Electronic supplementary materials *Mendeleev Commun*., 2024, **34**, 265–267

Reactions of 1-amino-2-nitroguanidine with 3-nitroacrylates

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Experimental part

Physico-chemical studies were carried out at the Center for Collective Use of the Herzen State Pedagogical University of Russia. ^{1}H, ^{13}C-{^{1}H}, ^{1}H-^{13}C HMQC, HMBC, COSY, NQESY NMR spectra were recorded on a JEOL ECX400A spectrometer [399.78 (^{1}H), 100.52 (^{13}C) MHz] in DMSO-d_6 using the residual signal from non-deuterated solvents as internal standard. IR spectra were obtained on an IRPrestige-21 Fourier spectrometer in KBr tablets. Elemental analysis was performed on an analyzer EuroVectorEA 3000 (CHN Dual mode). For the literature references met below, see the main text.

X-Ray Crystallography. X-ray diffraction analysis of the structure **4a** was performed on a Bruker D8 QUEST automatic three-circle diffractometer with a PHOTON III two-dimensional detector and an IμS DIAMOND microfocus X-ray tube (λ [Mo Kα] = 0.71073 Å) at cooling conditions (100 K). Data collection and processing of diffraction data were performed using an APEX3 software package. All of the structures were solved by the direct method using the SHELXT program[13] and refined by the full-matrix least squares method over F^2 using the SHELXL program.[14] All of the calculations were performed in the WinGX software package[14], the calculation of the geometry of the molecules and the intermolecular interactions in the crystals was carried out using the PLATON program[15] and the drawings of the molecules were performed using the MERCURY[16] programs. The non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the "riding" model. The crystallographic data of structure were deposited at the Cambridge Crystallographic Data Center, registration number 2301778.

Crystal **4a,** $C_5H_9N_5O_4$, M = 203.17, triclinic, space group *P*-1, at 100(2) K: a = 7.2127(4), b = 9.2346(5), c = 14.8660(8) Å, α = 96.229(2), β = 96.708(2), γ = 111.099(2)°, V = 905.27(9) Å^3, Z = 4 (two independent molecules), d_{calc} = 1.491 g·cm^{-3}, μ(MoKα) 0.129 mm^{-1}, F(000) = 424. A total of 49771 reflections were collected (6273 independent reflections, R_{int} = 0.068, 4831 observed with $I \geq 2\sigma(I)$), GOOF 1.014, final R indexes (observed reflections) R_1 = 0.0434, wR_2 = 0.1209, all data R_1 = 0.0613, wR_2 = 0.1313, 257 refined parameters.

The X-ray diffraction study was performed at the Department of X-ray Diffraction Research of the Multiple-Access Center on the basisof the Laboratory of Diffraction Research Methods of theA. E. Arbuzov Institute of Organic and Physical Chemistry, theKazan Scientific Center of the Russian Academy of Sciences.

The synthesis of 1-amino-2-nitroguanidine **1** (ANG) was carried out according to the literature method.[17] The synthesis of methyl and ethyl 3-nitroacrylates **2a**,**b** was carried out according to the literature method.[18]

Methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate 3a. A solutionof methyl 3-nitroacrylate **2a** (0.26 g, 2 mmol) in methanol (30 ml) was added dropwise to a solution of ANG **1** (0.23 g, 2 mmol) in water (10 ml) at a temperature of 60°C. The reaction mixture was stirred for 4.5 hours at a temperature of 60°C, then cooled to 18-20°C. The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.25 g (51%), mp. 118-120°C (decomposed) (water : methanol = 1 : 1.5). IR spectrum, ν cm^{-1}: 1749 (C=O), 1622 (C=N), 1274, 1433 (C=NNO$_2$), 1379 1555 (CH$_2$NO$_2$), 3423, 3302 (NH). NMR spectrum ^{1}H, δ, ppm (*J*, Hz): 3.72 (s, 3H, OCH$_3$), 4.28 (m, 1H, CH), 4.94, 4.97 (dd, 2H, CH$_2$NO$_2$, $^{2}J_{CH'CH''}$ 5.5, $^{3}J_{CH'CH}$ 15.1, $^{3}J_{CH''CH}$ 15.1), 6.04 (s, 1H, C-NH), 7.48, 8.39 (br. s, 2H, NH$_2$), 9.58 (br. s, 1H, NHC=NO$_2$.). NMR spectrum ^{13}C{^{1}H} δ, ppm: 53.2 (OCH$_3$), 59.8 (CH), 74.7 (CH$_2$), 161.8 (C=NNO$_2$), 170.4 (C=O). Found, %: C 23.74; H 4.08; N 33.53. $C_5H_{10}N_6O_6$. Calculated, %: C 24.00; H 4.00; N 33.60.

Ethyl 3-nitro-2-[2-(*N′*-nitrocarbamidoyl)hydrazinyl]propanoate 3b. A solution of ethyl 3-nitroacrylate **3b** (0.28 g, 2 mmol) in ethanol (30 ml) was added dropwise to a solution of ANG **1** (0.23 g, 2 mmol) of in water (10 ml) at a temperature of 60°C. The reaction mixture was stirred for 4.5 hours at a temperature of 60°C, then cooled to 18-20°C. The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.19 g (36.5%), mp. 76-80°C (decomposition) (water : ethanol = 1 : 1.5). IR spectrum, ν cm^{-1}: 1736 (C=O), 1629 (C=N), 1289, 1424 (C=NNO_2), 1383, 1558 (CH_2NO_2), 3469, 3352, 3298 (NH). NMR spectrum ^1H, δ, ppm (*J*, Hz): 1.22 (t, 3H, CH_2CH_3 , ^3J 7.1) , 4.18 (dq, 2H, CH_2CH_3 , ^3J 7.1) 4.04 (dd, 1H, CH_2NO_2, $^2J_{CH'CH''}$ 5.4, $^3J_{CH'CH}$ 15.1, $^3J_{CH''CH}$ 15.1), 4.25 (m, 1H, CH), 4.99 (dd, 1H, CH_2NO_2, $^2J_{CH'CH''}$ 5.4, $^3J_{CH''CH}$ 15.1), 6.02 (s, 1H, C-NH), 7.46, 8.35 (br. s, 2H, NH_2), 9.63 (br. s, 1H, NHC=NO_2). NMR spectrum $^{13}C\{^1H\}$ δ, ppm: 14.4, 59.8 (CH_2CH_3), 62.1 (CH), 74.8 (CH_2), 161.8 (C=NNO_2), 169.9 (C=O). Found, %: N 32.23. $C_6H_{12}N_6O_6$. Calculated, %: N 31.81.

Methyl 2-[2-(*N′*-nitrocarbamidoyl)hydrazinylidene]propanoate 4a.

a) From methyl 3-nitro-2-[2-(*N′*-nitrocarbamidoyl)hydrazinyl]propanoate 3a in the presence KOH. To a solution of methyl 3-nitro-2-[2-(*N′*-nitrocarbamidoyl)-hydrazinyl]propanoate **3a** (0.2 g, 0.8 mmol) in methanol (20 ml) was added KOH (0.045 g, 0.8 mmol) in water (10 ml). The mixture was refluxed at a temperature of 80-85ºC for 30 min, then cooled to 18-20ºC and acidified with conc. HCl to pH~5 (according to the universal indicator). The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.12 g (75%), mp. 146-148ºC (decomposed) (methanol : water = 1 : 1).

b) From 1-amino-2-nitroguanidine 1 and methyl 3-nitroacrylate. A solution of methyl 3-nitroacrylate **2a** (0.38 g, 2.9 mmol) in methanol (45 ml) was added dropwise to a solution of ANG **1** (0.35 g, 2.9 mmol) in water (15 ml) at a temperature of 60°C. The reaction mixture was stirred for 4.5 h at a temperature of 60°C. Then KOH (0.16 g, 2.9 mmol) in water (2 ml) was added to the reaction mass. The mixture was refluxed at a temperature of 80-85ºC for 30 minutes, cooled to 18-20ºC and acidified with conc. HCl to pH~5 (according to the universal indicator). The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.25 g (42%), mp. 147-148ºC (decomposed) (methanol : water = 1 : 1).). IR spectrum, ν cm^{-1}: 1716, 1727 (C=O), 1620 (C=N), 1319, 1429 (C=NNO_2), 3438, 3428, 3280 (NH). NMR spectrum ^1H, δ, ppm (*J*, Hz): 2.12 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 8.08, 9.05 (br. s, 2H, NH_2), 11.27 (s, 1H, NH). NMR spectrum $^{13}C\{^1H\}$ δ, ppm: 11.4 (CH_3), 50.3 (OCH_3), 141.74 (C=N), 157.0 (C=NNO_2), 162.3 (C=O). Found, %: C 28.11; H 4.21; N 34.15. $C_5H_9N_5O_4$. Calculated, %: C 29.55; H 4.43; N 34.48.

A mixed sample of samples obtained using methods *a* and *b* did not produce a depression in the melting point.

Ethyl 2-[2-(*N′*-nitrocarbamidoyl)hydrazinylidene]propanoate 4b.

a) From ethyl 3-nitro-2-[2-(*N′*-nitrocarbamidoyl)hydrazinyl]propanoate 3b in the presence KOH. To a solution of ethyl 3-nitro-2-[2-(*N′*-nitrocarbamidoyl)hydrazinyl]propanoate **3b** (0.15 g, 0.6 mmol) in ethanol (10 ml) was added KOH (0.03 g, 0.6 mmol) in water (5 ml). The mixture was refluxed at a temperature of 80-85ºC for 30 minutes, then cooled to 18-20ºC and acidified with conc. hydrochloric acid to pH~5 (according to a universal indicator). The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.06 g (50%), mp. 168-170ºC (decomposed) (ethanol: water = 1: 1).

b) From 1-amino-2-nitroguanidine 1 and ethyl 3-nitroacrylate. A solution of ethyl 3-nitroacrylate **2b** (0.69 g, 4.7 mmol) in ethanol (45 ml) was added dropwise to a solution of ANG **1** (0.56 g, 4.7 mmol) in water (15 ml) at a temperature of 60°C. The reaction mixture was stirred for 4.5 h at a temperature of 60°C. Then KOH (0.26 g, 4.7 mmol) in water (5 ml) was added. The mixture was refluxed at a temperature of 80-85ºC for 30 minutes, cooled to 18-20ºC and acidified with conc. HCl to pH~5 (according to the universal indicator). The solvent was evaporated on a rotary evaporator. The resulting crystalline precipitate was filtered off. Yield 0.38 g (42%), mp. 169-171ºC (decomposed) (ethanol : water = 1 : 1). IR spectrum, ν cm^{-1}: 1715, 1721(C=O), 1622 (C=N), 1305, 1455(C=NNO_2), 3436, 3293, 3251 (NH). NMR spectrum ^1H, δ, ppm (*J*, Hz): 1.27 t (3H, CH_2CH_3 , ^3J 7.0), 2.11 (s, 3H, CH_3), 4.22 (dq, 2H, CH_2CH_3 , ^3J 7.0), 8.03, 9.05 (br. s, 2H, NH_2), 11.25 (s, 1H, NH). NMR spectrum $^{13}C\{^1H\}$ δ, ppm: 11.0 (CH_3), 14.5, 61.9 (CH_2CH_3), 144.9 (C=N), 159.0 (C=NNO_2), 164.2 (C=O). Found, %: C N 31.38. $C_6H_{11}N_5O_4$. Calculated, %: N 32.26.

