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Systems with annulated thioxo azepinone moiety: an access through heterocyclic carbodithioate ring expansion

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1. General Information

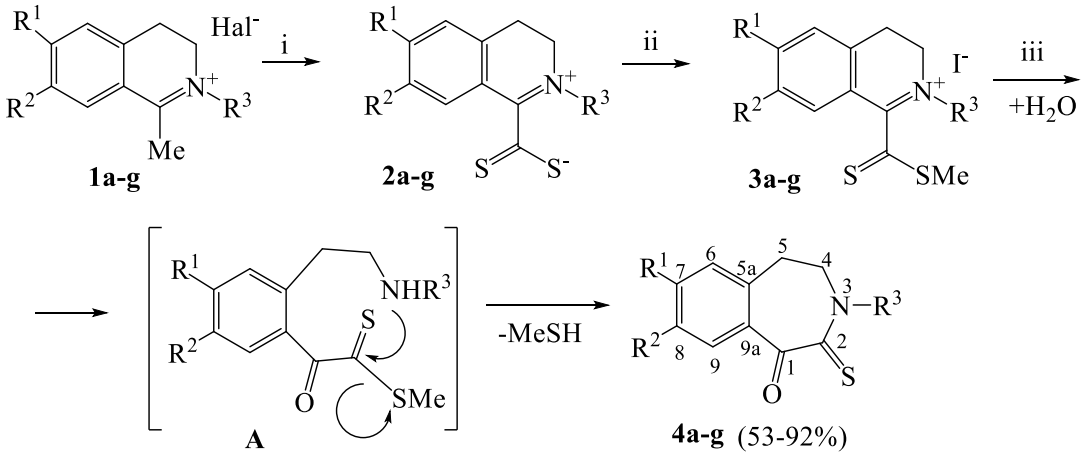
NMR spectra of newly synthesized compounds were recorded on a spectrometer Bruker Avance 600 (600 MHz) in DMSO-d_6. Chemical shifts of nuclei ^{1}H, ^{13}C and ^{15}N were measured relatively the residual signals of deuterosolvent at 30°C [δ =2.50 ppm for protons and 39.09 ppm for carbon; (see ref. [S1] and literature cited therein) and $^{15}NH_3$, respectively. Coupling constants (*J*) are reported in Hz. Melting points were determined by using Fisher-Johns Melting Point Apparatus (Fisher Scientific) and are uncorrected. High Resolution Mass Spectra for structures **4a,c** were registered on a Bruker UHR-TOF MaxisTM Impact instrument. Elemental analysis was performed by the classical method of microanalysis. The reaction and purity of the obtained compounds were monitored by TLC (plates with Al_2O_3, activity III grade, eluent $CHCl_3$, development of TLC plates by exposition to iodine vapors in iodine chamber).

The crystallographic data for structure **4c** were obtained on an Agilent SuperNova diffractometer by using a microfocus X-ray source with copper anode and an Atlas S2 two-dimensional CCD detector. The reflections were collected, unit cell parameters determined and refined by using the specialized CrysAlisPro 1.171.38.41 software suite (Rigaku Oxford Diffraction, 2015) [S2]. The structures were solved by using the ShelXT program (Sheldrick, 2015) [S3] and refined with the ShelXL program (Sheldrick, 2015) [S4].

Molecular graphics for structure **4c** were performed with the Olex2 software suite (ver 1.2.7) [S5]. CCDC 1897576 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

The solvents were purified according to standard procedures. Starting and intermediate compounds **1a, 1c** [S6], 1**e** [S7], **2a,c** [S8], **3c** [S8] were synthesized as described previously. 6,7-Dimethoxy-1-methyl-3,4-dihydroisoquinoline, used for preparation salt **1c**, and hydrogenated pyrido[3,4-*b*]indol-2-ium iodide **5** were provided by InterBioscreen Ltd (Russia).

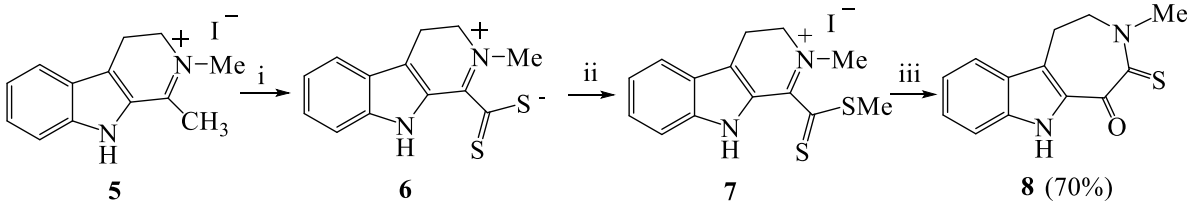
2. Synthesis and characterization of compounds 1-4, 6, 8.



1a-f Hal = I
1g Hal = Br

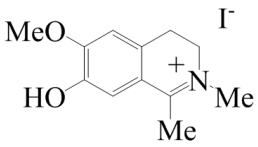
a $R^1 = R^2 = H$, $R^3 = Me$
b $R^1 = OMe$, $R^2 = OH$, $R^3 = Me$
c $R^1 = R^2 = OMe$, $R^3 = Me$
d $R^1 = R^2 = OMe$, $R^3 = Et$
e $R^1 = R^2 = OMe$, $R^3 = Bu$
f $R^1 = R^2 = OMe$, $R^3 = n\text{-}C_6H_{13}$
g $R^1 = R^2 = OMe$, $R^3 = PhO(CH_2)_2$

Reagents and conditions: i, S_8, K_2CO_3, DMF, 30-45°C; ii, MeI, CH_2Cl_2, boiling; iii, $NaHCO_3$, H_2O, EtOH, 20-60°C.



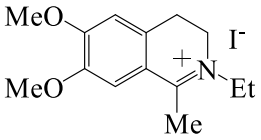
Reagents and conditions: i, S_8, K_2CO_3, DMF, 30-45ºC; ii, MeI, CH_2Cl_2, reflux; iii, $NaHCO_3$, H_2O, EtOH, boiling.

7-Hydroxy-6-methoxy-1,2-dimethyl-3,4-dihydroisoquinolin-2-ium iodide (**1b**).



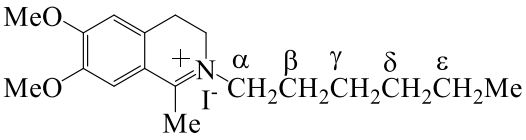
7-Hydroxy-6-methoxy-1,2-dimethyl-3,4-dihydroisoquinoline required for quaternization was obtained from 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline by O-demethylation upon action of conc. HBr [S9]. ^{1}H NMR, δ, ppm: 2.20 (s, 3H, Me), 2.51-2.54 (m, C(4)H_2), 3.44-3.47 (m, 2H, C(3)H_2), 3.81 (s, 3H, OMe), 6.81 (s, 1H, H-5); 6.96 (s, 1H, H-8), 8.97 (s, 1H, OH) (cf., [9]).Mp 184-186 °C (EtOH). ^{1}H NMR, δ, ppm: 2.20 (s, 3H, Me), 2.51-2.54 (m, C(4)H_2), 3.44-3.47 (m, 2H, C(3)H_2), 3.81 (s, 3H, OMe), 6.81 (s, 1H, H-5), 6.96 (s, 1H, H-8), 8.97 (s, 1H, OH). ^{13}C NMR (150 MHz) δ: 22.83, 25.08, 46.39, 55.57, 110.79, 112.72, 122.08, 128.58, 144.73, 149.35, 162.35. Next, a mixture of 7-hydroxy-6-methoxy-1-methyl-3,4-dihydroisoquinoline (0.75 g, 0.003 mol), $CHCl_3$ (12 mL) and MeI (0.25 mL, 0.57 g, 0.004 mol) were boiled for 3 h, cooled, the precipitate was filtered off and washed with $CHCl_3$ (3×3 mL). Yield of salt **1b** was almost quantitative. Colorless crystals, mp 235-237°C (EtOH). ^{1}H NMR, δ, ppm: 2.69 (s, 3H, Me), 3.04 (t, *J* 7.7, 2H, C(4)H_2), 3.66 (s, 3H, Me), 3.93-3.96 (m, 5H, OMe, C(3)H_2), 7.09 (s, 1H, H-5), 7.38 (s, 1H, H-8), 9.54 (s, 1H, OH). ^{13}C NMR (150 MHz) δ: 18.32, 24.70, 44.14, 51.97, 56.21, 110.96, 116.29, 119.52, 130.45, 145.55, 154.24, 173.66. Found (%): C, 43.00; H, 4.63; I, 37.66; N, 4.03. Calc. for $C_{12}H_{16}INO_2$ (%): C, 43.26; H, 4.84; I, 38.09; N, 4.20.

2-Ethyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide (**1d**).



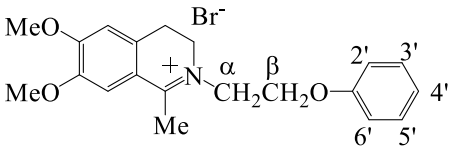
A mixture of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (0.62 g, 0.003 mol), ethyl iodide (0.78 g, 0.40 mL, 0.005 mol) in dry acetone (5 mL) was refluxed 8 h. The mixture was cooled, and the precipitate was filtered off and washed with acetone (10 mL). Yield of compound **1d** was 0.81 g (75%). Colorless crystals with mp 169-170 °C (*n*-PrOH). ^{1}H NMR, δ, ppm: 1.36 (t, *J* 7.2, 3H, CH_2Me), 2.83 (s, 3H, Me), 3.05 (t, *J* 7.7, 2H, C(4)H_2), 3.86 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.94-4.02 (m, 4H, C(3)H_2, CH_2Me), 7.13 (s, 1H, H-8), 7.47 (s, 1H, H-5). ^{13}C NMR (150 MHz) δ: 12.33, 18.00, 25.03, 49.29, 51.37, 56.24, 56.27, 110.75, 112.96, 119.54, 132.65, 147.80, 155.20, 173.37. Found (%): C, 46.24; H, 5.29; I, 35.41, N, 3.69. Calc. for $C_{14}H_{20}INO_2$ (%): C, 46.55; H, 5.58; I, 35.13, N, 3.88.

2-n-Hexyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide (**1f**).



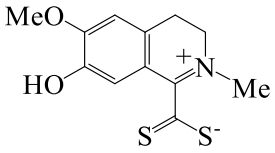
A mixture of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (4.11 g, 0.02 mol), *n*-hexyl iodide (5.30 g, 3.60 mL, 0.025 mol) in *n*-PrOH (20 mL) was refluxed 6 h. The mixture was cooled, then ether (100 mL) was added, the liquid was decanted from a viscous mass. Toluene (15 mL) was added, and this was heated until the product crystallized, the hot mixture was filtered and the precipitate was washed with hot toluene (2×10 mL). Yield of compound **1f** was 6.17 g (74%). Colorless crystals with mp 133-135°C (dioxane). ^{1}H NMR, δ, ppm: 0.82 (s, 3H, Me), 1.23-1.43 [m, 6H, C(γ)H$_2$ – C(ε)H$_2$], 1.71-1.81 (m, 2H, C(β)H$_2$), 2.82 (s, 3H, Me), 3.03 (dd, *J* 9.8, 5.5, 2H, C(4)H$_2$), 3.85 (s, 3H, OMe), 3.88-3.98 (m, 7H, OMe, C(α)H$_2$), 7.13 (s, 1H, H-8), 7.47 (s, 1H, H-5). Found (%): C, 51.46; H, 6.43; I, 29.89, N, 3.08.Calc. for $C_{18}H_{28}INO_2$ (%): C, 51.80; H, 6.76; I, 30.41, N, 3.36.

6,7-Dimethoxy-1-methyl-2-(2-phenoxyethyl)-3,4-dihydroisoquinolin-2-ium bromide (**1g**).



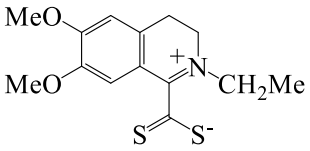
A mixture of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (0.62 g, 0.003 mol), 2-phenoxyethyl bromide (0.60 g, 0.003 mol) in dry acetone (10 mL) was refluxed 2 h. Acetone was evaporated, the residue was heated with EtOAc (8 mL), the resulting precipitate was filtered off and treated with boiling acetone (7 mL). Yield of compound **1g** was 1.07 g (88%). Colorless crystals with mp 179-180°C (EtOH). ^{1}H NMR, δ, ppm: 2.93 (s, 3H, Me), 3.04 (t, *J* 7.6, 2H, C(4)H$_2$), 3.87 (s, 3H, OMe), 3.90 (s, 3H, OMe), 4.07 (t, *J* 7.7, 2H, C(3)H$_2$), 4.42-4.48 (m, 4H, C(α)H$_2$, C(β)H$_2$), 6.93-7.00 (m, 3H, H-2', H-4', H-6'), 7.14 (s, 1H, H-8), 7.27-7.33 (m, 2H, H-3', H-5'), 7.52 (s, 1H, H-5). Found (%): C, 59.33; H, 5.60; Br, 19.74, N, 3.31. Calc. for $C_{20}H_{24}BrNO_3$ (%): C, 59.12; H, 5.95; Br, 19.67; N, 3.45.

7-Hydroxy-6-methoxy-2-methyl-3,4-dihydroisoquinolinium-1-carbodithioate (**2b**).



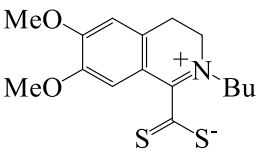
A mixture of 7-hydroxy-6-methoxy-1,2-dimethyl-3,4-dihydroisoquinolin-2-ium iodide **1c** (1.1 g, 0.005 mol), sulfur (0.33 g; 0.01 mol), morpholine (1.75 g; 2 mL, 0.02 mol) and DMF (10 mL) was stirred vigorously 4 h at 40-42°C. After reaction completion, water (30 mL) and AcOH (3 mL) were added, and this was kept at 10-15°C for 10 h. Product **2c** was filtered off and washed with water (4×3 mL), the yield was 0.5 g (54%). Red crystals with mp 238-240°C (EtOH). ^{1}H NMR, δ, ppm: 3.07 (t, *J* 7.7, 2H, C(4)H_2), 3.43 (s, 3H, Me), 3.88-3.93 (m, 5H, OMe, C(3)H_2), 6.99 (s, 1H, H-5), 7.27 (s, 1H, H-8), 9.53 (s, 1H, OH). ^{13}C NMR (150 MHz) δ: 24.80, 41.73, 50.29, 55.96, 110.88, 116.70, 117.15, 131.31, 145.41, 153.86, 169.26, 235.96. Found (%): C, 53.55; H, 4.72; N, 5.03, S 23.59. Calc. for $C_{12}H_{13}NO_2S_2$ (%): C, 53.91; H, 4.90; N, 5.24, S 23.98.

2-Ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium-1-carbodithioate (**2d**).



A mixture of 2-ethyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide **1d** (1.08 g, 0.003 mol), sulfur (0.96 g; 0.03 mol), morpholine (0.87 g; 0.86 mL, 0.01 mol), K_2CO_3 (1.38 g; 0.01 mol) and DMF (10mL) was stirred vigorously 4 h under 30-35°C. After reaction completion, water (30 mL) was added, and this was kept 20-25°C for 10 h. Dithiocarboxylate **2d** was filtered off and washed with water (3×10 mL). Yield of compound **2d** was 0.74g (83%). Red crystals with mp 195-197°C (EtOH). ^{1}H NMR, δ, ppm: 1.35 (t, *J* 7.2, 3H, CH_2Me), 3.08 (t, *J* 7.6, 2H, C(4)H_2), 3.64 (s, 3H, OMe), 3.81-3.85 (m, 2H, CH_2Me), 3.88-3.90 (m, 5H, OMe, C(3)H_2), 7.06 (s, 1H, H-5), 7.28 (s, 1H, H-8). ^{13}C NMR (150 MHz) δ: 11.91, 25.03, 46.93, 49.67, 55.66, 56.13, 110.81, 113.43, 116.45, 133.72, 147.51, 154.75, 169.03, 235.34. Found (%): C, 56.58; H, 5.49; N, 4.60; S, 21.86. Calc. for $C_{14}H_{17}NO_2S_2$ (%): C, 56.92; H, 5.80; N, 4.74; S, 21.71.

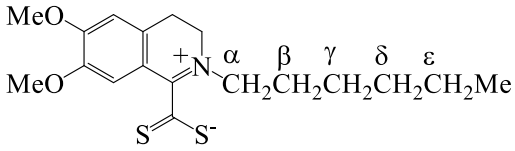
2-Butyl-6,7-dimethoxy-3,4-dihydroisoquinolinium-1-carbodithioate (**2e**).



A mixture of 2-butyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide **1e** [S7] (3.9 g , 0.01 mol), sulfur (0.96 g; 0.03 mol), morpholine (3 g, 3 mL, 0.035 mol), K_2CO_3 (2.76

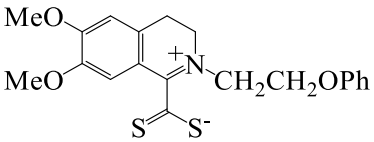
g; 0.02 mol) and DMF (15 mL) was stirred vigorously 3 h under 28-32°C. After the reaction was complete, water (60 mL) was added, dithiocarboxylate **2e** was filtered off and washed with water (4×15 mL). Yield of compound **2e** was 2.0 g (63%). Red crystals with mp 176-178°C (EtOH). ^{1}H NMR, δ, ppm: 0.87 (t, *J* 7.4, 3H, Me), 1.27-1.31 (m, 2H, C(γ)H$_2$), 1.78-1.83 (m, 2H, CH$_2$), 3.06-3.08 (m, 2H, C(α)H$_2$), 3.63 (s, 3H, OMe), 3.73-3.79 (m, 2H, C(4)H$_2$), 3.88-3.90 (m, 5H, OMe, C(3)H$_2$), 7.06 (s, 1H, H-5), 7.28 (s, 1H, H-8). ^{13}C NMR (150 MHz) δ: 13.45, 19.46, 25.05, 28.40, 47.50, 54.13, 55.66, 56.13, 110.79, 113.47, 116.53, 133.74, 147.52, 154.76, 169.08, 235.34. Found (%): C, 59.20; H, 6.32; N, 4.52; S, 19.49. Calc. for C$_{16}$H$_{21}$NO$_2$S$_2$ (%): C, 59.41; H, 6.54; N, 4.33; S, 19.82.

2-Hexyl-6,7-dimethoxy-3,4-dihydroisoquinolinium-1-carbodithioate (**2f**).



A mixture of 2-hexyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide **1f** (6.26 g, 0.015 mol), sulfur (1.28 g; 0.04 mol), morpholine (3 g, 3 mL, 0.035 mol), K$_2$CO$_3$ (6.21 g; 0.045 mol) and DMF (20 mL) was stirred vigorously 4 h under 40-45°C. After reaction completion, water (100 mL) was added, dithiocarboxylate **2f** was filtered off, washed with water (3×20 mL) and treated with boiling EtOAc (12 mL). Yield of compound **2f** was 1.74 g (33%). Red crystals with mp 169-170°C (MeOH). ^{1}H NMR, δ, ppm: 0.82-0.87 (m, 3H, Me), 1.21-1.29 (m, 6H, C(ε)H$_2$ – C(γ)H$_2$), 1.79-1.83 (m, 2H, C(β)H$_2$), 3.06 (t, *J* 7.6, 2H, C(α)H$_2$), 3.62 (s, 3H, OMe), 3.72-3.77 (m, 2H, C(4)H$_2$), 3.87-3.90 (m, 5H, OMe, C(3)H$_2$), 7.06 (s, 1H, H-5), 7.26 (s, 1H, H-8). Found (%): C, 61.22; H, 6.94; N, 3.65; S, 19.49. Calc. for C$_{18}$H$_{25}$NO$_2$S$_2$ (%): C, 61.50; H, 7.17; N, 3.98; S, 18.24.

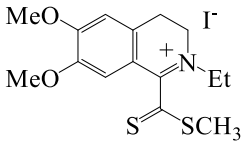
6,7-Dimethoxy-2-(2-phenoxyethyl)-3,4-dihydroisoquinolinium-1-carbodithioate (**2g**).



Compound **2g** was synthesized from 6,7-dimethoxy-1-methyl-2-(2-phenoxyethyl)-3,4-dihydroisoquinolin-2-ium bromide **1g** (4.06 g, 0.01 mol) analogously to compound **2f**. Yield of compound **2g** was 2.0 g (52%). Red crystals with mp 188-190°C (MeOH). ^{1}H NMR, δ, ppm: 3.08 (t, *J* 7.5, 2H, C(4)H$_2$), 3.63 (s, 3H, OMe), 3.88 (s, 3H, OMe), 4.02-4.07 (m, 2H, C(3)H$_2$), 4.21-4.25 (m, 2H, CH$_2$), 4.44-4.48 (m, 2H, CH$_2$), 6.93-6.98 (m, 3H, H-2', H-4', H-6'), 7.07 (s, 1H, H-5), 7.27-7.32 (m, 3H, H-3', H-5', H-8). Found (%): C, 61.72; H, 5.24; N, 3.65; S, 16.89. Calc. for C$_{20}$H$_{21}$NO$_3$S$_2$ (%): C, 61.99; H, 5.46; N, 3.61; S, 16.55.

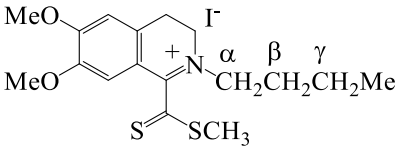
General procedure for the synthesis of 3,4-dihydroisoquinolinium iodides (**3d**,**e**). A mixture of 3,4-dihydroisoquinolinium-1-carbodithioate **2d** or **2e** (3 mmol), MeI (5 mmol) in CH_2Cl_2 (15 mL) was boiled 5 h. Then the excess of MeI and CH_2Cl_2 was distilled off, and the residue is recrystallized from a suitable solvent.

3,4-Dihydroisoquinolinium iodide **3d**.



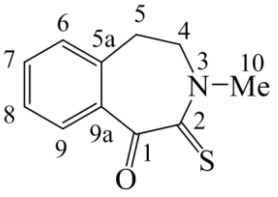
Yield of salt **3d** was 1.23 g (94%). Red crystals with mp 163-165°C (EtOH: EtOAc 1:1). ^{1}H NMR, δ, ppm: 1.35 (t, *J* 7.1, 3H, $CH_2\underline{Me}$), 3.05 (s, 3H, SMe), 3.16-3.21 (m, 1H, C(4)H_2), 3.30-3.36 (m, 1H, C(4)H_2), 3.70 (s, 3H, OMe), 3.86-3.99 (m, 5H,OMe, $\underline{CH_2}$Me), 4.14-4.25 (m, 2H, C(3)H_2), 6.91 (s, 1H, H-5), 7.26 (s, 1H, H-8). ^{13}C NMR (150 MHz) δ: 12.73, 19.99, 24.60, 48.75, 51.97, 55.22, 56.68, 111.65, 113.00, 115.55, 135.16, 148.02, 157.08, 168.99, 216.56. Found (%): C, 41.00; H, 4.21; I, 28.66; N, 3.44; S, 14.35. Calc. for $C_{15}H_{20}INO_2S_2$ (%): C, 41.19; H, 4.61; I, 29.02; N, 3.20; S, 14.66.

3,4-Dihydroisoquinolinium iodide **3e**.



Yield of compound **3e** was 1.37g (98%). Red crystals with mp 137-140°C (dioxane). ^{1}H NMR, δ, ppm: 0.87 (t, *J* 7.3, 3H, Me), 1.29-1.35 (m, 2H, C(γ)H_2), 1.70-1.76 (m, 1H, C(β)H_2), 1.80-1.85 (m, 1H, C(β)H_2), 3.05 (s, 3H, SMe), 3.15-3.21 (m, 1H, C(4)H_2), 3.30-3.35 (m, 1H, C(4)H_2), 3.70 (s, 3H, OMe), 3.80-3.86 (m, 1H, C(3)H_2), 3.87-3.90 (m, 1H, C(3)H_2), 3.95 (s, 3H, OMe), 4.14-4.26 (m, 2H, C(α)H_2), 6.91 (s, 1H, H-5), 7.25 (s, 1H, H-8). ^{13}C NMR (150 MHz) δ: 13.42, 19.20, 19.99, 24.65, 29.16, 49.23, 56.18, 56.21, 56.68, 111.63, 113.05, 115.62, 135.23, 148.05, 157.13, 169.12, 216.60. Found (%): C, 43.49; H, 5.00; I, 27.02; N, 3.34; S, 13.49. Calc. for $C_{17}H_{24}INO_2S_2$ (%): C, 43.87; H, 5.20; I, 27.27; N, 3.01; S, 13.78.

3-Methyl-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4a**).



Compound **4a** was prepared without isolation of poorly stable 2-methyl-1-(methylsulfanyl)carbonothioyl-3,4-dihydroisoquinolinium iodide **3a** in one-pot regime from 2-

methyl-3,4-dihydroisoquinolinium-1-carbodithioate **2a** [S8]. A mixture of **2a** (1.16 g, 0.003 mol), MeI (1.48 g, 0.65 mL, 0.01 mol) in $CHCl_3$ (10 mL) was boiled for 24 h, the solvent was distilled off in vacuum. Then of EtOH (15 mL) and saturated solution of $NaHCO_3$ (4 mL) were added to the residue, and this was stirred at 55-60°C for 2 h. Water (30 mL) was added, the formed precipitate of azepinones **4a** was filtered off and washed with water (3×5 mL). The total yield was 0.33 g (53%). Colorless crystals with mp 181-183°C (EtOH). ^{1}H NMR, δ, ppm: 3.24-3.25 (t, *J* 3.9, 2H, C(5)H_2), 3.44 (s, 3H, Me), 4.05-4.08 (m, 2H, C(4)H_2), 7.35 (d, *J* 7.8, 1H, H-6), 7.37 (t, *J* 7.5, 1H, H-8), 7.52 (d, 1H, H-9), 7.55 (t, *J* 7.5, 1H, H-7).^{13}C NMR (150 MHz) δ: 31.03 (C-5), 38.95 (Me), 52.82 (C-4), 126.75 (C-8), 129.23 (C-9), 130.45 (C-6), 132.47 (C-7), 133.74 (C-5a), 139.29 (C-9a), 192.81 (C=O), 196.20 (C=S). HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{11}H_{11}NNaOS$: 228.0454; found: 228.0452.

