SUPPORTING INFORMATION

Base-controlled Regioselectivity via Distinct Mechanisms During C–H Thionation of Azinium Salts with Elemental Sulfur

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S-I. General Information

Materials. All commercially available chemicals and solvents of high purity were used without purification unless otherwise stated. DMSO and THF were dried with 3A MS.

Chromatography. Flash-column chromatography was performed using silica gel (0.040–0.063 mm). Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F254 plates that were visualized by exposure to UV light.

Instrumentation. ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR were recorded at 400, 100 and 376 MHz respectively, for solutions in $CDCl_3$ or DMSO-d_6. Chemical shifts are referenced relative to the signal of $CDCl_3$ or DMSO-d_6 and quoted in δ (ppm). Coupling constants (J) are reported in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet – doublet (dd), doublet – doublet – doublet (ddd), doublet – doublet – triplet (ddt), multiplet (m), and broad signal (brs). High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) on an Orbitrap spectrometer. Single crystal X-ray analysis for **2c, 2p, 3h, 3s, 3t** was carried out at 100(2) K on the Bruker D8 Quest diffractometer (MoKα, λ = 0.71073 Å, ω- and ϕ-scan mode). Using Olex2 software package (*J. Appl. Crystallogr.*, **2009**, 42, 339-341), the structures were solved with the SHELXT (*Acta Crystallogr. A*., **2015**, *71*, 3-8) structure solution program and refined with the least-squares method against F^2 in anisotropic approximation for non-hydrogen atoms (*Acta Crystallogr. C Struct. Chem*., **2015**, *71*, 3-8). All hydrogen atoms were placed in calculated positions and refined within riding model.

Melting points were determined in open capillaries and are uncorrected.

Yields refer to isolated and analytically pure compounds.

S-II. General Procedure for the Synthesis of Azinium Salts (*General Procedure A*)[a]

N-Heterocycle (3 mmol, 1.0 equiv) and acetonitrile (5 mL, 1 M) were added to an 8 mL vial with a screw cap equipped with a magnetic stir bar. Alkylating reagent (15 mmol, 5.0 equiv) was slowly added at room temperature. Then the reaction mixture was stirred at 80 °C in an oil bath for 2 – 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature. The precipitate was filtered (see Note), washed with diethyl ether (3 x 20 mL) and dried under vacuum. The products were used in the next step without additional purification.

Note: If the product did not precipitate, the solvent was removed under reduced pressure. The resulting mixture was triturated with acetone (10 mL) and diethyl ether (3 mL). The crystallized solid was filtered, washed with diethyl ether (3 x 20 mL) and dried under vacuum. The amorphous solid was washed with diethyl ether (2 × 10 mL), the solvent was decanted and the amorphous product was dried under reduced pressure. The resulting products were used in the next step without additional purification.

[a]Salts **1m** [1], **1ee** [2] and **1jj** [3] were synthesized according to the literature methods.

Salt **1u** was synthesized according to the procedure below:

Step 1. Ethyl nicotinate (8.31 g, 55 mmol, 1.0 equiv) and 2,4-dinitrophenyl *p*-toluenesulfonate (20.43 g, 60 mmol, 1.1 equiv) were added to toluene (183 mL, 0.3 M) and stirred at reflux for 12 h. The mixture was cooled to rt, the product was filtered, washed thoroughly with toluene (3 x 30 mL) and dried under vacuum. **1-(2,4-Dinitrophenyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate**: yield 21.53 g (80%). The product was used in the next step without additional purification.

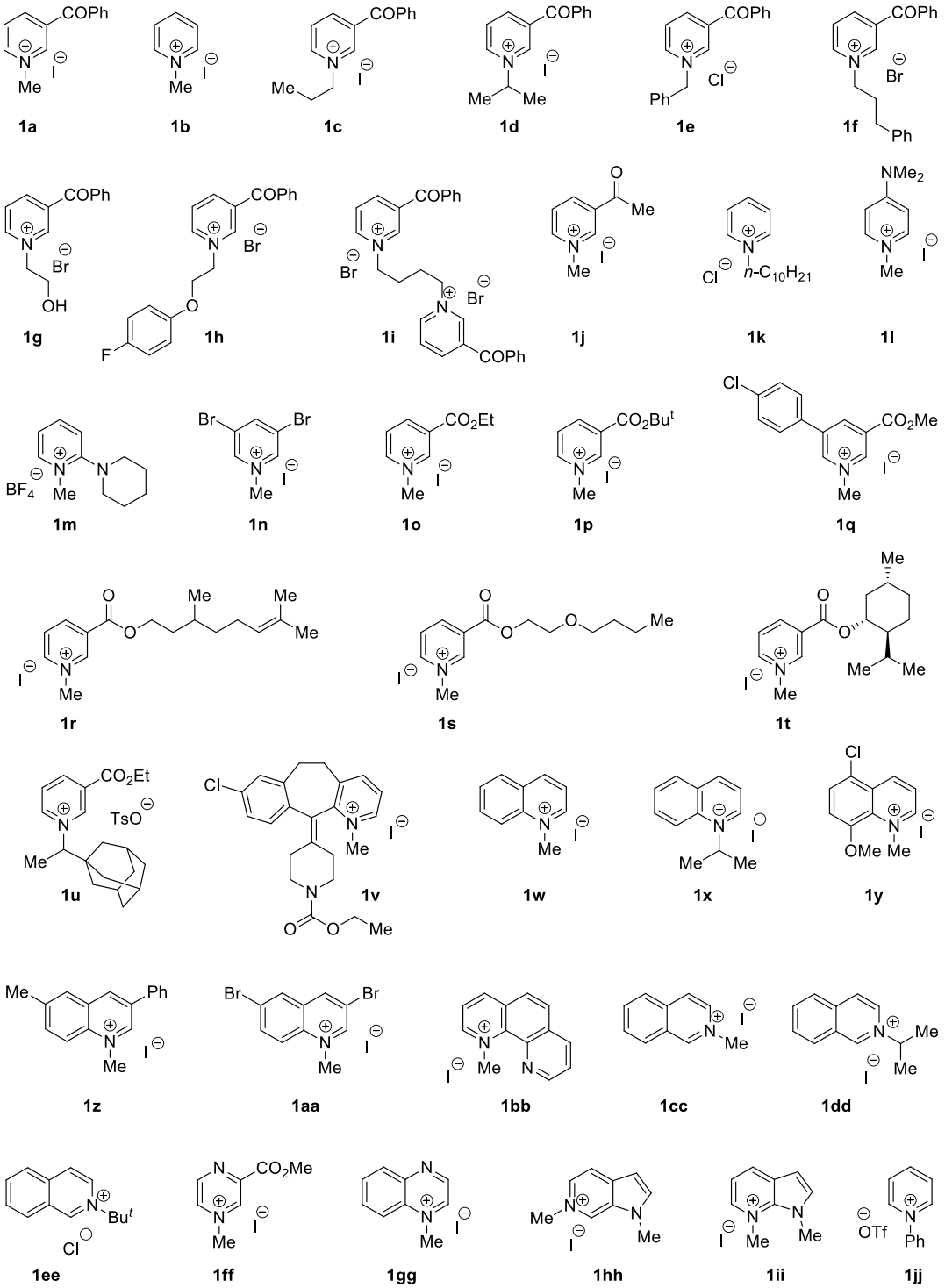
Step 2. 1-(2,4-Dinitrophenyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate (1,91 g, 3.9 mmol, 1.0 equiv) and ethanol (20 mL, 0.2 M) were taken in a 50 mL round bottom flask equipped with a magnetic stir bar. The racemic 1-(adamantan-1-yl)ethanamine (0.70 g, 3.9 mmol, 1.0 equiv) was added, and the reaction mixture was stirred at reflux for about 10 h. Upon complete consumption of salt (monitored by TLC), the reaction mixture was concentrated under reduced pressure. EtOAc (80 mL) and H_2O (40 mL) were added to the crude mass, and organic layer was separated. The aqueous layer was washed with EtOAc (3 x 40 mL) to eliminate 2,4-dinitroaniline. Then aqueous layer was extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. **1-(1-(Adamantan-1-yl)ethyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate** (**1u**): yield 1.12 g (59 %).

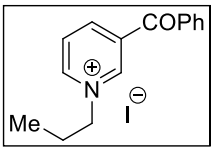
Characterization data obtained for these compounds matched those previously reported in the literature*:*

3-benzoyl-1-methylpyridin-1-ium iodide (**1a**) [4], **1-methylpyridin-1-ium iodide** (**1b**) [5], **3-acetyl-1-methylpyridin-1-ium iodide** (**1j**) [6], **1-decylpyridin-1-ium chloride** (**1k**) [7], **4-(dimethylamino)-1-**

methylpyridin-1-ium iodide (**1l**) [8], **1-methyl-2-(piperidin-1-yl)pyridin-1-ium tetrafluoroborate** (**1m**) [1], **3-(ethoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1o**) [9], **3-(*tert*-butoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1p**) [10], **1-methylquinolin-1-ium iodide** (**1w**) [6], **1-isopropylquinolin-1-ium iodide** (**1x**) [11], **1-methyl-1,10-phenanthrolin-1-ium iodide** (**1bb**) [12], **2-methylisoquinolin-2-ium iodide** (**1cc**) [6], **2-isopropylisoquinolin-2-ium iodide** (**1dd**) [11], **2-(*tert*-butyl)isoquinolin-2-ium chloride** (**1ee**) [2], **1-methylquinoxalin-1-ium iodide** (**1gg**) [13], **1,6-dimethyl-*1H*-pyrrolo[2,3-c]pyridin-6-ium iodide** (**1hh**) [14], **1-phenylpyridin-1-ium trifluoromesylate** (**1jj**) [3].

_N_-alkyl heterocyclic salts used in this work





3-Benzoyl-1-propylpyridin-1-ium iodide (**1c**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.88 g (83%).

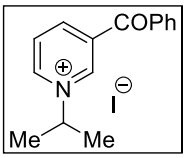
Physical state: yellow solid.

Melting point (Et_2O): 130 – 132 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.46 (s, 1H), 9.30 (d, *J* = 6.1 Hz, 1H), 8.83 – 8.86 (m, 1H), 8.32 (dd, *J* = 8.0, 6.1 Hz, 1H), 7.89 – 7.92 (m, 2H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.63 – 7.67 (m, 2H), 4.67 (t, *J* = 7.4 Hz, 2H), 1.91 – 2.04 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, D_2O): 192.4, 146.4, 145.5, 145.1, 136.7, 134.5, 134.1, 129.9, 128.7, 127.9, 63.4, 23.8, 9.2.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{16}NO^+$ 226.1226; Found 226.1227 (0.4 ppm).



3-Benzoyl-1-isopropylpyridin-1-ium iodide (**1d**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.86 g (81%).

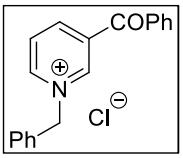
Physical state: yellow solid.

Melting point (Et_2O): 178 – 180 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.42 – 9.49 (m, 2H), 8.82 (d, *J* = 8.1 Hz, 1H), 8.24 – 8.44 (m, 1H), 7.86 – 8.01 (m, 2H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.72 (m, 2H), 5.17 (hept, *J* = 7.3, 6.5 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 190.8, 145.3, 144.8, 144.1, 137.0, 134.9, 134.5, 130.4, 129.1, 128.3, 64.9, 22.3.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{16}NO^+$ 226.1226; Found 226.1230 (1.7 ppm).



3-Benzoyl-1-benzylpyridin-1-ium chloride (**1e**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

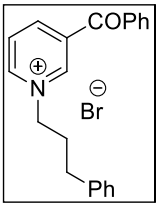
Yield: 0.68 g (73%).

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.68 (s, 1H), 9.53 (d, *J* = 6.1 Hz, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.34 (dd, *J* = 8.0, 6.1 Hz, 1H), 7.85 – 7.92 (m, 2H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.70 (m, 4H), 7.40 – 7.50 (m, 3H), 6.06 (s, 2H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 193.9, 148.4, 147.9, 147.0, 138.7, 136.6, 136.0, 133.9, 131.9, 131.8, 131.3, 130.9, 130.8, 130.2, 66.6.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{19}H_{16}NO^+$ 274.1226; Found 274.1223 (1 ppm).



3-Benzoyl-1-(3-phenylpropyl)pyridin-1-ium bromide (**1f**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.71 g (62%).

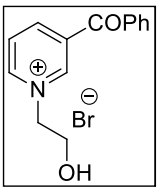
Physical state: white solid.

Melting point (Et_2O): 122 – 124 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.47 (s, 1H), 9.35 (d, *J* = 6.1 Hz, 1H), 8.83 (d, *J* = 8.0 Hz, 1H), 8.30 (dd, *J* = 8.0, 6.1 Hz, 1H), 7.89 – 7.91 (m, 2H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.70 (m, 2H), 7.17 – 7.30 (m, 5H), 4.78 (t, *J* = 7.4 Hz, 2H), 2.67 – 2.71 (m, 2H), 2.24 – 2.37 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 190.7, 147.0, 145.7, 145.3, 140.4, 136.7, 134.9, 134.4, 130.4, 129.1, 128.4, 128.3, 128.1, 126.2, 61.1, 32.1, 31.6.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{21}H_{20}NO^+$ 302.1539; Found 302.1548 (2.9 ppm).



3-Benzoyl-1-(2-hydroxyethyl)pyridin-1-ium bromide (**1g**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.48 g (52%).

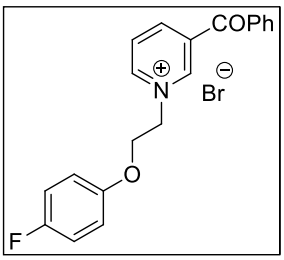
Physical state: light brown solid.

Melting point (Et_2O): 135 – 137 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.39 (s, 1H), 9.24 (dd, *J* = 6.1, 1.3 Hz, 1H), 8.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.33 (dd, *J* = 8.1, 6.1 Hz, 1H), 7.88 – 7.94 (m, 2H), 7.77 – 7.84 (m, 1H), 7.61 – 7.68 (m, 2H), 4.78 (t, *J* = 4.9 Hz, 2H), 3.85 – 3.93 (m, 2H), 3.55 (brs, 1H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 190.7, 147.6, 145.9, 145.5, 136.3, 134.9, 134.5, 130.4, 129.1, 127.8, 63.5, 60.0.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{14}NO_2^+$ 228.1019; Found 228.1016 (1.3 ppm).



3-Benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide (**1h**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.85 g (70%).

Physical state: white solid.

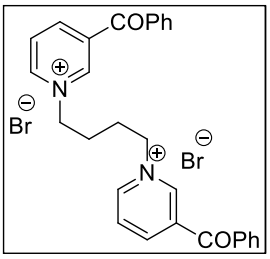
Melting point (Et_2O): 140 – 142 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.51 (s, 1H), 9.35 (d, *J* = 6.1 Hz, 1H), 8.90 (d, *J* = 8.2 Hz, 1H), 8.35 (dd, *J* = 8.0, 6.1 Hz, 1H), 7.86 – 7.96 (m, 2H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.69 (m, 2H), 7.10 – 7.19 (m, 2H), 6.91 – 6.99 (m, 2H), 5.14 (t, *J* = 4.9 Hz, 2H), 4.52 (t, *J* = 4.9 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 190.6, 157.0 (d, *J* = 236.6 Hz), 153.8 (d, *J* = 1.8 Hz), 147.8, 146.3, 145.9, 136.4, 134.8, 134.5, 130.4, 129.1, 127.9, 116.1 (d, *J* = 2.9 Hz), 116.0 (d, *J* = 12.1 Hz), 66.6, 60.3.

^{19}F NMR (376 MHz, DMSO-*d6*): δ -122.86 – -122.78 (m).

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{20}H_{17}FNO_2^+$ 322.1238; Found 322.1233 (1.5 ppm).



1,1'-(Butane-1,4-diyl)bis(3-benzoylpyridin-1-ium) bromide (**1i**) was obtained to the **General Procedure A** from **3-benzoyl pyridine** (0.55 g, 3 mmol).

Yield: 0.58 g (66%).

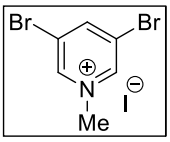
Physical state: white solid.

Melting point (Et_2O): more than 230 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.47 (s, 2H), 9.33 (d, *J* = 6.1 Hz, 2H), 8.86 (d, *J* = 8.0 Hz, 2H), 8.29 – 8.40 (m, 2H), 7.86 – 7.96 (m, 4H), 7.81 (t, *J* = 7.4 Hz, 2H), 7.58 – 7.70 (m, 4H), 4.70 – 4.84 (m, 4H), 1.97 – 2.07 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 190.7, 147.0, 145.7, 145.5, 136.8, 134.8, 134.5, 130.4, 129.1, 128.2, 60.3, 27.2.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{28}H_{26}N_2O_2^{2+}$ 211.0992; Found 211.1000 (3.7 ppm).



3,5-Dibromo-1-methylpyridin-1-ium iodide (**1n**) was obtained to the **General Procedure A** from **3,5-dibromopyridine** (0.70 g, 3 mmol).

Yield: 0.90 g (80%).

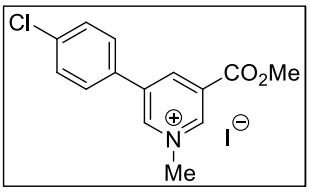
Physical state: light yellow solid.

Melting point (Et_2O): more than 230 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.45 (d, *J* = 1.7 Hz, 2H), 9.28 (t, *J* = 1.8 Hz, 1H), 4.28 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 149.1, 145.9, 121.8, 48.2.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_6H_6Br_2N^+$ 249.8862; Found 249.8863 (0.4 ppm).



3-(4-Chlorophenyl)-5-(methoxycarbonyl)-1-methylpyridin-1-ium iodide (**1q**) was obtained to the **General Procedure A** from **methyl 5-(4-chlorophenyl)nicotinate** (0.74 g, 3 mmol).

Yield: 0.94 g (81%).

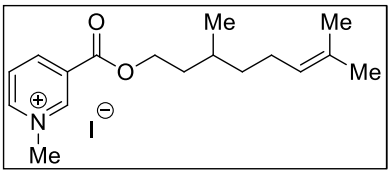
Physical state: yellow solid.

Melting point (Et_2O): 146 – 148 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.65 (s, 1H), 9.55 (s, 1H), 9.17 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 4.48 (s, 3H), 4.02 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 162.4, 147.2, 145.1, 141.8, 138.3, 135.8, 131.5, 129.77, 129.73, 129.7, 53.8, 48.7.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{13}ClNO_2^+$ 262.0629; Found 262.0626 (1.1 ppm).



3-(((3,7-Dimethyloct-6-en-1-yl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1r**) was obtained to the **General Procedure A** from **3,7-dimethyloct-6-en-1-yl nicotinate** (0.78 g, 3 mmol).

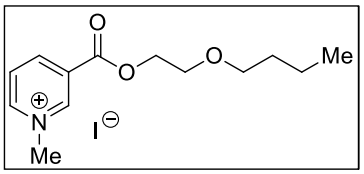
Yield: 0.88 g (73%).

Physical state: brown viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 – 9.80 (m, 1H), 9.34 (s, 1H), 8.84 – 8.93 (m, 1H), 8.35 (dd, *J* = 8.1, 6.1 Hz, 1H), 4.99 – 5.14 (m, 1H), 4.79 (s, 3H), 4.40 – 4.50 (m, 2H), 1.90 – 2.04 (m, 2H), 1.78 – 1.88 (m, 1H), 1.53 – 1.73 (m, 8H), 1.32 – 1.44 (m, 1H), 1.16 – 1.26 (m, 1H), 0.95 (d, *J* = 6.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.9, 148.9, 146.0, 144.7, 131.2, 130.1, 128.6, 124.1, 65.8, 50.3, 36.6, 34.9, 29.2, 25.5, 25.1, 19.1, 17.5.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{17}H_{26}NO_2^+$ 276.1958; Found 276.1965 (2.5 ppm).



3-((2-Butoxyethoxy)carbonyl)-1-methylpyridin-1-ium iodide (**1s**) was obtained to the **General Procedure A** from **2-butoxyethyl nicotinate** (0.67 g, 3 mmol).

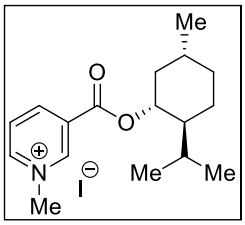
Yield: 0.82 g (75%).

Physical state: brown viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (d, *J* = 6.0 Hz, 1H), 9.41 (s, 1H), 8.93 (d, *J* = 8.2 Hz, 1H), 8.34 (dd, *J* = 8.2, 6.1 Hz, 1H), 4.79 (s, 3H), 4.52 – 4.62 (m, 2H), 3.75 – 3.84 (m, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 1.51 – 1.60 (m, 2H), 1.28 – 1.41 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1, 149.4, 146.3, 145.3, 130.4, 128.8, 71.4, 68.1, 66.4, 50.6, 31.7, 19.3, 14.0.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{13}H_{20}NO_3^+$ 238.1438; Found 238.1434 (1.6 ppm).



3-((((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1t**) was obtained to the **General Procedure A** from **(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl nicotinate** (0.78 g, 3 mmol).

Yield: 0.84 g (70%).

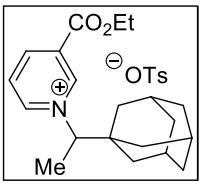
Physical state: yellow solid.

Melting point (Et_2O): 181 – 183 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (d, *J* = 6.1 Hz, 1H), 9.23 (s, 1H), 8.91 (d, *J* = 8.1 Hz, 1H), 8.34 (dd, *J* = 8.1, 6.1 Hz, 1H), 5.05 (td, *J* = 10.9, 4.5 Hz, 1H), 4.82 (s, 3H), 2.05 – 2.14 (m, 1H), 1.83 – 1.91 (m, 1H), 1.71 – 1.79 (m, 2H), 1.49 – 1.69 (m, 3H), 1.05 – 1.28 (m, 2H), 0.90 – 0.97 (m, 6H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 149.4, 145.8, 145.0, 130.8, 128.8, 78.2, 50.7, 46.8, 40.6, 33.9, 31.5, 26.3, 23.2, 22.0, 20.9, 16.2.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{17}H_{26}NO_2^+$ 276.1958; Found 276.1959 (0.3 ppm).



1-(1-(Adamantan-1-yl)ethyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate (**1u**) was obtained to the **General Procedure A** from **1-(2,4-dinitrophenyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate** (1.91 g, 3.9 mmol).

Yield: 1.12 g (59%).

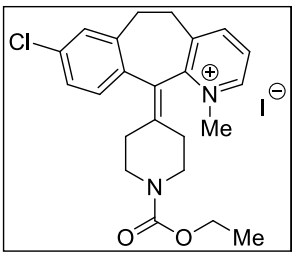
Physical state: light yellow solid.

Melting point (Et_2O): 152 – 154 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.53 (brs, 0.5H), 9.21 (d, *J* = 6.2 Hz, 1H), 9.02 (d, *J* = 8.0 Hz, 1H), 8.29 (dd, *J* = 8.1, 6.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.29 (brs, 0.5H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.70 – 4.97 (m, 1H), 4.38 – 4.52 (m, 2H), 2.28 (s, 3H), 1.92 – 2.00 (m, 3H), 1.59 – 1.69 (m, 6H), 1.48 – 1.57 (m, 7H), 1.32 – 1.41 (m, 5H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 161.8, 149.0, 146.7, 146.5, 145.6, 145.6, 137.8, 129.5, 128.2, 125.6, 76.3, 62.7, 55.7, 37.0, 36.2, 35.9, 34.1, 27.6, 27.5, 20.8, 14.0, 13.2, 12.8.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{20}H_{28}NO_2^+$ 314.2115; Found 314.2113 (0.6 ppm).



8-Chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-1-methyl-6,11-dihydro-*5H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-1-ium iodide (**1v**) was obtained to the **General Procedure A** from **ethyl 4-(8-chloro-*5H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11(6H)-ylidene)piperidine-1-carboxylate** (1.15 g, 3 mmol).

Yield: 1.15 g (73%).

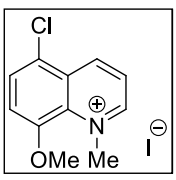
Physical state: yellow solid.

Melting point (Et_2O): 150 – 152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (d, *J* = 5.9 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.03 (dd, *J* = 7.9, 6.2 Hz, 1H), 7.10 – 7.25 (m, 3H), 4.47 (s, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.89 – 4.03 (m, 2H), 3.38 – 3.56 (m, 2H), 2.88 – 3.21 (m, 4H), 2.48 – 2.62 (m, 2H), 2.36 – 2.46 (m, 1H), 1.98 – 2.04 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 154.5, 153.8, 144.8, 144.3, 143.9, 139.9, 139.1, 133.2, 132.4, 131.2, 130.7, 126.4, 126.2, 123.2, 60.9, 45.7, 43.4, 43.2, 31.0, 30.6, 29.8, 28.9, 14.6.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{23}H_{26}ClN_2O_2^+$ 397.1677; Found 397.1675 (0.5 ppm).



5-Chloro-8-methoxy-1-methylquinolin-1-ium iodide (**1y**) was obtained to the **General Procedure A** from **5-chloro-8-methoxyquinoline** (0.58 g, 3 mmol).

Yield: 0.82 g (82%).

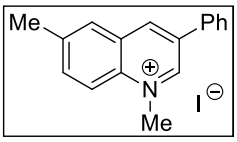
Physical state: yellow solid.

Melting point (Et_2O): 197 – 199 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.45 (d, *J* = 5.8 Hz, 1H), 9.33 (d, *J* = 8.7 Hz, 1H), 8.24 (dd, *J* = 8.6, 5.7 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 4.81 (s, 3H), 4.09 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 152.6, 150.9, 143.0, 131.7, 130.5, 128.6, 123.6, 122.8, 116.2, 57.8, 52.5.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{11}H_{11}ClNO^+$ 208.0524; Found 208.0525 (0.4 ppm).



1,6-Dimethyl-3-phenylquinolin-1-ium iodide (**1z**) was obtained to the **General Procedure A** from **6-methyl-3-phenylquinoline** (0.66 g, 3 mmol).

Yield: 0.87 g (80%).

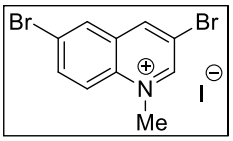
Physical state: yellow solid.

Melting point (Et_2O): more than 230 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.90 (d, *J* = 2.1 Hz, 1H), 9.50 (d, *J* = 2.0 Hz, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.25 (s, 1H), 8.13 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.02 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.63 – 7.71 (m, 2H), 7.55 – 7.62 (m, 1H), 4.69 (s, 3H), 2.64 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 148.2, 142.0, 140.5, 137.2, 135.8, 133.6, 133.4, 129.8, 129.6, 129.4, 128.9, 127.4, 118.8, 45.5, 21.0.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{17}H_{16}N^+$ 234.1277; Found 234.1277 (0 ppm).



3,6-Dibromo-1-methylquinolin-1-ium iodide (**1aa**) was obtained to the **General Procedure A** from **3,6-dibromoquinoline** (0.86 g, 3 mmol).

Yield: 1.22 g (95%).

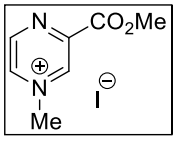
Physical state: orange solid.

Melting point (Et_2O): more than 230 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.93 (s, 1H), 9.52 (s, 1H), 8.68 (s, 1H), 8.40 – 8.50 (m, 2H), 4.61 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 152.0, 147.0, 138.0, 136.2, 131.2, 130.7, 124.0, 121.6, 115.8, 45.6.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{10}H_8Br_2N^+$ 299.9018; Found 299.9020 (0.6 ppm).



3-(Methoxycarbonyl)-1-methylpyrazin-1-ium iodide (**1ff**) was obtained to the **General Procedure A** from **methyl pyrazine-2-carboxylate** (0.41 g, 3 mmol).

Yield: 0.76 g (92%).

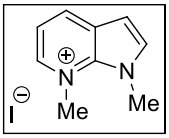
Physical state: yellow solid.

Melting point (Et_2O): 142 – 144 °C.

^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.79 (s, 1H), 9.62 (d, *J* = 3.3 Hz, 1H), 9.37 (d, *J* = 3.4 Hz, 1H), 4.48 (s, 3H), 4.03 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 161.5, 149.8, 147.6, 140.8, 139.7, 53.8, 48.9.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_7H_9N_2O_2^+$ 153.0659; Found 153.0653 (3.9 ppm).



1,7-Dimethyl-*1H*-pyrrolo[2,3-*b*]pyridin-7-ium iodide (**1ii**) was obtained to the **General Procedure A** from **1-methyl-*1H*-pyrrolo[2,3-*b*]pyridine** (0.40 g, 3 mmol).

Yield: 0.71 g (85%).

Physical state: yellow solid.

Melting point (Et_2O): more than 230 °C.

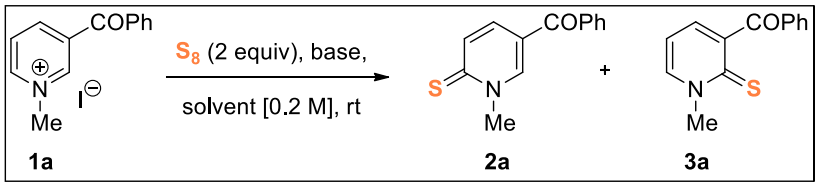
^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.70 (d, *J* = 7.9 Hz, 1H), 8.59 (d, *J* = 6.2 Hz, 1H), 7.83 (d, *J* = 3.6 Hz, 1H), 7.59 (dd, *J* = 7.9, 6.2 Hz, 1H), 6.93 (d, *J* = 3.5 Hz, 1H), 4.71 (s, 3H), 4.29 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): 139.6, 138.5, 137.5, 136.2, 127.8, 116.0, 102.3, 44.5, 37.4.

HRMS (ESI) m/z: $[M]^+$ Calcd for $C_9H_{11}N_2^+$ 147.0917; Found 147.0918 (0.6 ppm).

S-III. Optimization of the Reaction Conditions for the Preparation of Pyridine and Quinoline Thiones

Table S1. Optimization of the reaction conditions



1a **2a** **3a**

№	base (equiv)	solvent	conditions	time, h	ratio, **2a** : **3a**	total yield, %
1[a]	Cs_2CO_3 (1.5)	THF	hv, air	12	1 : 0	18
2[a]	Cs_2CO_3 (1.5)	THF	hv, Ar	12	1 : 0	35
3	Cs_2CO_3 (1.5)	THF	hv, Ar	12	1 : 0	39
4	Cs_2CO_3 (1.5)	MeCN	hv, Ar	12	1 : 0	39
5	Cs_2CO_3 (1.5)	DMF	hv, Ar	12	1 : 0	30
6	Cs_2CO_3 (1.5)	DMSO	hv, Ar	12	1 : 0	58
7	Cs_2CO_3 (1.5)	DMSO	100 °C, Ar	12	1 : 0	65
8	Cs_2CO_3 (1.5)	DMSO	Ar	12	1 : 0	76
9	K_2CO_3 (1.5)	DMSO	Ar	12	1 : 0	51
10	K_3PO_4 (1.5)	DMSO	Ar	12	1 : 0	42
11	(*i*-Pr)$_2$EtN (1.5)	DMSO	Ar	12	1 : 0	40
12	DABCO (1.5)	DMSO	Ar	12	1 : 0	34
13	Cs_2CO_3 (1.0)	DMSO	Ar	24	1 : 0	67
14	Cs_2CO_3 (1.5)	DMSO	Ar	24	1 : 0	86
15[b]	Cs_2CO_3 (1.5)	DMSO	Ar	24	1 : 0	80
16	LiHMDS (1.5)	THF	Ar	24	1 : 1.38	76[c]
17	LiHMDS (1.5)	THF	Ar	2	1 : 1.42	87[d]
18	LiHMDS (1.5)	THF	-100 °C, Ar	2	1 : 0.14	79[e]
19	LiHMDS (1.5)	THF	-50 °C, Ar	2	1 : 0.64	75[f]
20	KHMDS (1.5)	THF	Ar	2	1 : 0.70	80[g]

hv – white LED (6500K, 12 W), the distance to the source is 4 cm; [a]photocatalyst Eosin Y was added; [b]tetrafluoroborate salt **1a** was used; yields of individual compounds: [c]**2a** (32%), **3a** (44%); [d]**2a** (36%), **3a** (51%); [e]**2a** (69%), **3a** (10%); [f]**2a** (46%), **3a** (29%); [g]**2a** (47%), **3a** (33%). Yields were determined with ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

S-IV-I. General Procedure for the Synthesis of Pyridine and Quinoline Thiones 2 using Cs_2CO_3 as the Base (*General Procedure B)*

To the solution of *N*-alkylheterocyclic salt **1** (0.6 mmol, 1.0 equiv) in DMSO (3 mL, 0.2 M) in a screw cap vial with septum cap, S_8 (38.4 mg, 1.2 mmol, 2.0 equiv) and Cs_2CO_3 (293.2 mg, 0.9 mmol, 1.5 equiv) were added. The vial was evacuated and refilled with argon five times. The reaction mixture was stirred for 24 h at rt. Then the mixture was poured into brine (20 mL). The water layer was extracted with EtOAc (3 × 15 mL), and the combined organic layers were washed with brine (3 × 30 mL). The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using gradient mixtures of *n*-hexane : EtOAc (from 8:1 to 1:1) as an eluent (See Note).

Note: For **2p** and **2q** mixtures of CH_2Cl_2 : MeOH = 30:1 was used as eluent. Some products (**2a**, **2t**, **2u**) were obtained with a high degree of purity without the need for flash chromatography.

S-IV-II. General Procedure for the Synthesis of Pyridine and Quinoline Thiones 3 using LiHMDS as the Base (*General Procedure C)*

To the solution of *N*-alkylheterocyclic salt **1** (0.6 mmol, 1.0 equiv) in THF (3 mL, 0.2 M) in a screw cap vial with septum cap, S_8 (38.4 mg, 1.2 mmol, 2.0 equiv) was added. The vial was evacuated, refilled with argon five times and cooled to 0 °C. The solution of LiHMDS in 1.0 M *n*-hexane (0.9 mL, 0.9 mmol, 1.5 equiv) was added dropwise to the cooled stirring solution. The vial was evacuated and refilled with argon three times. The resulting reaction mixture was stirred for 2 h at rt. Then the solution of citric acid (10%, 1 mL) was added to the reaction mixture, THF was removed under reduced pressure. The residue was dissolved in EtOAc (30 mL) and washed with water (3 × 30 mL). The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using gradient mixtures of *n*-hexane : EtOAc (from 8:1 to 1:1) as an eluent (See Note).

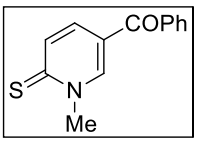
Note: For **3j** and **3o** mixtures of CH_2Cl_2 : MeOH = 40:1 was used as eluent. Some products (**3c**, **3n, 3s**) were obtained with a high degree of purity without the need for flash chromatography.

S-V. Scale-Up Procedure for Obtaining 2a and 3c

To the solution of 3-benzoyl-1-methylpyridin-1-ium iodide **1a** (1.02 g, 3.1 mmol, 1.0 equiv) in DMSO (15.5 mL, 0.2 M) in a round bottom flask with septum cap, S_8 (0.20 mg, 6.2 mmol, 2.0 equiv) and Cs_2CO_3 (1.52 g, 4.7 mmol, 1.5 equiv) were added. The flask with septum cap were evacuated and refilled with argon five times. The reaction mixture was stirred for 24 h at rt. Then the mixture was poured into brine (100 mL). The water layer was extracted with EtOAc (3 × 60 mL), the combined organic layers were washed with brine (3 × 100 mL). The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using mixture of *n*-hexane : EtOAc = 4:1 as an eluent. **(1-Methyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone** (**2a**) was in obtained in high purity with yield 81% (0.58 g).

To the solution of 1-methylpyridin-1-ium iodide **1b** (1.04 g, 4.7 mmol, 1.0 equiv) in THF (23.5 mL, 0.2 M) in a round bottom flask with septum cap, S_8 (0.30 g, 9.4 mmol, 2.0 equiv) was added. The flask with septum cap was evacuated, refilled with argon five times and cooled to 0 °C. The solution of LiHMDS in 1.0 M *n*-hexane (7.1 mL, 7.1 mmol, 1.5 equiv) was slowly added to the cooled stirring solution. The flask was evacuated and refilled with argon three times. The resulting reaction mixture was stirred for 2 h at rt. Then the solution of citric acid (10%, 8 mL) was added to the reaction mixture, THF was removed under reduced pressure. The residue was dissolved in EtOAc (100 mL) and washed with water (3 × 100 mL). The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using mixture of *n*-hexane : EtOAc = 1:1 as an eluent. **1-Methylpyridine-2(1*H*)-thione** (**3c**) was in obtained in high purity with yield 58% (0.34 g).

S-VI-I. Characterization Data for the Synthesis of Pyridine and Quinoline Thiones 2



(1-Methyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2a**) was obtained to the **General Procedure B** from **3-benzoyl-1-methylpyridin-1-ium iodide** (**1a**) (0.20 g, 0.6 mmol). **Yield:** 0.12 g (83%).

Physical state: yellow solid.

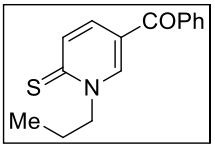
Melting point (EtOAc): 135 – 137 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.68 – 7.72 (m, 3H), 7.59 – 7.66 (m, 2H), 7.53 (dd, *J* = 8.3, 7.0 Hz, 2H), 4.01 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5, 183.5, 145.1, 136.6, 135.3, 133.0, 132.6, 129.2, 128.8, 123.2, 46.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}NOS^+$ 230.0634; Found 230.0634 (0 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.16.



Phenyl(1-propyl-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2b**) was obtained to the **General Procedure B** from **3-benzoyl-1-propylpyridin-1-ium iodide** (**1c**) (0.21 g, 0.6 mmol). **Yield:** 0.15 g (86%).

Physical state: brown solid.

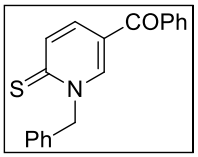
Melting point (*n*-hexane : EtOAc): 95 – 97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 2.1 Hz, 1H), 7.67 – 7.73 (m, 2H), 7.60 – 7.66 (m, 2H), 7.49 – 7.55 (m, 3H), 4.45 – 4.48 (m, 2H), 1.86 – 1.98 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.6, 183.1, 144.5, 136.7, 136.0, 133.0, 132.2, 129.3, 128.9, 123.3, 59.0, 21.6, 11.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NOS^+$ 258.0947; Found 258.0949 (0.7 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.73.



(1-Benzyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2c)** was obtained to the **General Procedure B** from **3-benzoyl-1-benzylpyridin-1-ium chloride** (**1e**) (0.19 g, 0.6 mmol). **Yield:** 0.14 g (74%).

Physical state: yellow solid.

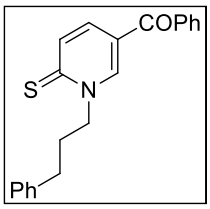
Melting point (*n*-hexane : EtOAc): 145 – 147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.56 – 7.60 (m, 4H), 7.32 – 7.46 (m, 7H), 5.79 (s, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.3, 184.0, 144.5, 136.6, 135.9, 134.6, 133.0, 132.1, 129.4, 129.3, 128.8, 128.69, 128.67, 123.3, 59.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}NOS^+$ 306.0947; Found 306.0950 (0.9 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.30.



Phenyl(1-(3-phenylpropyl)-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2d**) was obtained to the **General Procedure B** from **3-benzoyl-1-(3-phenylpropyl)pyridin-1-ium bromide** (**1f**) (0.23 g, 0.6 mmol). **Yield:** 0.15 g (77%).

Physical state: orange solid.

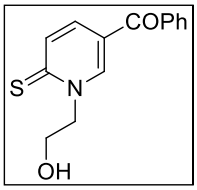
Melting point (*n*-hexane : EtOAc): 75 – 77 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.1 Hz, 1H), 7.61 – 7.70 (m, 4H), 7.50 – 7.55 (m, 3H), 7.25 – 7.29 (m, 2H), 7.17 – 7.20 (m, 3H), 4.53 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.31 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.2, 182.8, 144.4, 140.0, 136.5, 135.7, 132.8, 132.1, 129.1, 128.7, 128.5, 128.1, 126.2, 123.1, 56.8, 32.4, 29.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1268 (2.3 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.29.



(1-(2-Hydroxyethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2e**) was obtained to the **General Procedure B** from **3-benzoyl-1-(2-hydroxyethyl)pyridin-1-ium bromide** (**1g**) (0.18 g, 0.6 mmol). **Yield:** 0.11 g (70%).

Physical state: yellow solid.

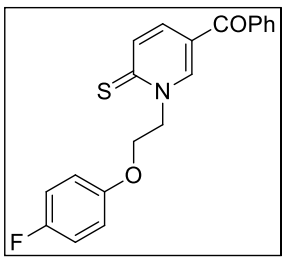
Melting point (*n*-hexane : EtOAc): 114 – 116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 2.1 Hz, 1H), 7.67 – 7.77 (m, 3H), 7.61 – 7.66 (m, 2H), 7.48 – 7.55 (m, 2H), 4.75 (t, *J* = 4.9 Hz, 2H), 4.15 (t, *J* = 4.9 Hz, 2H), 1.68 (brs, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.8, 183.0, 146.5, 136.5, 135.6, 133.1, 132.9, 129.4, 128.9, 122.8, 59.3, 59.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2S^+$ 260.0740; Found 260.0750 (3.8 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.40.



(1-(2-(4-Fluorophenoxy)ethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2f**) was obtained to the **General Procedure B** from **3-benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide** (**1h**) (0.24 g, 0.6 mmol). **Yield:** 0.16 g (76%).

Physical state: yellow solid.

Melting point (*n*-hexane : EtOAc): 135 – 137 °C.

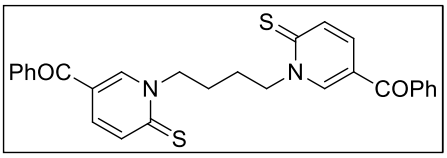
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 2.1 Hz, 1H), 7.63 – 7.73 (m, 5H), 7.50 – 7.54 (m, 2H), 6.94 – 6.99 (m, 2H), 6.77 – 6.81 (m, 2H), 4.94 (t, *J* = 4.6 Hz, 2H), 4.43 (t, *J* = 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5, 183.1, 157.7 (d, *J* = 239.6 Hz), 154.1 (d, *J* = 2.0 Hz), 146.3, 136.7, 135.9, 133.1, 132.8, 129.4, 128.9, 123.0, 116.2 (d, *J* = 23.2 Hz), 115.6 (d, *J* = 8.1 Hz), 65.0, 56.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -122.56 – -122.48 (m).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}FNO_2S^+$ 354.0959; Found 354.0963 (1.1 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.33.



(1,1'-(Butane-1,4-diyl)bis(6-thioxo-1,6-dihydropyridine-3,1-diyl))bis(phenylmethanone) (**2g**) was obtained to the **General Procedure B** from **1,1'-(butane-1,4-diyl)bis(3-benzoylpyridin-1-ium) bromide** (**1i**) (0.35 g, 0.6 mmol). **Yield:** 0.25 g (85%). **Physical state:** yellow solid.

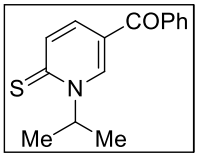
Melting point (*n*-hexane : EtOAc): 209 – 211 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.21 (m, 2H), 7.69 – 7.75 (m, 4H), 7.62 – 7.67 (m, 4H), 7.51 – 7.60 (m, 6H), 4.54 – 4.67 (m, 4H), 1.97 – 2.08 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5, 183.1, 144.5, 136.7, 136.2, 133.2, 132.6, 129.4, 129.0, 123.8, 56.6, 25.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{25}N_2O_2S_2^+$ 485.1352; Found 485.1354 (0.4 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.54.



(1-Isopropyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2h**) was obtained to the **General Procedure B** from **3-benzoyl-1-isopropylpyridin-1-ium iodide** (**1d**) (0.21 g, 0.6 mmol). **Yield:** 0.11 g (75%).

Physical state: yellow solid.

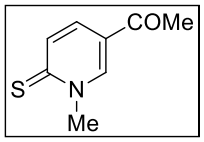
Melting point (*n*-hexane : EtOAc): 123 – 125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 2.1 Hz, 1H), 7.69 – 7.74 (m, 3H), 7.61 – 7.66 (m, 1H), 7.49 – 7.55 (m, 3H), 6.31 (hept, *J* = 6.8 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.7, 183.3, 140.3, 136.8, 135.7, 133.1, 131.8, 129.4, 128.9, 123.9, 54.4, 22.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NOS^+$ 258.0947; Found 258.0956 (3.4 ppm).

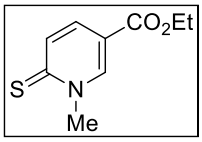
R_f (*n*-hexane : EtOAc = 4:1) = 0.30.



1-(1-Methyl-6-thioxo-1,6-dihydropyridin-3-yl)ethanone (**2i**) was obtained to the **General Procedure B** from **3-acetyl-1-methylpyridin-1-ium iodide** (**1j**) (0.16 g, 0.6 mmol). **Yield:** 0.08 g (79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 2.0 Hz, 1H), 7.60 – 7.67 (m, 2H), 4.02 (s, 3H), 2.50 (s, 3H).

Characterization data obtained for this compound matched those previously reported in the literature [15].



Ethyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2j**) was obtained to the **General Procedure B** from **3-(ethoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1o**) (0.18 g, 0.6 mmol). **Yield:** 0.08 g (69%). **Physical state:** yellow solid.

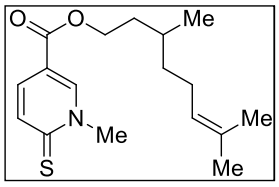
Melting point (*n*-hexane : EtOAc): 92 – 94 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 1.4 Hz, 1H), 7.60 – 7.69 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.8, 163.8, 144.1, 135.6, 132.2, 116.6, 61.7, 46.5, 14.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{12}NO_2S^+$ 198.0583; Found 198.0585 (1 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.50.



3,7-Dimethyloct-6-en-1-yl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2k**) was obtained to the **General Procedure B** from **3-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)-1-methylpyridin-1-ium iodide** (**1r**) (0.24 g, 0.6 mmol). **Yield:** 0.15 g (81%). **Physical state:** yellow solid.

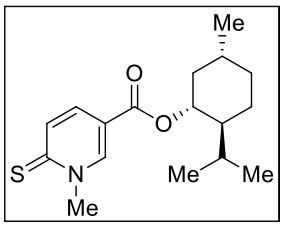
Melting point (*n*-hexane : EtOAc): 47 – 49 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dd, *J* = 1.3 Hz, 1H), 7.61 – 7.67 (m, 2H), 5.06 – 5.11 (m, 1H), 4.28 – 4.38 (m, 2H), 4.00 (s, 3H), 1.96 – 2.04 (m, 2H), 1.74 – 1.83 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.34 – 1.42 (m, 2H), 1.16 – 1.24 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.8, 163.8, 144.1, 135.6, 132.2, 131.7, 124.5, 116.6, 64.3, 46.5, 37.0, 35.5, 29.6, 25.9, 25.5, 19.6, 17.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_2S^+$ 308.1679; Found 308.1683 (1.2 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.29.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2l**) was obtained to the **General Procedure B** from **3-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1-methylpyridin-1-ium iodide** (**1t**) (0.24 g, 0.6 mmol). **Yield:** 0.14 g (77%). **Physical state:** yellow solid.

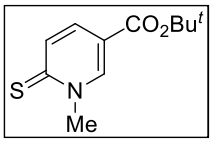
Melting point (*n*-hexane : EtOAc): 98 – 100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 1.6 Hz, 1H), 7.57 – 7.71 (m, 2H), 4.79 – 5.07 (m, 1H), 4.00 (s, 3H), 2.01 – 2.09 (m, 1H), 1.80 – 1.89 (m, 1H), 1.71 – 1.76 (m, 3H), 1.47 – 1.55 (m, 2H), 1.03 – 1.15 (m, 2H), 0.90 – 0.93 (m, 6H), 0.78 (d, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.7, 163.3, 144.1, 135.6, 132.3, 116.9, 75.8, 47.3, 46.5, 41.0, 34.3, 31.5, 26.6, 23.6, 22.1, 20.9, 16.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_2S^+$ 308.1679; Found 308.1686 (2.2 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.40.



***Tert*-butyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate** (**2m**) was obtained to the **General Procedure B** from **3-(tert-butoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1p**) (0.13 g, 0.6 mmol). **Yield:** 0.06 g (80%). **Physical state:** brown solid.

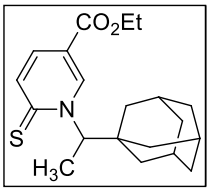
Melting point (*n*-hexane : EtOAc): 85 – 87 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 1.9 Hz, 1H), 7.58 – 7.65 (m, 2H), 4.00 (s, 3H), 1.57 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.3, 162.8, 143.9, 135.3, 132.5, 118.1, 82.6, 46.5, 28.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}NO_2S^+$ 226.0896; Found 226.0895 (0.4 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.42.



Ethyl 1-(1-(adamantan-1-yl)ethyl)-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2n**) was obtained to the **General Procedure B** from **1-(1-(adamantan-1-yl)ethyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate** (**1u**) (0.29 g, 0.6 mmol). **Yield:** 0.14 g (67%). **Physical state:** yellow solid.

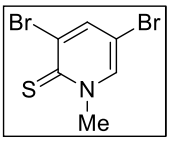
Melting point (*n*-hexane : EtOAc): 110 – 112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.31 (s, 1H), 7.85 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.99 (m, 1H), 2.01 – 2.03 (m, 3H), 1.81 – 1.93 (m, 1H), 1.65 – 1.71 (m, 3H), 1.51 – 1.58 (m, 8H), 1.39 – 1.46 (m, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.9, 166.5, 163.3, 154.8, 148.9, 124.7, 90.0, 62.6, 38.5, 36.7, 36.3, 28.0, 14.2. The compound was obtained as a mixture of rotamers. A number of rotamers complicate ^{13}C{^{1}H} NMR registration.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}NO_2S^+$ 346.1835; Found 346.1836 (0.2 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.52.



3,5-Dibromo-1-methylpyridine-2(1*H*)-thione (**2o**) was obtained to the **General Procedure B** from **3,5-dibromo-1-methylpyridin-1-ium iodide** (**1n**) (0.23 g, 0.6 mmol). **Yield:** 0.13 g (78%). **Physical state:** yellow solid.

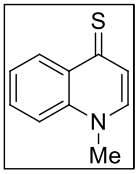
Melting point (*n*-hexane : EtOAc): 124 – 126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 2.2 Hz, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 4.05 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-*d6*): δ 175.8, 143.1, 139.9, 130.3, 102.9, 48.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_6H_6Br_2NS^+$ 281.8582; Found 281.8587 (1.7 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.63.



1-Methylquinoline-4(1*H*)-thione (**2p**) was obtained to the **General Procedure B** from **1-methylquinolin-1-ium iodide** (**1w**) (0.16 g, 0.6 mmol). **Yield:** 0.07 g (69%). **Physical state:** yellow solid.

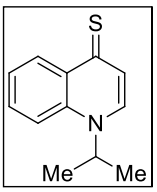
Melting point (CH_2Cl_2 : methanol): 123 – 125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.72 (ddd, *J* = 8.6, 6.9, 1.6 Hz, 1H), 7.41 – 7.53 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 3.90 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.7, 136.8, 136.8, 133.9, 132.9, 130.7, 125.8, 125.4, 116.2, 41.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{10}NS^+$ 176.0528; Found 176.0532 (2.2 ppm).

R_f (CH_2Cl_2 : methanol = 10:1) = 0.36.



1-Isopropylquinoline-4(1*H*)-thione (**2q**) was obtained to the **General Procedure B** from **1-isopropylquinolin-1-ium iodide** (**1x**) (0.18 g, 0.6 mmol). **Yield:** 0.10 g (78%). **Physical state:** yellow solid.

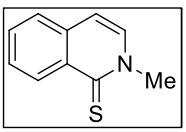
Melting point (CH_2Cl_2 : methanol): 110 – 112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.65 – 7.74 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.52 (m, 2H), 5.01 (hept, *J* = 6.7 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.3, 136.3, 134.5, 132.9, 131.6, 130.7, 126.0, 125.5, 115.4, 51.4, 22.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}NS^+$ 204.0841; Found 204.0846 (2.4 ppm).

R_f (CH_2Cl_2 : methanol = 10:1) = 0.48.



2-Methylisoquinoline-1(2*H*)-thione (**2r**) was obtained to the **General Procedure B** from **2-methylisoquinolin-2-ium iodide** (**1cc**) (0.16 g, 0.6 mmol). **Yield:** 0.06 g (55%). **Physical state:** yellow solid.

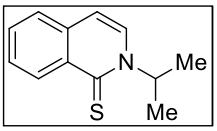
Melting point (*n*-hexane : EtOAc): 87 – 89 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 – 9.16 (m, 1H), 7.65 – 7.69 (m, 1H), 7.54 – 7.61 (m, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 4.09 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 184.1, 134.1, 133.8, 132.4, 132.1, 128.65, 128.62, 126.8, 112.3, 46.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{10}NS^+$ 176.0528; Found 176.0530 (1.1 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.29.



2-Isopropylisoquinoline-1(2*H*)-thione (**2s**) was obtained to the **General Procedure B** from **2-isopropylisoquinolin-2-ium iodide** (**1dd**) (0.18 g, 0.6 mmol). **Yield:** 0.06 g (50%). **Physical state:** yellow solid.

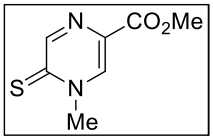
Melting point (*n*-hexane : EtOAc): 51 – 53 °C.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.16 – 9.19 (m, 1H), 7.63 – 7.67 (m, 1H), 7.52 – 7.59 (m, 2H), 7.47 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.68 (hept, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 183.6, 134.1, 133.4, 132.3, 132.1, 128.4, 128.1, 126.6, 113.0, 54.0, 21.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}NS^+$ 204.0841; Found 204.0850 (4.4 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.50.



Methyl 4-methyl-5-thioxo-4,5-dihydropyrazine-2-carboxylate (**2t**) was obtained to the **General Procedure B** from **3-(methoxycarbonyl)-1-methylpyrazin-1-ium iodide** (**1ff**) (0.17 g, 0.6 mmol). **Yield:** 0.10 g (89%). **Physical state:** brown solid.

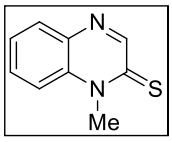
Melting point (EtOAc): 182 – 184 °C.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.73 (d, *J* = 1.1 Hz, 1H), 8.26 (d, *J* = 1.0 Hz, 1H), 3.97 (s, 3H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 177.9, 164.0, 158.2, 136.0, 129.9, 53.1, 45.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_7H_9N_2O_2S^+$ 185.0379; Found 185.0386 (3.7 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.26.



1-Methylquinoxaline-2(1*H*)-thione (**2u**) was obtained to the **General Procedure B** from **1-methylquinoxalin-1-ium iodide** (**1gg**) (0.16 g, 0.6 mmol). **Yield:** 0.10 g (93%). **Physical state:** yellow solid.

Melting point (EtOAc): 108 – 110 °C.

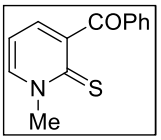
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.84 (s, 1H), 7.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.66 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 4.20 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 177.8, 156.6, 137.0, 133.9, 131.5, 130.8, 125.8, 114.7, 37.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9N_2S^+$ 177.0481; Found 177.0479 (1.1 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.58.

S-VI-II. Characterization Data for the Synthesis of Pyridine and Quinoline Thiones 3



(1-Methyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3a**) was obtained to the **General Procedure C** from **3-benzoyl-1-methylpyridin-1-ium iodide** (**1a**) (0.20 g, 0.6 mmol). **Yield:** 0.07 g (47%). **Physical state:** brown solid.

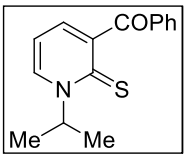
Melting point (*n*-hexane : EtOAc): 105 – 107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.94 (m, 2H), 7.81 (dd, *J* = 6.6, 1.7 Hz, 1H), 7.53 – 7.58 (m, 1H), 7.41 – 7.47 (m, 2H), 7.30 (dd, *J* = 7.1, 1.7 Hz, 1H), 6.75 (t, *J* = 6.8 Hz, 1H), 4.00 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.3, 177.5, 145.2, 142.1, 136.1, 133.6, 132.9, 129.6, 128.8, 112.5, 45.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}NOS^+$ 230.0634; Found 230.0634 (0 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.30.



(1-Isopropyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3b**) was obtained to the **General Procedure C** from **3-benzoyl-1-isopropylpyridin-1-ium iodide** (**1d**) (0.21 g, 0.6 mmol). **Yield:** 0.09 g (60%). **Physical state:** yellow solid.

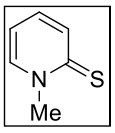
Melting point (*n*-hexane : EtOAc): 100 – 102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.94 (m, 2H), 7.81 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.51 – 7.58 (m, 1H), 7.40 – 7.47 (m, 2H), 7.22 (dd, *J* = 6.9, 1.6 Hz, 1H), 6.78 – 6.86 (m, 1H), 6.31 (hept, *J* = 6.7 Hz, 1H), 1.47 (d, *J* = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.1, 176.9, 145.3, 136.7, 136.2, 133.4, 131.9, 129.6, 128.8, 113.2, 52.9, 22.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NOS^+$ 258.0947; Found 258.0940 (2.7 ppm).

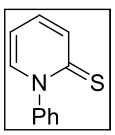
R_f (*n*-hexane : EtOAc = 1:1) = 0.60.



1-Methylpyridine-2(1*H*)-thione (**3c**) was obtained to the **General Procedure C** from **1-methylpyridin-1-ium iodide** (**1b**) (0.13 g, 0.6 mmol). **Yield:** 0.04 g (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.74 (m, 1H), 7.62 – 7.68 (m, 1H), 7.19 (ddd, *J* = 8.7, 6.9, 1.7 Hz, 1H), 6.58 – 6.67 (m, 1H), 3.99 (s, 3H).

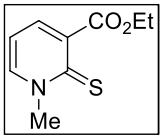
Characterization data obtained for this compound matched those previously reported in the literature [16].



1-Phenylpyridine-2(1H)-thione (**3d**) was obtained to the **General Procedure C** from **1-phenylpyridin-1-ium trifluoromesylate** (**1jj**) (0.18 g, 0.6 mmol). **Yield:** 0.08 g (71%). **Physical state:** yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (ddd, *J* = 8.8, 1.4, 0.8 Hz, 1H), 7.59 (ddd, *J* = 6.7, 1.7, 0.8 Hz, 1H), 7.46 – 7.57 (m, 3H), 7.31 – 7.38 (m, 2H), 7.22 – 7.28 (m, 1H), 6.65 – 6.72 (m, 1H).

Characterization data obtained for this compound matched those previously reported in the literature [17].



Ethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3e**) was obtained to the **General Procedure C** from **3-(ethoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1o**) (0.18 g, 0.6 mmol). **Yield:** 0.07 g (59%). **Physical state:** orange solid.

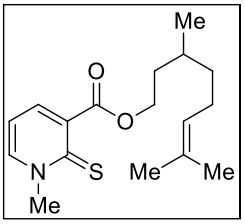
Melting point (*n*-hexane : EtOAc): 58 – 60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 6.6, 1.7 Hz, 1H), 7.41 (dd, *J* = 7.1, 1.7 Hz, 1H), 6.58 – 6.66 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.4, 166.9, 142.4, 139.6, 133.3, 111.6, 62.0, 46.3, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{12}NO_2S^+$ 198.0583; Found 198.0588 (2.5 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.33.



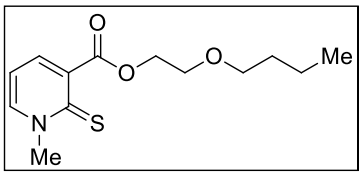
3,7-Dimethyloct-6-en-1-yl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3f**) was obtained to the **General Procedure C** from **3-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)-1-methylpyridin-1-ium iodide** (**1r**) (0.24 g, 0.6 mmol). **Yield:** 0.14 g (75%). **Physical state:** yellow viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 6.6, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.1, 1.7 Hz, 1H), 6.58 – 6.64 (m, 1H), 5.05 – 5.13 (m, 1H), 4.33 – 4.43 (m, 2H), 3.98 (s, 3H), 1.94 – 2.03 (m, 2H), 1.76 – 1.85 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.31 – 1.44 (m, 2H), 1.15 – 1.28 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.5, 167.1, 142.3, 139.8, 133.3, 131.4, 124.8, 111.5, 64.6, 46.4, 37.1, 35.4, 29.6, 25.9, 25.5, 19.5, 17.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_2S^+$ 308.1679; Found 308.1690 (3.5 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.46.



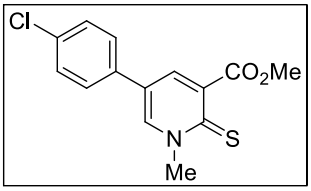
2-Butoxyethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3g**) was obtained to the **General Procedure C** from **3-((2-butoxyethoxy)carbonyl)-1-methylpyridin-1-ium iodide** (**1s**) (0.22 g, 0.6 mmol). **Yield:** 0.11 g (70%). **Physical state:** red viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 6.7, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.58 – 6.65 (m, 1H), 4.41 – 4.55 (m, 2H), 3.97 (s, 3H), 3.75 (dd, *J* = 5.7, 4.1 Hz, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 1.52 – 1.59 (m, 2H), 1.31 – 1.40 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.5, 166.8, 142.5, 139.2, 133.7, 111.5, 71.2, 68.4, 65.0, 46.4, 31.8, 19.4, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{20}NO_3S^+$ 270.1158; Found 270.1162 (2.2 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.42.



Methyl 5-(4-chlorophenyl)-1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3h**) was obtained to the **General Procedure C** from **3-(4-chlorophenyl)-5-(methoxycarbonyl)-1-methylpyridin-1-ium iodide** (**1q**) (0.23 g, 0.6 mmol). **Yield:** 0.08 g (48%). **Physical state:** orange solid.

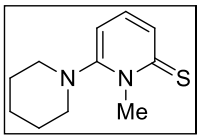
Melting point (*n*-hexane : EtOAc): 124 – 126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.2 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.41 – 7.46 (m, 2H), 7.35 – 7.40 (m, 2H), 4.06 (s, 3H), 3.96 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.1, 167.3, 139.8, 139.4, 134.8, 133.3, 132.5, 129.7, 127.4, 124.6, 53.1, 46.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}ClNO_2S^+$ 294.0350; Found 294.0342 (2.7 ppm).

R_f (*n*-hexane : EtOAc = 2:1) = 0.69.



1-Methyl-6-(piperidin-1-yl)pyridine-2(1*H*)-thione (**3i**) was obtained to the **General Procedure C** from **1-methyl-2-(piperidin-1-yl)pyridin-1-ium tetrafluoroborate** (**1m**) (0.16 g, 0.6 mmol). **Yield:** 0.08 g (65%). **Physical state:** yellow solid.

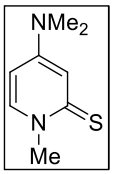
Melting point (*n*-hexane : EtOAc): 107 – 109 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.10 – 7.17 (m, 1H), 6.24 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.02 (s, 3H), 2.49 – 3.24 (m, 4H), 1.66 – 1.88 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 181.4, 159.4, 134.8, 129.8, 104.0, 52.7, 40.0, 25.7, 23.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{17}N_2S^+$ 209.1107; Found 209.1102 (2.3 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.59.



4-(Dimethylamino)-1-methylpyridine-2(1*H*)-thione (**3j**) was obtained to the **General Procedure C** from **4-(dimethylamino)-1-methylpyridin-1-ium iodide** (**1l**) (0.16 g, 0.6 mmol). **Yield:** 0.05 g (53%). **Physical state:** brown solid.

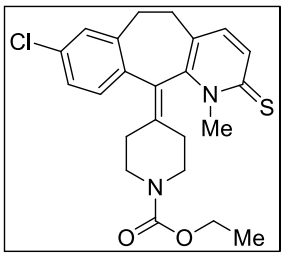
Melting point (CH_2Cl_2 : methanol): 162 – 164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 3.0 Hz, 1H), 6.12 (dd, *J* = 7.6, 3.0 Hz, 1H), 3.90 (s, 3H), 3.02 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.2, 152.6, 140.5, 111.8, 101.6, 44.1, 39.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_{13}N_2S^+$ 169.0794; Found 169.0793 (0.5 ppm).

R_f (CH_2Cl_2 : methanol = 20:1) = 0.22.



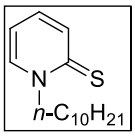
Ethyl 4-(8-chloro-1-methyl-2-thioxo-5,6-dihydro-1*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11(2*H*)-ylidene)piperidine-1-carboxylate (**3k**) was obtained to the **General Procedure C** from **8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-1-methyl-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-1-ium iodide** (**1v**) (0.31 g, 0.6 mmol). **Yield:** 0.20 g (80%). **Physical state:** orange viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.09 – 7.14 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.80 – 3.95 (m, 2H), 3.00 – 3.27 (m, 4H), 2.81 – 2.91 (m, 1H), 2.61 – 2.68 (m, 1H), 2.35 – 2.49 (m, 2H), 2.14 – 2.23 (m, 1H), 1.96 – 2.04 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.7, 155.4, 150.7, 140.6, 139.1, 134.8, 134.4, 134.3, 132.3, 131.4, 131.1, 128.2, 126.5, 123.8, 61.8, 44.4, 43.8, 41.2, 31.9, 31.2, 30.4, 29.4, 14.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}ClN_2O_2S^+$ 429.1398; Found 429.1405 (1.6 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.37.



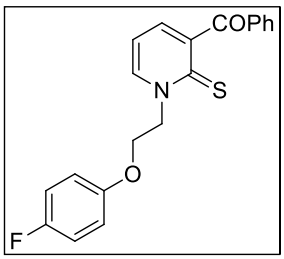
1-Decylpyridine-2(1*H*)-thione (**3l**) was obtained to the **General Procedure C** from **1-decylpyridin-1-ium chloride** (**1k**) (0.15 g, 0.6 mmol). **Yield:** 0.08 g (56%). **Physical state:** brown viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.73 (m, 1H), 7.59 (dd, *J* = 6.6, 1.7 Hz, 1H), 7.15 (ddd, *J* = 8.7, 6.8, 1.7 Hz, 1H), 6.60 – 6.66 (m, 1H), 4.45 – 4.55 (m, 2H), 1.88 (p, *J* = 7.4 Hz, 2H), 1.17 – 1.44 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.9, 140.2, 136.7, 133.7, 113.6, 57.2, 31.9, 29.5, 29.3, 29.3, 29.2, 28.3, 26.6, 22.7, 14.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{26}NS^+$ 252.1780; Found 252.1780 (0 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.32.



(1-(2-(4-Fluorophenoxy)ethyl)-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3m**) was obtained to the **General Procedure C** from **3-benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide** (**1h**) (0.24 g, 0.6 mmol). **Yield:** 0.05 g (26%). **Physical state:** yellow solid.

Melting point (*n*-hexane : EtOAc): 129 – 131 °C.

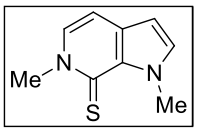
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 6.6, 1.7 Hz, 1H), 7.81 – 7.91 (m, 2H), 7.53 – 7.59 (m, 1H), 7.40 – 7.46 (m, 2H), 7.29 (dd, *J* = 7.0, 1.6 Hz, 1H), 6.94 – 7.00 (m, 2H), 6.74 – 6.84 (m, 3H), 4.92 – 4.98 (m, 2H), 4.40 – 4.46 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.2, 177.0, 157.7 (d, *J* = 239.4 Hz), 154.2 (d, *J* = 2.0 Hz), 145.4, 143.2, 136.0, 133.6, 133.1, 129.7, 128.8, 116.2 (d, *J* = 23.2 Hz), 115.7 (d, *J* = 7.9 Hz), 112.1, 65.1, 55.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -122.82 – -122.73 (m).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}FNO_2S^+$ 354.0959; Found 354.0964 (1.4 ppm).

R_f (*n*-hexane : EtOAc = 1:1) = 0.77.



1,6-Dimethyl-1*H*-pyrrolo[2,3-*c*]pyridine-7(6*H*)-thione (**3n**) was obtained to the **General Procedure C** from **1,6-dimethyl-1*H*-pyrrolo[2,3-*c*]pyridin-6-ium iodide** (**1hh**) (0.16 g, 0.6 mmol). **Yield:** 0.09 g (90%). **Physical state:** light yellow solid.

