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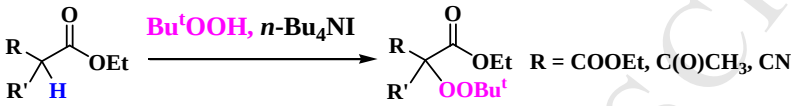

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Organocatalytic peroxidation of malonates, β-ketoesters, and cyanoacetic esters using *n*-Bu_4NI / *t*-BuOOH-mediated intermolecular oxidative C(sp^3)–O coupling

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ABSTRACT

A new organocatalytic approach for the synthesis of peroxides based on CH activation of a sp^3-hybridized carbon atom is reported. Peroxides were prepared in 31 – 89 % yield by the reaction of malonates, β-ketoesters, and cyanoacetic esters with a Bu_4NI / *tert*-butyl hydroperoxide system. The formation of the expected hydroxylation products was not observed. In the discovered reaction, *tert*-butyl hydroperoxide plays a dual role by acting as the oxidant and the O-reagent for the C-O coupling. The synthesis can be scaled up to generate gram quantities of the target products.

1. Introduction

Organic peroxides are widely used as radical polymerization initiators in the industrial synthesis of polymers such as polystyrene, polyvinyl chloride, polyacrylates, and polyethylene. A wide variety of commercial monomers and their composites requires for polymerization a wide assortment of peroxides, the most well-known of which are peroxy esters, peroxydicarbonates, peroxycarbonates, peracetals, cyclic triperoxides, organic hydroperoxides, dialkyl peroxides, diacyl peroxides, and geminal bishydroperoxides.[1,2] In the past decades, organic peroxides have received attention from researchers in the field of medicinal chemistry because these compounds were found to possess pronounced antimalarial,[3] anthelmintic,[4] and antitumor activities.[5] Peroxides obtained from lower aldehydes and ketones are attracting interest also as explosive compounds.[6]

The preparation of radical polymerization initiators and biologically active compounds is the major impetus for the development of new methods for the synthesis of peroxides. The present study is a part of our continuing research on the peroxidation of dicarbonyl compounds.[7] Earlier, it has been found that transition metals catalyze the peroxidation of β-dicarbonyl compounds at the α-position by *tert*-butyl hydroperoxide.[7a,b] In this study, we performed the organocatalytic peroxidation of malonates, β-ketoesters, and cyanoacetic esters at the α-position using the Bu_4NI / *tert*-butyl hydroperoxide system. This is a new approach for the synthesis of peroxides based on CH activation of a sp^3-hybridized carbon atom, which is generally accomplished by autooxidation, or under the action of hydroperoxides combined with variable-valence metal ions. Until recently, only the following two examples of peroxidation by the Bu_4NI / *tert*-butyl hydroperoxide system were described: the synthesis of peroxy esters from aldehydes (CH activation of a sp^2-hybridized carbon atom) [8a] and the peroxidation of C−H bonds adjacent to the amide nitrogen (CH activation of a sp^3-hybridized carbon atom).[8b]

The Bu_4NI / *tert*-butyl hydroperoxide system has been extensively studied in recent years.[9] It is assumed that a number of various reactive species are generated in this system, such as O-centered radicals and oxidized iodine species. Owing to this fact, this system is used in the oxidative synthesis resulting in the formation of C-C,[10] C-N,[11] C-S[12] and C-O[9f, 13] bonds.

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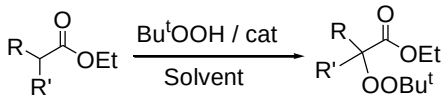
2. Results and discussion

Malonates **1a-h**, β-ketoesters **3a-d**, and cyanoacetic esters **5a-d** substituted at the α-position were used as the starting reagents for the synthesis of target peroxides **2a-h, 4a-d, 6a-d** (Scheme 1).



1a-h
3a-d
5a-d

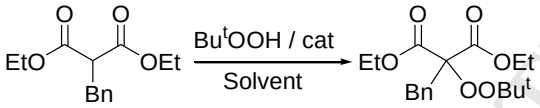
2a-h
4a-d
6a-d

1a, 2a: R = COOEt, R' = Me;
1b, 2b: R = COOEt, R' = Et;
1c, 2c: R = COOEt, R' = n-Bu;
1d, 2d: R = COOEt, R' = Bn;
1e, 2e: R = COOEt, R' = allyl;
1f, 2f: R = COOEt, R' = Ph;
1g, 2g: R = COOEt, R' = $CH_2CH_2C(O)CH_3$;
1h, 2h: R = COOEt, R' = CH_2CH_2CN;
3a, 4a: R = $CH_3C{=}O$, R' = Me;
3b, 4b: R = $CH_3C{=}O$, R' = n-Bu;
3c, 4c: R = $CH_3C{=}O$, R' = Bn;
3d, 4d: R = $CH_3C{=}O$, R' = $CH_2CH_2C(O)CH_3$;
5a, 6a: R = CN, R' = Bu;
5b, 6b: R = CN, R' = Bn;
5c, 6c: R = CN, R' = allyl;
5d, 6d: R = CN, R' = CH_2CH_2COOEt

Scheme 1. Synthesis of peroxides from malonates **1a-h**, β-ketoesters **3a-d**, and cyanoacetic esters **5a-d**.

A search for the conditions of peroxidation of diethyl benzylmalonate **1d** to form diethyl 2-benzyl-2-(*tert*-butylperoxy)malonate **2d** was performed using the catalysts Bu_4NI, Me_4NI, I_2, and KI in CH_3CN, EtOH, DMF, 1,2-dichloroethane, and benzene (Table 1).

Table 1. Peroxidation of diethyl benzylmalonate **1d** by *tert*-butyl hydroperoxide.



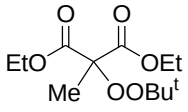
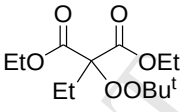
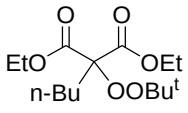
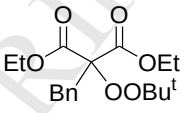
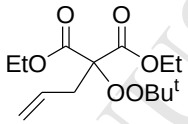
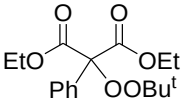
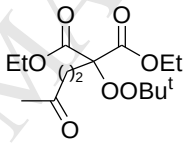
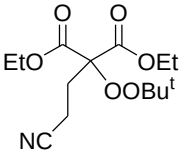
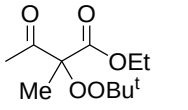
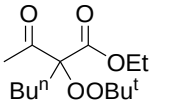
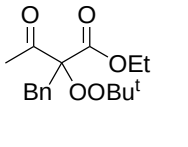
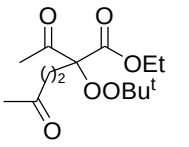
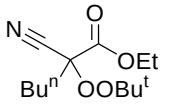
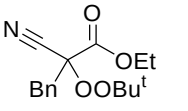
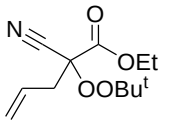
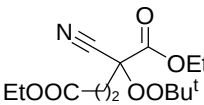
1d **2d**

Entry	Catalyst, % mol	Solvent	Yield of **2d**, %
1	Bu_4NI, 50	CH_3CN	80
2	Bu_4NI, 20	CH_3CN	85
3	Bu_4NI, 10	CH_3CN	60
4	Bu_4NI, 20	PhH	44
5	Bu_4NI, 20	EtOH	19
6	Bu_4NI, 20	1,2-Dichloroethane	16
7	Bu_4NI, 20	DMF	traces
8	Me_4NI, 50	CH_3CN	83
9	I_2, 50	CH_3CN	traces
10	KI, 50	CH_3CN	traces

General reaction conditions: 78-80 °C, 6 h, 3 mol of 70% aq. Bu^{t}OOH per mole of **1d**

In entries 1-3, performed in CH_3CN, the effect of the amount of the catalyst was studied; a 20% loading of the catalyst with respect to **1d** was found to be the optimal amount (entry 2). In entries 4-7, the possibility of using other solvents was examined; a moderate result was obtained using benzene (entry 4), while in ethanol, 1,2-dichloroethane, and dimethylformamide, the yield of **2d** was much lower (entries 5-7). In entries 8-10, other iodine-containing catalysts were examined, the related Me_4NI (entry 8) proved to be a good catalyst, whereas peroxidation in the presence of I_2 (entry 9) and KI (entry 10) was negligible. Using the optimised reaction conditions of entry 2 (Table 1), peroxides **2a-h, 4a-d, 6a-d** were synthesized (Table 2).

Table 2. Structures and yields of peroxides **2a-h**, **4a-d**, and **6a-d**.

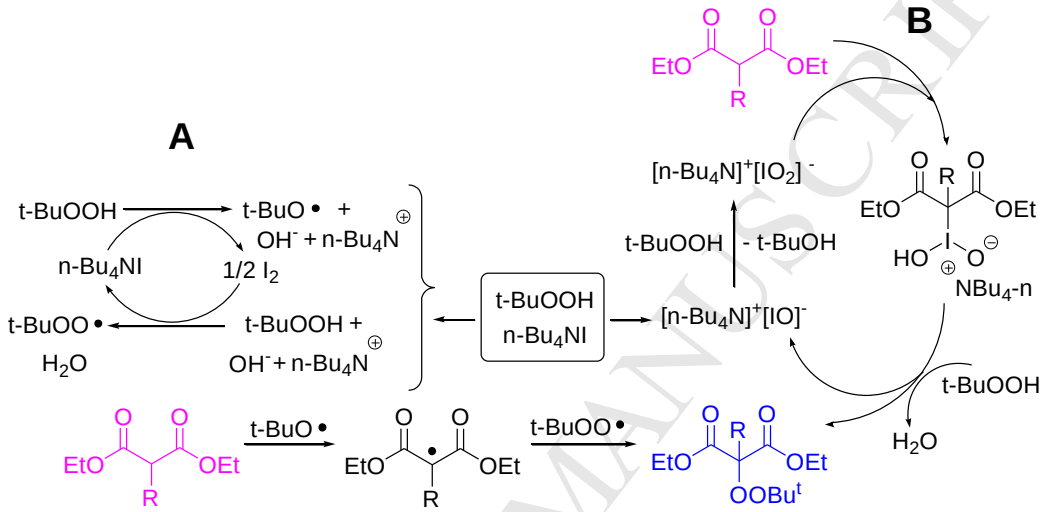
 **2a**, 76	 **2b**, 73
 **2c**, 83	 **2d**, 85 (81)[a]
 **2e**, 67	 **2f**, 89
 **2g**, 83	 **2h**, 83
 **4a**, 38	 **4b**, 47
 **4c**, 35	 **4d**, 33
 **6a**, 35	 **6b**, 39
 **6c**, 31	 **6d**, 42

[a] The experiment was scaled up by increasing the amounts of the reagents by a factor of five.

Based on the results presented in Table 2, it can be concluded that the Bu_4NI-catalyzed peroxidation provides a versatile approach to the synthesis of structurally different α-*tert*-butylperoxy malonates **2a-h**, β-ketoesters **4a-d**, and cyanoacetic esters **6a-d**. The yield of the resulting α-peroxidated malonates **2a-h** varies from 67 to 89%, or a range of substrates, including those containing reactive groups, such as CH_2 in the benzyl moiety and the allyl, carbonyl and nitrile groups. The yields of peroxides **4a-d** and **6a-d**, prepared from β-ketoesters **3a-d** and cyanoacetic esters **5a-d** were approximately two times lower, in comparison with **2a-h.** Attempts to peroxidise β-diketones (3-benzylpentane-2,4-dione and 3-butylpentane-2,4-dione) were unsuccessful; only complex mixtures of products were obtained.

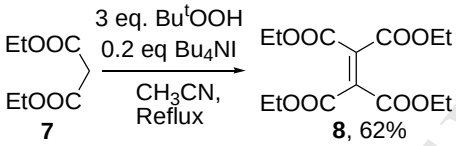
Plausible peroxidation mechanisms.

The published data suggest that the reaction may proceed by two different pathways. One of them (pathway A) is based on the formation of t-BuOO• and t-BuO• radicals in the Bu_4NI / t-BuOOH system followed by the generation of a C-centered radical from malonic ester and the recombination of the latter radical with the t-BuOO• radical to form the target peroxide.[8] Another pathway (pathway B) involves the oxidation of Bu_4NI to give $[Bu_4N]^+[IO]^-$ and then $[Bu_4N]^+[IO_2]^-$, which reacts with malonic ester at the α-position to form $[Bu_4N]^+[(COOEt)_2CH\text{-}I(OH)O]^-$. The final step is the replacement of hypervalent iodine bound to the organic moiety by *tert*-butyl hydroperoxide [14] (Scheme 2).



Scheme 2. Plausible peroxidation mechanisms in the example of malonates. Free radical pathway **A** and ionic pathway **B**.

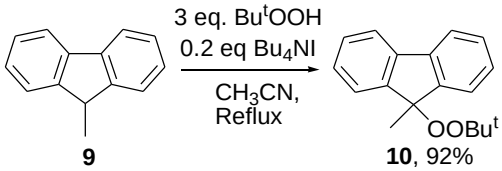
Based on literature data, pathways **A** [8] and **B** [14] are indirectly confirmed by the formation of dehydrogenated dimer **8** from malonic ester **7** (Scheme 3).



Scheme 3. Transformation of malonic ester **7** to tetraethyl ethene-1,1,2,2-tetracarboxylate **8**.

C-centered radicals formed *via* pathway **A** can dimerize with following oxidative dehydration with formation of product **8**. Product **8** can also be formed through nucleophilic substitution of iodine-containing moiety by malonate anion in iodinated intermediate prepared by pathway **B** with following oxidative dehydration.

Evidence to support pathway **A** concludes in the formation of 9-(*tert*-butylperoxy)-9-methyl-9*H*-fluorene **10** from 9-methyl-9*H*-fluorene **9** (Scheme 4).



Scheme 4. Transformation of 9-methyl-9*H*-fluorene **9** in to 9-(*tert*-butylperoxy)-9-methyl-9*H*-fluorene **10**.

Peroxide **10** is apparently formed via the abstraction of a hydrogen atom from CH fragment with formation of C-centered radical followed by the recombination of the latter radical with the t-BuOO• radical. The benzylic position is traditionally considered as a point for free radical reactions when free radical initiators are applied. Another evidence to support pathway **A** results from an additional experiment on catalyst isolation after peroxidation of diethyl benzylmalonate **1d**. Bu_4NI was isolated in 75% yield. In such a way pathway **B** seems to be less plausible, however based on the literature data it cannot be excluded.[14] Apparently, the mechanism of Bu_4NI-mediated peroxidation of β-dicarbonyl compounds differs essentially from that of transition metal-mediated peroxidation.[7b] In the metal-catalyzed reaction following reactivity order was observed: β-diketones>β-ketoesters>malonic esters.[7b] On the contrary, Bu_4NI-mediated reaction proceeds optimally with malonic esters, moderately with β-ketoesters, and peroxidations of β-diketones were unsuccessful.

3. Conclusions

A new approach is reported for the synthesis of peroxides from malonates, β-ketoesters, and cyanoacetic esters using the organocatalytic Bu_4NI / *tert*-butyl hydroperoxide system and activation of a $C(sp^3)$-H bond. α-*tert*-Butyl peroxides were prepared in 31 – 89 % yields. The synthesis can be scaled up to yield gram quantities of the target products.

4. Experimental section

Caution: Although we have encountered no difficulties in working with peroxides, precautions, such as the use of

shields, fume hoods, and the avoidance of heating and shaking, should be taken whenever possible.

^{1}H NMR spectra were recorded on a Bruker AM300 instrument (300.13 MHz for ^{1}H and 75.48 MHz for ^{13}C) in a $CDCl_3$ solution. Commercial diethyl ethylmalonate **1b**, diethyl phenylmalonate **1f**, diethyl malonate **7**, ethyl methylacetoacetate **3a**, 9-methylfluorene **9,** a 70 % aqueous solution of t-BuOOH, Bu_4NI, Me_4NI, I_2, and KI (Acros) were used as-is. Acetonitrile, 1,2-dichloroethane, and ethyl acetate (EA) were distilled over P_2O_5 before use. Benzene and petroleum ether (PE) (40/70) were distilled over Na before use. Ethanol 96% was used without additional purification. The filtration and column chromatography were performed on silica gel (0.060–0.200 mm, 60 A, Acros); MeCN (HPLC grade) for ESI-HRMS experiments was purchased from Merck and was used as-is. High-resolution mass spectra were recorded on a Bruker maXis instrument equipped with an electrospray ionization (ESI) ion source.[15] All measurements were carried out in positive (+MS) ion mode (interface capillary voltage e 4500 V) with the *m*/*z* scan range of 50 - 3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). The direct syringe injection was used for all the analyzed solutions in MeCN (flow rate 3 μL/min). Nitrogen was used as both the nebulizer gas (0.4 bar) and the dry gas (4.0 L/min); the interface temperature was set at 180 °C. Malonic esters **1a, 1c, 1d, 1e, 1g,** and **1h** were prepared according to known procedures.[7b] β-ketoesters **3b-d** and cyanoacetic esters **5a-d** were prepared as described [7a,b].

Synthesis of diethyl benzyl(*tert*-butylperoxy)malonate 2d (Table 1): To a solution of diethyl benzylmalonate **1d** (0.50 g, 2.00 mmol) in acetonitrile (10 mL) 70% t-BuOOH (0.77 g, 6.00 mmol) was added. The mixture was heated to reflux, and then Bu_4NI (0.07-0.37 g, 0.20-1.00 mmol), Me_4NI (0.20 g, 1.00 mmol), I_2 (0.25 g, 1.00 mmol), or KI (0.17 g, 1.00 mmol) was added. The solution was refluxed for 6 h. The solvent was removed under water aspirator pressure. The suspension that formed was diluted with diethyl ether (20 mL), and the precipitate was filtered using silica gel. The solvent was removed under water aspirator pressure. Product **2d** was isolated by chromatography on silica gel, eluting with PE-EtOAc (10/1).

General conditions for synthesis of peroxides 2a-h, 4a-d, and 6a-d (Table 2): To a solution of malonate **1a-h, 3a-d, 5a-d** (2.00 mmol) in acetonitrile (10 mL), 70% t-BuOOH (0.77 g, 6.00 mmol) was added. The mixture was heated to reflux, and then Bu_4NI (0.15 g, 0.40 mmol) was added. The solution was refluxed for 6 h. Products **2a-h, 4a-d,** and **6a-d** were isolated as described above.

Large-scale synthesis of diethyl benzyl(*tert*-butylperoxy)malonate 2d (Table 2): To a solution of diethyl benzylmalonate **1d** (2.50 g, 10.1 mmol) in acetonitrile (50 mL), 70% t-BuOOH (3.86 g, 30.0 mmol) was added. The mixture was heated to reflux, and then Bu_4NI (0.74 g, 2.00 mmol) was added. The solution was refluxed for 6 h. The solvent was removed under water aspirator pressure. The suspension that formed was diluted with diethyl ether (100 mL), and the precipitate was filtered using silica gel. The solvent was removed under water aspirator pressure. Product **2d** was isolated by chromatography on silica gel, eluting with PE-EtOAc (10/1). Yield of **2d** is (2.77 g, 8.20 mmol, 81 %).

Diethyl (*tert*-butylperoxy)(methyl)malonate 2a: Colorless oil. ^{1}H NMR 300.15 MHz, $CDCl_3$): δ = 1.22 (s, 9H, $C(CH_3)_3$), 1.25 (t, $J_{H\text{-}H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 1.66 (s, 3H,CCH_3), 4.21 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, $OC\underline{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 ($OCH_2\underline{C}H_3$), 19.6 ($C\underline{C}H_3$), 26.4 ($C(\underline{C}H_3)_3$), 61.7 ($O\underline{C}H_2CH_3$), 80.8 ($\underline{C}(CH_3)_3$), 84.9 ($CH_3\underline{C}$), 168.0 (CO). Calculated for $C_{12}H_{22}O_6$: % C 54.95; % H 8.45; found: % C 54.93; % H 8.43. HRMS-ESI: calculated 285.1309 [$C_{12}H_{22}O_6$+Na] found 285.1315 (Δ = 2.1 ppm). IR (film): 1749 (vs, υ_{CO}) cm^{-1}.

Diethyl (*tert*-butylperoxy)(ethyl)malonate 2b: Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 0.83 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H, $C\underline{H}_3CH_2$), 1.19 (s, 9H, $C(CH_3)_3$), 1.21 (t, $J_{H\text{-}H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 2.13 (q, $J_{H\text{-}H}$ = 7.4 Hz, 2H, $C\underline{H}_2CH_3$), 4.18 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, $OC\underline{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 7.2 ($CH_2\underline{C}H_3$), 14.1 ($OCH_2\underline{C}H_3$), 25.2 ($\underline{C}H_2CH_3$), 26.4 ($C(\underline{C}H_3)_3$), 61.4 ($O\underline{C}H_2CH_3$), 80.5 ($\underline{C}(CH_3)_3$), 87.8 ($CH_2\underline{C}$), 167.4 (CO). Calculated for $C_{13}H_{24}O_6$: % C 56.51; % H 8.75; found: % C 56.72; %H 8.78. HRMS-ESI: calculated 299.1465 [$C_{13}H_{24}O_6$+Na] found 299.1475 (Δ = 3.3 ppm). IR (film): 1748 (vs, υ_{CO}) cm^{-1}.

Diethyl butyl(*tert*-butylperoxy)malonate 2c: Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 0.85 (t, $J_{H\text{-}H}$ = 6.7 Hz, 3H, $\underline{C}H_3(CH_2)_3$), 1.20-1.26 (m, 21H, $C(CH_3)_3$, $(CH_2)_3$, $OCH_2C\underline{H}_3$), 4.19 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, $OC\underline{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.9 ($(CH_2)_3\underline{C}H_3$), 14.1 ($OCH_2\underline{C}H_3$), 22.6, 25.0, 31.8 (CH_2), 26.4 ($C(\underline{C}H_3)_3$), 61.6 ($O\underline{C}H_2CH_3$), 80.5 ($\underline{C}(CH_3)_3$), 87.5 ($CH_2\underline{C}$), 167.6 (CO). Calculated for $C_{15}H_{28}O_6$: % C 59.19; % H 9.27; found: % C 58.86; % H 9.23. HRMS-ESI: calculated 305.1959 [$C_{15}H_{28}O_6$+H] found 305.1958 (Δ = 0.3 ppm). IR (film): 1749 (vs, υ_{CO}) cm^{-1}.

Diethyl benzyl(*tert*-butylperoxy)malonate 2d[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.21 (t, $J_{H\text{-}H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 1.30 (s, 9H, $C(CH_3)_3$), 3.51 (s, 2H, CH_2Ph), 4.17 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, $OC\underline{H}_2CH_3$), 7.23-7.27 (m, 5H, Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 ($OCH_2\underline{C}H_3$), 26.6 ($C(\underline{C}H_3)_3$), 37.8 ($\underline{C}H_2Ph$), 61.7 ($O\underline{C}H_2CH_3$), 81.1 ($\underline{C}(CH_3)_3$), 88.0 ($CH_2\underline{C}$), 127.0, 128.0, 130.4, 135.0 (Ph), 167.0 (CO).

Diethyl allyl(*tert*-butylperoxy)malonate 2e[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.22 (s, 9H, $C(CH_3)_3$), 1.24 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, $OCH_2C\underline{H}_3$), 2.91 (d, $J_{H\text{-}H}$ = 7.1 Hz, 2H, $CHC\underline{H}_2C$), 4.20 (q, $J_{H\text{-}H}$ = 7.2 Hz, 4H, $OC\underline{H}_2CH_3$), 5.03-5.14 (m, 2H, $C\underline{H}_2$=$CHCH_2C$), 5.52-5.87 (m, 1H, CH_2=$C\underline{H}$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.1 ($OCH_2\underline{C}H_3$), 26.4 ($C(\underline{C}H_3)_3$), 36.6 ($\underline{C}H_2C$), 61.6 ($O\underline{C}H_2CH_3$), 80.8 ($\underline{C}(CH_3)_3$), 87.2 ($CH_2\underline{C}$), 119.0 ($\underline{C}H_2$=CH), 131.4 (CH_2=$\underline{C}H$), 167.0 (CO).

Diethyl (*tert*-butylperoxy)(phenyl)malonate 2f: Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.26 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, $OCH_2C\underline{H}_3$), 1.31 (s, 9H, CH_3), 4.25 (q, $J_{H\text{-}H}$ = 7.2 Hz, 4H, $OC\underline{H}_2CH_3$), 7.32-7.36 (m, 3H, Ph), 7.57-7.62 (m, 2H, Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 ($OCH_2\underline{C}H_3$), 26.5 ($C(\underline{C}H_3)_3$), 61.9 ($O\underline{C}H_2CH_3$), 81.5 ($\underline{C}(CH_3)_3$), 88.2 (Ph$\underline{C}$), 127.2, 128.0, 128.7, 134.6 (Ph), 166.8 (CO). Calculated for $C_{17}H_{24}O_6$: % C 62.95; % H 7.46; found: % C 62.50; % H 7.59. HRMS-ESI: calculated 347.1465 [$C_{17}H_{24}O_6$+Na] found 347.1462 (Δ=0.9 ppm). IR (film): 1750 (vs, υ_{CO}) cm^{-1}.

Diethyl (*tert*-butylperoxy)(3-oxobutyl)malonate 2g[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.19 (s, 9H, $C(CH_3)_3$), 1.22 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, $OCH_2C\underline{H}_3$), 2.10 (s, 3H, $COCH_3$), 2.41-2.50 (m, 4H, $(CH_2)_2$), 4.18 (q, $J_{H\text{-}H}$ = 7.2 Hz, 4H, $OC\underline{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 ($OCH_2\underline{C}H_3$), 25.9 ($COCH_2\underline{C}H_2$), 26.4 ($C(\underline{C}H_3)_3$), 29.9 ($\underline{C}H_3CO$), 37.2 ($CO\underline{C}H_2CH_2$), 61.8 ($O\underline{C}H_2CH_3$), 80.8 ($\underline{C}(CH_3)_3$), 86.3 ($CH_2\underline{C}$), 167.1, 207.3 (CO).

Diethyl (*tert*-butylperoxy)(2-cyanoethyl)malonate 2h[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.24 (s, 9H, $C(CH_3)_3$), 1.27 (t, J_{H-H} = 7.0 Hz, 6H, OCH_2CH_3), 2.37-2.62 (m, 4H, CH_2CH_2CN), 4.25 (q, J_{H-H} = 7.0 Hz, 4H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 11.4 (CH_2CH_2CN), 14.0 (OCH_2CH_3), 26.4 ($C(CH_3)_3$), 27.9 (CH_2CH_2CN), 62.4 (OCH_2CH_3), 81.5 ($C(CH_3)_3$), 85.6 (CH_2C), 119.1 (CN), 166.2 (CO).

Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate 4a: Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.22 (s, 9H, $(CH_3)_3C$), 1.23 (t, J_{H-H} = 6.7 Hz, 3H, OCH_2CH_3), 1.54 (s, 3H, CH_3COOBu-t), 2.25 (s, 3H, CH_3CO), 4.17 (q, J_{H-H} = 6.7 Hz, 2H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 (OCH_2CH_3), 18.3 (CH_3C), 25.7 (CH_3CO), 26.4 ($C(CH_3)_3$), 61.7 (OCH_2CH_3), 80.8 ($C(CH_3)_3$), 89.7 (CH_3C), 168.1, 203.8 (CO). Calculated for $C_{11}H_{20}O_5$: % C 56.88; % H 8.68; found: % C 57.00; % H 8.69. HRMS-ESI: calculated 255.1203 [$C_{11}H_{20}O_5$+Na] found 255.1212 (Δ = 1.5 ppm). IR (film): 1752 (vs, υ_{CO}), 1735 (vs, υ_{CO}) cm^{-1}.

Ethyl 2-acetyl-2-(*tert*-butylperoxy)hexanoate 4b[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 0.86 (t, J_{H-H} = 6.9 Hz, 3H, CH_3), 1.15-1.45 (m, 7H, CH_2CH_2, OCH_2CH_3), 1.25 (s, 9H, $(CH_3)_3C$), 2.00-2.25 (m, 2H, CH_2C), 2.23 (s, 3H, CH_3CO), 4.18 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.1 (OCH_2CH_3), 22.8, 25.0 (CH_2), 26.2 (CH_3CO), 26.5 ($C(CH_3)_3$), 30.9 (CH_2), 61.5 (OCH_2CH_3), 80.6 ($C(CH_3)_3$), 92.2 (CH_2C), 167.7, 203.7 (CO).

Ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate 4c[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.23 (t, J_{H-H} = 7.2 Hz, 3H, OCH_2CH_3), 1.32 (s, 9H, $(CH_3)_3C$), 1.90 (s, 3H, CH_3CO), 3.31 (d, J_{H-H} = 14.4 Hz, 1H, CH_2Ph), 3.62 (d, J_{H-H} = 14.4 Hz, 1H, CH_2Ph), 4.17 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3), 7.15-7.32 (m, 5H, Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 (OCH_2CH_3), 26.7 ($C(CH_3)_3$), 27.2 (CH_3CO), 37.2 (CH_2Ph), 61.7 (OCH_2CH_3), 81.2 ($C(CH_3)_3$), 92.7 (CH_2C), 126.8, 128.0, 130.7, 135.0 (Ph), 167.7, 203.7 (CO).

