Supporting Information

Part 1

Synthesis of unstrained Criegee intermediates: inverse α-effect and other protective stereoelectronic forces can stop Baeyer-Villiger rearrangement of γ-hydroperoxy-γ-peroxylactones

Vera A. Vil',[a] Yana A. Barsegyan,[a] Leah Kuhn,[b] Maria V. Ekimova, [a],[c] Egor A. Semenov, [a],[c] Alexander A. Korlyukov,[d],[e] Alexander O. Terent'ev, * [a],[c] Igor Alabugin * [b]

[a] N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, 47 Leninsky Prospect, Moscow, 119991, Russian Federation.

[b] Department of Chemistry and Biochemistry Florida State University, Tallahassee, 32309, USA.

[c] D. I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Square, Moscow 125047, Russian Federation.

[d] A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, 28 Vavilov Street, Moscow, 119991, Russian Federation.

[e] Pirogov Russian National Research Medical University, Moscow, 117997, Russian Federation.

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General materials and methods

Caution: Although we have encountered no difficulties in working with peroxides, precautions such as the performance of reactions within a fume hood and behind a safety shield should be taken. The use of redox-active transition-metal salts, heating and vigorous shaking should be avoided!

NMR spectra were recorded on commercial instrument (300.13 MHz for ^{1}H, 75.48 MHz for ^{13}C) in $CDCl_3$ at 25 °C. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI-TOF).[1] The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in MeCN (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

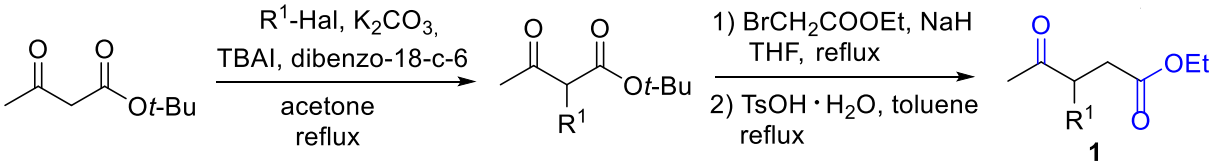
The TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (40-60 μm).

Ethyl levulinate **1m**, H_2O_2 (35% solution in water), $BF_3{\cdot}Et_2O$, $HClO_4$ (70% solution in water), HBF_4 (48% solution in water), $NaHCO_3$, phosphomolybdic acid hydrate (formula weight: 1,825.25 g/mol), $SnCl_4$ were purchased from commercial sources and were used as is. All solvents were distilled before use using standard procedures.

A solution of H_2O_2 in Et_2O (4.30 mol/L, ≈ 20 % weight) was prepared by the extraction with Et_2O (5 × 100 mL) from a 35% aqueous solution (100 mL) followed by drying over $MgSO_4$ and evaporating of approximately 2/3 volume of the solution.[2, 3]

Synthesis of starting γ-ketoesters 1

General procedure for synthesis of γ-ketoesters 1a-j. (GP1)



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Tert-butyl 3-oxobutanoate (2.37 g, 15.0 mmol, 1.3 eq.) was added dropwise to a suspension of K_2CO_3 (12.42 g, 90.0 mmol, 7.5 eq.) in dry acetone (50 mL). Then corresponding benzyl or alkyl halogenide (12.0 mmol, 1 eq.), TBAI (221.6 mg, 0.6 mmol, 0.05 eq.) and dibenzo-18-crown-6 (216.2 mg, 0.6 mmol, 0.05 eq.) were added. The reaction mixture was refluxed for 10 h. Then solid was filtered and washed acetone (3×10 mL). A filtrate was concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 30–35 °C). Later, Et_2O (60 mL) was added and a solution was washed with brine (3×10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath

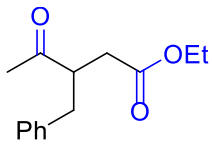
temperature, ca. 30–35 °C). The respective α-benzylated or α-alkylated β-ketoesters were isolated by column chromatography on SiO_2 (PE:EtOAc = from 20:1 to 2:1).

To a suspension of NaH (60% in mineral oil, 220.0 mg, 5.5 mmol, 1.1 eq.) in dry THF (15 mL) was added a solution of α-benzylated or α-alkylated β-ketoester from previous stage (5.0 mmol, 1.0 eq.) in THF (10 mL) dropwise over 30 min. The resulted solution was stirred for 1 h before addition of ethyl bromoacetate (918.5 mg, 5.5 mmol, 1.1 eq.) dropwise over 30 min. The addition funnel was replaced with a reflux condenser. The reaction mixture was refluxed for 6 h. After cooling, H_2O (15 mL) was added and the product from the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine (3×10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 30–35 °C).

A solution of unpurified resulting α,α-disubstituted β-ketoesters and *p*-toluenesulfonic acid monohydrate (47.6 mg, 0.25 mmol, 0.05 eq.) in toluene (15 mL) was refluxed for 5 h. The reaction mixture was then cooled to room temperature and diluted with Et_2O (50 mL). The mixture was washed with brine (10 mL), a 5% aqueous $NaHCO_3$ solution (2×10 mL), and again with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). The respective β-benzylated or β-alkylated γ-ketoesters **1** were isolated by column chromatography on SiO_2 (PE:EtOAc = from 20:1 to 2:1).

Characterization data of starting γ-ketoesters 1

Ethyl 3-benzyl-4-oxopentanoate, 1a [4]



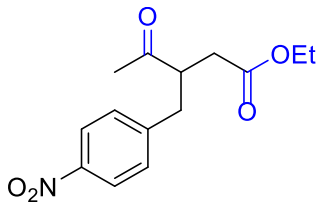
According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 57% (667.2 mg, 2.85 mmol) **1a**.

Colorless oil. R_f = 0.37 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.33 – 7.10 (m, 5H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.17 (m, 1H), 2.90 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.73 (dd, *J* = 17.0, 10.0 Hz, 1H), 2.59 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.31 (dd, *J* = 17.0, 4.2 Hz, 1H), 2.10 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.75, 172.27, 138.42, 129.03, 128.77, 126.82, 60.72, 49.78, 37.83, 35.53, 30.41, 14.21.

Ethyl 3-(4-nitrobenzyl)-4-oxopentanoate, 1b



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 63% (879.2 mg, 3.15 mmol) **1b**.

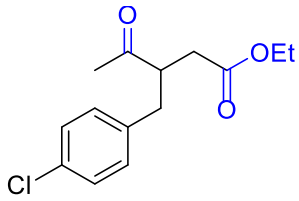
Colorless oil. R_f = 0.29 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.15 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.21 (m, 1H), 3.03 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.81 – 2.64 (m, 2H), 2.32 (dd, *J* = 16.9, 4.9 Hz, 1H), 2.13 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 209.58, 171.75, 147.06, 146.34, 130.00, 124.01, 61.04, 49.33, 37.19, 35.58, 30.39, 14.22.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{14}H_{17}NO_5Na]^+$: 302.0999. Found: 302.1000.

Ethyl 3-(4-chlorobenzyl)-4-oxopentanoate, 1c



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 36% (482.6 mg, 1.80 mmol) **1c**.

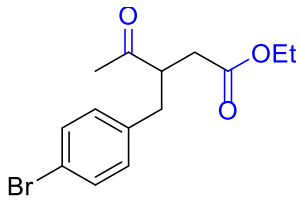
Colorless oil. R_f = 0.31 (PE:EtOAc = 2:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.25 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.30 – 3.14 (m, 1H), 2.88 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.71 (dd, *J* = 17.0, 9.7 Hz, 1H), 2.57 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.29 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.11 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.43, 172.11, 136.91, 132.71, 130.40, 128.92, 60.85, 49.63, 37.03, 35.50, 30.50, 14.21.

HRMS (ESI) m/z $[M + H]^+$. Calcd for $[C_{14}H_{18}ClO_3]^+$: 269.0939. Found: 269.0937.

Ethyl 3-(4-bromobenzyl)-4-oxopentanoate, 1d



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 78% (1216.8 mg, 3.90 mmol) **1d**.

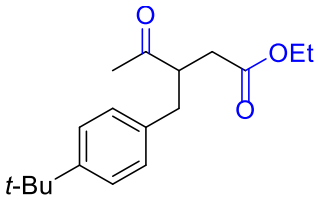
Yellow oil. R_f = 0.51 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.41 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.14 (m, 1H), 2.87 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.71 (dd, *J* = 17.0, 9.6 Hz, 1H), 2.56 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.30 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.11 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.32, 172.09, 137.46, 131.90, 130.79, 120.76, 60.87, 49.60, 37.11, 35.53, 30.48, 14.24.

HRMS (ESI) m/z $[M + H]^+$. Calcd for $[C_{14}H_{18}BrO_3]^+$: 313.0434, 315.0414. Found: 313.0432, 315.0414.

Ethyl 3-(4-(*tert*-butyl)benzyl)-4-oxopentanoate, 1e



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 45% (652.9 mg, 2.25 mmol) **1e**.

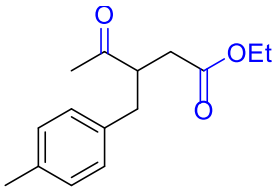
Colorless oil. R_f = 0.62 (PE:EtOAc = 2:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.31 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.19 (m, 1H), 2.90 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.73 (dd, *J* = 17.0, 10.1 Hz, 1H), 2.56 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.33 (dd, *J* = 17.0, 4.2 Hz, 1H), 2.14 (s, 3H), 1.30 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.95, 172.43, 149.74, 135.24, 128.72, 125.66, 60.73, 49.79, 37.23, 35.45, 34.54, 31.47, 30.33, 14.24.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{18}H_{26}O_3Na]^+$: 313.1774. Found: 313.1778.

Ethyl 3-(4-methylbenzyl)-4-oxopentanoate, 1f



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 46% (570.2 mg, 2.30 mmol) **1f**.

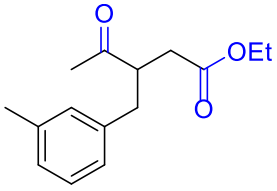
Colorless oil. R_f = 0.67 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.10 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.29 – 3.17 (m, 1H), 2.88 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.73 (dd, *J* = 17.0, 10.1 Hz, 1H), 2.55 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.31 (dd, *J* = 17.0, 4.2 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.98, 172.39, 136.38, 135.27, 129.45, 128.91, 60.72, 49.86, 37.41, 35.47, 30.46, 21.12, 14.23.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{15}H_{20}O_3Na]^+$: 271.1305. Found: 271.1310.

Ethyl 3-(3-methylbenzyl)-4-oxopentanoate, 1g



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 64% (793.9 mg, 3.20 mmol) **1g**.

Colorless oil. R_f = 0.43 (PE:EtOAc = 5:1).

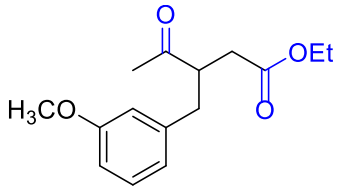
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.18 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.99 – 6.91 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.17 (m, 1H), 2.88 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.74 (dd, *J* = 17.0,

10.1 Hz, 1H), 2.54 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.36 – 2.27 (dd, *J* = 17.0, 4.2 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.92, 172.39, 138.42, 138.37, 129.81, 128.67, 127.58, 126.07, 60.73, 49.83, 37.77, 35.51, 30.40, 21.46, 14.23.

HRMS (ESI) m/z $[M + H]^+$. Calcd for $[C_{15}H_{21}O_3]^+$: 249.1485. Found: 249.1492.

Ethyl 3-(3-methoxybenzyl)-4-oxopentanoate, 1h



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 15% (198.2 mg, 0.75 mmol) **1h**.

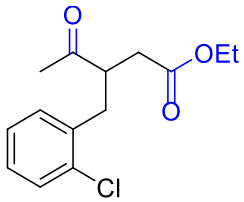
Colorless oil. R_f = 0.58 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.21 (t, *J* = 7.9 Hz, 1H), 6.86 – 6.60 (m, 3H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.35 – 3.18 (m, 1H), 2.89 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.74 (dd, *J* = 17.0, 10.0 Hz, 1H), 2.56 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.33 (dd, *J* = 17.0, 4.3 Hz, 1H), 2.13 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.76, 172.33, 159.98, 140.04, 129.81, 121.41, 114.86, 112.15, 60.77, 55.32, 49.72, 37.88, 35.57, 30.45, 14.25.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{15}H_{20}O_4Na]^+$: 287.1254. Found: 287.1255.

Ethyl 3-(2-chlorobenzyl)-4-oxopentanoate, 1i



According to **GP1** α-benzylated β-ketoester (5.0 mmol) given 36% (483.7 mg, 1.80 mmol) **1i**.

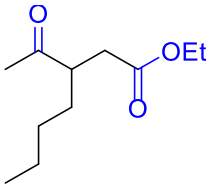
Colorless oil. R_f = 0.74 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.40 – 7.35 (m, 1H), 7.22 – 7.10 (m, 3H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.48 – 3.31 (m, 1H), 3.05 (dd, *J* = 13.4, 6.3 Hz, 1H), 2.85 – 2.62 (m, 2H), 2.32 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.16 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.55, 172.15, 136.16, 134.28, 131.63, 130.01, 128.49, 127.09, 60.78, 47.36, 35.59, 35.39, 30.31, 14.22.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{14}H_{17}O_3ClNa]^+$: 291.0758. Found: 291.0759.

Ethyl 3-acetylheptanoate, 1j[5]



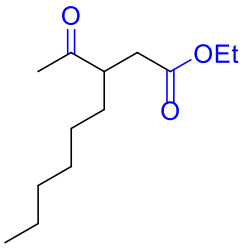
According to **GP1** α-alkylated β-ketoester (5.0 mmol) given 68% (681.0 mg, 3.40 mmol) **1j**.

Colorless oil. R_f = 0.63 (PE:EtOAc = 2:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 4.08 (q, *J* = 7.0 Hz, 2H), 3.06 – 2.86 (m, 1H), 2.71 (dd, *J* = 16.8, 9.8 Hz, 1H), 2.32 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.21 (s, 3H), 1.66 – 1.51 (m, 1H), 1.45 – 1.19 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.85, 172.43, 60.50, 47.89, 35.31, 31.01, 29.47, 29.04, 22.65, 14.12, 13.78.

Ethyl 3-acetylnonanoate, 1k



According to **GP1** α-alkylated β-ketoester (5.0 mmol) given 57% (650.3 mg, 2.85 mmol) **1k**.

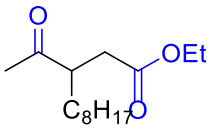
Colorless oil. R_f = 0.52 (PE:EtOAc = 2:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 4.08 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.88 (m, 1H), 2.71 (dd, *J* = 16.8, 9.8 Hz, 1H), 2.32 (dd, *J* = 16.8, 4.5 Hz, 1H), 2.21 (s, 3H), 1.67 – 1.51 (m, 1H), 1.46 – 1.32 (m, 1H), 1.32 – 1.17 (m, 11H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 211.13, 172.62, 60.67, 48.04, 35.42, 31.67, 31.45, 29.65, 29.37, 26.98, 22.65, 14.26, 14.12.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{13}H_{24}O_3Na]^+$: 251.1618. Found: 251.1625.

Ethyl 3-acetylundecanoate, 1l



According to **GP1** α-alkylated β-ketoester (5.0 mmol) given 60% (768.6 mg, 3.00 mmol) **1l**.

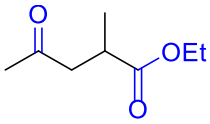
Colorless oil. R_f = 0.59 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 4.09 (q, *J* = 7.0 Hz, 2H), 3.07 – 2.87 (m, 1H), 2.71 (dd, *J* = 16.7, 9.8 Hz, 1H), 2.33 (dd, *J* = 16.7, 4.5 Hz, 1H), 2.21 (s, 3H), 1.64 – 1.52 (m, 1H), 1.46 – 1.33 (m, 1H), 1.29 – 1.18 (m, 15H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 211.01, 172.60, 60.67, 48.11, 35.47, 31.94, 31.49, 29.73, 29.60, 29.46, 29.31, 27.04, 22.75, 14.27, 14.17.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{15}H_{28}O_3Na]^+$: 279.1931. Found: 279.1929.

Ethyl 2-methyl-4-oxopentanoate, 1n [6]

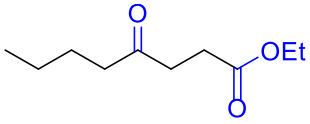


1n was prepared according to literature procedure.[6]

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 4.11 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.83 (m, 2H), 2.54 – 2.36 (m, 1H), 2.14 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 206.73, 175.83, 60.66, 46.72, 34.89, 30.15, 17.16, 14.24.

Ethyl 4-oxooctanoate, 1o[7]

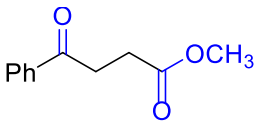


1o was prepared according to literature procedure.[7]

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 4.10 (q, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 6.5 Hz, 2H), 2.54 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.55 (quintet, *J* = 7.4 Hz, 2H), 1.36 – 1.25 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 209.25, 172.93, 60.66, 42.60, 37.11, 28.10, 26.00, 22.40, 14.25, 13.91.

Methyl 4-oxo-4-phenylbutanoate, 1p[8]



1p was prepared according to literature procedure.[9]

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.95 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 3.67 (s, 3H), 3.29 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 197.99, 173.29, 136.51, 133.19, 128.58, 127.99, 51.74, 33.35, 27.97.

Experimental procedure for Table 1.

An ethereal solution of H_2O_2 (4.30 M, 0.698-2.326 mL, 3.0-10.0 mmol, 3.0-10.0 eq.) was added with stirring to **1a** (234.3 mg, 1.00 mmol, 1.0 eq.) in Et_2O or CH_3CN (3.5 mL). Later, $BF_3{\cdot}Et_2O$ (425.7 mg-1.419 g, 3.00-10.00 mmol, 3.0-10.0 eq.), 70% aq. $HClO_4$ (1.435 g, 10.00 mmol, 10.0 eq.), 48% aq.

HBF_4 (1.829 g, 10.00 mmol, 10.0 eq.), $TsOH{\cdot}H_2O$ (1.902 g, 10.00 mmol, 10.0 eq.), or PMA (2340.0 mg, 1.00 mmol, 1.0 eq.) was added in portions with stirring to the solution at 0 °C. The reaction mixture was stirred at 20-25 °C for 24 h. After that time, CH_2Cl_2 (50 mL) was added and the organic layer was washed with brine (10 mL), a 5% aqueous $NaHCO_3$ solution (2 × 10 mL), and again with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Product **2a** was isolated by chromatography on SiO_2 with elution using PE-EtOAc mixture (4:1).

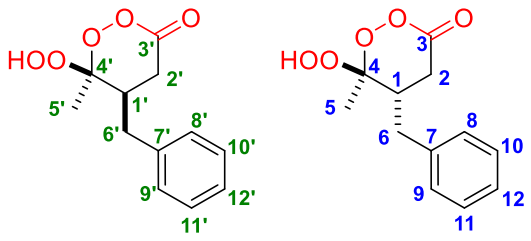
General experimental procedure for Scheme 5.

An ethereal solution of H_2O_2 (4.30 M, 1.163 mL, 5.0 mmol, 5.0 eq.) was added with stirring to **1** (1.00 mmol, 1.0 eq.) in Et_2O (3.5 mL). Later, $BF_3{\cdot}Et_2O$ (1.419 g, 10.00 mmol, 10.0 eq.) was added dropwise with stirring to the solution at 0 °C. The reaction mixture was stirred at 20-25 °C for 24 h. After that time, CH_2Cl_2 (50 mL) and H_2O (2 mL) was added and the mixture was neutralized by $NaHCO_3$. The solid was filtrated. The solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Product **2** was isolated by chromatography on SiO_2 with elution using PE-EtOAc mixture (4:1).

Characterization data of synthesized γ-hydroperoxy-γ-peroxylactones

Correlation of *cis* and *trans* isomer signals is done based on H6-H5 cross-peaks of *trans*-isomer and H5'-H1' cross-peaks of *cis*-isomer in 2D NOESY.

5-Benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2a



cis *trans*

Yield 53% (126.2 mg, 0.53 mmol). White crystals. R_f = 0.31 (PE:EtOAc = 5:1).

Peroxide **2a** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 22:78 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.68 (br.s., 1H, OOH'), 7.35 – 7.24 (m, 3H, H10', H11', H12'), 7.14 (d, *J* = 6.9 Hz, 2H, H8', H9'), 3.12 (dd, *J* = 13.5, 4.5 Hz, 1H, H6'$_a$), 2.85 – 2.72 (m, 1H, H1'), 2.65 (dd, *J* = 15.8, 7.2 Hz, 1H, H2'$_a$), 2.45 – 2.30 (m, 1H, H'6$_b$), 2.40 – 2.28 (m, 1H, H'2$_b$), 1.67 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.41 (C3'), 138.18 (C7'), 129.19 (C8'+C9'), 128.91 (C10'+C11'), 126.95 (C12'), 109.49 (C4'), 44.95 (C1'), 34.07 (C6'), 30.13 (C2'), 20.26 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.77 (br.s, 1H, OOH), 7.35 – 7.24 (m, 3H, H10, H11, H12), 7.14 (d, *J* = 6.9 Hz, 2H, H8, H9), 3.09 (dd, *J* = 13.5, 3.8 Hz, 1H, $H6_a$), 2.54 (dd, *J* = 13.5, 10.6 Hz, 1H, $H6_b$), 2.49 – 2.32 (m, 2H, H2), 2.38 – 2.22 (m, 1H, H1), 1.61 (s, 3H, H5).

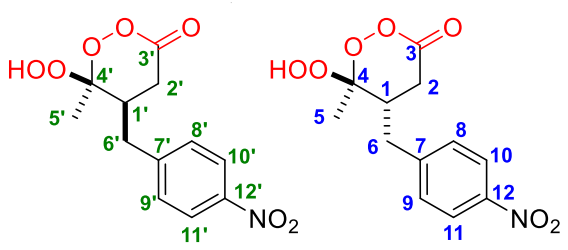
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.49 (C3), 137.34 (C7), 129.03 (C8+C9), 128.88 (C10+C11), 127.24 (C12), 112.76 (C4), 41.61 (C1), 36.65 (C6), 30.48 (C2), 15.56 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{12}H_{18}O_5N]^+$: 256.1179. Found: 256.1184.

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.72; H, 6.03.

IR (KBr): 3422, 3020, 2817, 1773, 1619, 1513, 1427, 1349, 1272, 1148, 1021, 858 cm^{-1}.

6-Hydroperoxy-6-methyl-5-(4-nitrobenzyl)-1,2-dioxan-3-one, 2b



cis *trans*

Yield 56% (158.6 mg, 0.56 mmol). White crystals. R_f = 0.28 (PE:EtOAc = 5:1).

Peroxide **2b** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 24:76 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.17 (br.s., 1H, OOH'), 8.14 (d, *J* = 8.6 Hz, 2H, H10', H11'), 7.33 (d, *J* = 8.6 Hz, 2H, H8', H9'), 3.15 (dd, *J* = 13.8, 5.6 Hz, 1H, $H6'_a$), 2.94 – 2.81 (m, 1H, H1'), 2.76 – 2.65 (m, 1H, $H2'_a$), 2.58 – 2.48 (m, 1H, $H6'_b$), 2.34 – 2.26 (m, 1H, $H2'_b$), 1.62 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.46 (C3'), 146.92 (C12'), 146.12 (C7'), 130.08 (C8'+C9'), 123.99 (C10'+C11'), 109.22 (C4'), 44.32 (C1'), 33.95 (C6'), 30.52 (C2'), 20.33 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.27 (br.s., 1H, OOH), 8.15 (d, *J* = 8.6 Hz, 2H, H10, H11), 7.35 (d, *J* = 8.6 Hz, 2H, H8, H9), 3.12 (dd, *J* = 13.8, 4.2 Hz, 1H, $H6_a$), 2.71 (dd, *J* = 13.8, 9.3 Hz, 1H, $H6_b$), 2.45 (d, *J* = 15.2 Hz, 1H, $H2_a$), 2.37 – 2.30 (m, 1H, H1), 2.30 (dd, *J* = 15.2, 2.8 Hz, 1H, $H2_b$), 1.56 (s, 3H, H5).

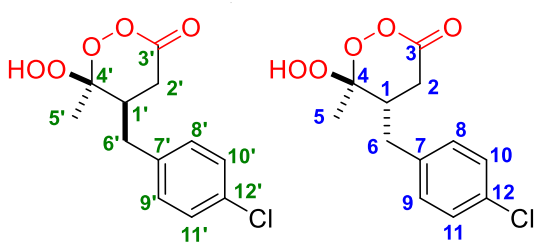
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.28 (C3), 147.08 (C12), 145.19 (C7), 129.83 (C8+C9), 124.12 (C10+C11), 112.43 (C4), 40.96 (C1), 36.20 (C6), 30.61 (C2), 15.45 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{12}H_{17}O_7N_2]^+$: 301.1030. Found: 301.1021.

Anal. Calcd for $C_{12}H_{13}NO_7$: C, 50.89; H, 4.63; N, 4.95. Found: C, 50.55; H, 4.89; N, 5.08.

IR (thin layer): 3401, 3081, 3010, 2945, 2859, 1779, 1602, 1518, 1425, 1346, 1259, 1149, 1110, 857 cm^{-1}.

5-(4-Chlorobenzyl)-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2c



cis *trans*

Yield 47% (128.2 mg, 0.47 mmol). Colorless oil. R_f = 0.30 (PE:EtOAc = 5:1).

Peroxide **2c** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 23:77 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.96 (br.s., 1H, OOH'), 7.27 (d, *J* = 8.3 Hz, 2H, H10', H11'), 7.07 (d, *J* = 8.3 Hz, 2H, H8', H9'), 3.03 (dd, *J* = 14.1, 4.6 Hz, 1H, H6'$_a$), 2.80 – 2.69 (m, 1H, H1'), 2.64 (dd, *J* = 15.5, 7.1 Hz, 1H, H2'$_a$), 2.43 – 2.33 (m, 1H, H6'$_b$), 2.38 – 2.27 (m, 1H, H2'$_b$), 1.63 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.52 (C3'), 136.65 (C7'), 132.78 (C12'), 130.53 (C8'+C9'), 129.01 (C10'+C11'), 109.38 (C4'), 44.80 (C1'), 33.41 (C6'), 30.22 (C2'), 20.31 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.07 (br.s., 1H, OOH), 7.28 (d, *J* = 8.3 Hz, 2H, H10, H11), 7.07 (2H, d, *J* = 8.3 Hz, H8, H9), 3.01 (dd, *J* = 13.6, 4.1 Hz, 1H, H6$_a$), 2.51 (dd, *J* = 13.6, 10.8 Hz, 1H, H6$_b$), 2.38 – 2.26 (m, 2H, H2), 2.31 – 2.19 (m, 1H, H1), 1.57 (s, 3H, H5).

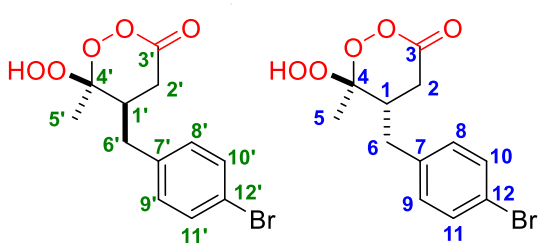
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.47 (C3), 135.83 (C7), 133.06 (C12), 130.20 (C8+C9), 129.15 (C10+C11), 112.61 (C4), 41.42 (C1), 35.92 (C6), 30.49 (C2), 15.49 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{12}H_{17}ClO_5N]^+$: 290.0790. Found: 290.0787.

Anal. Calcd for $C_{12}H_{13}ClO_5$: C, 52.86; H, 4.81; Cl, 13.00. Found: C, 52.54; H, 4.58; Cl, 12.90.

IR (thin layer): 3386, 2941, 1783, 1492, 1414, 1379, 1267, 1193, 1151, 1099, 856, 814, 510 cm^{-1}.

5-(4-Bromobenzyl)-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2d



cis *trans*

Yield 44% (139.5 mg, 0.44 mmol). Colorless oil. R_f = 0.25 (PE:EtOAc = 5:1).

Peroxide **2d** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 23:77 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.00 – 8.30 (br.s., OOH'), 7.43 (d, *J* = 8.2 Hz, 2H, H10', H11'), 7.02 (d, *J* = 8.2 Hz, 2H, H8', H9'), 3.03 (dd, *J* = 14.1, 4.8 Hz, 1H, H6'$_a$), 2.79 – 2.70 (m, 1H, H1'), 2.64 (dd, *J* = 15.4, 7.0 Hz, 1H, H2'$_a$), 2.42 – 2.32 (m, 1H, H6'$_b$), 2.42 – 2.26 (m, 1H, H2'$_b$), 1.64 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.21 (C3'), 137.16 (C7'), 132.04 (C10'+C11'), 130.93 (C8'+C9'), 120.91 (C12'), 109.41 (C4'), 44.87 (C1'), 33.50 (C6'), 30.26 (C2'), 20.42 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.00 – 8.30 (br.s., OOH), 7.44 (d, *J* = 8.2 Hz, 2H, H10, H11), 7.02 (d, *J* = 8.2 Hz, 2H, H8, H9), 3.00 (dd, *J* = 13.6, 4.1 Hz, 1H, H6$_a$), 2.50 (dd, *J* = 13.6, 10.7 Hz, 1H, H6$_b$), 2.42 – 2.28 (m, 2H, H2), 2.32 – 2.19 (m, 1H, H1), 1.58 (s, 3H, H5).

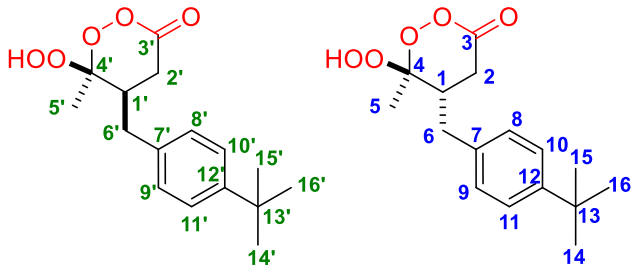
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.15 (C3), 136.31 (C7), 132.18 (C10+C11), 130.57 (C8+C9), 121.19 (C12), 112.61 (C4), 41.40 (C1), 36.07 (C6), 30.54 (C2), 15.57 (C5).

HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{12}H_{13}BrO_5Na]^+$: 338.9839, 340.9819. Found: 338.9835, 340.9821.

Anal. Calcd for $C_{12}H_{13}BrO_5$: C, 45.45; H, 4.13; Br, 25.20. Found: C, 45.11; H, 4.34; Br, 25.07.

IR (thin layer): 3383, 2931, 1783, 1717, 1488, 1410, 1378, 1266, 1193, 1150, 1071, 857, 810 cm^{-1}.

5-(4-(*Tert*-butyl)benzyl)-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2e



cis *trans*

Yield 67% (197.2 mg, 0.67 mmol). White crystals. R_f = 0.41 (PE:EtOAc = 5:1).

Peroxide **2e** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 21:79 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.51 (s, 1H, OOH'), 7.34 (d, 2H, *J* = 8.2 Hz, H10', H11'), 7.07 (d, *J* = 8.2 Hz, 2H, H8', H9'), 3.07 (dd, *J* = 13.5, 4.2 Hz, 1H, H6'$_a$), 2.82 – 2.70 (m, 1H, H1'), 2.62 (dd, *J* = 15.6, 7.0 Hz, 1H, H2'$_a$), 2.42 (dd, *J* = 13.5, 3.9 Hz, 1H, H6'$_b$), 2.45 – 2.28 (m, 1H, H2'$_b$), 1.68 (s, 3H, H5'), 1.31 (s, 9H, *t*-Bu').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.35 (C3'), 149.90 (C7'), 135.03 (C12'), 128.87 (C8'+C9'), 125.83 (C10'+C11'), 109.55 (C4'), 45.01 (C1'), 34.59 (C6'), 33.48 (C13'), 31.45 (C14'+C15'+C16'), 30.14 (C2'), 20.29 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.63 (s, 1H, OOH), 7.34 (d, *J* = 8.2 Hz, 2H, H10, H11), 7.06 (d, *J* = 8.2 Hz, 2H, H8, H9), 3.04 (dd, *J* = 13.3, 3.6 Hz, 1H, $H6_a$), 2.48 (dd, *J* = 13.3, 10.9 Hz, 1H, $H6_b$), 2.45 – 2.28 (m, 2H, H2), 2.34 – 2.19 (m, 1H, H1), 1.61 (s, 3H, H5), 1.32 (s, 9H, *t*-Bu).

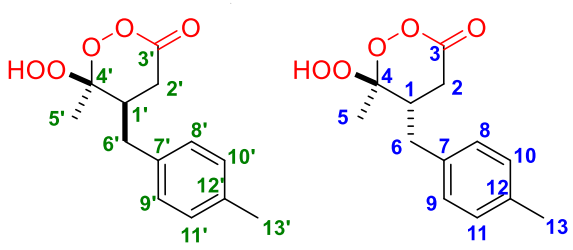
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.51 (C3), 150.20 (C7), 134.20 (C12), 128.57 (C8+C9), 125.96 (C10+C11), 112.82 (C4), 41.69 (C1), 36.14 (C6), 33.48 (C13), 31.45 (C14+C15+C16), 30.48 (C2), 15.58 (C5).