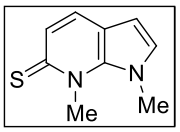
Melting point (EtOAc): 94 – 96 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 6.9 Hz, 1H), 7.14 (d, *J* = 2.9 Hz, 1H), 6.83 (d, *J* = 6.9 Hz, 1H), 6.30 (d, *J* = 2.9 Hz, 1H), 4.52 (s, 3H), 4.05 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.1, 136.2, 134.6, 132.1, 128.2, 107.6, 100.9, 44.7, 39.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{11}N_2S^+$ 179.0637; Found 179.0638 (0.5 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.58.



1,7-Dimethyl-1*H*-pyrrolo[2,3-*b*]pyridine-6(7*H*)-thione (**3o**) was obtained to the **General Procedure C** from **1,7-dimethyl-1*H*-pyrrolo[2,3-*b*]pyridin-7-ium iodide** (**1ii**) (0.16 g, 0.6 mmol). **Yield:** 0.03 g (33%). **Physical state:** brown solid.

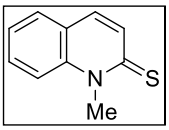
Melting point (CH_2Cl_2 : methanol): 123 – 125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 4.51 (s, 3H), 4.07 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 177.5, 139.8, 129.5, 127.6, 127.2, 117.0, 102.9, 39.1, 38.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{11}N_2S^+$ 179.0637; Found 179.0629 (4.4 ppm).

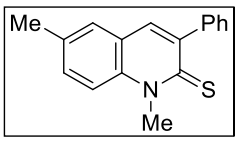
R_f (CH_2Cl_2 : methanol = 20:1) = 0.68.



1-Methylquinoline-2(1*H*)-thione (**3p**) was obtained to the **General Procedure C** from **1-methylquinolin-1-ium iodide** (**1w**) (0.16 g, 0.6 mmol). **Yield:** 0.06 g (62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.73 (m, 4H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.31 – 7.40 (m, 1H), 4.34 (s, 3H).

Characterization data obtained for this compound matched those previously reported in the literature [18].



1,6-Dimethyl-3-phenylquinoline-2(1*H*)-thione (**3q**) was obtained to the **General Procedure C** from **1,6-dimethyl-3-phenylquinolin-1-ium iodide** (**1z**) (0.22 g, 0.6 mmol). **Yield:** 0.09 g (55%). **Physical state:** orange solid.

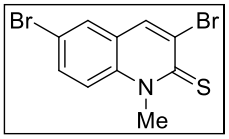
Melting point (*n*-hexane : EtOAc): 133 – 135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.35 – 7.55 (m, 8H), 4.40 (s, 3H), 2.46 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 184.1, 142.9, 141.4, 139.2, 134.2, 132.7, 132.0, 129.6, 128.7, 128.0, 127.9, 123.8, 115.8, 39.2, 20.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NS^+$ 266.0998; Found 266.1000 (0.7 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.60.



3,6-Dibromo-1-methylquinoline-2(1*H*)-thione (**3r**) was obtained to the **General Procedure C** from **3,6-dibromo-1-methylquinolin-1-ium iodide** (**1aa**) (0.26 g, 0.6 mmol). **Yield:** 0.12 g (58%). **Physical state:** orange solid.

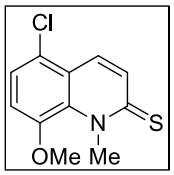
Melting point (*n*-hexane : EtOAc): 198 – 200 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.70 – 7.78 (m, 2H), 7.42 (d, *J* = 9.0 Hz, 1H), 4.39 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 181.9, 139.5, 134.5, 133.9, 130.2, 130.2, 124.5, 117.6, 117.6, 41.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8Br_2NS^+$ 331.8739; Found 331.8732 (2.1 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.58.



5-Chloro-8-methoxy-1-methylquinoline-2(1*H*)-thione (**3s**) was obtained to the **General Procedure C** from **5-chloro-8-methoxy-1-methylquinolin-1-ium iodide** (**1y**) (0.20 g, 0.6 mmol). **Yield:** 0.10 g (72%). **Physical state:** yellow solid.

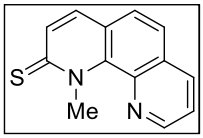
Melting point (EtOAc): 146 – 148 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 9.4 Hz, 1H), 7.69 (d, *J* = 9.4 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 4.35 (s, 3H), 3.94 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.6, 147.6, 135.1, 134.5, 127.5, 125.4, 124.4, 124.2, 113.4, 56.9, 46.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}ClNOS^+$ 240.0244; Found 240.0249 (2 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.54.



1-Methyl-1,10-phenanthroline-2(1*H*)-thione (**3t**) was obtained to the **General Procedure C** from **1-methyl-1,10-phenanthrolin-1-ium iodide** (**1bb**) (0.19 g, 0.6 mmol). **Yield:** 0.12 g (87%). **Physical state:** yellow solid.

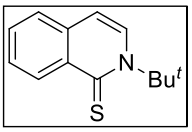
Melting point (*n*-hexane : EtOAc): 126 – 128 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 9.00 (dd, *J* = 4.2, 1.9 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.61 (m, 2H), 4.91 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.3, 147.8, 139.93, 139.89, 136.4, 135.7, 131.9, 130.2, 126.3, 125.3, 125.2, 122.6, 48.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}N_2S^+$ 227.0637; Found 227.0633 (1.7 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.28.



2-(*Tert*-butyl)isoquinoline-1(2*H*)-thione (**3u**) was obtained to the **General Procedure C** from **2-(*tert*-butyl)isoquinolin-2-ium chloride** (**1ee**) (0.10 g, 0.6 mmol). **Yield:** 0.04 g (41%). **Physical state:** yellow solid.

Melting point (*n*-hexane : EtOAc): 80 – 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.57 – 7.65 (m, 1H), 7.46 – 7.55 (m, 2H), 6.83 (d, J = 7.7 Hz, 1H), 2.06 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.8, 136.9, 132.9, 132.0, 131.5, 130.1, 128.2, 126.0, 112.0, 68.0, 29.3.

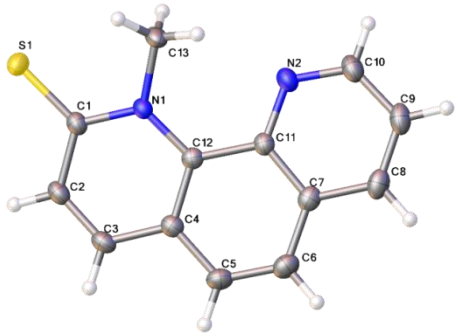
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}NS^+$ 218.0998; Found 218.0992 (2.7 ppm).

R_f (*n*-hexane : EtOAc = 4:1) = 0.64.

S-VII. X-Ray Crystallographic Data

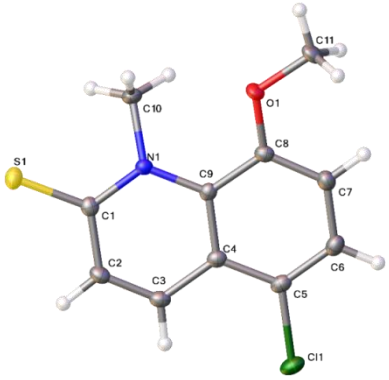
CCDC 2419945, 2419946, 2419948, 2419949, 2427527 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

General view of the molecule **3t** (non-hydrogen atoms are presented as thermal ellipsoids with 50% probability).



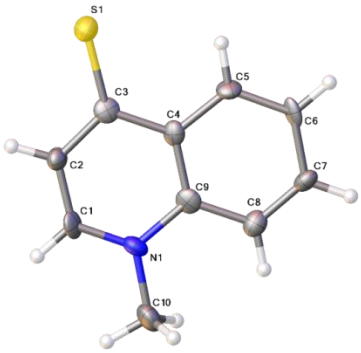
Crystal data and refinement parameters for **3r**: $C_{13}H_{10}N_2S$, M = 226.29, monoclinic, $P2_1/c$, a = 10.7446(7) Å, b = 14.6012(9) Å, c = 7.0569(6) Å, β = 108.194(3)°, V = 1051.76(13) Å^3, Z = 4, R_1(reflections with I>2σ)/ωR_2(all reflections) = 0.0478/0.1341 for 11353/3202 reflections and 146 parameters.

General view of the molecule **3s** (non-hydrogen atoms are presented as thermal ellipsoids with 50% probability).



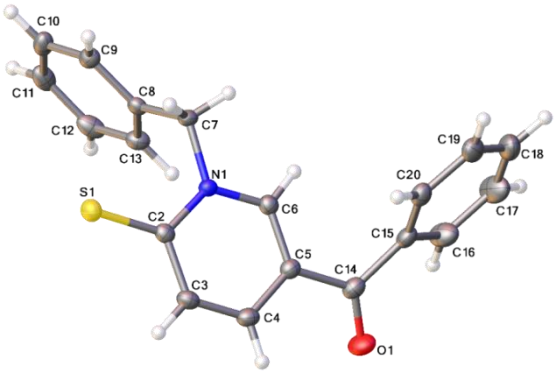
Crystal data and refinement parameters for **3q**: $C_{11}H_{10}NOSCl$, M = 239.71, monoclinic, $P2_1/n$, a = 17.8909(5) Å, b = 3.98570(10) Å, c = 29.2748(8) Å, β = 102.3060(10)°, V = 2039.56(10) Å^3, Z = 8, R_1(reflections with I>2σ)/ωR_2(all reflections) = 0.0435/0.1070 for 21097/6206 reflections and 275 parameters.

General view of the molecule **2p** (non-hydrogen atoms are presented as thermal ellipsoids with 50% probability).



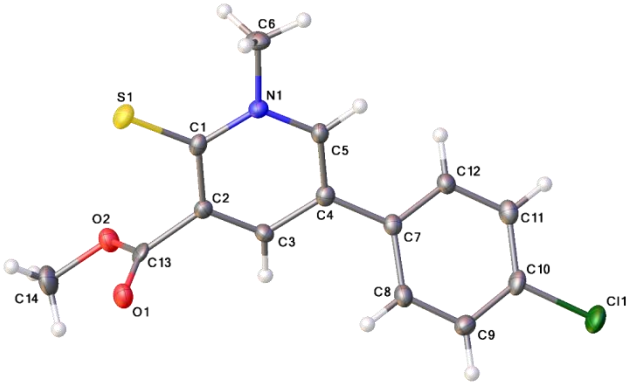
Crystal data and refinement parameters for **2p**: $C_{10}H_9NS$, M = 175.24, orthorhombic, $Pca2_1$, a = 15.077(3) Å, b = 7.584(2) Å, c = 28.746(7) Å, V = 3287.0(14) $Å^3$, Z = 16, R_1(reflections with I>2σ)/ωR_2(all reflections) = 0.0867/0.2392 for 21752/ 5748reflections and 438 parameters.

General view of the molecule **2c** (non-hydrogen atoms are presented as thermal ellipsoids with 50% probability).



Crystal data and refinement parameters for **2c**: $C_{19}H_{15}NOS$, M = 305.38, triclinic, P-1, a = 8.8568(3) Å, b = 10.5889(4) Å, c = 8.5261(3) Å, α = 77.1900(10)°, β = 78.4590(10)°, γ = 82.103(2)°, V = 760.31(5) $Å^3$, Z = 2, R_1(reflections with I>2σ)/ωR_2(all reflections) = 0.0472/0.1143 for 11184/4037 reflections and 259 parameters.

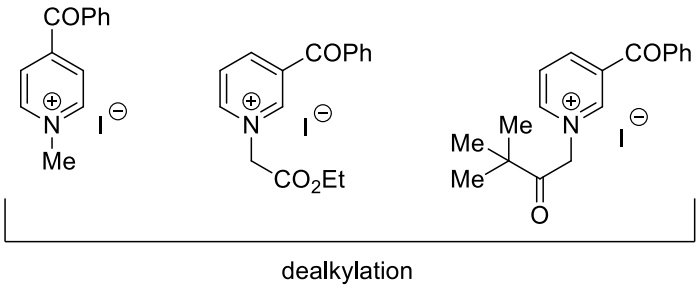
General view of the molecule **3h** (non-hydrogen atoms are presented as thermal ellipsoids with 50% probability).



Crystal data and refinement parameters for KO32: C14H12ClO2NS, M = 293.76, orthorhombic, Pca21, a = 26.6824(9) Å, b = 7.1838(3) Å, c = 13.9128(4) Å, α = β = γ = 90o, V = 2666.82(16) Å3, Z = 8, R1(reflections with I>2σ)/ωR2(all reflections) = 0.0485/0.1095 for 25468/5575 reflections and 348 parameters.

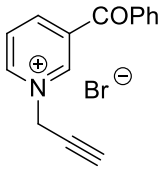
S-VIII. Unproductive Substrates

with Cs_2CO_3 as the base

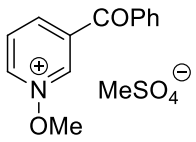


dealkylation

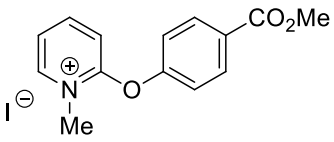
with LiHMDS as the base



dealkylation



N-O cleavage



S_NAr

S-IX. UV-vis Experiments

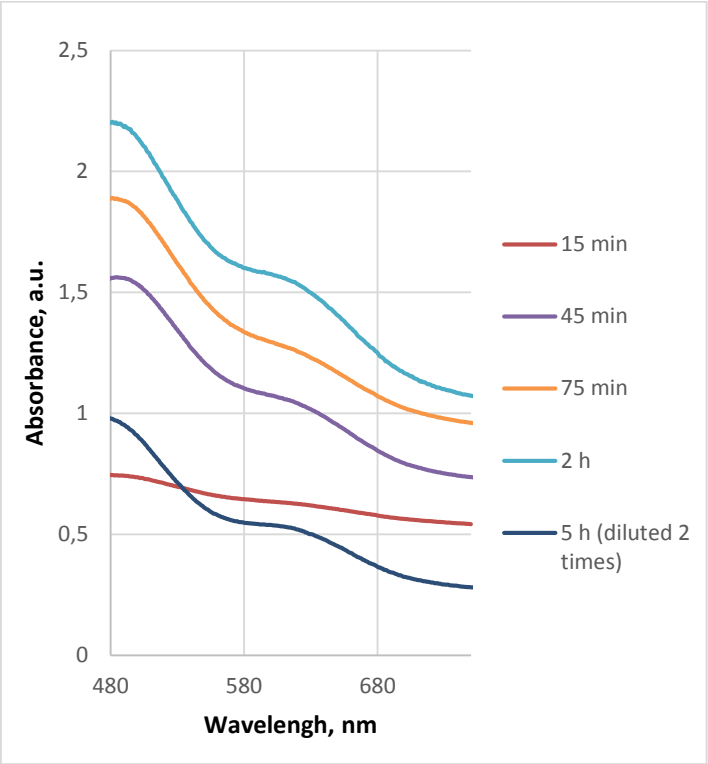


Fig. S1. Fragment of the UV-vis spectrum of a S_8 [0.02 M] – Cs_2CO_3 [0.015 M] mixture in DMSO

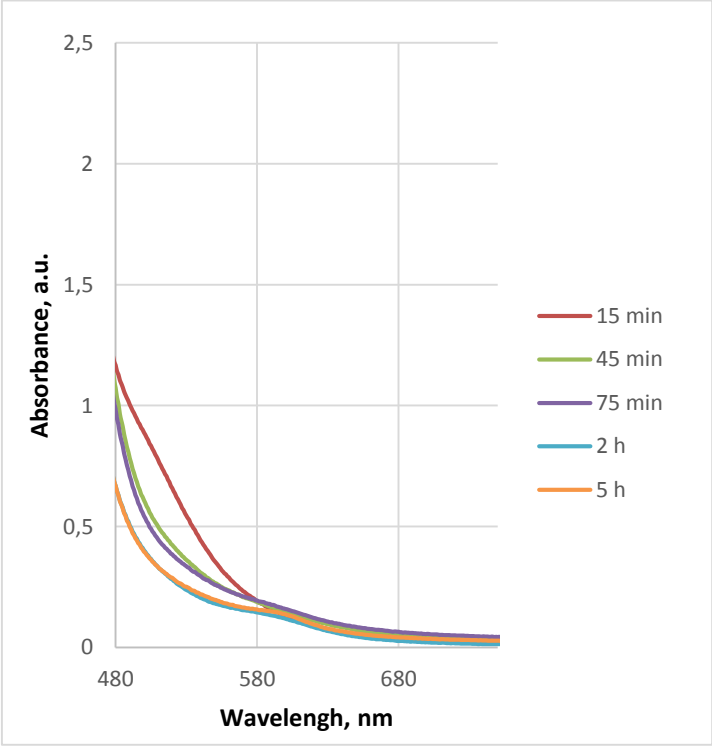
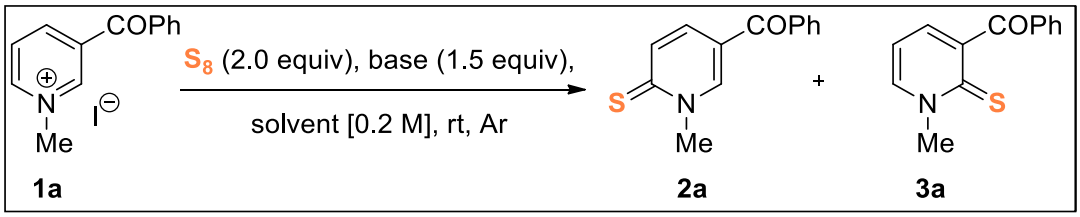


Fig. S2. Fragment of the UV-vis spectrum of a S_8 [0.02 M] – LiHMDS [0.015 M] mixture in THF

S- X. TEMPO Inhibition

Radical trapping experiments to study reaction mechanisms using Cs_2CO_3 and LiHMDS as the bases were carried out according to *General Procedure B* and *General Procedure C*, respectively, with the addition of 4 equivalents of the radical inhibitor (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO).

Table S2. Data on inhibition of reactions with and without TEMPO: comparison



entry	base	solvent	additive (equiv)	time, h	yield of 2a+3a, %
1	Cs_2CO_3	DMSO	-	24	83[a]
2	Cs_2CO_3	DMSO	TEMPO (4.0)	24	0
3	LiHMDS	THF	-	2	81
4	LiHMDS	THF	TEMPO (4.0)	2	56

[a]The yield of a single reaction product **2a** is given.

S-XI. Computational Data

Geometry optimizations were conducted using the PBE96 functional[19] a scalar-relativistic approximation,[20] L1 wavefunction,[21] and density-fitting[22] basis sets implemented in PRIRODA program.[23,24] Stationary points were characterized as minima (i=0) or first order transition states (i=1) by calculations of normal modes of vibrations at the same level. Single point energy calculations were done using the long-range- and dispersion-corrected L19[25]-PBE96[19]-VV10[26] density functional. Solvent effects for reactions in THF and DMSO using SMD[27] model were calculated using the PBE96 functional and def2-TZVP[28] basis set using Orca 5.0.3 release.[29] Optimized geometries are collected in the separate .xyz file.

Table S3. Calculated energy parameters (E = E_{total}(L19-PBE96-VV10/L1) a.u.; G = G(PBE96/L1) kcal/mol; $DG_S = DG_{ENP}$ (a.u.) + DG_{CDS} (kcal/mol) solvation free energy (PBE-D4(SMD)/def2-TZVP)).

Molecule	E	G	G_{ENP}	G_{CDS}
½ $(A)_2$ (THF)	-7662.59029	88.7	-0.02688	-2.0
A (DMSO)	-7662.57708	83.0	-0.03899	0.9
pre-TS-AB-2	-9242.09499	407.2	-0.05080	-4.0
pre-TS-AB-4	-9242.06986	406.5	-0.06756	-3.5
TS-AB-2	-9242.08128	406.1	-0.04819	-4.0
TS-AB-4	-9242.04211	405.9	-0.07136	-3.3
B-2	-440.92267	77.9	-0.02020	-2.8
B-4	-440.89679	77.7	-0.03381	-2.7
C-2 (THF)	-840.67903	78.9	-0.01541	-3.8
C-4 (THF)	-840.66954	78.9	-0.02371	-3.9
D-2	-1640.60572	82.6	-0.01958	-2.6
D-4	-1640.61187	82.8	-0.02092	-2.5
TS-DC-2	-1640.57844	80.5	-0.01775	-2.4
TS-DC-4	-1640.57668	79.6	-0.02343	-2.5
C-2 (DMSO)	-840.67903	78.9	-0.01541	-3.8
C-4 (DMSO)	-840.66954	78.9	-0.02371	-3.9
$Li(THF)_3HMDS$	-1579.49106	309.7	-0.01783	-2.4
HMDS	-875.34495	117.3	-0.00645	1.1
$Li(THF)_3I$	-7925.80058	183.0	-0.02401	-2.9
$Cs(DMSO)_5S_3$	-11882.93156	193.5	-0.04148	3.2
$1/4[Cs(DMSO)_3I]_4$	-16795.61446	119.1	-0.02547	3.9
DMSO	-554.64027	29.8	-0.01333	0.0
S_8 (THF)	-3197.45083	-17.7	-0.00062	-7.4

According to quantum chemical calculations in the Orcad program (version 5.0.3), the most electrophilic position of the pyridine ring is the C(6) position.* Charges were calculated using the Hirschfield model using the DLPNO-CSD method with def2-tzvpp def2/C bases. Geometry optimization was carried out using the B3LYP electron density functional method with the def2-tzvpp basis.

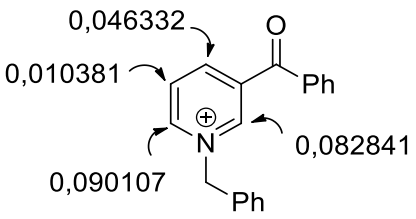


Fig. S3. DLPNO-CSD Quantum chemical calculation data for salt **1e**.

* We would like to thank Andreychev V.V. for conducting quantum chemical calculations.

S-XII. References

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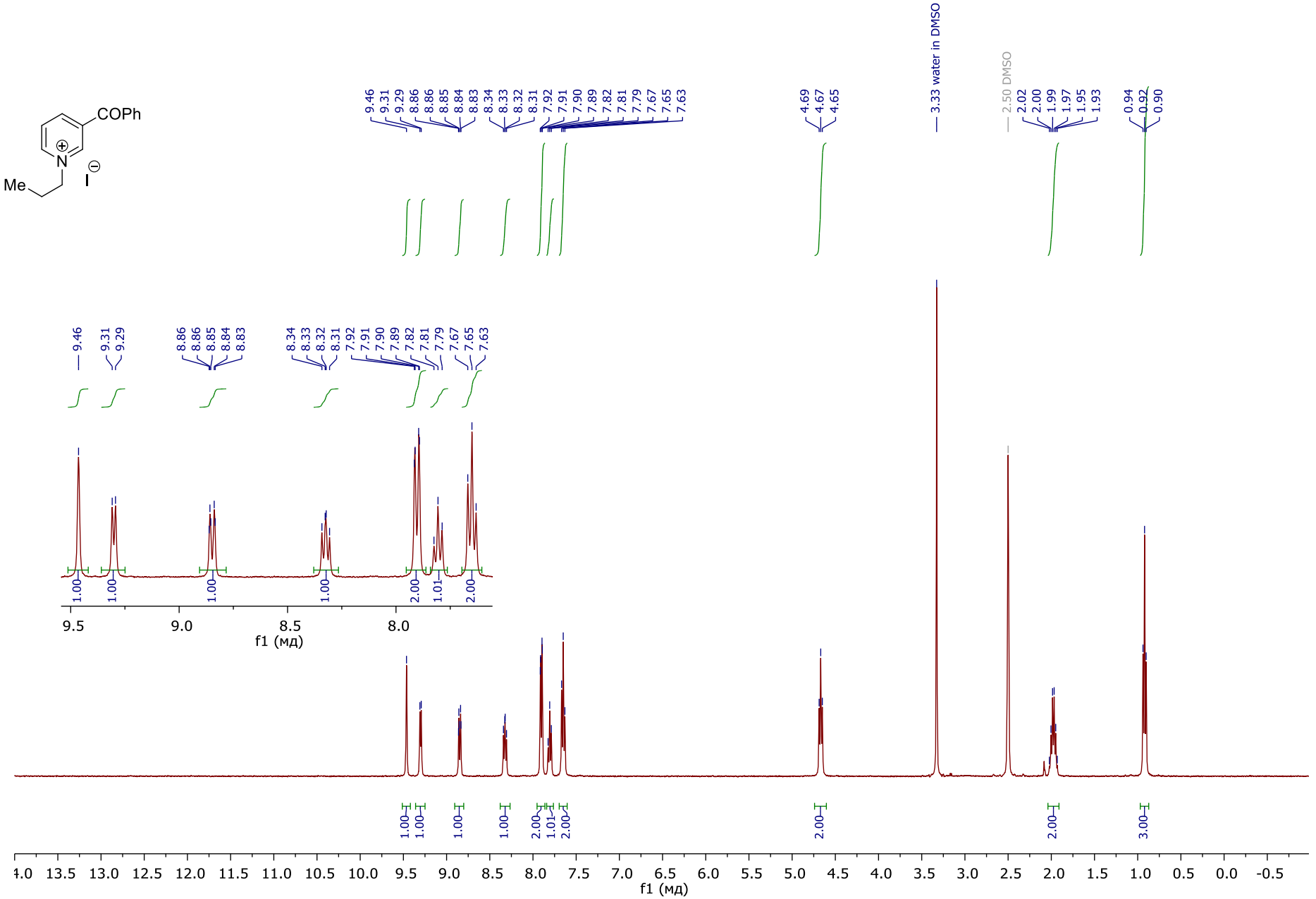
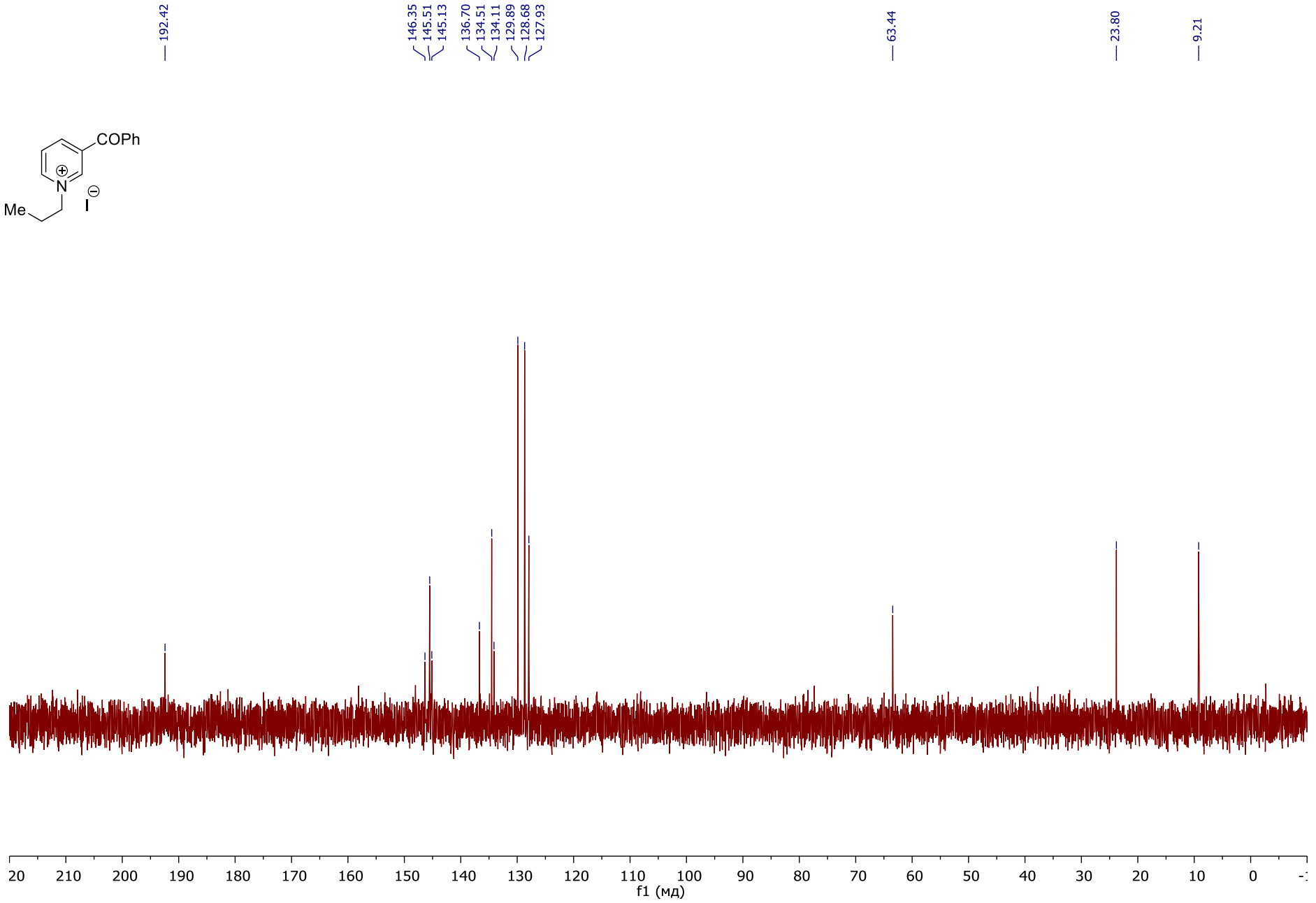
S-XIII. Copies of NMR Spectra

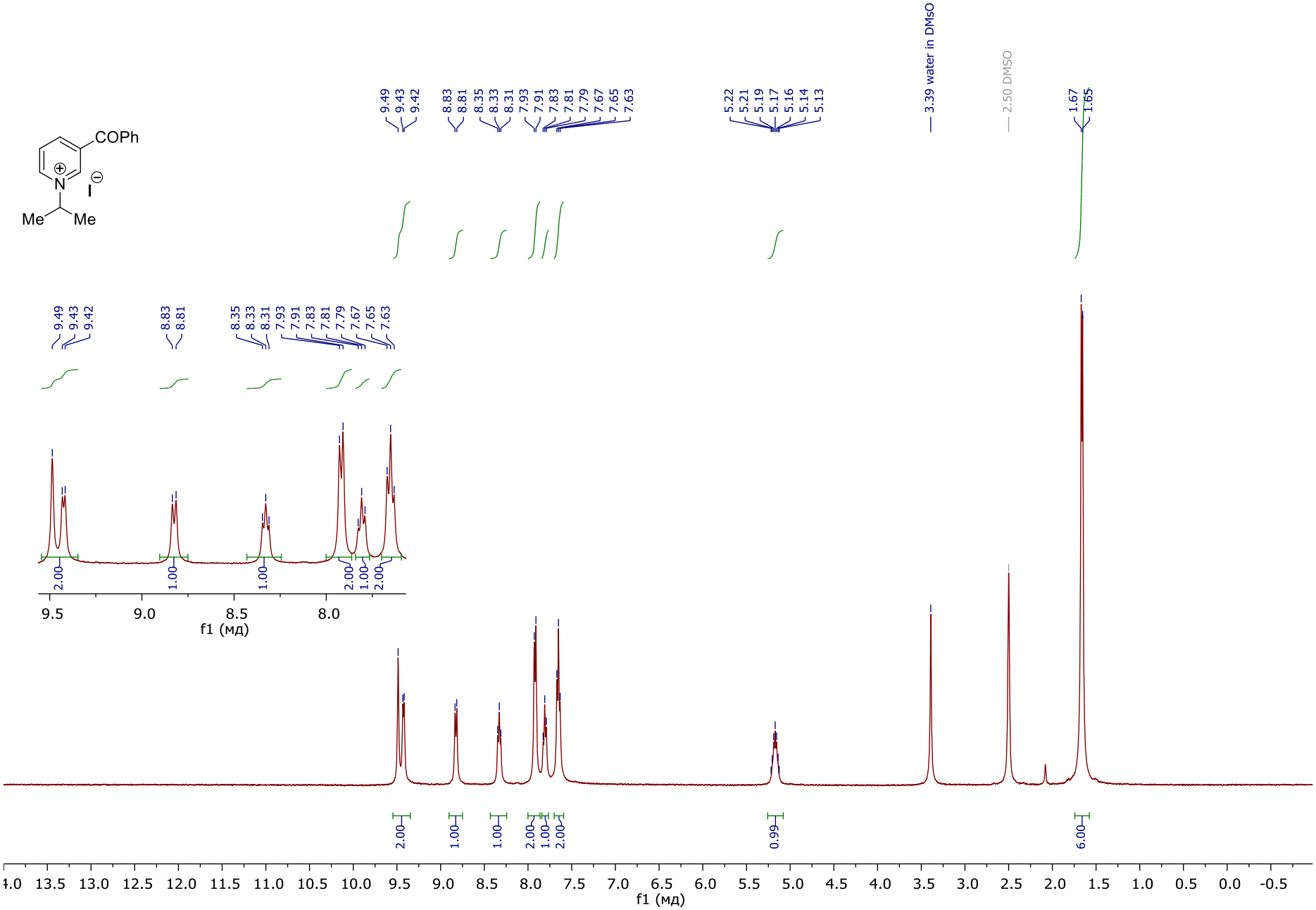
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-propylpyridin-1-ium iodide (**1c**)



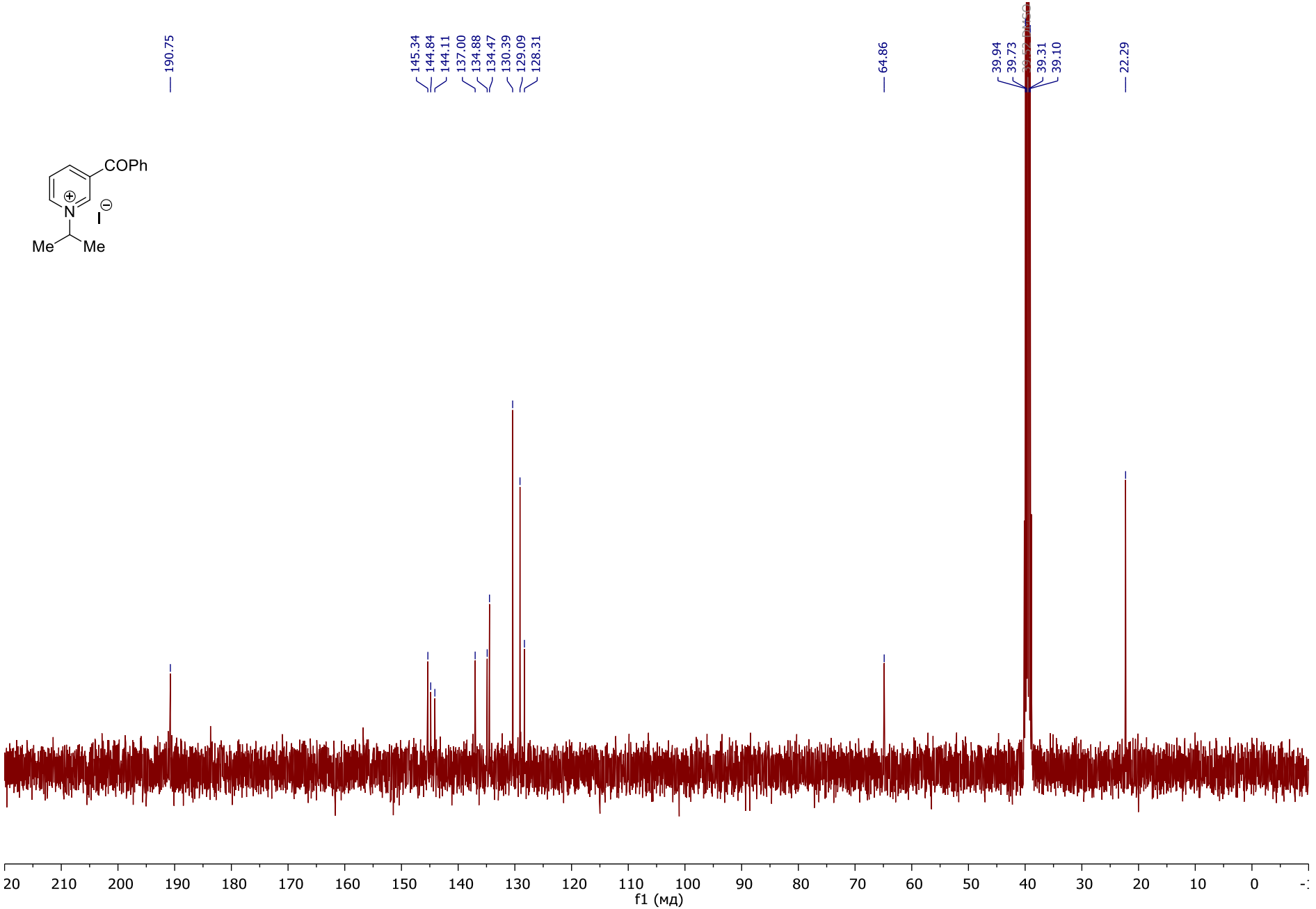
$^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O) of 3-benzoyl-1-propylpyridin-1-ium iodide (**1c**)



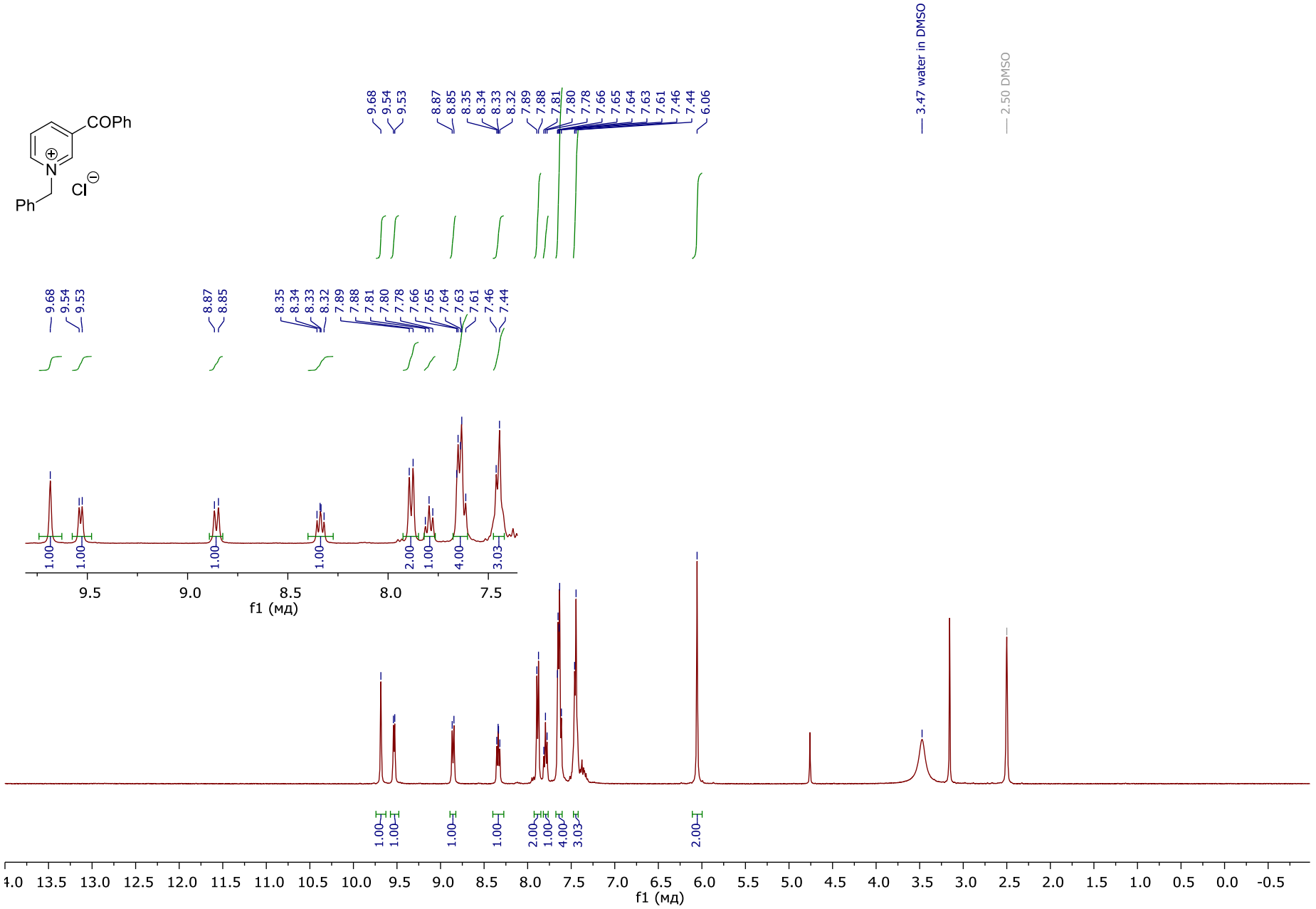
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-isopropylpyridin-1-ium iodide (**1d**)



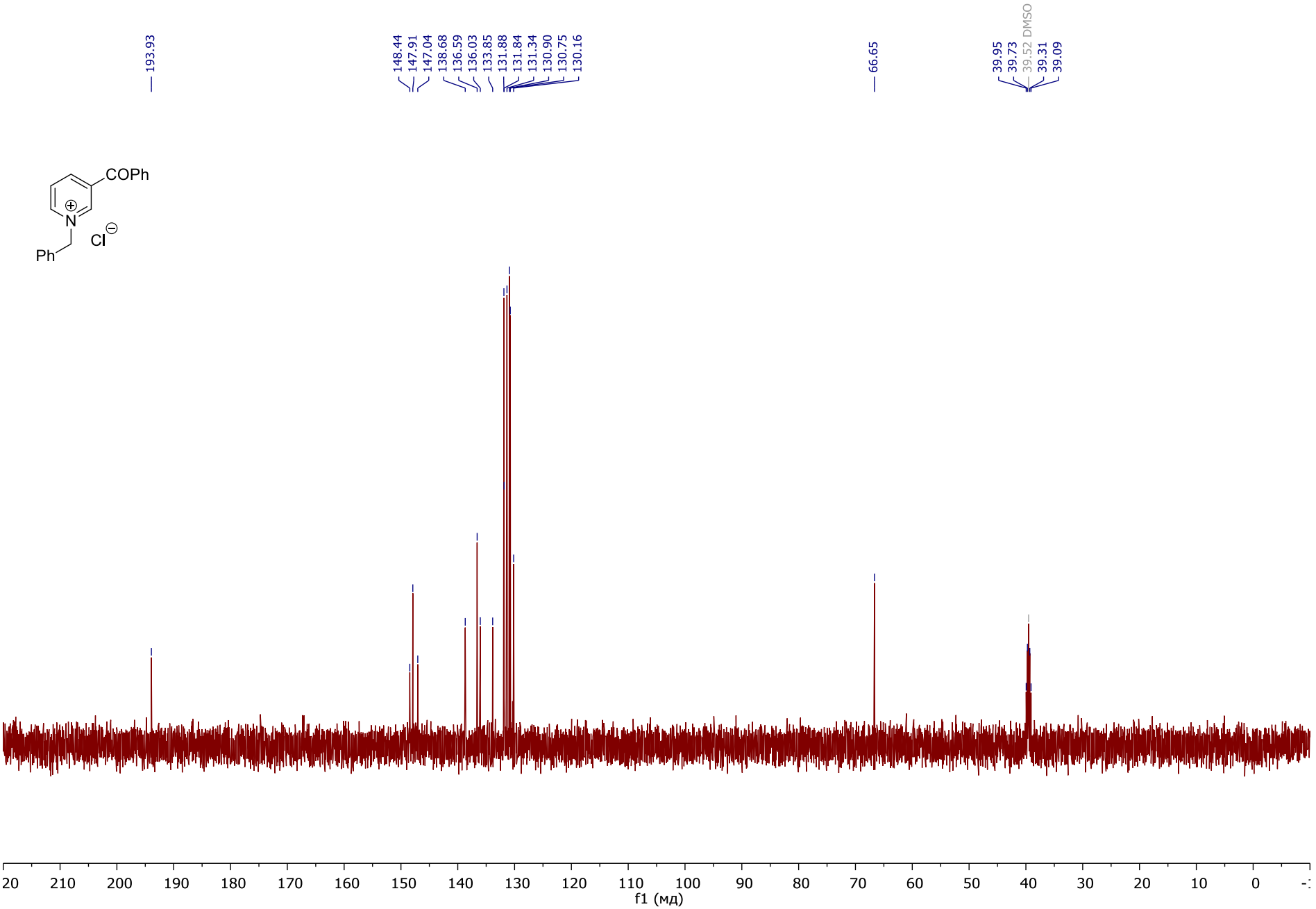
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-benzoyl-1-isopropylpyridin-1-ium iodide (**1d**)



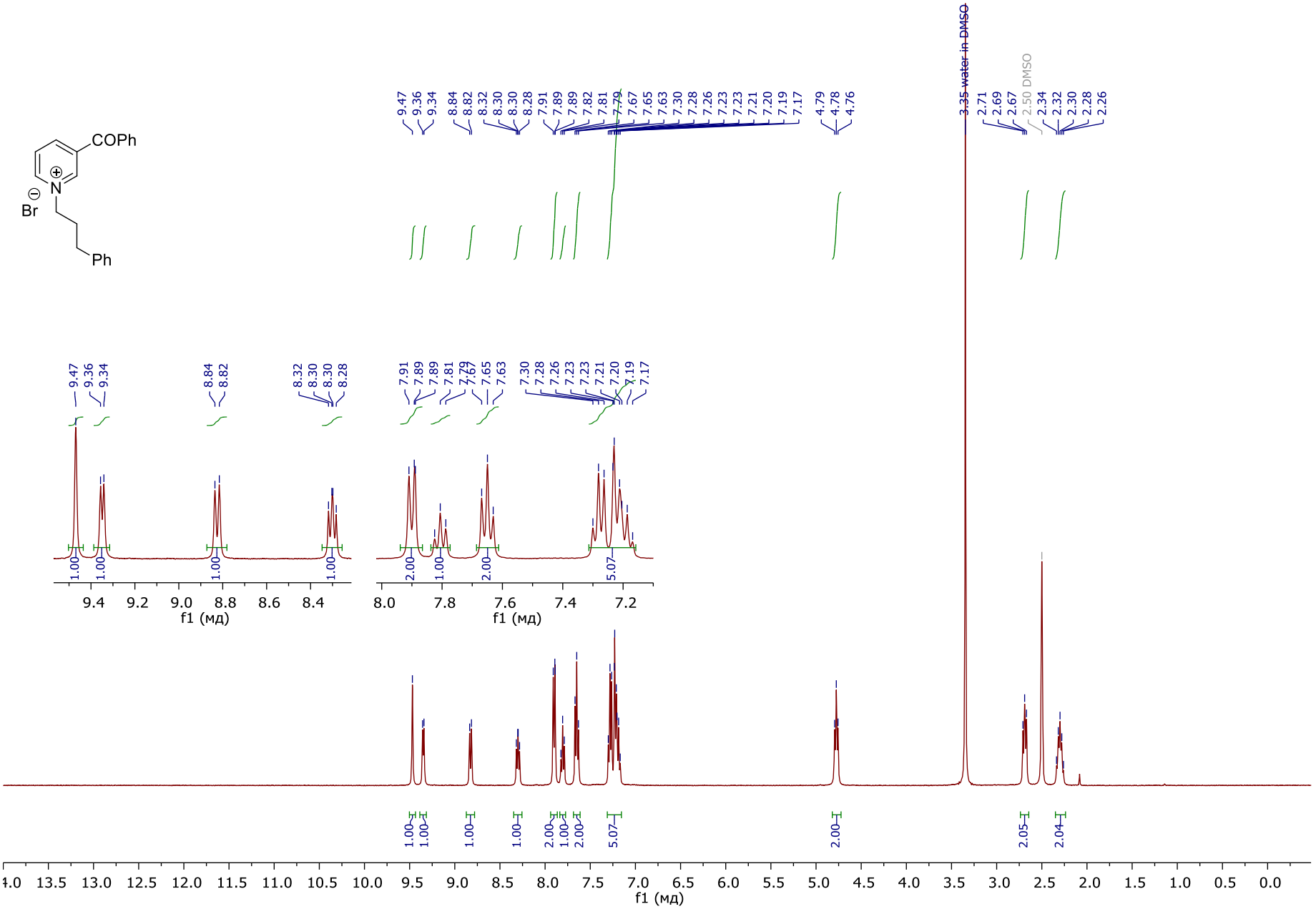
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-benzylpyridin-1-ium chloride (**1e**)



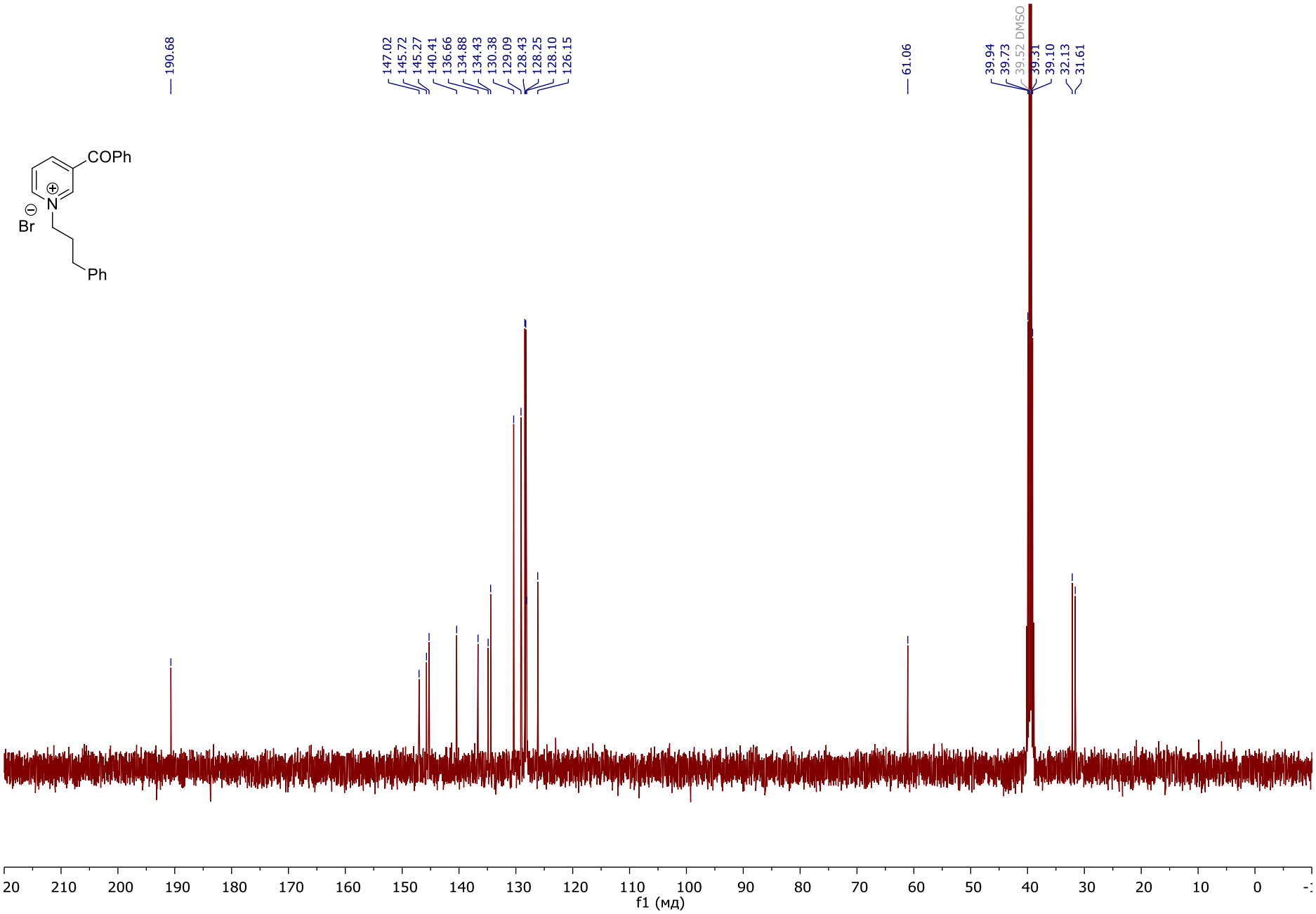
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-benzoyl-1-benzylpyridin-1-ium chloride (**1e**)



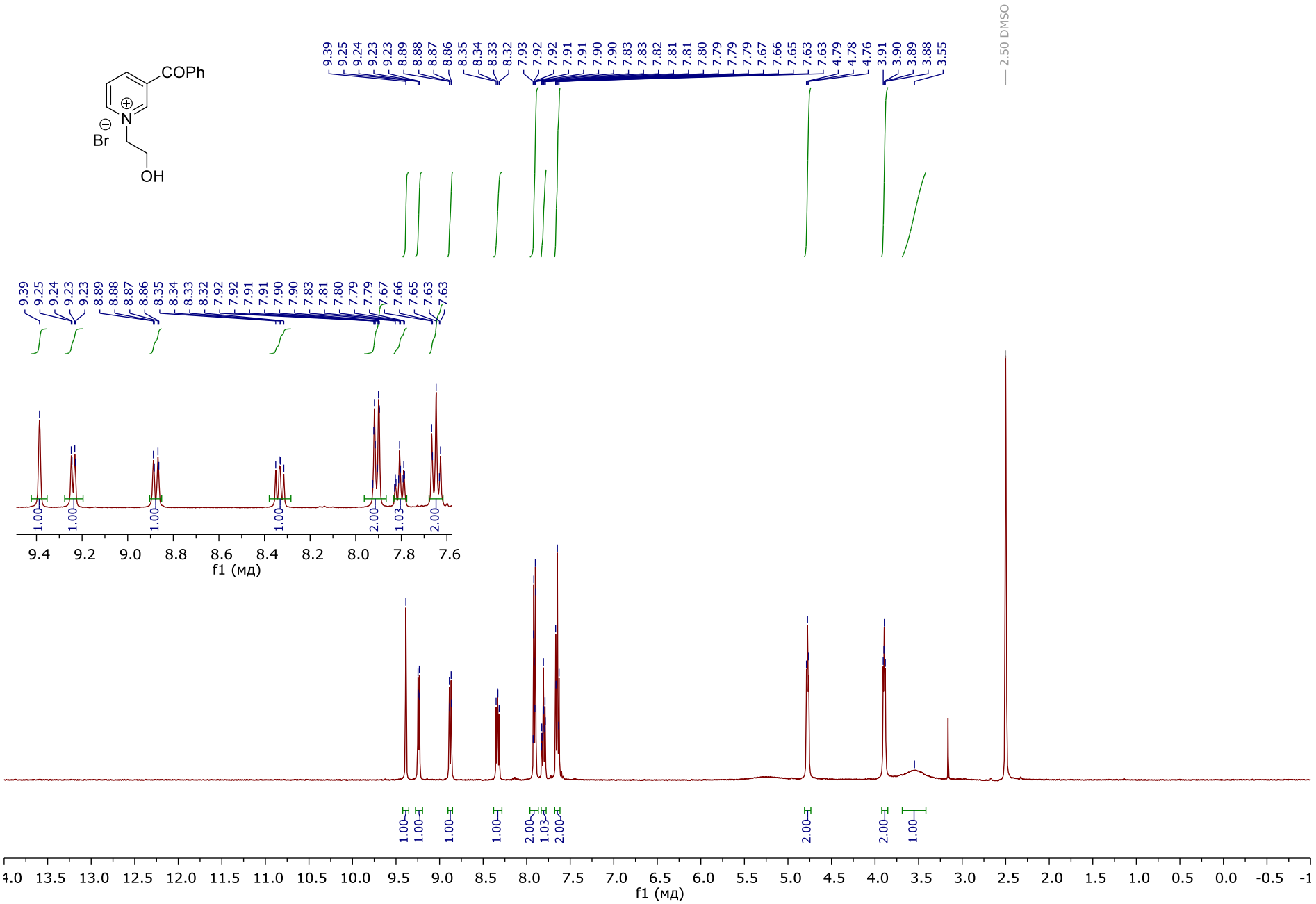
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-(3-phenylpropyl)pyridin-1-ium bromide (**1f**)



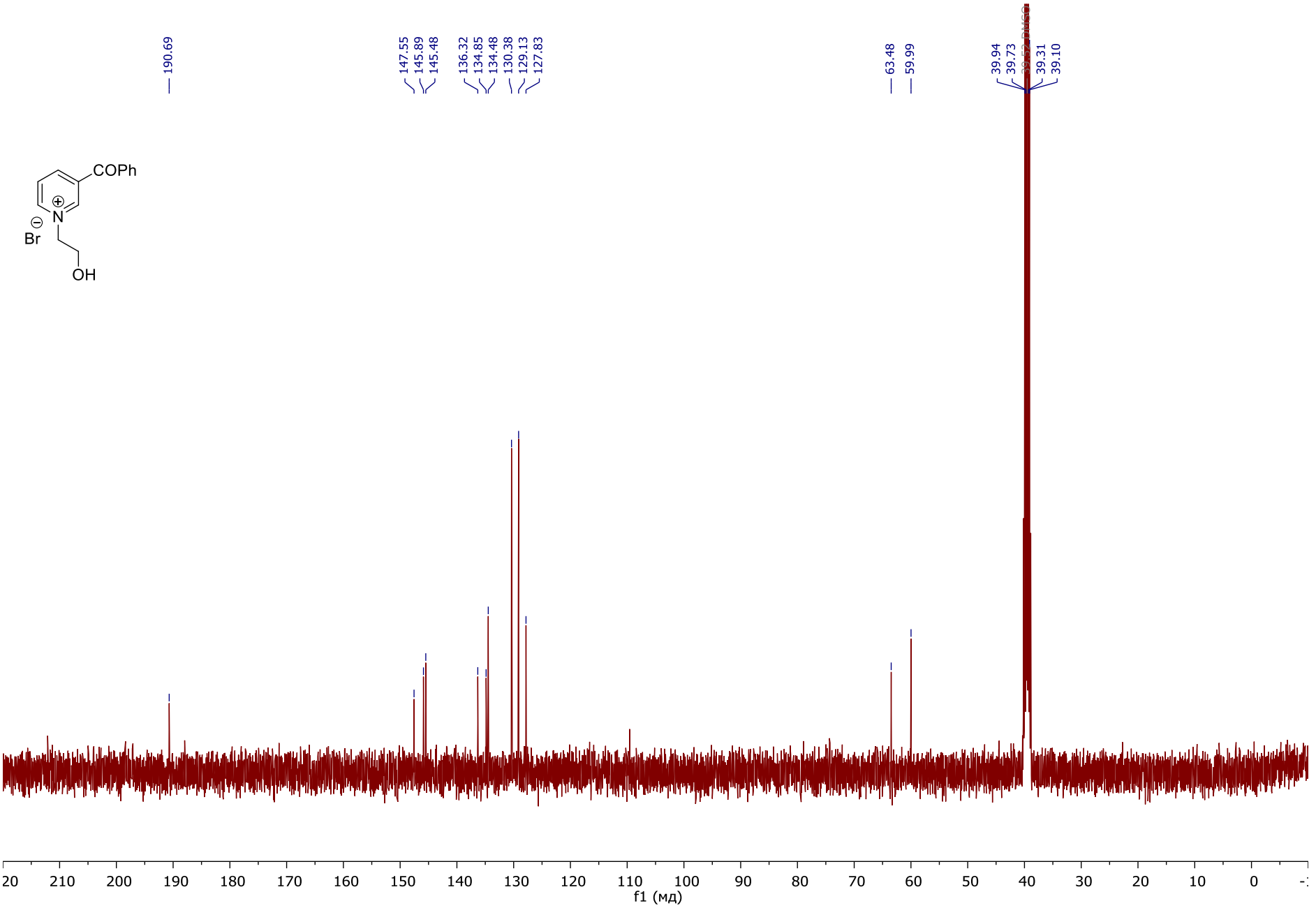
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-benzoyl-1-(3-phenylpropyl)pyridin-1-ium bromide (**1f**)



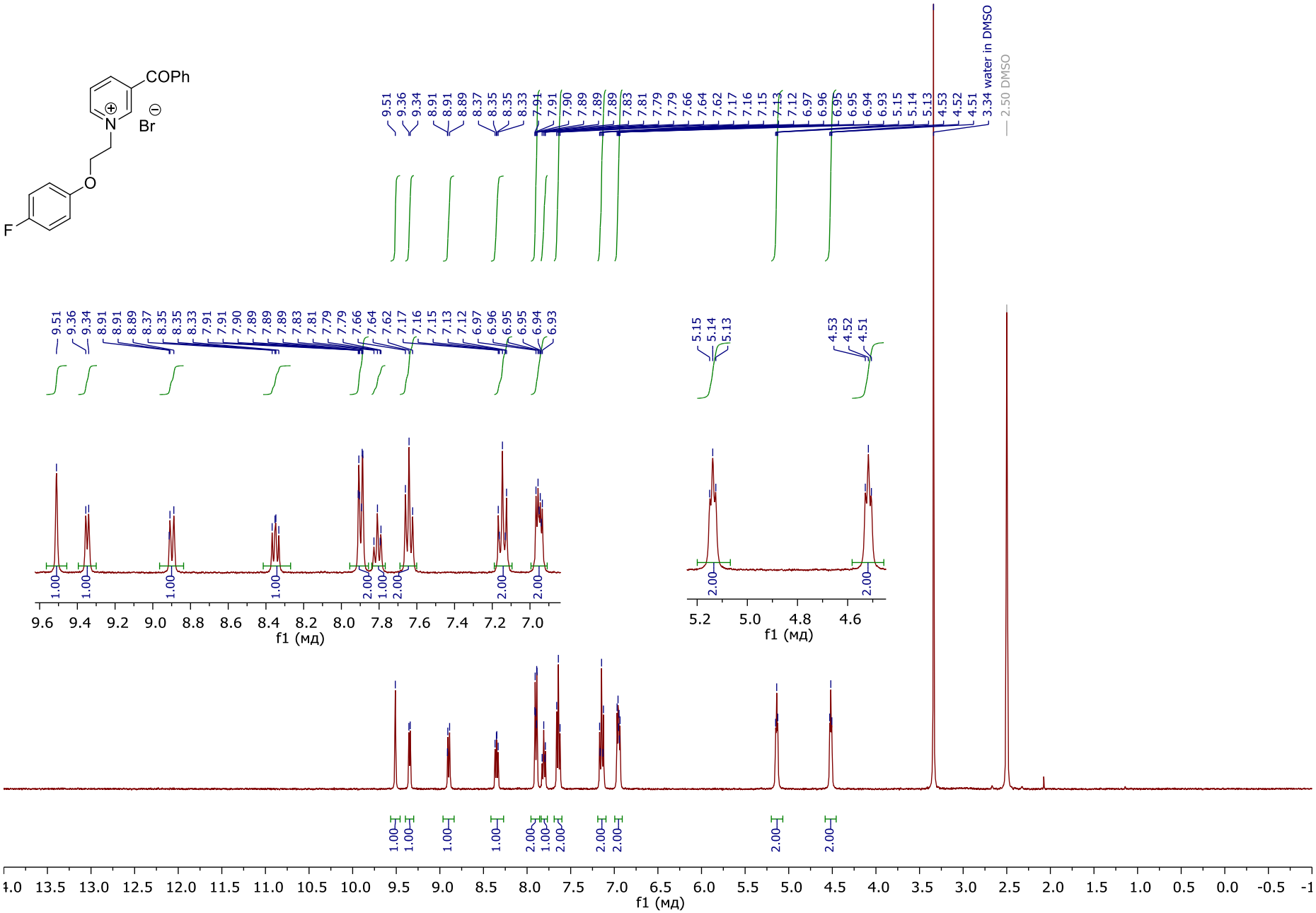
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-(2-hydroxyethyl)pyridin-1-ium bromide (**1g**)



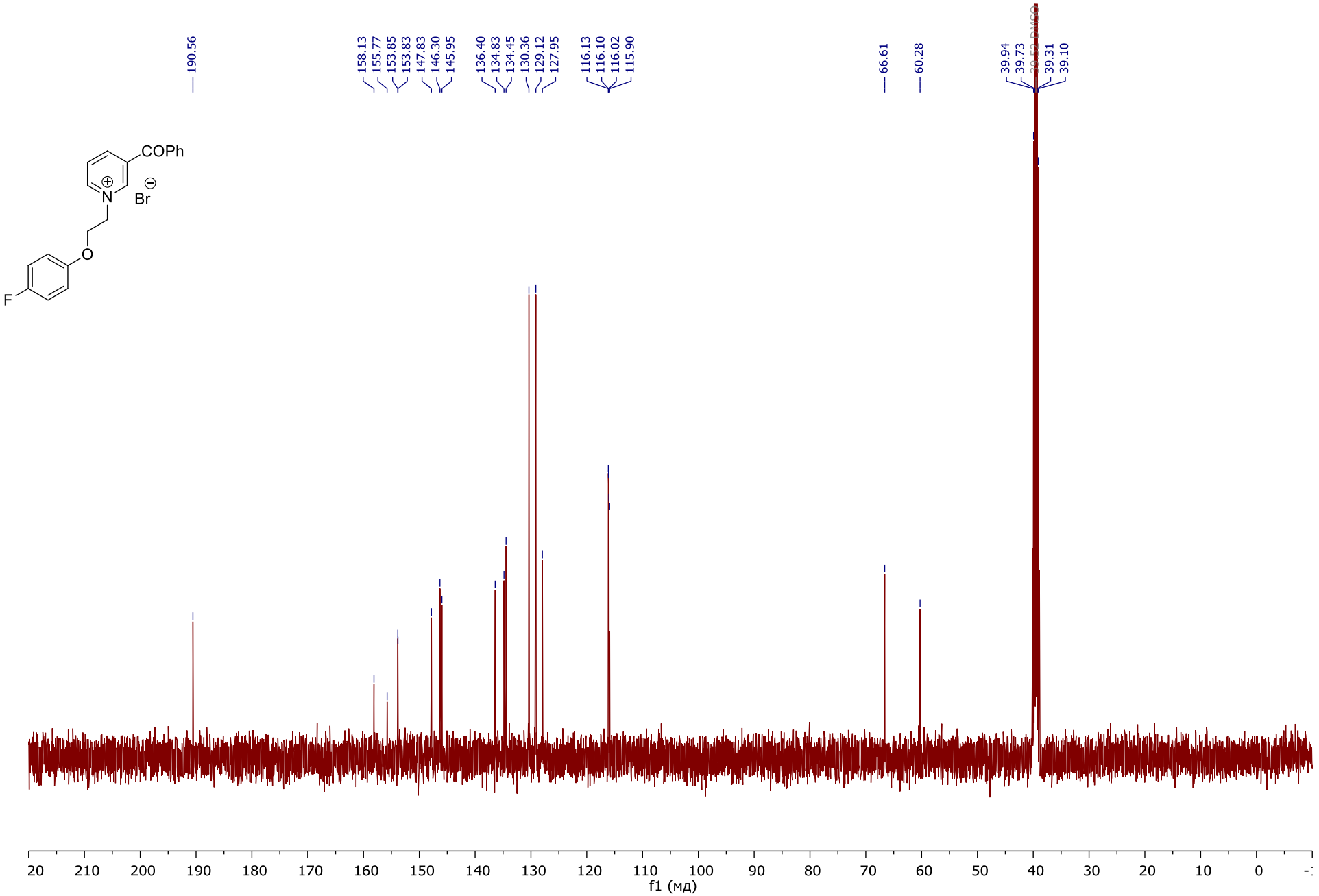
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-benzoyl-1-(2-hydroxyethyl)pyridin-1-ium bromide (**1g**)



