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Graphical Abstract

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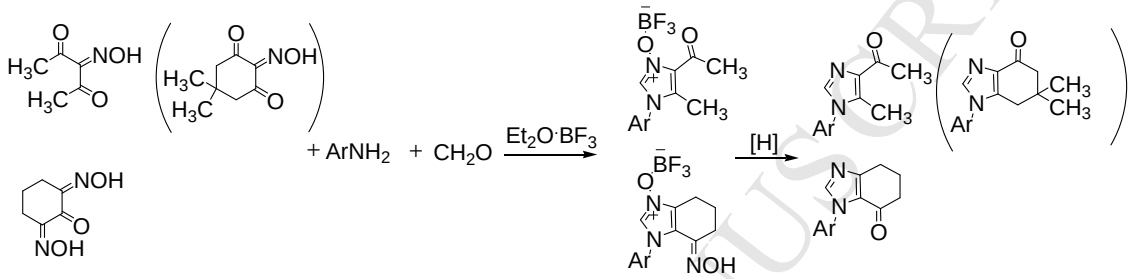

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Regioselective synthesis of 2-unsubstituted 1-aryl-4- and 1-aryl-5-acylimidazoles

Vitaly S. Mityanov[a], Ludmila G. Kuz'mina[b], Valery P. Perevalov[a] and Iosif I. Tkach[a*]

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ABSTRACT

An efficient and simple method for the synthesis of 2-unsubstituted 1-aryl-4- and 1-aryl-5-acylimidazoles has been developed. It consists in the condensation of α-diketone monooximes with aromatic amines and formaldehyde on the presence of boron trifluoride etherate, leading to the formation of stable boron trifluoride complexes of *N*-oxides. Further reduction of these complexes led to the corresponding imidazoles. This method permits broad variations of substituents in the aryl part of these compounds.

1. Introduction

1-Arylimidazoles have a wide range of biological activities[1] and great pharmacological potential.[2-5] 1-Arylimidazoles without a substituent at its position 2 are of particular importance. Several synthetic methods for the preparation of these compounds, are known.[6-10] However, most of them apply for the preparation of only a limited number of compounds, which hinders a comprehensive study of their properties. For this reason developing an efficient method for 2-unsubstituted 1-arylimidazoles synthesis is of considerable interest.

Our synthetic strategy consists of the preparation of 1-arylimidazole *N*-oxides followed by the reduction of the *N*-oxide functional group. First attempts to synthesize 2-unsubstituted 1-arylimidazole *N*-oxides[11-13] involved acid-catalyzed condensation of α-diketone monooximes either with aromatic amines and formaldehyde or previously obtained *N*-arylmethylenamines, but they failed, apparently, due to a rapid isomerization of the *N*-oxides to the corresponding imidazol-2-ones.[13] Other methods[14,15] are also ineffective, since suitable starting materials often prove to be not readily available.

We assumed that 2-unsabstituted imidazole *N*-oxides could be stabilized with respect to a rearrangement to 2-imidazolones by binding them in a complex. In our previous work[16] we have proved that the reaction of primary aromatic amines with formaldehyde and butane-2,3-dione monooxime in the presence of boron trifluoride etherate led to the formation of stable boron trifluoride complexes of 1-aryl-4,5-dimethylimidazole *N*-oxides (Fig. 1).

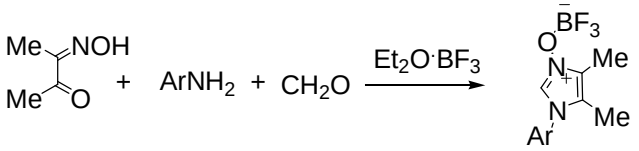

Figure 1. Synthesis of boron trifluoride complexes of 1-aryl-4,5-dimethylimidazole *N*-oxides.[16]

Aromatic amines containing different substituents, both electron donating and withdrawing groups and aromatic amines with bulky substituents at the ortho positions readily participate in this reaction. This shows the prospect of using this as a convenient and general method for the synthesis of 1-arylimidazoles. In the present study, we investigate the viability of this reaction for the preparation of 1-arylimidazoles containing an acyl group at positions 4 or 5.

2. Results and discussion

It is well-known that arylation of imidazoles containing dissimilar substituents at positions 4 and 5 leads to a mixture of regioisomers with predominance of the less sterically hindered compound.[6,17] Our method makes it possible to prepare any predetermined regioisomer. The nature of substituents at positions 4 and 5 depends on the structure of α-diketone monooxime.

Thus, for the synthesis of 1-aryl-4-acetylimidazoles easily available pentan-2,3,4-trione 3-oxime **7** can be used[18]. Indeed, the condensation of compound **7** with aromatic amines and formaldehyde in the presence of boron trifluoride etherate led to

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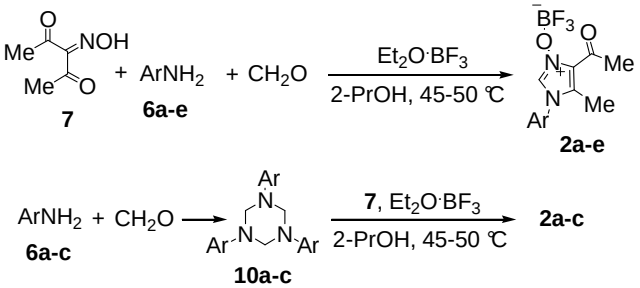
the formation of complexes of boron trifluoride with 1-aryl-4-acetyl-5-methylimidazole *N*-oxides **2** in good yield.

Boron trifluoride etherate not only stabilizes imidazole *N*-oxides but also acts as an excellent acid catalyst facilitating the reaction, so that it may proceed under mild conditions.

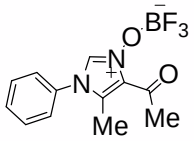
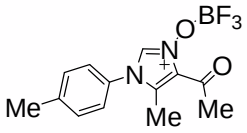
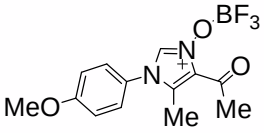
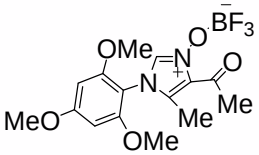
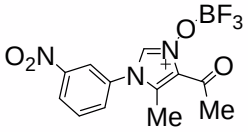
It is possible to use various solvents for the condensation (chloroform, alcohols, acetic acid); the choice is mainly determined by features of the isolation of products.



Scheme 1. Synthesis of boron trifluoride complexes **2**.

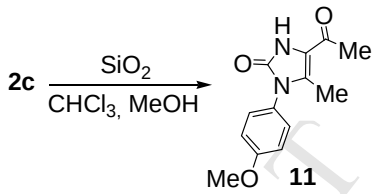
The use of the obtained 1,3,5-triarylhexahydro-1,3,5-triazinanes **10**[19] is an alternative to using a mixture of arylamines **6** and formaldehyde; compounds **10** possess a relatively high reactivity and the greater storage stability. Also, the use of triazinanes **10** makes it possible to minimize the amount of water entering with formaldehyde solution. In this case, the yields of **2** are generally higher (see Table 1, entries 1-3).

Table 1. Complexes of boron trifluoride with 1-aryl-4-acetyl-5-methylimidazole *N*-oxides **2** produced via scheme 1.

Entry	Compound 2		Yield, %
1		**2a**	61[1] (80)[2]
2		**2b**	48[1] (71)[2]
3		**2c**	33[1] (47)[2]
4		**2d**	55[1]
5		**2e**	83[1]

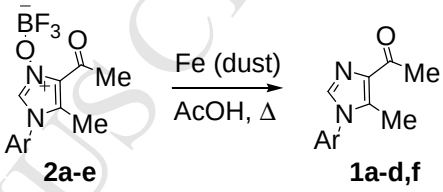
[1] Method A: 1.0 equiv oxime **7**, 1.1 equiv $Et_2O{\cdot}BF_3$, 2.0 equiv CH_2O, 1.0 equiv $ArNH_2$ **6**, IPA, 45-50 °C, 4h
[2] Method B: 1.0 equiv oxime **7**, 1.1 equiv $Et_2O{\cdot}BF_3$, 1.0 equiv triazinane **10**, IPA, room temperature, 4h

It is interesting to note that compounds **2** appeared to be less stable than their 4,5-dimethyl analogs. Thus, the attempt to isolate derivative **2c** from the reaction by column chromatography on silica gel led to the isolation imidazole-2-one **11**. Moreover, when pure compound **2c** was passed through a silica gel (eluent: chloroform-methanol) compound **11** was obtained in nearly quantitative yield (scheme 2). At the same time, complexes of boron trifluoride with 1-aryl-4,5-dimethylimidazole *N*-oxides were smoothly isolated by chromatography in high to moderate yields.



Scheme 2. Transformation of boron trifluoride complex to the imidazol-2-one

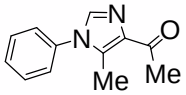
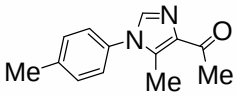
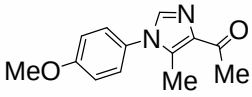
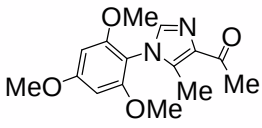
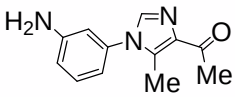
The reduction of compounds **2** proceeds facile by using various reducing agents and results in corresponding imidazoles **1** in high yields.



Scheme 3. Reduction of complexes **2**.

The fact that the condensation and reduction can be carried out in the same solvent (e.g., isopropyl alcohol or acetic acid) prompted us to obtain imidazoles **1** using one-pot procedure (see table 2).

Table 2. 4-Acetyl-5-methyl-1-aryl-1H-imidazoles **1**.

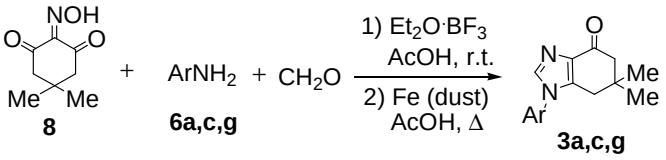
Entry	Compound 1		Yield, %
1		**1a**	57[1] (59)[2]
2		**1b**	41[1] (32)[2]
3		**1c**	27[1] (46)[2]
4		**1d**	54[1] (45)[2]
5		**1f**	50[1] (50)[2]

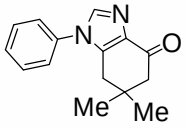
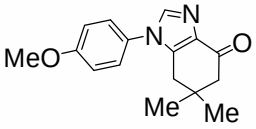
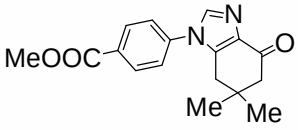
[1] Method A: 1.0 equiv compound **2**, 11.1 equiv iron powder, glacial acetic acid, reflux, 2.5 h (overall yield in stepwise procedure)
[2] Method B: 1.0 equiv oxime **7**, 1.1 equiv $Et_2O{\cdot}BF_3$, 2.0 equiv CH_2O, 1.0 equiv $ArNH_2$ **6**, IPA, 45-50 °C, 4h. Then 15 equiv HCO_2NH_4 and 3 mol % Pd/C (10%) were added and reflux for 3h (yield in one-pot procedure)

4-Acylimidazoles **3** were also obtained by using a one-pot procedure. As it is known, oxime **8**[20] is unstable under heating in solvents, especially in the presence of acids. For this reason the condensation was performed in acetic acid at room temperature

with an increased reaction time (20 h). The reduction step was carried out in the conventional manner.

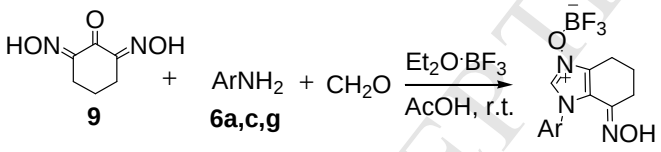
Table 3. The scope of 6,6-Dimethyl-1-aryl-4,5,6,7-tetrahydro-1H-benzimidazol-4-ones **3**.

