

Supporting Information

C–H amination of enolizable and nonenolizable ketones

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2. General information

NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers at room temperature (25 °C) unless otherwise stated. ¹H-NMR chemical shifts are given in ppm relative to Me₄Si with the solvent resonance used as the internal standard (CDCl₃ δ = 7.26 ppm). ¹³C-NMR (60, 101 or 150 MHz) chemical shifts are given in ppm relative to Me₄Si with the solvent resonance used as the internal standard (CDCl₃ = 77.16 ppm). IR spectra were recorded using an ATR sampler (Thermo Nicolet - Avatar 370 5T-IR) and are reported in wave numbers (cm⁻¹). Melting points (m.p.) were measured in open capillary tubes and are uncorrected. All reactions involving air sensitive compounds were carried out under anhydrous and inert atmosphere (N₂ or argon) by means of an inert gas/vacuum double manifold line and standard Schlenk techniques. High resolution mass spectra were recorded with Bruker Micro TOF LC.

3. Experimental procedures

3.1 Preparation and characterization of cyanohydrins **2**.

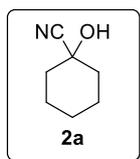
Method a): Sodium bisulfite (NaHSO_3 , 6 mmol) was dissolved in 8–15 mL of distilled water with continuous stirring until fully dissolved. The corresponding ketone (6 mmol) was then gradually added to the solution. The mixture was stirred thoroughly at 45°C for 10 minutes before being cooled to 10°C. Potassium cyanide (KCN, 7 mmol) was slowly introduced to the cooled reaction mixture with vigorous stirring. Once all reagents were added, the reaction was allowed to stir at room temperature overnight. The crude product was extracted with diethyl ether (Et_2O , 3×5 mL), dried over magnesium sulfate (MgSO_4), and concentrated under reduced pressure to yield the final product. According to this procedure cyanohydrines **2a** (87%), **2b** (74%), **2c** (81%), **2g** (89%), **2h** (91%) were obtained. Reference: CHOI, Dae Kyu et al. (2022), Korean Patent No WO2022025636 A1.

Method b): CO_2 was bubbled through ethanol (10 mL) at 35 °C for 5–10 minutes. Potassium cyanide (KCN, 5 mmol) was then gradually added to the stirring solution while maintaining CO_2 bubbling for an additional 15 minutes. The corresponding ketone (4 mmol) was introduced, and the reaction mixture was stirred at 35°C under a continuous CO_2 atmosphere for 18 hours. Upon completion of the reaction, 1M HCl (3 mL) was added, and the product was extracted with dichloromethane (3×5 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to yield the final product. According to this procedure cyanohydrin **2d** (72%), was obtained. Reference: T. Roy, M. Kim, Y. Yang, S. Kim, G. Kang, X. Ren, *ACS Catal.* 2019, **9**, 6006–6011.

Method c): Trimethylsilyl cyanide (3 mmol) and boron trifluoride diethyl etherate (2 mmol) were added to a solution of corresponding ketone (2 mmol) in dichloromethane (5 mL). The mixture was stirred at room temperature for 2 h and the solvent was evaporated to dryness. The residue, thus obtained, was dissolved in ethyl acetate (10 mL), washed with brine (2×5 mL) and dried (Na_2SO_4). After filtration and evaporation of the solvent, the residue was filtered through the silica using DCM:EtOAc (2:1 v/v) as the eluent. According to this procedure cyanohydrins **2a - 2h and 8** were obtained in yields **2a** (92%), **2b** (91%), **2c** (87%), **2d** (84%), **2e** (91%), **2f** (94%), **2g** (93%), **2h** (89%). Reference: de Castro, Sonia; et al. *Chem. Eur. J.* 2008, **14**, 9620-9632.

Method d): To a 4 mL vial were sequentially added ketone (5.0 mmol), anhydrous MeCN (1.0 mL), and phosphorane (0.1 mol%). Then the vial was put into a water bath at r.t., and stirred for 5 min before the addition of TMSCN (5.5 mmol, 695 μL). After TLC analysis indicated the full consumption of ketone, the mixture underwent column chromatography using petroleum ether/diethyl ether (from 10:0 to 10:1, v/v) as the eluent. According to this procedure cyanohydrine **2a** was obtained in high yield and can be used for next step. Reference: W-B. Wu, X-P. Zeng, and J. Zhou, *J. Org. Chem.* 2020, **85**, 14342–14350.

3.1.1 Compound 2a

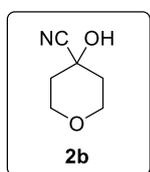


$^1\text{H NMR}$ (600 MHz, CDCl_3): δ/ppm = 1.23-1.32 (m, 1H), 1.50-1.68 (m, 5H), 1.74-1.83 (m, 2H), 2.04-2.10 (m, 2H), 3.22 (bs, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ/ppm = 22.6 (2 CH_2), 24.5 (2 CH_2), 38.0 (CH_2), 66.0 (C), 122.01 (CN).

Compound **2a** was prepared in one step from cyclohexanone according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2a** was obtained by eluting the reaction mixture through a pad of silica gel with hexane : Et_2O 2:1 and used in the next step without further purification.

3.1.2 Compound 2b

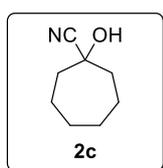


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ/ppm = 1.85-1.92 (m, 2H), 2.10-2.16 (m, 2H), 3.32 (bs, 1H), 3.65-3.71 (m, 2H), 3.92-3.98 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ/ppm = 37.7 (2 CH_2), 63.8 (2 CH_2), 66.6 (C), 121.2 (CN).

Compound **2b** was prepared in one step from tetrahydropyran-4-one according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2b** was obtained by eluting the reaction mixture through a pad of silica gel with hexane : Et_2O 1:1 and used in the next step without further purification.

3.1.3 Compound 2c

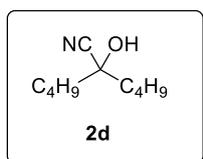


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ/ppm = 1.58-1.76 (m, 7H), 1.89-1.96 (m, 2H), 2.13-2.18 (m, 2H), 2.48-2.51 (m, 1H), 2.92 (bs, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ/ppm = 21.6 (2 CH_2), 27.8 (2 CH_2), 41.1 (2 CH_2), 72.5 (C), 123.05 (CN).

Compound **2c** was prepared in one steps from cycloheptanone according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2c** was obtained by eluting the reaction mixture through a pad of silica gel with hexane : Et_2O 1:1 and used in the next step without further purification.

3.1.4 Compound 2d



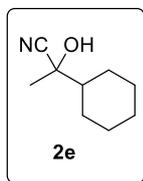
$^1\text{H NMR}$ (600 MHz, CDCl_3): δ/ppm = 0.94 (t, J = 8 Hz, 6H), 1.34-1.43 (m, 4H), 1.47-1.59 (m, 4H), 1.68-1.81 (m, 4H), 2.63 (bs, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ/ppm = 14.0 (2 CH_3), 22.6 (2 CH_2), 26.1 (2 CH_2), 40.0 (2 CH_2), 72.4 (C) 121.6 (CN).

Compound **2d** was prepared in one step from nonan-5-one according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product

2d was purified by silica gel column chromatography eluting with pure CHCl_3 and was isolated in a 73% yield.

3.1.5 Compound 2e

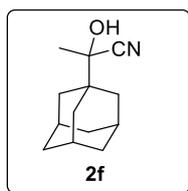


^1H NMR (600 MHz, CDCl_3): δ/ppm = 1.10-1.30 (m, 5H), 1.51-1.59 (m, 1H), 1.55 (s, 3H), 1.67-1.73 (m, 1H), 1.82-1.88 (m, 3H), 1.95-2.01 (m, 1H), 2.87 (bs, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 25.2 (CH_3), 25.8 (CH_2), 25.9 (CH_2), 26.0 (CH_2), 27.1 (CH_2), 27.3 (CH_2), 47.2 (CH), 72.2 (C) 121.8 (CN).

Compound **2e** was prepared in one step from cyclohexyl methyl ketone according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2e** was purified by silica gel column chromatography eluting with hexane : Et_2O 1:1 and isolated in a 78% yield.

3.1.6 Compound 2f

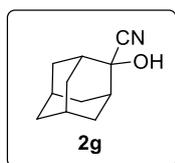


^1H NMR (400 MHz, CDCl_3): δ/ppm = 1.53 (s, 3H), 1.65-1.75 (m, 12H), 2.08-2.09 (m, 3H), 2.26 (bs, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 21.8 (CH_3), 28.2 (3 CH_2) 36.1 (3CH), 36.7 (3 CH_2), 39.0 (C), 75.81 (C), 121.6 (CN).

Compound **2f** was prepared in one step from 1-acetyladamantane according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2f** was purified by silica gel column chromatography eluting with hexane : Et_2O 1:1 and isolated in a 86% yield.

3.1.7 Compound 2g

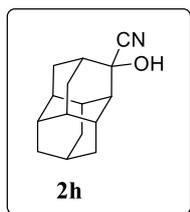


^1H NMR (400 MHz, CDCl_3): δ/ppm = 1.58-1.63 (m, 2H), 1.71-1.73 (m, 2H), 1.78-1.81- (m, 1H), 1.88-1.93 (m, 3H), 2.06-2.16 (m, 6H), 3.08 (bs, 1H)

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 26.3 (CH), 26.4 (CH), 30.8 (2 CH_2), 35.0 (2CH), 37.0 (2 CH_2), 37.1 (CH_2), 74.1 (C), 122.5 (CN).

Compound **2g** was prepared in one step from adamantan-2-one according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2g** was purified by silica gel column chromatography eluting with hexane : Et_2O 1:1 and isolated in a 83% yield.

3.1.8 Compound 2h



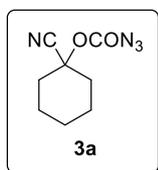
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.55-1.87 (m, 12H), 2.00-2.14 (m, 6H), 2.43-2.63 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 25.8 (CH), 31.0 (CH₂), 31.5 (CH), 35.0 (CH), 35.0 (CH), 35.2 (CH₂), 35.2 (CH₂), 35.2 (CH), 35.7 (CH), 36.8 (CH), 37.0 (CH₂), 37.4 (CH₂), 45.7 (CH), 74.9 (C), 122.3 (CN).

Compound **2h** was prepared in one step from diamantan-2-one according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **2h** was obtained by eluting the reaction mixture through a pad of silica gel with hexane : Et₂O 2:1 and used in the next step without further purification.

3.2 Preparation and characterisation of carbonazidates 3

3.2.1 Compound 3a



Starting material **2a** (200 mg, 1.60 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (210 mg, 3.20 mmol) was carefully added to the solution. Triphosgene (240 mg, 0.80 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was

heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using hexane:Et₂O 2:1 as a mobile phase. The compound **3a** was obtained as a white solid (230 mg) in 73% yield.

m.p. (cryst. from Et₂O/Hexane 1:1): 68.5 °C.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.7.

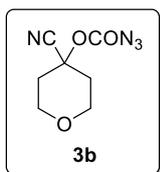
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.30-1.40 (m, 1H), 1.59-1.69 (m, 3H), 1.72-1.80 (m, 2H), 1.85-1.91 (m, 2H), 2.28-2.34 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 22.1 (2CH₂), 24.3 (2CH₂), 35.0 (CH₂), 76.2 (C), 117.5 (CN), 155.5(C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2945, 2866, 2673, 2383, 2189, 2156, 1738, 1450, 1267, 1227, 1209, 1165, 1144, 1095, 1041, 1028, 976, 951, 930, 906, 852, 748, 700, 656, 623, 588, 559, 525, 476, 449, 434, 407.

HRMS: *m/z* = 217.0698 ([M+Na]; calculated for C₈H₁₀N₄NaO₂⁺, *m/z* = 217.0696).

3.2.2 Compound 3b



Starting material **2b** (200 mg, 1.57 mmol) was dissolved in anhydrous Pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (204 mg, 3.14 mmol) was carefully added to the solution. Triphosgene (230 mg, 0.79 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using hexane: Et₂O 2:1 as a mobile phase. The compound **3b** was obtained as a colourless oil (210 mg) in 68% yield.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.6.

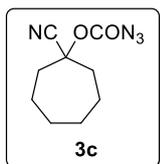
¹H NMR (400 MHz, CDCl₃): δ/ppm = 2.05-2.12 (m, 2H), 2.35-2.40 (m, 2H), 3.69-3.75 (m, 2H), 3.90-3.96 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 35.1 (2CH₂), 63.6 (2CH₂), 73.2 (C), 116.7 (CN), 155.6 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2976, 2943, 2866, 2702, 2387, 2197, 2168, 1755, 1471, 1452, 1431, 1360, 1279, 1255, 11167, 1151, 1103, 1053, 1009, 964, 935, 918, 889, 845, 771, 746, 594, 569, 557, 517, 498, 447, 413.

HRMS: *m/z* = 219.0501 ([M+Na]⁺; calculated for C₇H₈N₄NaO₃⁺, *m/z* = 219.0489).

3.2.3 Compound 3c



Starting material **2c** (200 mg, 1.44 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (187 mg, 2.88 mmol) was carefully added to the solution. Triphosgene (213 mg, 0.719 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using hexane: Et₂O 2:1 as a mobile phase. The compound **3c** was obtained as a colourless oil (200 mg) in 67% yield.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.7

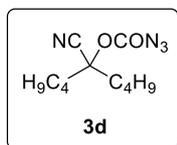
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.62-1.77 (m, 8H), 2.14-2.20 (m, 2H), 2.35-2.42 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 21.6 (2CH₂), 27.8 (2CH₂), 38.05 (2CH₂), 79.0 (C), 118.5 (CN), 155.6 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2937, 2664, 2389, 2191, 2137, 1738, 1464, 1448, 1367, 1290, 1248, 1228, 1166, 1149, 1122, 1011, 987, 951, 908, 847, 783, 748, 690, 658, 559, 498, 405.

HRMS: m/z = 231.0853 ([M+Na]; calculated for C₉H₁₂N₄NaO₂+ H₂O m/z = 231.0852).

3.2.4 Compound 3d



Starting material **2d** (200 mg, 1.18 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (154 mg, 2.36 mmol) was carefully added to the solution. Triphosgene (176 mg, 0.591 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using CHCl₃ as a mobile phase. The compound **3d** was obtained as a colourless oil (200 mg) in 71% yield.

R_f (silica gel; CHCl₃): 0.6

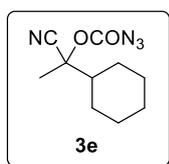
¹H NMR (400 MHz, CDCl₃): δ /ppm = 0.91-0.95 (m, 6H), 1.33-1.54 (m, 8H), 1.94-2.09 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ /ppm = 13.9 (2CH₃), 22.4 (2CH₂), 25.8 (2CH₂), 36.3 (2CH₂), 79.4 (C), 117.4 (CN), 155.7 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2960, 2933, 2868, 2736, 2193, 2139, 1734, 1468, 1381, 1246, 1209, 1163, 1147, 1130, 1059, 1039, 991, 899, 777, 750, 611, 559, 499, 415.

HRMS: m/z = 261.1322 ([M+Na]; calculated for C₁₁H₁₈N₄NaO₂⁺ m/z = 261.1322).

3.2.5 Compound 3e



Starting material **2e** (200 mg, 1.31 mmol) was dissolved in anhydrous Pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (170 mg, 2.61 mmol) was carefully added to the solution. Triphosgene (194 mg, 0.650 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using Hexane : EtOAc (15%) as a mobile phase. The compound **3e** was obtained as a colourless oil (226 mg) in 78% yield.

R_f (silica gel; *n*-hexane : EtOAc (15%)) : 0.8

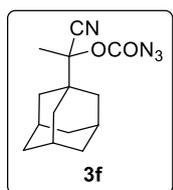
¹H NMR (400 MHz, CDCl₃): δ /ppm = 1.20-1.37 (m, 5H), 1.72-1.77 (m, 1H), 1.79 (s, 3H), 1.86-2.02 (m, 5H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 20.2 (CH₃), 25.3 (CH₂), 25.4 (CH₂), 25.6 (CH₂), 26.4 (CH₂), 26.7 (CH₂), 45.7 (CH), 78.7 (C), 117.1 (CN), 155.6 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2999, 2935, 2858, 2702, 2663, 2395, 2183, 2137, 1734, 1452, 1381, 1309, 1250, 1232, 1180, 1153, 1132, 1103, 1068, 1047, 960, 912, 895, 877, 849, 771, 750, 671, 625, 596, 625, 559, 509, 478, 434, 409.

HRMS: m/z = 245.1005 ([M+Na]; calculated for C₁₀H₁₄N₄NaO₂⁺ m/z = 245.1009).

3.2.6 Compound 3f



Starting material **2f** (200 mg, 0.97 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (127 mg, 1.94 mmol) was carefully added to the solution. Triphosgene (145 mg, 0.49 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using Hexane : Et₂O (1:1) as a mobile phase. The compound **3f** was obtained as a white solid (224 mg) in 84% yield.

m.p. (cryst. from Et₂O : *n*-hexane 1:1): 86.2 °C.

R_f (silica gel; *n*-hexane : Et₂O 1:1) : 0.7

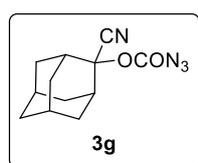
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.63-1.72 (m, 9H), 1.74 (s, 3H), 1.75-1.80 (m, 3H), 2.06-2.10 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 17.6 (CH₃), 28.1 (3CH), 35.9 (3CH₂), 36.4 (3CH₂), 39.9 (C), 82.1 (C), 116.8 (CN), 155.9 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3016, 2933, 2908, 2854, 2679, 2387, 2195, 2131, 1734, 1726, 1452, 1377, 1363, 1344, 1294, 1271, 1254, 1236, 1174, 1147, 1076, 1043, 978, 958, 941, 818, 752, 742, 698, 650, 596, 438, 426.

HRMS: m/z = 297.1317 ([M+Na]; calculated for C₁₄H₁₈N₄NaO₂⁺ m/z = 297.1322).

3.2.7 Compound 3g



Starting material **2g** (200 mg, 1.13 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (148 mg, 2.26 mmol) was carefully added to the solution. Triphosgene (168 mg, 0.056 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. The combined organic fractions were dried

over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using hexane: Et₂O 2:1 as a mobile phase. The compound **3g** was obtained as a white solid (225 mg) in 81% yield.

m.p. (cryst. from CHCl₃): 68.4 °C.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.7.

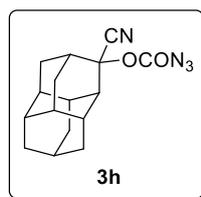
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.67-1.72 (m, 2H), 1.76-1.78 (m, 2H), 1.85-1.87 (m, 1H), 1.92-2.00 (m, 5H), 2.14-2.19 (m, 2H), 2.58-2.62 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 25.9 (CH), 26.1 (CH), 31.2 (2CH₂), 34.6 (CH), 34.6 (2CH₂), 36.8 (CH₂), 81.0 (C), 117.8 (CN), 155.6 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2937, 2910, 2866, 2848, 2673, 2393, 2191, 2143, 1739, 1454, 1354, 1342, 1282, 1217, 1120, 1101, 1049, 1014, 991, 926, 768, 748, 723, 673, 644, 555, 467.

HRMS: *m/z* = 269.1008 ([M+Na]; calculated for C₁₂H₁₄N₄NaO₂⁺, *m/z* = 269.1009).

3.2.8 Compound **3h**



Starting material **2h** (200 mg, 0.87 mmol) was dissolved in anhydrous Pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (113 mg, 1.74 mmol) was carefully added to the solution. C₃Cl₆O₃ (130 mg, 0.44 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. Reaction mixture was stirred for 15 min. at -10 °C then was allowed to reach r.t. and stirred for 1 h at r.t. After that the reaction mixture was heated at 50 °C for additional 5 hours. The reaction was quenched with water and the product was extracted using Et₂O. Combined organic fractions were dried over MgSO₄, concentrated *in vacuo* and the product was purified by column chromatography on silica gel using hexane: Et₂O 2:1 as a mobile phase. The compound **3h** was obtained as a white solid (260 mg) in a 72% yield.

m.p. (cryst. from CHCl₃): 93.1 °C.

R_f (silica gel; (Et₂O : *n*-hexane 2:1) 0.8

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.63 – 1.70 (m, 2H), 1.71-1.77 (m, 6H), 1.79-1.81 (m, 1H), 1.91–1.82 (m, 3H), 2.0 –1.92 (m, 2H), 2.13 (dq, *J* = 13.9, 3.0 Hz, 1H), 2.19-2.21 (m, 1H), 2.46-2.48 (m, 1H), 2.50-2.52 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 25.5 (CH), 31.5 (CH), 31.9 (CH₂), 32.6 (CH), 34.8 (CH₂), 34.8(CH), 35.1 (CH), 35.2 (CH), 36.6 (CH), 36.7 (CH₂), 36.8 (CH₂), 37.2 (CH₂), 42.9 (CH), 117.6 (CN), 155.6 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 2914, 2893, 2852, 2758, 2682, 2638, 2380, 2185, 2154, 2133, 1822, 1732, 1462, 1441, 1346, 1259, 1219, 1194, 1128, 1065, 1049, 1001, 984, 937, 779, 769, 752, 706, 559, 451.

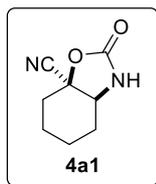
HRMS: *m/z* = 321.1321 ([M+Na]; calculated for C₁₆H₁₈N₄NaO₂ *m/z* = 321.1322).

3.3 Preparation and characterisation of carbamates 4.

3.3.1 Compound 4a

Carbonazidate **3a** (200 mg, 1.03 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a pale-yellow oil (144 mg) in a 84% yield combined. The ratio between *cis* and *trans* isomers was established from crude ¹H NMR to be 1:0.58 respectively.

2.3.1.1 Compound 4a1



Compound **4a1** was isolated by silica gel column chromatography eluting with pure Et₂O. Product **4a1** was obtained as a white crystalline solid (89 mg) in a 52% yield.

m.p. (cryst. from Et₂O): 128.9 °C.

R_f (silica gel; Et₂O): 0.6.

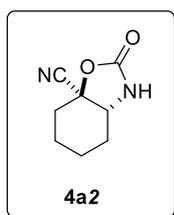
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.41-1.49 (m, 1H), 1.59-1.68 (m, 4H), 1.95-2.03 (m, 1H), 2.10-2.17 (m, 1H), 2.25-2.32 (m, 1H), 4.05 (t, *J* = 5.9 Hz, 1H), 6.10 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 18.5 (CH₂), 18.8 (CH₂), 27.8 (CH₂), 31.5 (CH₂), 55.7 (CH), 74.8 (C), 118.3 (CN), 157.2 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3492, 3402, 3236, 3157, 2954, 2871, 2775, 1851, 1778, 1739, 1620, 1556, 1466, 1448, 1392, 1371, 1366, 1311, 282, 1242, 1192, 1167, 1086, 1072, 1032, 941, 912, 876, 856, 775, 717, 694, 606, 584, 544, 526, 457.

HRMS: *m/z* = 189.0636 ([M+Na]; calculated for C₈H₁₀N₂NaO₂⁺, *m/z* = 189.0634).

2.3.1.2 Compound 4a2



Compound **4a2** was isolated by silica gel column chromatography eluting with pure Et₂O. Product **4a2** was obtained as a colourless oil (43 mg) in a 25% yield.

R_f (silica gel; Et₂O): 0.53.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.50 – 1.35 (m, 1H), 1.89 – 1.73 (m, 2H), 1.97 – 1.89 (m, 2H), 2.06 – 1.97 (m, 1H), 2.19 – 2.11 (m, 1H), 2.45 – 2.36 (m, 1H), 3.56 (dd, *J* = 12.4, 3.1 Hz, 1H), 6.15 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 22.6 (CH₂), 22.8 (CH₂), 26.5 (CH₂), 32.0 (CH₂), 62.6 (CH), 82.6 (C), 116.8 (CN), 158.1 (C).

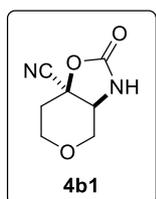
IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3292, 3182, 2929, 2862, 2692, 2239, 1836, 1776, 1755, 1537, 1462, 1408, 1302, 1265, 1149, 1134, 1097, 1080, 1070, 1045, 1020, 970, 947, 930, 918, 891, 868, 841, 800, 769, 721, 663, 633, 582, 557, 546, 523, 471, 461, 436.

HRMS: *m/z* = 189.0635 ([M+Na]; calculated for C₈H₁₀N₂NaO₂⁺, *m/z* = 189.0634).

3.3.2 Compound 4b

Carbonazidate **3b** (200 mg, 1.03 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a pale-yellow oil (152 mg) in a 87% yield combined. The ratio between *cis* and *trans* isomers was established from crude ¹H NMR to be 0.83:1 respectively.

2.3.2.1 Compound 4b1



Compound **4b1** was isolated by silica gel column chromatography eluting with pure DCM. Product **4b1** was obtained as a white crystalline solid (52 mg) in a 34% yield.

m.p. (cryst. from DCM): 136.9 °C.

R_f (DCM): 0.5.

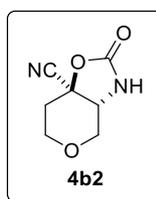
¹H NMR (400 MHz, CDCl₃): δ/ppm = 2.33-2.45 (m, 2H), 3.53-3.58 (m, 1H), 3.80-3.85 (m, 1H), 3.99-4.04 (m, 2H), 5.93 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 31.3 (CH₂), 53.3 (CH), 62.0 (CH₂), 67.0 (CH₂), 72.3 (C), 117.2 (CN), 156.2 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3286, 2940, 1781, 1209, 1072, 921, 746, 570.

HRMS: m/z = 169.0607 ([M+H]⁺; calculated for C₇H₉N₂O₃⁺, m/z = 169.0608).

2.3.2.2 Compound 4b2



Compound **4b2** was isolated by silica gel column chromatography eluting with pure DCM. Product **4b2** was obtained as a white crystalline solid (62 mg) in a 41% yield.

m.p. (cryst. from DCM): 136.9 °C.

R_f (silica gel; DCM): 0.5.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 2.24-2.44 (m, 4H), 3.91-3.95 (m, 2H), 5.15-5.17 (m, 1H), 6.29 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 33.2 (CH₂), 35.2 (CH₂), 55.2 (CH), 70.6 (CH₂), 74.3 (C), 116.6 (CN), 150.4 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3270, 3166, 2908, 1720, 1105, 1022, 800, 761, 624.

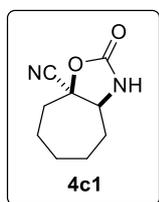
HRMS: m/z = 191.0427 ([M+Na]⁺; calculated for C₇H₈N₂NaO₃⁺, m/z = 191.0427).

3.3.3 Compound 4c

Carbonazidate **3c** (200 mg, 0.96 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained

as a pale-yellow oil (137 mg) in a 79% yield combined. The ratio between *cis* and *trans* isomers was established from crude ^1H NMR to be 0.87:1 respectively.

2.3.3.1 Compound 4c1



Compound **4c1** was isolated by silica gel column chromatography eluting with pure Et₂O. Product **4c1** was obtained as a colourless oil (63 mg) in a 36% yield.

R_f (silica gel; Et₂O): 0.5.

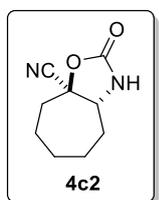
^1H NMR (400 MHz, CDCl₃): δ /ppm = 1.54 – 1.37 (m, 1H), 1.73 – 1.62 (m, 1H), 1.74-1.85 (m, 3H), 2.01 – 1.89 (m, 3H), 2.21 – 2.08 (m, 1H), 2.57 – 2.45 (m, 1H), 3.99 (dd, J = 11.6, 5.2 Hz, 1H), 6.36 (s, 1H).

^{13}C NMR (101 MHz, CDCl₃): δ /ppm = 23.7 (CH₂), 24.8 (CH₂), 26.2 (CH₂), 31.9 (CH₂), 35.4 (CH₂), 60.4 (CH), 82.5 (C), 116.8 (CN), 157.4 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3504, 3251, 3168, 2945, 2864, 1913, 1792, 1759, 1712, 1450, 1388, 1350, 1290, 1261, 1228, 1207, 1165, 1111, 1038, 1012, 999, 958, 945, 899, 858, 812, 771, 673, 609, 580, 526, 451, 440.

HRMS: m/z = 203.0793 ([M+Na]; calculated for C₉H₁₂N₂NaO₂⁺ m/z = 203.0791).

2.3.3.2 Compound 4c2



Compound **4c2-*cis*** was isolated by silica gel column chromatography eluting with pure Et₂O. Product **4c2-*cis*** was obtained as a colourless oil (69 mg) in a 40% yield.

R_f (silica gel; Et₂O): 0.65.

^1H NMR (400 MHz, CDCl₃): δ /ppm = 1.45-1.36 (m, 2H), 1.54 (m, 1H), 1.80-1.72 (m, 2H), 1.88-1.82 (m, 2H), 1.94 (m, 1H), 2.10 (m, 1H), 2.36 (m, 1H), 4.17 (m, 1H), 6.65 (s, 1H).

^{13}C NMR (101 MHz, CDCl₃): δ /ppm = 23.1 (CH₂), 25.2 (CH₂), 29.9 (CH₂), 31.9 (CH₂), 35.1 (CH₂), 62.1 (CH), 79.5 (C), 119.5 (CN), 156.3 (C).

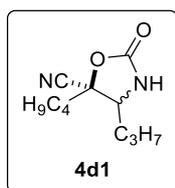
IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3305, 3188, 2927, 2866, 2698, 2025, 1780, 1755, 1739, 1462, 1381, 1363, 1327, 1290, 1244, 1225, 1211, 1153, 1084, 1026, 985, 970, 947, 924, 850, 800, 754, 655, 580, 507, 457.

HRMS: m/z = 203.0793 ([M+Na]; calculated for C₉H₁₂N₂NaO₂⁺ m/z = 203.0791).

3.3.4 Compound 4d

Carbonazidate **3d** (200 mg, 0.95 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a pale-yellow oil (176 mg) a 91% yield combined. The ratio between *cis* and *trans* isomers was established from crude ^1H NMR to be 1:1.

2.3.4.1 Compound 4d1



Compound **4d1** was isolated by silica gel column chromatography eluting with CHCl_3 : *n*-hexane 2:1. Product **4d1** was obtained as a colourless oil (71 mg) in a 37% yield.

R_f (silica gel; CHCl_3 : *n*-hexane 2:1): 0.5.

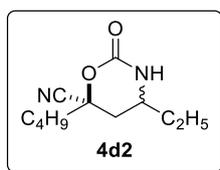
¹H NMR (400 MHz, CDCl_3): δ /ppm = 0.93-1.02 (m, 6H), 1.35-1.85 (m, 8H), 1.91-2.04 (m, 2H), 3.66-3.69 (m, 1H), 6.96 (brs, 1H).

¹³C NMR (101 MHz, CDCl_3): δ /ppm = 13.7 (CH_3), 13.8 (CH_3), 19.6 (CH_2), 22.2 (CH_2), 25.7 (CH_2), 35.1 (CH_2), 38.4 (CH_2), 60.1 (CH), 81.5 (C), 115.5 (CN), 156.9 (C).

IR (neat): $\tilde{\nu}$ / cm^{-1} = 3265, 3163, 2960, 2933, 2873, 2740, 2243, 1770, 1466, 1381, 1275, 1126, 1011, 951, 883, 762, 669, 617, 532, 474, 455, 436.

HRMS: m/z = 233.1260 ([M+Na]; calculated for $\text{C}_{11}\text{H}_{18}\text{N}_2\text{NaO}_2^+$, m/z = 233.1260).

2.3.4.2 Compound 4d2



Compound **4d2** was isolated by silica gel column chromatography eluting with CHCl_3 : *n*-hexane 2:1. Product was obtained as a white solid (60 mg) in a 31% yield.

m.p. (cryst. from Cyclohexane : CHCl_3 1:1): 116.7 °C

R_f (silica gel; CHCl_3 : *n*-hexane 2:1): 0.4

¹H NMR (400 MHz, CDCl_3): δ /ppm = 0.92-1.01 (m, 6H), 1.35-1.45 (m, 2H), 1.50-1.73 (m, 5H), 1.86-2.02 (m, 2H), 2.21-2.26 (m, 1H), 3.69-3.76 (m, 1H), 6.62 (brs, 1H).

¹³C NMR (101 MHz, CDCl_3): δ /ppm = 9.1 (CH_3), 13.7 (CH_3), 22.3 (CH_2), 25.4 (CH_2), 28.4 (CH_2), 35.7 (CH_2), 39.4 (CH_2), 50.2 (CH), 75.7 (C), 117.7 (CN), 151.9 (C).

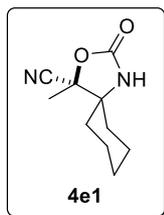
IR (neat): $\tilde{\nu}$ / cm^{-1} = 3402, 3246, 3136, 2965, 2935, 2875, 1759, 1722, 1462, 1406, 1346, 1325, 1304, 1182, 1120, 1103, 1080, 1028, 1014, 930, 868, 793, 766, 634, 523, 488, 440.

HRMS: m/z = 233.1260 ([M+Na]; calculated for $\text{C}_{11}\text{H}_{18}\text{N}_2\text{NaO}_2^+$, m/z = 233.1260).

3.3.5 Compound 4e

Carbonazidate **3e** (200 mg, 1.03 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a pale-yellow oil (152 mg) in a 87% yield combined. The ratio between the two isomers was established from crude ¹H NMR to be 1:0.83.

2.3.5.1 Compound 4e1



Compound **4e1** was isolated by silica gel column chromatography eluting with CHCl_3 : EtOAc 1:1. Product **4e1** was obtained as a white crystalline solid (69 mg) in a 47% yield.

m.p. (cryst. from DCM): 136.9 °C.

R_f (silica gel; CHCl_3 : EtOAc 1:1): 0.5.

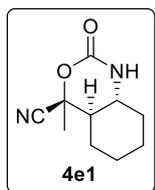
¹H NMR (400 MHz, CDCl_3): δ /ppm = 1.24-1.31(m, 1H), 1.48-1.61 (m, 3H), 1.64-1.71 (m, 3H), 1.72 (s, 3H), 1.75-1.85 (m, 2H), 1.95-1.99 (m, 1H), 3.35 (brs, 1H).

¹³C NMR (101 MHz, CDCl_3): δ /ppm = 20.1 (CH_3), 22.4 (CH_2), 23.5 (CH_2), 25.8 (CH_2), 32.5 (CH_2), 34.6 (CH_2), 63.4 (C), 82.9 (C), 118.6 (CN), 157.6 (C).

IR (neat): $\tilde{\nu}$ / cm^{-1} = 3475, 3219, 3140, 2989, 2937, 2688, 2517, 2386, 2326, 2237, 1763, 1604, 1444, 1385, 1363, 1327, 1300, 1217, 1161, 1107, 1034, 960, 933, 914, 899, 866, 831, 769, 706, 530, 496, 469, 432.

HRMS: m/z = 217.0951 ($[\text{M}+\text{Na}]$; calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{NaO}_2^+$, m/z = 217.0947).

2.3.5.2 Compound 4e2



Compound **4e2** was isolated by silica gel column chromatography eluting with CHCl_3 : EtOAc 1:1. Product **4e2** was obtained as a white crystalline solid (56 mg) in a 38% yield.

m.p. (cryst. from CHCl_3): 214.5 °C.

R_f (silica gel; CHCl_3 : EtOAc 1:1): 0.4.

¹H NMR (400 MHz, CDCl_3): δ /ppm = 1.22-1.46 (m, 4H), 1.69-1.73 (m, 1H), 1.75 (s, 3H), 1.81-2.06 (m, 4H), 3.26-3.31 (m, 1H), 3.37 (brs, 1H).

¹³C NMR (101 MHz, CDCl_3): δ /ppm = 24.6 (CH_3), 24.7 (CH_2), 25.9 (CH_2), 26.3 (CH_2), 32.7 (CH_2), 46.2 (CH), 53.9 (CH), 78.1 (C), 118.7 (CN), 153.2 (C).

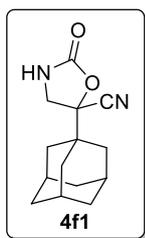
IR (neat): $\tilde{\nu}$ / cm^{-1} = 3211, 3118, 2949, 2993, 2871, 2362, 2268, 1716, 1522, 1448, 1414, 1358, 1342, 1298, 1238, 1207, 1140, 1084, 1049, 997, 924, 856, 843, 762, 746, 710, 665, 569, 523, 505, 476, 413

HRMS: m/z = 217.0951 ($[\text{M}+\text{Na}]$; calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{NaO}_2^+$, m/z = 217.0947).

3.3.6 Compound 4f

Carbonazidate **3f** (200 mg, 0.73 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a crystalline white solid (163 mg) in a 91% yield combined. The ratio between compound **4f1** and **4f2** according to crude ¹H NMR was 8:1. The ratio between the two **4f2** isomers was established from crude ¹H NMR to be 1:0.77.

2.3.6.1 Compound 4f1



Compound **4f1** was isolated by silica gel column chromatography eluting with Et₂O : *n*-hexane 1:1. Product **4f1** was obtained as a white crystalline solid (8.5 mg) in a 14% yield.

m.p. (cryst. from CHCl₃): 280.1 °C.

R_f (silica gel; Et₂O : *n*-hexane 1:1) : 0.7.

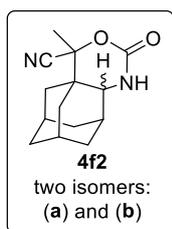
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.65-1.79 (m, 12H), 2.11-2.14 (m, 3H), 3.78 (dd, *J* = 47.2, 9.5 Hz, 2H), 5.36 (bs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 27.7 (3CH), 35.5 (3 CH₂), 36.4 (3CH₂), 38.5 (C), 44.9 (CH₂), 82.9 (C), 117.4 (CN), 156.3 (C).

IR (neat): /cm⁻¹ = 3408, 3359, 3226, 3128, 2920, 2904, 2864, 1716, 1450, 1388, 1379, 1338, 1327, 1228, 1207, 1194, 1144, 1120, 1082, 1005, 962, 904, 866, 810, 758, 714, 661, 648, 631, 519, 503, 490, 447.

HRMS: *m/z* = 247.1442 ([M+H]⁺); calculated for C₁₄H₁₉N₂O₂⁺, *m/z* = 247.1441).

2.3.6.2 Compound 4f2 (two isomers)



Compound 4f2a (first isomer)

Compound **4f2a** was isolated by silica gel column chromatography eluting with Et₂O : *n*-hexane 1:1. Product **4f2a** was obtained as a white crystalline solid (64mg) in a 39% yield.

m.p. (cryst. from CHCl₃): 205.8 °C.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.8.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.51-1.56 (m, 1H), 1.62 (s, 3H), 1.66-1.70 (m, 2H), 1.73-1.76 (m, 2H), 1.78-1.83 (m, 3H), 1.88-1.93 (m, 2H), 1.97-2.00 (m, 1H), 2.07-2.11 (m, 1H), 2.15-2.18 (m, 1H), 3.815 (d, *J* = 3.2 Hz, 1H), 5.89 (bs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 19.8 (CH₃), 26.7 (CH), 28.1 (CH), 28.7 (CH₂), 29.2 (CH₂), 31.9 (CH), 35.0 (CH₂), 35.3 (C), 36.2 (CH₂), 36.7 (CH₂), 56.8 (CH), 80.3 (C), 118.0 (CN), 151.3 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3400, 3230, 3128, 2904, 2862, 1786, 1716, 1450, 1388, 1379, 1338, 1327, 1281, 1265, 1207, 1194, 1144, 1120, 1076, 1005, 980, 904, 810, 758, 735, 714, 661, 648, 594, 519, 501, 490, 449.

HRMS: *m/z* = 247.1445 ([M+H]⁺); calculated for C₁₄H₁₉N₂O₂⁺, *m/z* = 247.1441).

Compound 4f2b (second isomer)

Compound **4f2b** was isolated by silica gel column chromatography eluting with Et₂O : *n*-hexane 1:1. Product **4f2b** was obtained as a white crystalline solid (66mg) in a 41% yield.

m.p. (cryst. from CHCl₃): 206.5 °C.

R_f (silica gel; Et₂O : *n*-hexane 1:1): 0.55.

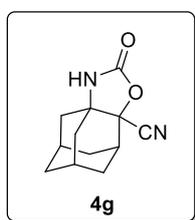
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.51-1.56 (m, 1H), 1.62 (s, 3H), 1.66-1.70 (m, 2H), 1.73-1.76 (m, 2H), 1.78-1.83 (m, 3H), 1.87-1.94 (m, 2H), 1.97-2.00 (m, 1H), 2.07-2.11 (m, 1H), 2.15-2.18 (m, 1H), 3.805 (d, *J* = 3.2 Hz, 1H), 6.02 (bs, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 19.8 (CH₃), 26.9 (CH), 28.0 (CH), 28.7 (CH₂), 29.2 (CH₂), 31.7 (CH), 35.0 (CH₂), 35.2 (C), 36.2 (CH₂), 36.8 (CH₂), 56.7 (CH), 80.3 (C), 118.0 (CN), 151.8 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3242, 3130, 2906, 1714, 1390, 1076, 1000, 760, 715.

HRMS: *m/z* = 247.1445 ([M+H]⁺); calculated for C₁₄H₁₉N₂O₂⁺, *m/z* = 247.1441).

3.3.7 Compound 4g



Carbonazidate **3g** (200 mg, 0.92 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was filtered off, washed with hexane and dried *in vacuo*. The compound **4g** was obtained as a white crystalline solid (204 mg) in a 83% yield.

m.p. (cryst. from CHCl₃): 179.7 °C.

R_f (silica gel; DCM : EtOAc 4:1): 0.6.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.64-1.67 (m, 1H), 1.73-1.82 (m, 2H), 1.86-1.98 (m, 4H), 2.04-2.10 (m, 2H), 2.26-2.37 (m, 3H), 2.63-2.65 (m, 1H), 6.03 (bs, 1H)

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 27.5 (CH), 28.8 (CH), 29.5 (CH₂), 33.7 (CH), 35.5 (CH₂), 35.6 (CH₂), 37.2 (CH₂), 40.2 (CH₂), 58.9 (C), 85.6 (C), 118.6 (CN), 158.3 (C).

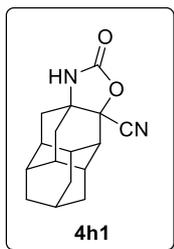
IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3292, 3182, 2929, 2862, 2692, 2239, 1836, 1776, 1755, 1537, 1462, 1408, 1302, 1265, 1149, 1134, 1097, 1080, 1070, 1045, 1020, 970, 947, 930, 918, 891, 868, 841, 800, 769, 721, 663, 633, 582, 557, 546, 523, 471, 461, 436.

HRMS: *m/z* = 241.0948 ([M+Na]⁺); calculated for C₁₂H₁₄N₂NaO₂⁺, *m/z* = 241.0947).

3.3.8 Compound 4h

Carbonazidate **3h** (200 mg, 0.67 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room temperature and concentrated *in vacuo*. The crude product was obtained as a white crystalline solid (156 mg) in a 86% yield. The ratio between compounds **3h1** and **3h2** was established from crude ¹H NMR to be 1:1.3 respectively.

2.3.8.1 Compound 4h1



Compound **4h1** was isolated by silica gel column chromatography eluting with DCM : EtOAc 4:1. Product **4h1** was obtained as a white crystalline solid (58 mg) in a 32% yield.

m.p. (cryst. from CHCl₃): 175.6 °C.

R_f (silica gel; DCM : EtOAc 4:1): 0.7.

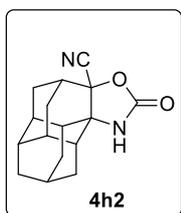
¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.63 (dt, J = 14.3, 2.6 Hz, 1H), 1.67-1.69 (m, 2H), 1.78 – 1.71 (m, 4H), 1.79-1.82 (m, 2H), 1.95 – 1.86 (m, 2H), 1.98 (q, J = 2.9 Hz, 1H), 2.05 – 2.00 (m, 1H), 2.16 – 2.12 (m, 2H), 2.33-2.35 (m, 1H), 2.38-2.39 (m, 1H), 6.53 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 27.4 (CH), 28.9 (CH₂), 33.4 (CH), 34.3 (CH₂), 34.7 (CH), 35.1 (CH), 36.1 (CH₂), 36.2 (CH₂), 37.7 (CH), 41.6 (CH₂), 42.7 (CH), 43.3 (CH), 52.2 (C), 80.1 (C), 117.4 (CN), 152.8 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3386, 3213, 3184, 3116, 2925, 2898, 2852, 1716, 1466, 1444, 1379, 1358, 1317, 1234, 1178, 1165, 1126, 1024, 995, 895, 872, 787, 756, 725, 650, 621, 525, 498, 467, 428.

HRMS: m/z = 293.1258 ([M+Na]; calculated for C₁₆H₁₈N₂NaO₂+ m/z = 293.1260).

2.3.8.2 Compound 4h2



Compound **4h2** was isolated by silica gel column chromatography eluting with DCM : EtOAc 4:1. Product **4h2** was obtained as a white crystalline solid (80 mg) in a 44% yield.

m.p. (cryst. from CHCl₃): 211.3 °C.

R_f (silica gel; DCM : EtOAc 4:1): 0.6.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.71-1.74 (m, 2H), 1.75-1.81 (m, 5H), 1.83-1.86 (m, 2H), 1.88-1.93 (m, 3H), 1.99 (dq, J = 13.4, 2.8 Hz, 1H), 2.04-2.08 (m, 1H), 2.36 (dq, J = 14.3, 3.1 Hz, 1H), 2.50 – 2.44 (m, 1H), 2.62 – 2.56 (m, 1H), 6.87 (s, 1H).

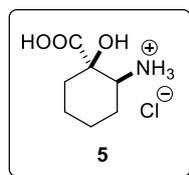
¹³C NMR (101 MHz, CDCl₃): δ/ppm = 24.8 (CH), 30.94 (CH₂), 32.4 (CH₂) 32.4 (CH), 33.2 (CH₂), 35.7 (CH), 35.9 (CH₂), 36.5 (CH₂), 36.7 (CH), 37.6 (CH), 37.7 (CH), 39.9 (CH), 62.5 (C), 86.7 (C), 118.5 (CN), 158.5 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3485, 3253, 3147, 3020, 2931, 2900, 2777, 2752, 2241, 1855, 1766, 1552, 1460, 1448, 1406, 1346, 1306, 1279, 1261, 1124, 1111, 1057, 1043, 985, 957, 930, 912, 858, 823, 806, 777, 754, 723, 652, 617, 582, 463, 424.

HRMS: m/z = 293.1260 ([M+Na]; calculated for C₁₆H₁₈N₂NaO₂ m/z = 293.1260).

3.4 Preparation and characterisation of compounds 5-13.

3.4.1 Compound 5

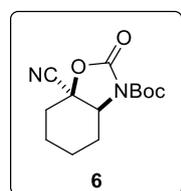


$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 1.20\text{-}1.82$ (m, 8H), 3.53-3.56 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta/\text{ppm} = 18.7$ (CH_2), 22.8 (2CH_2), 25.5 (CH_2), 34.1 (CH_2), 53.1 (CH), 73.9 (C), 176.9 (COOH).

Compound **4h1** (200 mg, 0.75 mmol) was dissolved in concentrated HCl and heated at 90 °C for 3 days. After that the reaction mixture was cooled down to room temperature and aqueous HCl was directly evaporated *in vacuo*. Compound **5** was obtained as a white crystalline solid (181 mg) in a 77% yield.

3.4.2 Compound 6

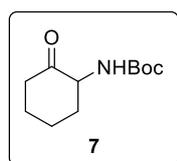


$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 1.32\text{-}1.49$ (m, 3H), 1.54 (s, 9H), 1.70-1.77 (m, 2H), 1.97-2.06 (m, 1H), 2.34-2.42 (m, 1H), 2.46-2.52 (m, 1H), 4.33-4.37 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta/\text{ppm} = 18.6$ (CH_2), 19.5 (CH_2), 27.4 (CH_2), 28.0 (3CH_3), 31.3 (CH_2), 58.4 (CH), 59.3 (CH), 72.5 (C), 82.1 (C), 118.4 (CN), 148.4 (C), 149.5 (C).

Compound **6** was prepared in one step from compound **4a1** according to the procedure described in Katsuo, S.; Kazuhiro, M.; Hideaki, W.; Yukio, M. *Chem. Pharm. Bull.* **1996**, *44*, 1823-1830. Product **6** was purified by silica gel column eluting with Et_2O : Hexane 1:1 and isolated in a 77% yield.

3.4.3 Compound 7

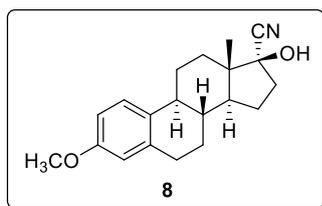


$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 1.35\text{-}1.39$ (m, 1H), 1.43 (s, 9H), 1.59-1.66 (m, 1H), 1.70-1.79 (m, 1H), 1.85-1.89 (m, 1H), 2.08-2.14 (m, 1H), 2.32-2.41 (m, 1H), 2.48-2.61 (m, 2H), 4.19-4.25 (m, 1H), 5.48 (bs, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta/\text{ppm} = 24.3$ (CH_2), 28.1 (2CH_2), 28.5 (3CH_3), 36.1 (CH_2), 41.2 (CH_2), 59.3 (CH), 79.7 (C), 155.1 (C), 207.8 (C).

Compound **6** (200 mg, 0.75 mmol) was dissolved in 2M aqueous KOH (2 mL)/EtOH (2 mL) solution, heated to 40 °C and left stirring overnight. After that the reaction mixture was cooled down to room temperature and extracted with EtOAc (3×4 mL). The combined organic phase was dried over MgSO_4 and concentrated *in vacuo*. Compound **7** was obtained as a white crystalline solid (134 mg) in a 84% yield.

3.4.4 Compound 8

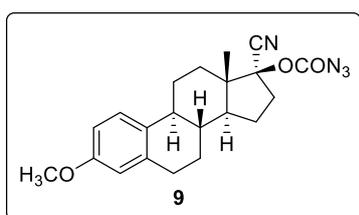


¹H NMR (600 MHz, CDCl₃): δ/ppm = 0.93 (s, 3H), 1.40-1.57 (m, 4H), 1.65-1.72 (m, 1H), 1.84-1.94 (m, 4H), 1.99-2.07 (m, 1H), 2.26-2.32 (m, 1H), 2.40-2.46 (m, 1H), 2.51-2.61 (m, 2H), 2.85-2.87 (m, 2H), 3.78 (s, 3H), 6.64-6.65 (m, 1H), 6.71-6.74 (m, 1H), 7.19-7.22 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 12.34 (CH₃), 23.05 (CH₂), 26.26 (CH₂), 27.25 (CH₂), 29.78 (CH₂), 33.48 (CH₂), 37.40 (CH), 39.32 (CH₂), 43.31 (CH), 47.58 (C), 49.82 (CH), 55.37 (OCH₃), 81.14 (C), 11.74 (CH), 114.00 (CH), 122.23 (CN), 126.48 (CH), 132.03 (C), 137.89 (C), 157.71 (C).

Compound **8** was prepared in one step from Estrone methyl ester according to the procedure described in de Castro, Sonia; et al. *Chemistry - A European Journal*. **2008**, 14(31), 9620-9632. Product **8** was purified silica gel column chromatography eluting with CH₂Cl₂ : EtOAc 2:1 and isolated in a 71% yield.

3.4.5 Compound 9



Starting material **8** (200 mg, 0.64 mmol) was dissolved in anhydrous pyridine (3 mL), the solution was cooled to -10 °C and NaN₃ (83.5 mg, 1.28 mmol) was carefully added to the solution. Triphosgene (954 mg, 0.32 mmol) was dissolved in anhydrous DCM (2 mL) at 0 °C and added dropwise to the reaction mixture at -10 °C. The reaction mixture was stirred for 15 min. at -10 °C After 10 minutes the reaction mixture was

allowed to warm up to room temperature and stirred for 1 h. After that the reaction mixture was heated at 50 °C and stirred for an additional 5 hours. The reaction was quenched with water and the product was extracted with Et₂O. The combined organic fractions were dried over anhydrous MgSO₄, concentrated *in vacuo* and the product was purified by silica gel column chromatography eluting with hexane: Et₂O 2:1. Compound **2a** was obtained as a white solid (225 mg) in a 92% yield.

m.p. (cryst. from CHCl₃): 58.2 °C.

R_f (silica gel; Hexane : Et₂O 2:1): 0.65.

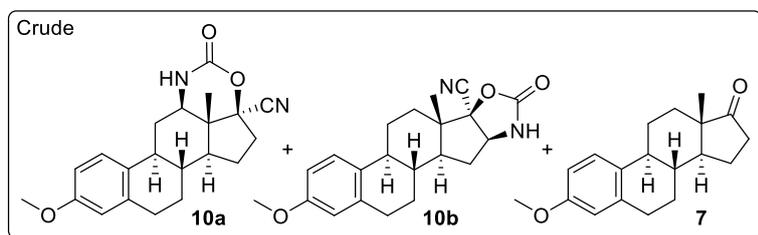
¹H NMR (400 MHz, CDCl₃): δ/ppm = 0.97 (s, 3H), 1.40-1.61 (m, 4H), 1.71-1.79 (m, 1H), 1.87-2.03 (m, 4H), 2.10-2.18 (m, 1H), 2.28-2.35 (m, 1H), 2.41-2.47 (m, 1H), 2.87-2.99 (m, 3H), 3.79 (s, 3H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.21 (dd, 8.6, 1.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 12.9 (CH₃), 23.2 (CH₂), 26.0 (CH₂) 27.1 (CH₂), 29.6 (CH₂), 33.7 (CH₂), 35.6 (CH₂), 38.9 (CH), 43.1 (CH), 48.4(C), 48.5 (CH), 55.2 (CH), 85.7 (C), 111.7 (CN), 126.4 (CH), 131.5 (CH), 137.6 (CH), 156.2 (C), 157.7 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3057, 2991, 2935, 2870, 2175, 2133, 1739, 1608, 1576, 1500, 1456, 1387, 1250, 1059, 1034, 1016, 912, 885, 868, 783, 739, 681, 648, 598, 557, 445.

