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The Vilsmeier-Haack formylation of 2,3-dihydro-4H-1,3-benzoxazin-4-ones and isomeric 1,2-dihydro-4H-3,1-benzoxazin-4-ones: an effective approach to functionalized 2H-/4H-Chromenes and Tetrahydroacridines

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Graphical Abstract

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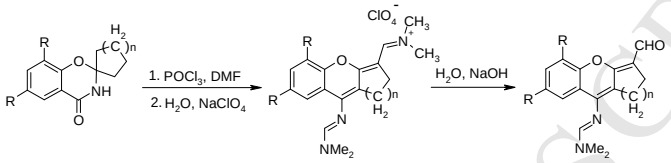

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Oleg K. Farat[a,b] *, Victor I. Markov[a], Svetlana A. Varenichenko[a], Victor V. Dotsenko[c] and Alexander V. Mazepa[d]

[a]*Ukrainian State University of Chemical Technology, 49005 Dnepropetrovsk, Ukraine*
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University, 119991Moscow, Russian Federation*
[c]*Kuban State University, 350040 Krasnodar, Russian Federation*
[d]*A. V. Bogatsky Physico-Chemical Institute, 65080 Odessa, Ukraine*

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ABSTRACT

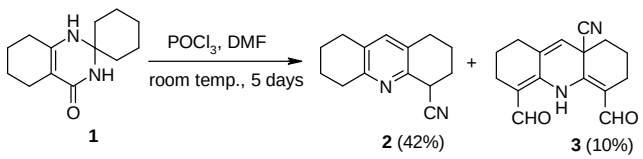
We found that 1,3- and isomeric 3,1-benzoxazin-4-ones react with the Vilsmeier reagent in vastly different ways. Thus, either 2*H*- or 4*H*-chromenes were obtained in good yields when 1,3-benzoxazin-4-ones were reacted at 75–80 ˚C, while the formylation of 3,1-benzoxazines at ambient temperature leads to acridine-9-one or 9-chloroacridine derivatives, depending on the amount of Vilsmeier reagent and the nature of substrate.

1. Introduction

The Vilsmeier-Haack reaction is a powerful tool in modern synthesis and is widely used not only to introduce the CHO group into activated aromatic and heteroaromatic substrates, but also as an approach for various condensations and cyclizations (for reviews on the Vilsmeier-Haack reaction see[1–6]).

The chemistry of the Vilsmeier reagent has attracted increasing interest during the past few decades: the great interest in this chemistry is supported by the significant increase in the number of publications (for recent examples see[7–10]).

Recently, we have reported the unexpected reaction of spirocyclic pyrimidine **1** with the Vilsmeier reagent that was accompanied by a deep-seated rearrangement of the carbon skeleton to give substituted acridines **2** and **3** (Scheme 1).[11]



1 **2** (42%) **3** (10%)

Scheme 1. Synthesis of substituted acridines.

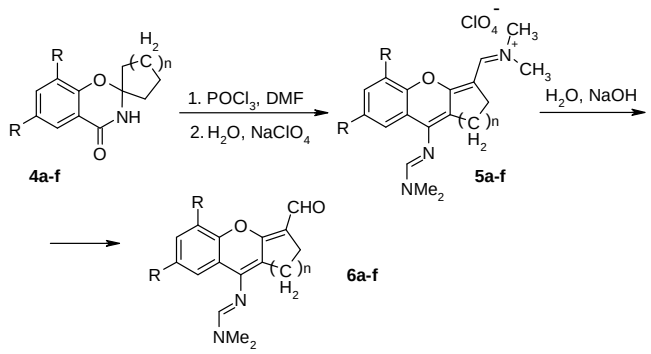
These results prompted us to examine the behavior of other heminal 1,3-diheteroatomic systems under the same conditions. Here we wish to report the results of the formylation of benzoxazine derivatives.

2. Results and discussion

The Vilsmeier reagent was obtained by the classical method with a molar ratio DMF : $POCl_3$ 3:1, then 0.5 mol of the corresponding benzoxazine was added and the mixture was maintained at 75–80 °C for 1 h (for compounds **4a–d**) or 4 h (for **4e,f**). When the mixture was neutralized by addition of aqueous NaOH immediately thereafter, as recommended by the classical Vilsmeier-Haack conditions, the yields were very poor and the isolation of products was very difficult due to tar formation. Therefore we had to use another work up procedure and we succeeded by using a sodium perchlorate solution. Thus, the reaction mixture was left to cool and treated with an excess of ice-cold aqueous $NaClO_4$, whereupon the solids of **5a–f** precipitated. The compounds **5a–f** could be easily hydrolyzed by aqueous alkali in DMF to form xanthene-type compounds **6a–f**. It should be noted that products **5a–d** were also obtained by

* Corresponding author. Tel.: +380562-47-46-70; fax: +380562-47-33-16; e-mail: faratok@mail.ru

maintaining the substrates **4a–d** with the Vilsmeier reagent at room temperature for 24 h (Scheme 2).



Scheme 2. Synthesis of xanthene-type compounds.

Table 1. The yields of compounds **4, 5** and **6**.

Compound	R	n	Yield %	Compound	R	n	Yield %
4a	H	2	92*	**5d**	*i*-Pr	1	87
4b	H	1	69*	**5e**	I	2	54**
4c	*i*-Pr	2	80	**5f**	I	1	57**
4d	*i*-Pr	1	73	**6a**	H	2	85
4e	I	2	66	**6b**	H	1	83
4f	I	1	68	**6c**	*i*-Pr	2	90
5a	H	2	96	**6d**	*i*-Pr	1	85
5b	H	1	80	**6e**	I	2	85
5c	*i*-Pr	2	95	**6f**	I	1	80

*Ref.:[16]

**crude product

The compounds were characterized by FTIR and mass spectrometry, multinuclear NMR spectroscopy, and elemental analysis. Finally, the structure of the compound **6a** was confirmed by a single crystal X-ray diffraction analysis (Fig. 1).

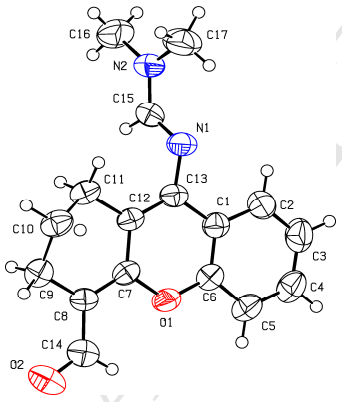
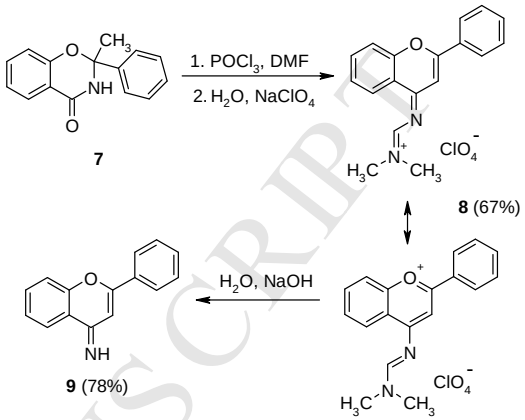


Fig.1. X-ray structure of **6a** (50% probability thermal ellipsoids).

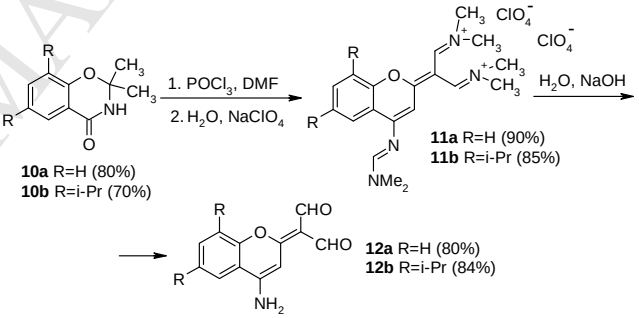
The cyclohexene ring has a *sofa* conformation. The atom C10 deviates by 0.628(3) Å from the plane of the other ring atoms. The latter, in turn, lie in the same plane as the dihydropyran and benzene rings (root mean square deviation of the atoms from the plane is 0.017 Å). The dimethylamidine substituent is heavily twisted by 119.0(2)° (C15-N1-C13-C1) with respect to the plane, while the formyl substituent is essentially in the plane to form a dihedral angle C9-C8-C14-O2 of 1.1(3)°. The orientation of CHO is additionally stabilized by intramolecular attractive shortened interaction O1…H14 (2.36 Å, the van der Waals sum is 2.46 Å).[12] In the crystal structure, the molecules **6a** are paired into centrosymmetric dimers linked by hydrogen bonds C15-H15…O2^{i} [i: 1-x,-y,-z] (H…O 2.29 Å, C-H…O 173°). These dimers are additionally stabilized by hydrogen bonds C-H…π : C9-H9b…C7^{i} (H…C 2.85 Å, C-H…C 144°) and C11-H11b…C14^{i} (H…C 2.85 Å, C-H…C 147°).

We found that benzoxazine **7** reacts in the same way and under Vilsmeier-Haack conditions undergoes the rearrangement to form (after hydrolysis) benzopyran **9**. The structure of the intermediate salt **8** can be best described by several resonance structures with an assumption that the pyrilium salt is probably the most contributing one (Scheme 3).



Scheme 3. Synthesis of benzopyran derivatives.

As we suggested, 2,2-dimethylbenzoxazines **10a,b** react further with the Vilsmeier reagent to afford dialdehydes **12a,b** (Scheme 4).



Scheme 4. Synthesis of substituted benzopyrans.

Compounds **12a** and **b** were characterized by spectroscopic data, the structure of the compound **12a** was confirmed by a single crystal X-ray diffraction analysis (Fig. 2). The compound **12a** is the hydrate 2:1. The independent part of the unit cell of **12a** contained two molecules (A and B) with very close geometrical parameters and a molecule of water.

All the non-hydrogen atoms in the molecule of **12a** lie in the same plane with RMSD less than 0.03 Å. The aldehyde groups oriented so to form the intramolecular hydrogen bonds C8-H8…O3 (H…O 2.26-2.27 Å, C-H…O 125°) and attractive contacts C11-H11…O1 (H…O 2.31-2.33 Å). The latter cannot be considered to be hydrogen bonds due to the small angle C-H…O of 103°. The analysis of the bond lengths shows a significant redistribution of the electron density in the molecule from the amino group to the =C(CHO)$_2$ moiety through the conjugated π bond system.

Thus, the C=O bonds are longer (1.226(3)-1.241(3) Å) than standard C=O double bond distances in aldehydes (1.192 Å), while C9-N1 bonds are slightly shortened to 1.316(3)-1.320(3) Å in comparison with the average distance of C(sp^2)-NH$_2$ bond of 1.336 Å.[13] In addition, the formal single bond C7-C8 (1.360(3)-1.364(3) Å) is even shorter than formal double bonds C8-C9 of 1.397(3)-1.400(3) Å and C7-C10 of 1.426(3)-1.429(3) Å. Such a

redistribution of the electron density in the crystal is stabilized by a network of intermolecular hydrogen bonds N1A-H1AA...O3B[i] [i: 1/2+x,1/2-y,-1/2+z] (H...O 2.01 Å, N-H...O 166°), N1A-H1AB...O2B[ii] [ii: 3/2-x,1/2+y,1/2-z] (H...O 2.10 Å, N-H...O 160°), N1B-H1BA...O3A[iii] [iii: 1/2+x,1/2-y,1/2+z] (H...O 2.01 Å, N-H...O 159°), N1B-H1BB...O1W[iv] [iv: 1/2-x,-1/2+y,1/2-z] (H...O 2.15 Å, N-H...O 152°), O1W-H1WA...O2B (H...O 2.04 Å, O-H...O 172°) и O1W-H1WB...O2A[iii] [iii: 1/2+x,1/2-y,1/2+z] (H...O 2.00 Å, O-H...O 166°). In the crystal structure, the molecules **12a** are linked through hydrogen bonds into tetramers; the latter consist of two pairs of A & B molecules, and are bonded together in a three-dimensional structure by hydrogen bonds with molecules of water.

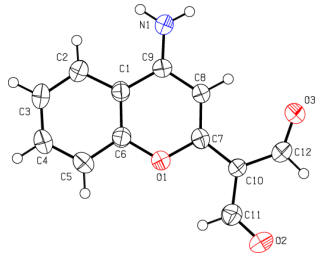
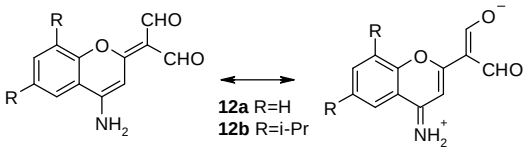


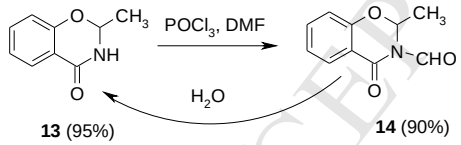
Fig. 2. X-ray structure of **12a** (50% probability thermal ellipsoids).

The structure of compounds **12** is best described by resonance structures shown below, from X-ray and ^{1}H NMR data (Scheme 5).



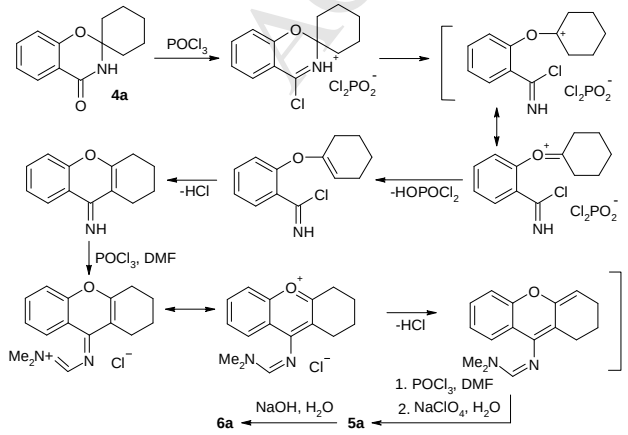
Scheme 5. Resonance structures of substituted benzopyrans.

Next, we found that compound **13** does not undergo recyclization even if maintained with Vilsmeier reagent at 75–80 °C for a couple of hours. Instead, the *N*-formylation occurs and imide **14** was isolated as the sole product. Under mild conditions, it could be easily hydrolyzed to form the starting benzoxazine **13** (Scheme 6).



Scheme 6. Synthesis of imide and his hydrolyze.

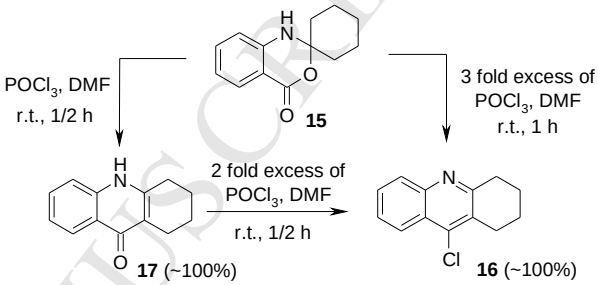
Based on these data, we suggest the following mechanism of the new rearrangement (Scheme 7).



Scheme 7. Proposed mechanism of the new rearrangement.

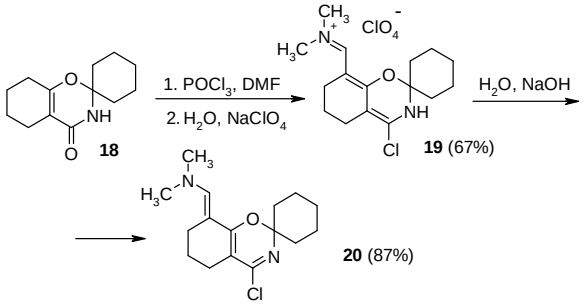
It was found that the reaction of benzoxazine **15** with a three-fold excess of Vilsmeier reagent at room temperature for 1 h leads to formation of 9-chloroacridine **16** in quantitative yield. Meanwhile, tetrahydroacridine-9-one **17** was isolated quantitatively when the same reaction was conducted with 1 eq. of Vilsmeier reagent for 0.5 h. The compound **17** could be quantitatively converted into chloride **16** by reaction with a two-fold excess of Vilsmeier reagent for 0.5 h.

The physical data of the compounds **16** and **17** appeared to be identical to that previously described in the literature.[14,15] According to LC–MS data, the purity of compound **16** was 96.3% prior to recrystallization. It is noteworthy that in all cases the isolation of products is very straightforward, and the isolation of acridines **16** and **17** is easily accomplished by simple filtration (Scheme 8).



Scheme 8. Synthesis of acridines derivatives.

In contrast to benzo analog **4**, hexahydro-4H-1,3-benzoxazin-4-one **18** failed to give xanthene derivatives. The perchlorate **19** was instead prepared in 67% yield by addition of the Vilsmeier reagent to compound **18** (room temperature, 0.5 h) followed by treatment with an aqueous $NaClO_4$ solution. The salt **19** has been found to be easily hydrolyzed by alkaline solution to form stable enamine **20** (Scheme 9).



Scheme 9. Synthesis of functionalized enamine.

The structures of the synthesized compounds were confirmed by means of spectroscopic data, and the compound **19** was studied by single crystal X-ray diffraction analysis (Fig. 3). Compound **19** is the salt consisting of an organic cation and perchlorate anion. The independent part of the unit cell of **19** contained two cations (molecules A and B) with very close geometrical parameters and three ClO_4^- ions, two of which are located on a second-order axis. Tetrahydrooxazine ring has a distorted *sofa* conformation with a flattened N1-C1-C2-C3-O1 fragment (root mean square deviation of the atoms from the plane is 0.048 and 0.054 Å for molecules A & B, respectively) with C4 atom deviation of 0.610(5) Å (molecule A) and 0.594(5) Å (molecule B) from the plane.

The cyclohexene ring has a *sofa* conformation with C8 atom deviation of 0.688(5) Å (molecule A), or 0.691(5) Å (molecule B) from the plane of other ring atoms. The positive charge is localized on the nitrogen N2 atom, as indicated by N2-C14 bond lengths of 1.306(5) Å (molecule A) and 1.303(5) Å (molecule B),

which values are close to the average N=C double bond distance of 1.28 Å.[13] The *cis*-orientation of the C14-N2 bond with respect to C8-C7 leads to a steric repulsion between the methyl C16 group and the methylene C7 fragment. It is evidenced by the shortened intramolecular contact H7B…C16 2.67 Å (molecule A) and 2.69 Å (molecule B) (the van der Waals sum is 2.87 Å),[12] the increase of the valence angles C16-N2-C14 126.4(4)° (A), 126.2(3)° (B) and C14-C8-C7 124.6(4)° (A), 123.8(4)° (B) in comparison with C15-N2-C14 120.1(4)° (A), 121.2(3)° (B) and C14-C8-C3 116.6(4)° (A), 117.3(4)° (B), respectively. A small twist along the C8-C14 bond (the dihedral torsion angles C7-C8-C14-N2 are of 19.8(7)° (A) and -18.6(7)° (B)) also lends support to the view of a steric repulsion. In the crystal structure, the cations and ClO_4^- anions are linked by intermolecular hydrogen bonds N1A-H1A…O3^{i} [i: 1/2-x,1/2+y,1/2-z] (H…O 2.06 Å, N-H…O 156°) and N1B-H1B…O2^{i} (H…O 2.03 Å, N-H…O 169°).

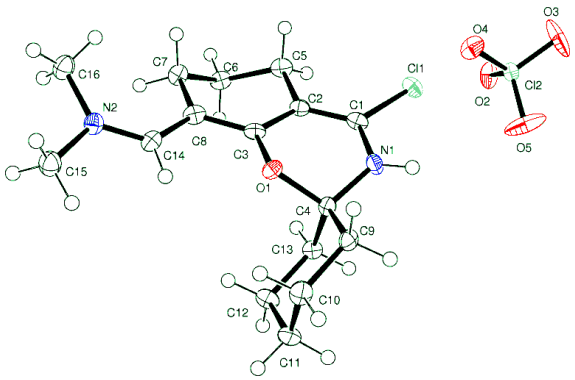


Fig. 3. X-ray structure of **19** (50% probability thermal ellipsoids).

In the summary, we have found that 1,3-benzoxazin-4-ones react with Vilsmeier reagent to form chromene derivatives, while the Vilsmeier-Haack reaction with isomeric 3,1-benzoxazin-4-ones leads to partially hydrogenated acridines in quantitative yields. The obtained compounds are highly functionalized and could serve as *low-molecular-weight* building blocks for organic synthesis.

3. Experimental section

The ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Avance II 400 instrument (400,13 MHz and 100,62 MHz for ^{1}H and ^{13}C respectively) in DMSO-d_6, DMSO-d_6/CCl_4 or DMSO-d_6/CF_3CO_2D with Me_4Si as internal standard. The FTIR spectra were recorded in KBr pellets using a Spectrum one (PerkinElmer) FT-IR Spectrometer. The mass spectra of compounds **4c–f**, **10b**, **6a,c–f**, **12b**, **14** and **20** were recorded on a MX1321 instrument with direct injection of the sample at an ionization chamber temperature of 200 °C and with 70 eV ionizing electrons. The FAB spectra of compounds were recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the samples in *meta*-nitrobenzyl alcohol was realized with a beam of argon atoms with energy 8 keV. Chromatographic analysis of compound **16** was realized on an Agilent 1100 liquid chromatograph with DAD and ELSD Sedex 75 detectors in conjunction with an LC-MS VL spectrometer with electrospray ionization. Elemental analysis was performed on a LECO CHNS-900 instrument. The reactions and the purity of the obtained compounds were monitored by TLC on Merck Silicagel 60 F-254 plates with 10:1 $CHCl_3$–*i*-PrOH as eluent.

Compounds **4a–f** were synthesized by the method described in literature.[16] Compounds **7,**[17] **15**[18] and **18**[19] were obtained by the known procedures.

3.1 Synthesis of Spirans 4a-f (General method). A mixture of the corresponding salicylamide (0.10 mol), ketone (0.12 mol) and p-TsOH × H_2O (0.05 mol) in toluene (70 mL) was refluxed for 8 h with continuous removal of water with a Dean–Stark trap. In the case of spirans **4a,b**, the mixture was cooled to 10 °C and stirred for 1 h at the same temperature. The resulting crystals were collected, washed with toluene (10 mL) and *i*-PrOH (10 mL) and dried at 50 °C. In all other cases, a solvent was evaporated to dryness under reduced pressure, the solid residue was washed with 5% aq. NaOH solution and filtered off.

3.1.1. 6,8-Diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3H)-one ***(4c)***. 80%, white powder, mp 165–167 °C (aq. MeOH); [Found: C, 75.86; H, 9.15; N, 4.69. $C_{19}H_{27}NO_2$ requires C, 75.71; H, 9.03; N, 4.65%]; ν_{max}(KBr) 3184 (N–H), 3066 (aromatic C–H), 2965–2862 (aliphatic C–H), 1674 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.43 (1H, s, NH), 7.41 (1H, s, H-5 Ar), 7.17 (1H, s, H-7 Ar), 3.22–3.31 (1H, m, C<u>H</u>$(CH_3)_2$), 2.79–2.88 (1H, m, C<u>H</u>$(CH_3)_2$), 1.95–2.07 (2H, m, spiro-ring), 1.50–1.70 (7H, m, spiro-ring), 1.25–1.32 (1H, m, spiro-ring), 1.21 (12H, d, *J* 6.1 Hz, 2CH(C<u>H</u>$_3)_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 161.4 (C=O), 140.6, 149.9, 128.6 (CH-7), 135.5, 121.4 (CH-5), 117.1, 86.9 (C-2), 35.4 ($2CH_2$), 32.9 (<u>C</u>H$(CH_3)_2$), 25.8 (<u>C</u>H$(CH_3)_2$), 23.9 ($2CH_2$), 23.8 (CH(<u>C</u>H$_3)_2$), 22.6 (CH(<u>C</u>H$_3)_2$), 21.6 (CH_2); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 128.3 (CH-7), 121.1 (CH-5), 35.1* ($2CH_2$), 32.5 (<u>C</u>H$(CH_3)_2$), 25.5 (<u>C</u>H$(CH_3)_2$), 23.9* ($2CH_2$), 23.5 (CH(<u>C</u>H$_3)_2$), 22.3 (CH(<u>C</u>H$_3)_2$), 21.3* (CH_2), *signals in antiphase; *m/z* (EI) 301 (9 M^+), 205 (20), 189 (5), 176 (7), 161 (5), 97 (100), 41 (7%).

3.1.2. 6,8-Diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3H)-one ***(4d)***. 73%, white powder, mp 137–140 °C (aq. MeOH); [Found: C, 75.37; H, 8.83; N, 4.91. $C_{18}H_{25}NO_2$ requires C, 75.22; H, 8.77; N, 4.87%]; ν_{max}(KBr) 3183 (N–H), 3066 (aromatic C–H), 2958–2871 (aliphatic C–H), 1669 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.54 (1H, s, NH), 7.41 (1H, s, H-5 Ar), 7.13 (1H, s, H-7 Ar), 3.11–3.23 (1H, m, C<u>H</u>$(CH_3)_2$), 2.77–2.91 (1H, m, C<u>H</u>$(CH_3)_2$), 2.03–2.13 (2H, m, spiro-ring), 1.72–1.88 (6H, m, spiro-ring), 1.22 (6H, d, *J* 6.1 Hz, CH(C<u>H</u>$_3)_2$), 1.19 (6H, d, *J* 6.1 Hz, CH(C<u>H</u>$_3)_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 161.9 (C=O), 150.9, 140.6, 135.6, 128.4 (CH-7), 121.5 (CH-5), 117.4, 96.7 (C-2), 37.9 ($2CH_2$), 32.9 (<u>C</u>H$(CH_3)_2$), 26.4 (<u>C</u>H$(CH_3)_2$), 23.8 (CH(<u>C</u>H$_3)_2$), 22.3 (CH(<u>C</u>H$_3)_2$), 22.2 ($2CH_2$); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 128.0 (CH-7), 121.1 (CH-5), 36.9* ($2CH_2$), 32.4 (<u>C</u>H$(CH_3)_2$), 26.0 (<u>C</u>H$(CH_3)_2$), 23.3 (CH(<u>C</u>H$_3)_2$), 21.9 (CH(<u>C</u>H$_3)_2$), 21.8* ($2CH_2$), *signals in antiphase; *m/z* (EI) 287 (8 M^+), 205 (29), 189 (6), 176 (10), 161 (9), 83 (100), 41 (10%).

3.1.3. 6,8-Diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3H)-one ***(4e)***. 66%, white powder, mp 235–237 °C (aq. DMF); [Found: C, 33.40; H, 2.84; N, 3.06. $C_{13}H_{13}I_2NO_2$ requires C, 33.29; H, 2.79; N, 2.99%]; ν_{max}(KBr) 3153 (N–H), 3070 (aromatic C–H), 2936–2850 (aliphatic C–H), 1689 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.90 (1H, s, NH), 8.19 (1H, s, H-5 Ar), 7.92 (1H, s, H-7 Ar), 1.79–2.08 (2H, m, spiro-ring), 1.42–1.75 (7H, m, spiro-ring), 1.12–1.28 (1H, m, spiro-ring); δ_C (100 MHz, DMSO-d_6) 159.0 (C=O), 154.1, 149.4, 135.2, 119.8, 89.1 (C-2), 87.6 (C-I), 85.5 (C-I), 35.4 ($2CH_2$), 24.1 ($2CH_2$), 21.5 (CH_2); *m/z* (EI) 469 (55 M^+), 373 (24), 245 (14), 97 (100%).

3.1.4. 6,8-Diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3H)-one ***(4f)***. 68%, white powder, mp 195–198 °C (aq. DMF); [Found: C, 31.79; H, 2.49; N, 3.14. $C_{13}H_{13}I_2NO_2$ requires C, 31.67; H, 2.44; N, 3.08%]; ν_{max}(KBr) 3177 (N–H), 3062 (aromatic C–H), 2971–2878 (aliphatic C–H), 1668 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.02 (1H, s, NH), 8.20 (1H, s, H-5 Ar),

7.93 (1H, s, H-7 Ar), 1.95–2.10 (2H, m, spiro-ring), 1.65–1.88 (6H, m, spiro-ring); δ_C (100 MHz, DMSO-d_6) 159.6 (C=O), 154.8, 149.3, 135.3, 119.9, 94.4 (C-2), 87.9 (C-I), 85.8 (C-I), 37.1 ($2CH_2$), 22.1 ($2CH_2$); *m/z* (EI) 455 (29 M^+), 373 (17), 245 (5), 83 (100%).

3.2. Synthesis of oxazines 10a,b and 13 (General method). Concentrated H_2SO_4 (1 mL) was added to glacial acetic acid (3 mL), and the solution formed was cooled on ice. A solution of corresponding salicylamide (0.01 mol), acetone or acetaldehyde (0.01 mol), and Ac_2O (1 mL) in glacial acetic acid (3 mL) was prepared separately. To the mixture obtained, the above ice-cold solution of H_2SO_4 and AcOH was added gradually with stirring on an ice bath. The resulted mixture was stirred for 40 min and left to stay overnight at room temperature, then pH was adjusted to ~7.0 with aq. Na_2CO_3 solution. The precipitate formed was filtered off and recrystallized from aqueous MeOH.
Yield of compound **10a** was 80%, mp 137–138 °C (Ref.[16]: 136–138 °C).
Yield of compound **13** was 98%, mp 150–152 °C (Ref.[20]: 143–147 °C).

*3.2.1. 6,8-Diisopropyl-2,2-dimethyl-2,3-dihydro-4H-1,3-benzoxazin-4-one **(10b)***. 70%, white powder, mp 145–147 °C (aq. MeOH); [Found: C, 73.42; H, 8.82; N, 5.30. $C_{16}H_{23}NO_2$ requires C, 73.53; H, 8.87; N, 5.36%]; ν_{max}(KBr) 3183 (N–H), 3066 (aromatic C–H), 2962–2871 (aliphatic C–H), 1674 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.57 (1H, s, NH), 7.45 (1H, s, H-5 Ar), 7.24 (1H, s, H-7 Ar), 3.01–3.15 (1H, m, C<u>H</u>$(CH_3)_2$), 2.78–2.89 (1H, m, C<u>H</u>$(CH_3)_2$), 1.49 (6H, s, $2CH_3$), 1.13–1.19 (12H, m, $2CH(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 161.5 (C=O), 150.7, 140.9, 135.7, 129.2, 121.3, 116.7, 86.7 (C-2), 32.8, 27.2, 27.1, 23.9, 22.3; *m/z* (EI) 261 (74 M^+), 246 (12), 205 (96), 189 (43), 176 (100), 161 (75), 91 (10), 58 (26), 41 (11%).

3.3 Synthesis of perchlorates 5a–f (General method). *Method A (with heating).*
The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **4a** (1.1 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was heated on a water bath at 75–85 °C for 1 h (an orange solid was separated within 0.5 h). Then the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate of the salt **5a** was filtered off, dried and purified by refluxing with toluene. In the case of salts **5b–d**, the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL); then pH was adjusted to 8.0–9.0 with aq. NaOH. The solid products were filtered off, washed and dried to give pure salts **5b–d**. For salts **5e,f**, the reaction time was 4 h. *Caution! Organic perchlorates are potentially explosive. The microanalysis were not performed in order to prevent an explosion.*

*3.3.1. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-2,3-dihydro-1H-xanthen-4-yl)methylene]-N-methylmethanaminium perchlorate **(5a)***. 96%, orange powder, mp 300 °C; ν_{max}(KBr) 2939 (aliphatic C–H), 1708, 1600 cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.56 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 8.20 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.76 (1H, d, *J* 7.6 Hz, H Ar), 7.60–7.68 (2H, m, H Ar), 7.34–7.42 (1H, m, H Ar), 3.52 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.27 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.25 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 2.74–2.81 (2H, m, 3-CH_2 or 1-CH_2), 2.59–2.74 (2H, m, 1-CH_2 or 3-CH_2), 1.61–1.78 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6/CCl_4) 172.0, 165.2, 158.3, 155.8, 152.1, 132.3, 125.0, 124.7, 121.5, 119.2, 116.5, 101.9, 42.0, 40.0, 24.6, 24.0, 20.6; *m/z* (FAB) 310 (100 M^+), 265 (6), 218 (11), 149 (33), 136 (35), 121 (12), 107 (24), 89 (19), 76 (27), 68 (21), 52 (29%).

*3.3.2. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[b]chromen-3-yl)methylene]-N-methylmethanaminium perchlorate **(5b)***. 80%, red needles, mp 262–265 °C (DMF); ν_{max}(KBr) 2964–2862 (aliphatic C–H), 1674, 1623 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.45 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 8.01–8.11 (1H, m, H Ar), 7.97 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.61–7.71 (1H, m, H Ar), 7.39–7.56 (2H, m, H Ar), 3.35 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.23 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.21 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 3.07 (4H, s, $2CH_2$); δ_C (100 MHz, DMSO-d_6) 172.8, 157.2, 153.1, 150.6, 144.0, 132.0, 125.6, 125.0, 121.4, 116.5, 114.1, 102.6, 41.0, 34.8, 25.1, 24.9; *m/z* (FAB) 296 (100 M^+), 137 (14), 107 (7), 91 (10), 80 (7), 53 (10%).

*3.3.3. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1H-xanthen-4-yl)methylene]-N-methylmethanaminium perchlorate **(5c)***. 95%, orange-red powder, mp 215–217 °C. ν_{max}(KBr) 2927 (aliphatic C–H), 1702, 1611 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.17 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 8.13 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.47 (2H, s, H-5,7 Ar), 3.53–3.59 (1H, m, C<u>H</u>$(CH_3)_2$), 3.46 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.22 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.19 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 2.95–3.05 (1H, m, C<u>H</u>$(CH_3)_2$), 2.77–2.82 (2H, m, 3-CH_2 or 1-CH_2), 2.63–2.68 (2H, m, 1-CH_2 or 3-CH_2), 1.65–1.75 (2H, m, 2-CH_2), 1.30 (6H, d, *J* 6.8 Hz, $CH(C\underline{H}_3)_2$), 1.23 (6H, d, *J* 6.8, $CH(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 172.2, 165.8, 156.0, 148.3, 148.1, 145.2, 135.5, 130.5, 127.8, 119.5, 110.7, 101.2, 41.5, 35.4, 33.2, 26.4, 24.6, 24.1, 24.0, 22.3, 21.0; *m/z* (FAB) 394 (100 M^+), 378 (5), 349 (6%).

*3.3.4. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[b]chromen-3-yl)methylene]-N-methylmethanaminium perchlorate **(5d)***. 87%, red powder, mp 258–260 °C; ν_{max}(KBr) 2960–2925 (aliphatic C–H), 1624 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.42 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 7.78 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.75 (1H, s, H Ar), 7.45 (s, 1H, H Ar), 3.65–3.75 (m, 1H, C<u>H</u>$(CH_3)_2$), 3.33 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.21 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.16 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 3.04–3.13 (4H, m, $2CH_2$), 2.95–3.03 (1H, m, C<u>H</u>$(CH_3)_2$), 1.29 (6H, d, *J* 6.8 Hz, $CH(C\underline{H}_3)_2$), 1.22 (6H, d, *J* 6.8 Hz, $CH(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 172.5, 157.3, 152.9, 149.1, 148.6, 145.4, 136.0, 127.4, 121.3, 119.4, 116.0, 101.9, 40.8, 34.5, 33.2, 26.0, 25.1, 24.9, 23.8, 22.8; *m/z* (FAB) 380 (100 M^+), 364 (9%).

*3.3.5. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-5,7-diiodo-2,3-dihydro-1H-xanthen-4-yl)methylene]-N-methylmethanaminium perchlorate **(5e)***. Yellow powder, yield ~54% (calculated for proposed structure), mp 245–252 °C. *This intermediate perchlorate was used on the next step without further purification.*

*3.3.6. N-[(9-{[(1E)-(Dimethylamino)methylene]amino}-5,7-diiodo-1,2-dihydrocyclopenta[b]chromen-3-yl)methylene]-N-methylmethanaminium perchlorate **(5f)***. Pink powder, yield ~57% (calculated for proposed structure), mp 225–233 °C. *This intermediate perchlorate was used on the next step without further purification.*

3.4. Synthesis of perchlorates 5a–d. *Method B (at room temperature).*
The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **4a** (1.1 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was stirred vigorously at room

temperature for 24 h and maintained as in the method A. The salts **5b–d** were obtained in the same way.
Yield of compound **5a** was 88 %.
Yield of compound **5b** was 75%.
Yield of compound **5c** was 85%.
Yield of compound **5d** was 80%.

3.5. Synthesis of benzopyrans 6a–f (General method).

The corresponding salt **5a-f** (1.0 g, 0.002 mol) was dissolved in hot DMF (5 mL). To the obtained solution, an aqueous 15 % NaOH solution (1.5 mL) was added and the mixture was stirred vigorously at 60–75 °C for 5 min. The precipitated solid of corresponding compound **6a–f** was filtered off. If no solid precipitated, the solution cooled to the room temperature and water was added.

*3.5.1. N'-(4-Formyl-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide **(6a)***. 85%, yellow-green needles, mp 175–177 °C (aq. MeOH); [Found: C, 72.41; H, 6.49; N, 9.98. $C_{17}H_{18}N_2O_2$ requires C, 72.32; H, 6.43; N, 9.92%]; ν_{max}(KBr) 2932–2852 (aliphatic C–H), 1632 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.13 (1H, s, CHO), 7.70 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.49–7.56 (1H, m, H Ar), 7.33–7.42 (1H, m, H Ar), 7.19–7.26 (1H, m, H Ar), 7.10–7.18 (1H, m, H Ar), 3.03 (3H, s, CH_3), 3.01 (3H, s, CH_3), 2.50 (2H, 3-CH_2 or 1-CH_2, overlapped with DMSO signals), 2.25–2.29 (2H, m, 1-CH_2 or 3-CH_2), 1.52–1.56 (2H, m, 2-CH_2); δ_H (400 MHz, DMSO-d_6/CF_3CO_2D) 10.00 (1H, s, CHO), 8.41 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.58 (1H, d, *J* 7.6 Hz, H-5 Ar), 7.50 (1H, t, *J* 7.6 Hz, H-6 Ar), 7.34 (1H, d, *J* 8.1 Hz, H-8 Ar), 7.25 (1H, t, *J* 7.4 Hz, H-7 Ar), 3.27 (3H, s, CH_3), 3.31 (3H, s, CH_3), 2.58–2.70 (2H, m, 3-CH_2 or 1-CH_2), 2.28–2.40 (2H, m, 1-CH_2 or 3-CH_2), 1.55–1.75 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6) 184.2 (CHO), 162.5, 154.6, 151.6, 146.9, 130.2, 124.0, 123.3, 120.8, 115.2, 110.9, 109.0, 33.8, 24.7, 27.0, 20.1; *m/z* (EI) 282 (100 M^+), 265 (16), 253 (60), 239 (13), 210 (10), 196 (6), 181 (11), 152 (5), 127 (7), 77 (8), 58 (6), 43 (17%).

*3.5.2. N'-(3-Formyl-1,2-dihydrocyclopenta[b]chromen-9-yl)-N,N-dimethylimidoformamide **(6b)***. 83%, yellow-green needles, mp 196–198 °C (aq. MeOH); [Found: C, 71.51; H, 5.97; N, 10.40. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%]; ν_{max}(KBr) 2924 (aliphatic C–H), 1630 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.77 (1H, s, CHO), 8.08 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.71–7.77 (1H, m, H Ar), 7.32–7.40 (1H, m, H Ar), 7.15–7.24 (2H, m, H Ar), 2.51–3.07 (3H, s, CH_3), 3.02 (3H, s, CH_3), 2.76–2.85 (2H, m, CH_2), 2.55 (2H, m, CH_2); δ_C (100 MHz, DMSO-d_6) 180.4 (CHO), 166.2, 155.5, 152.2, 143.2, 129.7, 124.0, 123.8, 122.2, 118.6, 155.5, 112.0, 33.8, 23.2; *m/z* (FAB) 269 (100 MH^+), 239 (11%).

*3.5.3. N'-(4-Formyl-5,7-diisopropyl-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide **(6c)***. 90%, yellow powder, mp 188–190 °C (aq. MeOH); [Found: C, 75.47; H, 8.32; N, 7.69. $C_{23}H_{30}N_2O_2$ requires C, 75.38; H, 8.25; N, 7.64%]; ν_{max}(KBr) 2927–2864 (aliphatic C–H), 1651 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.19 (1H, s, CHO), 7.66 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.24 (1H, s, H Ar), 7.19 (1H, s, H Ar), 3.35–3.43 (1H, m, C<u>H</u>(CH_3)$_2$), 3.05 (6H, m, N=CH–N(C<u>H</u>$_3$)$_2$), 2.86–2.91 (1H, m, C<u>H</u>(CH_3)$_2$), 2.49–2.53 (2H, m, 3-CH_2 or 1-CH_2), 2.29–2.34 (2H, m, 1-CH_2 or 3-CH_2), 1.56–1.62 (2H, m, 2-CH_2), 1.29 (6H, d, *J* 6.8 Hz, CH(C<u>H</u>$_3$)$_2$), 1.21 (6H, d, *J* 6.8 Hz, CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 183.4 (CHO), 162.8, 154.6, 148.0, 147.0, 142.9, 134.1, 125.3, 120.3, 118.9, 110.4, 108.7, 33.8, 33.1, 26.8, 24.4, 23.9, 22.3, 21.2, 20.3; *m/z* (EI) 366 (100 M^+), 349 (8), 337 (36), 322 (6), 59 (8), 43 (19%).

*3.5.4. N'-(3-Formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[b]-chromen-9-yl)-N,N-dimethylimidoformamide **(6d)***. 85%, yellow powder, mp 133–136 °C (aq. MeOH); [Found: C, 75.11; H, 8.08; N, 7.99. $C_{22}H_{28}N_2O_2$ requires C, 74.97; H, 8.01; N, 7.95%]; ν_{max}(KBr) 2925 (aliphatic C–H), 1630 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.79 (1H, s, CHO), 8.07 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.48 (1H, s, H Ar), 7.17 (1H, s, H Ar), 3.33 (1H, m, CH, overlapped with a peak of water), 3.07 (3H, s, N=CH–N(C<u>H</u>$_3$)CH_3), 3.03 (3H, s, N=CH–N(CH_3)C<u>H</u>$_3$), 2.89–2.99 (1H, m, C<u>H</u>(CH_3)$_2$), 2.79–2.89 (2H, m, CH_2), 2.51–2.60 (2H, m, CH_2), 1.22 (12H, d, *J* 6.8 Hz, 2CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 180.0 (CHO), 166.5, 158.4, 147.6, 144.2, 143.6, 134.2, 125.1, 121.6, 118.8, 118.0, 111.6, 33.9, 33.1, 27.2, 24.0, 23.3, 23.2, 22.4; *m/z* (EI) 352 (100 M^+), 337 (6), 323 (21), 308 (16), 280 (14), 44 (7%).

*3.5.5. N'-(4-Formyl-5,7-diiodo-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide **(6e)***. 85%, yellow powder, mp 295–300 °C (aq. DMF); [Found: C, 38.31; H, 3.05; N, 5.29. $C_{17}H_{16}I_2N_2O_2$ requires C, 38.23; H, 3.02; N, 5.24%]; ν_{max}(KBr) 2925 (aliphatic C–H), 1674 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.29 (1H, s, CHO), 8.05 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.73 (1H, s, H Ar), 7.72 (1H, s, H Ar), 3.04 (3H, s, CH_3), 3.01 (3H, s, CH_3), 2.50–2.55 (2H, m, 3-CH_2 or 1-CH_2), 2.24–2.30 (2H, m, 1-CH_2 or 3-CH_2), 1.51–1.57 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6) 185.1 (CHO), 166.0, 161.8, 155.1, 145.5, 144.8, 132.2, 123.6, 111.8, 110.2, 88.1 (C-I), 85.4 (C-I), 34.9, 33.9, 24.5, 20.8, 19.9; *m/z* (EI) 534 (100 M^+), 505 (19), 152 (7), 42 (34%).

*3.5.6. N'-(3-Formyl-5,7-diiodo-1,2-dihydrocyclopenta[b]-chromen-9-yl)-N,N-dimethylimidoformamide **(6f)***. 80%, pink powder, mp 300 °C (aq. DMF); [Found: C, 37.09; H, 2.75; N, 5.44. $C_{16}H_{14}I_2N_2O_2$ requires C, 36.95; H, 2.71; N, 5.39%]; ν_{max}(KBr) 2924 (aliphatic C–H), 1615 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CF_3CO_2D) 9.74 (1H, s, CHO), 8.42 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 8.09 (1H, s, H Ar), 7.81 (1H, s, H Ar), 3.28 (3H, s, CH_3), 3.21 (3H, s, CH_3), 2.84–2.88 (2H, m, CH_2), 2.52–2.60 (2H, m, CH_2); *m/z* (EI) 520 (100 M^+), 505 (7), 491 (13), 476 (7), 139 (9), 44 (40%).

3.6. Synthesis of salts 8 and 11 a,b (General procedure).

The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The corresponding oxazine **7** or **10** (0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was left to stand at room temperature for 24 h. Then the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate of the corresponding salt **8** or **11** was filtered off, dried and purified by refluxing with toluene.
The microanalysis were not performed in order to prevent an explosion.

*3.6.1. N-Methyl-N-({[(4Z)-2-phenyl-4H-chromen-4-ylidene]-amino}methylene)methanaminium perchlorate **(8)**.* 67%, yellow powder, mp 210–213 °C (MeOH); ν_{max}(KBr) 1630–1640 (C=N), 1614 (C=C), 1597 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.23 (1H, s, N–C<u>H</u>=N^+(CH_3)$_2$), 8.51–8.58 (1H, m, H Ar), 8.29–8.35 (2H, m, H Ar), 8.07 (1H, s, H-3), 8.01–8.13 (2H, m, H Ar), 7.62–7.82 (4H, m, H Ar), 3.52 (3H, s, CH_3), 3.49 (3H, s, CH_3); δ_C (100 MHz, DMSO-d_6) 166.4, 164.7, 161.6, 155.0, 136.4, 133.5, 130.2, 129.3, 127.3, 127.2, 125.7, 121.2, 118.6, 101.1, 42.9 (CH_3), 36.7 (CH_3); *m/z* (FAB) 277 (100 M^+), 222 (6%).

*3.6.2. N,N'-[2-(4-{[(1E)-(Dimethylamino)methylene]amino}-2H-chromen-2-ylidene)propane-1,3-diylidene]bis(N-methylmethanaminium) diperchlorate **(11a)**.* 90%, yellow

powder, mp 223–225 °C (MeOH); ν_{max}(KBr) 2929 (aliphatic C–H), 1622, 1526 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.94 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 8.42–8.48 (3H, m, H Ar and C<u>H</u>=N^+(CH_3)$_2$), 7.89–8.05 (2H, m, H Ar), 7.63–7.69 (1H, m, H Ar), 7.12 (1H, s, H-3), 3.61 (6H, s, CH=N^+(C<u>H</u>$_3$)$_2$), 3.46 (3H, s, N=CH–N(CH_3)C<u>H</u>$_3$), 3.42 (3H, s, N=CH–N(C<u>H</u>$_3$)CH_3), 3.24 (6H, s, CH=N^+(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 164.7, 162.4, 160.5, 154.3, 135.6, 127.0, 125.7, 120.4, 118.2, 101.4, 92.1, 48.5, 42.9, 42.6, 36.4; *m/z* (FAB) 427 (14 ($M^+$$^{37}ClO_4$)$^+$), 425 (42 ($M^+$$^{37}ClO_4$)$^+$), 326 (12), 311 (6), 280 (12), 270 (6), 225 (6), 165 (7%).

3.6.3. N,N'-[2-(4-{[(1E)-(Dimethylamino)methylene]amino}-6,8-diisopropyl-2H-chromen-2-ylidene)propane-1,3-diylidene]bis(N-methylmethanaminium) diperchlorate ***(11b).*** Yellow powder, yield 85% (calculated for proposed structure), mp 220–227 °C. *This intermediate diperchlorate was used on the next step without further purification.*

3.7. Synthesis of benzopyrans 9 and 12a, b (General method).
The corresponding salt **8** or **11** (1.0 g) was dissolved in MeOH (5 mL) and treated with 15 % aq. NaOH solution (1.5 mL) the mixture was slightly heated for a few minutes. After cooling to the room temperature, water (3–4 mL) was added, the precipitated solid was filtered off, washed with water to give benzopyrans **9**, **12**.

3.7.1. 2-Phenyl-4H-chromen-4-imine ***(9).*** 78%, white powder, mp 68–70 °C (Ref.:[21] 66–67 °C) (MeOH); δ_H (400 MHz, DMSO-d_6) 9.00 (1H, c, NH), 8.12–8.19 (1H, m, H Ar), 7.83–8.01 (2H, m, H Ar), 7.45–7.66 (5H, m, H Ph), 7.33–7.37 (1H, m, H Ar), 6.87 (1H, s, H-3); δ_C (100 MHz, DMSO-d_6) 178.1, 155.9, 152.2, 133.1, 130.9, 129.4, 127.8, 126.2, 125.1, 121.1, 118.2, 117.3, 94.0; *m/z* (FAB) 222 (100% MH^+); *m/z* (FAB+NaI) 244 (36% MNa^+).

3.7.2. (4-Amino-2H-chromen-2-ylidene)malonaldehyde ***(12a)***. 80%, pink powder, mp 300 °C (aq. DMF), mp of hydrate 220–222 °C (aq. MeOH); [Found: C, 66.89; H, 4.18; N, 6.46. $C_{12}H_9NO_3$ requires C, 66.97; H, 4.22; N, 6.51%]; ν_{max}(KBr) 3369, 3348 (NH_2), 1615 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.86 (2H, br. s, 2CHO), 9.14 (1H, br. s) and 8.85 (1H, br. s, NH_2), 8.20 (1H, d, *J* 8.1 Hz, H Ar), 7.79–7.86 (2H, m, H Ar), 7.69 (1H, d, *J* 8.1 Hz, H Ar), 7.53 (1H, t, *J* 7.6 Hz, H Ar); δ_C (100 MHz, DMSO-d_6) 185.8 (2CHO), 167.3, 156.5, 152.8, 134.4, 125.2, 123.2, 118.2, 114.5, 106.8, 91.4; *m/z* (FAB) 216 (83 MH^+) (83), 186 (26), 170 (11%); *m/z* (FAB+NaI) 238 (60% MNa^+).

3.7.3. (4-Amino-6,8-diisopropyl-2H-chromen-2-ylidene)malonaldehyde ***(12b)***. 84%, light gray powder, mp 295 °C (aq. DMF); [Found: C, 72.08; H, 6.97; N, 4.62. $C_{18}H_{21}NO_3$ requires C, 72.22; H, 7.07; N, 4.68%]; ν_{max}(KBr) 3323 (NH_2), 2959 (aliphatic C–H), 1692 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.77 (2H, br. s, 2CHO), 9.00 (1H, br. s) and 8.74 (1H, br. s, NH_2), 7.92 (1H, s, H Ar), 7.81 (1H, s, H Ar), 7.59 (1H, s, H-3), 3.65–3.69 (1H, m, C<u>H</u>(CH_3)$_2$), 2.98–3.02 (1H, m, C<u>H</u>(CH_3)$_2$), 1.24–1.30 (12H, m, 2CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 186.1 (2CHO), 165.8, 157.4, 148.5, 145.2, 137.5, 129.9, 117.7, 113.9, 106.9, 91.7, 33.4, 26.4, 23.8, 22.4; *m/z* (EI) 299 (8 M^+), 271 (100), 254 (87), 238 (5), 121 (5), 91 (5), 43 (17%).

3.8. 2-Methyl-4-oxo-2H-1,3-benzoxazine-3(4H)-carbaldehyde (14). The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **13** (0.82 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was heated on a water bath at 75–80 °C for 1 h. Then the reaction mixture was cooled to the room temperature, treated with water (10 mL) and left to stand at r.t. The precipitate was filtered off to give the imide **14** (0.86 g, 90%) as white powder, mp 60–62 °C (aq. MeOH); [Found: C, 62.98; H, 4.82; N, 7.39. $C_{10}H_9NO_3$ requires C C, 62.82; H, 4.74; N, 7.33%]; ν_{max}(KBr) 1714 (imide) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.27 (1H, s, CHO), 7.93 (1H, d, *J* 7.8 Hz, H-8 Ar), 7.69 (1H, t, *J* 7.7 Hz, H-7 or H-6 Ar), 7.23 (1H, t, *J* 7.6 Hz, H-6 or H-7 Ar), 7.12 (1H, d, *J* 8.3 Hz, H-5 Ar), 6.37–6.44 (1H, q, *J* 6.2 Hz, H-2), 1.42 (3H, d, *J* 6.2 Hz, CH_3); δ_C (100 MHz, DMSO-d_6) 160.0 (CHO), 159.8 (CO), 155.4, 137.1, 128.1, 123.0, 117.9, 115.5, 78.8 (C-2), 18.8 (CH_3); *m/z* (EI) 191 (6 M^+),163 (24), 148 (11), 120 (100), 92 (47), 65 (12), 39 (10), 31 (27%).

3.9. The hydrolysis of imide 14.
To a solution of compound **14** (1.91 g, 0.01 mol) in MeOH (10 mL), water (4 mL) was added and the mixture was left to stand at the room temperature for 12 h. The colorless needles of oxazine **13** were filtered off, the yield was 1.55 g (95 %), mp 150–152 °C (Ref.[20]: 143–147 °C).

3.10. 9-Chloro-1,2,3,4-tetrahydroacridine (16). *Method A.*
The compound **15** (2.17 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (6 mL) and $POCl_3$ (2.75 mL, 0.03 mol) under ice-cooling. A yellow solid precipitated abundantly within 10–15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **16** (2.17 g, ~100%), as yellow powder, mp 68–70 °C (Ref.:[14] mp 68–70 °C). Spectral data for **16** (NMR) were identical to the reported data.[14]

Method B.
The compound **17** (1.99 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (4 mL) and $POCl_3$ (1.83 mL, 0.02 mol) under ice-cooling. A yellow solid precipitated abundantly within 10–15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **16** (2.17 g, ~100%), as yellow powder, mp 68–70 °C.

3.11. 1,3,4,10-Tetrahydroacridin-9(2H)-one (17).
The compound **15** (2.17 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (2 mL) and $POCl_3$ (0.92 mL, 0.01 mol) under ice-cooling. A white solid precipitated abundantly within 10-15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **17** (1.99 g, (~100%), as a colorless crystals, mp 358–360 °C (Ref.:[22] mp 355–358 °C). Spectral data for **17** (FTIR, NMR) were identical to the reported data.[15]

3.12. N-[(4-Chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-N-methylmethanaminium perchlorate (19).
The Vilsmeier reagent was prepared from $POCl_3$ (2.76 mL, 0.03 mol) and DMF (6.9 mL, 0.03 mol) with ice cooling. The compound **18** (2.0 g, 0.009 mol) was added to the Vilsmeier reagent. The reaction mixture was left to stand at the room temperature for 0.5 h and then was treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate was filtered off to give perchlorate **19** (2.38 g, 67%), as yellow cubic crystals, mp 180–182 °C (*i*-PrOH), ν_{max}(KBr) 3263 (N–H), 2934–2862 (aliphatic C–H), 1637 cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 9.05

(1H, br. s, NH), 7.95 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 3.43 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 2.64–2.68 (2H, m, CH_2), 2.40–2.44 (2H, m, CH_2), 1.47–1.99 (12H, m, $6CH_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 165.7, 157.2, 143.9, 100.6, 99.2, 21.4, 21.8, 23.5, 89.5 (C-2), 32.0, 24.4; *m/z* (FAB) 297 (34 M($^{37}Cl)^+$), 295 (100 M($^{35}Cl)^+$), 259 (70), 217 (11), 175 (10%).

The microanalysis were not performed in order to prevent an explosion.

3.13. [(E)-(4-Chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine (20).

To a solution of salt **19** (1.00 g) in MeOH (5 mL), 15% aq. NaOH (1.5 mL) was added, the mixture was slightly heated for 5 min. After cooling to the room temperature, water (2–3 mL) was added, the precipitated solid was filtered off, washed with water to give compound **20** (0.65 g, 87%), as yellow powder, mp 91–93 °C (aq. MeOH); [Found: C, 65.09; H, 7.80; N, 9.45. $C_{16}H_{23}ClN_2O$ requires C, 65.18; H, 7.86; N, 9.50%]; δ_H (400 MHz, DMSO-d_6/CCl_4) 6.68 (1H, s, =C<u>H</u>-N($CH_3)_2$), 2.50–2.54 (2H, m, CH_2), 2.98 (6H, s, N($CH_3)_2$), 2.23–2.27 (2H, m, CH_2), 1.38–1.84 (12H, m, $6CH_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 157.1, 153.7, 140.4 (<u>C</u>H-N($CH_3)_2$), 98.0, 96.8, 92.3 (C-2), 42.9 ($2CH_3$), 34.1 (CH_2), 24.9 (CH_2), 24.5 (CH_2), 23.7 (CH_2), 22.5 (CH_2), 21.5 (CH_2); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 140.0 (<u>C</u>H-N($CH_3)_2$), 42.5 ($2CH_3$), 33.7* (CH_2), 24.4* (CH_2), 24.0* (CH_2), 23.2* (CH_2), 22.0* (CH_2), 21.0* (CH_2); *signals in antiphase; *m/z* (EI) 296 (29 M($^{37}Cl)^+$), 294 (79 M($^{35}Cl)^+$), 258 (100), 251 (50), 243 (31), 229 (15), 215 (21), 200 (16), 191 (11), 176 (30), 161 (21), 149 (16), 134 (32), 81 (40), 43 (46%).

X-ray diffraction study of **6a** ($C_{17}H_{18}N_2O_2$, M_r = 282.33) was performed at 298 K on a «Xcalibur 3» diffractometer. Crystal data: monoclinic, a = 14.610(2) Å, b = 8.8414(8) Å, c = 12.5150(19) Å, β = 115.25(2)°, V = 1462.2(4) Å^3, space group $P2_1/c$, Z = 4, d_{calc}= 1.283 g/cm^3, $\mu(MoK_a)$ = 0.085 мм$^{-1}$, F(000) = 600, 10870 reflections were collected up to $2\theta_{max}$= 58.3° (3477 unique, R_{int} = 0.046). Structure was solved by direct method and refined on F^2 with Shelx-2013 software.[23] Hydrogen atoms refined in riding model approximation with Uiso = nUeq of the carrier atom (n = 1.5 for the water molecule and n = 1.2 for the remaining H-atoms). Hydrogen atoms of the C17 methyl group are disordered over two positions with equal occupancies. Refinement converged at wR_2 = 0.159 for all 3477 data, R_1 = 0.058 for 1720 reflections with F>4σ(F). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1051305.

X-ray diffraction study of **12a** ($2(C_{12}H_9NO_3)\cdot H_2O$, M_r = 448.42) was performed at 298 K on a «Xcalibur 3» diffractometer. Crystal data: monoclinic, a = 14.8086(8) Å, b = 6.8292(4) Å, c = 21.3683(10) Å, β = 105.613(5)°, V = 2081.2(2) Å^3, space group $P2_1/n$, Z = 4, d_{calc}= 1.431 g/cm^3, $\mu(MoK_a)$ = 0.107 мм$^{-1}$, F(000) = 936, 13830 reflections were collected up to $2\theta_{max}$= 57.2° (4255 unique, R_{int} = 0.057). Structure was solved by direct method and refined on F^2 with Shelx-2013 software.[23] Hydrogen atoms refined in riding model approximation with Uiso = nUeq of the carrier atom (n = 1.5 for the water molecule and n = 1.2 for the remaining H-atoms). Refinement converged at wR_2 = 0.131 for all 4255 data, R_1 = 0.056 for 2239 reflections with F>4σ(F). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1051306.

X-ray diffraction study of **19** ($C_{16}H_{24}N_2OCl^+\cdot ClO_4^-$, M_r = 395.27) was performed at 120 K on an «Bruker APEX-II CCD» diffractometer. Crystal data: monoclinic, ***a*** = 24.667(3) Å, ***b*** = 14.1313(18) Å, ***c*** = 20.611(3) Å, ***β*** = 93.473(3)°, V = 7171.3(15) Å^3, space group C2/c, Z = 16, d_{calc}= 1.464 g/cm^3, $\mu(MoK_a)$ = 0.392 мм$^{-1}$, F(000) = 3328, 17805 reflections were collected up to $2\theta_{max}$= 52.792° (7319 unique, R_{int} = 0.053). Structure was solved by direct method and refined on F^2 with Shelx-2013 software.[23] Hydrogen atoms refined in riding model approximation with Uiso = nUeq of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for the remaining H-atoms). Refinement converged at wR_2 = 0.161 for all 7319 data, R_1 = 0.065 for 5138 reflections with F>4σ(F). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1051304.