Ethyl 2-acetyl-2-(*tert*-butylperoxy)-5-oxohexanoate 4d[7b]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.21 (s, 9H, $(CH_3)_3C$), 1.22 (t, J_{H-H} = 7.2 Hz, 3H, OCH_2CH_3), 2.08 (s, 3H, CH_3CO), 2.19 (s, 3H, CH_3CO), 2.30-2.49 (m, 4H, CH_2CH_2), 4.15 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 (OCH_2CH_3), 25.0 (CH_3CO), 26.4 ($C(CH_3)_3$), 29.8, 32.9, 37.3 (CH_3CO, CH_2CH_2), 61.8 (OCH_2CH_3), 80.9 ($C(CH_3)_3$), 91.0 (CH_2C), 167.1, 202.5, 207.4 (CO).

Ethyl 2-cyanohexanoate 6a: Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 0.90 (t, J_{H-H} = 6.9 Hz, 3H, $CH_3(CH_2)_3$), 1.24-1.40 (m, 7H, CH_2CH_2, OCH_2CH_3), 1.89-2.00 (m, 2H, CH_2C), 4.31 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.7 (CH_3), 14.1 (OCH_2CH_3), 22.3, 25.8, 35.1 (CH_2), 26.4 ($C(CH_3)_3$), 63.1 (OCH_2CH_3), 82.3 ($C(CH_3)_3$), 82.6 (CH_2C), 116.6 (CN), 165.9 (CO). Calculated for $C_{13}H_{23}NO_4$: % C 60.68; % H 9.01; % N 5.44 found: % C 60.59; % H 8.98; % N 5.54. HRMS-ESI: calculated 280.1519 [$C_{13}H_{23}O_4$+Na] found 280.1525 (Δ = 2.1 ppm). IR (film): 2245 (w, υ_{CN}), 1753 (vs, υ_{CO}) cm^{-1}.

Ethyl 2-(*tert*-butylperoxy)-2-cyano-3-phenylpropanoate 6b[7a]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.21 (t, J_{H-H} = 7.2 Hz, 3H, OCH_2CH_3), 1.25 (s, 9H, $(CH_3)_3C$), 3.22 (d, J_{H-H} = 13.6 Hz, 1H, CH_2Ph), 3.29 (d, J_{H-H} = 13.6 Hz, 1H, CH_2Ph), 4.24 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3), 7.20-7.40 (m, 5H, Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0 (OCH_2CH_3), 26.4 ($C(CH_3)_3$), 41.3 (CH_2Ph), 63.2 (OCH_2CH_3), 82.6 ($C(CH_3)_3$), 82.9 (CH_2C), 116.2 (CN), 128.3, 128.7, 130.5, 131.3, 133.5 (Ph), 165.3 (CO).

Ethyl 2-(*tert*-butylperoxy)-2-cyanopent-4-enoate 6c[7a]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.25 (s, 9H, $(CH_3)_3C$), 1.29 (t, J_{H-H} = 7.2 Hz, 3H, OCH_2CH_3), 2.69 (d, J_{H-H} = 7.4 Hz, 2H, CH_2), 4.25 (q, J_{H-H} = 7.2 Hz, 2H, OCH_2CH_3), 5.16-5.28 (m, 2H, CH_2=CH), 5.65-5.88 (m, 1H, CH_2=CH). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.1 (OCH_2CH_3), 26.3 ($C(CH_3)_3$), 39.6 (CH_2), 63.1 (OCH_2CH_3), 81.6 ($C(CH_3)_3$), 82.8 (CH_2C), 116.1 (CN), 122.1 (CH=CH_2), 130.6 (CH=CH_2), 165.1 (CO).

Diethyl 2-(*tert*-butylperoxy)-2-cyanopentanedioate 6d[7a]**:** Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.19-1.35 (m, 6H, OCH_2CH_3), 1.24 (s, 9H, $C(CH_3)_3$), 2.28-2.59 (m, 4H, CH_2CH_2CO), 4.12, (q, J_{H-H} = 6.9 Hz, 2H, OCH_2CH_3), 4.29 (q, J_{H-H} = 6.9 Hz, 2H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.0, 14.2 (OCH_2CH_3), 26.3 ($C(CH_3)_3$), 28.6, 30.5 (CH_2CH_2), 61.0, 63.3 (OCH_2CH_3), 81.0 ($C(CH_3)_3$), 82.9 (CH_2C), 115.9 (CN), 165.1, 171.1 (CO).

Reaction of malonic ester with the Bu_4NI / Bu^tOOH system: t-BuOOH 70 % (0.77 g, 6.00 mmol) was added to the solution of diethylmalonate **7** (0.32 g, 2.00 mmol) in acetonitrile (10 mL). The mixture was heated to boiling and Bu_4NI (0.15 g, 0.40 mmol) was added. The solution was refluxed for 6 hours. Product **8** was isolated as described for **2d.** Yield of **8** is (0.20 g, 0.60 mmol, 62 %).

Tetraethyl ethene-1,1,2,2-tetracarboxylate 8.[17] White crystals. m.p. 54–55 °C. Rf: 0.16 (1/10 EA / PE). ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.31 (t, J_{H-H} = 7.2 Hz, 12H, CH_3), 4.31 (q, J_{H-H} = 7.2 Hz, 8H, CH_2). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.9 (CH_3), 62.6 (CH_2), 135.5 (C=C), 162.4 (CO). HRMS-ESI: calculated 339.1050 [$C_{14}H_{20}O_8$+Na] found 339.1046 (Δ = 1.1 ppm).

Reaction of 9-methyl-9*H*-fluorene with the Bu_4NI / Bu^tOOH system: t-BuOOH 70 % (0.77 g, 6.00 mmol) was added to the solution of 9-methyl-9*H*-fluorene **9** (0.36 g, 2.00 mmol) in acetonitrile (10 mL). The mixture was heated to boiling and Bu_4NI (0.15 g, 0.40 mmol) was added. The solution was refluxed for 6 hours. A product **10** was isolated as described for **2d**. Yield of **10** is (0.49 g, 1.84 mmol, 92 %).

9-(*tert*-Butylperoxy)-9-methyl-9*H*-fluorene 10:[16] Colorless oil. ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.16 (s, 9H, $(CH_3)_3C$), 1.83 (s, 3H, CH_3), 7.31-7.68 (m, 8H, Ar). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 22.5 (CH_3), 26.6 ($C(CH_3)_3$), 79.5 ($C(CH_3)_3$), 87.9 (CH_3C), 119.9, 124.9, 127.5, 129.0, 140.0, 146.8 (Ar). Calculated for $C_{18}H_{20}O_2$: % C 80.56; % H 7.51; found: % C 80.44; % H 7.62. HRMS-ESI: calculated 307.1095 [$C_{18}H_{20}O_2$+K] found 307.1094 (Δ = 0.3 ppm). IR (film): 2976 (s), 1450 (s), 1363 (s), 1330 (m), 1246 (m), 1212 (m), 1196 (s), 1122 (m), 1096 (m), 877 (m), 761 (vs, $\upsilon_{CH\ Ar}$), 735 (vs, $\upsilon_{CH\ Ar}$) cm^{-1}.

Additional experiment on Bu_4NI isolation after peroxidation. To a solution of diethyl benzylmalonate **1d** (0.50 g, 2.00 mmol) in acetonitrile (10 mL) 70% t-BuOOH (0.77 g, 6.00 mmol) was added. The mixture was heated to reflux, and then Bu_4NI (0.15 g, 0.40 mmol) was added. The solution was refluxed for 6 h. The solvent was removed under water aspirator pressure. The suspension that formed was diluted with Et_2O (20 mL), the precipitate was filtered of, washed with Et_2O (20 mL), and collected. Yield of Bu_4NI is (0.11 g, 0.30 mmol, 75 %). ^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 0.91 (t, 12H, CH_3, J_{H-H} = 7.2 Hz), 1.28-1.68 (m, 16H, $CH_3CH_2CH_2CH_2$), 3.21-3.35 (m, 8H, CH_2N). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.8 (CH_3), 19.8, 24.3 (CH_2), 59.2 (CH_2N). Calculated for $C_{16}H_{36}IN$: % C 52.03; % H 9.82; % N 3.79; % I 34.36; found: % C 52.44; % H 9.88; % N 3.71; % I 33.58.

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Organocatalytic peroxidation of malonates, β-ketoesters, and cyanoacetic esters using *n*-Bu_4NI / *t*-BuOOH-mediated intermolecular oxidative C(sp^3)–O coupling

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Dmitri O. Levitsky,[b] Fabrice Fleury,[b]
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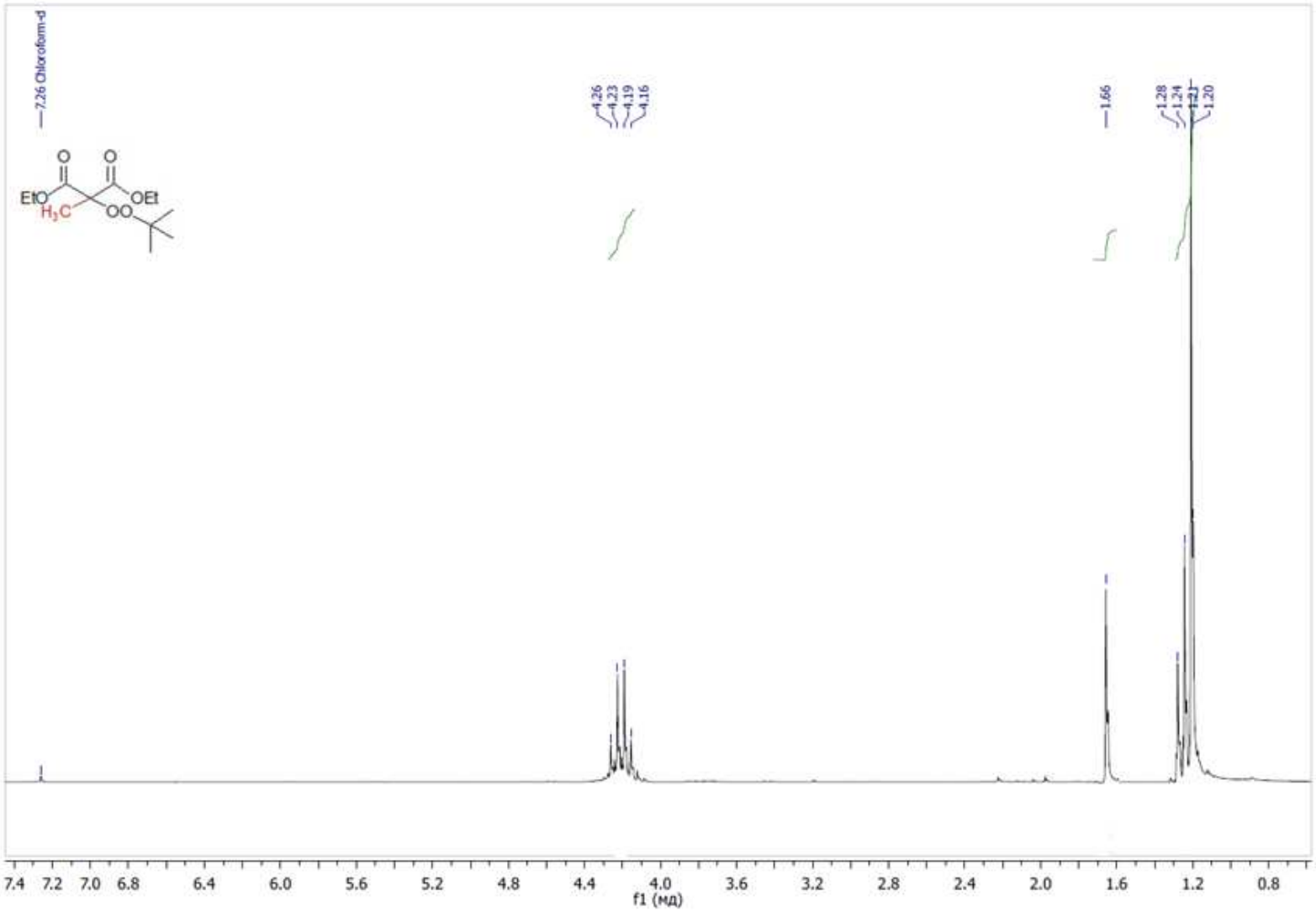
^{1}H NMR of Diethyl (*tert*-butylperoxy)(methyl)malonate 2a



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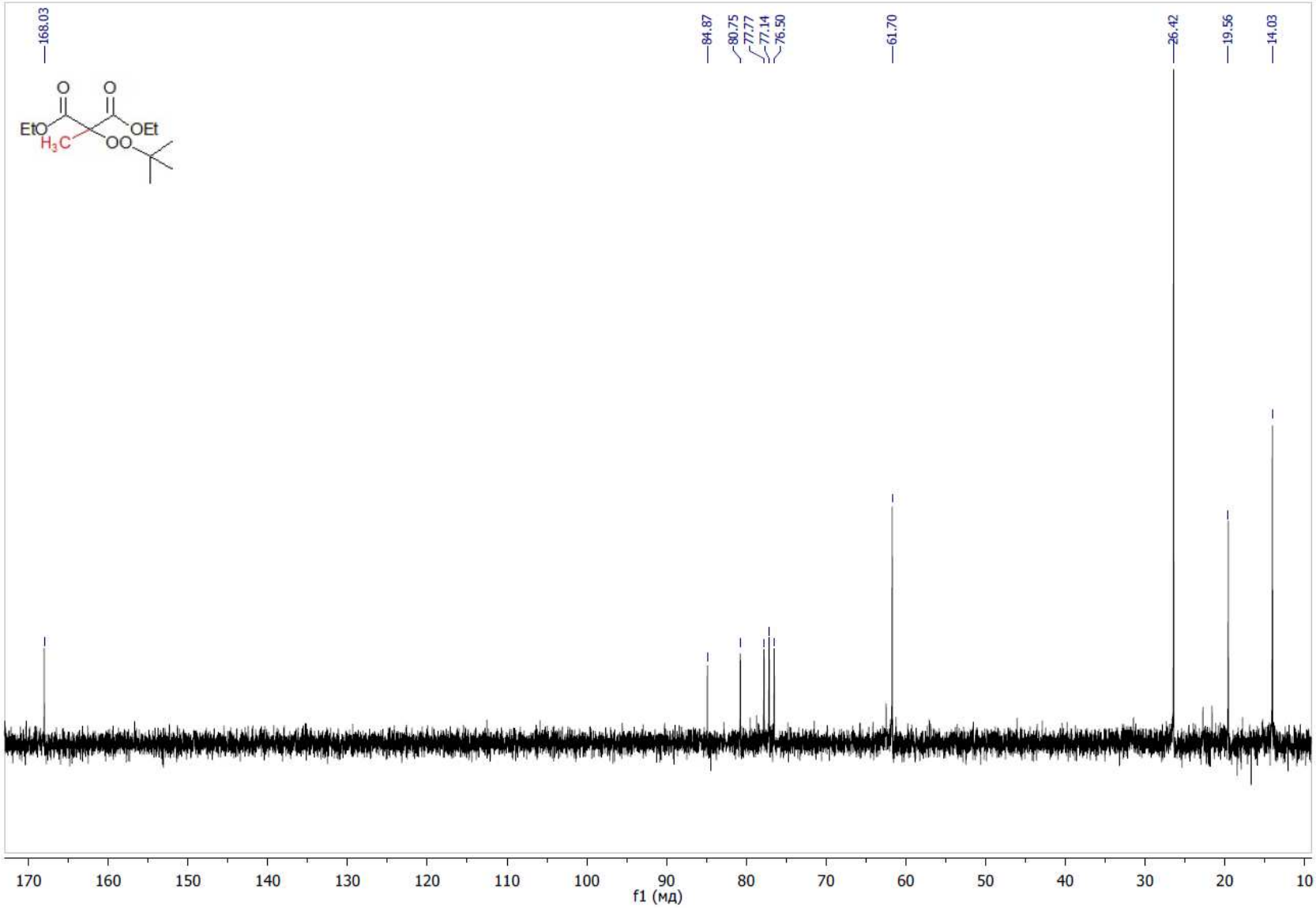

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Display Report

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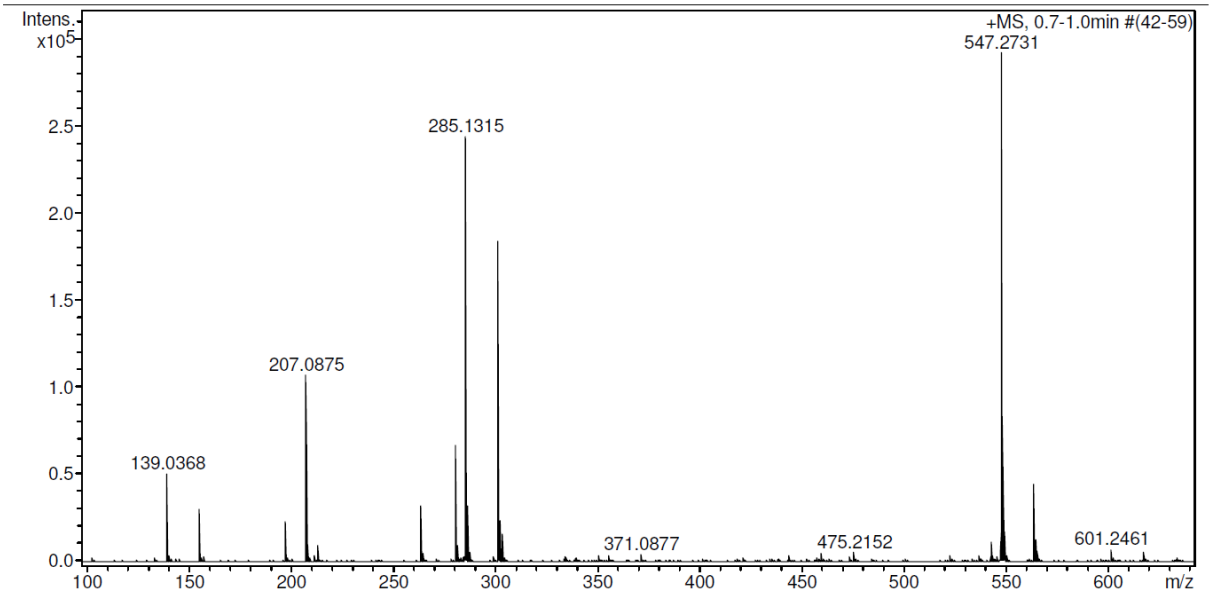

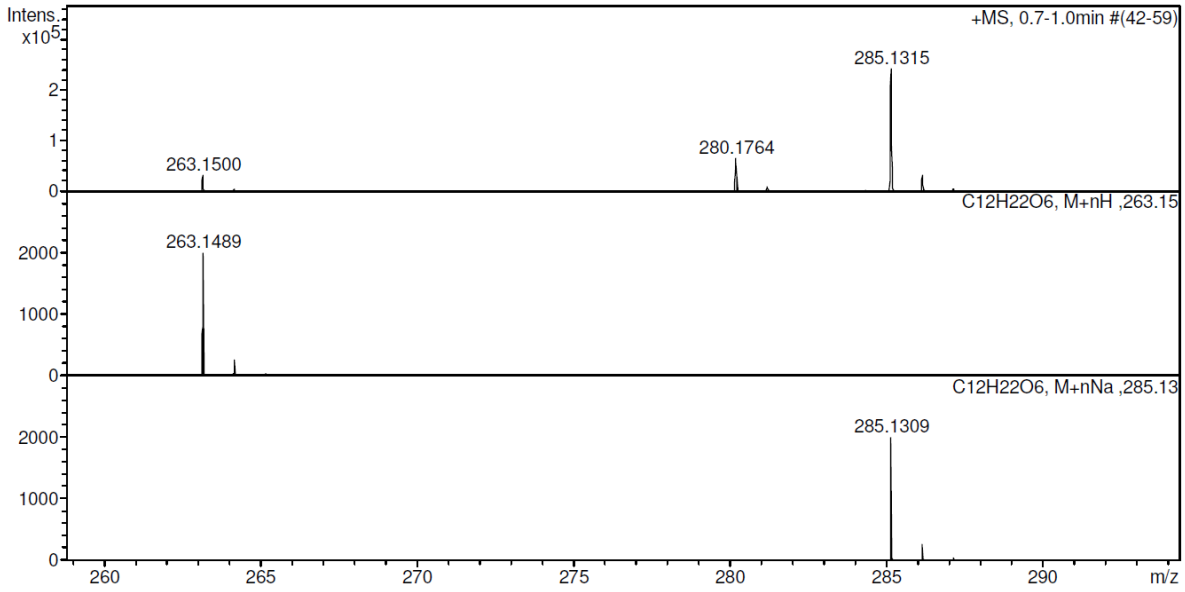

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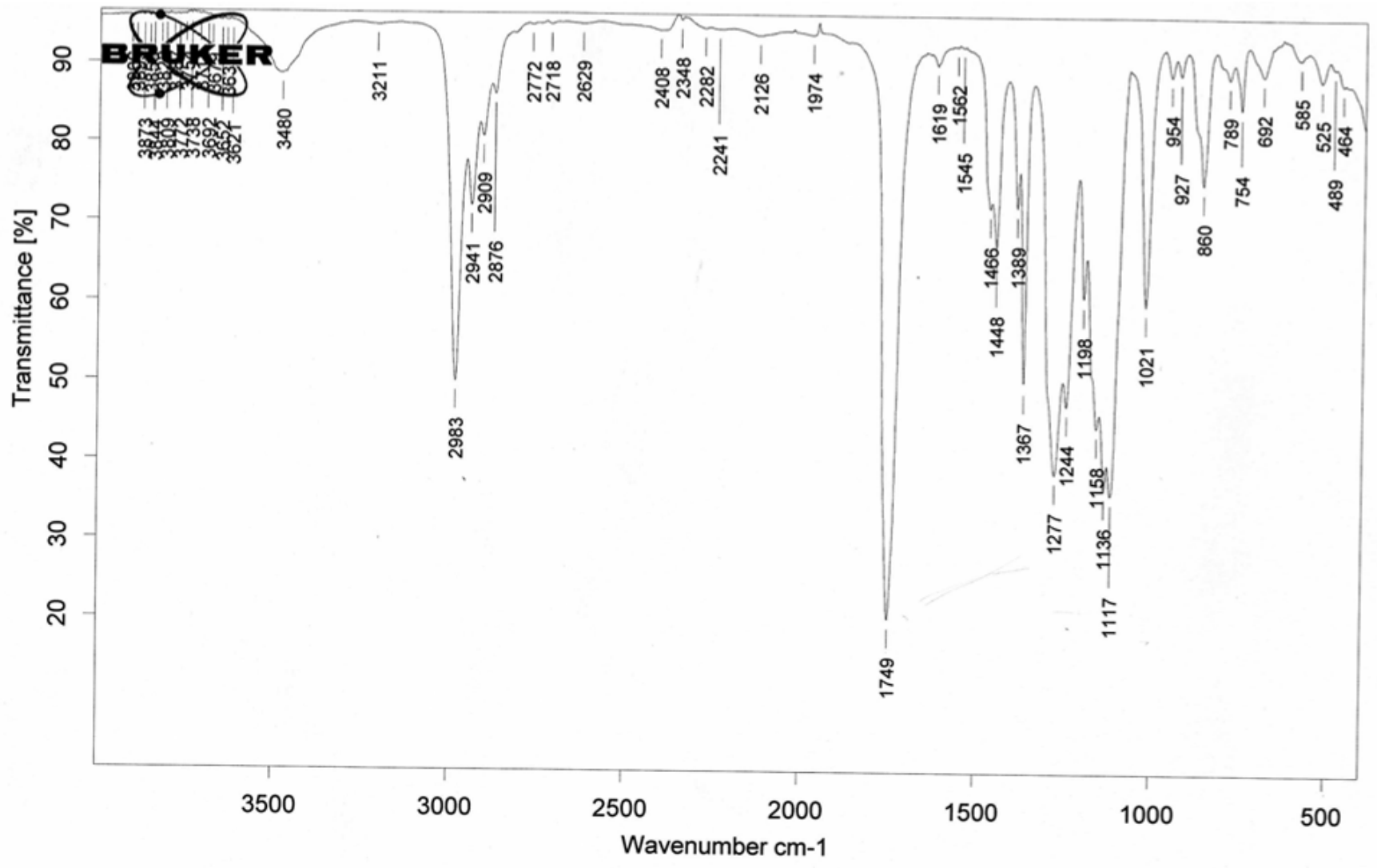

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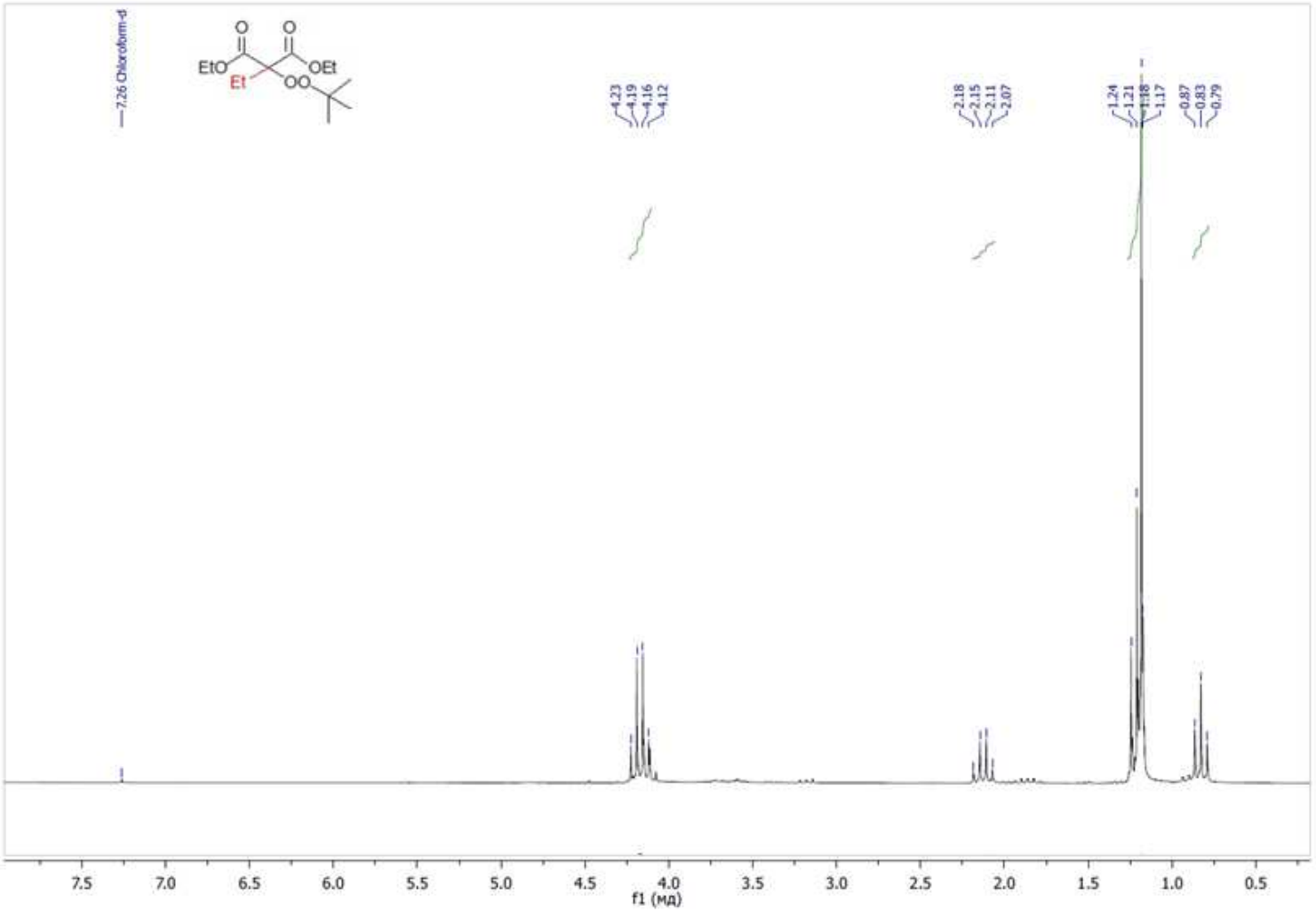