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{16}H_{22}O_5Na]^+$: 317.1359. Found: 317.1361.

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.27; H, 7.56.

IR (KBr): 3351, 2964, 1781, 1419, 1272, 1372, 1272, 1196, 1147, 1108, 858, 823, 560 cm^{-1}.

6-Hydroperoxy-6-methyl-5-(4-methylbenzyl)-1,2-dioxan-3-one, 2f



cis *trans*

Yield 64% (161.5 mg, 0.64 mmol). Colorless oil. R_f = 0.35 (PE:EtOAc = 5:1).

Peroxide **2f** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 24:76 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.00 – 8.00 (br.s., 1H, OOH'), 7.12 (d, *J* = 7.9 Hz, 2H, H10', H11'), 7.02 (d, *J* = 7.8 Hz, 2H, H8', H9'), 3.06 (dd, *J* = 13.9, 4.4 Hz, 1H, $H6'_a$), 2.80 – 2.67 (m, 1H, H1'), 2.61 (dd, *J* = 16.2, 7.0 Hz, 1H, $H2'_a$), 2.44 – 2.33 (m, 1H, $H6'_b$), 2.44 – 2.26 (m, 1H, $H2'_b$), 2.33 (s, 3H, H13'), 1.66 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 136.54 (C12'), 135.06 (C7'), 129.58 (C10'+C11'), 129.06 (C8'+C9'), 109.51 (C4'), 45.04 (C1'), 33.62 (C6'), 30.10 (C2'), 21.10 (C13'), 20.26 (C5'), (C3' carbon missing).

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.00 – 8.00 (br.s., 1H, OOH), 7.12 (d, *J* = 7.9 Hz, 2H, H10, H11), 7.02 (d, *J* = 7.8 Hz, 2H, H8, H9), 3.02 (dd, *J* = 13.3, 3.7 Hz, 1H, $H6_a$), 2.48 (dd, *J* = 13.3, 10.9 Hz, 1H, $H6_b$), 2.44 – 2.26 (m, 2H, H2), 2.33 (s, 3H, H13), 2.32 – 2.19 (m, 1H, H1), 1.59 (s, 3H, H5).

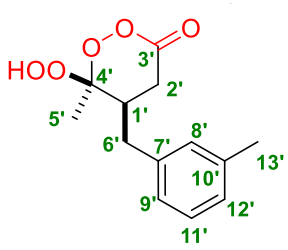
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.47 (C3), 136.85 (C12), 134.23 (C7), 129.69 (C10+C11), 128.74 (C8+C9), 112.79 (C4), 41.70 (C1), 36.24 (C6), 30.48 (C2), 21.10 (C13), 15.55 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{13}H_{20}O_5N]^+$: 270.1336. Found: 270.1342.

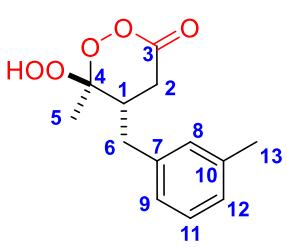
Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.94; H, 6.43.

IR (KBr): 3447, 3012, 2948, 1761, 1518, 1383, 1349, 1270, 1193, 1149, 1109, 880, 809, 513 cm^{-1}.

6-Hydroperoxy-6-methyl-5-(3-methylbenzyl)-1,2-dioxan-3-one, 2g



cis



trans

Yield 71% (180.0 mg, 0.71 mmol). White crystals. R_f = 0.35 (PE:EtOAc = 5:1).

Peroxide **2g** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 13:87 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.48 (br.s., 1H, OOH'), 7.20 (t, *J* = 7.5 Hz, 1H, H11'), 7.07 (d, *J* = 7.5 Hz, H12'), 6.99 – 6.87 (m, 2H, H8', H9'), 3.06 (dd, *J* = 13.9, 4.1 Hz, 1H, H6'$_a$), 2.84 – 2.70 (m, 1H, H1'), 2.61 (dd, *J* = 15.6, 7.2 Hz, 1H, H2'$_a$), 2.41 – 2.30 (m, 1H, H6'$_b$), 2.42 – 2.27 (m, 1H, H2'$_b$), 2.33 (s, 3H, H13'), 1.68 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.65 (C3'), 139.51 (C10'), 138.10 (C7'), 129.91 (C_{Ar}'), 128.82 (C11'), 127.71 (C12'), 126.22 (C_{Ar}'), 109.51 (C4'), 44.96 (C1'), 33.98 (C6'), 30.09 (C2'), 21.48 (C13'), 20.25 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.60 (br.s., 1H, OOH), 7.20 (t, *J* = 7.5 Hz, 1H, H11), 7.07 (d, *J* = 7.5 Hz, H12), 6.99 – 6.87 (m, 2H, H8, H9), 3.03 (dd, *J* = 13.2, 3.6 Hz, 1H, H6$_a$), 2.47 (dd, *J* = 13.2, 10.8 Hz, 1H, H6$_b$), 2.43 – 2.27 (m, 2H, H2), 2.33 (s, 3H, H13), 2.32 – 2.20 (m, 1H, H1), 1.60 (s, 3H, H5).

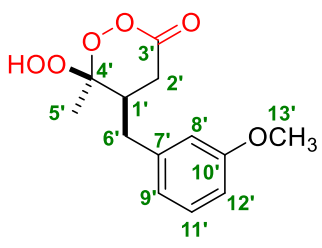
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.43 (C3), 138.75 (C10), 137.26 (C7), 129.63 (C_{Ar}), 128.91 (C11), 128.01 (C12), 125.93 (C_{Ar}), 112.79 (C4), 41.67 (C1), 36.60 (C6), 30.48 (C2), 21.48 (C13), 15.58 (C5).

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{13}H_{16}O_5Na]^+$: 275.0890. Found: 275.0884.

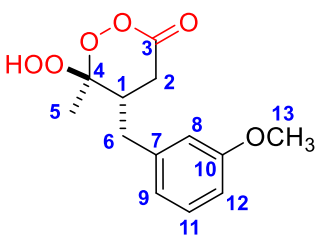
Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.85; H, 6.18.

IR (KBr): 3343, 3016, 1770, 1601, 1418, 1277, 1197, 1146, 1101, 856, 572 cm^{-1}.

6-Hydroperoxy-5-(3-methoxybenzyl)-6-methyl-1,2-dioxan-3-one, 2h



cis



trans

Yield 62% (166.3 mg, 0.62 mmol). Colorless oil. R_f = 0.20 (PE:EtOAc = 5:1).

Peroxide **2h** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 20:80 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.63 (br.s, 1H, OOH'), 7.24 (t, *J* = 7.8 Hz, 1H, H11'), 6.81 (dd, *J* = 8.3, 2.7 Hz, H12'), 6.73 (d, *J* = 7.8 Hz, H9'), 6.70 – 6.67 (m, 1H, H8'), 3.80 (s, 3H, H13'), 3.07 (dd, *J* = 13.8, 5.5 Hz, 1H, H6'$_a$), 2.84 – 2.71 (m, 1H, H1'), 2.62 (dd, *J* = 15.7, 7.0 Hz, 1H, H2'$_a$), 2.41 – 2.32 (m, 1H, H6'$_b$), 2.44 – 2.27 (m, 1H, H2'$_b$), 1.67 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 139.76 (C7'), 129.96 (C11'), 121.51 (C9'), 115.01 (C8'), 112.26 (C12'), 109.49 (C4'), 55.37 (C13'), 44.90 (C1'), 34.10 (C6'), 30.18 (C2'), 20.30 (C5') (C3' and C10' carbons missing).

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.63 (br.s, 1H, OOH), 7.24 (t, *J* = 7.8 Hz, 1H, H11), 6.81 (dd, *J* = 8.3, 2.7 Hz, H12), 6.73 (d, *J* = 7.8 Hz, H9), 6.70 – 6.67 (m, 1H, H8), 3.80 (s, 3H, H13), 3.04 (dd, *J* = 13.3, 3.5 Hz, 1H, H6$_a$), 2.48 (dd, *J* = 13.3, 10.9 Hz, 1H, H6$_b$),), 2.44 – 2.27 (m, 2H, H2), 2.37 – 2.19 (m, 1H, H1), 1.59 (s, 3H, H5).

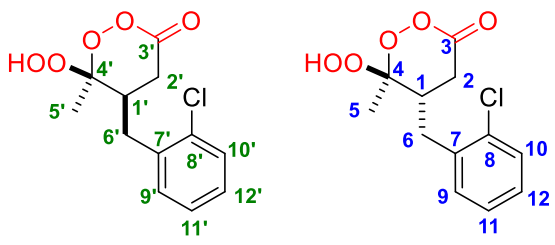
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.31 (C3), 160.08 (C10), 138.90 (C7), 130.08 (C11), 121.22 (C9), 114.83 (C8), 112.74 (C4), 112.42 (C12), 55.37 (C13), 41.57 (C1), 36.70 (C6), 30.53 (C2), 15.59 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{13}H_{20}O_6N]^+$: 286.1285. Found: 286.1288.

Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.16; H, 6.23.

IR (KBr): 3368, 3028, 2940, 2902, 1768, 1609, 1583, 1491, 1428, 1273, 1197, 1152, 1104, 1048, 857 cm^{-1}.

5-(2-Chlorobenzyl)-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2i



cis *trans*

Yield 78% (212.7 mg, 0.78 mmol). Colorless oil. R_f = 0.38 (PE:EtOAc = 5:1).

Peroxide **2i** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 28:72 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.40 – 7.33 (m, 1H, H10'), 7.24 – 7.15 (m, 3H, H9', H11', H12'), 3.29 (dd, *J* = 13.9, 4.1 Hz, 1H, H6'$_a$), 3.05 – 2.90 (m, 1H, H1'), 2.63 (dd, *J* = 15.9, 7.4 Hz, 1H, H2'$_a$), 2.53 – 2.31 (m, 1H, H2'$_b$), 2.46 – 2.33 (m, 1H, H6'$_b$), 1.68 (s, 3H, H5'), (OOH' protons missing).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.28 (C3'), 135.67 (C7'), 134.03 (C8'), 132.25 (C9'), 130.08 (C10'), 128.72 (C11'), 127.26 (C12'), 109.48 (C4'), 42.13 (C1'), 32.44 (C6'), 30.13 (C2'), 19.99 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.40 – 7.33 (m, 1H, H10), 7.24 – 7.15 (m, 3H, H9, H11, H12), 3.13 (dd, *J* = 13.4, 3.2 Hz, 1H, $H6_a$), 2.77 (dd, *J* = 13.4, 10.7 Hz, 1H, $H6_b$), 2.53 – 2.31 (m, 2H, H2), 2.48 – 2.31 (m, 1H, H1), 1.63 (s, 3H, H5), (OOH protons missing).

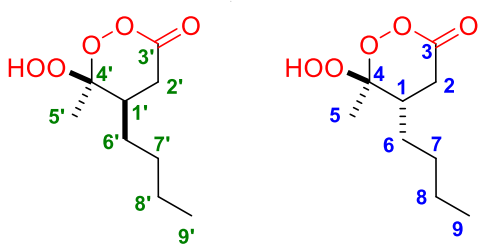
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.32 (C3), 135.10 (C7), 134.23 (C8), 131.10 (C9), 130.20 (C10), 128.86 (C11), 127.40 (C12), 112.69 (C4), 40.26 (C1), 33.84 (C6), 30.42 (C2), 15.57 (C5).

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_{12}H_{17}ClO_5N]^+$: 290.0790. Found: 290.0796.

Anal. Calcd for $C_{12}H_{13}ClO_5$: C, 52.86; H, 4.81; Cl, 13.00. Found: C, 52.99; H, 5.02; Cl, 12.83.

IR (KBr): 3366, 3060, 2940, 1763, 1441, 1411, 1274, 1195, 1153, 1104, 1051, 858, 751 cm^{-1}.

5-Butyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2j



cis *trans*

Yield 72% (147.0 mg, 0.72 mmol). Colorless oil. R_f = 0.44 (PE:EtOAc = 5:1).

Peroxide **2j** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 13:87 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.91 (br.s., 1H, OOH'), 2.79 (dd, *J* = 16.8, 8.4 Hz, 1H, $H2'_a$), 2.51 – 2.37 (m, 1H, $H2'_b$), 2.48 – 2.38 (m, 1H, H1'), 1.59 (s, 3H, H5'), 1.53 – 1.43 (m, 1H, $H6'_a$), 1.39 – 1.18 (m, 3H, $H6'_b$, H7', H8'), 0.88 (t, *J* = 6.5 Hz, 3H, H9').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 174.68 (C3'), 109.47 (C4'), 42.87 (C1'), 31.02 (C2'), 29.71 (C6'), 27.95 (C7'), 22.72 (C8'), 20.03 (C5'), 13.84 (C9').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.10 (br.s., 1H, OOH), 2.53 (dd, *J* = 14.9, 3.5 Hz, 1H, $H2_a$), 2.34 (dd, *J* = 14.9, 13.7 Hz, 1H, $H2_b$), 2.03 – 1.80 (m, 1H, H1), 1.64 – 1.52 (m, 1H, $H6_a$), 1.47 (s, 3H, H5), 1.39 – 1.18 (m, 3H, $H6_b$, H7, H8), 0.88 (t, *J* = 6.5 Hz, 3H, H9).

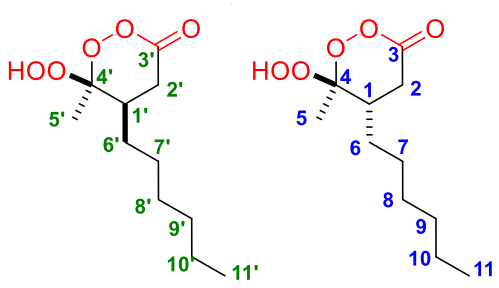
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 176.26 (C3), 113.20 (C4), 39.84 (C1), 31.45 (C2), 29.97 (C6), 29.62 (C7), 22.50 (C8), 15.06 (C5), 13.84 (C9).

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_9H_{16}O_5Na]^+$: 227.0890. Found: 227.0890.

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.22; H, 8.28.

IR (thin layer): 3393, 2957, 2935, 1784, 1461, 1423, 1380, 1265, 1214, 1163, 1111, 859 cm^{-1}.

5-Hexyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one, 2k



cis *trans*

Yield 26% (60.4 mg, 0.26 mmol). Colorless oil. R_f = 0.38 (PE:EtOAc = 5:1).

Peroxide **2k** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 14:86 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.45 (s., 1H, OOH'), 2.80 (dd, *J* = 16.7, 8.5 Hz, 1H, H2'$_a$), 2.53 – 2.38 (m, 1H, H2'$_b$), 2.52 – 2.44 (m, 1H, H1'), 1.70 – 1.55 (m, 1H, H6'$_a$), 1.62 (s, 3H, H5'), 1.39 – 1.20 (m, 9H, H6'$_b$, H7', H8', H9', H10'), 0.88 (t, *J* = 6.4 Hz, 3H, H11').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 43.04 (C1'), 31.64 (C9'), 31.09 (C2'), 28.30 (C_{Alk}'), 27.63 (C_{Alk}'), 20.15 (C5'), 14.11 (C11') (C3', C4', C6' and C_{Alk}' carbons missing)

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.63 (s., 1H, OOH), 2.55 (dd, *J* = 14.9, 3.5 Hz, 1H, H2$_a$), 2.35 (dd, *J* = 14.9, 13.6 Hz, 1H, H2$_b$), 1.98 – 1.90 (m, 1H, H1), 1.70 – 1.55 (m, 1H, H6$_a$), 1.49 (s, 3H, H5), 1.39 – 1.20 (m, 9H, H6$_b$, H7, H8, H9, H10,), 0.88 (t, *J* = 6.4 Hz, 3H, H11).

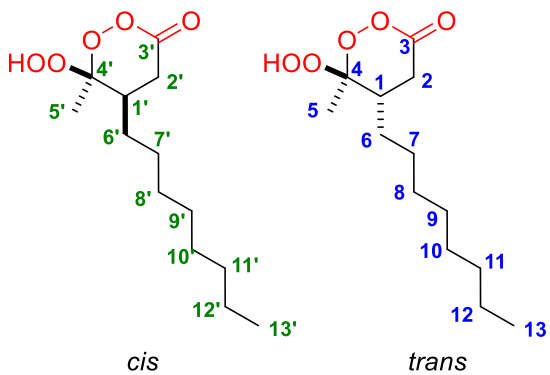
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.89 (C3), 113.26 (C4), 39.93 (C1), 31.64 (C9), 31.53 (C2), 30.41 (C6), 29.16 (C_{Alk}), 27.55 (C_{Alk}), 22.65 (C_{Alk}), 15.18 (C5), 14.11 (C11).

HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{11}H_{20}O_5Na]^+$: 255.1203. Found: 255.1210.

Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.33; H, 8.42.

IR (thin layer): 3395, 2930, 2861, 1786, 1718, 1461, 1424, 1379, 1270, 1246, 1159, 859 cm^{-1}.

6-Hydroperoxy-6-methyl-5-octyl-1,2-dioxan-3-one, 2l



cis *trans*

Yield 68% (177.0 mg, 0.68 mmol). Colorless oil. R_f = 0.48 (PE:EtOAc = 5:1).

Peroxide **2l** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 17:83 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.53 (br.s, 1H, OOH'), 2.80 (dd, *J* = 16.7, 8.4 Hz, 1H, H2'$_a$), 2.59 – 2.29 (m, 1H, H2'$_b$), 2.49 – 2.42 (m, 1H, H1'), 1.72 – 1.53 (m, 1H, H6'$_a$), 1.61 (s, 3H, H5'), 1.38 – 1.22 (m, 13H, H6'$_b$, H7', H8', H9', H10', H11', H12'), 0.87 (t, *J* = 7.0 Hz, 3H, H13').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 109.53 (C4'), 43.00 (C1'), 31.07 (C2'), 28.29 (C6'), 27.65 (C_{Alk}'), 20.12 (C5'), 14.18 (C13') (C3' and 5 C_{Alk}' carbons missing).

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.71 (br.s, 1H, OOH), 2.55 (dd, *J* = 14.9, 3.5 Hz, 1H, H2$_a$), 2.35 (dd, *J* = 14.9, 13.5 Hz, 1H, H2$_b$), 2.04 – 1.83 (m, 1H, H1), 1.72 – 1.53 (m, 1H, H6$_a$), 1.49 (s, 3H, H5), 1.38 – 1.22 (m, 13H, H6$_b$, H7, H8, H9, H10, H11, H12), 0.87 (t, *J* = 7.0 Hz, 3H, H13).

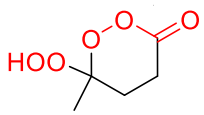
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.97 (C3), 113.25 (C4), 39.92 (C1), 31.90 (C_{Alk}), 31.52 (C2), 30.40 (C6), 29.50 (C_{Alk}), 29.42 (C_{Alk}), 29.28 (C_{Alk}), 27.58 (C_{Alk}), 22.74 (C_{Alk}), 15.16 (C5), 14.18 (C13).

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{13}H_{24}O_5Na]^+$: 283.1516. Found: 283.1512.

Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 60.05; H, 9.36.

IR (thin layer): 3386, 2928, 2858, 1785, 1461, 1379, 1263, 1159, 1111, 859 cm^{-1}.

6-Hydroperoxy-6-methyl-1,2-dioxan-3-one, 2m



Yield 60% (88.9 mg, 0.60 mmol). White solid, mp = 69-70 °C. R_f = 0.17 (PE:EtOAc = 2:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.71 (s, 1H), 2.72 – 2.56 (m, 2H), 2.36 (ddd, *J* = 14.5, 6.2, 2.6 Hz, 1H), 1.97 (ddd, *J* = 13.9, 13.9, 5.4 Hz, 1H), 1.64 (s, 3H).

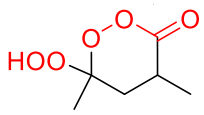
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.54, 109.64, 30.26, 26.06, 19.97.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_5H_8O_5Na]^+$: 171.0264. Found: 171.0260.

Anal. Calcd for $C_5H_8O_5$: C, 40.55; H, 5.44. Found: C, 40.65; H, 5.32.

IR (thin layer): 3335, 2820, 1777, 1714, 1566, 1416, 1157, 1107, 1013, 923, 855, 764 cm^{-1}.

6-Hydroperoxy-4,6-dimethyl-1,2-dioxan-3-one, 2n



Yield 83% (134.6 mg, 0.83 mmol). White solid, mp = 63-64 °C. R_f = 0.18 (PE:EtOAc = 5:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.96 (br.s, 1H), 2.90 – 2.71 (m, 1H), 2.32 (dd, *J* = 14.3, 6.1 Hz, 1H), 1.73 (t, *J* = 13.9 Hz, 1H), 1.62 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 178.56, 110.34, 38.31, 30.93, 20.11, 13.29.

HRMS (ESI) m/z $[M + NH_4]^+$. Calcd for $[C_6H_{14}O_5N]^+$: 180.0866. Found: 180.0864.

Anal. Calcd for $C_6H_{10}O_5$: C, 44.45; H, 6.92. Found: C, 44.58; H, 6.13.

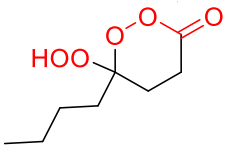
IR (KBr): 3360, 2990, 2943, 1757, 1458, 1379, 1268, 1166, 1064, 850, 568 cm^{-1}.

General experimental procedure for Scheme 7.

An ethereal solution of H_2O_2 (4.30 M, 1.163 mL, 5.0 mmol, 5.0 eq.) was added with stirring to **1** (1.00 mmol, 1.0 eq.) in Et_2O (3.5 mL). Later, $BF_3{\cdot}Et_2O$ (1.419 g, 10.00 mmol, 10.0 eq.) was added dropwise with stirring to the solution at 0 °C. The reaction mixture was stirred at 20-25 °C for 24 h. After that time, CH_2Cl_2 (50 mL) and H_2O (2 mL) was added and the mixture was neutralized by $NaHCO_3$. The solid was filtrated. The solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Products **6**, **7** and the least polar compound were isolated by chromatography on SiO_2 with elution using PE-EtOAc mixture (2:1).

Presumably, the least polar compound isolated in trace amount (12.0 mg) is peroxide **2o** with purity ≈85-90%.

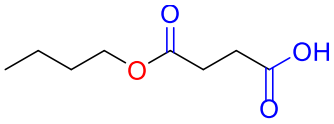
6-Butyl-6-hydroperoxy-1,2-dioxan-3-one, 2o



^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 175.65, 111.30, 31.68, 27.99, 26.17, 25.32, 22.76, 13.93.

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_8H_{14}O_5Na]^+$: 213.0733. Found: 213.0723.

4-Butoxy-4-oxobutanoic acid, 6o[10]

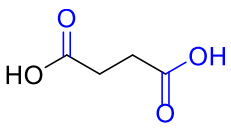


Yield 34% (59.2 mg, 0.34 mmol). Colorless oil. R_f = 0.32 (PE:EtOAc = 5:1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 4.09 (t, *J* = 6.6 Hz, 2H), 2.75 – 2.53 (m, 4H), 1.60 (quintet, *J* = 6.8 Hz, 2H), 1.36 (sextet, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 178.39, 172.34, 64.89, 30.72, 29.12, 29.05, 19.20, 13.76.

Succinic acid, 7 [11]



In the experiment with **1o** yield was 23% (27.1 mg, 0.23 mmol). In the experiment with **1p** yield was 36% (42.5 mg, 0.36 mmol). White solid, mp = 187 °C.

^1H NMR (300.13 MHz, DMSO-d_6, δ): 11.74 (s, 2H), 2.02 (s, 4H).

^{13}C NMR (75.48 MHz, DMSO-d_6, δ): 173.71, 28.87.

Phenol [12]

Yield 68% (64.0 mg, 0.68 mmol).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.26 (t, *J* = 7.9 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 5.26 (s, 1H).

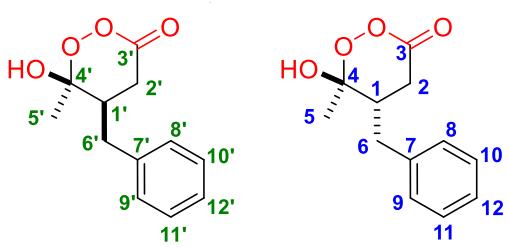
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 155.43, 129.84, 121.03, 115.47.

Experimental procedures for Scheme 8.

The reaction of 5-benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one (2a) with Ph_3P during 5 min.

Solution of Ph_3P (288.5 mg, 1.10 mmol, 1.1 eq.) in CH_2Cl_2 (2 mL) was added dropwise with stirring to solution of 5-benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one **2a** (238.2 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) at 0-10 °C. The reaction mixture was stirred at 20-25 °C for 5 min and transferred onto chromatographic column. Product **3a** was isolated by chromatography on SiO_2 (PE:EtOAc = 3:1).

5-Benzyl-6-hydroxy-6-methyl-1,2-dioxan-3-one, 3a



cis *trans*

Yield 25% (55.6 mg, 0.25 mmol). White solid. R_f = 0.18 (PE:EtOAc = 3:1).

Peroxide **3a** was obtained as an inseparable mixture of *cis* and *trans* isomers. Isomer ratio = 22:78 (*cis : trans*).

cis-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.19 (br.s., 1H, OH'), 7.34 – 7.29 (m, 2H, H10', H11'), 7.25 – 7.21 (m, 1H, H12'), 7.16 (d, *J* = 7.3 Hz, 2H, H8', H9'), 3.08 (dd, *J* = 13.1, 4.7 Hz, 1H, H6'$_a$), 3.02 – 2.96 (m, 1H, H1'), 2.78 – 2.70 (m, 1H, H2'$_a$), 2.47 – 2.39 (m, 1H, H6'$_b$), 2.30 (dd, *J* = 18.1, 5.0 Hz, 1H, H2'$_b$), 1.66 (s, 3H, H5').

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 176.16 (C3'), 137.97 (C7'), 129.04 (C_{Ar}'), 128.97 (C_{Ar}'), 127.01 (C12'), 115.19 (C4'), 42.22 (C1'), 36.55 (C6'), 35.02 (C2'), 18.21 (C5').

trans-isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.24 (br.s., 1H, OH), 7.34 – 7.29 (m, 2H, H10, H11), 7.25 – 7.20 (m, 3H, H8, H9, H12), 3.06 (dd, *J* = 13.9, 5.1 Hz, 1H, H6$_a$), 2.93 (dd, *J* = 13.9, 8.6 Hz, 1H, H6$_b$), 2.76 – 2.69 (m, 2H, H2$_a$, H1), 2.55 – 2.47 (m, 1H, H2b$_a$), 1.48 (s, 3H, H5).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 176.88 (C3), 139.28 (C7), 128.85 (C_{Ar}), 128.81 (C_{Ar}), 126.74 (C12), 113.13 (C4), 47.16 (C1), 35.76 (C2), 34.44 (C6), 21.39 (C5).

HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{12}H_{14}O_4Na]^+$: 245.0784. Found: 245.0783.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.89; H, 6.38.

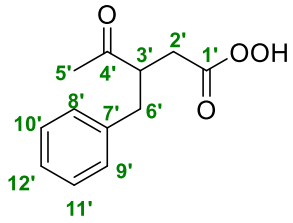
IR (KBr): 3253, 3026, 2931, 2855, 1775, 1450, 1380, 1271, 1084, 955, 699 cm^{-1}.

The reaction of 5-benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one (2a) with Ph_3P during 1 day.

With 1.1 eq. Ph_3P

Solution of Ph_3P (288.5 mg, 1.10 mmol, 1.1 eq.) in CH_2Cl_2 (2 mL) was added dropwise with stirring to solution of 5-benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one **2a** (238.2 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) at 0-10 °C. The reaction mixture was stirred at 20-25 °C for 1 day. The solution was concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). 3-Benzyl-4-oxopentaneperoxoic acid (**4a**) and 3-benzyl-4-oxopentanoic acid (**5a**) were isolated by chromatography on SiO_2 (PE:EtOAc = 3:1) as an inseparable mixture. **4a** / **5a** ratio = 1:2. Total yield 79% (165 mg).

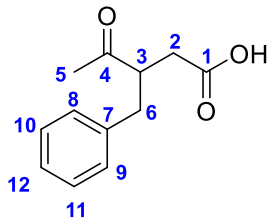
3-Benzyl-4-oxopentaneperoxoic acid, 4a



^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 10.14 (br.s., 1H, OOH'), 7.36 – 7.20 (m, 3H, H10', H11', H12'), 7.19 – 7.14 (m, 2H, H8', H9'), 3.31 – 3.18 (m, 1H, H3'), 3.00 (dd, *J* = 13.1, 6.7 Hz, 1H, H6'$_a$), 2.79 (dd, *J* = 17.1, 9.8 Hz, 1H, H2'$_a$), 2.66 (dd, *J* = 13.1, 8.3 Hz, 1H, H6'$_b$), 2.38 (dd, *J* = 17.1, 4.0 Hz, 1H, H2'$_b$), 2.15 (s, 3H, H5).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.02 (C4'), 172.91 (C1'), 137.52 (C7'), 128.94 (C8', C9'), 128.81 (C10', C11'), 127.14 (C12'), 49.55 (C3'), 37.58 (C6'), 31.24 (C2'), 30.02 (C5').

3-Benzyl-4-oxopentanoic acid, 5a[13]



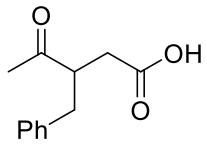
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 10.14 (br.s., 1H, OH), 7.36 – 7.20 (m, 3H, H10, H11, H12), 7.19 – 7.14 (m, 2H, H8, H9), 3.31 – 3.18 (m, 1H, H3), 2.94 (dd, *J* = 13.5, 6.8 Hz, 1H, H6$_a$), 2.80 (dd, *J* = 17.5, 10.0 Hz, 1H, H2$_a$), 2.62 (dd, *J* = 13.5, 8.3 Hz, 1H, H6$_b$), 2.38 (dd, *J* = 17.5, 3.9 Hz, 1H, H2$_b$), 2.11 (s, 3H, H5).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 211.01 (C4), 178.06 (C1), 138.09 (C7), 128.96 (C8, C9), 128.81 (C10, C11), 126.91 (C12), 49.57 (C3), 37.63 (C6), 34.98 (C2), 30.25 (C5).

With 2.0 eq. Ph_3P

Solution of Ph_3P (524.6 mg, 2.00 mmol, 2.0 eq.) in CH_2Cl_2 (2 mL) was added dropwise with stirring to solution of 5-benzyl-6-hydroperoxy-6-methyl-1,2-dioxan-3-one **2a** (238.2 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) at 0-10 °C. The reaction mixture was stirred at 20-25 °C for 1 day. Later, Et_2O (15 mL) was added and precipitate of Ph_3PO was filtered. A solution was washed with 5% aq. NaOH (3×10 mL). The combined aqueous layers were acidified by diluted aq. HCl (10 mL). The products were extracted by Et_2O (3×15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 30–35 °C).

3-Benzyl-4-oxopentanoic acid, 5a[13]



Yield 68% (140.2 mg, 0.68 mmol). White solid. mp = 95-96 °C (lit.[14] 96-97 °C). R_f = 0.23 (PE:EtOAc = 3:1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 7.36 – 7.20 (m, 3H), 7.16 (d, *J* = 7.1 Hz, 2H), 3.31 – 3.18 (m, 1H), 2.94 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.80 (dd, *J* = 17.5, 10.0 Hz, 1H), 2.62 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.37 (dd, *J* = 17.5, 3.9 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 210.69, 178.18, 138.14, 129.01, 128.87, 126.97, 49.60, 37.71, 35.02, 30.29.

