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Synthesis and properties of the salts of 1-nitropropan-2-one and 1-nitrobutan-2-one

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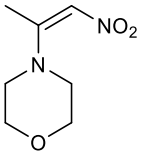
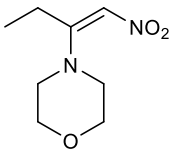
General. Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were determined on Electrothermal IA9100 apparatus. ^{1}H, ^{13}C NMR spectra were acquired on a Bruker Avance II spectrometer (400 and 100 MHz respectively) using DMSO-d_6 and acetonitrile-d_3 with TMS as internal reference. Elemental analysis was performed on a Perkin Elmer 2400 CHNS instrument. IR spectra were recorded on the IR spectrometer «Bruker Alpha, ZnSe (FTIR)». The XRD analysis was accomplished on an automated "Xcalibur 3" diffractometer on standard procedure (MoK-irradiation 0.71073 Å, graphite monochromator, "omega"-scans with step 1° at T=295 (2)K). Monitoring of the reaction course was carried out by TLC on Silufol UV-254 plates using EtOAc as eluent. Silica gel is Merck Grade 9385.

2-Morpholino-1-nitroprop-1-ene (1a)



A mixture of morpholine (17.23 ml, 0.2 mol), triethyl orthoacetate (73.06 ml, 0.4 mol), nitromethane (53.60 ml, 1.0 mol) and *p*-toluenesulfonic acid (1.72 g, 0.01 mol) was refluxed for 3 h at 140 °C. The mixture was concentrated under reduce pressure, the precipitate was filtered off, washed with isopropanol and the product was dried in air. The yield 23.05 g (67%). Yellow crystals, mp = 124-126 °C (126-127 °C)[25]. ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 2.54 (s, 3H, CH_3), 3.44 – 3.46 (m, 4H, $2CH_2$), 3.64 – 3.66 (m, 4H, $2CH_2$), 6.95 (s, 1H, CH). ^{13}C NMR spectrum, δ, ppm: 15.33, 47.14, 65.51, 114.00, 160.08. Found (%): C 48.97; H 7.08; N 16.41. Calc. for $C_7H_{12}N_2O_3$ (%): C 48.83; H 7.02; N 16.27. IR, ν, cm^{-1}: 1644 (C=C), 1529, 1330 (NO_2), 990 (C–O–C).

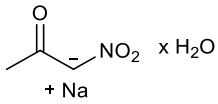
2-Morpholino-1-nitrobut-1-ene (1b)



A mixture of morpholine (17.23 ml, 0.2 mol), triethyl orthopropionate (86.00 ml, 0.4 mol), nitromethane (53.60 ml, 1.0 mol) and *p*-toluenesulfonic acid (1.72 g, 0.01 mol) was refluxed for 3 h at 140 °C. The mixture was concentrated under reduce pressure, the precipitate was filtered off,

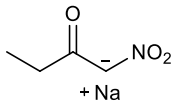
washed with isopropanol and the product was dried in air. The yield 28.30 g (76%). Yellow crystalls, mp = 114-116 °C. ^{1}H NMR (DMSO-*d*$_6$) spectrum, δ, ppm: 1.10 (t, 3H, CH_3, *J* = 7.4 Hz), 3.01 (q, 2H, CH_2, *J* = 7.4 Hz), 3.44 – 3.47 (m, 4H, $2CH_2$,), 3.65 – 3.67 (m, 4H, $2CH_2$), 6.88 (s, 1H, CH). ^{13}C NMR (DMSO-*d6*) spectrum, δ, ppm: 11.83, 20.89, 47.17, 65.74, 113.33, 164.63. Found (%): C 51.78; H 7.62; N 15.24. Calc. for $C_8H_{14}N_2O_3$ (%): C 51.60; H 7.58; N 15.04. IR, ν, cm^{-1}: 1645 (C=C), 1537, 1344 (NO_2), 1007 (C–O–C).

1-Nitro-2-propanone sodium salt monohydrate (2a)



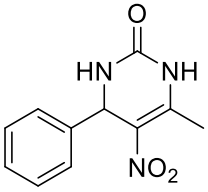
To finely ground 2-morpholino-1-nitroprop-1-ene **1a** (3.44 g, 0.02 mol) in EtOH (15 ml) a solution of NaOH (0.8 g) in EtOH (15 ml) was added. The mixture was stirred for 30 min at room temperature. The precipitate was filtered off, washed with methyl *tert*-butyl ether and dried in air. The filtrate was evaporated to dryness, the residue was suspended in EtOH (10 ml) and filtered off. The combined product was crystallized from EtOH. The yield was 2.0 g (70%), white powder, mp = 176-178 °C. ^{1}H NMR (DMSO-*d*$_6$) spectrum, δ, ppm: 2.02 (s, 3H, CH_3), 6.37 (s, 1H, CH). ^{13}C NMR (DMSO-*d*$_6$) spectrum, δ, ppm: 28.80, 113.65, 186.43. Found (%): C 25.15; H 4.11; N 9.60. Calc. for $C_3H_4NO_3Na*H_2O$ (%): C 25.18; H 4.23; N 9.76. IR, ν, cm^{-1}: 1612 (C=O), 1459, 1288 (NO_2).

1-Nitro-2-butanone sodium salt (2b)



To finely ground 2-morpholino-1-nitrobut-1-ene **1b** (3.72 g, 0.02 mol) in EtOH (15 ml) a solution of NaOH (0.8 g) in EtOH (15 ml) was added. The mixture was stirred for 30 min at room temperature. The precipitate was filtered off, washed with methyl *tert*-butyl ether and dried in air. The product was crystallized from EtOH. The yield was 2.47 g (93%), white powder, mp = 213-215 °C. ^{1}H NMR (DMSO-*d*$_6$) spectrum, δ, ppm: 0.94 (t, 3H, CH_3 *J* = 7.5 Hz), 2.25 (q, 2H, CH_2, *J* = 7.5 Hz), 6.51 (s, 1H, CH). ^{13}C NMR (DMSO-*d6*) spectrum, δ, ppm: 9.89, 33.06, 111.95, 188.83. Found (%): C 34.47; H 4.46; N 9.98. Calc. for $C_4H_6NO_3Na$ (%): C 34.54; H 4.35; N 10.07. IR, ν, cm^{-1}: 1648 (C=O), 1443, 1244 (NO_2).

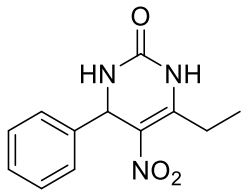
6-Methyl-5-nitro-4-phenyl-3,4-dihydropyrimidin-2-one (4a)



To a suspension of 1-nitropropan-2-one sodium salt monohydrate **2a** (0.59 g, 0.0041 mol) in EtOH (10 ml) were consecutively added 12 M HCl (1.025 ml, 0.0123 mol), urea (0.493 g, 0.0082 mol) and benzaldehyde (0.419 ml, 0.0041 mol). The mixture was refluxed for 7 h, cooled to room temperature and filtered. The precipitate was recrystallized from EtOH and dried in air.

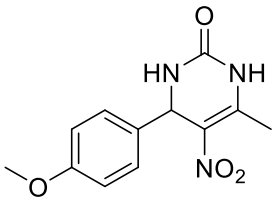
The yield 0.74 g (86%), yellow powder, mp = 198-203 °C (199-202 °C)[28]. ^{1}H NMR (CH_3CN-d_3) spectrum, δ, ppm: 2.50 (s, 3H, CH_3), 5.53 (d, 1H, CH *J* = 3.3 Hz,), 6.47 (s, 1H, NH), 7.31 – 7.40 (m, 5H, Ph), 7.92 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 19.33, 54.13, 123.11, 126.48, 127.95, 128.68, 142.31, 150.26, 150.99. Found (%): C 56.63; H 4.75; N 18.00. Calc. for $C_{11}H_{11}N_3O_3$ (%): C 56.65; H 4.75; N 18.02. IR, ν, cm^{-1}: 3300 (N–H), 1685 (C=O), 1452 (NO_2), 1306 (NO_2).

6-Ethyl-5-nitro-4-phenyl-3,4-dihydropyrimidin-2-one (4b)



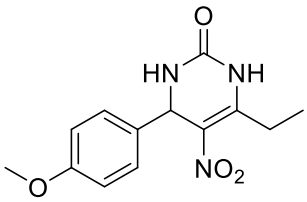
To a suspension of 1-nitrobutan-2-one sodium salt **2b** (0.682 g, 0.0041 mol) in EtOH (10 ml) were consecutively added 12 M HCl (1.025 ml, 0.0123 mol), urea (0.493 g, 0.0082 mol) and benzaldehyde (0.419 ml, 0.0041 mol). The mixture was refluxed for 7 h, cooled to room temperature and filtered. The precipitate was recrystallized from EtOH and dried in air. The yield was 0.86 g (87%), yellow powder, mp = 157-162 °C. ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 1.24 (t, 3H, CH_3, *J* = 7.4 Hz,), 2.77 – 2.90 (m, 2H, CH_2), 5.53 (d, 2H, CH, *J* = 3.4 Hz), 7.29 – 7.38 (m, 5H, Ph), 8.32 (s, 1H, NH), 10.06 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 12.59, 25.60, 54.60, 123.01, 128.44, 129.20, 142.80, 150.97, 156.03. Found (%): C 58.17; H 5.30; N 17.01. Calc. for $C_{12}H_{13}N_3O_3$ (%): C 58.29; H 5.30; N 16.99. IR, ν, cm^{-1}: 3349 (N–H), 1682 (C=O), 1444 (NO_2), 1309 (NO_2).

6-Methyl-4-(4-methoxyphenyl)-5-nitro-3,4-dihydropyrimidin-2-one (4c)



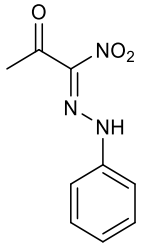
To a suspension of 1-nitropropan-2-one sodium salt monohydrate **2a** (0.59 g, 0.0041 mol) in EtOH (10 ml) were consecutively added 12 M HCl (1.025 ml, 0.0123 mol), urea (0.493 g, 0.0082 mol) and anisaldehyde (0.498 ml, 0.0041 mol). The mixture was refluxed for 7 h, cooled to room temperature and filtered. The precipitate was recrystallized from EtOH and dried in air. The yield was 0.87 g (81%), yellow powder, mp = 229-234 °C (227-228 °C)[29]. ^{1}H NMR (CH_3CN-d_3) spectrum, δ, ppm: 2.48 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 5.58 (d, 1H, CH, *J* = 3.1 Hz), 6.35 (s, 1H, NH), 6.89 – 6.92 (m, 2H, 2CH), 7.26 – 7.30 (m, 2H, 2CH), 7.75 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 19.42, 53.64, 55.20, 114.09, 123.56, 127.83, 134.60, 150.48, 150.77, 159.06. Found (%):C 54.57; H 5.03; N 15.89. Calc. for $C_{12}H_{13}N_3O_4$ (%): C 54.75; H 4.98; N 15.96. IR, ν, cm^{-1}: 3318 (N–H), 1695 (C=O), 1452 (NO_2), 1314 (NO_2), 1240 (Ph–OMe).