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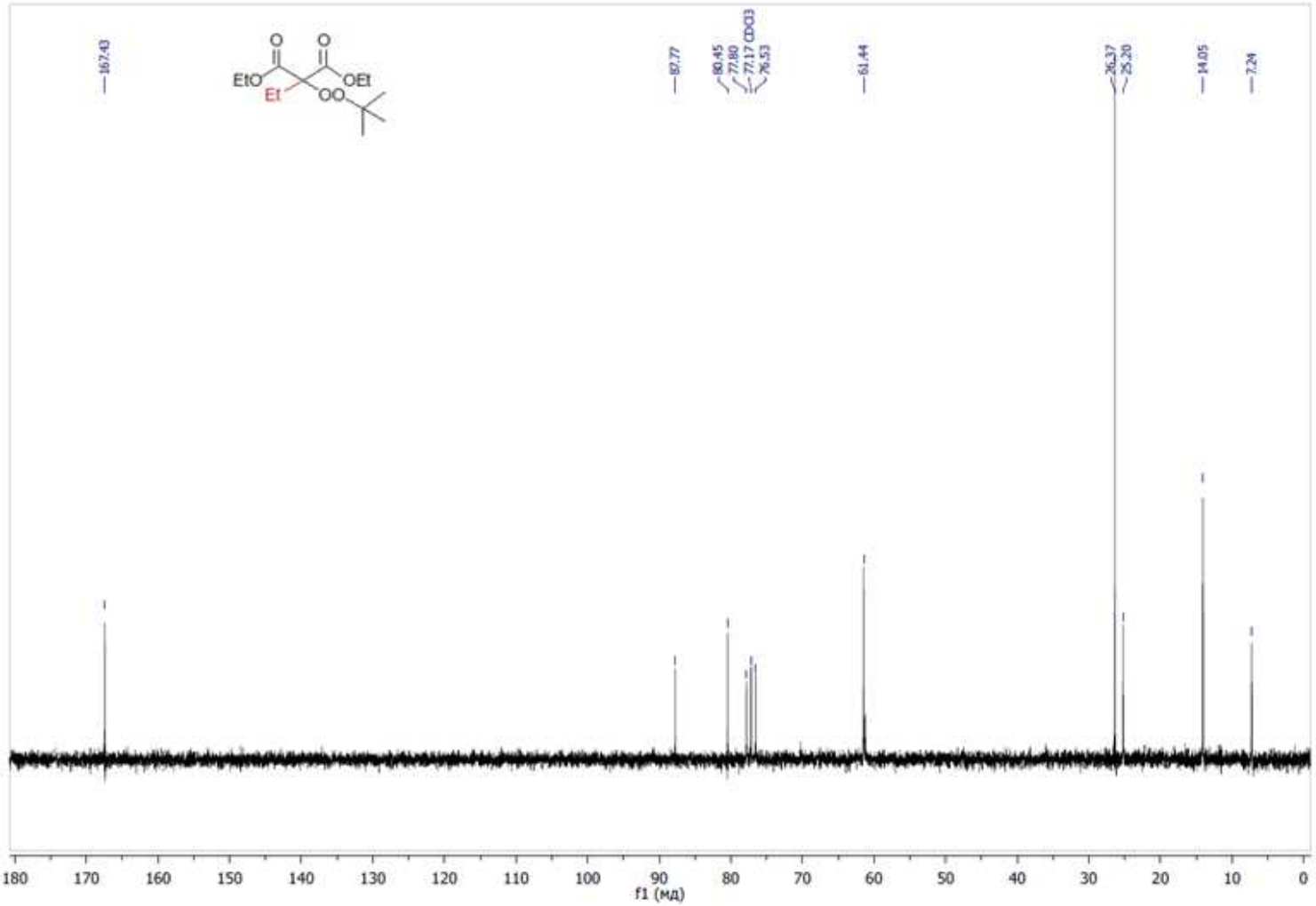

HRMS of Diethyl (*tert*-butylperoxy)(ethyl)malonate 2b

Display Report

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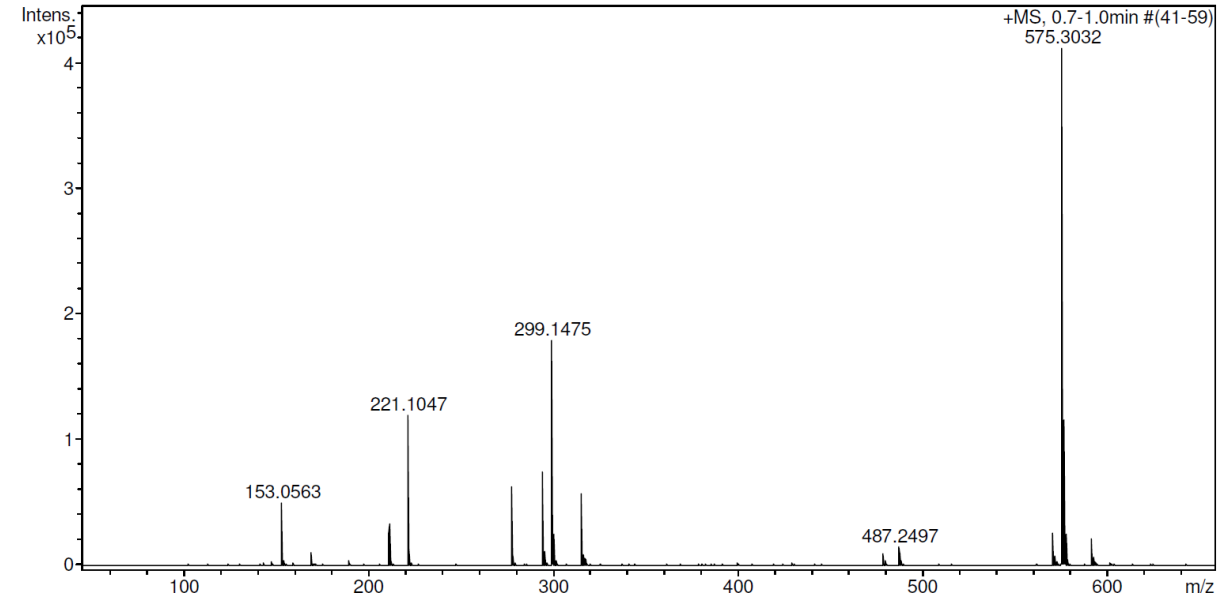

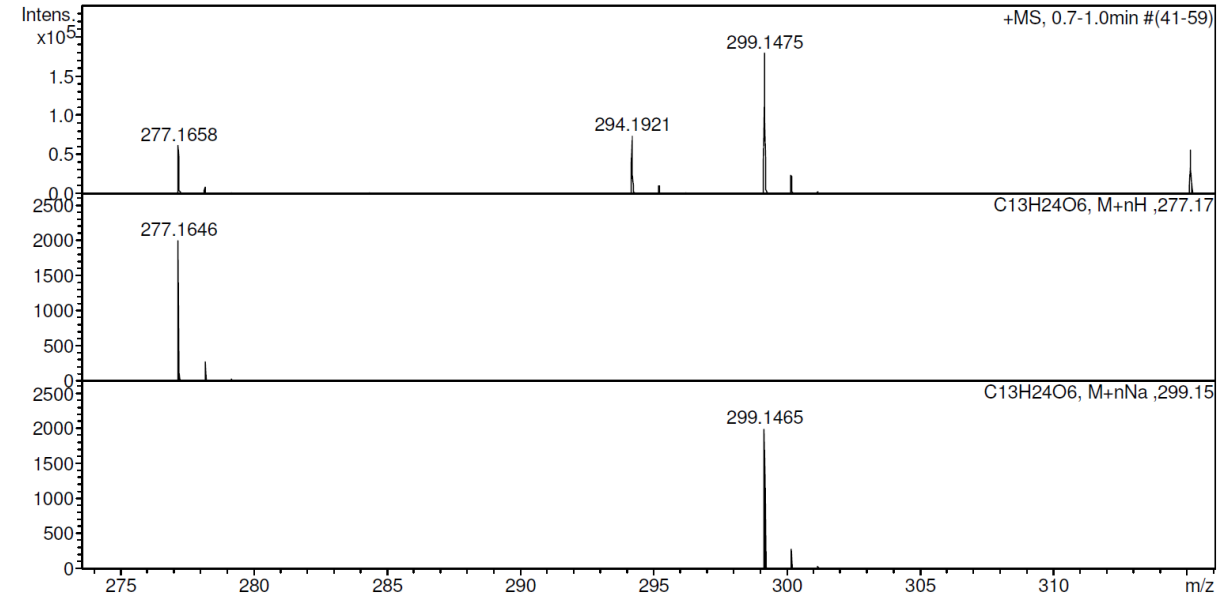

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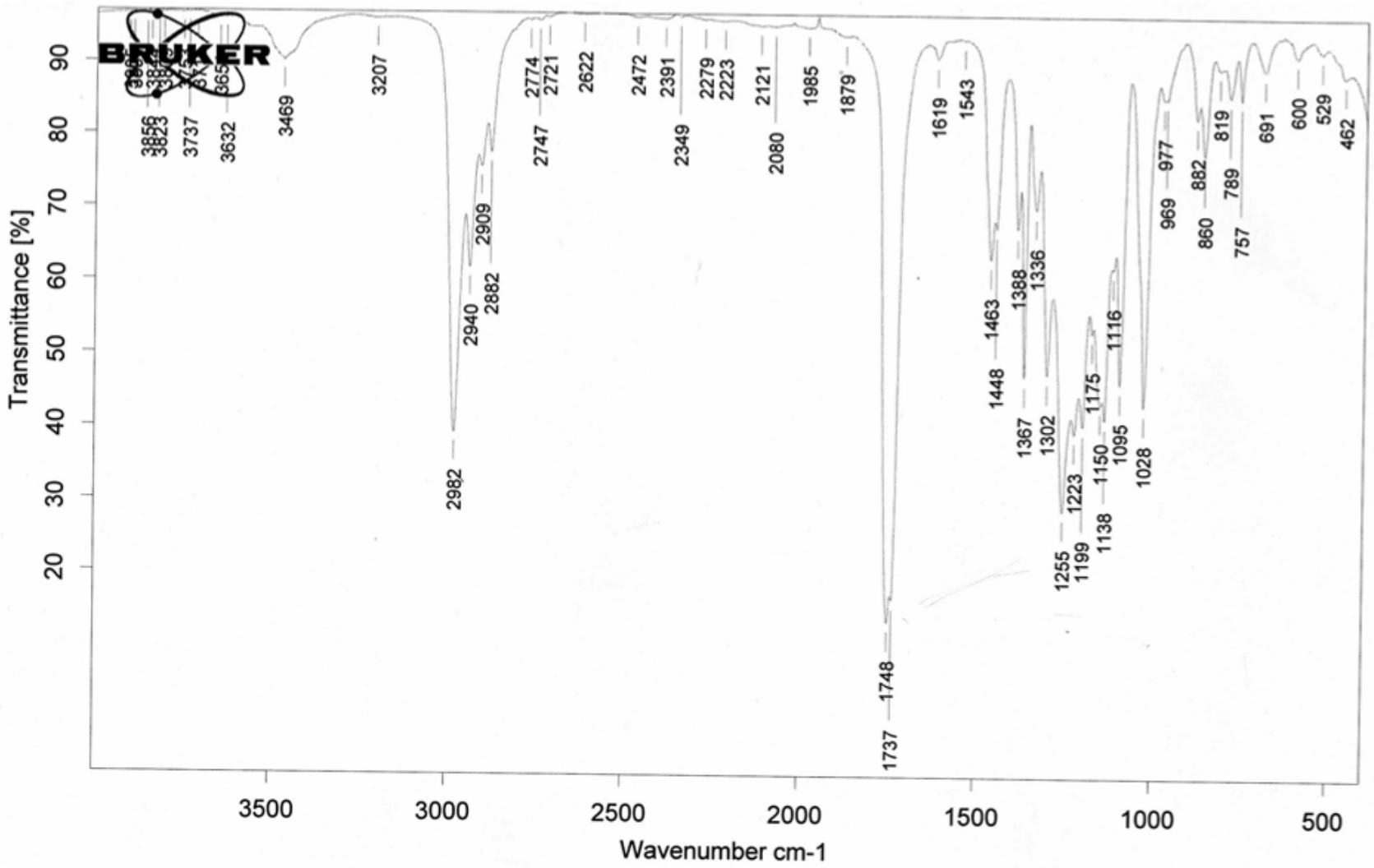

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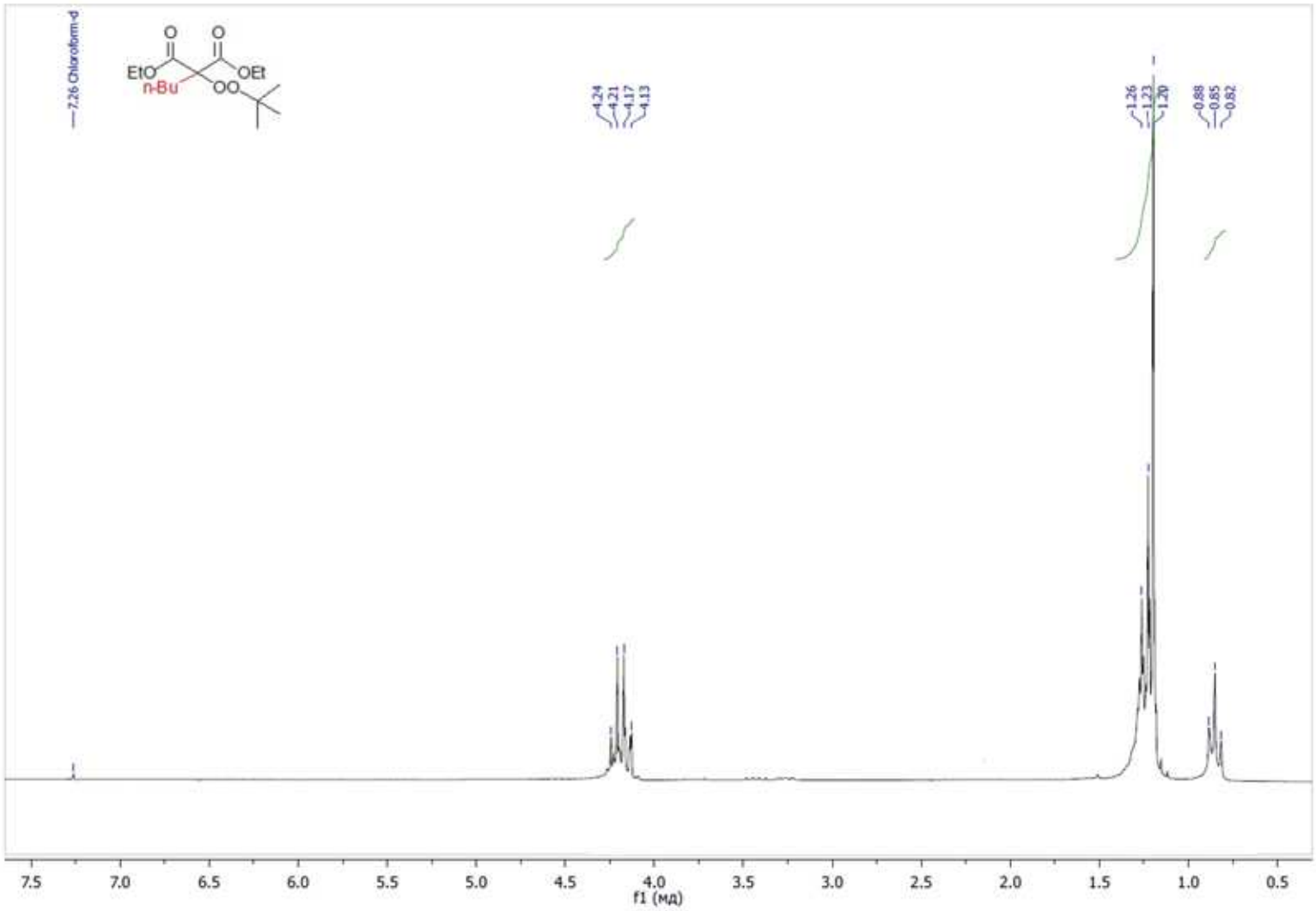

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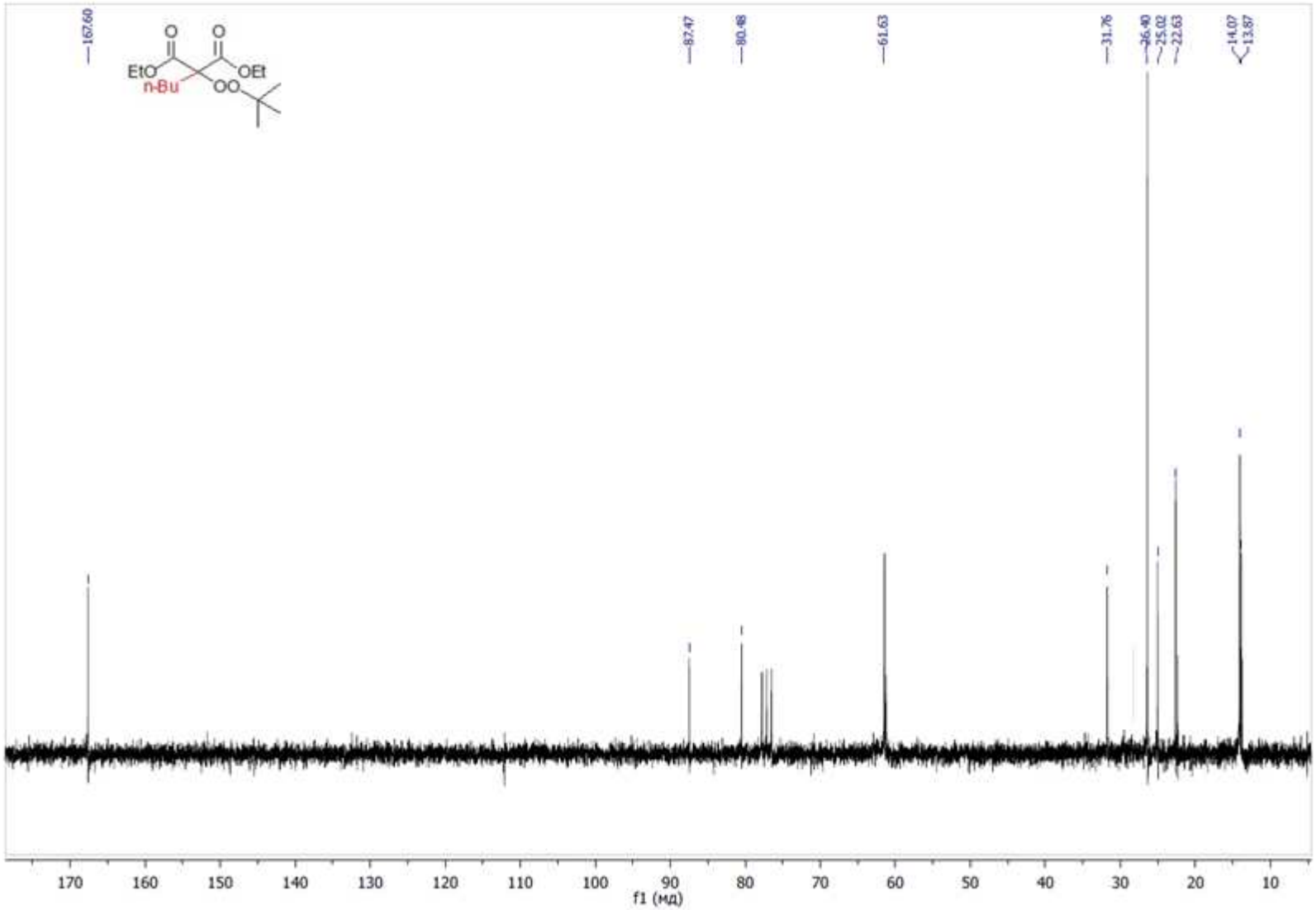

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Display Report

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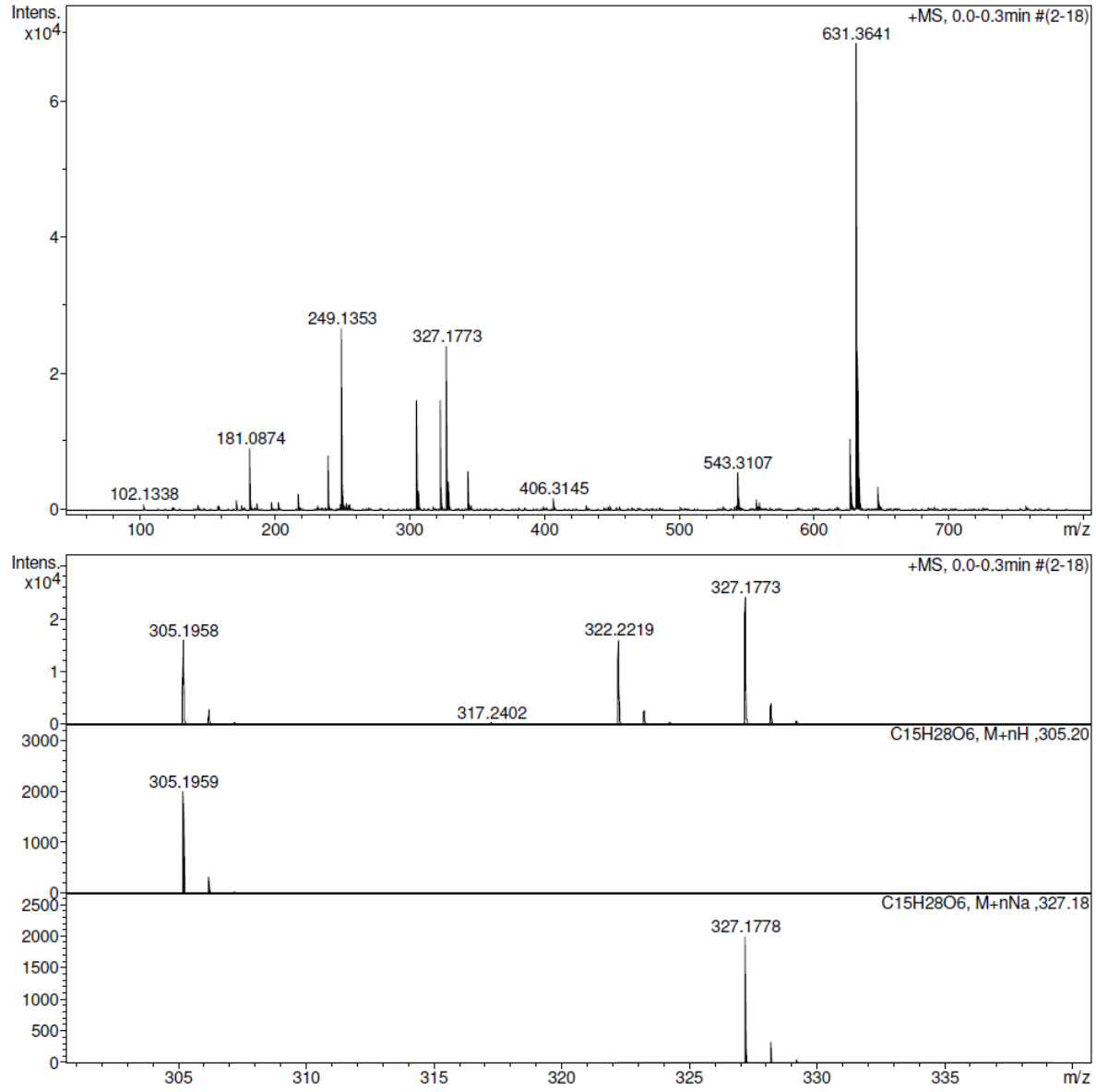

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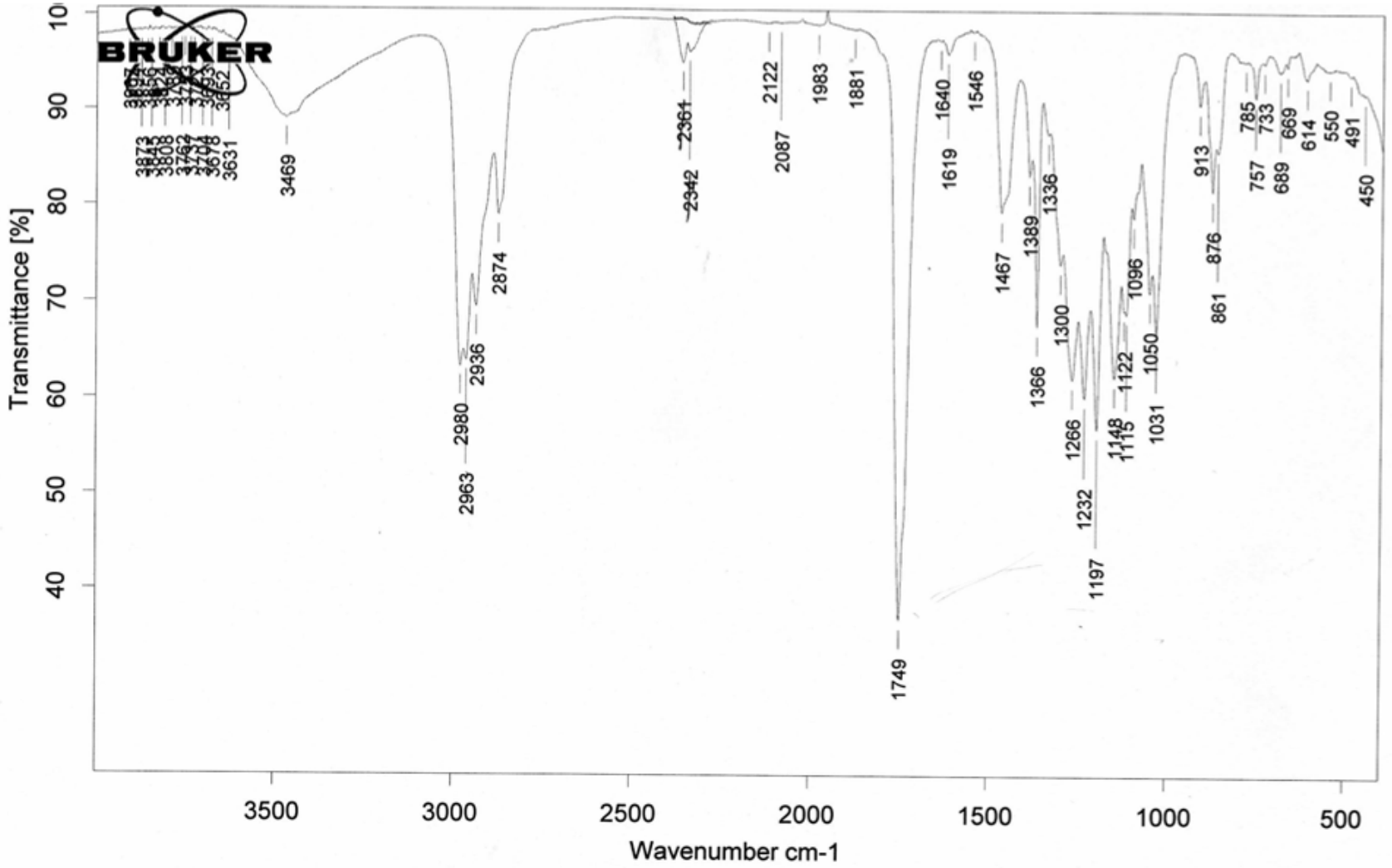

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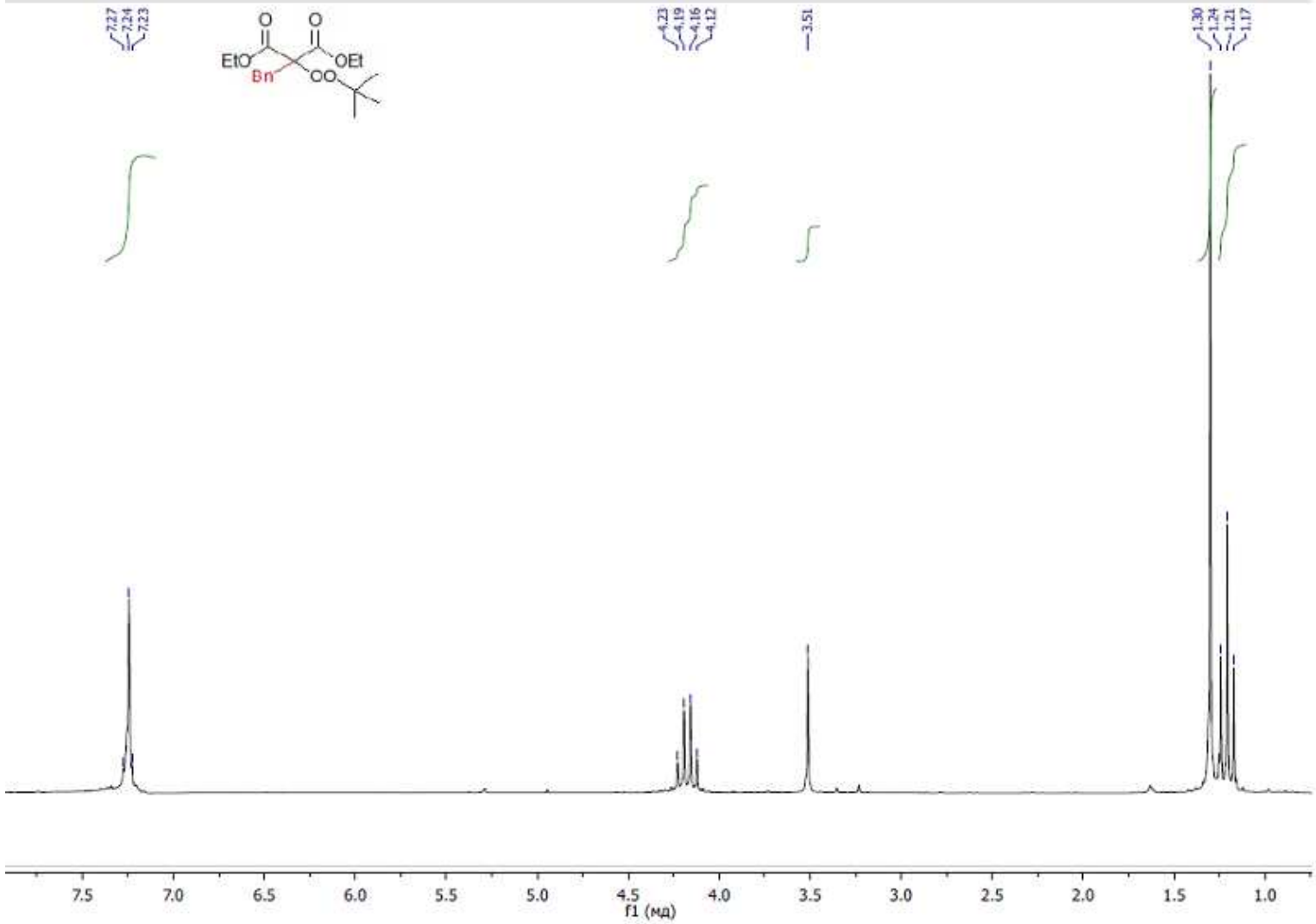