^{13}C -^{1}H HMBC NMR, δ^H, δ^C, multiplicity, J^{C-H} (Hz), integral (cross-peak assignment): 3.3, 31.0, dd, *J* 132.0, 32.1 (H-5, C-5); 3.3, 52.8, m, 102.3 (H-5, C-4); 3.3, 126.8, d, 22.3 (H-5, C-8); 3.3, 129.2, d, 4.5 (H-5, C-9); 3.3, 130.5, d, 163.1 (H-5, C-6); 3.3, 132.5, d, 20.0 (H-5, C-7); 3.3, 133.7, d, 182.8 (H-5, C-9a); 3.3, 139.3, t, 186.6 (H-5, C-5a); 3.4, 39.0, d, *J* 138, 1212.5 (H-10, C-10); 3.4, 52.8, d, 681.9 (H-10, C-4); 3.4, 196.2, d, 1202.3 (H-10, C-2); 4.0, 31.03, m, 270.0 (H-4, C-5); 4.0, 39.0, m, 278.5 (H-4, C-10); 4.0, 52.82, d.t, *J* 138, 160.5 (H-4, C-4); 4.0, 139.3, m, 594.9 (H-4, C-5a); 4.0, 196.2, m, 491.2 (H-4, C-2); 7.4, 31.0, d, 53.8 (H-6, C-5); 7.4, 126.8, tm, *J* 98, 155.5 (H-6, H-8, C-8); 7.4, 129.2, m, 98.7 (H-6, H-8, C-9); 7.36, 130.45, tm, *J* 102, 119.6 (H-6, H-8, C-6); 7.4, 132.5, m, 95.6 (H-6, H-8, C-7); 7.4, 192.8, d, 3.0 (H-6, C-1); 7.5, 126.8, m, 149.2, (H-7, H-9, C-8); 7.5, 129.2, tm, *J* 87.9,132.9 (H-7, H-9, C-9); 7.5, 130.5, m, 21.2 (H-7, H-9, C-6); 7.5, 132.5, tm, *J* 91.2, 67.0 (H-7, H-9, C-7); 7.5, 192.8, d, 25.2 (H-9, C-1); 7.5, 133.7, m, 25.8 (H-9, C-9a); 7.6, 139.3, m, 172.1 (H-7, C-5a); 7.5, 192.8, d, 25.1 (H-9, C-1).

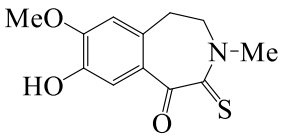
^{15}N–^{1}H HMBC spectrum, δ^H, δ^N, multiplicity, J^{N-H} (Hz), integral (cross-peak assignment): 3.25, 158.1, d, 68.6 (H-5, N-3); 3.44, 158.1, s, 179.43 (H-10, N-3); 4.04, 158.1, d, 10.6 (H-4, N-3).

General procedure for the synthesis of 2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-ones **4c-e**. A suspension of the corresponding 3,4-dihydroisoquinolinium iodide **3** (3 mmol) in a mixture of saturated aqueous solution $NaHCO_3$ and EtOH was stirred for the time indicated in Table S1. Then water (10 mL) was added, the formed precipitate of azepinone **4** was filtered off, washed with water (4×5 mL). The final purification was carried out by recrystallization from suitable solvents.

Table S1 Reaction conditions for the synthesis and yields of benzazepinones **4c-e.**

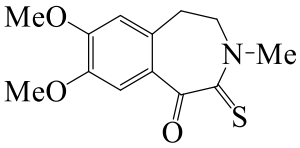
Product	EtOH (mL)	$NaHCO_3$ (8.8%), mL	*T*/°C	*t*/h	Yield %
4c	4	4	20-25	20	92
4d	10	10	25-30	20	56
4e	6	6	23-27	24	64

7-Hydroxy-8-methoxy-3-methyl-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4b**).



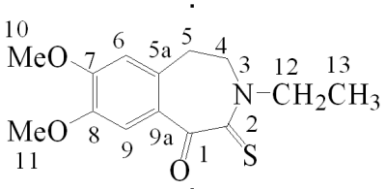
A mixture of 3,4-dihydroisoquinolinium-1-carbodithioate **2b** (0.41 g, 0.001 mol), MeI (0.33 g, 0.14 mL, 2 mmol) in EtOH (10 mL) was boiled for 2 h. Then the excess of MeI and EtOH was distilled off, EtOH (10 mL) and saturated aqueous solution of $NaHCO_3$ (5 mL) were added, and this was refluxed with stirring for 1 h. The mixture was evaporated to dryness in vacuum, water (4 mL) was added, the precipitate was filtered off and washed with water (3×1 mL). The total yield from two stages was 0.25 g (65%, as calculated on starting betaine). Colorless crystals with mp 246-248°C (EtOH). ^{1}H NMR, δ, ppm: 3.06-3.13 (m, 2H, C(5)H_2), 3.43 (s, 3H, Me), 3.81 (s, 3H, OMe), 3.94-4.04 (m, 2H, C(4)H_2), 6.84 (s, 1H, H-6), 6.93 (s, 1H, H-9), 9.44 (s, 1H, OH). ^{13}C NMR (150 MHz) δ: 30.93, 39.13, 53.28, 55.71, 112.95, 115.05, 125.86, 131.91, 145.37, 151.59, 191.43, 196.31. Found (%): C, 57.08; H, 5.39; N, 5.32; S, 12.87. Calc. for $C_{12}H_{13}NO_3S$ (%): C, 57.35; H, 5.21; N, 5.57; S, 12.76.

7,8-Dimethoxy-3-methyl-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4c**).



The starting compound was 6,7-dimethoxy-2-methyl-1-[(methylsulfanyl)carbonothioyl]-3,4-dihydroisoquinolinium iodide **3c**. Yield of compound **4c** was 0.73g (92%). Colorless crystals with mp 210-212 ºC (EtOH). ^{1}H NMR, δ, ppm: 3.13-3.18 (m, 2H, C(5)H2), 3.44 (s, 3H, Me), 3.77 (s, 3H, OMe), 3.81 (s, 3H, OMe), 4.00-4.04 (m, 2H, C(4)H2), 6.90 (s, 1H, H-6), 7.01 (s, 1H, H-9). ^{13}C NMR (150 MHz) δ: 31.14, 39.19, 53.21, 55.57, 55.78, 111.19, 112.71, 125.60, 133.90, 147.60, 152.35, 191.13, 196.17. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{15}NNaO_3S$: 288.0665; found: 288.0660.

3-Ethyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4d**).



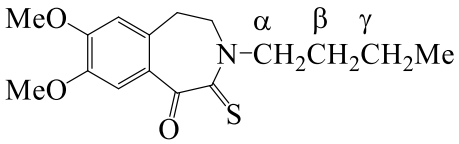
The starting compound was 3,4-dihydroisoquinolinium iodide **3d**. Yield of product **4d** was 0.50 g (56%). Colorless crystals with mp 158-160°C (EtOAc). ^{1}H NMR, δ, ppm: 1.23 (t, *J* 7.1, 3H, $CH_2\underline{Me}$), 3.10-3.18 (m, 2H, C(5)H_2), 3.77 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.94-4.00 (m, 4H, C(4)H_2, $\underline{CH_2}CH_3$), 6.90 (s, 1H, H-6), 6.99 (s, 1H, H-9). ^{13}C NMR (150 MHz) δ: 11.50 (C-13), 32.16 (C-5), 46.30 (C-12), 50.73 (C-4), 55.59 (C-11) , 55.76 (C-10) , 111.15 (C-9) , 112.66 (C-6) , 125.64 (C-9a) , 133.56 (C-5a), 147.64 (C-8) , 152.36 (C-7) , 191.19 (C-1), 195.68 (C-2) . ^{15}N, δ (from ^{15}N – ^{1}H HMBC spectrum): 169.87 ppm.

^{13}C-^{1}H HMBC spectrum, δ^{H}, δ^{C}, multiplicity, $J_{C\text{-}H}$ (Hz), integral (cross-peak assignment): 1.2, 11.5, d, *J* 126.0, 4.2 (H-13, C-13); 1.2, 46.3, m, 231.4 (H-13, C-12); 3.1, 50.73, dd, 59.6 (H-5, C-4); 3.1, 112.7, d, 71.4 (H-5, C-6); 3.1, 125.7, d, 101.2 (H-5, C-9a); 3.1, 133.6, dd, 130.5 (H-5, C-5a); 3.8, 55.6, d, *J* 144, 133.2 (H-11, C-11); 3.8, 147.6, d, 1173.4 (H-11, C-8); 3.8, 55.8, d, *J* 144, 168.9 (H-10, C-10); 3.8, 152.4, d, 1038.1 (H-10, C-7); 4.0, 11.5, m, 78.8 (H-12, C-13); 4.0, 32.2, d, 43.40 (H-4, C-5); 3.96, 46.3, tm, 61.2 (H-12, C-12); 4.0, 50.7, tm, 136.9 (H-4, C-4); 4.0, 133.6, m, 266.3 (H-4, C-5a); 4.0, 195.7, m, 298.1 (H-4, C-2); 6.9, 32.2, d, 141.1 (H-6, C-5); 6.9, 112.7, t, *J* 81, 49.9 (H-6, C-6); 6.9, 111.2, s, 13.5 (H-6, C-9); 6.90, 112.7, d, *J* 162, 39.2 (H-6, C-6); 6.9, 125.6, d, 379.4 (H-6, C-9a); 6.9, 133.6, s, 46.5 (H-6, C-5a); 6.9, 147.7, d, 317.3 (H-6, C-8); 6.9, 152.4, s, 170.2 (H-6, C-7); 6.9, 191.2, s, 67.1 (H-6, C-1); 7.0, 32.2, s, 25.8 (H-9, C-5); 7.0, 111.2, d, *J* 162, 48.9 (H-9, C-9); 7.0, 125.7, s,106.3 (H-9, C-9a); 7.0, 133.6, d, 464.9 (H-9, C-5a); 7.0, 147.7, d, 211.9 (H-9, C-8); 7.0, 152.4, d, 494.0 (H-9, C-7); 7.0, 191.2, d, 201.9 (H-9, C-1).

^{15}N–^{1}H HMBC spectrum, δ^{H}, δ^{N}, multiplicity, $J^{N\text{-}H}$ (Hz), integral (cross-peak assignment): 1.2, 169.9, t, 148.2 (H-13, N-3); 3.1, 169.9, d,71.9 (H-5, N-3); 4.0, 169.9, m, 25.3 (H-12, H-4, N-3); 3.1, 169.9, d, 71.9 (H-5, N-3).

Found (%): C, 60.42; H, 5.78; N, 5.34; S, 11.90. Calc. for $C_{14}H_{17}NO_3S$ (%): C, 60.19; H, 6.13; N, 5.01; S, 11.48.

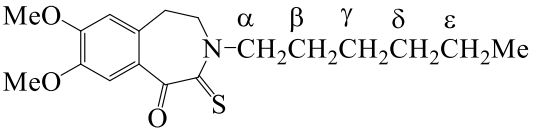
3-Butyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4e**).



The starting compound was 6,7-dimethoxy-2-butyl-1-(methylsulfanyl)carbonothioyl-3,4-dihydroisoquinolinium iodide **3e**. Yield of compound **4e** was 0.59 g (64%). Colorless crystals with mp 149-150°C (EtOAc). ^{1}H NMR, δ, ppm: 0.92 (t, *J* 7.4, 3H, Me), 1.30-1.35 (m, 2H, C(γ)H_2),

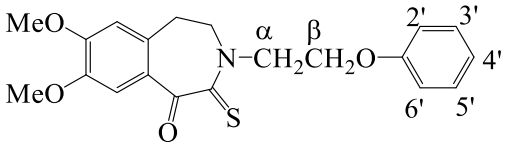
1.64-1.69 (m, 2H, C(β)H_2), 3.10-3.17 (m, 2H, C(5)H_2), 3.77 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.93 (t, *J* 7.6, 2H, C(4)H_2), 3.96-4.00 (m, 2H, C(α)H_2), 6.90 (s, 1H, H-6), 6.99 (s, 1H, H-9). ^{13}C NMR (150 MHz) δ: 13.62, 19.50, 28.29, 31.99, 50.76, 51.09, 55.57, 55.76, 111.11, 112.64, 125.63, 133.49, 147.63, 152.34, 191.18, 196.24.Found (%): C, 62.60; H, 6.70; N, 4.21; S, 10.09. Calc. for $C_{16}H_{21}NO_3S$ (%): C, 62.51; H, 6.89; N, 4.56; S, 10.43.

3-Hexyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4f**).



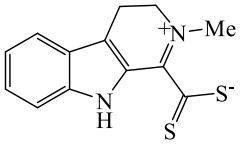
Compound **4f** was prepared without isolation of low stable 2-hexyl-1-(methylsulfanyl)carbonothioyl-3,4-dihydroisoquinolinium iodide **3f** in one-pot regime from 2-hexyl-3,4-dihydroisoquinolinium-1-carbodithioate **2f** similarly as azepinone **4a**. The total yield of **4f** was 0.64 g (64%). Colorless crystals with mp 149-150°C (EtOAc). ^{1}H NMR, δ, ppm: 0.80-0.86 (m, 3H, Me), 1.24-1.29 (m, 6H, C(γ)H_2-C(ε)H_2), 1.62-1.67 (m, 2H, C(β)H_2), 3.06-3.14 (m, 2H, C(5)H_2), 3.75 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.86-3.91 (m, 2H, C(α)H_2), 3.93-3.98 (m, 2H, C(4)H_2), 6.87 (s, 1H, H-6), 6.97 (s, 1H, H-9). ^{13}C NMR (150 MHz) δ: 13.78, 24.89, 25.83, 26.10, 30.83, 32.01, 51.05, 51.12, 55.58, 55.77, 111.13, 112.65, 125.65, 133.51, 147.64, 152.35, 191.19, 196.22. Found (%): C, 64.12; H, 7.36; N, 4.00; S, 9.24. Calc. for $C_{18}H_{25}NO_3S$ (%): C, 64.45; H, 7.51; N, 4.18; S, 9.56.

7,8-Dimethoxy-3-(2-phenoxyethyl)-2-thioxo-2,3,4,5-tetrahydro-1H-benz[d]azepin-1-one (**4g**).



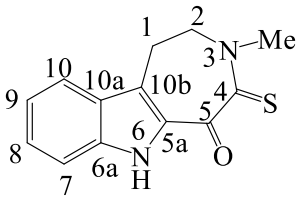
Azepine **4g** was obtained similarly as azepine **4a** from 6,7-dimethoxy-2-(2-phenoxyethyl)-3,4-dihydroisoquinolinium-1-carbodithioate (**2g**). The overall yield from both stages was 0.72 g (65%). Colorless crystals with mp 166-168°C (EtOAc). ^{1}H NMR, δ, ppm: 3.19-3.20 (m, 2H, C(5)H_2), 3.74 (s, 3H, OMe), 3.78 (s, 3H, OMe), 4.06-4.10 (m, 2H, C(α)H_2), 4.27-4.28 (m, 2H, C(4)H_2), 4.29-4.33 (m, 2H, C(β)H_2), 6.87 (s, 1H, H-6), 6.91-6.97 (m, 3H, H-3' – H-5'), 6.98 (s, 1H, H-9), 7.25-7.29 (m, 2H, H-2', H-6'). ^{13}C NMR (150 MHz) δ: 31.80, 51.04, 52.73, 55.59, 55.79, 64.04, 111.17, 112.66, 114.45, 120.98, 125.46, 129.53, 133.80, 147.67, 152.48, 157.93, 191.08, 197.40. Found (%): C, 64.46; H, 5.41; N, 3.50; S, 8.63. Calc. for $C_{20}H_{21}NO_4S$ (%): C, 64.67; H, 5.70; N, 3.77; S, 8.63.

2-Methyl-4,9-dihydro-3H-pyrido[3,4-b]indol-1-carbodithioate **6.**



Compound **6** was synthesized from 1,2-dimethyl-4,4a,9,9a-tetrahydro-3*H*-pyrido[3,4-*b*]-indol-2-ium iodide **5** (1.6 g) similarly to dithiocarboxylate **2f**. Yield of compound **6** was 1.2 g (95%). Red crystals with mp 225°C (EtOH). ^{1}H NMR, δ, ppm: 3.28-3.32 (m, 5H, Me, C(4)H$_2$), 4.08 (t, *J* 8.4, C(3)H$_2$), 7.14 (t, *J* 7.5, H-6), 7.34-7.35 (m, 1H, H-7), 7.47 (d, *J* 8.4, 1H, H-8), 7.69 (d, *J* 8.2, 1H, H-5), 11.58 (s, 1H, NH). ^{13}C NMR (150 MHz) δ: 18.87, 40.03, 51.54, 113.43, 120.73, 120.79, 122.52, 123.70, 124.10, 127.24, 140.52, 161.55, 232.28. Found (%): C, 60.12; H, 4.84; N, 10.54; S, 24.86. Calc. for $C_{13}H_{12}N_2S_2$ (%): C, 59.97; H, 4.65; N, 10.76; S, 24.63.

3-Methyl-4-thioxo-1,2,3,6-tetrahydroazepino[4,5-b]indol-5(2H)-one (**8**).



Compound **8** was prepared without isolation of poorly stable 2-methyl-1-(methylsulfanyl)carbonothioyl-4,9-dihydro-3*H*-pyrido[3,4-*b*]indol-2-ium iodide **7** in one-pot regime from 2-methyl-4,9-dihydro-3*H*-pyrido[3,4-*b*]indole-1-carbodithioate **6**. A mixture of compound **6** (0.7 g, 0.002 mol), MeI (1.14 g, 0.5 mL, 0.007 mol) in EtOH (10 mL) was boiled for 1 h, the solvent was distilled off in vacuum. Crude yield 0.87 (87%). Then of EtOH (10 mL) and saturated solution of $NaHCO_3$ (4 mL) were added, and the solution was boiled 2 h, then water (20 mL) was added, the formed precipitate of azepinone **8** was filtered off and washed with water (3×10 mL). The yield was 0.4 g (70%). Colorless crystals with mp 294-296°C (EtOH). ^{1}H NMR, δ, ppm: 3.13 (d, *J* 15.2, 2H, C(1)H$_2$), 3.57 (s, 3H, Me), 4.17 (t, *J* 5.0, 2H, C(2)H$_2$), 7.05-7.13 (m, 1H, H-7), 7.27-7.44 (m, 2H, H-8,9), 7.64 (d, *J* 8.2, 1H, H-10), 11.81 (s, 1H, NH). ^{13}C NMR (150 MHz) δ: 23.74, 41.60, 55.92, 112.51, 120.14, 120.78, 123.72, 126.15, 126.18, 129.09, 137.47, 180.27, 194.25. Found (%): C, 63.59; H, 4.59; N, 11.15; S, 13.00. Calc. for $C_{13}H_{12}N_2OS$ (%): C, 63.91; H, 4.95; N, 11.47; S, 13.12.

Table S2 Recyclization of salts **3a**,**b**,**f**,**g** and **7** into oxo thioxo derivatives **4a,b,f**,**g** and **8**.

Product	*T*/ºC	*t*/h	Yield, %
4a	20-25	20	53*
4b	73-75	1	65*
4f	50-60	2	64*
4g	25-30	20	65*
8	73-75	2	70*

* Overall yield from the two stages.

5. References

[S1] NMR Solvent Reference Shift, http://chem.ch.huji.ac.il/nmr/software/solvent.html.
[S2] *CrysAlisPro, version 1.171.38.41, Rigaku Oxford Diffraction*, Oxford, 2015.
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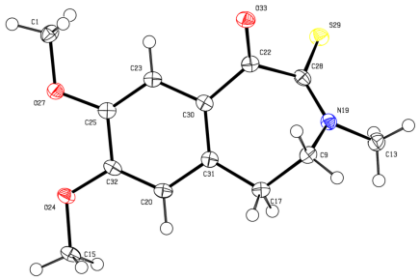
[S4] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.
[S5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.
[S6] I. V. Shcherbakova, V. G. Brovchenko and E. V. Kuznetsov, *Chem. Nat. Compd*., 1985, **21**, 774.
[S7] N. V. Sastry, N. M. Vaghela, P. M. Macwan, S. S. Soni, V. K. Aswal and A. J. Gibaud, *J. Colloid Interface Sci.*, 2012, **371**, 52.
[S8] A. S. Morkovnik, A. A. Zubenko, L. N. Divaeva, O. P. Demidov, T. N. Gribanova, A. I. Klimenko, N. M. Dobaeva, G. S. Borodkin, Y. D. Drobin, L. N. Fetisov and K. N. Kononenko, *Tetrahedron Lett*., 2020, **61**, 152228.
[S9] H. Bruderer and A. Brossi, *Helv. Chim. Acta*, 1965, **48**, 1945.

4. Structure and crystal data for compound 4c.

Table S3 Crystal data and structure refinement for **4c**.



CCDC Number	2049405
Empiricalformula	$C_{13}H_{15}NO_3S$
Formulaweight	265.32
Temperature/K	99.99(13)
Crystalsystem	orthorhombic
Space group	Pbca
a/Å	7.7726(2)
b/Å	16.3989(5)
c/Å	19.1123(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2436.09(13)
Z	8
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	2.375
F(000)	1120.0
Crystalsize/mm^3	0.375 × 0.238 × 0.157
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.254 to 152.026
Indexranges	$-9 \leq h \leq 6$, $-20 \leq k \leq 20$, $-24 \leq l \leq 23$
Reflectionscollected	16162
Independentreflections	2530 [R_{int} = 0.0607, R_{sigma} = 0.0309]
Data/restraints/parameters	2530/0/166
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1126
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1154
Largest diff. peak/hole / e Å^{-3}	0.35/-0.33

Table S4 Bond lengths for **4c**.

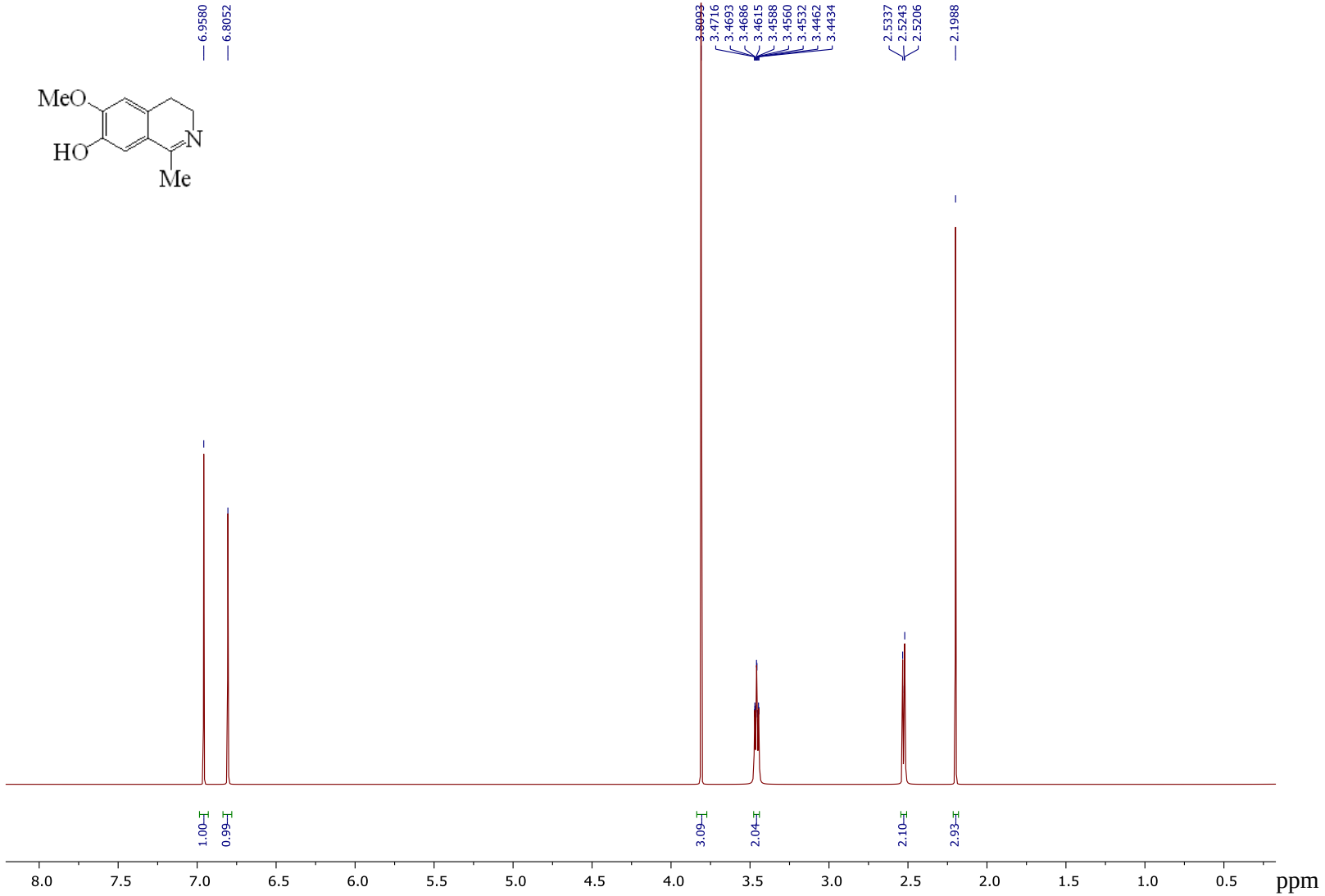
Atom	Atom	Bond length/Å	Atom	Atom	Bond length/Å
S29	C28	1.667(2)	C25	C23	1.376(3)
O27	C25	1.364(2)	C30	C31	1.397(3)
O27	C1	1.431(2)	C30	C22	1.486(3)
O33	C22	1.215(2)	C30	C23	1.413(3)
O24	C32	1.355(2)	C31	C20	1.397(3)
O24	C15	1.440(2)	C31	C17	1.516(3)
N19	C28	1.320(2)	C32	C20	1.383(3)
N19	C9	1.469(2)	C22	C28	1.533(3)
N19	C13	1.462(2)	C17	C9	1.517(3)
C25	C32	1.417(3)			