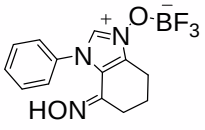
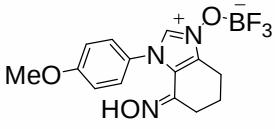
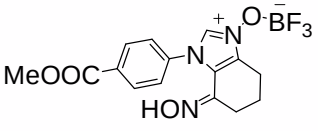


Entry	Compound 3		Yield, %
1		**3a**	44
2		**3c**	40
3		**3g**	52

Readily available cyclic dioxime **9**[21] was chosen as a precursor in the synthesis of sterically hindered 5-acylimidazoles. In this case the condensation was carried out with two equivalents of boron trifluoride etherate because of the potential possibility of complexation of the BF_3 with both *N*-oxide and oxime groups. However, compounds **5** contain only one BF_3 group.

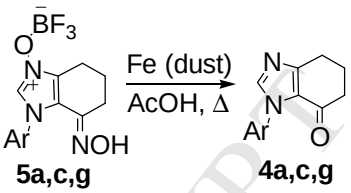
Table 4. The scope of boron trifluoride complexes of 1-aryl-7-hydroxyimino-4,5,6,7-tetrahydro-1H-benzimidazole 3-oxides **5**.

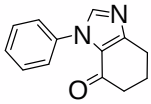
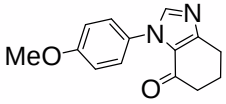
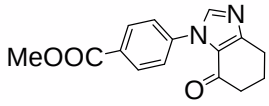


Entry	Compound 5		Yield, %
1		**5a**	65
2		**5c**	68
3		**5g**	67

The oxime group in these compounds is hidden the carbonyl function. So, the reduction of compounds **5** by iron dust in boiling acetic acid is accompanied by the hydrolysis of oxime function and led to the formation of imidazoles **4**. The isolation of these compounds is easy and can be carried out even without chromatography.

Table 5. The scope of 1-aryl-4,5,6,7-tetrahydro-1H-benzimidazol-7-ones **4**.



Entry	Compound 4		Yield[1], %
1		**4a**	50
2		**4c**	45
3		**4g**	55

[1] Yield can be increased by isolation additional amounts of product from the filtrates.

In the ^{1}H NMR spectra of imidazoles *N*-oxides **2** the signal of proton at position 2 of the imidazole ring is found as a narrow singlet in the 9.53-9.78 (in DMSO-*d6*) and 8.18-8.44 (in $CDCl_3$) ppm ranges. Thus, the signal of this proton in DMSO-*d6* is shifted downfield to 1.2-1.4 ppm over that in $CDCl_3$, while changes to the positions of other proton signals are negligible. It should be noted that in DMSO-*d6* doubling signals of all protons is observed (see supplementary materials). In addition to the main signal of each proton an additional signal with a close chemical shift, but much less intense appeared. When recording spectra in $CDCl_3$ this effect is not observed. For previously obtained 4,5-dimethyl derivatives such an effect was also lacking.

The signal of the proton at the imidazole ring C-2 atom of the compounds **5** are in the same range (9.50 - 9.62 ppm in DMSO-*d6*), however, unlike compounds **2**, doubling of the signals is not observed. For imidazoles **1**, **3** and **4** the proton signal at the imidazole ring C-2 atom is a narrow singlet in the range usual for imidazoles (7.27 - 7.78 ppm in $CDCl_3$).

The mass spectra of compounds **2** shows low-intensity signals corresponding to the $[M-F]^+$ cation, as well as a rather strong signal for the fragment with *m/z* = 49, corresponding to the BF_2^+ cation. Previously,[16] on the basis of similar mass spectra we erroneously ascribed to boron trifluoride complexes with 1-aryl-4,5-dimethylimidazole *N*-oxides structure of 1-aryl-3-[(difluoroboryl)oxy]-4,5-dimethyl-1H-imidazolium fluorides. However, as shown by single-crystal X-ray diffraction, 1-phenyl-4,5-dimethylimidazole *N*-oxide **12** and 1-aryl-4-acetyl-5-methylimidazole *N*-oxide **2b** formed similar complexes with BF_3.

While the signal for the fragment $[M-F]^+$ can be observed in the mass spectra not for all compounds **2** and **5**, the signal for the BF_2^+ is always present. The signal for the fragment with *m/z* = 68, that would correspond to the BF_3^+ cation in the mass spectra of these compounds is not detected, although in the mass spectra

of boron trifluoride etherate such a signal is present. The structure of boron trifluoride complexes of imidazole *N*-oxides (**12** and **2b**) has been determined by X-ray diffraction study. Compound **12** crystallizes as a benzene solvate of composition **12** × $1/6C_6H_6$. The structure of formula units of this compound is shown at figure 2.

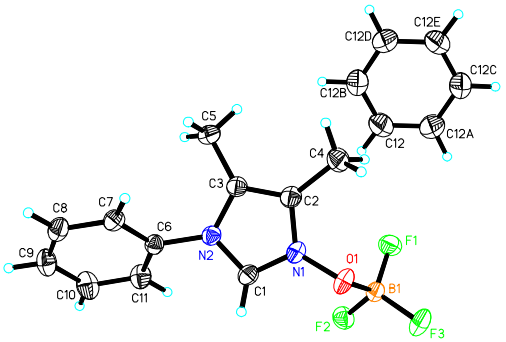


Figure 2. Structure of formula units of **12** × $1/6C_6H_6$; thermal ellipsoids displacement parameters are given at the 50% probability level.

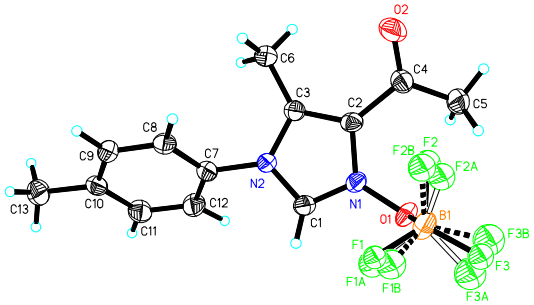


Figure 3. Structure of compound **2b**; thermal ellipsoids displacement parameters are given at the 50% probability level.

Selected geometric parameters for molecules **12** and **2b** are listed in table 6. The corresponding values agree within experimental errors.

Table 6. Selected geometric parameters (Å, deg.) for **12** and **2b**.

Parameter	12	2b
O1-N1	1.369(1)	1.365(2)
O1-B1	1.501(2)	1.501(3)
N1-C1	1.319(1)	1.315(3)
N1-C2	1.379(2)	1.387(2)
N2-C1	1.340(1)	1.333(3)
N2-C3	1.390(1)	1.385(2)
C2-C3	1.361(2)	1.363(3)
N1-O1-B1	113.26(8)	111.8(2)

Boron atom in these compounds has tetrahedral geometry with maximum coordination number four. Therefore, no additional binding with the oxygen atom of the carbonyl group in the compound **2b** and further stabilizing this structure does not occur. Furthermore, as mentioned above, boron trifluoride complexes of 1-aryl-4-acetyl-5-methylimidazole *N*-oxides **2** compared with analogous complexes of 1-aryl-4,5-dimethylimidazole *N*-oxides are less stable. Perhaps this is due to a repulsion between the negatively charged boron atom and the electron pairs of the carbonyl group.

3. Conclusion

In conclusion, we have developed a new simple and efficient method for the synthesis of 2-unsubsituted 1-arylimidazoles. This facilitates the synthesis of imidazole derivatives that are not easily accessible by other methods. A wide range of arylamines can enter in the reaction, most of starting materials being readily available compounds. The condensation and reduction steps can be carried out in one-pot.

At the moment we are trying to apply our method to the synthesis of 1,4- and 1,5-diarylimidazoles that are very interesting compounds due to the great diversity of their biological activity. The reactivity of complexes of 1-arylimidazole *N*-oxides with boron trifluoride is under further investigation.

4. Experimental

4.1. General

Chemicals were purchased from commercial sources and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AM 300 and Bruker AV 600 spectrometers with the residual solvents as internal standards (N.D. Zelinsky Institute of Organic Chemistry of RAS, Moscow). Mass-spectra were recorded with a LKB-2000 mass spectrometer (N.D. Zelinsky Institute of Organic Chemistry of RAS, Moscow). The TLC analysis was performed with Merck Silica Gel 60 F254 pre-coated plates. Column chromatography was performed with the use of 63-200 mesh silica gel (Merck). IR spectra were recorded on a Shimadzu IRAffinity-1 FTIR spectrophotometer. The elemental analysis was performed on CHN analyzer 1108 (Carlo Erba, Italy) (Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow). The melting points were determined on a Kofler hot stage and are uncorrected.

4.2. General procedure for the synthesis of boron trifluoride complexes of 4-acetyl-5-methyl-1-aryl-1H-imidazole 3-oxides (2).

Method A. A mixture of oxime **7** (2.00 g, 15.5 mmol), boron trifluoride diethyl etherate (2.09 mL, 2.40 g, 16.9 mmol), 40% formalin (2.13 mL, 2.33 g, 31.0 mmol) and amine **6** (15.5 mmol) in isopropyl alcohol (20 mL) was stirred at 45-50 ºC for 4 h. The solvent was removed under reduced pressure, and the residue was treated with water. Resulting precipitate was filtered off, washed with water and dried under reduced pressure over alkali to yield the corresponding product **2**. It may be crystallized from suitable solvent if needed.

Method B. A mixture of oxime **7** (3.70 g, 28.7 mmol), boron trifluoride diethyl etherate (3.90 mL, 4.49 g, 31.6 mmol) and methylene(aryl)amine **10** (28.7 mmol) in isopropyl alcohol (50 mL) was stirred at room temperature for 4 h. The precipitate was filtered off and washed with isopropyl alcohol yielding the corresponding product **2**. It may be crystallized from suitable solvent if needed.

4.2.1 Boron trifluoride complex of 4-acetyl-5-methyl-1-phenyl-1H-imidazole 3-oxide ***(2a)***. White powder; yield 61% (Method A), 80% (Method B); mp 169–173 ºC (toluene); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ = 9.72 (s, 1H, H–Im); 7.66 (s, 5H, H–Ar); 2.65 (s, 3H, CH_3); 2.32 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 188.9, 134.3, 133.1, 132.5, 130.9, 130.0, 129.3, 128.1, 126.8, 29.9, 10.4 ppm; MS (EI): *m/z* (*I*, %) = 265 $[M\text{-}F]^+$ (3), 216 $[M\text{-}BF_3]^+$. (17), 49 $[BF_2]^+$ (25); IR ν_{max} (KBr): 3124, 3066, 1683, 1386, 1273, 1138, 1095, 920, 833, 765, 696, 603, 588, 517 cm^{-1}; Anal. $C_{12}H_{12}BF_3N_2O_2$ (284): calcd C 50.74, H 4.26, N 9.86; found C 50.70, H 4.21, N 9.90.

4.2.2. Boron trifluoride complex of 4-acetyl-5-methyl-1-(4-methylphenyl)-1H-imidazole 3-oxide ***(2b)***. White powder; yield 48% (Method A), 71% (Method B); mp 179–180 ºC (2-propanol); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ = 9.72 (s, 1H, H–Im); 7.53 (d, *J*=8.07 Hz, 2H, H–Ar); 7.45 (d, *J*=8.79 Hz, 2H, H–Ar); 2.64 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 2.31 (s, 3H, CH_3) ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.34 (s, 1H, H–Im); 7.32 (d, *J*=8.07 Hz, 2H, H–Ar); 7.16 (d, *J*=7.35 Hz, 2H, H–Ar); 2.68 (s, 3H, CH_3); 2.37 (s, 3H, CH_3); 2.33 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 188.9, 140.9, 134.3, 133.1, 132.5, 130.4, 129.9, 129.8, 127.9, 126.5, 29.9, 20.7, 10.4 ppm; MS (EI): *m/z* (I, %)=279 $[M\text{-}F]^+$ (8), 230 $[M\text{-}BF_3]^+$. (32), 49 $[BF_2]^+$ (22); IR ν_{max} (KBr): 3138, 3074, 1683, 1578, 1512, 1389, 1159, 925, 824, 793, 677, 633, 613, 586, 523 cm^{-1}; Anal. $C_{13}H_{14}BF_3N_2O_2$ (298): calcd C 52.38, H 4.73, N 9.40; found C 52.33, H 4.70, N 9.45.

