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Synthesis of substituted furan-3-carboxylates from alkyl 3-bromo-3-nitroacrylates

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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, $^{13}C\{^{1}H\}$, $^{1}H—^{1}H$ dqf-COSY, $^{1}H—^{13}C$ 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}). Elemental analysis was performed on a Euro Vector EA 3000 analyzer (CHN Dual).

The starting alkyl 3-bromo-3-nitroacrylates **1a,b** were synthesized according to a procedure described previously.[22]

Methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate (2a).

To a solution of pentane-2,4-dione (143 mg, 1.43 mmol) and freshly fused of AcOK (140 mg, 1.43 mmol) in anhydrous MeOH (8 ml), a solution of methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol) in anhydrous MeOH (5 ml) was added dropwise. The resulted mixture was stirred for 1 h at 18-20 °C. The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The solvent evaporated. The yield was 270 mg (83%), light yellow oil, *Rf* 0.2 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1367 (s), 1576 (s, NO_2), 1746 (br. s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.30 (3H, s, CH_3); 2.41 (3H, d, ^{5}J = 1.4, $C^{5}CH_3$); 3.80 (3H, s, OCH_3); 4.38-4.40 (1H, m, $C^{3}H$); 6.11 (1H, d, ^{3}J = 2.0, $C^{2}H$). ^{13}C NMR ($CDCl_3$), δ: 14.7 ($C^{5}\underline{C}H_3$); 29.5 (CH_3); 53.5 (OCH_3); 55.0 (C^{3}); 104.9 (C^{2}); 112.7 (C^{4}); 167.2 (C^{5}); 168.8 (O-C=O); 192.3 (C=O). Found (%):C 47.01; H 4.55; N 6.03. $C_9H_{11}NO_6$. Calculated (%): C 47.17; H 4.84; N 6.11.

Dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate (2b) was synthesized as described for compound **2a** starting from methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol), methyl 3-oxobutanoate (166 mg, 1.43 mmol) and freshly fused of AcOK (140 mg, 1.43 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 260 mg (74%), yellow oil, *Rf* 0.47 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1366 (s), 1576 (s, NO_2), 1717 (s), 1744 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.40 (3H, d, ^{5}J = 1.5, $C^{5}CH_3$); 3.73 (3H, s, $C^{4}OCH_3$); 3.80 (3H, s, $C^{3}OCH_3$); 4.32-4.34 (1H, m, $C^{3}H$); 6.09 (1H, d, ^{3}J = 2.1, $C^{2}H$). ^{13}C NMR ($CDCl_3$), δ: 13.9 ($C^{5}CH_3$); 51.8 ($C^{4}O\underline{C}H_3$); 53.5 ($C^{3}O\underline{C}H_3$); 54.5 (C^{3}); 103.4 (C^{4}); 105.2 (C^{2}); 163.4 ($C^{4}O\text{-}\underline{C}$=O); 168.7 ($C^{5}$); 168.9 ($C^{3}O\text{-}\underline{C}$=O). Found (%): C 43.73; H 4.39; N 5.35. $C_9H_{11}NO_7$. Calculated (%): C 44.09; H 4.52; N 5.71.

4-Ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate (2c) was synthesized as described for compound **2a** starting from methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol), ethyl 3-oxobutanoate (186 mg, 1.43 mmol) and freshly fused of AcOK (140 mg, 1.43 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 270 mg (72%), yellow oil, *Rf* 0.87 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1369 (m), 1576 (s, NO_2), 1711 (s), 1744 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*,

Hz): 1.26 (3H, t, ^3J = 7.1, $OCH_2C\underline{H}_3$); 2.40 (3H, d, ^5J = 1.5, C^5CH_3); 3.80 (3H, s, OCH_3); 4.15 (1H, d. q, ^2J = 10.8 , ^3J = 7.1, $OC\underline{H}_2CH_3$); 4.23 (1H, d. q, ^2J = 10.8, ^3J = 7.1, $OC\underline{H}_2CH_3$); 4.22 (1H, d. q, ^3J = 2.1, ^5J = 1.5, C^3H); 6.09 (1H, d, ^3J = 2.1, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.9 ($C^5\underline{C}H_3$); 14.3 ($OCH_2\underline{C}H_3$); 53.4 (CH_3); 54.6 (C^3); 60.7 ($O\underline{C}H_2CH_3$); 103.6 (C^4); 105.2 (C^2); 163.0 (C^4O-C=O); 168.4 (C^5); 169.0 (C^3O-C=O). Found (%):C 46.84; H 4.74; N 4.99. $C_{10}H_{13}NO_7$. Calculated (%): C 46.34; H 5.06; N 5.40.

Ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate (2d) was synthesized as described for compound **2a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (400 mg, 1.78 mmol), pentane-2,4-dione (179 mg, 1.78 mmol) and freshly fused of AcOK (175 mg, 1.78 mmol). The solvent was removed and the oily residue was chromatographed on silica gel (C_6H_{14} : EtOAc = 3 : 1 as the eluent). The yield was 370 mg (74%), yellow oil, *Rf* 0.36 (C_6H_{14} : EtOAc = 3 : 1). IR ($CHCl_3$), ν/cm^{-1}: 1370 (s), 1575 (s, NO_2), 1689 (s), 1739 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.30 (3H, t, ^3J = 7.2, $OCH_2C\underline{H}_3$); 2.31 (3H, s, CH_3); 2.41 (3H, d, ^5J = 1.4, C^5CH_3); 4.25 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$); 4.36-4.39 (1H, m, C^3H); 6.12 (1H, d, ^3J = 2.0, C^2H). ^{13}C NMR ($CDCl_3$), δ: 14.1 ($OCH_2\underline{C}H_3$); 14.7 ($C^5\underline{C}H_3$); 29.6 (CH_3); 55.2 (C^3); 62.9 ($O\underline{C}H_2CH_3$); 105.0 (C^2); 112.6 (C^4); 167.2 (C^5); 168.4 (O-C=O); 192.4 (C=O). Found (%): C 48.96.; H 5.14; N 5.53. $C_{10}H_{13}NO_6$. Calculated (%): C 49.38; H 5.39; N 5.76.

3-Ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate (2e) was synthesized as described for compound **2a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (400 mg, 1.78 mmol), methyl 3-oxobutanoate (207 mg, 1.78 mmol) and freshly fused of AcOK (175 mg, 1.78 mmol). The solvent was removed and the oily residue was chromatographed on silica gel (C_6H_{14} : EtOAc = 3 : 1 as the eluent). The yield was 380 mg (75%), yellow oil, *Rf* 0.34 (C_6H_{14} : EtOAc = 3 : 1). IR ($CHCl_3$), ν/cm^{-1}: 1369 (s), 1576 (s, NO_2), 1670 (s), 1719 (s), 1740 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.29 (3H, t, ^3J = 7.2, $OCH_2C\underline{H}_3$); 2.40 (3H, d, ^5J = 1.5, $C^5C\underline{H}_3$); 3.73 (3H, s, OCH_3); 4.24 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$); 4.31 (1H, d. q, ^3J = 2.1, ^5J = 1.5, C^3H), 6.09 (1H, d, ^3J = 2.1, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.9 ($C^5\underline{C}H_3$); 14.1 ($OCH_2\underline{C}H_3$); 51.7 (OCH_3); 54.7 (C^3); 62.6 ($O\underline{C}H_2CH_3$); 103.4 (C^4); 105.3 (C^2); 163.5 (C^4O-$\underline{C}$=O); 168.4 (C^5); 168.5 (C^3O-$\underline{C}$=O). Found (%): C 45.93; H 4.93; N 5.15. $C_{10}H_{13}NO_7$. Calculated (%): C 46.34; H 5.06; N 5.40.

Diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate (2f) was synthesized as described for compound **2a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (400 mg, 1.43 mmol), ethyl 3-oxobutanoate (174 mg, 1.43 mmol) and freshly fused of AcOK (131 mg, 1.43 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 380 mg (75%), yellow oil, *Rf* 0.6 (CHCl3). IR ($CHCl_3$), ν/cm^{-1}: 1370 (s), 1575 (s, NO_2), 1712 (s), 1738 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.27 (3H, t, ^3J = 7.2, $C^4OCH_2C\underline{H}_3$); 1.30 (3H, t, $C^3OCH_2C\underline{H}_3$); 2.40 (3H, d, ^5J = 1.5, C^5CH_3); 4.17 (1H, d. q, ^3J = 7.2, ^2J = 10.8, $C^4OC\underline{H}_2CH_3$); 4.22 (1H, d. q, ^3J = 7.2, ^2J = 10.8, $C^4OC\underline{H}_2CH_3$); 4.22-4.28 (2H, m, $C^3OC\underline{H}_2CH_3$); 4.32 (1H, d. q, ^3J = 2.1, ^5J = 1.5, C^3H); 6.09 (1H, d, ^3J = 2.1, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.9 ($C^5\underline{C}H_3$); 14.1 ($C^3OCH_2\underline{C}H_3$); 14.3 ($C^4OCH_2\underline{C}H_3$); 54.8 (C^3); 60.7 ($C^4O\underline{C}H_2CH_3$); 62.6 ($C^3O\underline{C}H_2CH_3$); 103.6 (C^4); 105.3 (C^2); 163.0 (C^4O-$\underline{C}$=O); 168.3 (C^5); 168.6 (C^3O-$\underline{C}$=O). Found (%): C 48.15; H 5.60; N 5.37. $C_{11}H_{15}NO_7$. Calculated (%): C 48.35; H 5.53; N 5.13.

Methyl 4-acetyl-5-methylfuran-3-carboxylate (3a).

To a solution of pentane-2,4-dione (95 mg, 0.95 mmol) and freshly fused of AcOK (187 mg, 1.91 mmol) in anhydrous MeOH (8 ml), a solution of methyl 3-bromo-3-nitroacrylate (**1a**)

(200 mg, 0.95 mmol) in anhydrous MeOH (5 ml) was added dropwise. The resulted mixture was refluxed for 1 h. The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 122 mg (70%), yellow crystals, melting point 62-64ºC (EtOH). IR ($CHCl_3$), ν/cm^{-1}: 1679 (s), 1727 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.43 (3H, s, C^5CH_3); 2.52 (3H, s, CH_3); 3.83 (3H, s, OCH_3); 7.78 (1H, s, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.6 ($C^5\underline{C}H_3$); 31.3 (CH_3); 52.0 (OCH_3); 117.8 (C^3); 121.7 (C^4); 146.5 (C^2); 158.2 (C^5); 163.1 (O-C=O); 196.6 (C=O). Found (%): C 58.96; H 5.43. $C_9H_{10}O_4$. Calculated (%): C 59.34; H 5.53.

Dimethyl 2-methylfuran-3,4-dicarboxylate (3b) was synthesized as described for compound **3a** starting from methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol), methyl 3-oxobutanoate (166 mg, 1.43 mmol) and freshly fused of AcOK (280 mg, 2.86 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 173 mg (62%), yellow oil, *Rf* 0.3 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1719 (s), 1738 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.50 (3H, s, C^2CH_3); 3.82 (3H, s, C^3OCH_3); 3.85 (3H, s, C^4OCH_3); 7.74 (1H, s, C^5H). ^{13}C NMR ($CDCl_3$), δ: 13.6 ($C^2\underline{C}H_3$); 52.0 ($C^3O\underline{C}H_3$); 52.0 ($C^4O\underline{C}H_3$); 113.0 (C^3); 118.8 (C^4); 145.7 (C^5); 159.5 (C^2); 162.7 (C^4O-$\underline{C}$=O); 163.7 (C^3O-$\underline{C}$=O). Found (%): C 54.32; H 4.98. $C_9H_{10}O_5$. Calculated (%): C 54.55; H 5.09.

3-Ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate (3c) was synthesized as described for compound **3a** starting from methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol), ethyl 3-oxobutanoate (186 mg, 1.43 mmol) and freshly fused of AcOK (280 mg, 2.86 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 220 mg (73%), yellow oil, *Rf* 0.38 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1716 (s), 1738 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.33 (3H, t, ^3J = 7.2, $OCH_2C\underline{H}_3$); 2.49 (3H, s, C^2CH_3); 3.81 (3H, s, OCH_3); 4.30 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$); 7.72 (1H, s, C^5H). ^{13}C NMR ($CDCl_3$), δ: 13.6 ($C^2\underline{C}H_3$); 14.3 ($OCH_2\underline{C}H_3$); 51.9 (OCH_3); 60.9 ($O\underline{C}H_2CH_3$); 113.2 (C^3); 118.9 (C^4); 145.5 (C^5); 159.2 (C^2); 162.8 (C^4O-$\underline{C}$=O); 163.2 (C^3O-$\underline{C}$=O). Found (%): C 56.31; H 5.54. $C_{10}H_{12}NO_5$. Calculated (%): C 56.60; H 5.70.

Ethyl 4-acetyl-5-methylfuran-3-carboxylate (3d).

Method A. The compound was synthesized as described for compound **3a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (300 mg, 1.34 mmol), pentane-2,4-dione (134 mg, 1.34 mmol) and freshly fused of AcOK (263 mg, 2.68 mmol). The solvent was removed and the oily residue was chromatographed on silica gel (C_6H_{14} : EtOAc = 3 : 1 as the eluent). The yield was 179 mg (68%), yellow oil, *Rf* 0.34 (C_6H_{14} : EtOAc = 3 : 1).

Method B. To a solution of **2d** (207 mg, 0.854 mmol) and freshly fused of AcOK (84 mg, 0.854 mmol) in anhydrous MeOH (6 ml) was refluxed for 4 h. The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The solvent evaporated. The yield was 108 mg (65%), light yellow oil, *Rf* 0.34 (C_6H_{14} : EtOAc = 3 : 1).

IR ($CHCl_3$), ν/cm^{-1}: 1683 (m), 1729 (m, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.34 (3H, t, ^3J = 7.2, $OCH_2C\underline{H}_3$); 2.43 (3H, s, C^5CH_3); 2.52 (3H, s, CH_3); 4.30 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$); 7.78 (1H, s, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.6 ($C^5\underline{C}H_3$); 14.3 ($OCH_2\underline{C}H_3$); 31.3 (CH_3); 61.0 ($O\underline{C}H_2CH_3$); 118.2 (C^3); 121.7 (C^4); 146.4 (C^2); 158.1 (C^5); 162.7 (O-C=O); 196.8 (C=O). Found (%):C 61.12; H 6.10. $C_{10}H_{12}O_4$. Calculated (%): C 61.22; H 6.17.

4-Ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate (3e) was synthesized as described for compound **3a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (300 mg, 1.34 mmol), methyl 3-oxobutanoate (155 mg, 1.34 mmol) and freshly fused of AcOK (263 mg, 2.68 mmol). The

solvent was removed and the oily residue was chromatographed on silica gel (CHCl3 as the eluent). The yield was 174 mg (61%), yellow oil, *Rf* 0.38 ($CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 1730 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.31 (3H, t, ^3J = 7.2, $OCH_2C\underline{H}_3$); 2.49 (3H, s, $C^2C\underline{H}_3$); 3.83 (3H, s, OCH_3); 4.28 (2H, q, ^3J = 7.2, $OC\underline{H}_2CH_3$); 7.72 (1H, s, C^5H). ^{13}C NMR ($CDCl_3$), δ: 13.6 ($C^2\underline{C}H_3$); 14.3 ($OCH_2\underline{C}H_3$); 51.9 (OCH_3); 60.9 ($O\underline{C}H_2CH_3$); 112.9 (C^3); 119.2 (C^4); 145.5 (C^5); 159.3 (C^2); 162.3 (C^4O-$\underline{C}$=O); 163.8 (C^3O-$\underline{C}$=O). Found (%): C 56.36; H 5.42. $C_{10}H_{12}O_5$. Calculated (%): C 56.60; H 5.70.

Diethyl 2-methylfuran-3,4-dicarboxylate (3f)

Method A. The compound was synthesized as described for compound **3a** starting from ethyl 3-bromo-3-nitroacrylate (**1b**) (300 mg, 1.34 mmol), ethyl 3-oxobutanoate (174 mg, 1.34 mmol) and freshly fused of AcOK (263 mg, 2.68 mmol). The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The yield was 173 mg (57%), yellow oil, *Rf* 0.45 ($CHCl_3$).

Method B. The compound was synthesized as described for compound **3d** starting from compound (**2f**) (100 mg, 0.366 mmol) and freshly fused of AcOK (36 mg, 0.366 mmol, refluxed for 2 h. The solvent was removed and the oily residue was chromatographed on silica gel ($CHCl_3$ as the eluent). The solvent evaporated. The yield was 54 mg (65%), light yellow oil, *Rf* 0.45 ($CHCl_3$).

IR ($CHCl_3$), ν/cm^{-1}: 1716 (s), 1731 (s, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.31 (3H, t, ^3J = 7.2, $C^4OCH_2C\underline{H}_3$); 1.32 (3H, t, ^3J = 7.2, $C^3OCH_2C\underline{H}_3$); 2.48 (3H, s, C^5CH_3); 4.27 (2H, q, ^3J = 7.2, $C^4OC\underline{H}_2CH_3$); 4.30 (2H, q, ^3J = 7.2, $C^3OC\underline{H}_2CH_3$); 7.71 (1H, s, C^2H). ^{13}C NMR ($CDCl_3$), δ: 13.5 ($C^2\underline{C}H_3$); 14.3 ($C^4OCH_2\underline{C}H_3$); 14.3 ($C^3OCH_2\underline{C}H_3$); 60.9 ($C^3O\underline{C}H_2CH_3$); 60.9 ($C^4O\underline{C}H_2CH_3$); 113.2 (C^3); 119.3 (C^4); 145.3 (C^5); 159.0 (C^2); 162.4 (C^4O-C=O); 163.3 (C^3O-C=O). Found (%):C 58.29; H 6.19. $C_{11}H_{14}O_5$. Calculated (%): C 58.40; H 6.24.

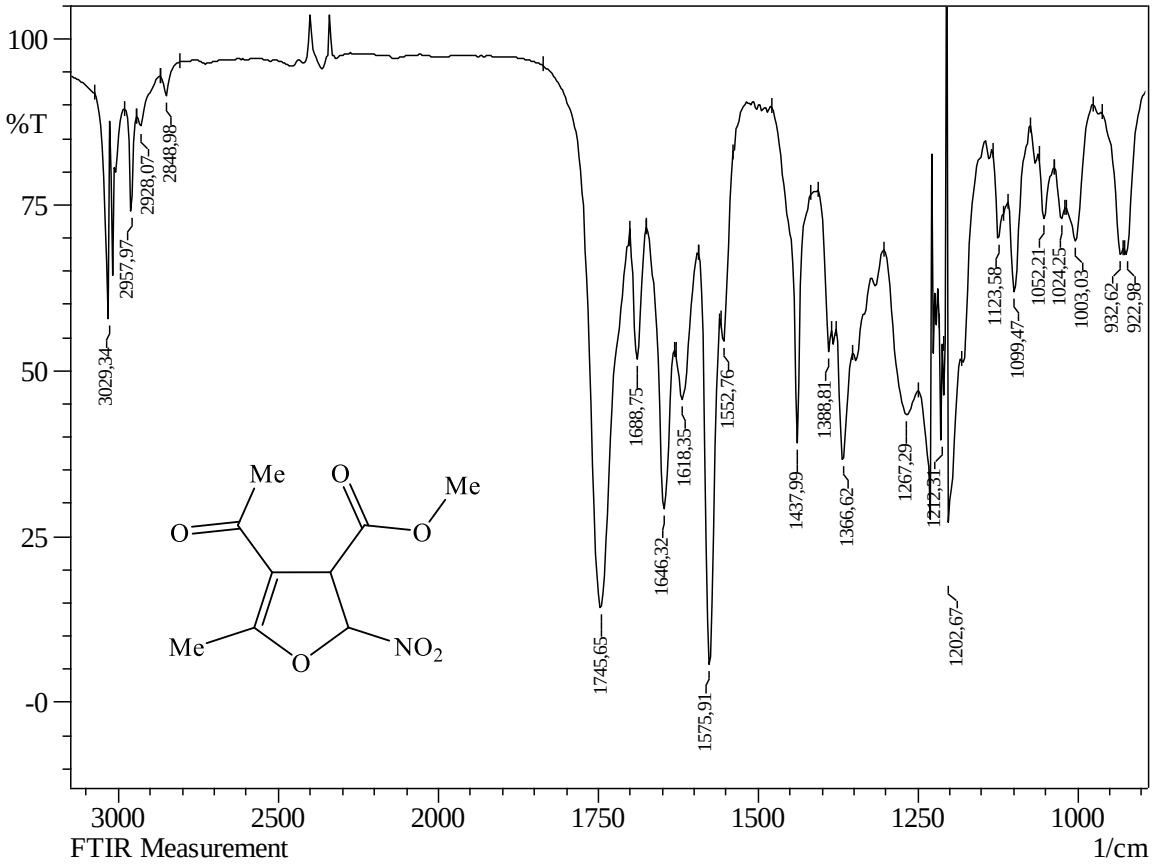

Figure S1. IR spectrum of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2a** in $CHCl_3$

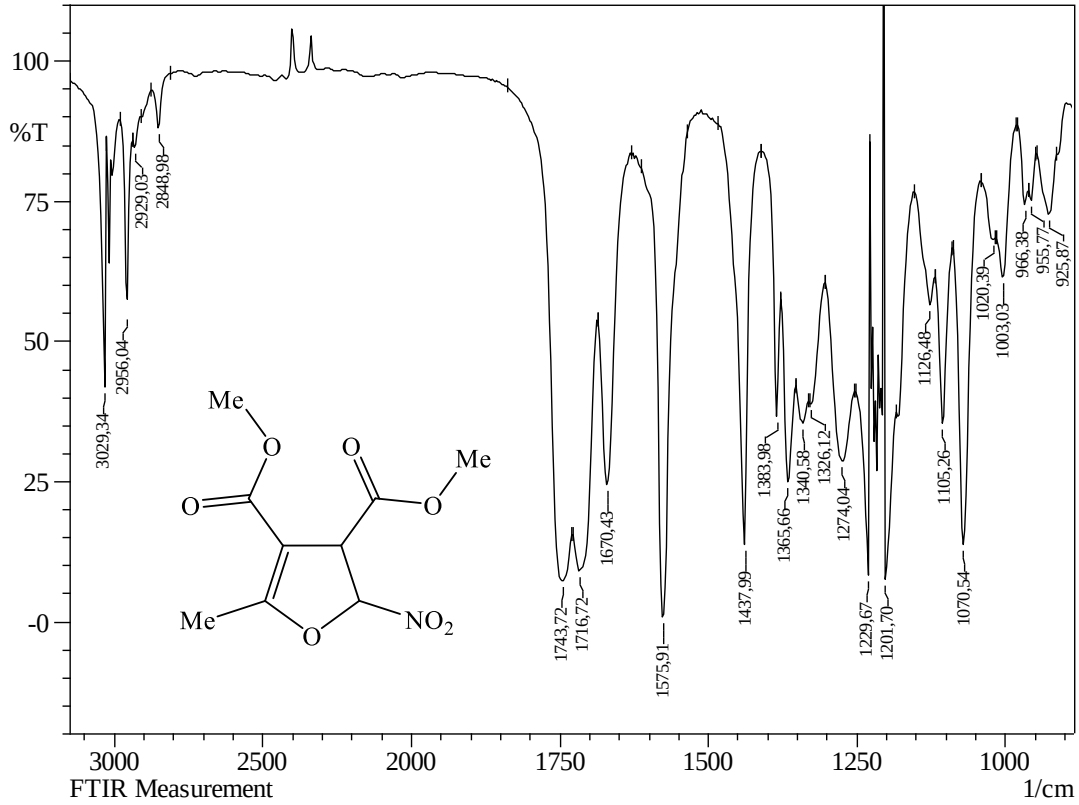

Figure S2. IR spectrum of dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2b** in $CHCl_3$

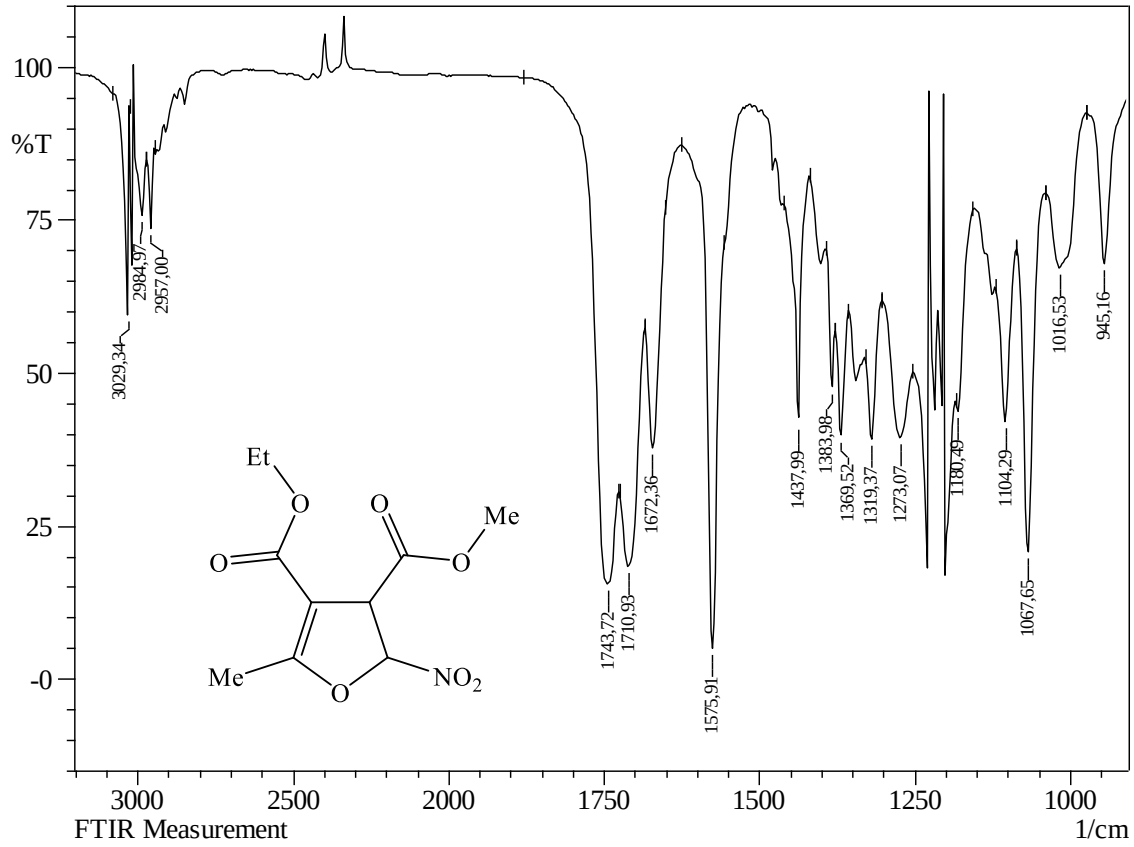

Figure S3. IR spectrum of 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2c** in $CHCl_3$