Computational Details

Calculations were carried out using the M06-2X functional with the 6-311++G(d,p) basis set for all atoms. The SMD solvation model was used to simulate water. Grimme's D3 method was used to simulate empirical dispersion. Additionally, an ultrafine (99,590) grid was used for all structure optimizations. Frequency calculations were performed on all structures to confirm that they were either a minimum or a transition state. All calculations were performed using Gaussian 09 software.[15] Visualization of all three-dimensional structures and orbital plots was achieved using CYLView Beta v1.0.565[16] and IQmol v2.14.0.[17]

Calculations:

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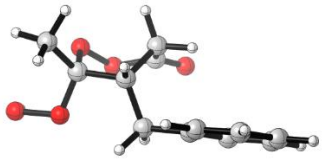

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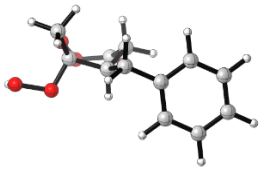

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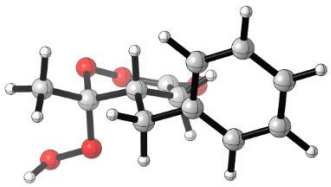

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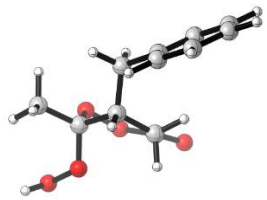
Trans Chair



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O	0.919429912660	-0.403582623324	-1.075038626734
O	1.770045106053	-1.522211157710	-0.898347566797
H	2.567984421497	-1.267995032744	-1.387076798948
C	-0.254959264736	2.468862142296	0.967236412390
H	0.717197312444	2.942238462887	1.118604806991
H	-0.516317109682	1.934914218391	1.885459615090
C	-1.280416048314	3.542045302711	0.692903200388
C	-2.491255645659	3.577308043618	1.385612831755
C	-1.036606901974	4.512196836242	-0.283555012178
C	-3.439907117082	4.561048840534	1.111966948400
H	-2.691206444595	2.827415723011	2.144619106214
C	-1.981461409525	5.494665029341	-0.560933931513
H	-0.096315626896	4.496385530924	-0.826647341846
C	-3.187988950810	5.521236074051	0.136855578144
H	-4.375020853330	4.575014517550	1.660198160974
H	-1.776372351832	6.241567072224	-1.319420203025
H	-3.924308130200	6.287048984024	-0.077689586062

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8 2 1.000 6 1.000 9 1.000 10 1.000

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10 8 1.000

11 5 1.000 12 1.000 13 1.000 14 1.000

12 11 1.000

13 11 1.000

14 11 1.000

15 5 1.000 16 0.100

16 15 0.100 17 1.000

17 16 1.000

18 6 1.000 19 1.000 20 1.000 21 1.000

19 18 1.000

20 18 1.000

21 18 1.000 22 1.500 23 1.500

22 21 1.500 24 1.500 25 1.000

23 21 1.500 26 1.500 27 1.000

24 22 1.500 28 1.500 29 1.000

25 22 1.000

26 23 1.500 28 1.500 30 1.000

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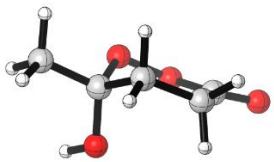
29 24 1.000

30 26 1.000

31 28 1.000

OH Chair R = Me Reactant



Imaginary Frequencies = 0

E = -496.13643327

0,1

O	2.840055567029	-0.241894590534	0.062792448377
C	1.658546920234	-0.052821025971	-0.070771823015
O	-0.454982408378	-1.064827701662	-0.590732075247
O	0.904701321570	-1.191045390113	-0.171981941044
C	-1.141332946115	0.034926972601	0.052031131031
C	-0.474147535127	1.313972116346	-0.400730664671
H	-0.587947706955	1.380399441937	-1.483210800585
H	-0.971646991548	2.170931064484	0.053346342868
C	0.998265046621	1.290076410599	-0.010331507570
H	1.597662129620	1.968215617138	-0.617881672540
H	1.129377107641	1.597538902789	1.031867728272
C	-2.567680000391	-0.124967505661	-0.423318224730
H	-2.979203061030	-1.069421207318	-0.061845243795
H	-3.155500212449	0.701222267102	-0.021484831562
H	-2.614810060904	-0.099843282052	-1.512075562483
O	-1.008729576074	-0.071477554906	1.440304933589
H	-1.499873593744	-0.847794534778	1.741949763104

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9 2 1.000 6 1.000 10 1.000 11 1.000

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11 9 1.000

12 5 1.000 13 1.000 14 1.000 15 1.000

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14 12 1.000

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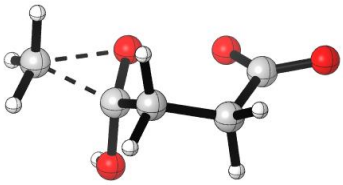
16 5 1.000 17 1.000

17 16 1.000

OH Chair R = Me Transition State



Imaginary Frequencies = 1

E = -496.08321742

0,1

O	3.024151696487	-0.186904825180	-0.165216858155
C	1.791654160220	-0.180657777059	-0.054328031599
O	-0.765793707691	-1.125052682501	-0.196604172653
O	1.133795396516	-1.261050451010	0.178199041404
C	-1.096679738617	0.078973321339	0.120267912476
C	-0.376208159051	1.175728619293	-0.611571874536
H	-0.418638148994	0.968031364388	-1.680162016306
H	-0.848689777174	2.134644846877	-0.403916593977
C	1.071638905993	1.163547875602	-0.106730991505
H	1.672861316321	1.825006153279	-0.729046694062
H	1.104685370410	1.548453646773	0.917188830063
C	-2.557432710427	-0.405388593831	-0.693421949103
H	-3.042768100551	-1.220612742289	-0.169023758330
H	-3.026673380449	0.558912855329	-0.474820609997
H	-2.387258732366	-0.564966335675	-1.750184382653
O	-1.332600482677	0.367808422610	1.422256681182
H	-1.585968187952	-0.436535347946	1.901777597750

1 2 2.000

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3 5 2.000

4 2 2.000

5 3 2.000 6 1.000 12 0.100 16 1.000

6 5 1.000 7 1.000 8 1.000 9 1.000

7 6 1.000

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9 2 1.000 6 1.000 10 1.000 11 1.000

10 9 1.000

11 9 1.000

12 5 0.100 13 1.000 14 1.000 15 1.000

13 12 1.000

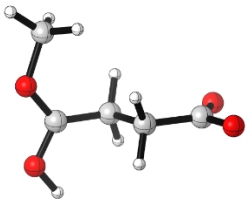
14 12 1.000

15 12 1.000

16 5 1.000 17 1.000

17 16 1.000

OH R = Me Product



Imaginary Frequencies = 0

E = -496.20176181

0,1

O	-2.463641733966	0.266112196926	1.177505257970
O	1.927879795033	-1.726685405381	-0.122264266147
H	1.278211782839	-2.399273689154	0.148028442379
C	2.095461384475	1.772267509597	-0.061185253083
H	2.943543806263	2.266819232727	-0.521572147191
H	1.169346788864	2.035532622590	-0.566626334483
H	2.053996002468	1.980572938457	1.005441811821
C	-2.259702852897	0.076981335579	-0.044226165638
O	2.364114303219	0.351687486111	-0.247762529228
O	-3.130136011219	0.098076987650	-0.950877172243
C	1.518778836160	-0.530036761220	0.102563794880
C	0.174661511648	-0.247661639840	0.652553405240
H	-0.084712422151	-1.051531476846	1.342241169474
H	0.180291478411	0.697690143158	1.191499576654
C	-0.827607862650	-0.209029477629	-0.515884325344
H	-0.551005284306	0.562717863272	-1.238260115006
H	-0.828387522191	-1.164363865996	-1.045288150057

1 8 2.000

2 3 1.000 11 2.000

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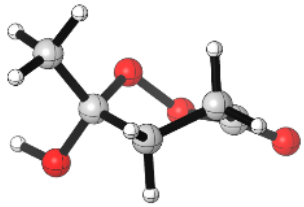
16 15 1.000

17 15 1.000

OH Boat R = Me Reactant



Imaginary Frequencies = 0

E = -496.14031146

0,1

O	-0.355725770154	-0.743155108207	-0.884731765887
O	0.895597133182	-1.115251670430	-0.319982780213
O	-1.592678749946	-0.903315986220	1.083335965189
O	2.849368060726	-0.226040929393	0.136222095727
C	-1.166461462230	-0.027214626006	0.078753468776
C	-0.320770841828	1.072991307261	0.723984340926
H	-0.060105521050	0.771311625200	1.739694336678
H	-0.895677702461	1.996350048331	0.779291440819
C	0.957570232276	1.285862230987	-0.092728691624
H	0.719249411381	1.567477597876	-1.122028643567
H	1.607747683975	2.041529259363	0.341797094200
C	1.692791484624	-0.013592857266	-0.103133685409
C	-2.307002463463	0.487122329115	-0.774236750289
H	-2.802957680997	-0.342464976155	-1.282925777400
H	-1.935463329438	1.197737258608	-1.513479242470
H	-3.023025867338	0.989098327176	-0.122826645676
H	-2.252057127259	-1.505086550243	0.711691580221

1 5 1.000

2 12 1.000

3 5 1.000 17 1.000

4 12 2.000

5 1 1.000 3 1.000 6 1.000 13 1.000

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7 6 1.000

8 6 1.000

9 6 1.000 10 1.000 11 1.000 12 1.000

10 9 1.000

11 9 1.000

12 2 1.000 4 2.000 9 1.000

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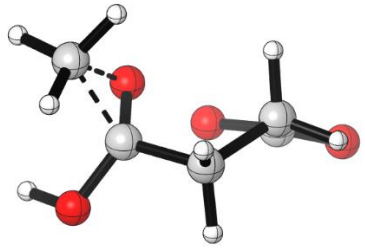
14 13 1.000

15 13 1.000

16 13 1.000

17 3 1.000

OH Boat R = Me Transition State



Imaginary Frequencies = 1

E = -496.08139542

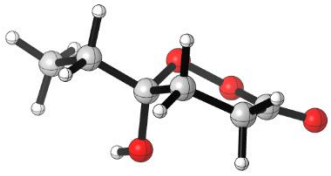
0,1

O	-0.662614101614	-0.726190384457	-0.801754453830
O	1.126898706755	-1.224621281388	-0.264863834608
O	-1.663292876929	-0.753568038444	1.239625152259
O	2.995075431369	-0.097495911514	0.064433642465
C	-1.116166159912	-0.067413959970	0.210563466270
C	-0.319148496462	1.150238322705	0.646952472252
H	-0.129321038185	1.032321727478	1.714901876659
H	-0.895717547202	2.063034714332	0.502734107609
C	0.987965562463	1.190151450434	-0.143818173387
H	0.782872073314	1.415408798591	-1.194697535871
H	1.632537802639	1.973612966781	0.250689686622

C	1.771293128857	-0.118101817881	-0.105907678378
C	-2.308295554949	0.352344574414	-0.998057267098
H	-2.782526656531	-0.508013503926	-1.457662388328
H	-1.876644835168	1.066271944782	-1.688266942476
H	-2.950810313573	0.806640473854	-0.238980019619
H	-2.031315194872	-1.593813475793	0.922394539456

1 5 1.500
2 12 1.500
3 5 1.000 17 1.000
4 12 2.000
5 1 1.500 3 1.000 6 1.000 13 0.100
6 5 1.000 7 1.000 8 1.000 9 1.000
7 6 1.000
8 6 1.000
9 6 1.000 10 1.000 11 1.000 12 1.000
10 9 1.000
11 9 1.000
12 2 1.500 4 2.000 9 1.000
13 5 0.100 14 1.000 15 1.000 16 1.000
14 13 1.000
15 13 1.000
16 13 1.000
17 3 1.000

OH Chair R = Et Reactant



# Imaginary Frequencies = 0
E = -535.43901143
0,1

O	3.099687669797	-0.653718926005	0.148666747911
C	1.974121397200	-0.264382043001	-0.026724831847
O	-0.260568001115	-0.893318439433	-0.611393243000
O	1.035160876068	-1.254523886997	-0.134683408632
C	-0.769792983402	0.310692791304	0.007907954124

C	0.120083601502	1.453077047882	-0.427231735979
H	0.041664532382	1.538211888634	-1.511569842060
H	-0.229161983710	2.383966703961	0.019593076415
C	1.558499342290	1.174714302189	-0.007188999884
H	2.279259390520	1.722772479610	-0.614224736631
H	1.724896019494	1.477286574827	1.031322008855
C	-2.191727704314	0.411434146840	-0.529454236529
H	-2.135330161799	0.409575691368	-1.620338406976
H	-2.560625847606	1.394335770778	-0.225329868376
O	-0.692480419244	0.196755305428	1.399630811220
C	-3.130233903129	-0.686374095429	-0.038144582956
H	-3.271451653244	-0.646338755380	1.044855662233
H	-4.112731108700	-0.557763284297	-0.494467373591
H	-2.763142432987	-1.678923944671	-0.304990661384
H	-1.276256960003	-0.515084297609	1.694961097087

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2 1 2.000 4 1.000 9 1.000
3 5 1.000
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5 3 1.000 6 1.000 12 1.000 15 1.000
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7 6 1.000
8 6 1.000
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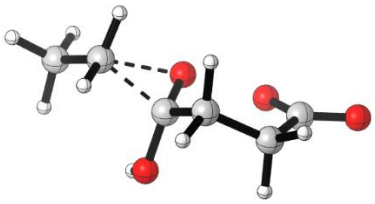
OH Chair R = Et Transition State



Imaginary Frequencies = 1

E = -535.3914918

0,1

O	3.062083452528	-0.081072725363	-0.155277356776
C	1.832051344796	-0.110255317187	-0.037157567756
O	-0.663818735729	-1.124063236202	-0.216395891283
O	1.209665394101	-1.220456844081	0.165283400657
C	-1.058848142984	0.041408295674	0.144593247791
C	-0.378904812303	1.202357624494	-0.528726272443
H	-0.423975436779	1.052782409471	-1.607136366019
H	-0.879759584346	2.133334205295	-0.266365619518
C	1.071928506038	1.211571856685	-0.035272468849
H	1.652986222442	1.913083390252	-0.632493084218
H	1.101601023226	1.554365631827	1.003780640981
C	-2.558186795129	-0.372120921482	-0.723653889633
H	-2.935972128690	0.640433828266	-0.552599864086
H	-2.291803479397	-0.526261646157	-1.763324620177
O	-1.307783754280	0.269707199462	1.462895645964
H	-1.469147643171	-0.569353603023	1.920711124675
C	-3.391466780175	-1.440716898886	-0.086892680467
H	-3.003036700105	-2.438425213365	-0.282091262304
H	-3.498790983834	-1.285588009807	0.987693755427
H	-4.390154866209	-1.365454415873	-0.528792041964

1 2 2.000

2 1 2.000 4 2.000 9 1.000

3 5 1.500

4 2 2.000

5 3 1.500 6 1.000 12 0.100 15 1.000

6 5 1.000 7 1.000 8 1.000 9 1.000

7 6 1.000

8 6 1.000

9 2 1.000 6 1.000 10 1.000 11 1.000

10 9 1.000

11 9 1.000

12 5 0.100 13 1.000 14 1.000 17 1.000

13 12 1.000

14 12 1.000

15 5 1.000 16 1.000

16 15 1.000

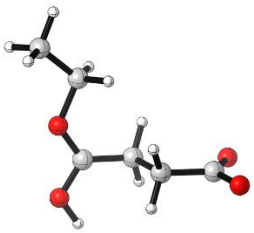
17 12 1.000 18 1.000 19 1.000 20 1.000

18 17 1.000

19 17 1.000

20 17 1.000

OH R = Et Product



Imaginary Frequencies = 0

E = -535.51098623

0,1

O	2.877566304203	-0.901199293656	1.138225396270
O	-0.333925984220	2.767650047646	0.039525953469
H	0.525345905766	3.106691722846	0.346674040548
C	-1.888588391641	-0.389073339124	-0.164074761388
C	2.805226075123	-0.529568567817	-0.056158827064
O	-1.558258947439	1.047628898778	-0.226544038231
O	3.628923068723	-0.800813411929	-0.966278648158
C	-0.439760917783	1.492637231009	0.174589364001
C	0.673861731259	0.664786674640	0.688234347242
H	1.207018278409	1.247960777147	1.440160357143
H	0.287890103469	-0.243630815260	1.145343243753
C	1.612086043959	0.333406177290	-0.486956190360
H	1.074622784525	-0.207006376888	-1.270157712386
H	1.999954871796	1.251448881077	-0.933704979484
C	-3.242022273074	-0.539428665572	-0.800629383893
H	-3.520688500962	-1.593832214105	-0.765727725439
H	-3.991581578891	0.037027404463	-0.257478722427
H	-3.219064118581	-0.219008392355	-1.842631305942

H	-1.110753670765	-0.925883790957	-0.705008591580
H	-1.889114223877	-0.666645527234	0.888710483928

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15 4 1.000 16 1.000 17 1.000 18 1.000
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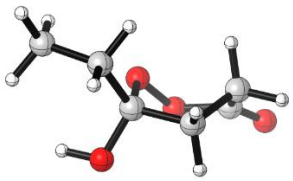
20 4 1.000

OH Boat R = Et Reactant



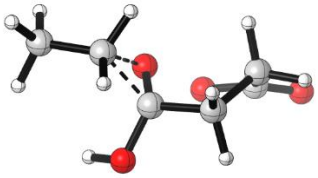
# Imaginary Frequencies = 0
E = -535.44272321
0,1

O	-0.206091144206	-0.851002074092	-0.448037768079
O	1.093257010144	-1.190756796586	0.019359800139
O	-1.060272861943	-0.247510045721	1.632792168999
O	3.158014244025	-0.460315032199	-0.115081674106
C	-0.775746158822	0.217803874583	0.343498475787

C	0.246691673874	1.351316985942	0.460989305866
H	0.657984901193	1.355392688412	1.471566945629
H	-0.241354710583	2.309644183285	0.287762198010
C	1.375540131786	1.136195714954	-0.552049774230
H	0.983430841435	1.115868593164	-1.572484434376
H	2.147333199559	1.899233520000	-0.482203704285
C	1.996948395809	-0.186066825343	-0.244740432695
C	-2.017063210845	0.612865048894	-0.450211521911
H	-1.678147782096	1.043982742927	-1.395865186670
H	-2.492412420646	1.414111053915	0.120958307709
C	-3.007223870891	-0.520737948594	-0.703643061306
H	-3.875678066535	-0.131559889090	-1.237150371784
H	-2.566986685652	-1.313561214527	-1.309732384985
H	-3.373505934124	-0.960845655608	0.227669989752
H	-1.794261951482	-0.874989204315	1.590631152535

1 5 1.000
2 12 1.000
3 5 1.000 20 1.000
4 12 2.000
5 1 1.000 3 1.000 6 1.000 13 1.000
6 5 1.000 7 1.000 8 1.000 9 1.000
7 6 1.000
8 6 1.000
9 6 1.000 10 1.000 11 1.000 12 1.000
10 9 1.000
11 9 1.000
12 2 1.000 4 2.000 9 1.000
13 5 1.000 14 1.000 15 1.000 16 1.000
14 13 1.000
15 13 1.000
16 13 1.000 17 1.000 18 1.000 19 1.000
17 16 1.000
18 16 1.000
19 16 1.000
20 3 1.000

OH Boat R = Et Transition State



Imaginary Frequencies = 1

E = -535.38935595

0,1

O	0.284771137423	-0.076429204171	-0.839518825576
O	-1.402577900831	0.803658388165	-0.979416972780
O	1.064267062957	0.995932901043	1.007366216637
O	-3.460678469933	0.314457480769	-0.364698222559
C	0.533366566889	-0.108239207609	0.419299151347
C	-0.486028245133	-0.820045745974	1.296907791350
H	-0.724127403351	-0.146146929915	2.120704480628
H	-0.071294108238	-1.736456456215	1.715650229934
C	-1.726662375148	-1.121632179559	0.454608573771
H	-1.502010838005	-1.910258180092	-0.269639786145
H	-2.532945894435	-1.470557721200	1.097440485968
C	-2.250917281348	0.071295650551	-0.334941605435
C	1.819847265614	-1.255599615682	-0.073652323336
H	1.301649620418	-2.143947541326	-0.419903345522
H	2.122763370802	-1.344964582218	0.973198374742
C	2.903998472898	-0.724541343893	-0.960642271545
H	3.747060885403	-1.417868007560	-0.882486562537
H	2.595883919628	-0.668154497522	-2.002711284162
H	3.252863480516	0.252981657403	-0.622800523776
H	1.530996403876	1.533851165006	0.348700098995

1 5 2.000

2 12 1.500

3 5 1.000 20 1.000

4 12 2.000

5 1 2.000 3 1.000 6 1.000 13 0.100

6 5 1.000 7 1.000 8 1.000 9 1.000

7 6 1.000

8 6 1.000

9 6 1.000 10 1.000 11 1.000 12 1.000

10 9 1.000

11 9 1.000

12 2 1.500 4 2.000 9 1.000

13 5 0.100 14 1.000 15 1.000 16 1.000

14 13 1.000

15 13 1.000

16 13 1.000 17 1.000 18 1.000 19 1.000

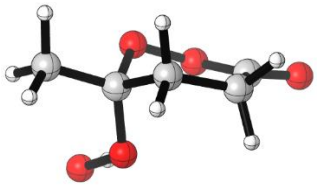
17 16 1.000

18 16 1.000

19 16 1.000

20 3 1.000

OOH Chair R = Me Reactant



Imaginary Frequencies = 0

E = -571.26030203

0,1

O	-2.944980160476	-0.603985142454	-0.029665914500
C	-1.838754461417	-0.140663350173	0.055570917600
O	0.263460892475	-0.261667738310	1.204557062523
O	-0.970721335981	-0.871610944654	0.825772869206
C	0.909246080617	0.407317029763	0.115918167394
C	0.037495979557	1.560185476003	-0.332673481370
H	-0.006832530149	2.259537403369	0.502655494026
H	0.496741432877	2.066367567821	-1.181368648655
C	-1.356479409414	1.060906085338	-0.697640916972
H	-2.112020222657	1.837130117004	-0.574880936413
H	-1.397014420896	0.743532208656	-1.743922981921
C	2.253345091974	0.816172967683	0.670185473713
H	2.818537229153	-0.053961917017	0.999247110709
H	2.801791219694	1.333179601480	-0.118398057430
H	2.111461196013	1.497250562910	1.509090230200
O	0.988778974161	-0.461988382231	-0.995553443473
O	1.737419271209	-1.617628777449	-0.664389111598
H	1.052904303261	-2.239241677741	-0.369173533040

1 2 2.000

2 1 2.000 4 1.000 9 1.000

3 5 1.000

4 2 1.000

5 3 1.000 6 1.000 12 1.000 16 1.000

6 5 1.000 7 1.000 8 1.000 9 1.000

7 6 1.000

8 6 1.000

9 2 1.000 6 1.000 10 1.000 11 1.000

10 9 1.000

11 9 1.000

12 5 1.000 13 1.000 14 1.000 15 1.000

13 12 1.000

14 12 1.000

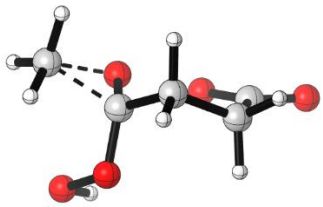
15 12 1.000

16 5 1.000 17 0.100

17 16 0.100 18 1.000

18 17 1.000

OOH Chair R = Me Transition State



Imaginary Frequencies = 1

E = -571.20213242

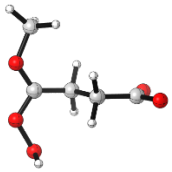
0,1

O	3.031594453210	-0.198859183776	-0.073621927812
C	1.794803882234	-0.182831231989	-0.021626552466
O	-0.803826564902	-1.077986462132	-0.252895236634
O	1.112482104876	-1.259033851556	0.134439461277
C	-1.089764224443	0.114537461933	0.095703303871
C	-0.346299597700	1.239658130322	-0.562510448474
H	-0.390469209263	1.083234264831	-1.639819741960
H	-0.806104064772	2.194057762502	-0.311025001108
C	1.101172913108	1.177585171085	-0.055449770242
H	1.715536761709	1.834916599046	-0.669432390651
H	1.144615882183	1.547756321114	0.973026803601

C	-2.570409582478	-0.322024311154	-0.719683351642
H	-2.985438341088	-1.279285103934	-0.426638854468
H	-3.102670186877	0.506982079128	-0.241489322846
H	-2.400521070852	-0.196764013242	-1.781042360755
O	-1.291280820544	0.386499055498	1.431303933103
O	-1.855541717421	-0.720977436155	2.097477440585
H	-1.077271636979	-1.238895611520	2.364536336619

1 2 2.000
2 1 2.000 4 2.000 9 1.000
3 5 1.500
4 2 2.000
5 3 1.500 6 1.000 12 0.100 16 1.000
6 5 1.000 7 1.000 8 1.000 9 1.000
7 6 1.000
8 6 1.000
9 2 1.000 6 1.000 10 1.000 11 1.000
10 9 1.000
11 9 1.000
12 5 0.100 13 1.000 14 1.000 15 1.000
13 12 1.000
14 12 1.000
15 12 1.000
16 5 1.000 17 1.000
17 16 1.000 18 1.000
18 17 1.000

<u>OOH R = Me Product</u>



# Imaginary Frequencies = 0
E = -571.31007525
0,1

O	-2.472310393594	0.275705482238	1.110195449284
O	2.007889162807	-1.712867880901	0.041448974422
C	2.128246508653	1.784706265052	-0.050903682478
H	3.002891412511	2.243272621713	-0.498084463957

H	1.230214302334	2.006936385031	-0.622596651582
H	2.029952314473	2.056579210801	0.997107838645
C	-2.227218175765	0.016586090173	-0.090338224010
O	2.401080130996	0.349582911633	-0.133194149455
O	-3.062454582052	-0.008581615739	-1.028885975048
C	1.540773003601	-0.505524425824	0.223536360936
C	0.180910198489	-0.223826386461	0.711388393244
H	-0.087146149609	-0.960573230997	1.465058397450
H	0.162194587388	0.771345127236	1.150429134305
C	-0.780674172391	-0.304988787127	-0.492464582618
H	-0.480124146954	0.398383692350	-1.272574240729
H	-0.762319824114	-1.306502283122	-0.927906477544
O	1.115826411694	-2.714880744109	0.464457197991
H	0.871263681534	-3.130412471945	-0.382328108858

1 7 2.000
2 10 2.000 17 1.000
3 4 1.000 5 1.000 6 1.000 8 1.000
4 3 1.000
5 3 1.000
6 3 1.000
7 1 2.000 9 2.000 14 1.000
8 3 1.000 10 2.000
9 7 2.000
10 2 2.000 8 2.000 11 1.000
11 10 1.000 12 1.000 13 1.000 14 1.000
12 11 1.000
13 11 1.000
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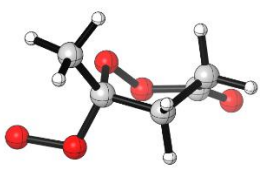
17 2 1.000 18 1.000
18 17 1.000

OOH Boat R = Me Reactant



Imaginary Frequencies = 0

E = -571.26502377

0,1

O	-0.175731436109	-0.368374164750	-1.005081500649
O	0.951256236478	-1.061286078643	-0.481750341459
O	-1.414436963696	-0.515370794831	0.957400625236
O	-2.457285523676	-1.261473673726	0.353053717386
H	-2.000148249481	-2.056467392969	0.037062055794
O	3.023376998443	-0.671354420623	0.124005288621
C	-0.842752809858	0.376511562470	0.022977440538
C	0.169866566490	1.195394856196	0.827188849897
H	0.314110092043	0.735061710053	1.806541229741
H	-0.210084825509	2.204507309727	0.975558672458
C	1.501065092392	1.224554729305	0.070271326698
H	1.375721440477	1.678658080614	-0.916444961680
H	2.272651719027	1.762989217590	0.615268292822
C	1.949333257001	-0.189058803896	-0.101849229233
C	-1.854346702305	1.205061953157	-0.736520488628
H	-2.436698745385	0.590964251754	-1.421398883898
H	-1.329003904469	1.978106905571	-1.298492390072
H	-2.519921241864	1.678798753001	-0.013872703572

1 7 1.000

2 14 1.000

3 4 0.100 7 1.000

4 3 0.100 5 1.000

5 4 1.000

6 14 2.000

7 1 1.000 3 1.000 8 1.000 15 1.000

8 7 1.000 9 1.000 10 1.000 11 1.000

9 8 1.000

10 8 1.000

11 8 1.000 12 1.000 13 1.000 14 1.000

12 11 1.000

13 11 1.000

14 2 1.000 6 2.000 11 1.000

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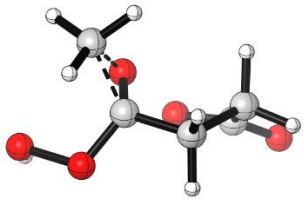
16 15 1.000

17 15 1.000

18 15 1.000

OOH Boat R = Me Transition State



Imaginary Frequencies = 1

E = -571.20115975

0,1

O	0.476282578169	-0.169479531082	0.996183311566
O	-1.107242070904	-1.224797452141	0.540327108276
O	1.592741075531	-0.427279677140	-0.981570501452
O	2.528681329220	-1.203050915033	-0.264517030777
H	2.053841074108	-2.036805708740	-0.109575140670
O	-3.147580700323	-0.730128783128	-0.144208386501
C	0.823774469169	0.329182447104	-0.127460694618
C	-0.182299280711	1.150628836650	-0.907146144160
H	-0.218552177381	0.733910037545	-1.915620690513
H	0.145276479195	2.186810393664	-0.979378055924
C	-1.537450311566	1.036995561008	-0.209278531142
H	-1.506147281735	1.560127106202	0.751131524053
H	-2.302530647413	1.505631473337	-0.825448610549
C	-1.976444041260	-0.397733070227	0.070313198142
C	1.791133350822	1.286526707885	0.972941430710
H	2.280324865570	0.753656696539	1.780393495817
H	1.152471767194	2.102950577757	1.286487350515
H	2.499818522316	1.532624299800	0.176253367225

1 7 1.667 15 0.333

2 14 1.500

3 4 0.067 7 1.167

4 3 0.067 5 1.000

5 4 1.000

6 14 2.000

7 1 1.667 3 1.167 8 1.000 15 0.333

8 7 1.000 9 1.000 10 1.000 11 1.000

9 8 1.000

10 8 1.000

11 8 1.000 12 1.000 13 1.000 14 1.000

12 11 1.000

13 11 1.000

14 2 1.500 6 2.000 11 1.000

15 1 0.333 7 0.333 16 1.000 17 1.000 18 1.000

16 15 1.000

17 15 1.000

18 15 1.000

OOH Chair R = Et Reactant

Imaginary Frequencies = 0

E = -610.55954301

0,1

O	-2.954812979918	-0.519528106401	-0.023971466779
C	-1.834953883721	-0.091040177504	0.065839930009
O	0.265850497320	-0.290789801308	1.194650944695
O	-0.986714510458	-0.862193926608	0.818233424699
C	0.930834809112	0.347179875176	0.104437740853
C	0.105476358506	1.540619482604	-0.335252503173
H	0.118207068189	2.251835689301	0.490767412088
H	0.568211265740	2.013398346743	-1.201349295286
C	-1.321949150903	1.113393448957	-0.662072480569
H	-2.036942501829	1.917078925152	-0.483536911559
H	-1.416728508121	0.836711018028	-1.716033673955
C	2.293345743822	0.750494593683	0.651050617849
H	2.756007399670	1.355682192876	-0.133019070033
H	2.095675761510	1.420839807895	1.491286160157
O	0.948363221255	-0.510620988491	-1.023531701437
O	1.457070637541	-1.791110433107	-0.691473645046
H	0.647337702557	-2.305743929299	-0.543514795567
C	3.236834455522	-0.366646301211	1.087915230401
H	4.099983884225	0.079230625389	1.585662528095

H	2.757019297206	-1.048636784958	1.791533544347
H	3.598786192775	-0.944878176916	0.239008190212

1 2 2.000
2 1 2.000 4 1.000 9 1.000
3 5 1.000
4 2 1.000
5 3 1.000 6 1.000 12 1.000 15 1.000
6 5 1.000 7 1.000 8 1.000 9 1.000
7 6 1.000
8 6 1.000
9 2 1.000 6 1.000 10 1.000 11 1.000
10 9 1.000
11 9 1.000
12 5 1.000 13 1.000 14 1.000 18 1.000
13 12 1.000
14 12 1.000
15 5 1.000 16 0.100
16 15 0.100 17 1.000
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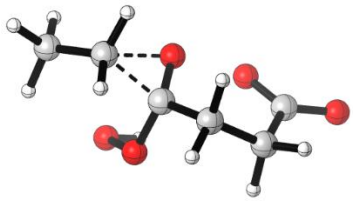
19 18 1.000
20 18 1.000
21 18 1.000

OOH Chair R = Et Transition State



# Imaginary Frequencies = 1
E = -610.50993129
0,1

O	3.475962704369	-0.533080395929	-0.253444694945
C	2.258673404847	-0.328204253690	-0.173173104894
O	-0.400590767792	-0.564828761870	-0.769050743622
O	1.406067662451	-1.241010855117	-0.476761803608
C	-0.548300706275	0.383543216976	0.051001930861

C	0.417149501799	1.537381135116	-0.024357406200
H	0.423635132050	1.893591325520	-1.054745767788
H	0.093501376671	2.340920099928	0.636326174324
C	1.792189582771	1.008952873933	0.394519312812
H	2.550721218806	1.745986348884	0.133135525459
H	1.815816051672	0.878103418894	1.480668754733
C	-2.066988908242	0.792625207331	-0.829052229664
H	-2.106318310841	1.760907811761	-0.322743390616
H	-1.795061252277	0.893536263511	-1.873769433086
O	-0.830440499547	0.089958533893	1.380165163252
O	-1.341002165846	-1.215835816710	1.530130492770
H	-0.537683011532	-1.763336773822	1.555665365992
C	-3.210860791774	-0.111776766535	-0.518727007711
H	-3.097537197539	-1.099471382776	-0.961884927893
H	-3.392492336828	-0.191489412218	0.551582638632
H	-4.088318796944	0.366547782920	-0.971112708806

1 2 2.000

2 1 2.000 4 2.000 9 1.000

3 5 2.000

4 2 2.000

5 3 2.000 6 1.000 12 0.100 15 1.000

6 5 1.000 7 1.000 8 1.000 9 1.000

7 6 1.000

8 6 1.000

9 2 1.000 6 1.000 10 1.000 11 1.000

10 9 1.000

11 9 1.000

12 5 0.100 13 1.000 14 1.000 18 1.000

13 12 1.000

14 12 1.000

15 5 1.000 16 0.100

16 15 0.100 17 1.000

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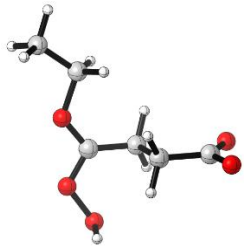
20 18 1.000