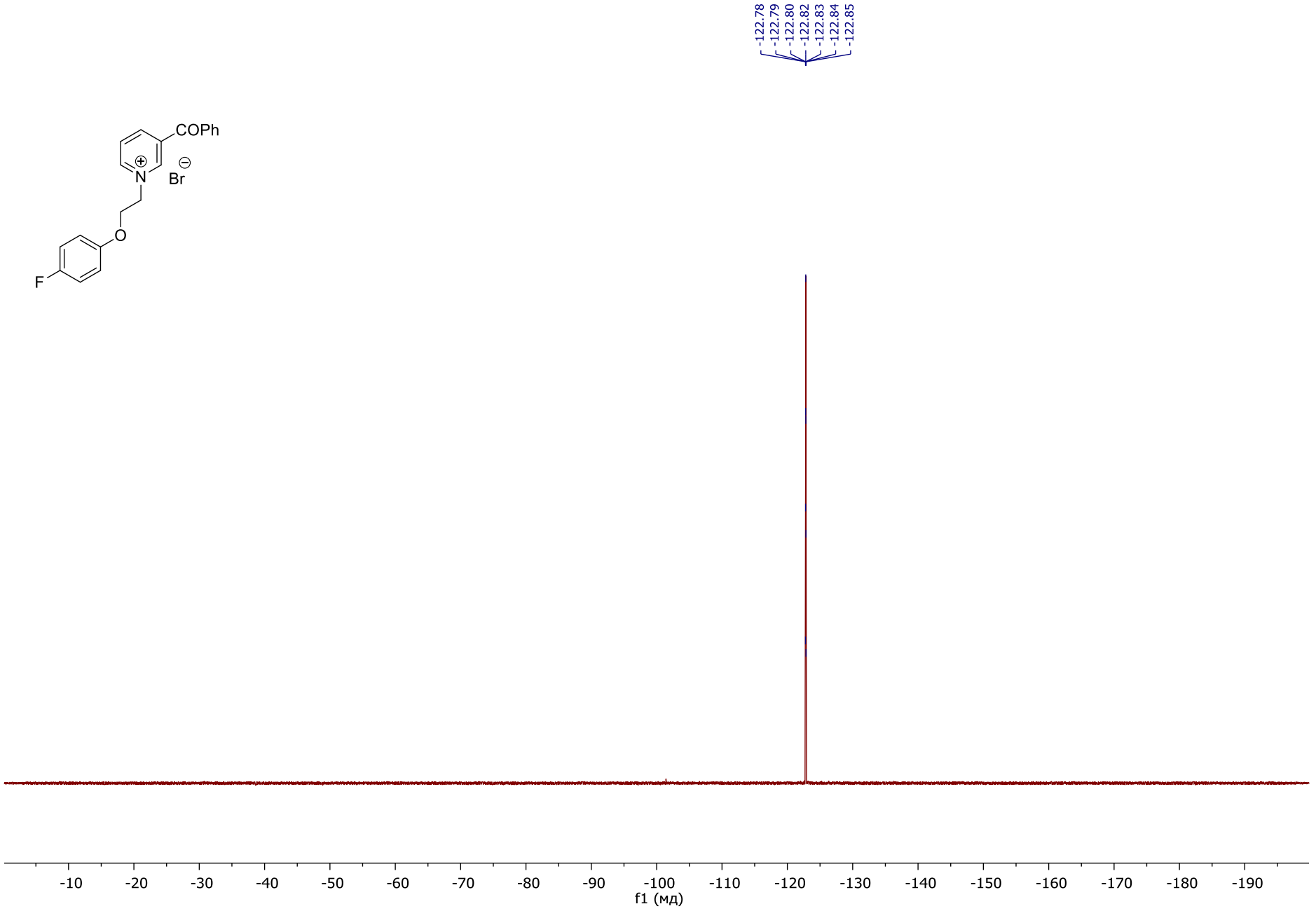
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide (**1h**)



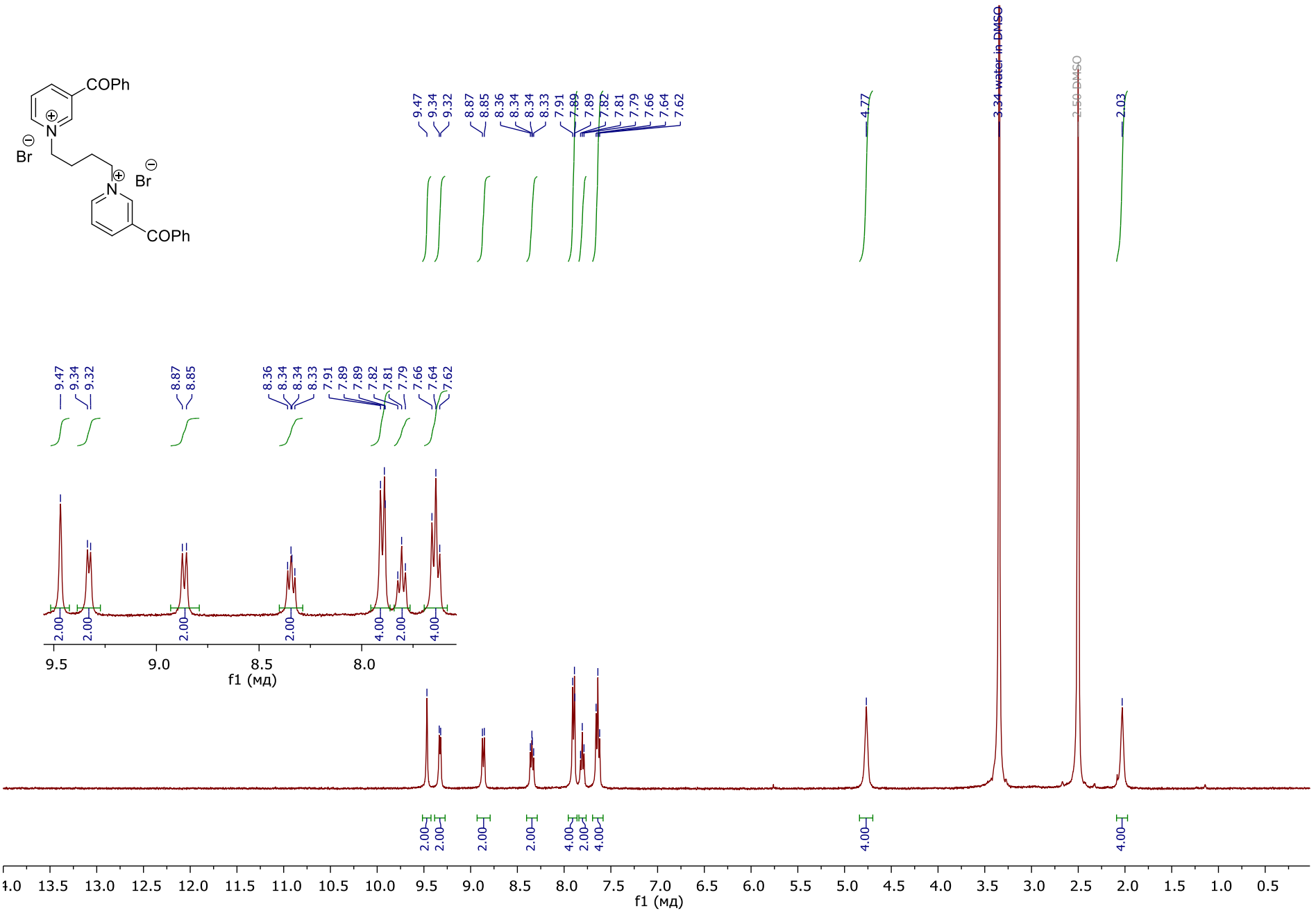
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide (**1h**)



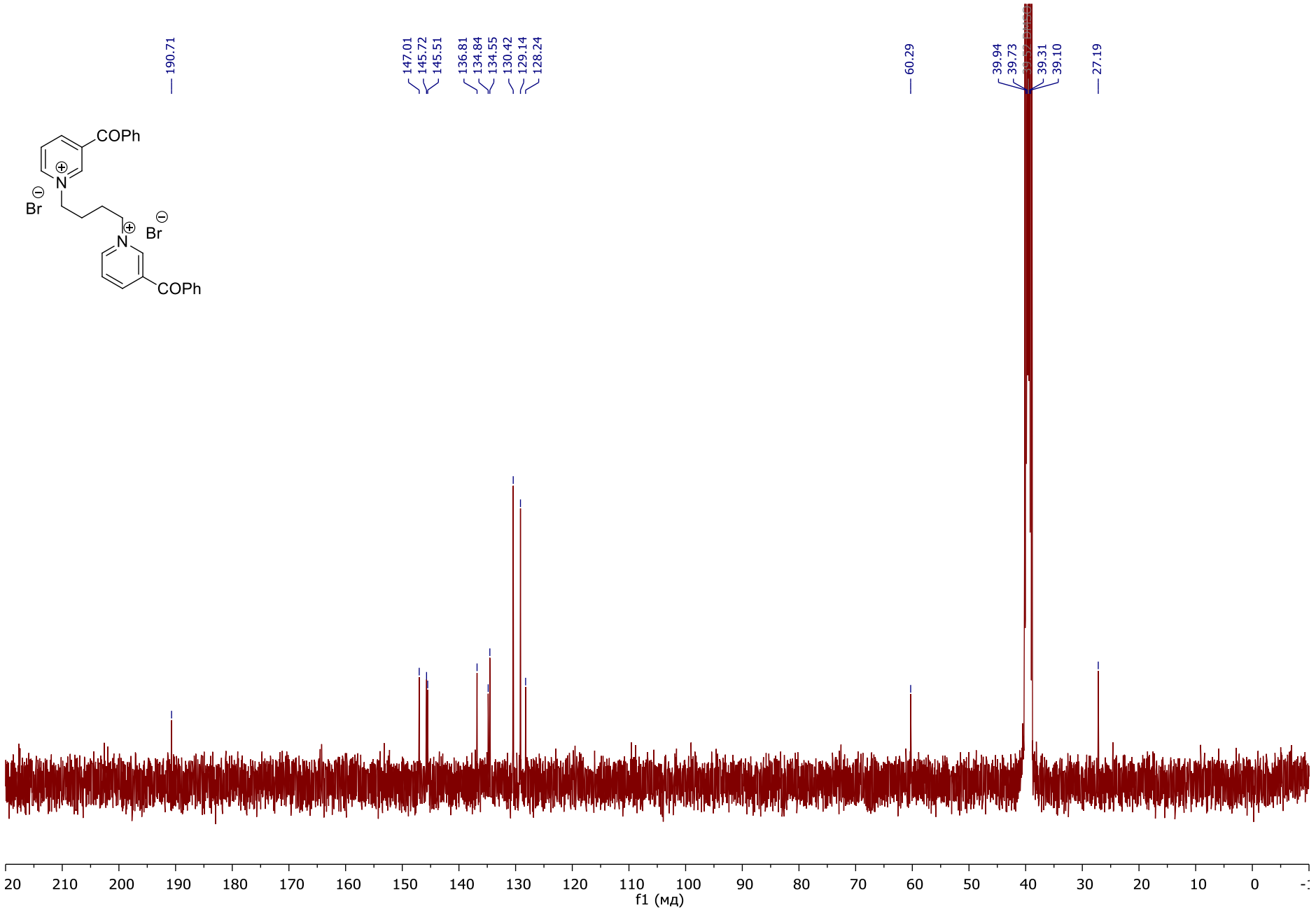
^{19}F NMR (376 MHz, DMSO-*d6*) of 3-benzoyl-1-(2-(4-fluorophenoxy)ethyl)pyridin-1-ium bromide (**1h**)



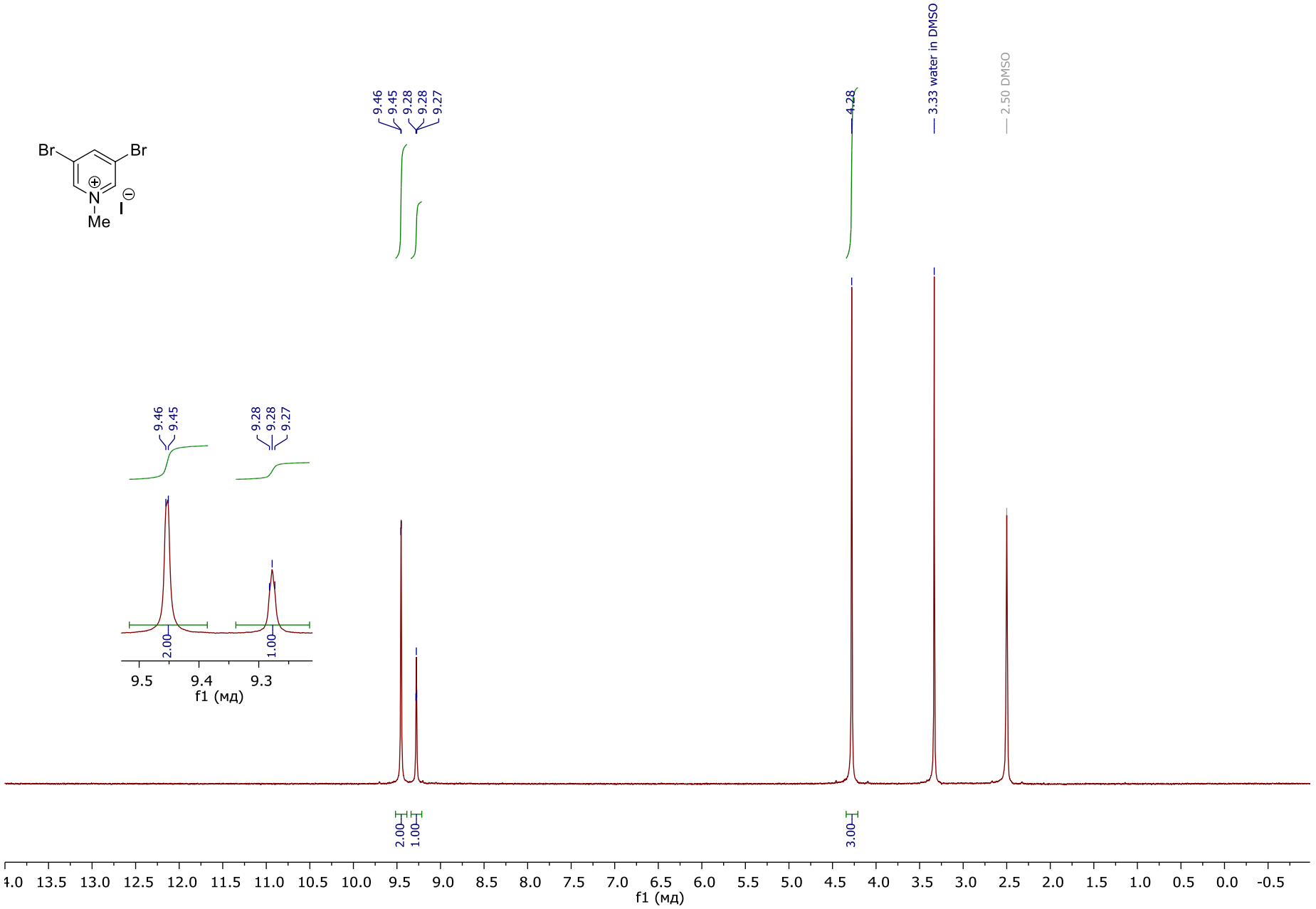
^{1}H NMR (400 MHz, DMSO-*d6*) of 1,1'-(butane-1,4-diyl)bis(3-benzoylpyridin-1-ium) bromide (**1i**)



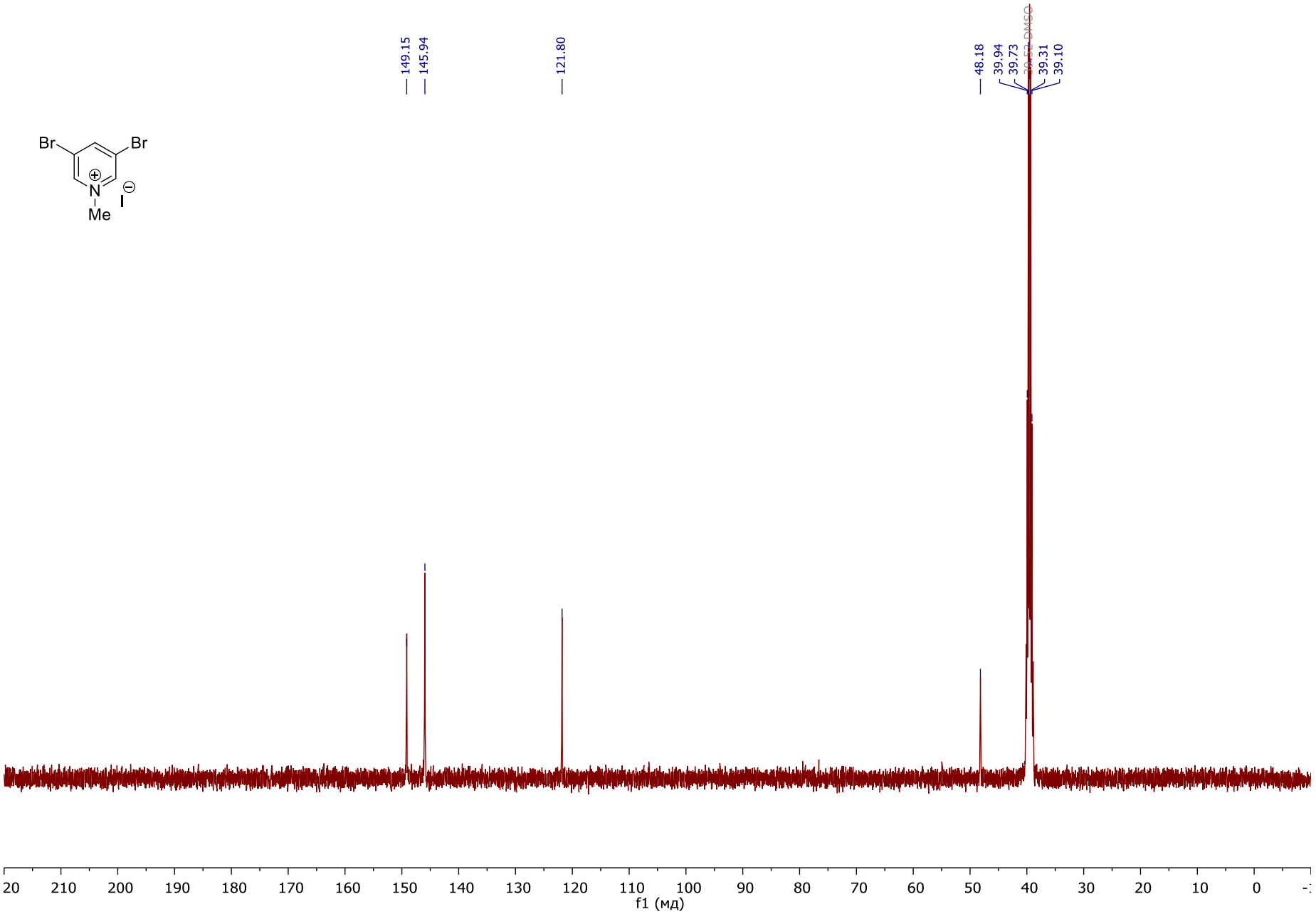
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 1,1'-(butane-1,4-diyl)bis(3-benzoylpyridin-1-ium) bromide (**1i**)



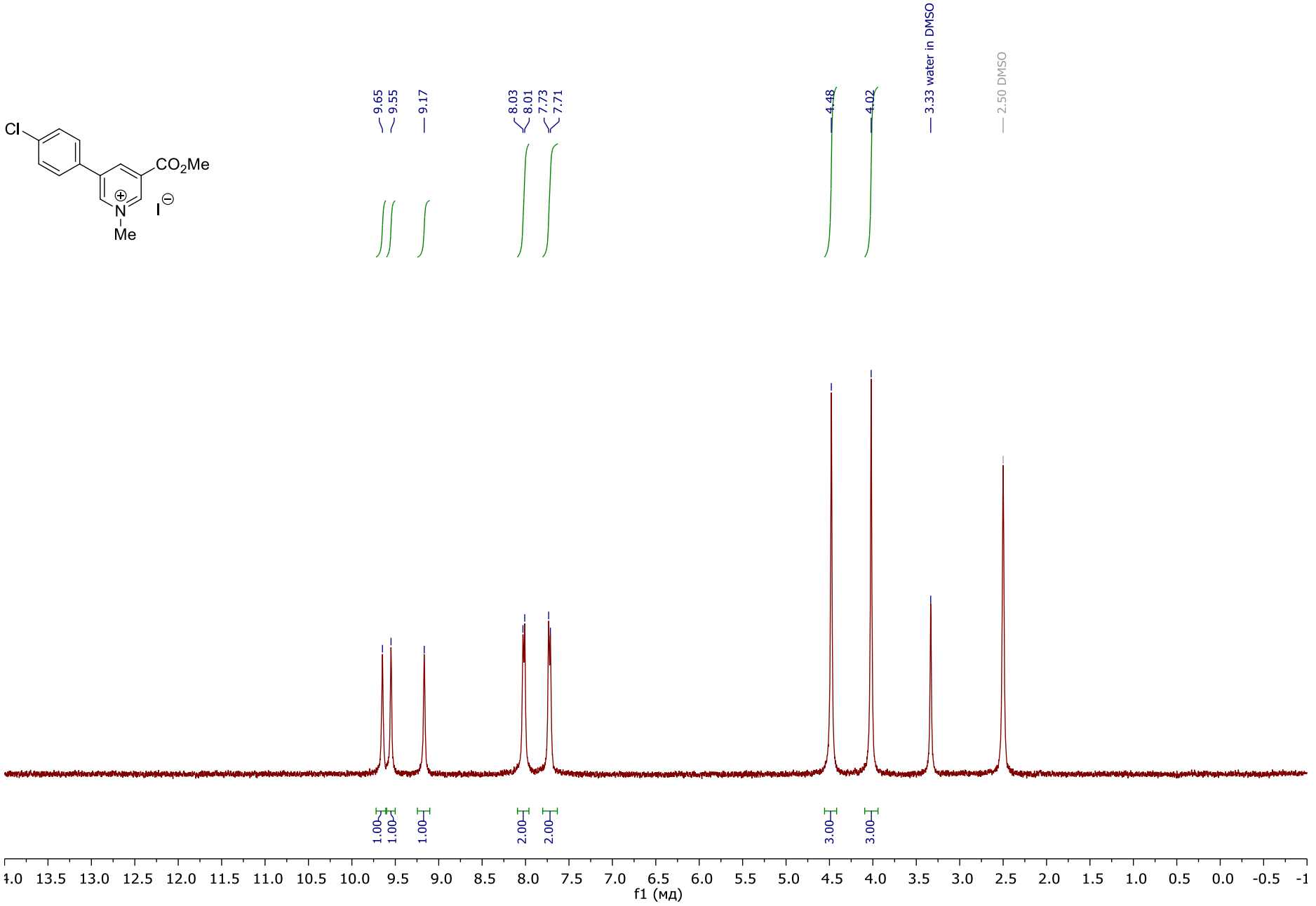
^{1}H NMR (400 MHz, DMSO-*d6*) of 3,5-dibromo-1-methylpyridin-1-ium iodide (**1n**)



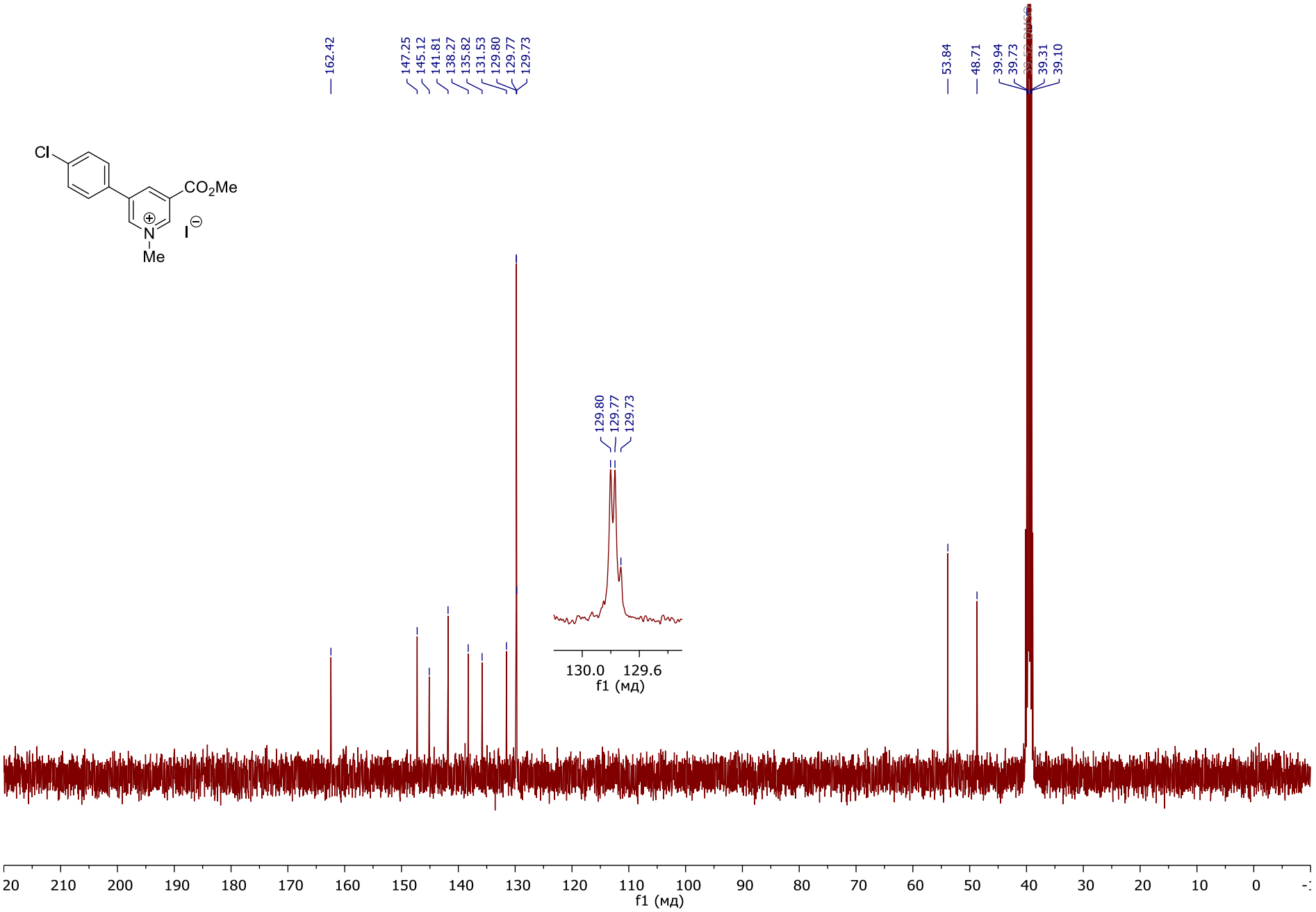
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3,5-dibromo-1-methylpyridin-1-ium iodide (**1n**)



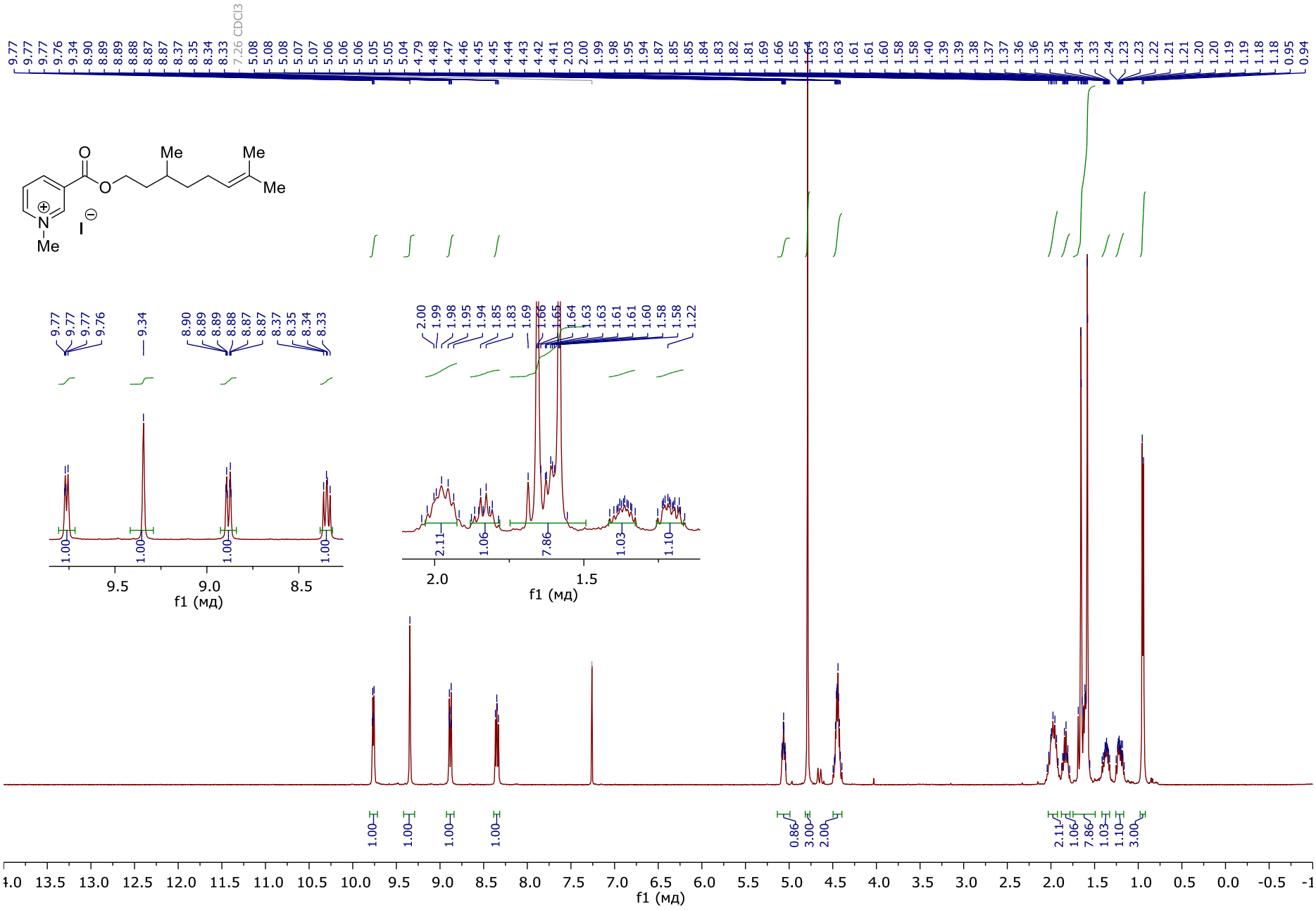
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-(4-chlorophenyl)-5-(methoxycarbonyl)-1-methylpyridin-1-ium iodide (**1q**)



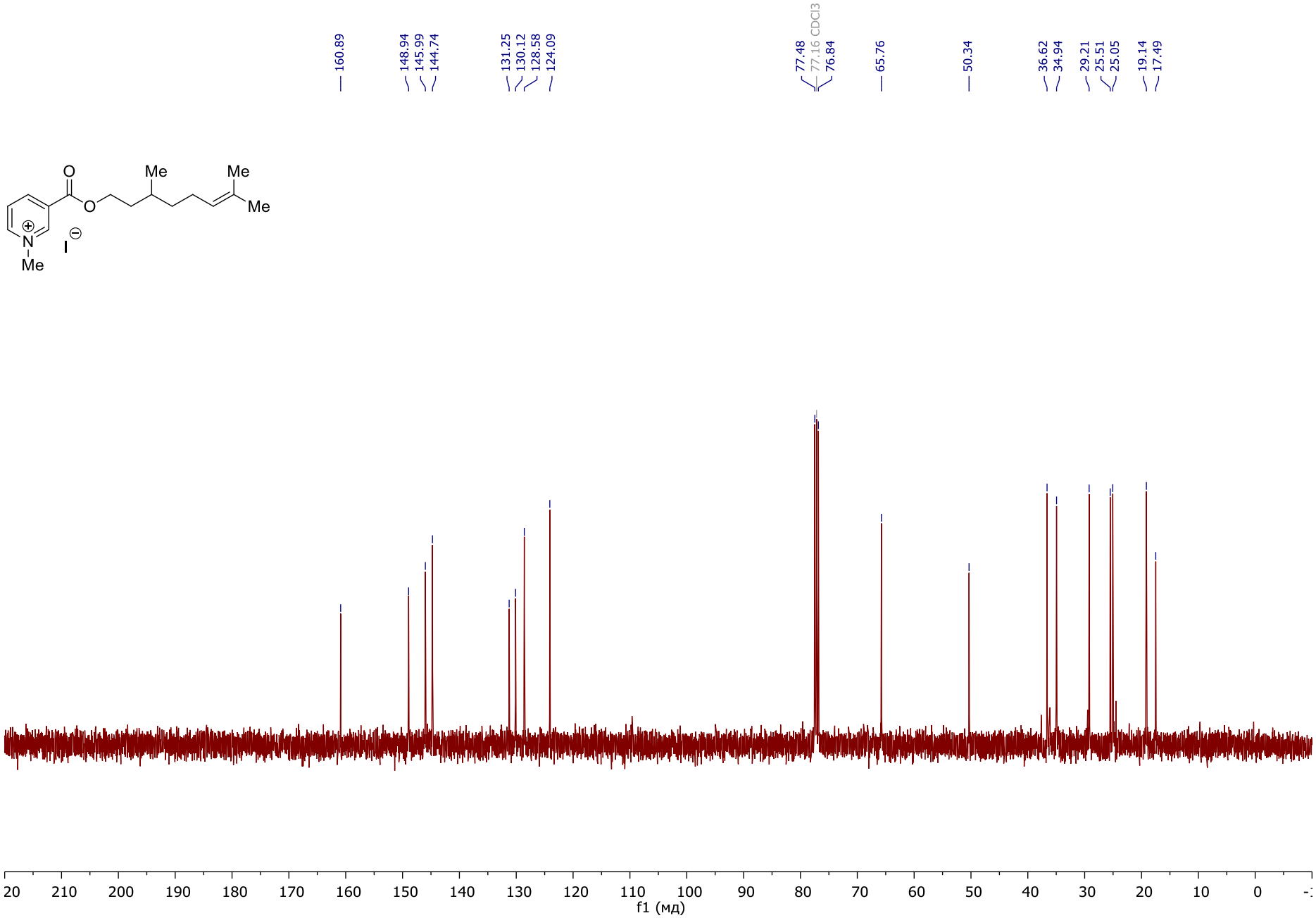
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-(4-chlorophenyl)-5-(methoxycarbonyl)-1-methylpyridin-1-ium iodide (**1q**)



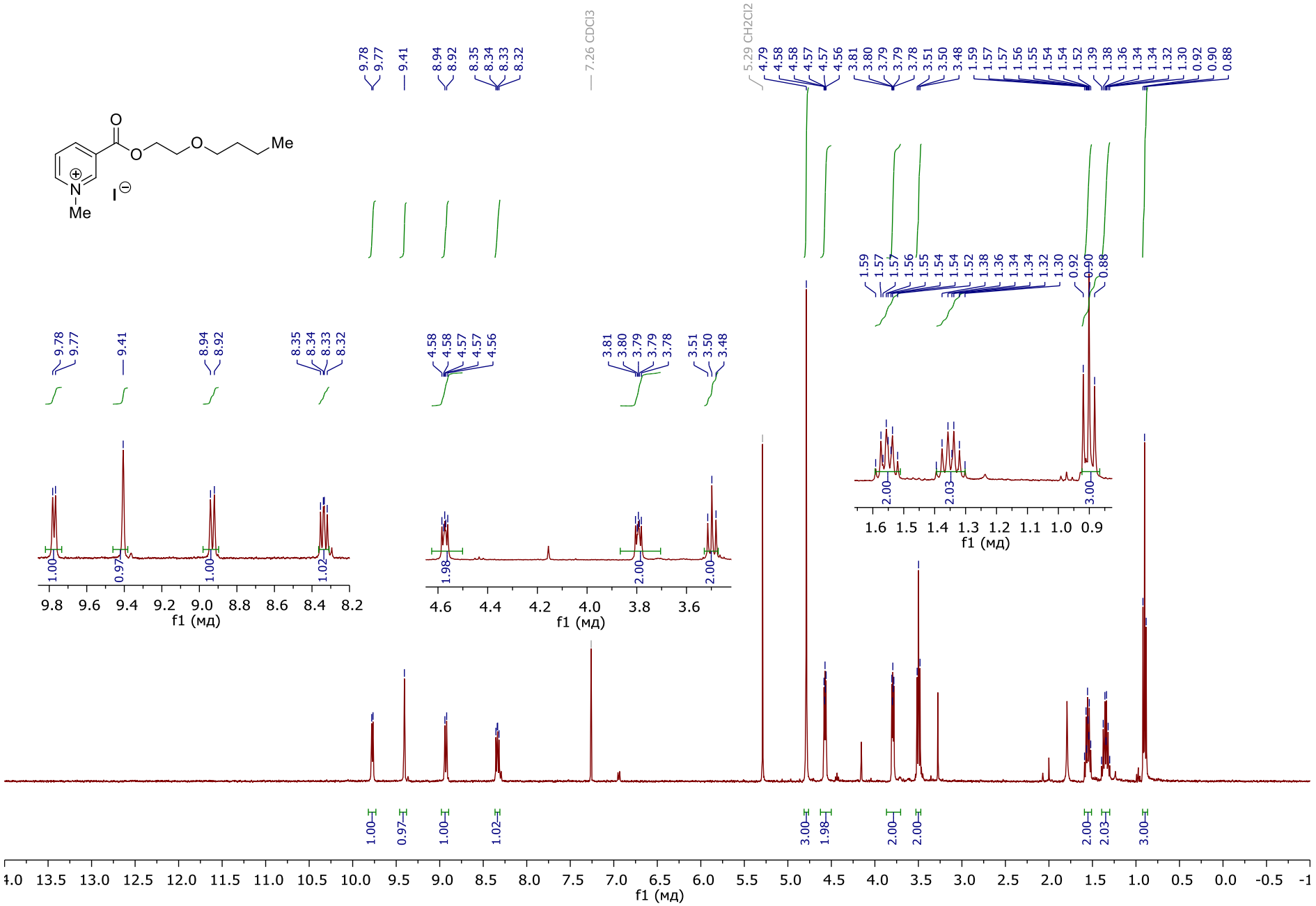
^{1}H NMR (400 MHz, $CDCl_3$) of 3-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1r**)



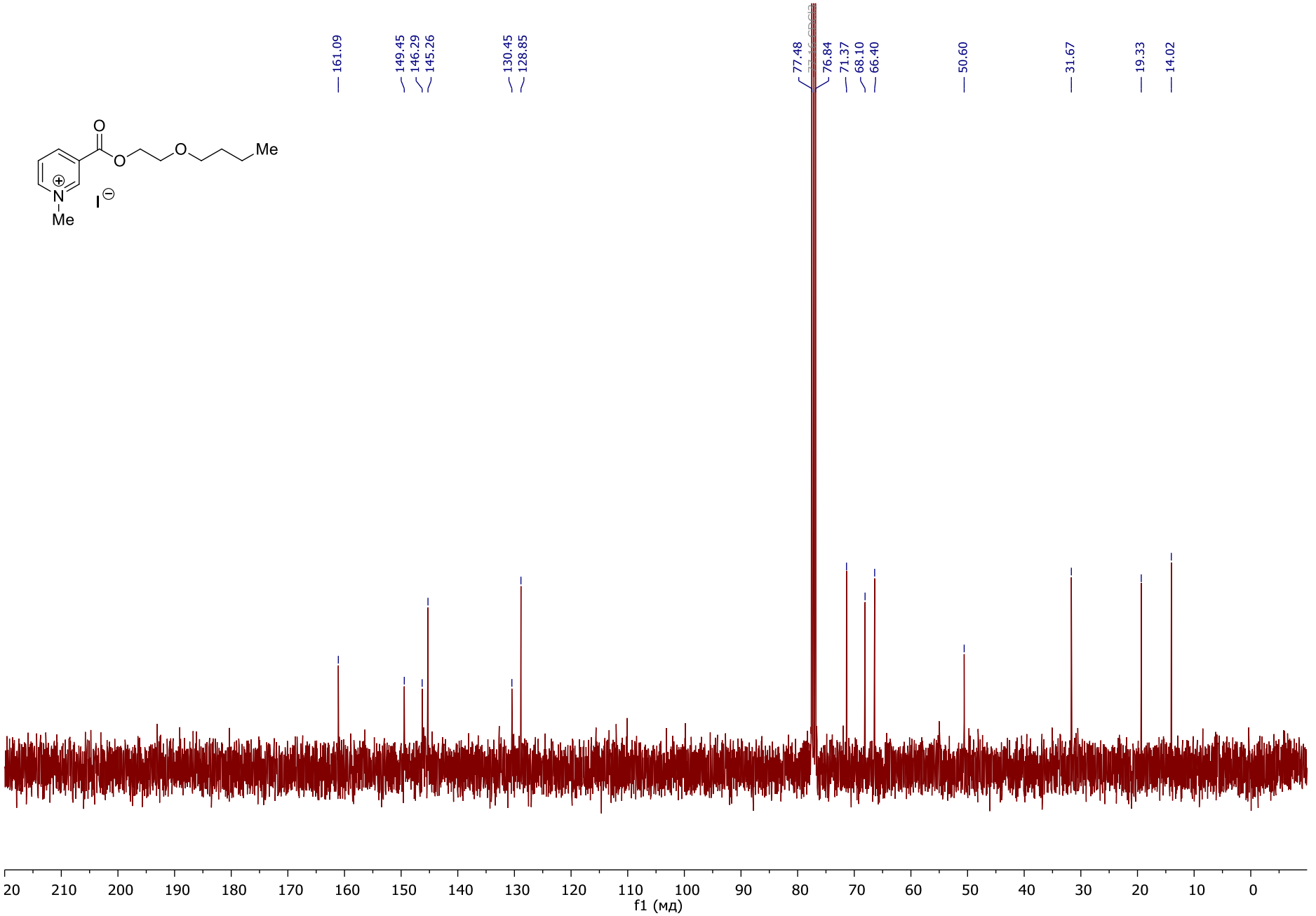
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1r**)



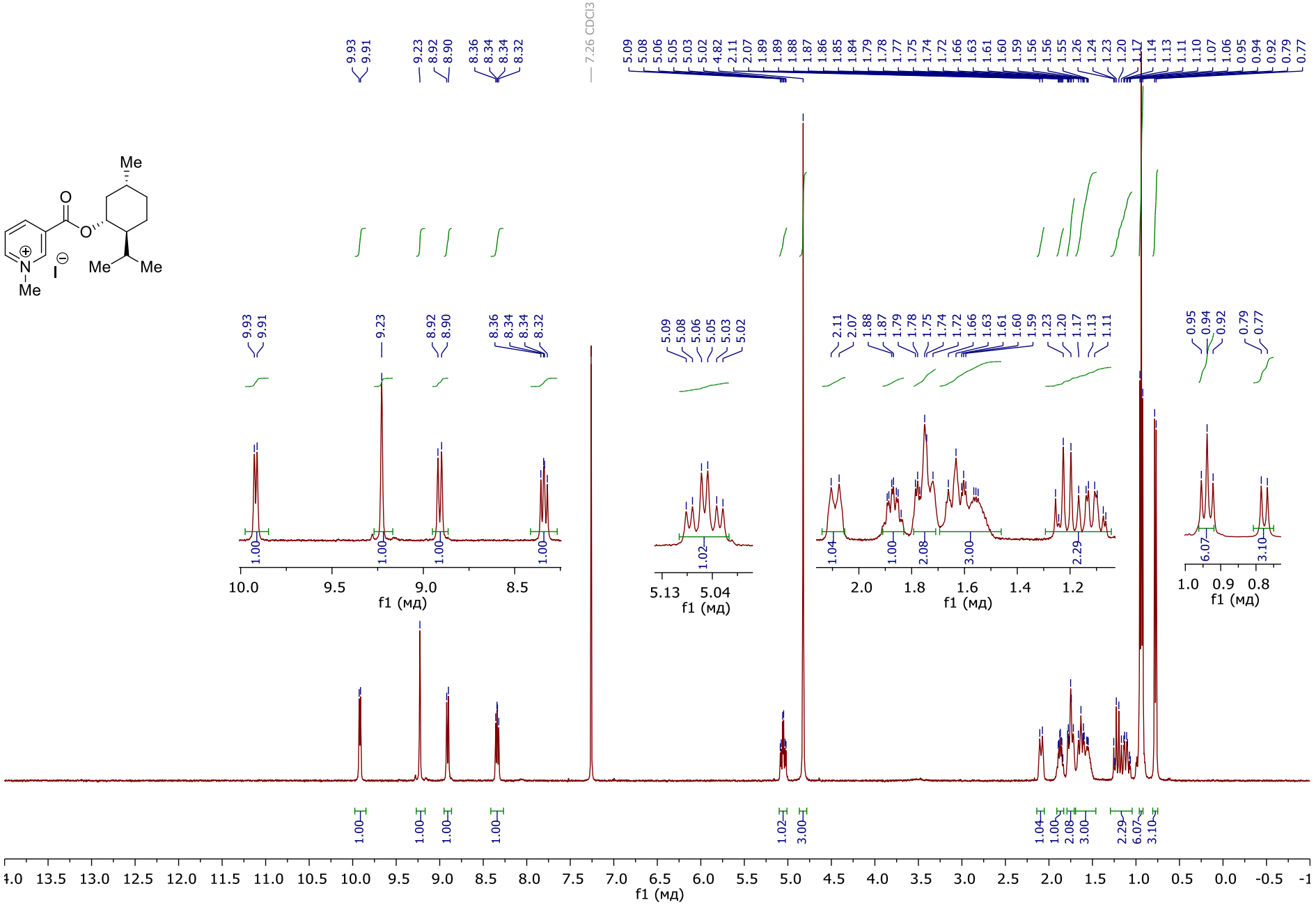
^{1}H NMR (400 MHz, $CDCl_3$) of 3-((2-butoxyethoxy)carbonyl)-1-methylpyridin-1-ium iodide (**1s**)



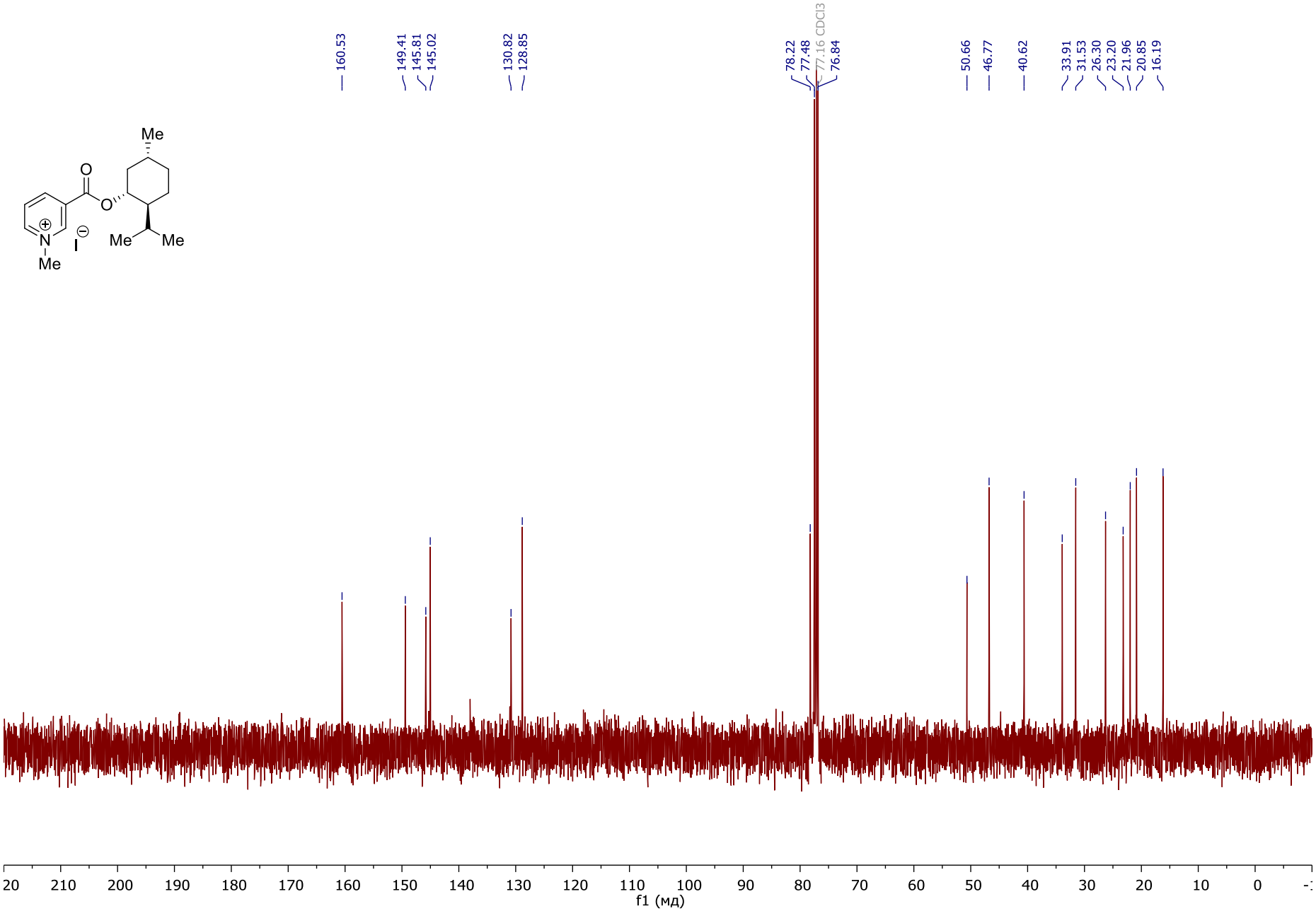
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3-((2-butoxyethoxy)carbonyl)-1-methylpyridin-1-ium iodide (**1s**)



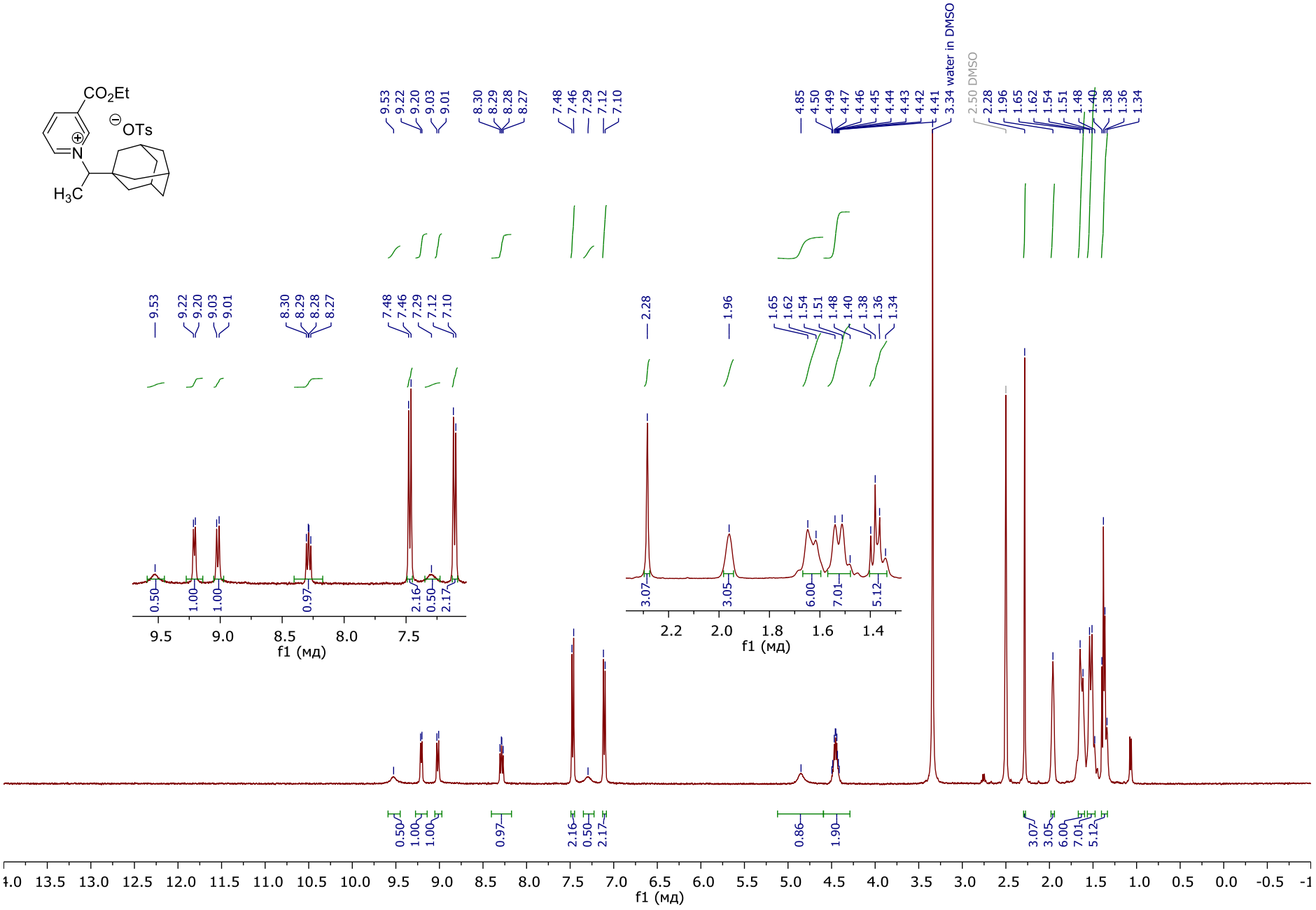
^{1}H NMR (400 MHz, $CDCl_3$) of 3-((((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1t**)



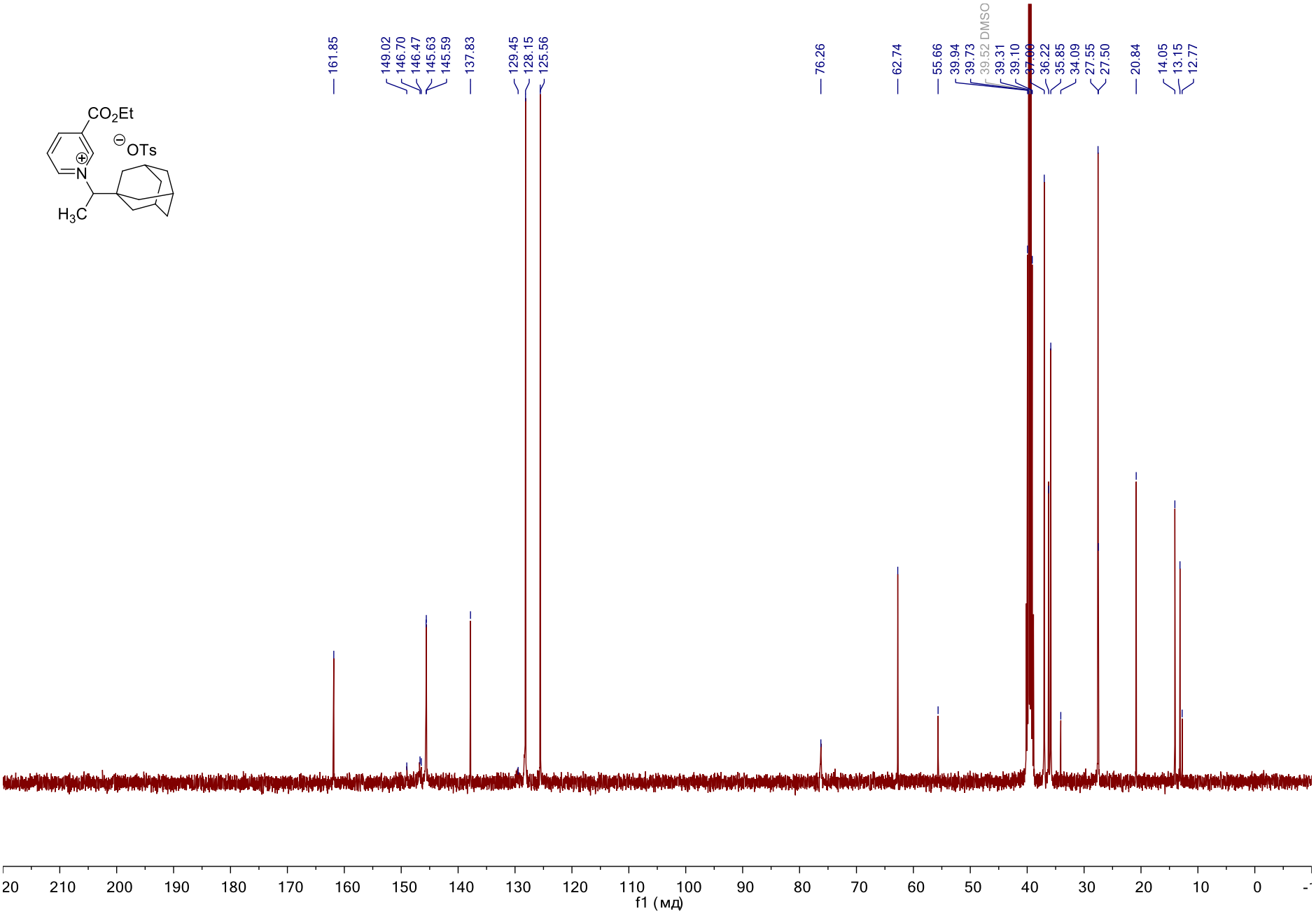
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3-((((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1-methylpyridin-1-ium iodide (**1t**)



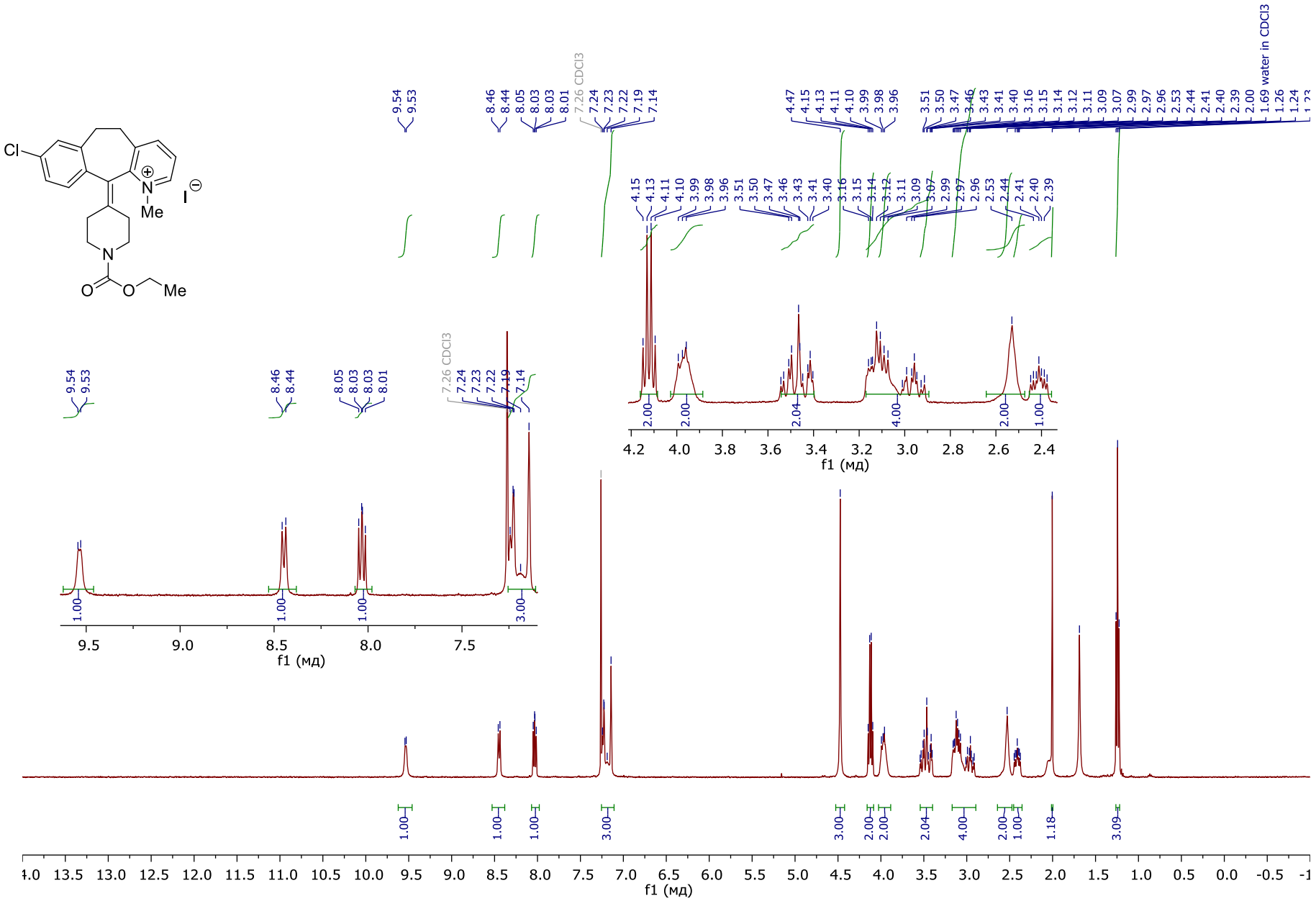
^{1}H NMR (400 MHz, DMSO-*d6*) of 1-(1-(adamantan-1-yl)ethyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate (**1u**)



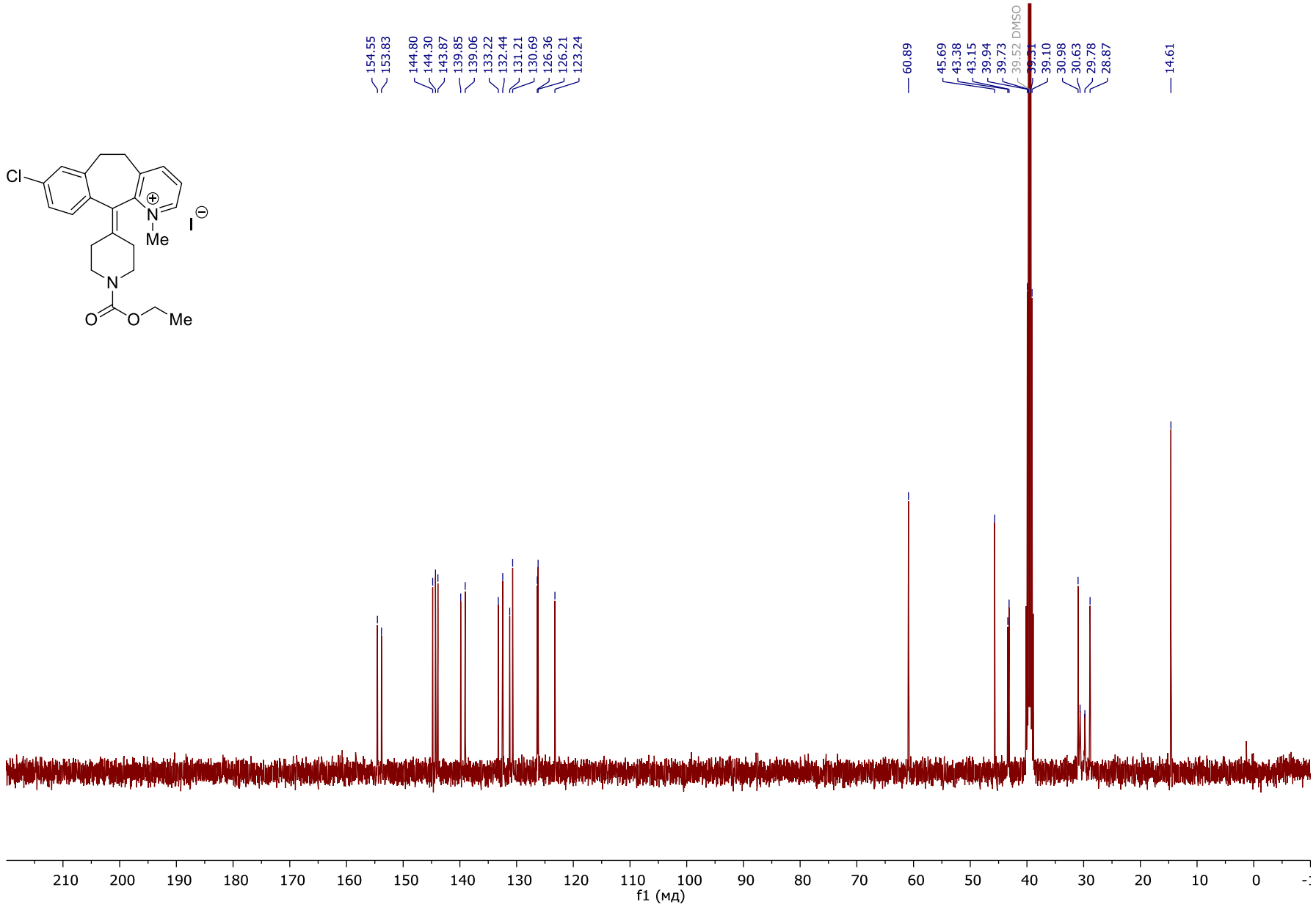
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 1-(1-(adamantan-1-yl)ethyl)-3-(ethoxycarbonyl)pyridin-1-ium *p*-toluenesulfonate (**1u**)



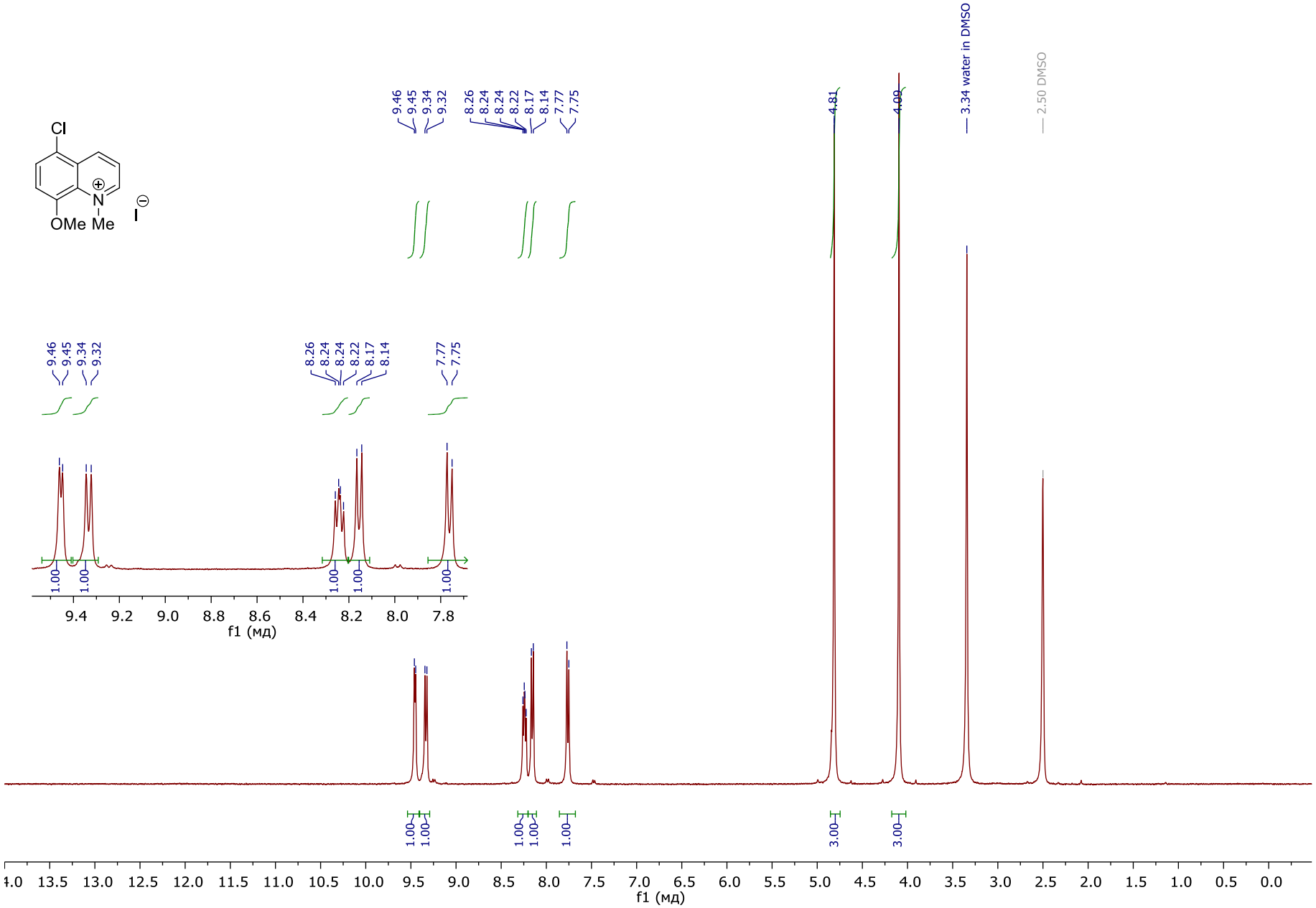
^{1}H NMR (400 MHz, $CDCl_3$) of 8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-1-methyl-6,11-dihydro-*5H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-1-ium iodide (**1v**)



