Supporting information for

Nitration of aromatics with dinitrogen pentoxide in liquefied 1,1,1,2-tetrafluoroethane medium

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1. Materials

The reactions were carried out in 22.4 cm^3 steel autoclave equipped with sapphire windows, magnetic stirrer, and pressure/temperature sensors. An auxiliary 12 cm^3 steel dosing vessel with sapphire windows and magnetic stirrer was used for preparation of DNP solutions. Melting points were measured on Stuart® SMP40. ^1H and ^{13}C NMR spectra were recorded on Bruker® AM-300 (300.13 or 75.47 MHz respectively). The high-resolution mass spectra (HRMS) were measured with Bruker microTOF II spectrometer by using electrospray ionization (ESI).

1,1,1,2-Tetrafluoroethane (TFE), O_2 (Grade 3.5), N_2 (Grade 5) and nitrogen dioxide (NO_2) were obtained from «Linde Gas Rus». Unless otherwise mentioned, all substrates were purchased from Acros Organics. Substrates **35** and **38** were prepared via the routine etherification procedure.[1]

Substrate **39** – methyl-2-(4-methoxyphenyl)-2-oxoacetate – was obtained via following procedure. A mixture of MeOH (2.08 g, 2.6 mL, 65 mmol) and DCM (5 mL) was added dropwise to the solution of $(COCl)_2$ (8.89 g, 6.0 mL 70 mmol) in DCM (8 mL) at 0-5°C under argon during 40 min. The mixture was further stirred at ambient temperature for 2 h and then added dropwise under argon to a stirred solution of $AlCl_3$ (6.00 g, 45 mmol) in DCM (10 mL) during 15 min. Anisole (3.24 g, 3.3 mL, 30 mmol) was added to the resulting solution within 10 min and the reaction mixture was stirred overnight. Then it was poured into an ice-cold concentrated aqueous HCl (100 mL). The aqueous and organic phases were separated and the aqueous phase was extracted with DCM (3 x 25 mL). The combined organic phases were washed with distilled water (3 x 25 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by column chromatography (silica gel, EtOAc/petroleum ether = 1:4) to afford compound **39** (4.71 g, 81%) as colorless crystals, m.p. 48-49°C (Lit.[2] m.p. 49°C).

[1] D. Chavez-Flores, J. M. Salvador, *Tetrahedron Asymmetry* **2012**, *23*, 237–239.
[2] A. J. Muller, K. Nishiyama, G. W. Griffin, K. Ishikawa, D. M. Gibson, *J. Org. Chem.* **1982**, *47*, 2342–2352.

2. Synthesis of DNP

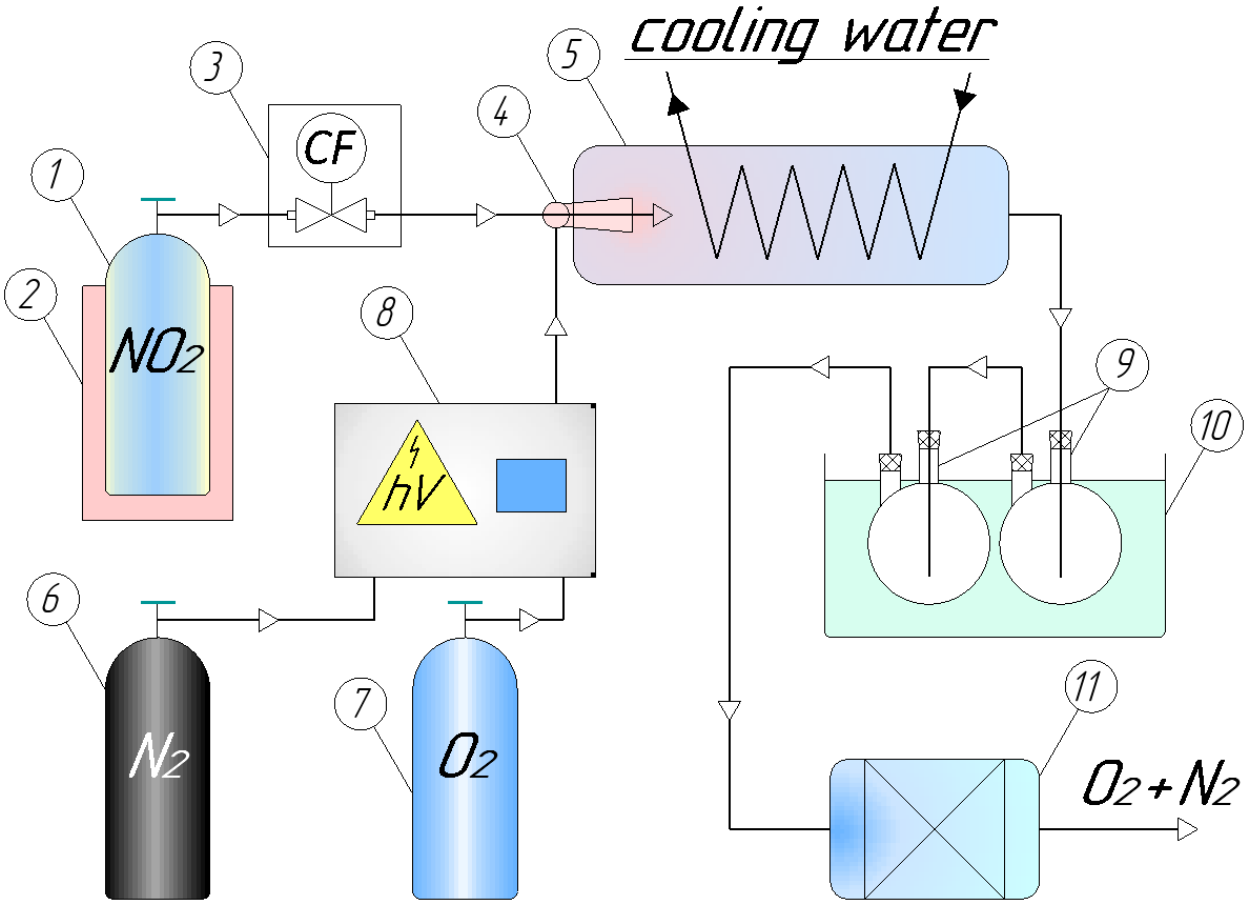


Figure 1. Principle scheme of N_2O_5 production laboratory setup:
1 – cylinder with NO_2; 2 – heating bath; 3 – flowmeter; 4 – coaxial nozzle; 5 – glass reactor with an inner coiled tube cooler; 6 – cylinder with nitrogen; 7 – cylinder with oxygen; 8 – ozone generation unit; 9 – DNP glass traps; 10 – cooling bath; 11 – ozone destructor.

The fresh and pure DNP was obtained via NO_2 oxidation with O_3. The detailed scheme of the experimental setup is given in Figure 1. The process was arranged in a 2 L gas-flow reactor with an inner coiled tube cooler **5**, operating in a continuous mode. The NO_2 gas was fed into the reactor from the cylinder **1** heated up to 35-40°C through the flowmeter **3** with the flow rate of 22.4 mL/min (1 mmol/min). The O_3 was delivered by an ozone generation unit **8** in the form of its 20 wt.% mixture with O_2. The O_2 and N_2 (doping gas) were delivered to **8** from cylinders **7** and **6** respectively. The O_3 flow rate was sufficient to have the brownish NO_2 fully engaged in the oxidation reaction (the discoloration was determined visually). The gases entered the reactor through the coaxial nozzle **4** for the better mixing and more uniform distribution throughout the vessel **5**. The process temperature was maintained by cooling water and did not exceed 25 °C in the first third of

the reactor, according to the thermocouple readings. The resultant gaseous DNP was condensed in two successive traps **9** cooled at -80 °C giving its snow-white crystalline flakes (Figure 2), which could be stored in a freezer at -18°C under the oxygen atmosphere without decomposition for two weeks. The process yield is nearly quantitative (~ 7 g/h). After the desired DNP quantity was obtained, the NO_2 feed and O_3 generation were stopped, the system was insufflated with pure O_2, and the product was weighed and used as intended. During the process, O_3 excess was being streamed in destructor **11** for its decomposition.

Figure 2. The obtained DNP in 500 ml round-bottom flask.

3. General nitration procedure

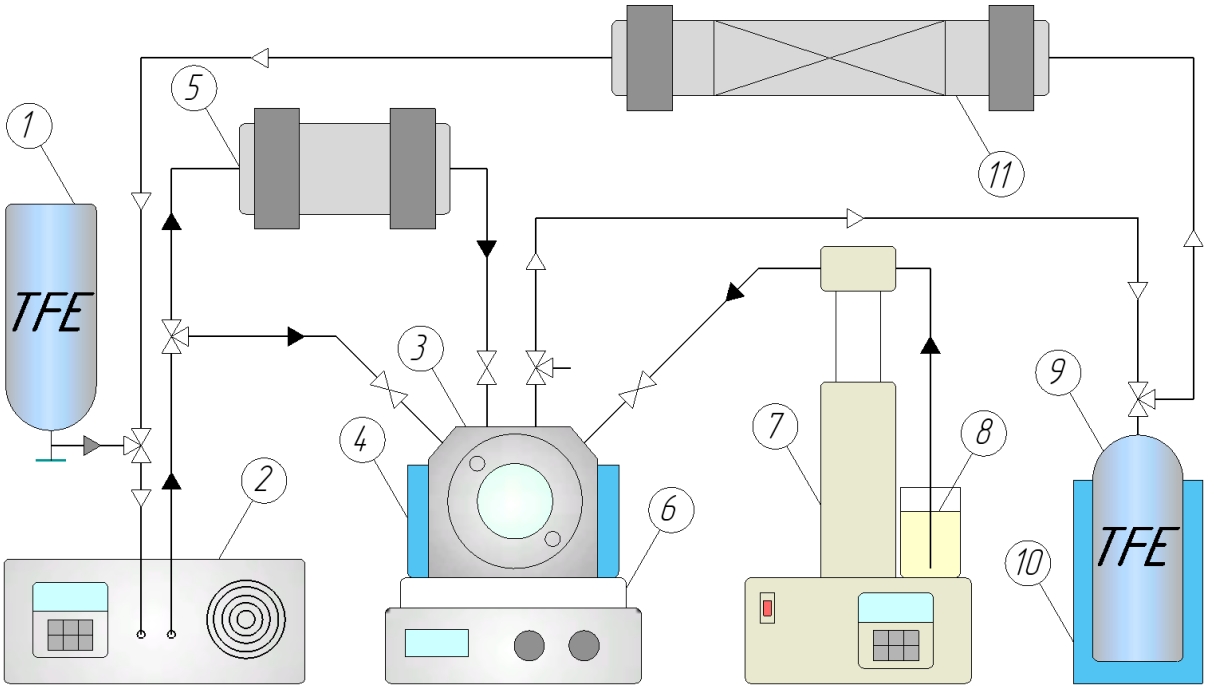


Figure 3. Laboratory setup for nitration of aromatics with DNP in TFE medium: 1 – cylinder with TFE; 2 – piston pump with gas condensation chamber; 3 – autoclave-reactor equipped with two looking-through windows, stir-bar and sensors of temperature and pressure; 4,10 – thermostats; 5 – auxiliary dosing vessel; 6 – magnetic stirrer; 7 – syringe pump; 8 – beaker with aqueous $NaHCO_3$; 9 – cylinder for TFE re-condensation; 11 – desiccant tube.

The nitration of aromatics was carried out using the laboratory setup given in Figure 3. A steel autoclave-reactor **3** containing 5.0 mmol of substrate was filled with liquefied TFE at room temperature by one third of the volume and cooled to 5°C. Here and then TFE was delivered from steal cylinder **1** by piston pump **2**, equipped with the gas condensation chamber cooled by a Peltier element. The auxiliary dosing vessel **5** was charged with 1.1 – 10.0 equivalents of DNP (depending on the arene structure and a number of introducing nitro groups) and then filled with TFE fluid by half at room temperature. Using the pressure difference (ΔP ~0.3 MPa) between the vessels, the N_2O_5 solution was slowly moved into the reactor **3** (*temperature growth more than 5°C should be avoided*) at constant stirring. The dosing vessel **5** was refilled with TFE by one third to dissolve and wash residuals of the nitrating agent into the reactor **3**. The reaction mixture was stirred at room temperature and 0.6 MPa. After the reaction was complete, 5 ml of 2N aqueous $NaHCO_3$ was added by the syringe pump **7** to the reactor **3** to neutralize an excess of the nitrating agent and the

formed nitric acid. The TFE was removed by decompression and streamed through the desiccant tube **11** filled with molecular sieves and dry potassium hydroxide into the precooled cylinder **9** for condensation, storage and further re-use (TFE recuperation yield is over 95% by weight). The autoclave **3** was opened, and the nitration products were isolated according to one of the following procedures.

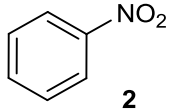
Work-up procedure A

The products were filtered off, washed with distilled water (2x3 mL), dried in the air to afford corresponding nitro compounds as individual substances or mixtures of isomers. The structures and isomer ratios of all nitro compounds were determined by ^{1}H NMR spectroscopy.

Work-up procedure B

The products were extracted from the aqueous suspension with ethyl acetate (2×25 ml). The combined organic extracts were washed with distilled water (2×25 ml) and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to afford the targeted nitro compounds. The structures and isomer ratios of all nitro compounds were determined by ^{1}H NMR spectroscopy.

