Unusual Kinetic Isotope Effects of Deuterium Reinforced Polyunsaturated Fatty Acids in Tocopherol Mediated Free Radical Chain Oxidations

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Supporting Information

General Methods and Materials:

Deuterium reinforced PUFAs were synthesized as described previously.[1-4] The synthesis of novel deuterated PUFAs are described below. All other PUFAs were purchased from Nu-Chek, Prep. MeOAMVN was purchased from Wako Chemicals. α-Tocopherol (α-Toc) was purchased from Sigma-Aldrich Co. and purified by flash column chromatography (10% ethyl acetate in hexanes). All HPLC solvents were purchased from Sigma-Aldrich Co.

HPLC analyses were carried out with a Waters 717plus Autosampler coupled to a Waters 1525 Binary HPLC Pump, both of which were interfaced to a Waters 2996 Photodiode Array Detector. Mass spectrometry was carried out on a Thermo Scientific TSQ Quantum Ultra Triple Stage Quadrupole mass spectrometer. Atmospheric-pressure chemical ionization in negative mode was used for the ionization of PUFAs and their oxidation products. Samples were introduced by direct liquid infusion (DLI) and monitored by full-scan in order to minimize any isotope effects which may occur during ionization and fragmentation of oxidation products.[5]

For oxidations where the products differ by 1 m/z (e.g. D1-LA oxidations and D0/D2-LA co-oxidations), analyses of products containing one deuterium had to be corrected for normal isotope contribution from D0-products. This was done by subtracting 13.1% of the value of the

integrated D0 product peak from the peak area of the D1 product peak. This isotopic distribution was determined by injections of a standard mixture of D0-LA oxidation products.

High resolution mass spectrometry isotope ratio analysis:

For isotope ratio analysis it is crucial to have unbiased sensitivity for isotopic labeled molecules. Also, integration functions capable of calculating peak areas are needed in order to compare the abundance (concentrations) of these molecules.

A Synapt G2 equipped with MassLynx (Waters, Milford, MA) was used to analyze H4/D4-αLn cooxidations. Three functions are available to obtain integration values for peaks of interest depending on the instrumentation used: Integrate (predominately for quadrupole mass analyzers), Center (for TDC data) and Automatic Peak Detection (for ADC data). Data was collected utilizing a combination of all three approaches thus a comparison of the three strategies is warranted. All three functions were used to calculate the KIE values for the H0/D4-αLn Cooxidation. They provided the results shown in Figure S1 and are summarized in Table 1, where the results do not vary significantly from function to function and all fall within a 10% variance. Using a 1-sample t-test with a hypothesis mean of 32.9 no significant difference between these three K_{IE} values is found (*p*-value of 0.968 with $\alpha = 0.05$).

The data in the Synapt G2 was acquired with DLI (15 µL/min) (11 Plus, Harvard Apparatus, Holliston, MA) in negative ion mode with an ESI source (T 80º C and capillary voltage of 2.7kV).

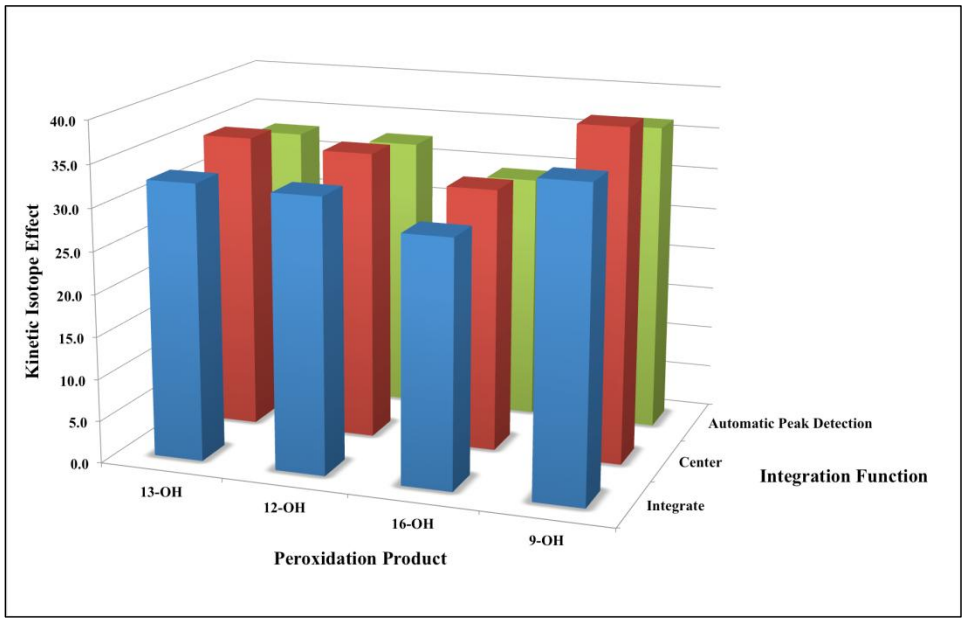


Figure S1. Kinetic Isotope effect values of 4 peroxidation products with 3 different integration functions.

Table S1. Average K_{IE}, Standard Deviation. and Percent Error of the 3 integration functions for three technical replicates.

Function	Average K_{IE}	Standard Deviation	Percent Error
Integrate	**32.1**	**1.7**	**5.3**
Center	**34.4**	**3.1**	**8.9**
Automatic Peak Detection	**32.3**	**1.8**	**5.5**

IR spectra were recorded with Vertex 70 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AC 400 instrument at 400 and 100 MHz respectively, in $CDCl_3$ (TMS at $\delta = 0.00$ or $CHCl_3$ at $\delta = 7.26$ for ^{1}H and $CHCl_3$ at $\delta = 77.0$ for ^{13}C as an internal standard).

General Oxidation Procedure:

All PUFAs were purified by flash column chromatography (10% EtOAc in hexanes to 20% EtOAc in hexanes) and dried for 2 to 3 hours under vacuum before use. Stock solutions of 2,2'-azobis(4-methoxy-2,4-dimethyl)-valeronitrile (MeOAMVN, 0.1 M) and α-Toc (1.0 M) were prepared in benzene. For all experiments, reagents were added in the order of: (1) benzene, (2)

PUFA, (3) α-Toc (if appropriate), (4) MeOAMVN. Reaction vials were vortexed for 5 s and heated at 37 °C for 1 h. Each reaction was quenched by the addition of 25 µL of both 0.5 M butylated hydroxytoluene (BHT) and 0.5 M PPh_3. All experiments were carried out in triplicate. Additionally, t=0 samples were prepared by dispensing purified PUFA into a vial and quenching via procedure outlined above without being oxidized, done concurrently with the corresponding experiment.

HPLC Separations:

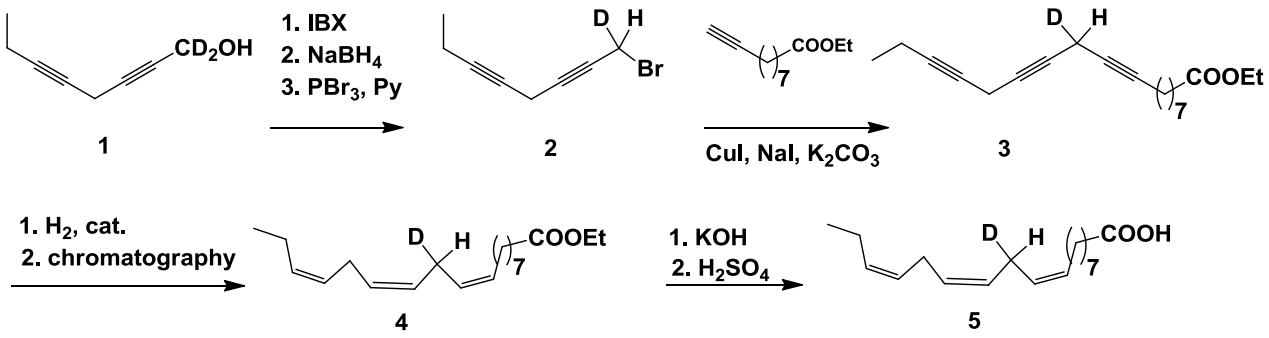
Oxidation products of PUFAs (as the free acid) were separated by HPLC-UV (250 x 4.6 mm silica column; 5 µm; elution solvent, 1.4% isopropanol, 0.1 % acetic acid in hexanes; 1.0 ml/min; monitoring wavelength, 234 nm). For samples where mass spectrometry was used, oxidation products were collected using HPLC-UV (same conditions as above) into vials contianing BHT. Collected products were introduced to the ion source (- APCI) by direct liquid introduction (DLI) using the same solvent conditions listed above.

Oxidation products of PUFA methyl esters were separated by HPLC-UV (250 x 4.6 mm silica column; 5 µm; elution solvent, 0.5% isopropanol in hexanes; 1.0 ml/min; monitoring wavelength, 234 nm).

Table S2: Table of KIEs

	0.5 M* α-*TOC		***0.05 M* α-*TOC***		
PUFA	k_H/k_D	**10% variance**	k_H/k_D	**10% variance**	**Method of Analysis**
11-D2-Ln	36.1	3.6	30.9	3.1	HPLC-UV
14-D2-Ln	35.9	3.6	31.0	3.1	HPLC-UV
14-D2-Ln Methyl Ester	45.6	4.6			HPLC-UV
D0/D4-Ln Cooxidation	32.3	3.2	36.3	3.6	DLI-MS
11-D1-Lin	8.9	0.9			DLI-MS
D0/D2-Lin Cooxidation	23.0	2.3			DLI-MS

Synthesis of 11-D_1-linolenic acid



1-Deutero-1-bromo-octa-2,5-diyne (**2**) 2-Iodoxybenzoic acid (IBX, 35.0 g) was added in one portion to a solution of 1,1-dideuteroocta-2,5-diyn-1-ol (**1**) [1] (5.50 g) in ethyl acetate (400 ml) (1,2-dichloroethane can be applied alternatively). The reaction mixture was stirred with simultaneous heating under reflux for 15 h until disappearance of (**1**) (TLC control). The reaction mixture was diluted with pentane (300 ml) and kept at 0°C for 3 h. The reaction mixture was filtered, and precipitate additionally washed with pentane. Methanol (20 ml) was added to the filtrate followed by $NaBH_4$ (0.60 g). After stirring for 15 min (TLC control) the reaction mixture was washed with brine (50 ml). The organic layer was dried over Na_2SO_4 and solvent was gently removed under reduced pressure. CC of the residue on silica gel (eluent: *n*-pentane/diethyl ether 10:1) yielded 1-deuteroocta-2,5-diyn-1-ol (3.02 g, 55%). IR (CCl_4): $\tilde{\nu}$ = 3622 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 4.25 (m, 1H, CHD), 3.19 (m, 2H, CH_2), 2.16 (m, 2H, CH_2), 1.63 (br. s., 1H, OH), 1.09 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 82.3, 80.6, 78.2, 72.7, 51.0 (t, J = 23 Hz), 13.7, 12.2, 9.7.