4.2.3. Boron trifluoride complex of 4-acetyl-5-methyl-1-(4-methoxylphenyl)-1H-imidazole 3-oxide ***(2c)***. White powder; yield 33% (Method A), 47% (Method B); mp 154–157 ºC (toluene); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ=9.63 (s, 1H, H–Im); 7.57 (d, *J*=8.04 Hz, 2H, H–Ar); 7.17 (d, *J*=8.79 Hz, 2H, H–Ar); 3.86 (s, 3H, OCH_3); 2.64 (s, 3H, CH_3); 2.30 (s, 3H, CH_3) ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ=8.44 (s, 1H, H–Im); 7.30 (d, *J*=8.79 Hz, 2H, H–Ar); 7.09 (d, *J*=8.82 Hz, 2H, H–Ar); 3.89 (s, 3H, OCH_3); 2.75 (s, 3H, CH_3); 2.42 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ=188.8, 160.8, 134.6, 133.1, 132.2, 128.2, 126.4, 125.0, 115.0, 55.7, 29.9, 10.3 ppm; MS (EI): *m/z* (I, %)=295 $[M\text{-}F]^+$ (3), 246 $[M\text{-}BF_3]^+$. (39), 49 $[BF_2]^+$ (70); IR ν_{max} (KBr): 3117, 3049, 1683, 1514, 1394, 1257, 831, 806, 660, 650, 615, 577, 529 cm^{-1}; Anal. $C_{13}H_{14}BF_3N_2O_3$ (314): calcd C 49.72, H 4.49, N 8.92; found C 49.68, H 4.43, N 8.90.

4.2.4. Boron trifluoride complex of 4-acetyl-5-methyl-1-(2.4.6-trimethoxylphenyl)-1H-imidazole 3-oxide ***(2d)***. White powder; yield 55% (Method A); mp 200–204 ºC (toluene-ethanol, 7:2); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ=9.53 (s, 1H, H–Im); 6.49 (s, 2H, H–Ar); 3.89 (s, 3H, OCH_3); 3.81 (s, 6H, OCH_3); 2.64 (s, 3H, CH_3); 2.16 (s, 3H, CH_3) ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ=8.18 (s, 1H, H–Im); 6.24 (s, 2H, H–Ar); 3.89 (s, 3H, OCH_3); 3.80 (s, 6H, OCH_3); 2.79 (s, 3H, CH_3); 2.27 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ=189.0, 163.5, 156.5, 136.0, 135.3, 133.8, 129.3, 128.6, 91.9, 57.0, 56.4, 30.3, 9.9 ppm; MS (EI): *m/z* (I, %)=355 $[M\text{-}F]^+$ (3), 306 $[M\text{-}BF_3]^+$. (20), 49 $[BF_2]^+$ (10); IR ν_{max} (KBr): 3163, 2992, 2951, 2848, 1683, 1512, 1387, 829, 746, 621, 586, 482 cm^{-1}; Anal. $C_{15}H_{18}BF_3N_2O_5$ (374): calcd C 48.16, H 4.85, N 7.49; found C 48.12, H 4.80, N 7.53.

4.2.5. Boron trifluoride complex of 4-acetyl-5-methyl-1-(3-nitrophenyl)-1H-imidazole 3-oxide ***(2e)***. Pale yellow powder; yield 83% (Method A); mp 193–195 ºC (acetic acid); ^{1}H NMR (300 MHz, DMSO-d6, 300 K): δ = 9.75 (s, 1H, H–Im); 8.65–7.92 (m, 4H, H–Ar); 2.65 (s, 3H, CH3); 2.34 (s, 3H, CH3) ppm; ^{13}C NMR (75 MHz, DMSO-d6): δ = 188.8, 148.3, 134.8, 133.6, 133.4, 131.4, 126.5, 125.7, 122.8, 29.9, 10.4 ppm; MS (EI): m/z (I, %) = 310 $[M\text{-}F]^+$ (2), 261 $[M\text{-}BF_3]^+$. (27), 49 $[BF_2]^+$ (26); IR ν_{max} (KBr): 3175, 1693, 1587, 1357, 825, 810, 754, 743, 727, 685, 646, 631, 602, 586, 527 cm^{-1}; Anal. $C_{12}H_{11}BF_3N_3O_4$ (329): calcd C 43.80, H 3.37, N 12.77; found C 43.77; H 3.32; N 12.99.

4.3. General procedure for the synthesis of 4-acetyl-5-methyl-1-aryl-1H-imidazoles (1).

Method A. Mixture of compound **2** (7.00 mmol) and iron powder (3.90 g, 79.6 mmol) in glacial acetic acid (30 mL) was stirred under reflux for 2.5 h. Then it was cooled to room temperature, poured into water (60 mL), extracted with chloroform (15 mL × 2). The extract was sequentially washed with 10% solution of sodium hydrocarbonate (50 mL), 10% solution of sodium chloride (50 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. and the residue was purified by column chromatography on silica gel (eluent: chloroform) to give the corresponding product **1**.

Method B. Mixture of oxime **7** (2.0 g; 15.5 mmol), boron trifluoride diethyl etherate (2.09 mL, 2.40 g; 16.9 mmol), 40% formalin (2.13 mL; 2.33 g; 31.0 mmol) and amine **6** (15.5 mmol) in isopropyl alcohol (30 mL) was stirred at 45–50 ºC for 4 h. Then ammonium formate (15.0 g, 240 mmol) and 10% Pd/C (0.5 g) were added. Reaction mixture was stirred under reflux for 3 h. Then it was cooled, filtered, diluted with water (100 mL) and extracted with chloroform (20 mL × 2). The extract was washed with 10% solution of sodium chloride (50 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. and the residue was purified by column chromatography on silica gel (eluent: chloroform) to give the corresponding product **1**.

4.3.1. 4-Acetyl-5-methyl-1-phenyl-1H-imidazole ***(1a)***. White powder; yield 93% (Method A), 59% (Method B); mp 88–90 ºC (heptane); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.52–7.50 (m, 4H, H–Im, H–Ar); 7.27–7.25 (m, 2H, H–Ar); 2.59 (s, 3H, CH_3); 2.45 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=195.4, 137.2, 135.4, 134.8, 134.0, 129.4, 128.8, 125.5, 27.0, 10.3 ppm; MS (EI): *m/z* (I, %) = 200 $[M]^+$ (87), 185 $[M\text{-}CH_3]^{+\cdot}$ (99); IR ν_{max} (KBr): 3101, 3055, 1680, 1597, 1253, 1182, 1070, 926, 777, 702, 658, 631, 611, 565, 494 cm^{-1}; Anal. $C_{12}H_{12}N_2O$ (200): calcd C 71.98, H 6.04, N 13.99; found C 71.95, H 6.01, N 14.05.

4.3.2. 4-Acetyl-5-methyl-1-(4-methylphenyl)-1H-imidazole ***(1b)***. White powder; yield 86% (Method A), 32% (Method B); mp 80–82 ºC (heptane); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.45 (s, 1H, H–Im); 7.28 (d, *J* = 8.07 Hz, 2H, H–Ar); 7.12 (d, *J* = 8.07 Hz, 2H, H–Ar); 2.59 (s, 3H, CH_3); 2.41 (s, 3H, CH_3); 2.39 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=195.9, 139.3, 137.4, 135.7, 134.6, 132.5, 130.2, 125.6, 27.3, 21.0, 10.5 ppm; MS (EI): *m/z* (I, %) = 214 $[M]^+$ (68), 199 $[M\text{-}CH_3]^{+\cdot}$ (100); IR ν_{max} (KBr): 3107, 2920, 1694, 1548, 1255, 1175, 930, 822, 675, 660, 631, 561, 501 cm^{-1}; Anal. $C_{13}H_{14}N_2O$ (214): calcd C 72.87, H 6.59, N 13.07; found C 72.85, H 6.52, N 13.10.

4.3.3. 4-Acetyl-5-methyl-1-(4-methoxylphenyl)-1H-imidazole ***(1c)***. White powder; yield 82% (Method A), 46% (Method B); mp 82–86 ºC (heptane); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.45 (s, 1H, H–Im); 7.15 (d, *J*=8.07 Hz, 2H, H–Ar); 6.98 (d, *J*=8.07 Hz, 2H, H–Ar); 3.84 (s, 3H, OCH_3); 2.57 (s, 3H, CH_3); 2.40 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.9, 160.0, 137.3, 135.9, 134.8, 127.8, 127.2, 114.8, 55.5, 27.4, 10.5 ppm; MS (EI): *m/z* (I, %)=230 $[M]^+$ (63), 215 $[M\text{-}CH_3]^{+\cdot}$ (100); IR ν_{max} (KBr): 3107, 1662, 1375, 1362, 1305, 1066, 1030, 928, 831, 673, 660, 627, 563, 513 cm^{-1}; Anal. $C_{13}H_{14}N_2O_2$ (230): calcd C 67.81, H 6.13, N 12.17; found C 67.75, H 6.10, N 12.15.

4.3.4. 4-Acetyl-5-methyl-1-(2,4,6-trimethoxylphenyl)-1H-imidazole ***(1d)***. White powder; yield 98% (Method A), 45% (Method B); mp 158–161 ºC (heptane); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.27 (s, 1H, H–Im); 6.19 (s, 2H, H–Ar); 3.85 (s, 3H, OCH_3); 3.71 (s, 6H, OCH_3); 2.59 (s, 3H, CH_3); 2.25 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.9, 162.0, 156.7, 137.4, 136.9, 136.5, 105.5, 90.7, 55.9, 55.6, 27.3, 9.9 ppm; MS (EI): *m/z* (I, %)=290 $[M]^+$ (54), 275 $[M\text{-}CH_3]^{+\cdot}$ (100); IR ν_{max} (KBr): 3123, 3015, 2970, 2943, 2845, 1658, 1130, 1070, 947, 926, 814, 683, 640, 474 cm^{-1}; Anal. $C_{15}H_{18}N_2O_4$ (290): calcd C 62.06, H 6.25, N 9.65; found C 62.01, H 6.27, N 9.60.

*4.3.5. 4-Acetyl-5-methyl-1-(3-aminophenyl)-1H-imidazole **(1f)***. White powder; yield 60% (Method A), 50% (Method B); mp 137–140 ºC (heptane); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.48 (s, 1H, H–Im); 7.27–7.21 (m, 1H, H–Ar); 6.75 (d, *J*=8.07 Hz, 1H, H–Ar); 6.60–6.52 (m, 2H, H–Ar); 4.01 (bs, 2H, NH_2); 2.59 (s, 3H, CH_3); 2.45 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.0, 148.1, 137.2, 135.7, 134.6, 130.2, 115.2, 114.8, 111.6, 27.3, 10.6 ppm; MS (EI): *m/z* (I, %)=215 $[M]^+$ (72), 200 $[M\text{-}CH_3]^{+\cdot}$ (100); IR ν_{max} (KBr): 3408, 3392, 3313, 3200, 3103, 1662, 1610, 1379, 1366, 1286, 1230, 934, 791, 779 cm^{-1}; Anal. $C_{12}H_{13}N_3O$ (215): calcd C 66.96, H 6.09, N 19.52; found C 66.92, H 6.03, N 19.50.

4.4. General procedure for the synthesis of 6,6-dimethyl-1-aryl-4,5,6,7-tetrahydro-1H-benzimidazol-4-ones (3).

Mixture of oxime **8** (3.00 g, 17.7 mmol), boron trifluoride diethyl etherate (2.41 mL, 2.77 g, 19.5 mmol), 40% formalin (2.44 mL, 2.66 g, 35.4 mmol) and amine **6** (17.7 mmol) in glacial acetic acid (50 mL) was stirred at room temperature for 50 hours. Then iron powder (5.00 g, 89.3 mmol) was added and mixture was stirred under reflux for 2.5 h. Then it was cooled to room temperature, poured into water (150 mL), extracted with chloroform (25 mL × 4). The extract was sequentially washed with 10% solution of sodium hydrocarbonate (50 mL), 10% solution of sodium chloride (50 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: chloroform) to give the corresponding imidazole product **3**.

