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Nitrofuran-3-carboxylates: synthesis and structure

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Experimental

Physicochemical studies were performed using the equipment of the Center for Collective Use "Physicochemical methods for the study of nitro compounds, coordination, biologically active substances and nanostructured materials" of the Interdisciplinary Resource Center for collective use "Modern physicochemical methods for the formation and study of materials for the needs of industry, science and education» Herzen State Pedagogical University of Russia. The ^{1}H, $^{13}C\{^{1}H\}$, $^{1}H–^{1}H$ NOESY, $^{1}H–^{13}C$ HMQC, and HMBC NMR spectra were recorded on a JEOL ECX400A spectrometer operating at 399.78 MHz (^{1}H) and 100.53 MHz (^{13}C) in $CDCl_3$ using residual signals of the nondeuterated solvent (δ_H 7.26, δ_C 77.16) as the references. The vibrational spectra were measured on a Shimadzu IR-Prestige-21 Fourier-transform IR spectrometer in chloroform (*c* 40 mg mL^{-1}). Electronic absorption spectra were recorded on a Shimadzu UV2401PC spectrophotometer in chloroform in 1.01 mm matched quartz cells. Elemental analysis was performed on a Euro Vector EA 3000 analyzer (CHN Dual). Melting points were determined on a PTP-M melting point apparatus.

The starting *trans*-2,3-dihydro-2-nitrofuran-3-carboxylates **1a-f** were synthesized according to a procedure described previously.[35]

Methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate (2a).

To a solution of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **1a** (757 mg, 3.3 mmol) in toluene (40 mL) MnO_2 (23 g, 0.26 mol) was added. The resulting mixture was stirred for 7 days at 18-20 °C. After filtration of MnO_2 and evaporation of the solvent, the oily residue was treated with hot hexane (40 mL). The precipitate was filtered off, after cooling. The yield was 325 mg (44%), light yellow crystals, melting point 79-81°C (C_6H_{14}) (conformer ratio **2a′**:**2a″** = 12:1). IR (KBr), ν/cm^{-1}: 1360 (s), 1531 (s, NO_2), 1684 (s), 1744 (s, C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 231 (4380), 310 (5324). Found, %: C 47.95; H 3.67, N 6.01. $C_9H_9NO_6$. Calculated, %: C 47.58; H 3.99, N 6.17.

major **2a′** ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.42 (3H, s, CH_3); 2.71 (3H, s, C^5CH_3); 4.00 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$), δ: 15.13 ($C^5\underline{C}H_3$); 29.45 (CH_3); 53.86 (OCH_3); 118.46 (C^3); 123.08 (C^4); 145.91 (C^2); 159.56 (C^5); 161.79 (O-C=O); 190.74 (C=O).

minor **2a″** ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.34 (3H, s, CH_3); 2.59 (3H, s, C^5CH_3); 3.91 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$), δ: 14.83 ($C^5\underline{C}H_3$); 31.75 (CH_3); 54.69 (OCH_3); 122.21 (C^3); 125.77 (C^4); 147.25 (C^2); 160.65 (C^5); 162.62 (O-C=O); 200.10 (C=O).

Dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (2b) was synthesized as described for compound **2a** starting from dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **1b** (650 mg, 2.65 mmol) and MnO_2 (18.46 g, 0.21 mol). The yield was 340 mg (53%), light yellow crystals, melting point 76-79°C (C_6H_{14}). IR (KBr), ν/cm^{-1}: 1361 (s), 1520 (s, NO_2), 1728 (s), 1759 (s, C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 230 (5260), 307 (8937). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.70 (3H, s, C^2CH_3); 3.85 (3H, s, C^3OCH_3); 3.97 (3H, s, C^4OCH_3). ^{13}C NMR ($CDCl_3$), δ: 14.31 ($C^2\underline{C}H_3$); 52.67 ($C^3O\underline{C}H_3$); 53.70 ($C^4O\underline{C}H_3$); 115.26 (C^3); 119.23 (C^4); 145.68 (C^5); 160.93 (C^2); 161.02 (C^3O-C=O); 161.08 (C^4O-C=O). Found, %: C 44.50; H 3.97, N 5.43. $C_9H_9NO_7$. Calculated, %: C 44.45; H 3.73, N 5.76.

3-Ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (2c) was synthesized as described for compound **2a** starting from 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **1c** (700 mg, 2.7 mmol) and MnO_2 (18.8 g, 0.22 mol). The yield was 0.356 г (51%), light yellow crystals, melting point 50-53°C (C_6H_{14}). IR (KBr), ν/cm^{-1}: 1359 (s), 1520 (s, NO_2), 1724 (s), 1754 (s, C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 231 (5652), 309 (9363). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.33 (3H, t, ^{3}J = 7.1, $OCH_2C\underline{H}_3$); 2.71 (3H, s, C^2CH_3); 3.98 (3H, s, OCH_3); 4.31 (2H, q, ^{3}J = 7.1, $OC\underline{H}_2CH_3$). ^{13}C NMR ($CDCl_3$), δ: 14.07 ($OCH_2\underline{C}H_3$); 14.25 ($C^2\underline{C}H_3$); 53.59 (OCH_3); 61.81 ($O\underline{C}H_2CH_3$); 115.44 (C^3); 119.27 (C^4); 145.68 (C^5); 160.55 (C^3O-C=O); 160.92 (C^2); 161.14 (C^4O-C=O). Found, %: C 46.79; H 4.20, N 4.95. $C_{10}H_{11}NO_7$. Calculated, %: C 46.70; H 4.31, N 5.45.

Ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate (2d) was synthesized as described for compound **2a** starting from ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **1d** (1.04 g, 4.27 mmol) and MnO_2 (29.8 g, 0.34 mol). The yield was 0.586 г (57%), light yellow crystals, melting point 84-86°C (C_6H_{14}) (conformer ratio **2d′**:**2d″** = 17:1). IR (KBr), ν/cm^{-1}: 1354 (s), 1528 (s, NO_2), 1673 (s), 1745 (s, C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 231 (6504), 309 (7630). C 46.41; H 4.13, N 5.32. $C_{10}H_{11}NO_6$. Calculated, %: C 46.70; H 4.31, N 5.45.

major **2d′** ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.41 (3H, t, ^3J = 7.1, $OCH_2C\underline{H}_3$); 2.43 (3H, s, CH_3); 2.72 (3H, s, C^5CH_3); 4.49 (2H, q, ^{3}J = 7.1, $OC\underline{H}_2CH_3$). ^{13}C NMR ($CDCl_3$), δ: 13.93 ($OCH_2\underline{C}H_3$); 15.15 ($C^5\underline{C}H_3$); 29.55 (CH_3); 63.36 ($O\underline{C}H_2CH_3$); 118.82 (C^3); 122.96 (C^4); 145.85 (C^2); 159.63 (C^5); 161.32 (O-C=O); 190.84 (C=O).

minor **2d″** ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.32 (3H, t, ^3J = 7.1, $OCH_2C\underline{H}_3$); 2.32 (3H, s, CH_3); 2.59 (3H, s, C^5CH_3); 4.34 (2H, q, ^{3}J = 7.1, $OC\underline{H}_2CH_3$).

4-Ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (2e) was synthesized as described for compound **2a** starting from 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **1e** (440 mg, 1.71 mmol) and MnO_2 (11.9 g, 0.14 mol). The yield was 0.227 г (52%), light yellow crystals, melting point 50-53°C (C_6H_{14}). IR (KBr), ν/cm^{-1}: 1360 (s), 1525 (s, NO_2), 1722 (s), 1755 (s, C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 231 (6055), 308 (10205). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.39 (3H, t, ^3J = 7.1, $OCH_2C\underline{H}_3$); 2.70 (3H, s, C^2CH_3); 3.86 (3H, s, OCH_3); 4.46 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$). ^{13}C NMR ($CDCl_3$), δ: 14.03 ($OCH_2\underline{C}H_3$); 14.31 ($C^2\underline{C}H_3$); 52.55 (OCH_3); 63.04 ($O\underline{C}H_2CH_3$); 115.21 (C^3); 119.55 (C^4); 145.73 (C^5); 160.95 (C^2); 160.57 (C^4O-C=O); 161.07 (C^3O-C=O). Found, %: C 46.87; H 3.99, N 5.15. $C_{10}H_{11}NO_7$. Calculated, %: C 46.70; H 4.31, N 5.45.

Diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (2f) was synthesized as described for compound **2a** starting from diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **1f** (600 mg, 2.18 mmol) and MnO_2 (15.2 g, 0.22 mol). The yield was 0.258 г (44%), light yellow oil, *Rf* 0.64 (C_6H_{14} : EtOAc = 3 : 1). IR ($CHCl_3$), ν/cm^{-1}: 1359 (s), 1530 (s, NO_2), 1730 (s C=O). UV ($CHCl_3$), λ_{max}/nm (ε): 231 (6223), 308 (9021).^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.33 (3H, t, ^3J = 7.2, $C^3OCH_2C\underline{H}_3$); 1.40 (3H, t, ^3J = 7.2, $C^4OCH_2C\underline{H}_3$); 2.71 (3H, s, C^2CH_3); 4.32 (2H, q, ^3J = 7.2, $C^3OC\underline{H}_2CH_3$); 4.46 (2H, q, ^3J = 7.2, $C^4OC\underline{H}_2CH_3$). ^{13}C NMR ($CDCl_3$), δ: 13.90 ($C^4OCH_2\underline{C}H_3$); 14.00 ($C^3OCH_2\underline{C}H_3$); 14.16 ($C^2\underline{C}H_3$); 61.70 ($C^4O\underline{C}H_2CH_3$); 62.87 ($C^2O\underline{C}H_2CH_3$); 115.32 (C^3); 119.57 (C^4); 145.61 (C^5); 160.53 (C^4O-C=O); 160.53 (C^3O-C=O); 160.96 (C^2). Found, %: C 48.56; H 4.57, N 5.02. $C_{11}H_{13}NO_7$. Calculated, %: C 48.71; H 4.83, N 5.16.

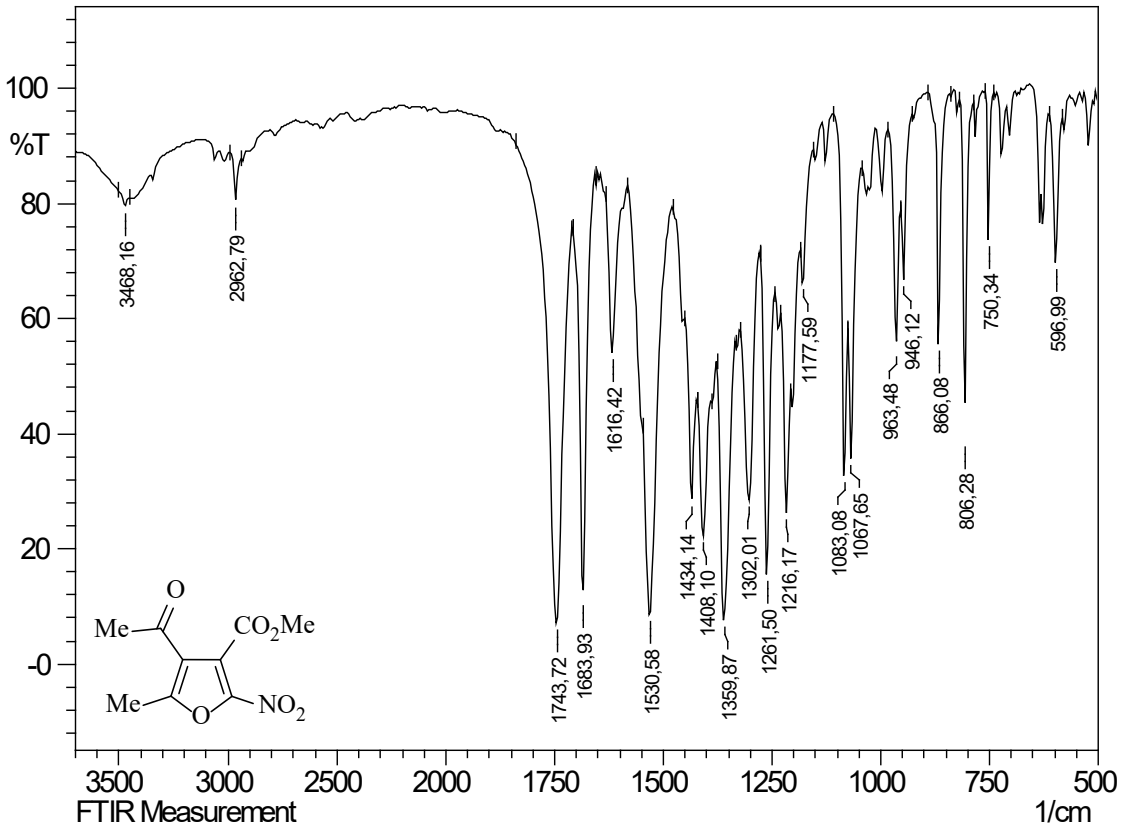

Figure S1. IR spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2a** in KBr

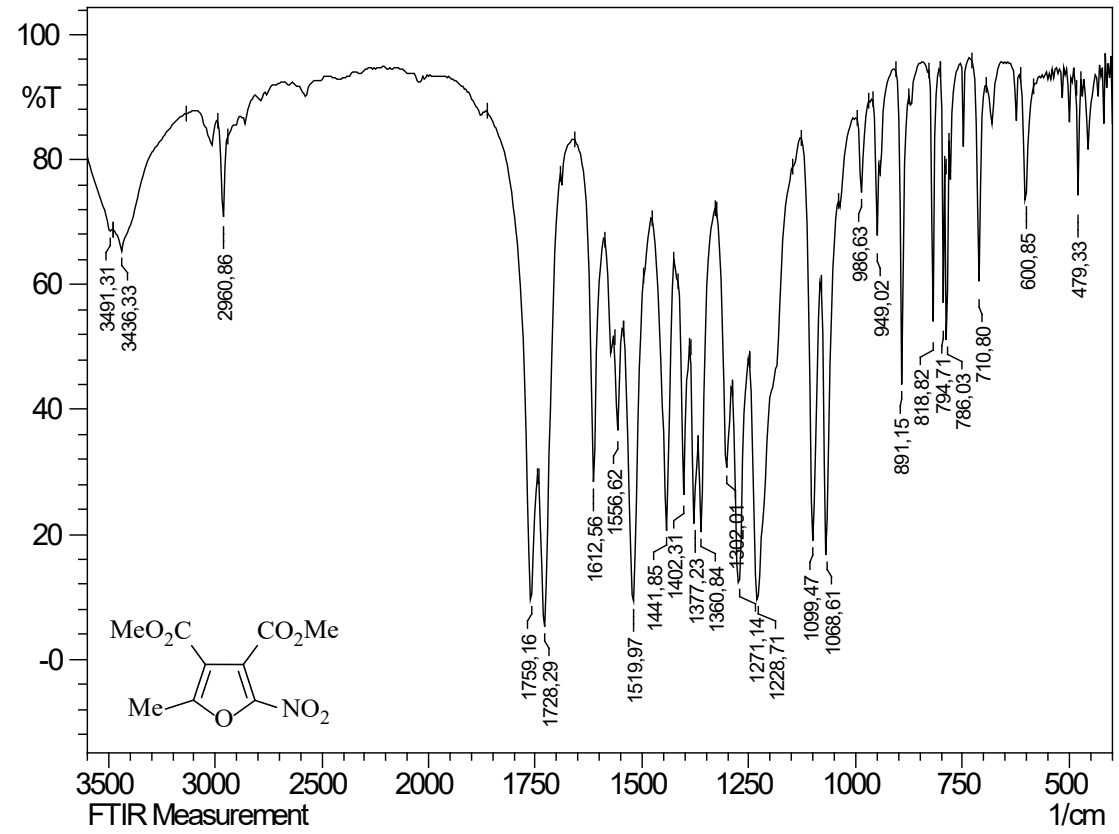

Figure S2. IR spectrum of dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2b** in KBr