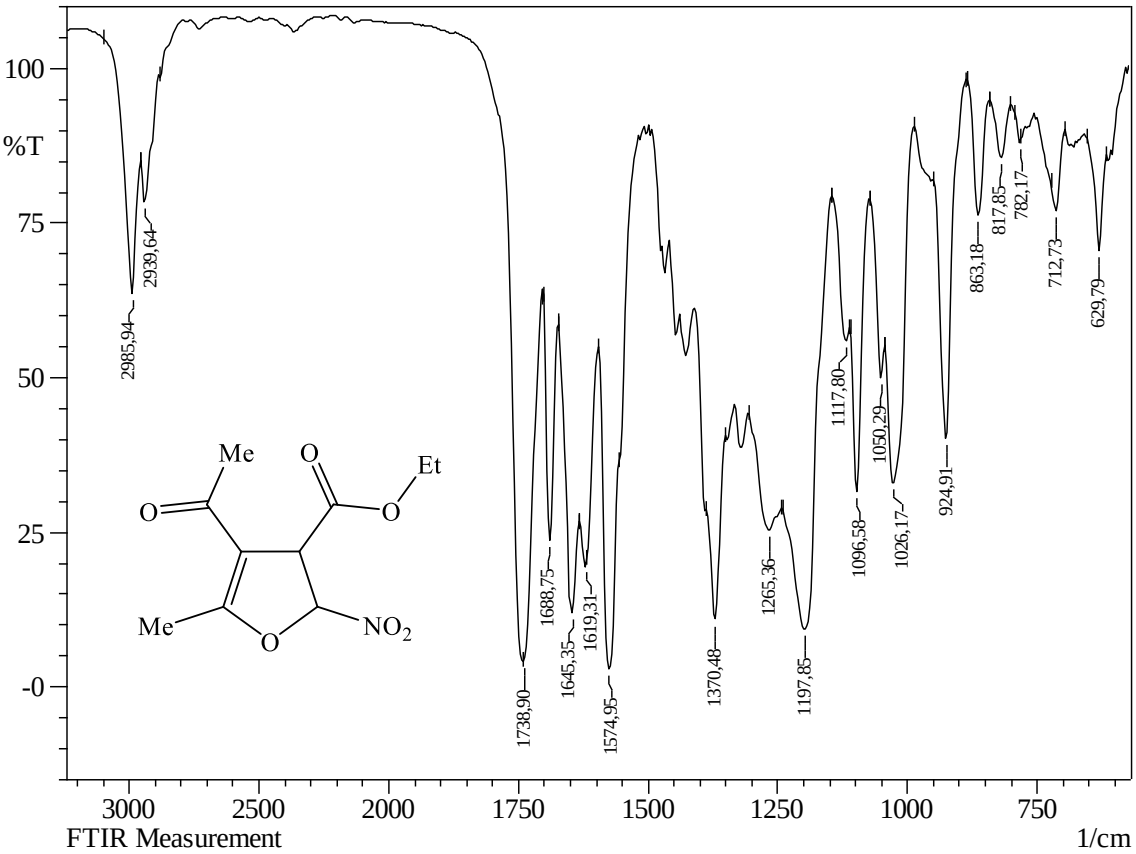

Figure S4. IR spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CHCl_3$

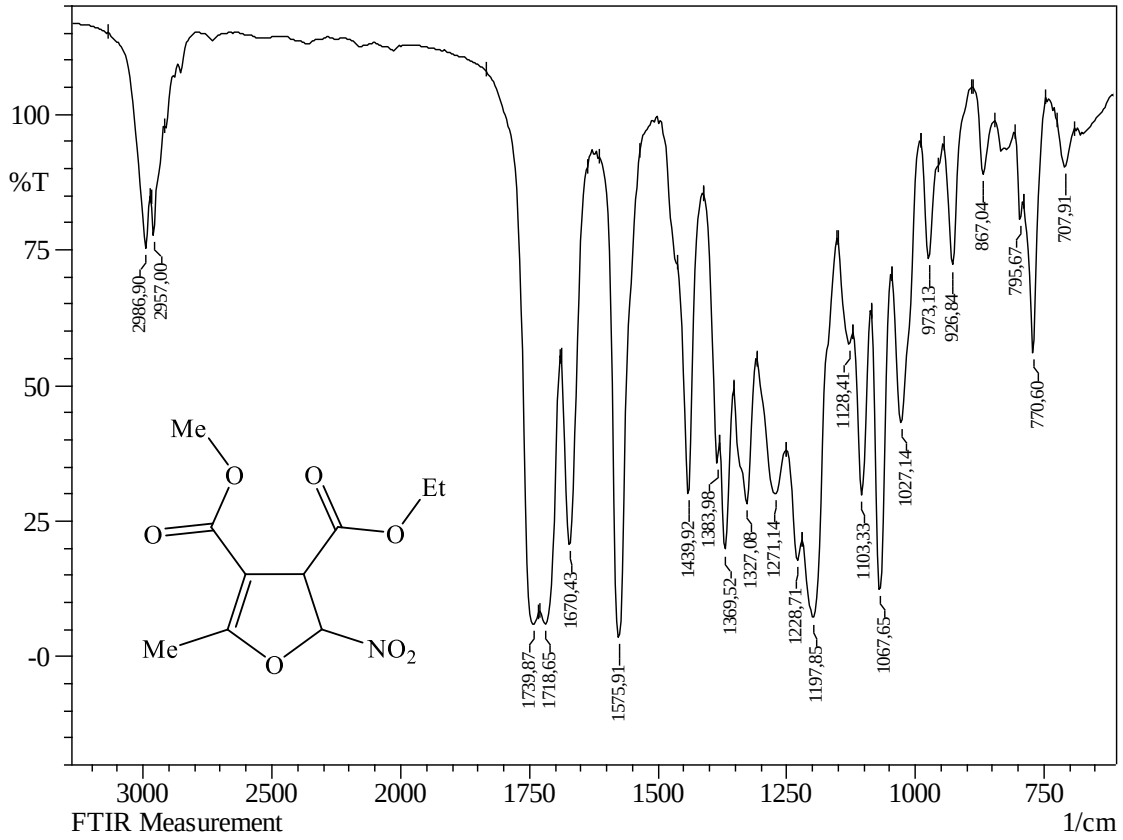

Figure S5. IR spectrum of 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2e** in $CHCl_3$

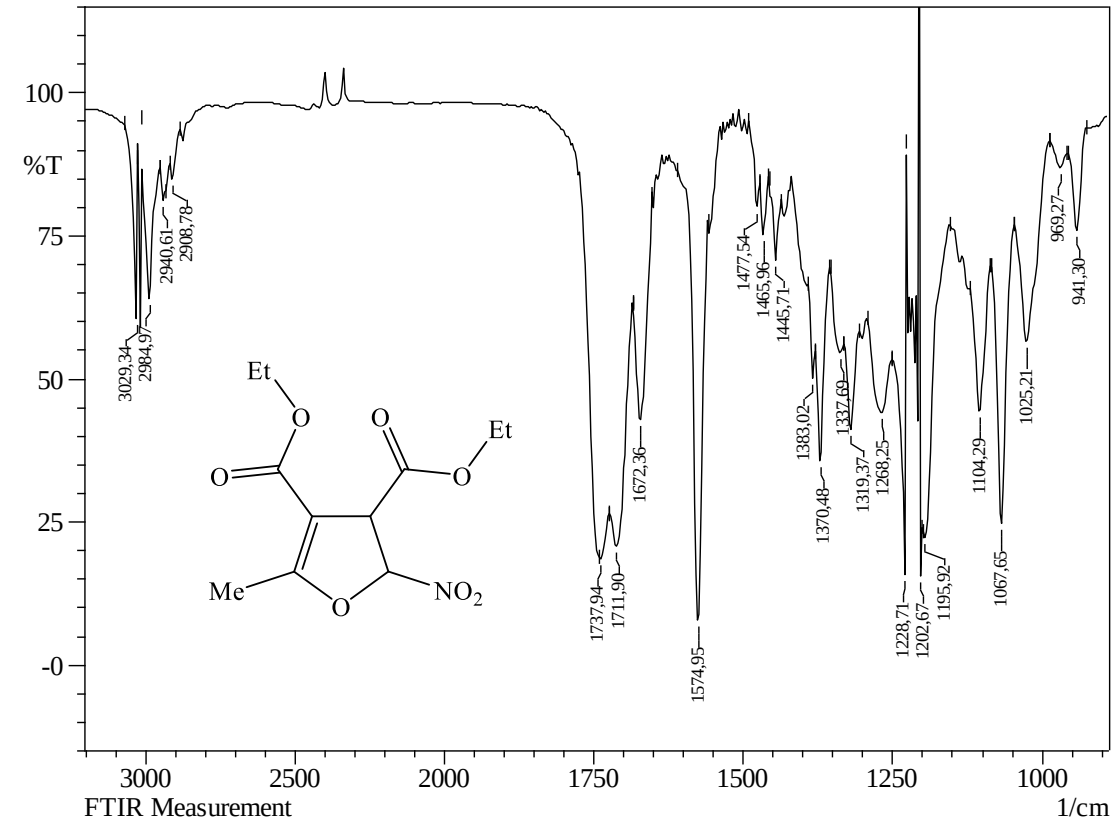

Figure S6. IR spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CHCl_3$

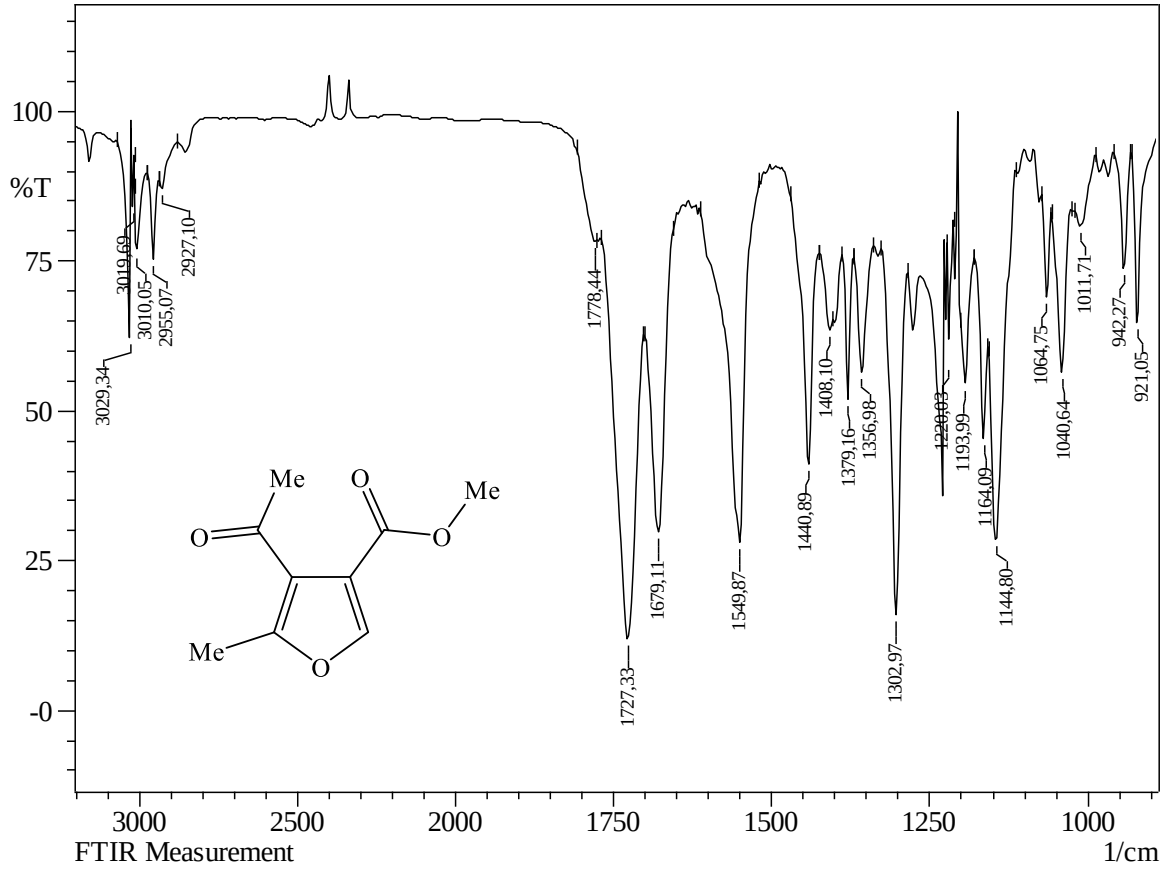

Figure S7. IR spectrum of methyl 4-acetyl-5-methylfuran-3-carboxylate **3a** in $CHCl_3$

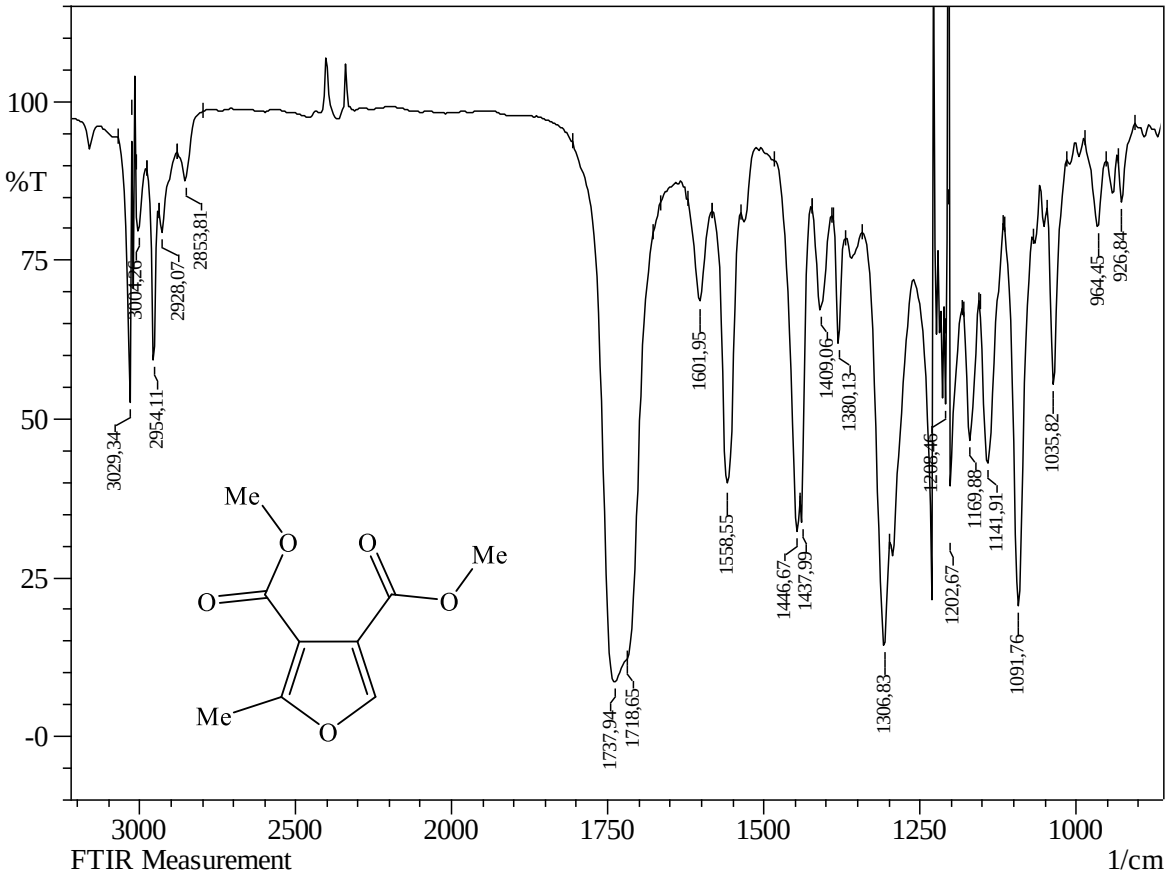

Figure S8. IR spectrum of dimethyl 2-methylfuran-3,4-dicarboxylate **3b** in $CHCl_3$

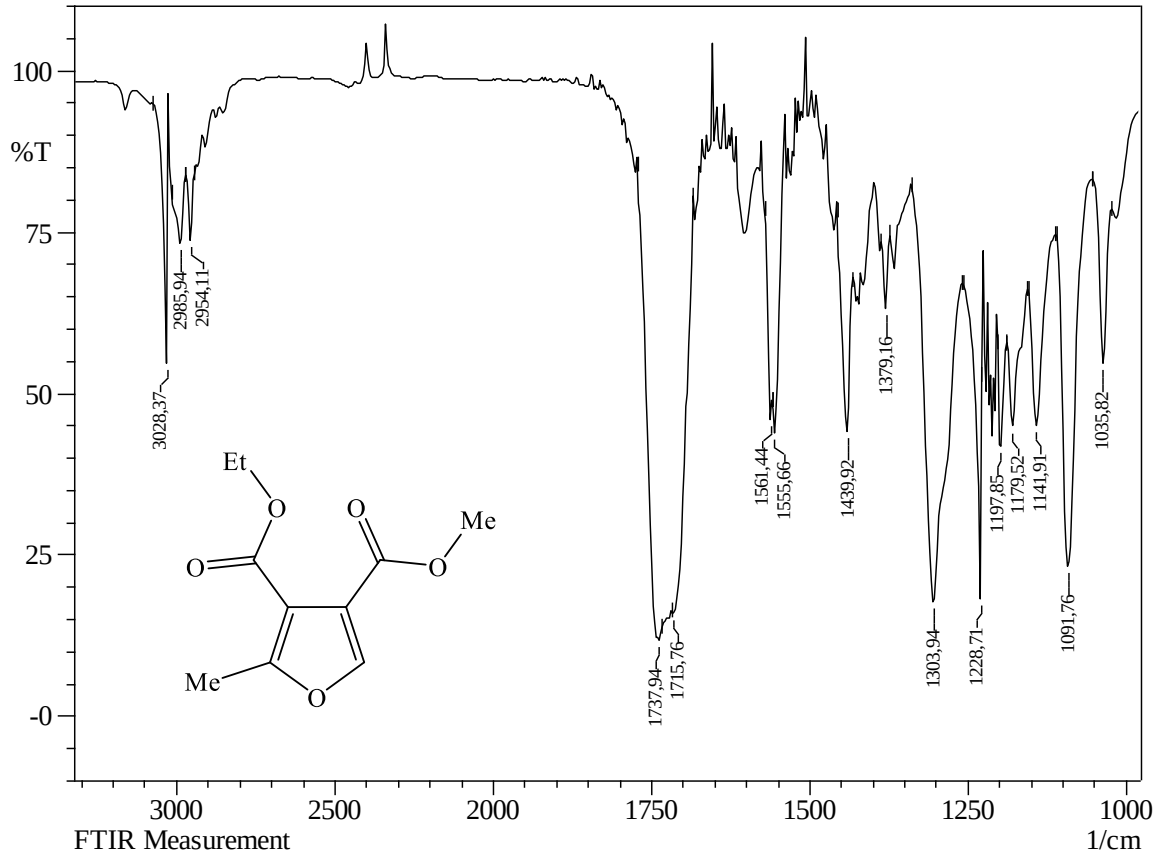

Figure S9. IR spectrum of 3-ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate **3c** in $CHCl_3$

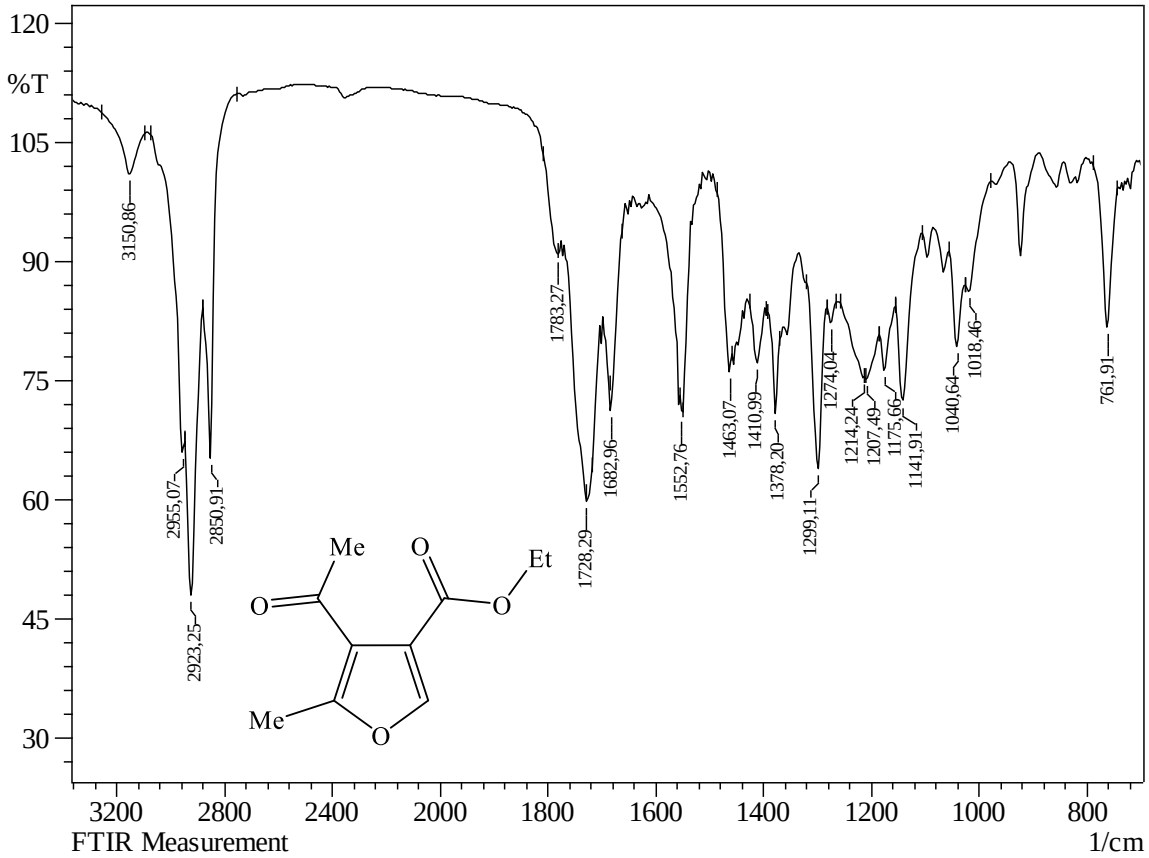

Figure S10. IR spectrum of ethyl 4-acetyl-5-methylfuran-3-carboxylate **3d** in $CHCl_3$

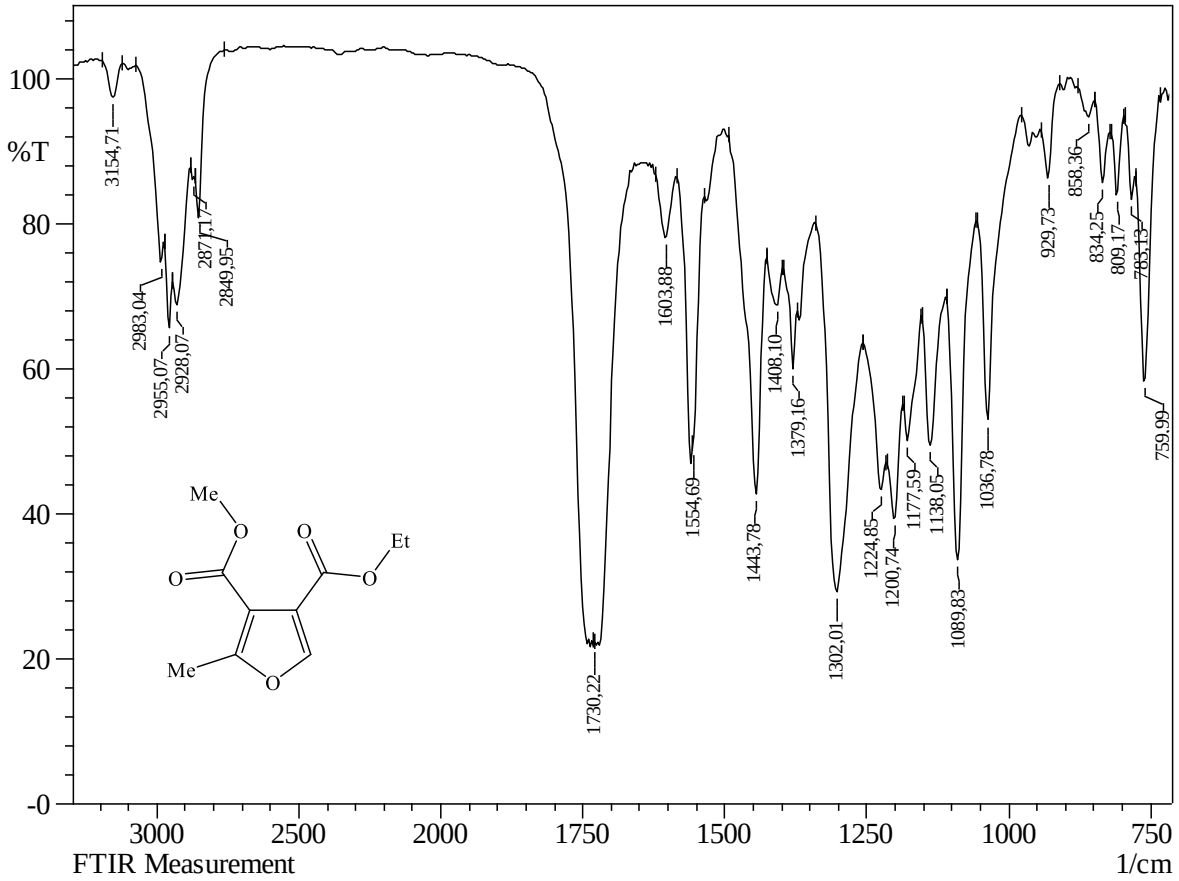

Figure S11. IR spectrum of 4-ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate **3e** in $CHCl_3$

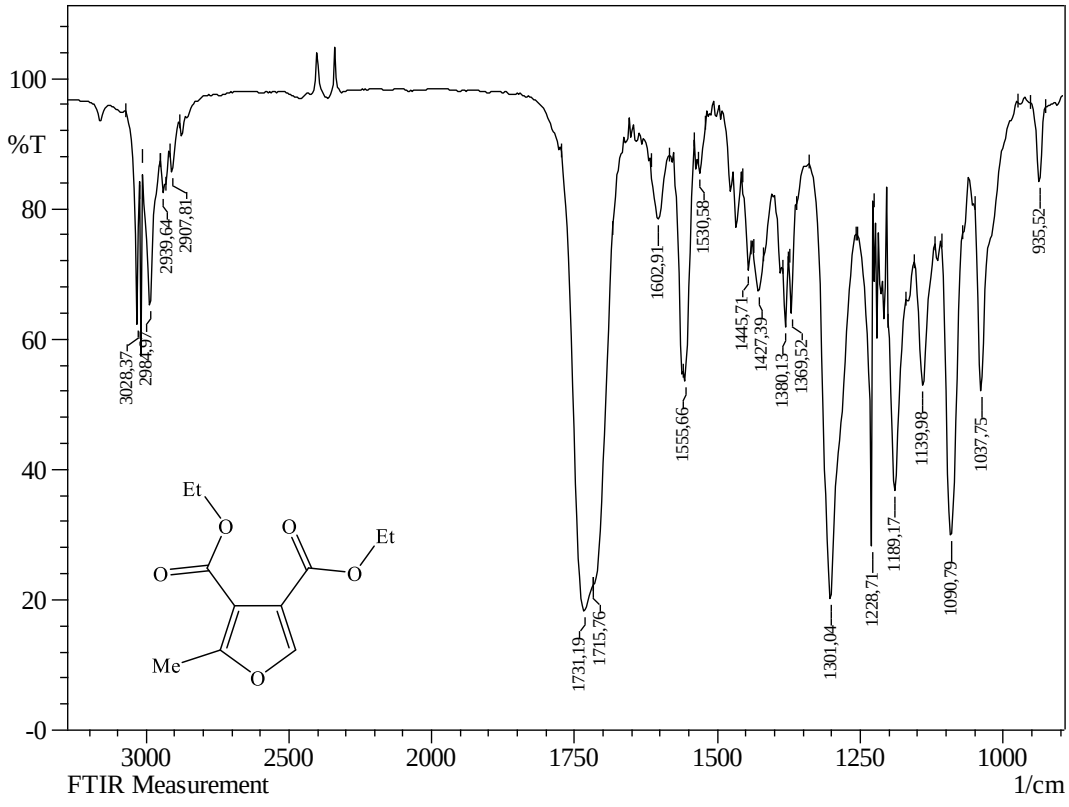

Figure S12. IR spectrum of diethyl 2-methylfuran-3,4-dicarboxylate **3f** in $CHCl_3$

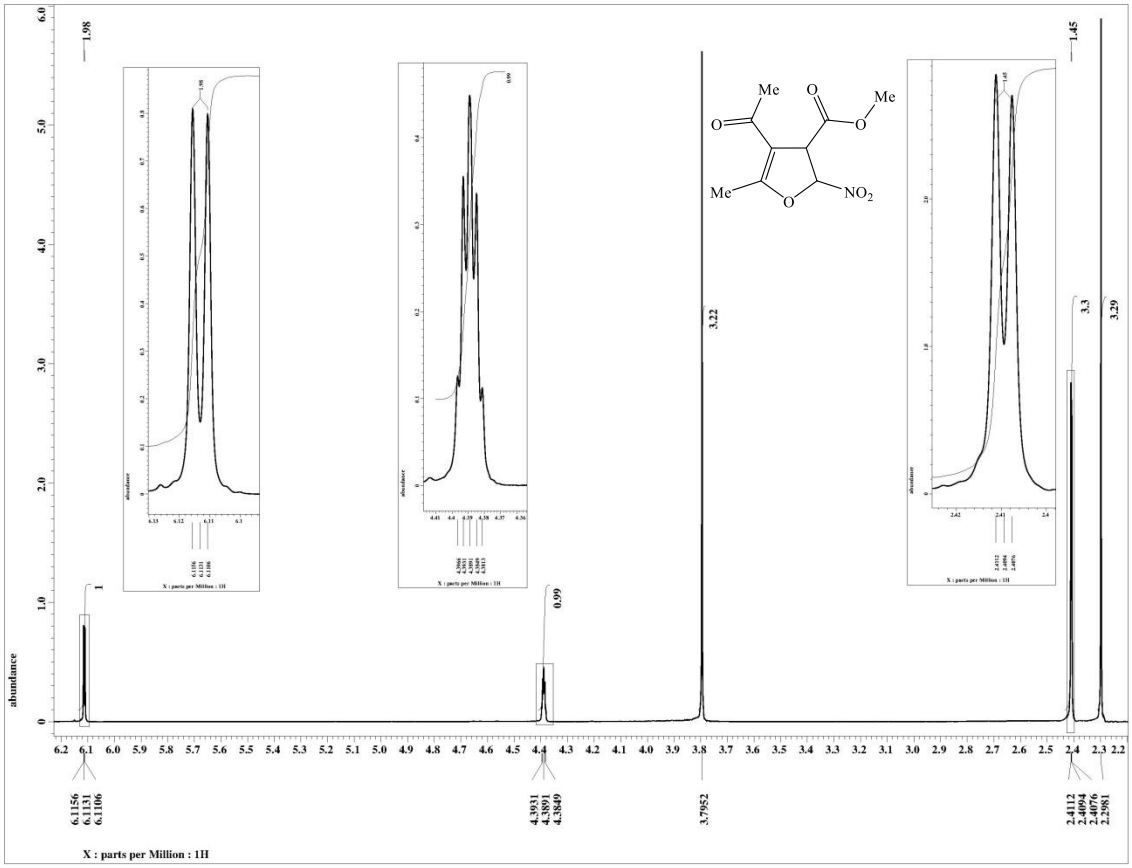

Figure S13. ^{1}H NMR spectrum of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2a** in $CDCl_3$