*4.4.1. 6,6-Dimethyl-1-phenyl-4,5,6,7-tetrahydro-1H-benzimidazol-4-one **(3a)***. White powder; yield 44%; mp 130–132 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.68 (s, 1H, H–Im); 7.53–7.47 (m, 3H, H–Ar); 7.31–7.29 (m, 2H, H–Ar); 2.67 (s, 2H, CH_2); 2.44 (s, 2H, CH_2); 1.09 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.1, 142.3, 138.7, 136.1, 135.1, 130.0, 129.0, 124.5, 52.1, 35.8, 35.6, 28.5 ppm; MS (EI): *m/z* (I, %)=240 $[M]^+$ (25), 225 $[M\text{-}CH3]^{+\cdot}$ (3); IR ν_{max} (KBr): 3045, 2956, 2924, 1662, 1597, 1504, 1390, 1180, 1107, 1059, 964, 777, 767, 624, 521 cm^{-1}; Anal. $C_{15}H_{16}N_2O$ (240): calcd C 74.97, H 6.71, N 11.66; found C 74.92, H 6.65, N 11.70.

*4.4.2. 6,6-Dimethyl-1-(4-methoxyphenyl)-4,5,6,7-tetrahydro-1H-benzimidazol-4-one **(3c)***. White powder; yield 40%; mp 182–184 ºC (CCl_4–benzene, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.64 (s, 1H, H–Im); 7.22 (d, *J*=8.07 Hz, 2H, H–Ar); 7.01 (d, *J*=8.79 Hz, 2H, H–Ar); 3.85 (s, 3H, OCH_3); 2.62 (s, 2H, CH_2); 2.43 (s, 2H, CH_2); 1.09 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.1, 159.9, 152.5, 142.7, 138.9, 135.7, 127.8, 125.9, 115.0, 55.6, 52.1, 35.9, 35.7, 35.4, 28.4, 28.3 ppm; MS (EI): *m/z* (I, %)=270 $[M]^+$ (80), 255 $[M\text{-}CH_3]^{+\cdot}$ (10); IR ν_{max} (KBr): 3118, 2966, 2953, 1666, 1514, 1394, 1248, 1177, 1034, 964, 847, 667, 646, 586, 534 cm^{-1}; Anal. $C_{16}H_{18}N_2O_2$ (270): calcd C 71.09, H 6.71, N 10.36; found C 71.05, H 6.65, N 10.41.

*4.4.3. 6,6-Dimethyl-1-(4-methoxycarbonylphenyl)-4,5,6,7-tetrahydro-1H-benzimidazol-4-one **(3g)***. White powder; yield 52%; mp 132–134 ºC (CCl_4); ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.22 (d, *J*=8.16 Hz, 2H, H–Ar);7.78 (s, 1H, H–Im); 7.42 (d, *J*=8.07 Hz, 2H, H–Ar); 3.96 (s, 3H, $COOCH_3$); 2.72 (s, 2H, CH_2); 2.48 (s, 2H, CH_2); 1.13 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.1, 165.7, 141.9, 138.9, 138.5, 136.7, 131.5, 130.6, 124.2, 52.6, 52.1, 36.0, 35.9, 28.5 ppm; MS (EI): *m/z* (I, %)=298 $[M]^+$ (47), 283 $[M\text{-}CH_3]^{+\cdot}$ (1); IR ν_{max} (KBr): 3053, 2951, 1716, 1674, 1606, 1437, 1278, 1101, 964, 870, 775, 702, 629, 586, 505 cm^{-1}; Anal. $C_{17}H_{18}N_2O_3$ (298): calcd C 68.44, H 6.08, N 9.39; found C 68.40, H 6.05, N 9.35.

4.5. General procedure for the synthesis of boron trifluoride complexes of 1-aryl-7-hydroxyimino-4,5,6,7-tetrahydro-1H-benzimidazole 3-oxides (5).

Mixture of oxime **9** (1.00 g, 6.40 mmol), boron trifluoride diethyl etherate (1.74 mL, 2.00 g, 14.1 mmol), 40% formalin (0.44 mL, 0.48 g, 6.40 mmol) and amine **6** (6.40 mmol) in glacial acetic acid (10 mL) was stirred at room temperature for 20 h. The precipitate was filtered off and washed with glacial acetic acid (5 mL) and diethyl ether (5 mL) yielding corresponding product **5** as a white powder. In the case of amine **6c** solvent was removed under reduced pressure, and the residue was treated with water yielding product **5c** as an off-white powder.

*4.5.1. Boron trifluoride complex of 1-phenyl-7-hydroxyimino-4,5,6,7-tetrahydro-1H-benzimidazole 3-oxide **(5a)***. White powder; yield 65%; mp 232 ºC (decomp.); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ = 11.25 (s, 1H, NOH); 9.51 (s, 1H, H–Im); 7.56 (s, 1H, H–Ar); 2.85–2.80 (m, 2H, CH_2); 2.72–2.69 (m, 2H, CH_2); 1.96–1.91 (m, 2H, CH_2) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 145.2, 135.4, 134.2, 133.4, 130.1, 129.2, 126.7, 121.4, 22.3, 20.2, 18.9 ppm; MS (EI): *m/z* (I, %) = 243 $[M\text{-}BF_3]^+$ (5), 227 $[M\text{-}BF_3\text{-}O]^{+\cdot}$ (17), 49 $[BF_2]^+$ (47); IR ν_{max} (KBr): 3489, 3143, 1494, 1155, 941, 903, 821, 770, 696, 611, 526, 486 cm^{-1}; Anal. $C_{13}H_{13}BF_3N_3O_2$ (311): calcd C 50.20, H 4.21, N 13.51; found C 50.15, H 4.19, N 13.55.

*4.5.2. Boron trifluoride complex of 1-(4-methoxyphenyl)-7-hydroxyimino-4,5,6,7-tetrahydro-1H-benzimidazole 3-oxide **(5c)***. Off-white powder; yield 68%; mp 212 ºC (decomp.); ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ = 11.28 (s, 1H, NOH); 9.50 (s, 1H, H–Im); 7.50 (d, *J*=8.07 Hz, 2H, H–Ar); 7.06 (d, *J*=8.79 Hz, 2H, H–Ar); 3.82 (s, 3H, OCH_3); 2.81–2.82 (m, 2H, CH_2); 2.69–2.67 (m, 2H, CH_2); 1.92–1.90 (m, 2H, CH_2) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 160.1, 145.2, 134.2, 133.1, 128.0, 127.5, 121.5, 114.1, 55.6, 22.2, 20.2, 18.8 ppm; MS (EI): *m/z* (I, %) = 257 $[M\text{-}BF_3]^+$ (31), 241 $[M\text{-}BF_3\text{-}O]^{+\cdot}$ (15), 49 $[BF_2]^+$ (95); IR ν_{max} (KBr): 3502, 3292 (br), 3142, 3115, 1514, 1255, 900, 835, 827, 621, 600, 538 cm^{-1}; Anal. $C_{14}H_{15}BF_3N_3O_3$ (341): calcd C 49.30, H 4.43, N 12.32; found C 49.25, H 4.40, N 12.35.

*4.5.3. Boron trifluoride complex of 1-(4-methoxycarbonylphenyl)-7-hydroxyimino-4,5,6,7-tetrahydro-1H-benzimidazole 3-oxide **(5g)***. White powder; yield 67%; mp 194–196 ºC; ^{1}H NMR (300 MHz, DMSO-*d6*, 300 K): δ = 11.26 (s, 1H, NOH); 9.62 (s, 1H, H–Im); 8.09 (d, *J*=8.04 Hz, 2H, H–Ar); 7.77 (d, *J*=8.79 Hz, 2H, H–Ar); 3.91 (s, 3H, $COOCH_3$); 2.83–2.80 (m, 2H, CH_2); 2.70–2.67 (m, 2H, CH_2); 1.94–1.91 (m, 2H, CH_2) ppm; ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 165.5, 145.1, 139.1, 134.2, 133.6, 132.9, 131.1, 130.0, 127.4, 121.4, 52.7, 22.3, 21.1, 20.2, 18.9 ppm; MS (EI): *m/z* (I, %) = 285 $[M\text{-}BF_3\text{-}O]^{+\cdot}$ (22), 49 $[BF_2]^+$ (98); IR ν_{max} (KBr): 3497, 3143, 1732, 1282, 947, 901, 864, 818, 773, 696, 617, 532 cm^{-1}; Anal. $C_{15}H_{15}BF_3N_3O_4$ (369): calcd C 48.81, H 4.10, N 11.38; found C 48.75, H 4.06, N 11.41.

4.6. General procedure for the synthesis of 1-aryl-4,5,6,7-tetrahydro-1H-benzimidazol-7-ones (4).

Mixture of compound **5** (5.00 mmol) and iron powder (1.96 g, 35.0 mmol) in glacial acetic acid (30 mL) was stirred under reflux for 7 h. Then it was cooled to room temperature, poured into water (100 mL), extracted with chloroform (25 mL × 2). The extract was sequentially washed with 10% solution of sodium hydrocarbonate (50 mL) and water (50 mL). The solvent was removed under reduced pressure, and the residue was dissolved in ethanol (30 mL). This solution was refluxed with activated charcoal (2 g) for 0.5 h. Then it was filtered and concentrated

under reduced pressure yielding chromatographically pure corresponding product **4**.

*4.6.1. 1-Phenyl-4,5,6,7-tetrahydro-1H-benzimidazol-7-one **(4a)***. White powder; yield 50%; mp 130–132 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.76 (s, 1H, H–Im); 7.43–7.37 (m, 5H, H–Ar); 3.00–2.97 (m, 2H, CH_2); 2.56–2.52 (m, 2H, CH_2); 2.22–2.18 (m, 2H, CH_2) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.2, 156.5, 141.8, 135.9, 129.2, 129.0, 125.8, 125.5, 39.2, 25.1, 23.8 ppm; MS (EI): *m/z* (I, %) = 212 $[M]^+$ (62), 184 $[M\text{-}CO]^{+\cdot}$ (35); IR ν_{max} (KBr): 3090, 3055, 2945, 1666 (br), 1068, 1011, 899, 764, 746, 692, 598, 557, 511, 430 cm^{-1}; Anal. $C_{13}H_{12}N_2O$ (212): calcd C 73.57, H 5.70, N 13.20; found C 73.55, H 5.65, N 13.24.

*4.6.2. 1-(4-Methoxyphenyl)-4,5,6,7-tetrahydro-1H-benzimidazol-7-one **(4c)***. White powder; yield 45%; mp 144–146 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.66 (s, 1H, H–Im); 7.27 (d, *J*=8.79 Hz, 2H, H–Ar); 6.95 (d, *J*=8.79 Hz, 2H, H–Ar); 3.85 (s, 3H, CH_3); 2.95–2.93 (m, 2H, CH_2); 2.56–2.52 (m, 2H, CH_2); 2.21–2.17 (m, 2H, CH_2) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.3, 159.7, 156.5, 141.9, 128.8, 126.6, 125.9, 114.2, 55.6, 39.1, 25.1, 23.7 ppm; MS (EI): *m/z* (I, %) = 242 $[M]^+$ (86), 214 $[M\text{-}CO]^{+\cdot}$ (15); IR ν_{max} (KBr): 3092, 1645 (br), 1516, 1390, 1253, 1223, 1032, 1016, 837, 661, 631, 590, 567, 525, 426 cm^{-1}; Anal. $C_{14}H_{14}N_2O_2$ (242): calcd C 69.41, H 5.82, N 11.56; found C 69.35, H 5.81, N 11.61.

*4.6.3. 1-(4-Methoxycarbonylphenyl)-4,5,6,7-tetrahydro-1H-benzimidazol-7-one **(4g)***. White powder; yield 55%; mp 162–165 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.13 (d, *J*=8.04 Hz, 2H, H–Ar); 7.73 (s, 1H, H–Im); 7.45 (d, *J*=8.07 Hz, 2H, H–Ar); 3.94 (s, 3H, CH_3); 2.98–2.94 (m, 2H, CH_2); 2.58–2.54 (m, 2H, CH_2); 2.22–2.18 (m, 2H, CH_2) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.2, 166.0, 157.4, 141.7, 139.5, 130.5, 130.3, 125.5, 125.1, 52.4, 39.1, 25.1, 23.6 ppm; MS (EI): *m/z* (I, %) = 270 $[M]^+$ (83), 242 $[M\text{-}CO]^{+\cdot}$ (26); IR ν_{max} (KBr): 3097, 2953, 1732 (br), 1386, 1282 (br), 1012, 897, 862, 771, 700, 613, 601, 561, 518, 434 cm^{-1}; Anal. $C_{15}H_{14}N_2O_3$ (270): calcd C 66.66, H 5.22, N 10.36; found C 66.61, H 5.19, N 10.41.