A mixed sample of samples obtained using methods *a* and *b* did not produce a depression in the melting point.

2-[2-(*N′*- Nitrocarbamidoyl)hydrazinylidene]propanoic acid 5.

a) From methyl 2-[2-(*N′*-nitrocarbamidoyl)hydrazinylidene]propanoate 4a in the presence of KOH. To a solution of methyl 2-[2-(*N′*-nitrocarbamidoyl)-hydrazinylidene]propanoate **4a** (0.2 g, 1 mmol) in methanol (10 ml) was added KOH (0.055 g, 1 mmol) in water (10 ml). The mixture was refluxed at a temperature of 80-85ºC for 4 hours, then cooled to 18-20ºC and acidified with conc. HCl to pH~5 (according to the universal indicator). The resulting crystalline precipitate was filtered off. Yield 0.16 g (88%), mp. 172-174ºC (decomposed) (water), lit. m.p. 190-191ºC (decomposition) (water).[8]

b) From ethyl 2-[2-(*N′*-nitrocarbamidoyl)hydrazinylidene]propanoate 4b in the presence of KOH. To a solution of ethyl 2-[2-(*N′*-nitrocarbamidoyl)-hydrazinylidene]propanoate **4b** (0.2 g, 0.9 mmol) in methanol (10 ml) was added KOH (0.051 g, 0.9 mmol) in water (10 ml). The mixture was refluxed at a temperature of 80-85ºC for 4 hours, then cooled to 18-20ºC and acidified with conc. HCl to pH~5 (according to the universal indicator). The resulting crystalline precipitate was filtered off. Yield 0.14 g (82%), mp. 171-173ºC (decomposed) (water), lit. m.p. 190-191ºC (decomposed) (water).[8] IR spectrum, ν cm^{-1}: 1718, 1704 (C=O), 1643 (C=N), 1348, 1405(C=NNO_2), 3327, 3297, 3261 (NH), 3433, 3400 (OH). NMR spectrum ^1H, δ, ppm (*J*, Гц): 2.04 (s, 3H, CH_3), 9.11, 9.23 (br. s, 2H, NH_2), 11.20 (s, 1H, NH), 12.35 (br. s, 1H, OH). NMR spectrum $^{13}C\{^1H\}$ δ, ppm: 12.9 (CH_3), 144.0 (C=N), 159.0 (C=NNO_2), 164.7 (C=O).

A mixed sample of samples obtained using methods *a* and *b* did not show a depression in the melting point.

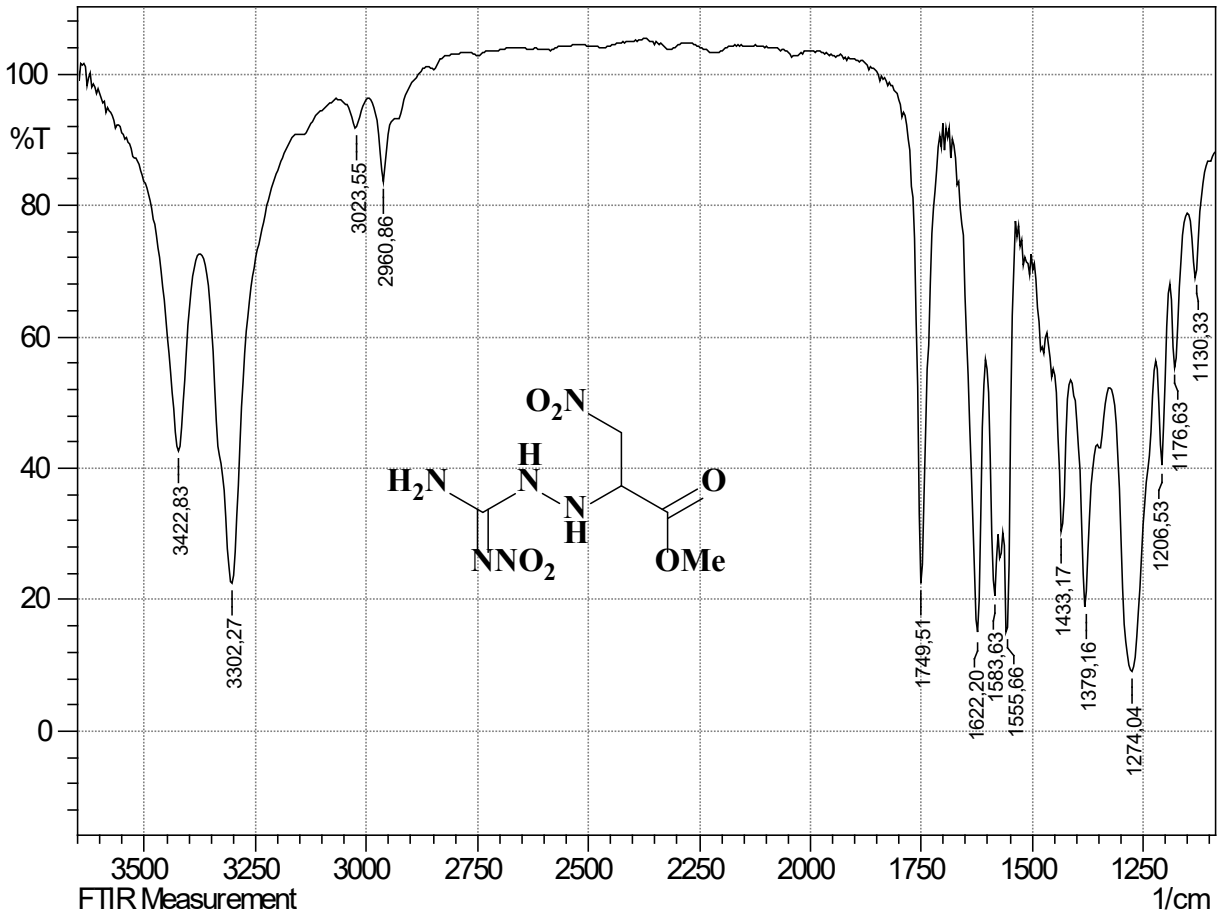

Figure S1. IR spectrum of methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3a** in KBr.

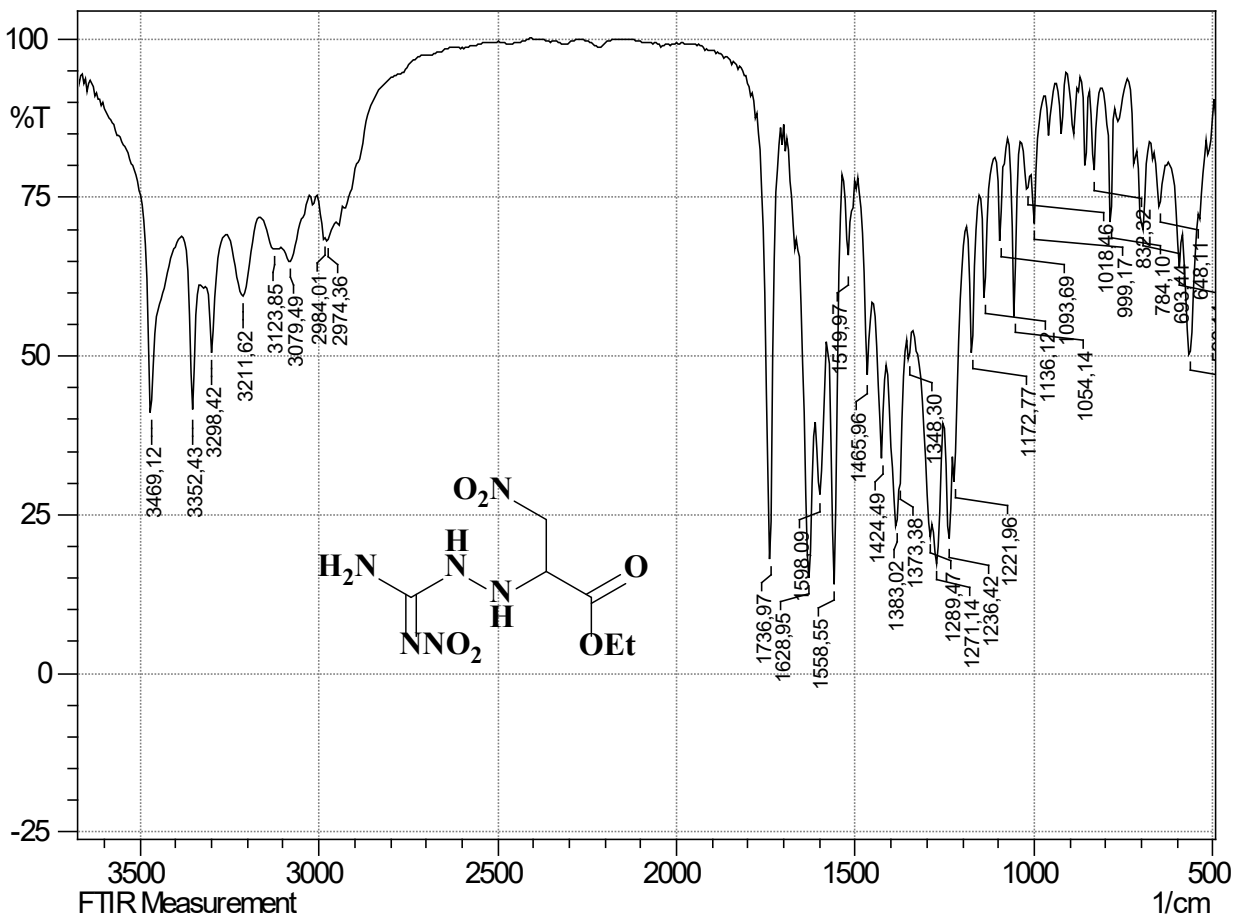

Figure S2. IR spectrum of ethyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3b** in KBr.