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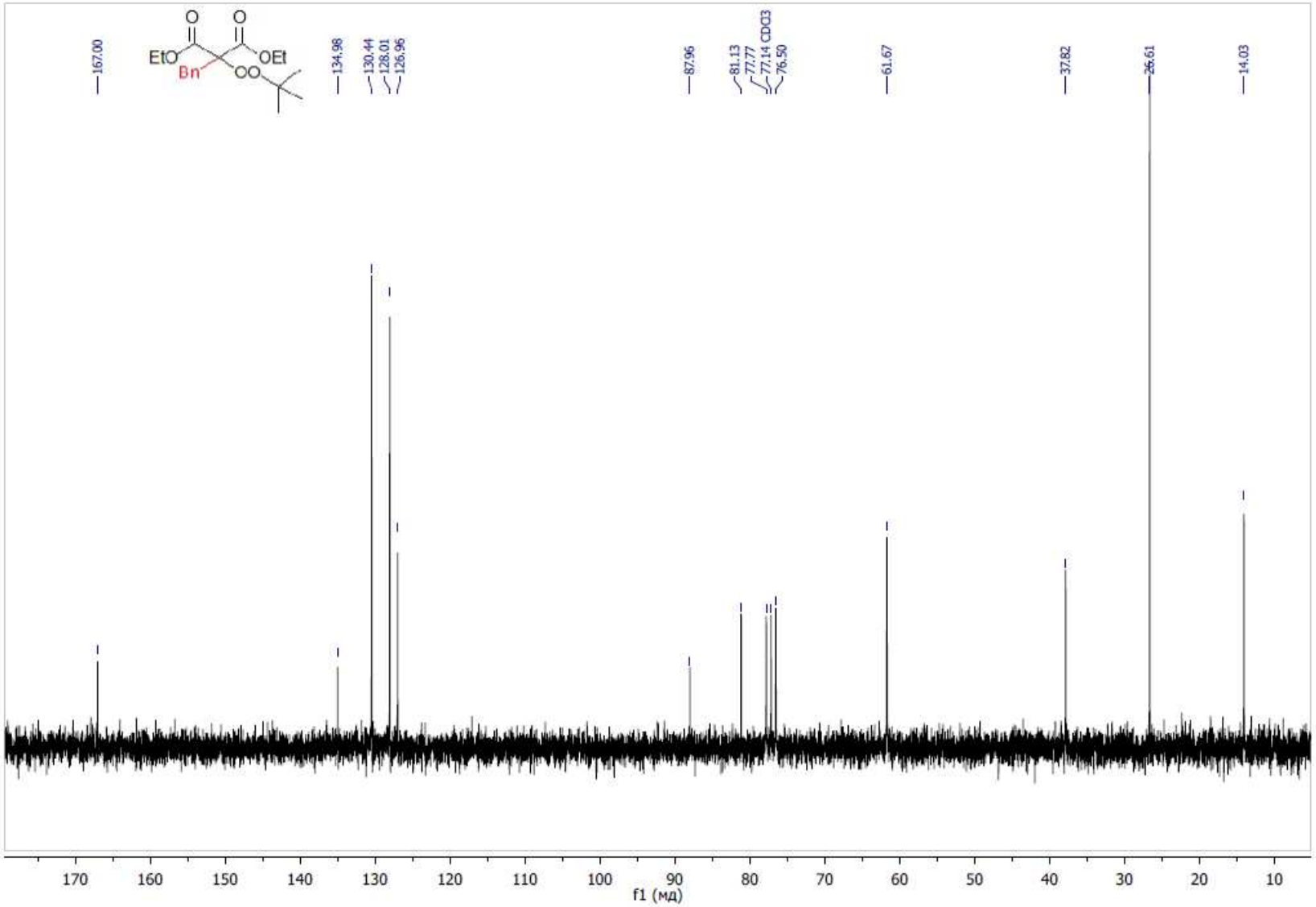

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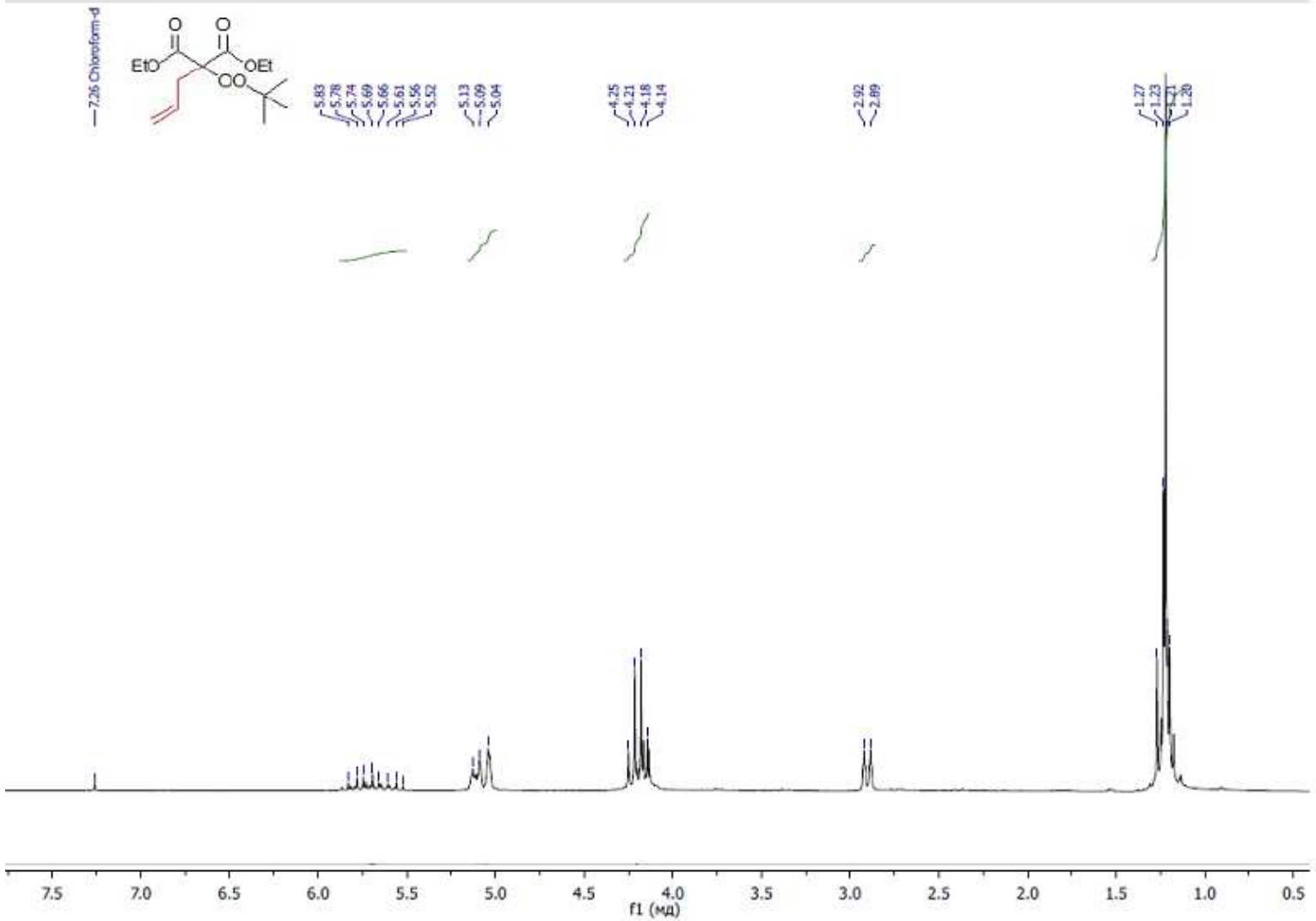

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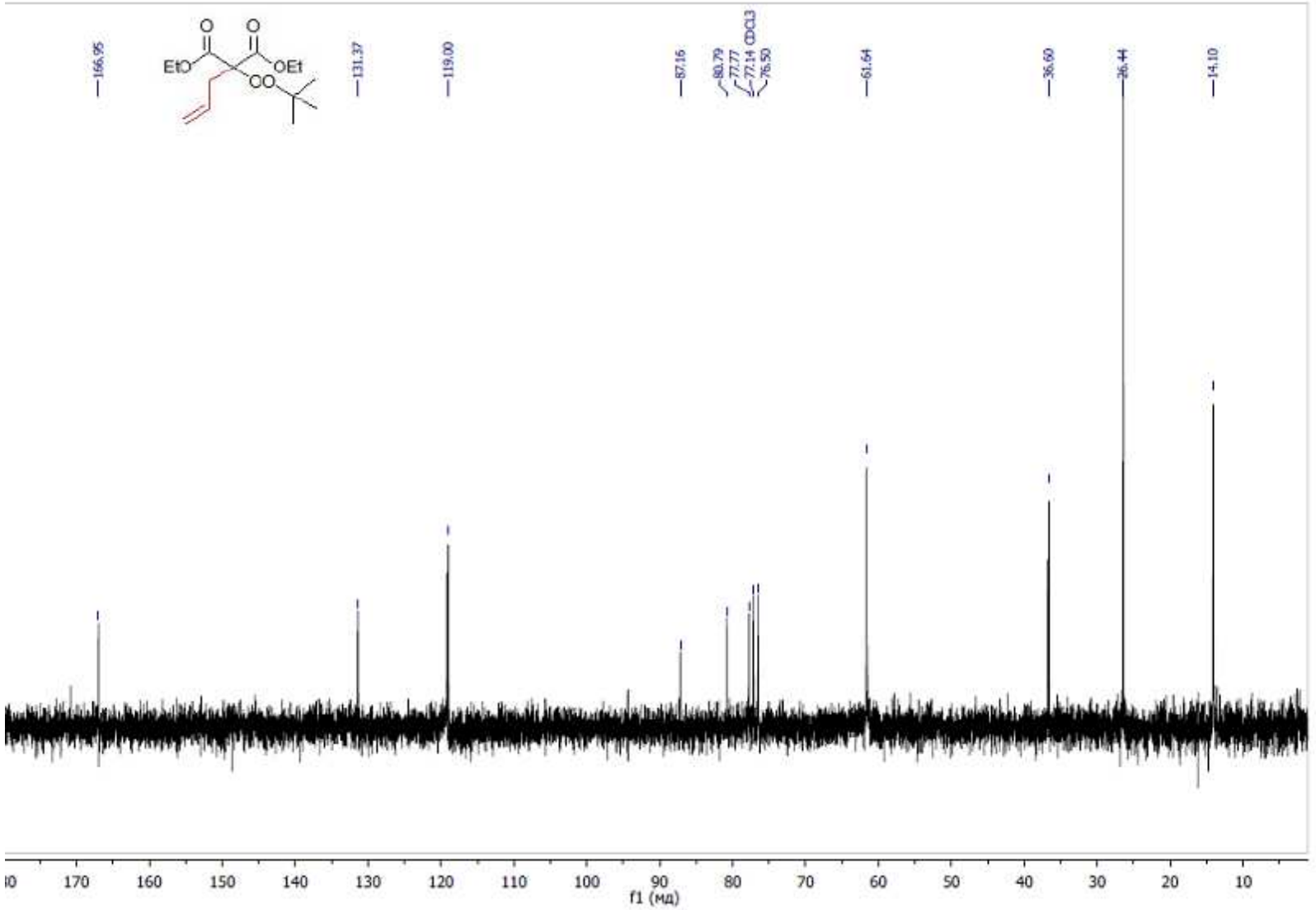

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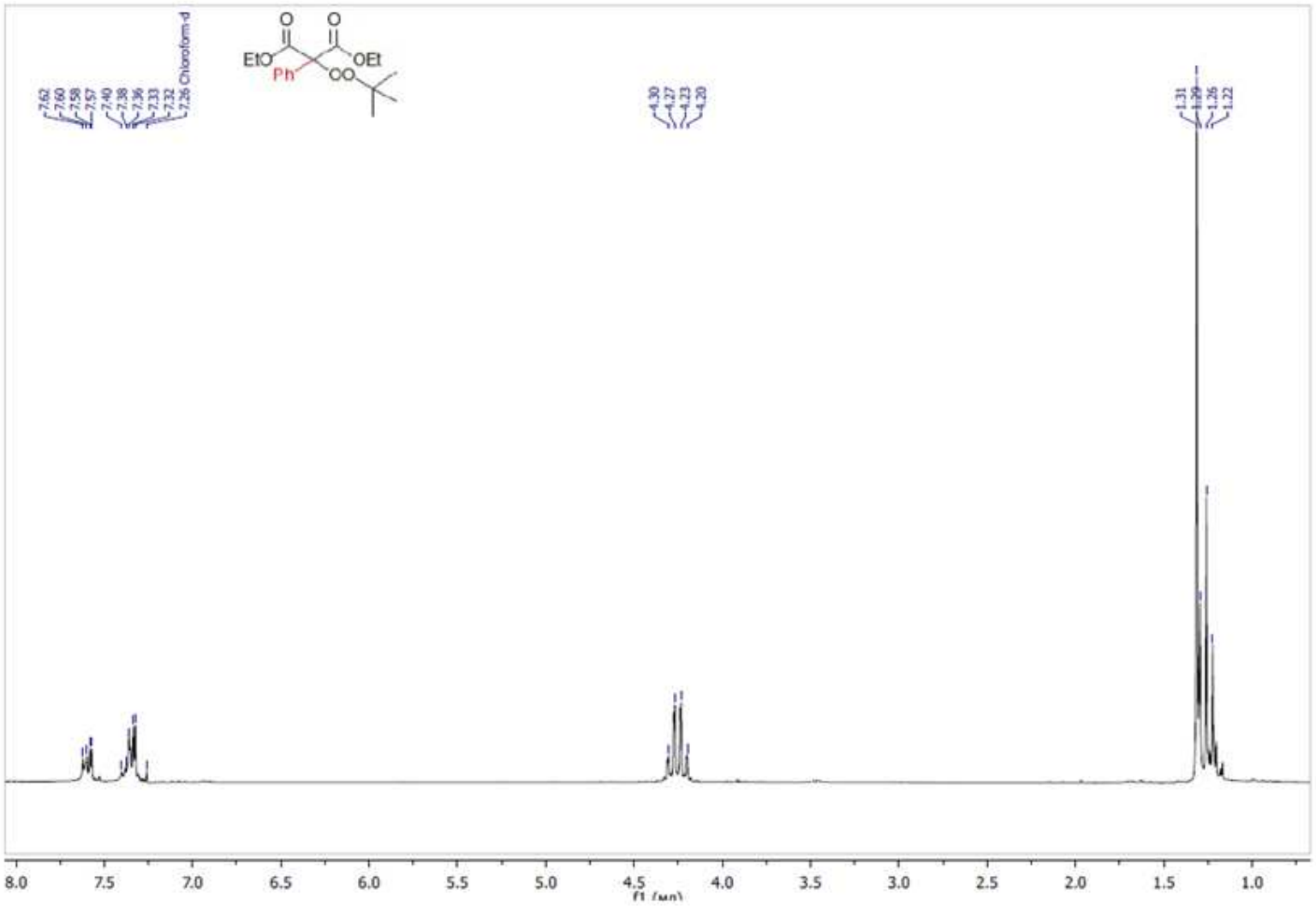

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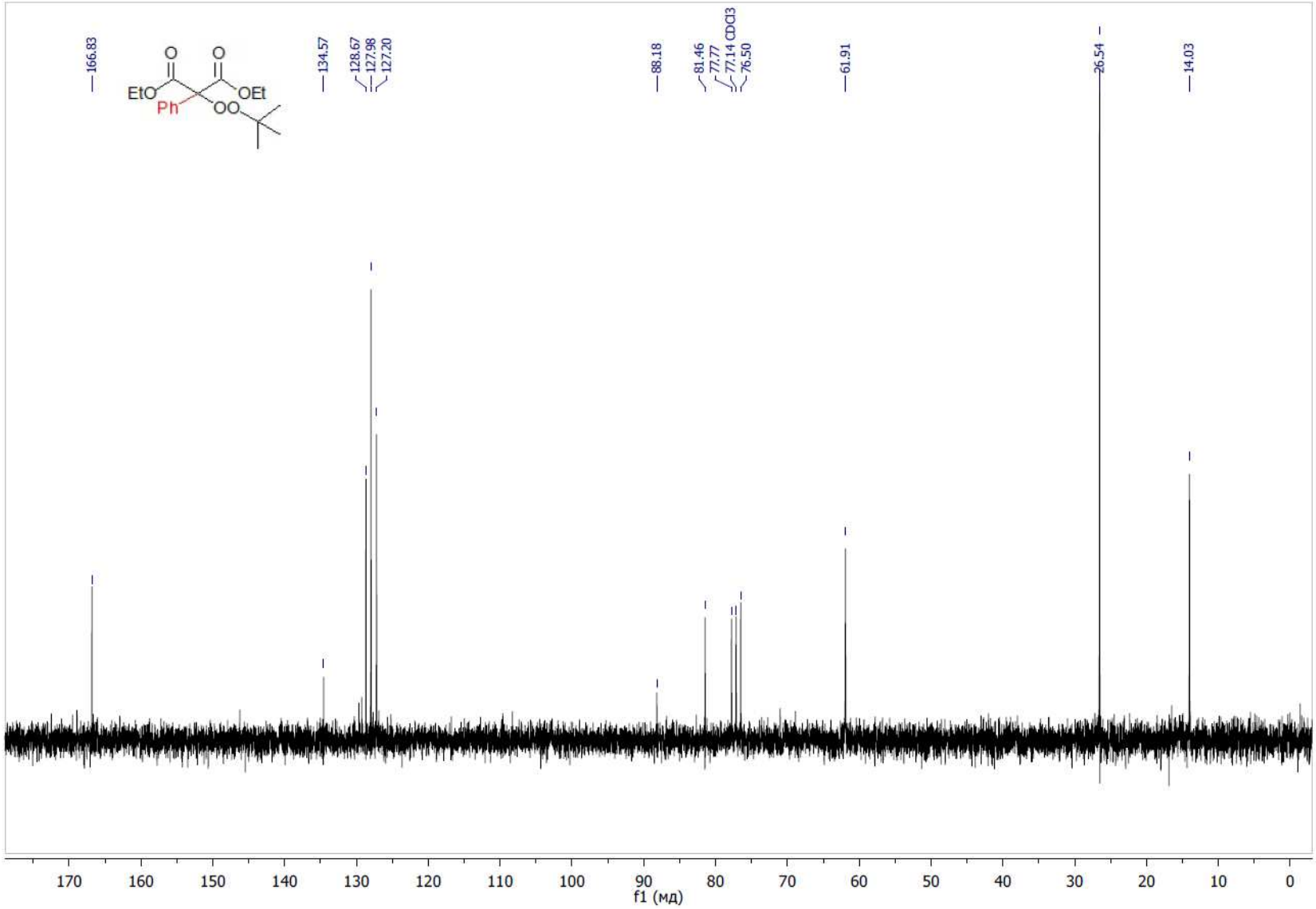

HRMS of Diethyl (*tert*-butylperoxy)(phenyl)malonate 2f

Display Report

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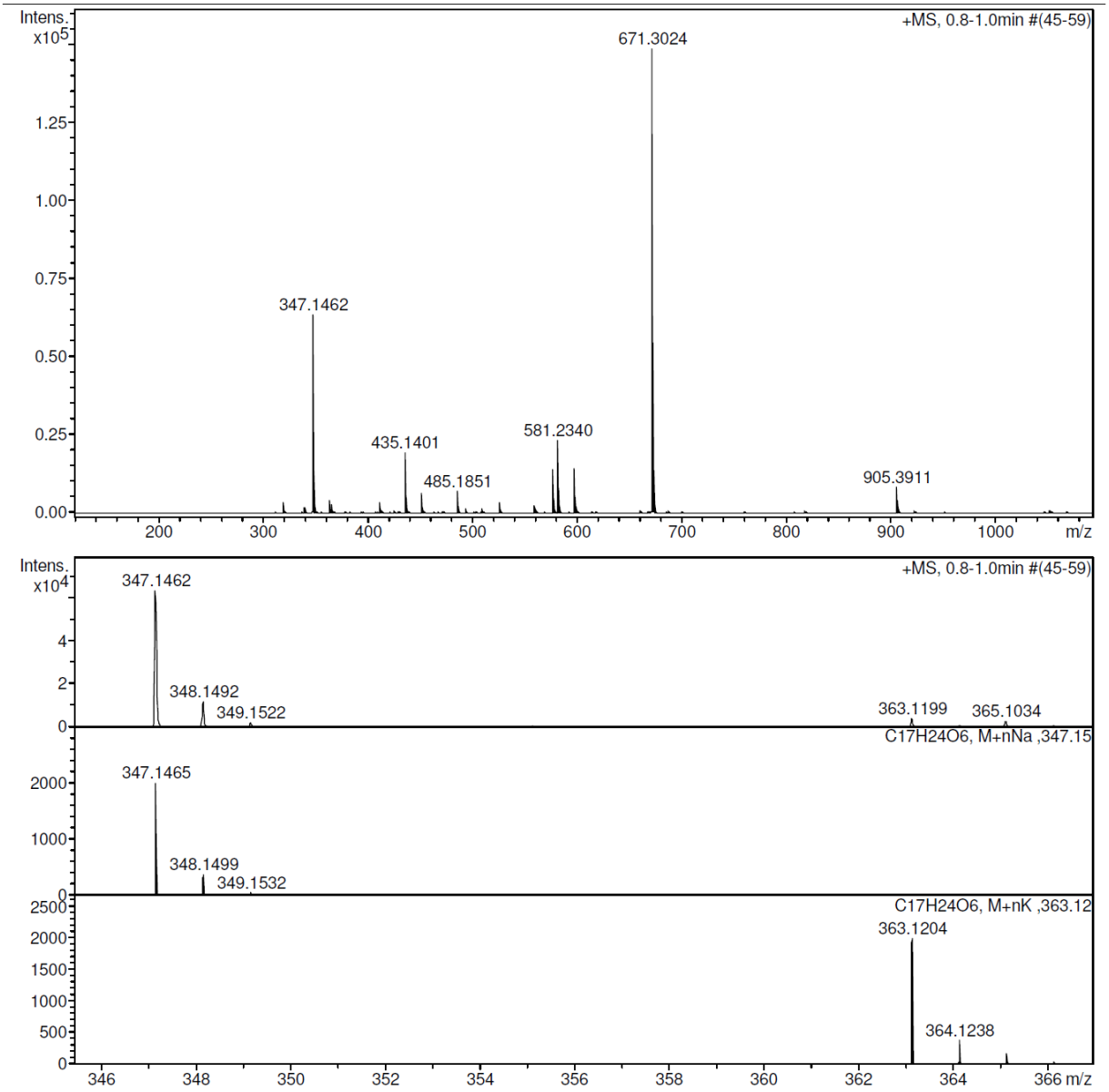

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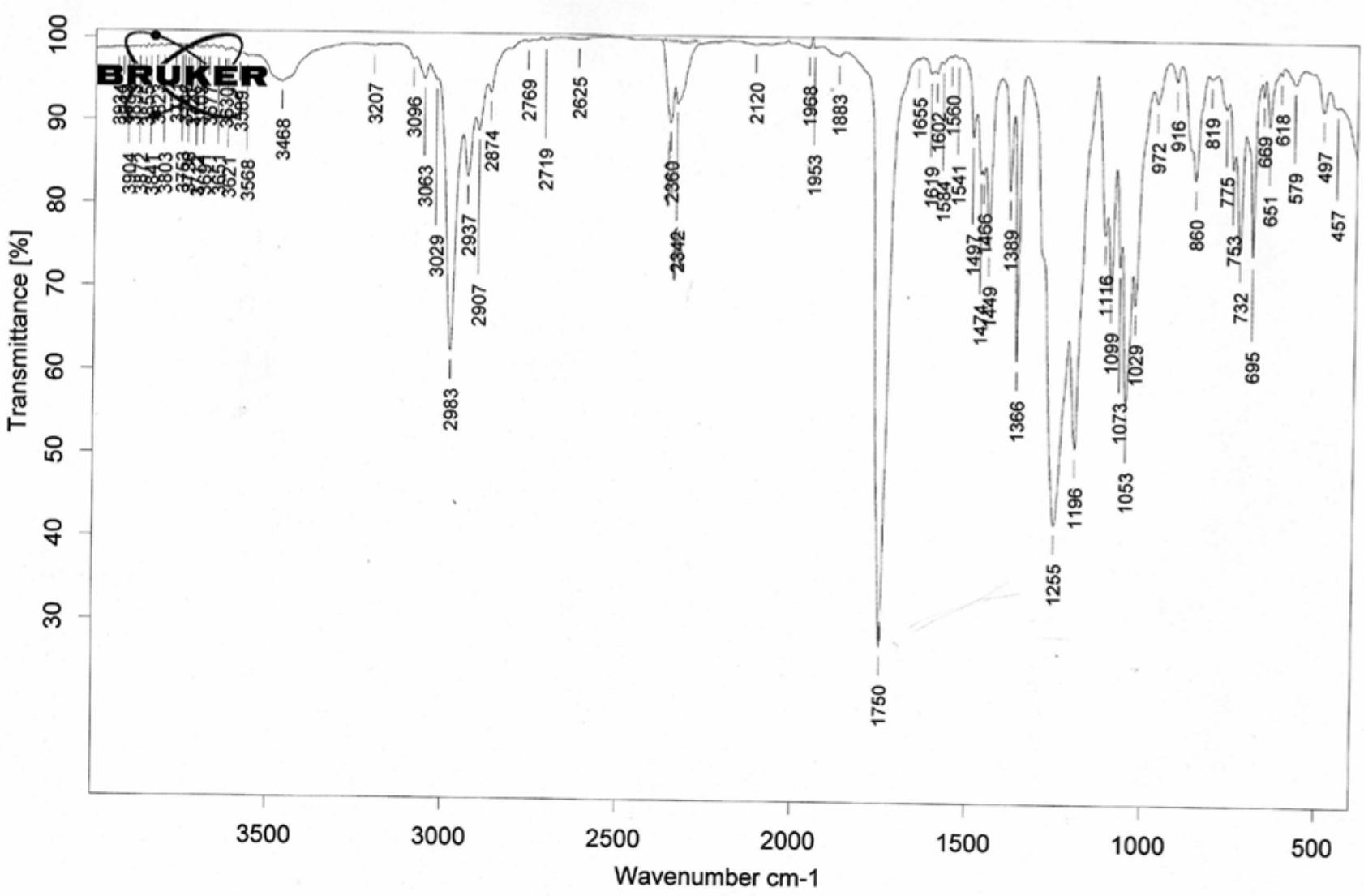
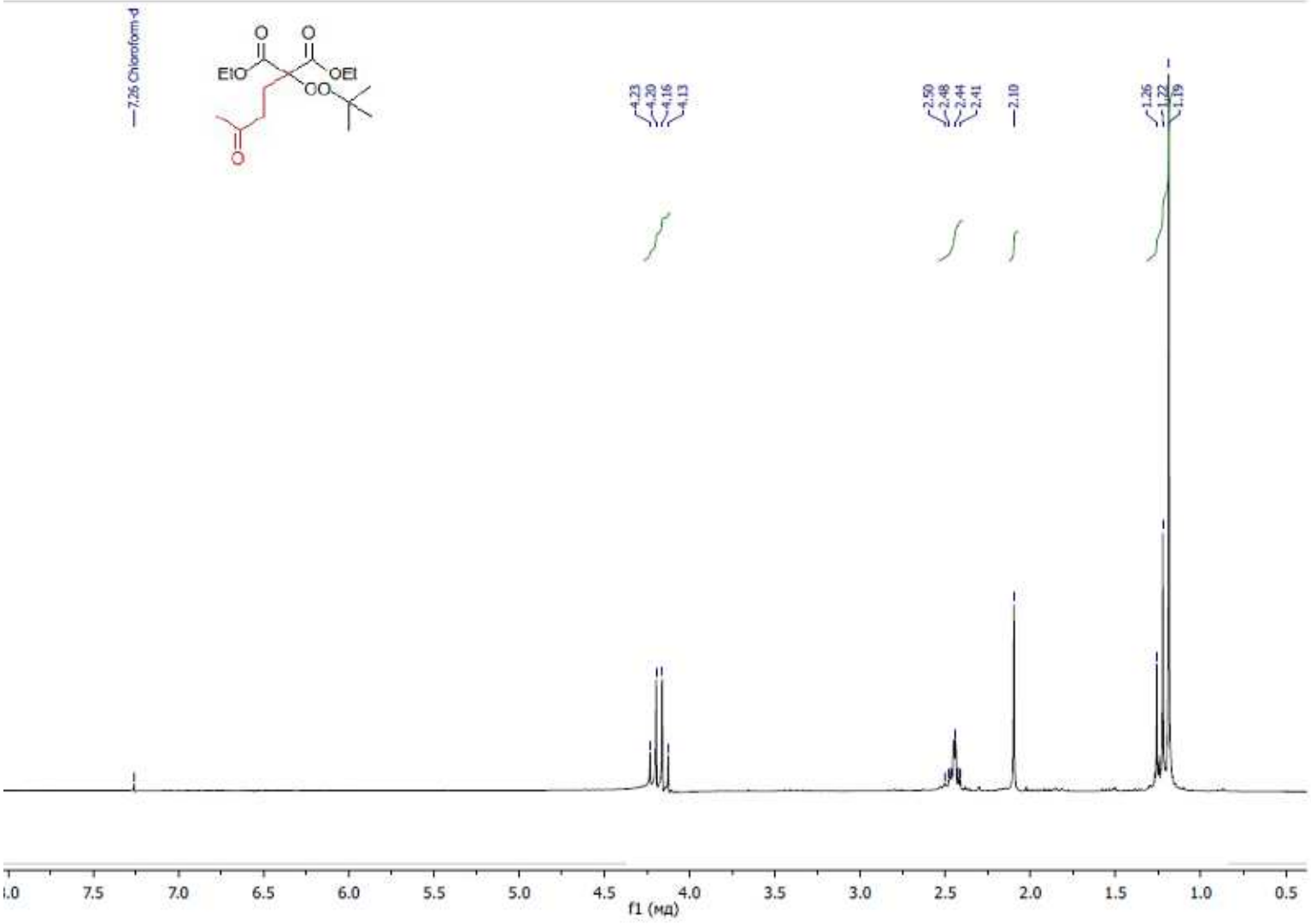
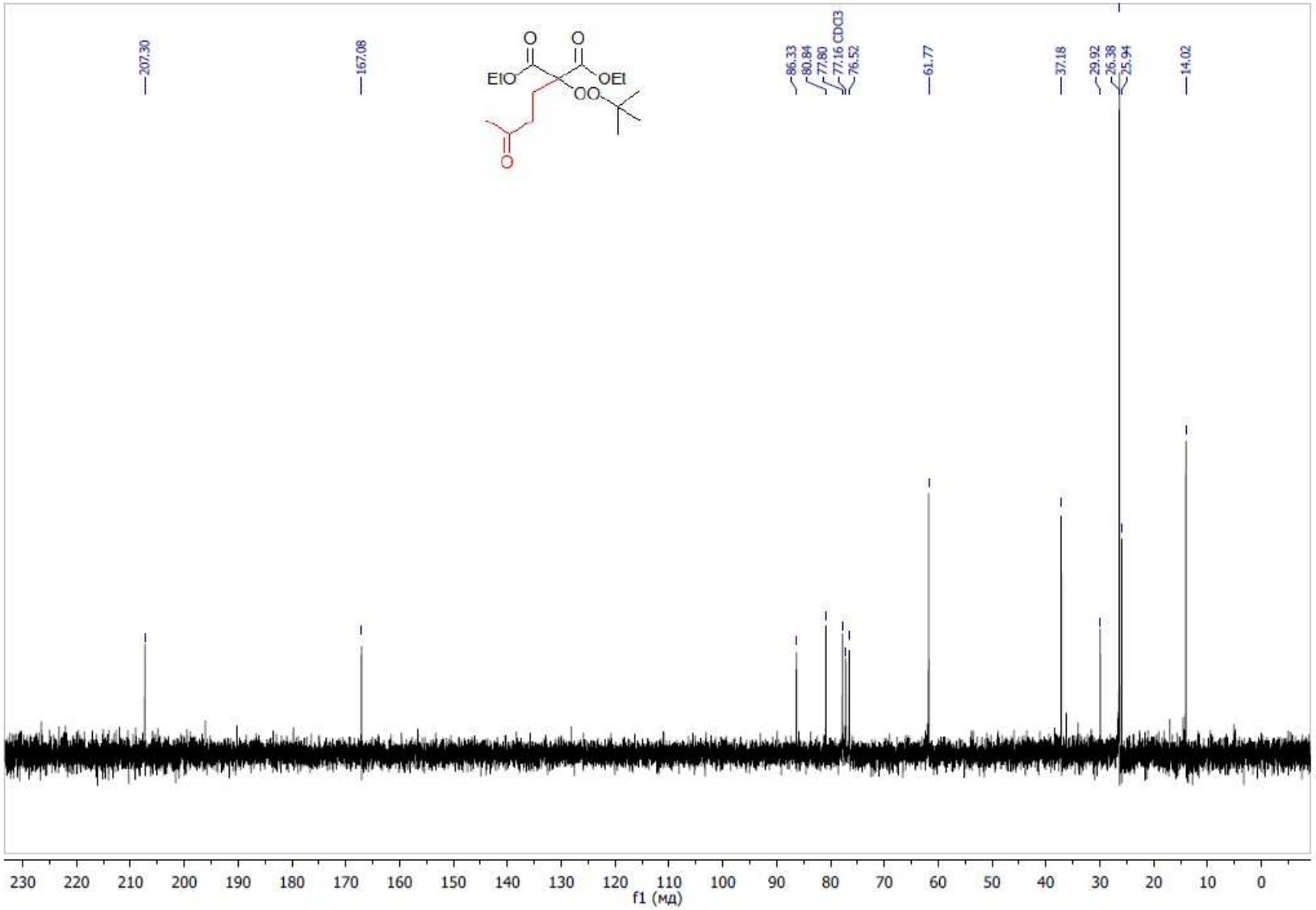