21 18 1.000

OOH R = Et Product



Imaginary Frequencies = 0

E = -610.61972403

0,1

O	-2.600245695776	0.289780819809	1.171904595340
O	1.983430673670	-1.244136118613	-0.189049327737
C	1.814772660447	2.274313423704	-0.068843288521
H	0.863677177735	2.410155767310	-0.581045022001
H	1.707870605993	2.432564603481	1.002757661444
C	-2.386324510635	0.097526781540	-0.047025877102
O	2.200279038405	0.852448577386	-0.246372450288
O	-3.257528309517	0.019139363945	-0.949375911896
C	1.428275861802	-0.089440418971	0.084388903978
C	0.070841193849	0.046621718903	0.639757959549
H	-0.096613205521	-0.749053589053	1.362528738072
H	-0.014417643098	1.012257035341	1.133043366718
C	-0.935826201640	-0.059977409440	-0.523798154883
H	-0.740435973741	0.713529946439	-1.270320966905
H	-0.845612368179	-1.026979215159	-1.023535822624
O	1.193066943581	-2.342525495722	0.195847739273
H	0.857735846585	-2.660878826860	-0.662717375215
C	2.924522061430	3.087077192392	-0.671367329188
H	2.674080398231	4.142301085283	-0.550004324308
H	3.868684608609	2.892227891910	-0.161971037277
H	3.030224777770	2.873467376374	-1.735270666428

1 6 2.000

2 9 1.500 16 0.100

3 4 1.000 5 1.000 7 1.000 18 1.000

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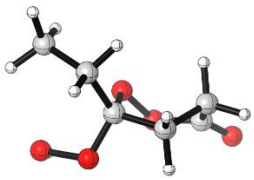
21 18 1.000

OOH Boat R = Et Reactant



Imaginary Frequencies = 0

E = -610.56398741

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O	1.011470630977	-1.215129956889	0.157897767790
O	-1.011711781627	-0.102608305692	1.751402339694
O	3.087533611838	-0.535475687914	-0.042209861901
C	-0.818159613370	0.241823580130	0.394067843399
C	0.214900214192	1.374652259150	0.440640665892
H	0.632553109914	1.446987449887	1.446310489905
H	-0.264624695589	2.321914929333	0.200544070996
C	1.332992596561	1.067707076187	-0.560088816622
H	0.932843297115	0.989140467476	-1.574771126924
H	2.118638310579	1.819216259921	-0.543925975433
C	1.932326055693	-0.244595429066	-0.176097905673
C	-2.074598839904	0.631158151347	-0.382276425213
H	-1.713028588841	1.161795113911	-1.267635700082

H	-2.588032400416	1.369238335901	0.239676592097
C	-3.032606809052	-0.474646293808	-0.823195954581
H	-3.774950271781	-0.042394467576	-1.496976613070
H	-2.511732245720	-1.263086831759	-1.368824667143
H	-3.558620493861	-0.924233011922	0.016175803903
O	-1.956999429467	-1.150257869635	1.877291408220
H	-1.404178175559	-1.946488498341	1.836299231572

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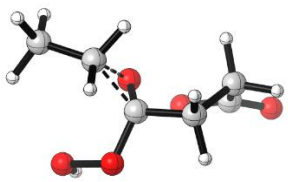
21 20 1.000

OOH Boat R = Et Transition State



Imaginary Frequencies = 1

E = -610.50779387

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O	-0.377342535359	-0.249657831043	-1.007373701423
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O	-1.529429053367	-0.520508006268	0.947321783569
O	3.190066025037	-0.624190181912	0.309983663760
C	-0.798326217717	0.262749656898	0.071596540271
C	0.126445459022	1.179268591208	0.856736917515
H	0.131243382564	0.828069375340	1.889802460919
H	-0.242707125961	2.203902506758	0.846959709308
C	1.519602613560	1.088080146986	0.232917259581
H	1.519980109920	1.577449018363	-0.745570967235
H	2.237650809319	1.601448943595	0.869935704026
C	2.025332191088	-0.334610780521	0.020758964225
C	-1.863407903703	1.246048778963	-1.013421744068
H	-1.165263879160	1.994928576398	-1.374144150364
H	-2.425874449362	1.577321661270	-0.136079197142
C	-2.706607216367	0.587776653007	-2.059310683442
H	-3.397390560002	1.362309732245	-2.411343191824
H	-2.118311688394	0.243107807993	-2.907399950110
H	-3.300033580086	-0.228573758037	-1.653126981655
O	-2.269916253248	-1.509060226027	0.266185202766
H	-1.643321157475	-2.249473196422	0.205941820275

1 5 1.667 13 0.333

2 12 1.500

3 5 1.167 20 0.067

4 12 2.000

5 1 1.667 3 1.167 6 1.000 13 0.333

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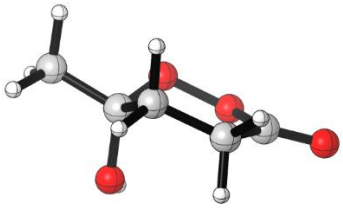
Anomeric Loss

OH Chair R = Me with HOCO dihedral from Transition State



Imaginary Frequencies = 1

E = -496.13300172

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O	2.856061919338	-0.232852626779	-0.006401271131
C	1.670773799071	-0.046579289290	-0.094900348501
O	-0.457518444368	-1.080833658509	-0.543872764946
O	0.915727492877	-1.190218775682	-0.149376779867
C	-1.132793921296	0.031401650958	0.058340595291
C	-0.468125060876	1.310325377102	-0.398690340457
H	-0.589901059854	1.380548670070	-1.480282959473
H	-0.966154232427	2.164352909241	0.060897730407
C	1.005219455925	1.291647056444	-0.016346368470
H	1.597864756319	1.980388273623	-0.618089453917
H	1.137730190456	1.585835734822	1.029674770362
C	-2.555825538233	-0.129264668612	-0.435971574550
H	-2.964506614890	-1.078056044571	-0.085277332162
H	-3.148619260275	0.689379756255	-0.025661054519
H	-2.596010825210	-0.088349322325	-1.524663946349
O	-1.054268148414	-0.061634040522	1.461397325405
H	-0.920347808143	-0.986532222226	1.707421662877

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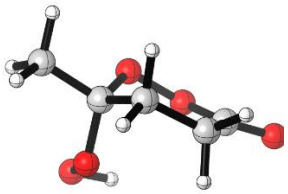
17 16 1.000

OOH Chair R = Me with OOCO Dihedral from Transition State



Imaginary Frequencies = 0

E = -571.25528849

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O	0.297929986619	-0.288076498008	1.174104538494
O	-0.980264823197	-0.841835975066	0.834783440053
C	0.907379381998	0.405278400717	0.101091663796
C	0.055723138584	1.574701544502	-0.328315195266
H	0.044507405599	2.280309997321	0.503501684394
H	0.512248190870	2.066075662829	-1.187629257893
C	-1.352899801734	1.106029667279	-0.669052856780
H	-2.086495742968	1.905202467501	-0.564999049149
H	-1.406358716759	0.757256183713	-1.705144666563
C	2.266795579960	0.776753419340	0.653354074705
H	2.830468187233	-0.127797636204	0.885136438388
H	2.797215675210	1.350527877394	-0.107331443924
H	2.161183115088	1.384405137709	1.552074029018
O	1.039453502713	-0.444280254150	-1.048786712496
O	1.247325287315	-1.792871257772	-0.676396958356

H	0.343987120154	-2.138956180760	-0.596921210480

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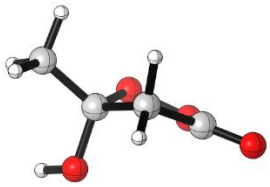
18 17 1.000

5 membered OH with R = Me Reactant



# Imaginary Frequencies = 0
E = -456.83446088
0,1

O	3.339010103435	0.586765794727	-0.046641801006
C	2.190801682952	0.256386662104	-0.110172951577
O	0.457961428885	-1.140606267732	-0.526376419719
O	1.878322890510	-1.041033591933	-0.425690691429
C	-0.078373763585	-0.098476274990	0.326032880600
C	0.922650136275	1.020190081000	0.115942514460
H	0.697112513734	1.583538128710	-0.792501996110
H	1.015248064399	1.694189966617	0.963947430356

O	0.011346814918	-0.495443231050	1.664812936879
H	-0.640616552077	-1.190352496430	1.829181297169
C	-1.494438680729	0.130534398453	-0.136578339422
H	-1.509823307001	0.426559468800	-1.184700619331
H	-2.075964929240	-0.784546644236	-0.004589912359
H	-1.934112912474	0.921705545960	0.471409011490

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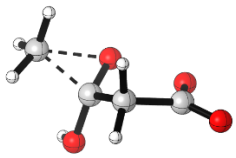
14 11 1.000

5 membered OH with R = Me Transition State



# Imaginary Frequencies = 1
E = -456.76995696
0,1

O	-2.653021419835	-0.465855661515	-0.110084994844
C	-1.512170566457	-0.000533421132	-0.091265860103
O	0.733612186150	1.077887735896	-0.185862818273
O	-1.197910498688	1.201458551920	0.192750872466
C	0.825262351983	-0.171615659604	0.123032685088
C	-0.314893518814	-0.930444620652	-0.461050963763
H	-0.264453569468	-0.956778742206	-1.550458234264
H	-0.443290832071	-1.929385163286	-0.053370895042
C	2.260889527598	-0.099042963992	-0.844083446520

H	2.971808319574	0.593233051162	-0.406919921884
H	2.519321914805	-1.140085273495	-0.633899840154
H	2.010731730836	0.085030170437	-1.880745335374
O	1.118189710165	-0.518312981553	1.403174868589
H	1.645694664222	0.178826978019	1.824130884078

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7 6 1.000
8 6 1.000
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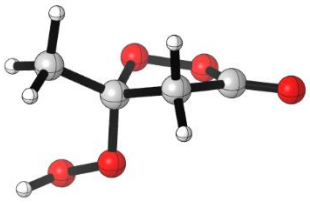
14 13 1.000

<u>5 membered OOH R = Me Reactant</u>



# Imaginary Frequencies = 0
E = -531.95720941
0,1

O	3.343956062744	0.634949598559	-0.177839599535
C	2.204051769166	0.276258393512	-0.174751305013
O	0.482715522206	-1.159003138164	-0.515170086878
O	1.903759951323	-1.027368645257	-0.481295994900
C	-0.040385739871	-0.132908544304	0.336359469701
C	0.934730169250	1.009565518285	0.135285045816
H	0.654666654980	1.609640073600	-0.733155414867
H	1.056107748760	1.648726223072	1.007278216040
O	0.139143516845	-0.506426741378	1.689817928060

C	-1.478549072448	0.078185805147	-0.055983746110
H	-1.523903896607	0.462865280141	-1.073761397633
H	-2.032197107013	-0.858369633935	0.002743240319
H	-1.921398609297	0.804782112231	0.626560809801
O	-0.614011541717	-1.672107127945	1.970393691088
H	-1.409313948322	-1.317650343565	2.398026984109

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13 10 1.000
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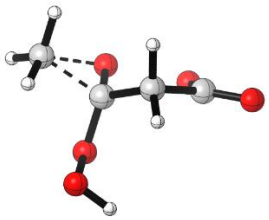
15 14 1.000

5 membered OOH R = Me Transition State



# Imaginary Frequencies = 1
E = -531.88642463
0,1

O	2.718382930799	-0.658337148112	0.408162463922
C	1.700469800683	-0.047912052906	0.074664589140
O	-0.303124419000	1.351474176189	-0.536705229391
O	1.572177983693	0.734949216055	-0.914512973636
C	-0.635231945249	0.263950347061	0.037633486523
C	0.421080383064	-0.223167232926	0.964587948565
H	0.538682050112	0.451048174080	1.814203551930

H	0.305759551395	-1.248935737960	1.301136676583
C	-1.899855264047	1.214581282787	0.729647115650
H	-2.493340510696	1.683119132565	-0.047031241050
H	-2.396942930342	0.335683295506	1.154810068179
H	-1.469440035879	1.881242762002	1.465394960365
O	-1.205558816160	-0.647542556461	-0.846979833840
O	-1.668489638037	-1.773046862219	-0.131008041349
H	-0.999484140338	-2.448062795664	-0.333821541591

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15 14 1.000

X-ray studies

Table S1. Crystallographic data for **2m**

datablock	**2m**
Brutto formula	$C_5H_8O_5$
Formula weight	148.11
Diffractometer	Bruker APEX-II CCD
Scan mode	ϕ and ω scans
Anode [Wavelength, Å]	MoKα [0.71073]
Crystal Dimensions, mm	0.05 × 0.2 × 0.4
Crystal color	colourless
Crystal system	monoclinic
a, Å	9.8512(13)
b, Å	5.7699(8)
c, Å	11.7734(16)
β, °	102.850(3)
Volume, Å³	652.45(15)
Density, gcm⁻³	1.508
Temperature, K	120
T_{min}/T_{max}	0.6102/0.7463
μ, mm⁻¹	0.138
Space group	$P2_1/c$
Z	4
F(000)	312
Reflections collected	9425
Independent reflections	2274
Reflections (I>2σ(I))	1852
Parameters	94
R_{int}	0.0357
$2\theta_{min}$ - $2\theta_{max}$, °	4.240 - 64.108
wR_2 (all reflections)	0.0970
R_1(I>σ(I))	0.0366
GOF	1.044
ρ_{min}/ρ_{max}, eÅ⁻³	-0.253/0.414
Restraints	0

Single crystal X-ray studies of **2m** were carried out in Center for molecule composition studies of INEOS RAS.

The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, X - cental atom of XH_2 group; $U_{eq}(H) = 1.5U_{eq}(Y)$, Y - central atom of YH_3 group. All structures were solved with the ShelXT[18] program and refined with the ShelXL[19] program. Molecular graphics was drawn using OLEX2[20] program.

CCDC 1980721 contains the supplementary crystallographic data for **2m**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

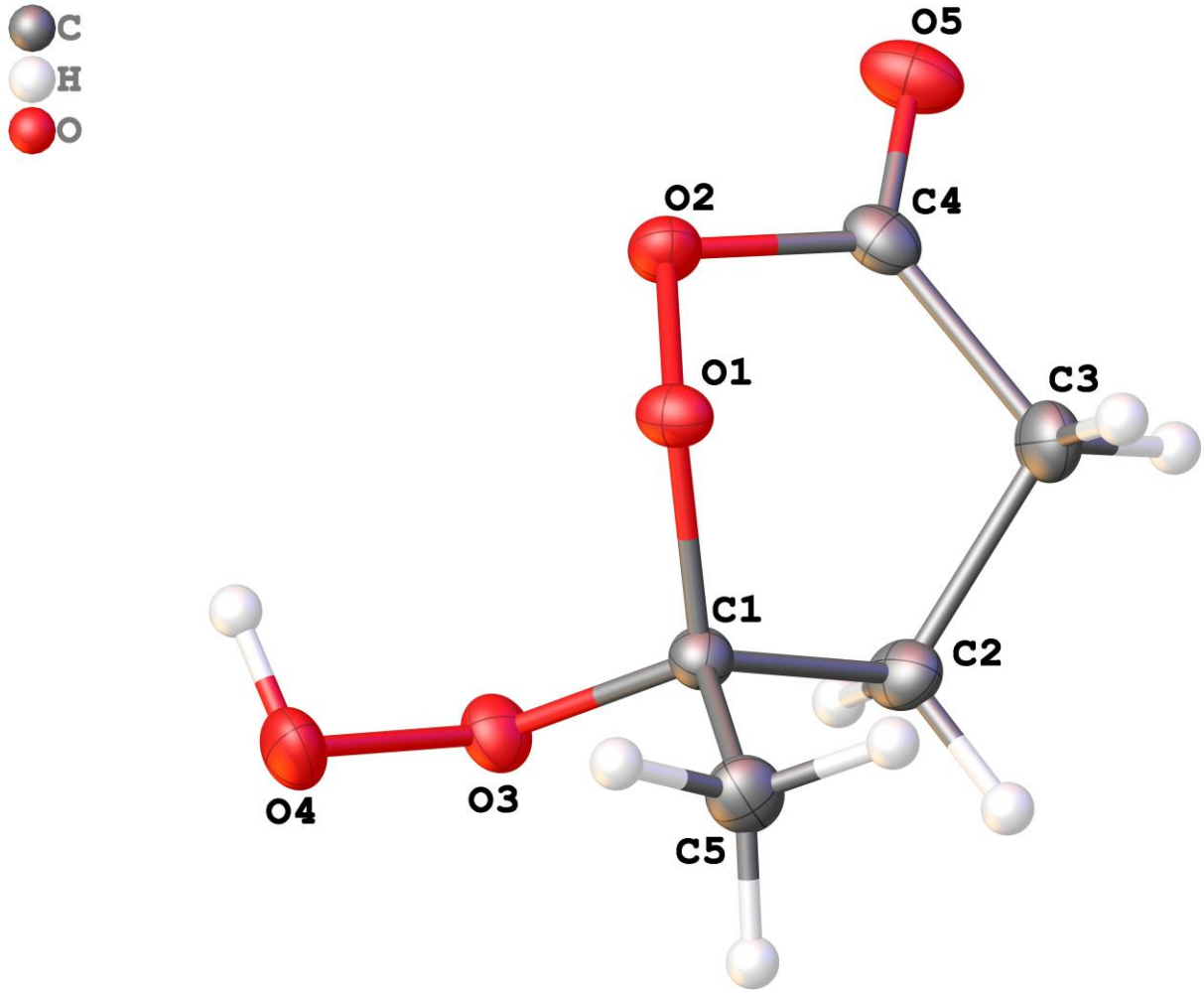

Figure S1. Molecular structure of **2m** presented in thermal ellipsoids.

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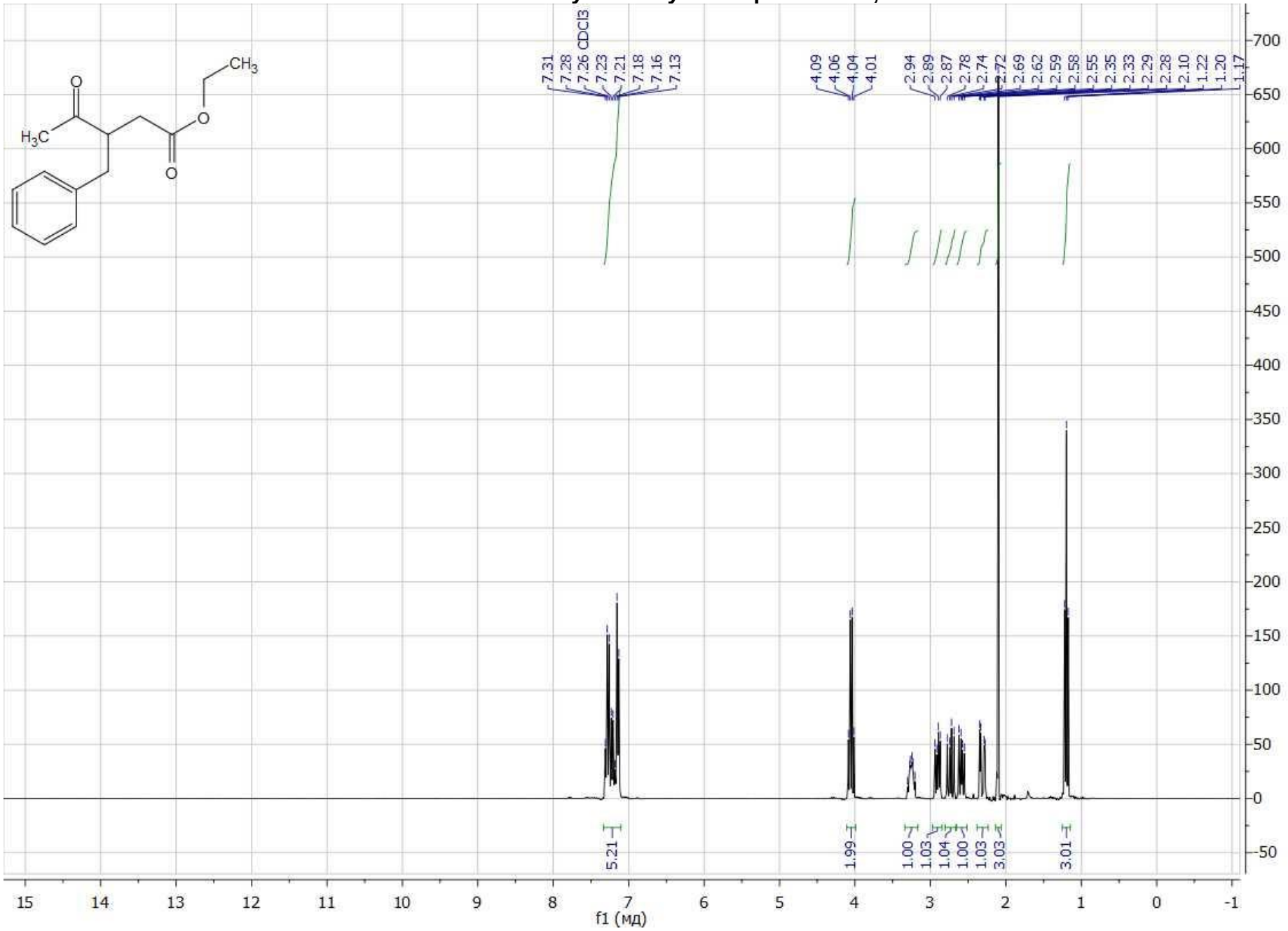
NMR of starting γ-ketoesters 1

^{1}H NMR of ethyl 3-benzyl-4-oxopentanoate, 1a



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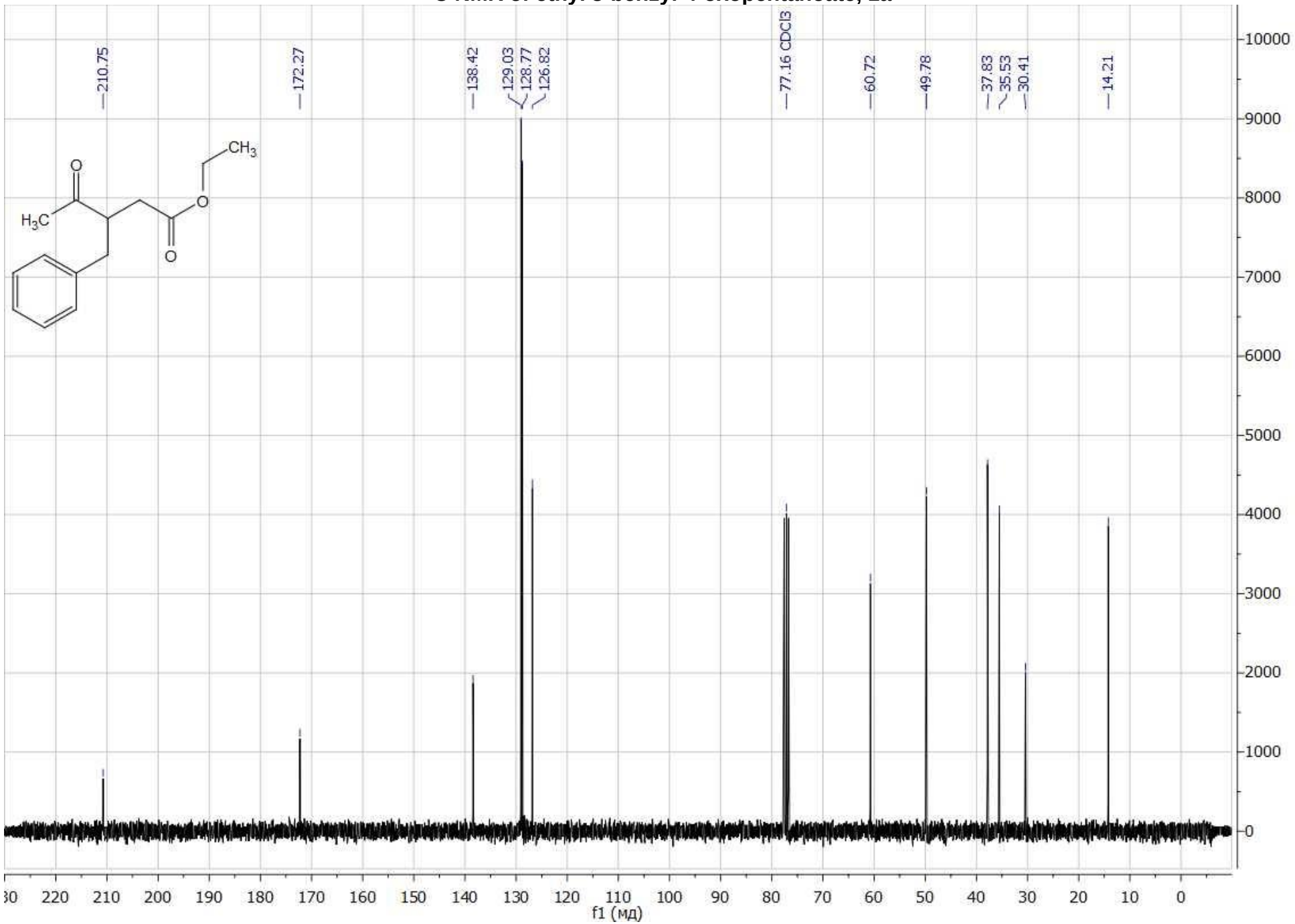

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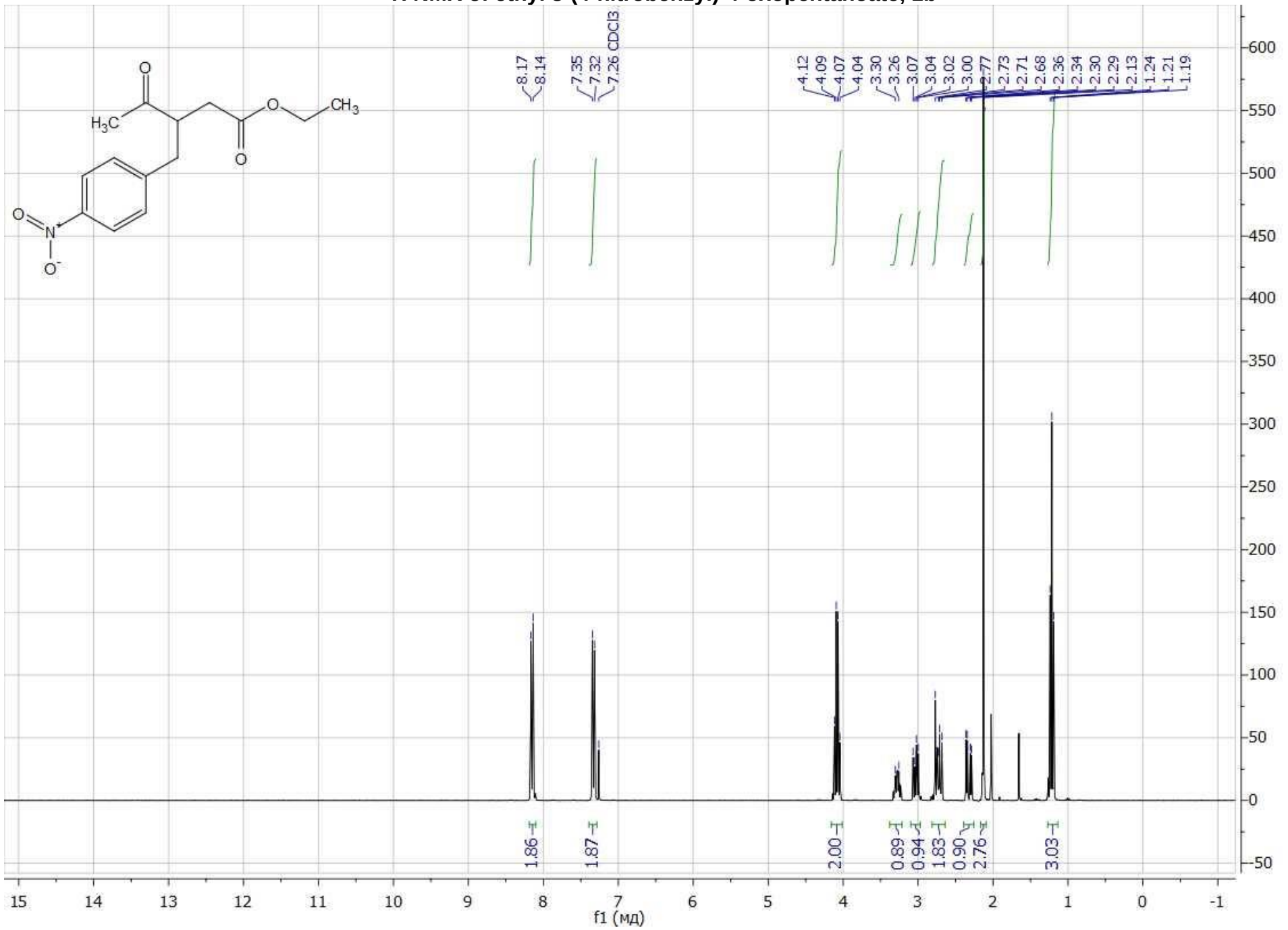

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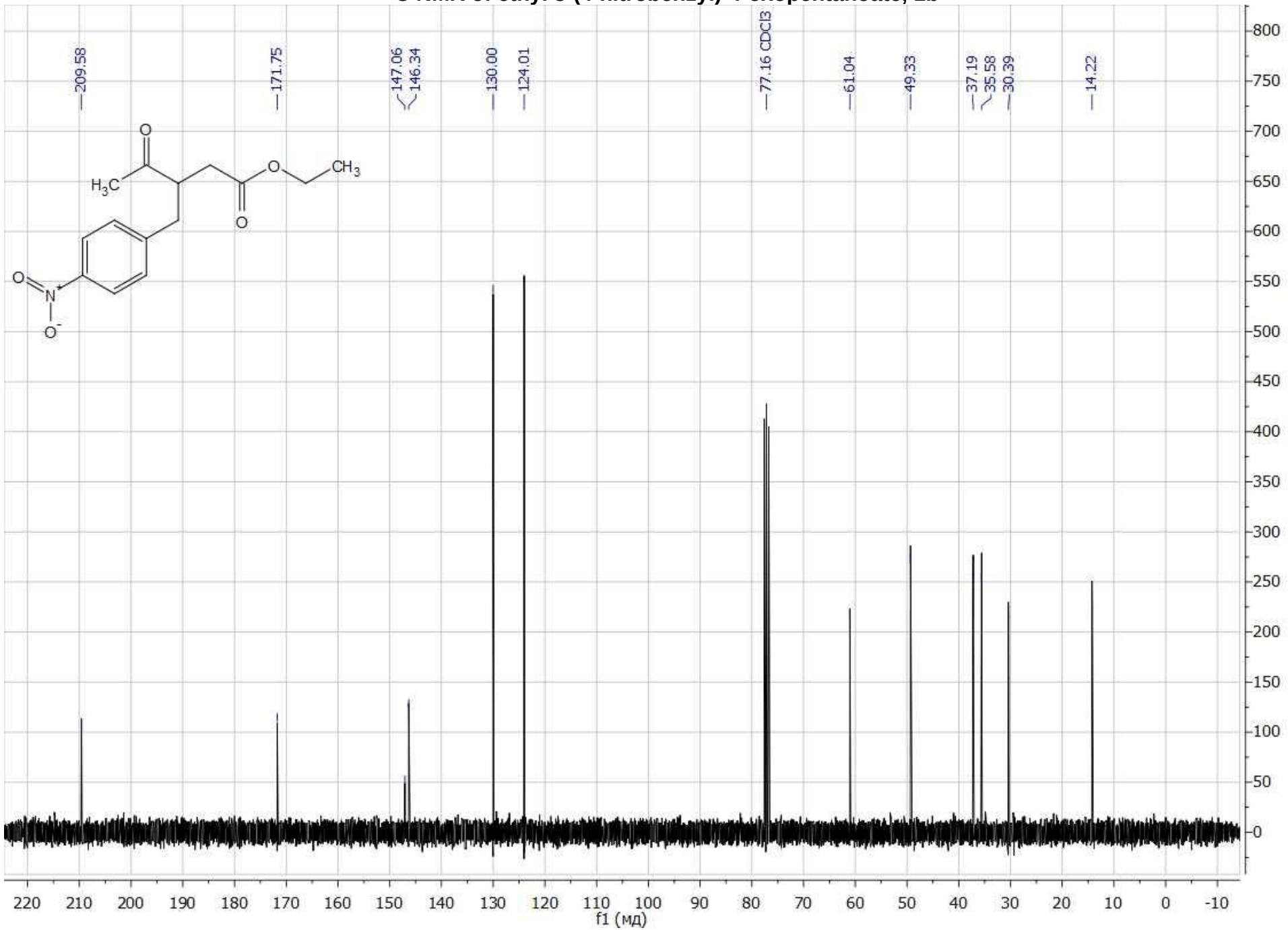