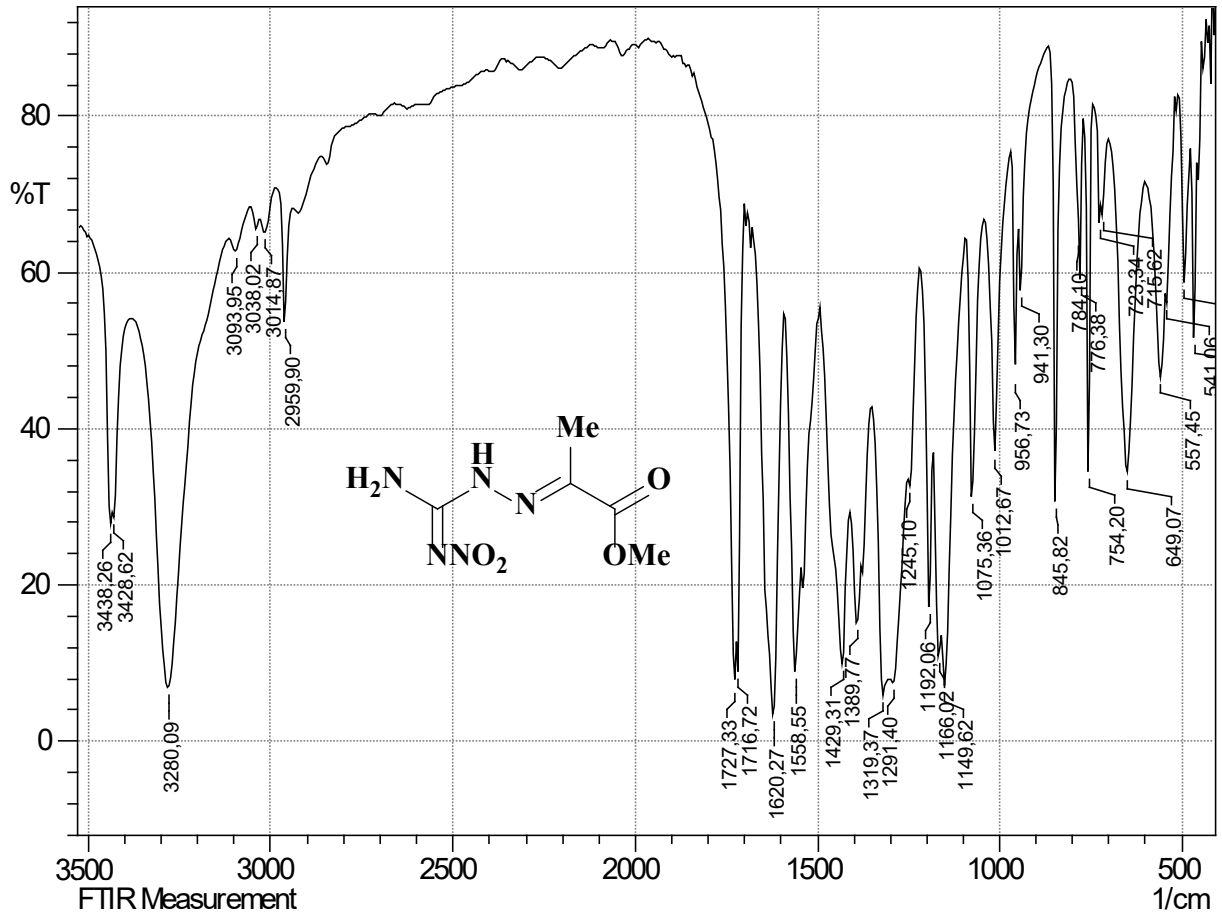

Figure S3. IR spectrum of methyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4a** in KBr.

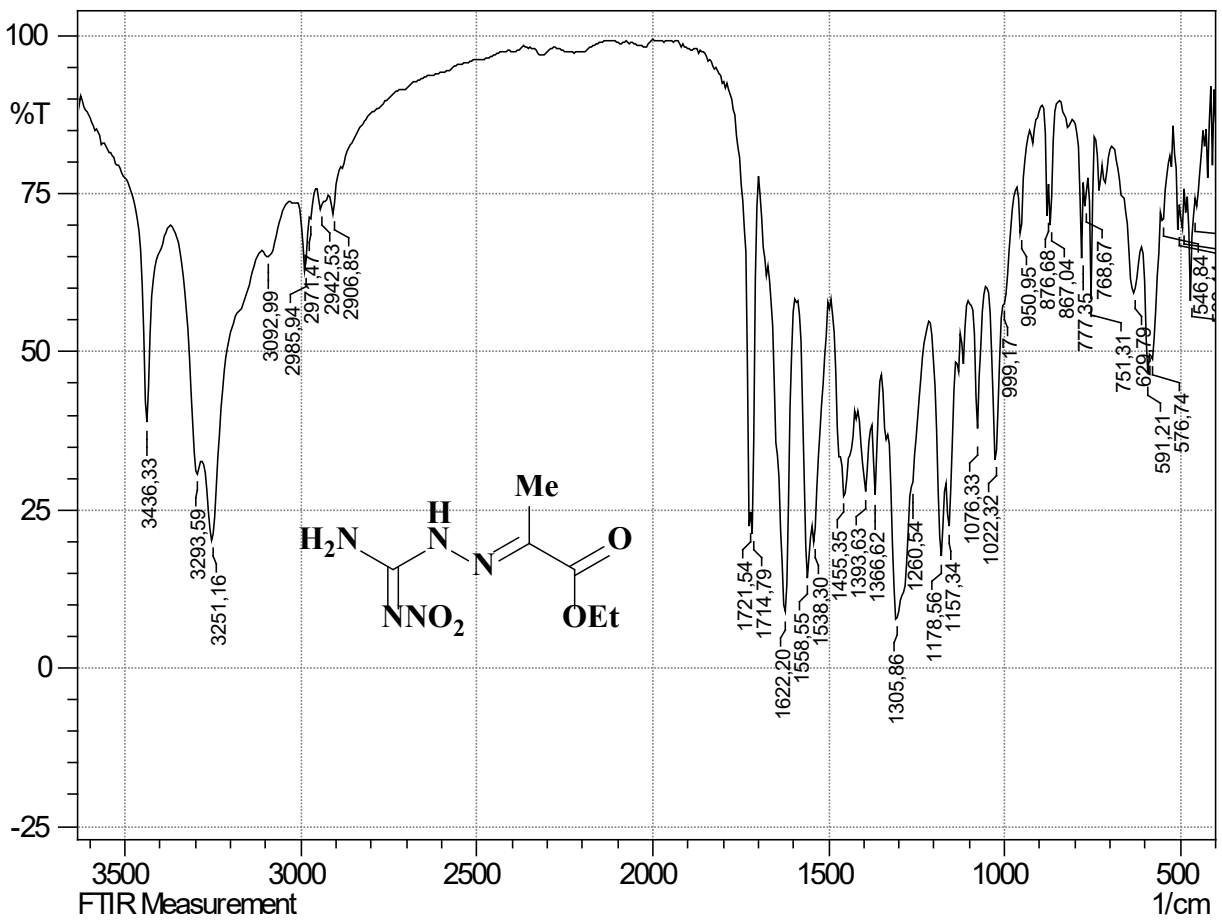

Figure S4. IR spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in KBr.

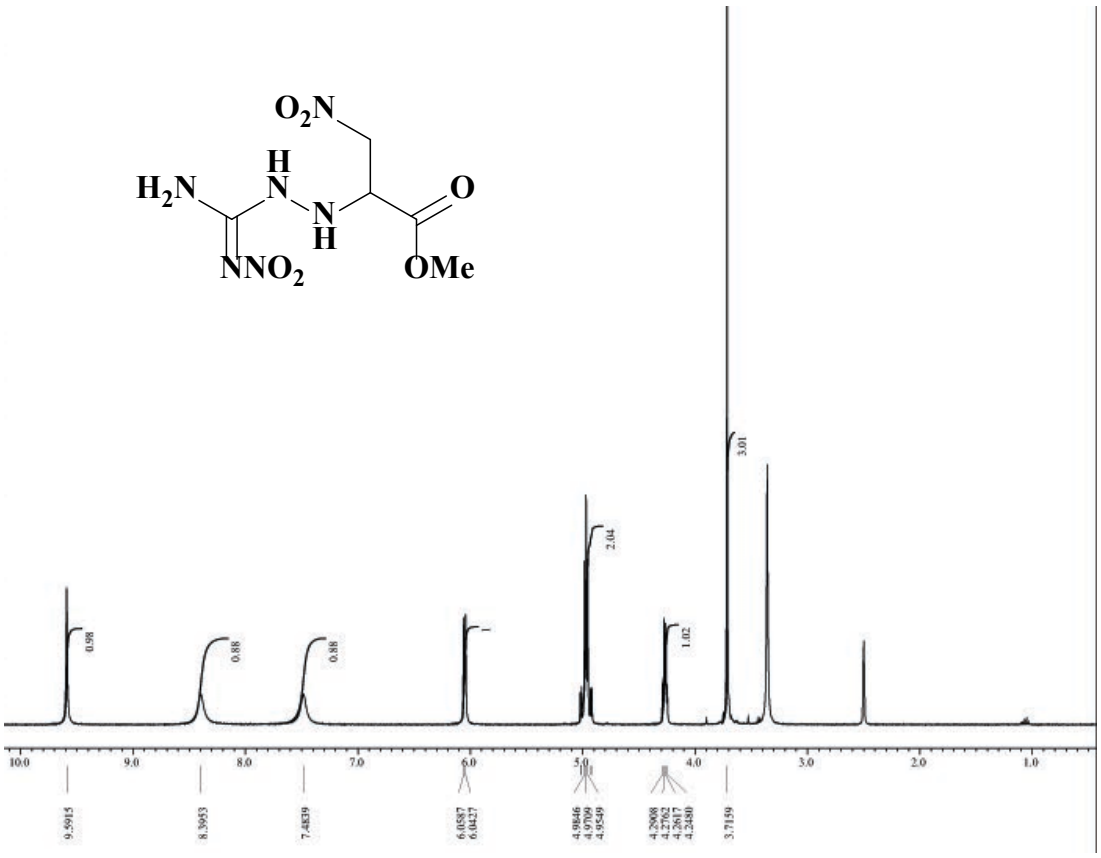

Figure S5. ^{1}H NMR spectrum of methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3a** in DMSO-d_6.