Nitrobenzene (2)

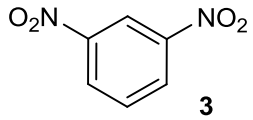


2

Treatment of benzene (**1**) (0.39 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** afforded compound **2** (0.60 g, yield 98%) as yellowish liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, J = 8.2 Hz, 2H), 7.70 (t, J = 8.2 Hz, 1H), 7.54 (t, J = 8.2 Hz, 2H).

***m*-Dinitrobenzene (3)**



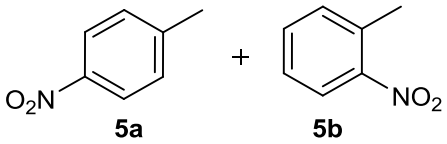
3

Treatment of benzene (**1**) (0.39 g, 5.0 mmol) with DNP (5.40 g, 50.0 mmol) followed by work-up **A** afforded compound **2** (0.80 g, yield 95%) as yellow solid m.p., 87-89°C (Lit. [3] m.p. 90°C).

[3] F. McCamish and A. Salathe, *J. Am. Chem. Soc.* **1928**, *50*, *6*, 1785.

^{1}H NMR (300 MHz, DMSO-d6) δ 8.85 (d, J = 2.0 Hz, 1H), 8.67 (dd, J = 8.2, 2.0 Hz, 2H), 7.99 (t, J = 8.2 Hz, 1H).

4-Nitrotoluene (5a) and 2-nitrotoluene (5b)



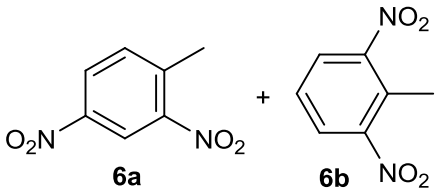
5a **5b**

Treatment of toluene (**4**) (0.46 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** afforded the mixture of isomers **5a** and **5b** (0.67 g, yield 98%) in a 1:1.4 ratio as yellowish liquid.

5a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.39 – 7.27 (m, 2H), 2.46 (s, 3H).

5b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 – 7.27 (m, 2H), 2.59 (s, 3H).

2,4-Dinitrotolune (6a) and 2,6-dinitrotolune (6b)



6a **6b**

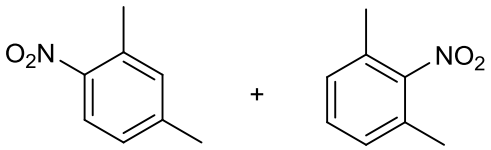
Method A: Treatment of toluene (**4**) (0.46 g, 5.0 mmol) with DNP (1.20 g, 11.0 mmol) followed by work-up **A** afforded the mixture of isomers **6a** and **6b** (0.90 g, yield 99%) in a 4:1 ratio as yellowish solid.

Method B: Treatment of 2-nitrotoluene (**5b**) (0.69 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded the mixture of isomers **6a** and **6b** (0.81 g, yield 89%) in a 2.3:1 ratio as yellowish solid.

6a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, J = 2.4 Hz, 1H), 8.38 (dd, J = 8.5, 2.4 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 2.76 (s, 3H).

6b ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 8.1 Hz, 1H), 2.61 (s, 3H).

1,3-Dimethyl-4-nitrobenzene (8a) and 1,3-dimethyl-2-nitrobenzene (8b)



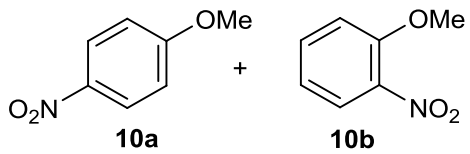
8a **8b**

Treatment of *m*-xylene (**7**) (0.53 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded the mixture of isomers **8a** and **8b** (0.86 g, yield 99%) in a 6:1 ratio as yellowish solid.

8a ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 1H), 7.15 (s, 1H), 7.12 (d, J = 8.9 Hz, 1H), 2.60 (s, 3H), 2.42 (s, 3H).

8b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 2.33 (s, 6H).

4-Nitroanisole (10a) and 2-nitroanisole (10b)



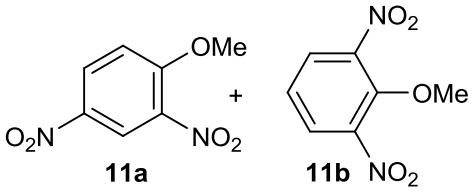
10a **10b**

Treatment of anisole (**9**) (0.54 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** afforded the mixture of isomers **10a** and **10b** (0.76 g, yield 99%) in a 1:2 ratio as yellowish oil.

10a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 9.3 Hz, 2H), 6.96 (d, J = 9.3 Hz, 2H), 3.91 (c, 3H).

10b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.1, 1.8 Hz, 1H), 7.54 (td, J = 8.1, 1.8 Hz, 1H), 7.13 – 7.00 (m, 2H), 3.96 (s, 3H).

2,4-Dinitroanisole (11a) and 2,6-dinitroanisole (11b)



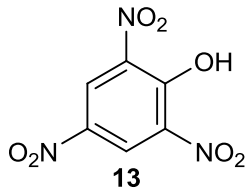
11a **11b**

Treatment of anisole (**9**) (0.54 g, 5.0 mmol) with DNP (1.20 g, 11.0 mmol) followed by work-up **A** afforded the mixture of isomers **11a** and **11b** (0.92 g, yield 93%) in a 6:1 ratio as yellowish solid.

11a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, J = 2.8 Hz, 1H), 8.50 (dd, J = 8.2, 2.8 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 4.15 (s, 3H).

11b ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 8.2 Hz, 1H), 4.13 (c, 3H).

2,4,6-Trinitrophenol (13)

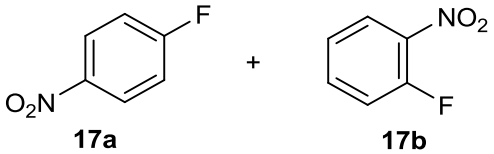


13

Treatment of phenol (**12**) (0.47 g, 5.0 mmol) with DNP (1.80 g, 16.5 mmol) followed by work-up **A** afforded compound **13** (0.93 g, yield 82%) as yellowish solid, m.p. 121-122°C (Lit.[4] m.p. 122°C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.95 (s, 1H), 9.22 (s, 2H).

4-Fluoronitrobenzene (17a) and 2-fluoronitrbenzene (17b)



17a **17b**

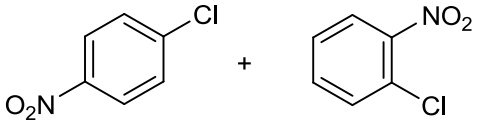
[4] Y. G. Khabarov, A. A. Patrakeev, V. A. Veshnyakov, D. S. Kosyakov, N. V. Ul'yanovskii, A. Y. Garkotin, *Org. Prep. Proced. Int.* **2017**, *49*, 178–181.

Treatment of fluorobenzene (**14**) (0.48 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** afforded the mixture of isomers **17a** and **17b** (0.64 g, yield 91%) in a 5:1 ratio as yellowish liquid.

17a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34-8.23 (m, 2H), 7.28–7.17 (m, 2H).

17b ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13-8.04 (m, 1H), 7.72-7.62 (m, 1H), 7.37-7.28 (m, 2H).

4-Chloronitrobenzene (18a) and 2-chloronitrobenzene (18b)



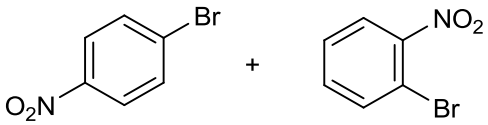
18a **18b**

Treatment of chlorobenzene (**15**) (0.56 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded the mixture of isomers **18a** and **18b** (0.73 g, yield: 93%) in a 1.5:1 ratio as yellowish solid.

18a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0, 2H), 7.54 (d, J = 8.0, 2H).

18b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.0, 1.5 Hz, 1H), 7.63–7.56 (m, 2H), 7.44 (td, J = 8.0, 1.5 Hz, 1H).

4-Bromonitrobenzene (19a) and 2-bromonitrobenzene (19b)



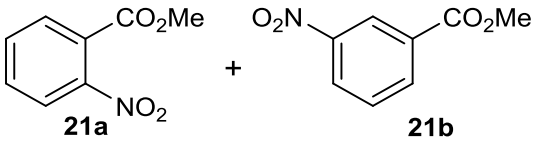
19a **19b**

Treatment of bromobenzene (**15**) (0.78 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded the mixture of isomers **19a** and **19b** (0.93 g, yield 92%) in a 1.2:1 ratio as yellowish solid.

19a ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 9.0 Hz, 2H).

19b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.5, 2.9 Hz, 1H), 7.78 (dd, J = 7.5, 2.9 Hz, 1H), 7.52 – 7.42 (m, 2H).

Methyl 2-nitrobenzoate (21a) and methyl 3-nitrobenzoate (21b)



21a **21b**

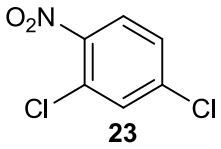
Treatment of methylbenzoate (**20**) (0.68 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** and separation of isomeric products by flash-chromatography (silica gel, ethyl acetate/petroleum ether gradient) afforded:

Methyl 2-nitrobenzoate (**21a**). Yellowish oil (0.17 g, yield 19%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.76 – 7.63 (m, 3H), 3.93 (s, 3H).

Methyl 3-nitrobenzoate (**21b**). Yellowish oil (0.65 g, yield 72%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 3.99 (s, 3H).

1,3-Dichloro-4-nitrobenzene (23)

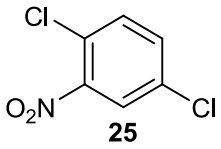


23

Treatment of 1,3-dichlorobenzene (**22**) (0.73 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded compound **23** (0.90 g, yield 94%) as light yellow solid, m.p. 30-31°C (Lit.[5] m.p. 31.5°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 2.2 Hz, 1H), 7.42 (dd, J = 8.7, 2.2 Hz, 1H).

1,4-Dichloro-2-nitrobenzene (25)

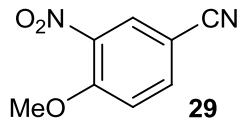


25

Treatment of 1,4-dichlorobenzene (**24**) (0.73 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded compound **25** (0.91 g, yield 95%) as light yellow solid, m.p. 54-55°C (Lit.[6] m.p. 54-57°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (t, J = 1.4 Hz, 1H), 7.53 (d, J = 1.4 Hz, 2H).

4-Methoxy-3-nitrobenzonitrile (29)



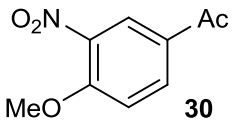
29

Treatment of 4-methoxybenzonitrile (**26**) (0.66 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded compound **29** (0.88 g, yield 99%) as light yellow solid, m.p. 149-150°C (Lit.[4] m.p. 150-151°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 2.5 Hz, 1H), 7.86 (dd, J = 8.8, 2.5 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 4.07 (s, 3H).

[5] R. J. Galbreath, R. K. Ingham, *J. Org. Chem.* **1958**, *23*, 1804–1806.
[6] S. Ichikawa, T. Seki, T. Ikariya, *Adv. Synth. Catal.* **2014**, *356*, 2643–2652.

4-Methoxy-3-nitroacetophenone (30)

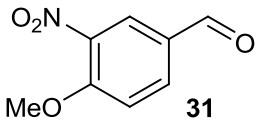


30

Treatment of 4-methoxyacetophenone (**27**) (0.75 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **A** afforded compound **30** (0.98 g, yield 91%) as yellowish solid, m.p. 97-98°C (Lit.[7] m.p. 97-99°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, J = 2.1 Hz, 1H), 8.16 (dd, J = 8.8, 2.1 Hz, 1H), 7.16 (d, J = 8.8 Hz, 1H), 4.04 (s, 3H), 2.60 (s, 3H).

4-Methoxy-3-nitrobenzaldehyde (31)

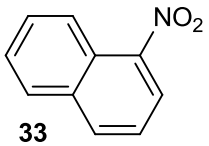


31

Treatment of 4-methoxybenzaldehyde (**28**) (0.68 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** and further purification of the residue by flash-chromatography (silica gel, EtOAc/petroleum ether gradient) afforded compound **31** (0.68 g, yield 75%) as yellowish solid, m.p. 82-84°C (Lit.[8] m.p. 83-84°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.37 (d, J = 2.5 Hz, 1H), 8.11 (dd, J = 8.7, 2.5 Hz, 1H), 7.27 (d, J = 8.7 Hz, 1H), 4.09 (s, 3H).

1-Nitronaphthalene (33)



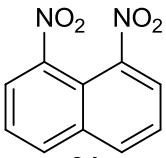
33

Treatment of naphthalene (**32**) (0.32 g, 2.5 mmol) with DNP (0.30 g, 2.75 mmol) followed by work-up **A** afforded compound **33** (0.43 g, yield 99%) as light yellow solid, m.p. 55-56°C (Lit.[9] m.p. 55-57°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.74 (td, J = 8.6, 1.5 Hz, 1H), 7.67 (td, J = 8.6, 1.5 Hz, 1H), 7.56 (t, J = 8.2 Hz, 1H).

[7] G. Aridoss, K. K. Laali, *J. Org. Chem.* **2011**, *76*, 8088–8094.
[8] Y. Zhao, V. Snieckus, *Org. Lett.* **2014**, *16*, 390–393.
[9] J. Liu, J. Li, J. Ren, B. B. Zeng, *Tetrahedron Lett.* **2014**, *55*, 1581–1584.