HRMS: $m/z = 403.1739$ ($[M+Na]$; calculated for $C_{21}H_{24}N_4NaO_3+$ $m/z = 403.1741$).

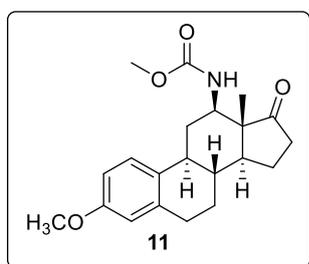
3.4.6 Compound 10



Carbonazidate **9** (200 mg, 0.53 mmol) was dissolved in anhydrous 1,2-DCE (5 mL) and the solution was heated in a sealed tube at 130 °C overnight. After that the reaction mixture was cooled down to room

temperature and concentrated *in vacuo*. The crude product was obtained as a pale-yellow oil. The crude mixture of five-membered **10a** and six-membered **10b** carbamates (1:1) was carried to the next step without further purification.

3.4.7 Compound 11



The crude mixture of carbamates **10** (60 mg) was dissolved in anhydrous methanol 15 mL and 120 mg of K_2CO_3 was added. The mixture was heated for 2 hours at 100 °C in seal tube. Then the mixture was cooled to room temperature, evaporated and directly transferred to a silica gel column for separation using $CHCl_3 : iPrOH : Et_3N$ 10:1:0.2. Product **11** was obtained as a light-yellow oil (26 mg) in a 41% yield.

R_f (silica gel; $CHCl_3 : iPrOH : Et_3N$ 10:1:0.2) 0.25

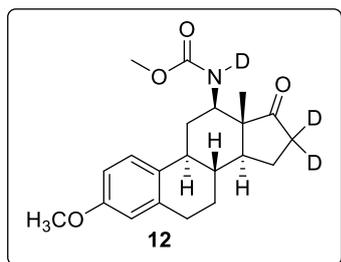
¹H NMR (400 MHz, $CDCl_3$): $\delta/ppm = 0.92$ (s, 3H), 1.38-1.55 (m, 3H), 1.62-1.69 (m, 2H), 1.98-2.24 (m, 3H), 2.38-2.50 (m, 2H), 2.81-2.92 (m, 3H), 3.85-3.91 (m, 1H), 5.12 (bs, 1H), 6.65 (d, $J = 2.8$ Hz, 1H), 6.73 (dd, $J = 8.6, 2.9$ Hz, 1H), 7.19 (d, $J = 6.7$ Hz, 1H).

¹³C NMR (101 MHz, $CDCl_3$): $\delta/ppm = 9.64$ (CH_3), 21.2 (CH_2), 26.3 (CH_2), 29.6 (CH_2), 33.3 (CH_2), 36.3 (CH_2), 37.7 (CH), 42.7 (CH), 49.4 (C), 50.4 (CH_3), 52.2 (CH), 53.9 (CH_3), 55.3 (CH), 111.7 (CH), 114.1 (CH), 126.4 (CH), 131.1 (C), 137.6 (C), 157.1 (C), 157.9 (C), 218.8 (C).

IR (neat): $\tilde{\nu}/cm^{-1} = 3330, 2929, 2885, 2837, 1736, 1701, 1608, 1518, 1498, 1464, 1377, 1344, 1254, 1236, 1188, 1153, 1049, 1039, 970, 939, 908, 818, 750, 712, 665, 598, 501, 455, 436$.

HRMS: $m/z = 380.1831$ ($[M+Na]$; calculated for $C_{21}H_{27}NNaO_4^+$, $m/z = 380.1832$).

3.4.8 Compound 12

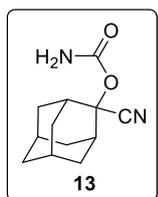


A vial was charged with carbamate **11** (70 mg, 0.2 mmol) and a magnetic stirbar. A mixture of D_2O (1 ml) and CD_3OD (2 ml) was added followed by solid NaOH (80 mg, 2 mmol). The vial was sealed and the reaction mixture was stirred at 40 °C for 16 h. After 16 h a sample was taken directly from the deuterated reaction mixture for NMR measurements.

¹H NMR (400 MHz, CD₃OD) δ/ppm = 0.9 (s, 3H), 1.3 – 1.5 (m, 3H), 1.6 – 1.7 (m, 2H), 2.0 – 2.1 (m, 2H), 2.3 – 2.5 (m, 2H), 2.8 – 2.9 (m, 2H), 3.7 (s, 3H), 3.7 (s, 3H), 3.9 (dd, *J* = 12.0, 4.1 Hz, 1H), 6.6 (d, *J* = 2.7 Hz, 1H), 6.7 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.1 (d, *J* = 8.6 Hz, 1H).

¹³C NMR (101 MHz, CD₃OD) δ/ppm = 9.7, 21.7, 27.1, 30.4, 34.8, 38.7, 44.0, 49.2, 51.2, 51.5, 52.8, 54.1, 55.8, 112.6, 114.8, 127.1, 132.5, 138.9, 158.8, 159.3, 222.6.

3.4.9 Compound 13



Cyanohydrin **2g** (286 mg, 1.62 mmol) was dissolved in anhydrous DCM and cooled to 0 °C. Trichloroacetylisocyanate (0.21 mL, 1.78 mmol) was added dropwise to the reaction mixture and stirred for 2h at 24 °C. After 2h the solvent was removed *in vacuo* and 1.5 mL MeOH was added together with 1.5 mL of saturated aqueous K₂CO₃. The reaction mixture was heated to 50 °C and stirred for 24h. The MeOH was evaporated *in vacuo* and the product precipitated from the water solution. The product was filtered off, washed with water and Et₂O. The compound **13** (280 mg) was obtained as colorless solid in a 78 % yield.

m.p. (cryst. from DCM): over 200 °C.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 5.73-5.96 (m, 10H), 6.16-6.27 (m, 4H), 8.83 (bs, 2H).

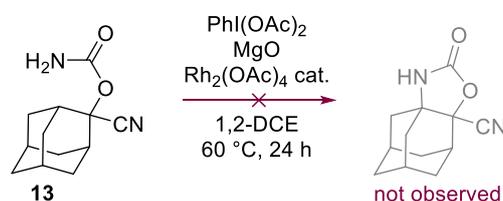
¹³C NMR (101 MHz, CD₃OD): δ/ppm = 27.1 (CH), 28.1 (CH), 33.7 (CH₂), 35.6 (CH₂), 36.4 (CH), 38.8 (CH₂), 90.6 (C), 168.5 (CN), 187.2 (C).

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3359, 3126, 3020, 2945, 2902, 2889, 2860, 2846, 2488, 2254, 1741, 1668, 1597, 1552, 1496, 1456, 1392, 1306, 1282, 1242, 1215, 1122, 1092, 1068, 1009, 980, 939, 930, 862, 787, 729, 683, 661, 627, 602, 521, 505.476,445.

HRMS: *m/z* = 221.1285 ([*M*+*H*]; calculated for C₁₂H₁₇N₂O₂⁺, *m/z* = 221.1285).

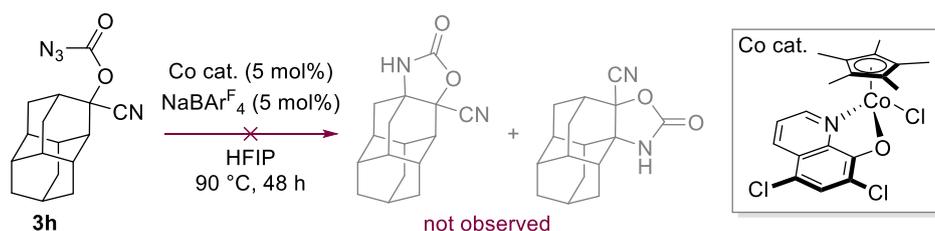
3.5 Additional experiments

3.5.1 Dirhodium acetate catalysed amination reaction of 13



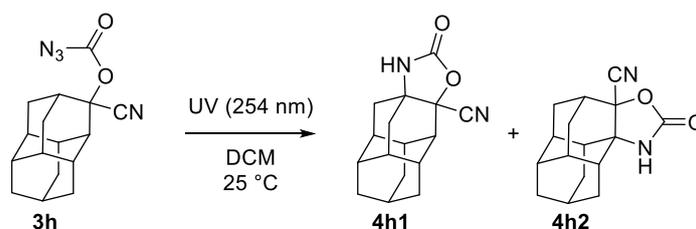
Compound **13** (30 mg, 0.14 mmol), PhI(OAc)₂ (59 mg, 0.18 mmol), MgO (13 mg) and Rh₂(OAc)₄ (2 mg, 0.004 mmol) were dissolved in anhydrous 1,2-dichloroethane and the reaction was stirred at 60 °C for 24h. The reaction turned into red/brown color indicating the deactivation of the dirhodium catalyst. No product formation was observed with complete retrieval of the starting material **13**.

3.5.2 Cobalt catalysed amination reaction of **3h**.



A vial with a septum cap was charged with the Co-catalyst (7 mg, 5 mol%), NaBARF₄ (15 mg, 5 mol%) and HFIP (2 ml). The mixture was stirred at room temperature for 1 minute. Next, azide **3h** (100 mg, 0.34 mmol) was added, the vial tightly sealed and the reaction mixture was heated to 90 °C and vigorously stirred for 48 h. After completion the crude reaction mixture was filtered through a pad of silica gel eluting with EtOAc. The filtrate was concentrated under vacuo and crude ¹H NMR was measured. Formation of the desired product was not observed. The procedure was adapted from: Lee, J.; Lee, J.; Jung, H.; Kim, D.; Park, J.; Chang, S. *J. Am. Chem. Soc.* **2020**, 142, 12324-12332.

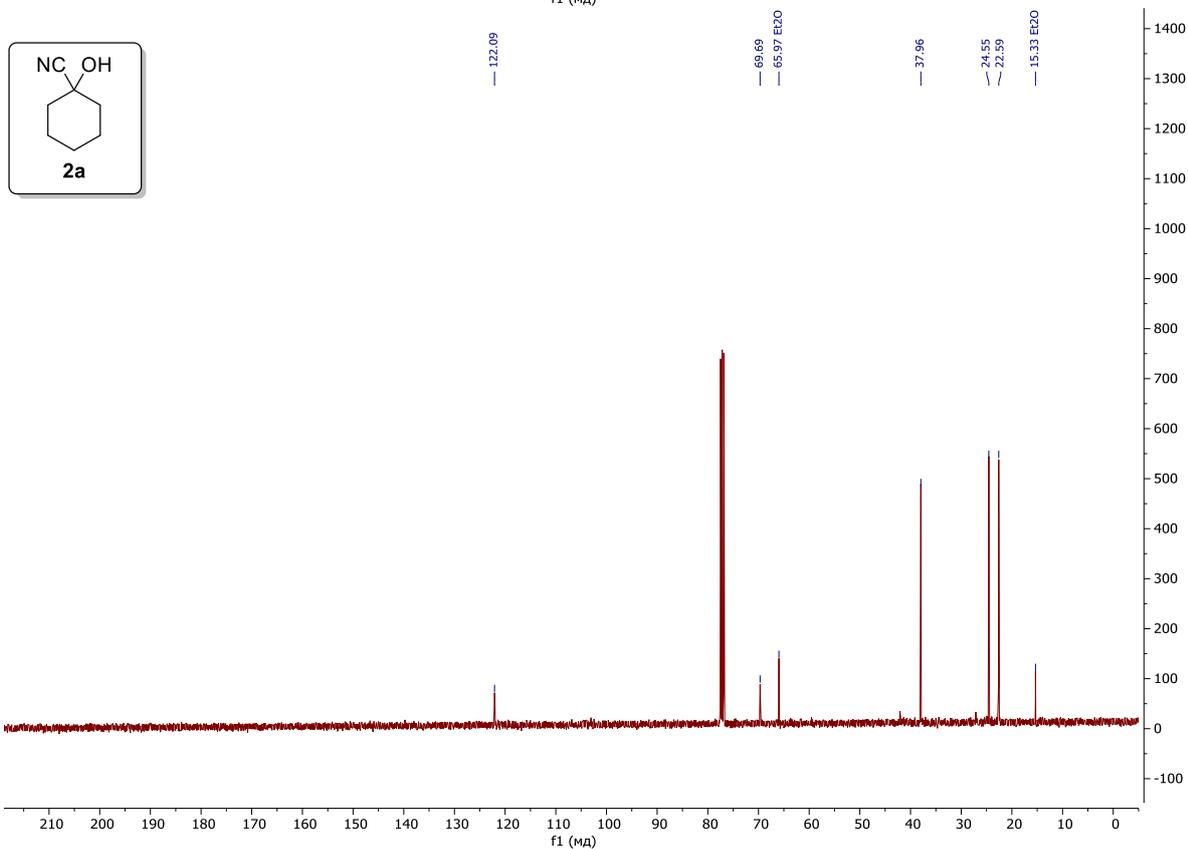
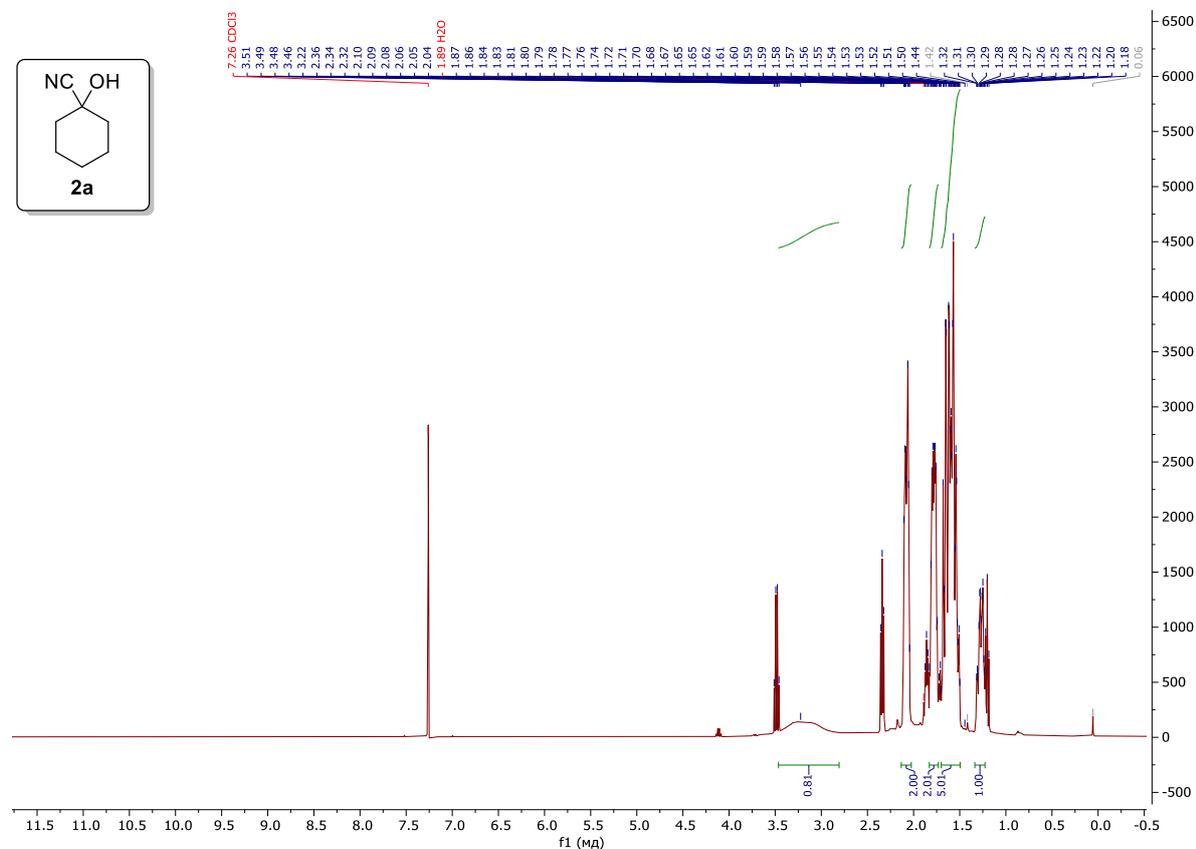
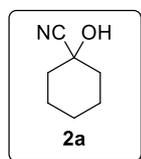
3.5.3 UV initiated amination reaction of **3h**



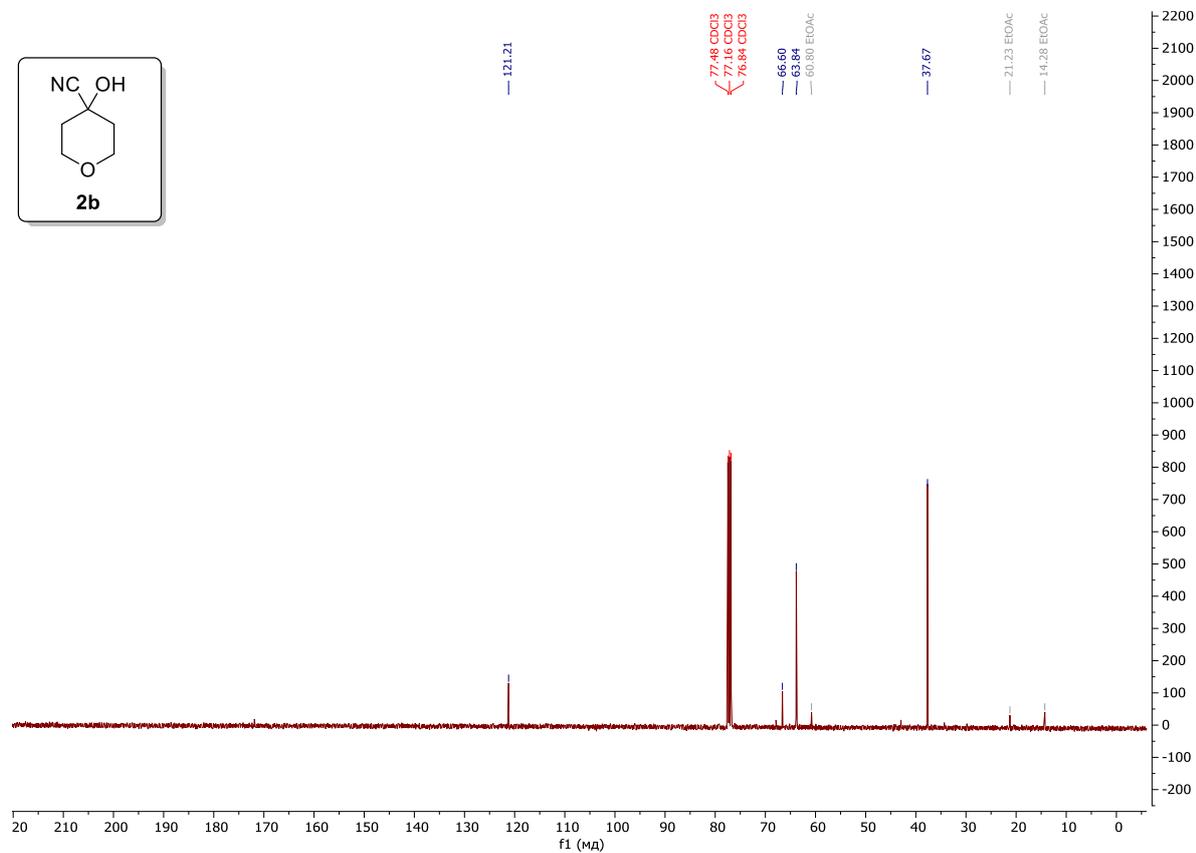
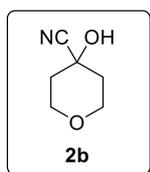
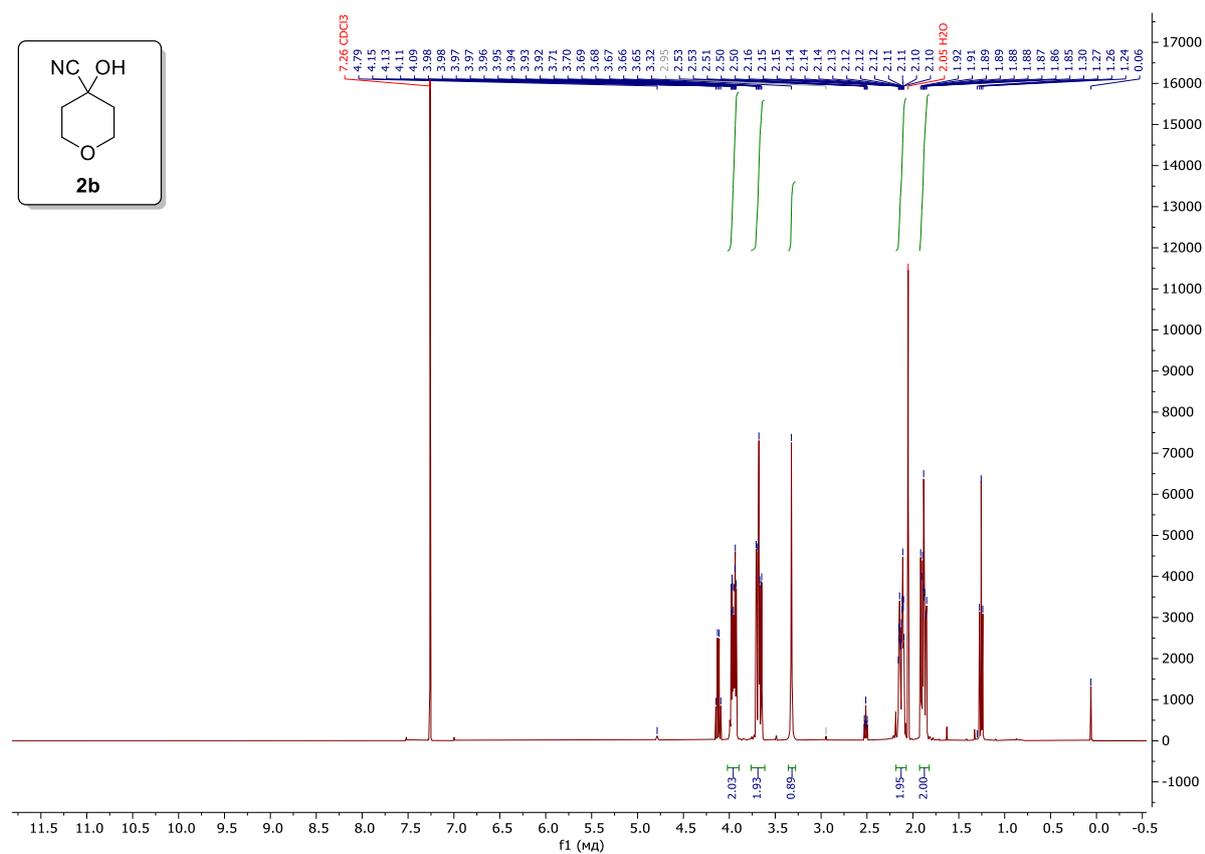
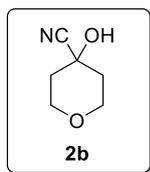
A quartz cuvette was charged with azide **3h** (20 mg, 0.067 mmol) and a stirbar, flushed with argon and anhydrous DCM (1 ml) was added. The cuvette was sealed with a septum connected to a argon balloon. The mixture was stirred and irradiated with a mercury lamp (254 nm). Progress of the reaction was monitored by TLC. Upon completion (3 h), DCM was evaporated under vacuo and the crude ¹H NMR was measured. The ratio of **4h1** and **4h2** was established to be 1:1.3 respectively, which is identical to the ratio of the thermal amination reaction.

4. NMR spectra of compounds 2-12

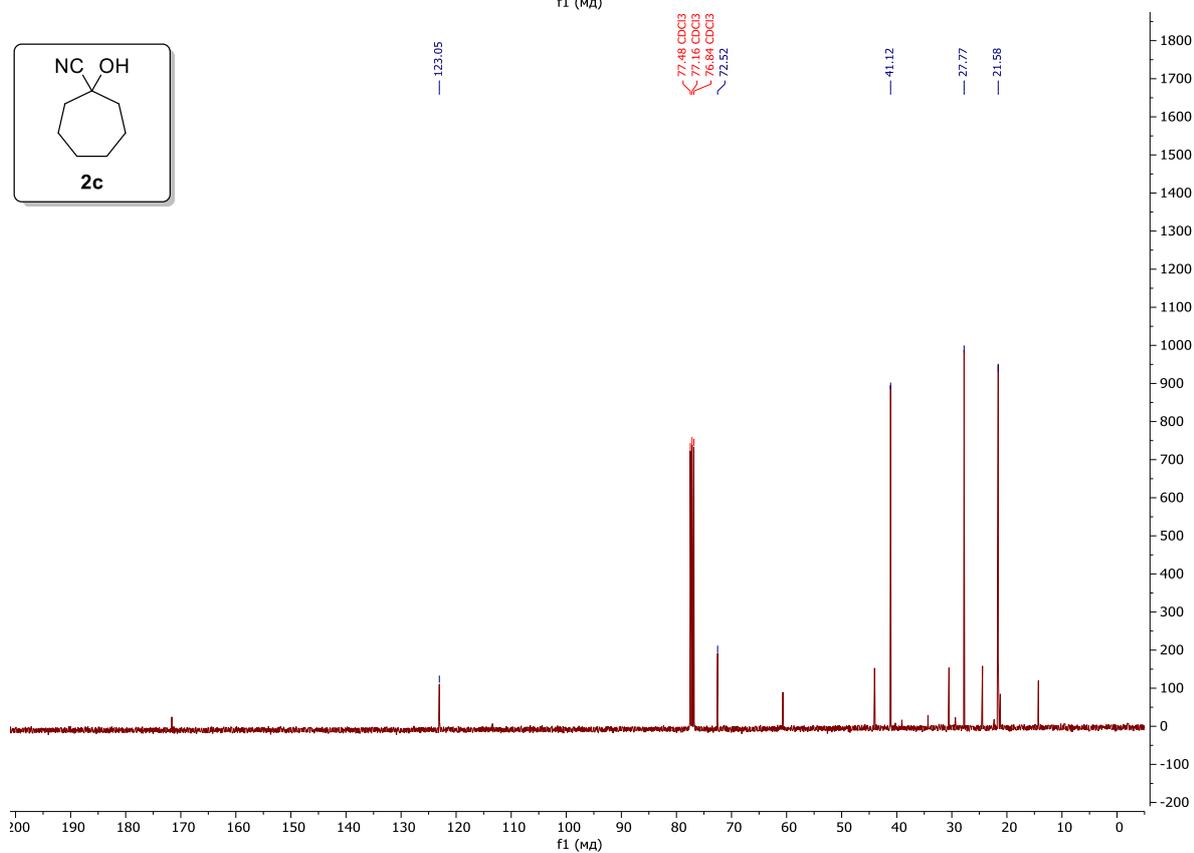
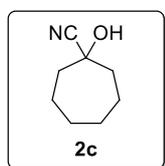
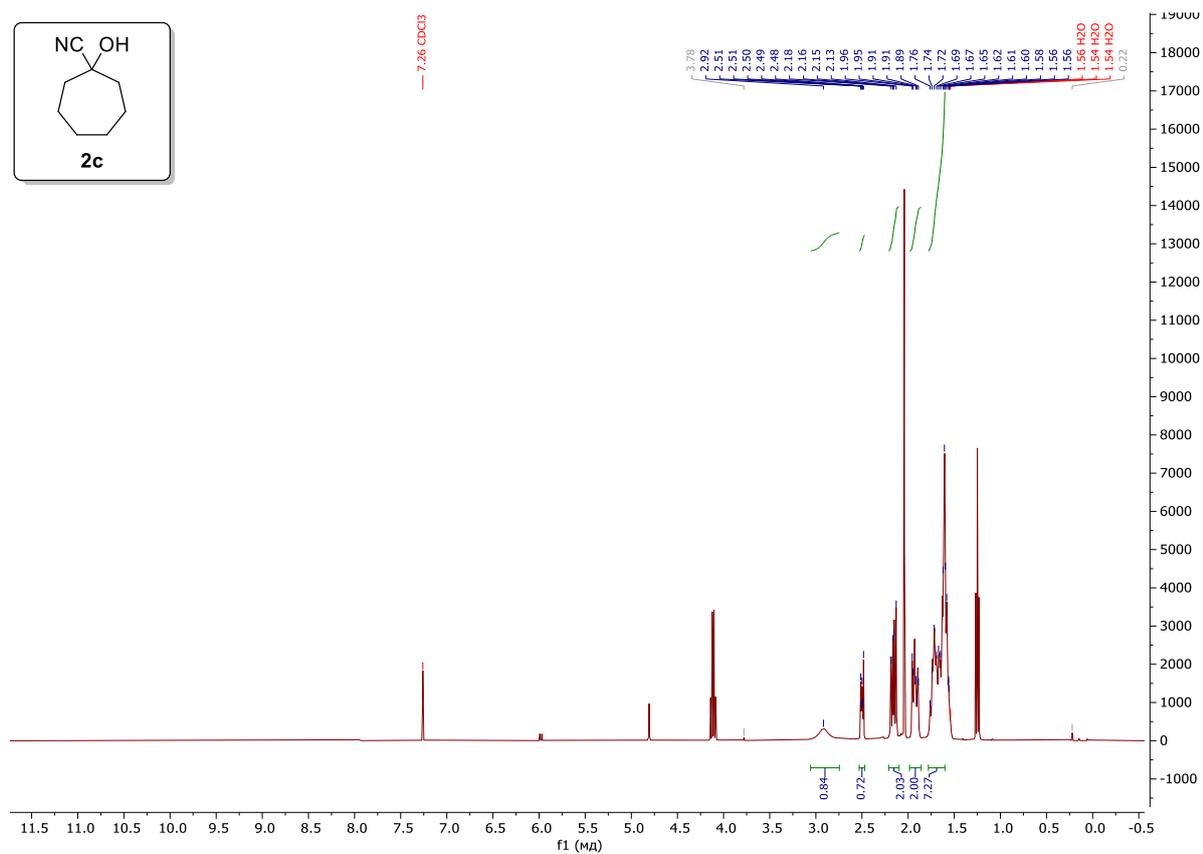
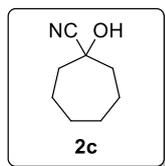
Compound 2



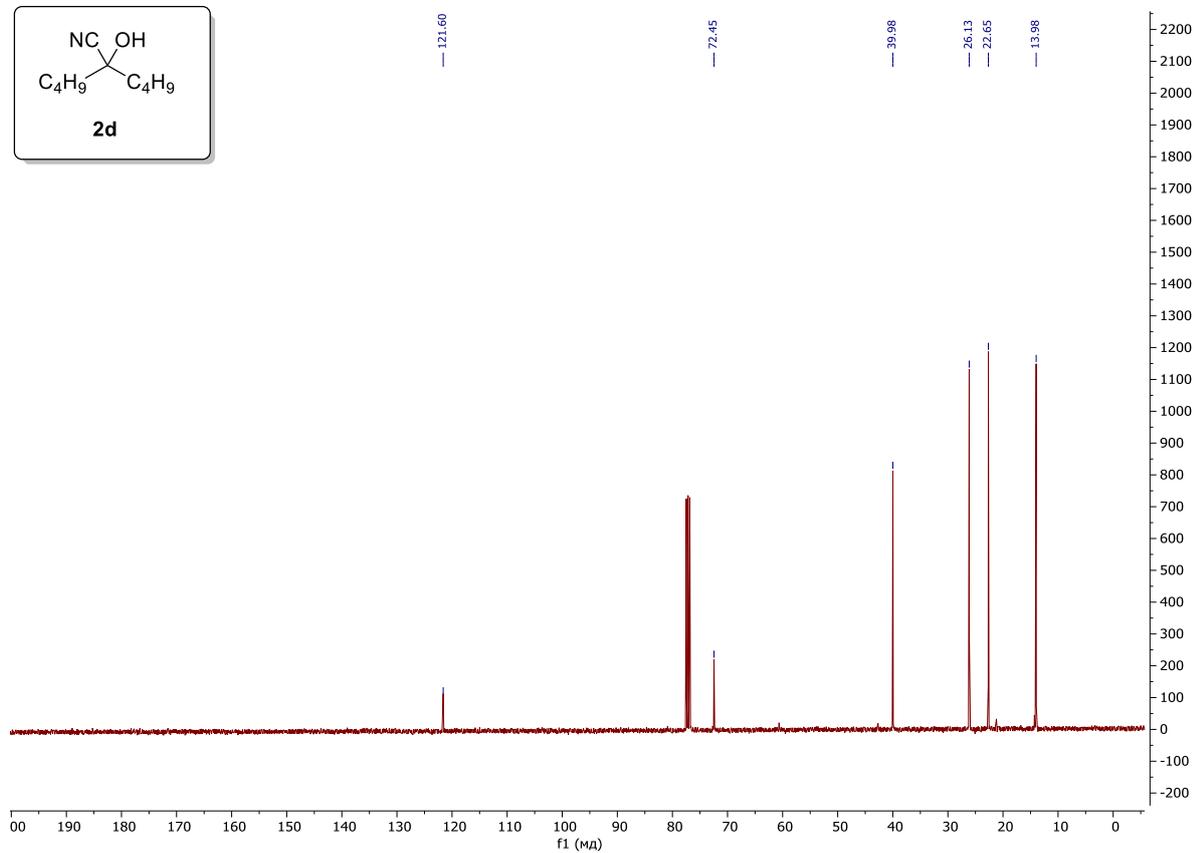
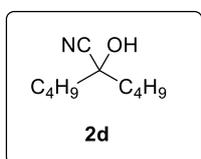
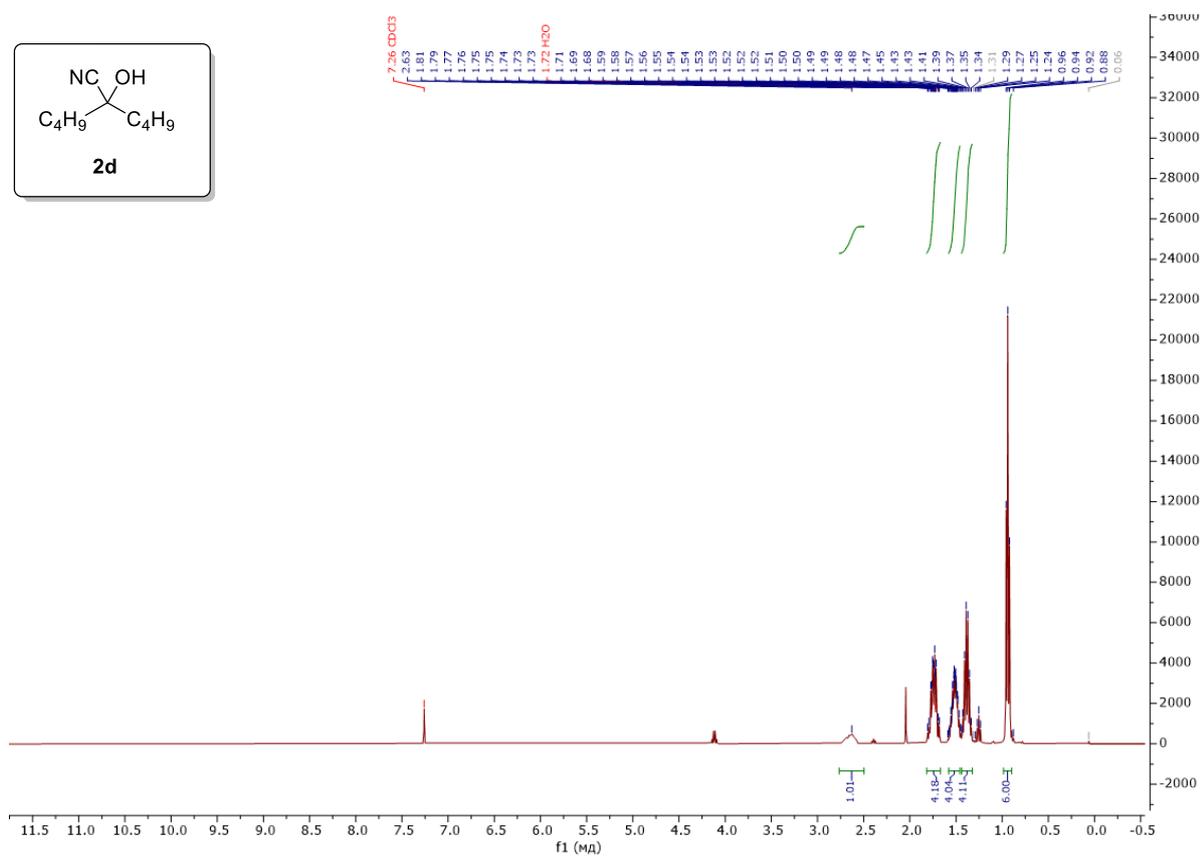
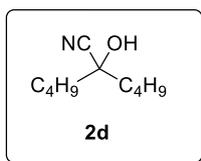
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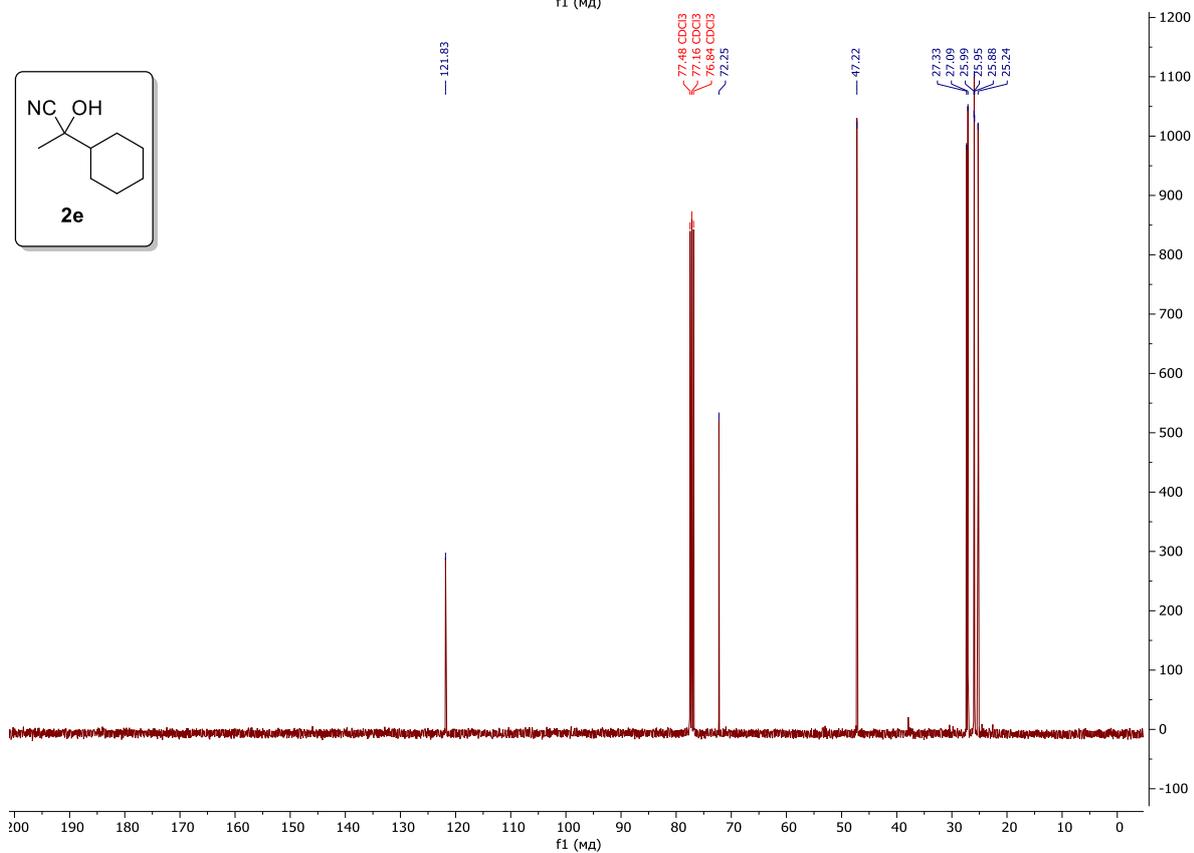
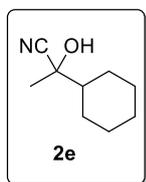
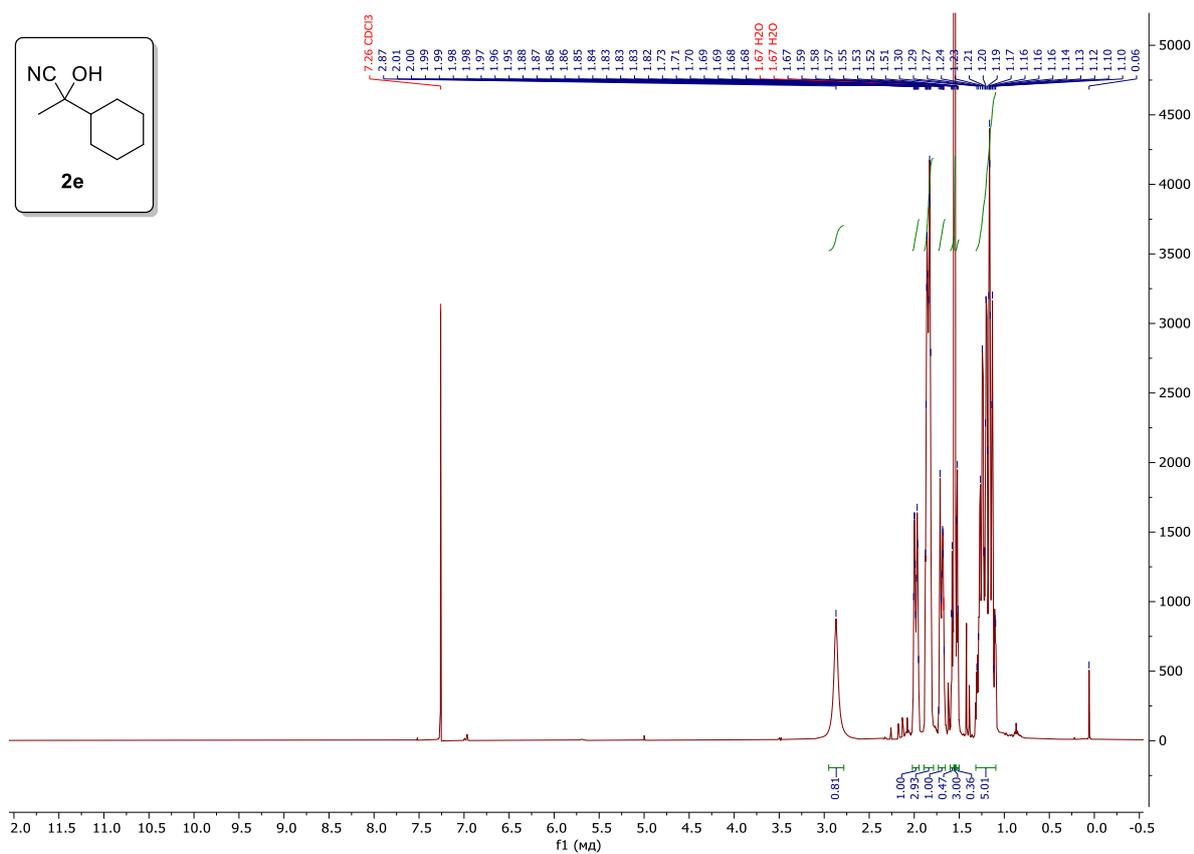
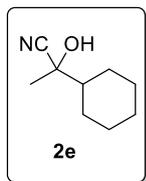
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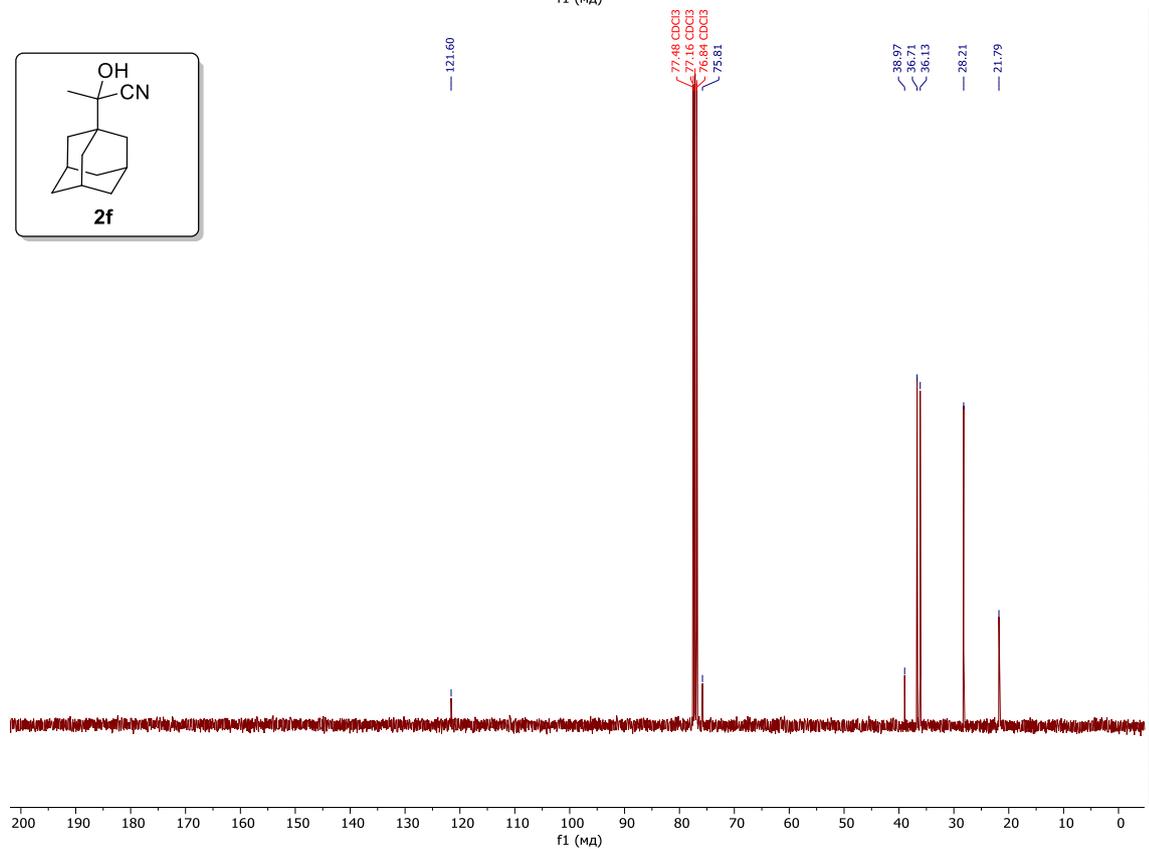
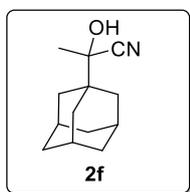
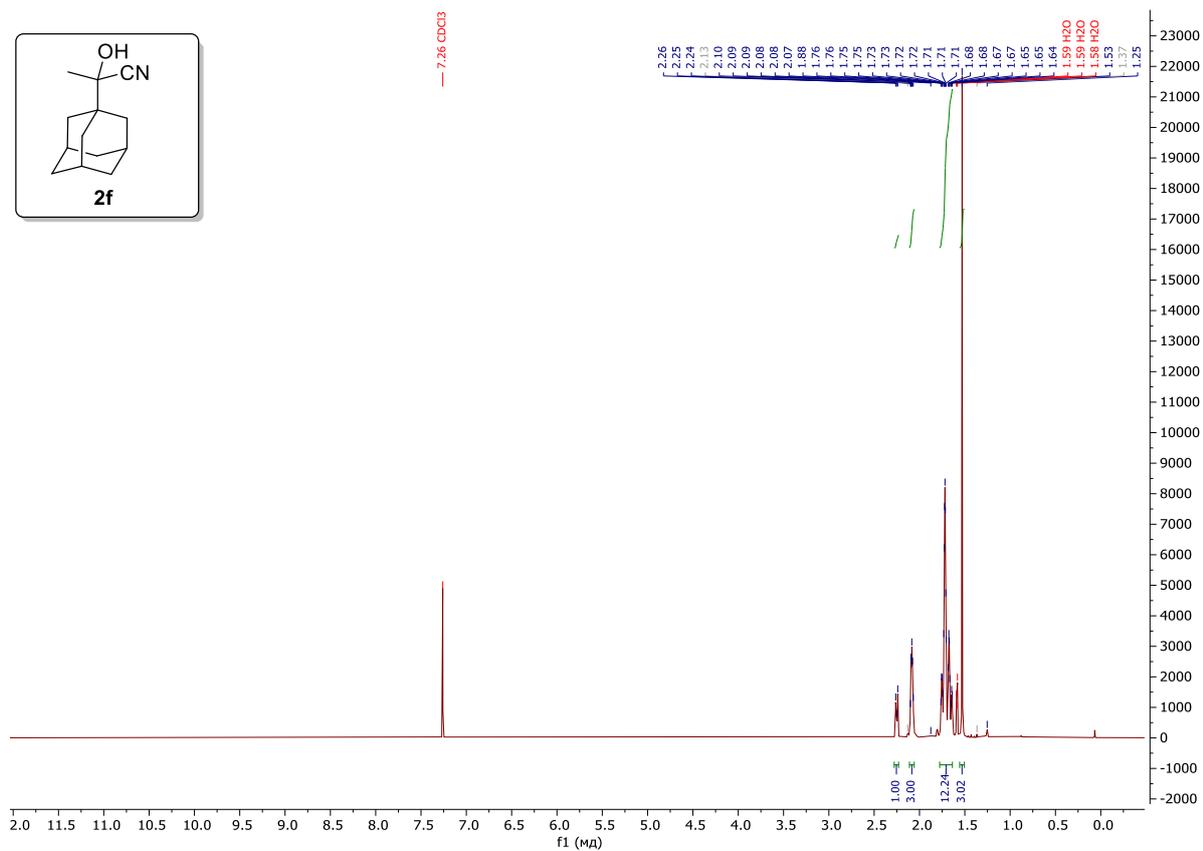
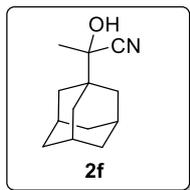
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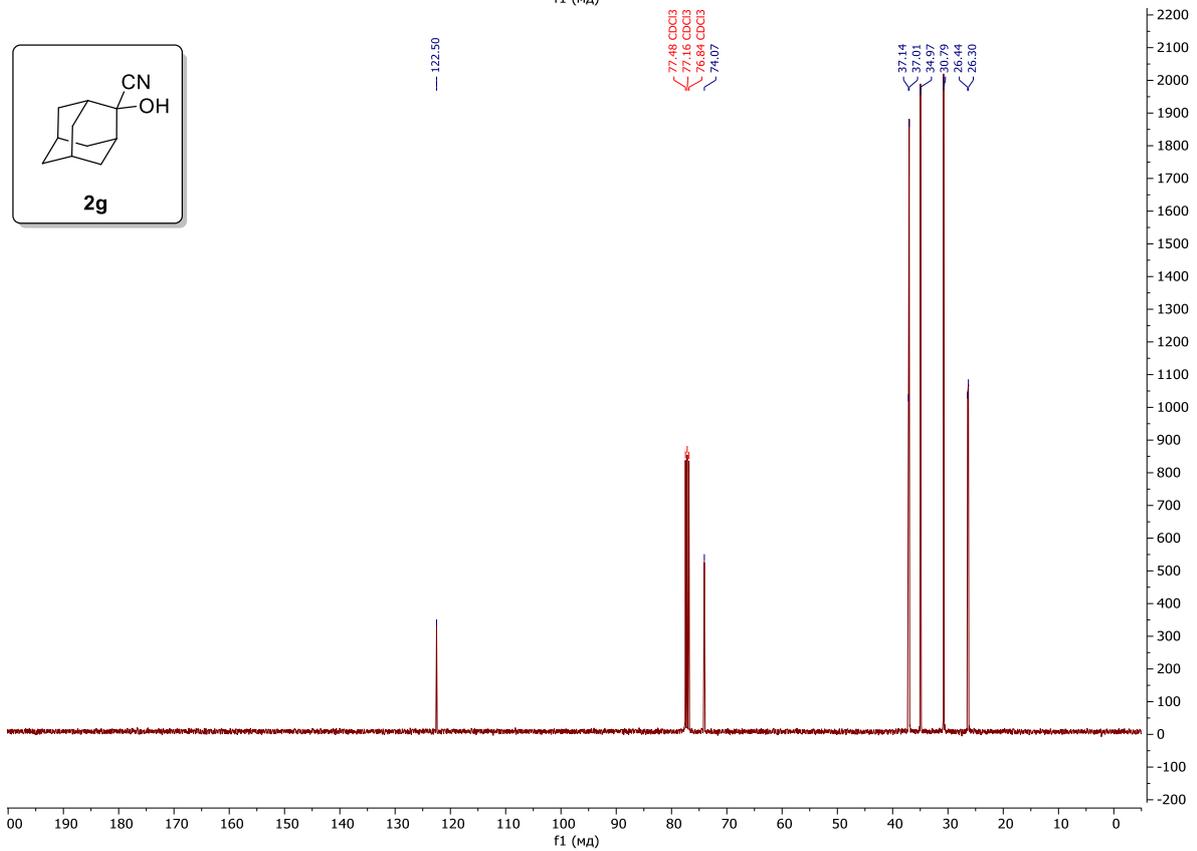
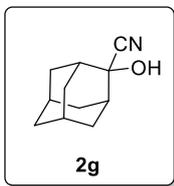
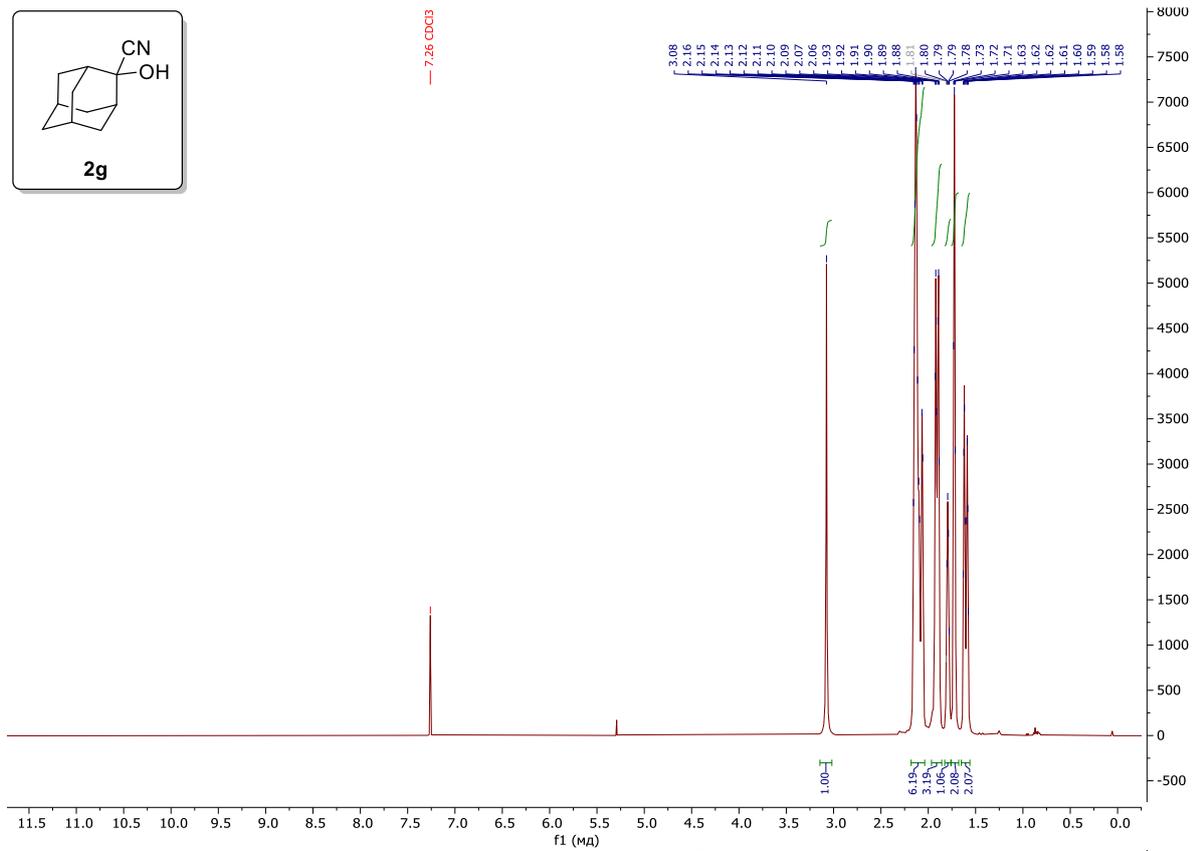
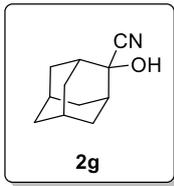
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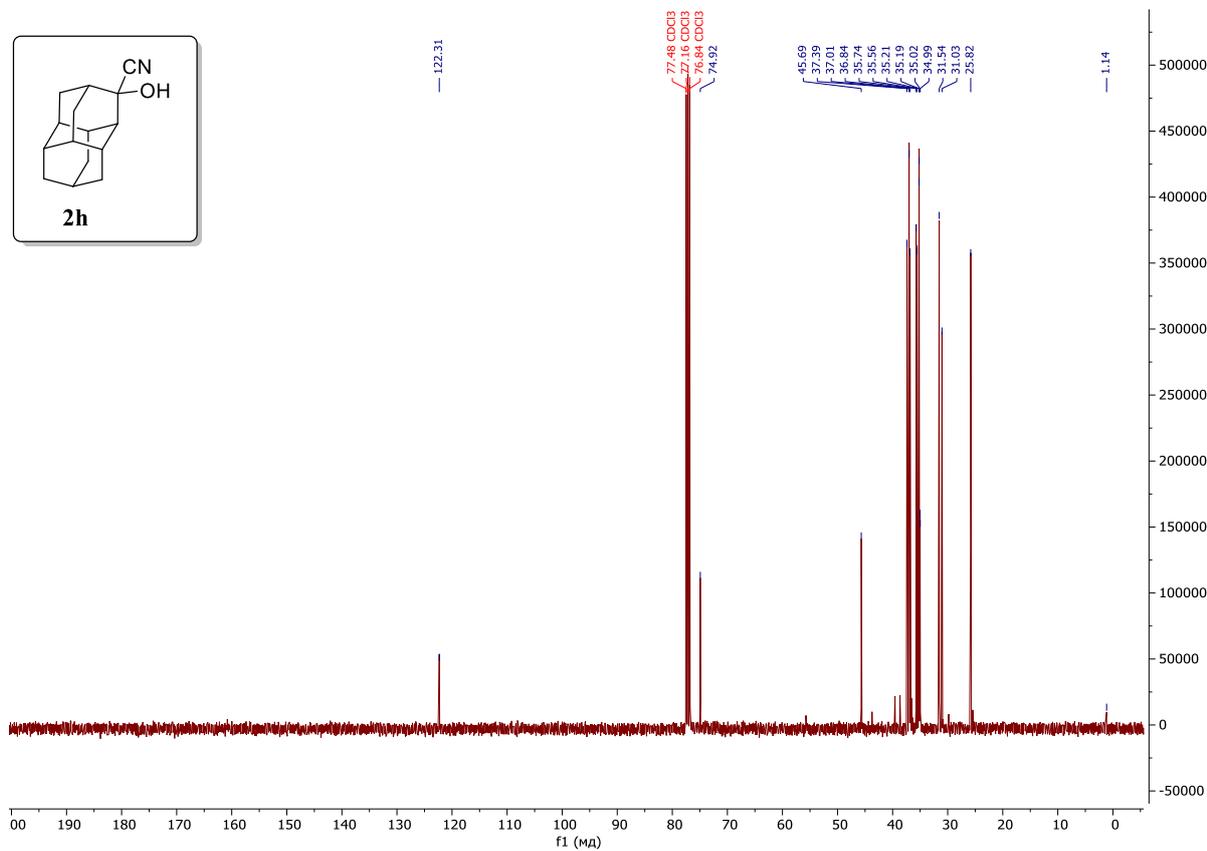
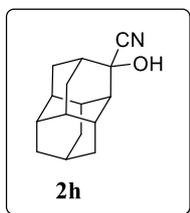
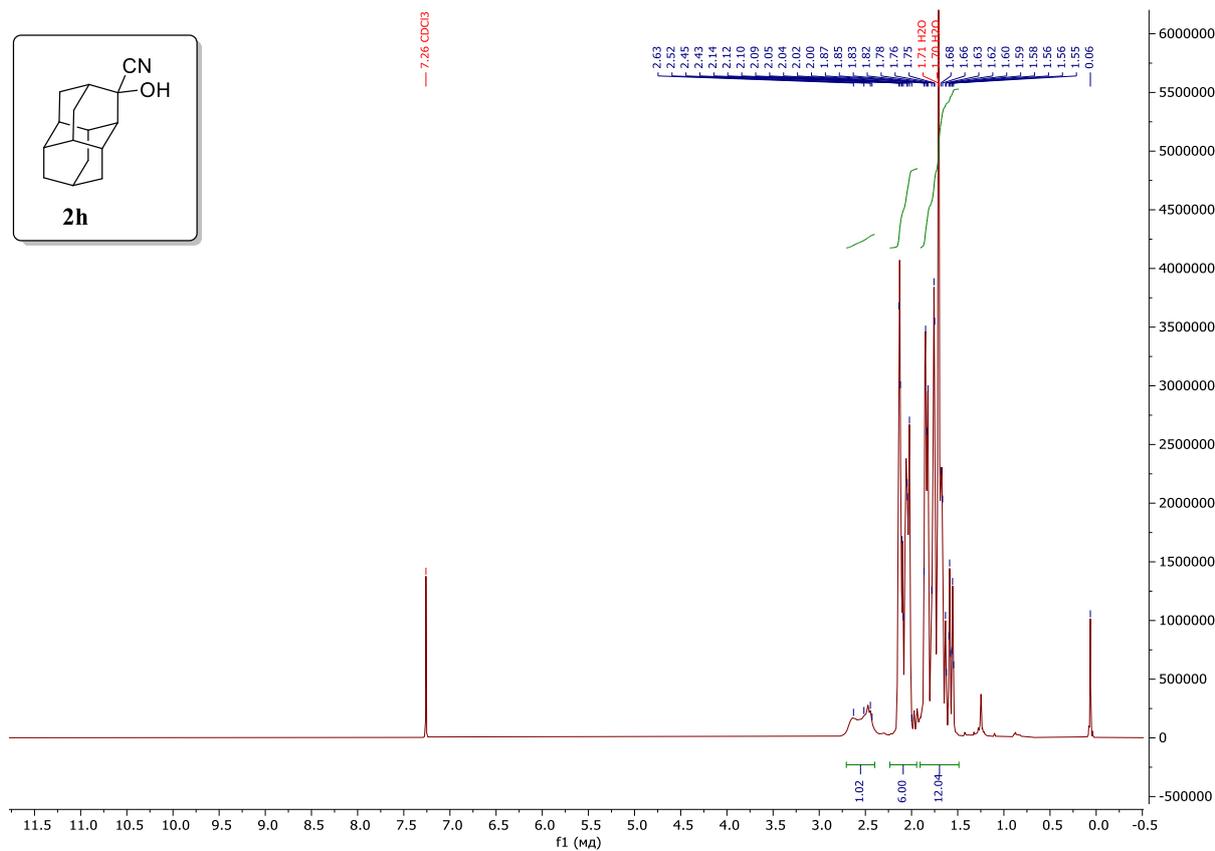
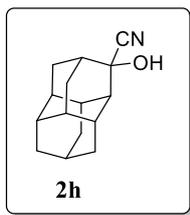
Compound 2f