4.7. 4-acetyl-1-(4-methoxyphenyl)-5-methyl-1,3-dihydro-2H-imidazol-2-one (11). White powder; mp 236-240 ºC; ^{1}H NMR (300 MHz, DMSO-d6, 300 K): δ = 10.55 (s, 1H, NH); 7.24 (d, J=8.79 Hz, 2H, H–Ar); 7.04 (d, J=8.07 Hz, 2H, H–Ar); 3.80 (s, 3H, OCH_3); 2.31 (s, 3H, CH_3); 2.17 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d6): δ = 186.5, 159.0, 151.8, 130.5, 129.3, 126.3, 118.8, 114.4, 55.4, 28.1, 11.4 ppm; MS (EI): m/z (I, %) = 246 $[M]^+$ (27), 231 $[M\text{-}CH_3]^{+\cdot}$ (3); IR ν_{max} (KBr): 3300-2900 (br), 1654-1685 (br), 1170, 1070, 821, 797, 754, 619, 590, 528, 467 cm^{-1}; Anal. $C_{13}H_{14}N_2O_3$ (246): calcd C 63.40, H 5.73, N 11.38; found C 63.43, H 5.70, N 11.41.

4.8. X-ray determination. Crystals of compounds **12**×1/6C_6H_6 and **2b** were grown from benzene and toluene solutions respectively. For each of compounds, a single crystal was set at a Bruker SMART-APEX-II diffractometer (graphite-monochromatized Mo-K_α radiation, ω scan technique) under a stream of cooled nitrogen, where crystallographic parameters and experimental reflections were measured. Data reduction was performed using SAINT program.[22] The structures were solved by direct methods and refined by least squares on F^2 in anisotropic approximation for non-hydrogen atoms. Positions of H atoms were calculated geometrically. The refinement of H atoms was carried out in isotropic approximation. In **2b**, the BF_3 group was found to be rotationally disordered over three positions with near equal occupancies (0.36:0.32:0.32). Structure **12**×1/6C_6H_6 represents a benzene solvate, the center of the benzene ring being situated at the special point at 3-fold axis. So 1/6 part of the solvate molecule falls per one main molecule in this structure. Crystallographic parameters and selected data for structure refinement are listed in table 7.

Table 7. Crystal data and structure refinement parameters for compounds **12**×1/6C_6H_6 and **2b**.

Compound	**12**	**2b**
empirical formula	$C_{12}H_{13}BF_3N_2O$	$C_{12}H_{14}BF_3N_2O_2$
formula weight	269.05	298.07
T [K]	123(2)	183(2)
Crystal system	trigonal	monoclinic
Space group	*R-3*	$P2_1/c$
a [Å]	24.0099(9)	12.1349(16)
b [Å]	24.0099(9)	9.9424(13)
c [Å]	11.1957(5)	11.8147(6)
β [°]	-	104.568(2)
V [Å$^{3]}$	5589.4(4)	1379.6(3)
Z	18	4
D_{calc} g cm^{-3}	1.439	1.435
μ [mm^{-1}]	0.122	0.123
F(000)	2502	616
reflections		
Collected/uniq	13527/2953	14420/3668
Number of parameters	224	246
GOF on F^2	1.072	0.981
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0348/0.0910	0.0559/0.1218
R_1 / wR_2 (all data)	0.0435/0.0939	0.1218/0.1451
Max/min residuals [e/A^3]	0.202 and -0.249	0.446 and -0.499

All the calculations were performed using SHELXTL-Plus software[23].

The experimental data for structures **12**×1/6C_6H_6 and **2b** were deposited with the Cambridge Crystallographic Data Centre (CCDC registration numbers are 971013 and 971014, respectively). Copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:

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Supporting Information

New regiocontrolled synthesis of 2-unsubstituted 1-aryl-4- and 1-aryl-5-acylimidazoles