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SUPPORTING INFORMATION

The Vilsmeier-Haack formylation of 2,3-dihydro-4H-1,3-benzoxazin-4-ones and isomeric 1,2-dihydro-4H-3,1-benzoxazin-4-ones: an effective approach to functionalized 2H-/4H-Chromenes and Tetrahydroacridines

Oleg K. Farat[a,b] ∗, Victor I. Markov[a], Svetlana A. Varenichenko[a], Victor V. Dotsenko[c] and Alexander V. Mazepa[d]

[a]Ukrainian State University of Chemical Technology, 49005 Dnepropetrovsk, Ukraine

[b]Department of Chemistry, M. V. Lomonosov Moscow State University, 119991Moscow, Russian Federation

[c]Kuban State University, 350040 Krasnodar, Russian Federation

[d]A. V. Bogatsky Physico-Chemical Institute, 65080 Odessa, Ukraine

∗ Corresponding author. Tel.: +380562-47-46-70; fax: +380562-47-33-16; e-mail: faratok@mail.ru

Corresponding Author

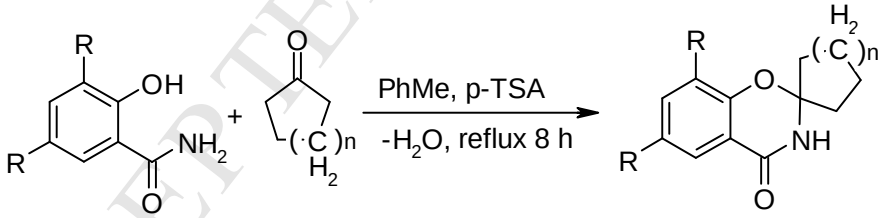
E-mail: faratok@mail.ru

General experimental details and procedures

The ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Avance II 400 instrument (400,13 MHz and 100,62 MHz for ^{1}H and ^{13}C respectively) in DMSO-d_6, DMSO-d_6/CCl_4 or DMSO-d_6/CF_3CO_2D with Me_4Si as internal standard. The FTIR spectra were recorded in KBr pellets using a Spectrum one (PerkinElmer) FT-IR Spectrometer. The mass spectra of compounds 4c–f, 10b, 6a,c–f, 12b, 14 and 20 were recorded on a MX1321 instrument with direct injection of the sample at an ionization chamber temperature of 200 °C and with 70 eV ionizing electrons. The FAB spectra of compounds were recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the samples in *meta*-nitrobenzyl alcohol was realized with a beam of argon atoms with energy 8 keV. Chromatographic analysis of compound 16 was realized on an Agilent 1100 liquid chromatograph with DAD and ELSD Sedex 75 detectors in conjunction with an LC-MS VL spectrometer with electrospray ionization. Elemental analysis was performed on a LECO CHNS-900 instrument. The reactions and the purity of the obtained compounds were monitored by TLC on Merck Silicagel 60 F-254 plates with 10:1 $CHCl_3$–*i*-PrOH as eluent.

Compounds 4a–f were synthesized by the method described in literature.[16] Compounds 7,[17] 15[18] and 18[19] were obtained by the known procedures.

Synthesis of Spirans 4a-f (General method).

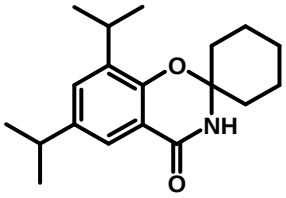


4a. R=H; n=2
4b. R=H; n=1
4c. R=i-Pr; n=2 (80%)
4d. R=i-Pr; n=1 (73%)
4e. R=I; n=2 (66%)
4f. R=I; n=1 (68%)

A mixture of the corresponding salicylamide (0.10 mol), ketone (0.12 mol) and p-TsOH × H_2O (0.05 mol) in toluene (70 mL) was refluxed for 8 h with continuous removal of water with a Dean–Stark trap. In the case of spirans **4a,b**, the mixture was cooled to 10 °C and stirred for 1 h at the same temperature. The resulting crystals were collected, washed with toluene (10 mL) and *i*-PrOH (10 mL) and dried at 50 °C. In all other cases, a solvent was evaporated to dryness

under reduced pressure, the solid residue was washed with 5% aq. NaOH solution and filtered off.

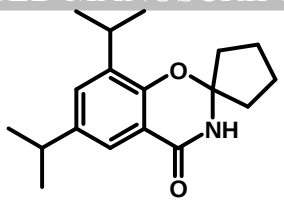
6,8-Diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one (4c).



80%, white powder, mp 165–167 °C (aq. MeOH); [Found: C, 75.86; H, 9.15; N, 4.69. $C_{19}H_{27}NO_2$ requires C, 75.71; H, 9.03; N, 4.65%]; ν_{max}(KBr) 3184 (N–H), 3066 (aromatic C–H), 2965–2862 (aliphatic C–H), 1674 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.43 (1H, s, NH), 7.41 (1H, s, H-5 Ar), 7.17 (1H, s, H-7 Ar), 3.22–3.31 (1H, m, C<u>H</u>$(CH_3)_2$), 2.79–2.88 (1H, m, C<u>H</u>$(CH_3)_2$), 1.95–2.07 (2H, m, spiro-ring), 1.50–1.70 (7H, m, spiro-ring), 1.25–1.32 (1H, m, spiro-ring), 1.21 (12H, d, *J* 6.1 Hz, 2CH(C<u>H</u>$_3)_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 161.4 (C=O), 140.6, 149.9, 128.6 (CH-7), 135.5, 121.4 (CH-5), 117.1, 86.9 (C-2), 35.4 ($2CH_2$), 32.9 (<u>C</u>H$(CH_3)_2$), 25.8 (<u>C</u>H$(CH_3)_2$), 23.9 ($2CH_2$), 23.8 (CH(<u>C</u>H$_3)_2$), 22.6 (CH(<u>C</u>H$_3)_2$), 21.6 (CH_2); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 128.3 (CH-7), 121.1 (CH-5), 35.1* ($2CH_2$), 32.5 (<u>C</u>H$(CH_3)_2$), 25.5 (<u>C</u>H$(CH_3)_2$), 23.9* ($2CH_2$), 23.5 (CH(<u>C</u>H$_3)_2$), 22.3 (CH(<u>C</u>H$_3)_2$), 21.3* (CH_2), *signals in antiphase; *m/z* (EI) 301 (9 M^+), 205 (20), 189 (5), 176 (7), 161 (5), 97 (100), 41 (7%).

^{1}H NMR signals, δ, ppm	Correlations	
	^{1}H-^{1}H COSY	HSQC
1.21 (d, 2CH(C<u>H</u>$_3)_2$)	2.79–2.88, 3.22–3.31	22.6, 23.8
1.25–1.32 (m, spiro-ring)	1.50–1.70	21.6
1.50–1.70 (m, spiro-ring)	1.95–2.07, 1.25–1.32	21.6, 23.9
1.95–2.07 (m, spiro-ring)	1.50–1.70	35.4
2.79–2.88 (m, C<u>H</u>$(CH_3)_2$)	1.21	32.9
3.22–3.31 (m, C<u>H</u>$(CH_3)_2$)	1.21	25.8
7.17 (s, H-7)	–	128.6
7.41 (s, H-5)	–	121.4

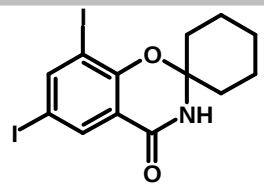
6,8-Diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one (4d).



73%, white powder, mp 137–140 °C (aq. MeOH); [Found: C, 75.37; H, 8.83; N, 4.91. $C_{18}H_{25}NO_2$ requires C, 75.22; H, 8.77; N, 4.87%]; ν_{max}(KBr) 3183 (N–H), 3066 (aromatic C–H), 2958–2871 (aliphatic C–H), 1669 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.54 (1H, s, NH), 7.41 (1H, s, H-5 Ar), 7.13 (1H, s, H-7 Ar), 3.11–3.23 (1H, m, C<u>H</u>$(CH_3)_2$), 2.77–2.91 (1H, m, C<u>H</u>$(CH_3)_2$), 2.03–2.13 (2H, m, spiro-ring), 1.72–1.88 (6H, m, spiro-ring), 1.22 (6H, d, *J* 6.1 Hz, CH(C<u>H</u>$_3)_2$), 1.19 (6H, d, *J* 6.1 Hz, CH(C<u>H</u>$_3)_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 161.9 (C=O), 150.9, 140.6, 135.6, 128.4 (CH-7), 121.5 (CH-5), 117.4, 96.7 (C-2), 37.9 ($2CH_2$), 32.9 (<u>C</u>H$(CH_3)_2$), 26.4 (<u>C</u>H$(CH_3)_2$), 23.8 (CH(<u>C</u>H$_3)_2$), 22.3 (CH(<u>C</u>H$_3)_2$), 22.2 ($2CH_2$); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 128.0 (CH-7), 121.1 (CH-5), 36.9* ($2CH_2$), 32.4 (<u>C</u>H$(CH_3)_2$), 26.0 (<u>C</u>H$(CH_3)_2$), 23.3 (CH(<u>C</u>H$_3)_2$), 21.9 (CH(<u>C</u>H$_3)_2$), 21.8* ($2CH_2$), *signals in antiphase; *m/z* (EI) 287 (8 M^+), 205 (29), 189 (6), 176 (10), 161 (9), 83 (100), 41 (10%).

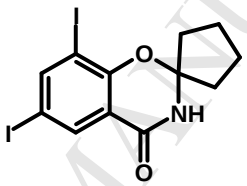
^{1}H NMR signals, δ, ppm	HSQC
1.19 (d, CH(C<u>H</u>$_3)_2$)	22.3
1.22 (d, CH(C<u>H</u>$_3)_2$)	23.8
1.72–1.88 (m, spiro-ring)	22.2, 37.9
2.03–2.13 (m, spiro-ring)	37.9
2.77–2.91 (m, C<u>H</u>$(CH_3)_2$)	32.9
3.11–3.23 (m, C<u>H</u>$(CH_3)_2$)	26.4
7.13 (s, H-7)	128.4
7.41 (s, H-5)	121.5

6,8-Diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one (4e).



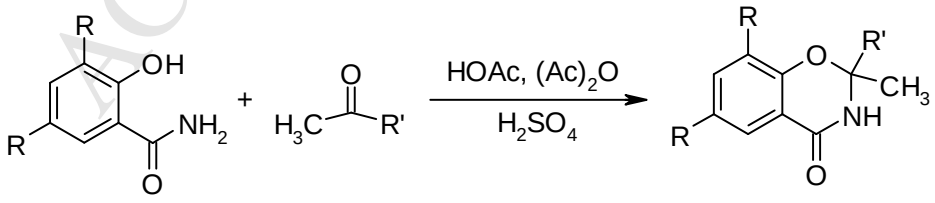
66%, white powder, mp 235–237 °C (aq. DMF); [Found: C, 33.40; H, 2.84; N, 3.06. $C_{13}H_{13}I_2NO_2$ requires C, 33.29; H, 2.79; N, 2.99%]; ν_{max}(KBr) 3153 (N–H), 3070 (aromatic C–H), 2936–2850 (aliphatic C–H), 1689 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.90 (1H, s, NH), 8.19 (1H, s, H-5 Ar), 7.92 (1H, s, H-7 Ar), 1.79–2.08 (2H, m, spiro-ring), 1.42–1.75 (7H, m, spiro-ring), 1.12–1.28 (1H, m, spiro-ring); δ_C (100 MHz, DMSO-d_6) 159.0 (C=O), 154.1, 149.4, 135.2, 119.8, 89.1 (C-2), 87.6 (C-I), 85.5 (C-I), 35.4 ($2CH_2$), 24.1 ($2CH_2$), 21.5 (CH_2); *m/z* (EI) 469 (55 M^+), 373 (24), 245 (14), 97 (100%).

6,8-Diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one (4f).



68%, white powder, mp 195–198 °C (aq. DMF); [Found: C, 31.79; H, 2.49; N, 3.14. $C_{13}H_{13}I_2NO_2$ requires C, 31.67; H, 2.44; N, 3.08%]; ν_{max}(KBr) 3177 (N–H), 3062 (aromatic C–H), 2971–2878 (aliphatic C–H), 1668 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.02 (1H, s, NH), 8.20 (1H, s, H-5 Ar), 7.93 (1H, s, H-7 Ar), 1.95–2.10 (2H, m, spiro-ring), 1.65–1.88 (6H, m, spiro-ring); δ_C (100 MHz, DMSO-d_6) 159.6 (C=O), 154.8, 149.3, 135.3, 119.9, 94.4 (C-2), 87.9 (C-I), 85.8 (C-I), 37.1 ($2CH_2$), 22.1 ($2CH_2$); *m/z* (EI) 455 (29 M^+), 373 (17), 245 (5), 83 (100%).

Synthesis of oxazines 10a,b and 13 (General method).



10a R=H; R'=Me (80%)
10b R=i-Pr; R'=Me (70%)
13 R=R'=H (98%)

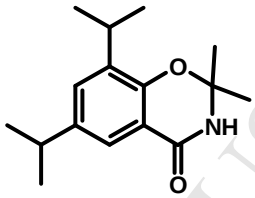
Concentrated H_2SO_4 (1 mL) was added to glacial acetic acid (3 mL), and the solution formed was cooled on ice. A solution of corresponding salicylamide (0.01

mol), acetone or acetaldehyde (0.01 mol), and Ac_2O (1 mL) in glacial acetic acid (3 mL) was prepared separately. To the mixture obtained, the above ice-cold solution of H_2SO_4 and AcOH was added gradually with stirring on an ice bath. The resulted mixture was stirred for 40 min and left to stay overnight at room temperature, then pH was adjusted to ~7.0 with aq. Na_2CO_3 solution. The precipitate formed was filtered off and recrystallized from aqueous MeOH.

Yield of compound **10a** was 80 %, mp 137–138 °C (Ref.[16]: 136–138 °C).

Yield of compound **13** was 98 %, mp 150–152 °C (Ref.[20]: 143–147 °C).

6,8-Diisopropyl-2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (10b).



70%, white powder, mp 145–147 °C (aq. MeOH); [Found: C, 73.42; H, 8.82; N, 5.30. $C_{16}H_{23}NO_2$ requires C, 73.53; H, 8.87; N, 5.36%]; ν_{max}(KBr) 3183 (N–H), 3066 (aromatic C–H), 2962–2871 (aliphatic C–H), 1674 (C=O) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.57 (1H, s, NH), 7.45 (1H, s, H-5 Ar), 7.24 (1H, s, H-7 Ar), 3.01–3.15 (1H, m, C<u>H</u>$(CH_3)_2$), 2.78–2.89 (1H, m, C<u>H</u>$(CH_3)_2$), 1.49 (6H, s, $2CH_3$), 1.13–1.19 (12H, m, $2CH(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 161.5 (C=O), 150.7, 140.9, 135.7, 129.2, 121.3, 116.7, 86.7 (C-2), 32.8, 27.2, 27.1, 23.9, 22.3; *m/z* (EI) 261 (74 M^+), 246 (12), 205 (96), 189 (43), 176 (100), 161 (75), 91 (10), 58 (26), 41 (11%).

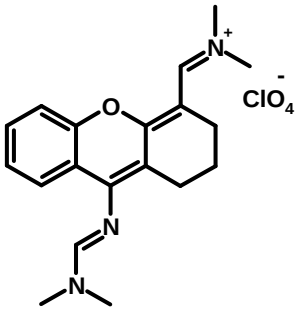
Synthesis of perchlorates 5a–f (General method).

Method A (with heating).

The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **4a** (1.1 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was heated on a water bath at 75–85 °C for 1 h (an orange solid was separated within 0.5 h). Then the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate of the salt **5a** was filtered off, dried and purified by refluxing with toluene. In the case of salts **5b–d**, the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL); then pH was adjusted to 8.0–9.0 with aq. NaOH. The solid products were filtered off, washed and dried to give pure salts **5b–d**. For salts **5e,f**, the reaction

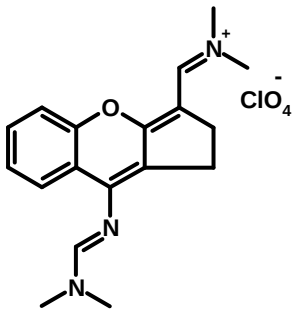
time was 4 h. *Caution! Organic perchlorates are potentially explosive. The microanalysis were not performed in order to prevent an explosion.*

_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-2,3-dihydro-1_H_-xanthen-4-yl)methylene]-_N_-methylmethanaminium perchlorate (5a).



96%, orange powder, mp 300 °C; ν_{max}(KBr) 2939 (aliphatic C–H), 1708, 1600 cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 8.56 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 8.20 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.76 (1H, d, *J* 7.6 Hz, H Ar), 7.60–7.68 (2H, m, H Ar), 7.34–7.42 (1H, m, H Ar), 3.52 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.27 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.25 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 2.74–2.81 (2H, m, 3-CH_2 or 1-CH_2), 2.59–2.74 (2H, m, 1-CH_2 or 3-CH_2), 1.61–1.78 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6/CCl_4) 172.0, 165.2, 158.3, 155.8, 152.1, 132.3, 125.0, 124.7, 121.5, 119.2, 116.5, 101.9, 42.0, 40.0, 24.6, 24.0, 20.6; *m/z* (FAB) 310 (100 M^+), 265 (6), 218 (11), 149 (33), 136 (35), 121 (12), 107 (24), 89 (19), 76 (27), 68 (21), 52 (29%).

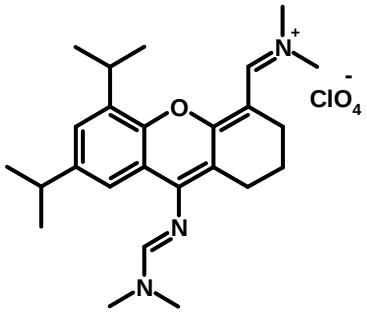
_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[_b_]chromen-3-yl)methylene]-_N_-methylmethanaminium perchlorate (5b).



80%, red needles, mp 262–265 °C (DMF); ν_{max}(KBr) 2964–2862 (aliphatic C–H), 1674, 1623 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.45 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 8.01–8.11 (1H, m, H Ar), 7.97 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.61–7.71 (1H, m, H Ar), 7.39–7.56 (2H, m, H Ar), 3.35 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.23 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.21 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 3.07 (4H, s, $2CH_2$); δ_C (100 MHz, DMSO-d_6) 172.8, 157.2, 153.1, 150.6, 144.0, 132.0, 125.6, 125.0, 121.4, 116.5, 114.1, 102.6,

41.0, 34.8, 25.1, 24.9; *m/z* (FAB) 296 (100 M^+), 137 (14), 107 (7), 91 (10), 80 (7), 53 (10%).

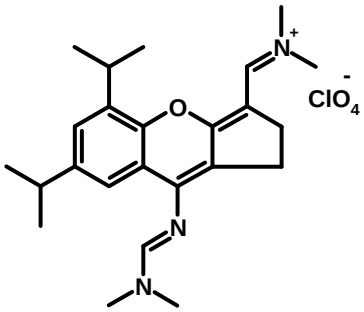
_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1_H_-xanthen-4-yl)methylene]-_N_-methylmethanaminium perchlorate (5c).



95%, orange-red powder, mp 215–217 °C. ν_{max}(KBr) 2927 (aliphatic C–H), 1702, 1611 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.17 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 8.13 (1H, s, C<u>H</u>=N^+(CH_3)$_2$), 7.47 (2H, s, H-5,7 Ar), 3.53–3.59 (1H, m, C<u>H</u>(CH_3)$_2$), 3.46 (6H, s, CH=N^+(C<u>H</u>$_3$)$_2$), 3.22 (3H, s, N=CH–N(CH_3)C<u>H</u>$_3$), 3.19 (3H, s, N=CH–N(C<u>H</u>$_3$)CH_3), 2.95–3.05 (1H, m, C<u>H</u>(CH_3)$_2$), 2.77–2.82 (2H, m, 3-CH_2 or 1-CH_2), 2.63–2.68 (2H, m, 1-CH_2 or 3-CH_2), 1.65–1.75 (2H, m, 2-CH_2), 1.30 (6H, d, *J* 6.8 Hz, CH(C<u>H</u>$_3$)$_2$), 1.23 (6H, d, *J* 6.8, CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 172.2, 165.8, 156.0, 148.3, 148.1, 145.2, 135.5, 130.5, 127.8, 119.5, 110.7, 101.2, 41.5, 35.4, 33.2, 26.4, 24.6, 24.1, 24.0, 22.3, 21.0; *m/z* (FAB) 394 (100 M^+), 378 (5), 349 (6%).

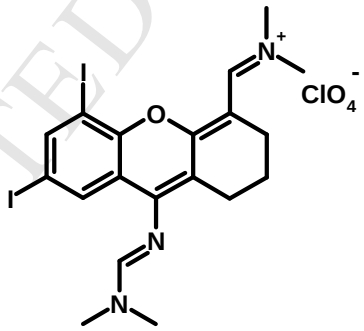
^{1}H NMR signals, δ, ppm	^{1}H-^{1}H COSY
1.23 (d, CH(C<u>H</u>$_3$)$_2$)	2.95–3.05
1.30 (d, CH(C<u>H</u>$_3$)$_2$)	3.53–3.59
1.65–1.75 (м, 2-CH_2)	2.63–2.68, 2.77–2.82
2.63–2.68 (м, 1-CH_2 or 3-CH_2)	1.65–1.75
2.77–2.82 (м, 3-CH_2 or 1-CH_2)	1.65–1.75
2.95–3.05 (м, 1H, C<u>H</u>(CH_3)$_2$)	1.23
3.53–3.59 (м, 1H, C<u>H</u>(CH_3)$_2$)	1.30

_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[_b_]chromen-3-yl)methylene]-_N_-methylmethanaminium perchlorate (5d).



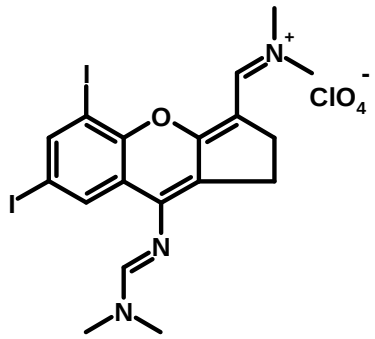
87%, red powder, mp 258–260 °C; ν_{max}(KBr) 2960–2925 (aliphatic C–H), 1624 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.42 (1H, s, N=C<u>H</u>–N$(CH_3)_2$), 7.78 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 7.75 (1H, s, H Ar), 7.45 (s, 1H, H Ar), 3.65–3.75 (m, 1H, C<u>H</u>$(CH_3)_2$), 3.33 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.21 (3H, s, N=CH–N$(CH_3)C\underline{H}_3$), 3.16 (3H, s, N=CH–N$(C\underline{H}_3)CH_3$), 3.04–3.13 (4H, m, $2CH_2$), 2.95–3.03 (1H, m, C<u>H</u>$(CH_3)_2$), 1.29 (6H, d, *J* 6.8 Hz, CH$(C\underline{H}_3)_2$), 1.22 (6H, d, *J* 6.8 Hz, CH$(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 172.5, 157.3, 152.9, 149.1, 148.6, 145.4, 136.0, 127.4, 121.3, 119.4, 116.0, 101.9, 40.8, 34.5, 33.2, 26.0, 25.1, 24.9, 23.8, 22.8; *m/z* (FAB) 380 (100 M^+), 364 (9%).

_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-5,7-diiodo-2,3-dihydro-1_H_-xanthen-4-yl)methylene]-_N_-methylmethanaminium perchlorate (5e).



Yellow powder, yield ~54% (calculated for proposed structure), mp 245–252 °C. *This intermediate perchlorate was used on the next step without further purification.*

_N_-[(9-{[(1_E_)-(Dimethylamino)methylene]amino}-5,7-diiodo-1,2-dihydrocyclopenta[_b_]chromen-3-yl)methylene]-_N_-methylmethanaminium perchlorate (5f).



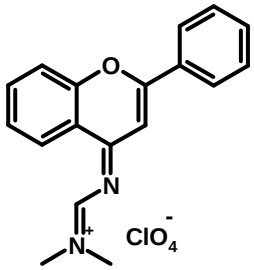
Pink powder, yield ~57% (calculated for proposed structure), mp 225–233 °C. *This intermediate perchlorate was used on the next step without further purification.*

Synthesis of perchlorates 5a–d. *Method B (at room temperature).*
The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **4a** (1.1 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was stirred vigorously at room temperature for 24 h and maintained as in the method A. The salts **5b–d** were obtained in the same way.

Yield of compound **5a** was 88 %.
Yield of compound **5b** was 75%.
Yield of compound **5c** was 85%.
Yield of compound **5d** was 80%.

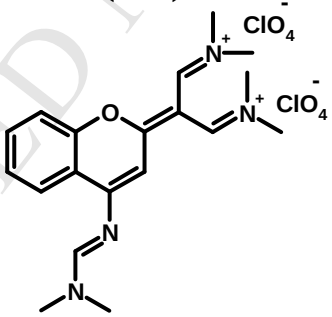
Synthesis of salts 8 and 11 a,b (General procedure).
The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The corresponding oxazine **7** or **10** (0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was left to stand at room temperature for 24 h. Then the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate of the corresponding salt **8** or **11** was filtered off, dried and purified by refluxing with toluene. *The microanalysis were not performed in order to prevent an explosion.*

_N_-Methyl-_N_-({[(4_Z_)-2-phenyl-4_H_-chromen-4-ylidene]amino}methylene)methanaminium perchlorate (8).



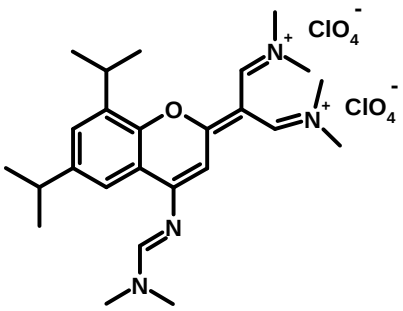
67%, yellow powder, mp 210–213 °C (MeOH); ν_{max}(KBr) 1630–1640 (C=N), 1614 (C=C), 1597 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.23 (1H, s, N–C<u>H</u>=$N^+(CH_3)_2$), 8.51–8.58 (1H, m, H Ar), 8.29–8.35 (2H, m, H Ar), 8.07 (1H, s, H-3), 8.01–8.13 (2H, m, H Ar), 7.62–7.82 (4H, m, H Ar), 3.52 (3H, s, CH_3), 3.49 (3H, s, CH_3); δ_C (100 MHz, DMSO-d_6) 166.4, 164.7, 161.6, 155.0, 136.4, 133.5, 130.2, 129.3, 127.3, 127.2, 125.7, 121.2, 118.6, 101.1, 42.9 (CH_3), 36.7 (CH_3); *m/z* (FAB) 277 (100 M^+), 222 (6%).

_N_,_N_'-[2-(4-{[(1_E_)-(Dimethylamino)methylene]amino}-2_H_-chromen-2-ylidene)propane-1,3-diylidene]bis(_N_-methylmethanaminium) diperchlorate (11a).



90%, yellow powder, mp 223–225 °C (MeOH); ν_{max}(KBr) 2929 (aliphatic C–H), 1622, 1526 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.94 (1H, s, N=C<u>H</u>–$N(CH_3)_2$), 8.42–8.48 (3H, m, H Ar and C<u>H</u>=$N^+(CH_3)_2$), 7.89–8.05 (2H, m, H Ar), 7.63–7.69 (1H, m, H Ar), 7.12 (1H, s, H-3), 3.61 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 3.46 (3H, s, N=CH–$N(CH_3)C\underline{H}_3$), 3.42 (3H, s, N=CH–$N(C\underline{H}_3)CH_3$), 3.24 (6H, s, CH=$N^+(C\underline{H}_3)_2$); δ_C (100 MHz, DMSO-d_6) 164.7, 162.4, 160.5, 154.3, 135.6, 127.0, 125.7, 120.4, 118.2, 101.4, 92.1, 48.5, 42.9, 42.6, 36.4; *m/z* (FAB) 427 (14 $(M+^{37}ClO_4)^+$), 425 (42 $(M+^{37}ClO_4)^+$), 326 (12), 311 (6), 280 (12), 270 (6), 225 (6), 165 (7%).

_N,N'_-[2-(4-{[(1E)-(Dimethylamino)methylene]amino}-6,8-diisopropyl-2H-chromen-2-ylidene)propane-1,3-diylidene]bis(N-methylmethanaminium) diperchlorate (11b).

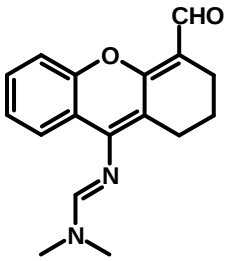


Yellow powder, yield 85% (calculated for proposed structure), mp 220–227 °C. *This intermediate diperchlorate was used on the next step without further purification.*

Synthesis of benzopyrans 6a–f (General method).

The corresponding salt **5a-f** (1.0 g, 0.002 mol) was dissolved in hot DMF (5 mL). To the obtained solution, an aqueous 15 % NaOH solution (1.5 mL) was added and the mixture was stirred vigorously at 60–75 °C for 5 min. The precipitated solid of corresponding compound **6a–f** was filtered off. If no solid precipitated, the solution cooled to the room temperature and water was added.

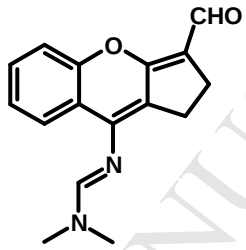
_N'_-(4-Formyl-2,3-dihydro-1_H_-xanthen-9-yl)-_N,N_-dimethylimidoformamide (6a).



85%, yellow-green needles, mp 175–177 °C (aq. MeOH); [Found: C, 72.41; H, 6.49; N, 9.98. $C_{17}H_{18}N_2O_2$ requires C, 72.32; H, 6.43; N, 9.92%]; ν_{max}(KBr) 2932–2852 (aliphatic C–H), 1632 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.13 (1H, s, CHO), 7.70 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.49–7.56 (1H, m, H Ar), 7.33–7.42 (1H, m, H Ar), 7.19–7.26 (1H, m, H Ar), 7.10–7.18 (1H, m, H Ar), 3.03 (3H, s, CH_3), 3.01 (3H, s, CH_3), 2.50 (2H, 3-CH_2 or 1-CH_2, overlapped with DMSO signals), 2.25–2.29 (2H, m, 1-CH_2 or 3-CH_2), 1.52–1.56 (2H, m, 2-CH_2); δ_H (400 MHz, DMSO-d_6/CF_3CO_2D) 10.00 (1H, s, CHO), 8.41 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.58 (1H, d, *J*

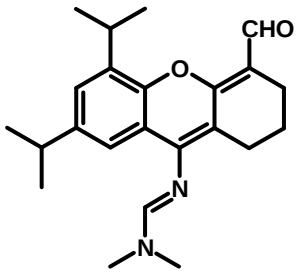
7.6 Hz, H-5 Ar), 7.50 (1H, t, *J* 7.6 Hz, H-6 Ar), 7.34 (1H, d, *J* 8.1 Hz, H-8 Ar), 7.25 (1H, t, *J* 7.4 Hz, H-7 Ar), 3.27 (3H, s, CH_3), 3.31 (3H, s, CH_3), 2.58–2.70 (2H, m, 3-CH_2 or 1-CH_2), 2.28–2.40 (2H, m, 1-CH_2 or 3-CH_2), 1.55–1.75 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6) 184.2 (CHO), 162.5, 154.6, 151.6, 146.9, 130.2, 124.0, 123.3, 120.8, 115.2, 110.9, 109.0, 33.8, 24.7, 27.0, 20.1; *m/z* (EI) 282 (100 M^+), 265 (16), 253 (60), 239 (13), 210 (10), 196 (6), 181 (11), 152 (5), 127 (7), 77 (8), 58 (6), 43 (17%).

_N_'-(3-Formyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide (6b).



83%, yellow-green needles, mp 196–198 °C (aq. MeOH); [Found: C, 71.51; H, 5.97; N, 10.40. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%]; ν_{max}(KBr) 2924 (aliphatic C–H), 1630 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.77 (1H, s, CHO), 8.08 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.71–7.77 (1H, m, H Ar), 7.32–7.40 (1H, m, H Ar), 7.15–7.24 (2H, m, H Ar), 2.51–3.07 (3H, s, CH_3), 3.02 (3H, s, CH_3), 2.76–2.85 (2H, m, CH_2), 2.55 (2H, m, CH_2); δ_C (100 MHz, DMSO-d_6) 180.4 (CHO), 166.2, 155.5, 152.2, 143.2, 129.7, 124.0, 123.8, 122.2, 118.6, 155.5, 112.0, 33.8, 23.2; *m/z* (FAB) 269 (100 MH^+), 239 (11%).

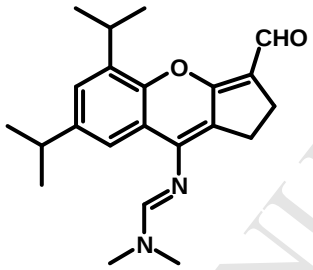
_N_'-(4-Formyl-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide (6c).



90%, yellow powder, mp 188–190 °C (aq. MeOH); [Found: C, 75.47; H, 8.32; N, 7.69. $C_{23}H_{30}N_2O_2$ requires C, 75.38; H, 8.25; N, 7.64%]; ν_{max}(KBr) 2927–2864

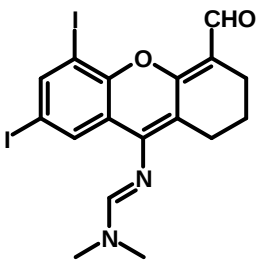
(aliphatic C–H), 1651 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.19 (1H, s, CHO), 7.66 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.24 (1H, s, H Ar), 7.19 (1H, s, H Ar), 3.35–3.43 (1H, m, C<u>H</u>(CH_3)$_2$), 3.05 (6H, m, N=CH–N(C<u>H</u>$_3$)$_2$), 2.86–2.91 (1H, m, C<u>H</u>(CH_3)$_2$), 2.49–2.53 (2H, m, 3-CH_2 or 1-CH_2), 2.29–2.34 (2H, m, 1-CH_2 or 3-CH_2), 1.56–1.62 (2H, m, 2-CH_2), 1.29 (6H, d, *J* 6.8 Hz, CH(C<u>H</u>$_3$)$_2$), 1.21 (6H, d, *J* 6.8 Hz, CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 183.4 (CHO), 162.8, 154.6, 148.0, 147.0, 142.9, 134.1, 125.3, 120.3, 118.9, 110.4, 108.7, 33.8, 33.1, 26.8, 24.4, 23.9, 22.3, 21.2, 20.3; *m/z* (EI) 366 (100 M^+), 349 (8), 337 (36), 322 (6), 59 (8), 43 (19%).

_N_'-(3-Formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide (6d).



85%, yellow powder, mp 133–136 °C (aq. MeOH); [Found: C, 75.11; H, 8.08; N, 7.99. $C_{22}H_{28}N_2O_2$ requires C, 74.97; H, 8.01; N, 7.95%]; ν_{max}(KBr) 2925 (aliphatic C–H), 1630 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.79 (1H, s, CHO), 8.07 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.48 (1H, s, H Ar), 7.17 (1H, s, H Ar), 3.33 (1H, m, CH, overlapped with a peak of water), 3.07 (3H, s, N=CH–N(C<u>H</u>$_3$)CH_3), 3.03 (3H, s, N=CH–N(CH_3)C<u>H</u>$_3$), 2.89–2.99 (1H, m, C<u>H</u>(CH_3)$_2$), 2.79–2.89 (2H, m, CH_2), 2.51–2.60 (2H, m, CH_2), 1.22 (12H, d, *J* 6.8 Hz, 2CH(C<u>H</u>$_3$)$_2$); δ_C (100 MHz, DMSO-d_6) 180.0 (CHO), 166.5, 158.4, 147.6, 144.2, 143.6, 134.2, 125.1, 121.6, 118.8, 118.0, 111.6, 33.9, 33.1, 27.2, 24.0, 23.3, 23.2, 22.4; *m/z* (EI) 352 (100 M^+), 337 (6), 323 (21), 308 (16), 280 (14), 44 (7%).

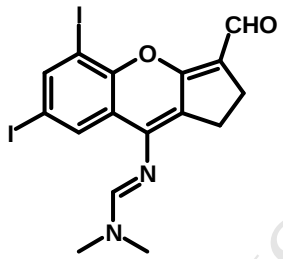
_N_'-(4-Formyl-5,7-diiodo-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide (6e).



85%, yellow powder, mp 295–300 °C (aq. DMF); [Found: C, 38.31; H, 3.05; N, 5.29. $C_{17}H_{16}I_2N_2O_2$ requires C, 38.23; H, 3.02; N, 5.24%]; ν_{max}(KBr) 2925

(aliphatic C–H), 1674 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 10.29 (1H, s, CHO), 8.05 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 7.73 (1H, s, H Ar), 7.72 (1H, s, H Ar), 3.04 (3H, s, CH_3), 3.01 (3H, s, CH_3), 2.50–2.55 (2H, m, 3-CH_2 or 1-CH_2), 2.24–2.30 (2H, m, 1-CH_2 or 3-CH_2), 1.51–1.57 (2H, m, 2-CH_2); δ_C (100 MHz, DMSO-d_6) 185.1 (CHO), 166.0, 161.8, 155.1, 145.5, 144.8, 132.2, 123.6, 111.8, 110.2, 88.1 (C-I), 85.4 (C-I), 34.9, 33.9, 24.5, 20.8, 19.9; *m/z* (EI) 534 (100 M^+), 505 (19), 152 (7), 42 (34%).

_N_'-(3-Formyl-5,7-diiodo-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide (6f).

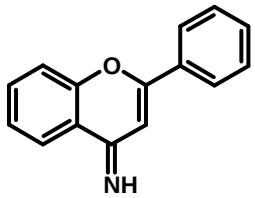


80%, pink powder, mp 300 °C (aq. DMF); [Found: C, 37.09; H, 2.75; N, 5.44. $C_{16}H_{14}I_2N_2O_2$ requires C, 36.95; H, 2.71; N, 5.39%]; ν_{max}(KBr) 2924 (aliphatic C–H), 1615 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6/CF_3CO_2D) 9.74 (1H, s, CHO), 8.42 (1H, s, N=C<u>H</u>–N(CH_3)$_2$), 8.09 (1H, s, H Ar), 7.81 (1H, s, H Ar), 3.28 (3H, s, CH_3), 3.21 (3H, s, CH_3), 2.84–2.88 (2H, m, CH_2), 2.52–2.60 (2H, m, CH_2); *m/z* (EI) 520 (100 M^+), 505 (7), 491 (13), 476 (7), 139 (9), 44 (40%).

Synthesis of benzopyrans 9 and 12a, b (General method).

The corresponding salt **8** or **11** (1.0 g) was dissolved in MeOH (5 mL) and treated with 15 % aq. NaOH solution (1.5 mL), the mixture was slightly heated for a few minutes. After cooling to the room temperature, water (3–4 mL) was added, the precipitated solid was filtered off, washed with water to give benzopyrans **9**, **12**.

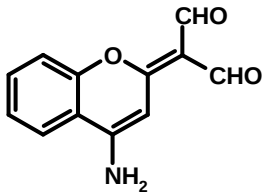
2-Phenyl-4*H*-chromen-4-imine (9).



78%, white powder, mp 68–70 °C (Ref.:[21] 66–67 °C) (MeOH); δ_H (400 MHz, DMSO-d_6) 9.00 (1H, c, NH), 8.12–8.19 (1H, m, H Ar), 7.83–8.01 (2H, m, H Ar), 7.45–7.66 (5H, m, H Ph), 7.33–7.37 (1H, m, H Ar), 6.87 (1H, s, H-3); δ_C (100

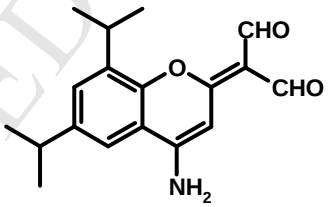
MHz, DMSO-d_6) 178.1, 155.9, 152.2, 133.1, 130.9, 129.4, 127.8, 126.2, 125.1, 121.1, 118.2, 117.3, 94.0; *m/z* (FAB) 222 (100% MH^+); *m/z* (FAB+NaI) 244 (36% MNa^+).

(4-Amino-2*H*-chromen-2-ylidene)malonaldehyde (12a).



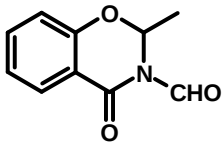
80%, pink powder, mp 300 °C (aq. DMF), mp of hydrate 220–222 °C (aq. MeOH); [Found: C, 66.89; H, 4.18; N, 6.46. $C_{12}H_9NO_3$ requires C, 66.97; H, 4.22; N, 6.51%]; ν_{max}(KBr) 3369, 3348 (NH_2), 1615 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.86 (2H, br. s, 2CHO), 9.14 (1H, br. s) and 8.85 (1H, br. s, NH_2), 8.20 (1H, d, *J* 8.1 Hz, H Ar), 7.79–7.86 (2H, m, H Ar), 7.69 (1H, d, *J* 8.1 Hz, H Ar), 7.53 (1H, t, *J* 7.6 Hz, H Ar); δ_C (100 MHz, DMSO-d_6) 185.8 (2CHO), 167.3, 156.5, 152.8, 134.4, 125.2, 123.2, 118.2, 114.5, 106.8, 91.4; *m/z* (FAB) 216 (83 MH^+) (83), 186 (26), 170 (11%); *m/z* (FAB+NaI) 238 (60% MNa^+).

(4-Amino-6,8-diisopropyl-2*H*-chromen-2-ylidene)malonaldehyde (12b).



84%, light gray powder, mp 295 °C (aq. DMF); [Found: C, 72.08; H, 6.97; N, 4.62. $C_{18}H_{21}NO_3$ requires C, 72.22; H, 7.07; N, 4.68%]; ν_{max}(KBr) 3323 (NH_2), 2959 (aliphatic C–H), 1692 (CHO) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.77 (2H, br. s, 2CHO), 9.00 (1H, br. s) and 8.74 (1H, br. s, NH_2), 7.92 (1H, s, H Ar), 7.81 (1H, s, H Ar), 7.59 (1H, s, H-3), 3.65–3.69 (1H, m, C<u>H</u>$(CH_3)_2$), 2.98–3.02 (1H, m, C<u>H</u>$(CH_3)_2$), 1.24–1.30 (12H, m, 2CH(C<u>H</u>$_3)_2$); δ_C (100 MHz, DMSO-d_6) 186.1 (2CHO), 165.8, 157.4, 148.5, 145.2, 137.5, 129.9, 117.7, 113.9, 106.9, 91.7, 33.4, 26.4, 23.8, 22.4; *m/z* (EI) 299 (8 M^+), 271 (100), 254 (87), 238 (5), 121 (5), 91 (5), 43 (17%).

2-Methyl-4-oxo-2*H*-1,3-benzoxazine-3(4*H*)-carbaldehyde (14).

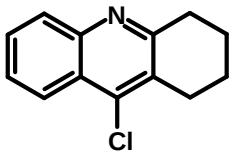


The Vilsmeier reagent was prepared from $POCl_3$ (0.92 mL, 0.01 mol) and DMF (2.3 mL, 0.03 mol) with ice cooling. The compound **13** (0.82 g, 0.005 mol) was added to the Vilsmeier reagent. The reaction mixture was heated on a water bath at 75–80 °C for 1 h. Then the reaction mixture was cooled to the room temperature, treated with water (10 mL) and left to stand at r.t. The precipitate was filtered off to give the imide **14** (0.86 g, 90%) as white powder, mp 60–62 °C (aq. MeOH); [Found: C, 62.98; H, 4.82; N, 7.39. $C_{10}H_9NO_3$ requires C C, 62.82; H, 4.74; N, 7.33%]; ν_{max}(KBr) 1714 (imide) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 9.27 (1H, s, CHO), 7.93 (1H, d, *J* 7.8 Hz, H-8 Ar), 7.69 (1H, t, *J* 7.7 Hz, H-7 or H-6 Ar), 7.23 (1H, t, *J* 7.6 Hz, H-6 or H-7 Ar), 7.12 (1H, d, *J* 8.3 Hz, H-5 Ar), 6.37–6.44 (1H, q, *J* 6.2 Hz, H-2), 1.42 (3H, d, *J* 6.2 Hz, CH_3); δ_C (100 MHz, DMSO-d_6) 160.0 (CHO), 159.8 (CO), 155.4, 137.1, 128.1, 123.0, 117.9, 115.5, 78.8 (C-2), 18.8 (CH_3); *m/z* (EI) 191 (6 M^+),163 (24), 148 (11), 120 (100), 92 (47), 65 (12), 39 (10), 31 (27%).

***The hydrolysis of imide 14*.**

To a solution of compound **14** (1.91 g, 0.01 mol) in MeOH (10 mL), water (4 mL) was added and the mixture was left to stand at the room temperature for 12 h. The colorless needles of oxazine **13** were filtered off, the yield was 1.55 g (95 %), mp 150–152 °C (Ref.[20]: 143–147 °C).

9-Chloro-1,2,3,4-tetrahydroacridine (16).



Method A.

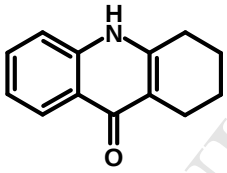
The compound **15** (2.17 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (6 mL) and $POCl_3$ (2.75 mL, 0.03 mol) under ice-cooling. A yellow solid precipitated abundantly within 10–15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **16**. The yield is 2.17 g (~100%), mp 68–70 °C

(Ref.:[14] mp 68–70 °C). Spectral data for **16** (FTIR, NMR) were identical to the reported data.[14]

Method B.

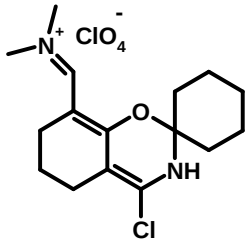
The compound **17** (1.99 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (4 mL) and $POCl_3$ (1.83 mL, 0.02 mol) under ice-cooling. A yellow solid precipitated abundantly within 10–15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **16**. The yield was 2.17 g (~100%), yellow crystals, mp 68–70 °C.

1,3,4,10-Tetrahydroacridin-9(2H)-one (17).



The compound **15** (2.17 g, 0.01 mol) was added to DMF (1 mL). The suspension formed was treated with the ice-cold Vilsmeier reagent obtained from DMF (2 mL) and $POCl_3$ (0.92 mL, 0.01 mol) under ice-cooling. A white solid precipitated abundantly within 10-15 min. After 0.5 h the reaction mixture was poured on ice and treated with aqueous ammonia, the obtained solid was filtered off and dried to give acridine **17**. The yield was 1.99 g (~100%), colorless crystals, mp 358–360 °C (Ref.:[22] mp 355–358 °C). Spectral data for **17** (FTIR, NMR) were identical to the reported data.[15]

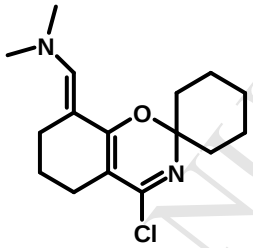
***N*-[(4-Chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-*N*-methylmethanaminium perchlorate (19).**



The Vilsmeier reagent was prepared from $POCl_3$ (2.76 mL, 0.03 mol) and DMF (6.9 mL, 0.03 mol) with ice cooling. The compound **18** (2.0 g, 0.009 mol) was added to the Vilsmeier reagent. The reaction mixture was left to stand at the room temperature for 0.5 h and then was treated with an ice-cold 15% aq. solution of

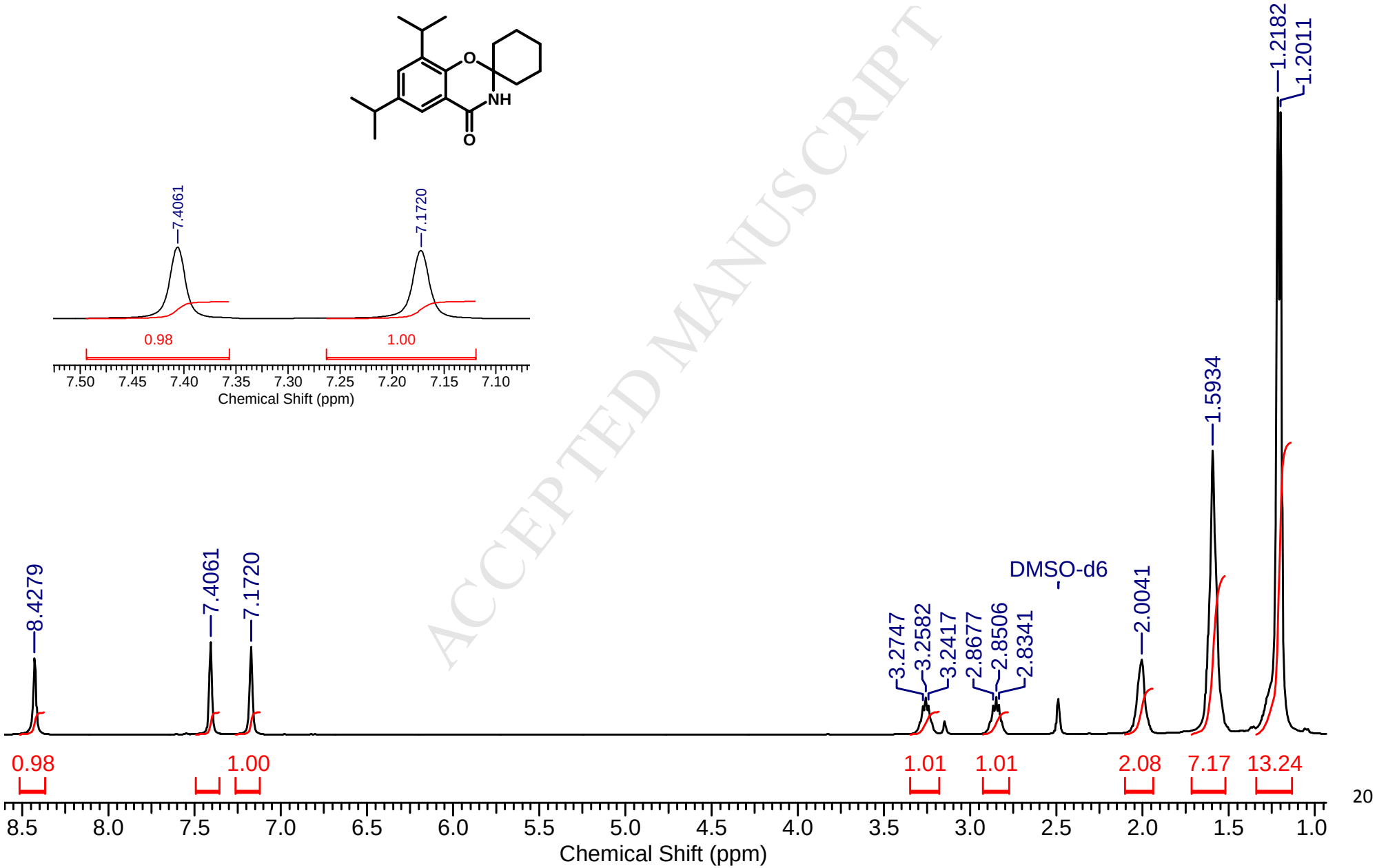
$NaClO_4$ (10 mL). The precipitate was filtered off to give perchlorate **19** (2.38 g, 67%), as yellow cubic crystals, mp 180–182 °C (*i*-PrOH), ν_{max}(KBr) 3263 (N–H), 2934–2862 (aliphatic C–H), 1637 cm^{-1}; δ_H (400 MHz, DMSO-d_6/CCl_4) 9.05 (1H, br. s, NH), 7.95 (1H, s, C<u>H</u>=$N^+(CH_3)_2$), 3.43 (6H, s, CH=$N^+(C\underline{H}_3)_2$), 2.64–2.68 (2H, m, CH_2), 2.40–2.44 (2H, m, CH_2), 1.47–1.99 (12H, m, $6CH_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 165.7, 157.2, 143.9, 100.6, 99.2, 21.4, 21.8, 23.5, 89.5 (C-2), 32.0, 24.4; *m/z* (FAB) 297 (34 M($^{37}Cl)^+$), 295 (100 M($^{35}Cl)^+$), 259 (70), 217 (11), 175 (10%). *The microanalysis were not performed in order to prevent an explosion.*

[(E)-(4-Chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine (20).

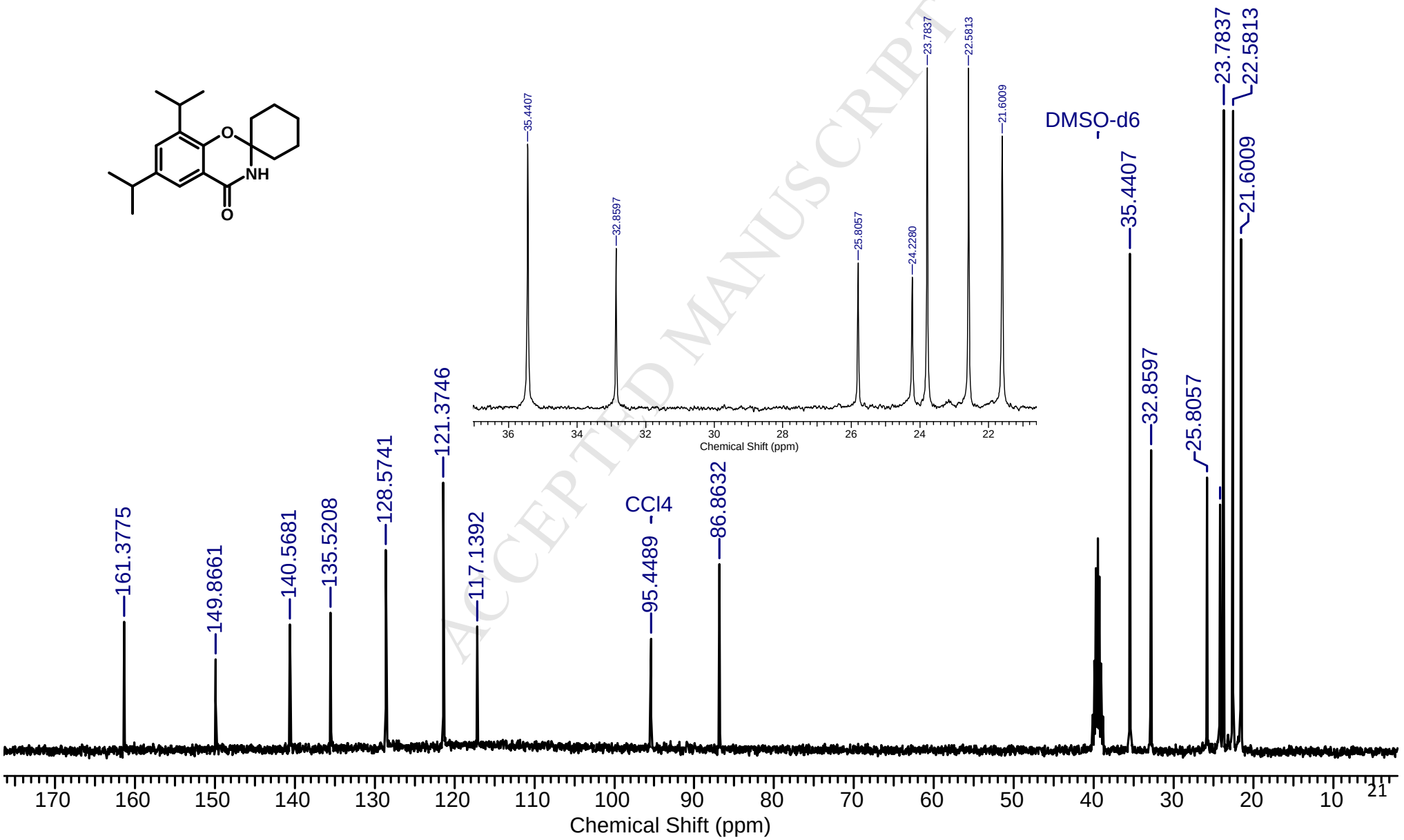


To a solution of salt **19** (1.00 g) in MeOH (5 mL), 15% aq. NaOH (1.5 mL) was added, the mixture was slightly heated for 5 min. After cooling to the room temperature, water (2–3 mL) was added, the precipitated solid was filtered off, washed with water to give compound **20** (0.65 g, 87%), as yellow powder, mp 91–93 °C (aq. MeOH); [Found: C, 65.09; H, 7.80; N, 9.45. $C_{16}H_{23}ClN_2O$ requires C, 65.18; H, 7.86; N, 9.50%]; δ_H (400 MHz, DMSO-d_6/CCl_4) 6.68 (1H, s, =C<u>H</u>-$N(CH_3)_2$), 2.50–2.54 (2H, m, CH_2), 2.98 (6H, s, $N(CH_3)_2$), 2.23–2.27 (2H, m, CH_2), 1.38–1.84 (12H, m, $6CH_2$); δ_C (100 MHz, DMSO-d_6/CCl_4) 157.1, 153.7, 140.4 (<u>C</u>H-$N(CH_3)_2$), 98.0, 96.8, 92.3 (C-2), 42.9 ($2CH_3$), 34.1 (CH_2), 24.9 (CH_2), 24.5 (CH_2), 23.7 (CH_2), 22.5 (CH_2), 21.5 (CH_2); δ_C DEPT-135 (100 MHz, DMSO-d_6/CCl_4) 140.0 (<u>C</u>H-$N(CH_3)_2$), 42.5 ($2CH_3$), 33.7* (CH_2), 24.4* (CH_2), 24.0* (CH_2), 23.2* (CH_2), 22.0* (CH_2), 21.0* (CH_2); *signals in antiphase; *m/z* (EI) 296 (29 M($^{37}Cl)^+$), 294 (79 M($^{35}Cl)^+$), 258 (100), 251 (50), 243 (31), 229 (15), 215 (21), 200 (16), 191 (11), 176 (30), 161 (21), 149 (16), 134 (32), 81 (40), 43 (46%).

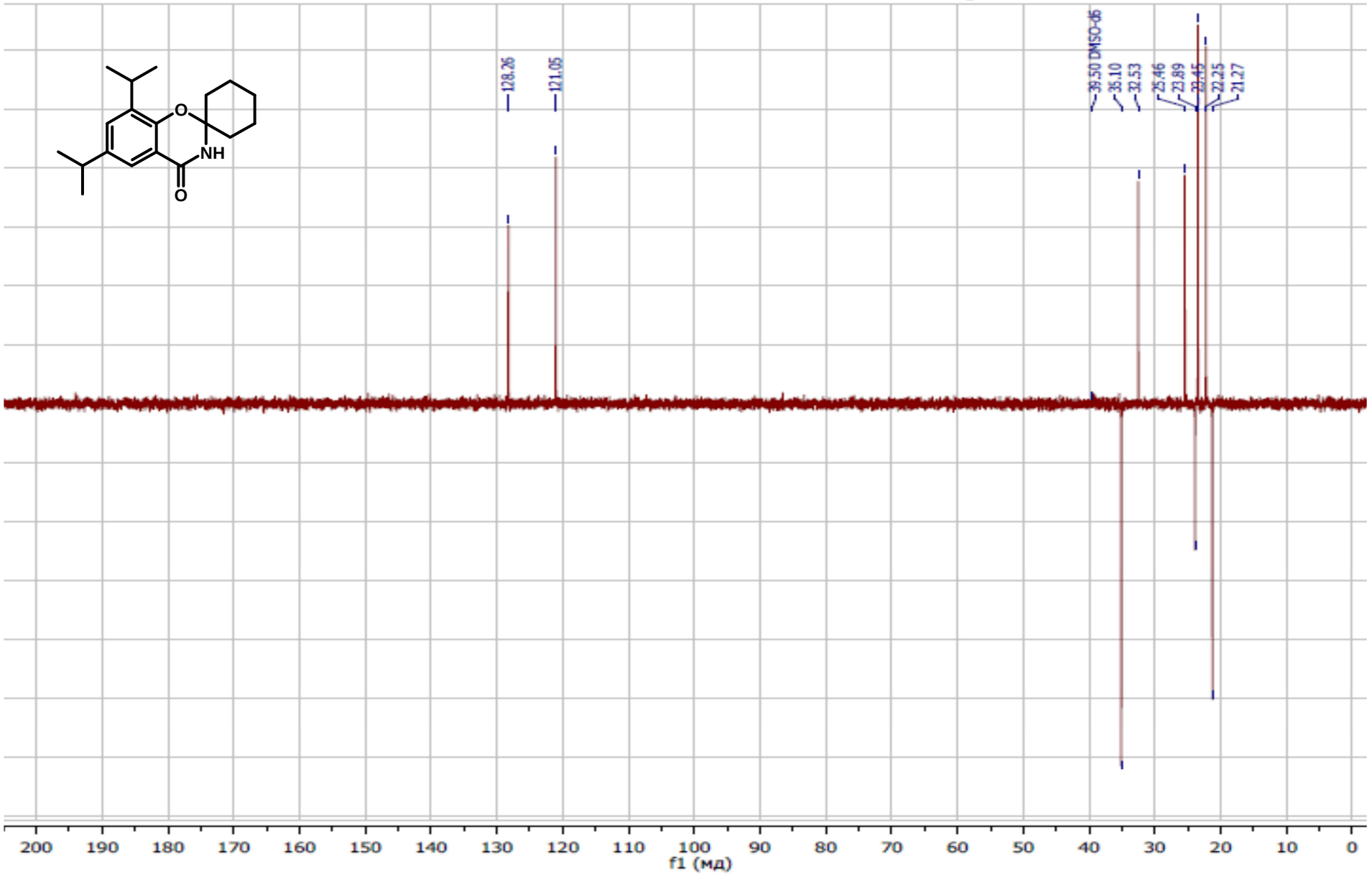
^{1}H NMR spectrum (DMSO-d_6/CCl_4, 400 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.