6-Ethyl-4-(4-methoxyphenyl)-5-nitro-3,4-dihydropyrimidin-2-one (4d)



To a suspension of 1-nitro-2-butanone sodium salt **2b** (0.682 g, 0.0041 mol) in EtOH (10 ml) were consecutively added 12 M HCl (1.025 ml, 0.0123 mol), urea (0.493 g, 0.0082 mol) and anisaldehyde (0.498 ml, 0.0041 mol). The mixture was refluxed for 7 h, cooled to room temperature and filtered. The precipitate was recrystallized from EtOH and dried in air. The yield was 1.01 g (89%), yellow powder, mp = 132-137 °C. ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 1.22 (t, 3H, CH_3, J = 7,4 Hz), 2.77–2.85 (m, 2H, CH_2), 3,73 (s, 3H, OMe), 5.47 (d, H, CH), 6.91–6.92 (m, 2H, 2CH), 7.19–7.20 (m, 2H, 2CH), 8,24 – 8.25 (m, 1H, NH), 10.02 (d, 1H, NH, J = 2.1 Hz). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 12.59, 25.58, 53.96, 55.57, 114.52, 123.31, 128.04, 134.94, 151.00, 155.67, 159.41. Found (%): C 56.23; H 5.54; N 14.74. Calc. for $C_{13}H_{15}N_3O_4$ (%): C 56.31; H 5.45; N 15.15. IR, ν, cm^{-1}: 3333 (N–H), 1695 (C=O), 1510 (NO_2), 1317 (NO_2), 1222 (Ph–OMe)

1-Nitro-1-(2-phenylhydrazono)propan-2-one (5a)



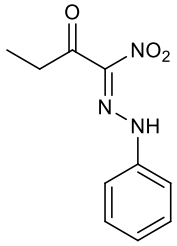
Method 1 (using 1-nitropropan-2-one sodium salt): A solution of 1-nitropropan-2-one sodium salt monohydrate **2a** (0.258 g, 0.0018 mol) in 3.9 M AcONa (1.5 ml, 0.00585 mol) was prepared. To a mixture of aniline (0.165 ml, 0.0018 mol) in water (5 ml) and 12 M HCl (0.45 ml, 0.0054 mol), a solution of $NaNO_2$ (0.138 g, 0.002 mol) in water (1 ml) was added portionwise at 0-5 °C. The mixture was kept for 10 min and poured into 1-nitro-2-propanone sodium salt solution. The mixture was stirred for 30 min at room temperature, the precipitate was filtered off, washed with water-ethanol mixture (15 ml) and dried in air.

Method 2 (using 2-morpholino-1-nitroprop-1-ene): To a solution of NaOH (0.072 g, 0.0018 mol) in water (3 ml), 2-morpholino-1-nitroprop-1-ene **1a** (0.31 g, 0.0018 mol) and 1.5 ml 3.9 M AcONa (0.00585 mol) were added consecutively. To a mixture of aniline (0.165 ml, 0.0018 mol) in water (5 ml) and 12 M HCl (0.45 ml, 0.0054 mol), a solution of $NaNO_2$ (0.138 g, 0.002 mol) in water (1 ml) was added portionwise at 0-5 °C. The mixture was kept for 10 min and poured into 2-morpholino-1-nitroprop-1-ene solution. The mixture was stirred for 30 min at room temperature, the precipitate was filtered off, washed with water-ethanol mixture (15 ml) and dried in air.

Yields for both methods 0.26 g (69%), pale-yellow powder, mp = 96-98 °C (98 °C)[29]. ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 3.33 (s, 3H, CH_3), 7.18 (t, 1H, CH, J = 7.3 Hz), 7.43 (t, 2H,

2CH, *J* = 7.7 Hz), 7.52 (d, 2H, 2CH, *J* = 8.0 Hz), 11.85 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 25.08, 117.38, 127.44, 129.64, 140.52, 158.15, 194.48. Found (%): C 52.13; H 4.53; N 20.32. Calc. for $C_9H_9N_3O_3$ (%): C 52.17; H 4.38; N 20.28. IR, ν, cm^{-1}: 1632 (C=O), 1539, 1294 (NO_2).

1-Nitro-1-(2-phenylhydrazono)butan-2-one (5b)