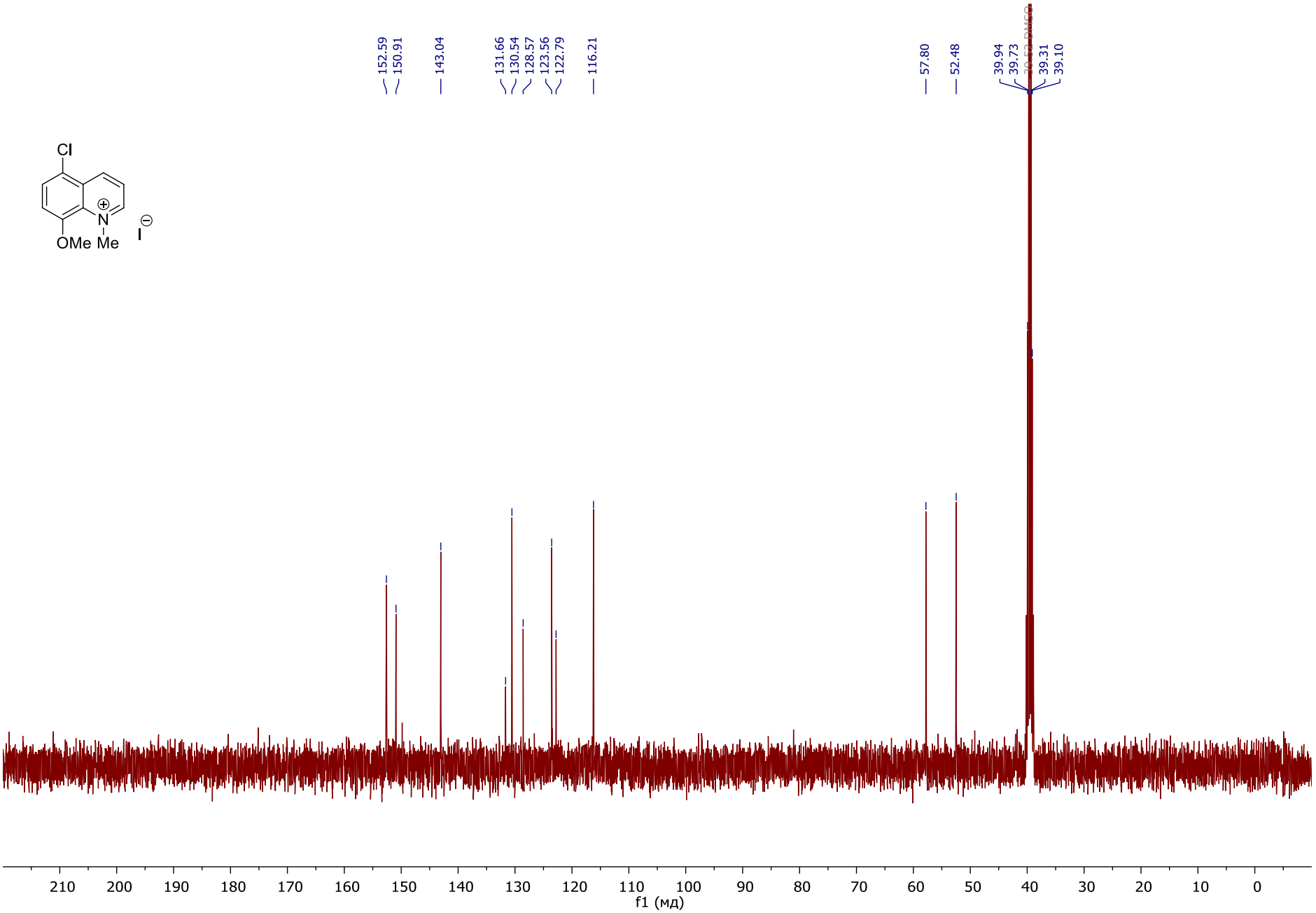
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-1-methyl-6,11-dihydro-*5H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-1-ium iodide (**1v**)



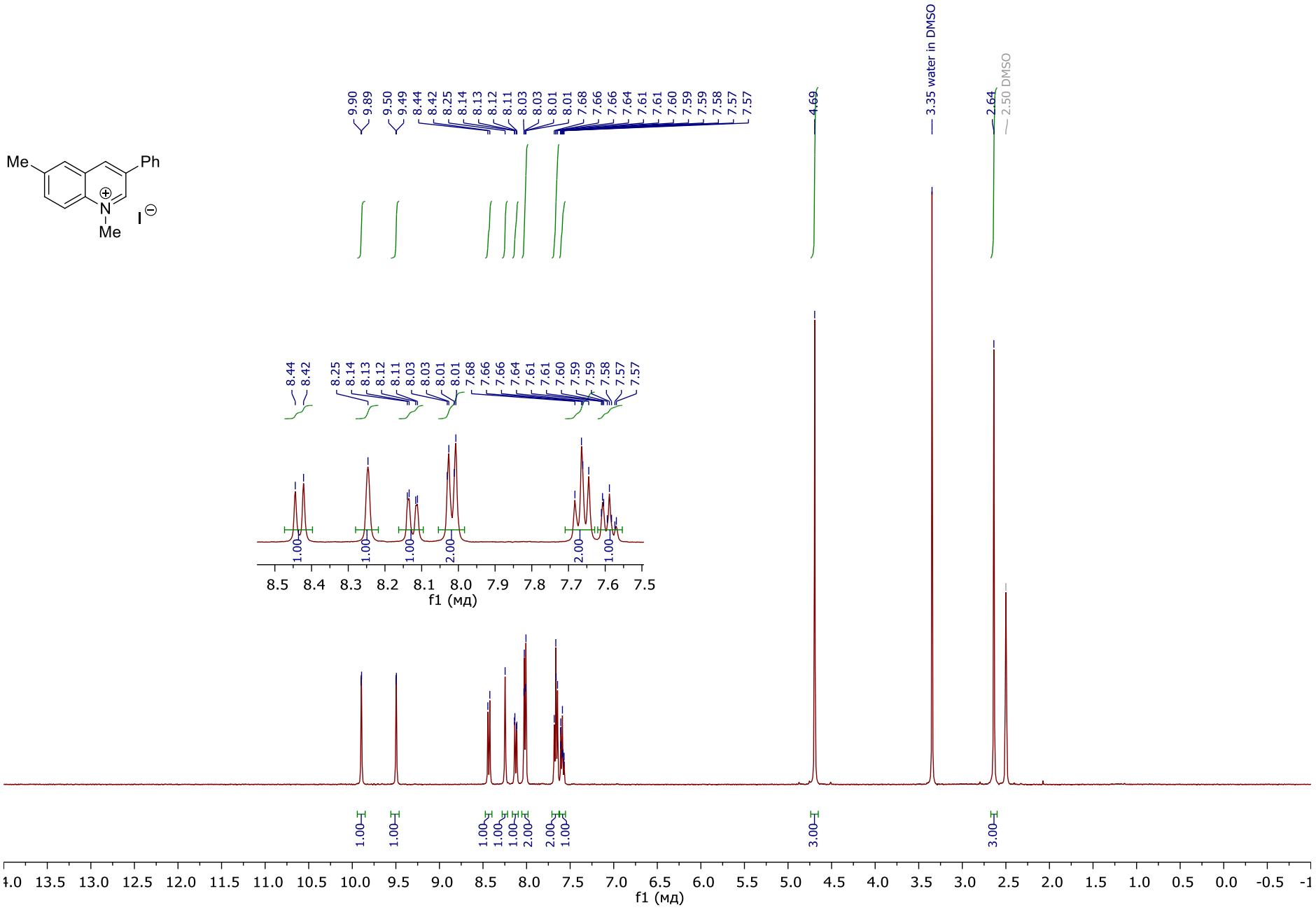
^{1}H NMR (400 MHz, DMSO-*d6*) of 5-chloro-8-methoxy-1-methylquinolin-1-ium iodide (**1y**)



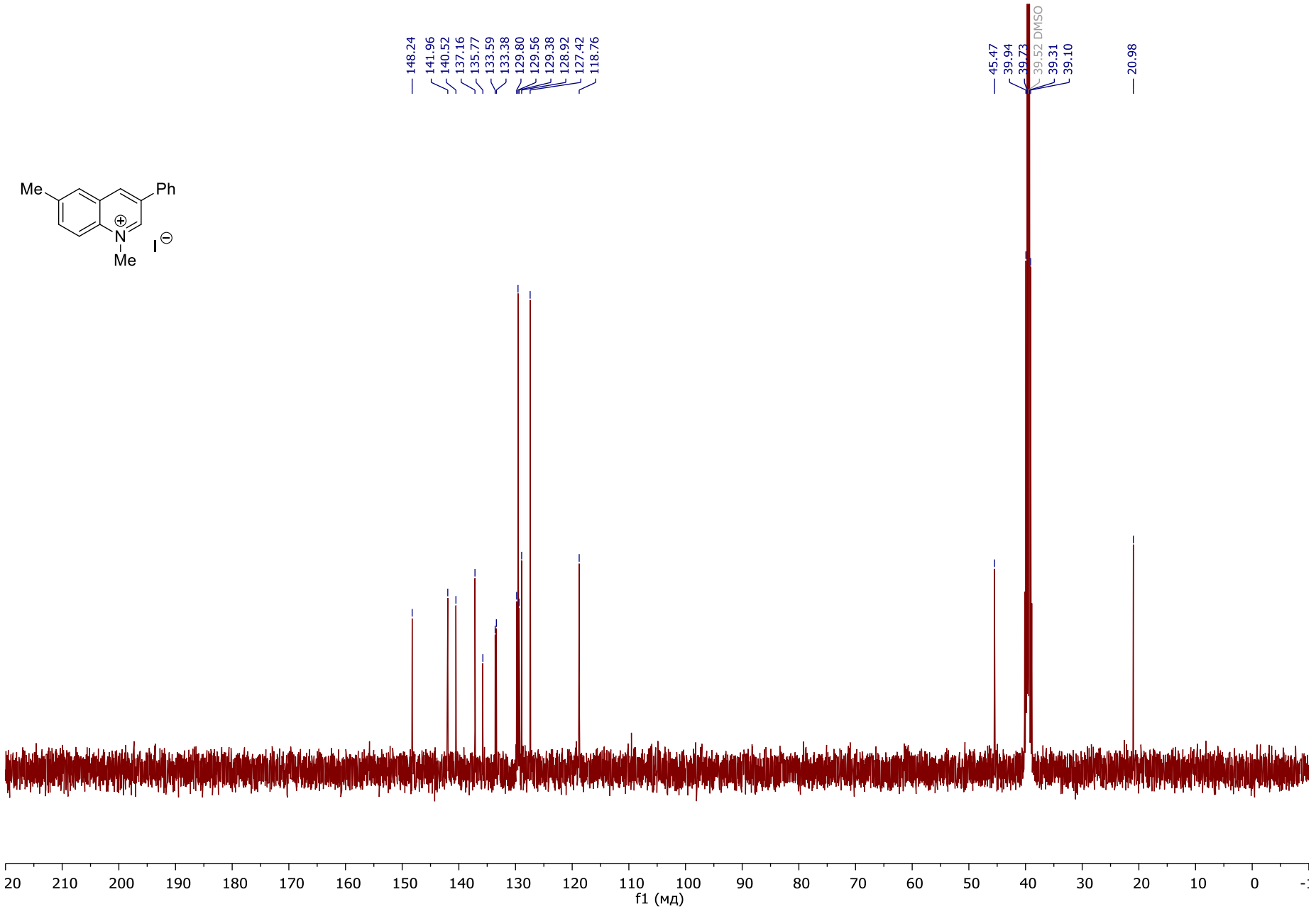
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 5-chloro-8-methoxy-1-methylquinolin-1-ium iodide (**1y**)



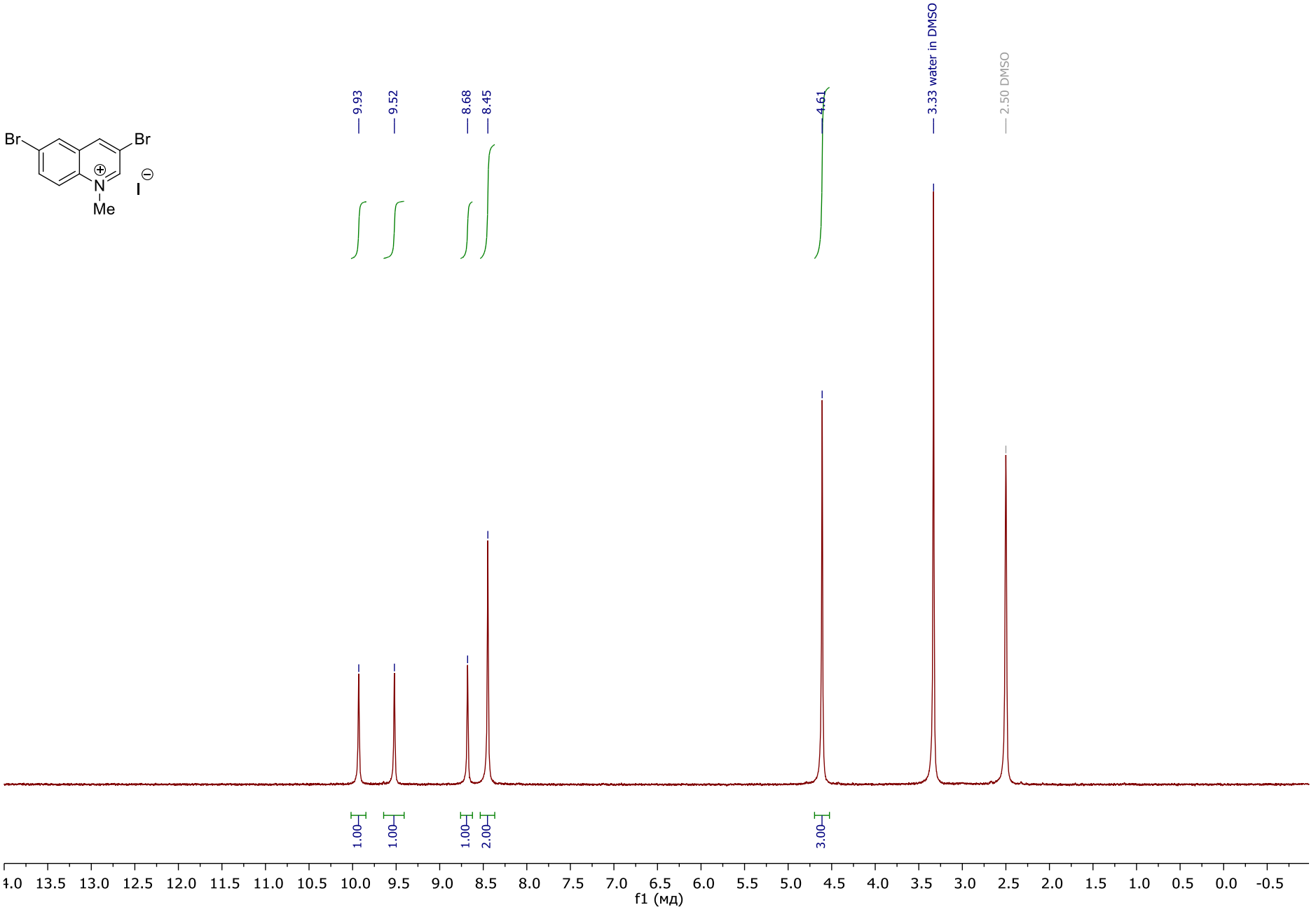
^{1}H NMR (400 MHz, DMSO-*d6*) of 1,6-dimethyl-3-phenylquinolin-1-ium iodide (**1z**)



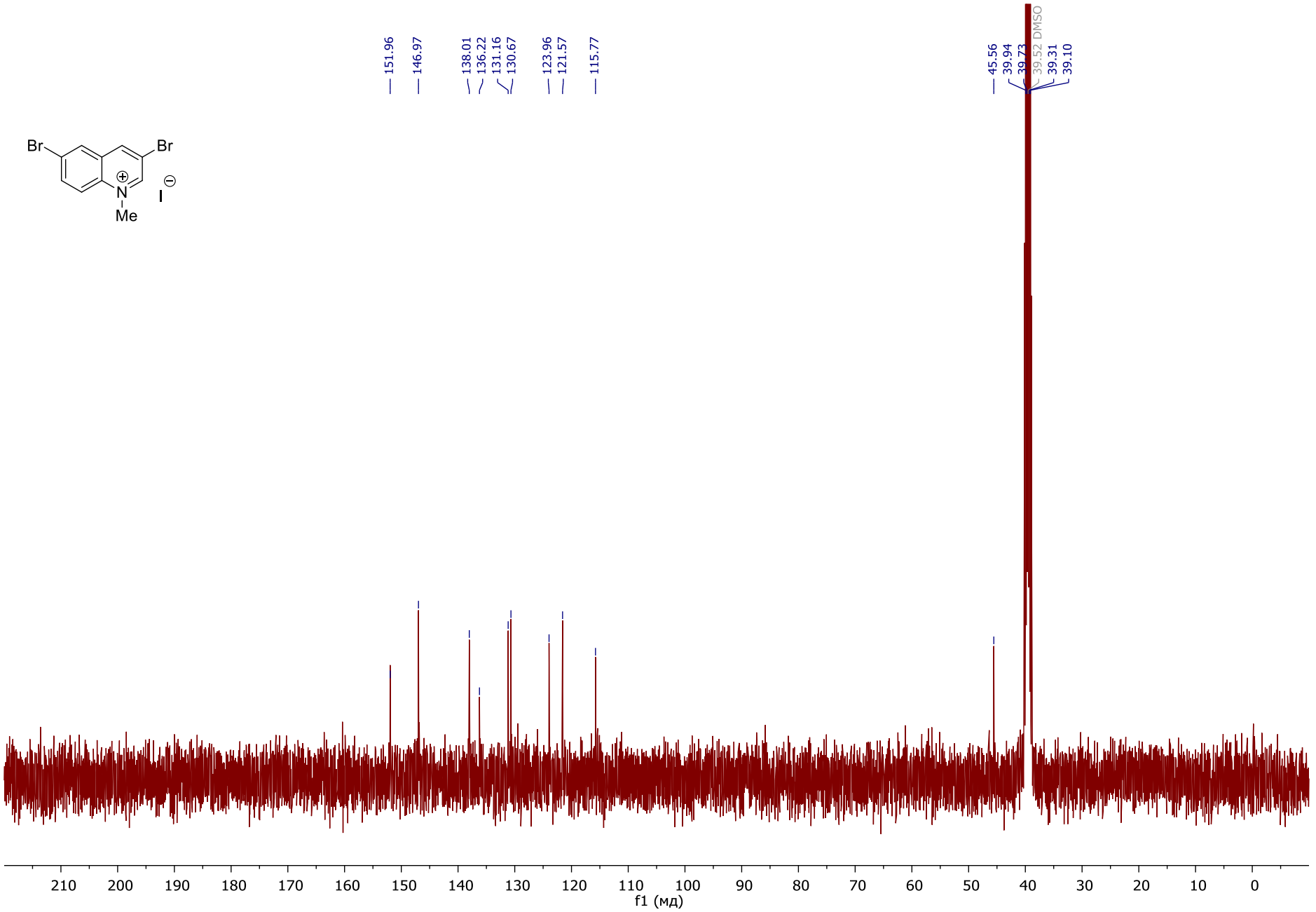
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 1,6-dimethyl-3-phenylquinolin-1-ium iodide (**1z**)



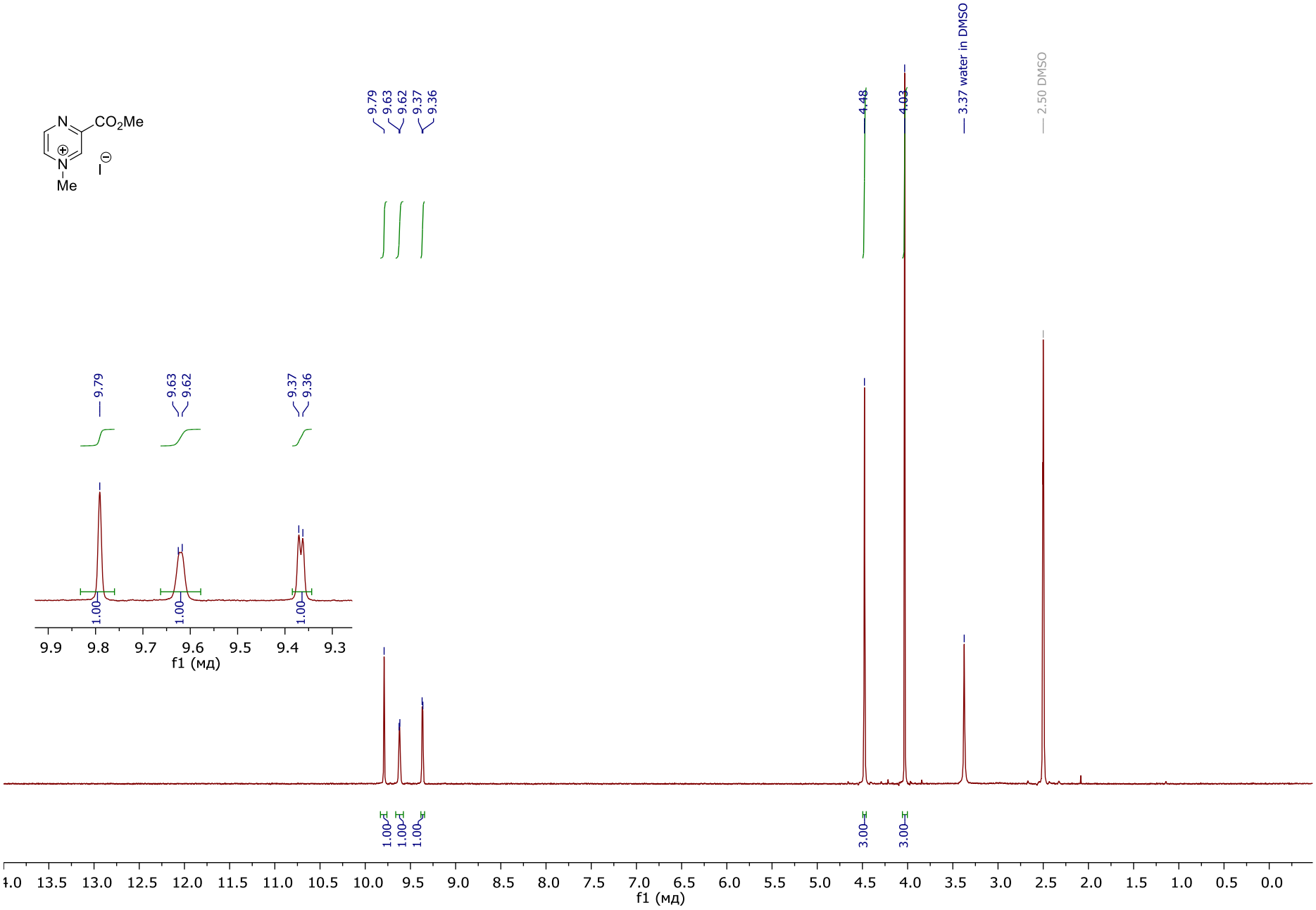
^{1}H NMR (400 MHz, DMSO-*d6*) of 3,6-dibromo-1-methylquinolin-1-ium iodide (**1aa**)



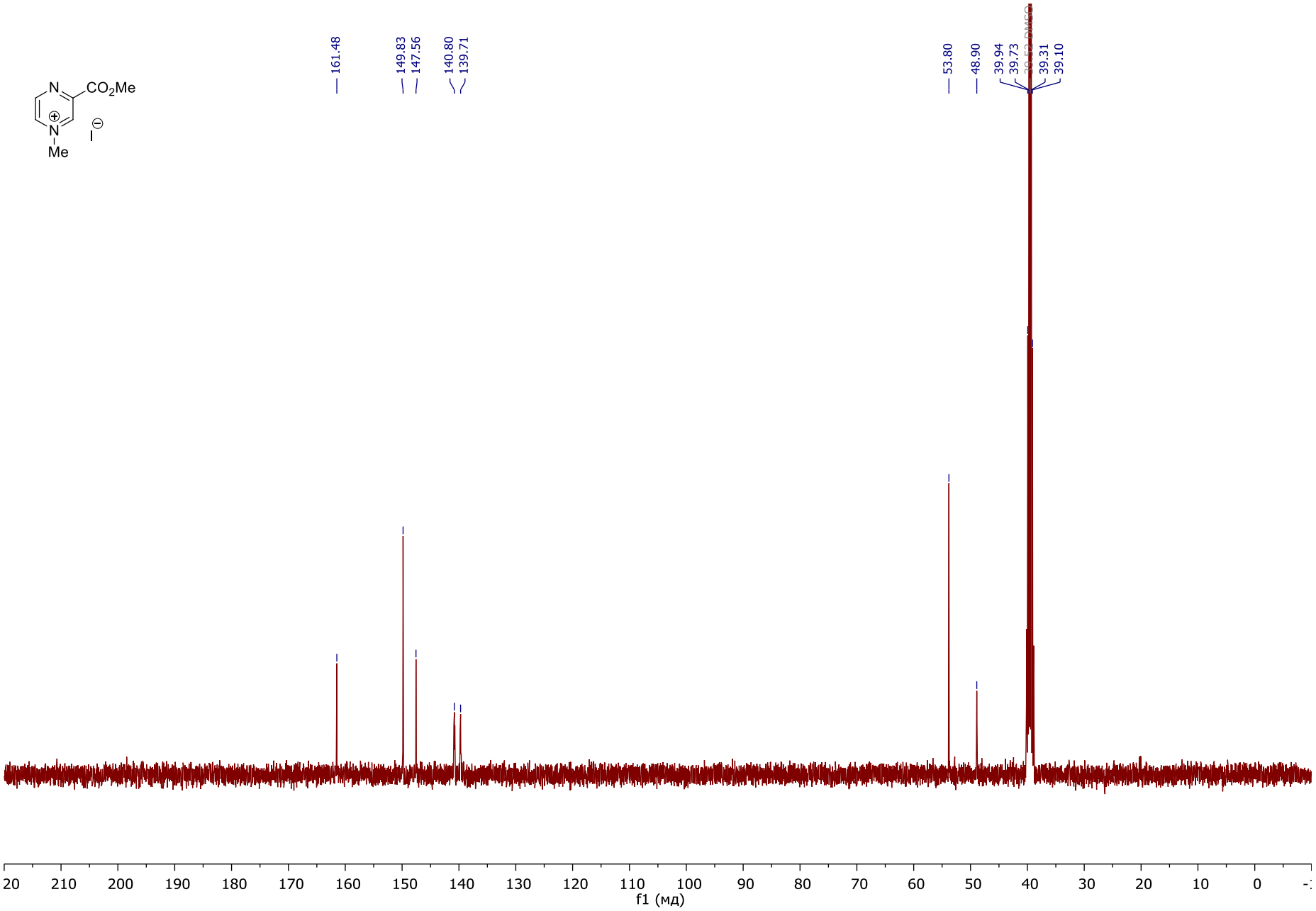
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3,6-dibromo-1-methylquinolin-1-ium iodide (**1aa**)



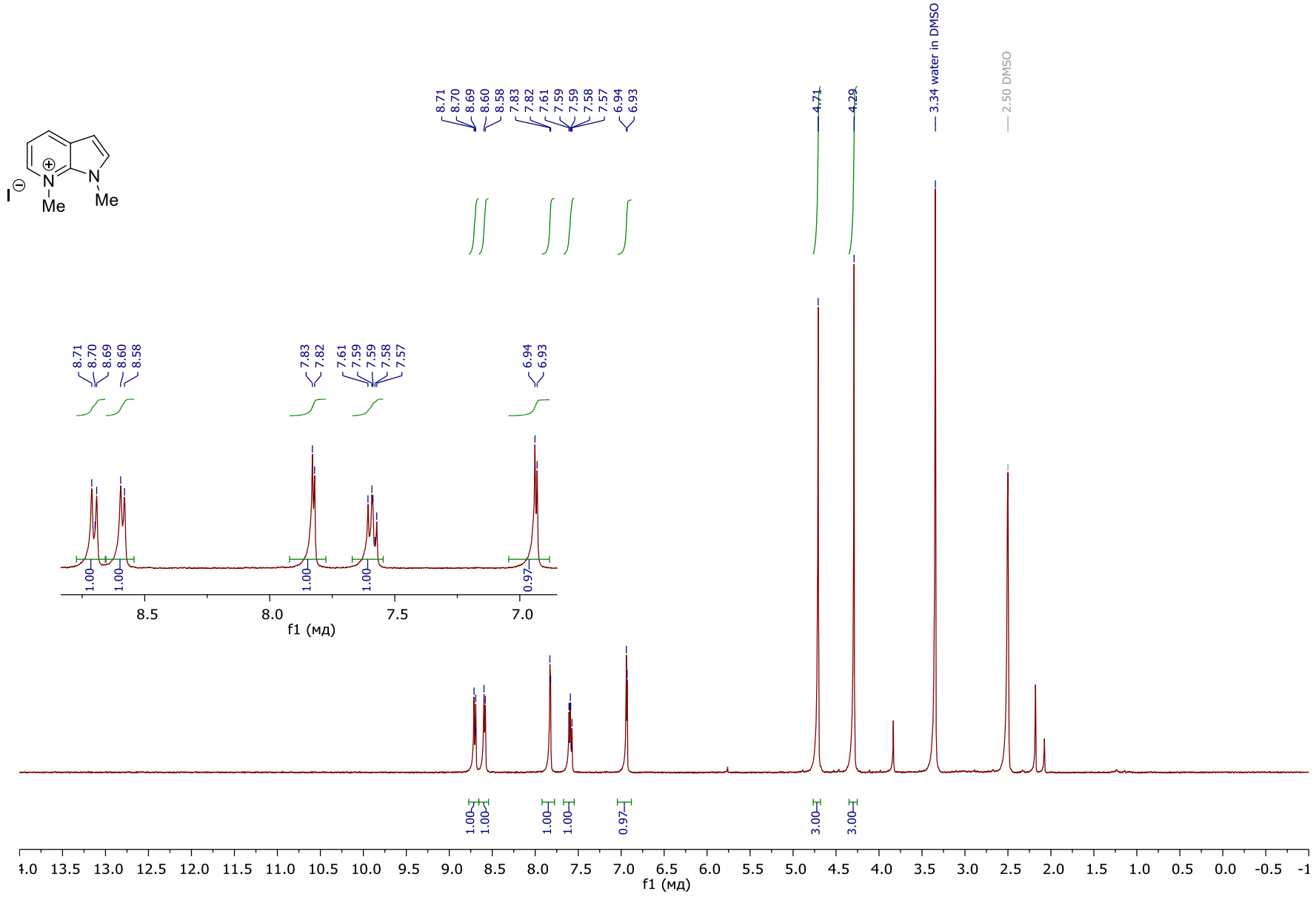
^{1}H NMR (400 MHz, DMSO-*d6*) of 3-(methoxycarbonyl)-1-methylpyrazin-1-ium iodide (**1ff**)



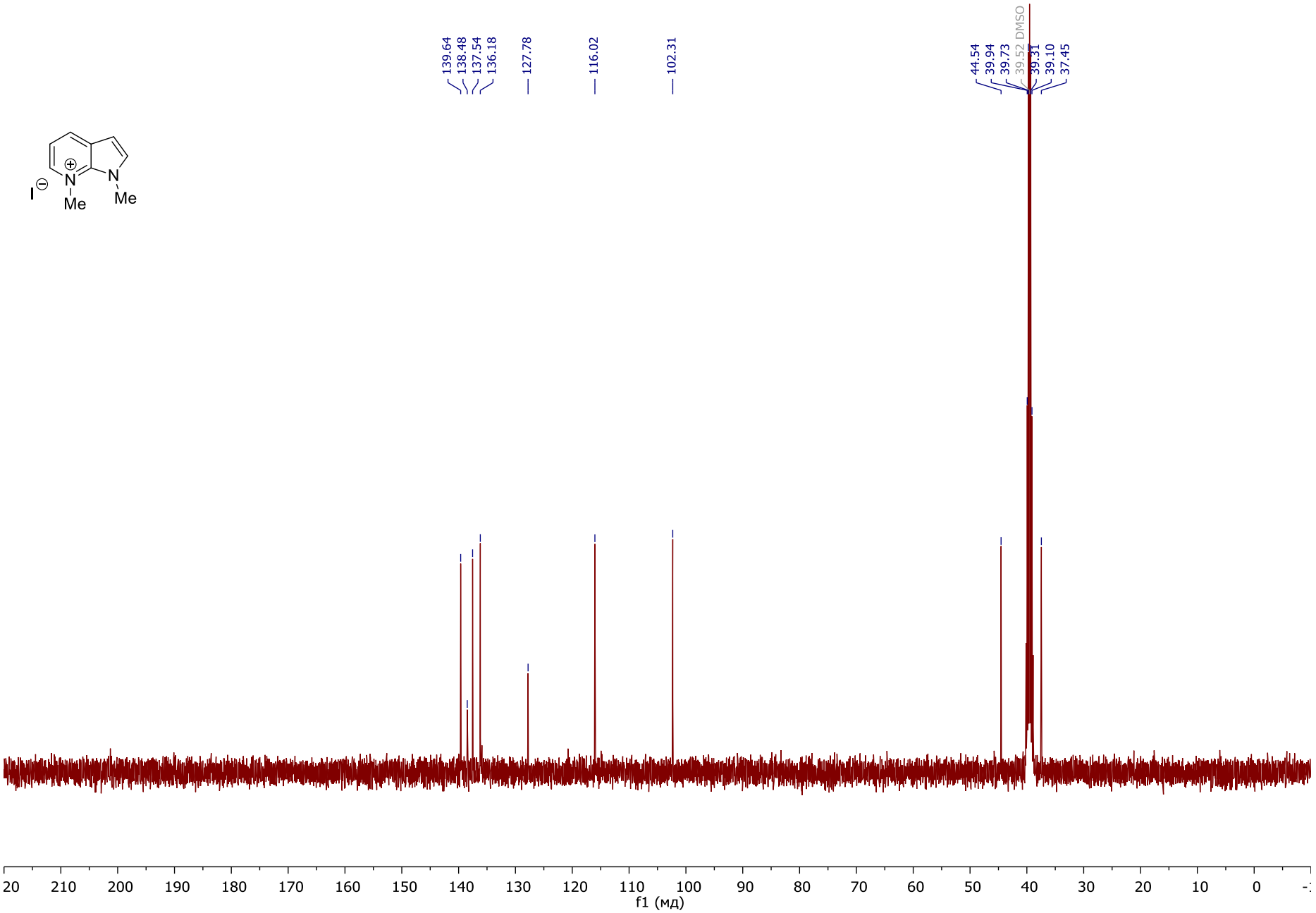
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 3-(methoxycarbonyl)-1-methylpyrazin-1-ium iodide (**1ff**)



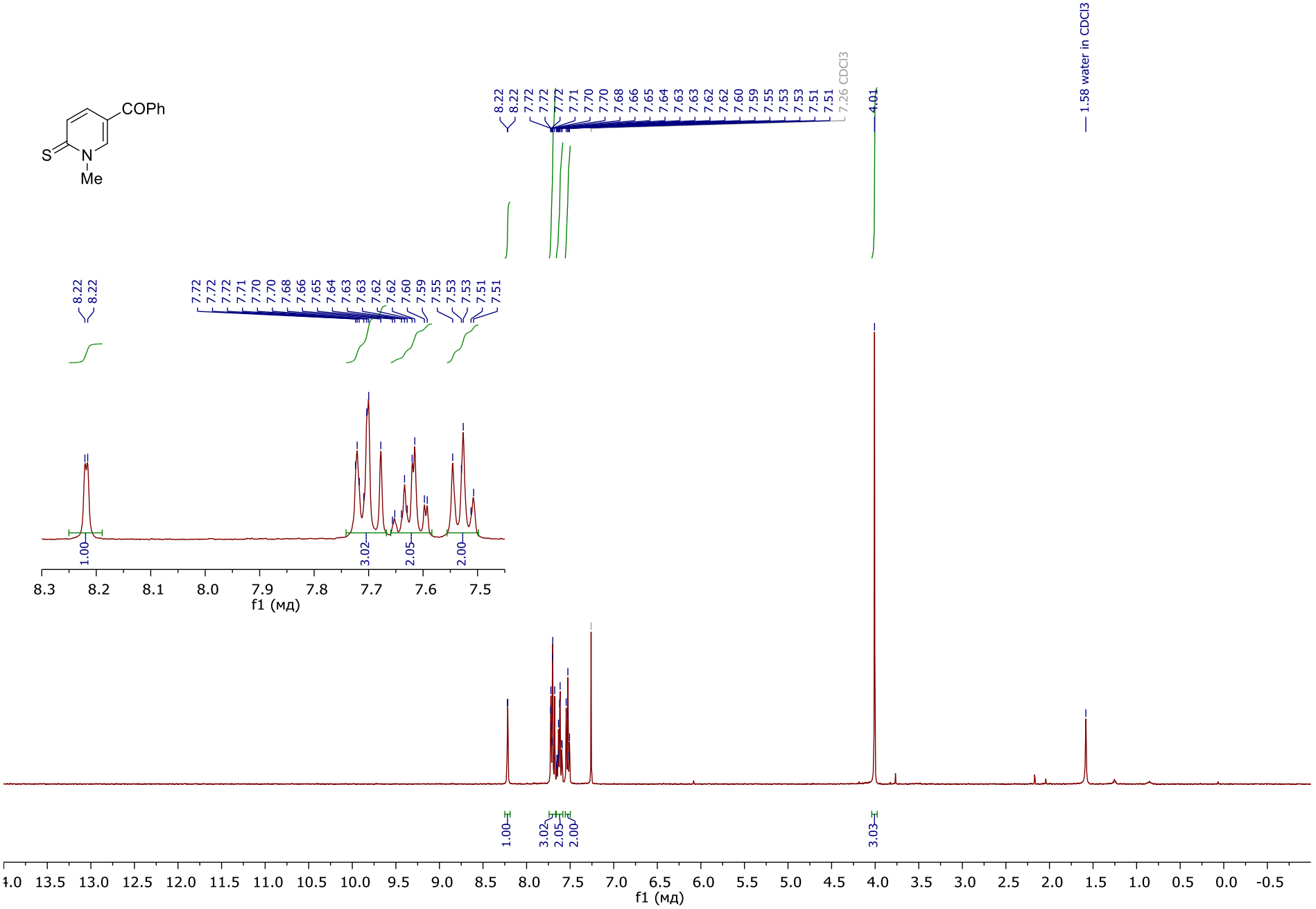
^{1}H NMR (400 MHz, DMSO-*d6*) of 1,7-dimethyl-*1H*-pyrrolo[2,3-*b*]pyridin-7-ium iodide (**1ii**)



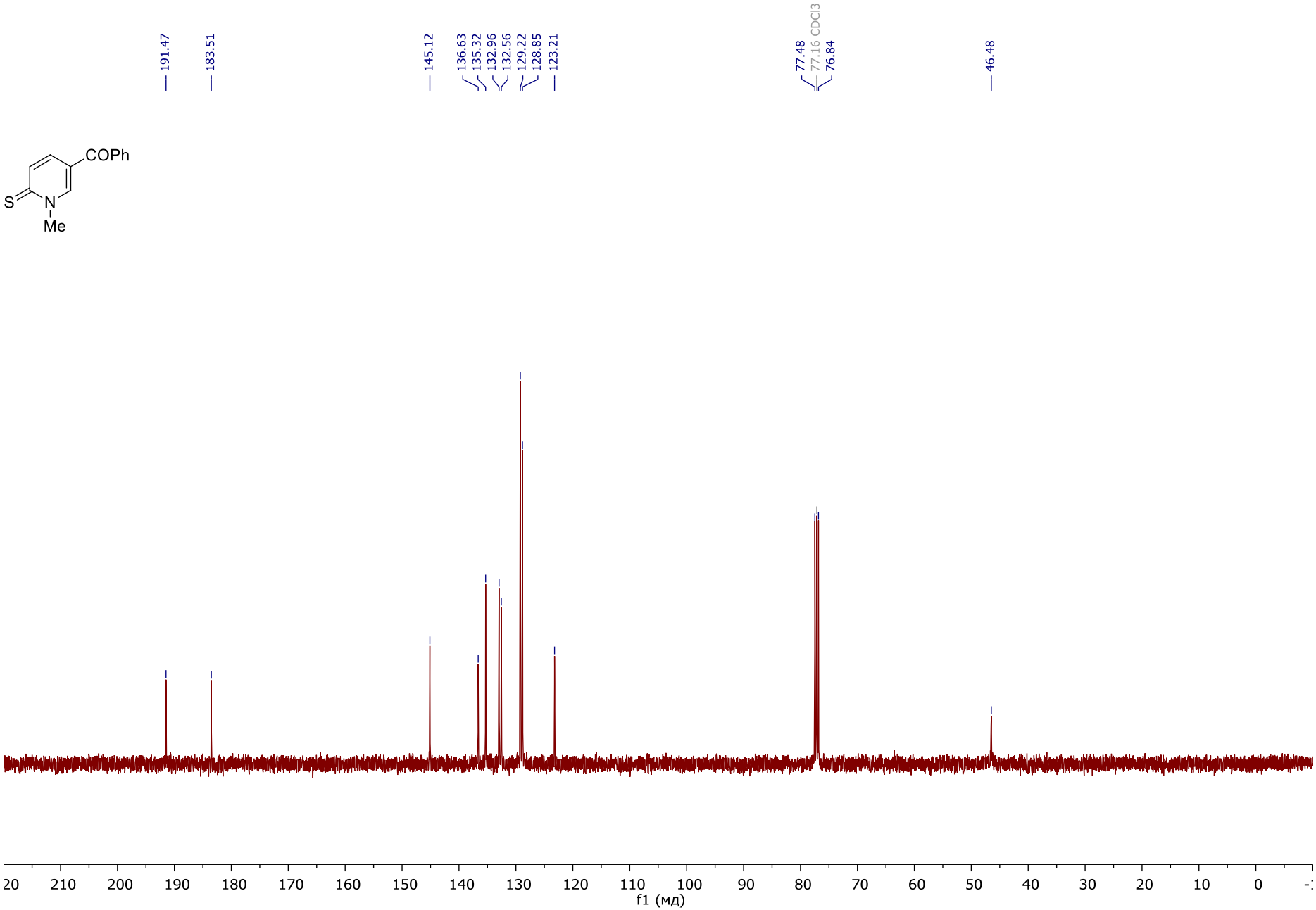
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-*d6*) of 1,7-dimethyl-*1H*-pyrrolo[2,3-*b*]pyridin-7-ium iodide (**1ii**)



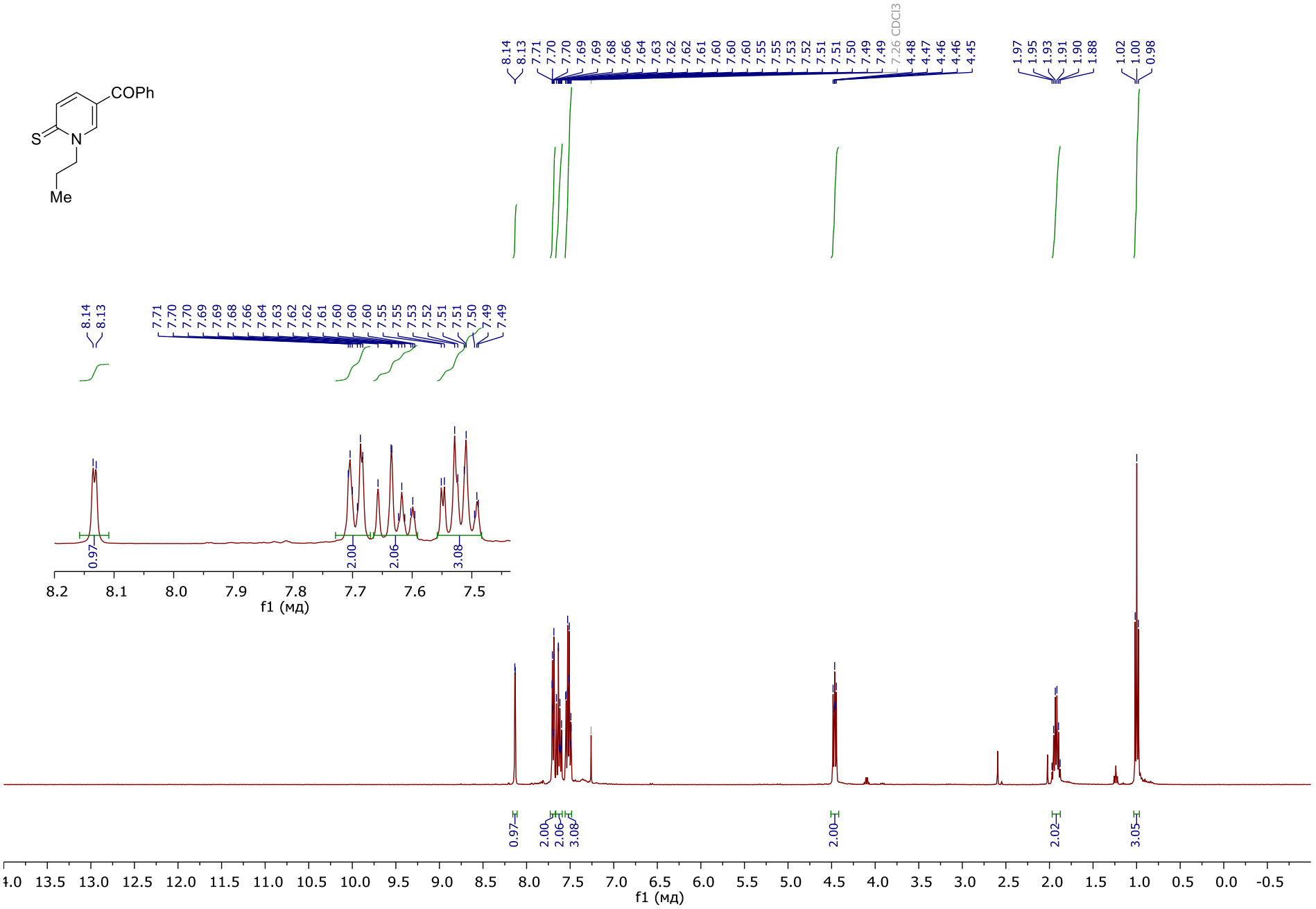
^{1}H NMR (400 MHz, $CDCl_3$) of (1-methyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2a**)



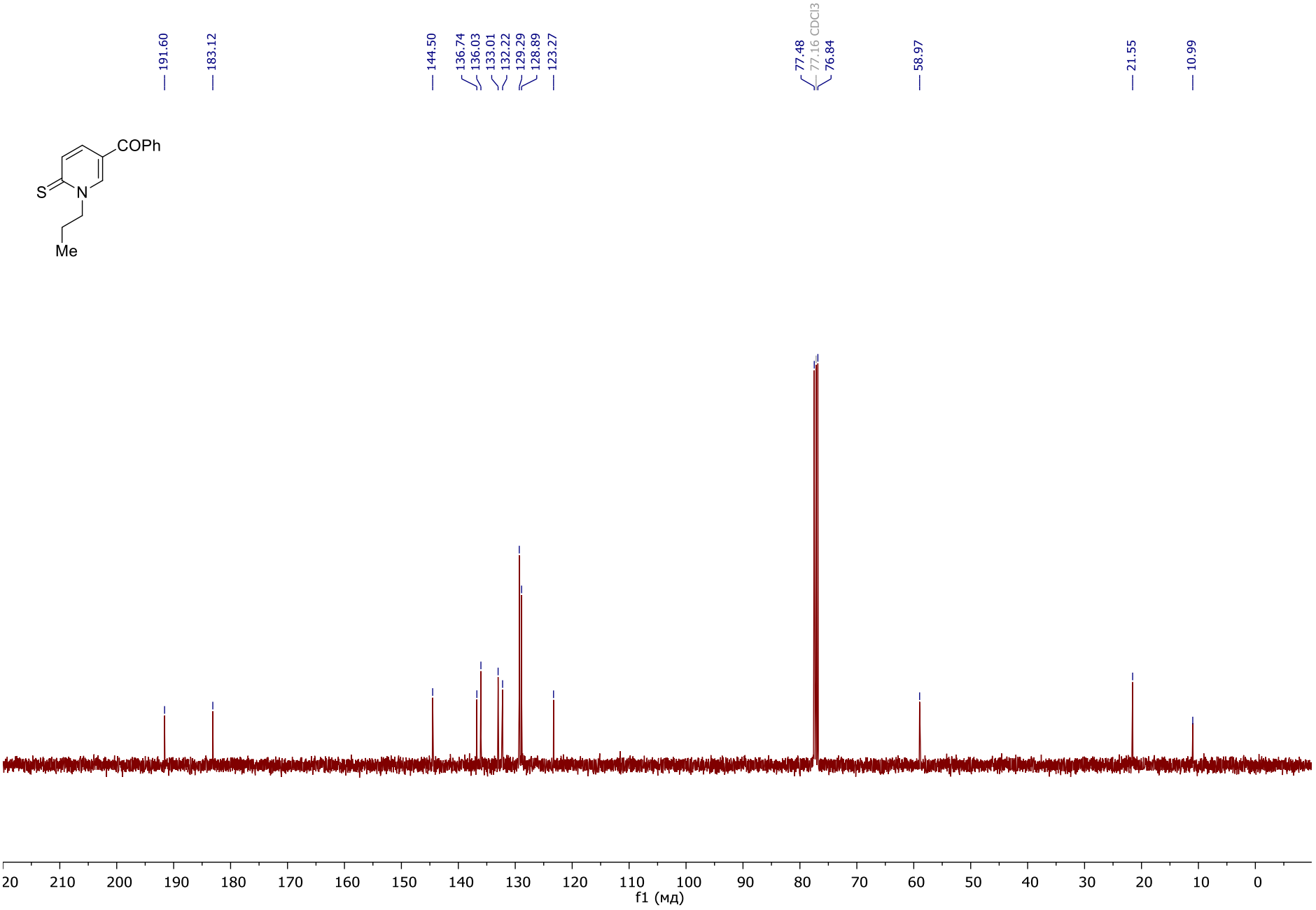
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-methyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2a**)



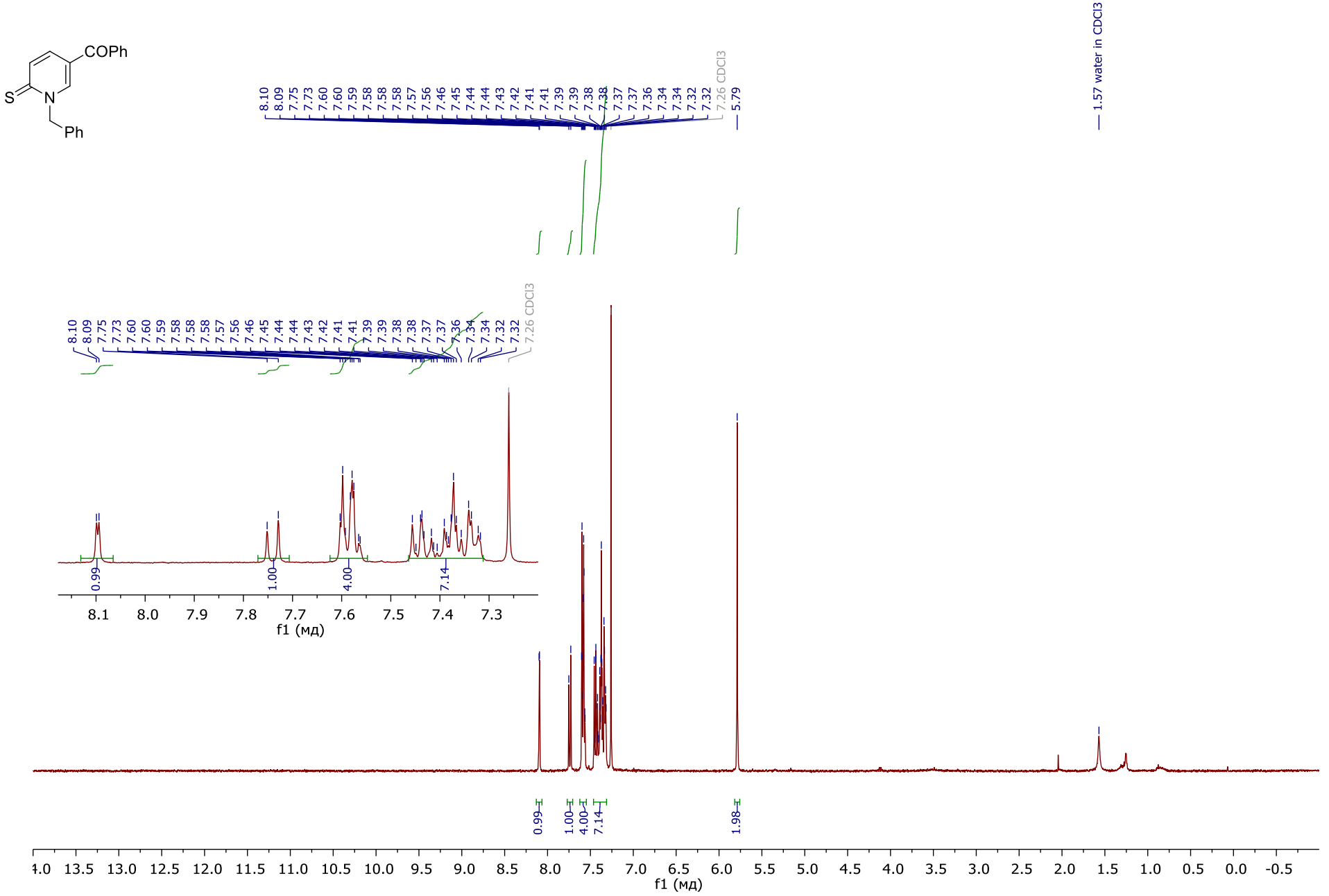
^{1}H NMR (400 MHz, $CDCl_3$) of phenyl(1-propyl-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2b**)



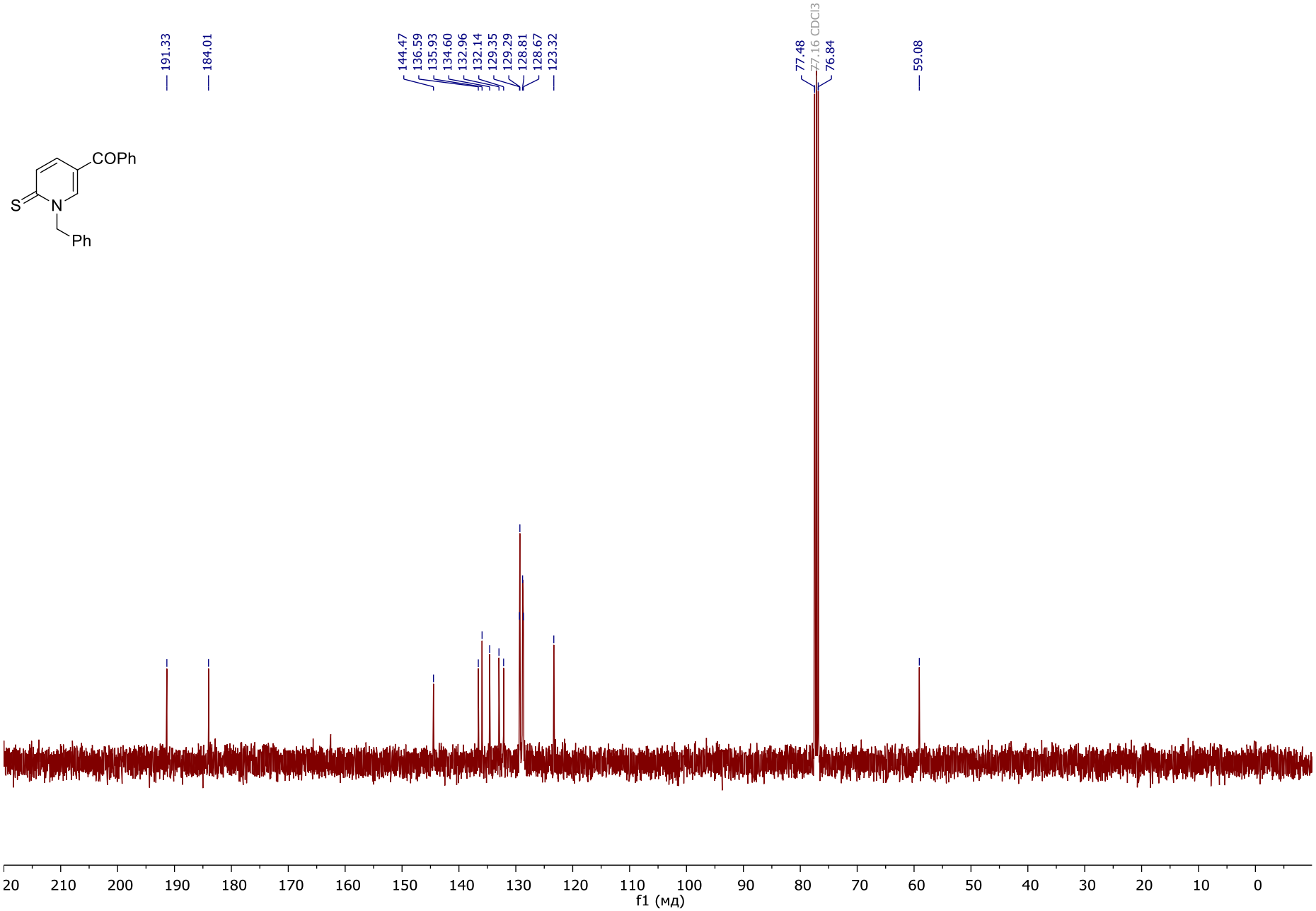
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of phenyl(1-propyl-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2b**)



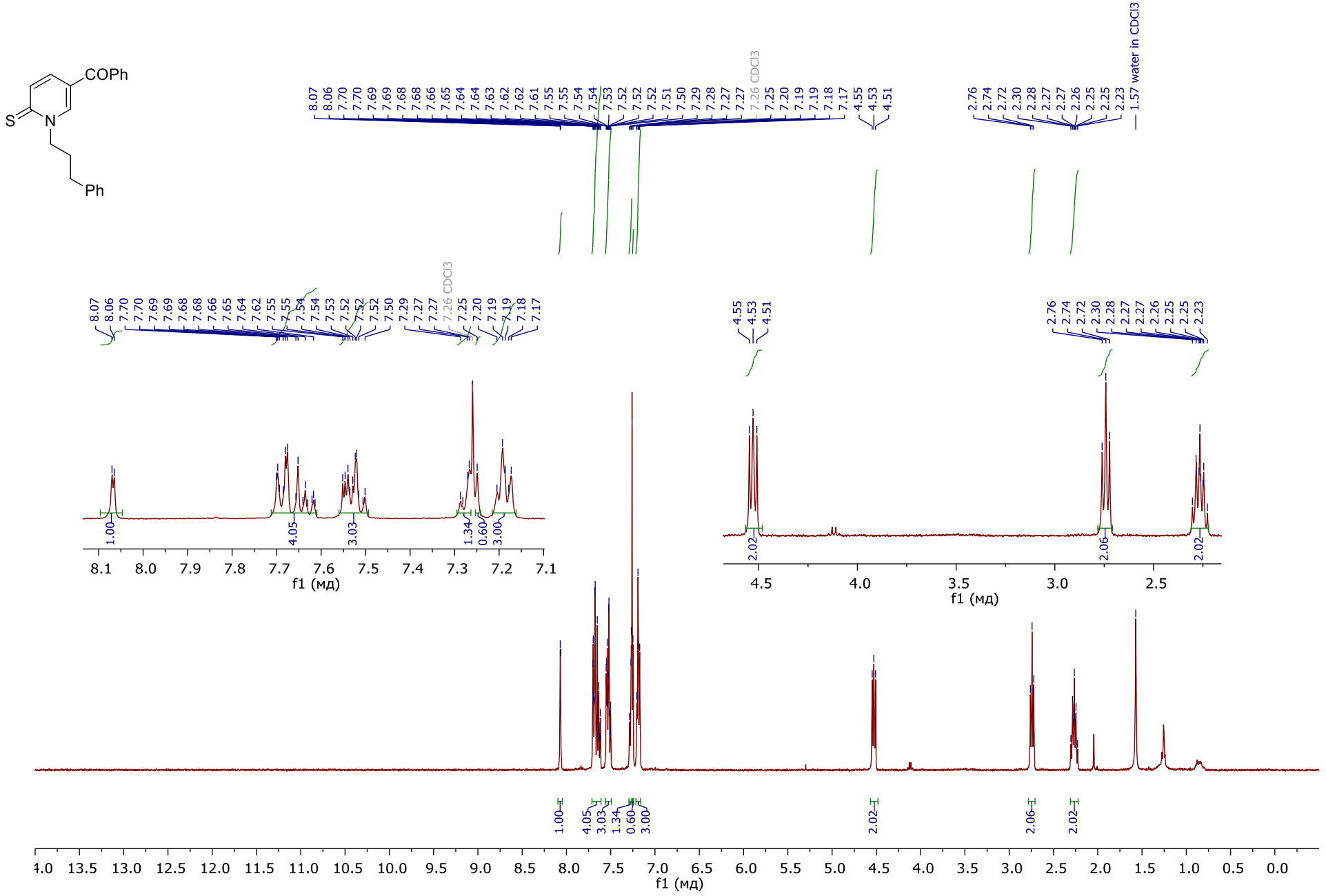
^{1}H NMR (400 MHz, $CDCl_3$) of (1-benzyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2c)**



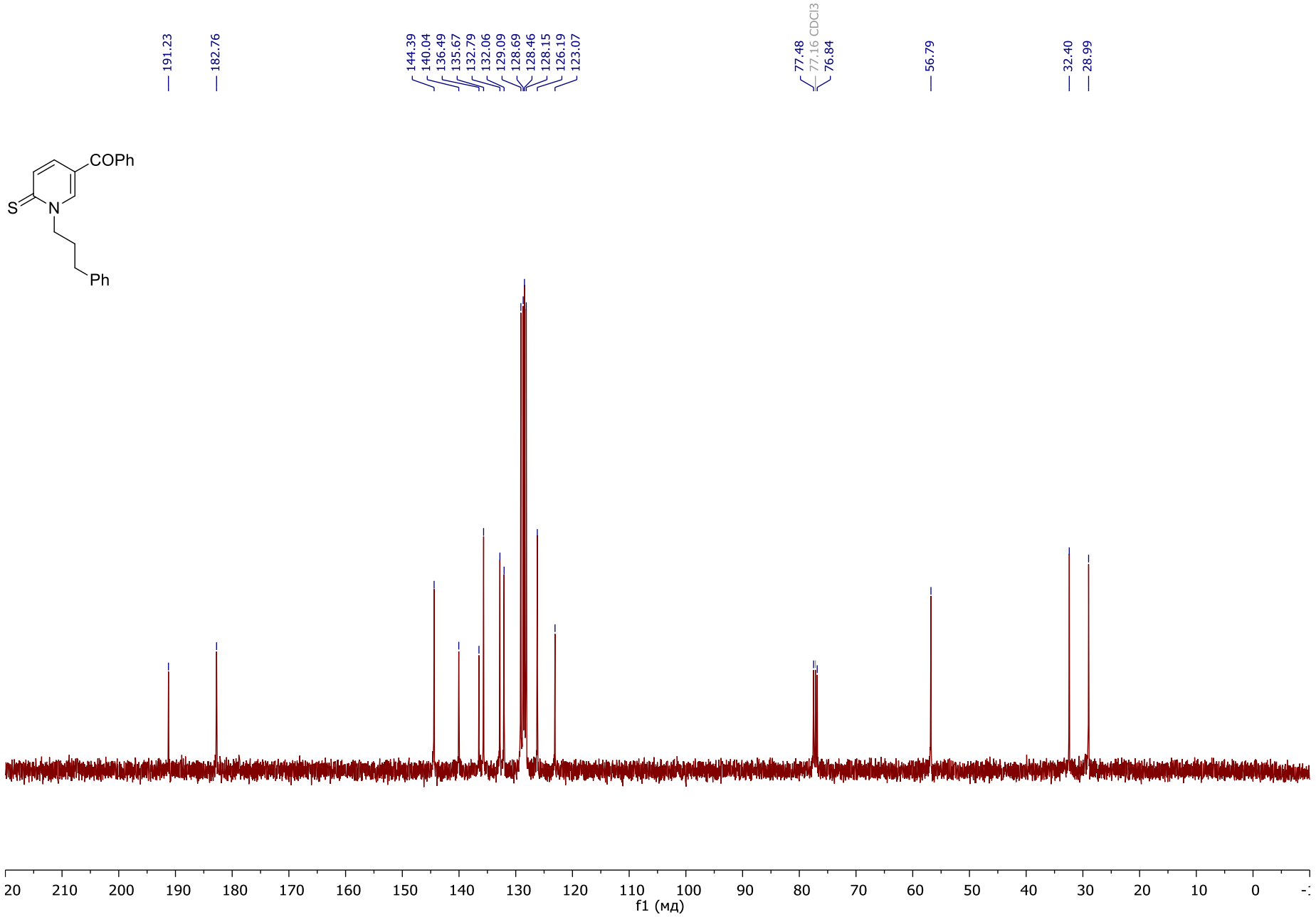
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-benzyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2c)**



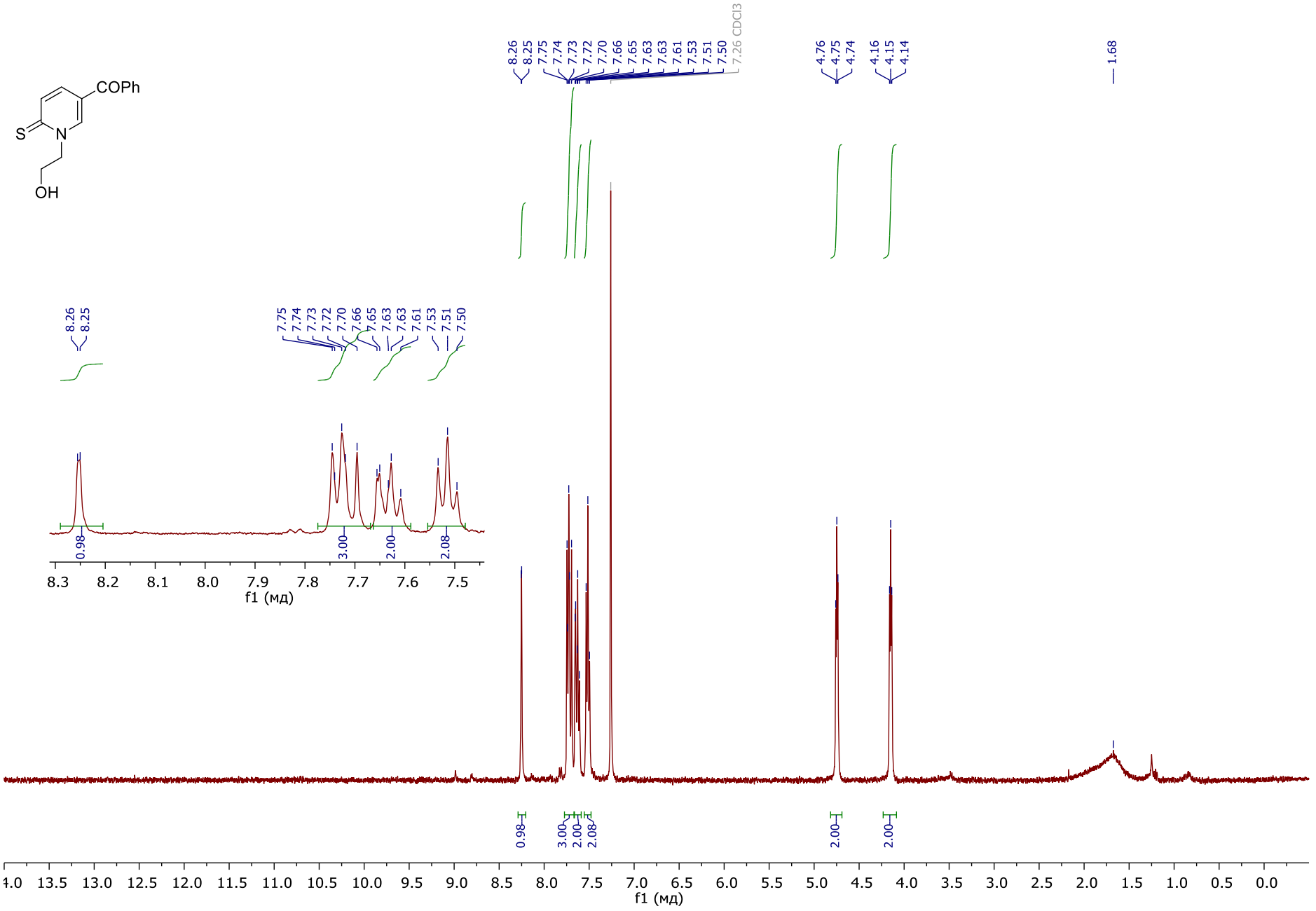
^{1}H NMR (400 MHz, $CDCl_3$) of phenyl(1-(3-phenylpropyl)-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2d**)