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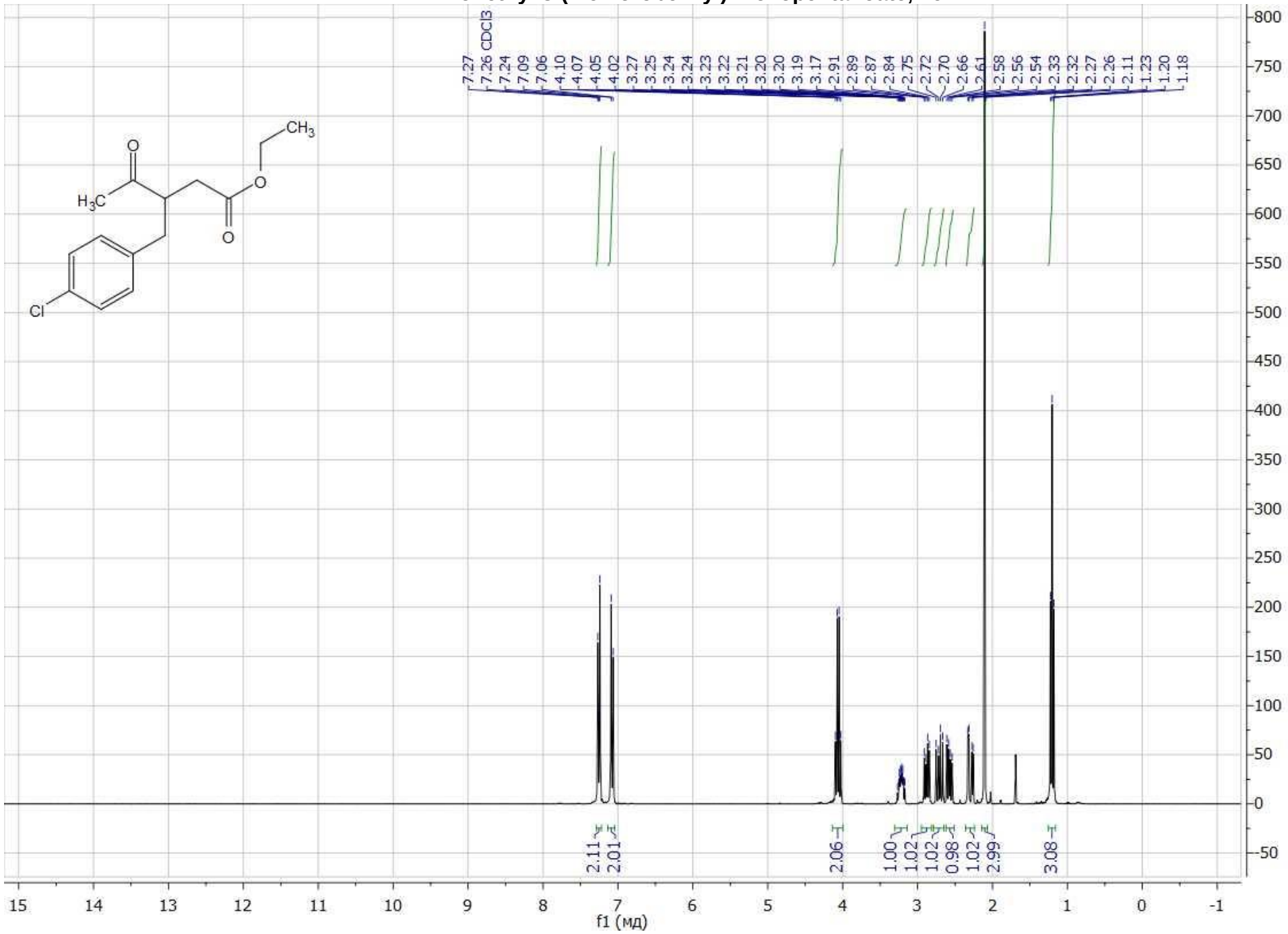

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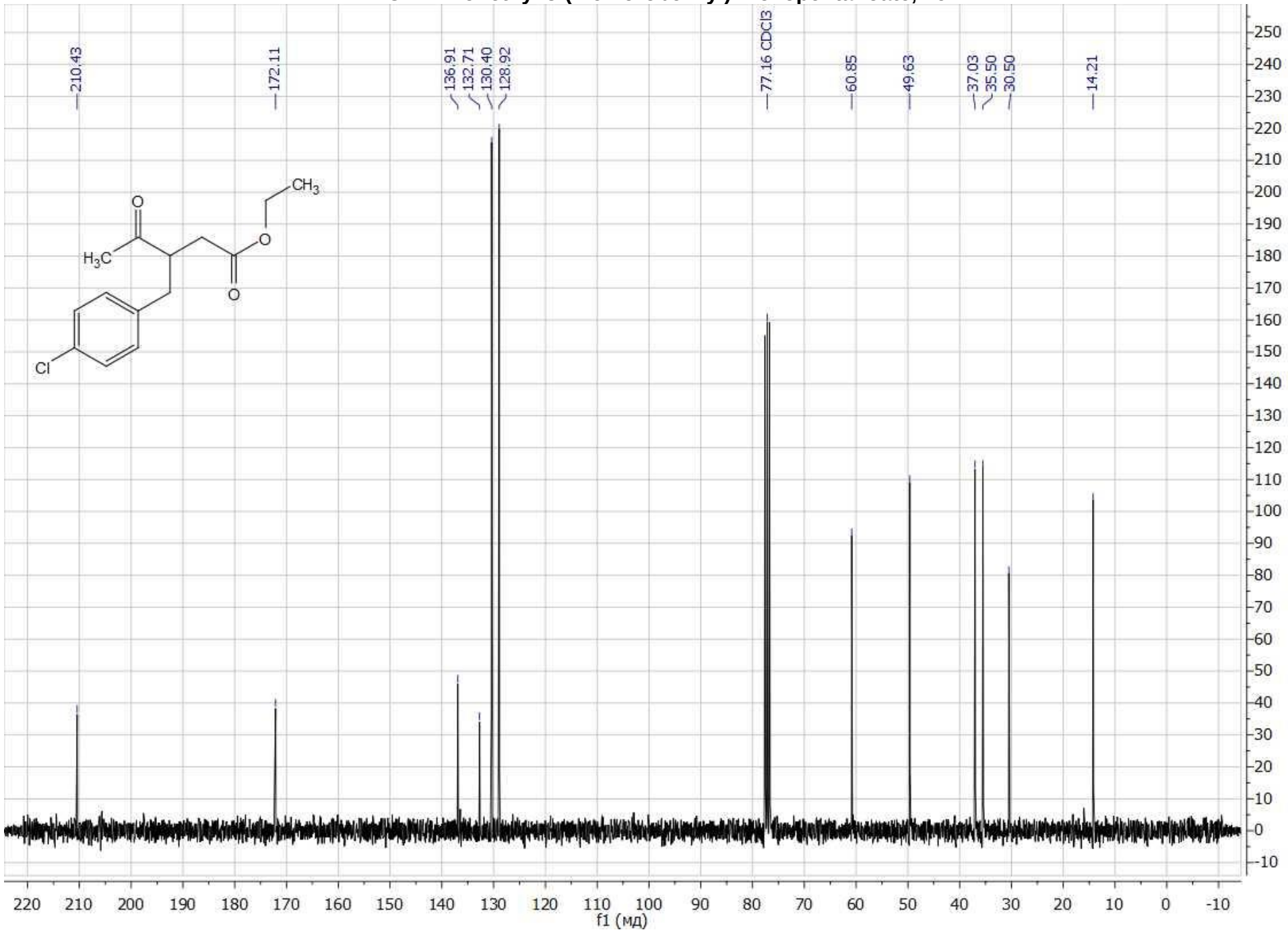
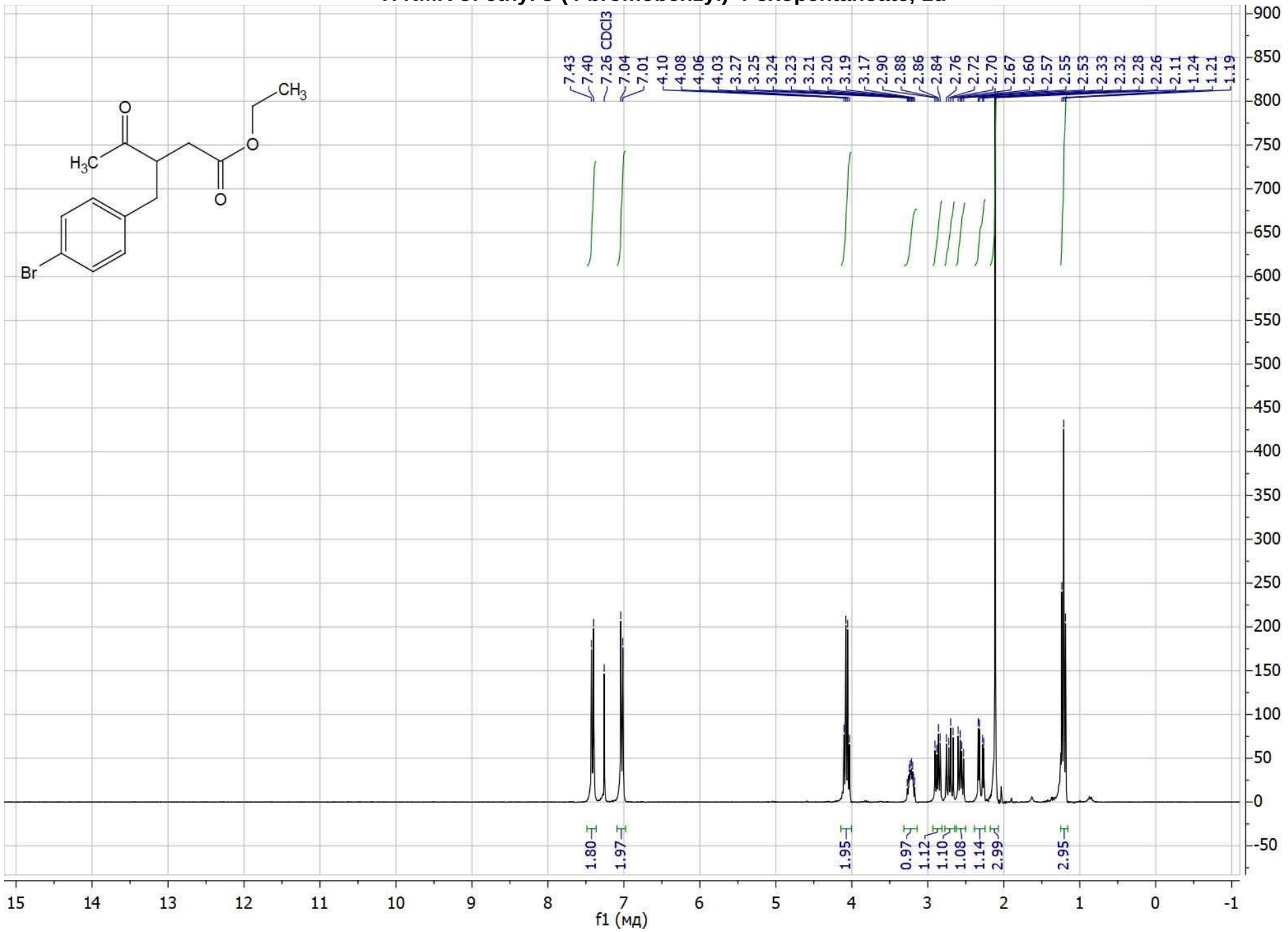


^{1}H NMR of ethyl 3-(4-bromobenzyl)-4-oxopentanoate, 1d



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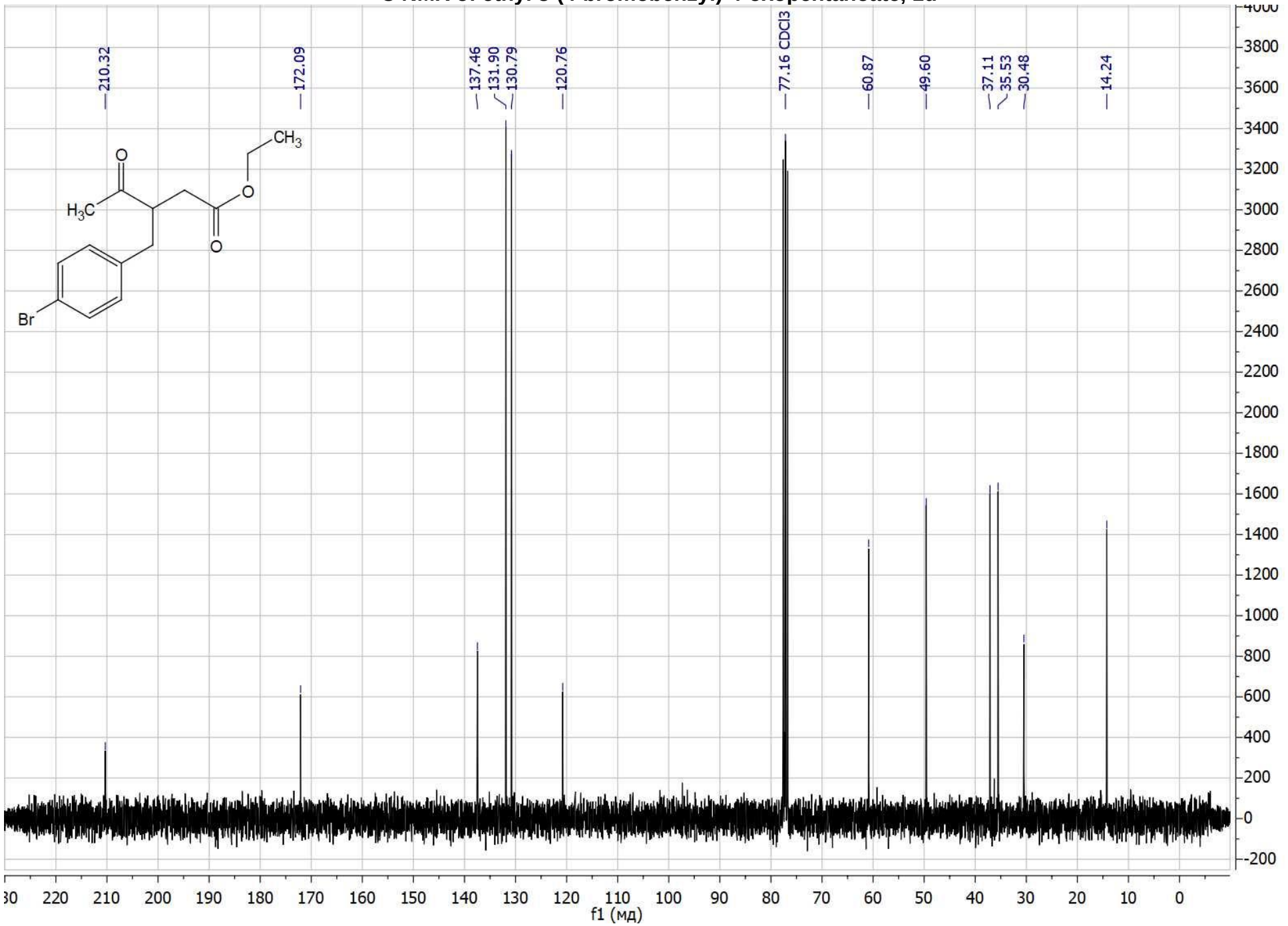
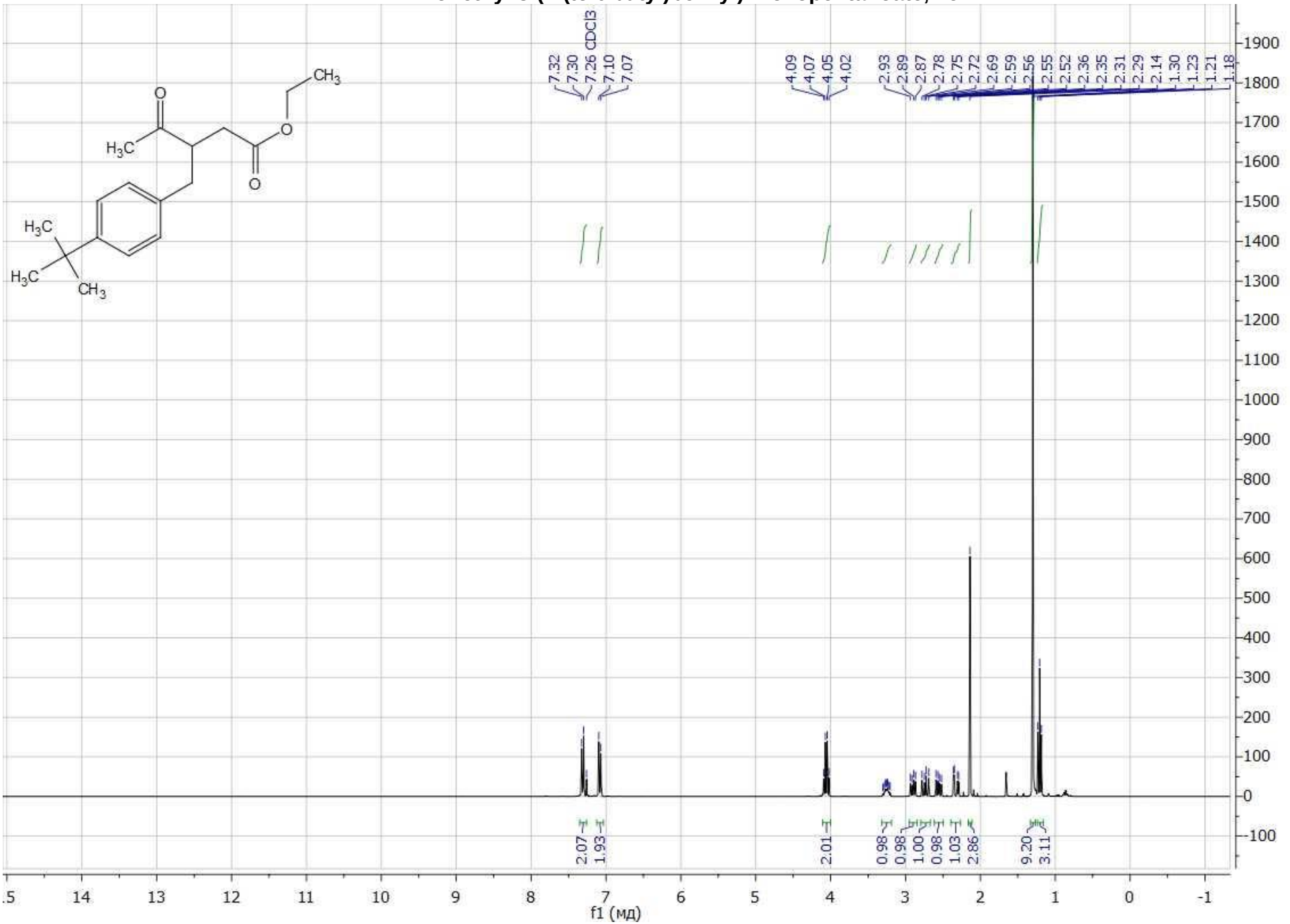


^{1}H NMR of ethyl 3-(4-(*tert*-butyl)benzyl)-4-oxopentanoate, 1e



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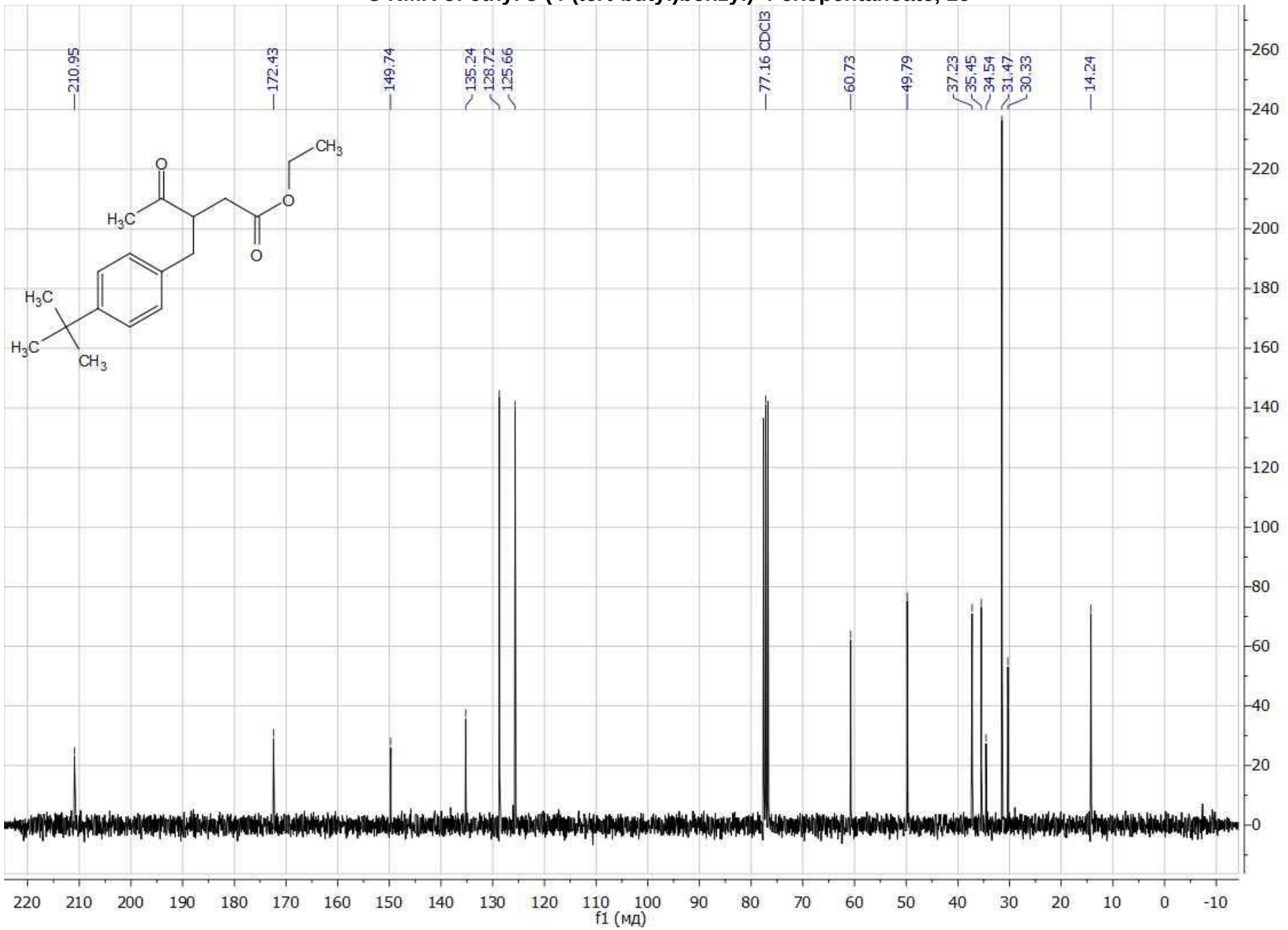

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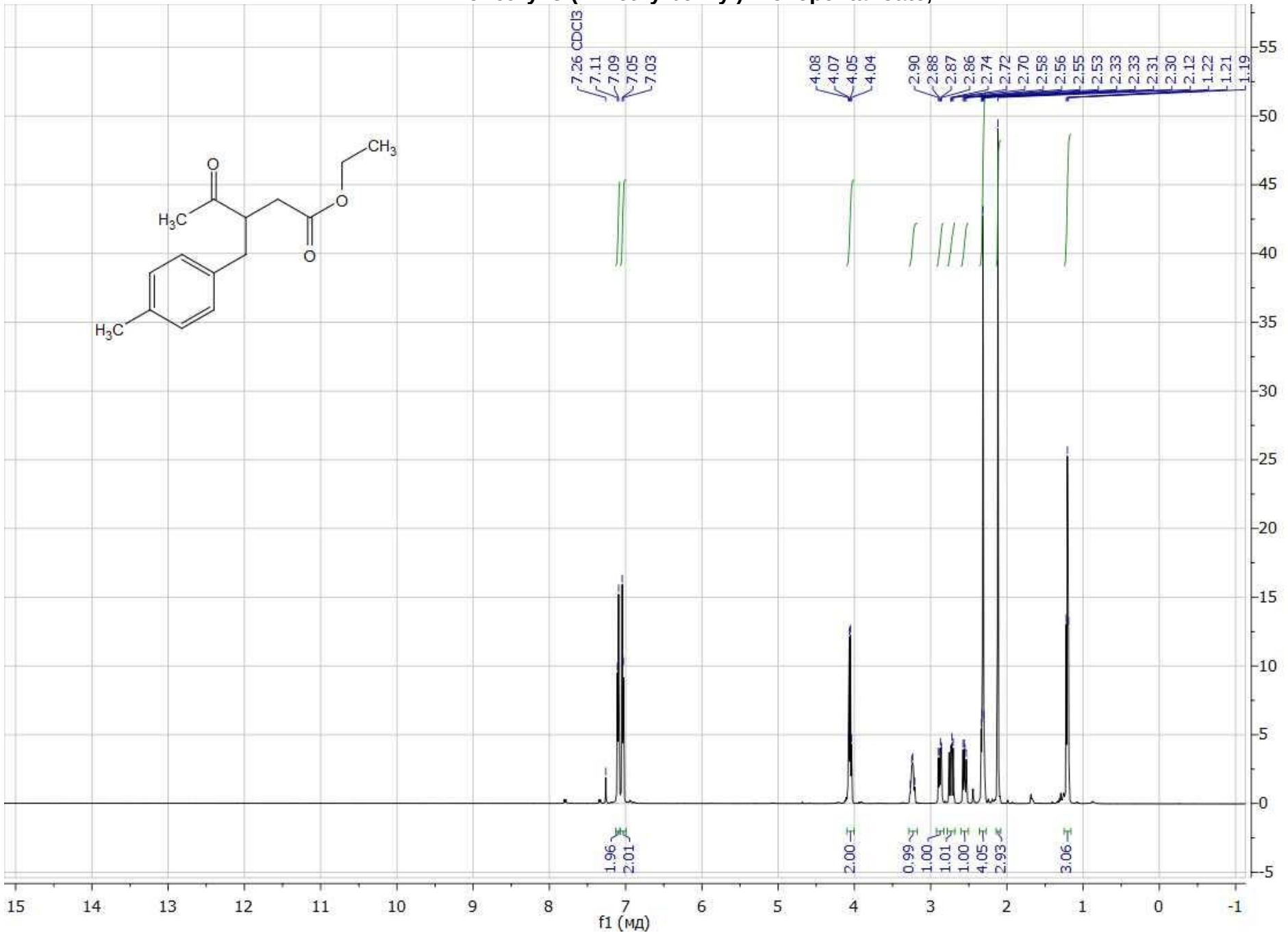

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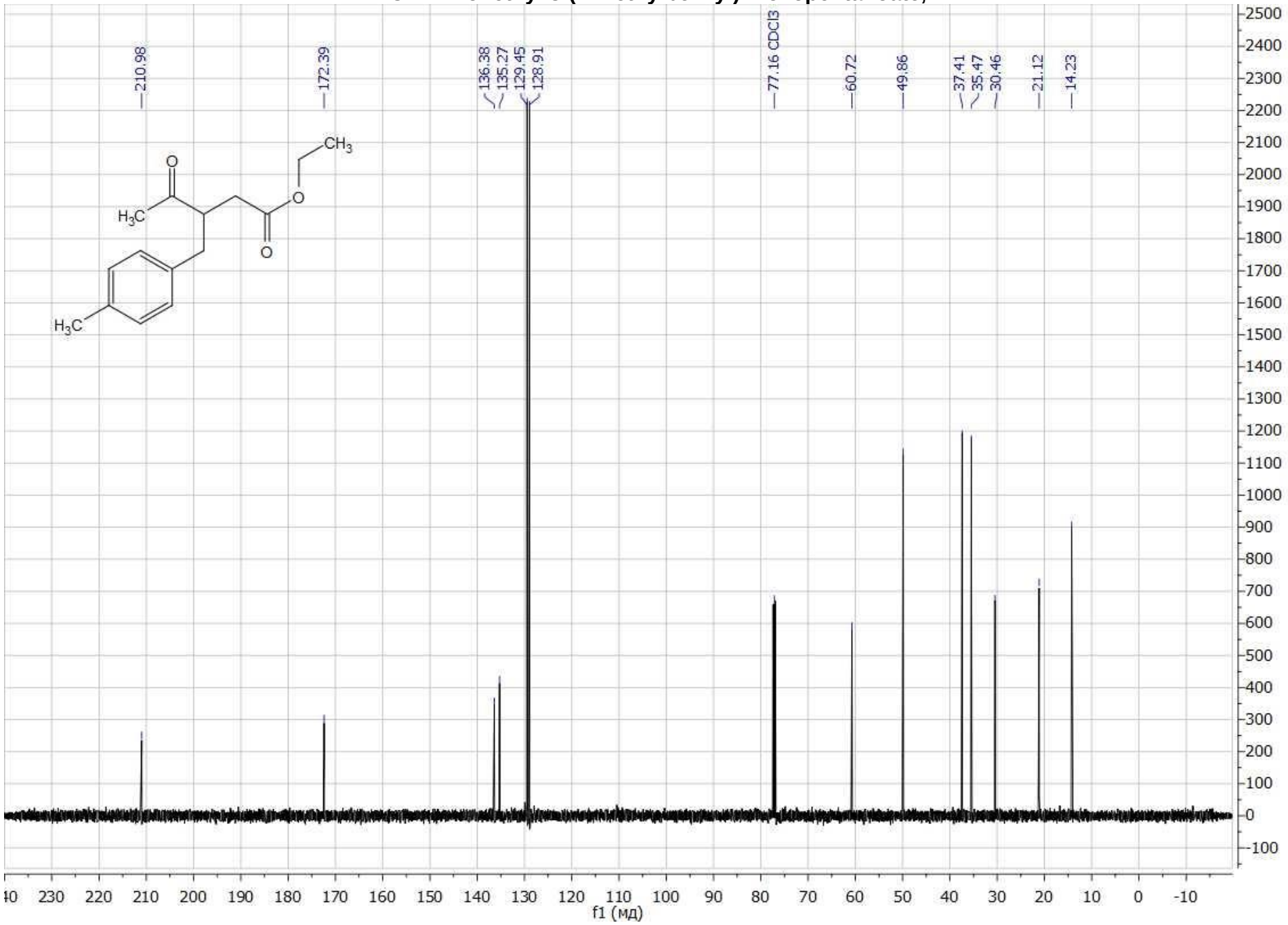

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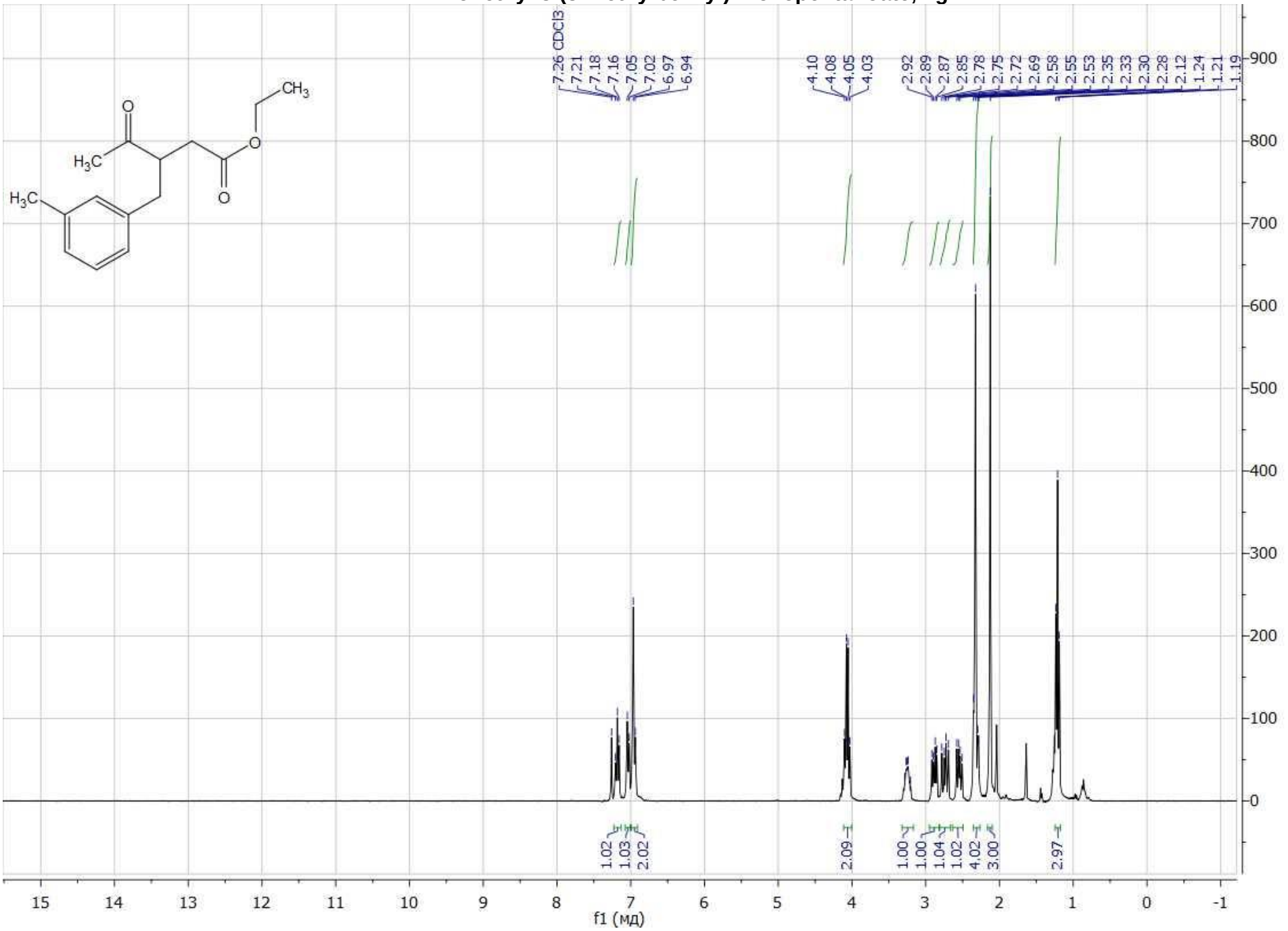