To a solution of 1-deuteroocta-2,5-diyn-1-ol (3.00 g, 24.2 mmol) and pyridine (0.15 ml) in dry diethyl ether (15 ml), a solution of PBr_3 (0.8 ml, 8.5 mmol) in diethyl ether (3 ml) was added dropwise with stirring over 10 min at -15°C under argon. The reaction mixture was allowed to gradually warm up to r.t. and then refluxed for 3.5 h with stirring. The reaction mixture was then cooled down to -10°C and 10 ml of cold water was added. When the residue dissolved, saturated NaCl (10 ml) and pentane (25 ml) were added, and the organic layer was separated. The aqueous fraction was washed with pentane (2 x 10 ml), and the combined organic fractions were washed with saturated $NaHCO_3$ (5 ml), saturated NaCl (5 ml) and dried over Na_2SO_4 in the presence of traces of hydroquinone. The solvent was removed under reduced

pressure. The residue was dissolved in pentane and filtered through silica gel (10 ml). Removal of the solvent gave the product (3.21 g, 71%, 39% starting from 1,1-dideuteroocta-2,5-diyn-1-ol (**1**)). IR (CCl_4): $\tilde{\nu}$ = 2255 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.90 (m, 1H, CHD), 3.21 (q, J = 2.3 Hz, 2H, CH_2), 2.16 (m, 2H, CH_2), 1.12 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 82.6, 81.9, 75.2, 72.0, 14.8 (t, J = 24 Hz), 13.7, 12.3, 9.8.

11-Deuterooctadeca-9,12,15-triynoic acid ethyl ester (**3**) was synthesized as described for the synthesis of 11,11-dideuterooctadeca-8,12,15-triynoic acid methyl ester [1, 2]. CuI (6.40 g) was quickly added to 15 ml of stirred DMF (freshly distilled over CaH_2), followed by dry NaI (5.10 g) and K_2CO_3 (7.20 g). Dec-9-ynoic acid ethyl ester (3.10 g) was then added in one portion, followed by bromide (**2**) (3.20 g). Additional 10 ml of DMF was used to rinse the reagents off the flask walls into the bulk of reaction mixture, which was then stirred for 16 h at r.t. Saturated aqueous NH_4Cl (25 ml) was then added with stirring, followed in a few minutes by saturated aqueous NaCl (15 ml) and then by a 5:1 mixture of hexane : ethyl acetate (30 ml). The mixture was further stirred for 15 min and then filtered through a fine mesh Schott glass filter. The residue was washed with hexane : ethyl acetate mixture several times. The organic fraction was separated, and the aqueous phase was additionally extracted with hexane (3 x 20 ml). The combined organic fractions were dried (Na_2SO_4), traces of hydroquinone were added, and the solvent was evaporated under reduced pressure. The residue was purified by CC (25:1 hexane : ethyl acetate) to give 4.53 g (95%) of the title compound. ^1H NMR ($CDCl_3$, δ): 4.11 (q, J = 7.2 Hz, 2H, OCH_2), 3.12 (m, 3H, CH_2 and CHD), 2.28 (t, J = 7.5 Hz, 2H, CH_2CO), 2.15 (m, 4H, CH_2), 1.61 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.31 (m, 6H, CH_2), 1.24 (t, J = 7.2 Hz, 3H, CH_3), 1.11 (t, J = 7.4 Hz, 3H, CH_3).

11-Deutero-cis,cis,cis-octadeca-9,12,15-trienoic acid ethyl ester (**4**) was synthesized as described for the synthesis of 11,11-dideutero-*cis,cis,cis*-octadeca-9,12,15-trienoic acid methyl ester [1, 2]. A suspension of nickel acetate tetrahydrate (1.87 g) in 96 % EtOH (25 ml) was heated with stirring to approx. 60 - 70°C until the salt dissolved. The flask was flushed with hydrogen, and then 7.7 ml of $NaBH_4$ solution (prepared by a 15 min stirring of $NaBH_4$

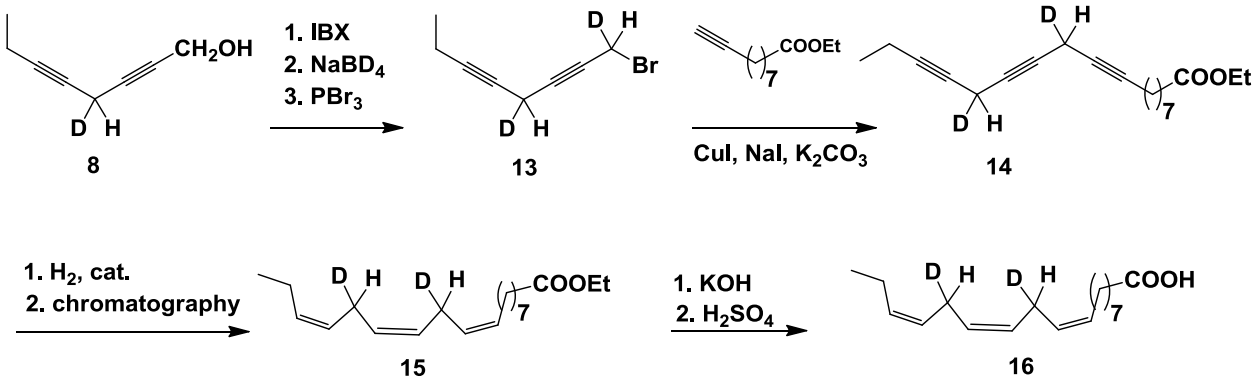
suspension (0.43 g) in EtOH (10 ml) followed by filtering) was added dropwise over 5-10 min with stirring. In 5 min ethylenediamine (2.3 ml) was added in one portion, followed in 5 min by an addition of (**3**) (4.50 g) in EtOH (15 ml). The reaction mixture was vigorously stirred under hydrogen (1 atm). The absorption of hydrogen stopped in about 2 h. To the reaction mixture, 70 ml of hexane and 3.3 ml of acetic acid were added, followed by water (6 ml) and the mixture was allowed to separate. Aqueous fractions were extracted by 5:1 mixture of hexane : ethyl acetate. The completion of extraction was monitored by TLC. The combined organic fractions were washed with diluted solution of HCl, followed by saturated NaCl and saturated $NaHCO_3$, and then dried over Na_2SO_4. The solvent was removed at reduced pressure.

Silica gel (Silica gel 60, Merck; 162 g) was added to a solution of silver nitrate (43 g) in anhydrous MeCN (360 ml), and the solvent removed on a rotavap. The obtained impregnated silica gel was dried for 3 h at 50°C (aspiration pump) and then 8 h on an oil pump. 30 g of this silica was used per gram of product. The reaction mixture was dissolved in a small volume of hexane and applied to the silver-modified silica gel, eluted with gradient of hexane: ether (from 50:1 to 20:1). When the non-polar contaminants were washed off (control by $AgNO_3$-impregnated TLC), the product was eluted with ether and the solvent evaporated under reduced pressure to give 1.91 g (42%) of the title ester (**4**). HRMS, *m/z* calculated for $C_{20}H_{33}DO_2$: 307.2622; found: 307.2624. IR (CCl_4): $\tilde{\nu}$ = 1740 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.36 (m, 6H, CH-double bonds), 4.12 (q, 2H, J = 7.2 Hz, OCH_2), 2.81 (m, 3H, CH_2 and CHD), 2.28 (t, J = 7.5 Hz, 2H, CH_2CO), 2.06 (m 4H, CH_2), 1.59 (m, 2H, CH_2), 1.30 (m, 8H, CH_2), 1.25 (t, J = 7.2 Hz, 3H, CH_3), 0.97 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 173.9, 131.9, 130.3, 128.3, 128.2, 127.6, 127.1, 60.1, 34.4, 29.5, 29.1, 29.08, 29.06, 27.2, 25.5, 25.3 (t, J = 19.5 Hz), 24.9, 20.5, 14.25, 14.23.

11-Deutero-cis,cis,cis-octadeca-9,12,15-trienoic acid (**5**) To a solution of (**4**) (1.20 g, 3.9 mmol) in ethanol (8 ml), a solution of KOH (1.10 g, 19.6 mmol) in water (2.5 ml) was added in one portion. The reaction mixture was stirred at 40-50 °C for 15 min (control by TLC) and then diluted with water (20 ml). Diluted sulfuric acid was added to pH 2, followed by diethyl ether (15 ml) and hexane (15 ml). The organic layer was separated and the aqueous layer washed with diethyl ether/hexane mixture (3 x 10 ml). The combined organic fractions were washed with

saturated aqueous NaCl and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was filtered through silica gel (2 ml, eluent: ethyl acetate/hexane 1:1). Evaporation of the solvent gave 1.08 g of (**5**) (98%). HRMS (ESI-QTOF) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{29}DO_2$ 278.2230; Found 278.2227. IR (CCl_4): $\tilde{\nu}$ = 1741, 1711 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 11.4 (br. s., 1 H, COOH), 5.36 (m, 6H, CH-double bonds), 2.81 (m, 3H, CH_2 and CHD), 2.35 (t, J = 7.5 Hz, 2H, CH_2), 2.06 (m, 4H, CH_2), 1.63 (m, 2H, CH_2), 1.31 (m, 8H, CH_2), 0.97 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 180.3, 131.9, 130.2, 128.3, 128.1, 127.7, 127.1, 34.0, 29.5, 29.1, 29.04, 28.99, 27.2, 25.5, 25.3 (t, J = 19.5 Hz), 24.6, 20.5, 14.2.