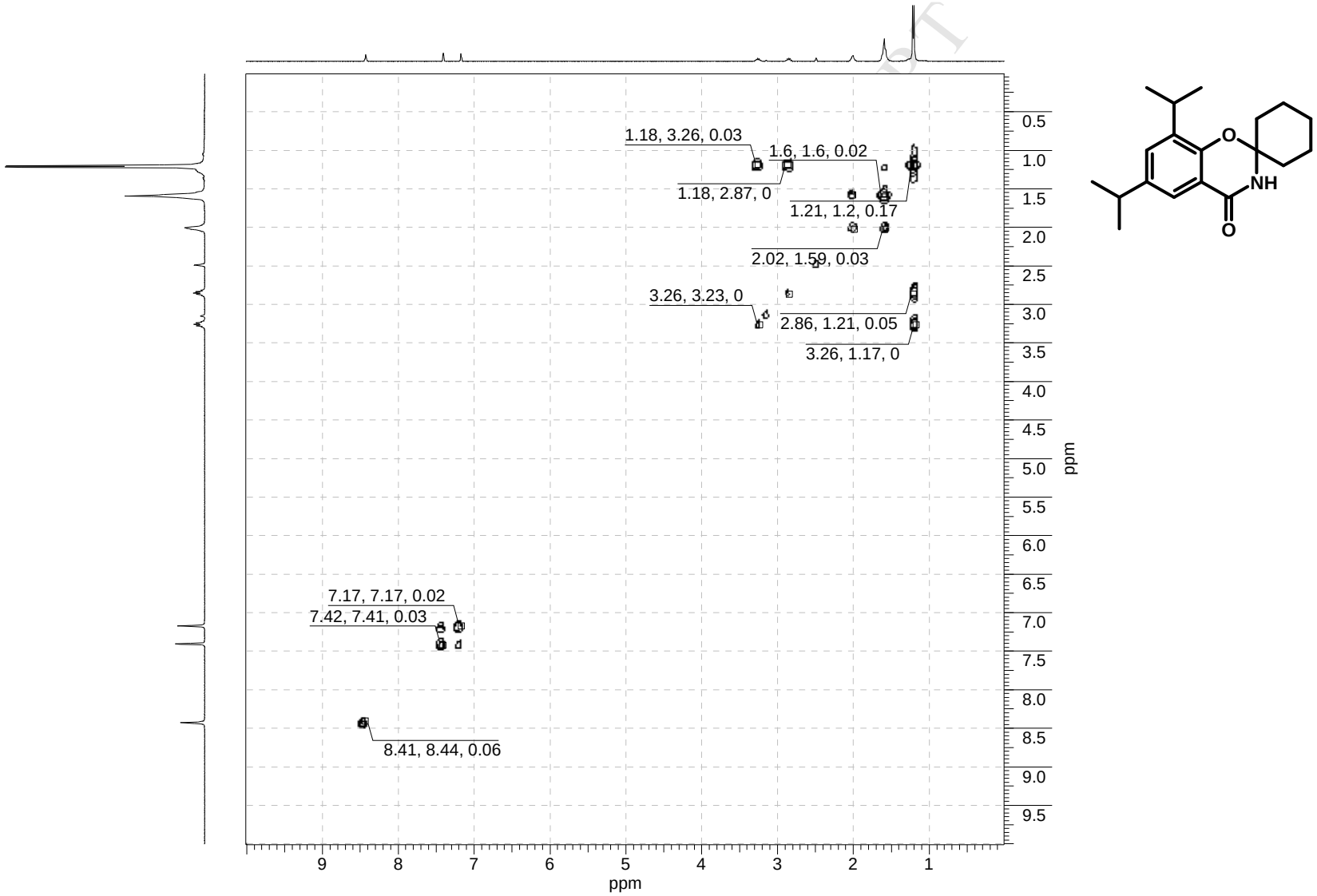
^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.



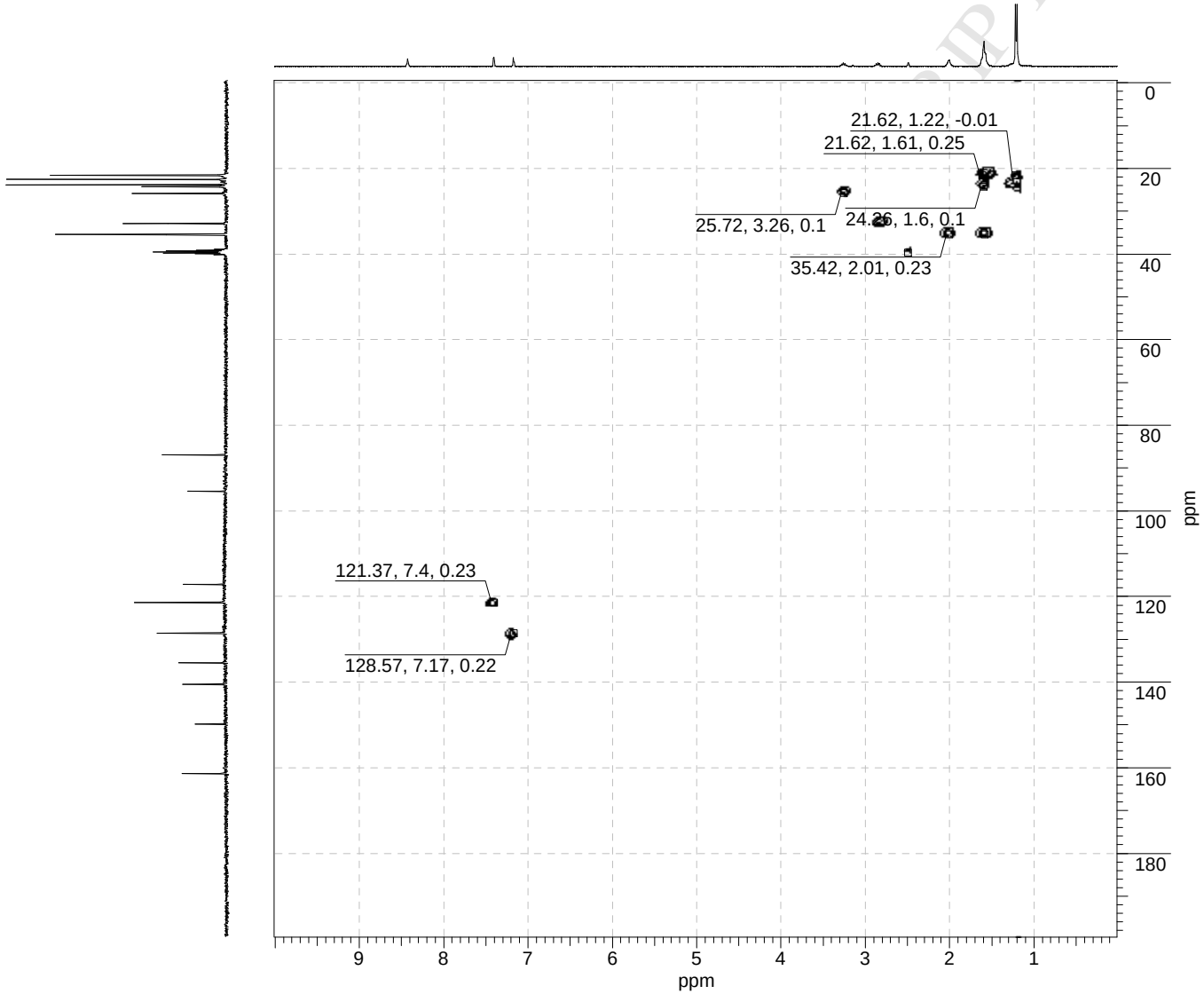
DEPT-135 ^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.

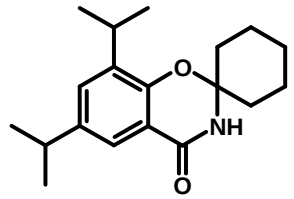


^{1}H-^{1}H COSY NMR spectrum (400 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.

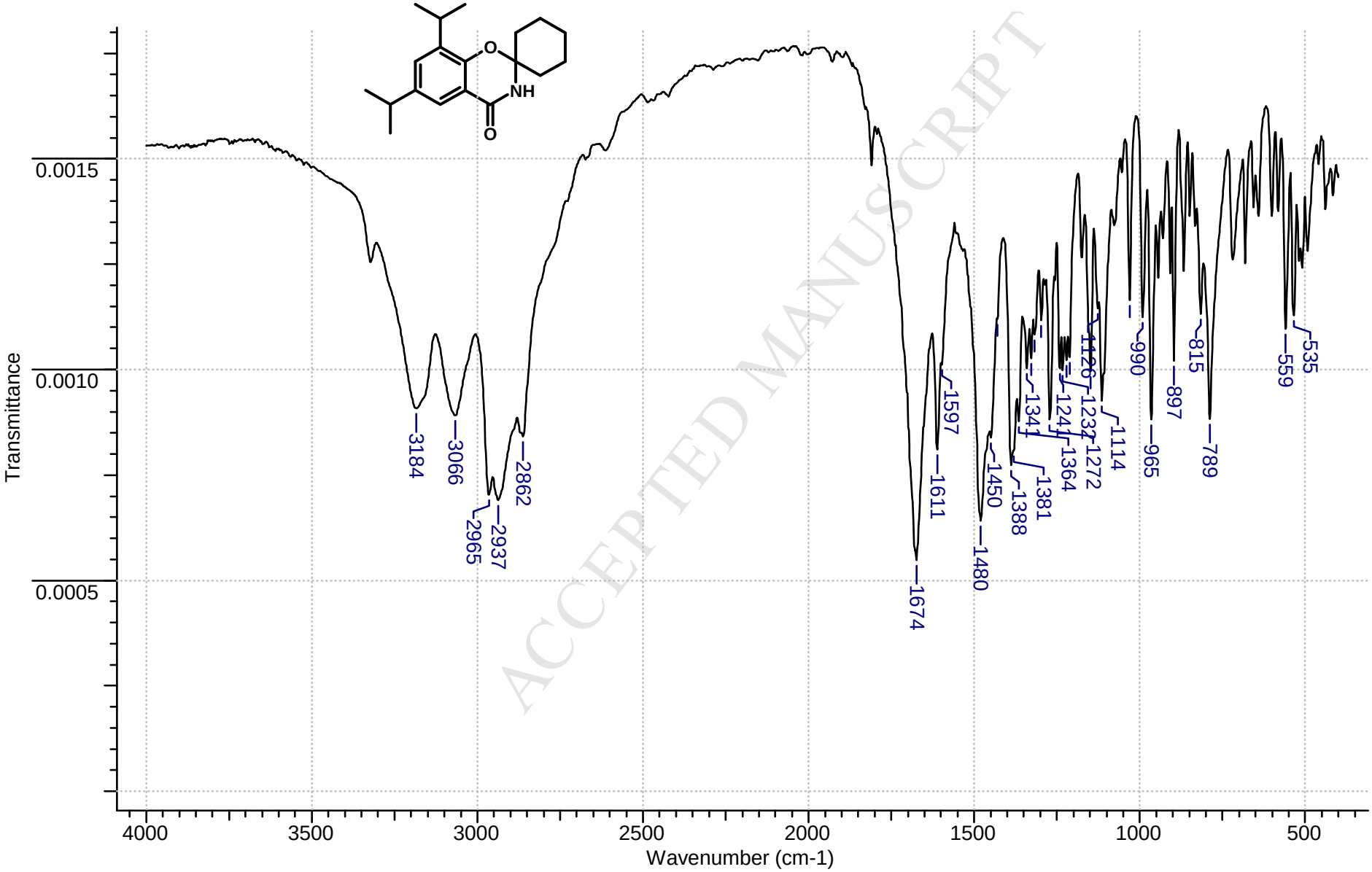


^{1}H-^{13}C HSQC NMR spectrum of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.

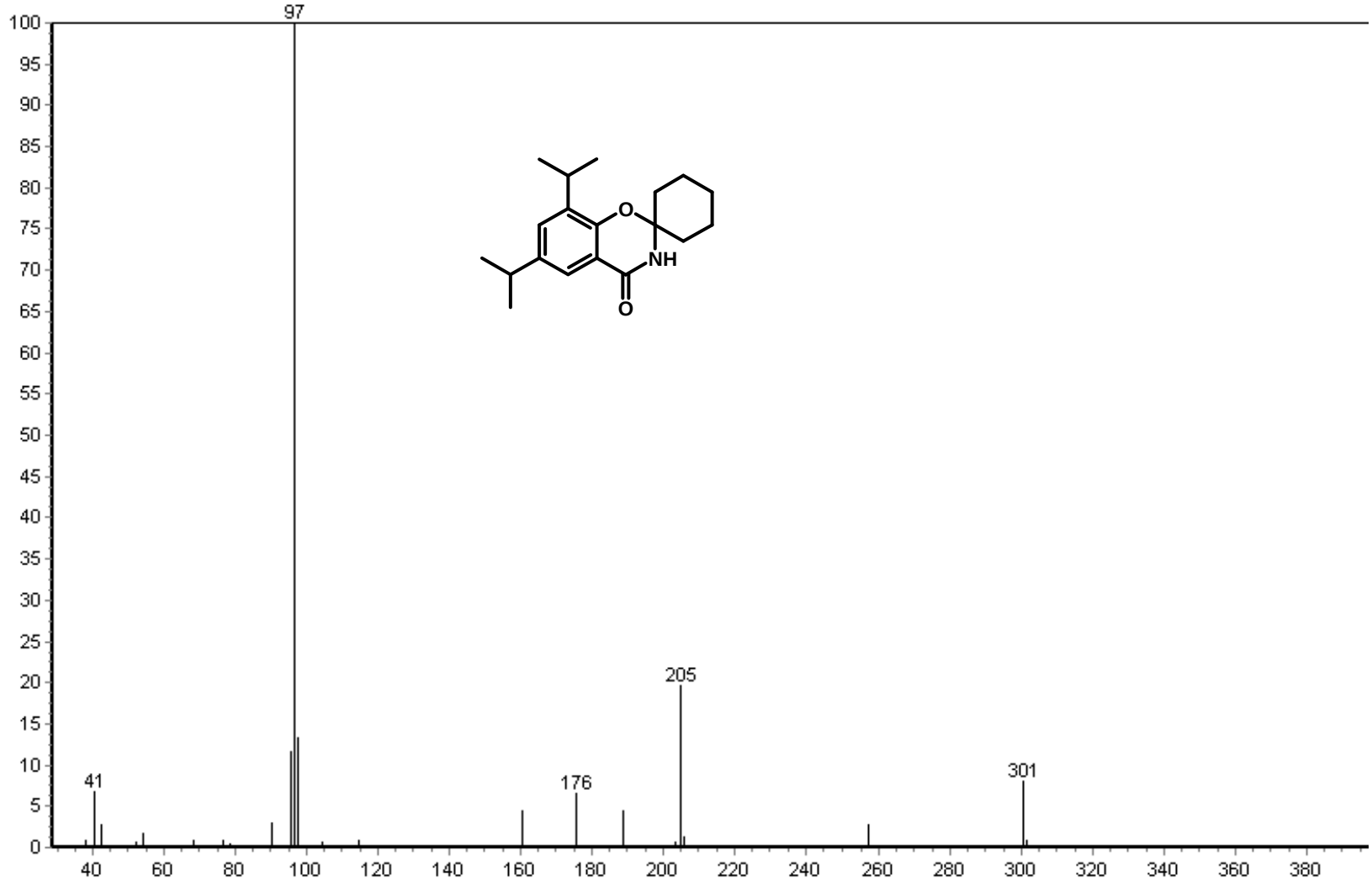




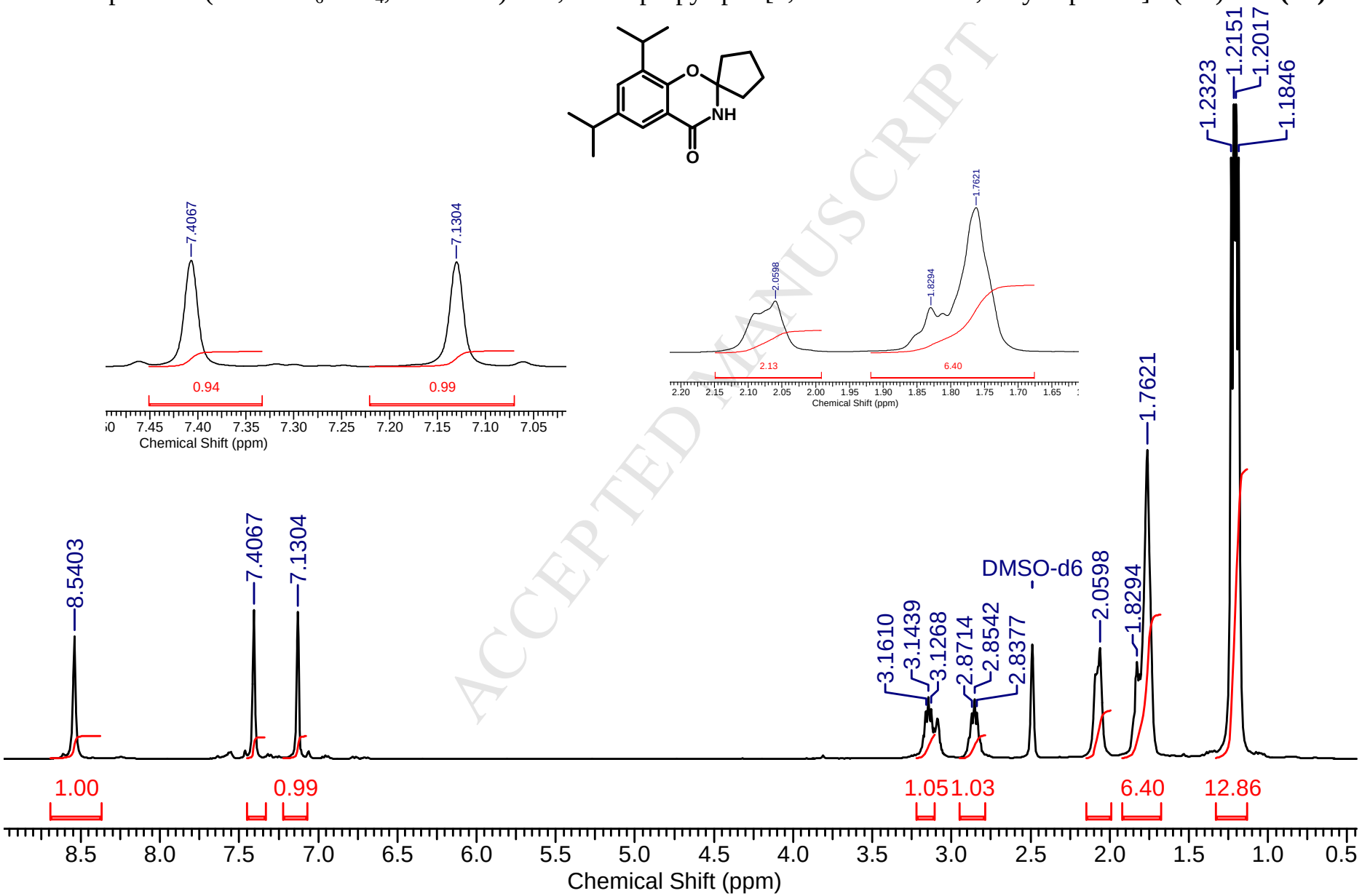
FTIR spectrum of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.



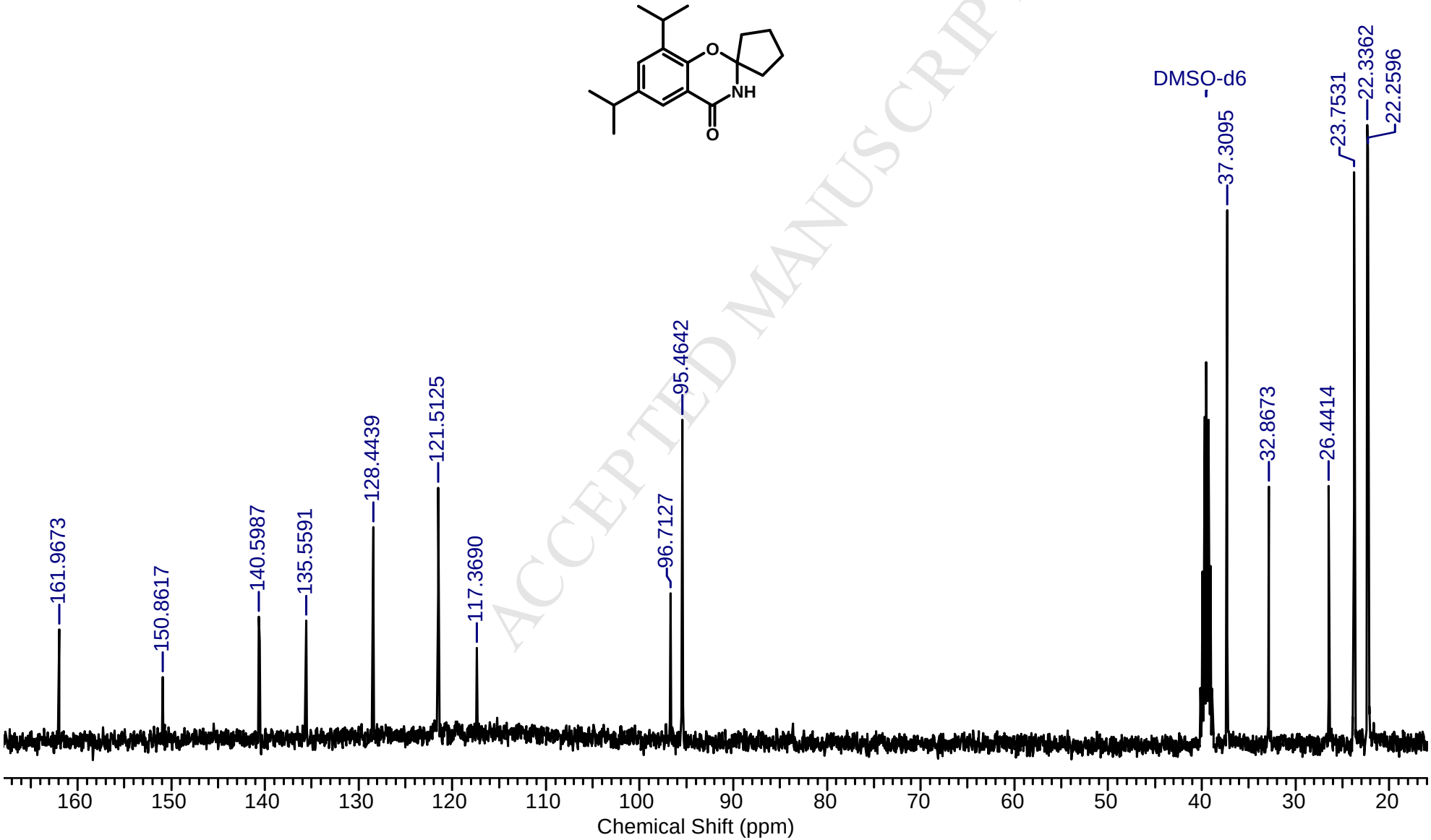
Mass spectrum (EI) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4c)**.



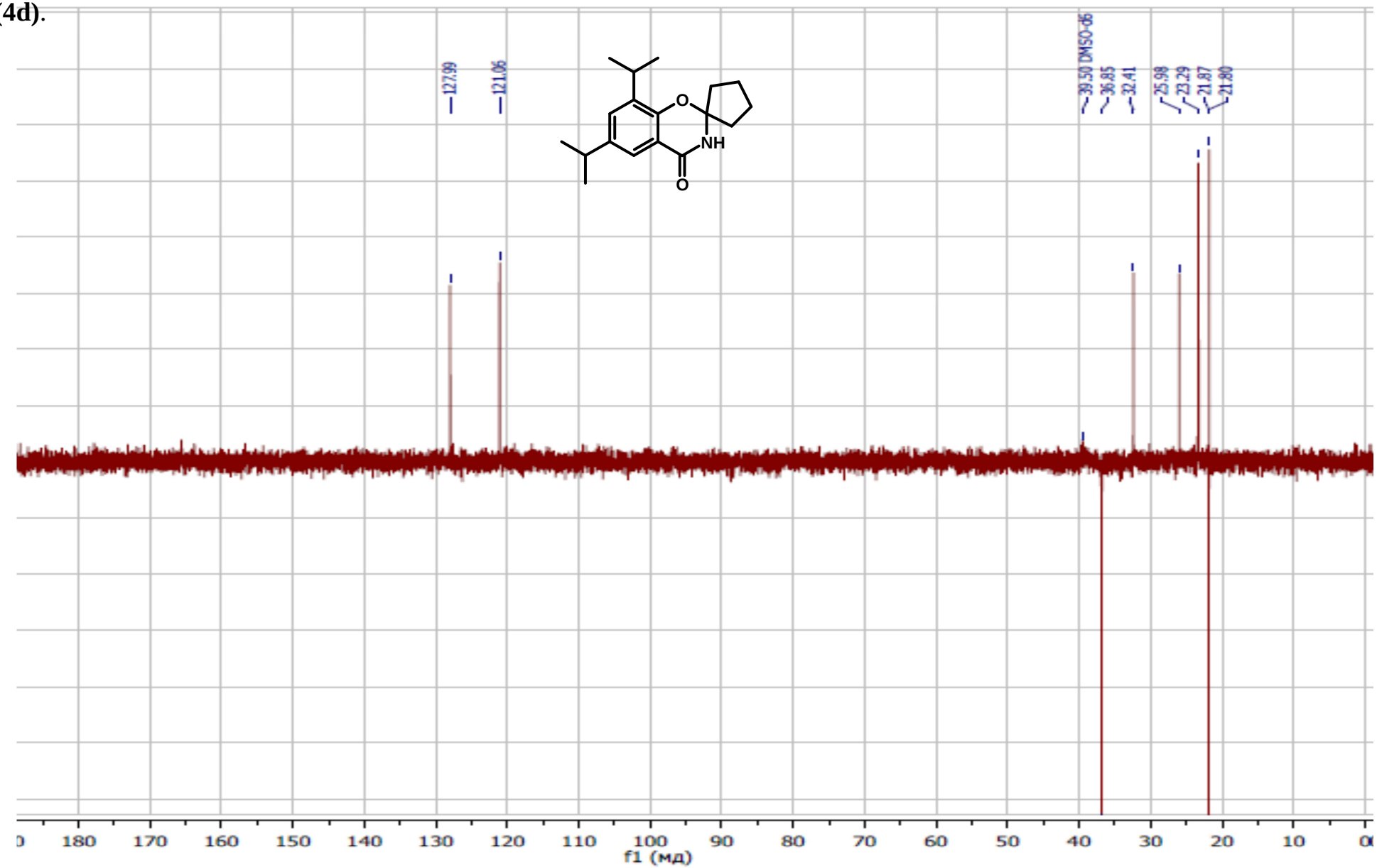
^{1}H NMR spectrum (DMSO-d_6/CCl_4, 400 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



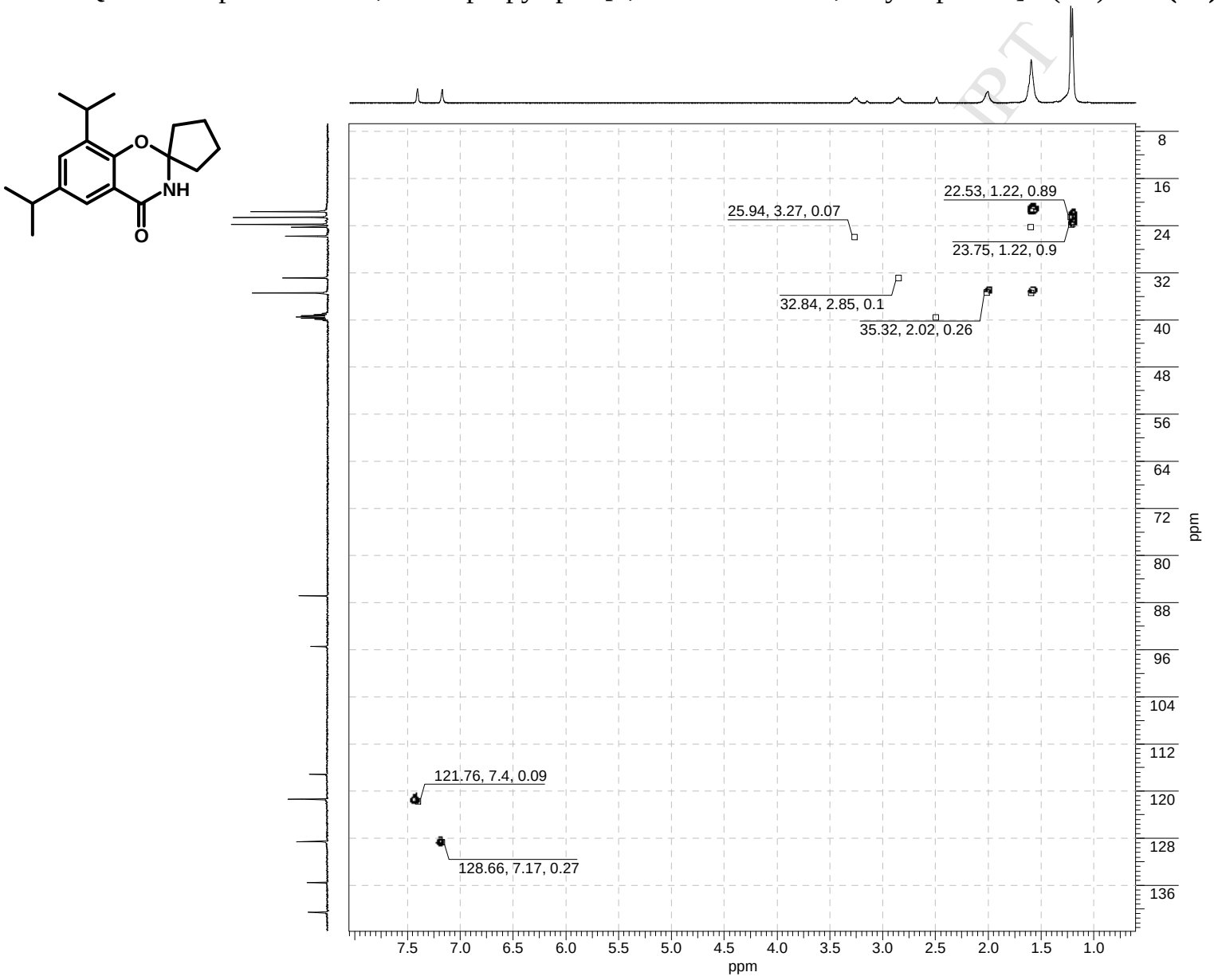
^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



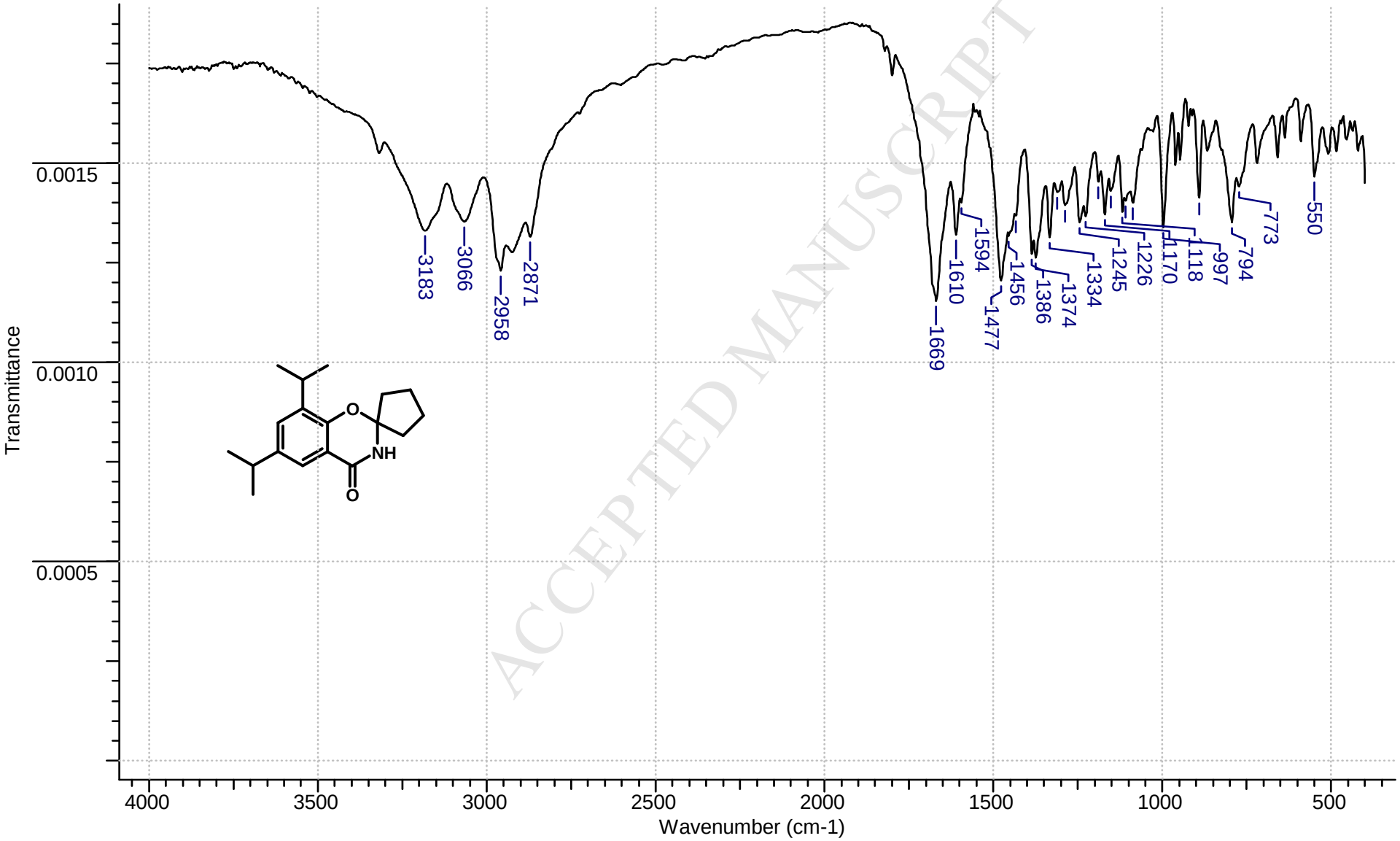
DEPT-135 ^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



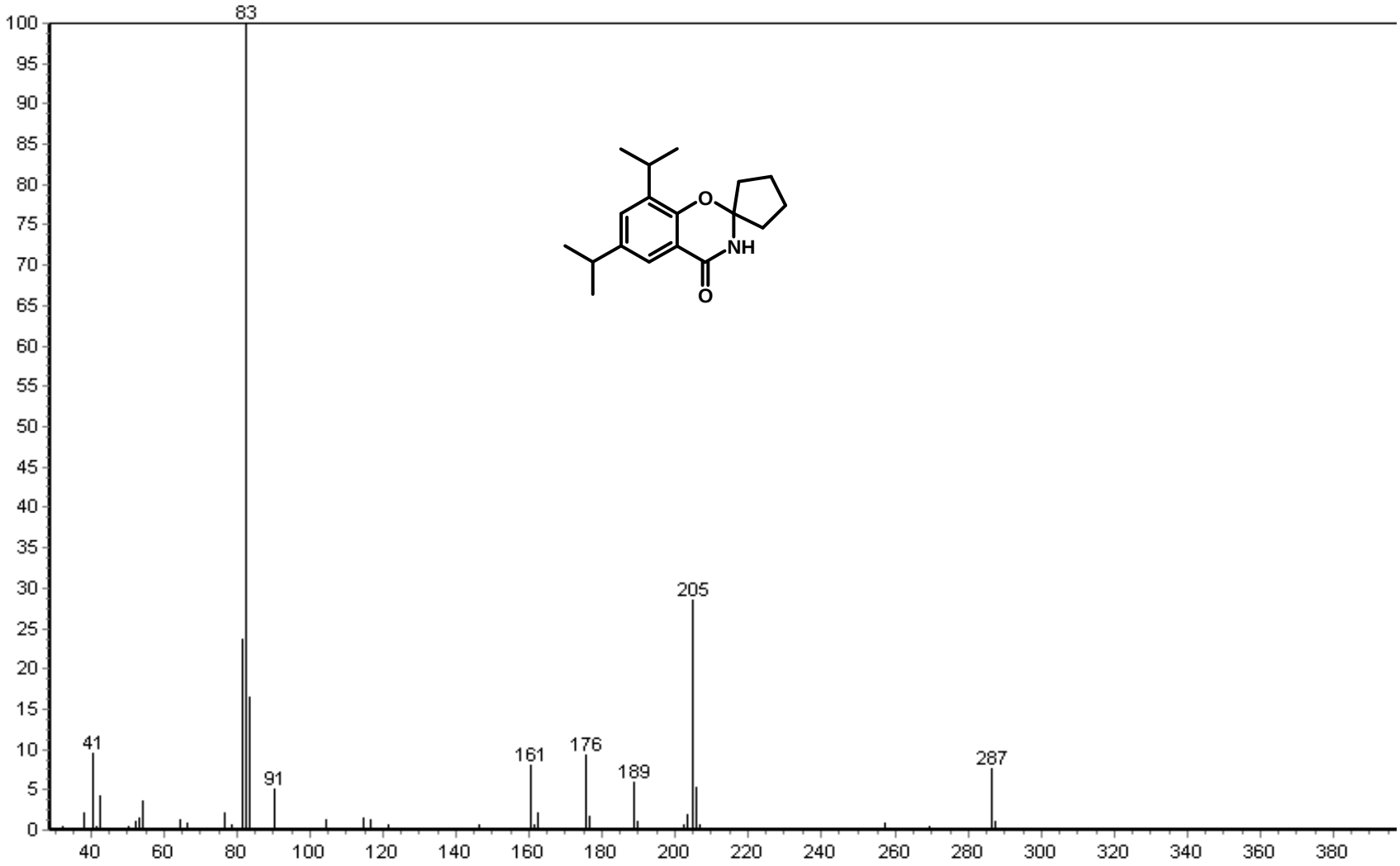
^{1}H-^{13}C HSQC NMR spectrum of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



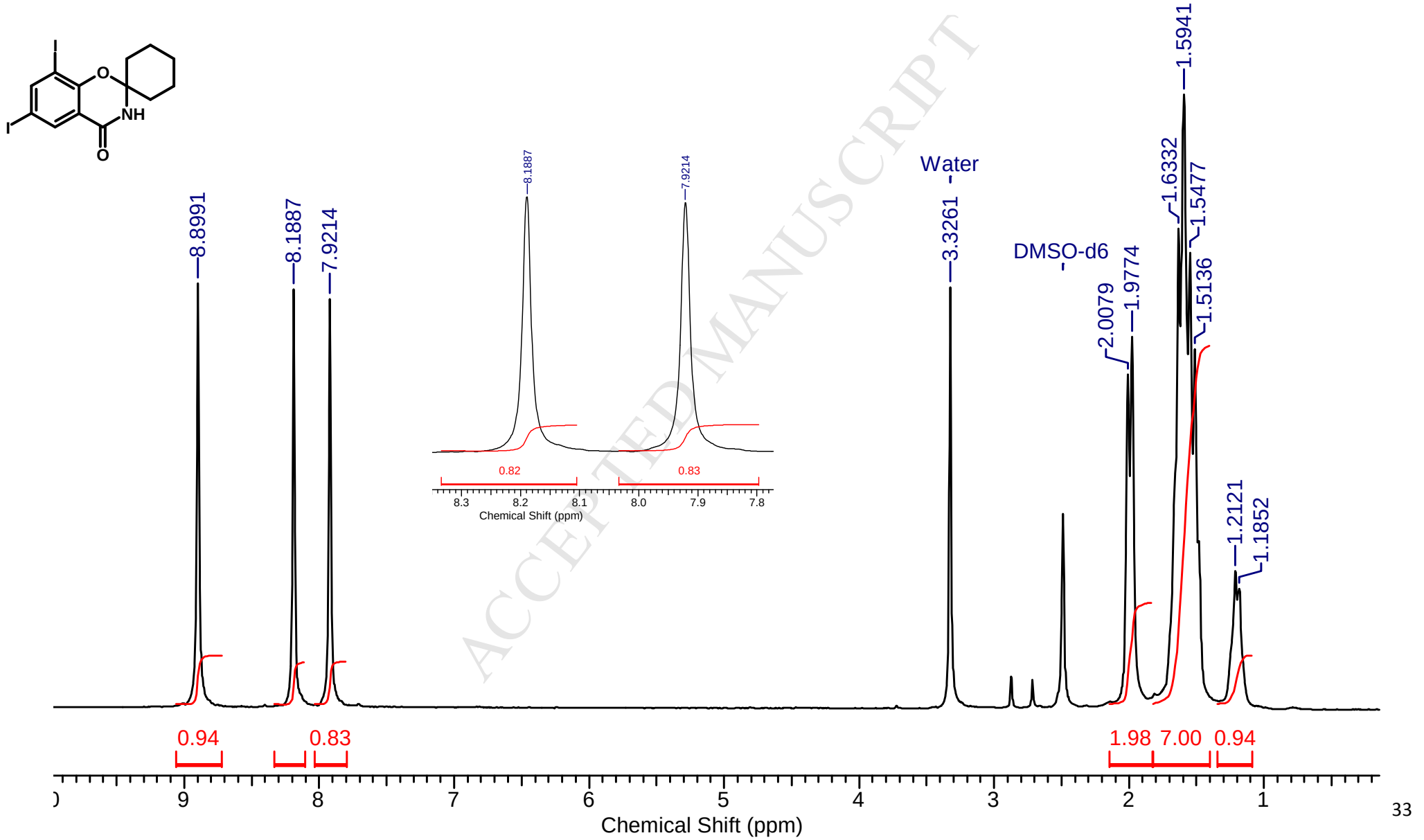
FTIR spectrum of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



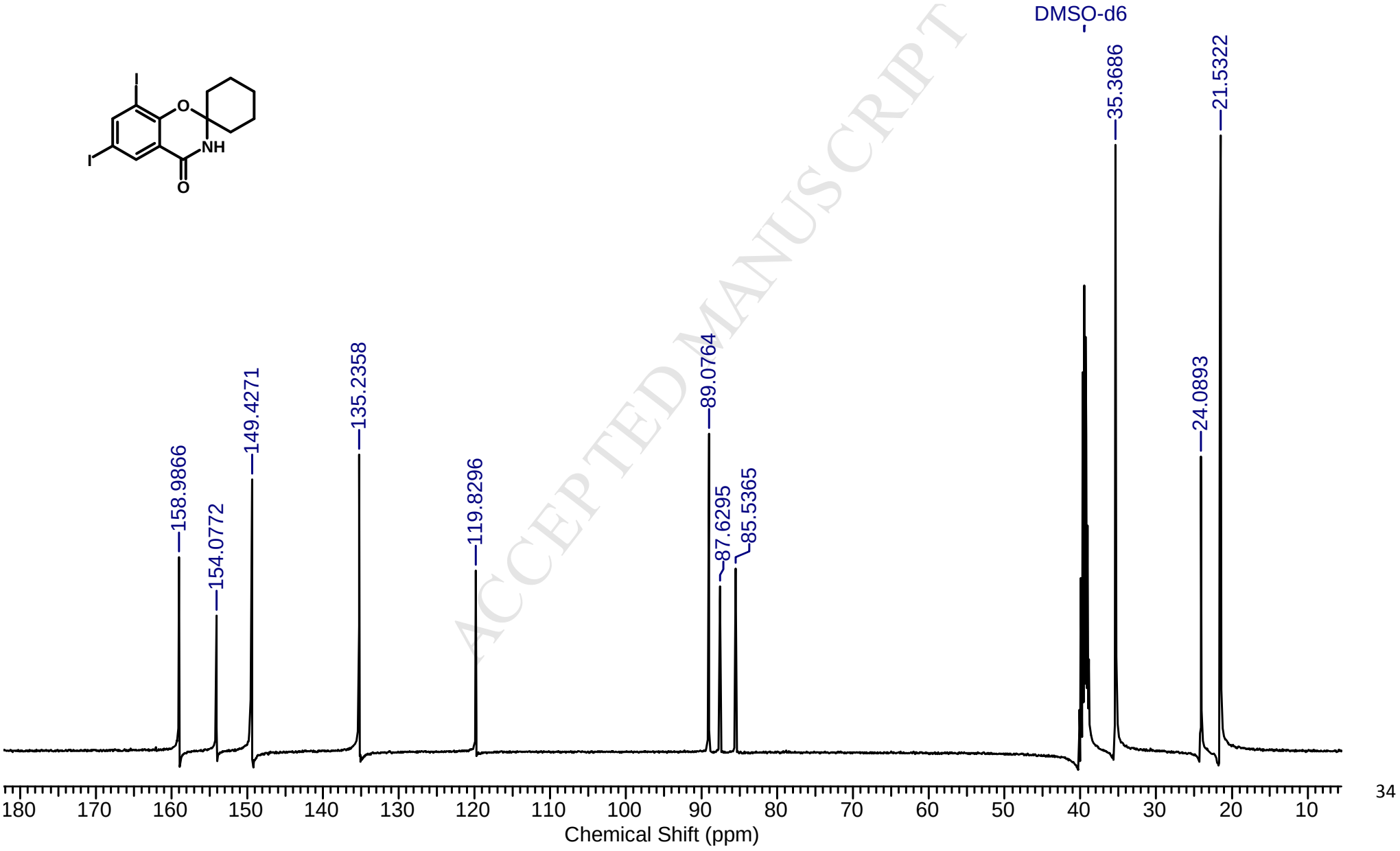
Mass spectrum (EI) of 6,8-diisopropylspiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4d)**.



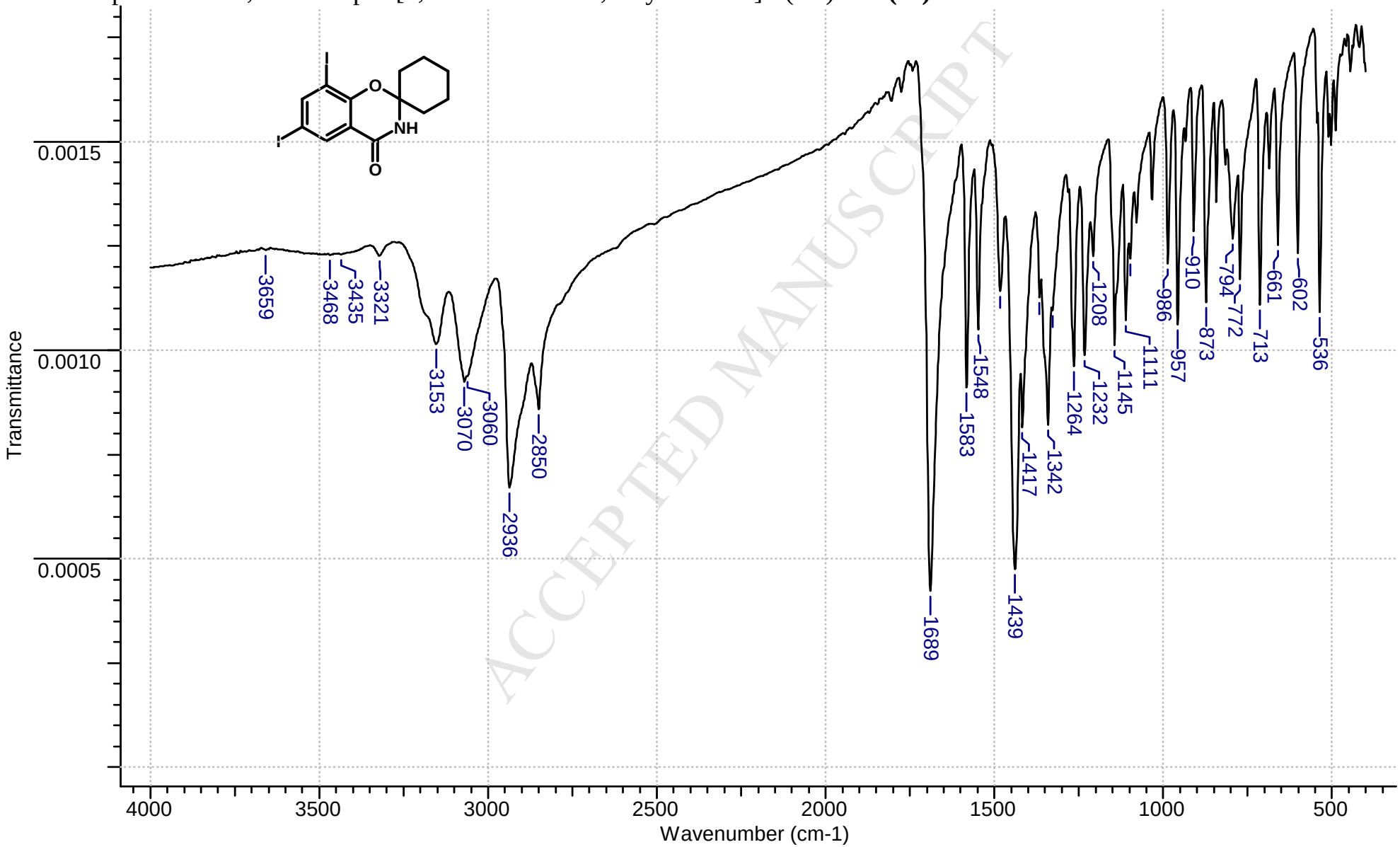
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4e)**.



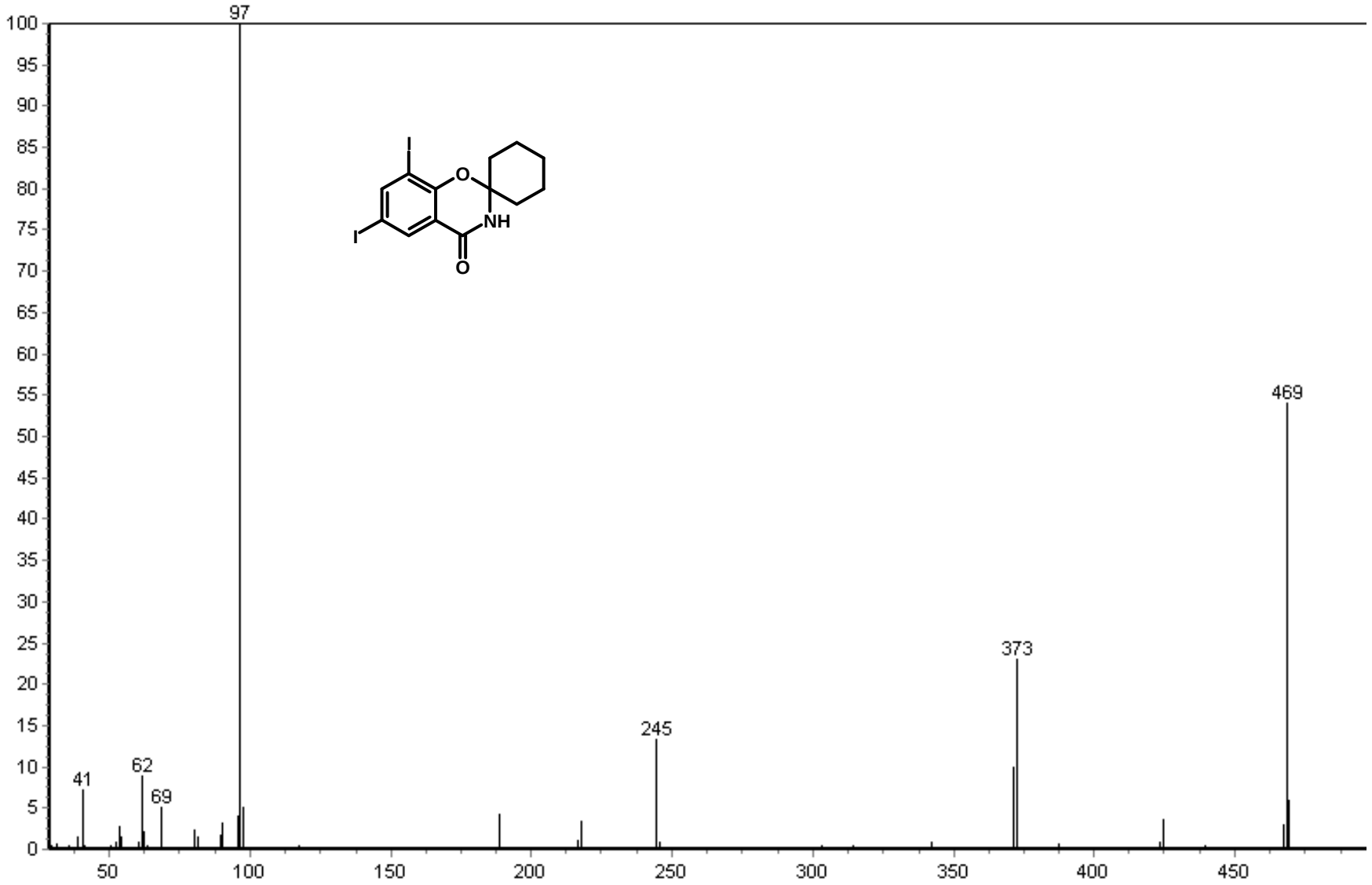
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4e)**.



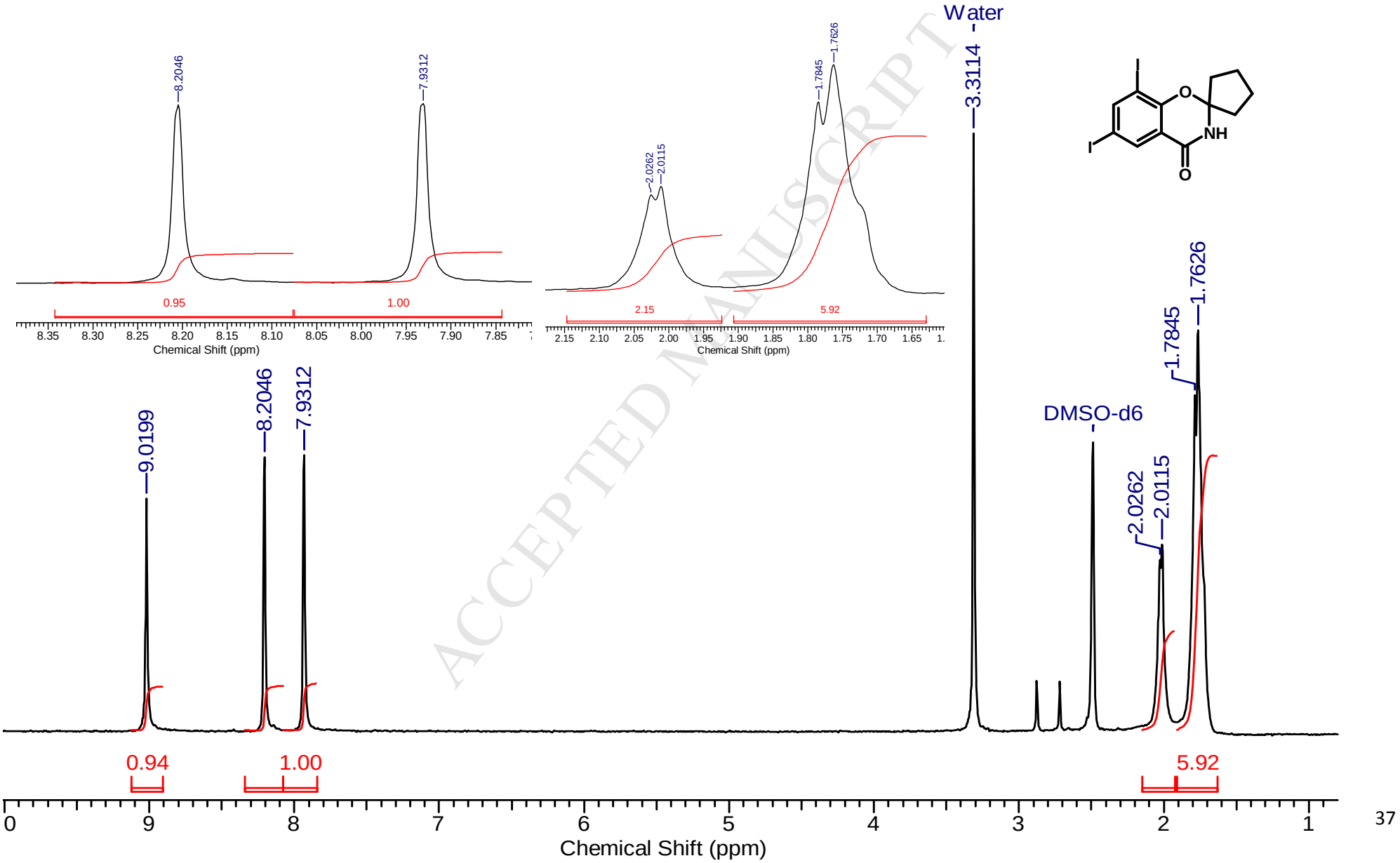
FTIR spectrum of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4e)**.



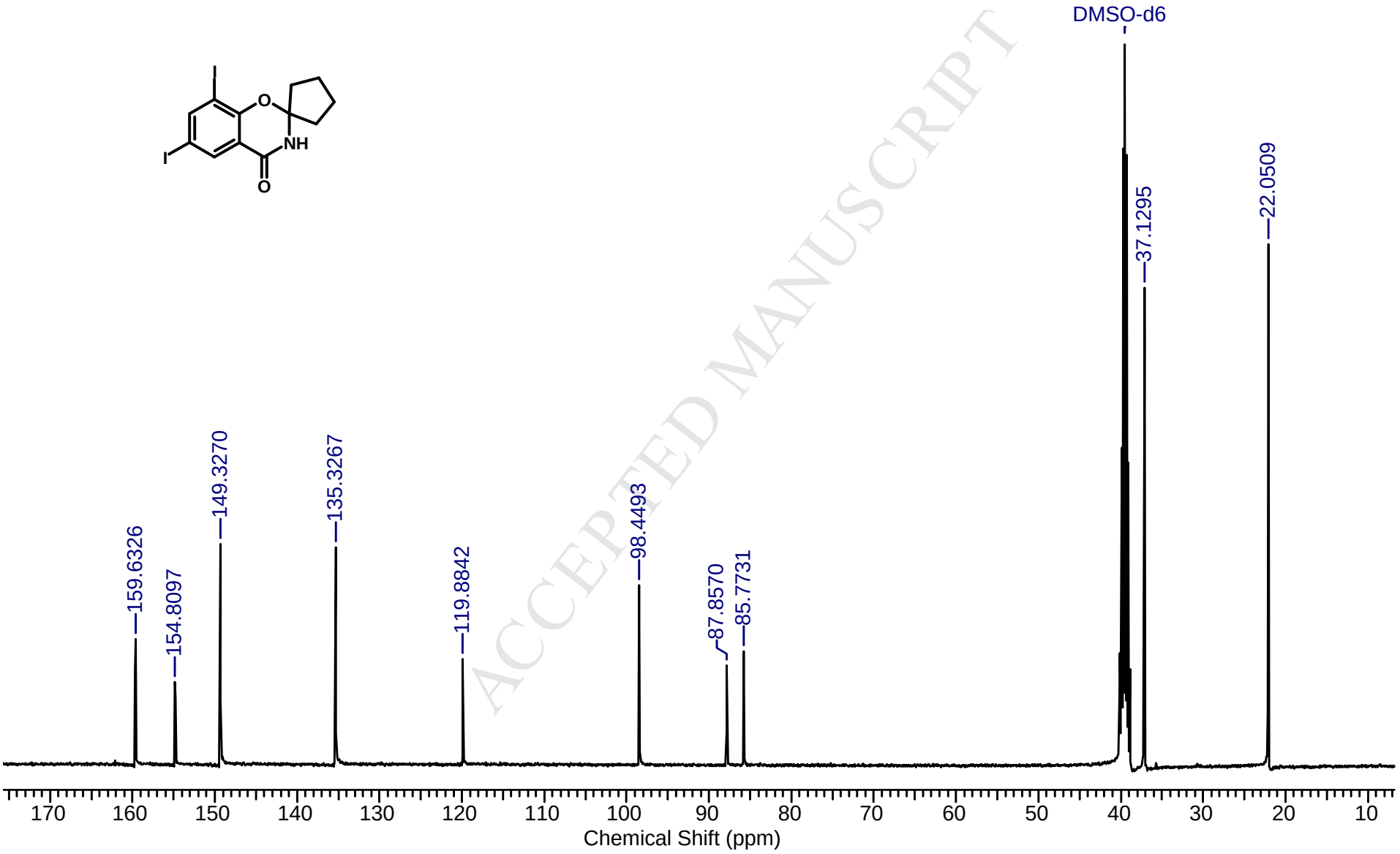
Mass spectrum (EI) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3*H*)-one **(4e)**.