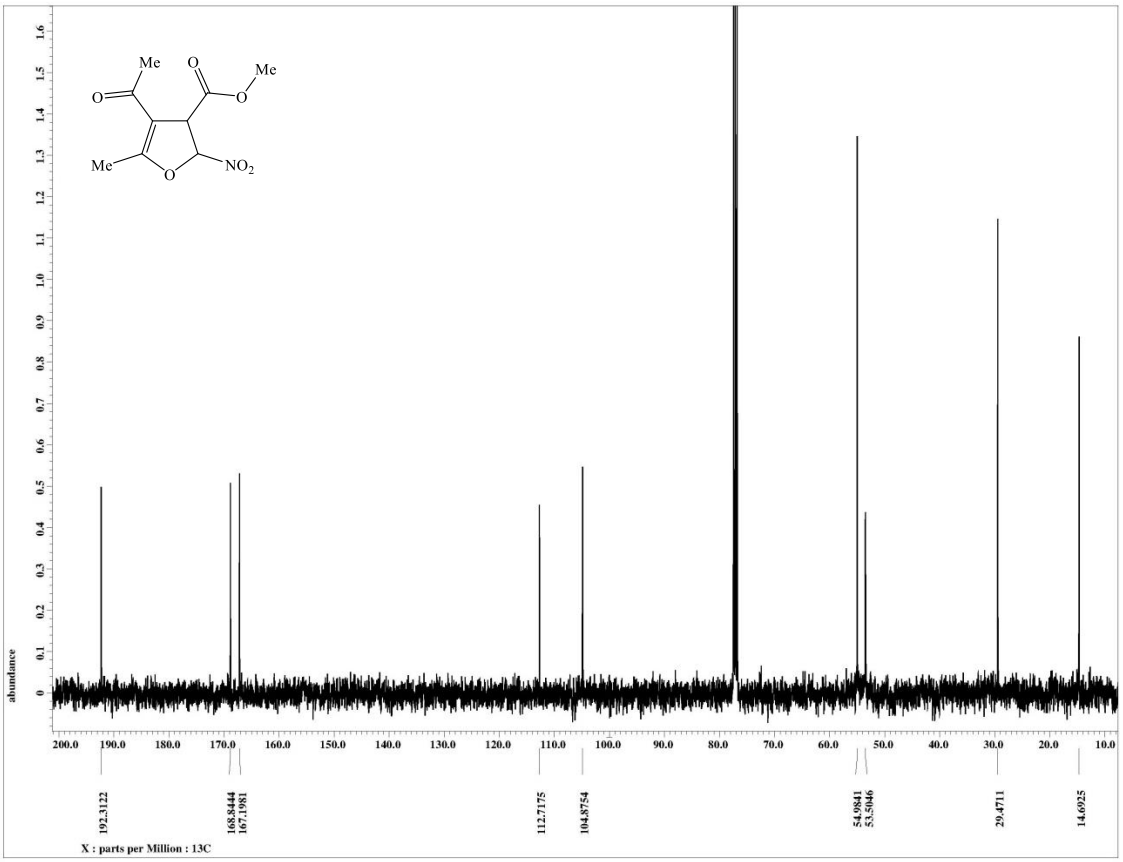

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2a** in $CDCl_3$

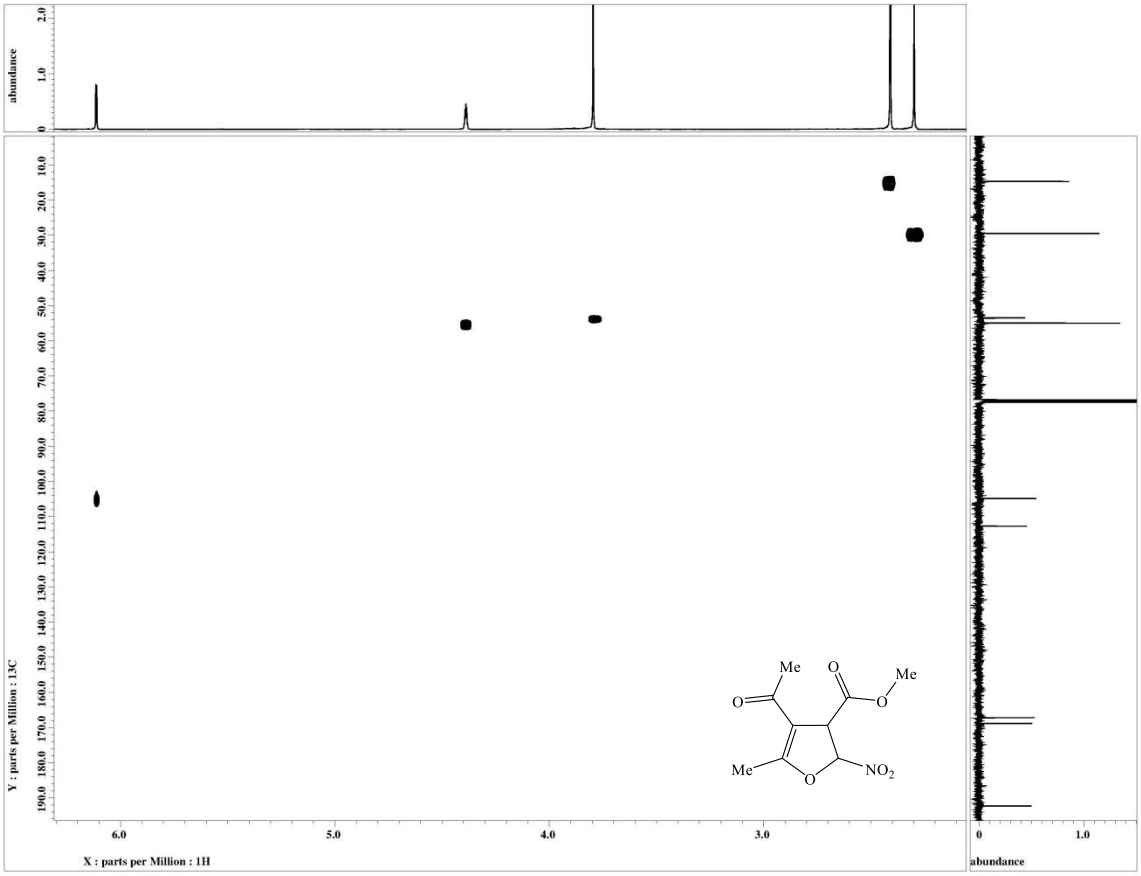

Figure S15. ^{1}H-^{13}C HMQC spectrum of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2a** in $CDCl_3$

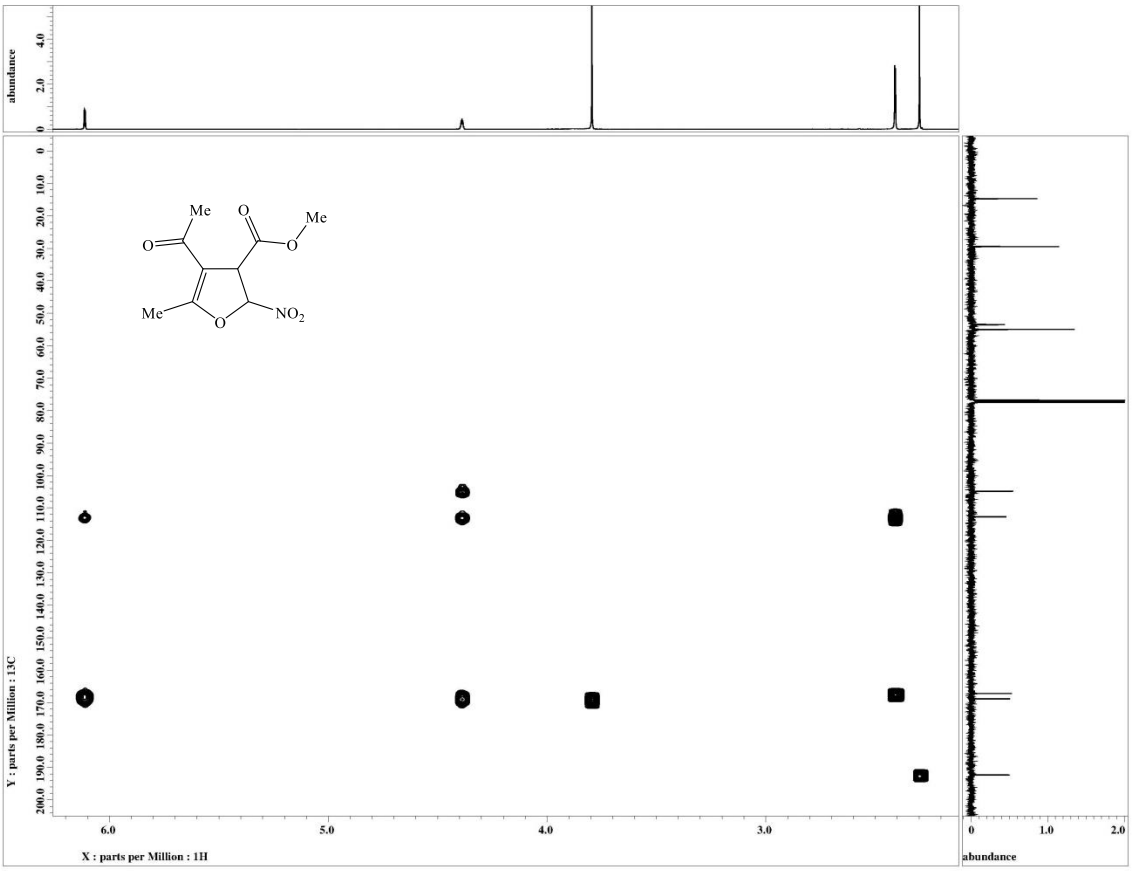

Figure S16. ^{1}H-^{13}C HMBC spectrum of methyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2a** in $CDCl_3$

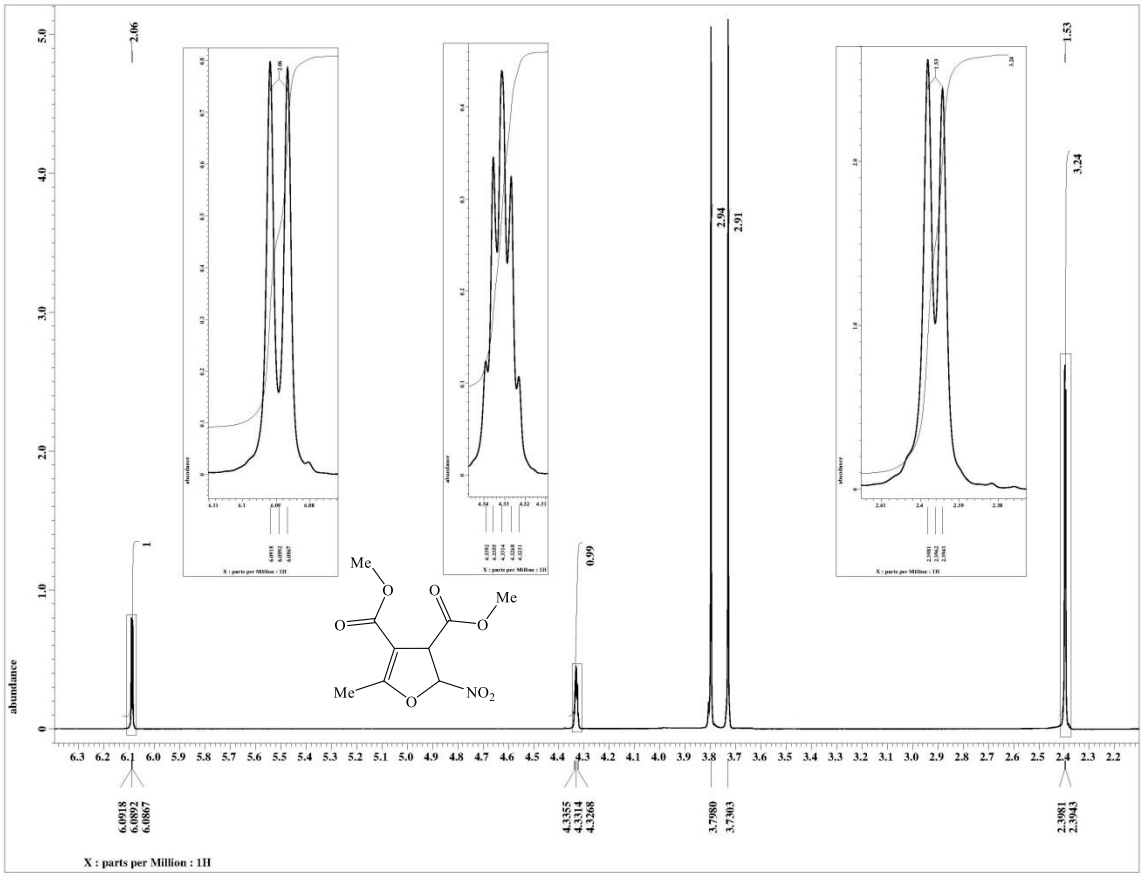

Figure S17. ^{1}H NMR spectrum of dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

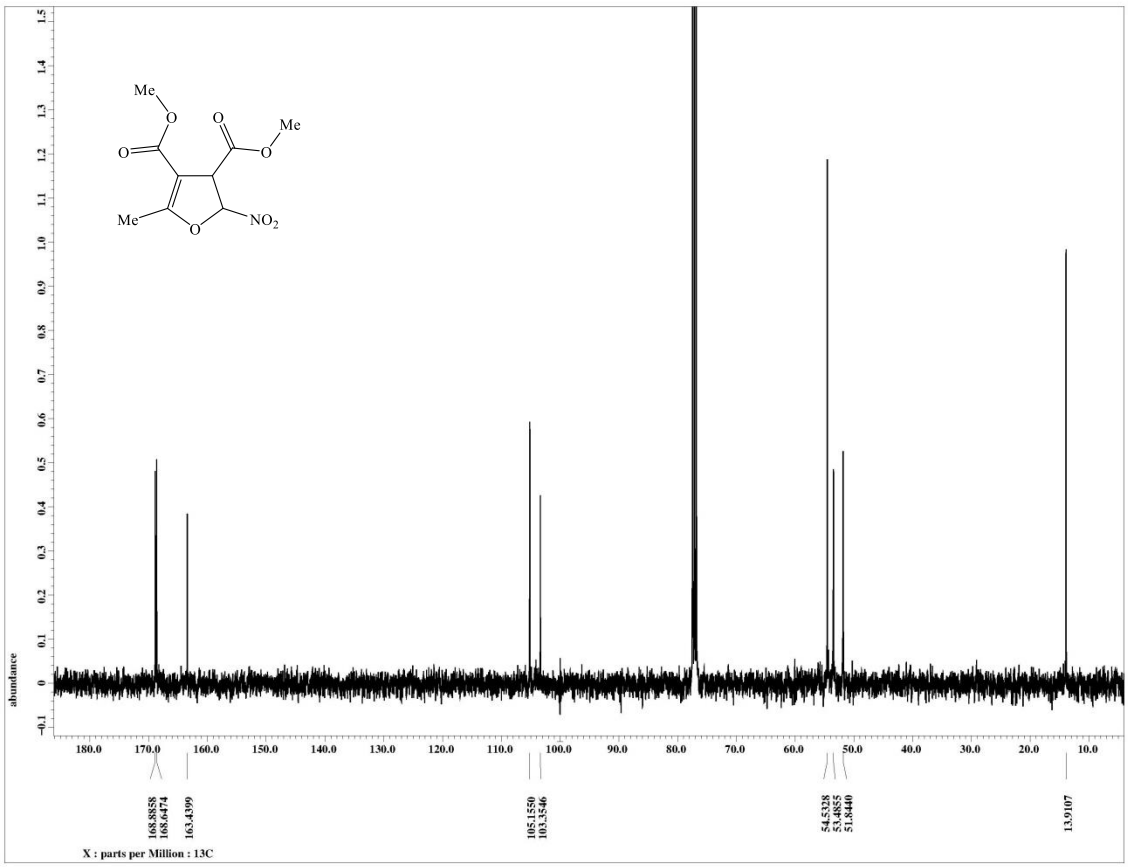

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

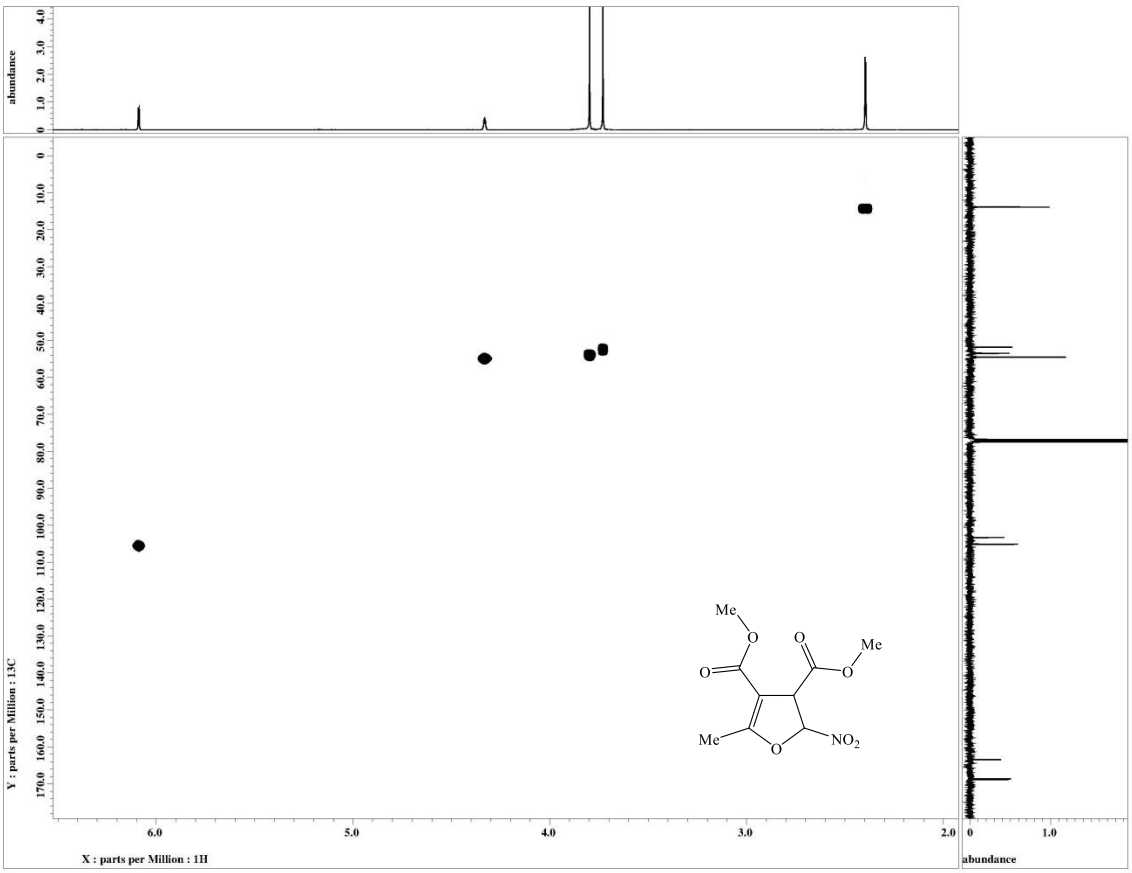

Figure S19. ^{1}H-^{13}C HMQC spectrum of dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

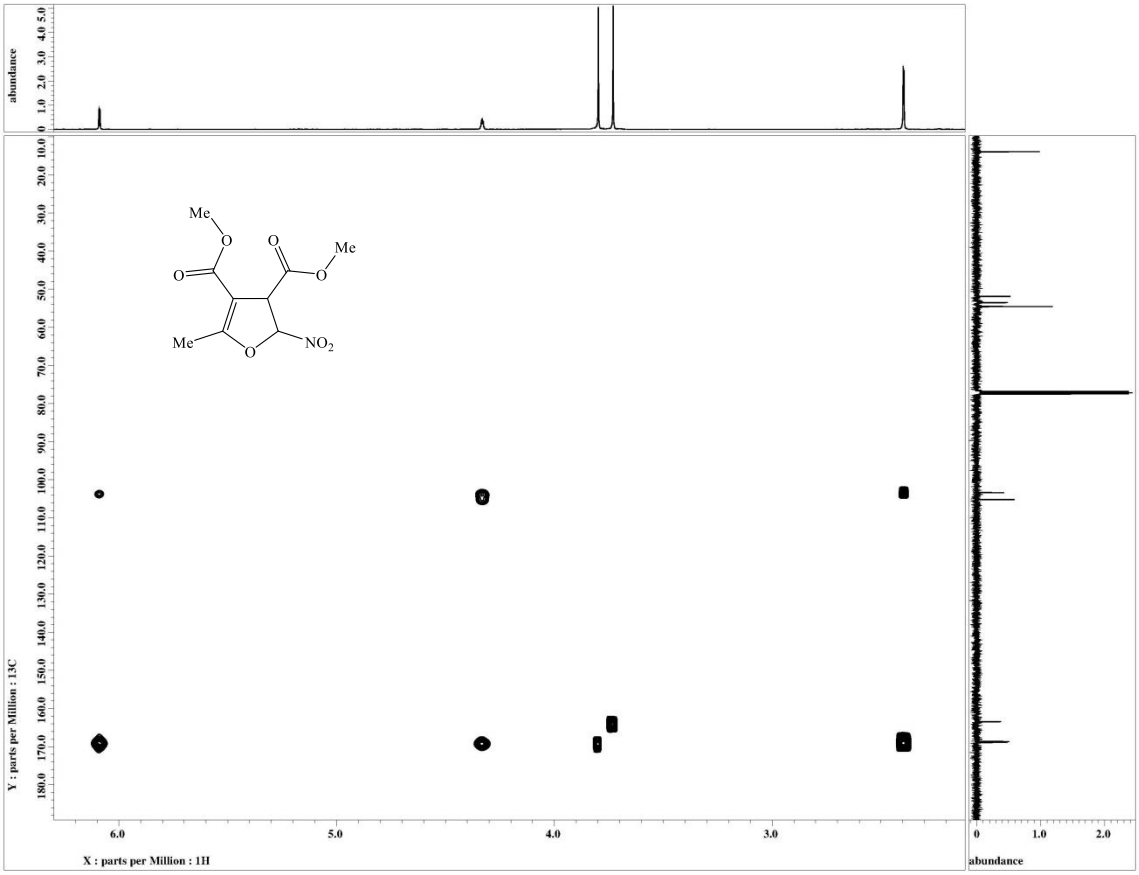

Figure S20. ^{1}H-^{13}C HMBC spectrum of dimethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2b** in $CDCl_3$

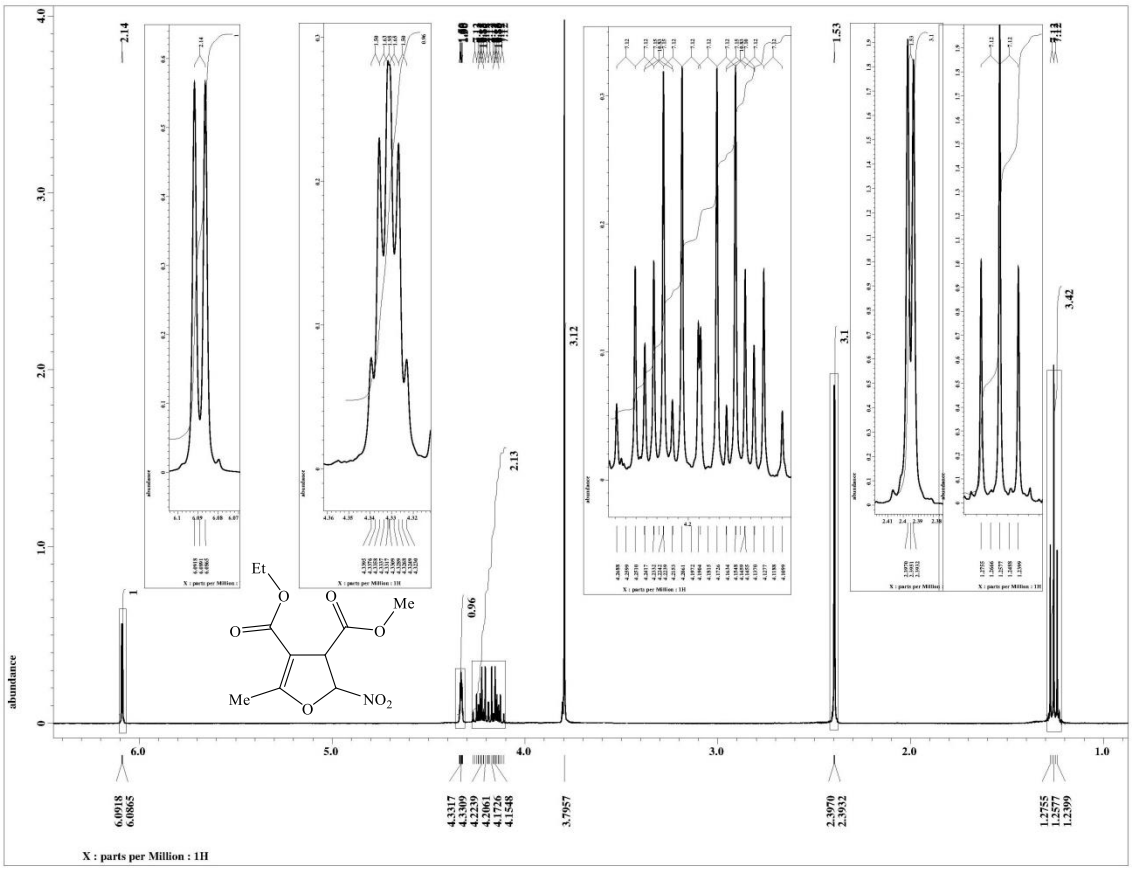

Figure S21. ^{1}H NMR spectrum of 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