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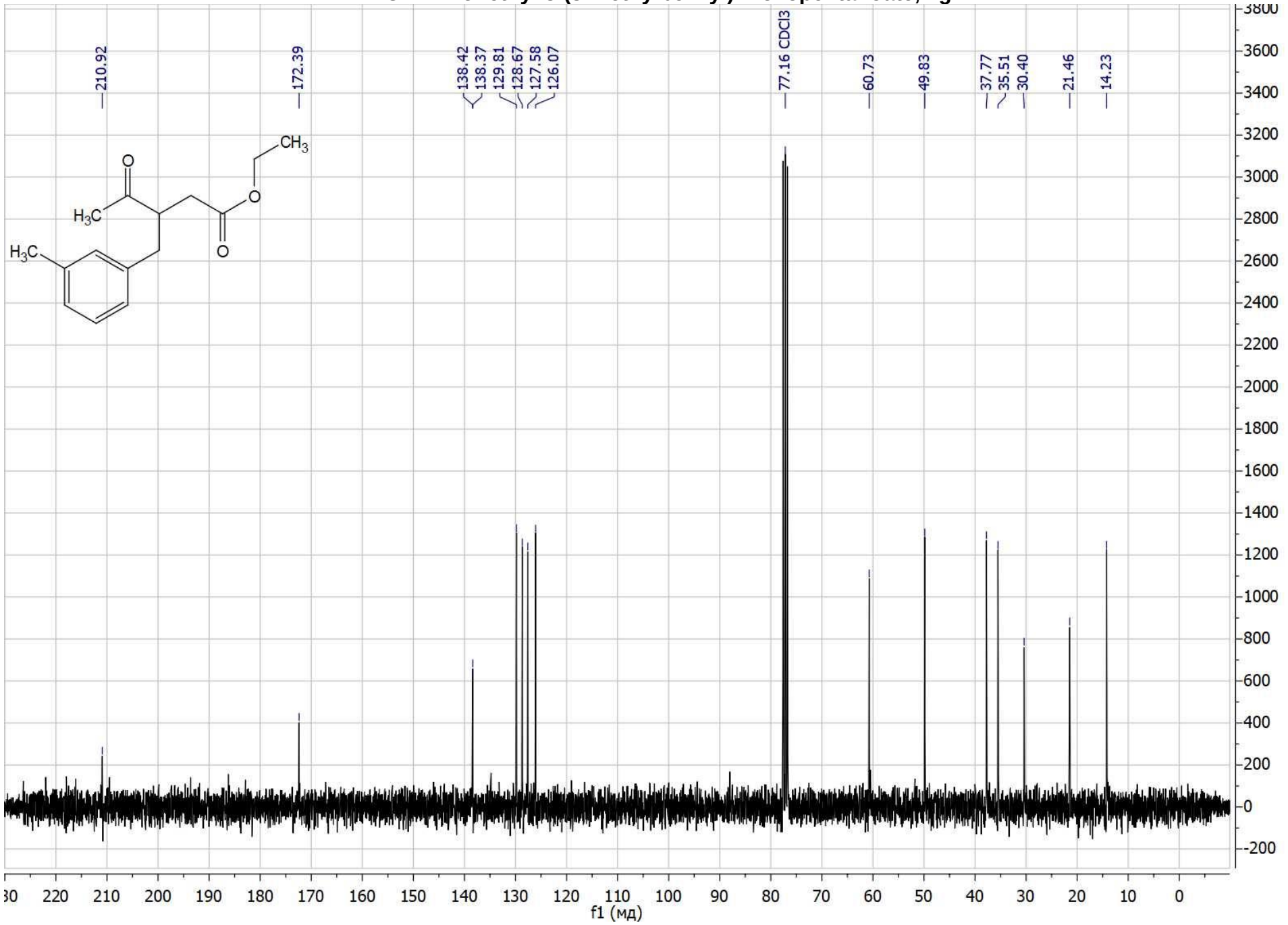

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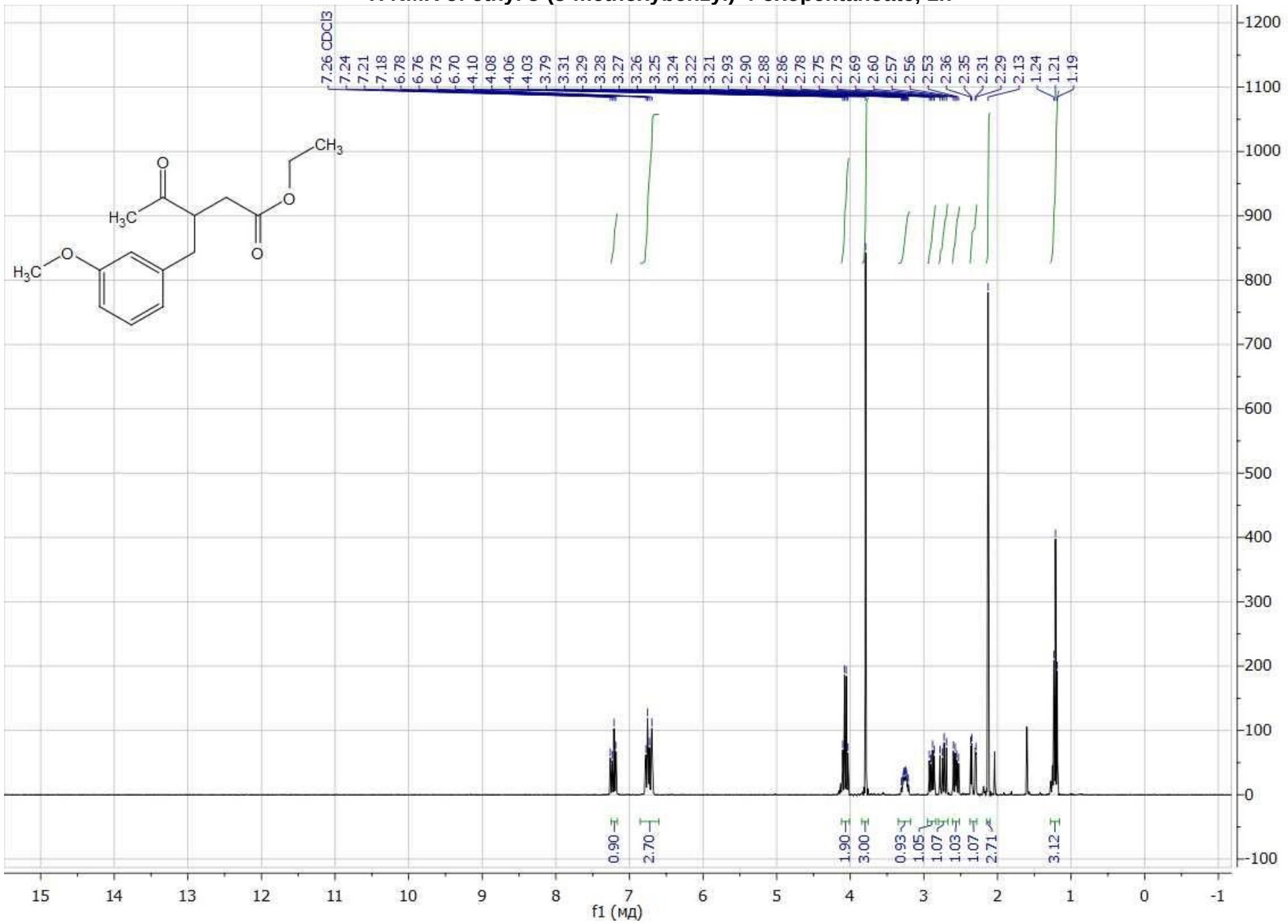

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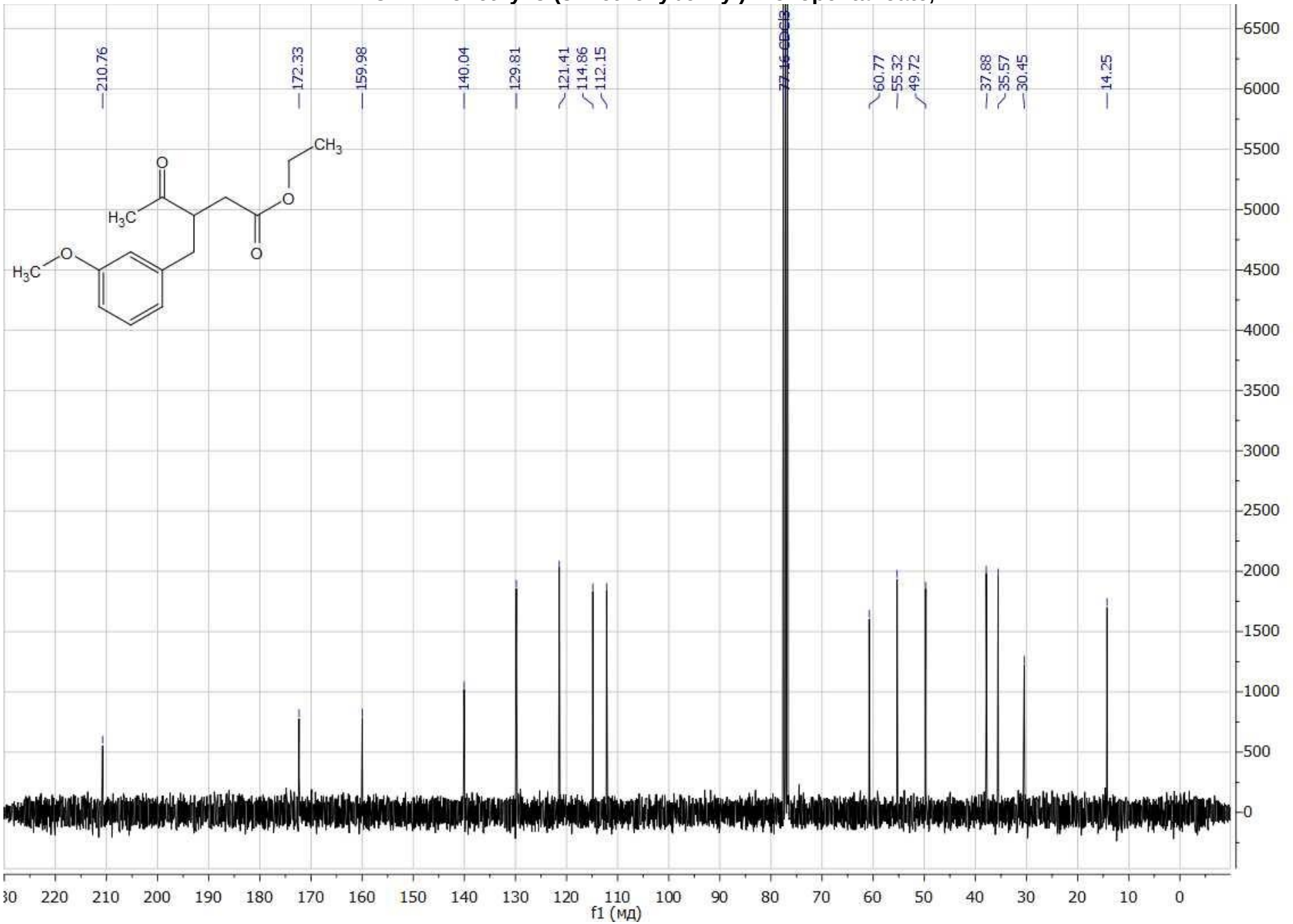
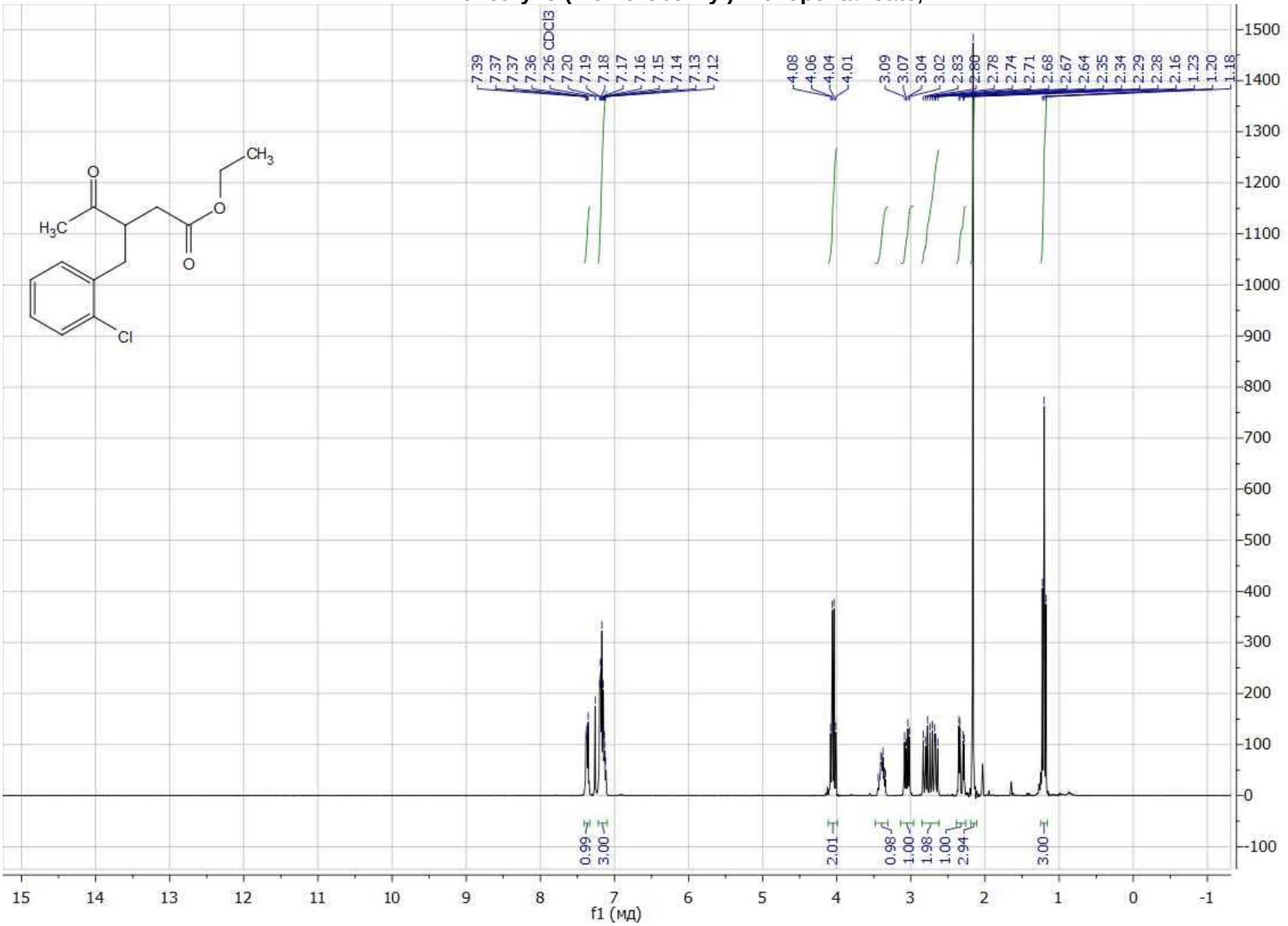


^{1}H NMR of ethyl 3-(2-chlorobenzyl)-4-oxopentanoate, 1i



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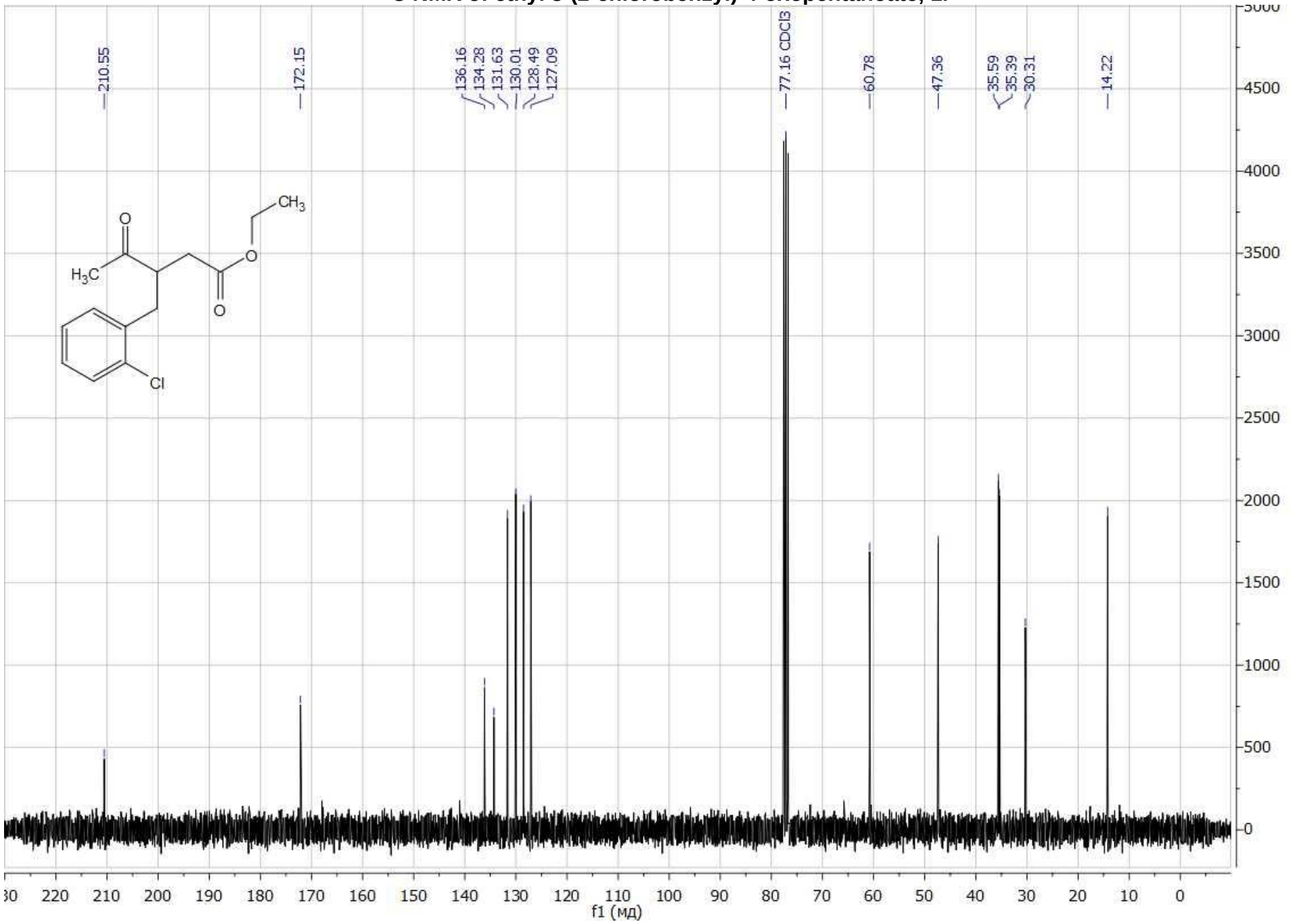

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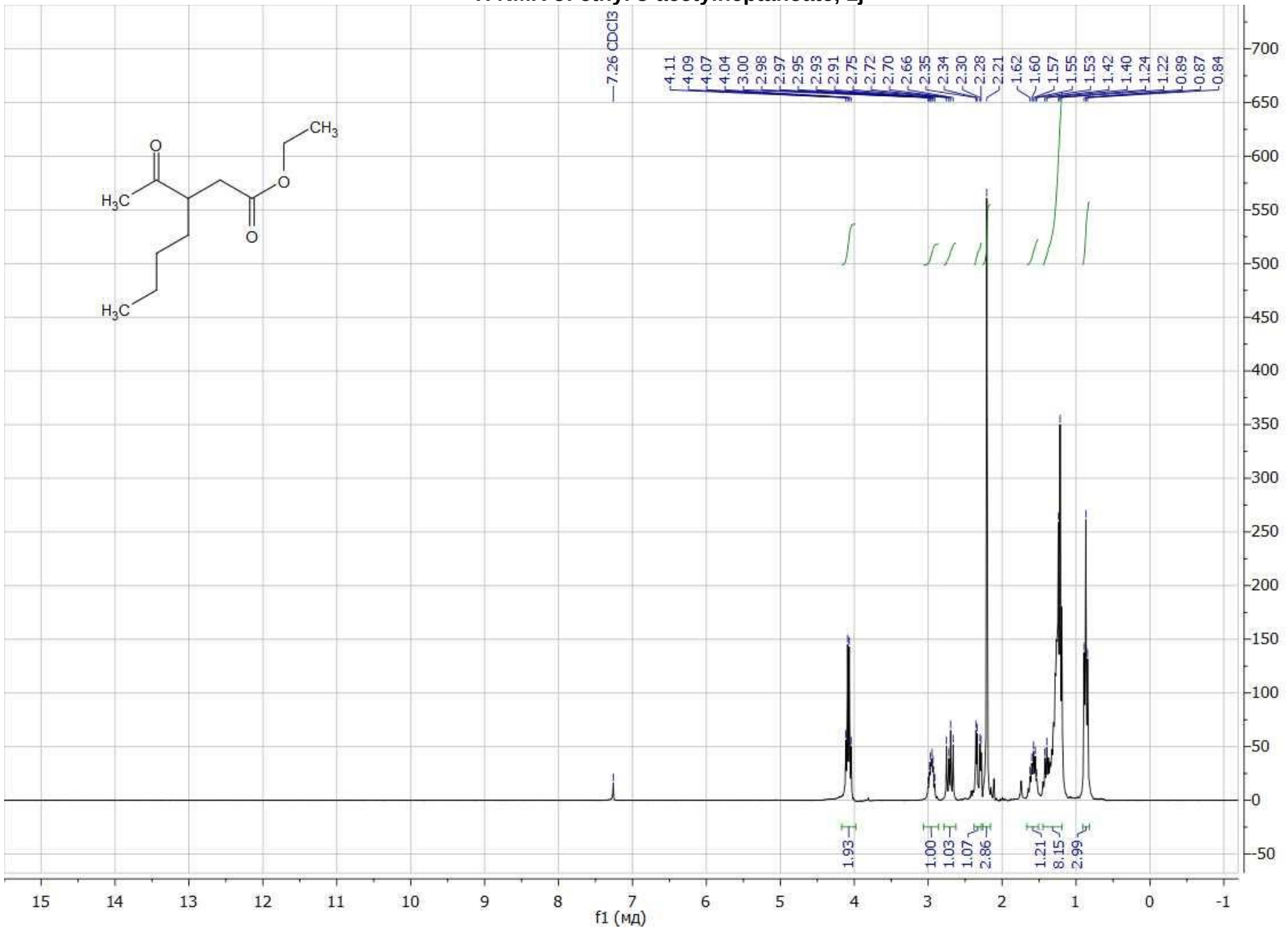

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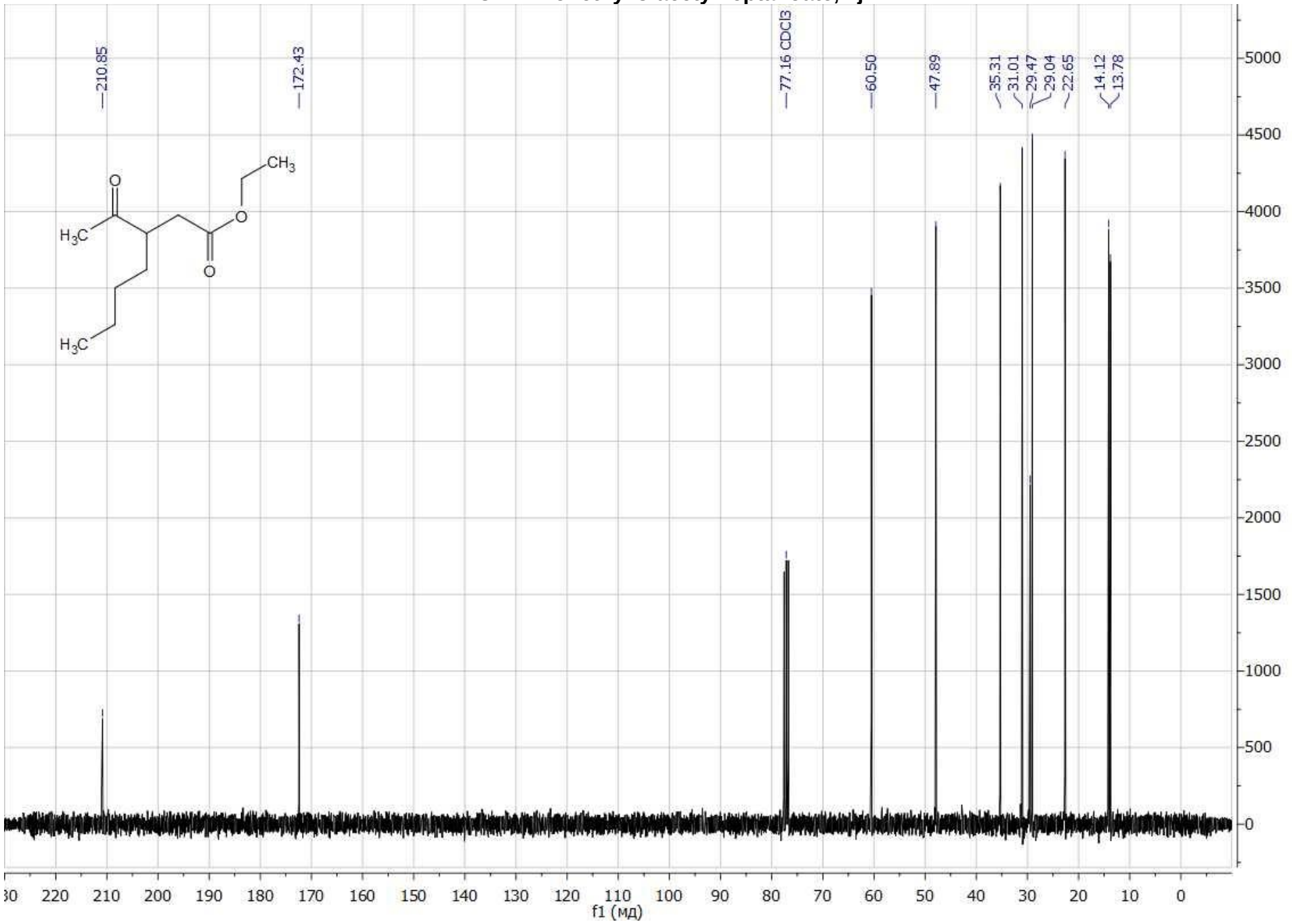

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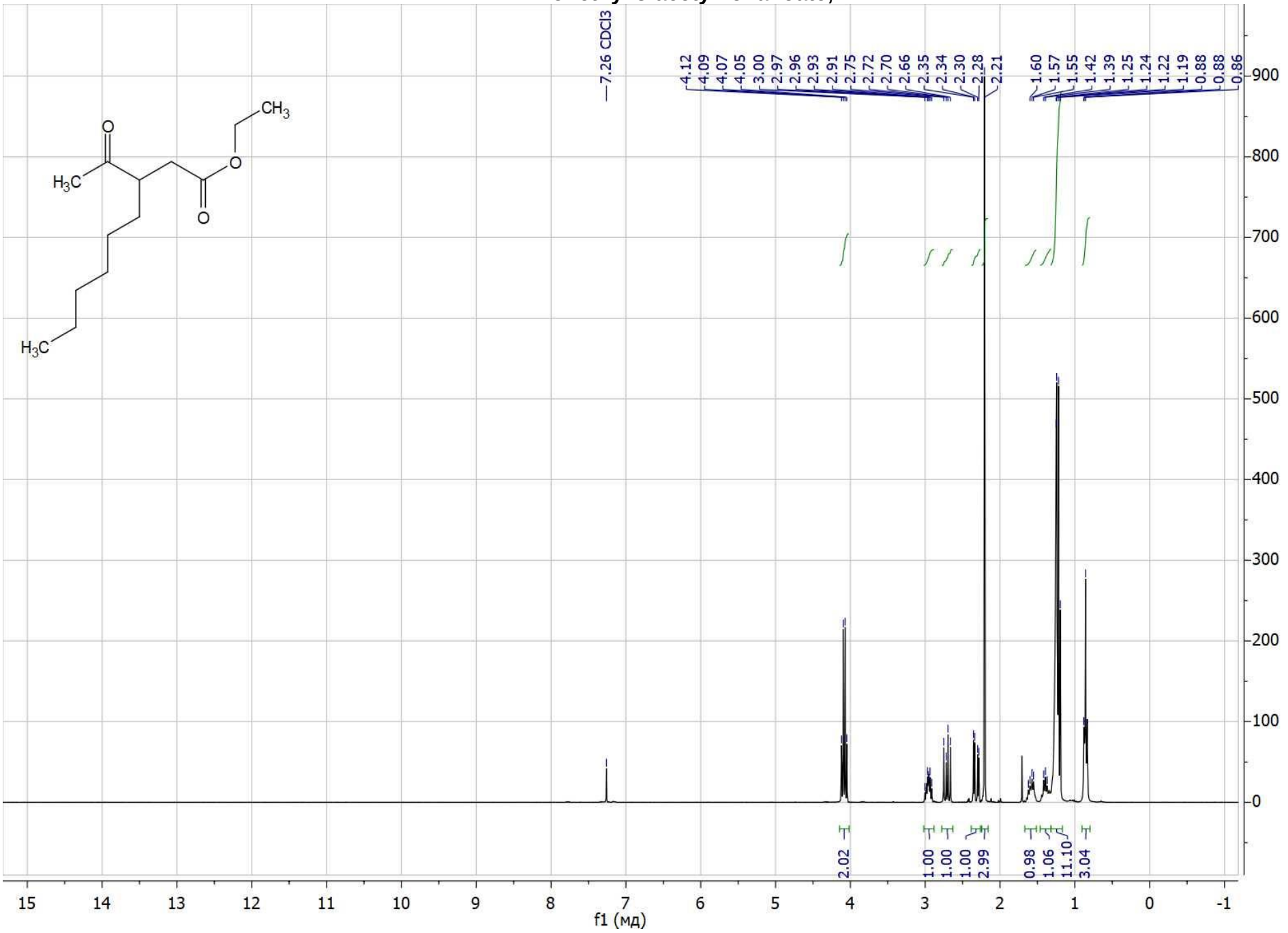