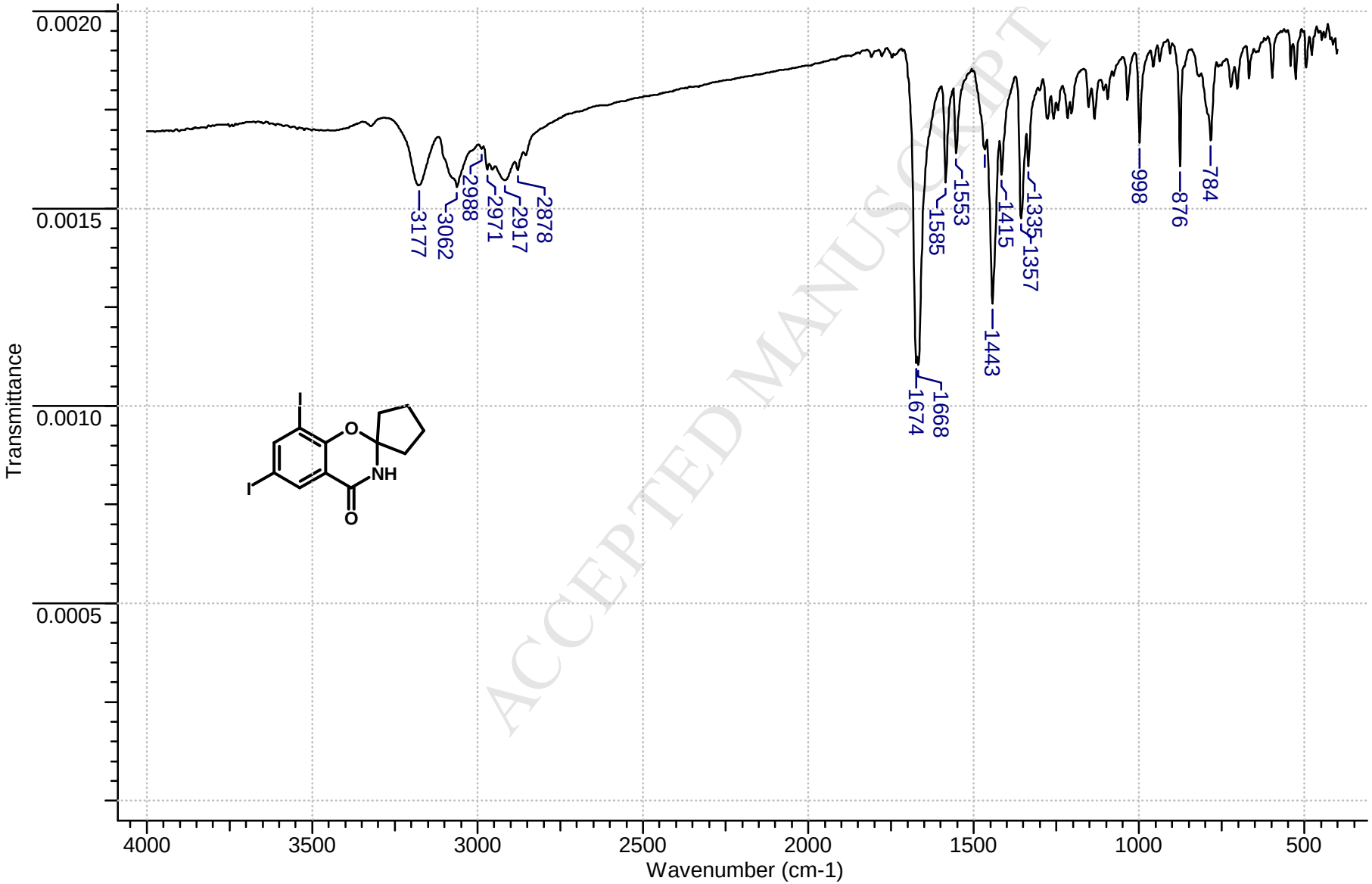
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4f)**.



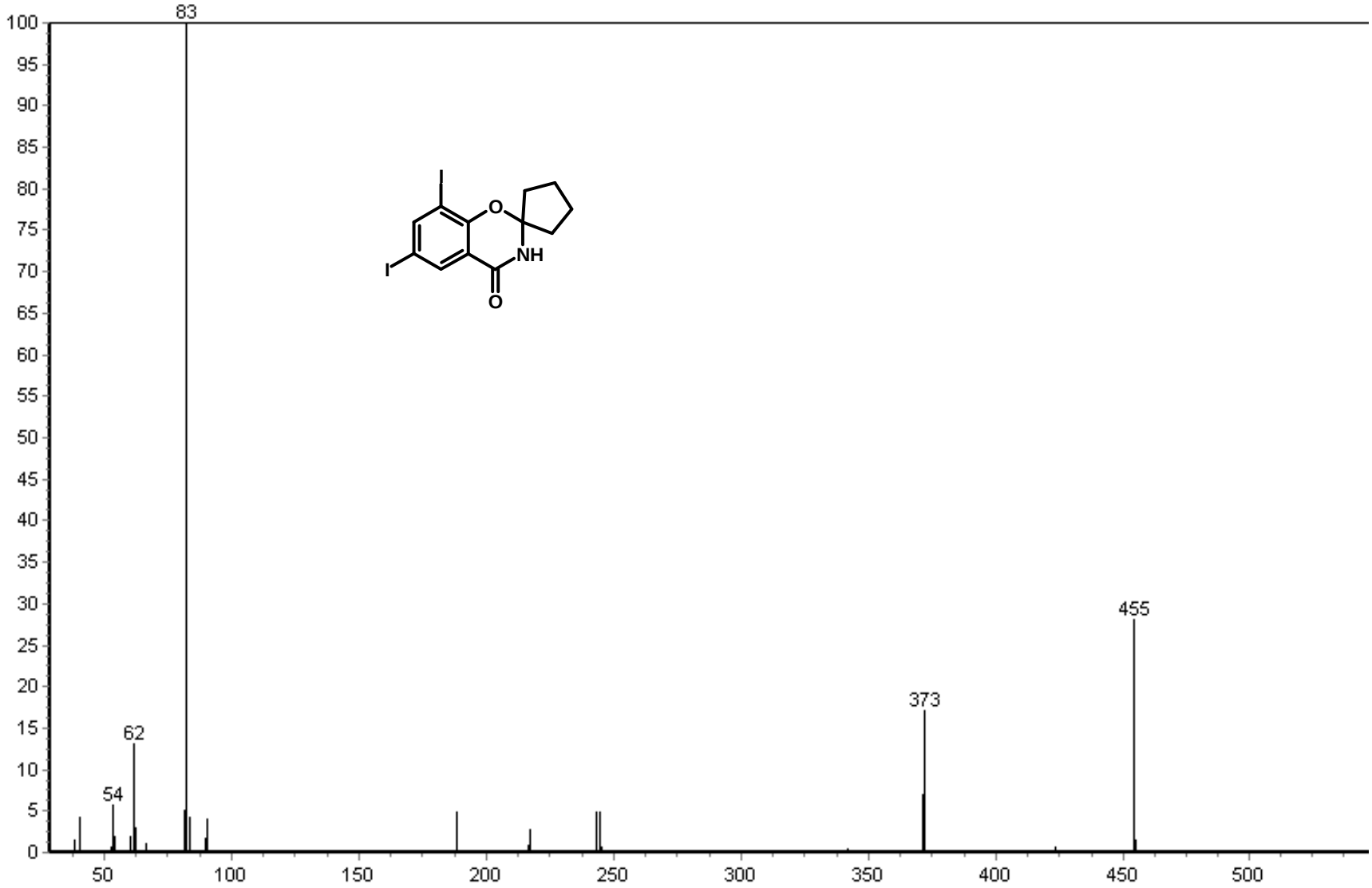
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4f)**.



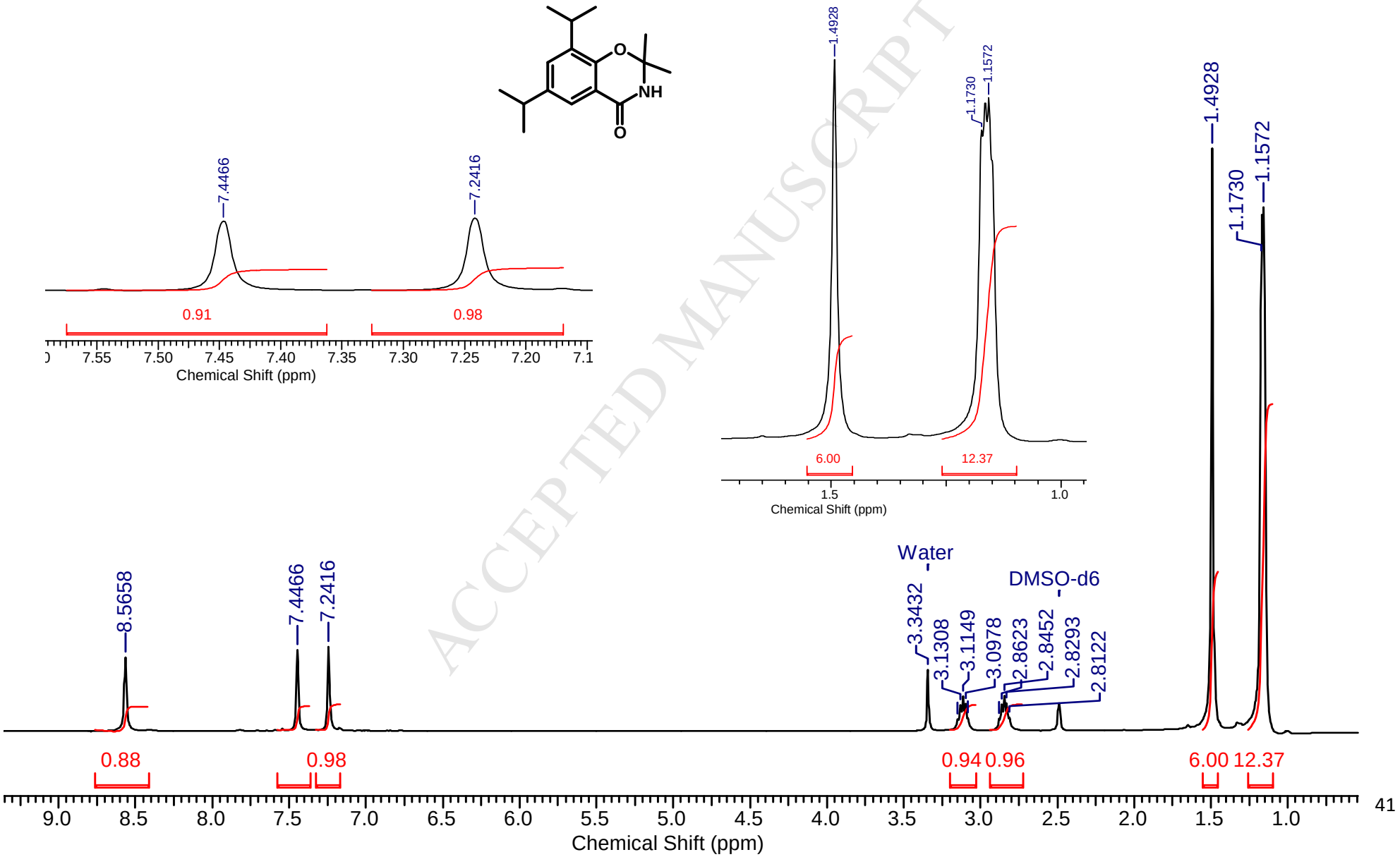
FTIR spectrum of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4f)**.



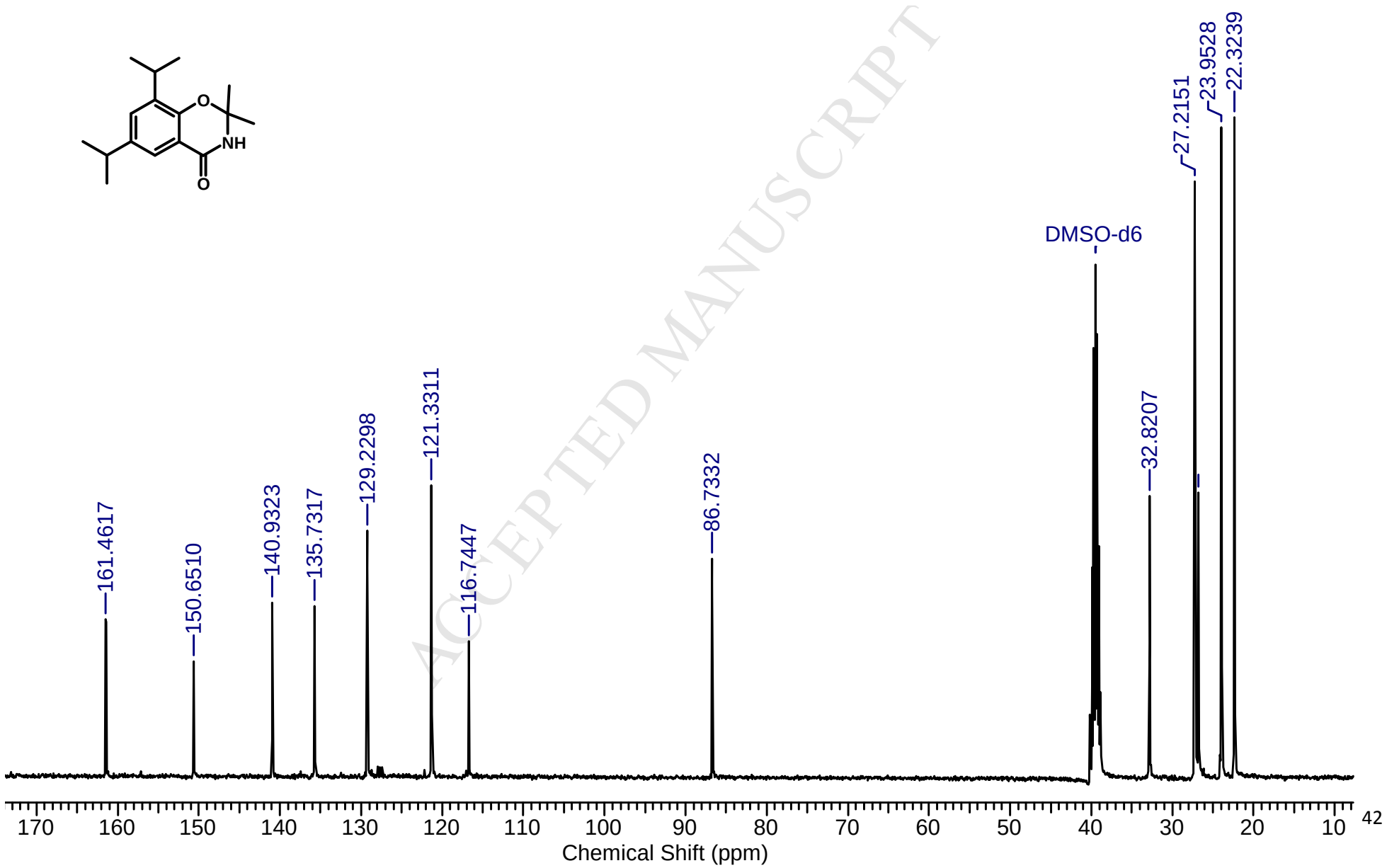
Mass spectrum (EI) of 6,8-diiodospiro[1,3-benzoxazine-2,1'-cyclopentan]-4(3*H*)-one **(4f)**.



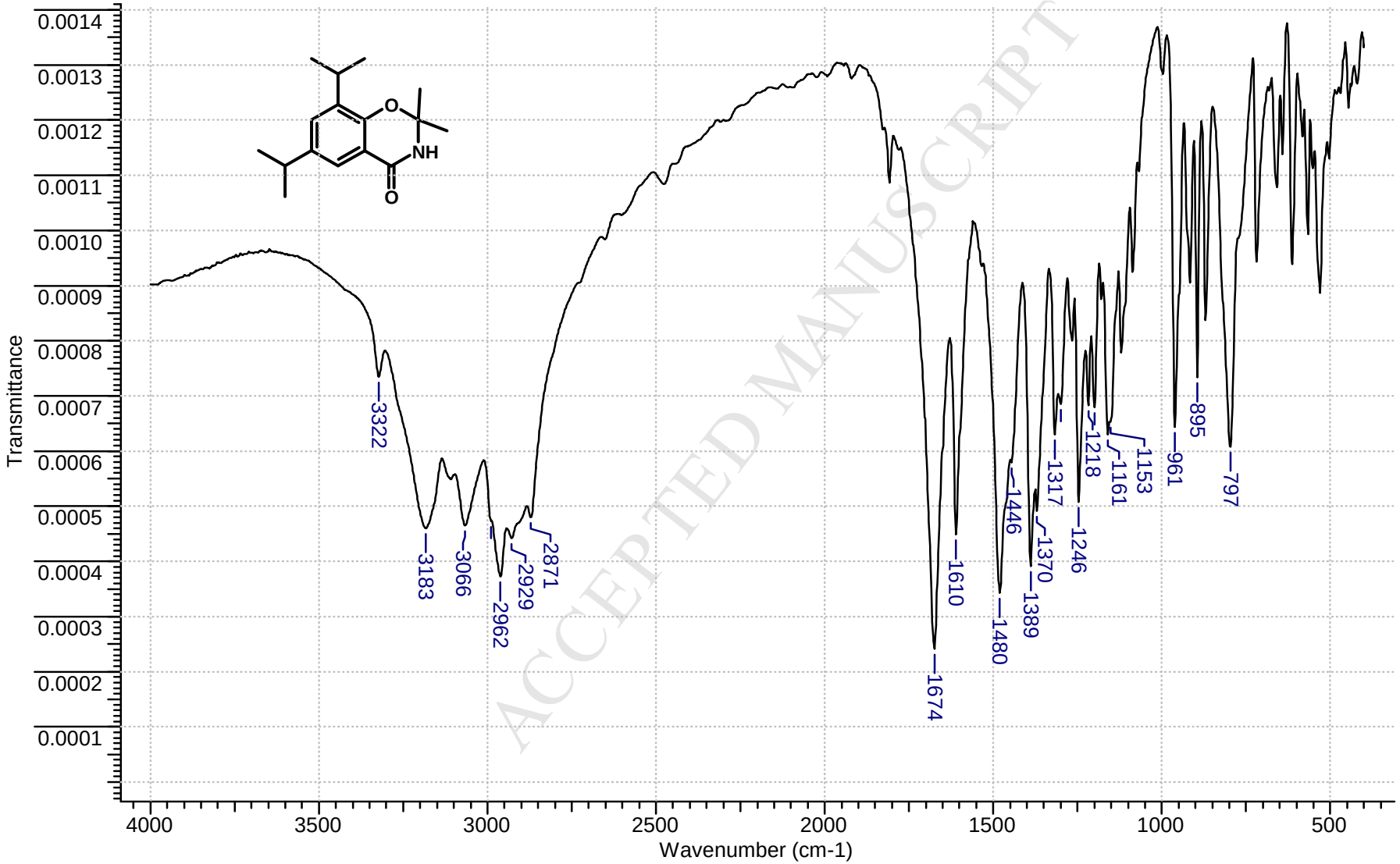
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of 6,8-diisopropyl-2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one **(10b)**.



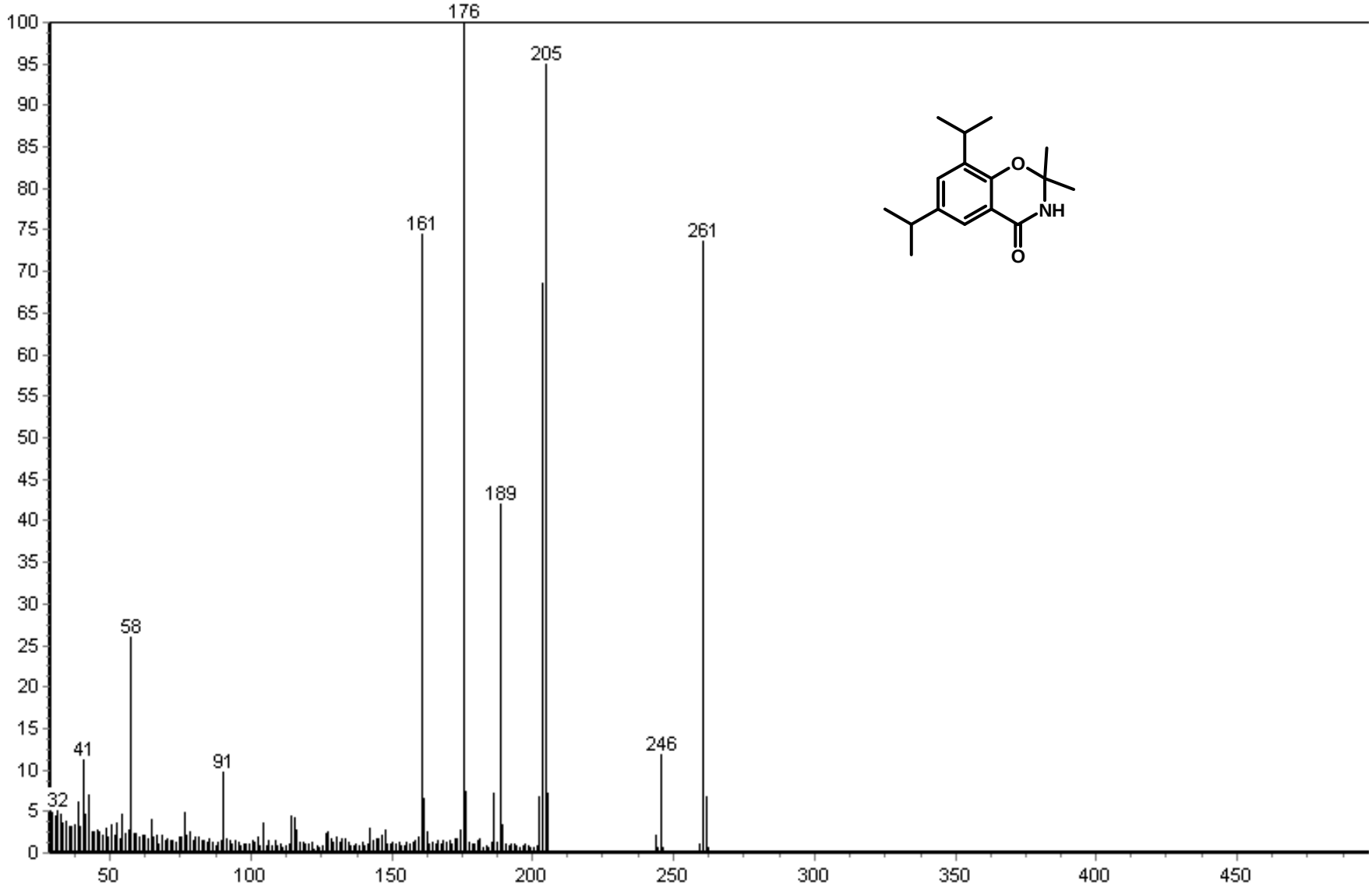
^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of 6,8-diisopropyl-2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one **(10b)**.



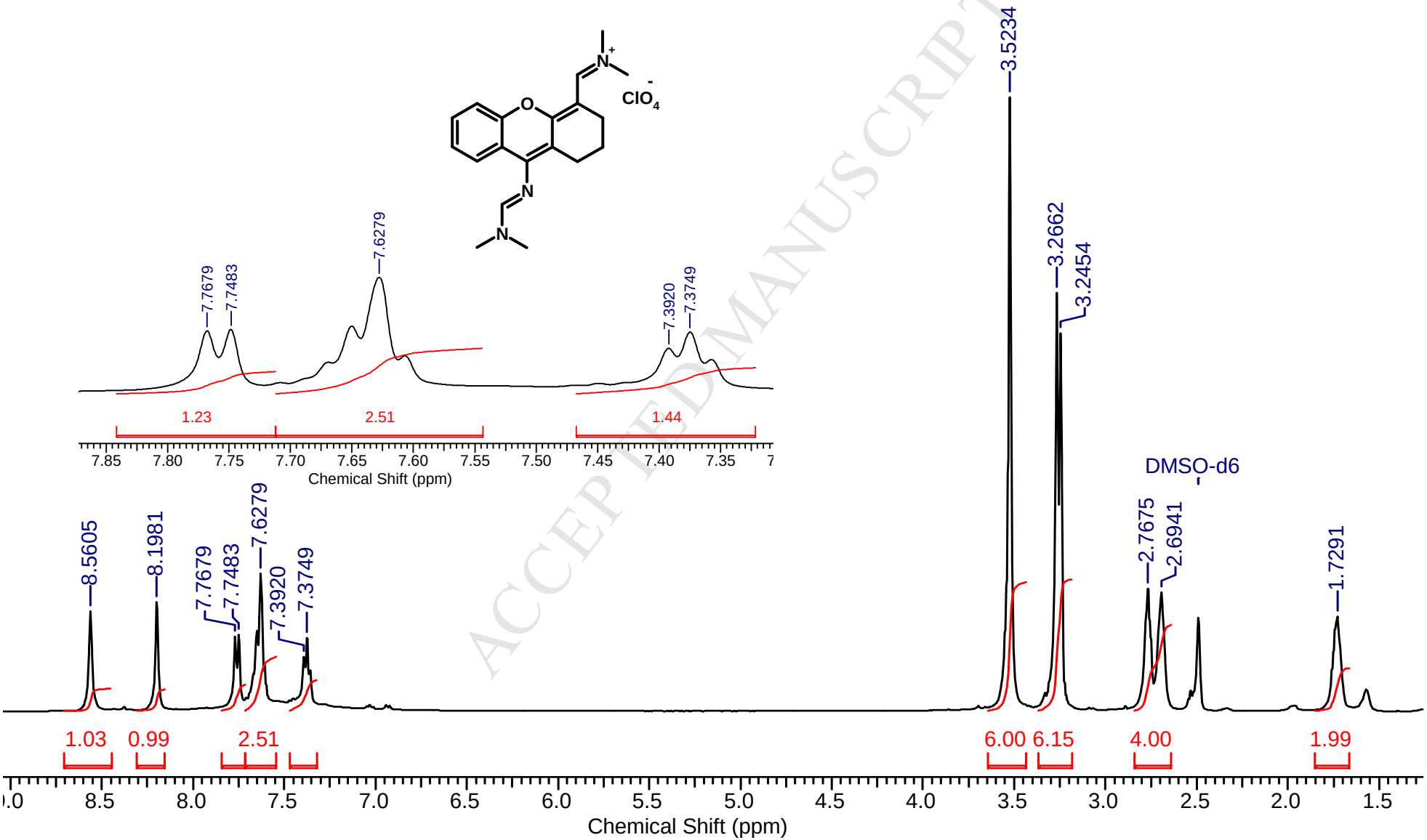
FTIR spectrum of 6,8-diisopropyl-2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one **(10b)**.



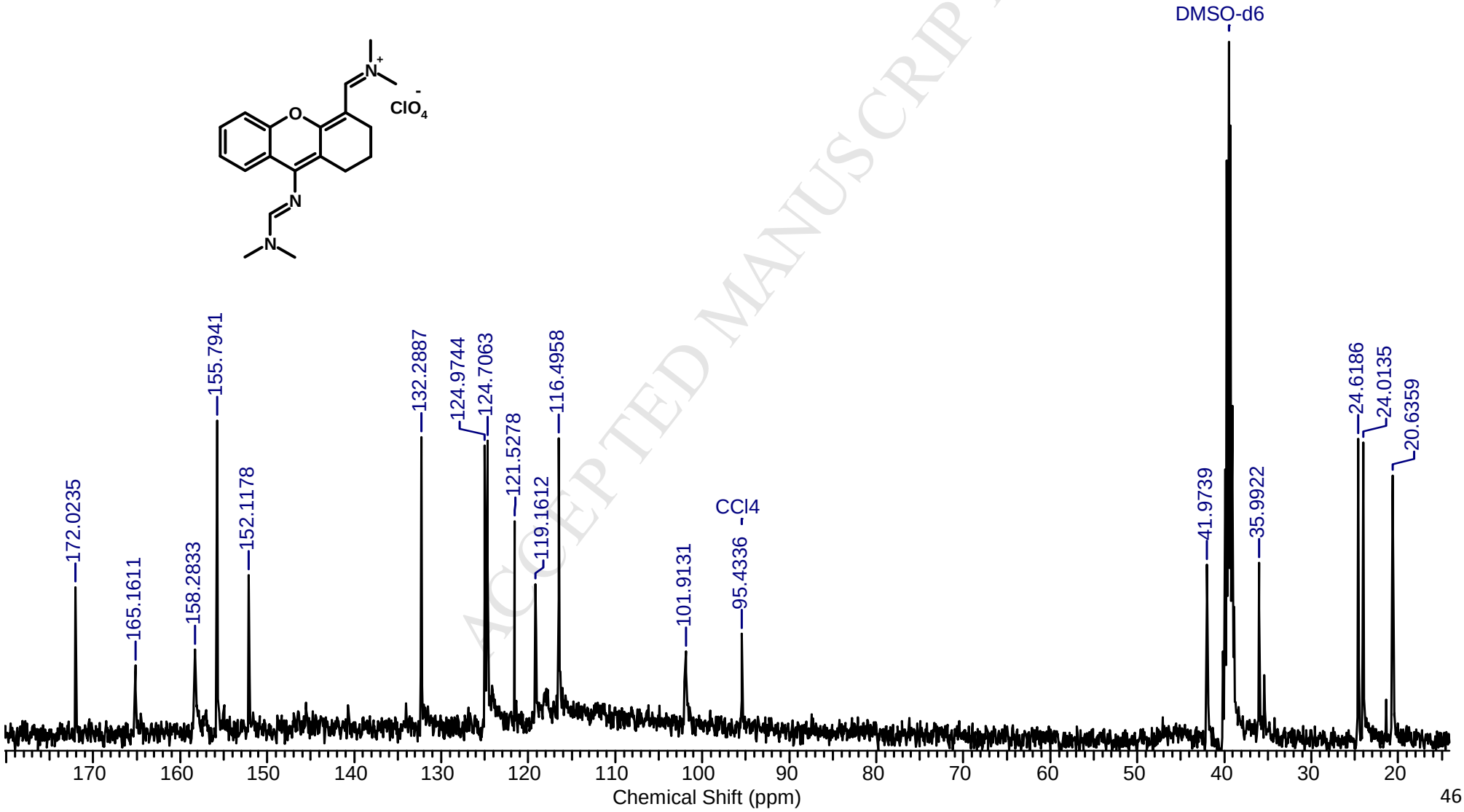
Mass spectrum (EI) of 6,8-diisopropyl-2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one **(10b)**.



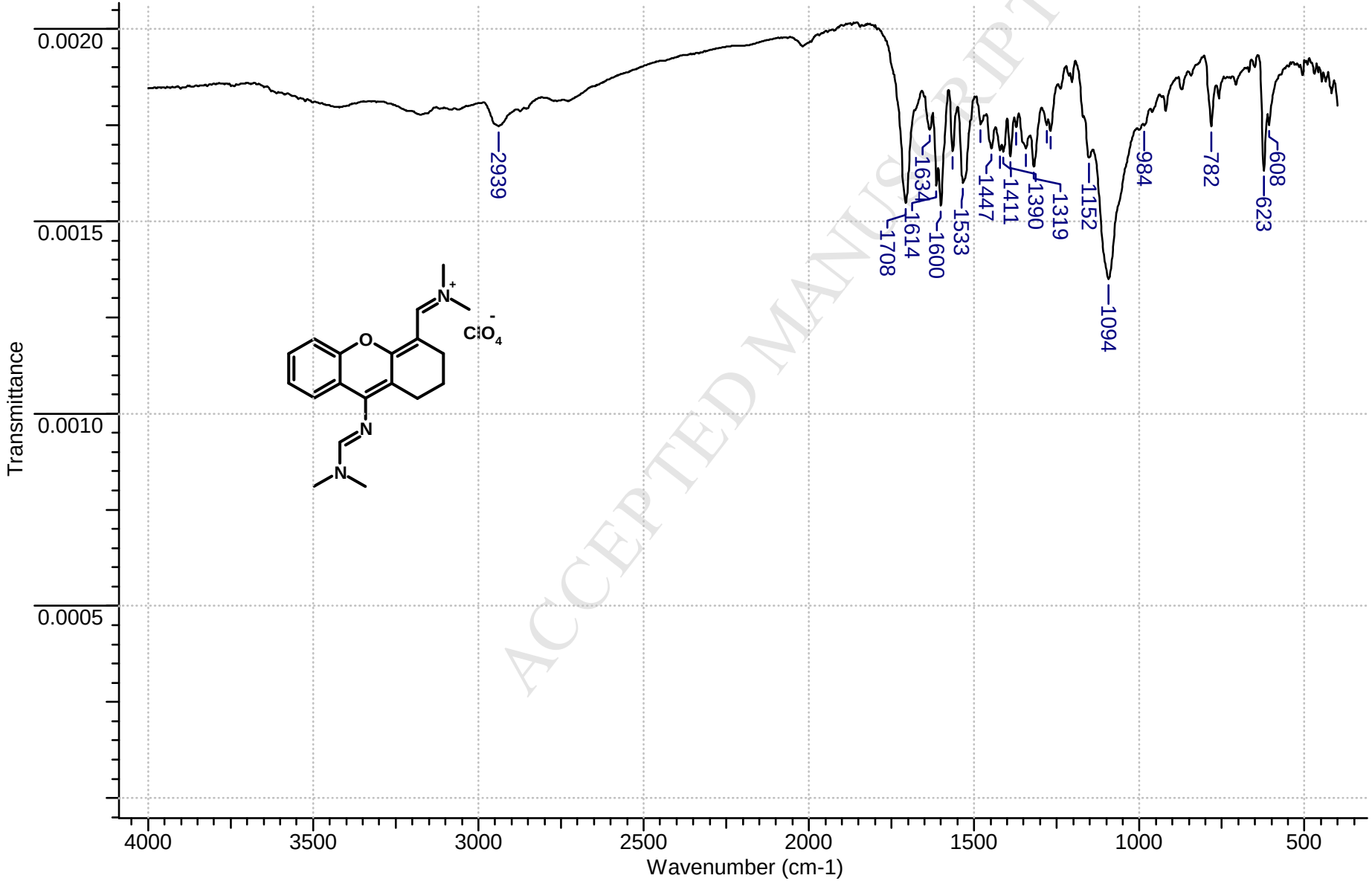
^{1}H NMR spectrum (DMSO-d_6/CCl_4, 400 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5a)**.



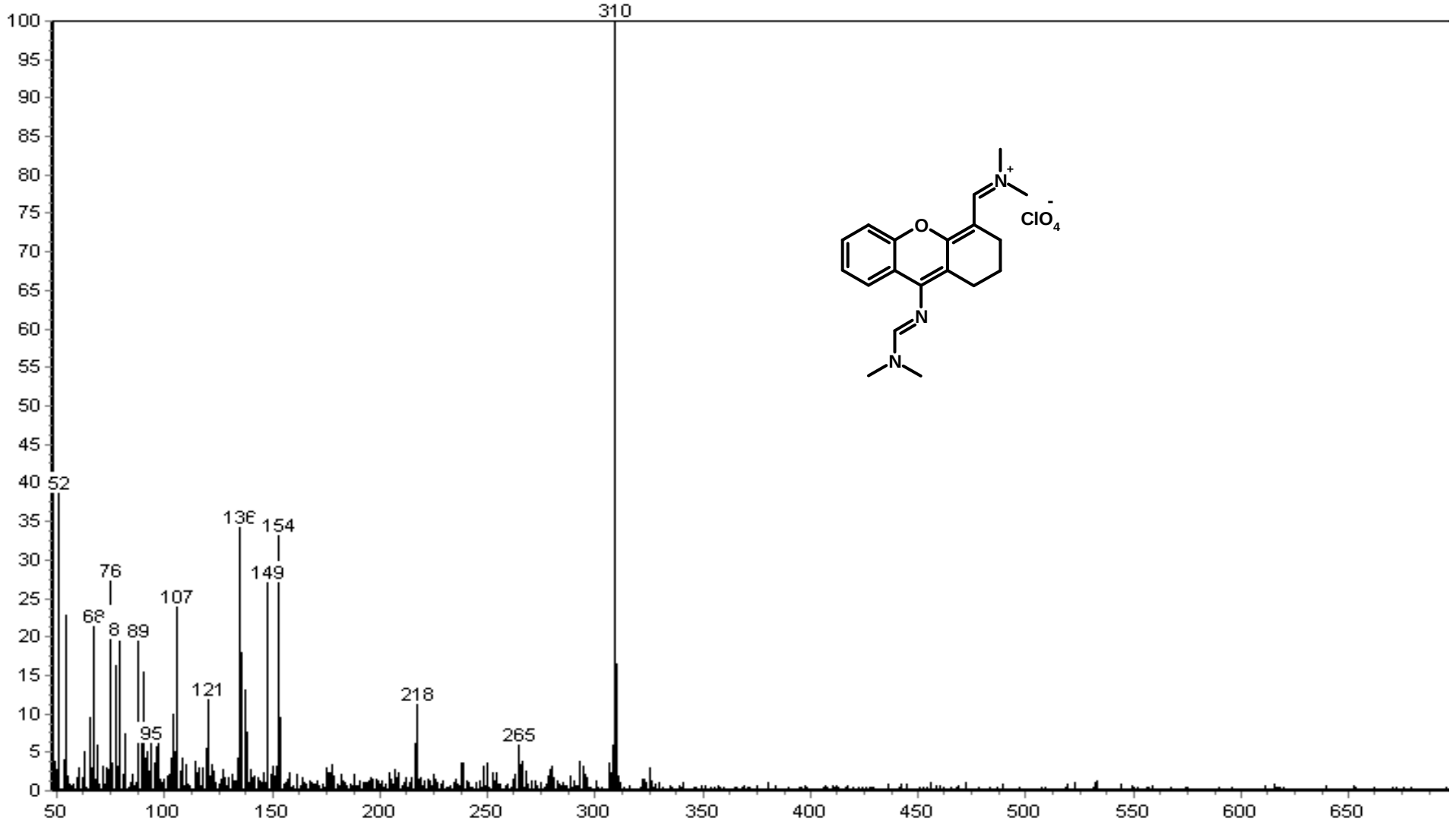
^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5a)**.



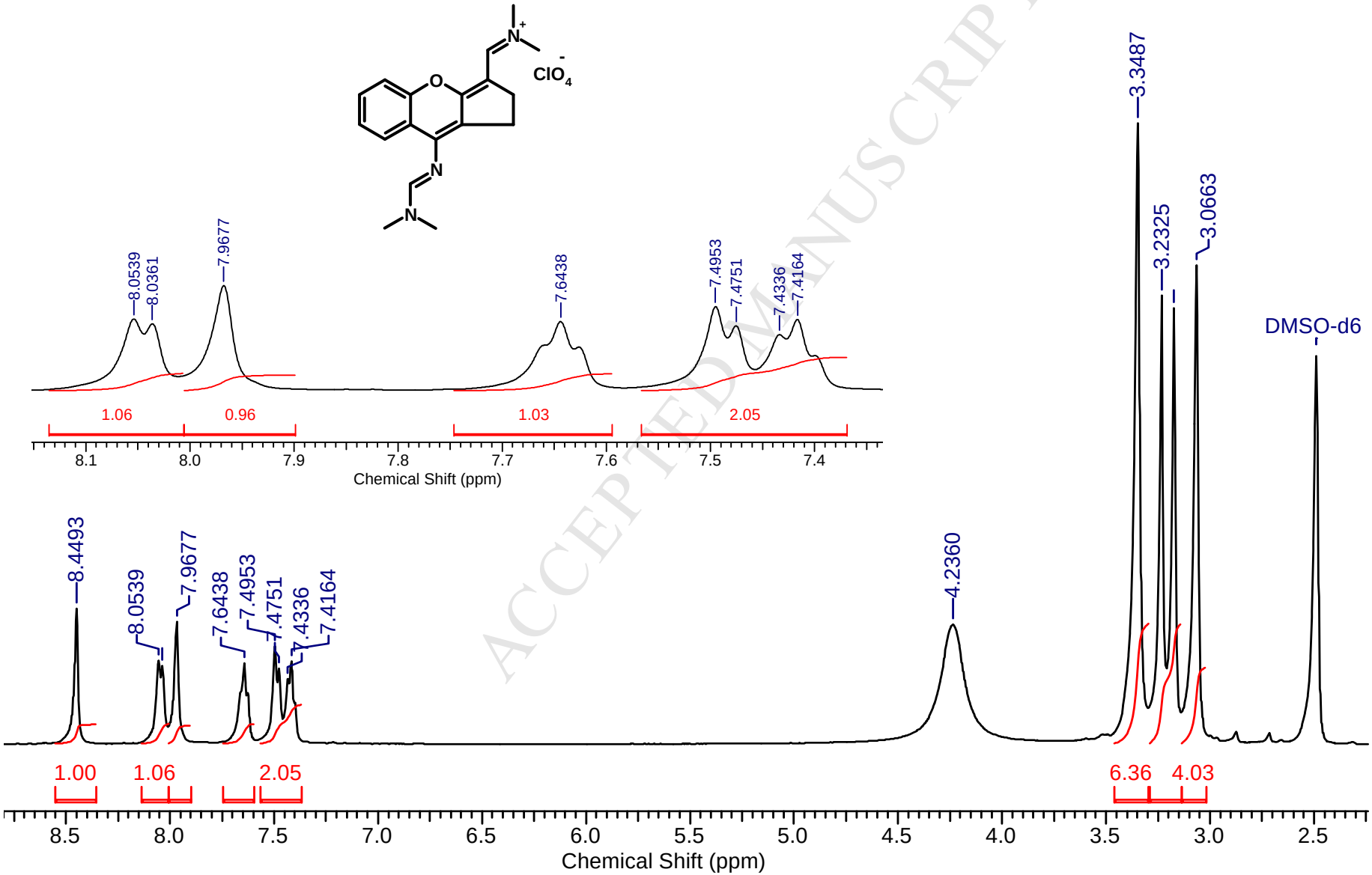
FTIR spectrum of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5a)**.



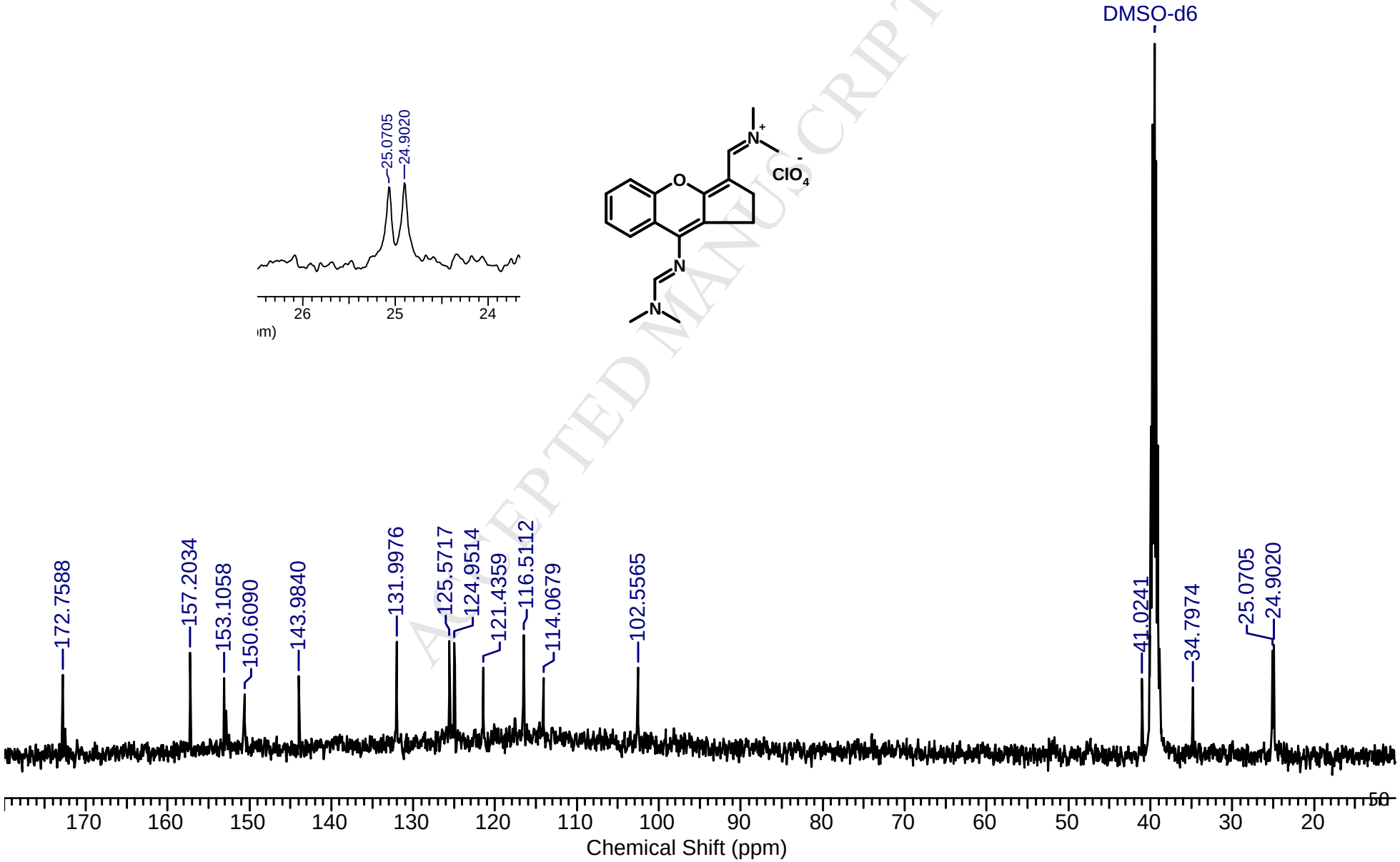
Mass spectrum (FAB) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5a)**.



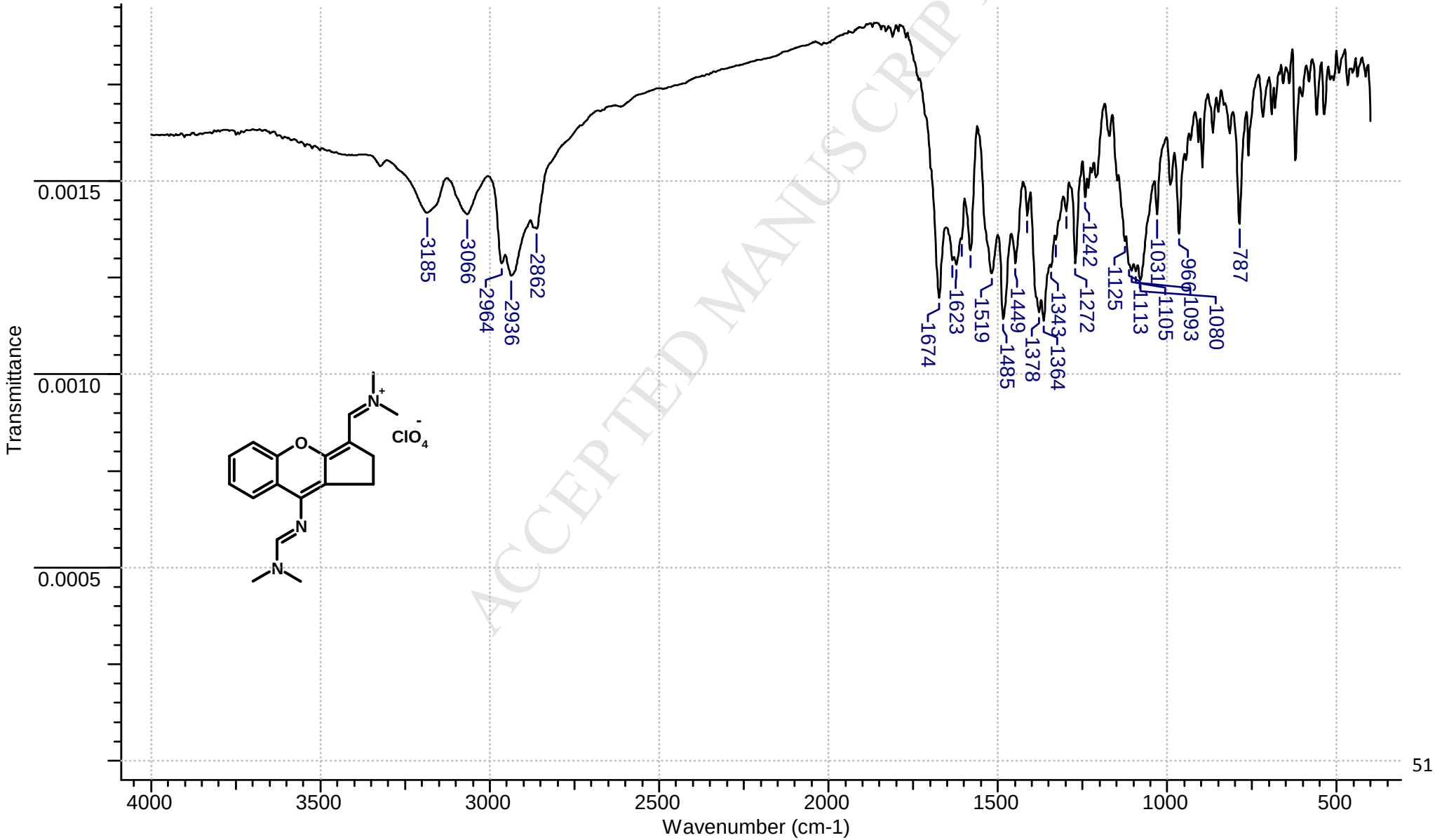
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5b)**.



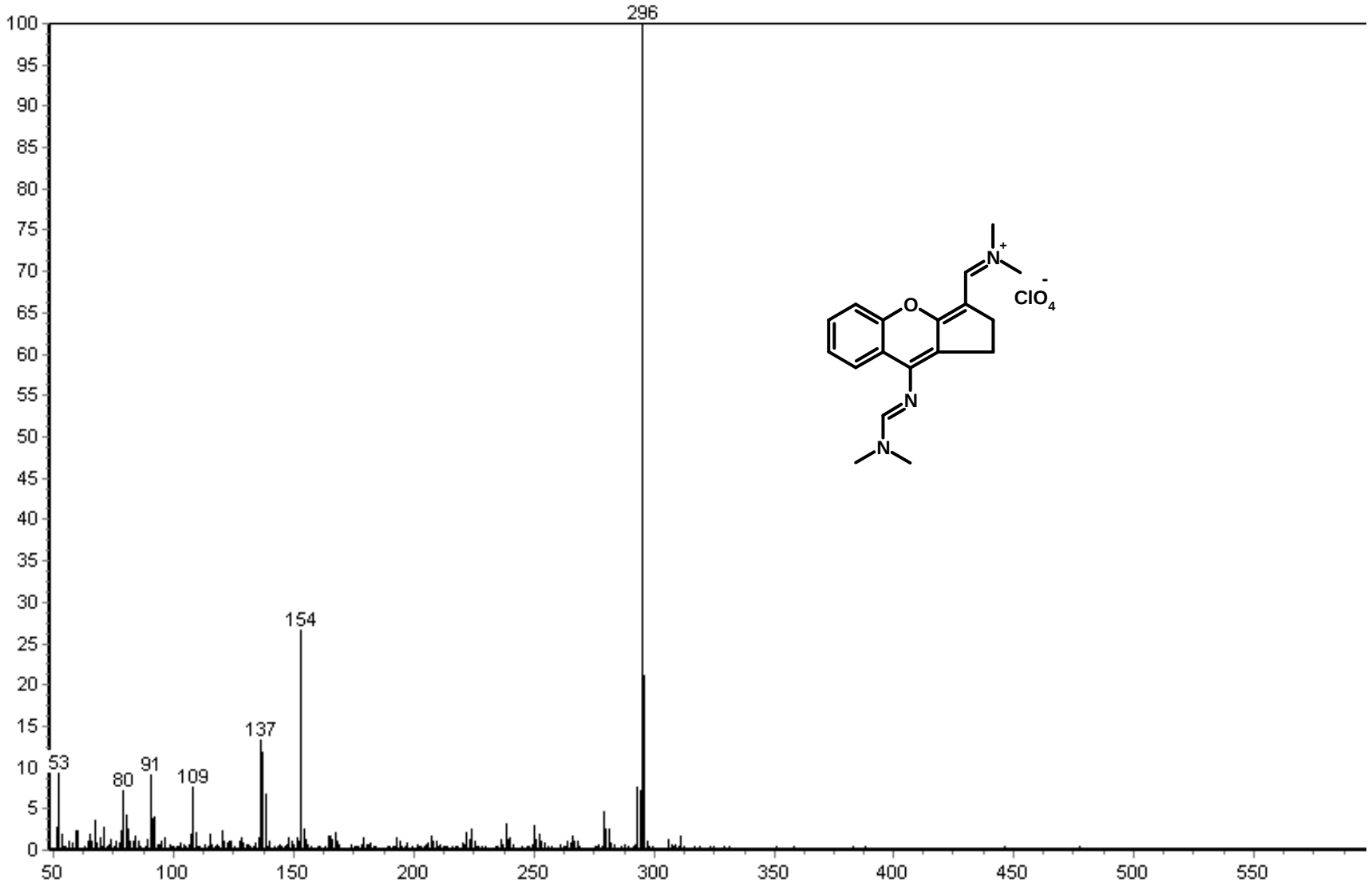
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5b)**.



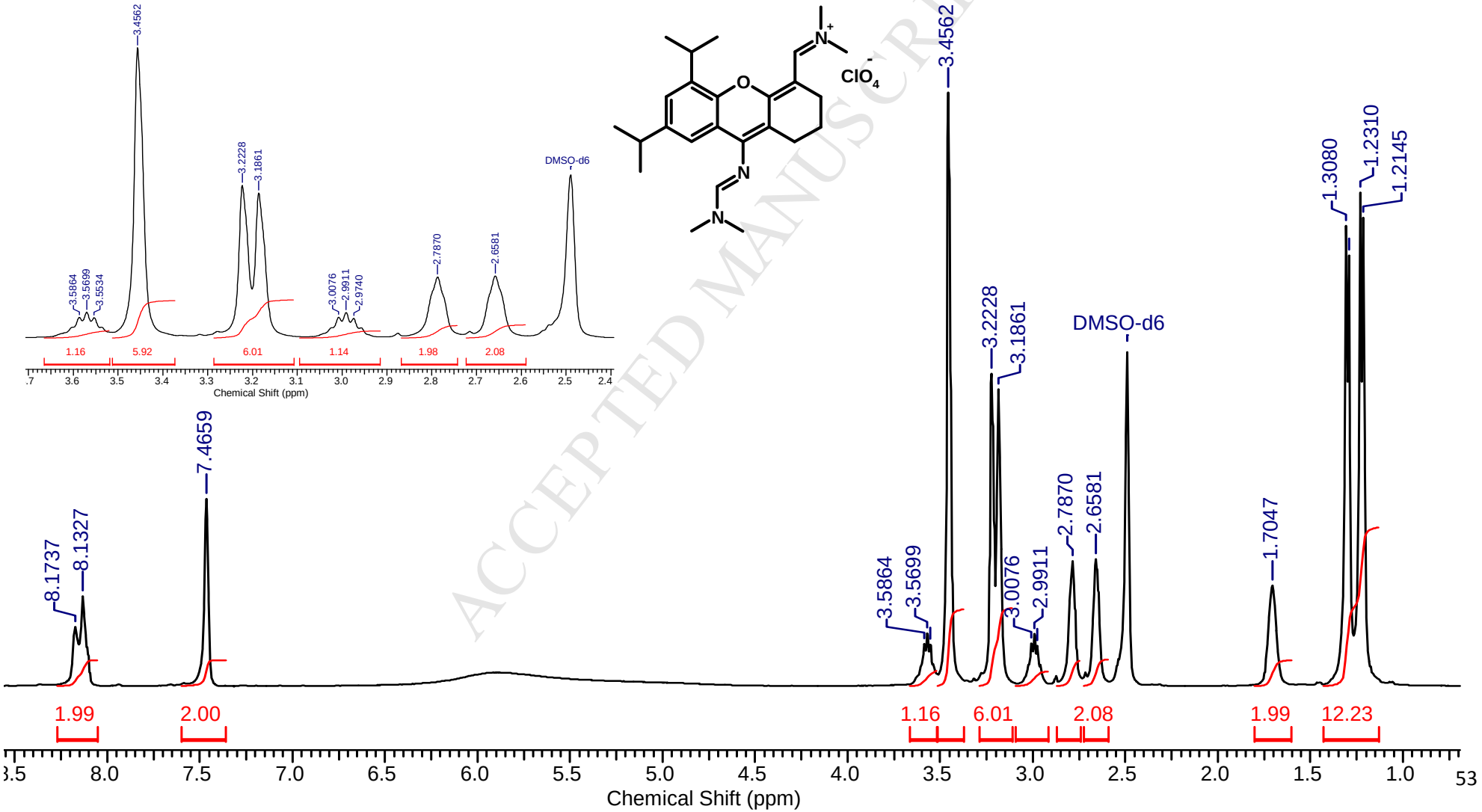
FTIR spectrum of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5b)**.



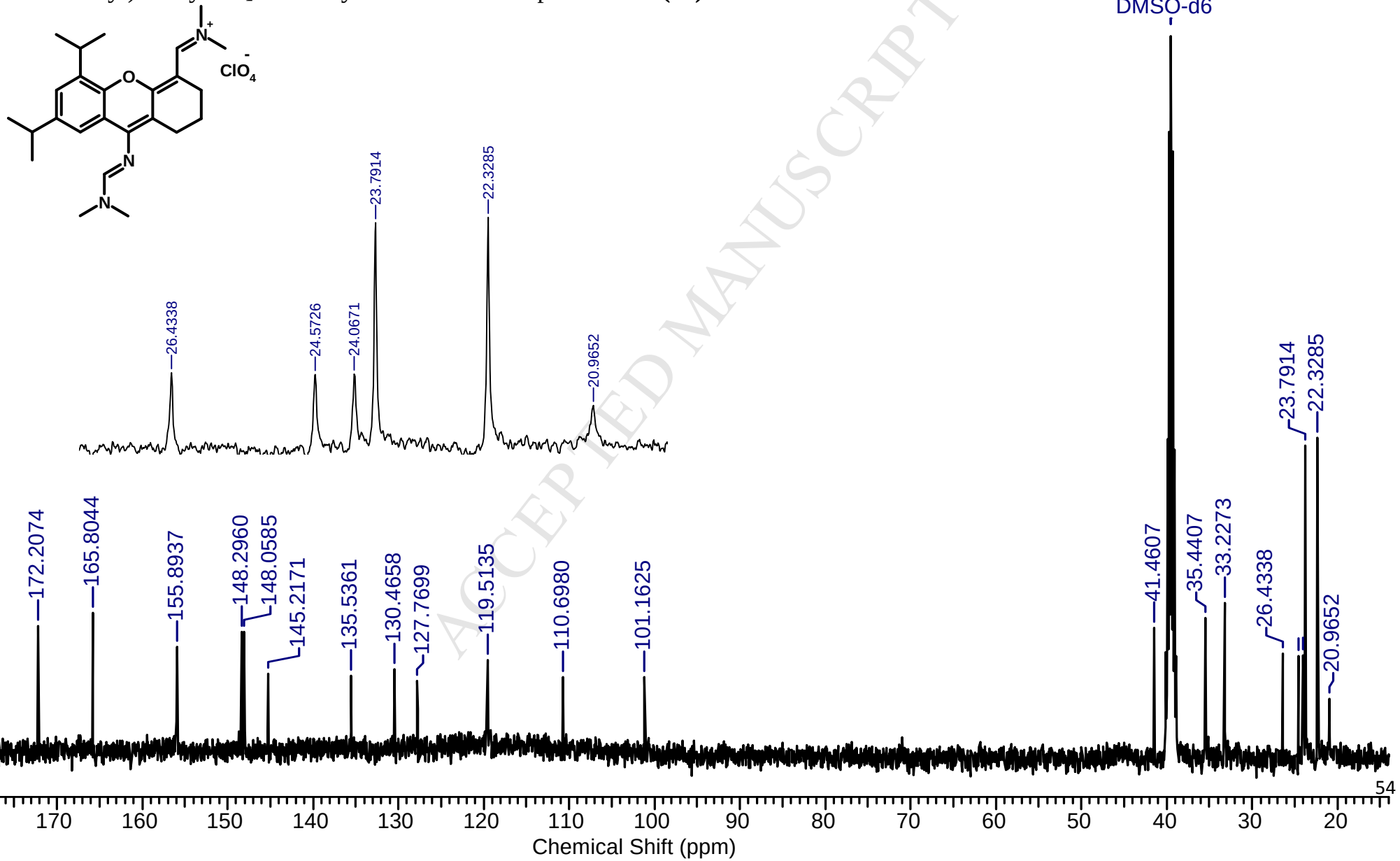
Mass spectrum (FAB) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5b)**.