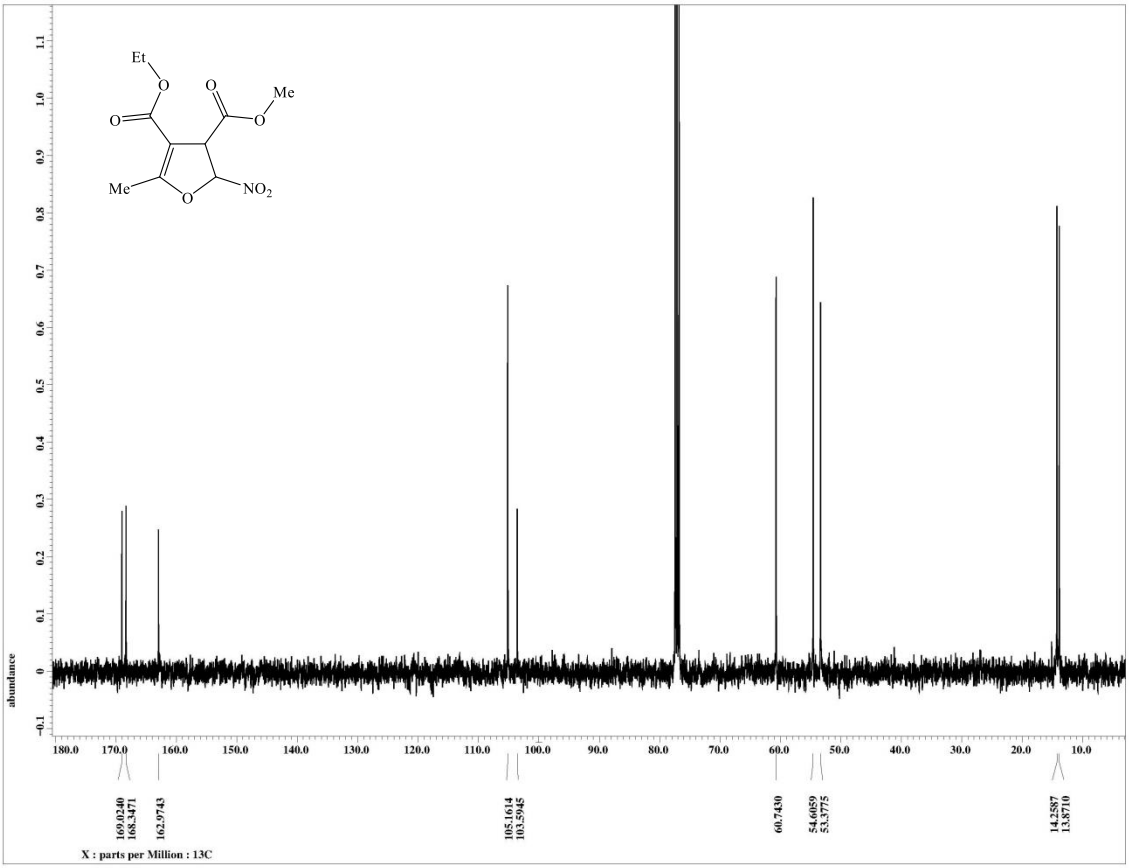

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

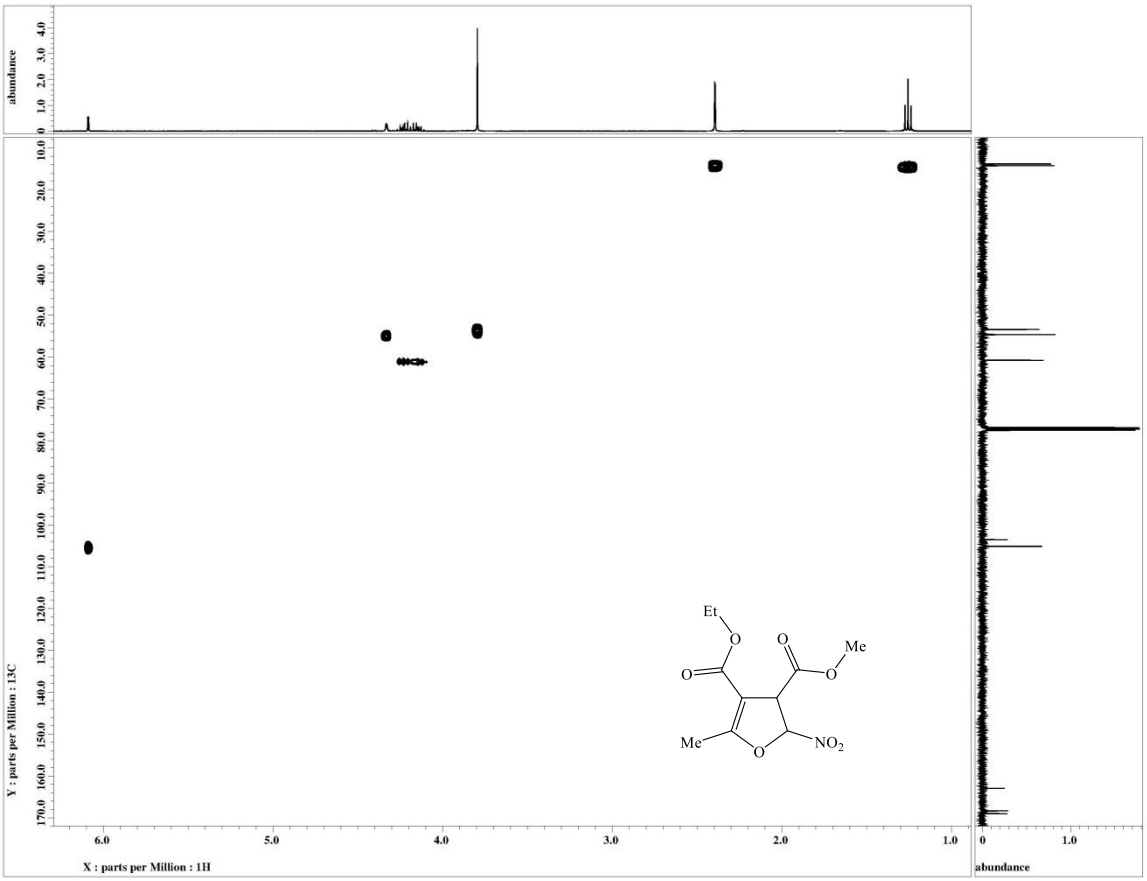

Figure S23. ^{1}H-^{13}C HMQC spectrum of 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

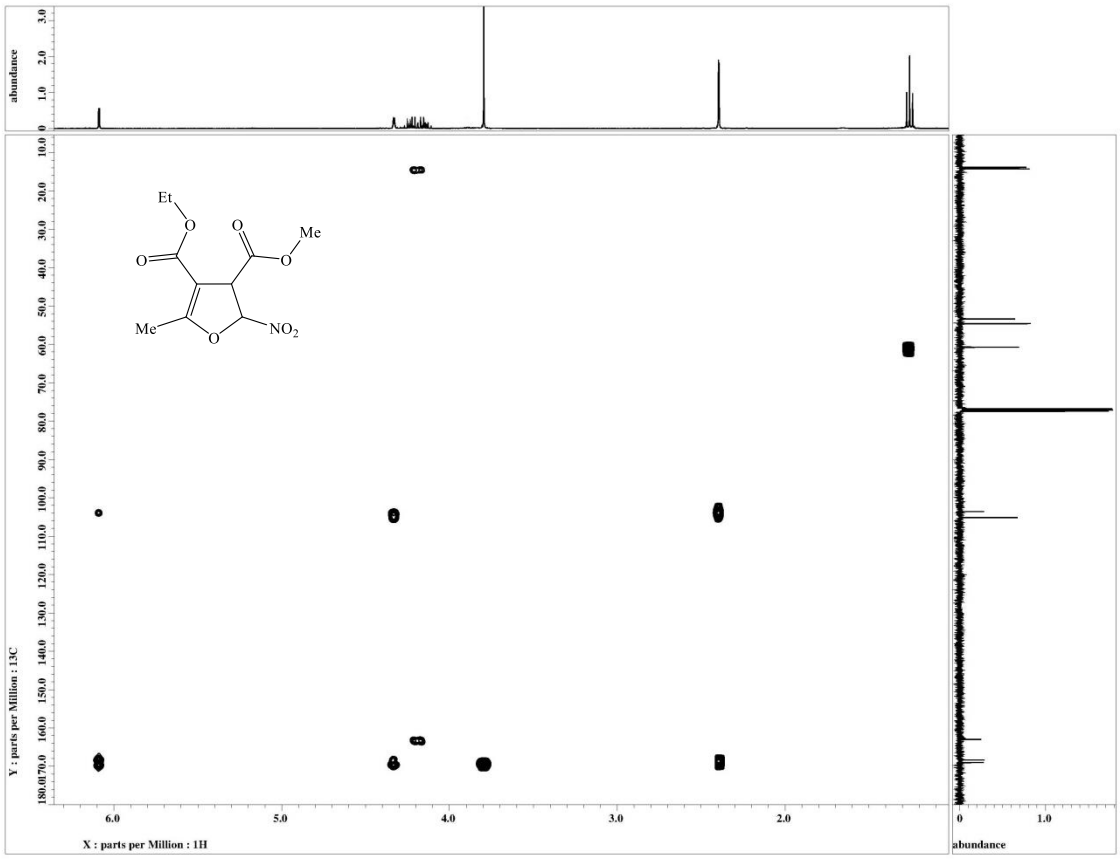

Figure S24. ^{1}H-^{13}C HMBC spectrum of 4-ethyl 3-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2c** in $CDCl_3$

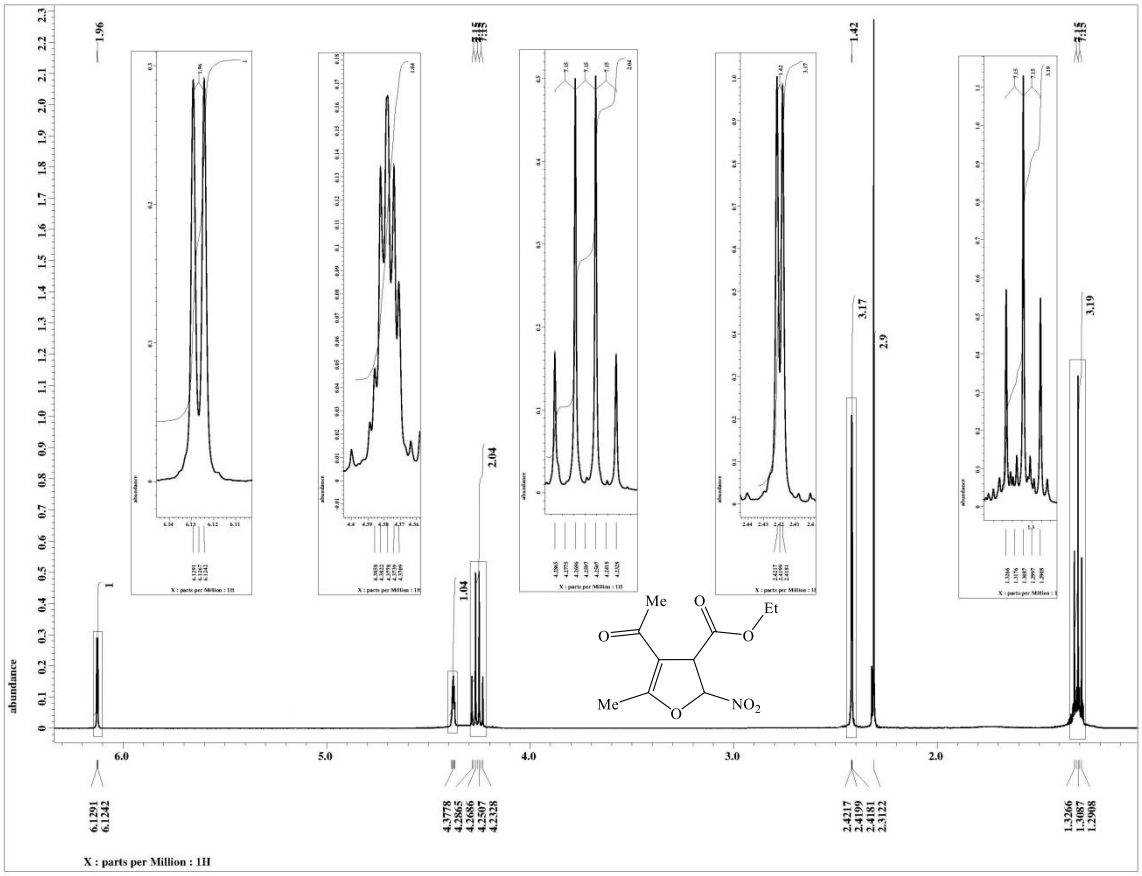

Figure S25. ^{1}H NMR spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CDCl_3$

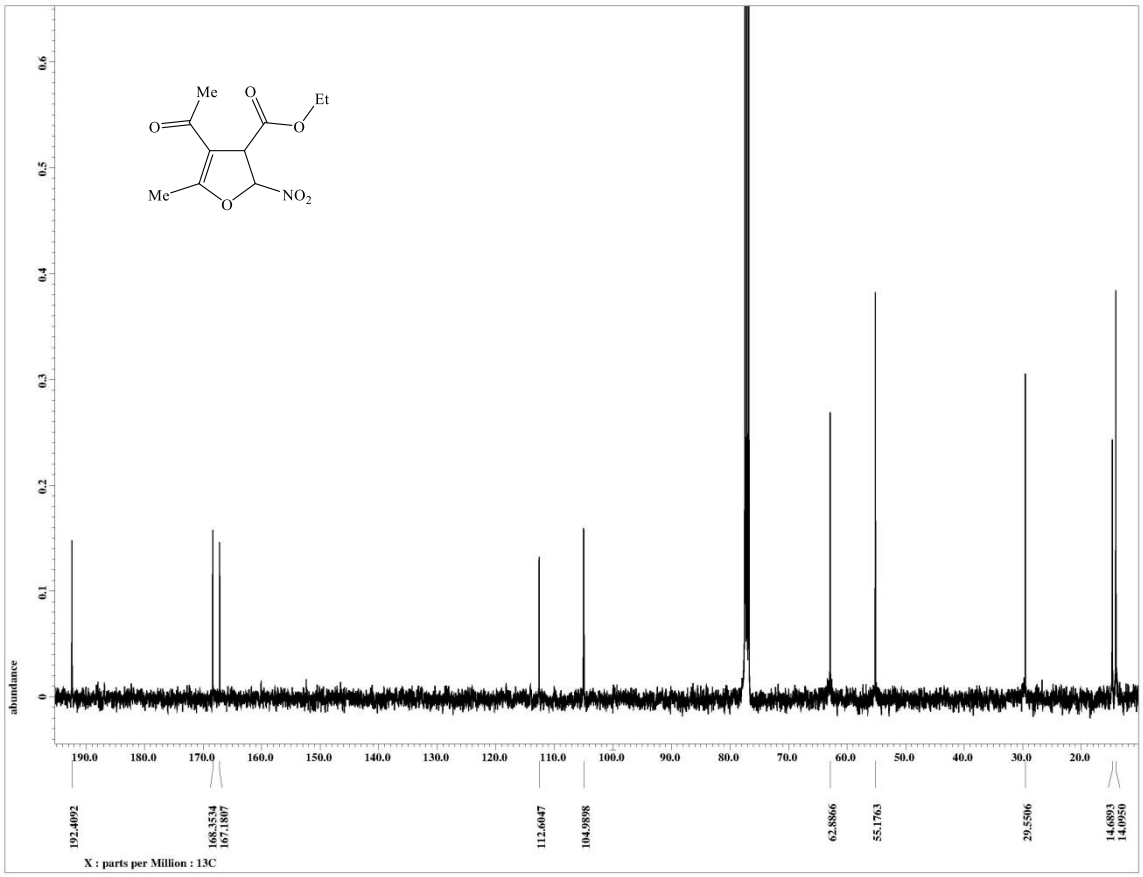

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CDCl_3$

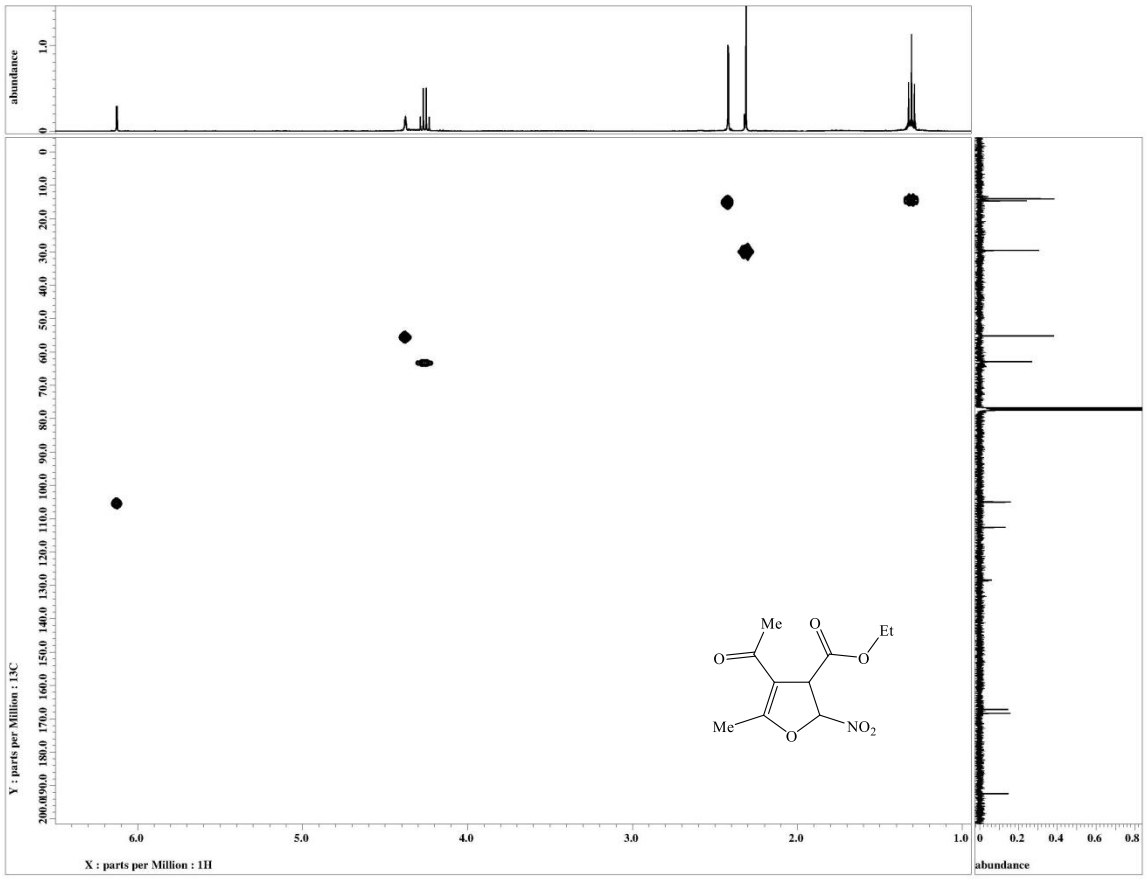

Figure S27. ^{1}H-^{13}C HMQC spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CDCl_3$

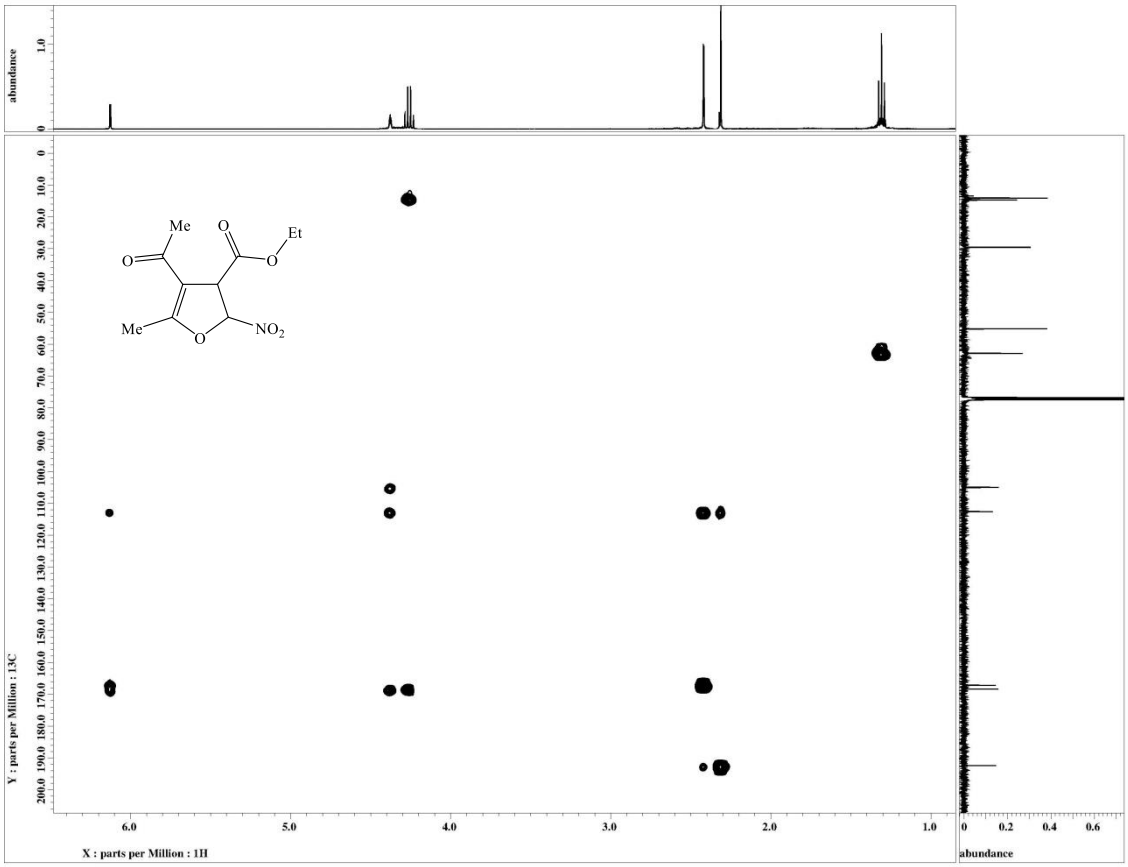

Figure S28. ^{1}H-^{13}C HMBC spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CDCl_3$

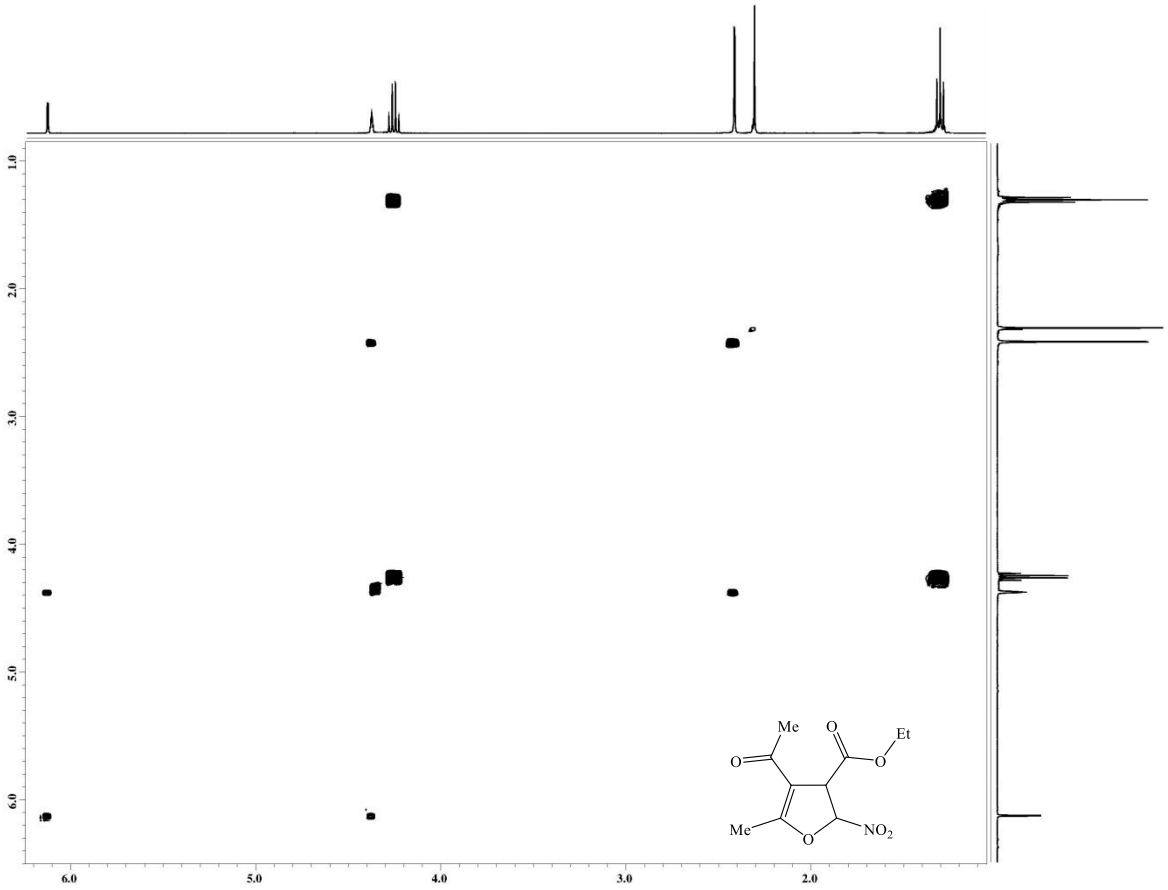

Figure S29. ^{1}H-^{1}H dqf-COSY spectrum of ethyl 4-acetyl-5-methyl-2-nitro-2,3-dihydrofuran-3-carboxylate **2d** in $CDCl_3$

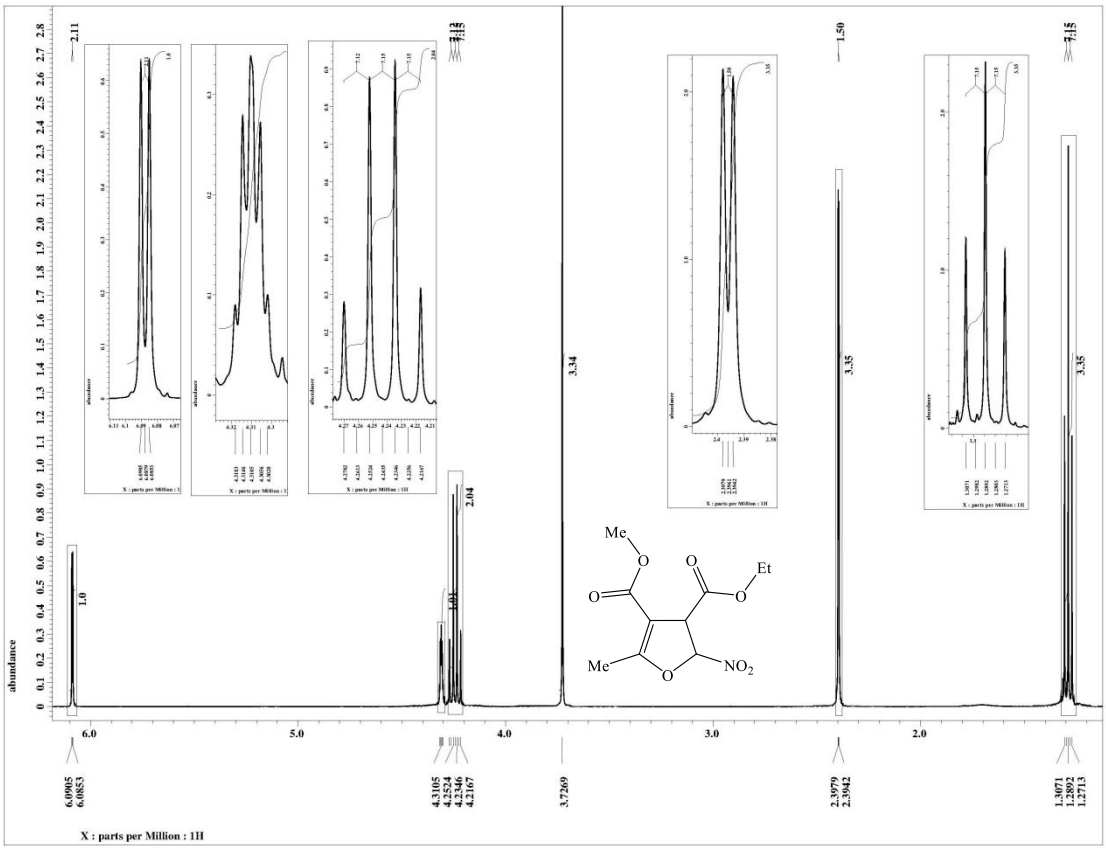

Figure S30. ^{1}H NMR spectrum of 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