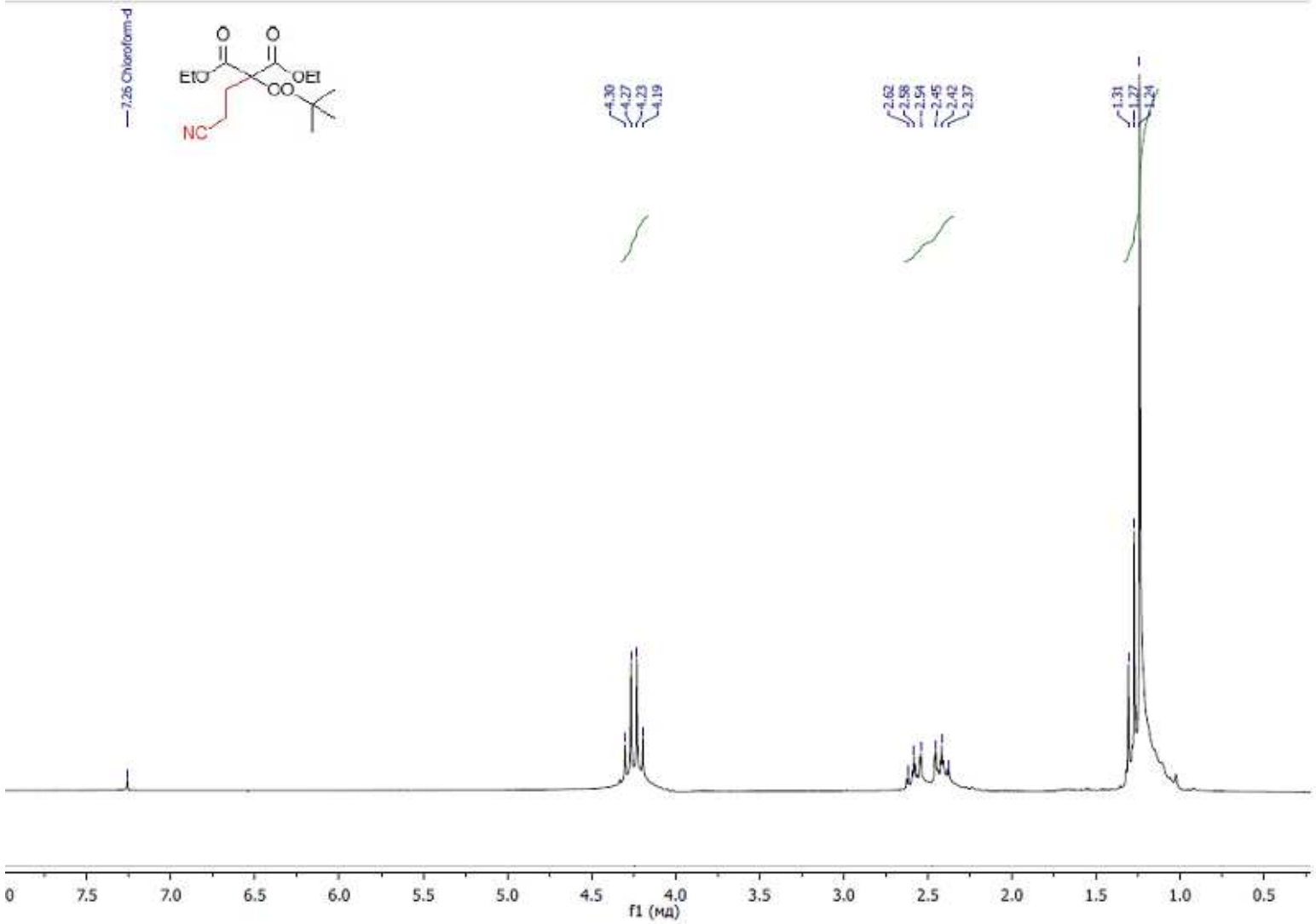
^{1}H NMR of Diethyl (*tert*-butylperoxy)(3-oxobutyl)malonate 2g



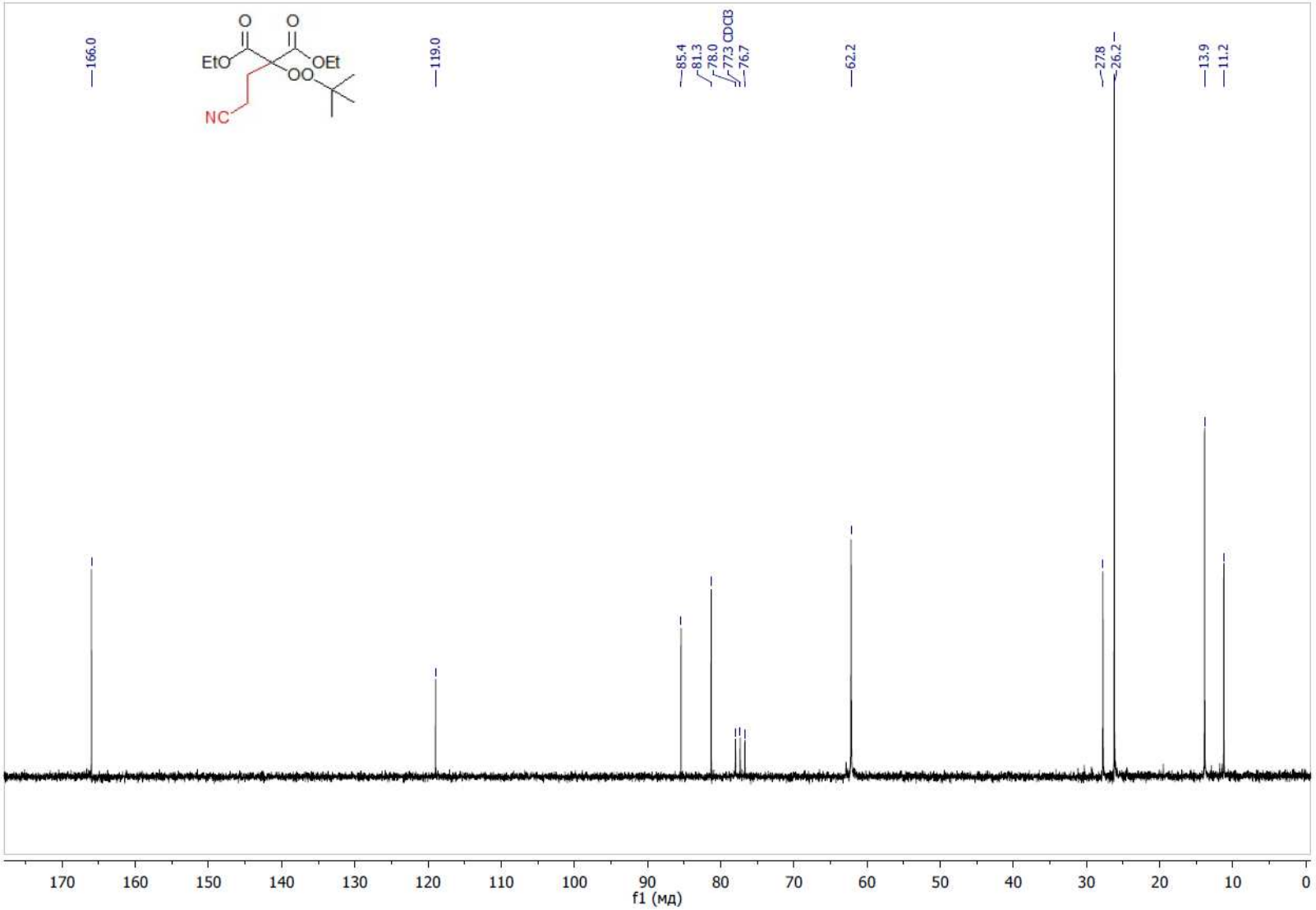
^{13}C NMR of Diethyl (*tert*-butylperoxy)(3-oxobutyl)malonate 2g



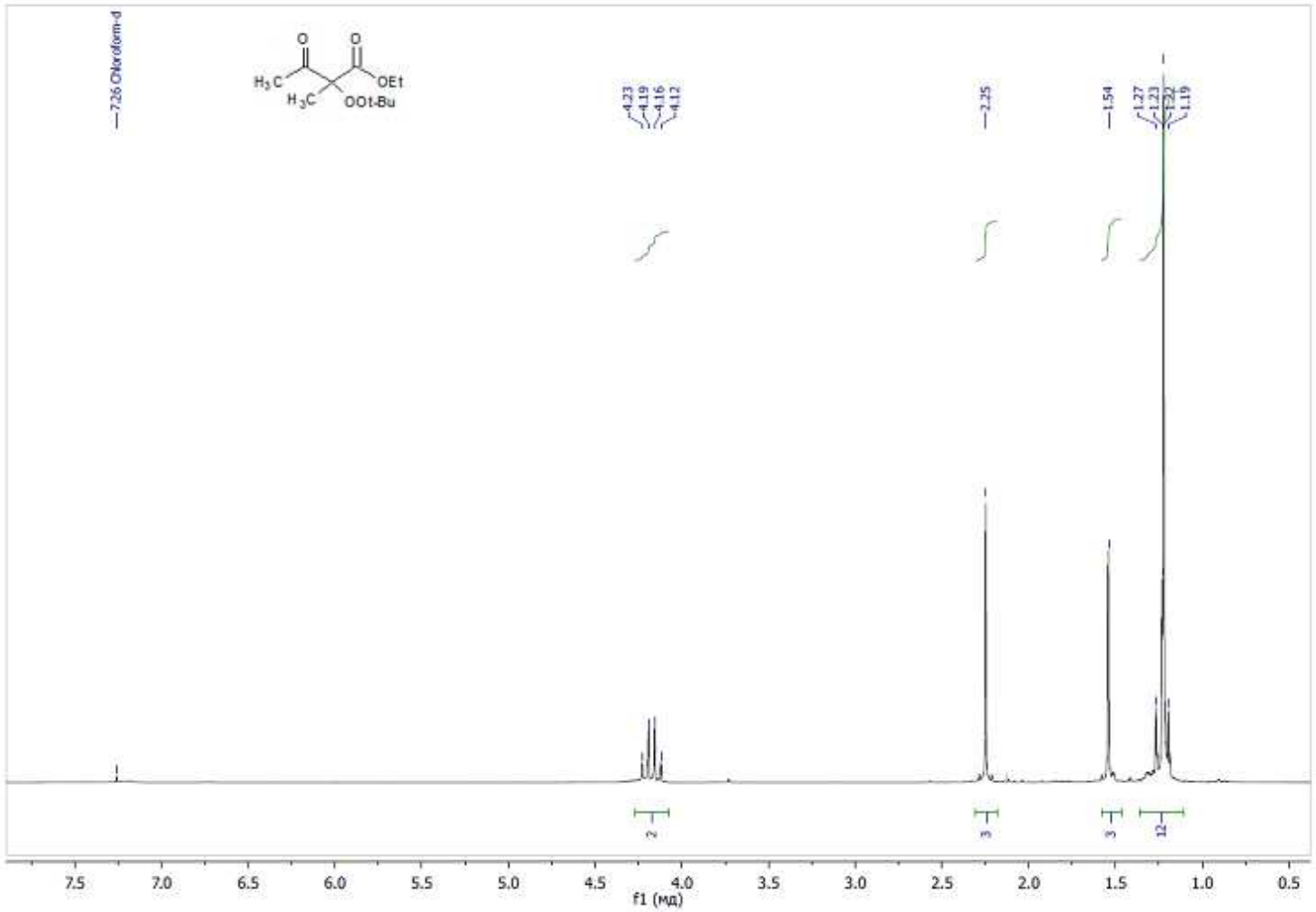
^{1}H NMR of Diethyl (*tert*-butylperoxy)(2-cyanoethyl)malonate 2h



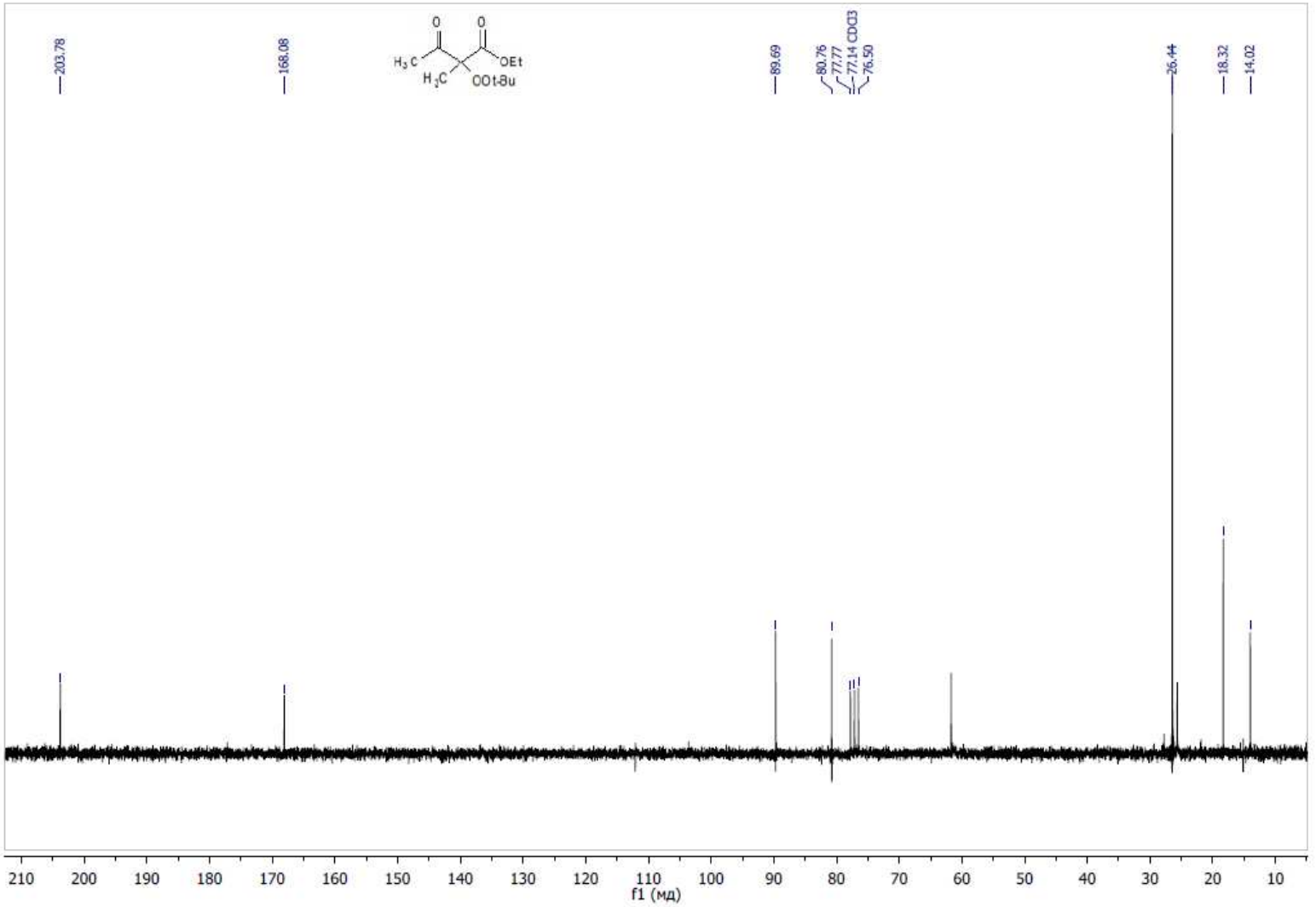
^{13}C NMR of Diethyl (*tert*-butylperoxy)(2-cyanoethyl)malonate 2h



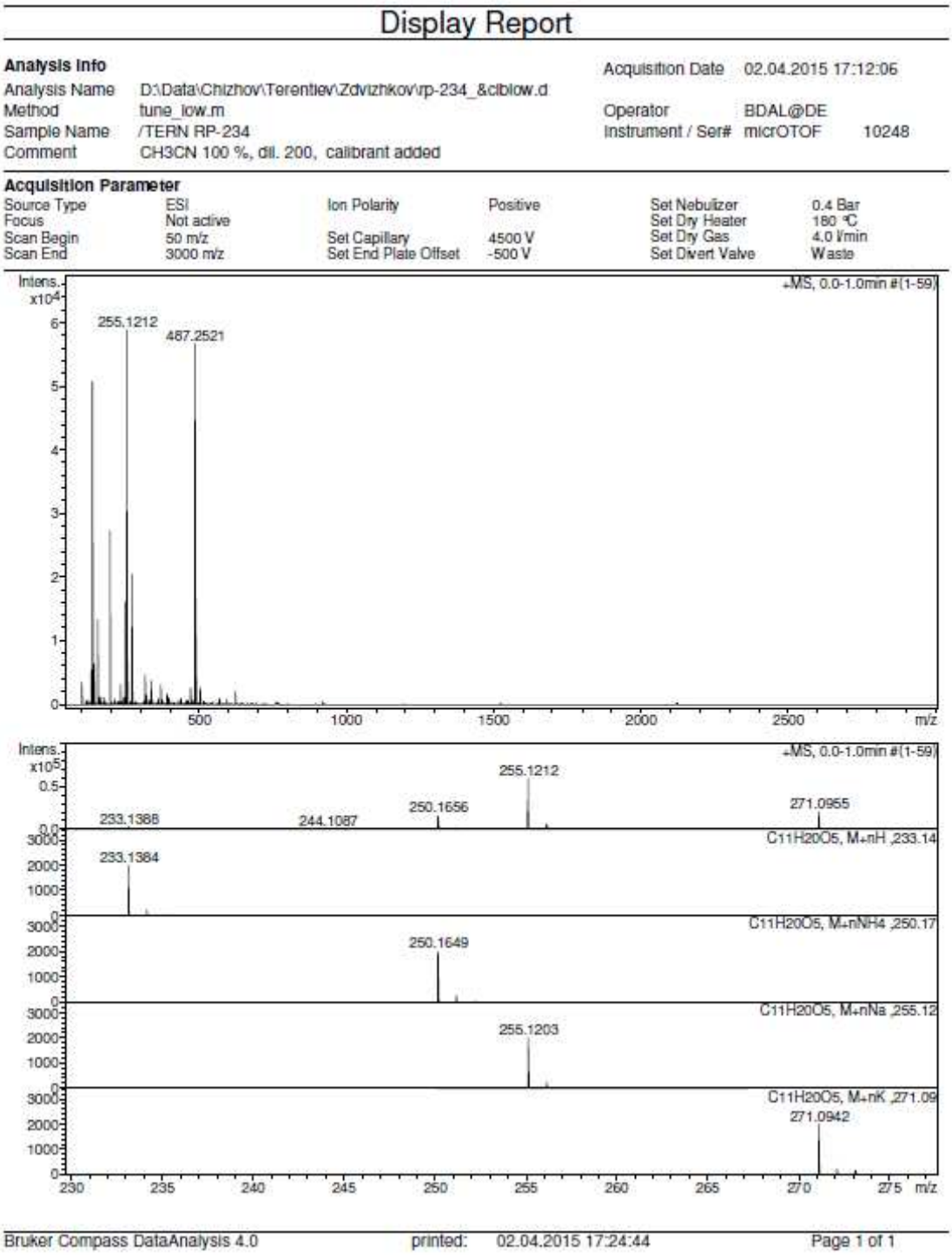
^{1}H NMR of Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate 4a



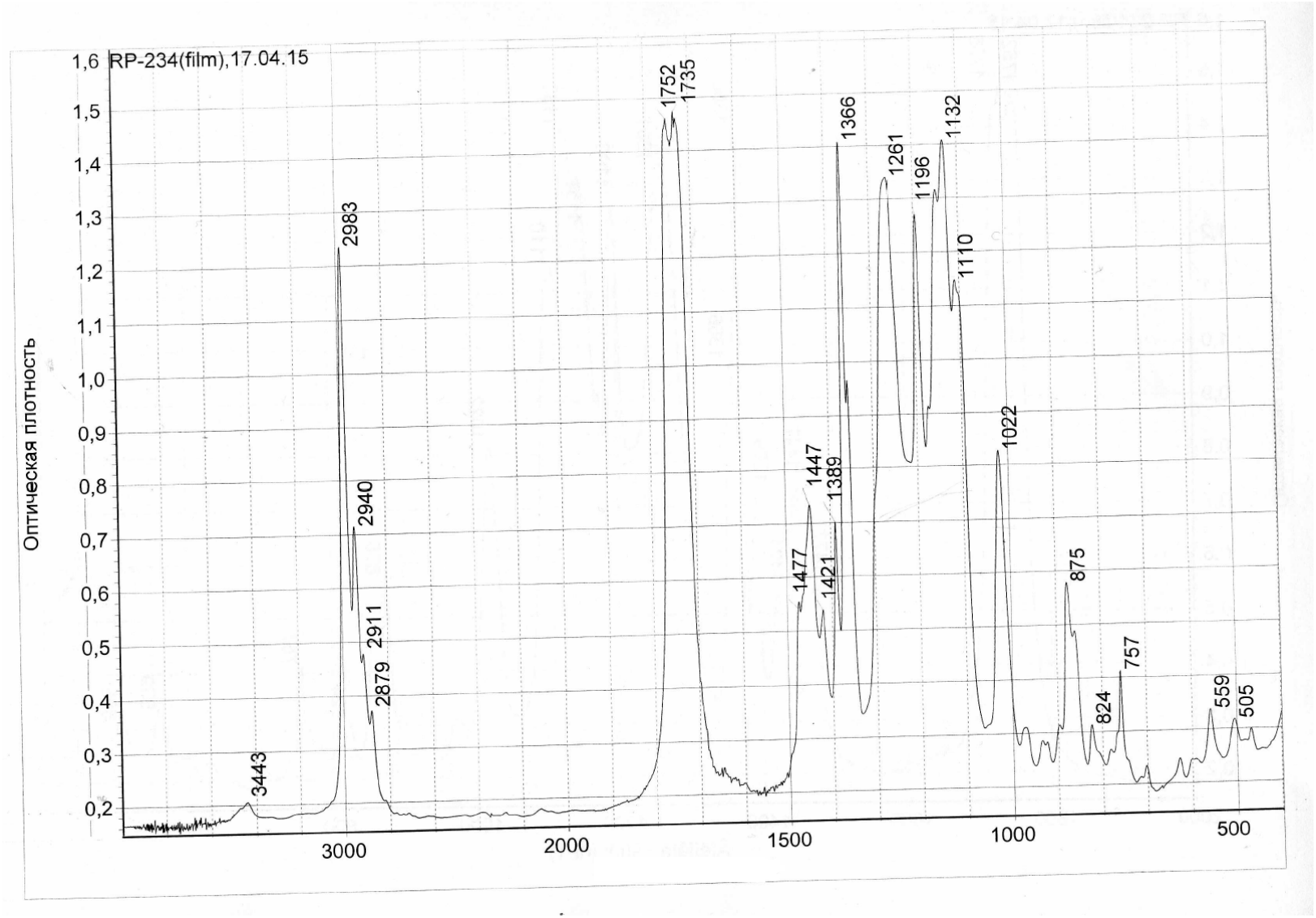
^{13}C NMR of Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate 4a