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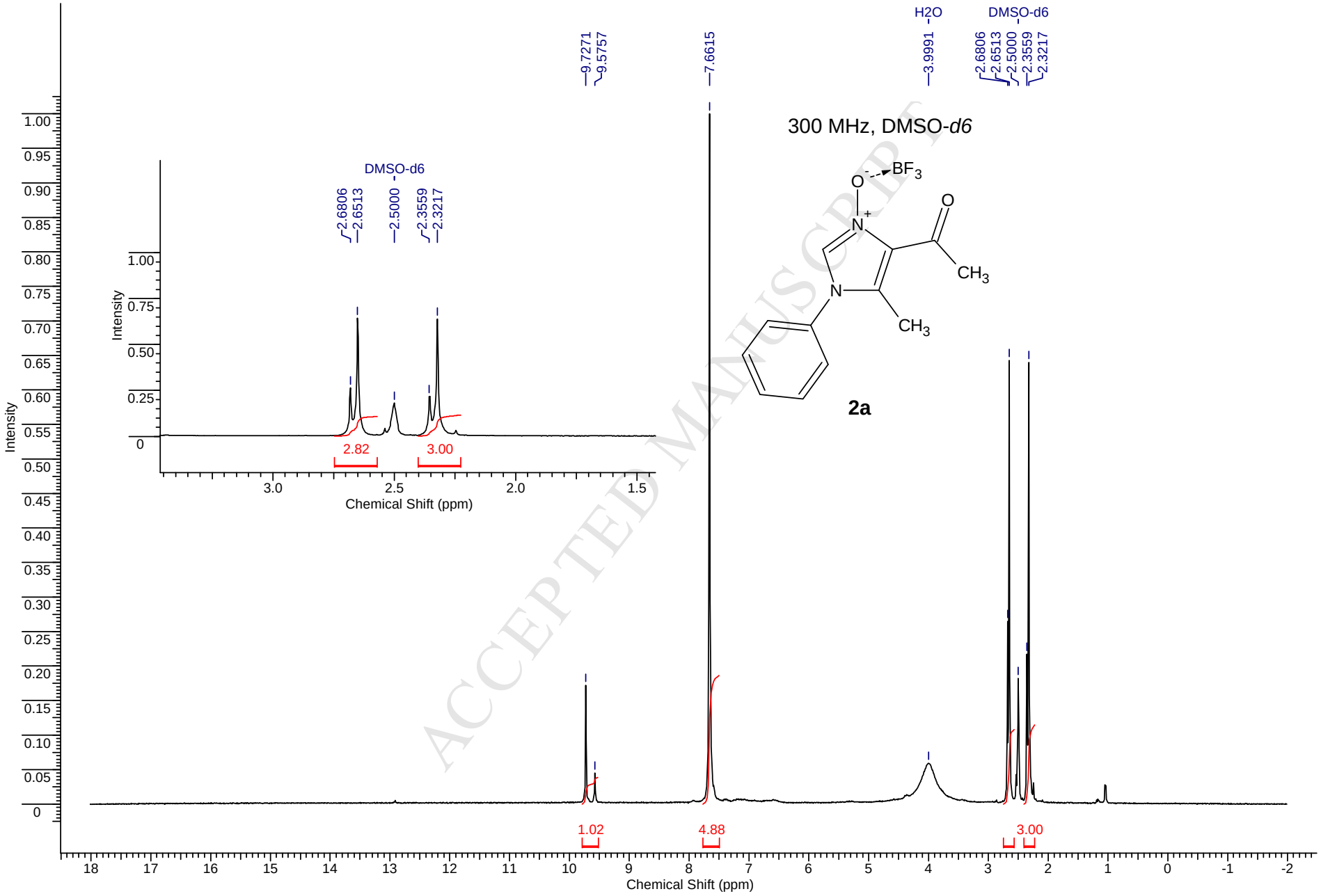
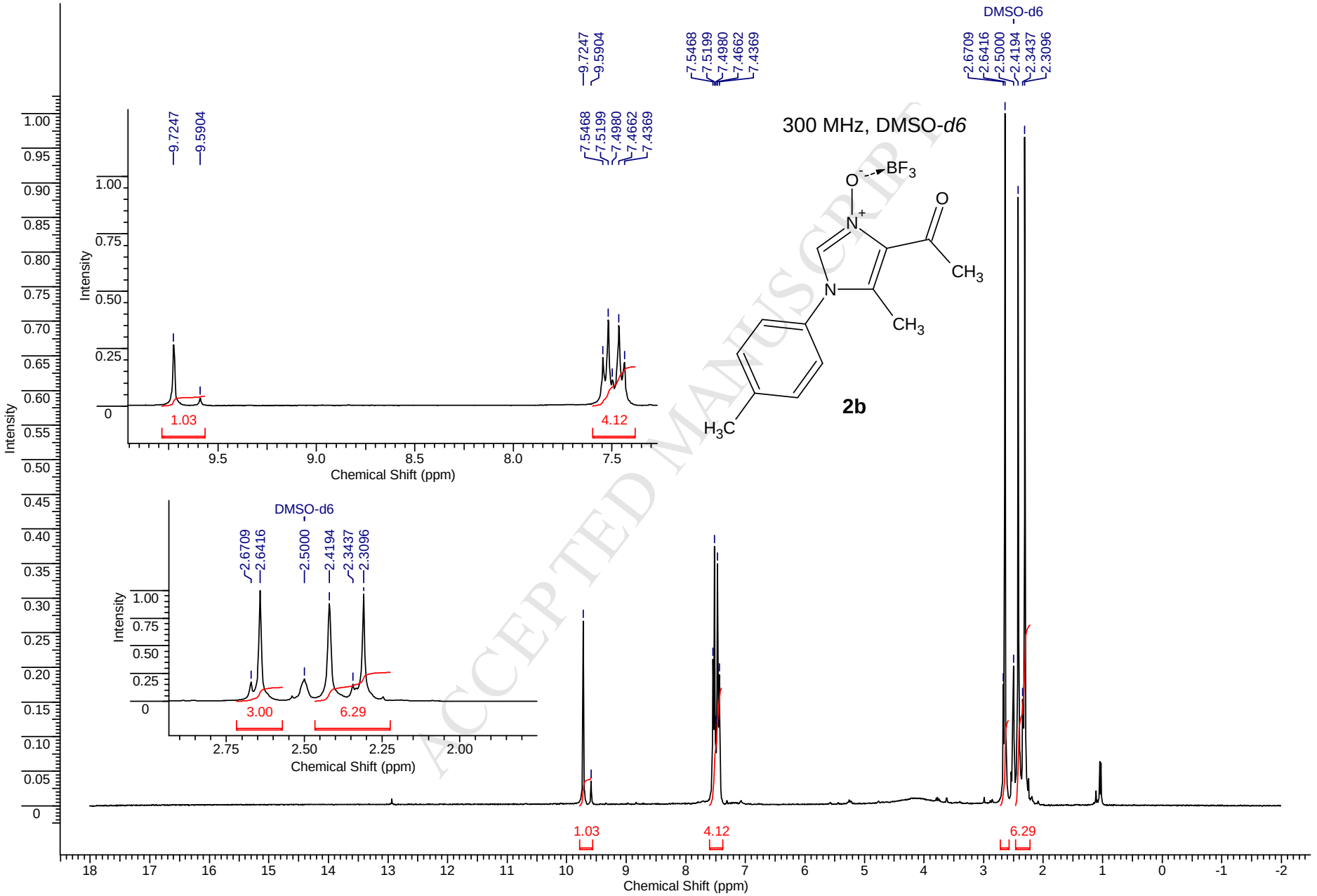
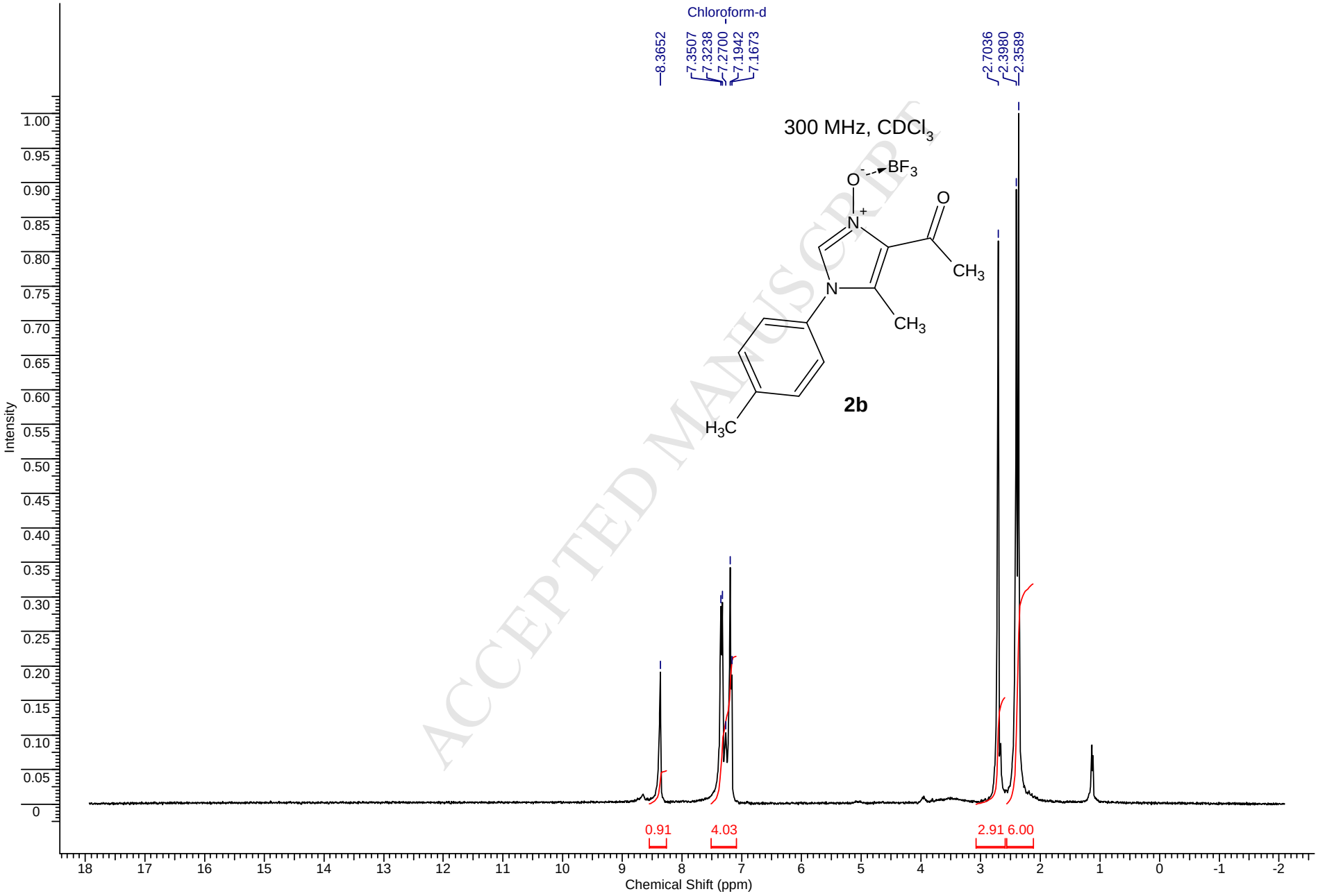
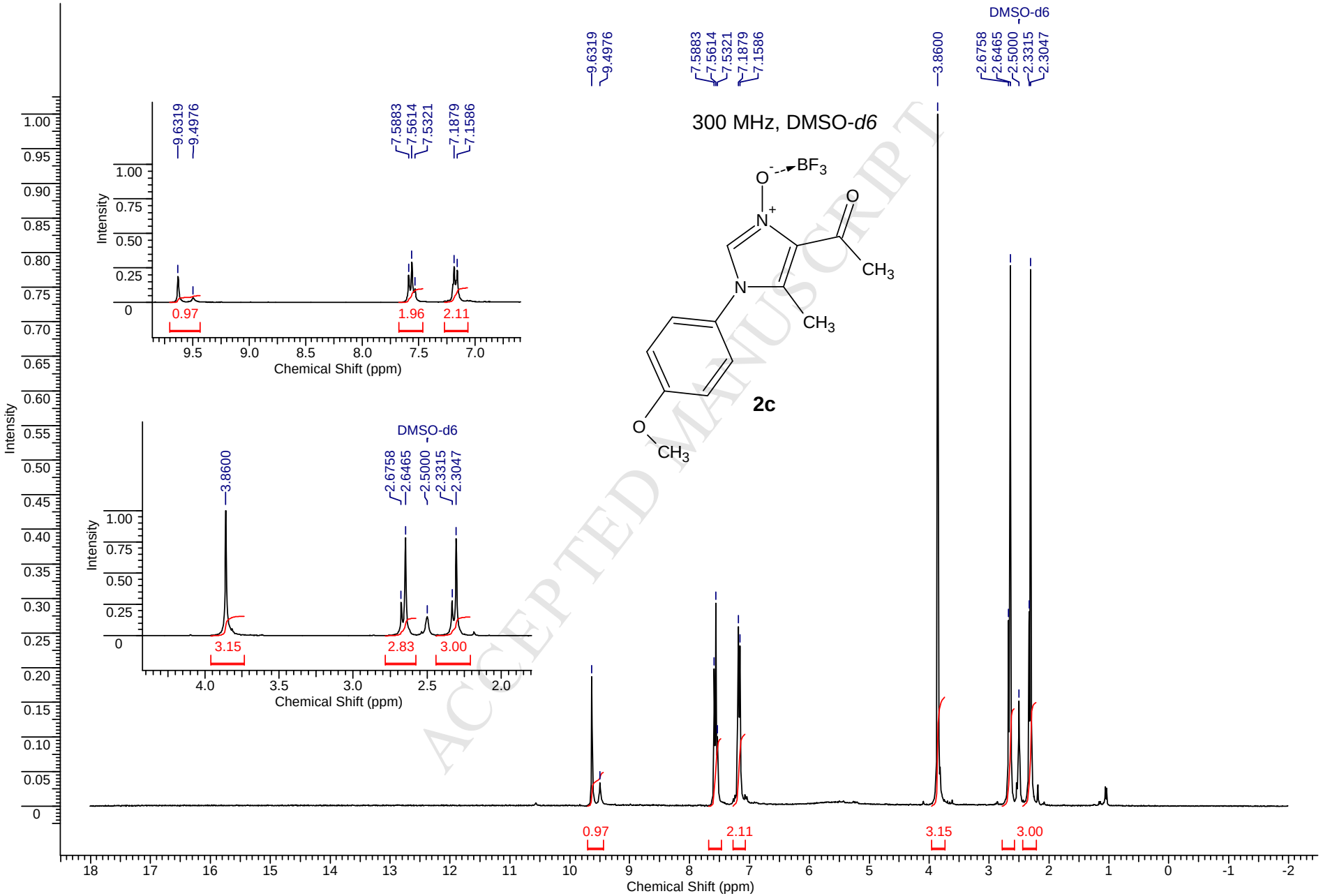
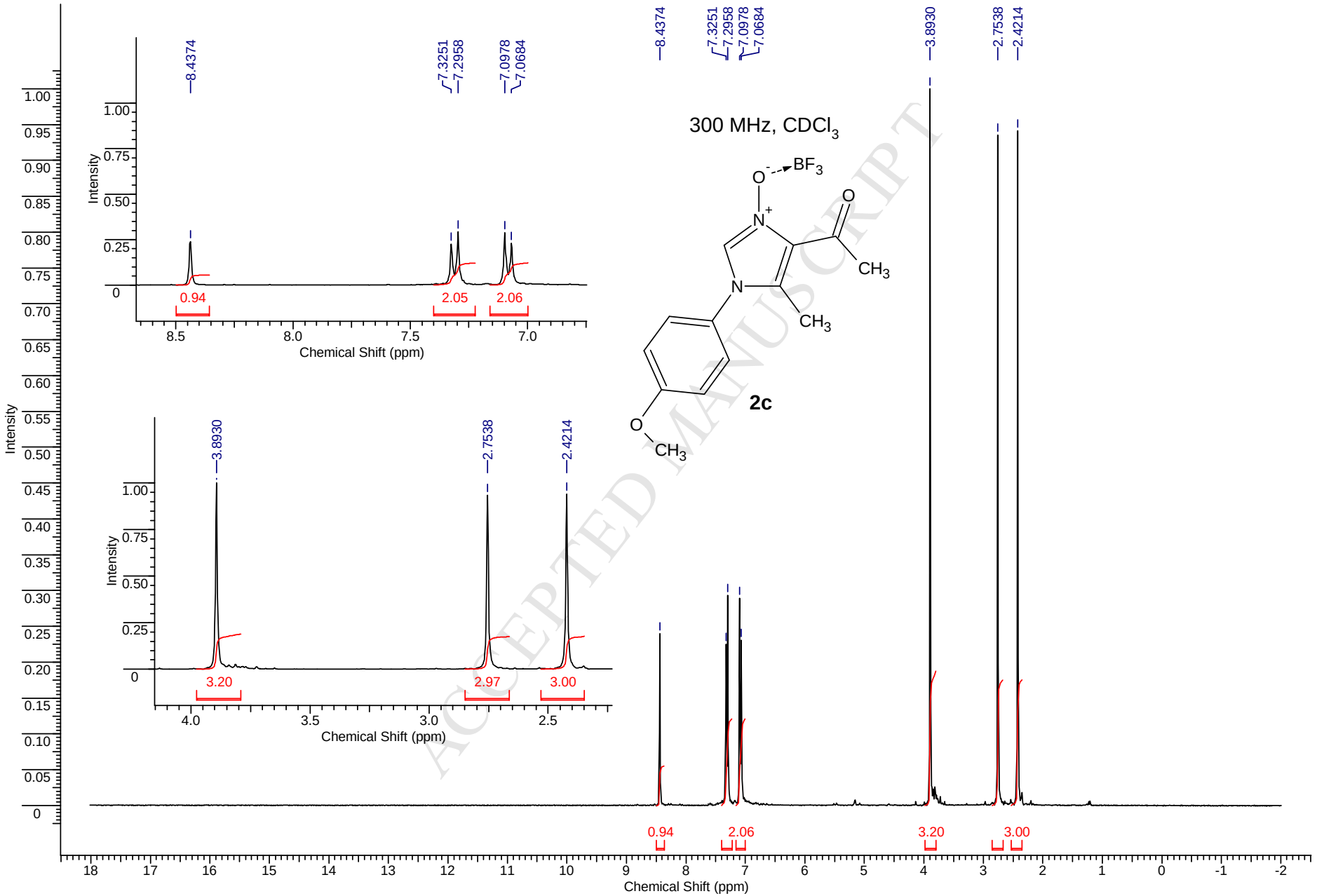
^{1}H, ^{13}C NMR, EIMS and IR spectra.