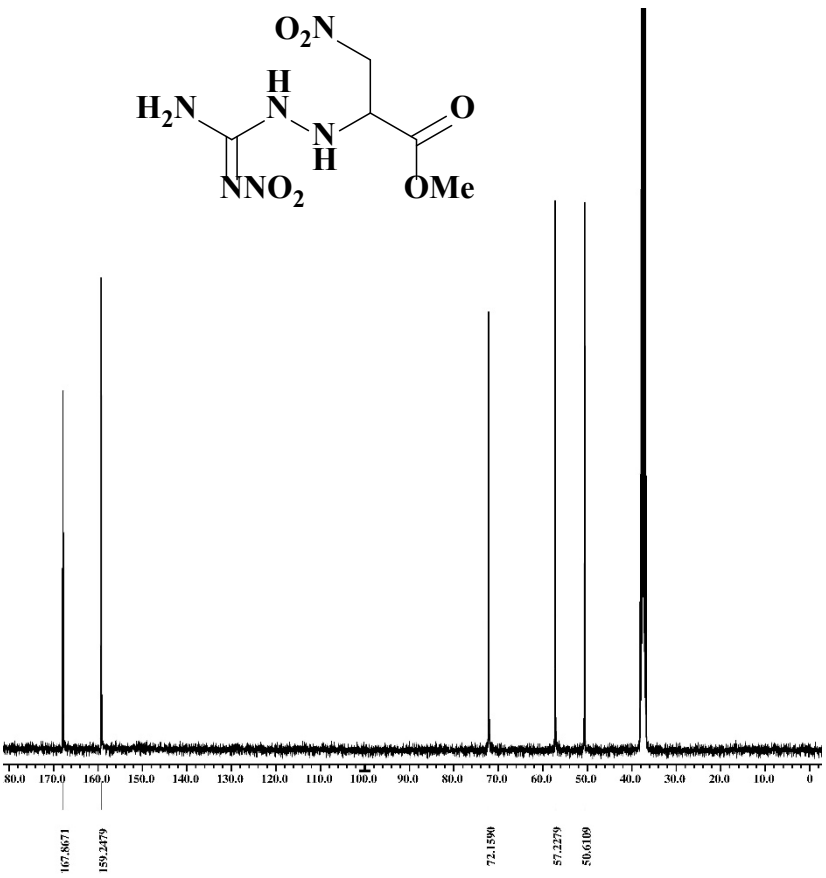

Figure S6. ^{13}C{^{1}H} NMR spectrum of methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3a** in DMSO-d_6.

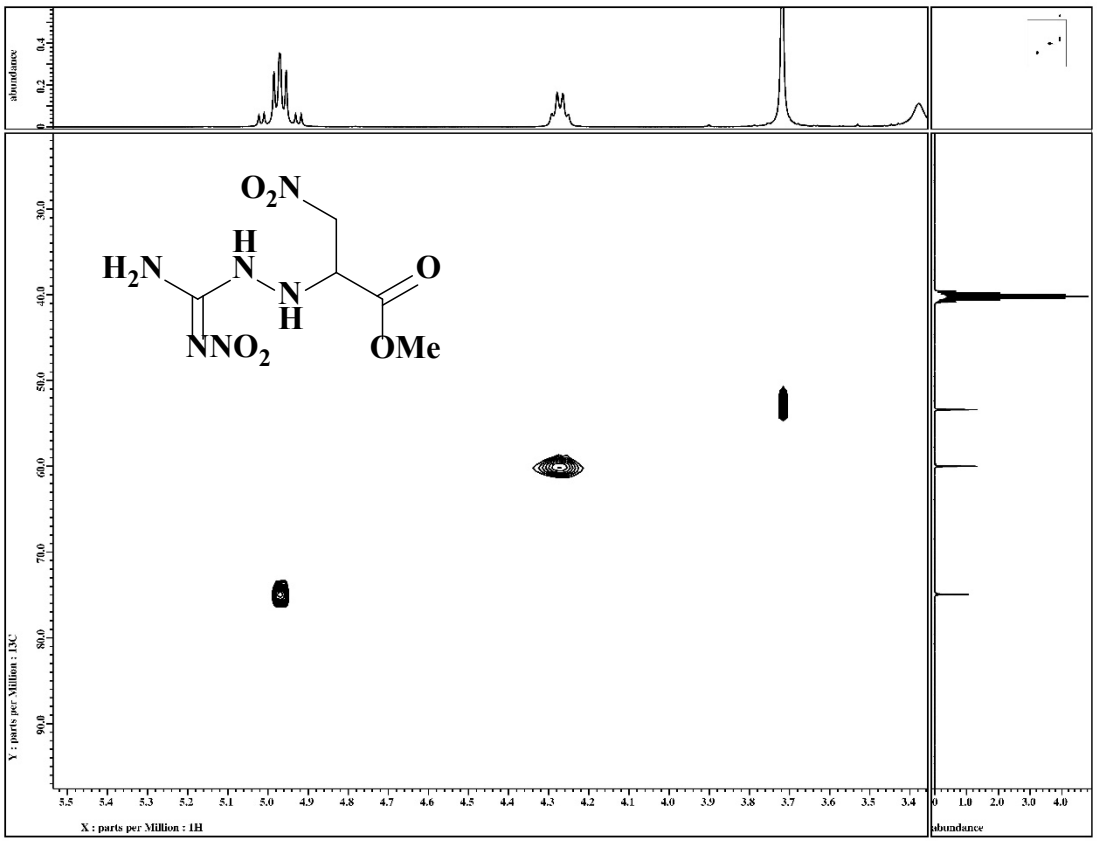

Figure S7. ^{1}H-^{13}C HMQC NMR spectrum of methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)-hydrazinyl]propanoate **3a** in DMSO-d_6.

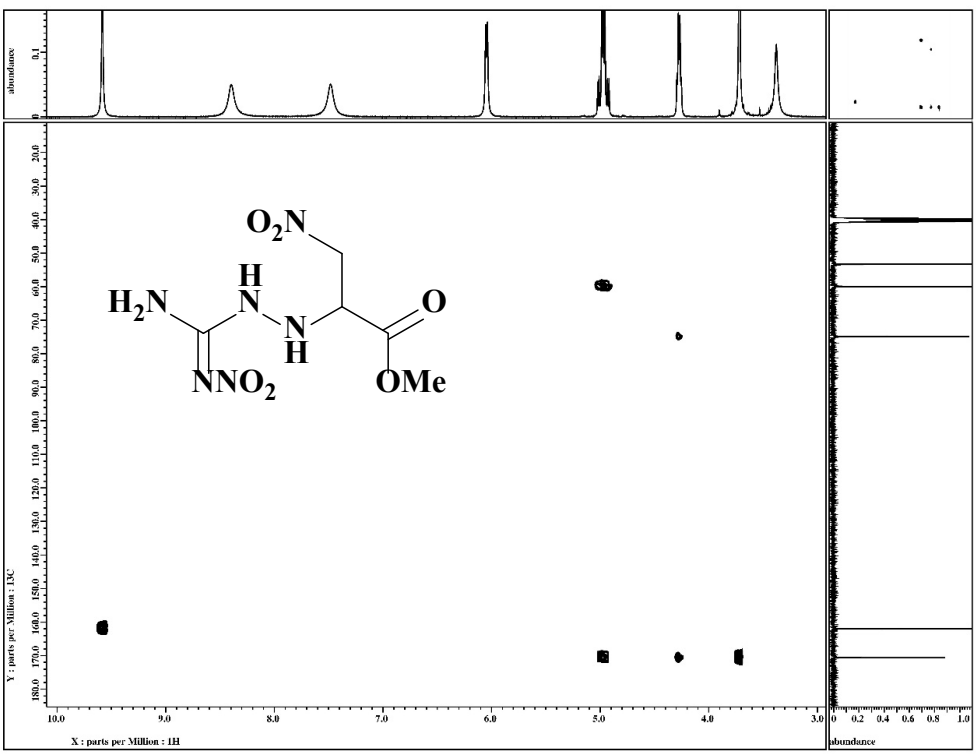

Figure S8. ^{1}H-^{13}C HMBC NMR spectrum of methyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)-hydrazinyl]propanoate **3a** in DMSO-d_6.

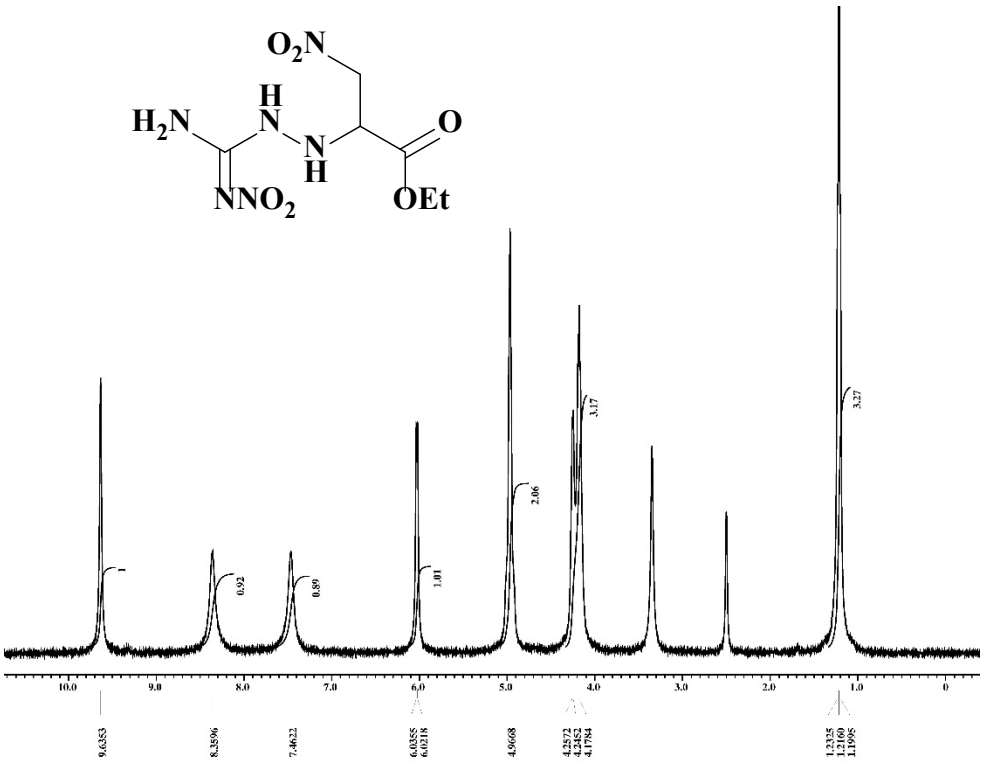

Figure S9. ^{1}H NMR spectrum of ethyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3b** in DMSO-d_6.