Synthesis of 11-D_1-14-D_1-linolenic acid



1,4-Dideutero-1-bromo-octa-2,5-diyne (**13**) 2-Iodoxybenzoic acid (IBX, 75.0 g) was added in one portion to a solution of 4-deuteroocta-2,5-diyn-1-ol (**8**) (8.90 g) in 1,2-dichloroethane (550 ml). The reaction mixture was stirred with simultaneous heating under reflux for 10 h until full starting alcohol consumption (TLC control). The reaction mixture was diluted with pentane (400 ml) and kept at 0^oC for 3 h. The reaction mixture was filtered; precipitate was additionally washed with pentane. Methanol (35 ml) was added to the filtrate followed by $NaBD_4$ (1.00 g). After stirring for 45 min (TLC control) the reaction mixture was washed with brine (50 ml). The organic layer was dried over Na_2SO_4. The bulk of the solvent was removed at atmospheric pressure from a flask equipped with 40 cm Vigreux column. The residual solvent was gently removed under reduced pressure. CC of the residue on silica gel led to 1,4-dideuteroocta-2,5-diyn-1-ol (4.70 g, 53%). IR (CCl_4): $\tilde{\nu}$ = 3622 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 4.25 (m, 1H, CHD), 3.17 (m, 1H, CHD), 2.17 (qd, J_1 = 7.5 Hz, J_2 = 2.3 Hz, 2H, CH_2), 1.59 (br. s., 1H, OH), 1.12 (t,

J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 82.3, 80.6, 78.2, 72.7, 51.0 (t, J = 23 Hz), 13.7, 12.2, 9.7 (t, J = 21 Hz).

To a solution of 1,4-dideuteroocta-2,5-diyn-1-ol (4.68 g, 37.7 mmol) and pyridine (0.25 ml) in dry diethyl ether (25 ml), a solution of PBr_3 (1.25 ml, 13.2 mmol) in diethyl ether (5 ml) was added dropwise with stirring over 10 min at -15°C under argon. The reaction mixture was allowed to gradually warm up to r.t. and then refluxed 3.5 h with stirring. The reaction mixture was then cooled down to -10°C and 10 ml of cold water was added. When the residue dissolved, saturated NaCl (10 ml) and pentane (30 ml) were added, and the organic layer was separated. The aqueous fraction was washed with pentane (2 x 10 ml), and the combined organic fractions were washed with saturated NaCl (5 ml), saturated $NaHCO_3$ (10 ml) and dried over Na_2SO_4 in the presence of traces of hydroquinone. The solvent was removed under reduced pressure. The residue was dissolved in pentane and filtered through silica gel (10 ml). Removal of the solvent gave the product (4.10 g, 58%, 30% starting from (**8**)). IR (CCl_4): $\tilde{\nu}$ = 2255 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.90 (m, 1H, CHD), 3.20 (m, 1H, CHD), 2.16 (qd, J_1 = 7.5 Hz, J_2 = 2.3 Hz, 2H, CH_2), 1.11 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 82.6, 82.0, 75.2, 72.1, 14.8 (t, J = 24 Hz), 13.8, 12.3, 9.8 (t, J = 22 Hz).

11,14-Dideuterooctadeca-9,12,15-triynoic acid ethyl ester (**14**) was synthesized as described for (**3**). The product obtained from 8.2 g CuI, 6.5 g NaI, 9.2 g K_2CO_3, 4.10 g of bromide (**13**), 4.00 g of ethyl ester of dec-9-ynoic acid and 35 ml of anhydrous DMF, was purified by CC (25:1 hexane:EtOAc) to give 5.58 g (91%) of the title compound. ^1H NMR ($CDCl_3$, δ): 4.11 (q, 2H, J = 7.2 Hz, OCH_2), 3.11 (m, 1H, CHD and CHD), 2.28 (t, J = 7.5 Hz, 2H, CH_2), 2.14 (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.30 (m, 6H, CH_2), 1.24 (t, J = 7.2 Hz, 3H, CH_3), 1.10 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 173.8, 82.1, 80.7, 74.8, 74.7, 73.7, 73.0, 60.1, 34.3, 29.0, 28.7, 28.63, 28.59, 24.9, 18.6, 14.2, 13.8, 12.3, 9.6 (t, J = 20.5 Hz), 9.5 (t, J = 20.5 Hz).

11,14-Dideutero-cis,cis,cis-octadeca-9,12,15-trienoic acid ethyl ester (**15**) was synthesized as described for ester (**4**). For a reduction of 6.00 g of (**14**), 2.50 g of nickel acetate tetrahydrate and 3.1 ml ethylenediamine were used. The product was purified on $AgNO_3$-impregnated silica gel

as described for (**4**) to give 3.48 g (57%) of the title ester (**15**). HRMS, *m/z* calculated for $C_{20}H_{32}D_2O_2$: 308.2684; found: 308.2680. IR (CCl_4): $\tilde{\nu}$ = 1740 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.35 (m, 6H, CH-double bonds), 4.12 (q, 2H, J = 7.2 Hz, OCH_2), 2.78 (m, 2H, CHD and CHD), 2.28 (t, J = 7.5 Hz, 2H, CH_2CO), 2.06 (m 4H, CH_2), 1.61 (m, 2H, CH_2), 1.30 (m, 8H, CH_2), 1.25 (t, J = 7.2 Hz, 3H, CH_3), 0.97 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 173.9, 131.9, 130.3, 128.22, 128.20, 127.6, 127.0, 60.1, 34.4, 29.6, 29.14, 29.09, 27.2, 25.5, 25.3 (t, J = 19.5 Hz), 25.2 (t, J = 19.5 Hz), 24.9, 20.5, 14.25, 14.23.

11,14-Dideutero-cis,cis,cis-octadeca-9,12,15-trienoic acid (**16**) was synthesized as described for acid (**5**). HRMS (ESI-QTOF) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{27}D_2O_2$ 279.2293; Found 279.2299. IR (CCl_4): $\tilde{\nu}$ = 1741, 1711 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 11.4 (br. s., 1 H, COOH), 5.36 (m, 6H, CH-double bonds), 2.78 (m, 2H, CHD and CHD), 2.34 (t, J = 7.5 Hz, 2H, CH_2), 2.06 (m, 4H, CH_2), 1.63 (m, 2H, CH_2), 1.31 (m, 8H, CH_2), 0.97 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 180.3, 131.9, 130.2, 128.21, 128.17, 127.7, 127.0, 34.0, 29.5, 29.1, 29.04, 28.99, 27.2, 25.3 (t, J = 19.5 Hz), 25.2 (t, J = 19.5 Hz), 24.6, 20.5, 14.2.