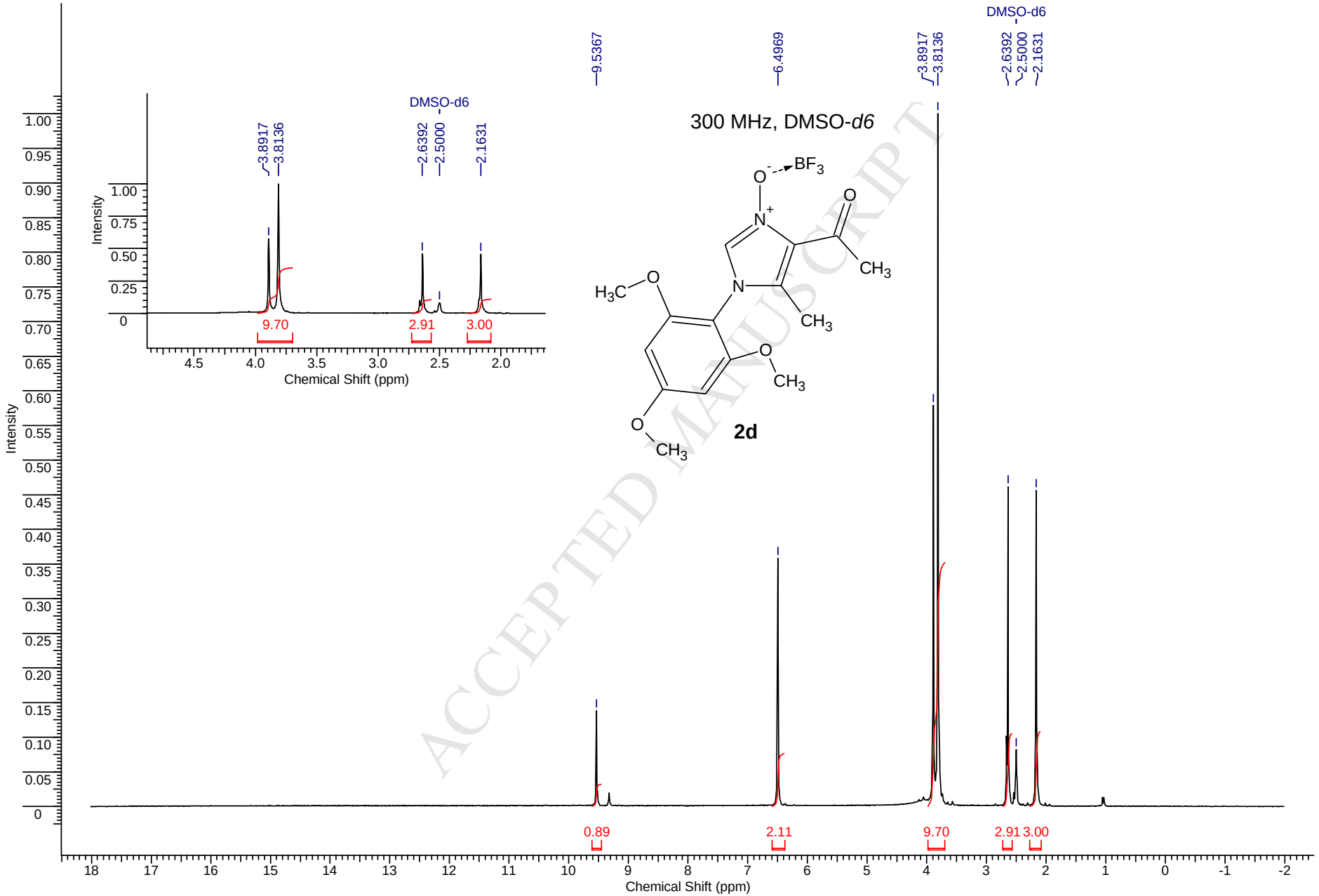


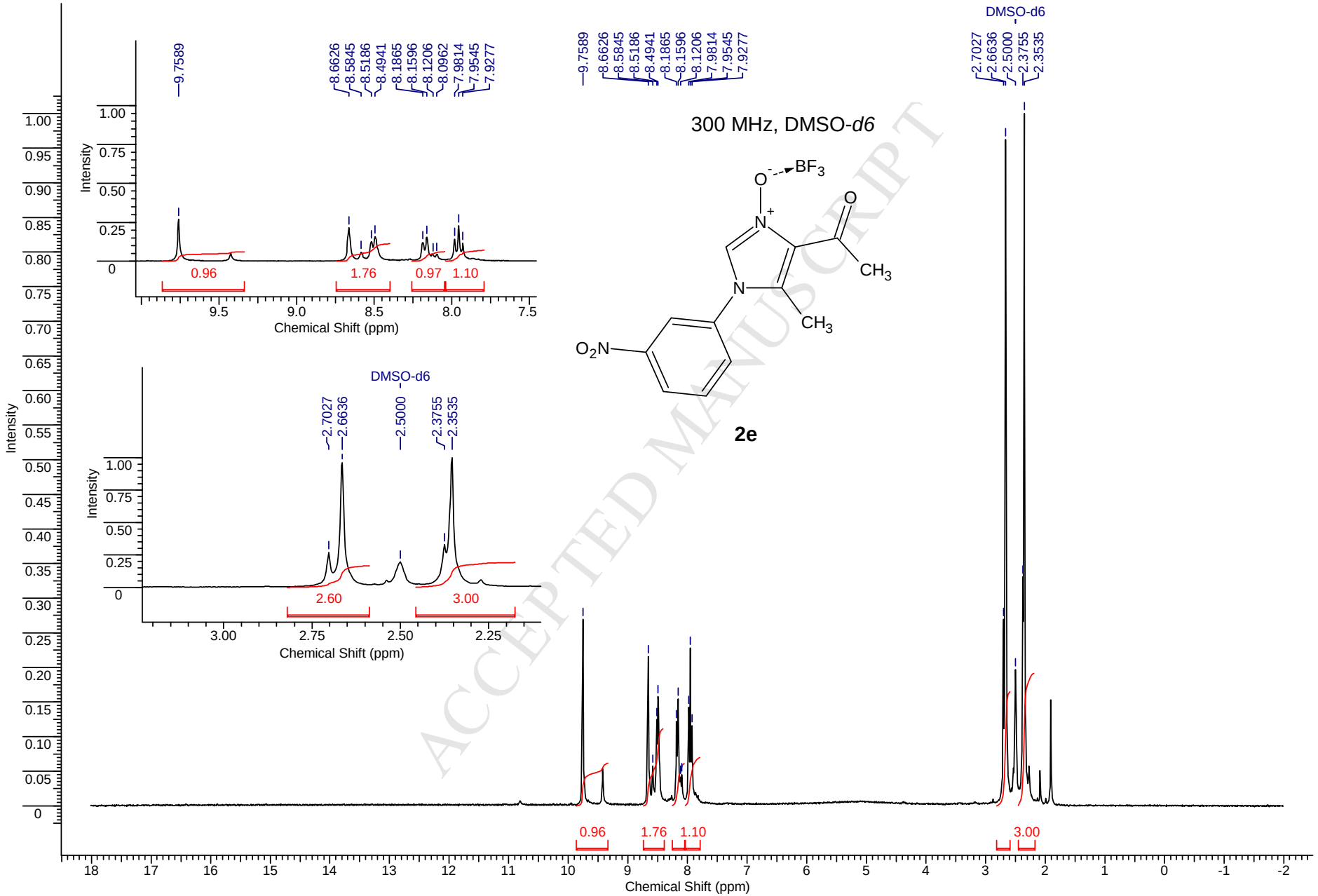


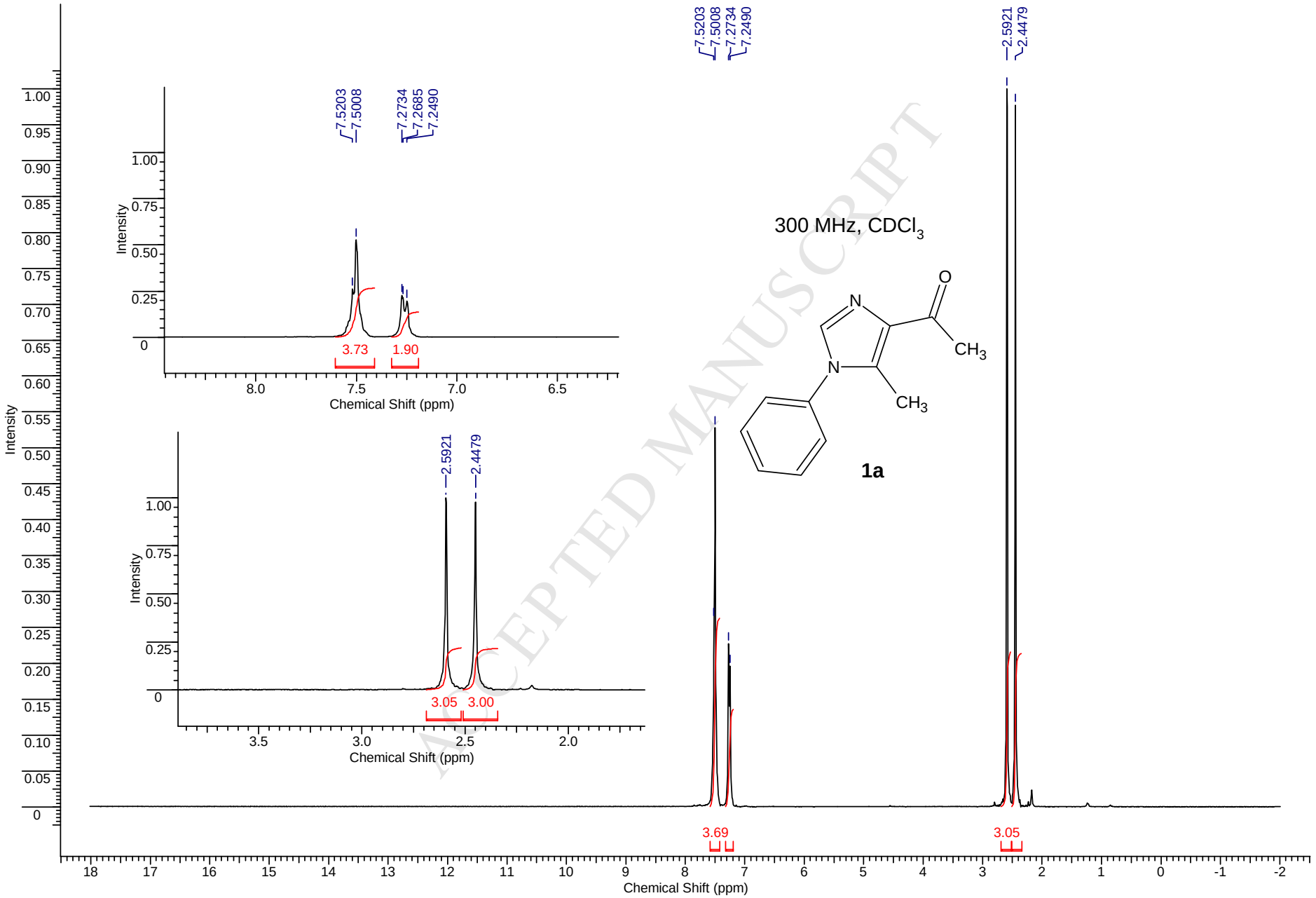