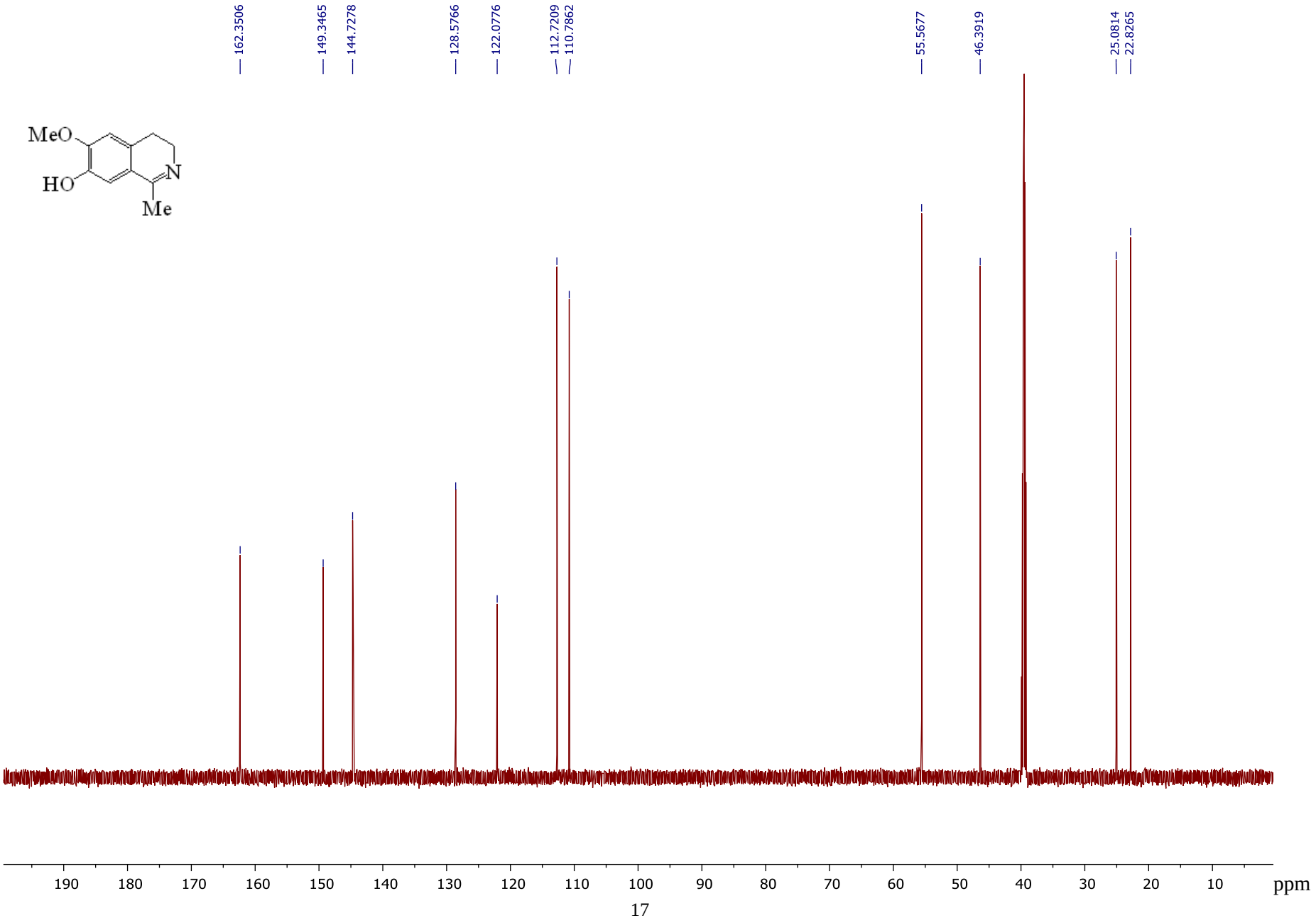
Table S5 Bond Angles for **4c**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C25	O27	C1	115.67(14)	O24	C32	C25	115.74(16)
C32	O24	C15	116.84(15)	O24	C32	C20	124.79(17)
C28	N19	C9	120.12(16)	C20	C32	C25	119.44(17)
C28	N19	C13	122.57(17)	C32	C20	C31	121.96(18)
C13	N19	C9	117.22(15)	O33	C22	C30	122.73(17)
O27	C25	C32	116.03(16)	O33	C22	C28	119.23(17)
O27	C25	C23	125.01(17)	C30	C22	C28	117.54(16)
C23	C25	C32	118.97(17)	C25	C23	C30	121.34(17)
C31	C30	C22	125.36(17)	N19	C28	S29	126.05(15)
C31	C30	C23	119.59(17)	N19	C28	C22	117.15(17)
C23	C30	C22	115.03(16)	C22	C28	S29	116.74(14)
C30	C31	C20	118.54(17)	C31	C17	C9	115.42(16)
C30	C31	C17	124.73(17)	N19	C9	C17	110.98(15)
C20	C31	C17	116.33(17)				

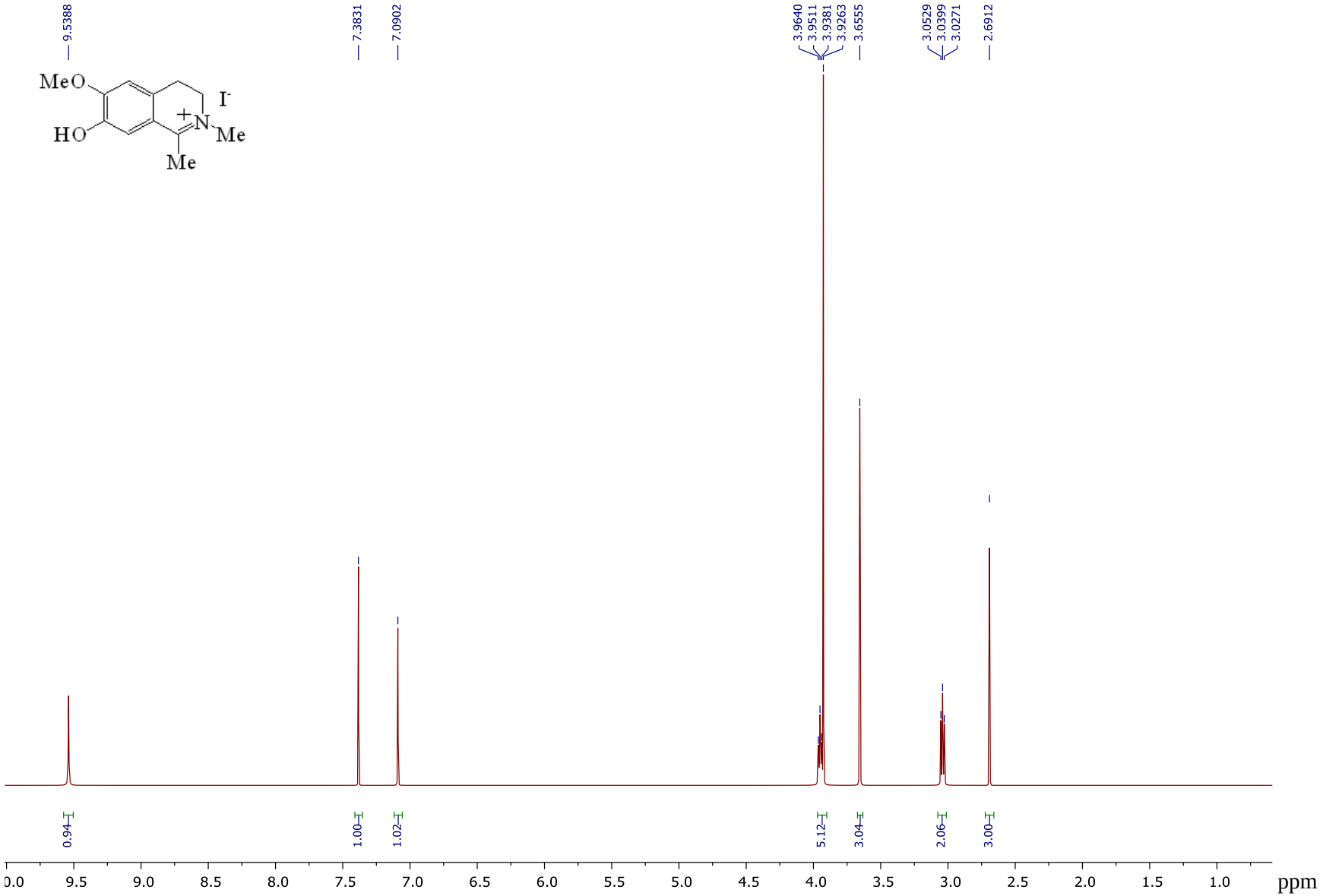
5. NMR spectra of compounds 1-4, 8.

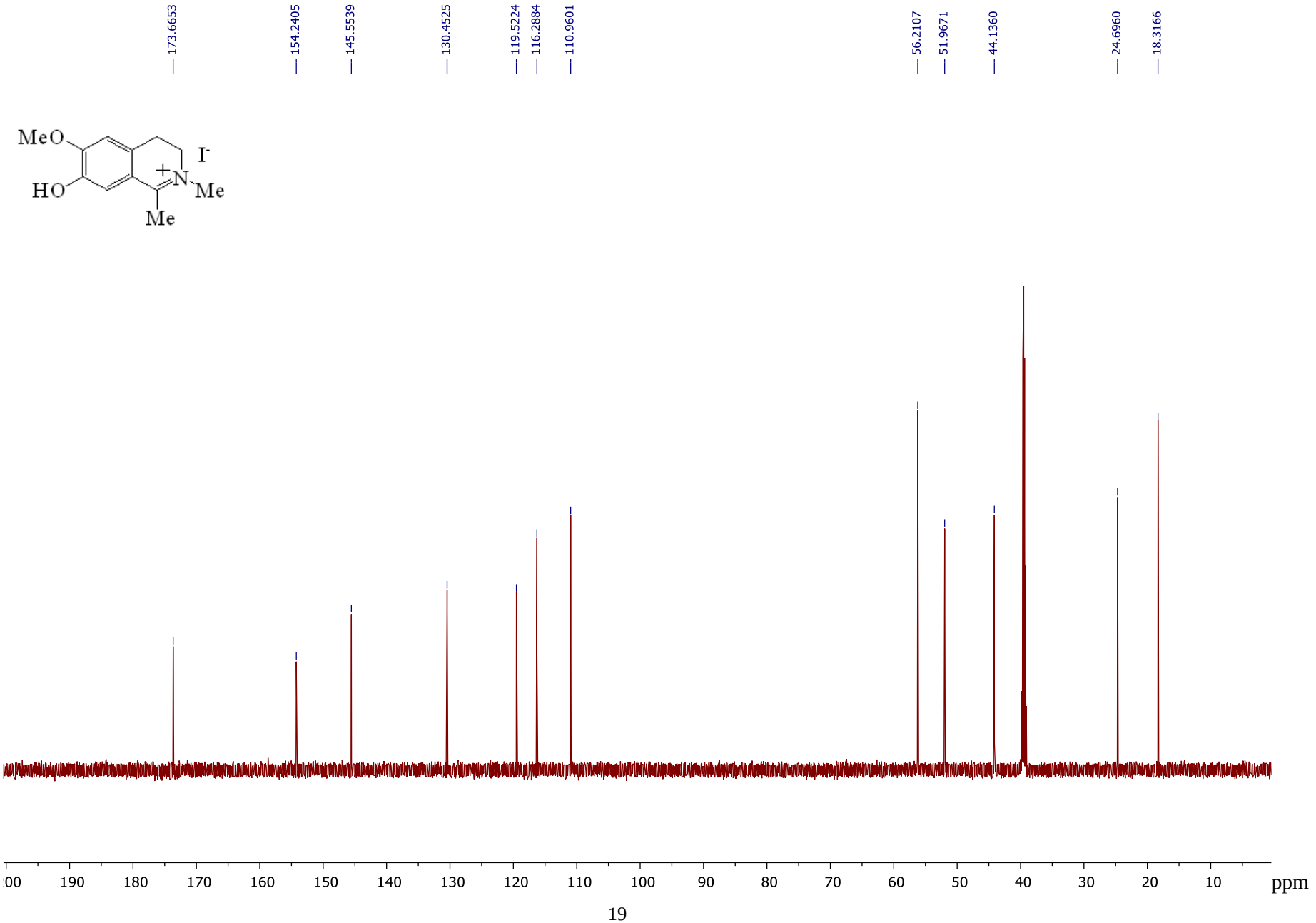
6-Methoxy-1-methyl-3,4-dihydroisoquinolin-7-ol



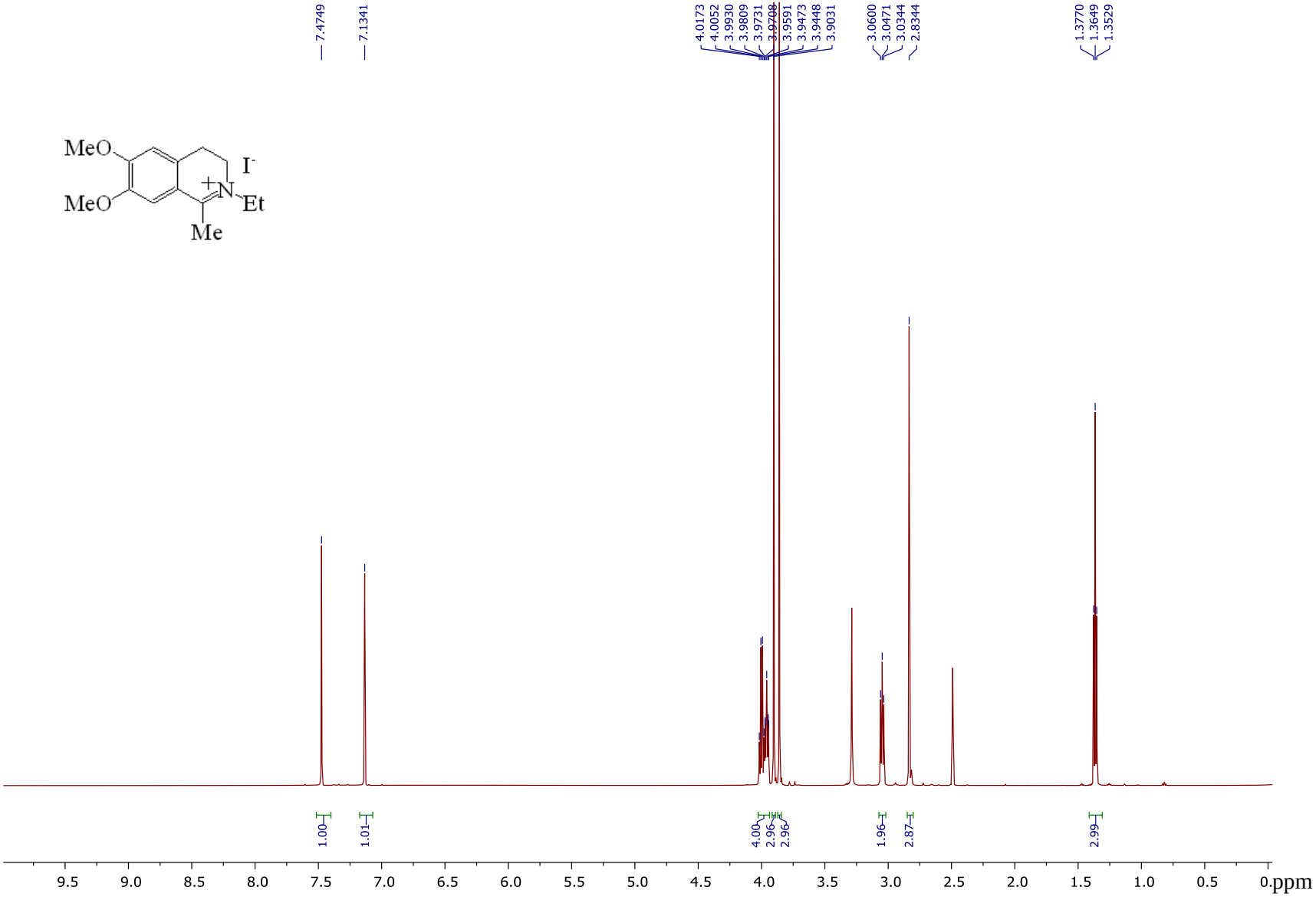

162.3506
149.3465
144.7278
128.5766
122.0776
112.7209
110.7862
55.5677
46.3919
25.0814
22.8265
MeO
HO
N
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

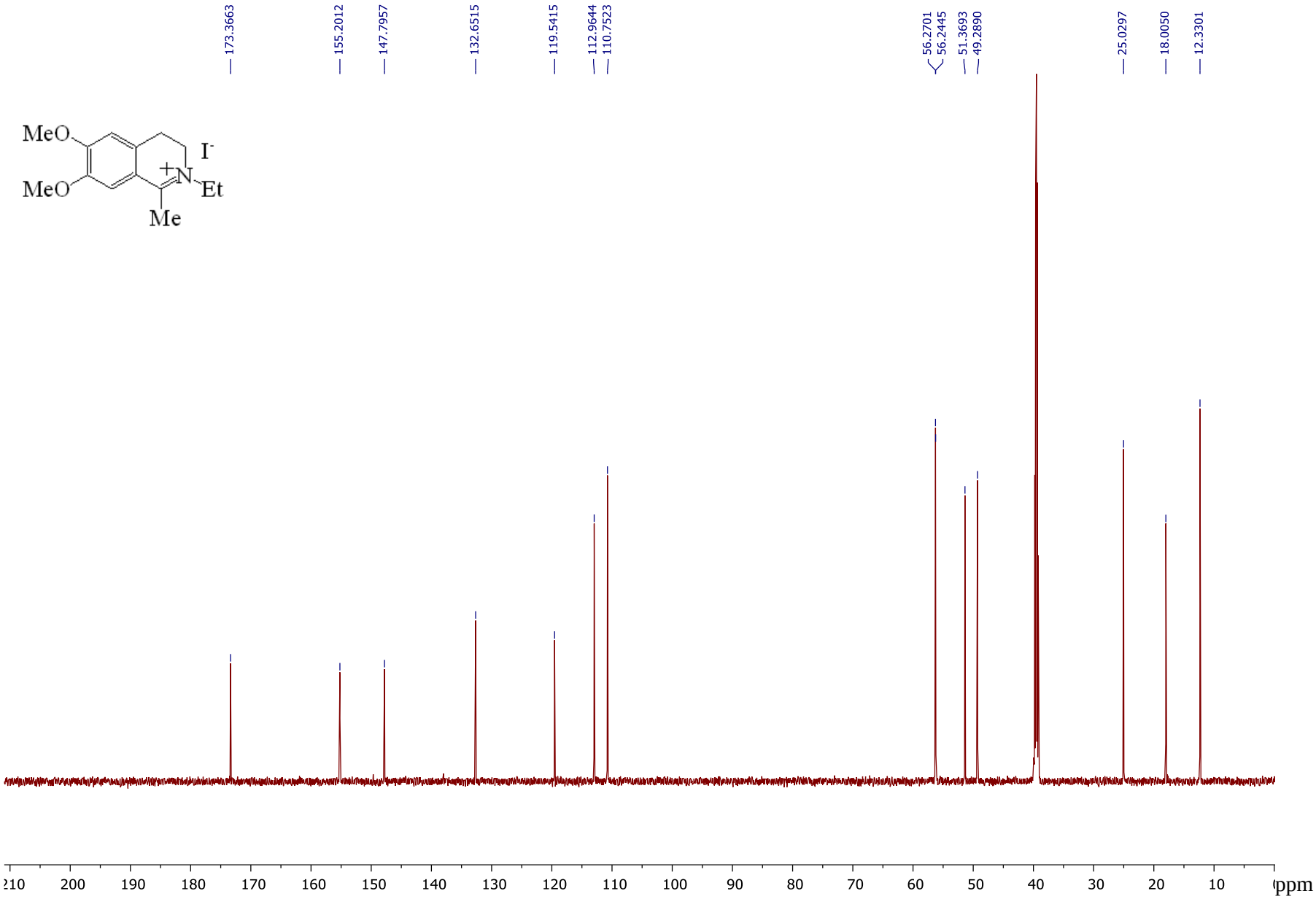
7-Hydroxy-6-methoxy-1,2-dimethyl-3,4-dihydroisoquinolin-2-ium iodide (**1b**).



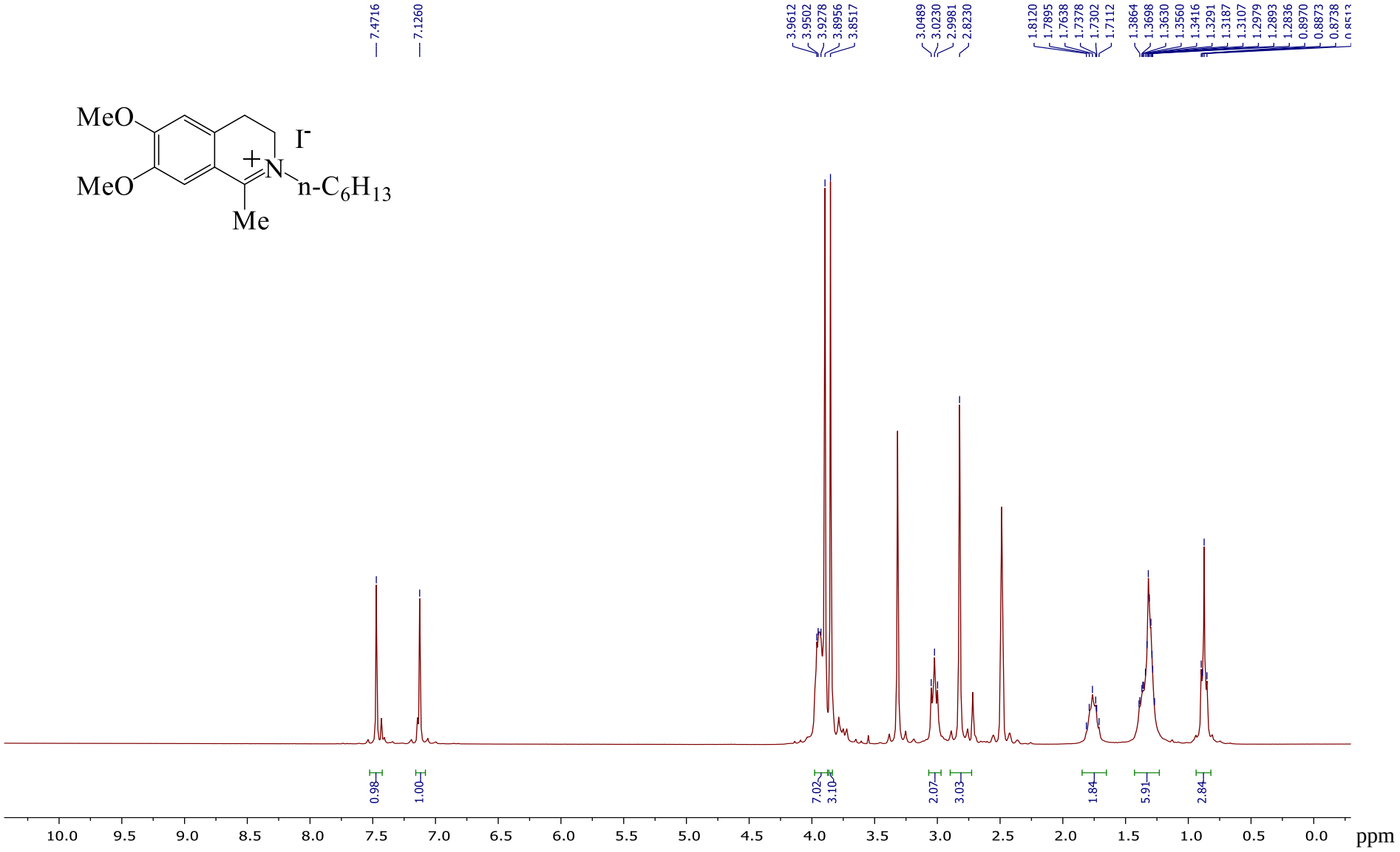

173.6653
154.2405
145.5539
130.4525
119.5224
116.2884
110.9601
56.2107
51.9671
44.1360
24.6960
18.3166
MeO
HO
I-
N
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

2-Ethyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide (**1d**).

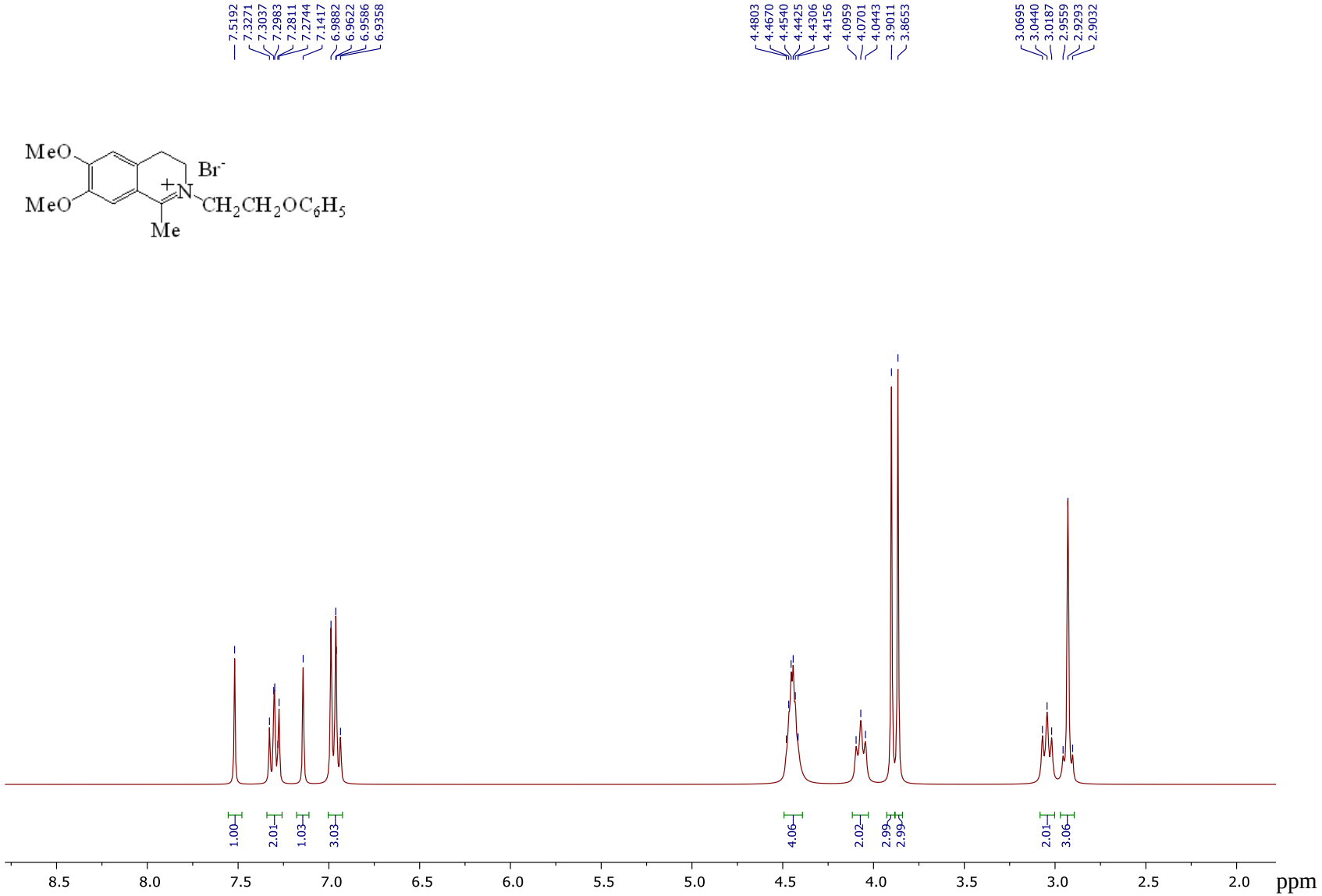



173.3663
155.2012
147.7957
132.6515
119.5415
112.9644
110.7523
56.2701
56.2445
51.3693
49.2890
25.0297
18.0050
12.3301
MeO
MeO
I-
+N
Et
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

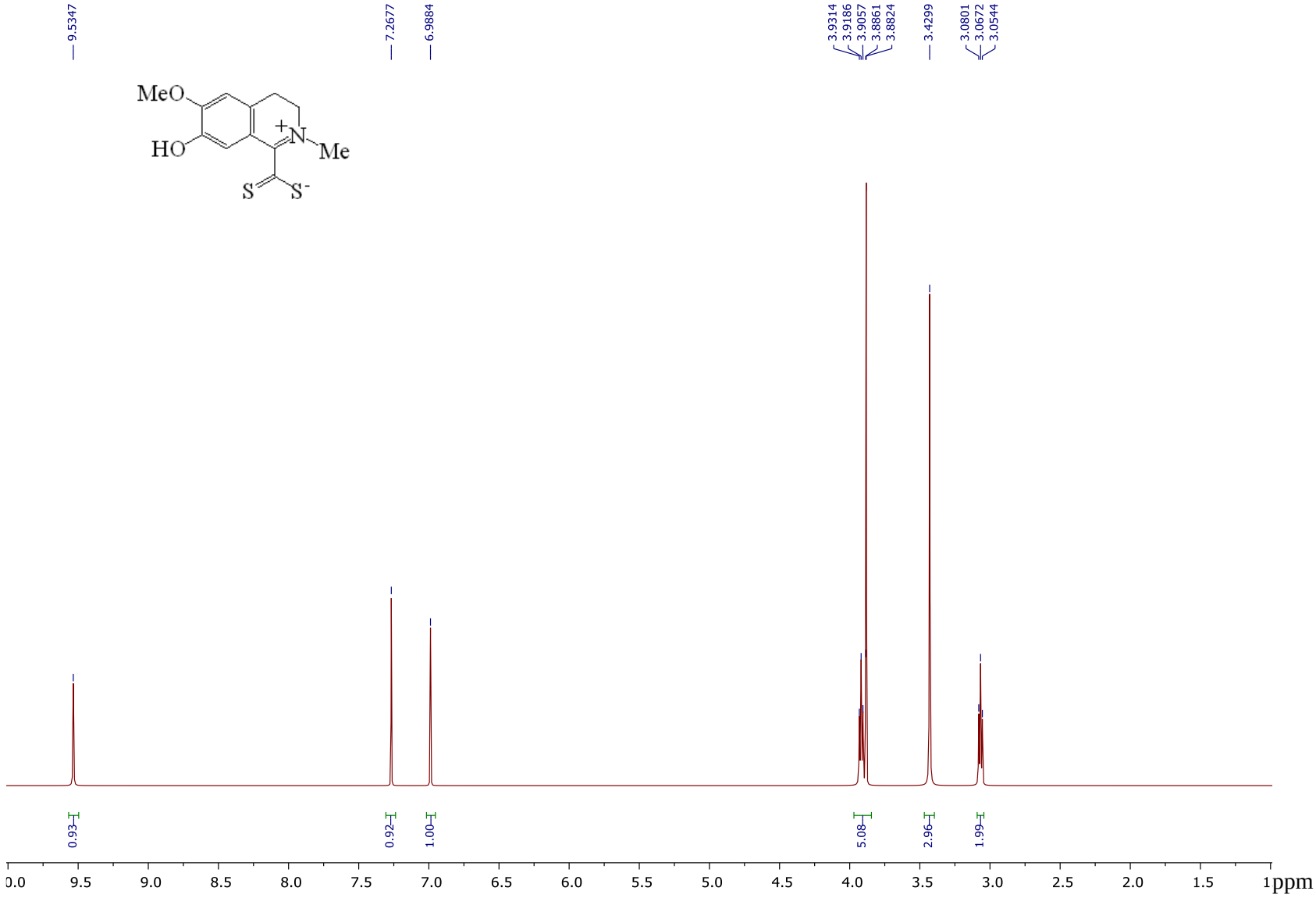
2-*n*-Hexyl-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinolin-2-ium iodide (**1f**).