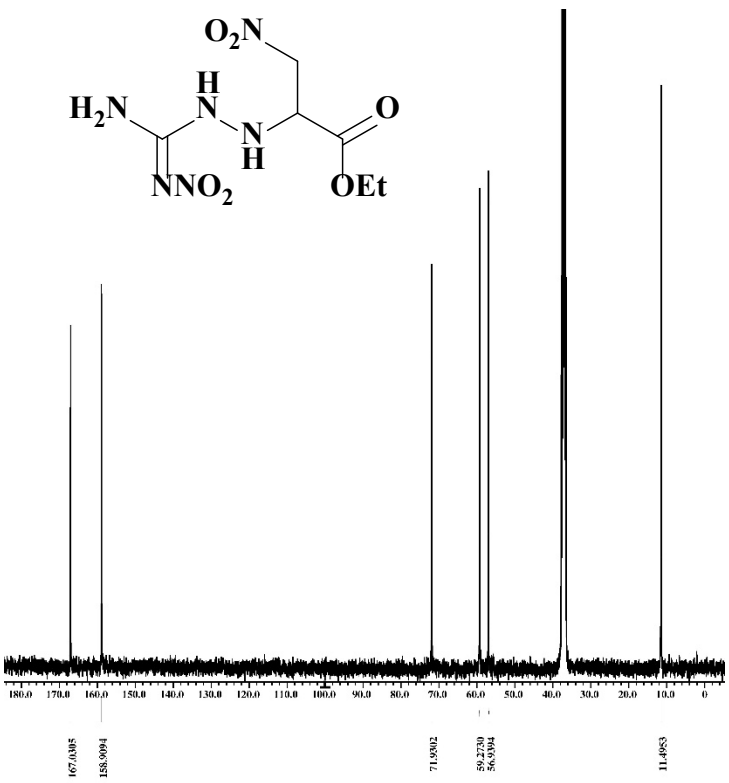

Figure S10. ^{13}C{^{1}H} NMR spectrum of ethyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3b** in DMSO-d_6.

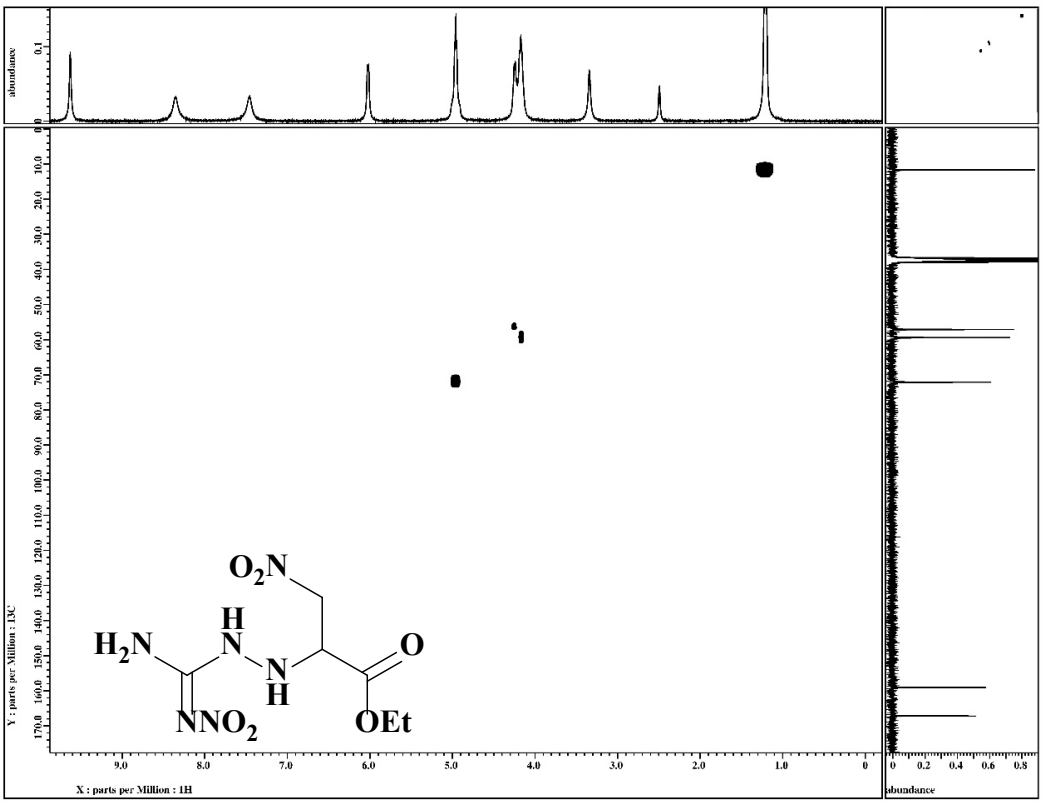

Figure S11. ^{1}H-^{13}C HMQC NMR spectrum of ethyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3b** in DMSO-d_6.

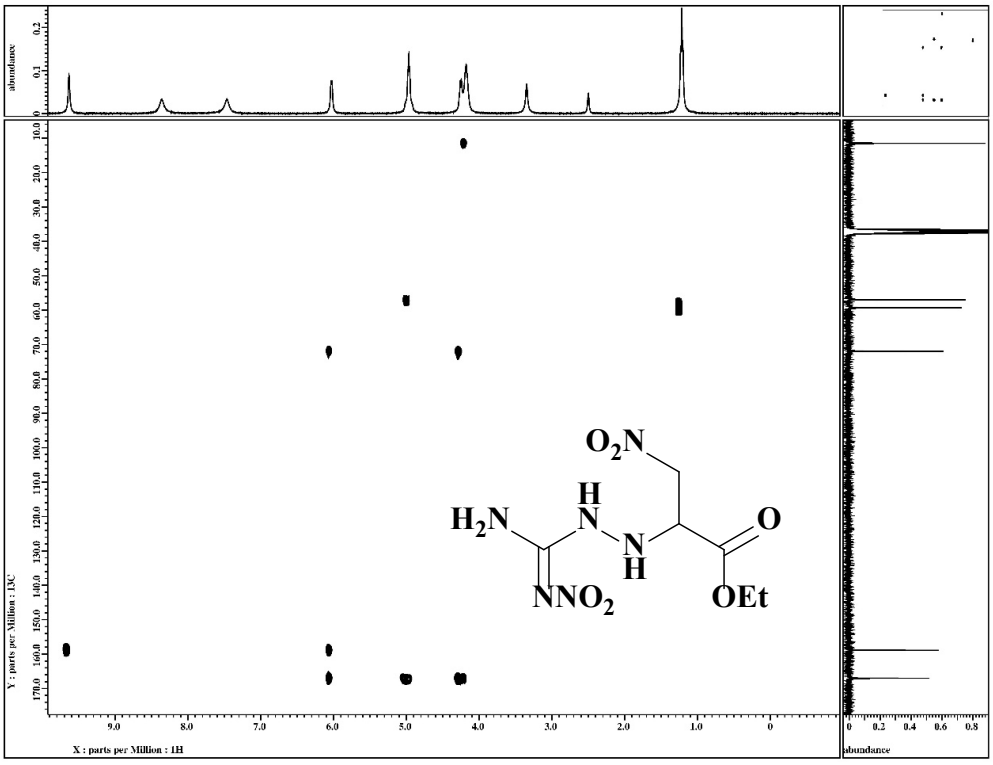

Figure S12. ^{1}H-^{13}C HMBC NMR spectrum of ethyl 3-nitro-2-[2-(*N*′-nitrocarbamidoyl)hydrazinyl]propanoate **3b** in DMSO-d_6.

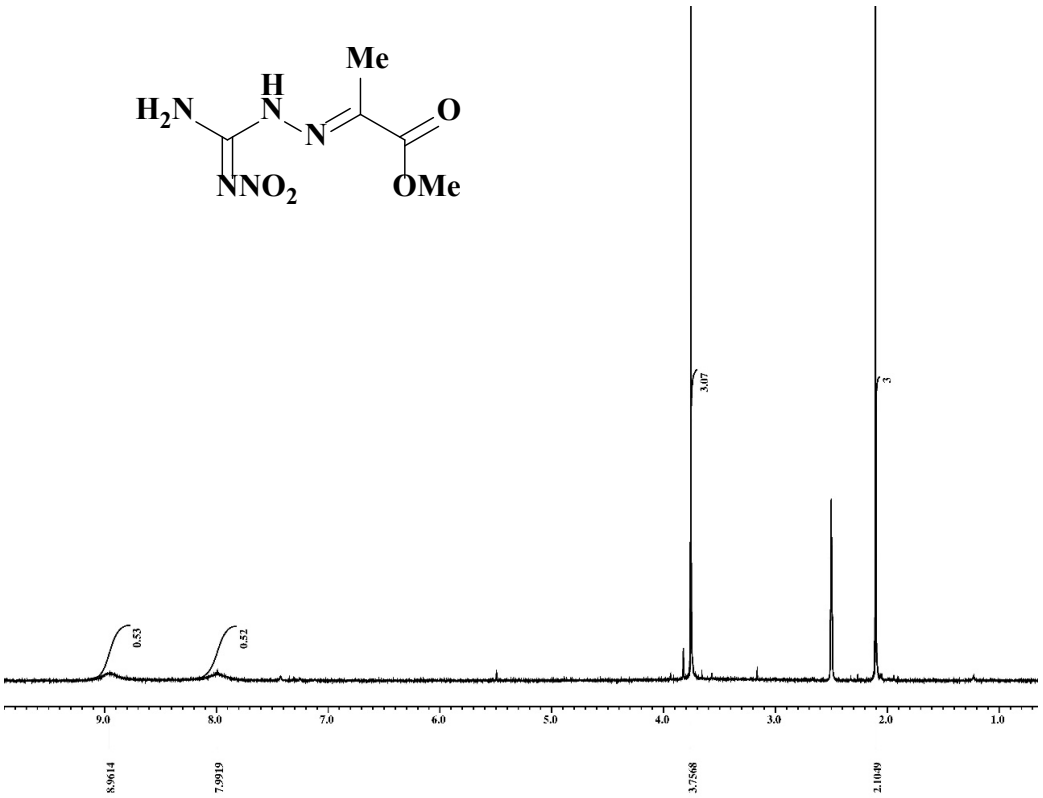

Figure S13. ^{1}H NMR spectrum of methyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4a** in DMSO-d_6.