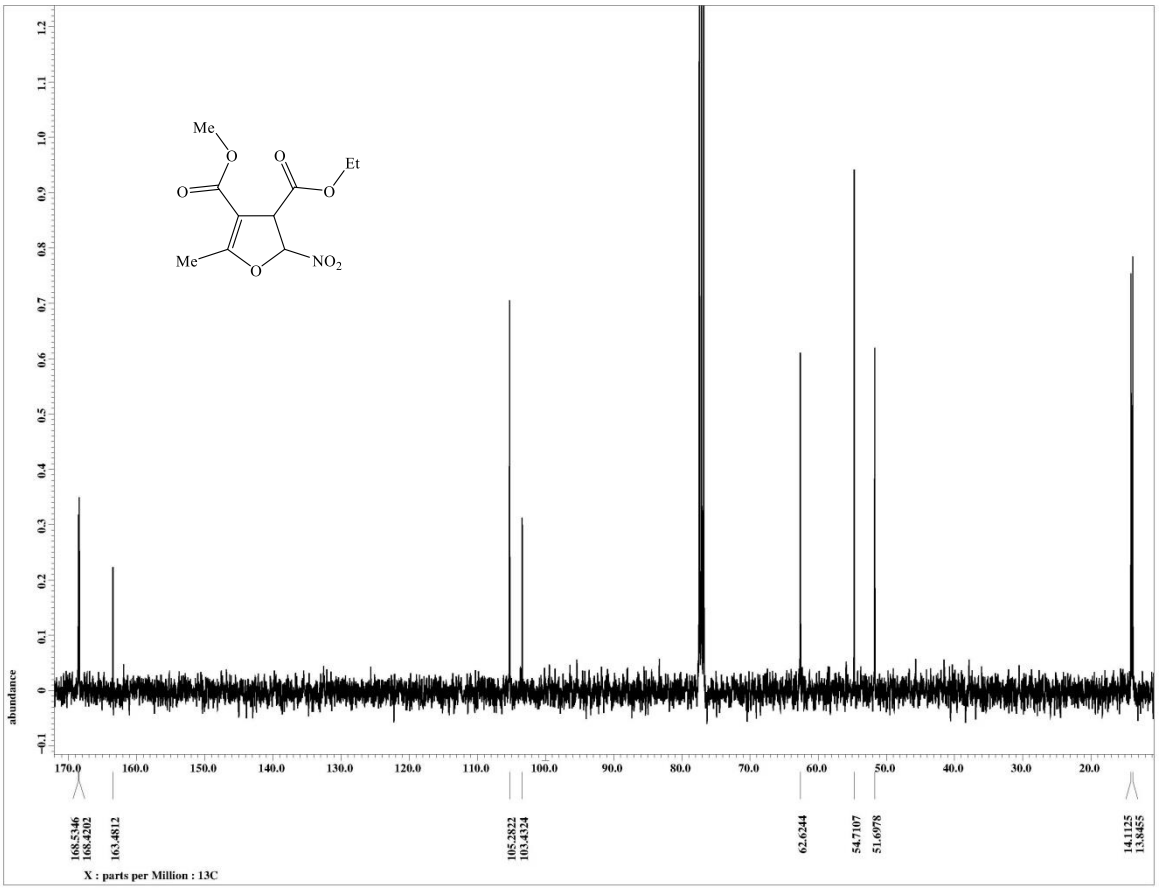

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

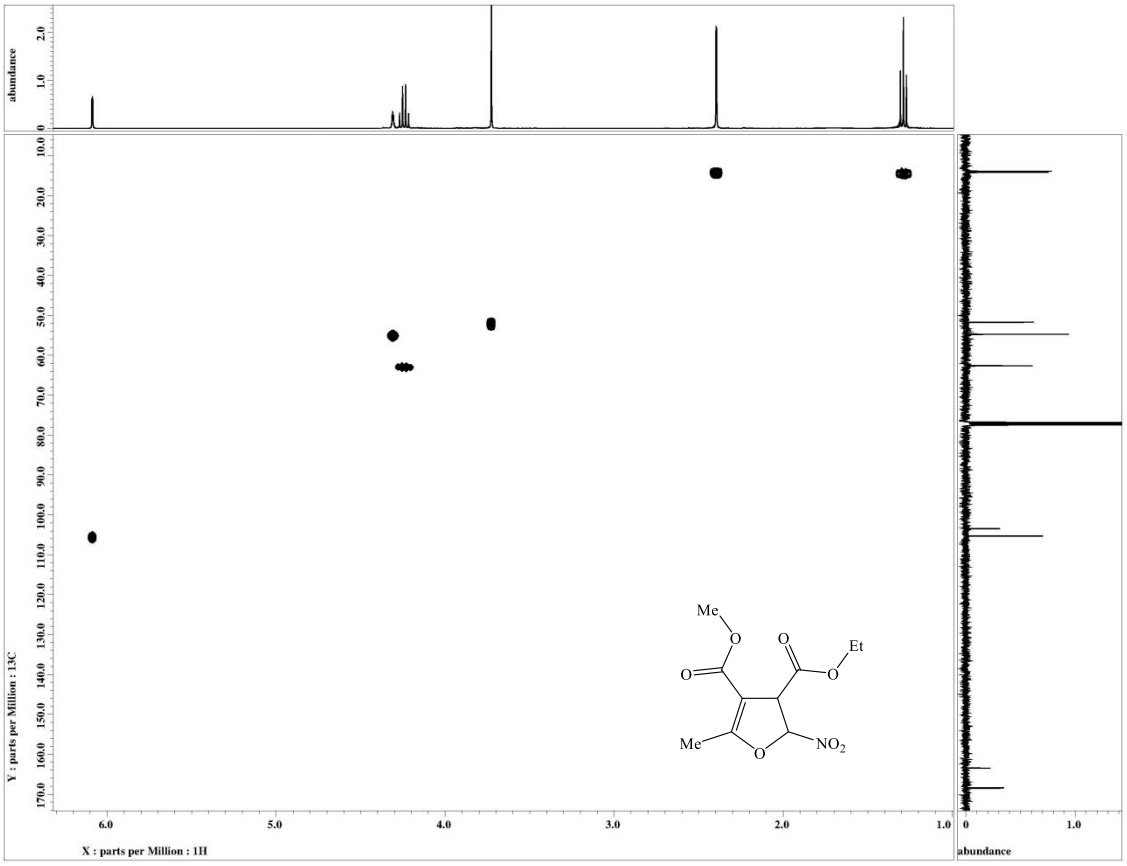

Figure S32. ^{1}H-^{13}C HMQC spectrum of 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

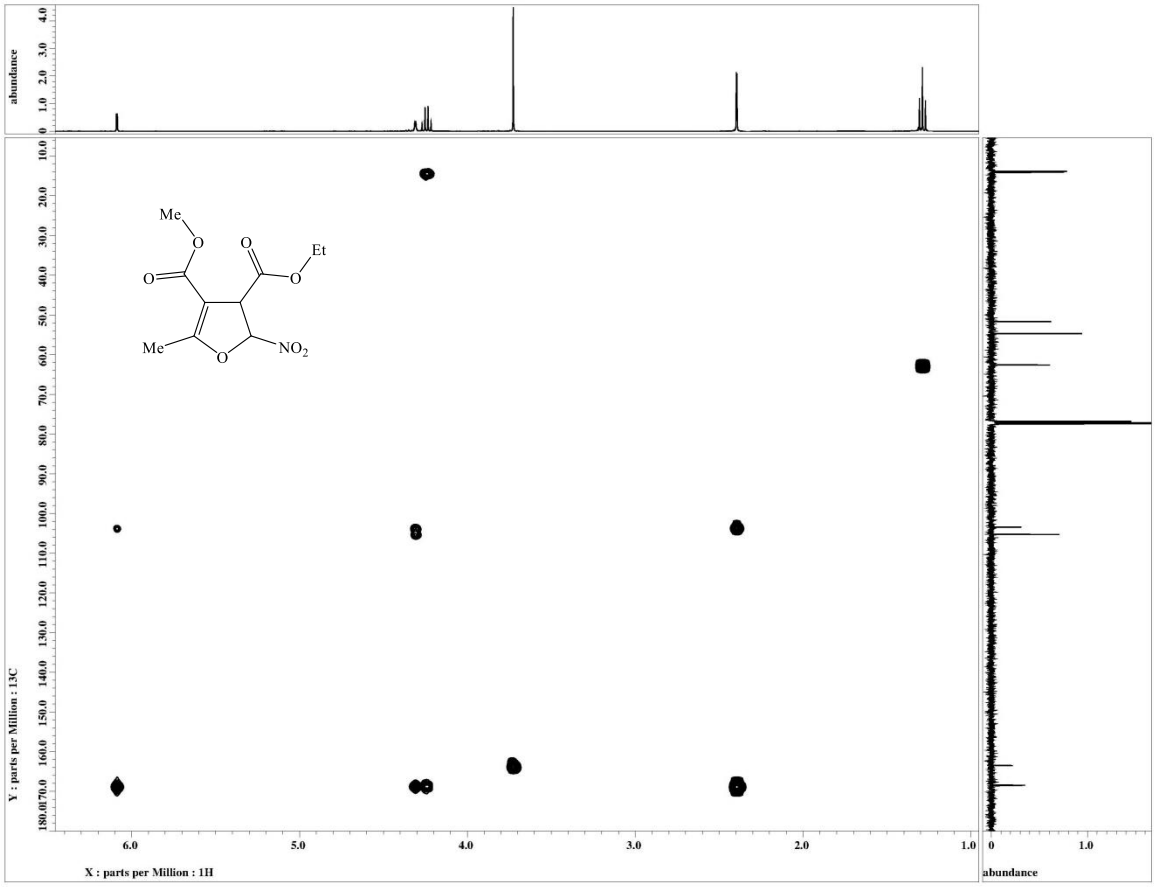

Figure S33. ^{1}H-^{13}C HMBC spectrum of 3-ethyl 4-methyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2e** in $CDCl_3$

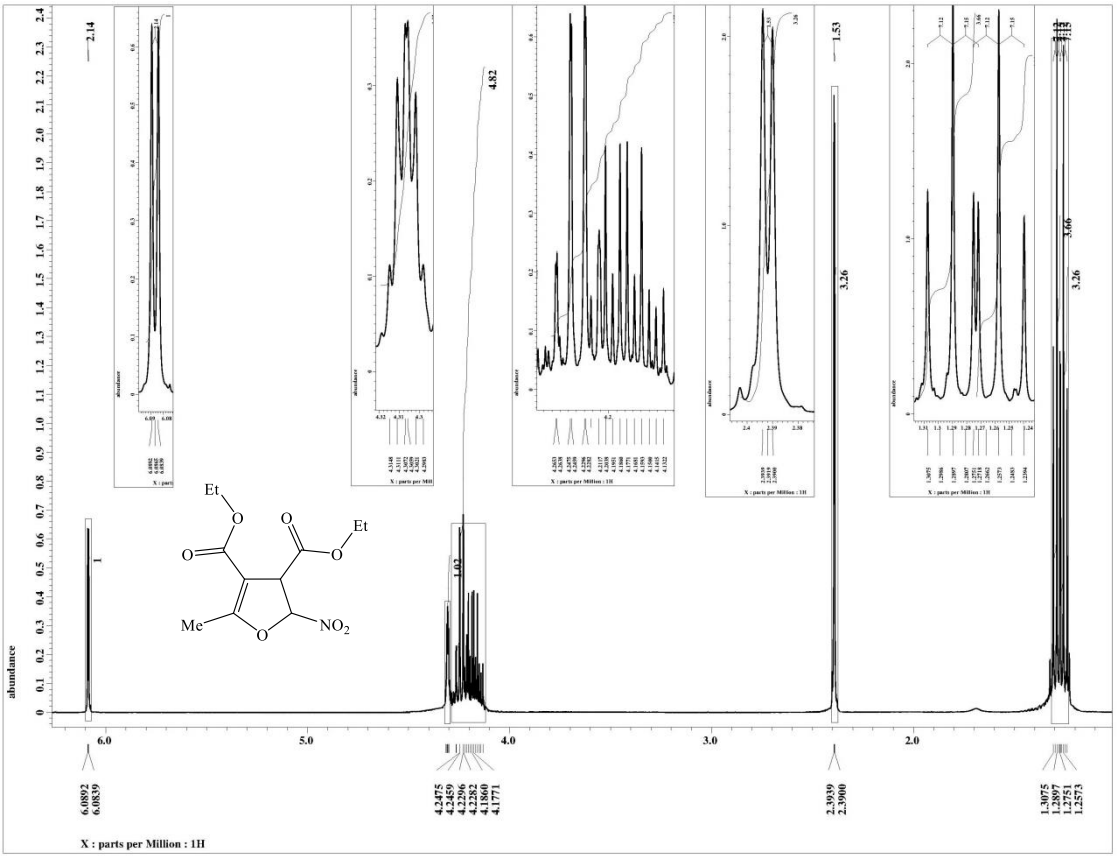

Figure S34. ^{1}H NMR spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

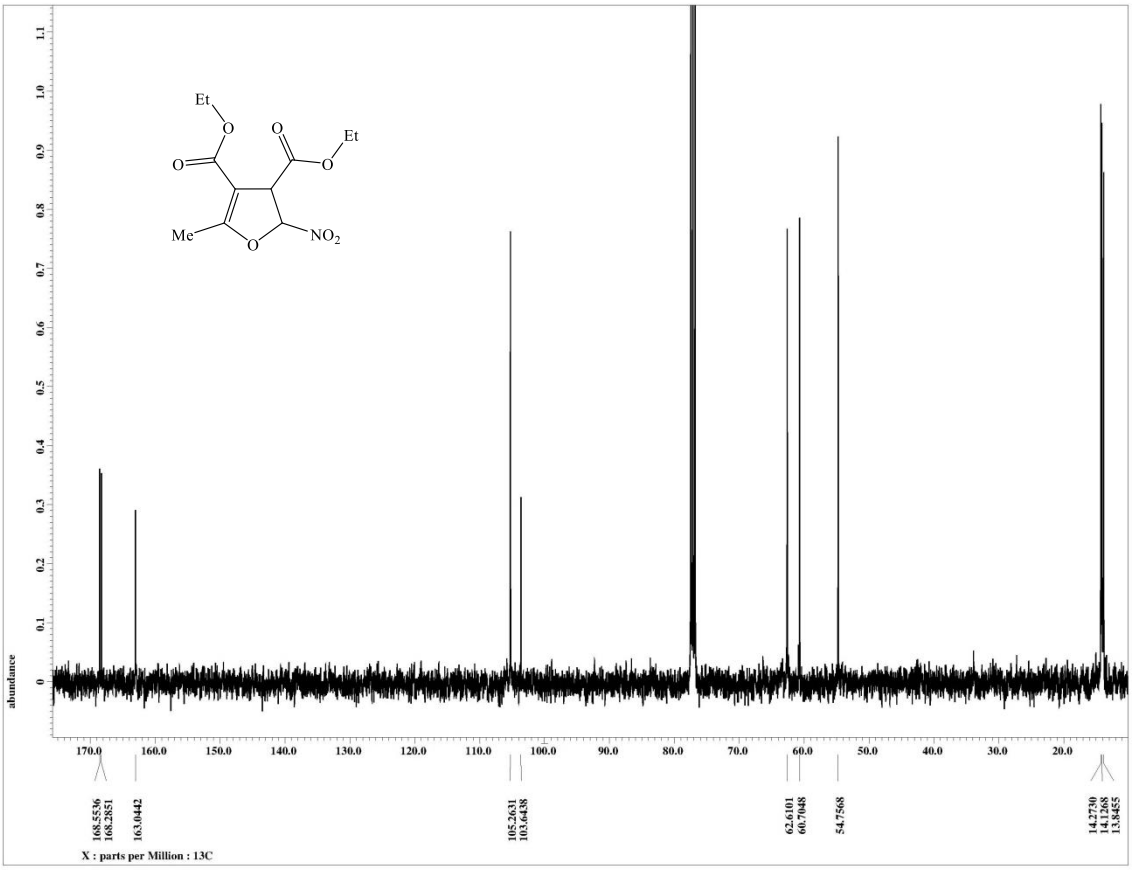

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

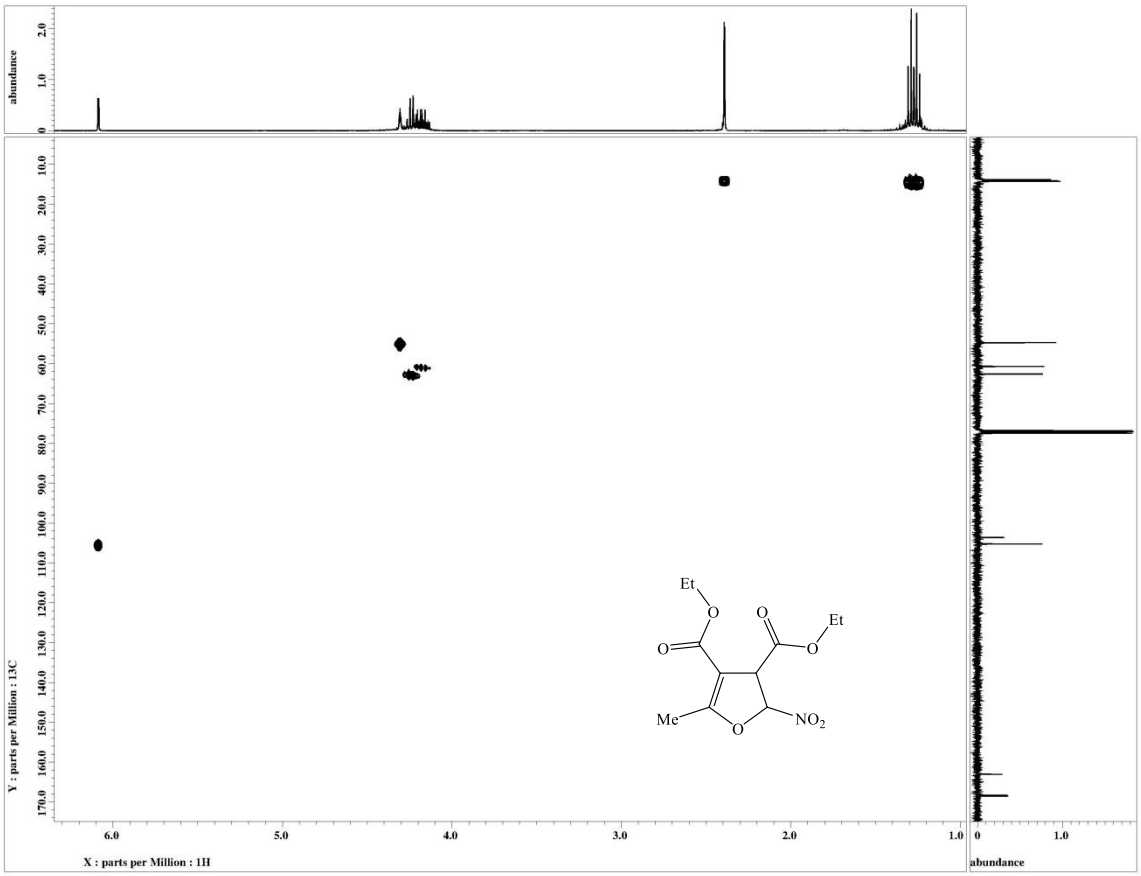

Figure S36. ^{1}H-^{13}C HMQC spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

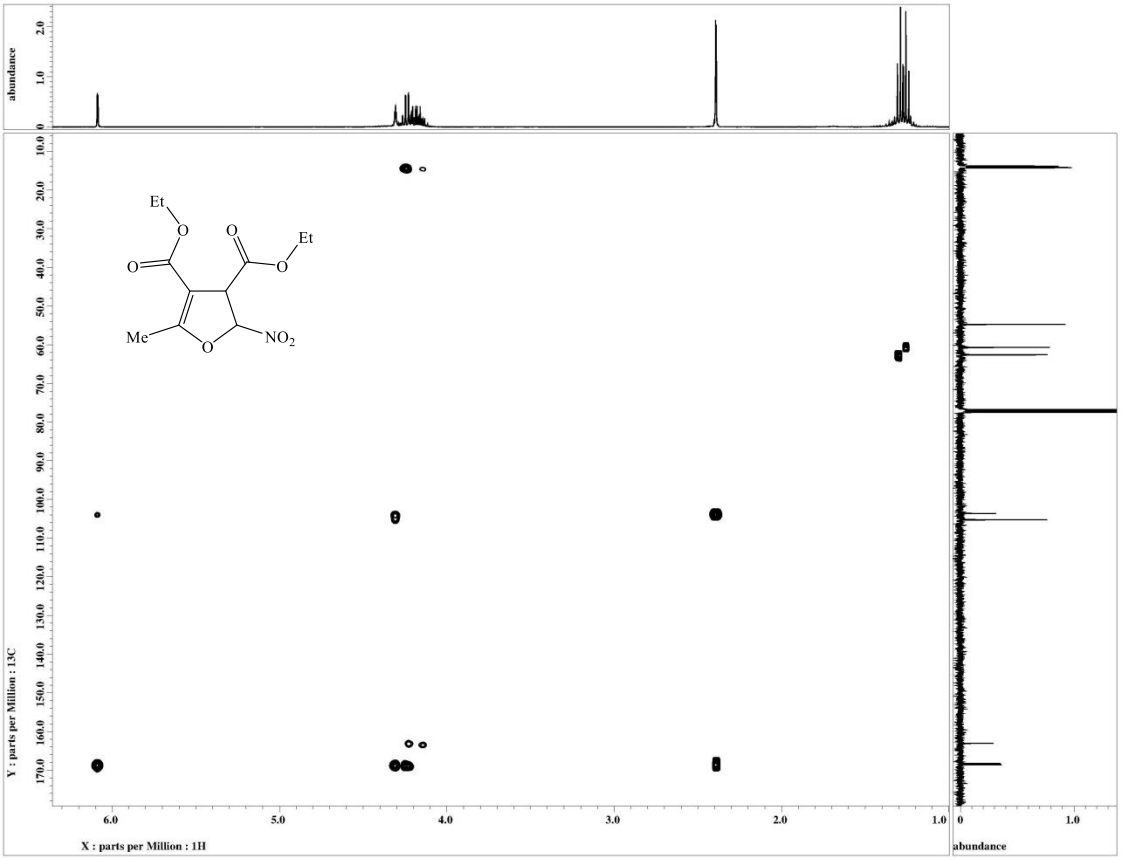

Figure S37. ^{1}H-^{13}C HMBC spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

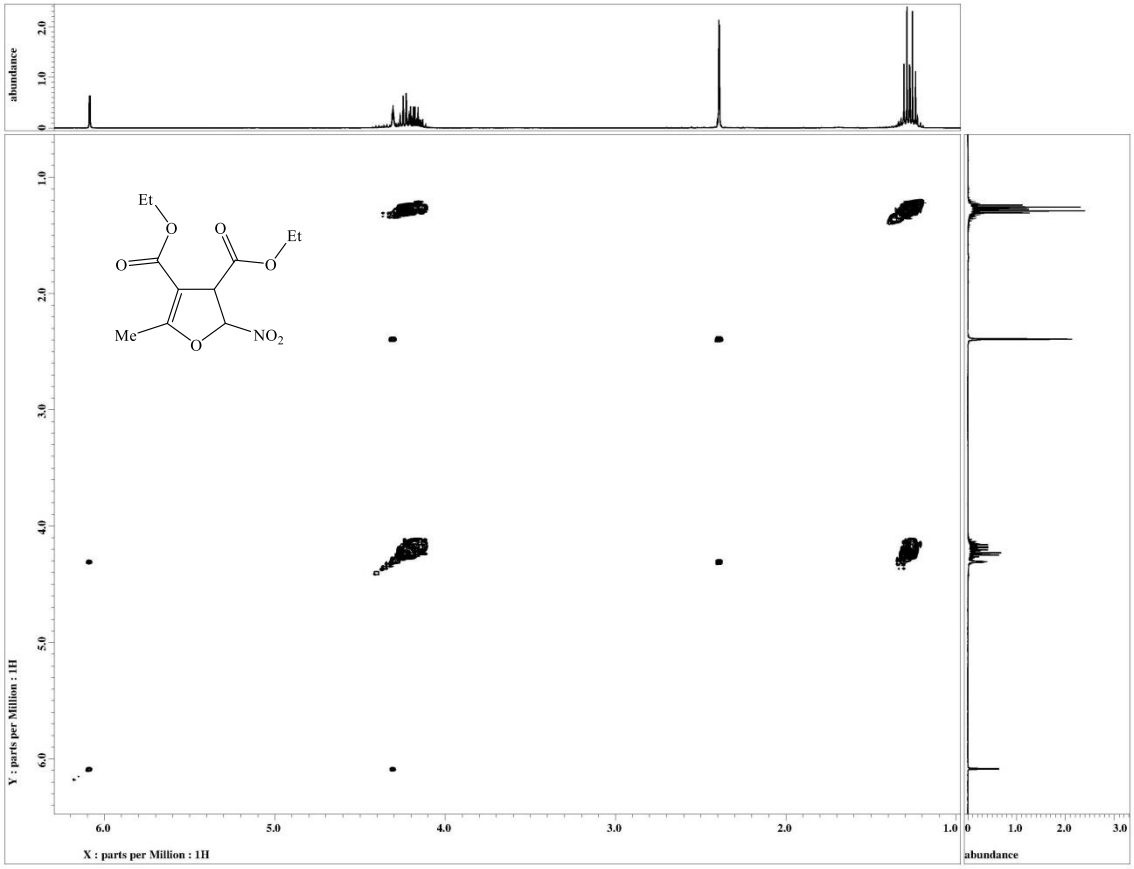

Figure S38. ^{1}H-^{1}H dqf-COSY spectrum of diethyl 5-methyl-2-nitro-2,3-dihydrofuran-3,4-dicarboxylate **2f** in $CDCl_3$

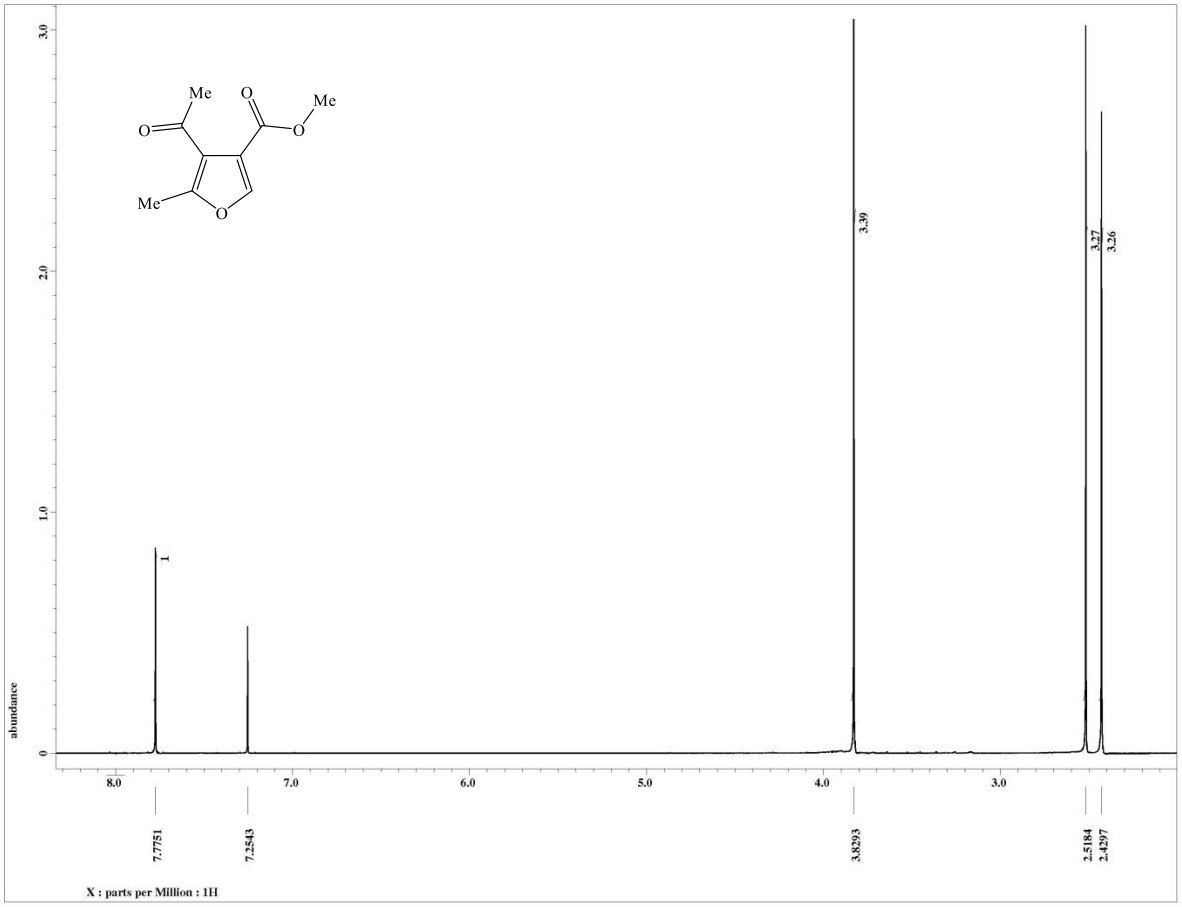

Figure S39. ^{1}H NMR spectrum of methyl 4-acetyl-5-methylfuran-3-carboxylate **3a** in $CDCl_3$