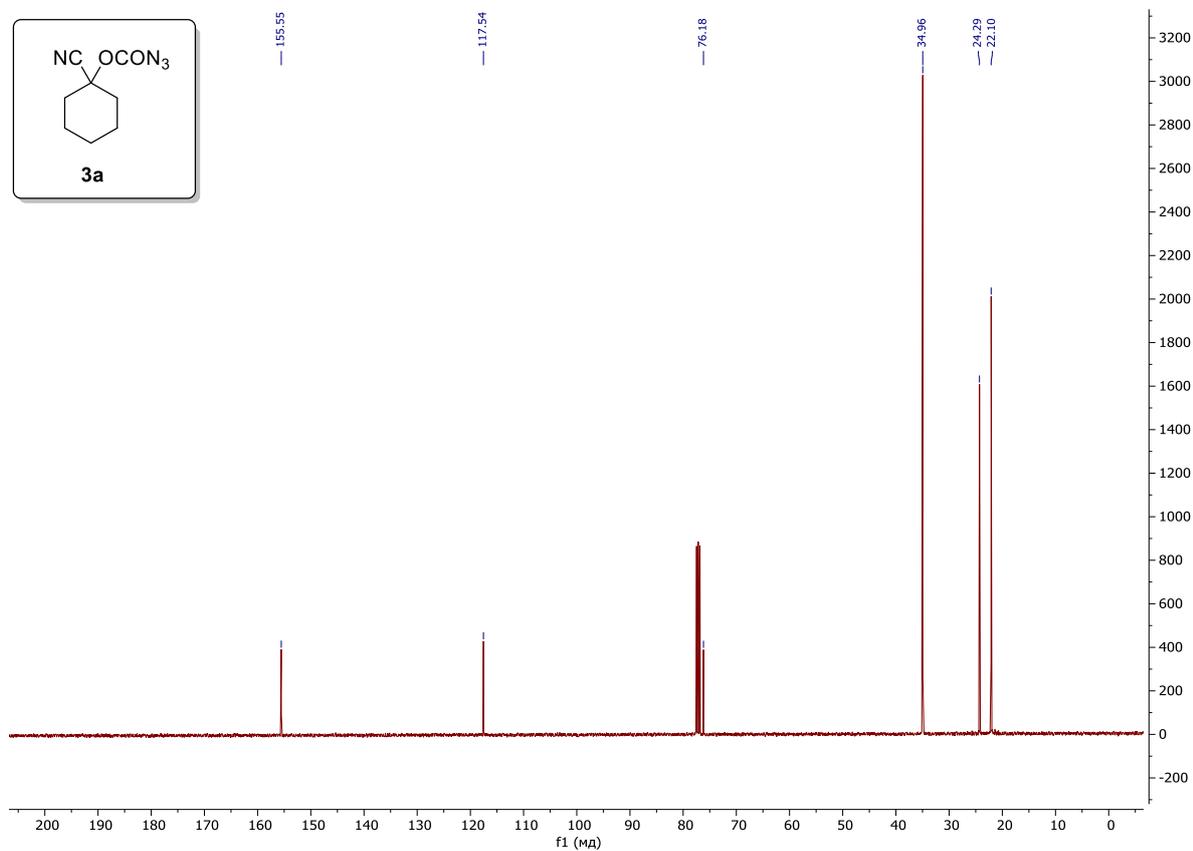
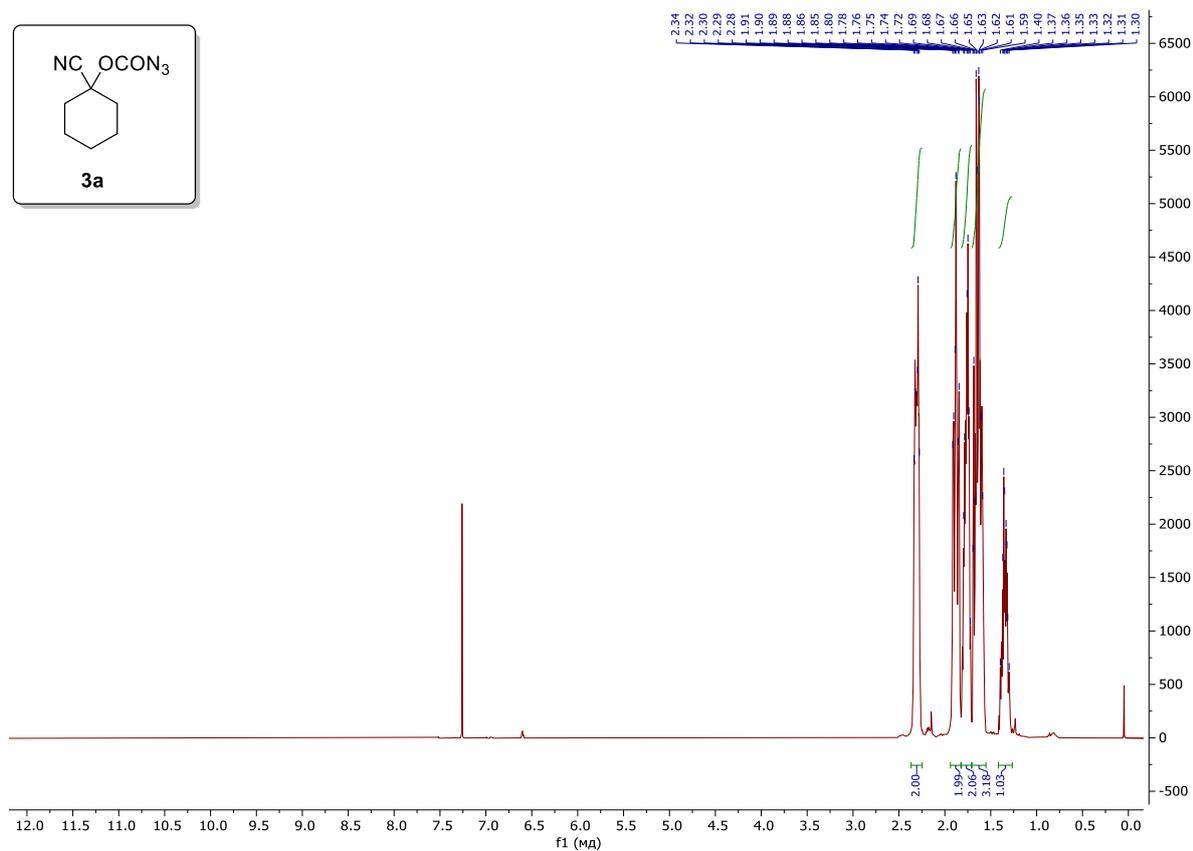
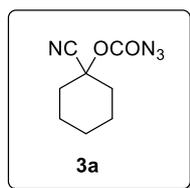
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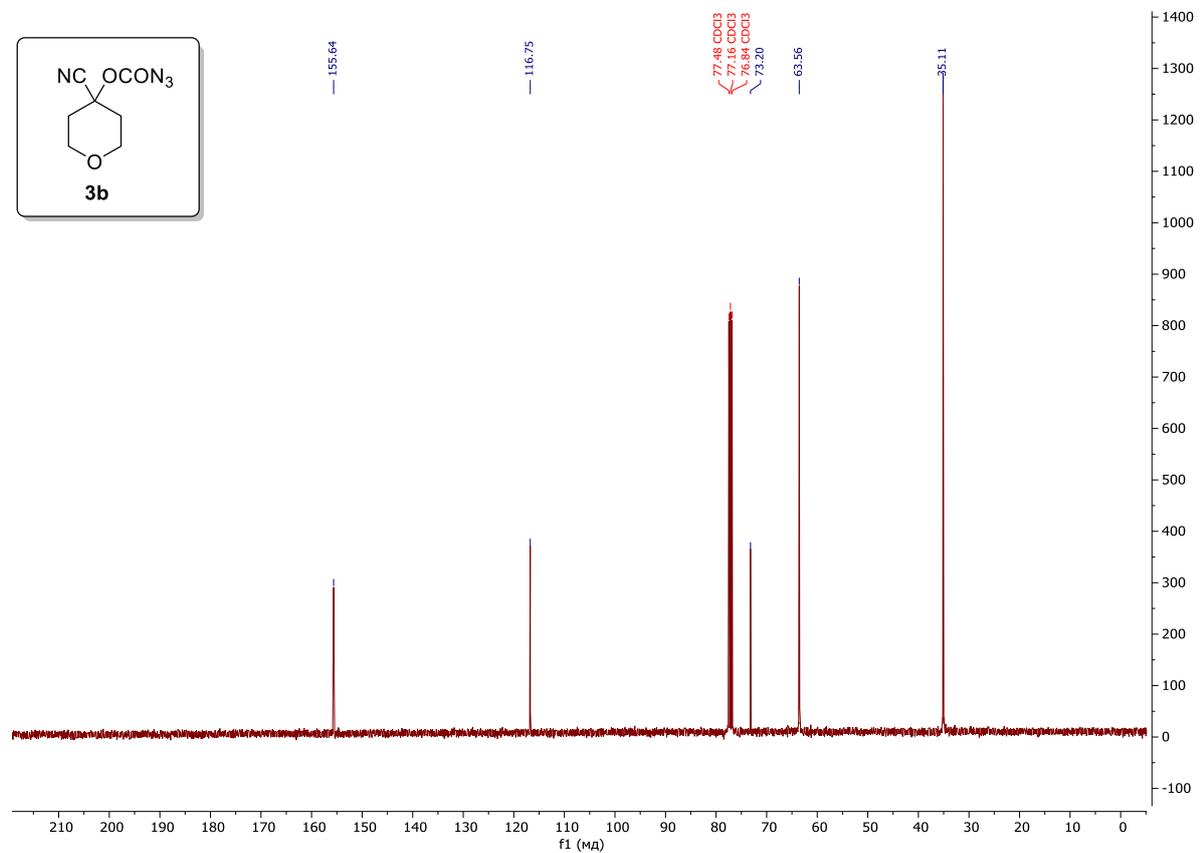
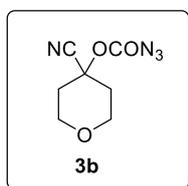
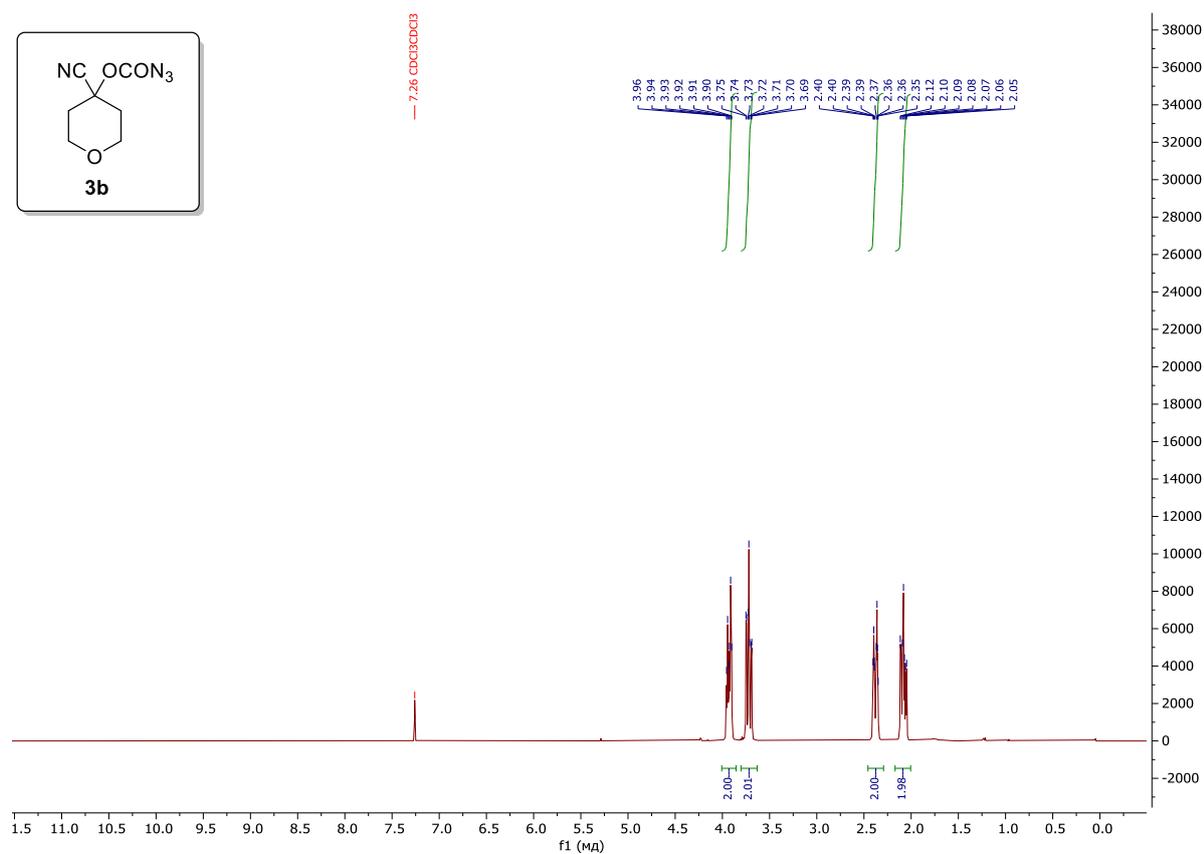
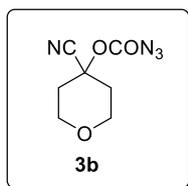
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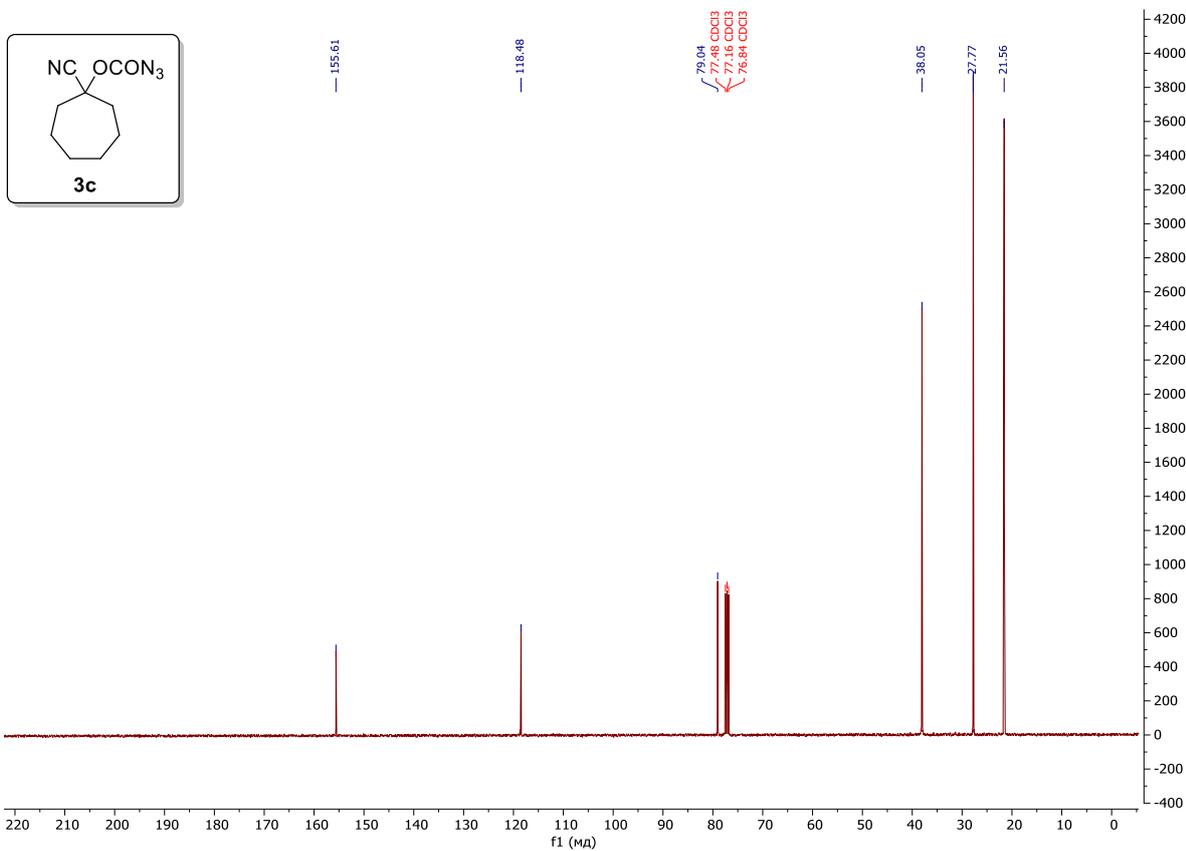
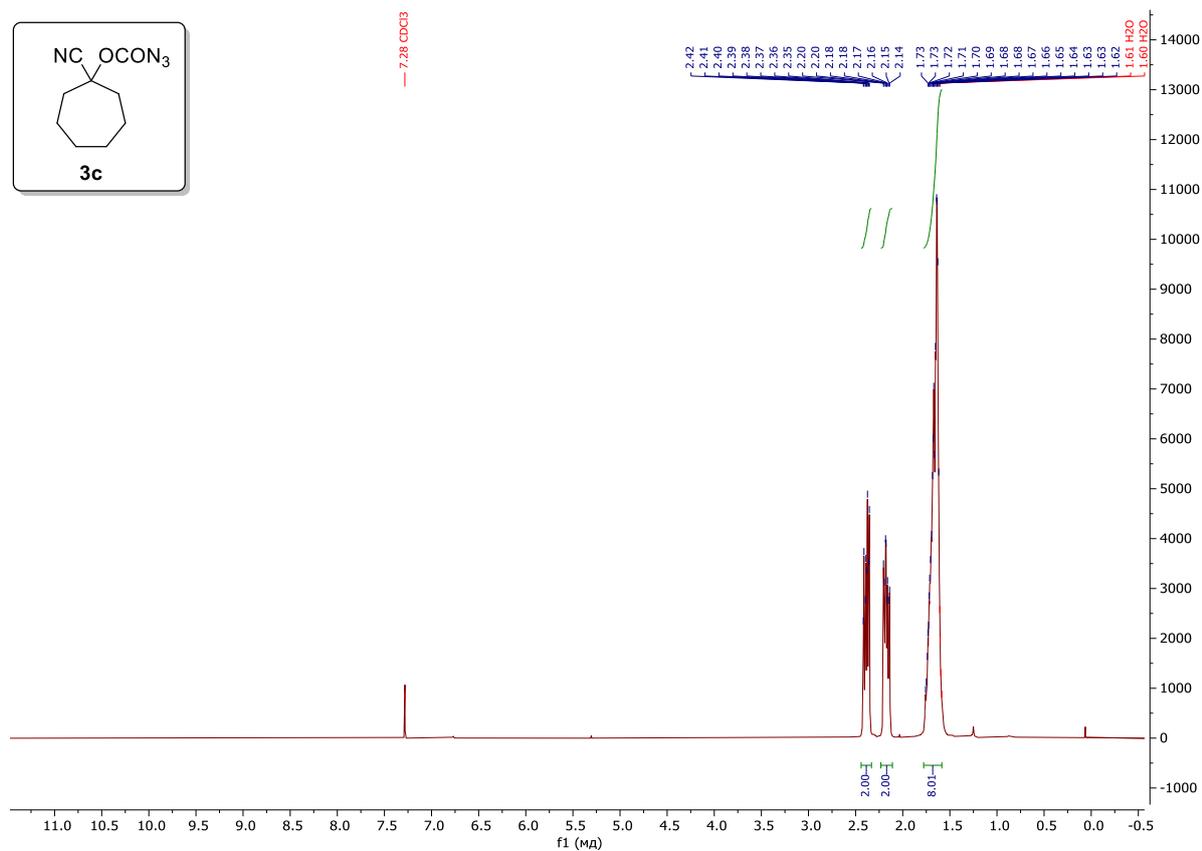
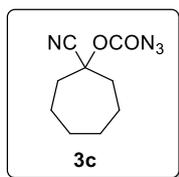
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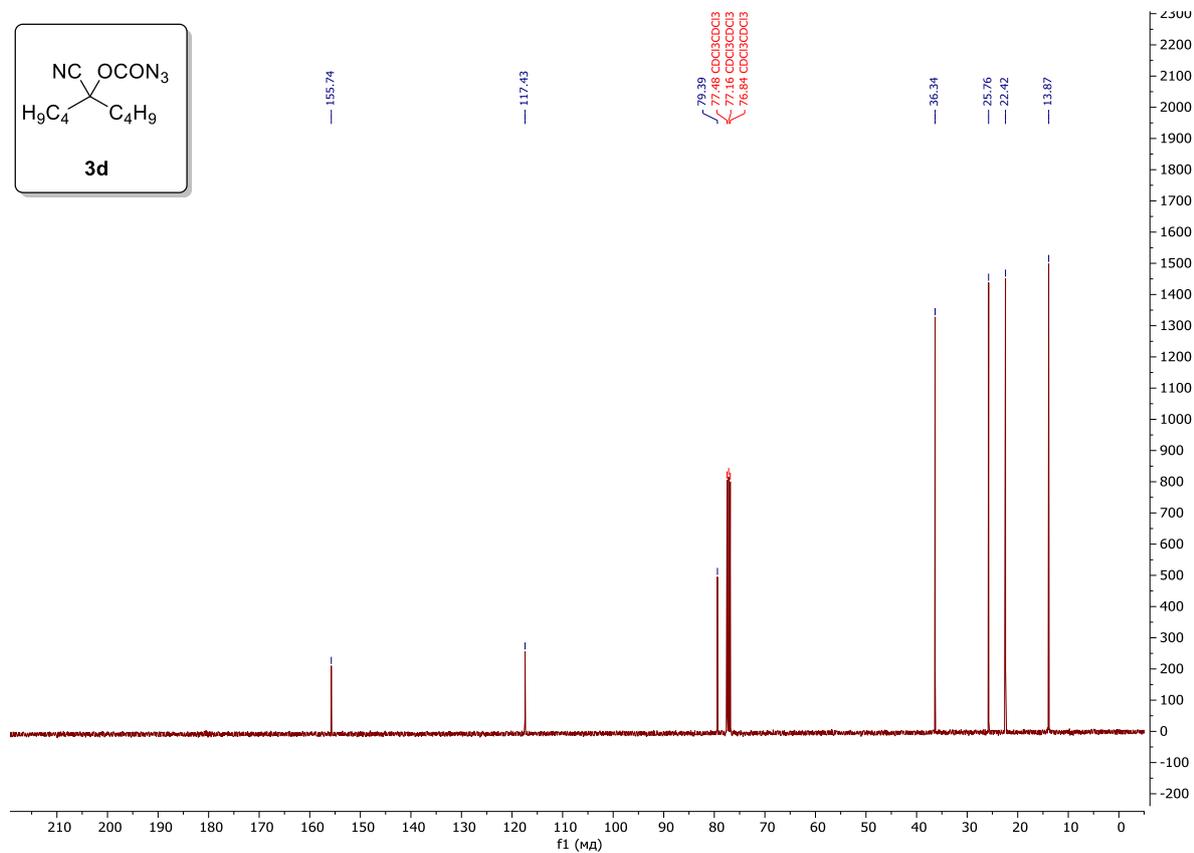
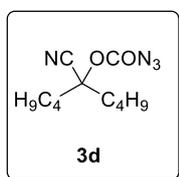
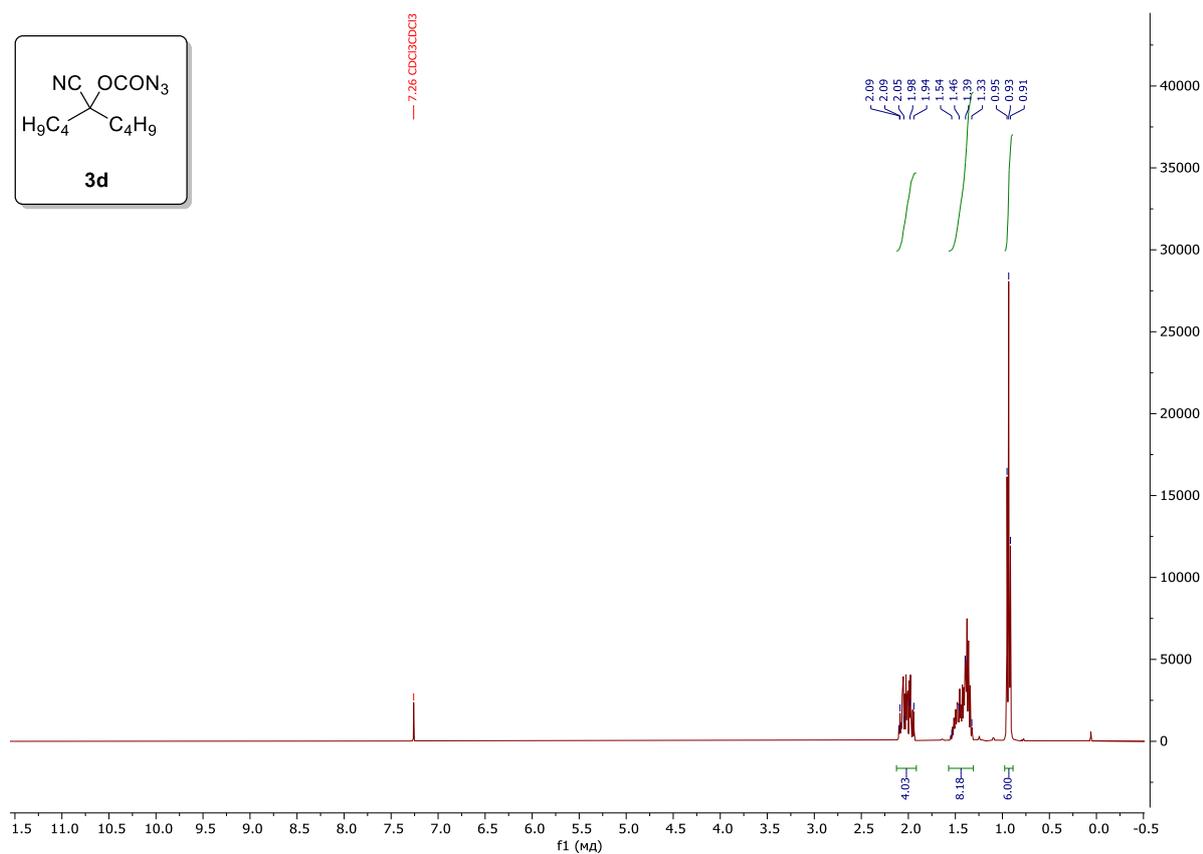
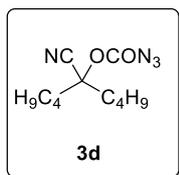
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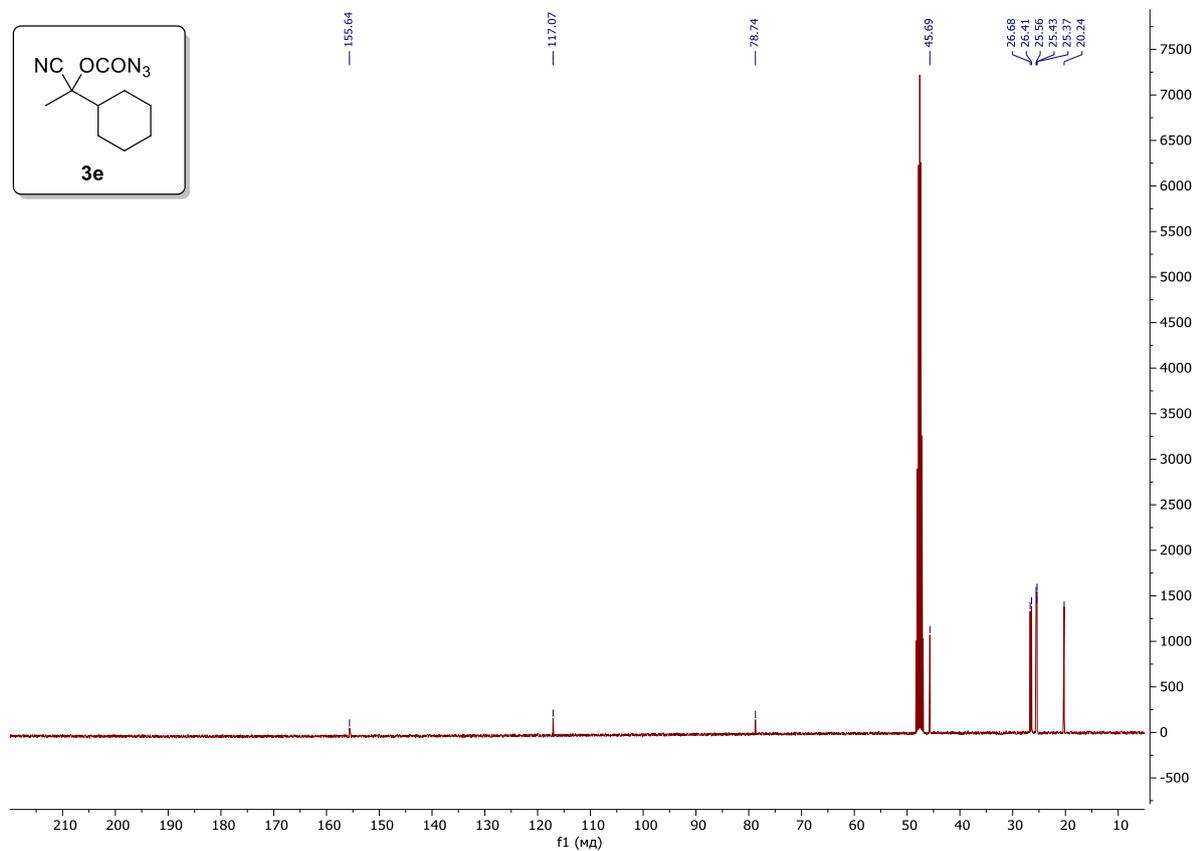
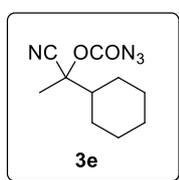
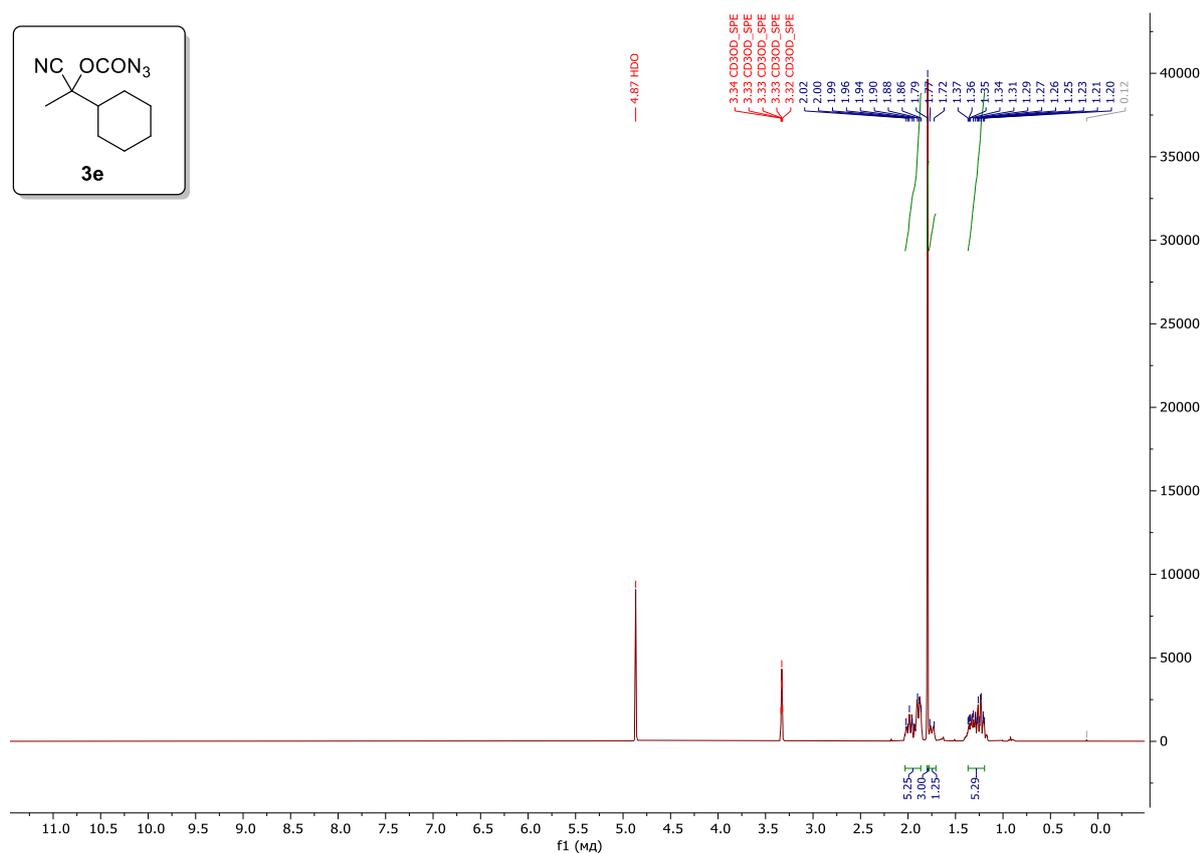
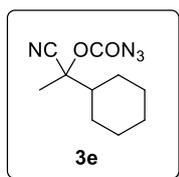
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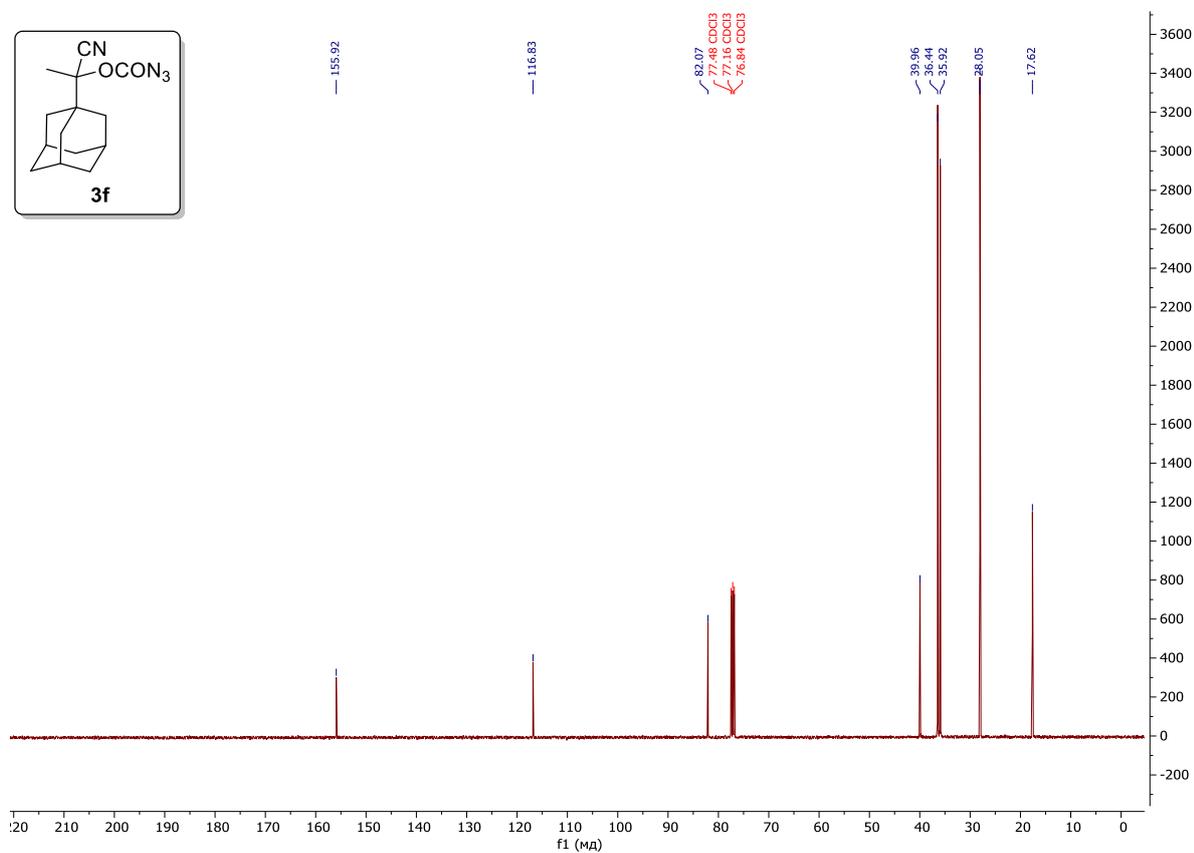
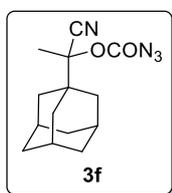
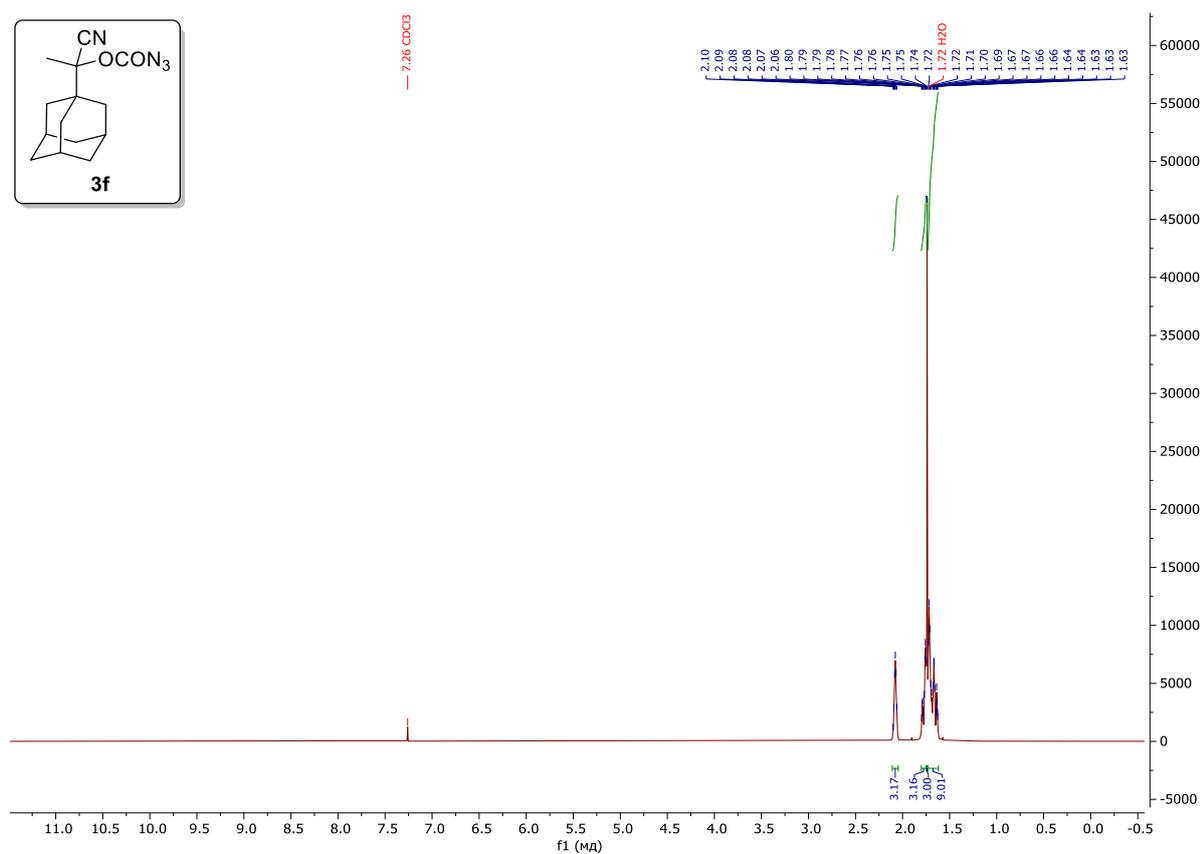
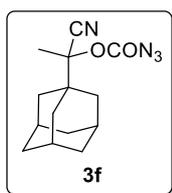
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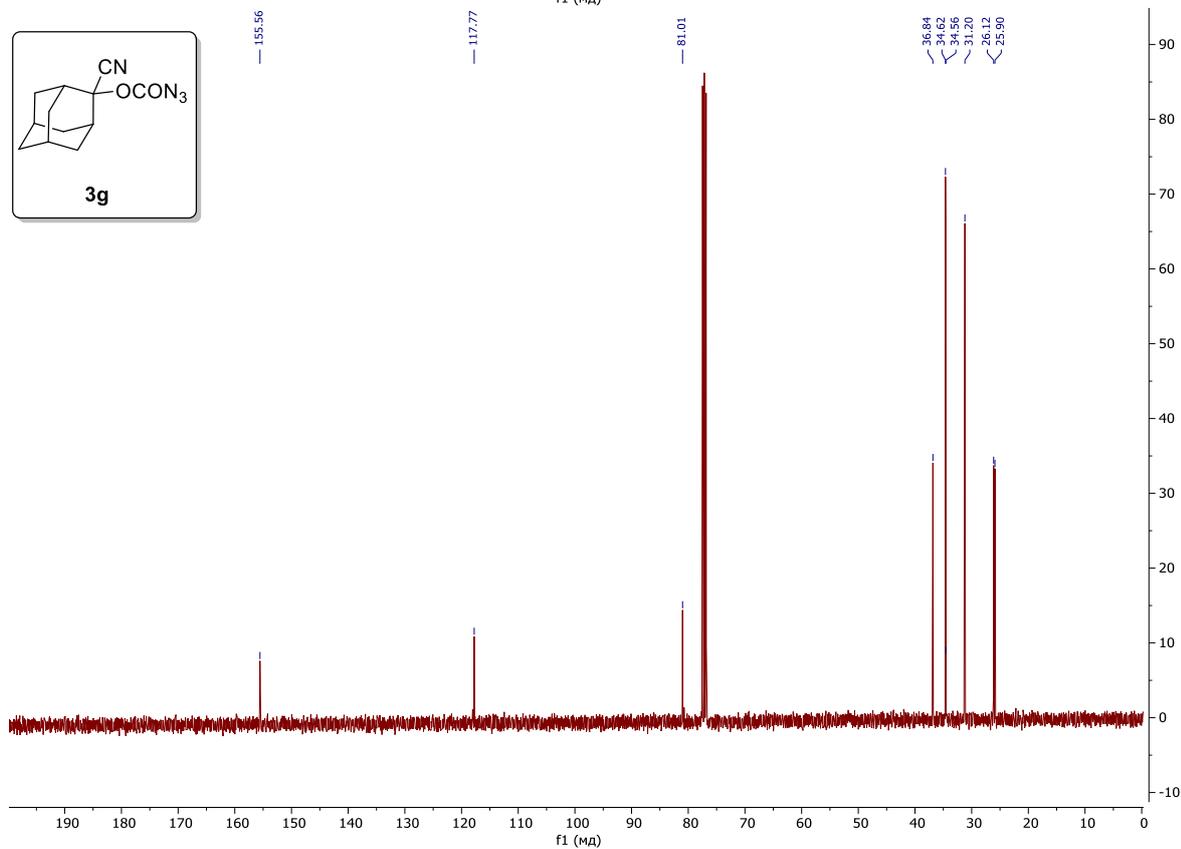
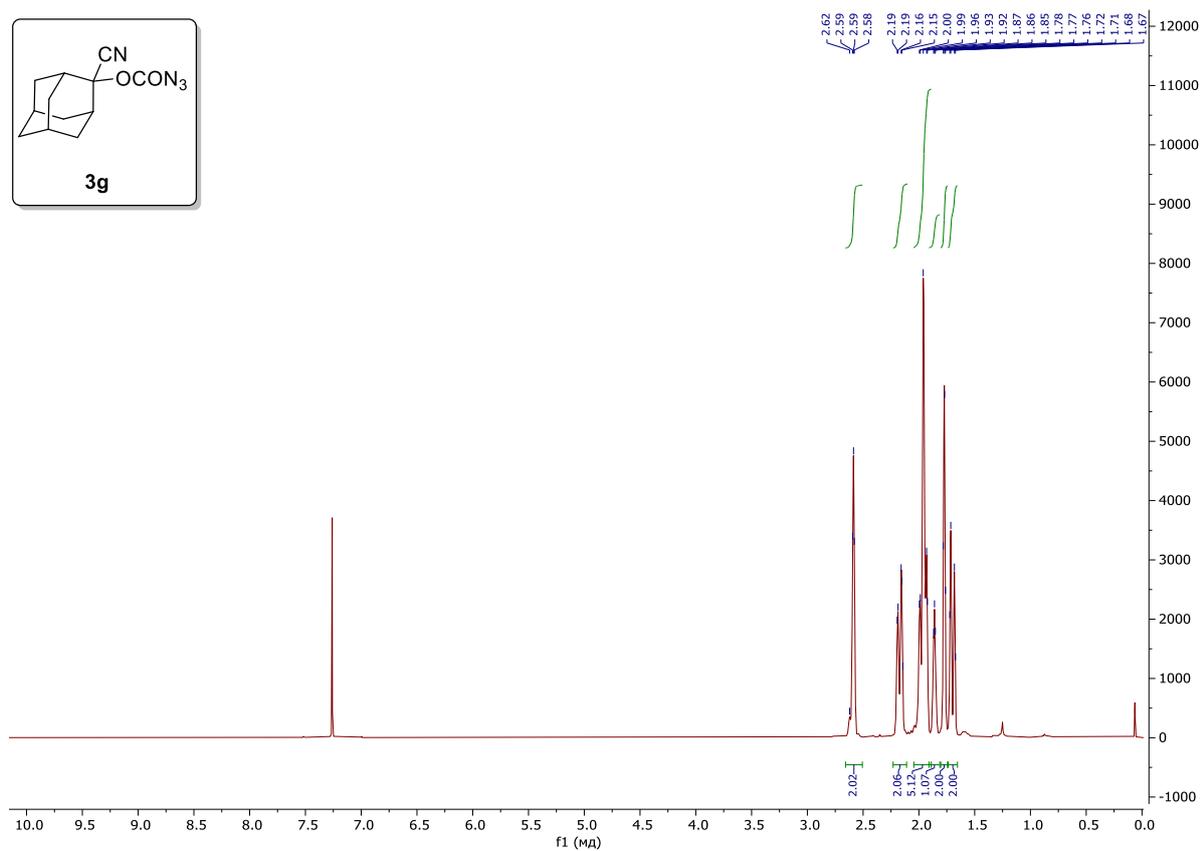
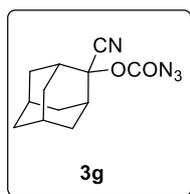
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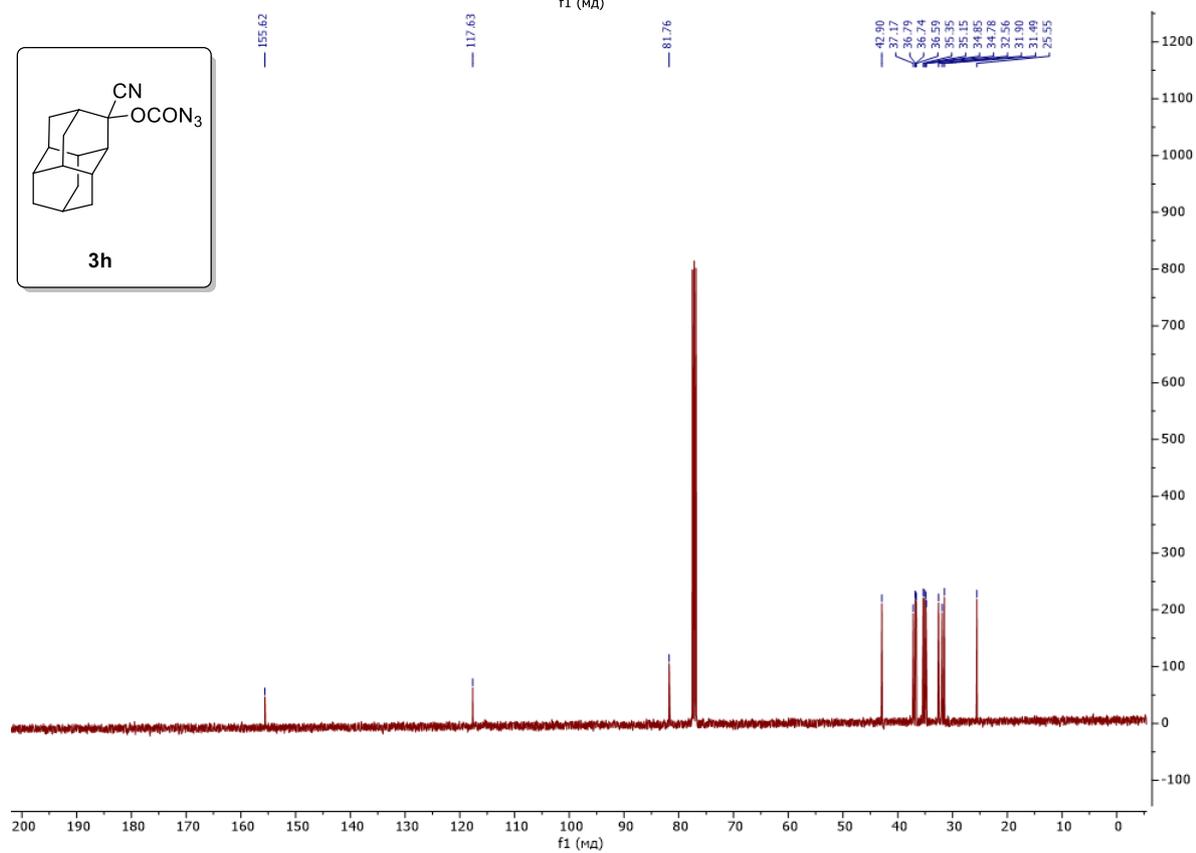
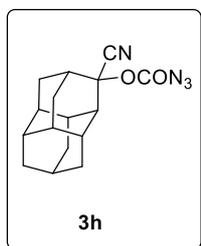
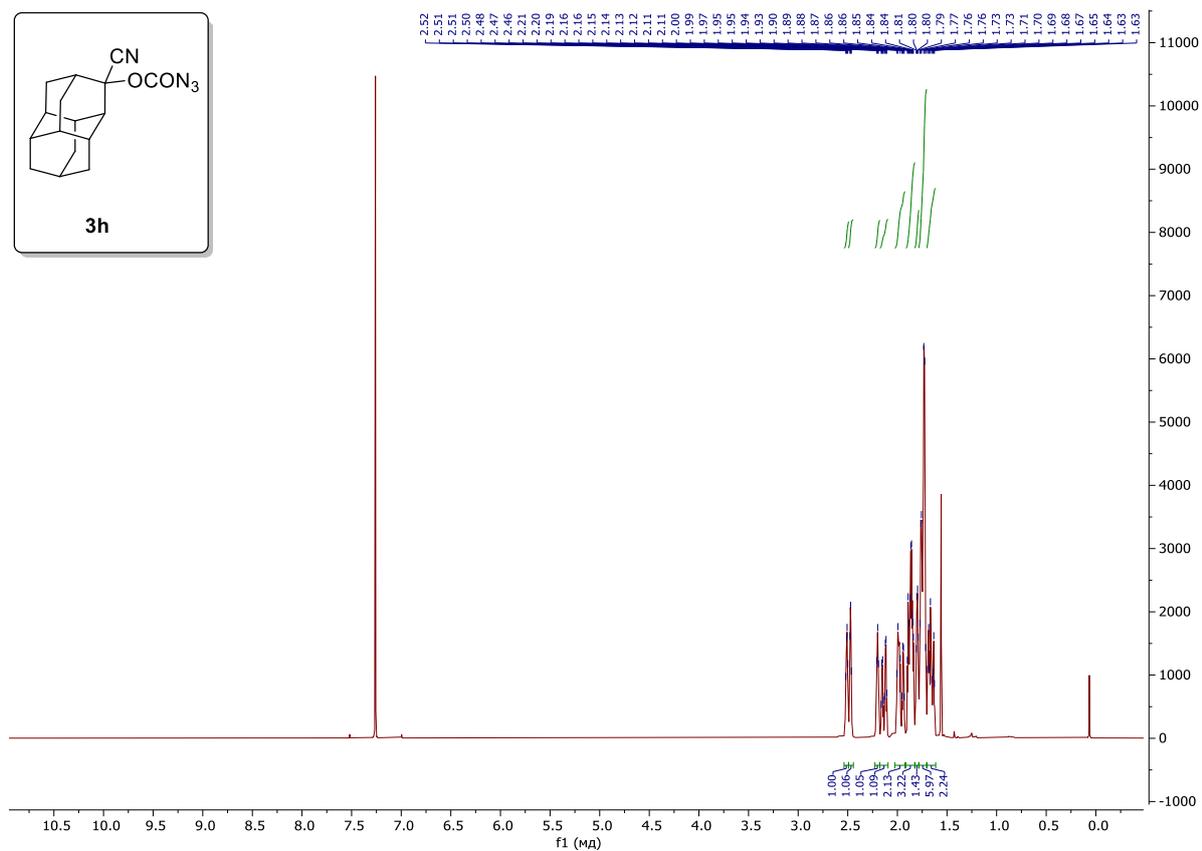
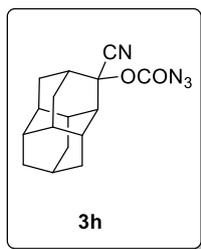
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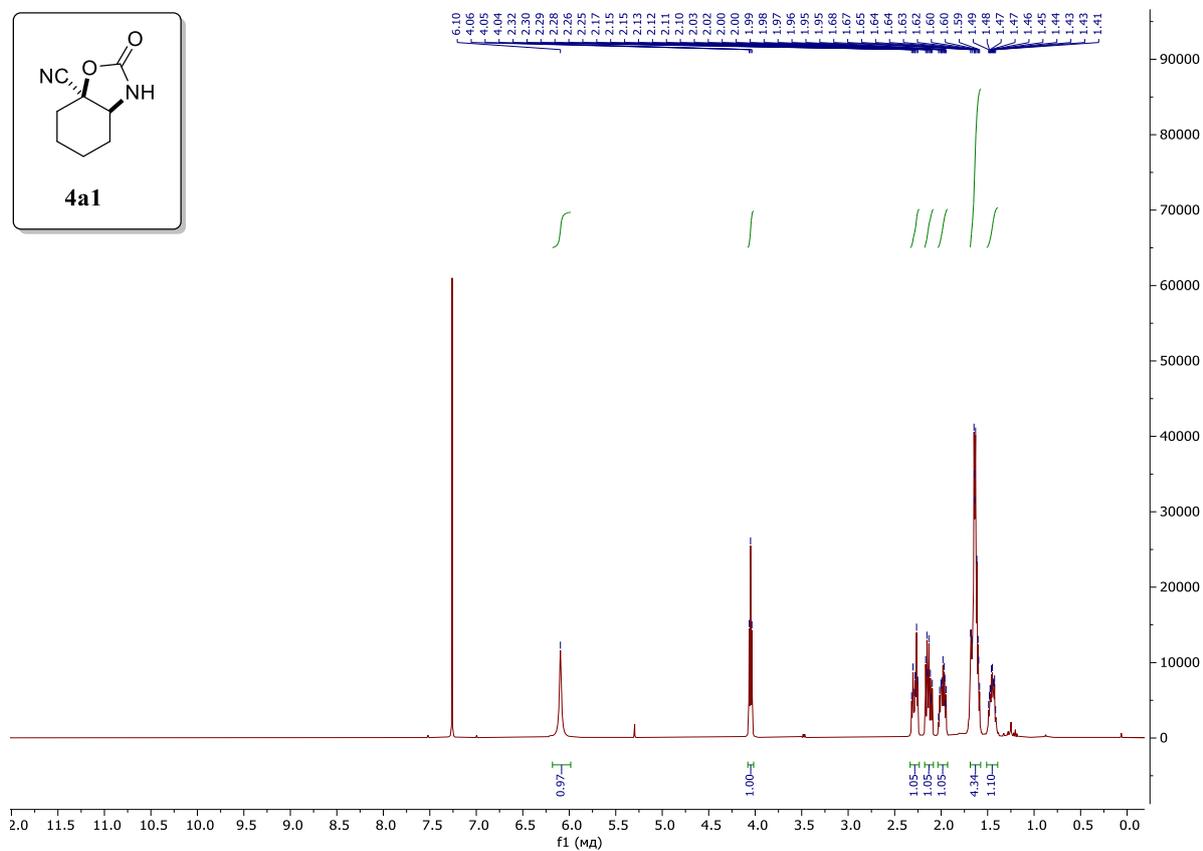
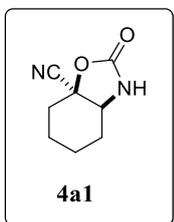
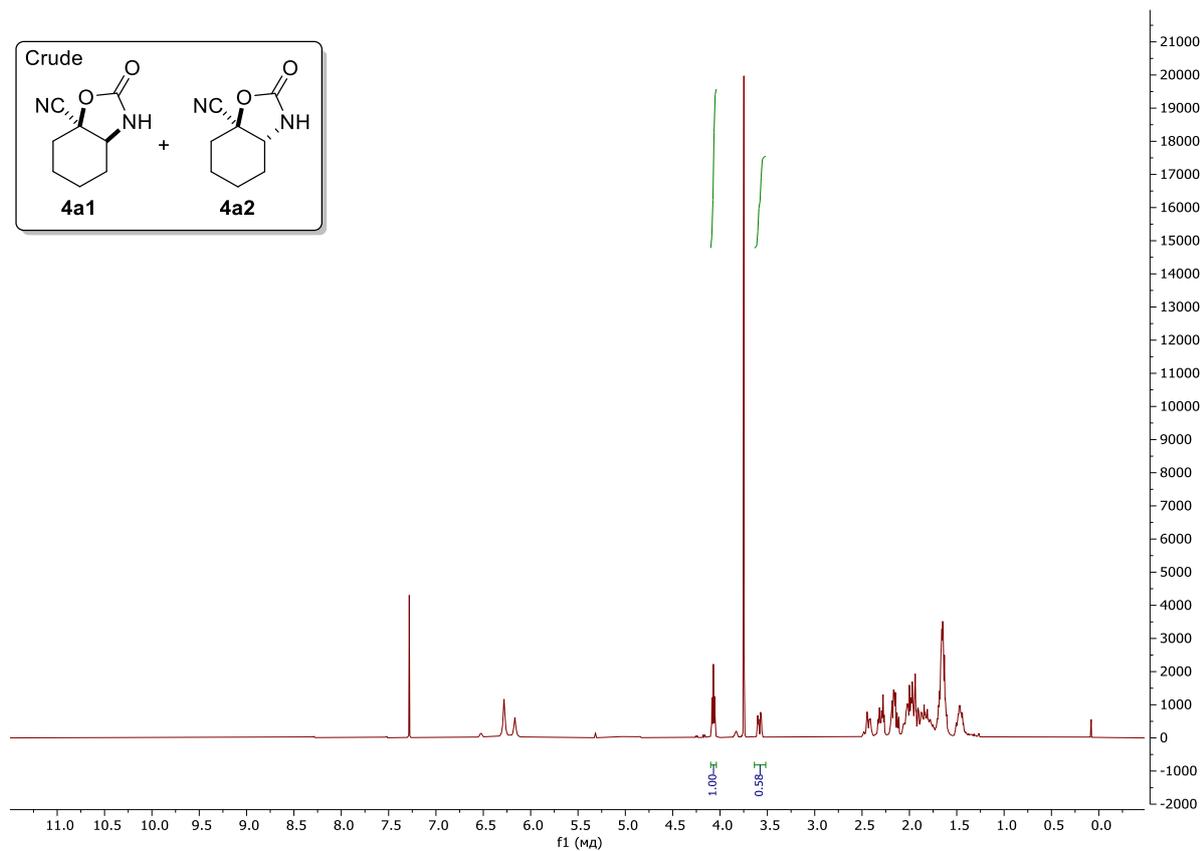
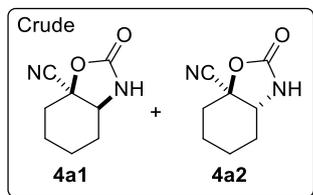
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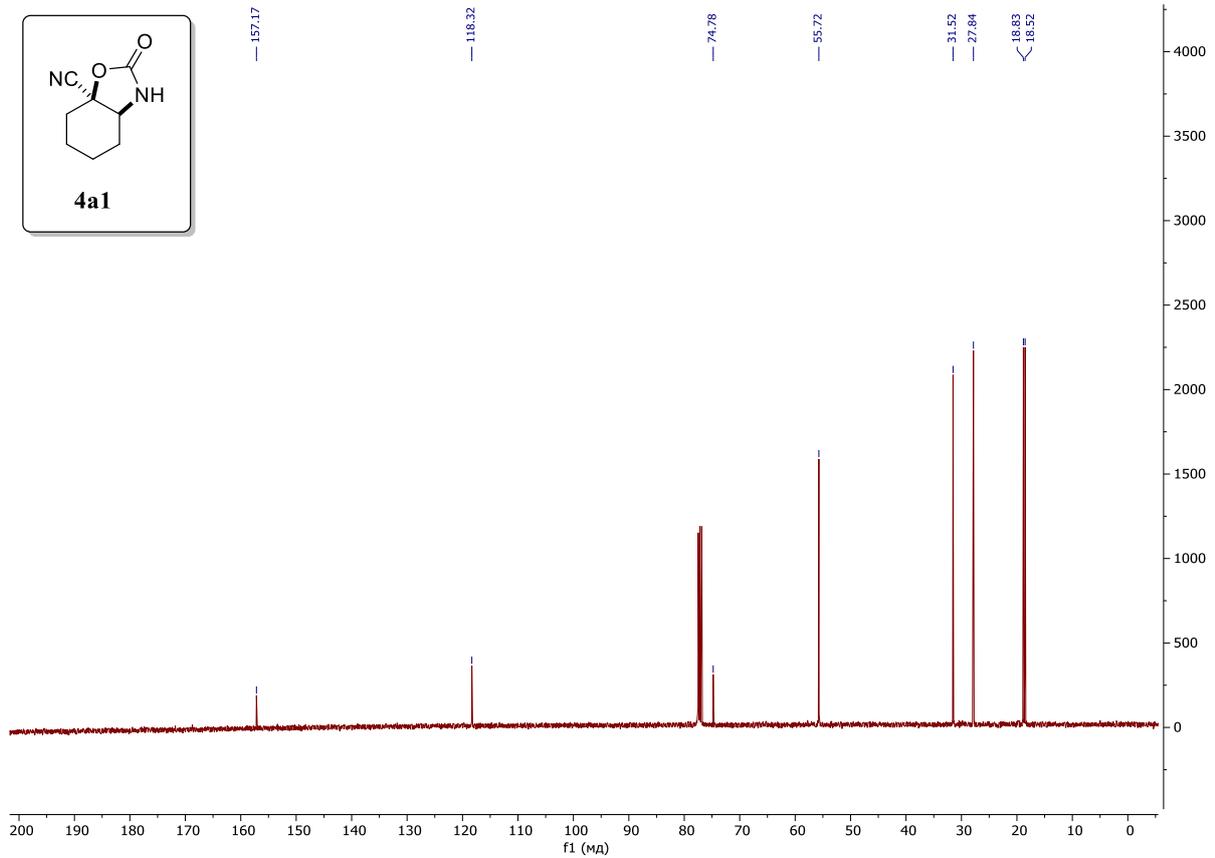
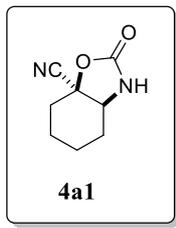