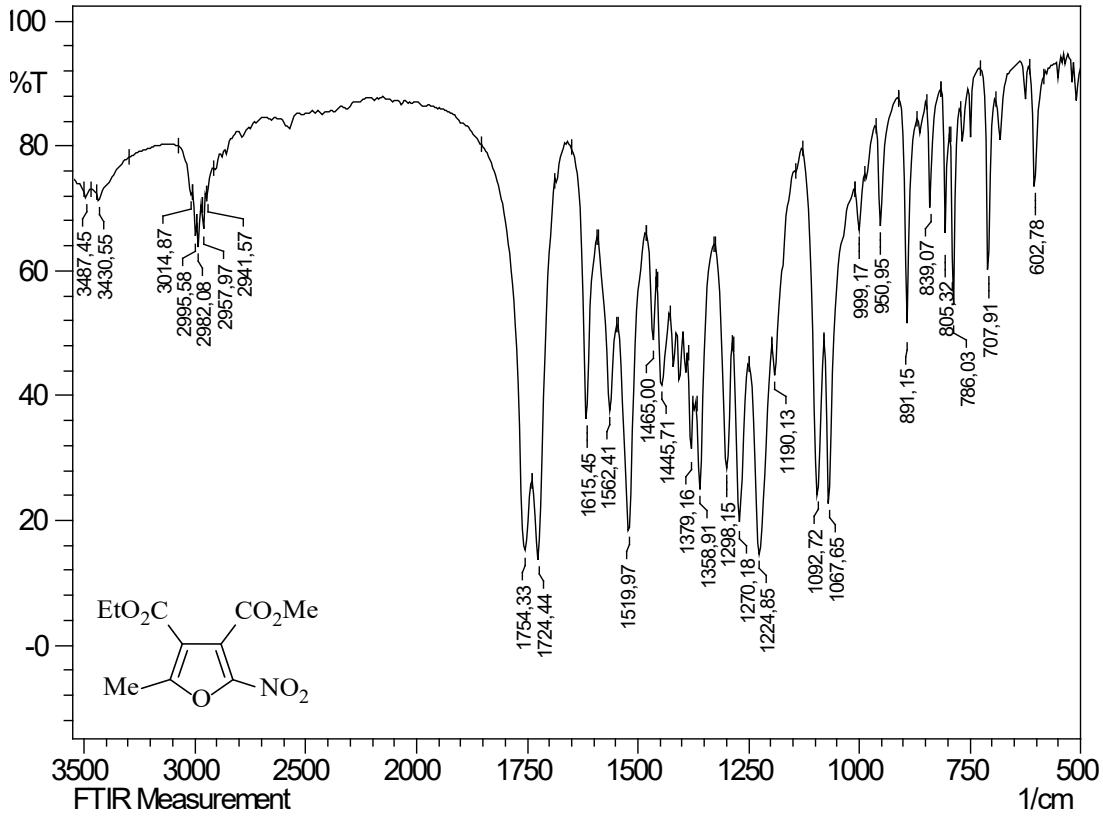

Figure S3. IR spectrum of 3-ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2c** in KBr

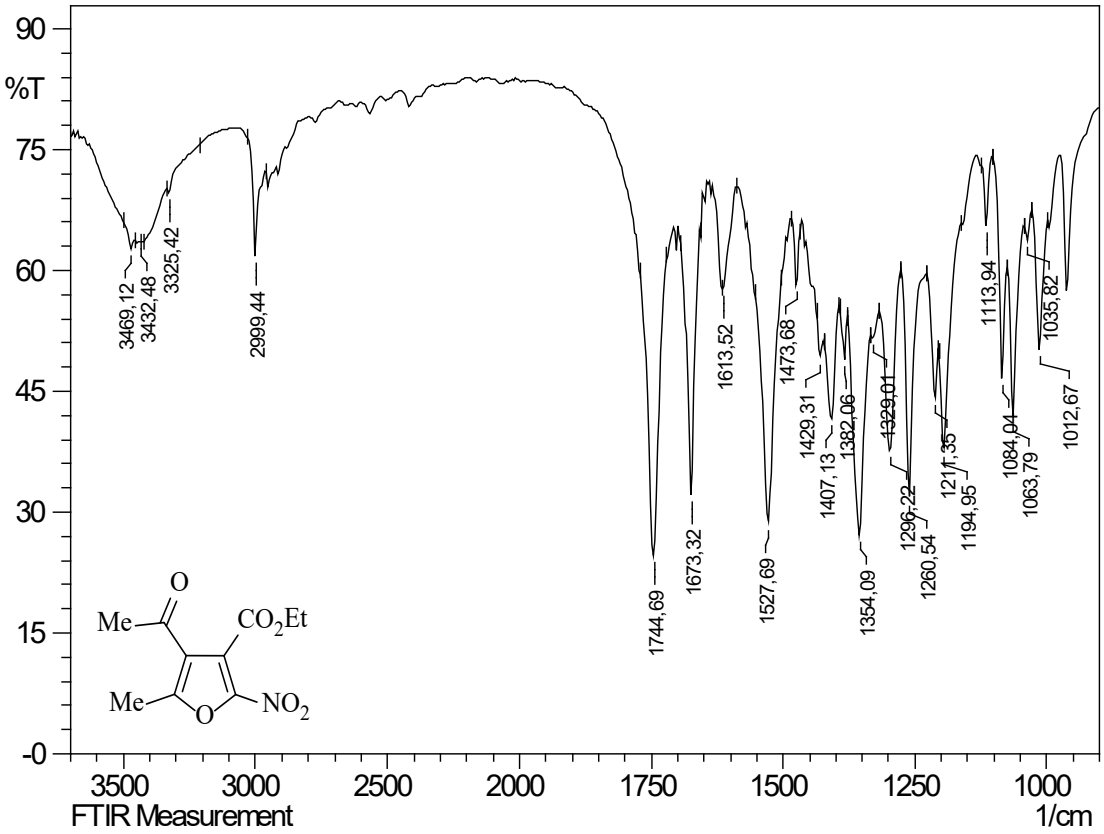

Figure S4. IR spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2d** in KBr

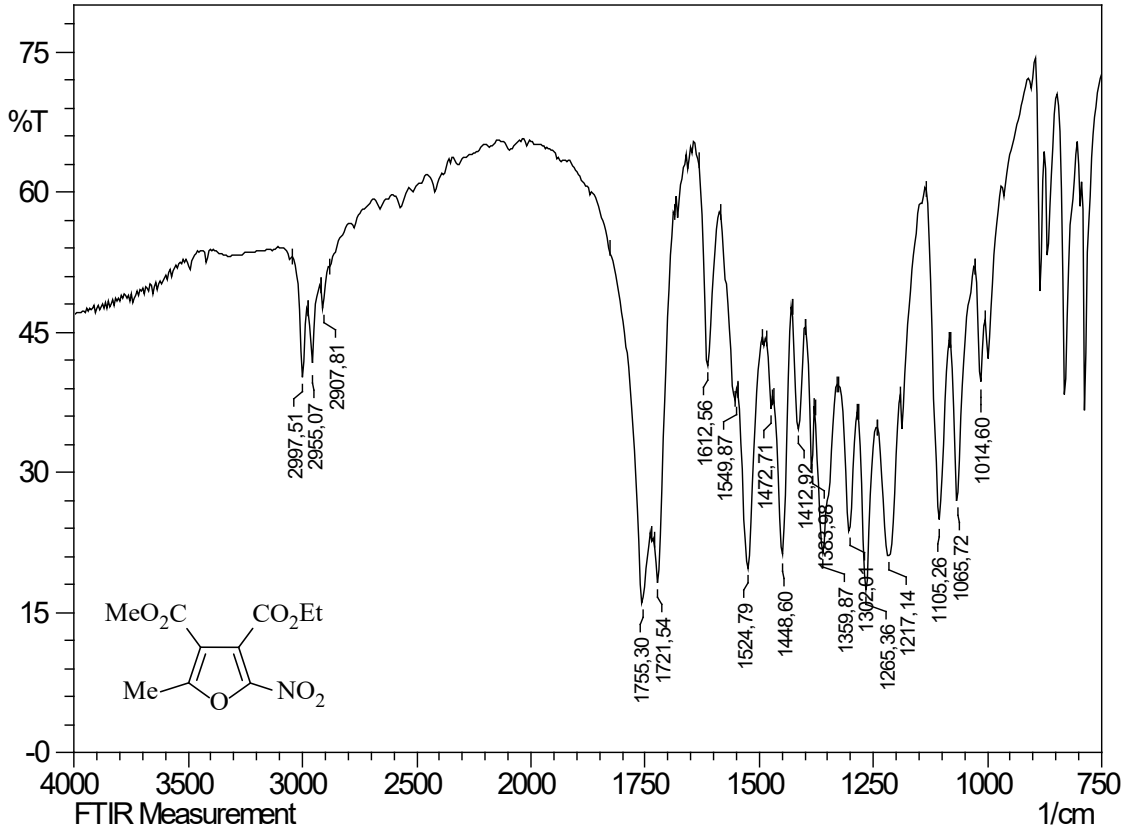

Figure S5. IR spectrum of 4-ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2e** in KBr

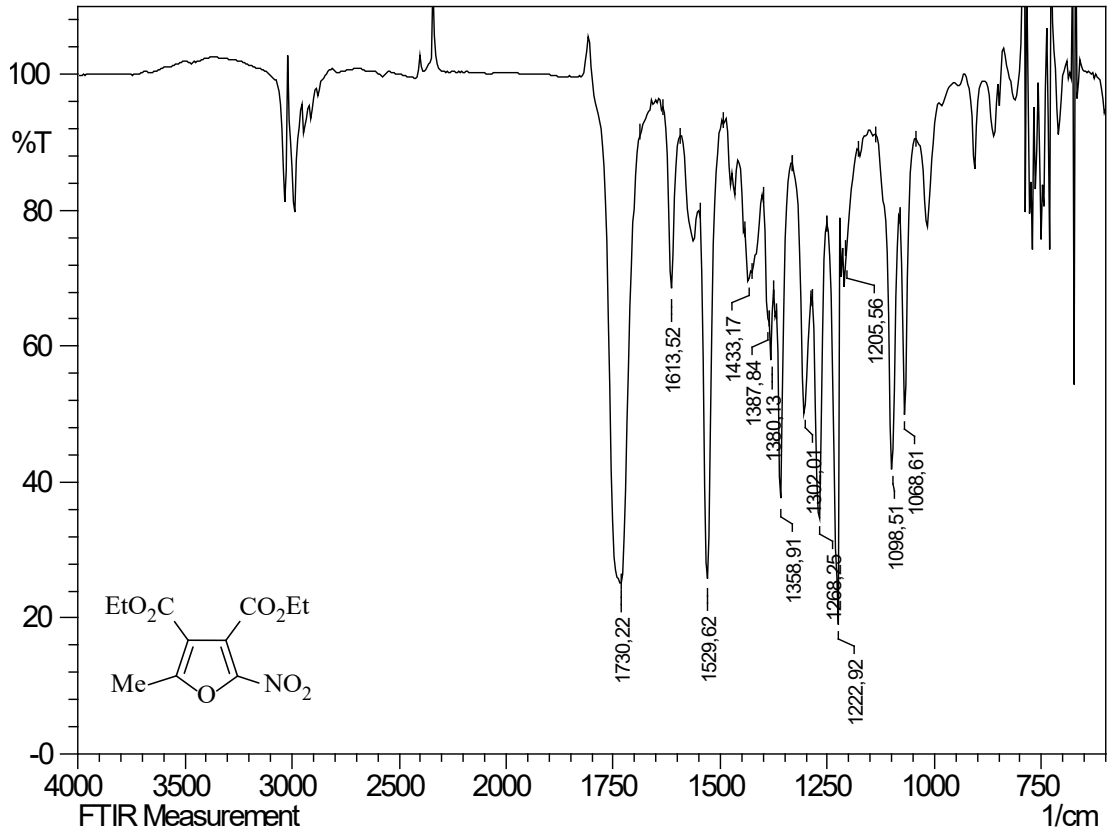

Figure S6. IR spectrum of diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2f** in $CHCl_3$

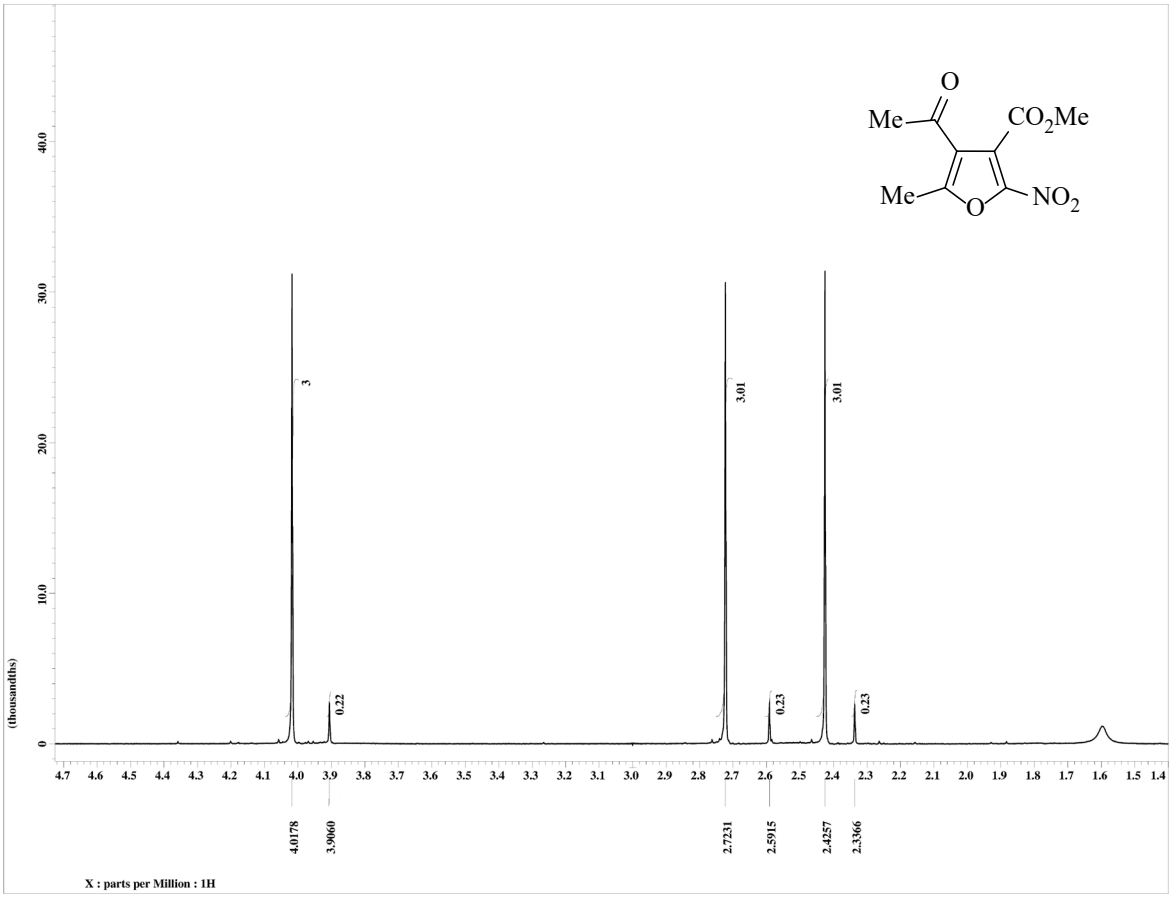

Figure S7. ^{1}H NMR spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2a′** and **2a″** in $CDCl_3$

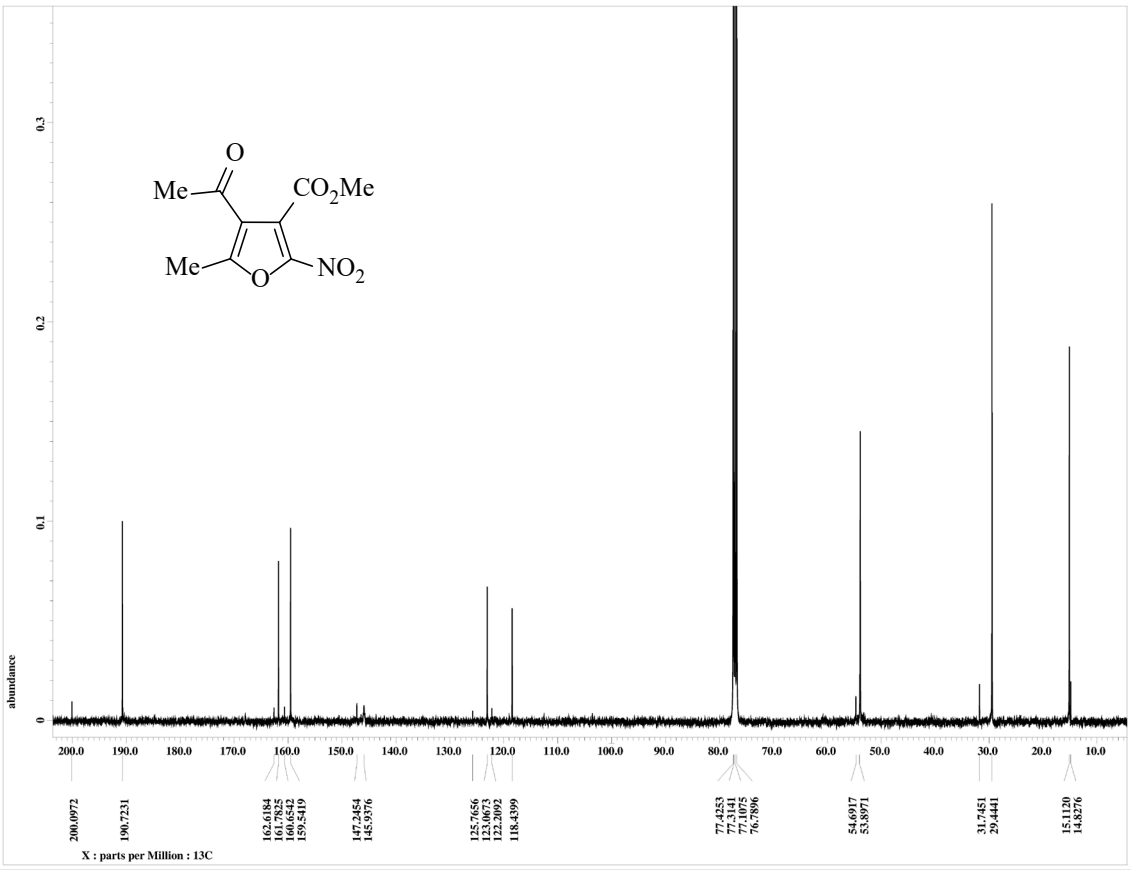

Figure S8. ^{13}C{^{1}H} NMR spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2a′** and **2a″** in $CDCl_3$