1,8-Dinitronaphthalene (34)

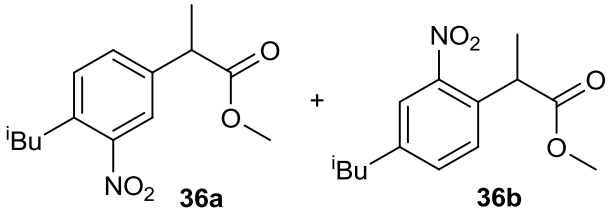


34

Treatment of naphthalene (**32**) (0.64 g, 5.0 mmol) with DNP (0.60 g, 5.5 mmol) followed by work-up **B** and further purification by flash-chromatography (silica gel, ethyl acetate/petroleum ether gradient) afforded compound **34** (0.25 g, yield 23%) as yellowish solid, m.p. 169-170°C (Lit.[10] m.p. 169-171°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.0 Hz, 2H), 7.76 (t, J = 8.0 Hz, 2H).

Methyl-2-(4-isobutyl-3-nitrophenyl)propionate (36a) and methyl-2-(4-isobutyl-2-nitrophenyl)propionate (36b)



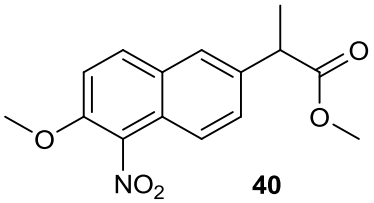
36a **36b**

Treatment of methyl-2-(4-isobutylphenyl)propionate (**35**) (0.55 g, 2.5 mmol) with DNP (0.30 g, 2.75 mmol) followed by work-up **B** and further purification by flash-chromatography (silica gel, ethyl acetate/petroleum ether gradient) afforded the mixture of isomers **36a** and **36b** (0.62 g, yield 93%) in a 2:1 ratio as yellowish oil.

36a ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 2.4 Hz, 1H), 7.47 (dd, J = 8.0, 2.4 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 3.79 (q, J = 7.2 Hz, 1H), 3.70 (s, 3H), 2.77 (d, J = 7.2 Hz, 2H), 2.02 – 1.82 (m, 1H), 1.55 (d, J = 7.2 Hz, 3H), 0.93 (d, J = 7.2 Hz, 6H).

36b ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.39 (s, 2H), 4.30 (q, J = 7.2 Hz, 1H), 3.68 (s, 3H), 2.55 (d, J = 7.2 Hz, 2H), 2.01 – 1.82 (m, 1H), 1.60 (d, J = 7.2 Hz, 3H), 0.94 (d, J = 7.2 Hz, 6H).

Methyl 2-(6-methoxy-5-nitronaphthalen-2-yl)propionate (40)



40

Treatment of methyl-2-(6-methoxynaphthalen-2-yl)propionate (**38**) (0.61 g, 2.5 mmol) with DNP (0.30 g, 2.75 mmol) followed by work-up **B** and further purification by flash-chromatography (silica gel, EtOAc/petroleum ether gradient) afforded compound **40** (0.60 g, yield 83%). Yellowish solid, m.p. 83-84°C.

[10] P. Natarajan, R. Chaudhary, P. Venugopalan, *J. Org. Chem.* **2015**, *80*, 10498–10504.

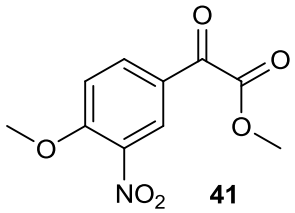
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 9.2 Hz, 1H), 7.75 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.33 (d, J = 9.2 Hz, 1H), 4.02 (s, 3H), 3.89 (q, J = 7.2 Hz, 1H), 3.68 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 174.6, 148.7, 137.5, 135.9, 132.1, 129.2, 128.3, 126.2, 124.9, 121.0, 113.4, 57.1, 52.21, 45.2, 18.4.

HRMS (ESI): *m/z* [M+H] calcd for $C_{15}H_{15}NO_5$: 290.1025. Found: 290.1023.

Anal calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.17; H, 5.42; N, 4.82.

Methyl 2-(4-methoxy-3-nitrophenyl)-2-oxoacetate (41)



41

Treatment of methyl-2-(4-methoxyphenyl)-2-oxoacetate (**39**) (0.48 g, 2.5 mmol) with DNP (0.30 g, 2.75 mmol) followed by work-up **B** and further purification by flash-chromatography (silica gel, EtOAc/petroleum ether gradient) afforded compound **41** (0.47 g, yield 79%). Yellowish wax.

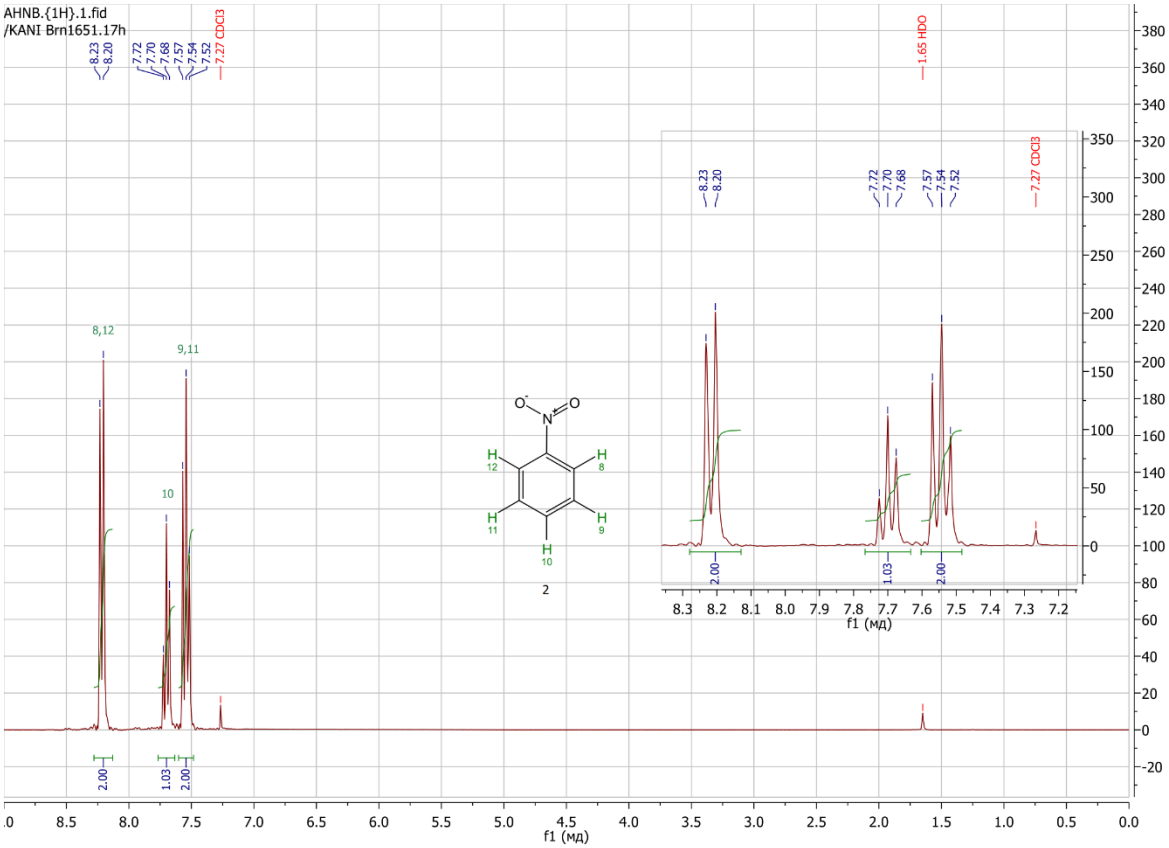
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, J = 2.2 Hz, 1H), 8.32 (dd, J = 8.8, 2.2 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 4.08 (s, 3H), 4.00 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 182.0, 162.7, 157.4, 139.6, 135.9, 128.1, 125.1, 113.6, 57.1, 53.2.

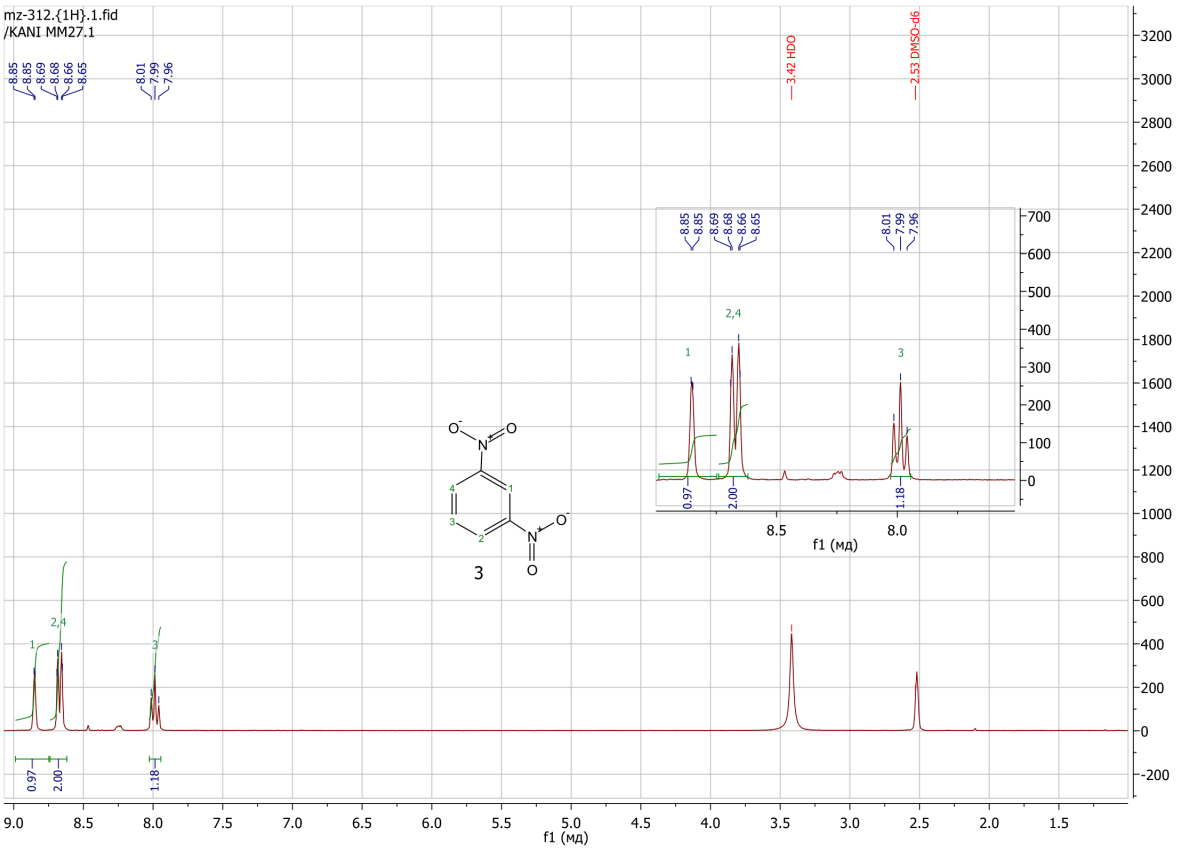
Anal calcd for $C_{10}H_9NO_6$: C, 50.22; H, 3.79; N, 5.86. Found: C, 50.31; H, 3.76; N, 5.82.

4. NMR pictures

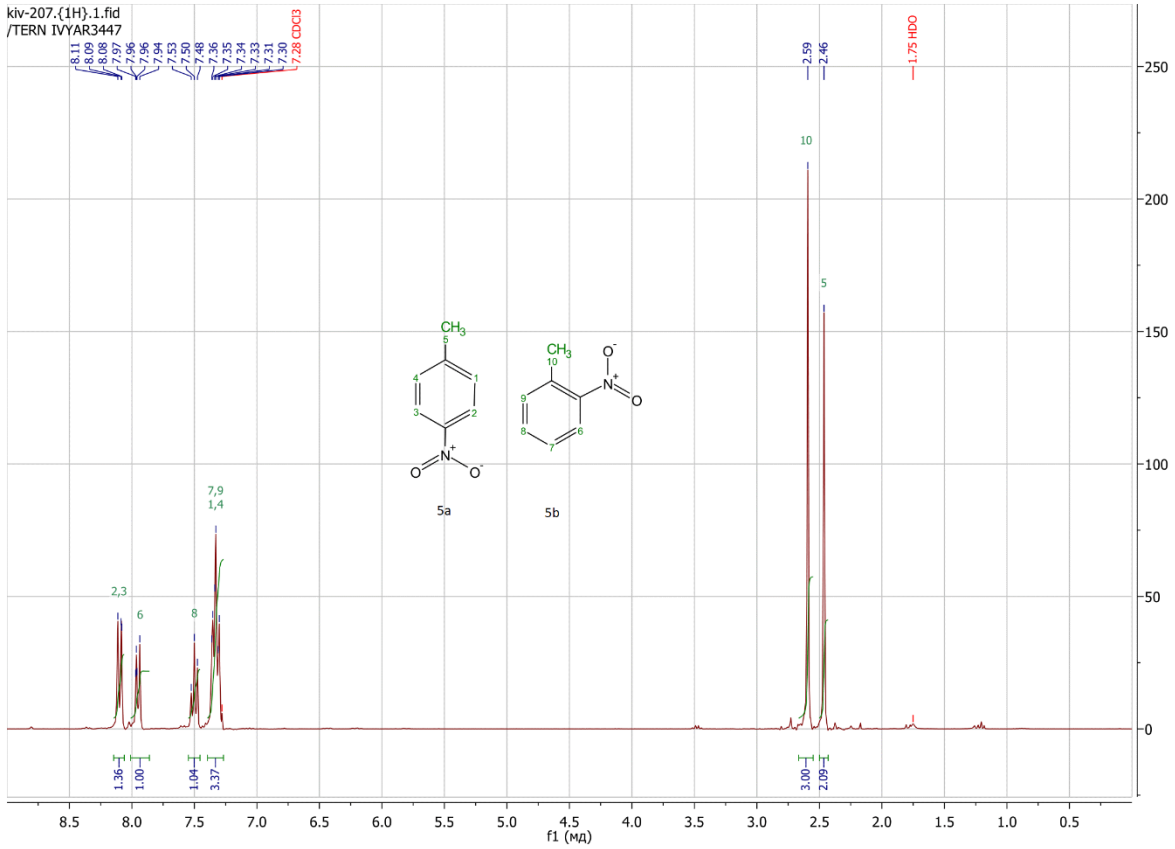
Nitrobenzene (2)