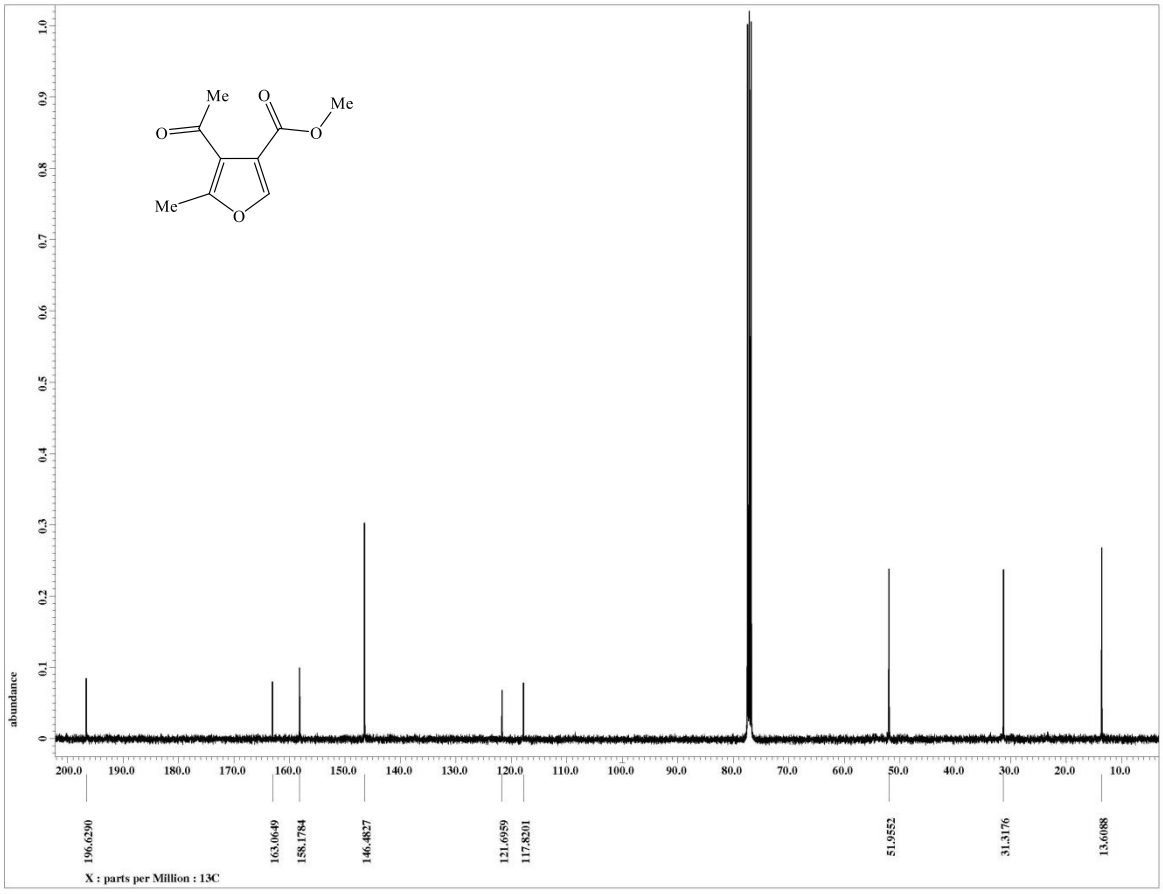

Figure S40. ^{13}C{^{1}H} NMR spectrum of methyl 4-acetyl-5-methylfuran-3-carboxylate **3a** in $CDCl_3$

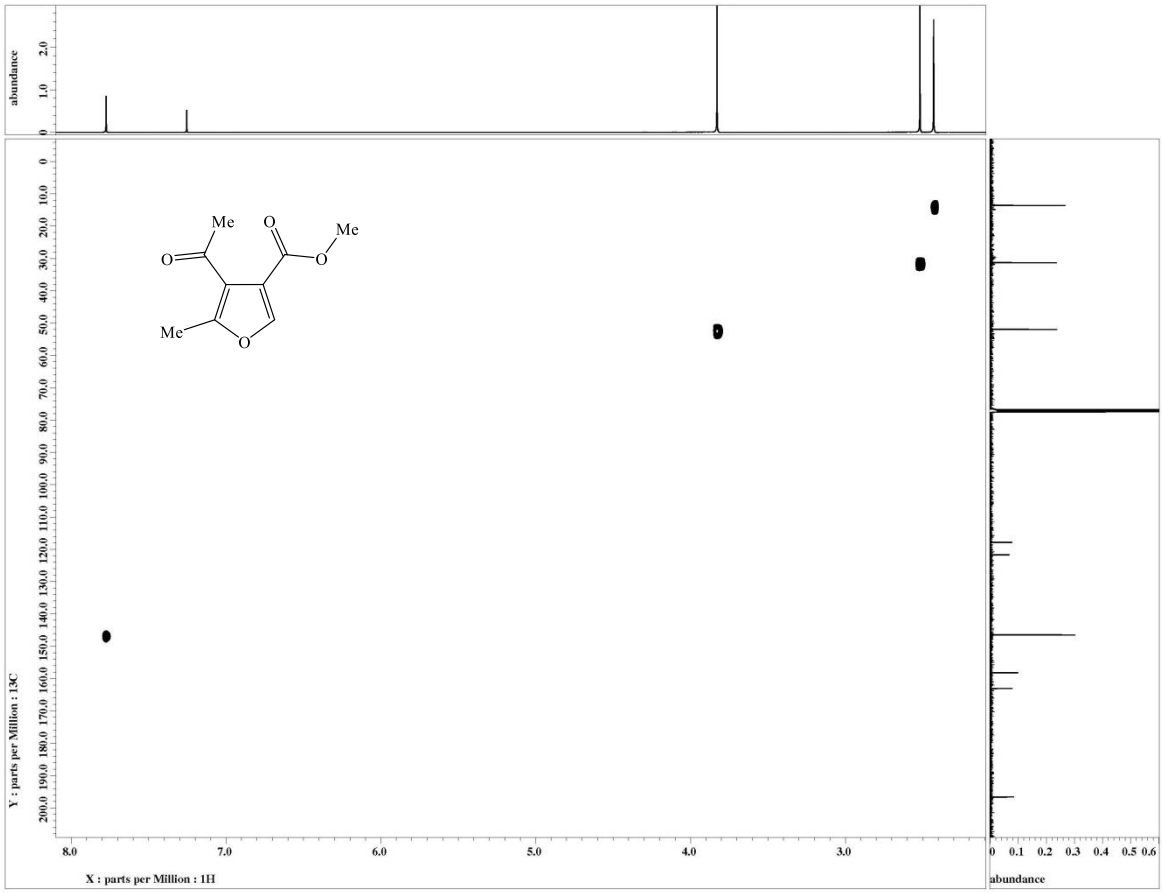

Figure S41. ^{1}H-^{13}C HMQC spectrum of methyl 4-acetyl-5-methylfuran-3-carboxylate **3a** in $CDCl_3$

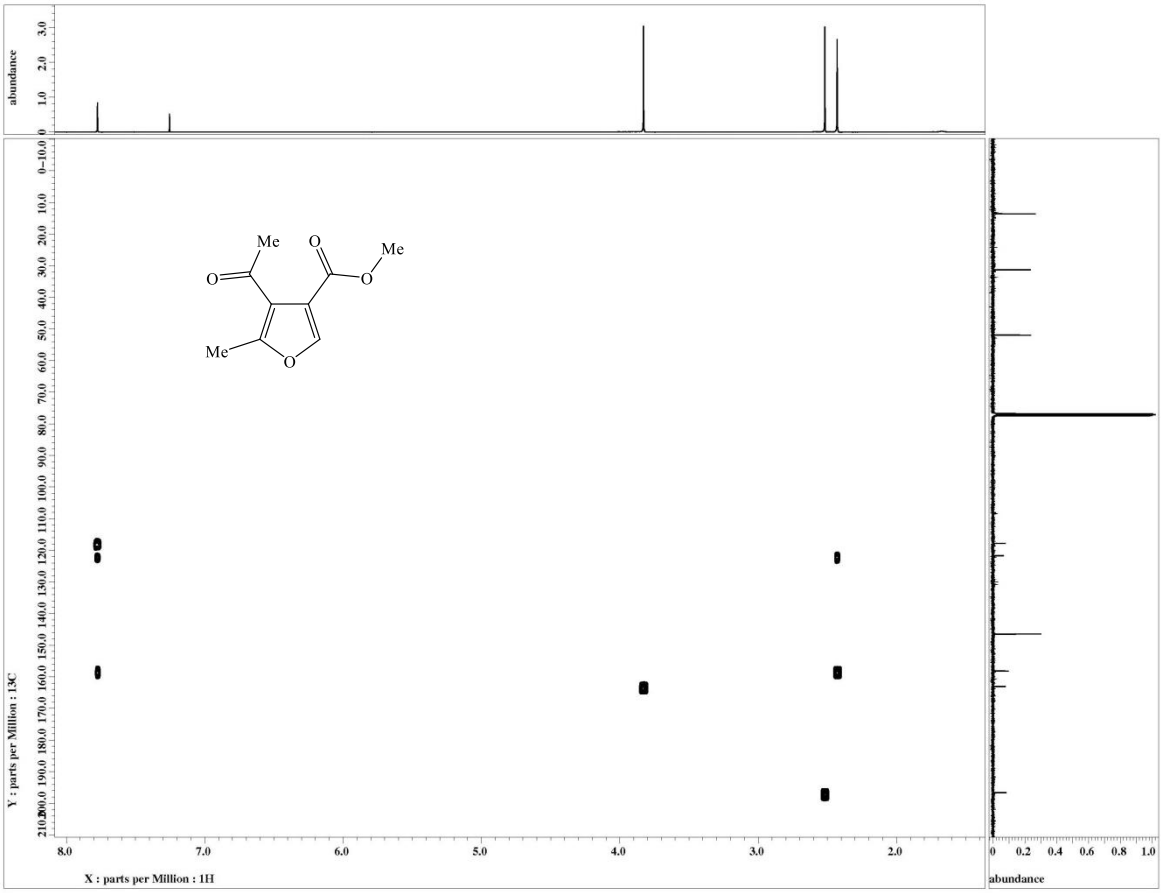

Figure S42. ^{1}H-^{13}C HMBC spectrum of methyl 4-acetyl-5-methylfuran-3-carboxylate **3a** in $CDCl_3$

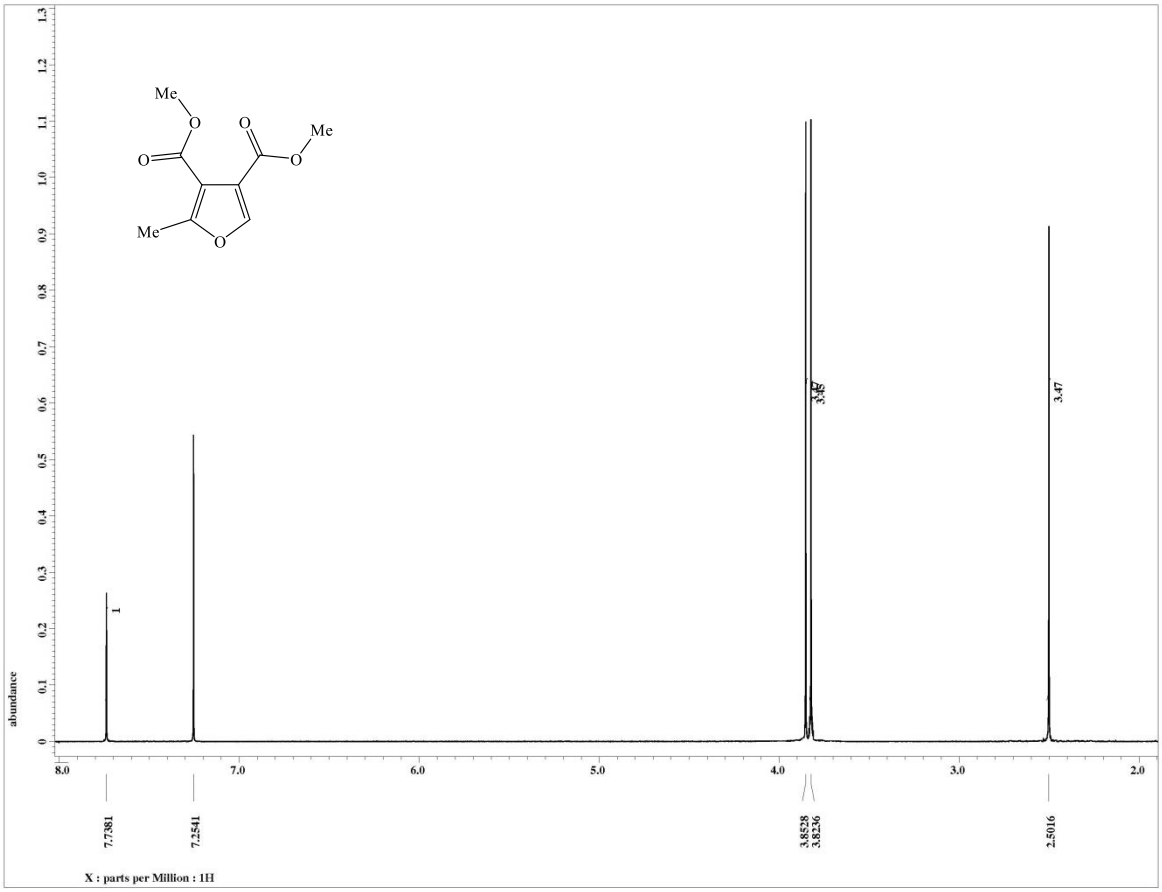

Figure S43. ^{1}H NMR spectrum of dimethyl 2-methylfuran-3,4-dicarboxylate **3b** in $CDCl_3$

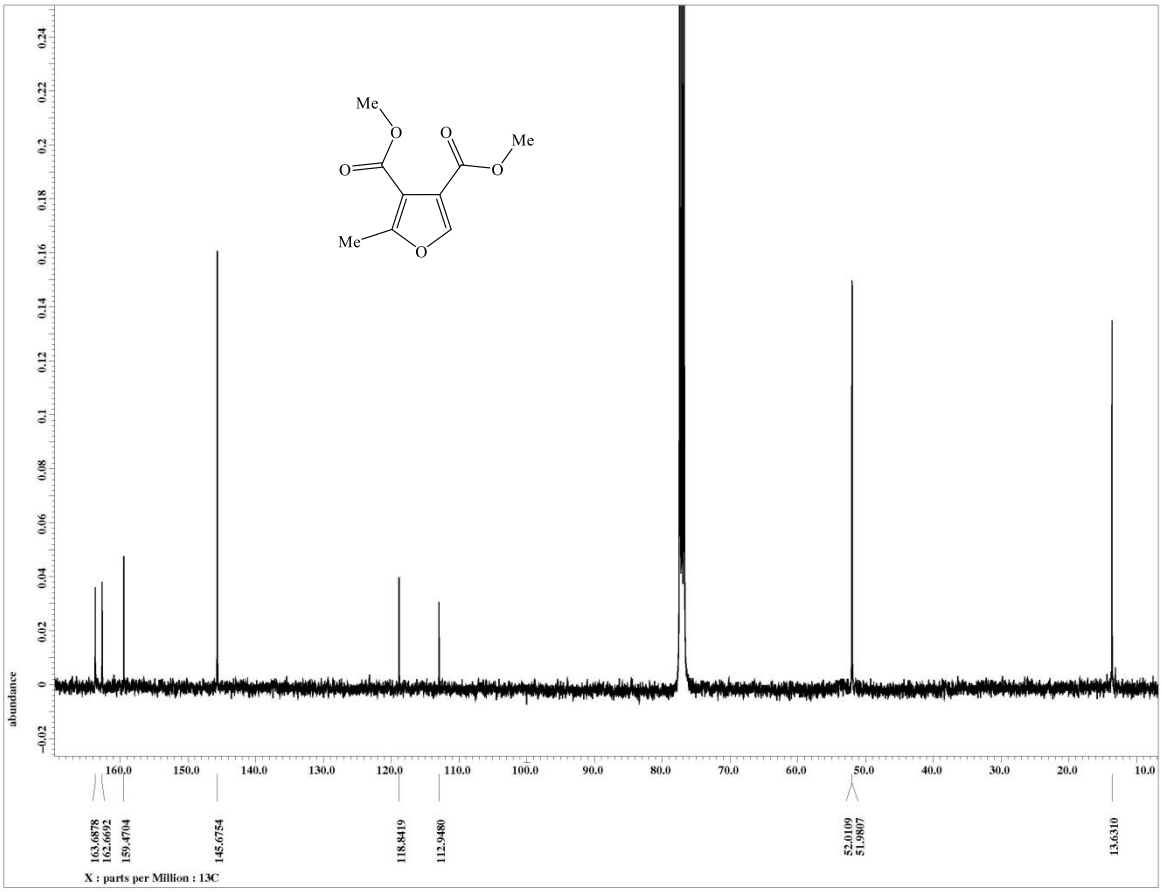

Figure S44. ^{13}C{^{1}H} NMR spectrum of dimethyl 2-methylfuran-3,4-dicarboxylate **3b** in $CDCl_3$

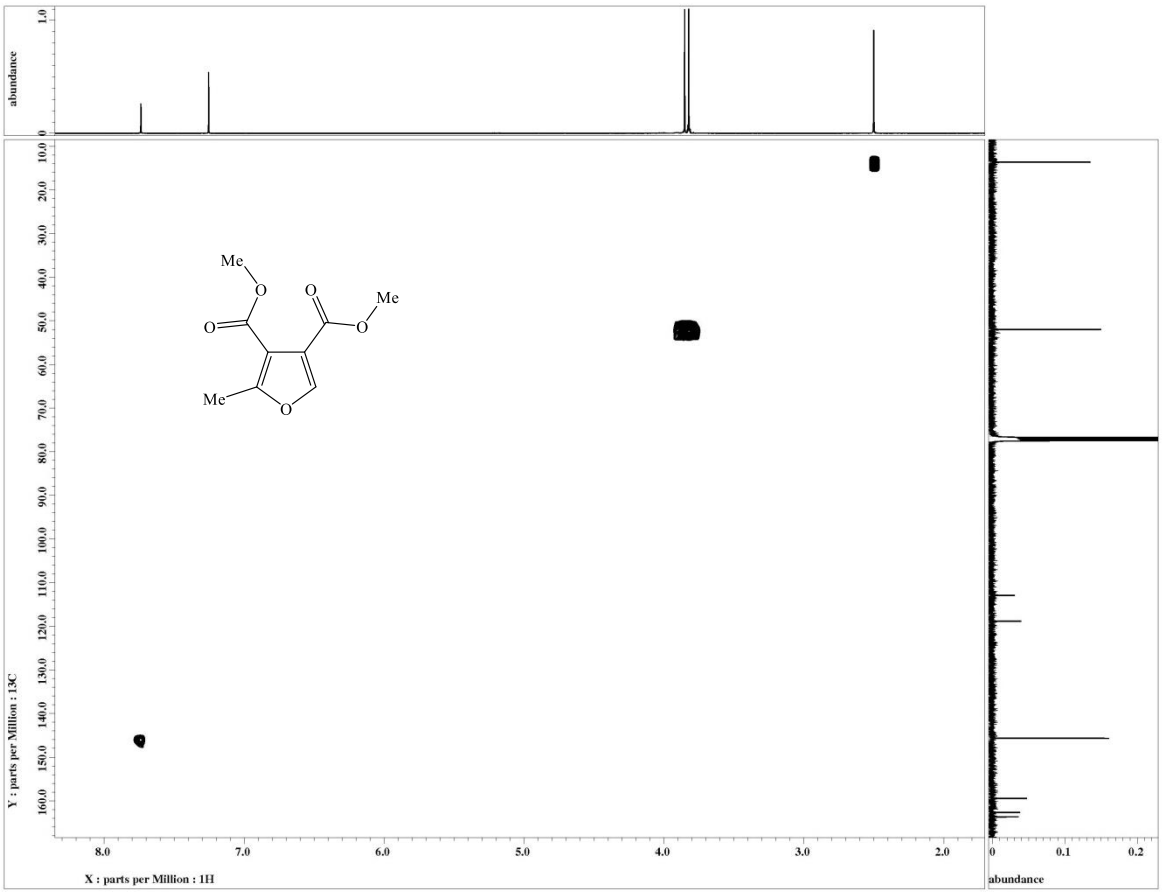

Figure S45. ^{1}H-^{13}C HMQC spectrum of dimethyl 2-methylfuran-3,4-dicarboxylate **3b** in $CDCl_3$

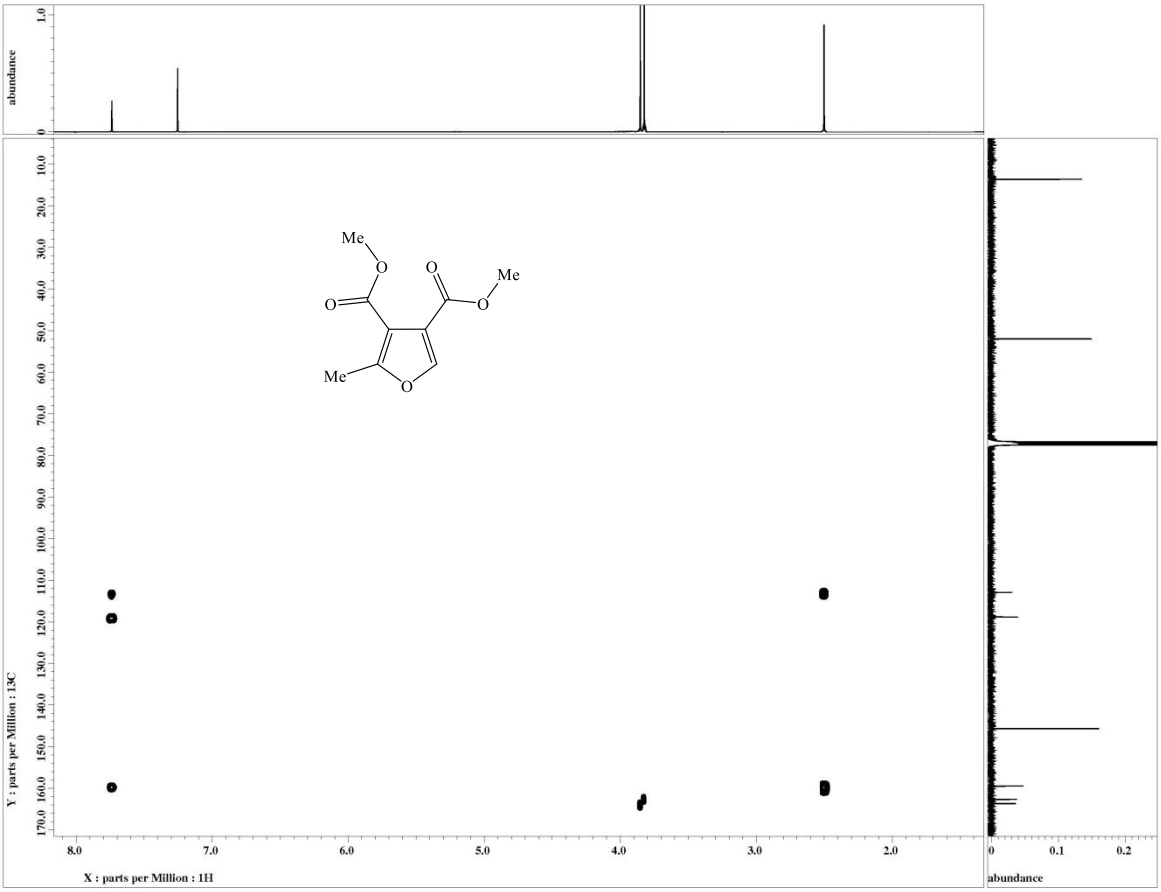

Figure S46. ^{1}H-^{13}C HMBC spectrum of dimethyl 2-methylfuran-3,4-dicarboxylate **3b** in $CDCl_3$

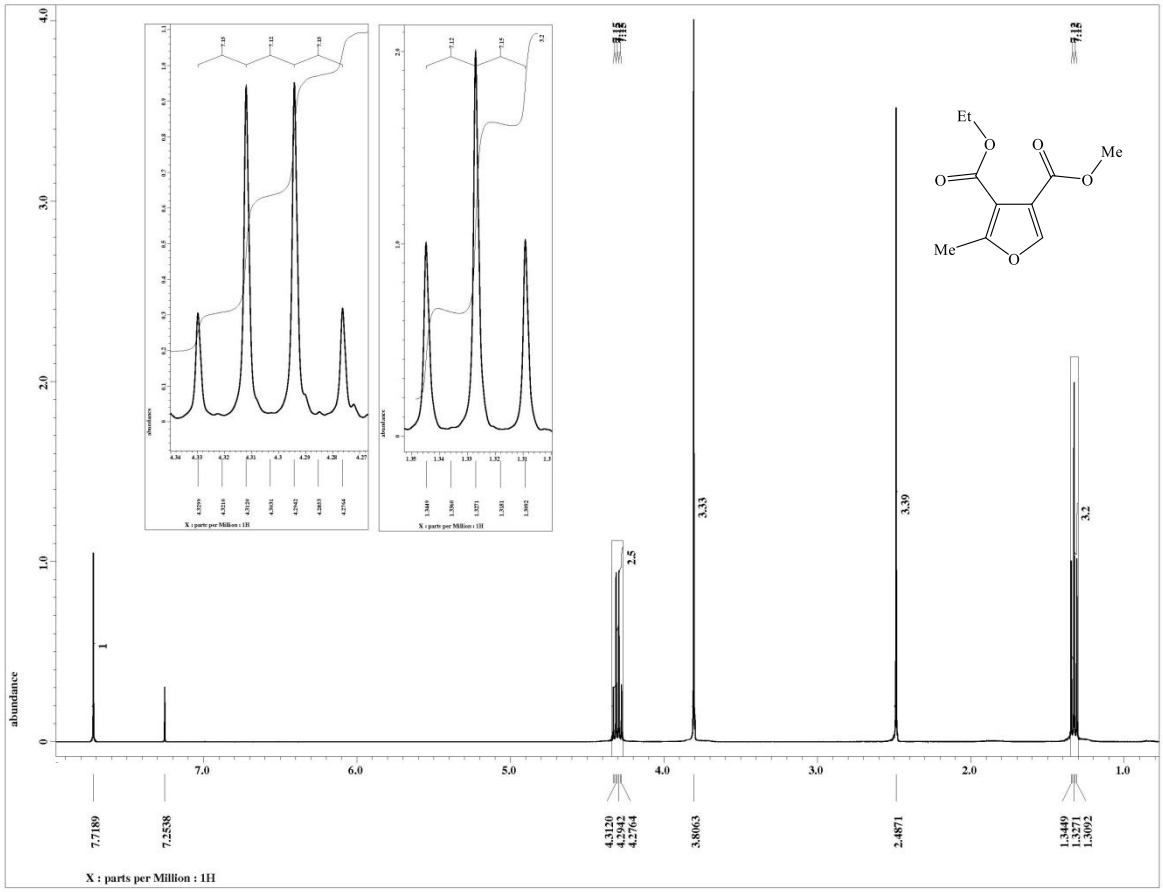

Figure S47. ^{1}H NMR spectrum of 3-ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate **3c** in $CDCl_3$

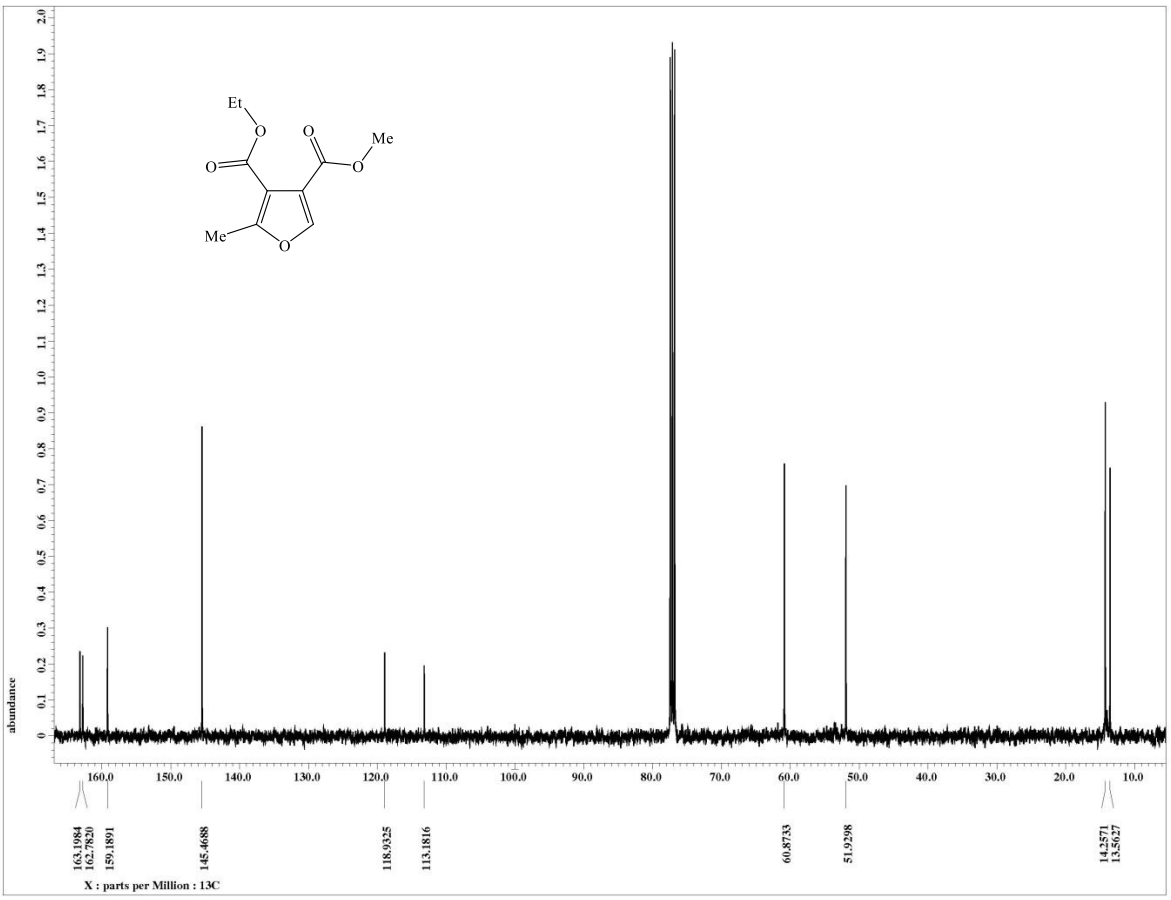

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of 3-ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate **3c** in $CDCl_3$