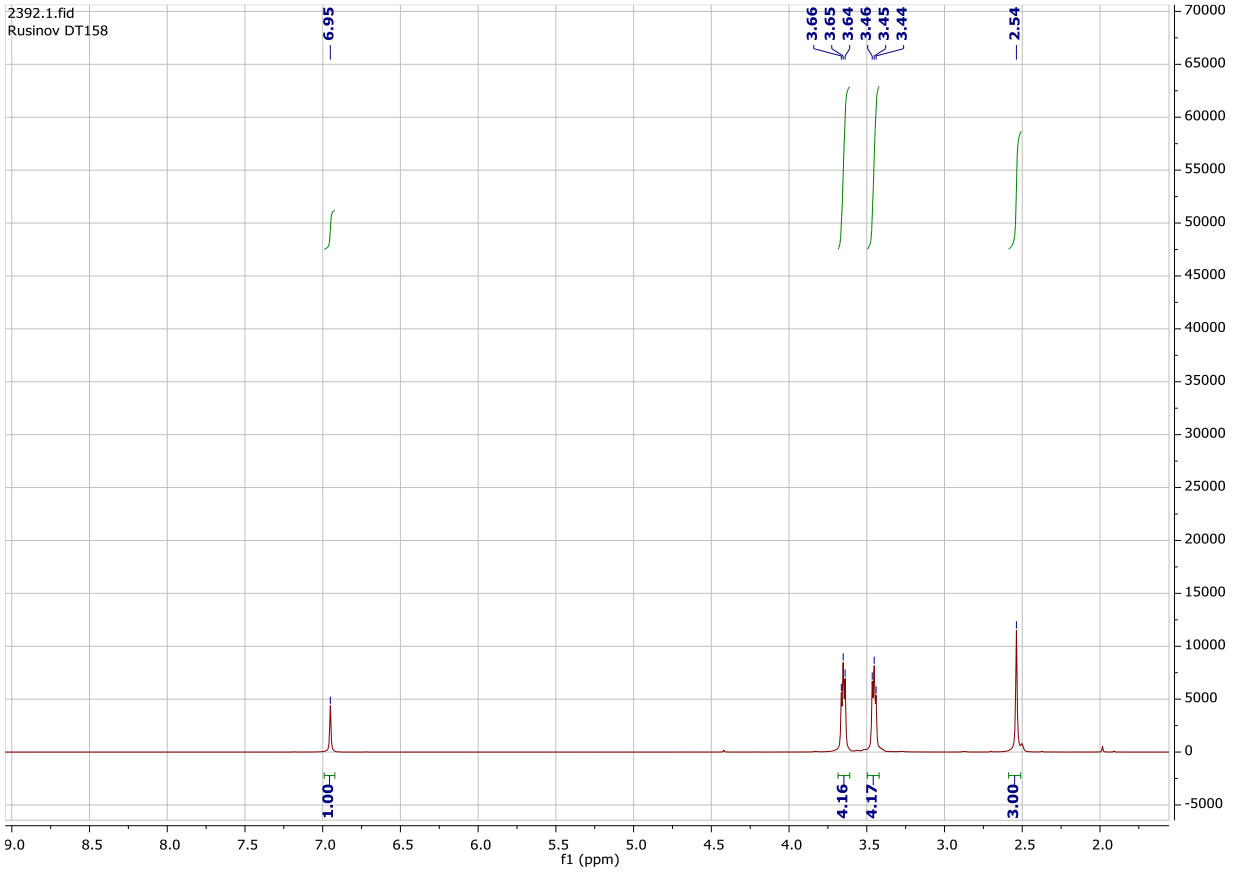


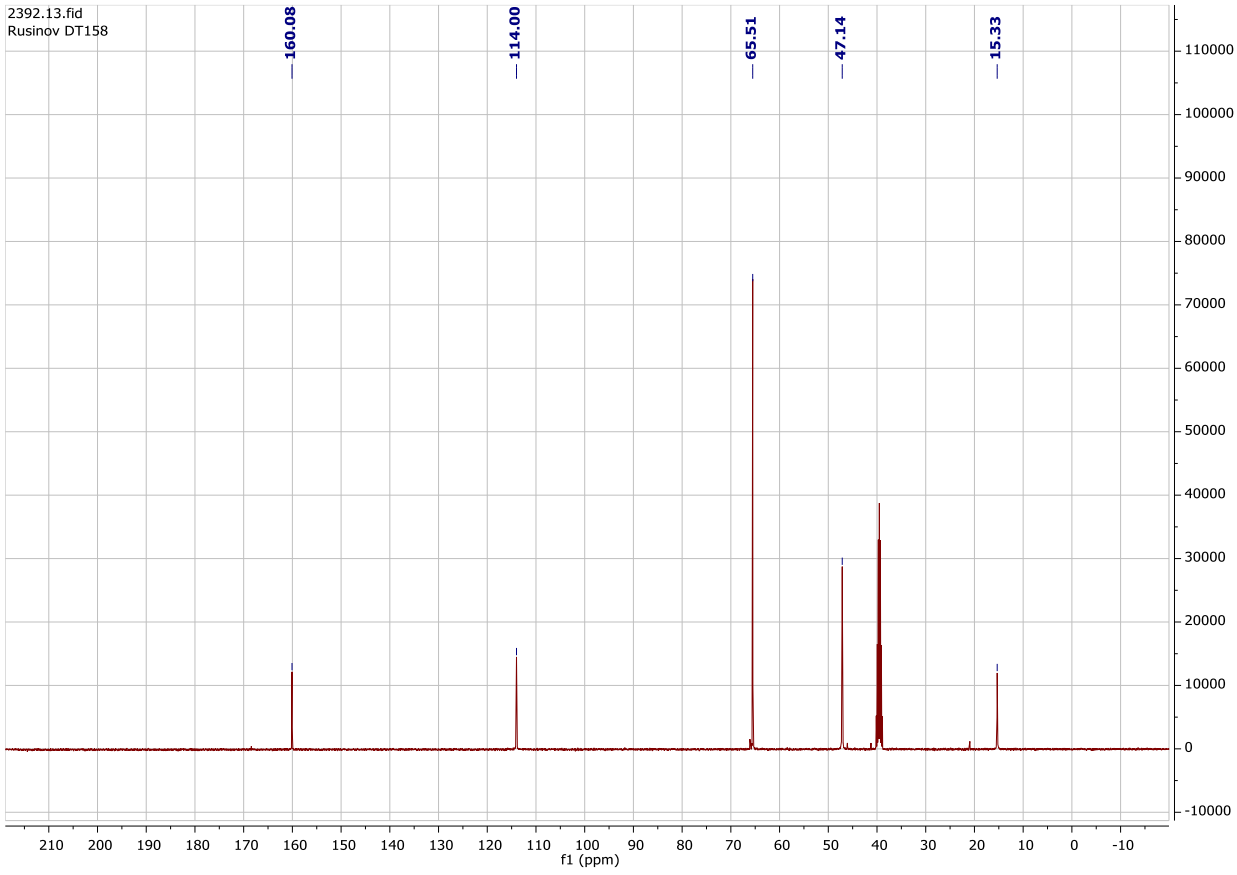
Method 1 (using 1-nitrobutan-2-one sodium salt): A solution of 1-nitrobutan-2-one sodium salt **2b** (0.252 g, 0.0018 mol) in 3.9 M AcONa (1.5 ml, 0.00585 mol) was prepared. To a mixture of aniline (0.165 ml, 0.0018 mol) in water (5 ml) and 12 M HCl (0.45 ml, 0.0054 mol), a solution of $NaNO_2$ (0.138 g, 0.002 mol) in water (1 ml) was added portionwise at 0-5 °C. The mixture was kept for 10 min and poured into the above solution of 1-nitrobutan-2-one sodium salt. The mixture was stirred for 30 min at room temperature, the precipitate was filtered off, washed with water-ethanol mixture (15 ml) solution and dried in air.

Method 2 (using 2-morpholino-1-nitrobut-1-ene): To a solution of NaOH (0.072 g, 0.0018 mol) in water (3 ml), 2-morpholino-1-nitrobut-1-ene **1b** (0.335 g, 0.0018 mol) and 3.9 M AcONa (1.5 ml, 0.00585 mol) were added consecutively. To a mixture of aniline (0.165 ml, 0.0018 mol) in water (5 ml) and 12 M HCl (0.45 ml, 0.0054 mol), a solution of $NaNO_2$ (0.138 g, 0.002 mol) in water (1 ml) was added portionwise at 0-5 °C. The mixture was kept 10 min and poured into the abovementioned 2-morpholino-1-nitrobut-1-ene solution. The mixture was stirred for 30 min at room temperature, the precipitate was filtered off, washed with water-ethanol mixture (15 ml) and dried in air.

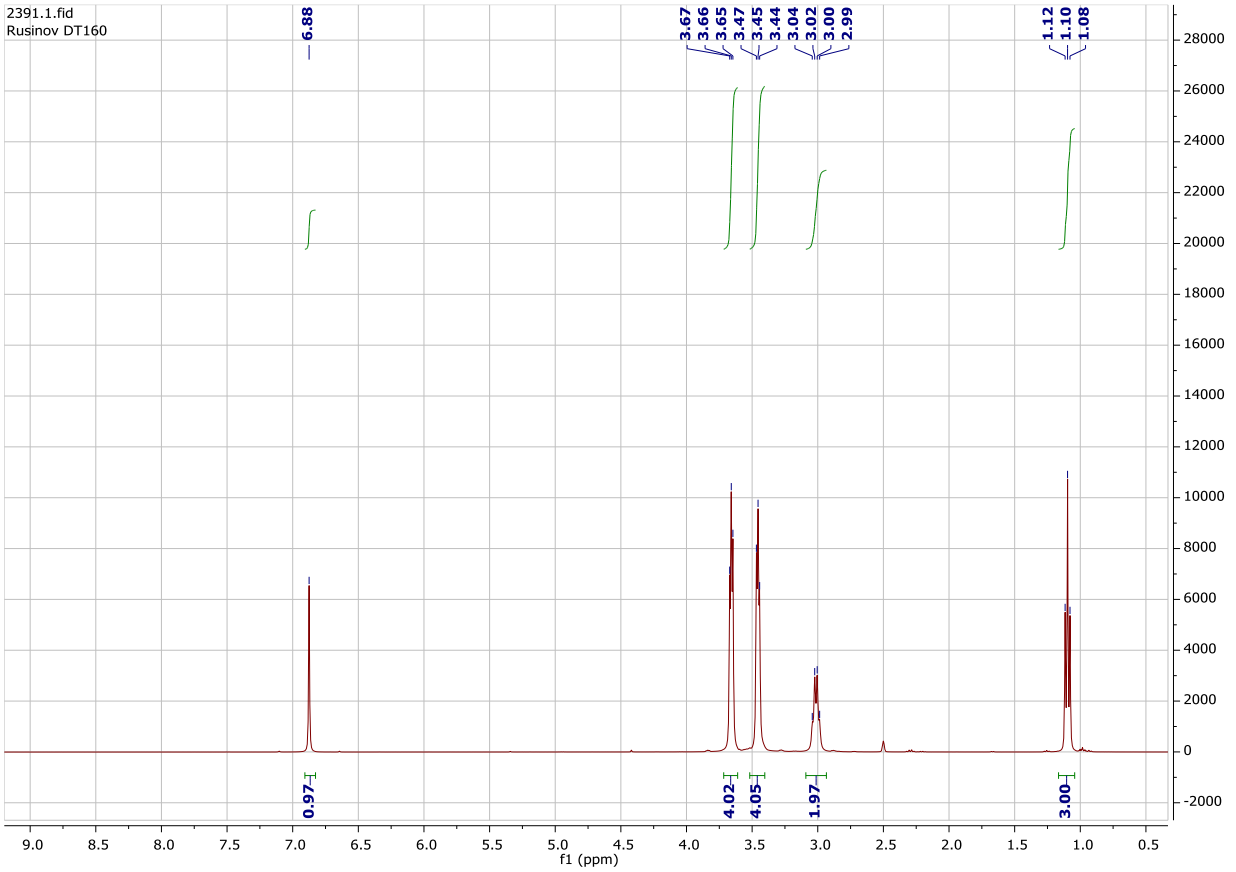
Yields in both methods was 0.29 g (73%), pale-yellow powder, mp = 82-84°C. ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 1.15 (t, 3H, CH_3, *J*=7.3 Hz), 2.93 (q, 2H, CH_2, *J* = 7.3 Hz), 7.12 (t, 1H, CH, *J* = 7.3 Hz), 7.36 (t, 2H, 2CH, *J*= 7.7 Hz), 7.47 (d, 2H, 2CH, *J* = 8.0 Hz), 11.68 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*) spectrum, δ, ppm: 6.80, 30.55, 117.37, 127.42, 129.51, 129.63, 140.52, 158.23, 197.03. Found (%): C 54.26; H 5.25; N 19.08. Calc. for $C_{10}H_{11}N_3O_3$ (%): C 54.29; H 5.01; N 19.00. IR, ν, cm^{-1}: 3239 (N-H), 1691 (C=O), 1522, 1236 (NO_2).

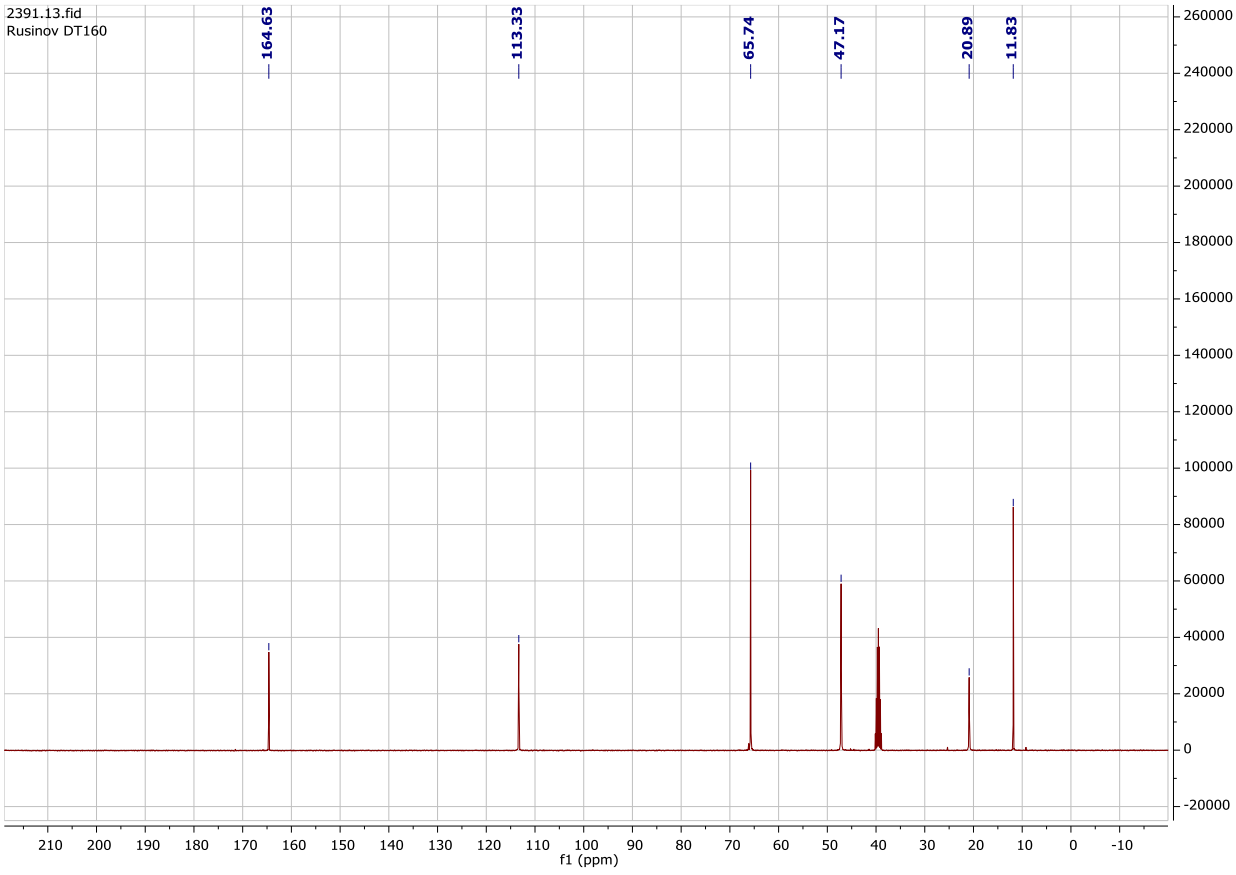
2-Morpholino-1-nitroprop-1-ene (1a)