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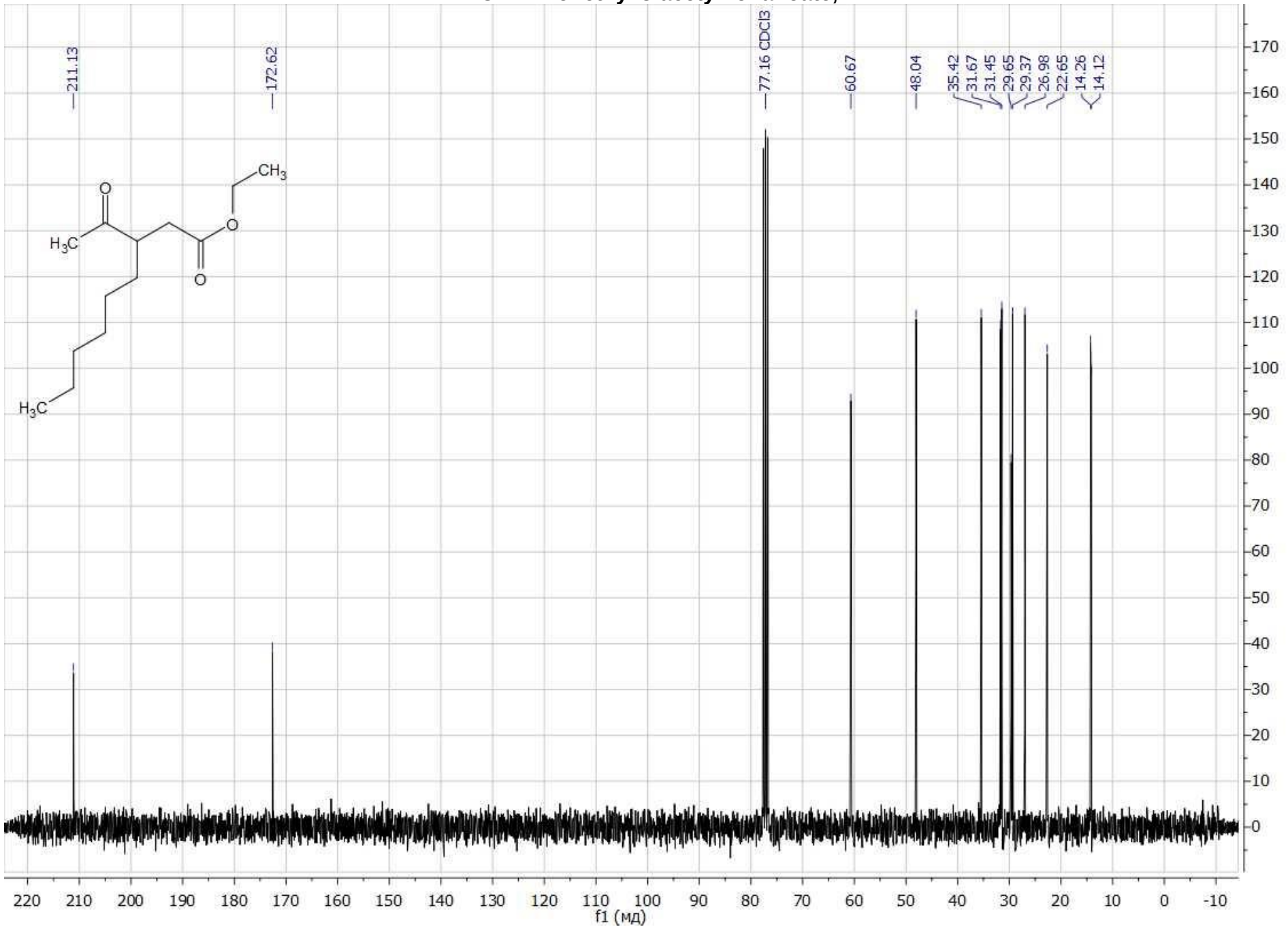
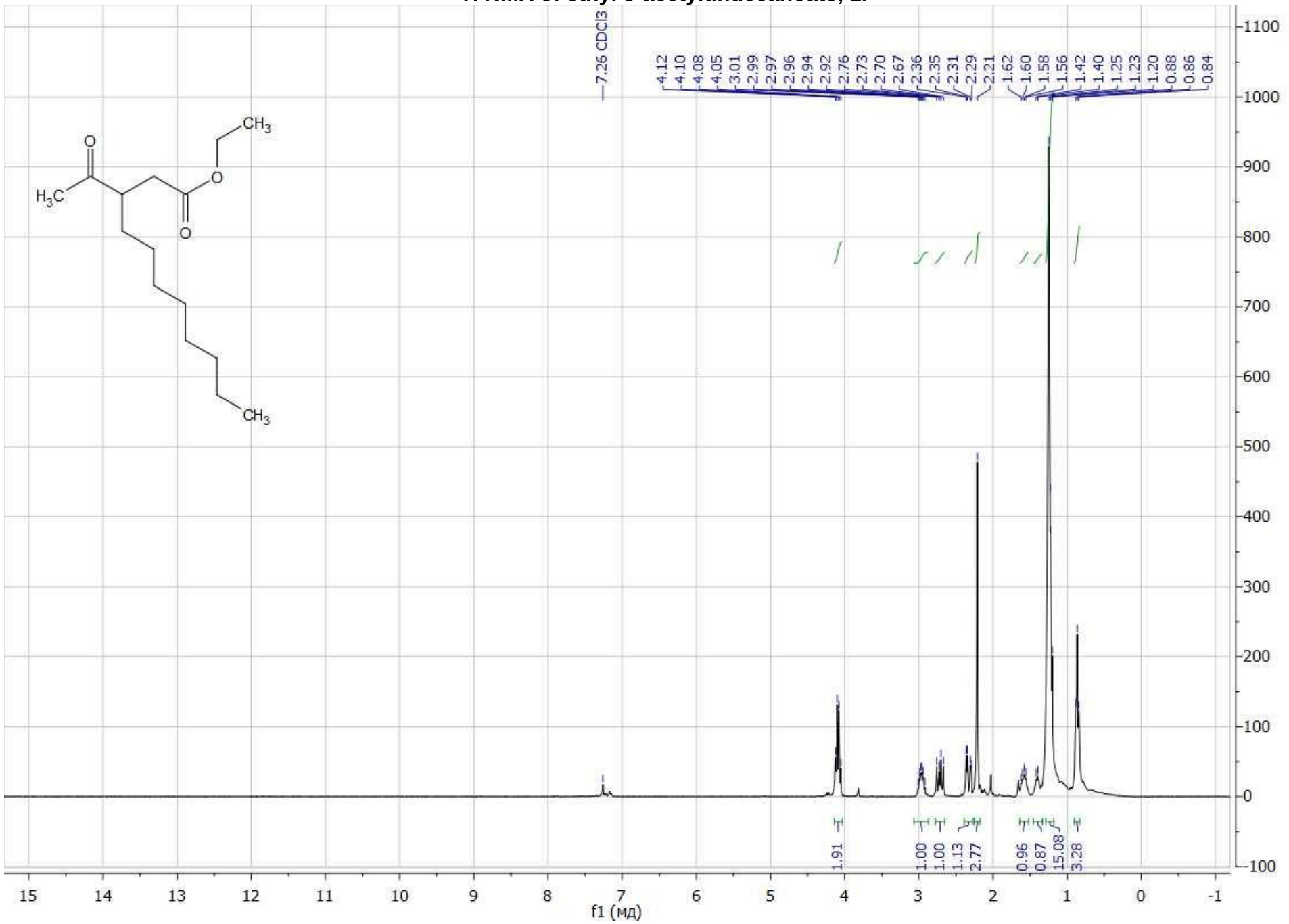


^{1}H NMR of ethyl 3-acetylundecanoate, 1l



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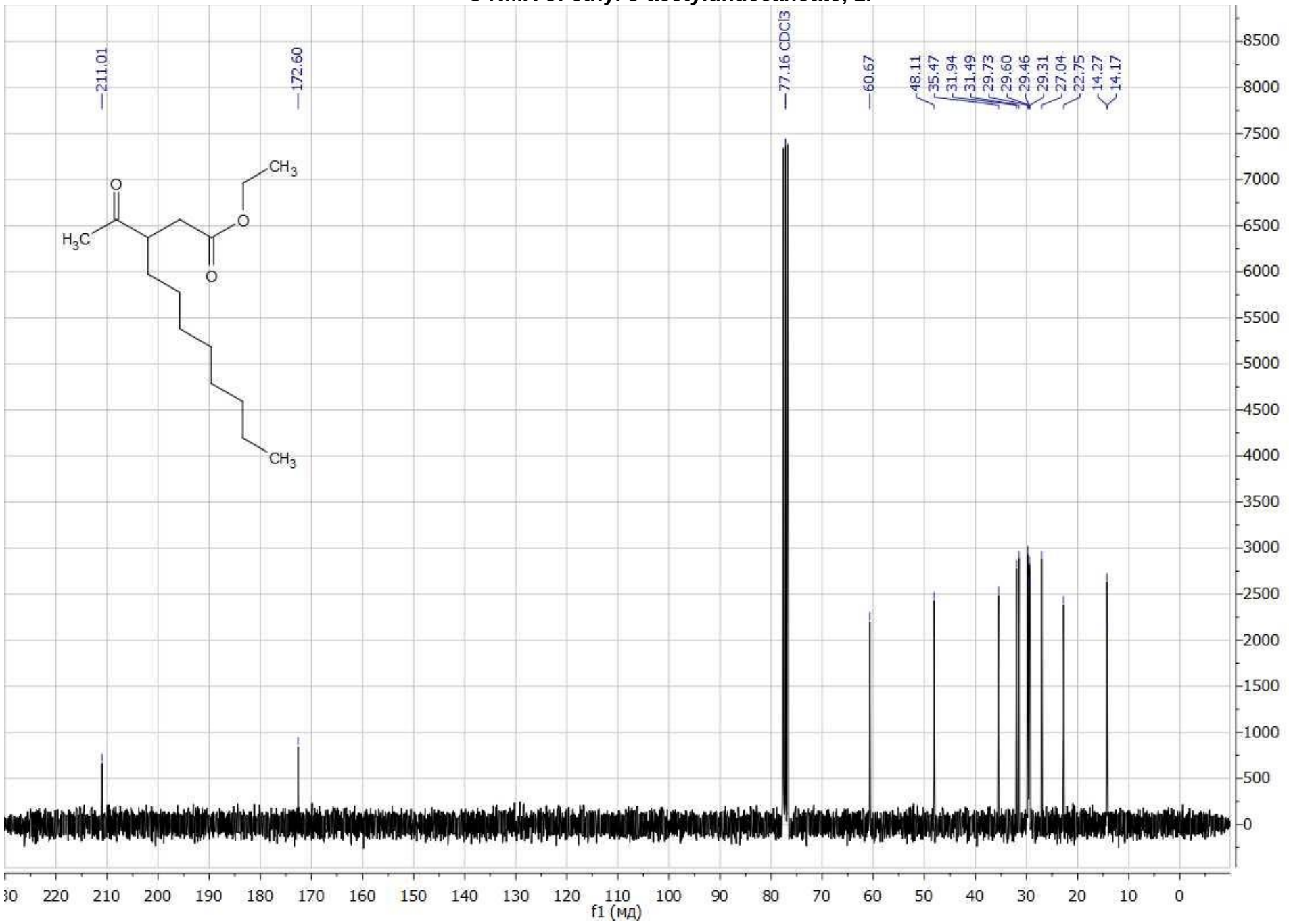
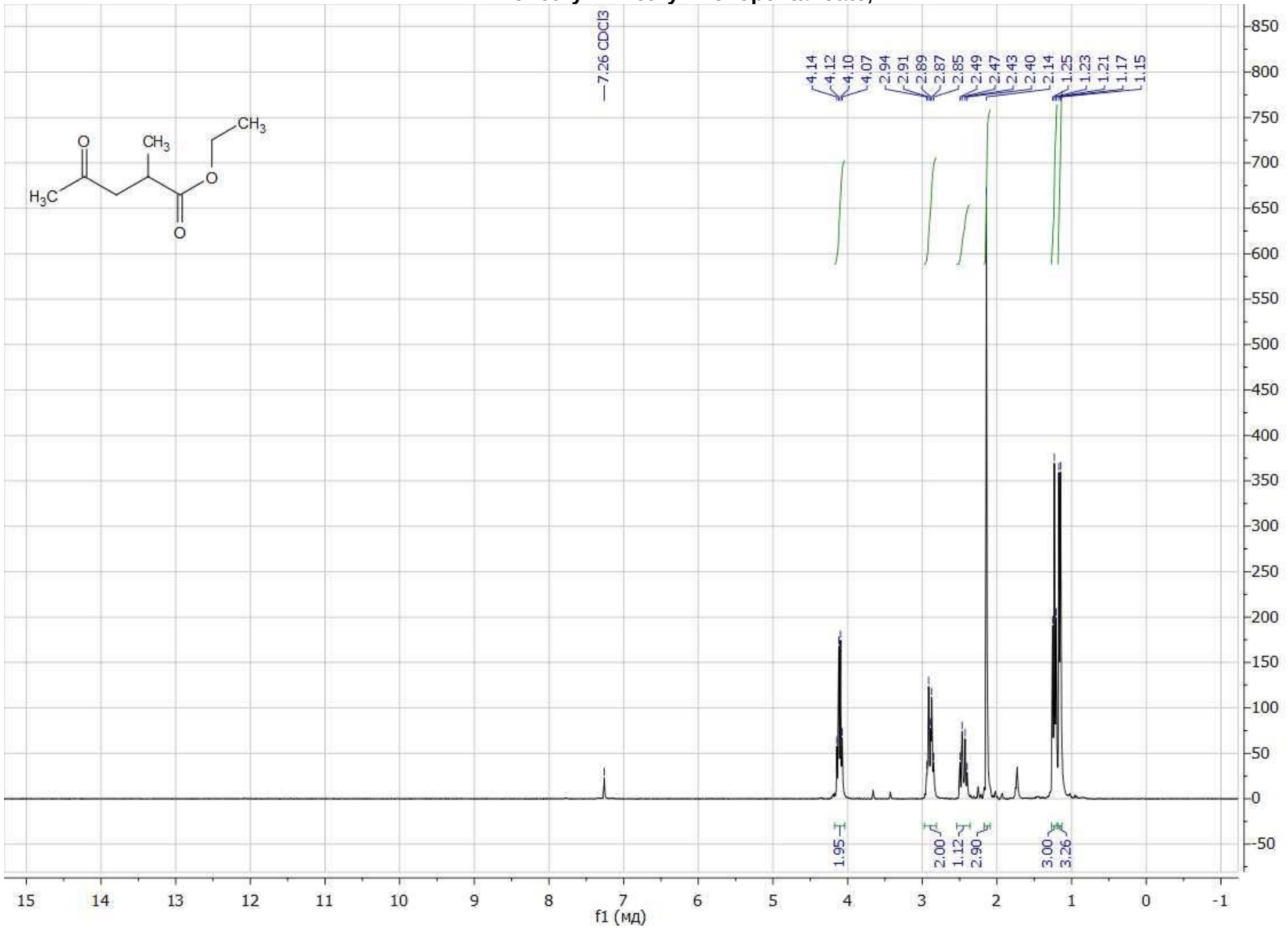


^{1}H NMR of ethyl 2-methyl-4-oxopentanoate, 1n



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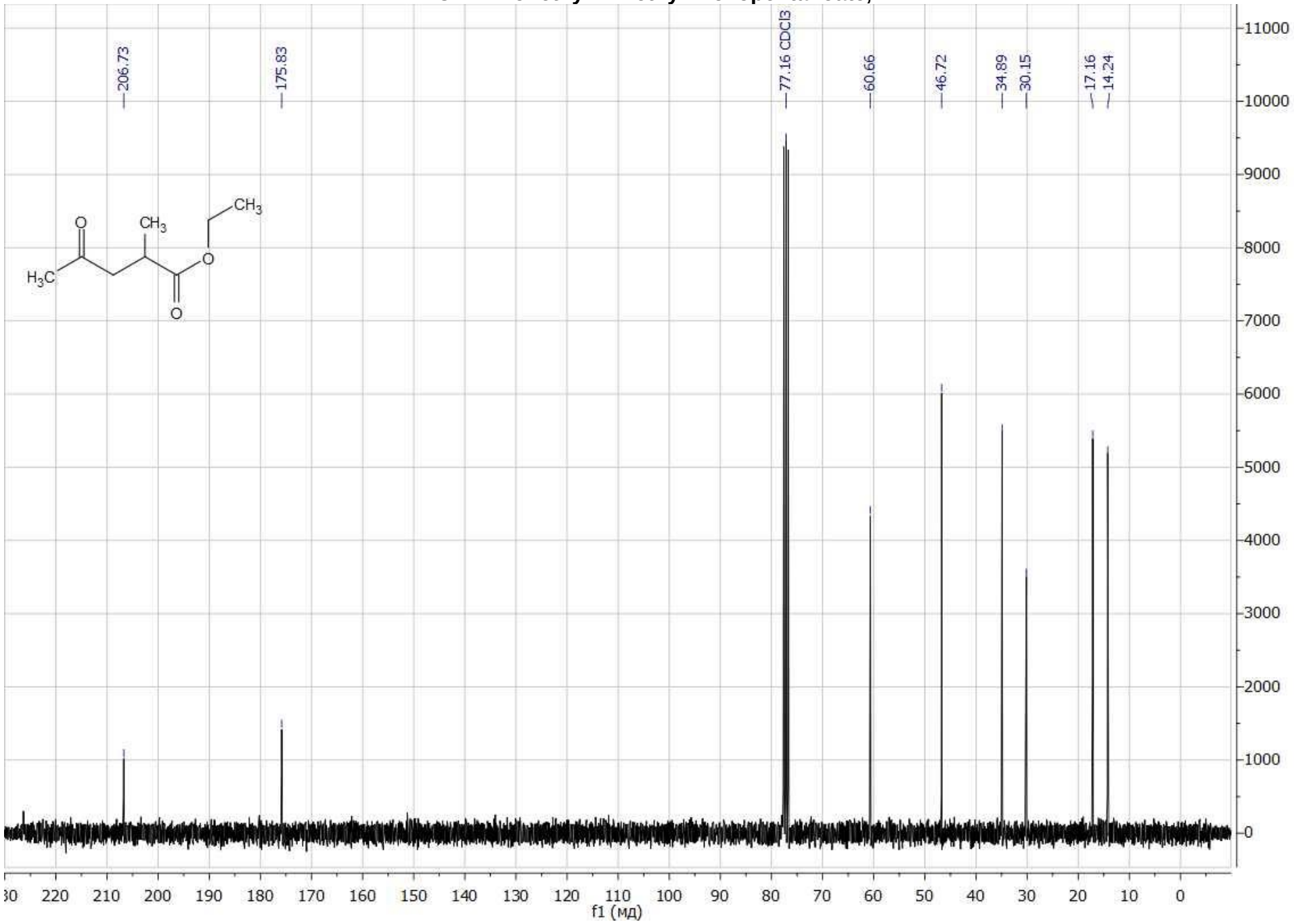
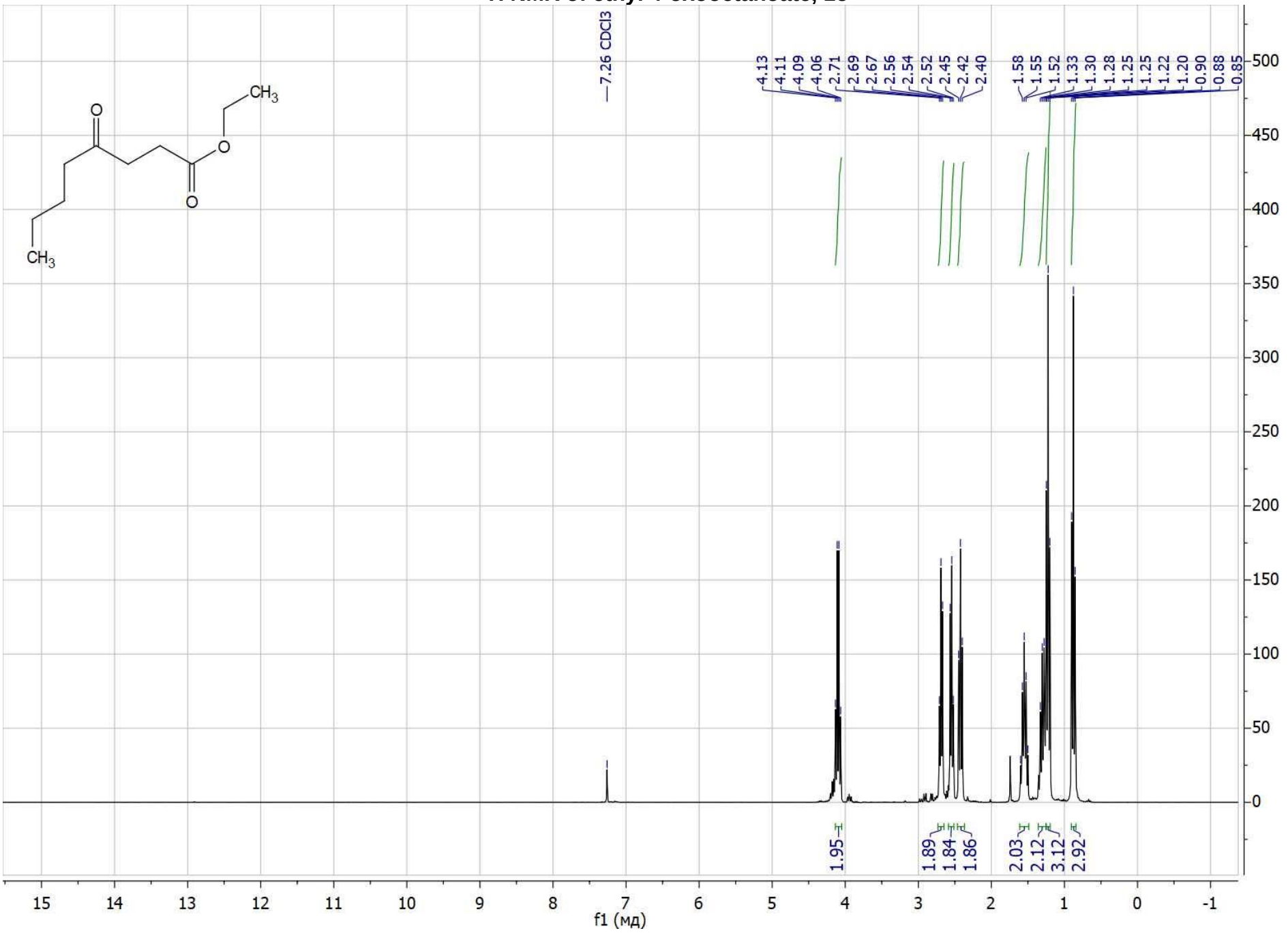


^{1}H NMR of ethyl 4-oxooctanoate, 1o



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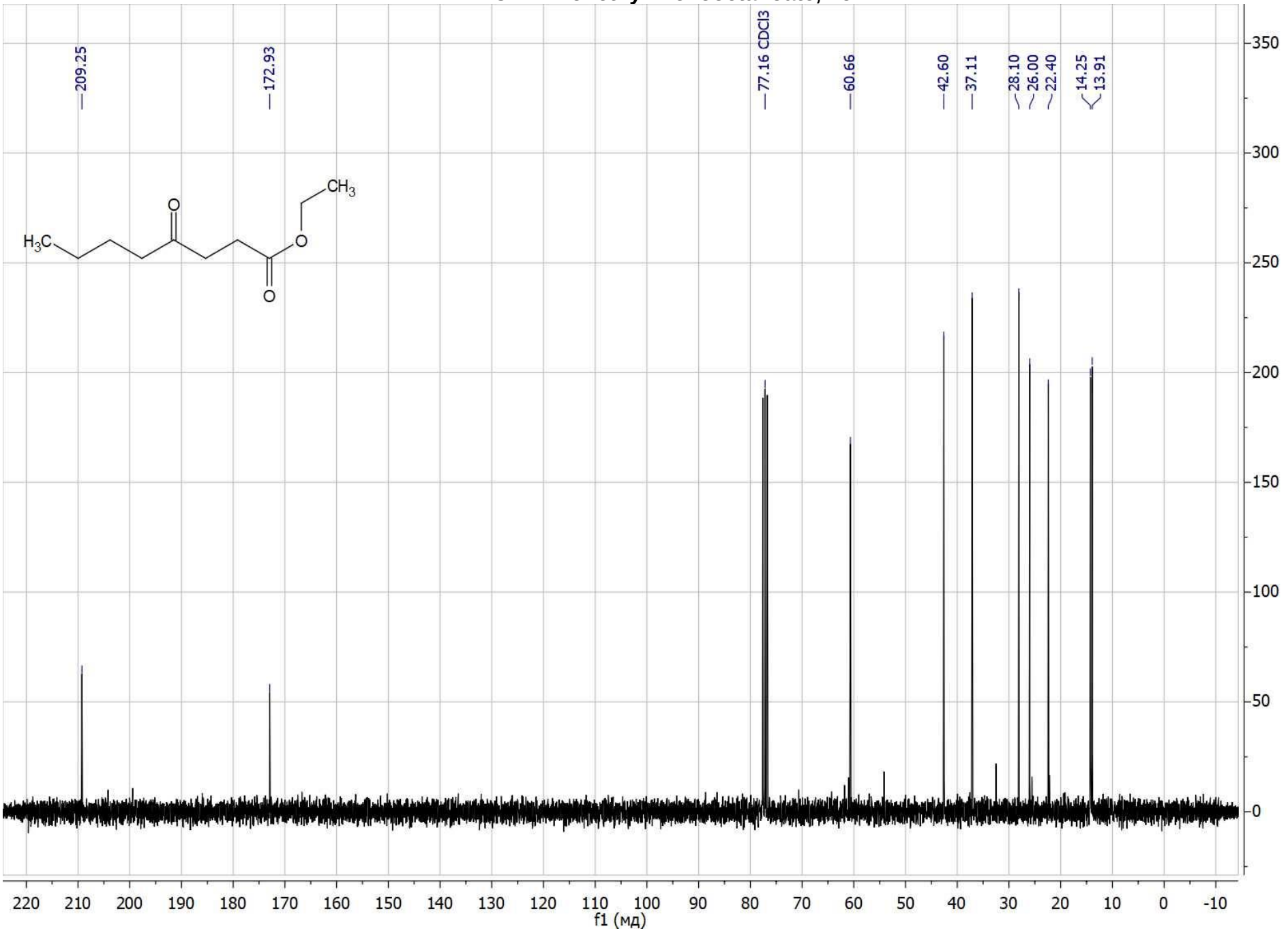

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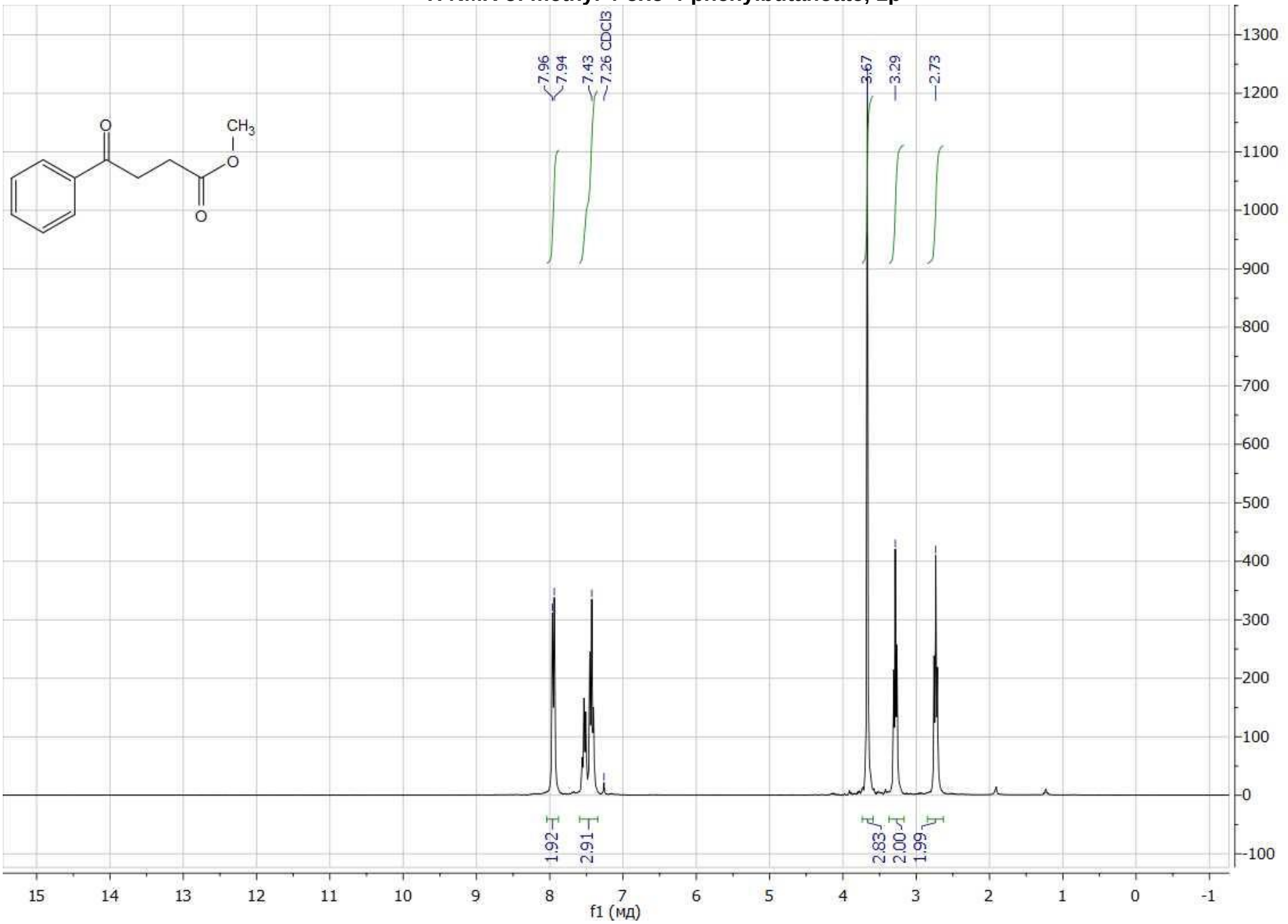

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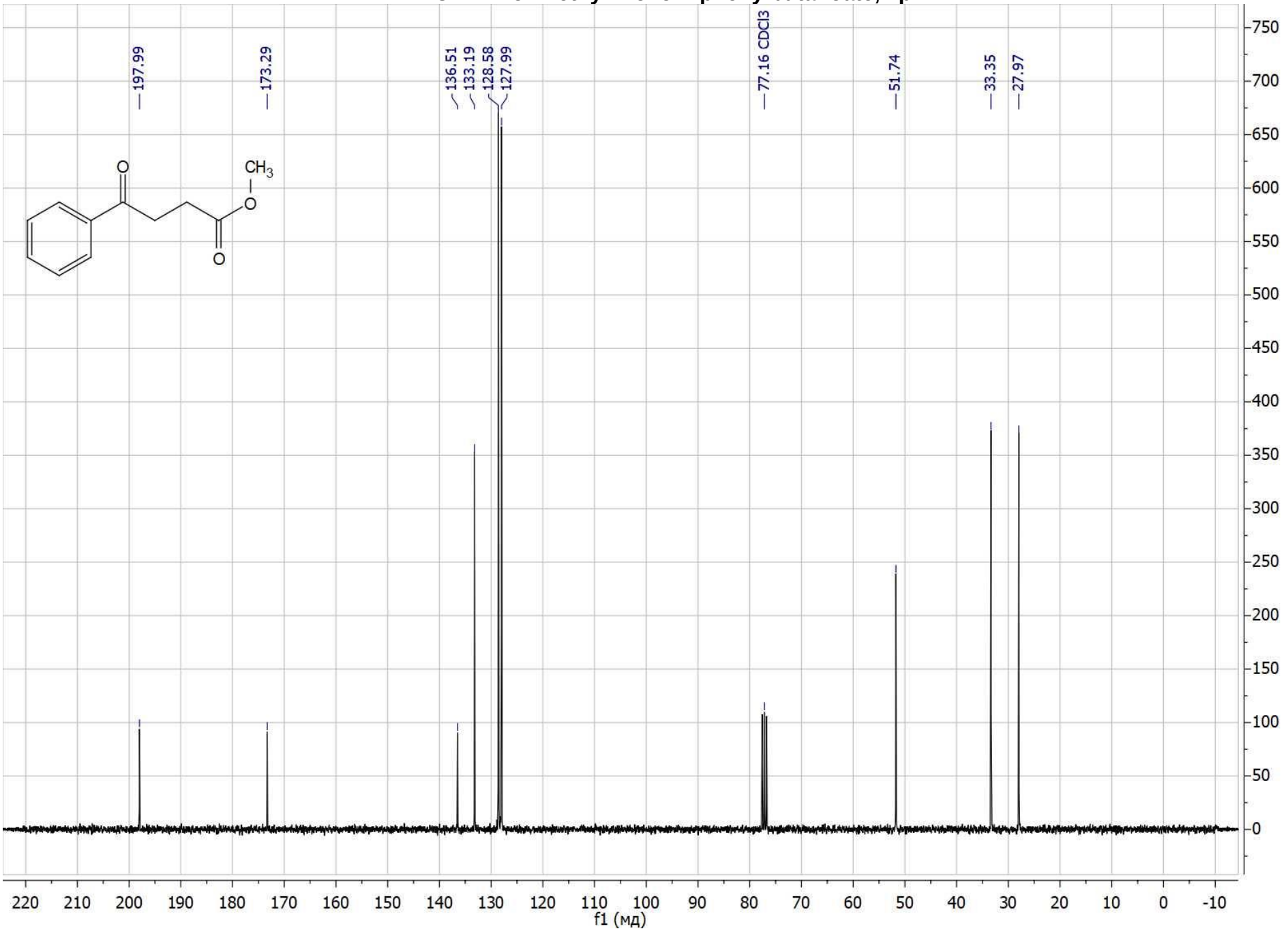