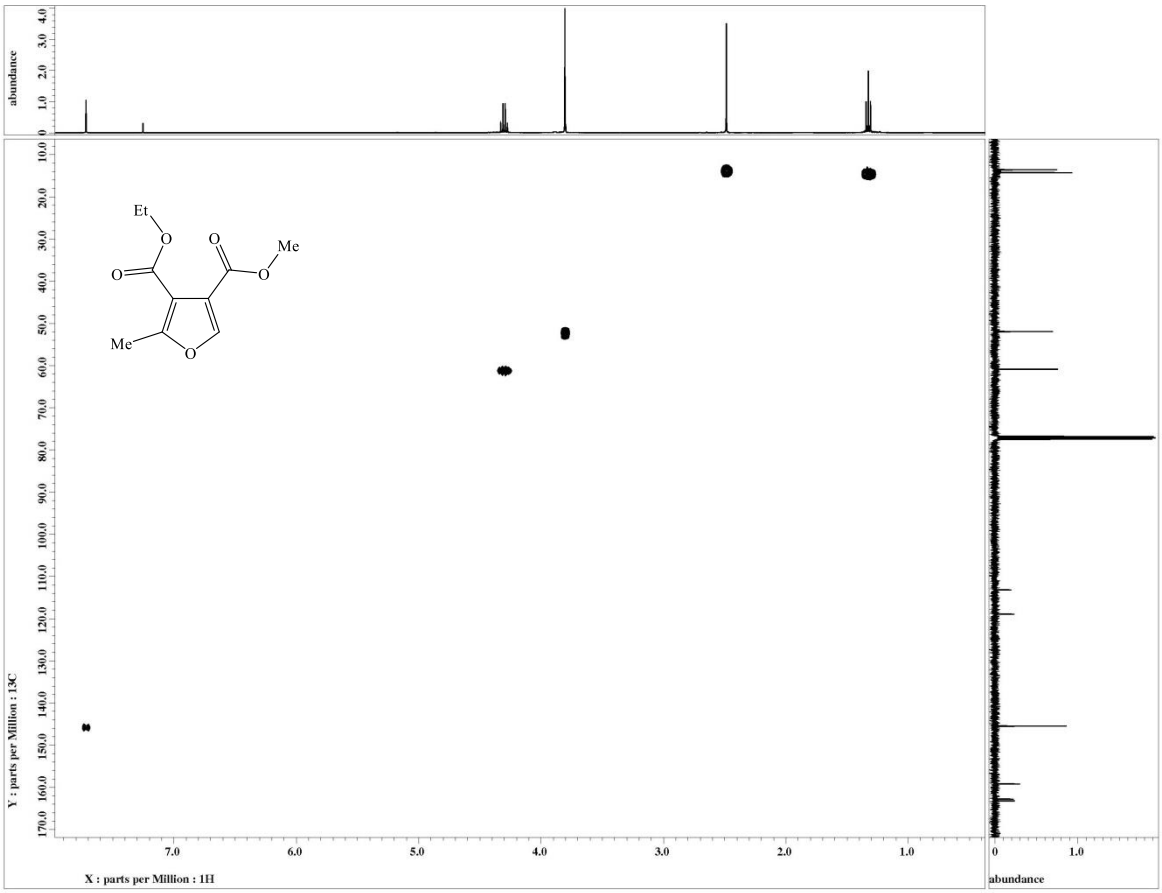

Figure S49. ^{1}H-^{13}C HMQC spectrum of 3-ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate **3c** in $CDCl_3$

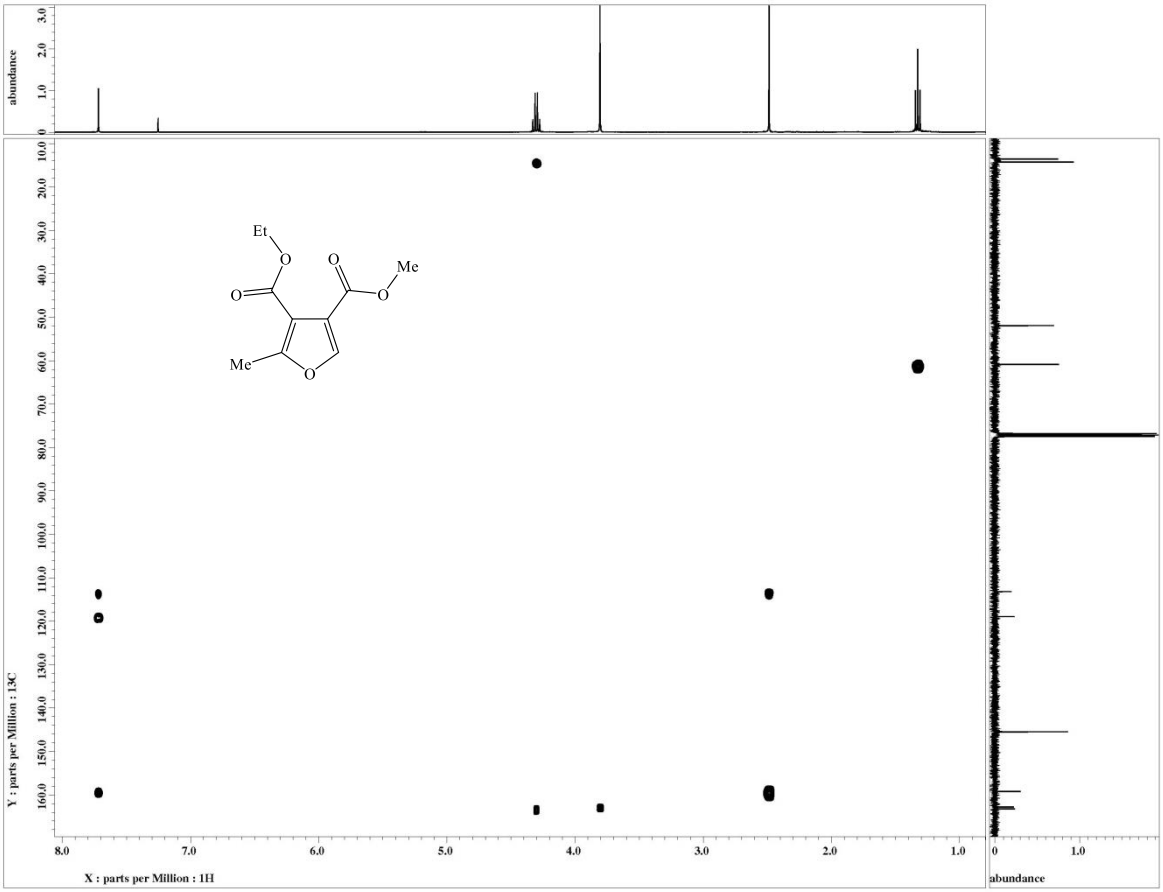

Figure S50. ^{1}H-^{13}C HMBC spectrum of 3-ethyl 4-methyl 2-methylfuran-3,4-dicarboxylate **3c** in $CDCl_3$

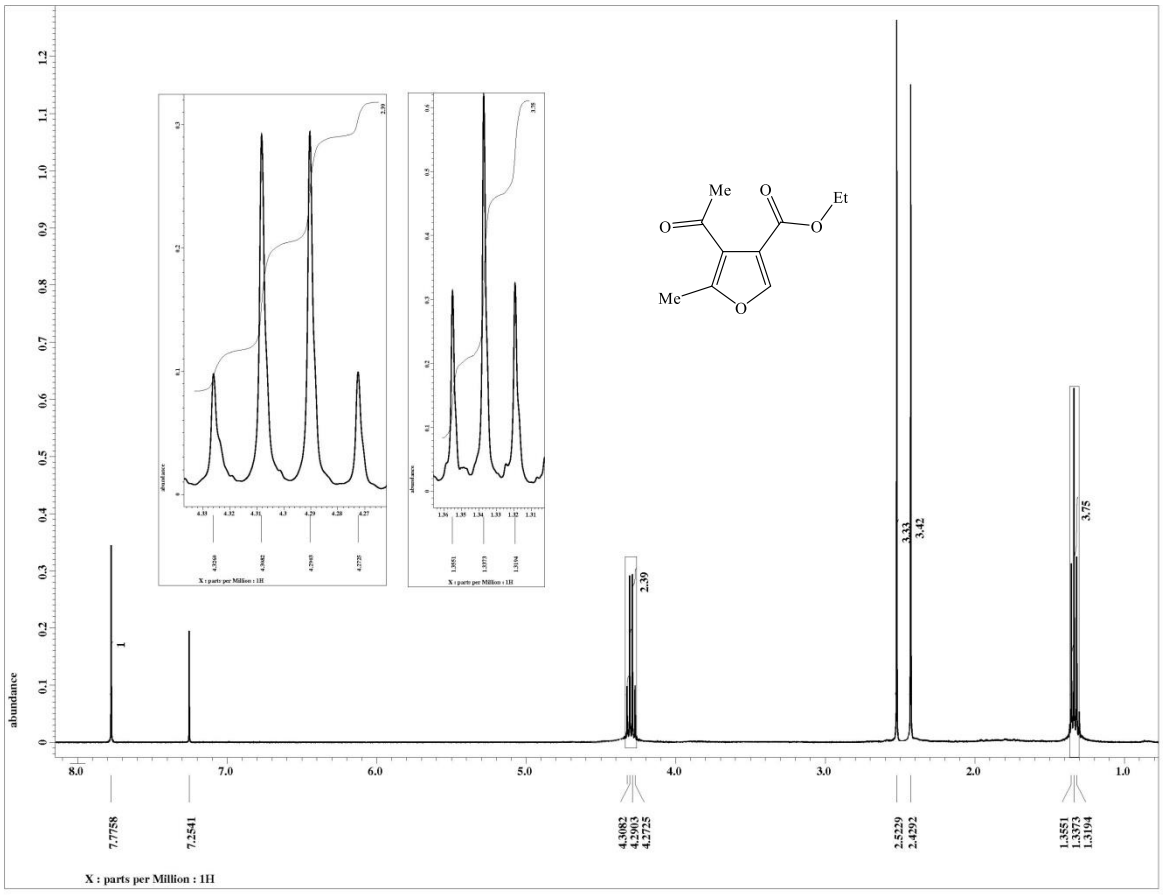

Figure S51. ^{1}H NMR spectrum of ethyl 4-acetyl-5-methylfuran-3-carboxylate **3d** in $CDCl_3$

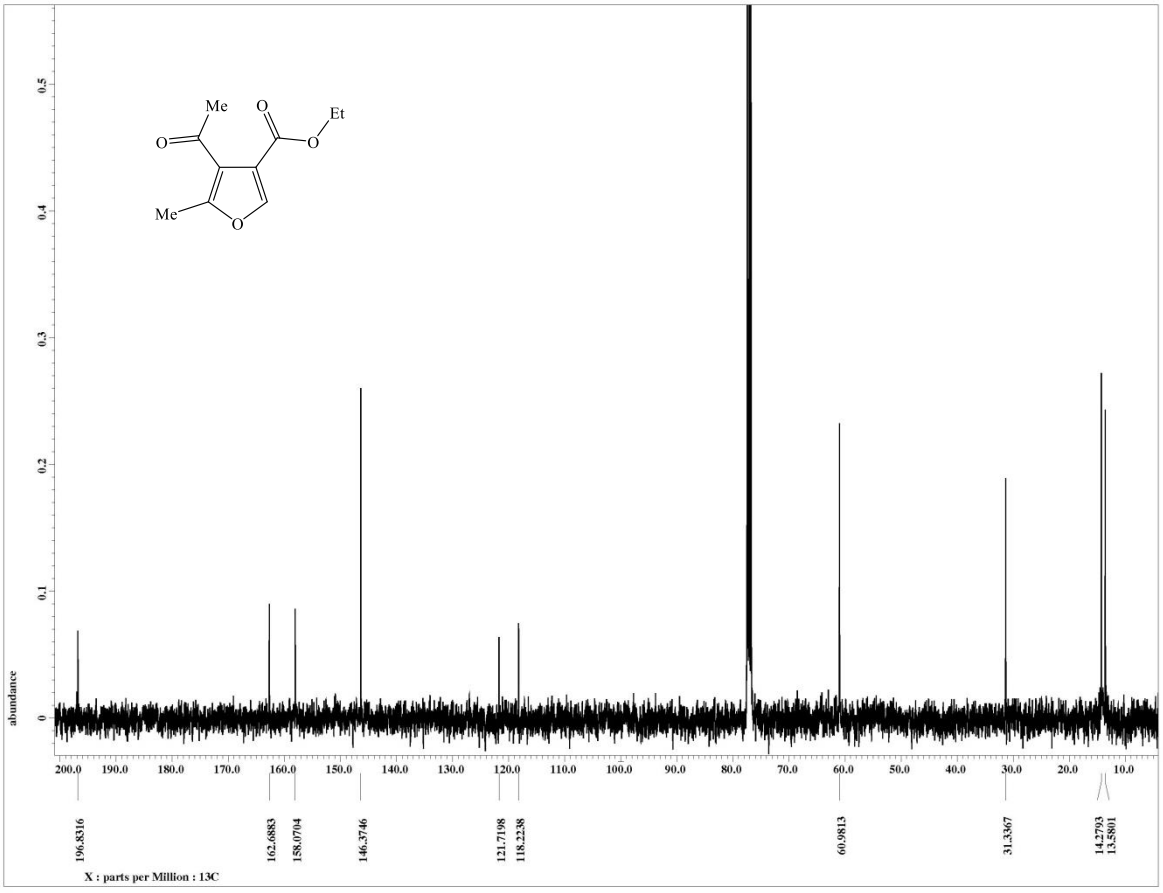

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 4-acetyl-5-methylfuran-3-carboxylate **3d** in $CDCl_3$

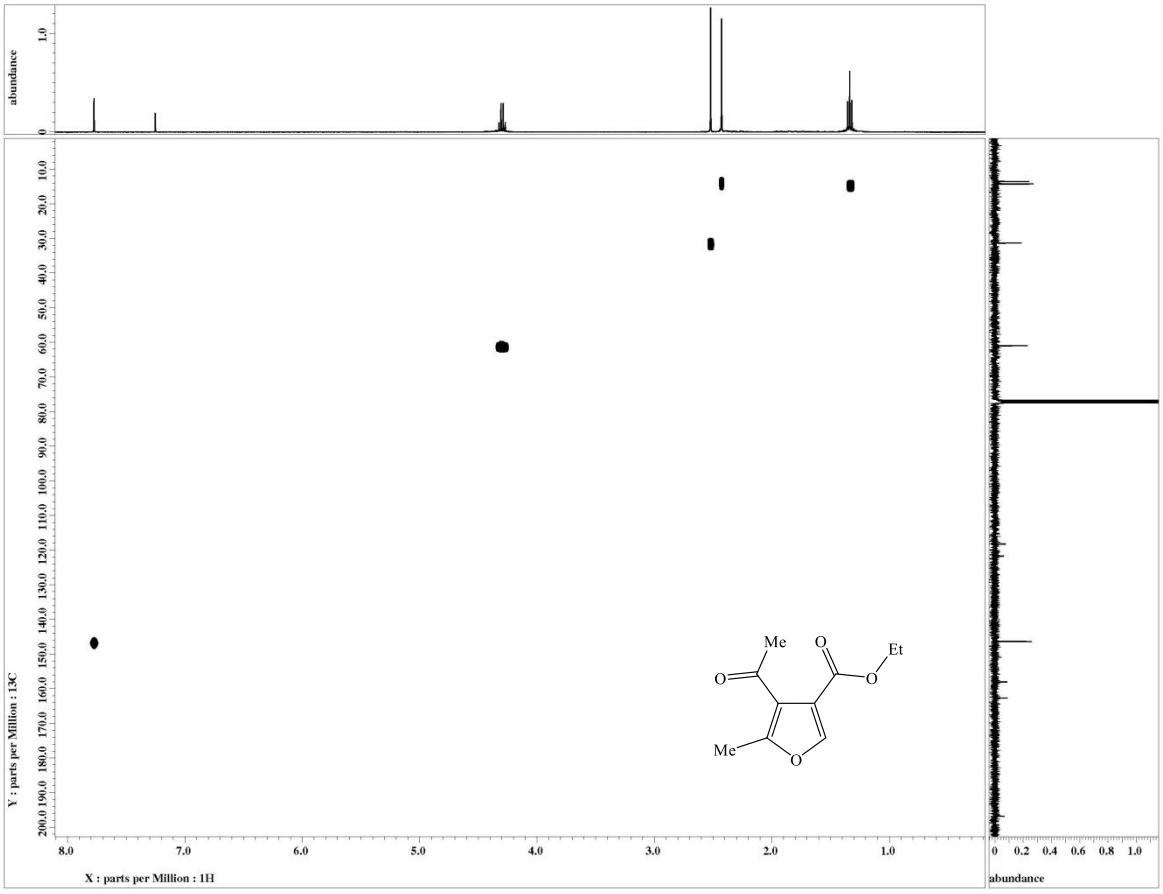

Figure S53. ^{1}H-^{13}C HMQC spectrum of ethyl 4-acetyl-5-methylfuran-3-carboxylate **3d** in $CDCl_3$

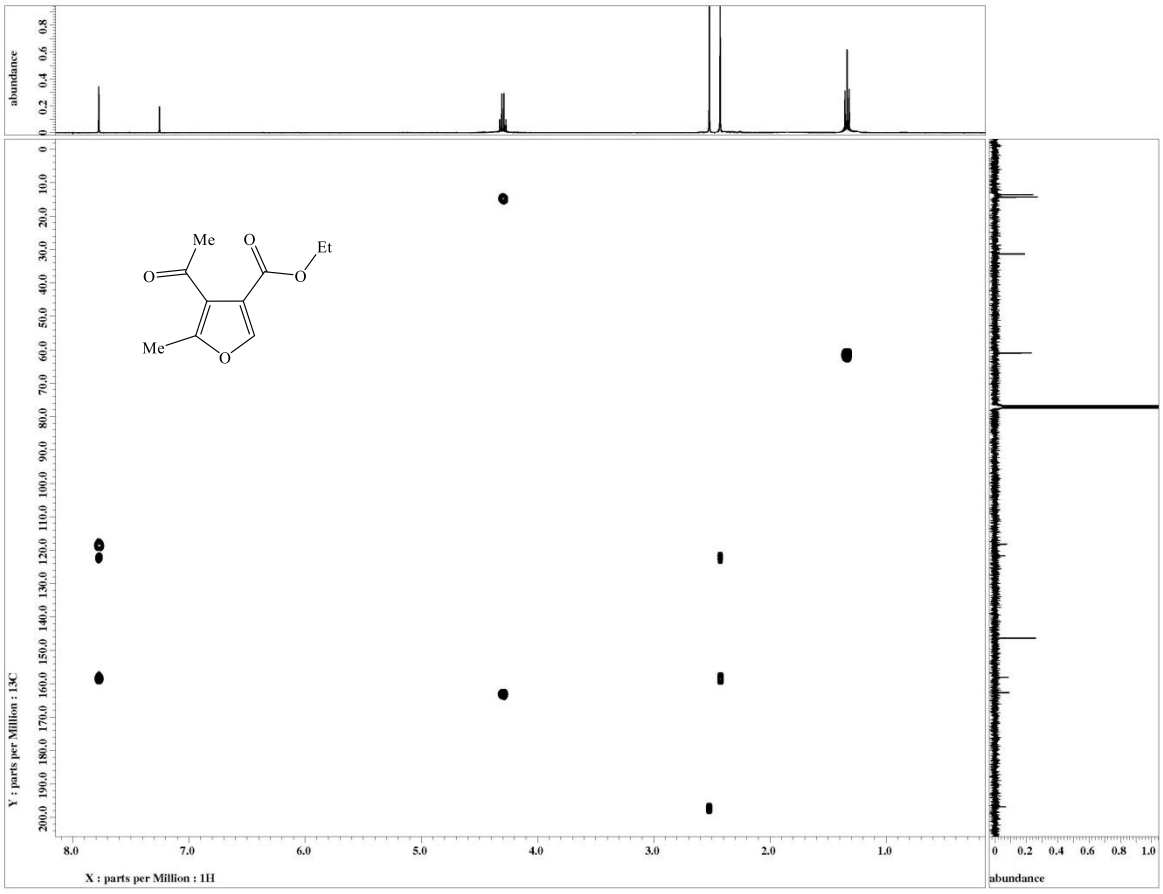

Figure S54. ^{1}H-^{13}C HMBC spectrum of ethyl 4-acetyl-5-methylfuran-3-carboxylate **3d** in $CDCl_3$

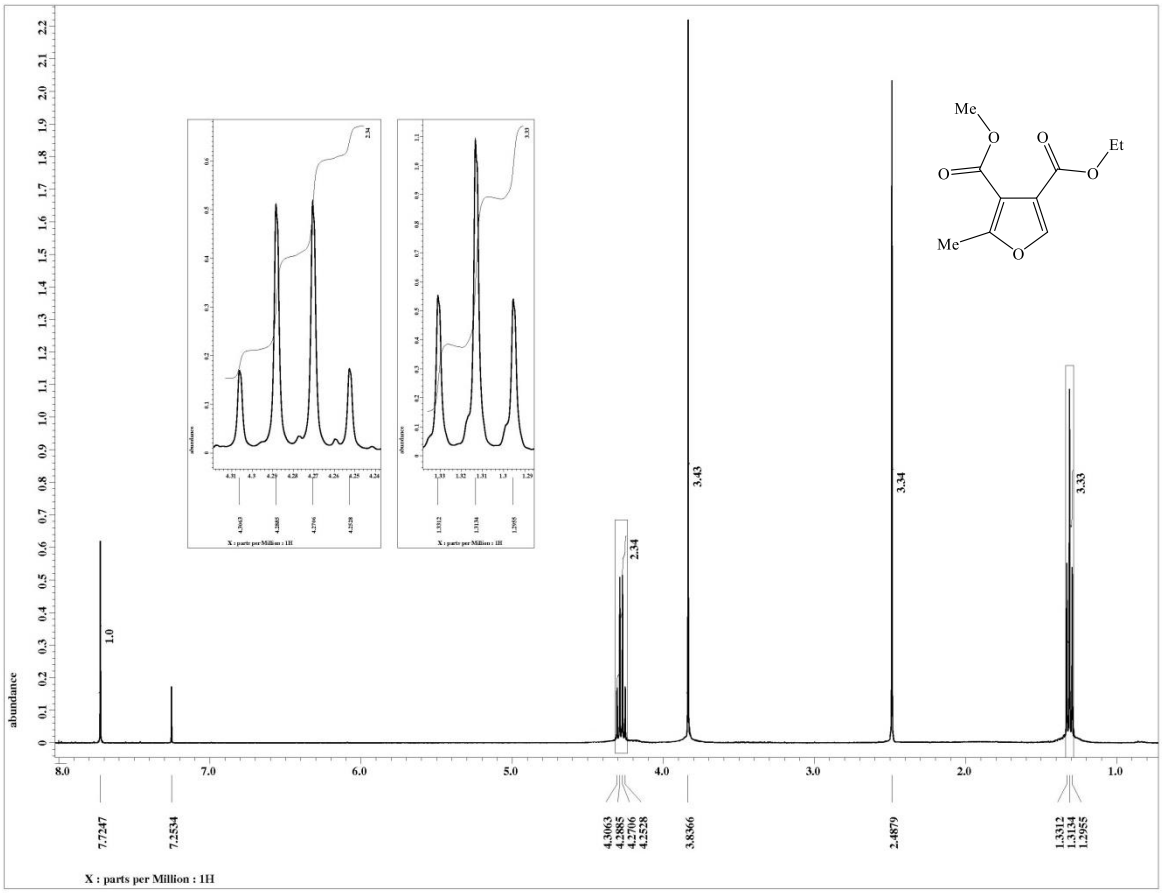

Figure S55. ^{1}H NMR spectrum of 4-ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate **3e** in $CDCl_3$

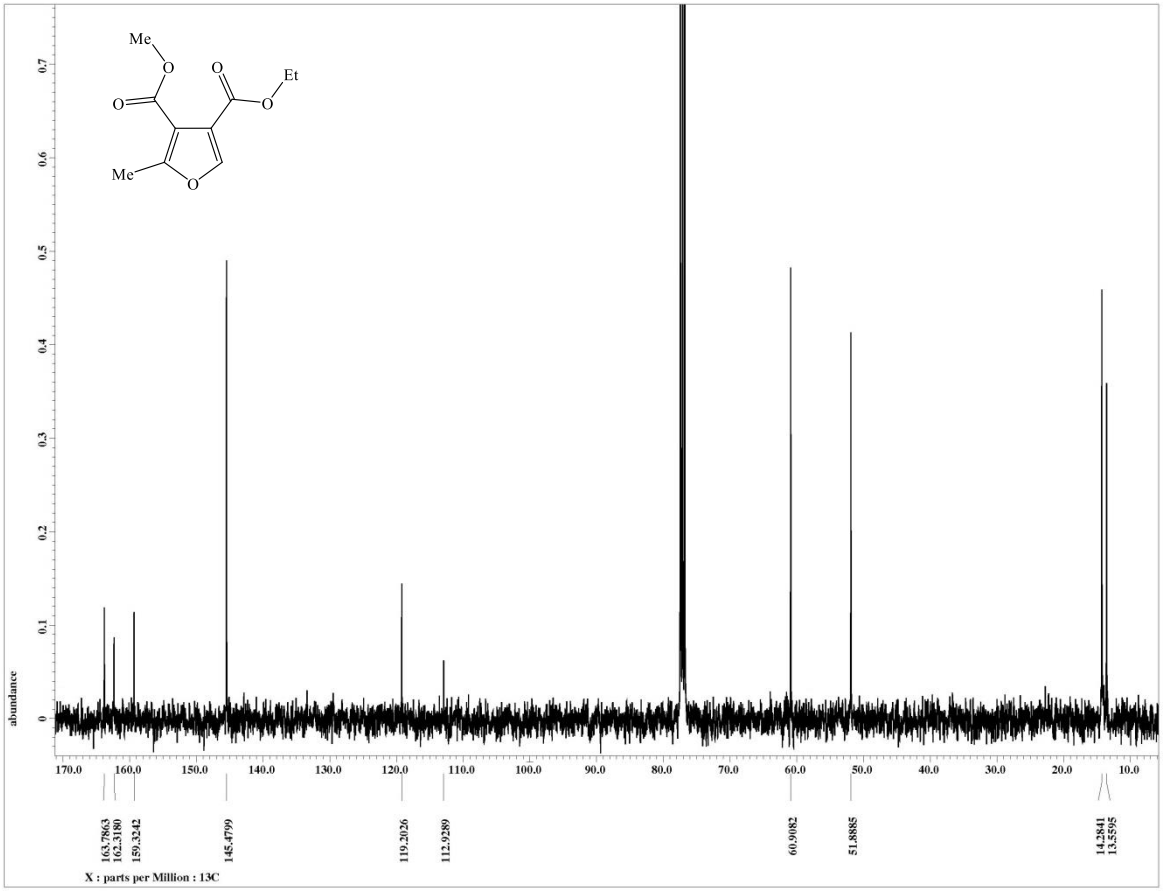

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate **3e** in $CDCl_3$

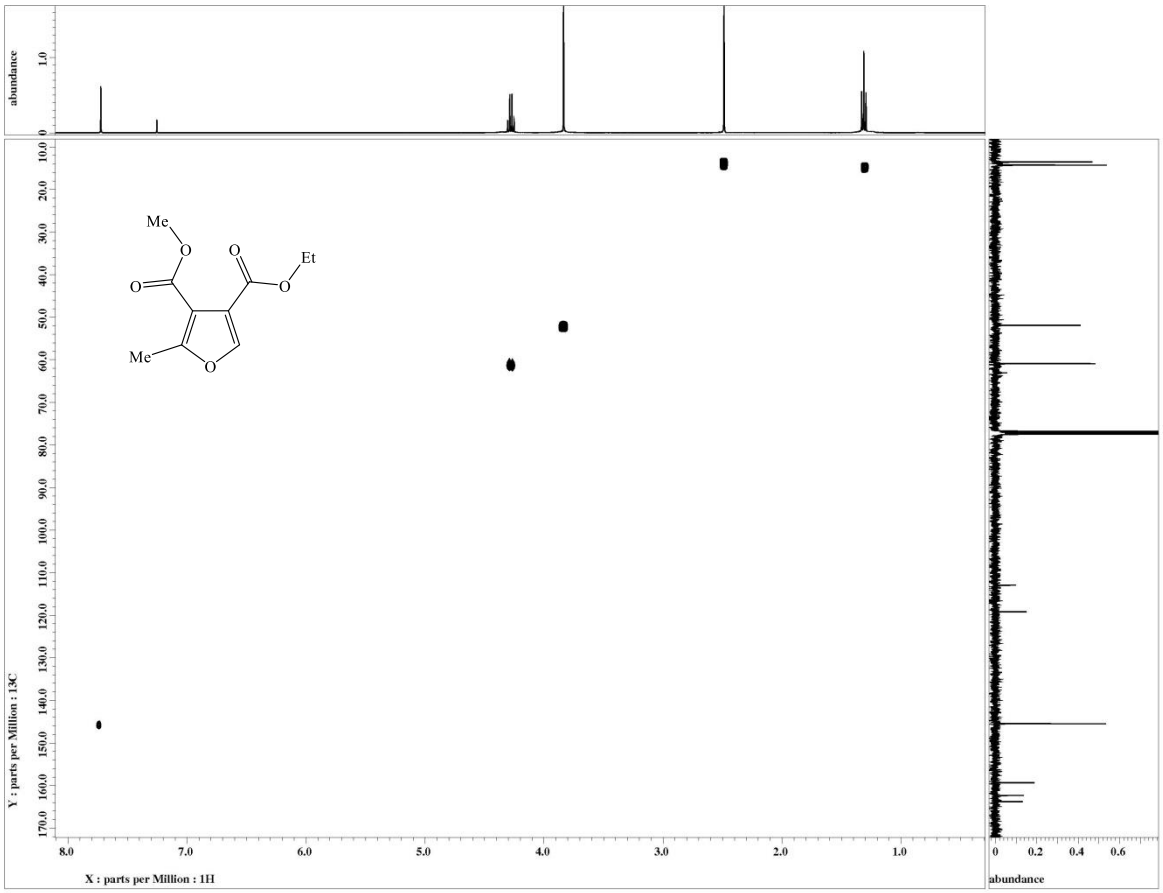

Figure S57. ^{1}H-^{13}C HMQC spectrum of 4-ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate **3e** in $CDCl_3$