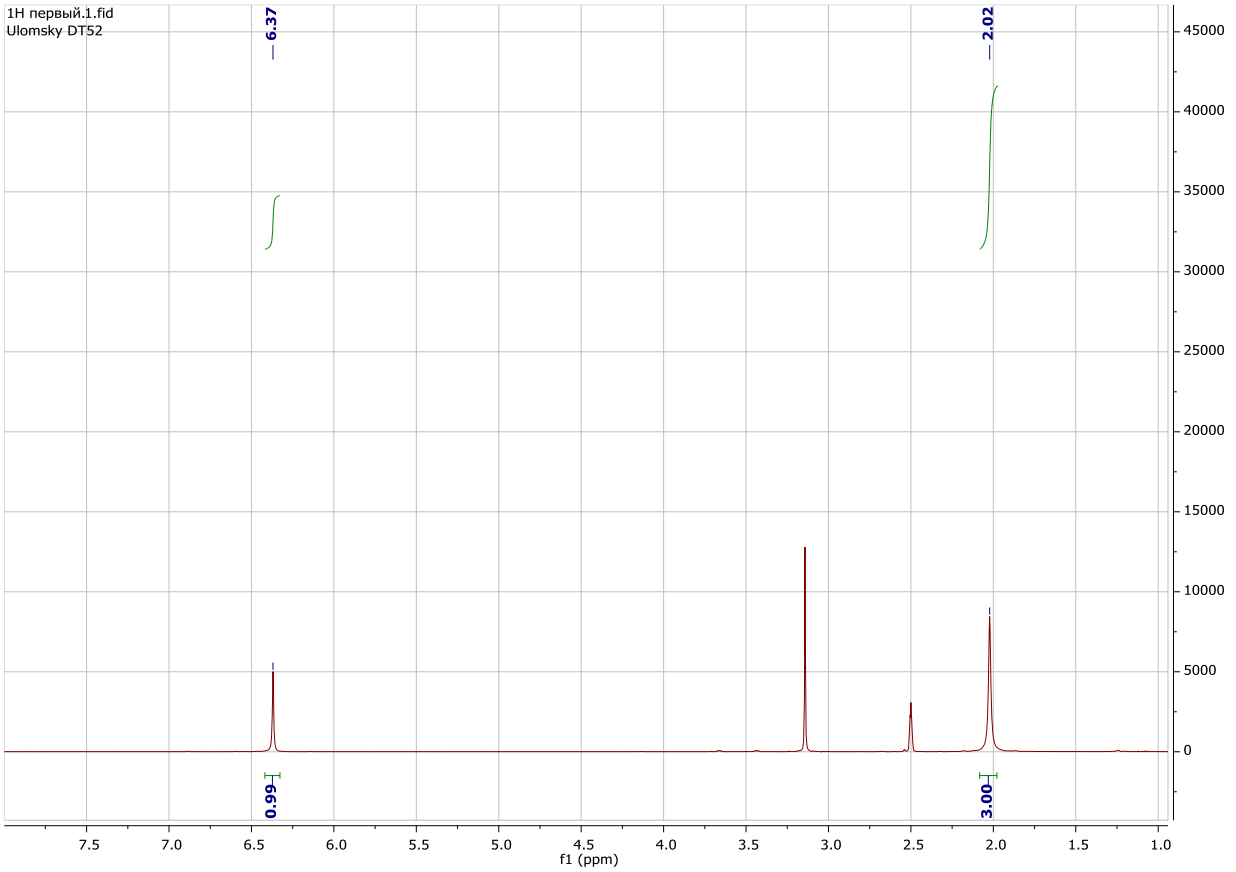


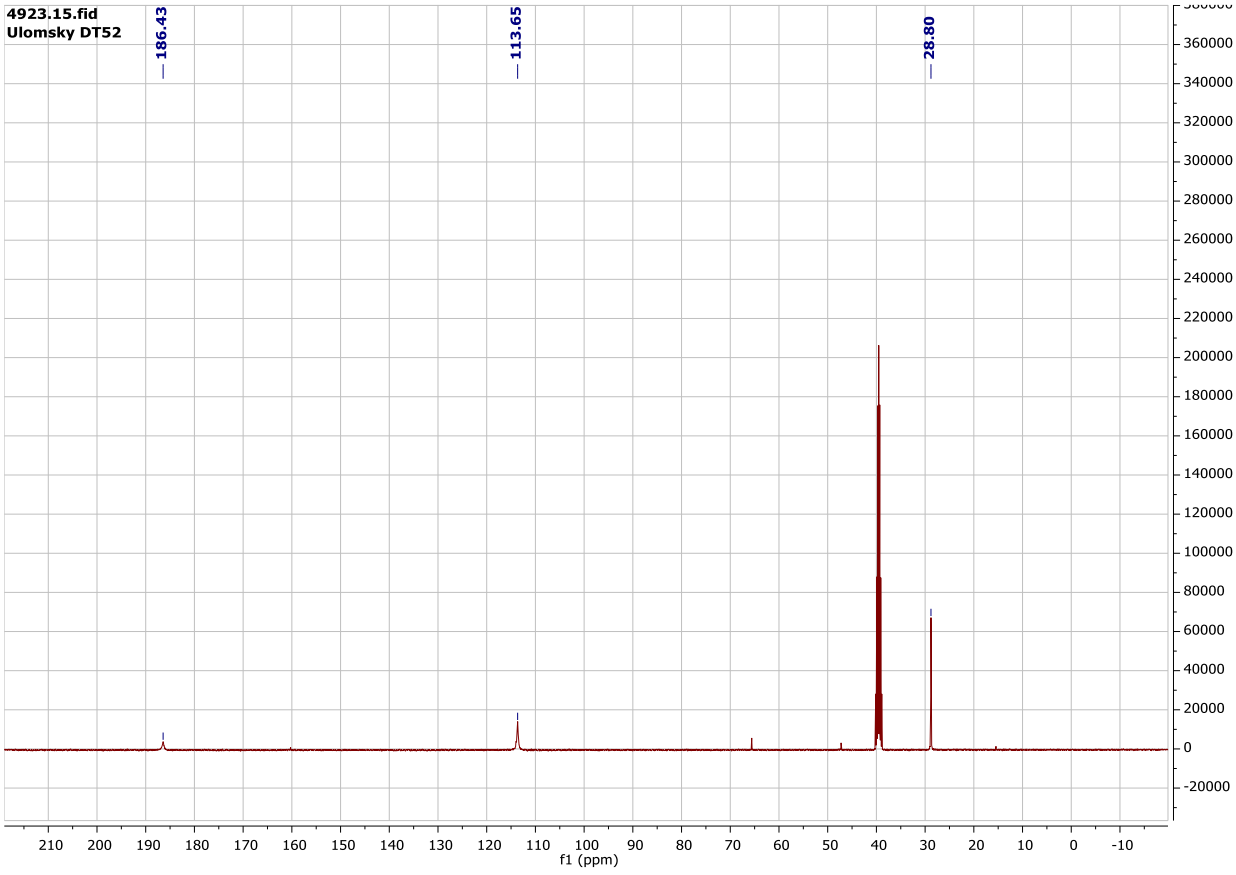
2-Morpholino-1-nitrobut-1-ene (1b)