Compound 3h

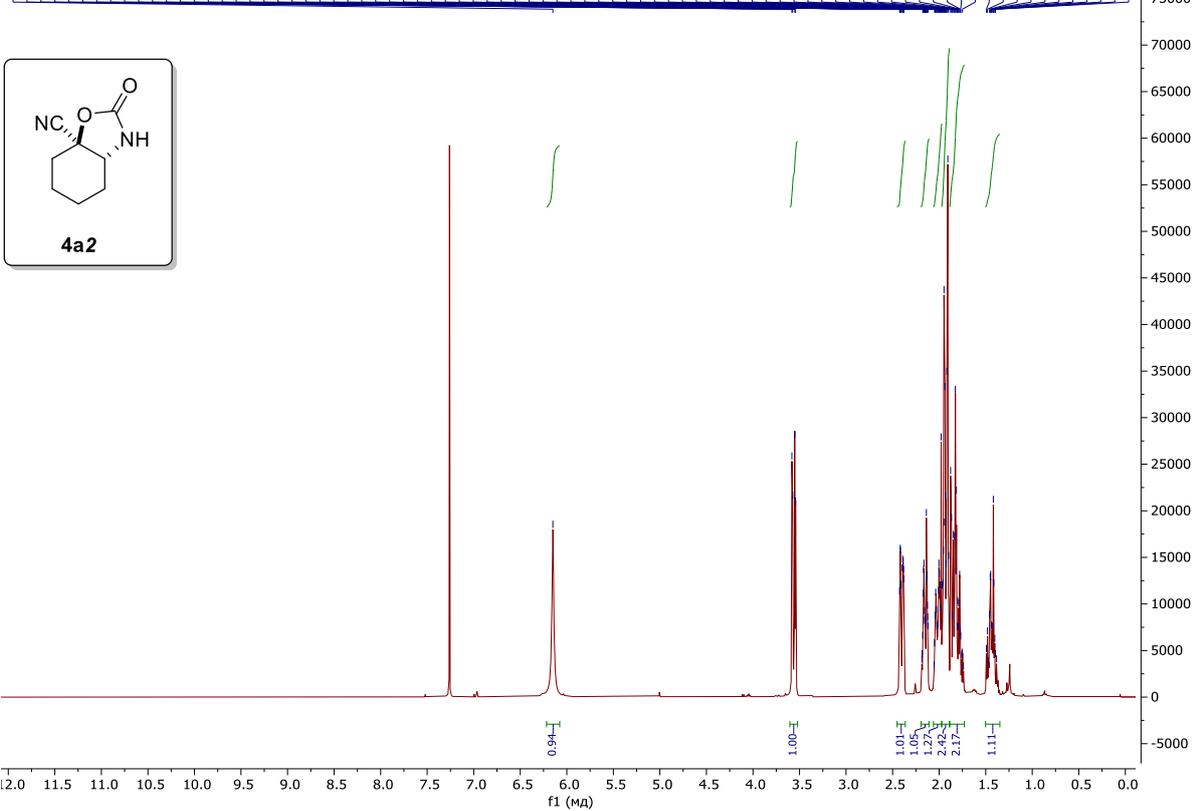


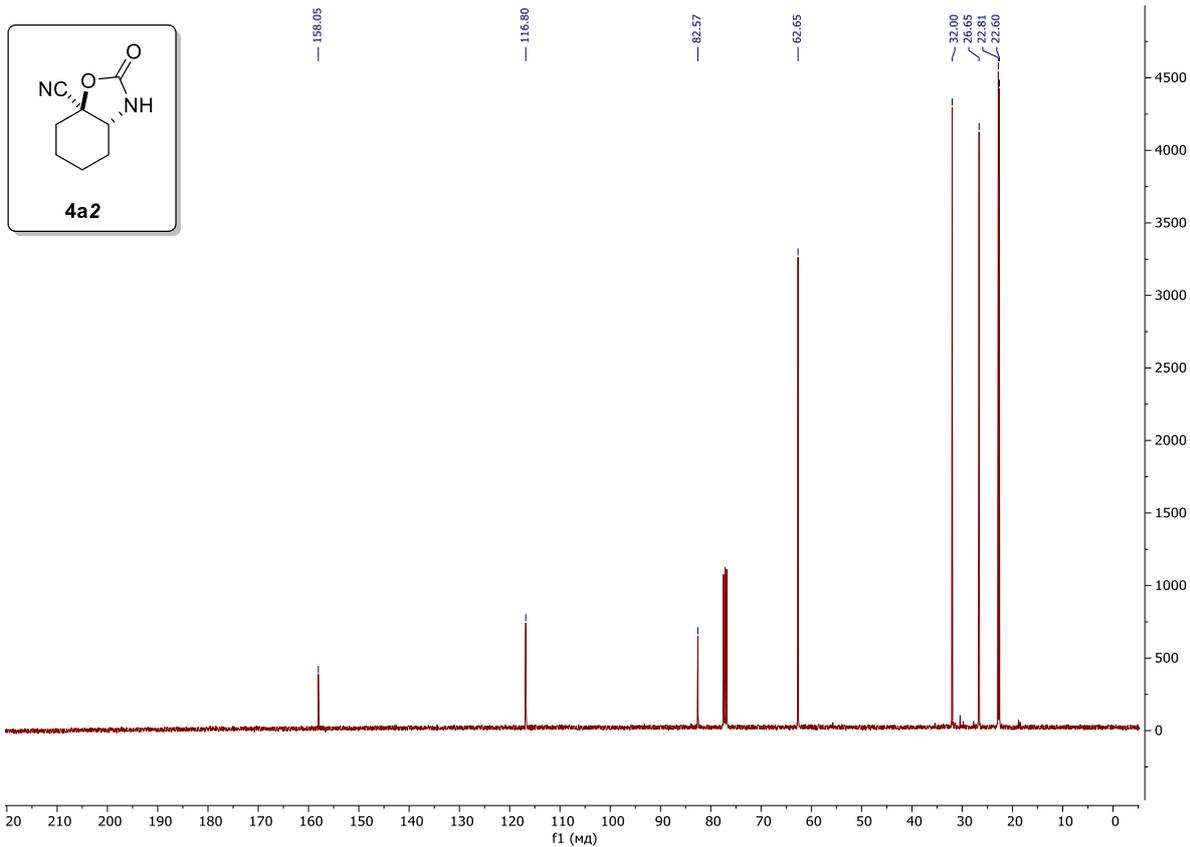
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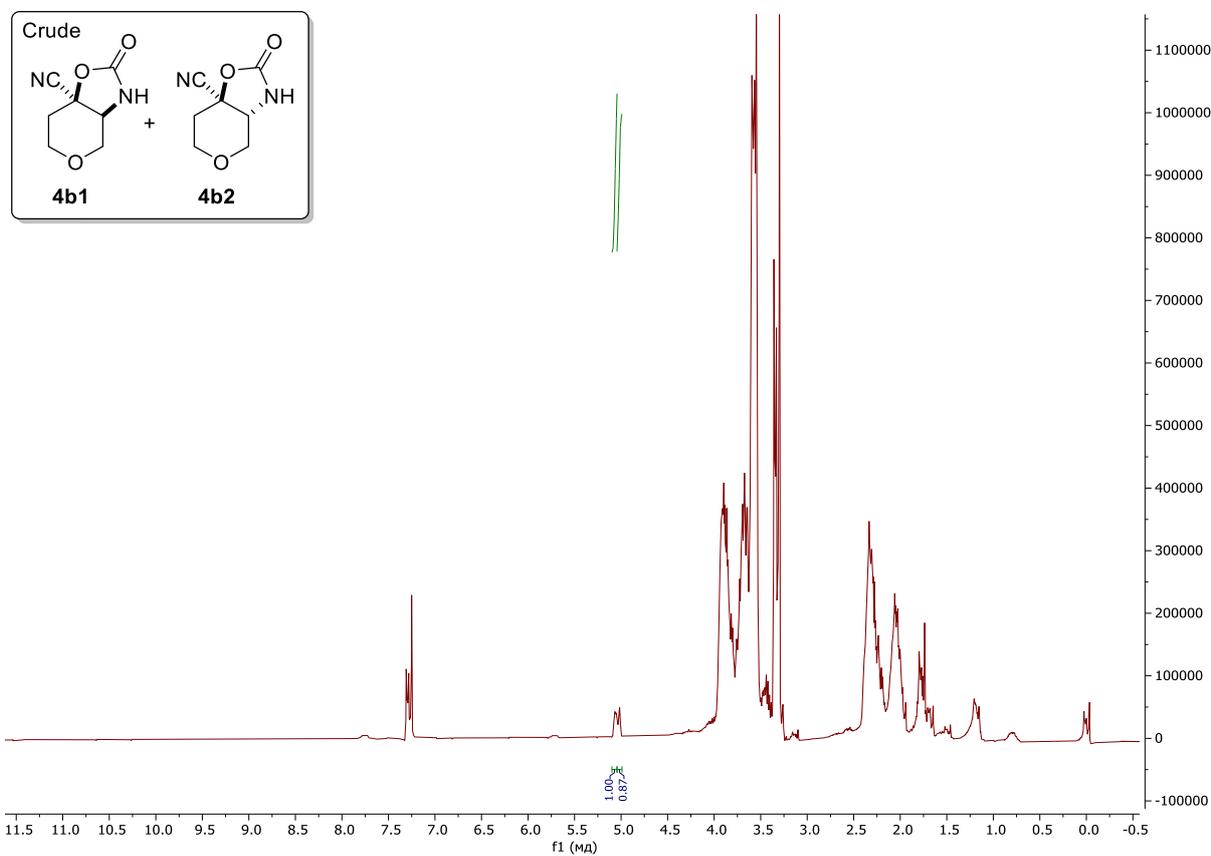


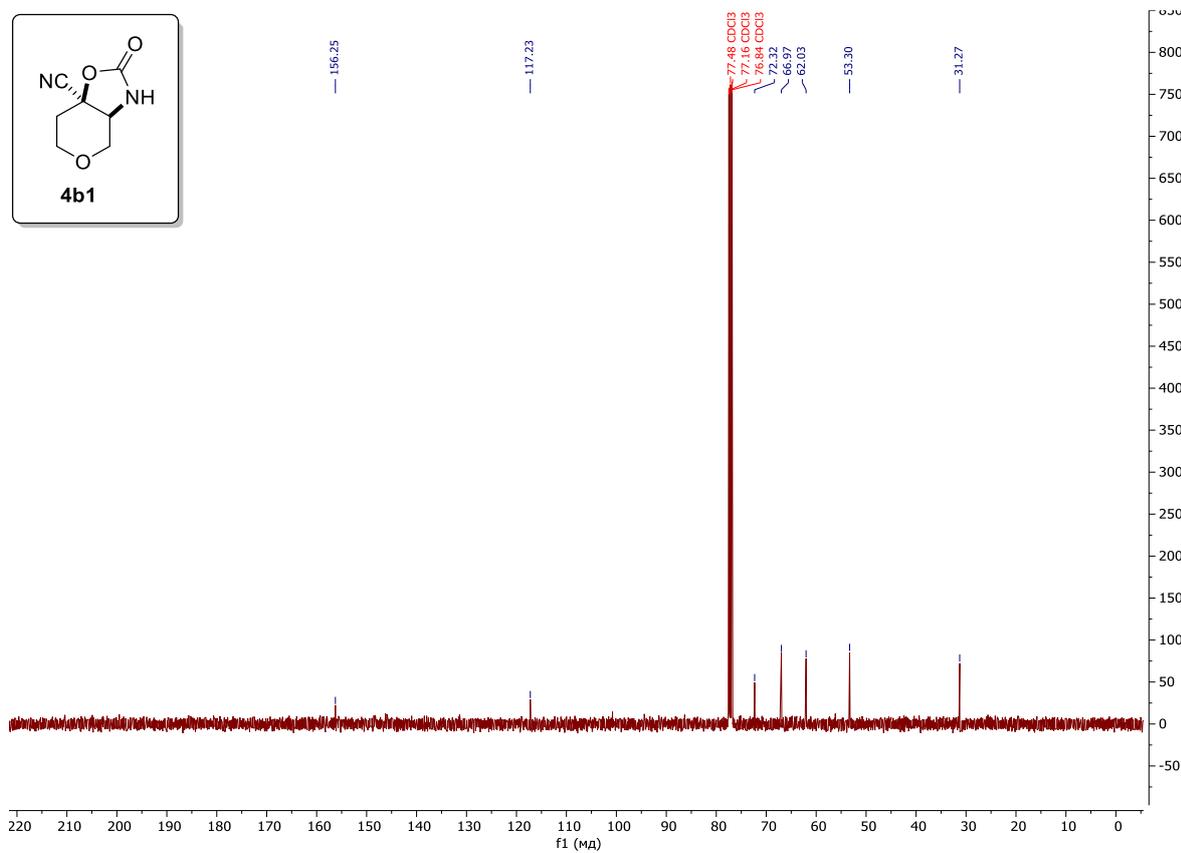
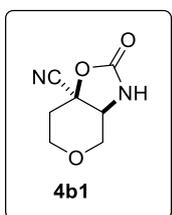
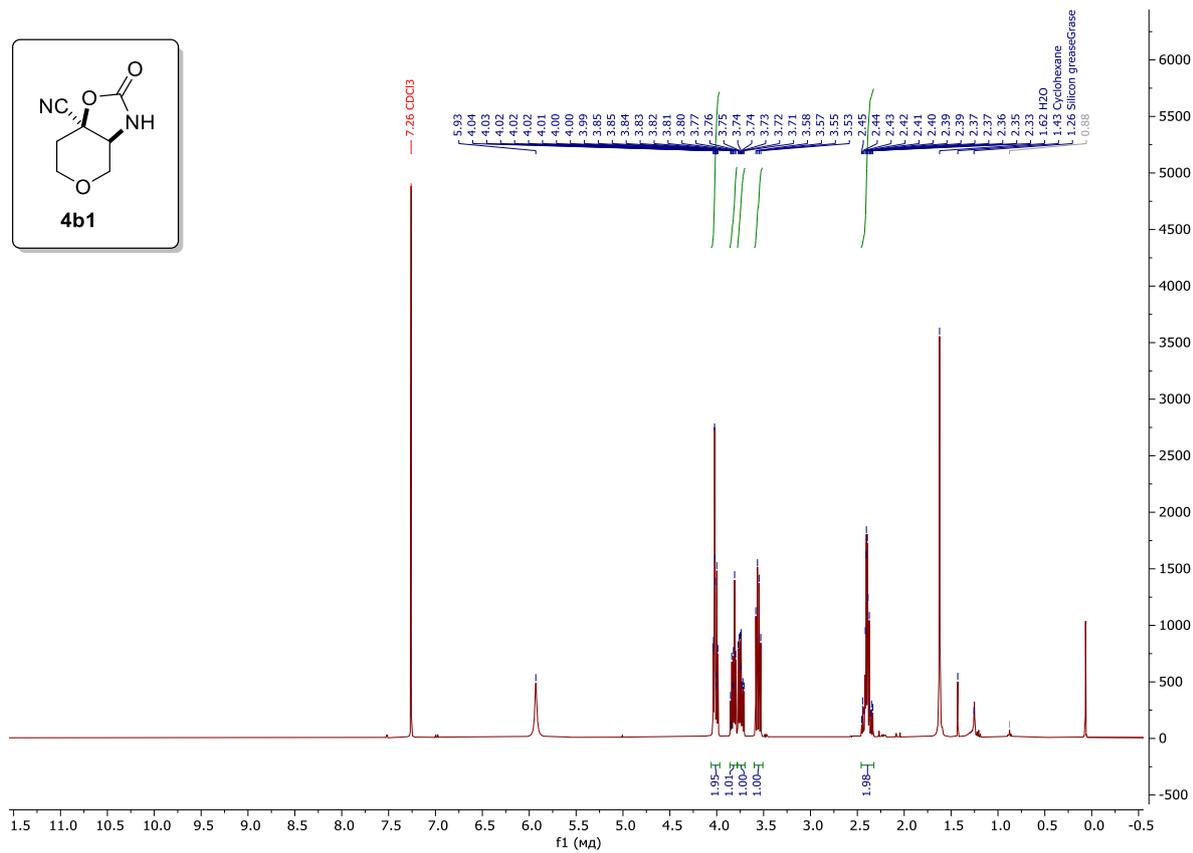
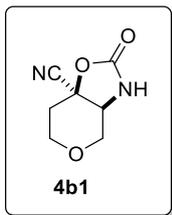
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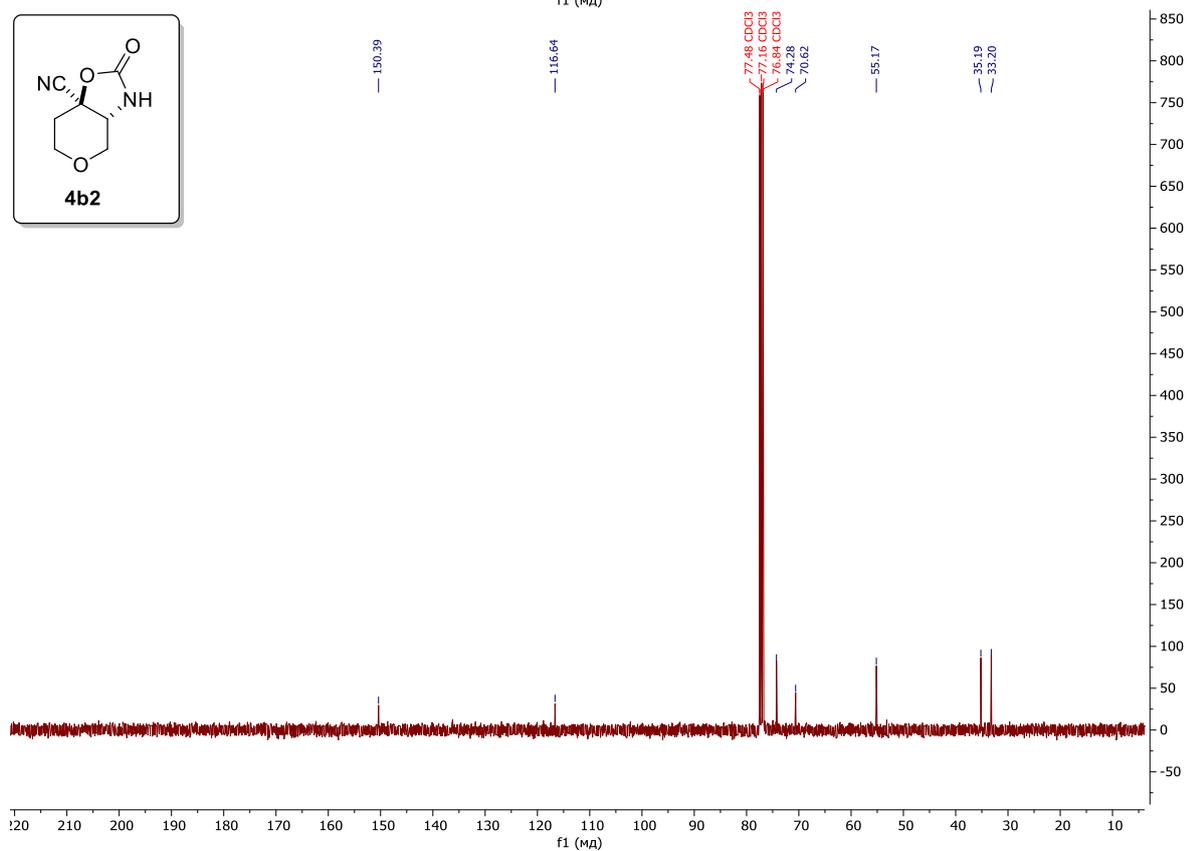
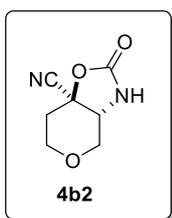
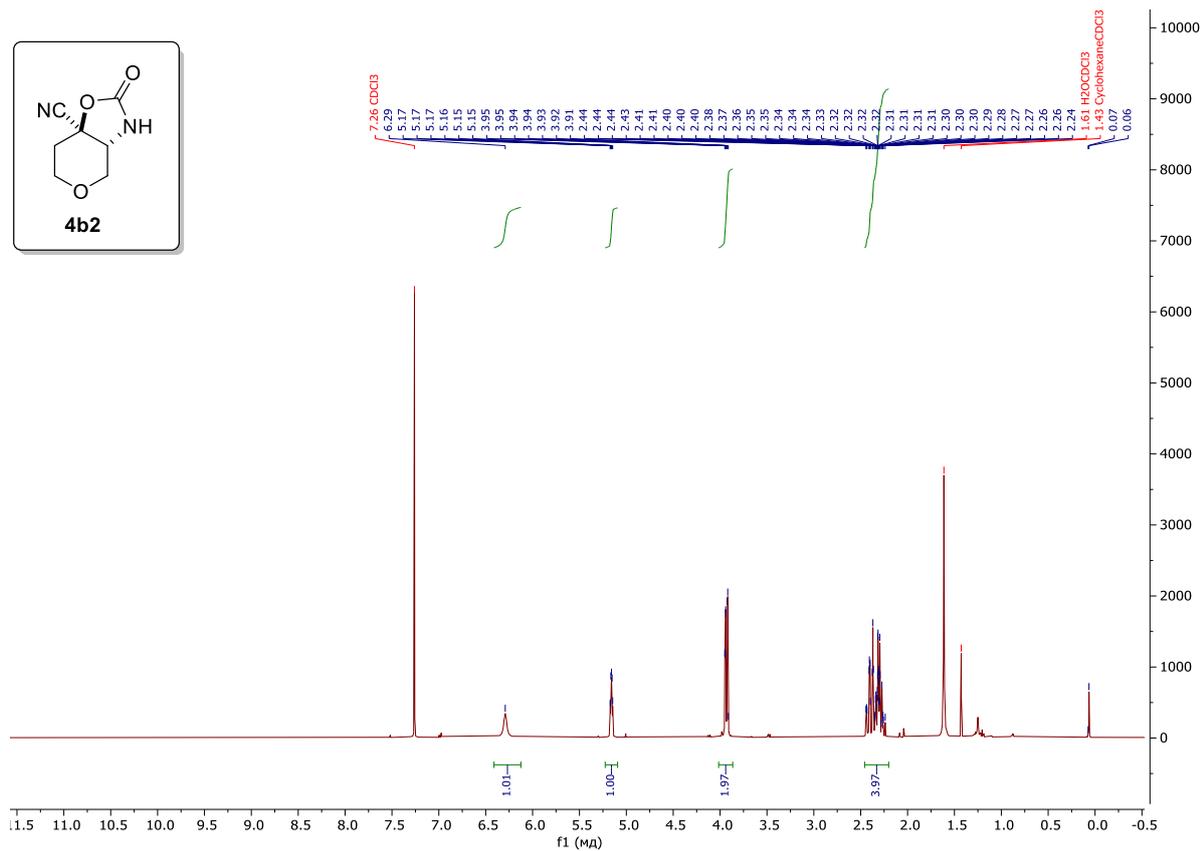
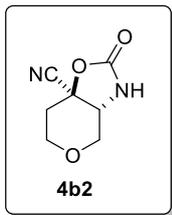




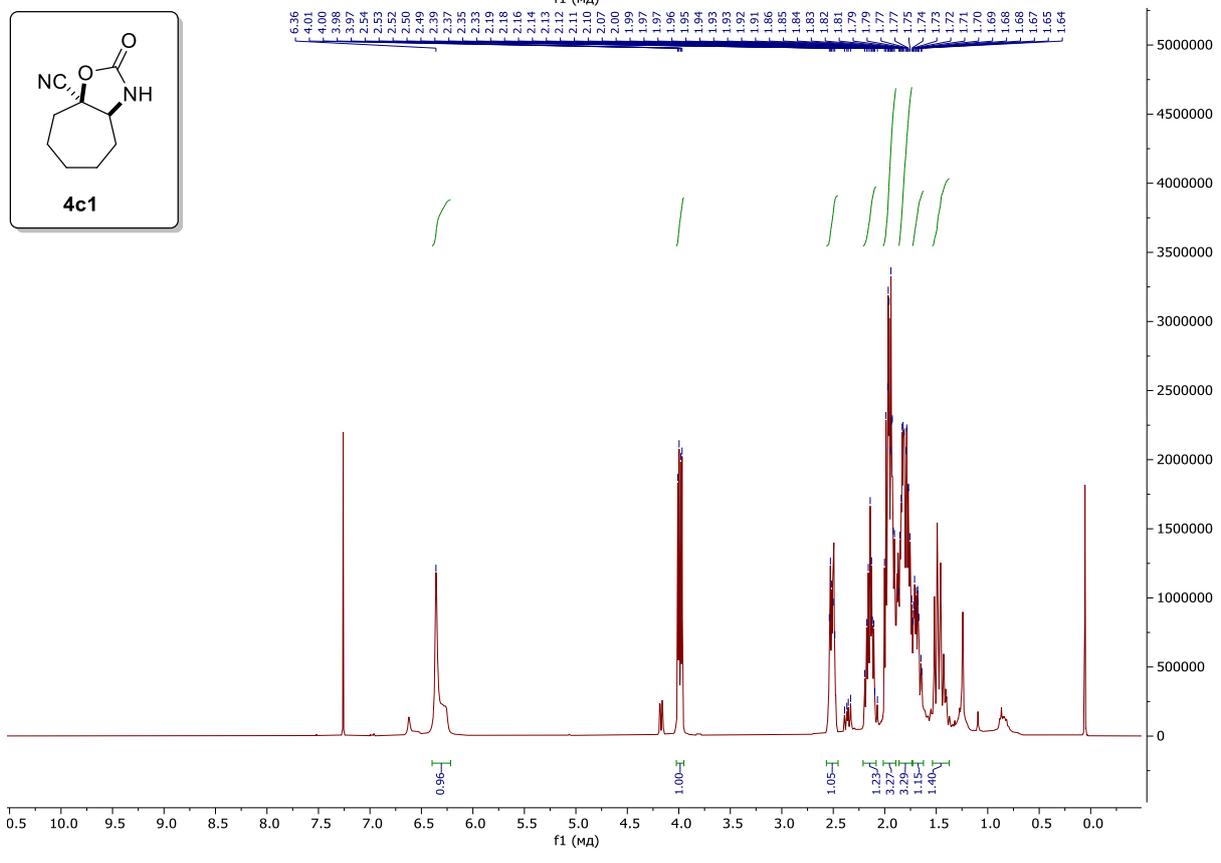
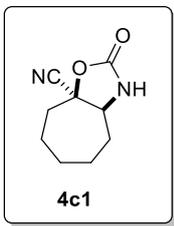
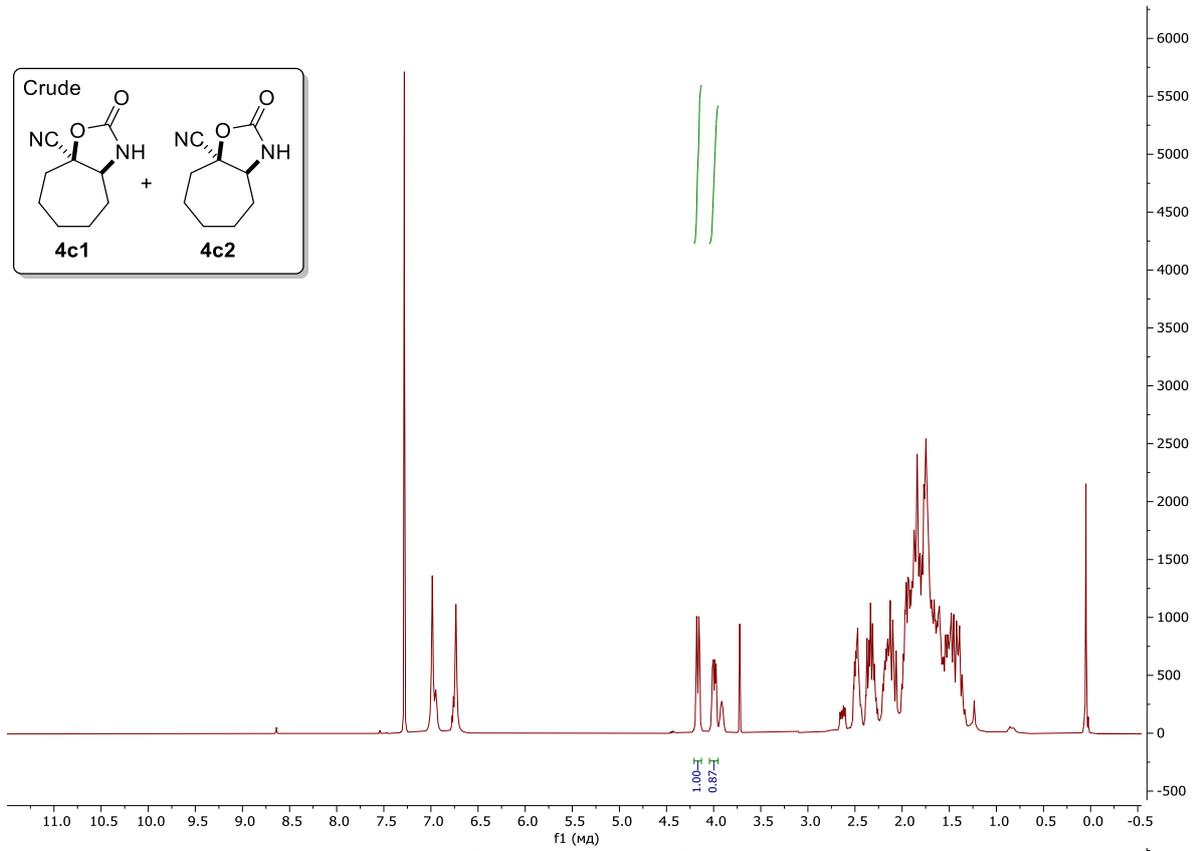
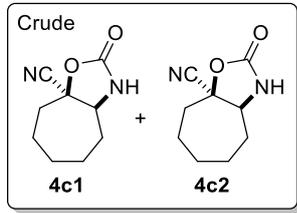
Compound 4b