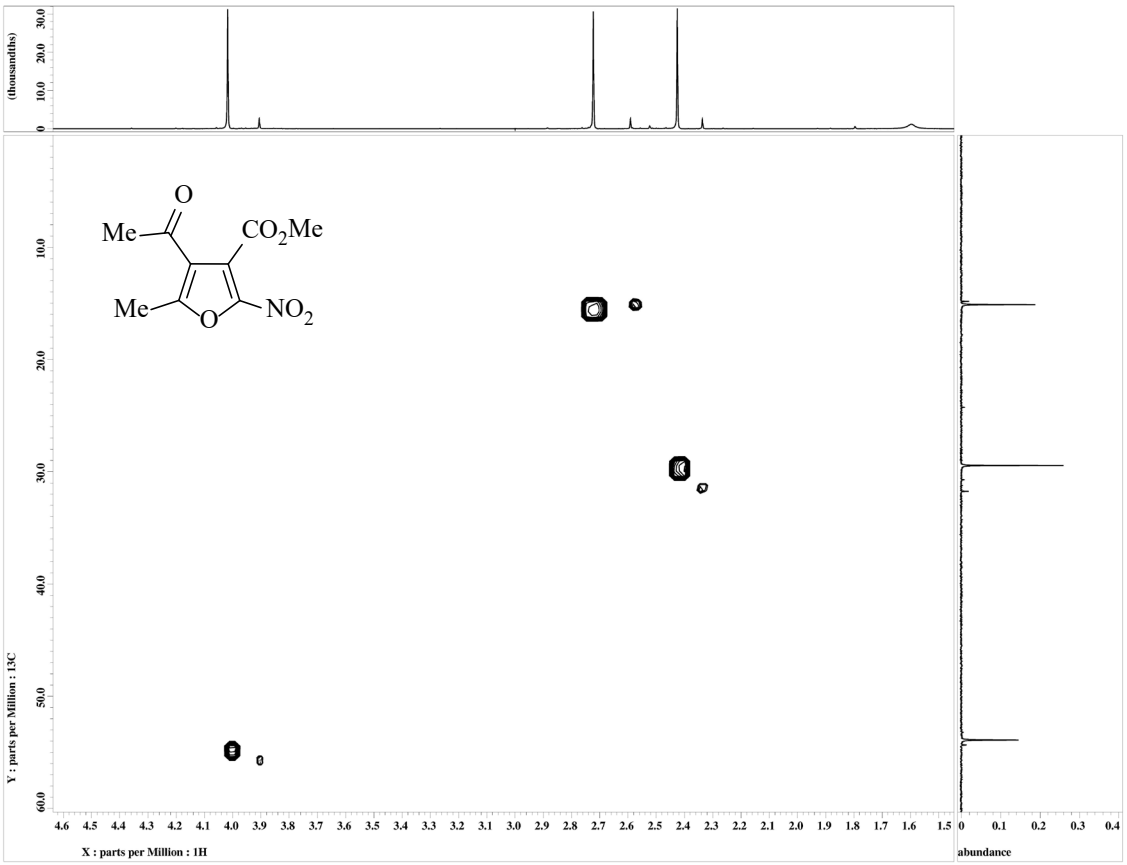

Figure S9. $^{1}H–^{13}C$ HMQC spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2a′** and **2a″** in $CDCl_3$

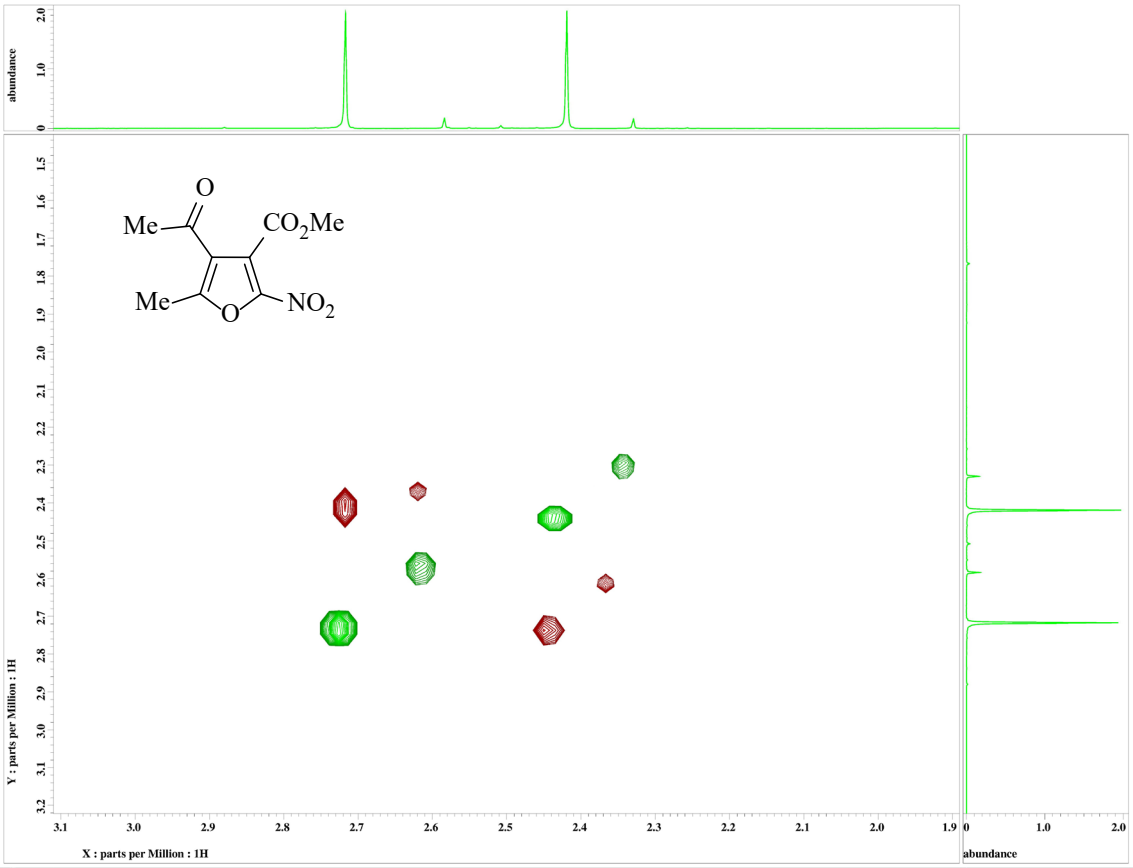

Figure S10. $^{1}H–^{1}H$ NOESY spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2a′** and **2a″** in $CDCl_3$

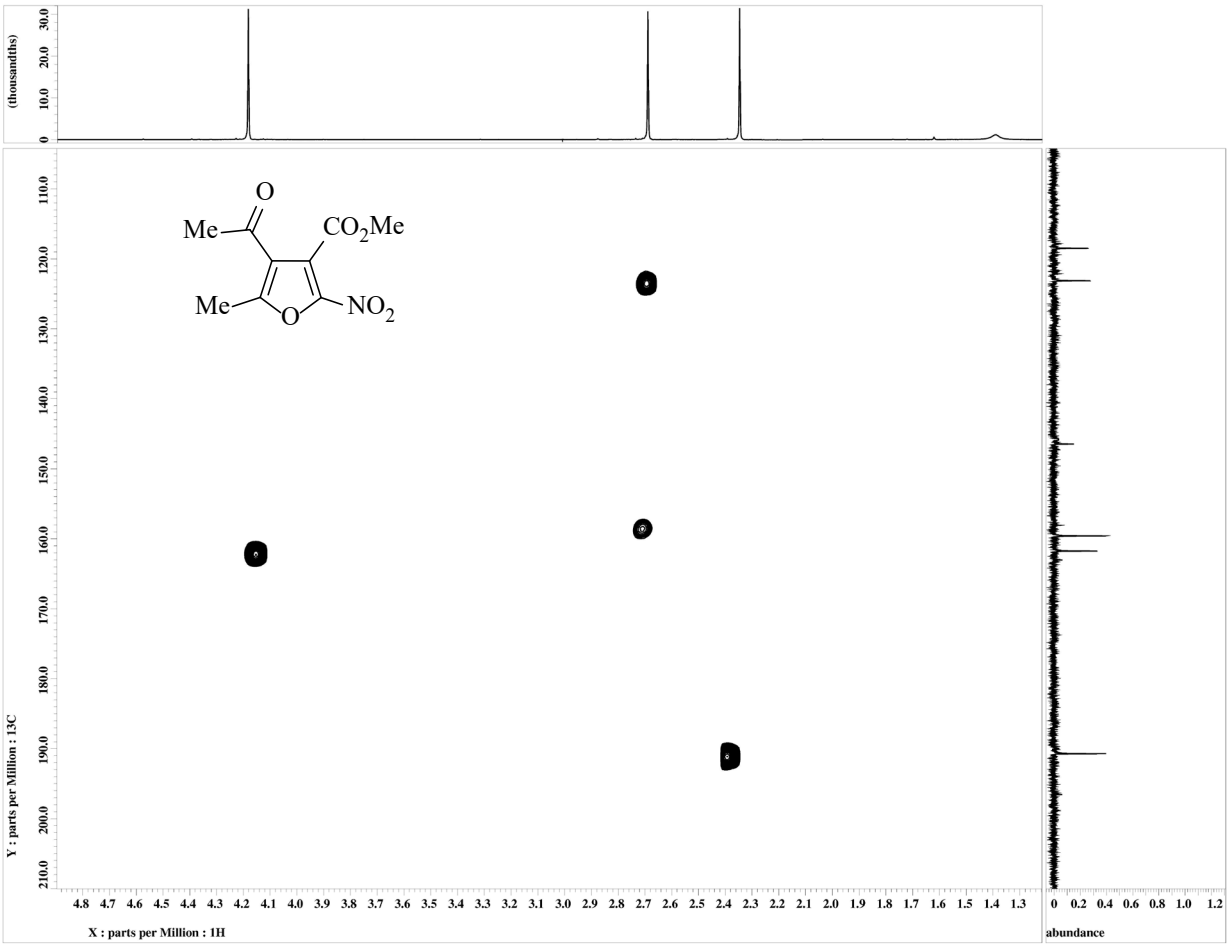

Figure S11. $^{1}H–^{13}C$ HMBC spectrum of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2a′** in $CDCl_3$

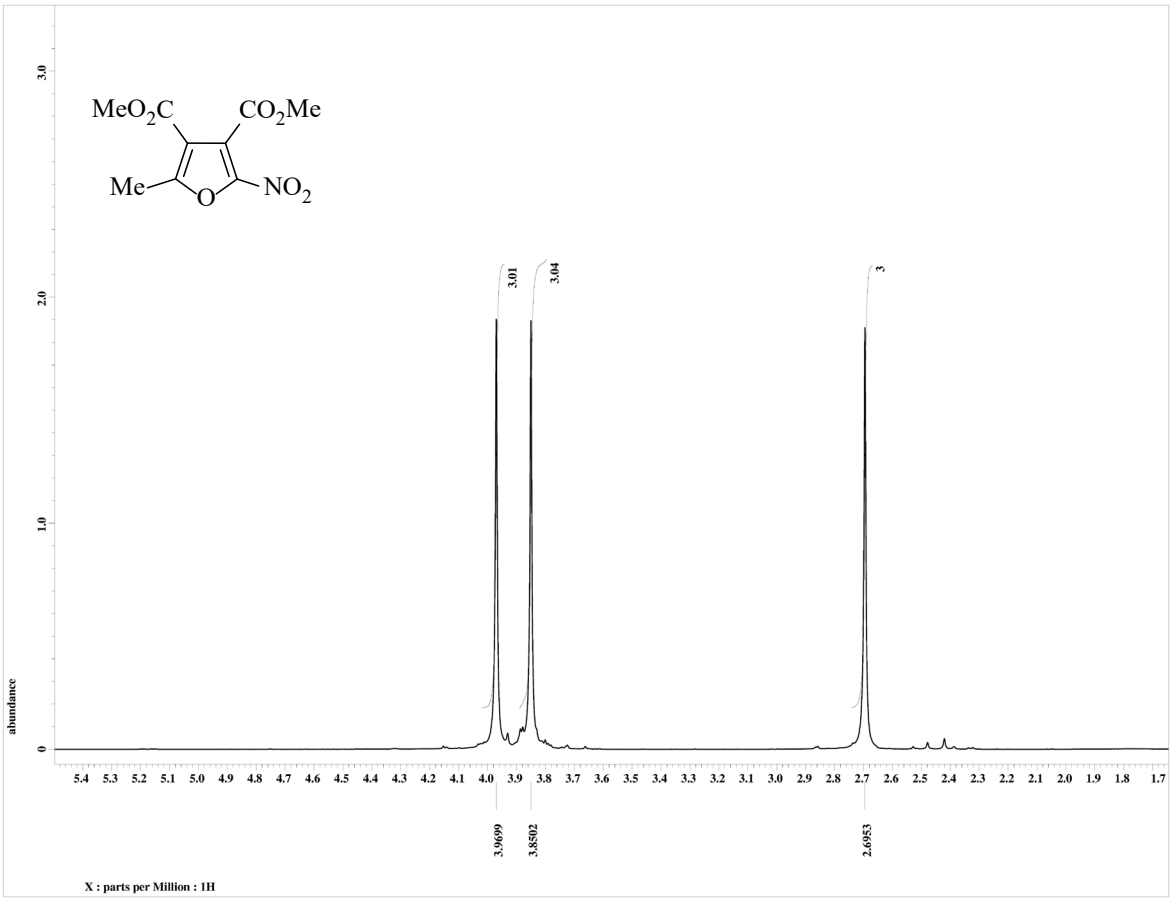

Figure S12. ^{1}H NMR spectrum of dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