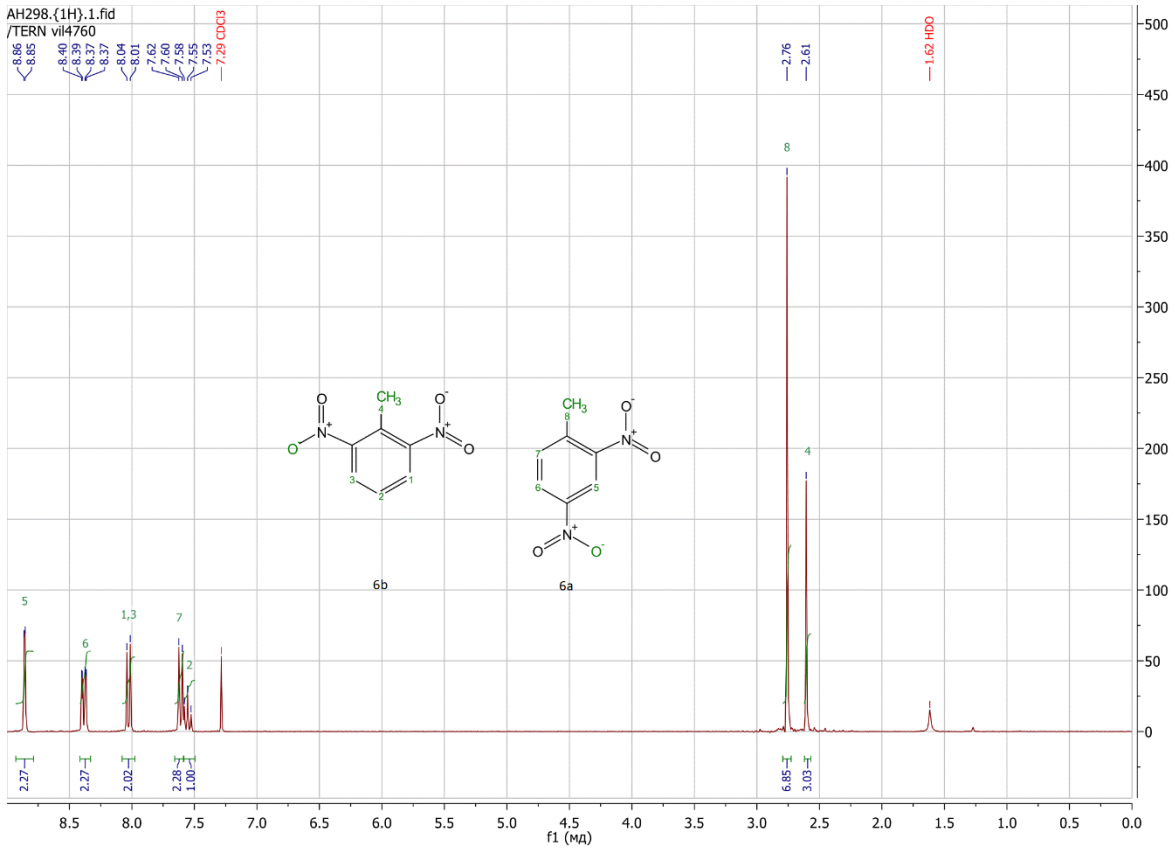
m-Dinitrobenzene (3)



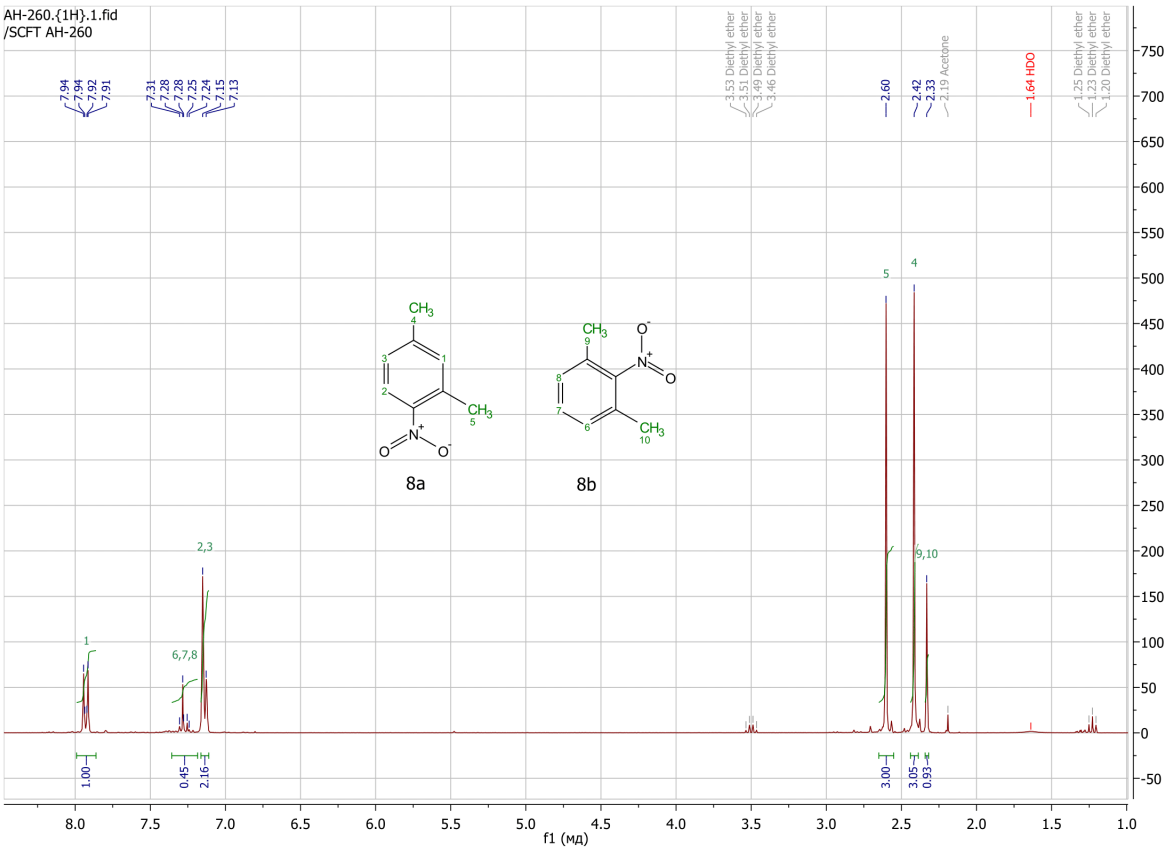
2-Nitrotoluene (5a) and 4-nitrotoluene (5b)



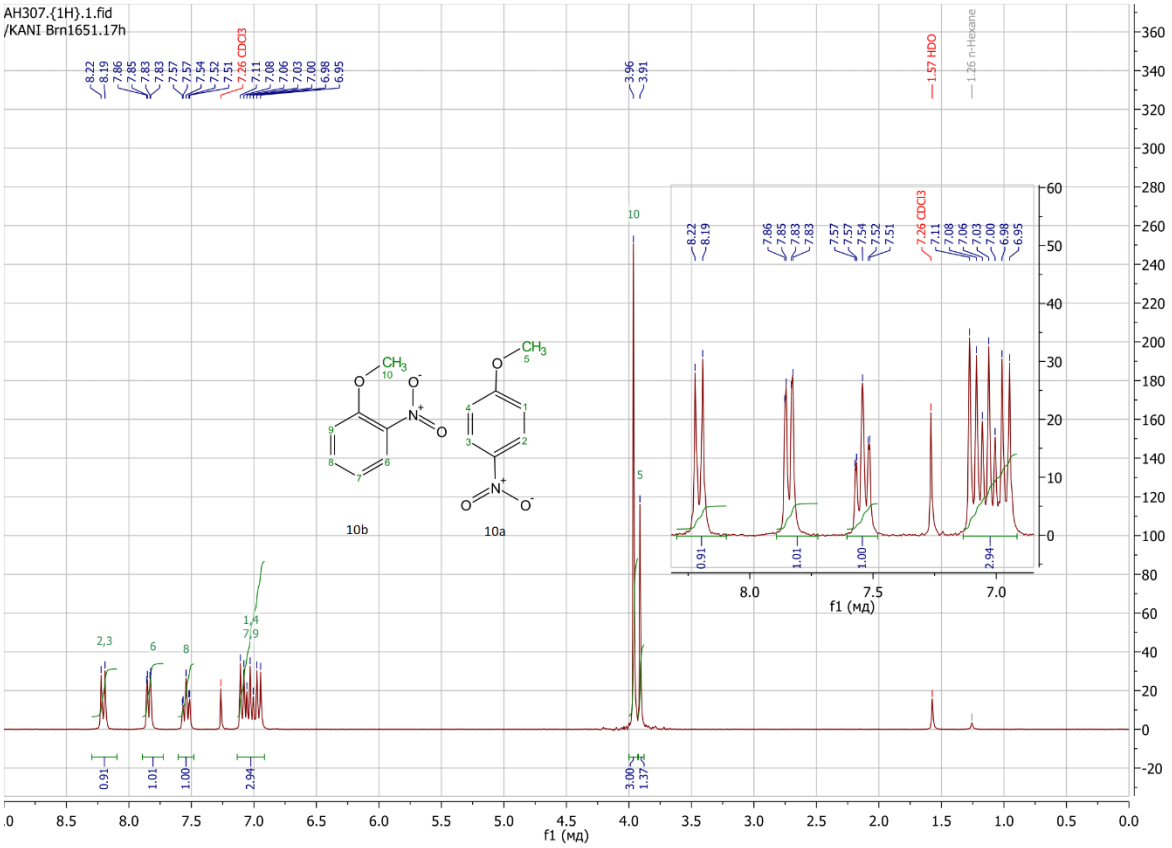
2,4-Dinitrotolune (6a) and 2,6-dinitrotolune (6b)



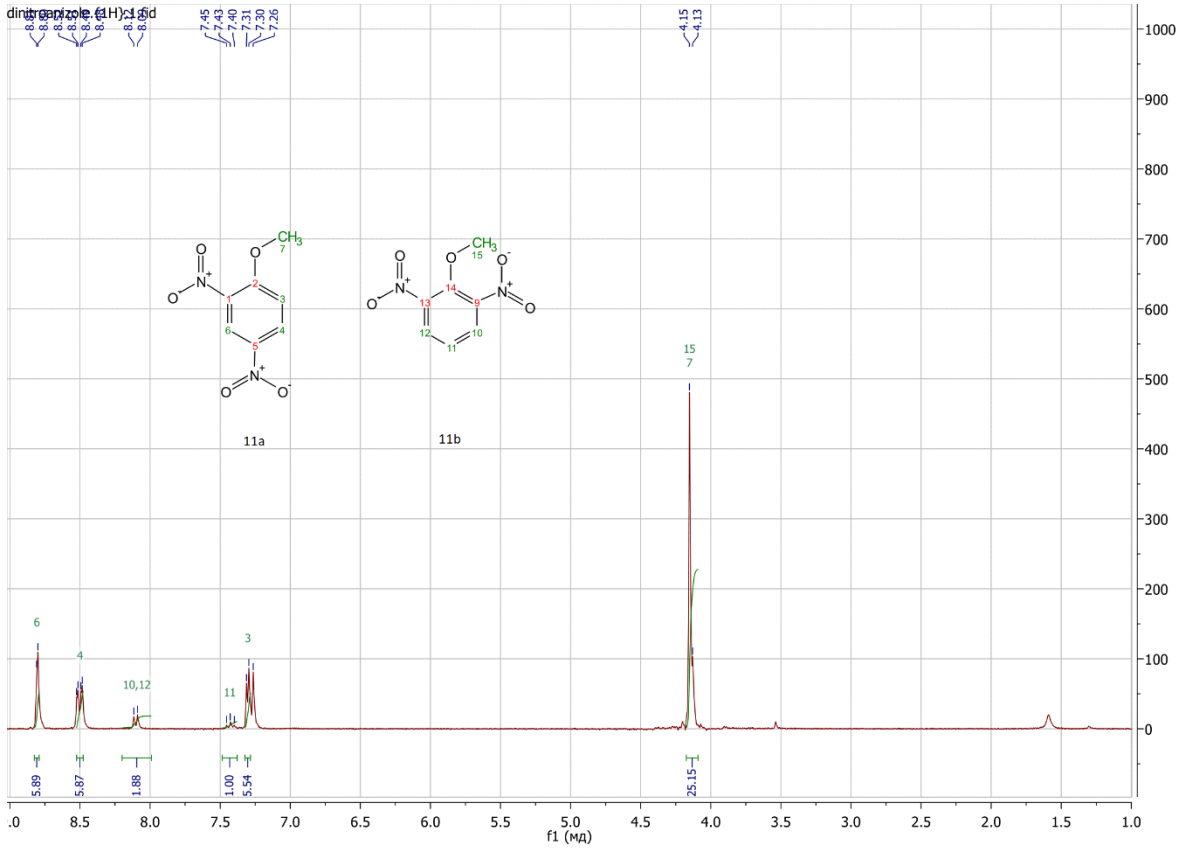
1,3-Dimethyl-4-nitrobenzene (8a) and 1,3-dimethyl-2-nitrobenzene (8b)