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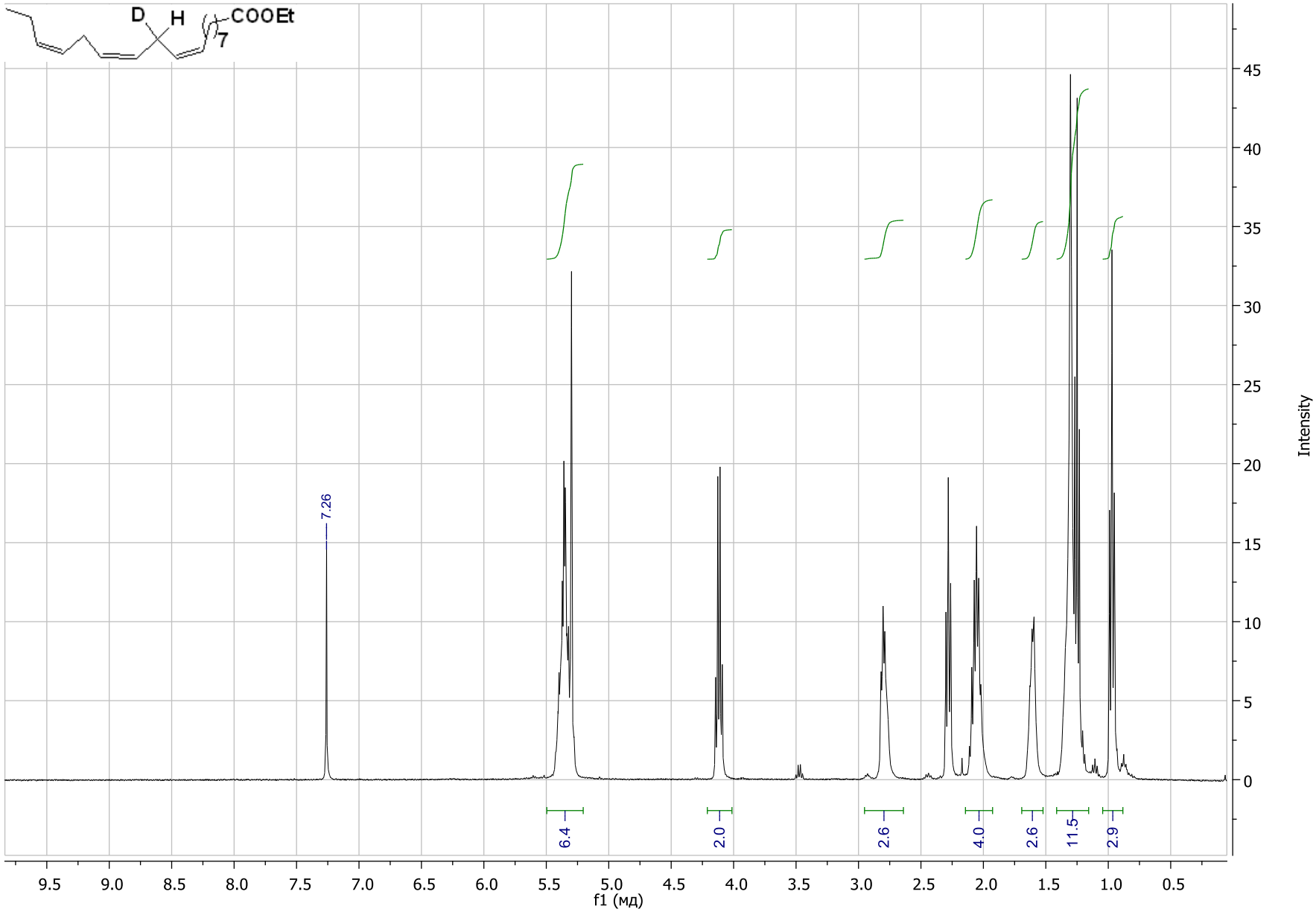
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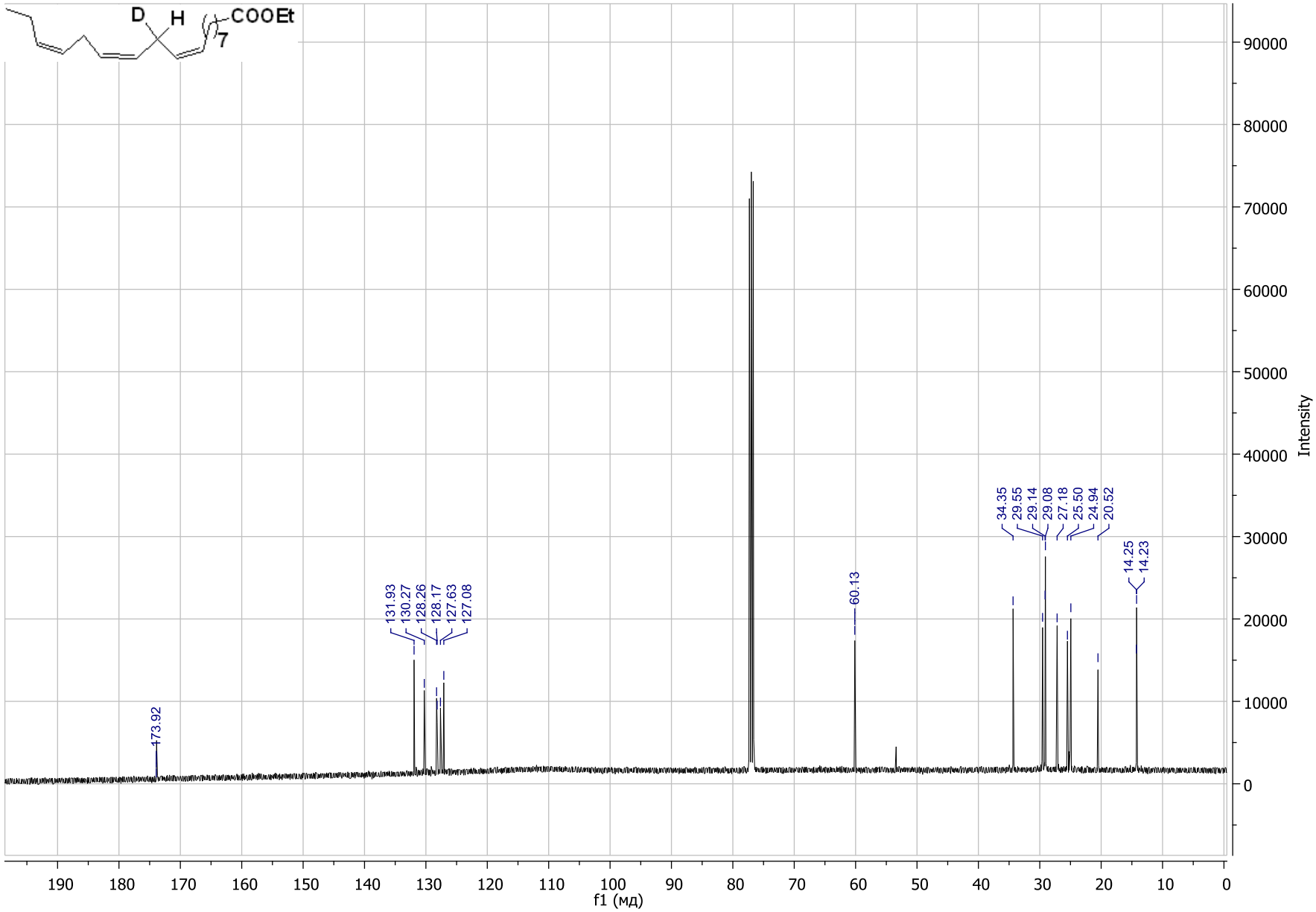
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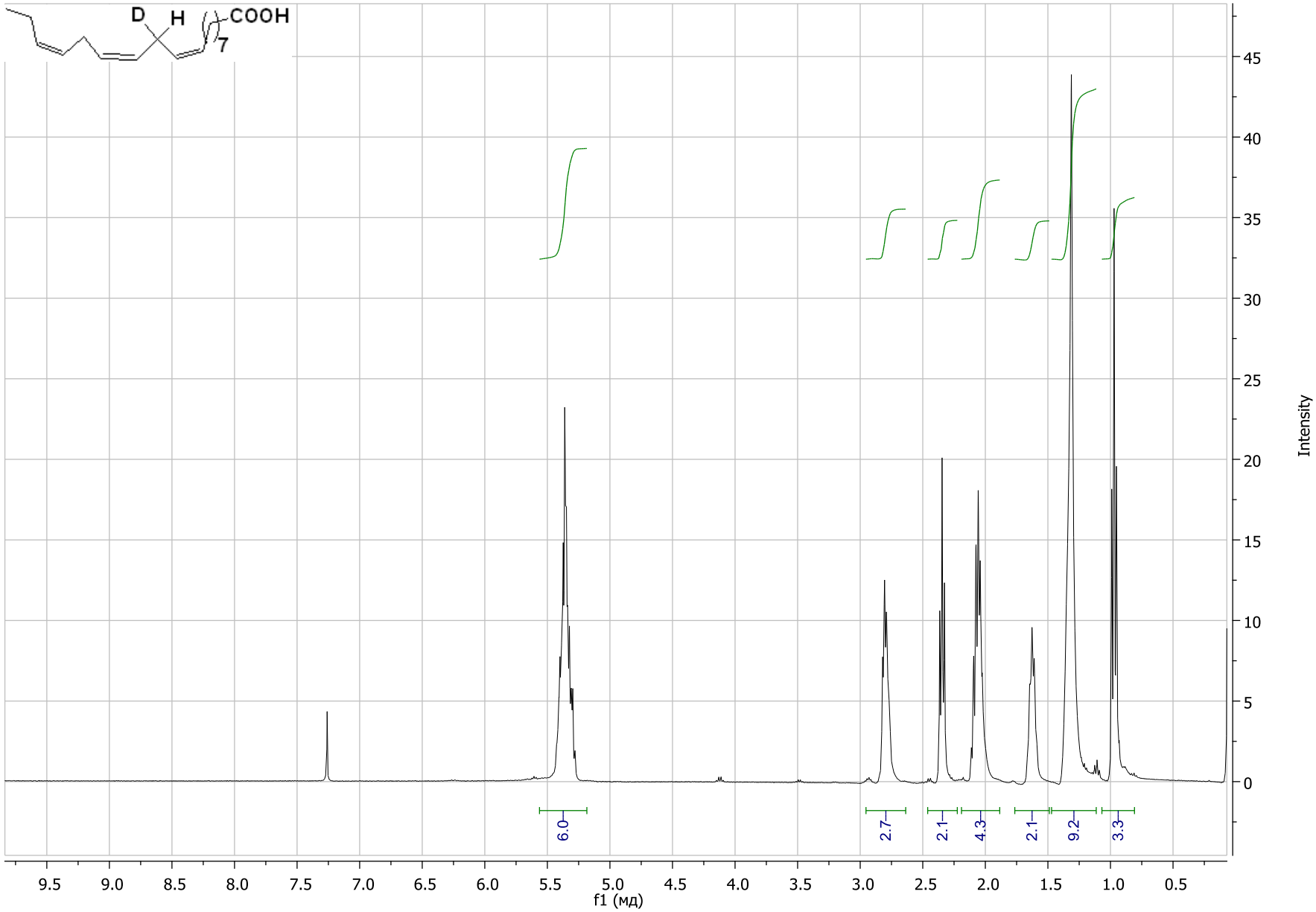
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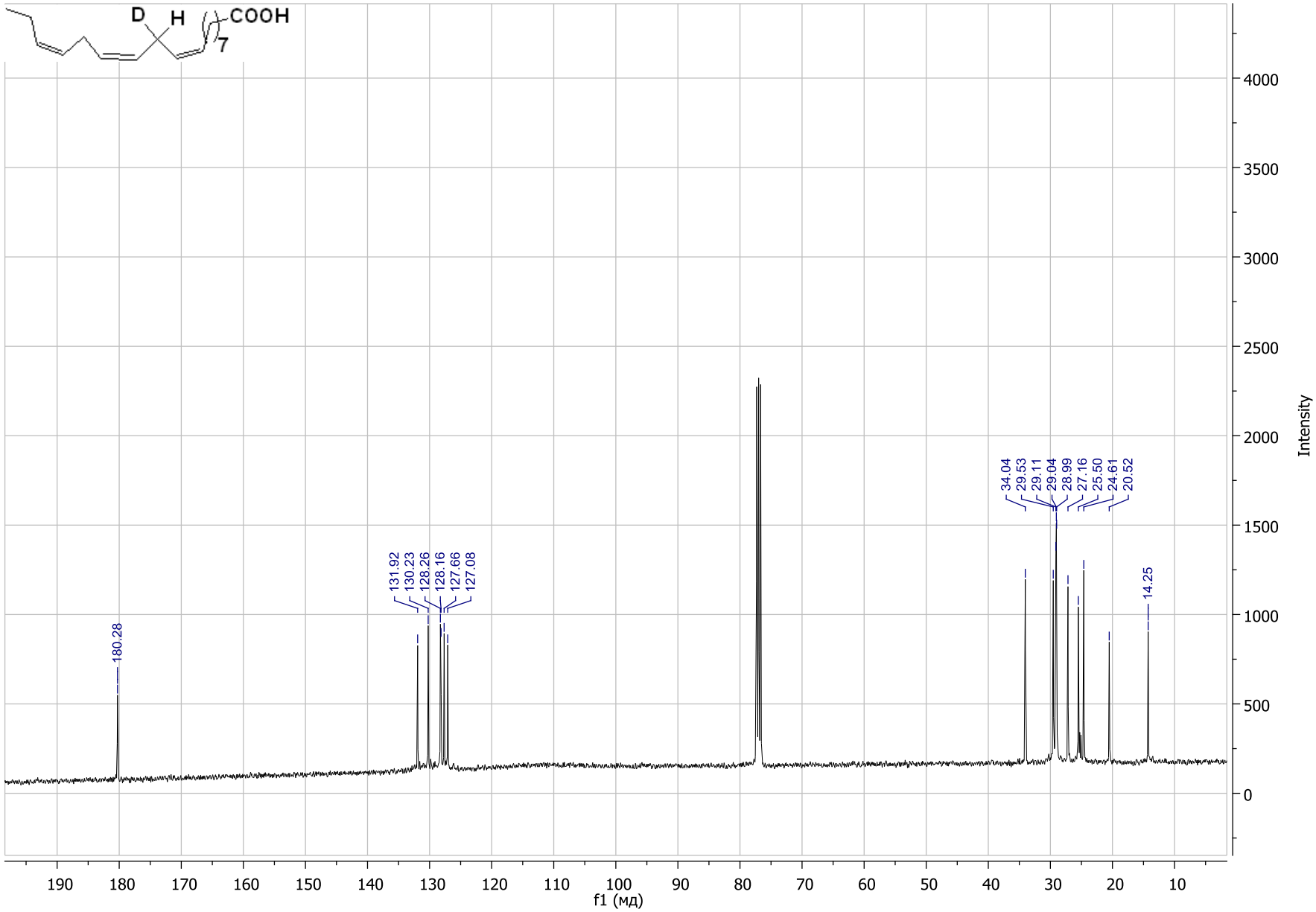