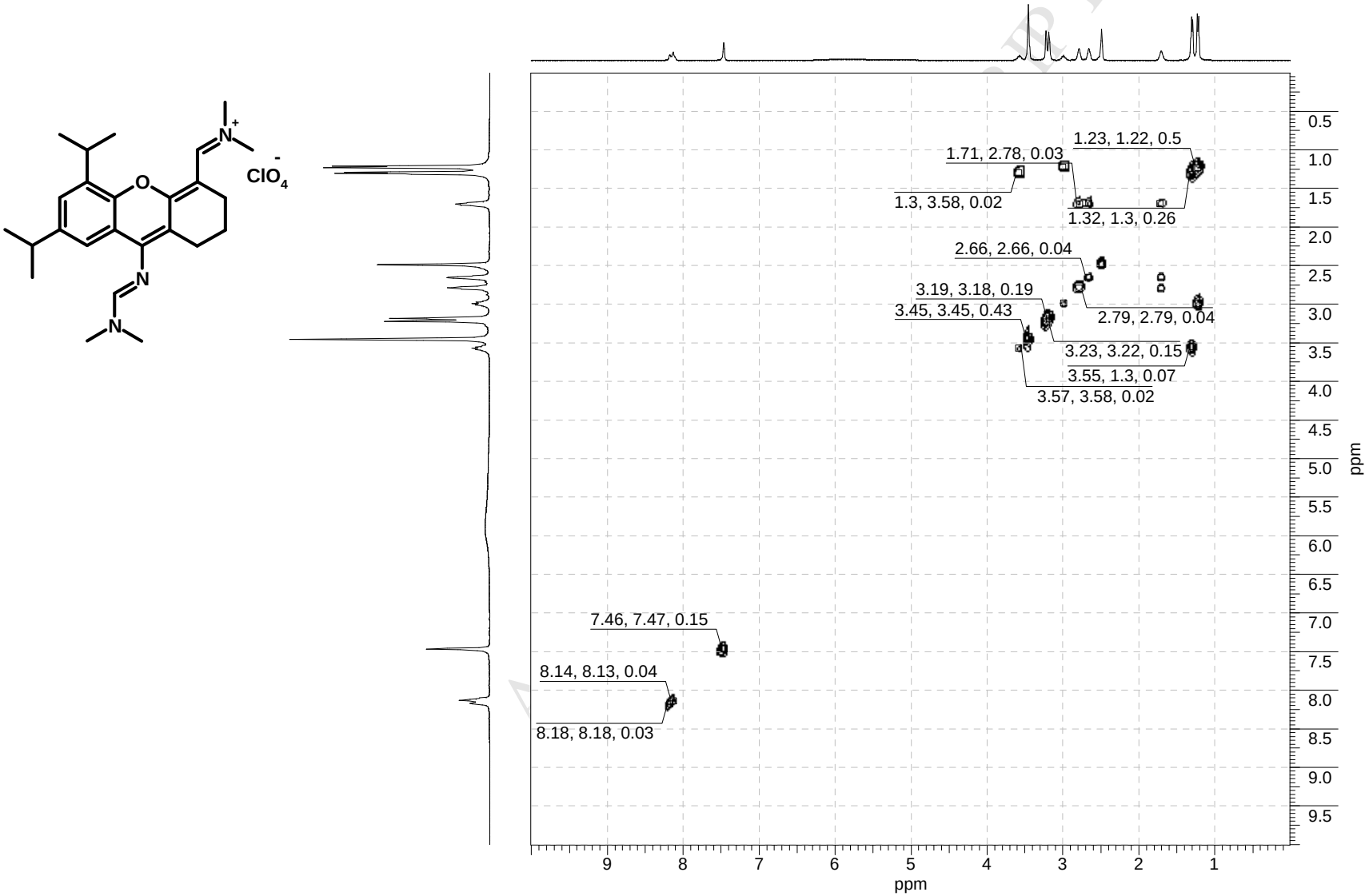
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5c)**.



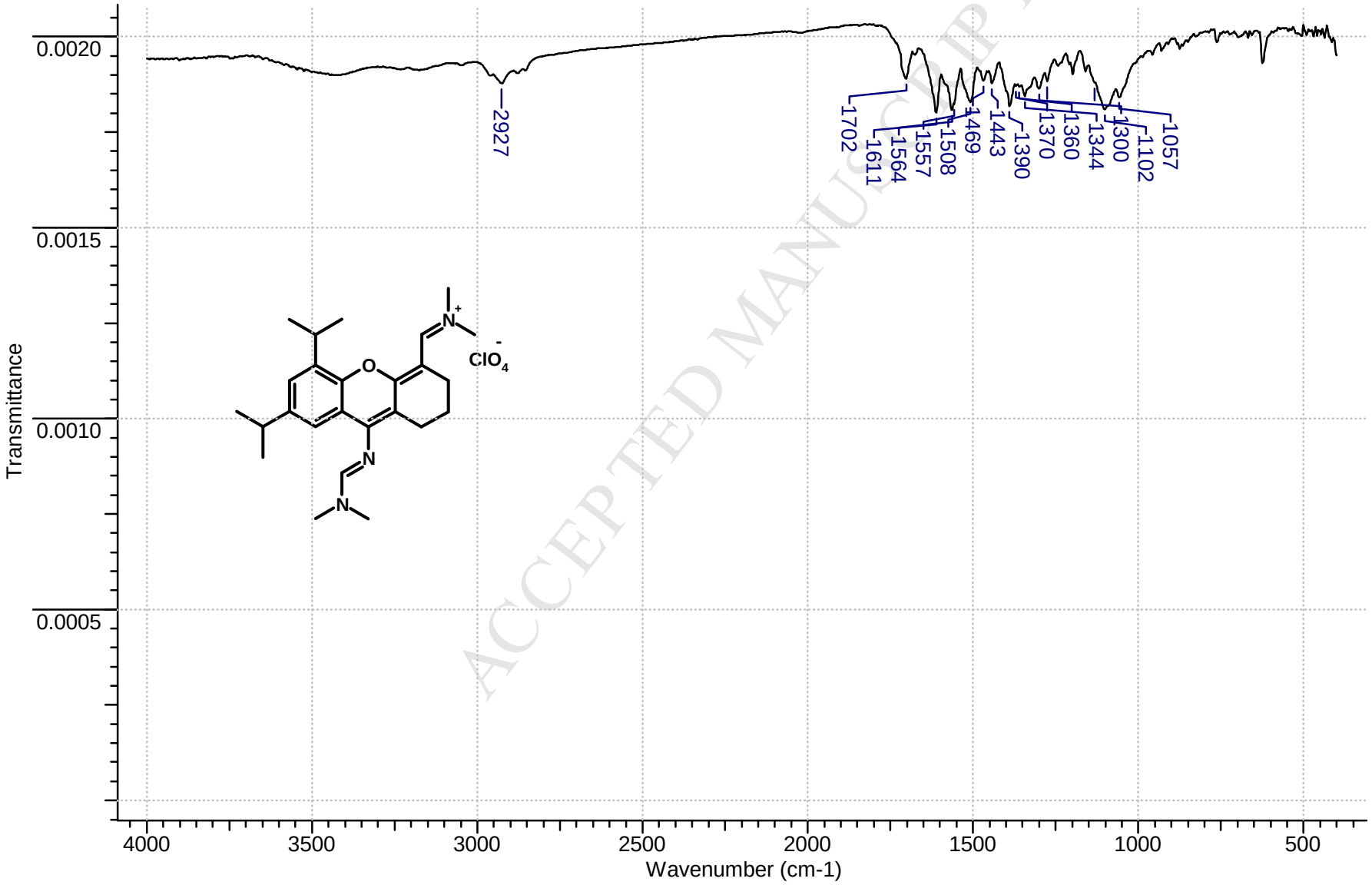
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5c)**.



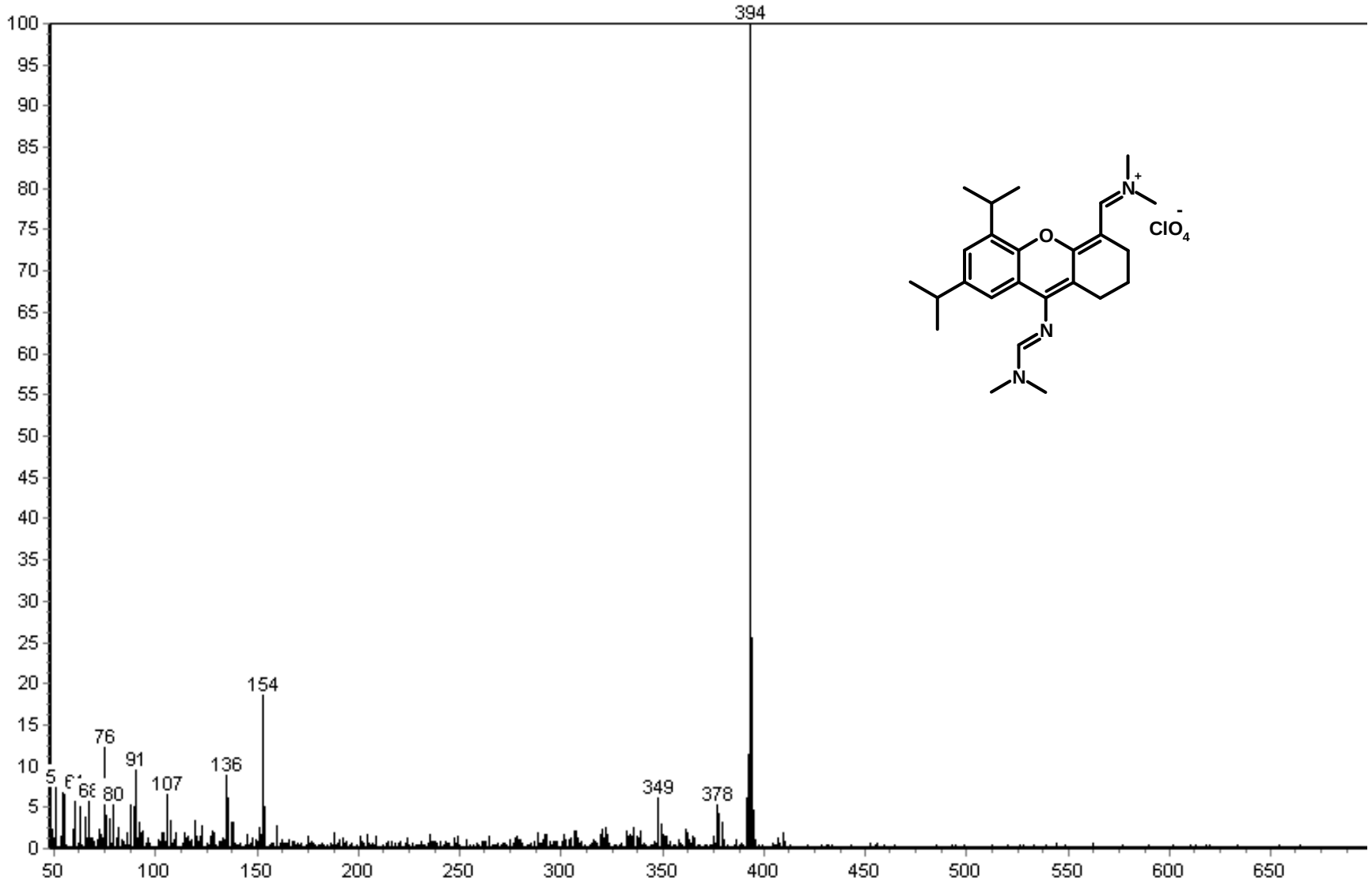
^{1}H-^{1}H COSY NMR spectrum (400 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5c)**.



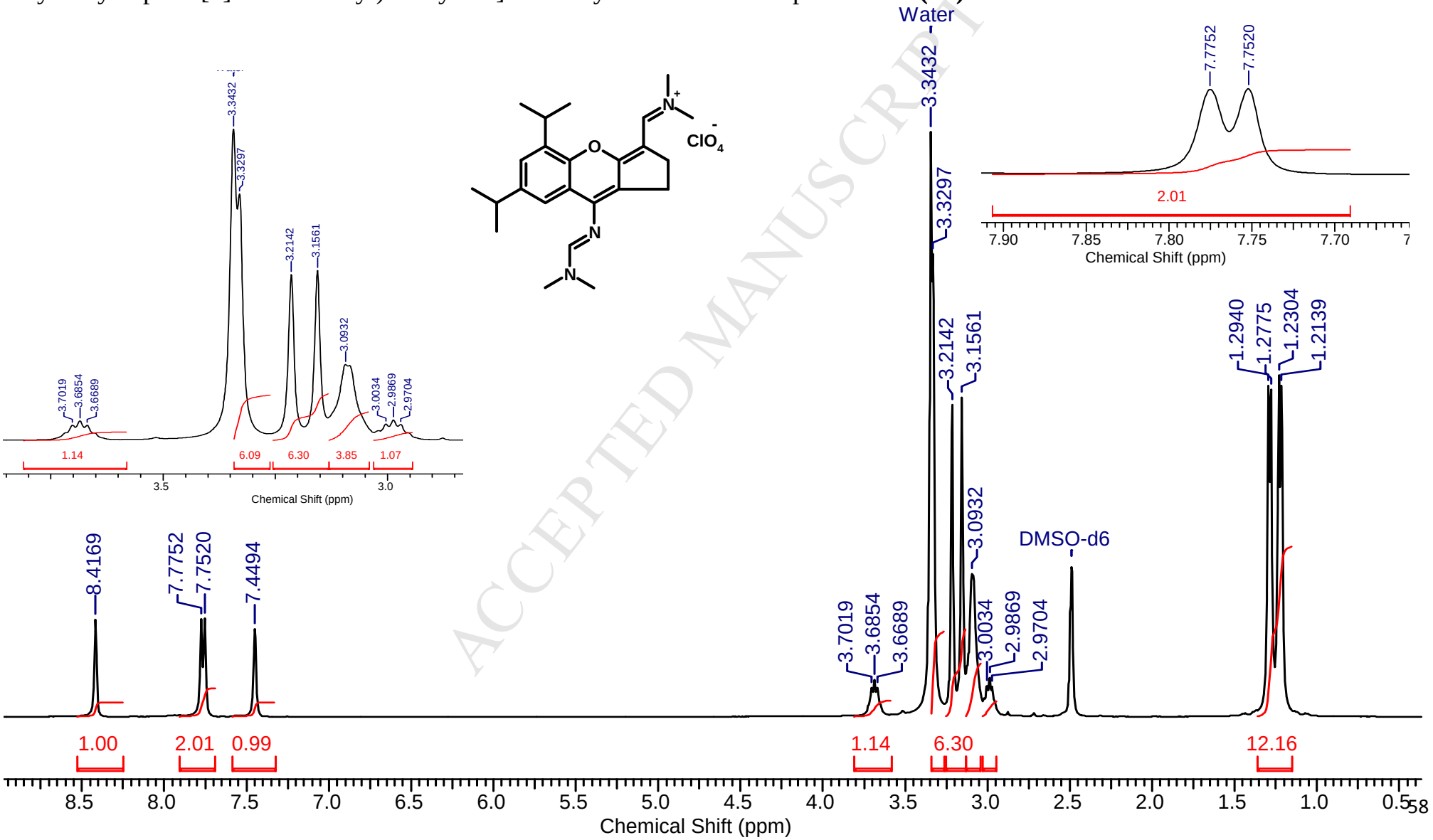
FTIR spectrum of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5c)**.



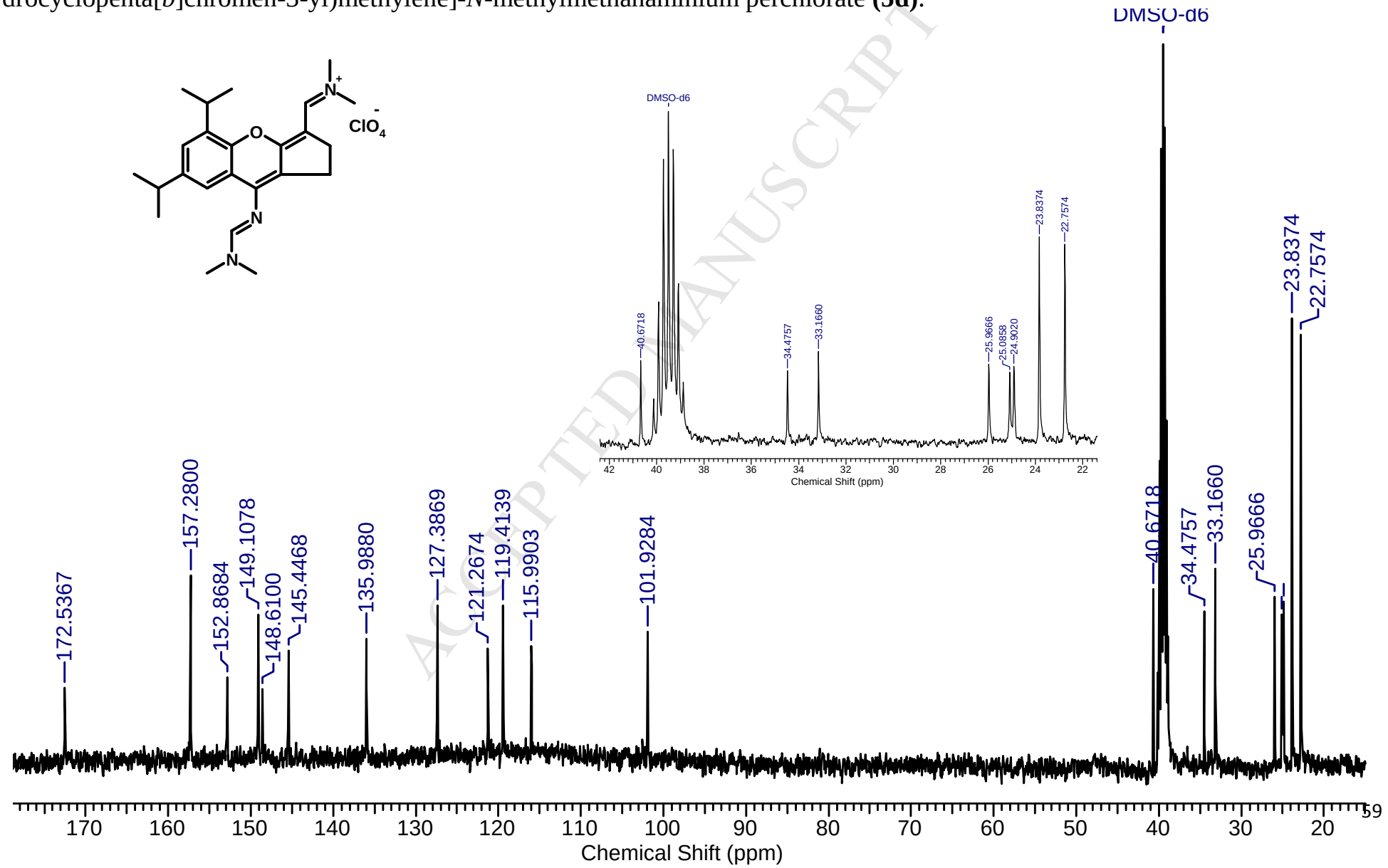
Mass spectrum (FAB) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-4-yl)methylene]-*N*-methylmethanaminium perchlorate **(5c)**.



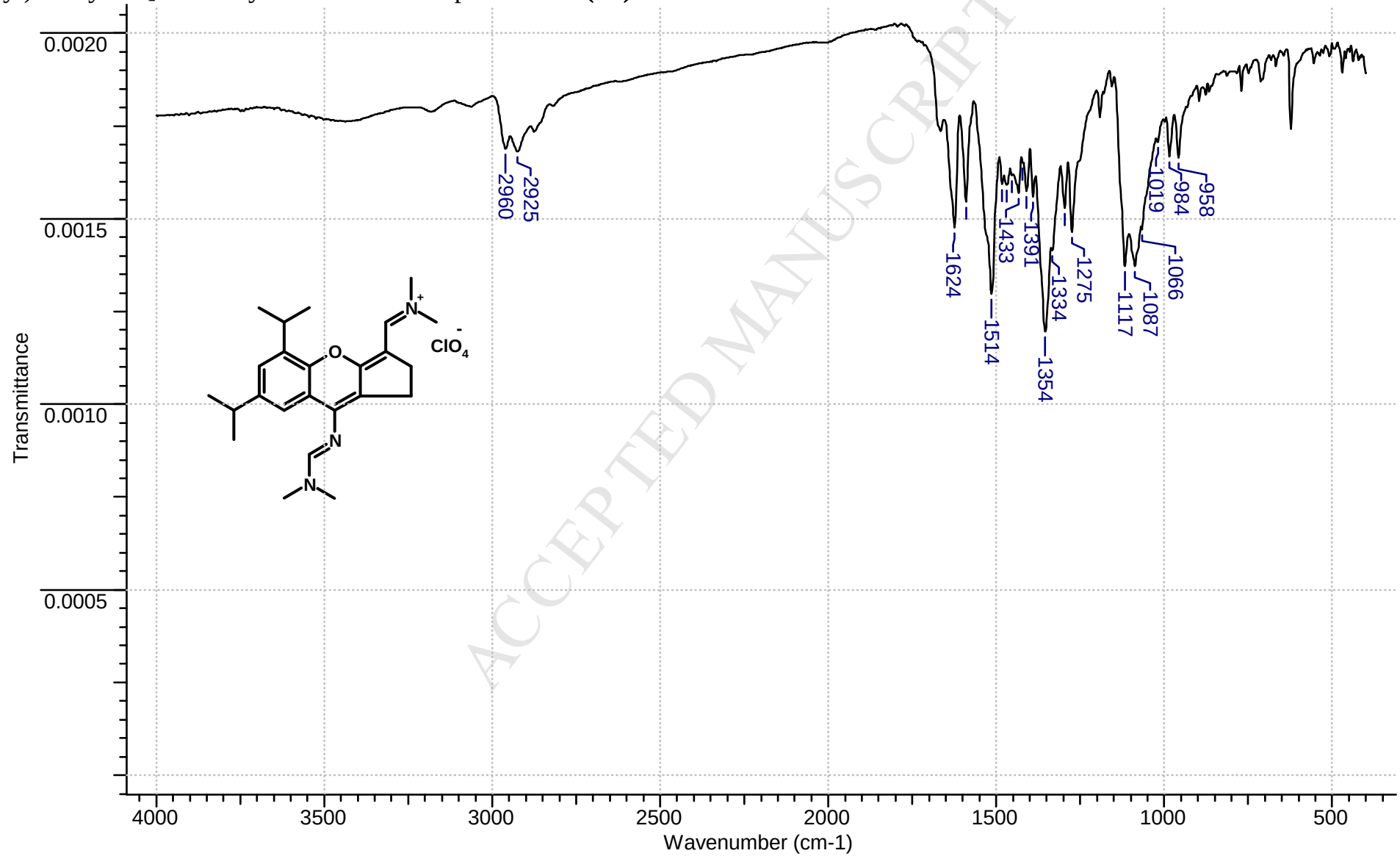
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5d)**.



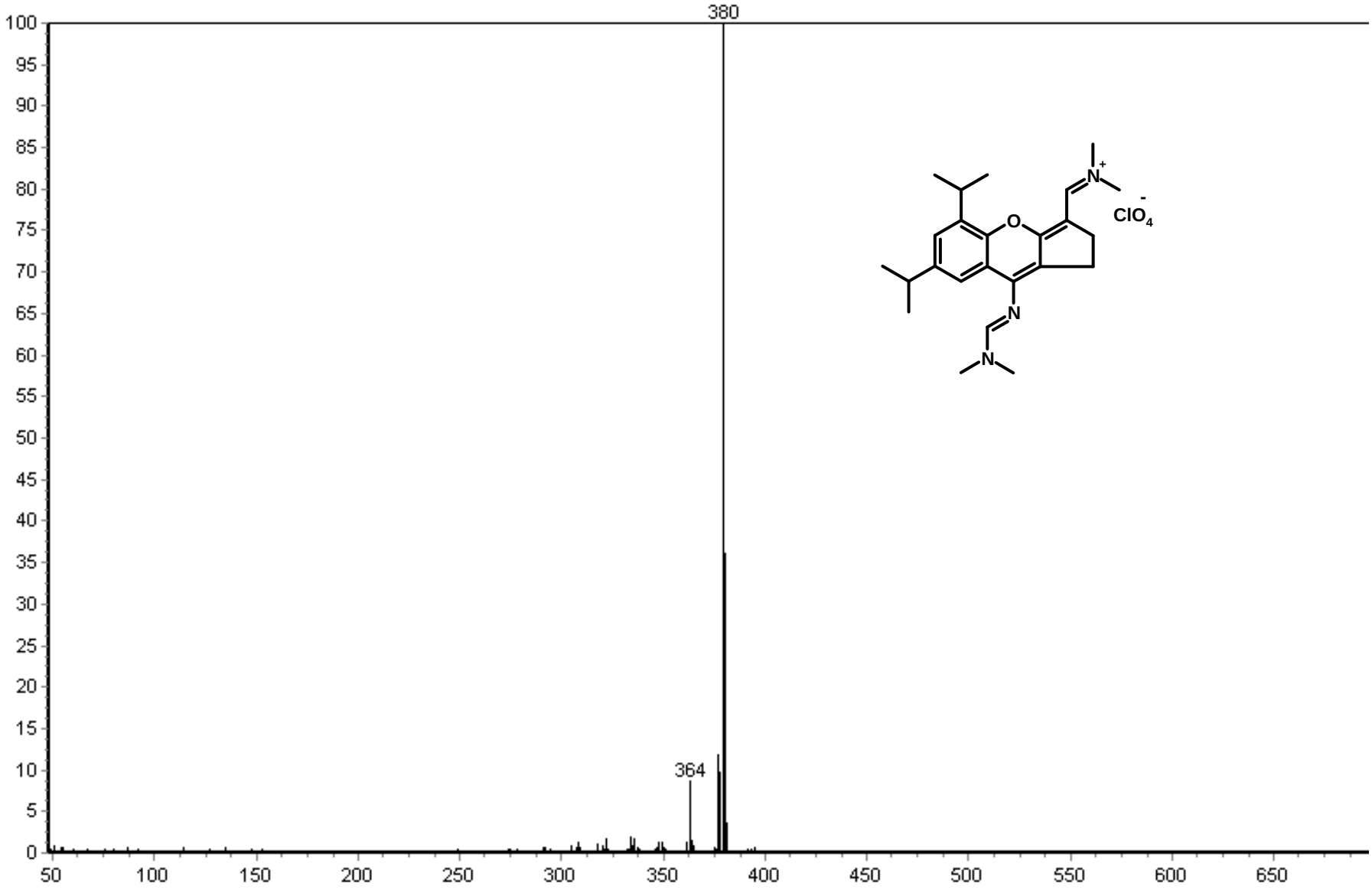
^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5d)**.



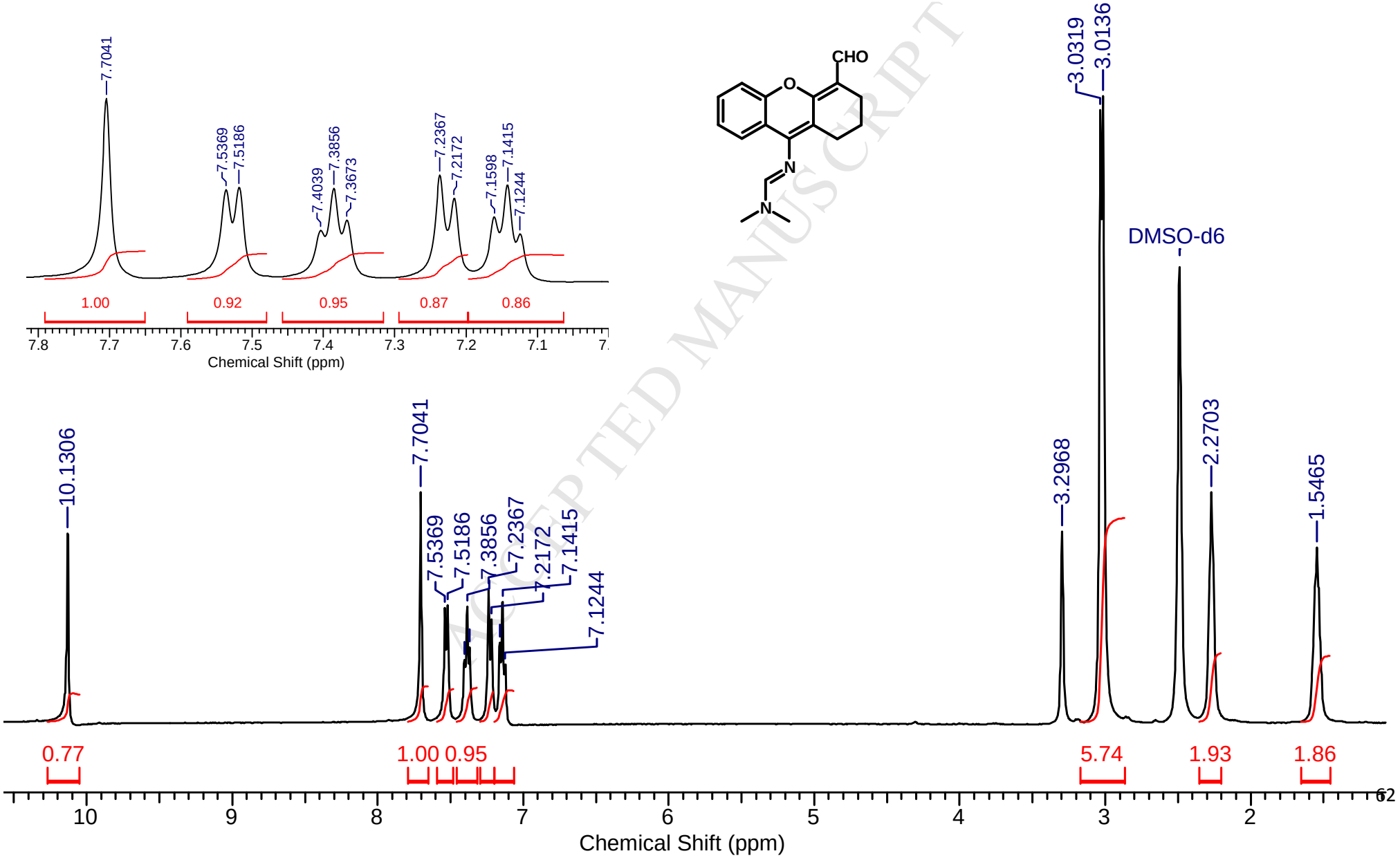
FTIR spectrum of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5d)**.



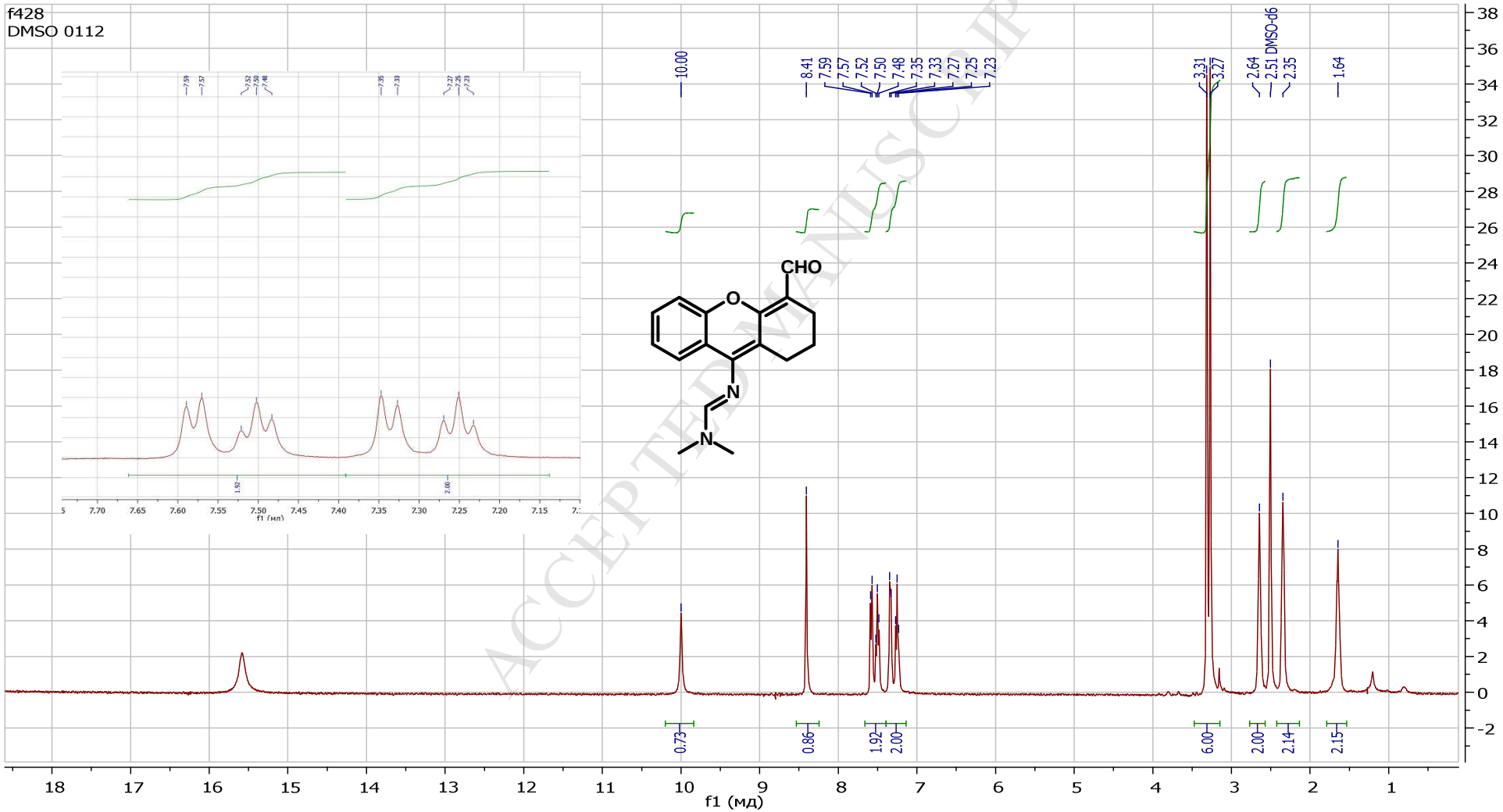
Mass spectrum (FAB) of *N*-[(9-{[(1*E*)-(dimethylamino)methylene]amino}-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-3-yl)methylene]-*N*-methylmethanaminium perchlorate **(5d)**.



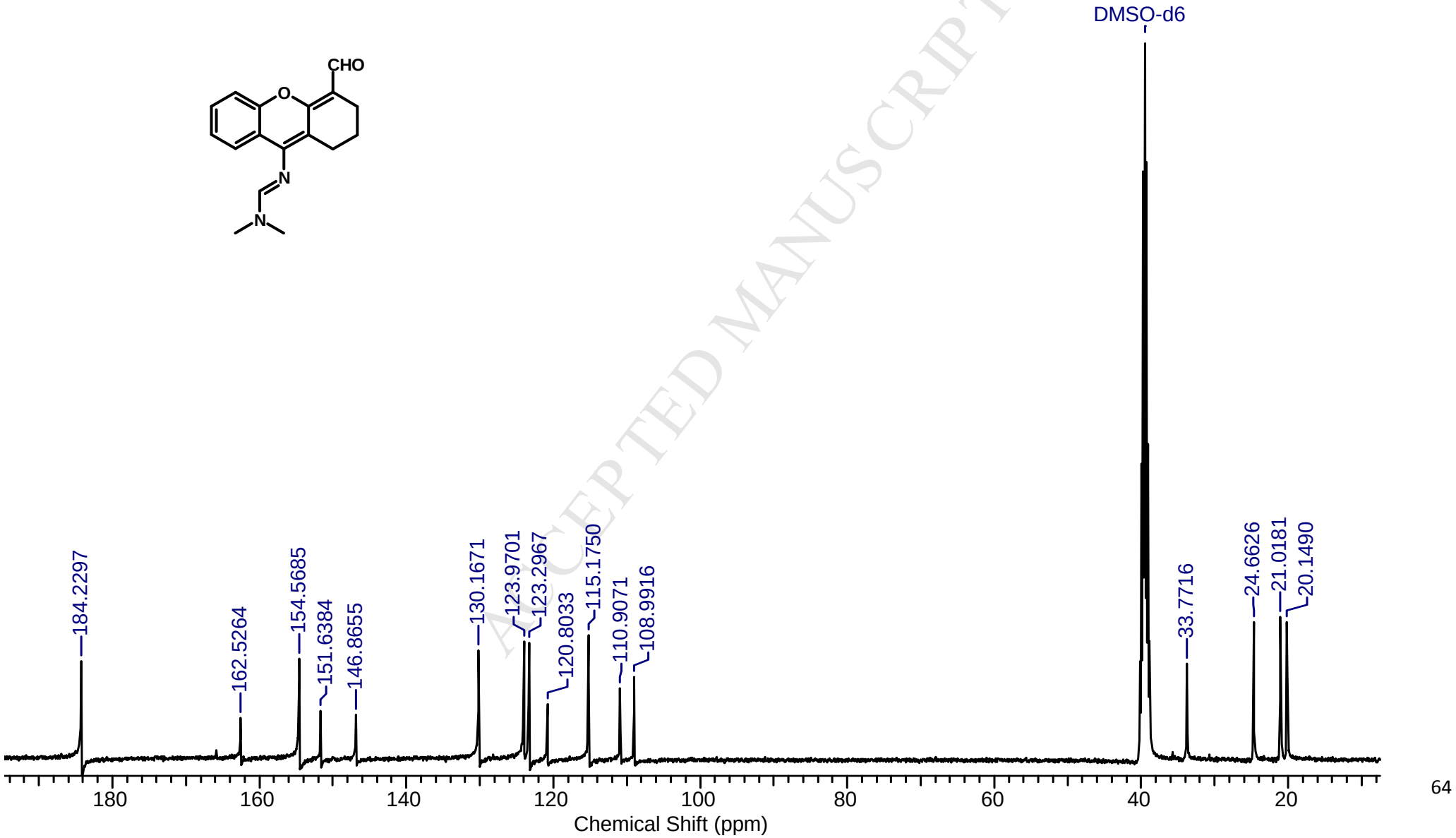
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*'-(4-formyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6a)**.



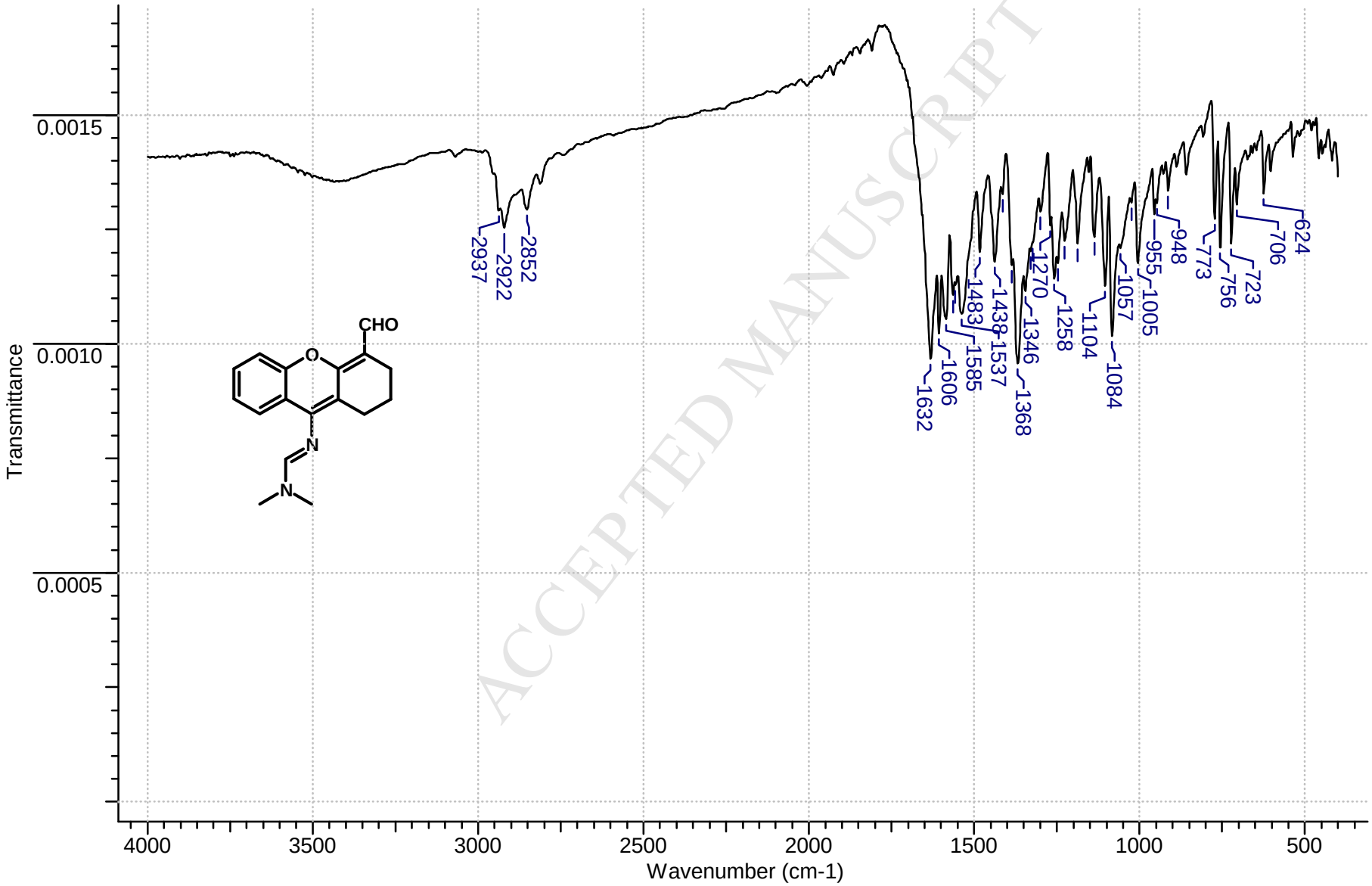
^{1}H NMR spectrum (DMSO-d_6/CF_3CO_2D, 400 MHz) of *N*'-(4-formyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6a)**.



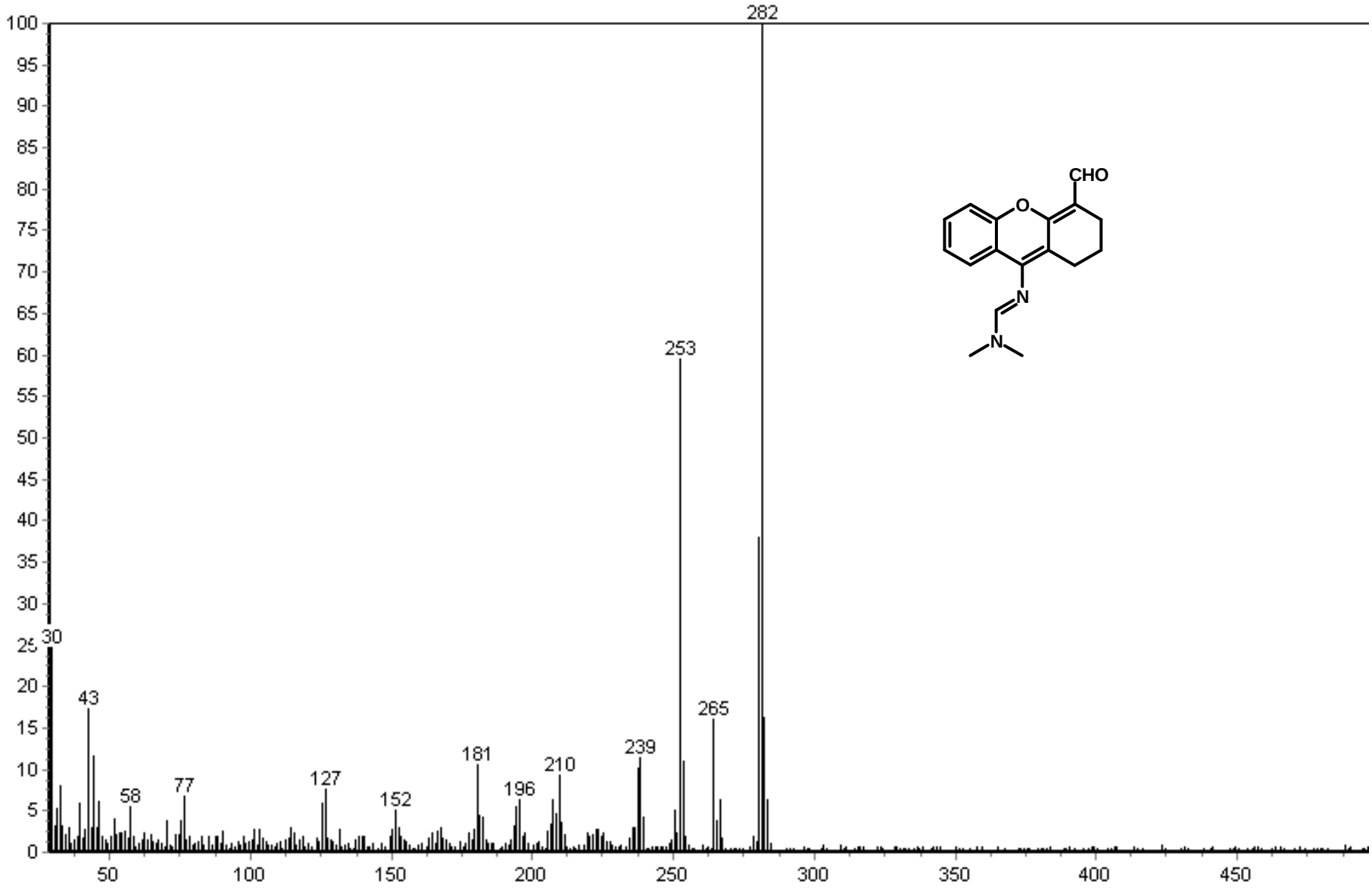
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*'-(4-formyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6a)**.



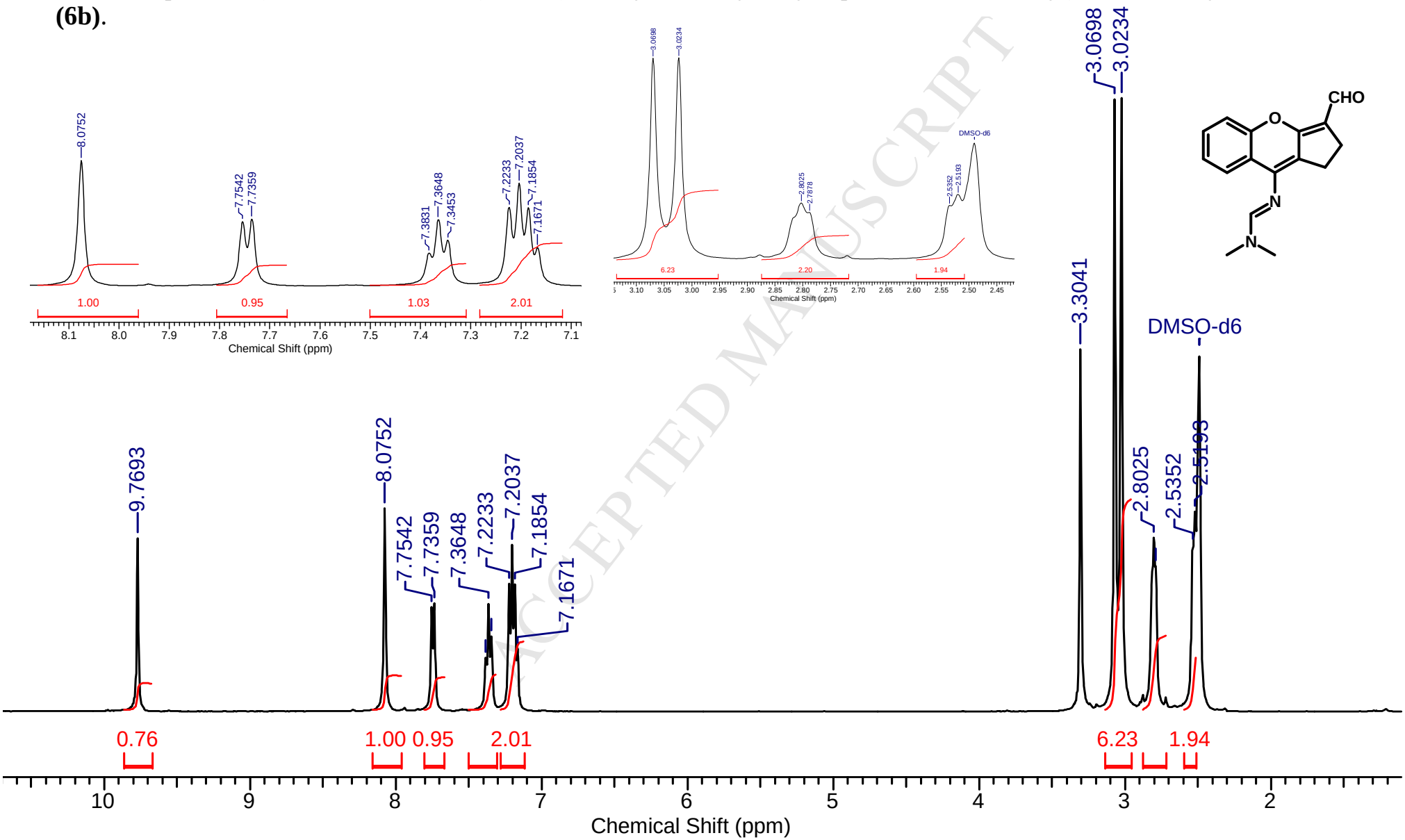
FTIR spectrum of *N*'-(4-formyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6a)**.



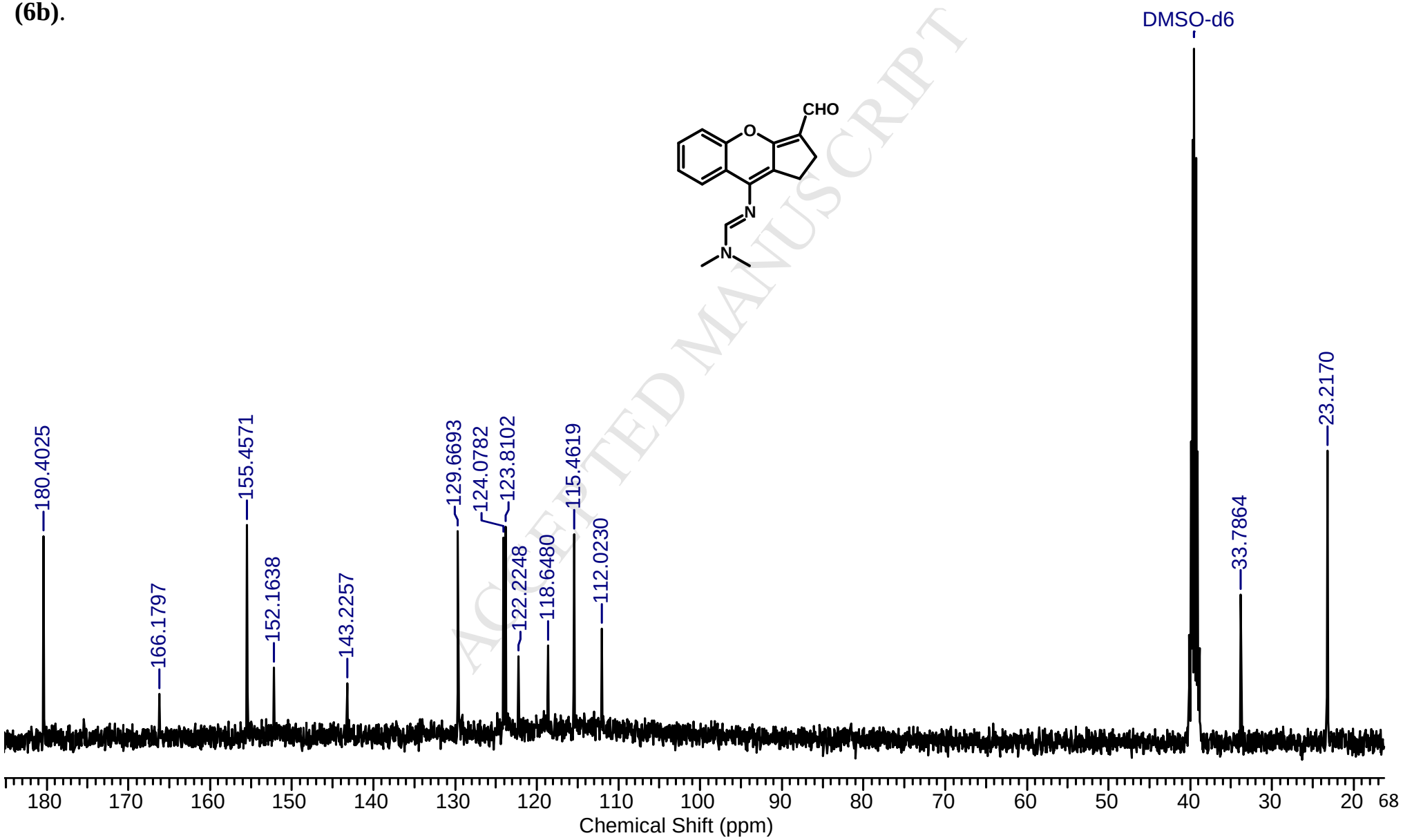
Mass spectrum (EI) of *N*'-(4-formyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6a)**.



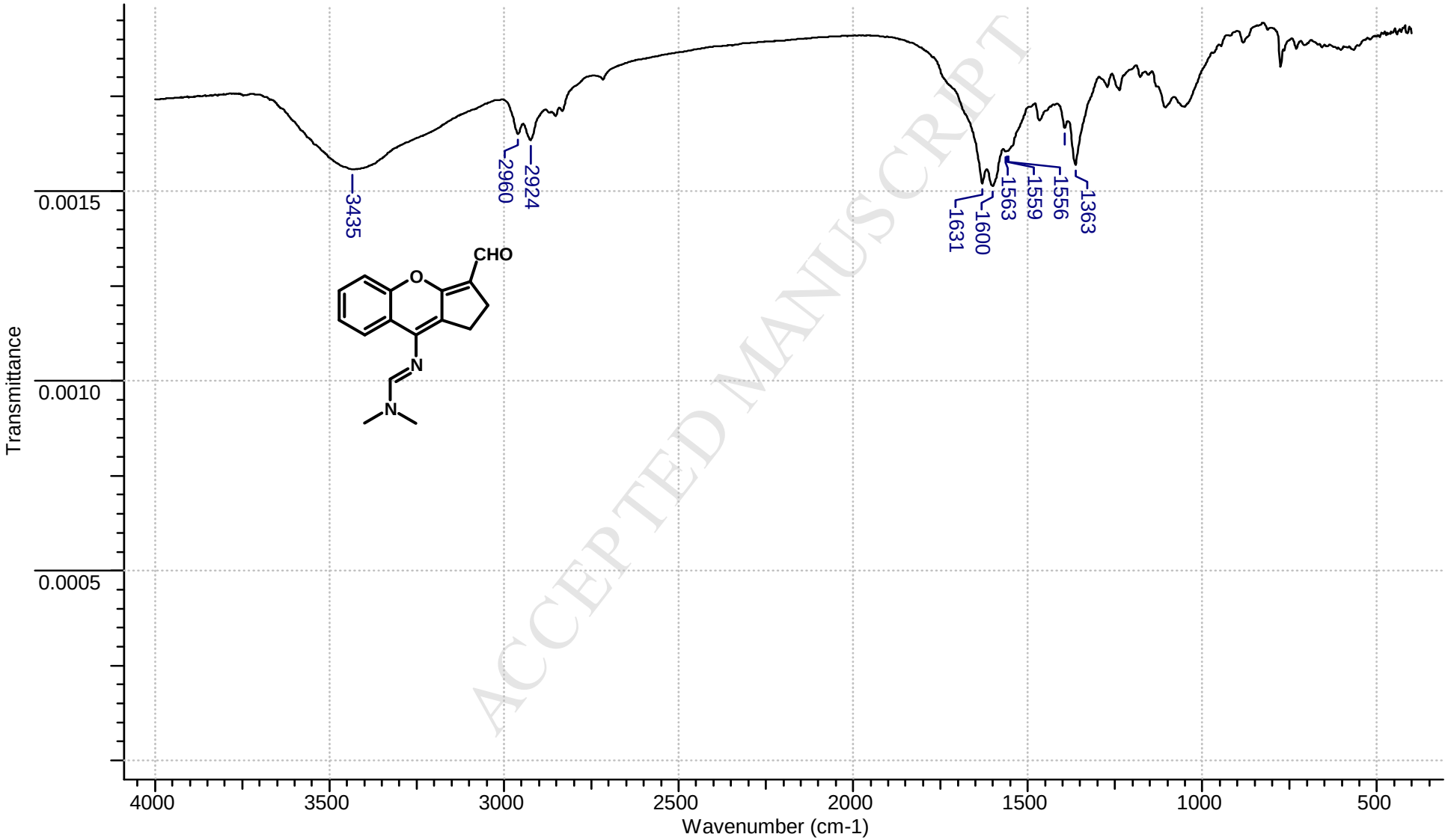
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*'-(3-formyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6b)**.



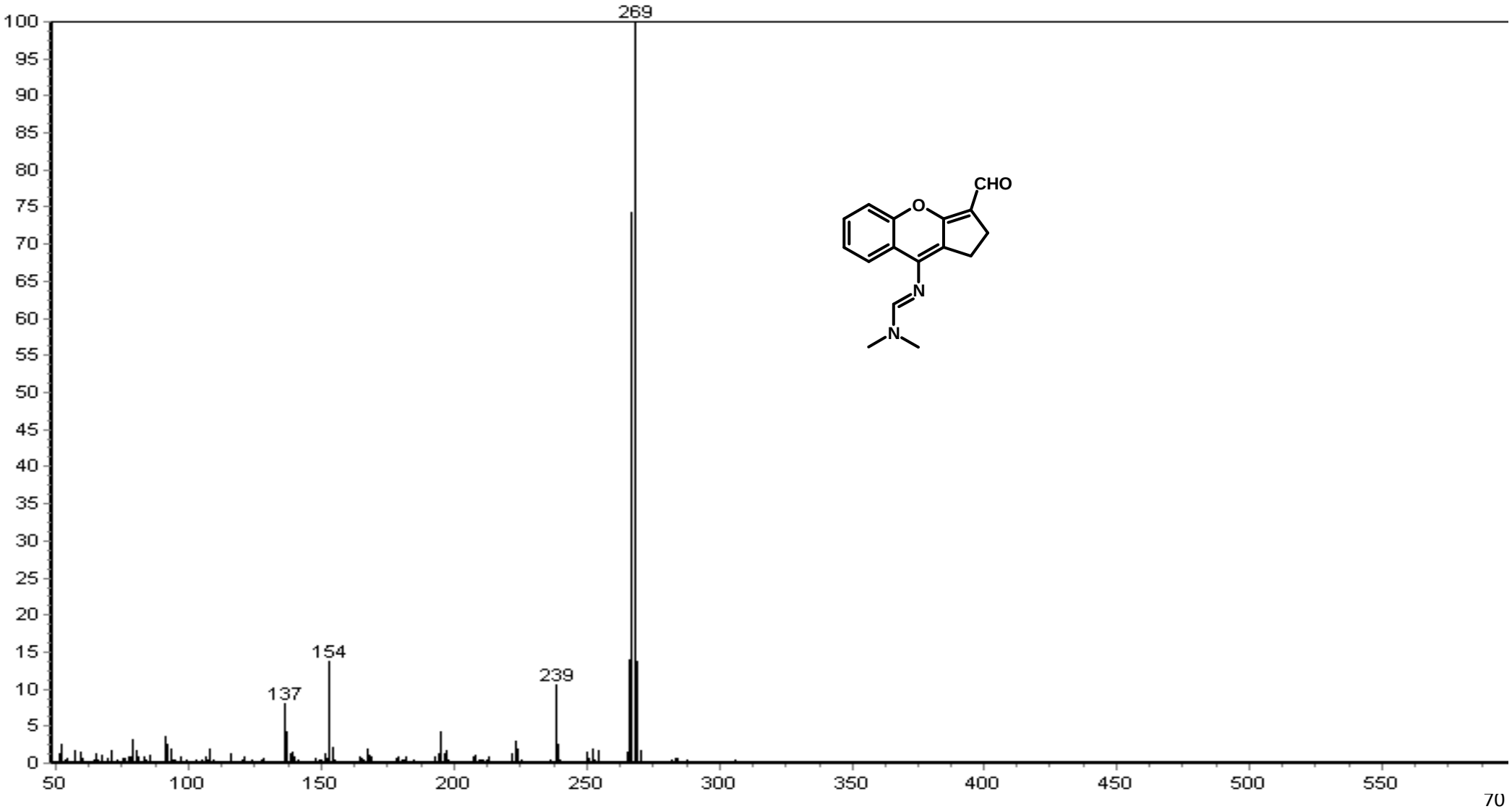
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*'-(3-formyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6b)**.