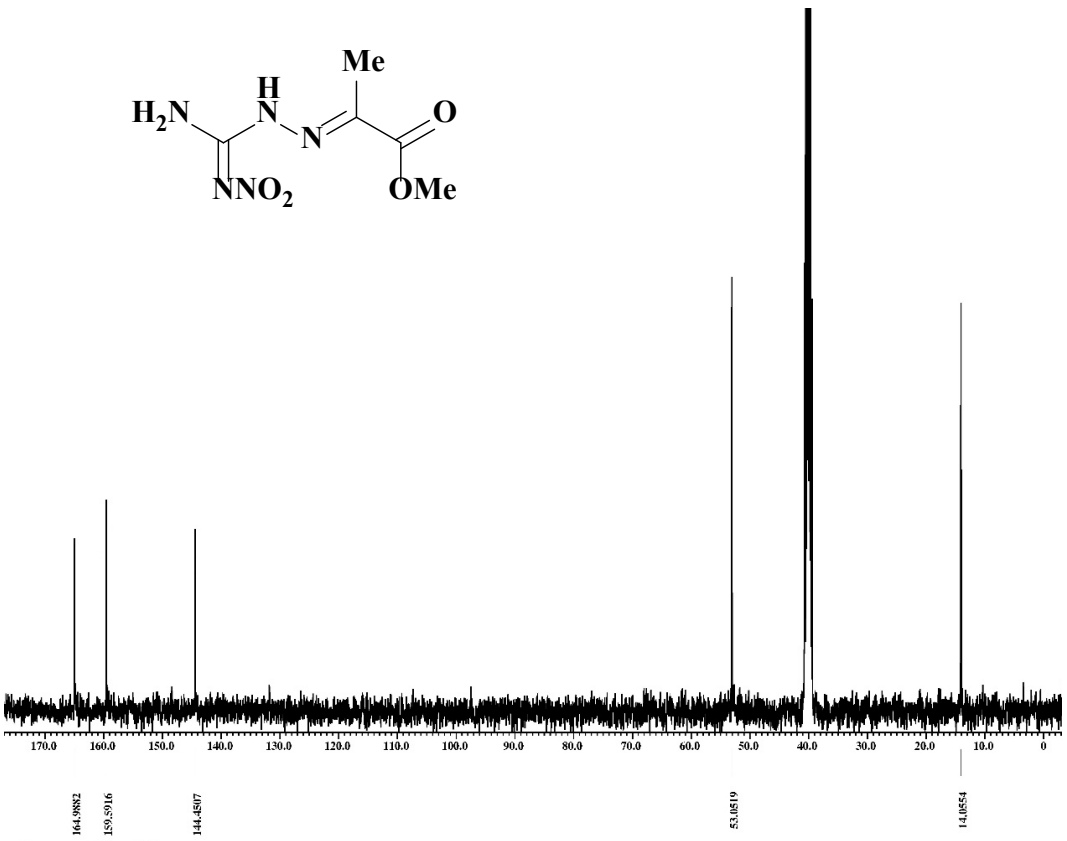

Figure S14. ^{13}C{^{1}H} NMR spectrum of methyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4a** in DMSO-d_6.

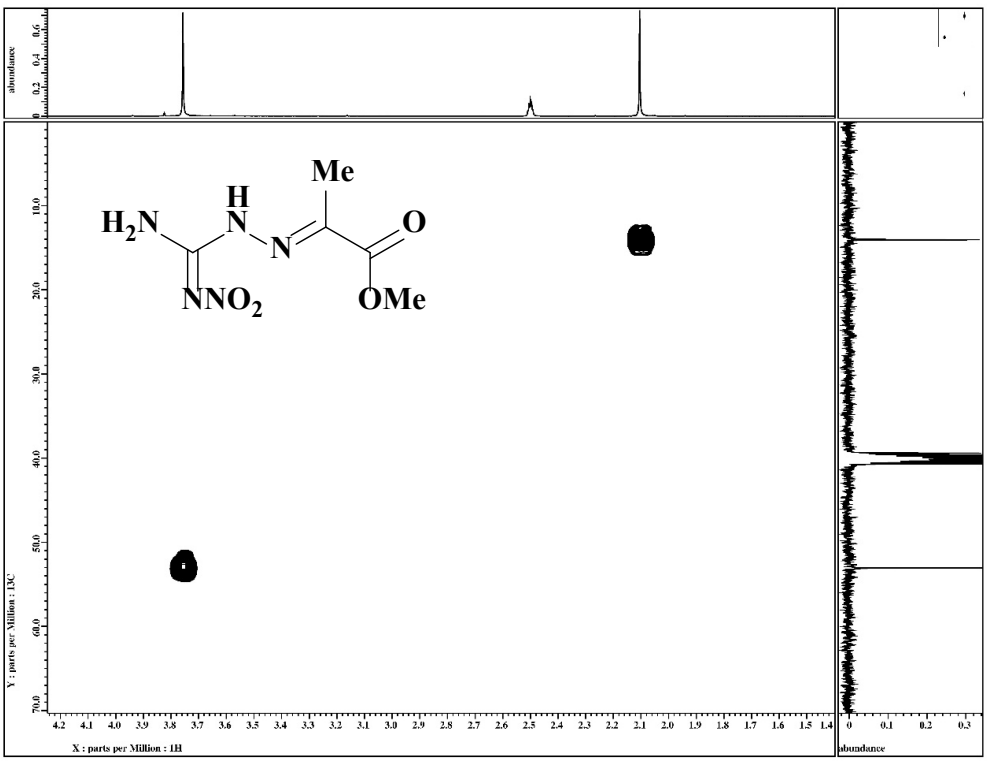

Figure S15. ^{1}H-^{13}C HMQC NMR spectrum of methyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4a** in DMSO-d_6.

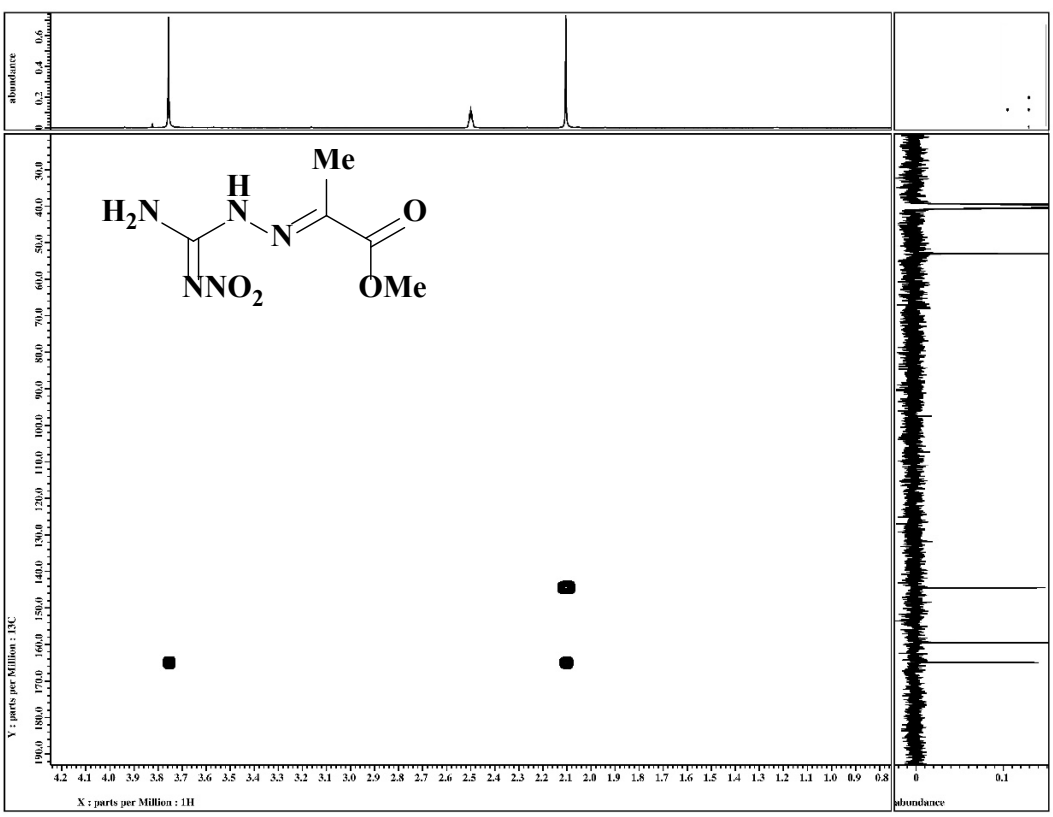

Figure S16. ^{1}H-^{13}C HMBC NMR spectrum of methyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4a** in DMSO-d_6.

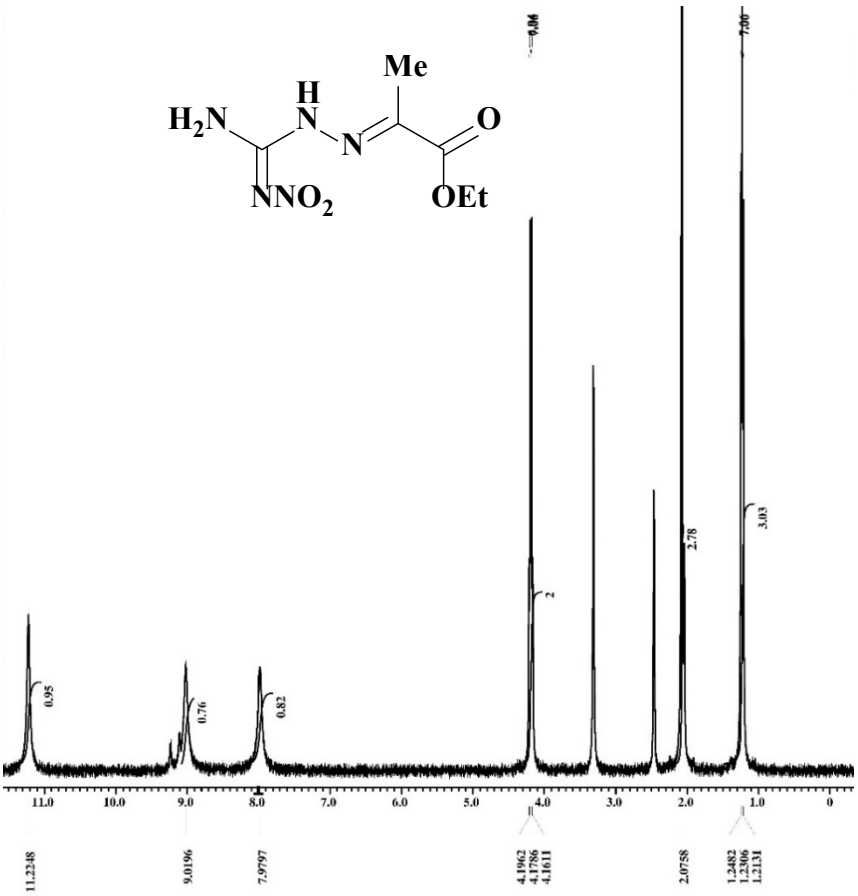

Figure S17. ^{1}H NMR spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in DMSO-d_6.