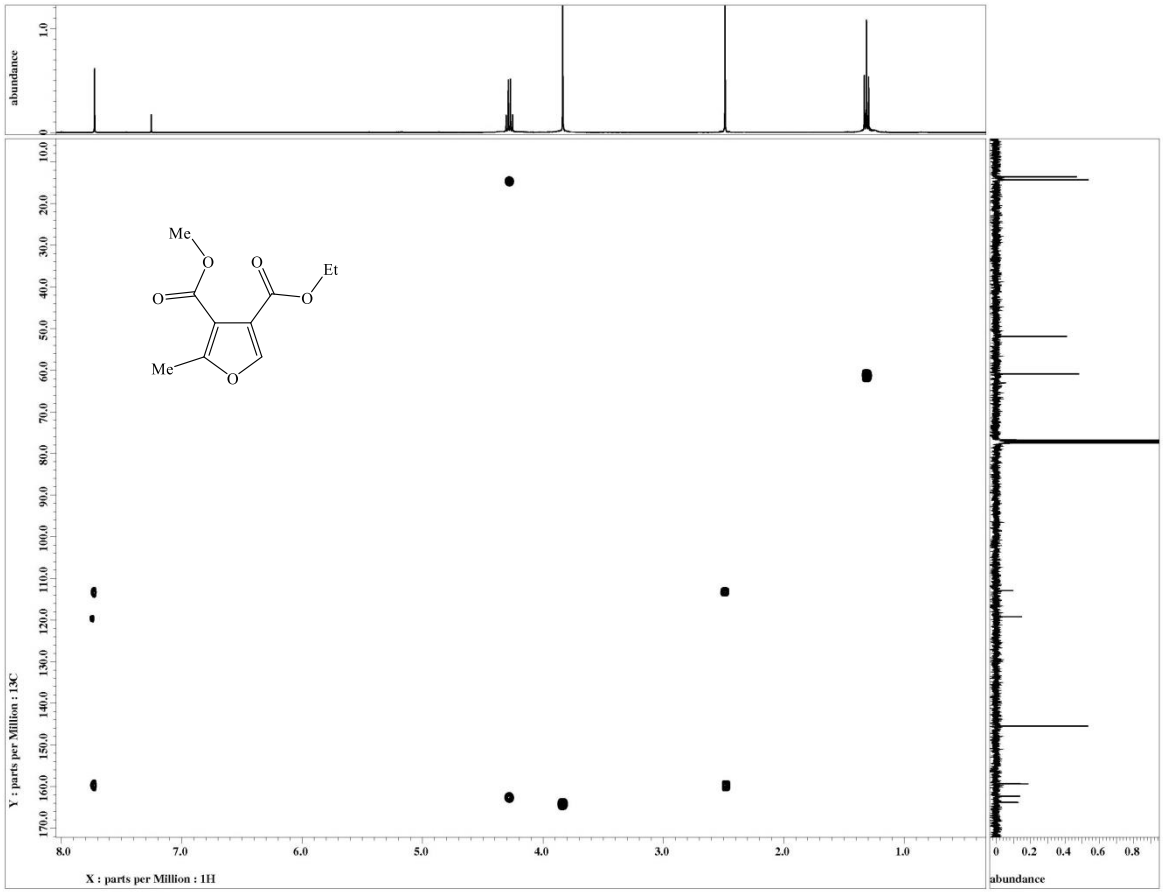

Figure S58. ^{1}H-^{13}C HMBC spectrum of 4-ethyl 3-methyl 2-methylfuran-3,4-dicarboxylate **3e** in $CDCl_3$

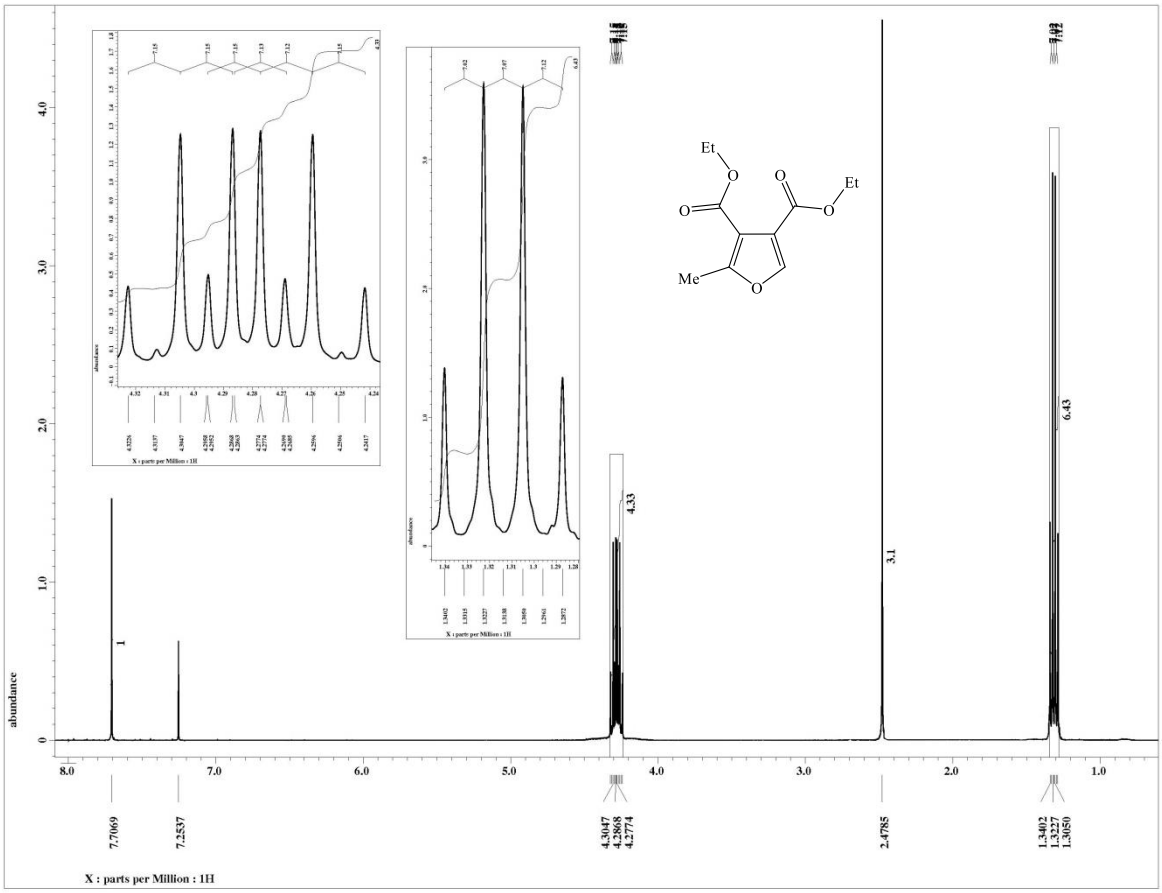

Figure S59. ^{1}H NMR spectrum of diethyl 2-methylfuran-3,4-dicarboxylate **3f** in $CDCl_3$

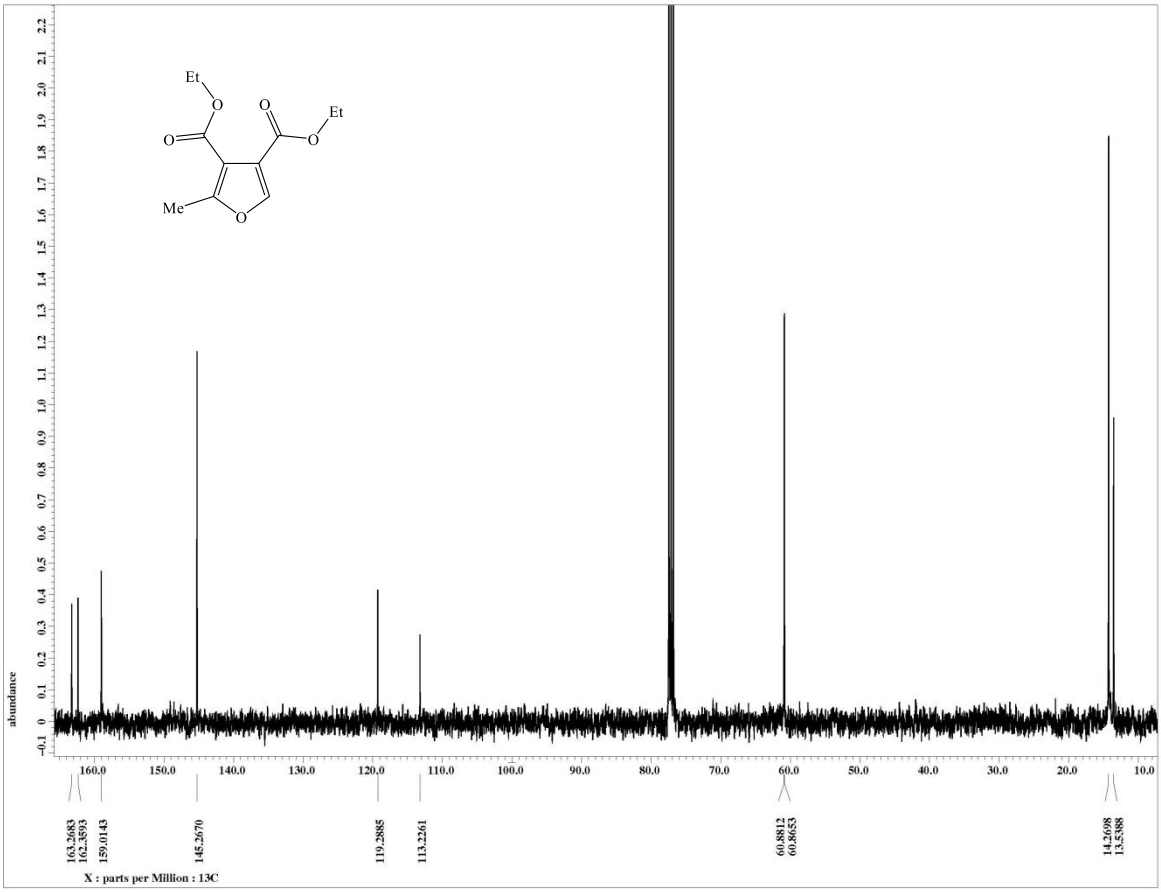

Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of diethyl 2-methylfuran-3,4-dicarboxylate **3f** in $CDCl_3$

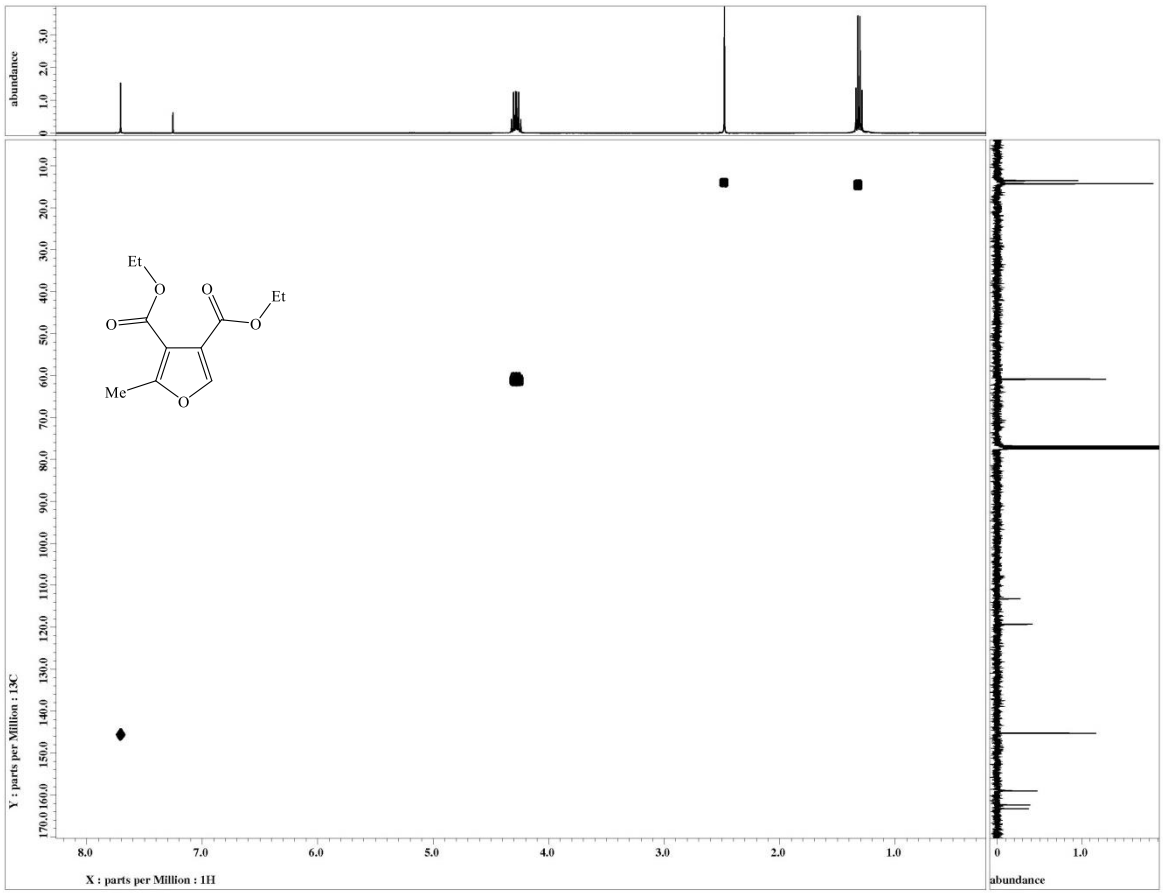

Figure S61. ^{1}H-^{13}C HMQC spectrum of diethyl 2-methylfuran-3,4-dicarboxylate **3f** in $CDCl_3$

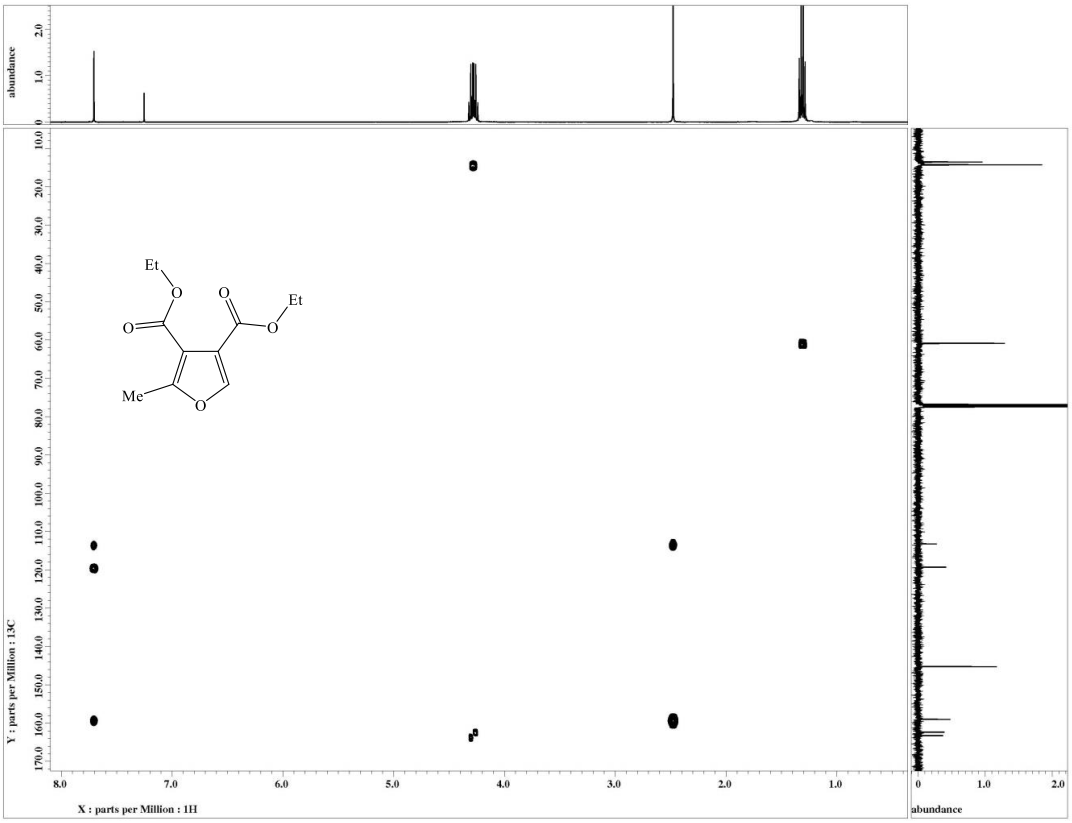

Figure S62. ^{1}H-^{13}C HMBC spectrum of diethyl 2-methylfuran-3,4-dicarboxylate **3f** in $CDCl_3$

In the ^{1}H-^{13}C HMQC spectrum of compound **2d**, the signal of $C^{2}H$ proton (δ_H 6.12 ppm) forms a cross-peak with the carbon atom at δ_C 105.00 ppm, $C^{3}H$ proton (δ_H 4.36-4.39 ppm) and carbon at δ_C 55.18 ppm, methyl group protons at C^5 (δ_H 2.41 ppm) and carbon at δ_C 14.69 ppm. The proton signals of the CH_3CH_2O ester fragment (δ_H 1.30, 4.25 ppm) form cross peaks with carbon atoms at δ_C 14.10 ppm and δ_C 62.89 ppm, respectively. The signal of the methyl protons of the acetyl fragment (δ_H 2.31 ppm) forms a cross peak with the signal of the carbon atom at δ_C 29.55 ppm.

The assignment of the signals of quaternary carbon atoms was based on the results of the ^{1}H-^{13}C HMBC experiment. The spectrum of compound **2d** shows cross peaks of the signal of the methylene protons CH_2O (δ_H 4.25 ppm) and the carbon atom at δ_C 168.35 ppm (O–C=O), methyl protons of the acetyl fragment (δ_H 2.31 ppm), and carbon atoms at δ_C 112.60 ppm (C^4) and δ_C 192.41 ppm (C=O), as well as cross peaks of protons of the methyl group at C^5 (δ_H 2.41 ppm)/C^5 (δ_C 167.18 ppm) (Fig. S63).

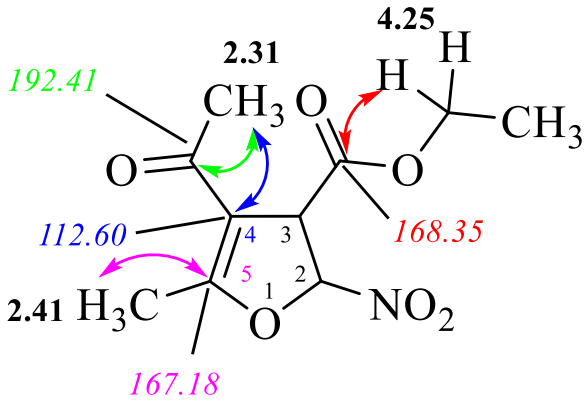

Figure S63. Key correlations in the ^{1}H-^{13}C HMBC NMR spectrum of compound **2d** ($CDCl_3$).

X-ray diffraction study of compounds 3a was performed on a Bruker D8 QUEST automatic three-circle diffractometer at 105 K (graphite monochromator, λMoK_α = 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 least-squares method based on *F*2 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 **3a** 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 **3a** based on X-ray diffraction data

Parameter	**3a**
Molecular formula	$C_9H_{10}O_4$
Molecular weight	182.17
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
Unit cell parameters	
a/Å	3.7735(5)
b/Å	29.786(4)
c/Å	7.7343(11)
β/deg	98.255(5)
V/Å^3	860.3(2)
d_{calc}/g cm^{-3}	1.406
Absorption coeffi cient, μ/mm^{-1}	0.111
F(000)	560
Θ (min, max)/deg	2.7, 26.5
Ranges of indices,	
h	$-4 \le h \le 4$
k	$-37 \le k \le 37$
l	$-9 \le l \le 9$
Number of reflections	
total	24393
unique	1774
R_{int}	0.150
Completeness up to θ = 27.0°	0.996
$T_{max/min}$	0.7472 / 0.5310
Number of observed reflections (I > 2σ(I))	1278
Number of reflections/of contraints/number of parameters	1774/0/121
GOOF	0.920
R [*I* > 2σ(*I*)]	
R_1	0.0358
wR_2	0.0917
R (based on all reflections)	
R_1	0.0540
wR_2	0.0950
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.279 / -0.206
CCDC	2178613

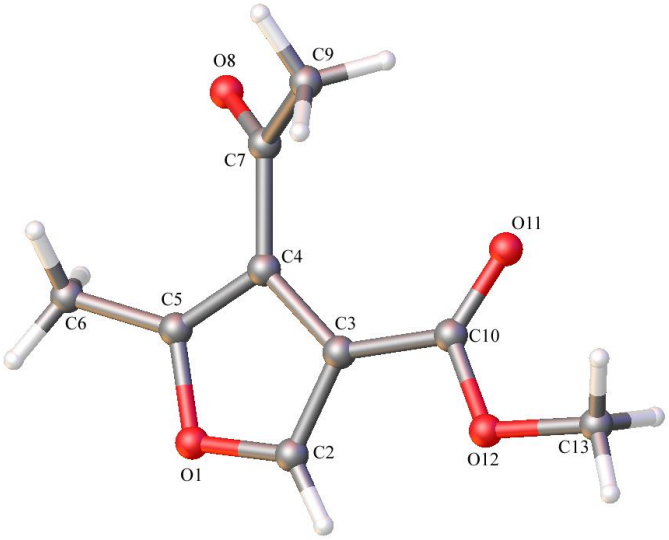

Table S2. Torsion angles (τ) in the molecule of compound **3a**

Angle	τ/deg	Angle	τ/deg
H2–C2–C3–C4	179.0	C5–C4–C7–O8	-38.2(2)
H2–C2–C3–C10	3.7	C4–C5–C6–H6A	-39.2
O1–C2–C3–C4	-1.0(2)	C4–C5–C6–H6B	-159.2
O1–C2–C3–C10	-176.3(1)	C4–C5–C6–H6C	80.8
H2–C2–O1–C5	-179.2	O1–C5–C6–H6A	135.2
C3–C2–O1–C5	0.8(2)	O1–C5–C6–H6B	15.2
C2–C3–C4–C5	0.8(2)	O1–C5–C6–H6C	-104.8
C2–C3–C4–C7	174.9(2)	C4–C5–O1–C2	-0.2(2)
C10–C3–C4–C5	175.8(2)	C6–C5–O1–C2	-175.9(1)
C10–C3–C4–C7	-10.1(3)	C4–C7–C9–H9A	97.1
C2–C3–C10–O11	163.4(2)	C4–C7–C9–H9B	-22.9
C2–C3–C10–O12	-16.0(2)	C4–C7–C9–H9C	-142.9
C4–C3–C10–O11	-10.8(3)	O8–C7–C9–H9A	-86.3
C4–C3–C10–O12	169.9(1)	O8–C7–C9–H9B	153.7
C3–C4–C5–C6	174.3(2)	O8–C7–C9–H9C	33.7
C3–C4–C5–O1	-0.4(2)	C3–C10–O12–C13	178.4(1)
C7–C4–C5–C6	-0.5(3)	O11–C10–O12–C13	-1.0(2)
C7–C4–C5–O1	-175.2(1)	H13A–C13–O12–C10	-67.3
C3–C4–C7–C9	-34.8(2)	H13B–C13–O12–C10	172.7
C3–C4–C7–O8	148.6(2)	H13C–C13–O12–C10	52.7
C5–C4–C7–C9	138.5(2)		

Table S3. Angles (τ) in the molecule of compound **3a**

Angle	τ/deg	Angle	τ/deg
H2–C2–C3	124.9	C4–C7–O8	119.8(1)
H2–C2–O1	124.9	C9–C7–O8	120.8(1)
C3–C2–O1	110.3(1)	C7–C9–H9A	109.5
C2–C3–C4	106.3(1)	C7–C9–H9B	109.5
C2–C3–C10	124.5(1)	C7–C9–H9C	109.5
C4–C3–C10	129.1(1)	H9A–C9–H9B	109.5
C3–C4–C5	105.9(1)	H9A–C9–H9C	109.5
C3–C4–C7	132.2(1)	H9B–C9–H9C	109.5
C5–C4–C7	121.6(1)	C3–C10–O11	125.9(1)
C4–C5–C6	133.5(1)	C3–C10–O12	110.8(1)
C4–C5–O1	109.8(1)	O11–C10–O12	123.4(1)
C6–C5–O1	116.5(1)	H13A–C13–H13B	109.5
C5–C6–H6A	109.5	H13A–C13–H13C	109.5
C5–C6–H6B	109.5	H13A–C13–O12	109.5
C5–C6–H6C	109.5	H13B–C13–H13C	109.5
H6A–C6–H6B	109.5	H13B–C13–O12	109.5
H6A–C6–H6C	109.5	H13C–C13–O12	109.5
H6B–C6–H6C	109.5	C2–O1–C5	107.7(1)
C4–C7–C9	119.3(1)	C10–O12–C13	115.4(1)

Table S4. Bond lengths (*d*) in the molecule of compound **3a**

Bond	*d*/Å	Bond	*d*/Å
C2–H2	0.950	C7–C9	1.501(2)
C2–C3	1.355(2)	C7–O8	1.219(2)
C2–O1	1.357(2)	C9–H9A	0.980
C3–C4	1.446(2)	C9–H9B	0.980
C3–C10	1.469(2)	C9–H9C	0.980
C4–C5	1.363(2)	C10–O11	1.205(2)
C4–C7	1.481(2)	C10–O12	1.348(2)
C5–C6	1.482(2)	C13–H13A	0.980
C5–O1	1.367(2)	C13–H13B	0.980
C6–H6A	0.980	C13–H13C	0.980
C6–H6B	0.980	C13–O12	1.444(2)
C6–H6C	0.980		