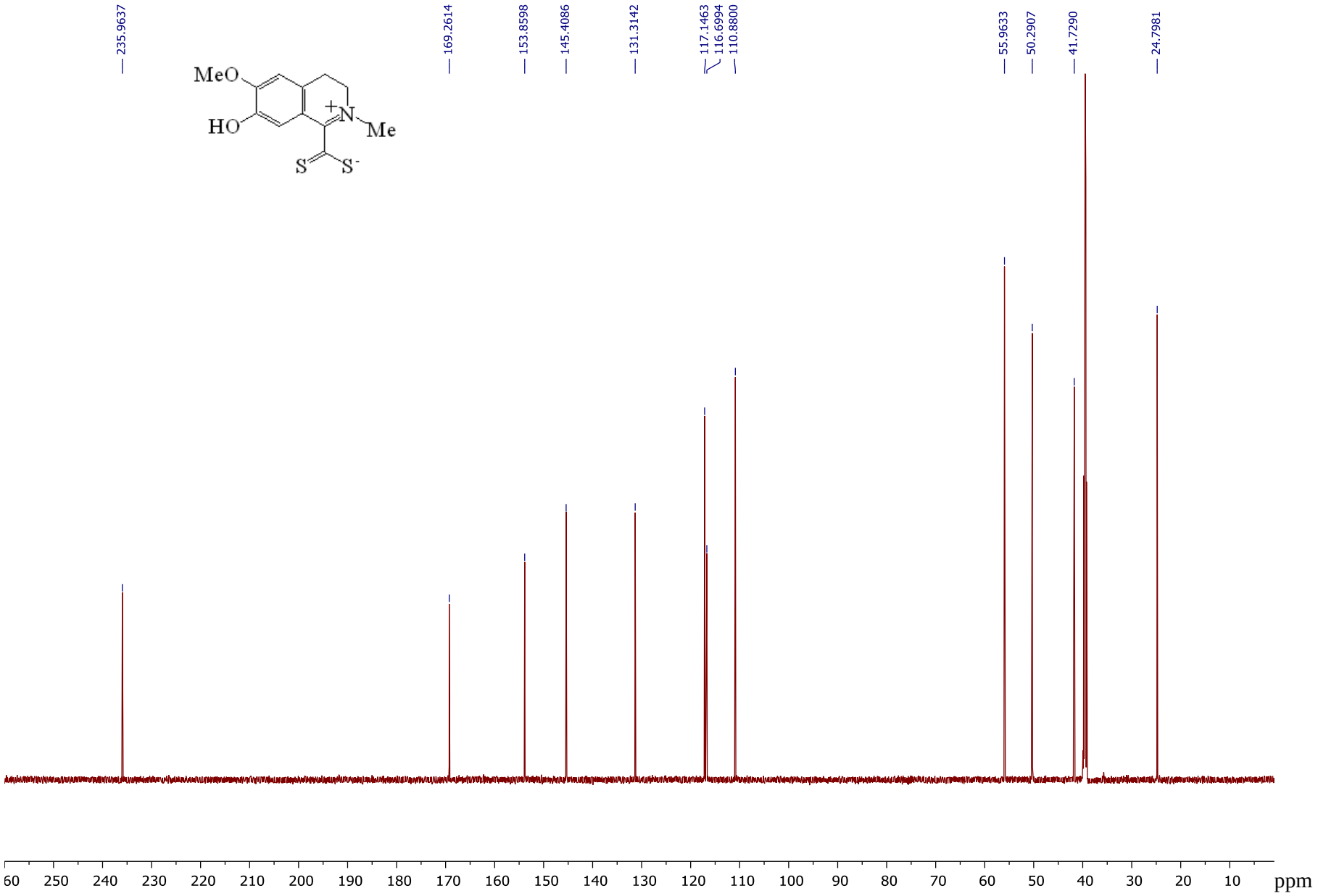


6,7-Dimethoxy-1-methyl-2-(2-phenoxyethyl)-3,4-dihydroisoquinolin-2-ium bromide (**1g**).

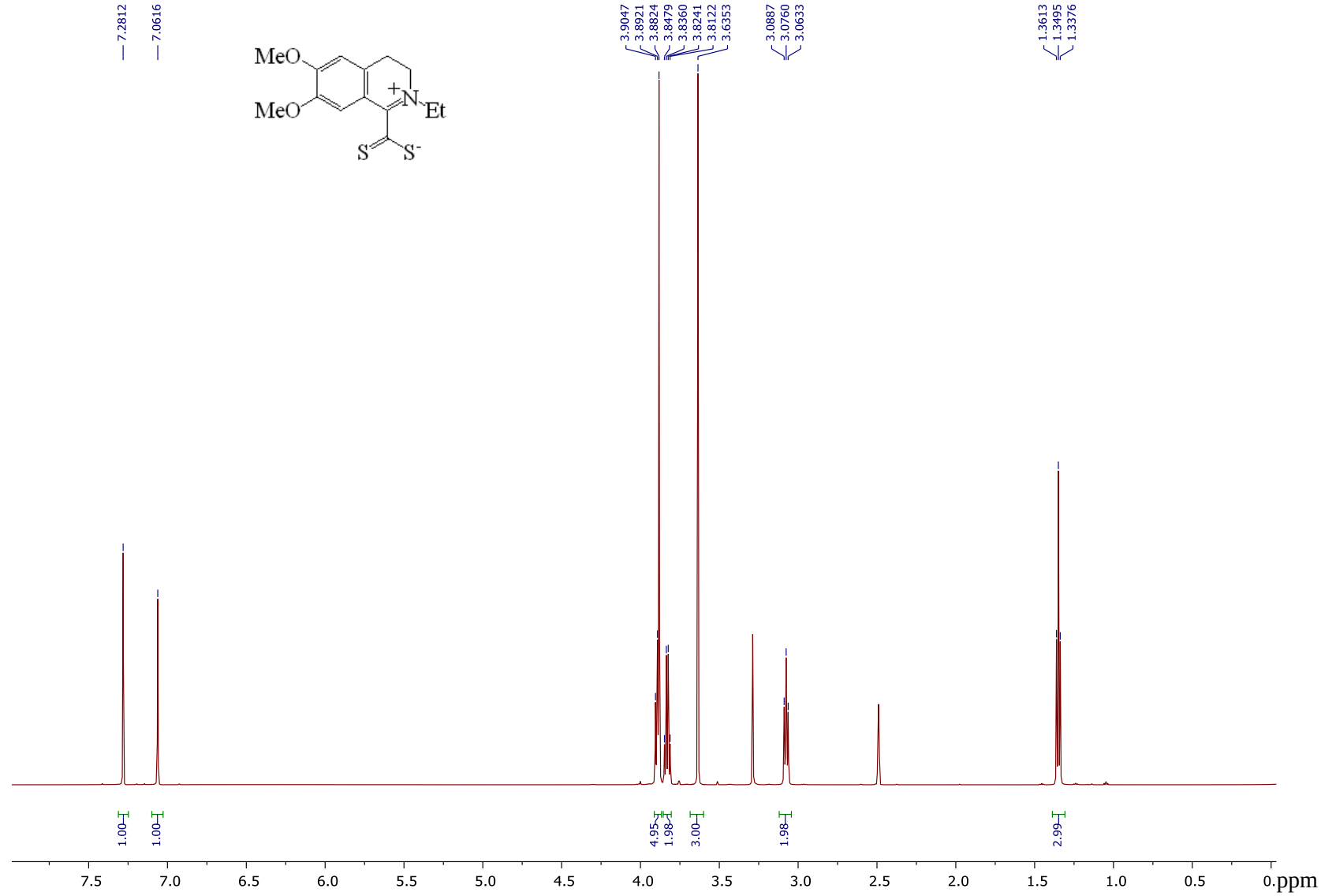


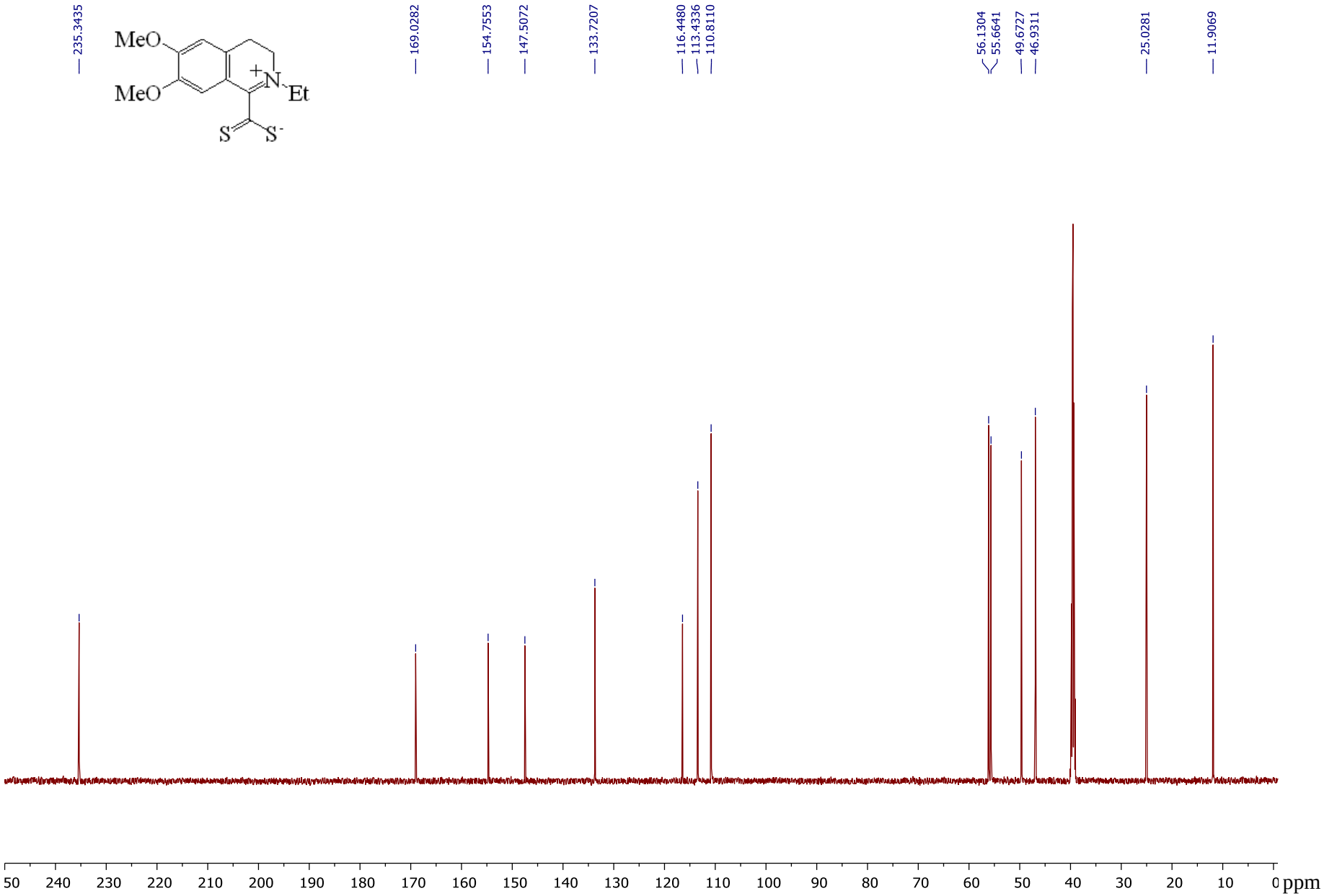
7-Hydroxy-6-methoxy-2-methyl-3,4-dihydroisoquinolinium-1-carbodithioate (**2b**).



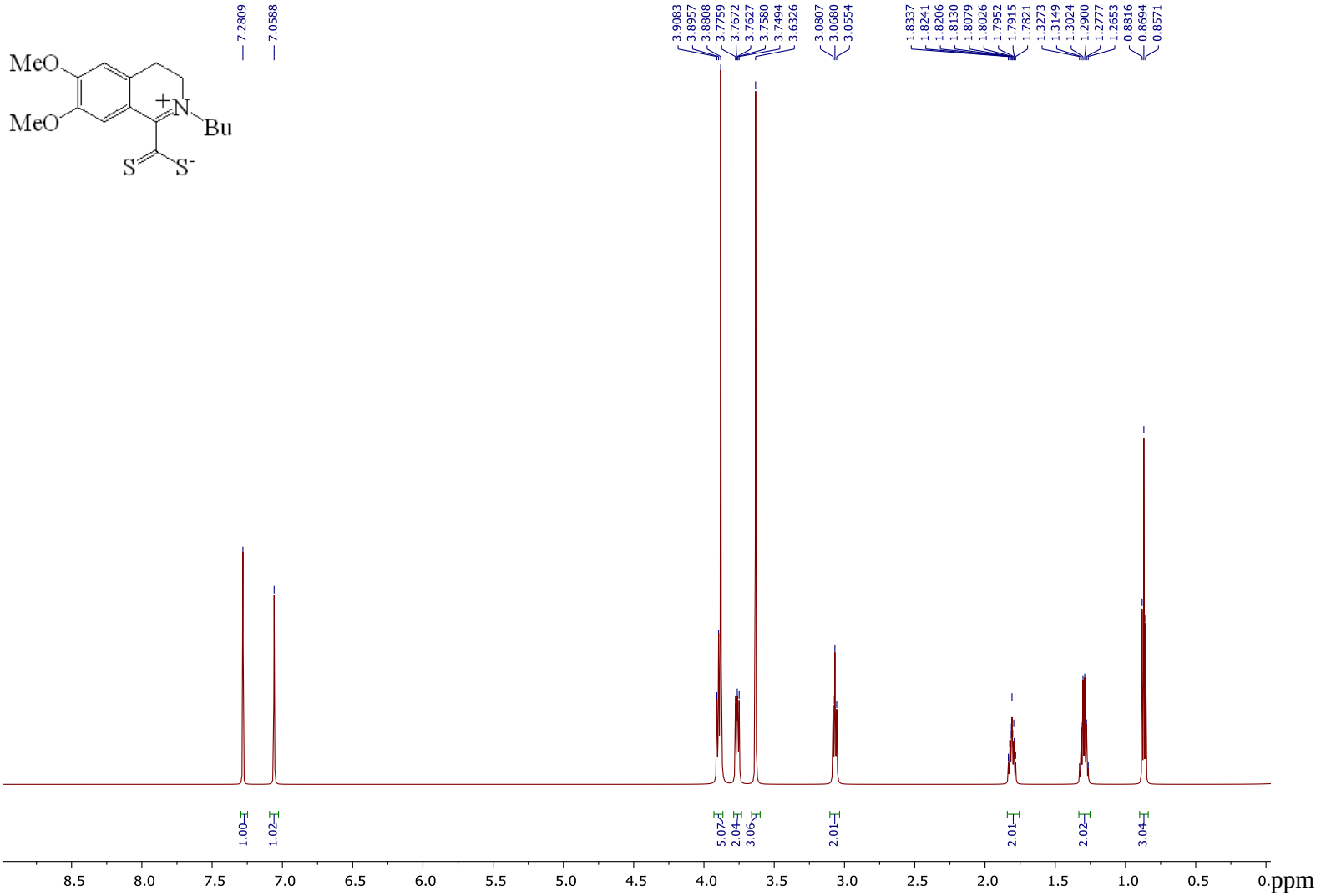

235.9637
169.2614
153.8598
145.4086
131.3142
117.1463
116.6994
110.8800
55.9633
50.2907
41.7290
24.7981
MeO
HO
N
Me
S
S-
60 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

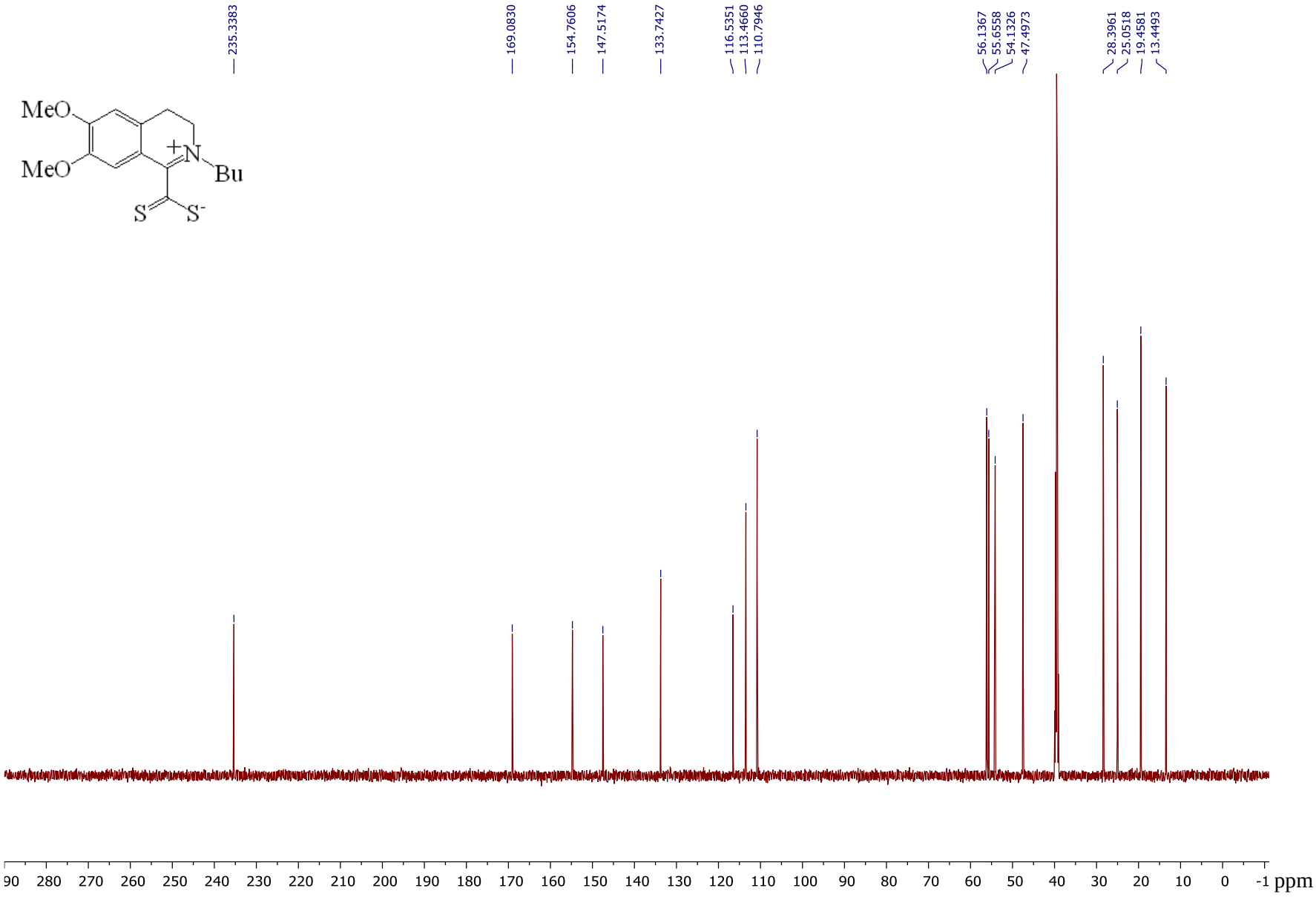
2-Ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium-1-dithiocarboxylate (**2d**).



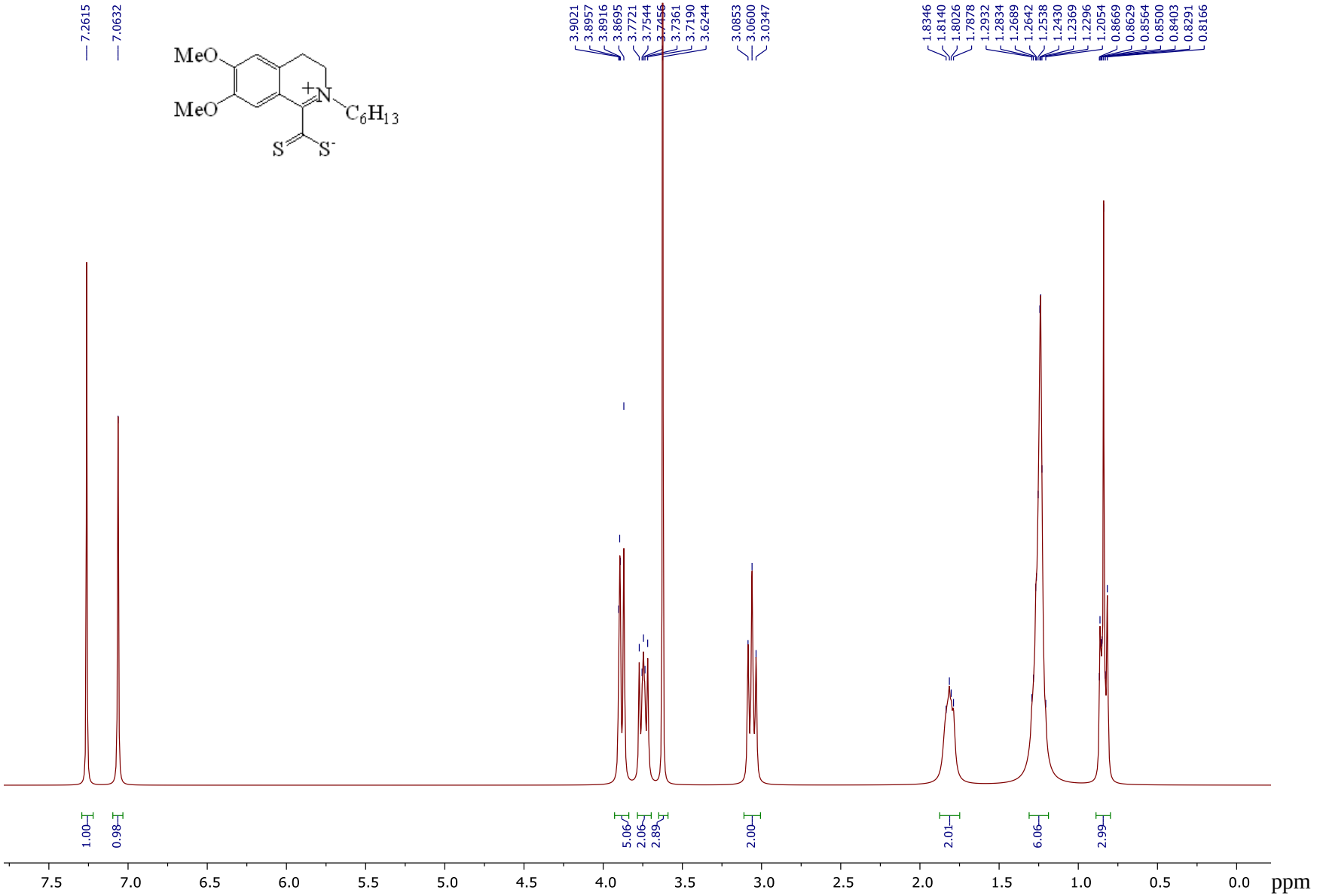

235.3435
169.0282
154.7553
147.5072
133.7207
116.4480
113.4336
110.8110
56.1304
55.6641
49.6727
46.9311
25.0281
11.9069
MeO
MeO
N
Et
S
S
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2-Butyl-6,7-dimethoxy-3,4-dihydroisoquinolinium-1-dithiocarboxylate (**2e**).