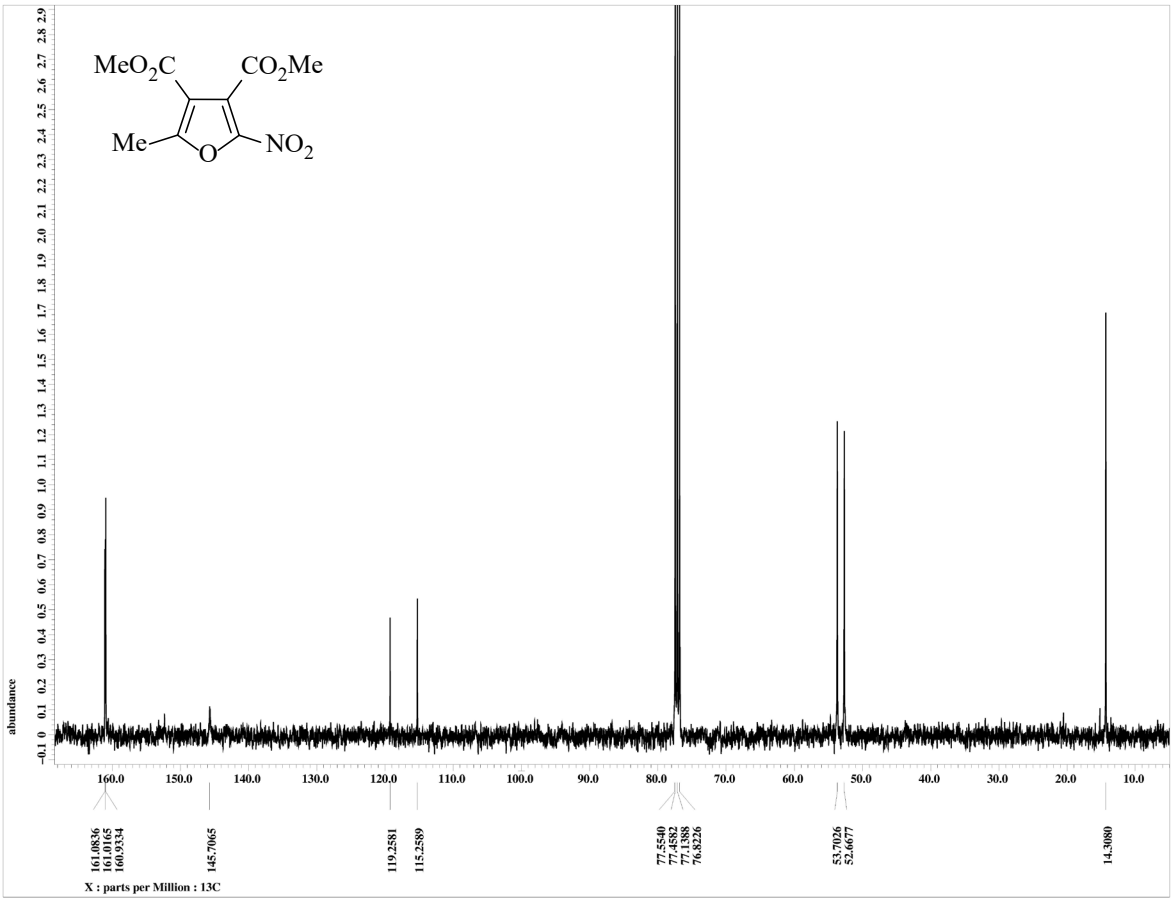

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

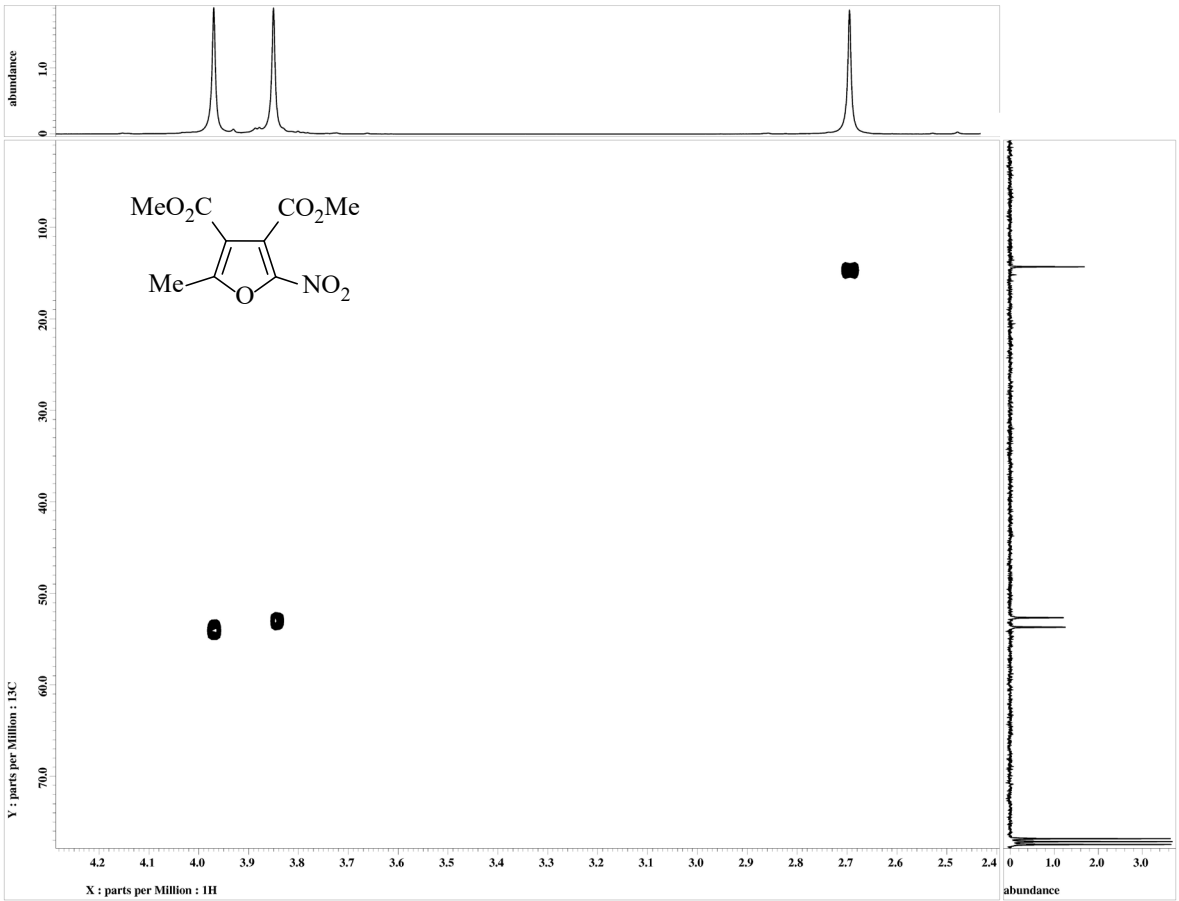

Figure S14. $^{1}H–^{13}C$ HMQC spectrum of dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

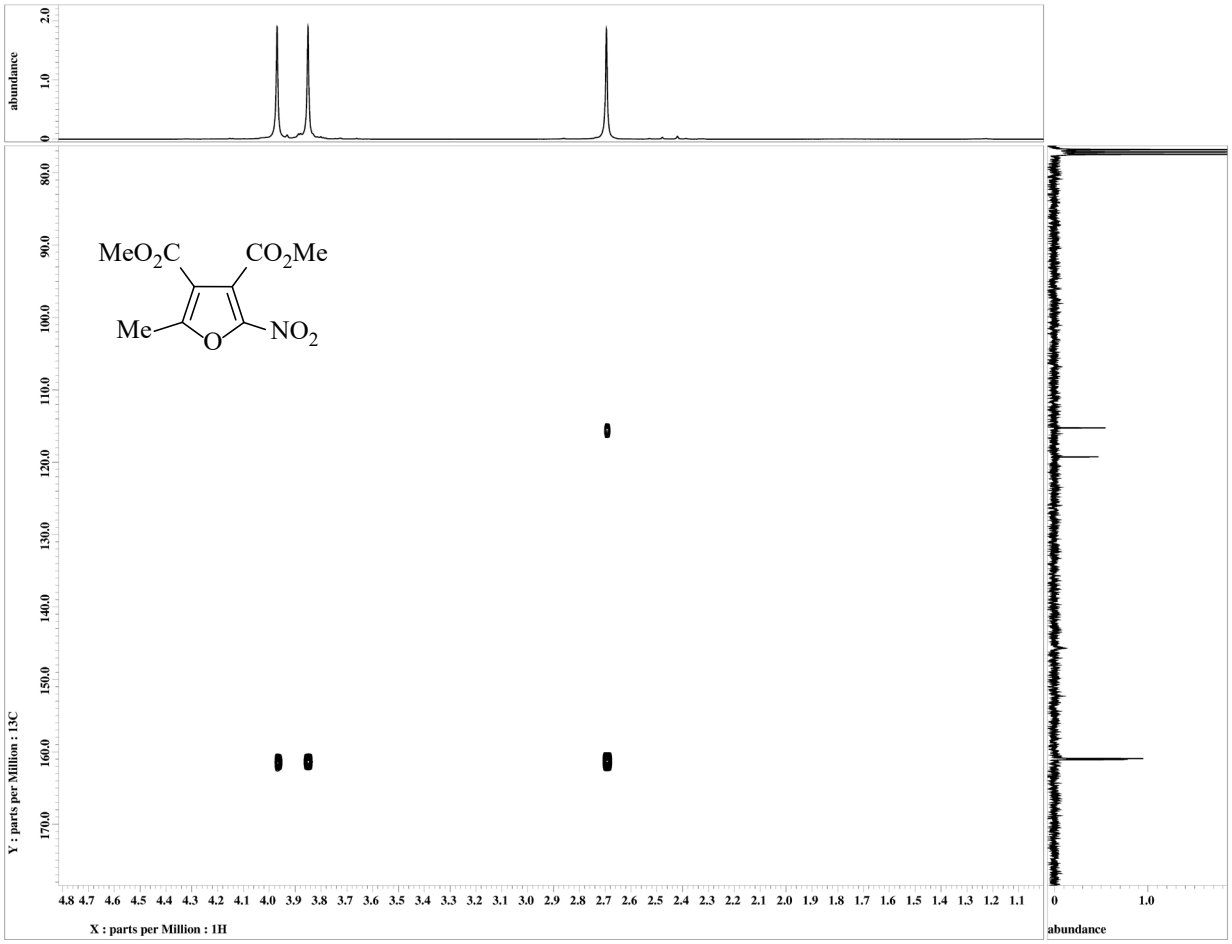

Figure S15. $^{1}H–^{13}C$ HMBC spectrum of dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

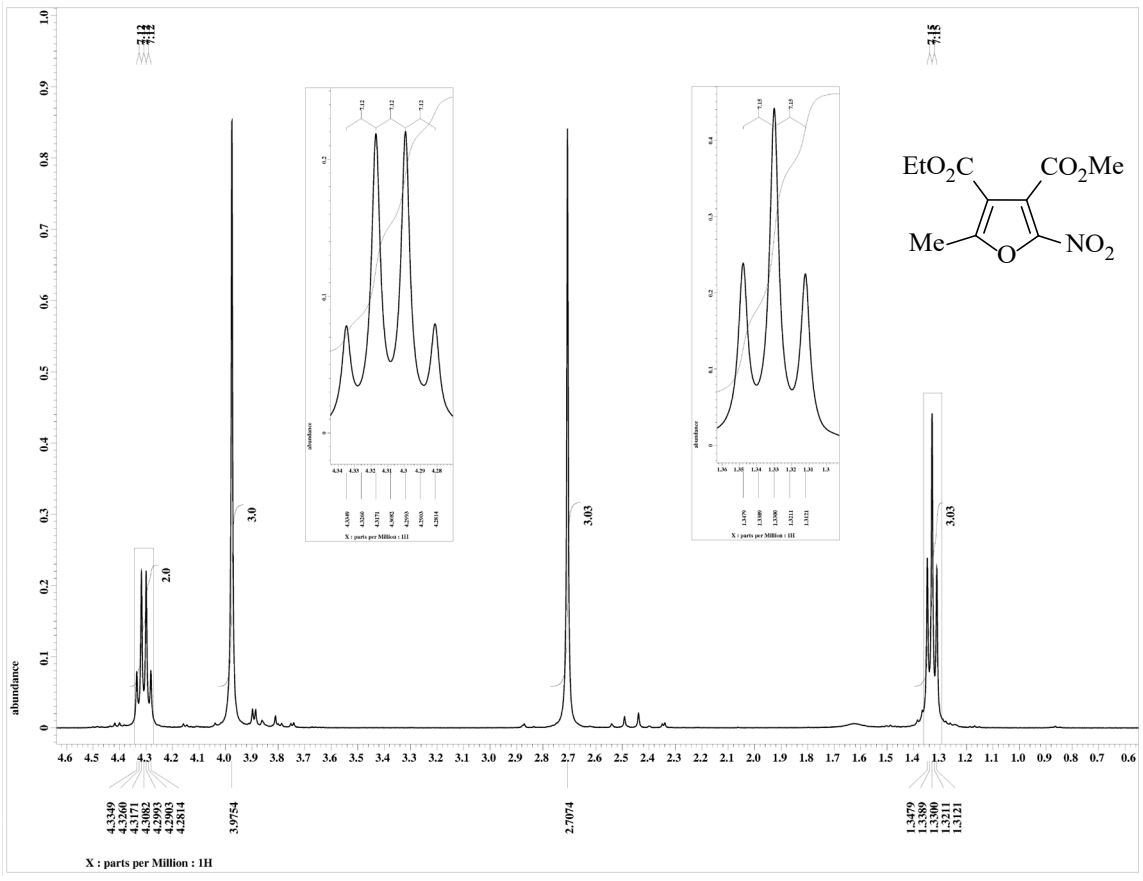

Figure S16. ^{1}H NMR spectrum of 3-ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

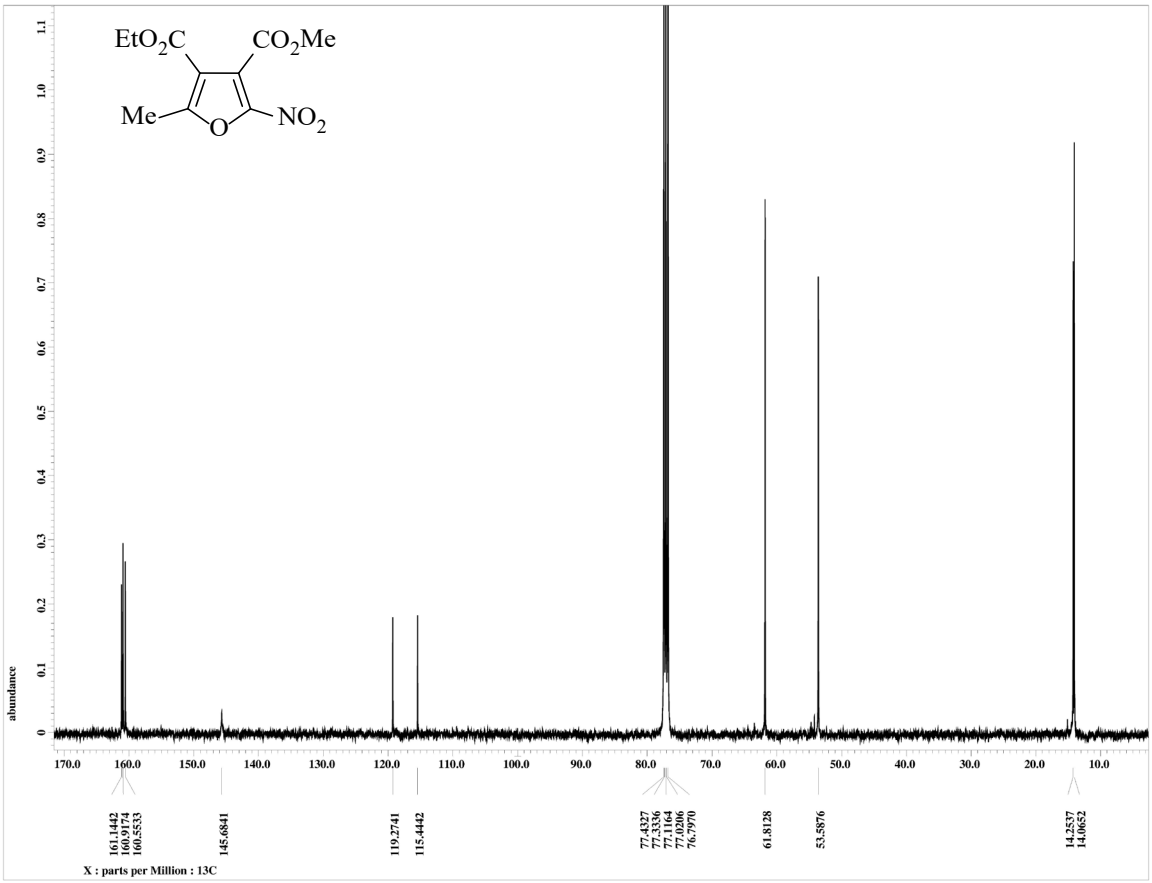

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of 3-ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

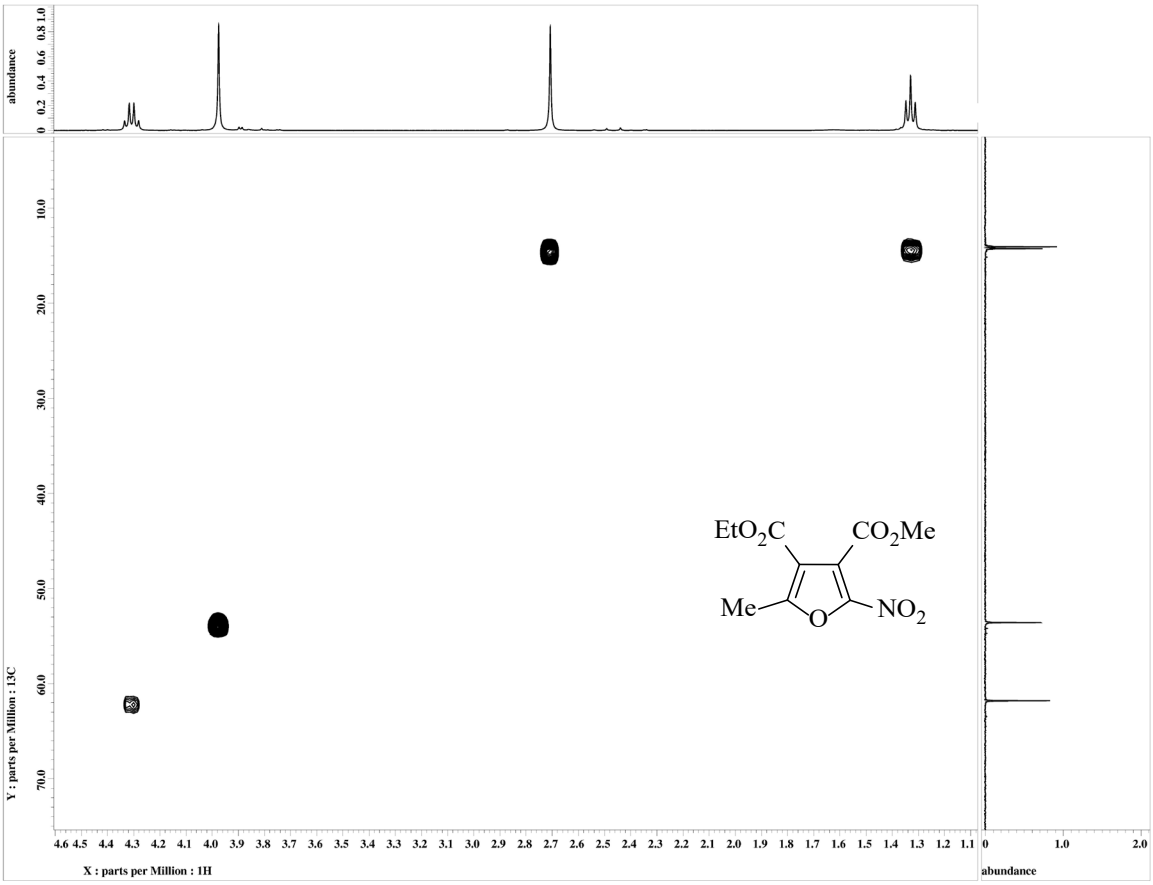

Figure S18. $^{1}H–^{13}C$ HMQC spectrum of 3-ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