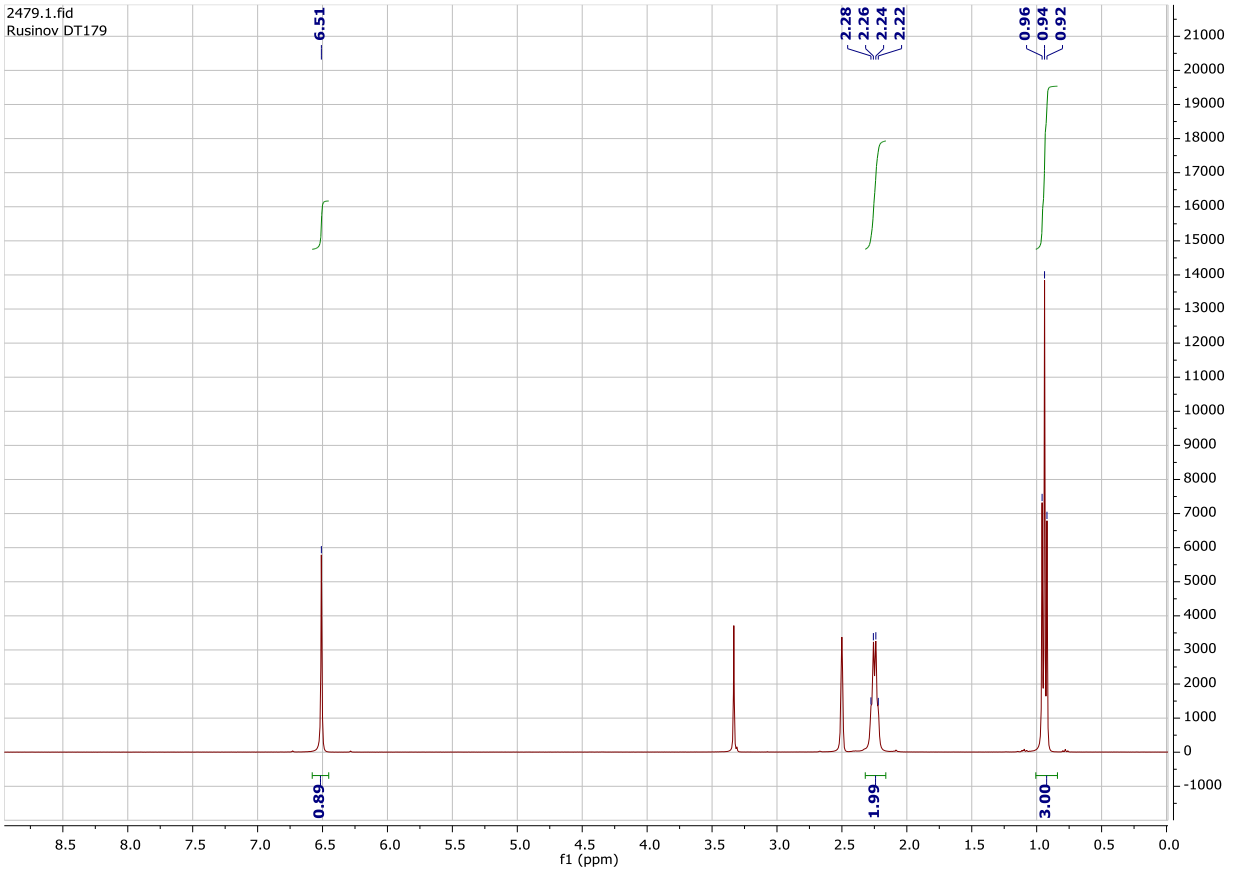


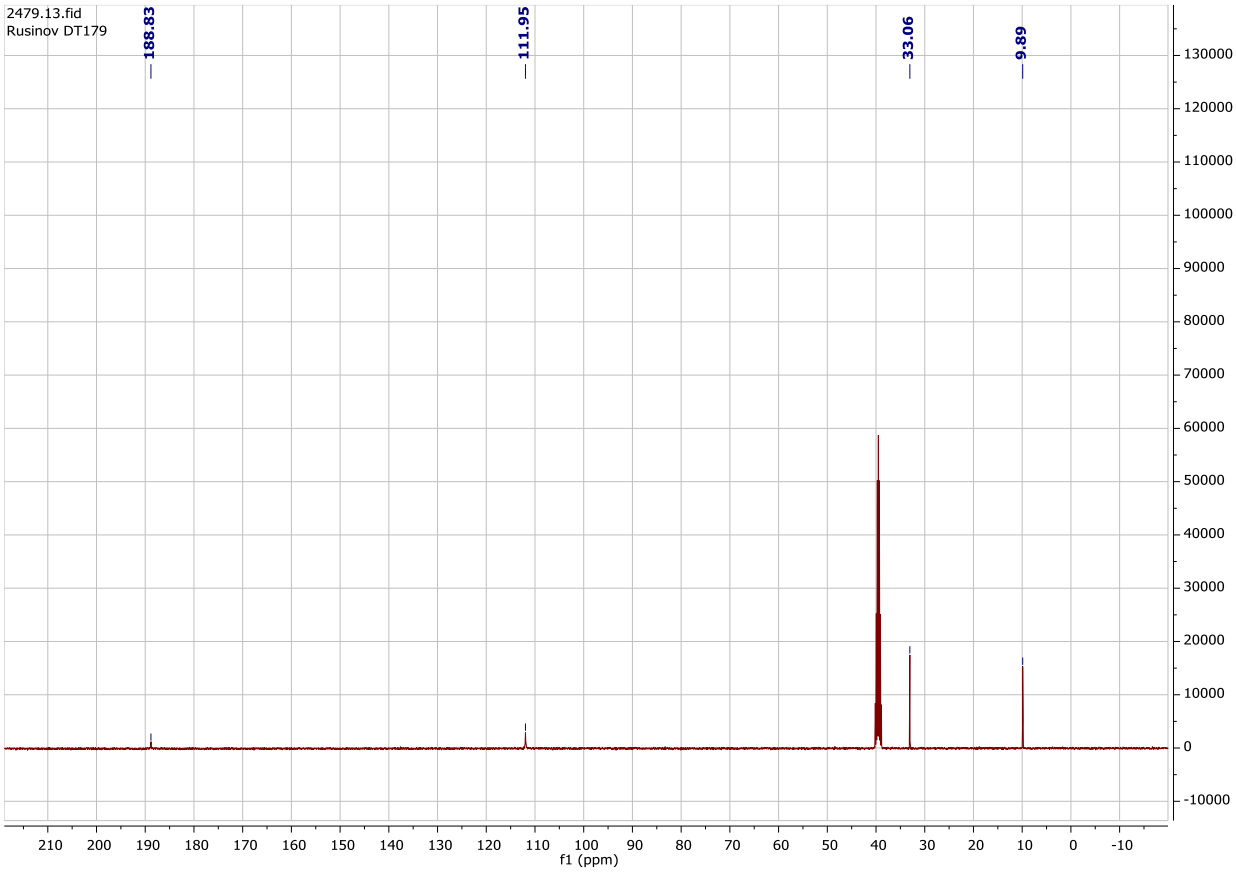
1-Nitropropan-2-one sodium salt monohydrate (2a)



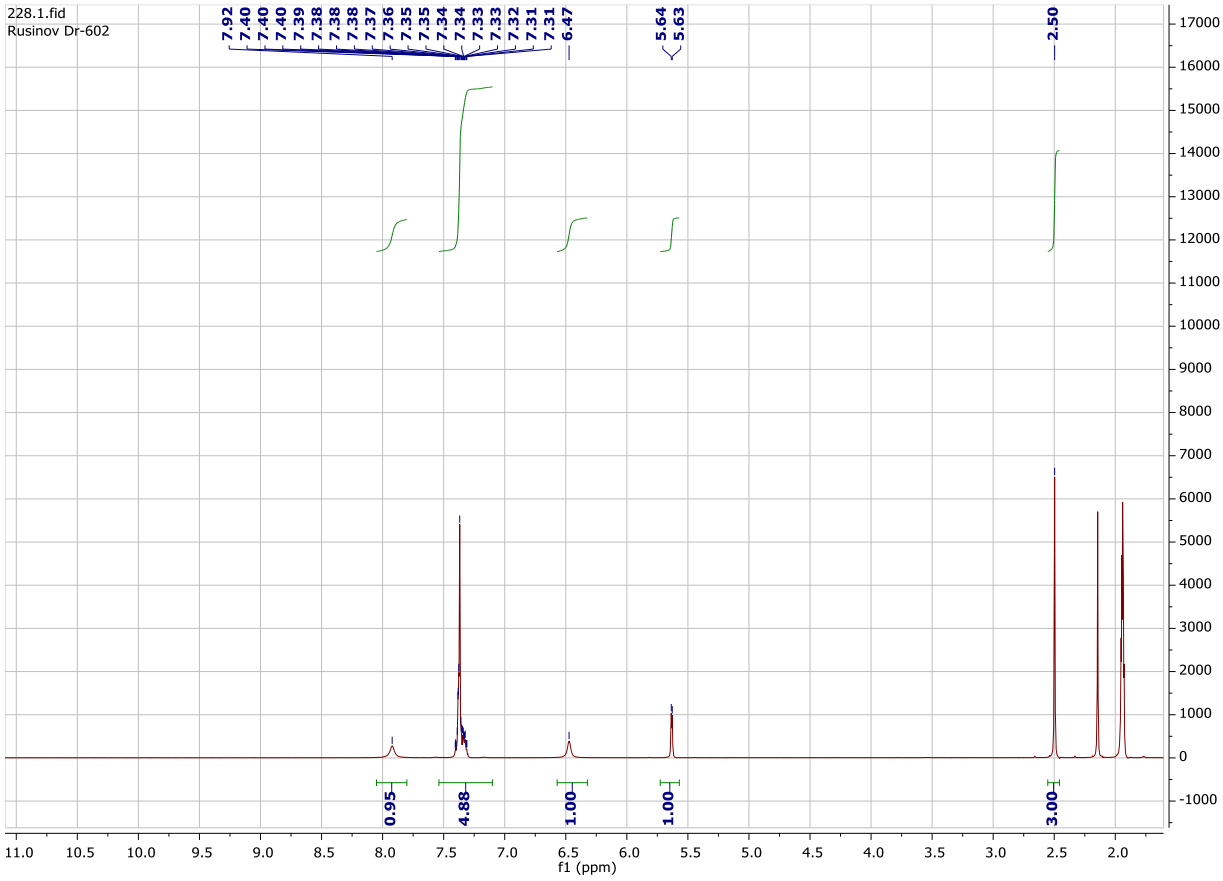


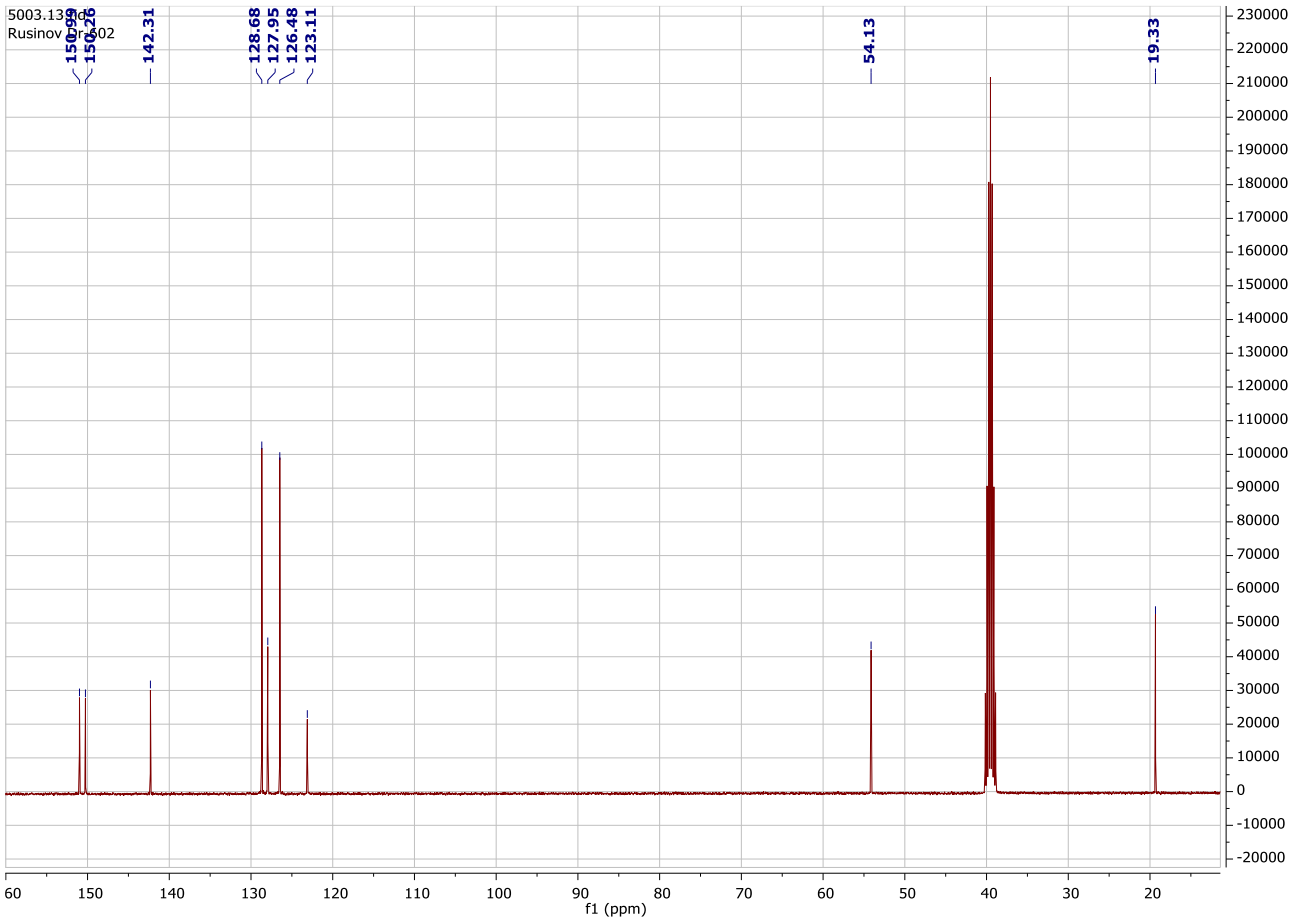
1-Nitrobutan-2-one sodium salt (2b)