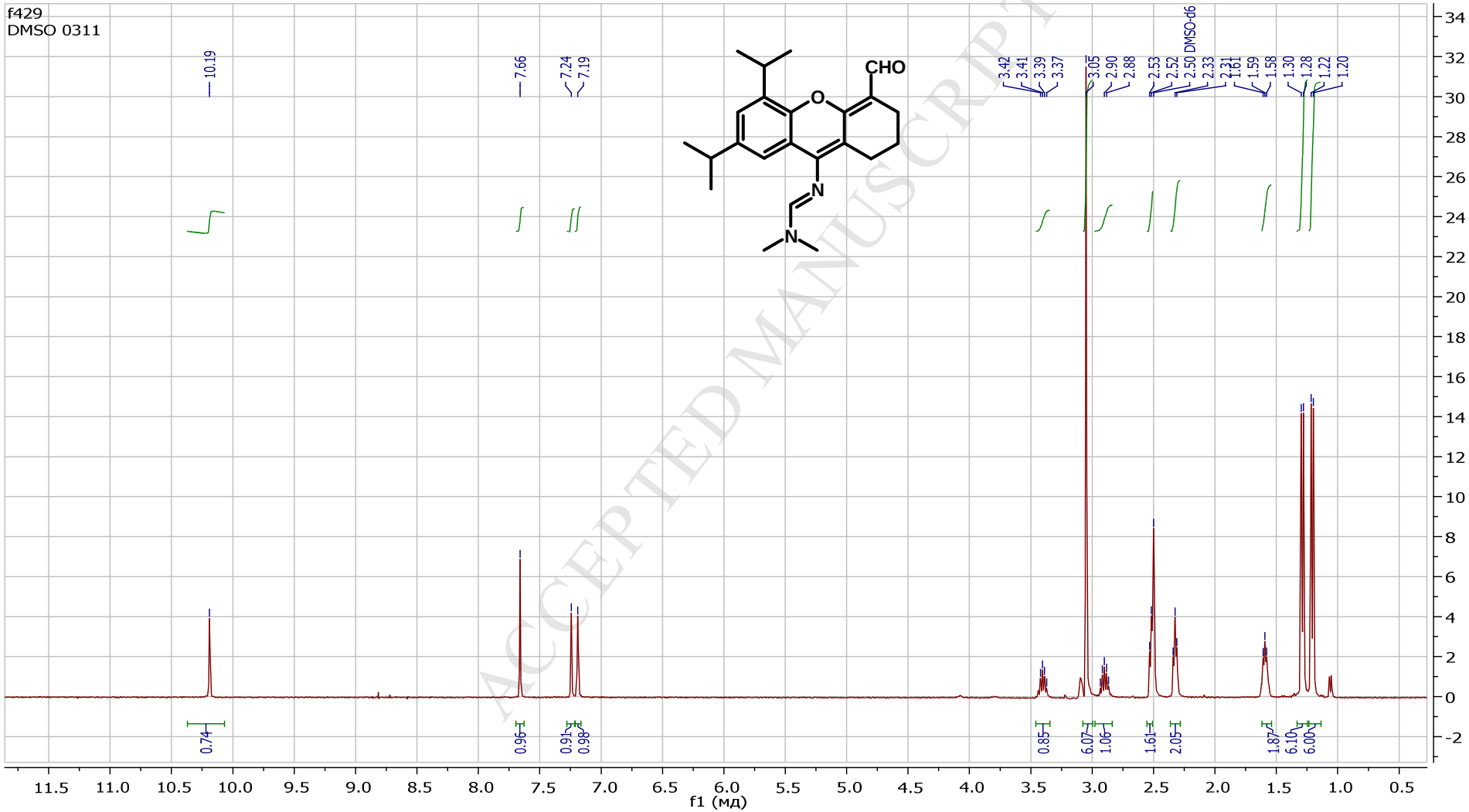
FTIR spectrum *N*'-(3-formyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6b)**.



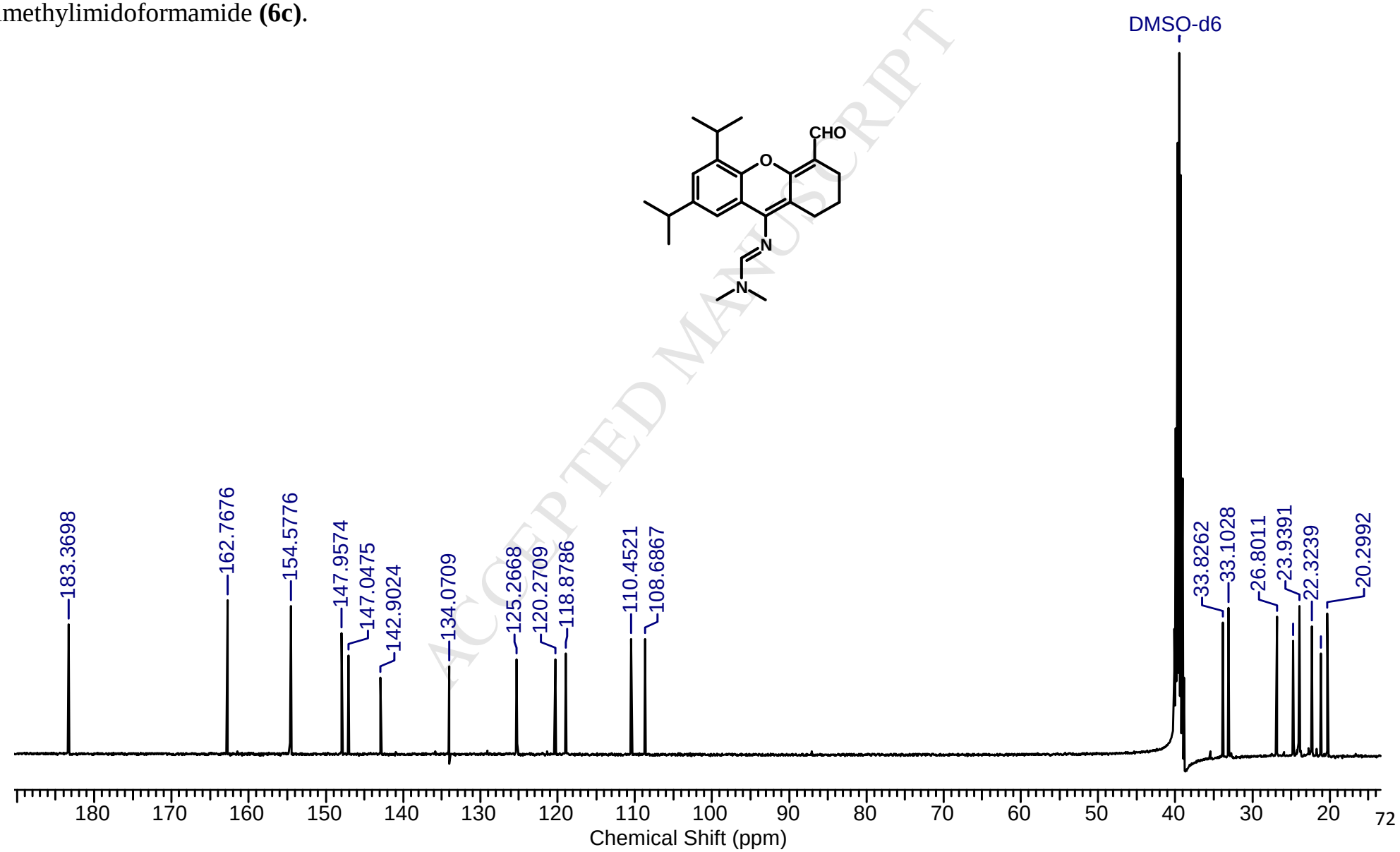
Mass spectrum (FAB) ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of *N*'-(3-formyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6b)**.



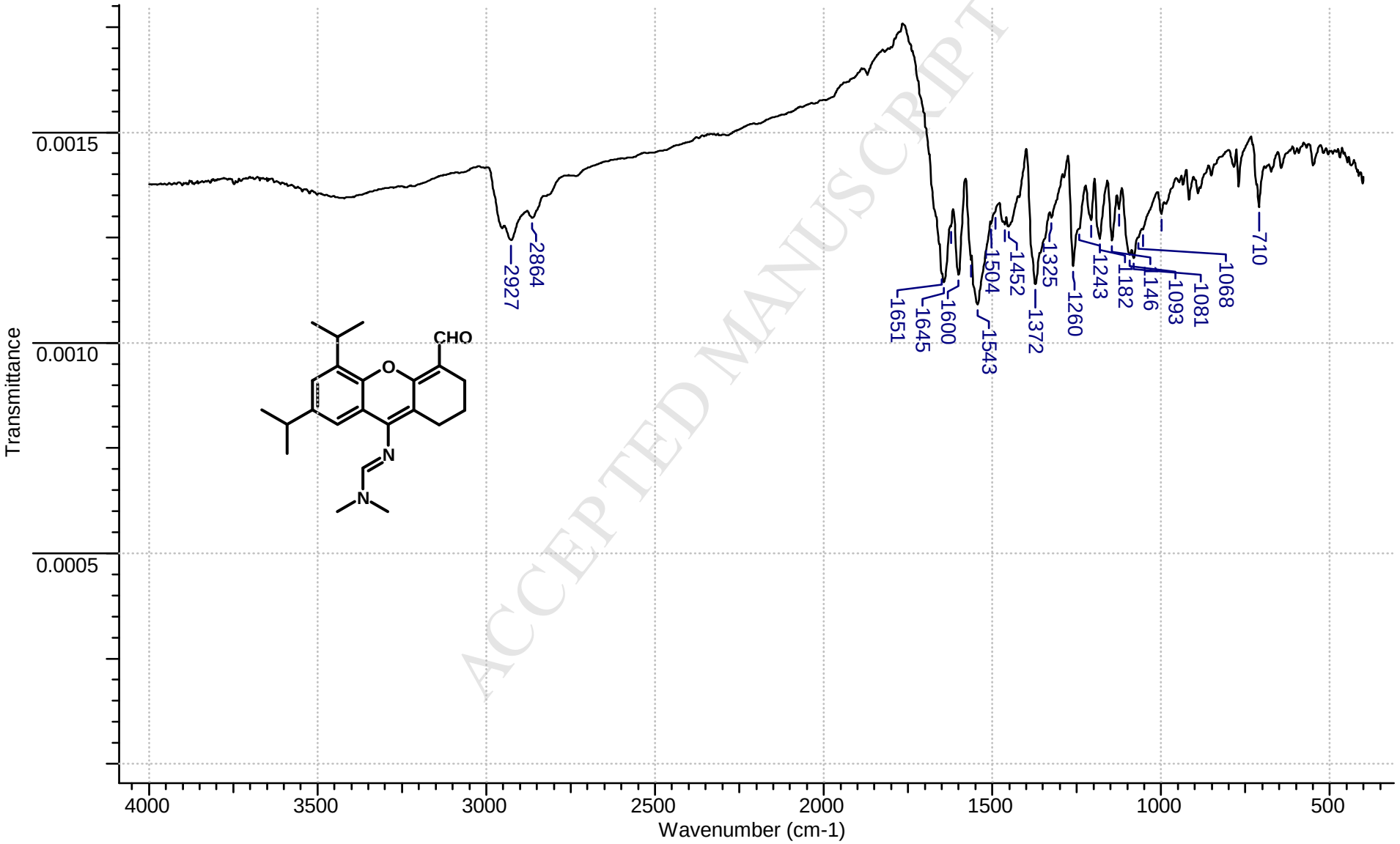
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of *N*'-(4-formyl-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6c)**.



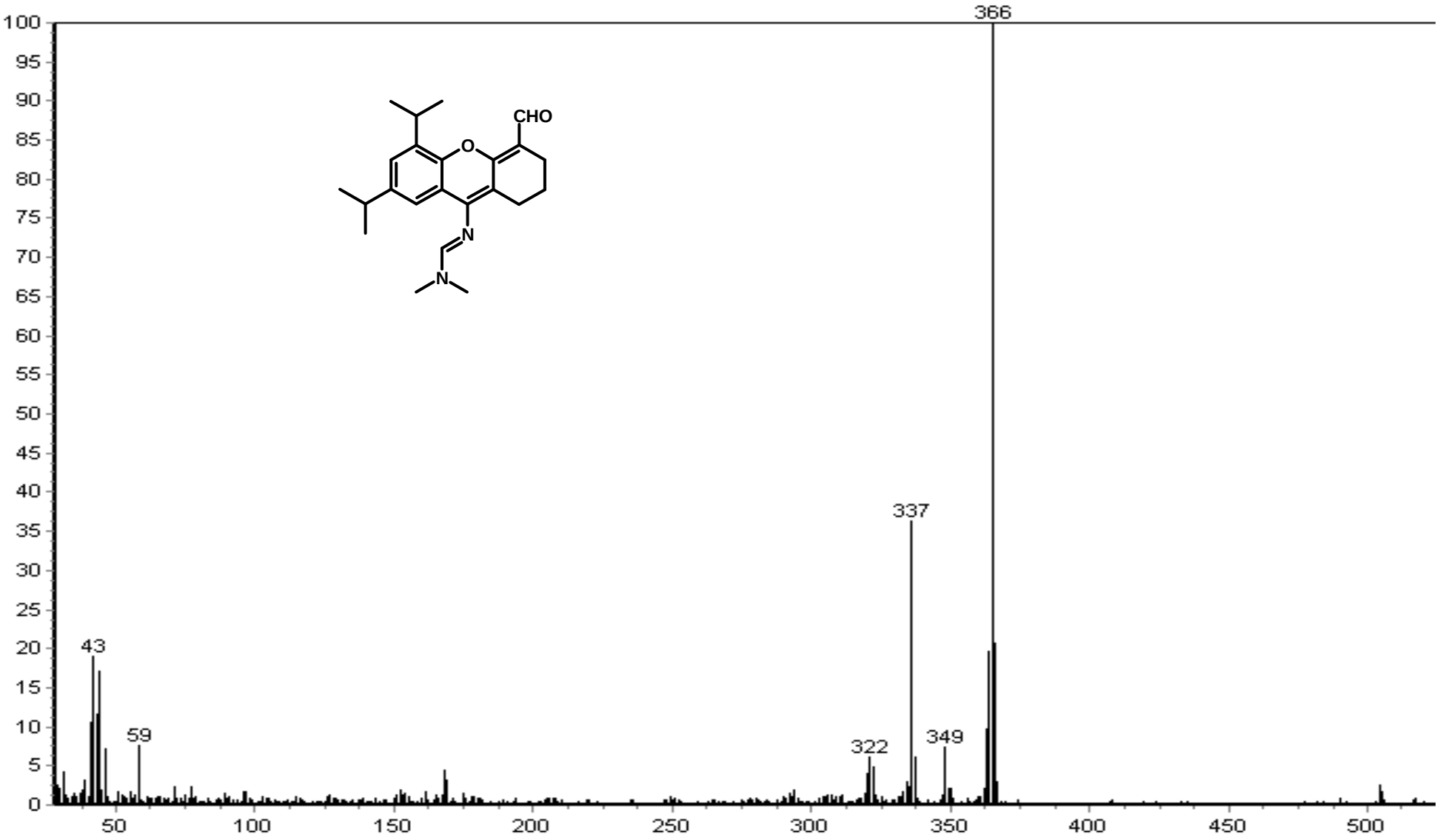
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*'-(4-formyl-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6c)**.



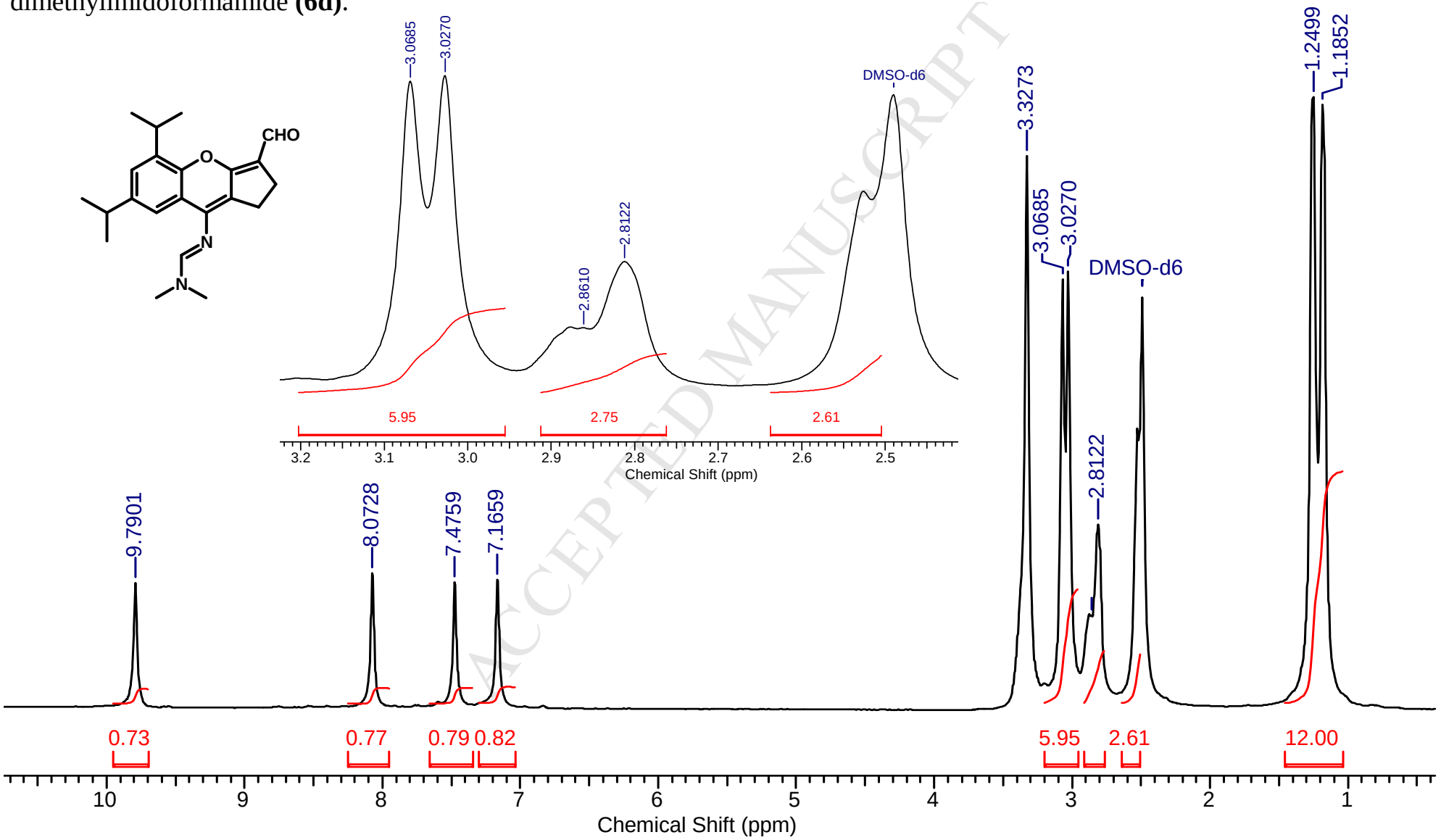
FTIR spectrum of *N*'-(4-formyl-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6c)**.



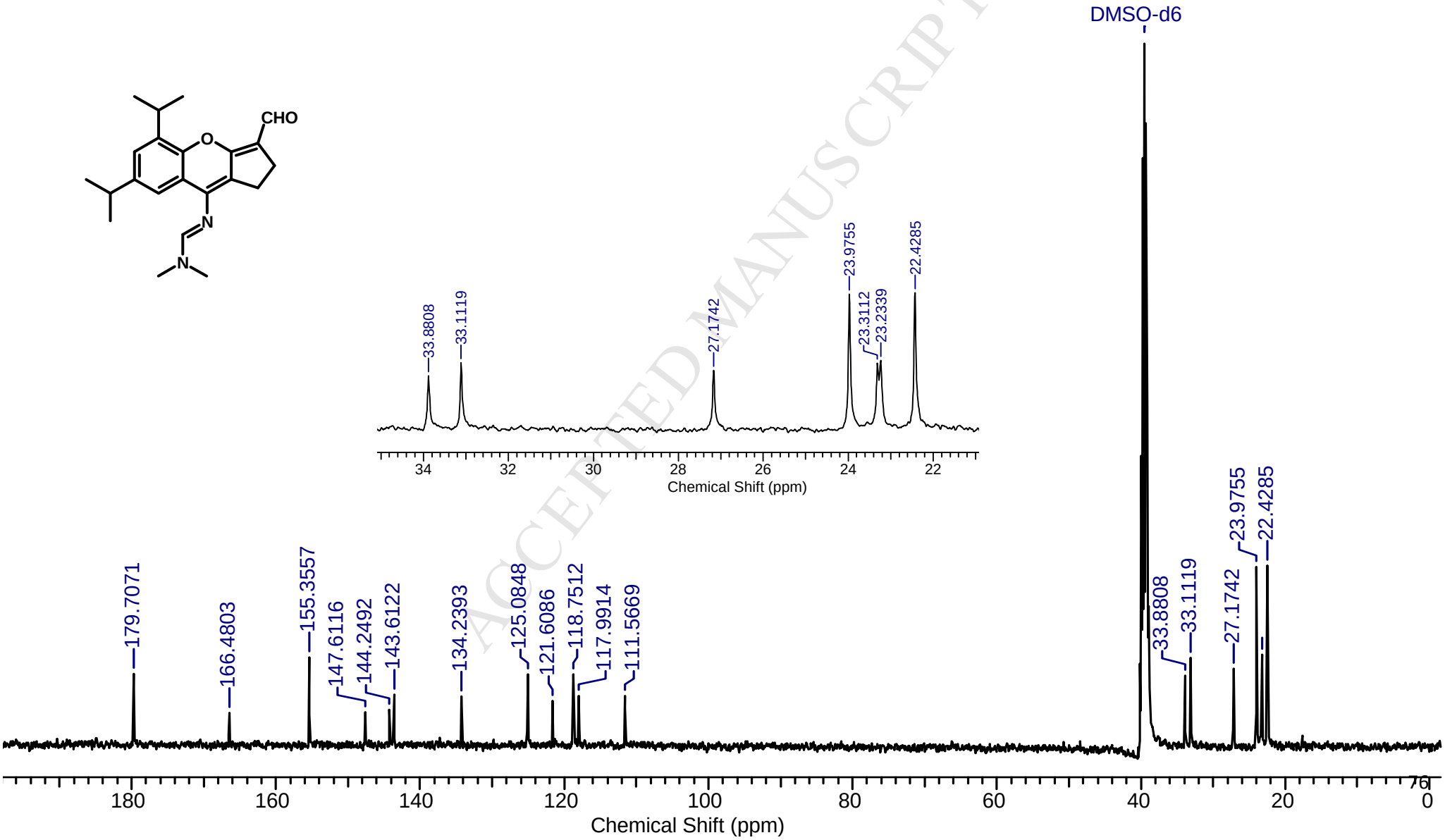
Mass spectrum (EI) of *N*'-(4-formyl-5,7-diisopropyl-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6c)**.



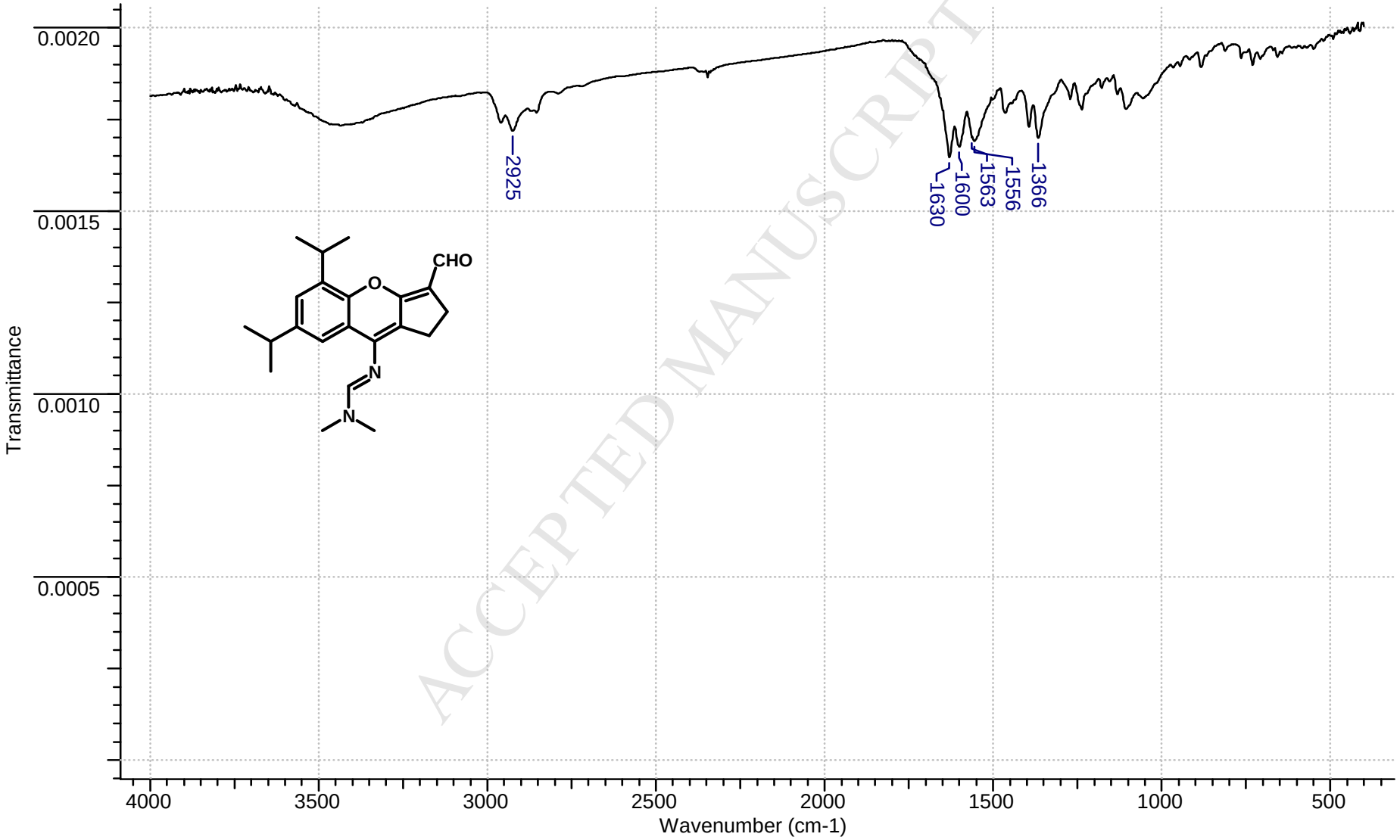
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of *N*'-(3-formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6d)**.



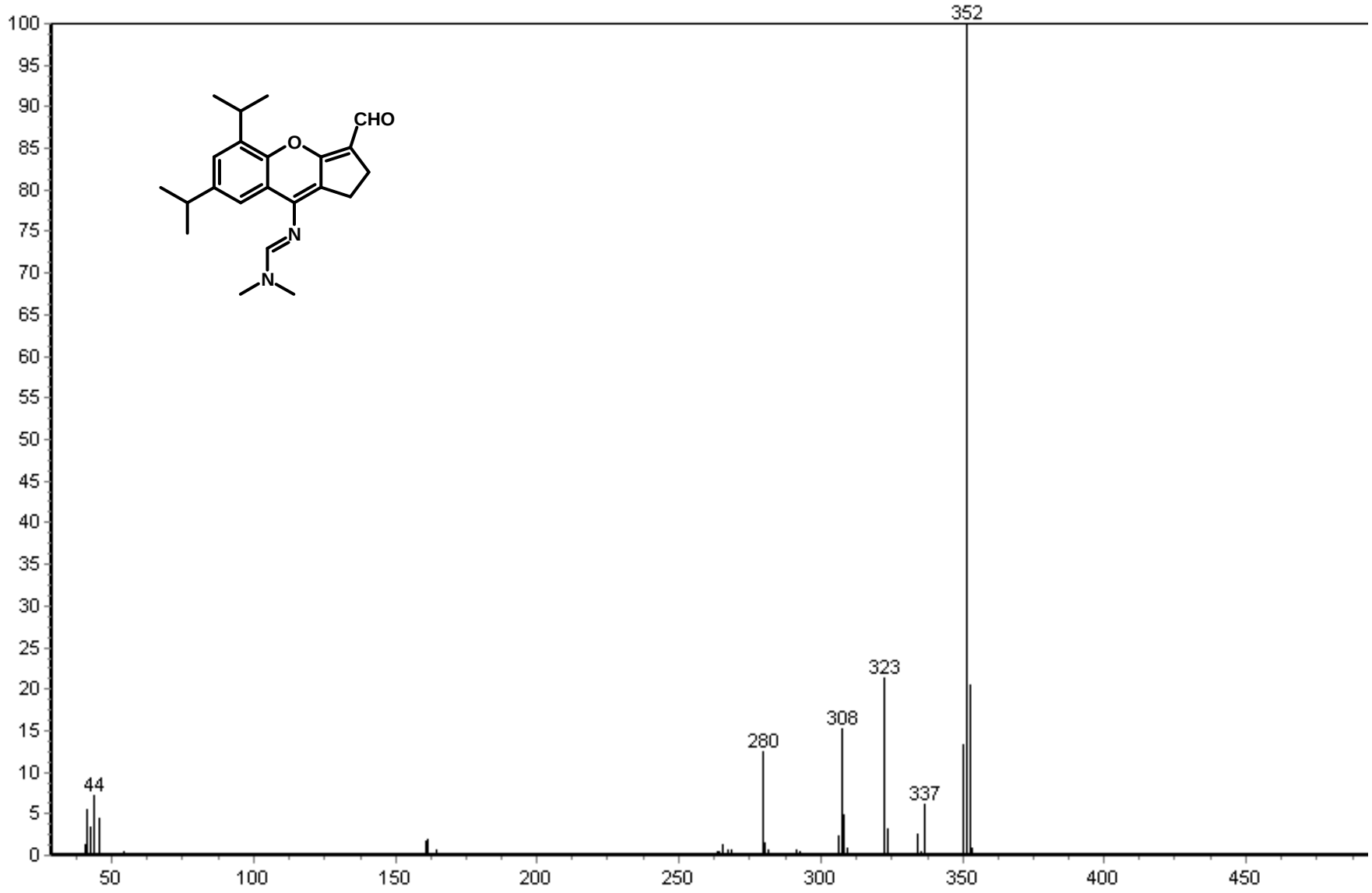
^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of *N*'-(3-formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6d)**.



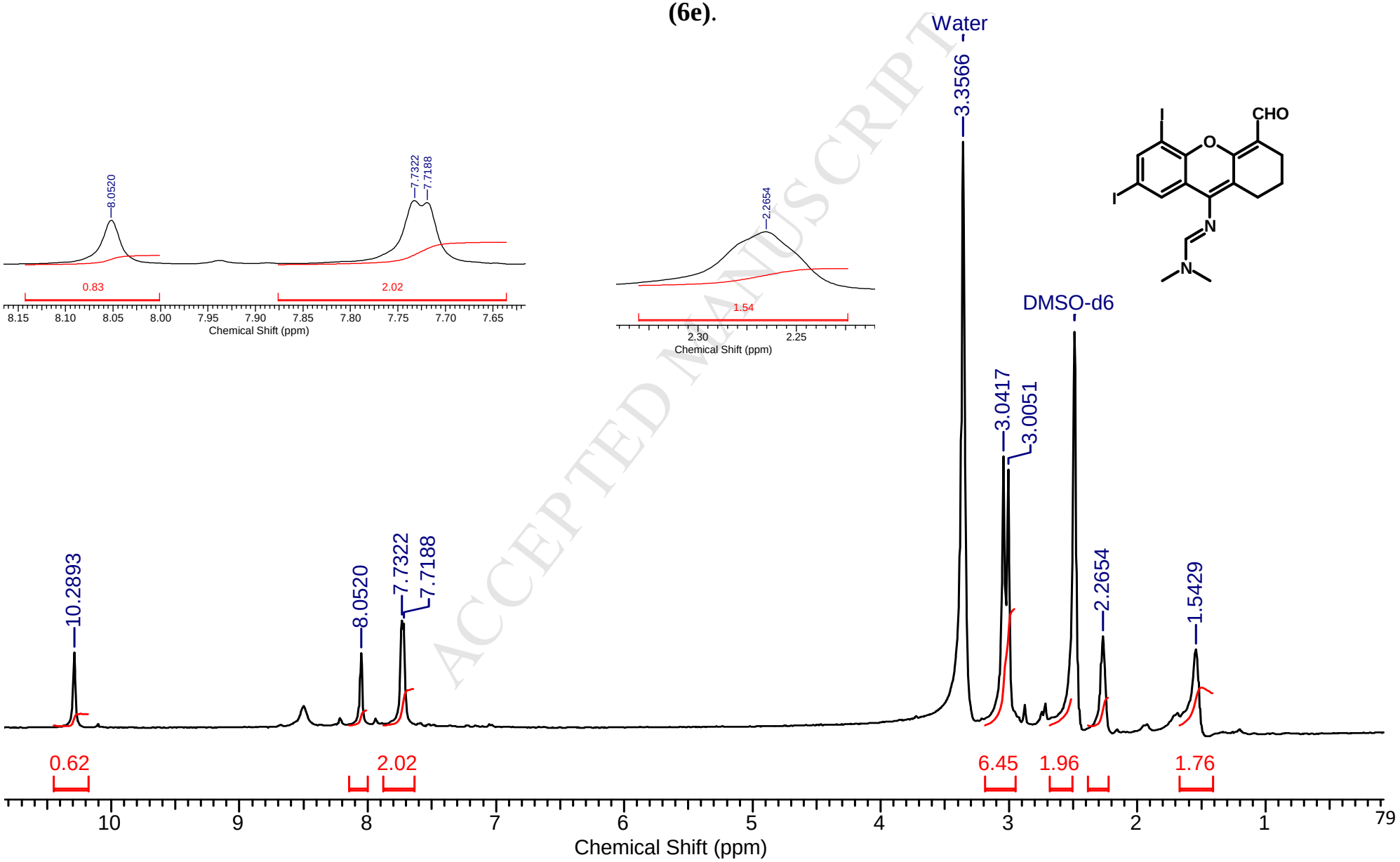
FTIR spectrum of *N*'-(3-formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6d)**.



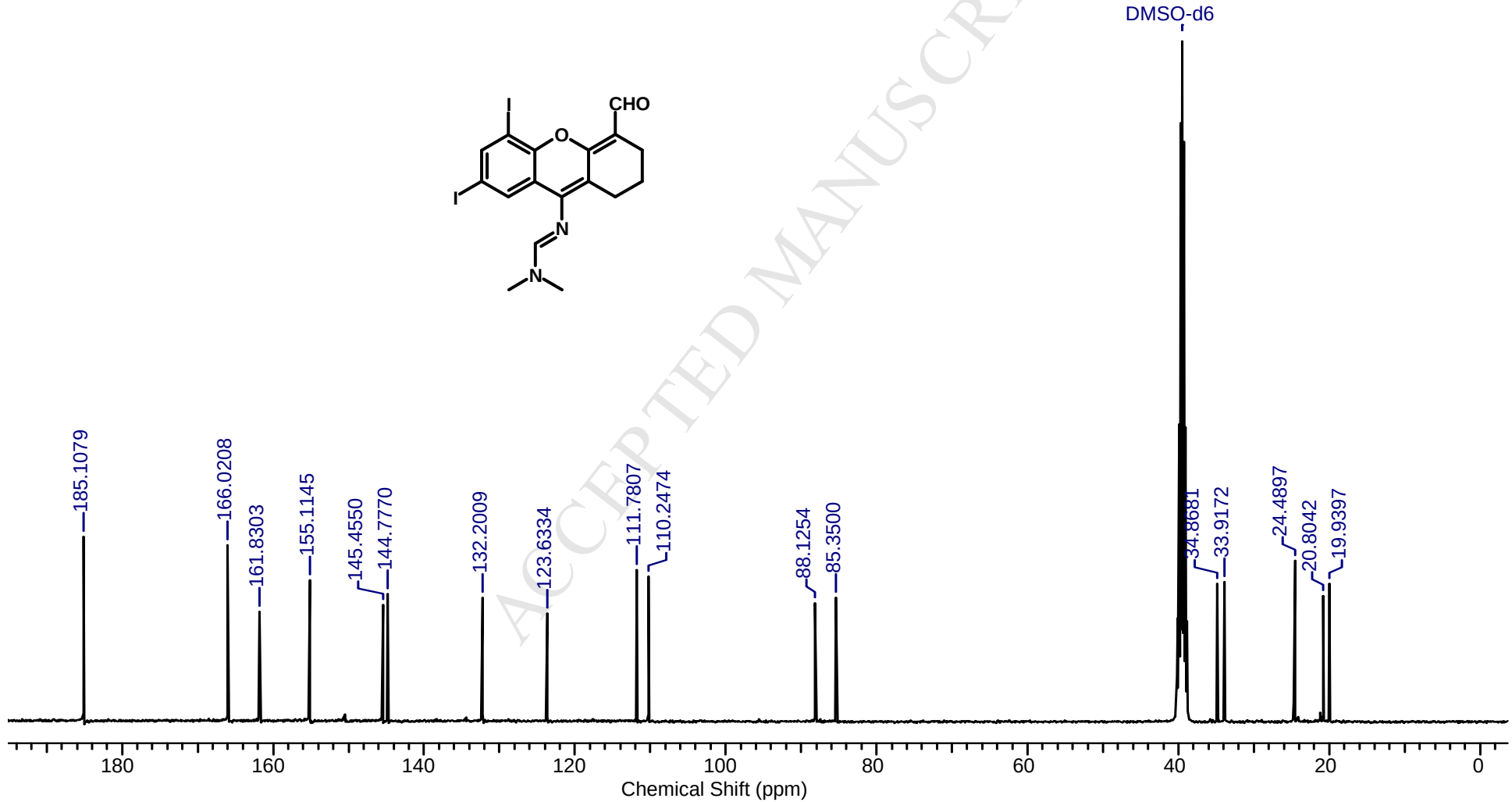
Mass spectrum EI of *N*'-(3-formyl-5,7-diisopropyl-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6d)**.



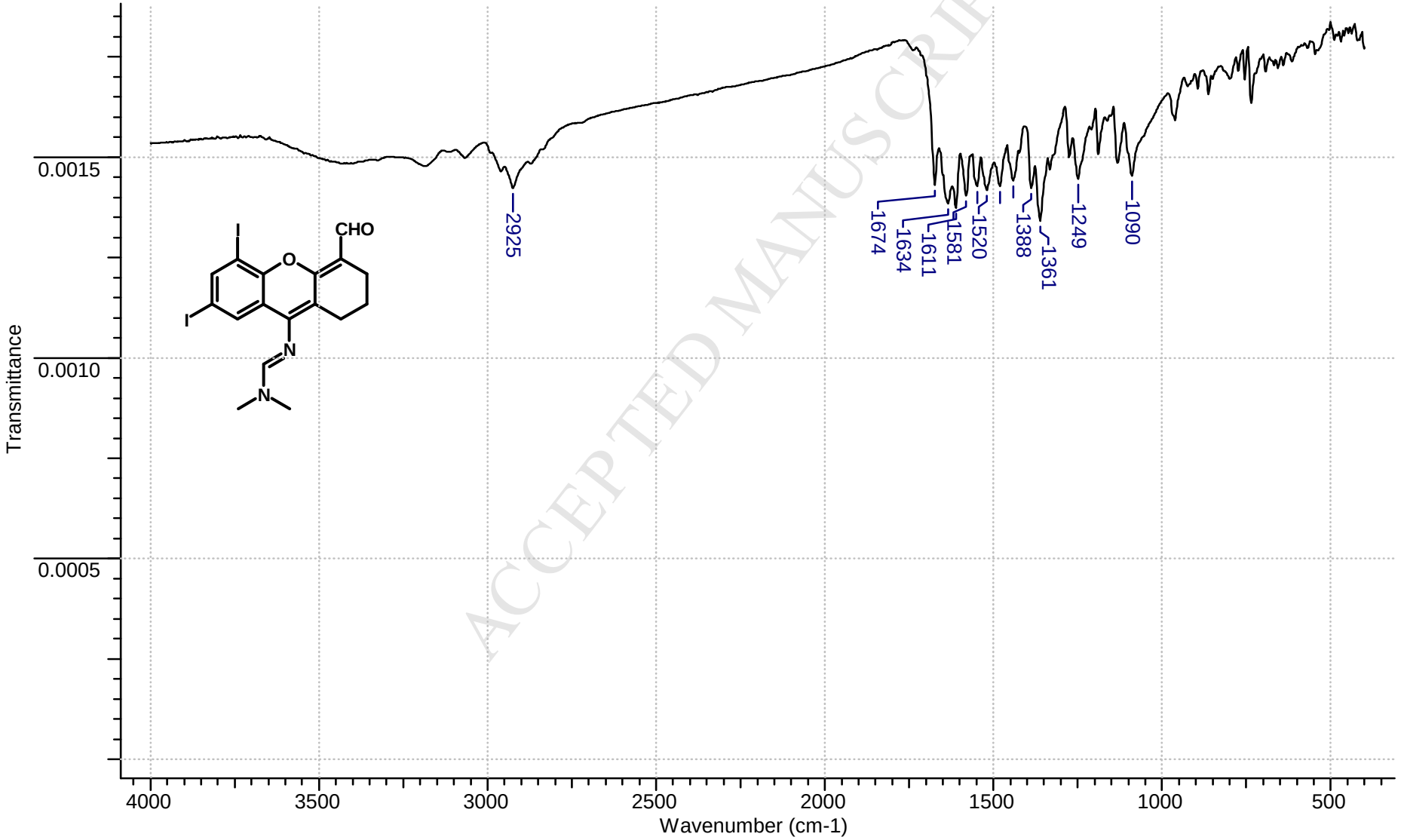
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*'-(4-formyl-5,7-diiodo-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6e)**.



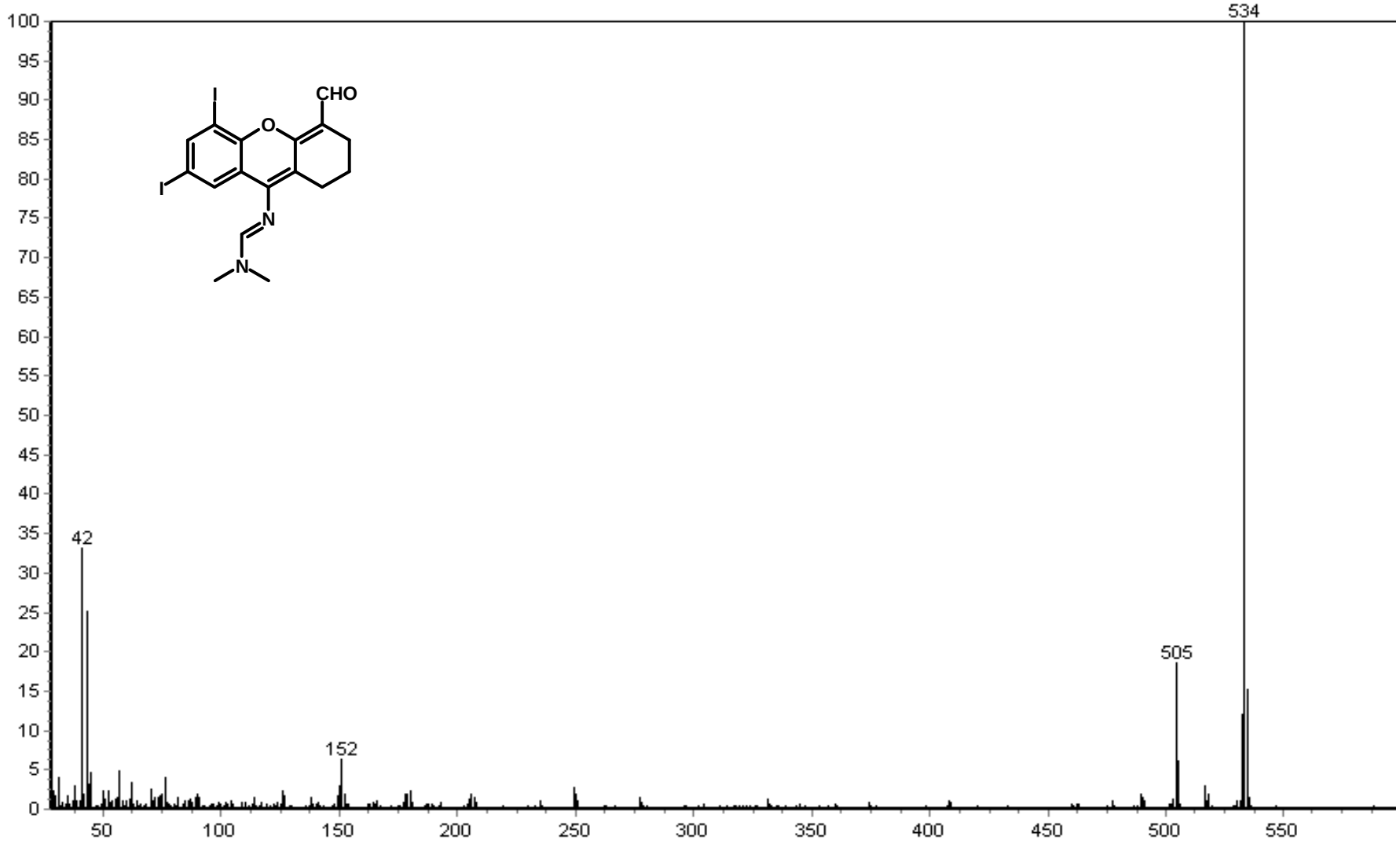
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*'-(4-formyl-5,7-diiodo-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6e)**.



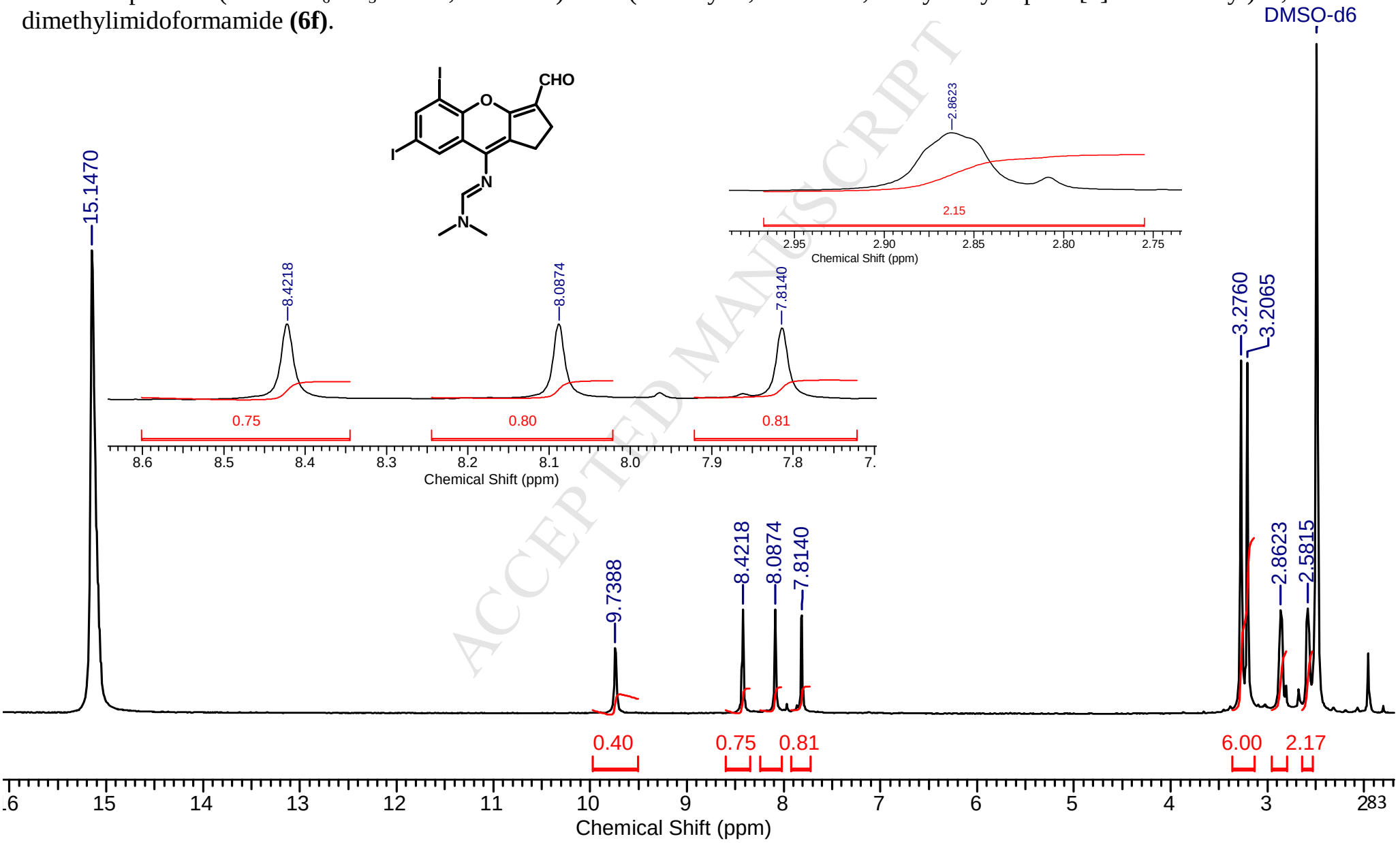
FTIR spectrum of *N*'-(4-formyl-5,7-diiodo-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6e)**.



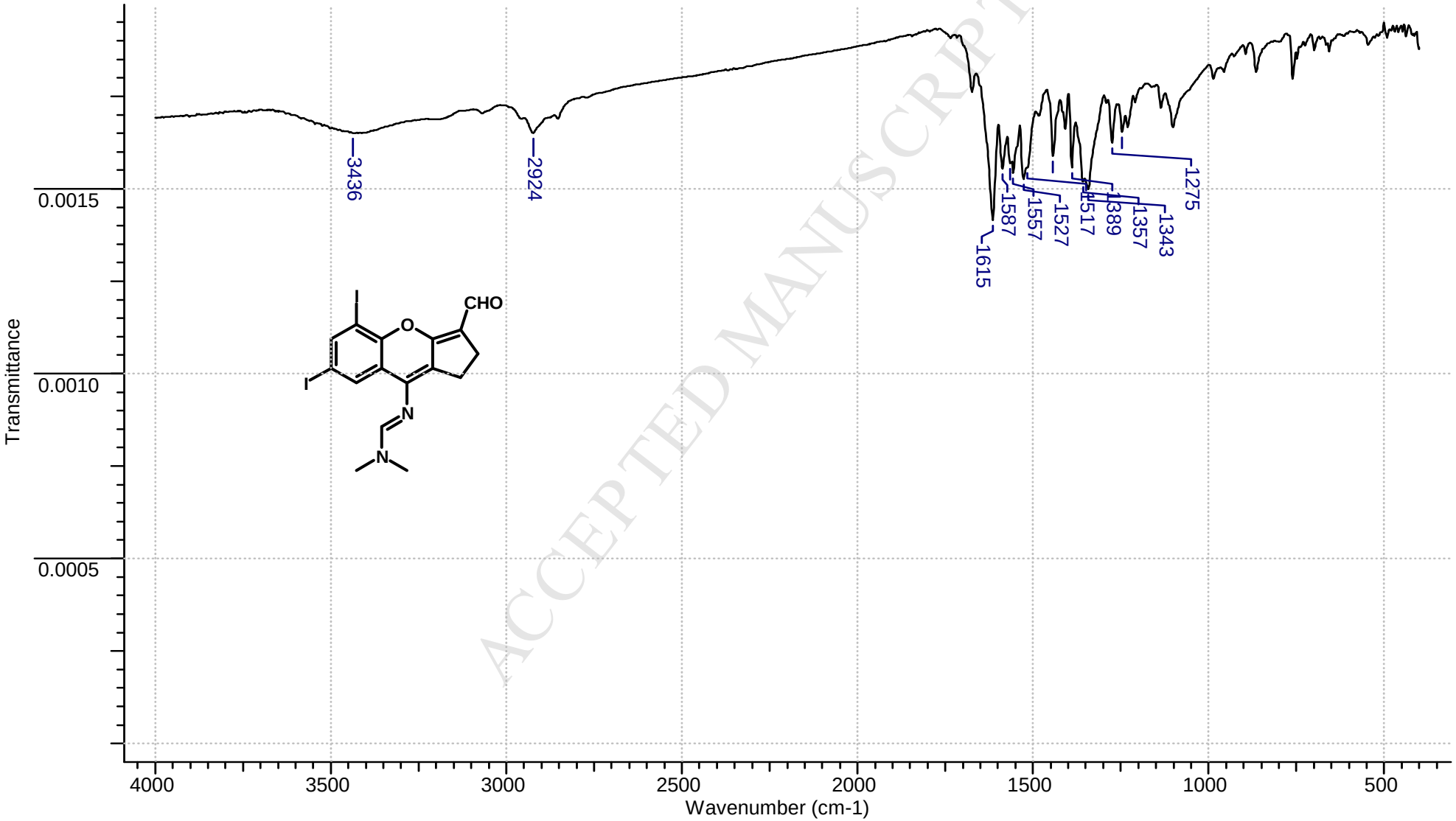
Mass spectrum (EI) of *N*'-(4-formyl-5,7-diiodo-2,3-dihydro-1*H*-xanthen-9-yl)-*N*,*N*-dimethylimidoformamide **(6e)**.



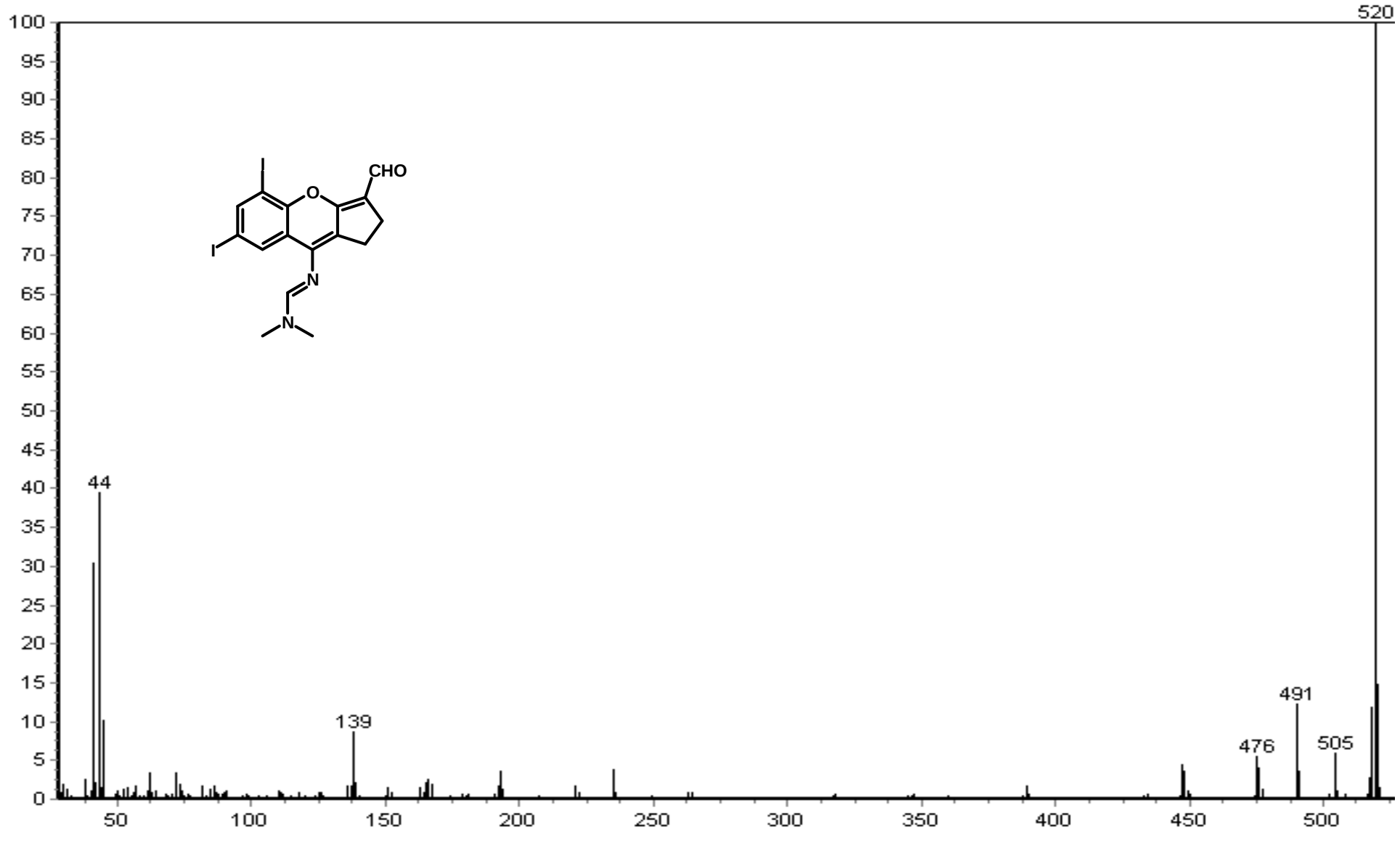
^{1}H NMR spectrum (DMSO-d_6/CF_3COOD, 400 MHz) of *N*'-(3-formyl-5,7-diiodo-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6f)**.



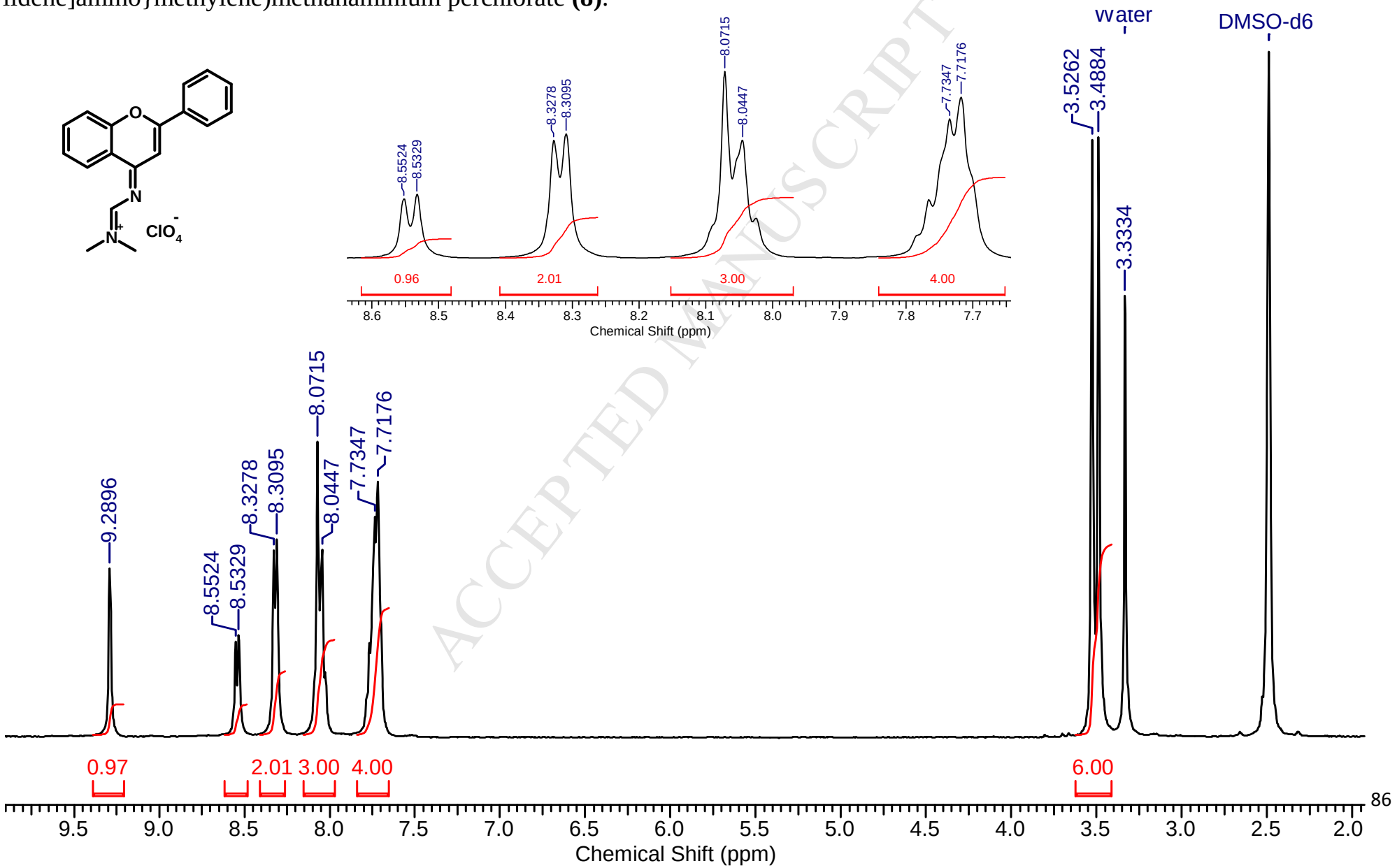
FTIR spectrum of *N*'-(3-formyl-5,7-diiodo-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6f)**.