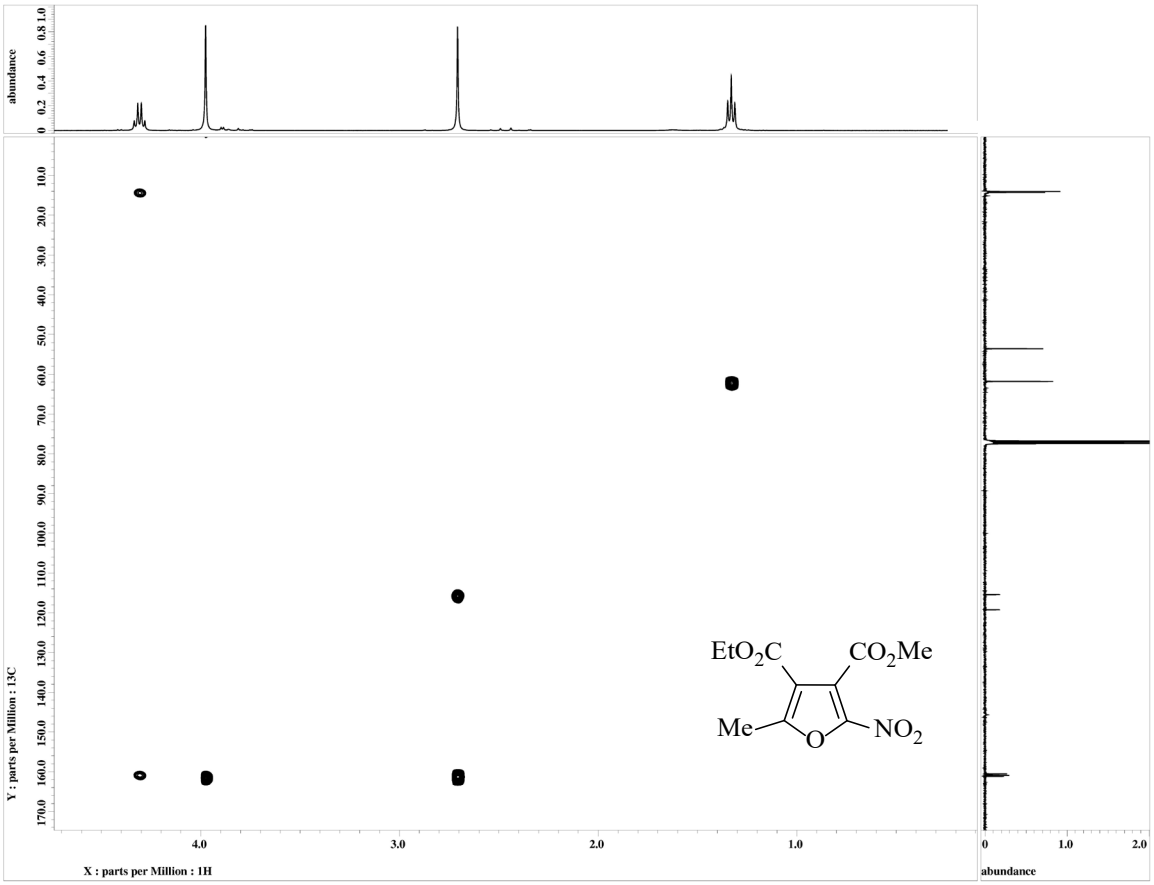

Figure S19. $^{1}H–^{13}C$ HMBC spectrum of 3-ethyl 4-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

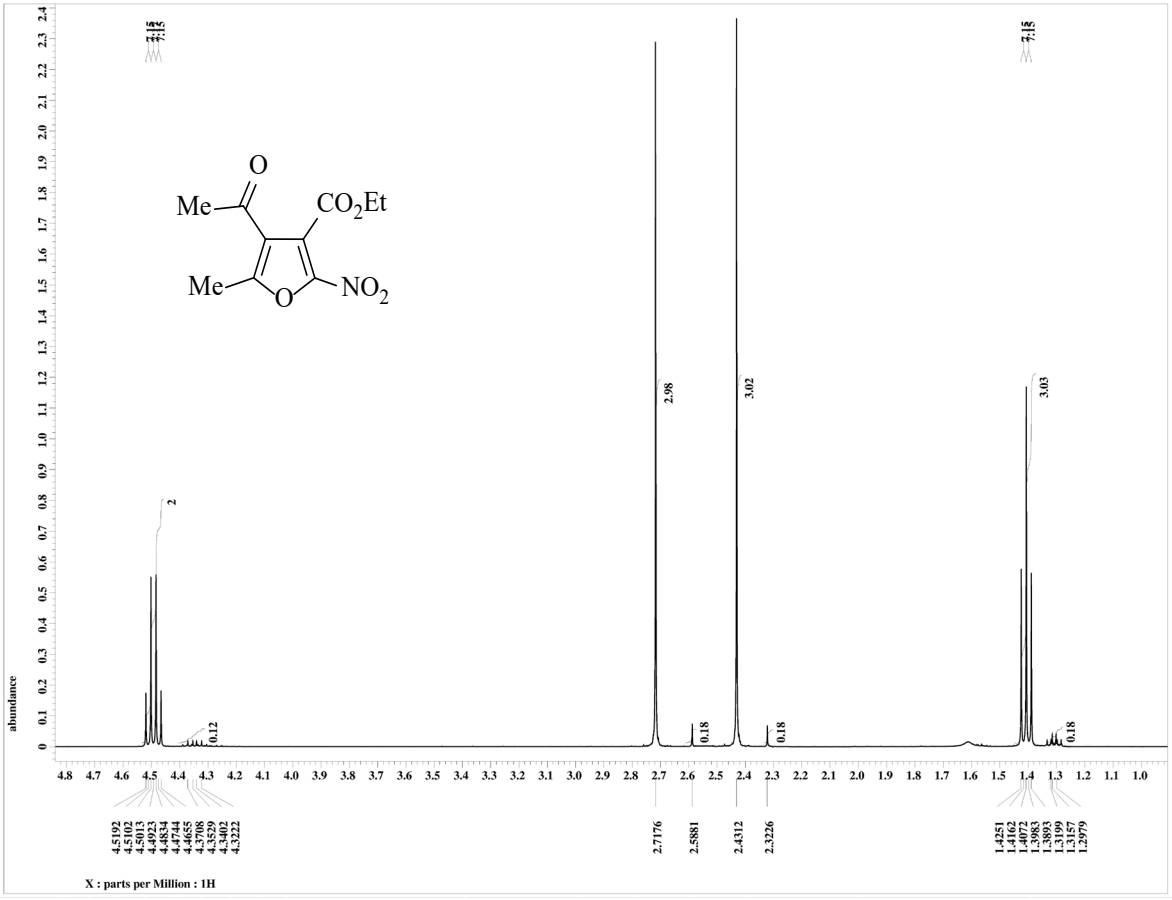

Figure S20. ^{1}H NMR spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2d′** and **2d″** in $CDCl_3$

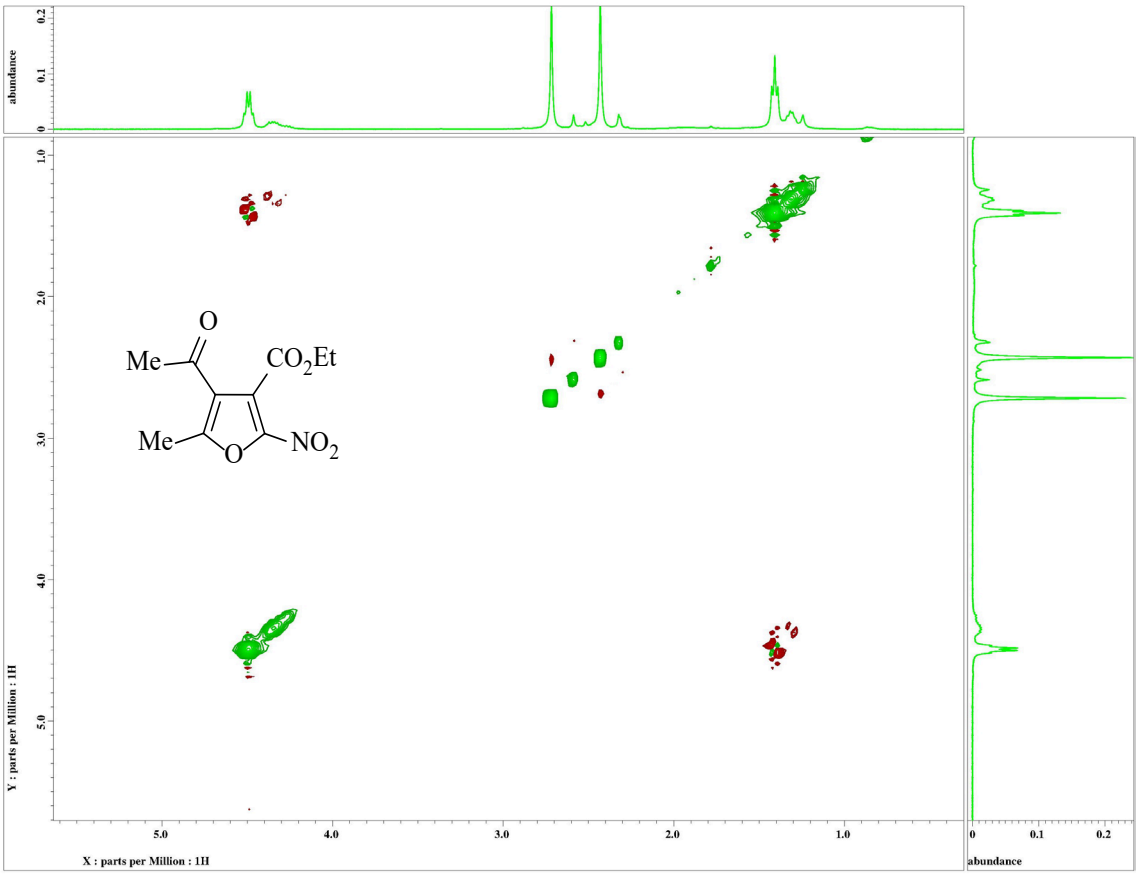

Figure S21. $^{1}H–^{1}H$ NOESY spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2d′** and **2d″** in $CDCl_3$

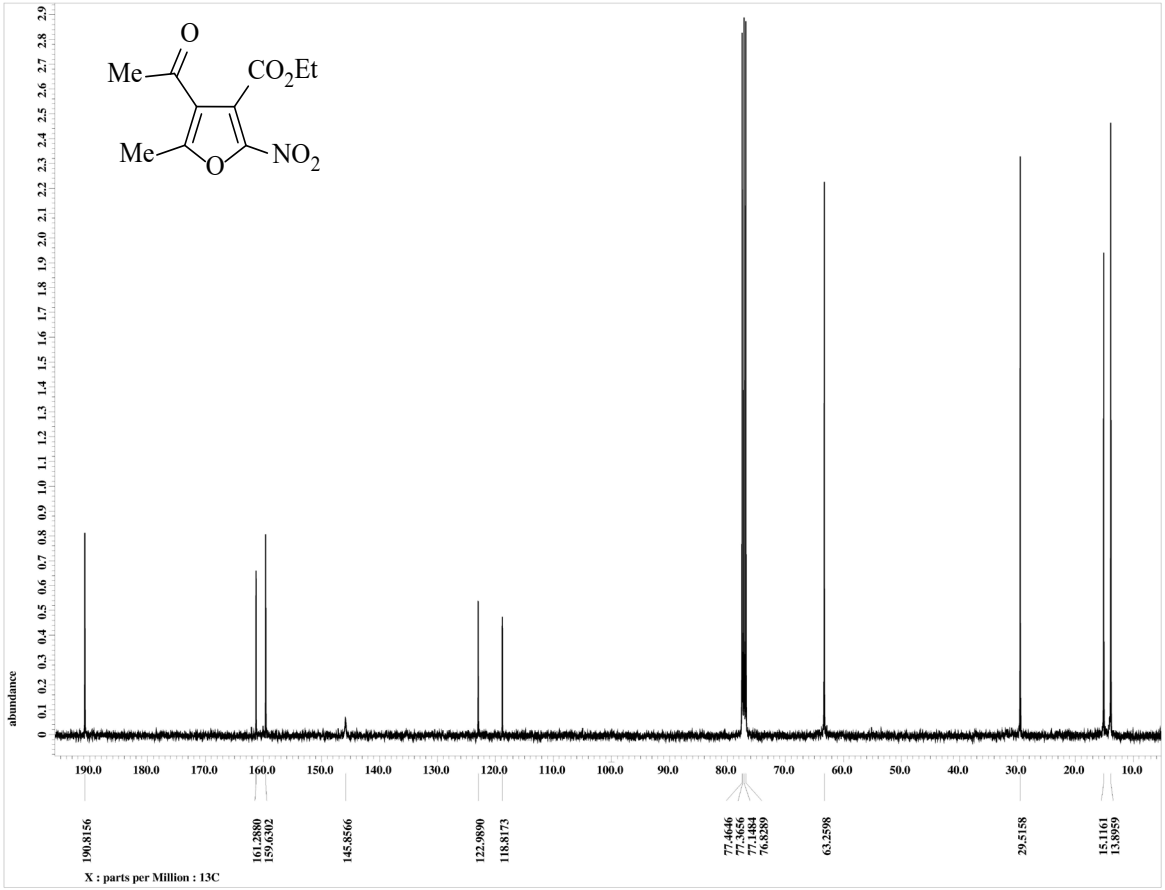

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2d′** in $CDCl_3$

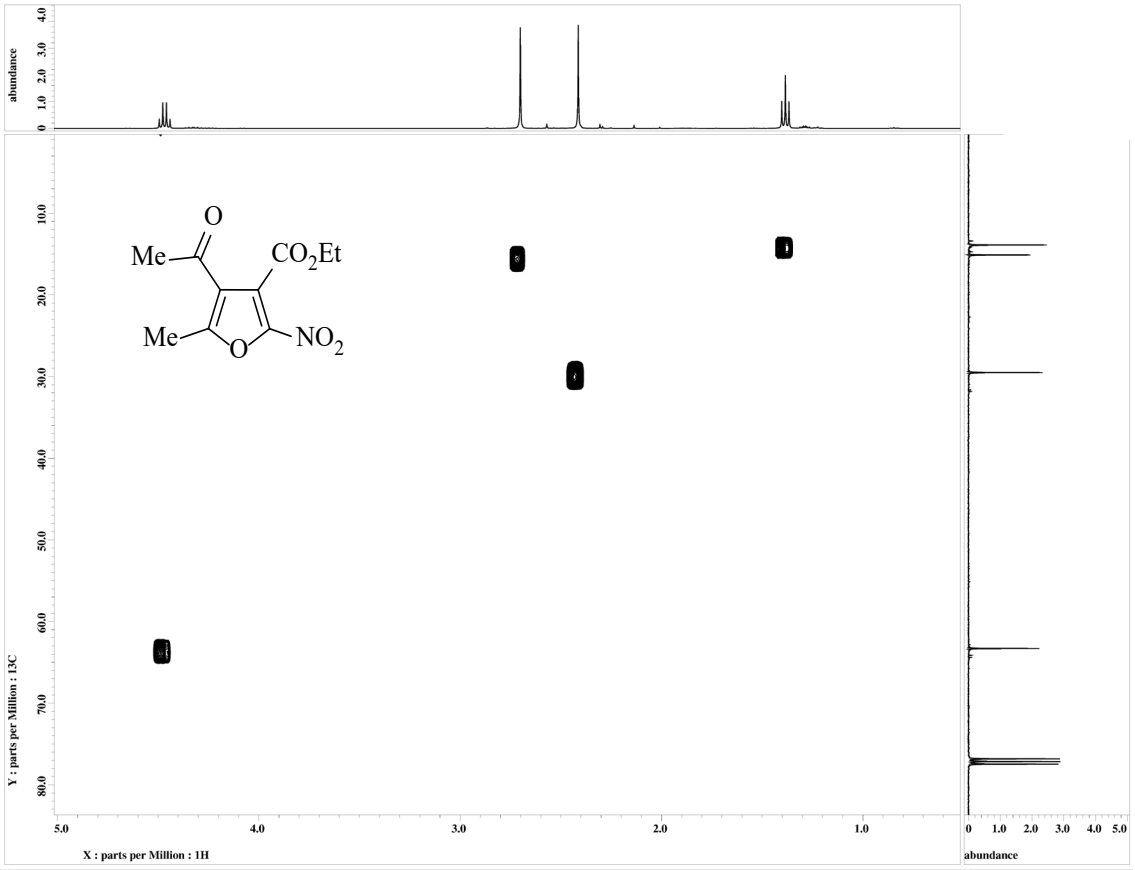

Figure S23. $^{1}H–^{13}C$ HMQC spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2d′** in $CDCl_3$