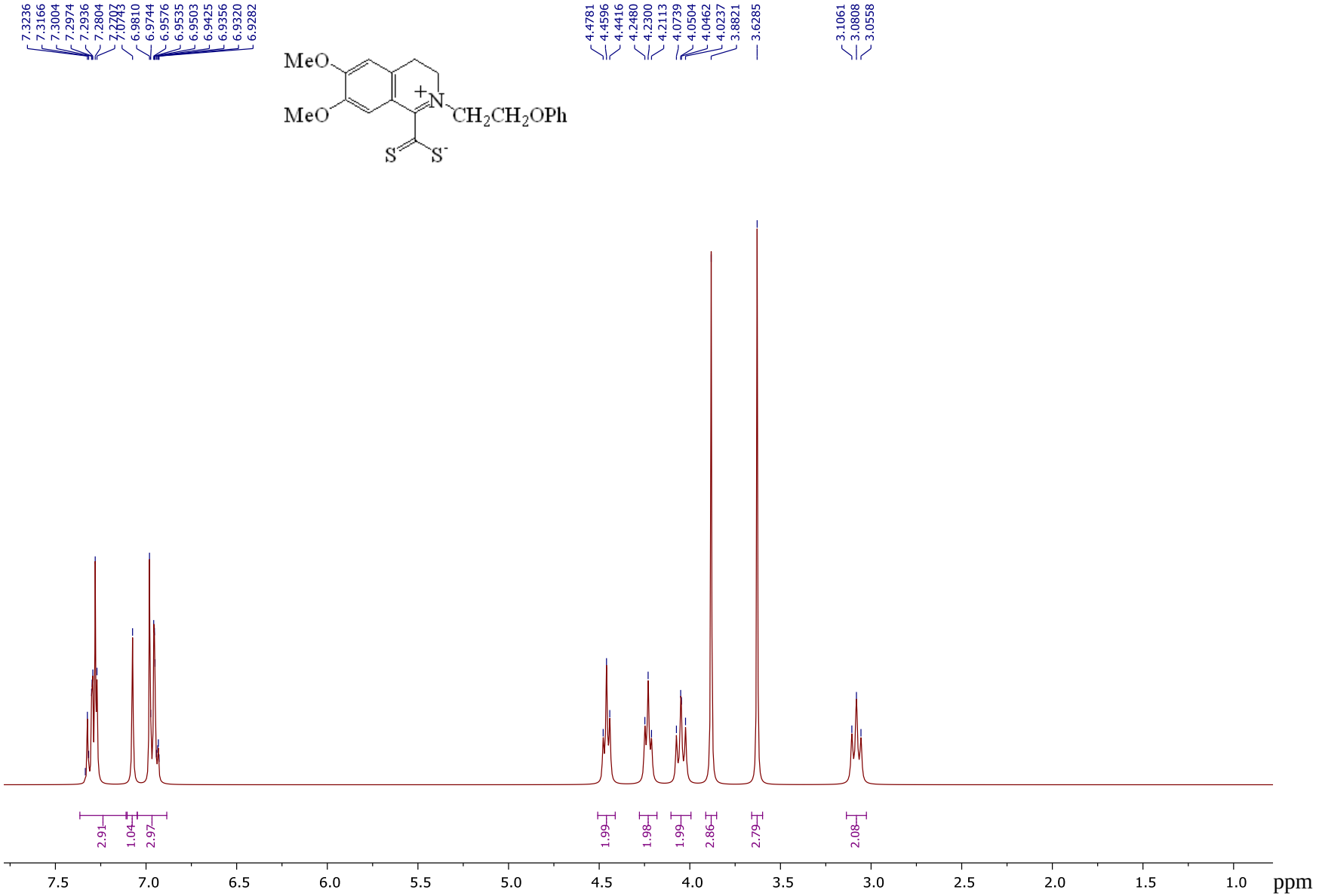



235.3383
169.0830
154.7606
147.5174
133.7427
116.5351
113.4660
110.7946
56.1367
55.6558
54.1326
47.4973
28.3961
25.0518
19.4581
13.4493
MeO
MeO
N
Bu
S
S
90 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 ppm

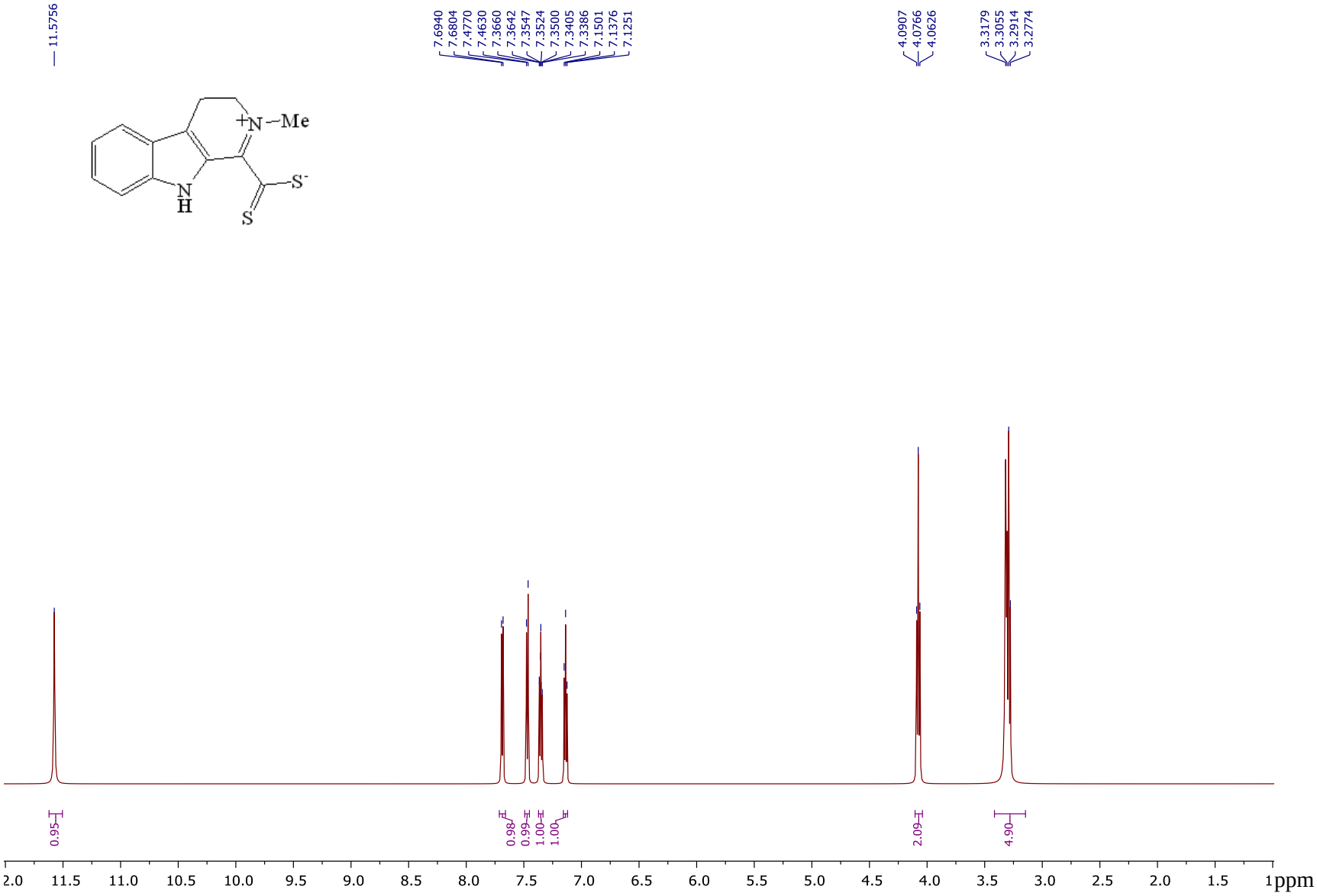
2-Hexyl-6,7-dimethoxy- -3,4-dihydroisoquinolinium-1-dithiocarboxylate (**2f**).

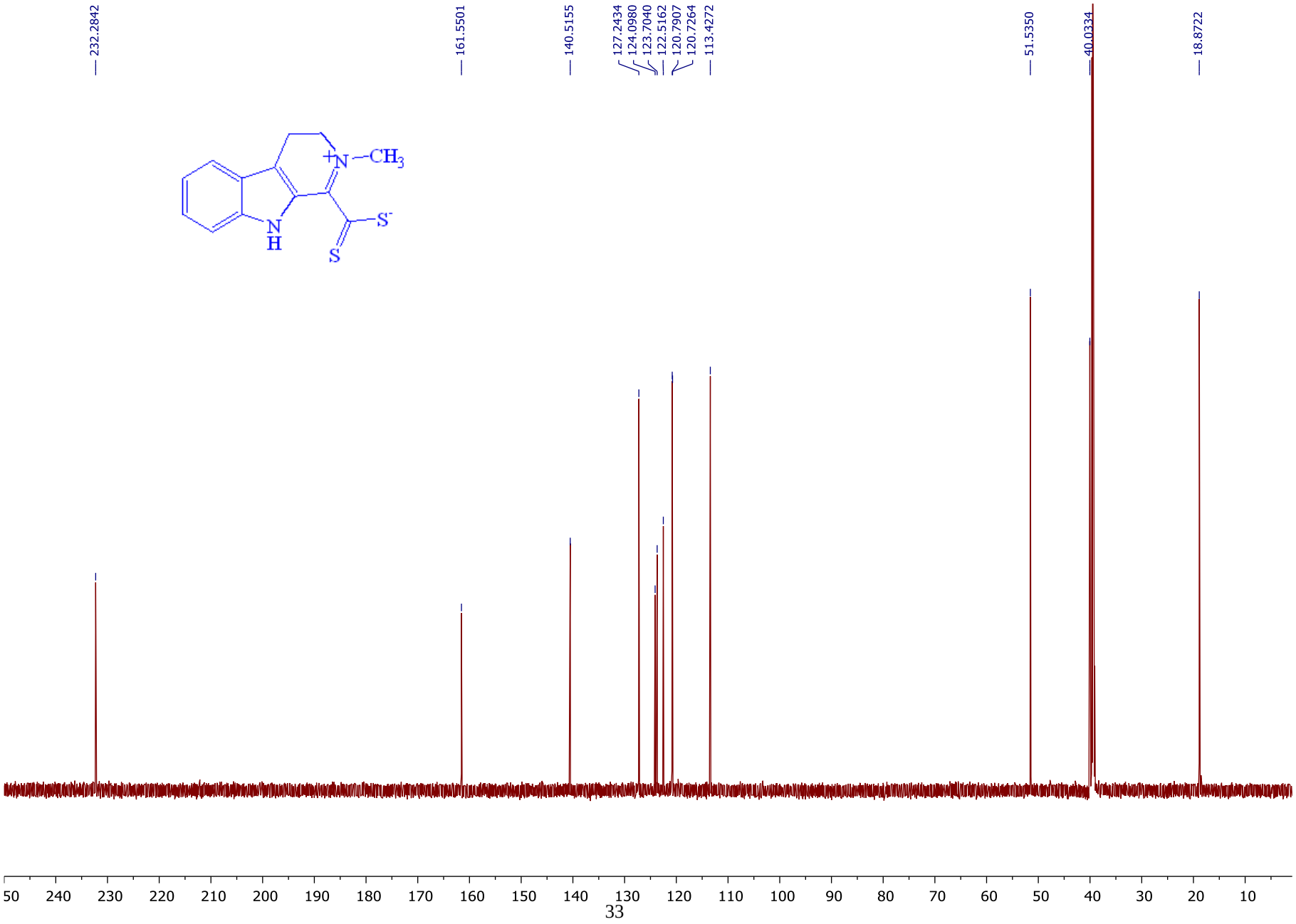


6,7-Dimethoxy-2-(2-phenoxyethyl)-3,4-dihydroisoquinolinium-1-dithiocarboxylate (**2g**).

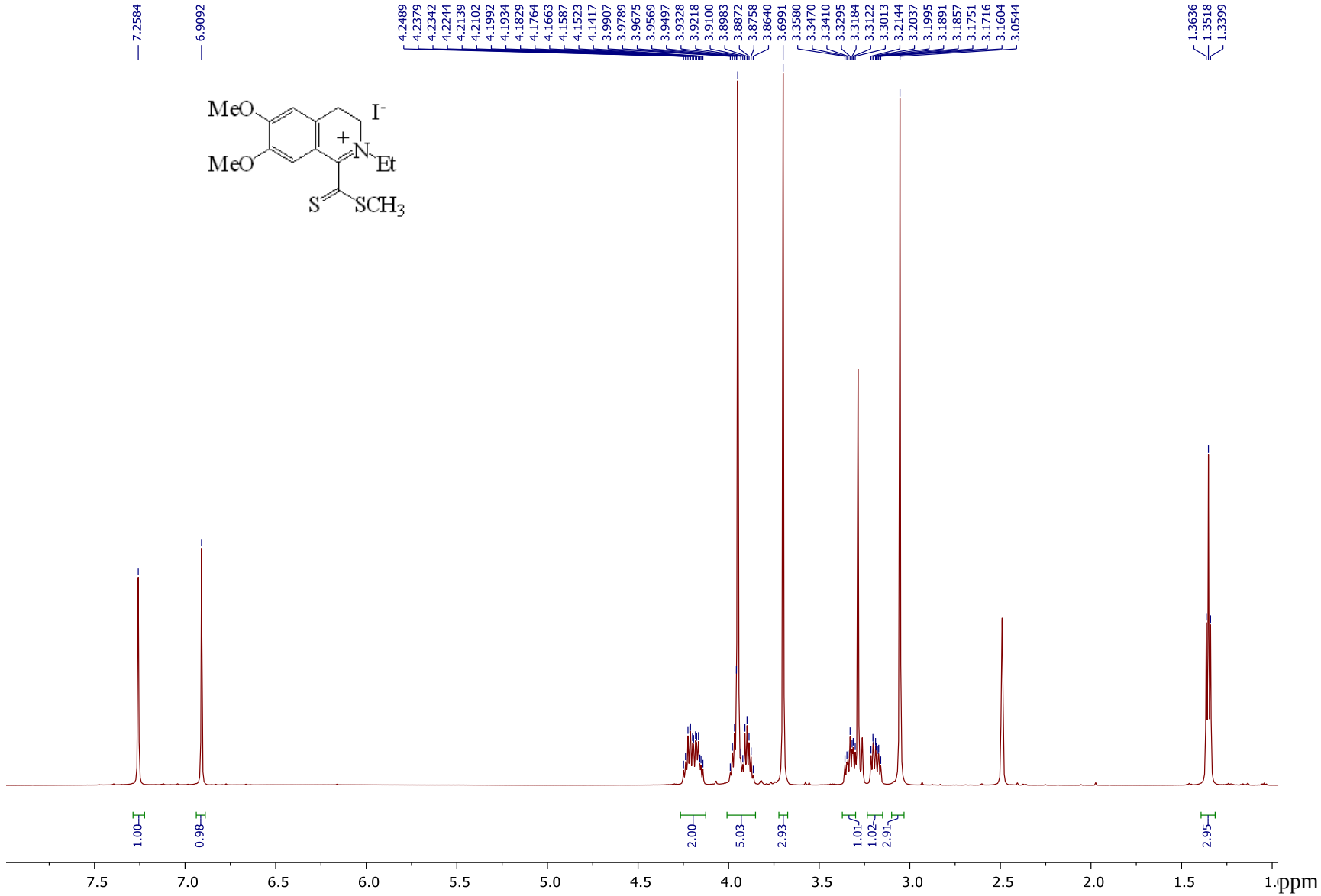


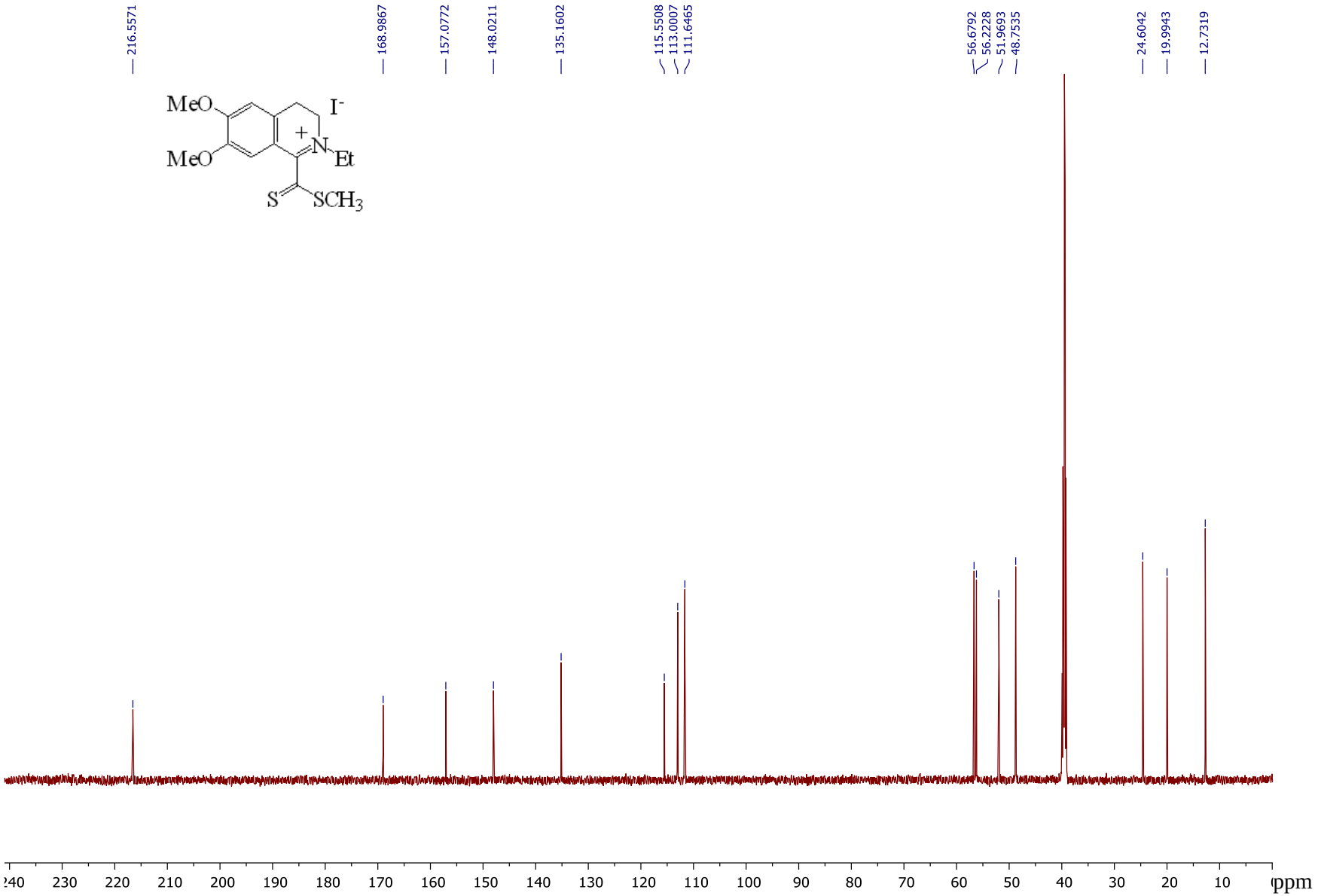
2-Methyl-4,9-dihydro-3*H*-pyrido[3,4-*b*]indol-1-dithiocarboxylate **6.**



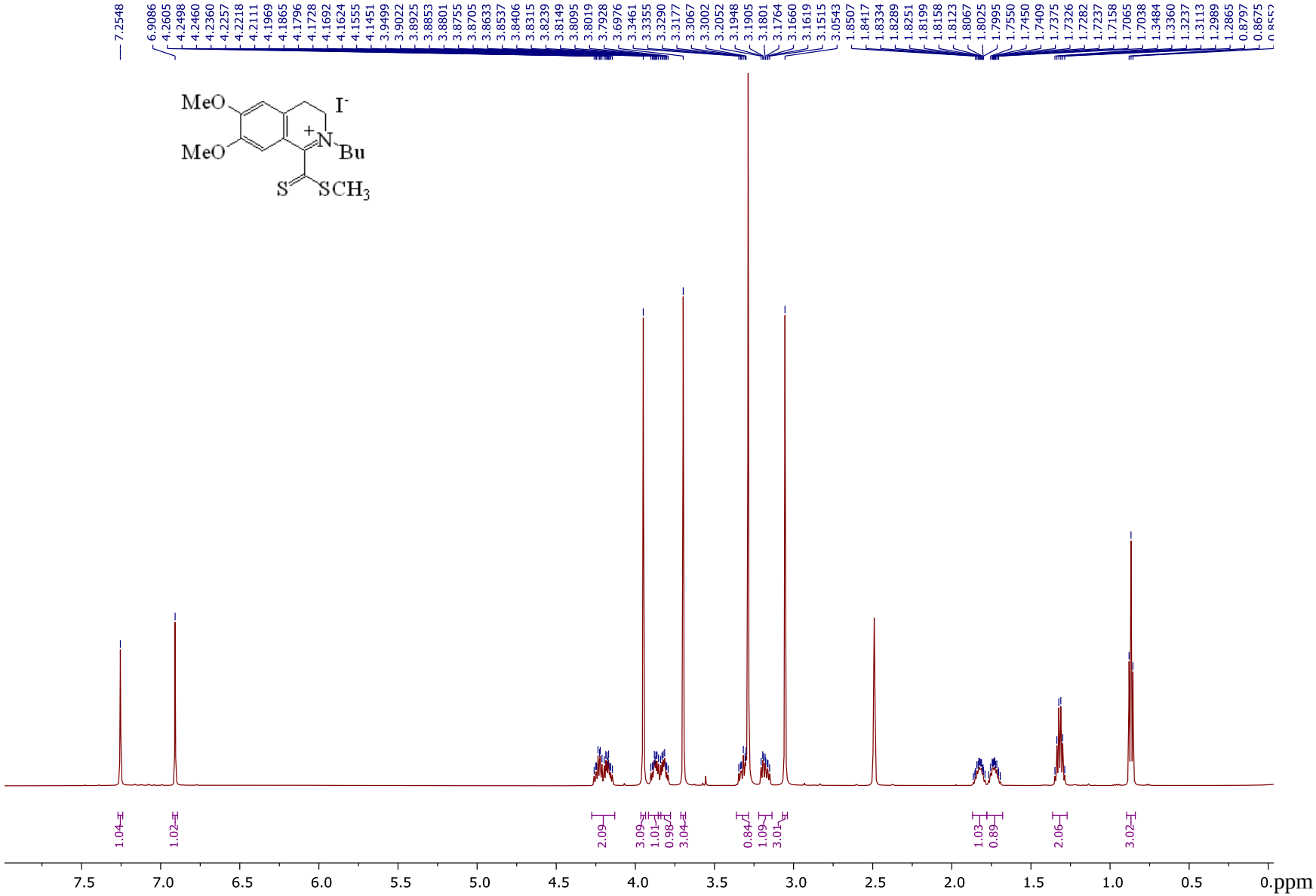

232.2842
161.5501
140.5155
127.2434
124.0980
123.7040
122.5162
120.7907
120.7264
113.4272
51.5350
40.0334
18.8722
+N—CH3
N
H
S-
S
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

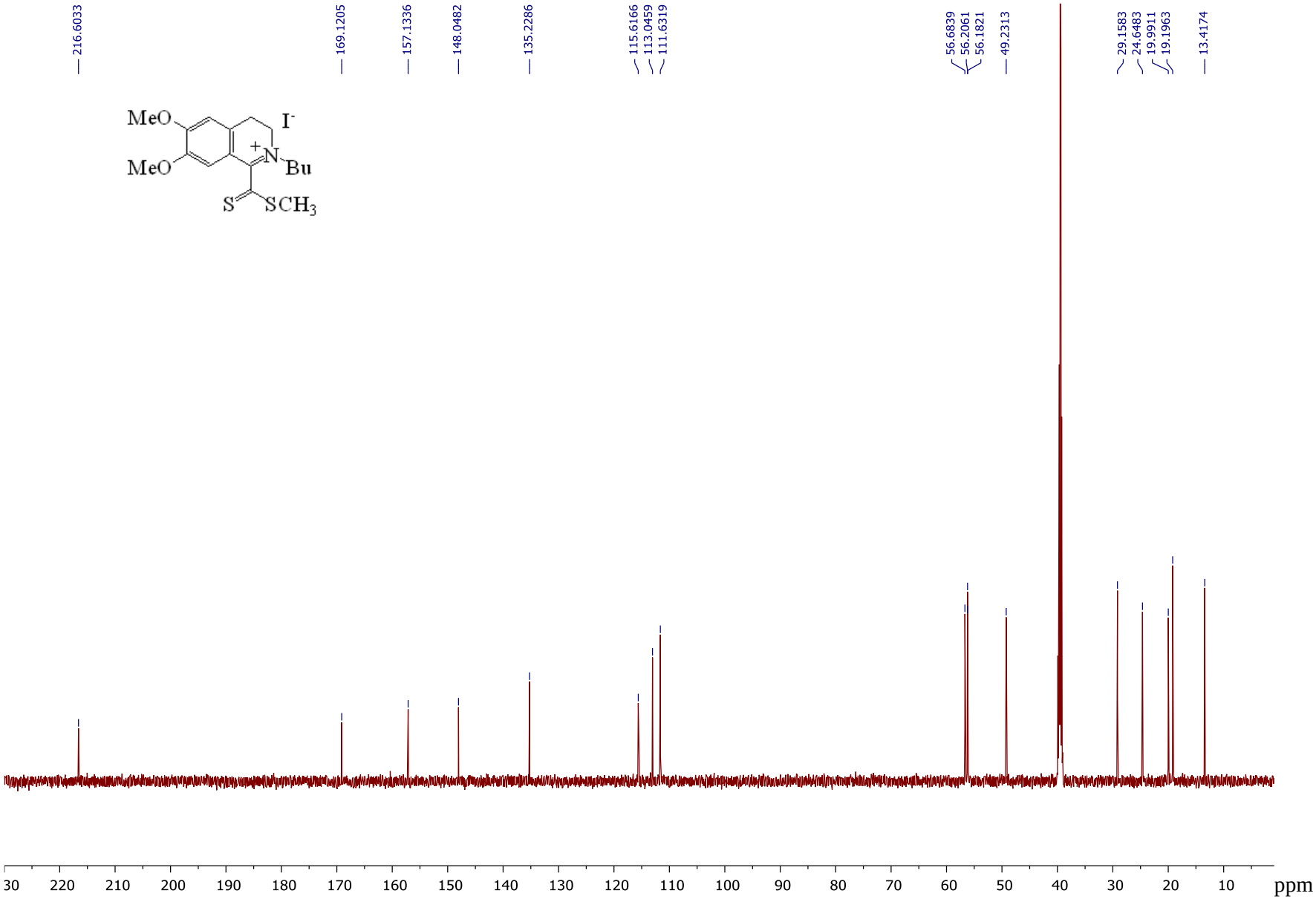
6,7-Dimethoxy-2-ethyl-1-[(methylsulfanyl)carbonothioyl]-3,4-dihydroisoquinolinium iodides (**3d**).