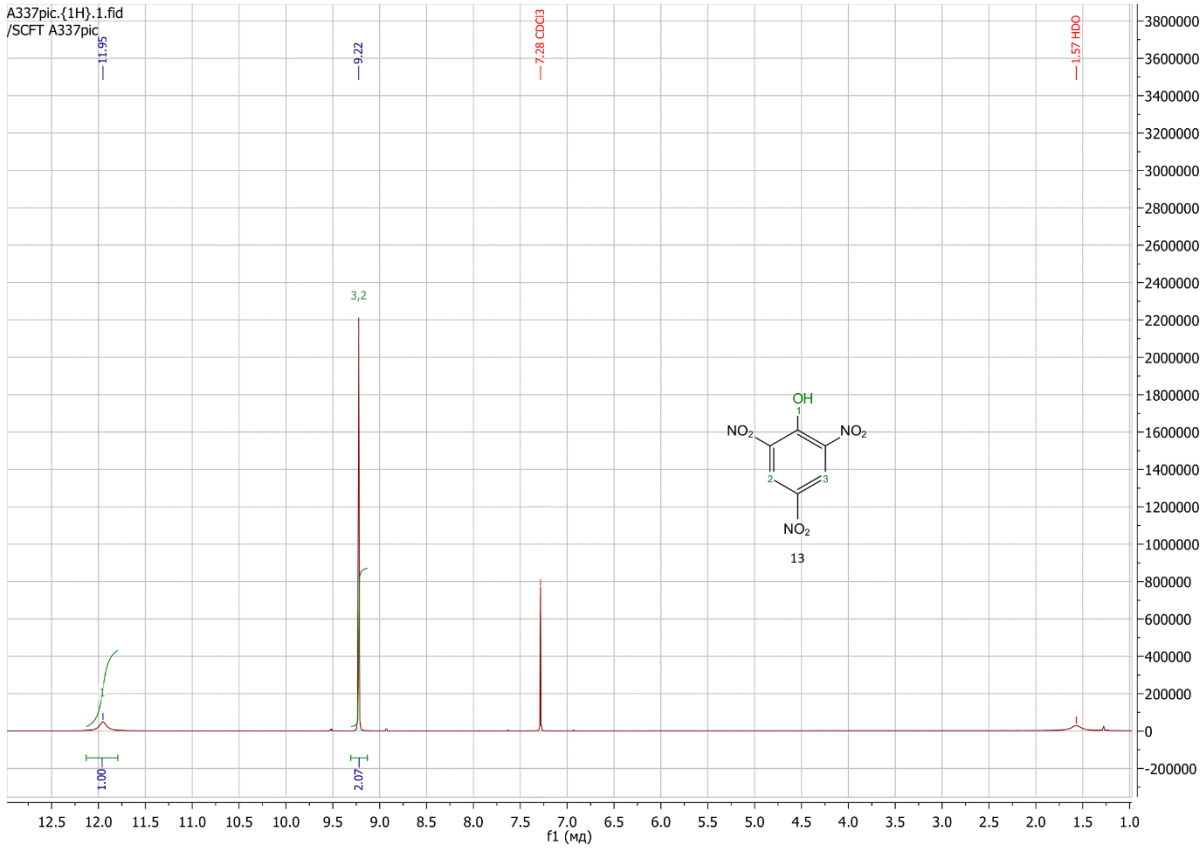
2-Nitroanisole (10a) and 2-nitroanisole (10b)



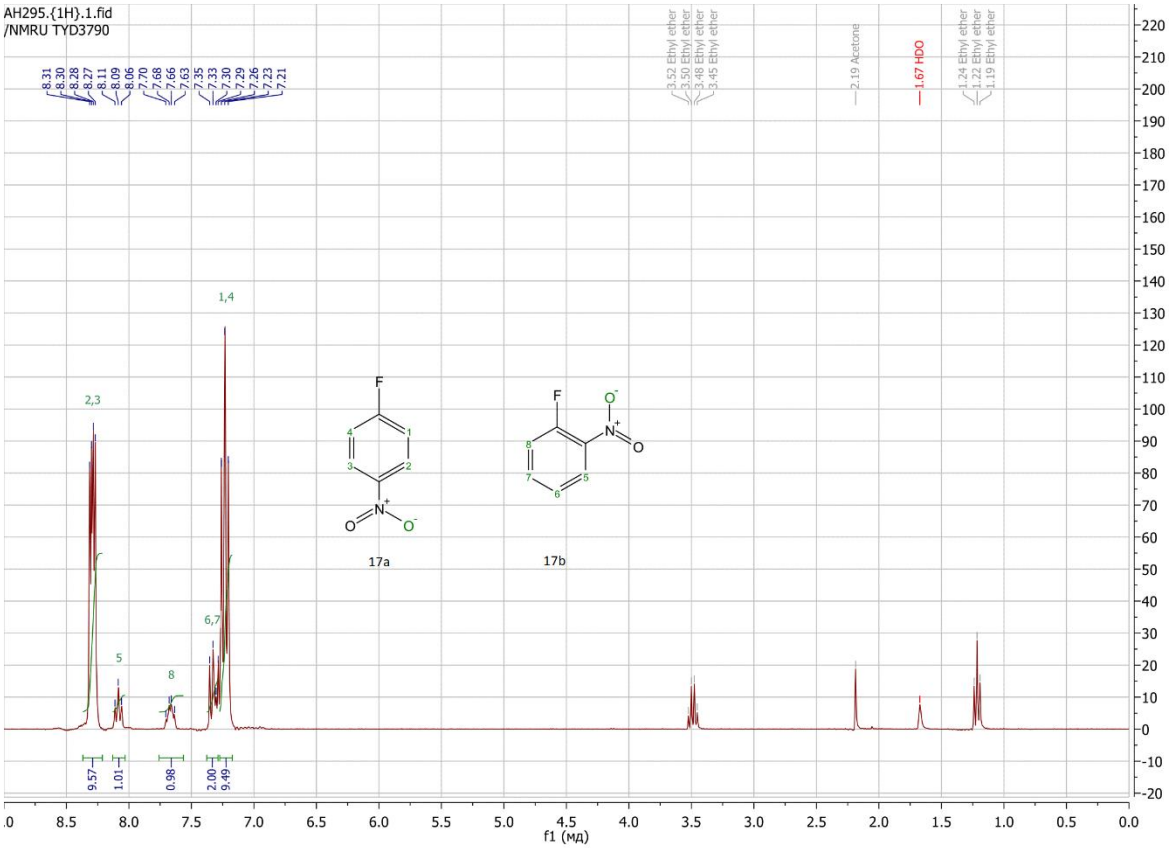
2-Dinitroanisole (11a) and 2-dinitroanisole (11b)



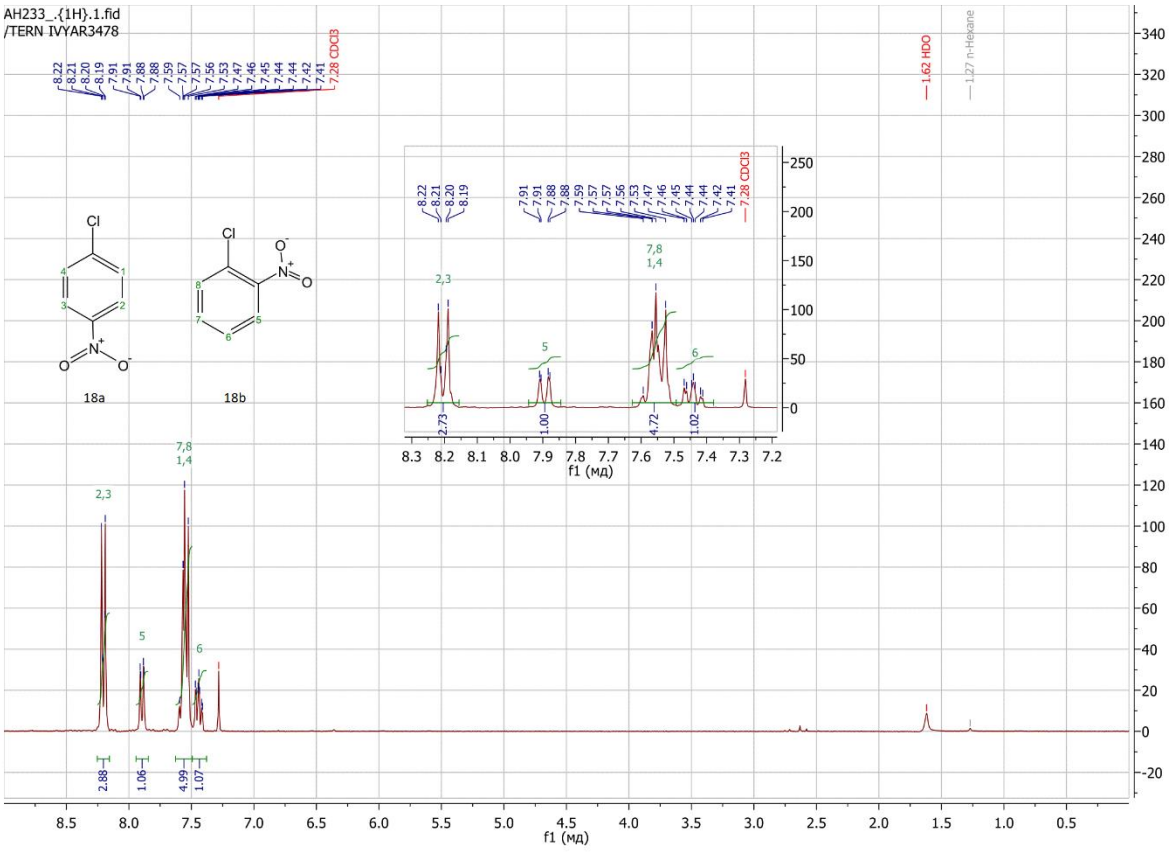
2,4,6-Trinitrophenol (13)



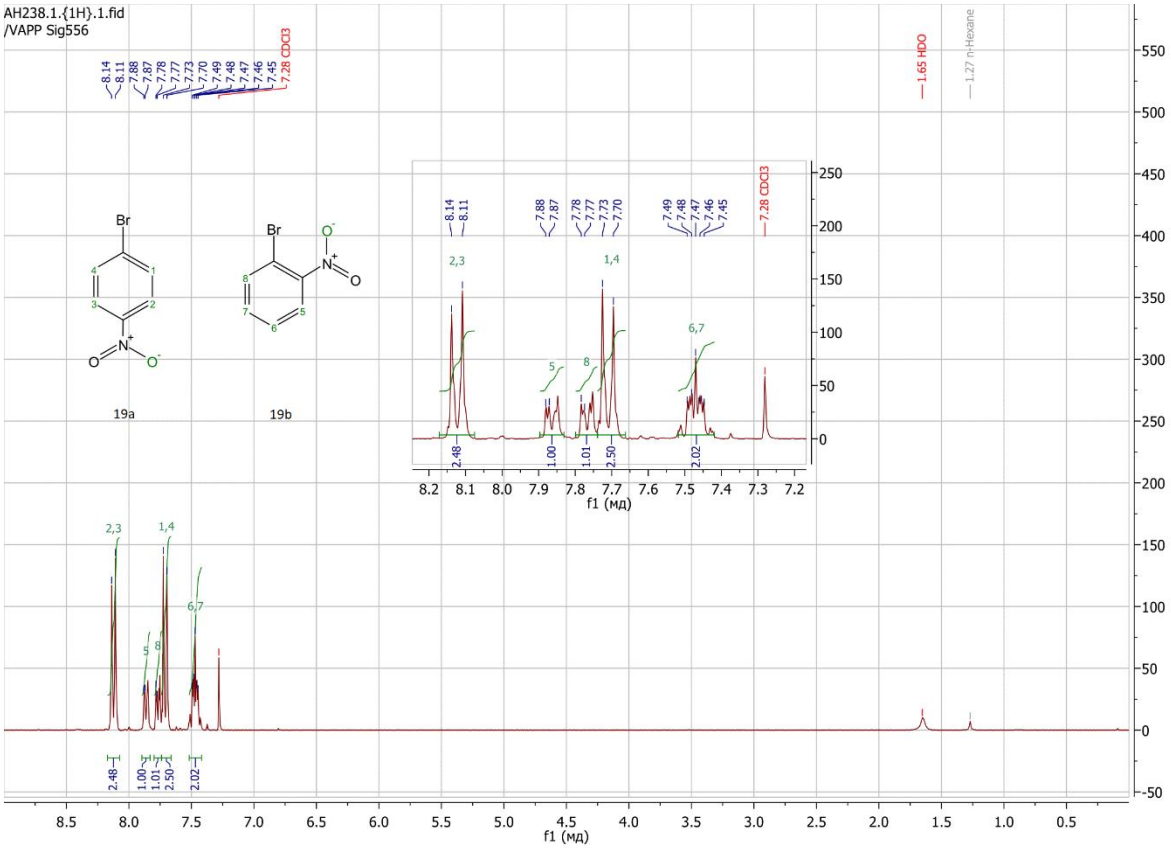
4-Fluoronitrobenzene (17a) and 2-fluoronitrobenzene (17b)