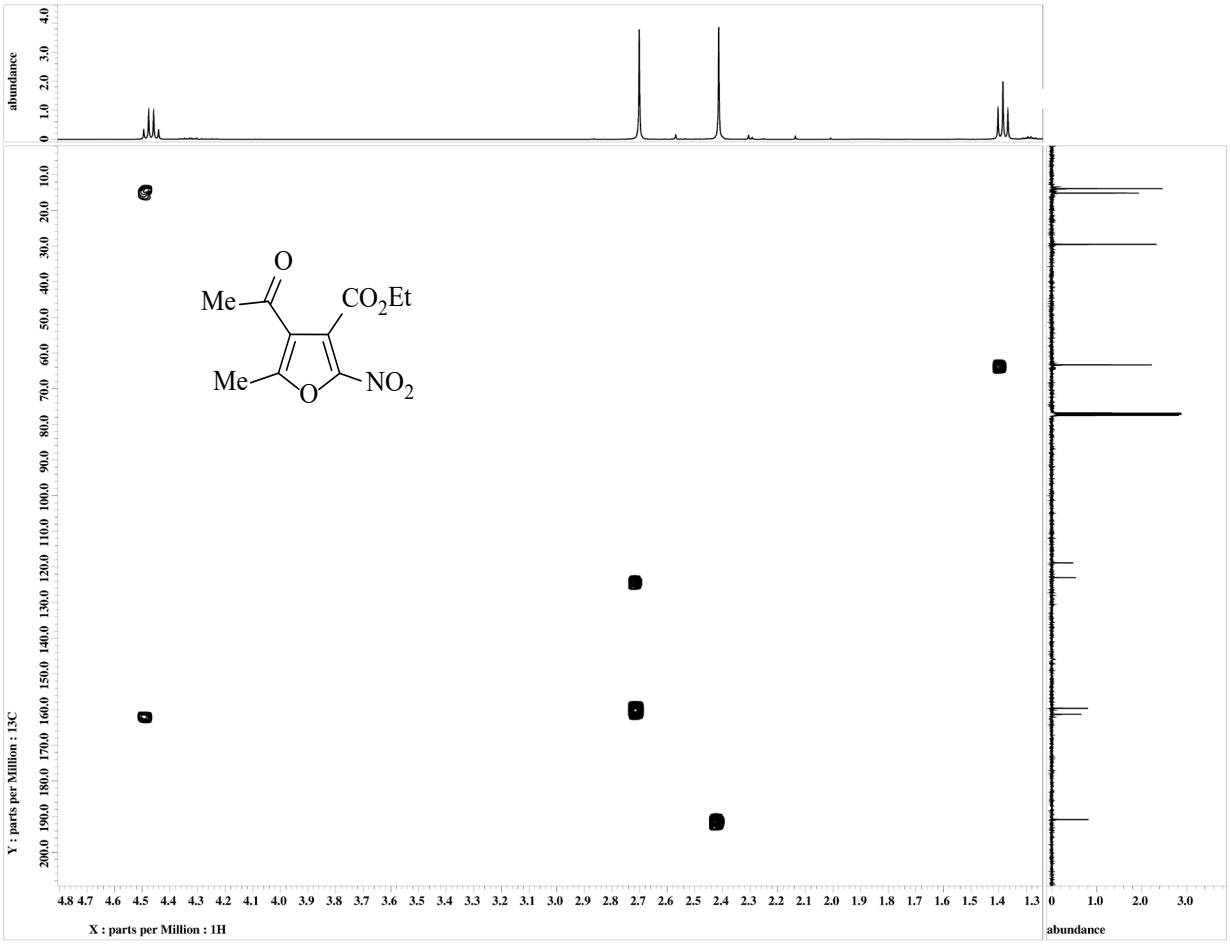

Figure S24. $^{1}H–^{13}C$ HMBC spectrum of ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate **2d′** in $CDCl_3$

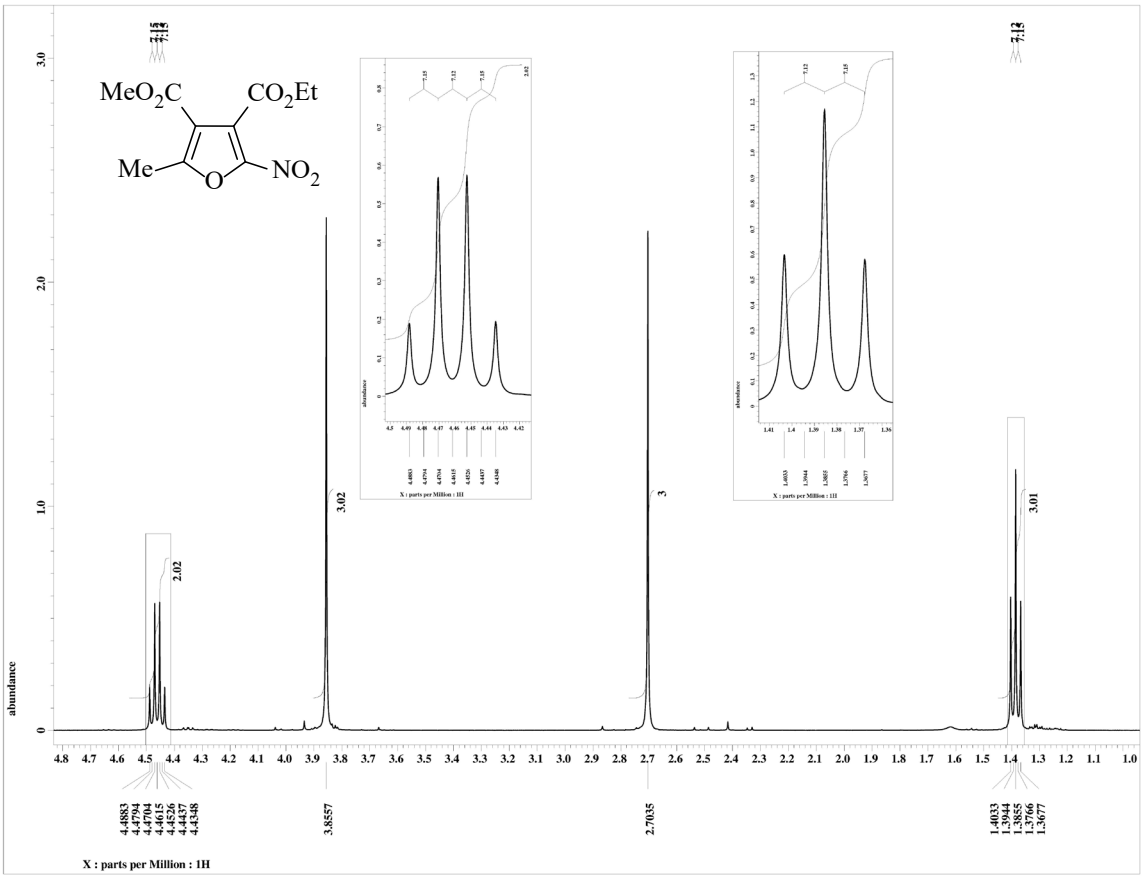

Figure S25. ^{1}H NMR spectrum of 4-ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

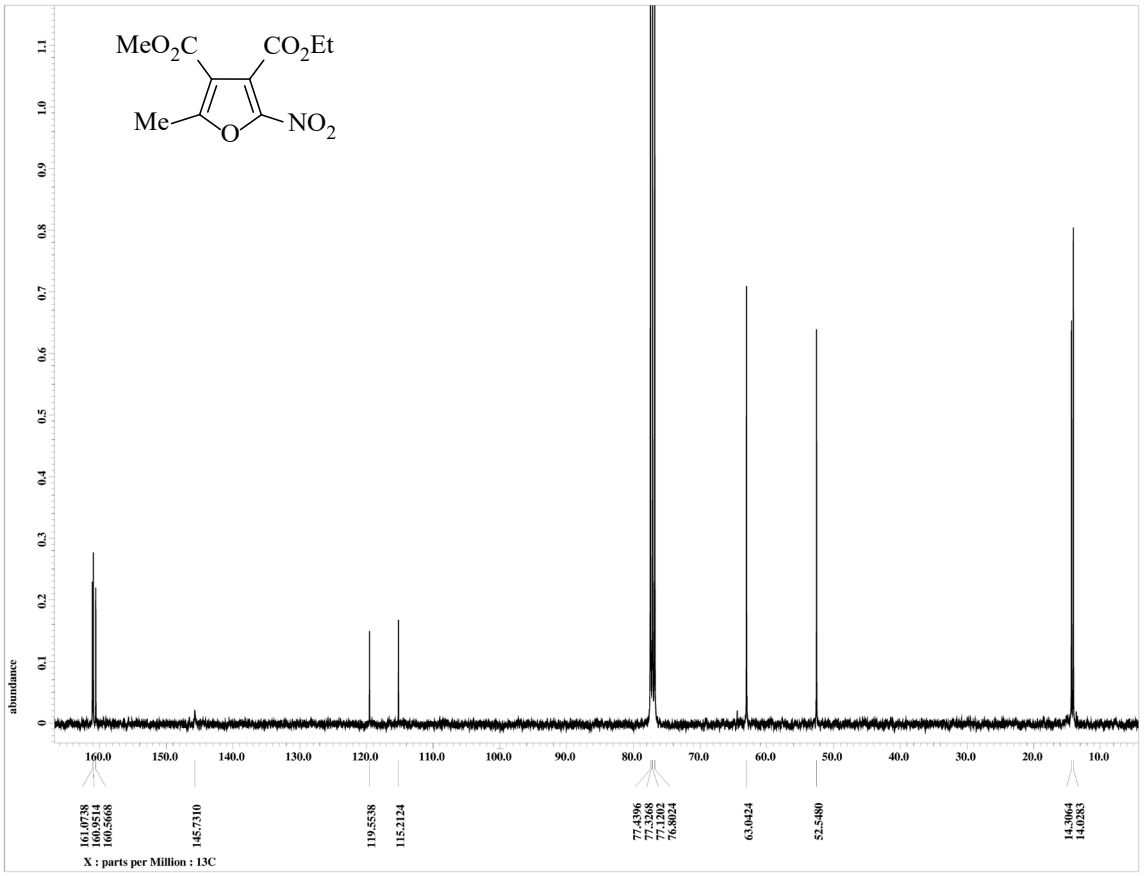

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

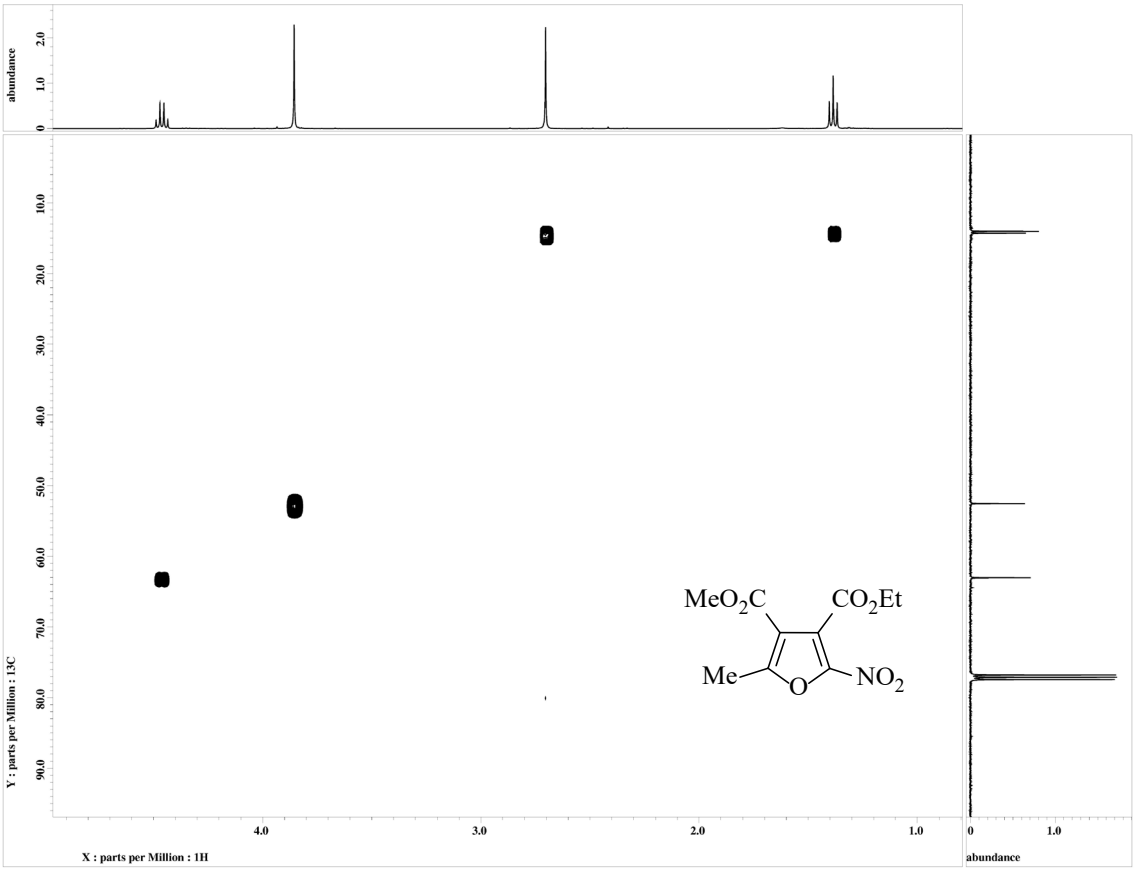

Figure S27. $^{1}H–^{13}C$ HMQC spectrum of 4-ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

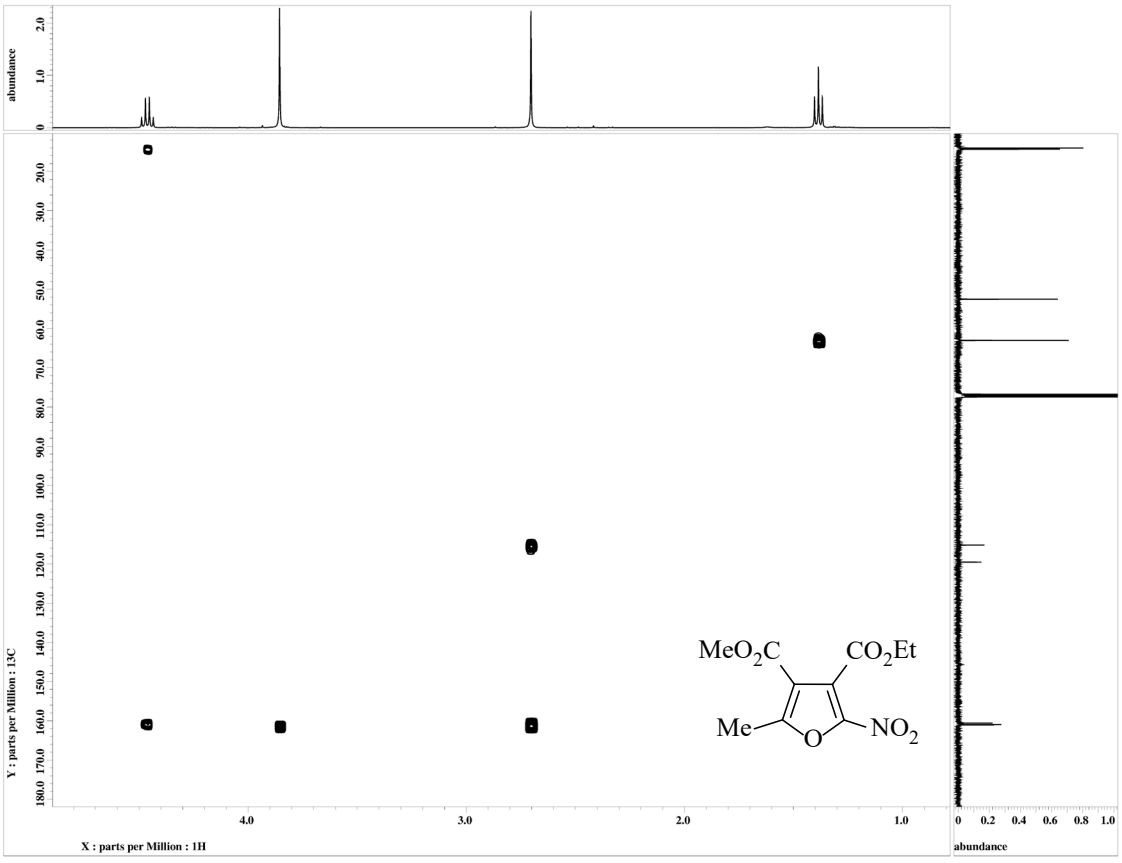

Figure S28. $^{1}H–^{13}C$ HMBC spectrum of 4-ethyl 3-methyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