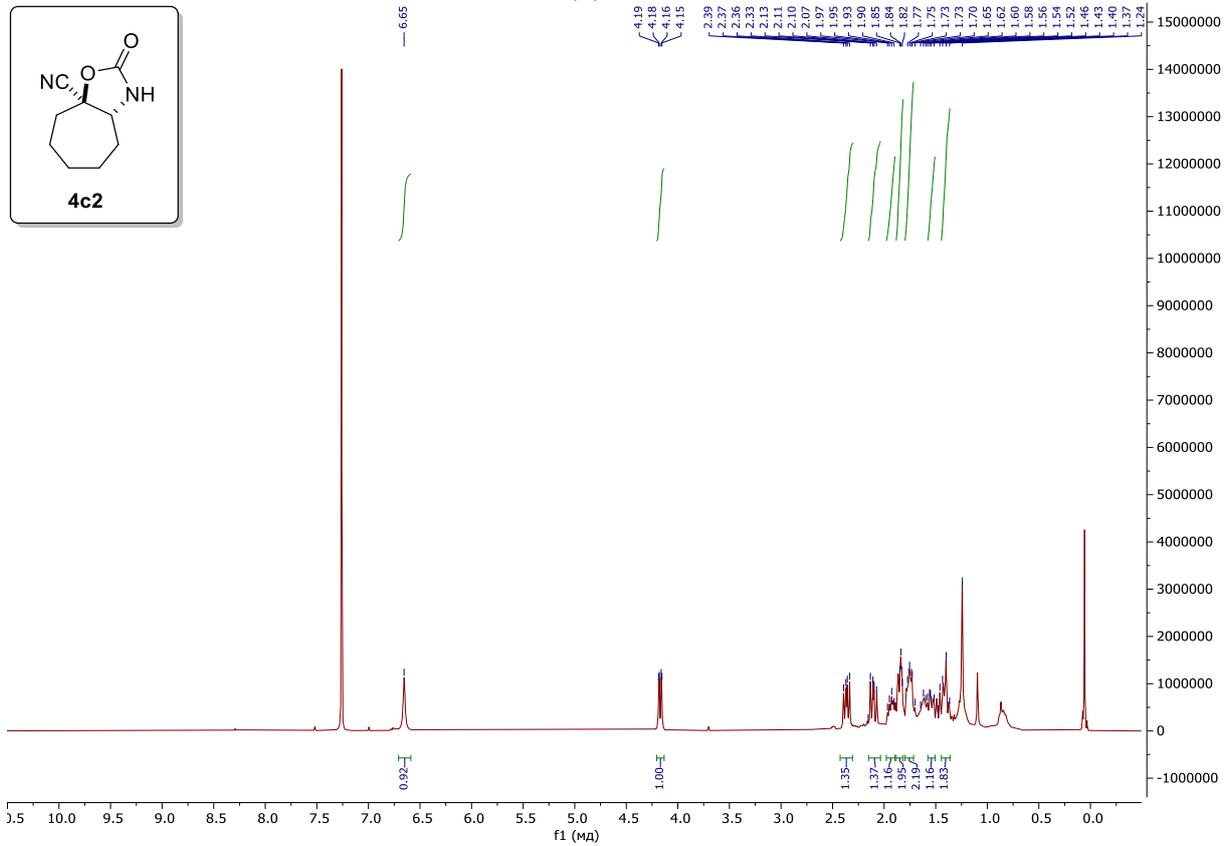
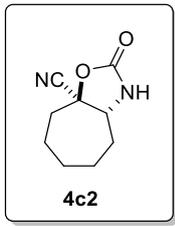
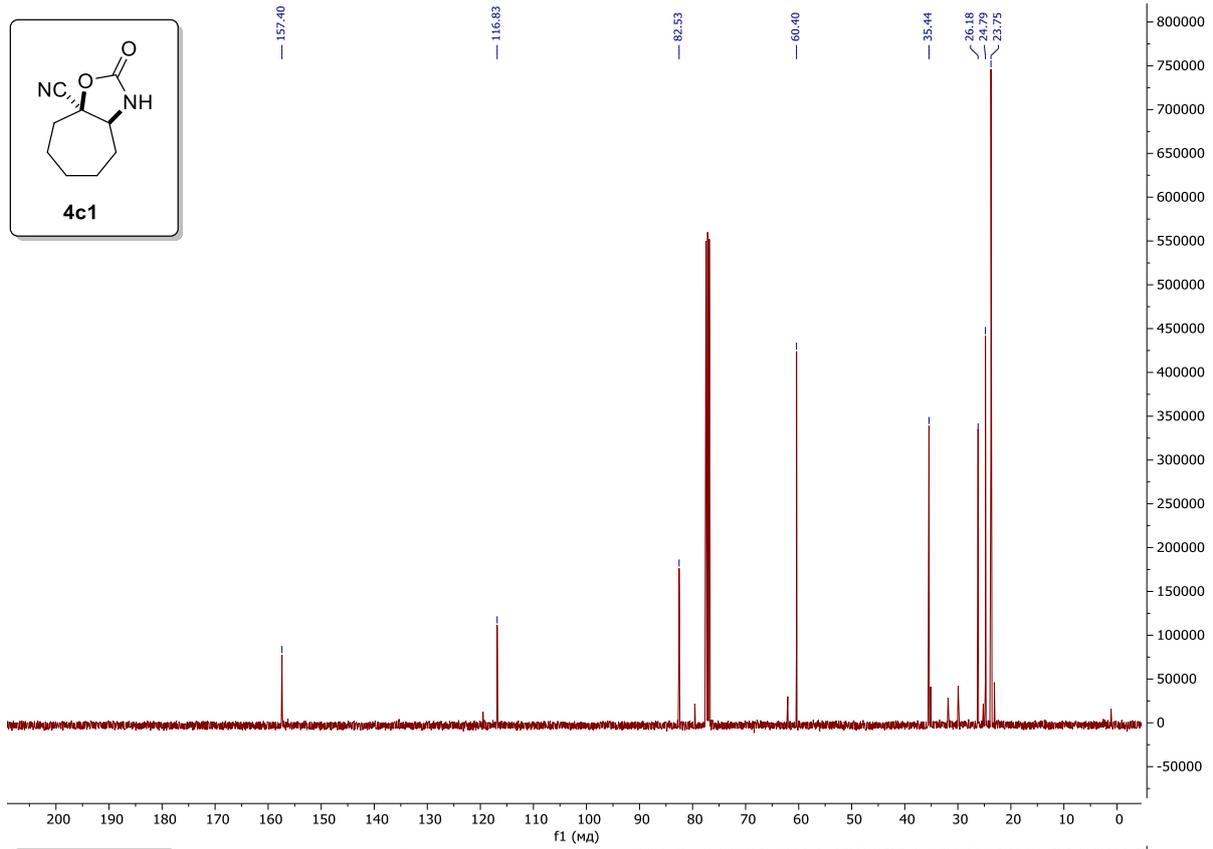
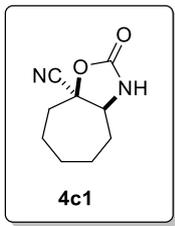


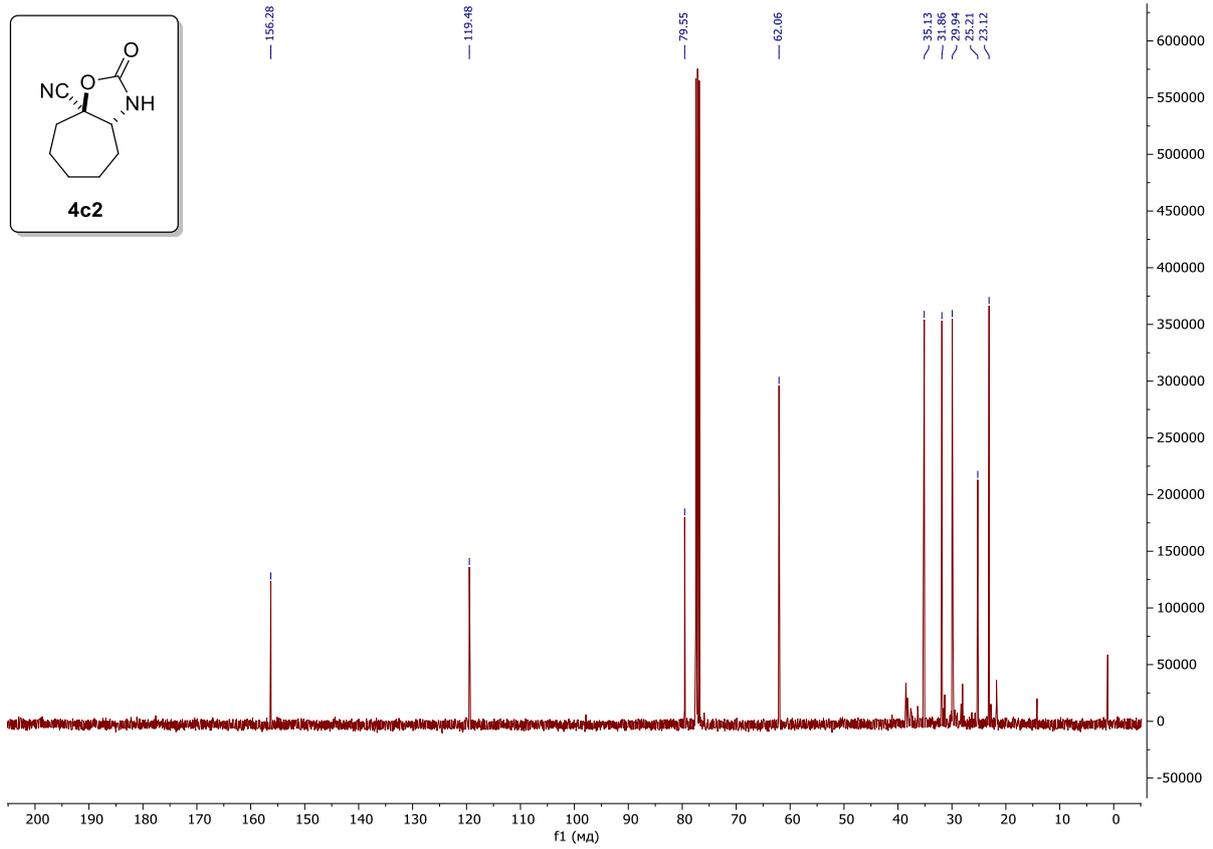
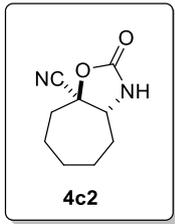




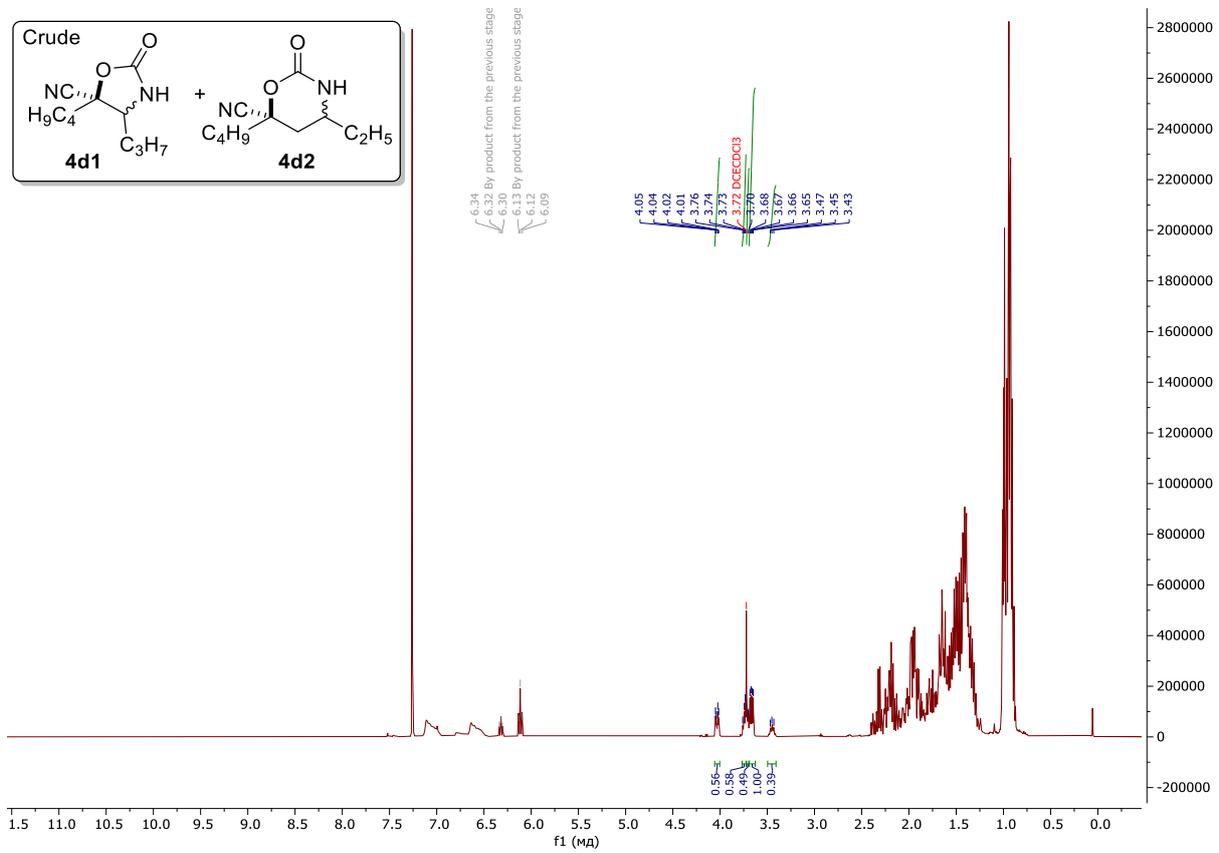
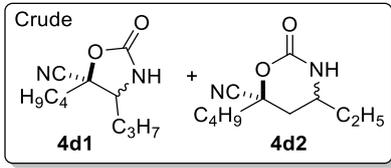
Compound 4c

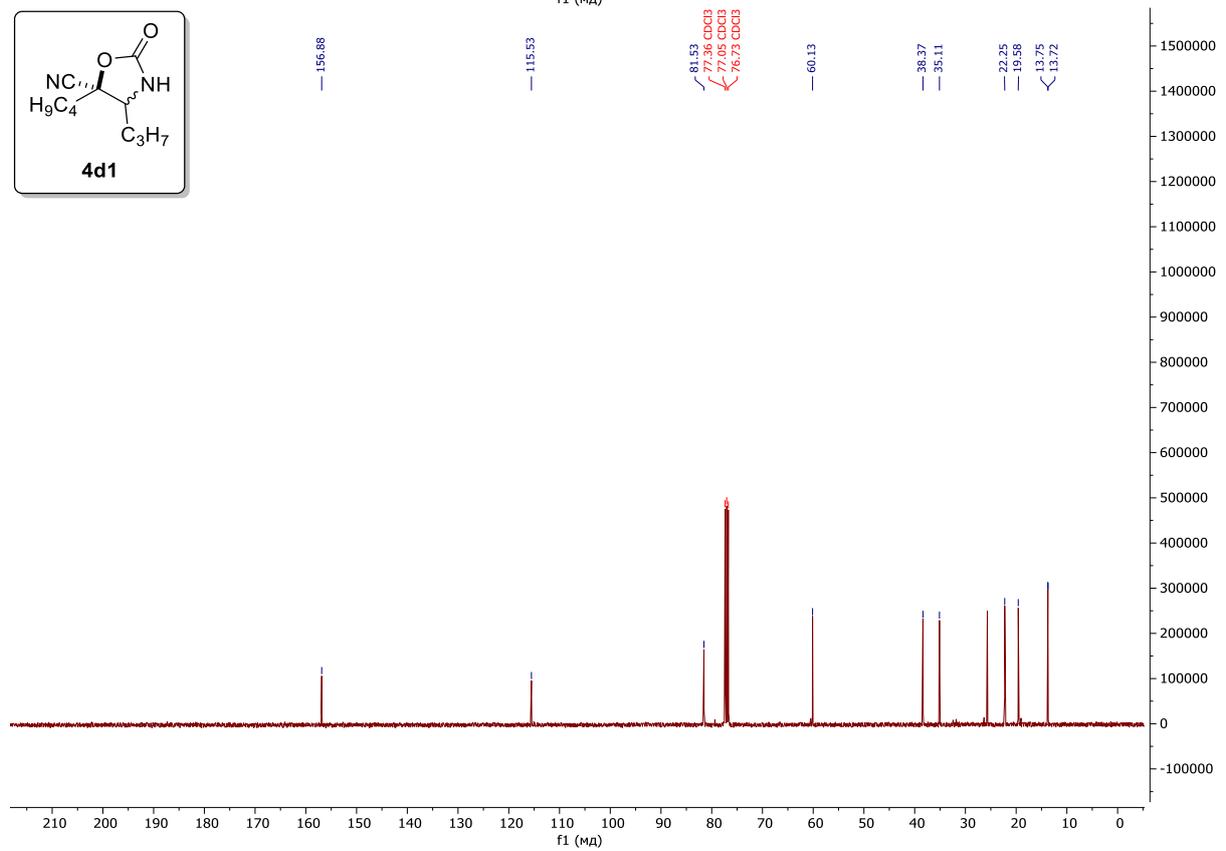
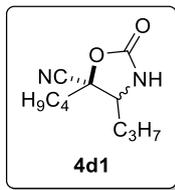
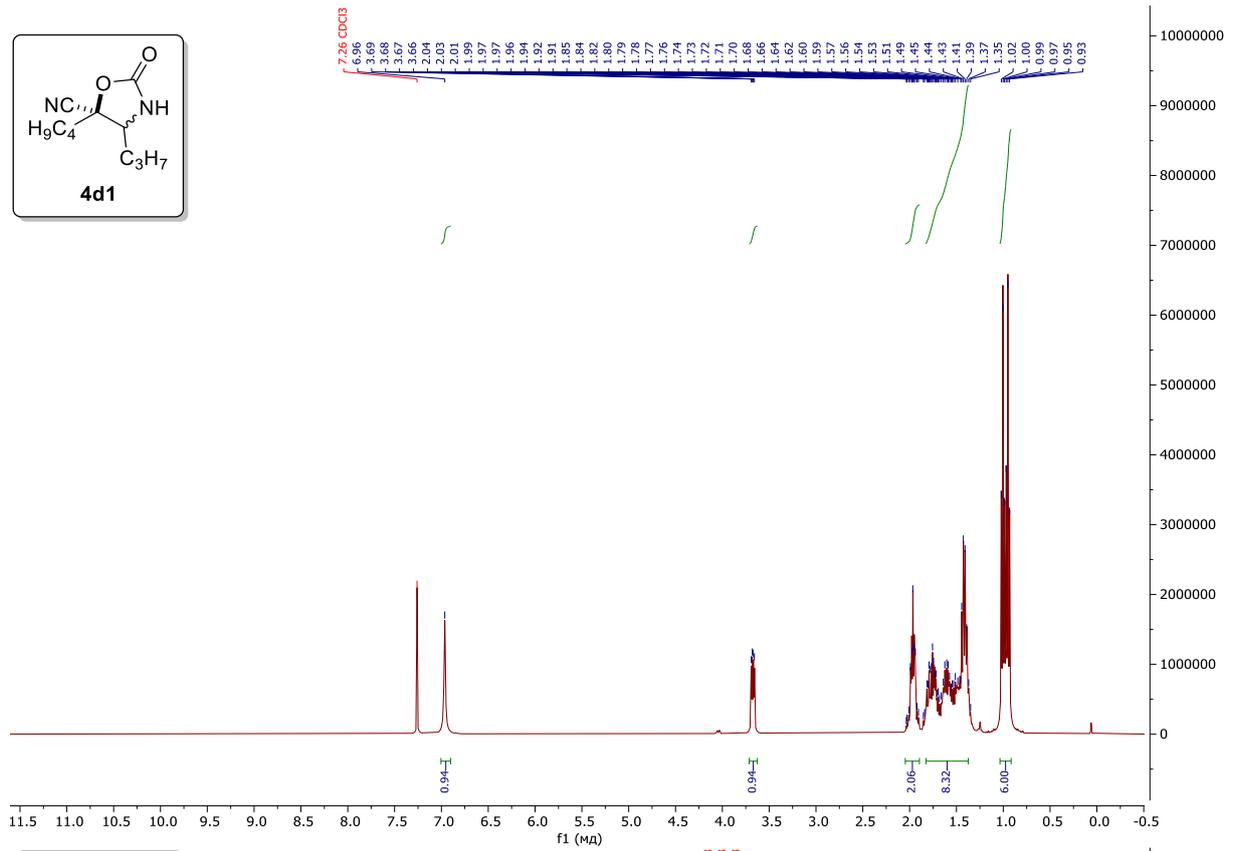
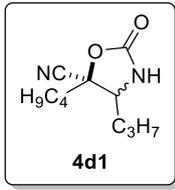




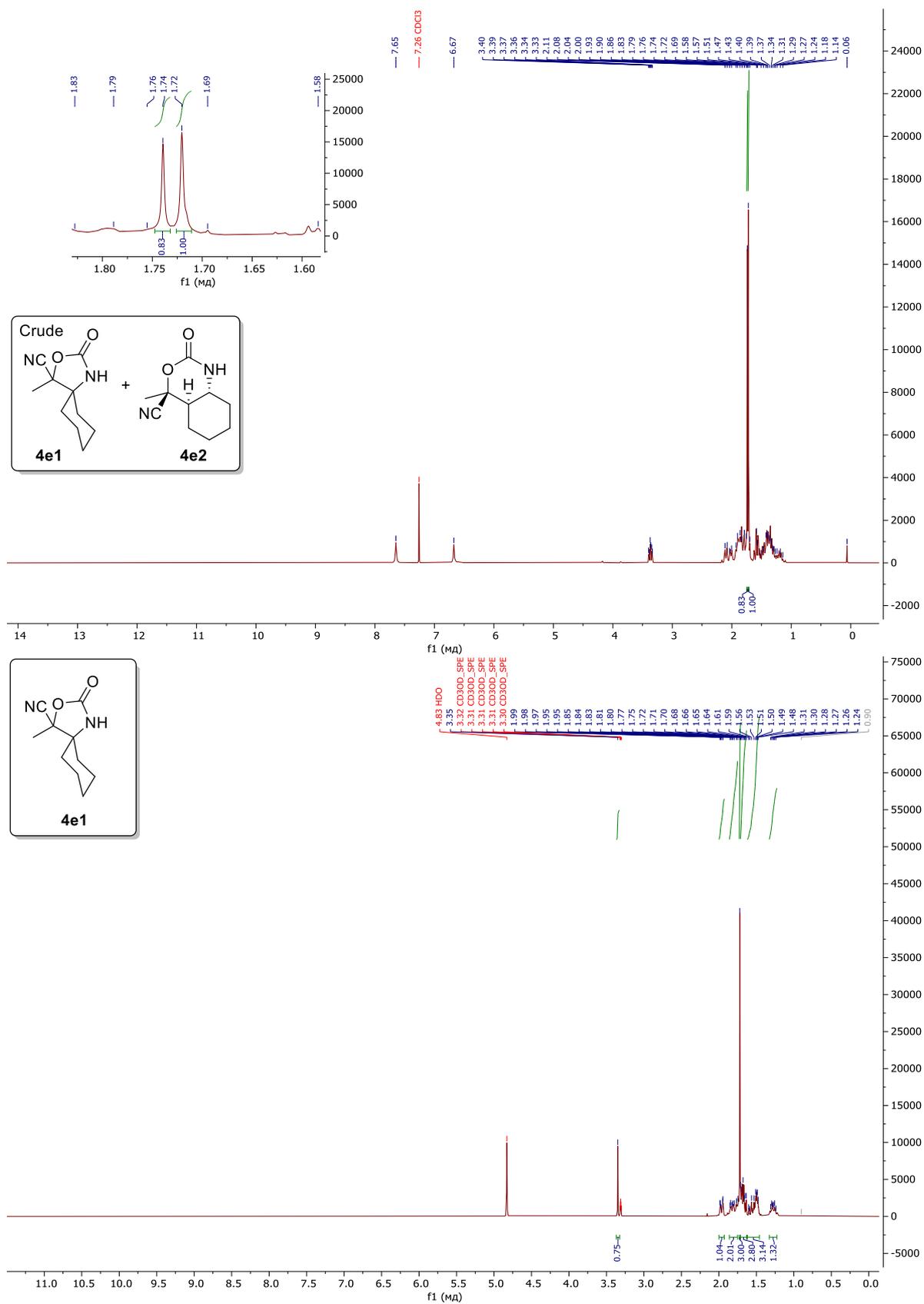


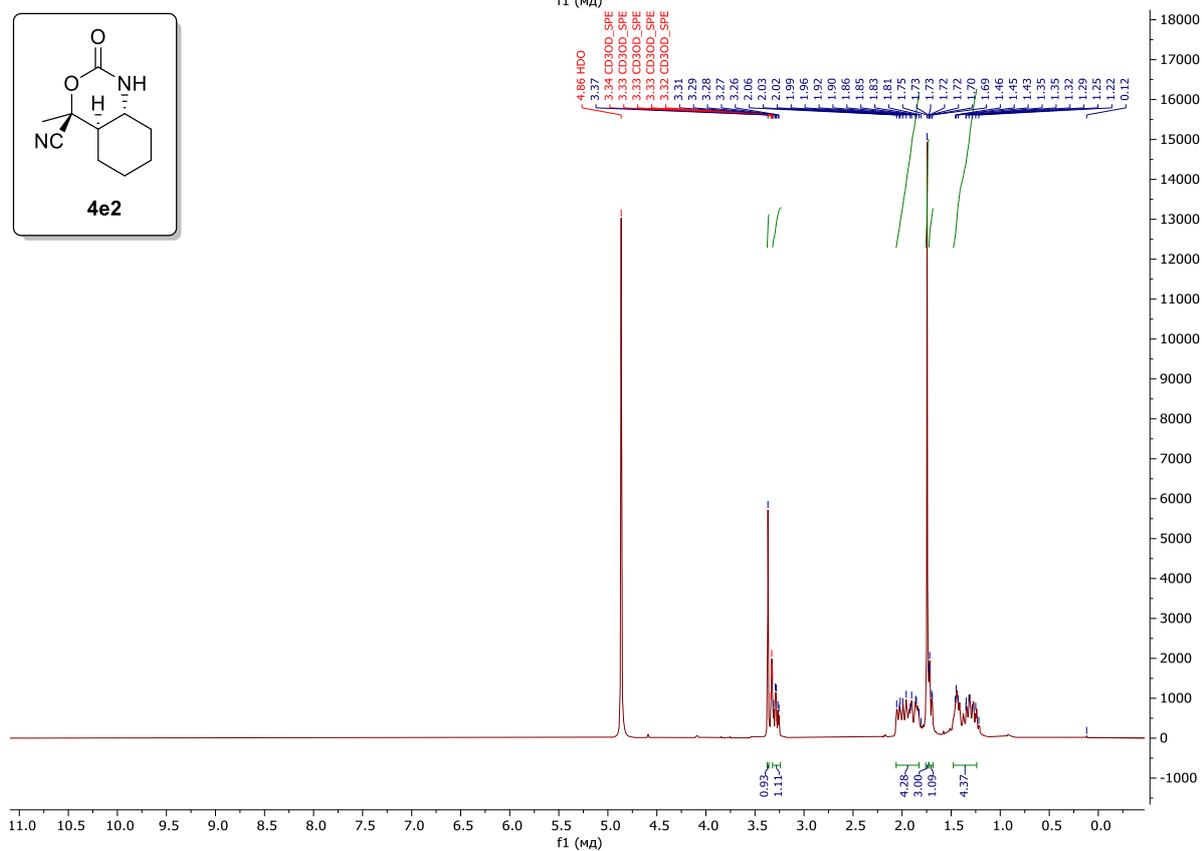
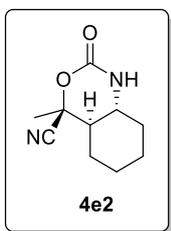
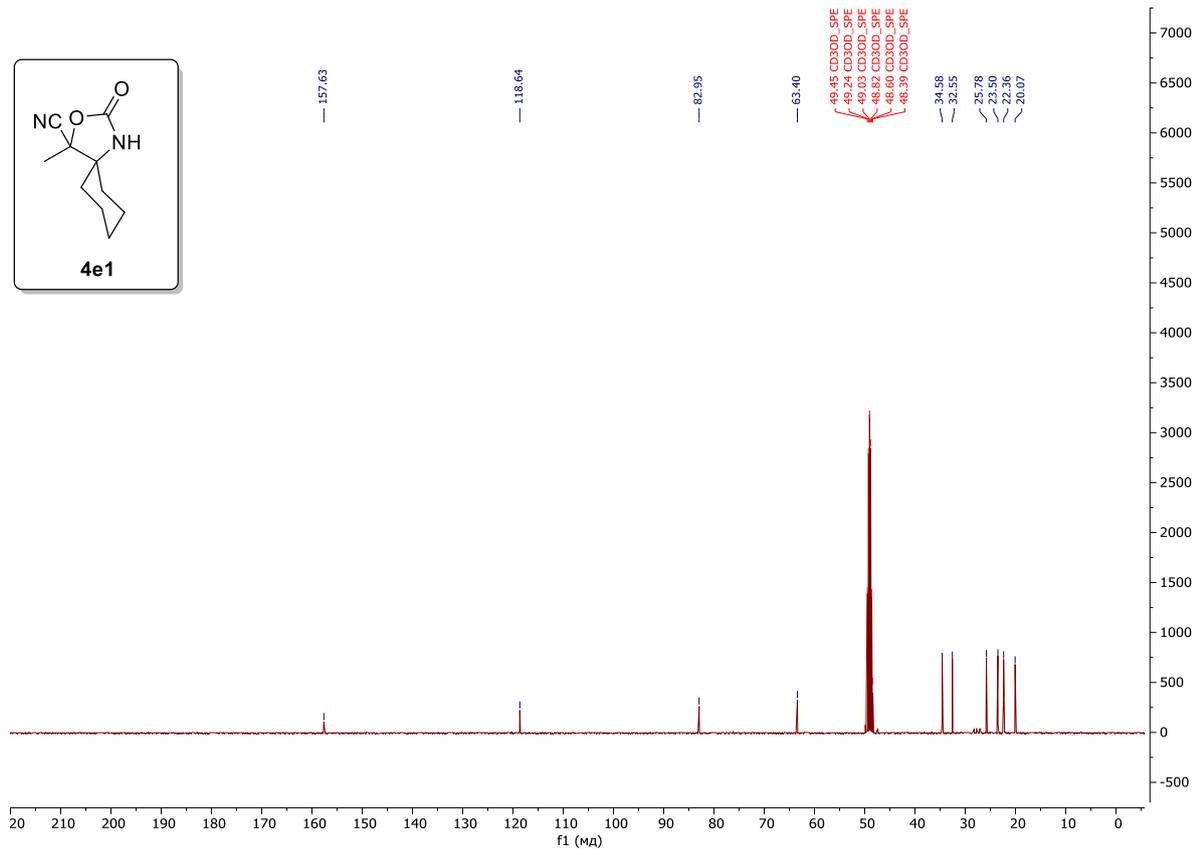
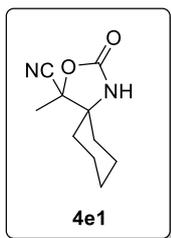
Compound 4d

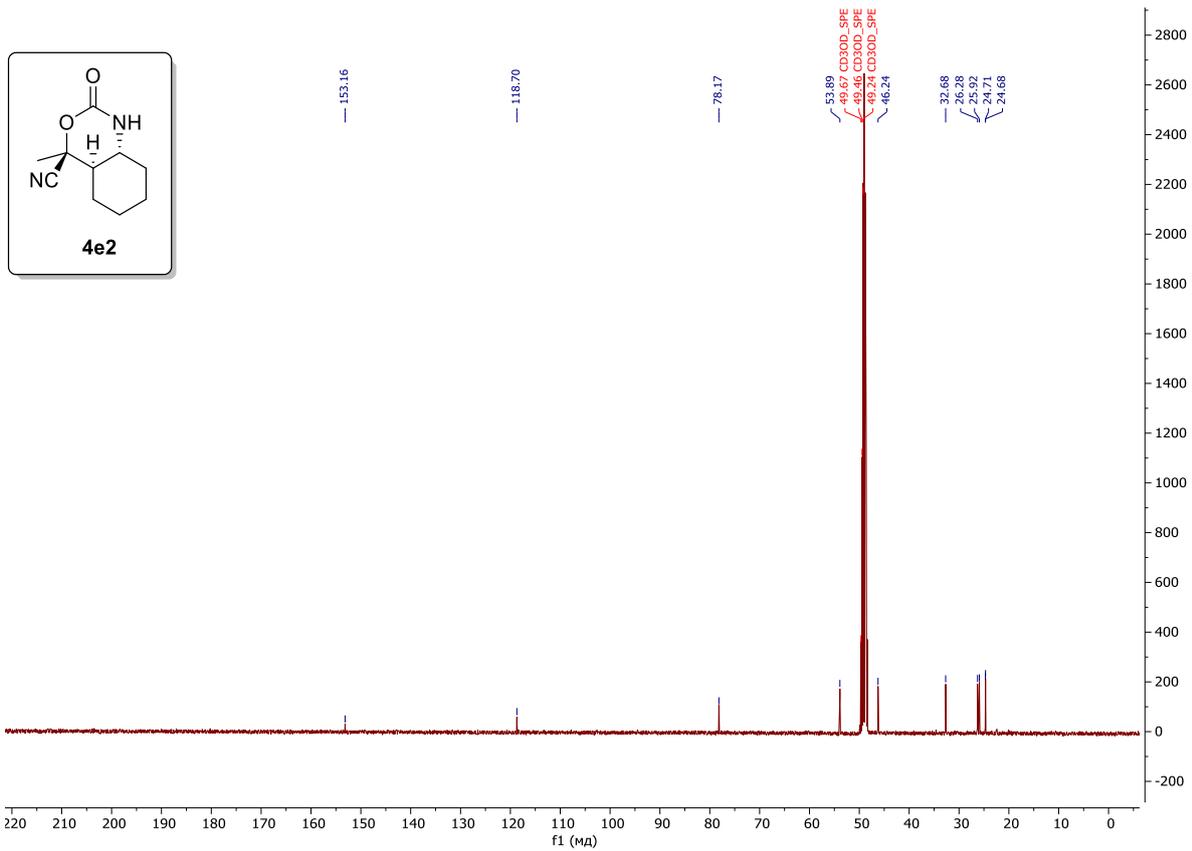




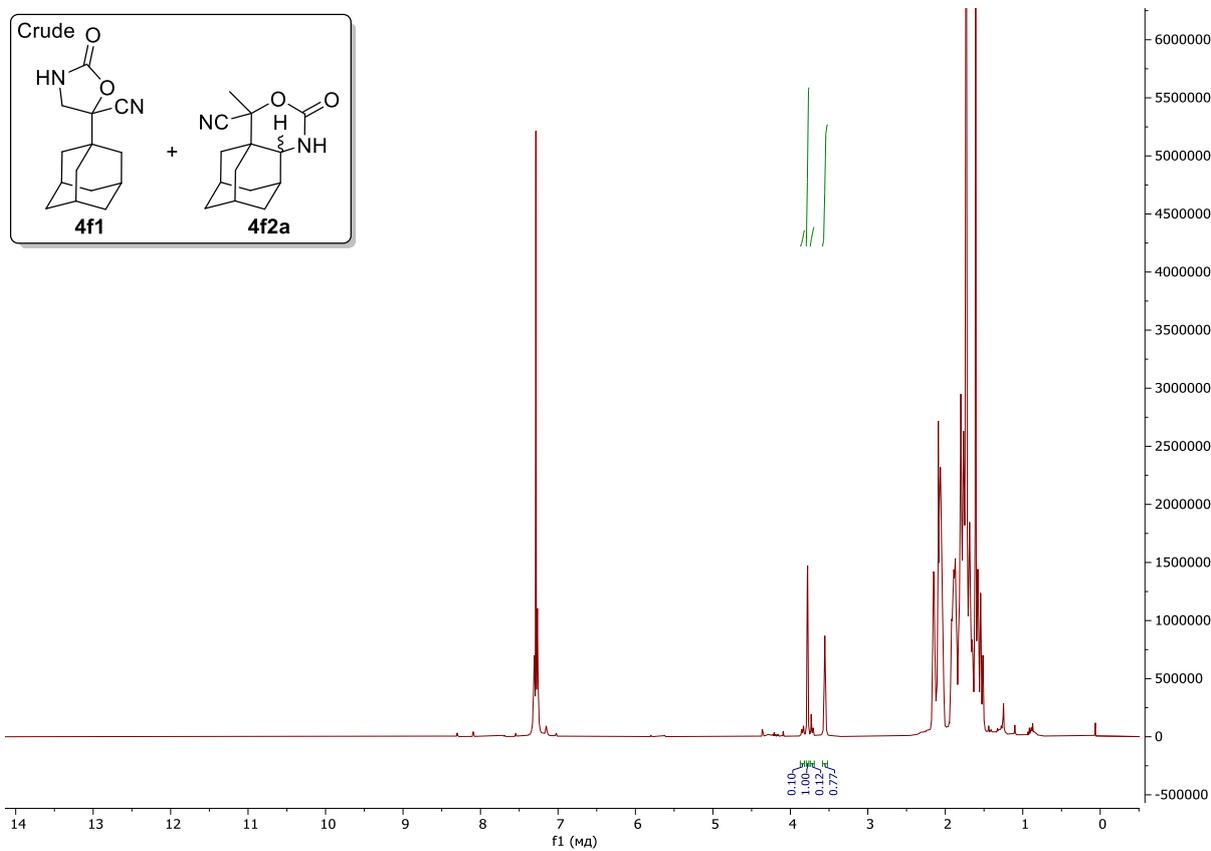
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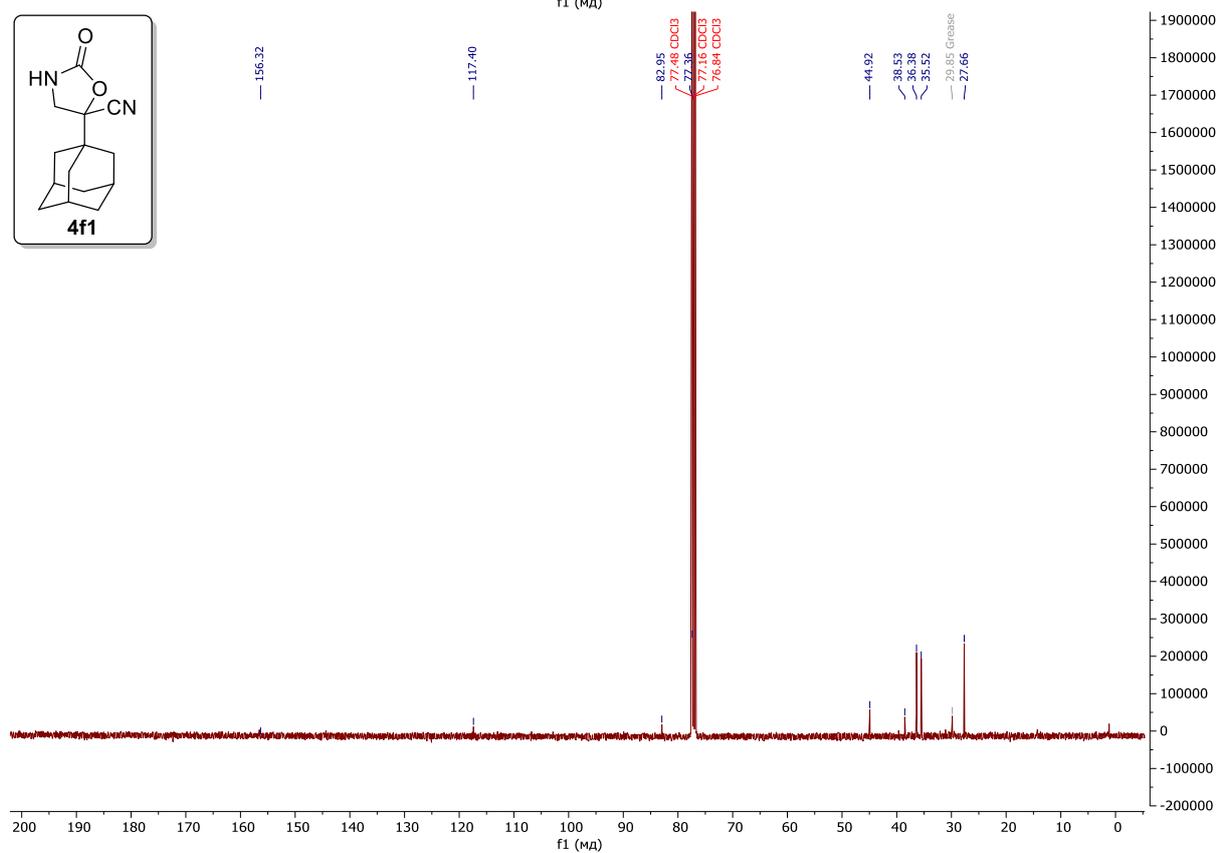
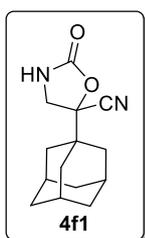
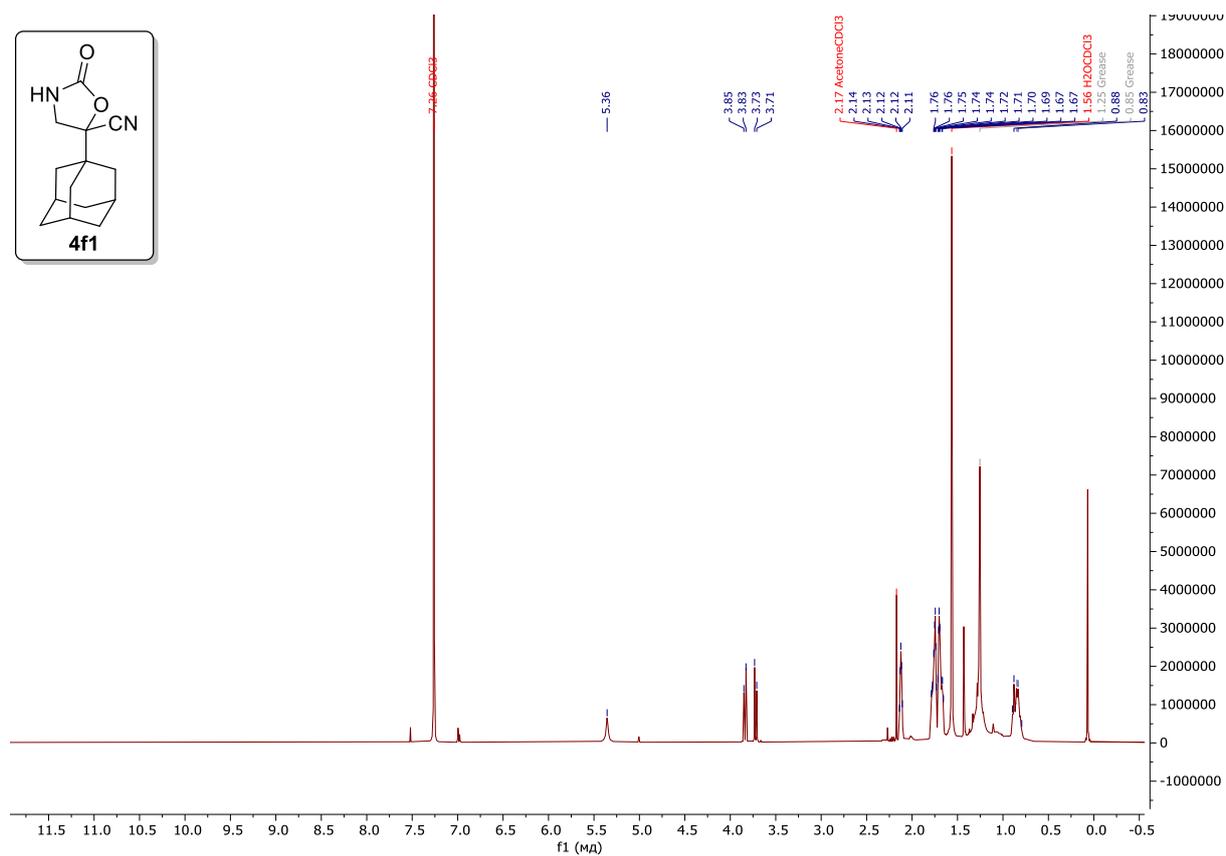
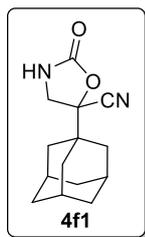


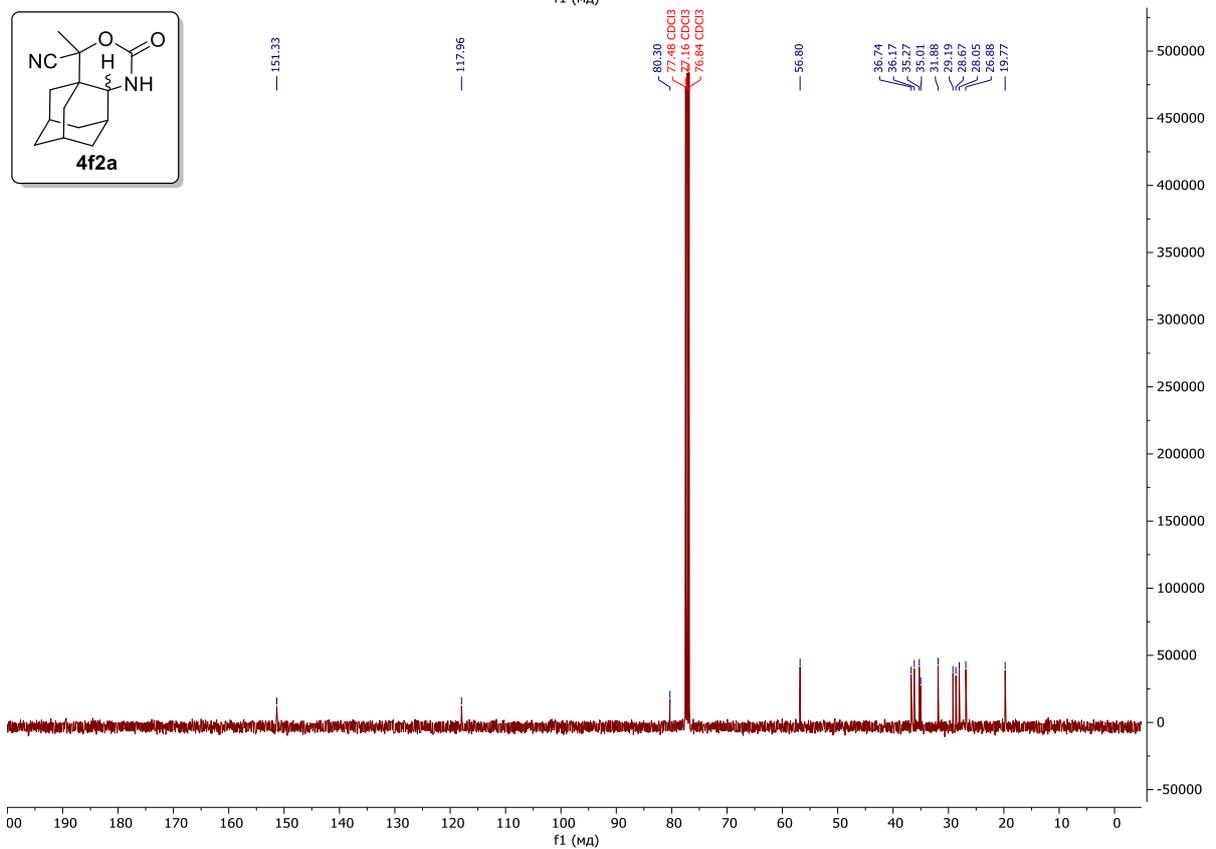
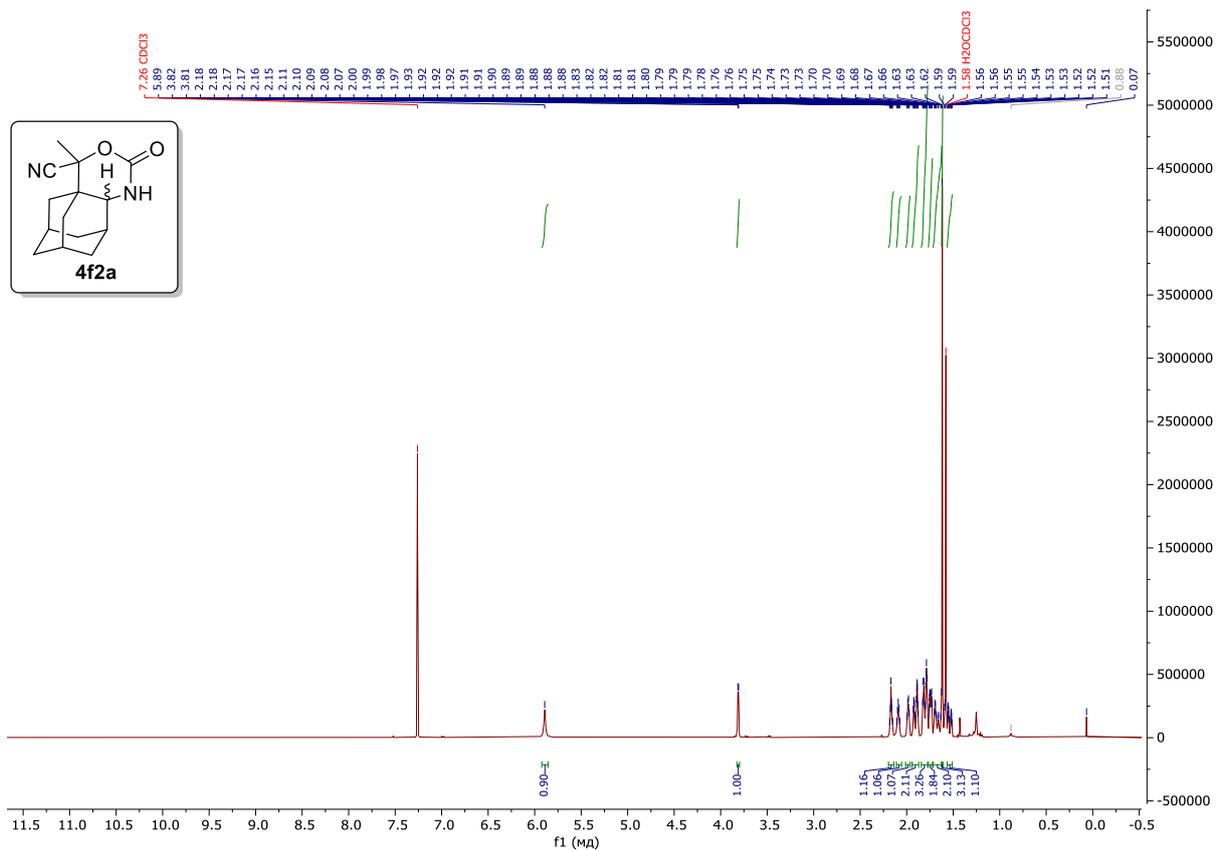


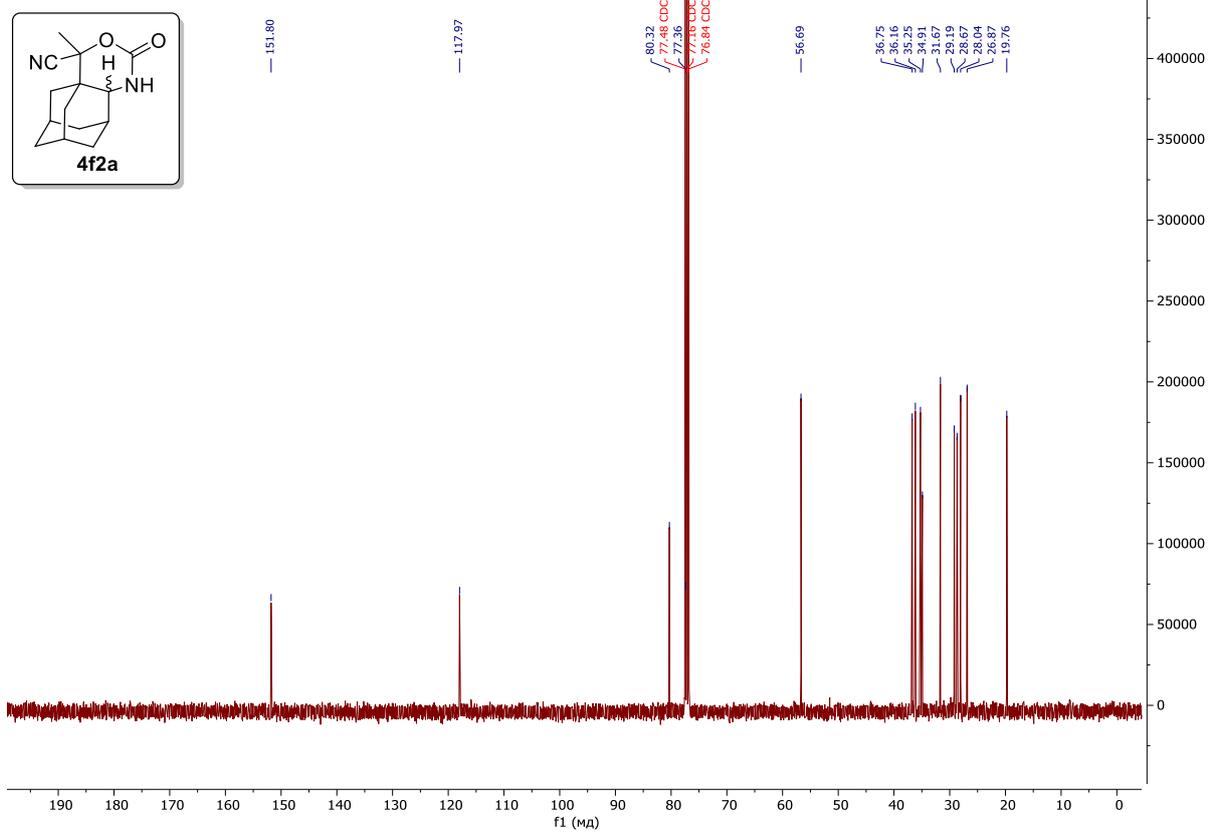
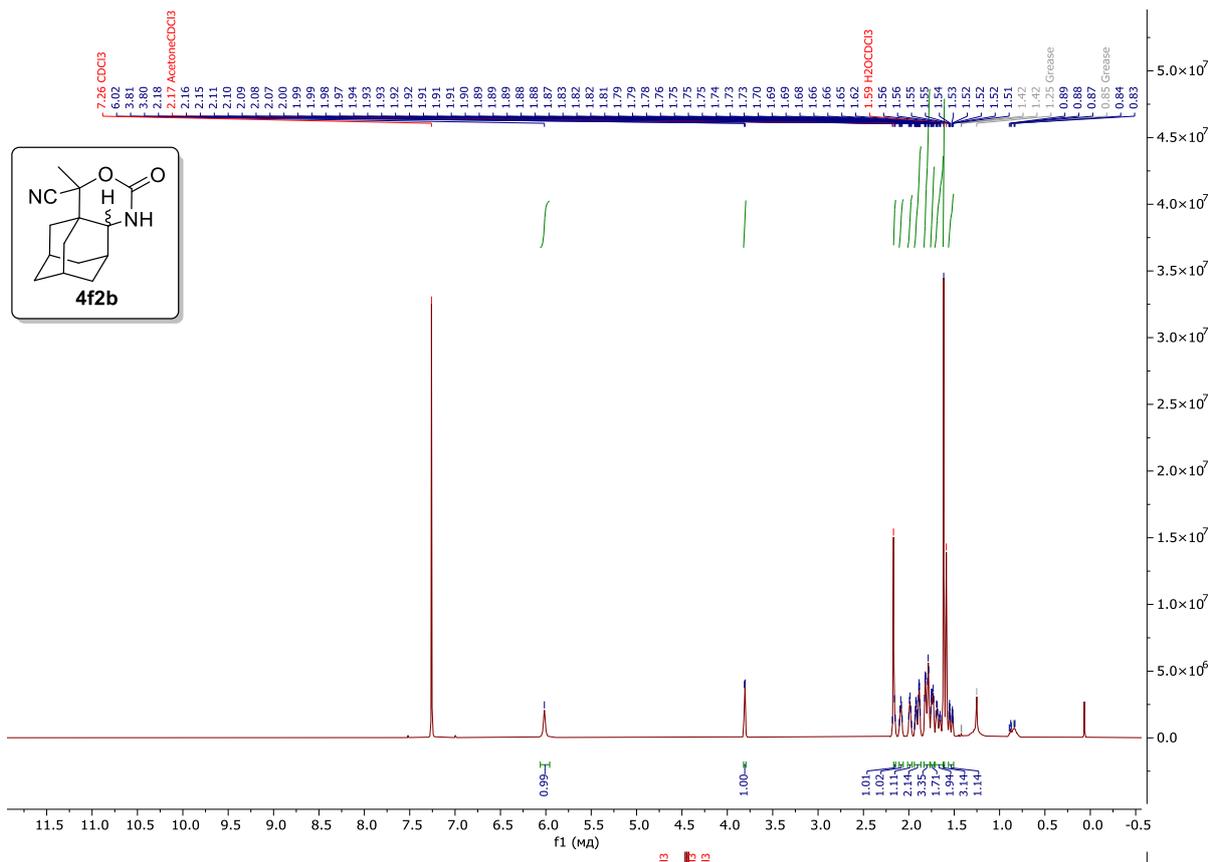