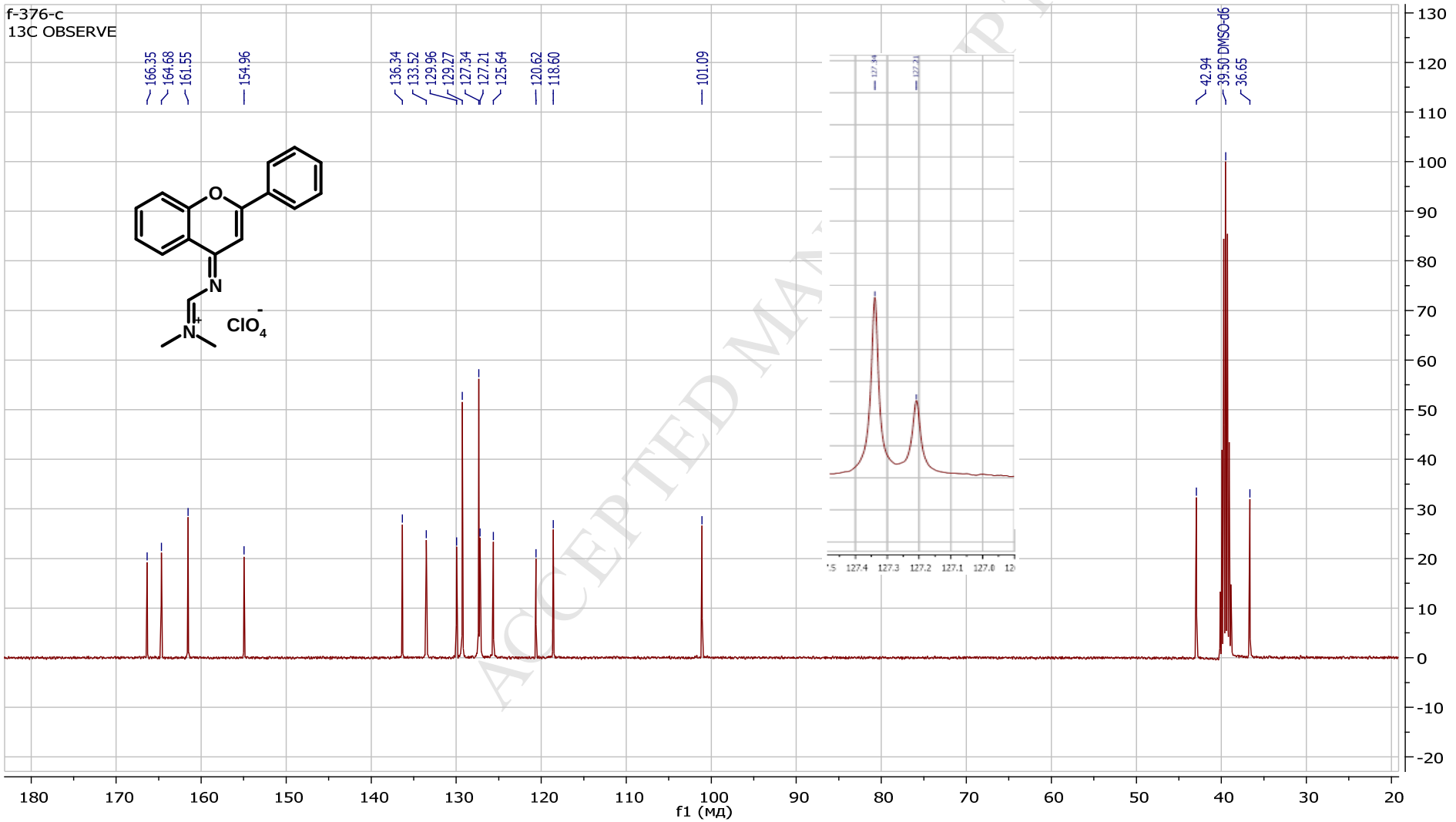
Mass spectrum (EI) of *N*'-(3-formyl-5,7-diiodo-1,2-dihydrocyclopenta[*b*]chromen-9-yl)-*N*,*N*-dimethylimidoformamide **(6f)**.



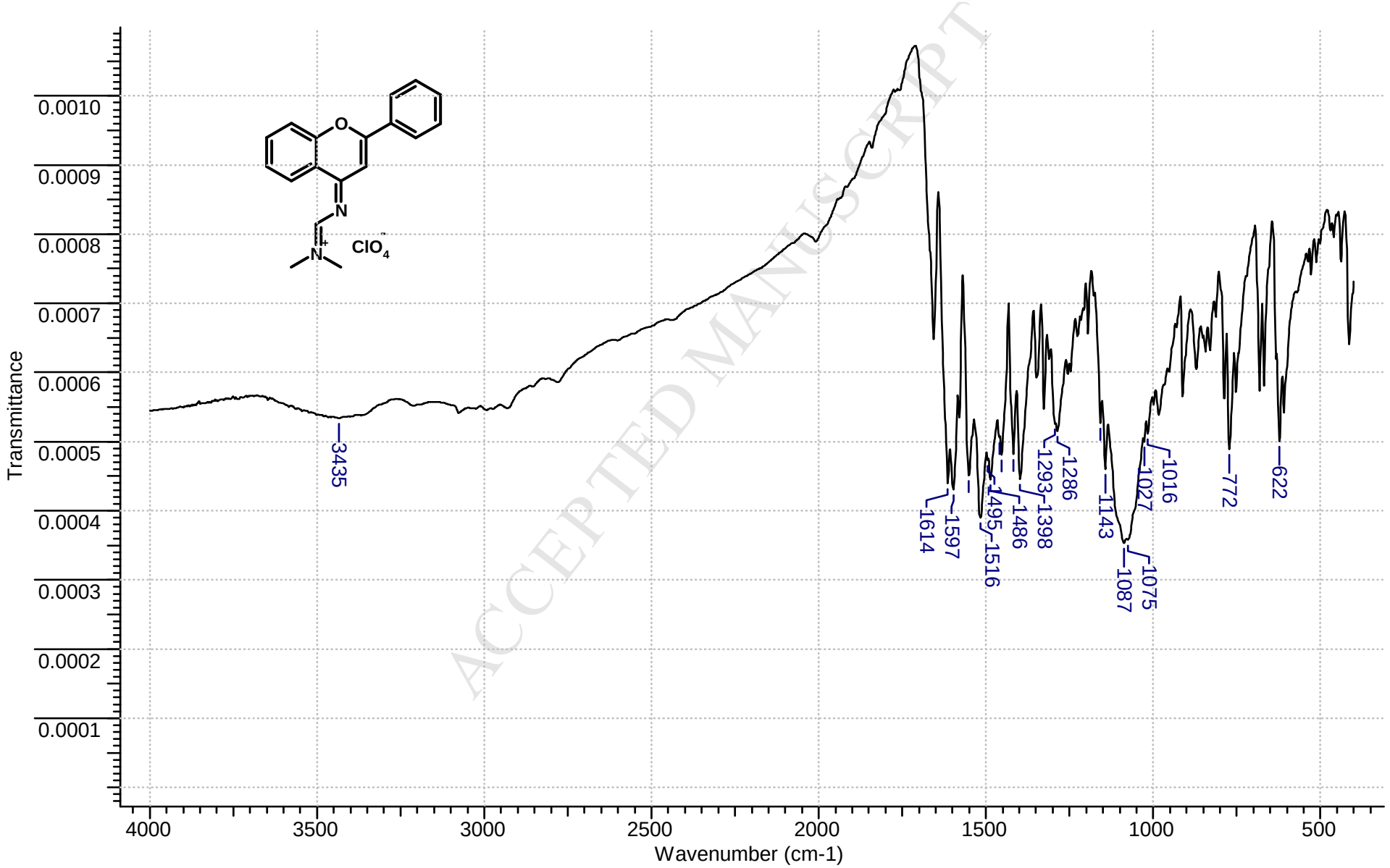
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of *N*-methyl-*N*-({[(4*Z*)-2-phenyl-4*H*-chromen-4-ylidene]amino}methylene)methanaminium perchlorate **(8)**.



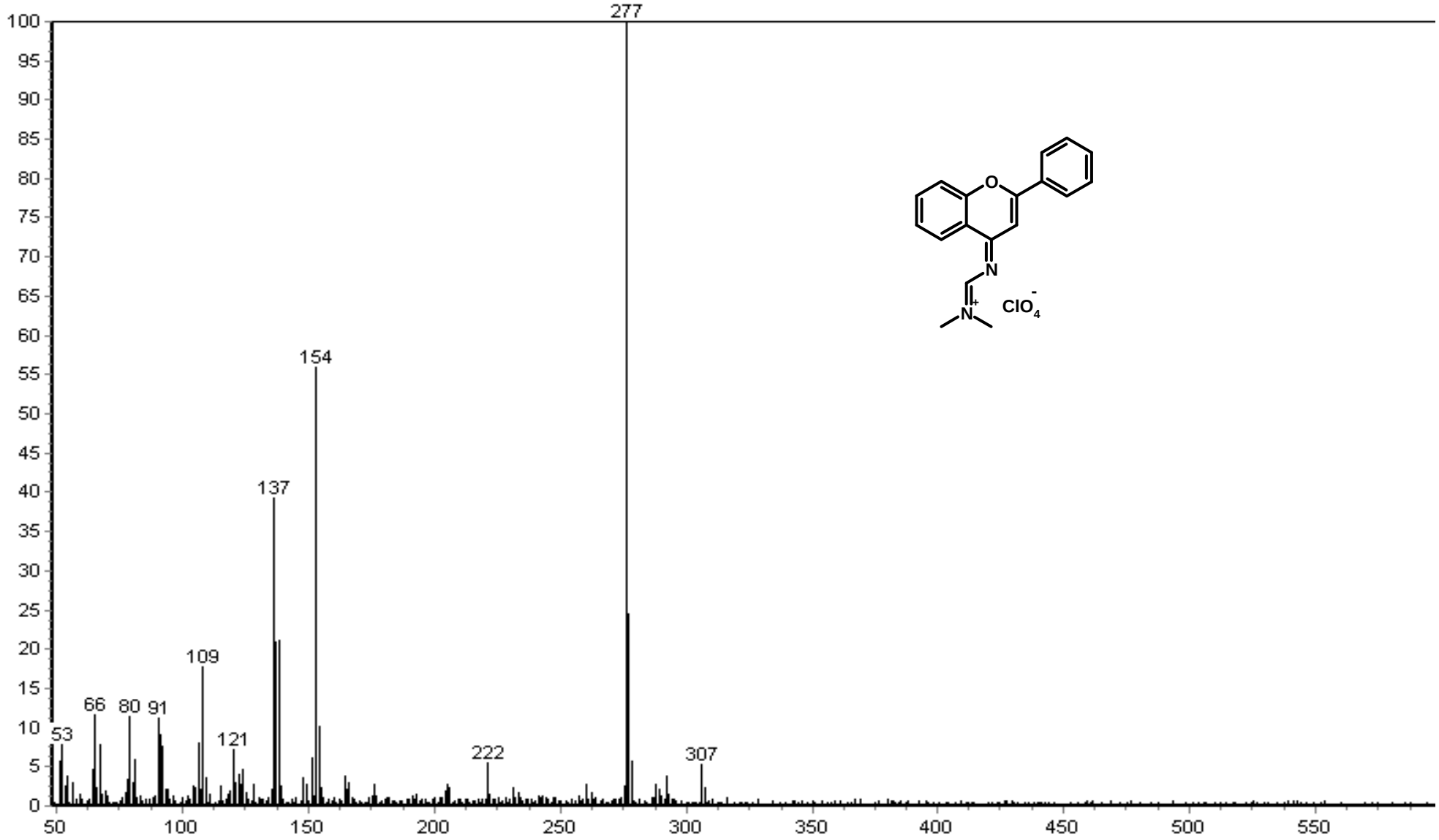
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*-methyl-*N*-({[(4*Z*)-2-phenyl-4*H*-chromen-4-ylidene]amino}methylene)methanaminium perchlorate **(8)**.



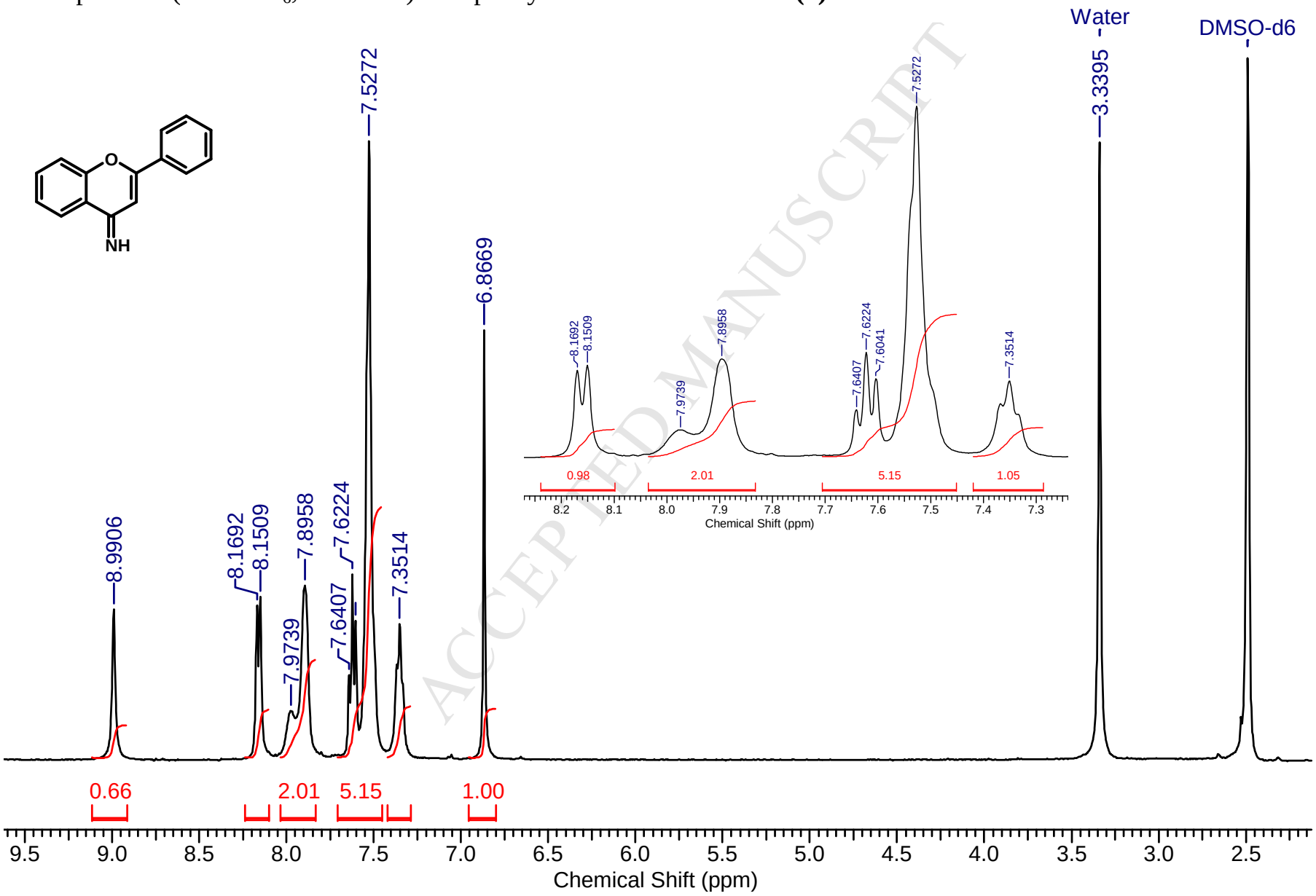
FTIR spectrum of *N*-methyl-*N*-({[(4*Z*)-2-phenyl-4*H*-chromen-4-ylidene]amino}methylene)methanaminium perchlorate **(8)**.



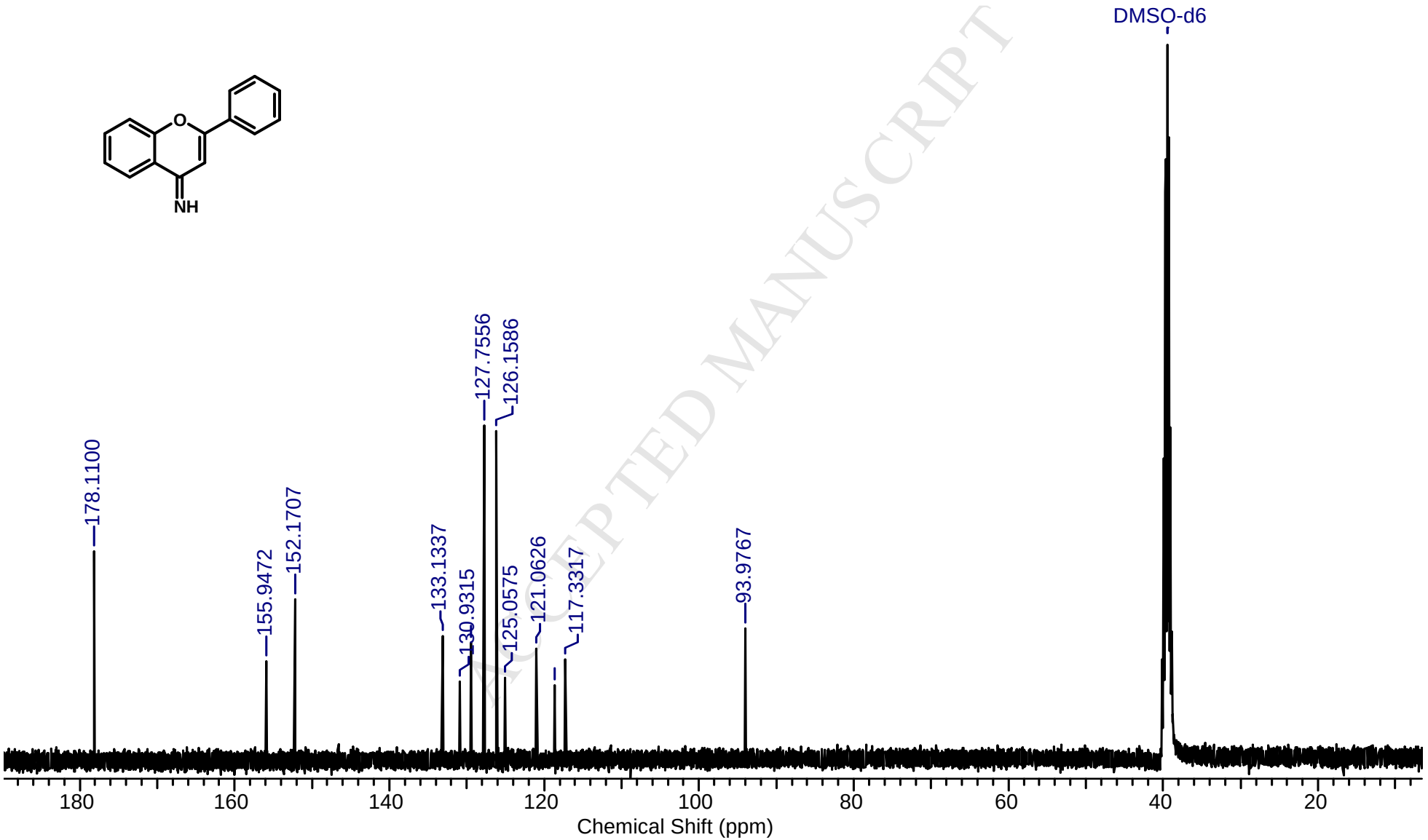
Mass spectrum (FAB) of *N*-methyl-*N*-({[(4*Z*)-2-phenyl-4*H*-chromen-4-ylidene]amino}methylene)methanaminium perchlorate **(8)**.



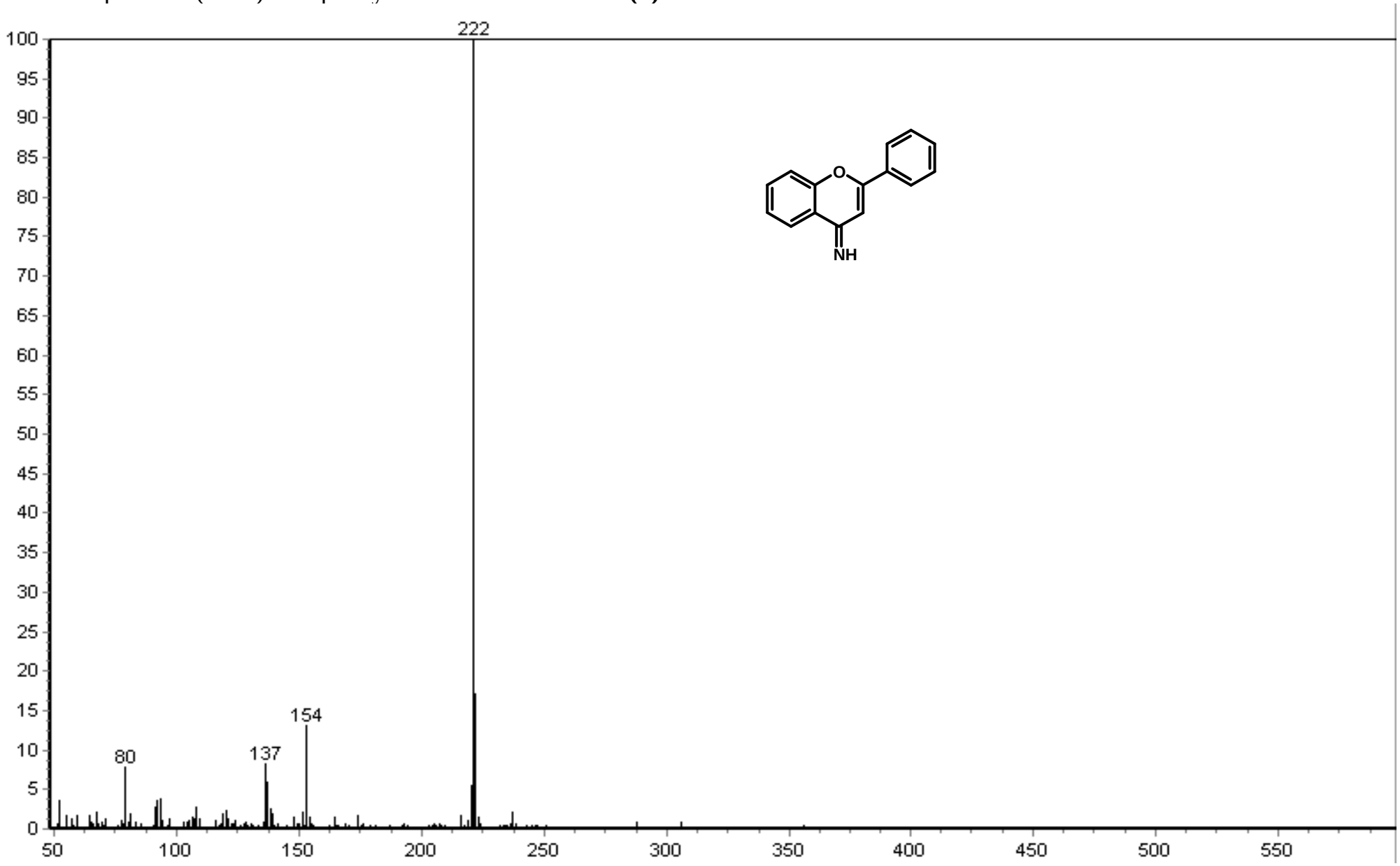
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of 2-phenyl-4*H*-chromen-4-imine **(9).**



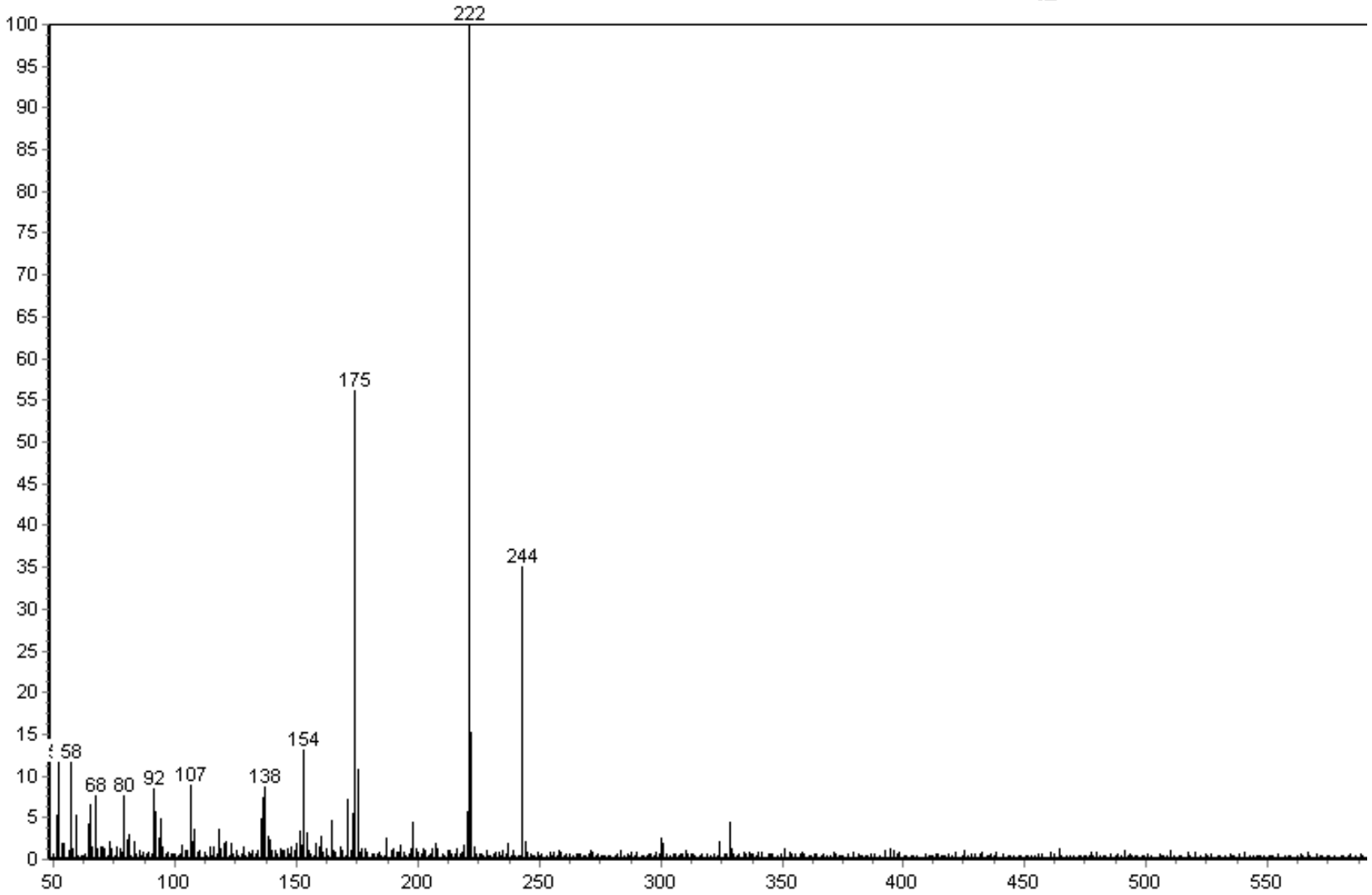
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of 2-phenyl-4*H*-chromen-4-imine **(9).**



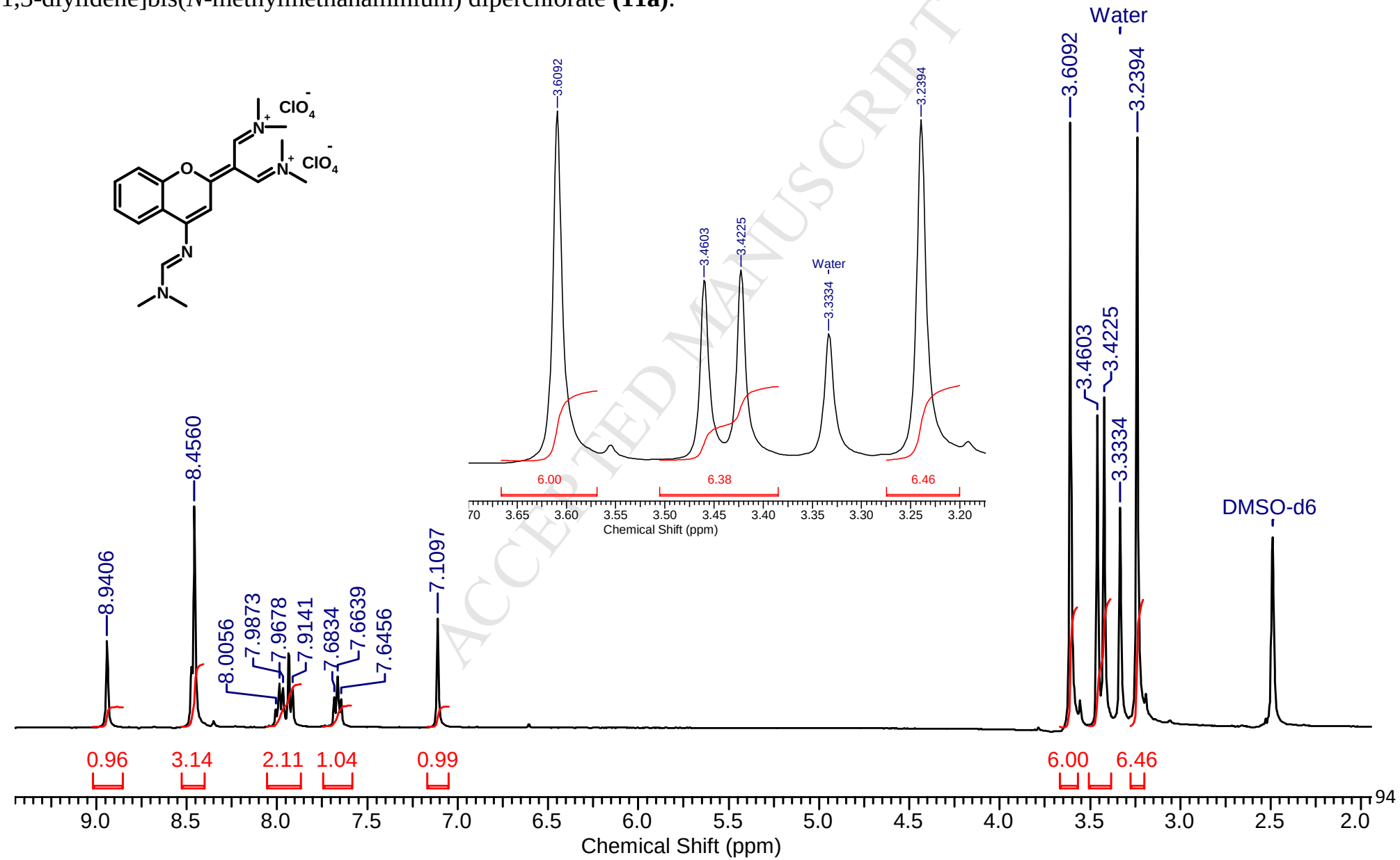
Mass spectrum (FAB) of 2-phenyl-4*H*-chromen-4-imine **(9).**



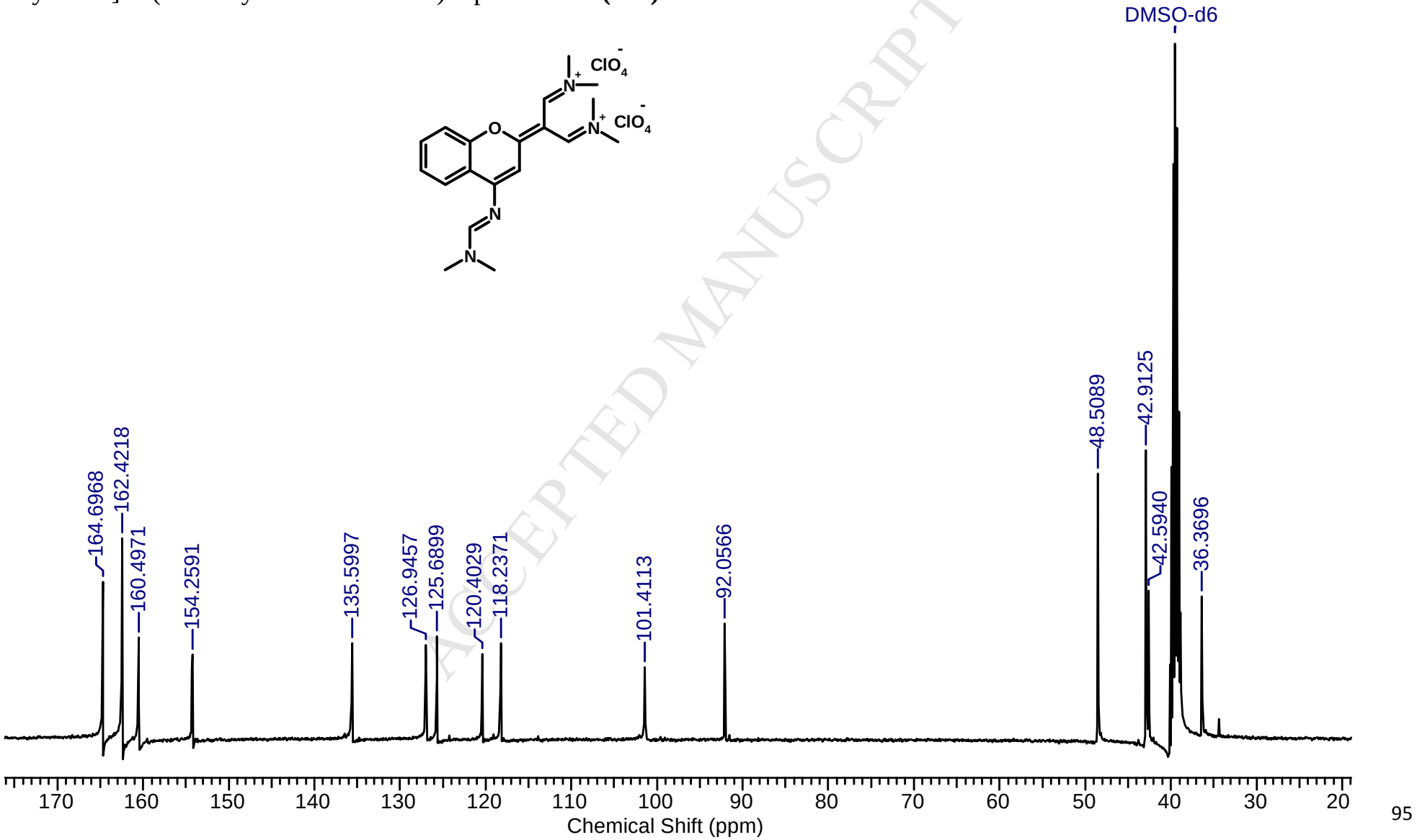
Mass spectrum (FAB+NaI) of 2-phenyl-4*H*-chromen-4-imine **(9).**



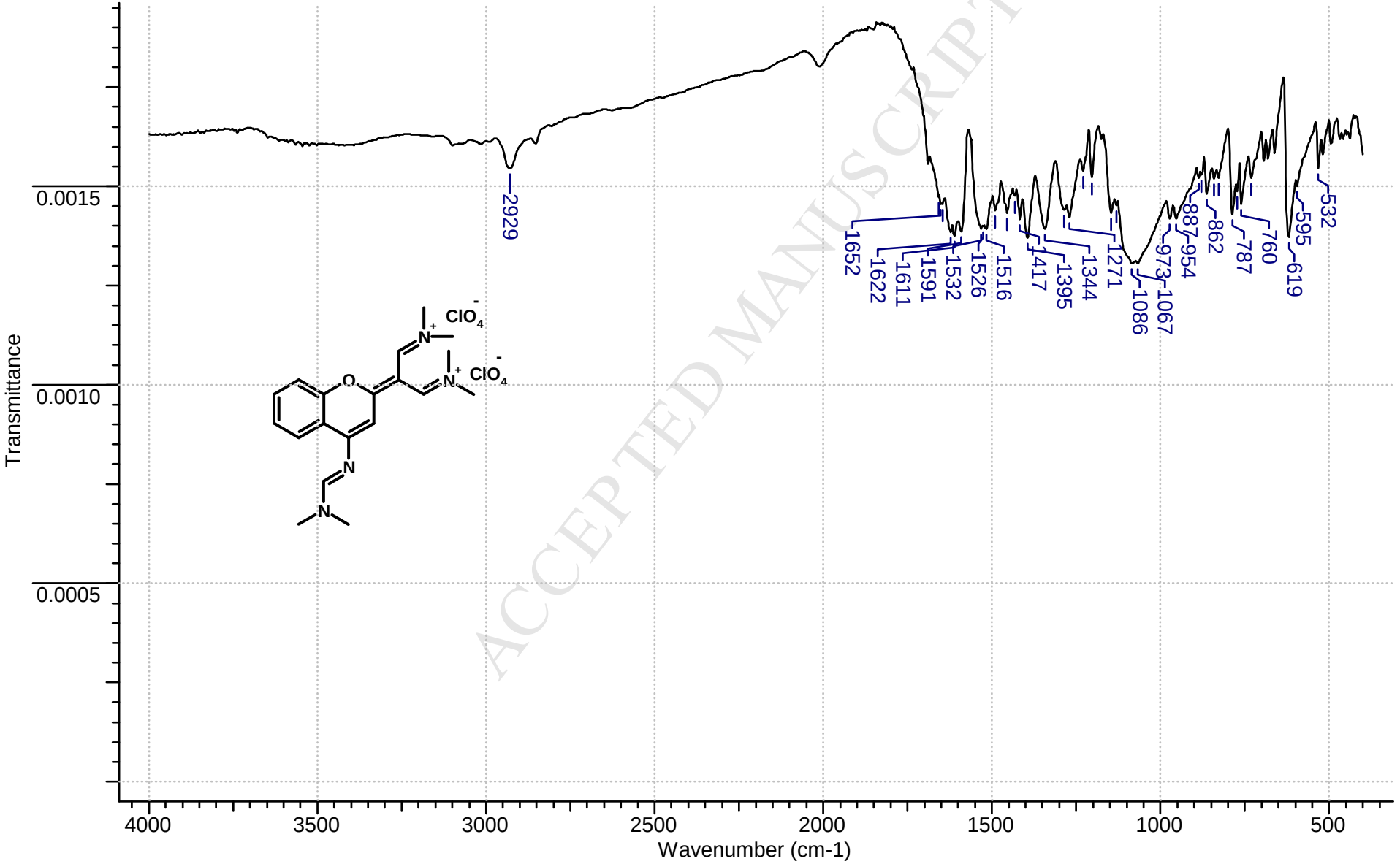
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of *N*,*N*'-[2-(4-{[(1*E*)-(dimethylamino)methylene]amino}-2*H*-chromen-2-ylidene)propane-1,3-diylidene]bis(*N*-methylmethanaminium) diperchlorate **(11a)**.



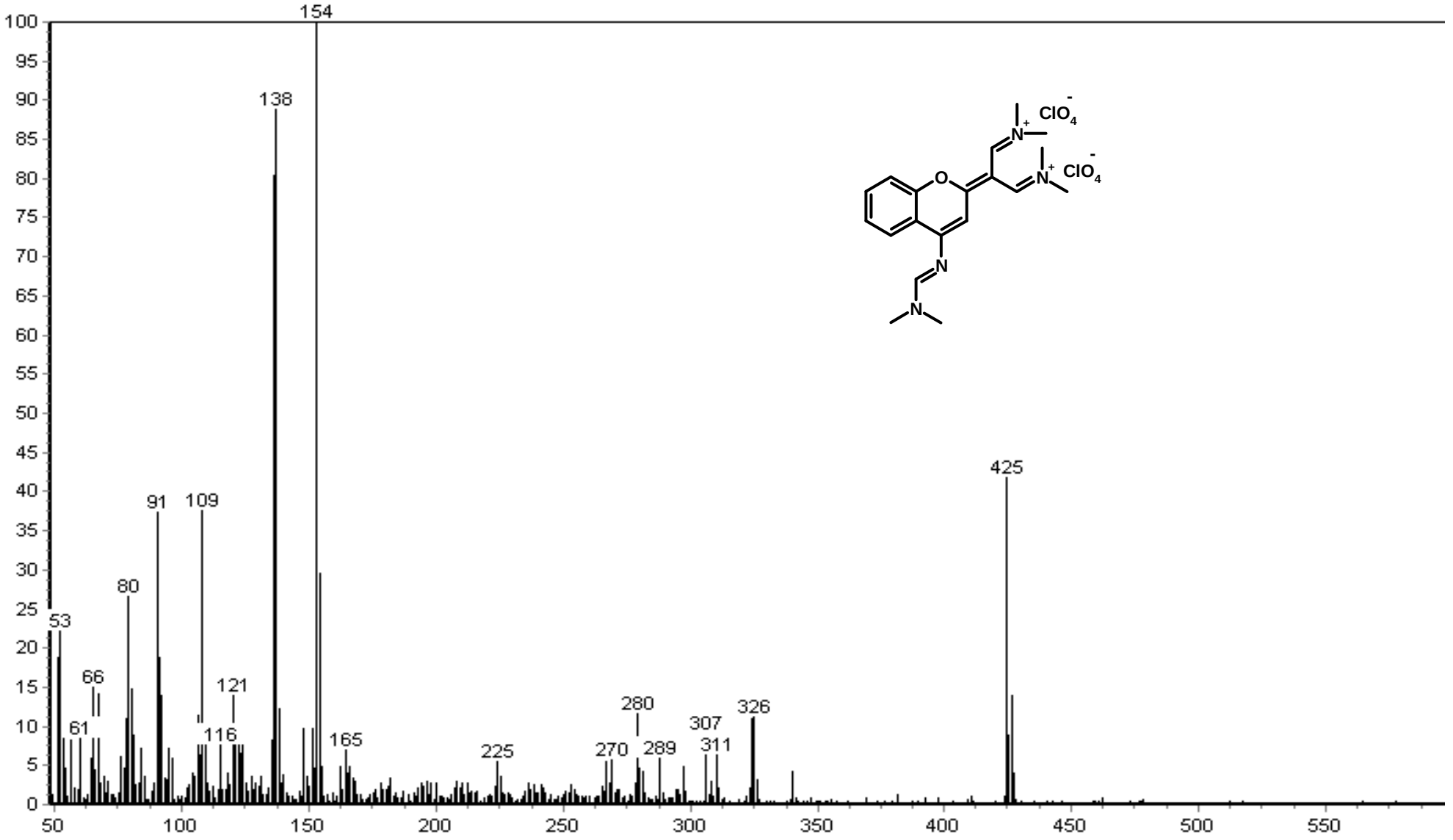
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of *N*,*N*'-[2-(4-{[(1*E*)-(dimethylamino)methylene]amino}-2*H*-chromen-2-ylidene)propane-1,3-diylidene]bis(*N*-methylmethanaminium) diperchlorate **(11a)**.



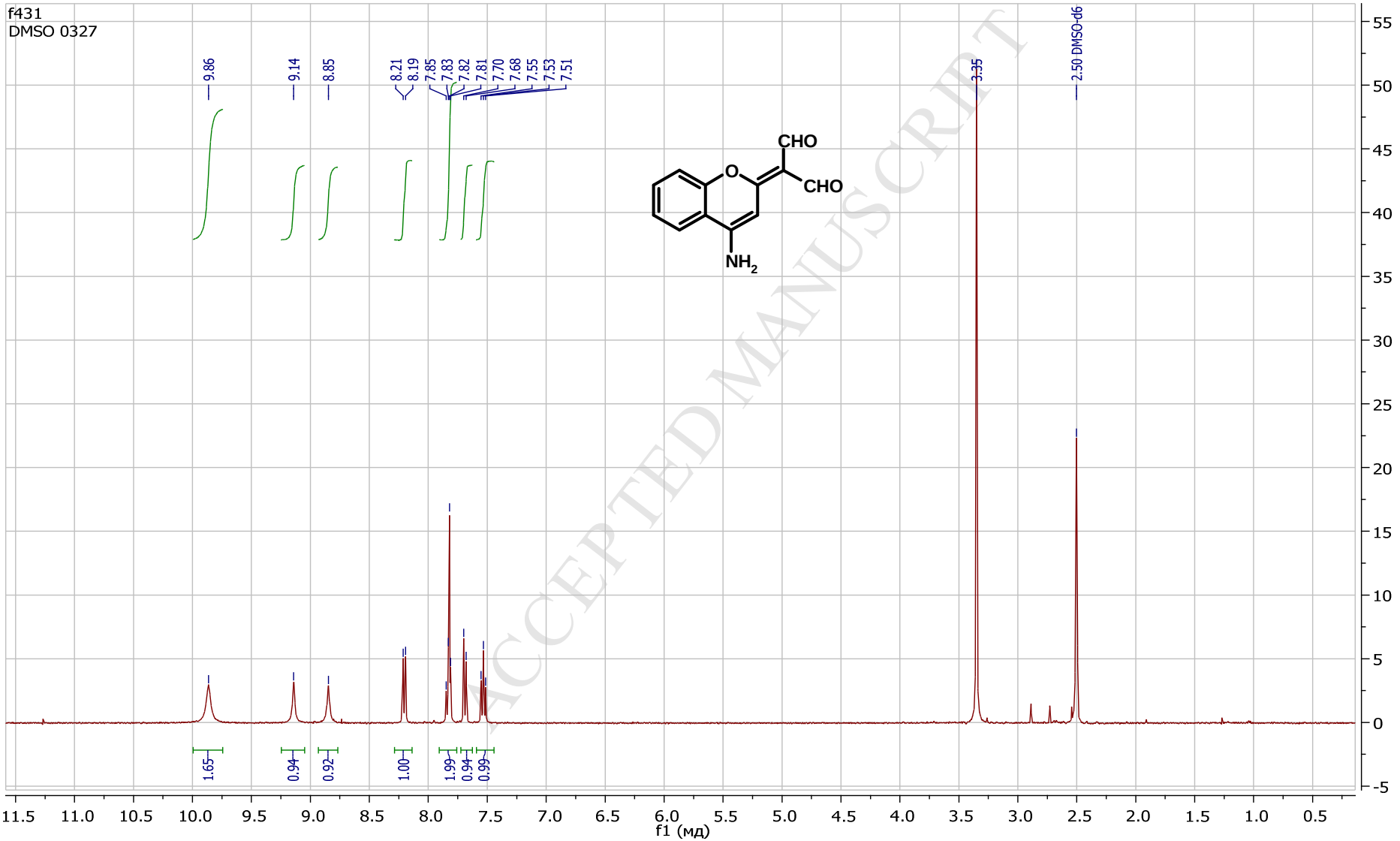
FTIR spectrum of *N*,*N*'-[2-(4-{[(1*E*)-(dimethylamino)methylene]amino}-2*H*-chromen-2-ylidene)propane-1,3-diylidene]bis(*N*-methylmethanaminium) diperchlorate **(11a)**.



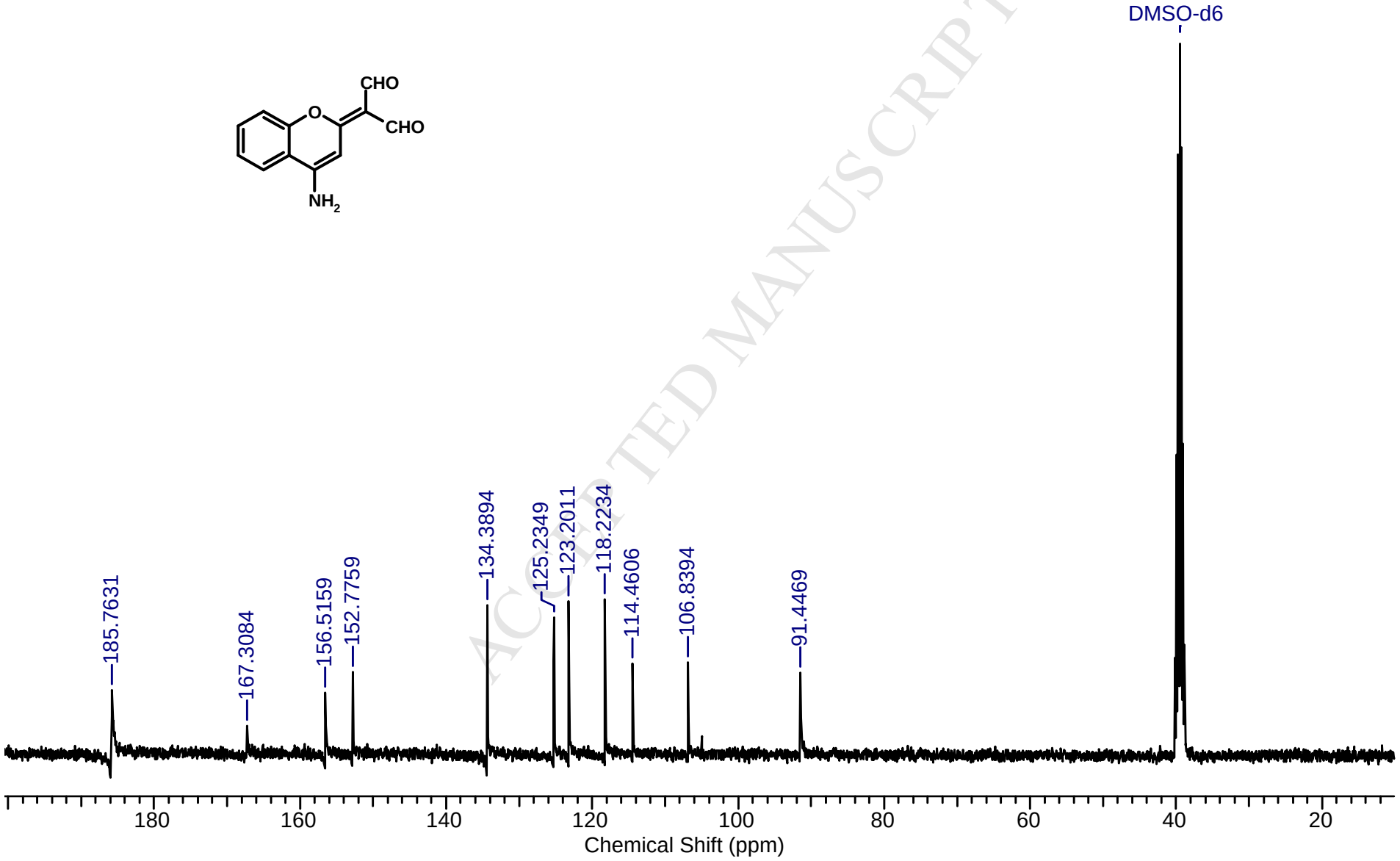
Mass spectrum (FAB) of *N*,*N*'-[2-(4-{[(1*E*)-(dimethylamino)methylene]amino}-2*H*-chromen-2-ylidene)propane-1,3-diylidene]bis(*N*-methylmethanaminium) diperchlorate **(11a)**.



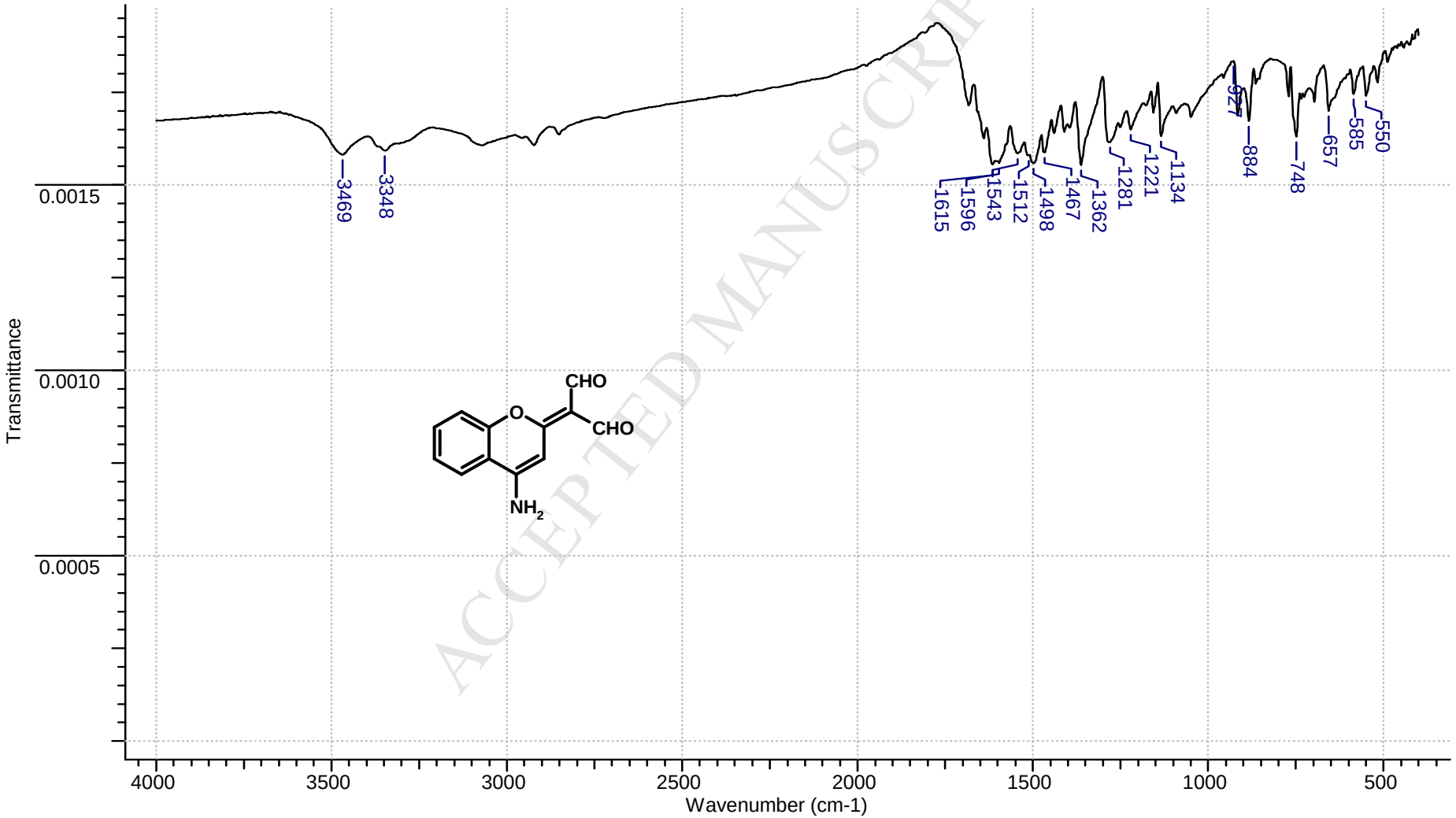
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of (4-amino-2*H*-chromen-2-ylidene)malonaldehyde **(12a)**.



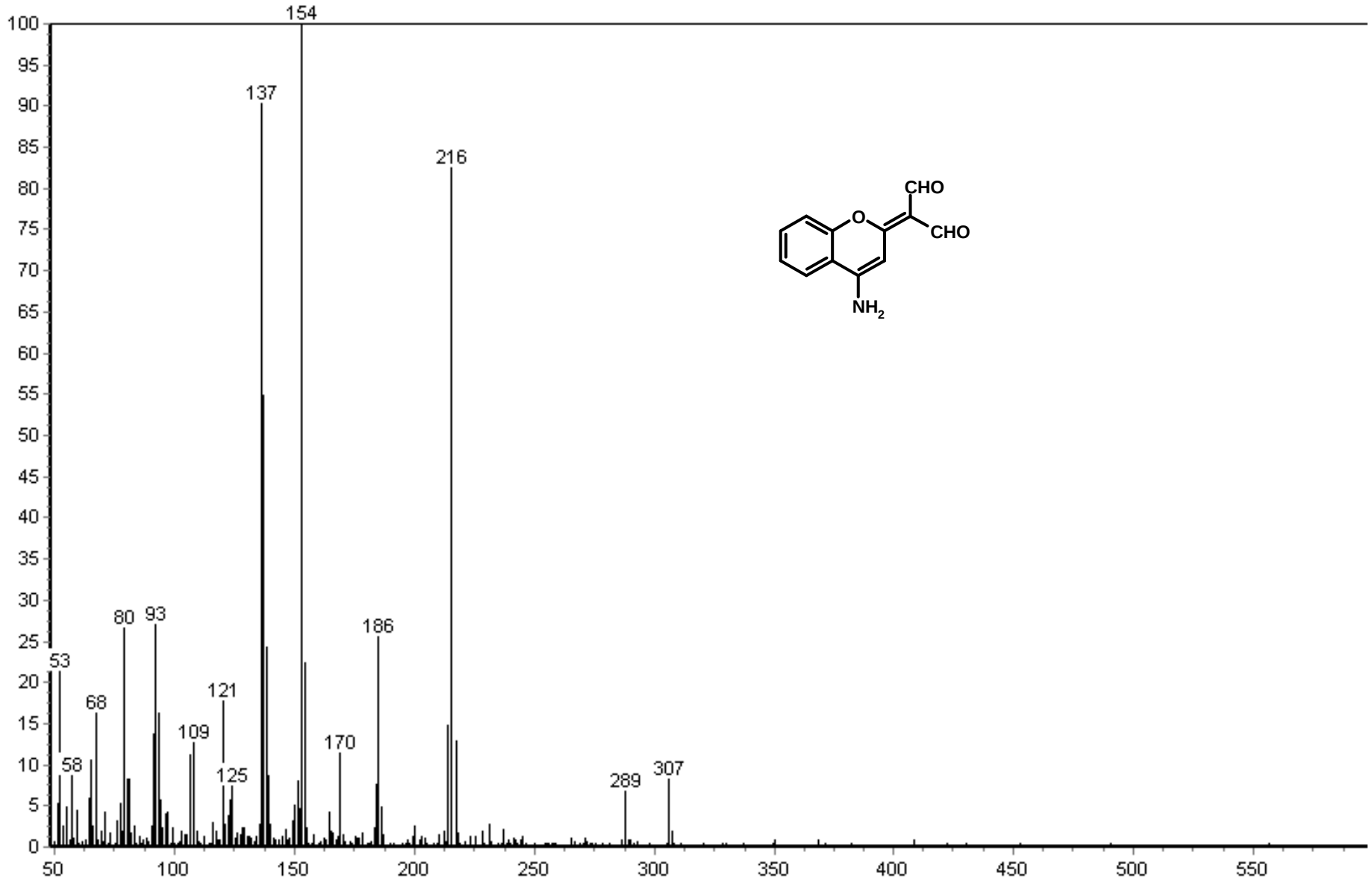
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of (4-amino-2*H*-chromen-2-ylidene)malonaldehyde **(12a)**.



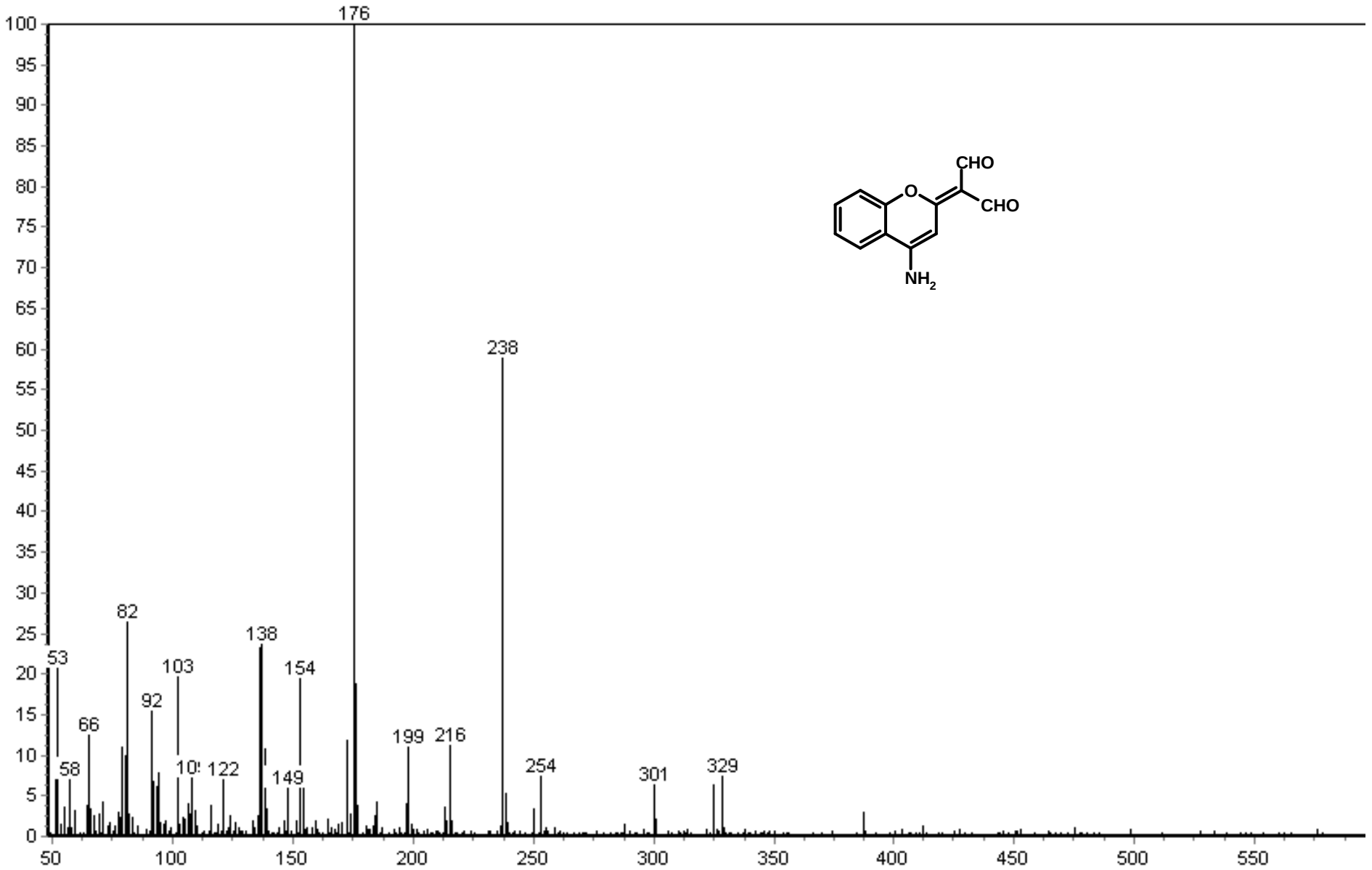
FTIR spectrum of (4-amino-2*H*-chromen-2-ylidene)malonaldehyde **(12a)**.