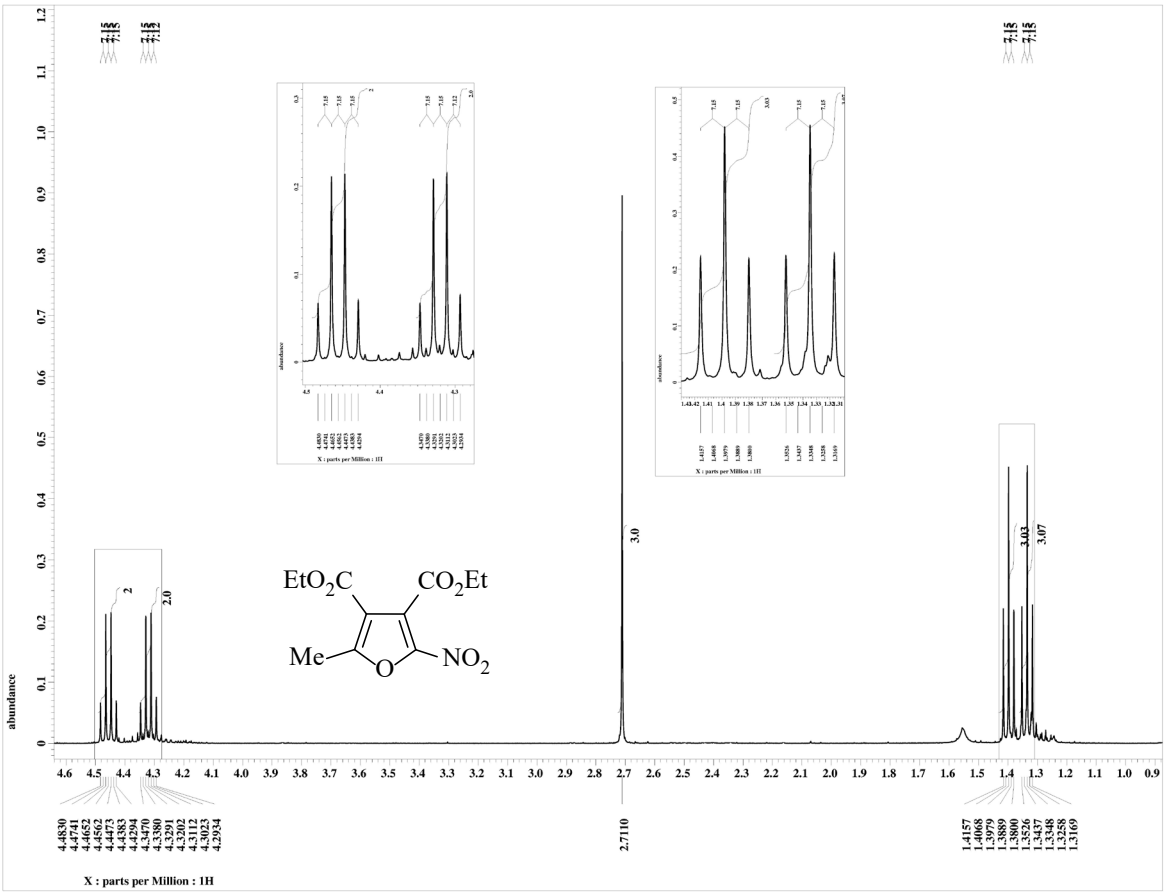

Figure S29. ^{1}H NMR spectrum of diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

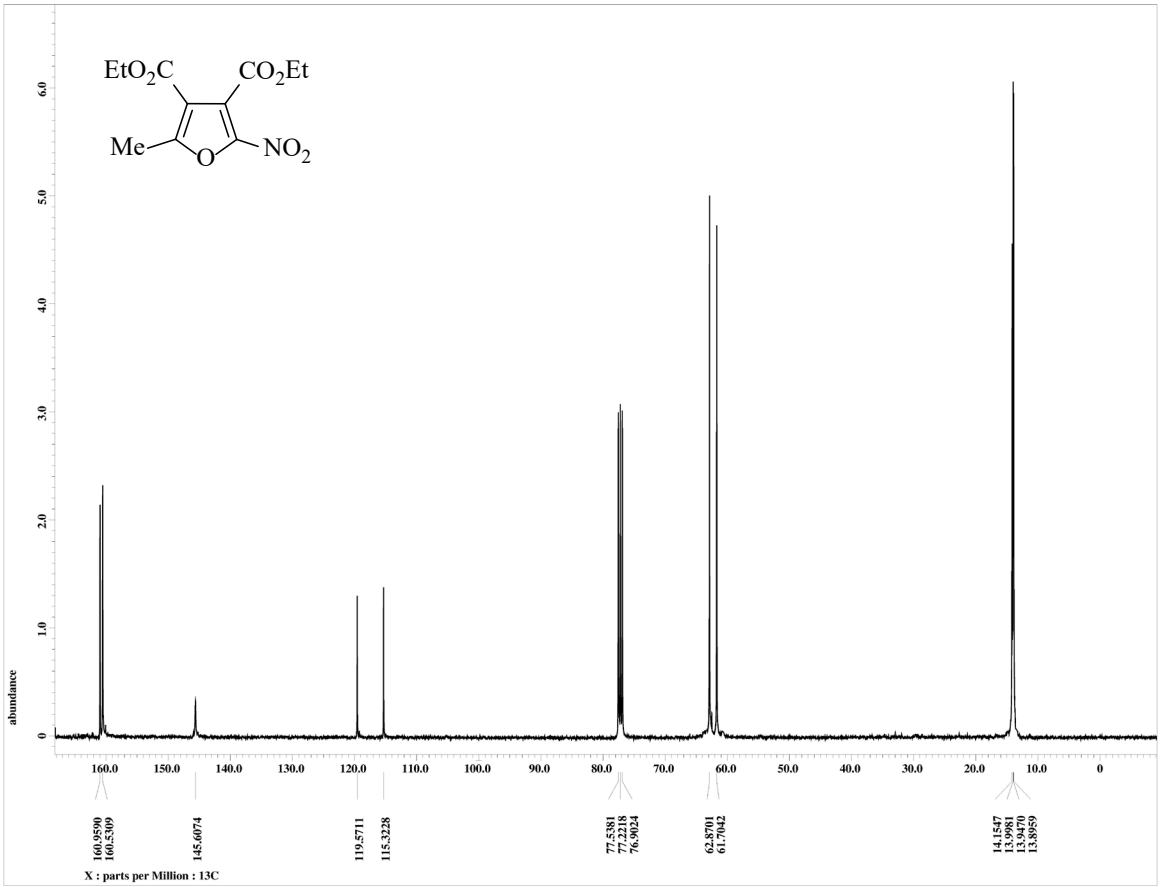

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

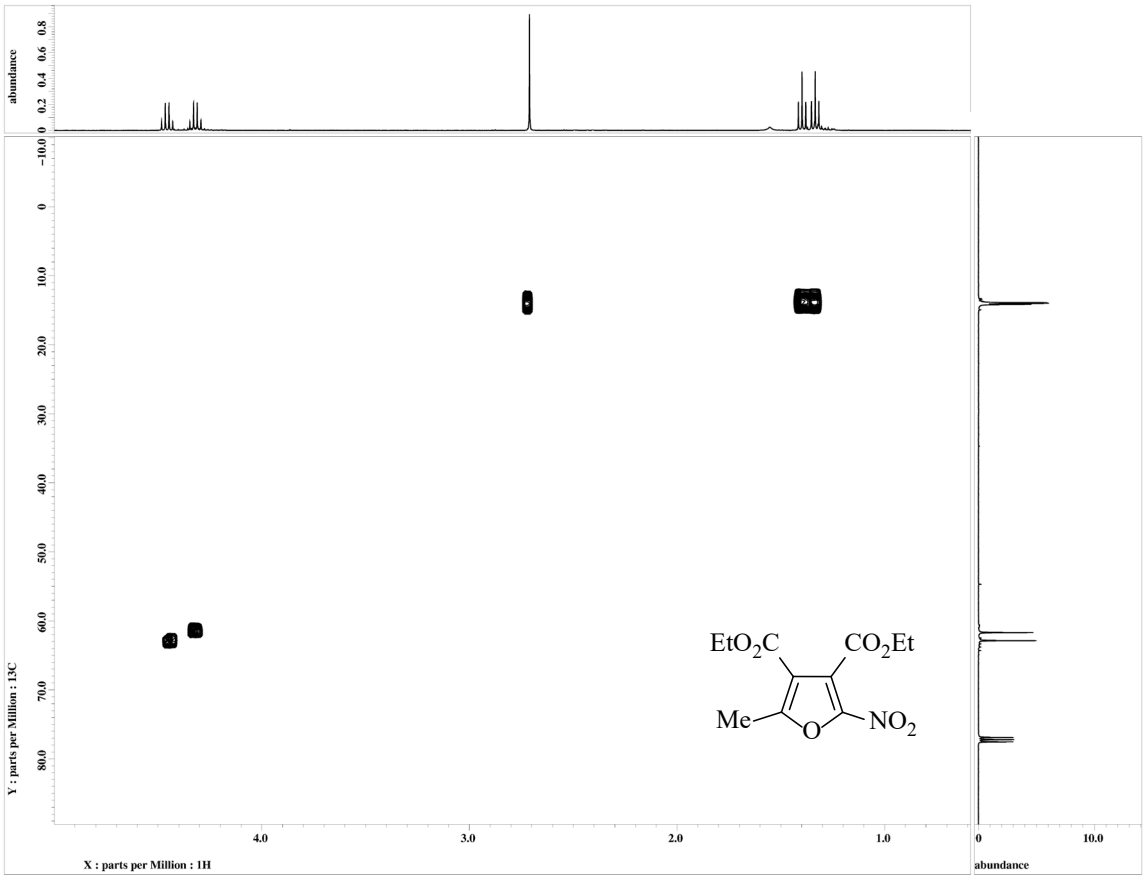

Figure S31. $^{1}H–^{13}C$ HMQC spectrum of diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

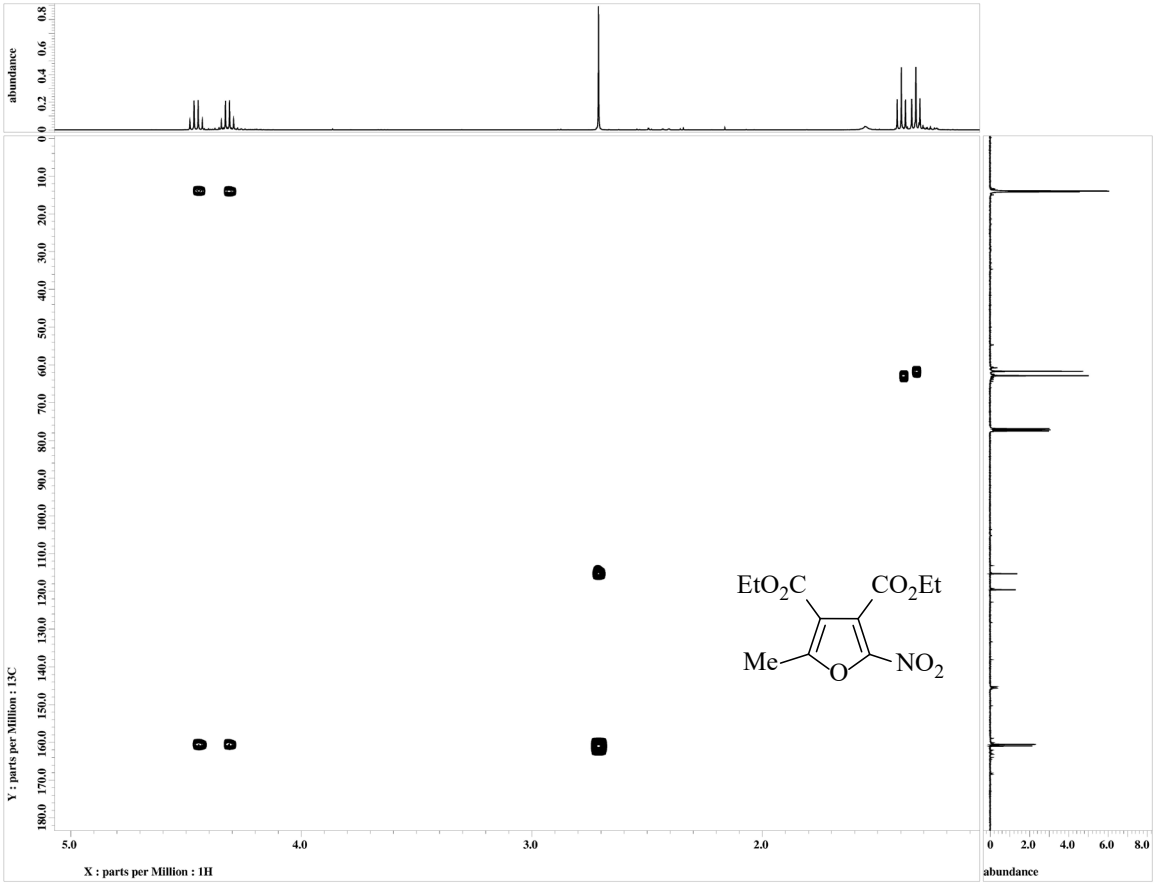

Figure S32. $^{1}H–^{13}C$ HMBC spectrum of diethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

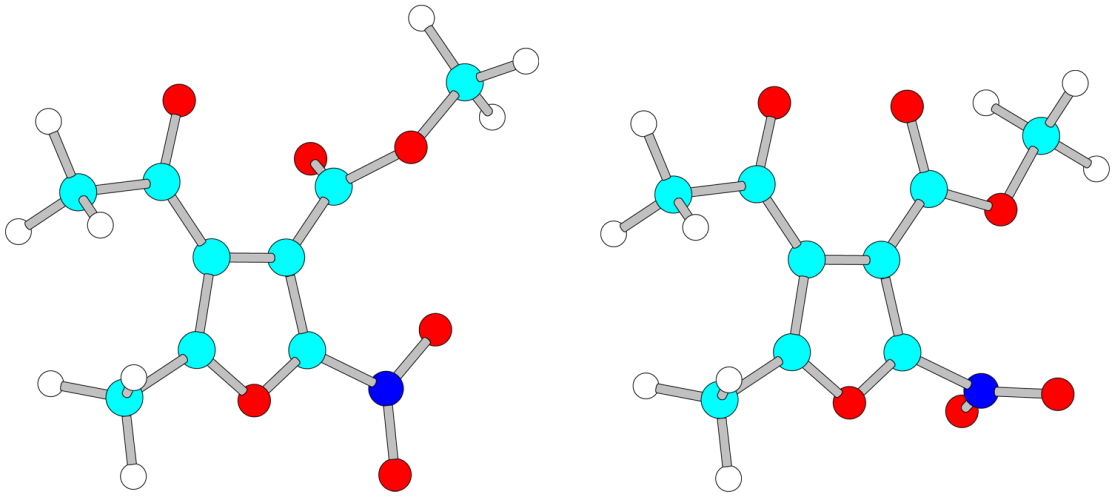

Figure S33. Conformer configuration of methyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylates **2a′** and **2a″**

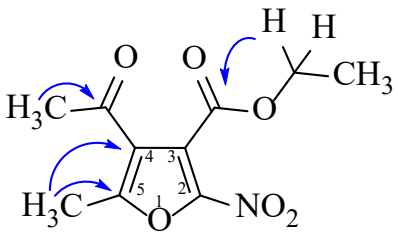

Figure S34. Key correlations in the $^{1}H–^{13}C$ HMBC NMR spectrum of compound **2d** ($CDCl_3$)

X-ray diffraction study of compounds 2b, **2d** was performed on a Bruker D8 QUEST automatic three-circle diffractometer at 105 K (graphite monochromator, λMoKα = 0.71073 Å, ω- and φ-scan with a step of 0.5°) at the Distributed Spectral-Analytical Center of Shared Facilities for Study of Structure, Composition and Properties of Substances and Materials of FRC Kazan Scientific Center of RAS. Single crystals of a suitable size were glued to the top of a glass fiber in a random orientation. The preliminary unit cell parameters were determined using three runs at different φ angle positions with 12 frames per run (φ-scan technique). The X-ray diffraction data were collected and indexed and the unit cell parameters were determined and refined using the APEX2 software package. The empirical absorption correction based on the crystal shape and an additional spherical correction were applied and systematic errors were corrected using the SADABS software. The structures were solved by direct methods using the SHELXT-2014/5 program package and refined by the full-matrix leastsquares method based on F2 using the SHELXL-2018/3 program package as implemented in WinGX-2020.1. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned geometrically and refined using a riding model. Intermolecular interactions were analyzed and the figures were generated with the PLATON and Mercury 2020.3 programs, respectively. Crystallographic data for the structures of **2b**, **2d** were deposited with the Cambridge Crystallographic Data Centre. The X-ray diffraction data collection and structure refinement statistics and the corresponding CCDC number are given in Table S1.