Compound 4f

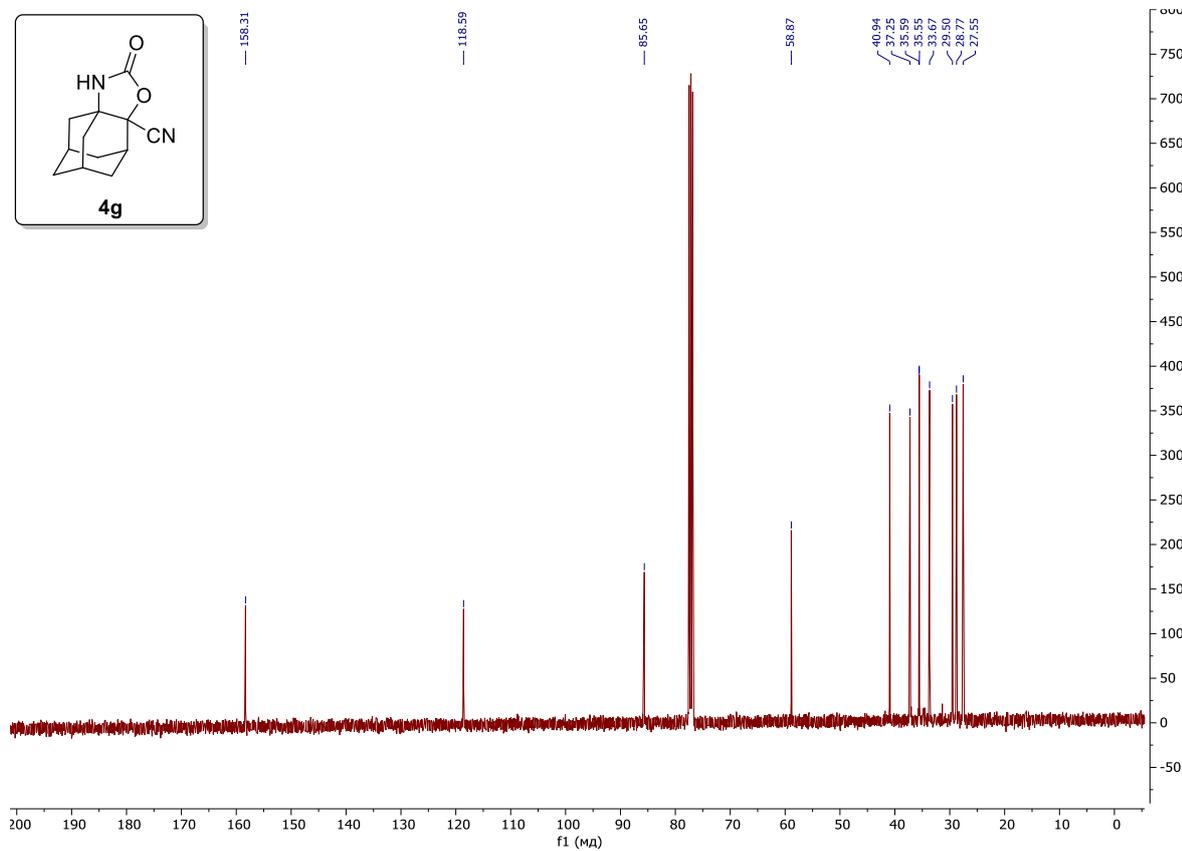
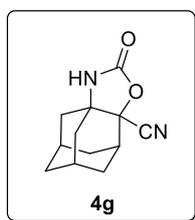
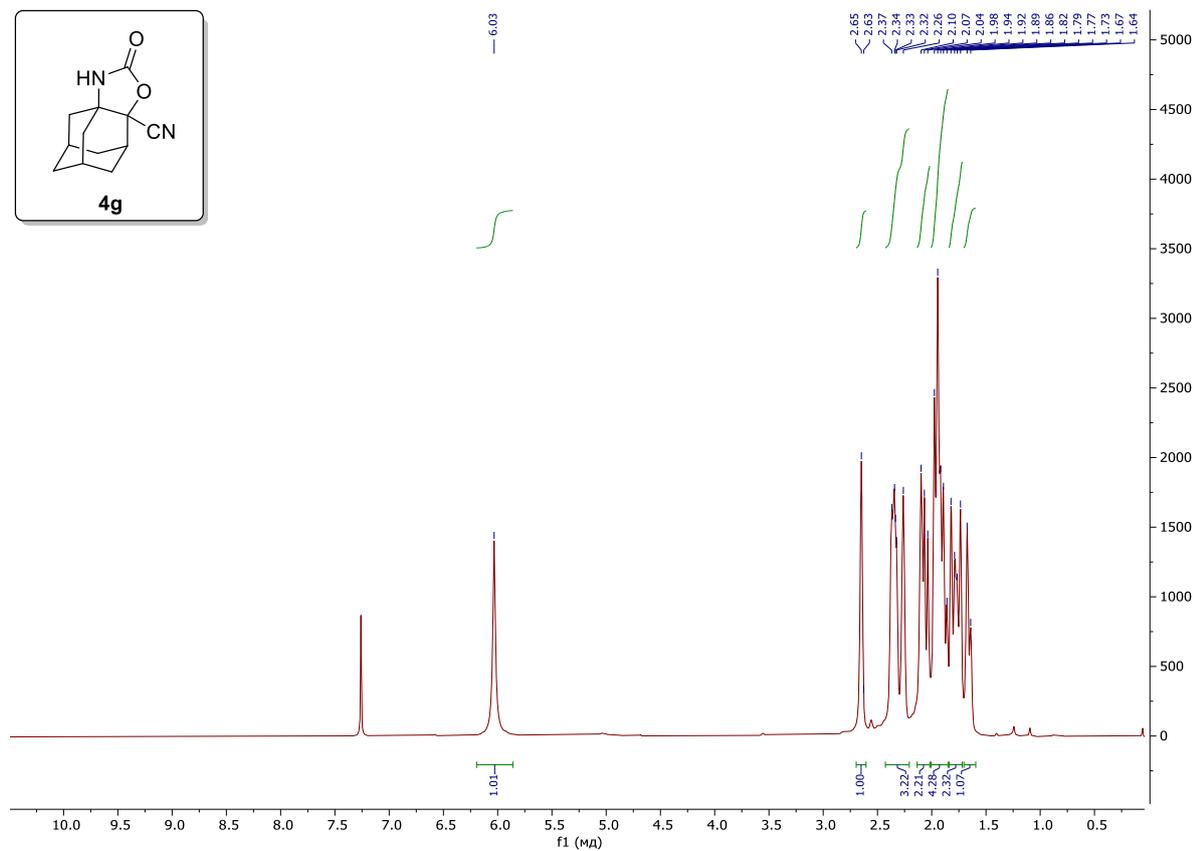
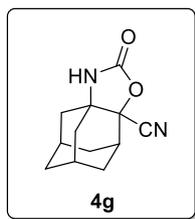




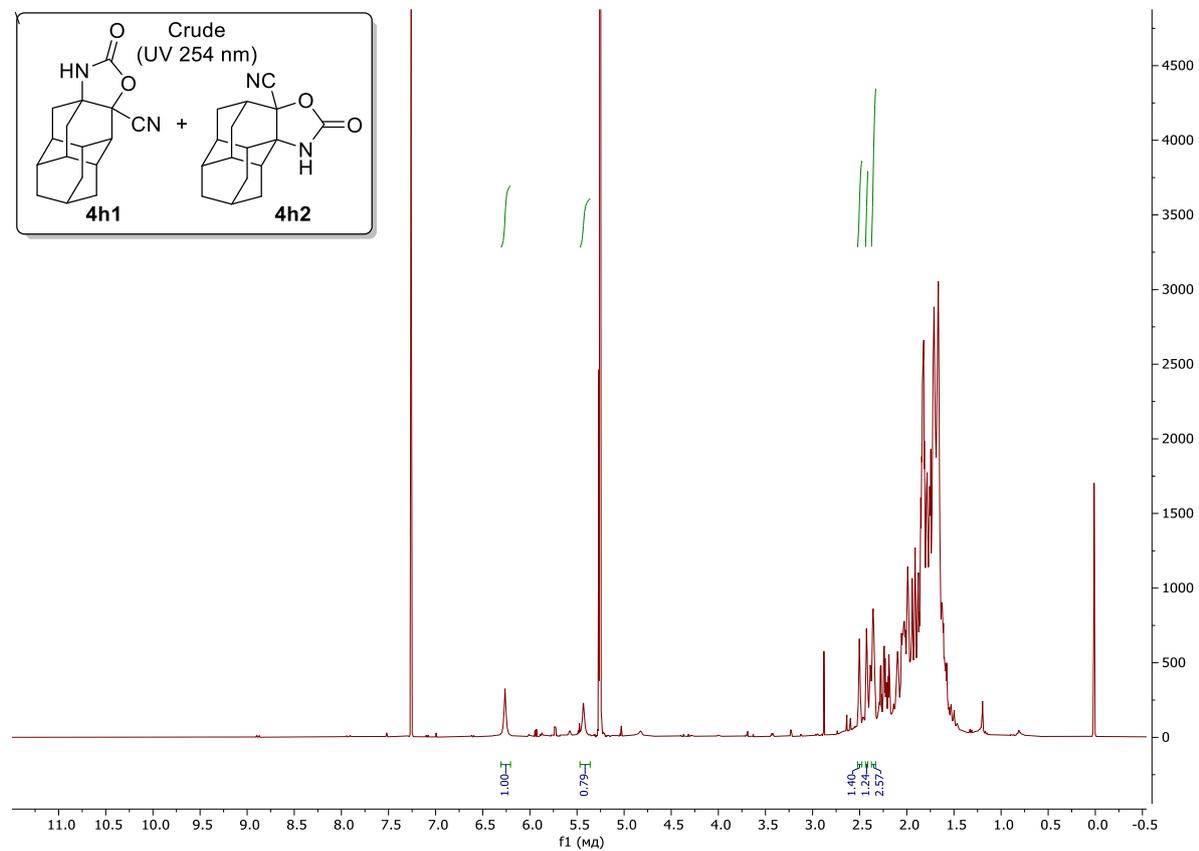
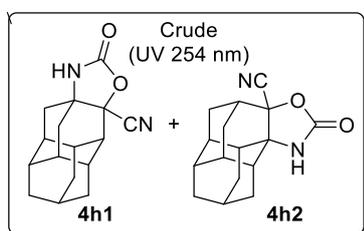
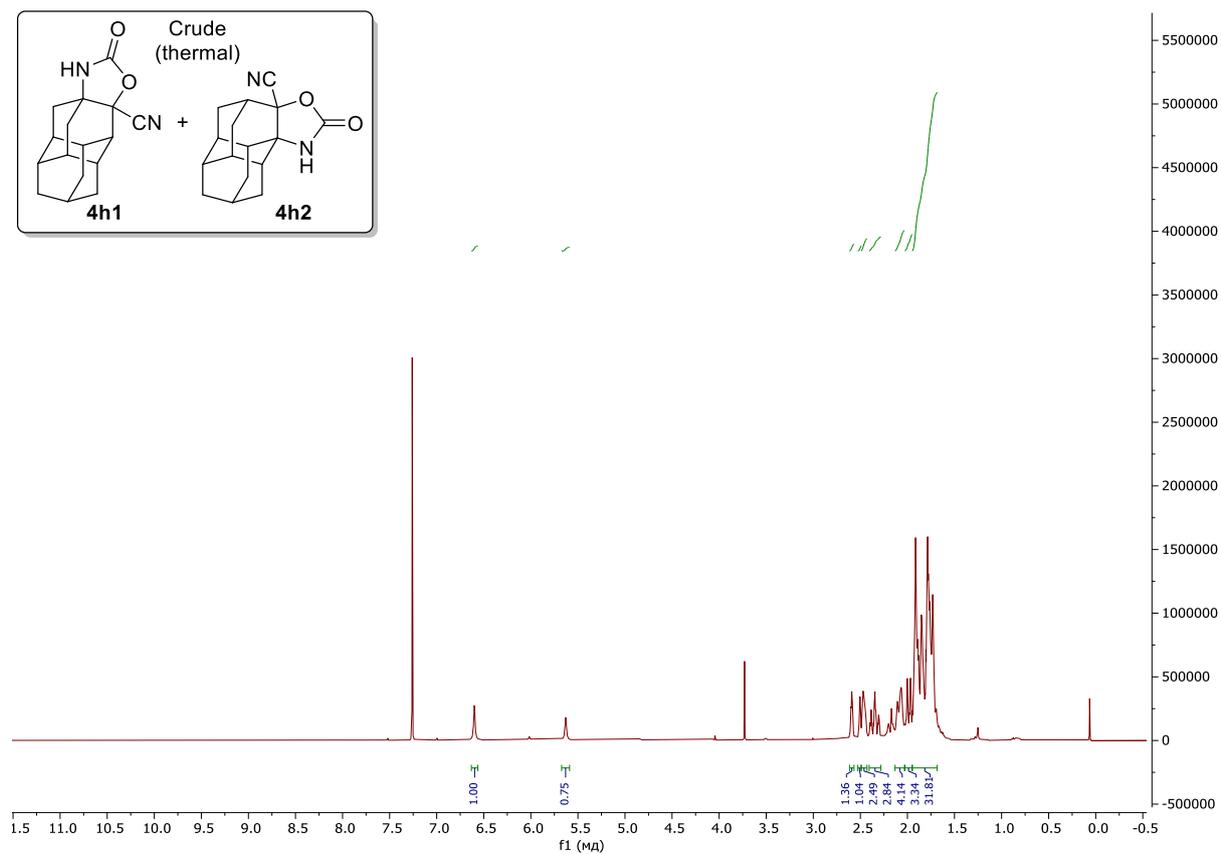
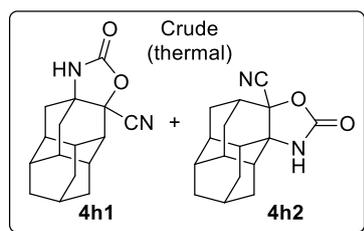


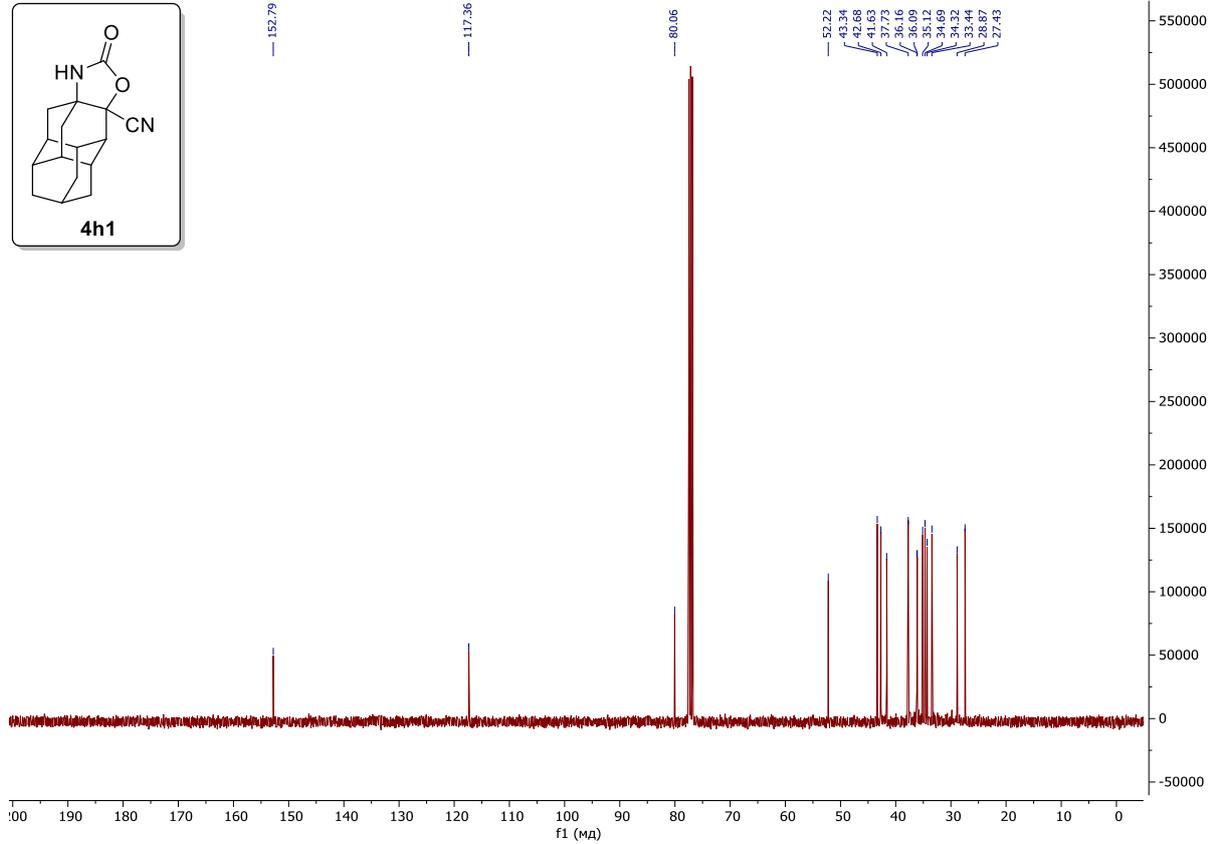
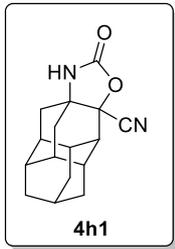
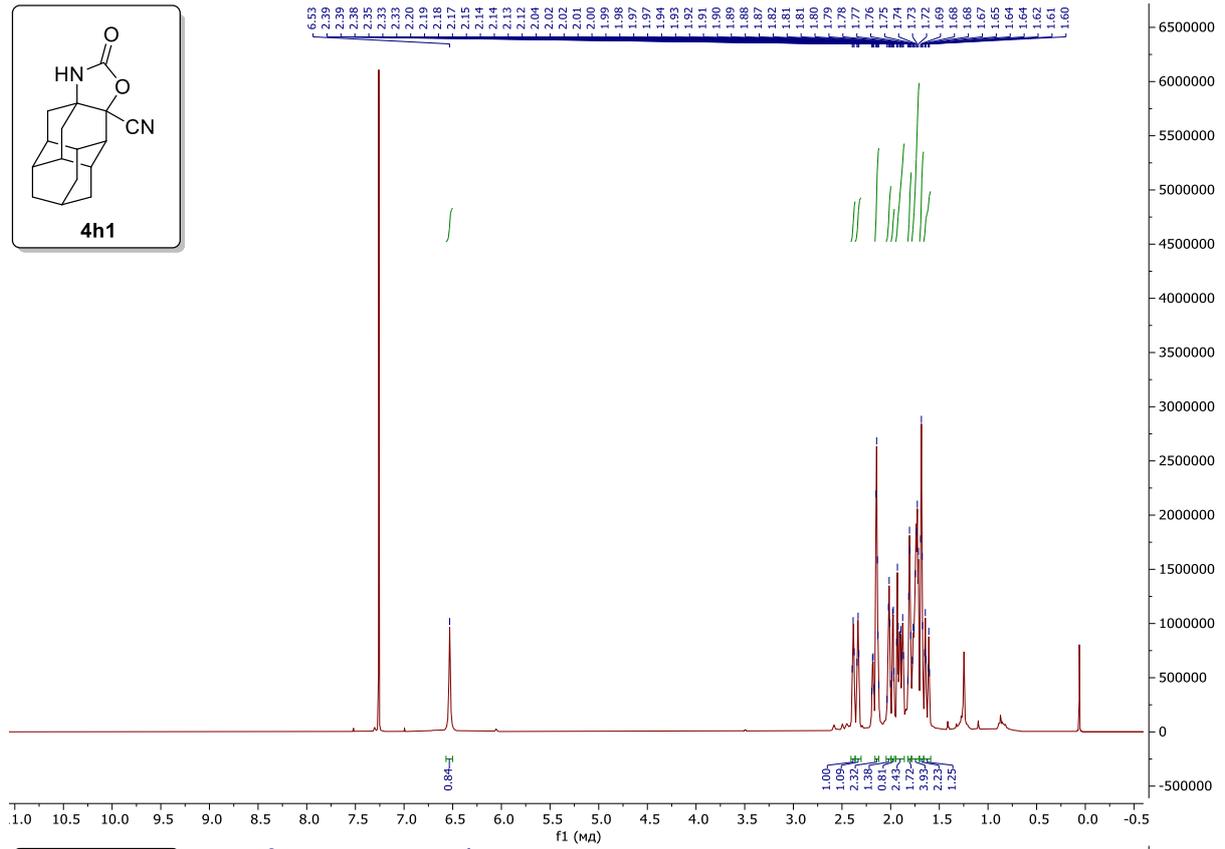
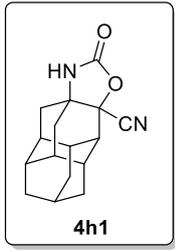


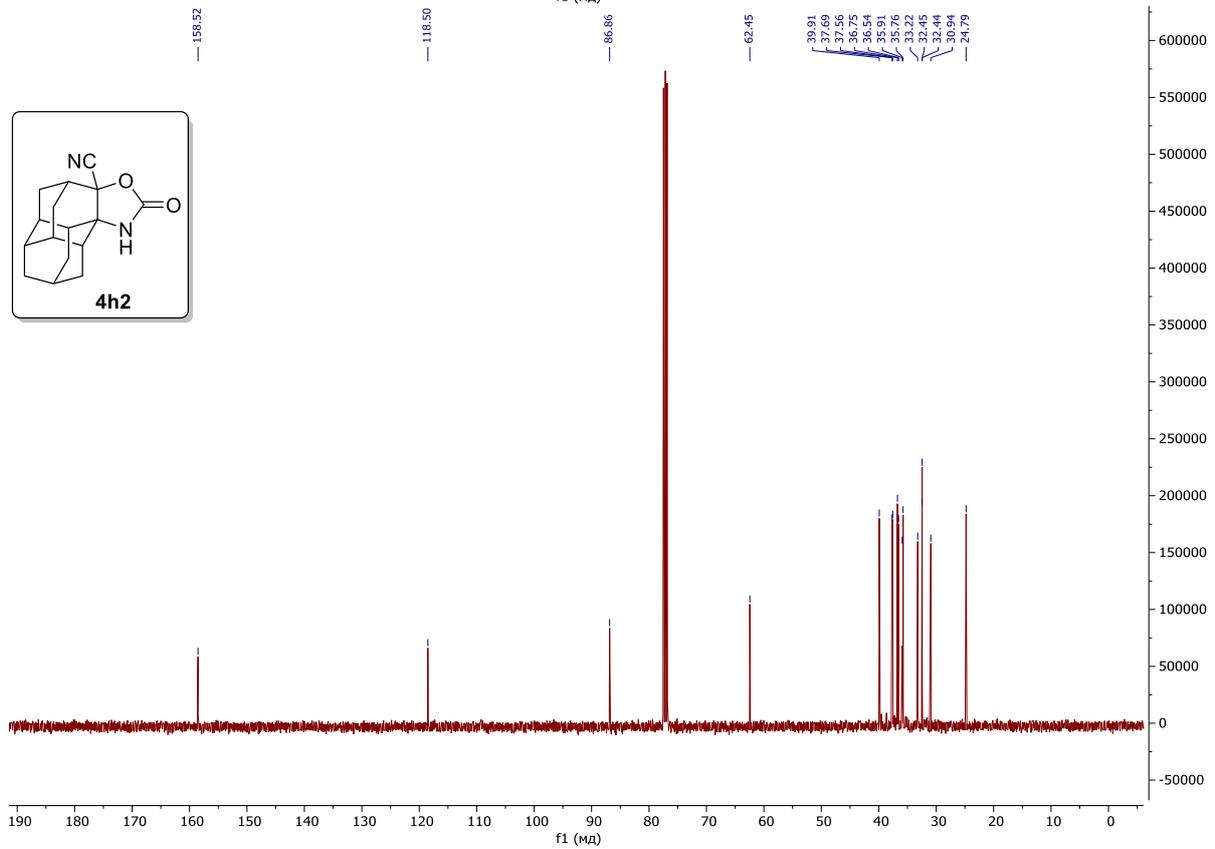
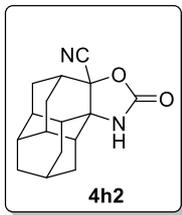
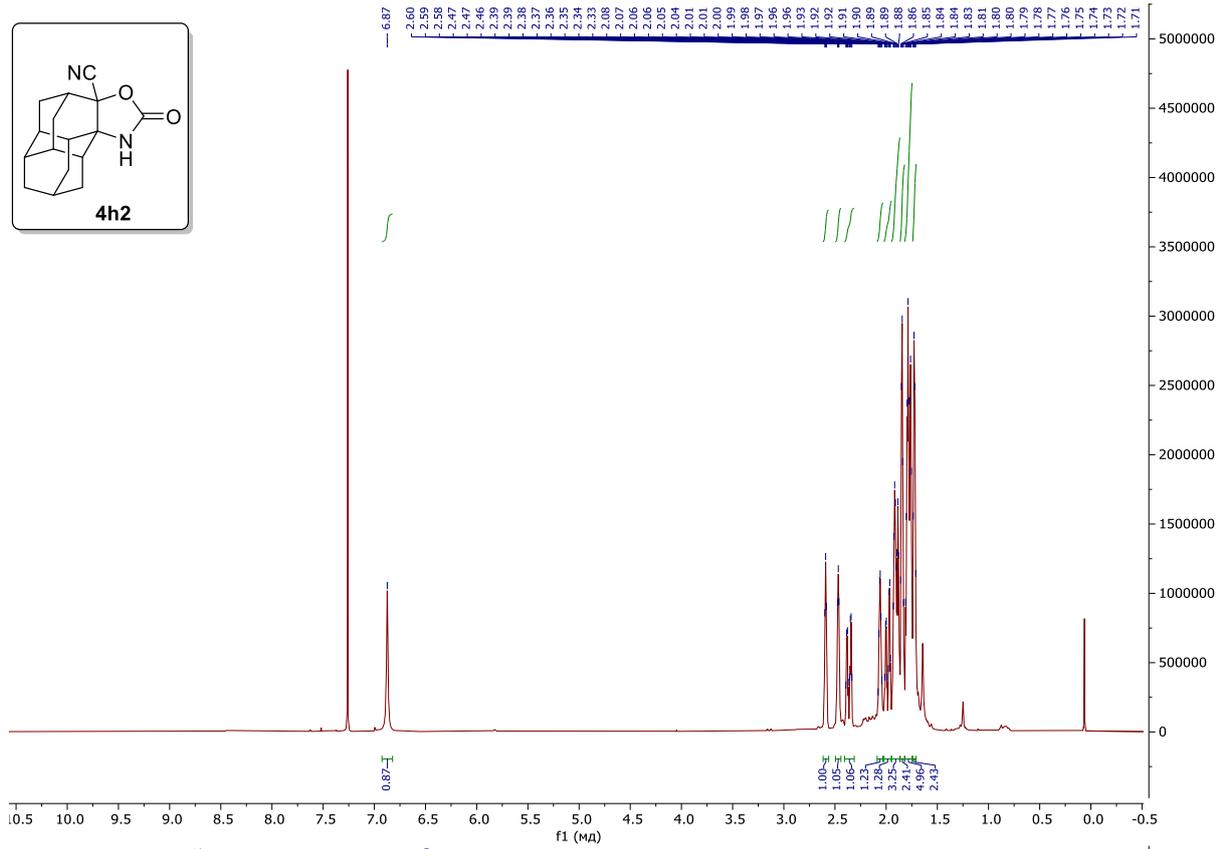
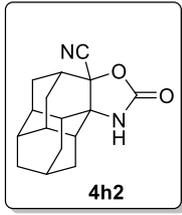
Compound 4g



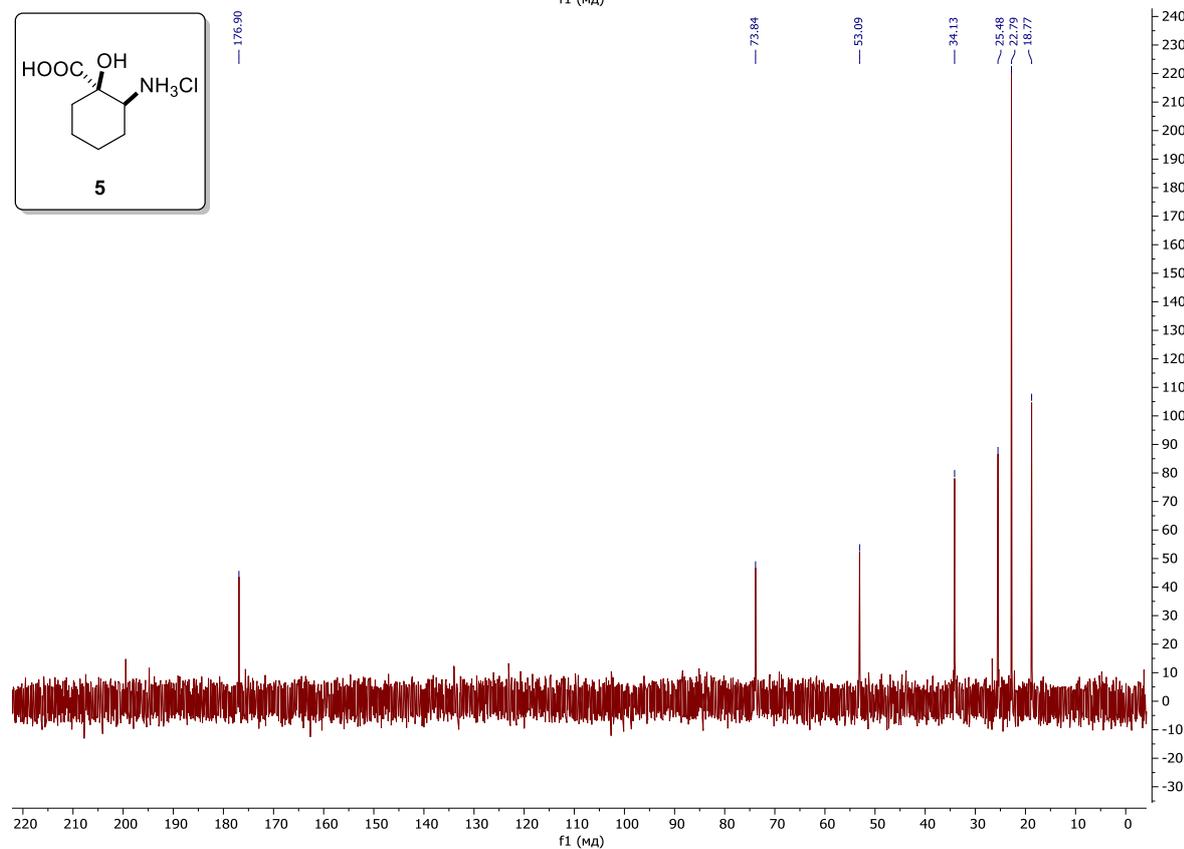
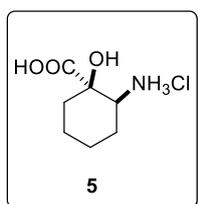
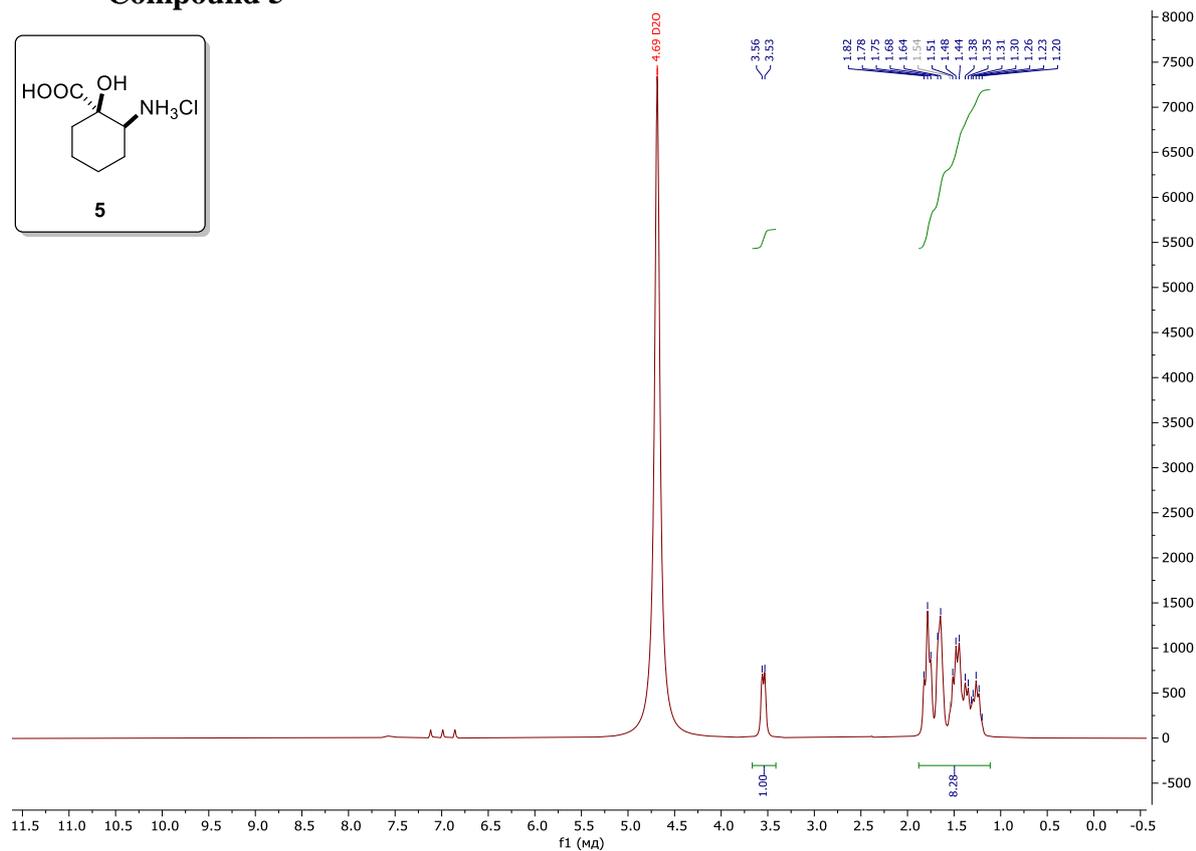
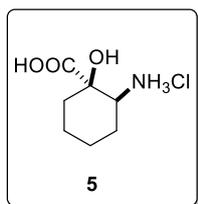
Compound 4h



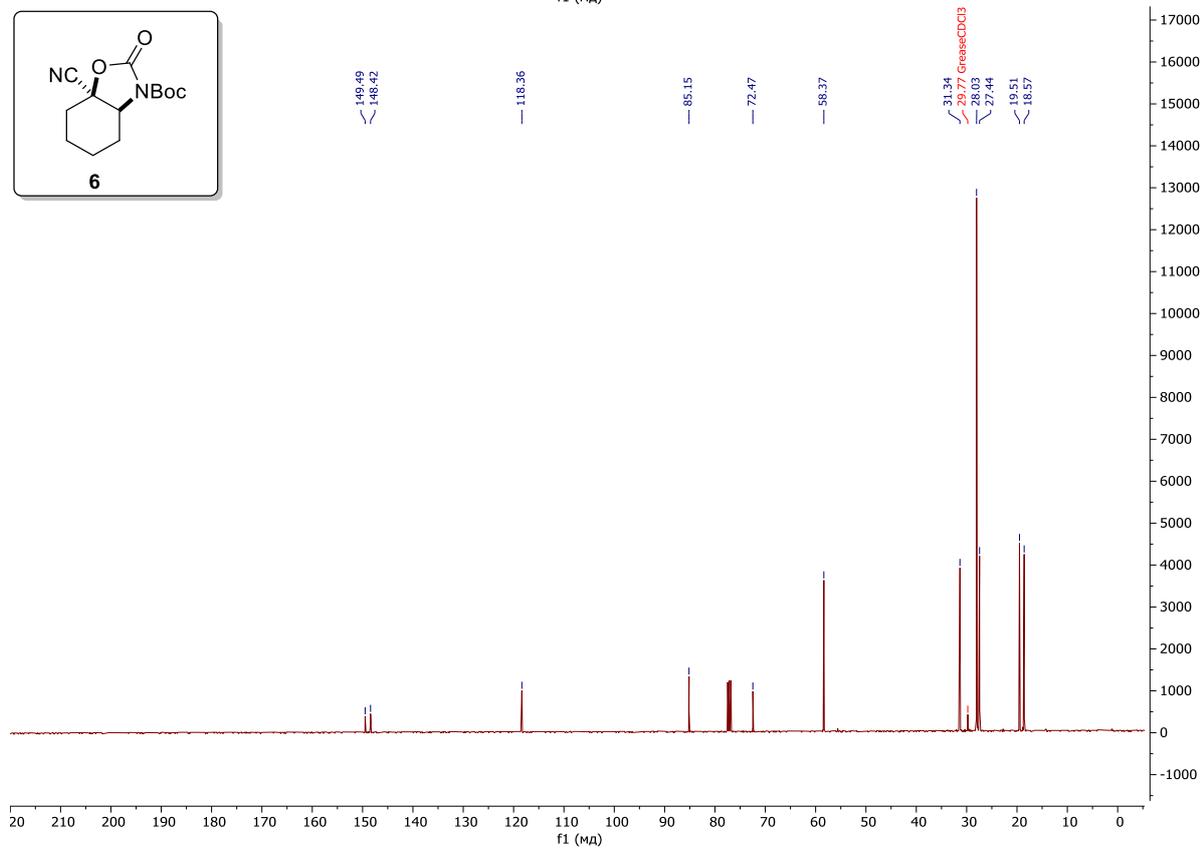
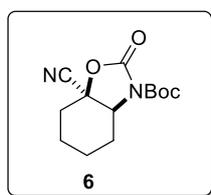
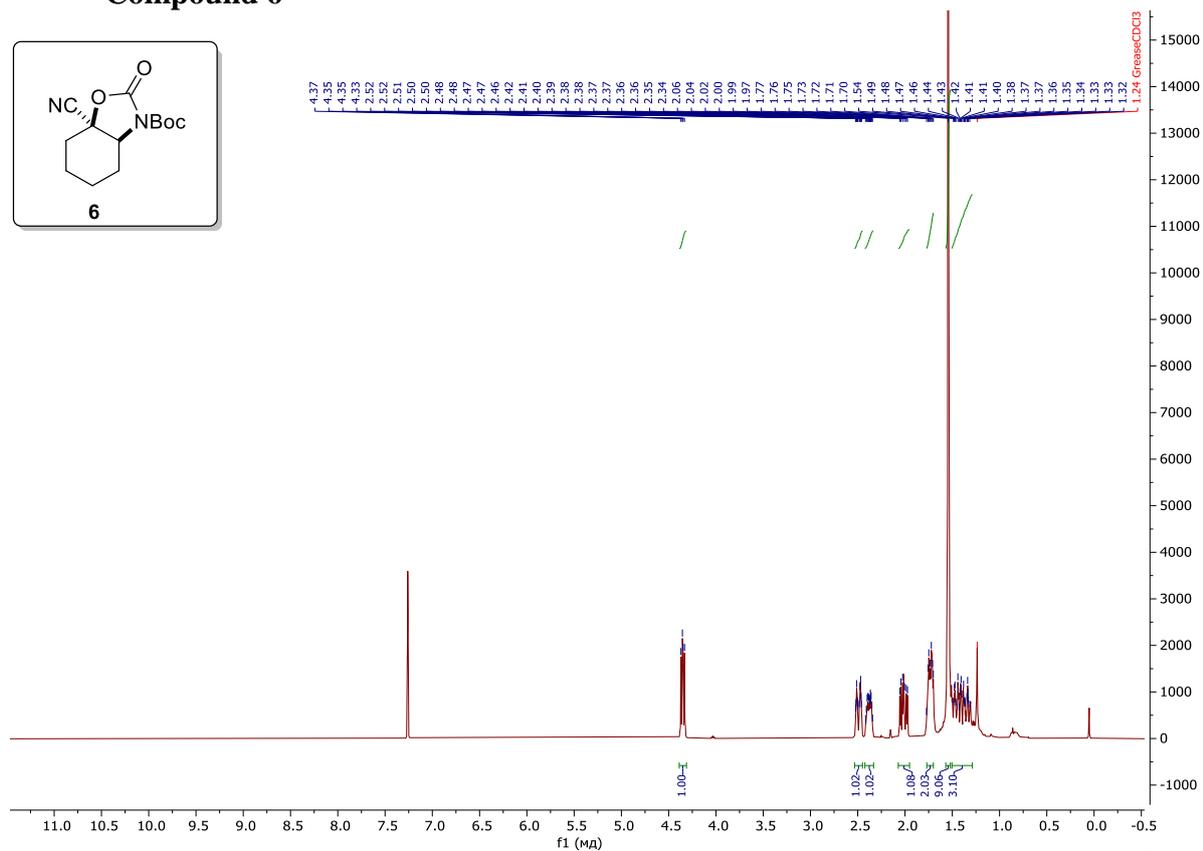
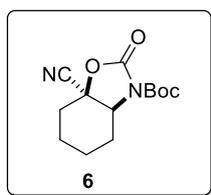




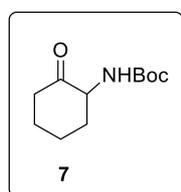
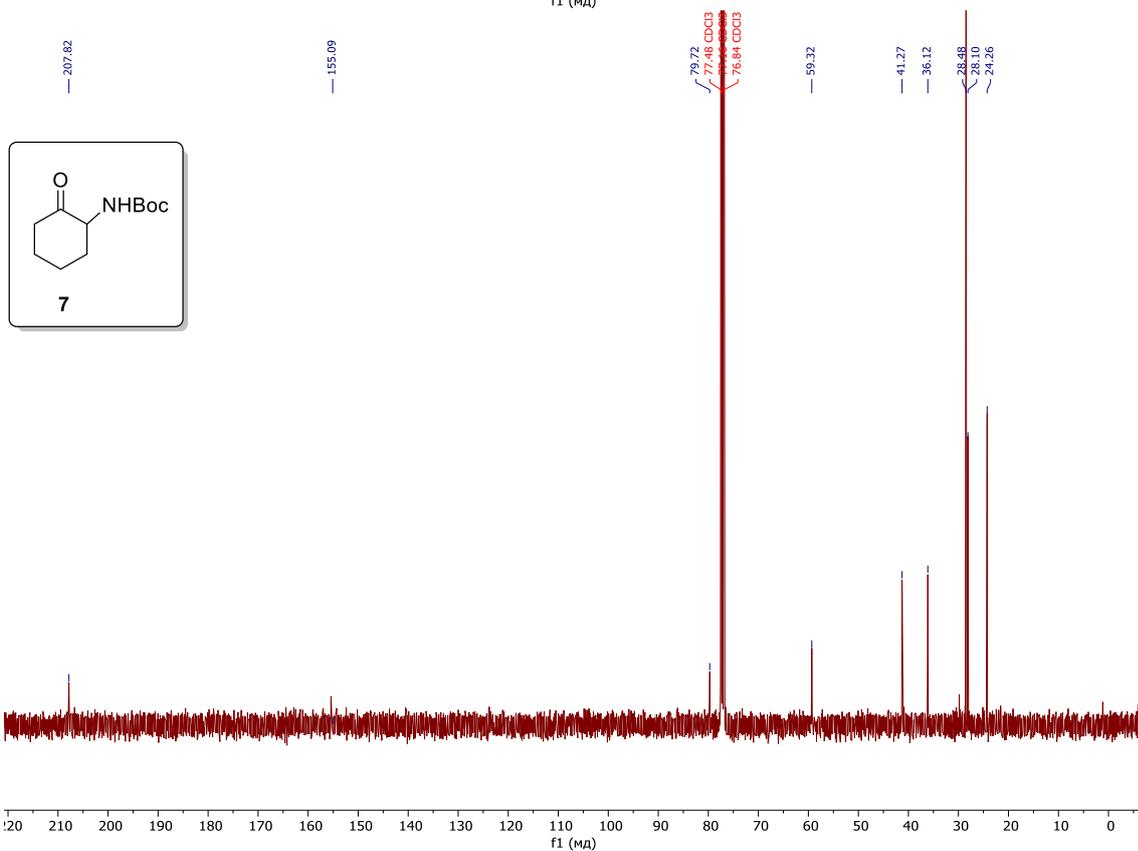
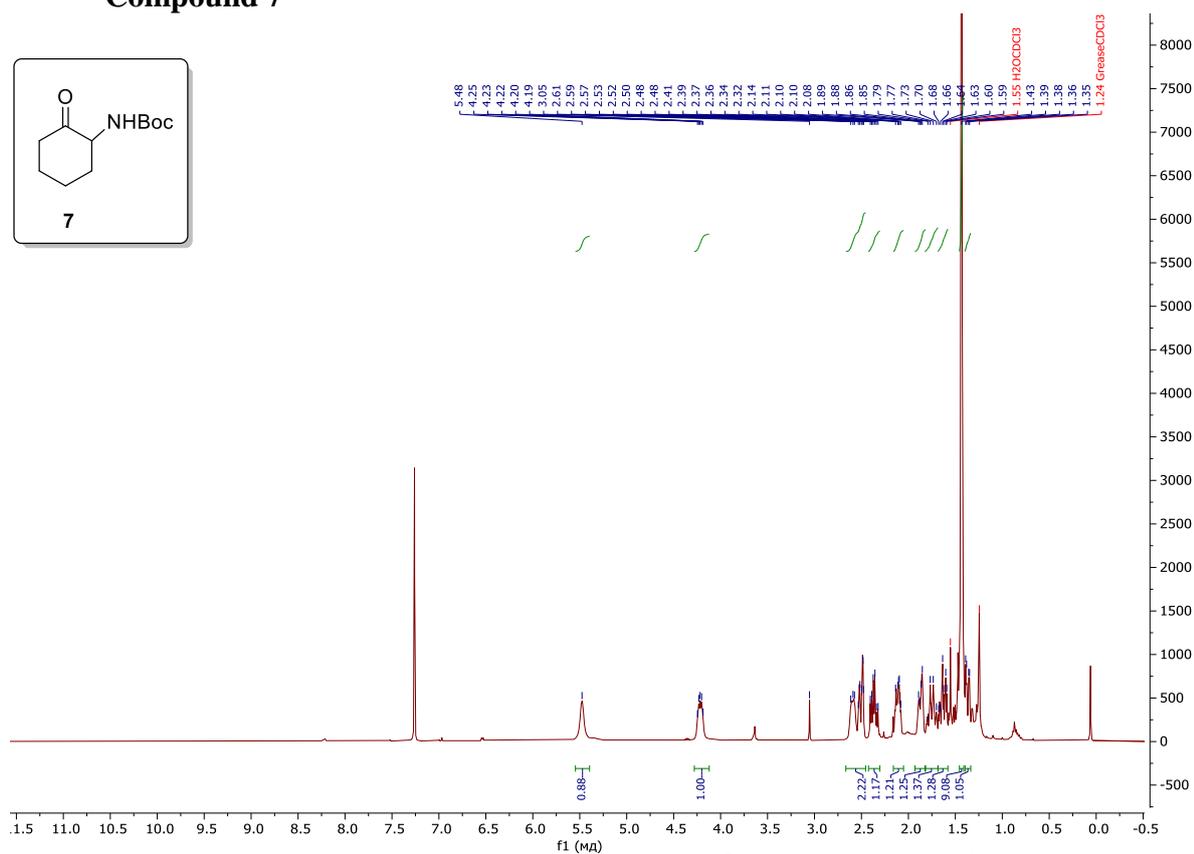
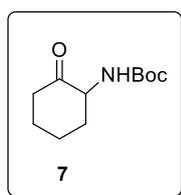
Compound 5



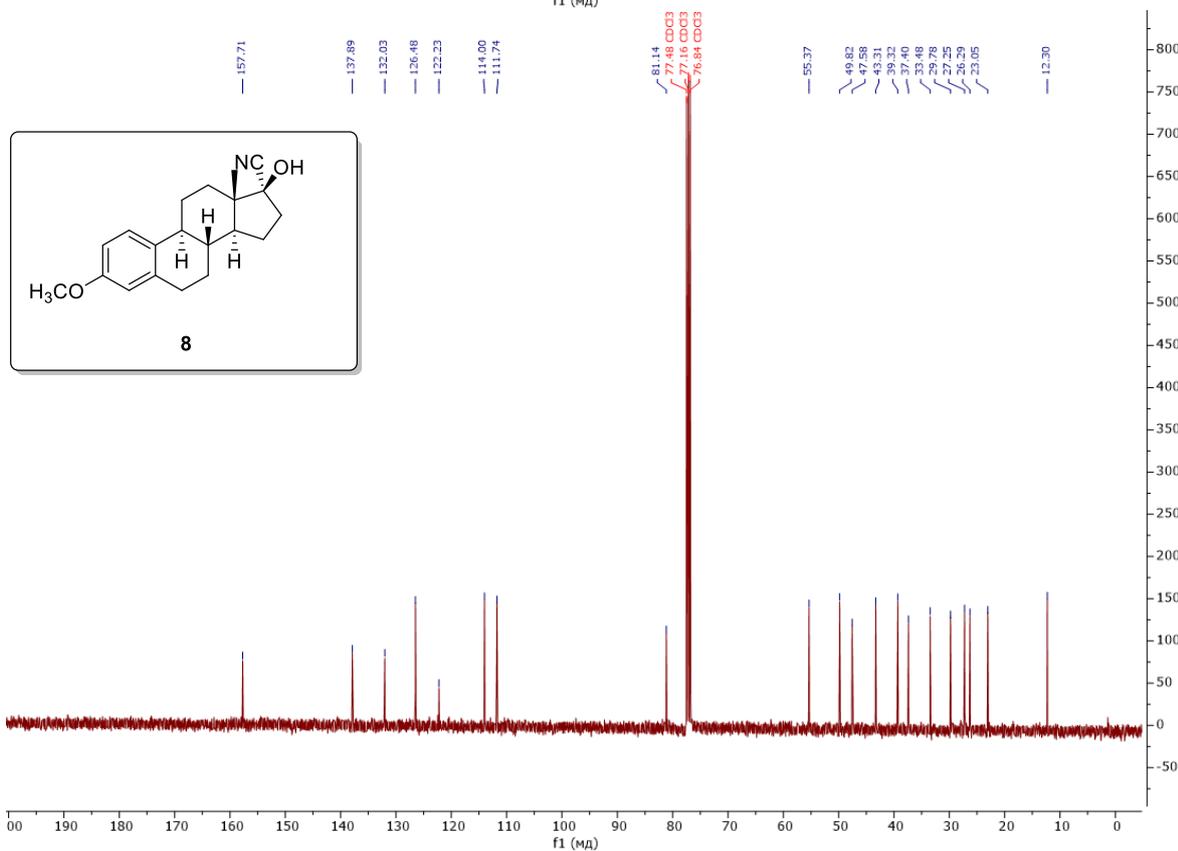
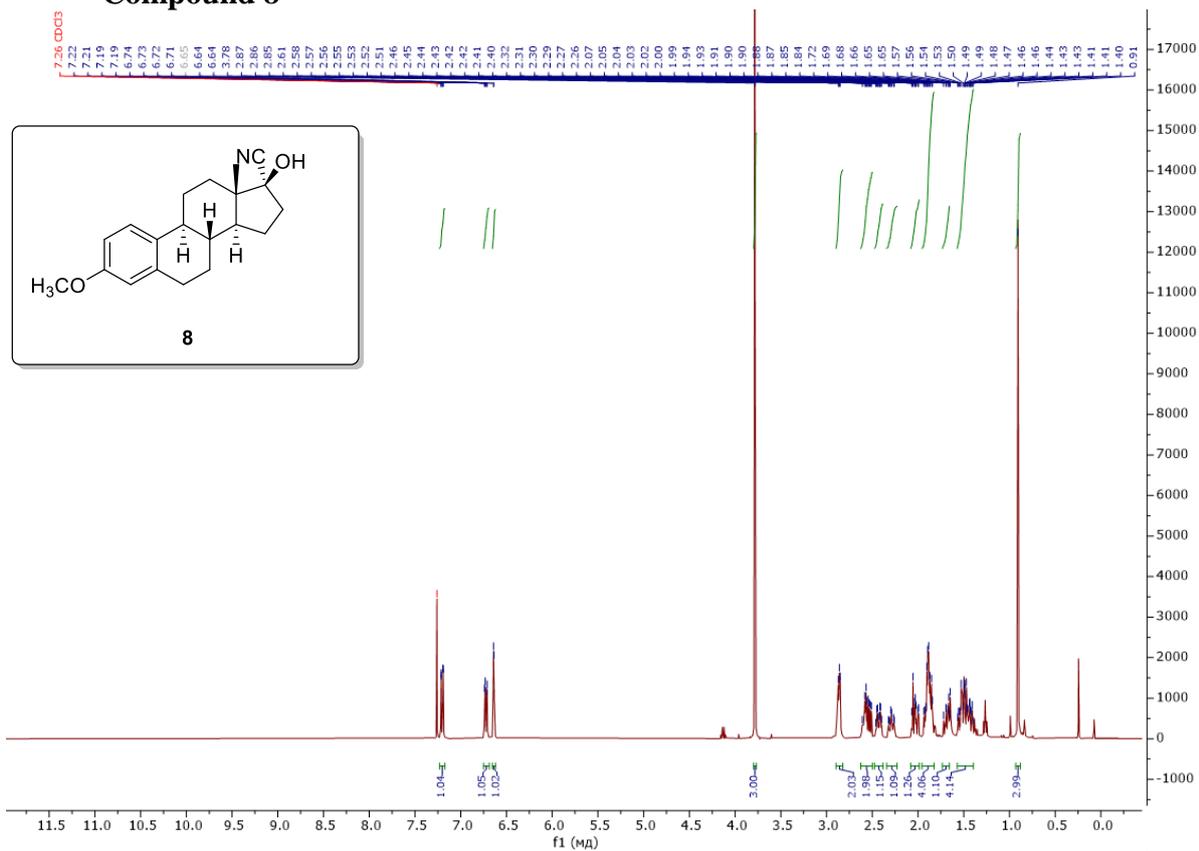
Compound 6