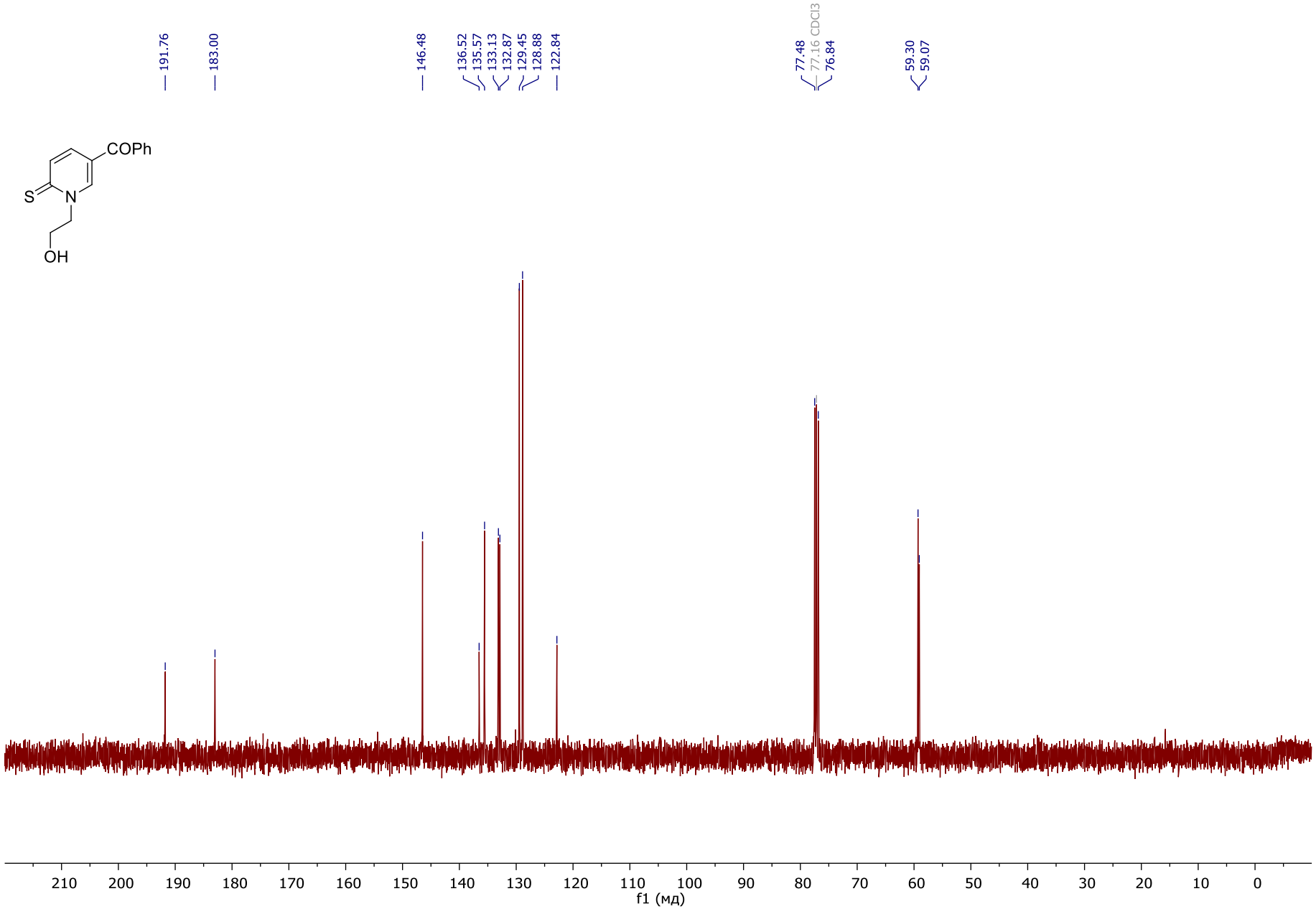
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of phenyl(1-(3-phenylpropyl)-6-thioxo-1,6-dihydropyridin-3-yl)methanone (**2d**)



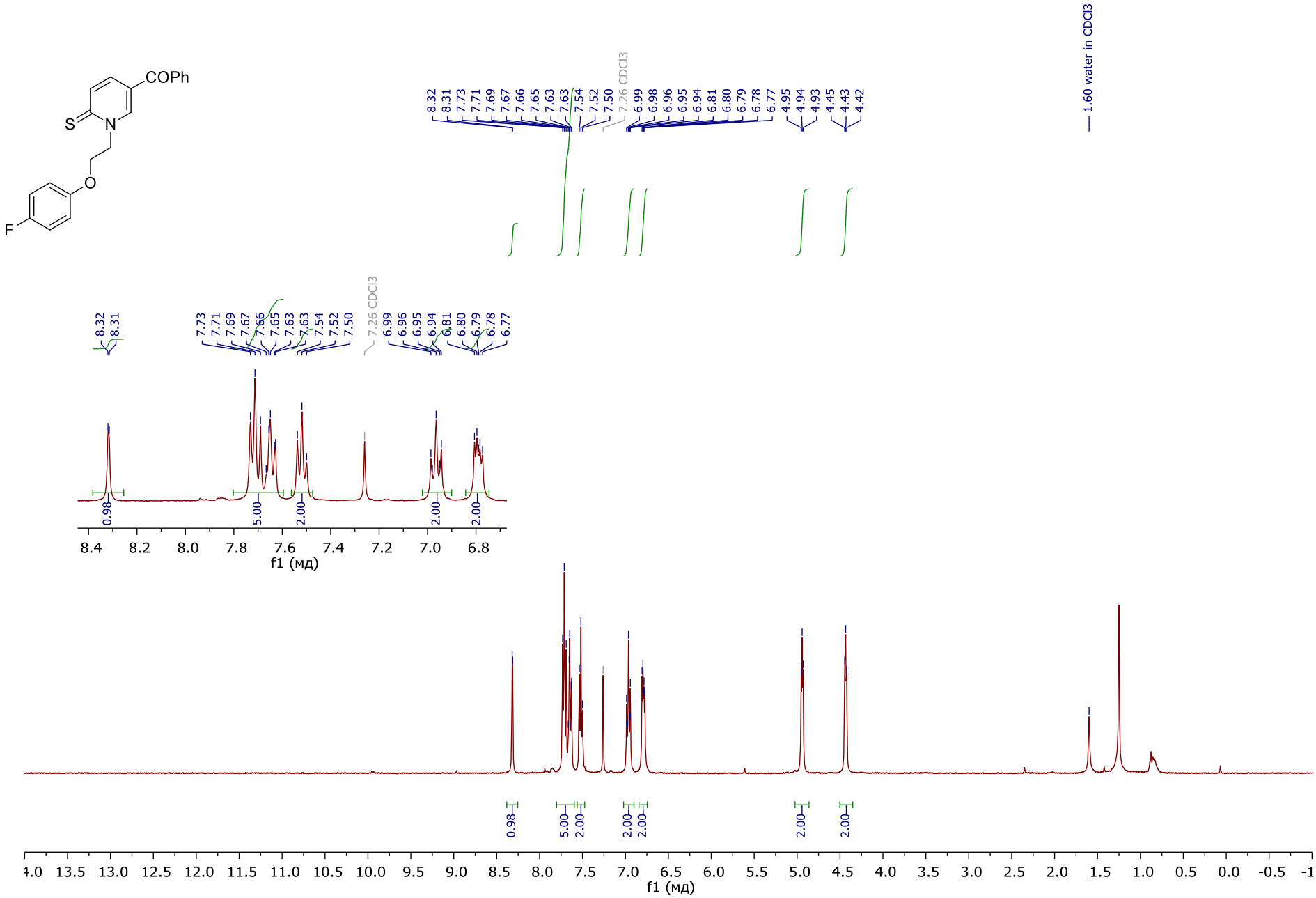
^{1}H NMR (400 MHz, $CDCl_3$) of (1-(2-hydroxyethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2e**)



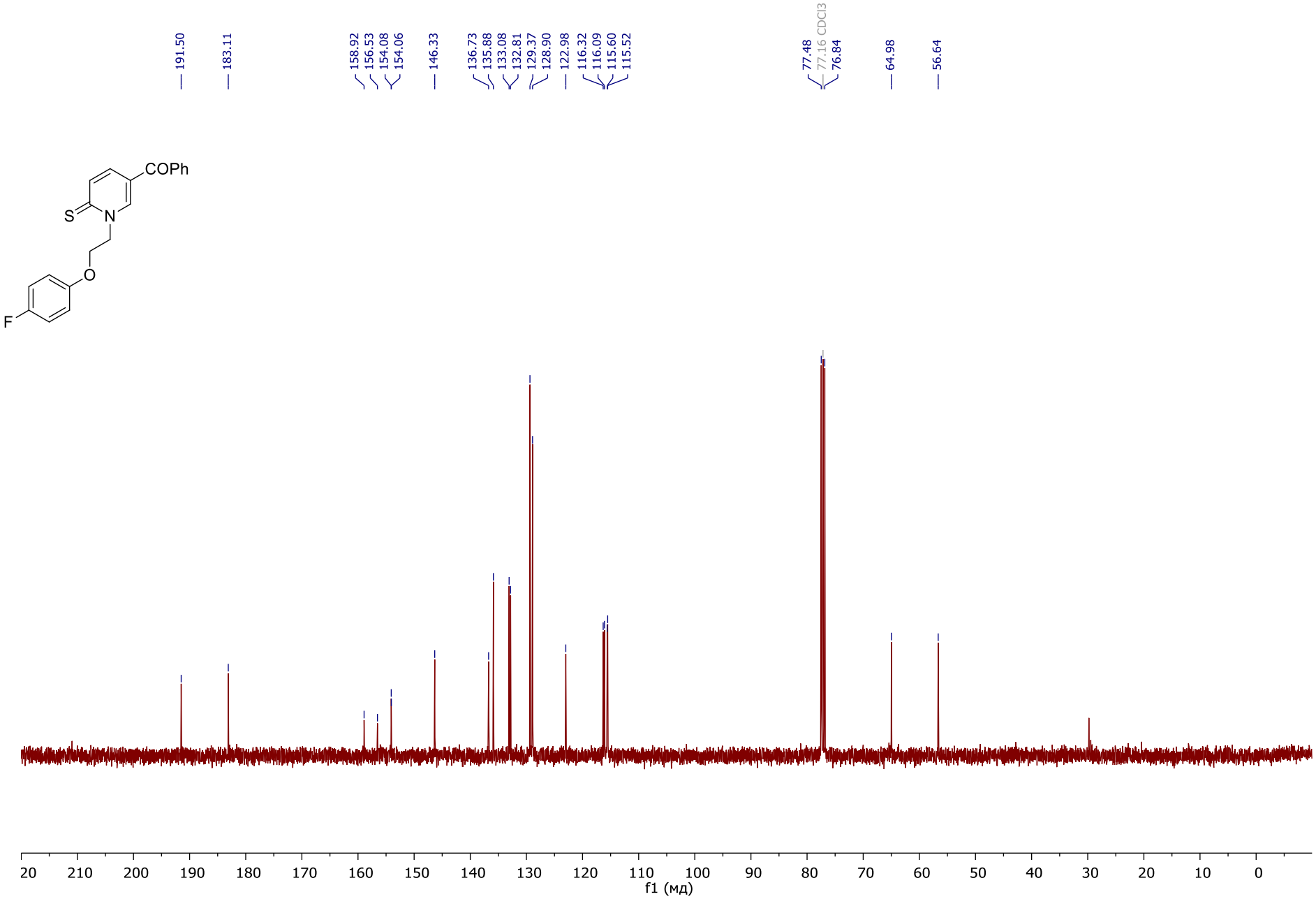
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-(2-hydroxyethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2e**)



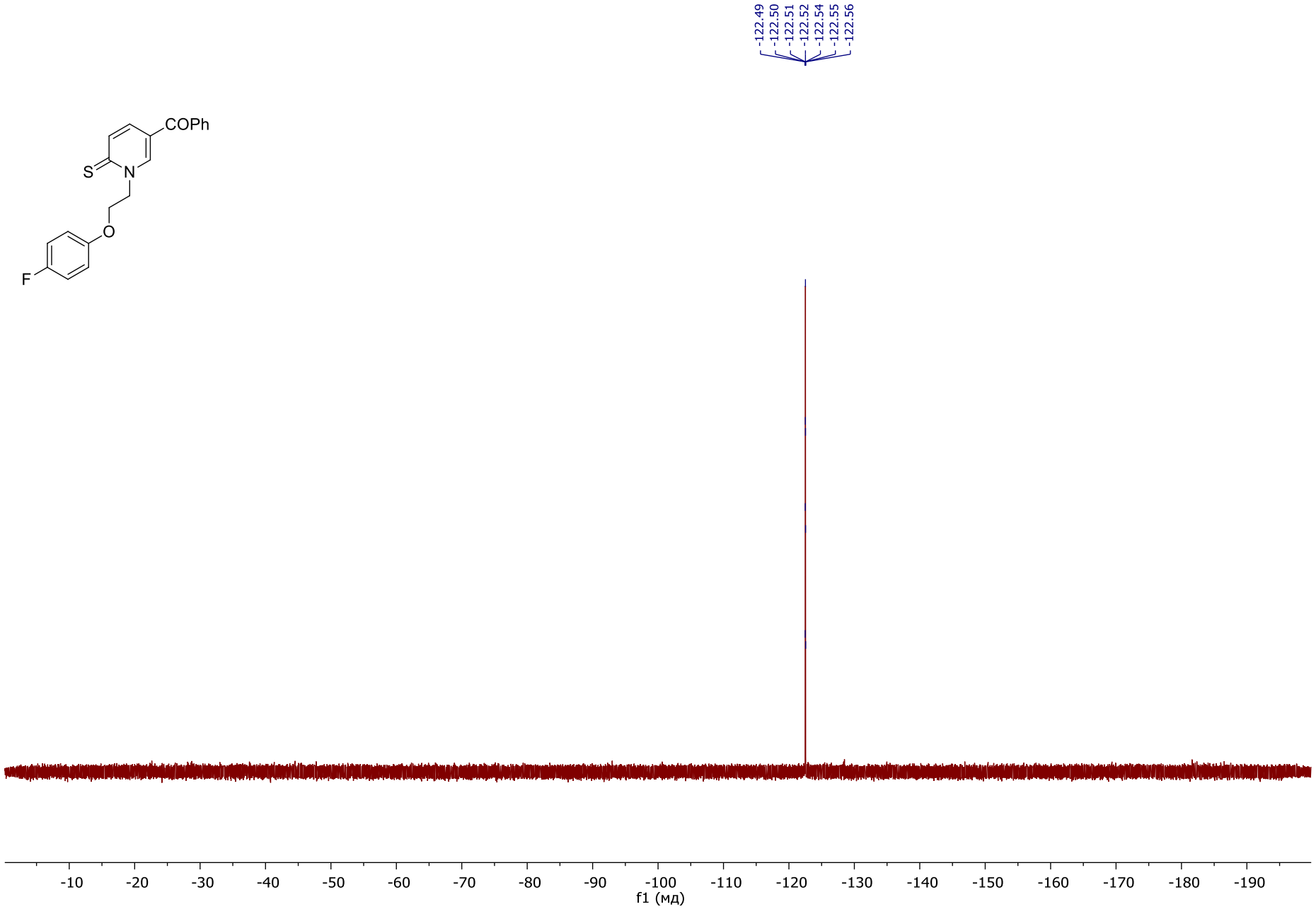
^{1}H NMR (400 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2f**)



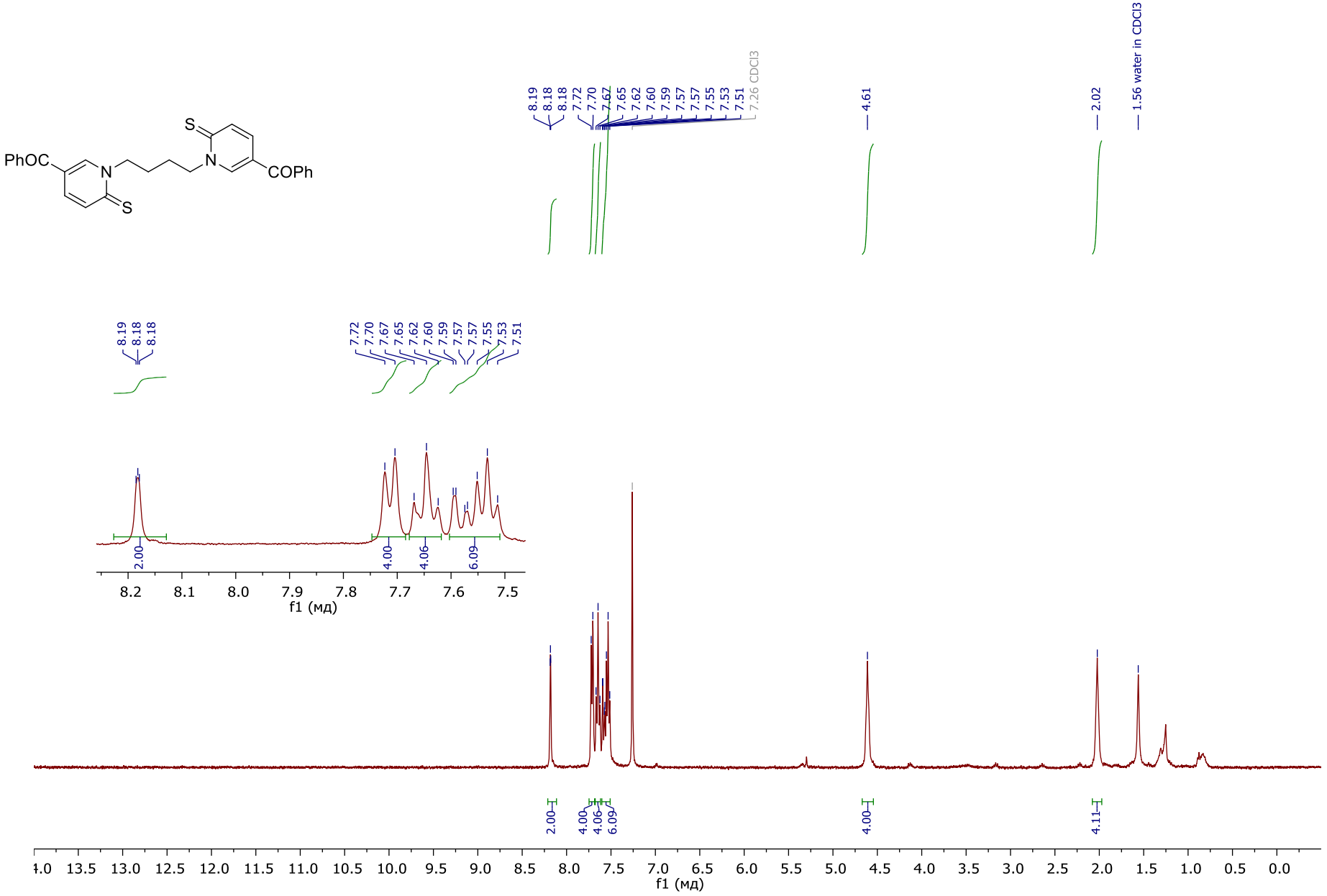
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2f**)



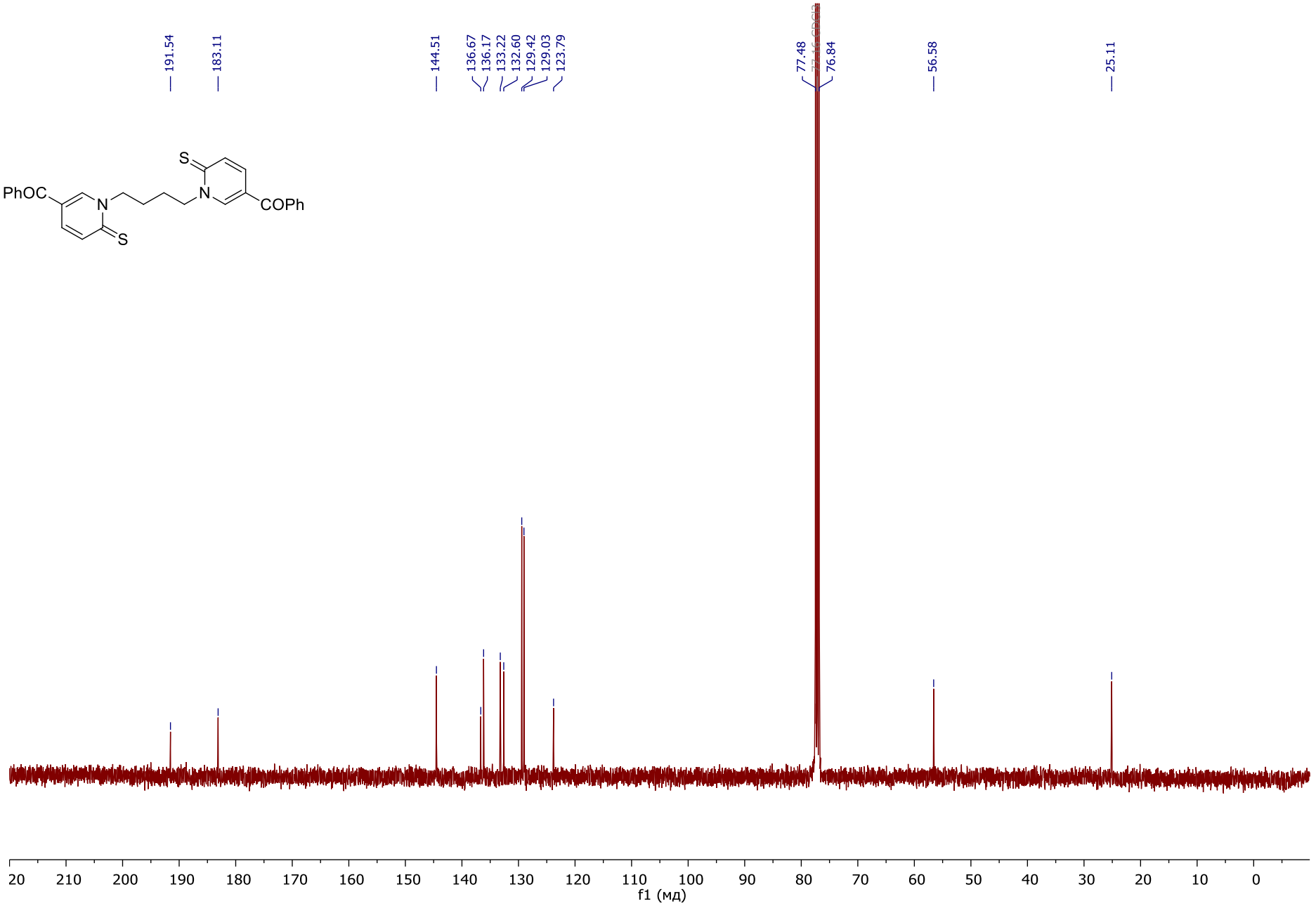
^{19}F NMR (376 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2f**)



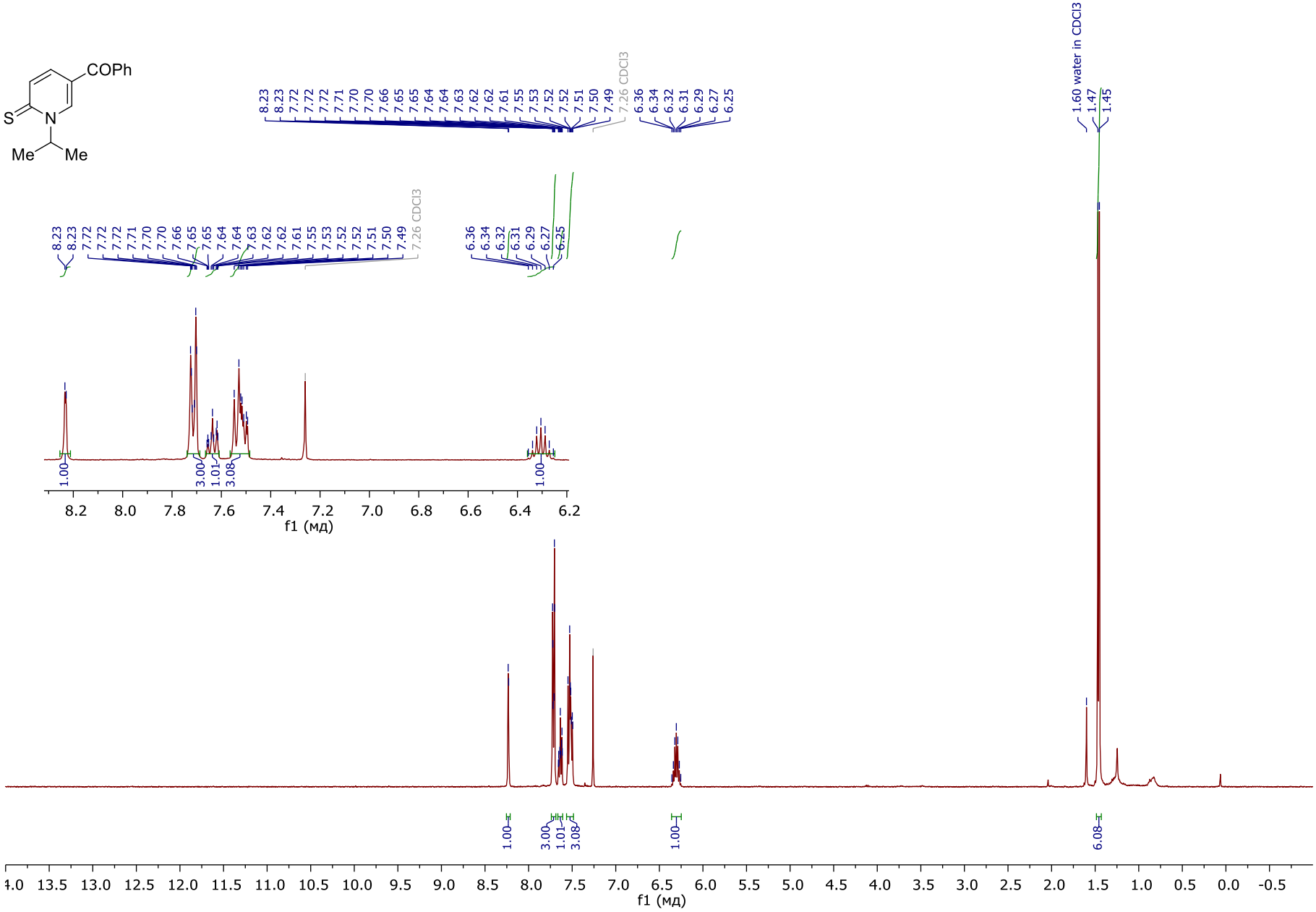
^{1}H NMR (400 MHz, $CDCl_3$) of (1,1'-(butane-1,4-diyl)bis(6-thioxo-1,6-dihydropyridine-3,1-diyl))bis(phenylmethanone) (**2g**)



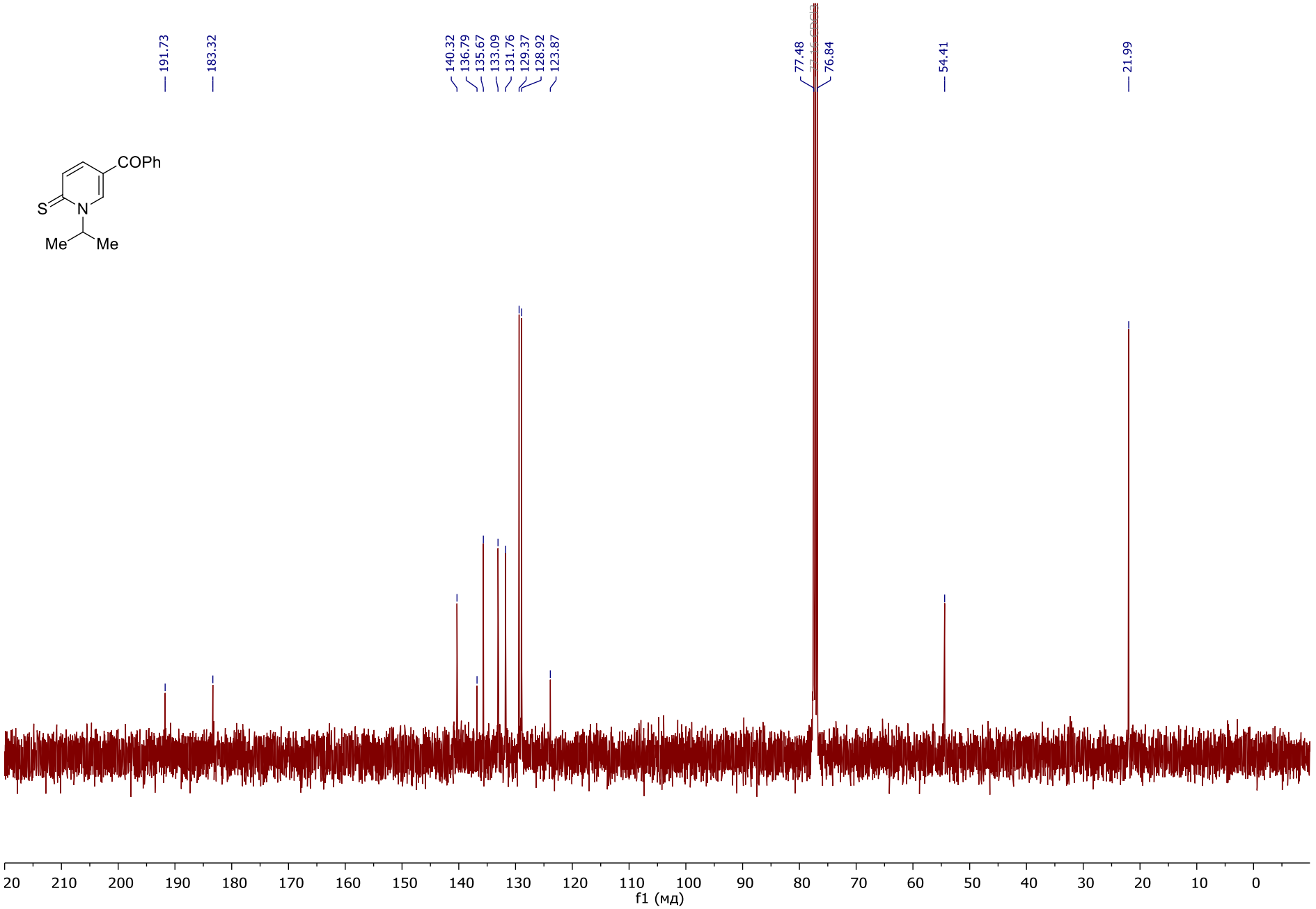
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1,1'-(butane-1,4-diyl)bis(6-thioxo-1,6-dihydropyridine-3,1-diyl))bis(phenylmethanone) (**2g**)



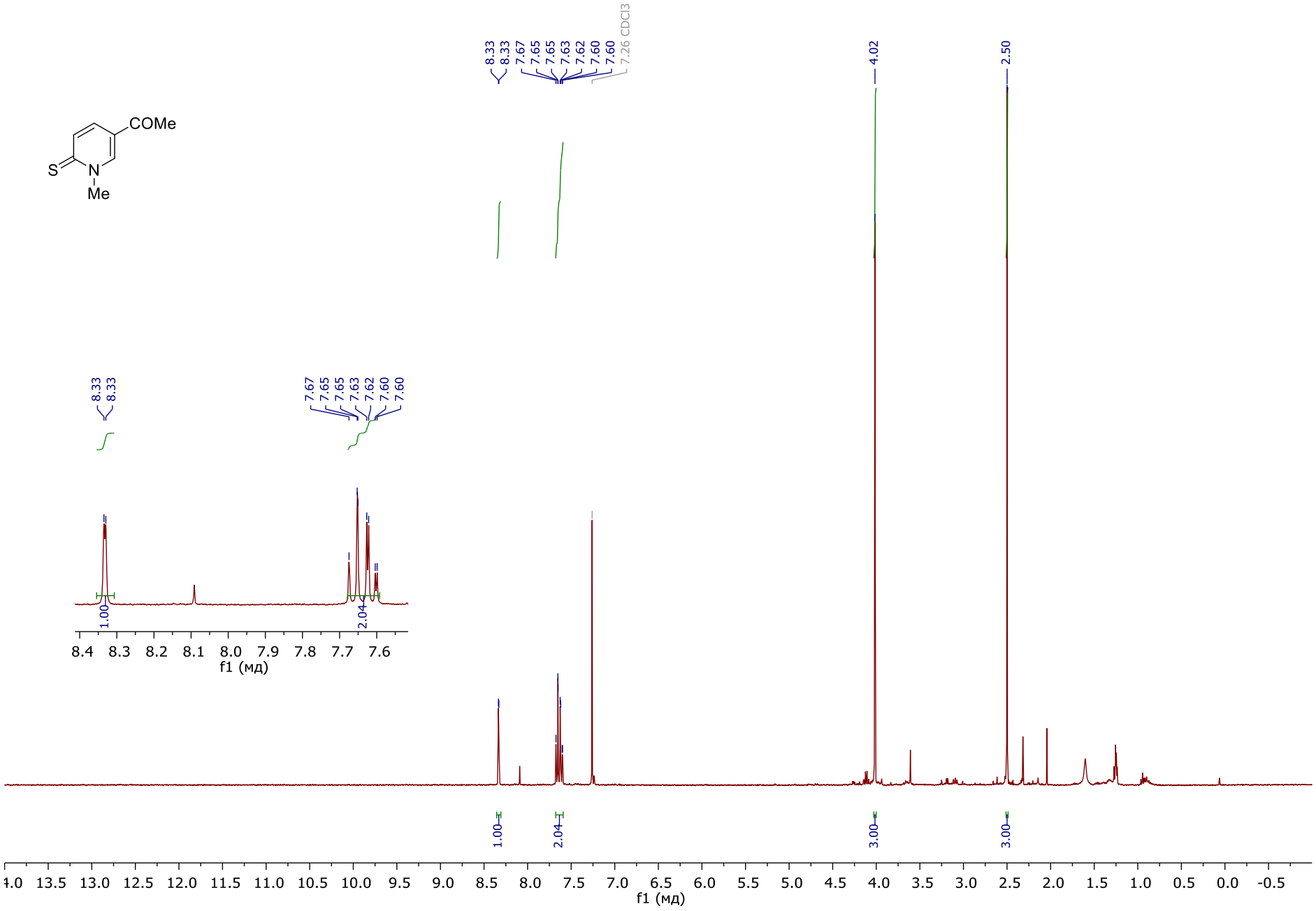
^{1}H NMR (400 MHz, $CDCl_3$) of (1-isopropyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2h**)



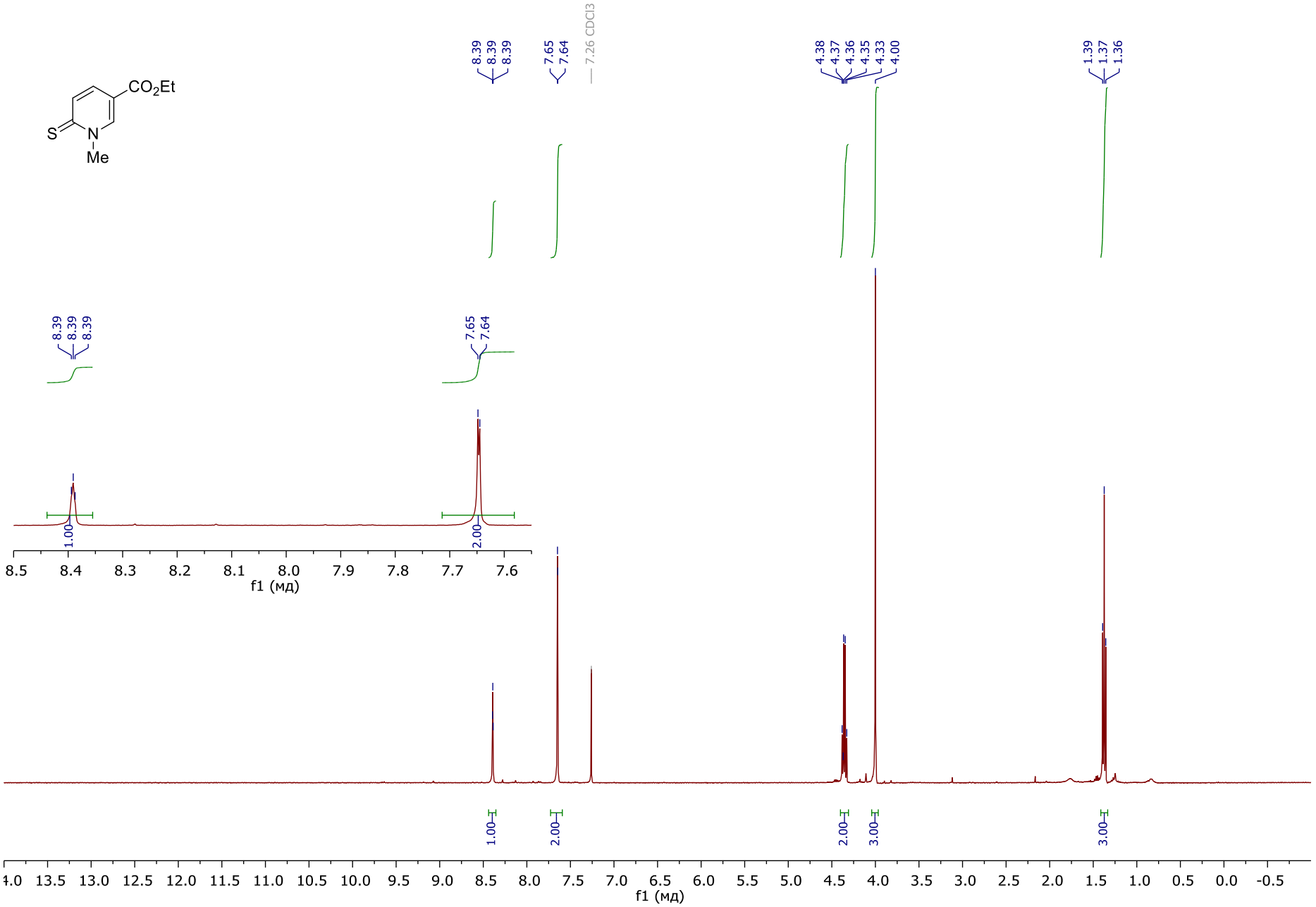
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-isopropyl-6-thioxo-1,6-dihydropyridin-3-yl)(phenyl)methanone (**2h**)



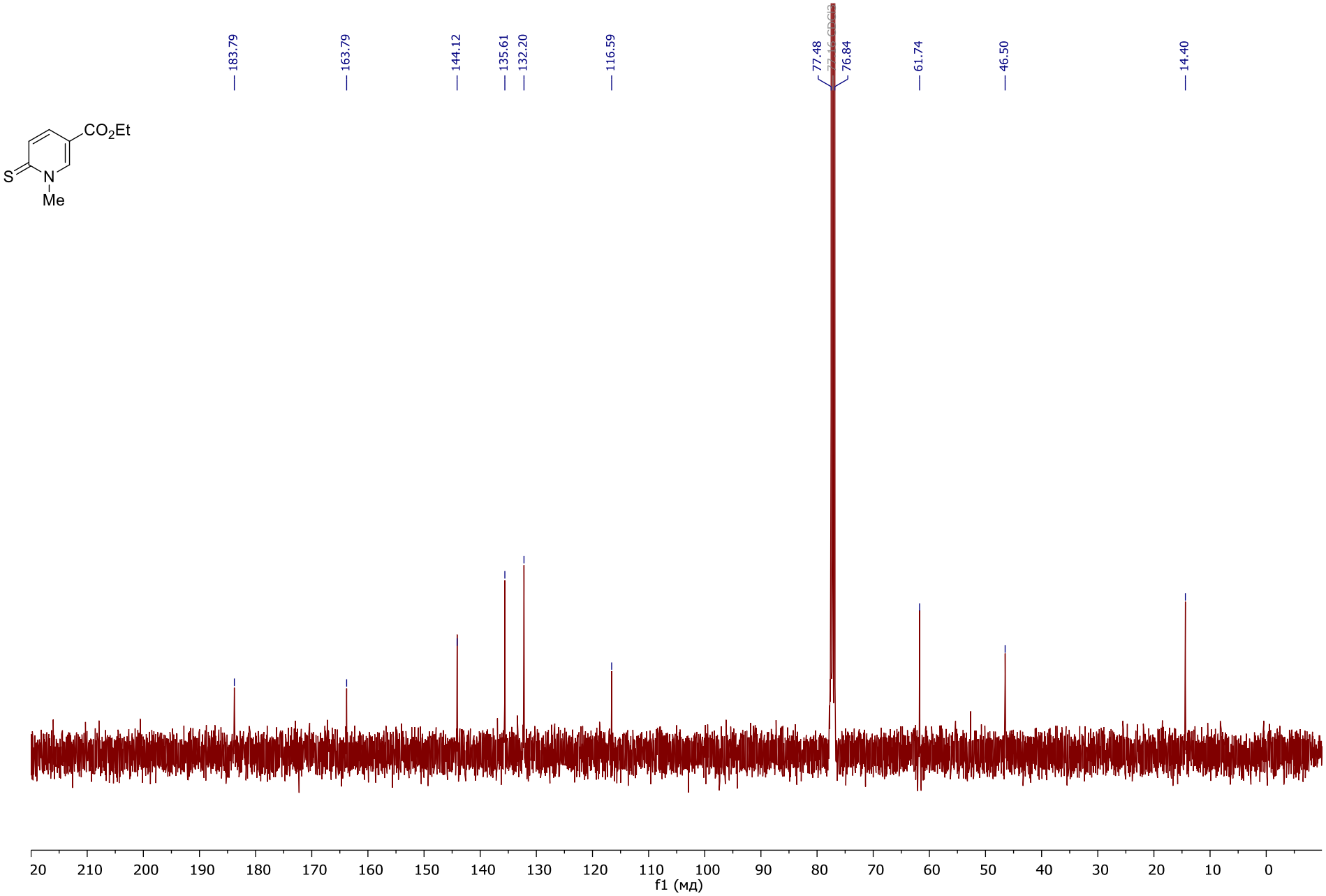
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(1-methyl-6-thioxo-1,6-dihydropyridin-3-yl)ethanone (**2i**)



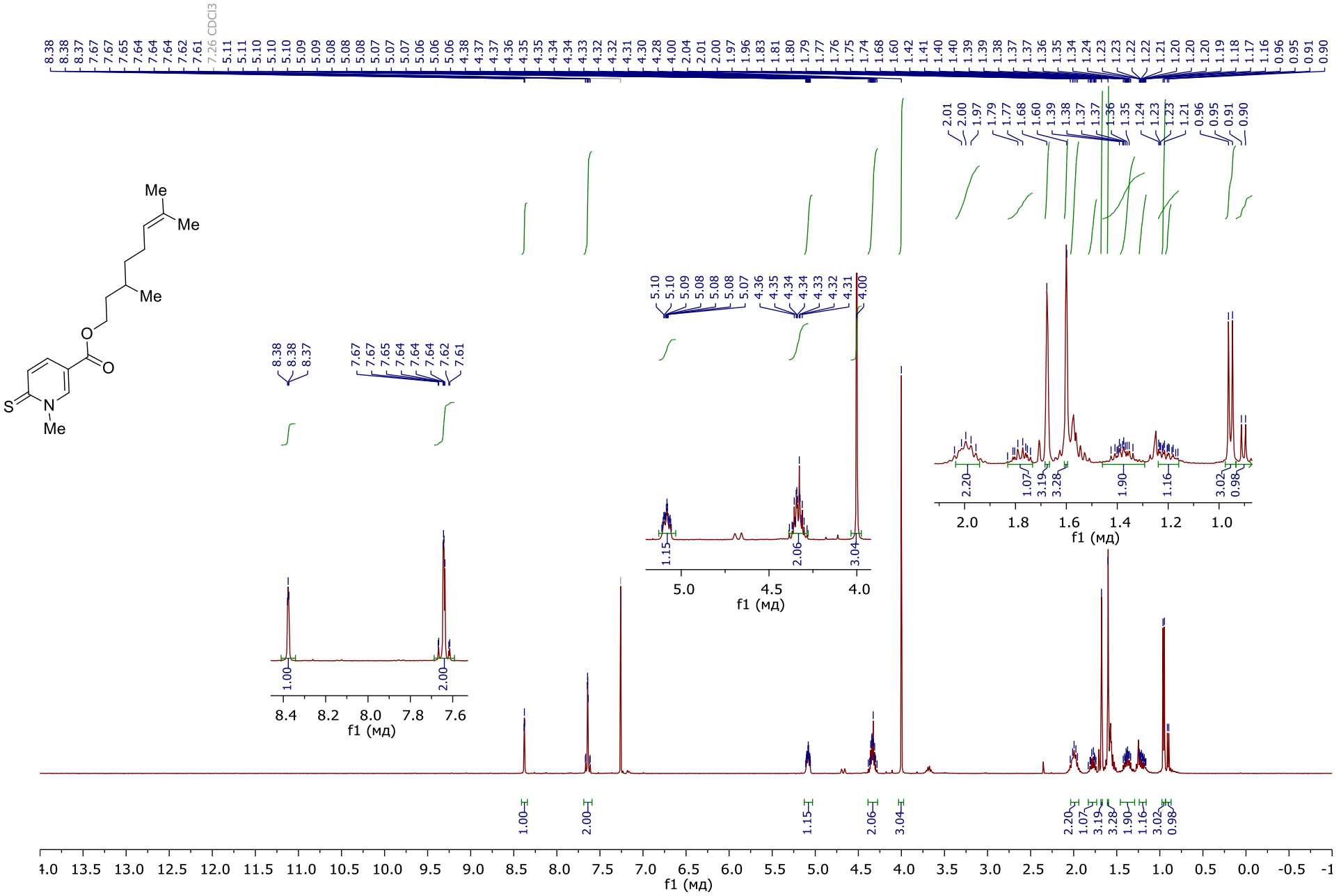
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2j**)



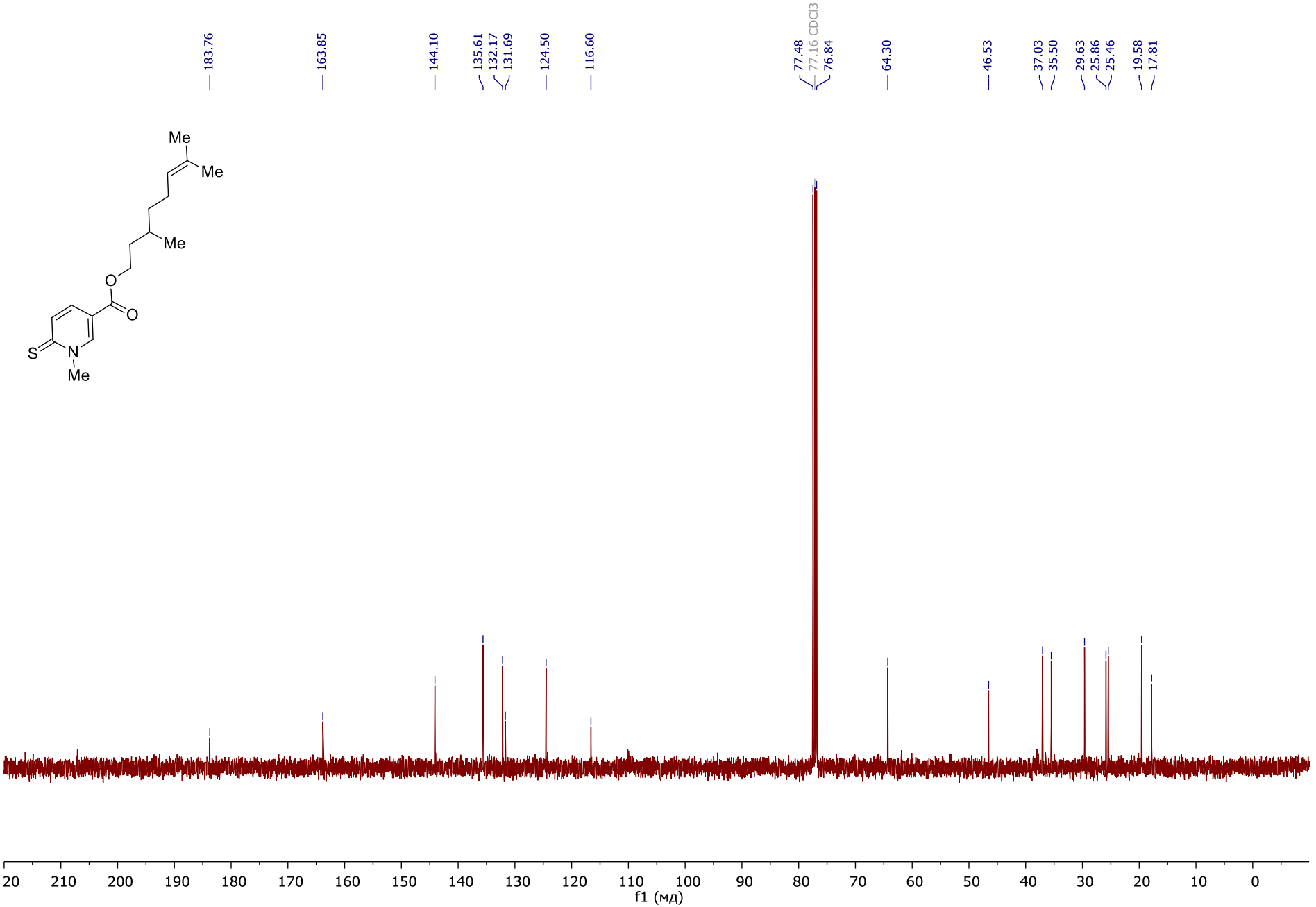
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of ethyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2j**)



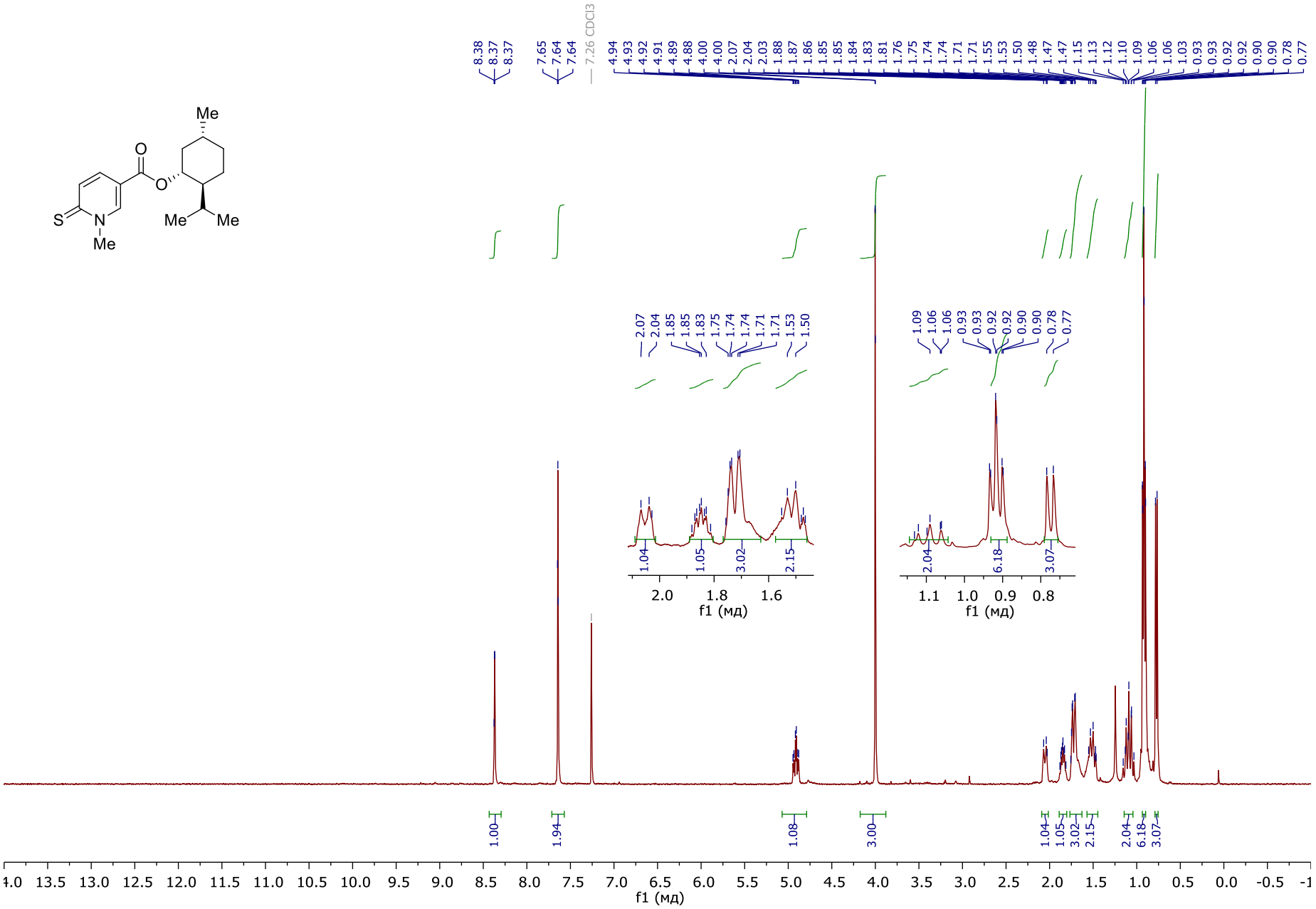
^{1}H NMR (400 MHz, $CDCl_3$) of 3,7-dimethyloct-6-en-1-yl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2k**)



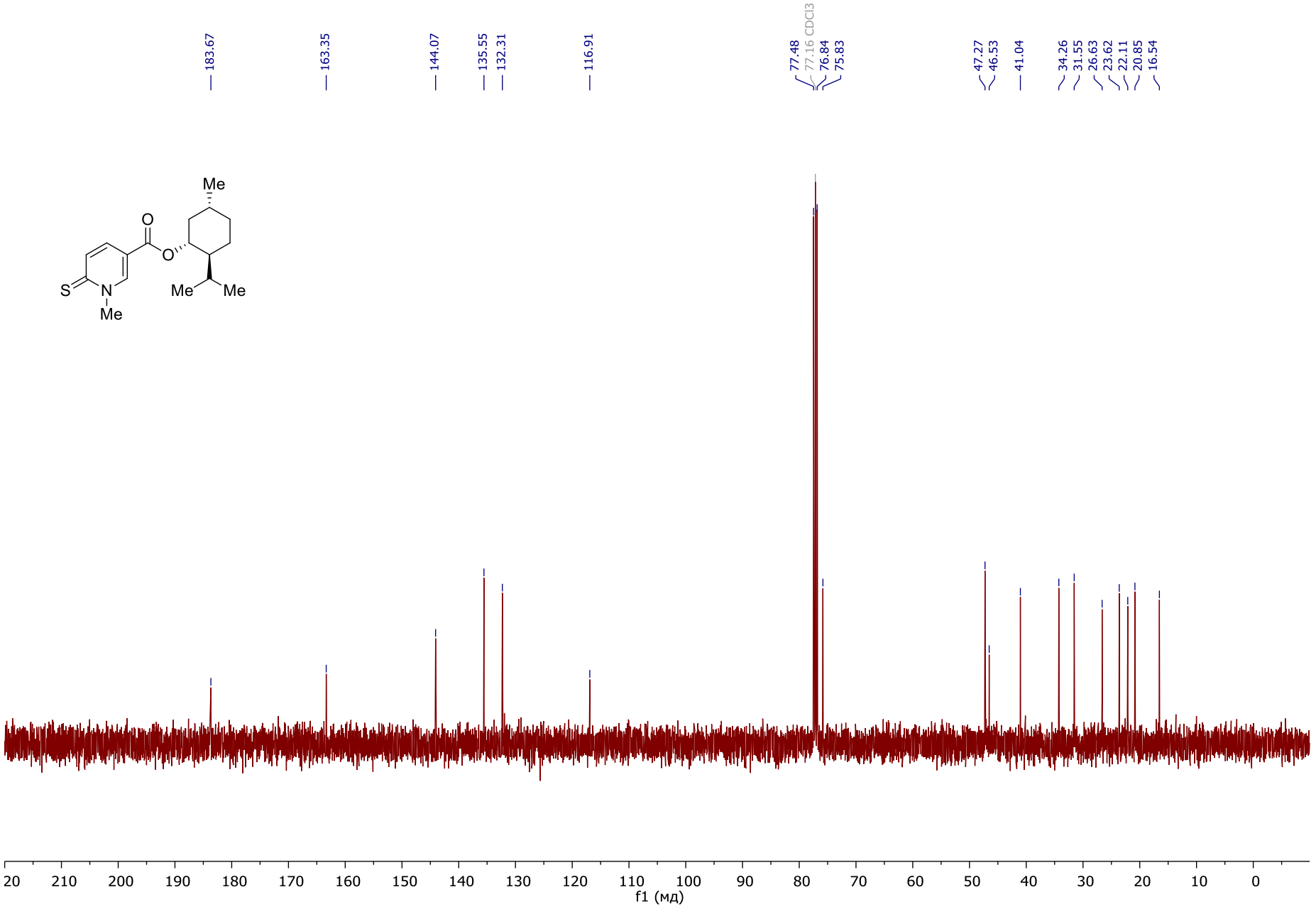
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3,7-dimethyloct-6-en-1-yl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2k**)



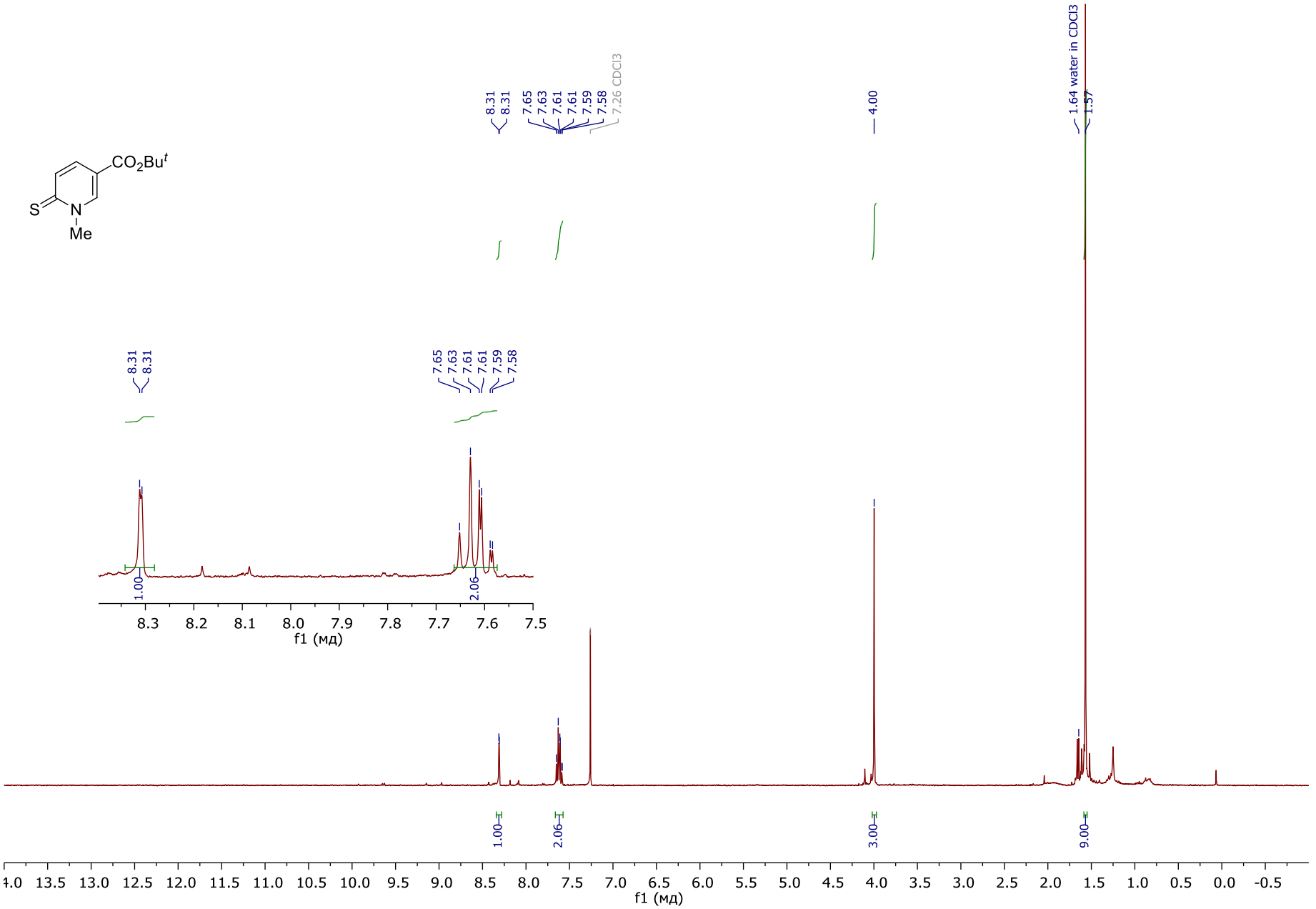
^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2l**)



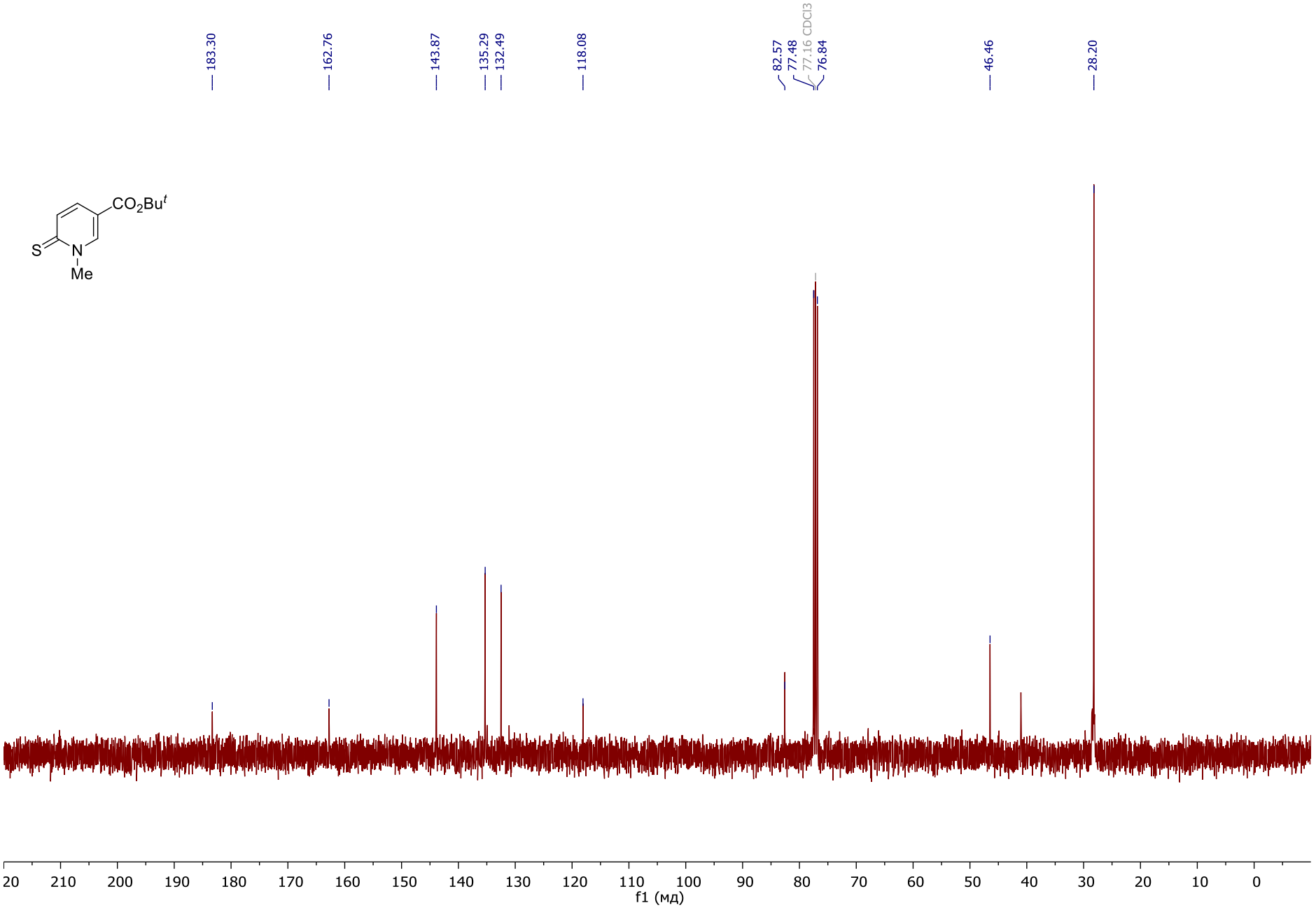
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2l**)



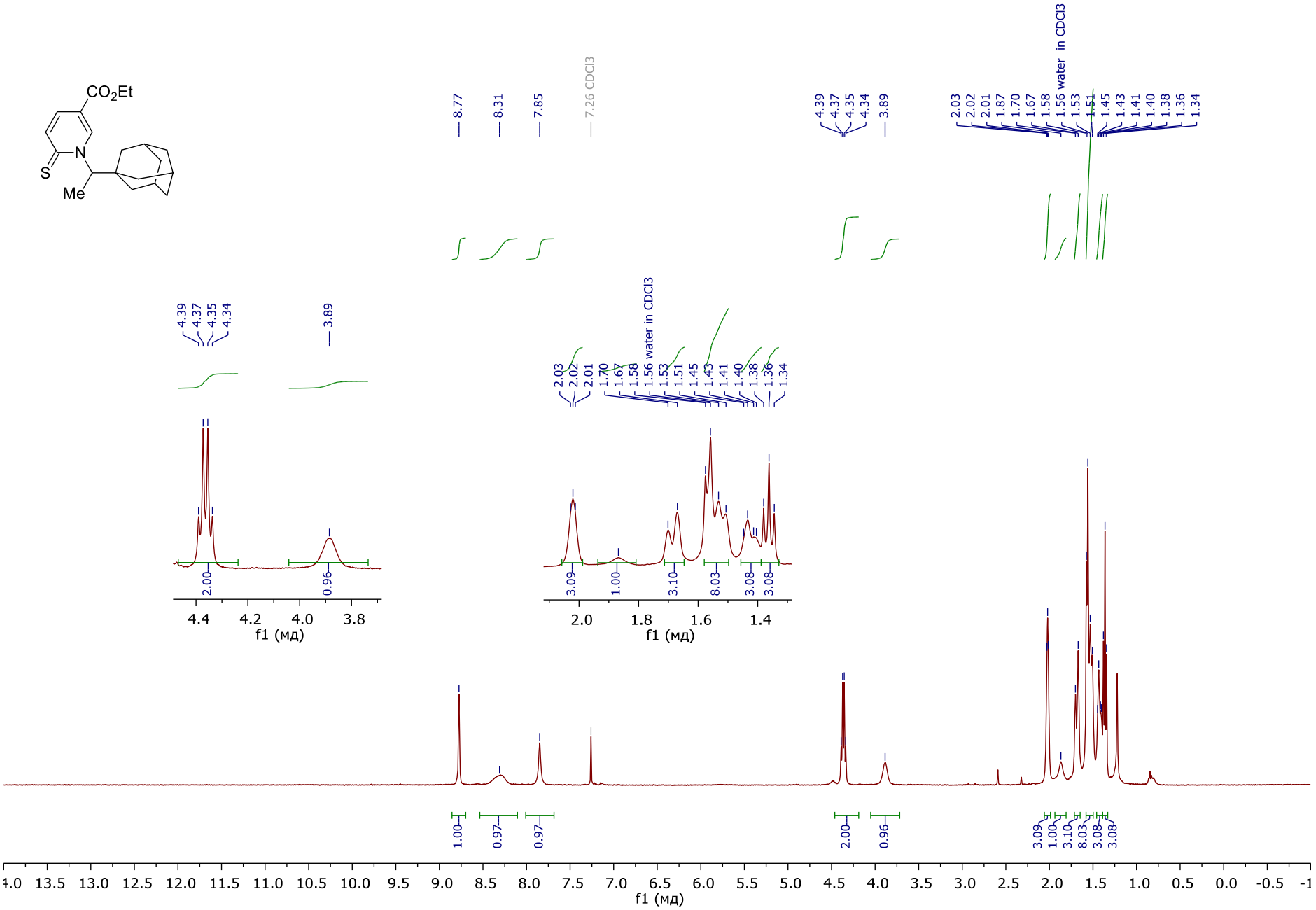
^{1}H NMR (400 MHz, $CDCl_3$) of *tert*-butyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2m**)