HRMS of starting γ-ketoesters 1

HRMS of ethyl 3-(4-nitrobenzyl)-4-oxopentanoate, 1b

Display Report

Analysis Info

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Acquisition Parameter

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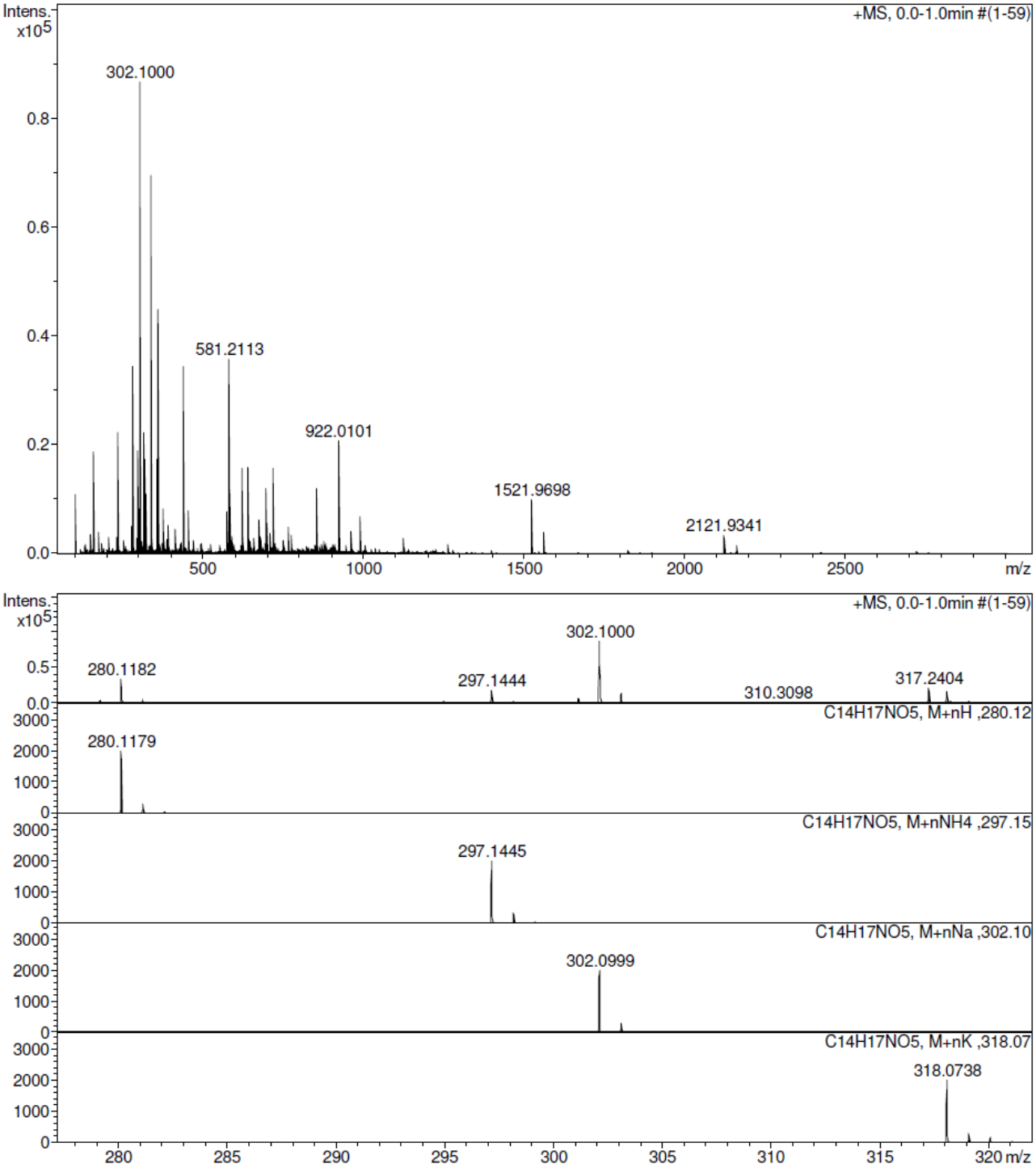

HRMS of ethyl 3-(4-chlorobenzyl)-4-oxopentanoate, 1c

Display Report

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Comment	CH3CN 100 %, dil. 200, calibrant added		

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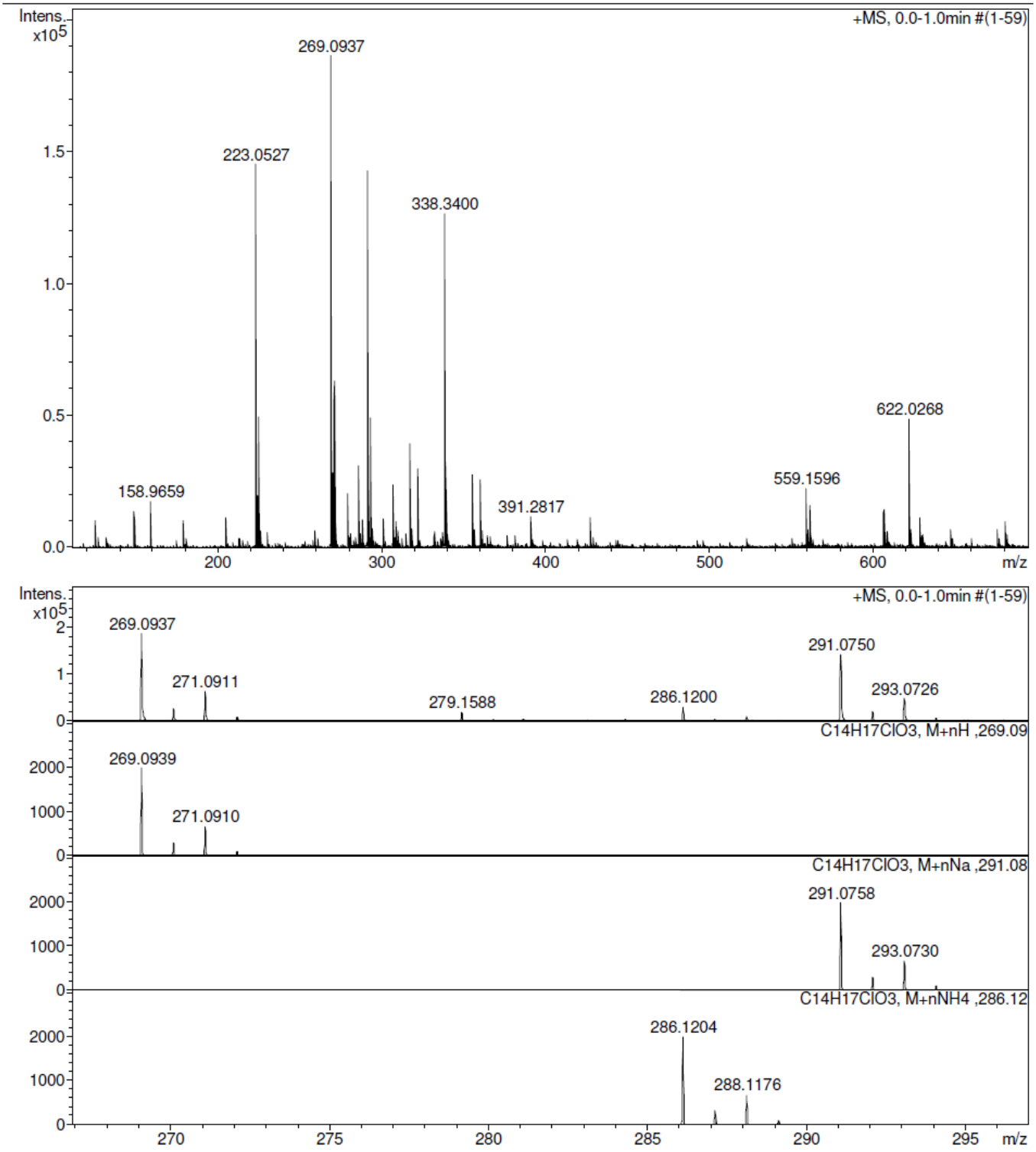

HRMS of ethyl 3-(4-bromobenzyl)-4-oxopentanoate, 1d

Display Report

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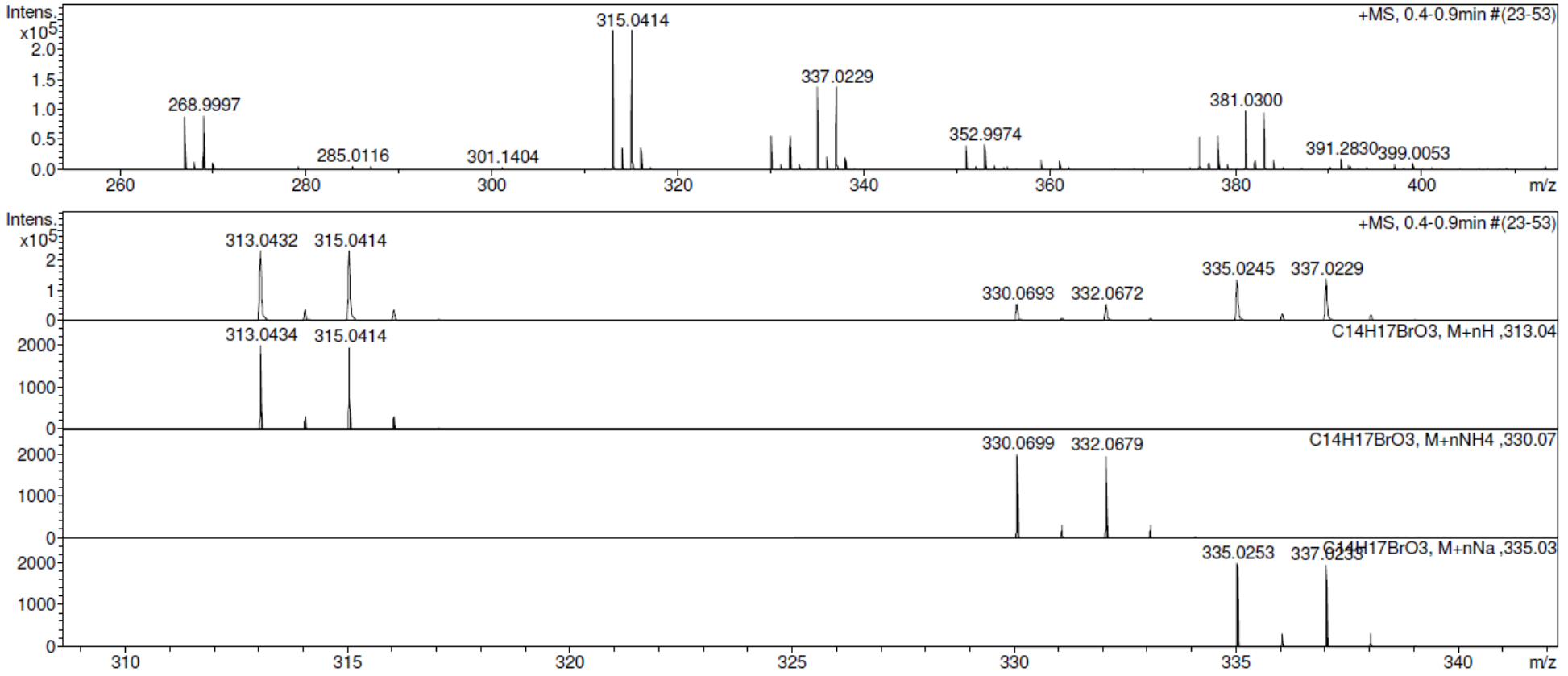

HRMS of ethyl 3-(4-(*tert*-butyl)benzyl)-4-oxopentanoate, 1e

Display Report

Analysis Info

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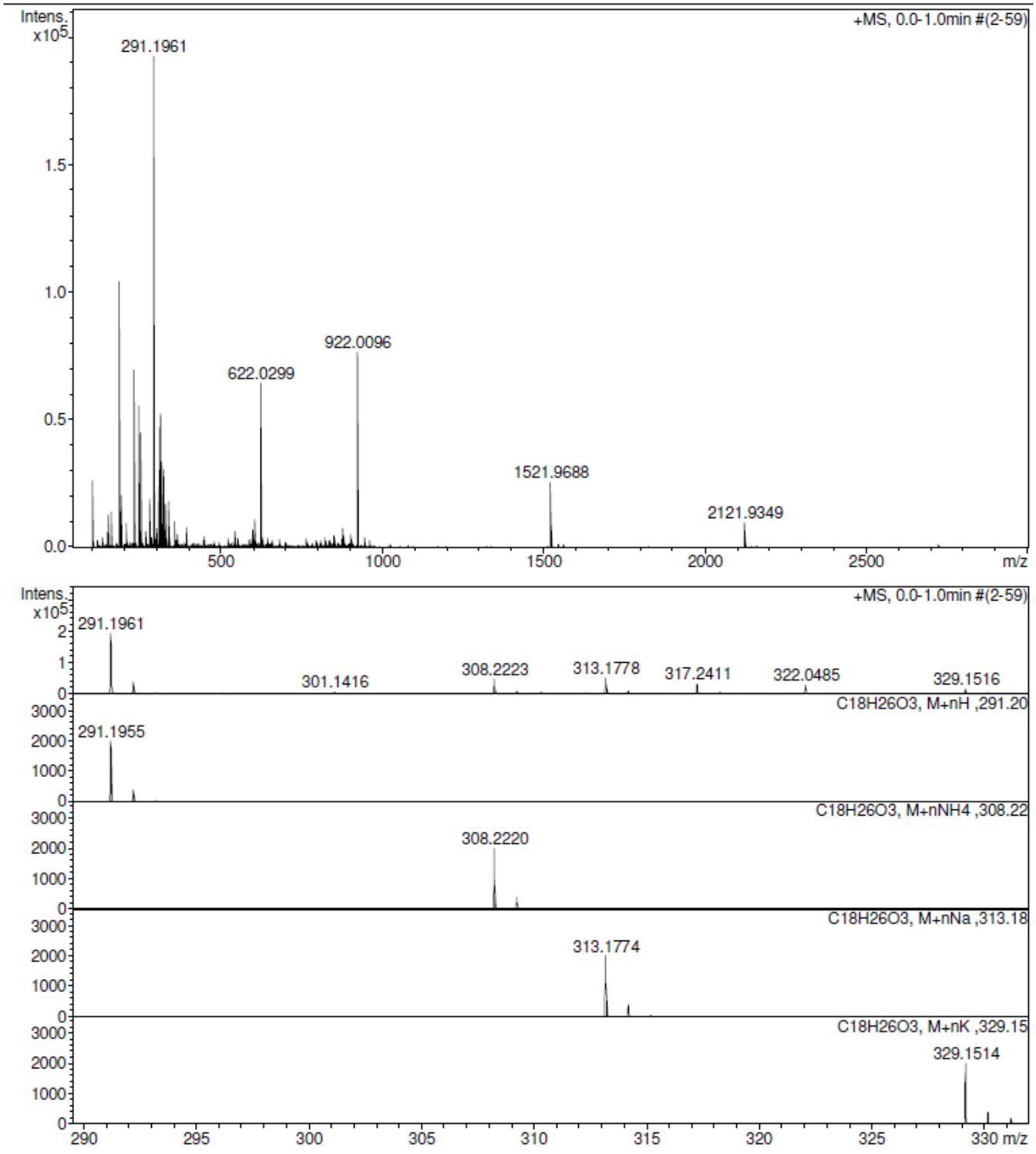

HRMS of ethyl 3-(4-methylbenzyl)-4-oxopentanoate, 1f

Display Report

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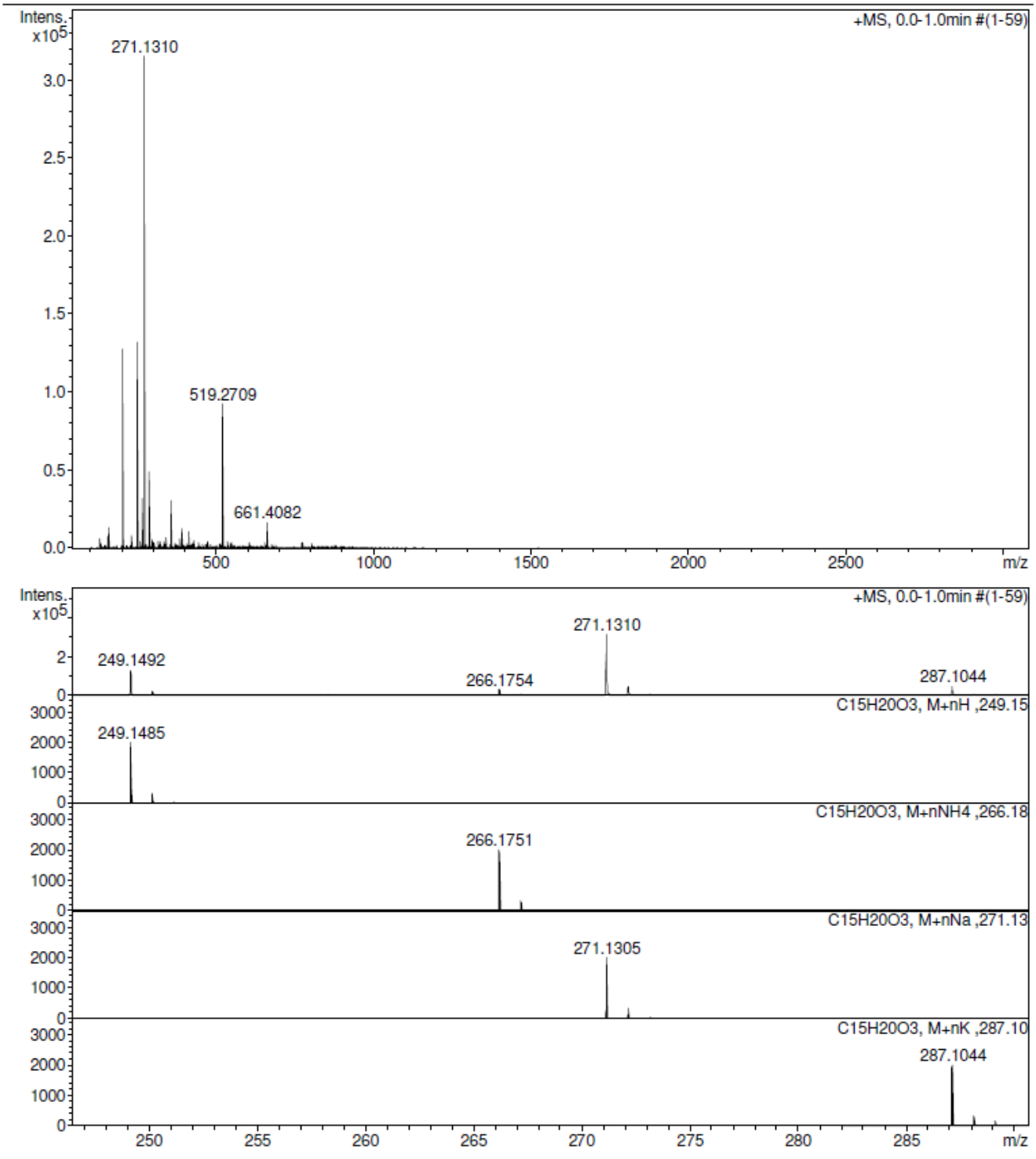


HRMS of ethyl 3-(3-methylbenzyl)-4-oxopentanoate, 1g

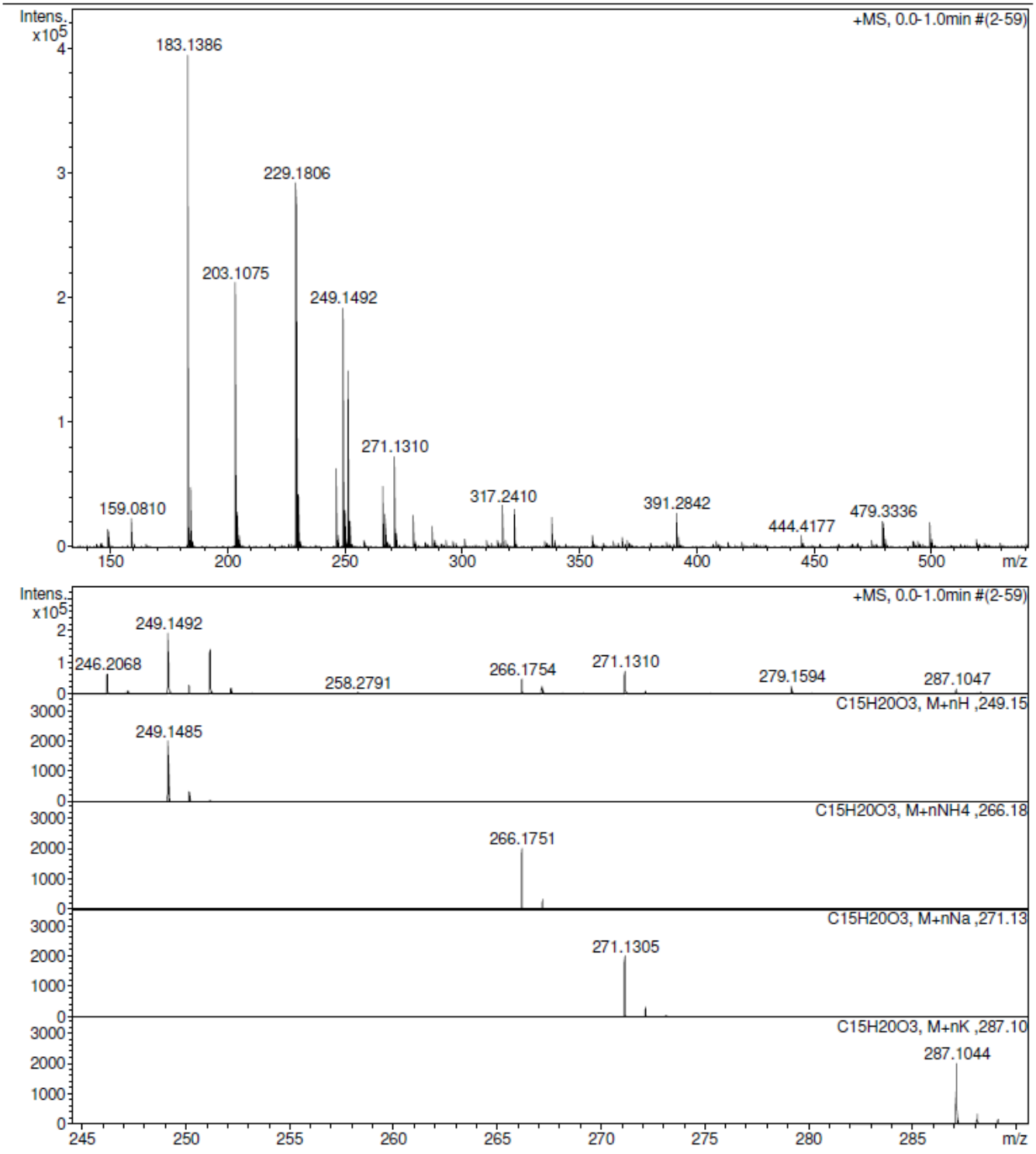
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Wil\se-28_&clblow.d	Acquisition Date	11.10.2019 18:48:57
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN SE-28	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of ethyl 3-(3-methoxybenzyl)-4-oxopentanoate, 1h

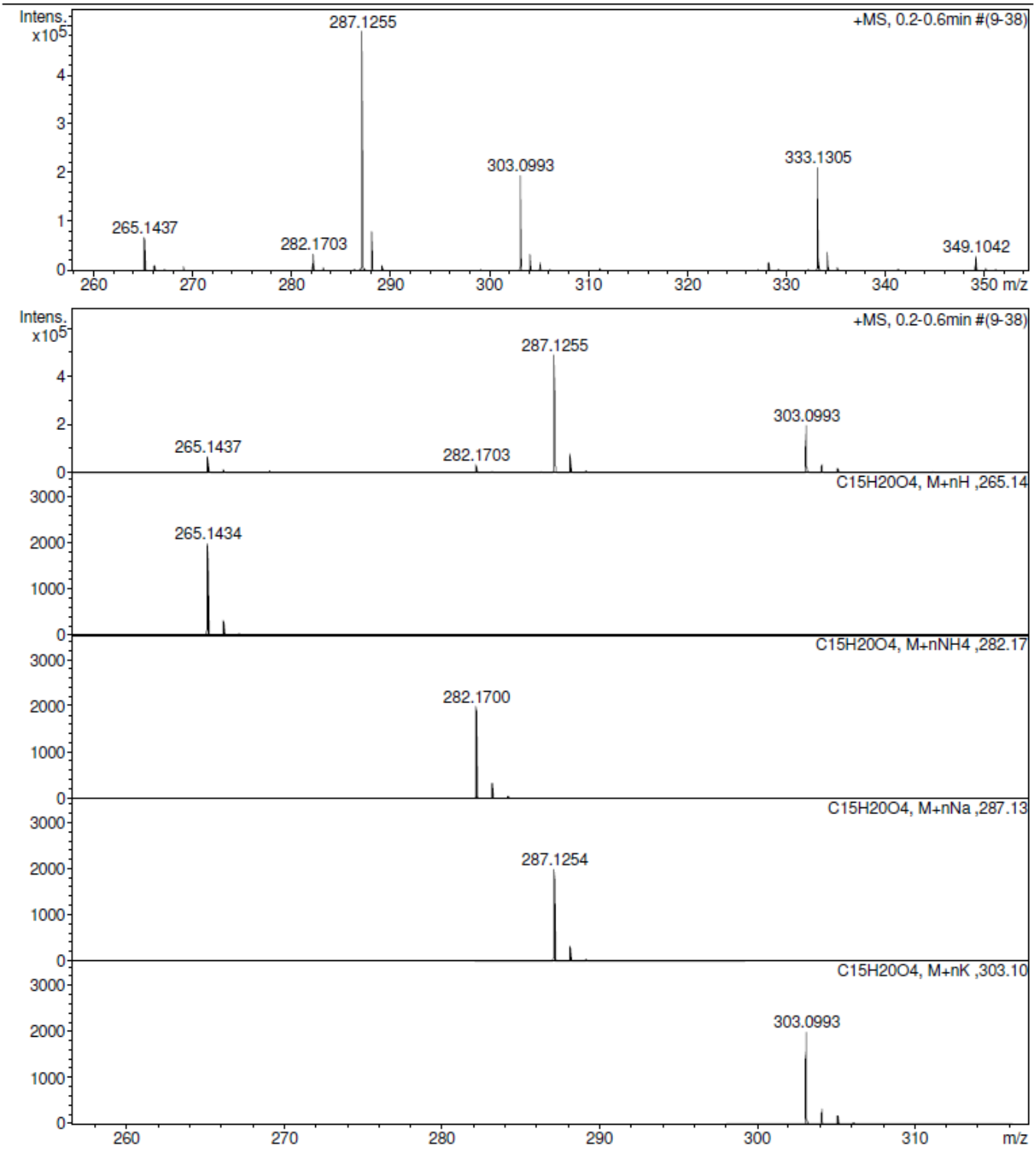
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2019\Vil\1031024.d	Acquisition Date	31.10.2019 17:02:48
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN SE-31	Instrument / Ser#	micrOTOF 10248
Comment	C15H20O4 mH 265.1434 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of ethyl 3-(2-chlorobenzyl)-4-oxopentanoate, 1i

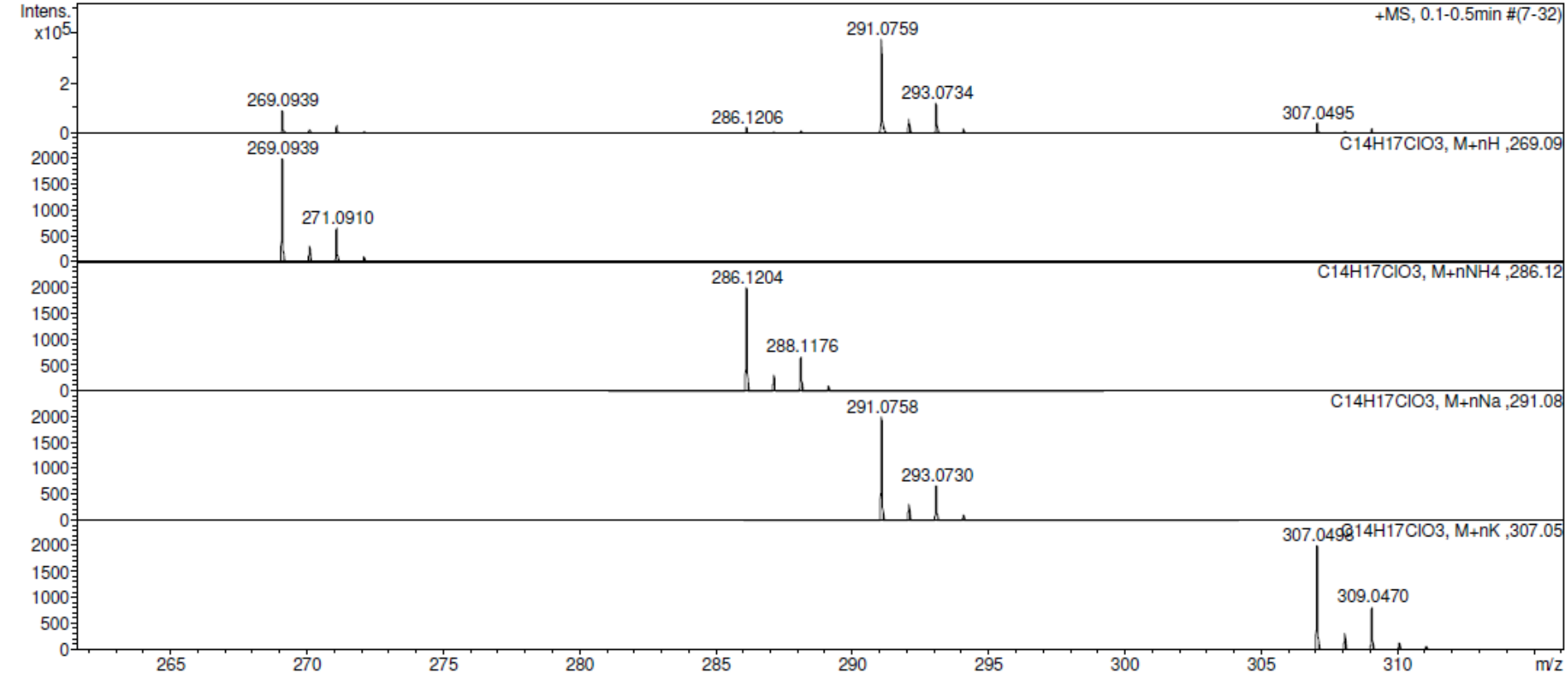
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2019\Barsegyan\1120064.d	Acquisition Date	20.11.2019 18:36:20
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN RES-10	Instrument / Ser#	micrOTOF 10248
Comment	C14H117ClO3 mH 269.0949 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of ethyl 3-acetylnonanoate, 1k

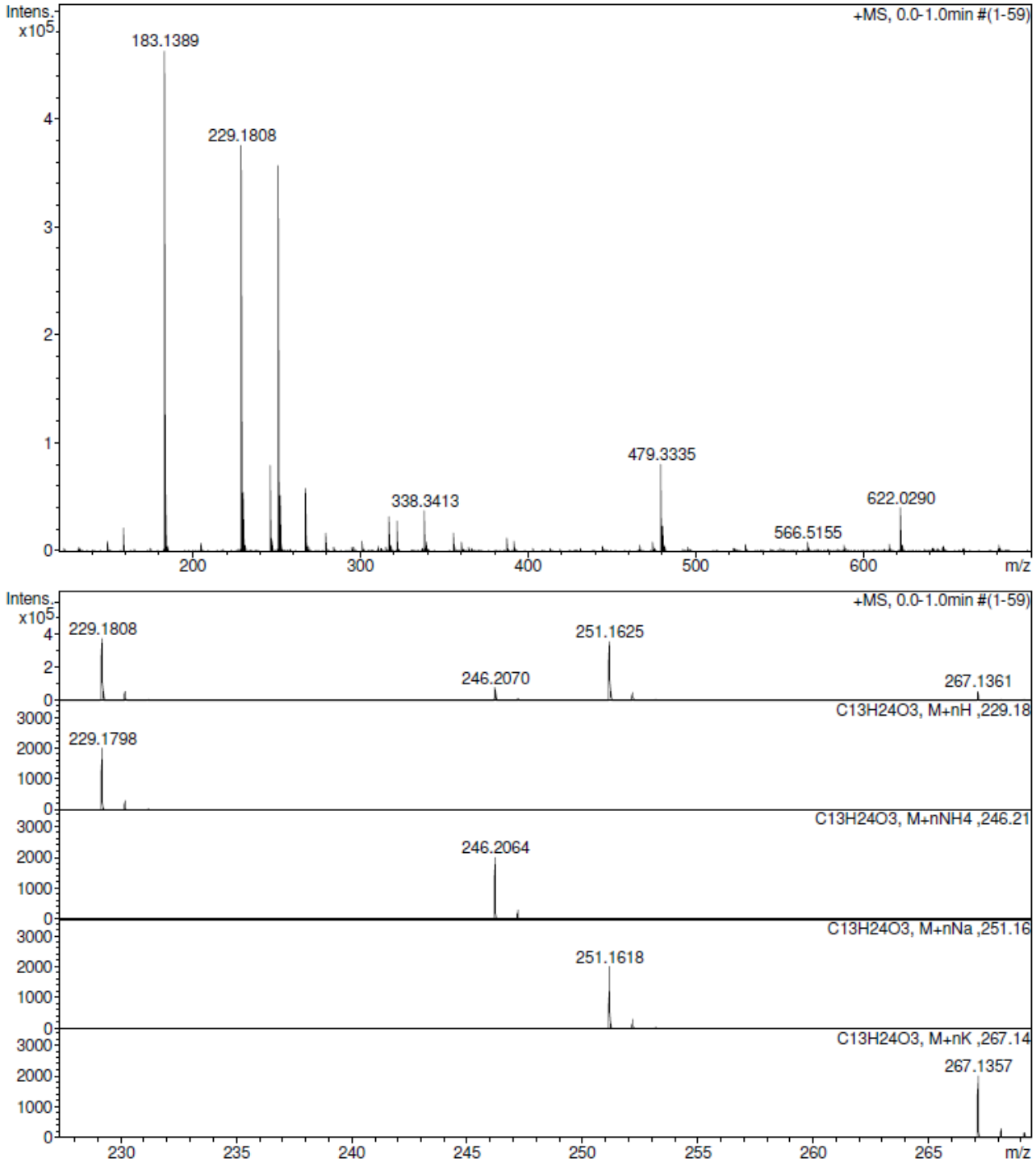
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Wil\bb-2143_&clblow.d	Acquisition Date	11.10.2019 18:35:15
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN BB-2143	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of ethyl 3-acetylundecanoate, 1l

Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Barsegyan\brs326_&clblow.d	Acquisition Date	27.09.2019 15:19:28
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN Brs326	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste