Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Contents

1. General information

Reagents and solvents. Commercially available reagents (Merck, ABCR, TCI, Fluorochem and Carbosynth) were used without additional purification. Commercially available solvents also were used without additional purification, except DMSO, which was redistilled over CaH_2.

Chromatography. Column chromatography was performed on silica gel obtained from Merck (Silica gel Si 60, 0.040-0.063 mm). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} glass-backed plates (Merck). Visualization was effected by UV light (254 or 312 nm).

Photochemistry. Photoinduced processes were performed on Evoluchem™ PhotoRedOx box. 365 nm (LG/CREE, HCK1012-01-011, 9 mW/cm^2), 380 nm (LG, HCK1012-01-013, 8 mW/cm^2), 405 nm (LG, HCK1012-01-010, 28 mW/cm^2) and 425 nm (EPILED, HCK1012-01-012, 33 mW/cm^2) LED lamps from Evoluchem™ were used. This device is equipped with a fan to maintain room temperature during the irradiation process. For large-scale experiment 365 nm (LG, HCK1012-01-006, 25 mW/cm^2) LED without Evoluchem™ PhotoRedOx box was used.

Absorption spectra. UV-VIS spectra were recorded on a Varian Cary 100 spectrophotometer.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on a 700 MHz Bruker Avance, 800 MHz Bruker Avance and Bruker Fourier 300 at 303 K. Chemical shifts are reported relative to solvent residual signals of DMSO-d_6 (2.50 ppm: for ^{1}H and 39.52 ppm: for ^{13}C) or $CDCl_3$ (7.26 ppm: for ^{1}H and 77.16 ppm: for ^{13}C).

Melting points. Melting points were measured on a SMP 30 apparatus without correction.

High Resolution Mass Spectrometry. High-resolution mass spectra (HRMS) were obtained using a TripleTOF 5600+ mass spectrometer from AB Sciex. The voltage on the capillary is 5.5 kV in the positive ion registration mode, 4.5 kV in the negative ion registration mode. Carrier gas flow (ion sourse gas 1) was 15 arb, curtain gas flow was 20 arb. Samples were injected using a syringe pump with a flow rate of 30 μl/min. Acetonitrile with the addition of 0.1% (v/v) formic acid was used as the eluent.

2. Solvent screening

Compound **1a** (5 mg) was dissolved in dry solvent (1.0 mL). Vials with obtained solutions were irradiated with 365 nm LED lamp (HCK1012-01-011) in Evoluchem™ PhotoRedOx box with stirring (Figure S1). After 24 hours of irradiation, solvents were removed in vacuum (with the use of a rotary evaporator, the temperature in bath is not higher than 35ºC). For solutions in DMSO, DMF and $MeNO_2$ reaction mixtures were dissolved in 10 mL of EtOAc and washed with saturated KCl solution (2-3 mL x 10 times). Next, organic solutions were dried over Na_2SO_4 and similarly evaporated. Finally all residues were analyzed by ^1H NMR in DMSO-d_6. Results are presented in Table S1.

Table S1. Solvents screening results.

Entry	Solvent	Conversion[a], %
1	CH_3CN	23
2	THF	13
3	DMF	45
4	1,4-Dioxane	~5
5	CH_2Cl_2	~5
6	**DMSO**	**60**
7	EtOH	33
8	EtOAc	9
9	$CHCl_3$	~5
10	$C_2H_4Cl_2$	-[b]
11	Et_2O	<2
12	p-Xylene	<1
13	Toluene	<1
14	MeOH	33
15	Hexane	-[c]
16	$MeNO_2$	-[b]

a - measured in single experiment, error is about 5% based on integration accuracy in NMR spectra; b – only products of decomposition observed; c – **1a** is not soluble, no reaction.

During the research, we found that in all cases, in addition to compound **2a**, some by-products were formed. Amount of these admixtures increased with the amount of **2a**. We repeated the process of irradiation in DMSO in an inert atmosphere and showed that in an oxygen-free environment the reaction proceeded without formation of such by-products.

Figure S1. Photochemical set-up. Solvent screening.

3. Kinetic study

First experiment.

Compound **1a** (5 mg) were dissolved in 1mL of DMSO-*d6* in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, a part of the solution (0.65 mL) was transferred to argon fused NMR tube and sealed. NMR tube with this solutions was irradiated with 365 nm LED lamp (HCK1012-01-011) in Evoluchem™ PhotoRedOx box.

The mixture was analyzed by NMR every 30 minutes. Results are presented on Figures S2 and S3.

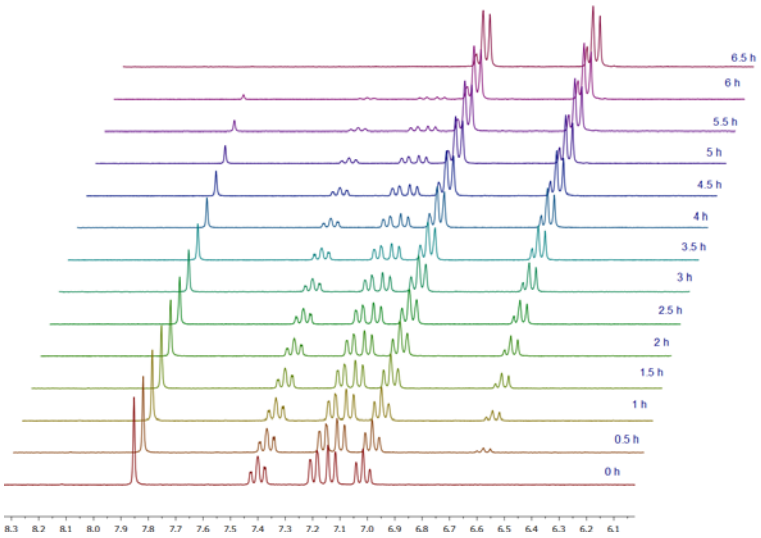


Figure S2. Fragments of NMR spectra of **1a** solution during irradiation.

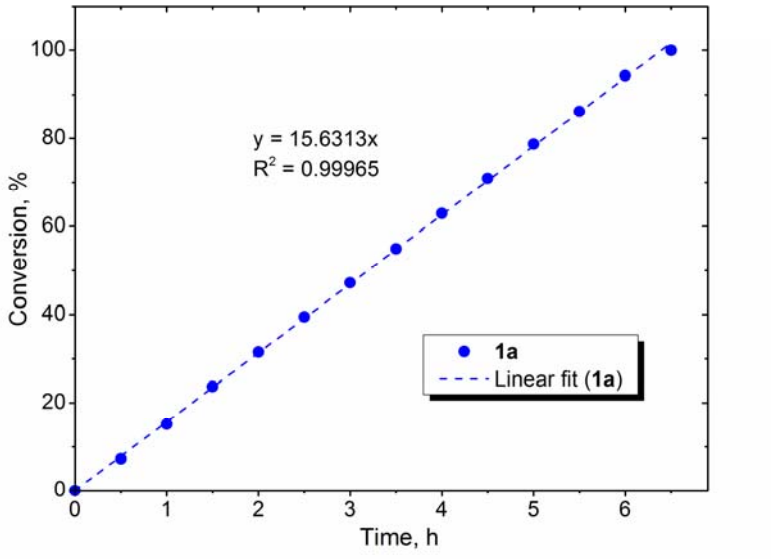


Figure S3. Kinetic study of compound **1a**.

Second experiment.

Compounds **1a**, and **1a-*d*$_6$** were dissolved in dry DMSO-*d6* in a Schlenk vessel in 5mg/mL concentration (1,5 mL for **1a** and 1 mL for **1a-*d*$_6$**). The mixtures were degassed under vacuum and filled with argon three times. Next, a part of solutions (0.65 mL) were transferred to argon fused NMR tubes and sealed. There were three samples – two with compounds **1a** and one with **1a-*d*$_6$**. All three samples were irradiated with 365 nm LED lamp (HCK1012-01-011) in Evoluchem™ PhotoRedOx box. However, one of two samples with derivative **1a** was wrapped in a foil and served as a blank standard confirming that the reaction does not proceed without irradiation at the similar conditions (solvent, time, temperature). Two other samples were placed directly in the middle of the reactor so that their irradiation was as identical as possible. (Figure S4).

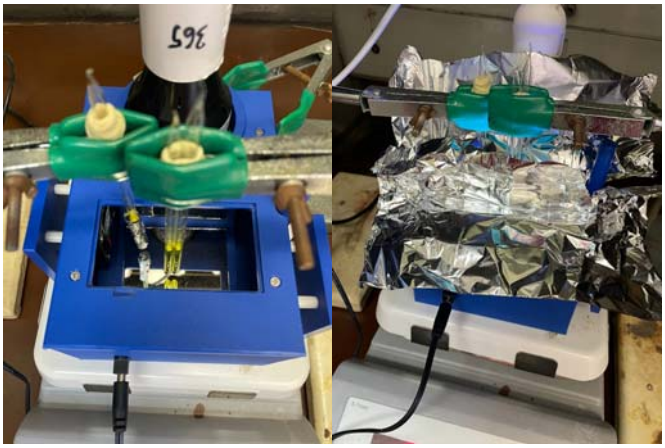


Figure S4. Photochemical set-up. Kinetic study.

All three mixtures were analyzed by NMR. Results are presented on Figure S5.

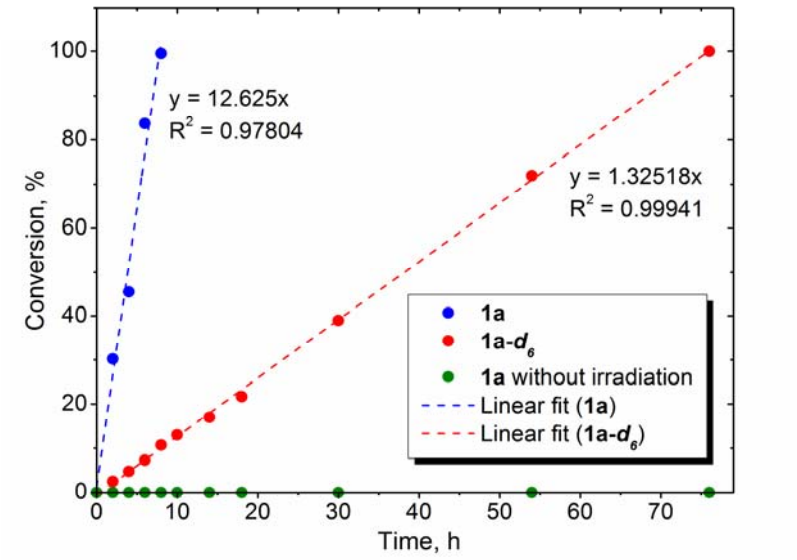


Figure S5. Comparative kinetic study of compounds **1a** and **1a-*d*$_6$**.

4. Synthesis of the starting aldehydes

General method

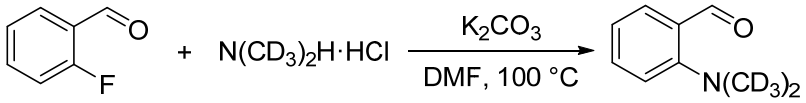
Mixture of the corresponding 2-fluorobenzaldehyde (10 mmol), amine (12 mmol) and K_2CO_3 (2.07 g, 15 mmol) in freshly distilled DMF (20 mL) was heated at 100 °C for 24 h. EtOAc (200 mL) was added and the resulted mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo and the residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 15:1).

The spectral properties of the obtained 2-aminobenzaldehydes corresponded to the literature data – Table S2.

Table S2. Starting aldehydes literature data.

Compounds	Reference
2-(dimethylamino)benzaldehyde, 2-(benzyl(methyl)amino)benzaldehyde	[1]
2-(dimethylamino)-4-methoxybenzaldehyde, 2-(dimethylamino)-4-(trifluoromethyl)benzaldehyde	[2]
2-bromo-6-(dimethylamino)benzaldehyde	[3]
2-(dimethylamino)-5-methylbenzaldehyde	[4]
2-chloro-6-(dimethylamino)benzaldehyde, 4-chloro-2-(dimethylamino)benzaldehyde, 2-(pyrrolidin-1-yl)benzaldehyde, 2-morpholinobenzaldehyde, 2-(diethylamino)benzaldehyde, 2-(benzyl(ethyl)amino)benzaldehyde	[5]
2-(piperidin-1-yl)benzaldehyde	[6]
2-(benzyl(methyl)amino)-5-nitrobenzaldehyde	[7]
2-(Dimethylamino)-5-methoxybenzaldehyde	[8]
2-(Dimethylamino)-4-bromobenzaldehyde	[9]

Synthesis of 2-(dimethyl-*d*$_6$-amino)benzaldehyde



Scheme S1. 2-(dimethyl-*d*$_6$-amino)benzaldehyde synthesis.

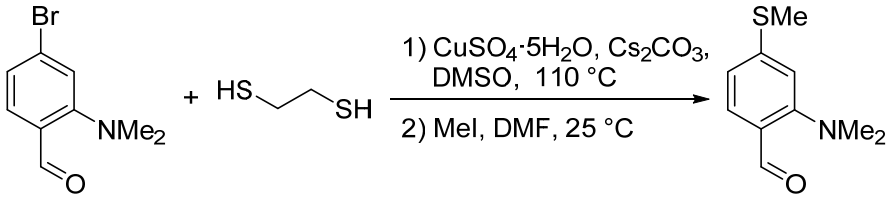
Mixture of 1.24 g (10 mmol) of 2-fluorobenzaldehyde, 1.05 g (12 mmol) of deuterated dimethylamine hydrochloride and 2.76 g (20 mmol) of K_2CO_3 in 50 mL of freshly distilled DMF was stirred in argon at 100 °C overnight. 300 mL of EtOAc was added, the organic layer was washed with brine (3×100 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 20:1). Yield 1.17 (75%), yellow viscous oil.

^{1}H NMR (700 MHz, DMSO-*d*$_6$) δ ppm: 10.12 (s, 1H), 7.67 (d, *J*=7.6 Hz, 1H), 7.51 (t, *J*=7.3 Hz, 1H), 7.12 (d, *J*=8.2 Hz, 1H), 7.00 (t, *J*=7.4 Hz, 1H),

^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ ppm: 190.4, 155.1, 134.7, 130.5, 125.9, 119.9, 117.6, 44.1 (sept, *J*=20 Hz, 2C).

HRMS found, *m/z*: 156.1291 $[M+H]^+$. $C_9H_6D_6NO^+$. Calculated, *m/z*: 156.1290.

Synthesis of 2-(dimethylamino)-4-(methylthio)benzaldehyde



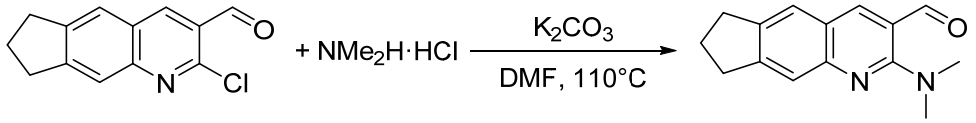
2-(Dimethylamino)-4-bromobenzaldehyde (2.3 g, 10 mmol), ethane-1,2-dithiol (1.9 g, 20 mmol), $Cu_2SO_4 \cdot 5H_2O$ (180 mg, 0.5 mmol) and Cs_2CO_3 (17.7 g, 50 mmol) were mixed in dry DMSO (30 mL) in argon and stirred at 110 °C for 5 h and cooled to 25 °C, MeI (4.3 g, 30 mmol) and DMF (10 mL) were added and the resulted mixture was stirred overnight at the same temperature. EtOAc (300 mL) was added, the resulted solution was washed with brine (3×100 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 10:1). Yield 1.1 g (56%), red oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 9.99 (s, 1H), 7.59 (d, *J*=8.2 Hz, 1H), 6.86 (dd, *J*=8.2, 1.3 Hz, 1H), 6.84 (d, *J*=1.5 Hz, 1H), 2.88 (s, 6H), 2.53 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 189.1, 155.0, 147.3, 131.3, 122.6, 116.4, 113.1, 44.8, 13.8.

HRMS found, *m/z*: 196.0792 $[M+H]^+$. $C_{10}H_{14}NOS^+$. Calculated, *m/z*: 196.0791.

Synthesis of 2-(dimethylamino)-7,8-dihydro-6*H*-cyclopenta[*g*]quinoline-3-carbaldehyde



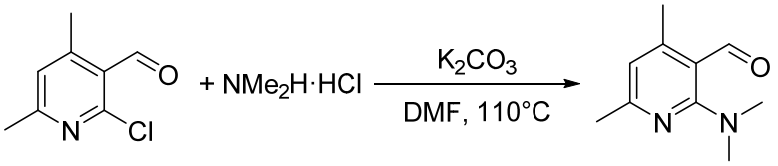
Mixture of 2.31 g (10 mmol) of 2-chloro-7,8-dihydro-6*H*-cyclopenta[*g*]quinoline-3-carbaldehyde, 1.63 g (20 mmol) of dimethylamine hydrochloride and 2.76 g (20 mmol) of K_2CO_3 in 50 mL of freshly distilled DMF was stirred in argon at 110 °C overnight. 300 mL of EtOAc was added, the organic layer was washed with brine (3×100 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 3:1). Yield 2.1 g (86%), orange solid, m.p. 123-125°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 10.07 (s, 1H), 8.54 (s, 1H), 7.71 (s, 1H), 7.51 (s, 1H), 3.04 (s, 6H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.07 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 190.1, 157.2, 150.9, 148.3, 143.3, 140.3, 123.2, 121.7, 120.8, 120.1, 41.7, 32.6, 31.5, 25.5.

HRMS found, *m/z*: 241.1337 $[M+H]^+$. $C_{15}H_{17}N_2O^+$. Calculated, *m/z*: 241.1335.

Synthesis of 2-(dimethylamino)-4,6-dimethylnicotinaldehyde



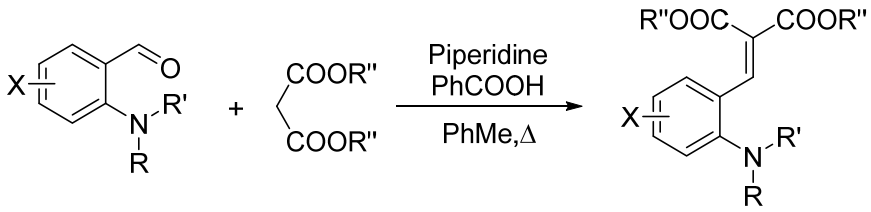
Mixture of 1.66 g (10 mmol) of 2-chloro-4,6-dimethylnicotinaldehyde, 1.63 g (20 mmol) of dimethylamine hydrochloride and 2.76 g (20 mmol) of K_2CO_3 in 50 mL of freshly distilled DMF was stirred in argon at 110 °C for 5 h. 300 mL of EtOAc was added, the organic layer was washed with brine (3×100 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 1:1). Yield 1.64 g (92%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 10.01 (s, 1H), 6.54 (s, 1H), 2.97 (s, 6H), 2.44 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 189.5, 161.9, 159.9, 151.1, 116.7, 113.2, 42.3, 24.3, 19.6.

HRMS found, *m/z*: 179.1177 $[M+H]^+$. $C_{10}H_{15}N_2O^+$. Calculated, *m/z*: 179.1179.

5. Synthesis of benzylidenemalonates 1

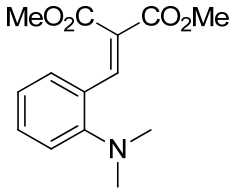


Scheme S2. Synthesis of compounds **1**.

General method

Mixture of 5 mmol of the corresponding 2-aminobenzaldehyde, 5.5 mmol of dialkylmalonate, 20 mg of benzoic acid and 20 mg of piperidine in 20 mL of toluene was refluxed for 10 h. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 10:1).

Dimethyl 2-(2-(dimethylamino)benzylidene)malonate (1a)



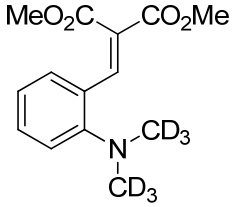
Yield 1.2 g (91%), yellow solid, m.p. 71-73°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.85 (s, 1H), 7.40 (t, *J*=7.1 Hz, 1H), 7.20 (d, *J*=7.8 Hz, 1H), 7.13 (d, *J*=8.2 Hz, 1H), 7.01 (t, *J*=7.3 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.70 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.3, 164.3, 153.6, 141.3, 131.5, 128.5, 125.6, 124.0, 121.8, 118.2, 52.6, 52.4, 44.5 (2C).

HRMS found, *m/z*: 264.1232 $[M+H]^+$. $C_{14}H_{18}NO_4^+$. Calculated, *m/z*: 264.1236.

Dimethyl 2-(2-(dimethyl-d$_6$-amino)benzylidene)malonate (1a-*d$_6$*)



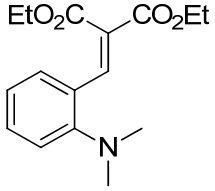
Yield 1.08 g (80%), yellow solid, m.p. 75-77°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.85 (s, 1H), 7.39 (t, *J*=7.1 Hz, 1H), 7.20 (d, *J*=7.6 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 1H), 7.01 (t, *J*=7.4 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.3, 164.3, 153.6, 141.4, 131.5, 128.5, 125.5, 124.0, 121.7, 118.2, 52.6, 52.4, 44.6 (sept, *J*=20 Hz, 2C).

HRMS found, *m/z*: 270.1610 $[M+H]^+$. $C_{14}H_{12}D_6NO_4^+$. Calculated, *m/z*: 270.1612.

Diethyl 2-(2-(dimethylamino)benzylidene)malonate (1a-Et)



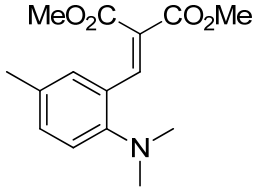
Yield 1.1 g (75%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.81 (s, 1H), 7.39 (t, *J*=7.1 Hz, 1H), 7.23 (d, *J*=7.8 Hz, 1H), 7.13 (d, *J*=7.6 Hz, 1H), 7.00 (t, *J*=7.6 Hz, 1H), 4.25 (q, *J*=7.1 Hz, 2H), 4.20 (q, *J*=7.1 Hz, 2H), 2.70 (s, 6H), 1.25 (t, *J*=7.1 Hz, 3H), 1.14 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 165.8, 163.9, 153.5, 140.9, 131.4, 128.7, 125.8, 124.9, 121.6, 118.1, 61.3, 61.1, 44.5 (2C), 14.0, 13.7.

HRMS found, *m/z*: 292.1542 $[M+H]^+$. $C_{16}H_{22}NO_4^+$. Calculated, *m/z*: 292.1549.

Dimethyl 2-(2-(dimethylamino)-5-methylbenzylidene)malonate (1b)



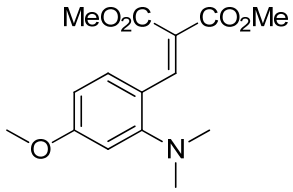
Yield 1.27 g (92%), yellow solid, m.p. 80-82°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.86 (s, 1H), 7.23 (bd, *J*=8.2 Hz, 1H), 7.04 (d, *J*=8.2 Hz, 1H), 6.99 (bs, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 2.65 (s, 6H), 2.23 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.4, 164.3, 153.5, 141.1, 132.2, 130.9, 128.7, 125.8, 124.0, 118.3, 52.6, 52.4, 44.8 (2C), 20.2.

HRMS found, *m/z*: 278.1388 $[M+H]^+$. $C_{15}H_{20}NO_4^+$. Calculated, *m/z*: 278.1392.

Dimethyl 2-(2-(dimethylamino)-4-methoxybenzylidene)malonate (1c)



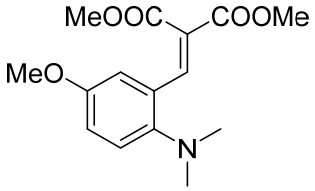
Yield 1.35 g (92%), yellow solid, m.p. 97-99°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.80 (s, 1H), 7.16 (d, *J*=8.6 Hz, 1H), 6.63-6.60 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 2.70 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.7, 164.6, 162.2, 155.7, 140.8, 130.1, 121.5, 117.9, 107.6, 104.2, 55.3, 52.4, 52.3, 44.5 (2C).

HRMS found, *m/z*: 294.1338 $[M+H]^+$. $C_{15}H_{20}NO_5^+$. Calculated, *m/z*: 294.1341.

Dimethyl 2-(2-(dimethylamino)-5-methoxybenzylidene)malonate (1d)



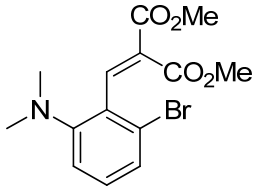
Yield 1.0 g (69%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.91 (s, 1H), 7.13 (d, J = 8.9 Hz, 1H), 7.03 (dd, J = 8.9, 3.0 Hz, 1H), 6.78 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 2.62 (s, 6H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 166.2, 164.1, 154.3, 147.4, 140.4, 127.1, 124.7, 119.9, 117.4, 112.8, 55.3, 52.6, 52.4, 45.1.

HRMS found, *m/z*: 294.1339 $[M+H]^+$. $C_{15}H_{20}NO_5^+$. Calculated, *m/z*: 294.1336.

Dimethyl 2-(2-bromo-6-(dimethylamino)benzylidene)malonate (1e)



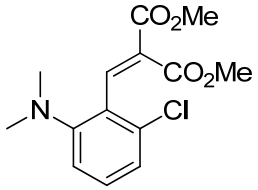
Yield 0.7 g (41%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.76 (s, 1H), 7.25-7.20 (m, 2H), 7.06 (d, J=7.8 Hz, 1H), 3.80 (s, 3H), 3.56 (s, 3H), 2.58 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 164.7, 164.1, 153.7, 143.2, 131.2, 126.9, 126.1, 125.2, 123.3, 117.3, 55.7, 51.9, 43.5 (2C).

HRMS found, *m/z*: 342.0344/344.0325 $[M+H]^+$. $C_{14}H_{17}BrNO_4^+$. Calculated, *m/z*: 342.0341/344.0320.

Dimethyl 2-(2-chloro-6-(dimethylamino)benzylidene)malonate (1f)



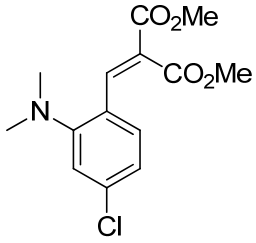
Yield 0.86 g (58%), yellow solid, m.p. 64-66°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.77 (s, 1H), 7.31 (t, J=8.0 Hz, 1H), 7.09 (d, J=8.0 Hz, 1H), 7.03 (d, J=8.1 Hz, 1H), 3.80 (s, 3H), 3.58 (s, 3H), 2.60 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 164.7, 164.3, 153.9, 143.3, 131.8, 131.0, 127.4, 124.6, 122.1, 116.9, 52.7, 52.0, 43.6 (2C).

HRMS found, *m/z*: 298.0837 $[M+H]^+$. $C_{14}H_{17}ClNO_4^+$. Calculated, *m/z*: 298.0846.

Dimethyl 2-(4-chloro-2-(dimethylamino)benzylidene)malonate (1g)



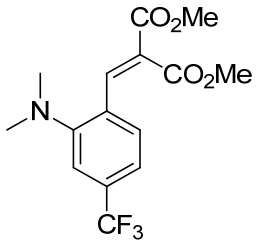
Yield 1.37 g (92%), yellow solid, m.p. 52-54°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.74 (s, 1H), 7.18 (d, *J*=8.4 Hz, 1H), 7.12 (d, *J*=1.91 Hz, 1H), 7.06 (dd, *J*=8.4, 1.9 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.72 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.0, 164.1, 154.6, 140.5, 135.9, 130.1, 124.5, 124.1, 121.4, 118.3, 52.7, 52.6, 44.2 (2C).

HRMS found, *m/z*: 298.0838 $[M+H]^+$. $C_{14}H_{17}ClNO_4^+$. Calculated, *m/z*: 298.0846.

Dimethyl 2-(2-(dimethylamino)-4-(trifluoromethyl)benzylidene)malonate (1h)



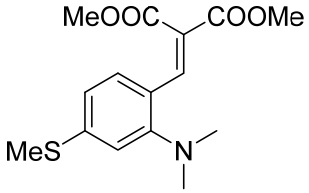
Yield 1.27 g (77%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.79 (s, 1H), 7.37 (d, *J*=8.0 Hz, 1H), 7.34-4.31 (m, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 2.77 (s, 6H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 165.6, 163.9, 153.5, 140.5, 131.0 (q, *J*=31.5 Hz), 129.7, 129.1, 126.0, 123.8 (q, *J*=272.7 Hz), 117.6 (q, *J*=3.7 Hz), 114.2 (q, *J*=3.6 Hz), 52.7, 52.5, 43.9 (2C).

HRMS found, *m/z*: 332.1102 $[M+H]^+$. $C_{15}H_{17}F_3NO_4^+$. Calculated, *m/z*: 332.1110.

Dimethyl 2-(2-(dimethylamino)-4-(methylthio)benzylidene)malonate (1i)



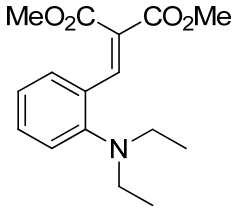
Yield 1.3 g (82%), yellow oil.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.96 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 2.77 (s, 6H), 2.49 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.4, 164.4, 153.9, 143.1, 140.8, 128.9, 122.8, 121.7, 118.4, 114.8, 52.5, 52.4, 44.4, 14.0.

HRMS found, *m/z*: 310.1111 $[M+H]^+$. $C_{15}H_{20}NO_4S^+$. Calculated, *m/z*: 310.1108.

Dimethyl 2-(2-(diethylamino)benzylidene)malonate (1k)



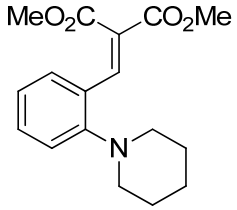
Yield 1.3 g (89%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.93 (s, 1H), 7.41 (t, *J*=7.1 Hz, 1H), 7.23 (d, *J*=6.9 Hz, 1H), 7.20 (d, *J*=8.0 Hz, 1H), 7.04 (t, *J*=6.3 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.02 (q, *J*=7.1 Hz, 4H), 0.98 (q, *J*=7.1 Hz, 4H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.4, 164.2, 151.2, 141.4, 131.0, 128.4, 128.0, 124.1, 122.3, 121.0, 52.6, 52.4, 47.3 (2C), 12.4 (2C).

HRMS found, *m/z*: 292.1543 $[M+H]^+$. $C_{16}H_{22}NO_4^+$. Calculated, *m/z*: 292.1549.

Dimethyl 2-(2-(piperidin-1-yl)benzylidene)malonate (1l)



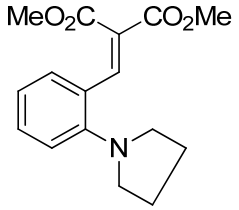
Yield 1.3 g (86%), yellow solid, m.p. 101-103°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.92 (s, 1H), 7.41 (t, *J*=7.1 Hz, 1H), 7.23 (d, *J*=7.4 Hz, 1H), 7.13 (d, *J*=8.0 Hz, 1H), 7.04 (t, *J*=7.6 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.86 (bt, *J*=5.0 Hz, 4H), 1.68-1.64 (m, 4H), 1.57-1.53 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.4, 164.3, 153.8, 140.5, 131.7, 128.2, 126.2, 124.0, 122.2, 118.9, 53.9 (2C), 52.6, 52.5, 26.0 (2C), 23.6.

HRMS found, *m/z*: 304.1542 $[M+H]^+$. $C_{17}H_{22}NO_4$. Calculated, *m/z*: 304.1549.

Dimethyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (1m)

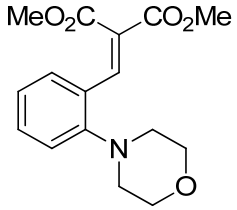


Yield 0.87 g (60%), yellow solid, m.p. 89-91°C.[10] lit m.p. 92-93°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.86 (s, 1H), 7.26 (t, *J*=7.1 Hz, 1H), 7.09 (d, *J*=7.6 Hz, 1H), 6.90 (d, *J*=8.4 Hz, 1H), 6.79 (t, *J*=7.4 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.24-3.20 (m, 4H), 1.90-1.86 (m, 4H).

The data correspond to previously described - [10].

Dimethyl 2-(2-morpholinobenzylidene)malonate (1n)

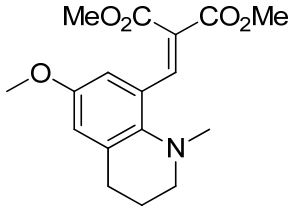


Yield 1.49 g (98%), yellow oil. [11]

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.94 (s, 1H), 7.45 (t, *J*=7.1 Hz, 1H), 7.26 (d, *J*=6.9 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 1H), 7.10 (t, *J*=7.4 Hz, 1H), 3.79 (s, 3H), 3.76-3.73 (m, 4H), 3.71 (s, 3H), 2.92-2.87 (m, 4H).

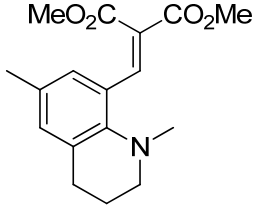
The data correspond to previously described - [11].

Dimethyl 2-((6-methoxy-1-methyl-1,2,3,4-tetrahydroquinolin-8-yl)methylene)malonate (1o)



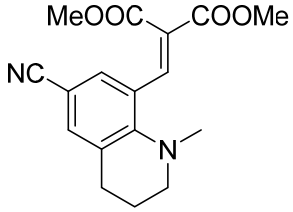
Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [12].

Dimethyl 2-((6-methyl-1-methyl-1,2,3,4-tetrahydroquinolin-8-yl)methylene)malonate (1p)



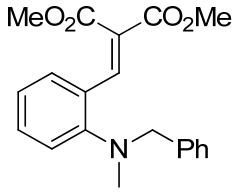
Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [12].

Dimethyl 2-((6-cyano-1-methyl-1,2,3,4-tetrahydroquinolin-8-yl)methylene)malonate (1q)



Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [12].

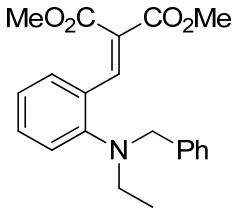
Dimethyl 2-(2-(benzyl(methyl)amino)benzylidene)malonate (1r)



Yield 1.32 g (78%), yellow solid, m.p. 97-100°C.[11] lit m.p. 93-95°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 8.06 (s, 1H), 7.39 (t, *J*=7.1 Hz, 1H), 7.33 (t, *J*=8.2 Hz, 2H), 7.28-7.25 (m, 3H), 7.23 (d, *J*=7.8 Hz, 1H), 7.13 (d, *J*=7.8 Hz, 1H), 7.06 (t, *J*=7.4 Hz, 1H), 4.09 (s, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 2.64 (s, 3H).

Dimethyl 2-(2-(benzyl(ethyl)amino)benzylidene)malonate (1s)



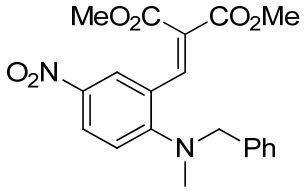
Yield 1.57 g (89%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 8.06 (s, 1H), 7.35 (t, *J*=7.1 Hz, 1H), 7.30-7.24 (m, 4H), 7.23-7.19 (m, 2H), 7.17 (d, *J*=8.0 Hz, 1H), 7.03 (t, *J*=7.6 Hz, 1H), 4.20 (s, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 3.00 (q, *J*=7.1 Hz, 2H), 1.01 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.3, 164.1, 150.8, 141.4, 138.2, 130.4, 128.2, 128.2 (2C), 128.1 (2C), 127.9, 127.0, 124.6, 122.6, 121.5, 56.4, 52.6, 52.5, 48.2, 12.1.

HRMS found, *m/z*: 354.1702 $[M+H]^+$. $C_{21}H_{24}NO_4^+$. Calculated, *m/z*: 354.1705.

Dimethyl 2-(2-(benzyl(methyl)amino)-5-nitrobenzylidene)malonate (1t)



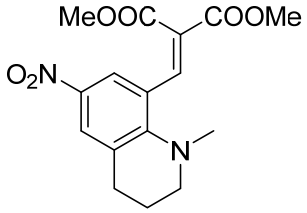
Yield 1.4 g (73%), yellow solid, m.p. 94-97°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 8.17 (dd, *J*=9.2, 2.7 Hz, 1H), 8.03 (d, *J*=2.7 Hz, 1H), 7.78 (s, 1H), 7.36 (t, *J*=7.6 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 1H), 7.24 (d, *J*=7.3 Hz, 2H), 7.15 (d, *J*=9.2 Hz, 1H), 4.46 (s, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 2.90 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.7, 164.4, 162.1, 154.7, 140.7, 137.5, 129.9, 128.4 (2C), 128.2 (2C), 127.3, 122.1, 118.7, 108.1, 105.9, 60.9, 52.4 (2C), 40.9.

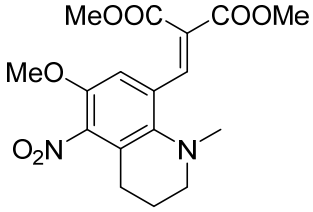
HRMS found, *m/z*: 385.1397 $[M+H]^+$. $C_{20}H_{21}N_2O_6^+$. Calculated, *m/z*: 385.1400.

Dimethyl 2-((1-methyl-6-nitro-1,2,3,4-tetrahydroquinolin-8-yl)methylene)malonate (1u)



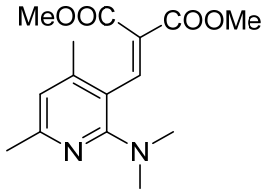
Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [12].

Dimethyl 2-((6-methoxy-1-methyl-5-nitro-1,2,3,4-tetrahydroquinolin-8-yl)methylene)malonate (1v)



Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [12].

Dimethyl 2-((2-(dimethylamino)-4,6-dimethylpyridin-3-yl)methylene)malonate (1w)



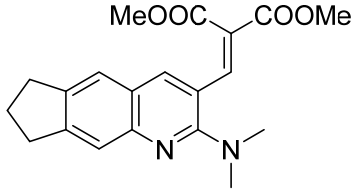
Yield 0.9 g (63%), yellow oil.

^{1}H NMR (700 MHz, DMSO-d$_6$) δ ppm: 7.88 (s, 1H), 6.60 (s, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 2.70 (s, 6H), 2.30 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 164.8, 164.7, 159.7, 155.8, 147.3, 142.7, 125.1, 116.5, 113.5, 52.43, 51.7, 41.4, 23.8, 19.0.

HRMS found, *m/z*: 293.1500 $[M+H]^+$. $C_{15}H_{21}N_2O_4^+$. Calculated, *m/z*: 293.1496.

Dimethyl 2-((2-(dimethylamino)-7,8-dihydro-6*H*-cyclopenta[*g*]quinolin-3-yl)methylene)malonate (1x)



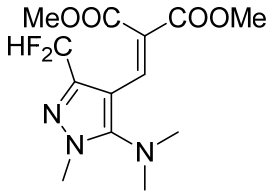
Yield 1.4 g (80%), yellow solid, m.p. 127-129°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ: ppm: 7.92 (s, 1H), 7.82 (s, 1H), 7.60 (s, 1H), 7.53 (s, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.00 (t, J = 7.4 Hz, 2H), 2.95 (t, J = 7.3 Hz, 2H), 2.90 (s, 6H), 2.06 (p, J = 7.3 Hz, 2H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 165.5, 164.0, 158.3, 148.8, 146.5, 141.8, 140.8, 137.4, 124.9, 122.4, 122.1, 121.1, 118.6, 52.6, 52.4, 41.6, 32.5, 31.6, 25.6.

HRMS found, *m/z*: 355.1655 $[M+H]^+$. $C_{20}H_{23}N_2O_4^+$. Calculated, *m/z*: 355.1652.

Dimethyl 2-((3-(difluoromethyl)-5-(dimethylamino)-1-methyl-1*H*-pyrazol-4-yl)methylene)malonate (1y)



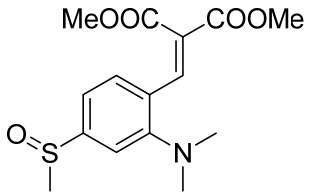
Yield 1.1 g (72%), yellow solid, m.p. 65-67°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.64 (s, 1H), 6.81 (t, J = 53.7 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.68 (s, 3H), 2.70 (s, 6H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 164.8, 164.3, 149.9, 141.7 (t, J = 26.8 Hz), 133.9, 126.3, 111.6 (t, J = 232.9 Hz), 103.5, 52.5, 51.9, 41.7, 36.9.

HRMS found, *m/z*: 318.1262 $[M+H]^+$. $C_{13}H_{18}F_2N_3O_4^+$. Calculated, *m/z*: 318.1260.

Synthesis of dimethyl 2-(2-(dimethylamino)-4-(methylsulfinyl)benzylidene)malonate (1j)



5 mL (49 mmol) of 30% H_2O_2 was added dropwise to a stirred solution of 0.93 g (3 mmol) of dimethyl 2-(2-(dimethylamino)-4-(methylsulfinyl)benzylidene)malonate in 25 mL of MeOH. The resulted mixture was stirred overnight. 300 mL of EtOAc was added, the organic layer was washed with brine (3×100 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of $CHCl_3$ and EtOH, v/v 30:1). Yield 1.64 g (51%), yellow oil.

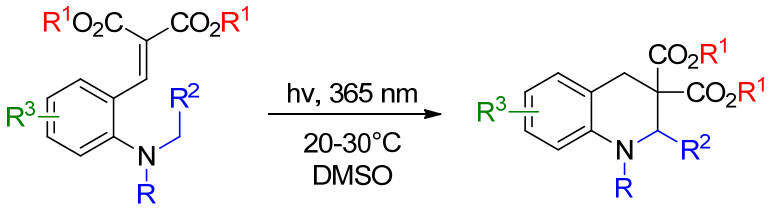
^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.80 (s, 1H), 7.37 (d, J = 1.7 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.27 (dd, J = 8.0, 1.6 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.773 (s, 3H), 2.768 (s, 6H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 164.8, 164.7, 159.7, 155.8, 147.3, 142.7, 125.1, 116.5, 113.5, 52.43, 51.7, 41.4, 23.8, 19.0.

HRMS found, *m/z*: 326.1057 $[M+H]^+$. $C_{15}H_{20}NO_5S^+$. Calculated, *m/z*: 326.1057.

6. Synthesis of tetrahydroquinolines 2

General method



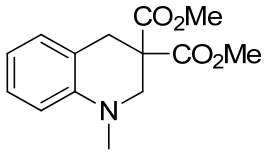
Scheme S3. Synthesis of tetrhydrochonolines **2**.

Compounds **1** (0.25 mmol) were dissolved in 10 mL of dry DMSO in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. Obtained solutions were irradiated with 365 nm LED lamp (HCK1012-01-011) in Evoluchem™ PhotoRedOx box with stirring (Figure S7). The process was carried out strictly with two samples at a time. This approach allowed us to claim approximately identical irradiation conditions for all samples, since the Schlenk vessels were installed symmetrically into the reactor each time.

Figure S6. Photochemical set-up. Examples of large-scale reactions. Reaction. Up - solutions of compounds **5a** and **4** with 405 nm LED lamp before irradiation. Down - solutions of compounds **1e** and **1f** with 365 nm LED lamp upon irradiation.

The progress of the reaction was monitored by TLC and also visually by the color disappearance. After the reaction completion (or 14 days for compound **2d**), reaction mixtures were dissolved in 150 mL of EtOAc, washed with saturated KCl solution (30 mL x 10 times) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography on silica using EtOAc as eluent or column chromatography on silica using CH_2Cl_2 for compound **2d** since in that case starting **1d** should be separated carefully.

Dimethyl 1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2a)



Yield 62 mg (94%), colorless solid, m.p. 98-100°C.

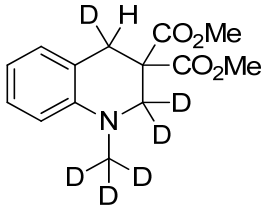
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.09 (t, *J*=7.4 Hz, 1H), 7.04 (d, *J*=7.1 Hz, 1H), 6.69 (t, *J*=7.3 Hz, 1H), 6.59 (d, *J*=8.2 Hz, 1H), 3.73 (s, 6H), 3.61 (s, 2H), 3.29 (s, 2H), 2.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 170.4 (2C), 145.3, 129.0, 127.5, 119.8, 117.4, 111.3, 54.7, 53.0, 53.9 (2C), 39.1, 33.5.

HRMS found, *m/z*: 264.1235 $[M+H]^+$. $C_{14}H_{18}NO_4^+$. Calculated, *m/z*: 264.1236.

Dimethyl 1-(methyl-d$_6$)-2,2,4-trideutero-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2a-*d$_6$*)



Yield 64 mg (95%), colorless solid, m.p. 92-95°C.

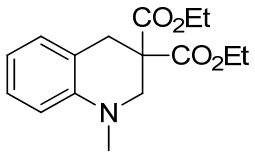
Reaction time ~ 20 days.

^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 7.09 (t, *J*=7.3 Hz, 1H), 7.04 (d, *J*=7.3 Hz, 1H), 6.68 (t, *J*=7.5 Hz, 1H), 6.59 (d, *J*=8.3 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.27 (s, 1H).

^{13}C NMR (200 MHz, $CDCl_3$) δ ppm: 170.4 (2C), 145.4, 129.1, 127.5, 119.8, 117.4, 111.3, 54.0 (p, *J*=21 Hz), 52.9 (3C), 38.3 (spt, *J*=20.5 Hz), 33.2 (t, *J*=20.5 Hz).

HRMS found, *m/z*: 270.1608 $[M+H]^+$. $C_{14}H_{12}D_6NO_4^+$. Calculated, *m/z*: 270.1612.

Diethyl 1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2a-Et)



Yield 57 mg (78%), colorless oil.

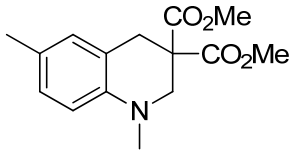
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.08 (t, *J*=7.3 Hz, 1H), 7.04 (d, *J*=7.4 Hz, 1H), 6.67 (t, *J*=7.3 Hz, 1H), 6.58 (d, *J*=8.2 Hz, 1H), 4.22-4.16 (m, 4H), 3.61 (s, 2H), 3.27 (s, 2H), 2.90 (s, 3H), 1.21 (t, *J*=7.2 Hz, 6H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.0 (2C), 145.4, 129.0, 127.4, 120.0, 117.3, 111.2, 61.7 (2C), 54.8, 53.1, 39.1, 33.6, 14.1 (2C).

HRMS found, *m/z*: 292.1545 $[M+H]^+$. $C_{16}H_{22}NO_4^+$. Calculated, *m/z*: 292.1549.

Dimethyl 1,6-dimethyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2b)



Yield 39 mg (56%), colorless oil. Decompose on SiO_2 during chromatography.

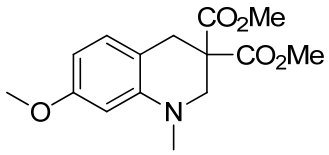
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.90 (d, *J*=8.2 Hz, 1H), 6.86 (s, 1H), 6.52 (d, *J*=8.2 Hz, 1H), 3.73(s, 6H), 3.56 (s, 2H), 3.25 (s, 2H), 2.86 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.5 (2C), 143.3, 129.7, 128.0, 126.7, 120.0, 111.6, 55.0, 53.3, 52.9 (2C), 39.3, 33.5, 20.4.

HRMS found, *m/z*: 276.1234 $[M\text{-}H_2+H]^+$. $C_{15}H_{18}NO_4^+$. Calculated, *m/z*: 276.1236. (Some kind of oxidizing process upon ionization.)

Dimethyl 7-methoxy-1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2c)



Yield 62 mg (85%), colorless solid, m.p. 87-89°C.

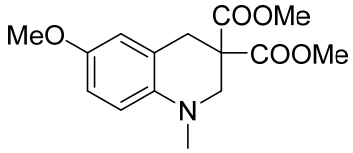
Reaction time ~ 5 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.94 (d, *J*=8.3 Hz, 1H), 6.25 (dd, *J*=8.3, 2.3 Hz, 1H), 6.15 (d, *J*=2.3 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 6H), 3.61 (s, 2H), 3.23 (s, 2H), 2.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 170.4 (2C), 159.4, 146.1, 129.6, 112.4, 101.9, 98.1, 55.3, 54.6, 53.1, 53.0 (2C), 39.2, 32.9.

HRMS found, *m/z*: 294.1337 $[M+H]^+$. $C_{15}H_{20}NO_5^+$. Calculated, *m/z*: 294.1341.

Dimethyl 6-methoxy-1-methyl-1,4-dihydroquinoline-3,3(2*H*)-dicarboxylate (2d)



Yield 70 mg (96%), colorless oil.

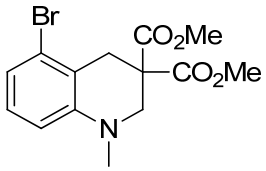
Reaction time ~ 3 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 6.67 (d, *J* = 2.9 Hz, 1H), 6.64 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 6H), 3.65 (s, 3H), 3.43 (s, 2H), 3.16 (s, 2H), 2.76 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 169.7, 151.5, 139.8, 121.4, 114.5, 112.5, 112.3, 104.5, 55.2, 54.5, 52.7, 52.6, 32.8.

HRMS found, *m/z*: 294.1336 $[M+H]^+$. $C_{15}H_{20}NO_5^+$. Calculated, *m/z*: 294.1336.

Dimethyl 5-bromo-1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2e)



Yield (~85%, brsm!, 50% isolated, incomplete reaction), colorless solid, m.p. 112-115°C.

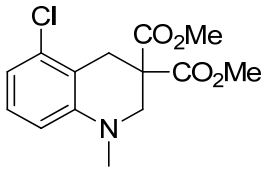
Reaction time 20+ days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.97-6.92 (m, 2H), 6.54 (dd, *J*=6.7, 2.5 Hz, 1H), 3.75 (s, 6H), 3.60 (s, 2H), 3.30 (s, 2H), 2.91 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.1 (2C), 147.1, 128.2, 125.3, 121.5, 119.7, 110.4, 54.4, 53.4, 53.1 (2C), 39.5, 34.5.

HRMS found, *m/z*: 342.0338/344.0319 $[M+H]^+$. $C_{14}H_{17}BrNO_4^+$. Calculated, *m/z*: 342.0341/344.0320.

Dimethyl 5-chloro-1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2f)



Yield 64 mg (86%), colorless solid, m.p. 96-98°C.

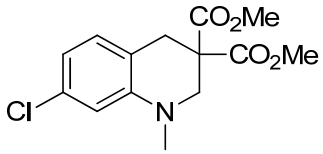
Reaction time ~ 13 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.02 (t, *J*=8.0, Hz, 1H), 6.76 (d, *J*=7.8, Hz, 1H), 6.50 (d, *J*=8.4, Hz, 1H), 3.75 (s, 6H), 3.60 (s, 2H), 3.31 (s, 2H), 2.91 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.2 (2C), 147.0, 134.5, 127.7, 118.1, 118.1, 109.8, 54.3, 53.0 (3C), 39.5, 31.6.

HRMS found, *m/z*: 298.0843 $[M+H]^+$. $C_{14}H_{17}ClNO_4^+$. Calculated, *m/z*: 298.0846.

Dimethyl 7-chloro-1-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2g)



Yield 62 mg (84%), colorless solid, m.p. 94-96°C.

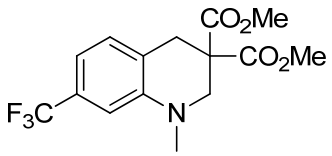
Reaction time ~ 4 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.93 (d, *J*=8.0 Hz, 1H), 6.63 (dd, *J*=8.0, 1.9 Hz, 1H), 6.54 (d, *J*=1.9 Hz, 1H), 3.73 (s, 6H), 3.62 (s, 2H), 3.23 (s, 2H), 2.90 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.1 (2C), 146.1, 133.1, 129.9, 118.1, 117.0, 111.1, 54.4, 53.0 (2C), 52.8, 39.1, 33.2.

HRMS found, *m/z*: 298.0843 $[M+H]^+$. $C_{14}H_{17}ClNO_4^+$. Calculated, *m/z*: 298.0846.

Dimethyl 1-methyl-7-(trifluoromethyl)-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2h)



Yield 73 mg (88%), colorless solid, m.p. 76-78°C.

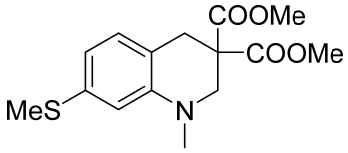
Reaction time ~ 5 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.11 (d, *J*=7.8 Hz, 1H), 6.91 (d, *J*=7.7 Hz, 1H), 6.76 (s, 1H), 3.74 (s, 6H), 3.66 (s, 2H), 3.31 (s, 2H), 2.95 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.0 (2C), 145.3, 130.0 (q, *J*=31.8 Hz), 129.3, 124.7 (q, *J*=272.1 Hz), 123.4, 113.8 (q, *J*=4.0 Hz), 107.6 (q, *J*=3.7 Hz), 54.5, 53.1 (2C), 52.6, 39.1, 33.6.

HRMS found, *m/z*: 332.1104 $[M+H]^+$. $C_{15}H_{17}F_3NO_4^+$. Calculated, *m/z*: 332.1110.

Dimethyl 1-methyl-7-(methylthio)-1,4-dihydroquinoline-3,3(2*H*)-dicarboxylate (2i)



Yield 69 mg (89%), yellowish solid, m.p. 86-88°C.

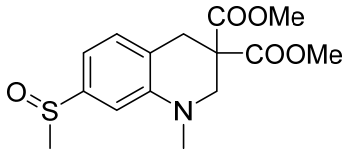
Reaction time ~ 3 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 6.94 (d, *J* = 7.8 Hz, 1H), 6.52 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.65 (s, 6H), 3.53 (s, 2H), 3.13 (s, 2H), 2.84 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 169.5, 145.4, 136.2, 129.1, 116.8, 114.8, 108.933, 53.9, 52.7, 52.1, 38.7, 32.4, 15.0.

HRMS found, *m/z*: 310.1109 $[M+H]^+$. $C_{15}H_{20}NO_4S^+$. Calculated, *m/z*: 310.1108.

Dimethyl 1-methyl-7-(methylthio)-1,4-dihydroquinoline-3,3(2*H*)-dicarboxylate (2j)



Yield 25 mg (31%), yellowish solid, m.p. 141-143°C.

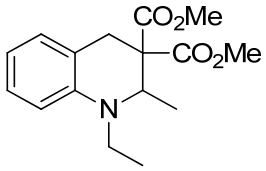
Reaction time ~ 1.5 days.The product decomposes upon irradiation.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.20 (d, *J* = 7.7 Hz, 1H), 6.88 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.83 (d, *J* = 1.6 Hz, 1H), 3.671 (s, 3H), 3.67 (s, 3H), 3.61 (s, 2H), 3.23 (s, 2H), 2.90 (s, 3H), 2.69 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 169.4, 169.3, 145.6, 145.0, 129.3, 122.3, 111.4, 105.4, 53.6, 52.8, 51.8, 43.1, 38.7, 32.6.

HRMS found, *m/z*: 326.1055 $[M+H]^+$. $C_{15}H_{20}NO_5S^+$. Calculated, *m/z*: 326.1057.

Dimethyl 1-ethyl-2-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2k)



Yield 68 mg (94%), colorless oil.

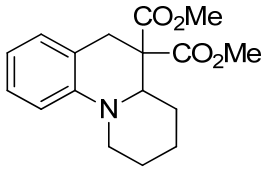
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.09-7.05 (m, 2H), 6.61 (t, *J*=7.3 Hz, 1H), 6.55 (d, *J*=8.0 Hz, 1H), 4.20 (q, *J*=6.7 Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 3.49-3.41 (m, 2H), 3.28 (dq, *J*=14.5, 7.4 Hz, 1H), 3.20 (d, *J*=16.8 Hz, 1H), 1.22 (t, *J*=7.4 Hz, 3H), 1.07 (d, *J*=6.5 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.1, 169.7, 142.2, 129.4, 127.5, 118.2, 115.9, 110.7, 56.5, 55.8, 52.9, 52.8, 44.8, 28.7, 15.6, 13.0.

HRMS found, *m/z*: 292.1542 $[M+H]^+$. $C_{16}H_{22}NO_4^+$. Calculated, *m/z*: 292.1549.

Dimethyl 2,3,4,4a-tetrahydro-1H-pyrido[1,2-a]quinoline-5,5(6H)-dicarboxylate (2l)



Yield 65 mg (86%), colorless oil.

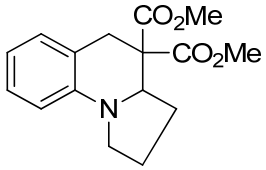
Reaction time ~ 6 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.07 (t, *J*=7.8 Hz, 1H), 7.04 (d, *J*=7.4 Hz, 1H), 6.72 (d, *J*=8.2 Hz, 1H), 6.65 (t, *J*=7.3 Hz, 1H), 4.04-3.99 (m, 2H), 3.76 (s, 3H), 3.62 (s, 3H), 3.35 (d, *J*=16.0 Hz, 1H), 3.15 (d, *J*=16.0 Hz, 1H), 3.02 (td, *J*=12.0, 2.5 Hz, 1H), 1.92-1.86 (m, 1H), 1.75-1.68 (m, 1H), 1.65-1.57 (m, 1H), 1.54-1.43 (m, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.0, 169.8, 143.9, 129.2, 127.7, 120.8, 117.2, 112.4, 60.1, 57.2, 53.0, 52.8, 48.8, 30.2, 26.1, 25.6, 22.9.

HRMS found, *m/z*: 304.1545 $[M+H]^+$. $C_{17}H_{22}NO_4^+$. Calculated, *m/z*: 304.1549.

Dimethyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2m)



Yield 67 mg (93%), colorless solid, m.p. 85-87°C.

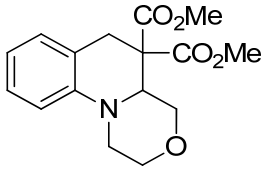
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.08 (t, *J*=7.6 Hz, 1H), 7.02 (d, *J*=7.4 Hz, 1H), 6.60 (t, *J*=6.5 Hz, 1H), 6.46 (d, *J*=8.0 Hz, 1H), 3.79 (s, 3H), 3.78 (dd, *J*=9.0, 6.9 Hz, 1H), 3.57 (s, 3H), 3.38 (d, *J*=15.8 Hz, 1H), 3.36-3.30 (m, 2H), 3.25 (d, *J*=15.8 Hz, 1H), 2.47-2.41 (m, 1H), 2.17-2.13 (m, 1H), 2.10-2.04 (m, 1H), 1.98-1.92 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 171.6, 169.2, 144.0, 128.6, 127.7, 118.8, 116.1, 111.1, 62.3, 53.4, 52.8, 52.2, 47.5, 37.0, 28.0, 23.6.

HRMS found, *m/z*: 290.1387 $[M+H]^+$. $C_{16}H_{20}NO_4^+$. Calculated, *m/z*: 290.1392.

Dimethyl 1,2,4,4a-tetrahydro-[1,4]oxazino[4,3-a]quinoline-5,5(6H)-dicarboxylate (2n)



Yield 70 mg (92%), colorless solid, m.p. 104-107°C.

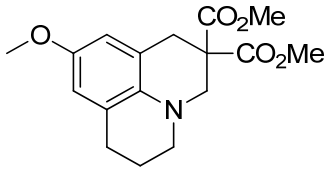
Reaction time ~ 13 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.12 (t, *J*=8.2 Hz, 1H), 7.03 (d, *J*=6.7 Hz, 1H), 6.77-6.73 (m, 2H), 3.95 (dd, *J*=10.5, 2.5 Hz, 1H), 3.93-3.89 (m, 1H), 3.84 (dd, *J*=10.9, 2.7 Hz, 1H), 3.75-3.67 (m, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 3.27 (d, *J*=15.5 Hz, 1H), 3.19 (d, *J*=15.5 Hz, 1H), 3.18-3.16 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.0, 169.0, 144.7, 128.8, 127.9, 121.9, 118.9, 112.8, 67.7, 66.2, 58.8, 55.7, 53.1, 52.8, 48.3, 33.5.

HRMS found, *m/z*: 306.1335 $[M+H]^+$. $C_{16}H_{20}NO_5^+$. Calculated, *m/z*: 306.1341.

Dimethyl 9-methoxy-3,5,6,7-tetrahydropyrido[3,2,1-ij]quinoline-2,2(1H)-dicarboxylate (2o)



Yield 58 mg (73%), colorless oil.

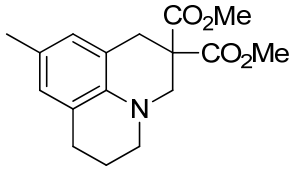
Reaction time ~ 6 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.48 (d, *J*=2.5 Hz, 1H), 6.42 (d, *J*=2.5 Hz, 1H), 3.73 (s, 6H), 3.70 (s, 3H), 3.45 (s, 2H), 3.24 (s, 2H), 3.06 (t, *J*=5.3 Hz, 2H), 2.73 (t, *J*=6.7 Hz, 2H), 1.97-1.91 (m, 2H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.6 (2C), 151.6, 136.2, 123.6, 120.5, 113.3, 112.5, 55.7, 53.0, 53.2, 52.9 (2C), 50.4, 33.7, 27.8, 22.4.

HRMS found, *m/z*: 320.1496 $[M+H]^+$. $C_{17}H_{22}NO_5^+$. Calculated, *m/z*: 320.1498.

Dimethyl 9-methyl-3,5,6,7-tetrahydropyrido[3,2,1-ij]quinoline-2,2(1H)-dicarboxylate (2p)



Yield 51 mg (67%), colorless oil.

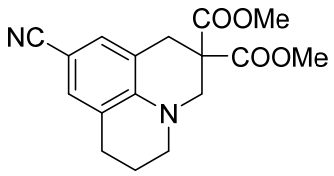
Reaction time ~ 5 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 6.69 (s, 1H), 6.63 (s, 1H), 3.74 (s, 6H), 3.49 (s, 2H), 3.24 (s, 2H), 3.11 (t, *J*=5.3 Hz, 2H), 2.71 (t, *J*=6.7 Hz, 2H), 2.18 (s, 3H), 1.97-1.93 (m, 2H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 170.6 (2C), 139.4, 128.1, 127.5, 126.1, 122.1, 119.1 53.7, 53.1, 52.9 (2C), 50.3, 33.5, 27.5, 22.4, 20.4.

HRMS found, *m/z*: 304.1546 $[M+H]^+$. $C_{17}H_{22}NO_4^+$. Calculated, *m/z*: 304.1549.

Dimethyl 9-cyano-6,7-dihydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-2,2(3*H*)-dicarboxylate (2q)



Yield 76 mg (97%), colorless oil.

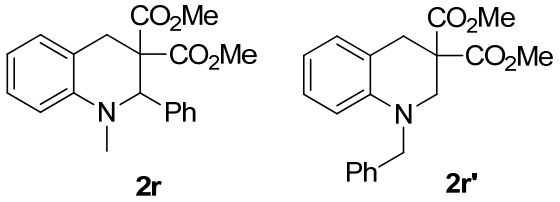
Reaction time ~ 2 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.24 (s, 1H), 7.11 (s, 1H), 3.66 (s, 6H), 3.60 (s, 2H), 3.25 (t, J = 5.7 Hz, 2H), 3.16 (s, 2H), 2.65 (t, J = 6.3 Hz, 2H), 1.81 (p, J = 6.1 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 169.1, 144.3, 130.6, 130.3, 121.5, 120.4, 118.3, 95.7, 53.0, 52.3, 51.0, 49.3, 32.4, 26.5, 20.4.

HRMS found, *m/z*: 315.1335 $[M+H]^+$. $C_{17}H_{19}N_2O_4^+$. Calculated, *m/z*: 315.1339.

Dimethyl 1-methyl-2-phenyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate and dimethyl 1-benzyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2r and 2r')



Can not be separated.

2r/**2r'** ratio ~ 2/1.

Overall yield 81 mg (95%), colorless viscous oil.

Reaction time ~ 1 day.

The structures were confirmed using two-dimensional NMR spectroscopy by experiments ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC together with conventional ^{1}H and ^{13}C NMR data. Signal assignment are presented on Scheme below. There are likely to be some inaccuracies in the assignment of the signals of the carbonyl groups and the phenyl ring.

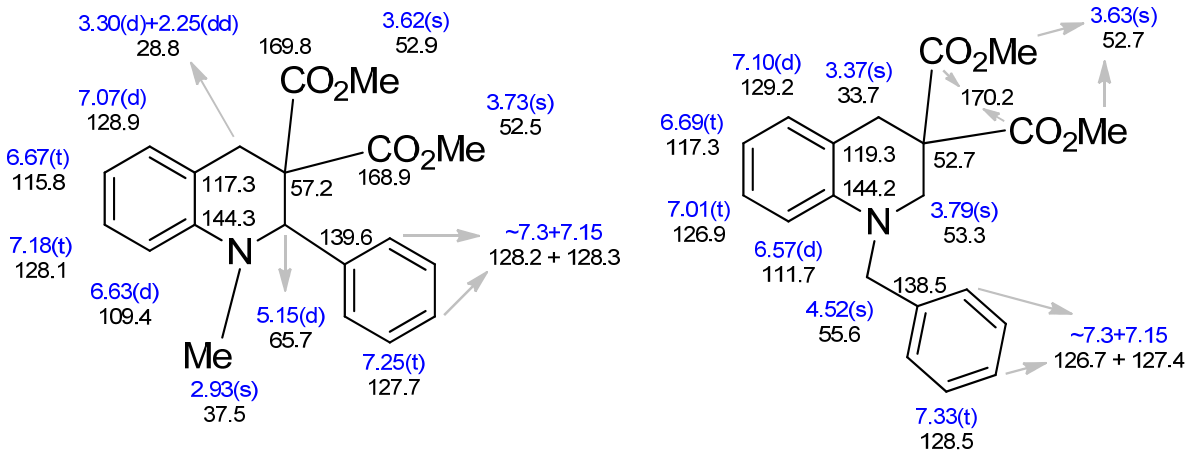
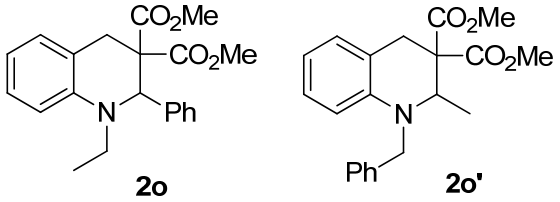


Figure S8. NMR study of compounds **2r** and **2r'** mixture ($CDCl_3$).

Dimethyl 1-ethyl-2-phenyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate and dimethyl 1-benzyl-2-methyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (2s and 2s')



Can not be separated.

2s/**2s'** ratio ~ 1/2.

Overall yield 83 mg (94%), colorless viscous oil.

Reaction time ~ 1 day.

The structures were confirmed using two-dimensional NMR spectroscopy by experiments ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC together with conventional ^{1}H and ^{13}C NMR data. Signal assignment are presented on Scheme below. There are likely to be some inaccuracies in the assignment of the signals of the carbonyl groups and the phenyl ring.

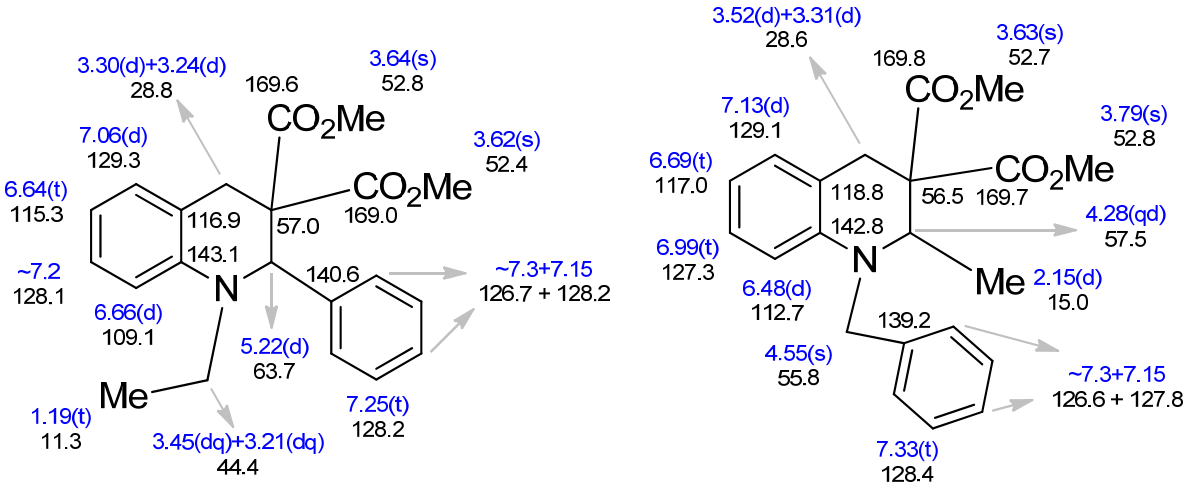


Figure S9. NMR study of compounds **2s** and **2s'** mixture ($CDCl_3$).

7. Optical properties and wavelength screening

Optical properties

Absorbance spectra were recorded on a Varian Cary 100 spectrophotometer. For this experiment compounds **1a**, **3**, **4**, **5a** and **6** were dissolved in DMSO in final concentration 10-30 mkM.

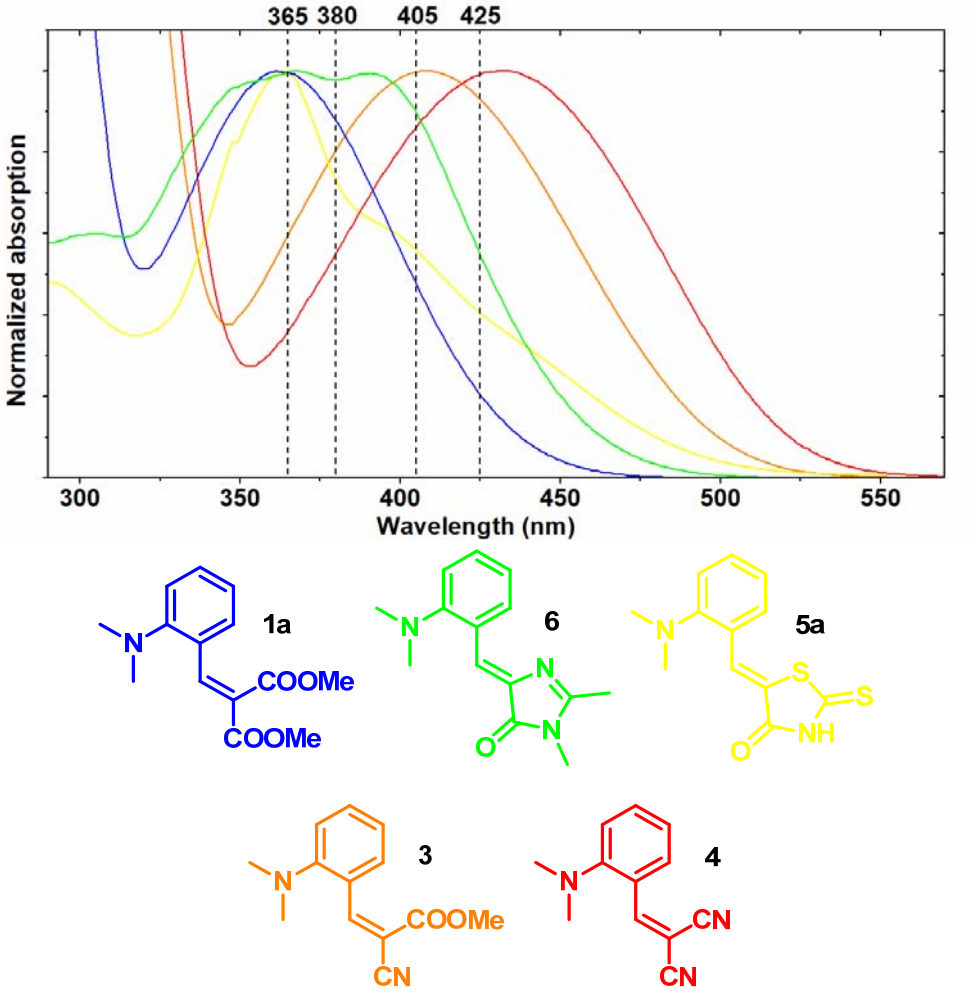


Figure S7. Absorbance spectra of compounds **1a**, **3**, **4**, **5a** and **6**. The figure also indicates the wavelengths of the LED lamps used.

Wavelength screening

Compounds **1a**, **3**, **4**, **5a** and **6** (12 mg) were dissolved in 4 mL of DMSO-d_6. Vials with 1 mL of obtained solutions were irradiated with various LED lamp in Evoluchem™ PhotoRedOx box with stirring (set-up is similar to Figure S1). After 24 hours of irradiation solutions were analyzed by NMR. In each case, for various LEDs, each specific compound always occupied the same position in the rack.

Results are presented in Table S3.

Table S3. LED screening results. Irradiation time – 24 hours.

Compound	LED, nm	LED power[a], mW/cm^2	Conversion[b], %
1a	365	9	-[c]
	380	8	-[c]
	405	28	-[c]
	425	33	-[c]
3	365	9	-[c]
	380	8	-[c]
	405	28	-[c]
	425	33	-[c]
4	365	9	24
	380	8	29
	405	28	57
	425	33	52
5a	365	9	7.1
	380	8	7.9
	405	28	19
	425	33	19
6	365	9	<1.5
	380	8	<2.0
	405	28	2.7
	425	33	2.7

a – not measured but obtained from the manufacturer's site - https://www.hepatochem.com/photoreactors-leds-accessories/led-evoluchem; b - measured in single experiment, error is about 5% based on integration accuracy in NMR spectra; c – irradiation time is too long, 100% conversion, in several cases significant degradation of the product observed.

Compounds **1a** and **3** (12 mg) were dissolved in 4 mL of DMSO-d_6. Vials with 1 mL of obtained solution were irradiated with various LED lamp in Evoluchem™ PhotoRedOx box with stirring (set-up is similar to Figure S1). After 3 hours of irradiation solutions were analyzed by NMR. In each case, for various LEDs, each specific compound always occupied the same position in the rack.

Results are presented in Table S4.

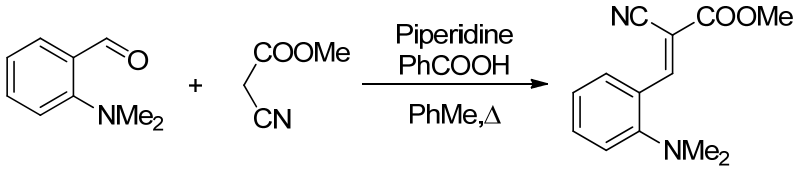
Table S4. LED screening results. Irradiation time – 3 hours.

Compound	LED, nm	LED power[a], mW/cm^2	Conversion[b], %
1a	365	9	66
	380	8	64
	405	28	27
	425	33	33
3	365	9	8.0
	380	8	9.1
	405	28	19
	425	33	18

a – not measured but obtained from the manufacturer's site - https://www.hepatochem.com/photoreactors-leds-accessories/led-evoluchem; b - measured in single experiment, error is about 5% based on integration accuracy in NMR spectra.

8. Synthesis of compounds 3-6

Synthesis of methyl 2-cyano-3-(2-(dimethylamino)phenyl)acrylate (3)



Scheme S4. Synthesis of compound **3**.

Mixture of 745 mg (5 mmol) of 2-(dimethylamino)benzaldehyde, 545 mg (5.5 mmol) of methyl 2-cyanoacetate, 20 mg of benzoic acid and 20 mg of piperidine in 20 mL of toluene was refluxed for 5 h. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 7:1).

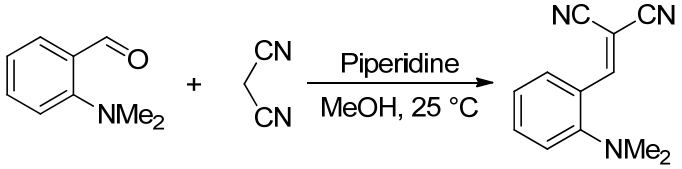
Yield 1.12 g (97%), yellow solid, m.p. 76-78°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 8.41 (s, 1H), 7.96 (d, *J*=7.8 Hz, 1H), 7.54 (t, *J*=7.1 Hz, 1H), 7.21 (d, *J*=8.4 Hz, 1H), 7.13 (t, *J*=7.6 Hz, 1H), 3.87 (s, 3H), 2.76 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 162.9, 155.1, 152.7, 133.9, 129.1, 123.4, 121.5, 118.6, 115.7, 101.0, 53.3, 45.1 (2C).

HRMS found, *m/z*: 231.1129 $[M+H]^+$. $C_{13}H_{15}N_2O_2^+$. Calculated, *m/z*: 231.1134.

Synthesis of 2-(2-(dimethylamino)benzylidene)malononitrile (4)



Scheme S5. Synthesis of compound **4**.

Mixture of 745 mg (5 mmol) of 2-(dimethylamino)benzaldehyde and 330 mg (5 mmol) of malononitrile in 20 mL of methanol was stirred at 25 °C overnight. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 10:1).

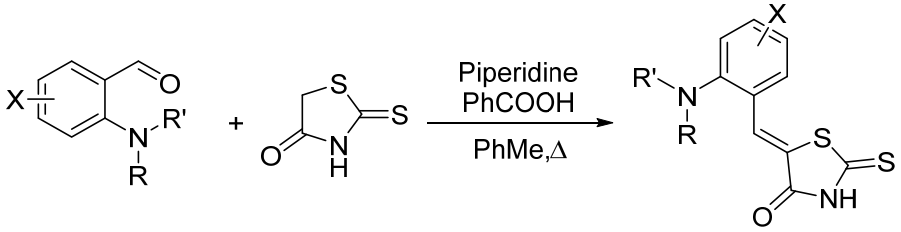
Yield 690 mg (70%), orange solid, m.p. 79-81°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 8.29 (s, 1H), 7.85 (d, *J*=7.1 Hz, 1H), 7.56 (t, *J*=8.6 Hz, 1H), 7.20 (d, *J*=8.4 Hz, 1H), 7.10 (t, *J*=7.6 Hz, 1H), 2.81 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 159.2, 154.9, 134.7, 129.3, 122.8, 121.1, 118.5, 114.7, 113.4, 80.0, 45.0 (2C).

HRMS found, *m/z*: 198.1027 $[M+H]^+$. $C_{12}H_{12}N_3^+$. Calculated, *m/z*: 198.1031.

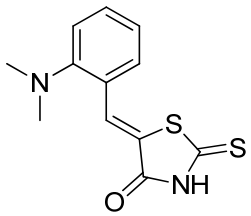
Synthesis of 5-(2-aminobenzylidene)-2-thioxothiazolidin-4-ones



Scheme S6. Synthesis of compounds **5**.

General method

Mixture of 5 mmol of the corresponding 2-aminobenzaldehyde, 665 mg (5 mmol) of 2-thioxothiazolidin-4-one, 20 mg of benzoic acid and 20 mg of piperidine in 20 mL of toluene was refluxed for 6 h. All volatiles were removed in vacuo and the residue was purified by flash chromatography (eluent – mixture of hexane and EtOAc, v/v 8:1).



(Z)-5-(2-(dimethylamino)benzylidene)-2-thioxothiazolidin-4-one (5a)

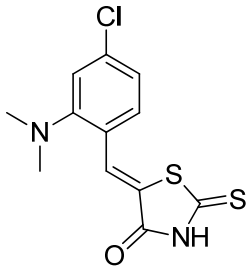
Yield 1.17 g (89%), yellow solid, m.p. 156-158°C.

Contain ~ 10% of E-isomer.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 13.6 (bs, 1H), 7.69 (s, 1H), 7.46 (d, *J*=7.8 Hz, 1H), 7.44 (t, *J*=8.7 Hz, 1H), 7.21 (d, *J*=7.8 Hz, 1H), 7.11 (t, *J*=7.4 Hz, 1H), 2.68 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 197.3, 169.8, 153.0, 131.8, 131.3, 130.8, 125.5, 124.6, 122.3, 118.9, 44.0 (2C).

HRMS found, *m/z*: 265.0465 $[M+H]^+$. $C_{12}H_{13}N_2OS_2^+$. Calculated, *m/z*: 265.0469.



(Z)-5-(4-chloro-2-(dimethylamino)benzylidene)-2-thioxothiazolidin-4-one (5b)

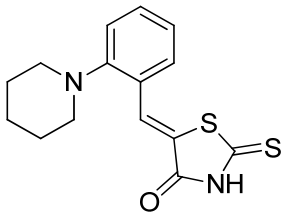
Yield 1.15 g (78%), yellow solid, m.p. 225-228°C.

Contain ~ 10% of E-isomer.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 13.6 (bs, 1H), 7.62 (s, 1H), 7.48 (d, *J*=8.4 Hz, 1H), 7.20 (d, *J*=1.9 Hz, 1H), 7.15 (dd, *J*=8.4 1.9 Hz, 1H), 2.70 (s, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 197.0, 169.8, 154.0, 136.2, 132.8, 129.8, 125.1, 124.1, 122.0, 119.0, 43.7 (2C).

HRMS found, *m/z*: 299.0077 $[M+H]^+$. $C_{12}H_{12}ClN_2OS_2^+$. Calculated, *m/z*: 299.0080.



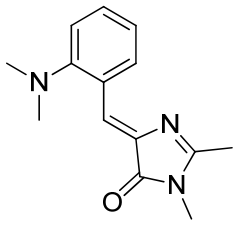
(Z)-5-(2-(piperidin-1-yl)benzylidene)-2-thioxothiazolidin-4-one (5c)

Yield 1.21 g (80%), yellow solid, m.p. 182-185°C.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 13.7 (bs, 1H), 7.76 (s, 1H), 7.44 (t, *J*=7.0 Hz, 1H), 7.40 (d, *J*=6.3 Hz, 1H), 7.18-7.13 (m, 2H), 2.89-2.84 (m, 4H), 1.72-1.65 (m, 4H), 1.57-1.53 (m, 2H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 195.9, 169.5, 154.2, 131.8, 129.2, 128.7, 126.3, 124.7, 122.6, 119.4, 54.0 (2C), 25.8 (2C), 23.5.

HRMS found, *m/z*: 305.0772 $[M+H]^+$. $C_{15}H_{17}N_2OS_2^+$. Calculated, *m/z*: 305.0782.

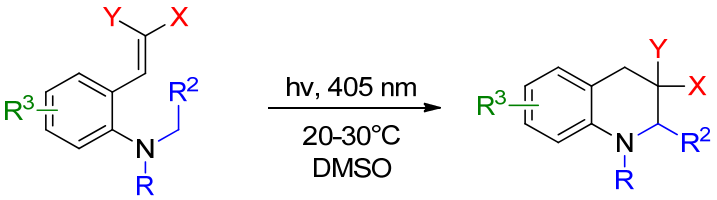


(Z)-4-(2-(dimethylamino)benzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (6)

Previously obtained in our laboratory. Synthetic procedures, yields and spectral data are presented in our previous work – [3].

9. Synthesis of tetrahydroquinolines 7-10

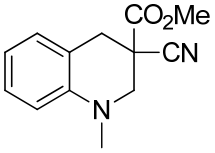
General method



Scheme S7. Synthesis of tetrhydrochonolines **2**.

Compounds **3-6** (0.25 mmol) were dissolved in 10 mL of dry DMSO in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. Obtained solutions were irradiated with 405 nm LED lamp in Evoluchem™ PhotoRedOx box with stirring (similary to mentioned above – see Figure S6). The progress of the reaction was monitored by TLC and also visually by the color disappearance (only for compounds **7** and **8**). After the reaction completion (or 14 days for compound **9b** and 21 days for compound **10**), reaction mixtures were dissolved in 150 mL of EtOAc, washed with saturated KCl solution (30 mL x 10 times) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by column chromatography on silica (eluent – EtOAc for **7** and **8** and CH_2Cl_2 for **9** and **10**).

Methyl 3-cyano-1-methyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (7)



Yield 53 mg (92%), colorless solid, m.p. 75-77°C.

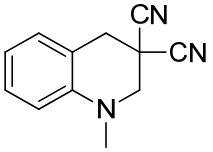
Reaction time ~ 6 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.11 (t, *J*=7.8 Hz, 1H), 7.04 (d, *J*=7.3 Hz, 1H), 6.72 (d, *J*=8.2 Hz, 1H), 6.67 (t, *J*=7.4 Hz, 1H), 3.82 (s, 3H), 3.72 (dd, *J*=11.7, 2.1 Hz, 1H), 3.51 (d, *J*=11.6 Hz, 1H), 3.32 (d, *J*=16.2 Hz, 1H), 3.25 (d, *J*=16.2 Hz, 1H), 2.94 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 167.2, 144.3, 129.0, 127.9, 118.3, 117.2, 117.1, 111.6, 54.5, 53.8, 41.2, 28.6, 34.7.

HRMS found, *m/z*: 231.1132 $[M+H]^+$. $C_{13}H_{15}N_2O_2^+$. Calculated, *m/z*: 231.1134.

1-Methyl-1,2-dihydroquinoline-3,3(4H)-dicarbonitrile (8)



Yield 45 mg (92%), colorless solid, m.p. 129-132°C.

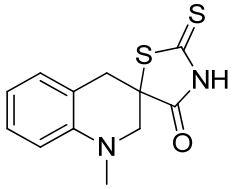
Reaction time ~ 5 days.

^{1}H NMR (700 MHz, $CDCl_3$) δ ppm: 7.23 (t, *J*=7.6 Hz, 1H), 7.03 (d, *J*=7.4 Hz, 1H), 6.80 (t, *J*=7.4 Hz, 1H), 6.74 (d, *J*=8.2 Hz, 1H), 3.73 (s, 2H), 3.47 (s, 2H), 3.06 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ ppm: 143.6, 129.3, 129.3, 118.9, 114.6, 114.6, 112.7 (2C), 56.4, 39.5, 37.3, 30.1.

HRMS found, *m/z*: 198.1027 $[M+H]^+$. $C_{12}H_{12}N_3^+$. Calculated, *m/z*: 198.1031.

1-Methyl-2'-thioxo-2,4-dihydro-1H-spiro[quinoline-3,5'-thiazolidin]-4'-one (9a)



Yield 58 mg (88%), yellow solid, m.p. 193-195°C.

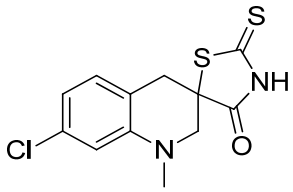
Reaction time ~ 12 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 13.4 (bs, 1H), 7.10 (t, *J*=8.0 Hz, 1H), 7.00 (d, *J*=7.4 Hz, 1H), 6.69 (d, *J*=8.2 Hz, 1H), 6.64 (t, *J*=7.3 Hz, 1H), 3.71 (dd, *J*=11.7, 2.9 Hz, 1H), 3.61 (d, *J*=11.6 Hz, 1H), 3.42 (d, *J*=16.2 Hz, 1H), 3.20 (dd, *J*=16.2, 2.9 Hz, 1H), 2.92 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 202.3, 178.6, 144.2, 129.2, 128.0, 117.7, 116.9, 111.4, 61.0, 57.2, 38.6, 38.1.

HRMS found, *m/z*: 265.0465 $[M+H]^+$. $C_{12}H_{13}N_2OS_2^+$. Calculated, *m/z*: 265.0469.

7-Chloro-1-methyl-2'-thioxo-2,4-dihydro-1H-spiro[quinoline-3,5'-thiazolidin]-4'-one (9b)



Yield (~85%, brsm!, 45% isolated, incomplete reaction), yellow solid, m.p. over 250°C with decomposition.

Reaction time >35 days.

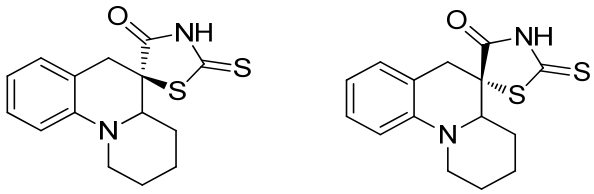
Isolated in 90+% purity with ~10% of starting material.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 13.4 (bs, 1H), 7.00 (d, *J*=8.0 Hz, 1H), 6.69 (d, *J*=1.8 Hz, 1H), 6.64 (dd, *J*=8.0, 1.8 Hz, 1H), 3.71 (dd, *J*=12.0, 2.7 Hz, 1H), 3.61 (d, *J*=12.0 Hz, 1H), 3.42 (d, *J*=16.2 Hz, 1H), 3.20 (dd, *J*=16.2, 2.5 Hz, 1H), 2.93 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 202.1, 178.5, 145.3, 132.5, 130.5, 116.7, 116.1, 110.6, 60.3, 56.9, 38.6, 37.5.

HRMS found, *m/z*: 299.0078 $[M+H]^+$. C12H12ClN2OS2$^+$. Calculated, *m/z*: 299.0080.

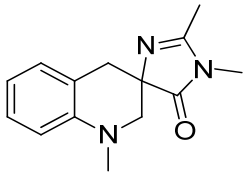
(5S)-2'-Thioxo-1,2,3,4,4a,6-hexahydrospiro[pyrido[1,2-a]quinoline-5,5'-thiazolidin]-4'-one (9c)



Reaction time >30 days.

Obtained as inseparable mixture of two isomers with starting material. Isomer ratio – 2:3.

1,1',2-Trimethyl-2',4'-dihydro-1'H-spiro[imidazole-4,3'-quinolin]-5(1H)-one (10)



Yield (~85%, brsm!, 30% isolated, incomplete reaction), colorless solid, m.p. 101-103°C.

Reaction time > 50 days.

^{1}H NMR (700 MHz, DMSO-d_6) δ ppm: 7.04 (t, *J*=7.8 Hz, 1H), 6.88 (d, *J*=7.4 Hz, 1H), 6.63 (d, *J*=8.0 Hz, 1H), 6.54 (t, *J*=7.3 Hz, 1H), 3.34 (d, *J*=11.6 Hz, 1H), 3.01 (s, 3H), 2.94-2.90 (m, 2H), 2.86 (s, 3H), 2.45 (dd, *J*=15.8, 2.1 Hz, 1H), 2.14 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6) δ ppm: 182.6, 160.8, 144.9, 128.6, 127.0, 119.4, 115.6, 110.4, 66.4, 55.6, 38.5, 35.1, 26.3, 15.1.

HRMS found, *m/z*: 244.1447 $[M+H]^+$. $C_{14}H_{18}N_3O^+$. Calculated, *m/z*: 244.1450.

10. Large scale synthesis

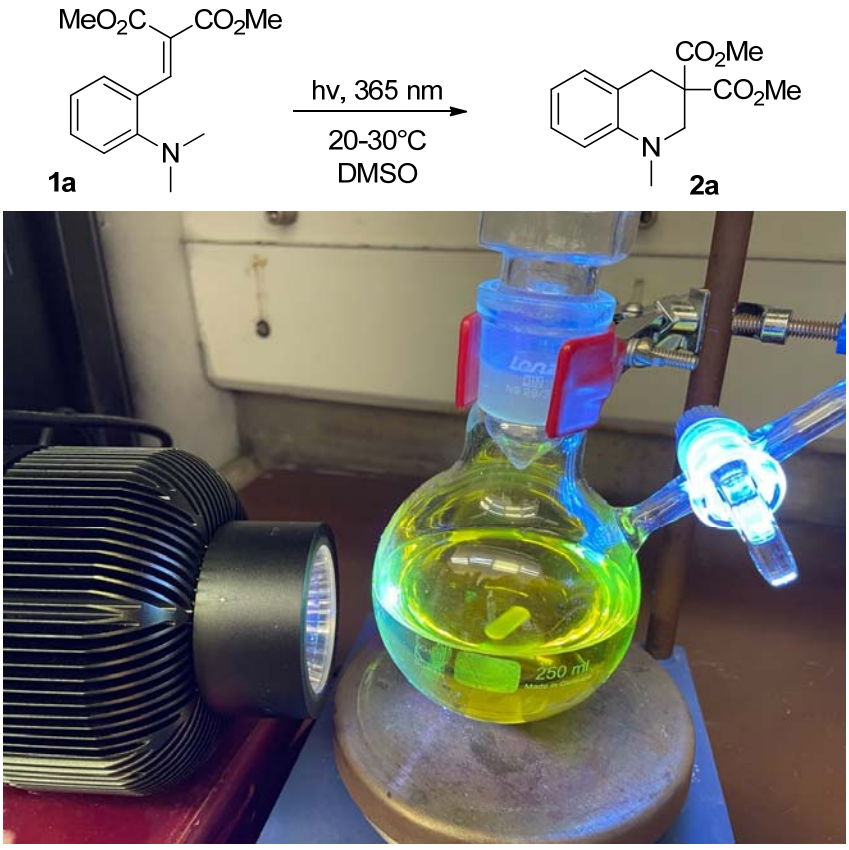


Figure S8. Large scale synthesis set-up.

Compound **1a** (1.32 g, 5 mmol) was dissolved in 150 mL of dry DMSO in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. Obtained solution was irradiated with 365 nm LED lamp (HCK1012-01-006) with stirring (Figure S8).

The progress of the reaction was monitored by TLC and also visually by the color disappearance. After the reaction completion (10 days), reaction mixtures were dissolved in 750 mL of EtOAc, washed with saturated KCl solution (75 mL x 10 times) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified by flash chromatography on silica using EtOAc as eluent.

Yield 1.25g (95%).

11. References

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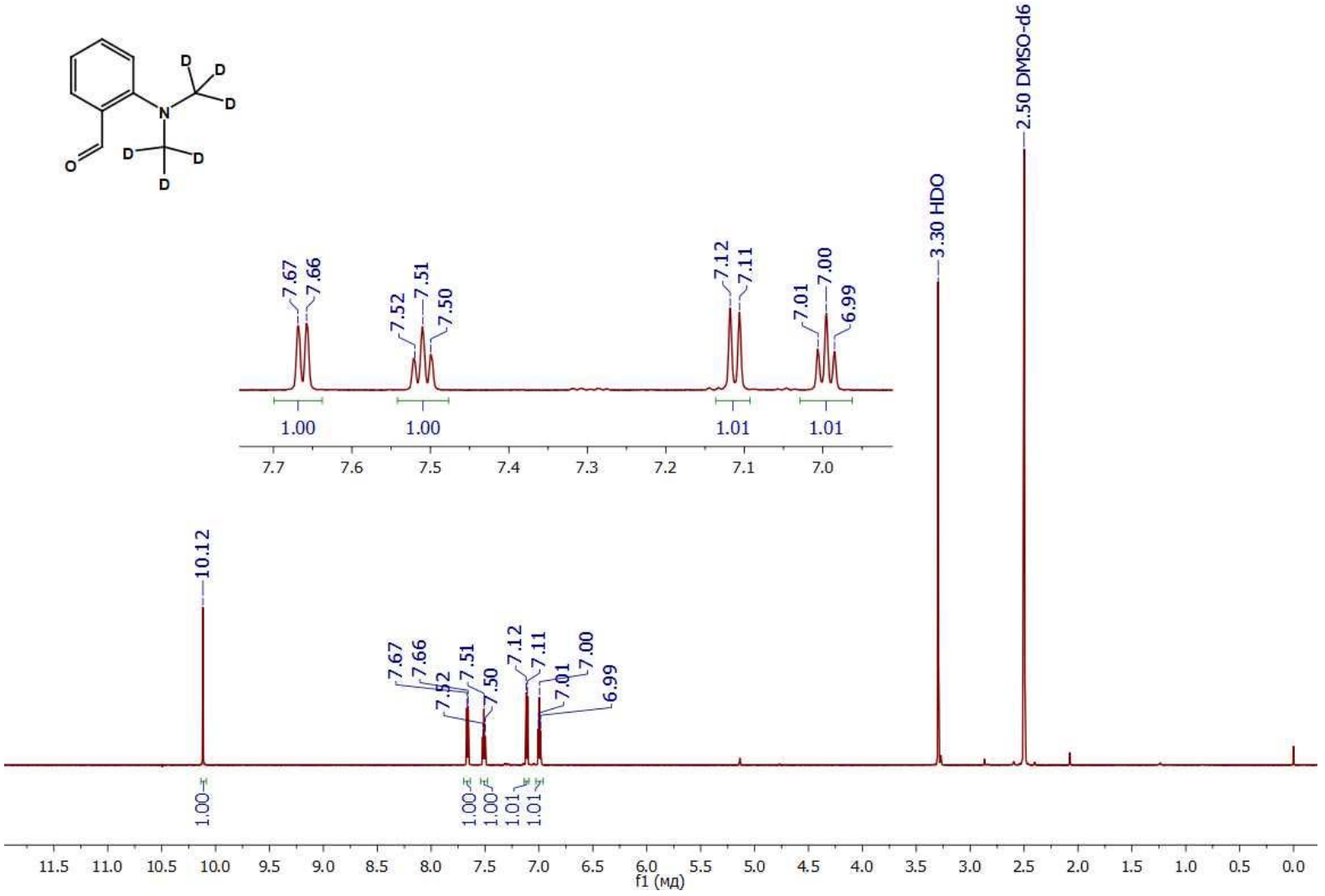
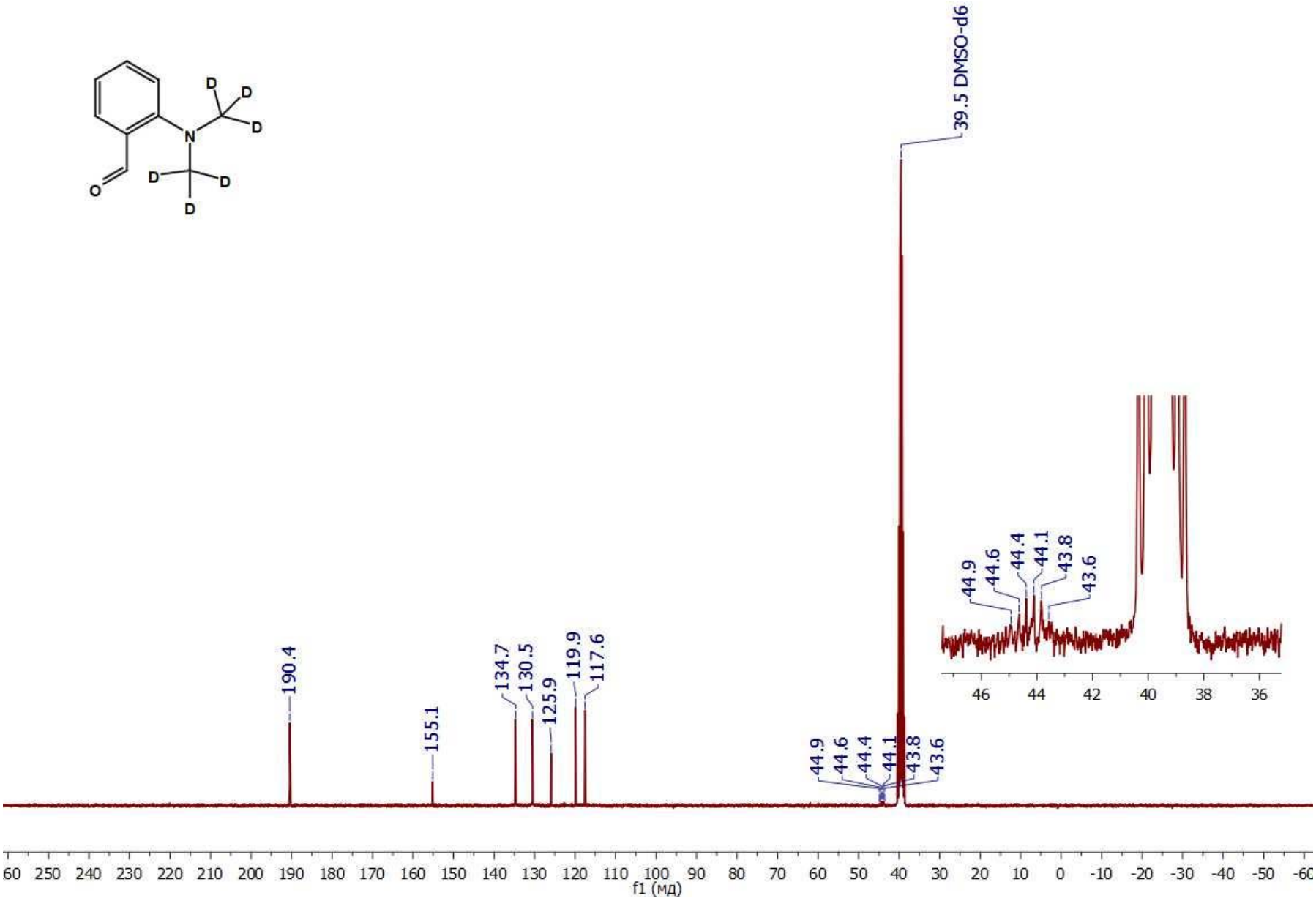
12. Copies of ^{1}H and ^{13}C NMR spectra

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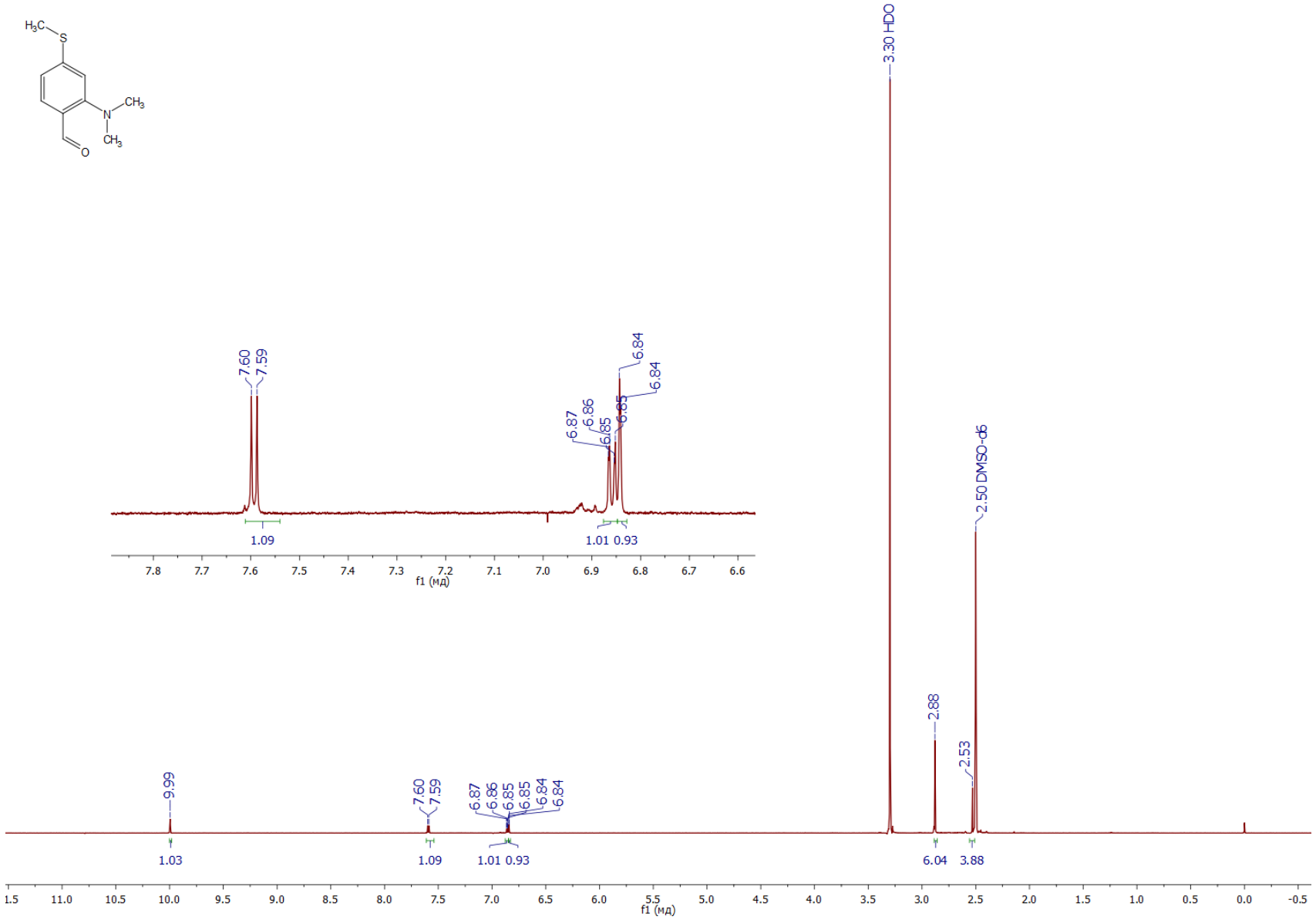
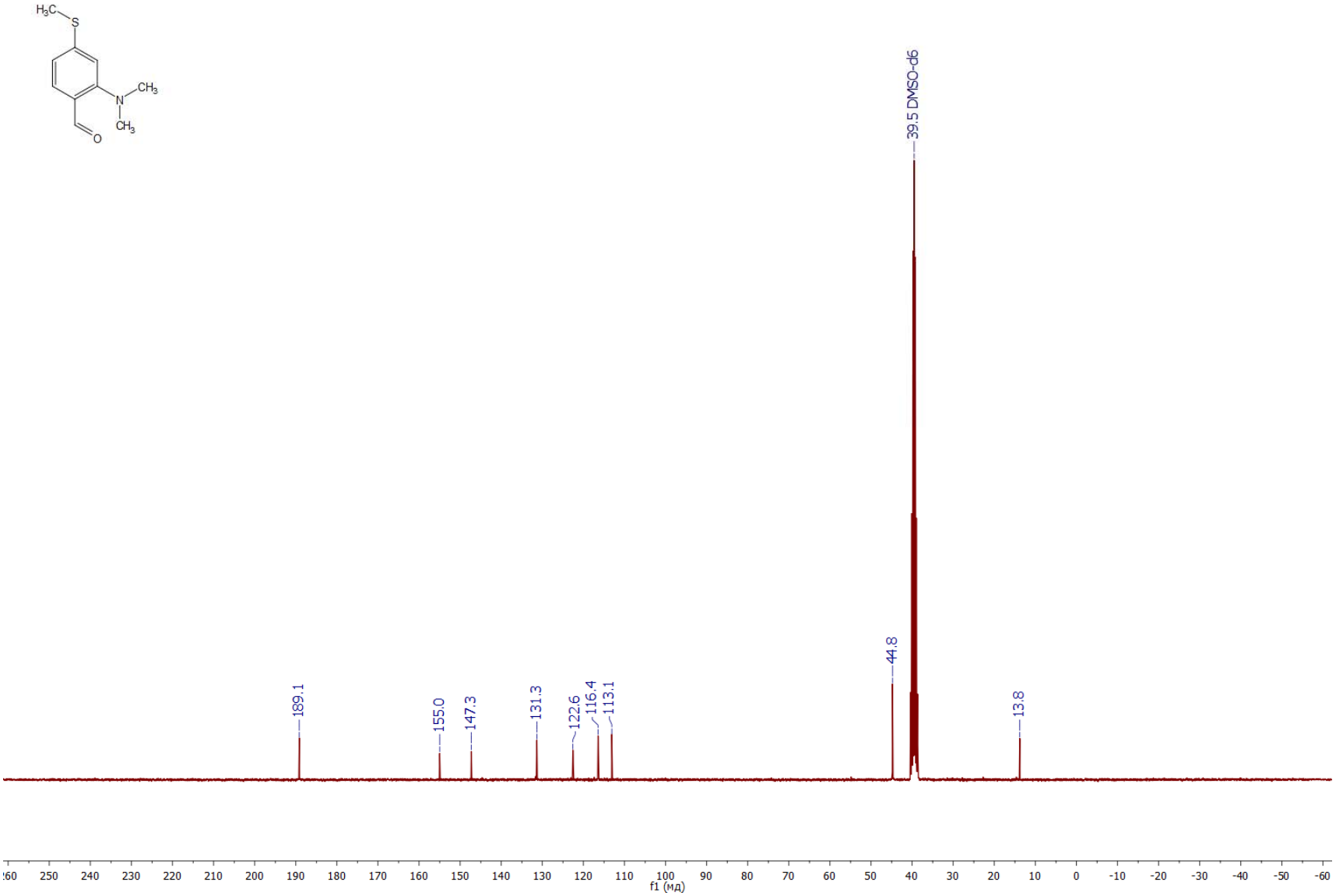
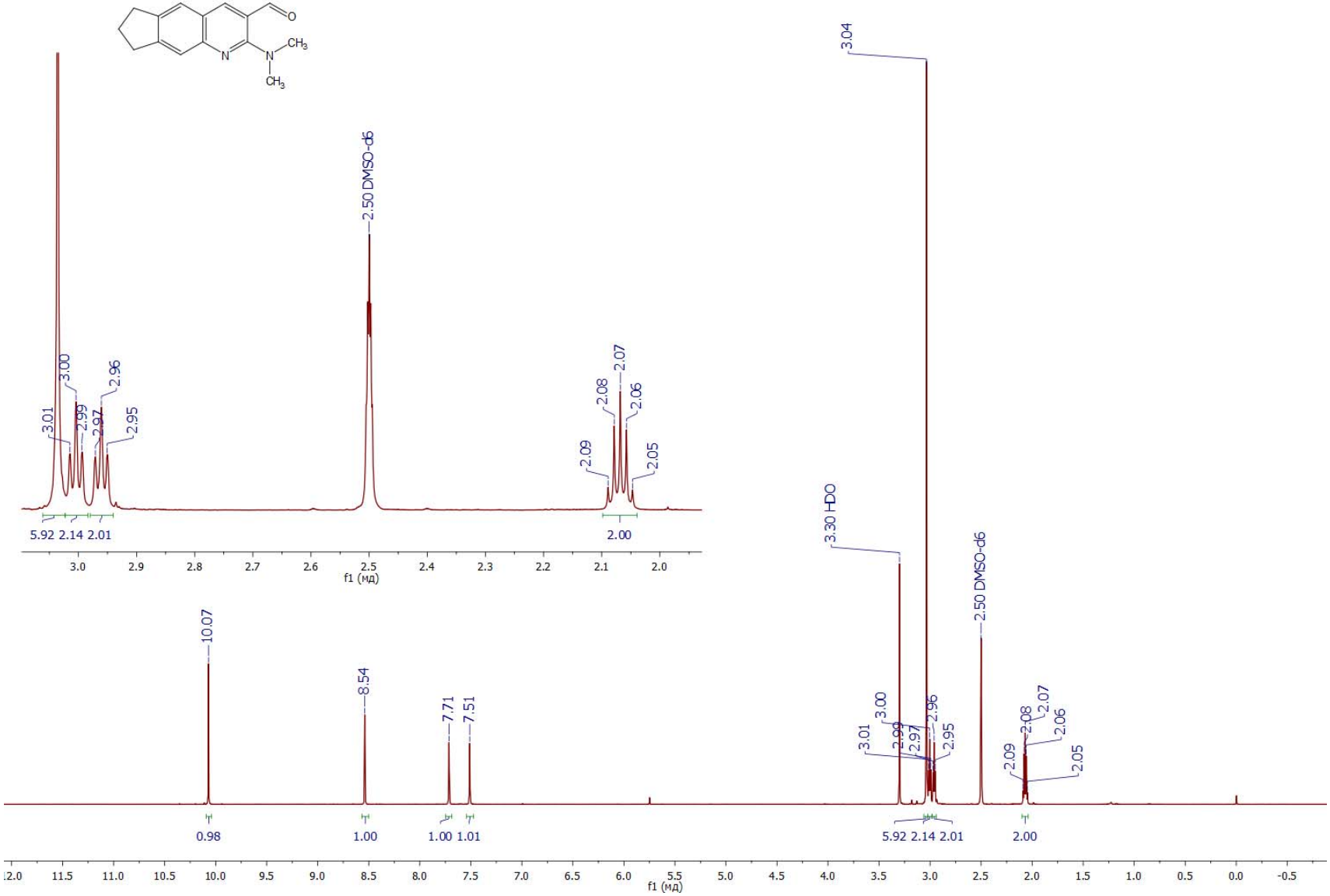
N
D
D
D
D
D
D
39.5 DMSO-d6
190.4
155.1
134.7
130.5
125.9
119.9
117.6
44.9
44.6
44.4
44.1
43.8
43.6
f1 (мд)


H3C
S
N
CH3
CH3
O
3.30 HDO
2.50 DMSO-d6
2.88
2.53
9.99
7.60
7.59
6.87
6.86
6.85
6.84
6.84
1.03
1.09
1.01 0.93
6.04
3.88
f1 (мд)


H3C
S
CH3
N
CH3
O
39.5 DMSO-d6
189.1
155.0
147.3
131.3
122.6
116.4
113.1
44.8
13.8
f1 (мд)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N
CH3
CH3
10.07
8.54
7.71
7.51
3.04
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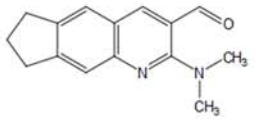
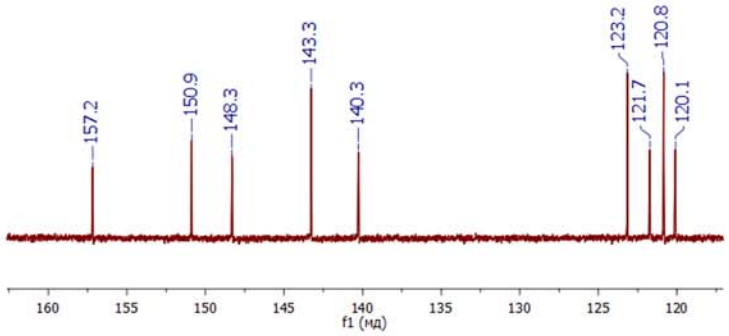
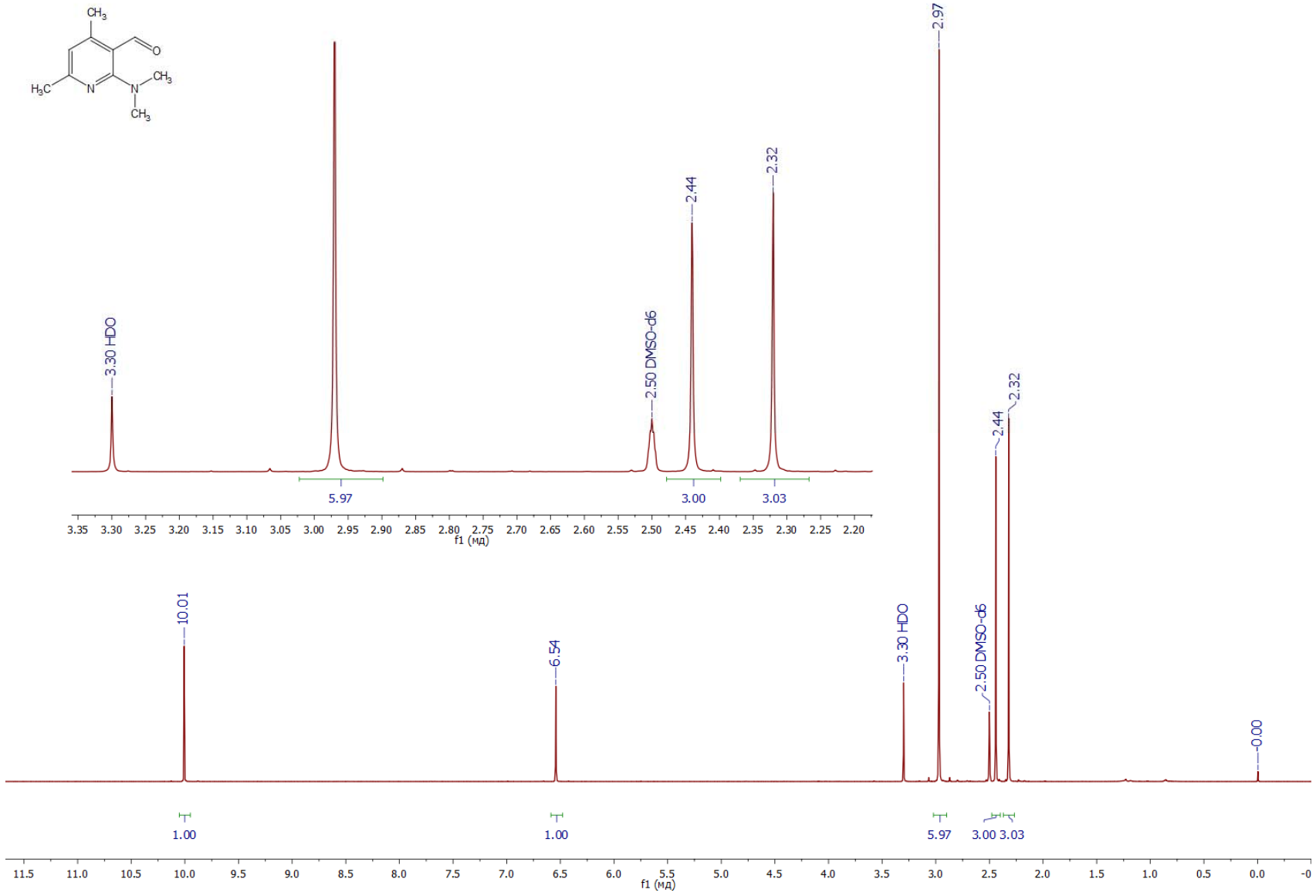
2.50 DMSO-d6
3.01
3.00
2.99
2.97
2.96
2.95
2.09
2.08
2.07
2.06
2.05
0.98
1.00
1.00 1.01
5.92 2.14 2.01
2.00
f1 (мд)


O
N
N
CH3
CH3


157.2
150.9
148.3
143.3
140.3
123.2
121.7
120.8
120.1
160
155
150
145
140
135
130
125
120
f1 (мд)

190.1
157.2
150.9
148.3
143.3
140.3
123.2
121.7
120.8
120.1
41.7
39.5 DMSO-d6
32.6
31.5
25.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (мд)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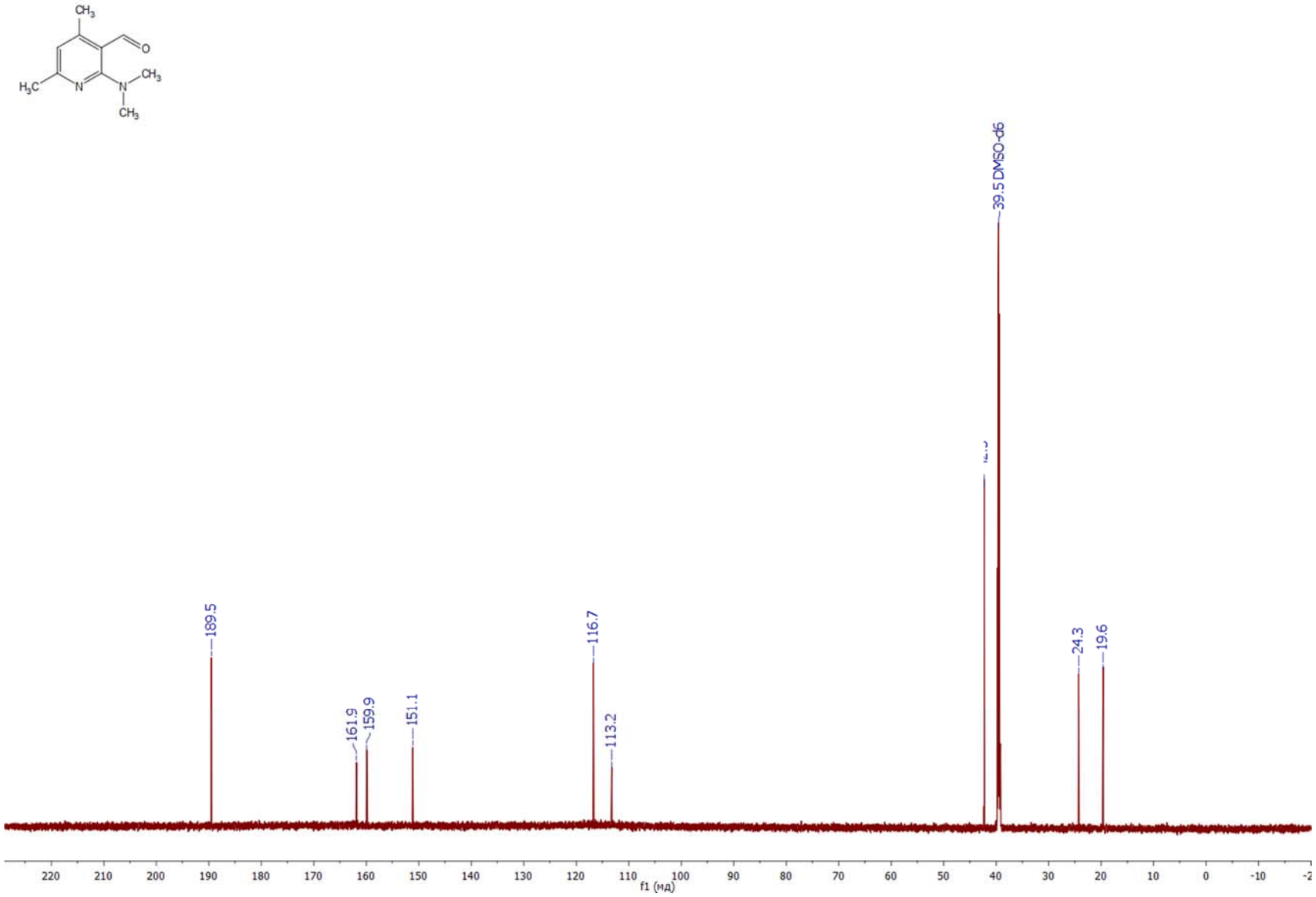
O
H3C
N
N
CH3
CH3
3.30 HDO
2.50 DMSO-d6
2.44
2.32
2.97
5.97
3.00
3.03
f1 (мд)
10.01
6.54
0.00
1.00
1.00
5.97
3.00 3.03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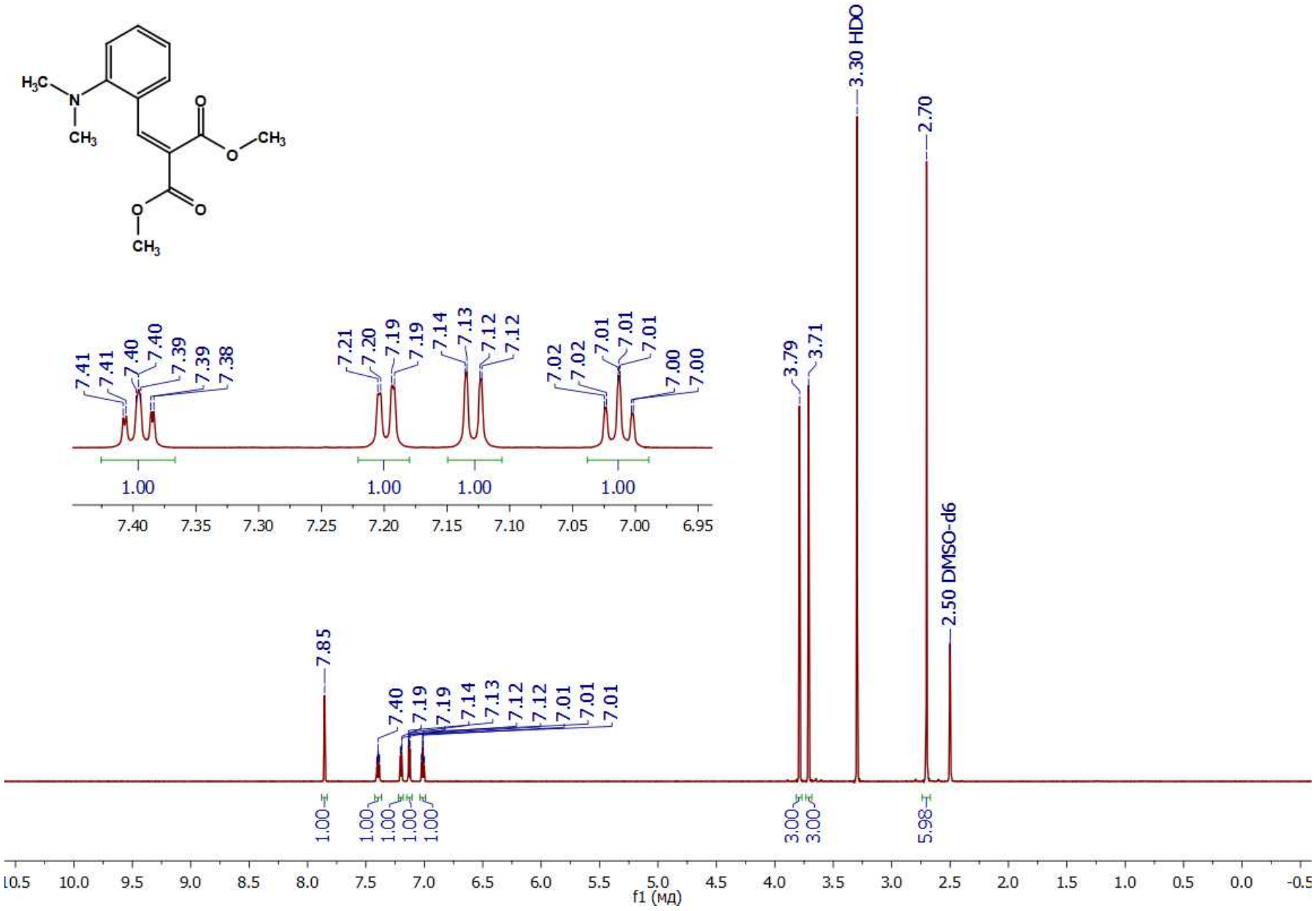
161.9
159.9
151.1
116.7
113.2
39.5 DMSO-d6
24.3
19.6
f1 (ppm)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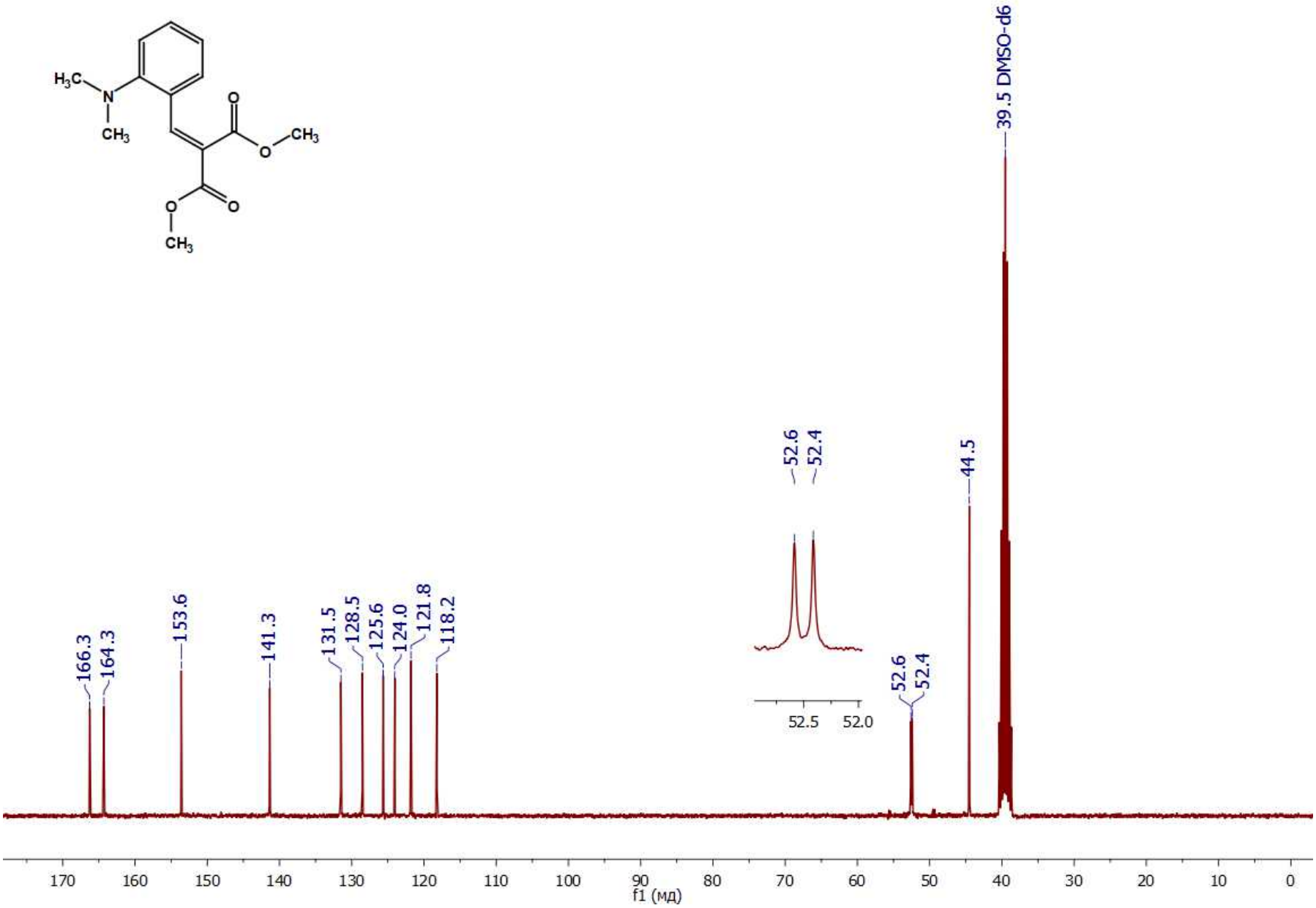
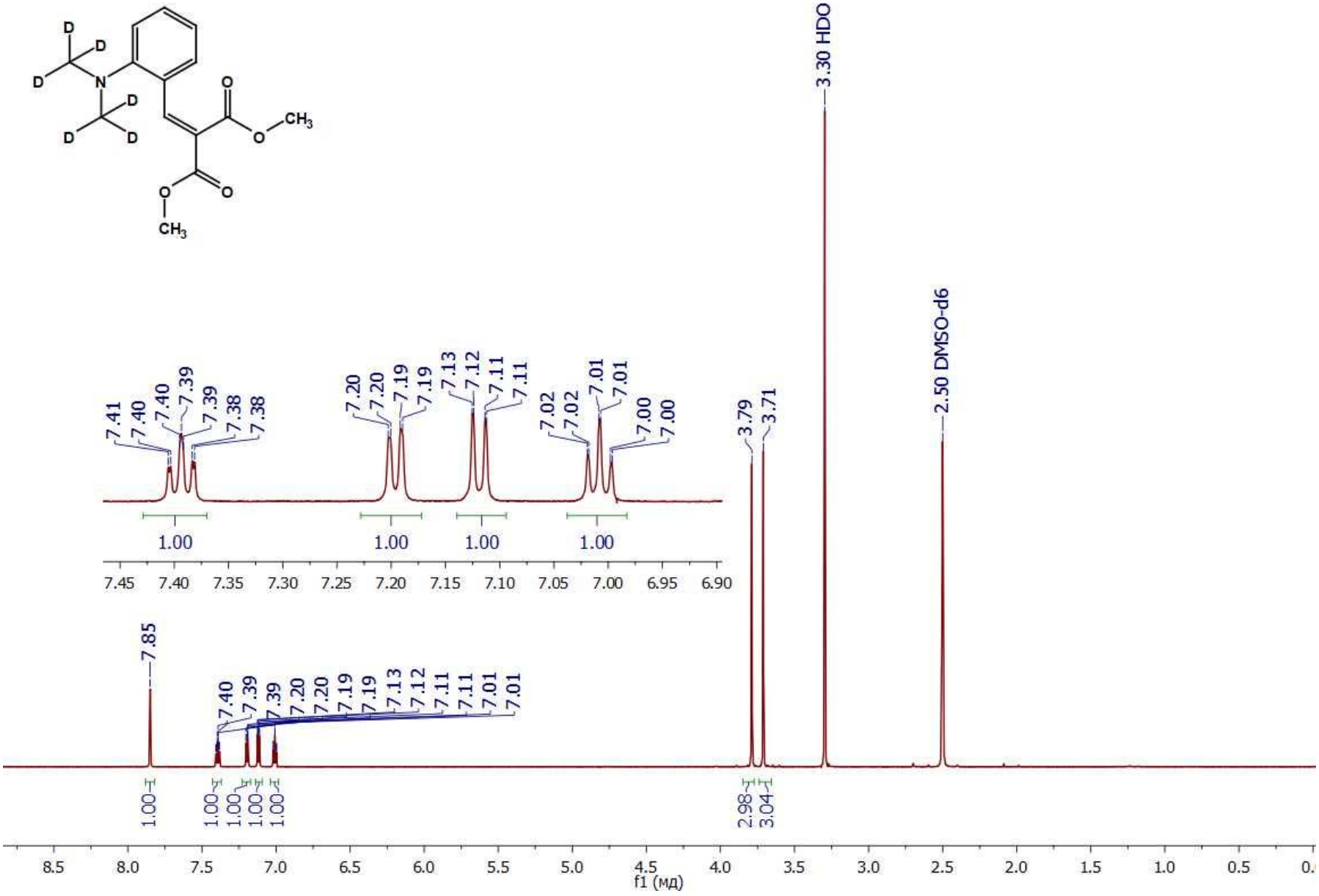
7.85
3.79
3.71
f1 (мд)


H3C
N
CH3
O
O
CH3
O
O
O
CH3
166.3
164.3
153.6
141.3
131.5
128.5
125.6
124.0
121.8
118.2
52.6
52.4
52.5
52.0
52.6
52.4
44.5
39.5 DMSO-d6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


D
D
D
N
D
D
D
D
O
O
CH3
O
O
O
CH3
3.30 HDO
2.50 DMSO-d6
7.85
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.20
7.20
7.19
7.19
7.13
7.12
7.11
7.11
7.02
7.02
7.01
7.01
7.00
7.00
3.79
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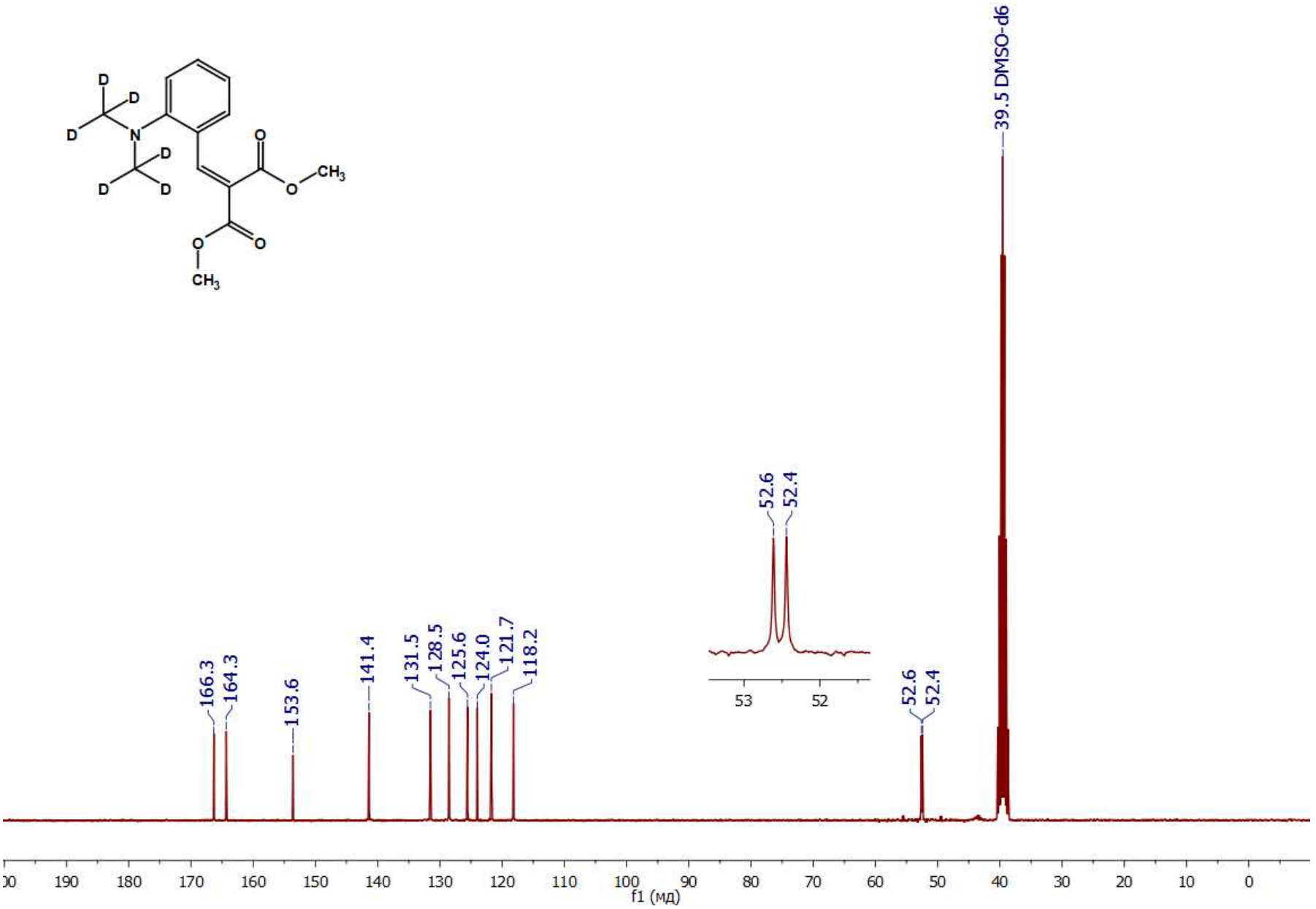
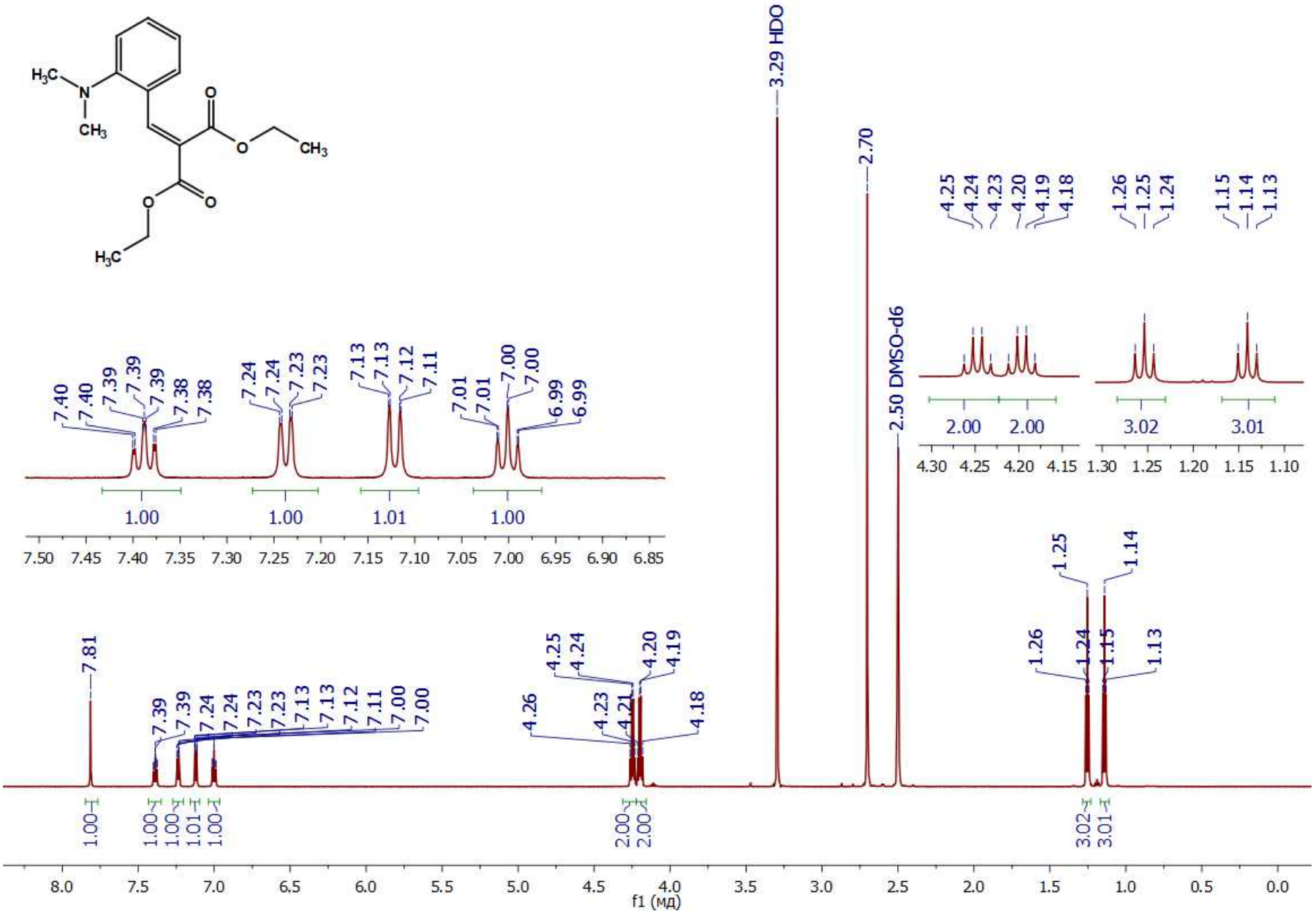
1.00
1.00
2.98
3.04
f1 (мд)


D
D
D
N
D
D
D
O
O
CH3
O
O
CH3
39.5 DMSO-d6
52.6
52.4
166.3
164.3
153.6
141.4
131.5
128.5
125.6
124.0
121.7
118.2
53
52
52.6
52.4
f1 (мд)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2.70
2.50 DMSO-d6
7.81
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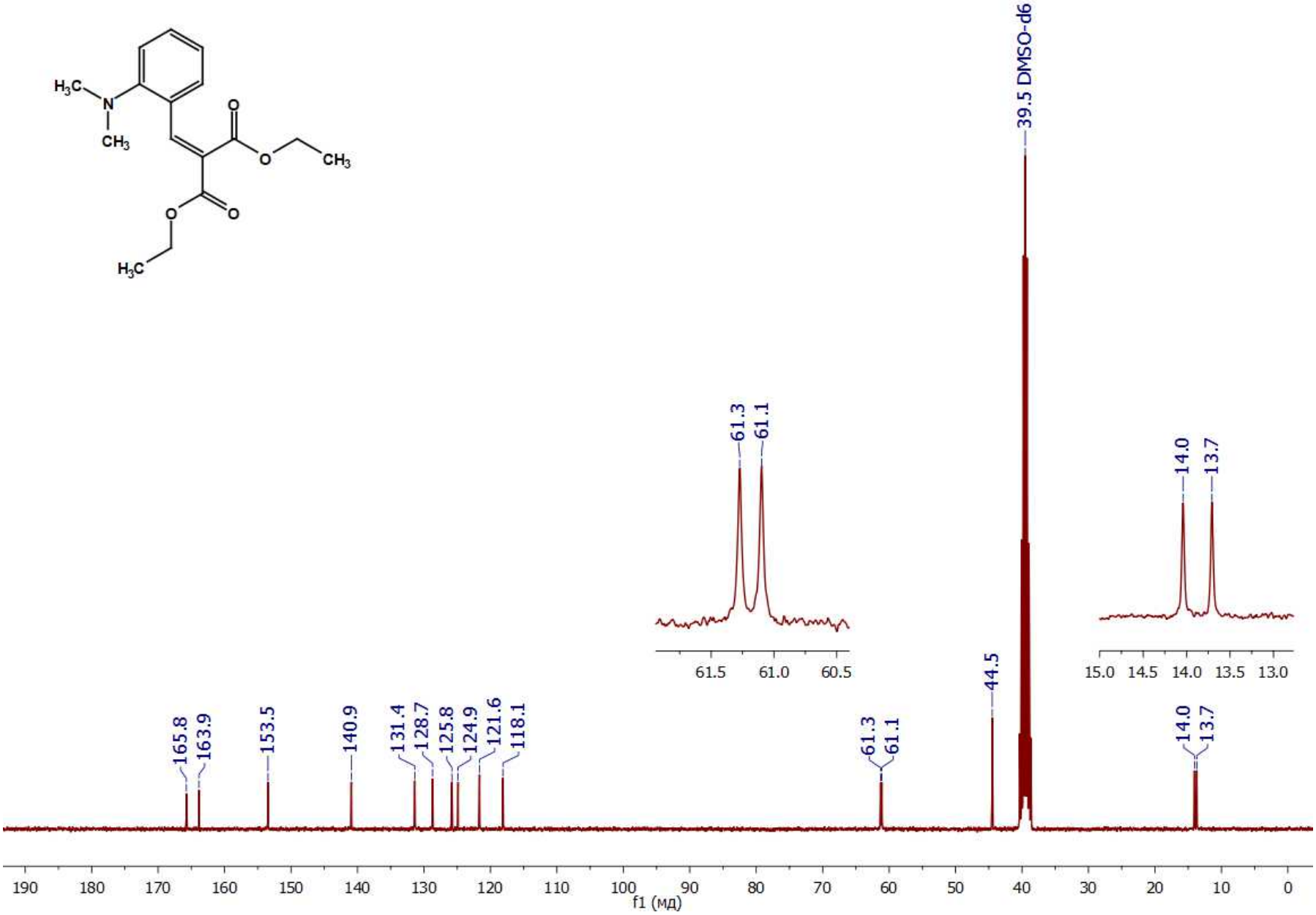
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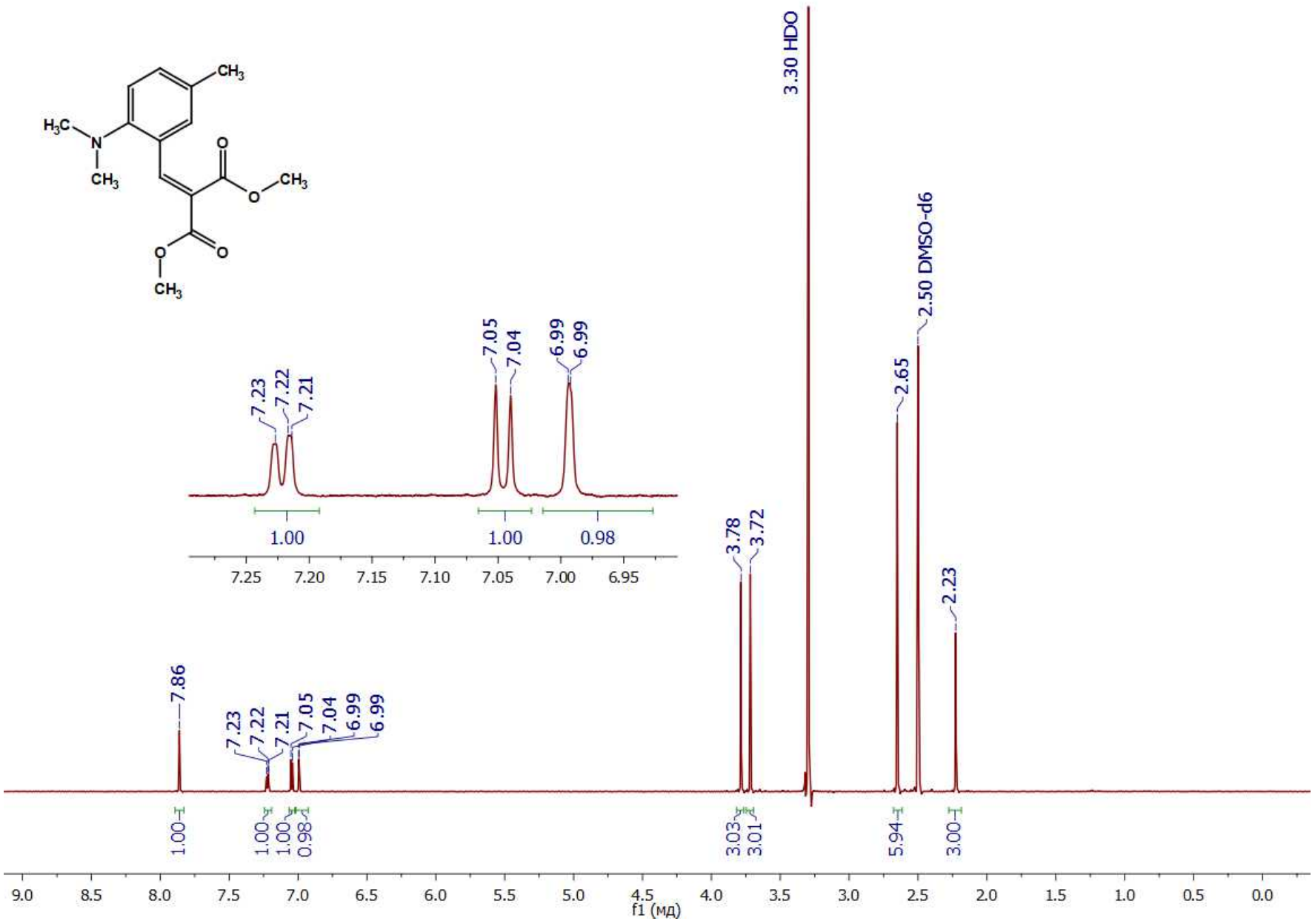
61.1
14.0
13.7
165.8
163.9
153.5
140.9
131.4
128.7
125.8
124.9
121.6
118.1
44.5
f1 (мд)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2.50 DMSO-d6
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3.78
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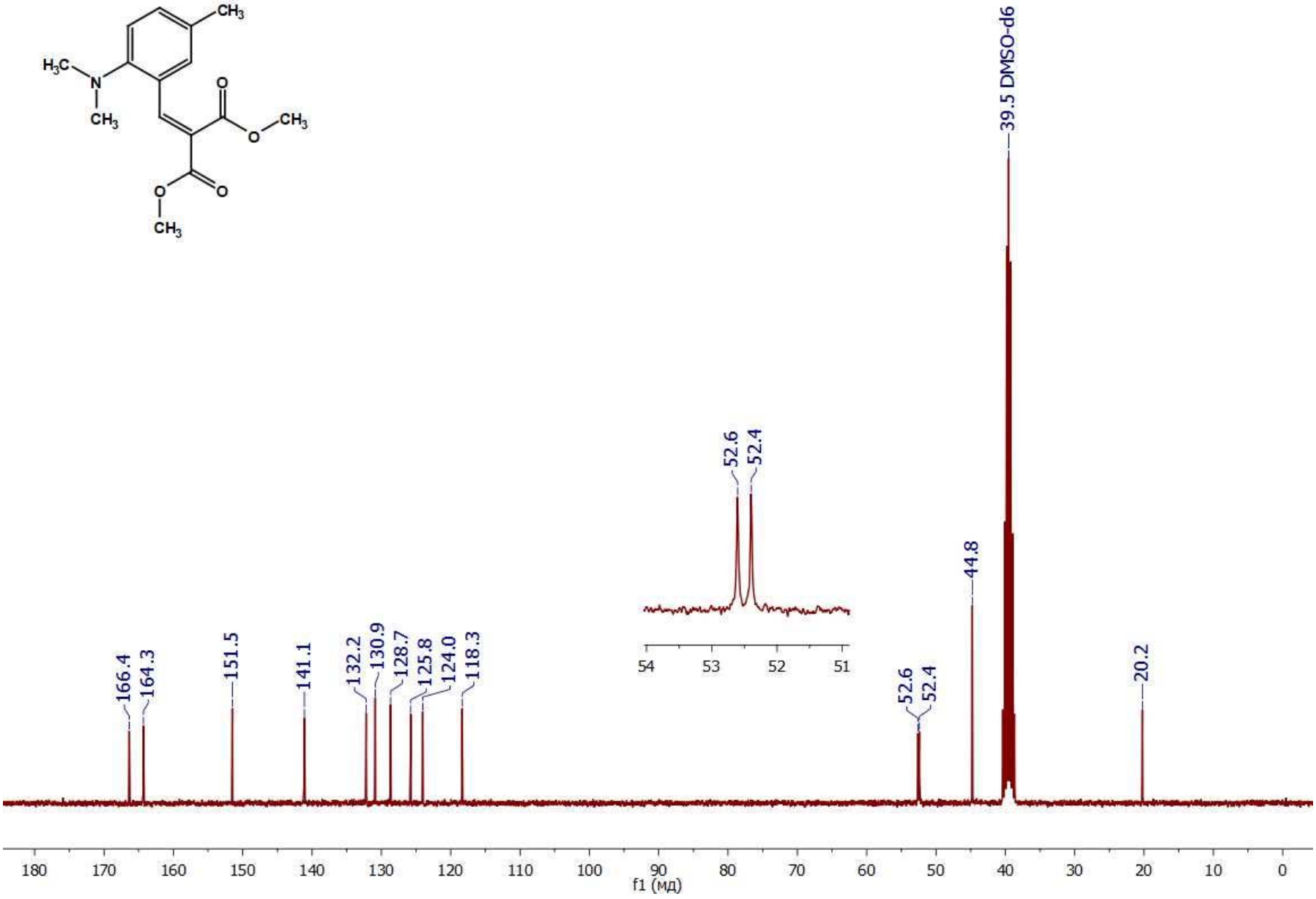
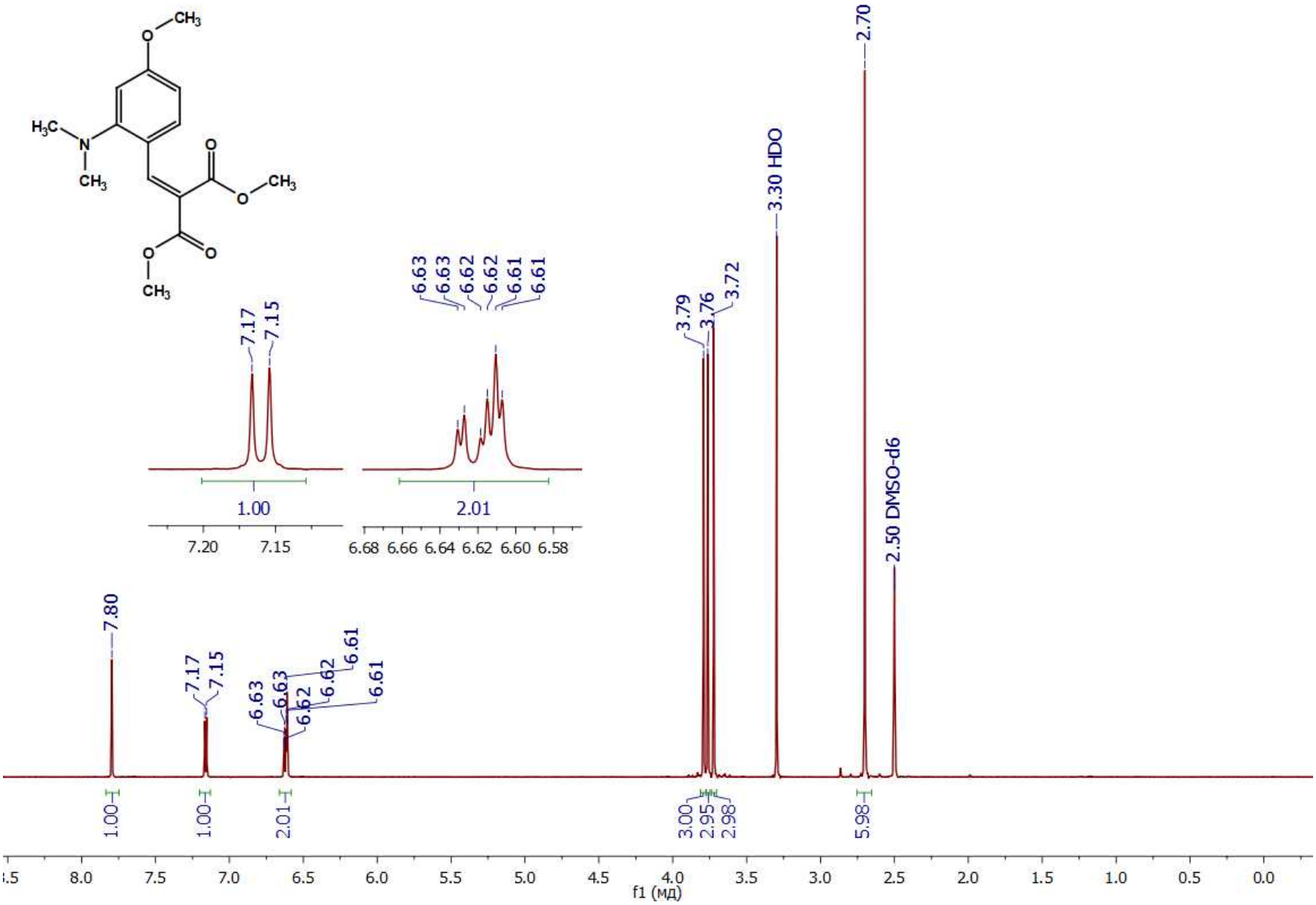
7.86
7.23
7.22
7.21
7.05
7.04
6.99
6.99
1.00
1.00
1.00
0.98
3.03
3.01
5.94
3.00
f1 (мд)


H3C
N
CH3
CH3
O
O
CH3
O
O
CH3
39.5 DMSO-d6
52.6
52.4
44.8
166.4
164.3
151.5
141.1
132.2
130.9
128.7
125.8
124.0
118.3
52.6
52.4
20.2
54
53
52
51
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)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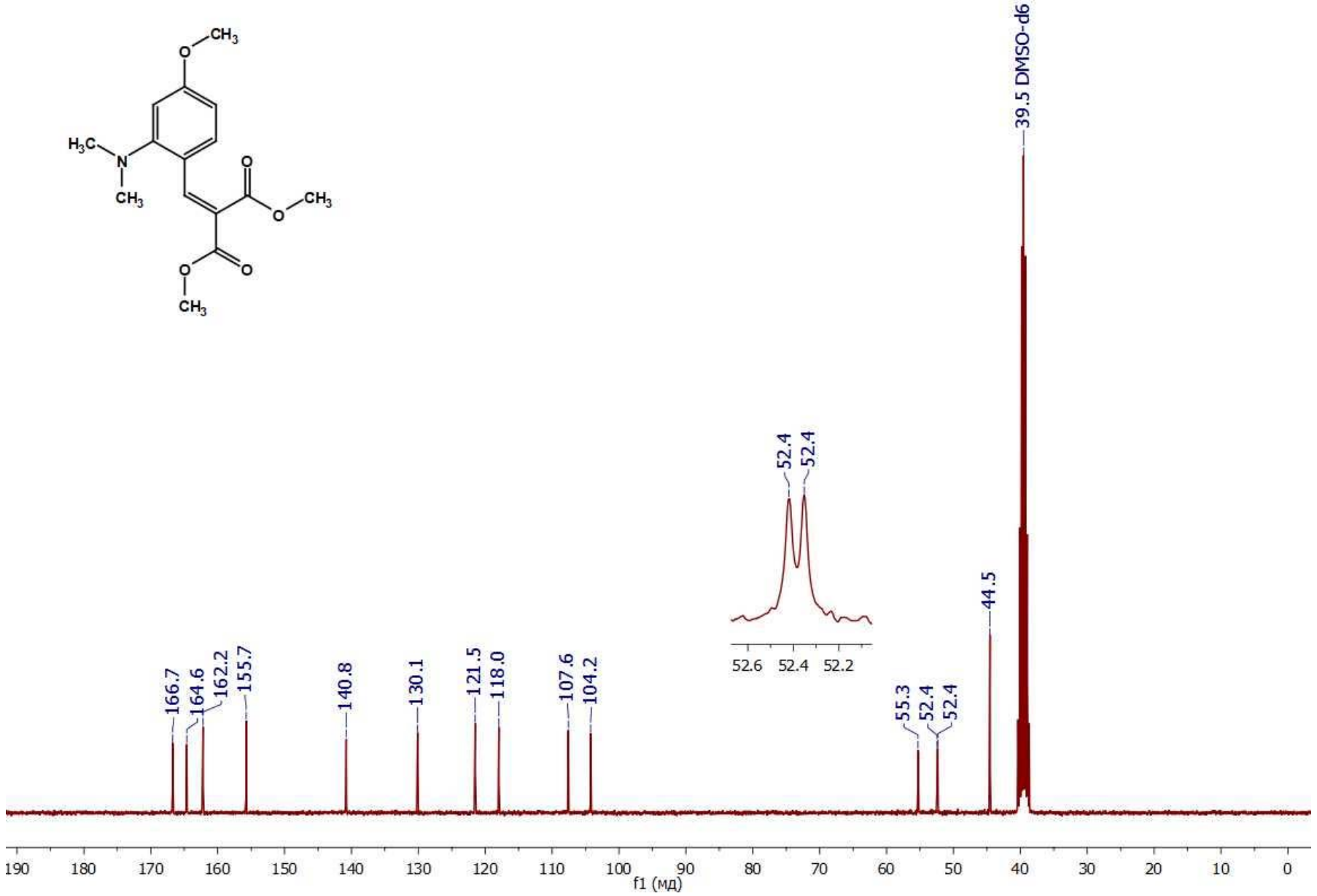
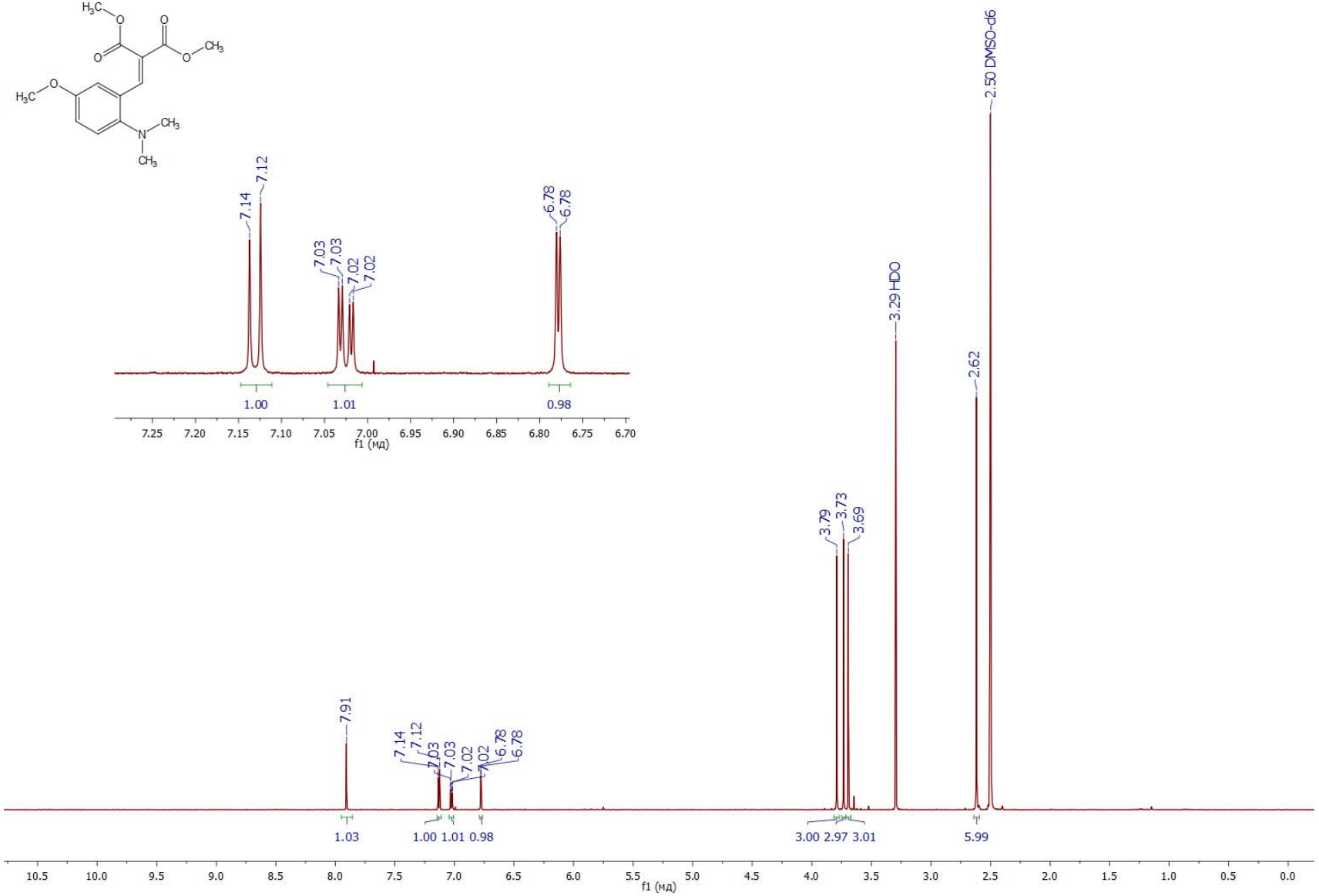
7.17
7.15
6.63
6.63
6.62
6.62
6.61
6.61
3.79
3.76
3.72
3.30 HDO
2.70
2.50 DMSO-d6
1.00
2.01
1.00
2.01
3.00
2.95
2.98
5.98
f1 (мд)


39.5 DMSO-d6
166.7
164.6
162.2
155.7
140.8
130.1
121.5
118.0
107.6
104.2
55.3
52.4
52.4
44.5
52.4
52.4
52.6 52.4 52.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)


H3C
O
O
O
O
CH3
H3C
O
N
CH3
CH3
7.14
7.12
7.03
7.03
7.02
7.02
6.78
6.78
1.00
1.01
0.98
7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (мд)
2.50 DMSO-d6
3.29 HDO
2.62
3.79
3.73
3.69
7.91
7.14
7.12
7.03
7.03
7.02
7.02
6.78
6.78
1.03
1.00 1.01 0.98
3.00 2.97 3.01
5.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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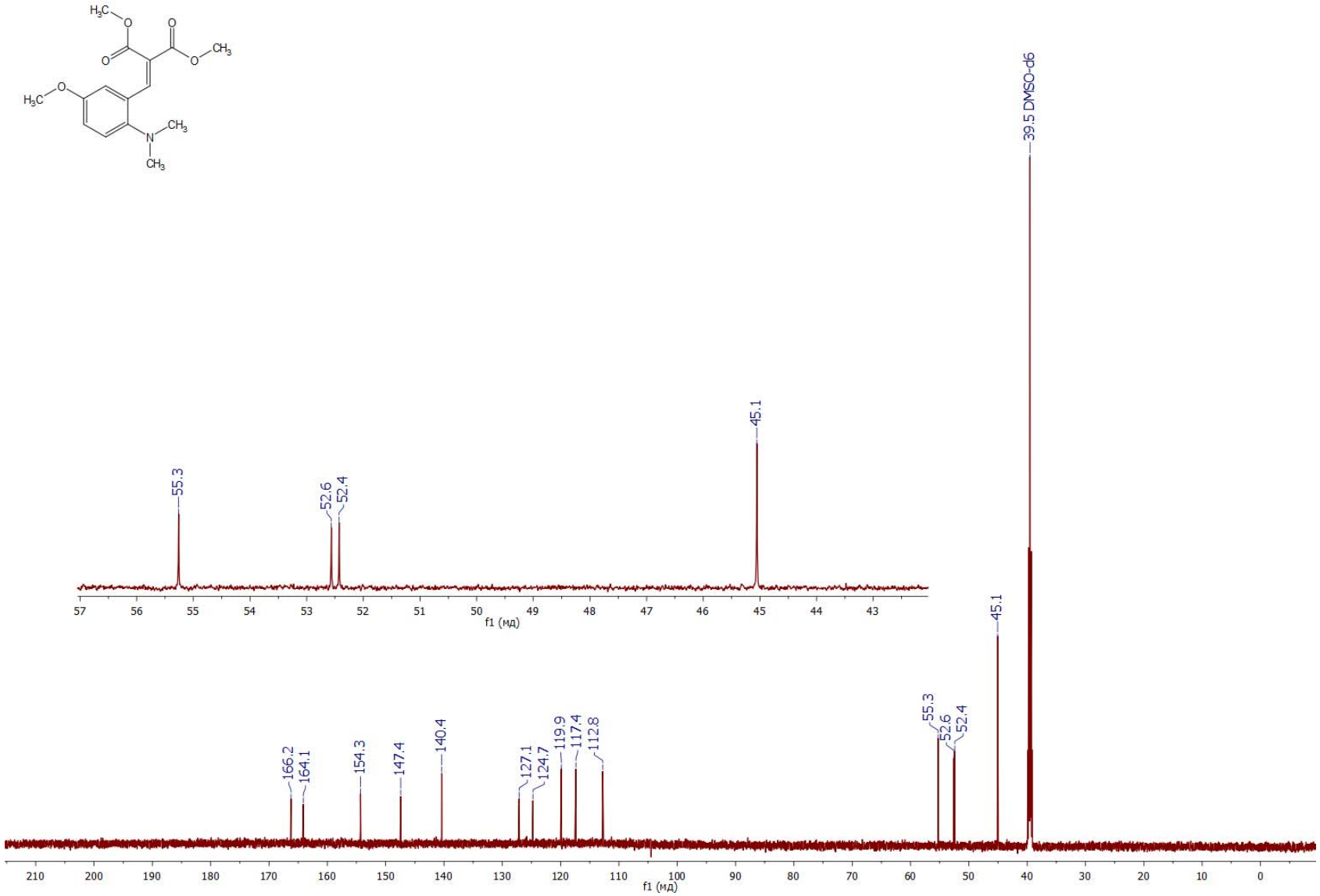
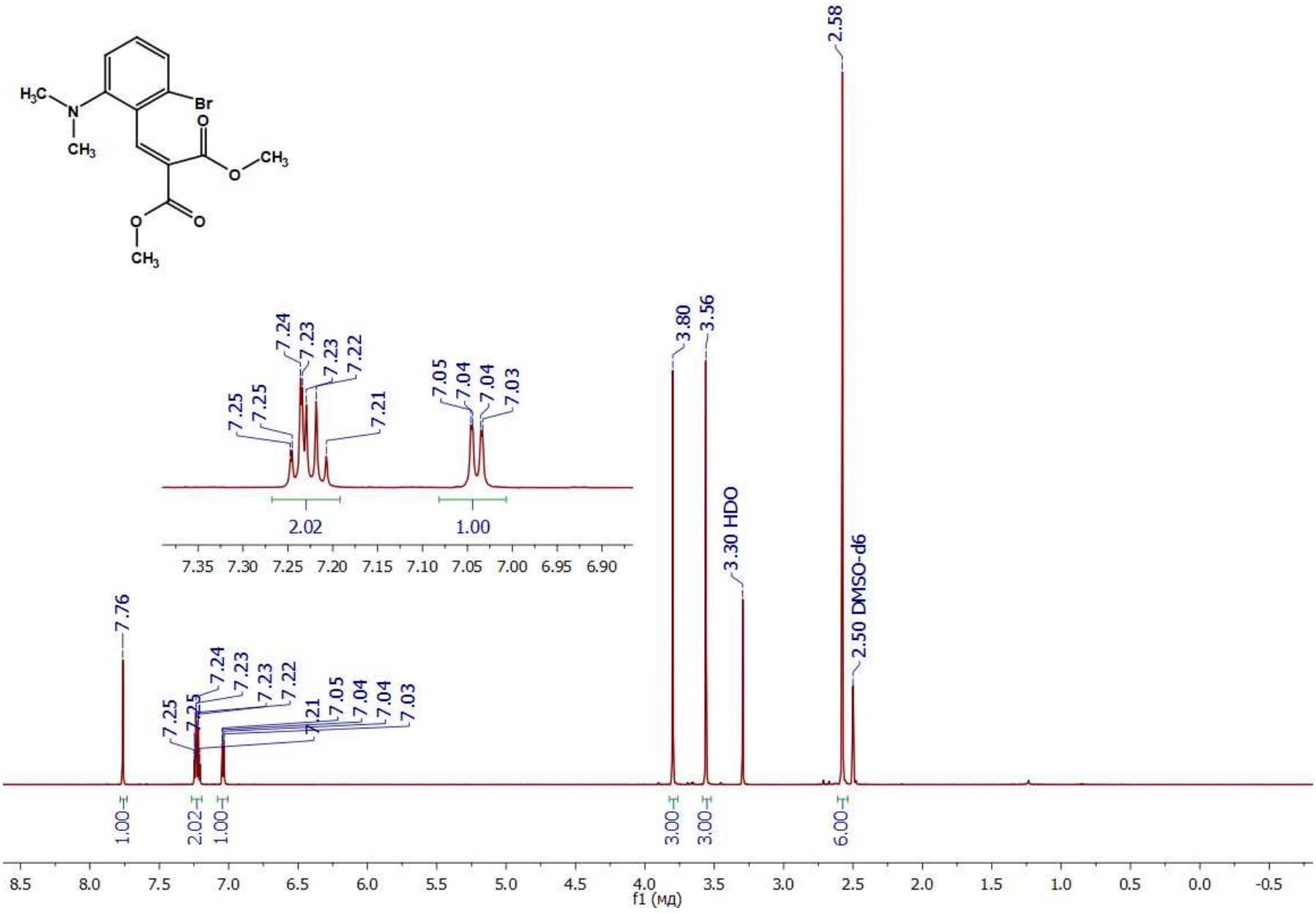


* The inverted peak at 105 ppm is an artifact at exact center of spectrum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O
CH3
O
O
O
CH3
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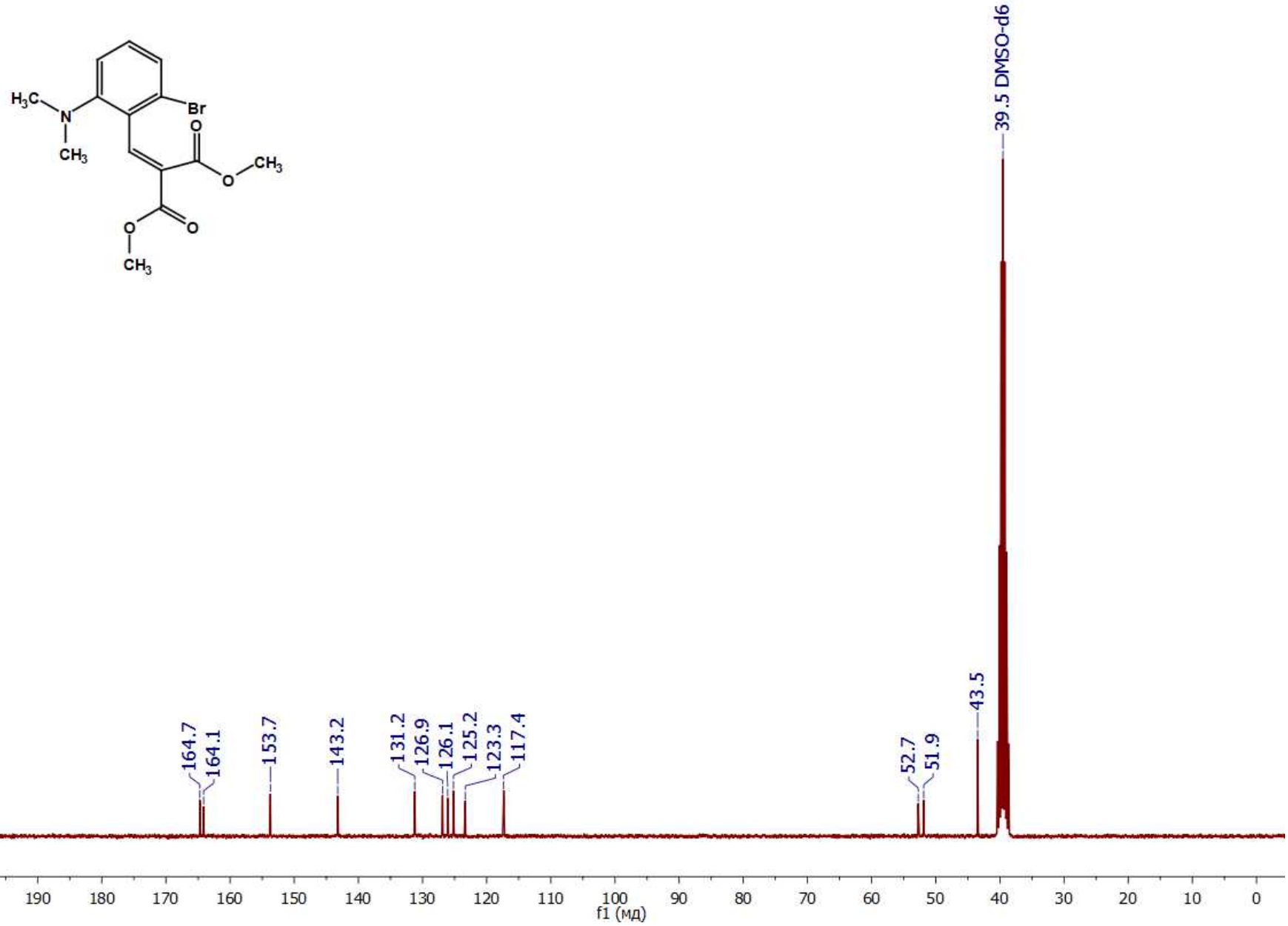
7.24
7.23
7.23
7.22
7.25
7.25
7.21
7.05
7.04
7.04
7.03
3.80
3.56
2.02
1.00
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
7.76
3.30 HDO
2.50 DMSO-d6
1.00
2.02
1.00
3.00
3.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (мд)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CH3
Br
O
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O
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O
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39.5 DMSO-d6
164.7
164.1
153.7
143.2
131.2
126.9
126.1
125.2
123.3
117.4
52.7
51.9
43.5
200
190
180
170
160
150
140
130
120
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100
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80
70
60
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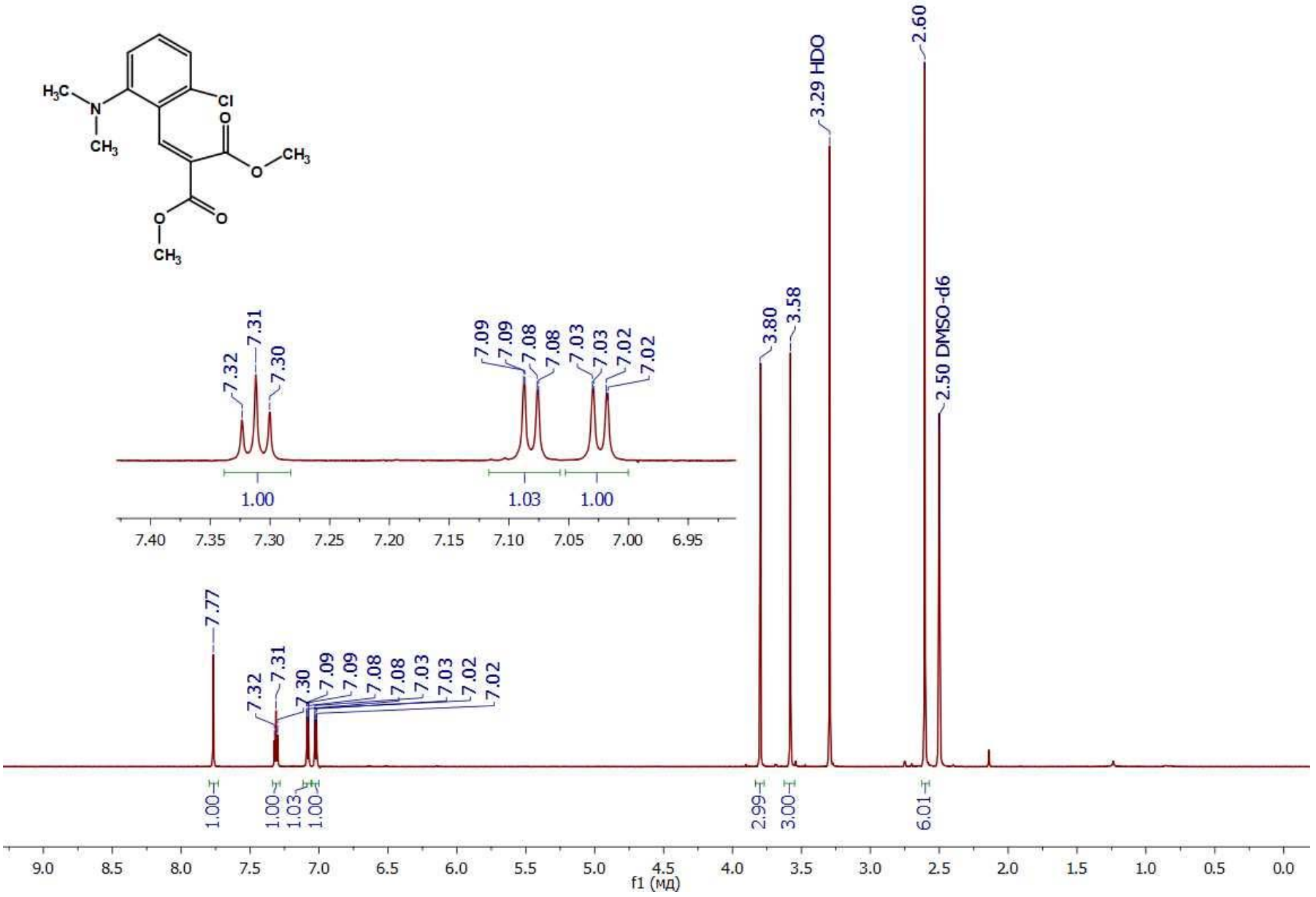
40
30
20
10
0
f1 (мд)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7.08
7.03
7.03
7.02
7.02
1.00
1.03
1.00
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
3.80
3.58
3.29 HDO
2.60
2.50 DMSO-d6
7.77
7.32
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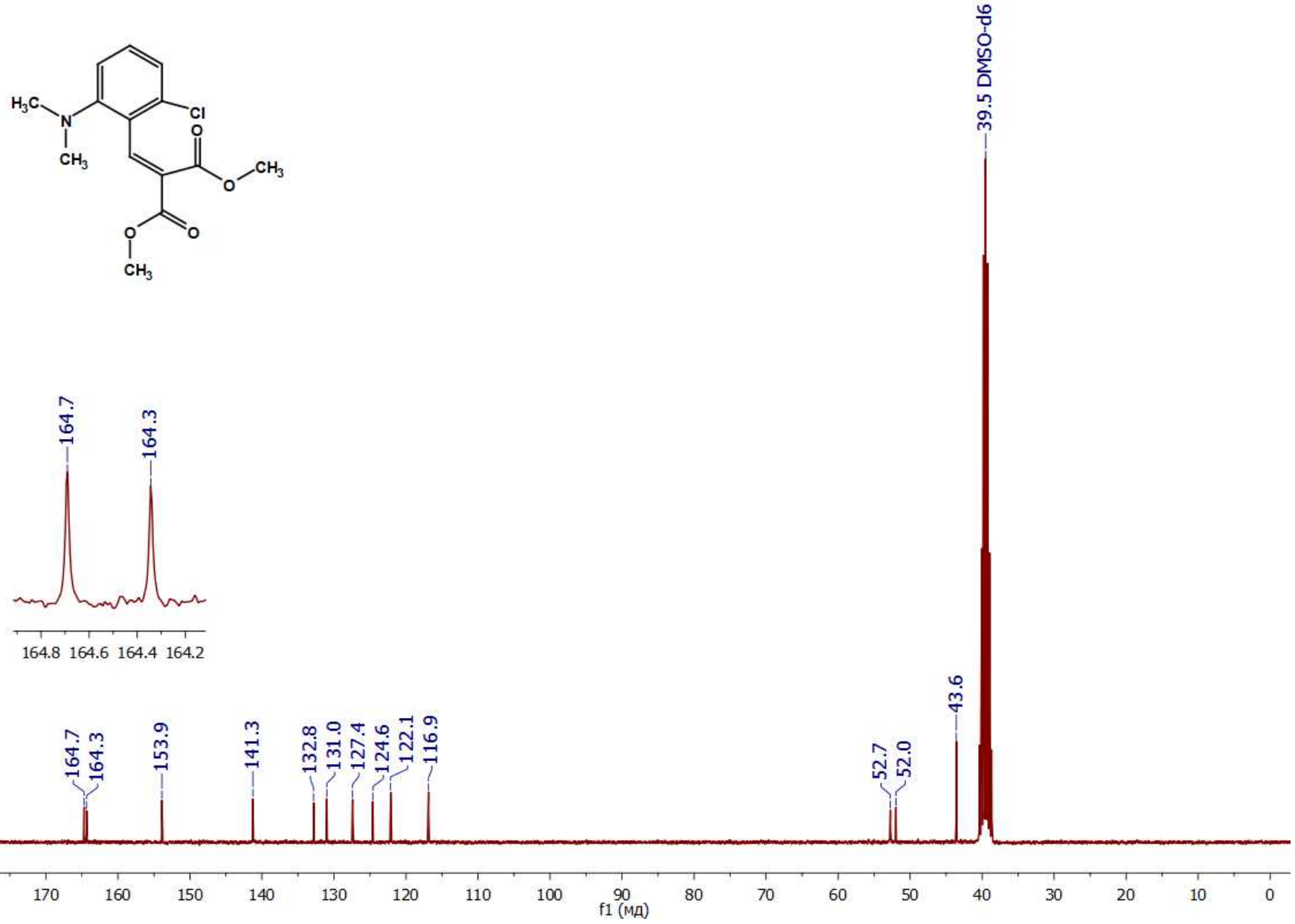
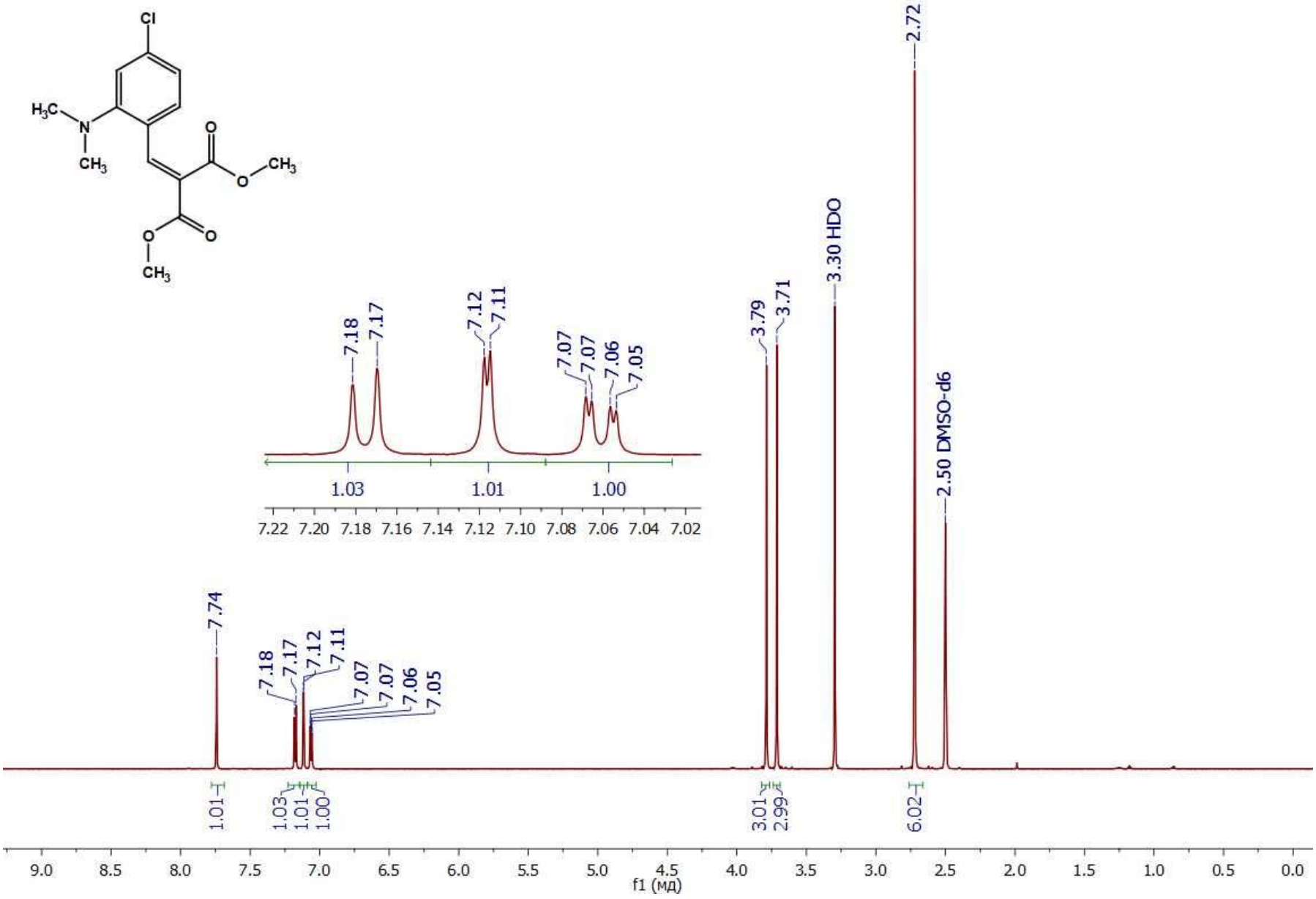
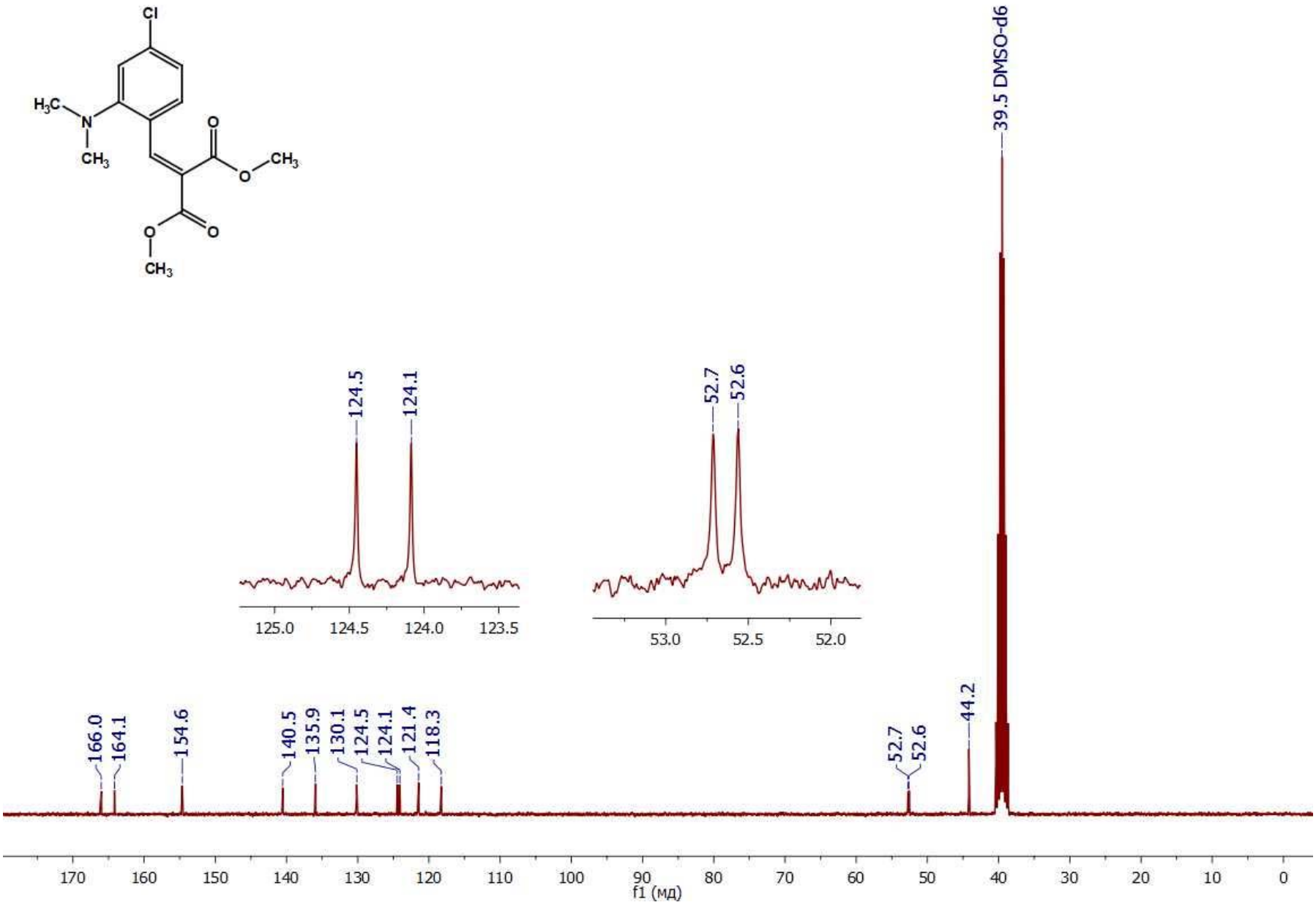
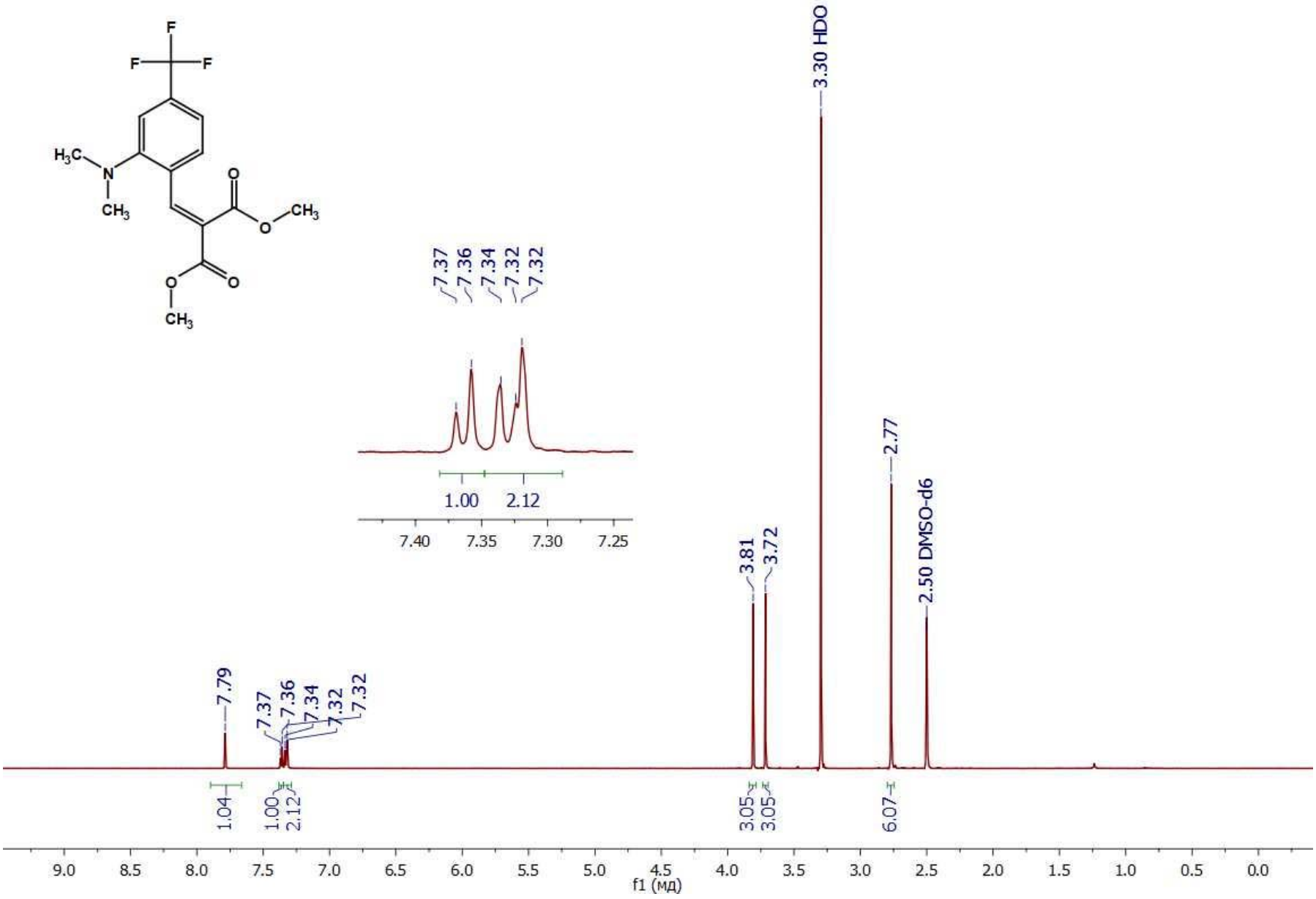
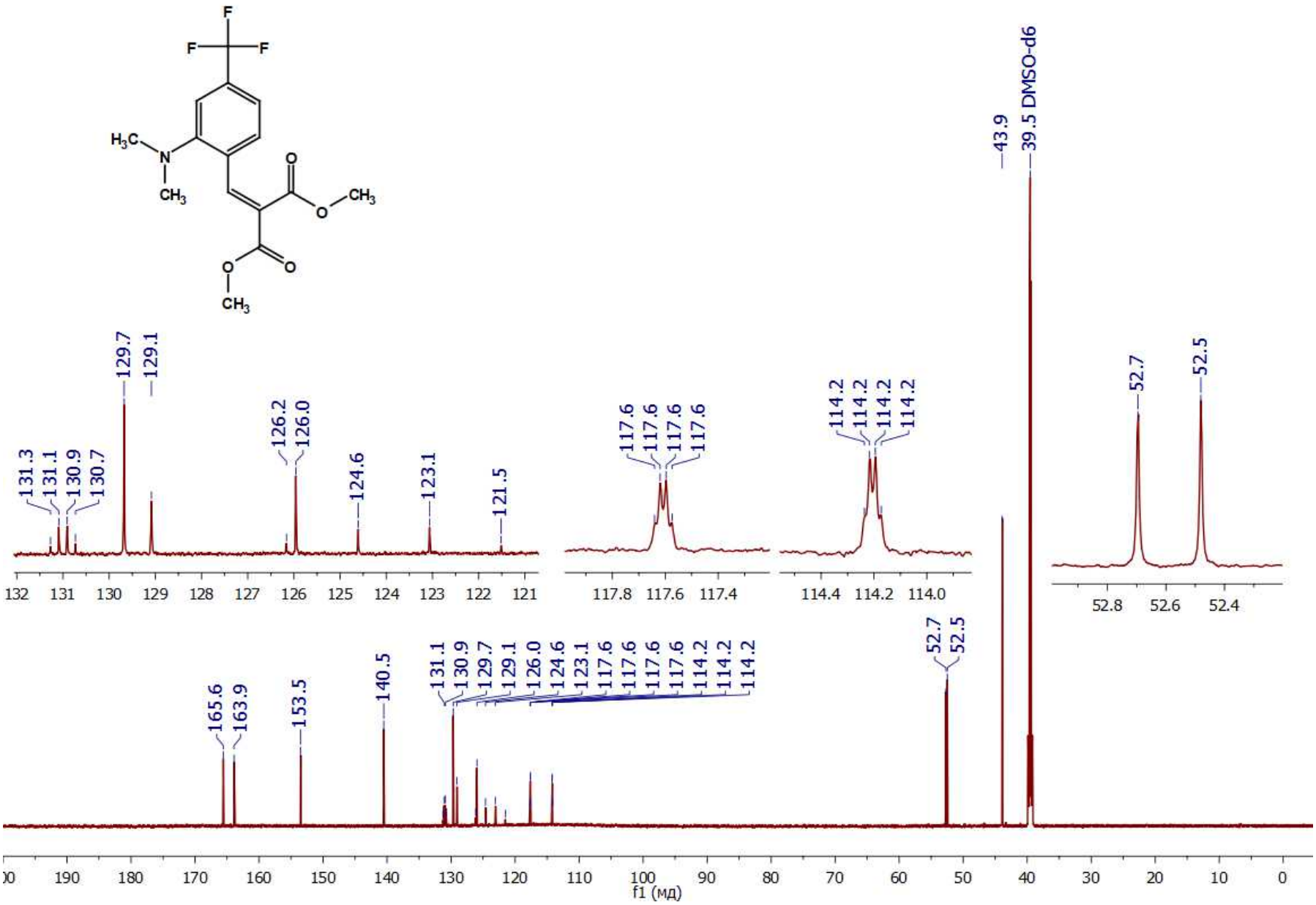
7.30
7.09
7.09
7.08
7.08
7.03
7.03
7.02
7.02
1.00
1.00
1.03
1.00
2.99
3.00
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

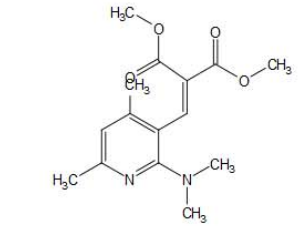

H3C
N
CH3
Cl
O
O
CH3
O
O
CH3
164.7
164.3
164.8 164.6 164.4 164.2
39.5 DMSO-d6
164.7
164.3
153.9
141.3
132.8
131.0
127.4
124.6
122.1
116.9
52.7
52.0
43.6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

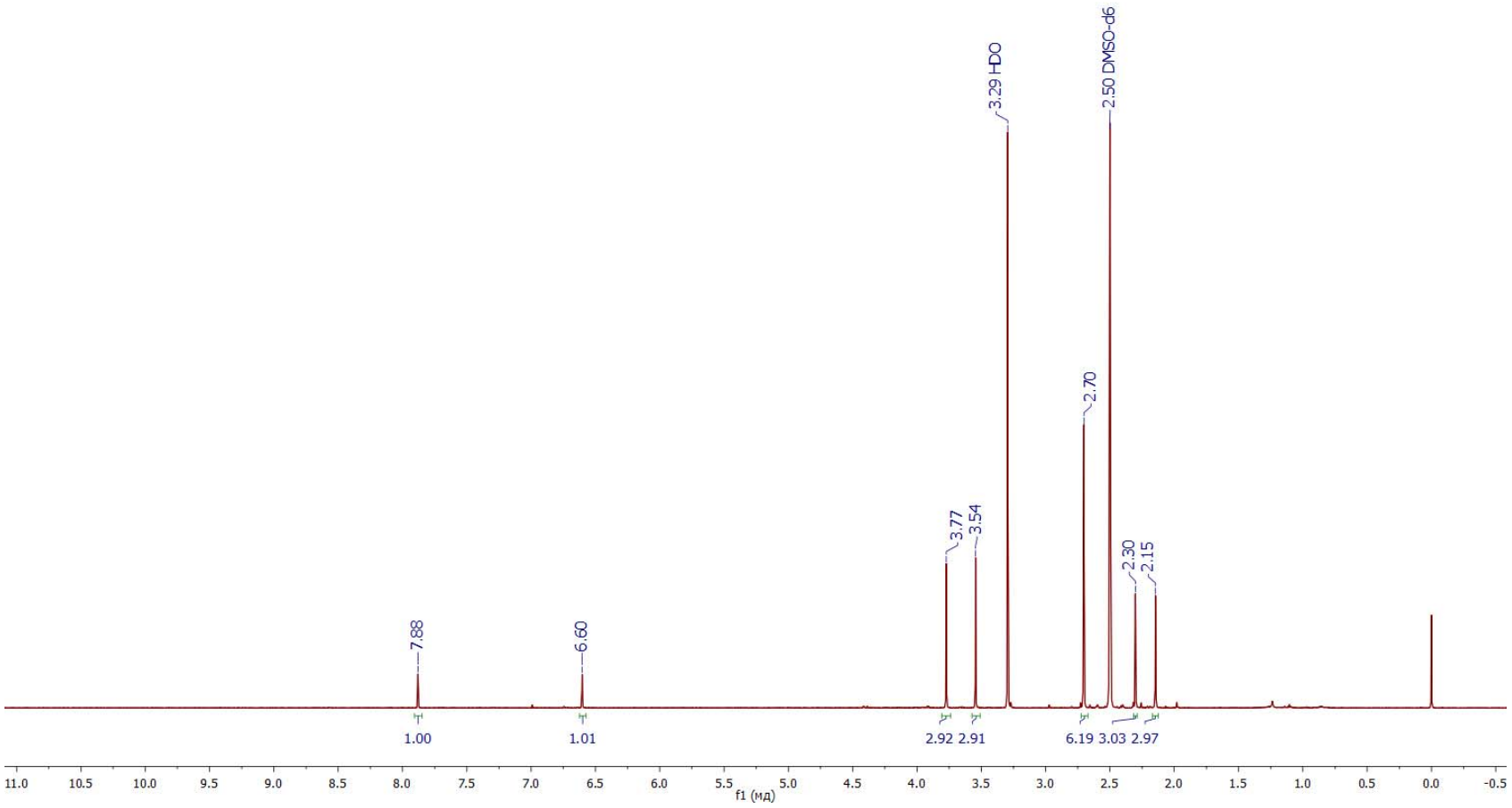

Cl
H3C
N
CH3
O
O
CH3
O
O
O
CH3
7.74
7.18
7.17
7.12
7.11
7.07
7.07
7.06
7.05
3.79
3.71
3.30 HDO
2.72
2.50 DMSO-d6
1.01
1.03
1.01
1.00
3.01
2.99
6.02
f1 (мд)

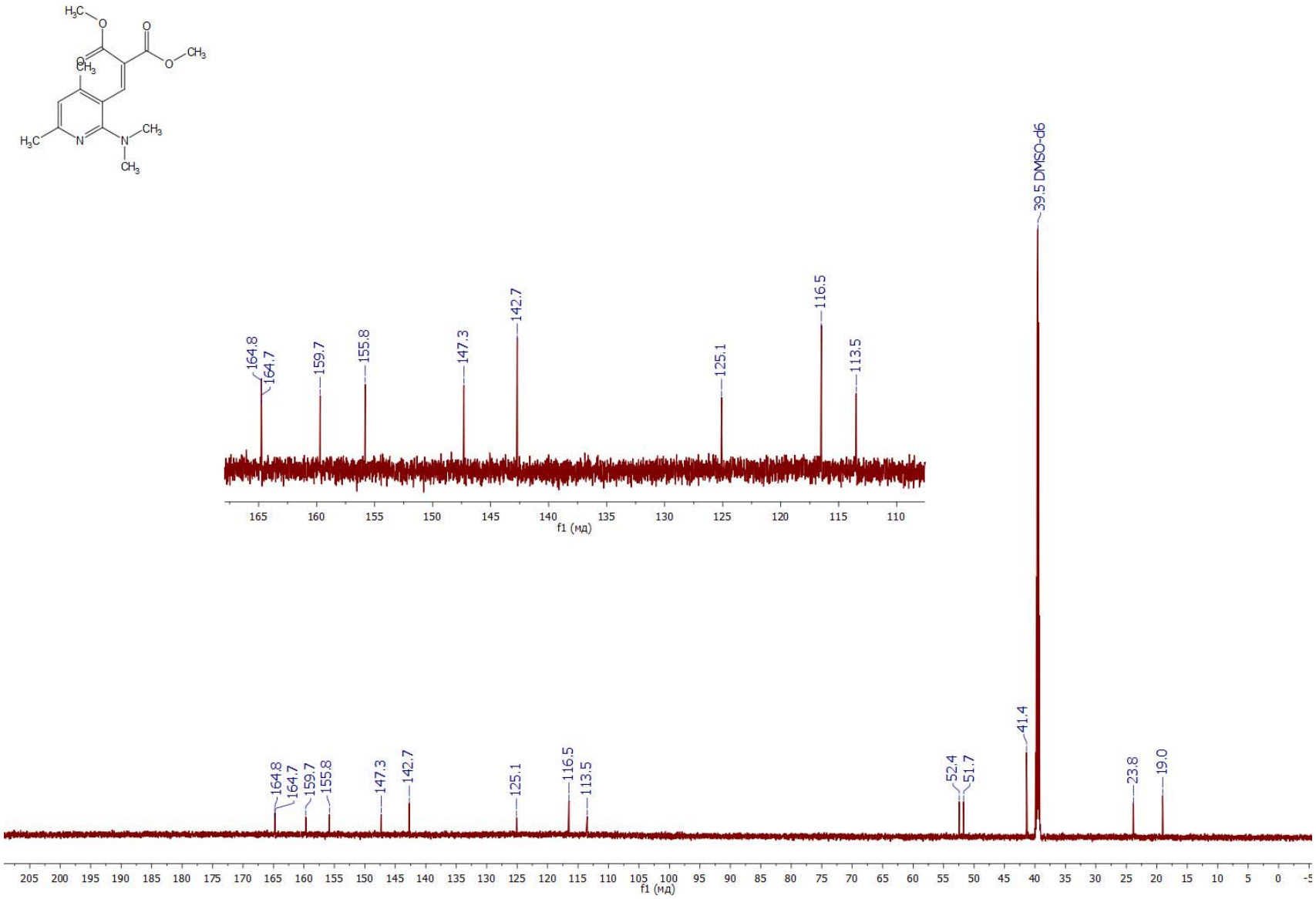

Cl
H3C
N
CH3
O
O
CH3
O
O
O
CH3
39.5 DMSO-d6
124.5
124.1
52.7
52.6
125.0
124.5
124.0
123.5
53.0
52.5
52.0
166.0
164.1
154.6
140.5
135.9
130.1
124.5
124.1
121.4
118.3
52.7
52.6
44.2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

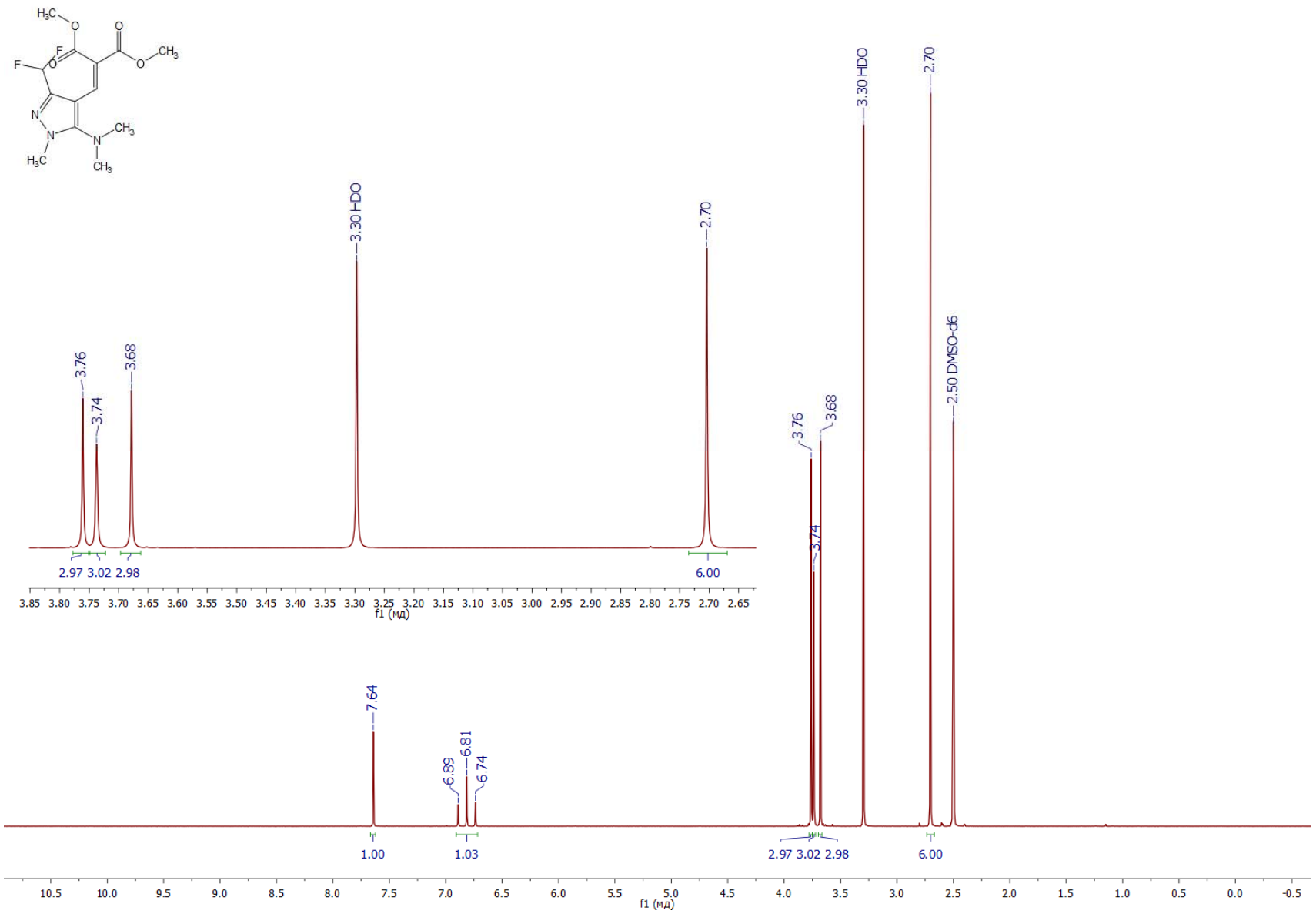

F
F
F
H3C
N
CH3
O
O
CH3
O
O
CH3
7.37
7.36
7.34
7.32
7.32
1.00
2.12
7.40
7.35
7.30
7.25
3.30 HDO
2.77
2.50 DMSO-d6
3.81
3.72
7.79
7.37
7.36
7.34
7.32
7.32
1.04
1.00
2.12
3.05
3.05
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

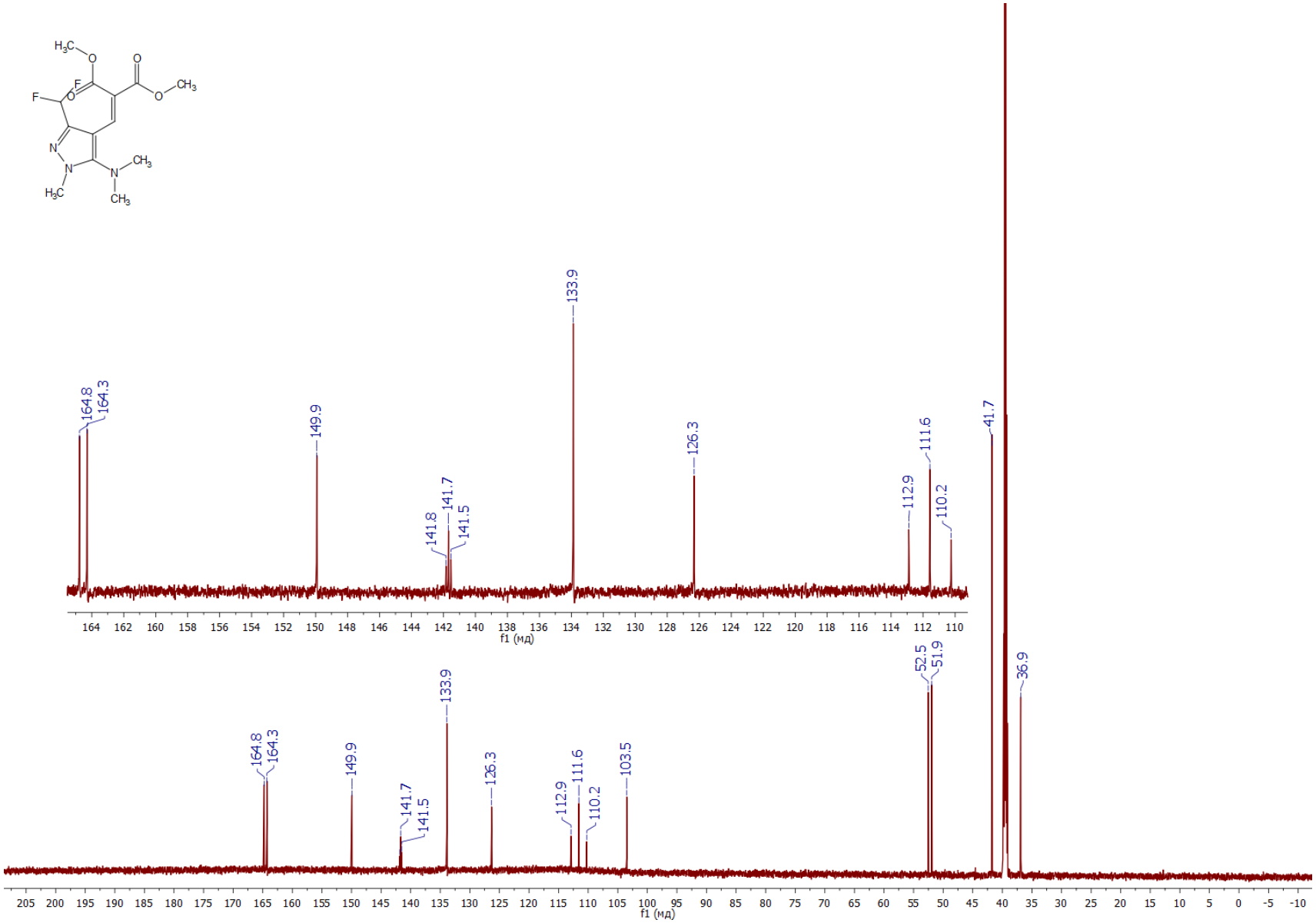

F
F
F
H3C
N
CH3
CH3
O
O
O
O
CH3
43.9
39.5 DMSO-d6
129.7
129.1
131.3
131.1
130.9
130.7
126.2
126.0
124.6
123.1
121.5
117.6
117.6
117.6
117.6
114.2
114.2
114.2
114.2
52.7
52.5
165.6
163.9
153.5
140.5
131.1
130.9
129.7
129.1
126.0
124.6
123.1
117.6
117.6
117.6
117.6
114.2
114.2
114.2
52.7
52.5
f1 (мд)

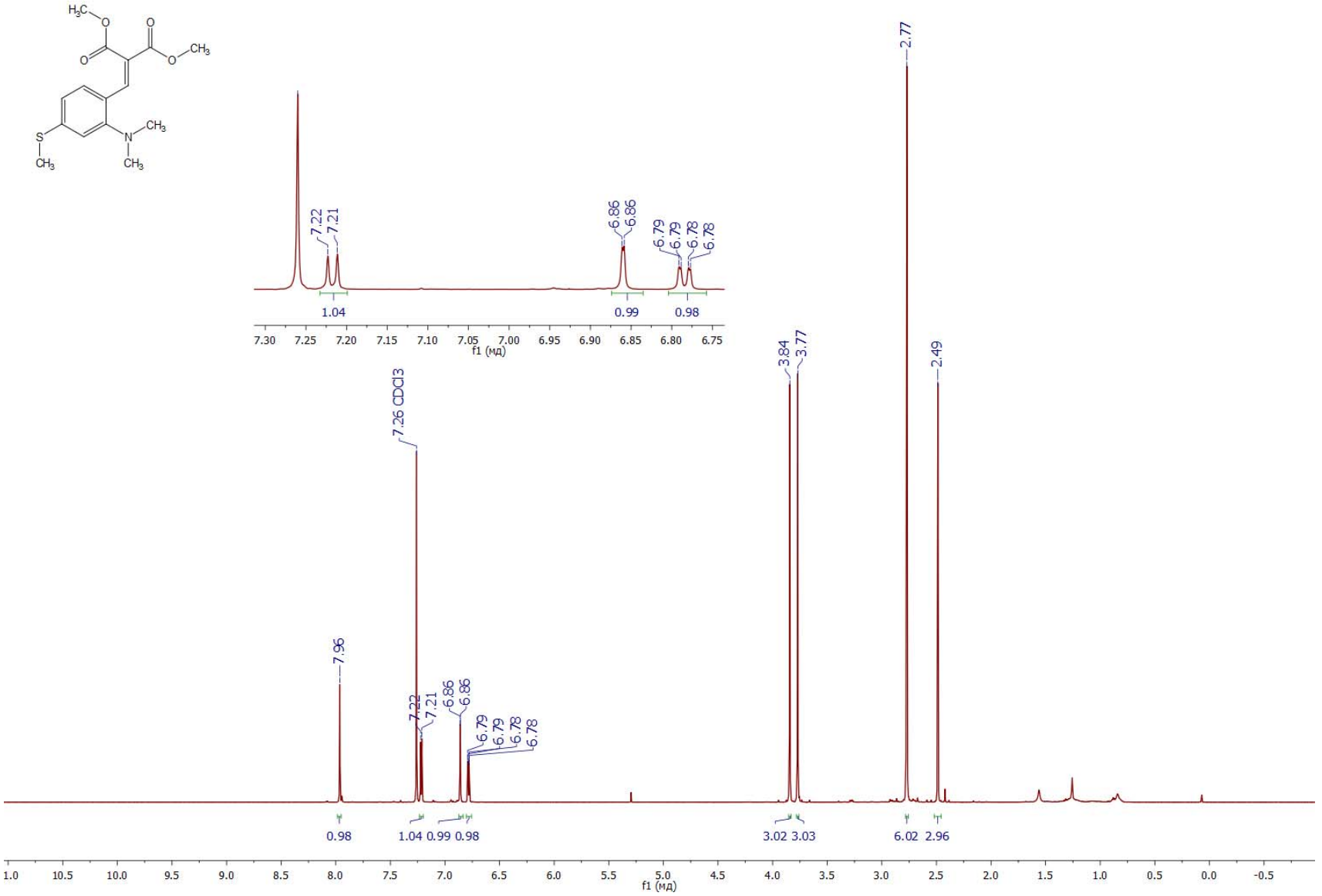


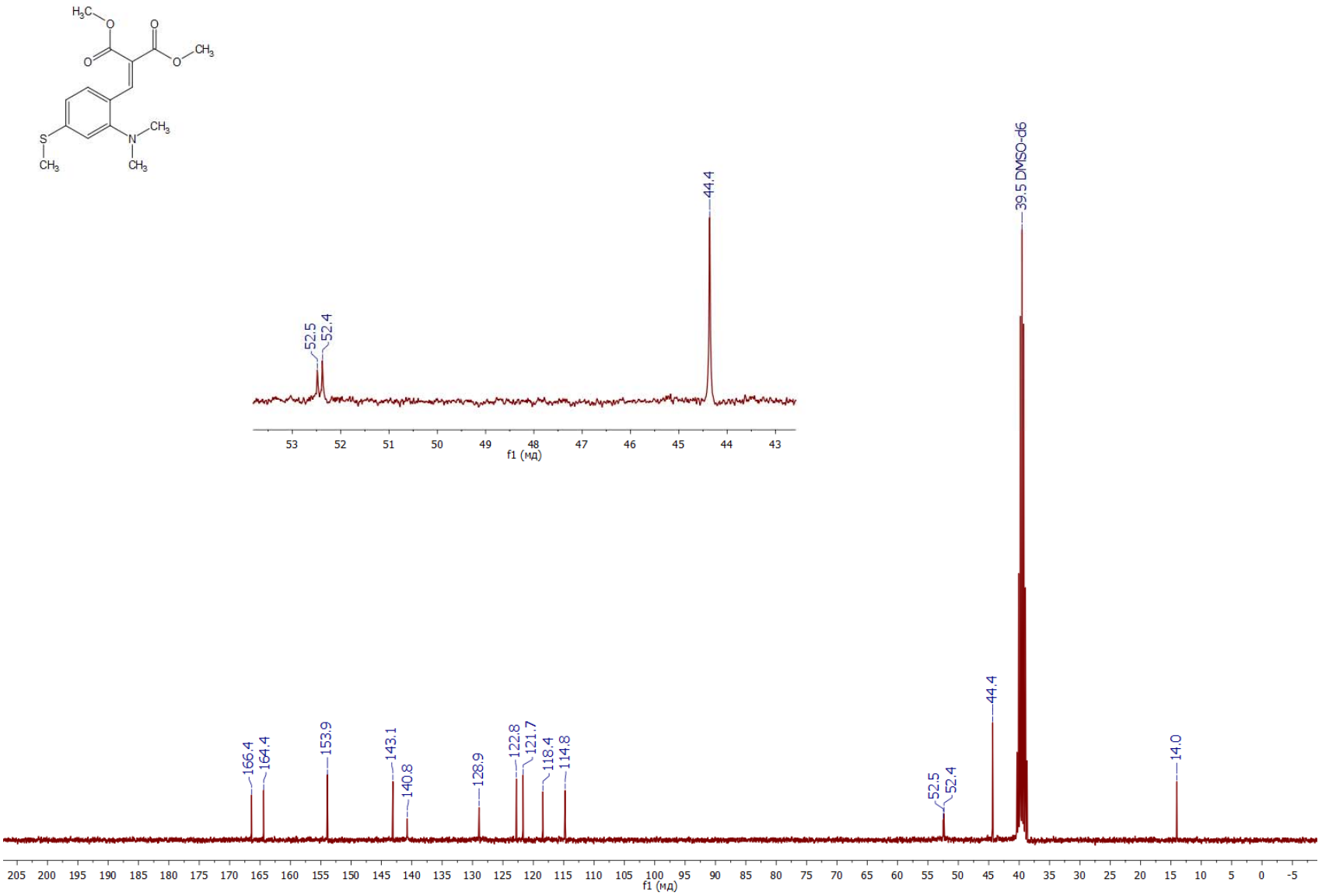

7.88
6.60
3.77
3.54
3.29 HDO
2.70
2.50 DMSO-d6
2.30
2.15
1.00
1.01
2.92 2.91
6.19 3.03 2.97
f1 (мд)

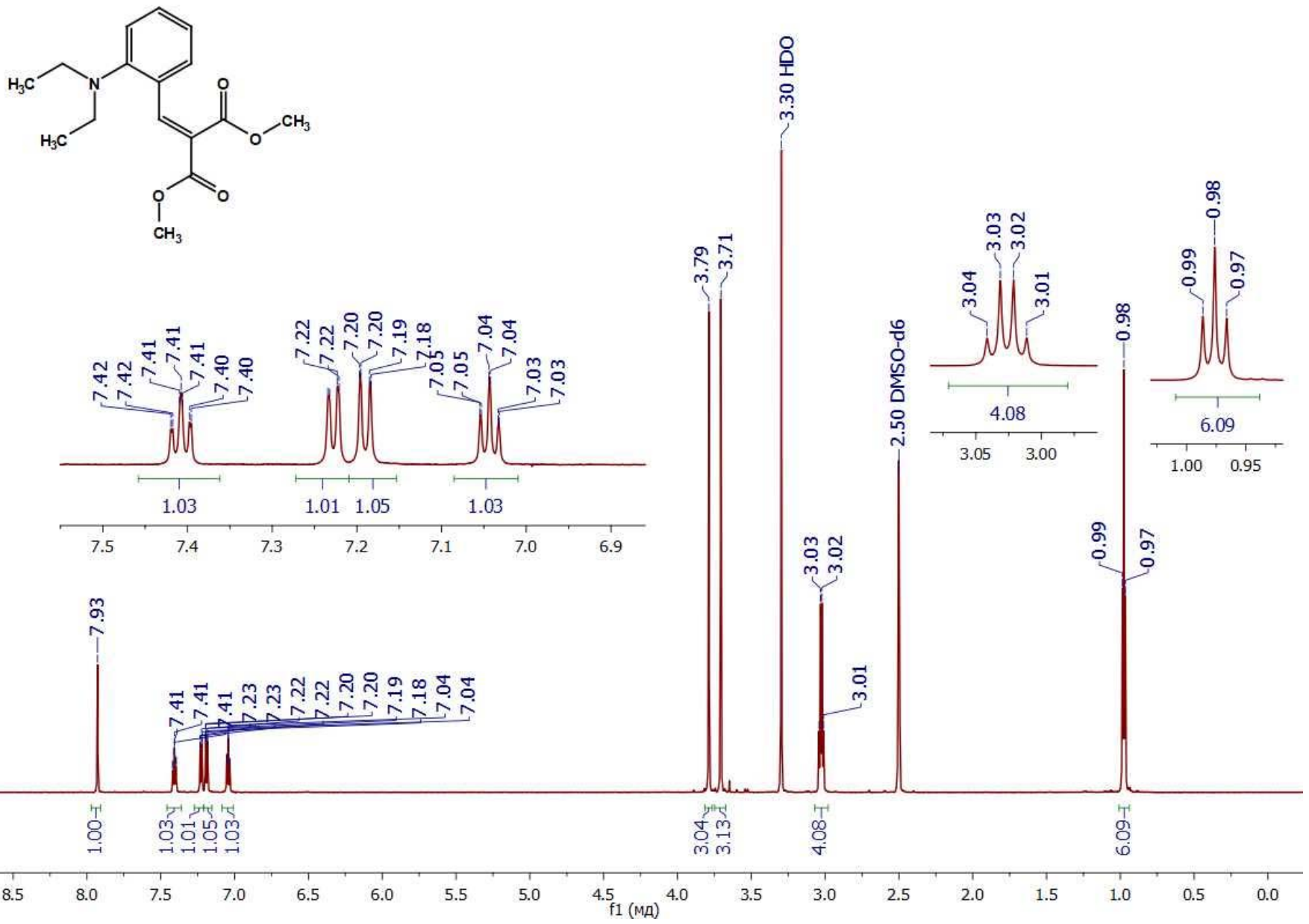

164.8
164.7
159.7
155.8
147.3
142.7
125.1
116.5
113.5
39.5 DMSO-d6
52.4
51.7
41.4
23.8
19.0
f1 (мд)

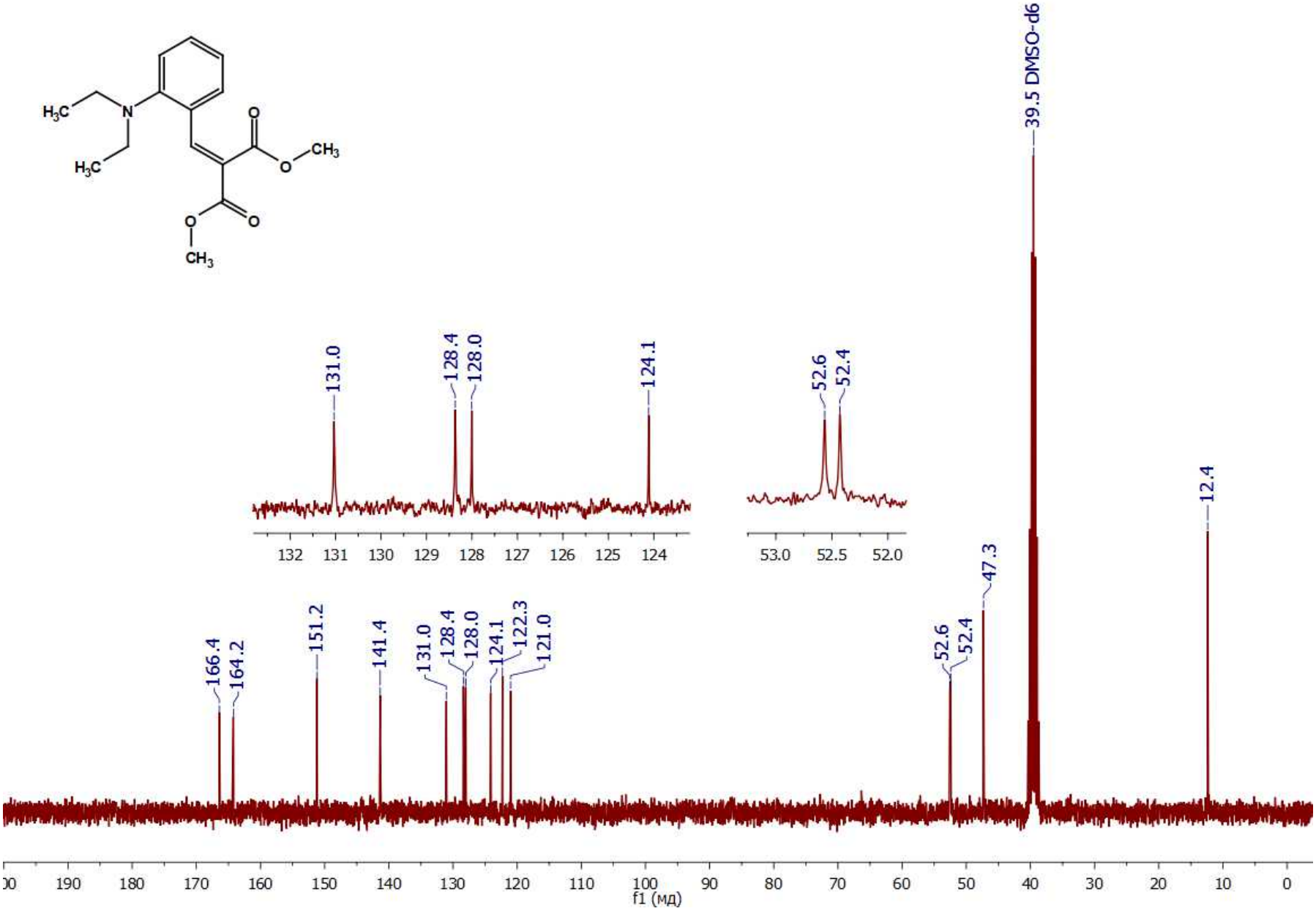

3.30 HDO
2.70
3.76
3.74
3.68
2.97 3.02 2.98
6.00
f1 (мд)
7.64
6.89
6.81
6.74
1.00
1.03
2.50 DMSO-d6

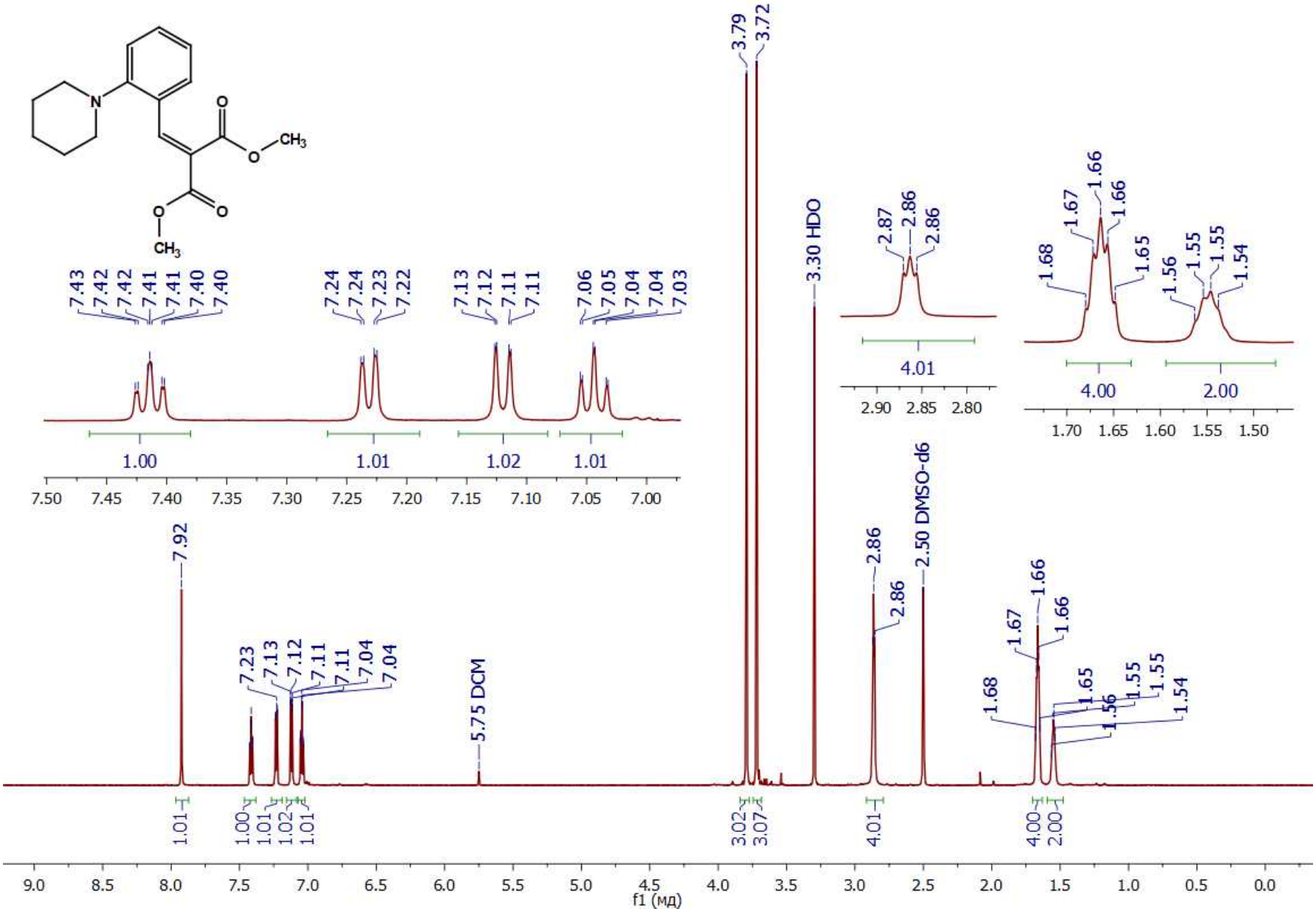

H3C
O
O
F
F
O
O
CH3
N
N
H3C
N
CH3
CH3
164.8
164.3
149.9
141.8
141.7
141.5
133.9
126.3
112.9
111.6
110.2
41.7
164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (мд)
52.5
51.9
36.9
164.8
164.3
149.9
141.7
141.5
133.9
126.3
112.9
111.6
110.2
103.5
205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (мд)

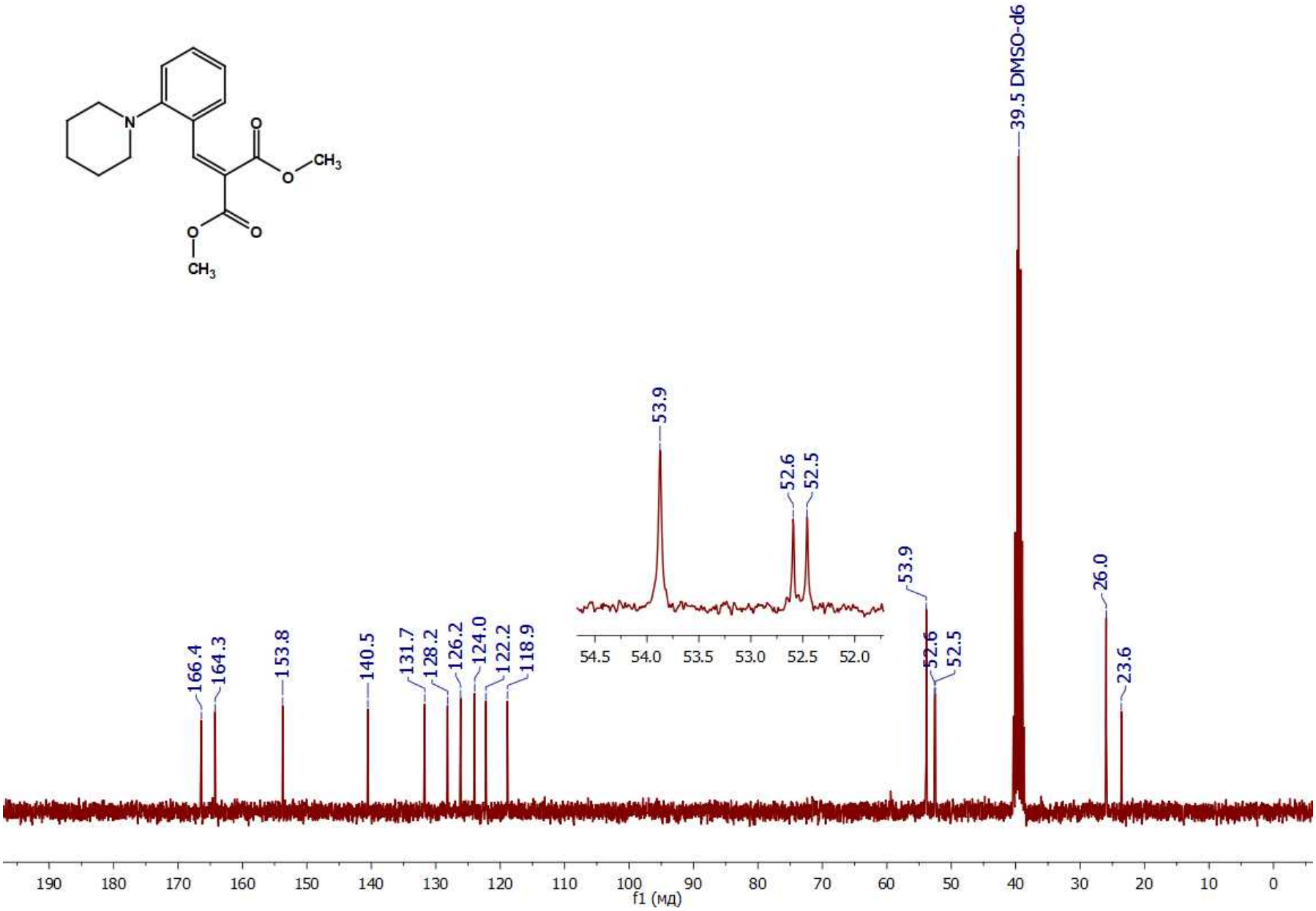

7.22
7.21
6.86
6.86
6.79
6.79
6.78
6.78
1.04
0.99
0.98
f1 (мд)
7.26 CDCl3
7.96
3.84
3.77
2.77
2.49
0.98
1.04
0.99
0.98
3.02
3.03
6.02
2.96

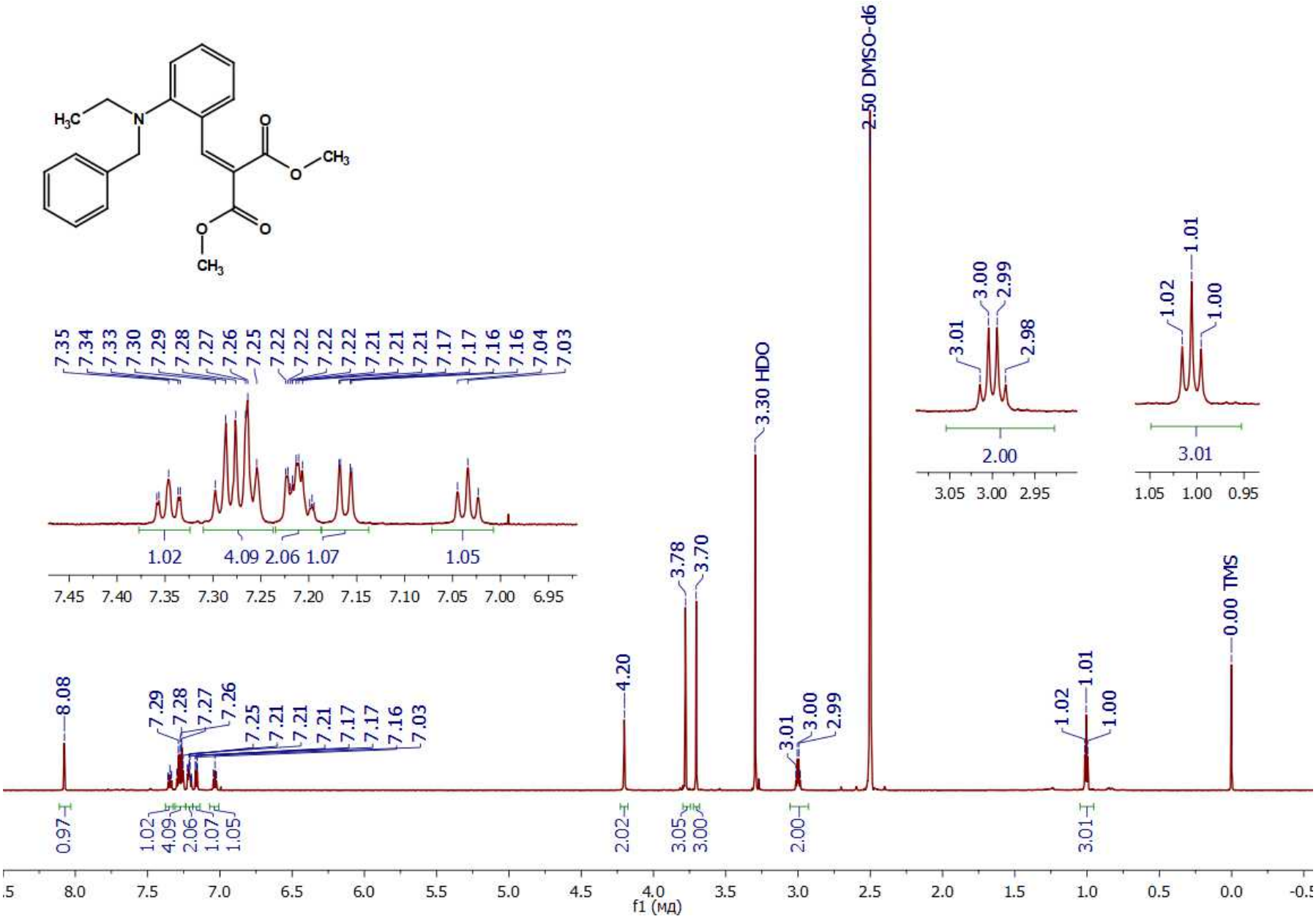

H3C
O
O
O
O
CH3
S
CH3
N
CH3
CH3
52.5
52.4
44.4
f1 (мд)
166.4
164.4
153.9
143.1
140.8
128.9
122.8
121.7
118.4
114.8
52.5
52.4
44.4
39.5 DMSO-d6
14.0
f1 (мд)

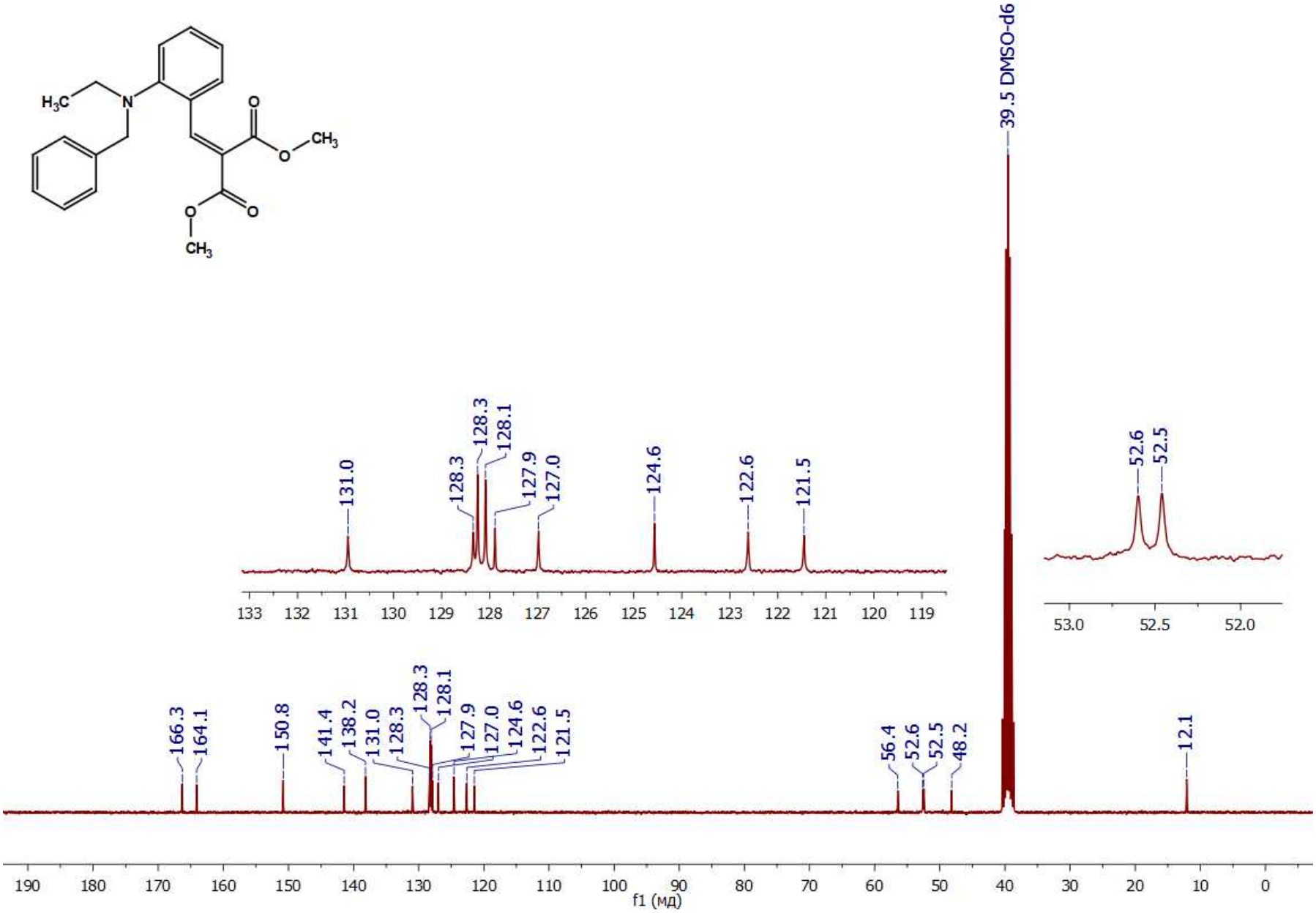

H3C
N
H3C
O
O
CH3
O
O
O
CH3
7.93
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.41
7.41
7.41
7.23
7.23
7.22
7.22
7.20
7.20
7.19
7.18
7.04
7.04
7.22
7.22
7.20
7.20
7.19
7.18
7.05
7.05
7.04
7.04
7.03
7.03
3.79
3.71
3.30 HDO
3.03
3.02
3.01
2.50 DMSO-d6
0.99
0.97
0.98
3.04
3.03
3.02
3.01
4.08
3.05
3.00
0.99
0.98
0.97
6.09
1.00
0.95
1.03
1.01
1.05
1.03
1.00
1.03
1.01
1.05
1.03
3.04
3.13
4.08
6.09
f1 (мд)

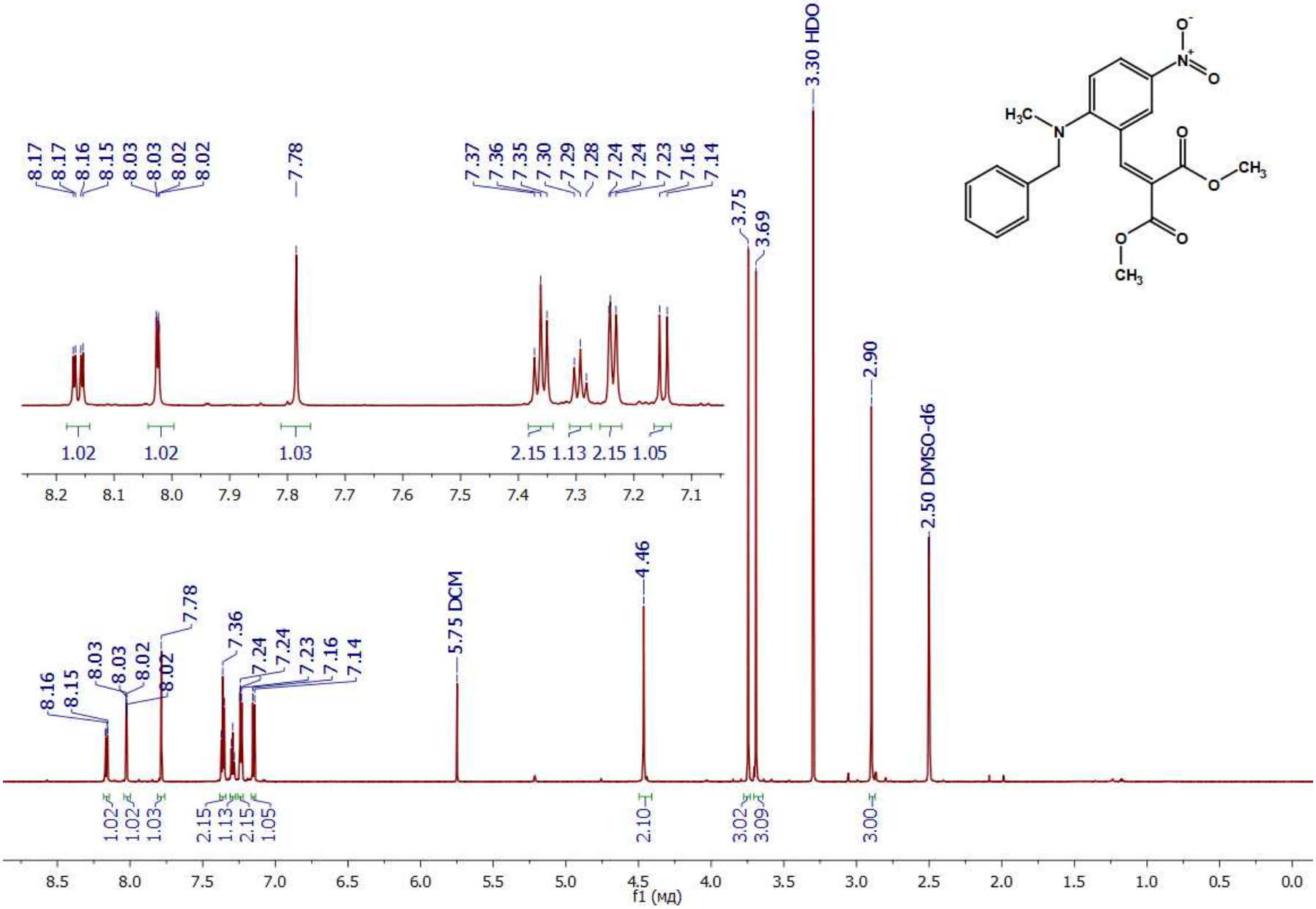

H3C
N
H3C
O
O
CH3
O
O
O
CH3
39.5 DMSO-d6
131.0
128.4
128.0
124.1
52.6
52.4
12.4
47.3
166.4
164.2
151.2
141.4
131.0
128.4
128.0
124.1
122.3
121.0
52.6
52.4
f1 (мд)

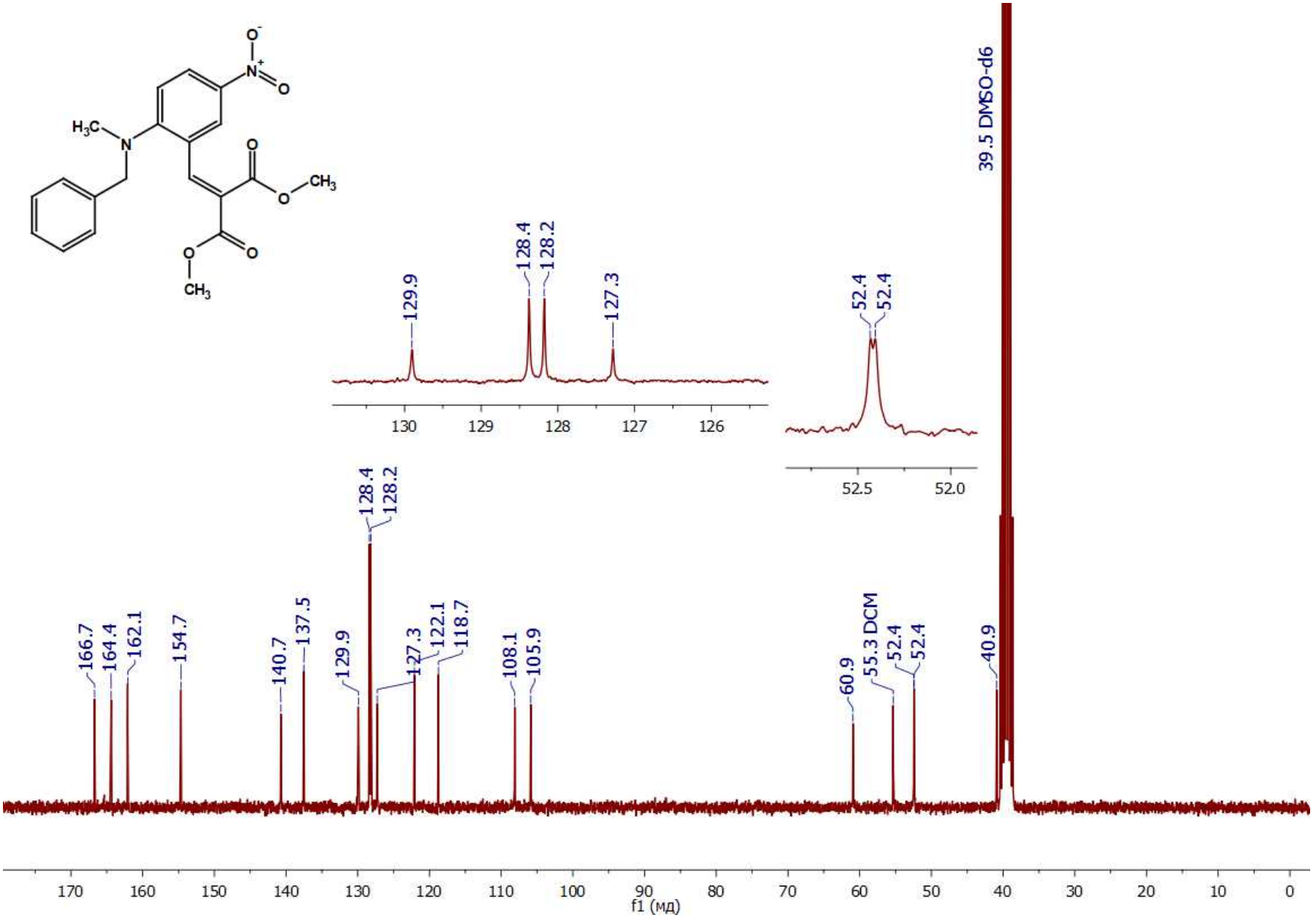

N
O
O
CH3
O
O
CH3
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.24
7.24
7.23
7.22
7.13
7.12
7.11
7.11
7.06
7.05
7.04
7.04
7.03
1.00
1.01
1.02
1.01
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
3.79
3.72
3.30 HDO
2.87
2.86
2.86
4.01
2.90 2.85 2.80
1.68
1.67
1.66
1.66
1.65
1.56
1.55
1.55
1.54
4.00
2.00
1.70 1.65 1.60 1.55 1.50
7.92
7.23
7.13
7.12
7.11
7.11
7.04
7.04
5.75 DCM
2.86
2.86
2.50 DMSO-d6
1.68
1.67
1.66
1.66
1.65
1.56
1.55
1.55
1.54
1.01
1.00
1.01
1.02
1.01
3.02
3.07
4.01
4.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)

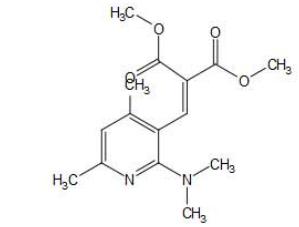

N
O
O
CH3
O
O
CH3
39.5 DMSO-d6
53.9
52.6
52.5
26.0
23.6
166.4
164.3
153.8
140.5
131.7
128.2
126.2
124.0
122.2
118.9
54.5
54.0
53.5
53.0
52.5
52.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

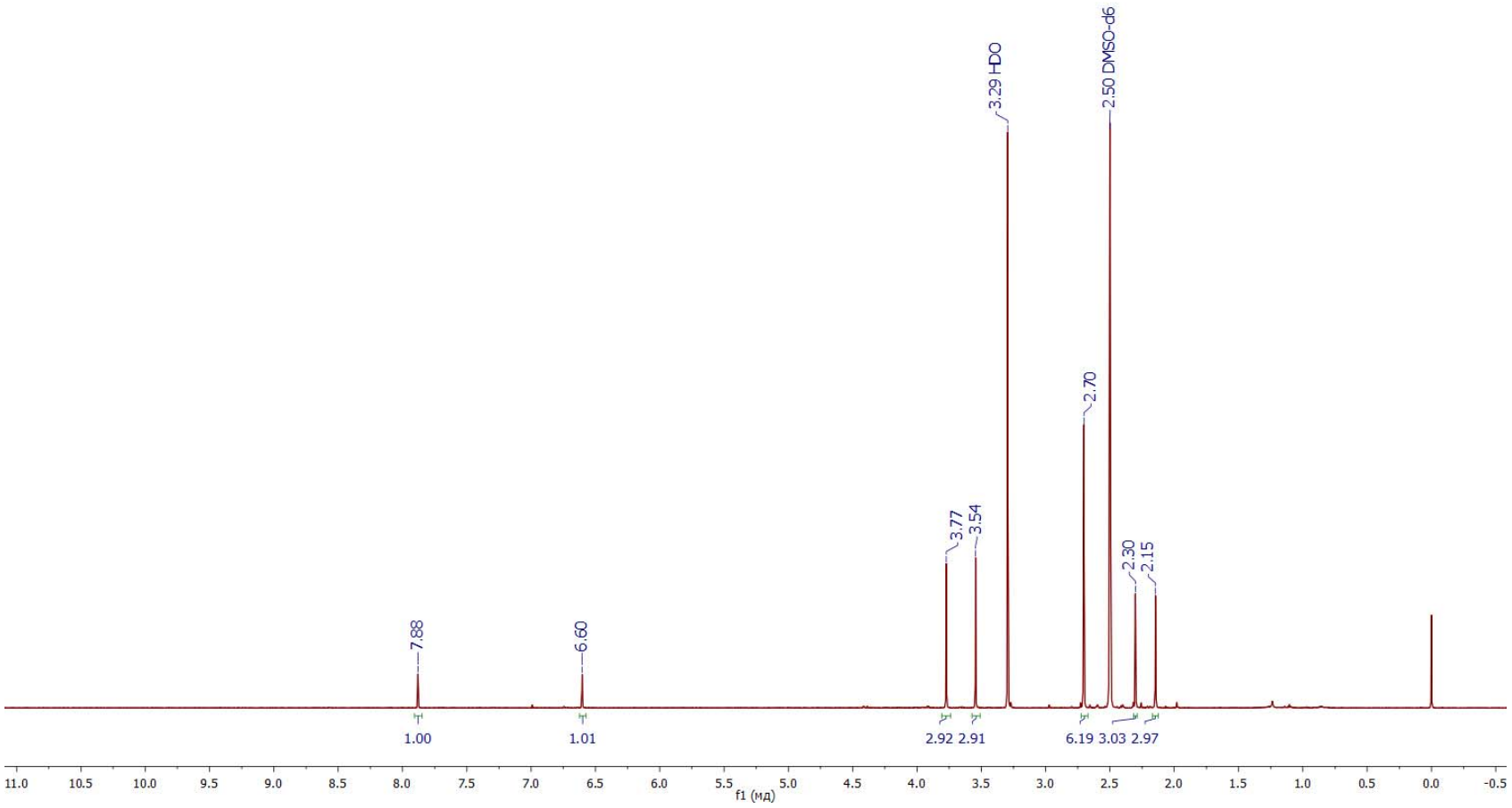

H3C
N
O
O
CH3
O
O
CH3
2.50 DMSO-d6
3.30 HDO
3.78
3.70
4.20
8.08
0.00 TMS
f1 (мд)

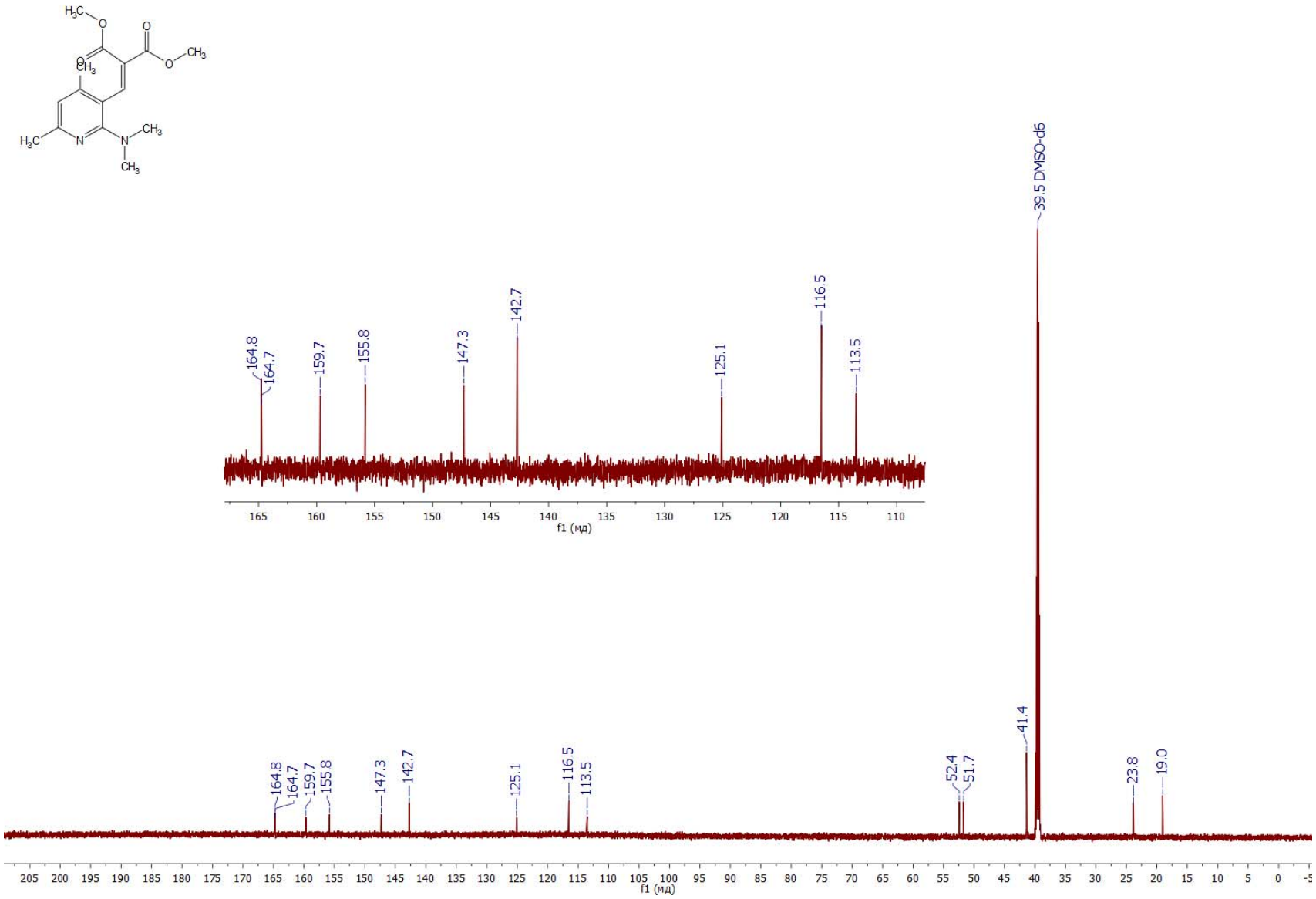

H3C
N
O
O
CH3
O
O
O
CH3
39.5 DMSO-d6
131.0
128.3
128.3
128.1
127.9
127.0
124.6
122.6
121.5
52.6
52.5
166.3
164.1
150.8
141.4
138.2
131.0
128.3
128.3
128.1
127.9
127.0
124.6
122.6
121.5
56.4
52.6
52.5
48.2
12.1
f1 (мд)

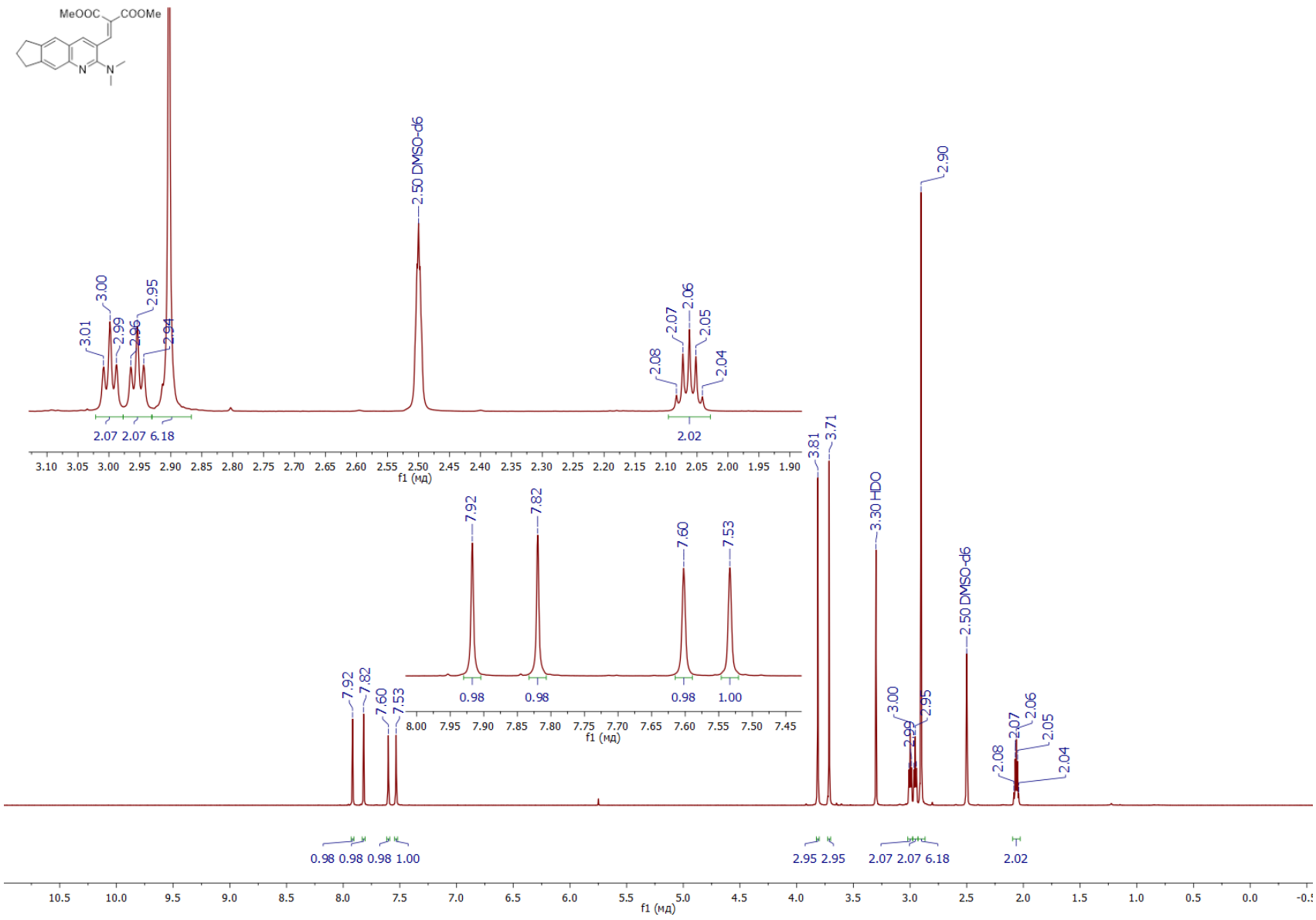

3.30 HDO
2.90
2.50 DMSO-d6
5.75 DCM
4.46
3.75
3.69
8.17
8.16
8.15
8.03
8.02
7.78
7.37
7.36
7.35
7.30
7.29
7.28
7.24
7.23
7.16
7.14
1.02
1.02
1.03
2.15
1.13
2.15
1.05
2.10
3.02
3.09
3.00
f1 (мд)

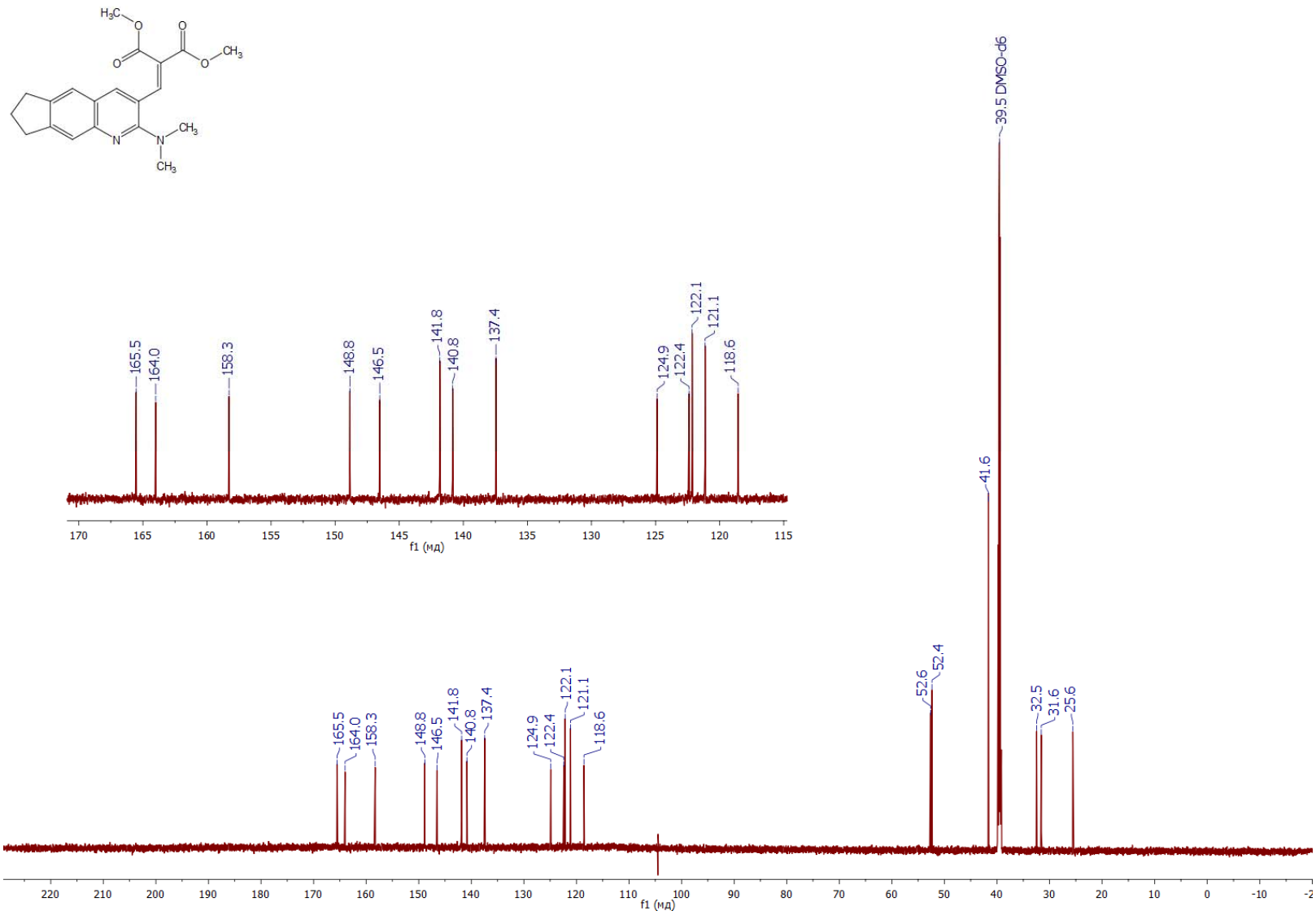

39.5 DMSO-d6
129.9
128.4
128.2
127.3
52.4
52.4
166.7
164.4
162.1
154.7
140.7
137.5
129.9
128.4
128.2
127.3
122.1
118.7
108.1
105.9
60.9
55.3 DCM
52.4
52.4
40.9
f1 (мд)



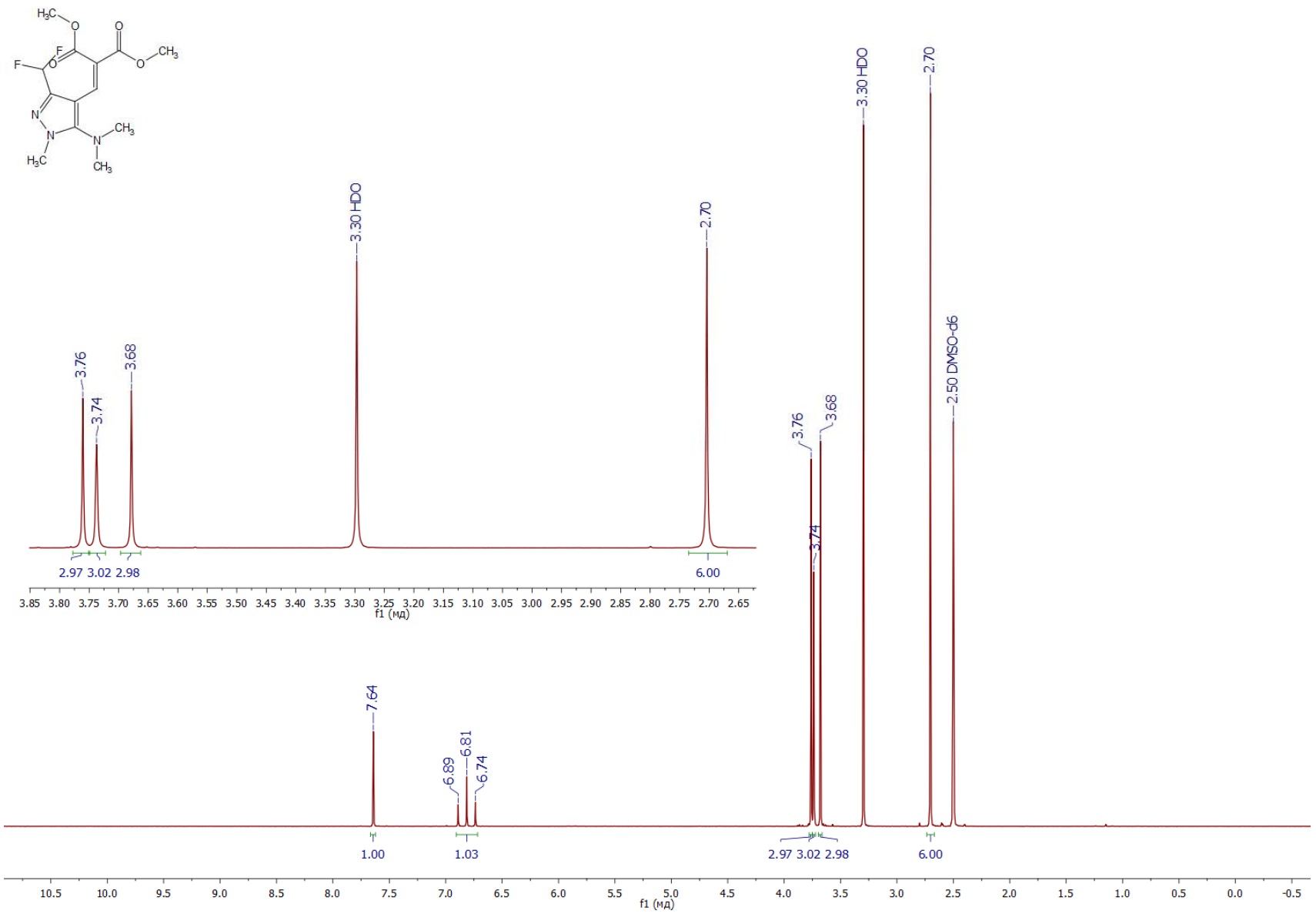

7.88
6.60
3.77
3.54
3.29 HDO
2.70
2.50 DMSO-d6
2.30
2.15
1.00
1.01
2.92 2.91
6.19 3.03 2.97
f1 (мд)

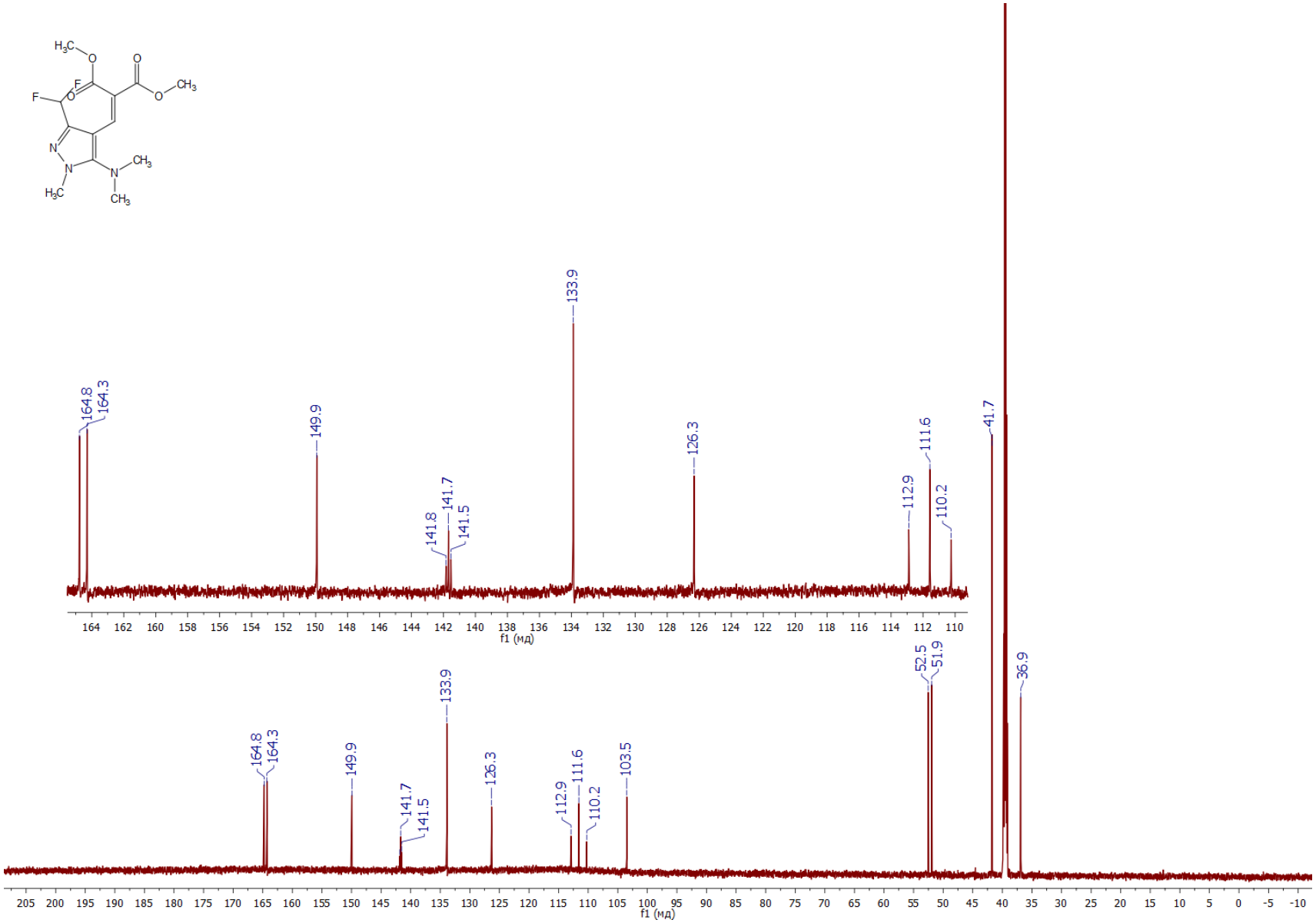

164.8
164.7
159.7
155.8
147.3
142.7
125.1
116.5
113.5
39.5 DMSO-d6
52.4
51.7
41.4
23.8
19.0
f1 (мд)

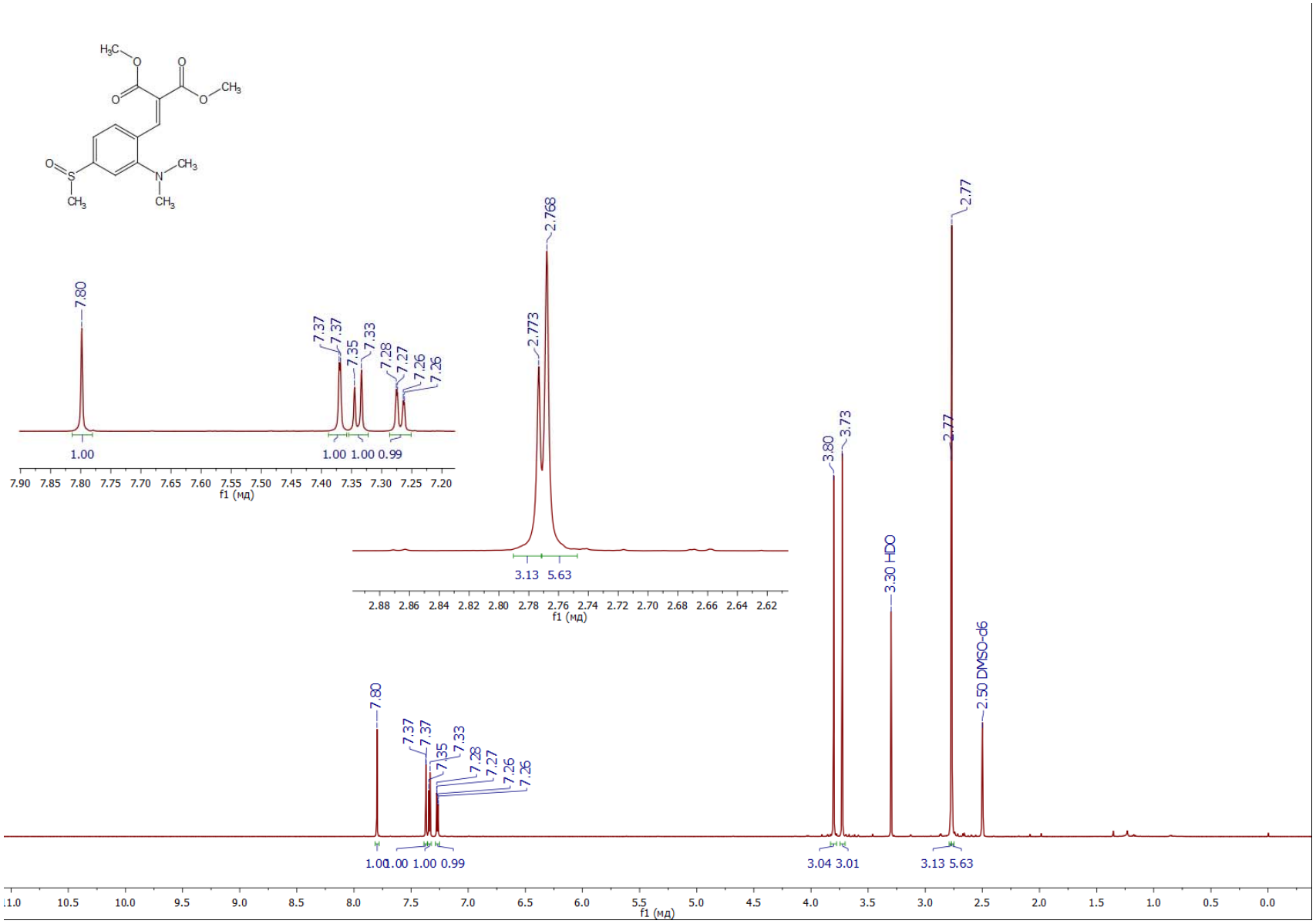

MeOOC
COOMe
N
N
2.50 DMSO-d6
3.01
3.00
2.99
2.96
2.95
2.94
2.08
2.07
2.06
2.05
2.04
2.07 2.07 6.18
2.02
3.10 3.05 3.00 2.95 2.90 2.85 2.80 2.75 2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.95 1.90
f1 (мд)
7.92
7.82
7.60
7.53
0.98
0.98
0.98
1.00
8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45
f1 (мд)
3.81
3.71
3.30 HDO
2.90
2.50 DMSO-d6
0.98 0.98 0.98 1.00
2.95 2.95
2.07 2.07 6.18
2.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)

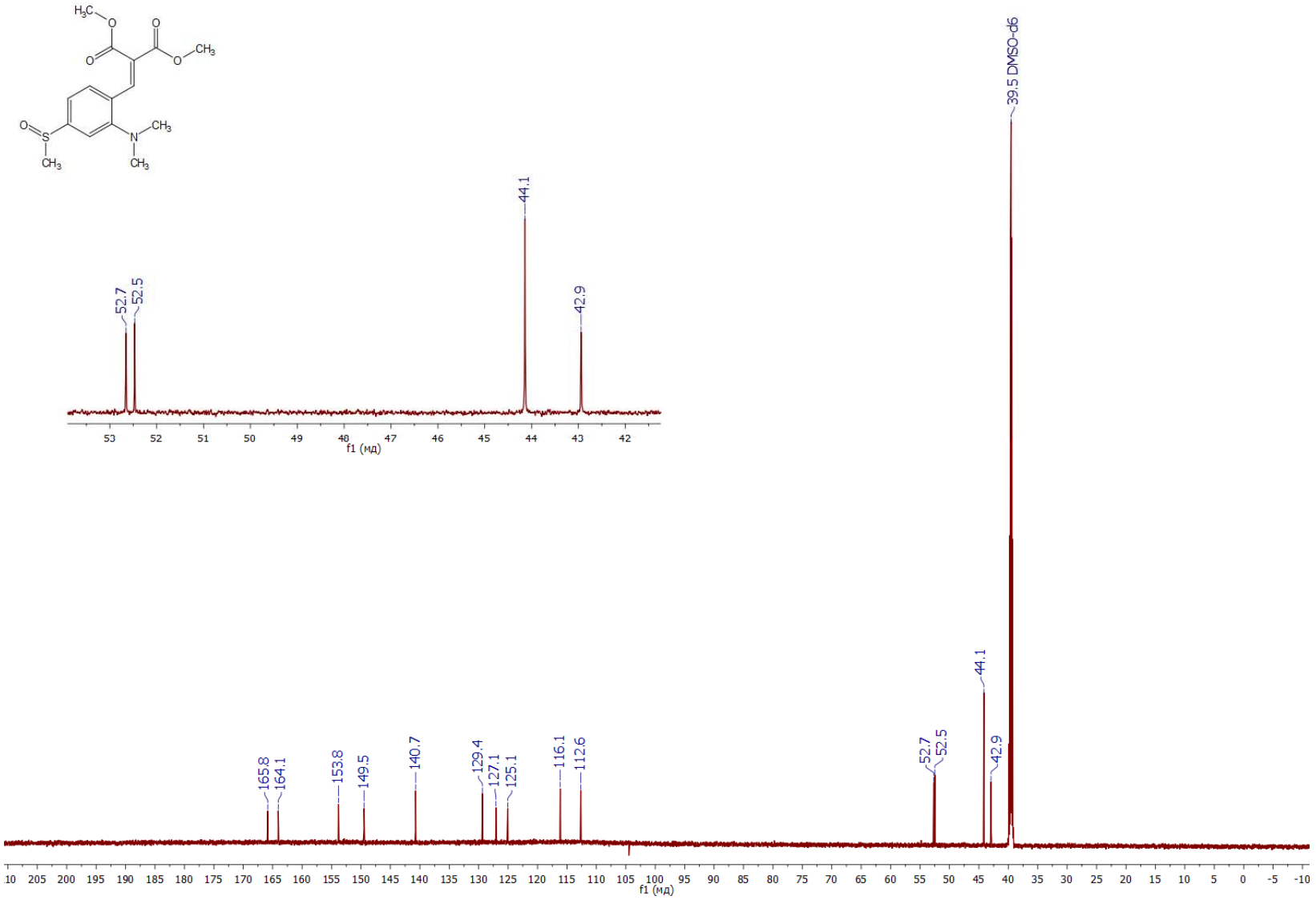


* The inverted peak at 105 ppm is an artifact at exact center of spectrum

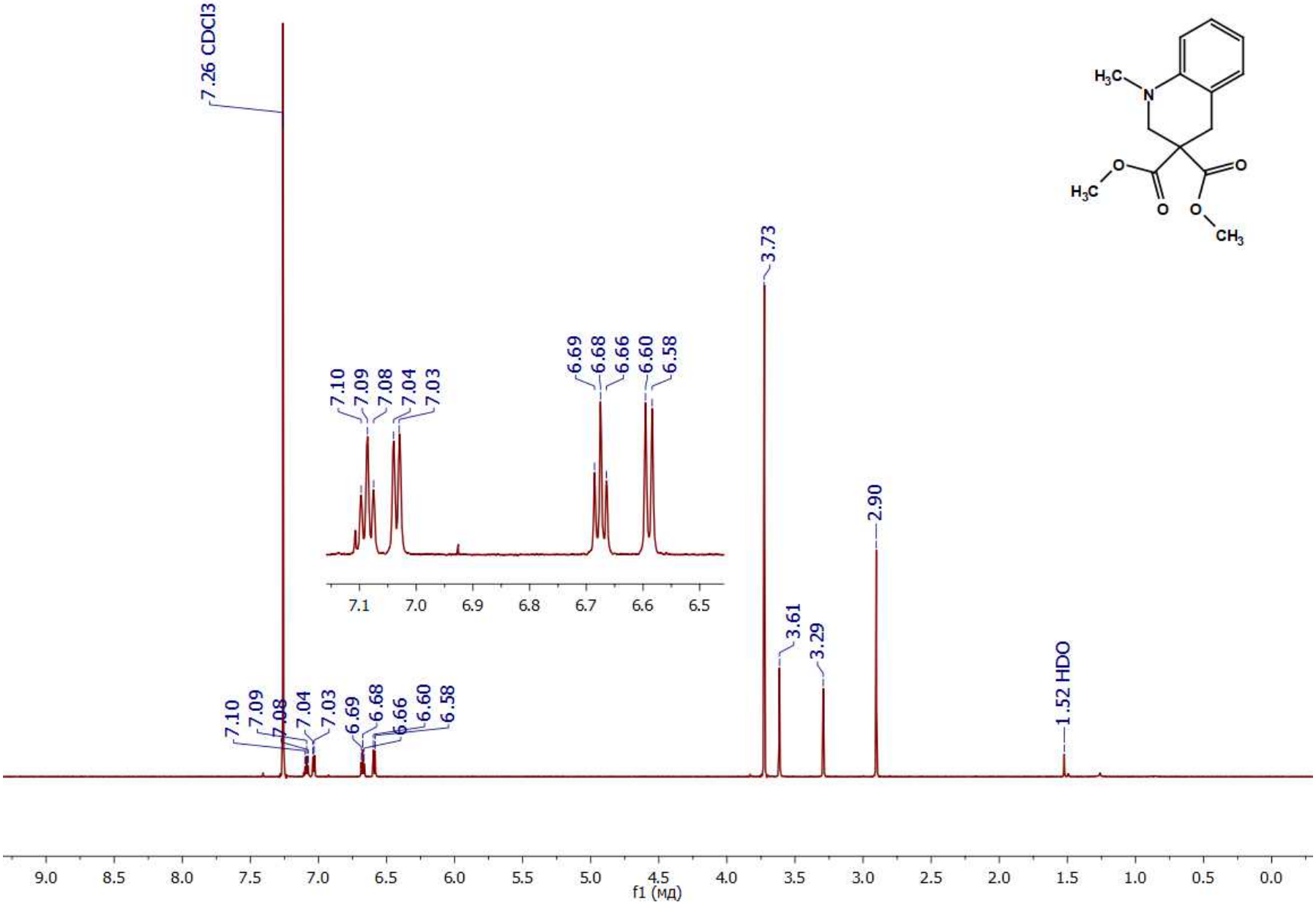

3.30 HDO
2.70
3.76
3.74
3.68
2.97 3.02 2.98
6.00
f1 (мд)
7.64
6.89
6.81
6.74
1.00
1.03
2.50 DMSO-d6

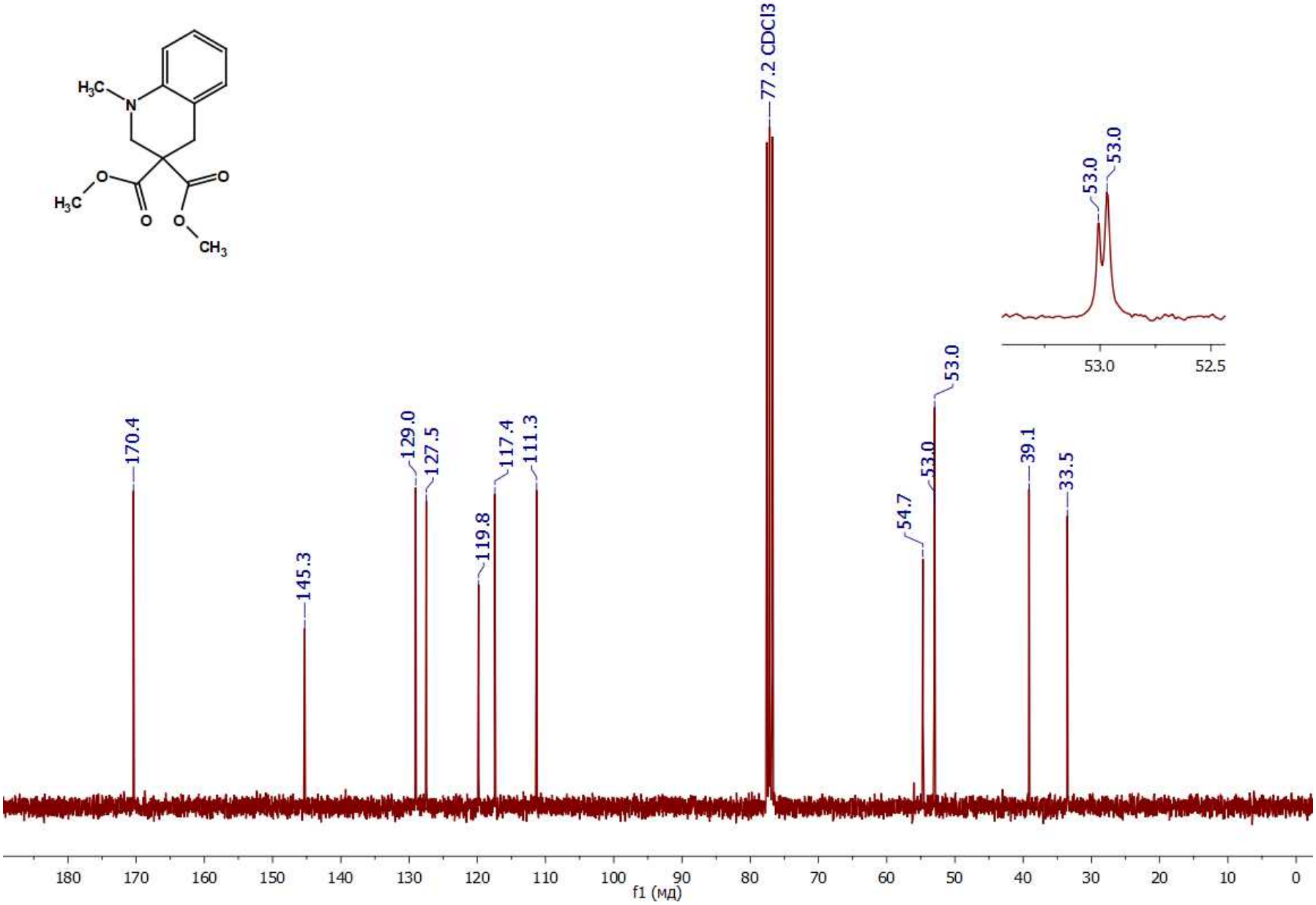

H3C
O
O
F
F
O
O
CH3
N
N
H3C
N
CH3
CH3
164.8
164.3
149.9
141.8
141.7
141.5
133.9
126.3
112.9
111.6
110.2
41.7
164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (мд)
52.5
51.9
36.9
164.8
164.3
149.9
141.7
141.5
133.9
126.3
112.9
111.6
110.2
103.5
205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (мд)

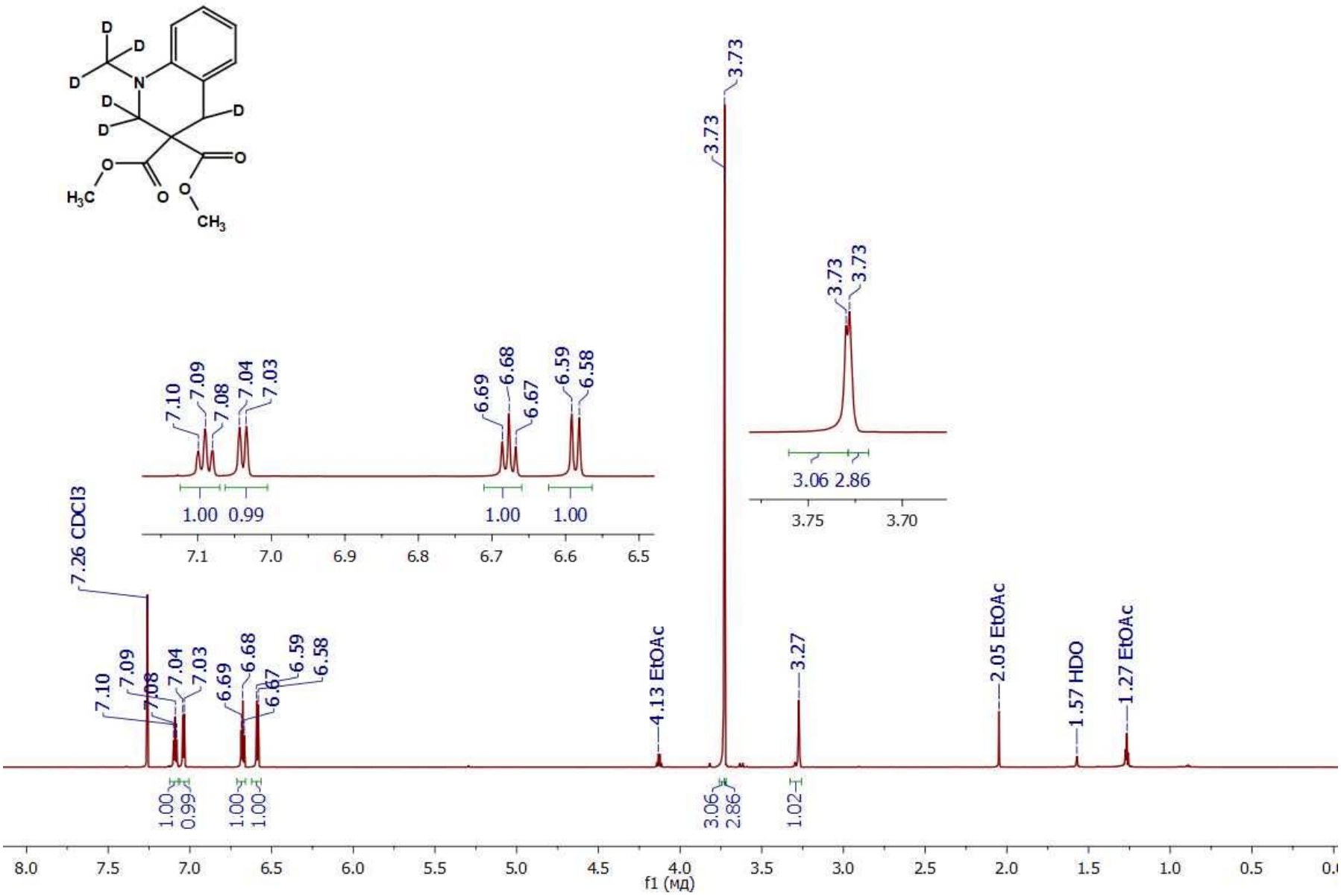

7.80
7.37
7.37
7.35
7.33
7.28
7.27
7.26
7.26
1.00
1.00 1.00 0.99
2.768
2.773
3.13 5.63
3.80
3.73
3.30 HDO
2.77
2.77
2.50 DMSO-d6
1.00 1.00 1.00 0.99
3.04 3.01
3.13 5.63
f1 (мд)

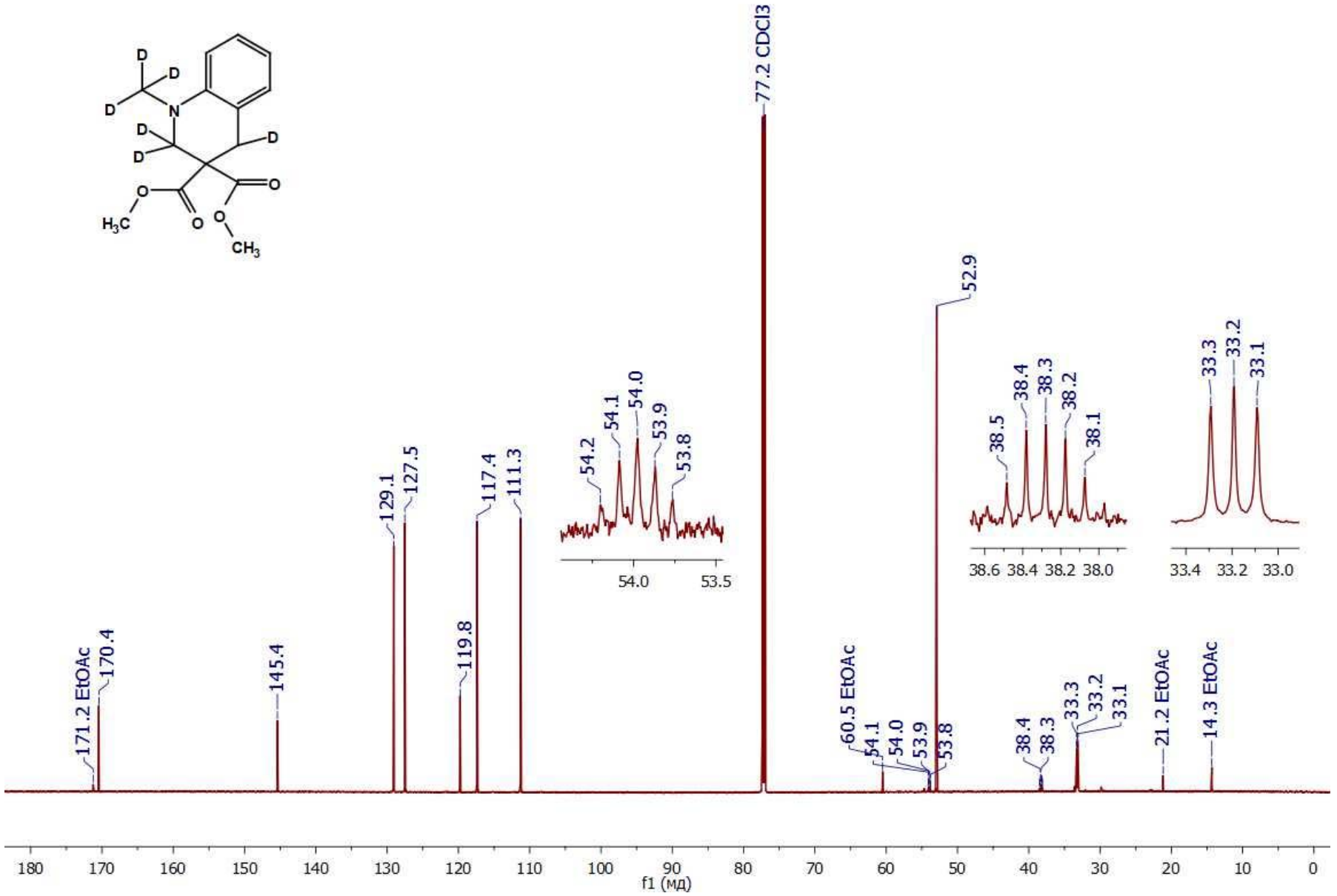


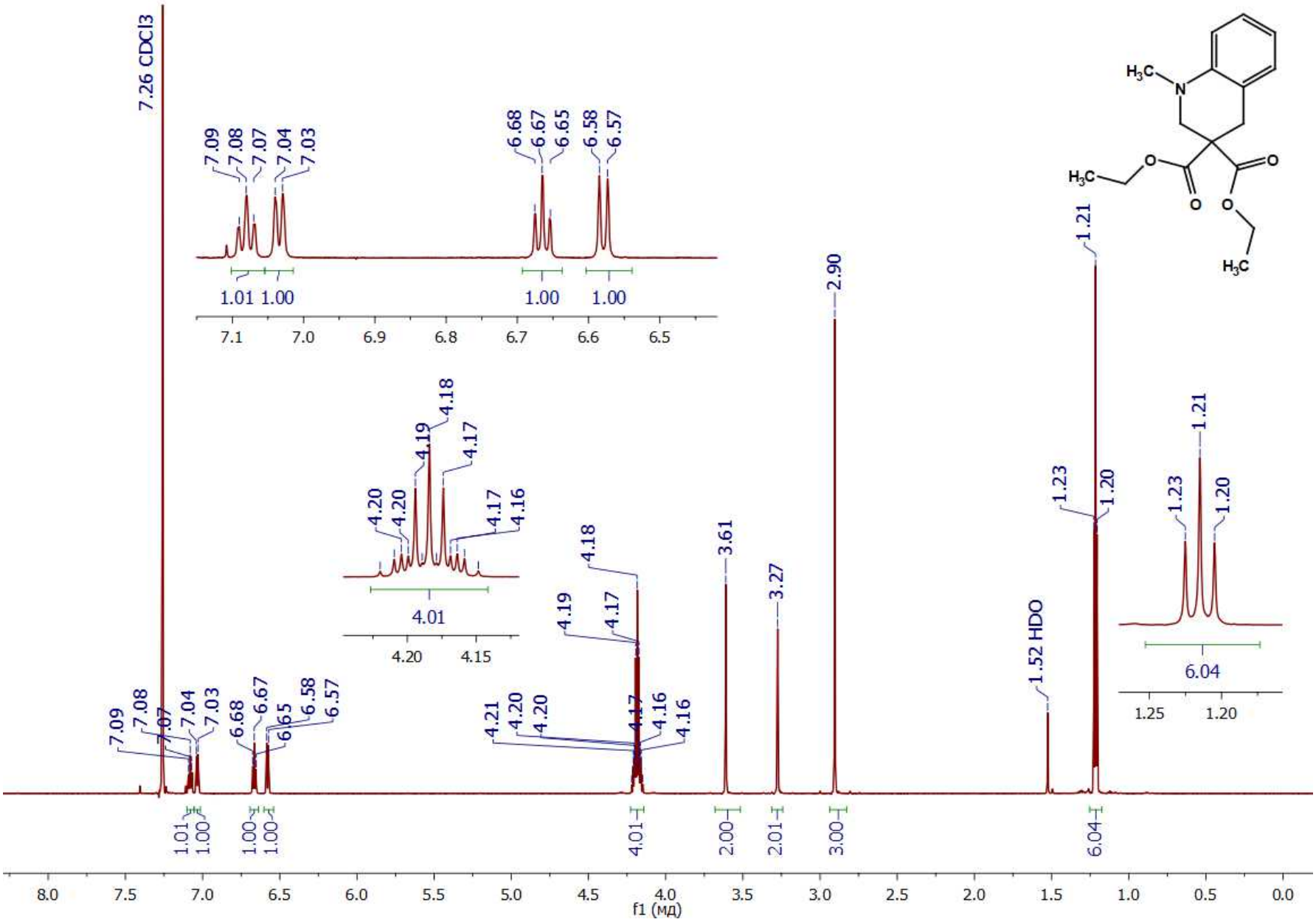
* The inverted peak at 105 ppm is an artifact at exact center of spectrum

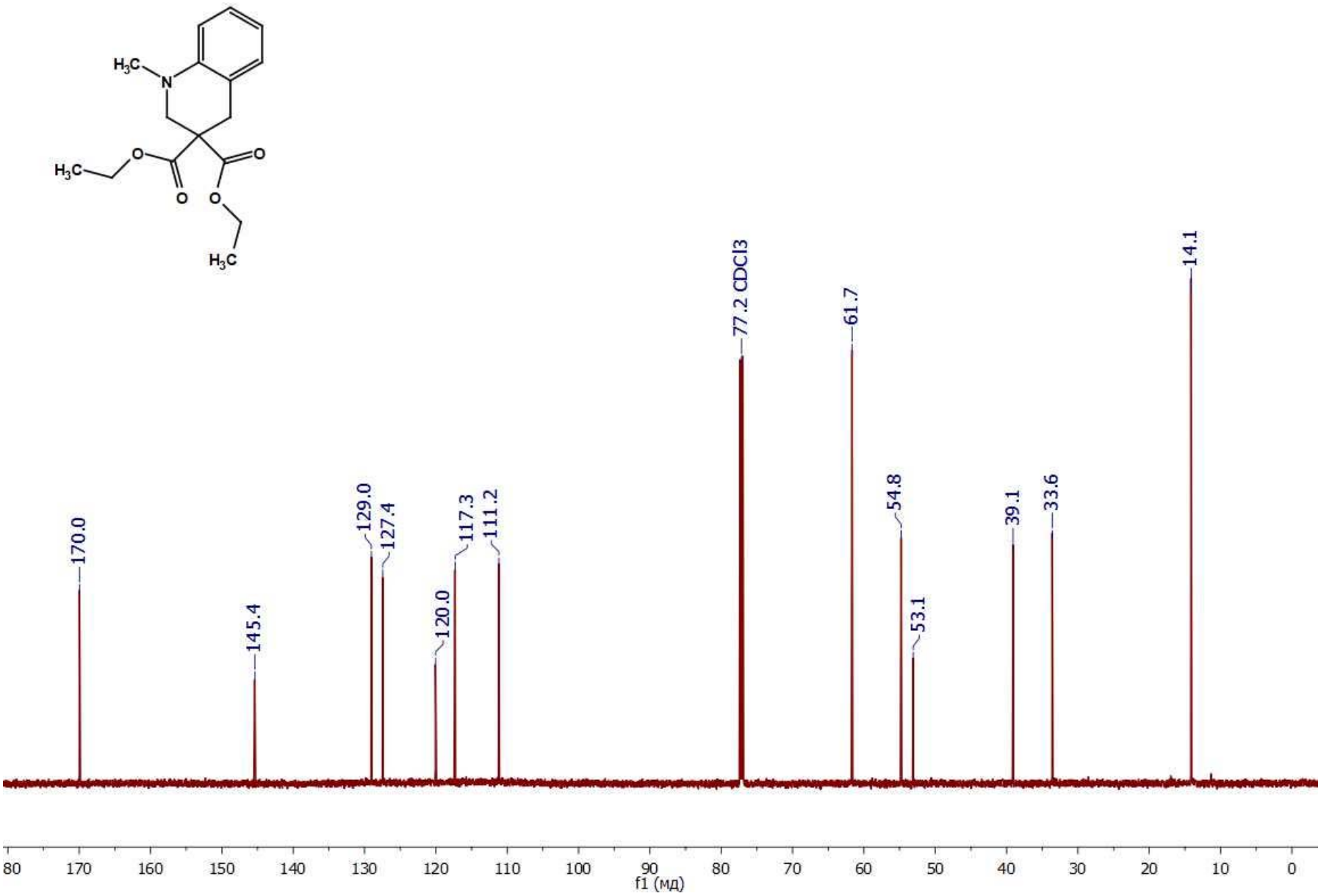

7.26 CDCl3
7.10
7.09
7.08
7.04
7.03
6.69
6.68
6.66
6.60
6.58
3.73
3.61
3.29
2.90
1.52 HDO
f1 (мд)

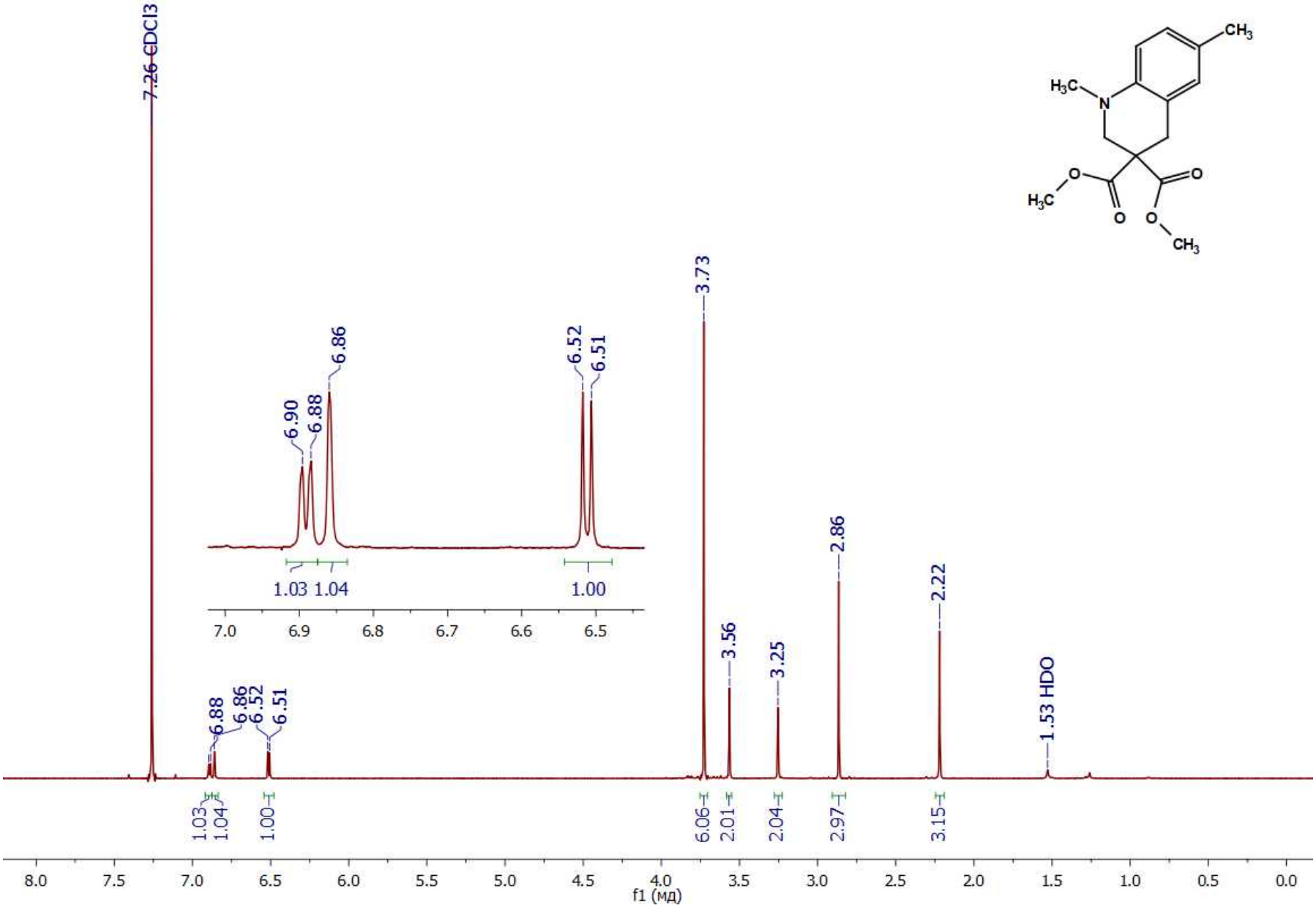

77.2 CDCl3
170.4
145.3
129.0
127.5
119.8
117.4
111.3
54.7
53.0
53.0
39.1
33.5
53.0
53.0
53.0
52.5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

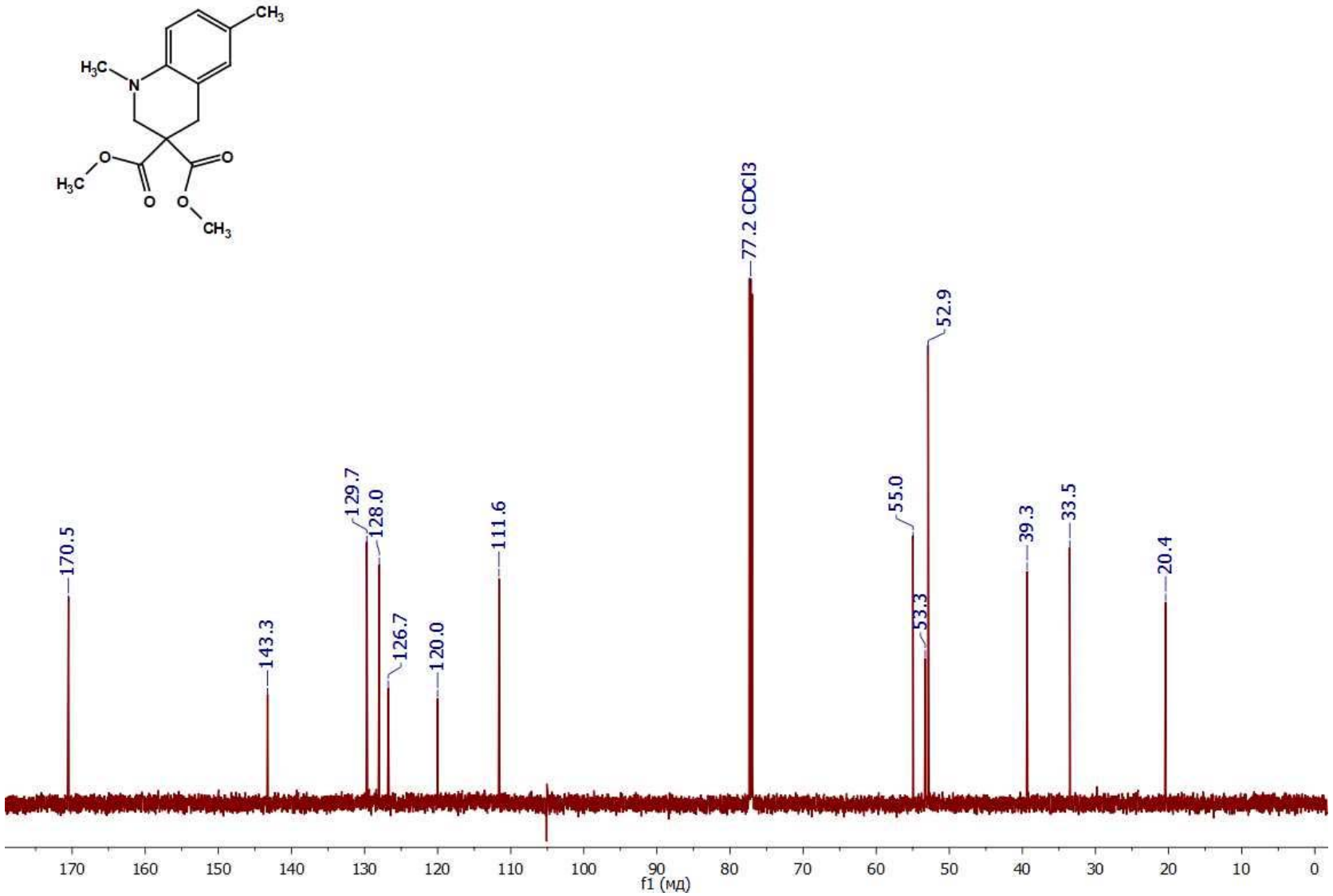

D
D
D
N
D
D
D
O
O
H3C
O
O
CH3
7.26 CDCl3
7.10
7.09
7.08
7.04
7.03
6.69
6.68
6.67
6.59
6.58
4.13 EtOAc
3.73
3.27
2.05 EtOAc
1.57 HDO
1.27 EtOAc
1.00
0.99
1.00
1.00
3.06
2.86
1.02
3.06 2.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (мд)


D
D
D
N
D
D
D
O
O
H_3C
O
O
CH_3
77.2 CDCl3
52.9
129.1
127.5
117.4
111.3
119.8
145.4
171.2 EtOAc
170.4
60.5 EtOAc
54.1
54.0
53.9
53.8
38.4
38.3
33.3
33.2
33.1
21.2 EtOAc
14.3 EtOAc
54.2
54.1
54.0
53.9
53.8
54.0
53.5
38.5
38.4
38.3
38.2
38.1
38.6 38.4 38.2 38.0
33.3
33.2
33.1
33.4 33.2 33.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

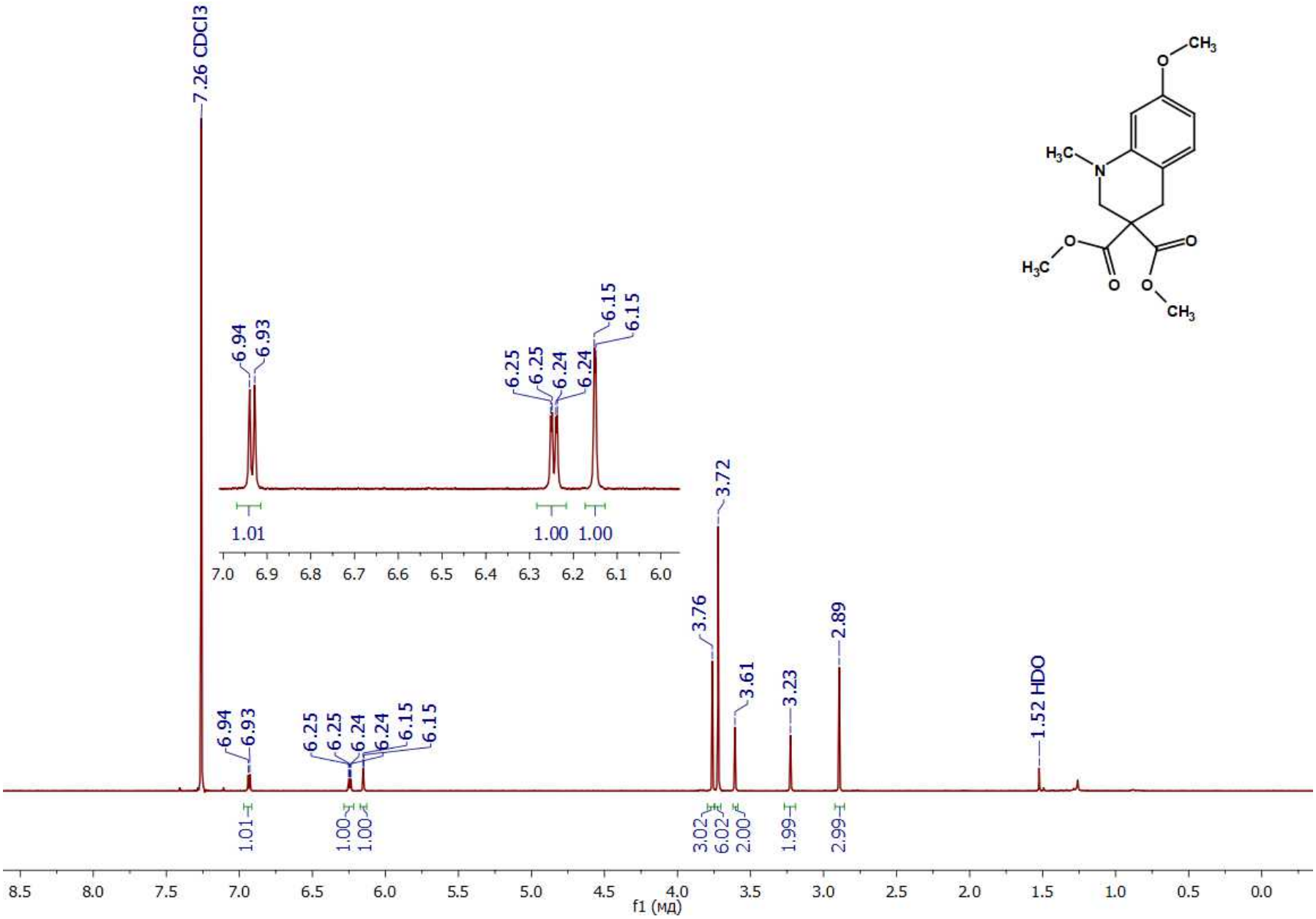

7.26 CDCl3
7.09
7.08
7.07
7.04
7.03
6.68
6.67
6.65
6.58
6.57
4.21
4.20
4.20
4.19
4.18
4.17
4.17
4.16
4.16
3.61
3.27
2.90
1.52 HDO
1.23
1.21
1.20
1.01
1.00
1.00
1.00
4.01
2.00
2.01
3.00
6.04
f1 (мд)

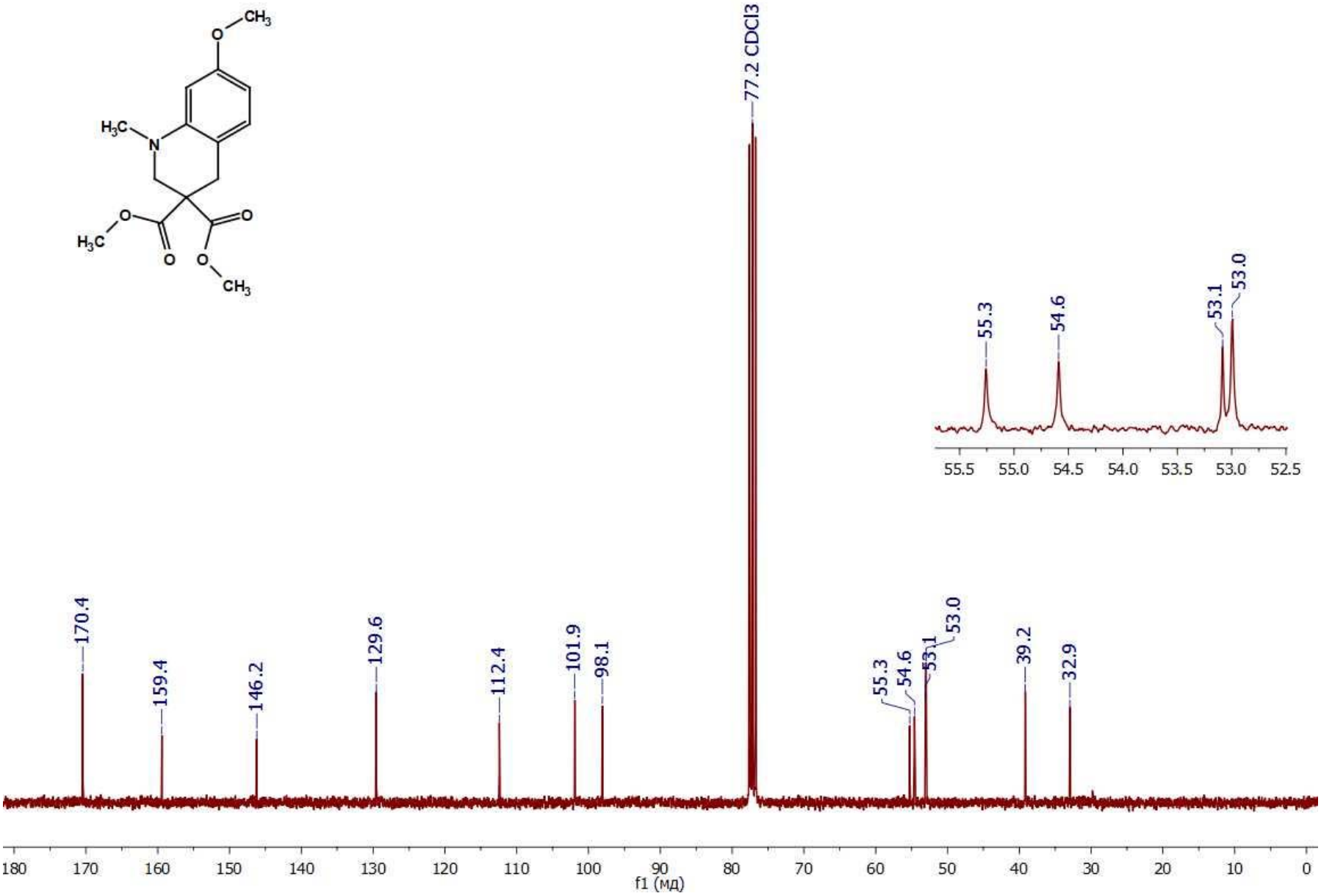

H3C
N
O
O
O
O
H3C
H3C
170.0
145.4
129.0
127.4
120.0
117.3
111.2
77.2 CDCl3
61.7
54.8
53.1
39.1
33.6
14.1
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

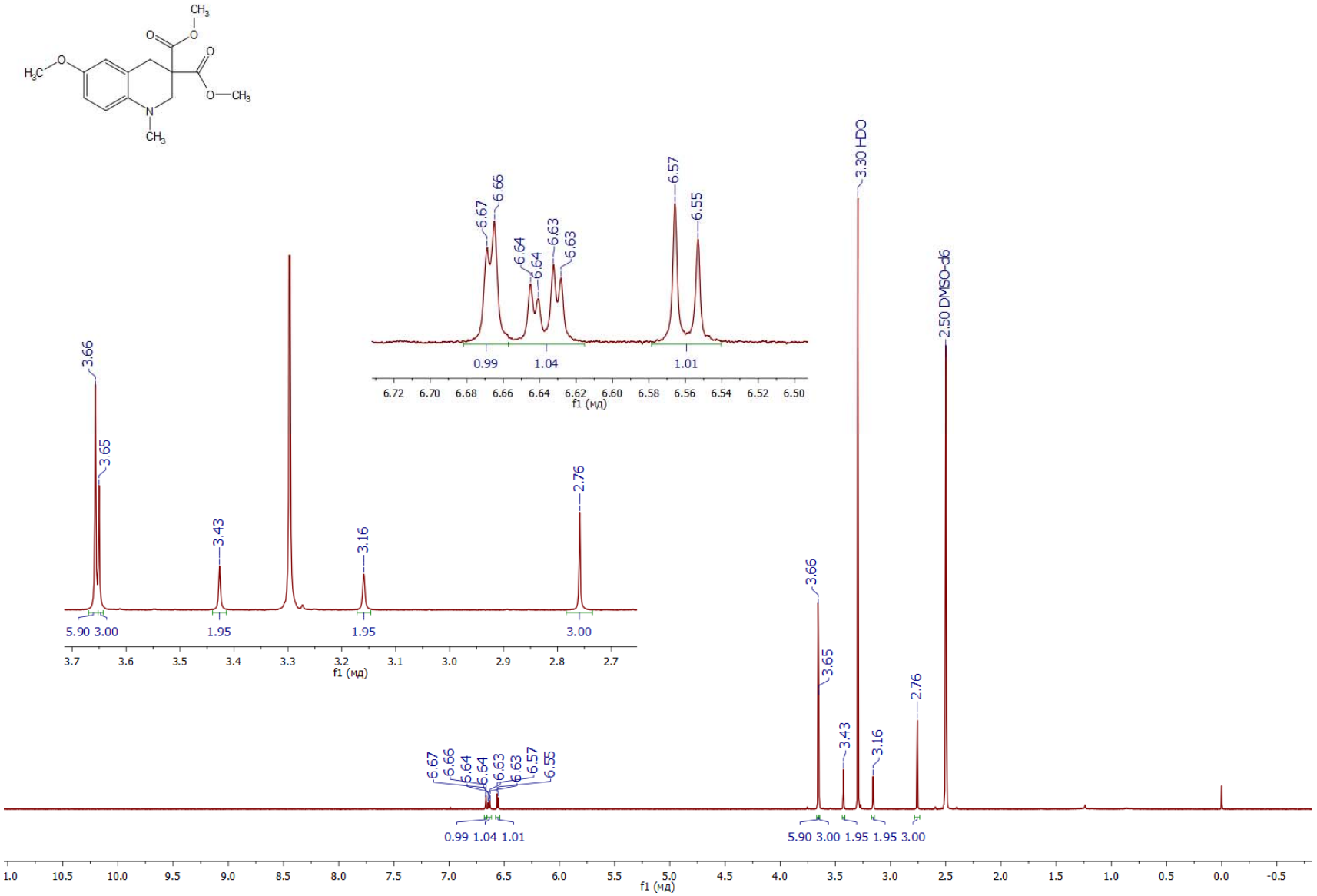

7.26 CDCl3
6.90
6.88
6.86
6.52
6.51
1.03 1.04
1.00
3.73
3.56
3.25
2.86
2.22
1.53 HDO
1.03
1.04
1.00
6.06
2.01
2.04
2.97
3.15
f1 (мд)

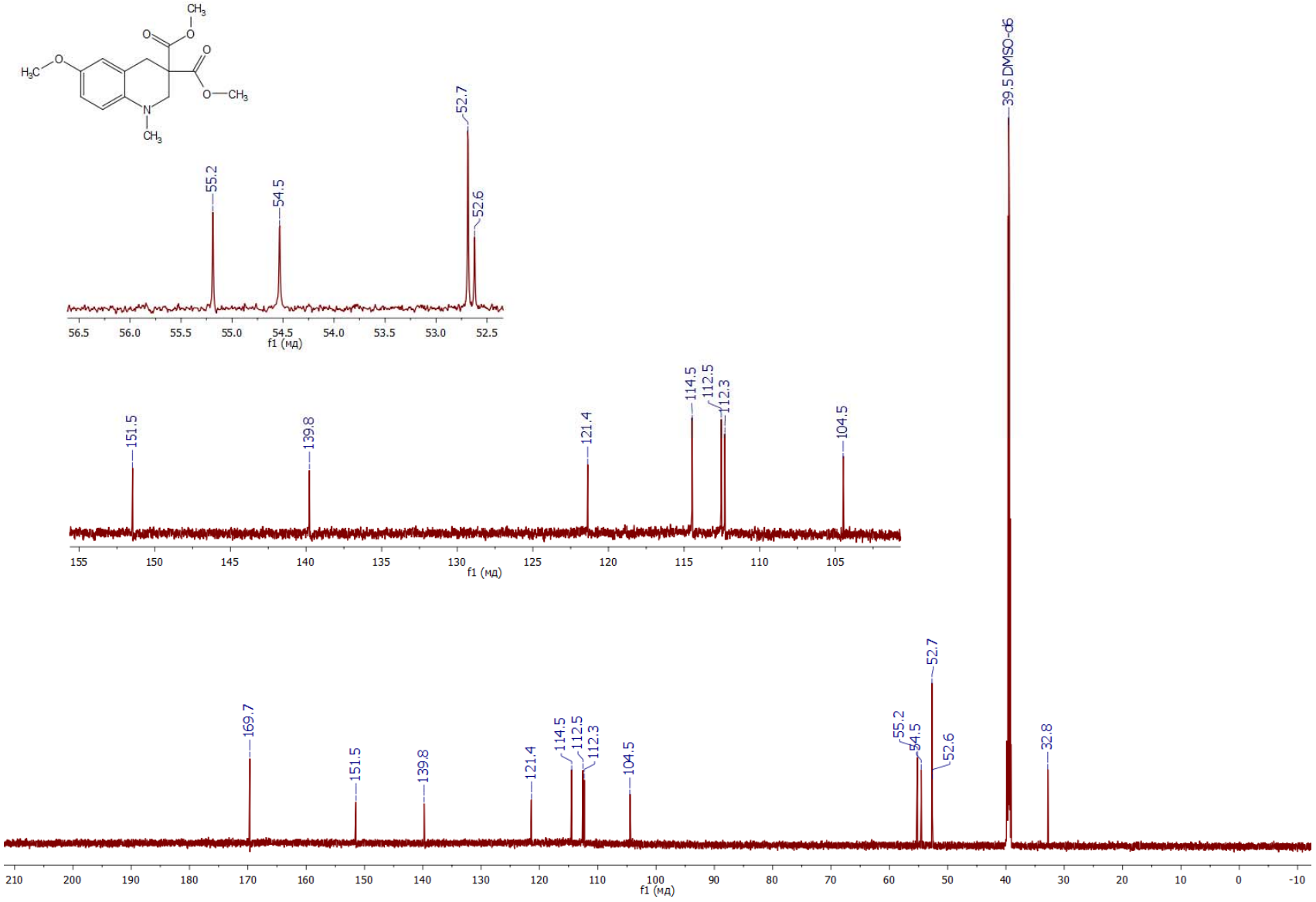


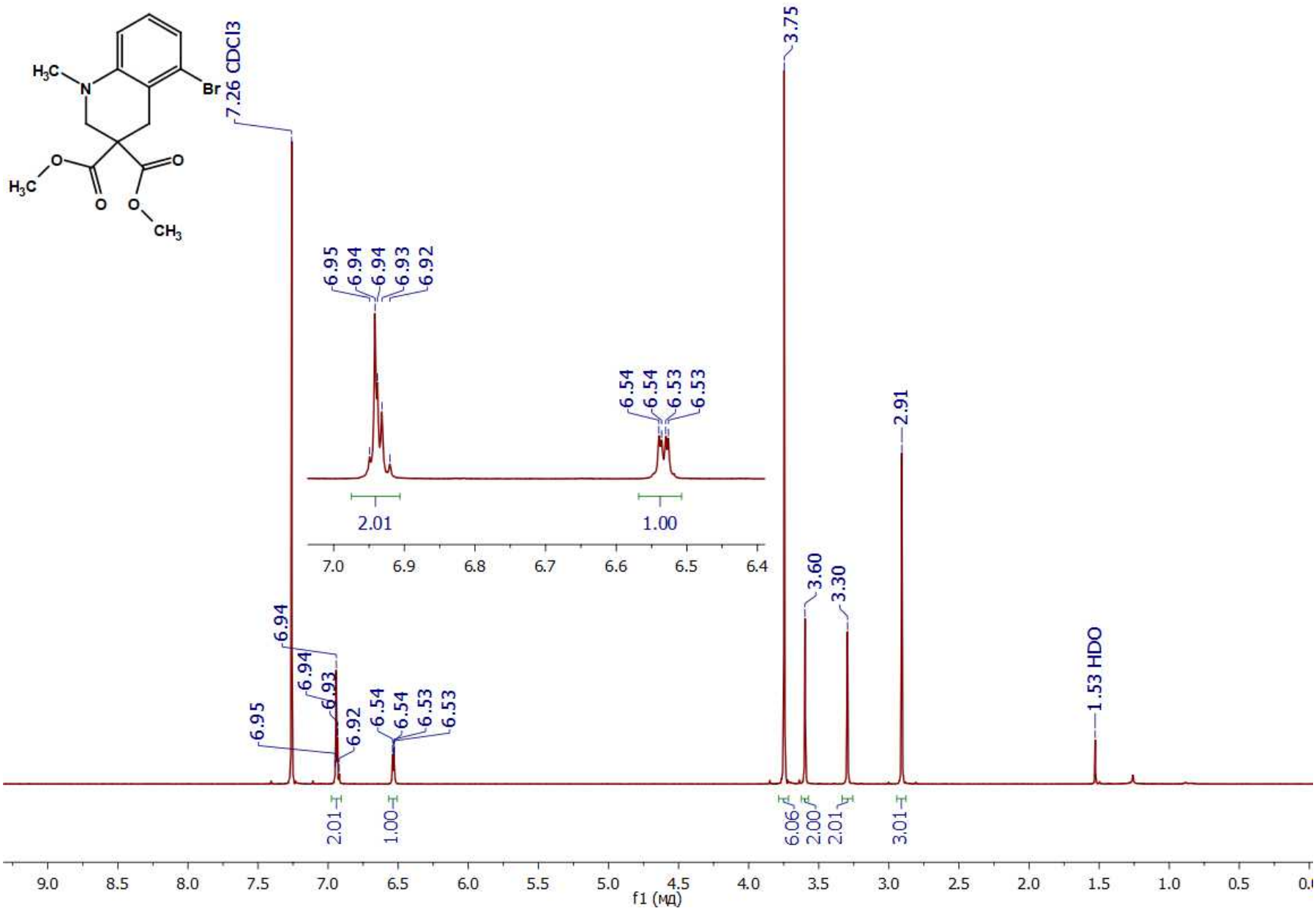
* The inverted peak at 105 ppm is an artifact at exact center of spectrum

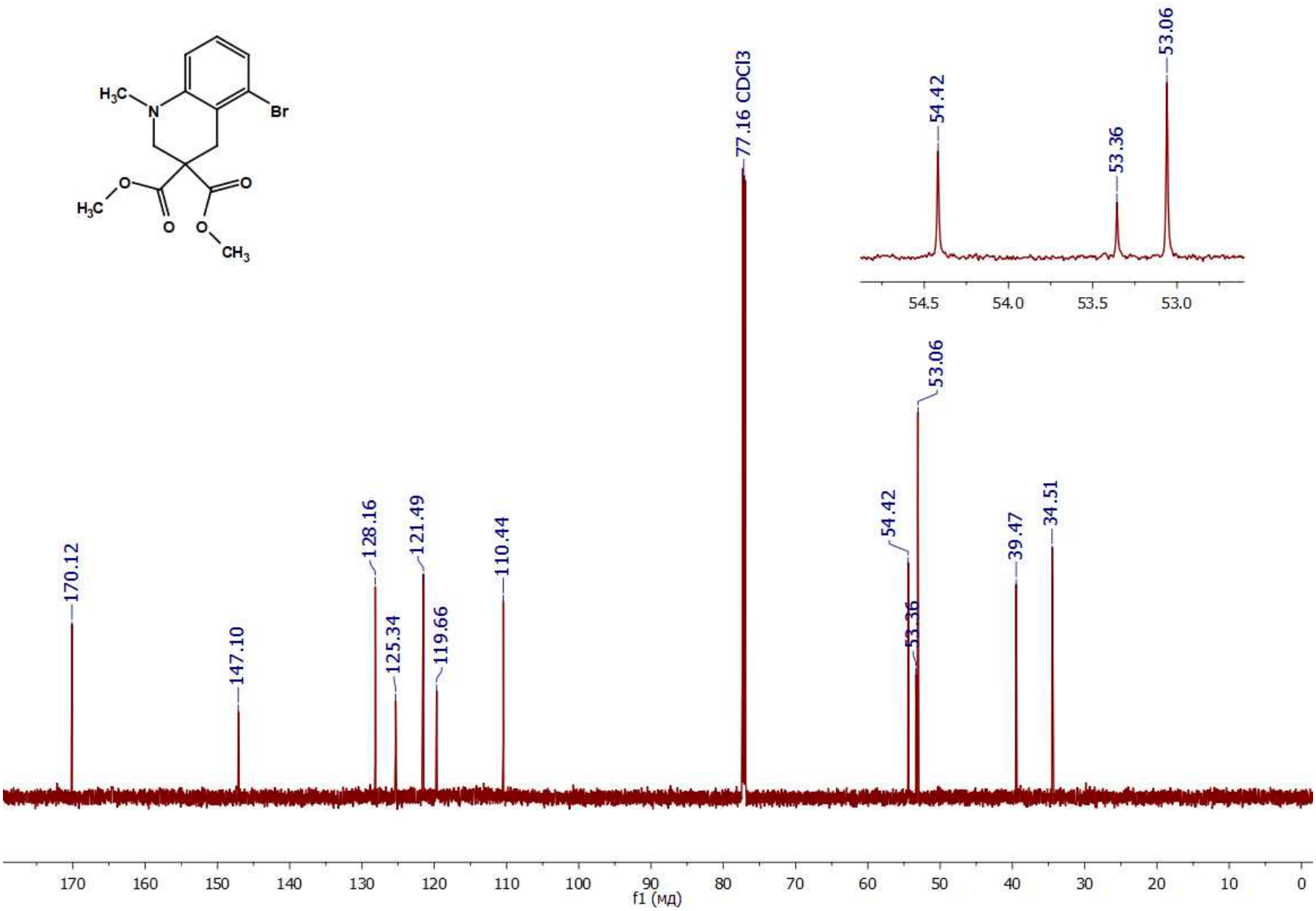

7.26 CDCl3
6.94
6.93
6.25
6.25
6.24
6.24
6.15
6.15
1.01
1.00
1.00
3.76
3.72
3.61
3.23
2.89
1.52 HDO
1.01
1.00
1.00
3.02
6.02
2.00
1.99
2.99
f1 (мд)

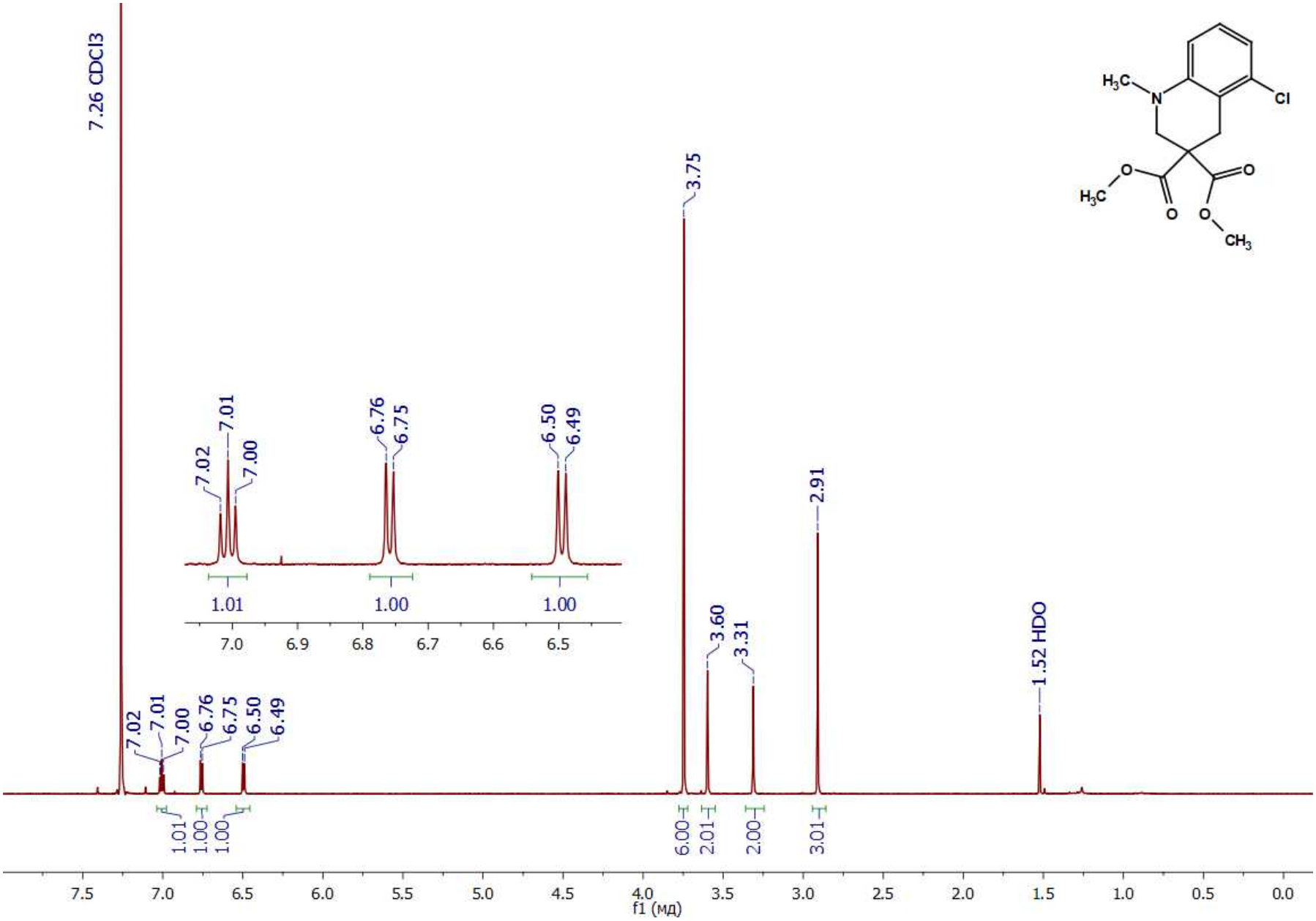

O
CH3
H3C
N
O
O
H3C
O
O
O
CH3
77.2 CDCl3
55.3
54.6
53.1
53.0
55.5
55.0
54.5
54.0
53.5
53.0
52.5
170.4
159.4
146.2
129.6
112.4
101.9
98.1
55.3
54.6
53.1
53.0
39.2
32.9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

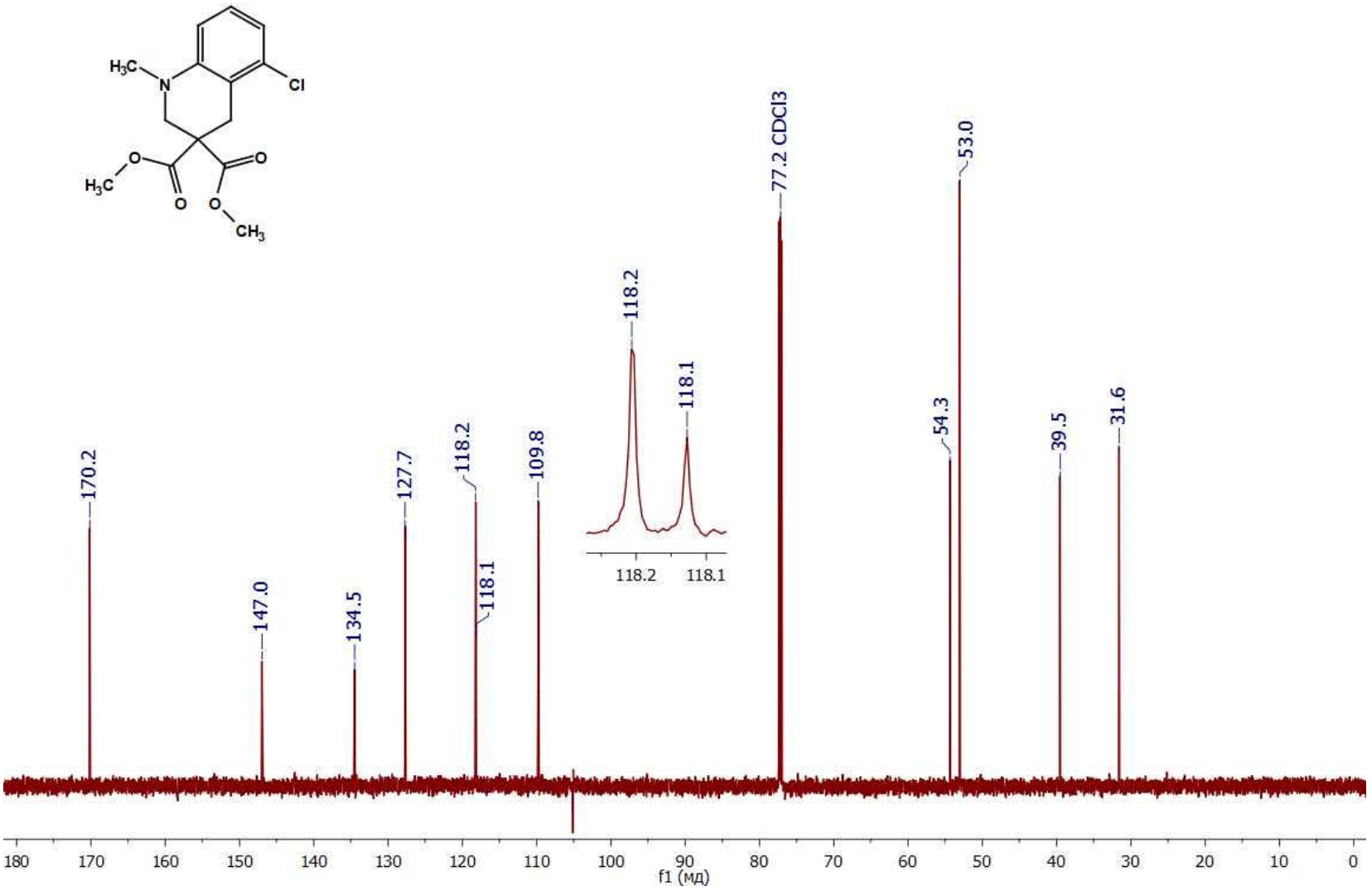

3.66
3.65
3.43
3.16
2.76
5.90 3.00
1.95
1.95
3.00
f1 (мд)
6.67
6.66
6.64
6.64
6.63
6.63
6.57
6.55
0.99
1.04
1.01
f1 (мд)
3.30 HDO
2.50 DMSO-d6
0.99 1.04 1.01
5.90 3.00 1.95 1.95 3.00
f1 (мд)


CH3
O
O
O
H3C
O
O
CH3
N
CH3
52.7
55.2
54.5
52.6
56.5
56.0
55.5
55.0
54.5
54.0
53.5
53.0
52.5
f1 (мд)
151.5
139.8
121.4
114.5
112.5
112.3
104.5
155
150
145
140
135
130
125
120
115
110
105
f1 (мд)
39.5 DMSO-d6
169.7
151.5
139.8
121.4
114.5
112.5
112.3
104.5
55.2
54.5
52.7
52.6
32.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (мд)

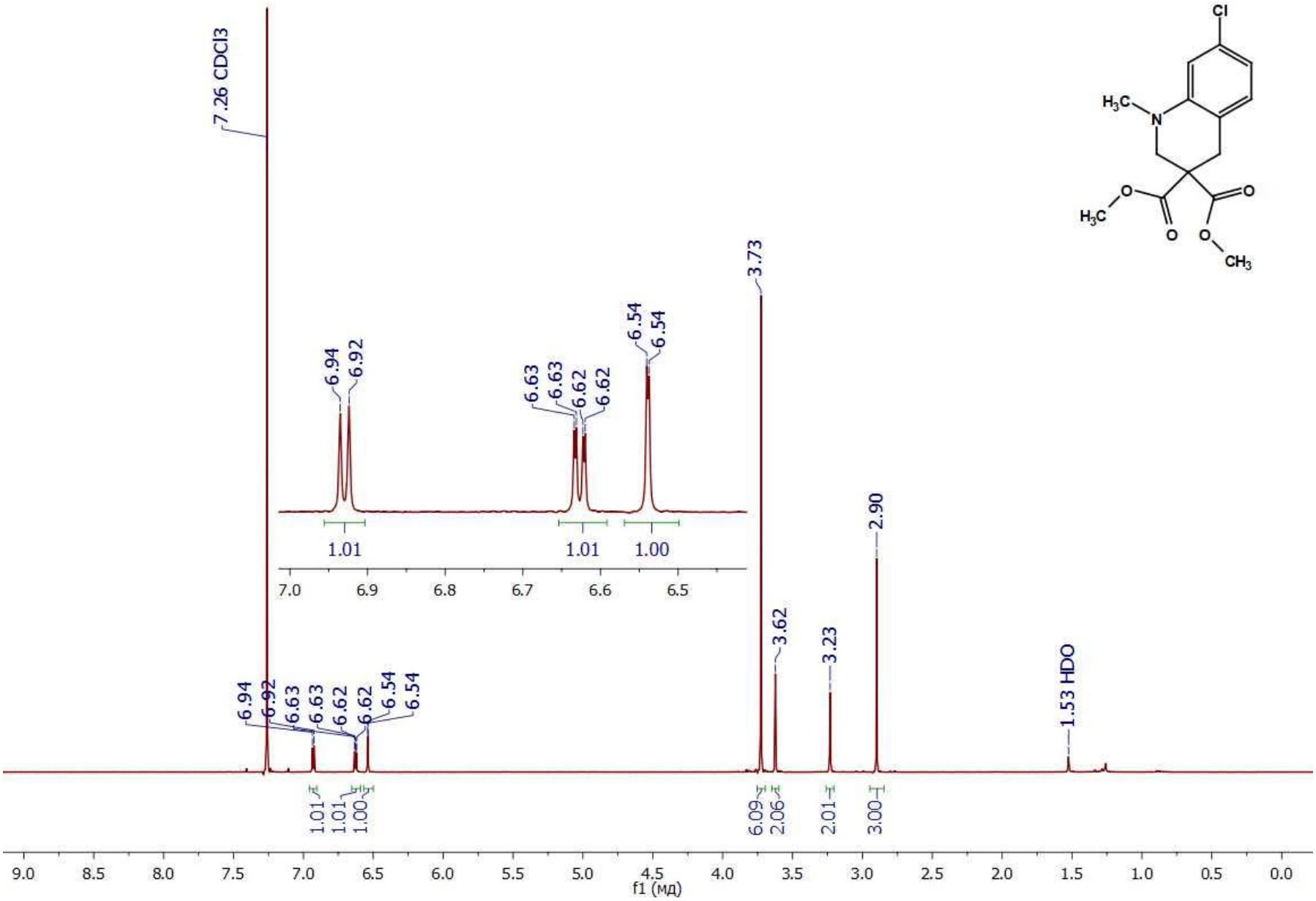

H3C
N
Br
O
O
H3C
O
O
O
CH3
7.26 CDCl3
3.75
6.95
6.94
6.94
6.93
6.92
6.54
6.54
6.53
6.53
2.91
2.01
1.00
3.60
3.30
1.53 HDO
6.95
6.94
6.94
6.93
6.92
6.54
6.54
6.53
6.53
2.01
1.00
6.06
2.00
2.01
3.01
f1 (мд)

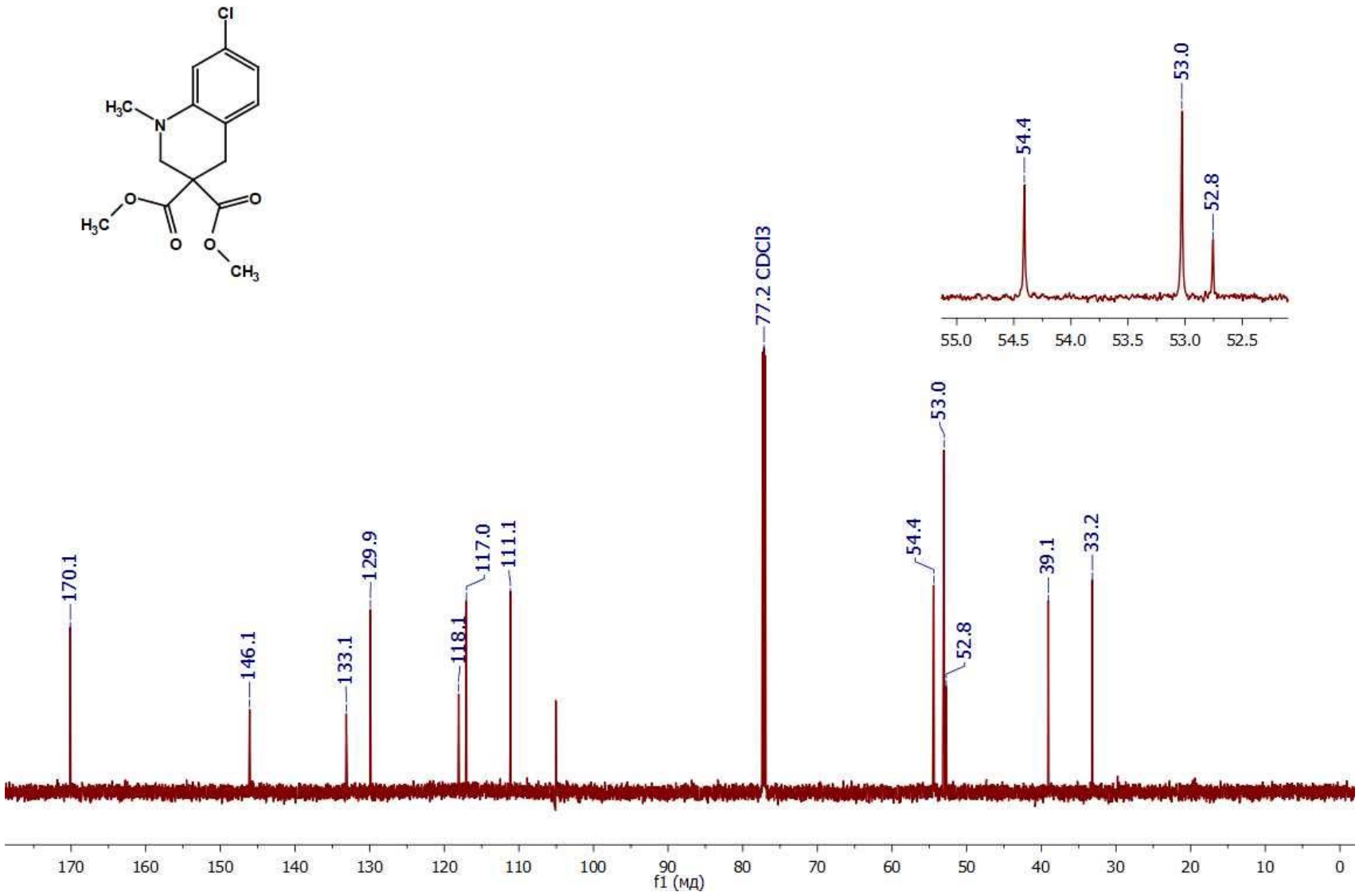

H3C
N
Br
O
H3C
O
O
O
O
CH3
77.16 CDCl3
54.42
53.36
53.06
54.5
54.0
53.5
53.0
170.12
147.10
128.16
125.34
121.49
119.66
110.44
54.42
53.36
53.06
39.47
34.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


7.26 CDCl3
7.02
7.01
7.00
6.76
6.75
6.50
6.49
3.75
3.60
3.31
2.91
1.52 HDO
1.01
1.00
1.00
6.00
2.01
2.00
3.01
f1 (мд)

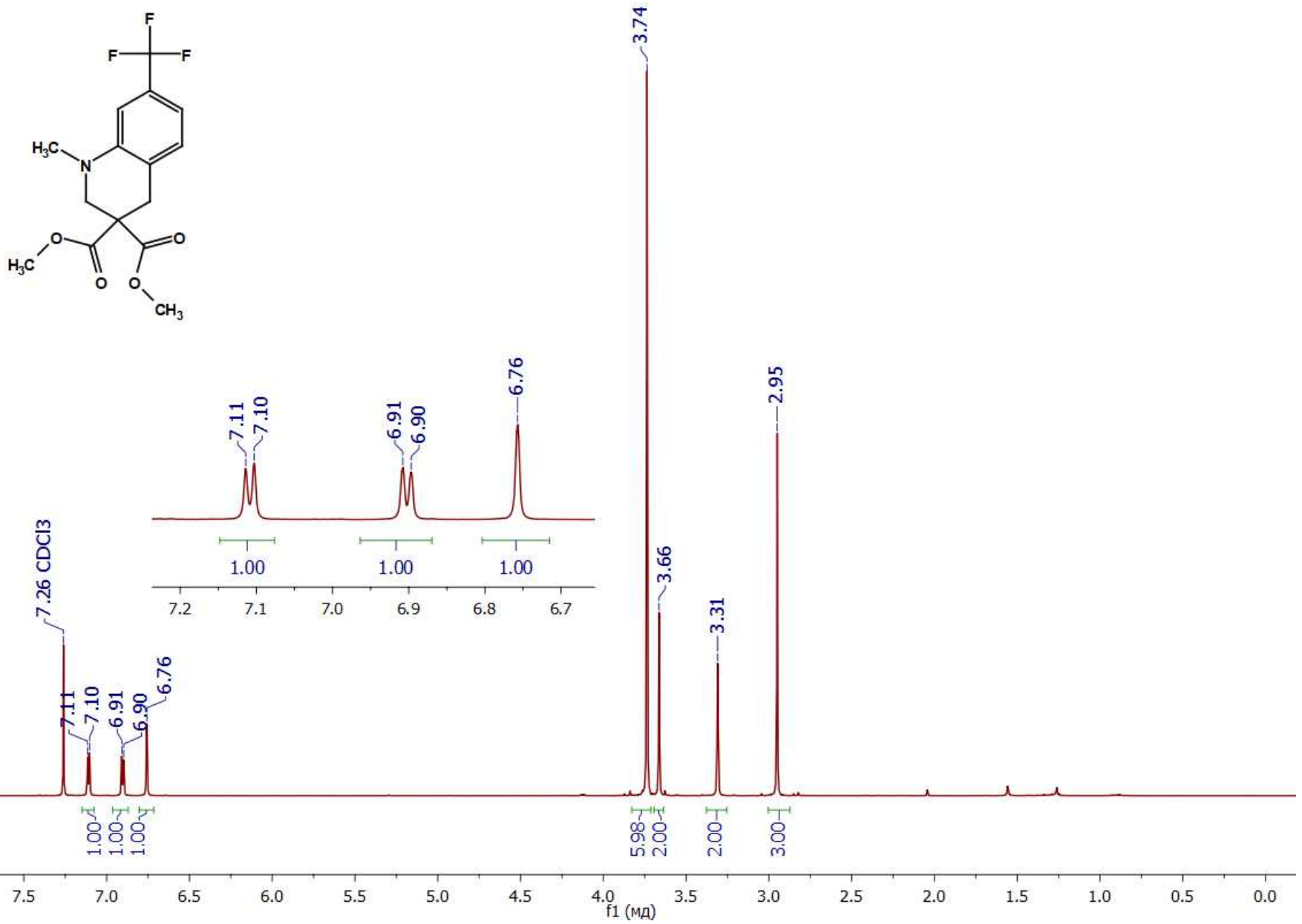


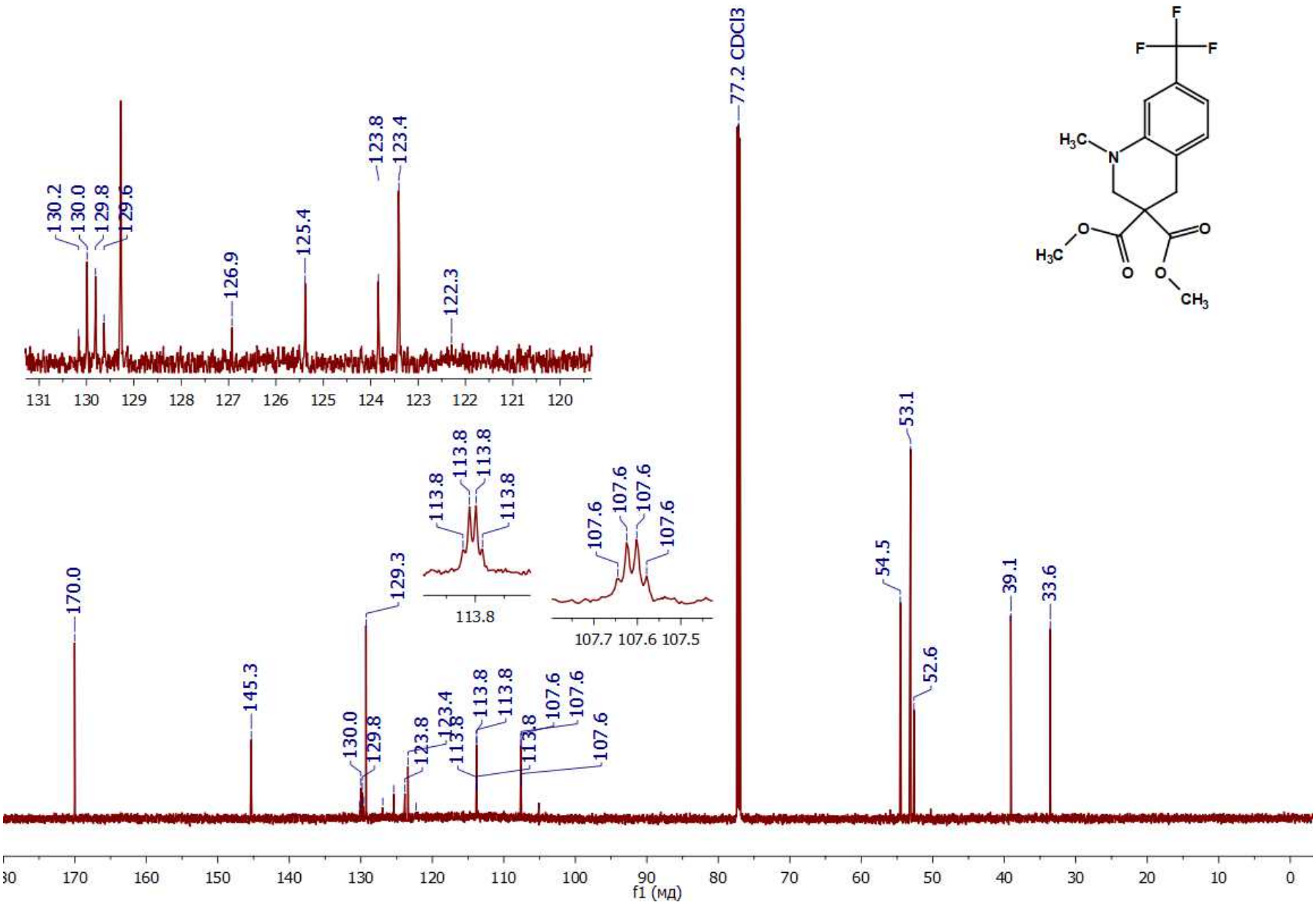
* The inverted peak at 105 ppm is an artifact at exact center of spectrum

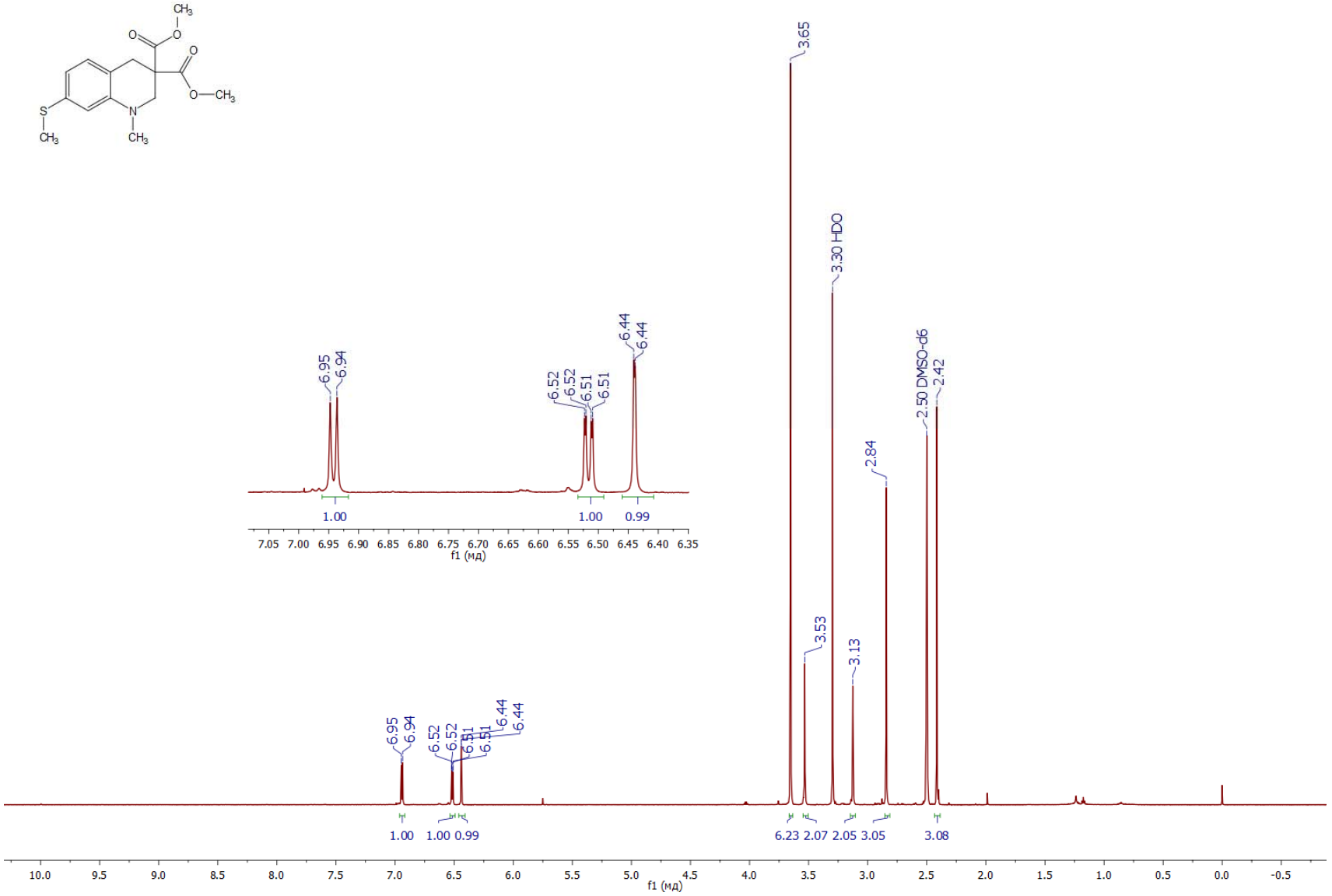

7.26 CDCl3
Cl
H3C
N
O
O
H3C
O
O
O
CH3
6.94
6.92
6.63
6.63
6.62
6.62
6.54
6.54
1.01
1.01
1.00
7.0
6.9
6.8
6.7
6.6
6.5
3.73
3.62
3.23
2.90
1.53 HDO
6.09
2.06
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

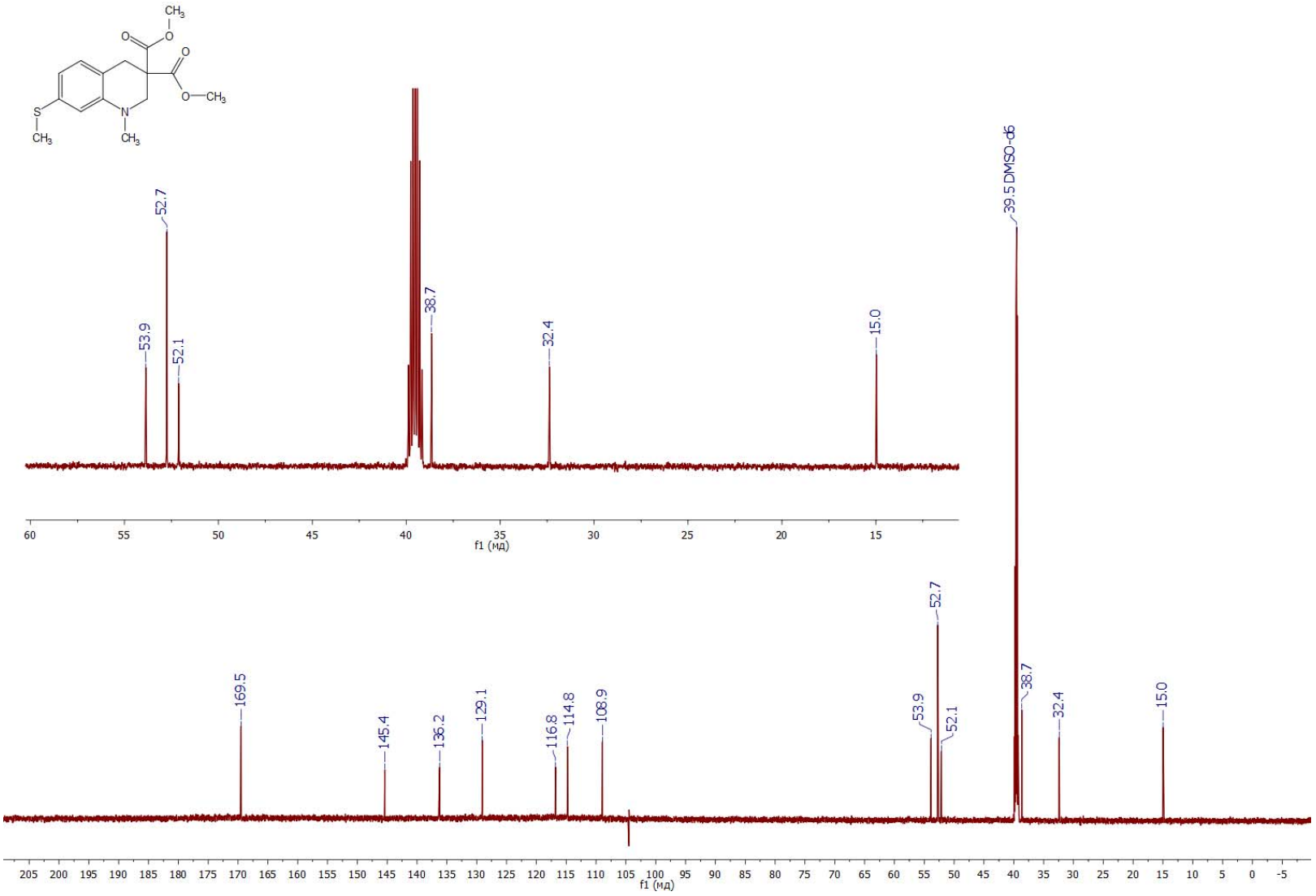


* The peak at 105 ppm is an artifact at exact center of spectrum

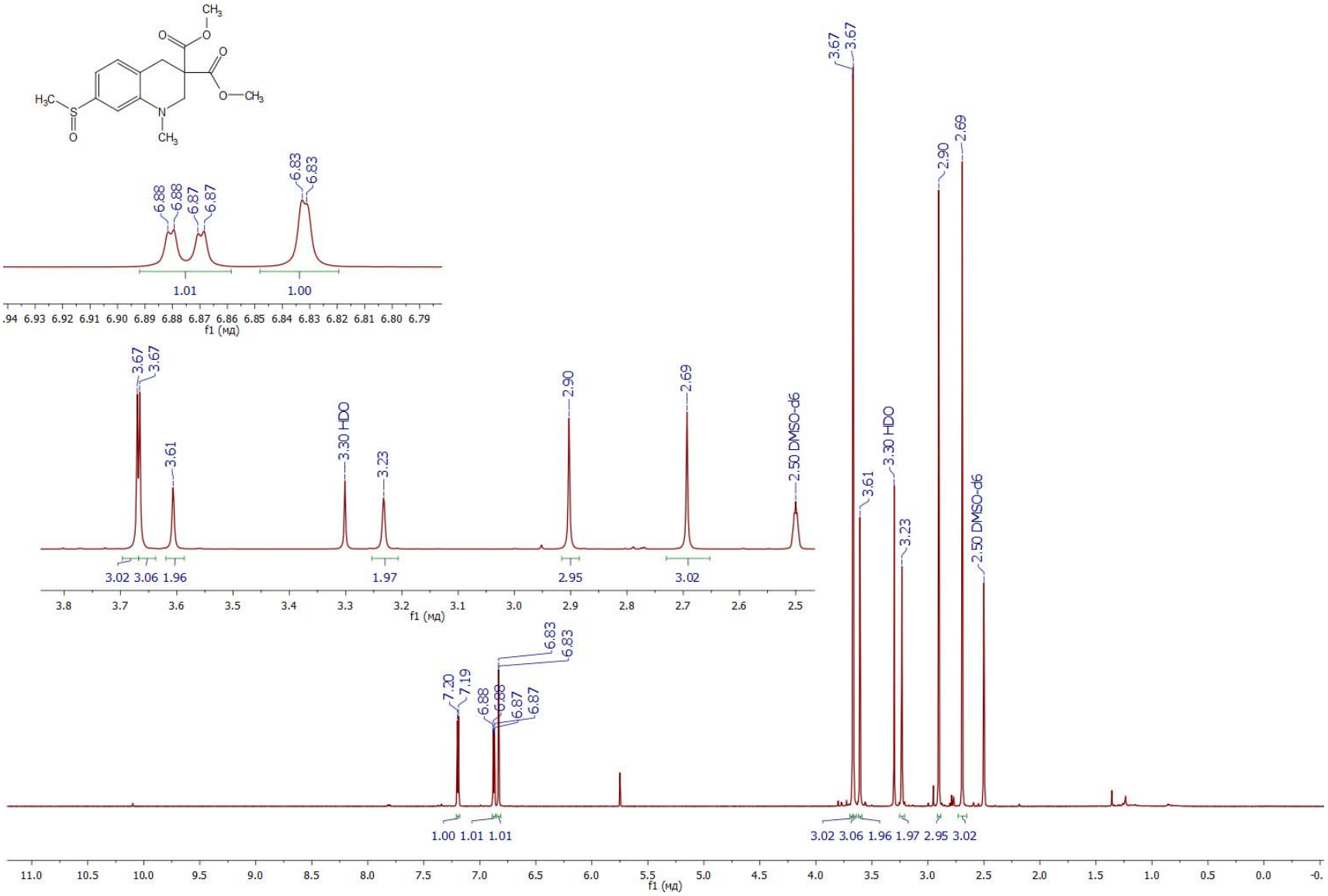

F
F
F
H3C
N
O
H3C
O
O
O
CH3
7.26 CDCl3
7.11
7.10
6.91
6.90
6.76
3.74
3.66
3.31
2.95
1.00
1.00
1.00
1.00
1.00
1.00
5.98
2.00
2.00
3.00
f1 (мд)

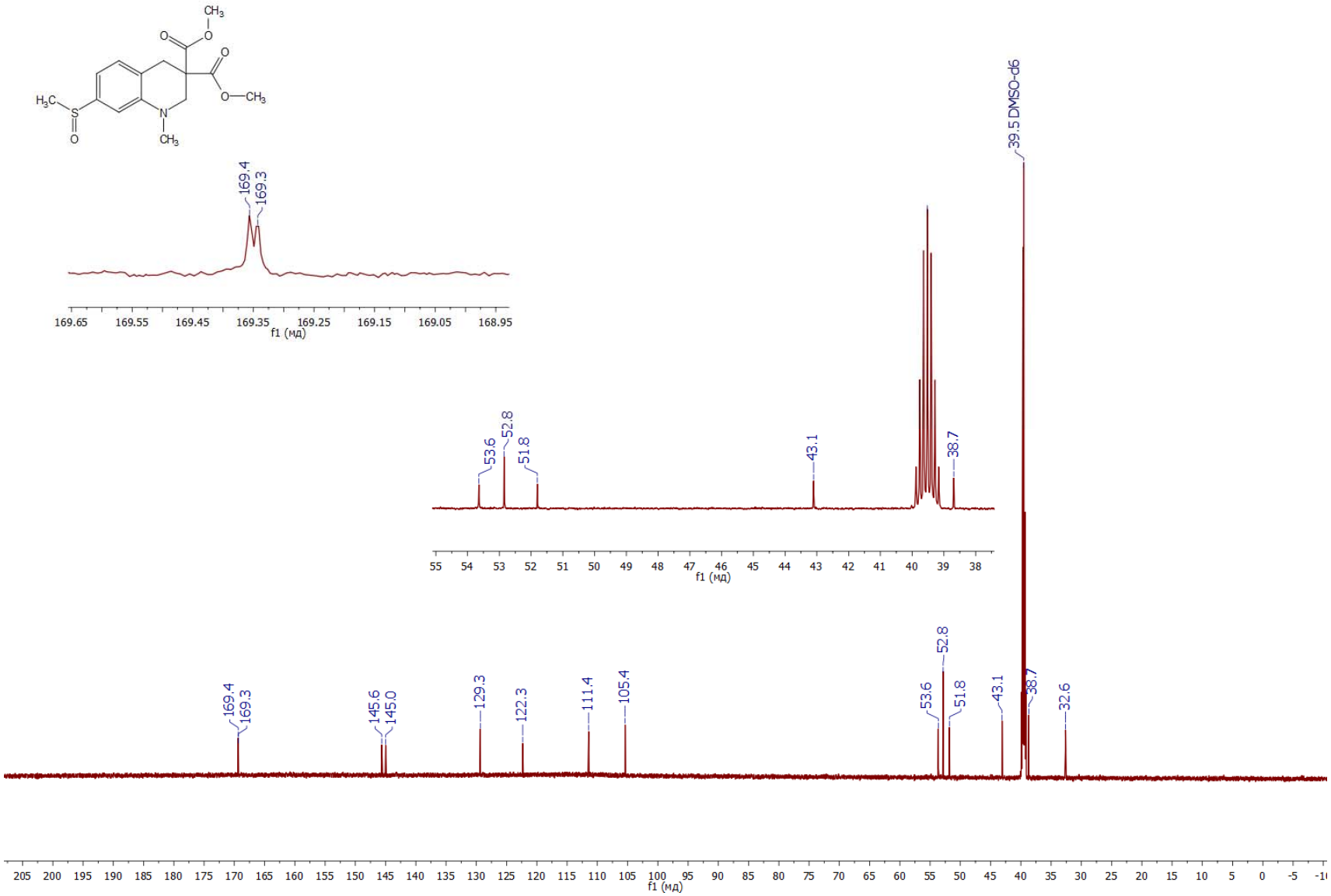

77.2 CDCl3
170.0
145.3
129.3
130.2
130.0
129.8
129.6
126.9
125.4
123.8
123.4
122.3
113.8
107.6
54.5
53.1
52.6
39.1
33.6
F
F
F
H3C
N
O
O
O
O
H3C
CH3
f1 (мд)

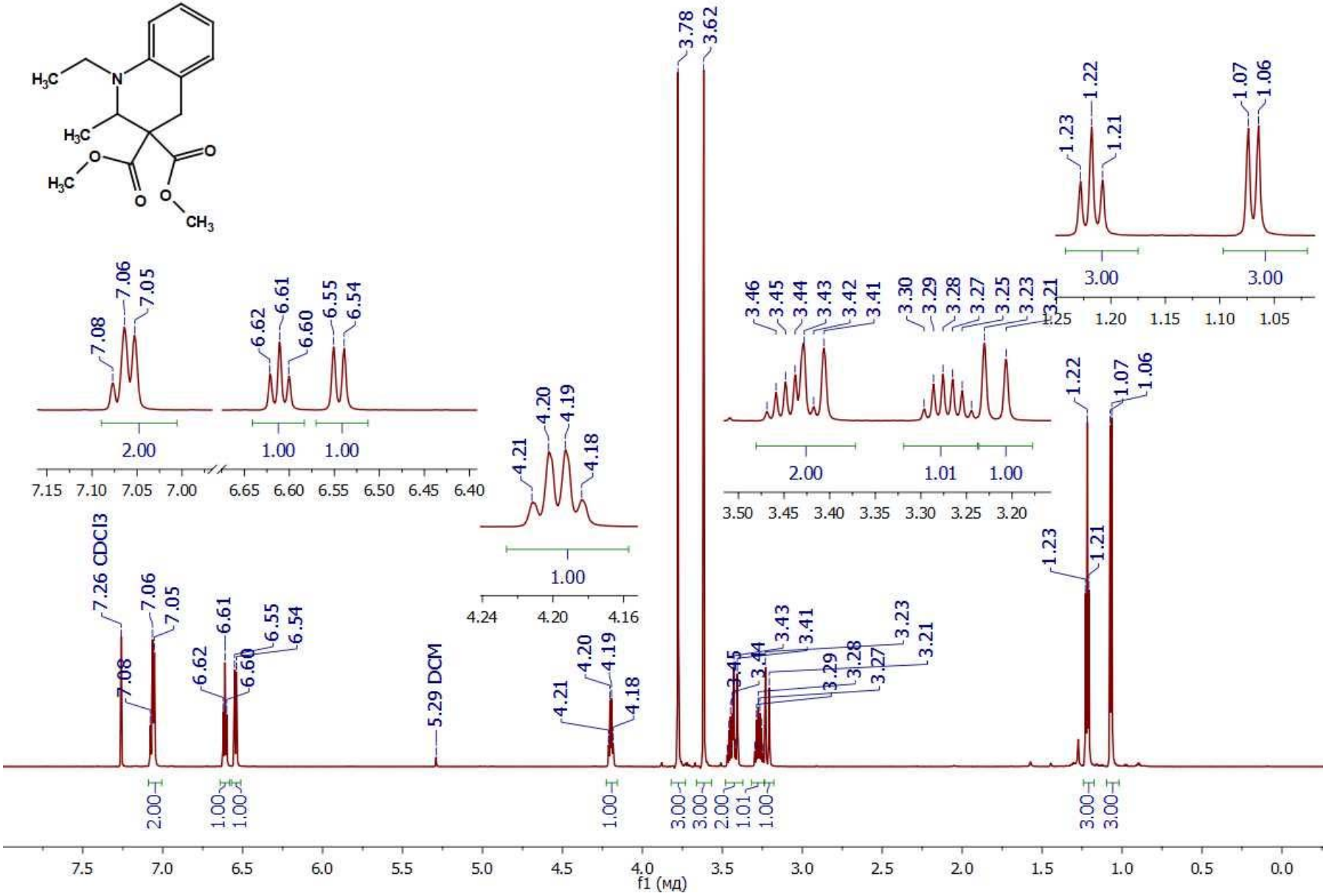

3.65
3.30 HDO
2.84
2.50 DMSO-d6
2.42
3.53
3.13
6.95
6.94
6.52
6.52
6.51
6.51
6.44
6.44
1.00 1.00 0.99
6.23 2.07 2.05 3.05 3.08
f1 (мд)

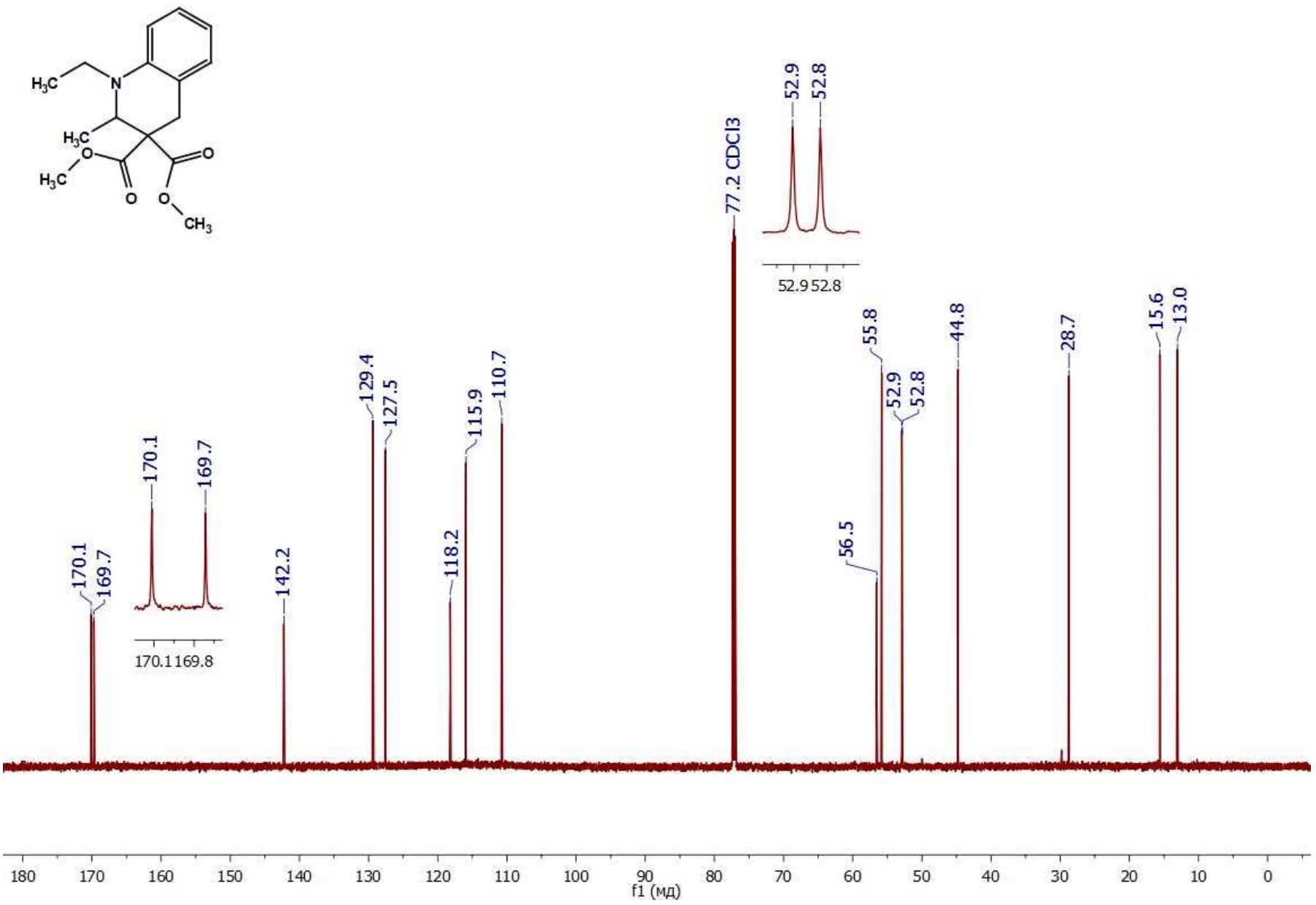


* The inverted peak at 105 ppm is an artifact at exact center of spectrum


3.67
3.67
2.90
2.69
3.61
3.30 HDO
3.23
2.50 DMSO-d6
6.83
6.83
6.88
6.88
6.87
6.87
7.20
7.19
1.00 1.01 1.01
3.02 3.06 1.96 1.97 2.95 3.02
f1 (мд)


CH3
O
O
O
O
O—CH3
H3C
S
O
N
CH3
169.4
169.3
169.65 169.55 169.45 169.35 169.25 169.15 169.05 168.95
f1 (мд)
39.5 DMSO-d6
53.6
52.8
51.8
43.1
38.7
55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38
f1 (мд)
169.4
169.3
145.6
145.0
129.3
122.3
111.4
105.4
53.6
52.8
51.8
43.1
38.7
32.6
205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (мд)


H3C
N
H3C
O
H3C
O
O
O
O
CH3
7.26 CDCl3
7.08
7.06
7.05
6.62
6.61
6.60
6.55
6.54
5.29 DCM
4.21
4.20
4.19
4.18
3.78
3.62
3.46
3.45
3.44
3.43
3.42
3.41
3.30
3.29
3.28
3.27
3.25
3.23
3.21
1.23
1.22
1.21
1.07
1.06
2.00
1.00
1.00
1.00
3.00
3.00
2.00
1.01
1.00
3.00
3.00
f1 (мд)


H3C
N
H3C
O
H3C
O
O
O
O
CH3
77.2 CDCl3
52.9
52.8
52.9 52.8
170.1
169.7
170.1 169.8
142.2
129.4
127.5
118.2
115.9
110.7
56.5
55.8
52.9
52.8
44.8
28.7
15.6
13.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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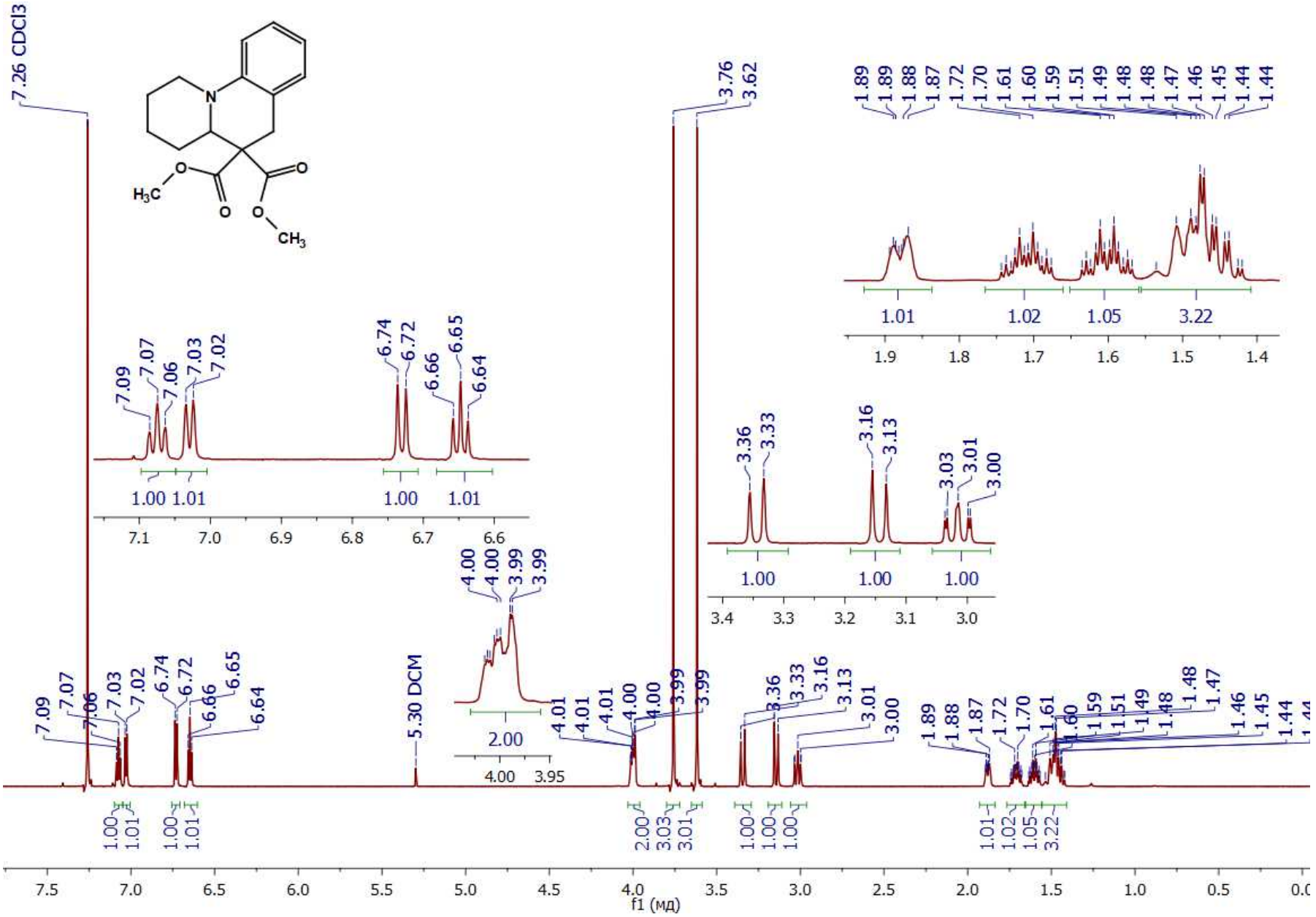
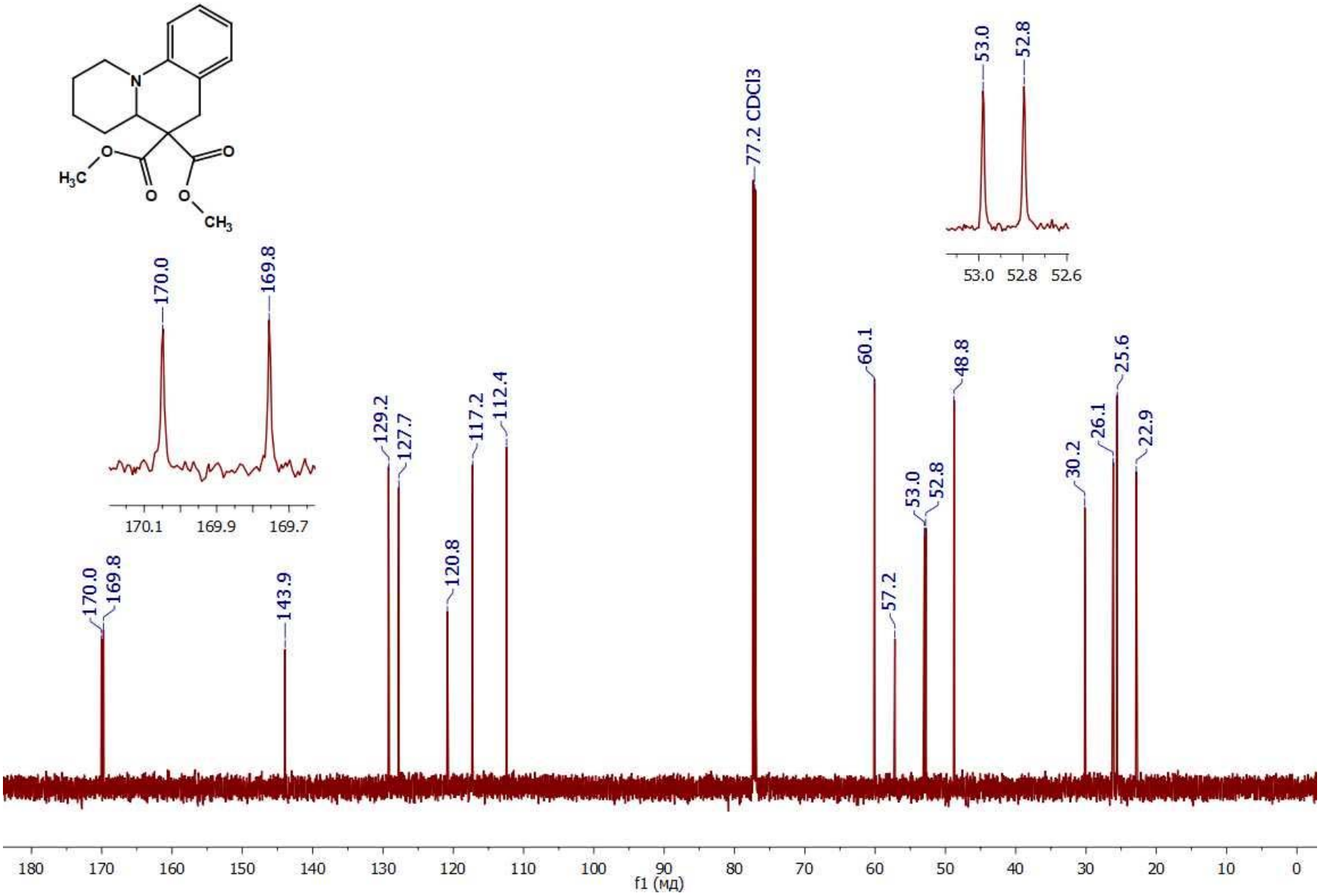
0
f1 (мд)


7.26 CDCl3
5.30 DCM
f1 (мд)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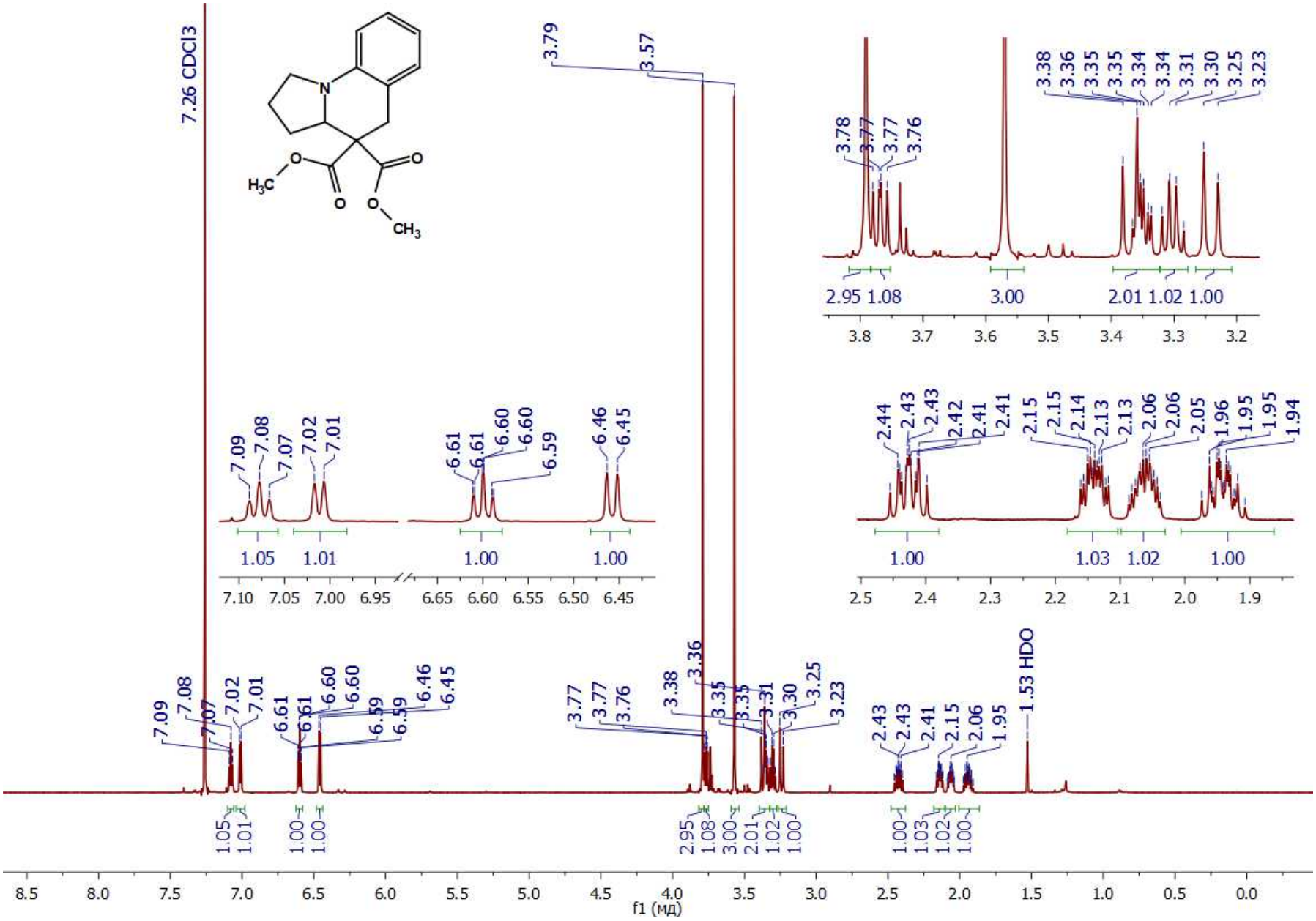
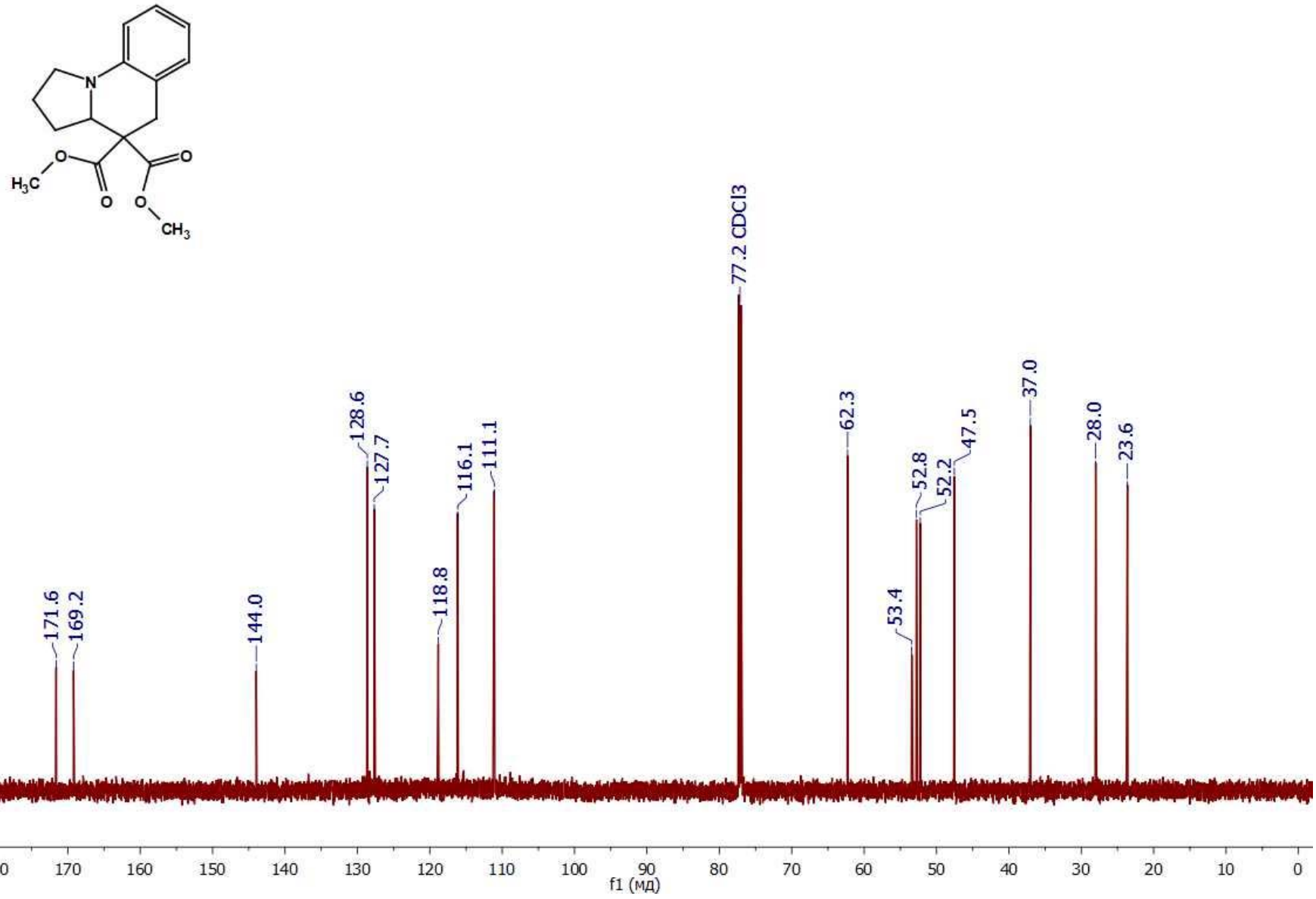
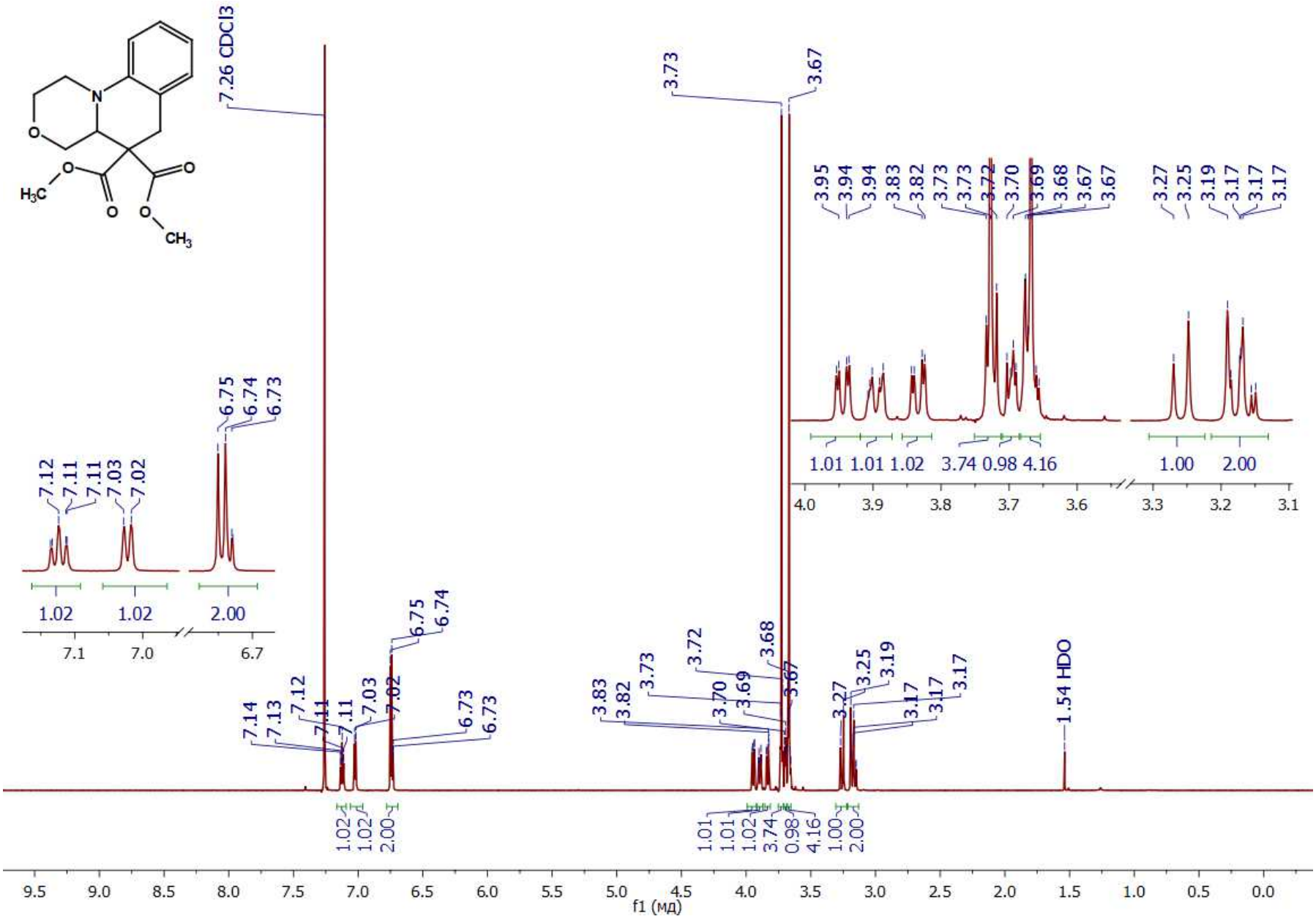
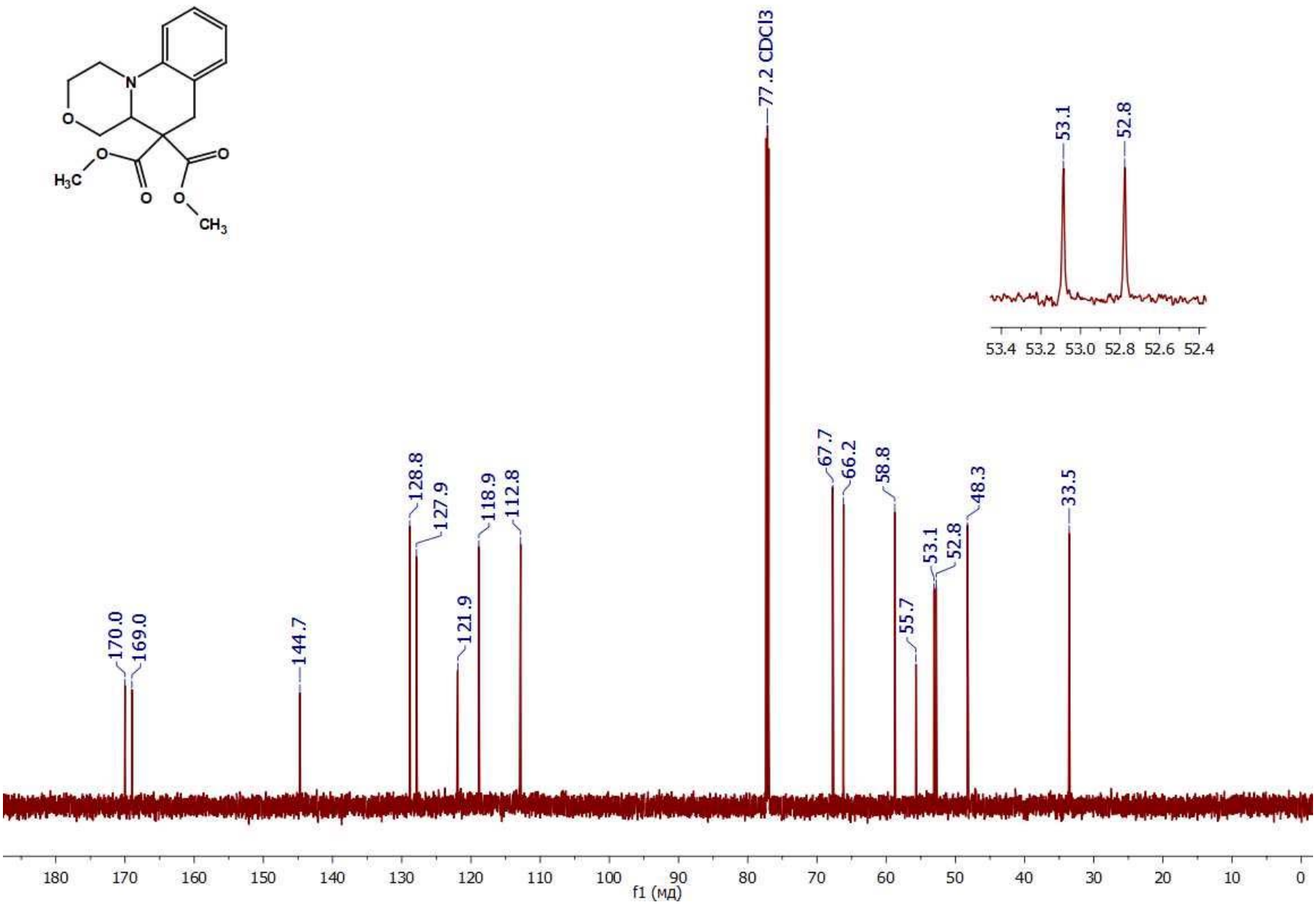
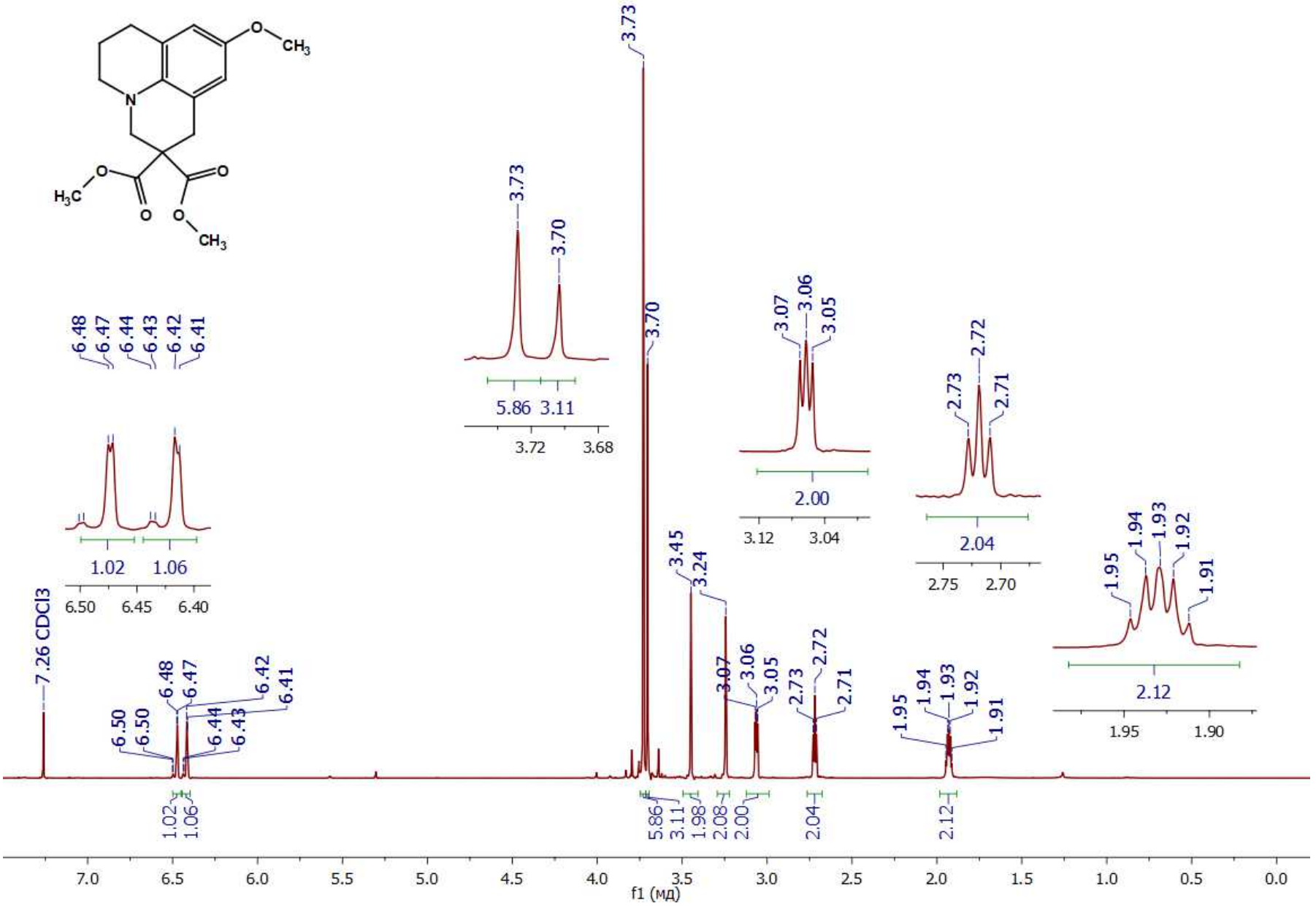
O
O
O
O
H_3C
CH_3
170.0
169.8
170.1
169.9
169.7
53.0
52.8
53.0
52.8
52.6
77.2 CDCl3
129.2
127.7
120.8
117.2
112.4
143.9
60.1
57.2
53.0
52.8
48.8
30.2
26.1
25.6
22.9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

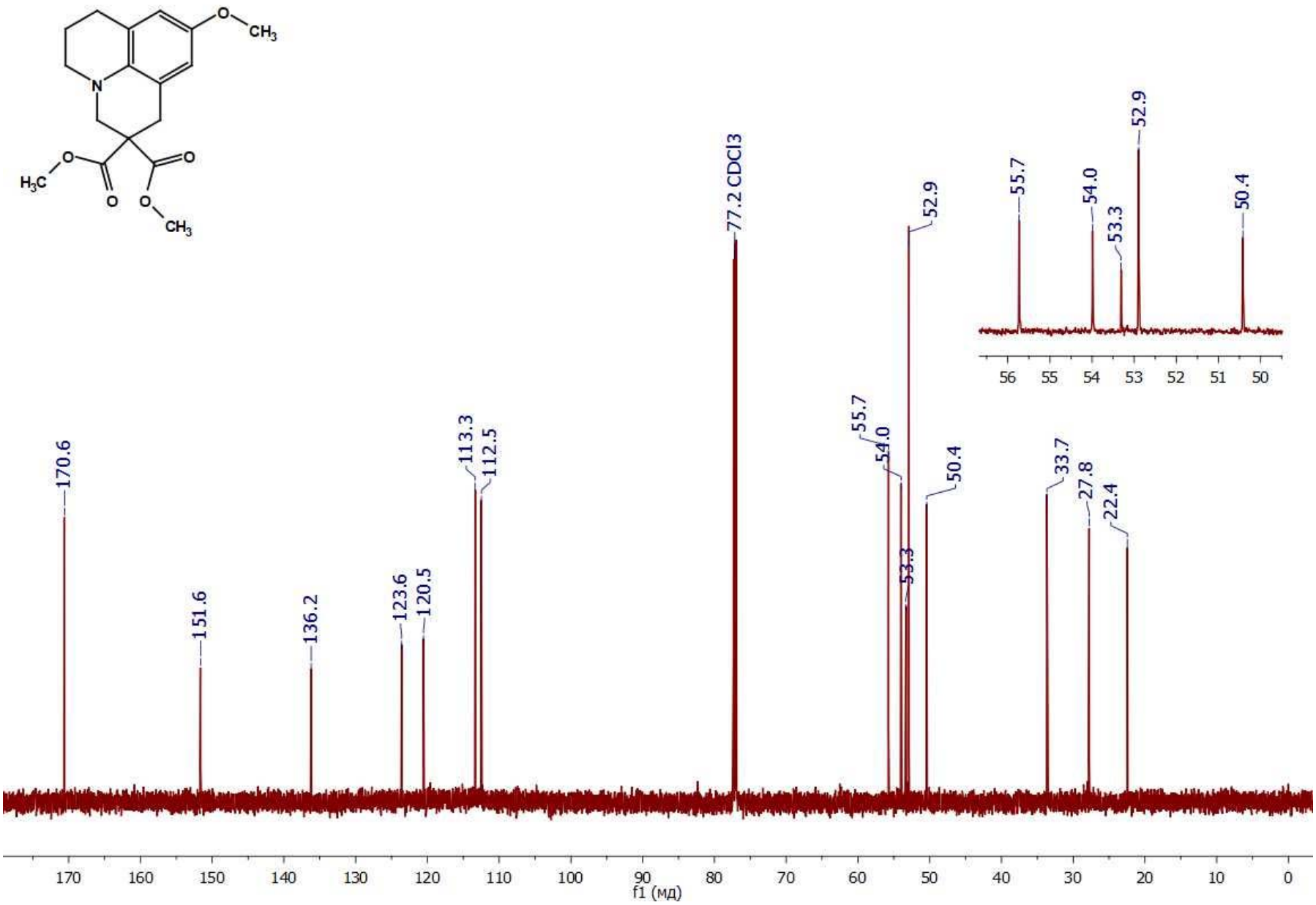

7.26 CDCl3
3.79
3.57
1.53 HDO
f1 (мд)

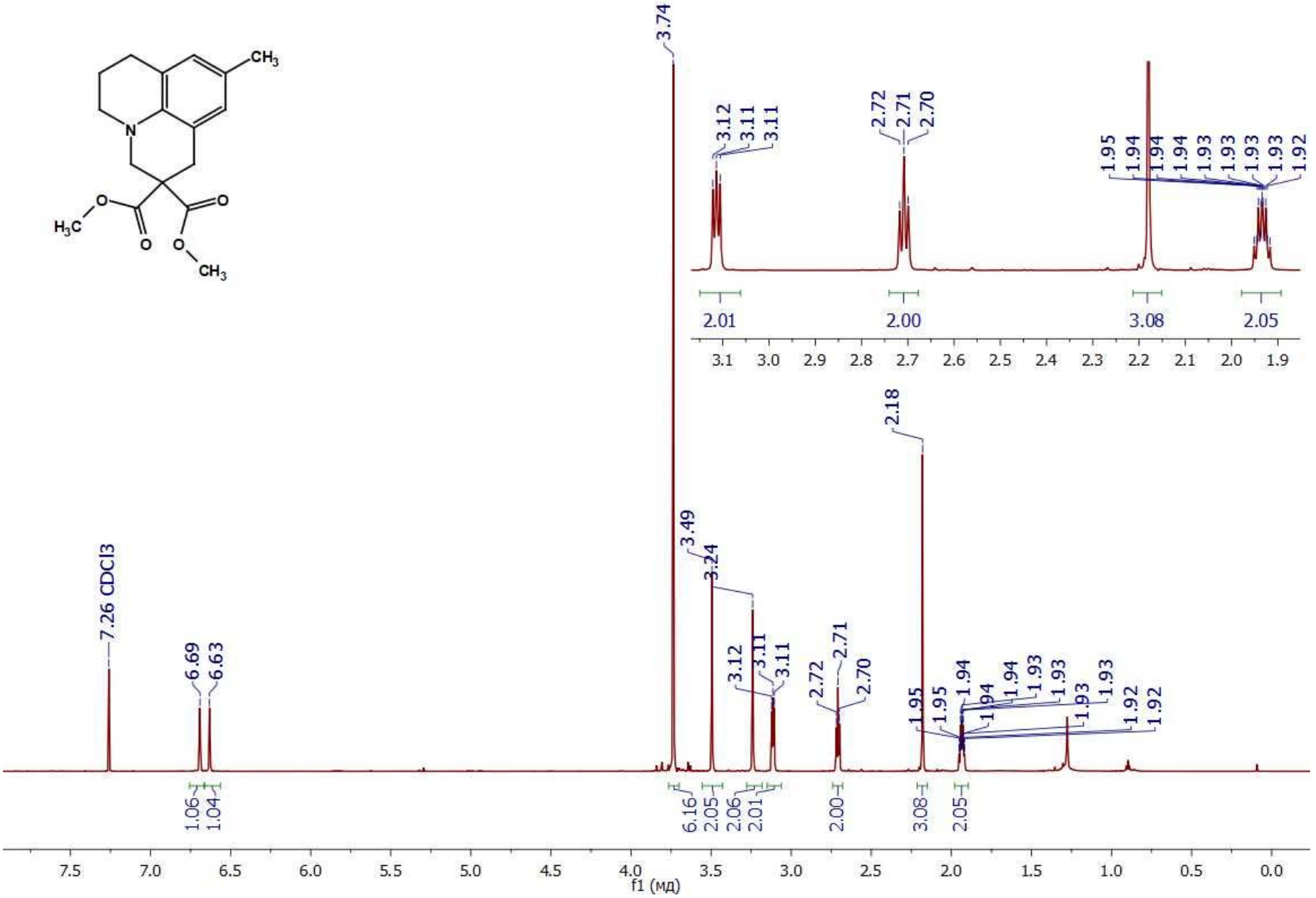

N
O
O
O
O
O
H_3C
CH_3
171.6
169.2
144.0
128.6
127.7
118.8
116.1
111.1
77.2 CDCl3
62.3
53.4
52.8
52.2
47.5
37.0
28.0
23.6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


7.26 CDCl3
3.73
3.67
1.54 HDO
f1 (мд)


77.2 CDCl3
53.1
52.8
53.4 53.2 53.0 52.8 52.6 52.4
170.0
169.0
144.7
128.8
127.9
121.9
118.9
112.8
67.7
66.2
58.8
55.7
53.1
52.8
48.3
33.5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)


O
CH3
N
O
H3C
O
O
O
CH3
7.26 CDCl3
6.50
6.50
6.48
6.47
6.44
6.43
6.42
6.41
3.73
3.70
3.45
3.24
3.07
3.06
3.05
2.73
2.72
2.71
1.95
1.94
1.93
1.92
1.91
1.02
1.06
5.86
3.11
1.98
2.08
2.00
2.04
2.12
f1 (мд)


O
CH3
N
O
H3C
O
O
O
O
CH3
170.6
151.6
136.2
123.6
120.5
113.3
112.5
77.2 CDCl3
55.7
54.0
53.3
52.9
50.4
33.7
27.8
22.4
f1 (мд)


CH3
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O
H3C
O
O
O
CH3
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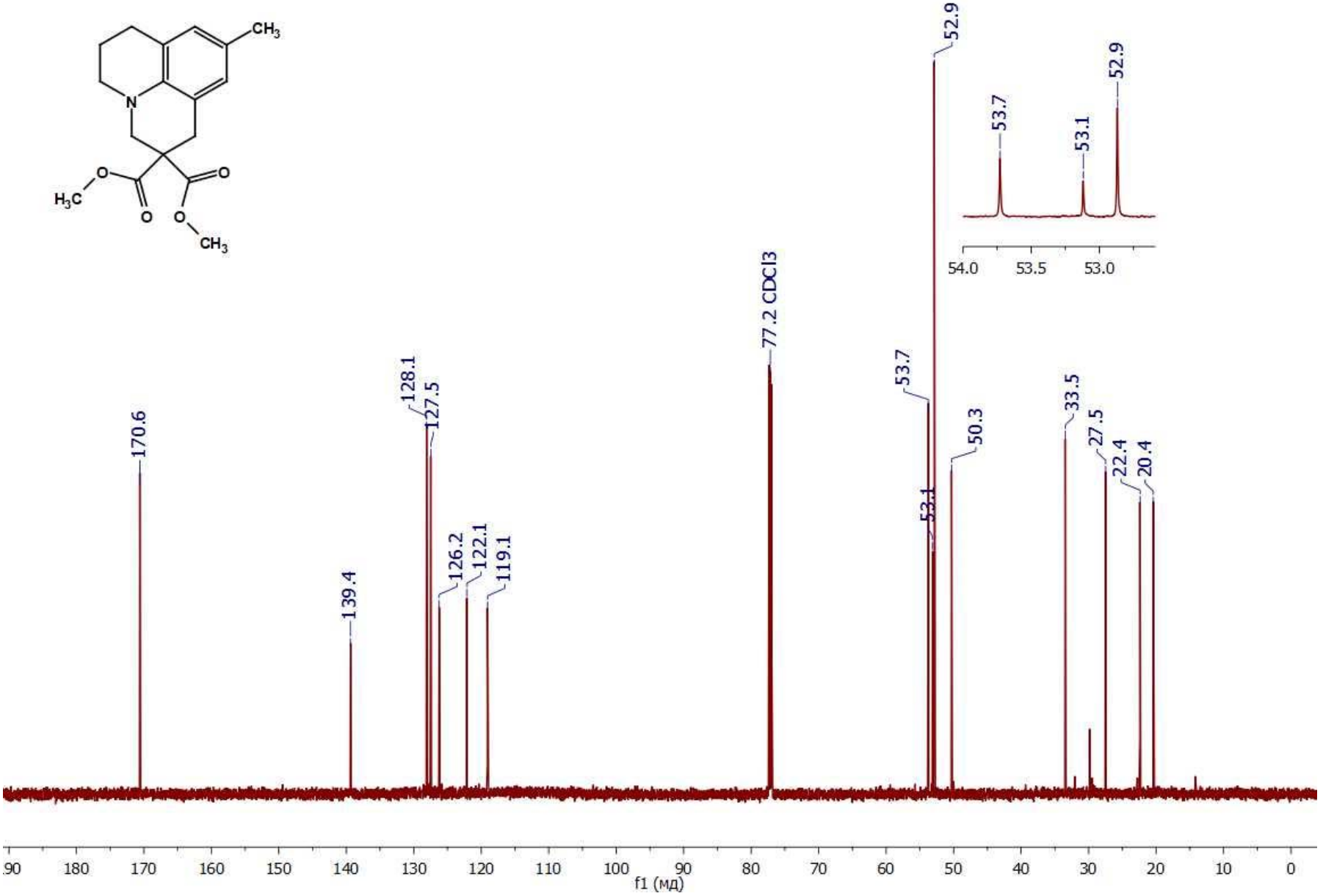
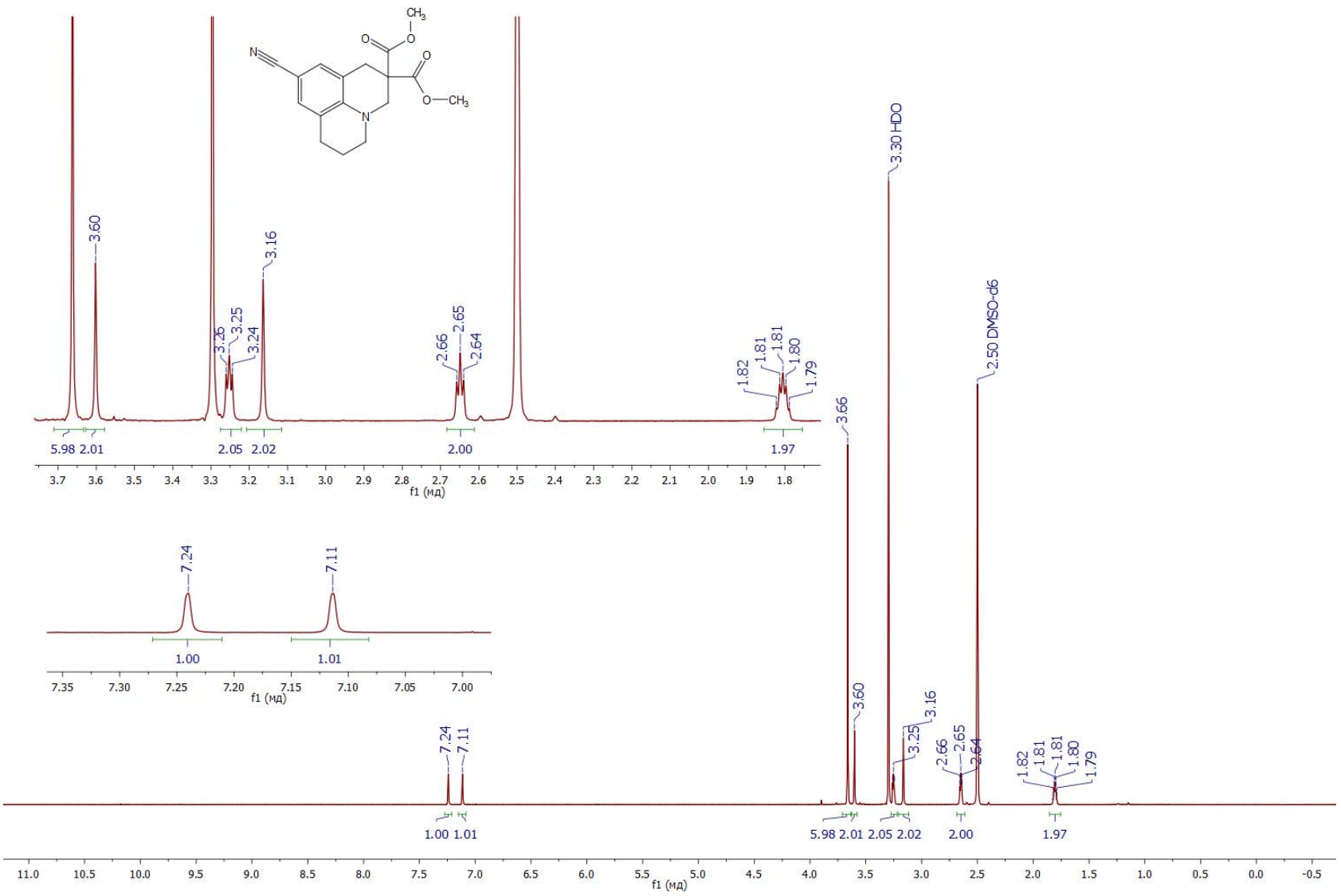
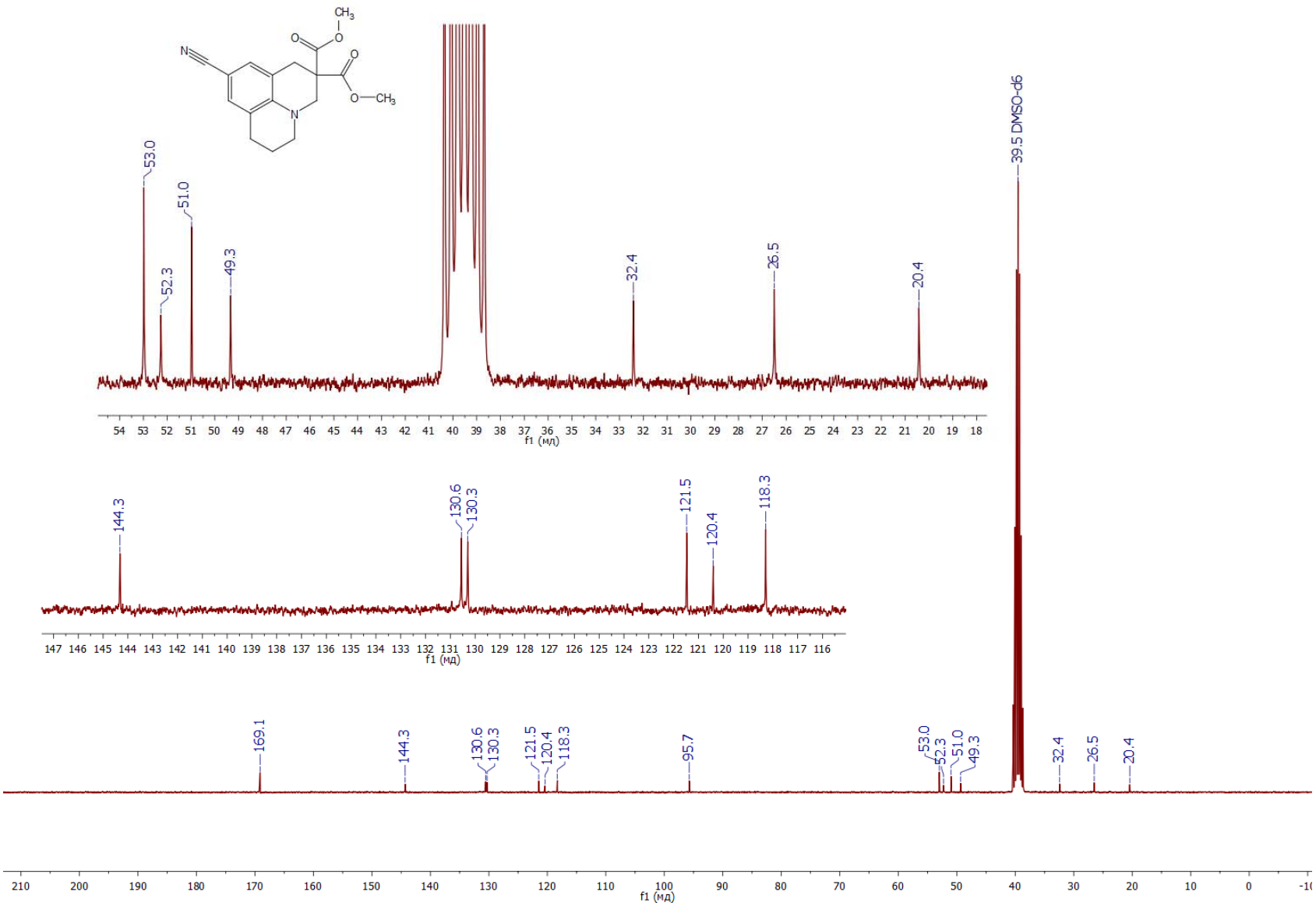
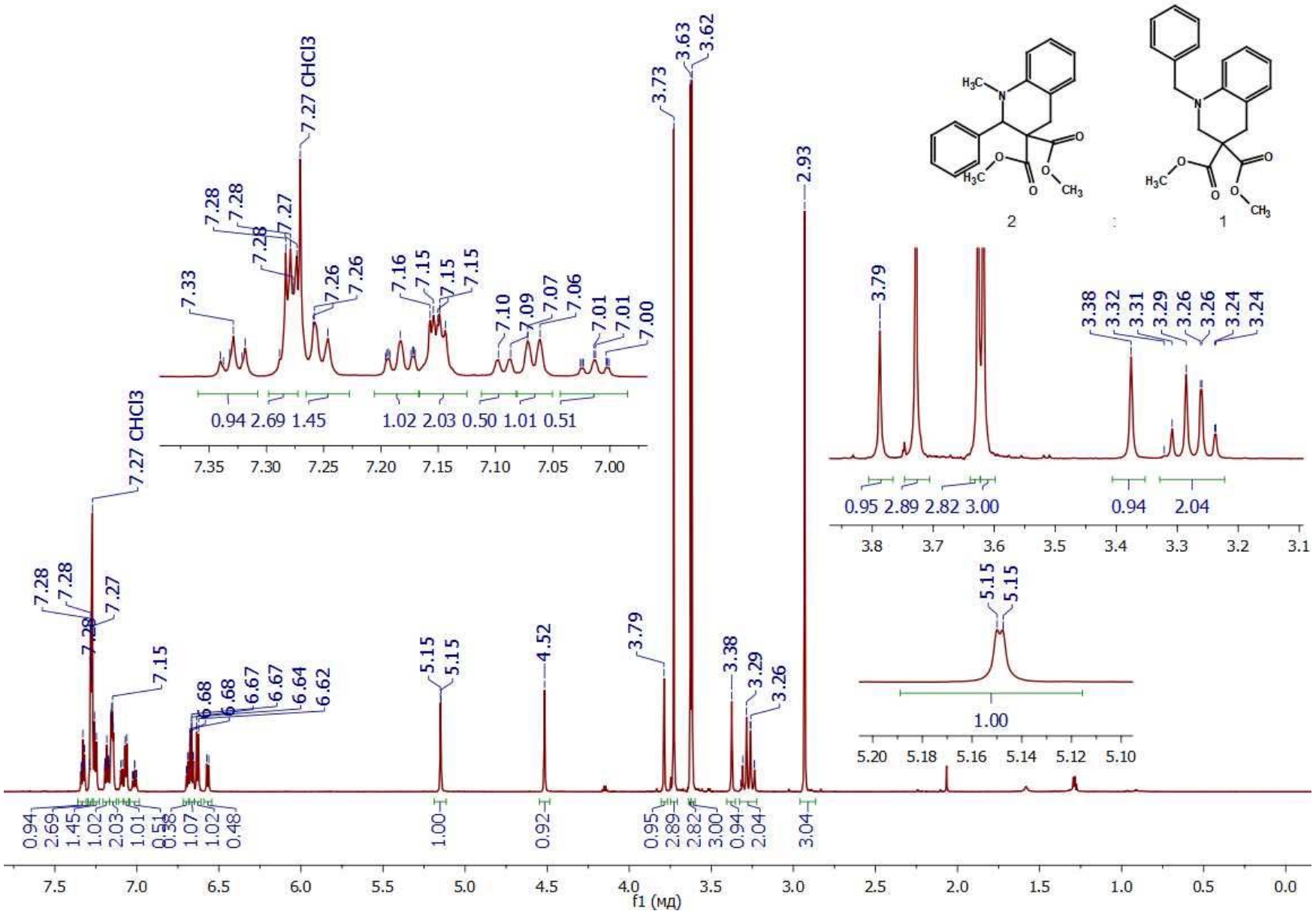
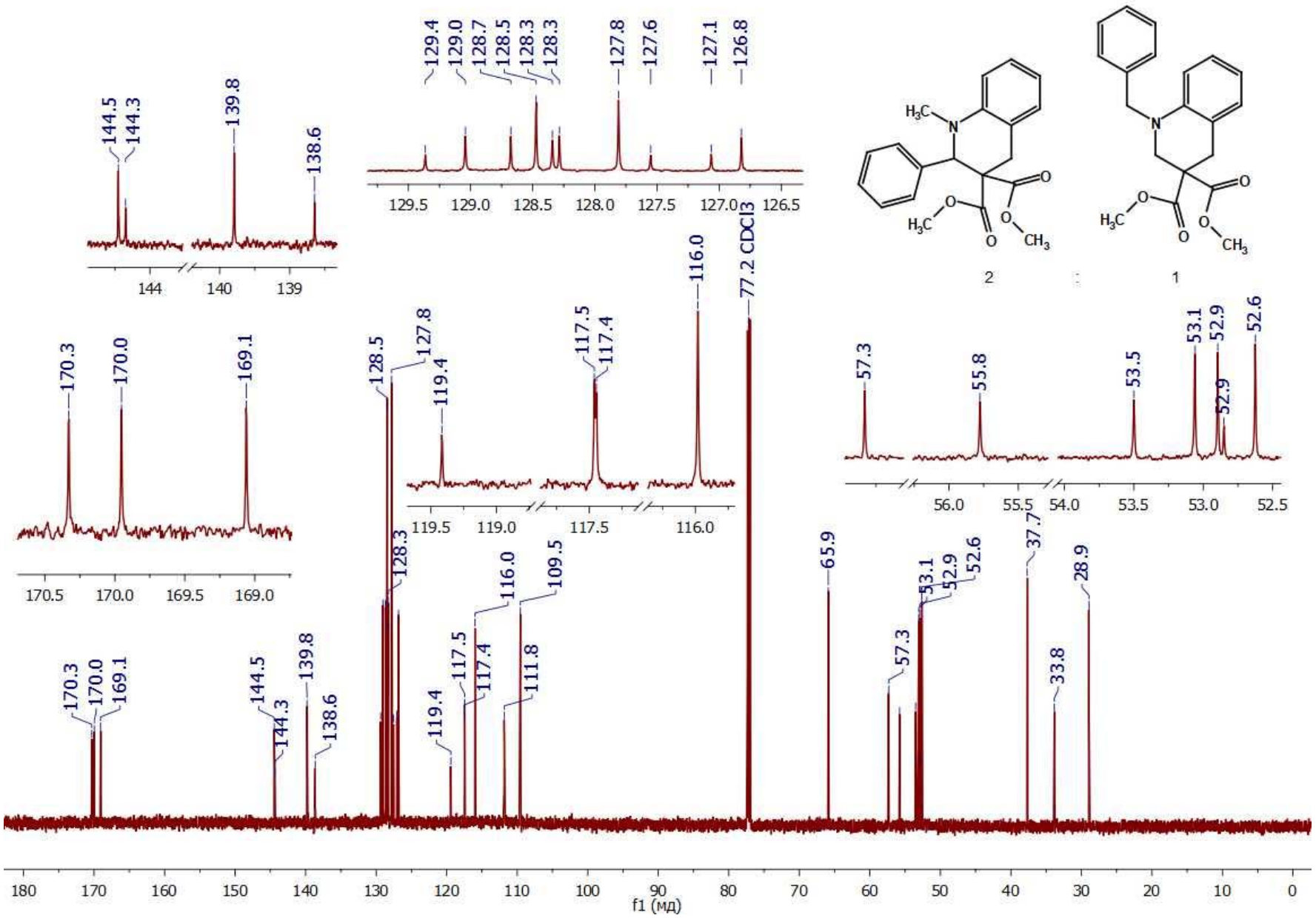
3.12
3.11
3.11
2.72
2.71
2.70
1.95
1.94
1.94
1.94
1.93
1.93
1.93
1.93
1.92
2.01
2.00
3.08
2.05
3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
2.18
7.26 CDCl3
6.69
6.63
3.49
3.24
3.12
3.11
3.11
2.72
2.71
2.70
1.95
1.95
1.94
1.94
1.94
1.93
1.93
1.93
1.93
1.92
1.92
1.06
1.04
6.16
2.05
2.06
2.01
2.00
3.08
2.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)

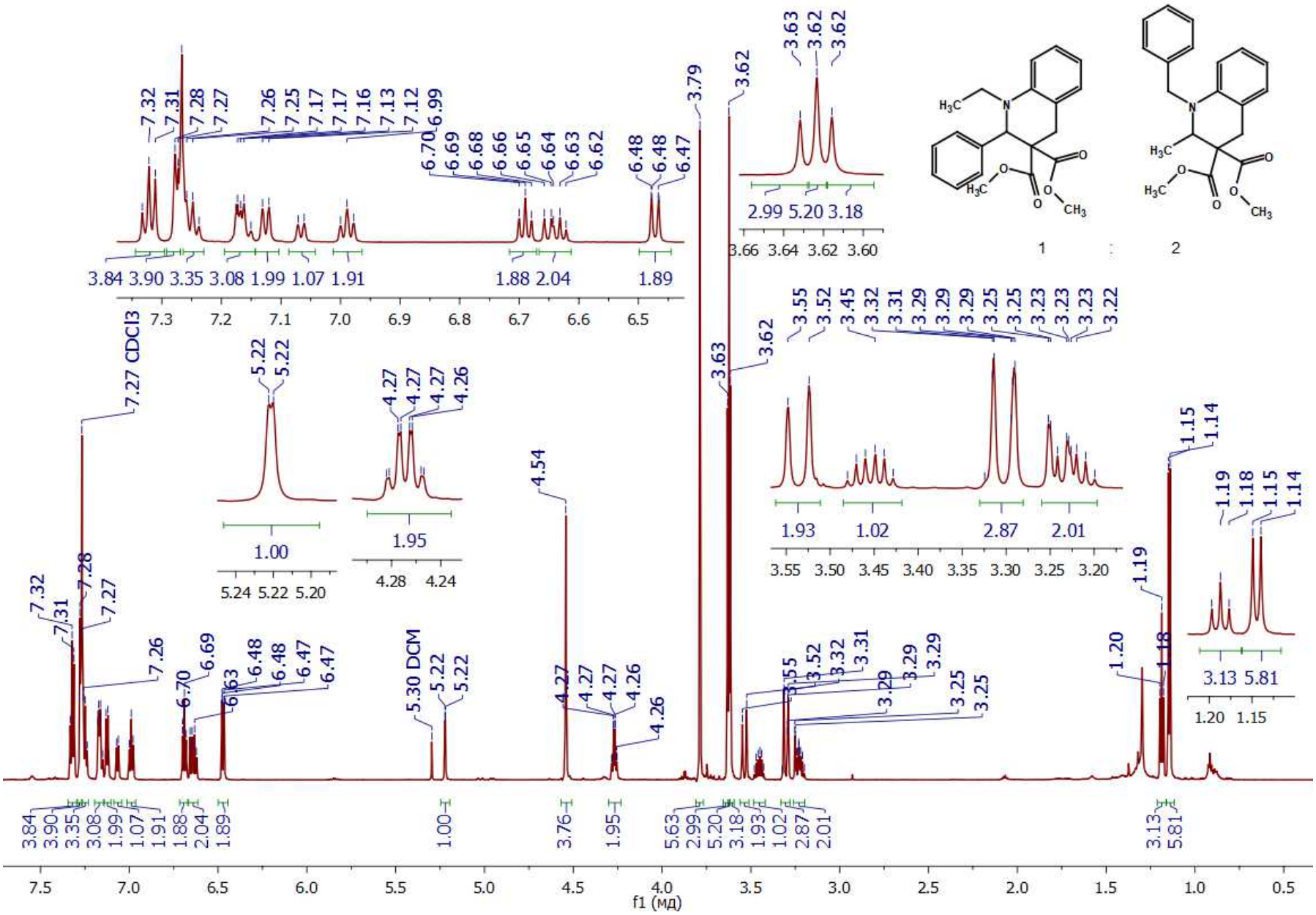

CH3
N
O
H3C
O
O
O
O
CH3
52.9
53.7
53.1
52.9
54.0
53.5
53.0
77.2 CDCl3
170.6
139.4
128.1
127.5
126.2
122.1
119.1
53.7
53.1
52.9
50.3
33.5
27.5
22.4
20.4
f1 (мд)

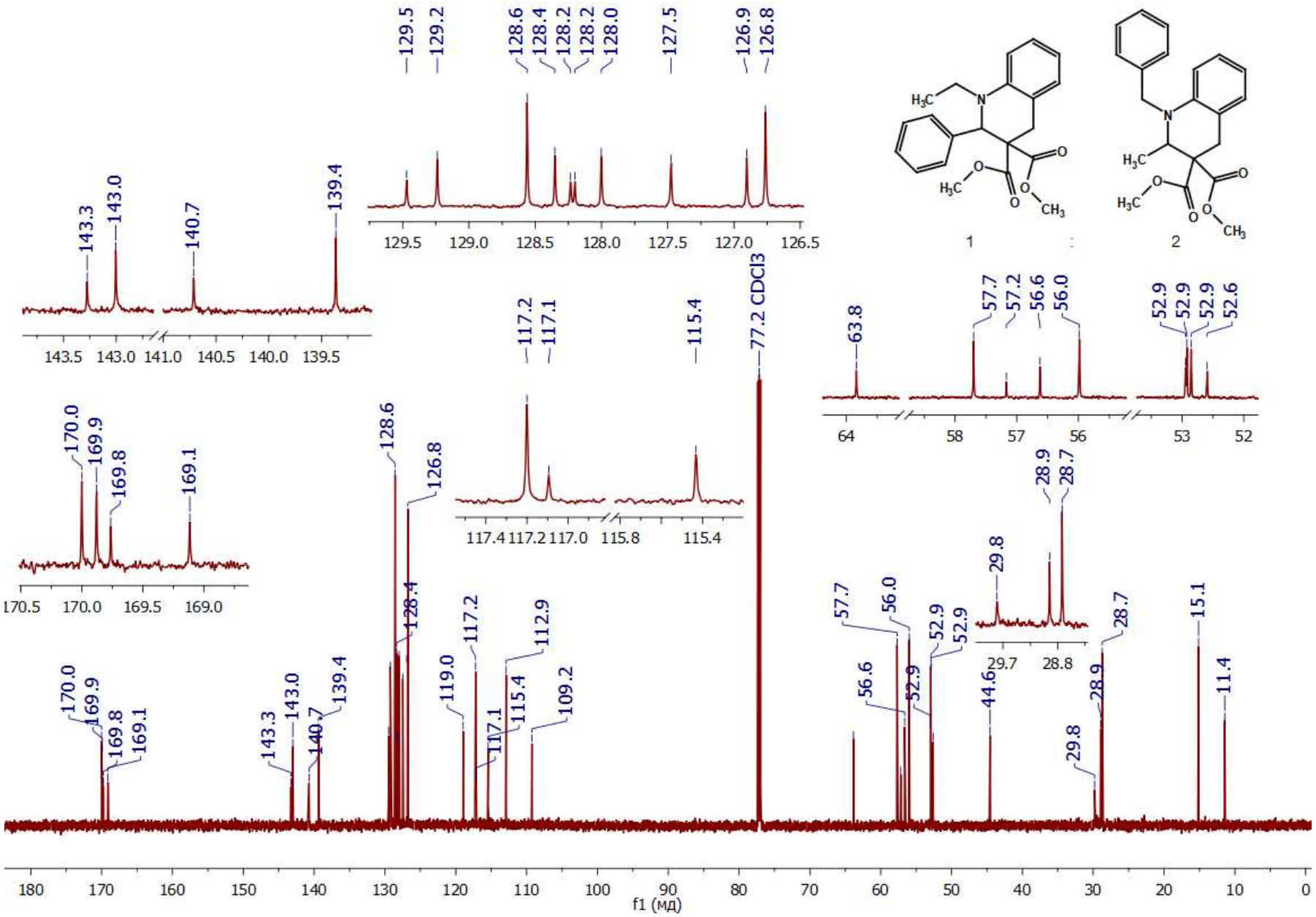

CH3
O
O
O
O
O—CH3
N
N
3.60
3.16
3.26
3.25
3.24
2.66
2.65
2.64
1.82
1.81
1.81
1.80
1.79
3.66
3.30 HDO
2.50 DMSO-d6
5.98 2.01
2.05 2.02
2.00
1.97
f1 (мд)
7.24
7.11
1.00
1.01
f1 (мд)
7.24
7.11
1.00 1.01
5.98 2.01 2.05 2.02
2.00
1.97
f1 (мд)


CH3
O
O
O
O
O—CH3
N
N
53.0
52.3
51.0
49.3
32.4
26.5
20.4
39.5 DMSO-d6
f1 (мл)
144.3
130.6
130.3
121.5
120.4
118.3
f1 (мд)
169.1
144.3
130.6
130.3
121.5
120.4
118.3
95.7
53.0
52.3
51.0
49.3
32.4
26.5
20.4
f1 (мд)


7.27 CHCl3
7.28
7.28
7.28
7.27
7.33
7.26
7.26
7.16
7.15
7.15
7.15
7.10
7.09
7.07
7.06
7.01
7.01
7.00
0.94 2.69 1.45 1.02 2.03 0.50 1.01 0.51
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
7.27 CHCl3
7.28
7.28
7.27
7.28
7.15
6.68
6.68
6.67
6.67
6.64
6.62
5.15
5.15
4.52
3.79
3.73
3.63
3.62
3.38
3.29
3.26
2.93
0.94 2.69 1.45 1.02 2.03 1.01 0.51 0.38 1.07 1.02 0.48
1.00
0.92
0.95 2.89 2.82 3.00 0.94 2.04
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)
3.79
3.38
3.32
3.31
3.29
3.26
3.26
3.24
3.24
0.95 2.89 2.82 3.00
0.94 2.04
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
5.15
5.15
1.00
5.20 5.18 5.16 5.14 5.12 5.10
2
1


144.5
144.3
139.8
138.6
129.4
129.0
128.7
128.5
128.3
128.3
127.8
127.6
127.1
126.8
170.3
170.0
169.1
128.5
127.8
119.4
117.5
117.4
116.0
77.2 CDCl3
57.3
55.8
53.5
53.1
52.9
52.9
52.6
2
1
170.3
170.0
169.1
144.5
144.3
139.8
138.6
128.5
128.3
119.4
117.5
117.4
116.0
111.8
109.5
65.9
57.3
53.1
52.9
52.6
37.7
33.8
28.9
f1 (мд)


7.27 CDCl3
5.30 DCM
4.54
3.79
3.62
3.63
1
2
f1 (мд)


129.5
129.2
128.6
128.4
128.2
128.2
128.0
127.5
126.9
126.8
143.3
143.0
140.7
139.4
117.2
117.1
115.4
77.2 CDCl3
63.8
57.7
57.2
56.6
56.0
52.9
52.9
52.9
52.6
170.0
169.9
169.8
169.1
128.6
126.8
128.4
119.0
117.2
112.9
115.4
109.2
117.1
57.7
56.0
52.9
52.9
56.6
52.9
44.6
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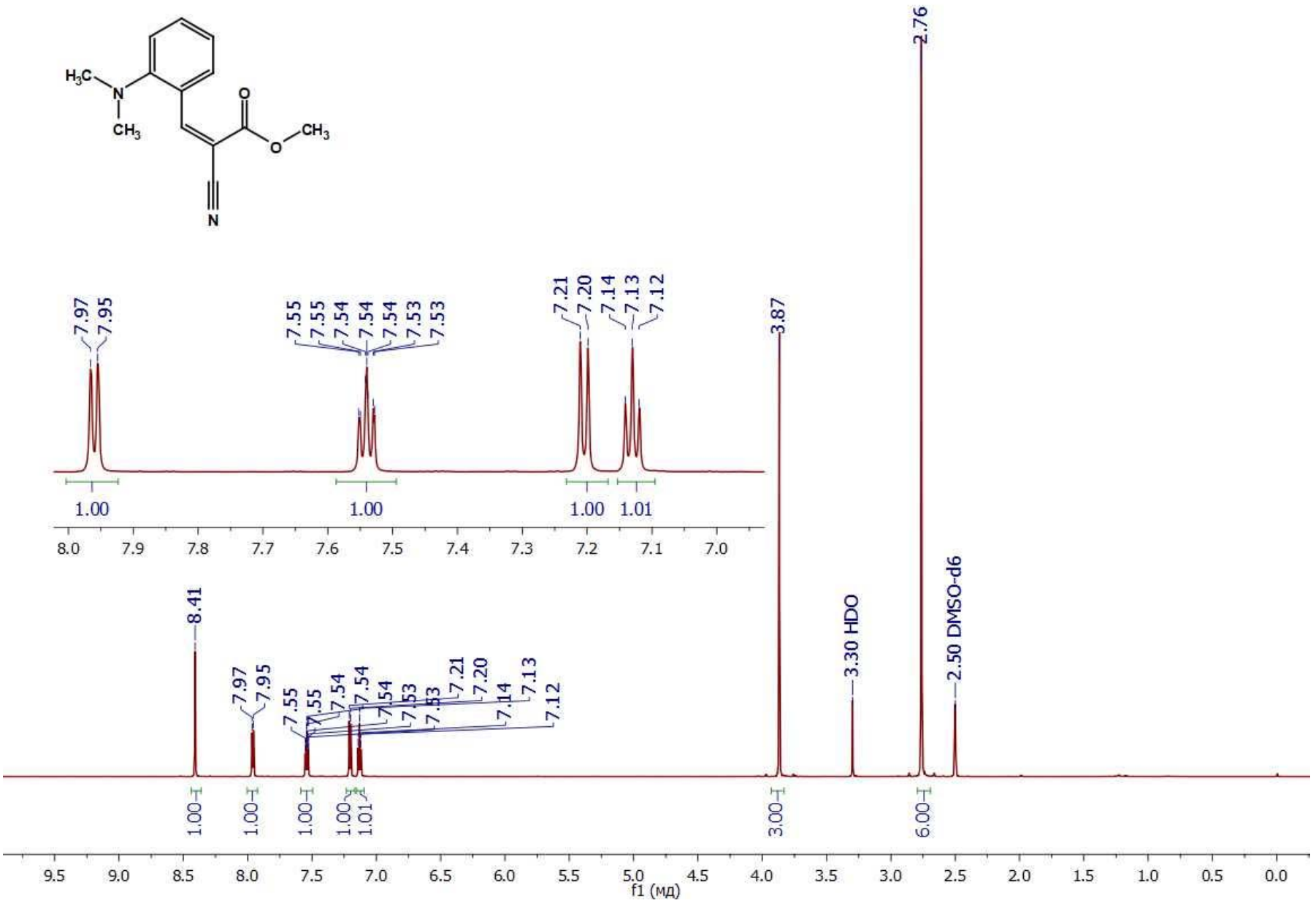
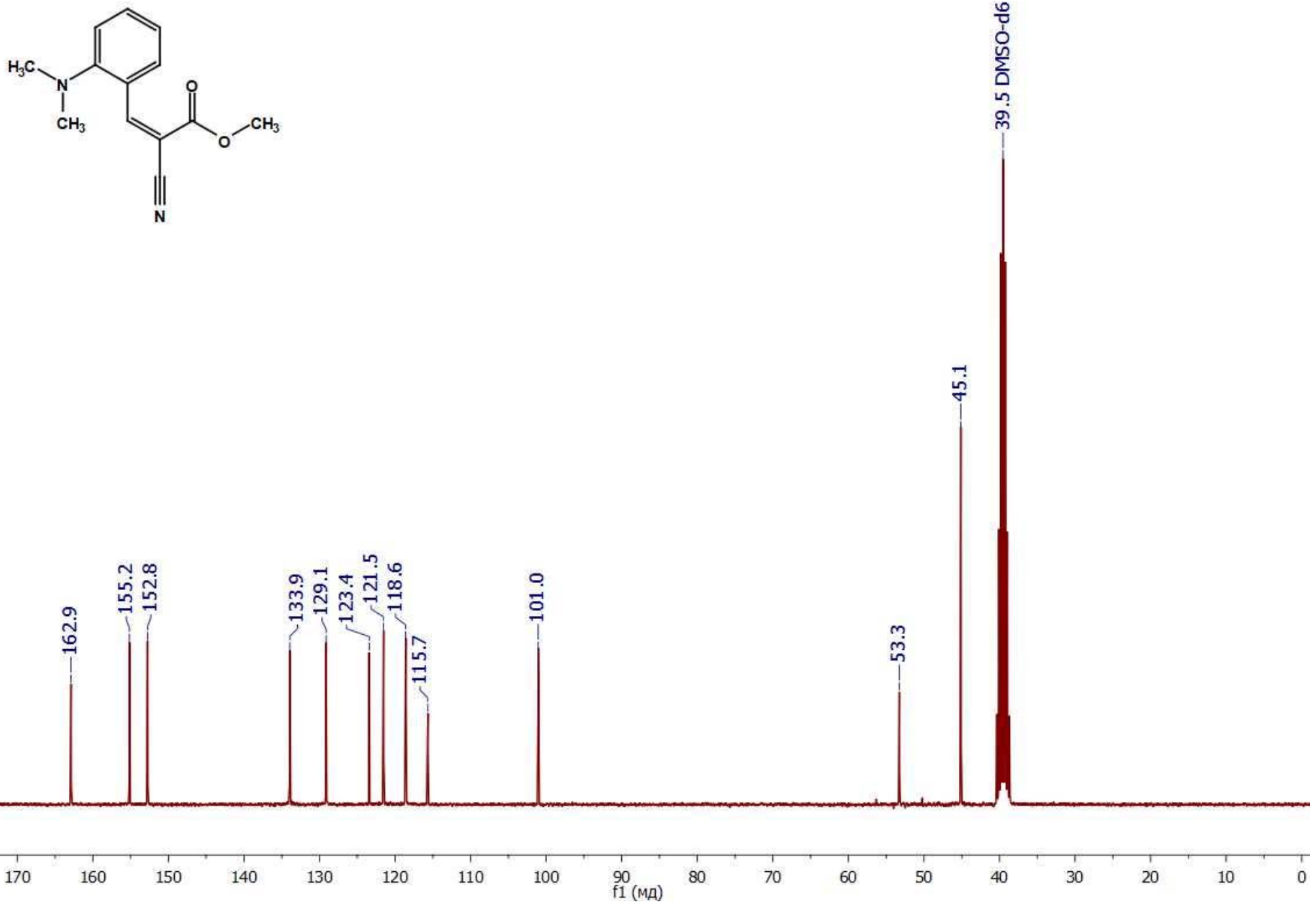
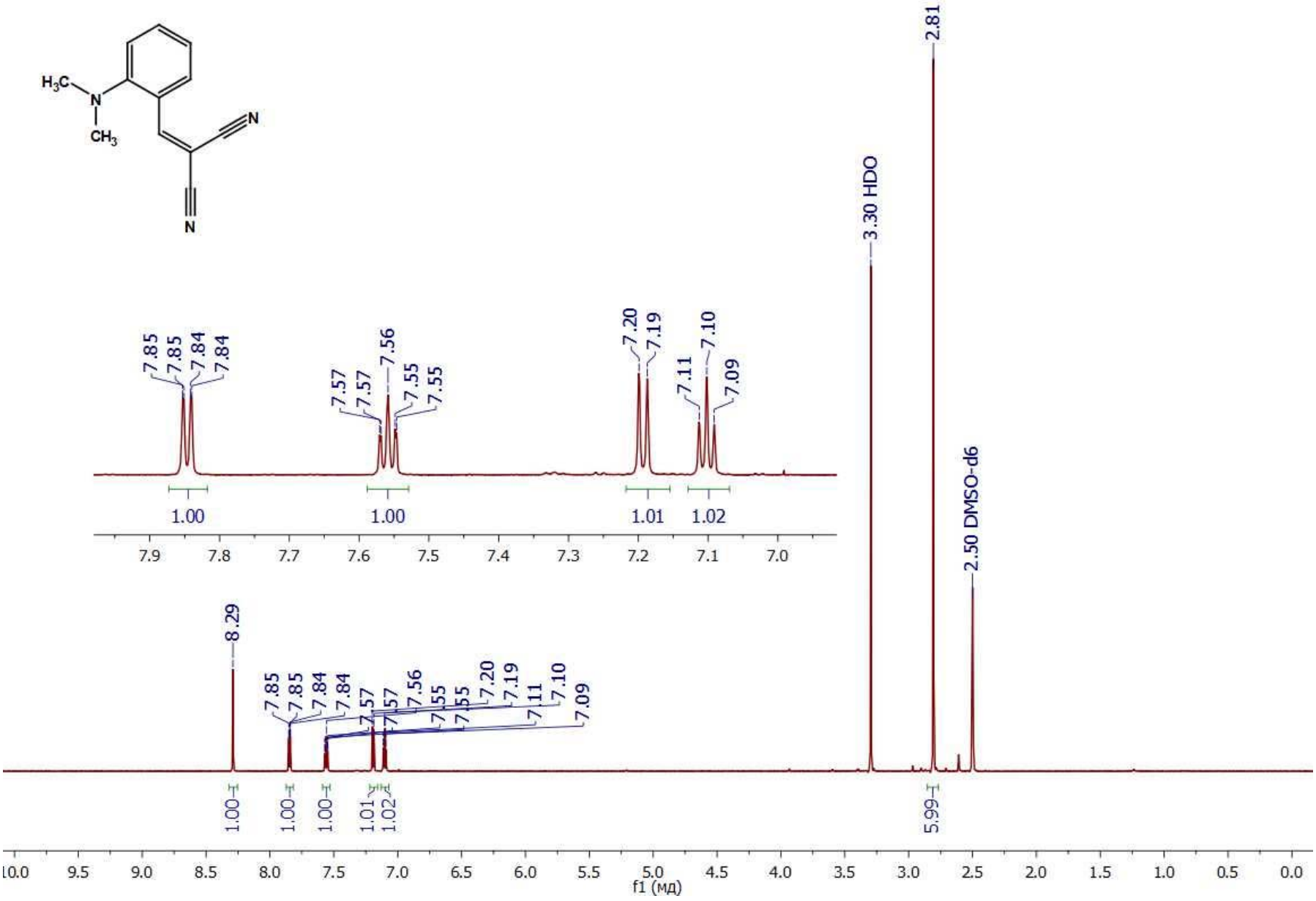
28.9
28.7
15.1
11.4
29.8
28.9
28.7
1
2
f1 (мд)


H3C
N
CH3
O
O
CH3
N
8.41
7.97
7.95
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.21
7.20
7.14
7.13
7.12
3.87
3.30 HDO
2.76
2.50 DMSO-d6
1.00
1.00
1.00
1.00
1.01
3.00
6.00
f1 (мд)


H3C
N
CH3
O
O
CH3
N
162.9
155.2
152.8
133.9
129.1
123.4
121.5
118.6
115.7
101.0
53.3
45.1
39.5 DMSO-d6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