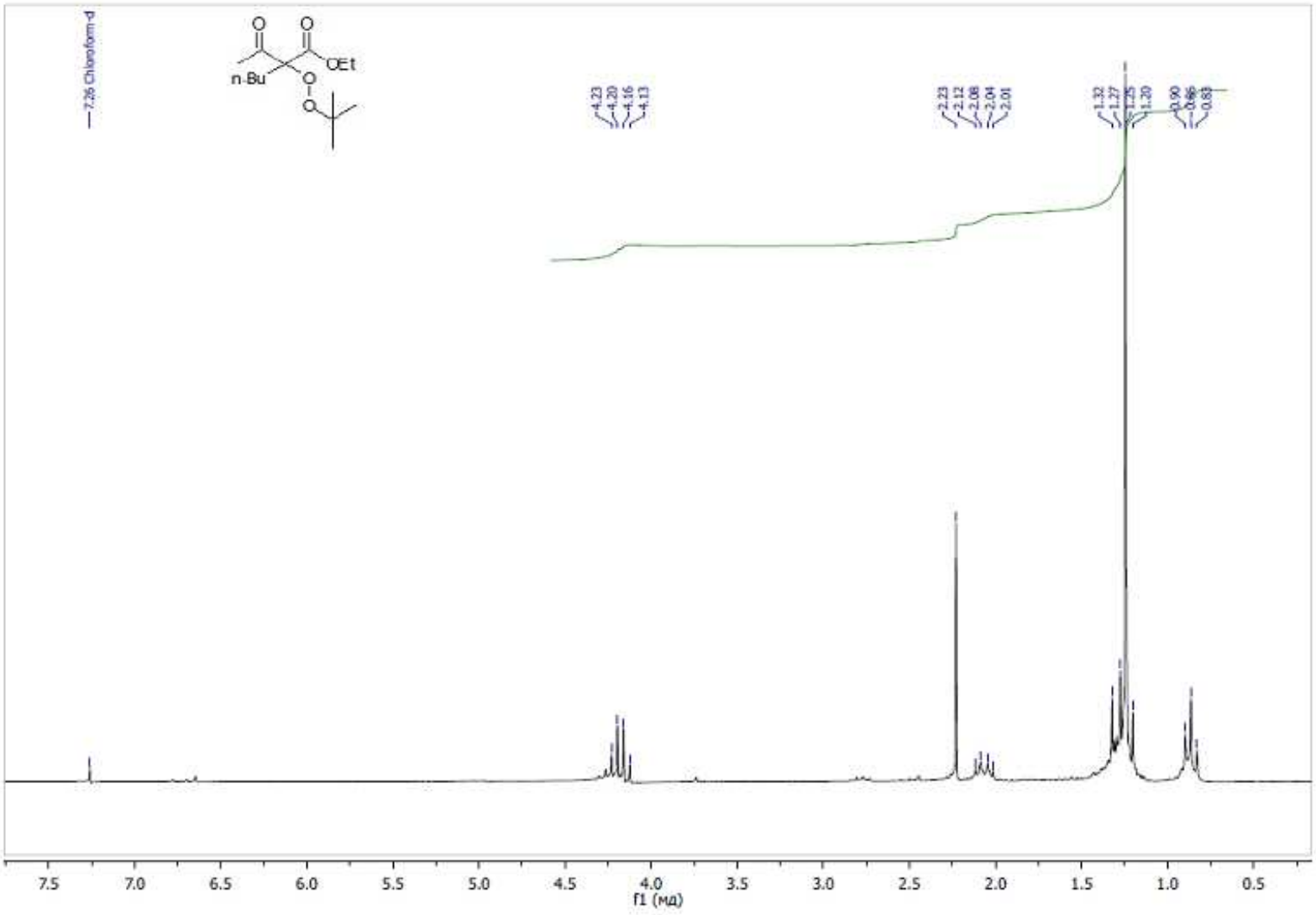
HRMS of Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate 4a



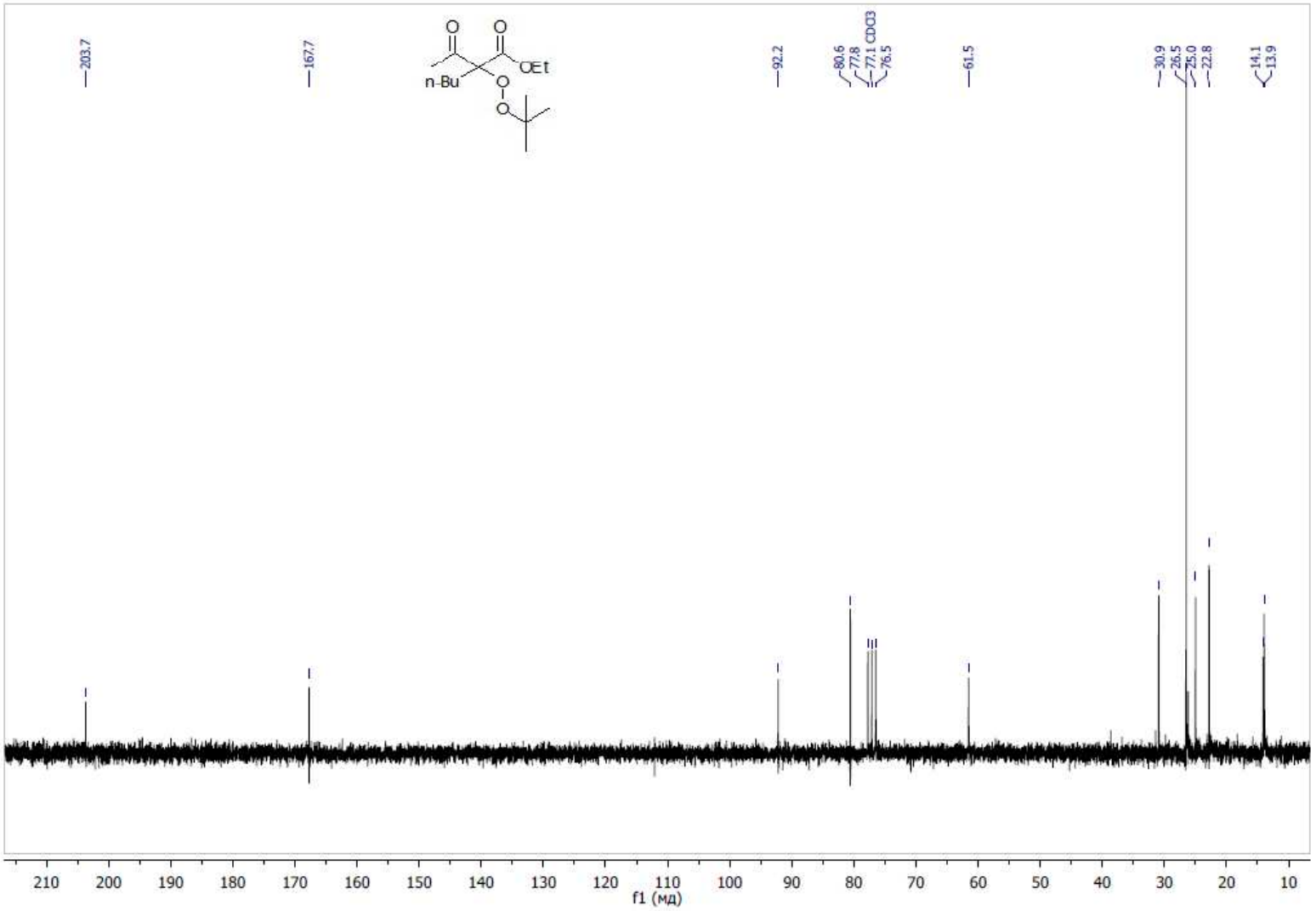
IR of Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate 4a



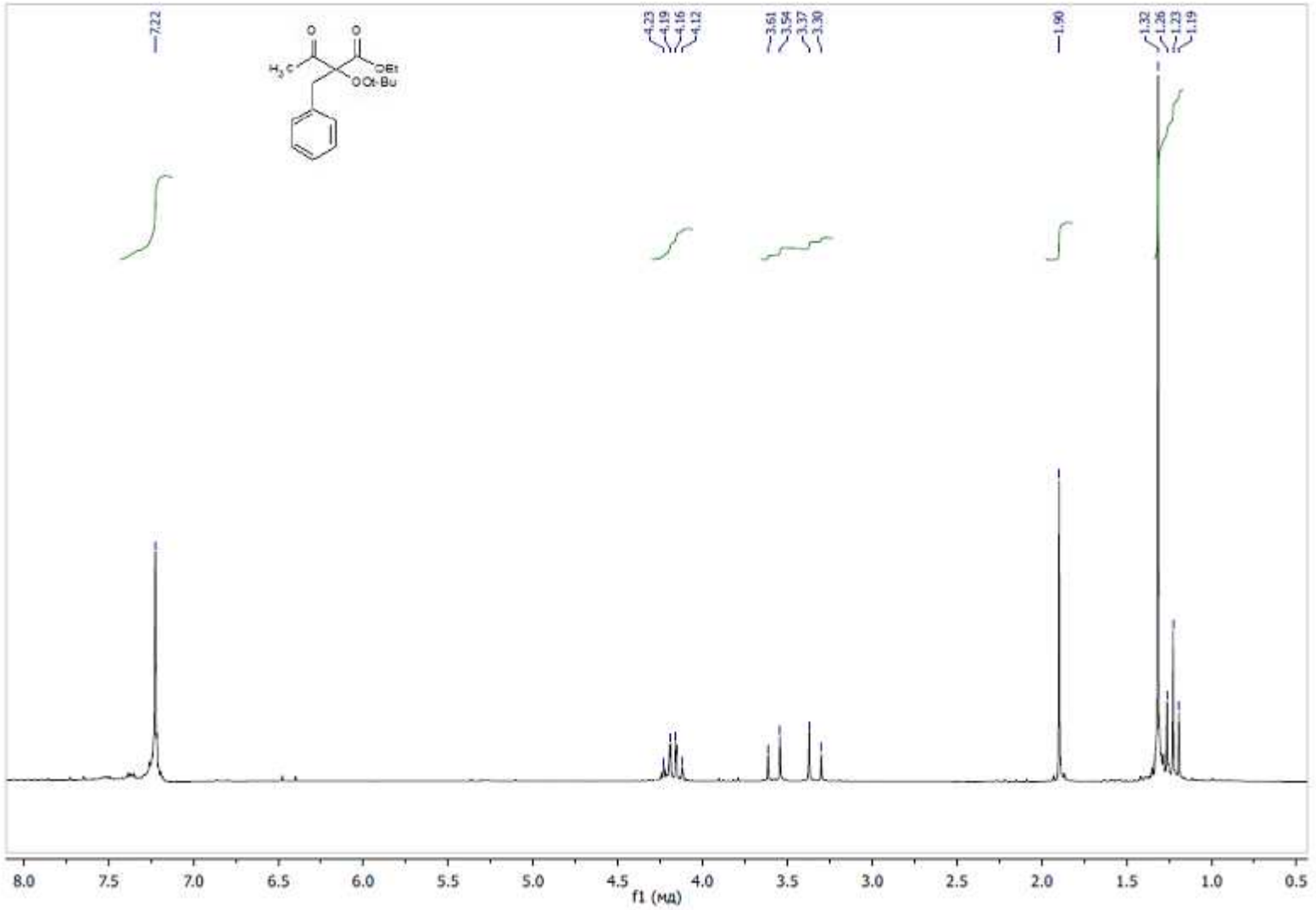
^{1}H NMR of Ethyl 2-acetyl-2-(*tert*-butylperoxy)hexanoate 4b



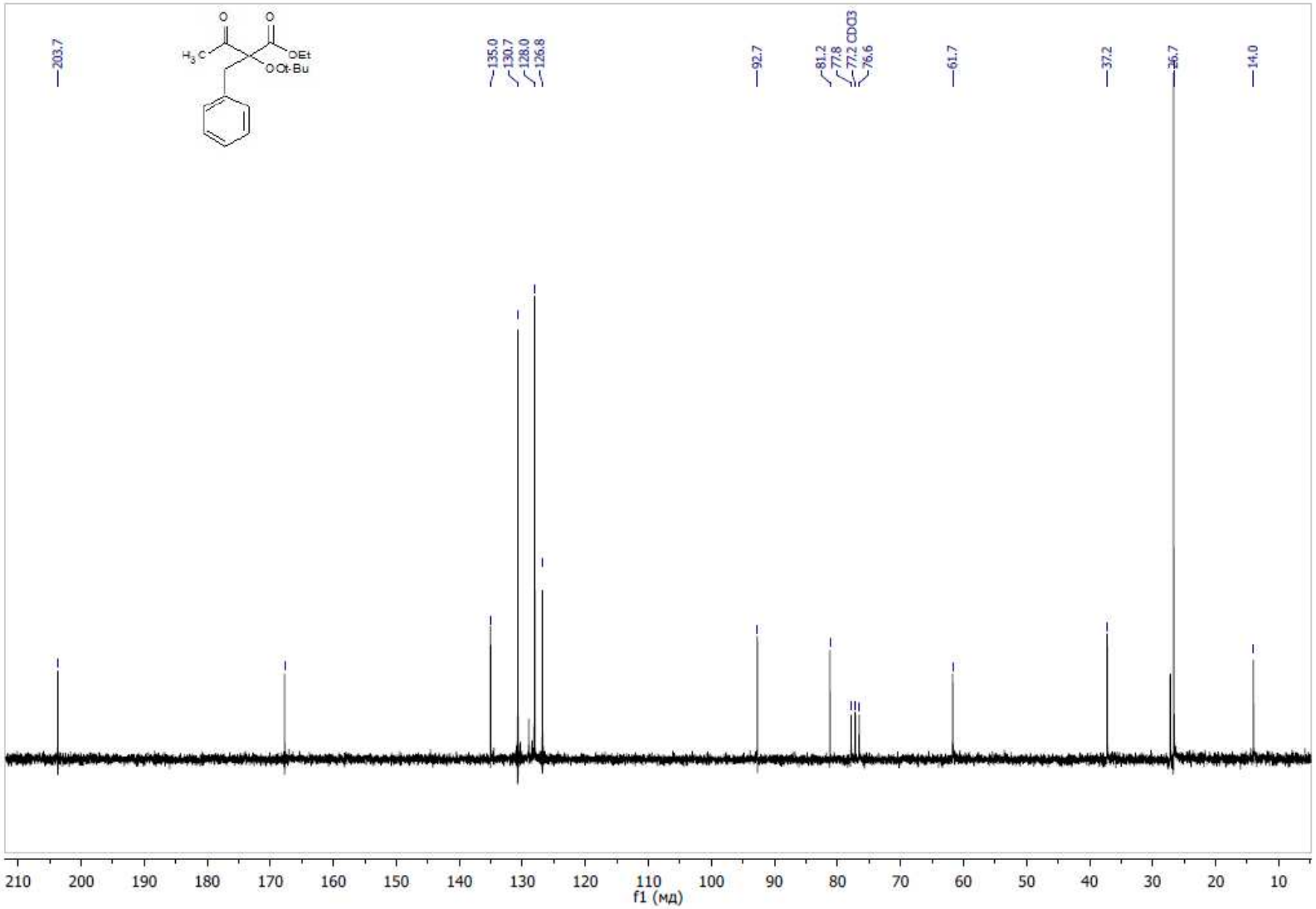
^{13}C NMR of Ethyl 2-acetyl-2-(*tert*-butylperoxy)hexanoate 4b



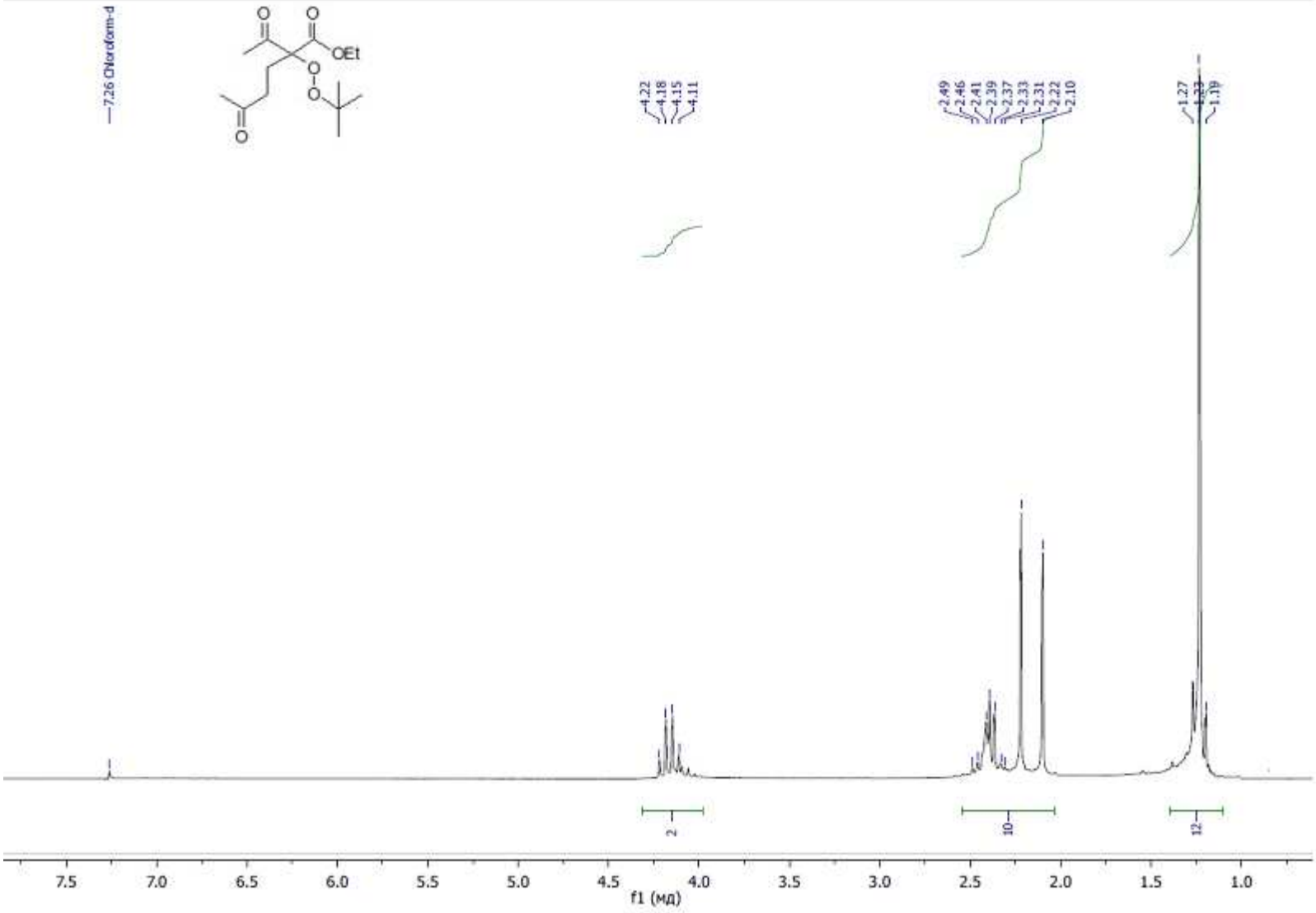
^{1}H NMR of Ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate 4c



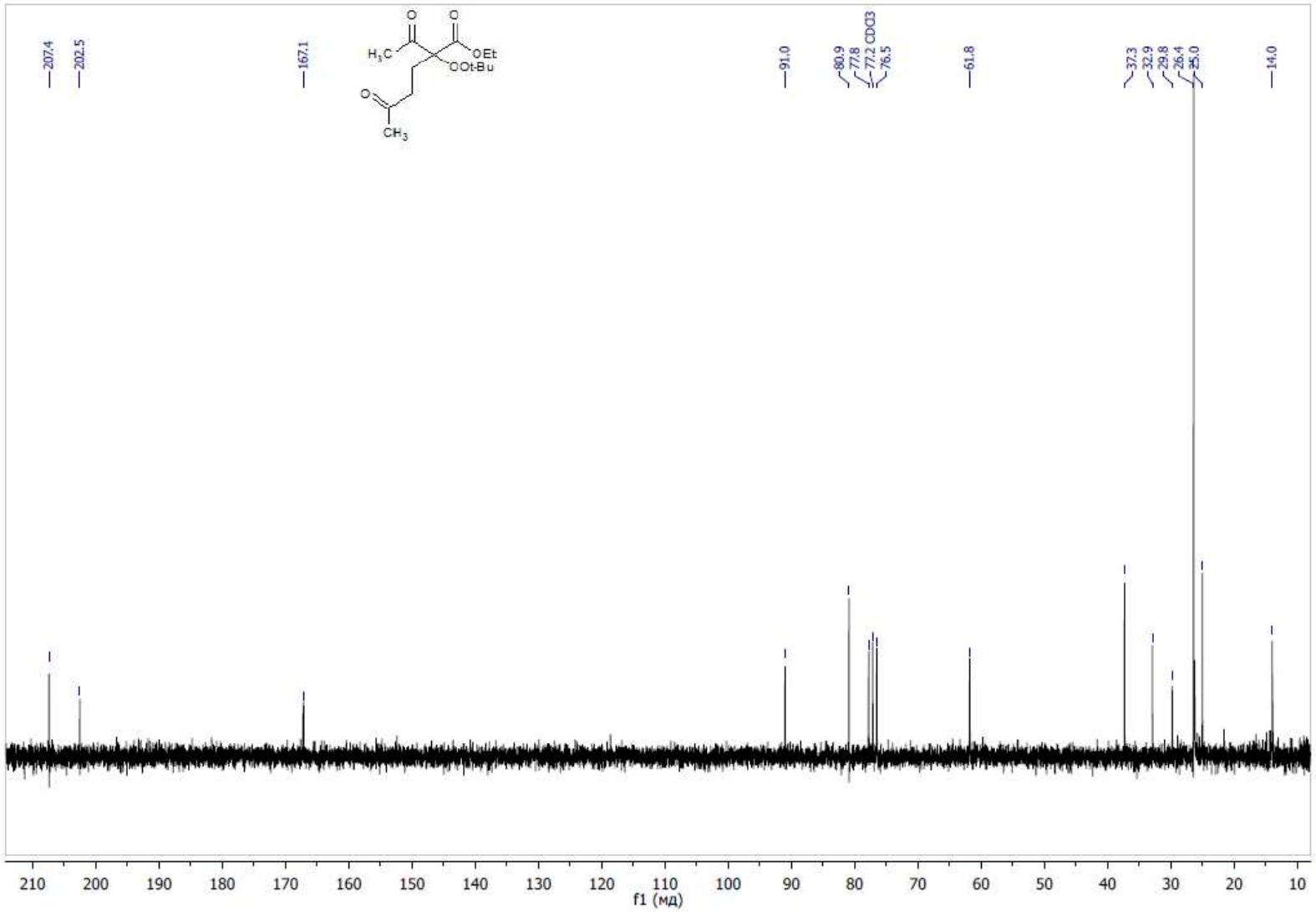
^{13}C NMR of Ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate 4c



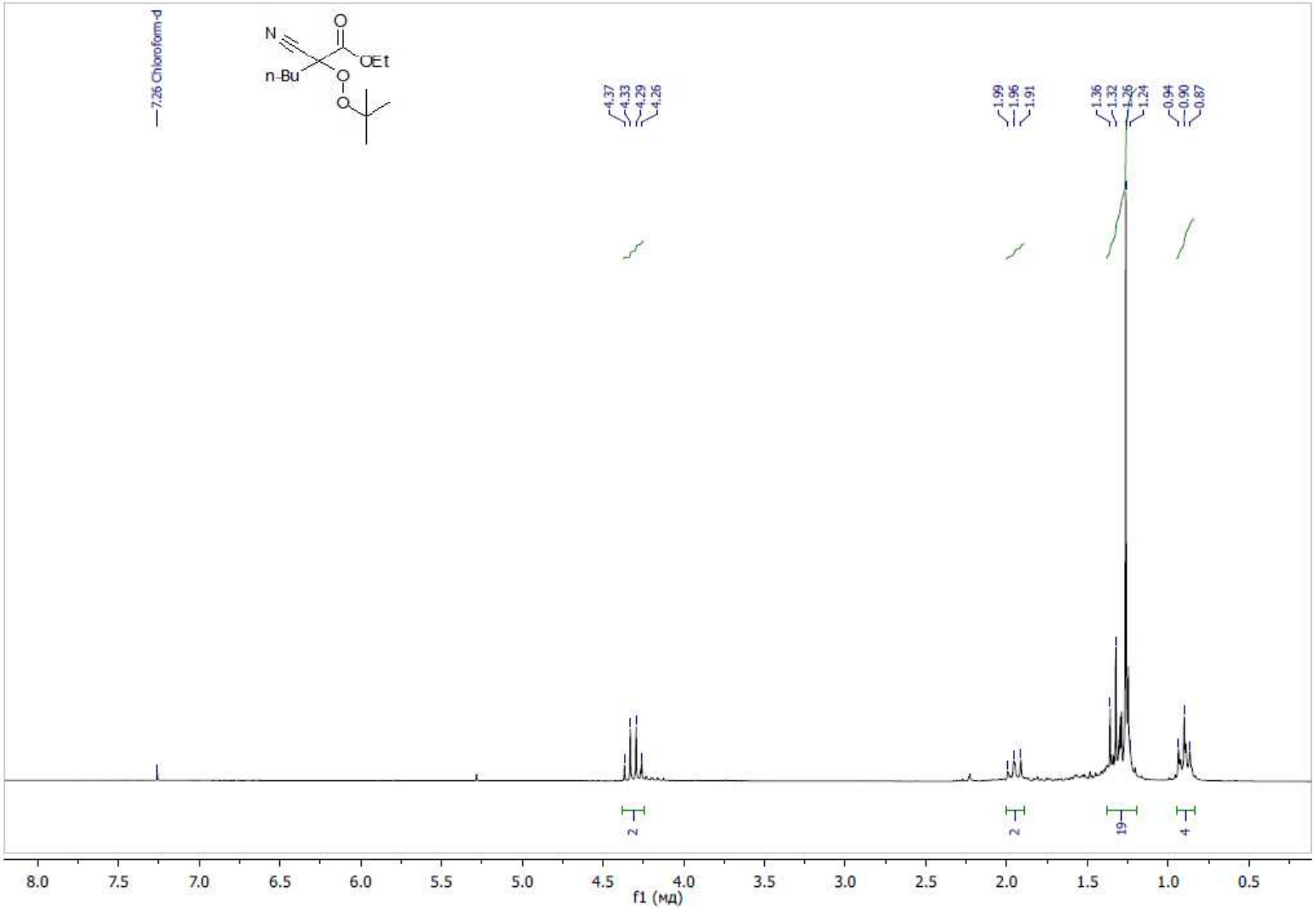
^{1}H NMR of Ethyl 2-acetyl-2-(*tert*-butylperoxy)-5-oxohexanoate 4d



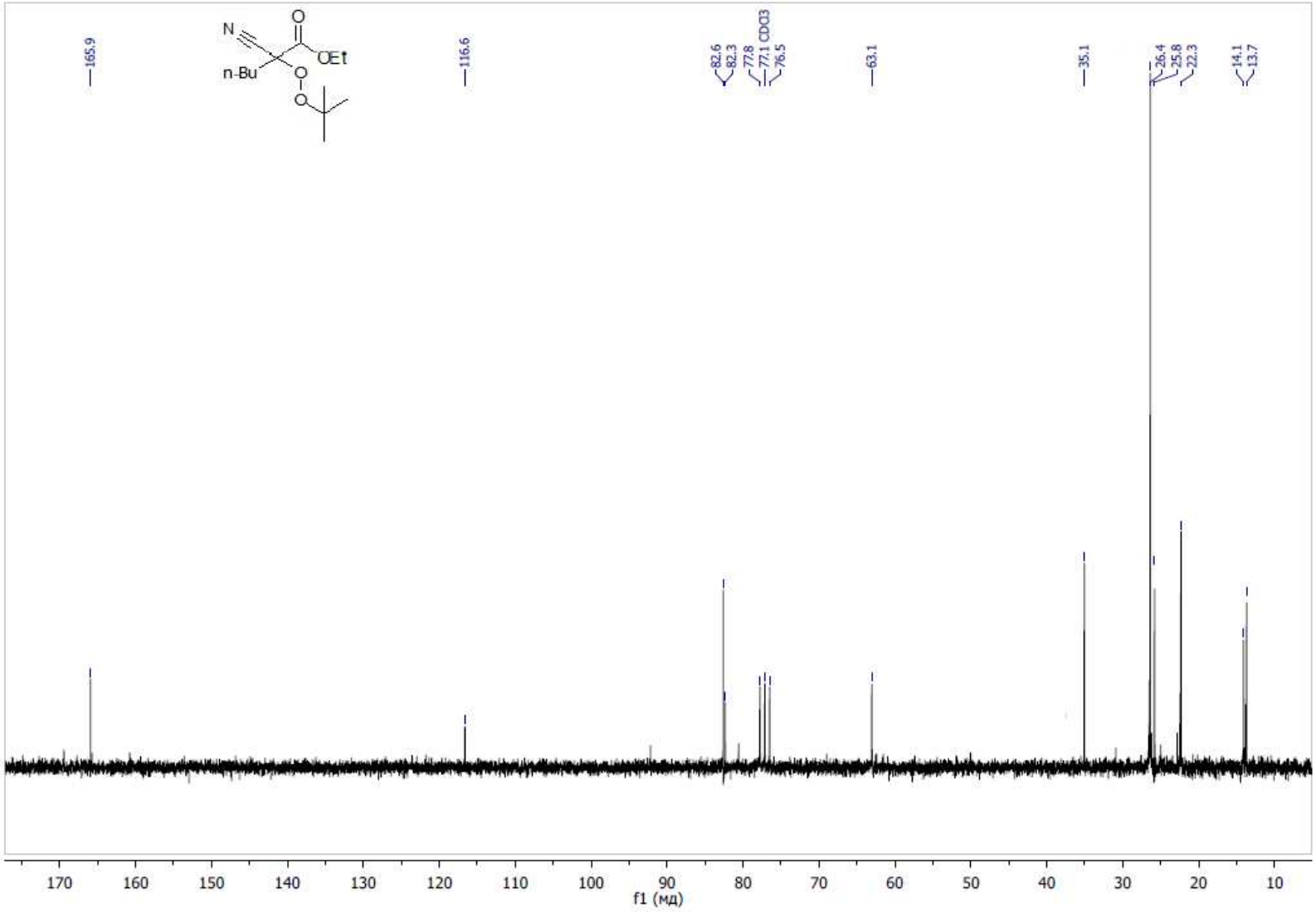
^{13}C NMR of Ethyl 2-acetyl-2-(*tert*-butylperoxy)-5-oxohexanoate 4d