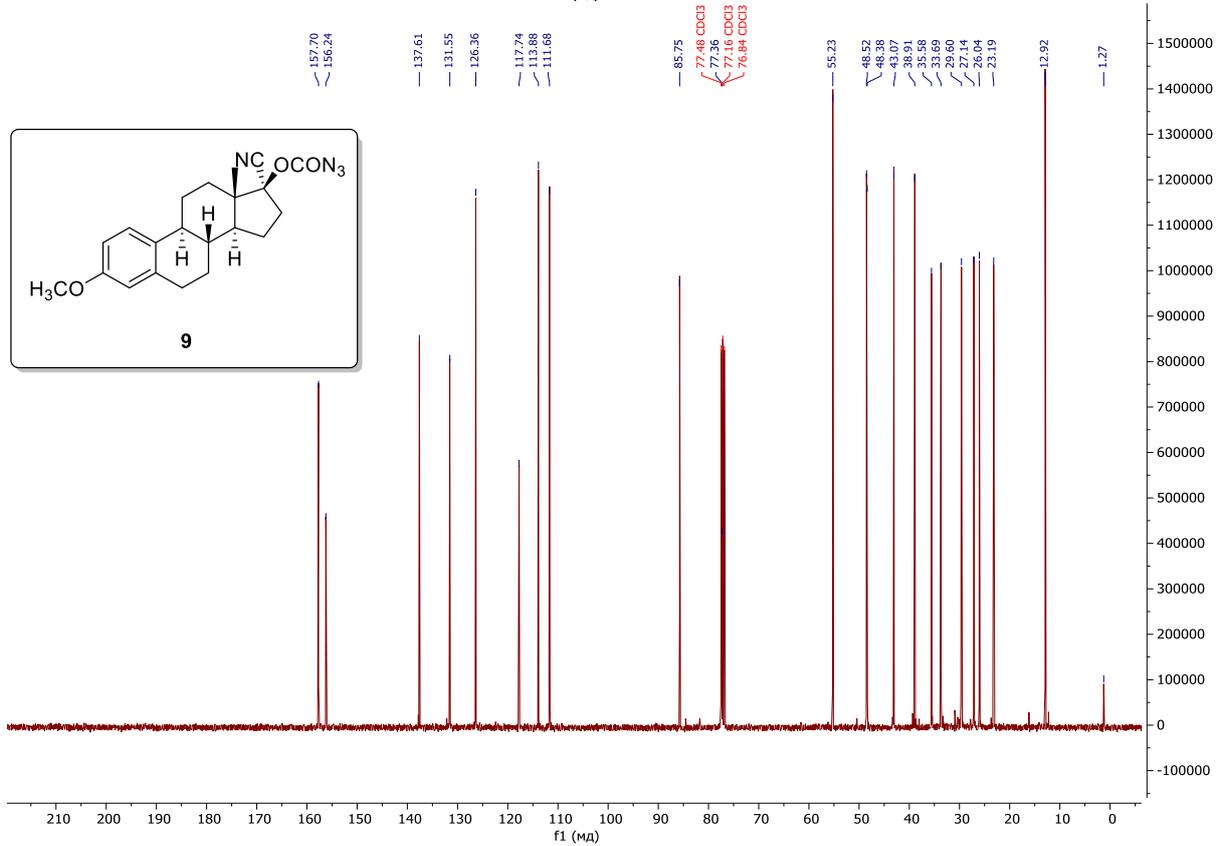
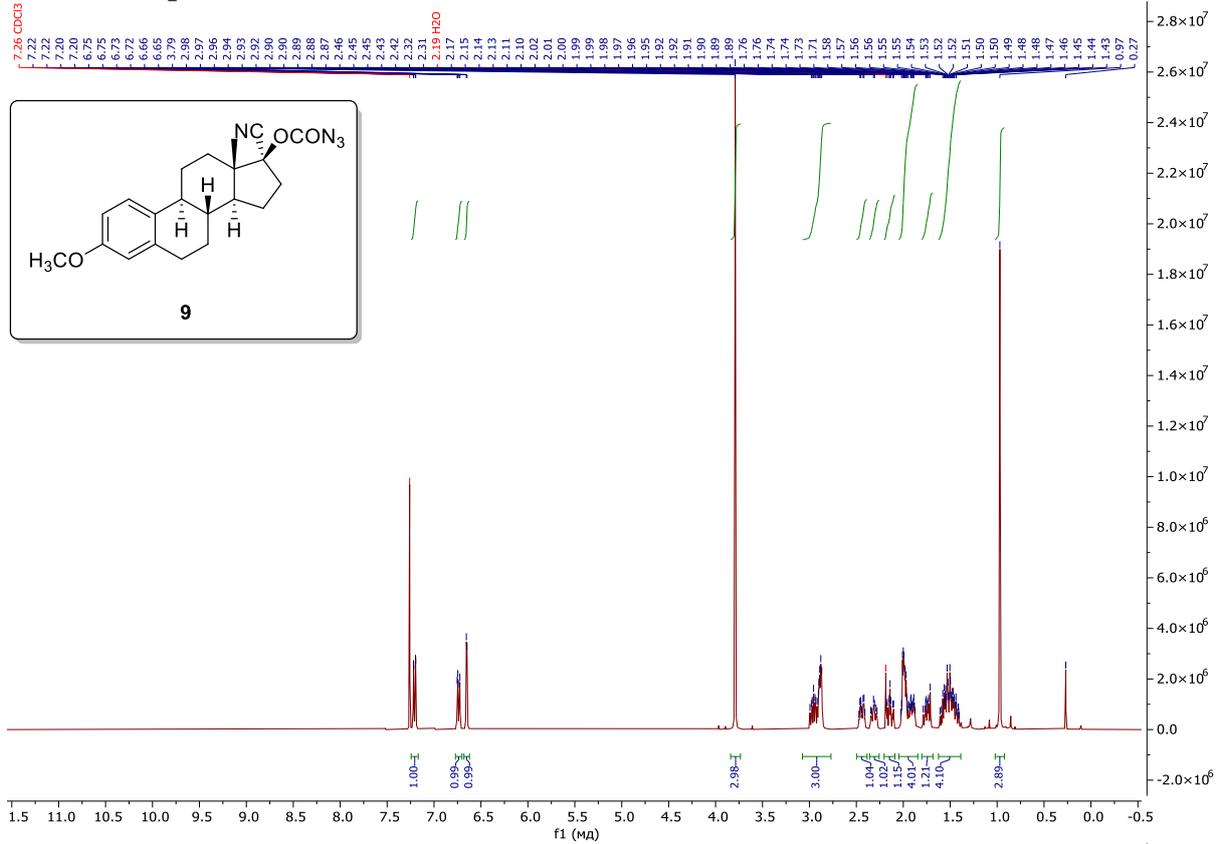
Compound 7



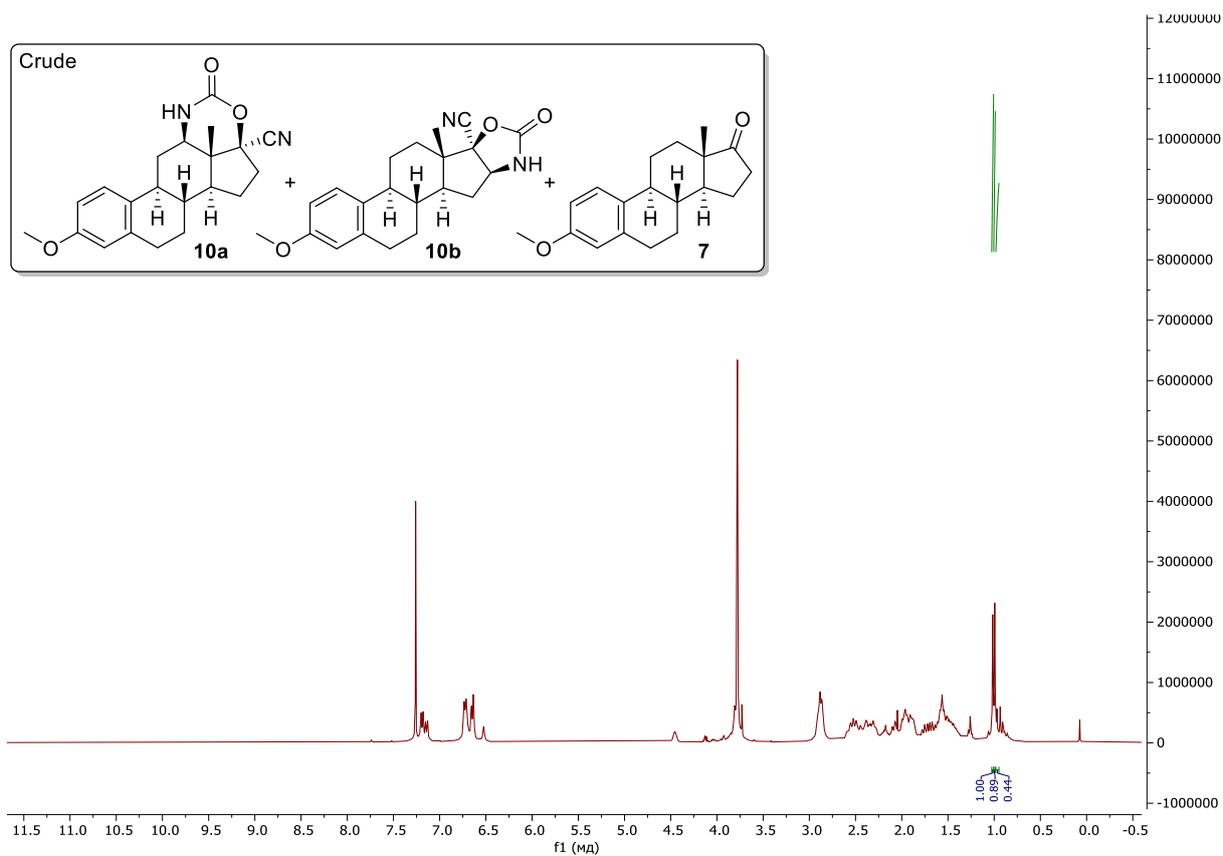
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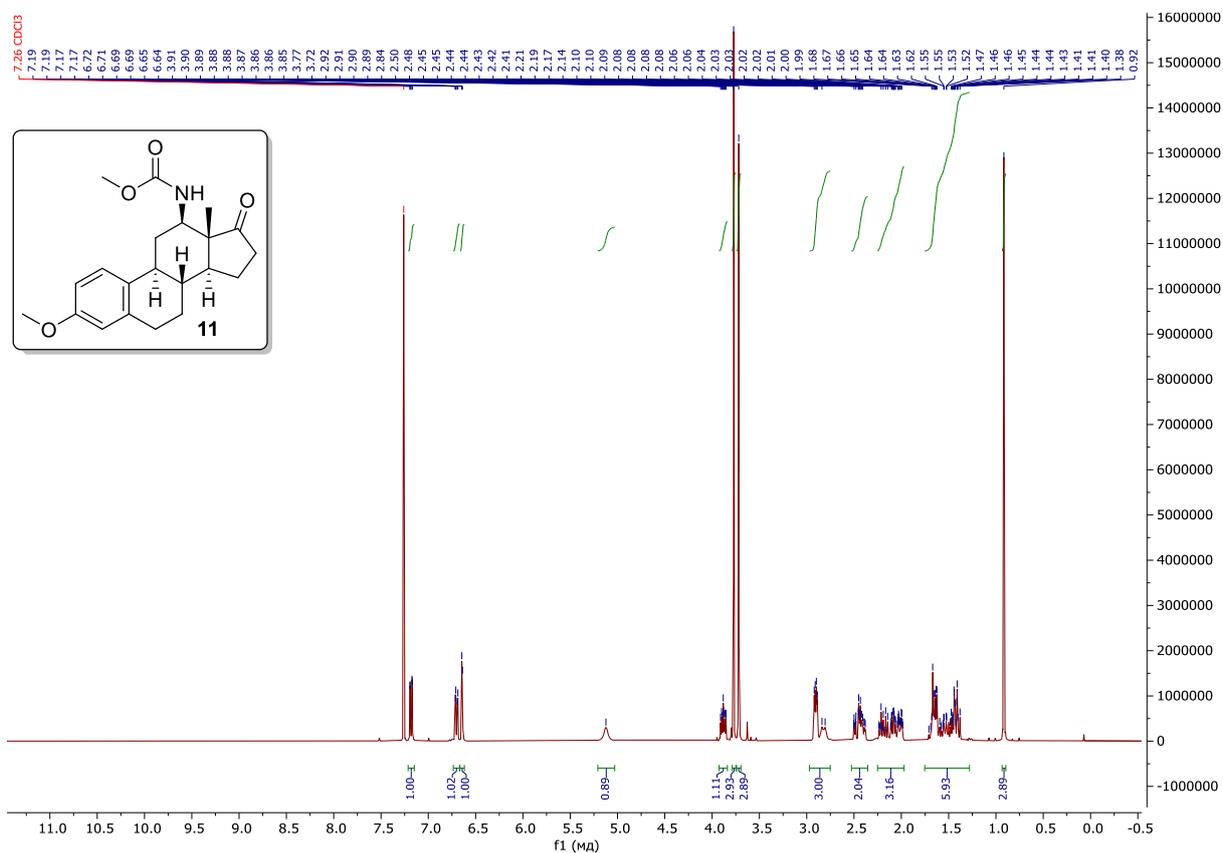
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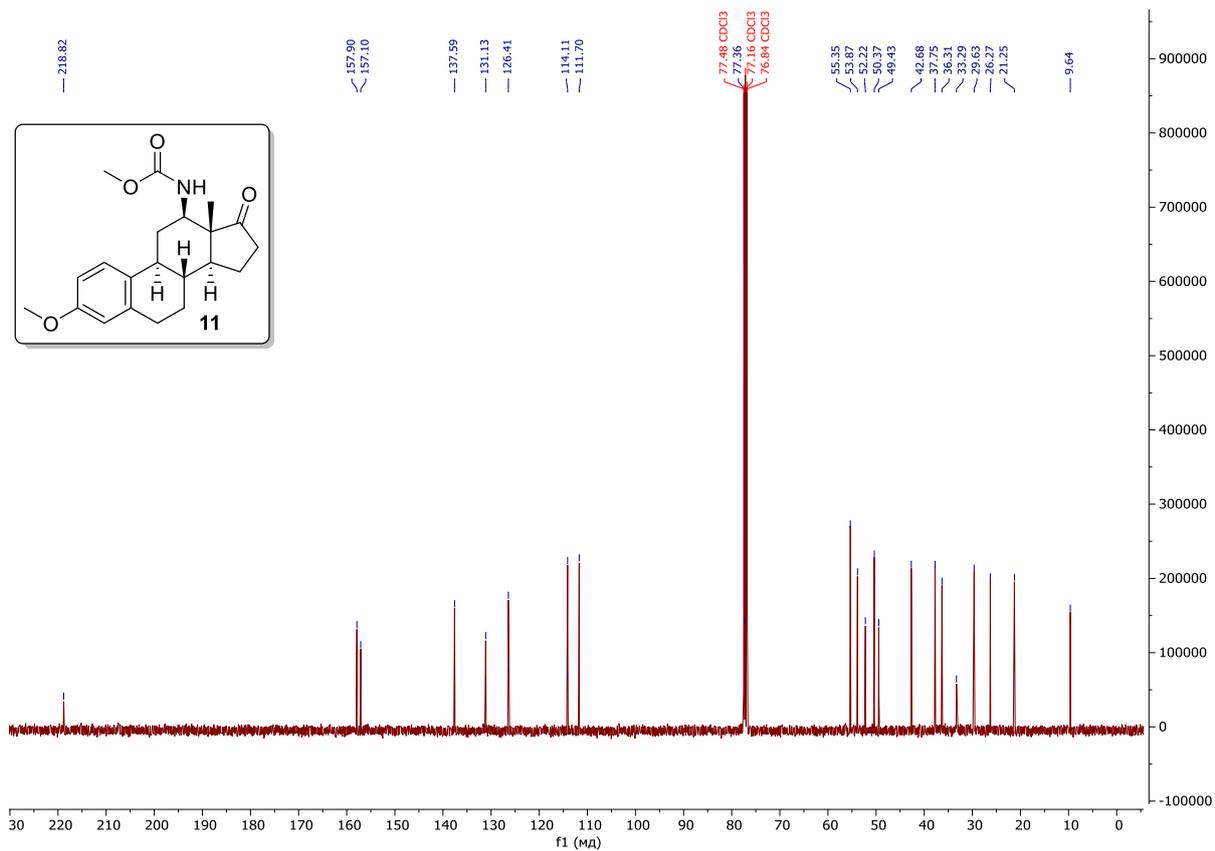


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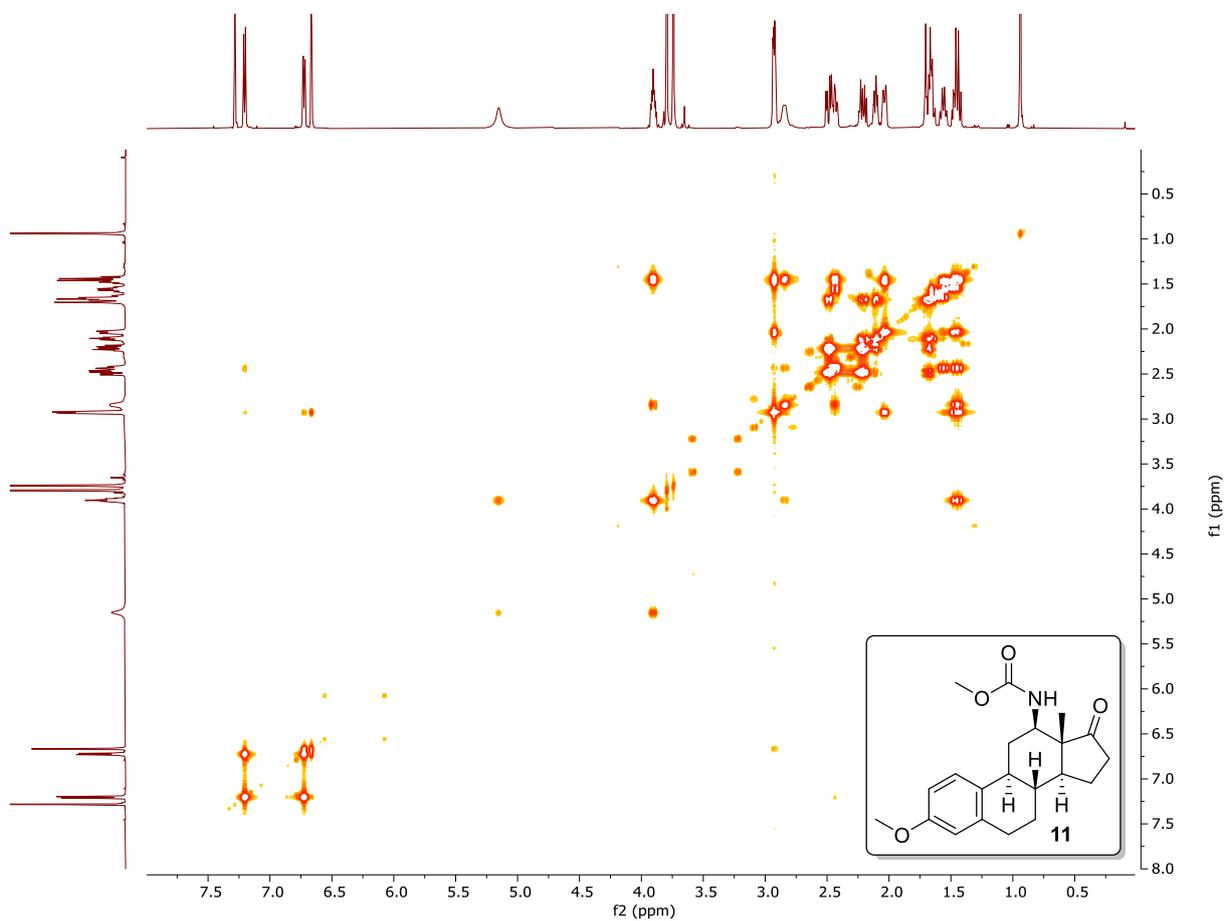


Compound 11

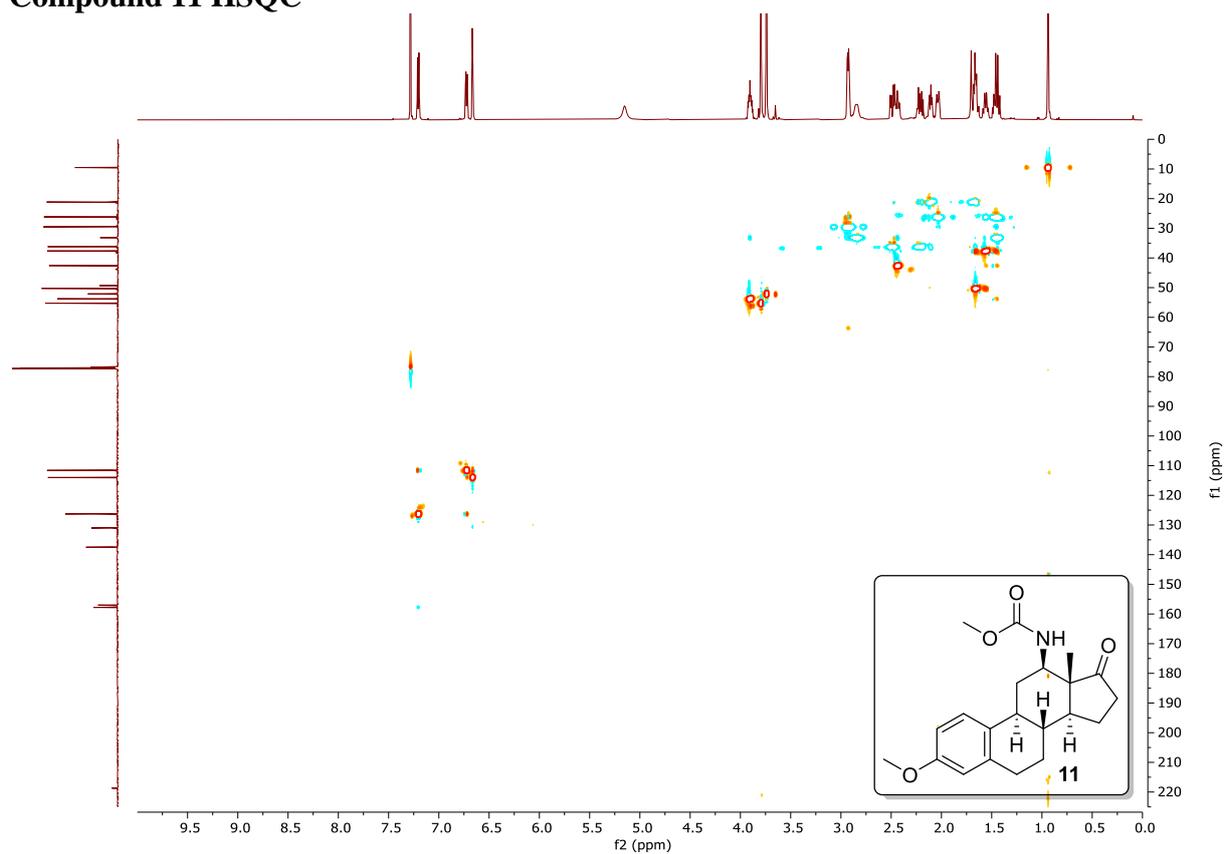




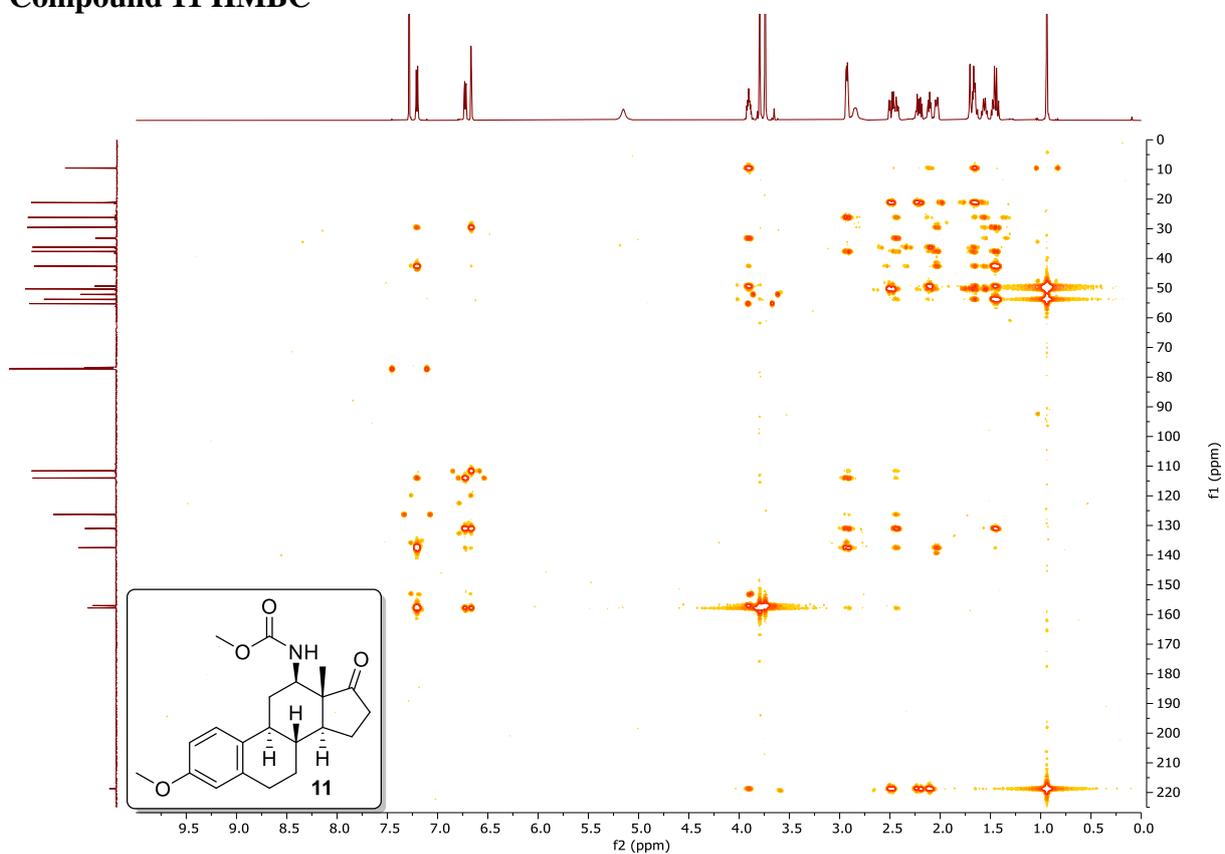
Compound 11 COSY



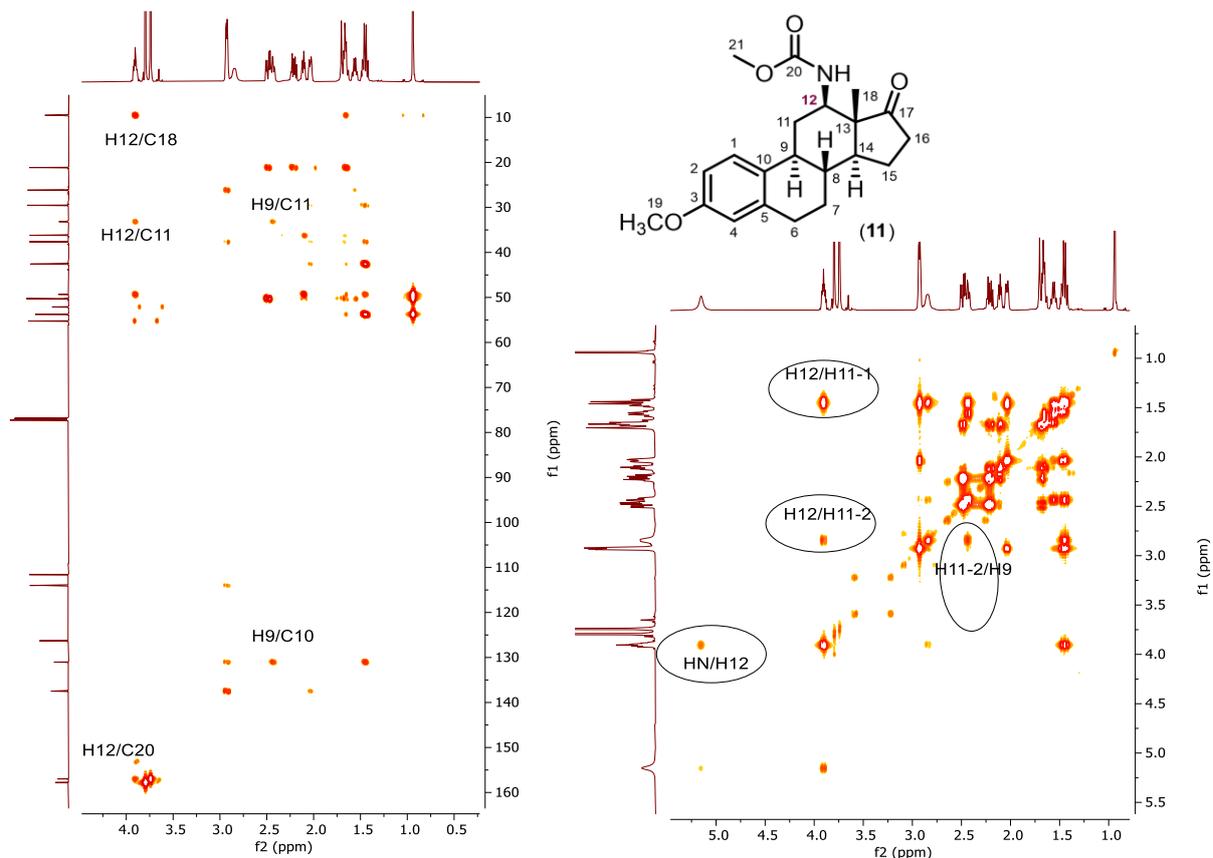
Compound 11 HSQC



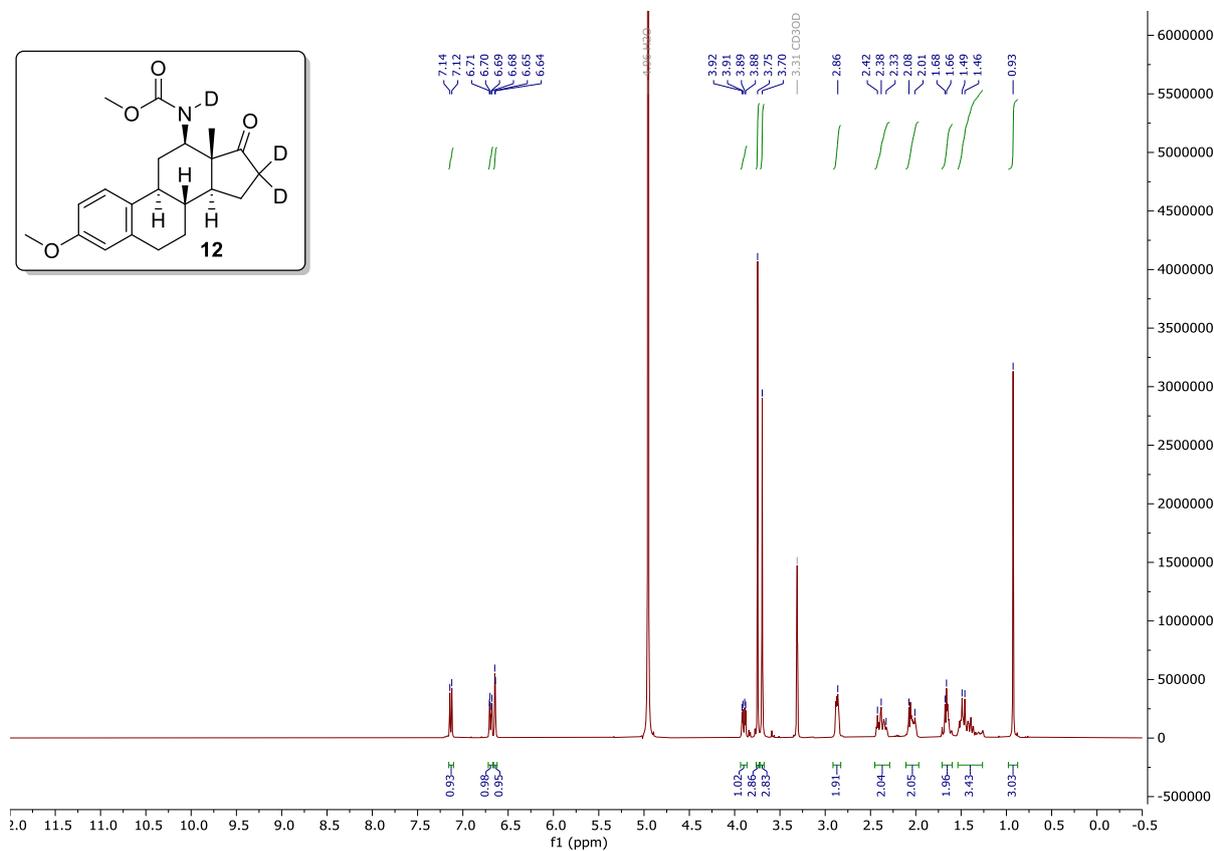
Compound 11 HMBC

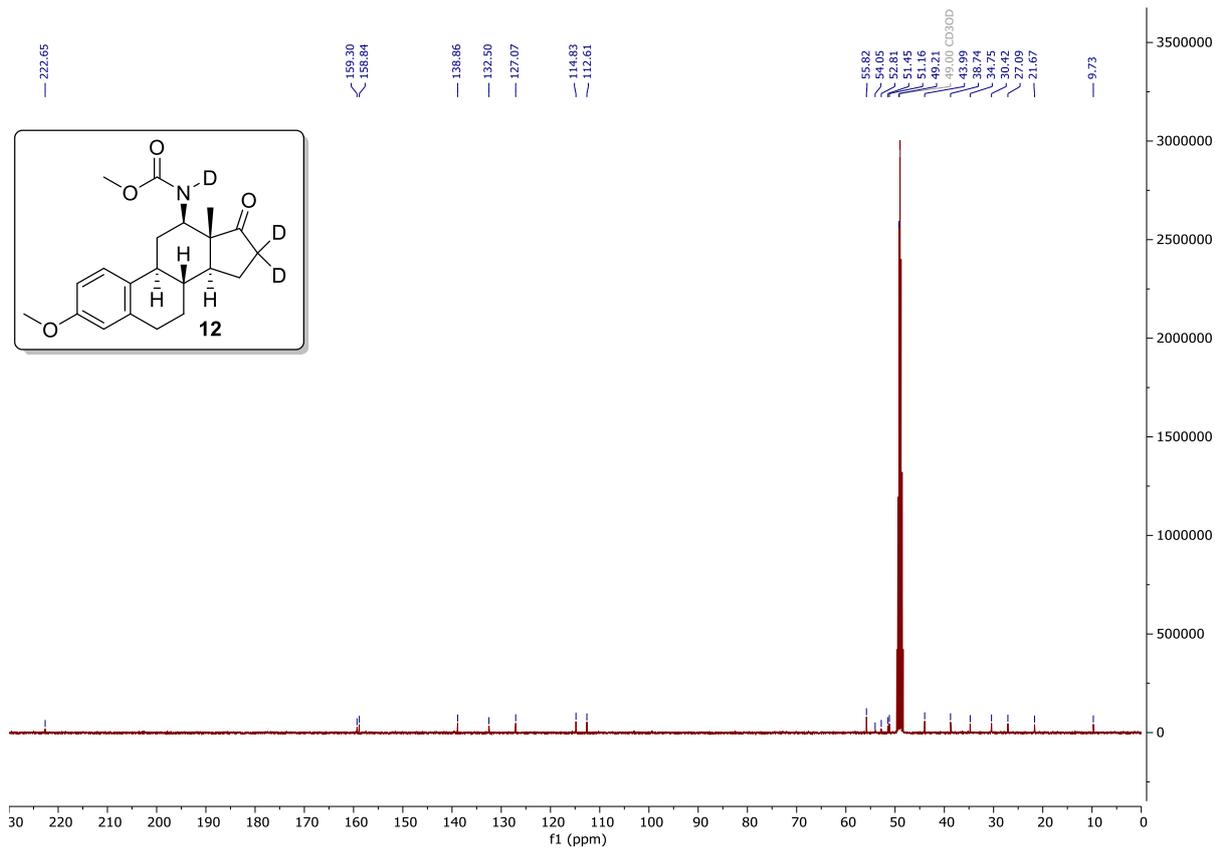


Compound 11 Crosspeak Analysis

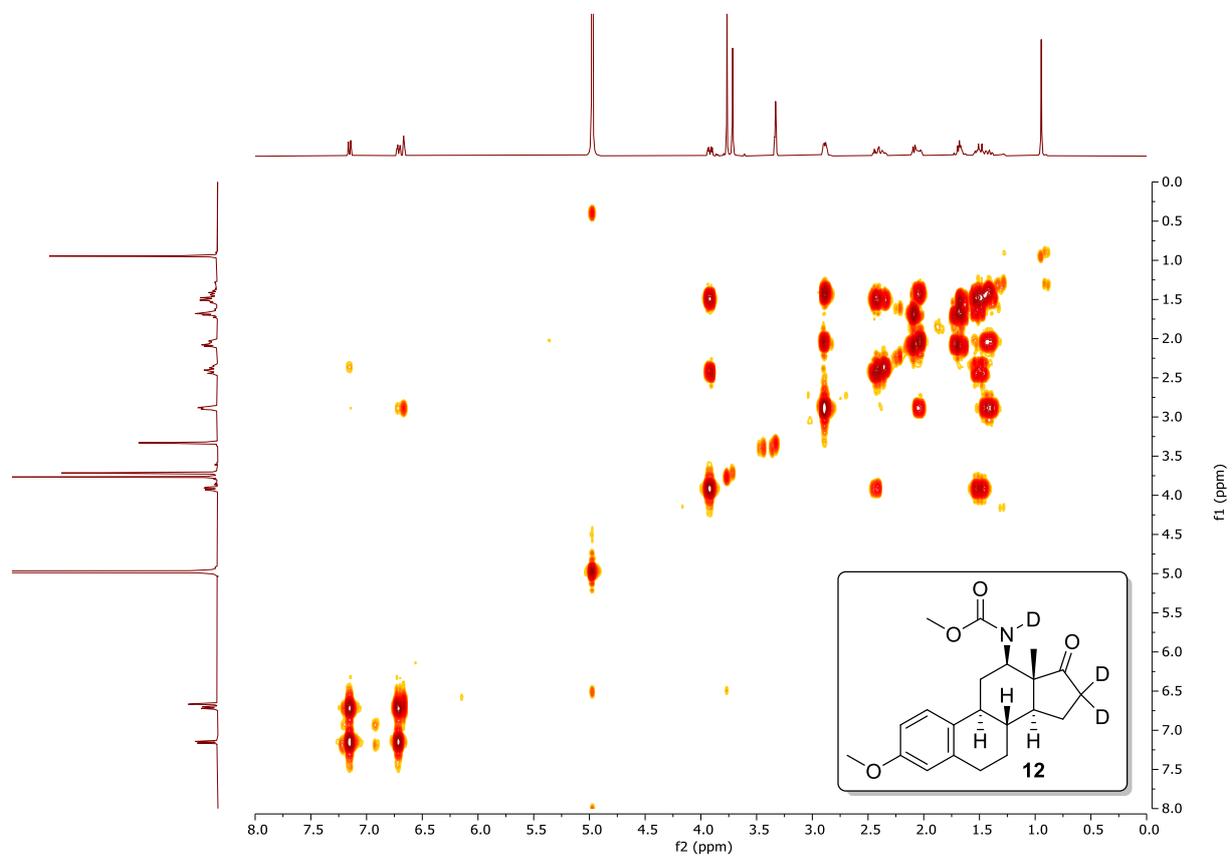


Compound 12

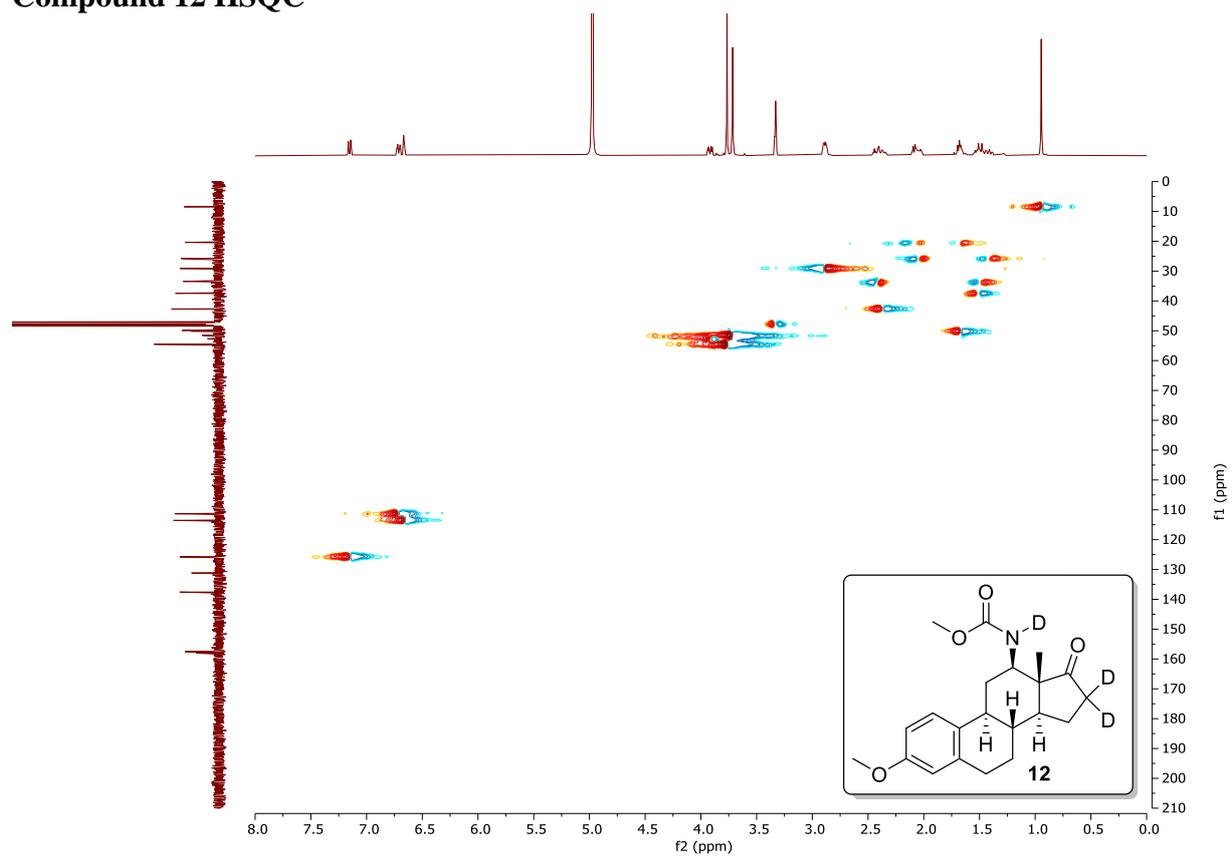




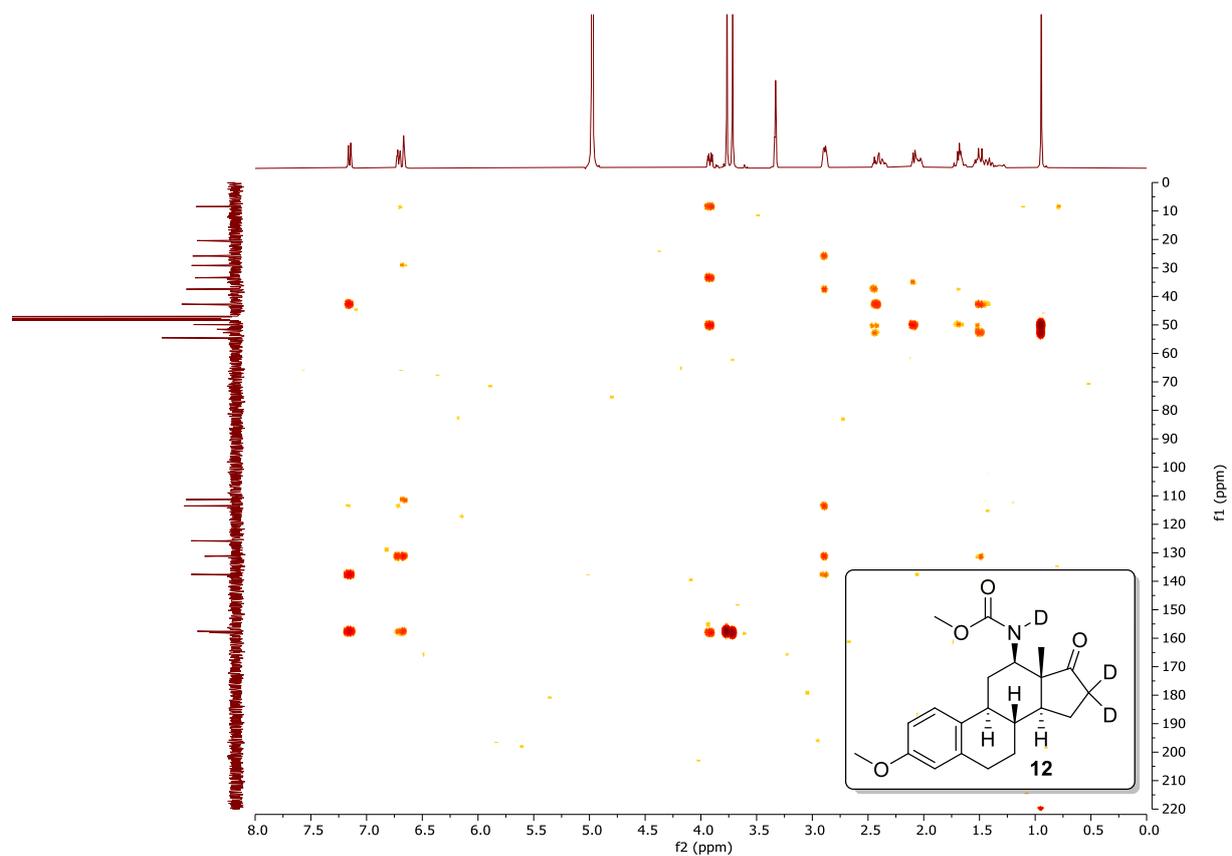
Compound 12 COSY



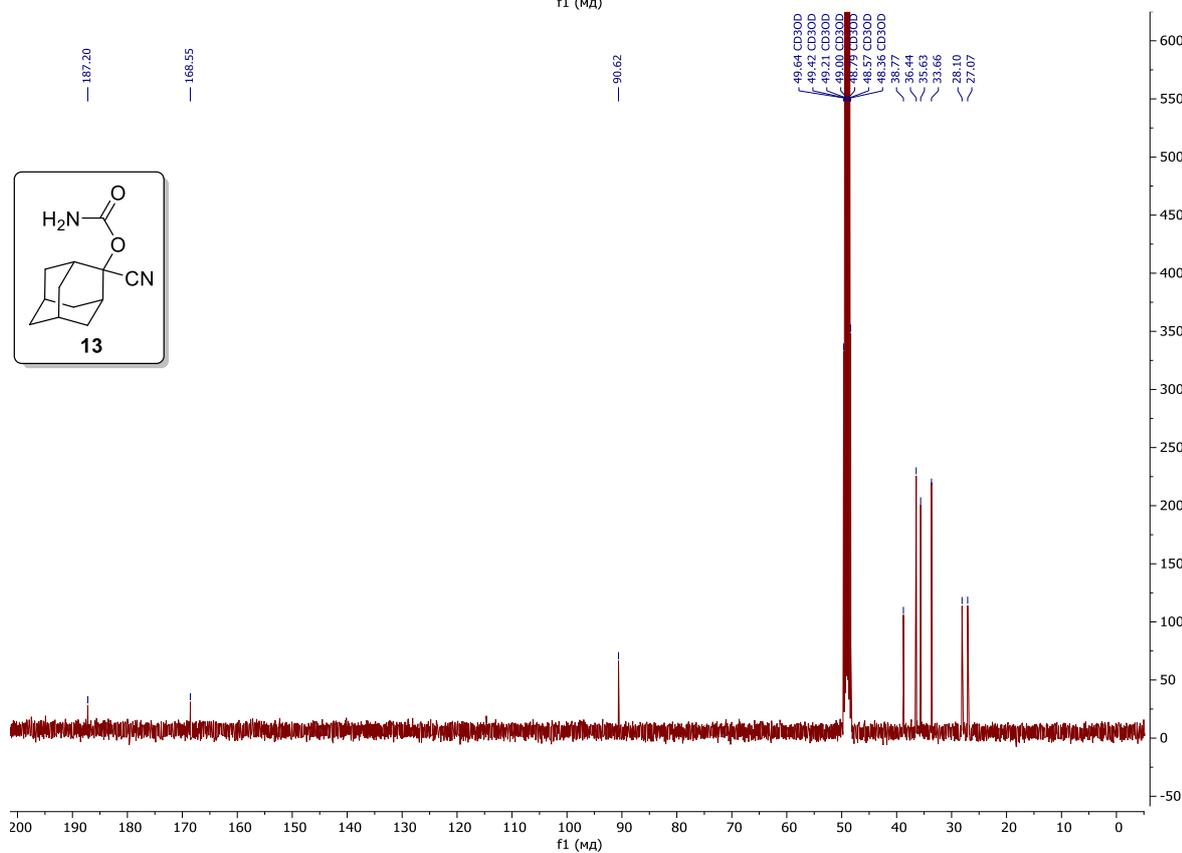
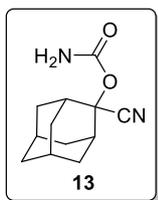
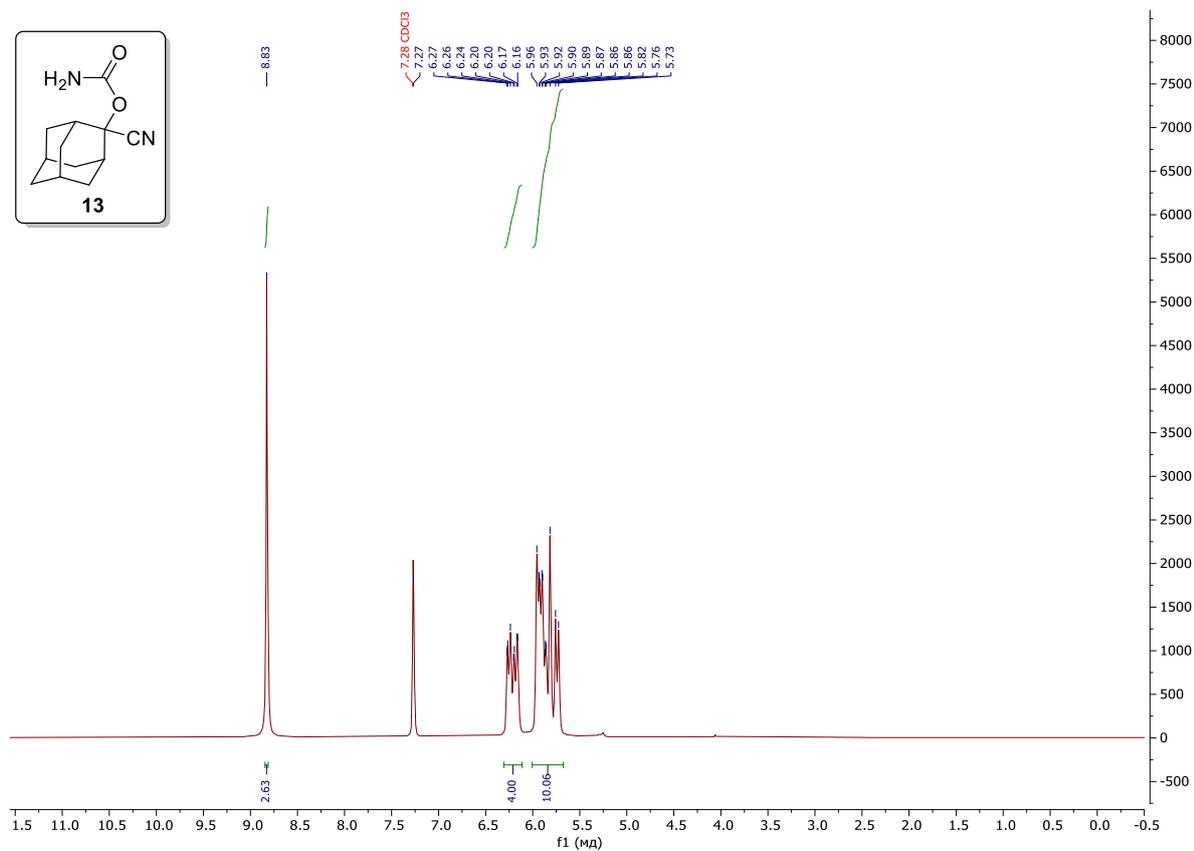
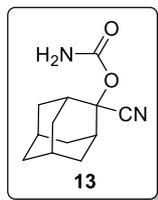
Compound 12 HSQC



Compound 12 HMBC



Compound 13



5. Crystallographic data collection and refinement details

The diffraction pattern for crystal structure determination of **4a1**, **4d2a** and **4h2** were measured on Bruker D8 VENTURE Kappa Duo PHOTONIII using I μ S micro-focus sealed tube at low temperature preserved by Cryostream Cooler. The structures were solved by direct methods (XT^{39a}) and refined by full matrix least squares based on F^2 (SHELXL2019^{39b}). The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or $H_{iso}(H) = 1.5 U_{eq}$ (pivot atom) for methyl moiety. The hydrogen atoms in -N-H moiety was found on difference Fourier map and refined under rigid-body approximation. Basic crystallographic data are given in Table 1.