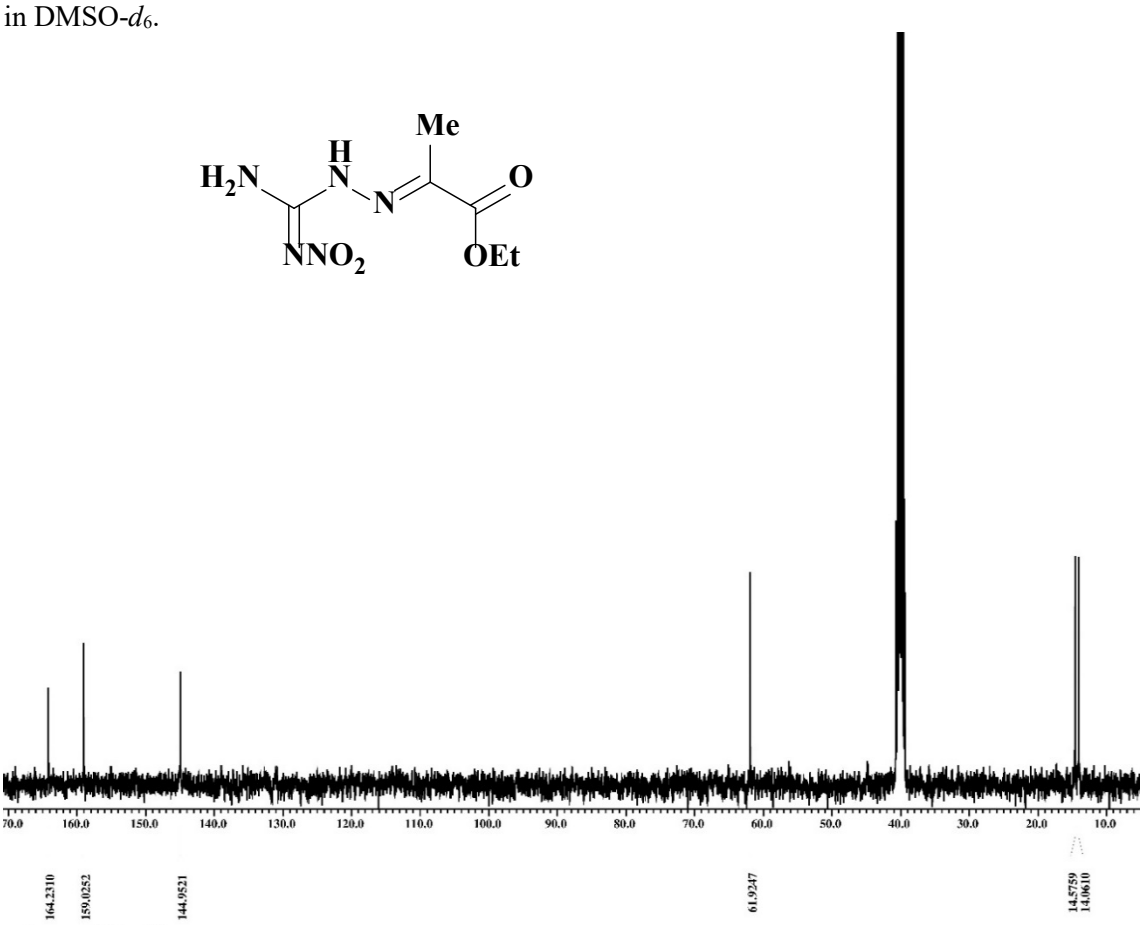

Figure S18. ^{13}C{^{1}H} NMR spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in DMSO-d_6.

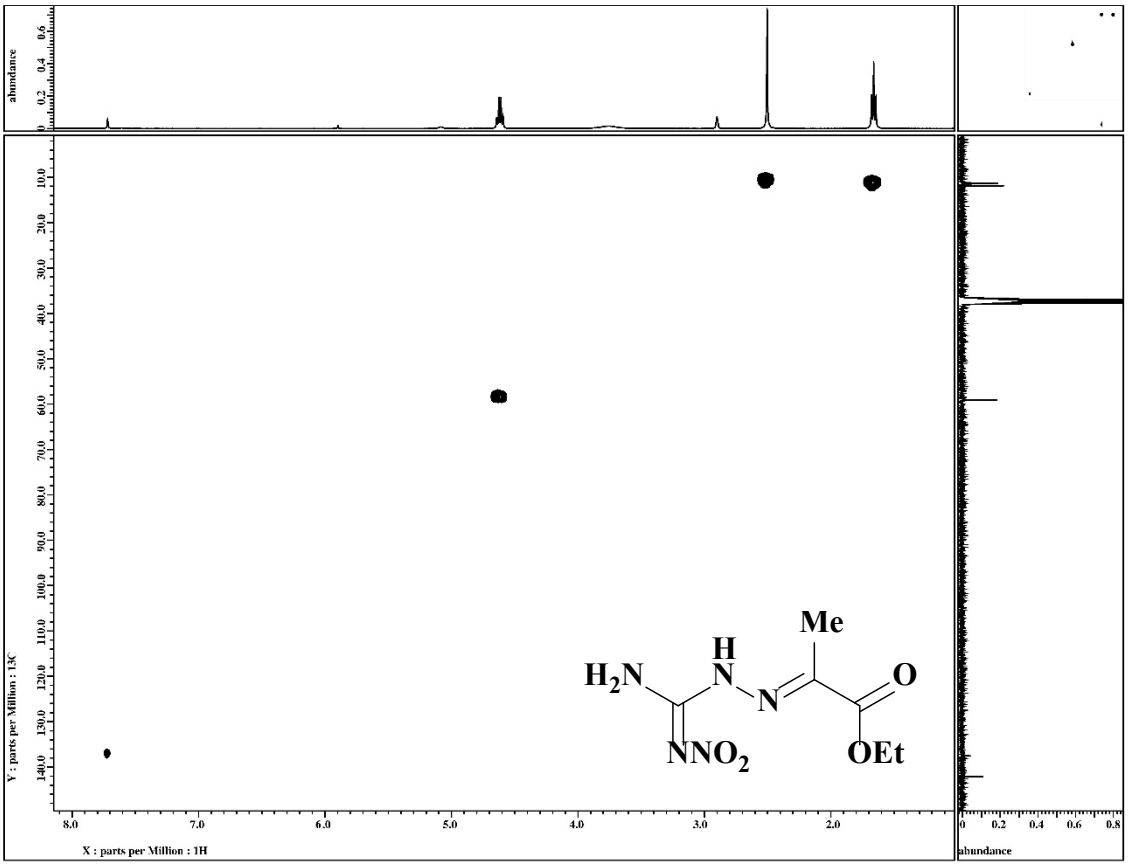

Figure S19. ^{1}H-^{13}C HMQC NMR spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in DMSO-d_6.

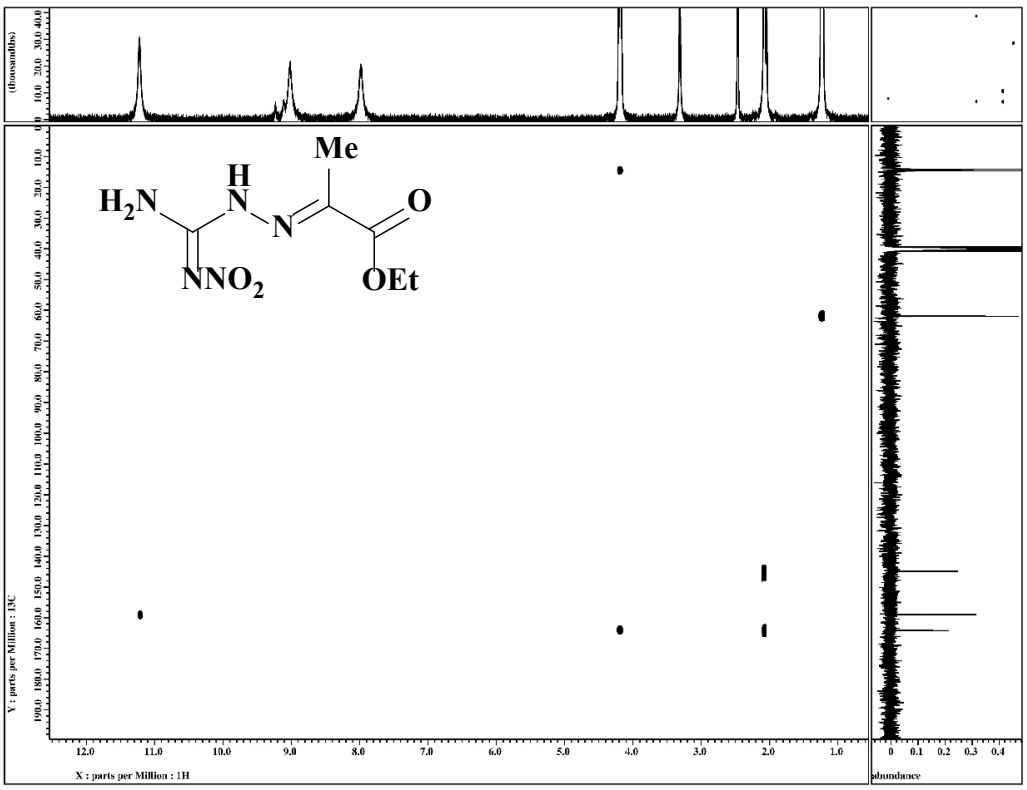

Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in DMSO-d_6.