H3C
N
CH3
N
N
2.81
3.30 HDO
2.50 DMSO-d6
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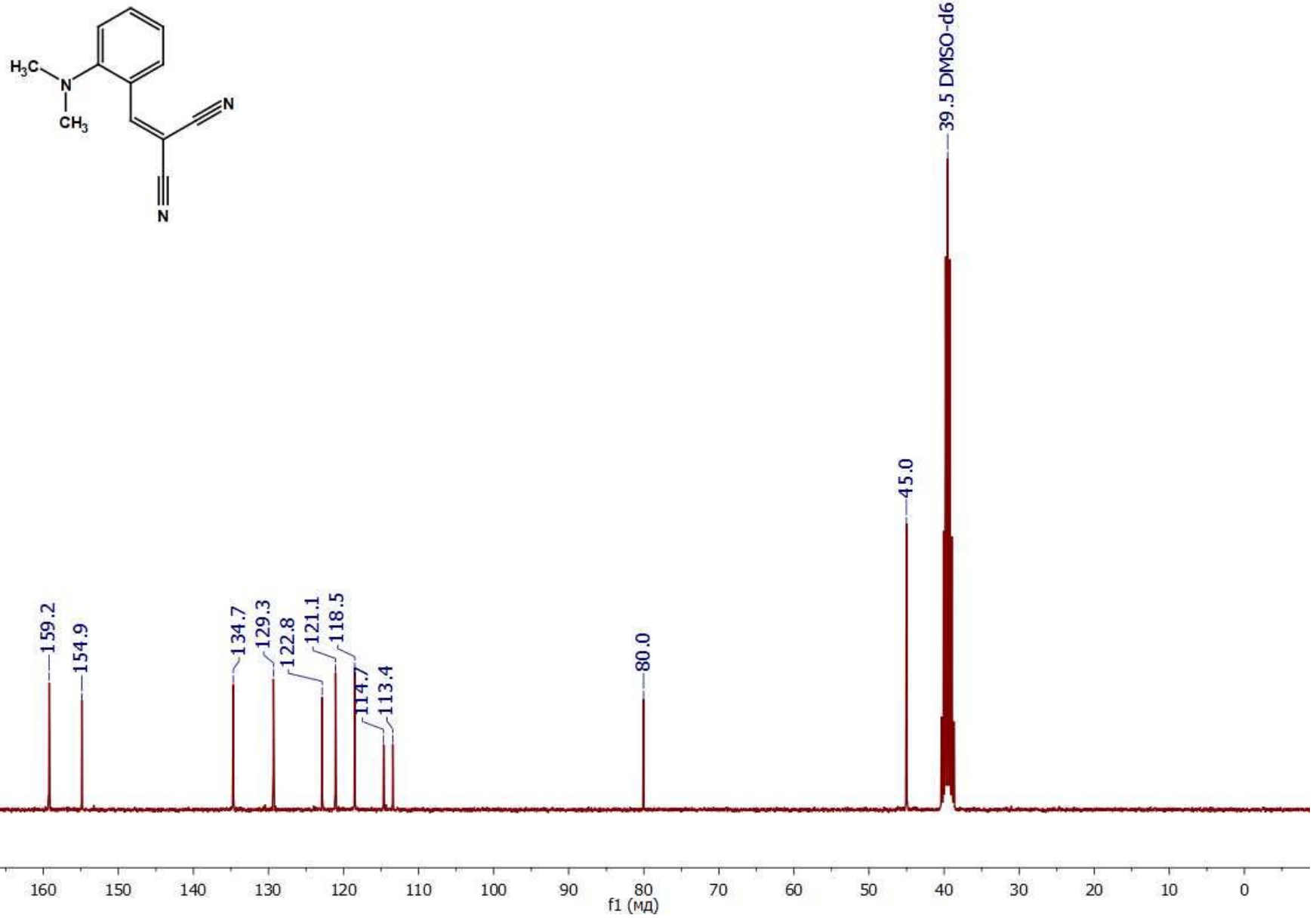
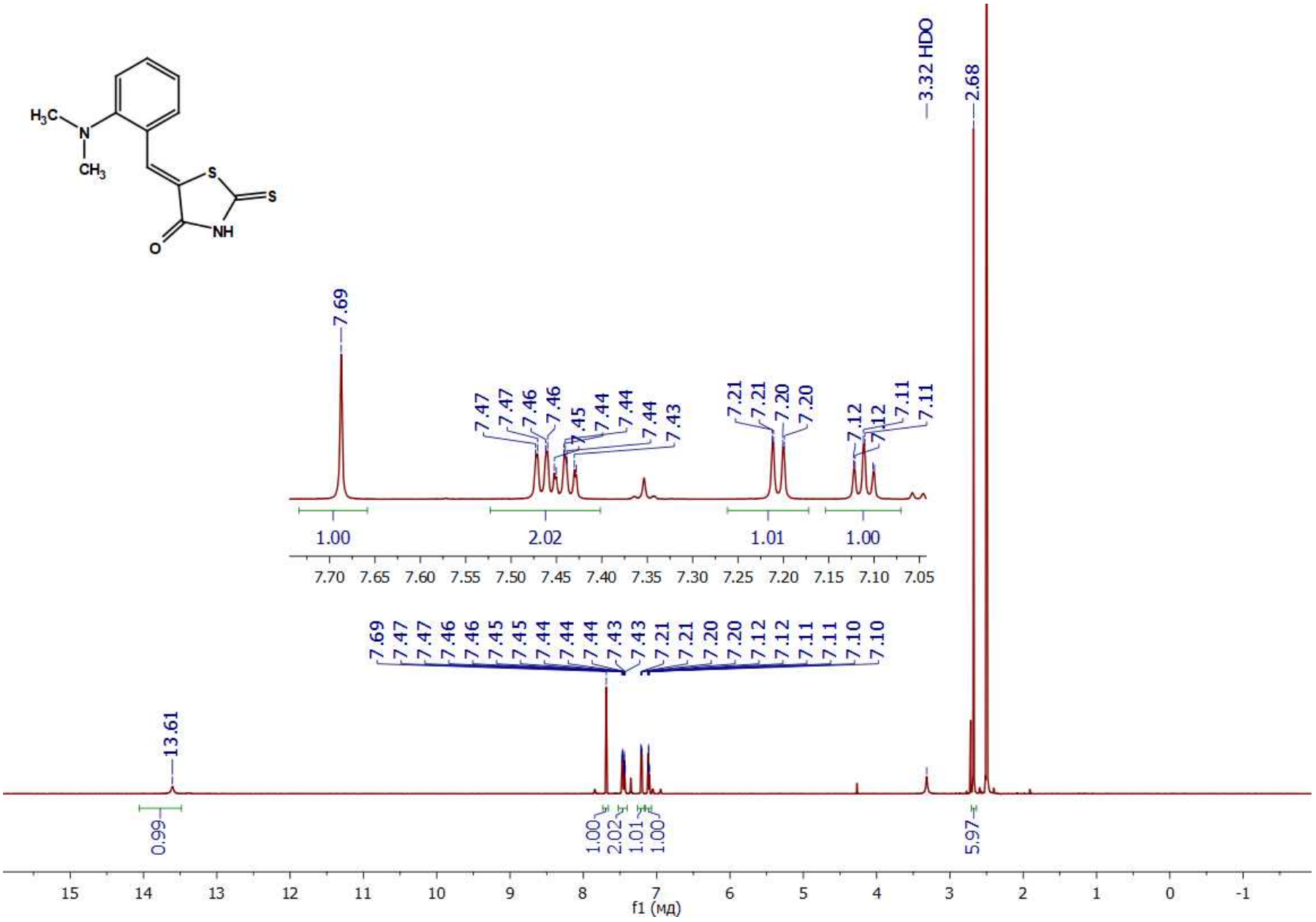
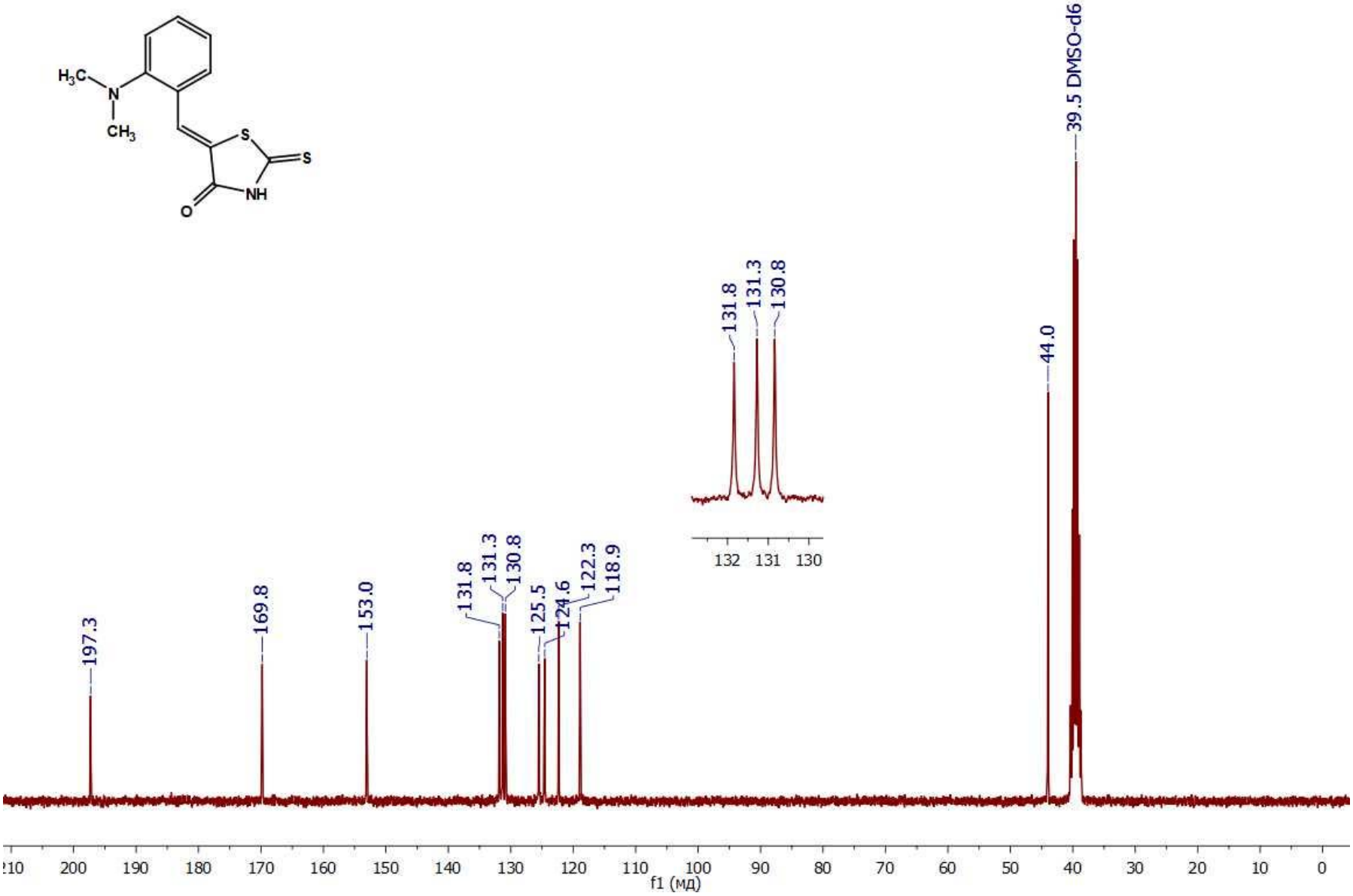
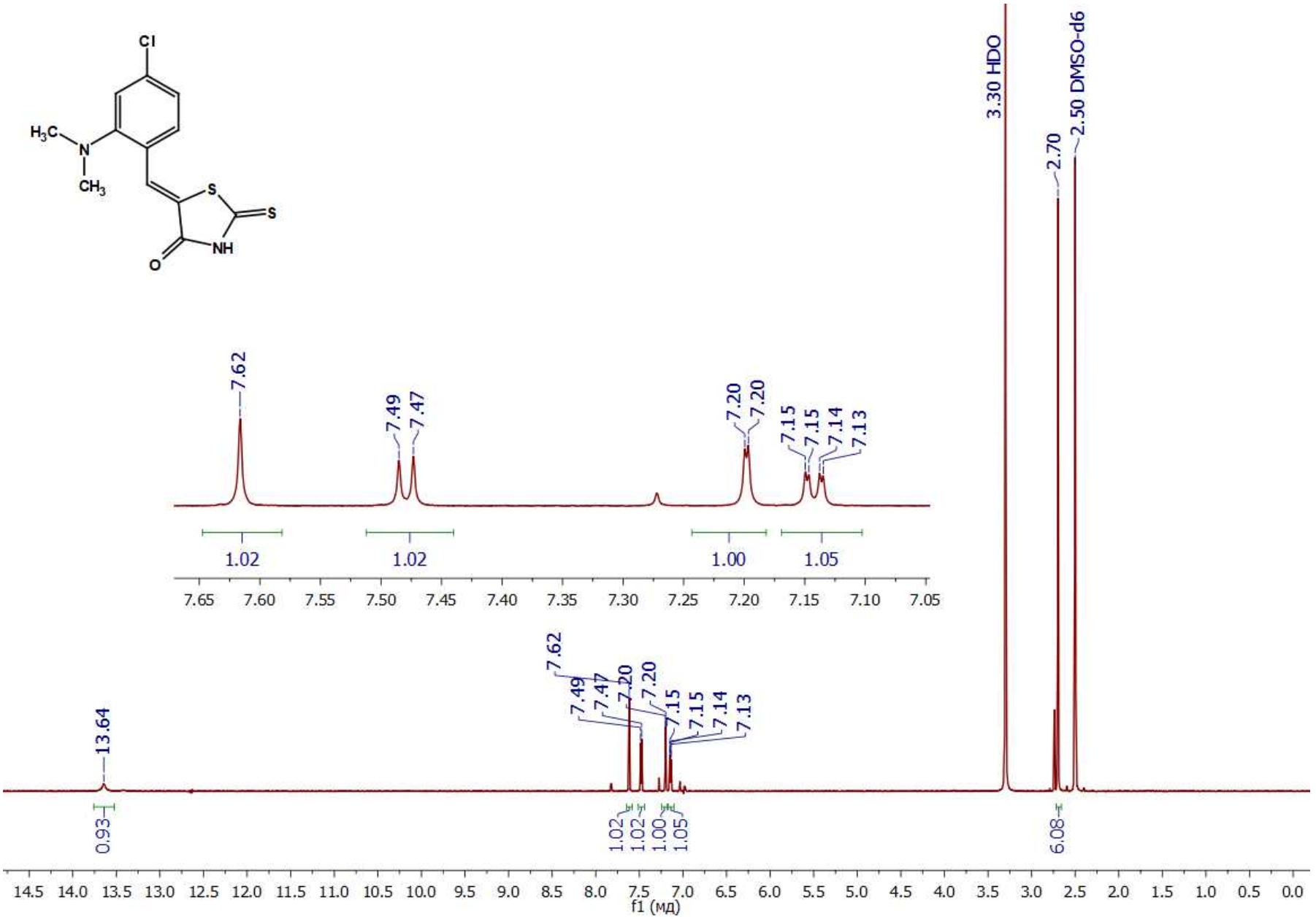
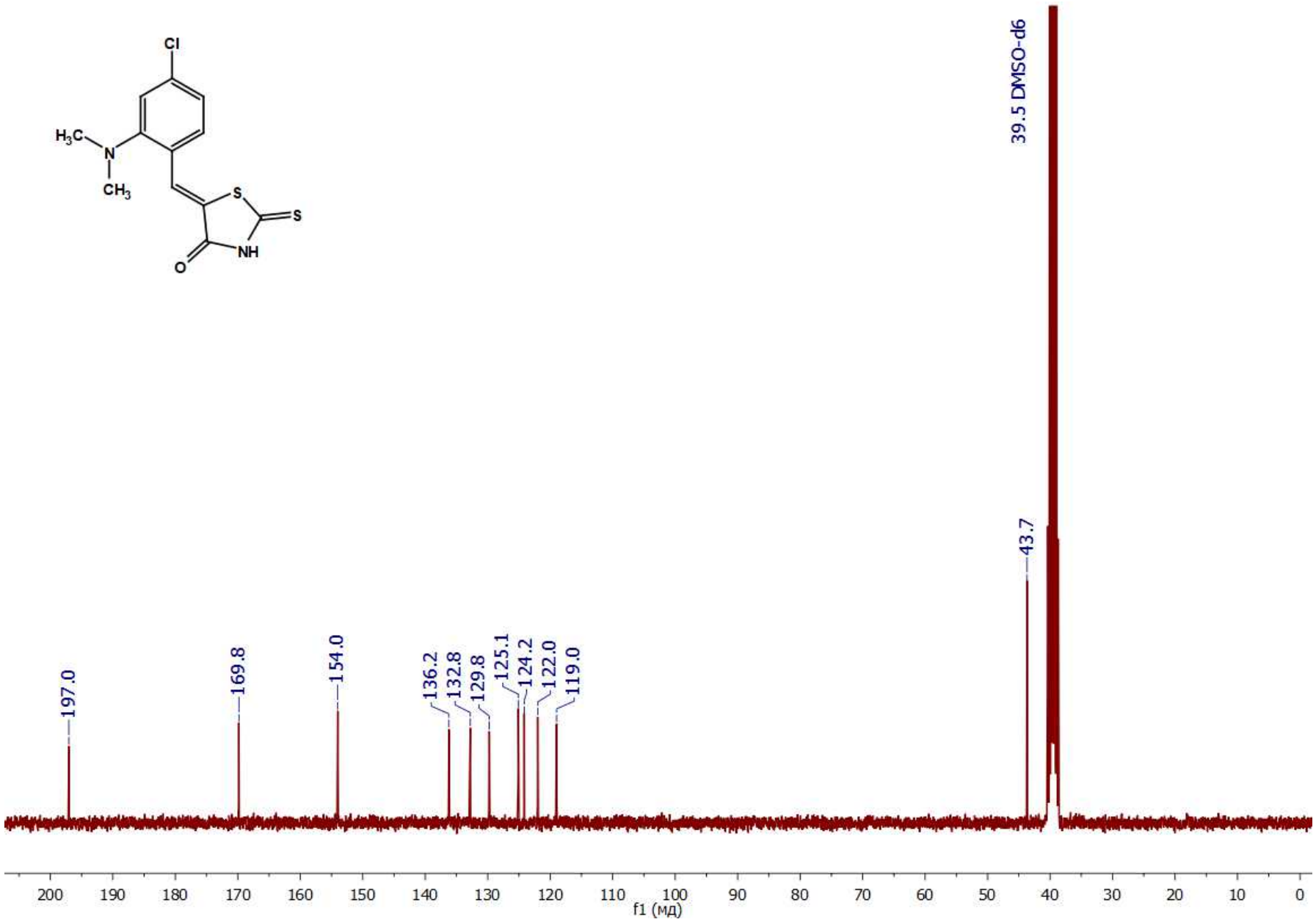
7.85
7.85
7.84
7.84
7.57
7.57
7.56
7.55
7.55
7.20
7.19
7.11
7.10
7.09
1.00
1.00
1.01
1.02
1.00
1.00
1.01
1.02
5.99
f1 (мд)

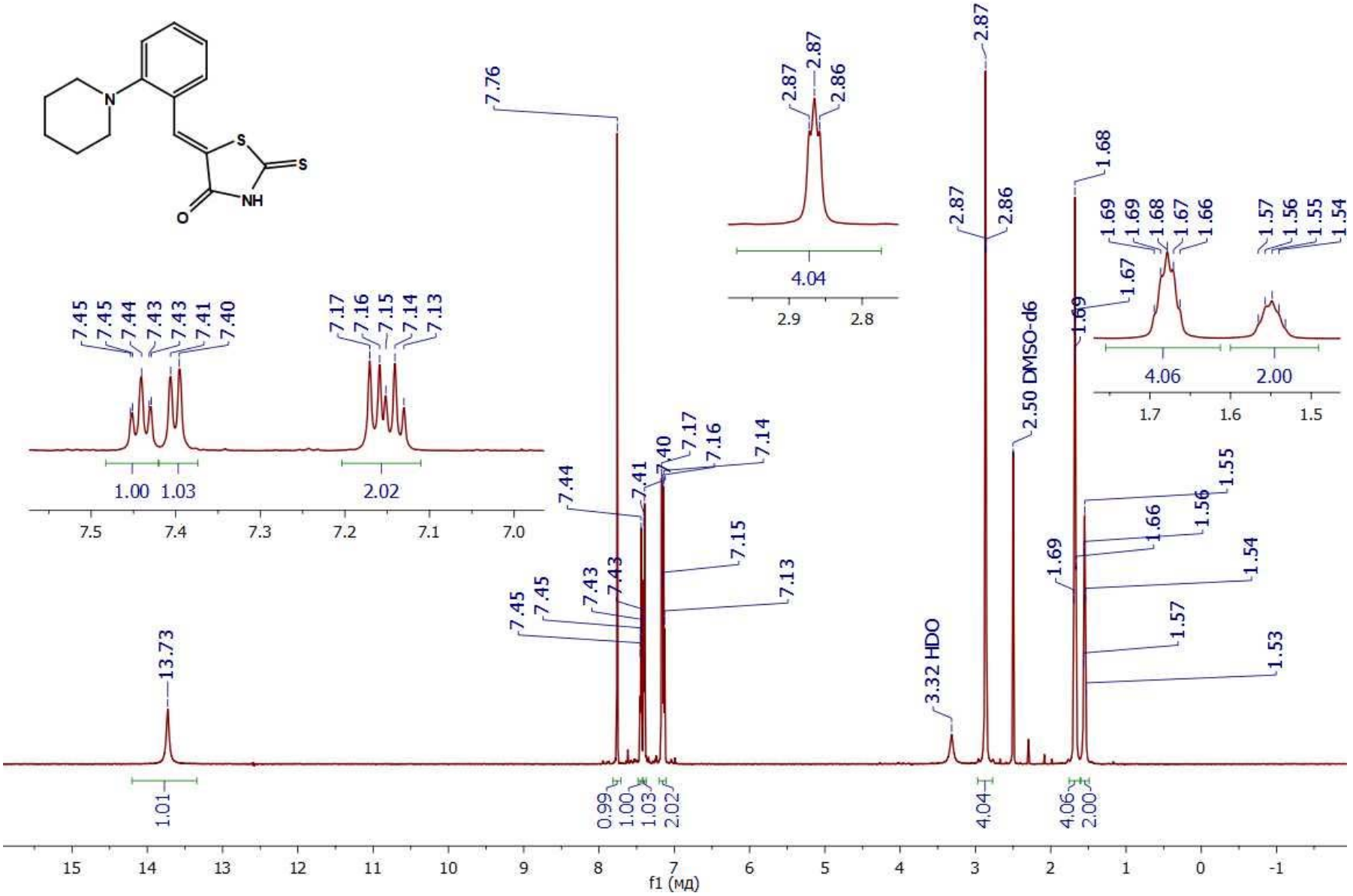

H3C
N
CH3
N
N
159.2
154.9
134.7
129.3
122.8
121.1
118.5
114.7
113.4
80.0
45.0
39.5 DMSO-d6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

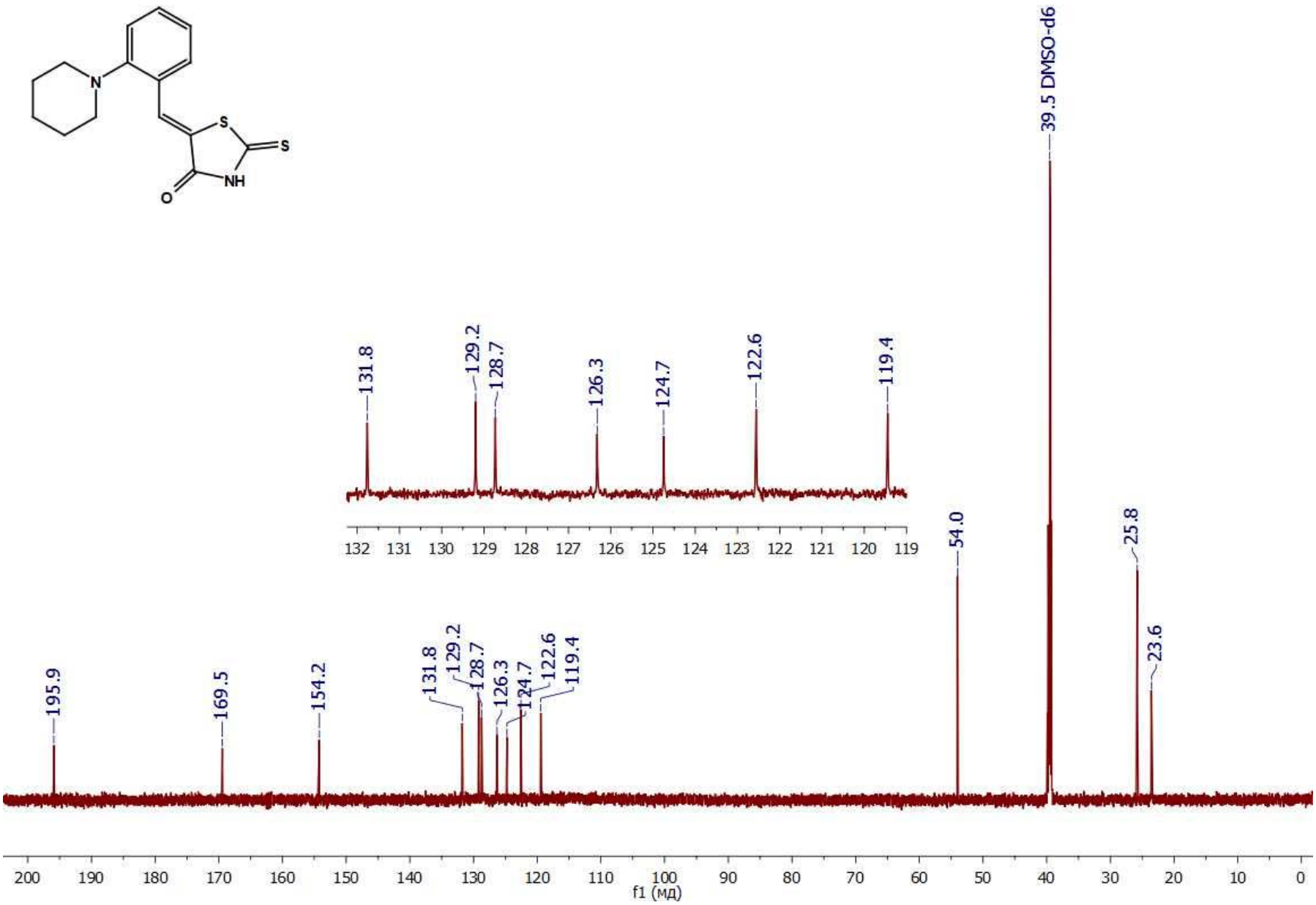

H3C
N
CH3
S
S
NH
O
3.32 HDO
2.68
7.69
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.21
7.21
7.20
7.20
7.12
7.12
7.11
7.11
1.00
2.02
1.01
1.00
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
7.69
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.21
7.21
7.20
7.20
7.12
7.12
7.11
7.11
7.10
7.10
13.61
0.99
1.00
2.02
1.01
1.00
5.97
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (мд)

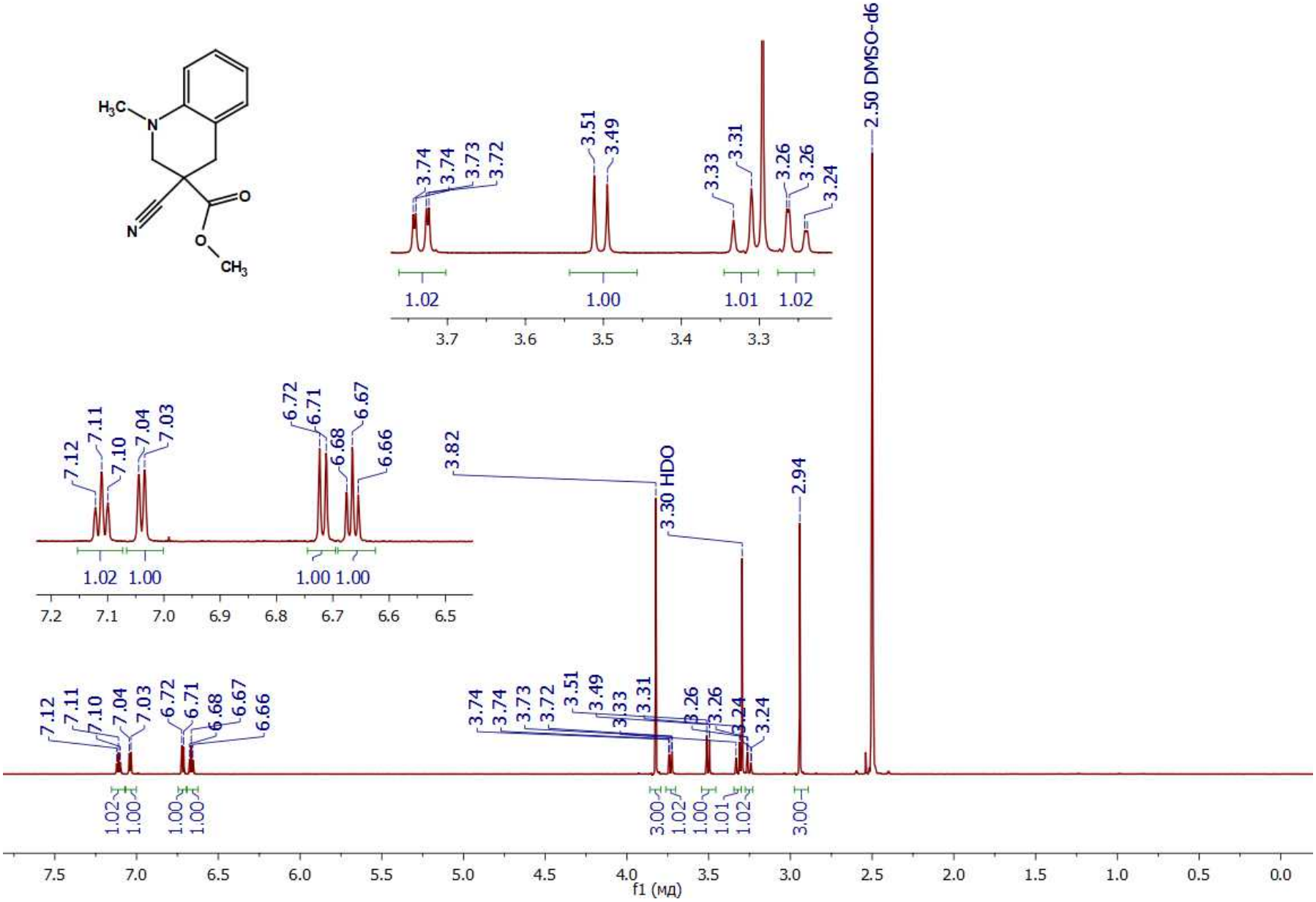

H3C
N
CH3
S
S
NH
O
197.3
169.8
153.0
131.8
131.3
130.8
125.5
124.6
122.3
118.9
44.0
39.5 DMSO-d6
132
131
130
f1 (мд)

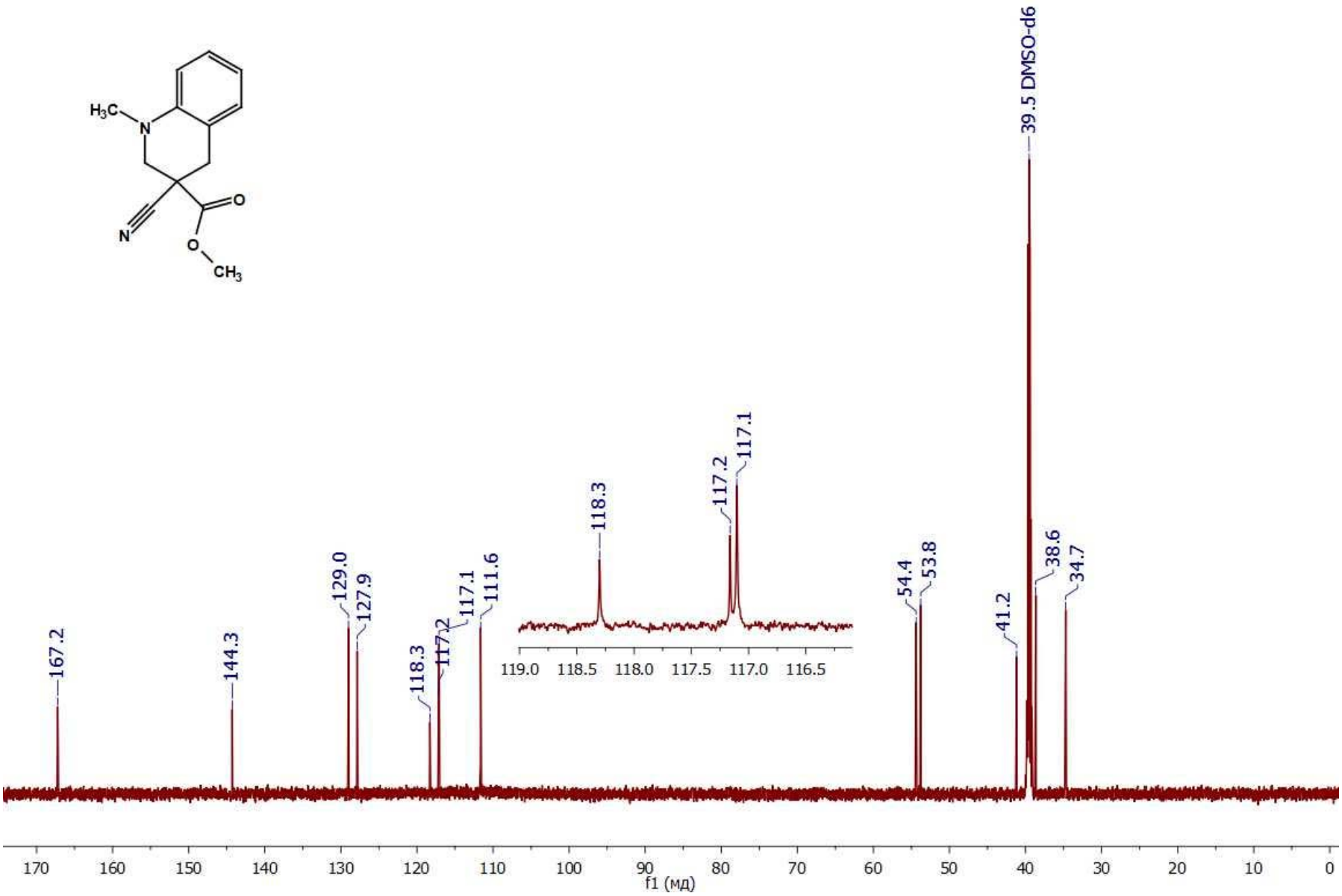

Cl
H3C
N
CH3
S
S
NH
O
3.30 HDO
2.70
2.50 DMSO-d6
7.62
7.49
7.47
7.20
7.20
7.15
7.15
7.14
7.13
1.02
1.02
1.00
1.05
13.64
0.93
6.08
f1 (мд)

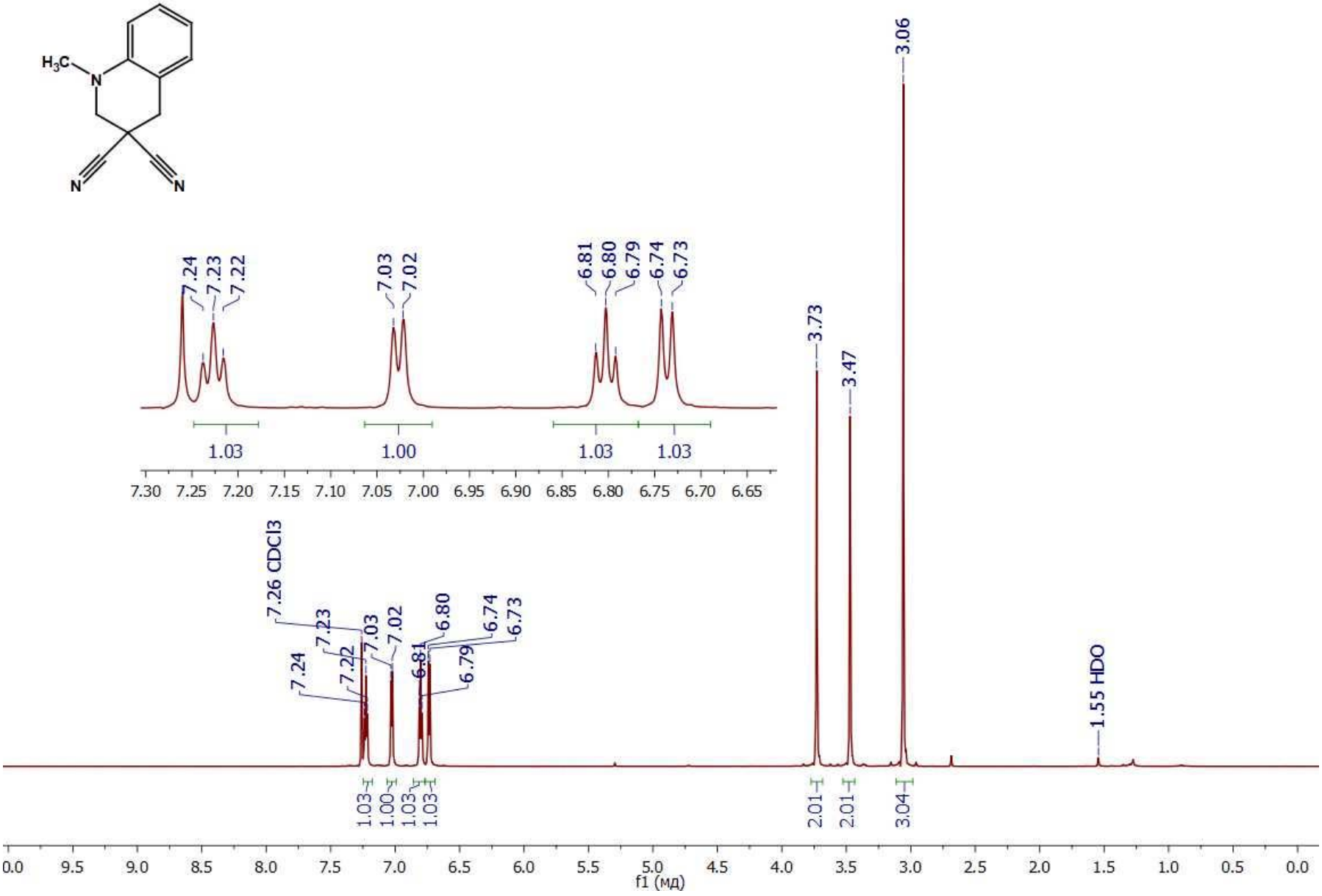

Cl
H3C
N
CH3
S
S
NH
O
39.5 DMSO-d6
43.7
197.0
169.8
154.0
136.2
132.8
129.8
125.1
124.2
122.0
119.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

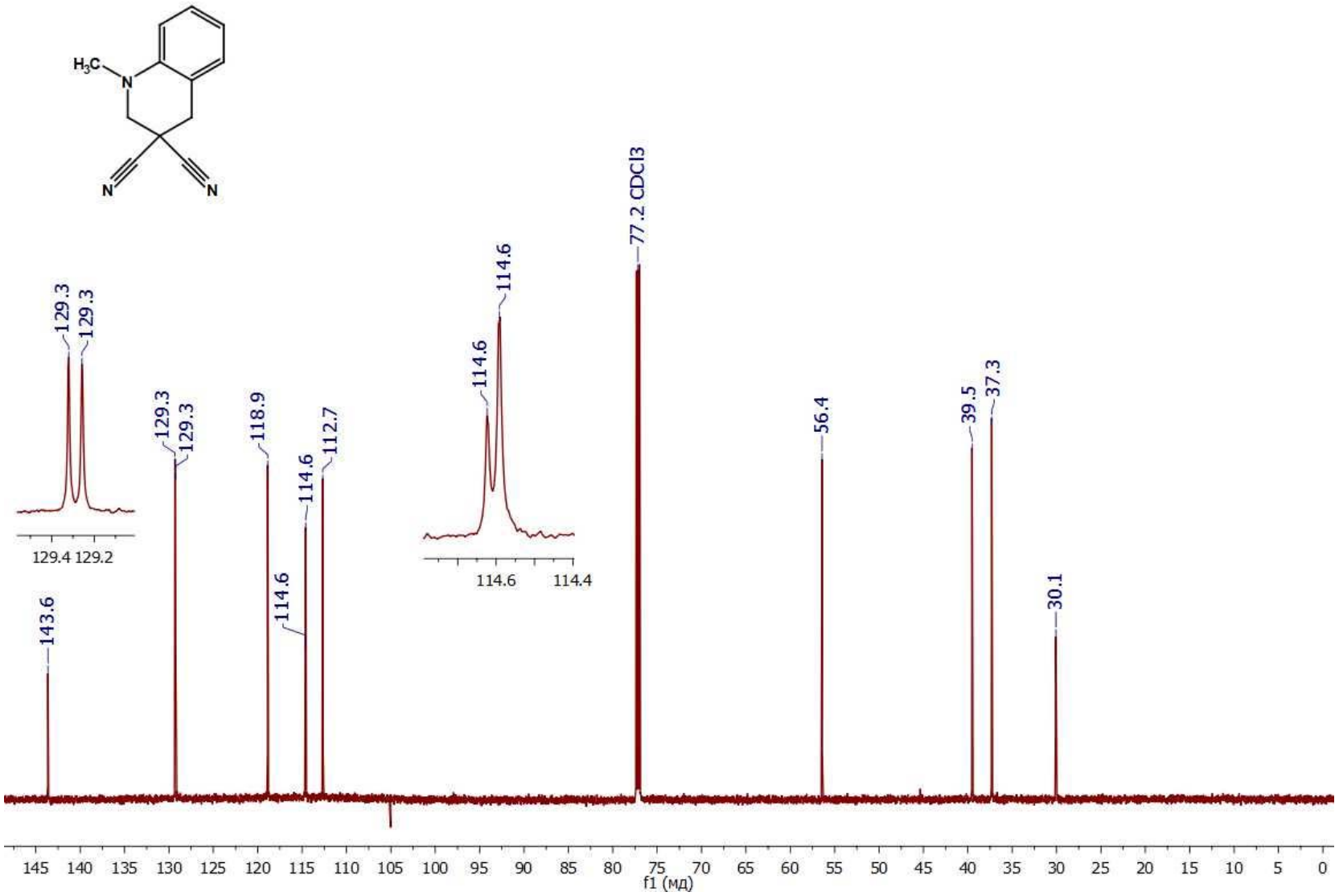

N
S
S
NH
O
7.76
7.45
7.45
7.44
7.43
7.43
7.41
7.40
7.17
7.16
7.15
7.14
7.13
1.00 1.03
2.02
2.87
2.87
2.86
4.04
2.87
2.86
2.50 DMSO-d6
3.32 HDO
1.68
1.69
1.69
1.68
1.67
1.66
1.57
1.56
1.55
1.54
1.67
1.69
4.06
2.00
13.73
1.01
0.99
1.00
1.03
2.02
4.04
4.06
2.00
f1 (мд)


N
S
S
NH
O
39.5 DMSO-d6
131.8
129.2
128.7
126.3
124.7
122.6
119.4
54.0
25.8
23.6
195.9
169.5
154.2
f1 (мд)

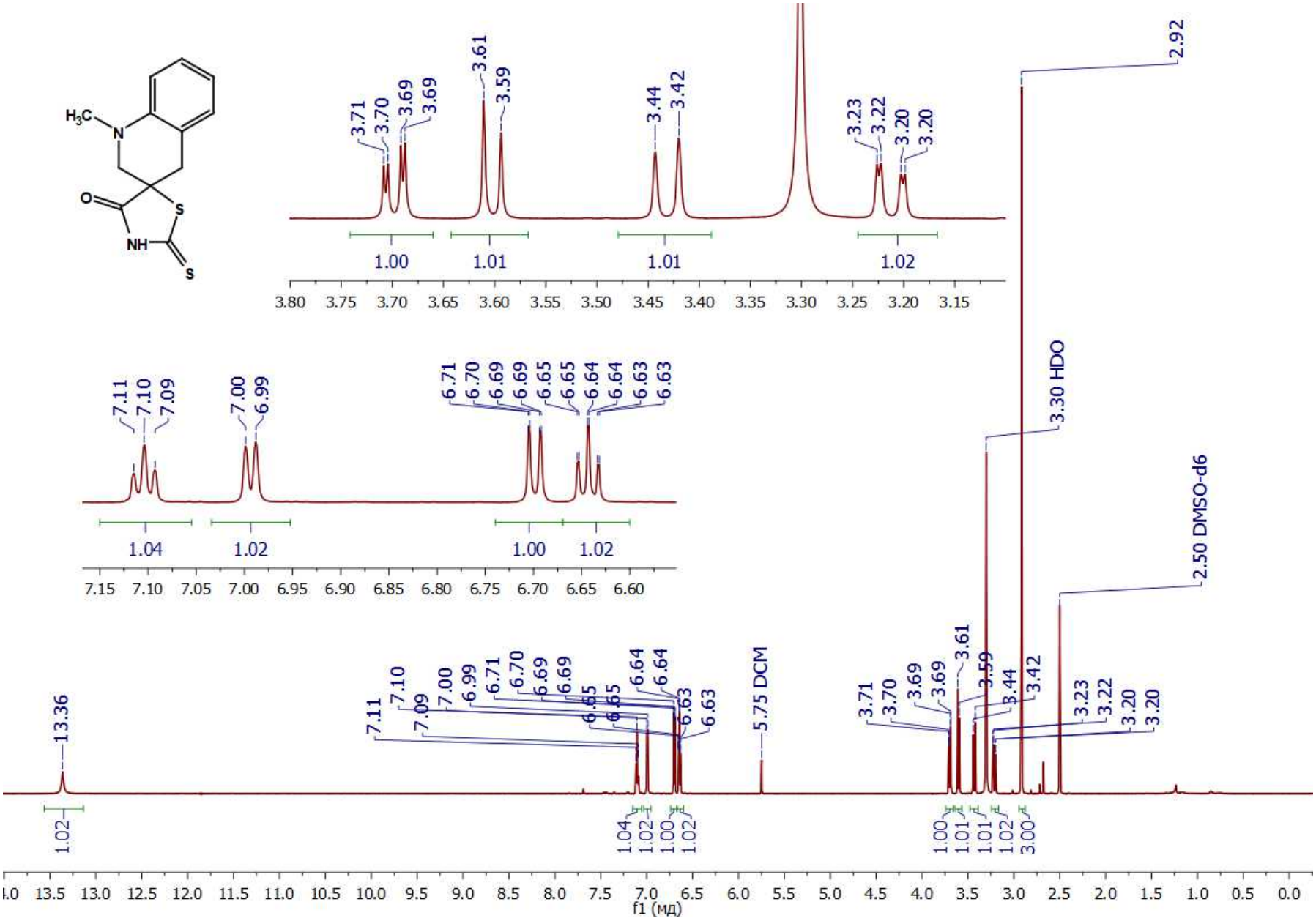

H3C
N
N
O
O
CH3
2.50 DMSO-d6
3.30 HDO
3.82
2.94
f1 (мд)

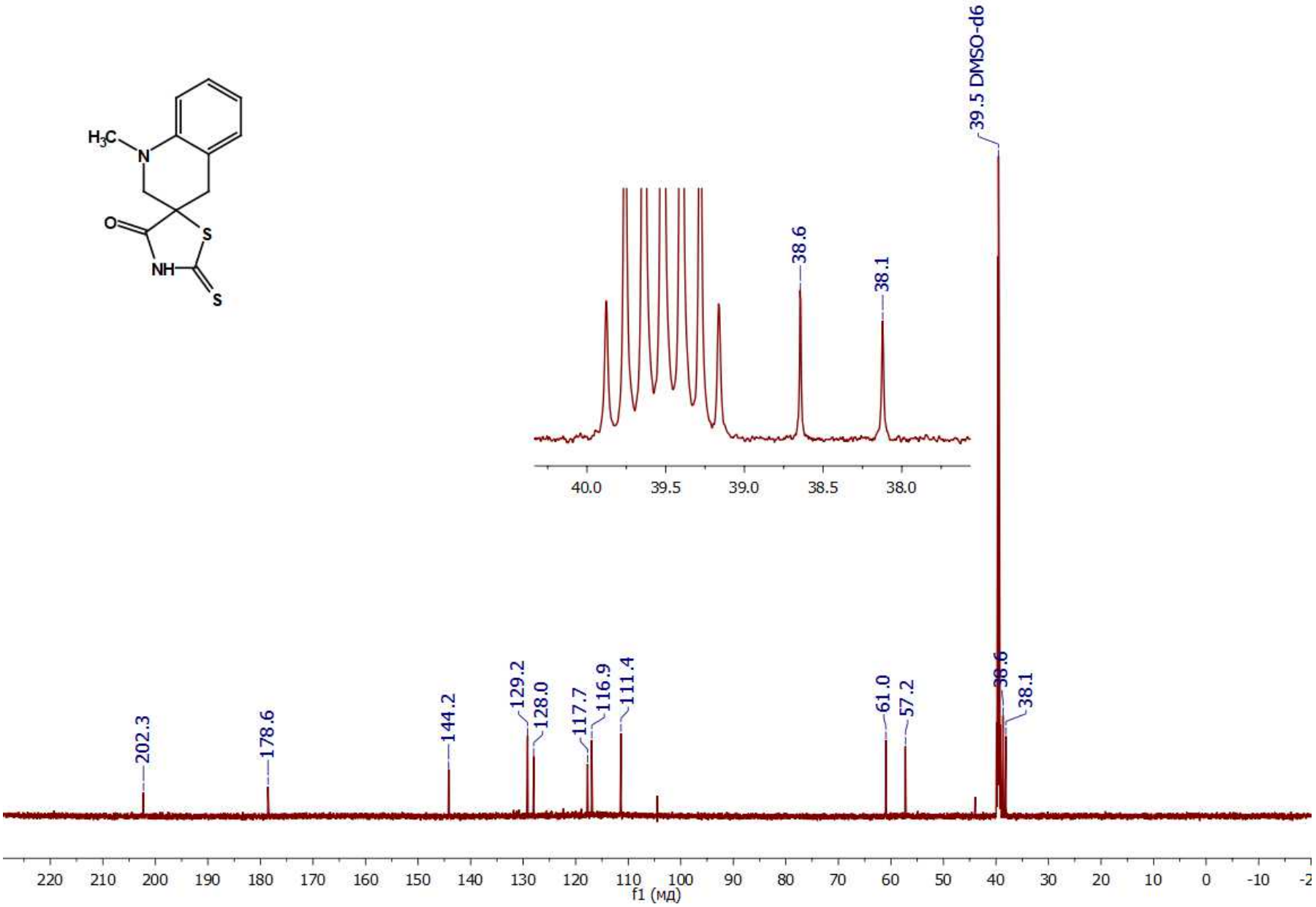

H3C
N
N
O
O
CH3
39.5 DMSO-d6
167.2
144.3
129.0
127.9
118.3
117.2
117.1
111.6
54.4
53.8
41.2
38.6
34.7
119.0
118.5
118.0
117.5
117.0
116.5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

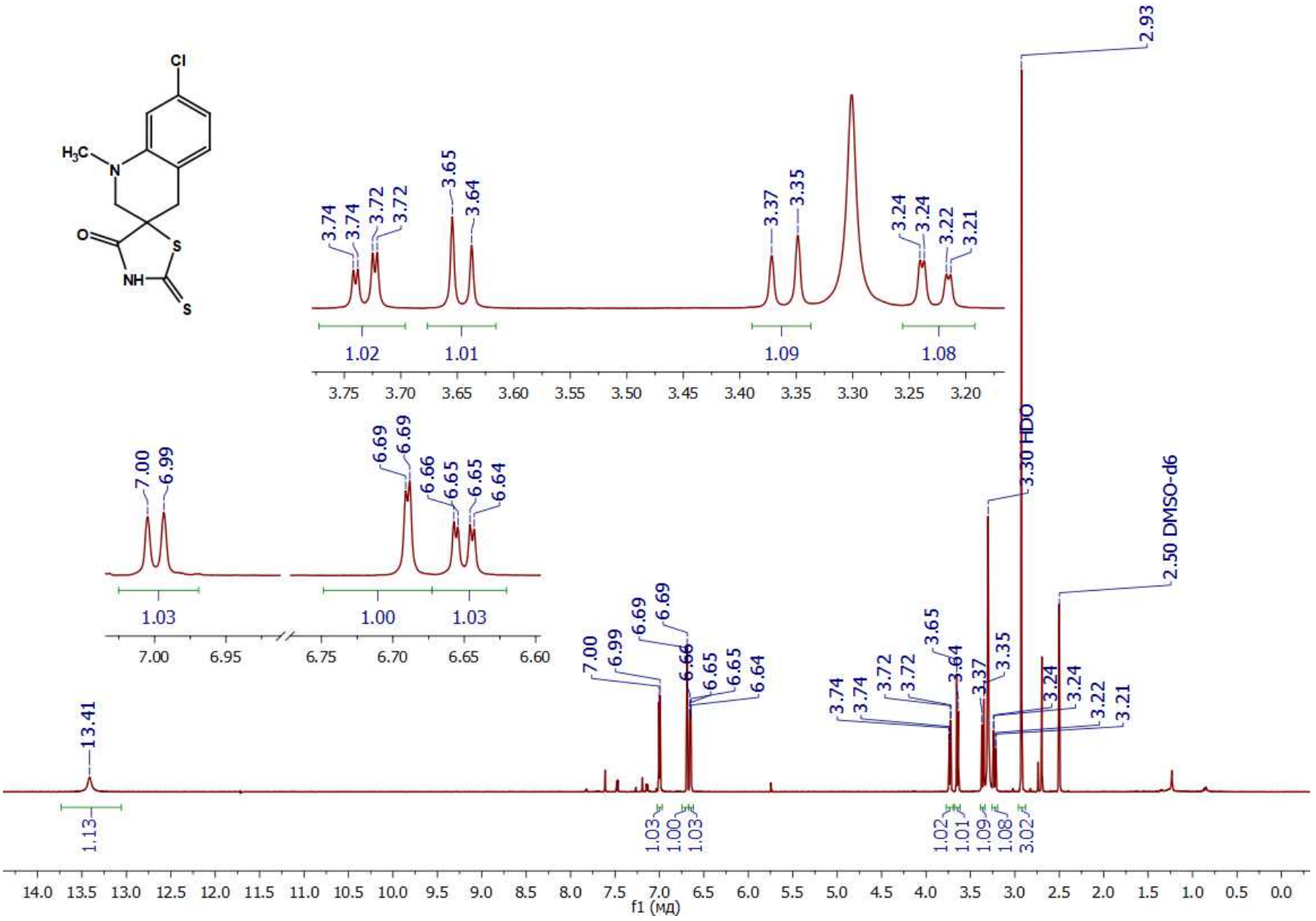

H3C
N
N
N
7.24
7.23
7.22
7.03
7.02
6.81
6.80
6.79
6.74
6.73
1.03
1.00
1.03
1.03
7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65
7.26 CDCl3
3.73
3.47
3.06
1.55 HDO
2.01
2.01
3.04
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)

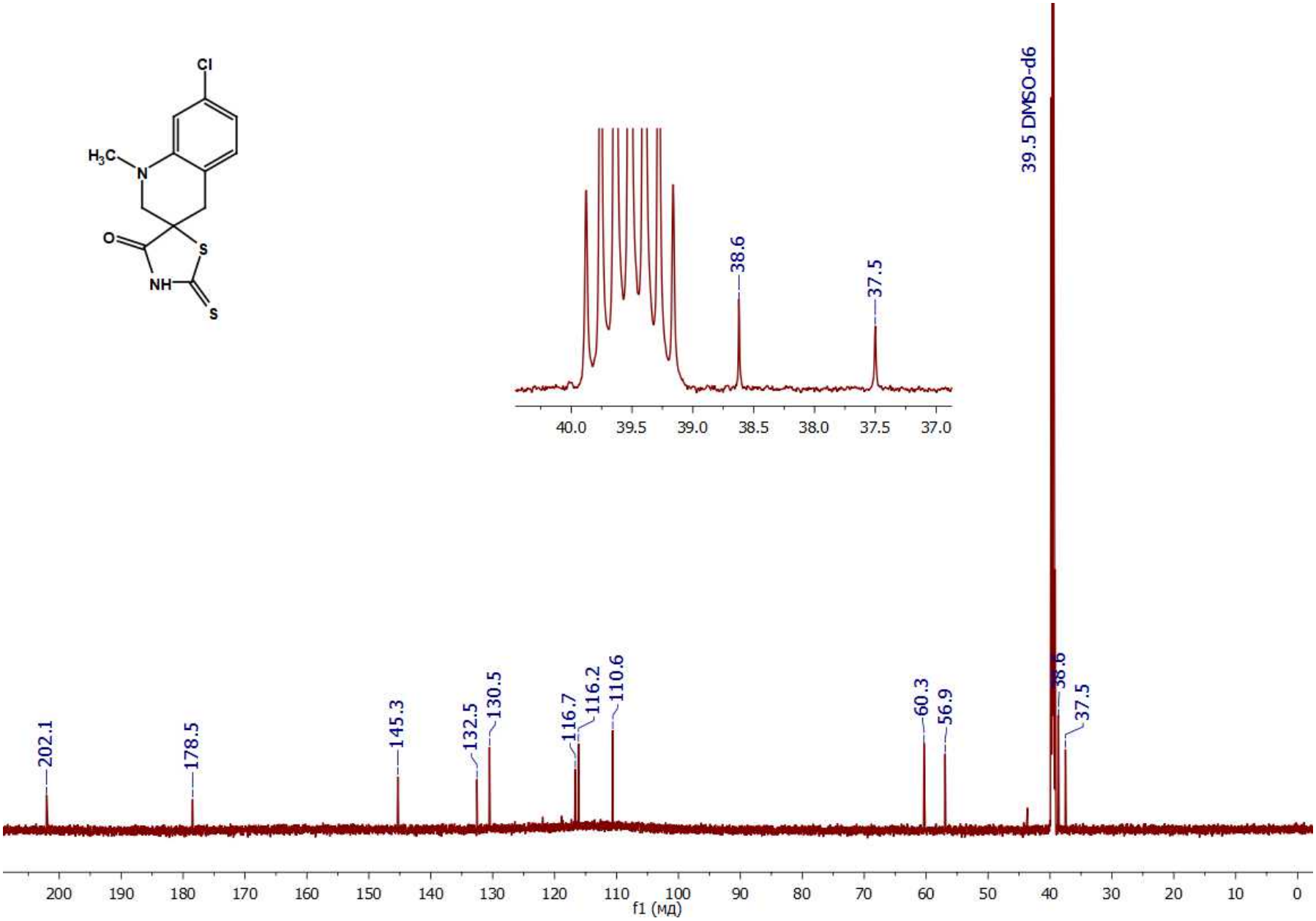


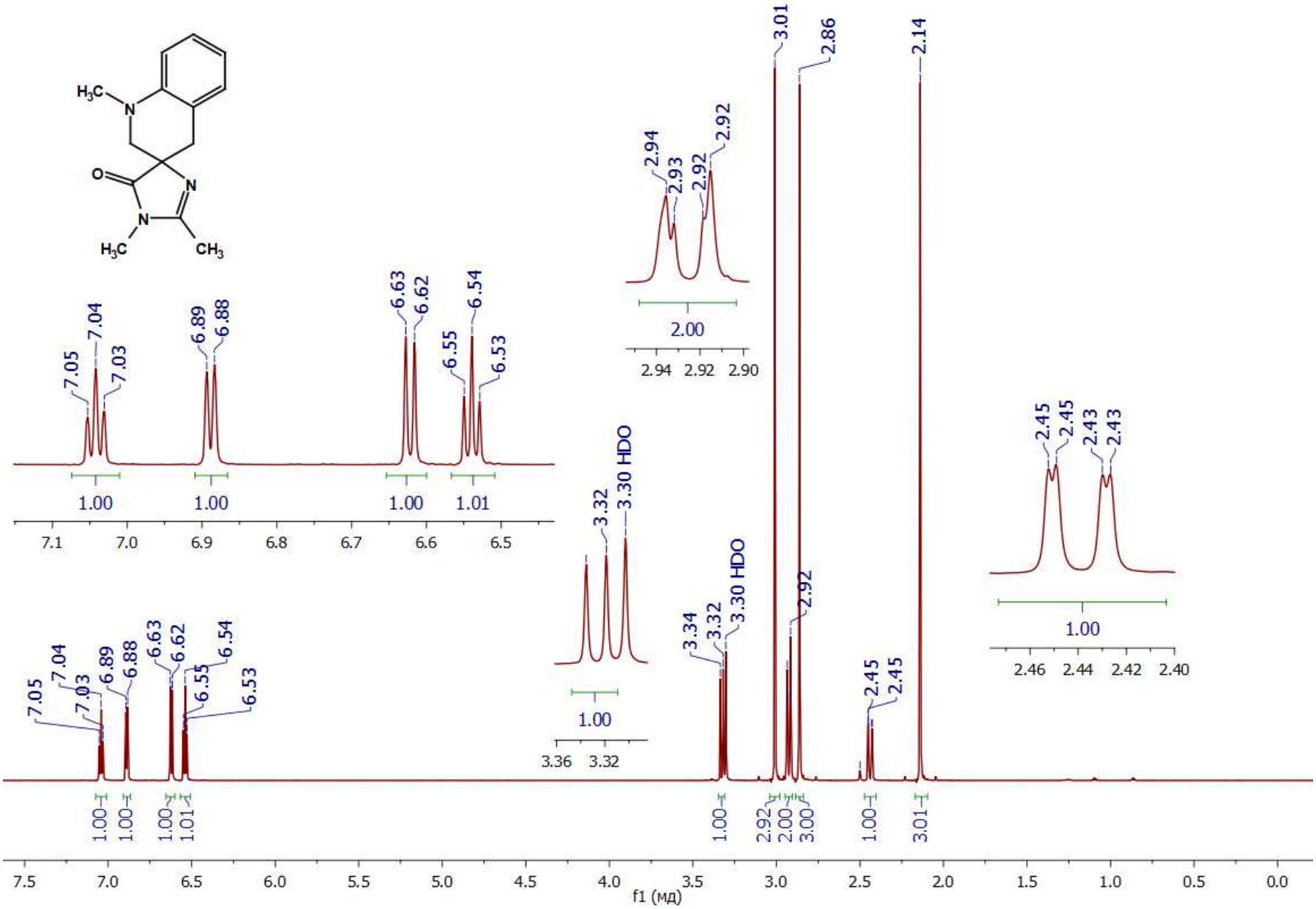
* The inverted peak at 105 ppm is an artifact at exact center of spectrum

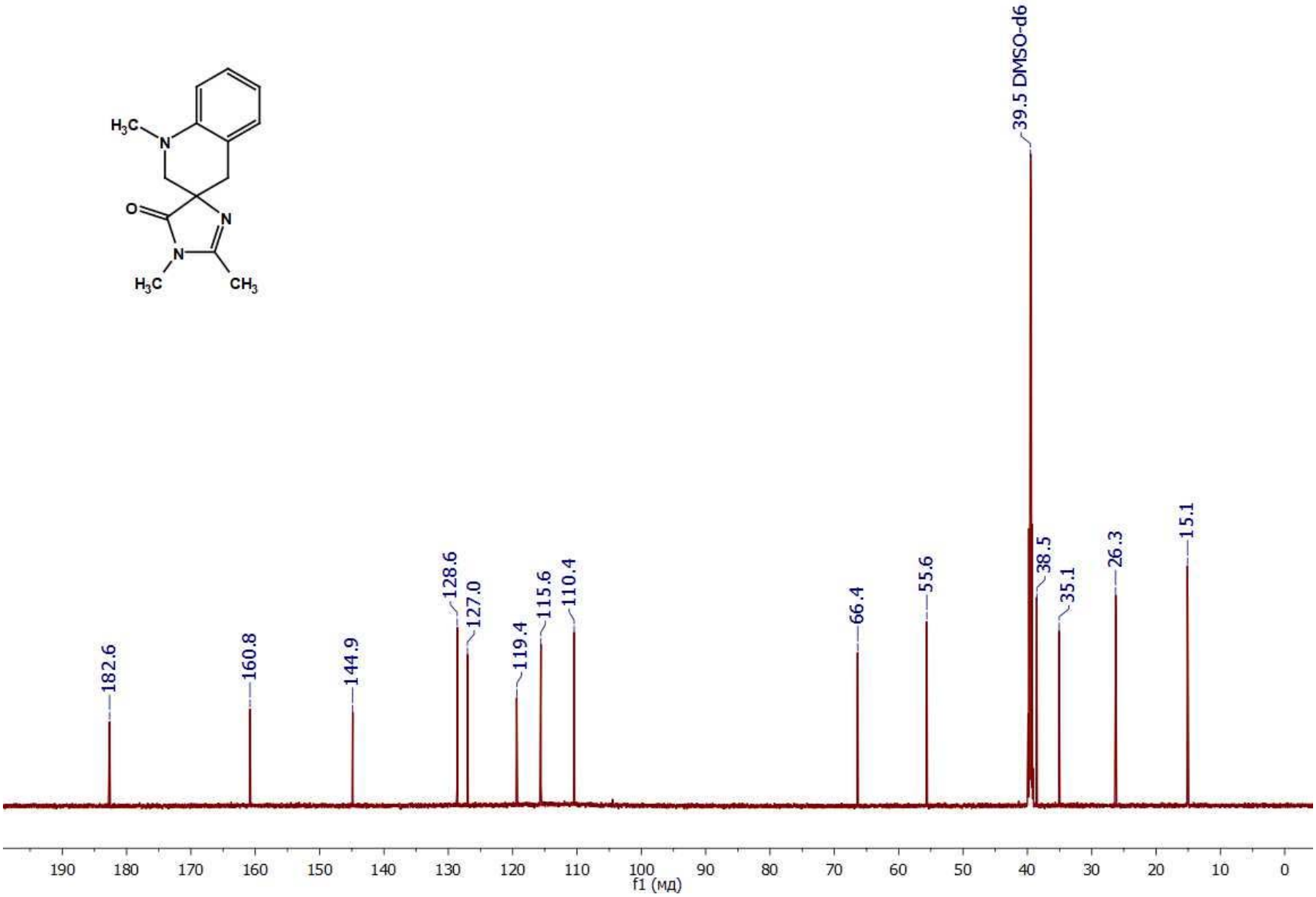

H3C
N
O
S
NH
S
3.71
3.70
3.69
3.69
3.61
3.59
3.44
3.42
3.23
3.22
3.20
3.20
2.92
1.00
1.01
1.01
1.02
3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15
7.11
7.10
7.09
7.00
6.99
6.71
6.70
6.69
6.69
6.65
6.65
6.64
6.64
6.63
6.63
1.04
1.02
1.00
1.02
7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
3.30 HDO
2.50 DMSO-d6
13.36
5.75 DCM
1.02
1.04
1.02
1.00
1.02
1.00
1.01
1.01
1.02
3.00
f1 (мд)


H3C
N
O
S
NH
S
39.5 DMSO-d6
38.6
38.1
40.0
39.5
39.0
38.5
38.0
202.3
178.6
144.2
129.2
128.0
117.7
116.9
111.4
61.0
57.2
38.6
38.1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (мд)


Cl
H3C
N
O
S
NH
S
2.93
3.74
3.74
3.72
3.72
3.65
3.64
3.37
3.35
3.24
3.24
3.22
3.21
1.02
1.01
1.09
1.08
3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20
7.00
6.99
6.69
6.69
6.66
6.65
6.65
6.64
1.03
1.00
1.03
7.00 6.95 6.75 6.70 6.65 6.60
3.30 HDO
2.50 DMSO-d6
13.41
1.13
1.03
1.00
1.03
1.02
1.01
1.09
1.08
3.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)


Cl
H3C
N
O
S
NH
S
39.5 DMSO-d6
38.6
37.5
40.0
39.5
39.0
38.5
38.0
37.5
37.0
202.1
178.5
145.3
132.5
130.5
116.7
116.2
110.6
60.3
56.9
38.6
37.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


H3C
N
O
N
N
H3C
CH3
7.05
7.04
7.03
6.89
6.88
6.63
6.62
6.55
6.54
6.53
1.00
1.00
1.00
1.01
7.1
7.0
6.9
6.8
6.7
6.6
6.5
2.94
2.93
2.92
2.92
2.00
2.94
2.92
2.90
3.32
3.30 HDO
1.00
3.36
3.32
3.34
3.32
3.30 HDO
2.92
2.45
2.45
3.01
2.86
2.14
2.45
2.45
2.43
2.43
1.00
2.46
2.44
2.42
2.40
1.00
1.00
1.00
2.92
2.00
3.00
1.00
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)


H3C
N
O
N
N
H3C
CH3
39.5 DMSO-d6
182.6
160.8
144.9
128.6
127.0
119.4
115.6
110.4
66.4
55.6
38.5
35.1
26.3
15.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)