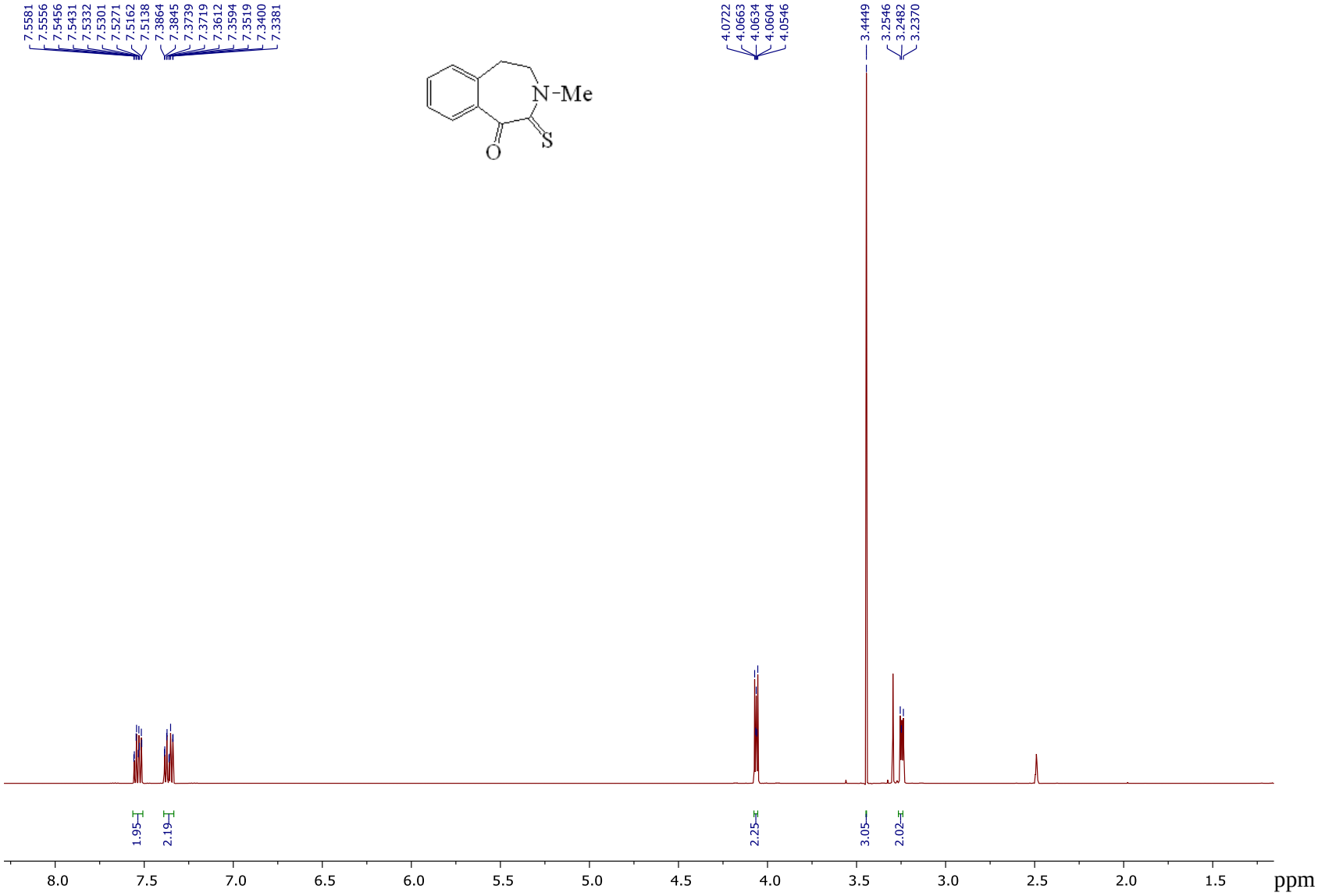

216.5571
168.9867
157.0772
148.0211
135.1602
115.5508
113.0007
111.6465
56.6792
56.2228
51.9693
48.7535
24.6042
19.9943
12.7319
MeO
MeO
I-
+
N
Et
S
SCH3
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

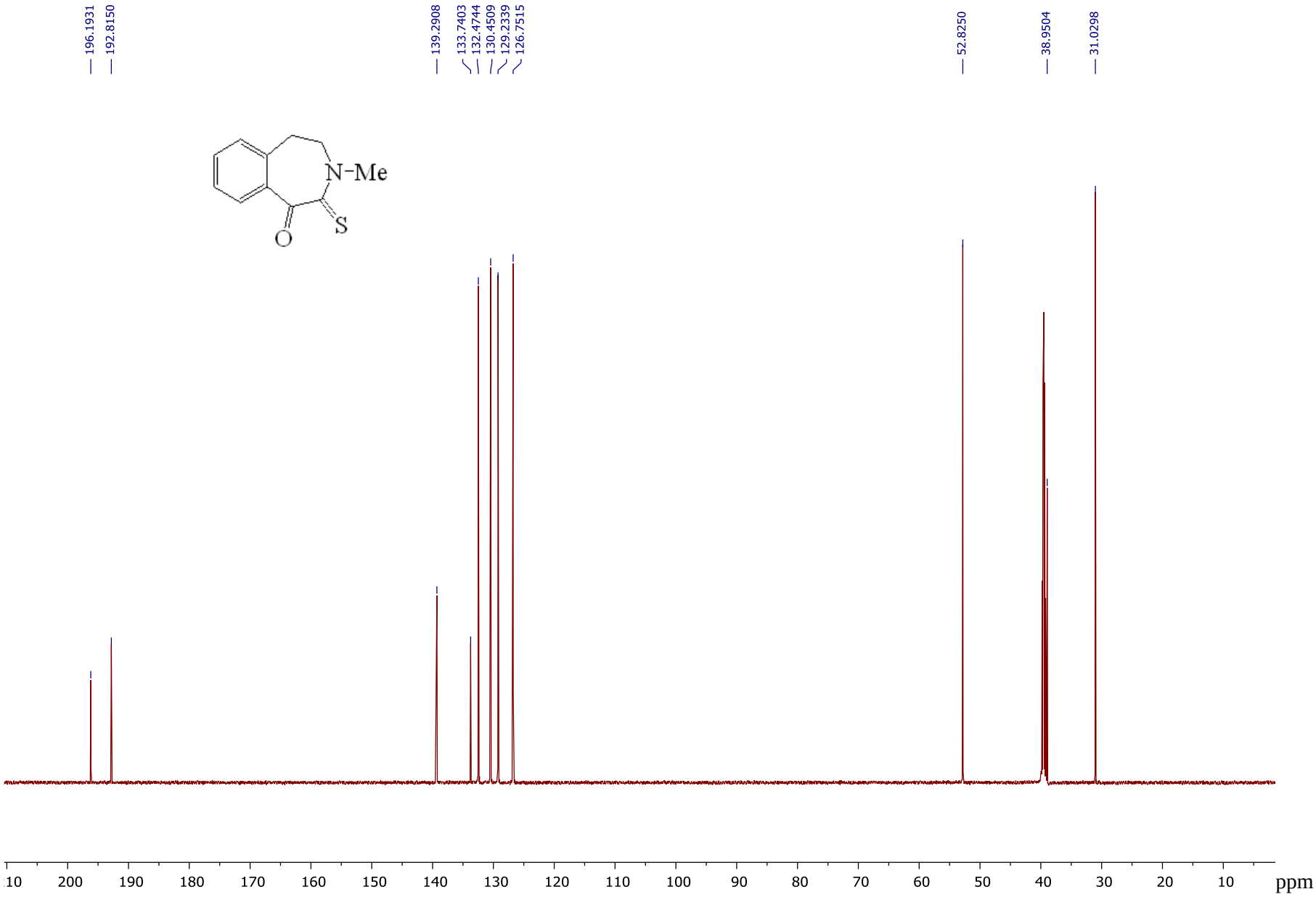
6,7-Dimethoxy-2-butyl-1-[(methylsulfanyl)carbonothioyl]-3,4-dihydroisoquinolinium Iodides (**3e**).

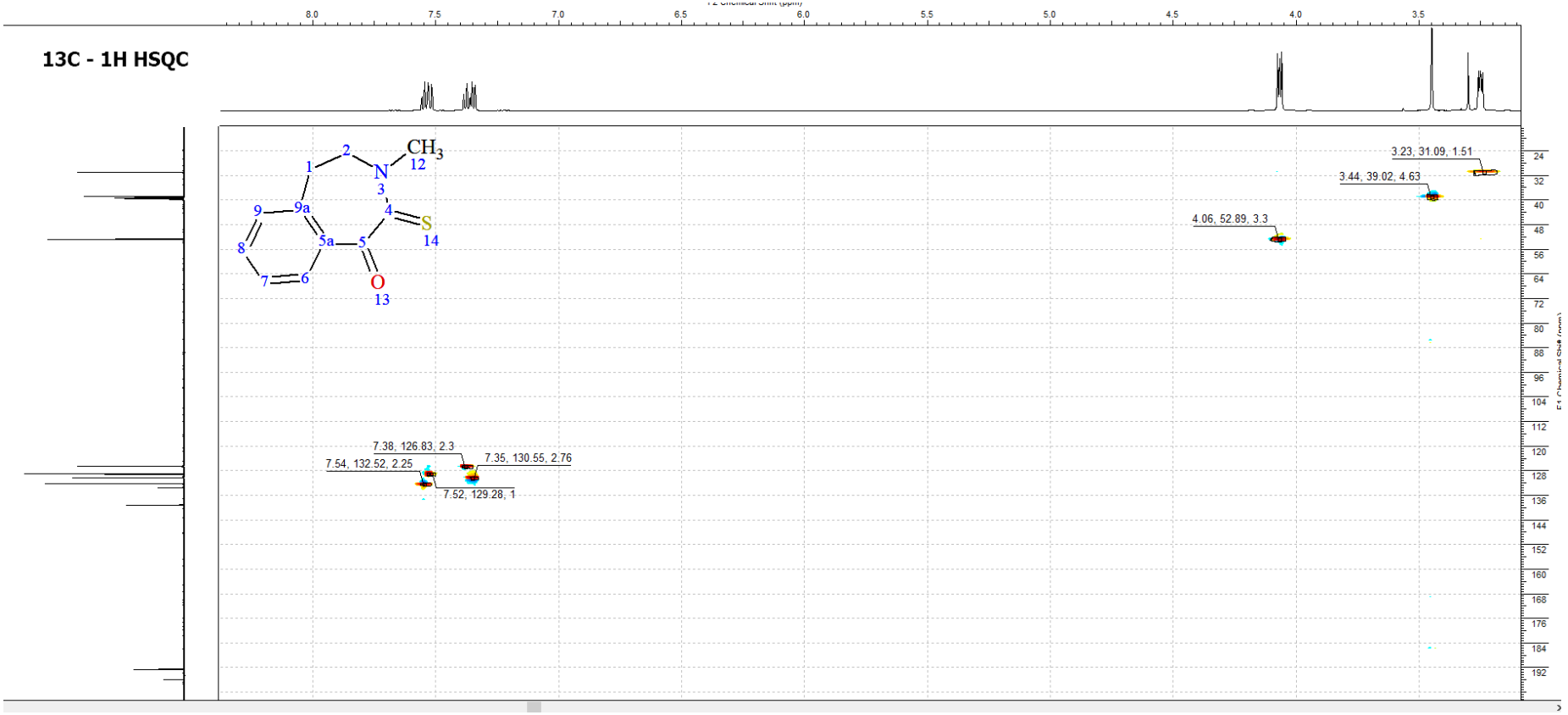


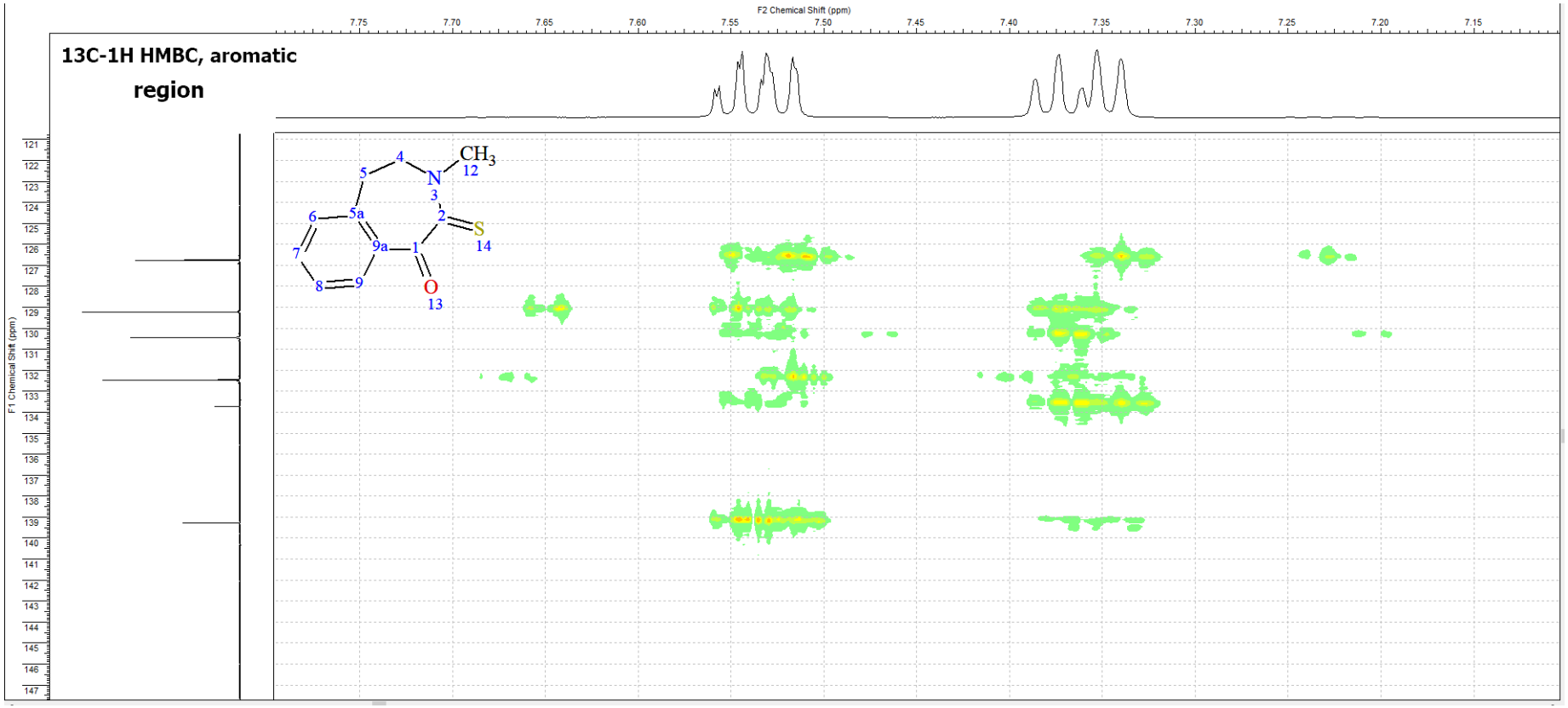

216.6033
169.1205
157.1336
148.0482
135.2286
115.6166
113.0459
111.6319
56.6839
56.2061
56.1821
49.2313
29.1583
24.6483
19.9911
19.1963
13.4174
MeO
MeO
I-
N
Bu
S
SCH3
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

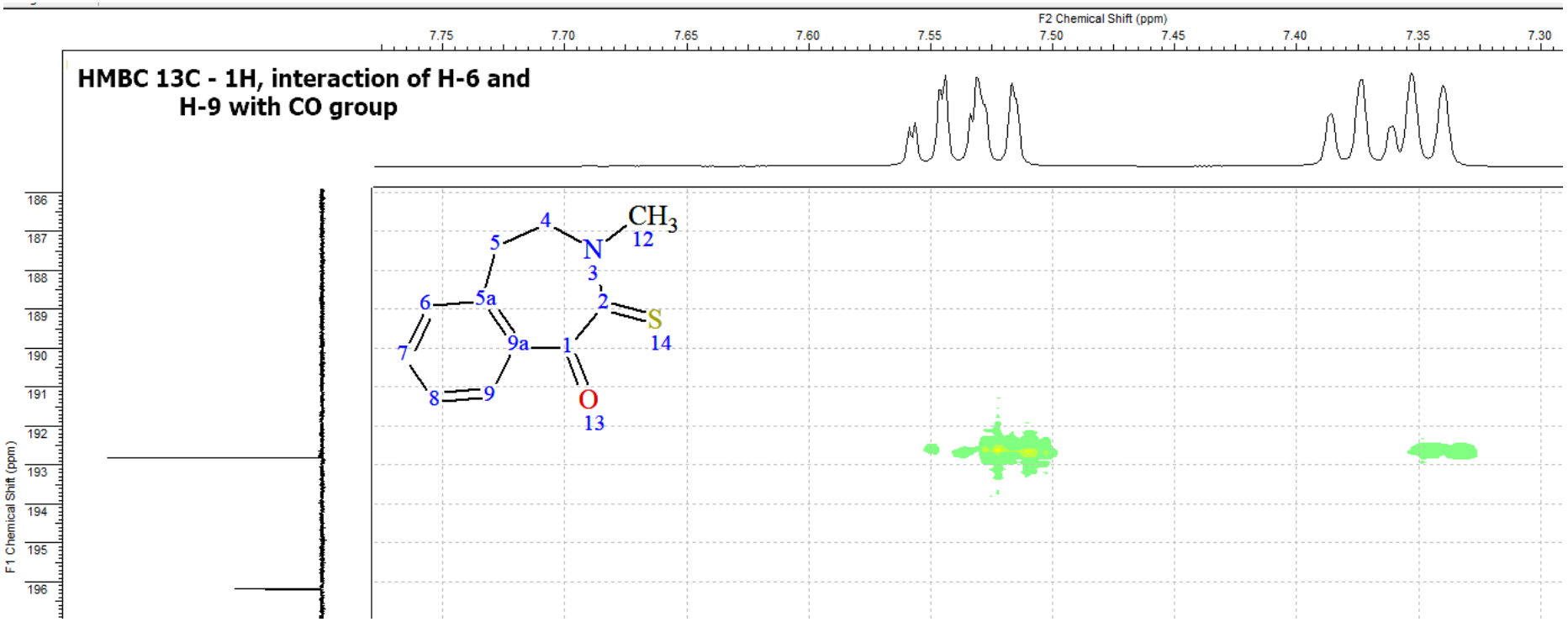
3-Methyl-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4a**).

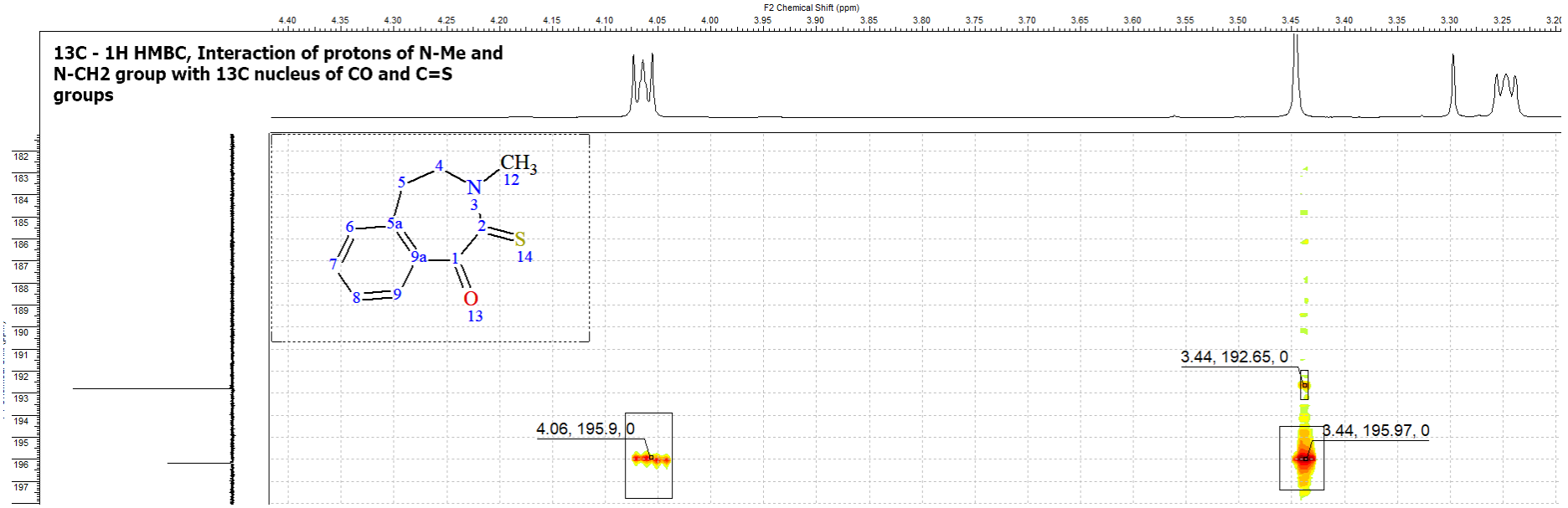


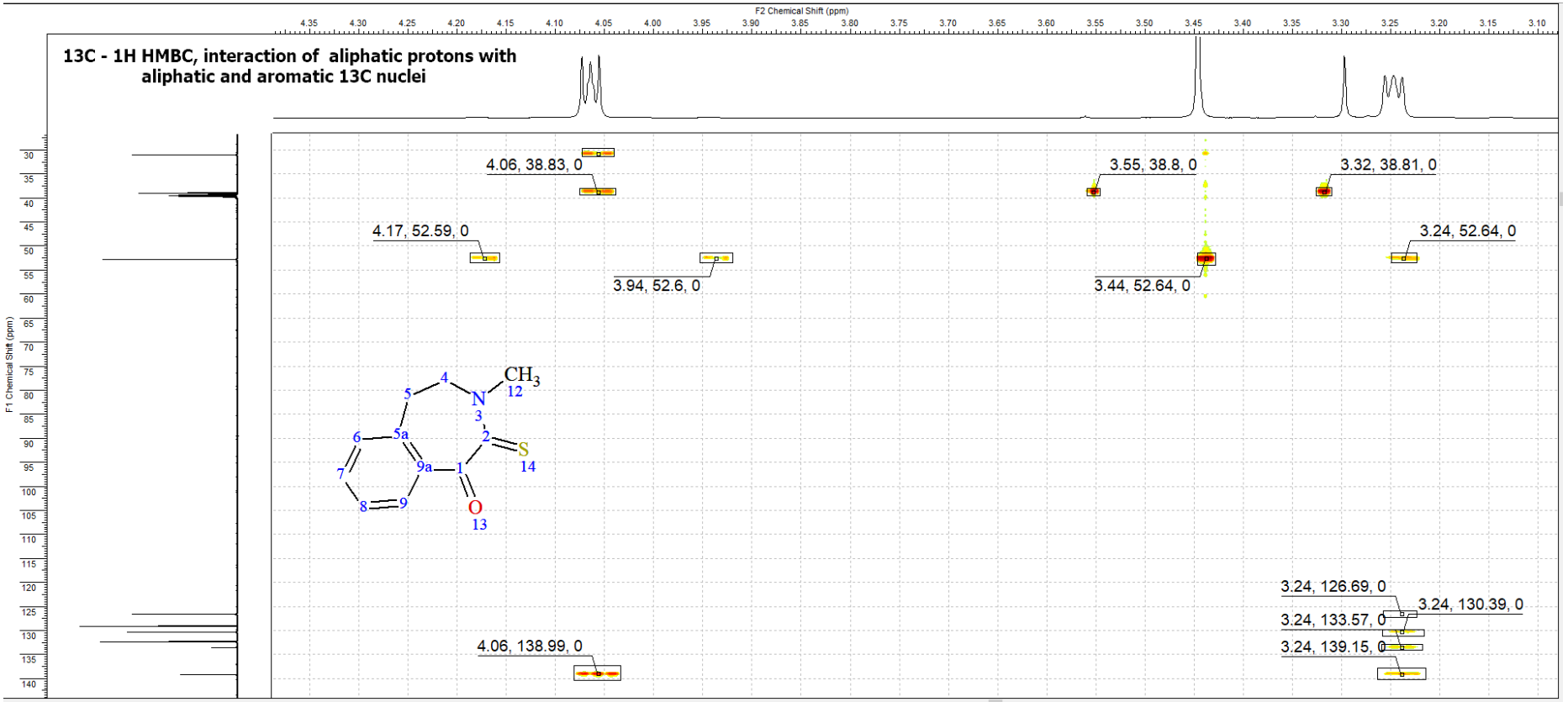

196.1931
192.8150
139.2908
133.7403
132.4744
130.4509
129.2339
126.7515
52.8250
38.9504
31.0298
N-Me
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13C - 1H HSQC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
CH3
12
N
3
1
2
9
9a
4
S
14
8
5a
5
7
6
O
13
3.23, 31.09, 1.51
3.44, 39.02, 4.63
4.06, 52.89, 3.3
7.38, 126.83, 2.3
7.54, 132.52, 2.25
7.35, 130.55, 2.76
7.52, 129.28, 1
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176
184
192

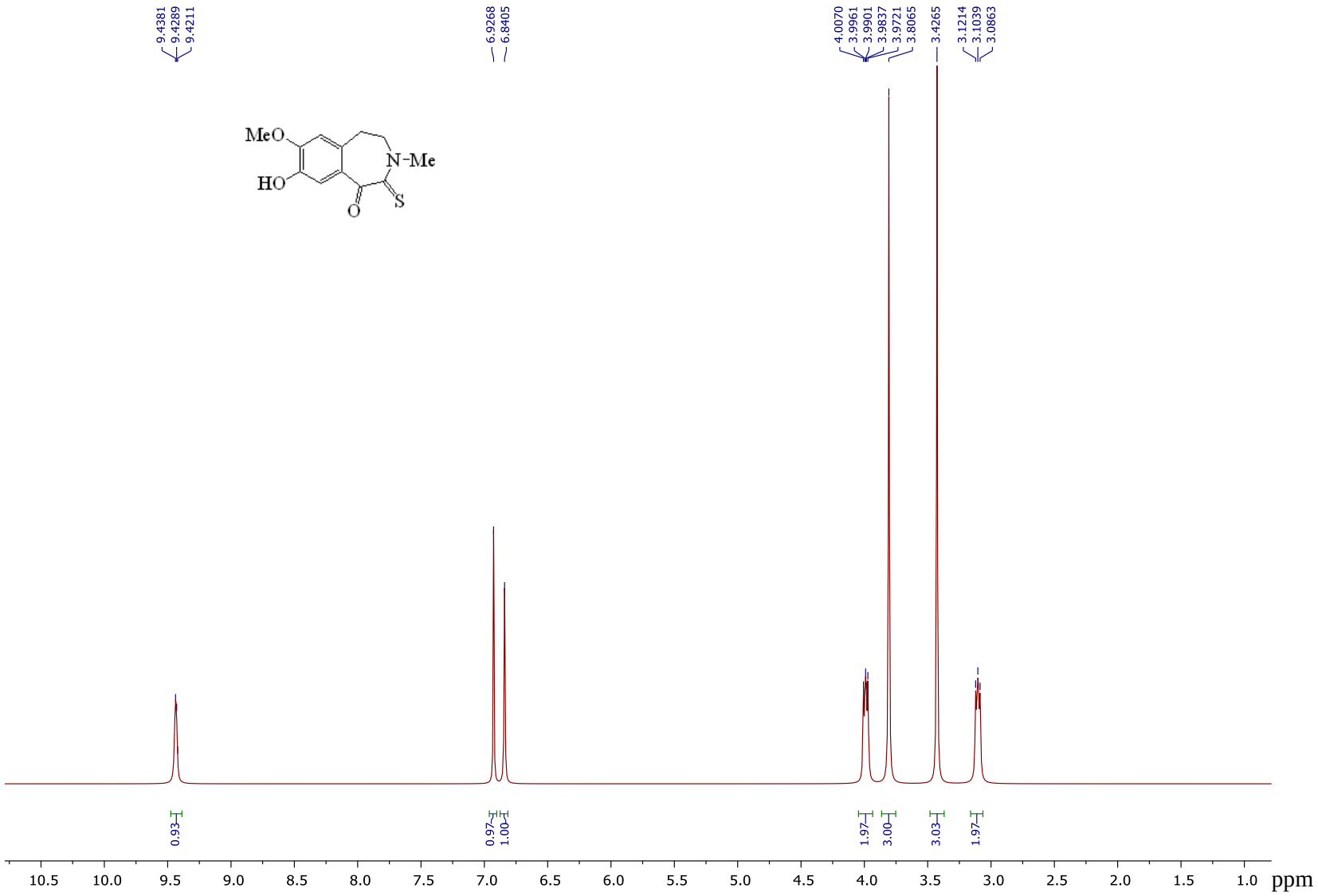

13C-1H HMBC, aromatic region
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
CH3
12
N
3
4
5
5a
6
7
8
9
9a
1
2
S
14
O
13