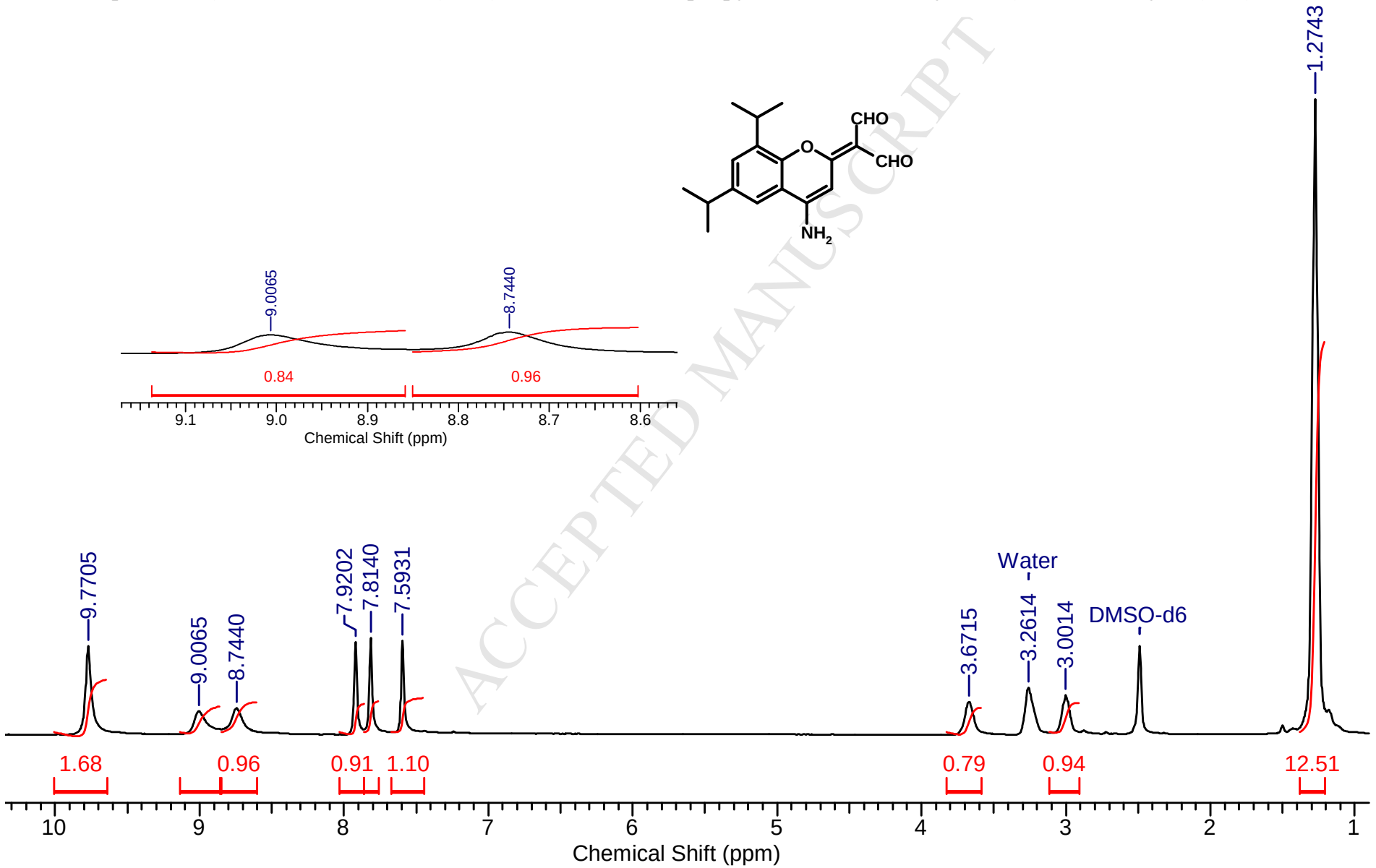
Mass spectrum (FAB) of (4-amino-2*H*-chromen-2-ylidene)malonaldehyde **(12a)**.



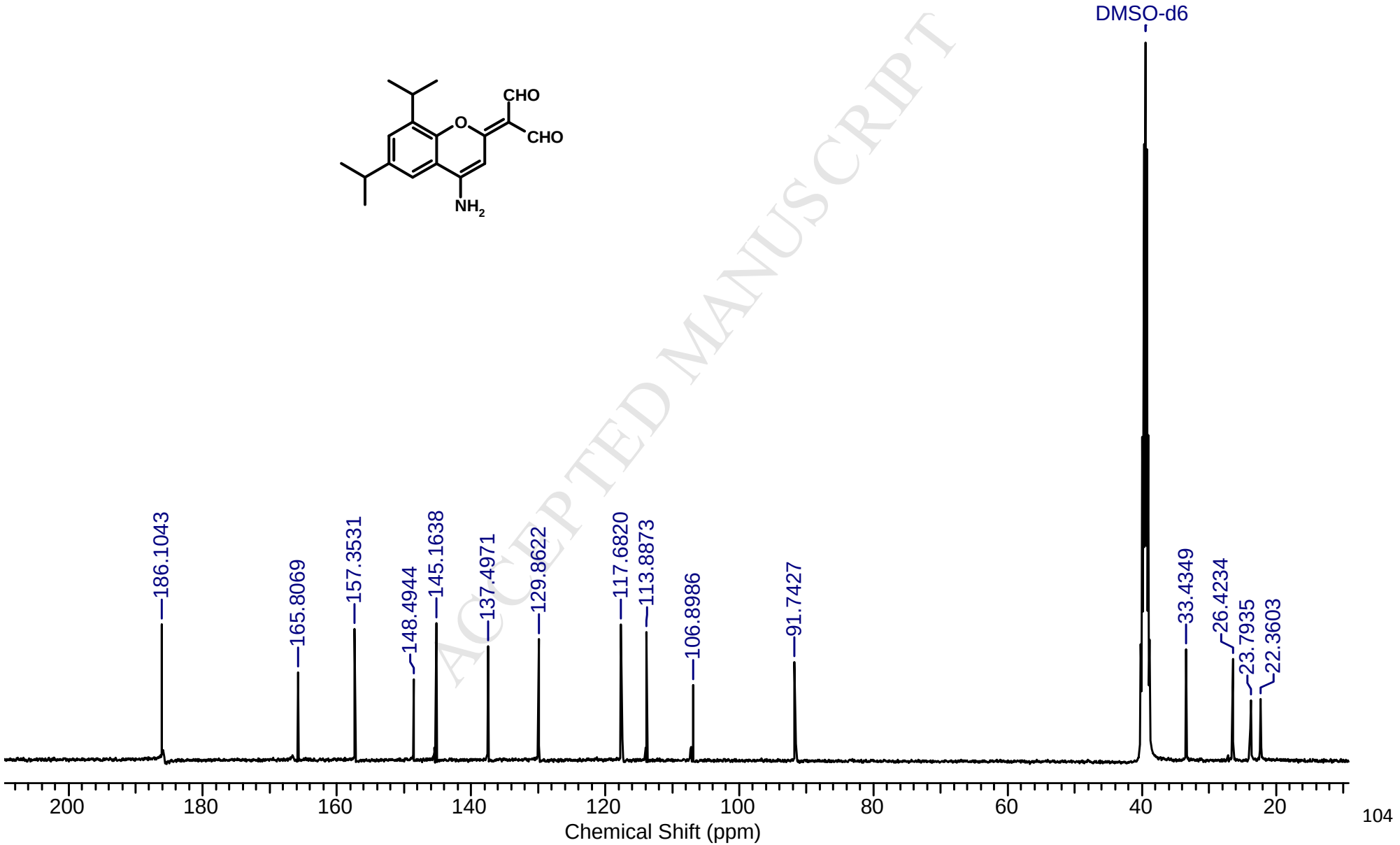
Mass spectrum (FAB+NaI) of (4-amino-2*H*-chromen-2-ylidene)malonaldehyde **(12a)**.



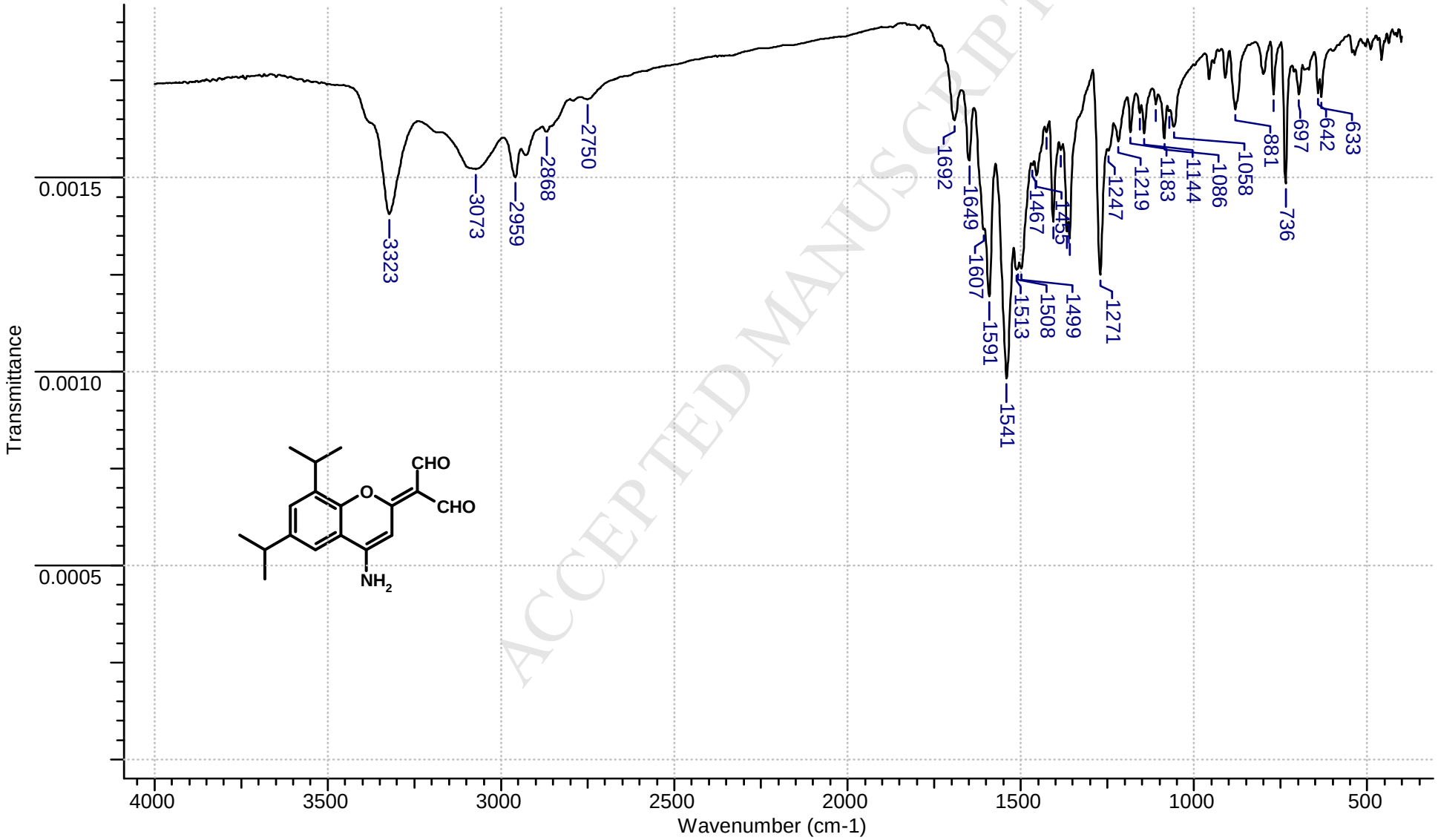
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of (4-amino-6,8-diisopropyl-2*H*-chromen-2-ylidene)malonaldehyde **(12b)**.



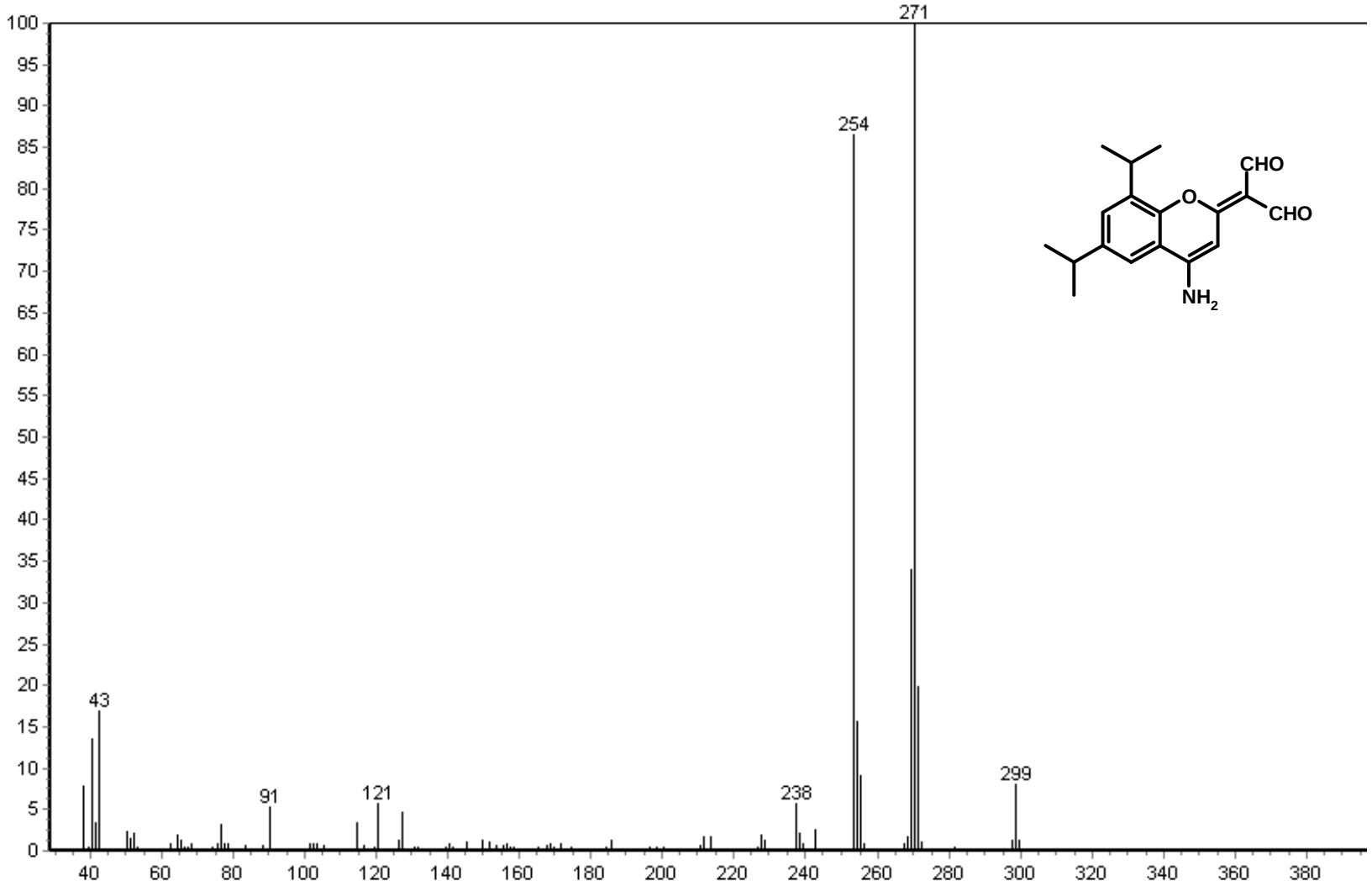
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of (4-amino-6,8-diisopropyl-2*H*-chromen-2-ylidene)malonaldehyde **(12b)**.



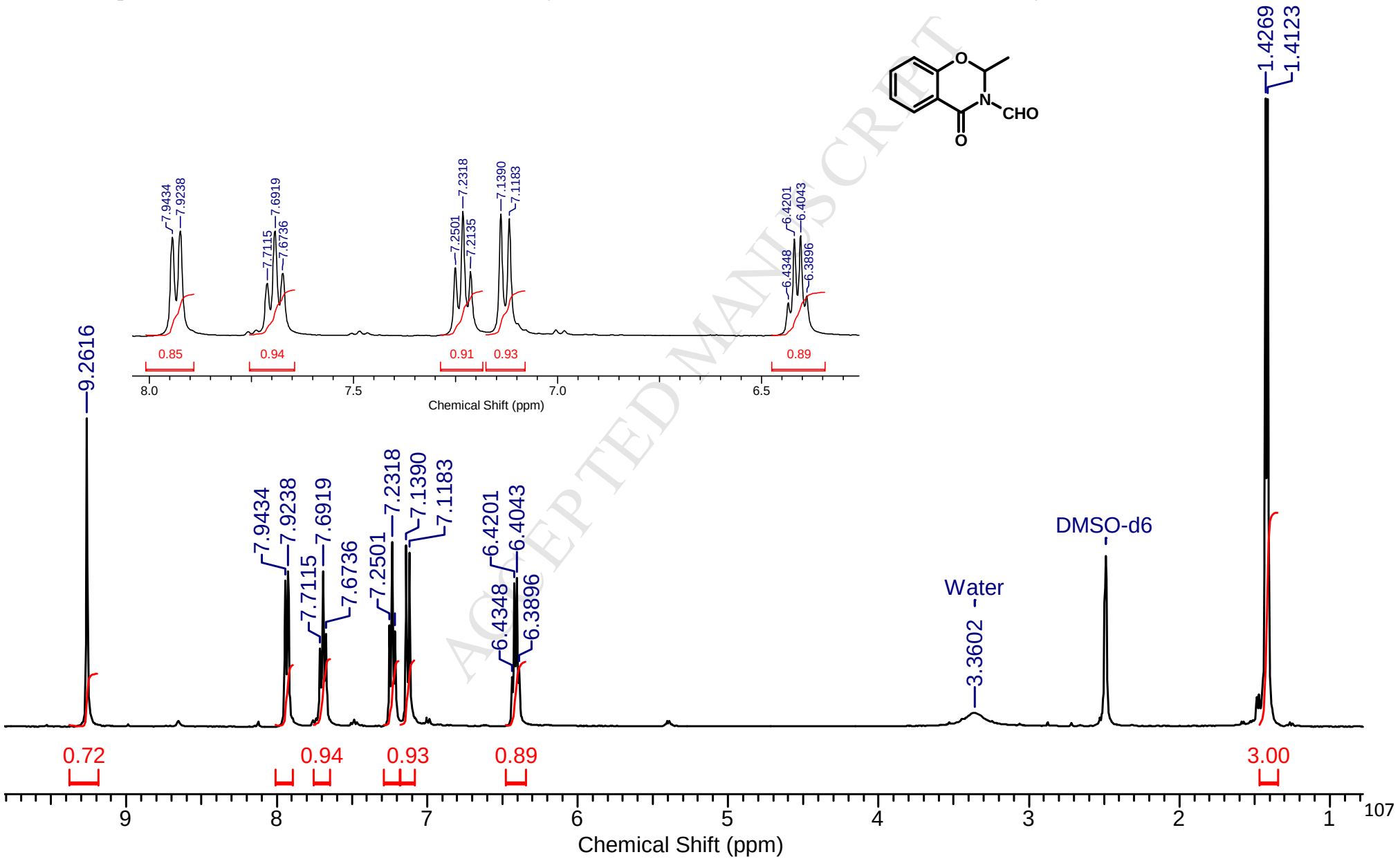
FTIR spectrum of (4-amino-6,8-diisopropyl-2*H*-chromen-2-ylidene)malonaldehyde **(12b)**.



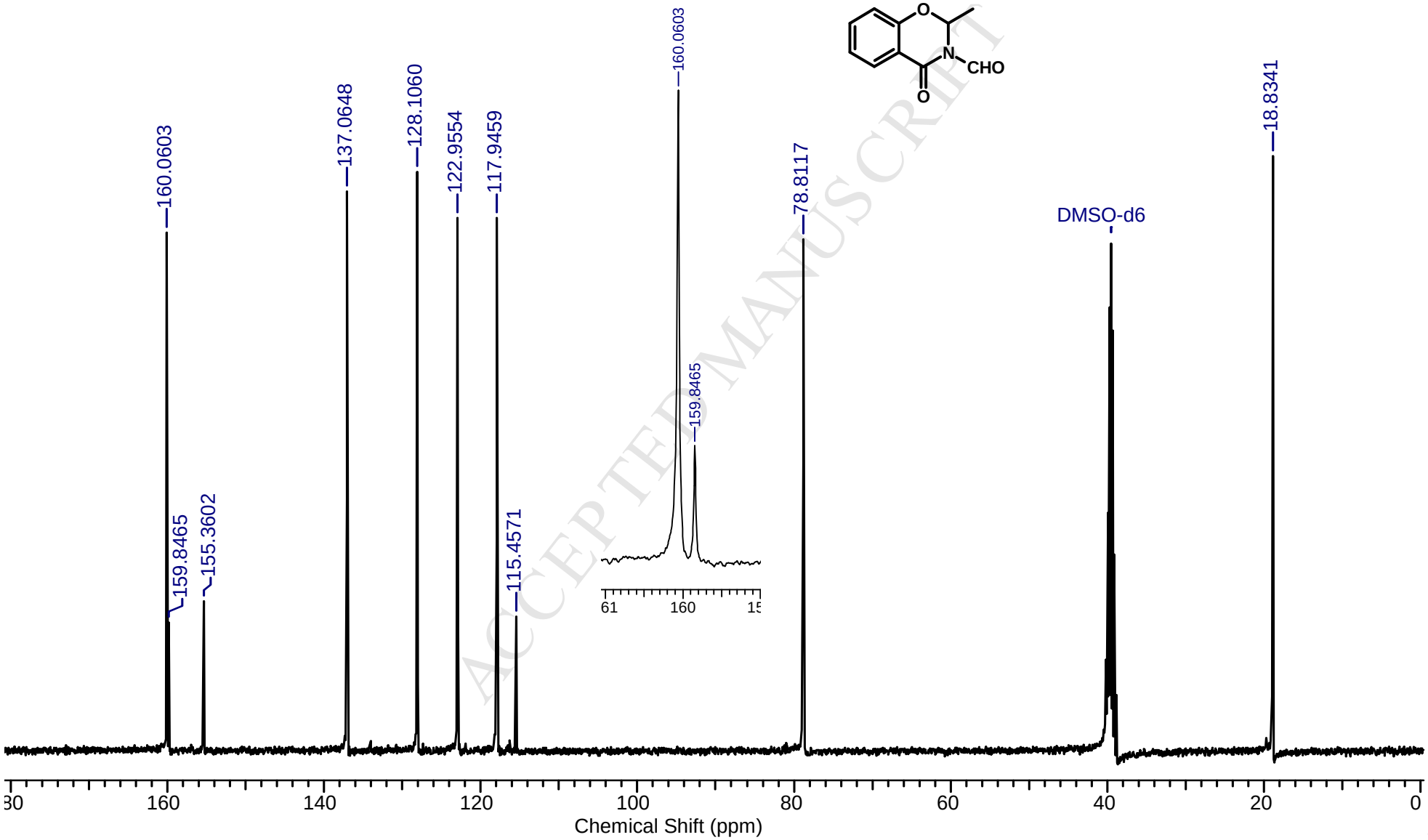
Mass spectrum (EI) of (4-amino-6,8-diisopropyl-2*H*-chromen-2-ylidene)malonaldehyde **(12b)**.



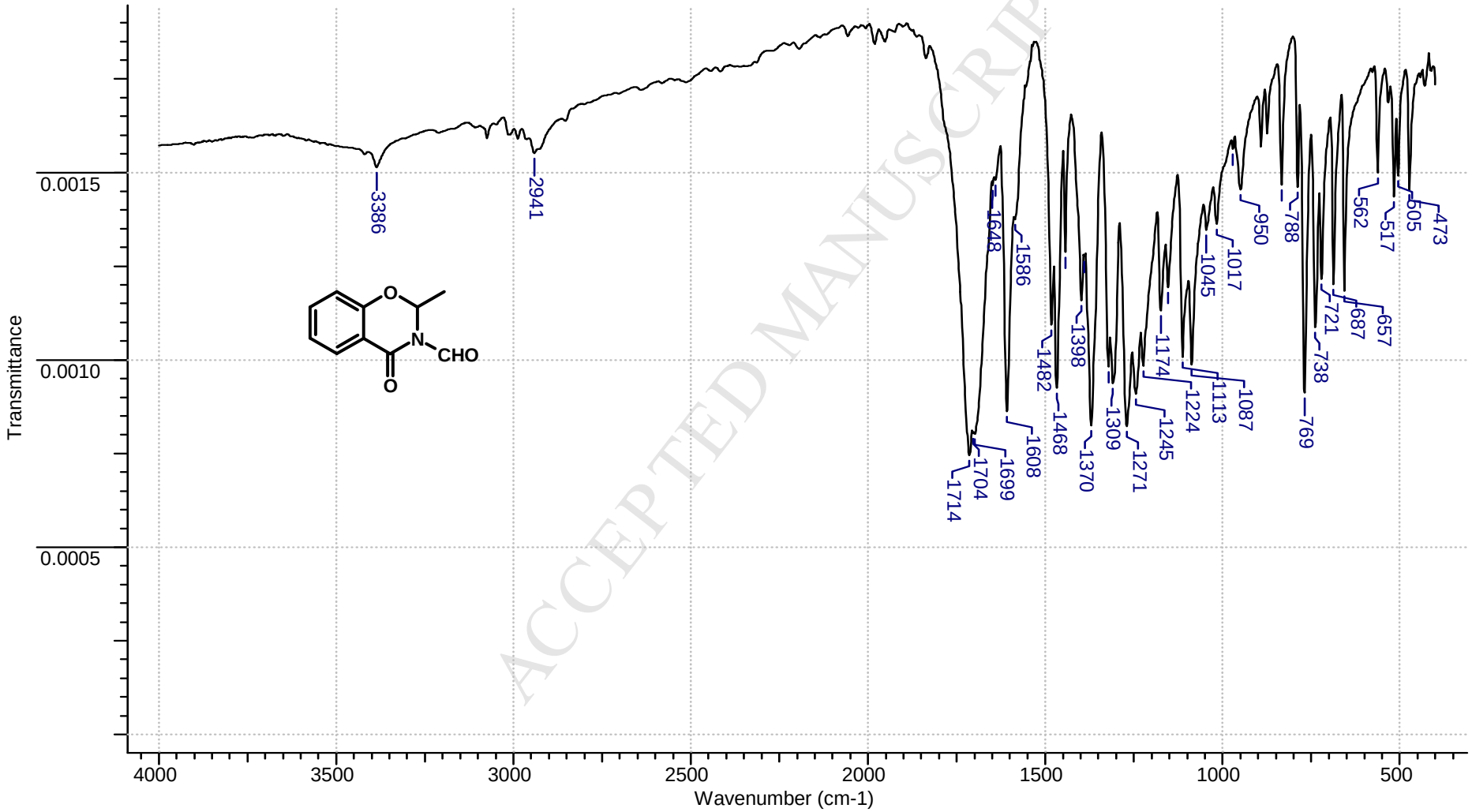
^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-methyl-4-oxo-2*H*-1,3-benzoxazine-3(4*H*)-carbaldehyde **(14)**.



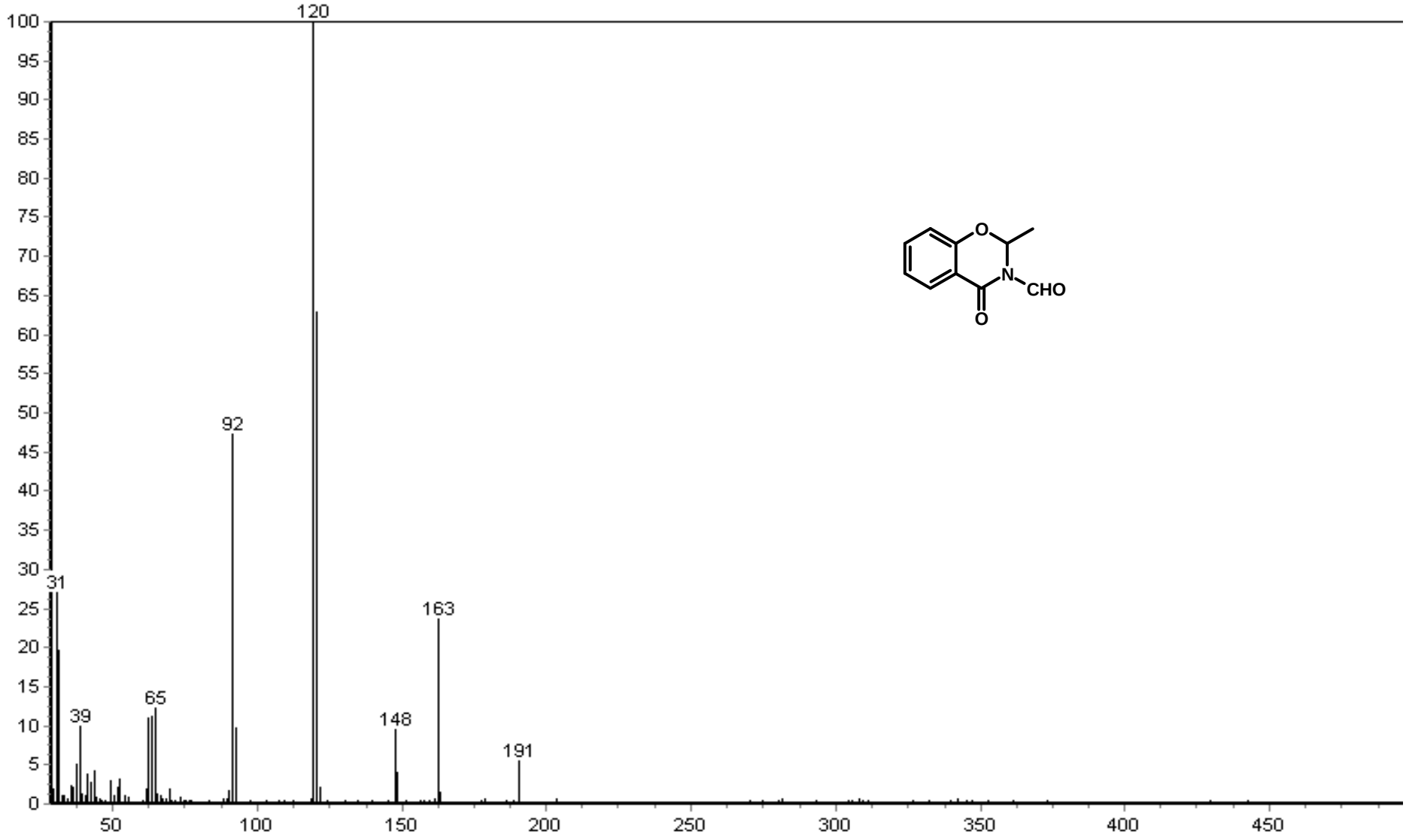
^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz) of 2-methyl-4-oxo-2*H*-1,3-benzoxazine-3(4*H*)-carbaldehyde **(14)**.



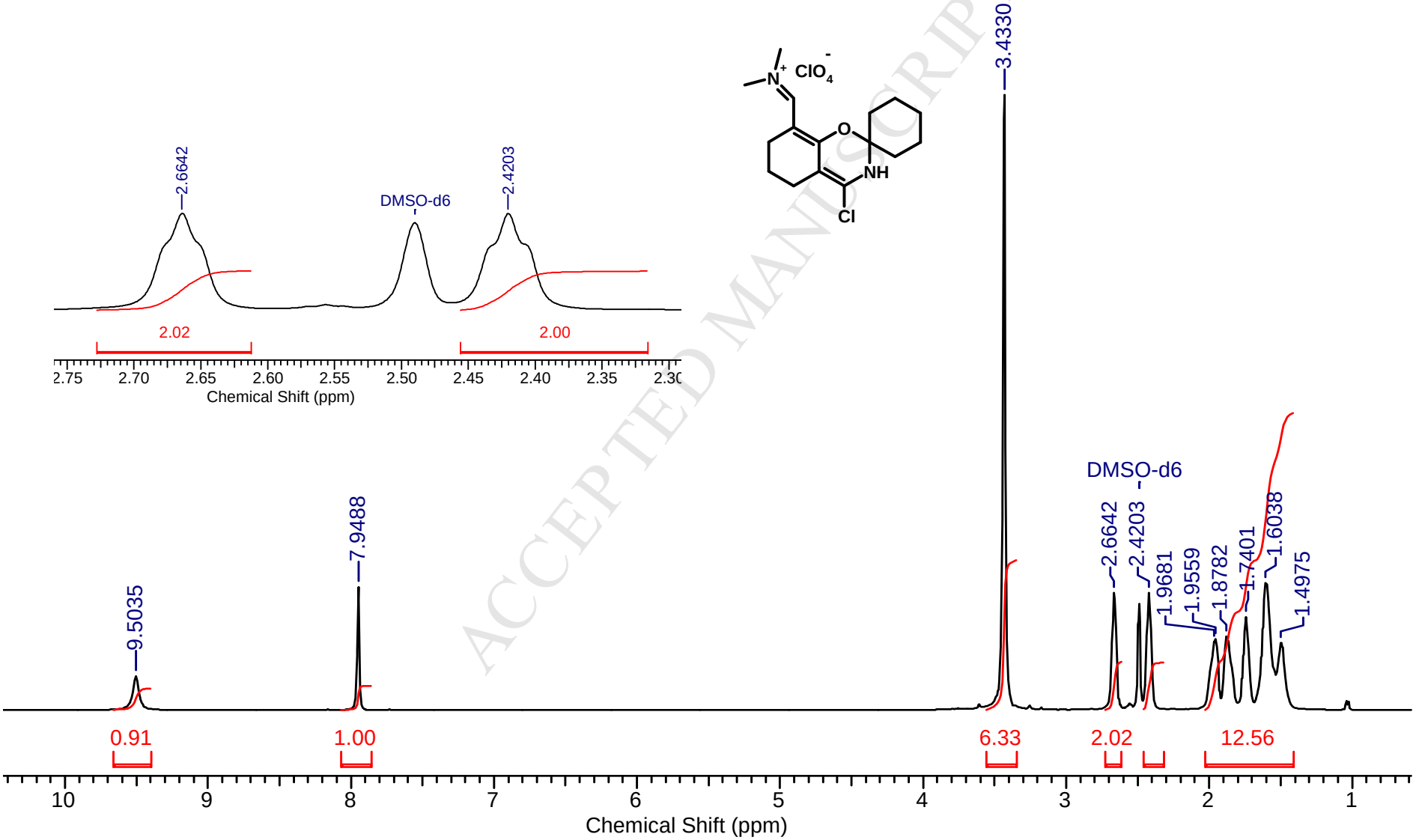
FTIR spectrum of 2-methyl-4-oxo-2*H*-1,3-benzoxazine-3(4*H*)-carbaldehyde **(14)**.



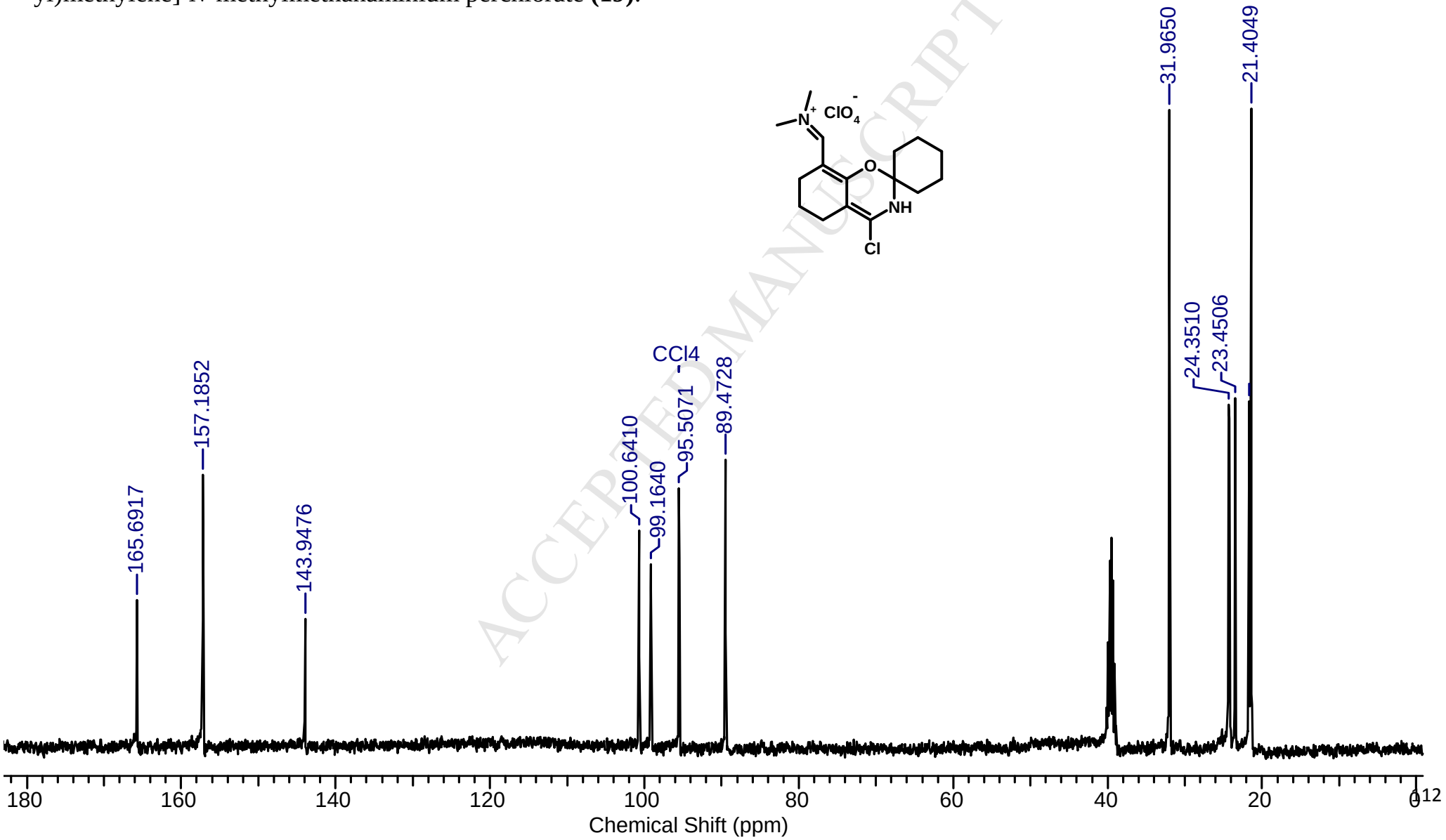
Mass spectrum (EI) of 2-methyl-4-oxo-2*H*-1,3-benzoxazine-3(4*H*)-carbaldehyde **(14)**.



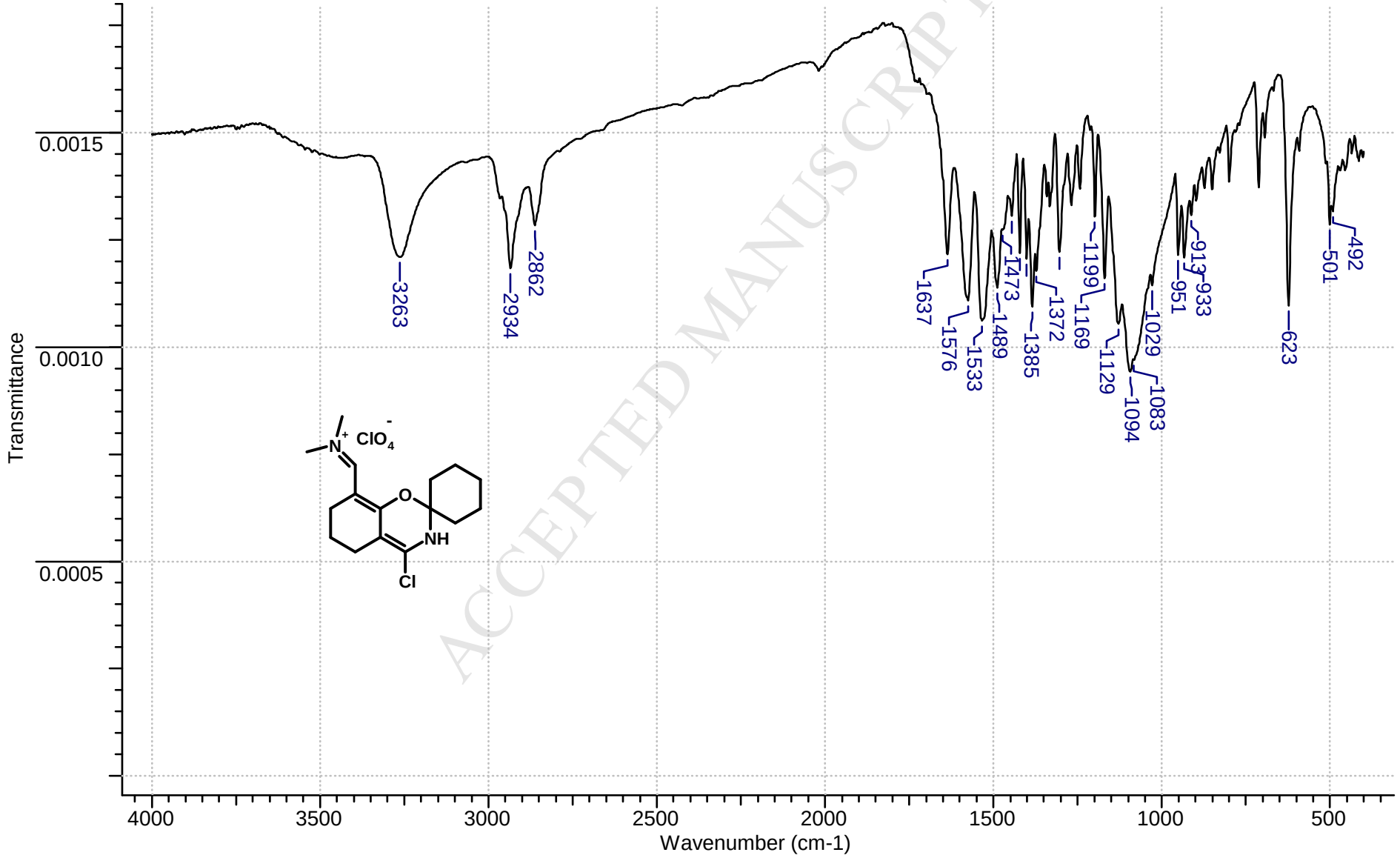
^{1}H NMR spectrum (DMSO-d_6/CCl_4, 400 MHz) of *N*-[(4-chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-*N*-methylmethanaminium perchlorate **(19)**.



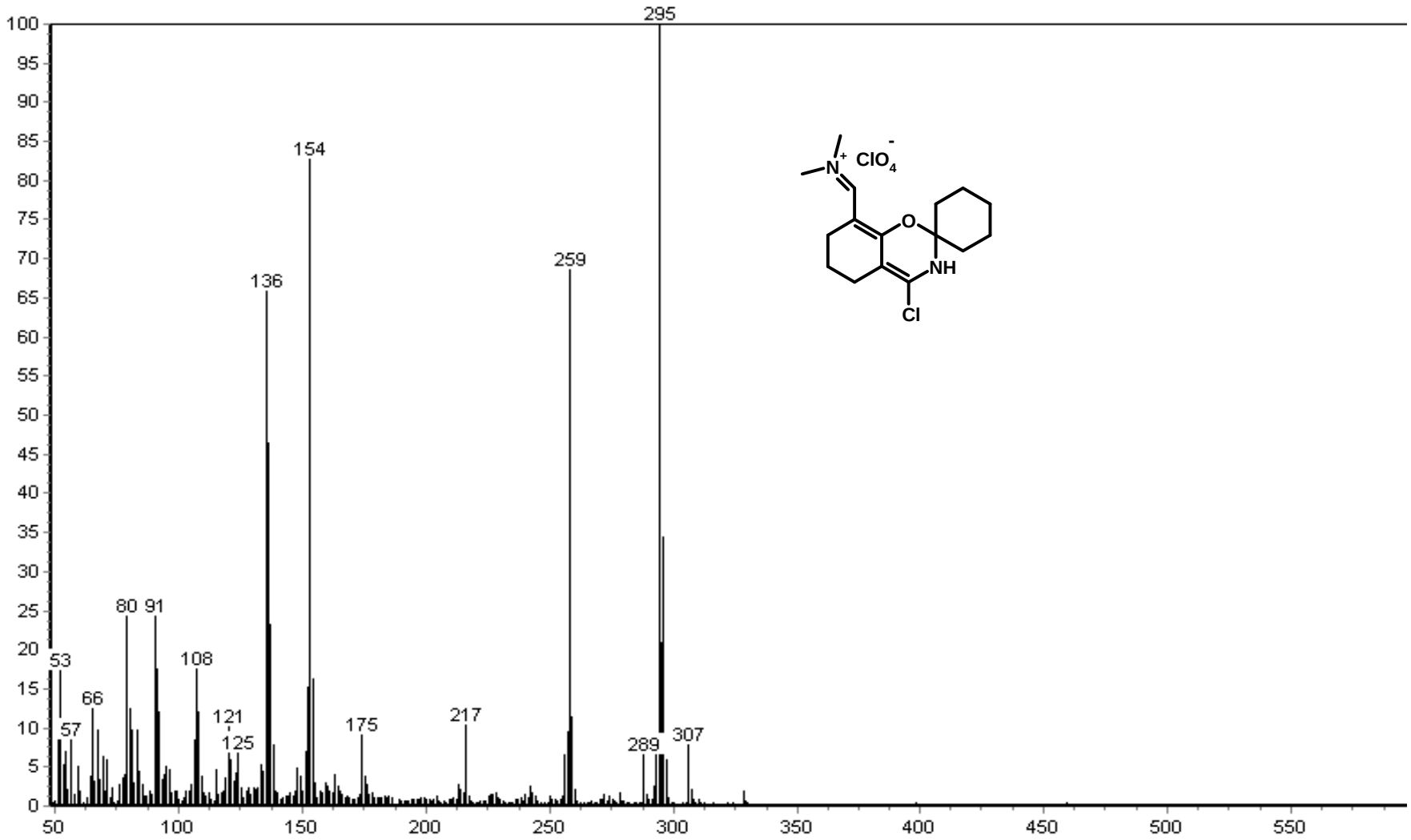
^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of *N*-[(4-chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-*N*-methylmethanaminium perchlorate **(19)**.



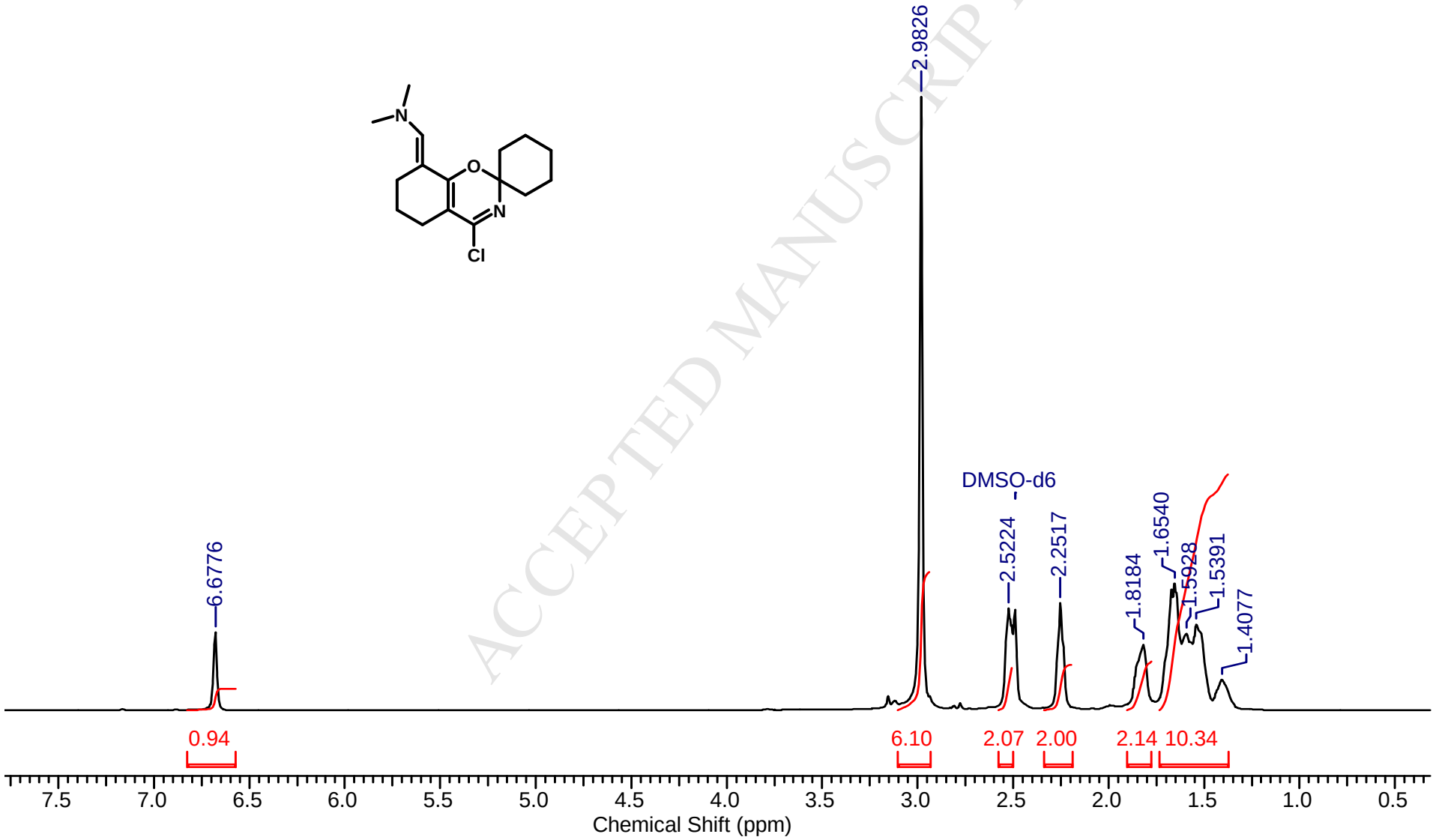
FTIR spectrum of *N*-[(4-chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-*N*-methylmethanaminium perchlorate **(19)**.



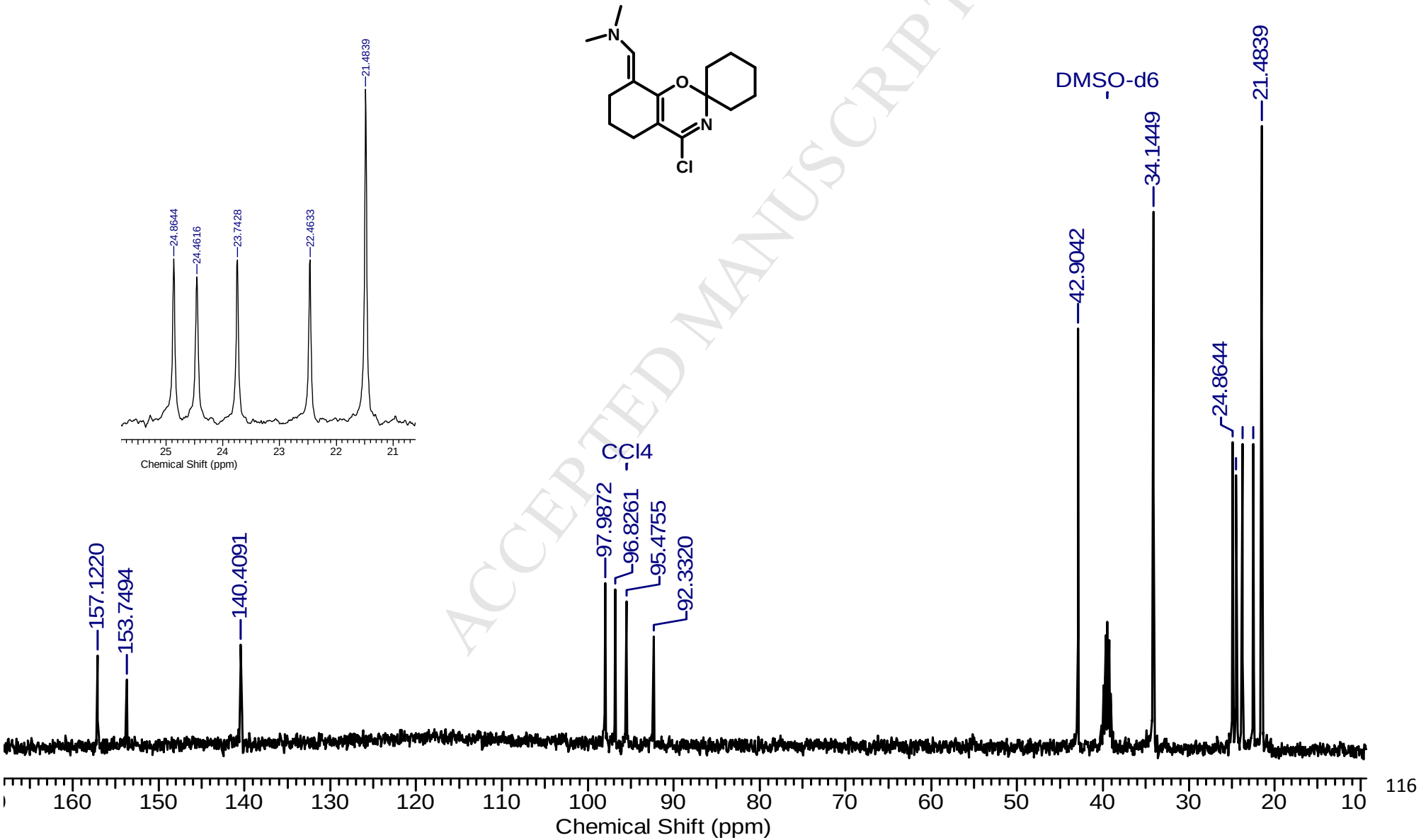
Mass spectrum (FAB) of *N*-[(4-chloro-3,5,6,7-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8-yl)methylene]-*N*-methylmethanaminium perchlorate **(19)**.



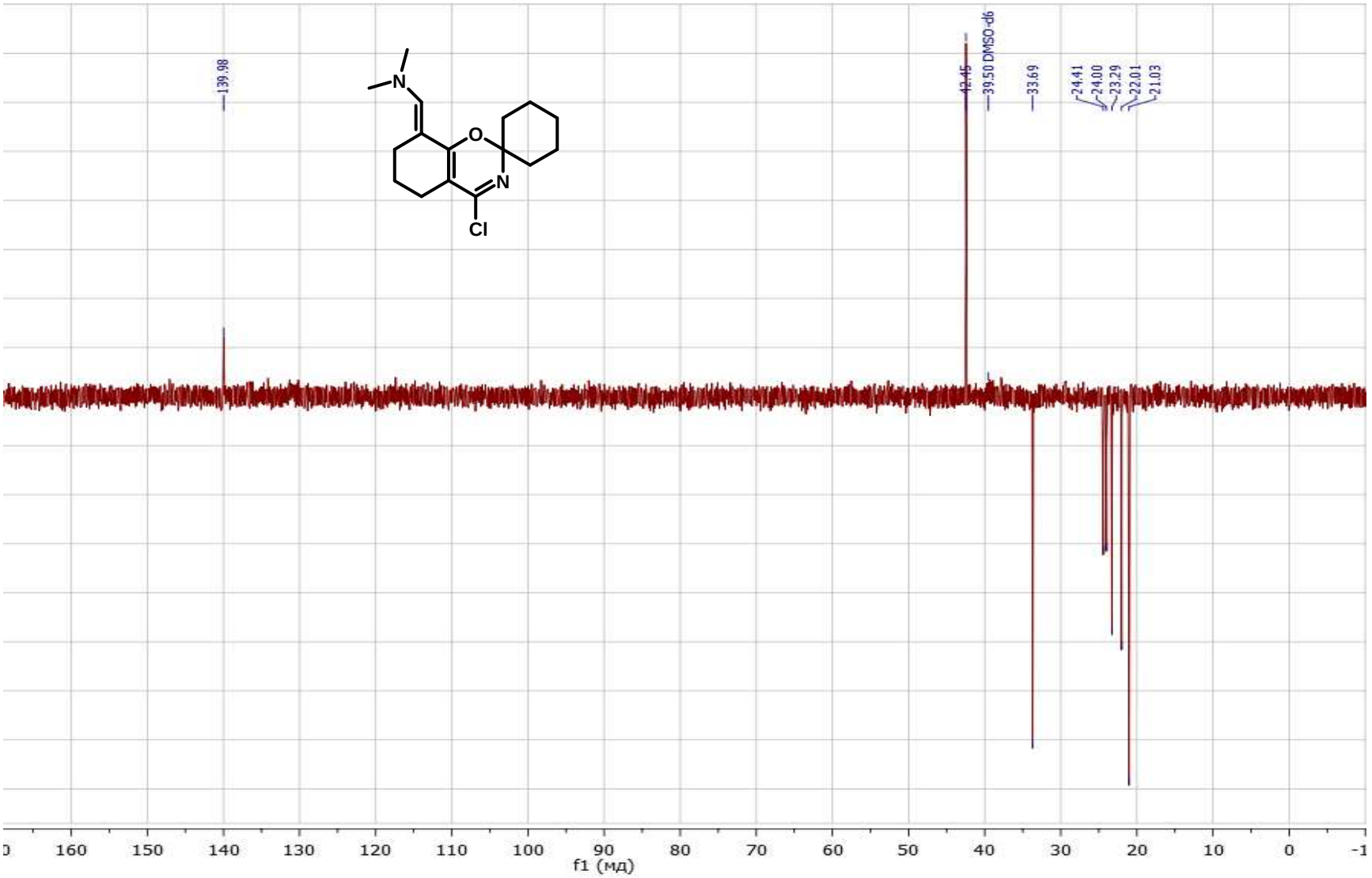
^{1}H NMR spectrum (DMSO-d_6/CCl_4, 400 MHz) of [(E)-(4-chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine **(20)**.



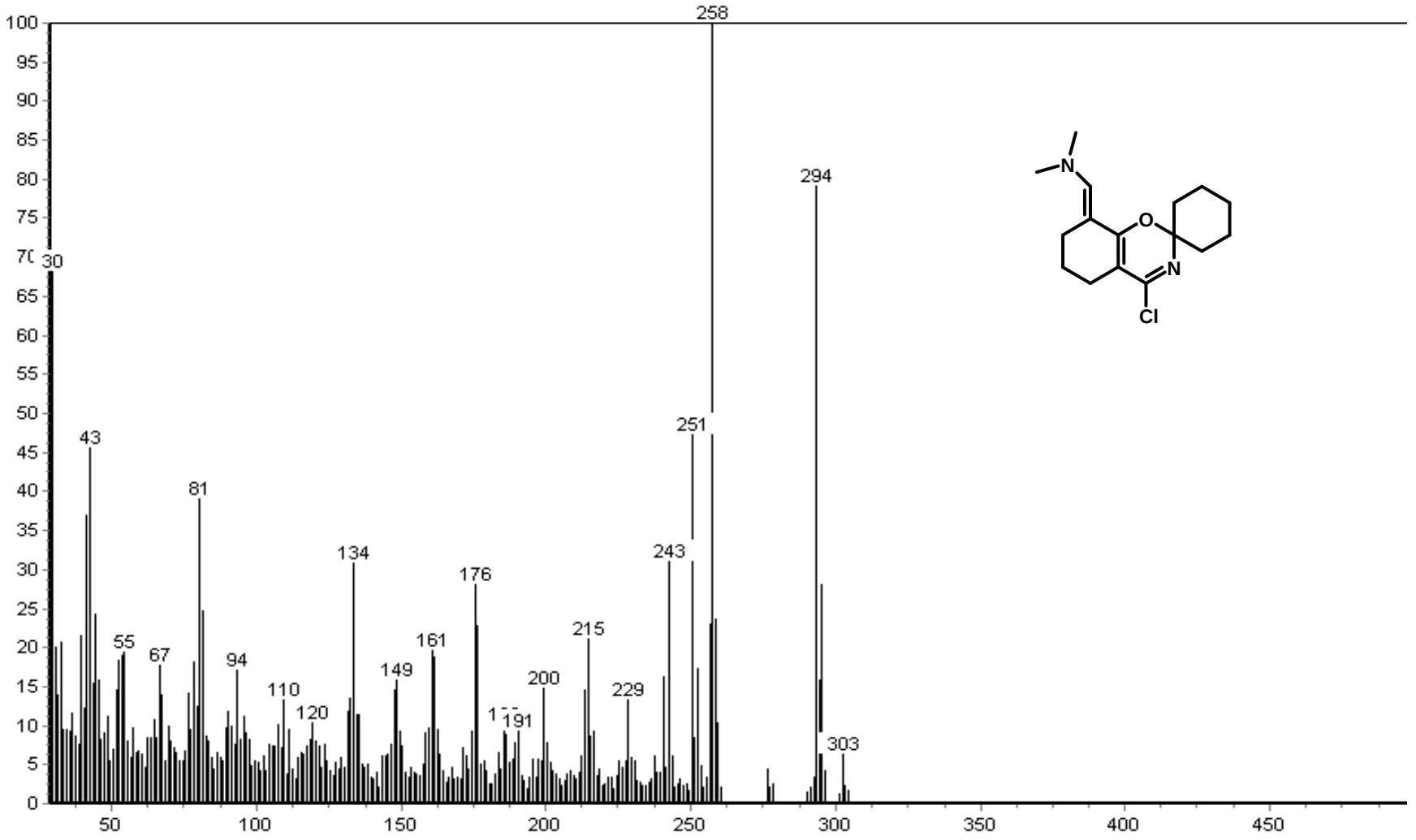
^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of [(E)-(4-chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine **(20)**.



DEPT-135 ^{13}C NMR spectrum (DMSO-d_6/CCl_4, 100 MHz) of [(E)-(4-chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine **(20)**.



Mass spectrum (EI) of [(E)-(4-chloro-6,7-dihydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-8(5H)-ylidene)methyl]dimethylamine **(20)**.



LC-MS data for 9-chloro-1,2,3,4-tetrahydroacridine **(16)**.