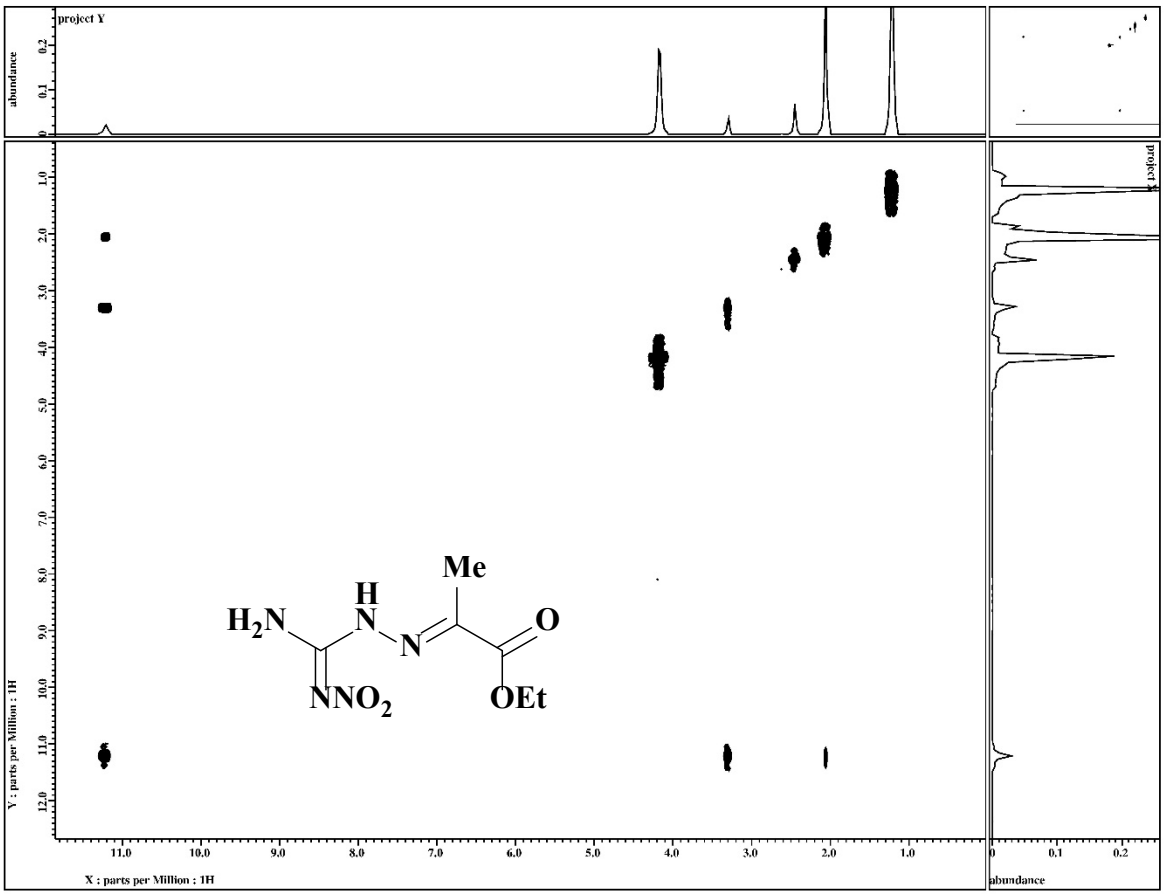

Figure S21. ^{1}H-^{1}H NOESY spectrum of ethyl 2-[2-(*N*′-nitrocarbamidoyl)hydrazinylidene]propanoate **4b** in DMSO-d_6.

Hydrogen bonds in crystal

Nr Typ Res Donor --- H....Acceptor [ARU] D - H H...A D...A D - H...A A..H..A* A'..H..A" Sum(XY,YZ) Sum(XZ)

1 1 N8 --H8 ..O13B [1665.02] 0.88 2.04 2.8725(11) 157
2 2 N8B --H8B ..O14 [1555.01] 0.88 2.05 2.8825(11) 158
3 Intra 1 N10 --H10A ..O14 [ ] 0.88 1.98 2.5642(12) 122
4 1 N10 --H10A ..N11B [1555.02] 0.88 2.23 2.9734(11) 142' 95' 359
5 1 N10 --H10B ..O14B [1555.02] 0.88 2.38 2.8632(11) 115
6 Intra 1 N10 --H10B ..N7 [ ] 0.88 2.21 2.5748(11) 104' 141' 360
7 Intra 2 N10B --H10C ..O13B [ ] 0.88 1.99 2.5655(12) 122
8 2 N10B --H10C ..N11 [1445.01] 0.88 2.27 2.9840(12) 139' 94' 355
9 2 N10B --H10D ..O13 [1445.01] 0.88 2.40 2.8905(11) 116
10 Intra 2 N10B --H10D ..N7B [ ] 0.88 2.23 2.5862(12) 104' 137' 357
11 2 C3B --H3B1 ..O14B [2666.02] 0.98 2.57 3.5212(13) 163
12 Intra 2 C3B --H3B2 ..O4B [ ] 0.98 2.46 2.8888(13) 106
13 Intra 1 C3 --H3B ..O4 [ ] 0.98 2.44 2.8816(14) 107
14 1 C3 --H3C ..O13 [2776.01] 0.98 2.54 3.4461(15) 154

Translation of ARU-Code to CIF and Equivalent Position Code

==========

[2666.] = [2_666] = 1-x,1-y,1-z
[1665.] = [1_665] = 1+x,1+y,z
[2776.] = [2_776] = 2-x,2-y,1-z
[1445.] = [1_445] = -1+x,-1+y,z

Table S1. Principal crystallographic parameters of compound **4a** based on X-ray diffraction data

Parameter	**4a**
Molecular formula	$C_5H_9N_5O_5$
Molecular weight	203.07
Crystal system	triclinic
Space group	P -1
Z	4
a/Å	7.2127(4)
b/Å	9.2346(5)
c/Å	14.8660(8)
γ/deg	111.099(2)
V/Å^3	905.27(9)
d_{calc}/g cm^{-3}	1.491
μ(MoKα)/mm^{-1}	0.129
F(000)	424.0
R_{int}	0.068
GOOF	1.014
R_1	0.0434
wR_2	0.1209
R_1	0.0613
wR_2	0.1313
CCDC	2301778

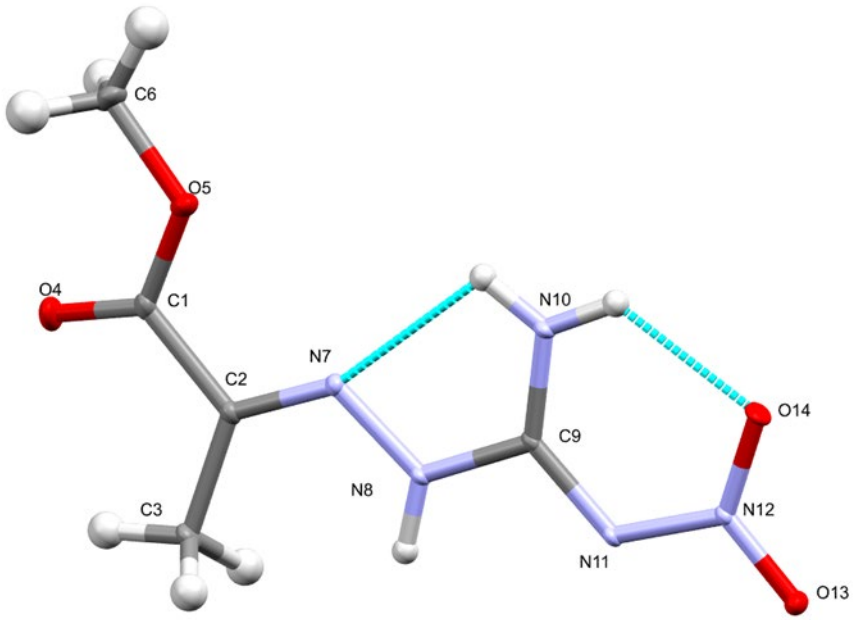

Figure S22. Geometry of molecule **4a** in crystal with intramolecular hydrogen bonds indicated.

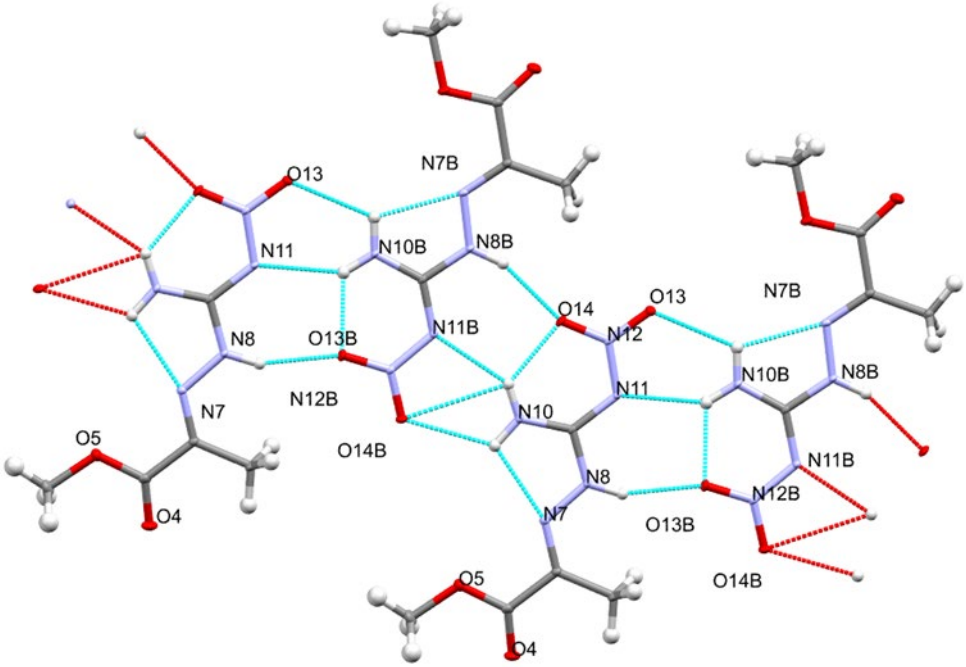

Figure S23. System of hydrogen bonds in crystal **4a**. Hydrogen bonds are shown with dotted lines.

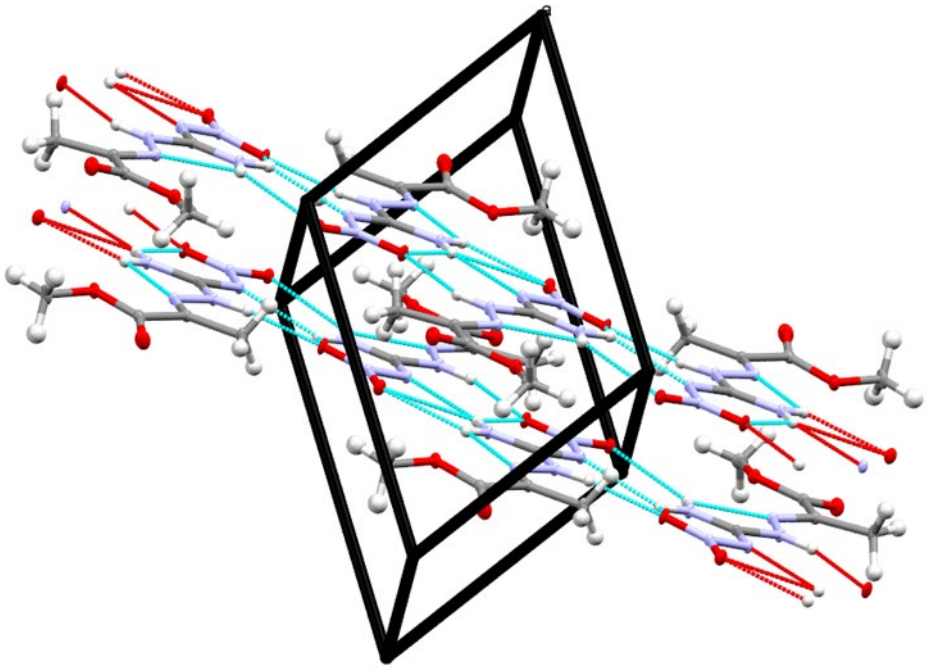

Figure S24. Fragment of crystal packaging. Hydrogen bonds are shown with dotted lines.