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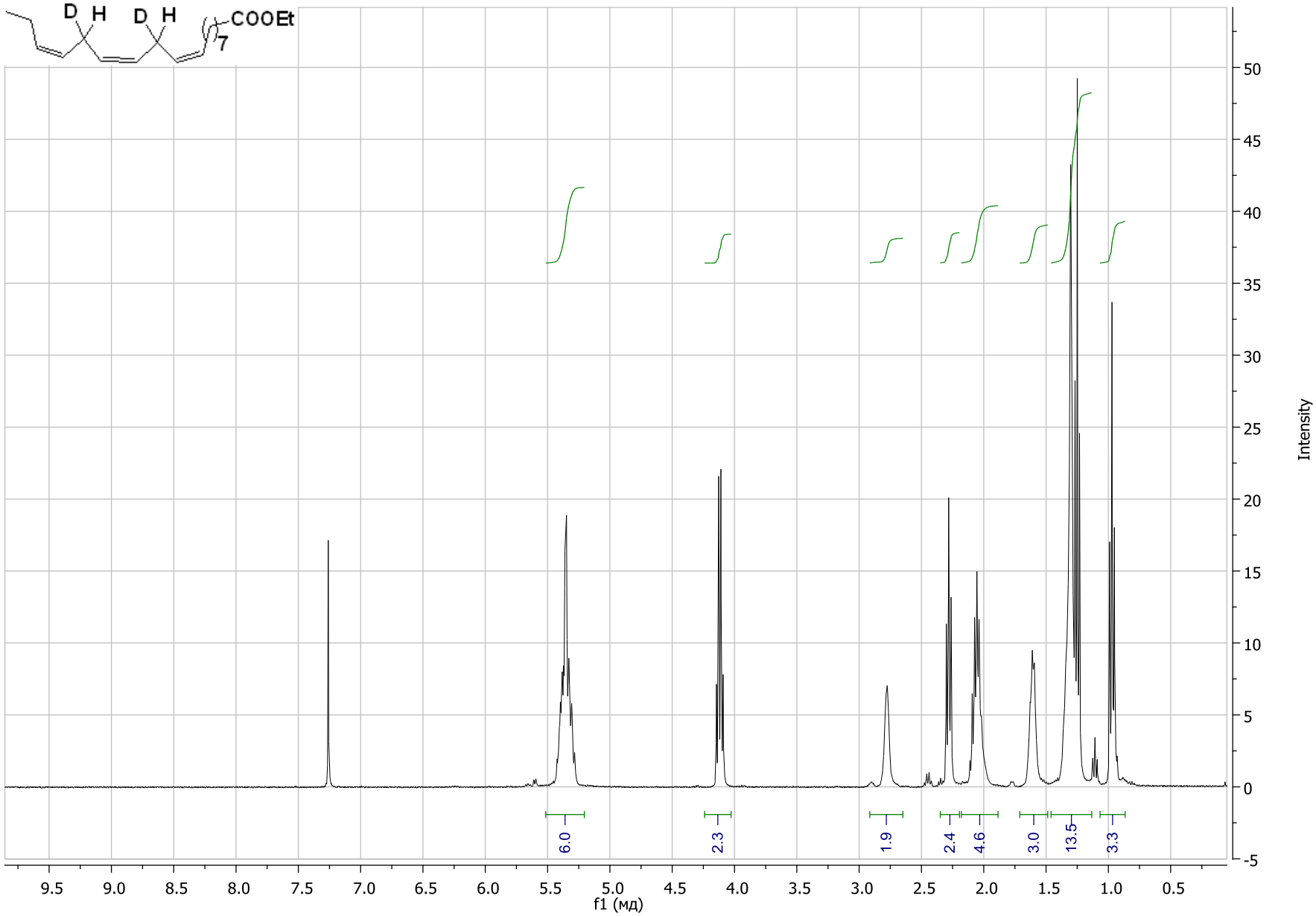
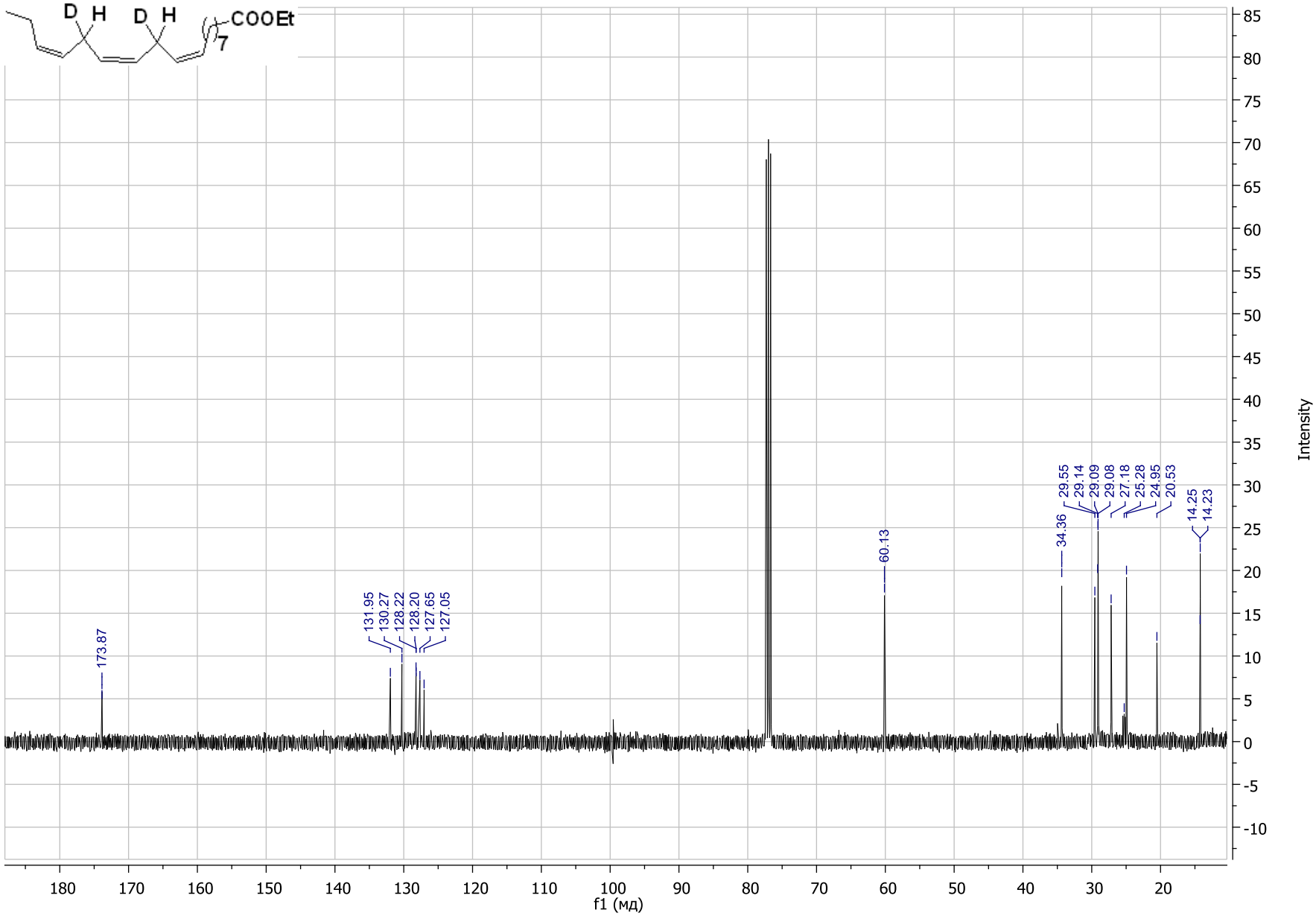
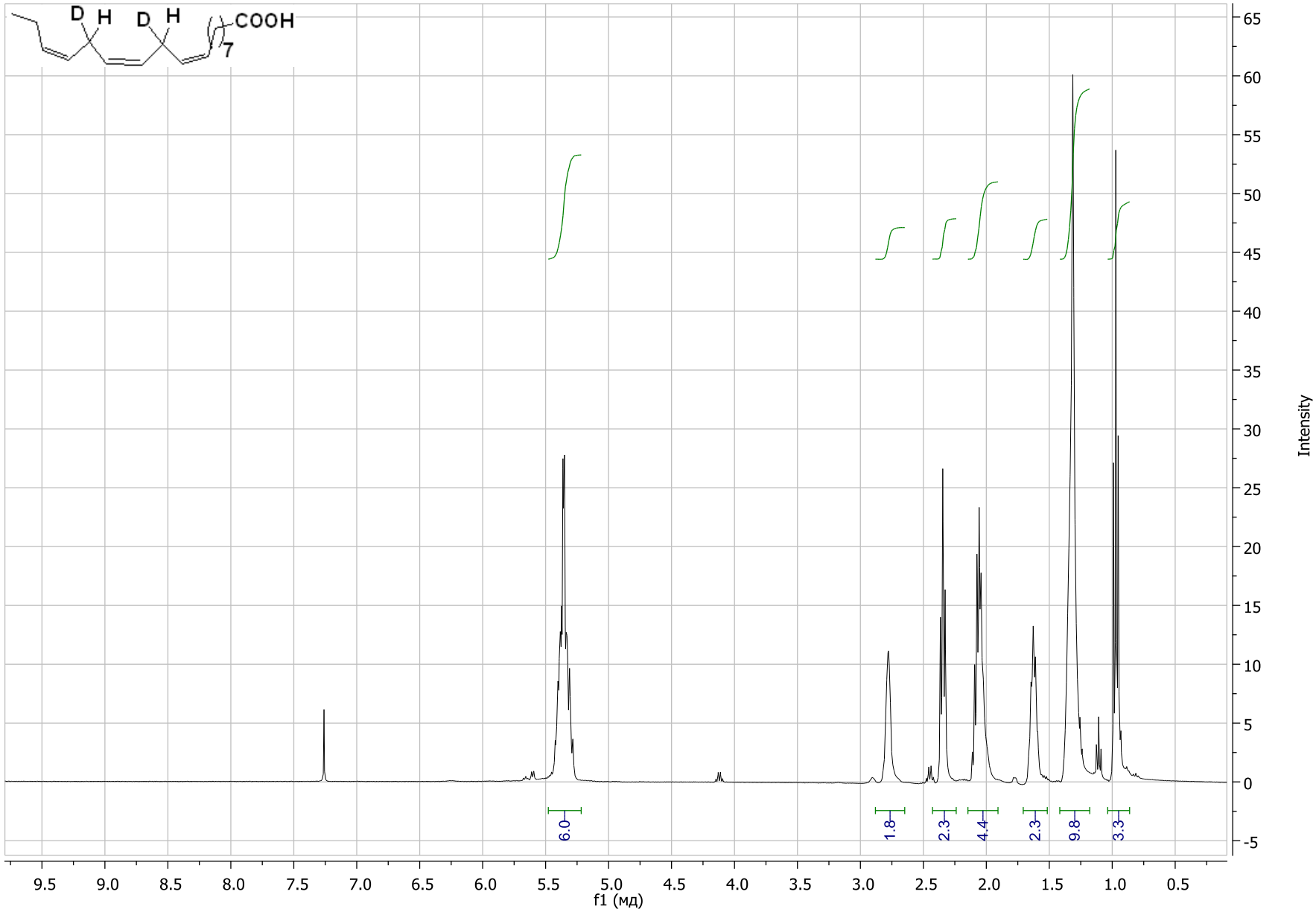
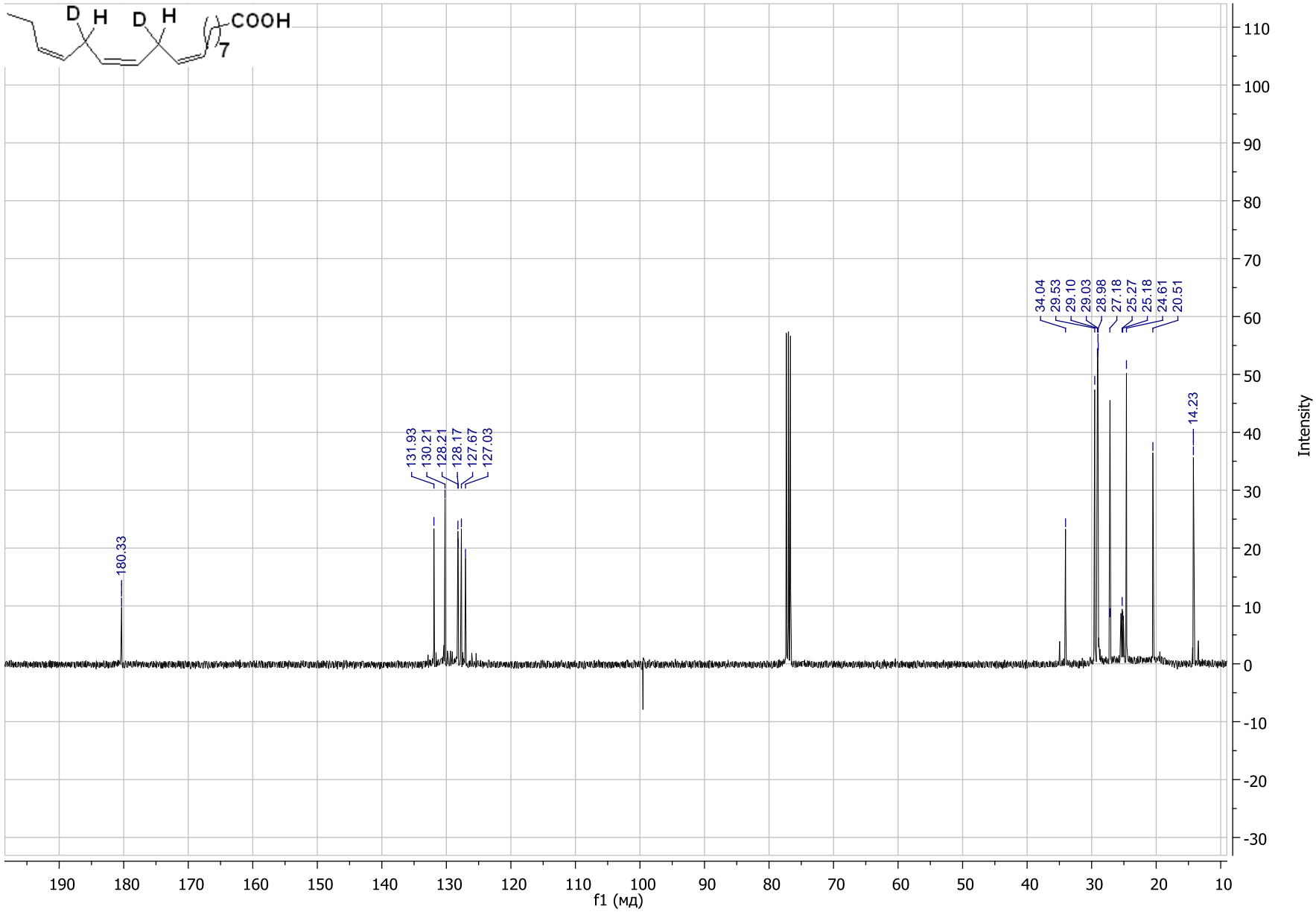
130.23
128.26
128.16
127.66
127.08
34.04
29.53
29.11
29.04
28.99
27.16
25.50
24.61
20.52
14.25
Intensity
f1 (мд)