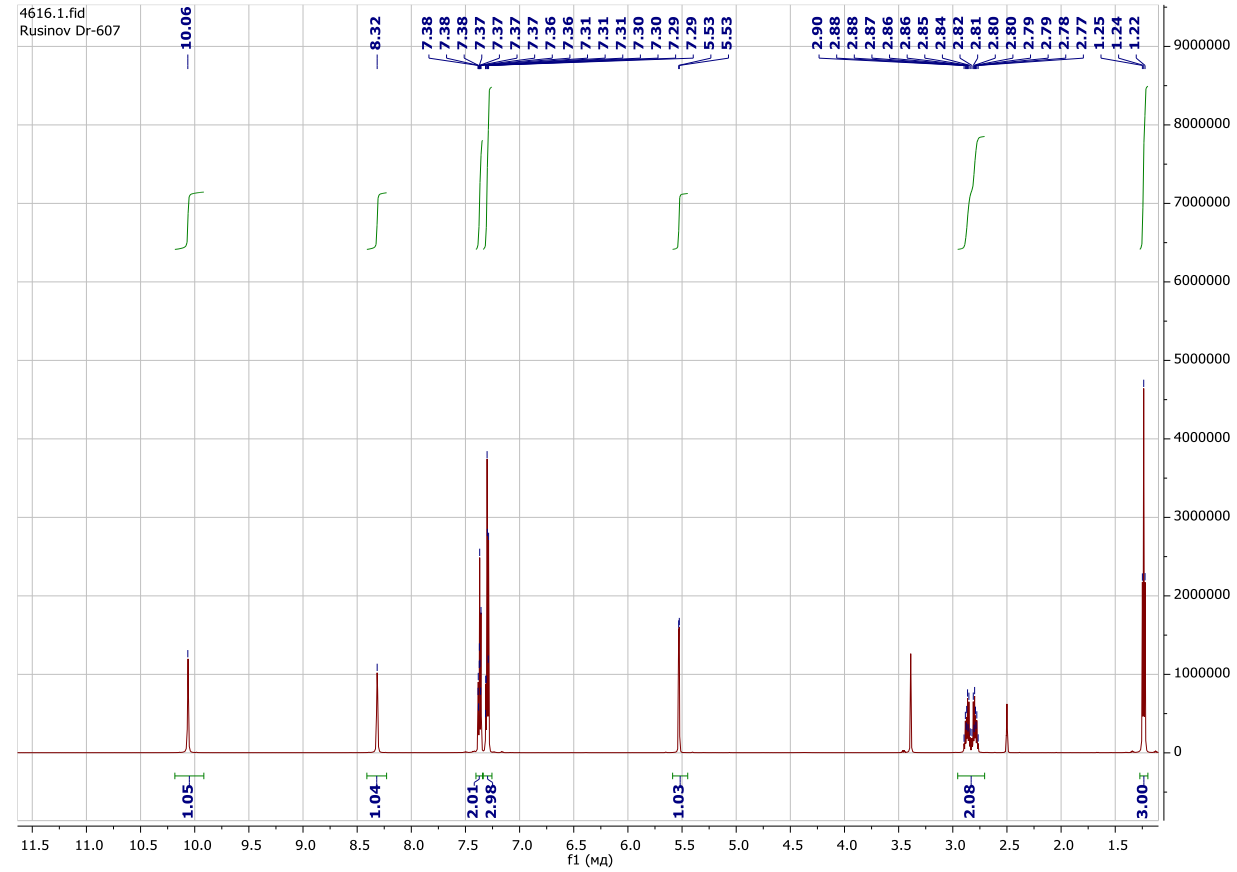


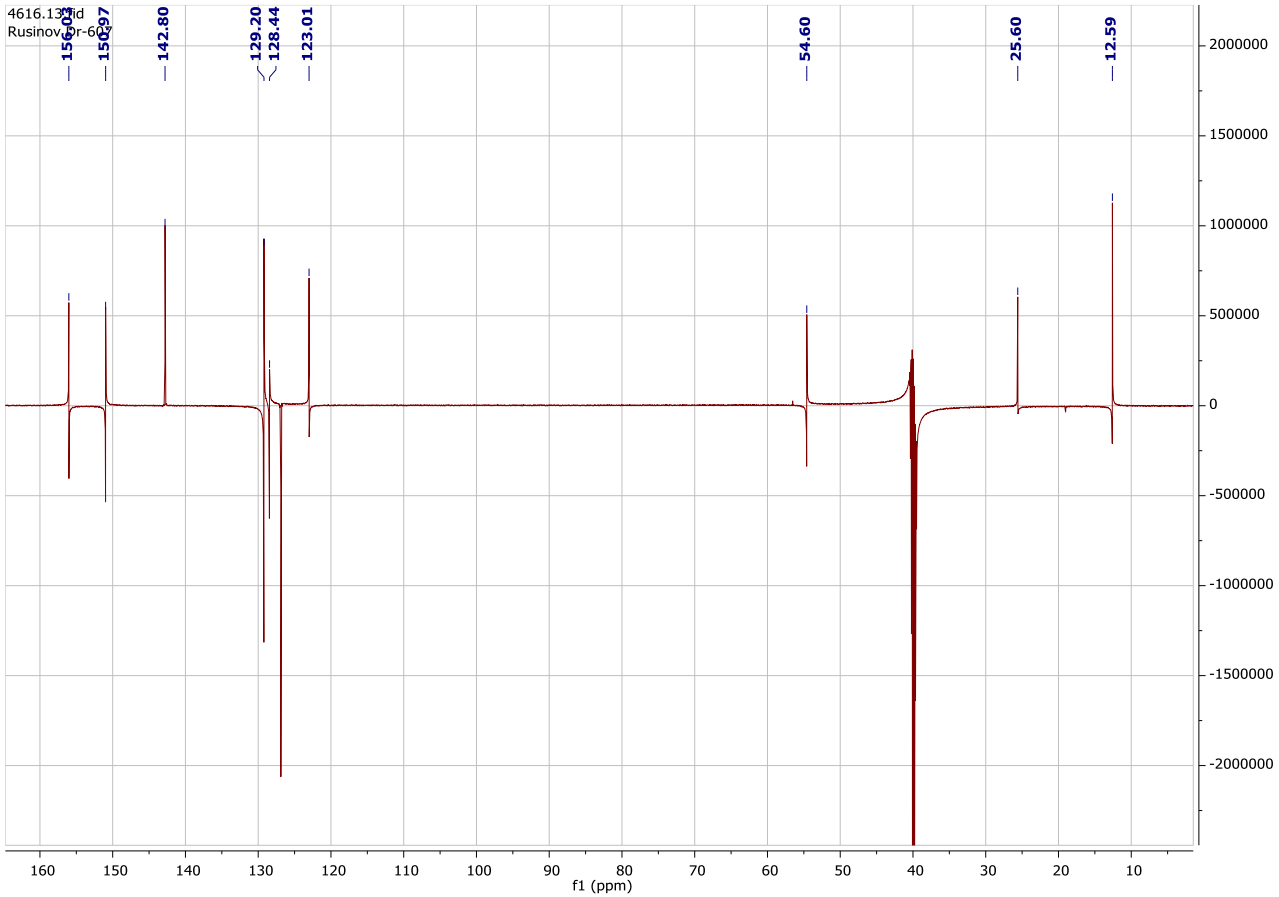
6-Methyl-5-nitro-4-phenyl-3,4-dihydropyrimidin-2-one (4a)