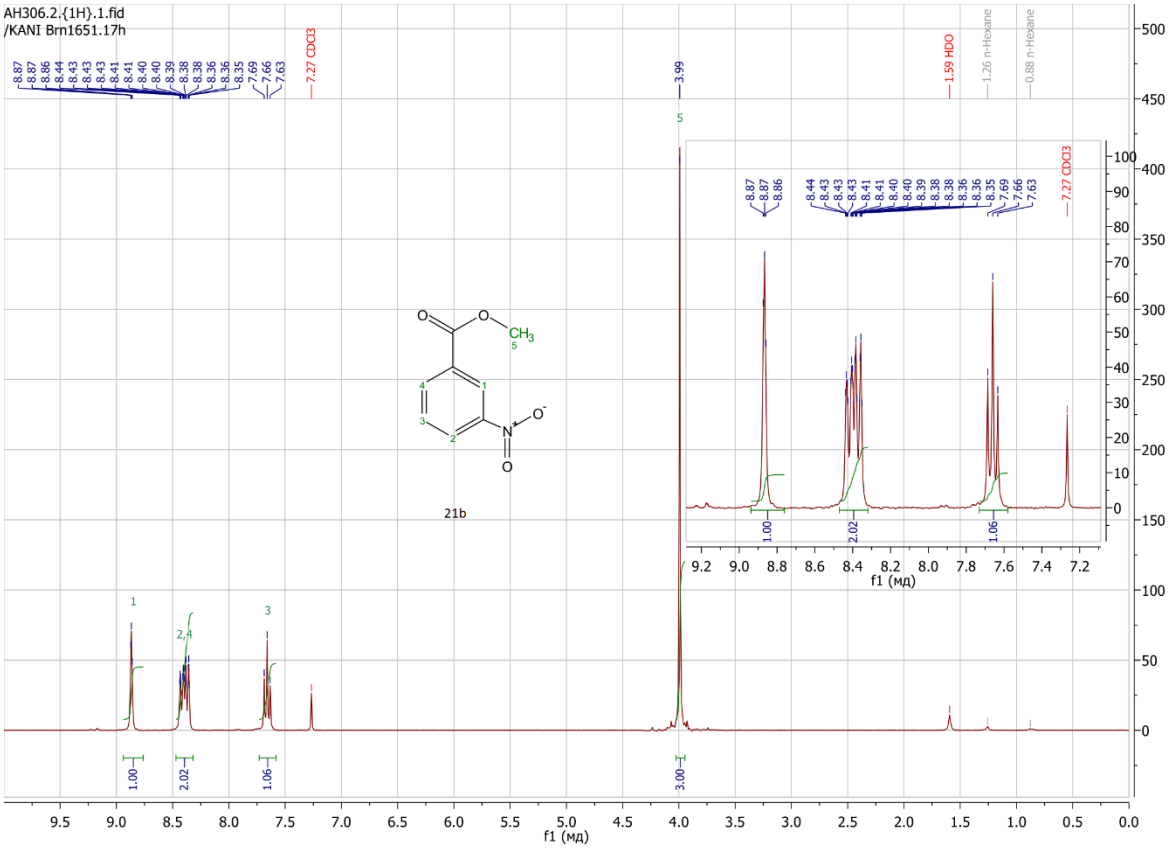
4-Chloronitrobenzene (18a) and 2-chloronitrobenzene (18b)



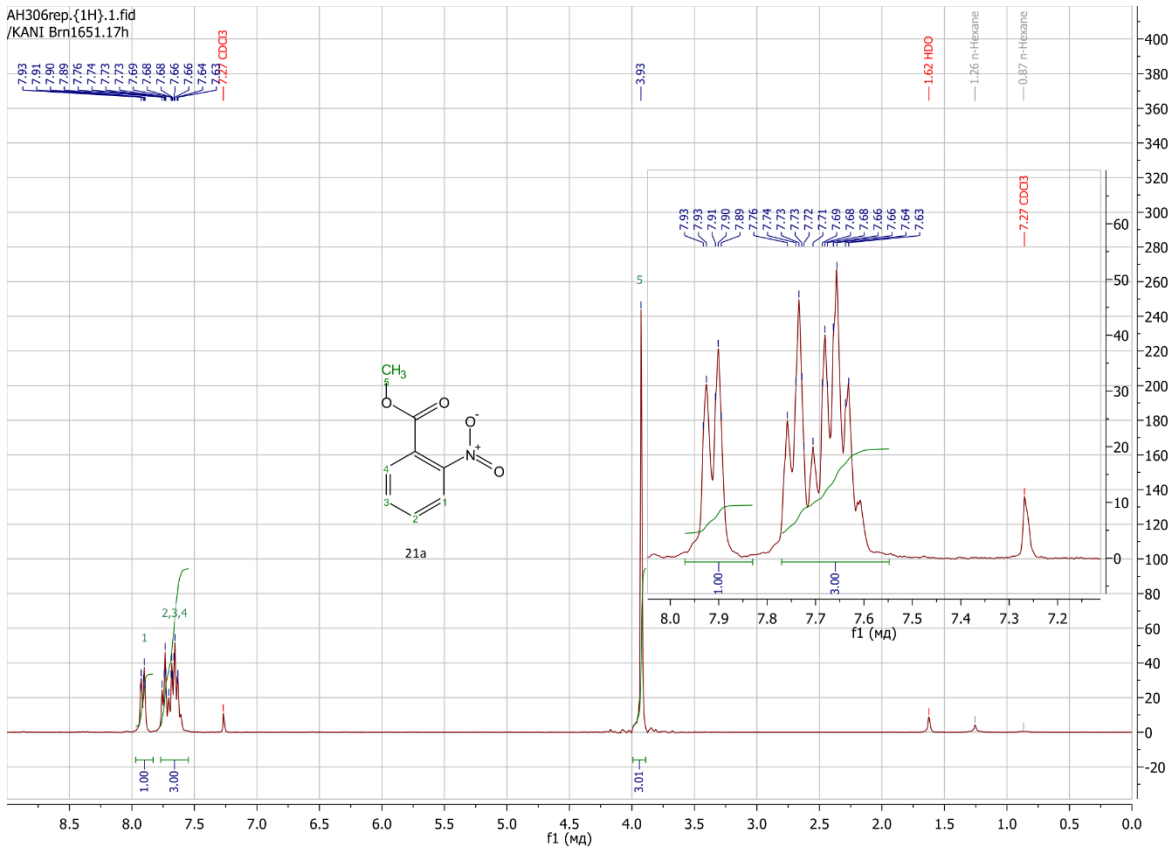
4-Bromonitrobenzene (19a) and 2-bromonitrobenzene (19b)



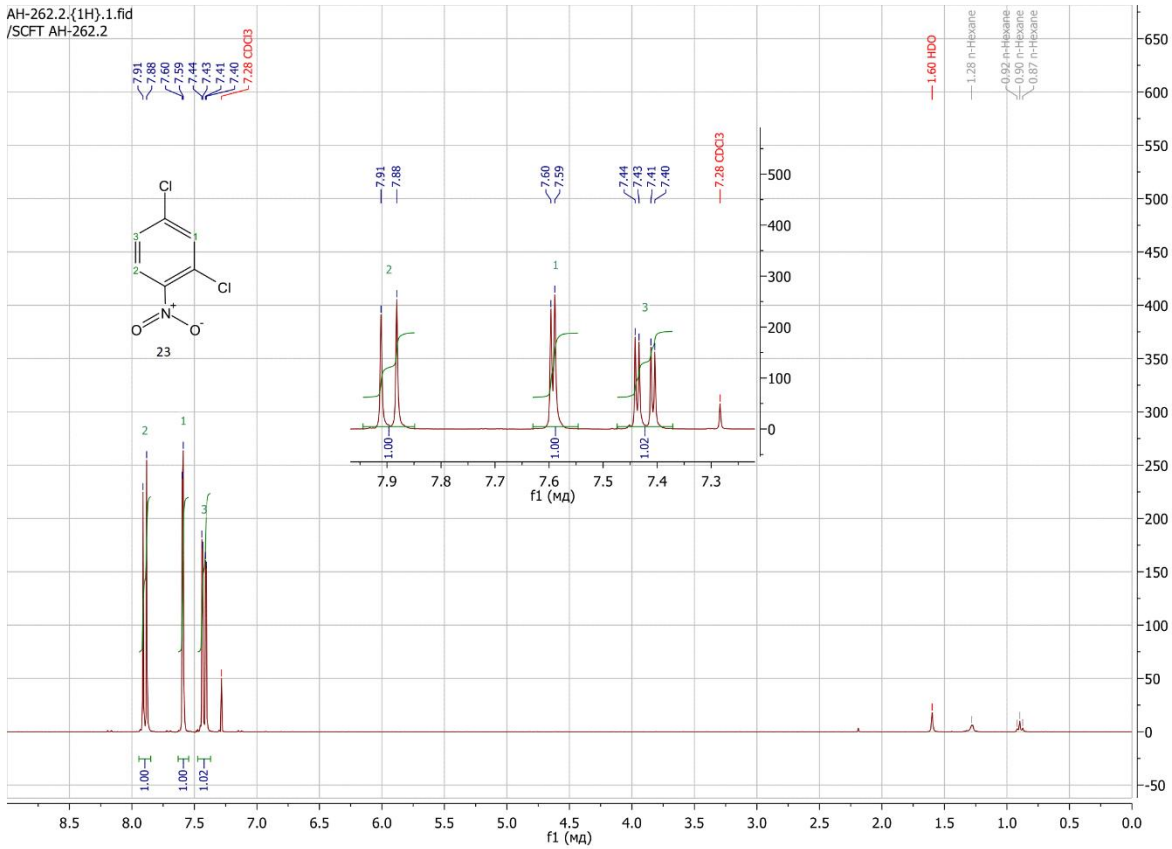
Methyl 2-nitrobenzoate (21a)



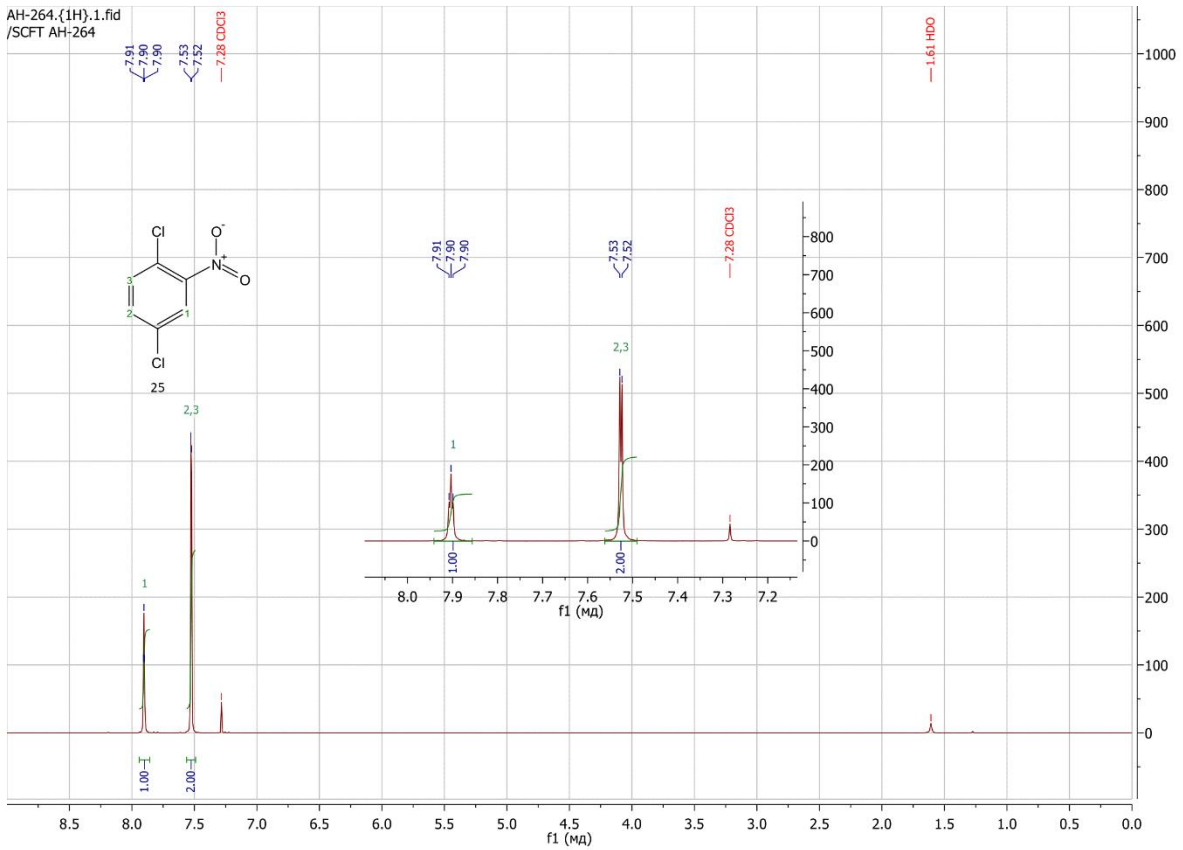
Methyl 3-nitrobenzoate (21b)