^{1}H NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyanohexanoate 6a



^{13}C NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyanohexanoate 6a



HRMS of Ethyl 2-(*tert*-butylperoxy)-2-cyanohexanoate 6a

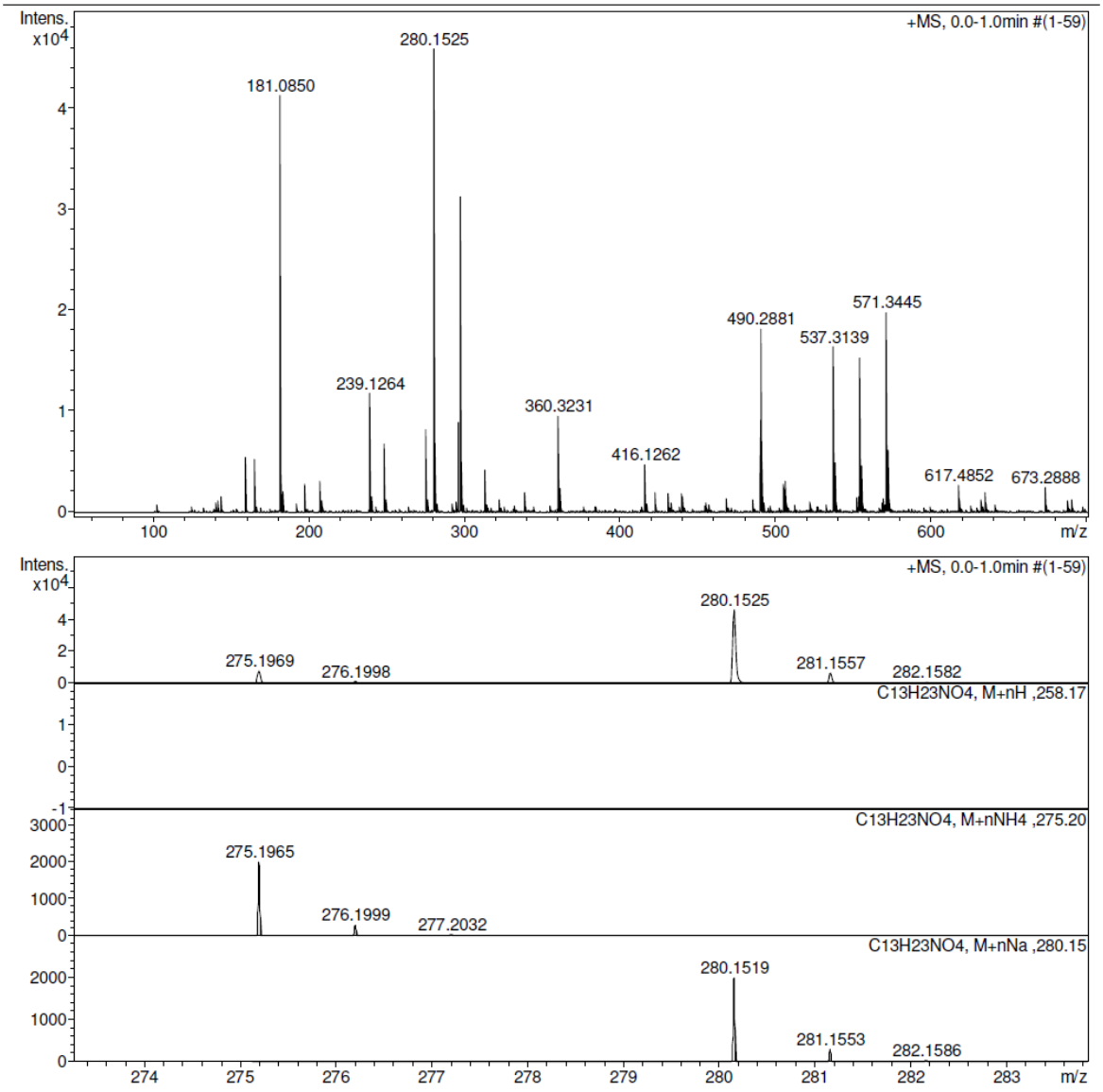
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Zdvizhkov\kl-122_&clblow.d	Acquisition Date	02.04.2015 17:34:18
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN KL-122	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



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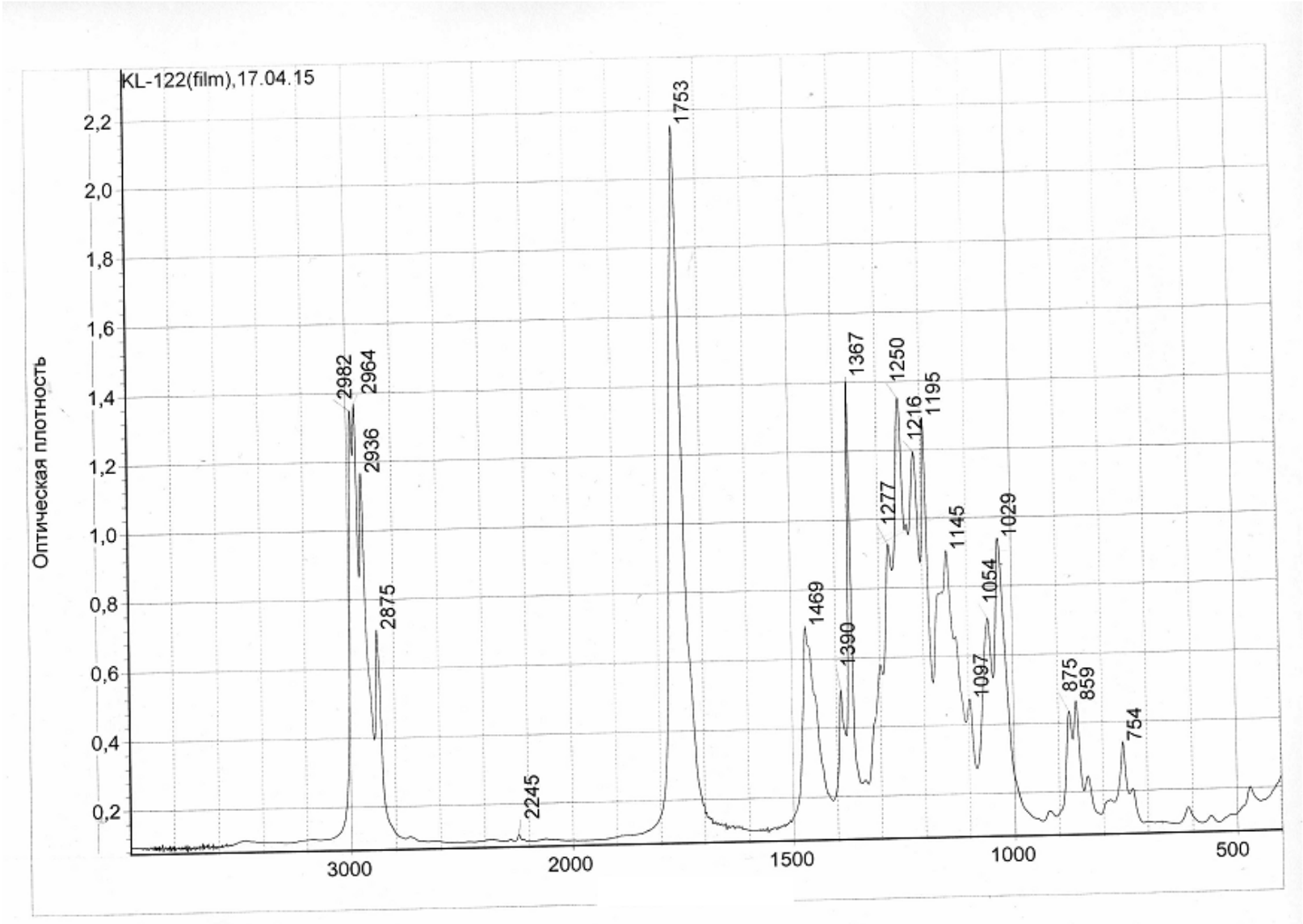
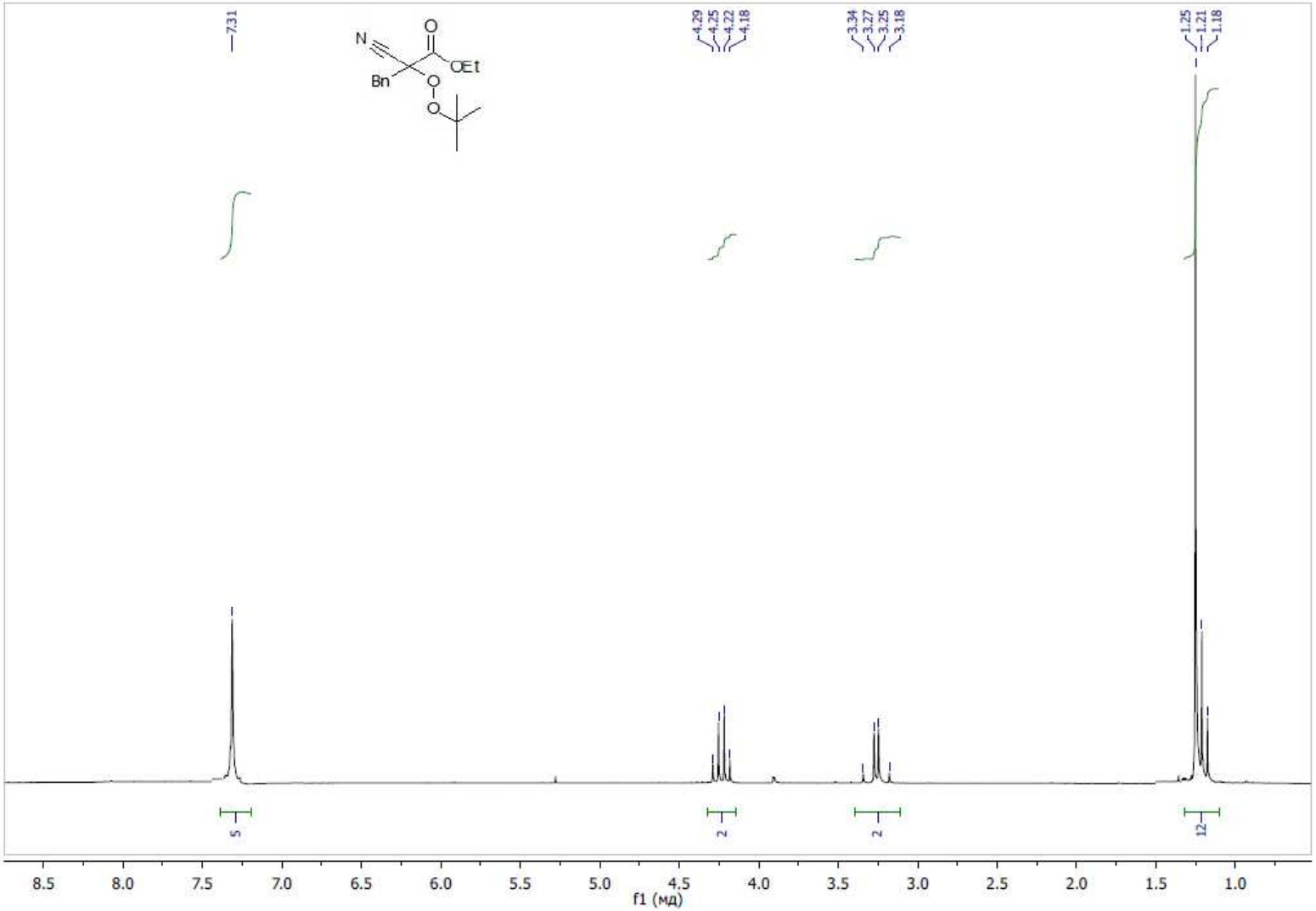
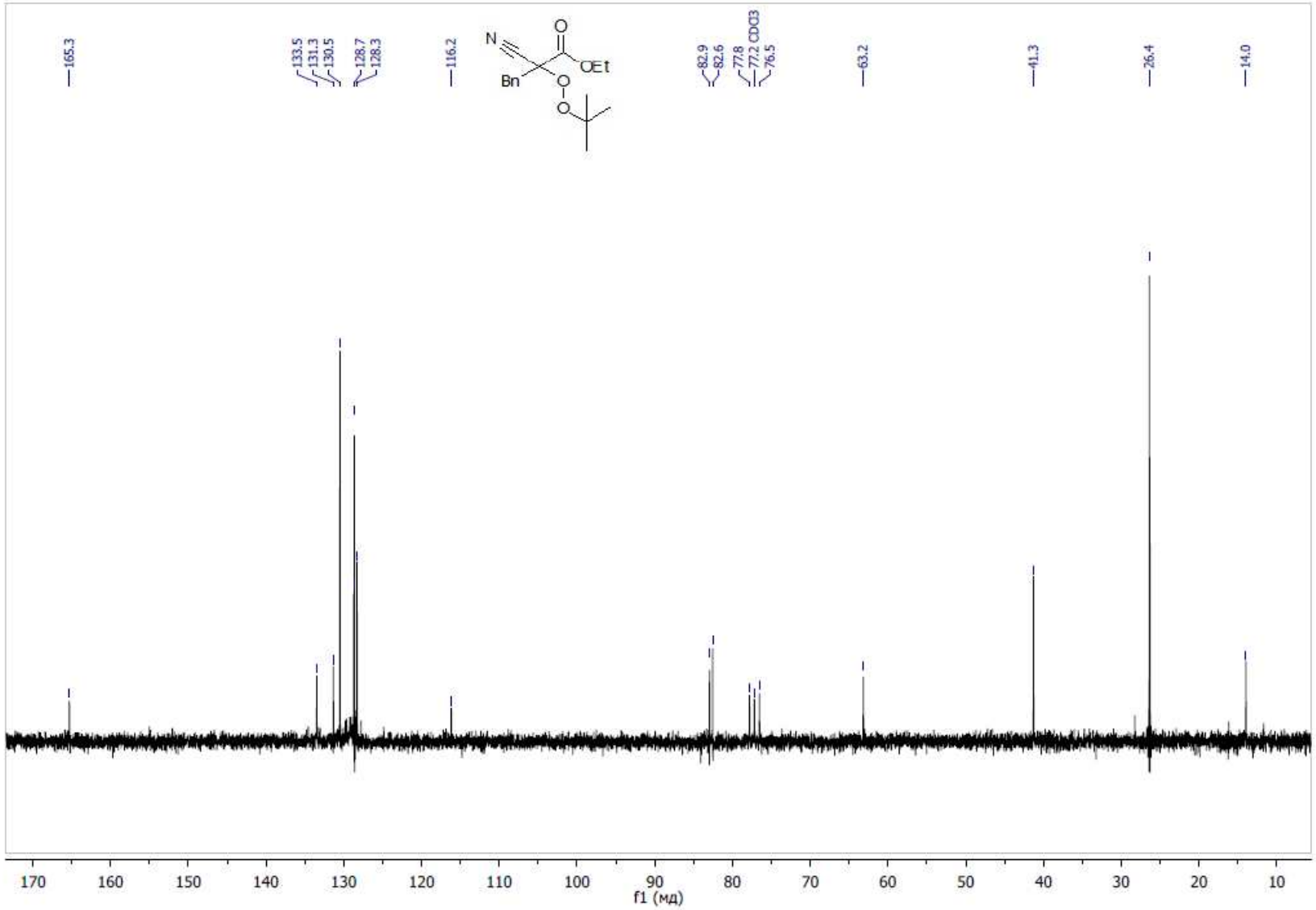
IR of Ethyl 2-(*tert*-butylperoxy)-2-cyanohexanoate 6a



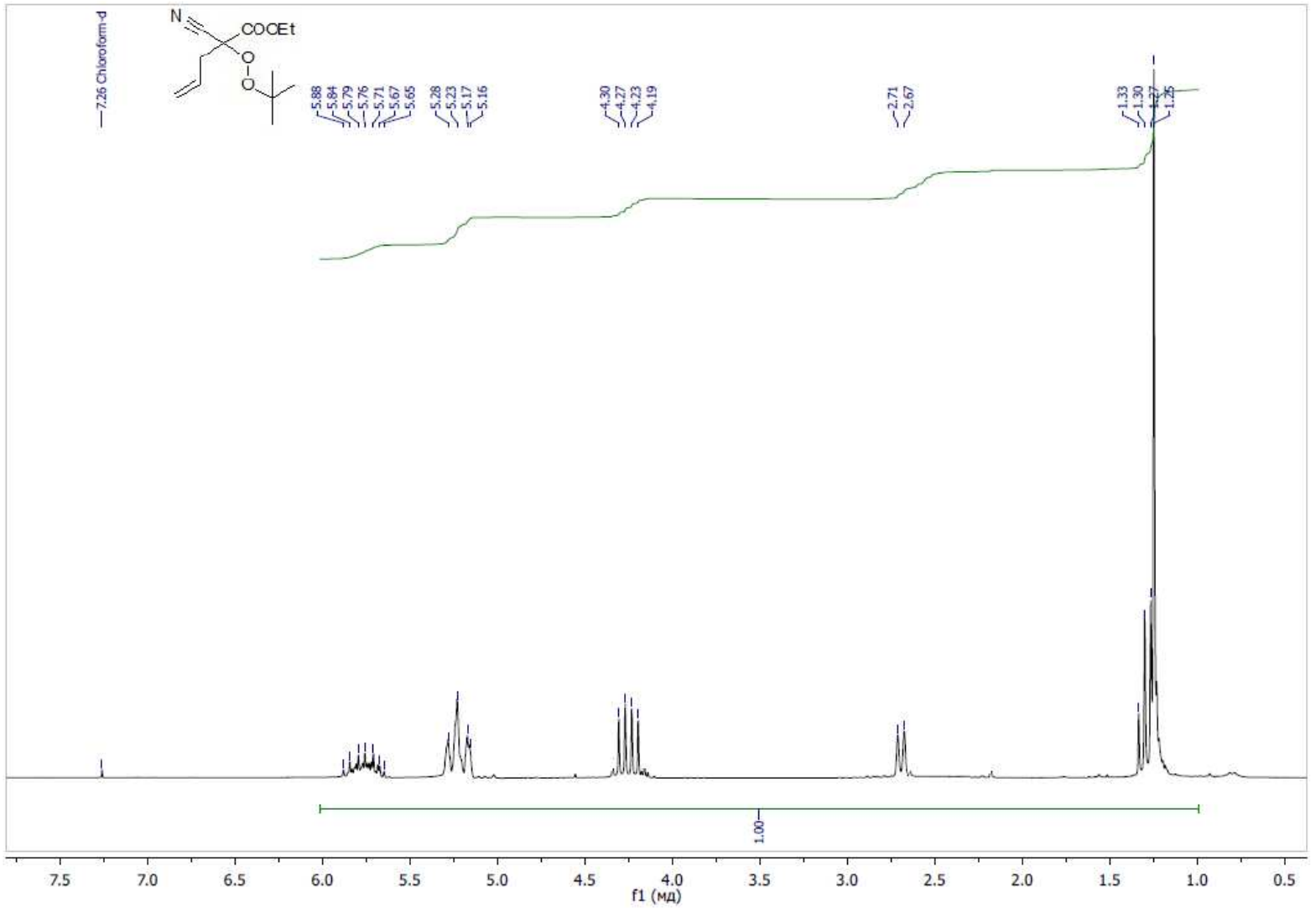
^{1}H NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyano-3-phenylpropanoate 6b



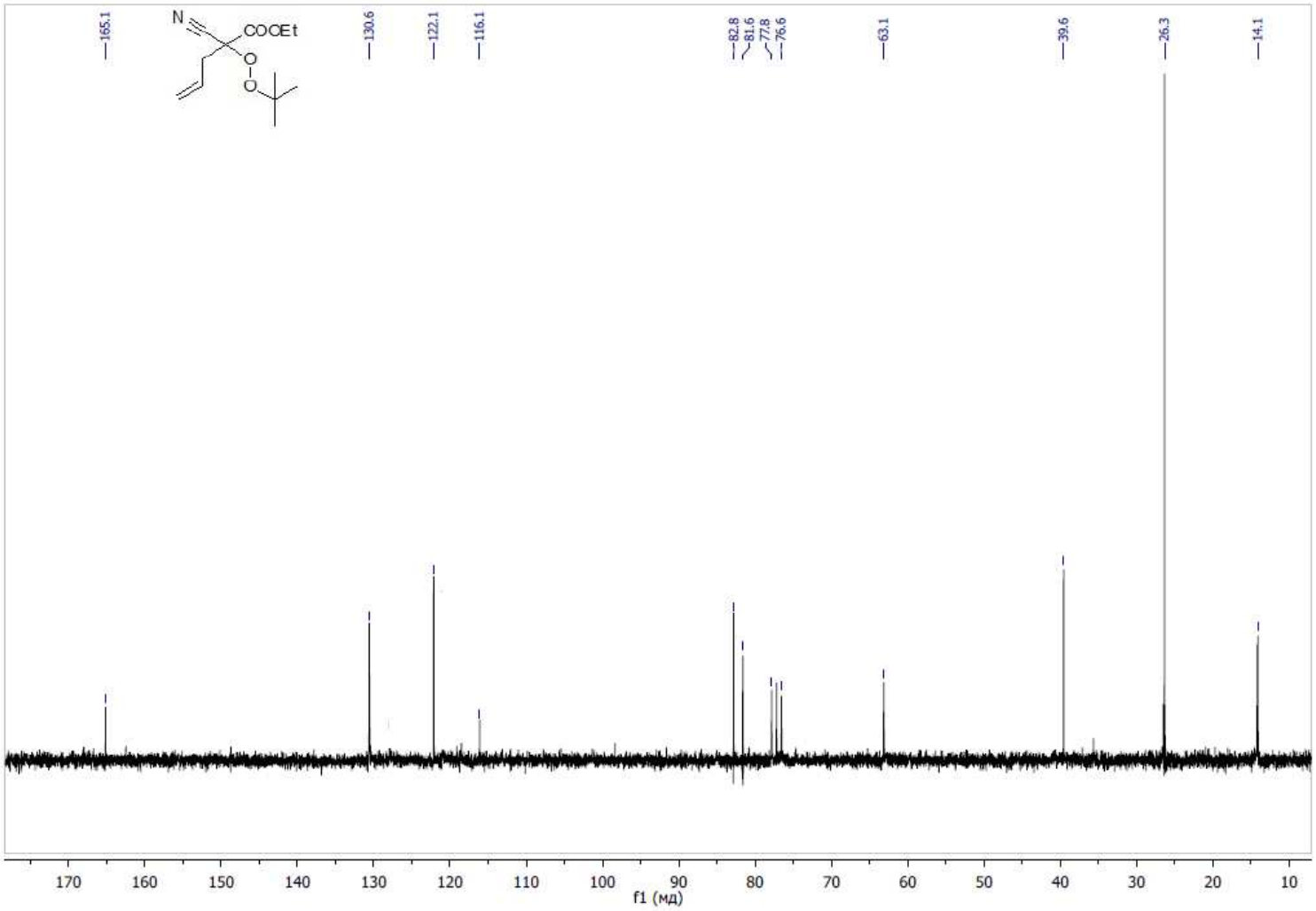
^{13}C NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyano-3-phenylpropanoate 6b



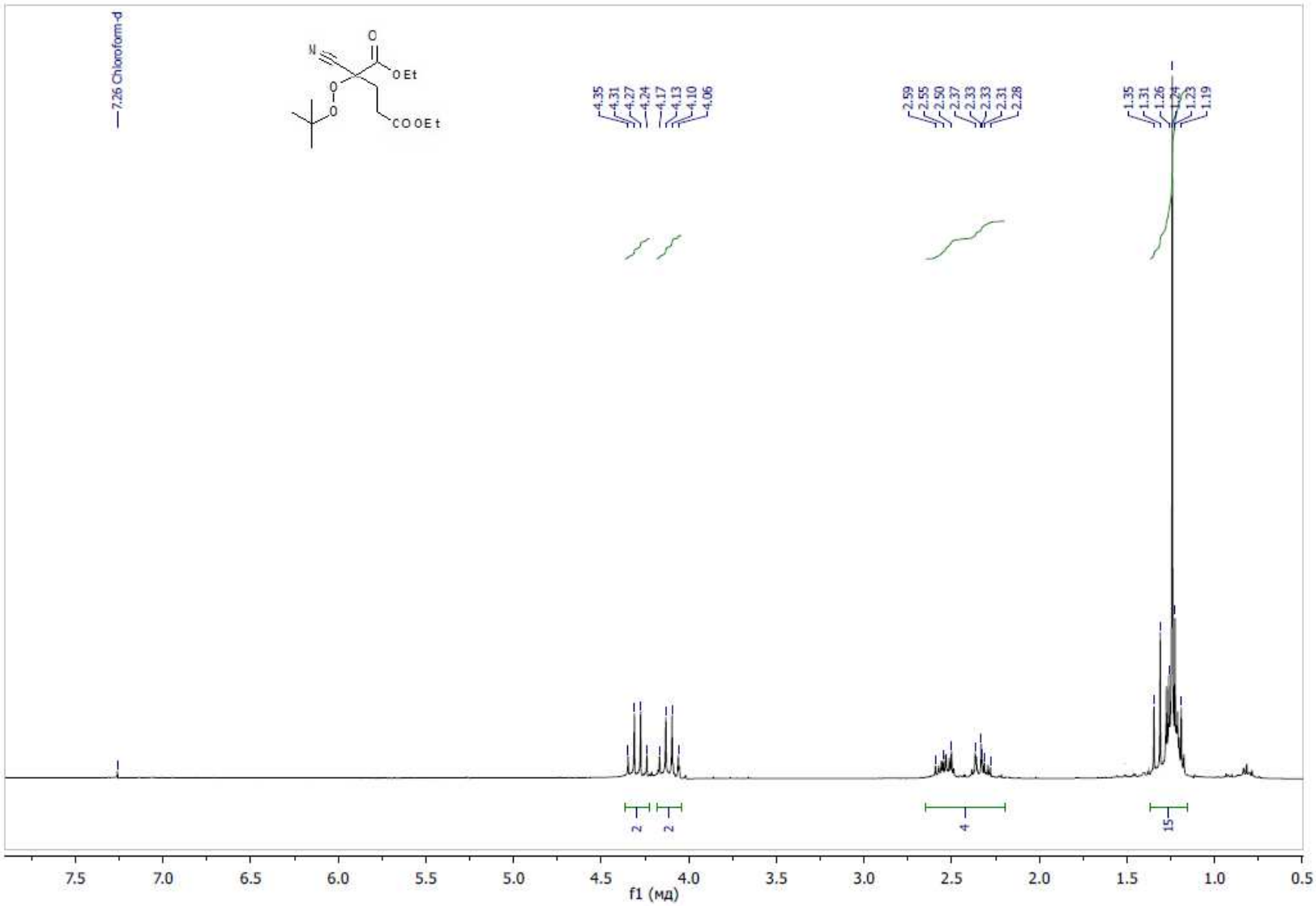
^{1}H NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyanopent-4-enoate 6c



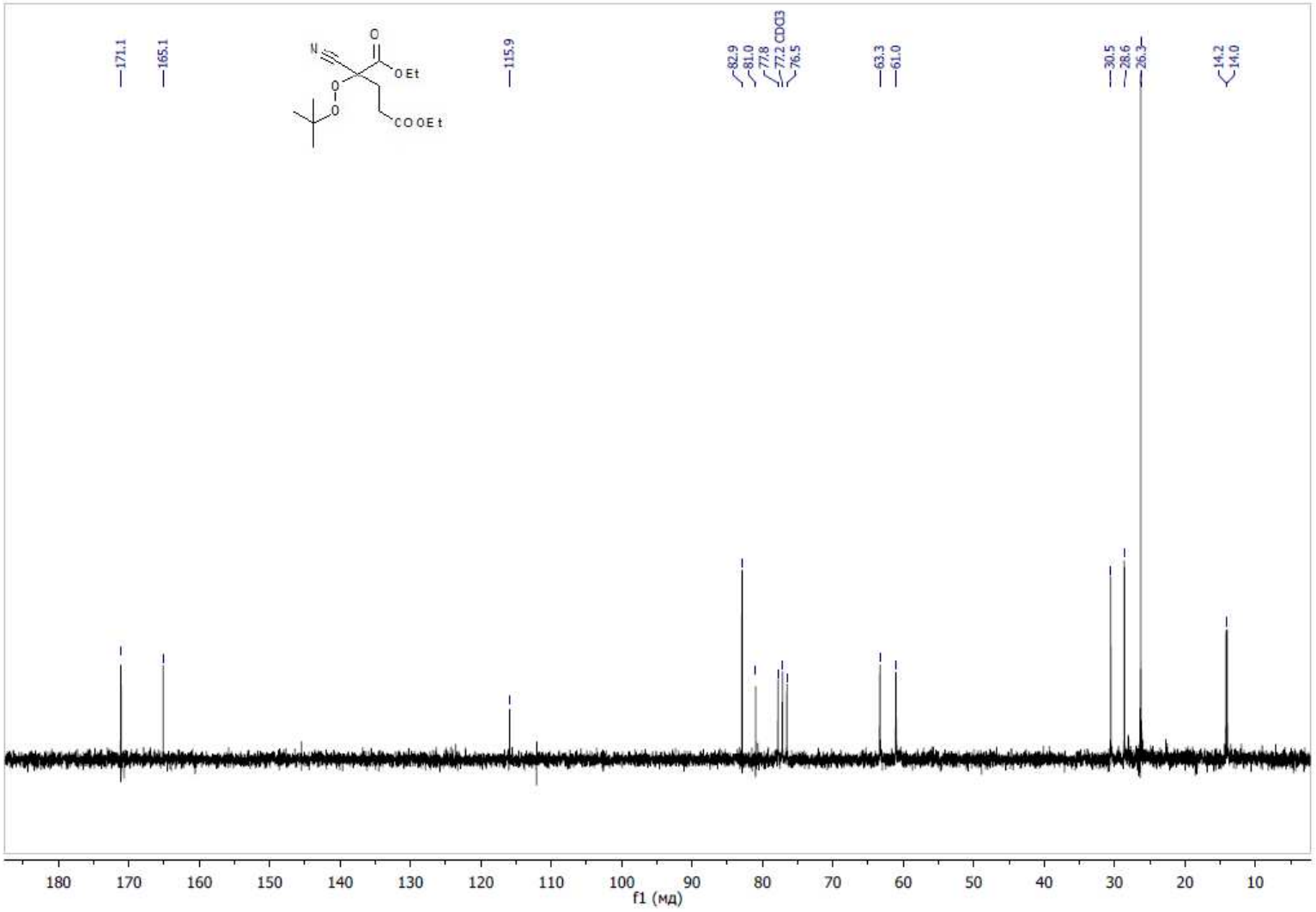
^{13}C NMR of Ethyl 2-(*tert*-butylperoxy)-2-cyanopent-4-enoate 6c