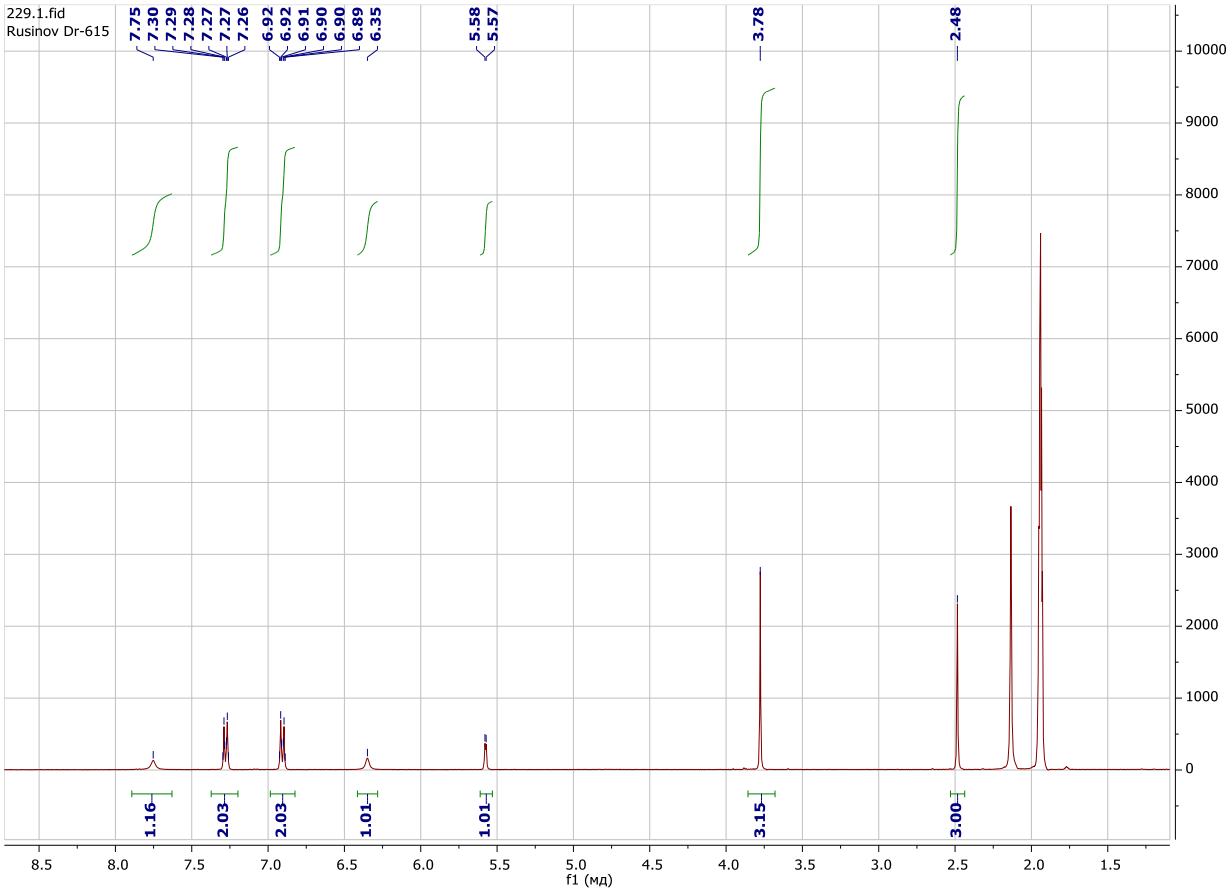


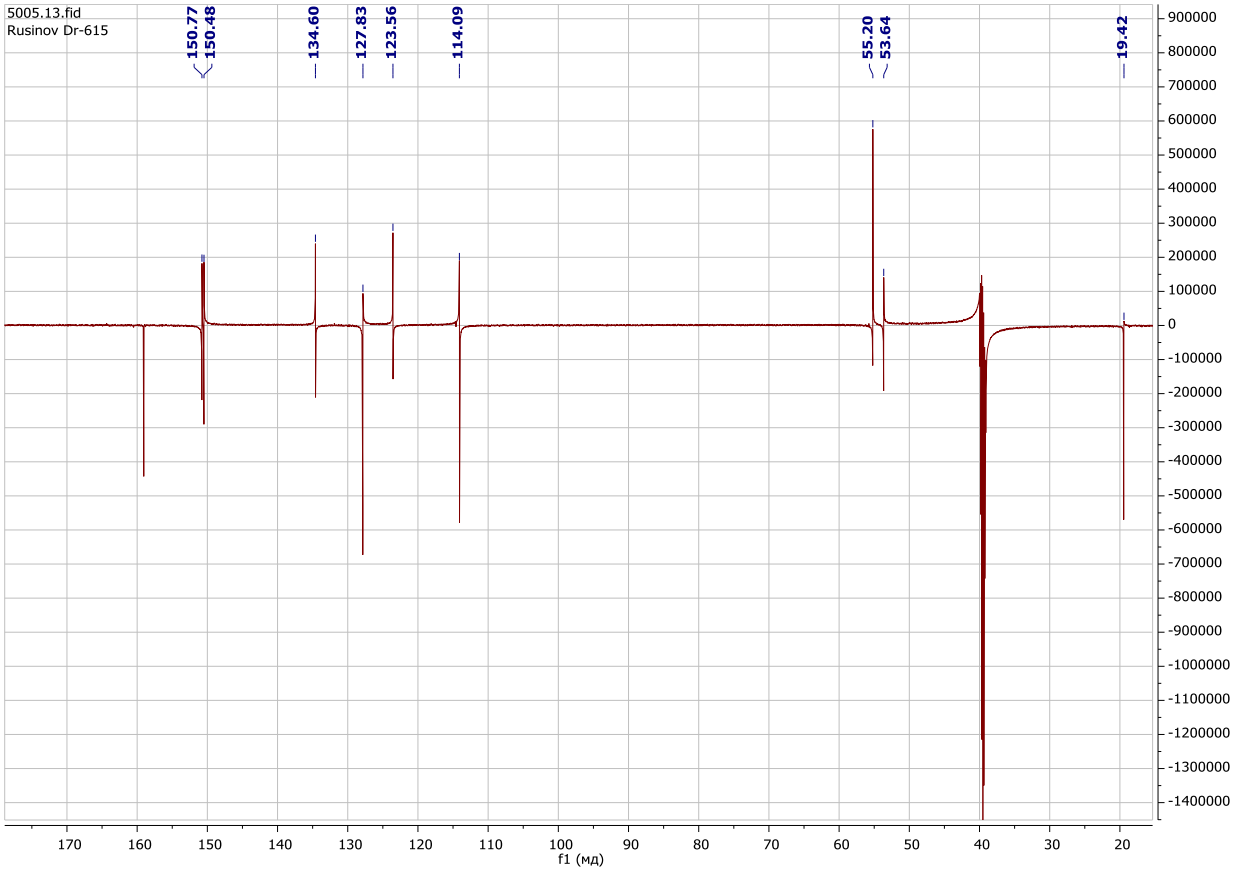
6-Ethyl-5-nitro-4-phenyl-3,4-dihydropyrimidin-2-one (4b)