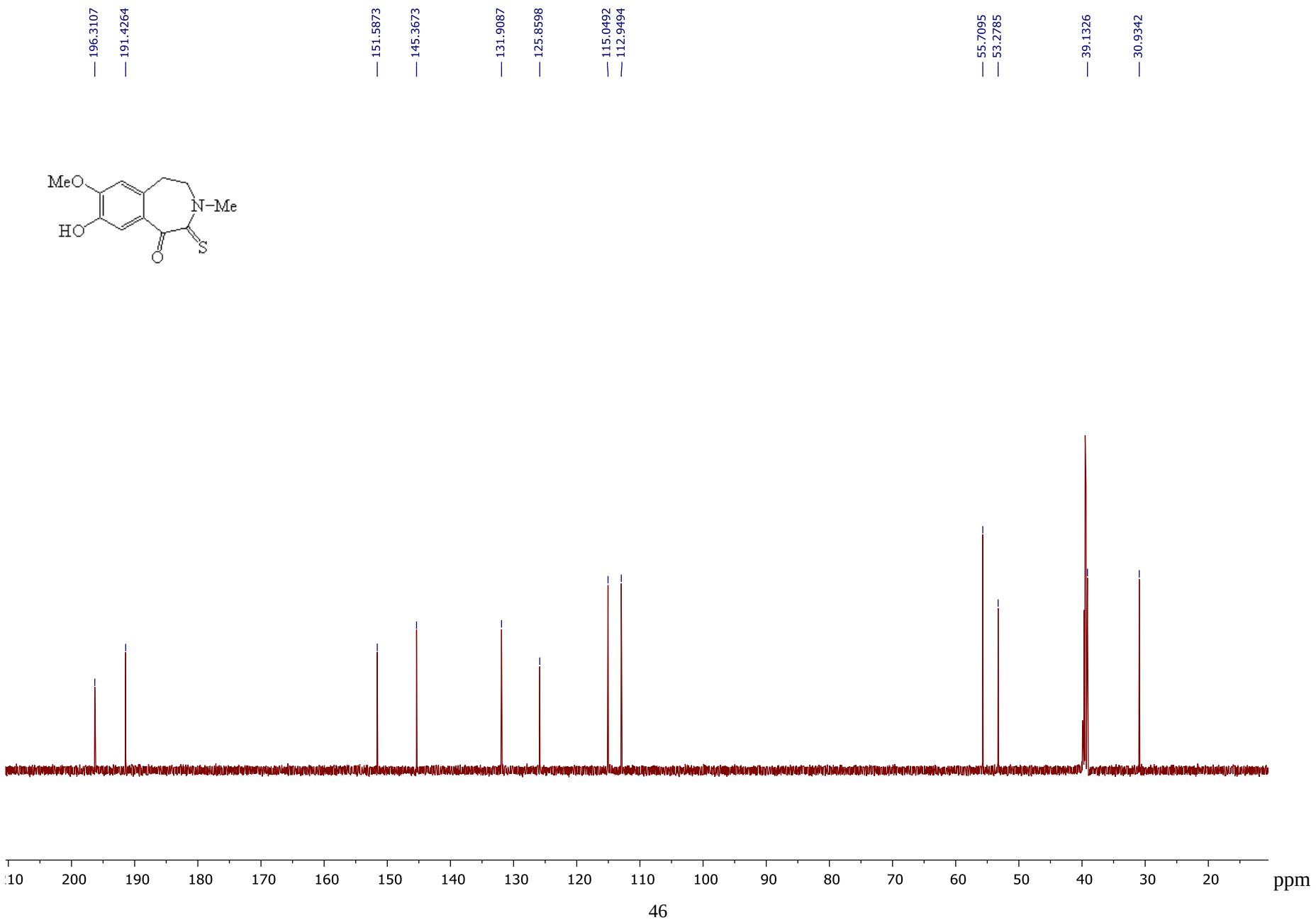

HMBC 13C - 1H, interaction of H-6 and
H-9 with CO group
F2 Chemical Shift (ppm)
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
F1 Chemical Shift (ppm)
186
187
188
189
190
191
192
193
194
195
196
CH3
12
N
3
4
5
5a
6
7
8
9
9a
1
2
S
14
O
13


F2 Chemical Shift (ppm)
13C - 1H HMBC, Interaction of protons of N-Me and N-CH2 group with 13C nucleus of CO and C=S groups
CH3
12
N
3
4
5
5a
6
7
8
9
9a
1
2
S
14
O
13
4.06, 195.9, 0
3.44, 192.65, 0
3.44, 195.97, 0

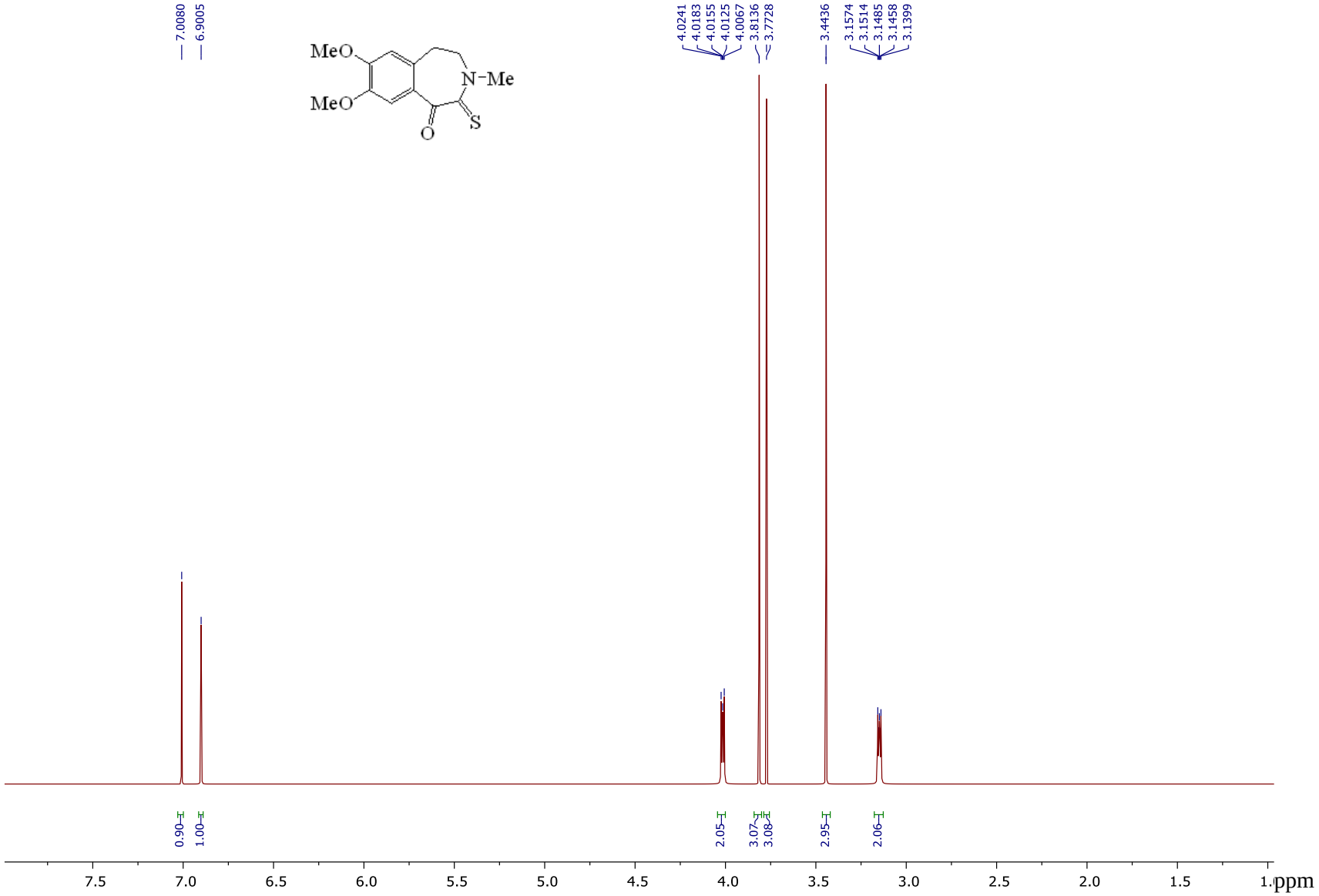

13C - 1H HMBC, interaction of aliphatic protons with aliphatic and aromatic 13C nuclei
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
4.06, 38.83, 0
3.55, 38.8, 0
3.32, 38.81, 0
4.17, 52.59, 0
3.24, 52.64, 0
3.94, 52.6, 0
3.44, 52.64, 0
CH3
12
N
3
4
5
6
5a
2
S
14
9a
1
7
8
9
O
13
3.24, 126.69, 0
3.24, 130.39, 0
3.24, 133.57, 0
3.24, 139.15, 0
4.06, 138.99, 0

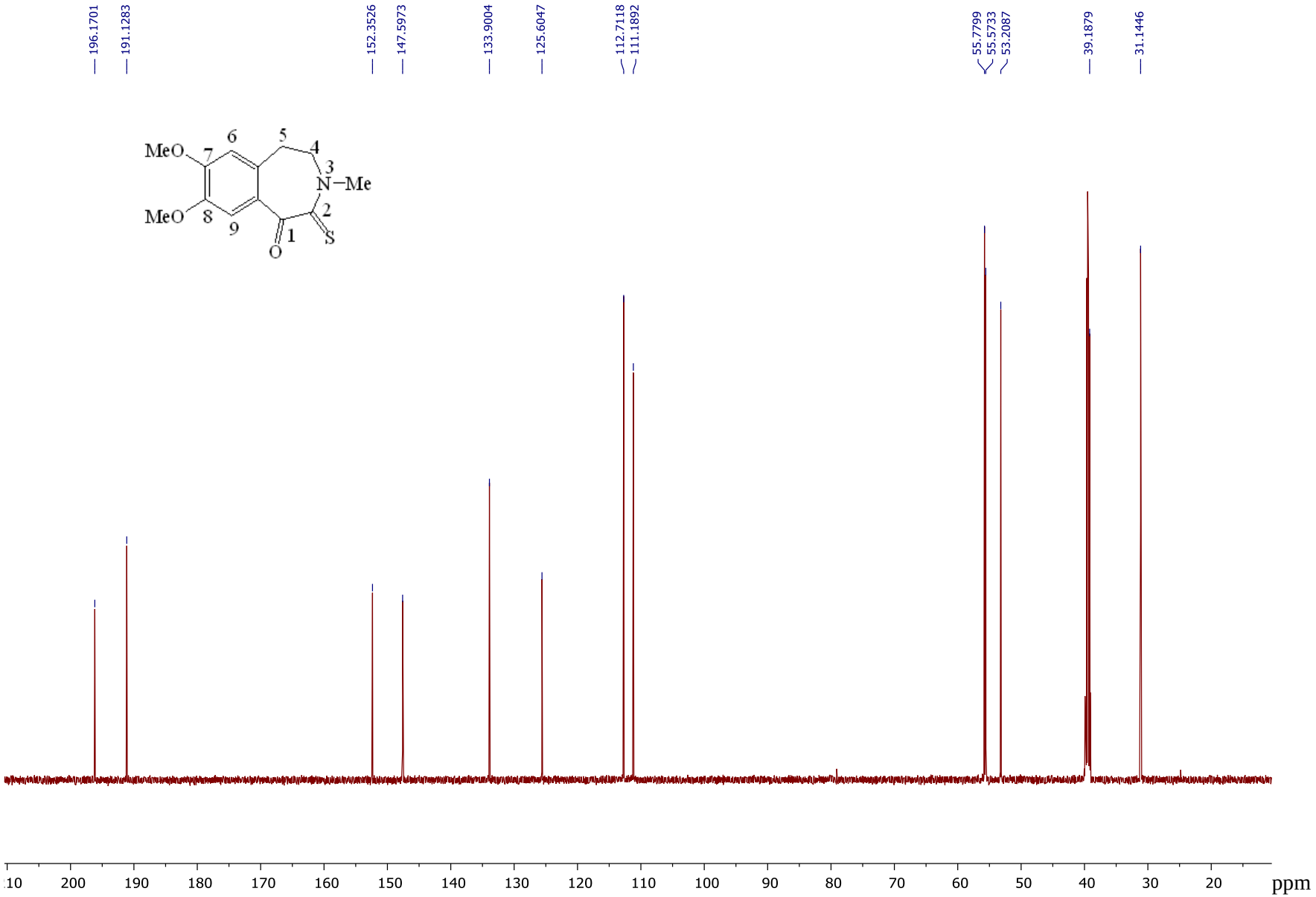
7-Hydroxy-8-methoxy-3-methyl-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4b**).



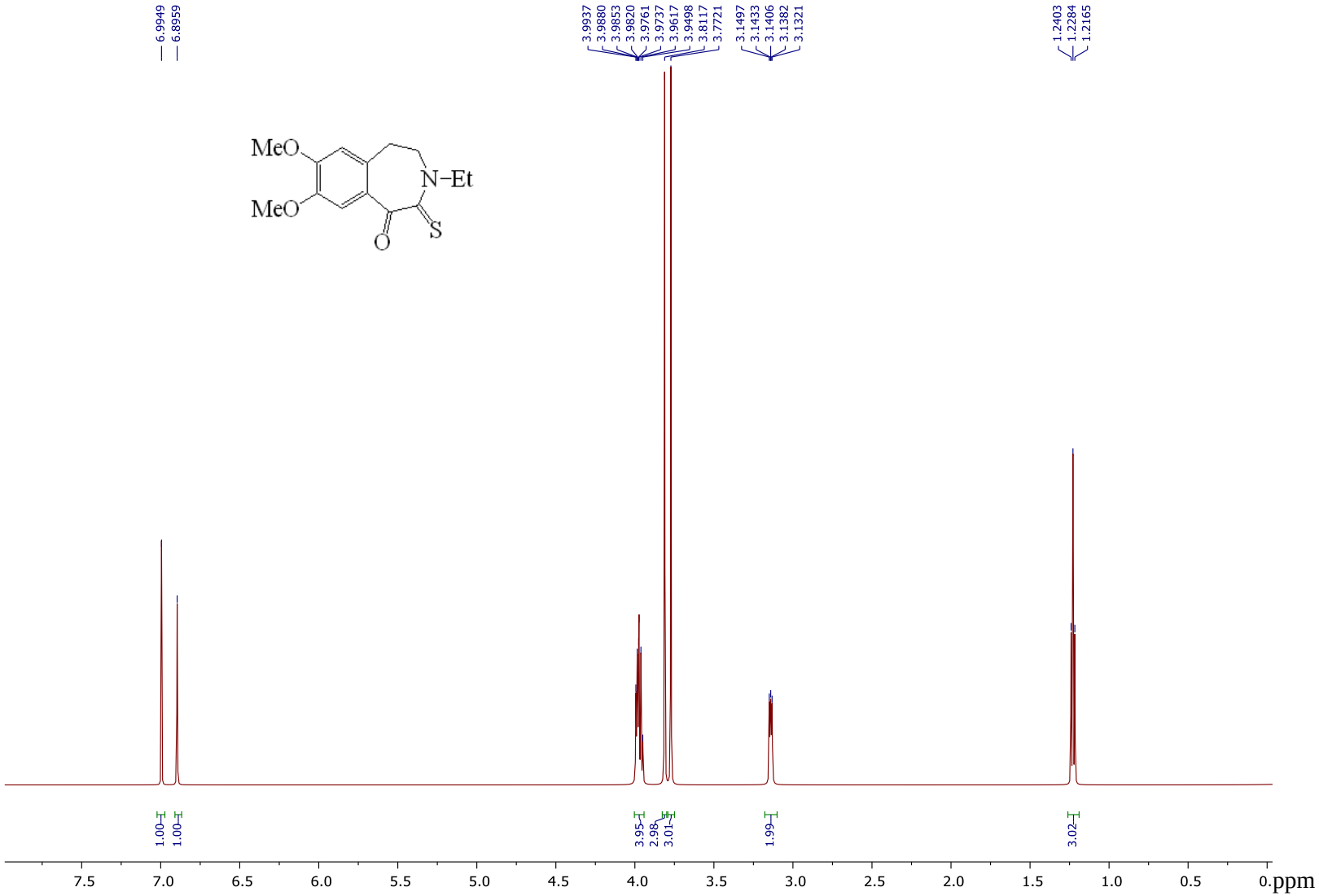

196.3107
191.4264
151.5873
145.3673
131.9087
125.8598
115.0492
112.9494
55.7095
53.2785
39.1326
30.9342
MeO
HO
N–Me
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

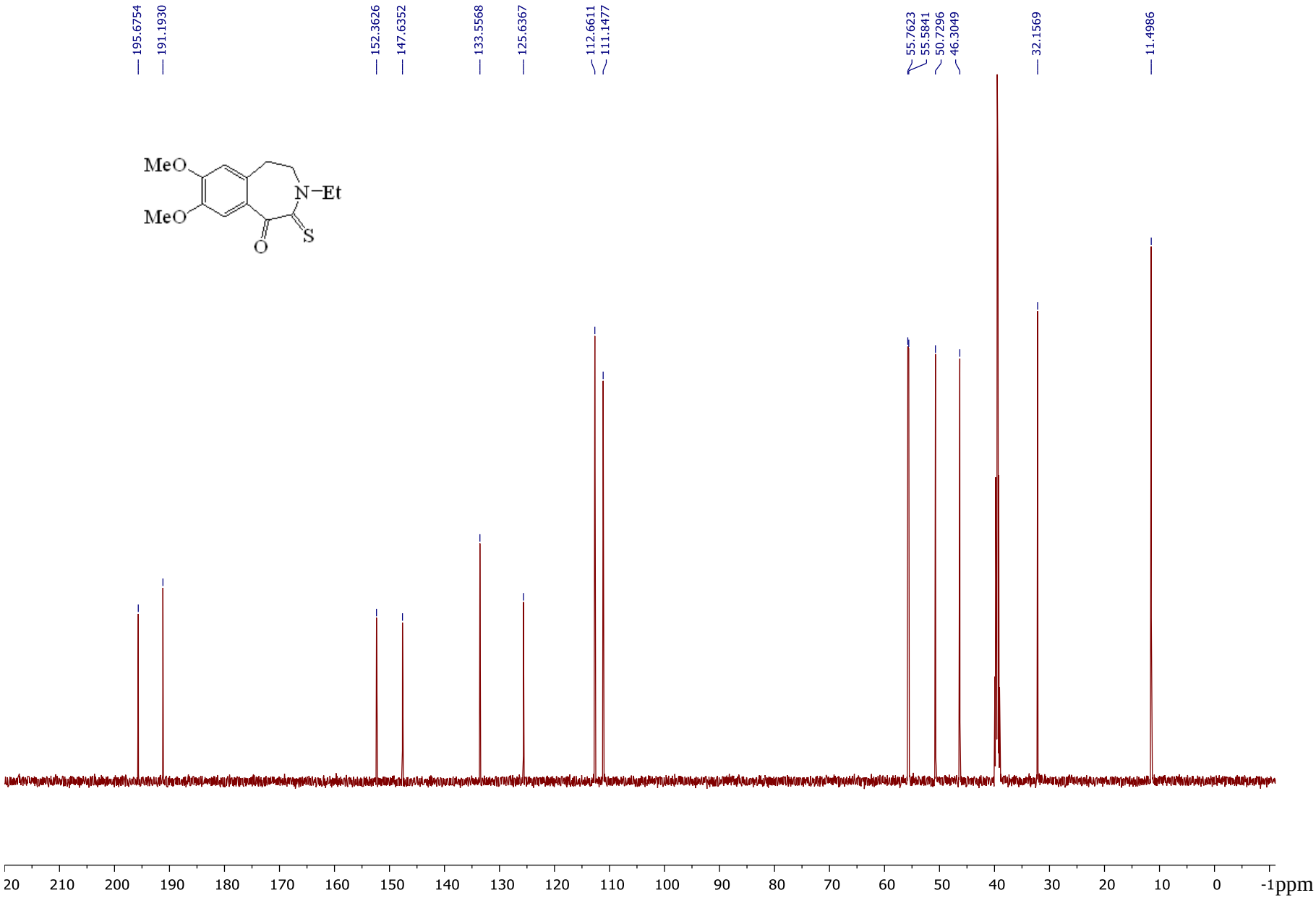
7,8-Dimethoxy-3-methyl-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4c**).



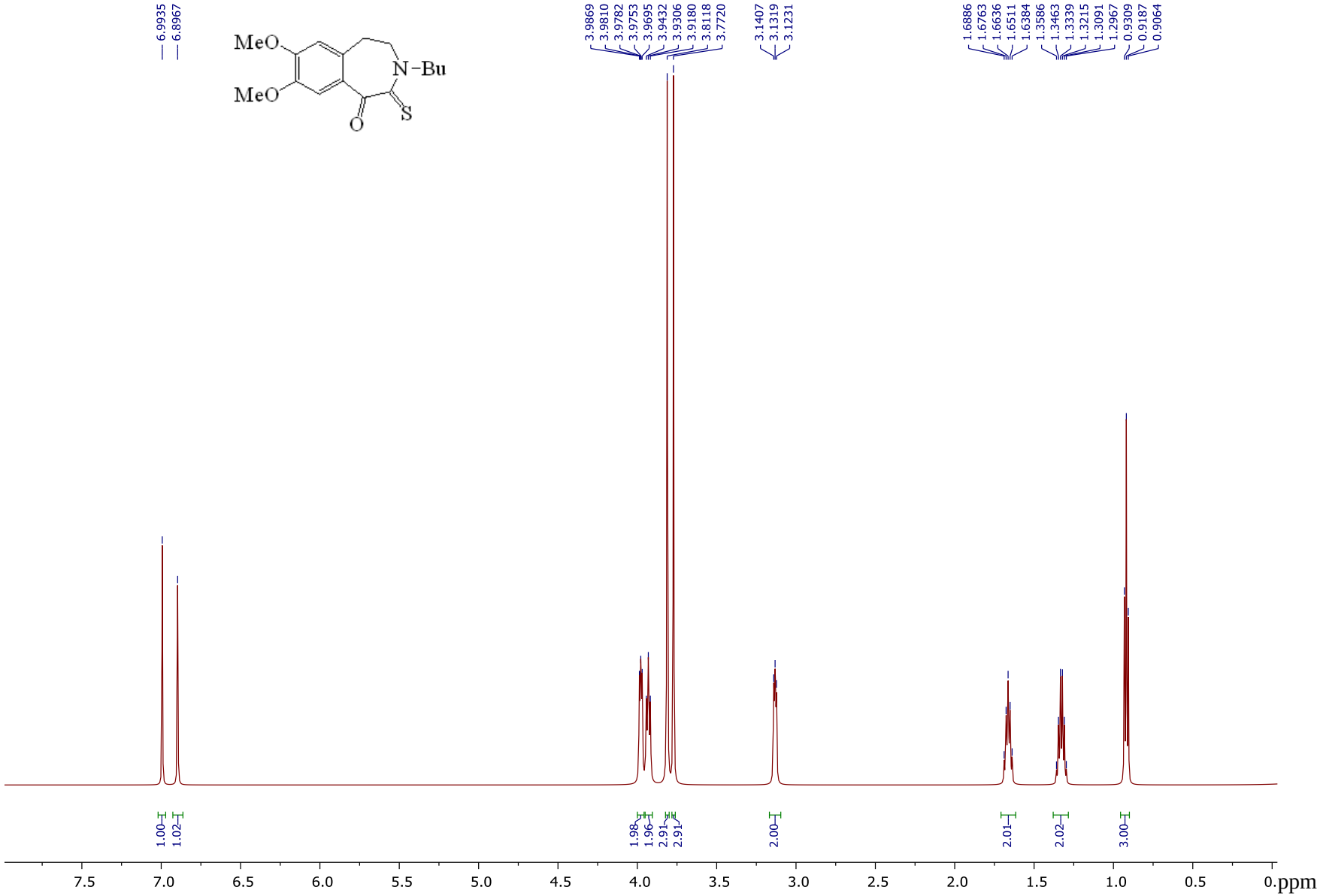

196.1701
191.1283
152.3526
147.5973
133.9004
125.6047
112.7118
111.1892
55.7799
55.5733
53.2087
39.1879
31.1446
MeO
MeO
N–Me
O
S
ppm

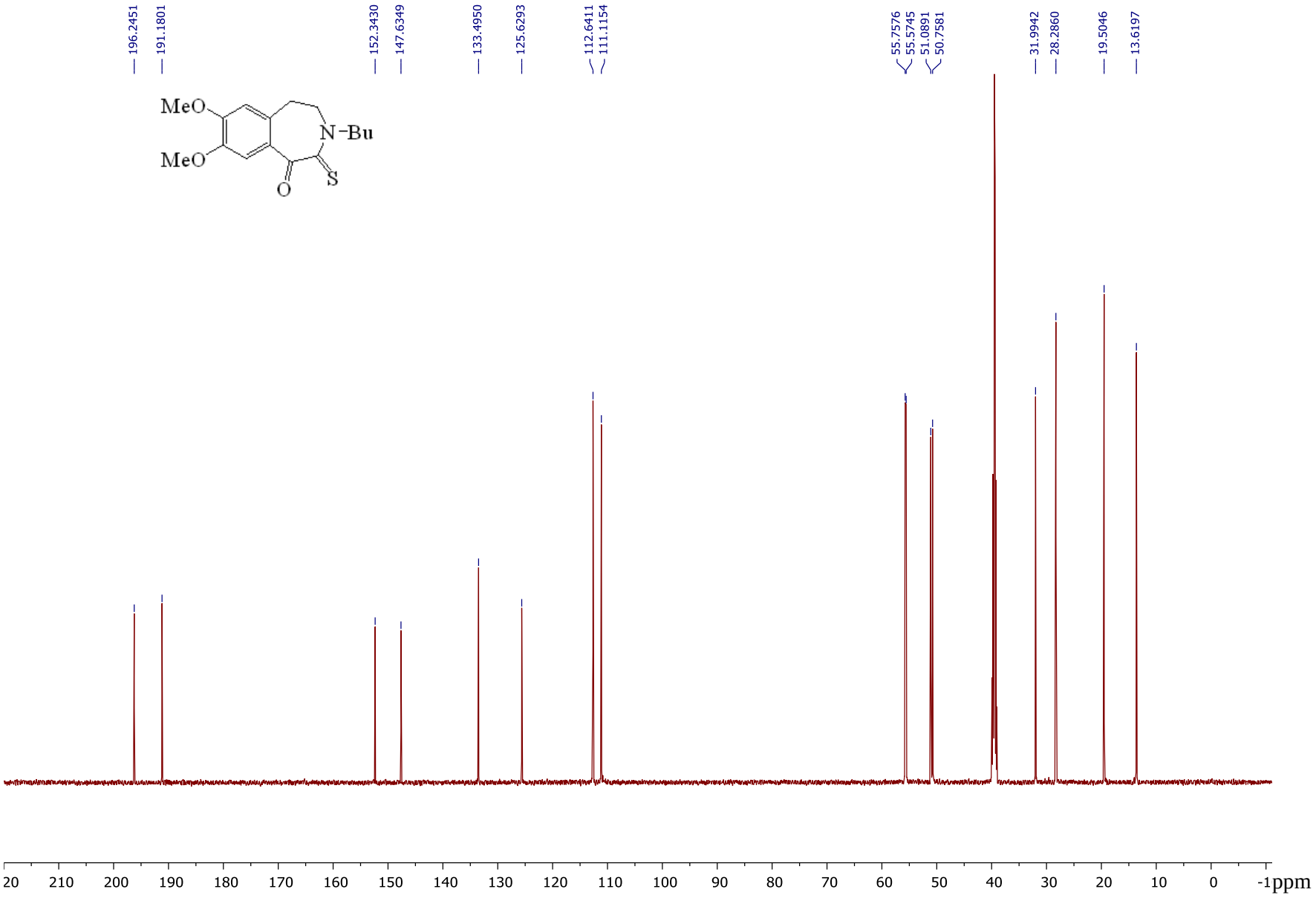
3-Ethyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4d**).