Table S1. Principal crystallographic parameters of compound **2b**, **2d** based on X-ray diffraction data

Parameter	**2b**	**2d**
Molecular formula	$C_9H_9NO_7$	$C_{10}H_{11}NO_6$
Molecular weight	243.17	241.20
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Z	2	2
Unit cell parameters		
a/Å	7.7836(4)	7.8477(4)
b/Å	8.5623(4)	7.9224(4)
c/Å	8.7753(4)	10.1121(5)
α/deg	82.783(2)	112.6770(10)
β/deg	76.963(2)	93.841(2)
γ/deg	67.3940(10)	106.8840(10)
V/Å^3	525.49(4)	543.57(5)
d_{calc}/g cm^{-3}	1.537	1.474
Absorption coeffi cient, μ/mm^{-1}	0.136	0.124
F(000)	252.0	252.0
Θ (min, max)/deg		3.2, 32.0
Ranges of indices,		
h	$-11 \le h \le 11$	$-11 \le h \le 11$
k	$-12 \le k \le 12$	$-11 \le k \le 11$
l	$-13 \le l \le 12$	$-15 \le l \le 15$
Number of reflections		
total	26117	43417
unique	3655	3745
R_{int}	0.0515	0.0683
Number of observed reflections (I > 2σ(I))	0.0409	3268
Number of reflections/of contraints/number of parameters	3655/0/157	3745/0/157
GOOF	1.016	1.046
R [$I > 2\sigma(I)$]		
R_1	0.0409	0.0406
wR_2	0.1052	0.1166
R (based on all reflections)		
R_1	0.0533	0.0461
wR_2	0.1109	0.1210
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.58/-0.23	0.61/-0.28
CCDC	2295211	2295213

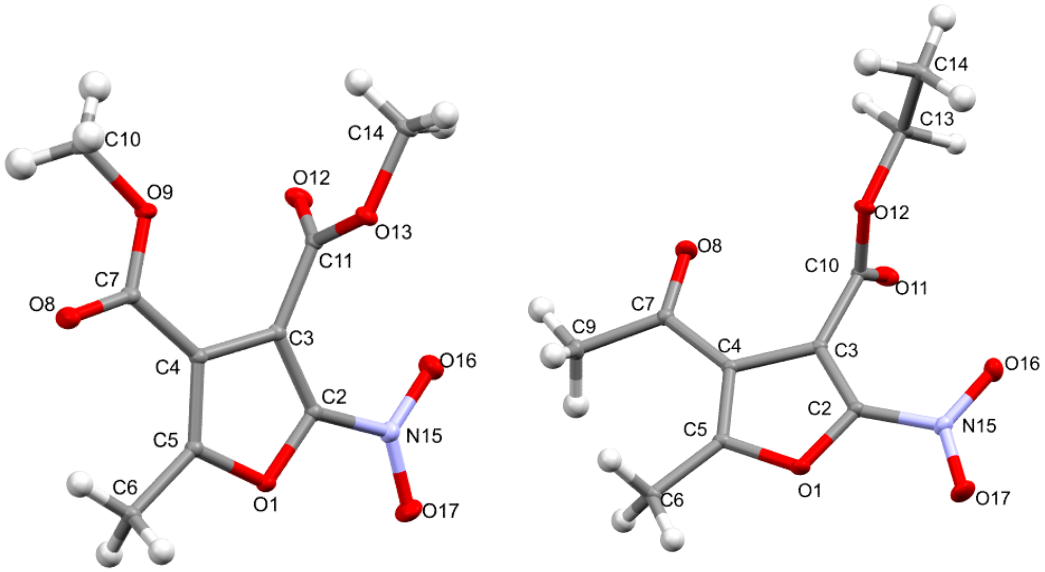

Figure 35. Geometry of the molecule **2b**, (*a*) and **2d** (*b*) in the crystals. Ellipsoids of anisotropic displacements are shown with 50% probability.

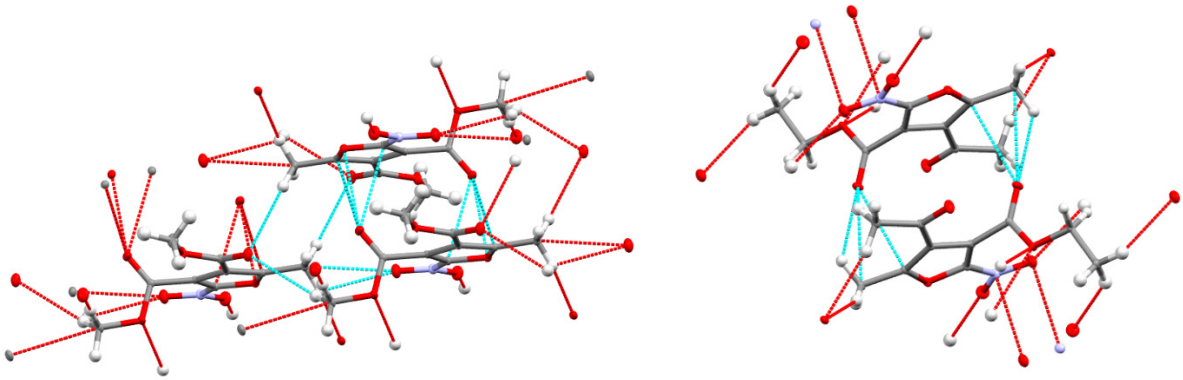

Figure 36. Short intermolecular contacts in the crystals **2b** and **2d.**

It is shown that the packing of crystal **2d** is determined by interactions of the C-H...O type, and in crystal **2b**, in addition, interactions of the LEP...π type are realized between the oxygen atoms of carbonyl groups and the π-system of the heteroaromatic ring.

Table S2. Torsion angles (τ) in the molecule of compounds **2b**, **2d**

*Dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (***2b***)*		*Ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate (***2d***)*	
Angle	**τ/deg**	**Angle**	**τ/deg**
N15–C2–C3–C4	176.0(1)	N15–C2–C3–C4	177.85(9)
N15–C2–C3–C11	-5.9(2)	N15–C2–C3–C10	-0.7(2)
O1–C2–C3–C4	-1.1(1)	O1–C2–C3–C4	-0.6(1)
O1–C2–C3–C11	177.04(9)	O1–C2–C3–C10	-179.09(8)
C3–C2–N15–O16	1.0(2)	C3–C2–N15–O16	6.2(1)
C3–C2–N15–O17	-178.6(1)	C3–C2–N15–O17	-173.79(9)
O1–C2–N15–O16	178.03(9)	O1–C2–N15–O16	-175.44(8)
O1–C2–N15–O17	-1.6(1)	O1–C2–N15–O17	4.6(1)
C3–C2–O1–C5	1.5(1)	C3–C2–O1–C5	0.1(1)

N15–C2–O1–C5	-176.02(9)	N15–C2–O1–C5	-178.54(7)
C2–C3–C4–C5	0.2(1)	C2–C3–C4–C5	0.79(9)
C2–C3–C4–C7	-176.5(1)	C2–C3–C4–C7	-176.71(8)
C11–C3–C4–C5	-177.8(1)	C10–C3–C4–C5	179.30(8)
C11–C3–C4–C7	5.4(2)	C10–C3–C4–C7	1.8(1)
C2–C3–C11–O12	88.9(1)	C2–C3–C10–O11	87.8(1)
C2–C3–C11–O13	-90.9(1)	C2–C3–C10–O12	-91.6(1)
C4–C3–C11–O12	-93.5(1)	C4–C3–C10–O11	-90.4(1)
C4–C3–C11–O13	86.8(1)	C4–C3–C10–O12	90.3(1)
C3–C4–C5–C6	-178.9(1)	C3–C4–C5–C6	178.4(1)
C3–C4–C5–O1	0.7(1)	C3–C4–C5–O1	-0.7(1)
C7–C4–C5–C6	-2.1(2)	C7–C4–C5–C6	-4.4(2)
C7–C4–C5–O1	177.42(9)	C7–C4–C5–O1	176.51(8)
C3–C4–C7–O8	-174.1(1)	C3–C4–C7–C9	171.09(8)
C3–C4–C7–O9	7.4(1)	C3–C4–C7–O8	-7.4(1)
C5–C4–C7–O8	9.8(2)	C5–C4–C7–C9	-5.8(1)
C5–C4–C7–O9	-168.7(1)	C5–C4–C7–O8	175.77(9)
C4–C5–C6–H6A	122.6	C4–C5–C6–H6A	-174.76
C4–C5–C6–H6B	2.6	C4–C5–C6–H6B	65.2
C4–C5–C6–H6C	-117.4	C4–C5–C6–H6C	-54.8
O1–C5–C6–H6A	-56.9	O1–C5–C6–H6A	4.3
O1–C5–C6–H6B	-176.92	O1–C5–C6–H6B	-115.67
O1–C5–C6–H6C	63.1	O1–C5–C6–H6C	124.33
C4–C5–O1–C2	-1.3(1)	C4–C5–O1–C2	0.40(9)
C6–C5–O1–C2	178.34(9)	C6–C5–O1–C2	-178.92(7)
C4–C7–O9–C10	178.83(9)	C4–C7–C9–H9A	-179.25
O8–C7–O9–C10	0.3(2)	C4–C7–C9–H9B	60.8
H10A–C10–O9–C7	-52.1	C4–C7–C9–H9C	-59.2
H10B–C10–O9–C7	-172.1	O8–C7–C9–H9A	-0.9
H10C–C10–O9–C7	67.9	O8–C7–C9–H9B	-120.9
C3–C11–O13–C14	-179.29(8)	O8–C7–C9–H9C	119.2
O12–C11–O13–C14	0.9(1)	C3–C10–O12–C13	-178.66(7)
H14A–C14–O13–C11	-58.6	O11–C10–O12–C13	2.0(1)
H14B–C14–O13–C11	-178.56	H13A–C13–C14–H14A	63.5
H14C–C14–O13–C11	61.4	H13A–C13–C14–H14B	-56.5
		H13A–C13–C14–H14C	-176.47
		H13B–C13–C14–H14A	-176.49
		H13B–C13–C14–H14B	63.5
		H13B–C13–C14–H14C	-56.5
		O12–C13–C14–H14A	-56.5
		O12–C13–C14–H14B	-176.48
		O12–C13–C14–H14C	63.5
		H13A–C13–O12–C10	73.2
		H13B–C13–O12–C10	-46.8
		C14–C13–O12–C10	-166.79(7)

Table S3. Angles (τ) in the molecule of compounds **2b**, **2d**

*Dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (**2b**)*		*Ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate (**2d**)*	
Angle	**τ/deg**	**Angle**	**τ/deg**
C3–C2–N15	130.59(9)	C3–C2–N15	130.86(8)
C3–C2–O1	112.93(9)	C3–C2–O1	112.55(8)
N15–C2–O1	116.43(9)	N15–C2–O1	116.58(8)
C2–C3–C4	104.20(8)	C2–C3–C4	104.70(7)
C2–C3–C11	127.08(9)	C2–C3–C10	127.69(8)
C4–C3–C11	128.69(9)	C4–C3–C10	127.60(7)
C3–C4–C5	106.97(9)	C3–C4–C5	106.71(7)
C3–C4–C7	127.14(9)	C3–C4–C7	123.06(7)
C5–C4–C7	125.80(9)	C5–C4–C7	130.18(8)
C4–C5–C6	134.82(9)	C4–C5–C6	135.47(8)
C4–C5–O1	109.75(9)	C4–C5–O1	109.59(7)
C6–C5–O1	115.42(9)	C6–C5–O1	114.93(7)
C5–C6–H6A	109.5	C5–C6–H6A	109.47
C5–C6–H6B	109.5	C5–C6–H6B	109.47
C5–C6–H6C	109.5	C5–C6–H6C	109.47
H6A–C6–H6B	109.5	H6A–C6–H6B	109.47
H6A–C6–H6C	109.5	H6A–C6–H6C	109.47
H6B–C6–H6C	109.5	H6B–C6–H6C	109.47
C4–C7–O8	124.8(1)	C4–C7–C9	119.44(8)
C4–C7–O9	110.66(9)	C4–C7–O8	118.47(8)
O8–C7–O9	124.6(1)	C9–C7–O8	122.07(8)
H10A–C10–H10B	109.5	C7–C9–H9A	109.47
H10A–C10–H10C	109.5	C7–C9–H9B	109.47
H10A–C10–O9	109.5	C7–C9–H9C	109.47
H10B–C10–H10C	109.5	H9A–C9–H9B	109.47
H10B–C10–O9	109.5	H9A–C9–H9C	109.47
H10C–C10–O9	109.5	H9B–C9–H9C	109.47
C3–C11–O12	124.54(9)	C3–C10–O11	123.45(8)
C3–C11–O13	109.64(8)	C3–C10–O12	110.49(7)
O12–C11–O13	125.8(1)	O11–C10–O12	126.05(8)
H14A–C14–H14B	109.5	H13A–C13–H13B	108.58
H14A–C14–H14C	109.5	H13A–C13–C14	110.33
H14A–C14–O13	109.5	H13A–C13–O12	110.33
H14B–C14–H14C	109.5	H13B–C13–C14	110.33
H14B–C14–O13	109.5	H13B–C13–O12	110.33
H14C–C14–O13	109.5	C14–C13–O12	106.93(8)
C2–N15–O16	116.16(9)	C13–C14–H14A	109.47
C2–N15–O17	118.54(9)	C13–C14–H14B	109.47
O16–N15–O17	125.3(1)	C13–C14–H14C	109.47
C2–O1–C5	106.13(8)	H14A–C14–H14B	109.5
C7–O9–C10	116.10(9)	H14A–C14–H14C	109.5

C11–O13–C14	115.23(8)	H14B–C14–H14C	109.5
		C2–N15–O16	115.92(8)
		C2–N15–O17	118.70(8)
		O16–N15–O17	125.38(9)
		C2–O1–C5	106.45(7)
		C10–O12–C13	116.34(7)

Table S4. Bond lengths (*d*) in the molecule of compounds **2b**, **2d**

*Dimethyl 2-methyl-5-nitrofuran-3,4-dicarboxylate (***2b***)*		*Ethyl 4-acetyl-5-methyl-2-nitrofuran-3-carboxylate (***2d***)*	
Bond	***d*/Å**	**Bond**	***d*/Å**
C2–C3	1.353(1)	C2–C3	1.353(1)
C2–N15	1.421(1)	C2–N15	1.422(1)
C2–O1	1.351(1)	C2–O1	1.353(1)
C3–C4	1.433(1)	C3–C4	1.434(1)
C3–C11	1.495(2)	C3–C10	1.494(1)
C4–C5	1.375(2)	C4–C5	1.380(1)
C4–C7	1.473(1)	C4–C7	1.477(1)
C5–C6	1.477(2)	C5–C6	1.479(1)
C5–O1	1.359(1)	C5–O1	1.362(1)
C6–H6A	0.9800	C6–H6A	0.9800
C6–H6B	0.980	C6–H6B	0.9800
C6–H6C	0.980	C6–H6C	0.980
C7–O8	1.206(1)	C7–C9	1.497(1)
C7–O9	1.331(2)	C7–O8	1.221(1)
C10–H10A	0.980	C9–H9A	0.980
C10–H10B	0.980	C9–H9B	0.980
C10–H10C	0.980	C9–H9C	0.9800
C10–O9	1.449(1)	C10–O11	1.201(1)
C11–O12	1.197(2)	C10–O12	1.3250(9)
C11–O13	1.325(1)	C13–H13A	0.990
C14–H14A	0.980	C13–H13B	0.990
C14–H14B	0.980	C13–C14	1.501(1)
C14–H14C	0.980	C13–O12	1.461(1)
C14–O13	1.454(1)	C14–H14A	0.980
N15–O16	1.228(1)	C14–H14B	0.9800
N15–O17	1.224(1)	C14–H14C	0.980
		N15–O16	1.236(1)
		N15–O17	1.222(1)