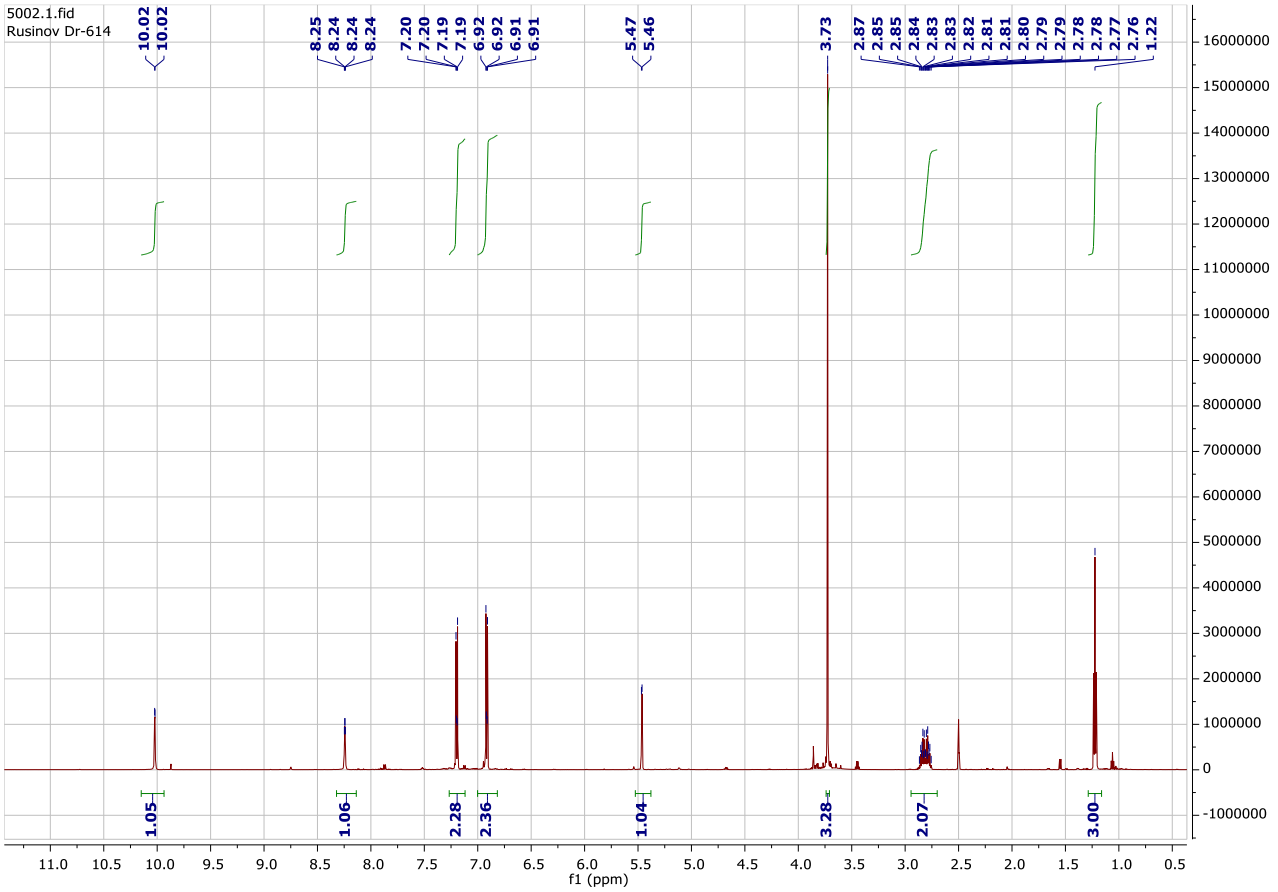


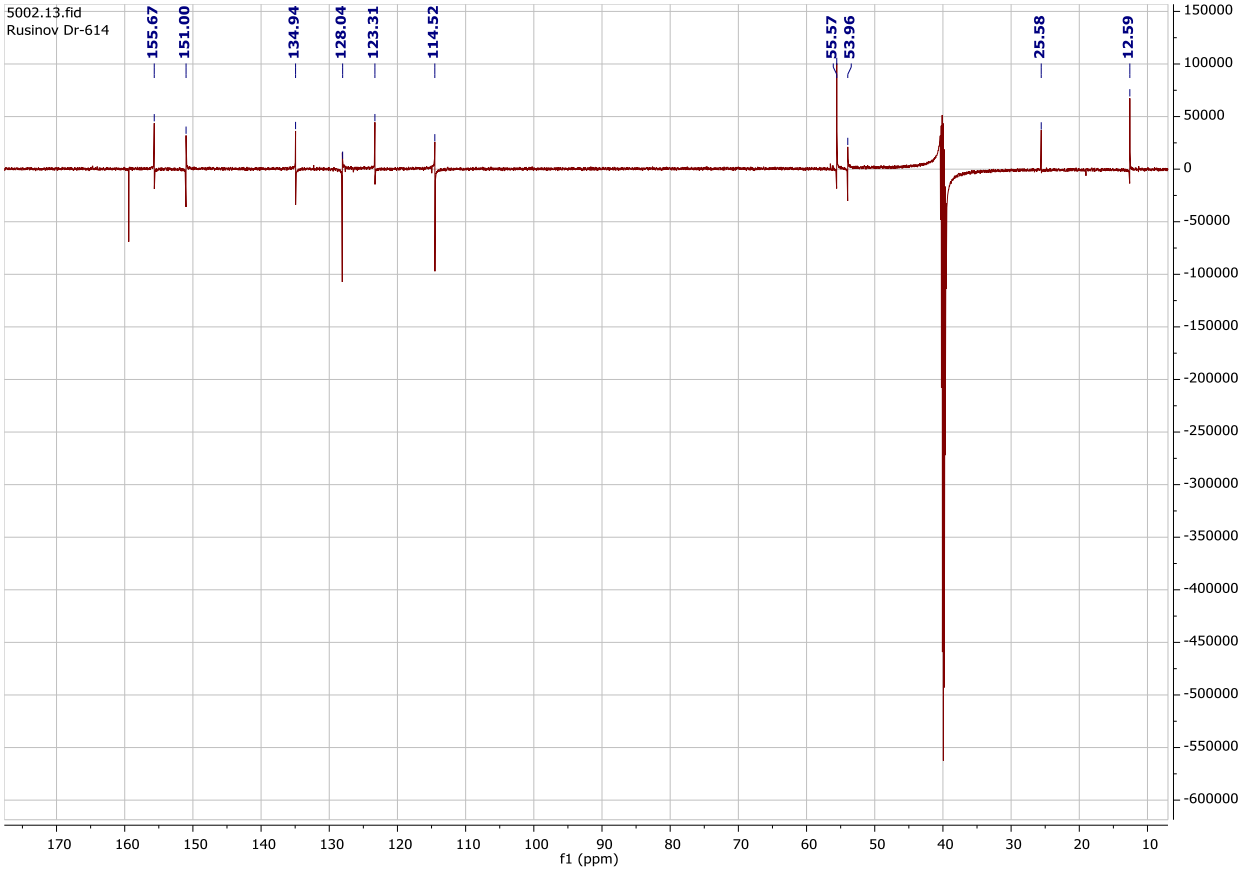
6-Methyl-4-(4-methoxyphenyl)-5-nitro-3,4-dihydropyrimidin-2-one (4c)



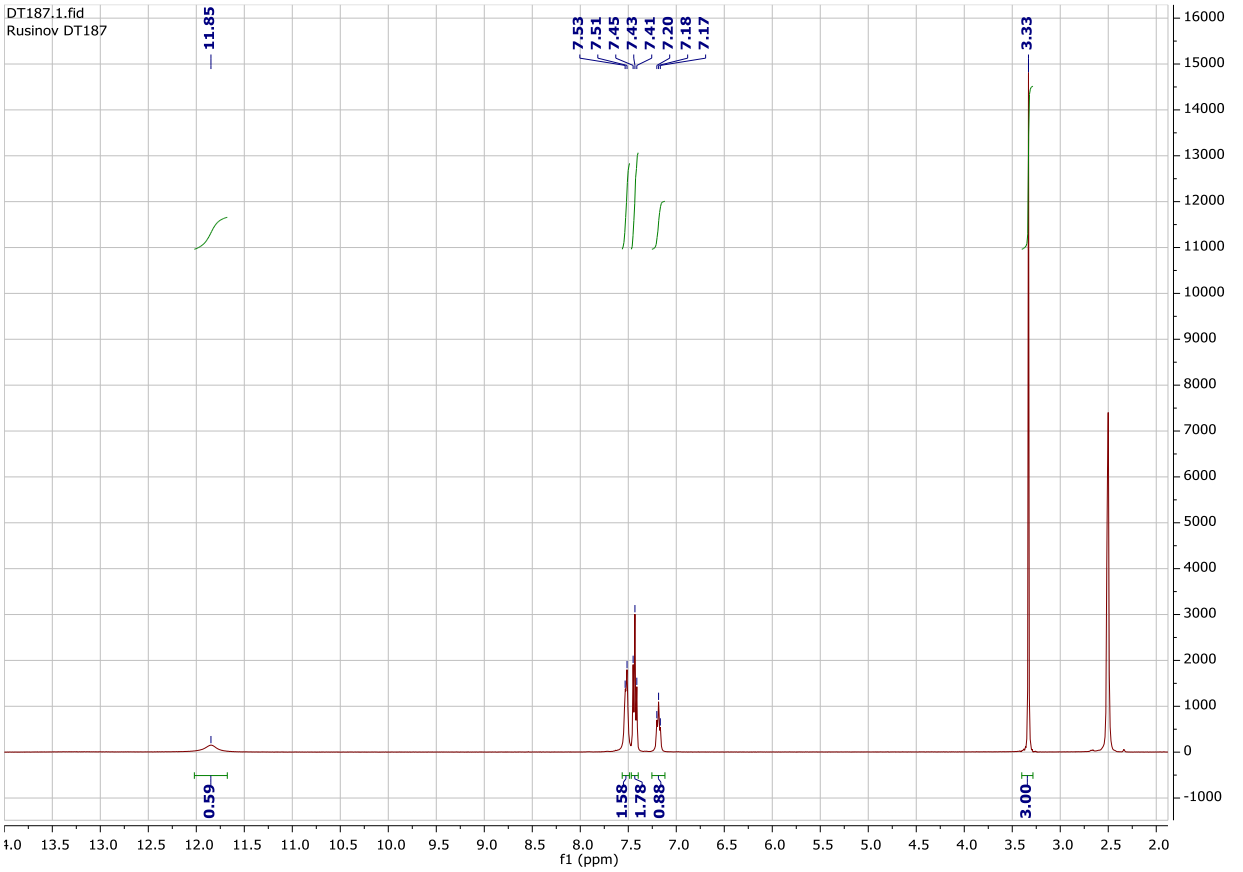


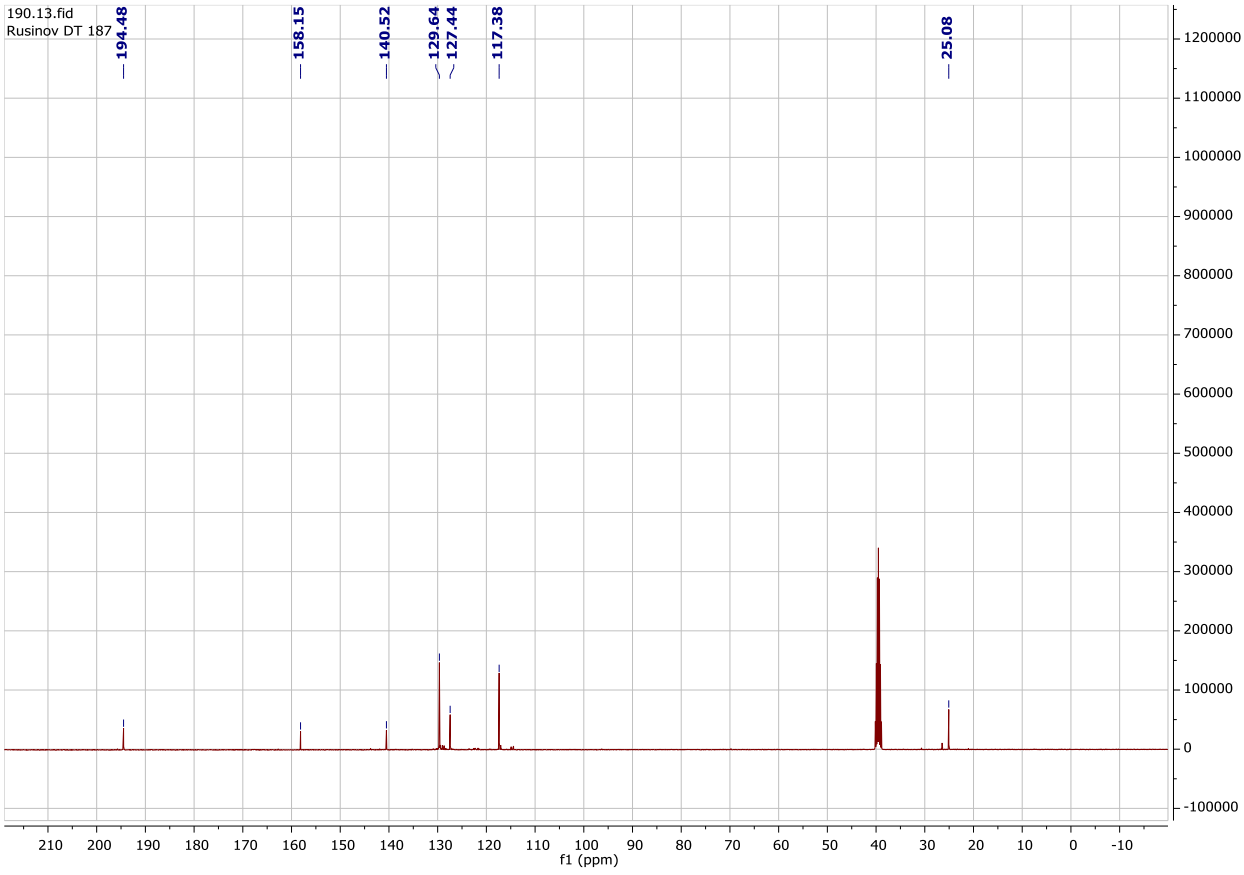
6-Ethyl-4-(4-methoxyphenyl)-5-nitro-3,4-dihydropyrimidin-2-one (4d)





1-Nitro-1-(2-phenylhydrazono)propan-2-one (5a)





1-Nitro-1-(2-phenylhydrazono)butan-2-one (5b)