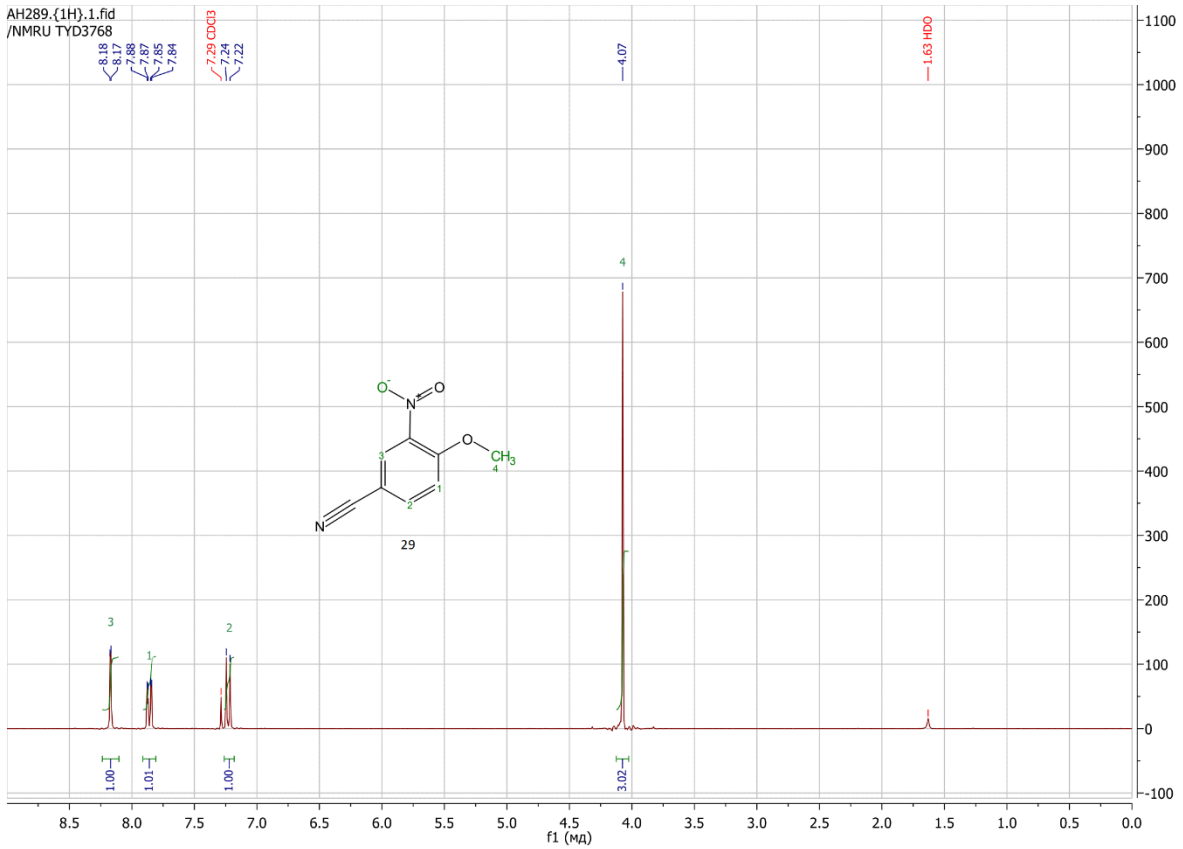
1,3-Dichloro-4-nitrobenzene (23)



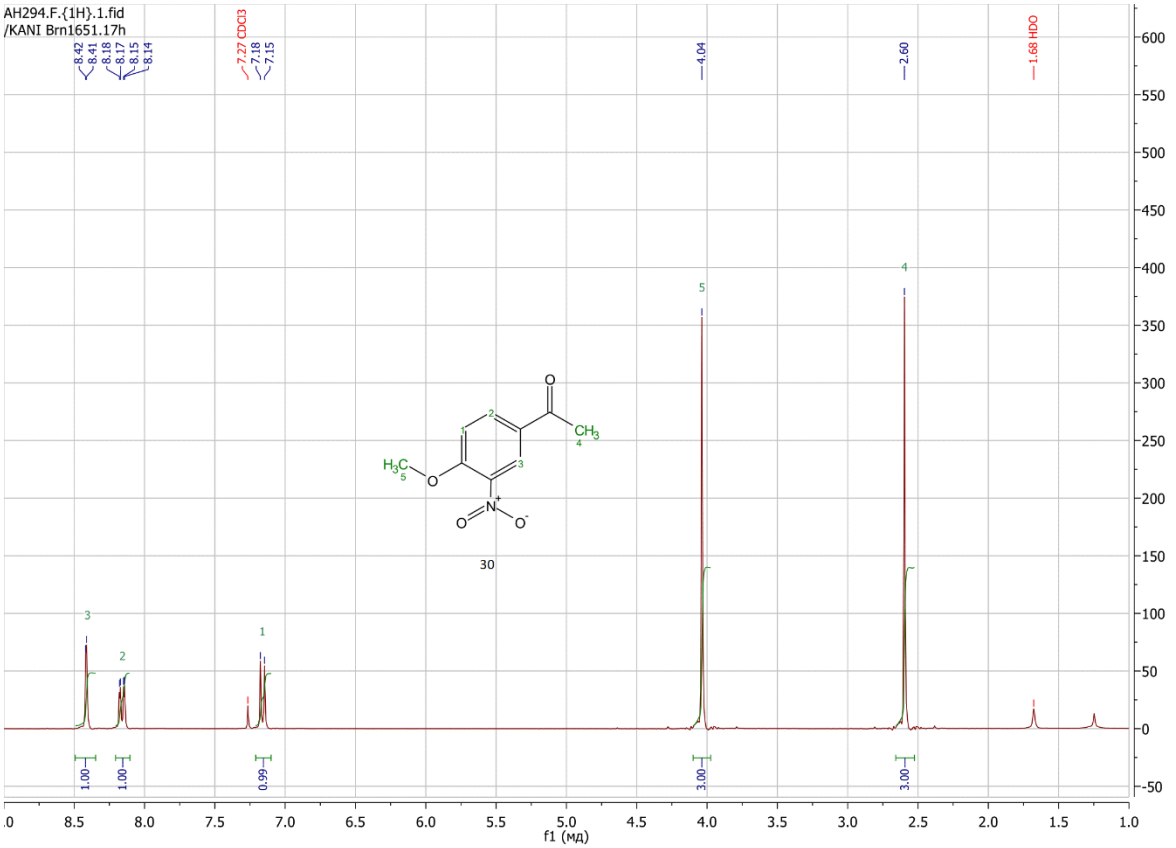
1,4-Dichloro-2-nitrobenzene (25)



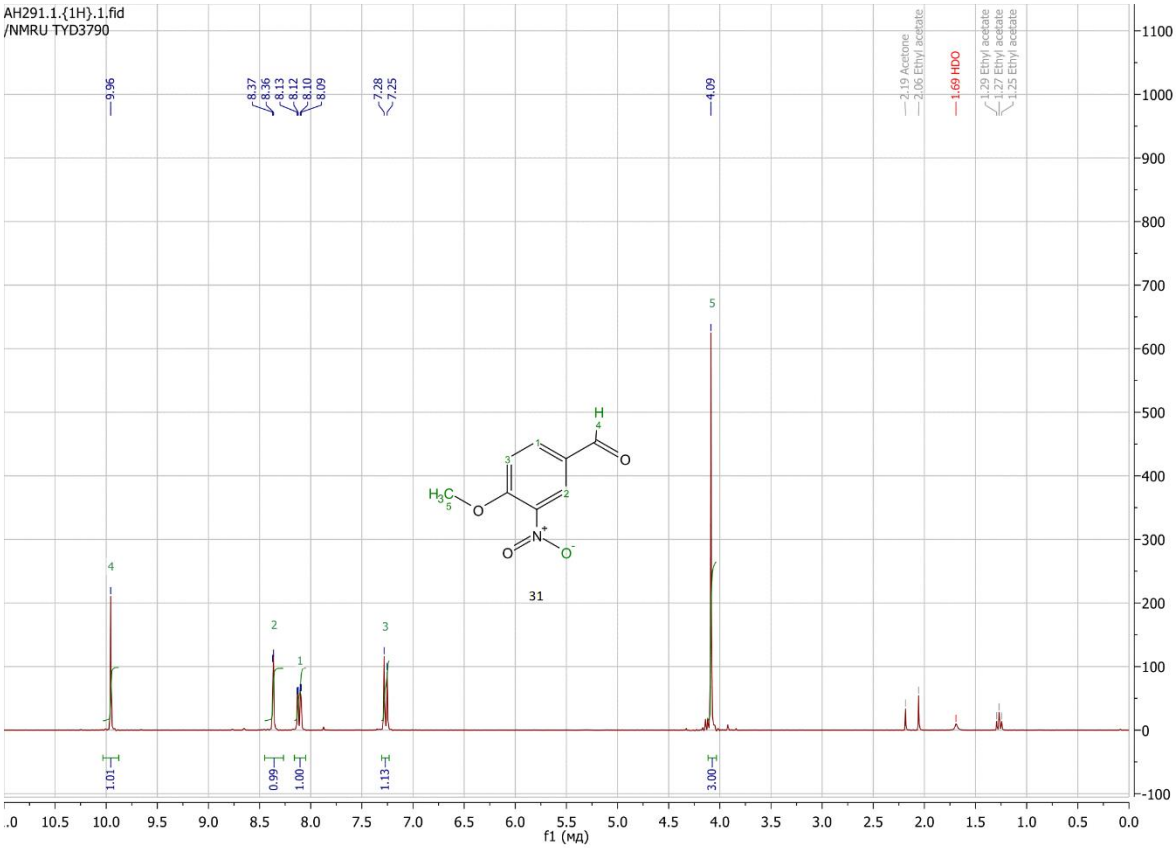
4-Methoxy-3-nitrobenzonitrile (29)



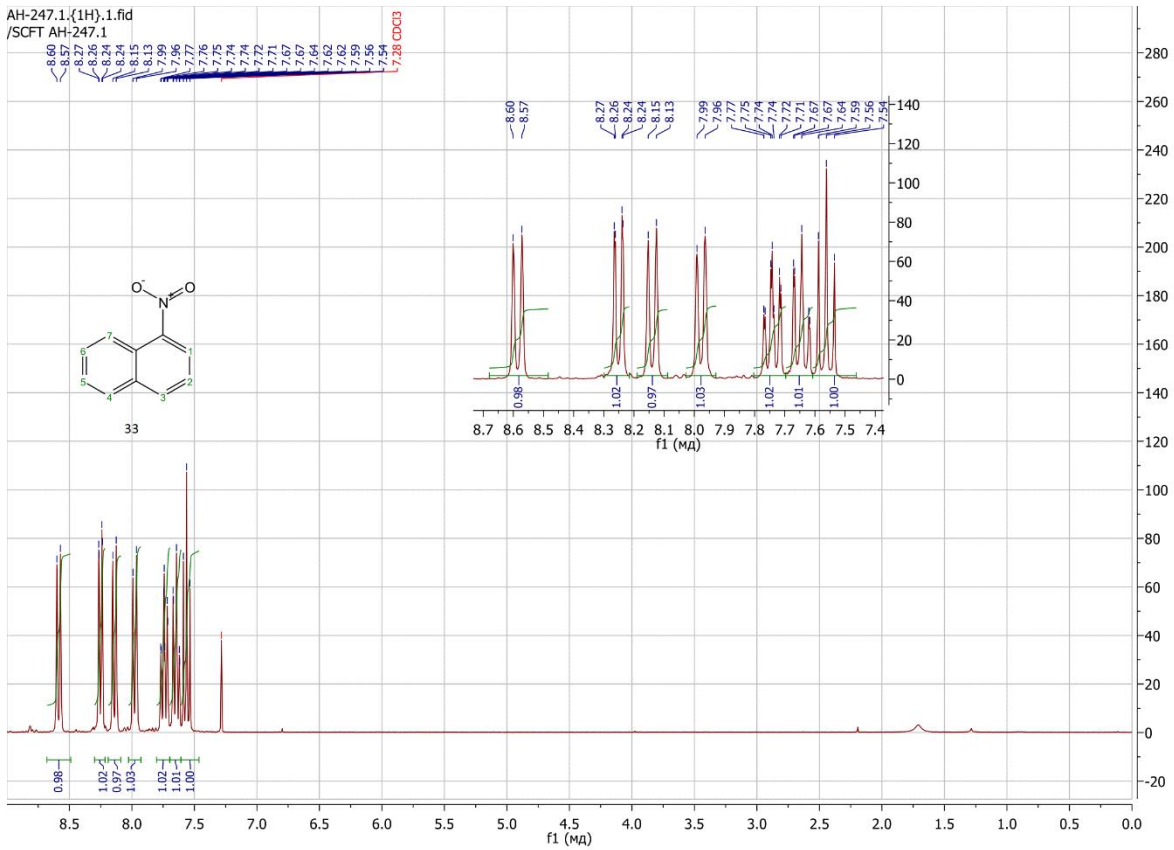
4-Methoxy-3-nitroacetophenone (30)