D H D H
COOEt
7
6.0
2.3
1.9
2.4
4.6
3.0
13.5
3.3
f1 (мд)
Intensity

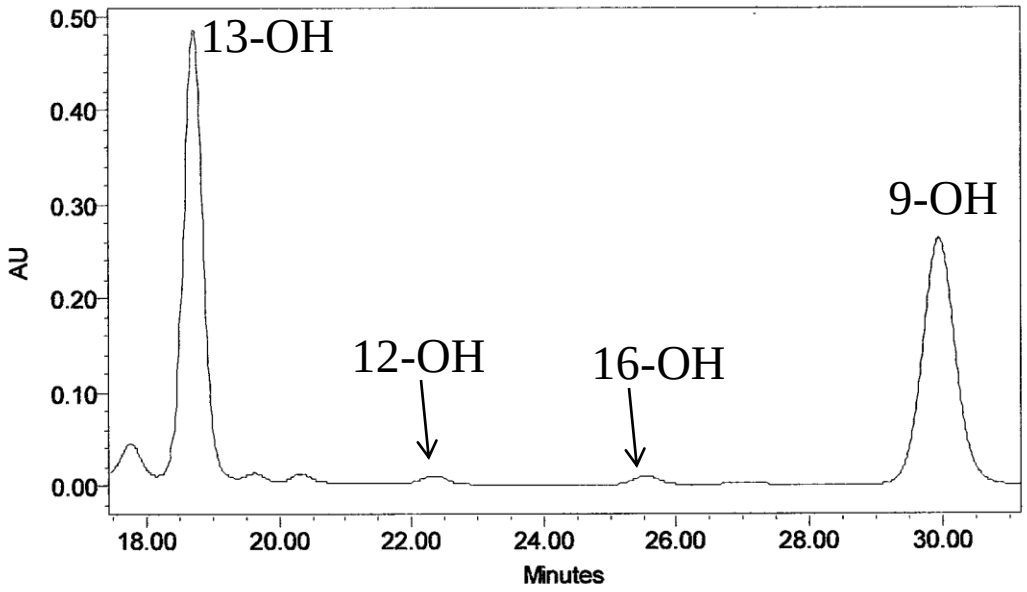

D H D H
COOEt
7
173.87
131.95
130.27
128.22
128.20
127.65
127.05
60.13
34.36
29.55
29.14
29.09
29.08
27.18
25.28
24.95
20.53
14.25
14.23
f1 (мд)
Intensity


D H D H COOH
7
6.0
1.8
2.3
4.4
2.3
9.8
3.3
f1 (мд)
Intensity

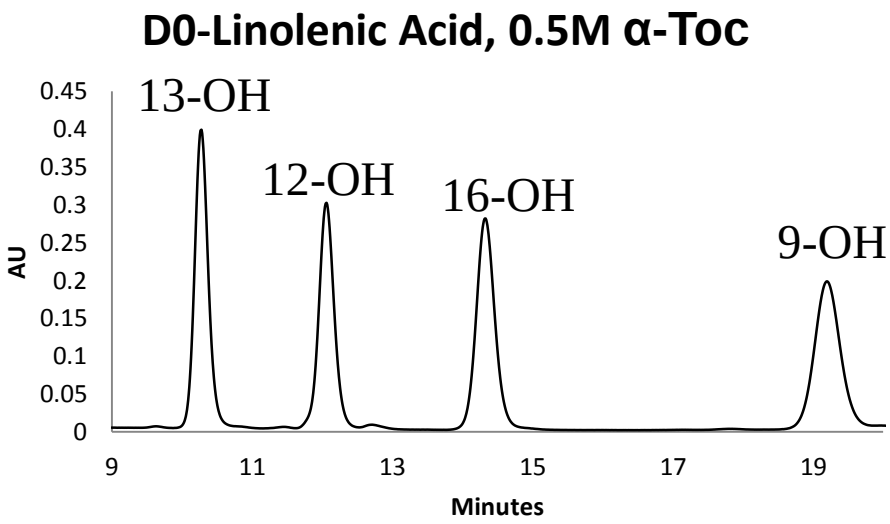

D H D H COOH
7
180.33
131.93
130.21
128.21
128.17
127.67
127.03
34.04
29.53
29.10
29.03
28.98
27.18
25.27
25.18
24.61
20.51
14.23
Intensity
f1 (мд)