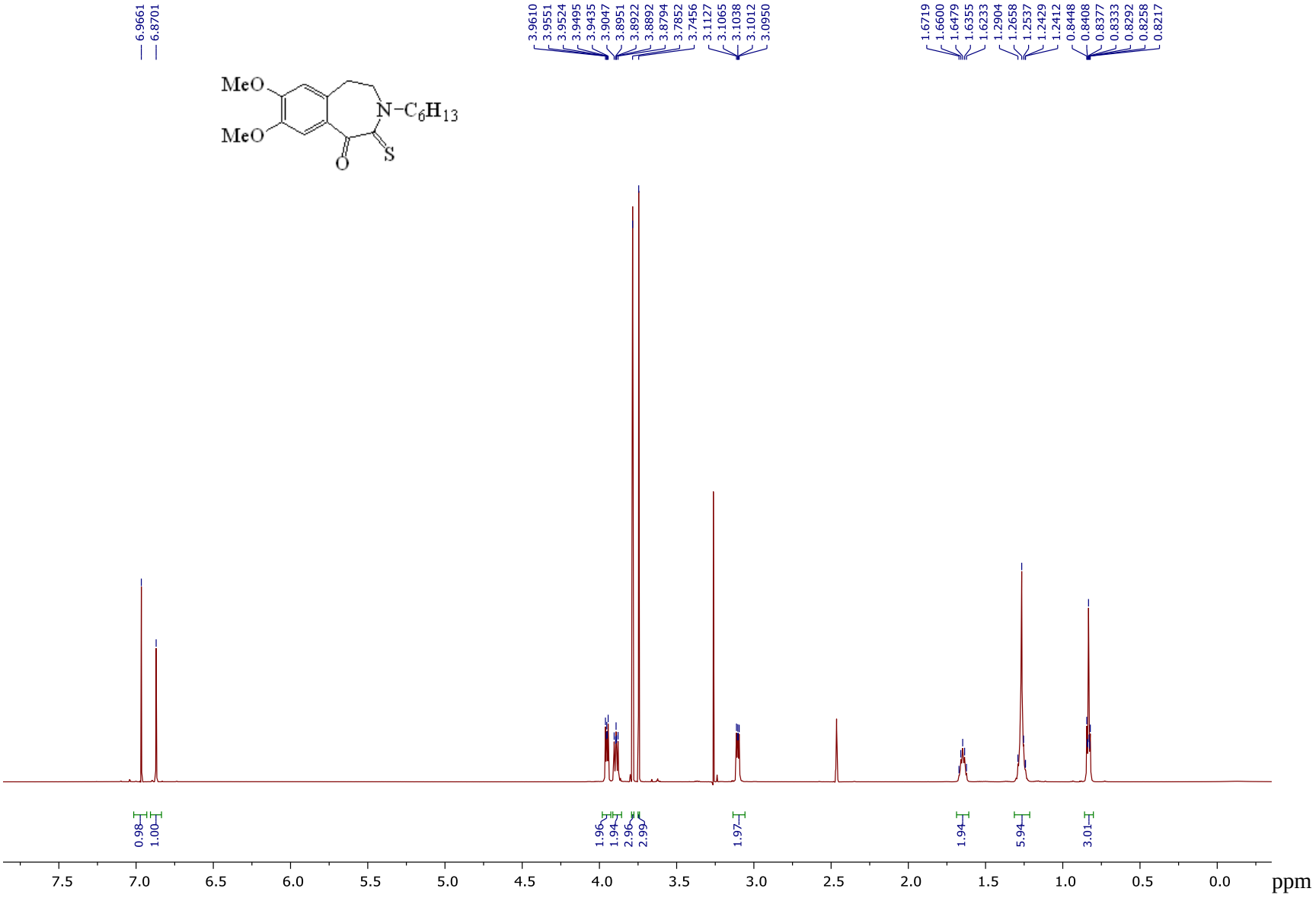

195.6754
191.1930
152.3626
147.6352
133.5568
125.6367
112.6611
111.1477
55.7623
55.5841
50.7296
46.3049
32.1569
11.4986
MeO
MeO
N−Et
O
S
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1ppm

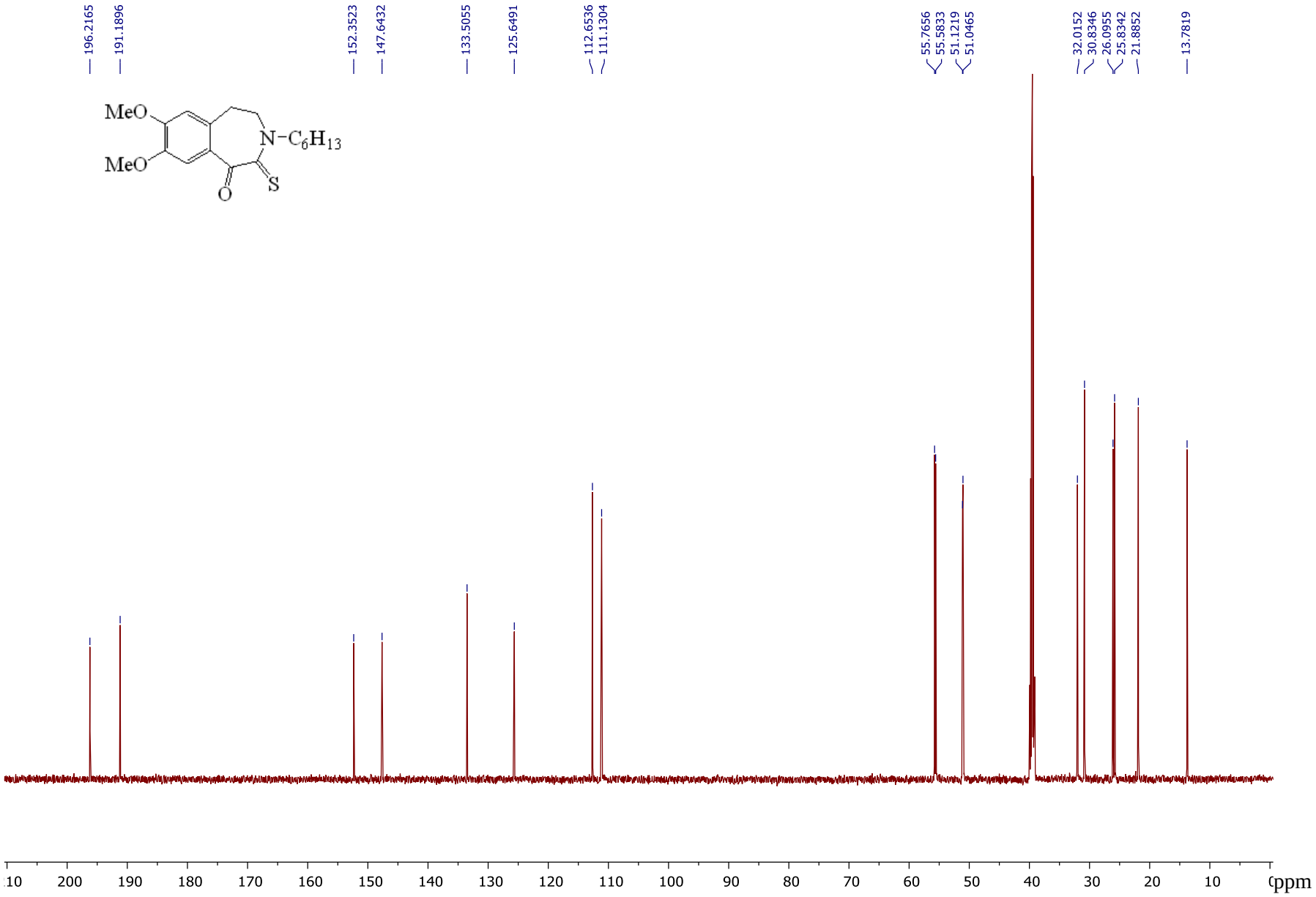
3-Butyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4e**).



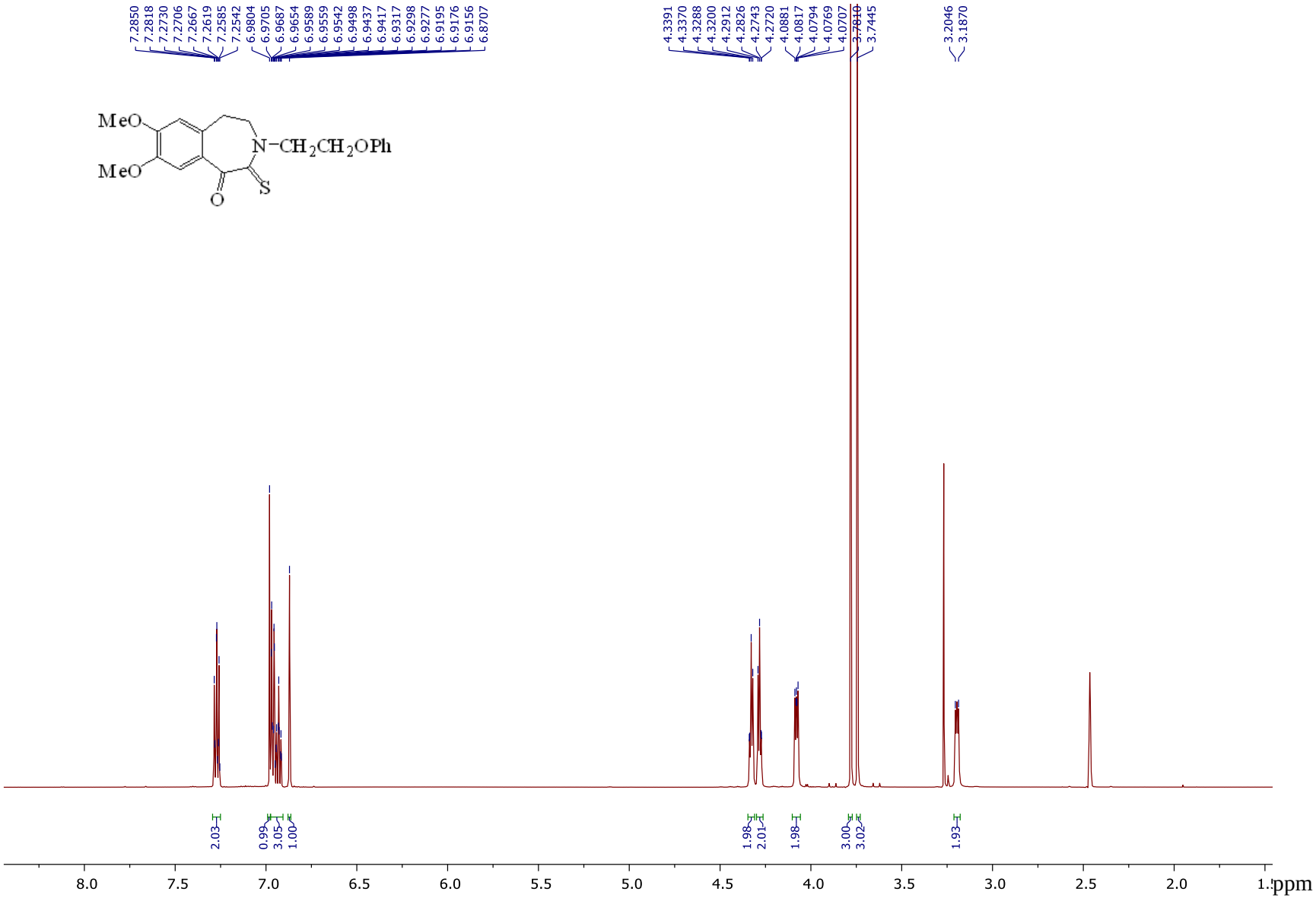

196.2451
191.1801
152.3430
147.6349
133.4950
125.6293
112.6411
111.1154
55.7576
55.5745
51.0891
50.7581
31.9942
28.2860
19.5046
13.6197
MeO
MeO
N-Bu
O
S
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1ppm

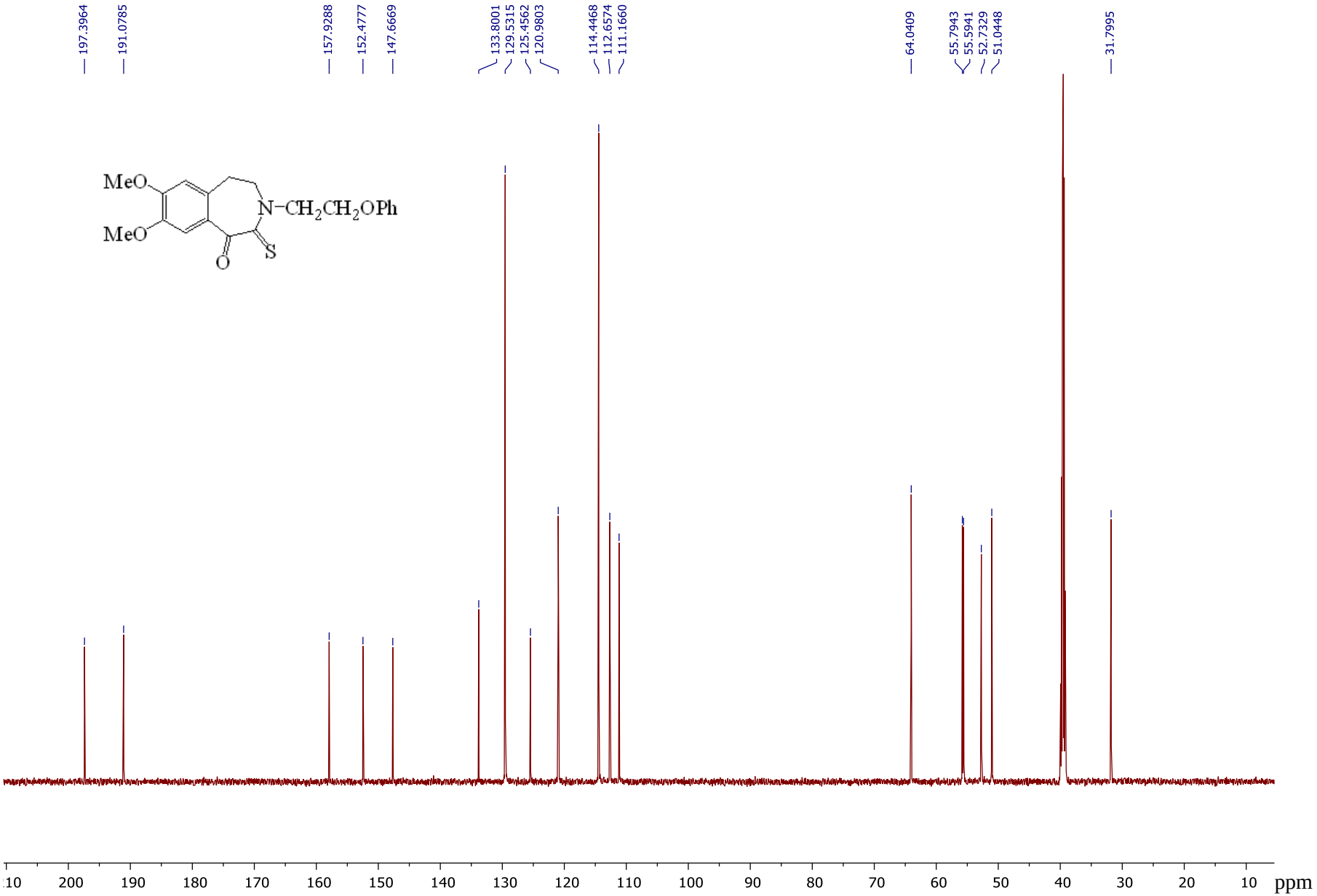
3-Hexyl-7,8-dimethoxy-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4f**).



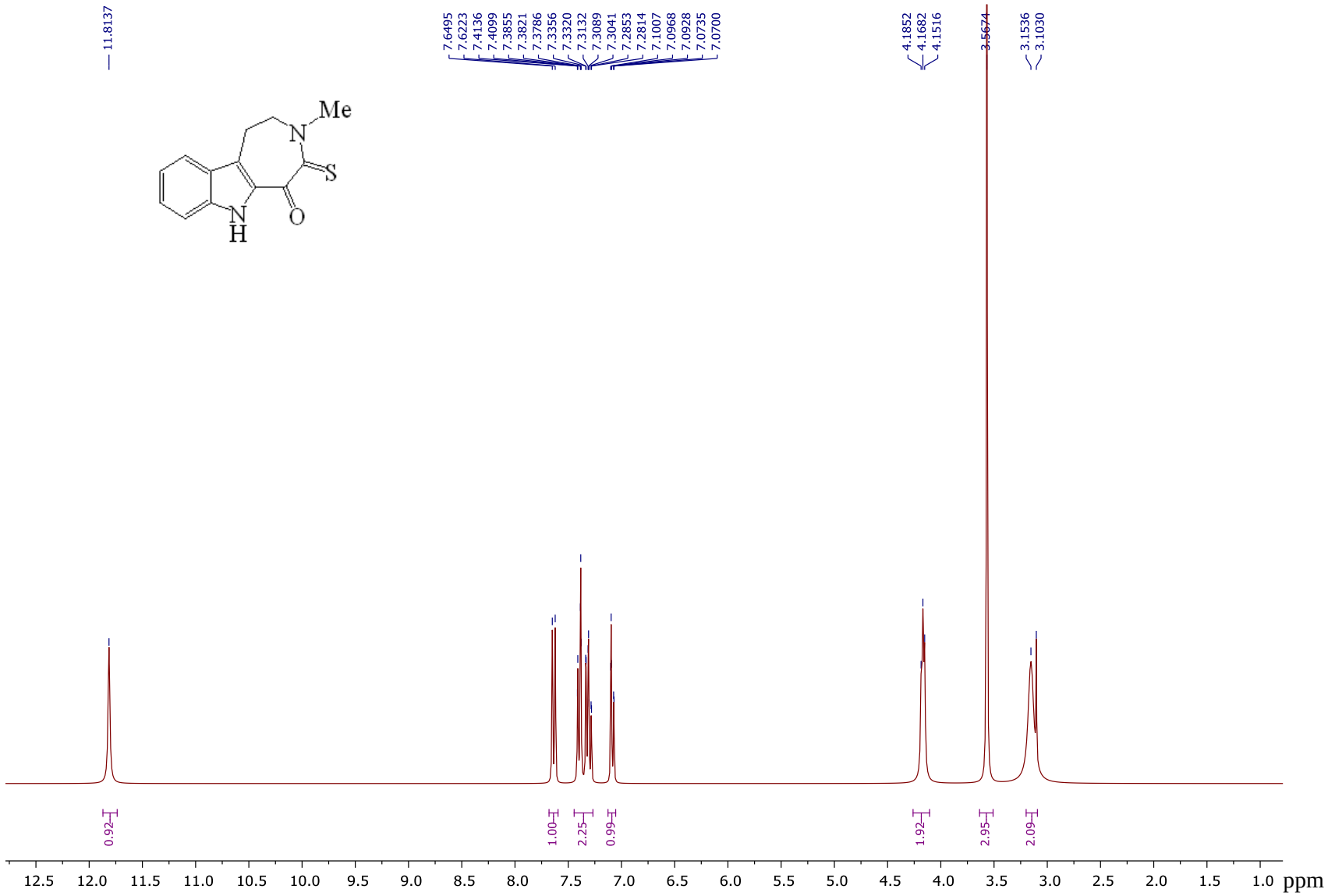

196.2165
191.1896
152.3523
147.6432
133.5055
125.6491
112.6536
111.1304
55.7656
55.5833
51.1219
51.0465
32.0152
30.8346
26.0955
25.8342
21.8852
13.7819
MeO
MeO
N−C6H13
O
S
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

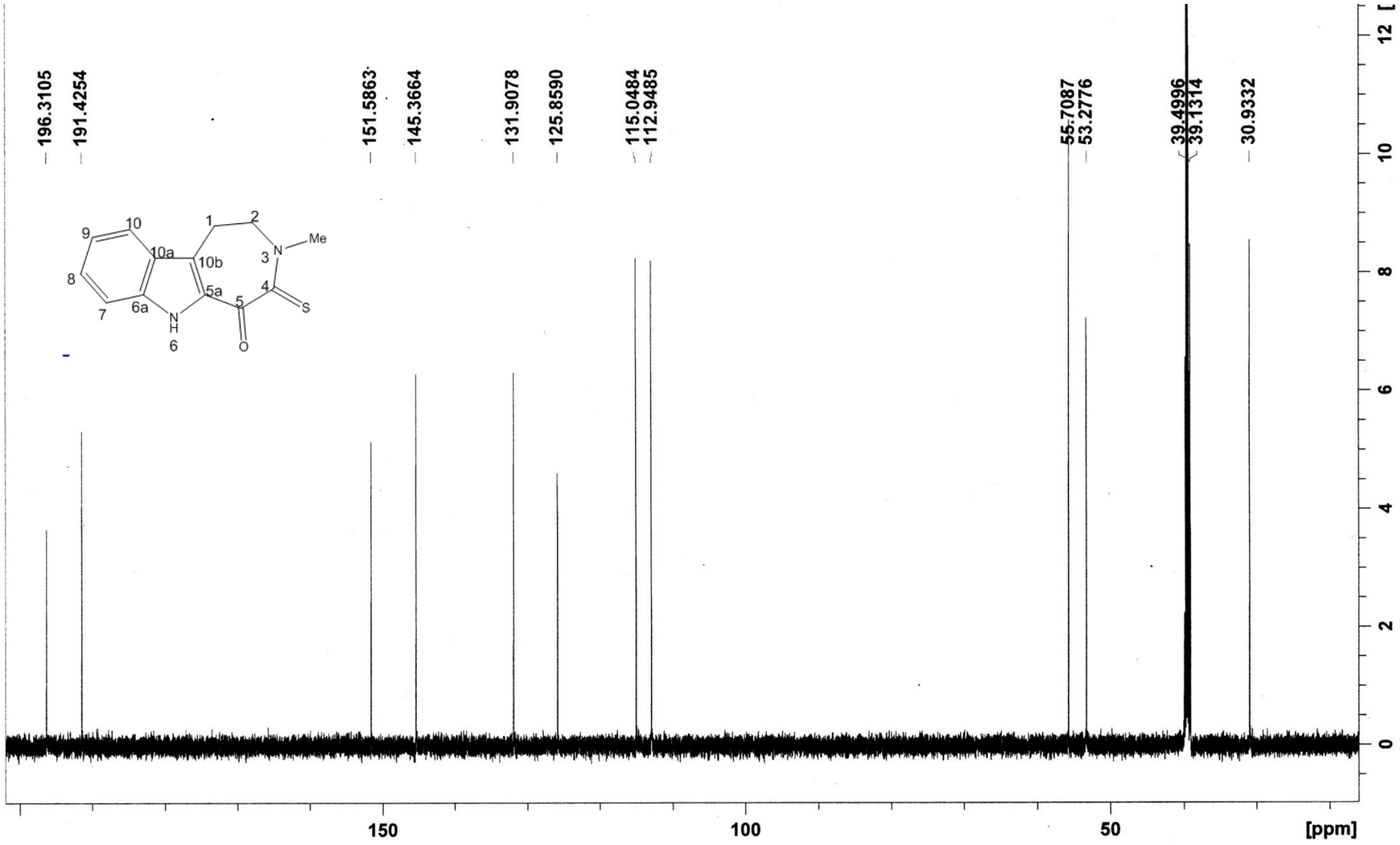
7,8-Dimethoxy-3-(2-phenoxyethyl)-2-thioxo-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-one (**4g**).




197.3964
191.0785
157.9288
152.4777
147.6669
133.8001
129.5315
125.4562
120.9803
114.4468
112.6574
111.1660
64.0409
55.7943
55.5941
52.7329
51.0448
31.7995
MeO
MeO
N−CH2CH2OPh
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3-Methyl-4-thioxo-1,2,3,6-tetrahydroazepino[4,5-*b*]indol-5(2*H*)-one (**8**).




196.3105
191.4254
151.5863
145.3664
131.9078
125.8590
115.0484
112.9485
55.7087
53.2776
39.4996
39.1314
30.9332
Me
150
100
50
[ppm]