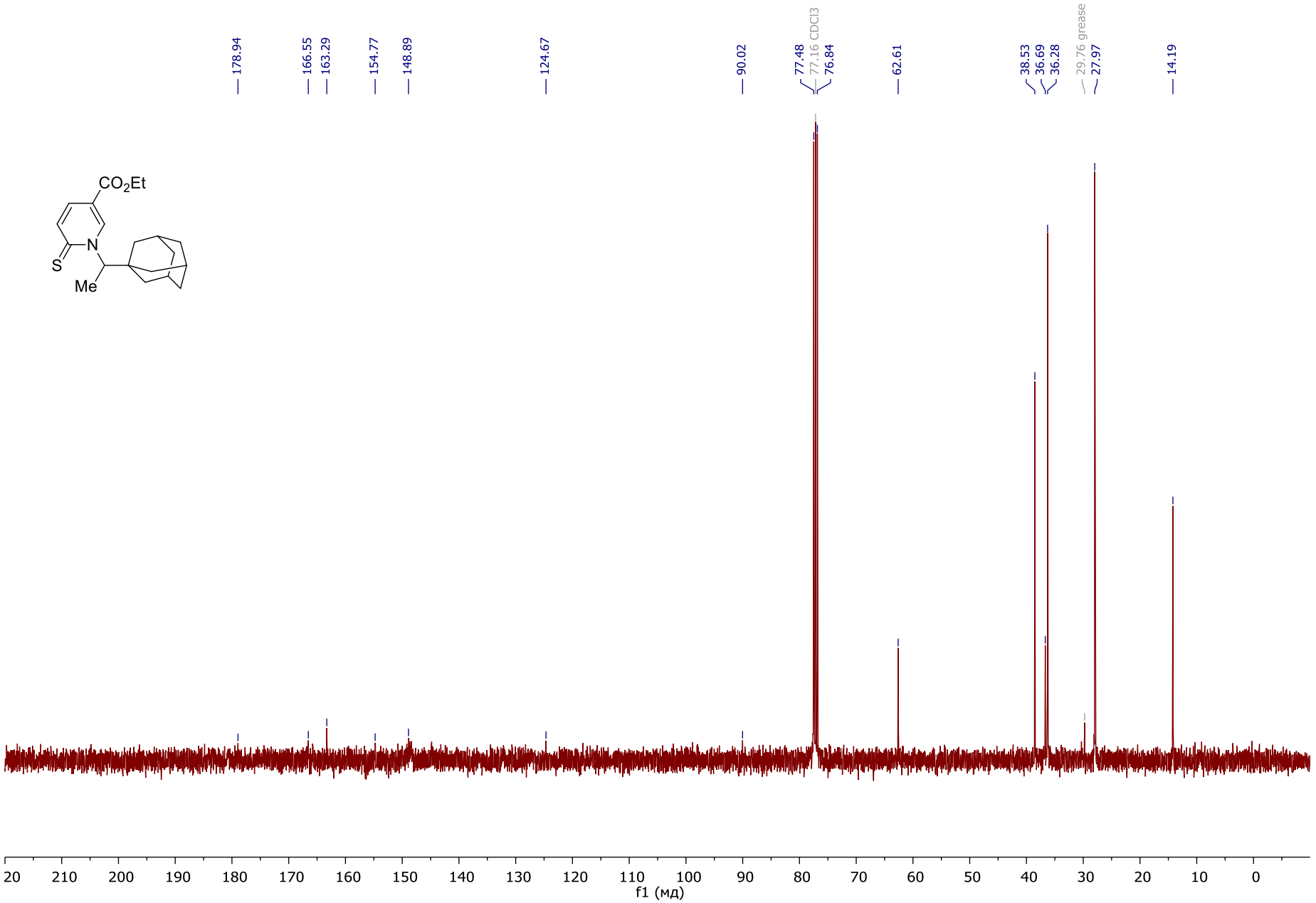
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *tert*-butyl 1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2m**)



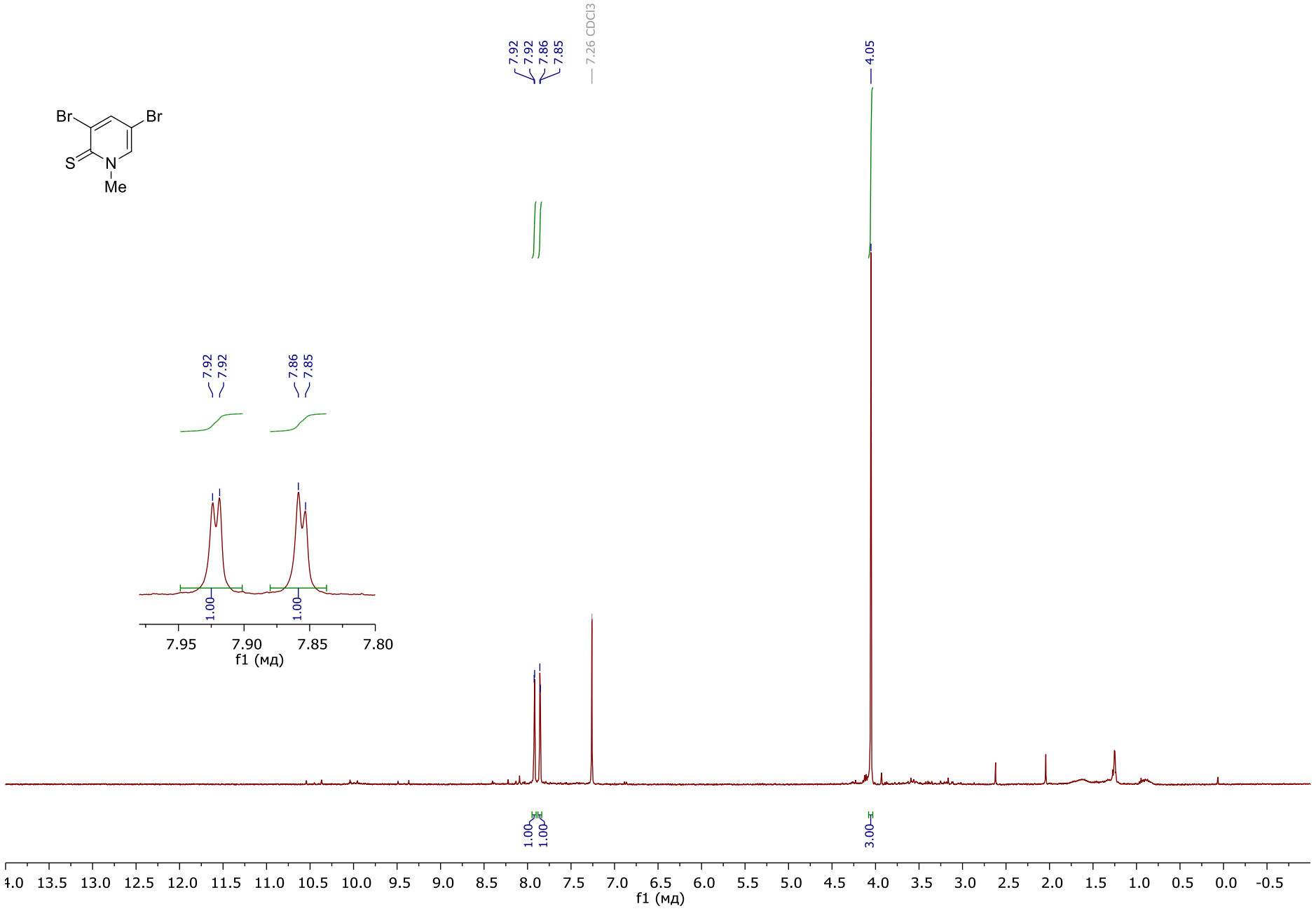
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 1-(1-(adamantan-1-yl)ethyl)-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2n**)



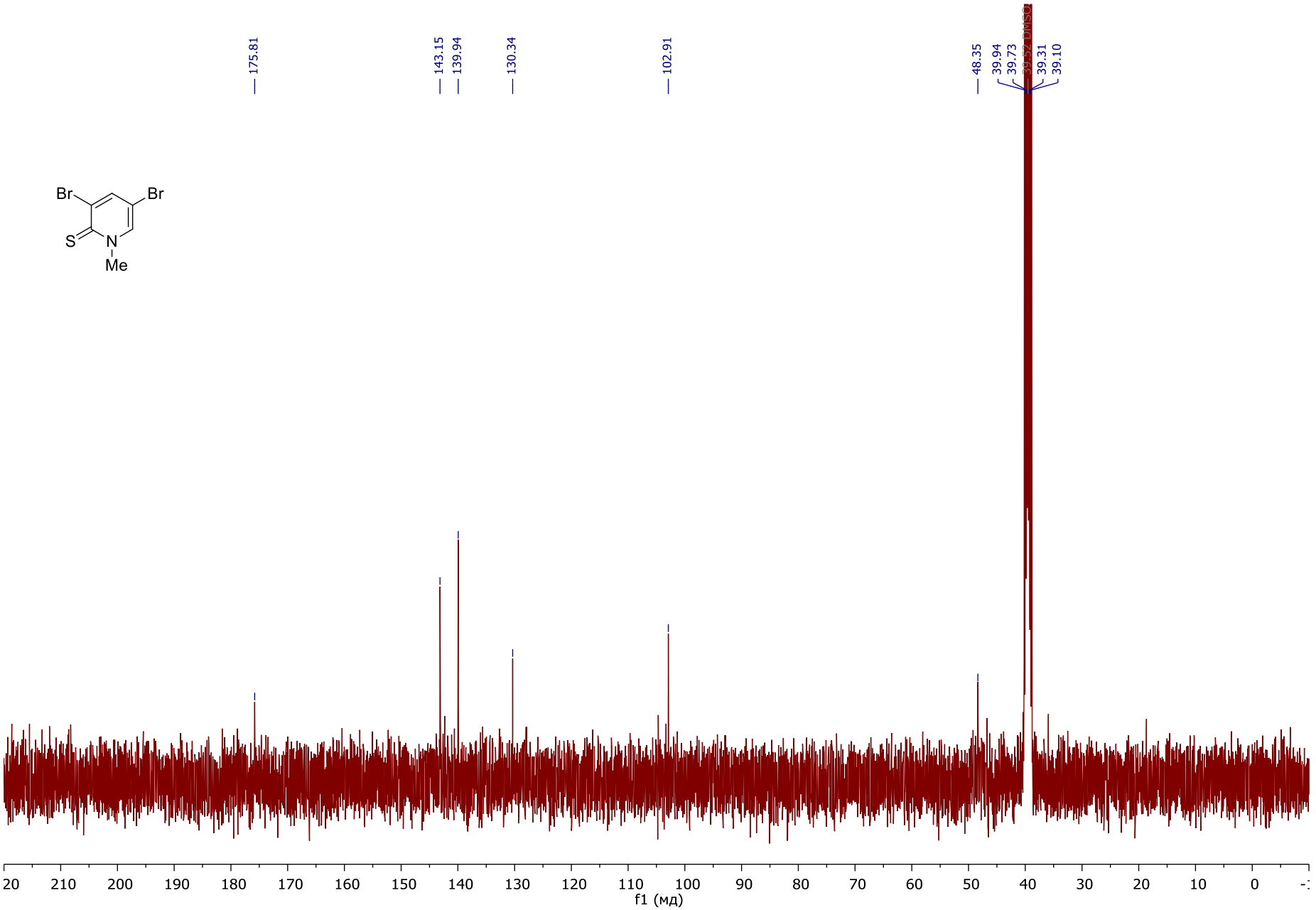
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of ethyl 1-(1-(adamantan-1-yl)ethyl)-6-thioxo-1,6-dihydropyridine-3-carboxylate (**2n**)



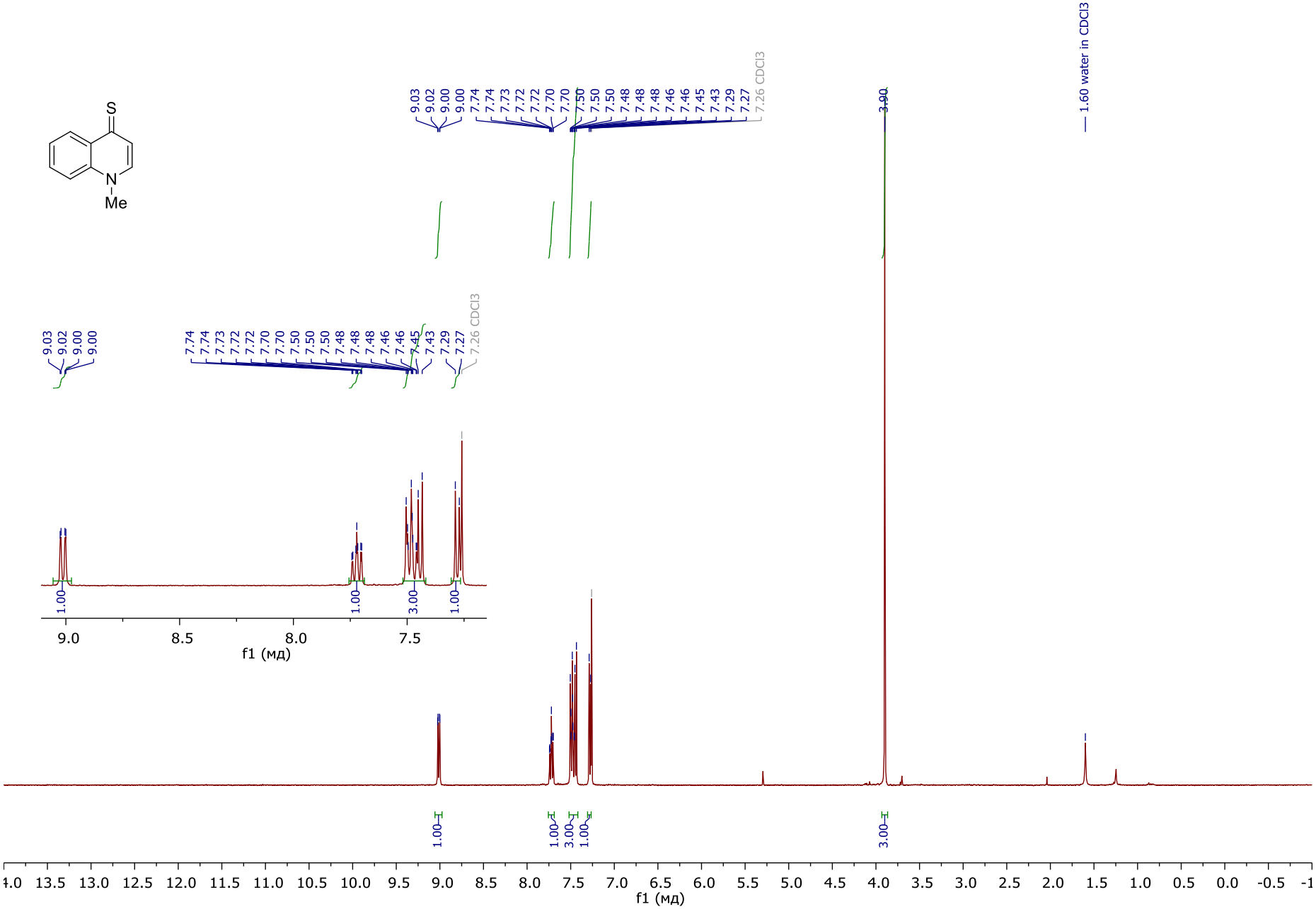
^{1}H NMR (400 MHz, $CDCl_3$) of 3,5-dibromo-1-methylpyridine-2(1*H*)-thione (**2o**)



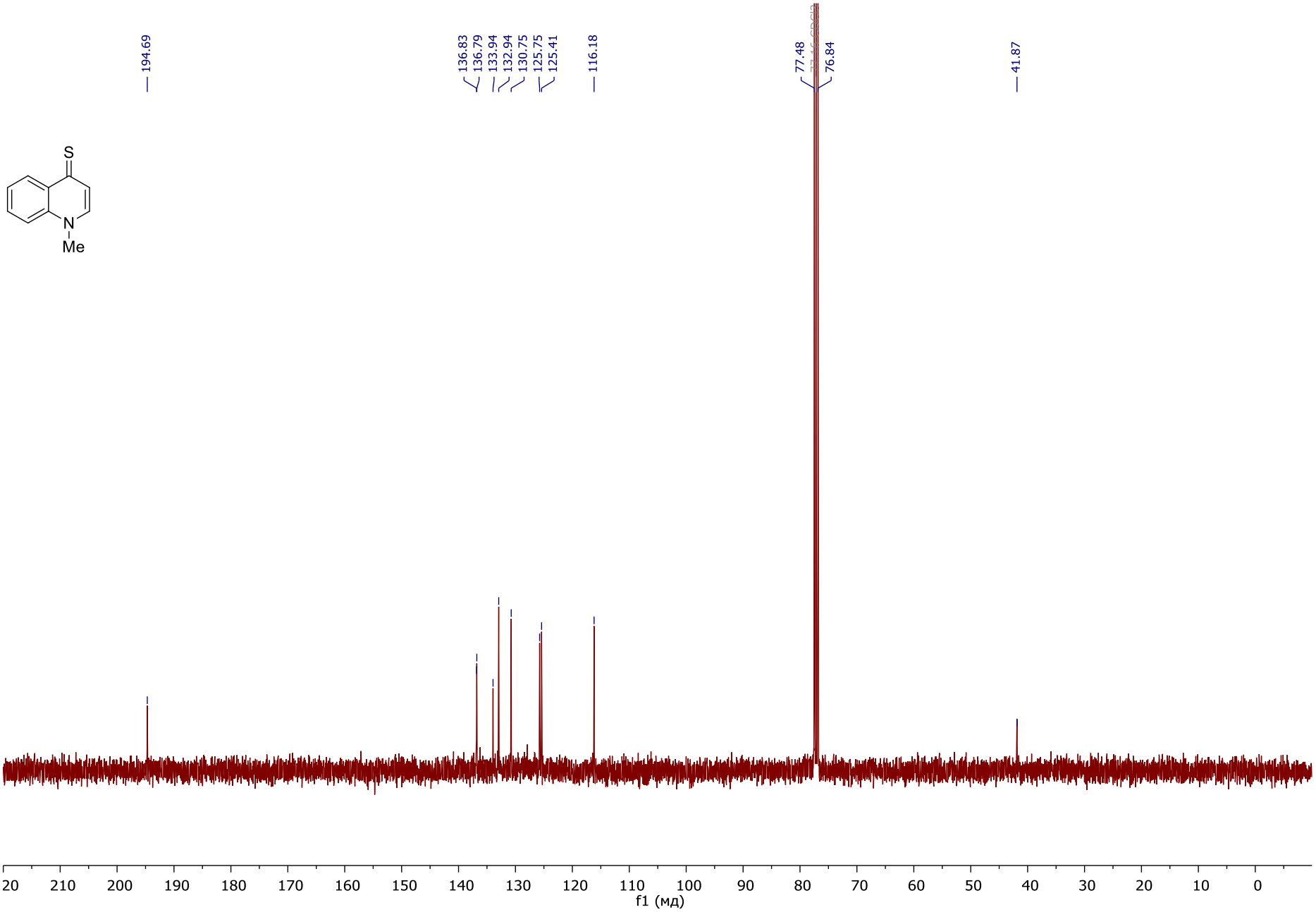
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3,5-dibromo-1-methylpyridine-2(1*H*)-thione (**2o**)



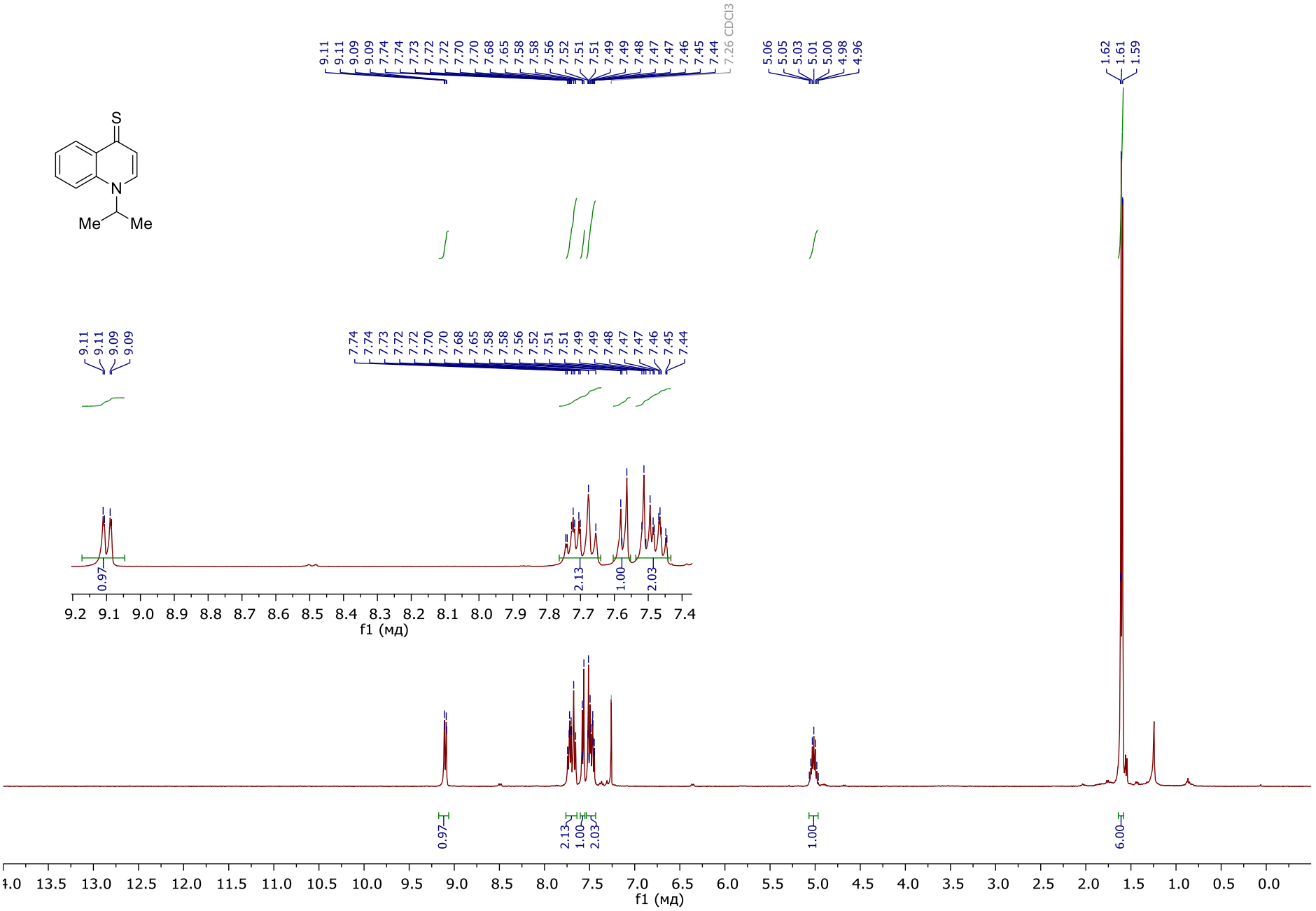
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methylquinoline-4(1*H*)-thione (**2p**)



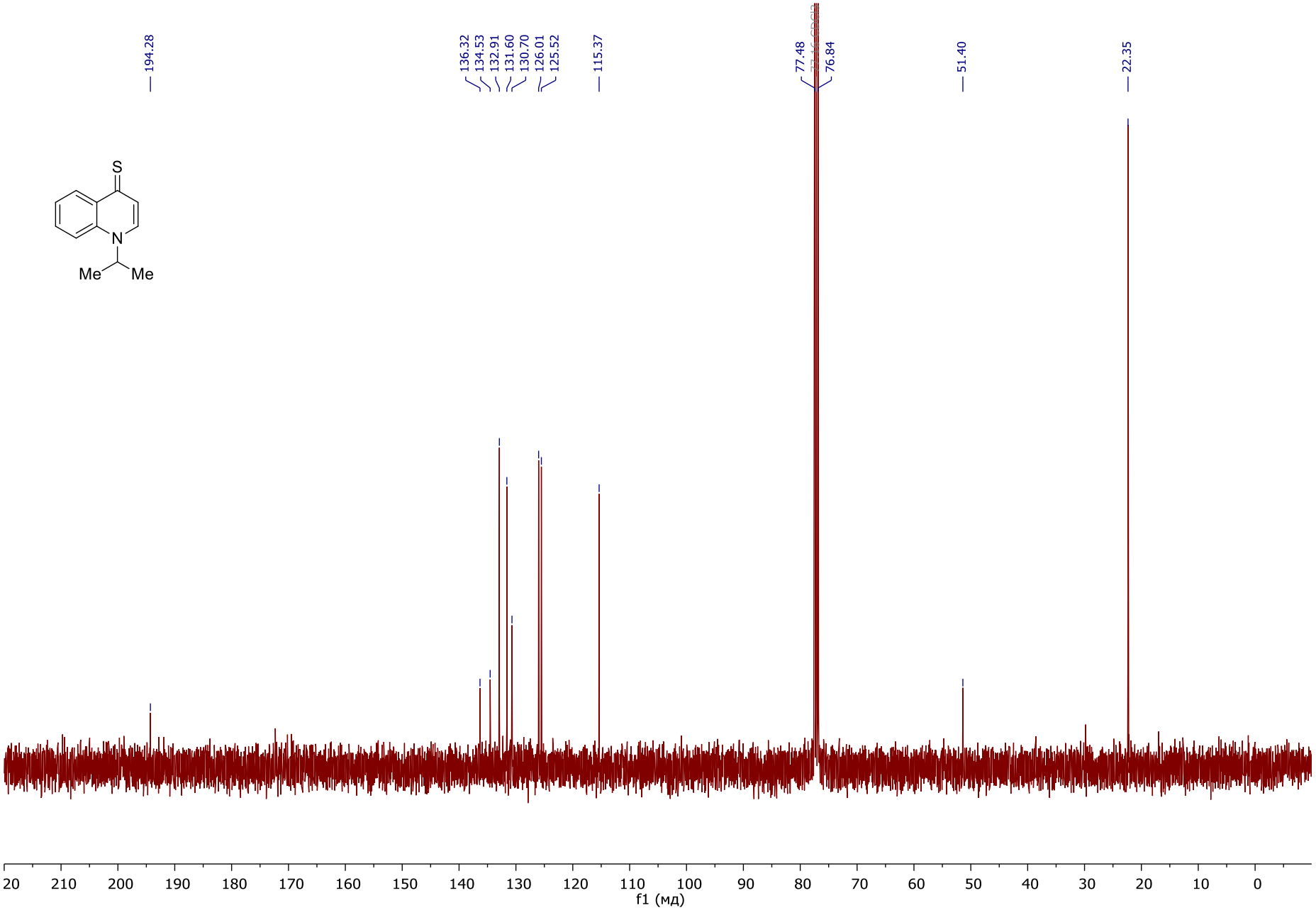
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-methylquinoline-4(1*H*)-thione (**2p**)



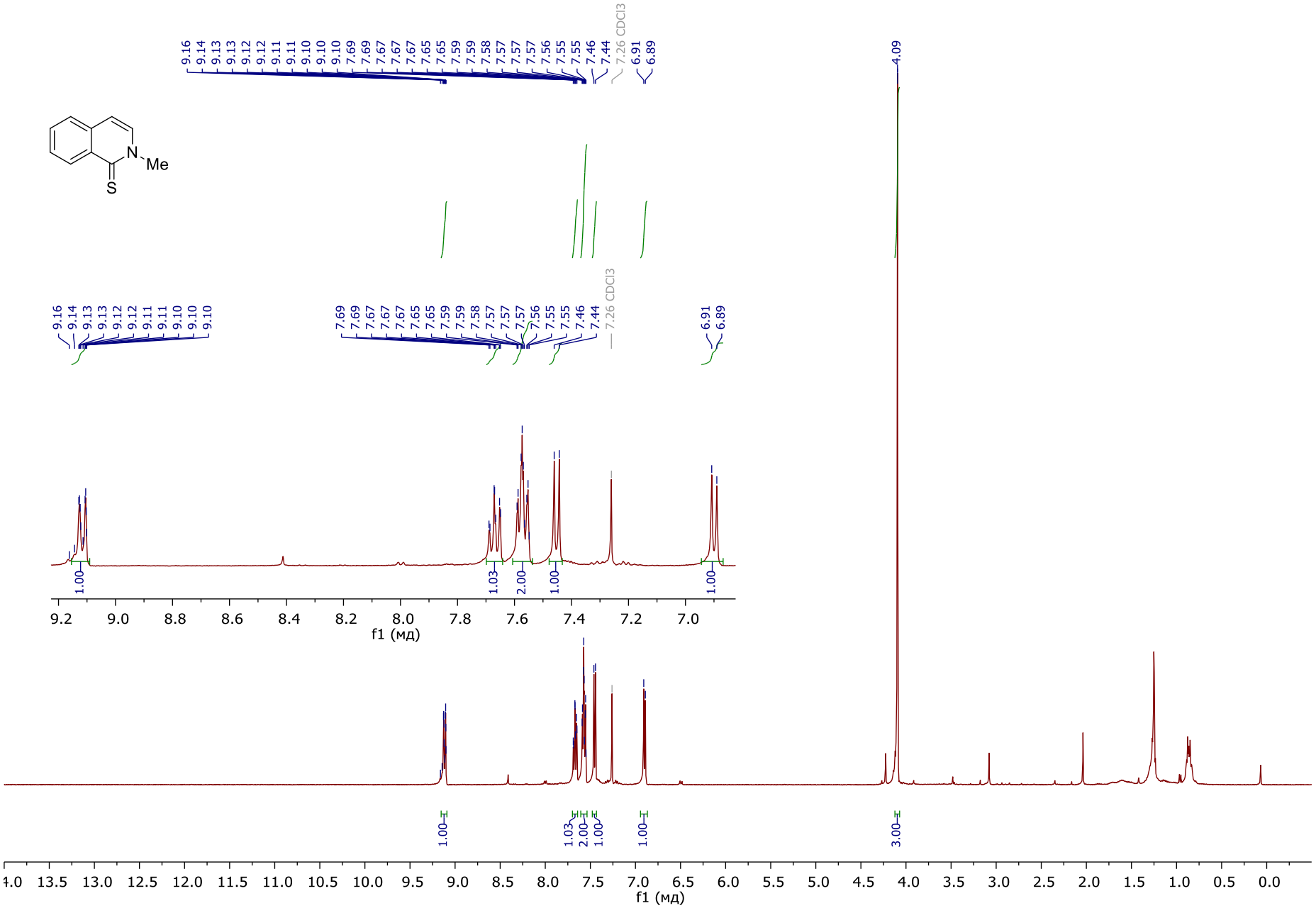
^{1}H NMR (400 MHz, $CDCl_3$) of 1-isopropylquinoline-4(1*H*)-thione (**2q**)



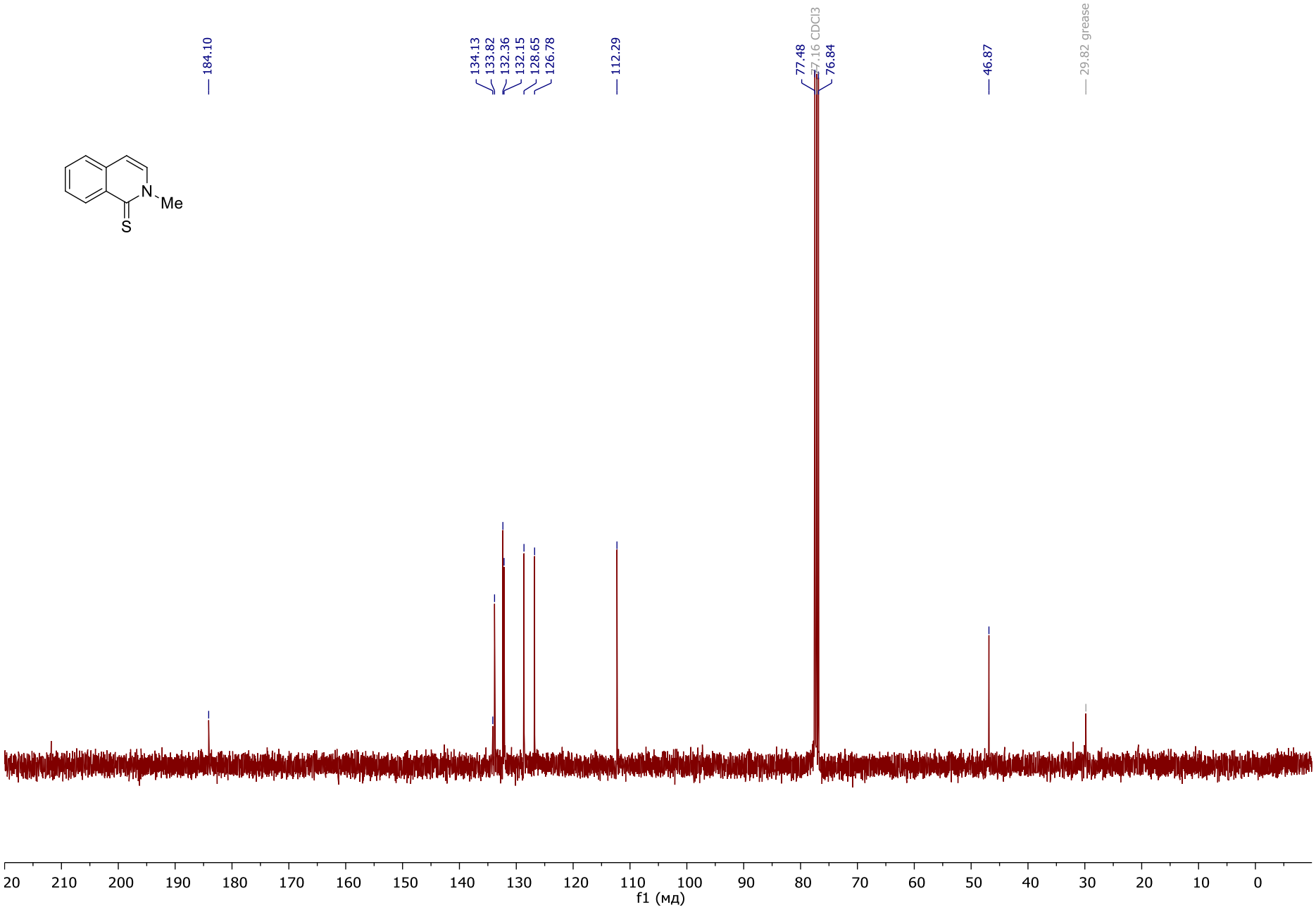
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-isopropylquinoline-4(1*H*)-thione (**2q**)



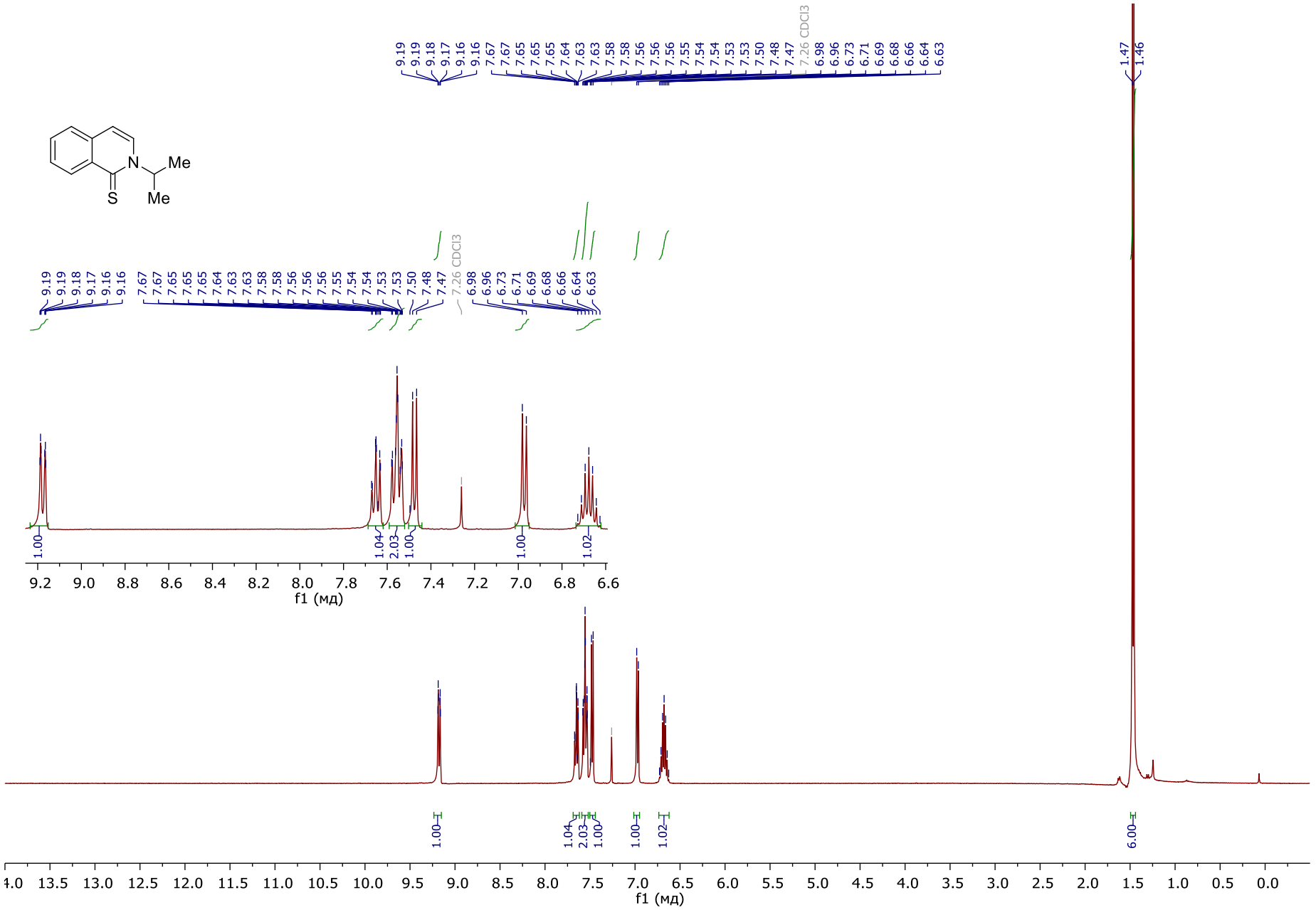
^{1}H NMR (400 MHz, $CDCl_3$) of 2-methylisoquinoline-1(2*H*)-thione (**2r**)



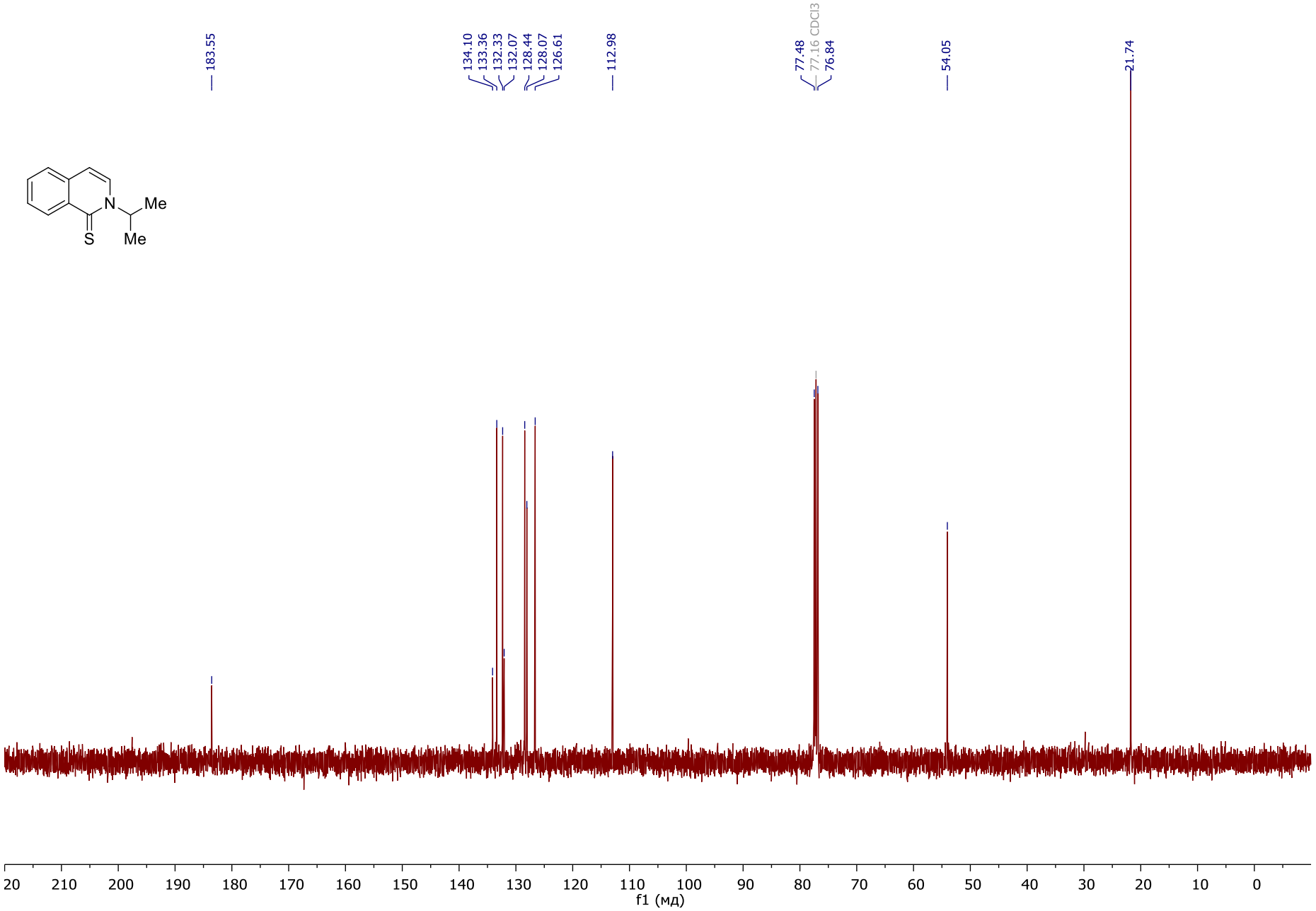
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 2-methylisoquinoline-1(2*H*)-thione (**2r**)



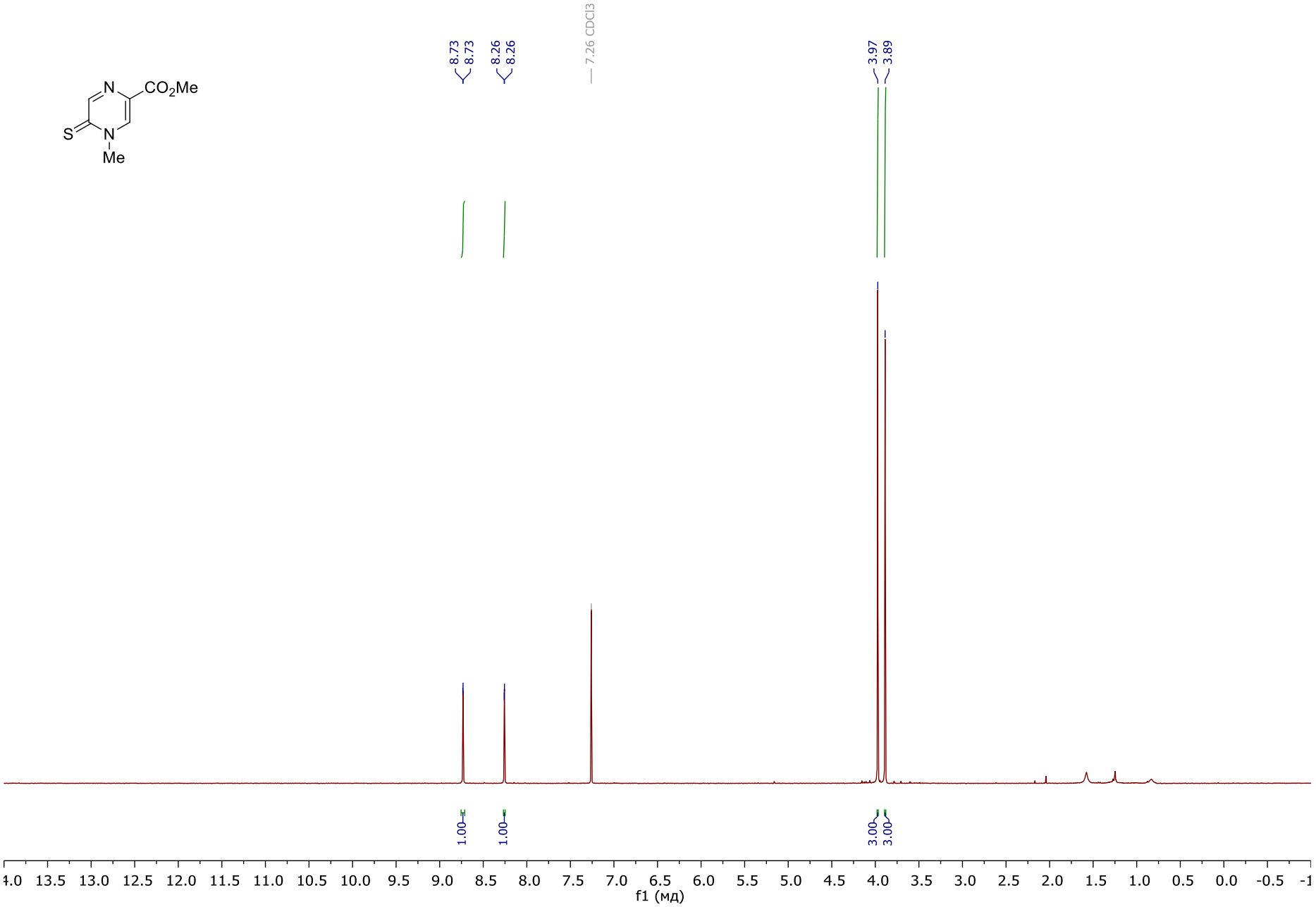
^{1}H NMR (400 MHz, $CDCl_3$) of 2-isopropylisoquinoline-1(2*H*)-thione (**2s**)



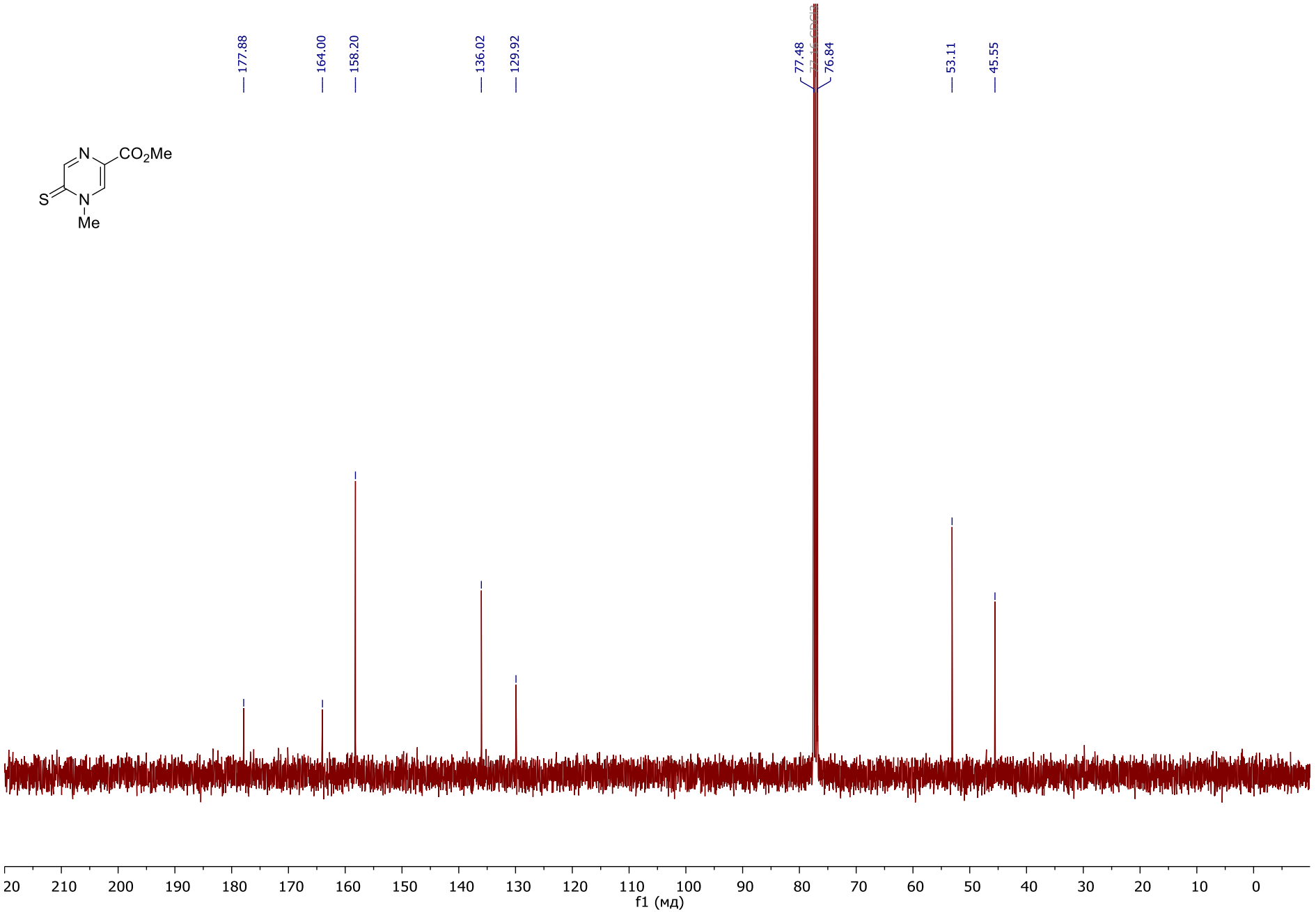
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 2-isopropylisoquinoline-1(2*H*)-thione (**2s**)



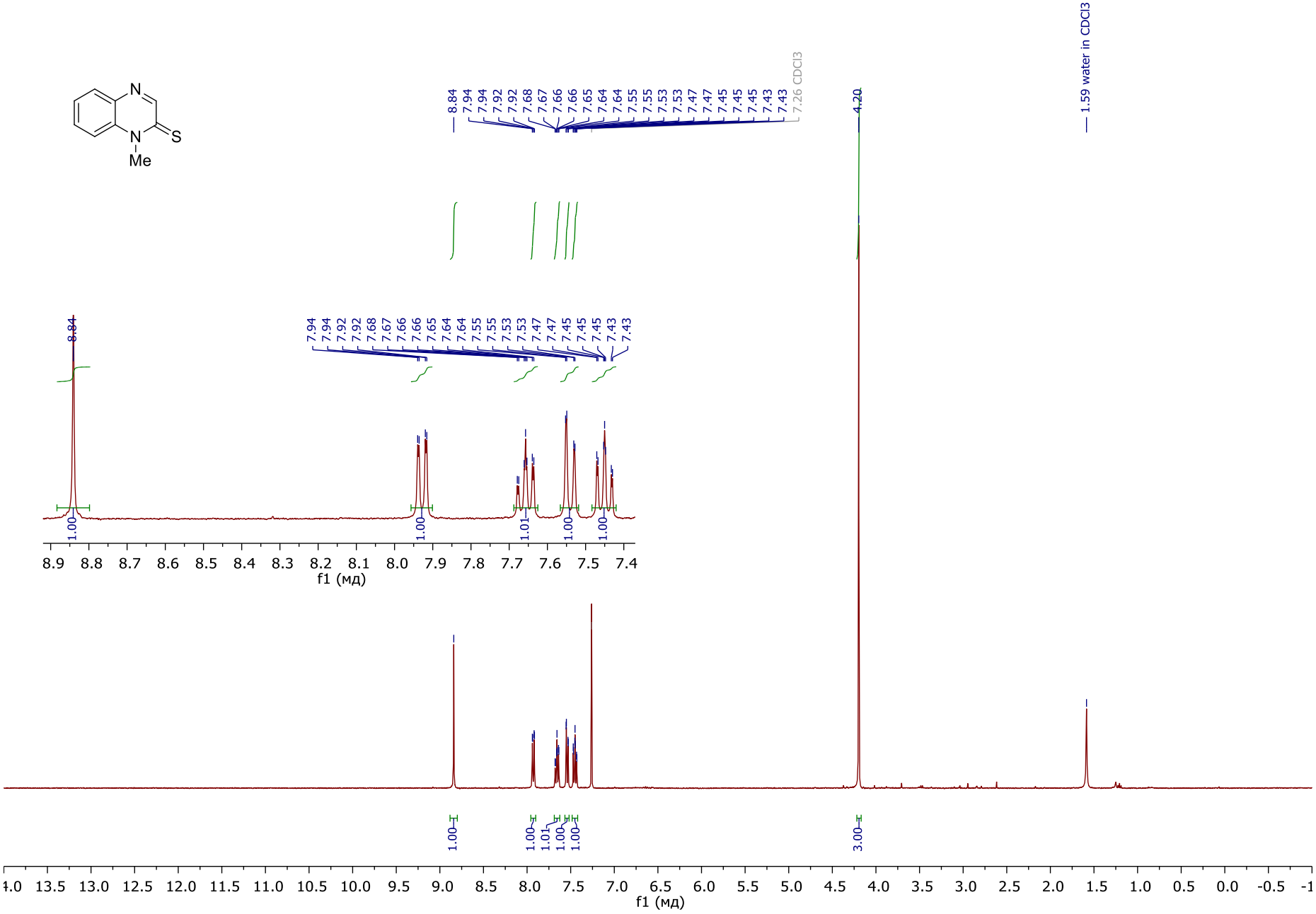
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 4-methyl-5-thioxo-4,5-dihydropyrazine-2-carboxylate (**2t**)



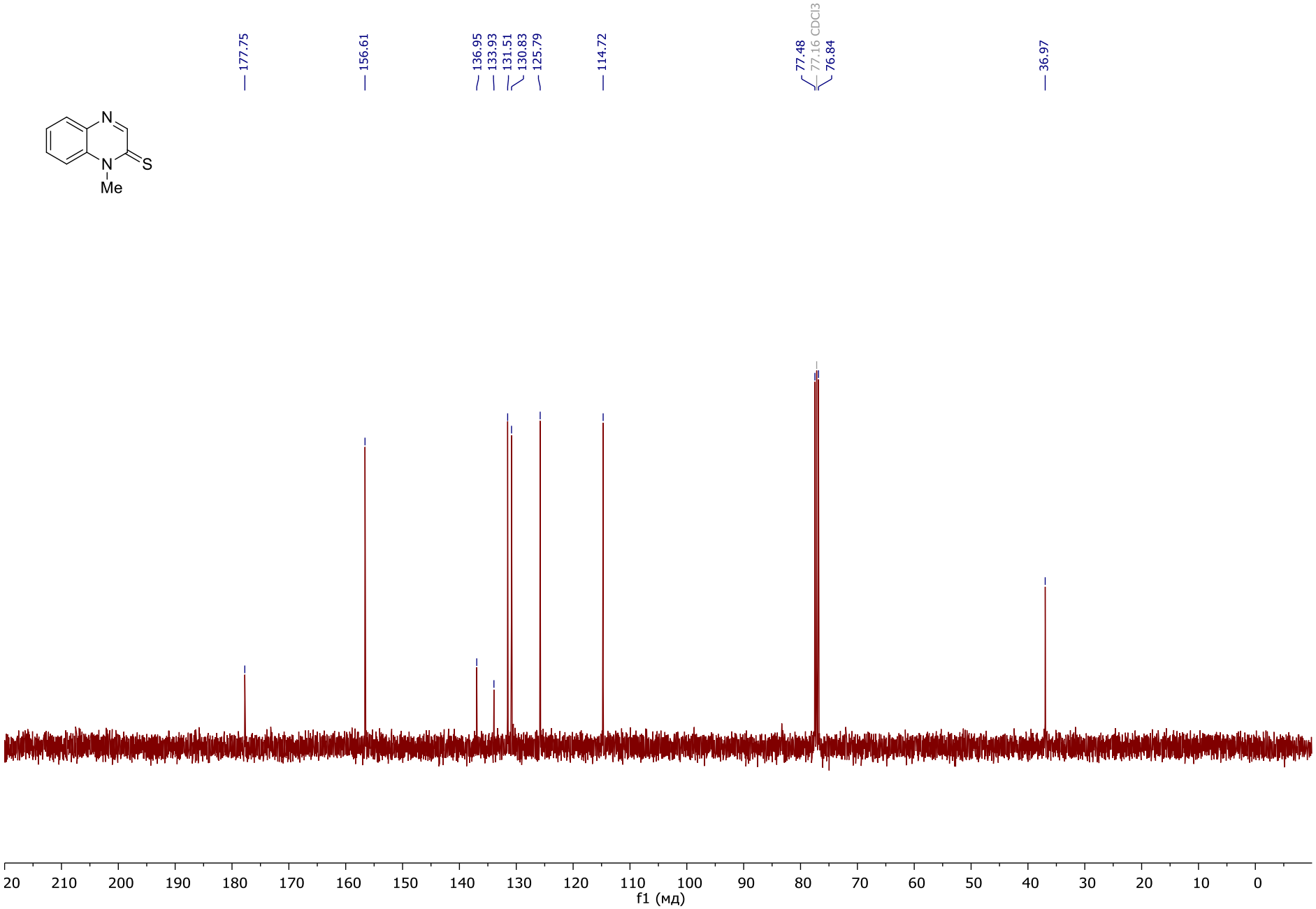
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of methyl 4-methyl-5-thioxo-4,5-dihydropyrazine-2-carboxylate (**2t**)



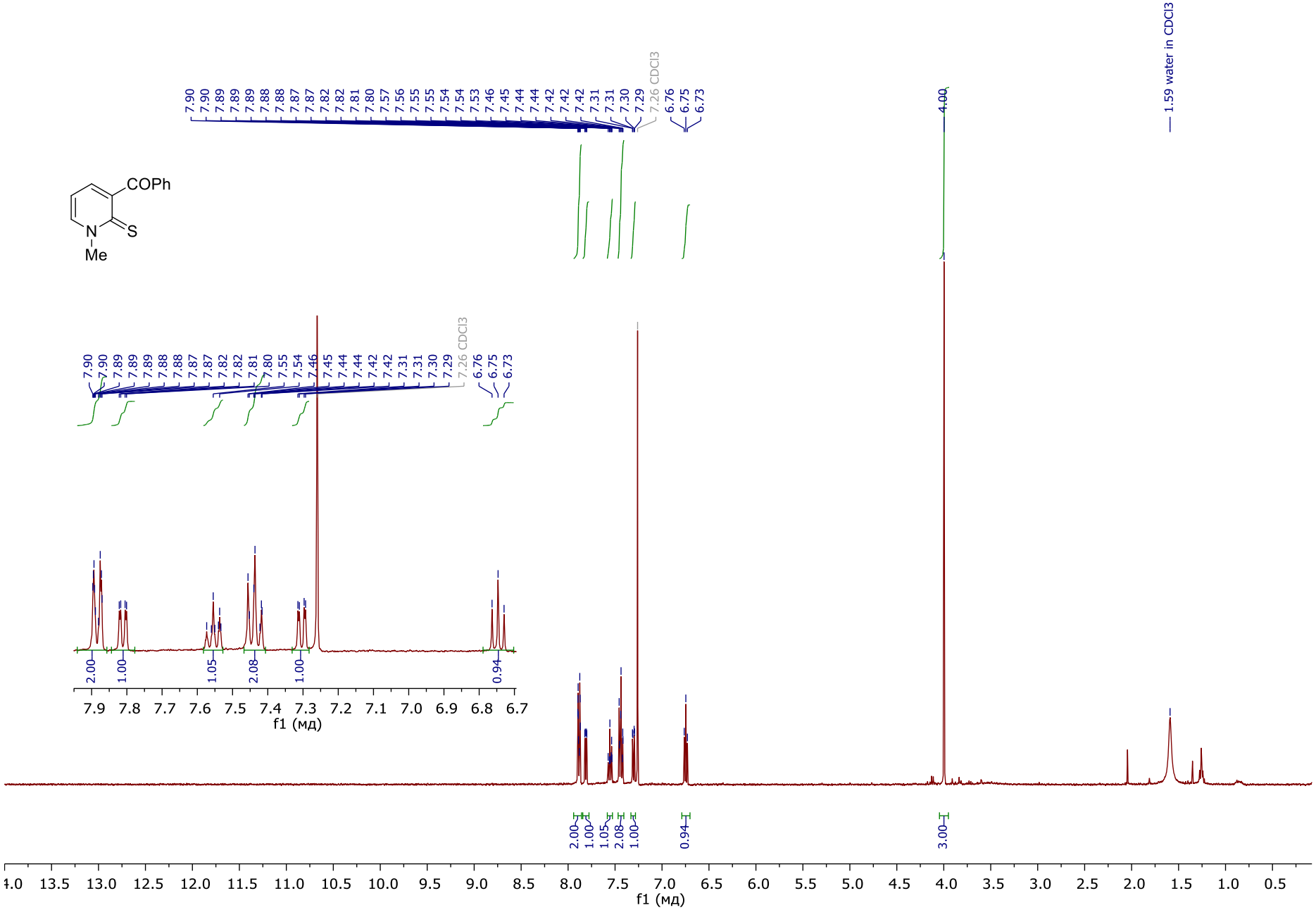
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methylquinoxaline-2(1*H*)-thione (**2u**)



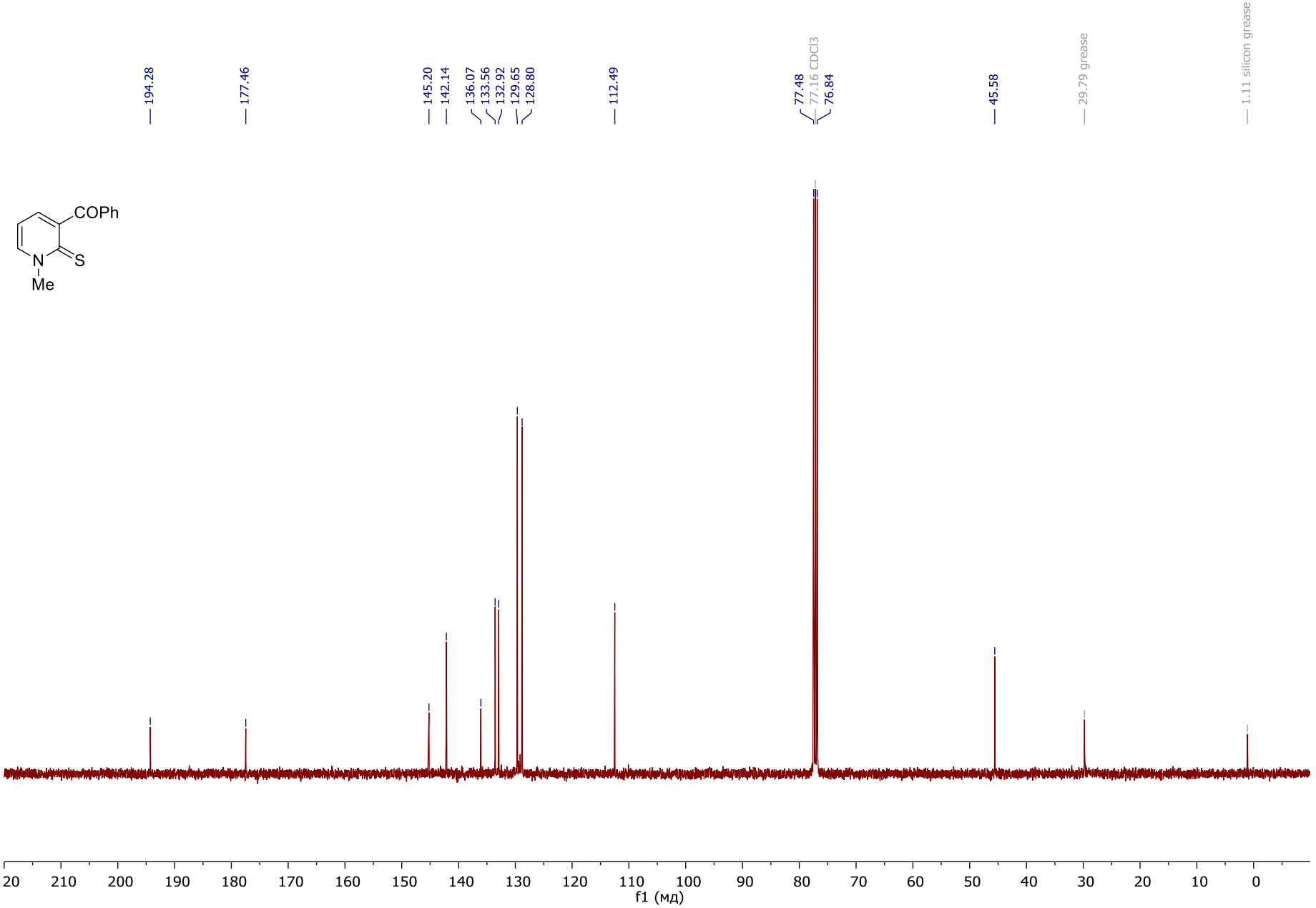
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-methylquinoxaline-2(1*H*)-thione (**2u**)



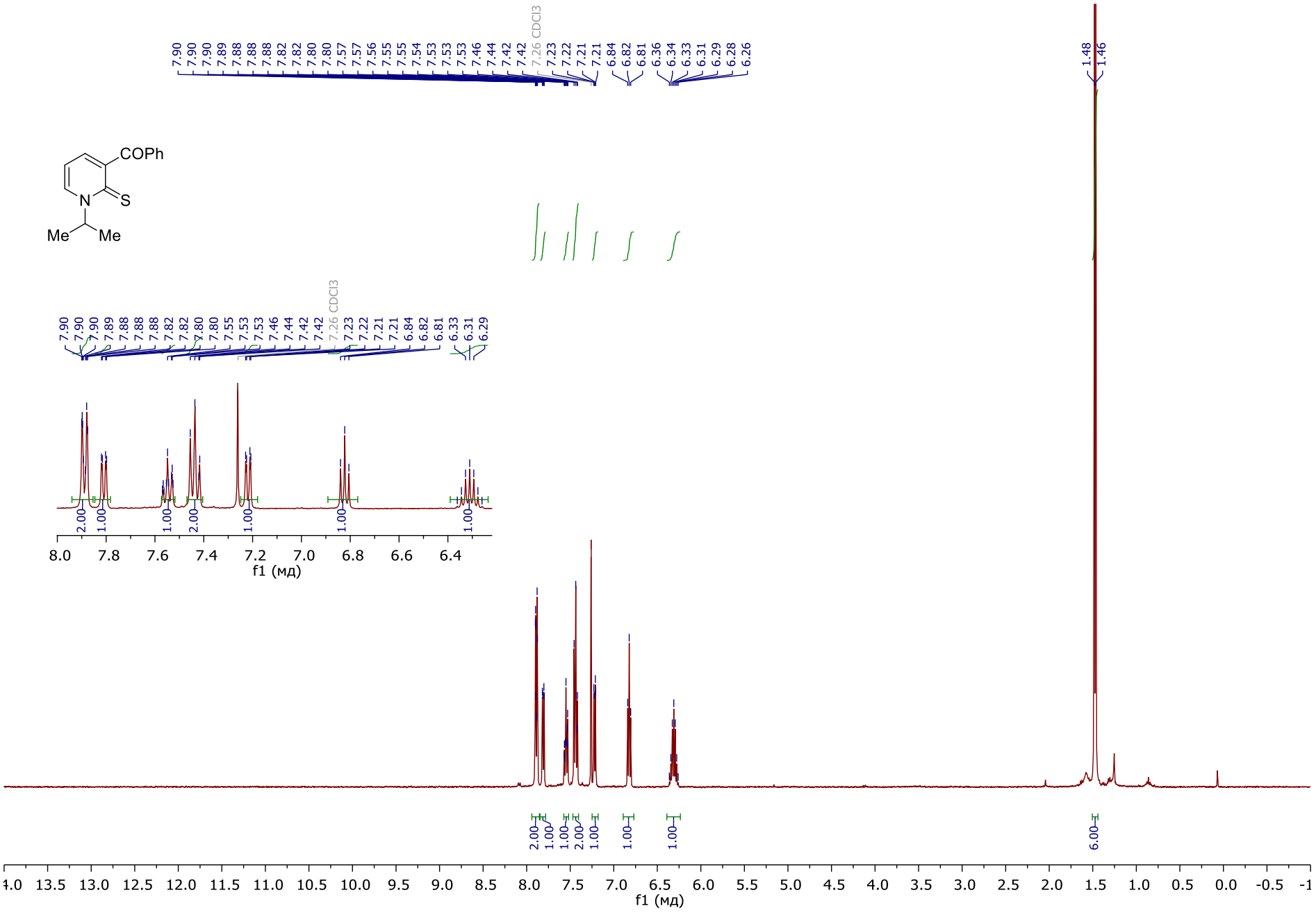
^{1}H NMR (400 MHz, $CDCl_3$) of (1-methyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3a**)