Typical Chromatograms/Mass Spectrum

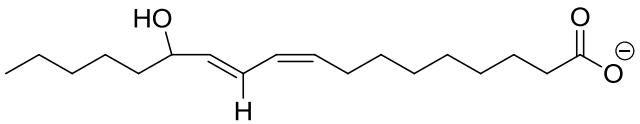
14-D2-Lnn Methyl Ester



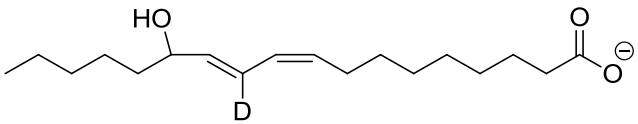
D0-Linolenic Acid + 0.5 M α-Toc



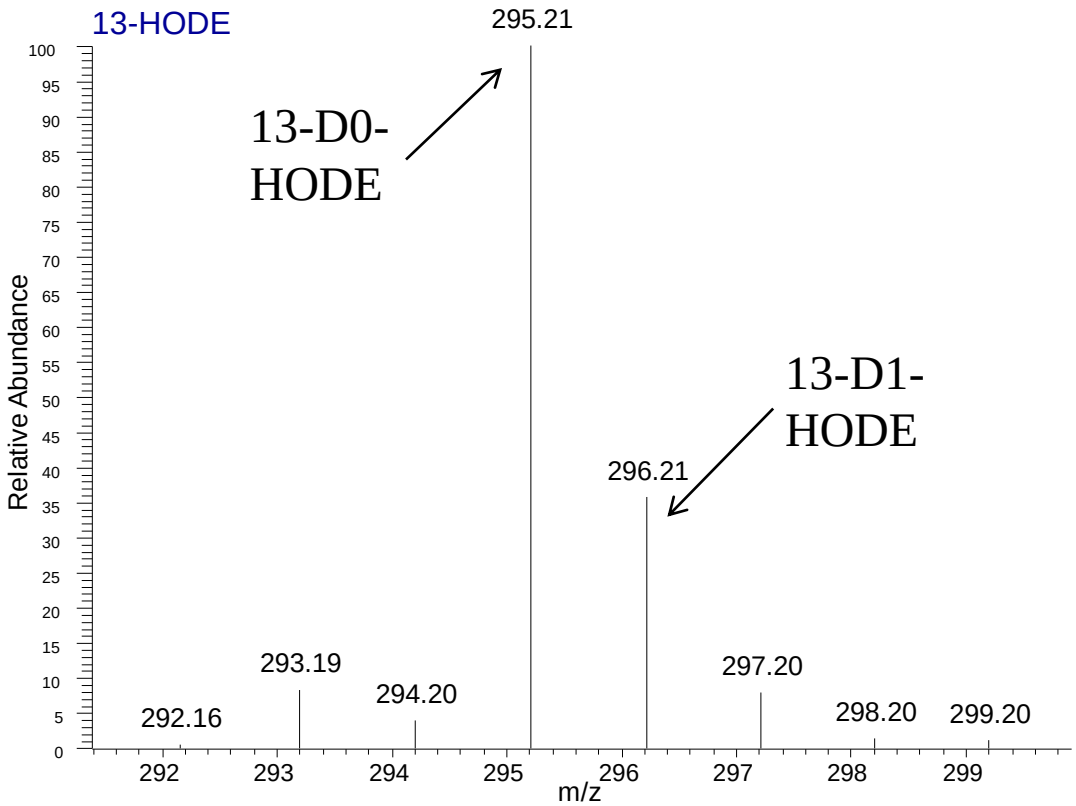
D0/D2-LA (1:5.1) CoOx
13-HODE



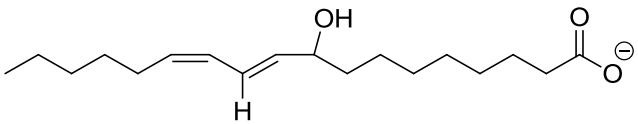
Chemical Formula: $C_{18}H_{31}O_3^-$
Exact Mass: 295.23



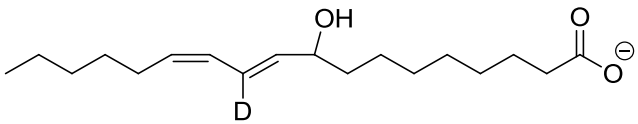
Chemical Formula: $C_{18}H_{30}DO_3^-$
Exact Mass: 296.23



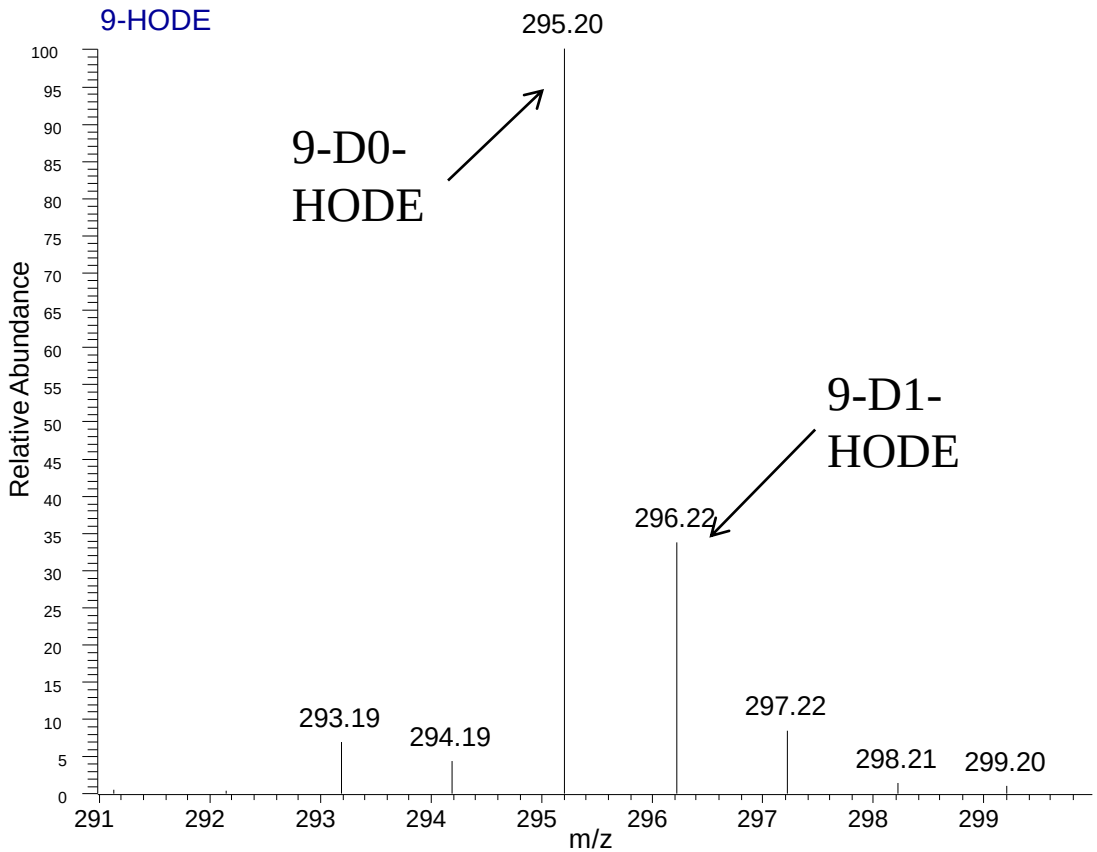
D0/D2-LA (1:5.1) CoOx 9-HODE



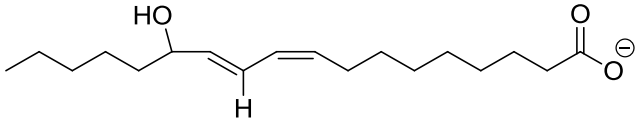
Chemical Formula: $C_{18}H_{31}O_3^-$
Exact Mass: 295.23



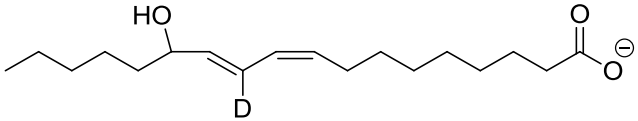
Chemical Formula: $C_{18}H_{30}DO_3^-$
Exact Mass: 296.23



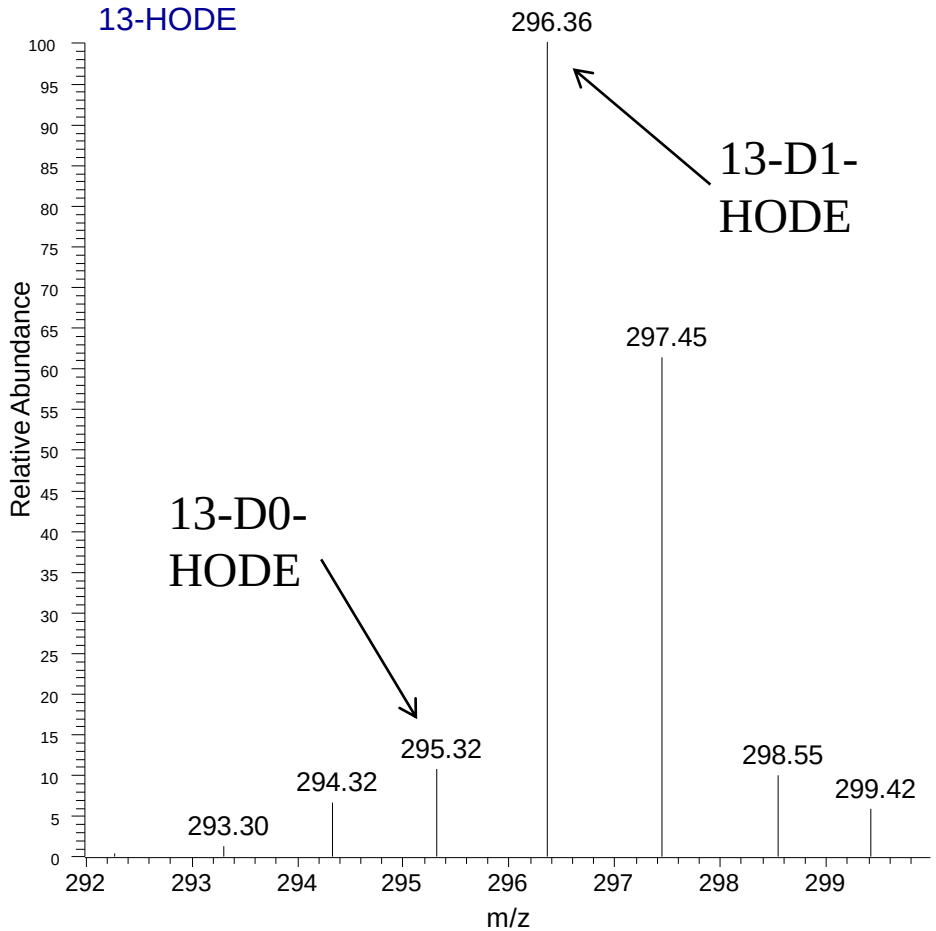
11-D1-LA
13-HODE



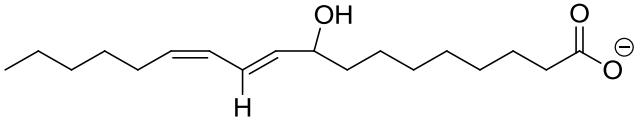
Chemical Formula: $C_{18}H_{31}O_3^-$
Exact Mass: 295.23



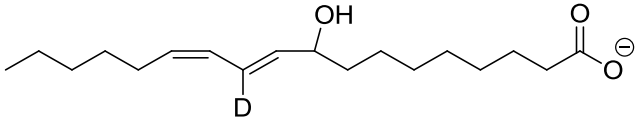
Chemical Formula: $C_{18}H_{30}DO_3^-$
Exact Mass: 296.23