Table 1 Crystal data, data collection, and refinement parameters for **4a1**, **4d2a** and **4h2**

Compound	4a1	4d2a	4h2
CCDC	2388740	2388741	2388739
Formula	C ₈ H ₁₀ N ₂ O ₂	C ₁₁ H ₁₈ N ₂ O ₂	C ₁₆ H ₁₈ N ₂ O ₂
M.w.	166.18	210.27	270.32
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P 2_1/c$ (No. 14)	$P 2_1/c$ (No. 14)	$P -1$ (No. 2)
a [Å]	11.5155 (8)	8.9496 (3)	8.2209 (3)
b [Å]	5.6145 (3)	6.5680 (2)	11.6407 (4)
c [Å]	12.6912 (9)	20.8721 (7)	13.6236 (5)
α [°]	90	90	83.587 (1)
β [°]	100.496 (2)	96.166 (1)	81.241 (1)
γ [°]	90	90	73.437 (1)
Z	4	4	4
V [Å ³]	806.80 (9)	1219.78 (7)	1231.86 (8)
Temperature	120	150	120
D_x [g cm ⁻³]	1.368	1.145	1.458
Wavelength, Å	0.71073	1.54178	1.54178
Crystal size [mm]	0.46 × 0.19 × 0.15	0.52 × 0.16 × 0.16	0.42 × 0.21 × 0.10
Crystal color, shape	prism, colourless	Bar, colourless	Plate, colourless
μ [mm ⁻¹]	0.10	0.64	0.78
T_{min}, T_{max}	0.85, 0.98	0.77, 0.90	0.78, 0.93
Measured reflections	26237	33316	15385
Independent diffractions (R_{int}^a)	1859, (0.040)	2634, (0.029)	4444 (0.027)
Observed diffract. [$I > 2\sigma(I)$]	1600	2477	4176
No. of parameters	109	158	361

R^b	0.035	0.038	0.035
$wR(F^2)$ for all data	0.094	0.110	0.099
GOF ^c	1.06	1.06	1.03
Residual electron density [e/Å ³]	0.35, -0.26	0.25, -0.17	0.31, -0.20

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), the deposition numbers are in Table 1 and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/structures/).

References:

39a. SHELXT: Sheldrick, G.M. (2015). *Acta Cryst.* **A71**, 3-8.

39b. SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.

40. Parsons, S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst.* **B69**, 249-259.

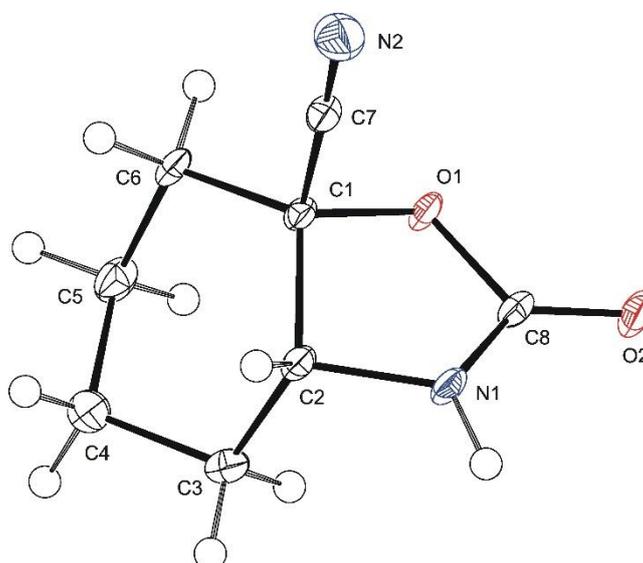


Fig. 1 View on the molecule of **4a1** with atom numbering schema. The displacement ellipsoids are drawn on 50% probability level.

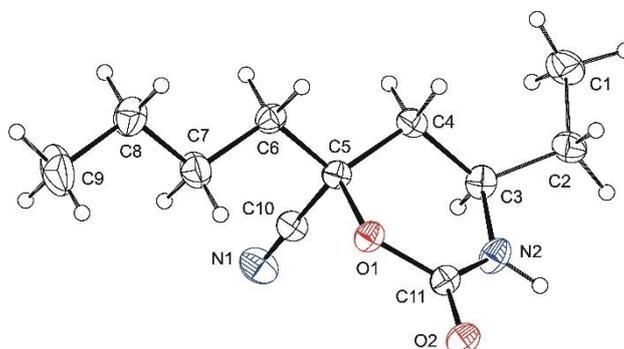


Fig. 2 View on the molecule of **4d2a** with atom numbering schema. The displacement ellipsoids are drawn on 30% probability level.

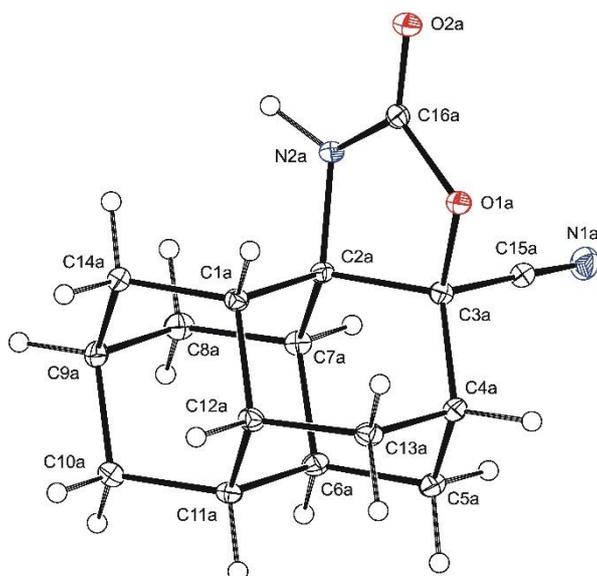


Fig. 3 View on the molecule of **4h2** with atom numbering schema. The displacement ellipsoids are drawn on 30% probability level.

Computing details

Data collection: Bruker Instrument Service v2021.1.0.5; cell refinement: *SAINT* V8.40B (Bruker AXS LLC, 2019); data reduction: *SAINT* V8.40B (Bruker AXS LLC, 2019); program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2019).

Compound 4a1

Crystal data

$C_8H_{10}N_2O_2$	$F(000) = 352$
$M_r = 166.18$	$D_x = 1.368 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 11.5155 (8) \text{ \AA}$	Cell parameters from 8634 reflections
$b = 5.6145 (3) \text{ \AA}$	$\theta = 3.3\text{--}27.5^\circ$
$c = 12.6912 (9) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 100.496 (2)^\circ$	$T = 120 \text{ K}$
$V = 806.80 (9) \text{ \AA}^3$	Prism, colourless
$Z = 4$	$0.46 \times 0.19 \times 0.15 \text{ mm}$

Data collection

NoniusKappa+Bruker diffractometer	APEX-II	CCD	1859 independent reflections
Radiation source: fine-focus sealed tube			1600 reflections with $I > 2\sigma(I)$
Graphite monochromator			$R_{\text{int}} = 0.040$

ϕ and ω scans	$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.3^\circ$
Absorption correction: multi-scan Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. (2015). "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination" J. Appl. Cryst. 48, 3-10. doi:10.1107/S1600576714022985	$h = -14 \rightarrow 14$
$T_{\min} = 0.85$, $T_{\max} = 0.98$	$k = -7 \rightarrow 7$
26237 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: mixed
$wR(F^2) = 0.094$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.2426P]$ where $P = (F_o^2 + 2F_c^2)/3$
1859 reflections	$(\Delta/\sigma)_{\max} < 0.001$
109 parameters	$\Delta_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for **4a1**.

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.23541 (6)	0.20858 (13)	0.64259 (6)	0.01394 (19)
O2	0.07667 (7)	0.09720 (14)	0.71135 (6)	0.0192 (2)
N1	0.12970 (8)	0.49357 (16)	0.70130 (7)	0.0147 (2)
H1	0.065400	0.560668	0.719321	0.018*
N2	0.45305 (9)	0.4397 (2)	0.82730 (8)	0.0242 (2)
C1	0.30288 (9)	0.42747 (19)	0.64360 (8)	0.0119 (2)
C2	0.20814 (9)	0.62253 (19)	0.64263 (8)	0.0128 (2)
H2	0.242273	0.766459	0.683302	0.015*
C3	0.14546 (9)	0.6897 (2)	0.52988 (9)	0.0172 (2)

H3A	0.089003	0.562012	0.501617	0.021*
H3B	0.099835	0.837946	0.533542	0.021*
C4	0.23161 (10)	0.7267 (2)	0.45315 (9)	0.0209 (3)
H4A	0.187930	0.773695	0.381641	0.025*
H4B	0.288011	0.855376	0.480132	0.025*
C5	0.29803 (10)	0.4958 (2)	0.44462 (9)	0.0192 (3)
H5A	0.349366	0.513543	0.390453	0.023*
H5B	0.241047	0.365900	0.421048	0.023*
C6	0.37306 (9)	0.4323 (2)	0.55257 (9)	0.0148 (2)
H6A	0.437800	0.549809	0.569908	0.018*
H6B	0.409250	0.273825	0.547131	0.018*
C7	0.38706 (9)	0.43270 (19)	0.74797 (9)	0.0154 (2)
C8	0.13798 (9)	0.2577 (2)	0.68853 (8)	0.0137 (2)

Atomic displacement parameters (\AA^2) for 4a1.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0092 (4)	0.0124 (4)	0.0223 (4)	-0.0020 (3)	0.0082 (3)	-0.0021 (3)
O2	0.0139 (4)	0.0186 (4)	0.0277 (5)	-0.0043 (3)	0.0107 (3)	-0.0002 (3)
N1	0.0100 (4)	0.0157 (5)	0.0205 (5)	0.0006 (3)	0.0086 (4)	-0.0012 (4)
N2	0.0215 (5)	0.0253 (5)	0.0240 (5)	-0.0015 (4)	-0.0010 (4)	0.0025 (4)
C1	0.0080 (5)	0.0119 (5)	0.0162 (5)	-0.0015 (4)	0.0031 (4)	-0.0001 (4)
C2	0.0096 (5)	0.0130 (5)	0.0168 (5)	-0.0005 (4)	0.0049 (4)	-0.0009 (4)
C3	0.0117 (5)	0.0200 (5)	0.0196 (5)	0.0027 (4)	0.0017 (4)	0.0013 (4)
C4	0.0183 (6)	0.0260 (6)	0.0185 (6)	0.0020 (5)	0.0037 (4)	0.0059 (5)
C5	0.0154 (5)	0.0276 (6)	0.0157 (5)	-0.0003 (5)	0.0061 (4)	-0.0009 (5)
C6	0.0088 (5)	0.0183 (5)	0.0187 (5)	-0.0011 (4)	0.0066 (4)	-0.0010 (4)
C7	0.0119 (5)	0.0147 (5)	0.0204 (5)	-0.0006 (4)	0.0054 (4)	0.0018 (4)
C8	0.0090 (5)	0.0179 (5)	0.0152 (5)	0.0000 (4)	0.0050 (4)	-0.0008 (4)

Geometric parameters (\AA , $^\circ$) for 4a1.

O1—C8	1.3833 (12)	C3—C4	1.5257 (15)
O1—C1	1.4528 (12)	C3—H3A	0.9900
O2—C8	1.2120 (13)	C3—H3B	0.9900
N1—C8	1.3396 (14)	C4—C5	1.5191 (17)
N1—C2	1.4628 (13)	C4—H4A	0.9900
N1—H1	0.8968	C4—H4B	0.9900
N2—C7	1.1462 (15)	C5—C6	1.5230 (15)
C1—C7	1.4925 (15)	C5—H5A	0.9900
C1—C6	1.5260 (14)	C5—H5B	0.9900
C1—C2	1.5443 (14)	C6—H6A	0.9900

C2—C3	1.5278 (15)	C6—H6B	0.9900
C2—H2	1.0000		
C8—O1—C1	107.52 (8)	C5—C4—C3	108.88 (9)
C8—N1—C2	111.32 (8)	C5—C4—H4A	109.9
C8—N1—H1	121.8	C3—C4—H4A	109.9
C2—N1—H1	122.5	C5—C4—H4B	109.9
O1—C1—C7	106.52 (8)	C3—C4—H4B	109.9
O1—C1—C6	111.37 (8)	H4A—C4—H4B	108.3
C7—C1—C6	108.88 (8)	C4—C5—C6	110.25 (9)
O1—C1—C2	102.95 (8)	C4—C5—H5A	109.6
C7—C1—C2	109.68 (9)	C6—C5—H5A	109.6
C6—C1—C2	116.89 (9)	C4—C5—H5B	109.6
N1—C2—C3	111.63 (9)	C6—C5—H5B	109.6
N1—C2—C1	98.38 (8)	H5A—C5—H5B	108.1
C3—C2—C1	113.27 (9)	C5—C6—C1	113.16 (9)
N1—C2—H2	111.0	C5—C6—H6A	108.9
C3—C2—H2	111.0	C1—C6—H6A	108.9
C1—C2—H2	111.0	C5—C6—H6B	108.9
C4—C3—C2	112.34 (9)	C1—C6—H6B	108.9
C4—C3—H3A	109.1	H6A—C6—H6B	107.8
C2—C3—H3A	109.1	N2—C7—C1	178.69 (12)
C4—C3—H3B	109.1	O2—C8—N1	130.45 (10)
C2—C3—H3B	109.1	O2—C8—O1	120.33 (10)
H3A—C3—H3B	107.9	N1—C8—O1	109.22 (9)

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Computing details

Data collection: Bruker Instrument Service v8.5.1.2 Release; cell refinement: *SAINT* V8.40B (Bruker AXS LLC, 2019); data reduction: *SAINT* V8.40B (Bruker AXS LLC, 2019); program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *SHELXL*2019/2 (Sheldrick, 2019).

Compound 4d2a

Crystal data

$C_{11}H_{18}N_2O_2$	$F(000) = 456$
$M_r = 210.27$	$D_x = 1.145 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
$a = 8.9496 (3) \text{ \AA}$	Cell parameters from 9949 reflections

$b = 6.5680 (2) \text{ \AA}$	$\theta = 5.6\text{--}79.2^\circ$
$c = 20.8721 (7) \text{ \AA}$	$\mu = 0.64 \text{ mm}^{-1}$
$\beta = 96.166 (1)^\circ$	$T = 150 \text{ K}$
$V = 1219.78 (7) \text{ \AA}^3$	Bar, colourless
$Z = 4$	$0.52 \times 0.16 \times 0.16 \text{ mm}$

Data collection

Bruker D8 VENTURE Kappa Duo PHOTONIII CMOS diffractometer	2634 independent reflections
Radiation source: I μ S micro-focus sealed tube	2477 reflections with $I > 2\sigma(I)$
Helios Cu multilayer optic monochromator	$R_{\text{int}} = 0.029$
ϕ and ω scans	$\theta_{\text{max}} = 79.4^\circ$, $\theta_{\text{min}} = 5.0^\circ$
Absorption correction: multi-scan Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. (2015). "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination" J. Appl. Cryst. 48, 3-10. doi:10.1107/S1600576714022985	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.77$, $T_{\text{max}} = 0.90$	$k = -7 \rightarrow 8$
33316 measured reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: mixed
$wR(F^2) = 0.110$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.264P]$ where $P = (F_o^2 + 2F_c^2)/3$
2634 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
158 parameters	$\Delta_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
0 restraints	$\Delta_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for **4d2a**.

	x	Y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.36976 (8)	0.41541 (11)	0.41711 (3)	0.03477 (19)	
O2	0.34871 (8)	0.15675 (12)	0.48210 (3)	0.0402 (2)	
N1	0.39740 (12)	0.30191 (17)	0.26247 (5)	0.0508 (3)	
N2	0.57067 (10)	0.19747 (15)	0.44110 (4)	0.0425 (2)	
H2	0.600256	0.092927	0.461065	0.051*	
C1	0.9471 (2)	0.3997 (4)	0.41483 (12)	0.0545 (7)	0.594 (4)
H1A	1.044805	0.366873	0.438410	0.082*	0.594 (4)
H1B	0.929718	0.546740	0.416734	0.082*	0.594 (4)
H1C	0.946416	0.357423	0.369764	0.082*	0.594 (4)
C2	0.8225 (6)	0.2868 (7)	0.4455 (3)	0.0442 (9)	0.594 (4)
H2A	0.848840	0.140792	0.450244	0.053*	0.594 (4)
H2B	0.813831	0.343003	0.488937	0.053*	0.594 (4)
C1B	0.9206 (3)	0.1546 (6)	0.46784 (17)	0.0558 (10)	0.406 (4)
H1BA	1.023939	0.184164	0.485934	0.084*	0.406 (4)
H1BB	0.922050	0.060319	0.431508	0.084*	0.406 (4)
H1BC	0.865815	0.092423	0.501043	0.084*	0.406 (4)
C2B	0.8444 (8)	0.3480 (10)	0.4450 (4)	0.0439 (13)	0.406 (4)
H2BA	0.908364	0.420691	0.416598	0.053*	0.406 (4)
H2BB	0.833143	0.436389	0.482604	0.053*	0.406 (4)
C3	0.67815 (12)	0.30798 (17)	0.40553 (5)	0.0389 (2)	
H3	0.682847	0.232926	0.364003	0.058*	
C4	0.61722 (11)	0.52024 (16)	0.39059 (5)	0.0353 (2)	
H4A	0.670586	0.581355	0.356138	0.042*	
H4B	0.636390	0.606583	0.429480	0.042*	
C5	0.44966 (11)	0.51607 (15)	0.36911 (4)	0.0316 (2)	
C6	0.37949 (12)	0.72728 (16)	0.36103 (5)	0.0366 (2)	
H6A	0.397964	0.801351	0.402429	0.044*	
H6B	0.430039	0.803421	0.328551	0.044*	
C7	0.21126 (15)	0.7244 (2)	0.34026 (7)	0.0550 (3)	
H7A	0.193335	0.651335	0.298648	0.066*	
H7B	0.161324	0.646079	0.372450	0.066*	
C8	0.13900 (15)	0.9304 (2)	0.33277 (7)	0.0563 (3)	
H8A	0.187621	1.008852	0.300214	0.068*	
H8B	0.156568	1.004250	0.374243	0.068*	
C9	-0.0279 (2)	0.9208 (3)	0.31254 (10)	0.0882 (6)	
H9A	-0.068600	1.059233	0.308255	0.132*	
H9B	-0.077346	0.846683	0.345152	0.132*	
H9C	-0.046238	0.850172	0.271075	0.132*	
C10	0.41940 (11)	0.39575 (16)	0.30850 (5)	0.0361 (2)	
C11	0.42985 (11)	0.24834 (15)	0.44824 (4)	0.0338 (2)	

Atomic displacement parameters (\AA^2) for **4d2a**.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0359 (4)	0.0377 (4)	0.0323 (4)	0.0016 (3)	0.0111 (3)	0.0049 (3)
O2	0.0446 (4)	0.0403 (4)	0.0377 (4)	-0.0007 (3)	0.0141 (3)	0.0052 (3)
N1	0.0509 (6)	0.0611 (7)	0.0412 (5)	-0.0058 (5)	0.0087 (4)	-0.0151 (5)
N2	0.0445 (5)	0.0435 (5)	0.0419 (5)	0.0095 (4)	0.0158 (4)	0.0114 (4)
C1	0.0315 (10)	0.0638 (14)	0.0696 (14)	-0.0065 (9)	0.0111 (9)	0.0015 (11)
C2	0.0314 (17)	0.051 (2)	0.0513 (14)	-0.0067 (15)	0.0088 (11)	0.0026 (18)
C1B	0.0344 (15)	0.067 (2)	0.066 (2)	0.0045 (13)	0.0054 (13)	0.0137 (16)
C2B	0.025 (2)	0.053 (4)	0.052 (2)	-0.005 (2)	-0.0013 (16)	0.013 (3)
C3	0.0365 (5)	0.0472 (6)	0.0345 (5)	0.0040 (4)	0.0110 (4)	0.0028 (4)
C4	0.0340 (5)	0.0398 (5)	0.0326 (5)	-0.0038 (4)	0.0061 (4)	-0.0020 (4)
C5	0.0346 (5)	0.0351 (5)	0.0261 (4)	-0.0032 (4)	0.0072 (4)	-0.0006 (4)
C6	0.0427 (6)	0.0342 (5)	0.0335 (5)	-0.0007 (4)	0.0068 (4)	0.0012 (4)
C7	0.0514 (7)	0.0456 (7)	0.0633 (8)	0.0071 (5)	-0.0148 (6)	-0.0062 (6)
C8	0.0563 (7)	0.0517 (7)	0.0602 (8)	0.0122 (6)	0.0021 (6)	0.0053 (6)
C9	0.0733 (10)	0.0801 (11)	0.1014 (13)	0.0339 (9)	-0.0364 (9)	-0.0165 (10)
C10	0.0359 (5)	0.0412 (5)	0.0320 (5)	-0.0024 (4)	0.0071 (4)	-0.0021 (4)
C11	0.0406 (5)	0.0341 (5)	0.0276 (4)	0.0006 (4)	0.0077 (4)	-0.0012 (4)

Geometric parameters (\AA , $^\circ$) for **4d2a**.

O1—C11	1.3566 (12)	C2B—H2BB	0.9900
O1—C5	1.4513 (11)	C3—C4	1.5171 (15)
O2—C11	1.2242 (12)	C3—H3	1.0019
N1—C10	1.1406 (14)	C4—C5	1.5185 (13)
N2—C11	1.3276 (13)	C4—H4A	0.9900
N2—C3	1.4685 (13)	C4—H4B	0.9900
N2—H2	0.8316	C5—C10	1.4915 (13)
C1—C2	1.535 (5)	C5—C6	1.5246 (14)
C1—H1A	0.9800	C6—C7	1.5215 (16)
C1—H1B	0.9800	C6—H6A	0.9900
C1—H1C	0.9800	C6—H6B	0.9900
C2—C3	1.467 (6)	C7—C8	1.5007 (17)
C2—H2A	0.9900	C7—H7A	0.9900
C2—H2B	0.9900	C7—H7B	0.9900
C1B—C2B	1.495 (8)	C8—C9	1.510 (2)
C1B—H1BA	0.9800	C8—H8A	0.9900
C1B—H1BB	0.9800	C8—H8B	0.9900
C1B—H1BC	0.9800	C9—H9A	0.9800

C2B—C3	1.643 (7)	C9—H9B	0.9800
C2B—H2BA	0.9900	C9—H9C	0.9800
C11—O1—C5	119.98 (7)	C5—C4—H4A	109.3
C11—N2—C3	127.85 (9)	C3—C4—H4B	109.3
C11—N2—H2	114.0	C5—C4—H4B	109.3
C3—N2—H2	118.1	H4A—C4—H4B	108.0
C2—C1—H1A	109.5	O1—C5—C10	106.62 (8)
C2—C1—H1B	109.5	O1—C5—C4	110.40 (8)
H1A—C1—H1B	109.5	C10—C5—C4	110.09 (8)
C2—C1—H1C	109.5	O1—C5—C6	105.26 (7)
H1A—C1—H1C	109.5	C10—C5—C6	110.68 (8)
H1B—C1—H1C	109.5	C4—C5—C6	113.47 (8)
C3—C2—C1	110.6 (4)	C7—C6—C5	113.79 (9)
C3—C2—H2A	109.5	C7—C6—H6A	108.8
C1—C2—H2A	109.5	C5—C6—H6A	108.8
C3—C2—H2B	109.5	C7—C6—H6B	108.8
C1—C2—H2B	109.5	C5—C6—H6B	108.8
H2A—C2—H2B	108.1	H6A—C6—H6B	107.7
C2B—C1B—H1BA	109.5	C8—C7—C6	114.87 (11)
C2B—C1B—H1BB	109.5	C8—C7—H7A	108.6
H1BA—C1B—H1BB	109.5	C6—C7—H7A	108.6
C2B—C1B—H1BC	109.5	C8—C7—H7B	108.6
H1BA—C1B—H1BC	109.5	C6—C7—H7B	108.6
H1BB—C1B—H1BC	109.5	H7A—C7—H7B	107.5
C1B—C2B—C3	112.4 (4)	C7—C8—C9	113.19 (13)
C1B—C2B—H2BA	109.1	C7—C8—H8A	108.9
C3—C2B—H2BA	109.1	C9—C8—H8A	108.9
C1B—C2B—H2BB	109.1	C7—C8—H8B	108.9
C3—C2B—H2BB	109.1	C9—C8—H8B	108.9
H2BA—C2B—H2BB	107.9	H8A—C8—H8B	107.8
C2—C3—N2	104.5 (2)	C8—C9—H9A	109.5
C2—C3—C4	118.62 (19)	C8—C9—H9B	109.5
N2—C3—C4	108.52 (8)	H9A—C9—H9B	109.5
N2—C3—C2B	115.6 (3)	C8—C9—H9C	109.5
C4—C3—C2B	104.0 (3)	H9A—C9—H9C	109.5
C2—C3—H3	109.2	H9B—C9—H9C	109.5
N2—C3—H3	106.5	N1—C10—C5	179.16 (12)
C4—C3—H3	108.8	O2—C11—N2	124.77 (10)
C2B—C3—H3	113.1	O2—C11—O1	116.40 (9)
C3—C4—C5	111.46 (8)	N2—C11—O1	118.82 (9)

C3—C4—H4A	109.3		
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Computational details

Data collection: Bruker Instrument Service v8.5.1.2 Release; cell refinement: *SAINT* V8.40B (Bruker AXS LLC, 2019); data reduction: *SAINT* V8.40B (Bruker AXS LLC, 2019); program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2019).

Compound 4h2

Crystal data

$C_{16}H_{18}N_2O_2$	$Z = 4$
$M_r = 270.32$	$F(000) = 576$
Triclinic, $P\bar{1}$	$D_x = 1.458 \text{ Mg m}^{-3}$
$a = 8.2209 (3) \text{ \AA}$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
$b = 11.6407 (4) \text{ \AA}$	Cell parameters from 9927 reflections
$c = 13.6236 (5) \text{ \AA}$	$\theta = 3.3\text{--}68.2^\circ$
$\alpha = 83.587 (1)^\circ$	$\mu = 0.78 \text{ mm}^{-1}$
$\beta = 81.241 (1)^\circ$	$T = 120 \text{ K}$
$\gamma = 73.437 (1)^\circ$	Plate, colourless
$V = 1231.86 (8) \text{ \AA}^3$	$0.42 \times 0.21 \times 0.10 \text{ mm}$

Data collection

Bruker D8 VENTURE Kappa Duo PHOTONIII CMOS diffractometer	4444 independent reflections
Radiation source: $I\mu S$ micro-focus sealed tube	4176 reflections with $I > 2\sigma(I)$
Helios Cu multilayer optic monochromator	$R_{\text{int}} = 0.027$
ϕ and ω scans	$\theta_{\text{max}} = 68.2^\circ$, $\theta_{\text{min}} = 3.3^\circ$
Absorption correction: multi-scan Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. (2015). "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination" <i>J. Appl. Cryst.</i> 48 , 3-10. doi:10.1107/S1600576714022985	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.78$, $T_{\text{max}} = 0.93$	$k = -14 \rightarrow 14$
15385 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: mixed
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.5741P]$ where $P = (F_o^2 + 2F_c^2)/3$
4444 reflections	$(\Delta/\sigma)_{\max} = 0.001$
361 parameters	$\Delta_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for **4h2**.

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1A	0.88783 (11)	0.94049 (7)	0.57155 (6)	0.0163 (2)
O2A	0.67173 (11)	1.06765 (8)	0.49683 (7)	0.0202 (2)
N1A	1.12792 (15)	0.74735 (11)	0.40787 (8)	0.0262 (3)
N2A	0.69450 (13)	0.86314 (9)	0.52322 (7)	0.0149 (2)
H2A	0.577884	0.873994	0.514034	0.018*
C1A	0.68466 (15)	0.79889 (10)	0.70194 (9)	0.0139 (2)
H1A	0.653661	0.887297	0.709326	0.017*
C2A	0.78237 (15)	0.77307 (11)	0.59666 (8)	0.0134 (2)
C3A	0.94966 (15)	0.81057 (11)	0.58108 (9)	0.0150 (3)
C4A	1.06031 (15)	0.75340 (11)	0.66361 (9)	0.0167 (3)
H4A	1.166245	0.781387	0.654653	0.020*
C5A	1.10575 (16)	0.61644 (11)	0.65242 (9)	0.0183 (3)
H5AA	1.172393	0.597960	0.586450	0.022*
H5AB	1.177540	0.572657	0.704167	0.022*
C6A	0.94229 (15)	0.57417 (11)	0.66272 (9)	0.0165 (3)
H6A	0.976079	0.485700	0.655189	0.020*
C7A	0.82219 (16)	0.63840 (11)	0.58294 (9)	0.0158 (3)
H7A	0.883309	0.620888	0.514702	0.019*

C8A	0.65891 (17)	0.59635 (11)	0.59924 (10)	0.0195 (3)
H8AA	0.688741	0.508950	0.591507	0.023*
H8AB	0.583373	0.638298	0.548715	0.023*
C9A	0.56482 (16)	0.62314 (11)	0.70382 (10)	0.0189 (3)
H9A	0.457711	0.596476	0.713857	0.023*
C10A	0.68121 (16)	0.55649 (11)	0.78198 (10)	0.0197 (3)
H10A	0.620083	0.572720	0.849577	0.024*
H10B	0.711128	0.468851	0.775348	0.024*
C11A	0.84446 (16)	0.59796 (11)	0.76776 (9)	0.0161 (3)
H11A	0.919682	0.553168	0.818601	0.019*
C12A	0.80053 (16)	0.73359 (11)	0.78045 (9)	0.0157 (3)
H12A	0.737246	0.750522	0.848309	0.019*
C13A	0.95970 (16)	0.78016 (11)	0.76659 (9)	0.0175 (3)
H13C	0.924925	0.867896	0.773428	0.021*
H13D	1.033224	0.740979	0.818777	0.021*
C14A	0.52005 (15)	0.75865 (11)	0.71441 (9)	0.0169 (3)
H14C	0.455373	0.777582	0.780782	0.020*
H14D	0.447061	0.802432	0.663208	0.020*
C15A	1.04979 (16)	0.77568 (11)	0.48237 (9)	0.0183 (3)
C16A	0.74096 (15)	0.96586 (11)	0.52677 (8)	0.0156 (3)
O1B	0.38411 (11)	0.43140 (8)	0.86772 (6)	0.0172 (2)
O2B	0.16847 (11)	0.56109 (8)	0.95524 (7)	0.0218 (2)
N1B	0.62731 (15)	0.23549 (11)	1.02103 (9)	0.0252 (3)
N2B	0.18899 (13)	0.35643 (9)	0.96733 (7)	0.0155 (2)
H2B	0.079831	0.364596	0.995302	0.019*
C1B	0.17417 (15)	0.29345 (11)	0.80324 (9)	0.0145 (3)
H1B	0.144961	0.381853	0.784701	0.017*
C2B	0.27372 (15)	0.26617 (11)	0.89487 (9)	0.0136 (3)
C3B	0.44237 (15)	0.30143 (11)	0.87142 (9)	0.0149 (3)
C4B	0.54958 (15)	0.24366 (11)	0.77900 (9)	0.0167 (3)
H4B	0.656596	0.270248	0.762405	0.020*
C5B	0.59266 (15)	0.10714 (11)	0.80779 (9)	0.0173 (3)
H5BA	0.662912	0.063066	0.750941	0.021*
H5BB	0.660300	0.087853	0.864614	0.021*
C6B	0.42787 (15)	0.06636 (11)	0.83654 (9)	0.0159 (3)
H6B	0.460198	-0.022133	0.854696	0.019*
C7B	0.31072 (15)	0.13156 (11)	0.92658 (9)	0.0151 (3)
H7B	0.373234	0.112972	0.986403	0.018*
C8B	0.14568 (16)	0.09171 (11)	0.94975 (9)	0.0185 (3)
H8BA	0.173691	0.004342	0.968738	0.022*
H8BB	0.072033	0.134309	1.006396	0.022*

C9B	0.05011 (16)	0.11988 (11)	0.85803 (10)	0.0185 (3)
H9B	-0.058179	0.094764	0.873587	0.022*
C10B	0.16341 (16)	0.05183 (11)	0.77087 (10)	0.0195 (3)
H10C	0.191915	-0.035701	0.789136	0.023*
H10D	0.100831	0.068419	0.711985	0.023*
C11B	0.32840 (16)	0.09164 (11)	0.74552 (9)	0.0166 (3)
H11B	0.401720	0.046500	0.689036	0.020*
C12B	0.28663 (16)	0.22740 (11)	0.71541 (9)	0.0161 (3)
H12B	0.221916	0.245426	0.656499	0.019*
C13B	0.44755 (16)	0.27187 (12)	0.69000 (9)	0.0184 (3)
H13A	0.519396	0.232123	0.631552	0.022*
H13B	0.414568	0.359634	0.672812	0.022*
C14B	0.00785 (15)	0.25540 (11)	0.82982 (9)	0.0172 (3)
H14A	-0.063260	0.299640	0.886357	0.021*
H14B	-0.057956	0.275227	0.772188	0.021*
C15B	0.54490 (15)	0.26502 (11)	0.95730 (9)	0.0174 (3)
C16B	0.23643 (15)	0.45898 (11)	0.93420 (9)	0.0163 (3)

Atomic displacement parameters (\AA^2) for 4h2.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0157 (4)	0.0153 (4)	0.0179 (4)	-0.0046 (3)	-0.0041 (3)	0.0021 (3)
O2A	0.0203 (5)	0.0171 (5)	0.0222 (5)	-0.0041 (4)	-0.0055 (4)	0.0043 (4)
N1A	0.0206 (6)	0.0357 (7)	0.0204 (6)	-0.0064 (5)	0.0011 (5)	-0.0019 (5)
N2A	0.0147 (5)	0.0163 (5)	0.0137 (5)	-0.0036 (4)	-0.0044 (4)	0.0016 (4)
C1A	0.0144 (6)	0.0130 (6)	0.0132 (6)	-0.0023 (4)	-0.0011 (4)	-0.0009 (4)
C2A	0.0127 (6)	0.0146 (6)	0.0127 (6)	-0.0029 (4)	-0.0036 (4)	0.0002 (4)
C3A	0.0149 (6)	0.0151 (6)	0.0145 (6)	-0.0035 (5)	-0.0018 (5)	0.0001 (4)
C4A	0.0134 (6)	0.0189 (6)	0.0185 (6)	-0.0053 (5)	-0.0047 (5)	0.0016 (5)
C5A	0.0145 (6)	0.0190 (6)	0.0192 (6)	-0.0013 (5)	-0.0029 (5)	0.0007 (5)
C6A	0.0155 (6)	0.0136 (6)	0.0189 (6)	-0.0010 (5)	-0.0029 (5)	-0.0011 (5)
C7A	0.0174 (6)	0.0151 (6)	0.0144 (6)	-0.0026 (5)	-0.0024 (5)	-0.0029 (4)
C8A	0.0217 (7)	0.0166 (6)	0.0230 (6)	-0.0068 (5)	-0.0076 (5)	-0.0019 (5)
C9A	0.0149 (6)	0.0186 (6)	0.0245 (7)	-0.0075 (5)	-0.0040 (5)	0.0026 (5)
C10A	0.0193 (6)	0.0170 (6)	0.0220 (6)	-0.0056 (5)	-0.0028 (5)	0.0039 (5)
C11A	0.0168 (6)	0.0152 (6)	0.0157 (6)	-0.0035 (5)	-0.0046 (5)	0.0028 (4)
C12A	0.0177 (6)	0.0171 (6)	0.0118 (5)	-0.0043 (5)	-0.0022 (4)	-0.0002 (4)
C13A	0.0199 (6)	0.0185 (6)	0.0156 (6)	-0.0057 (5)	-0.0070 (5)	0.0000 (5)
C14A	0.0132 (6)	0.0179 (6)	0.0181 (6)	-0.0033 (5)	-0.0013 (5)	0.0015 (5)
C15A	0.0144 (6)	0.0202 (6)	0.0193 (6)	-0.0042 (5)	-0.0034 (5)	0.0024 (5)
C16A	0.0149 (6)	0.0195 (6)	0.0114 (5)	-0.0043 (5)	-0.0002 (4)	0.0000 (4)

O1B	0.0165 (4)	0.0146 (4)	0.0200 (4)	-0.0048 (3)	0.0018 (3)	-0.0030 (3)
O2B	0.0202 (5)	0.0174 (5)	0.0273 (5)	-0.0042 (4)	0.0003 (4)	-0.0073 (4)
N1B	0.0227 (6)	0.0288 (6)	0.0250 (6)	-0.0059 (5)	-0.0068 (5)	-0.0042 (5)
N2B	0.0147 (5)	0.0168 (5)	0.0144 (5)	-0.0043 (4)	0.0016 (4)	-0.0033 (4)
C1B	0.0151 (6)	0.0134 (6)	0.0141 (6)	-0.0023 (5)	-0.0027 (5)	-0.0004 (4)
C2B	0.0128 (6)	0.0146 (6)	0.0127 (5)	-0.0029 (5)	-0.0002 (4)	-0.0018 (4)
C3B	0.0146 (6)	0.0139 (6)	0.0161 (6)	-0.0035 (5)	-0.0014 (5)	-0.0020 (4)
C4B	0.0134 (6)	0.0188 (6)	0.0181 (6)	-0.0057 (5)	0.0023 (5)	-0.0042 (5)
C5B	0.0128 (6)	0.0179 (6)	0.0205 (6)	-0.0017 (5)	-0.0015 (5)	-0.0055 (5)
C6B	0.0142 (6)	0.0140 (6)	0.0189 (6)	-0.0022 (5)	-0.0029 (5)	-0.0023 (5)
C7B	0.0152 (6)	0.0152 (6)	0.0145 (6)	-0.0038 (5)	-0.0028 (4)	0.0005 (5)
C8B	0.0186 (6)	0.0178 (6)	0.0194 (6)	-0.0073 (5)	-0.0008 (5)	0.0019 (5)
C9B	0.0143 (6)	0.0195 (6)	0.0232 (6)	-0.0072 (5)	-0.0017 (5)	-0.0022 (5)
C10B	0.0184 (6)	0.0183 (6)	0.0236 (6)	-0.0051 (5)	-0.0057 (5)	-0.0039 (5)
C11B	0.0162 (6)	0.0166 (6)	0.0168 (6)	-0.0026 (5)	-0.0022 (5)	-0.0052 (5)
C12B	0.0170 (6)	0.0181 (6)	0.0131 (6)	-0.0036 (5)	-0.0027 (4)	-0.0021 (5)
C13B	0.0208 (6)	0.0196 (6)	0.0138 (6)	-0.0060 (5)	0.0021 (5)	-0.0021 (5)
C14B	0.0131 (6)	0.0194 (6)	0.0184 (6)	-0.0022 (5)	-0.0035 (5)	-0.0024 (5)
C15B	0.0144 (6)	0.0175 (6)	0.0207 (6)	-0.0051 (5)	0.0008 (5)	-0.0050 (5)
C16B	0.0154 (6)	0.0188 (6)	0.0145 (6)	-0.0035 (5)	-0.0030 (4)	-0.0027 (5)

Geometric parameters (Å, °) for 4h2.

O1A—C16A	1.3777 (15)	O1B—C16B	1.3802 (15)
O1A—C3A	1.4492 (14)	O1B—C3B	1.4485 (14)
O2A—C16A	1.2135 (15)	O2B—C16B	1.2066 (16)
N1A—C15A	1.1431 (17)	N1B—C15B	1.1449 (17)
N2A—C16A	1.3627 (16)	N2B—C16B	1.3683 (16)
N2A—C2A	1.4752 (15)	N2B—C2B	1.4726 (15)
N2A—H2A	0.9564	N2B—H2B	0.9027
C1A—C12A	1.5313 (16)	C1B—C12B	1.5300 (16)
C1A—C14A	1.5340 (16)	C1B—C14B	1.5347 (16)
C1A—C2A	1.5493 (16)	C1B—C2B	1.5503 (16)
C1A—H1A	1.0000	C1B—H1B	1.0000
C2A—C7A	1.5342 (16)	C2B—C7B	1.5335 (16)
C2A—C3A	1.5362 (16)	C2B—C3B	1.5339 (16)
C3A—C15A	1.4985 (17)	C3B—C15B	1.4982 (17)
C3A—C4A	1.5276 (16)	C3B—C4B	1.5256 (16)
C4A—C13A	1.5320 (17)	C4B—C13B	1.5315 (17)
C4A—C5A	1.5499 (17)	C4B—C5B	1.5450 (17)
C4A—H4A	1.0000	C4B—H4B	1.0000

C5A—C6A	1.5401 (17)	C5B—C6B	1.5419 (16)
C5A—H5AA	0.9900	C5B—H5BA	0.9900
C5A—H5AB	0.9900	C5B—H5BB	0.9900
C6A—C11A	1.5435 (17)	C6B—C11B	1.5437 (16)
C6A—C7A	1.5618 (16)	C6B—C7B	1.5619 (16)
C6A—H6A	1.0000	C6B—H6B	1.0000
C7A—C8A	1.5332 (17)	C7B—C8B	1.5334 (16)
C7A—H7A	1.0000	C7B—H7B	1.0000
C8A—C9A	1.5335 (18)	C8B—C9B	1.5319 (17)
C8A—H8AA	0.9900	C8B—H8BA	0.9900
C8A—H8AB	0.9900	C8B—H8BB	0.9900
C9A—C14A	1.5324 (17)	C9B—C14B	1.5329 (17)
C9A—C10A	1.5342 (17)	C9B—C10B	1.5354 (17)
C9A—H9A	1.0000	C9B—H9B	1.0000
C10A—C11A	1.5301 (17)	C10B—C11B	1.5342 (17)
C10A—H10A	0.9900	C10B—H10C	0.9900
C10A—H10B	0.9900	C10B—H10D	0.9900
C11A—C12A	1.5394 (17)	C11B—C12B	1.5402 (16)
C11A—H11A	1.0000	C11B—H11B	1.0000
C12A—C13A	1.5323 (17)	C12B—C13B	1.5326 (17)
C12A—H12A	1.0000	C12B—H12B	1.0000
C13A—H13C	0.9900	C13B—H13A	0.9900
C13A—H13D	0.9900	C13B—H13B	0.9900
C14A—H14C	0.9900	C14B—H14A	0.9900
C14A—H14D	0.9900	C14B—H14B	0.9900
C16A—O1A—C3A	105.69 (9)	C16B—O1B—C3B	105.93 (9)
C16A—N2A—C2A	107.55 (9)	C16B—N2B—C2B	107.38 (9)
C16A—N2A—H2A	115.7	C16B—N2B—H2B	117.6
C2A—N2A—H2A	123.0	C2B—N2B—H2B	121.4
C12A—C1A—C14A	111.25 (10)	C12B—C1B—C14B	111.11 (10)
C12A—C1A—C2A	109.38 (9)	C12B—C1B—C2B	109.56 (9)
C14A—C1A—C2A	109.55 (10)	C14B—C1B—C2B	109.53 (9)
C12A—C1A—H1A	108.9	C12B—C1B—H1B	108.9
C14A—C1A—H1A	108.9	C14B—C1B—H1B	108.9
C2A—C1A—H1A	108.9	C2B—C1B—H1B	108.9
N2A—C2A—C7A	120.50 (10)	N2B—C2B—C7B	120.67 (10)
N2A—C2A—C3A	96.64 (9)	N2B—C2B—C3B	96.76 (9)
C7A—C2A—C3A	109.58 (9)	C7B—C2B—C3B	109.65 (9)
N2A—C2A—C1A	108.96 (9)	N2B—C2B—C1B	108.89 (9)
C7A—C2A—C1A	109.11 (9)	C7B—C2B—C1B	108.91 (10)

C3A—C2A—C1A	111.46 (9)	C3B—C2B—C1B	111.41 (9)
O1A—C3A—C15A	105.43 (9)	O1B—C3B—C15B	105.34 (9)
O1A—C3A—C4A	117.78 (10)	O1B—C3B—C4B	117.72 (10)
C15A—C3A—C4A	109.15 (10)	C15B—C3B—C4B	109.05 (10)
O1A—C3A—C2A	102.07 (9)	O1B—C3B—C2B	102.25 (9)
C15A—C3A—C2A	110.85 (10)	C15B—C3B—C2B	111.09 (10)
C4A—C3A—C2A	111.25 (9)	C4B—C3B—C2B	111.12 (10)
C3A—C4A—C13A	111.11 (10)	C3B—C4B—C13B	111.41 (10)
C3A—C4A—C5A	104.66 (10)	C3B—C4B—C5B	104.71 (9)
C13A—C4A—C5A	108.84 (10)	C13B—C4B—C5B	108.92 (10)
C3A—C4A—H4A	110.7	C3B—C4B—H4B	110.5
C13A—C4A—H4A	110.7	C13B—C4B—H4B	110.5
C5A—C4A—H4A	110.7	C5B—C4B—H4B	110.5
C6A—C5A—C4A	110.66 (10)	C6B—C5B—C4B	110.75 (9)
C6A—C5A—H5AA	109.5	C6B—C5B—H5BA	109.5
C4A—C5A—H5AA	109.5	C4B—C5B—H5BA	109.5
C6A—C5A—H5AB	109.5	C6B—C5B—H5BB	109.5
C4A—C5A—H5AB	109.5	C4B—C5B—H5BB	109.5
H5AA—C5A—H5AB	108.1	H5BA—C5B—H5BB	108.1
C5A—C6A—C11A	108.84 (10)	C5B—C6B—C11B	108.75 (10)
C5A—C6A—C7A	112.77 (10)	C5B—C6B—C7B	112.46 (10)
C11A—C6A—C7A	109.37 (9)	C11B—C6B—C7B	109.47 (9)
C5A—C6A—H6A	108.6	C5B—C6B—H6B	108.7
C11A—C6A—H6A	108.6	C11B—C6B—H6B	108.7
C7A—C6A—H6A	108.6	C7B—C6B—H6B	108.7
C8A—C7A—C2A	111.48 (10)	C8B—C7B—C2B	111.56 (10)
C8A—C7A—C6A	110.44 (10)	C8B—C7B—C6B	110.51 (10)
C2A—C7A—C6A	105.31 (9)	C2B—C7B—C6B	105.52 (9)
C8A—C7A—H7A	109.8	C8B—C7B—H7B	109.7
C2A—C7A—H7A	109.8	C2B—C7B—H7B	109.7
C6A—C7A—H7A	109.8	C6B—C7B—H7B	109.7
C7A—C8A—C9A	109.97 (10)	C9B—C8B—C7B	109.74 (10)
C7A—C8A—H8AA	109.7	C9B—C8B—H8BA	109.7
C9A—C8A—H8AA	109.7	C7B—C8B—H8BA	109.7
C7A—C8A—H8AB	109.7	C9B—C8B—H8BB	109.7
C9A—C8A—H8AB	109.7	C7B—C8B—H8BB	109.7
H8AA—C8A—H8AB	108.2	H8BA—C8B—H8BB	108.2
C14A—C9A—C8A	108.89 (10)	C8B—C9B—C14B	108.95 (10)
C14A—C9A—C10A	109.23 (10)	C8B—C9B—C10B	109.59 (10)
C8A—C9A—C10A	109.54 (10)	C14B—C9B—C10B	109.52 (10)
C14A—C9A—H9A	109.7	C8B—C9B—H9B	109.6

C8A—C9A—H9A	109.7	C14B—C9B—H9B	109.6
C10A—C9A—H9A	109.7	C10B—C9B—H9B	109.6
C11A—C10A—C9A	109.97 (10)	C11B—C10B—C9B	109.81 (10)
C11A—C10A—H10A	109.7	C11B—C10B—H10C	109.7
C9A—C10A—H10A	109.7	C9B—C10B—H10C	109.7
C11A—C10A—H10B	109.7	C11B—C10B—H10D	109.7
C9A—C10A—H10B	109.7	C9B—C10B—H10D	109.7
H10A—C10A—H10B	108.2	H10C—C10B—H10D	108.2
C10A—C11A—C12A	110.36 (10)	C10B—C11B—C12B	110.43 (10)
C10A—C11A—C6A	110.84 (10)	C10B—C11B—C6B	110.44 (10)
C12A—C11A—C6A	108.21 (10)	C12B—C11B—C6B	108.16 (10)
C10A—C11A—H11A	109.1	C10B—C11B—H11B	109.3
C12A—C11A—H11A	109.1	C12B—C11B—H11B	109.3
C6A—C11A—H11A	109.1	C6B—C11B—H11B	109.3
C1A—C12A—C13A	108.97 (10)	C1B—C12B—C13B	108.82 (10)
C1A—C12A—C11A	107.58 (10)	C1B—C12B—C11B	107.82 (10)
C13A—C12A—C11A	112.58 (10)	C13B—C12B—C11B	112.46 (10)
C1A—C12A—H12A	109.2	C1B—C12B—H12B	109.2
C13A—C12A—H12A	109.2	C13B—C12B—H12B	109.2
C11A—C12A—H12A	109.2	C11B—C12B—H12B	109.2
C4A—C13A—C12A	110.14 (10)	C4B—C13B—C12B	109.99 (10)
C4A—C13A—H13C	109.6	C4B—C13B—H13A	109.7
C12A—C13A—H13C	109.6	C12B—C13B—H13A	109.7
C4A—C13A—H13D	109.6	C4B—C13B—H13B	109.7
C12A—C13A—H13D	109.6	C12B—C13B—H13B	109.7
H13C—C13A—H13D	108.1	H13A—C13B—H13B	108.2
C9A—C14A—C1A	109.70 (10)	C9B—C14B—C1B	109.63 (9)
C9A—C14A—H14C	109.7	C9B—C14B—H14A	109.7
C1A—C14A—H14C	109.7	C1B—C14B—H14A	109.7
C9A—C14A—H14D	109.7	C9B—C14B—H14B	109.7
C1A—C14A—H14D	109.7	C1B—C14B—H14B	109.7
H14C—C14A—H14D	108.2	H14A—C14B—H14B	108.2
N1A—C15A—C3A	178.82 (14)	N1B—C15B—C3B	177.97 (13)
O2A—C16A—N2A	128.92 (11)	O2B—C16B—N2B	129.37 (11)
O2A—C16A—O1A	121.11 (11)	O2B—C16B—O1B	120.99 (11)
N2A—C16A—O1A	109.97 (10)	N2B—C16B—O1B	109.64 (10)

Hydrogen-bond geometry (Å, °) for 4h2.

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
N2A— H2A···O2A ⁱ	0.96	1.99	2.9337 (13)	168

N2B— H2B...O2B ⁱⁱ	0.90	2.02	2.8885 (13)	162
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Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+1, -z+2$.

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