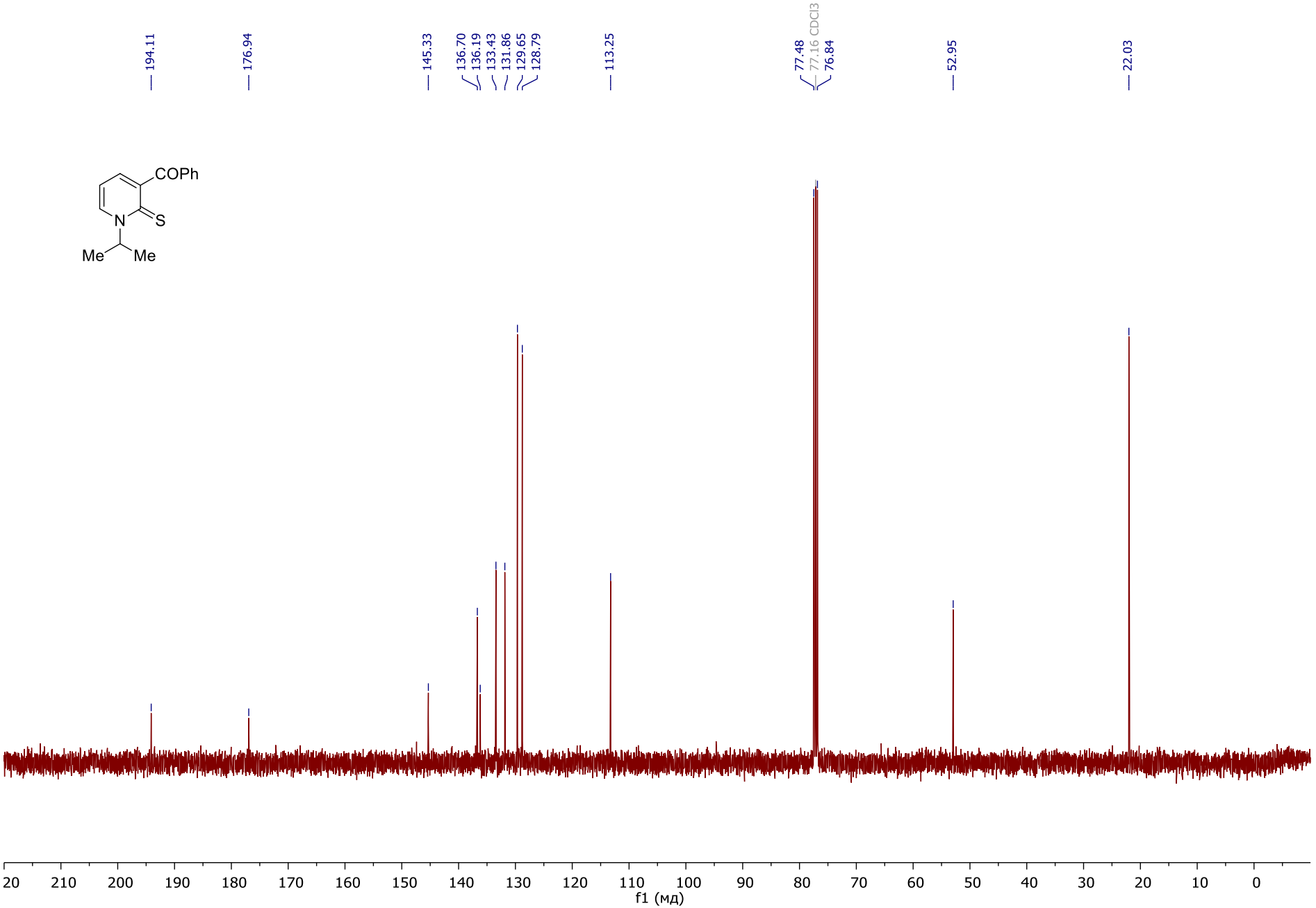
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-methyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3a**)



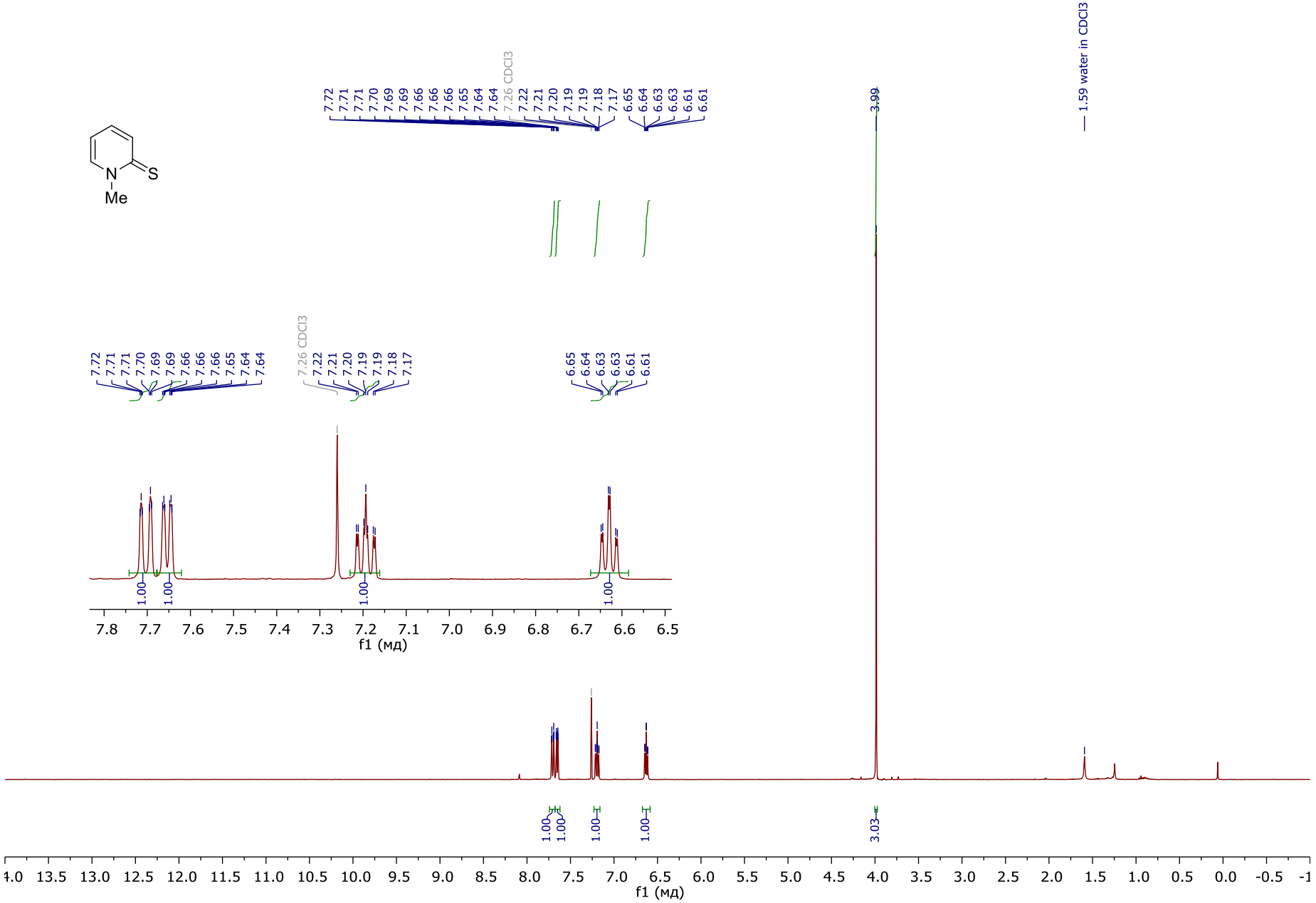
^{1}H NMR (400 MHz, $CDCl_3$) of (1-isopropyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3b**)



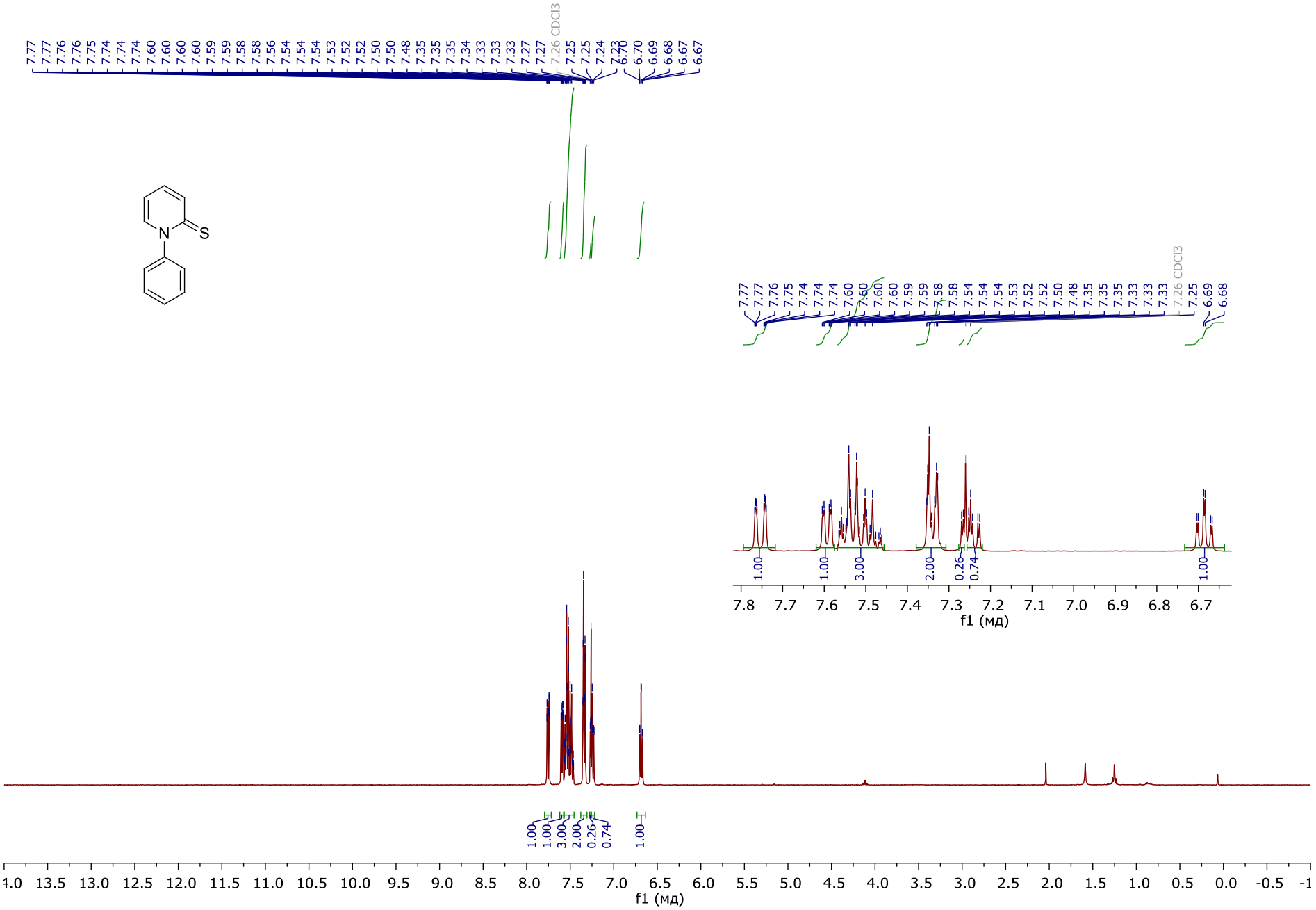
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-isopropyl-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3b**)



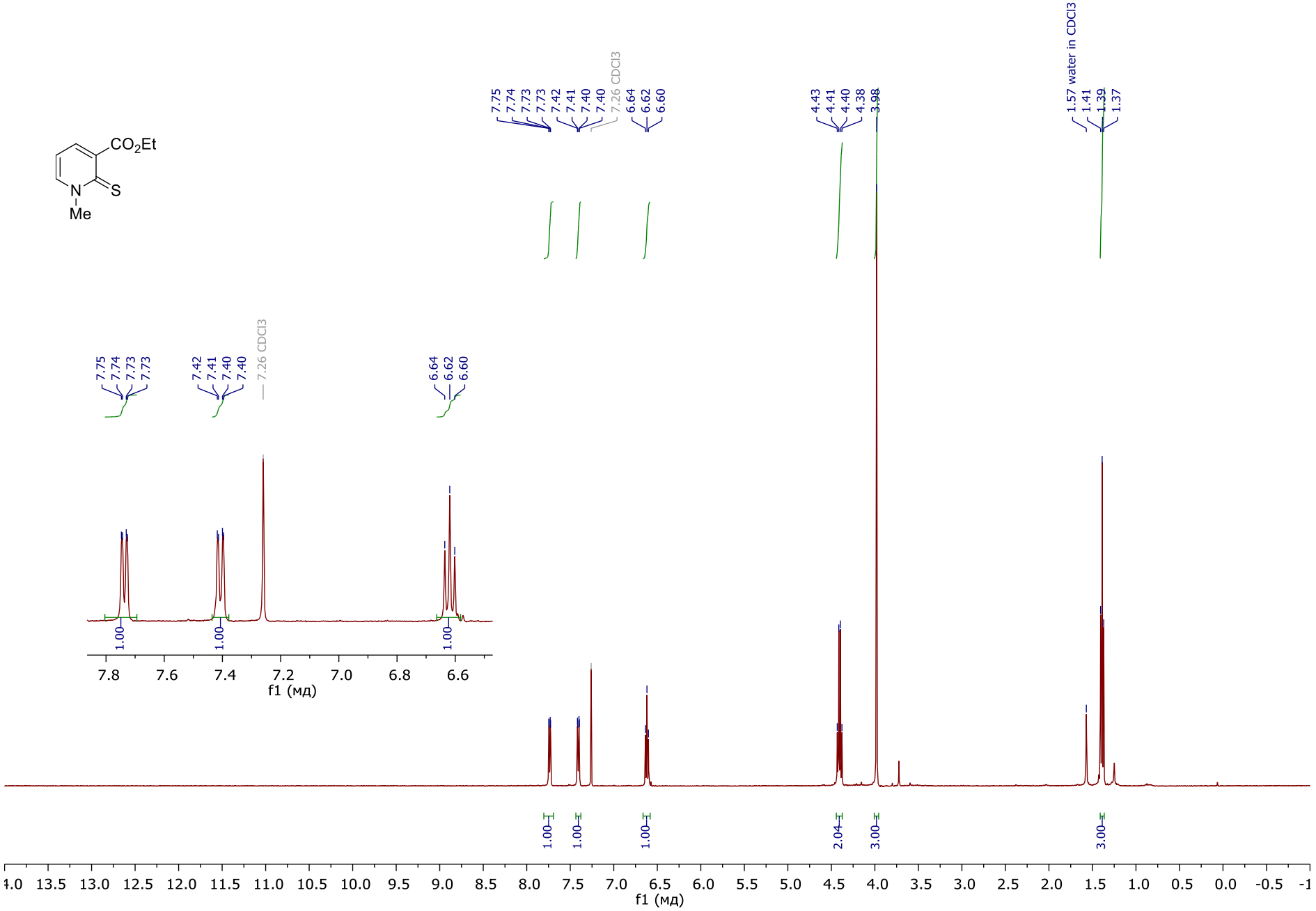
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methylpyridine-2(1*H*)-thione (**3c**)



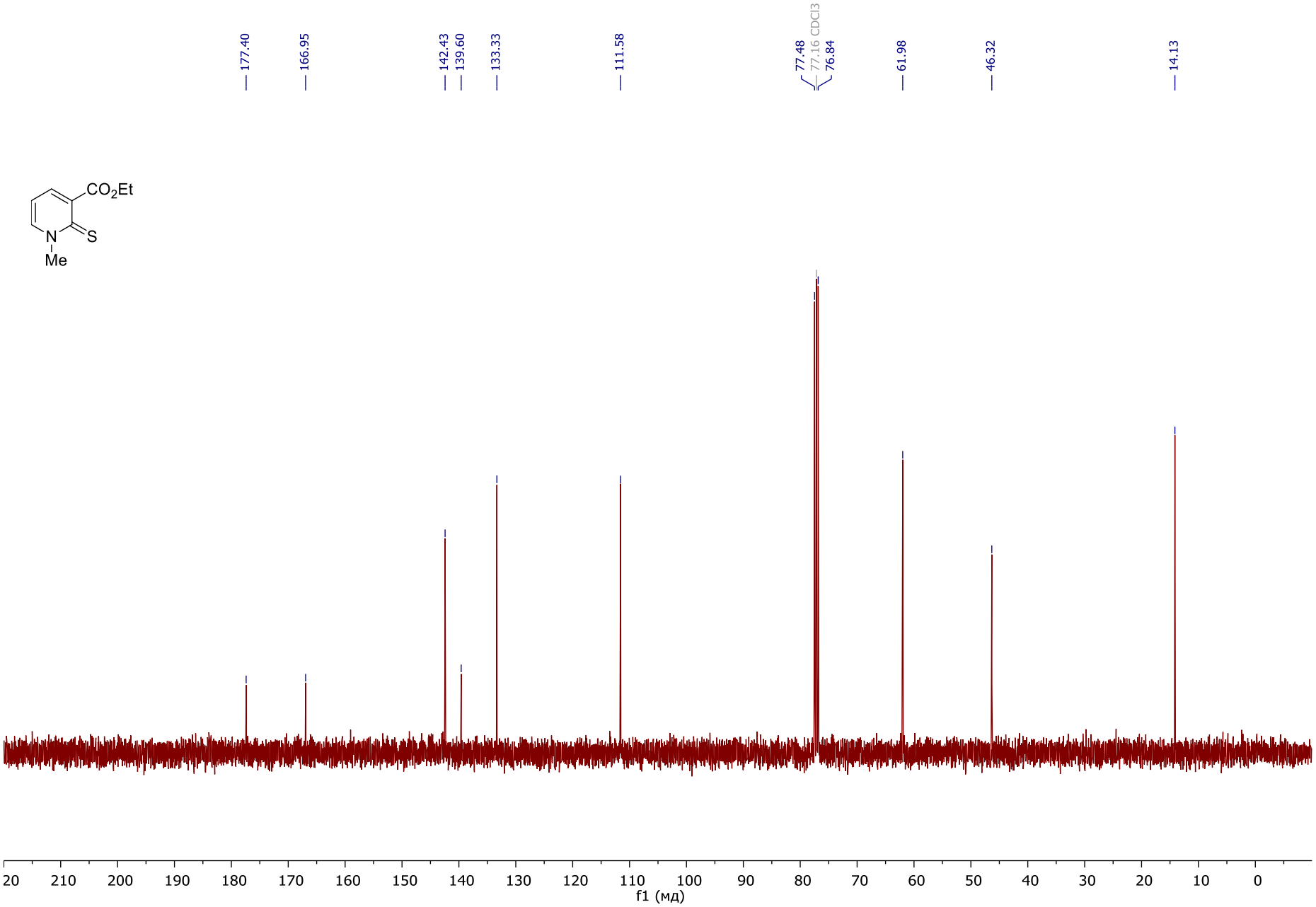
^{1}H NMR (400 MHz, $CDCl_3$) of 1-phenylpyridine-2(*1H*)-thione (**3d**)



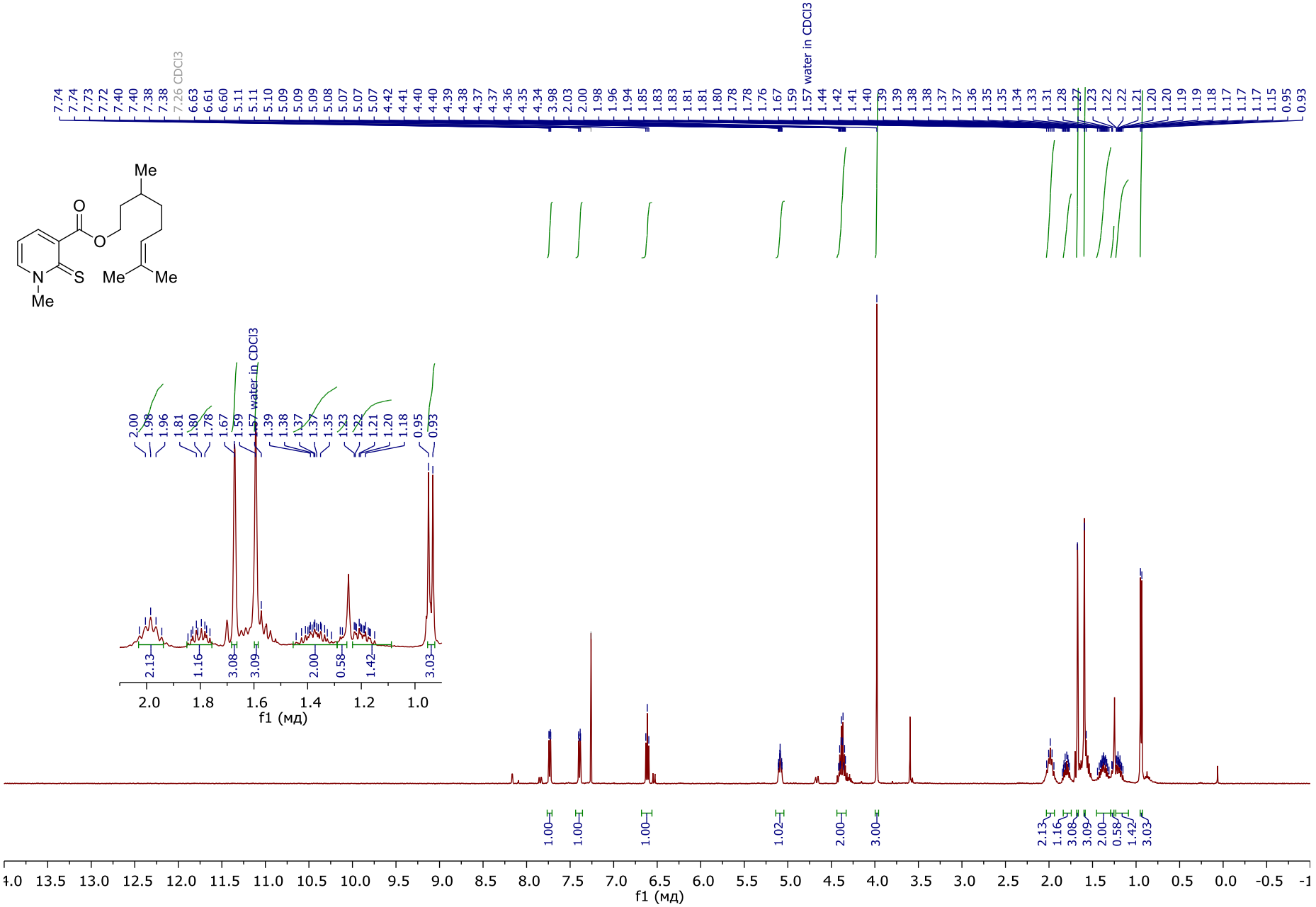
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3e**)



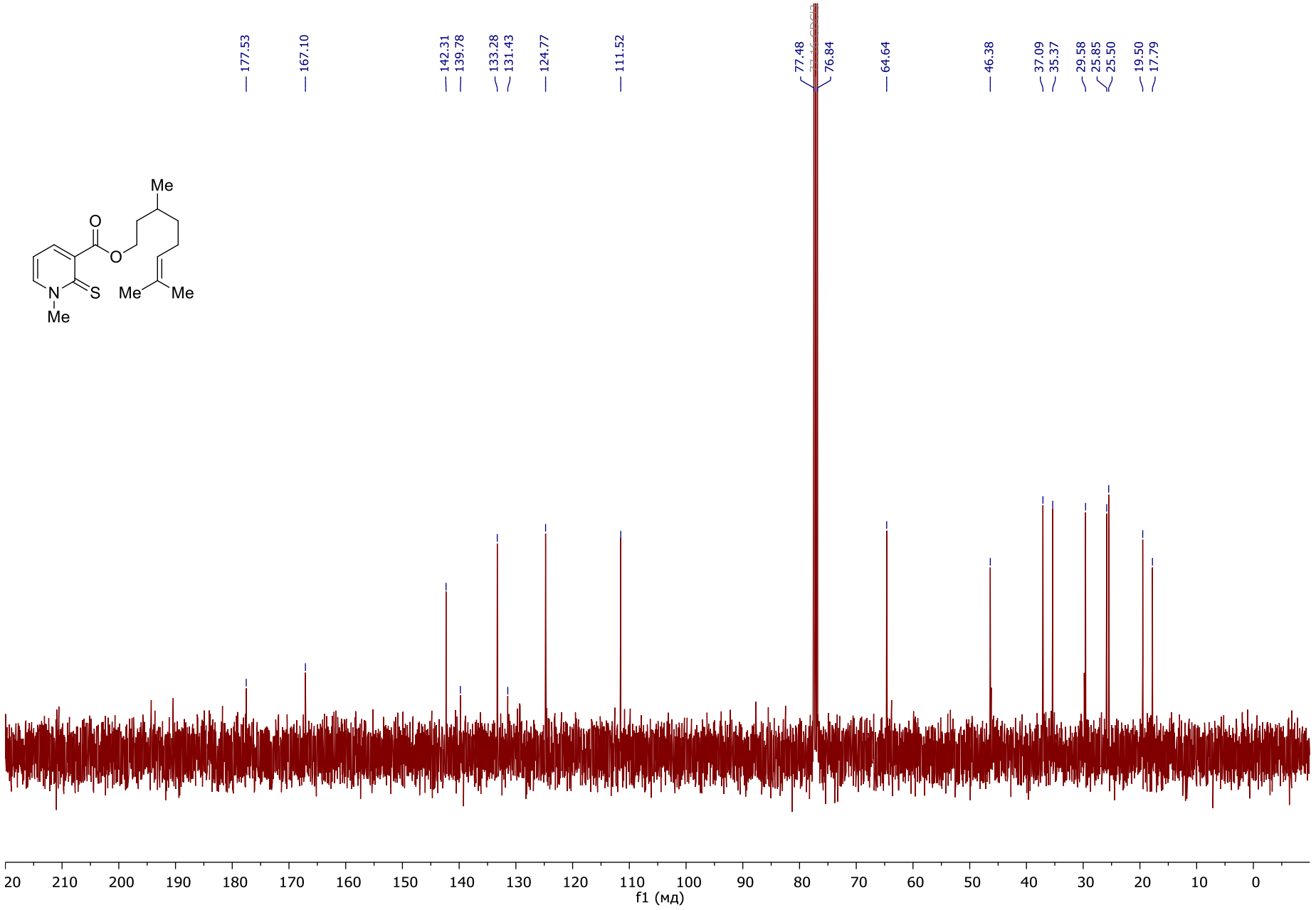
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of ethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3e**)



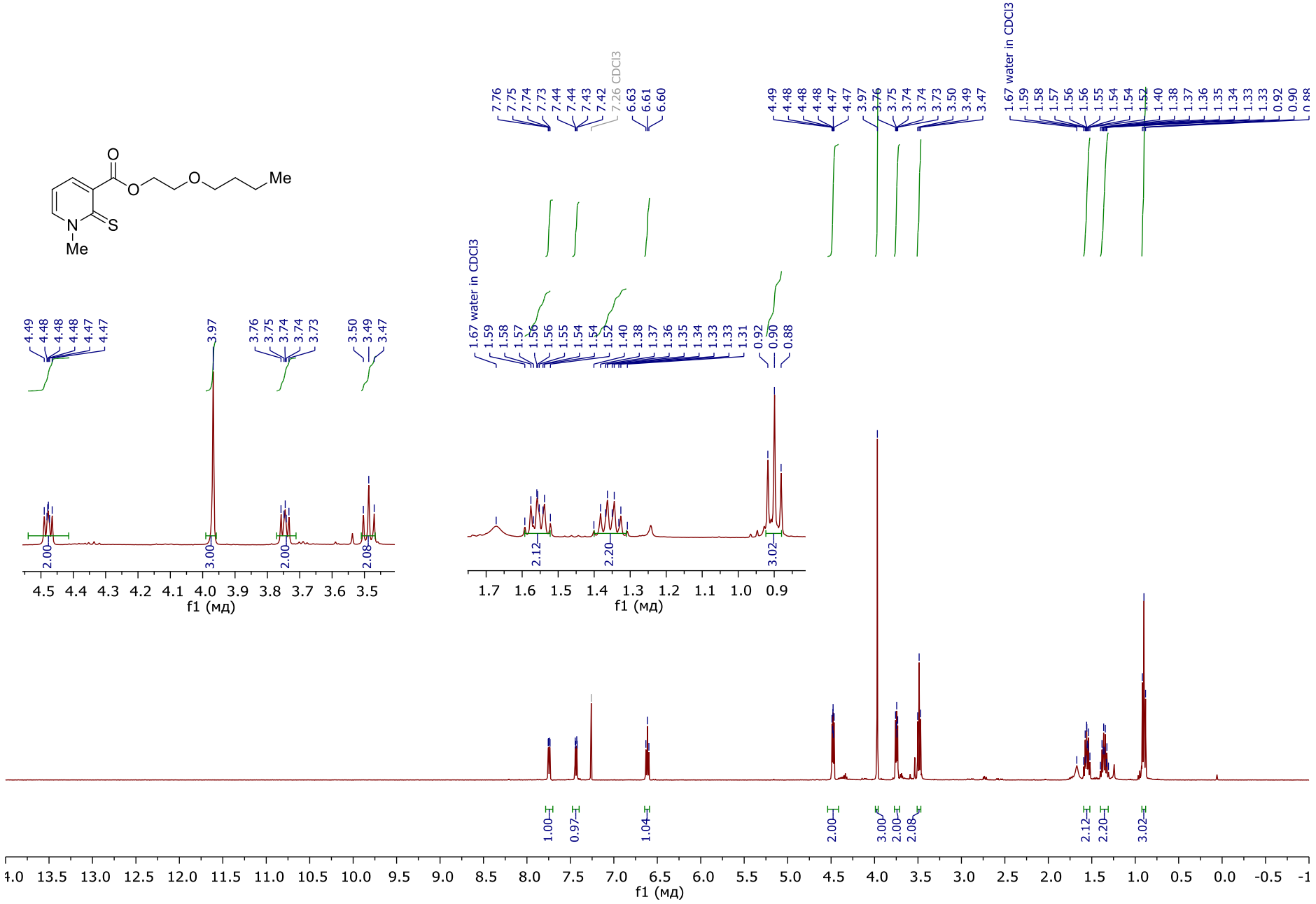
^{1}H NMR (400 MHz, $CDCl_3$) of 3,7-dimethyloct-6-en-1-yl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3f**)



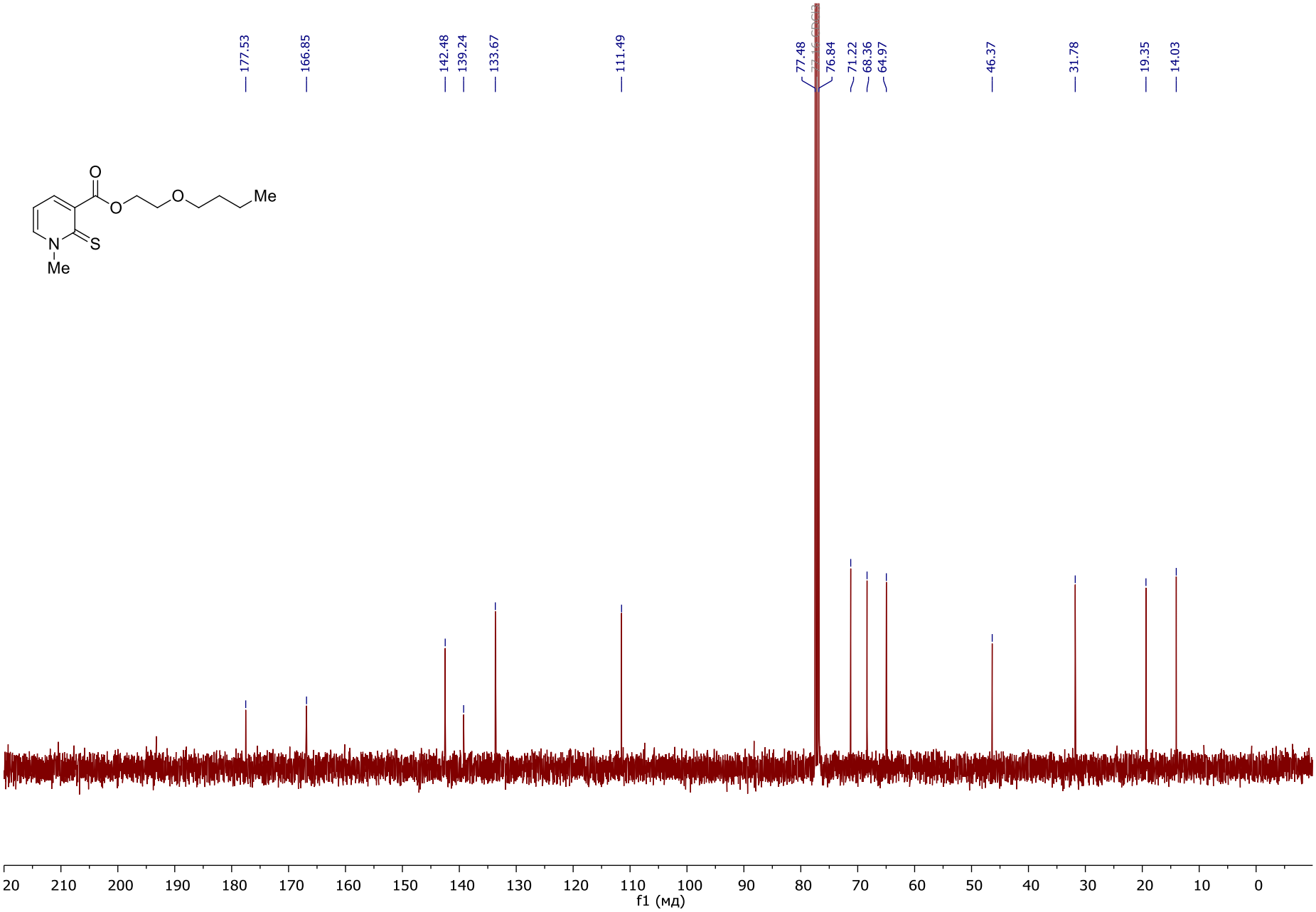
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3,7-dimethyloct-6-en-1-yl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3f**)



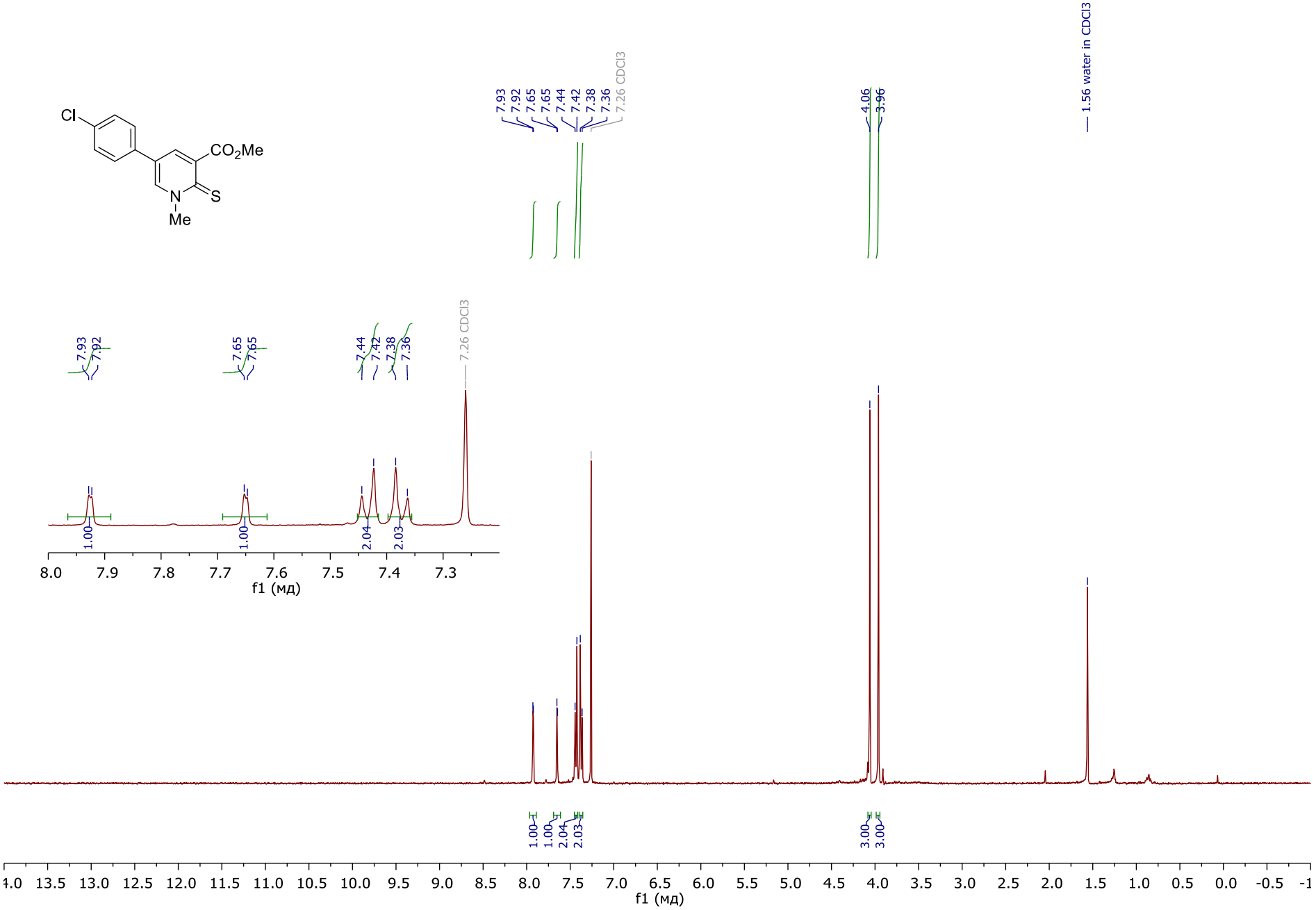
^{1}H NMR (400 MHz, $CDCl_3$) of 2-butoxyethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3g**)



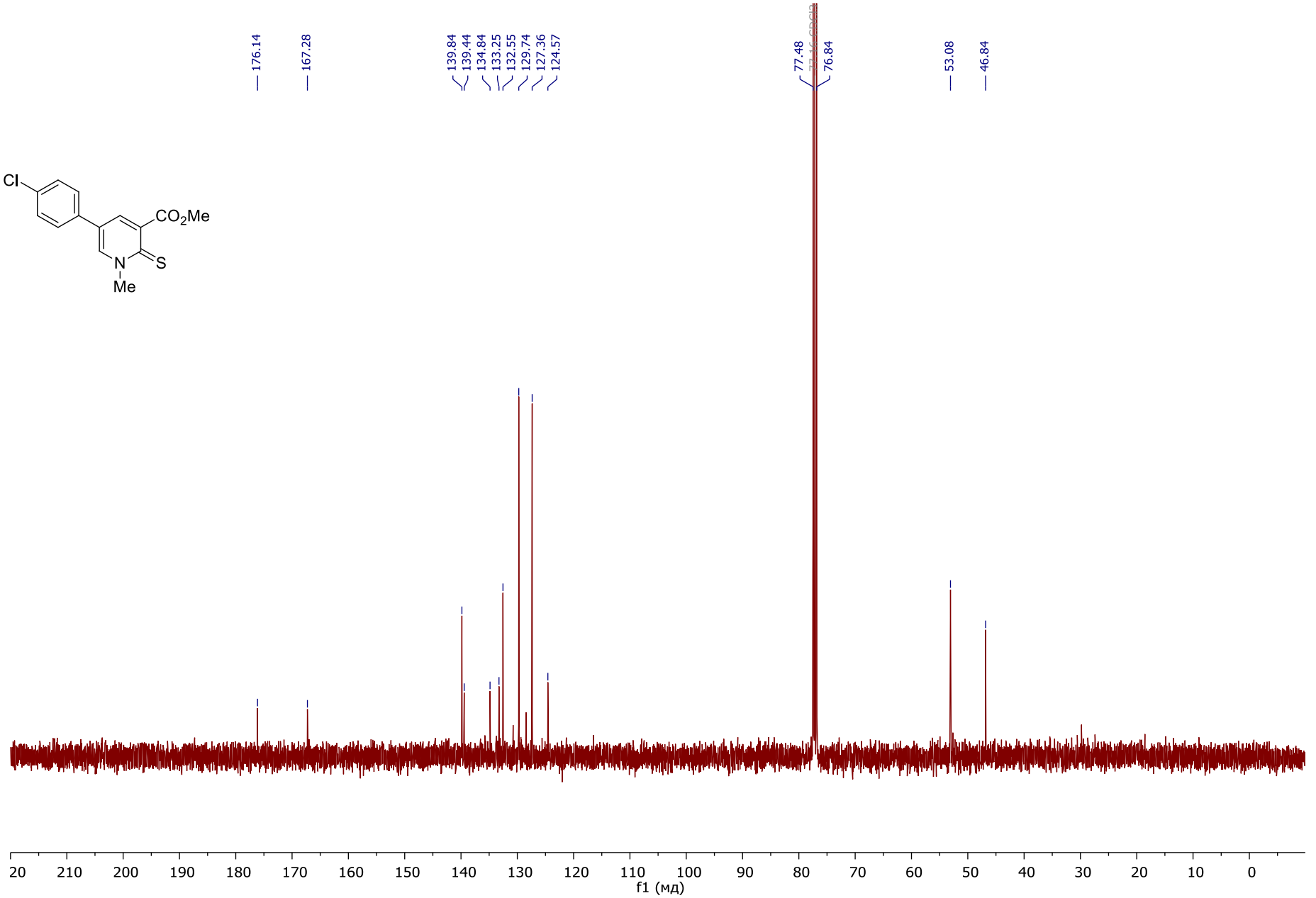
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 2-butoxyethyl 1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3g**)



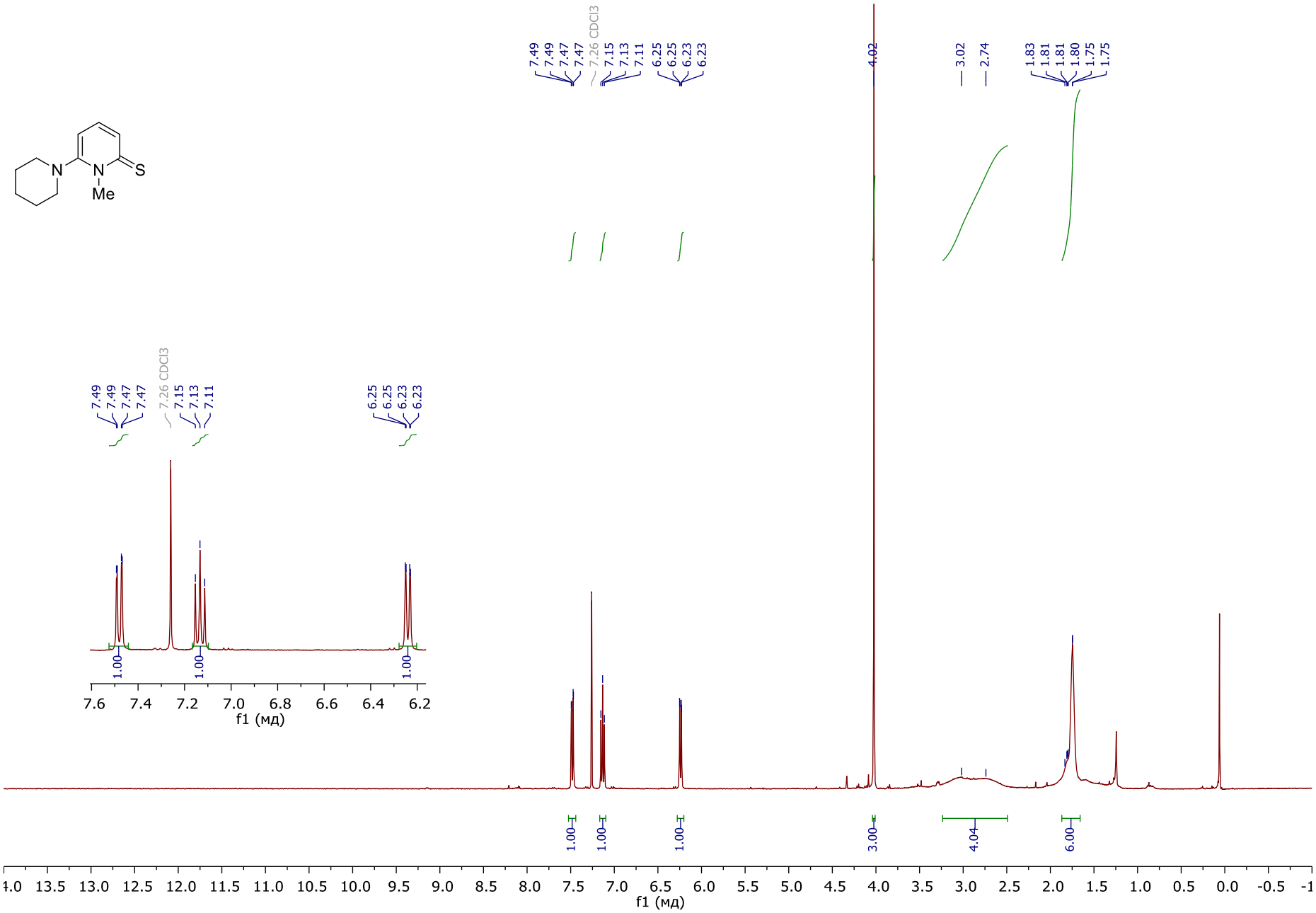
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 5-(4-chlorophenyl)-1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3h**)



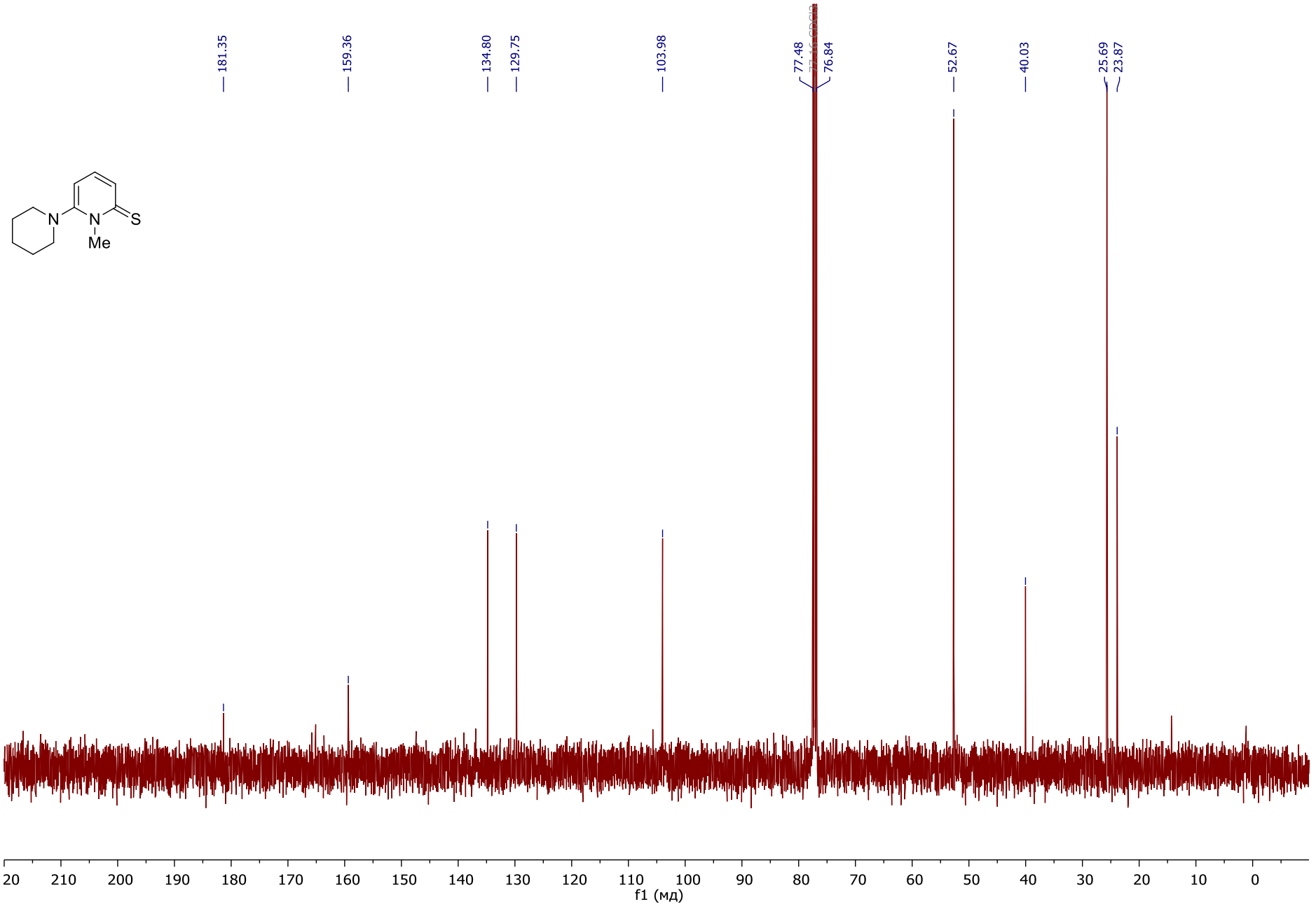
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of methyl 5-(4-chlorophenyl)-1-methyl-2-thioxo-1,2-dihydropyridine-3-carboxylate (**3h**)



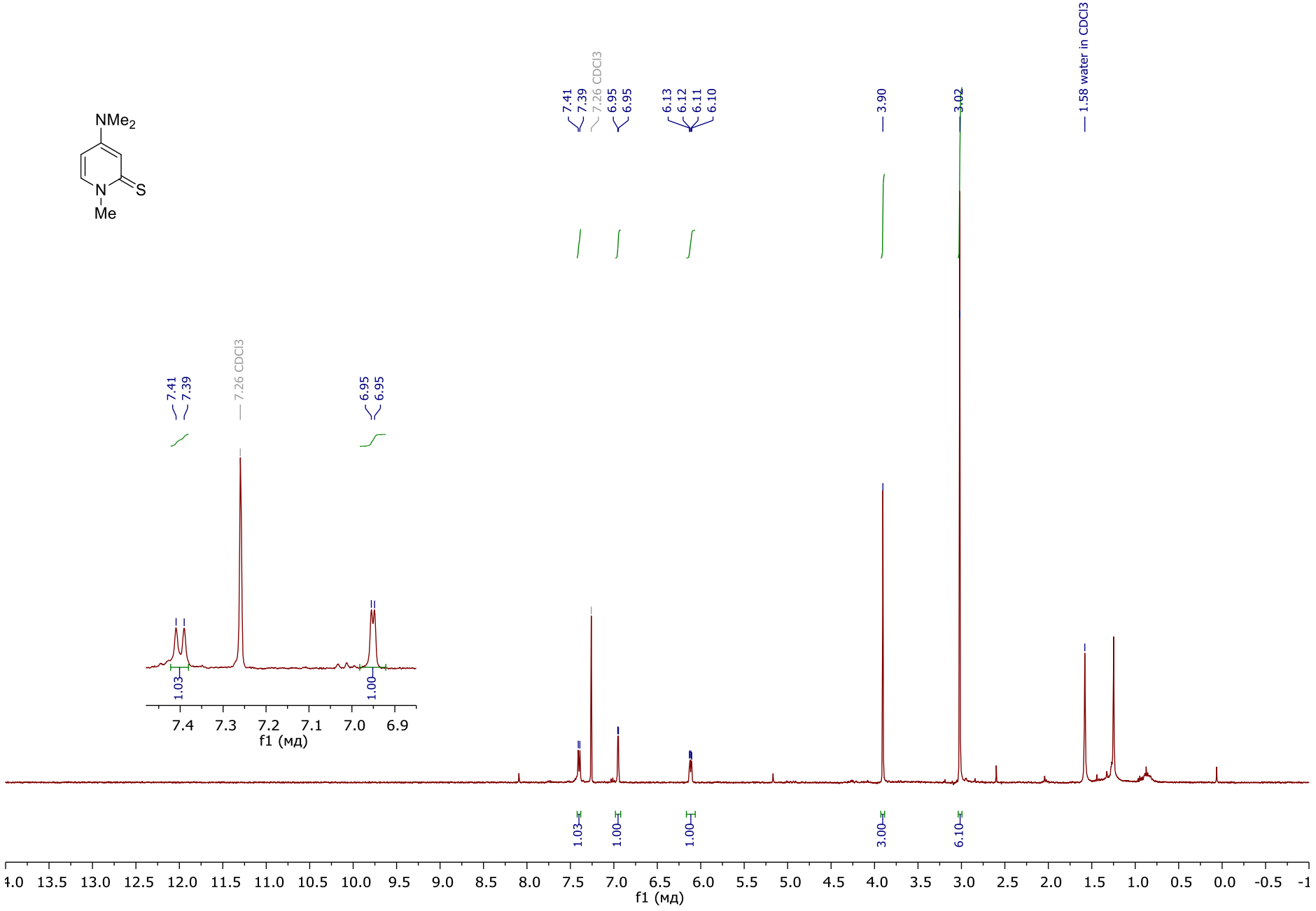
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methyl-6-(piperidin-1-yl)pyridine-2(1*H*)-thione (**3i**)



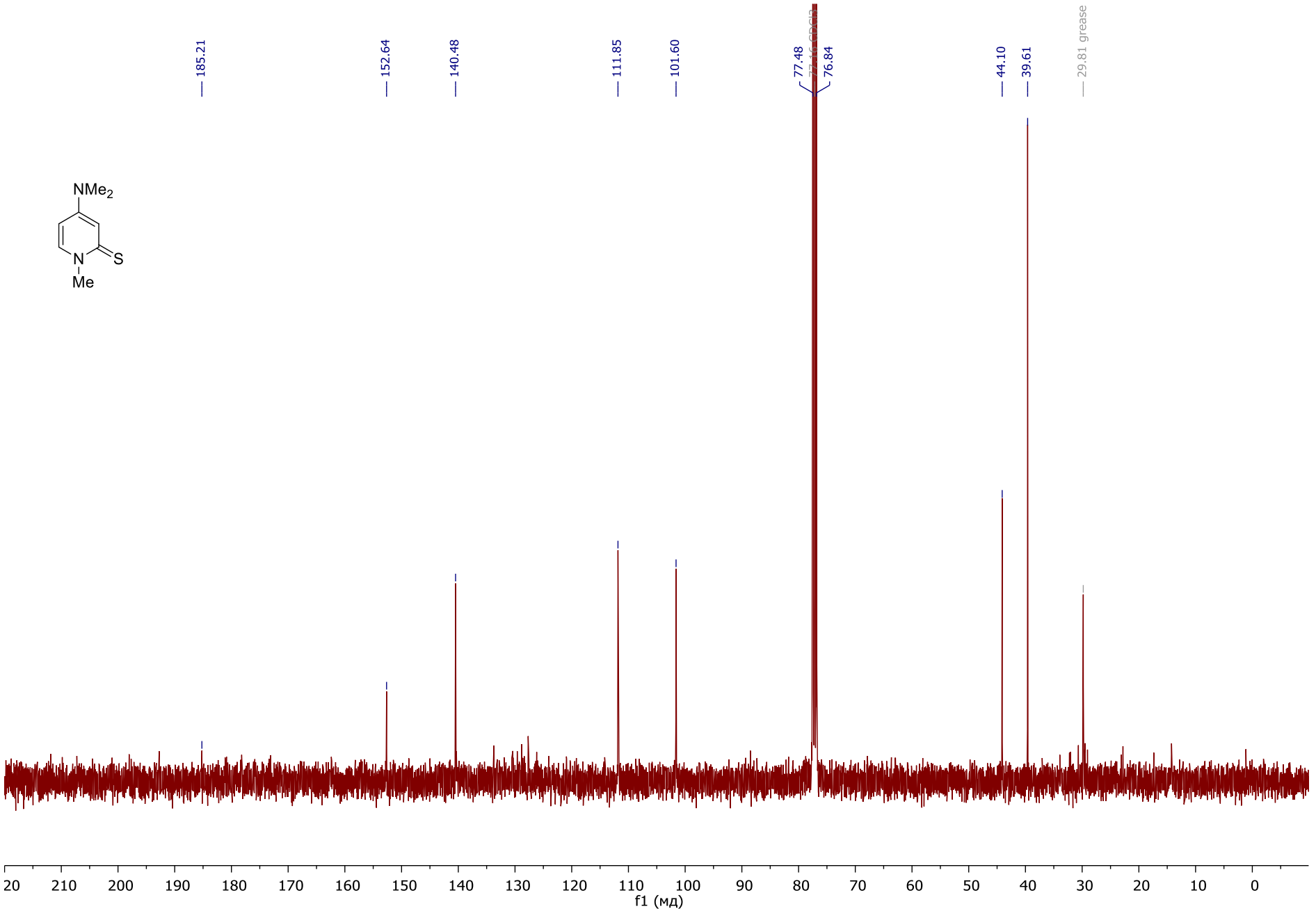
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-methyl-6-(piperidin-1-yl)pyridine-2(1*H*)-thione (**3i**)



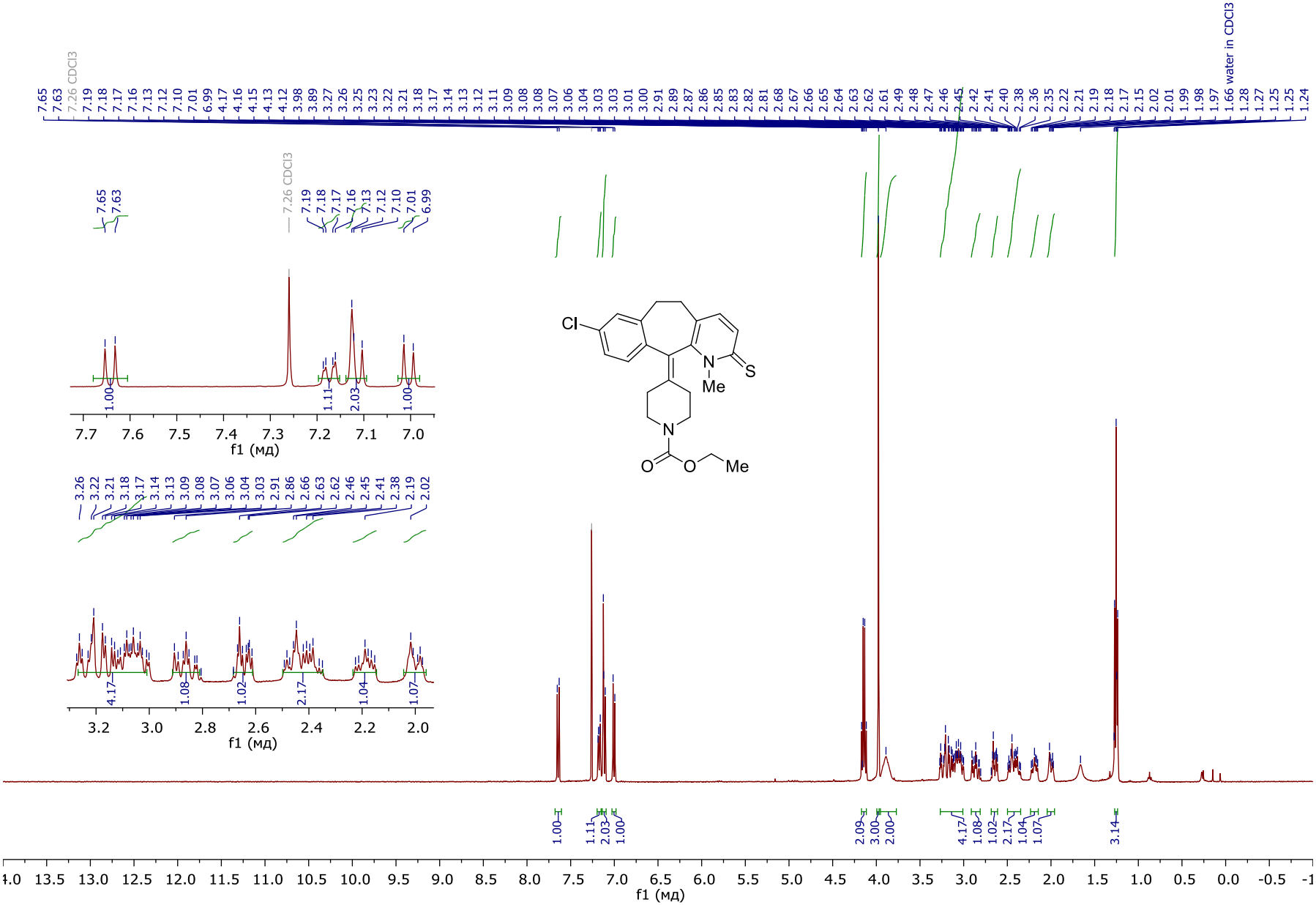
^{1}H NMR (400 MHz, $CDCl_3$) of 4-(dimethylamino)-1-methylpyridine-2(1*H*)-thione (**3j**)



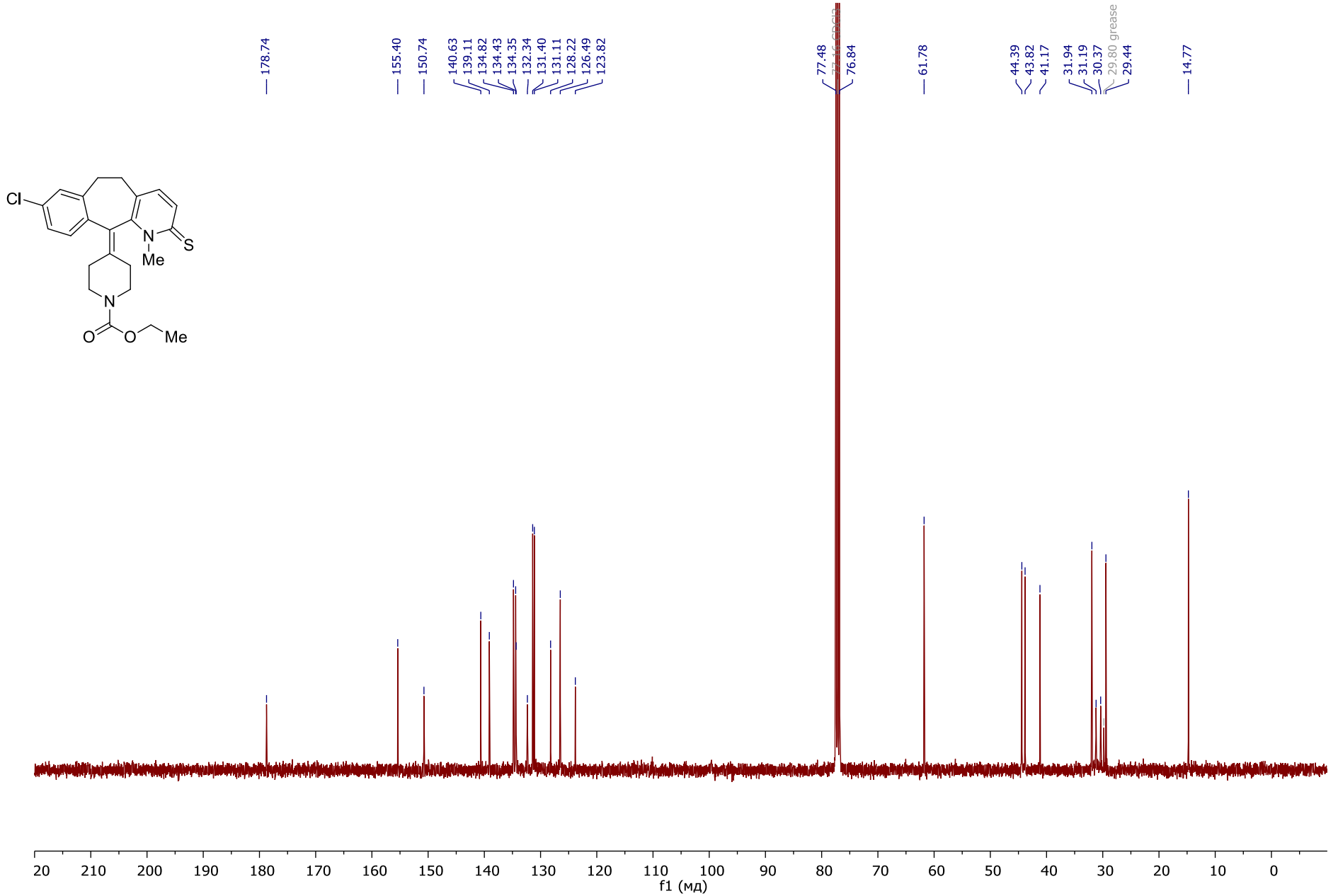
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 4-(dimethylamino)-1-methylpyridine-2(1*H*)-thione (**3j**)



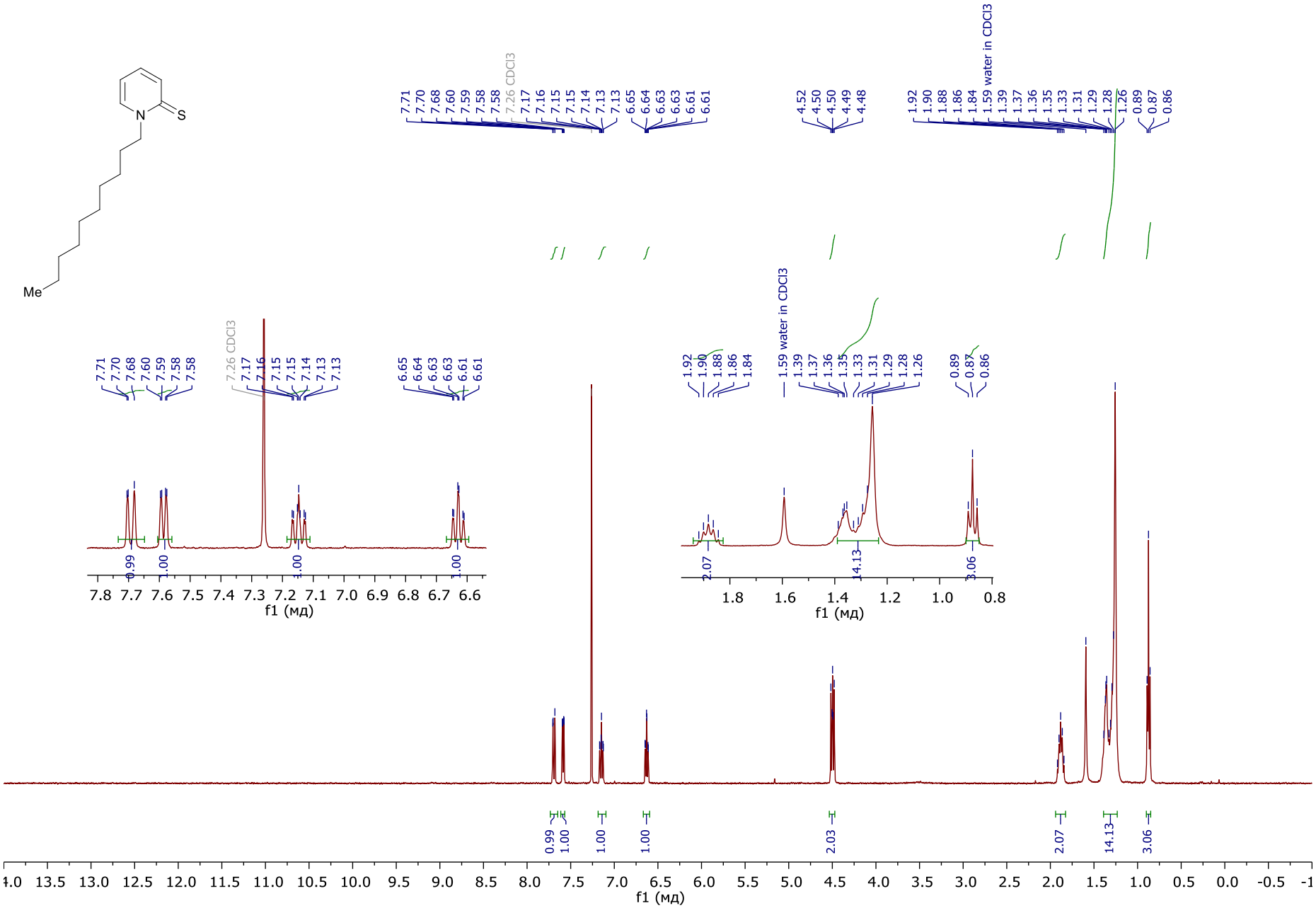
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 4-(8-chloro-1-methyl-2-thioxo-5,6-dihydro-1*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11(2*H*)-ylidene)piperidine-1-carboxylate (**3k**)