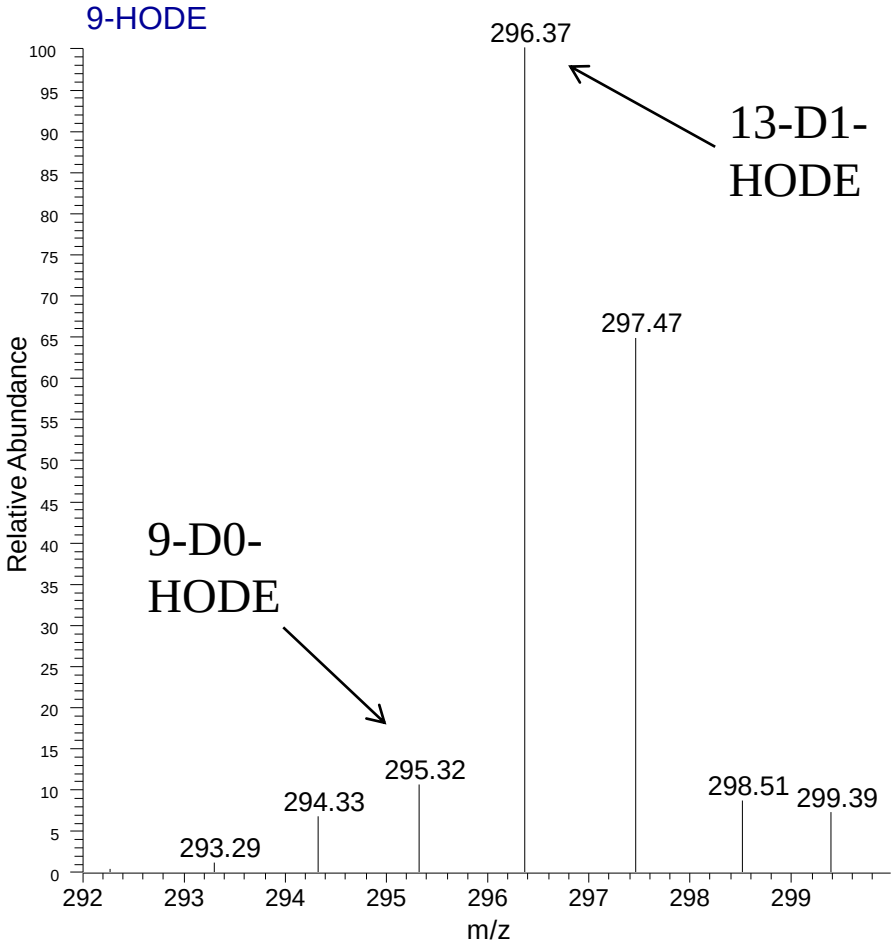
11-D1-LA
9-HODE



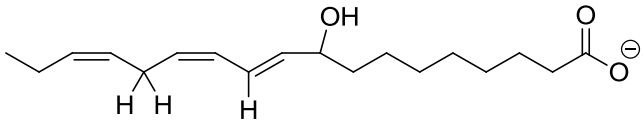
Chemical Formula: $C_{18}H_{31}O_3^-$
Exact Mass: 295.23



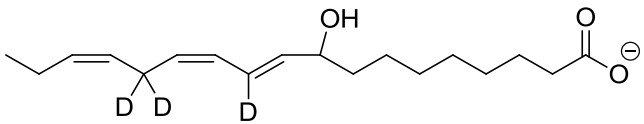
Chemical Formula: $C_{18}H_{30}DO_3^-$
Exact Mass: 296.23



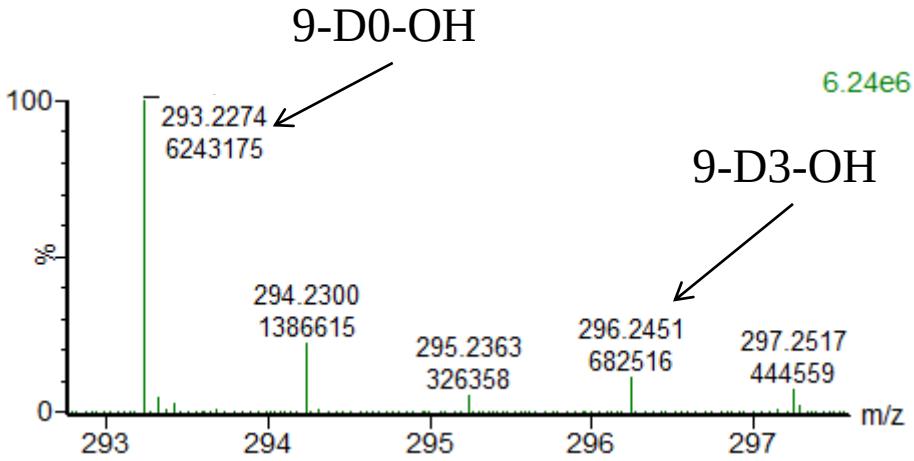
D0/D4-Ln (1:4) CoOx
9-OH



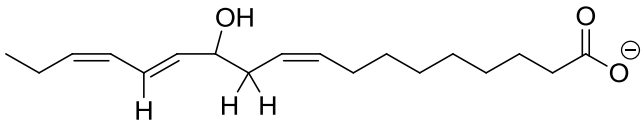
Chemical Formula: $C_{18}H_{29}O_3^-$
Exact Mass: 293.21



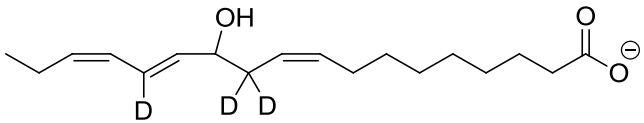
Chemical Formula: $C_{18}H_{26}D_3O_3^-$
Exact Mass: 296.23



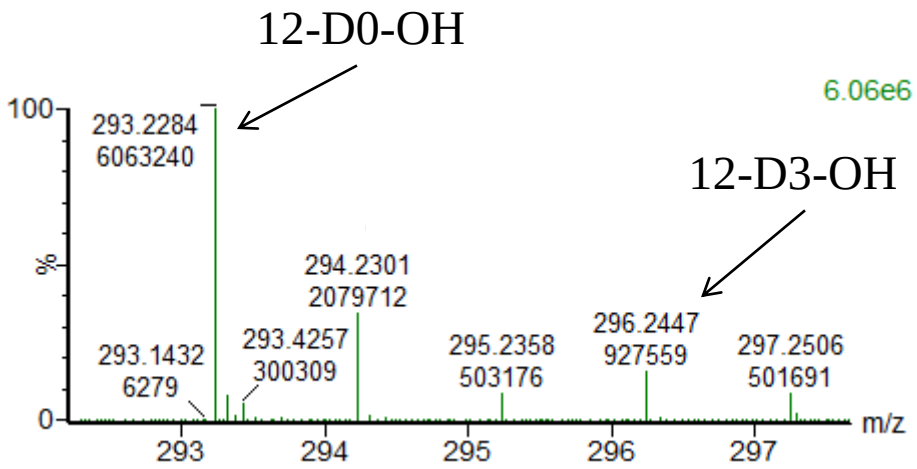
D0/D4-Ln (1:4) CoOx 12-OH



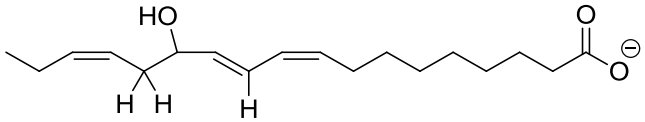
Chemical Formula: $C_{18}H_{29}O_3^-$
Exact Mass: 293.21



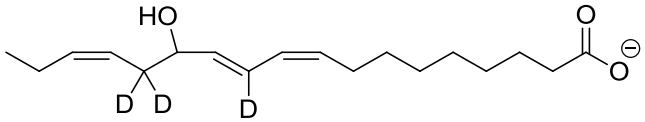
Chemical Formula: $C_{18}H_{26}D_3O_3^-$
Exact Mass: 296.23



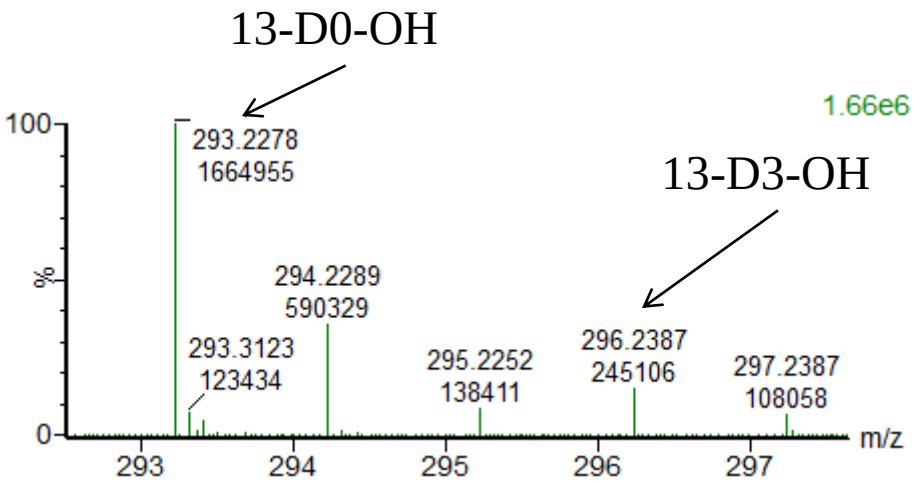
D0/D4-Ln (1:4) CoOx 13-OH



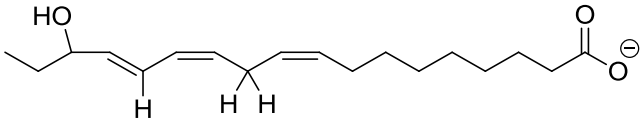
Chemical Formula: $C_{18}H_{29}O_3^-$
Exact Mass: 293.21



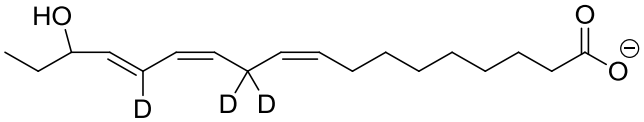
Chemical Formula: $C_{18}H_{26}D_3O_3^-$
Exact Mass: 296.23



D0/D4-Ln (1:4) CoOx 16-OH



Chemical Formula: $C_{18}H_{29}O_3^-$
Exact Mass: 293.21



Chemical Formula: $C_{18}H_{26}D_3O_3^-$
Exact Mass: 296.23