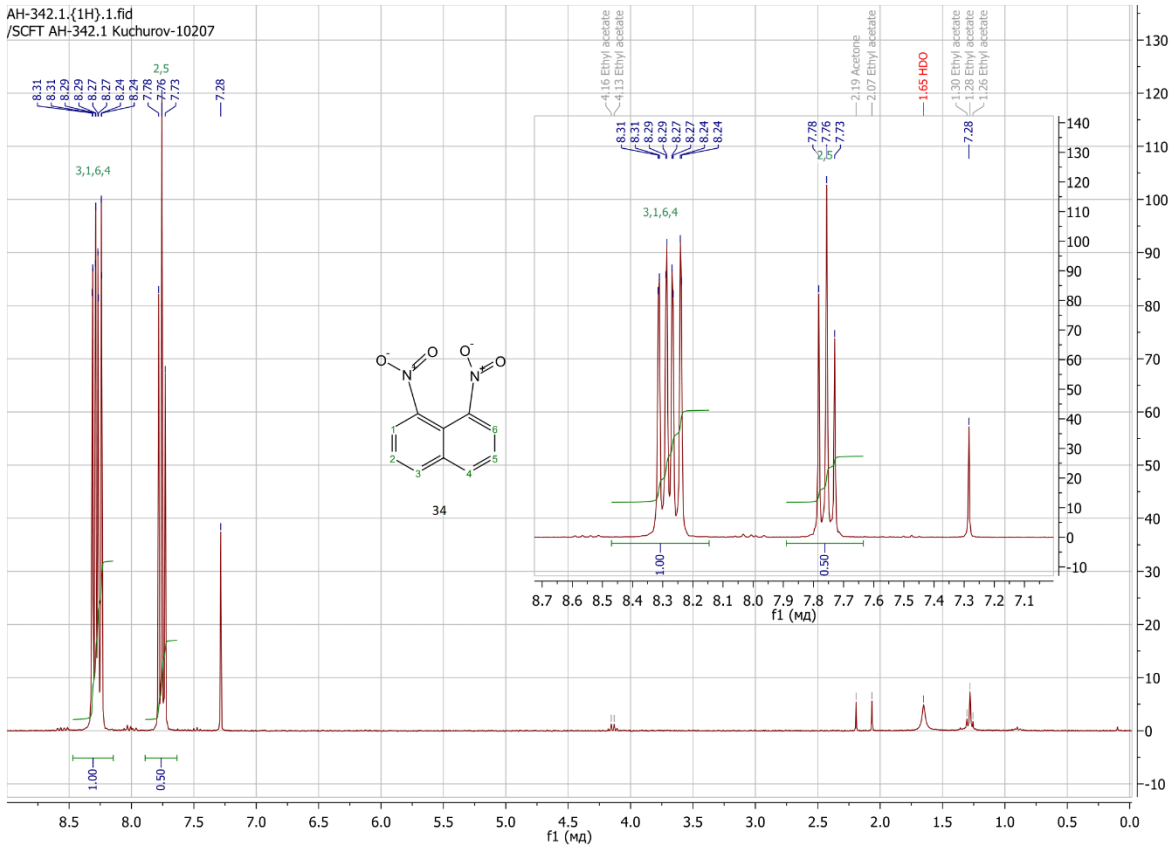
4-Methoxy-3-nitrobenzaldehyde (31)



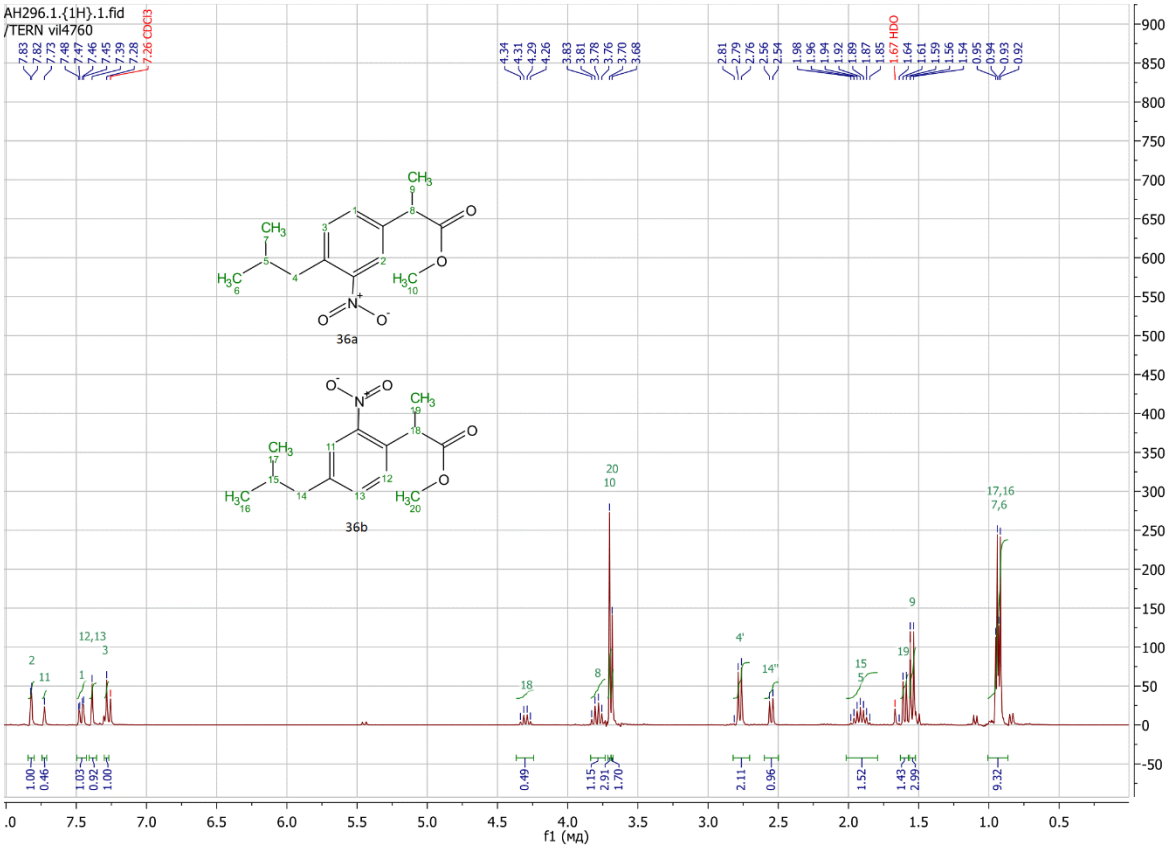
1-Nitronaphthalene (33)



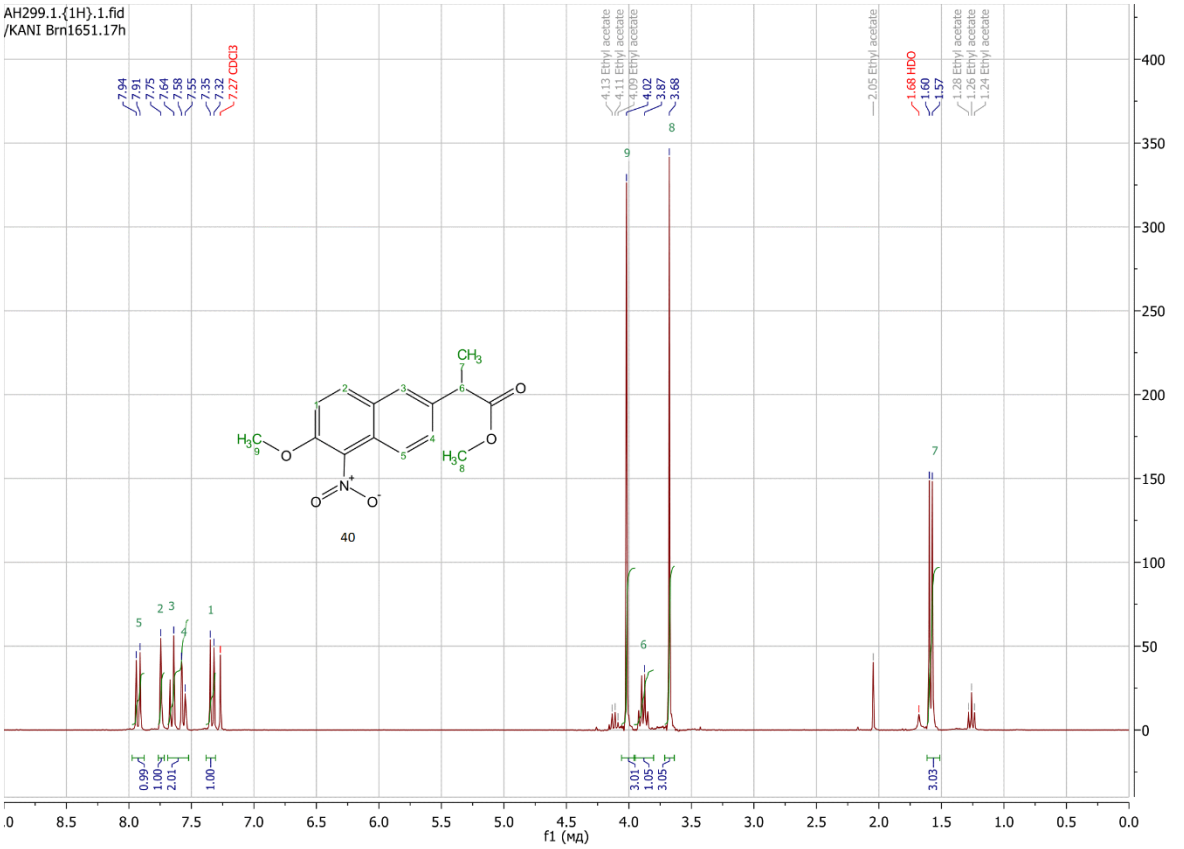
1,8-Dinitronaphthalene (34)

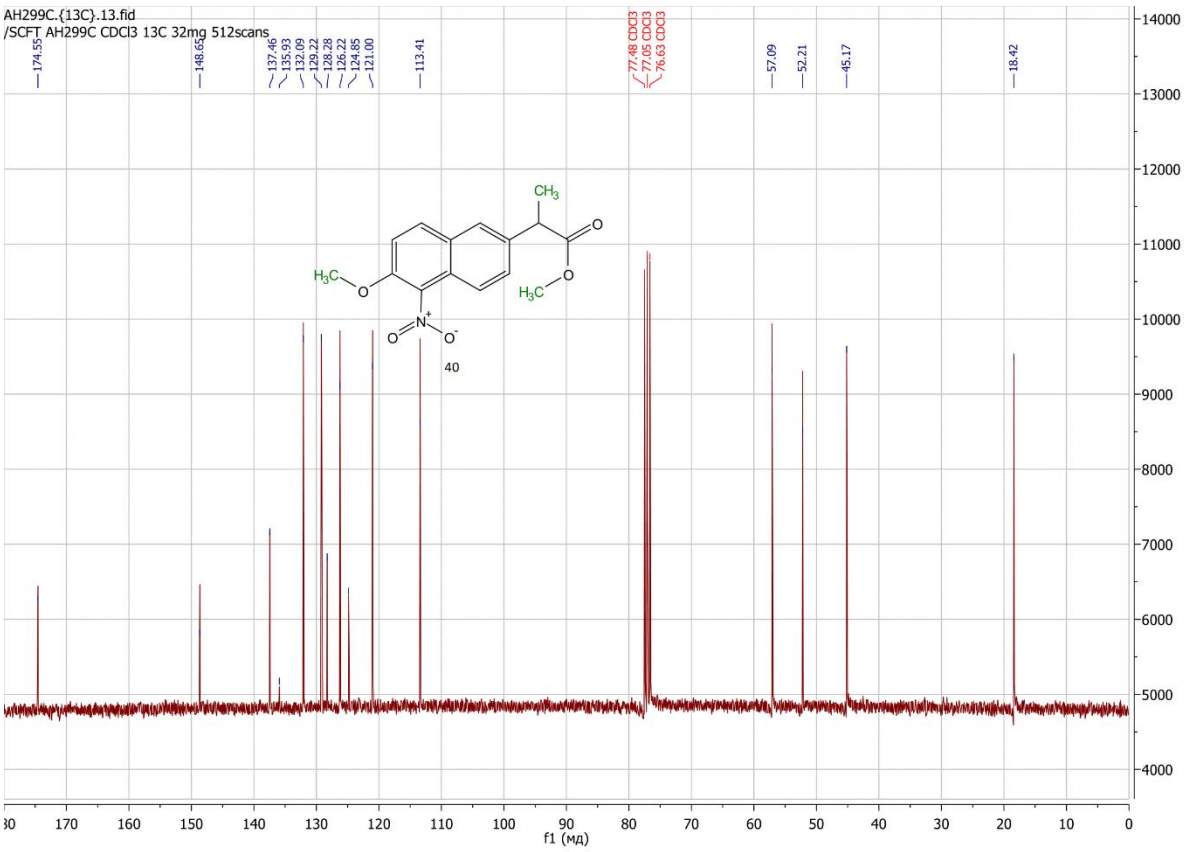


Methyl-2-(4-isobutyl-3-nitrophenyl)propionate (36a) and methyl-2-(4-isobutyl-2-nitrophenyl)propionate (36b)



Methyl-2-(6-methoxy-5-nitronaphthalen-2-yl)propionate (40)





Methyl-2-(4-methoxy-3-nitrophenyl)-2-oxoacetate (41)