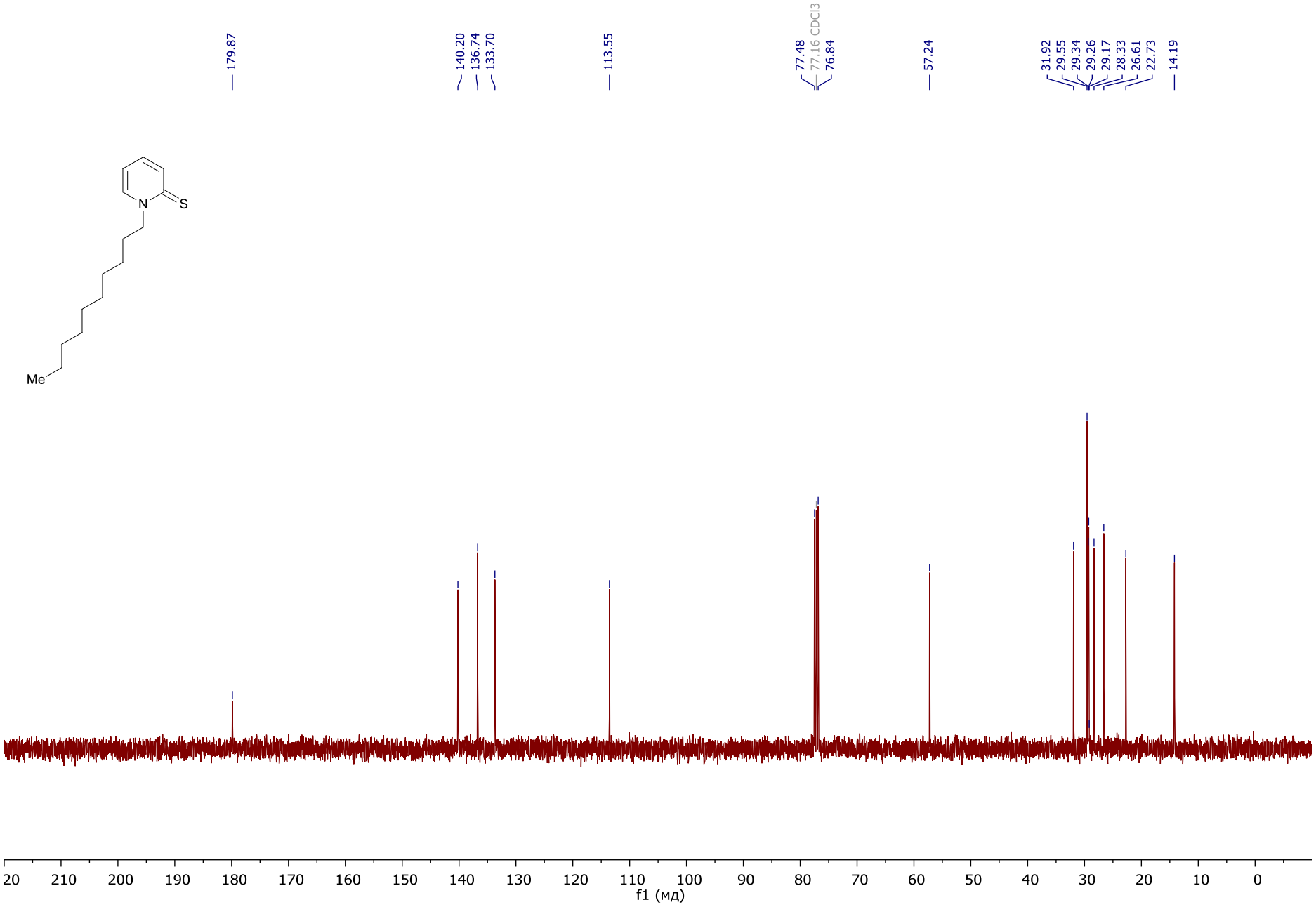
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of ethyl 4-(8-chloro-1-methyl-2-thioxo-5,6-dihydro-1*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11(2*H*)-ylidene)piperidine-1-carboxylate (**3k**)



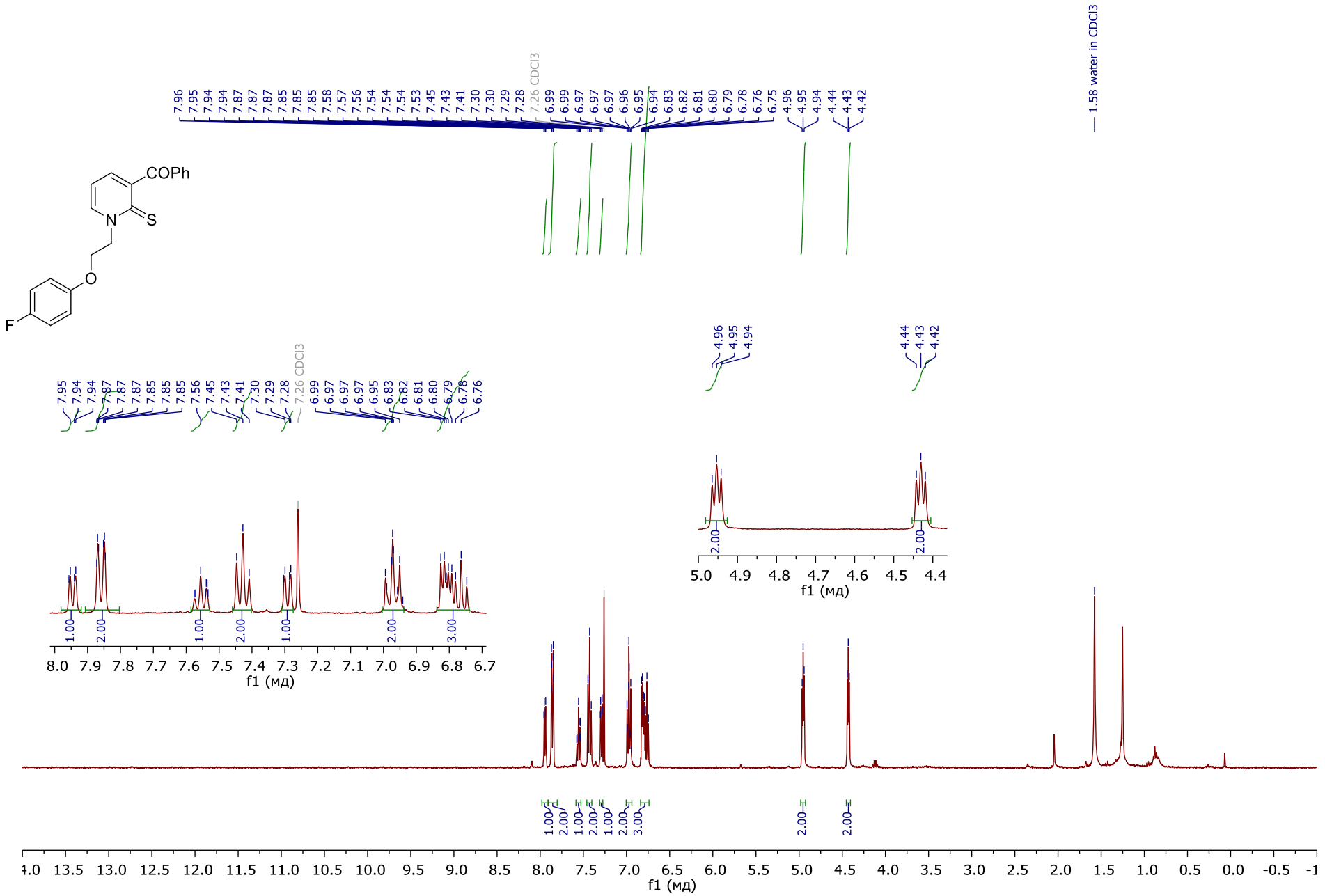
^{1}H NMR (400 MHz, $CDCl_3$) of 1-decylpyridine-2(1*H*)-thione (**3l**)



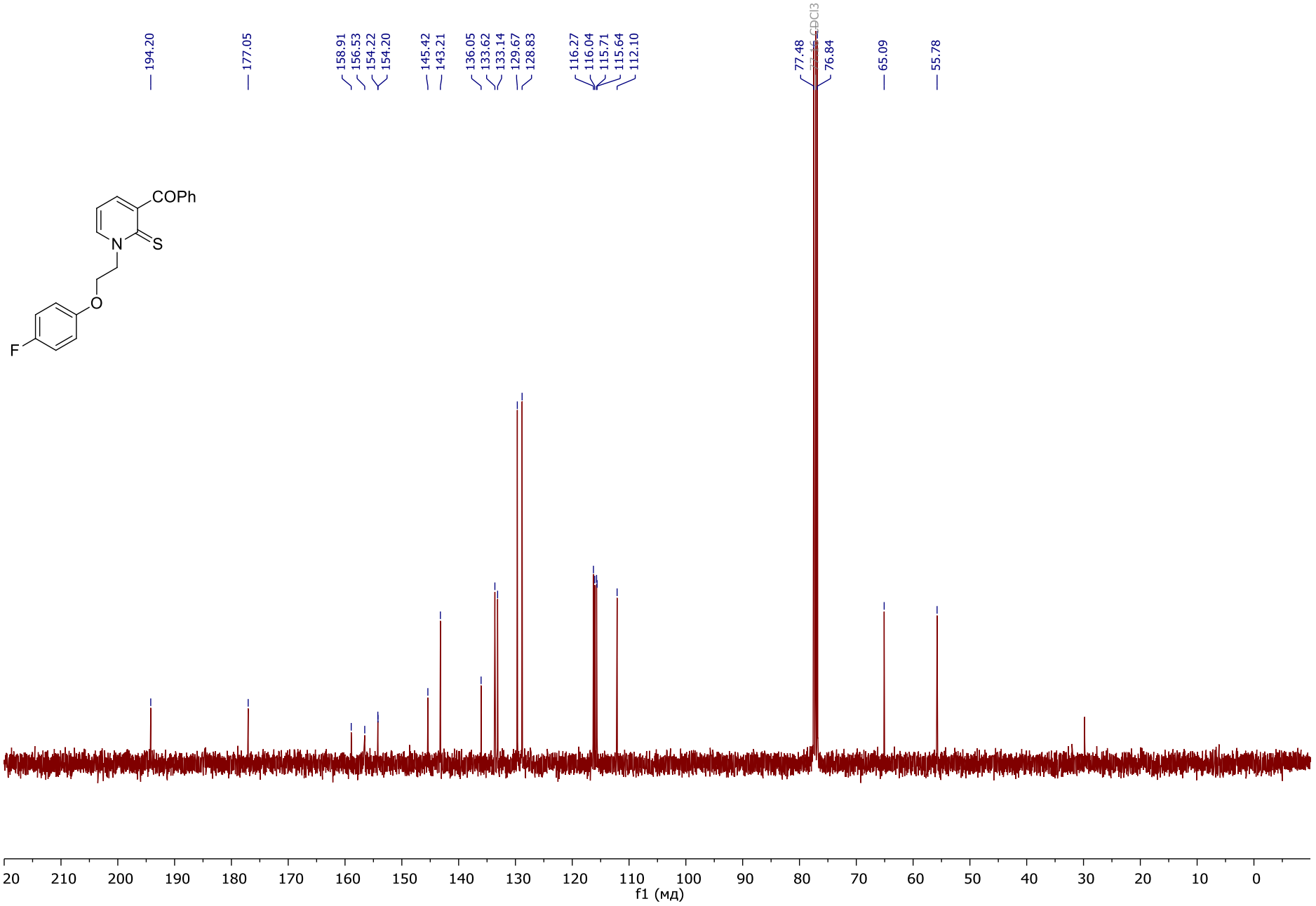
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-decylpyridine-2(1*H*)-thione (**3l**)



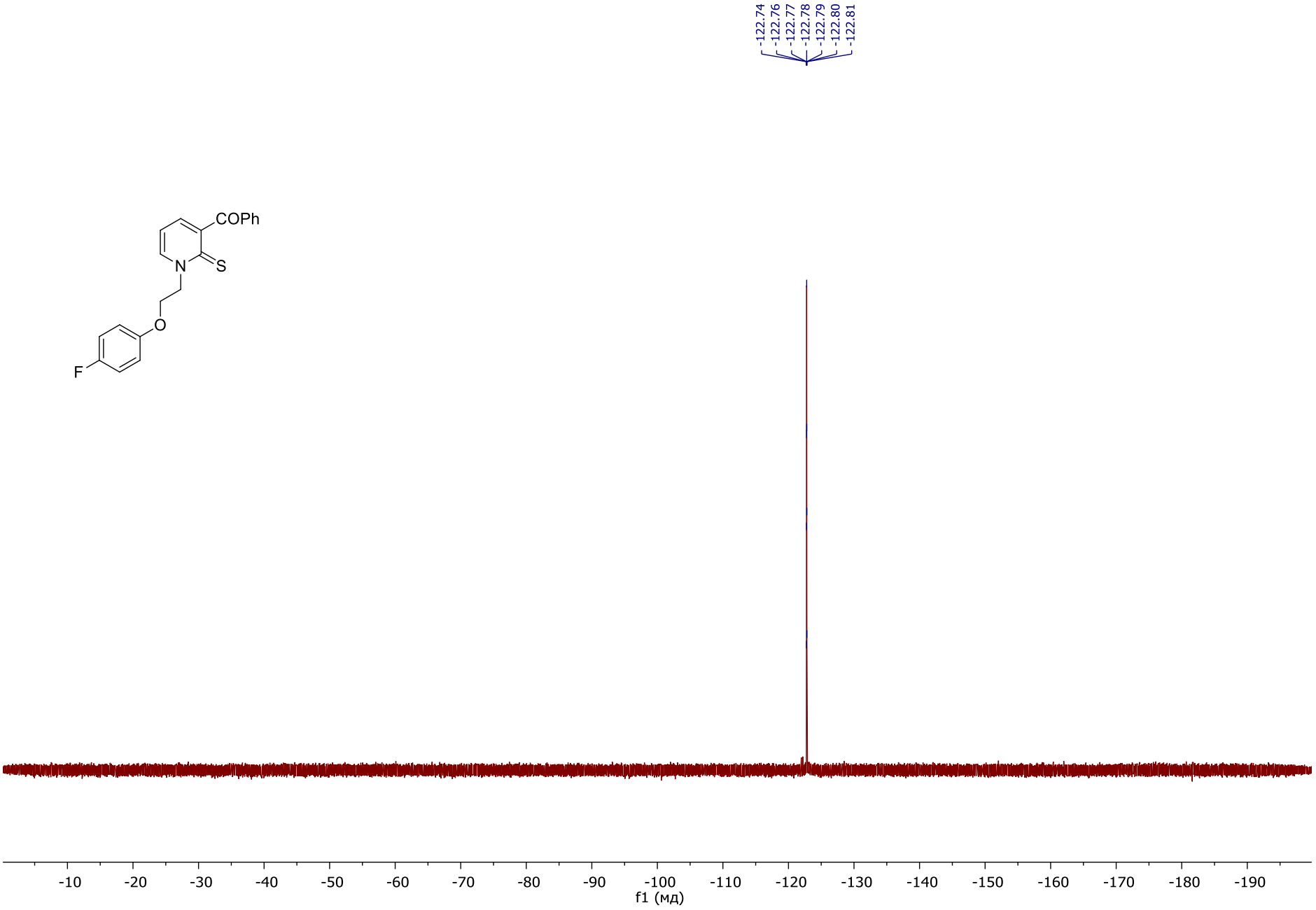
^{1}H NMR (400 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3m**)



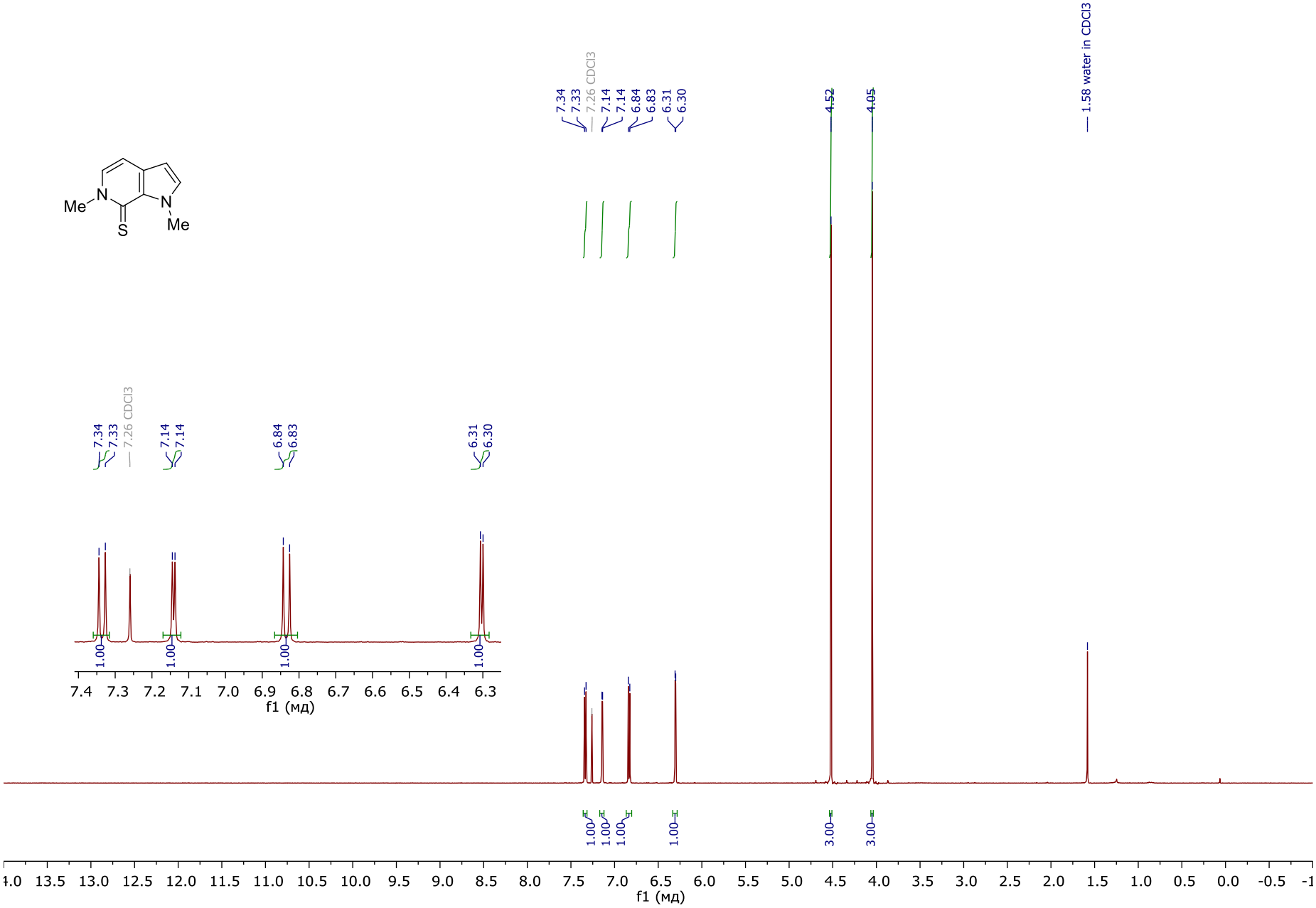
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3m**)



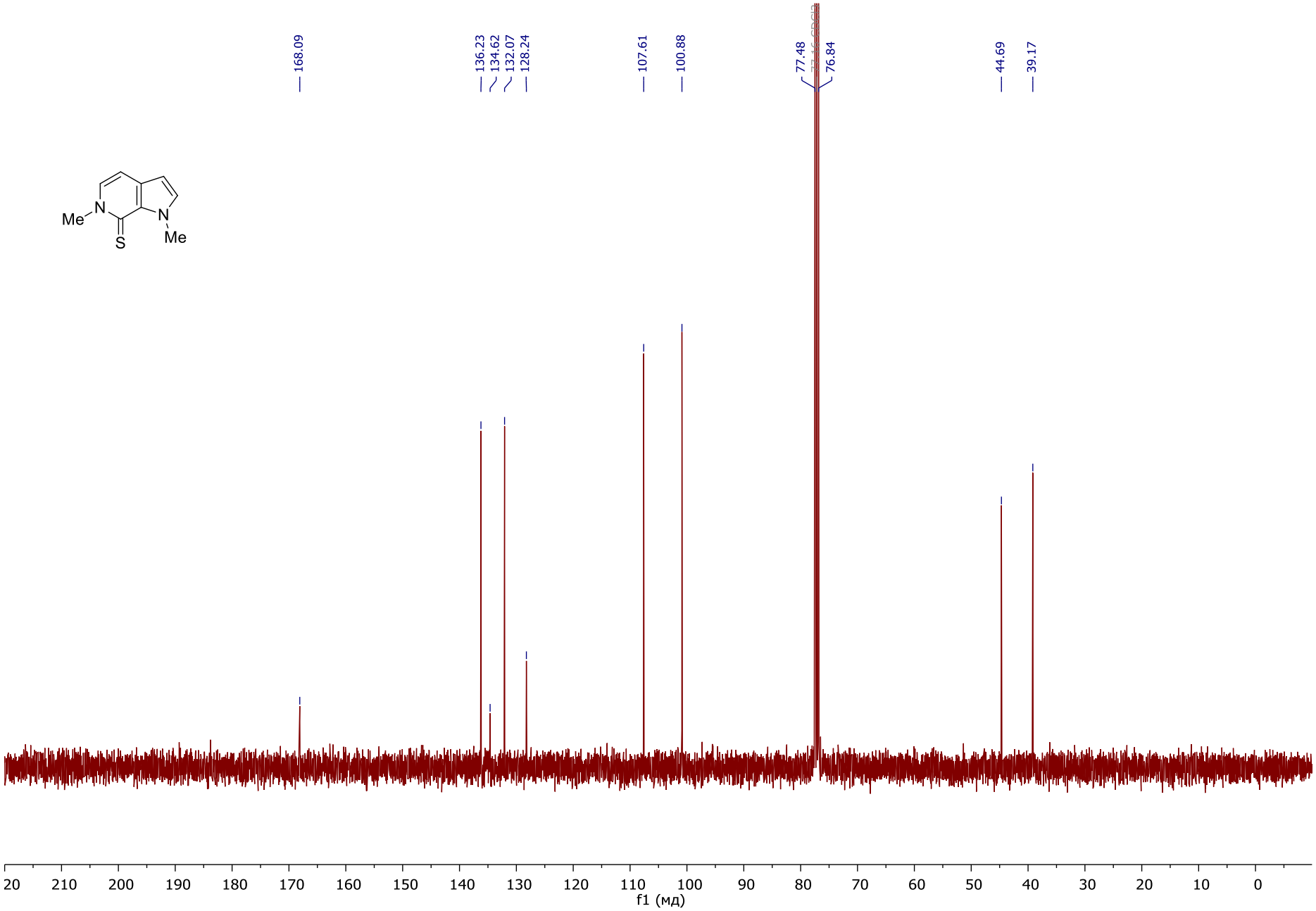
^{19}F NMR (376 MHz, $CDCl_3$) of (1-(2-(4-fluorophenoxy)ethyl)-2-thioxo-1,2-dihydropyridin-3-yl)(phenyl)methanone (**3m**)



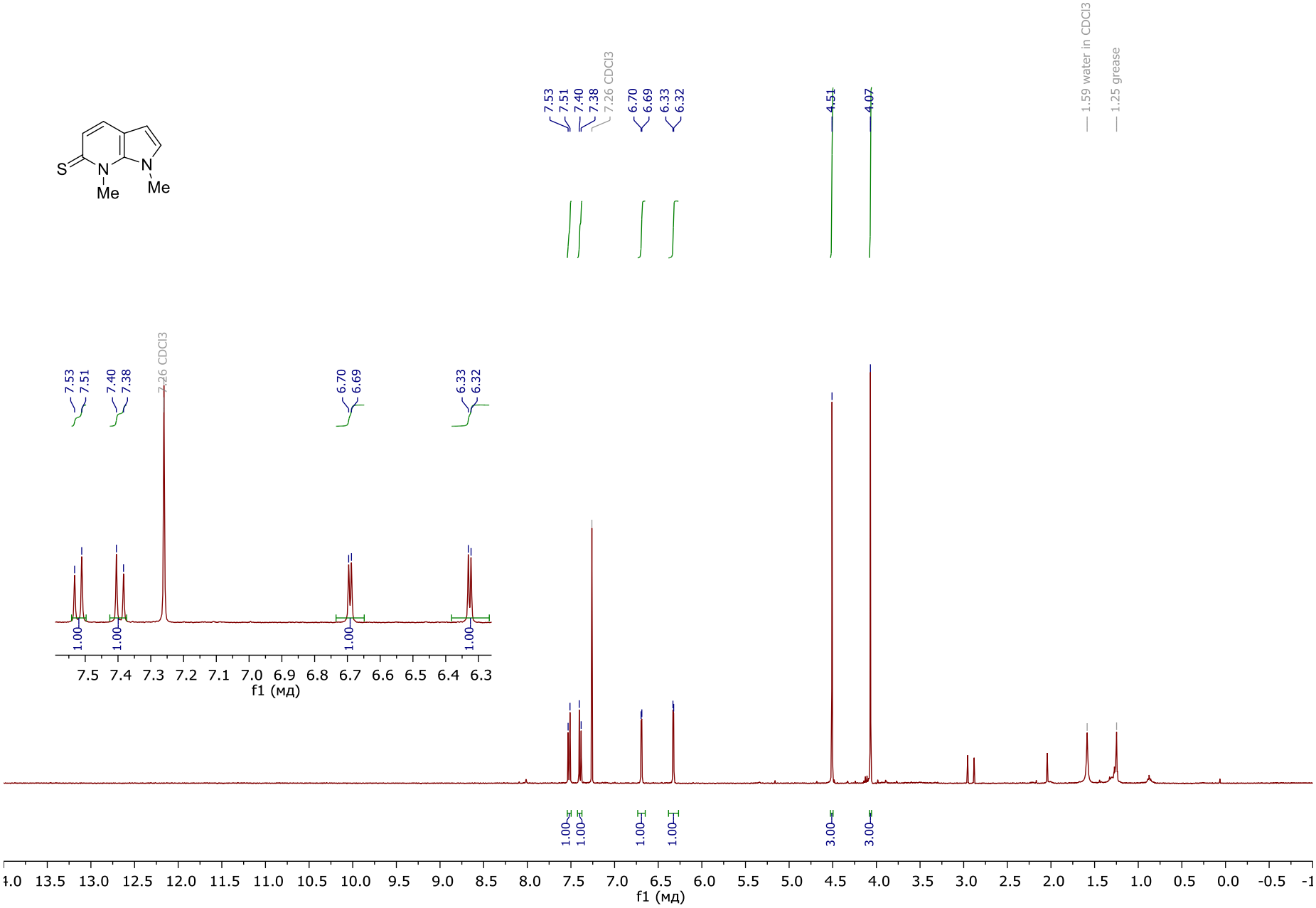
^{1}H NMR (400 MHz, $CDCl_3$) of 1,6-dimethyl-1*H*-pyrrolo[2,3-*c*]pyridine-7(6*H*)-thione (**3n**)



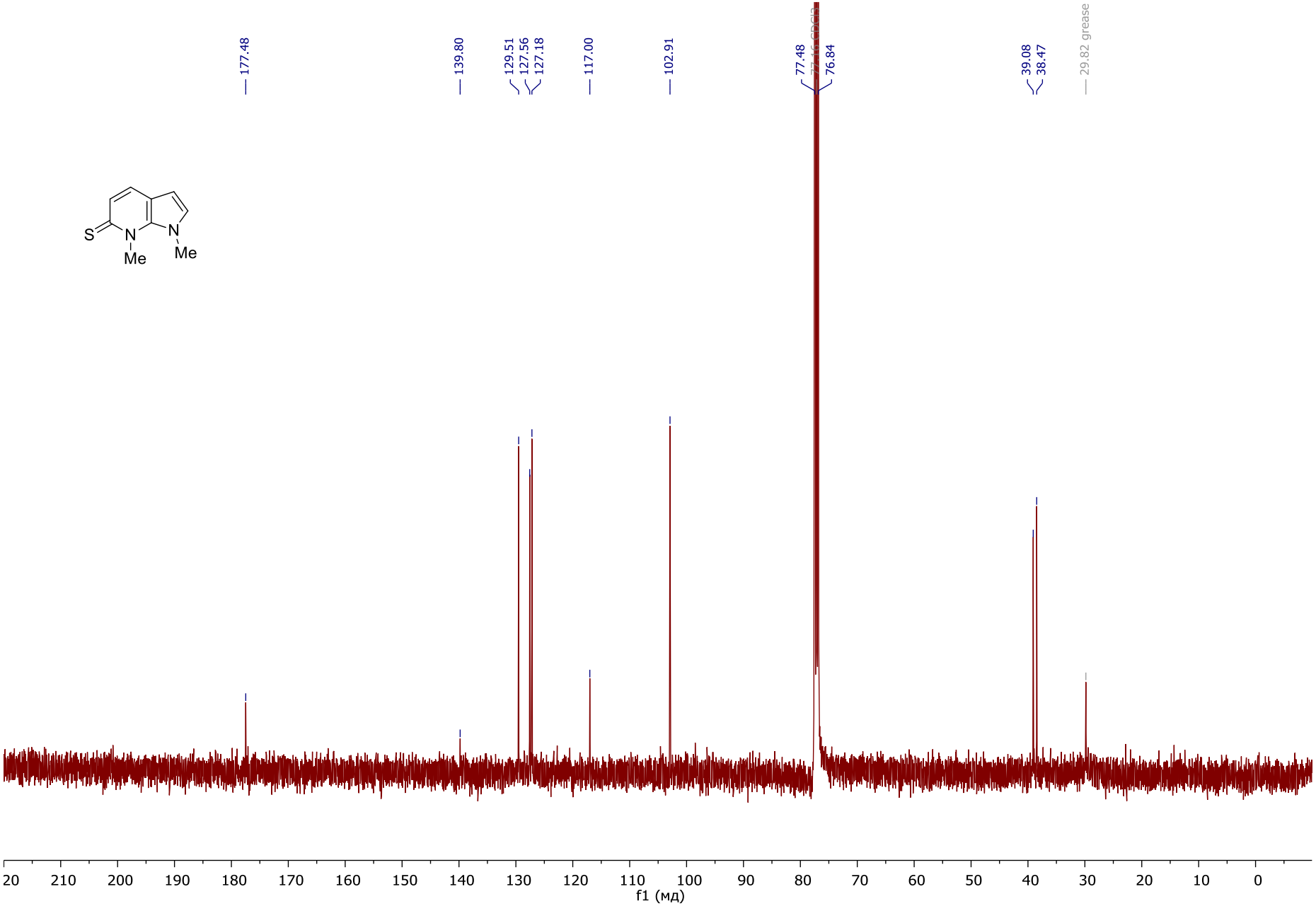
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1,6-dimethyl-1*H*-pyrrolo[2,3-*c*]pyridine-7(6*H*)-thione (**3n**)



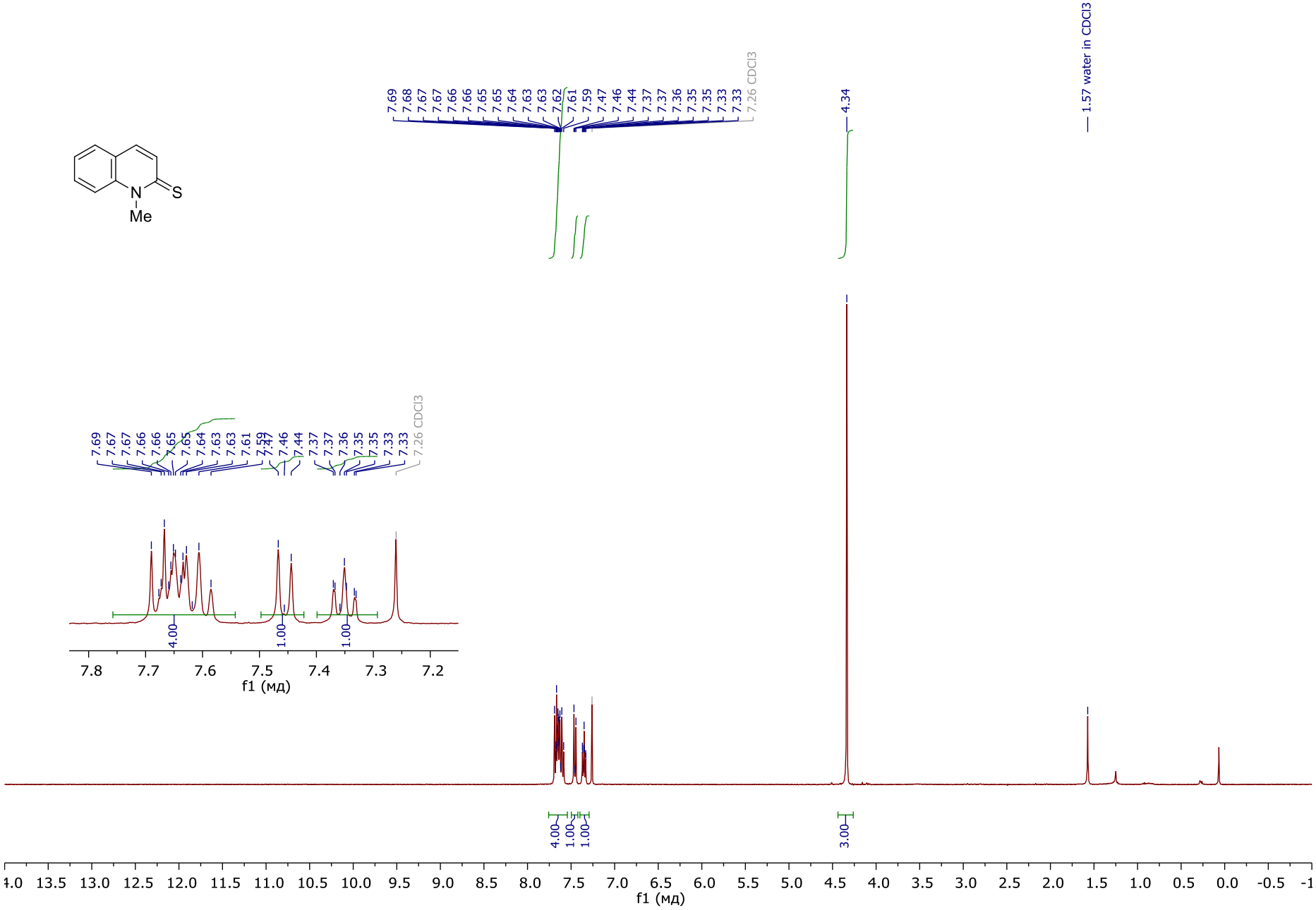
^{1}H NMR (400 MHz, $CDCl_3$) of 1,7-dimethyl-1*H*-pyrrolo[2,3-*b*]pyridine-6(7*H*)-thione (**3o**)



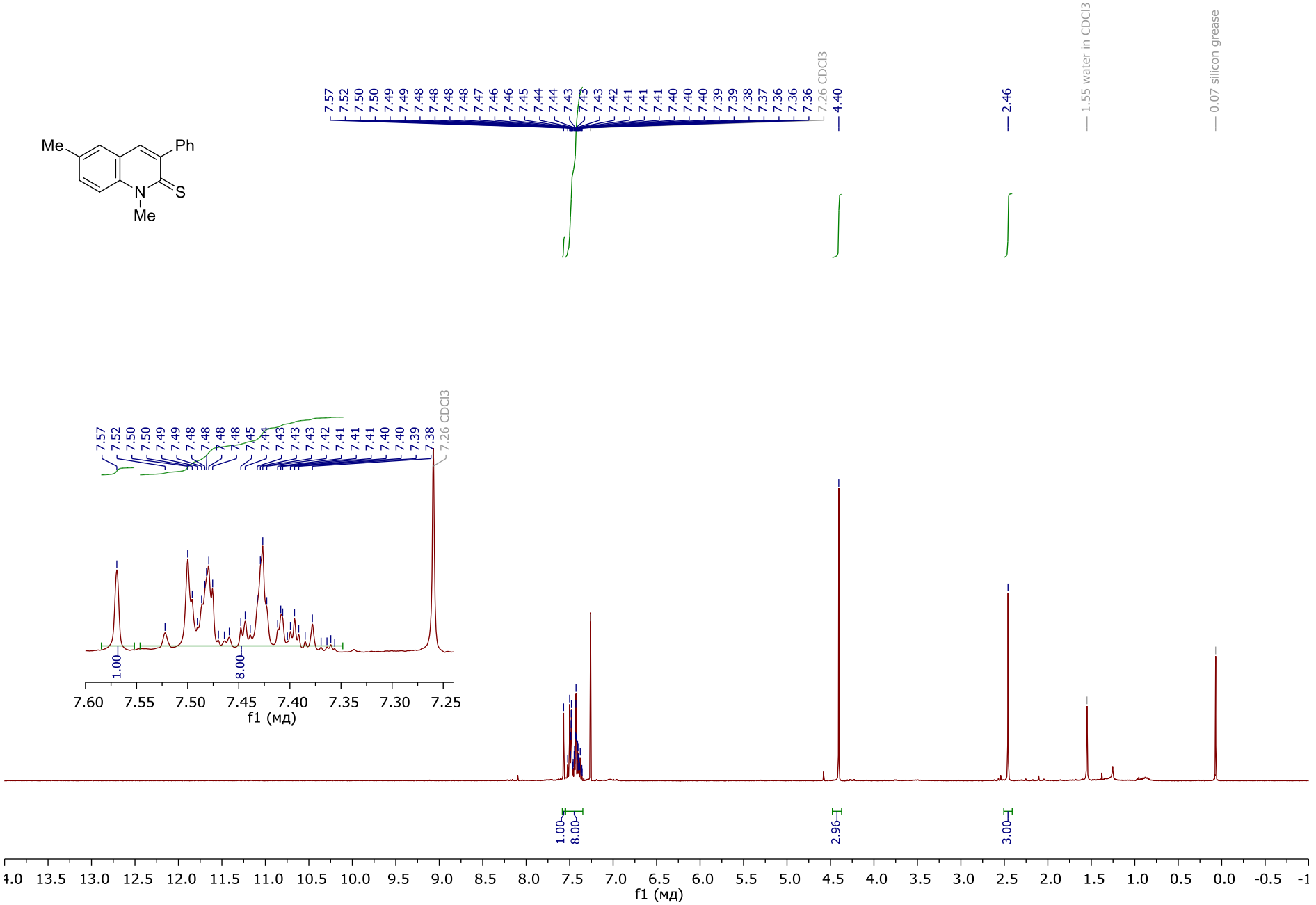
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1,7-dimethyl-1*H*-pyrrolo[2,3-*b*]pyridine-6(7*H*)-thione (**3o**)



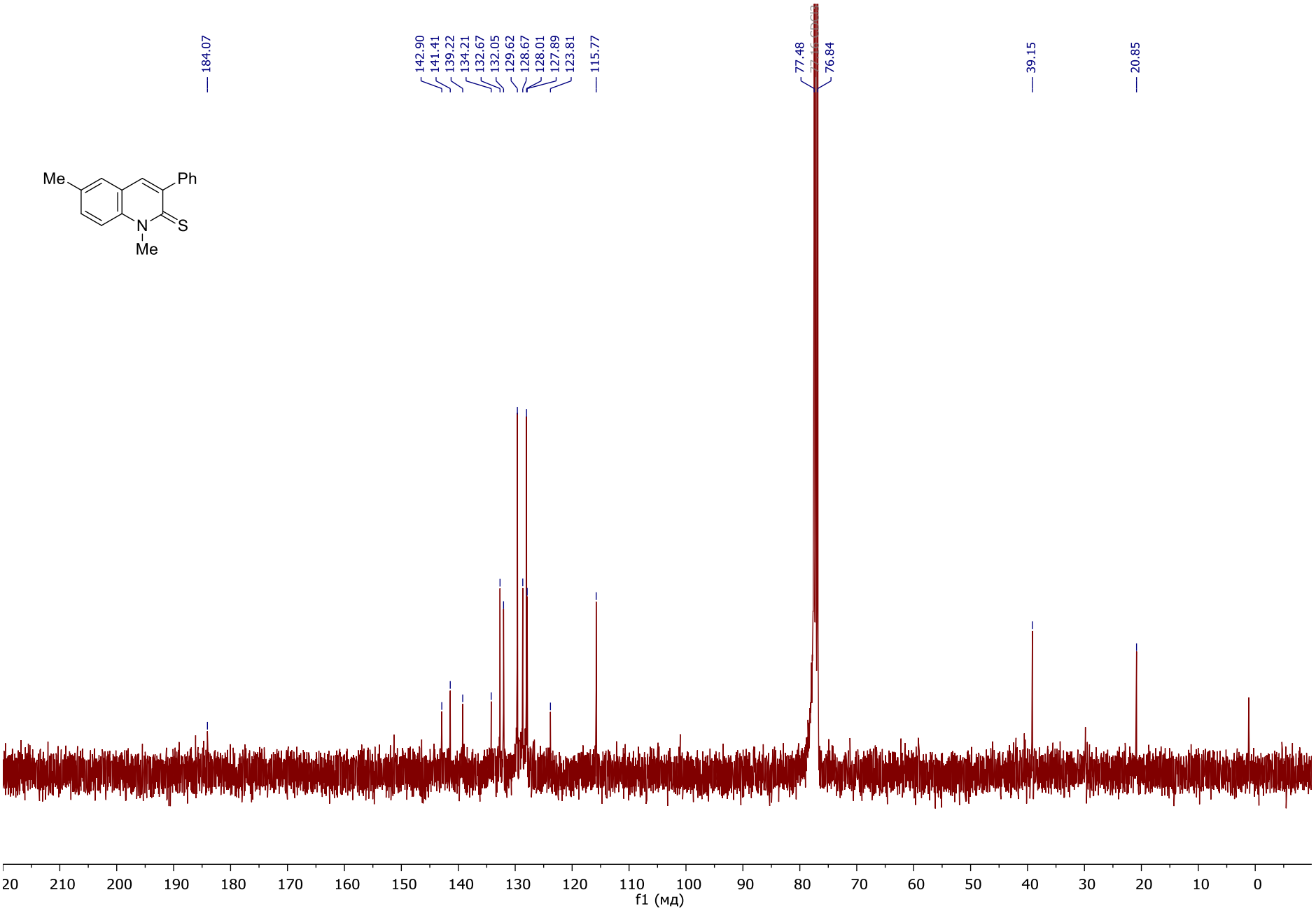
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methylquinoline-2(1*H*)-thione (**3p**)



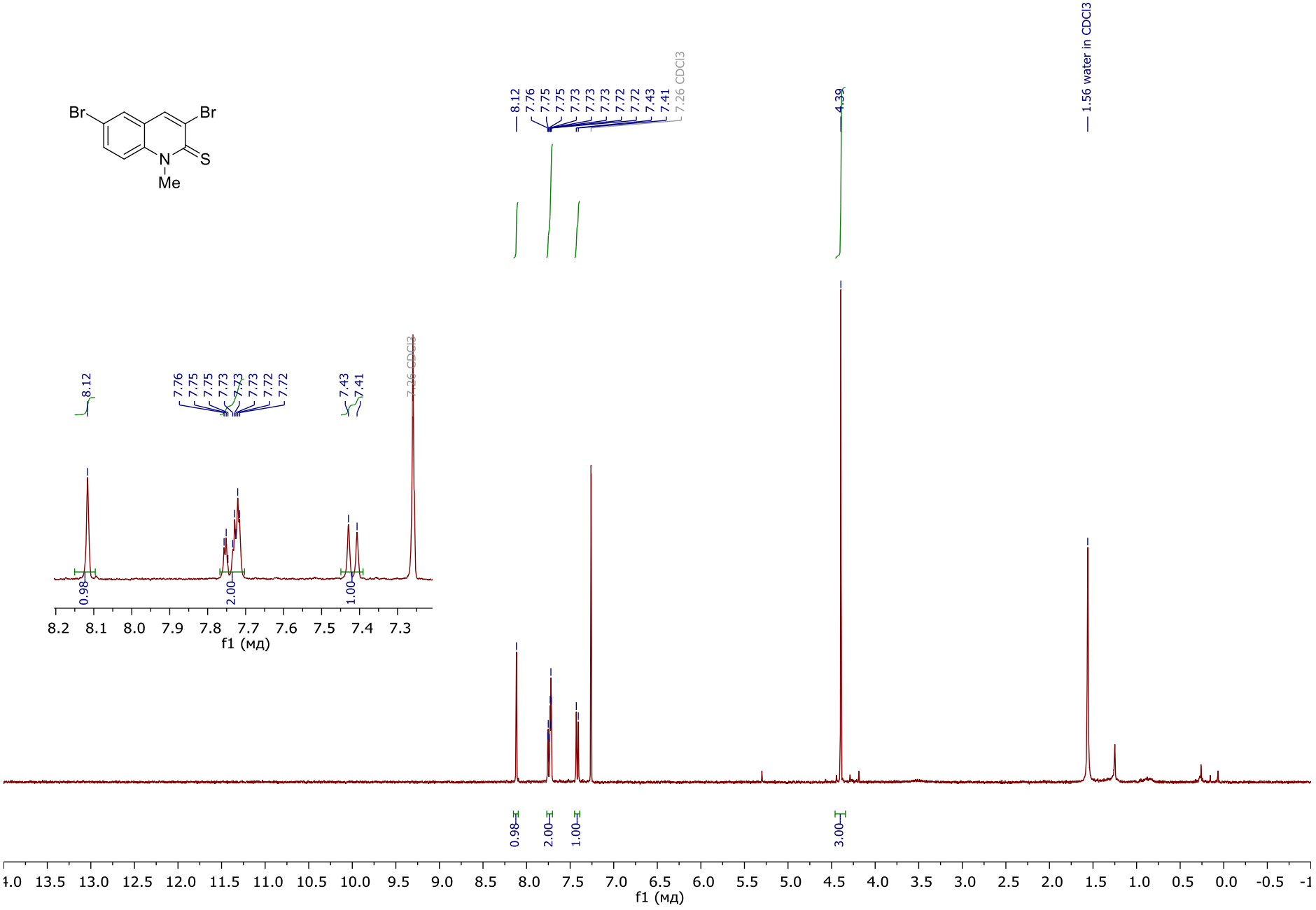
^{1}H NMR (400 MHz, $CDCl_3$) of 1,6-dimethyl-3-phenylquinoline-2(1*H*)-thione (**3q**)



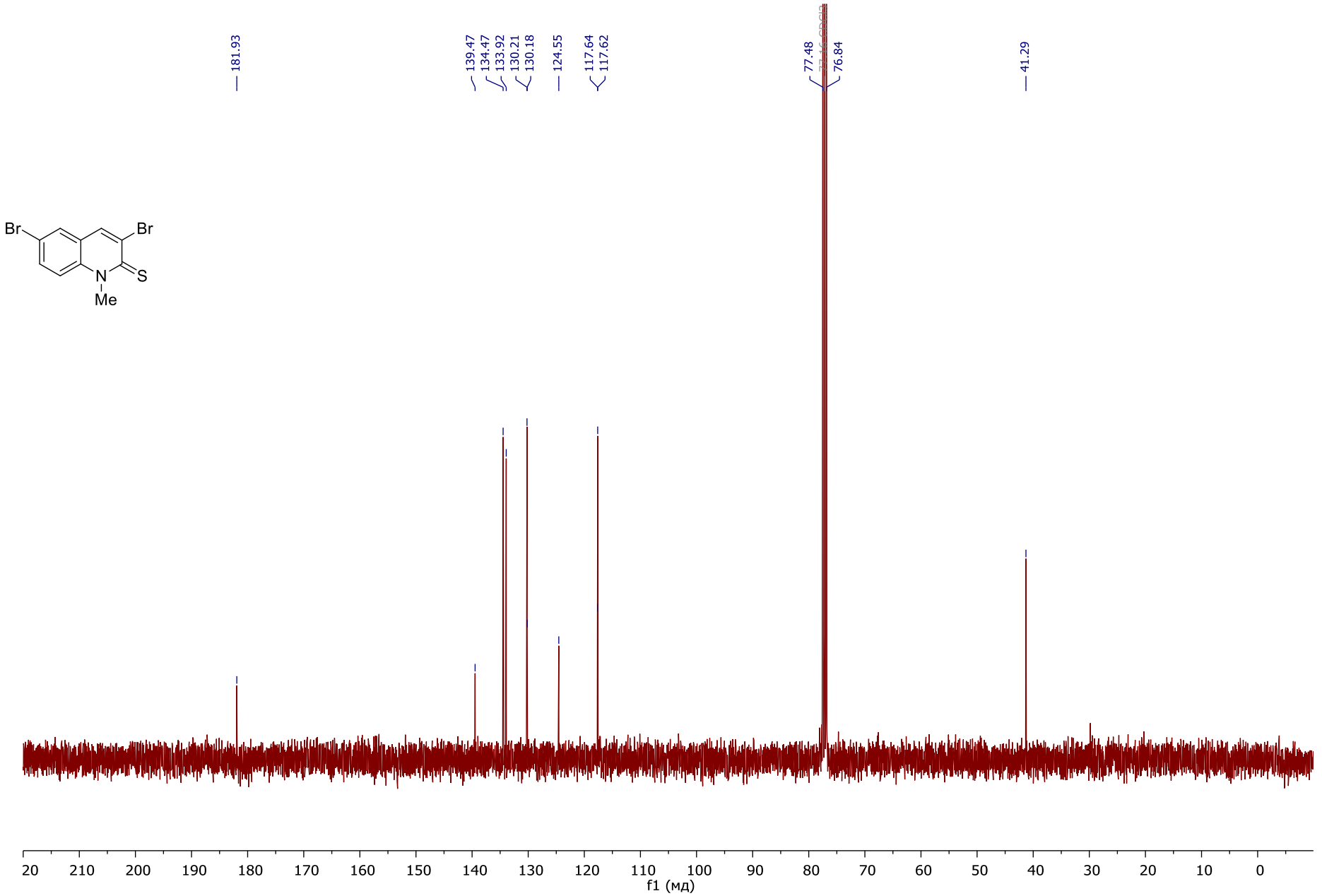
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1,6-dimethyl-3-phenylquinoline-2(1*H*)-thione (**3q**)



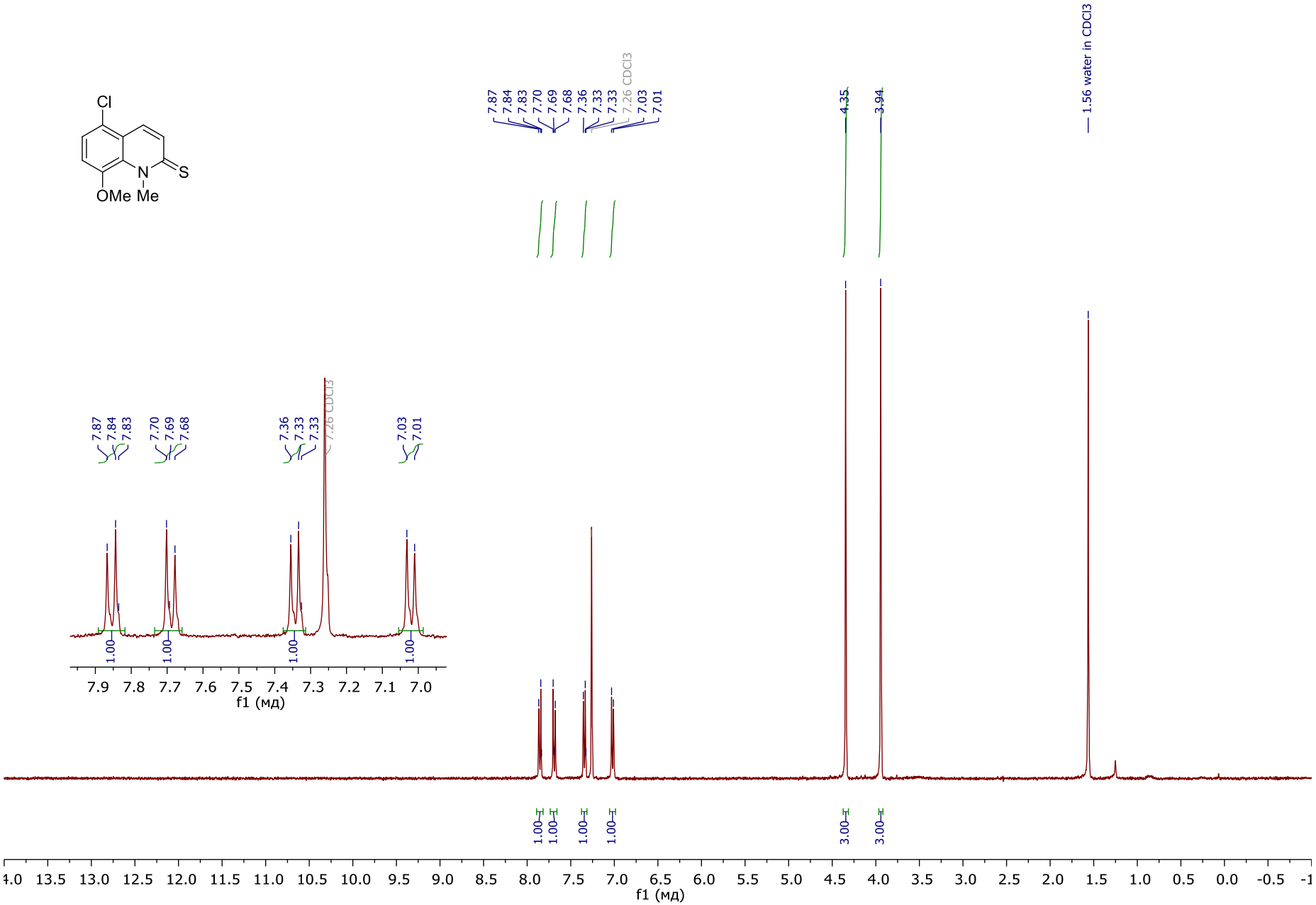
^{1}H NMR (400 MHz, $CDCl_3$) of 3,6-dibromo-1-methylquinoline-2(1*H*)-thione (**3r**)



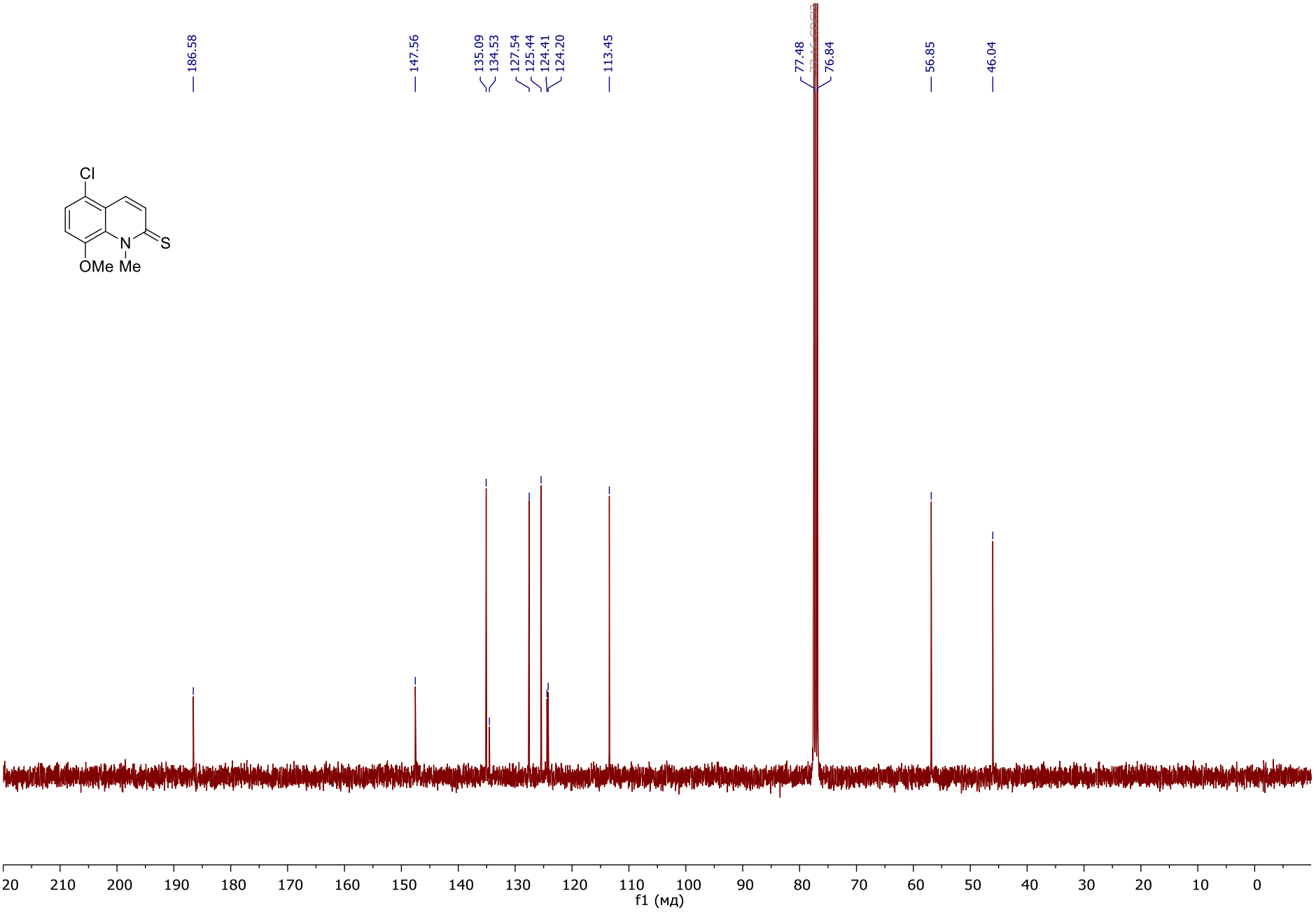
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 3,6-dibromo-1-methylquinoline-2(1*H*)-thione (**3r**)



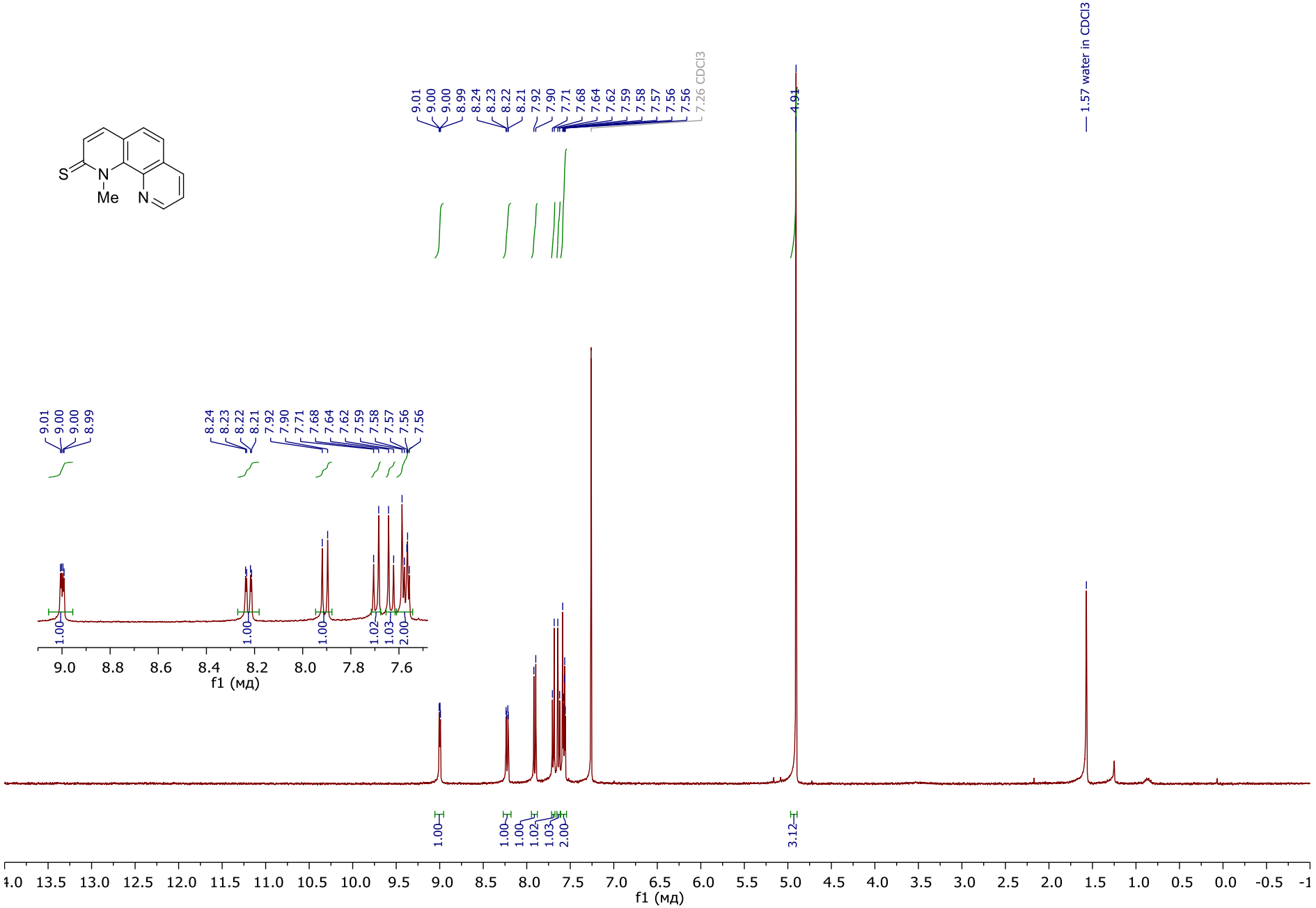
^{1}H NMR (400 MHz, $CDCl_3$) of 5-chloro-8-methoxy-1-methylquinoline-2(1*H*)-thione (**3s**)



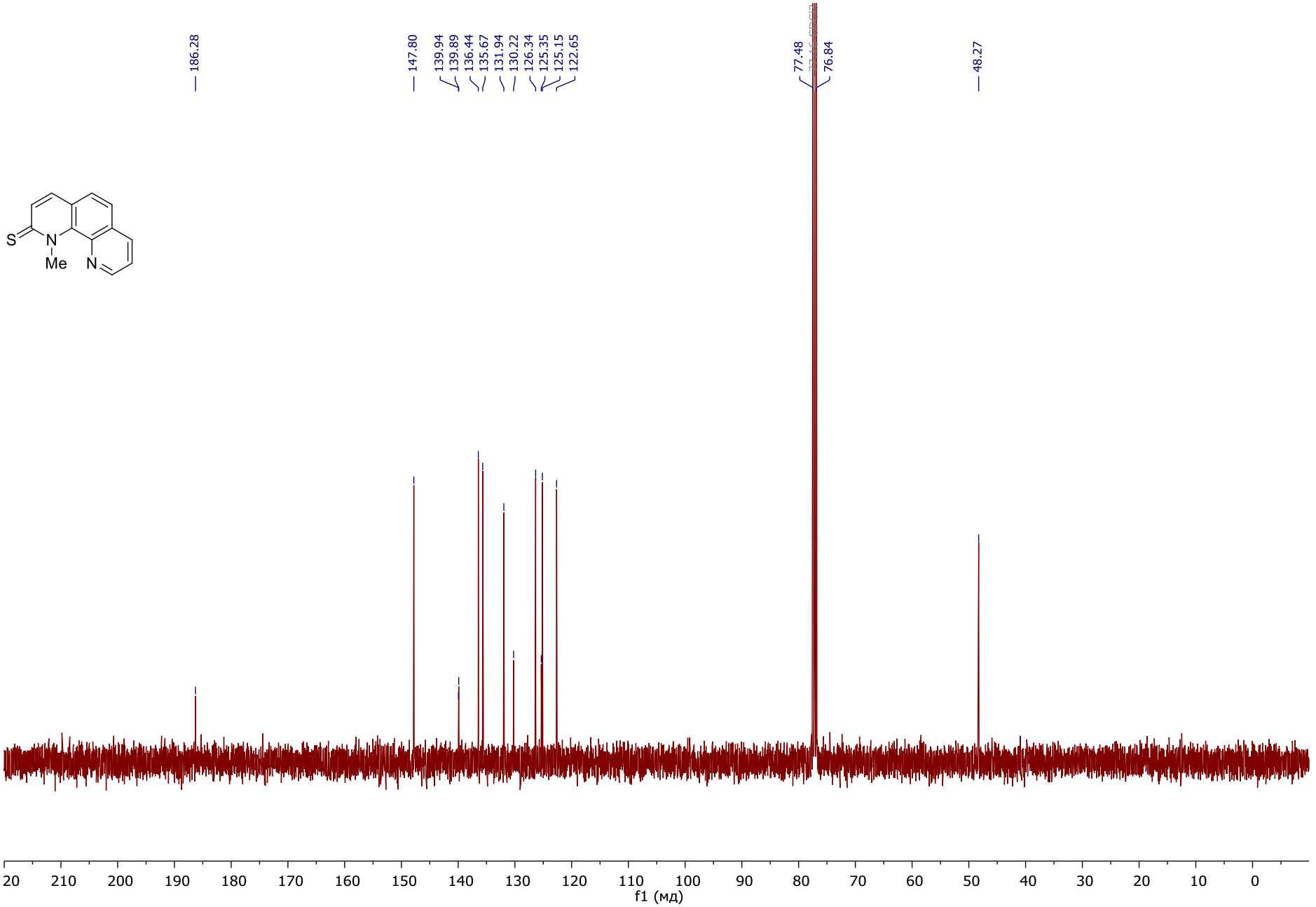
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 5-chloro-8-methoxy-1-methylquinoline-2(1*H*)-thione (**3s**)



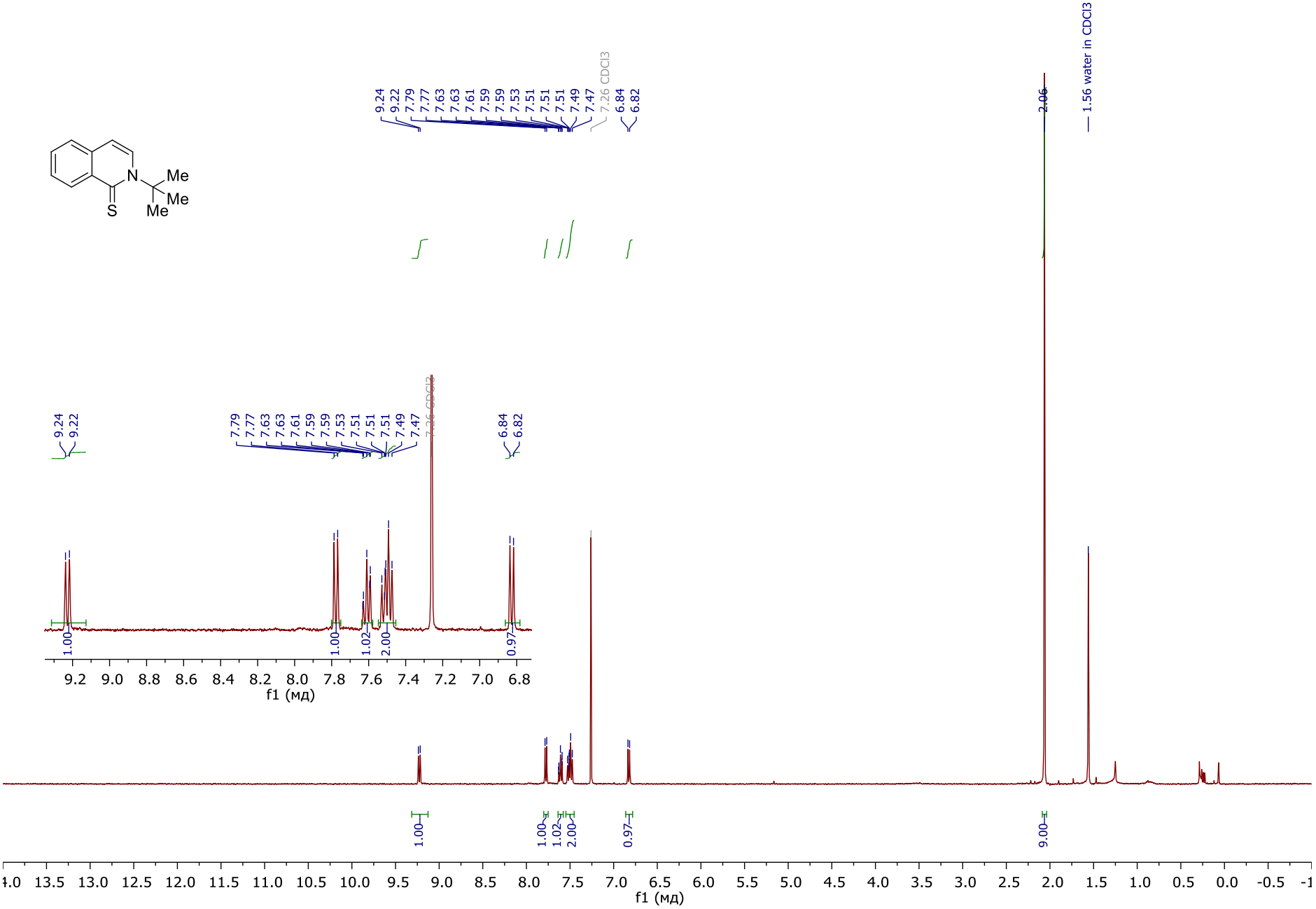
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methyl-1,10-phenanthroline-2(1*H*)-thione (**3t**)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 1-methyl-1,10-phenanthroline-2(1*H*)-thione (**3t**)



^{1}H NMR (400 MHz, $CDCl_3$) of 2-(*tert*-butyl)isoquinoline-1(2*H*)-thione (**3u**)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 2-(*tert*-butyl)isoquinoline-1(2*H*)-thione (**3u**)