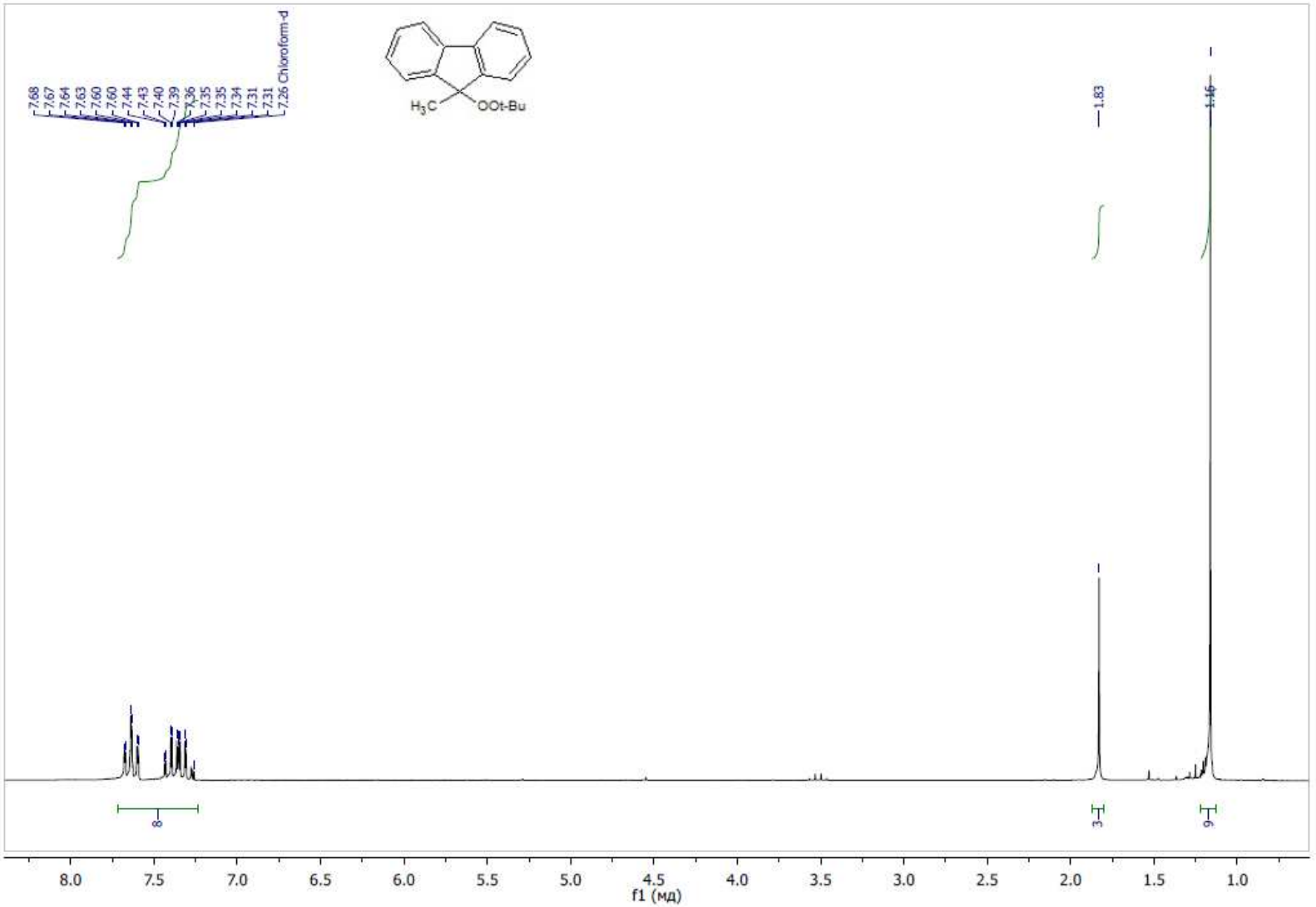
^{1}H NMR of Diethyl 2-(*tert*-butylperoxy)-2-cyanopentanedioate 6d



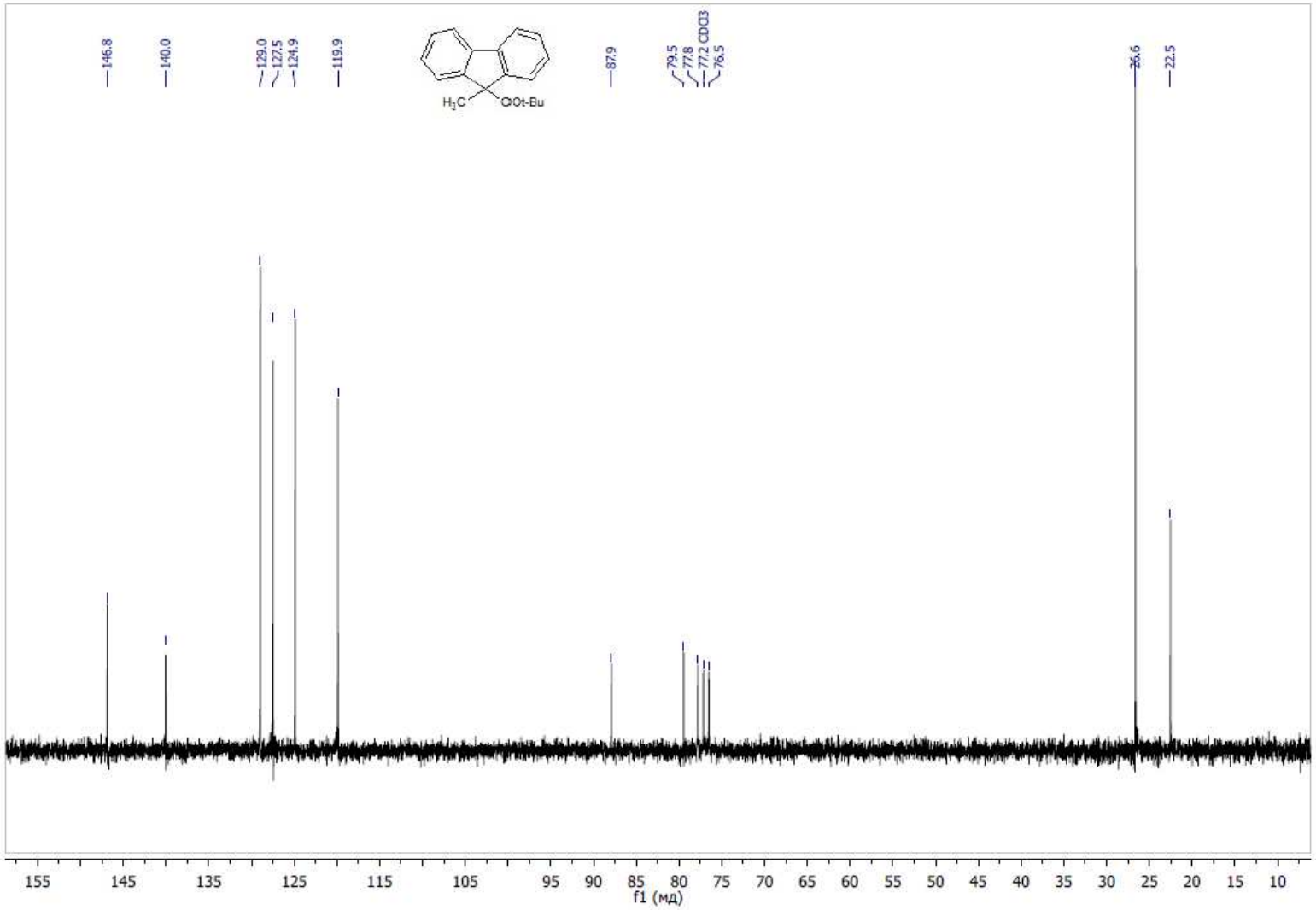
^{13}C NMR of Diethyl 2-(*tert*-butylperoxy)-2-cyanopentanedioate 6d



^{1}H NMR of *tert*-Butyl 9-methyl-9*H*-fluoren-9-yl peroxide



^{13}C NMR of *tert*-Butyl 9-methyl-9*H*-fluoren-9-yl peroxide



HRMS of *tert*-Butyl 9-methyl-9*H*-fluoren-9-yl peroxide

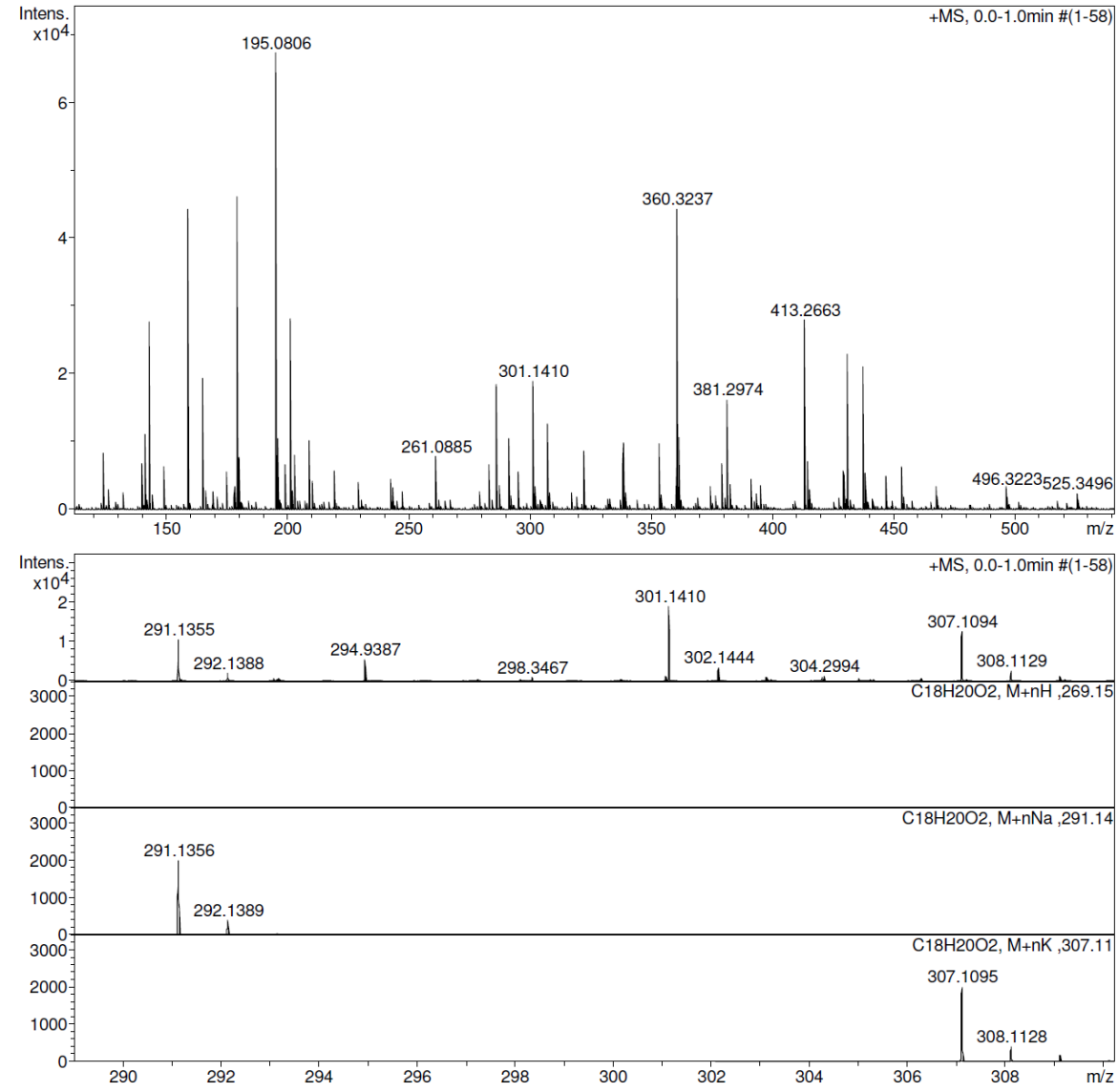
Display Report

Analysis Info

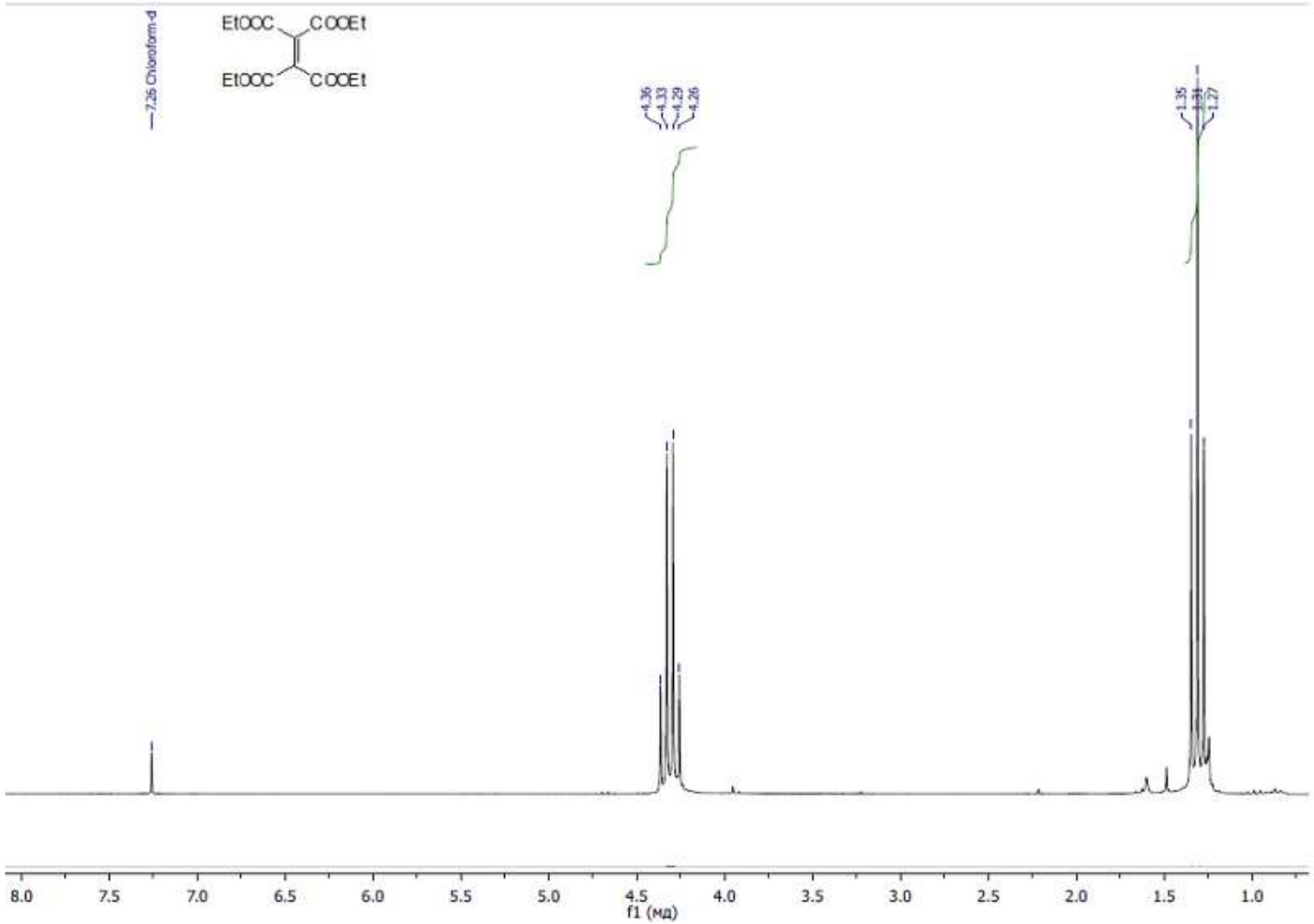
Analysis Name	D:\Data\Chizhov\Terentiev\Pototskii\rp-220_&clblow.d	Acquisition Date	03.03.2015 14:39:48
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN RP-220	Instrument	maXis 43
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

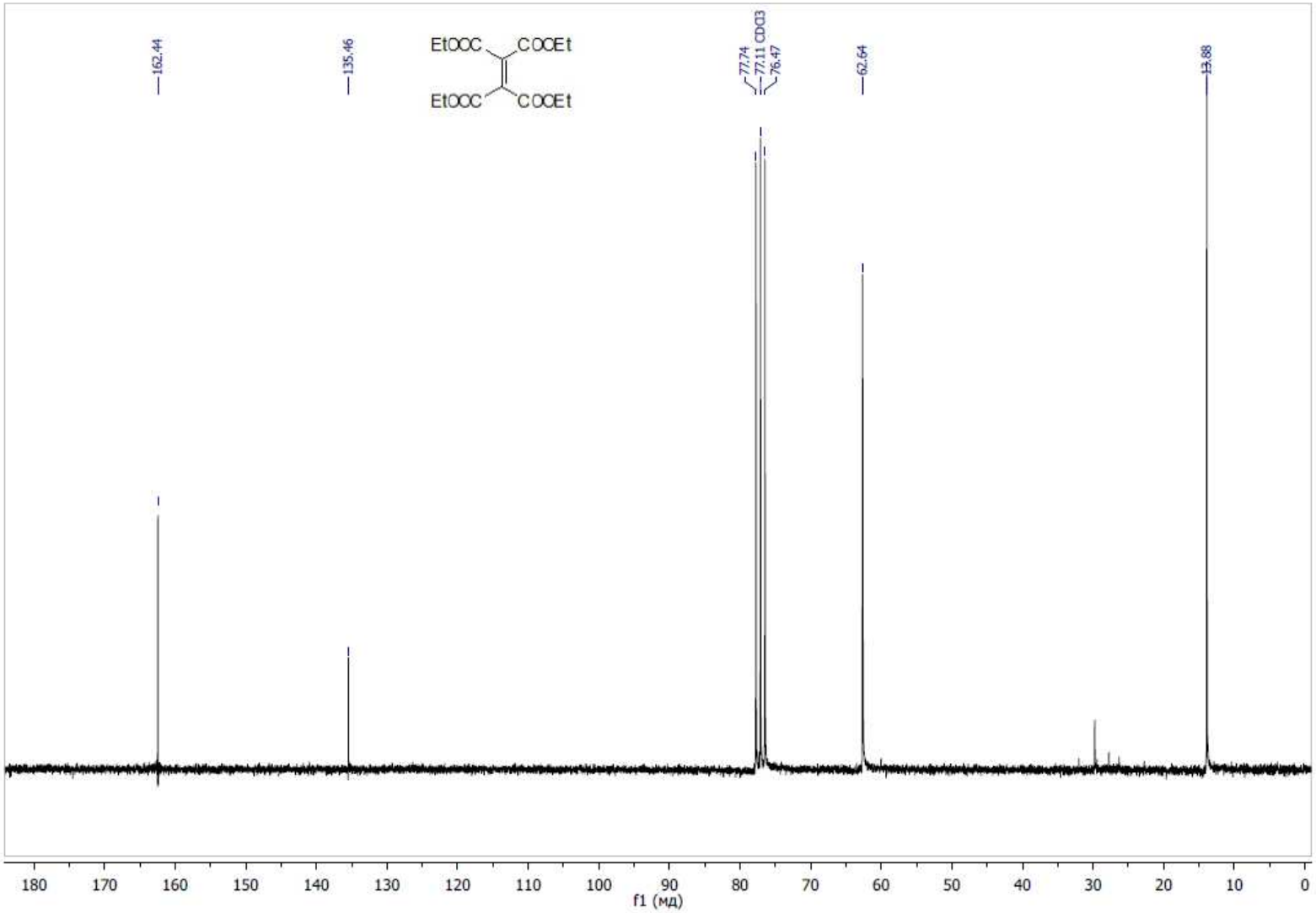
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source



^{1}H NMR of Tetraethyl ethene-1,1,2,2-tetracarboxylate 3



^{13}C NMR of Tetraethyl ethene-1,1,2,2-tetracarboxylate 3



HRMS of Tetraethyl ethene-1,1,2,2-tetracarboxylate 3

Display Report

Analysis Info

Analysis Name	D:\Data\Ivanova\ZD-576.d	Acquisition Date	10.02.2015 16:46:45
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	ZD-576	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100%, dil 40000		

Acquisition Parameter

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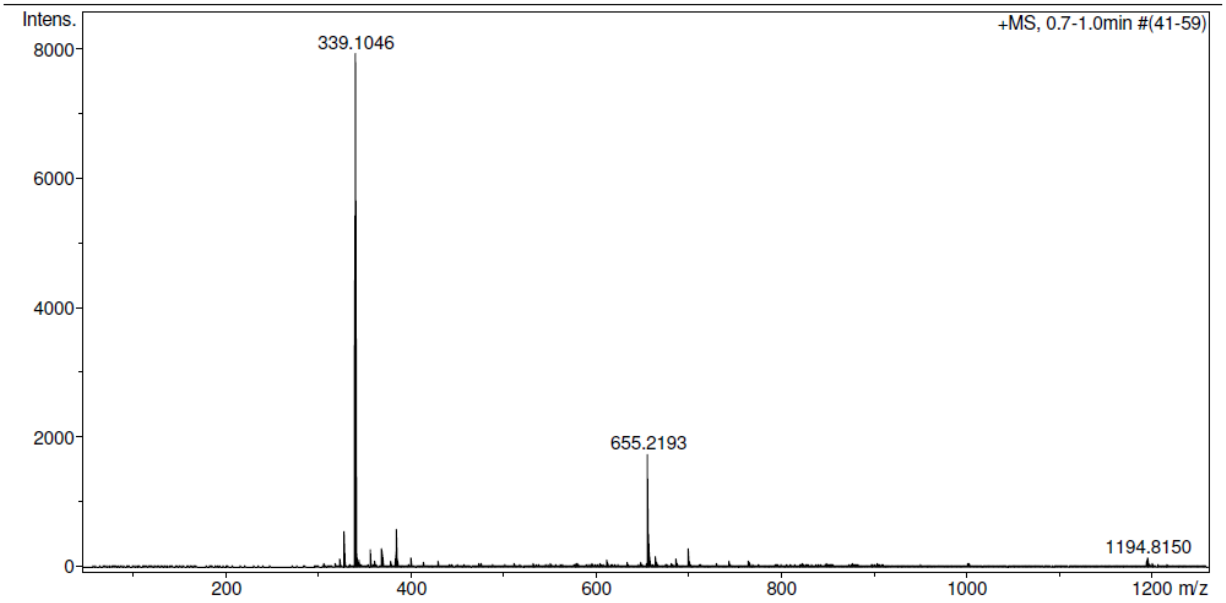
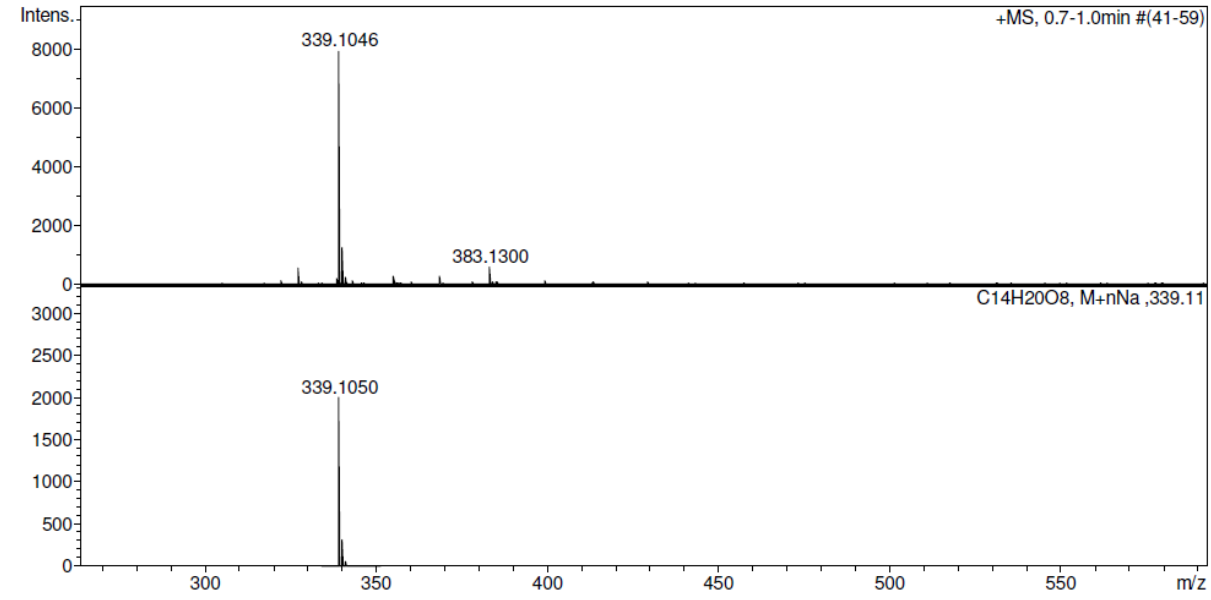
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





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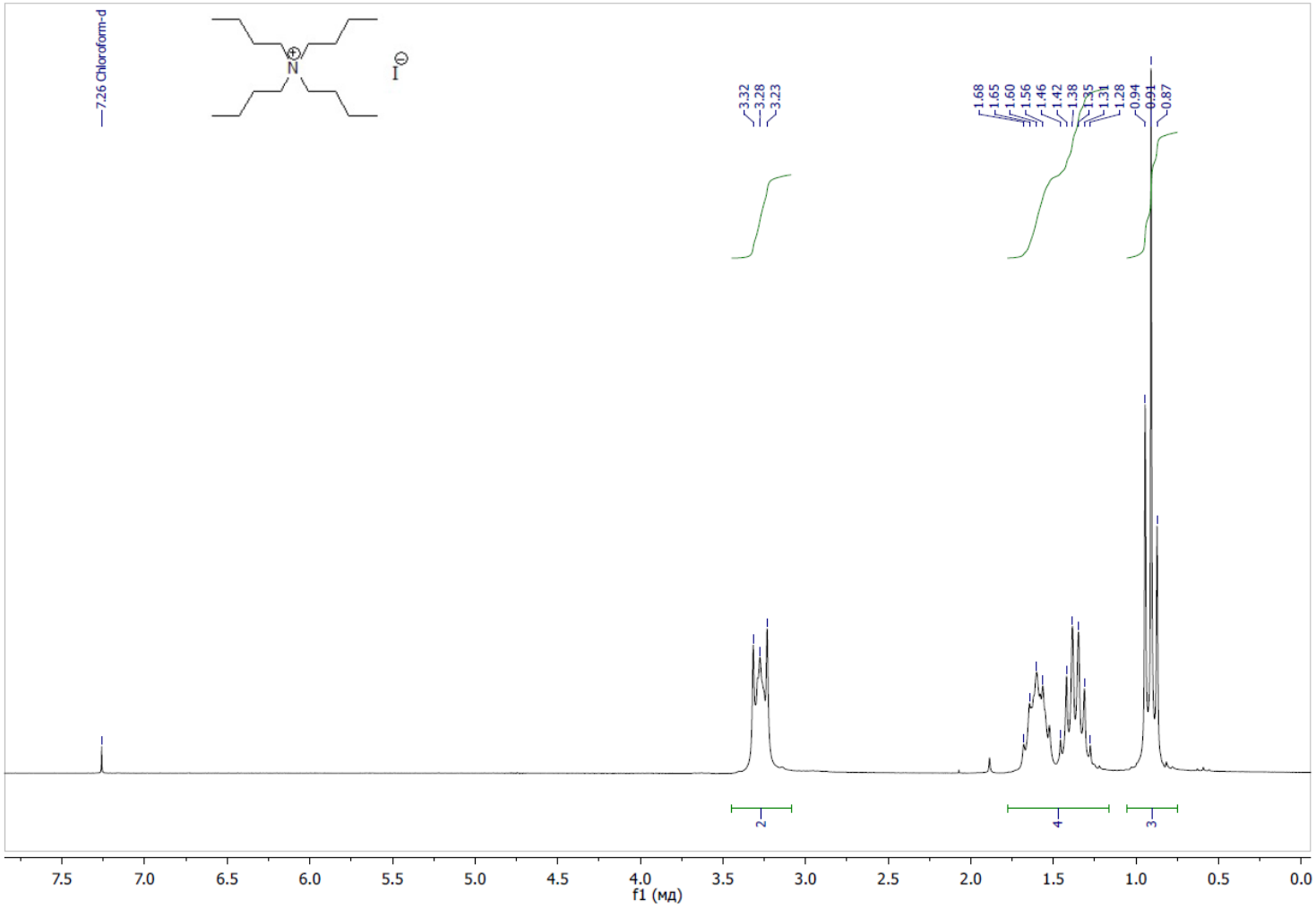
^{1}H NMR of tetrabuthylammonium iodide



^{13}C NMR of tetrabuthylammonium iodide