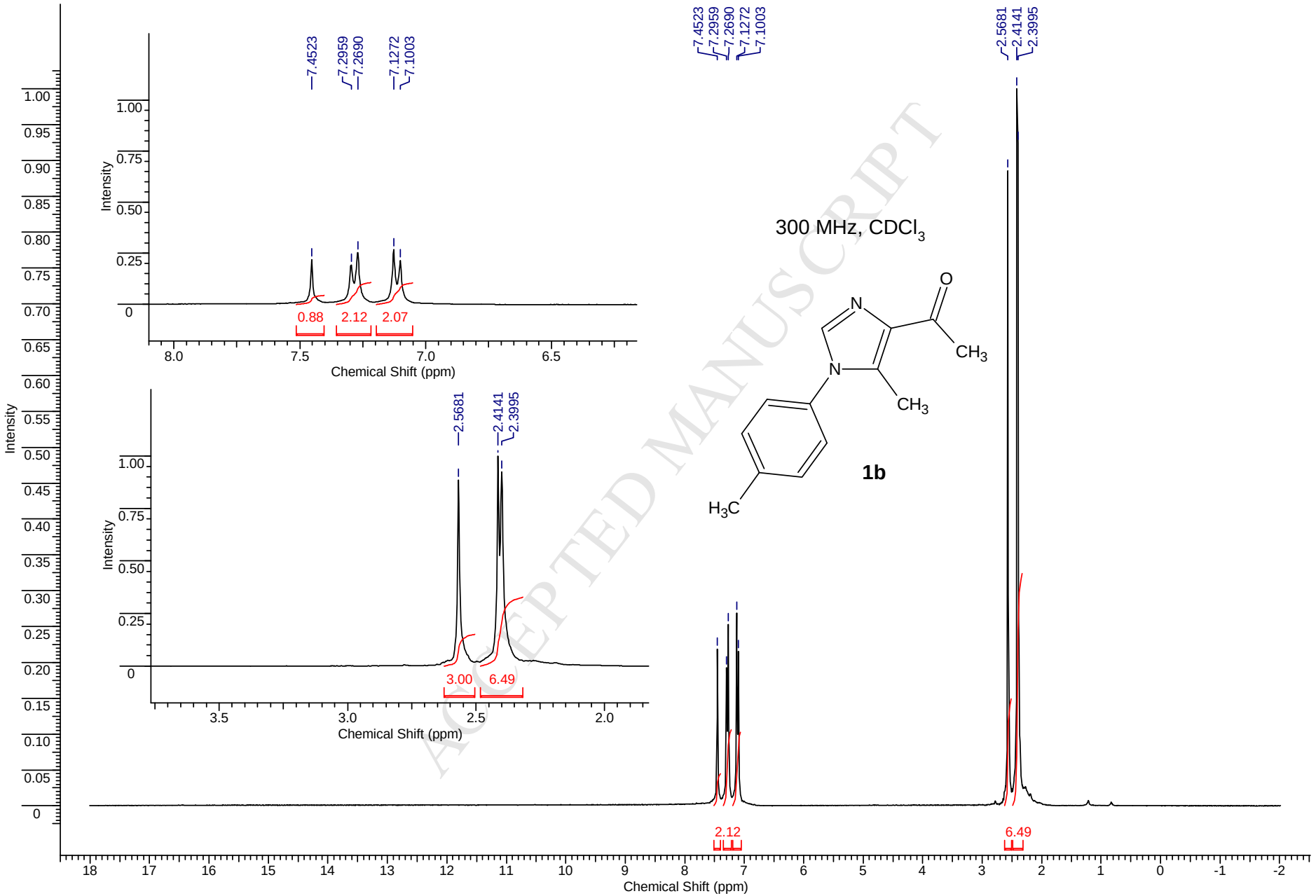


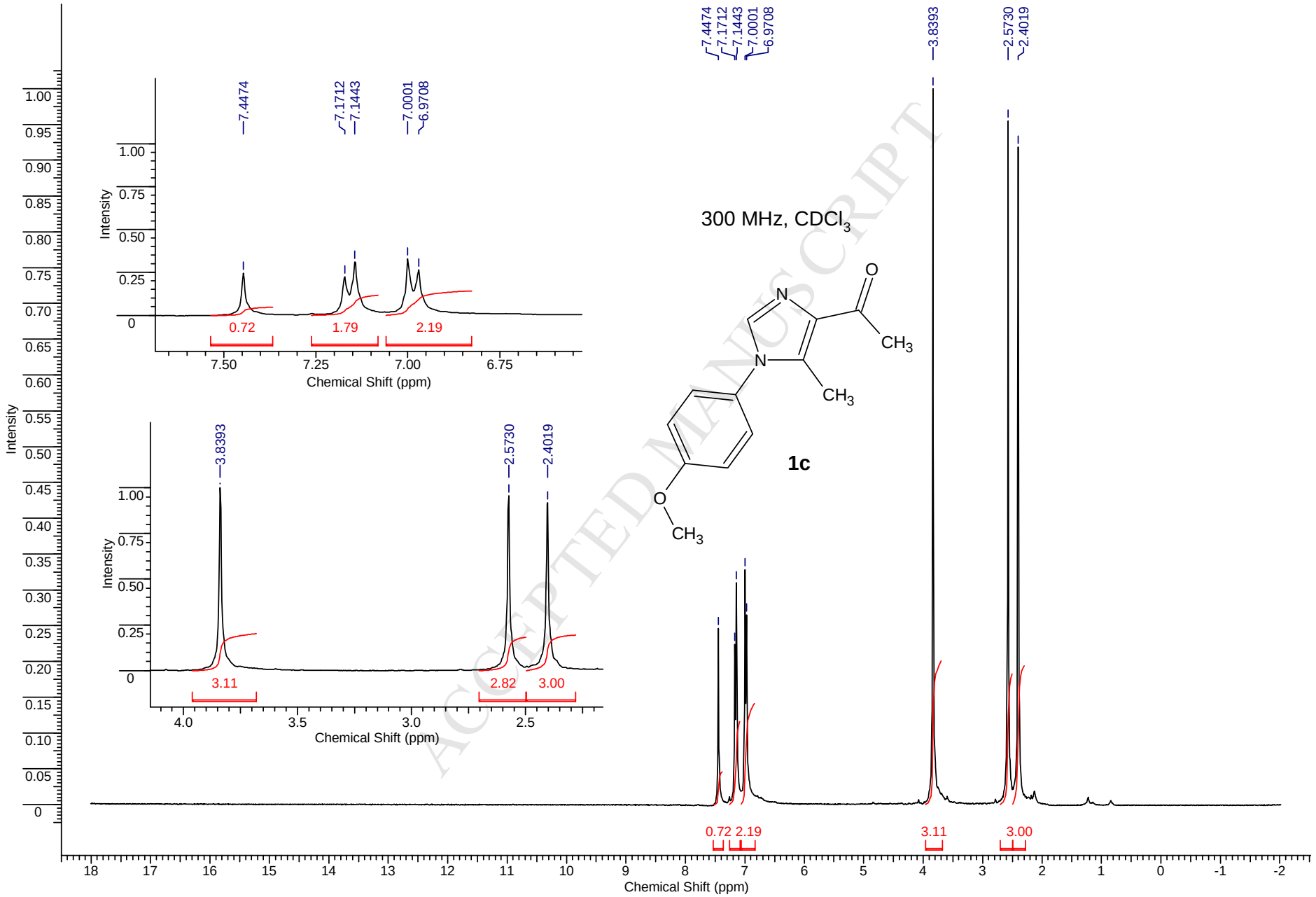


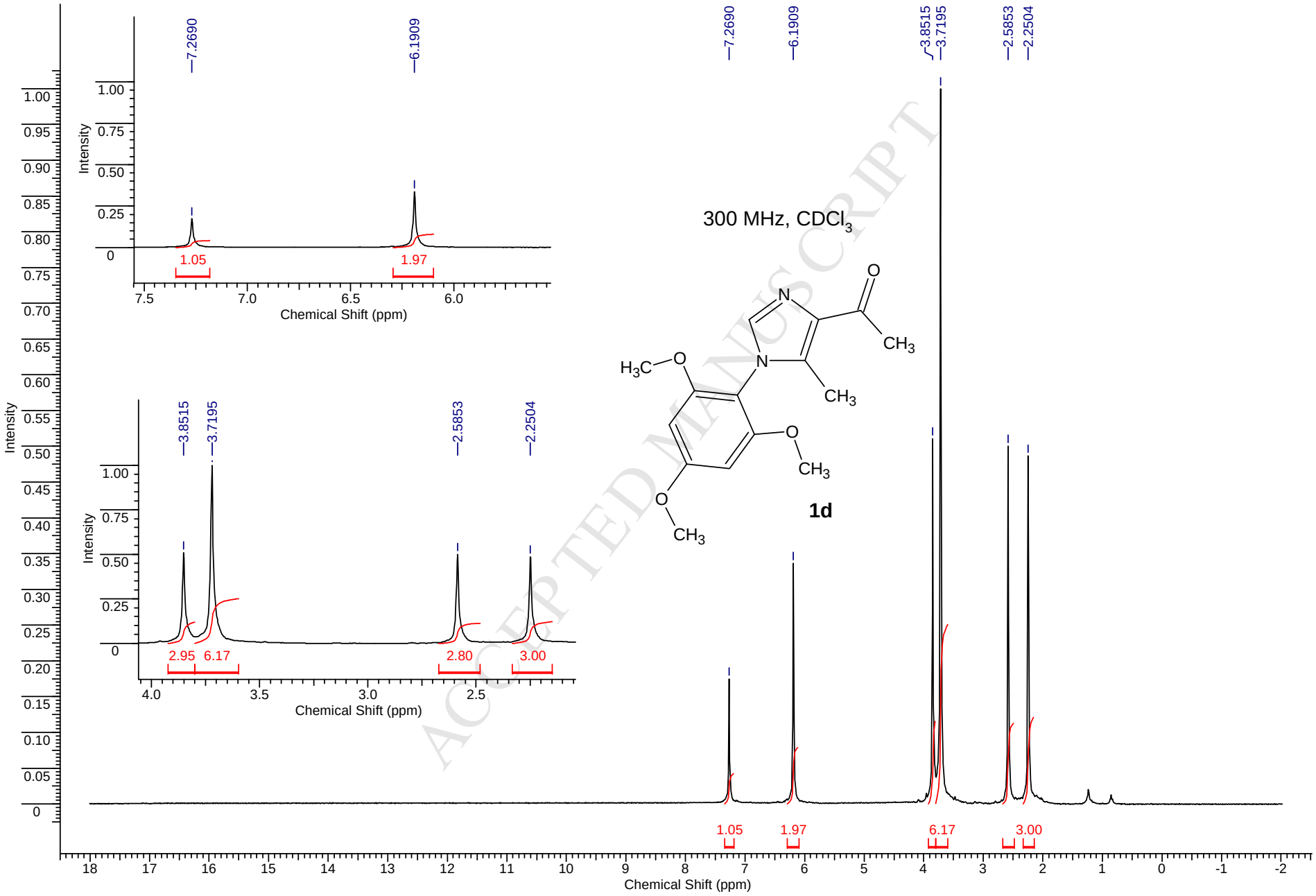


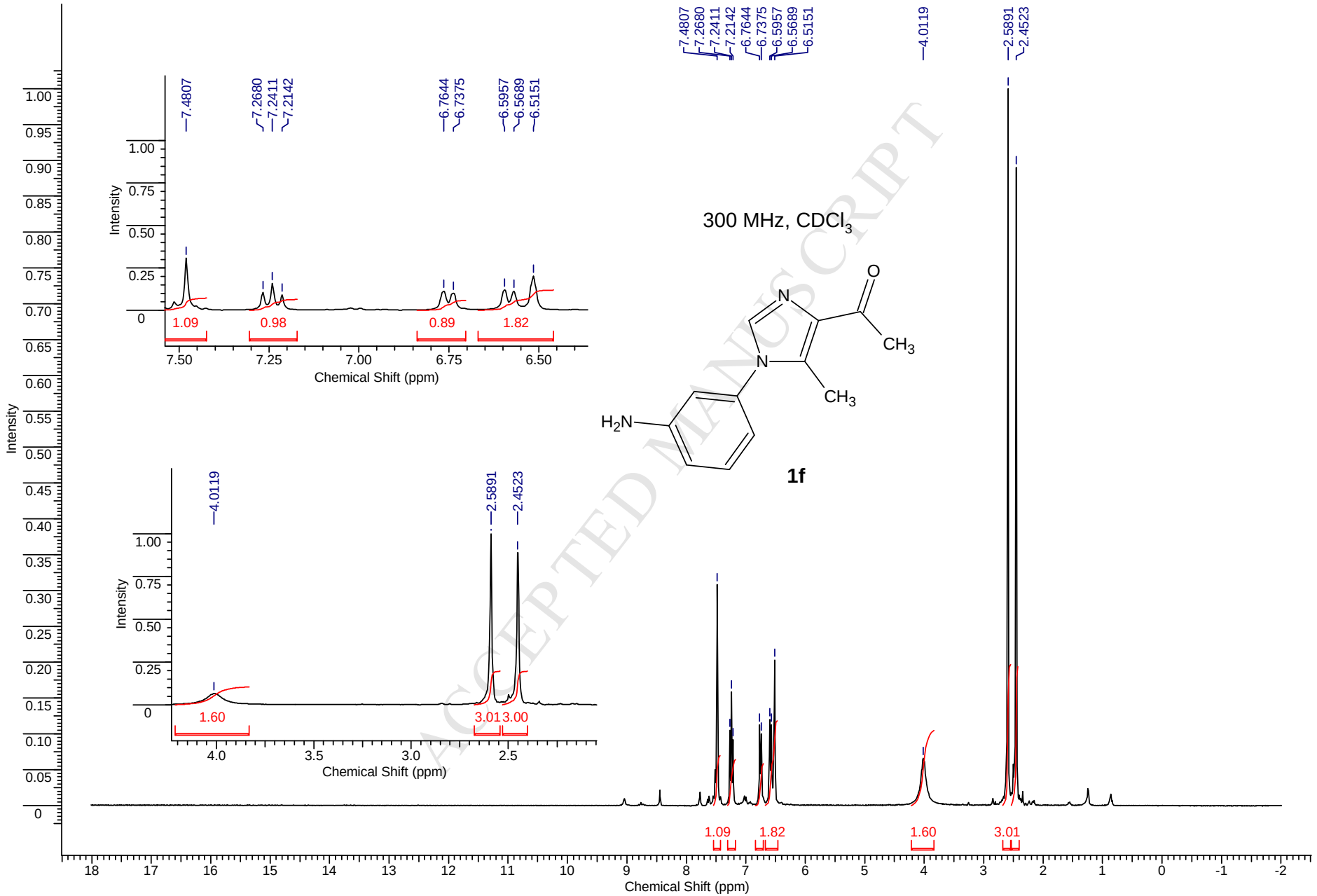


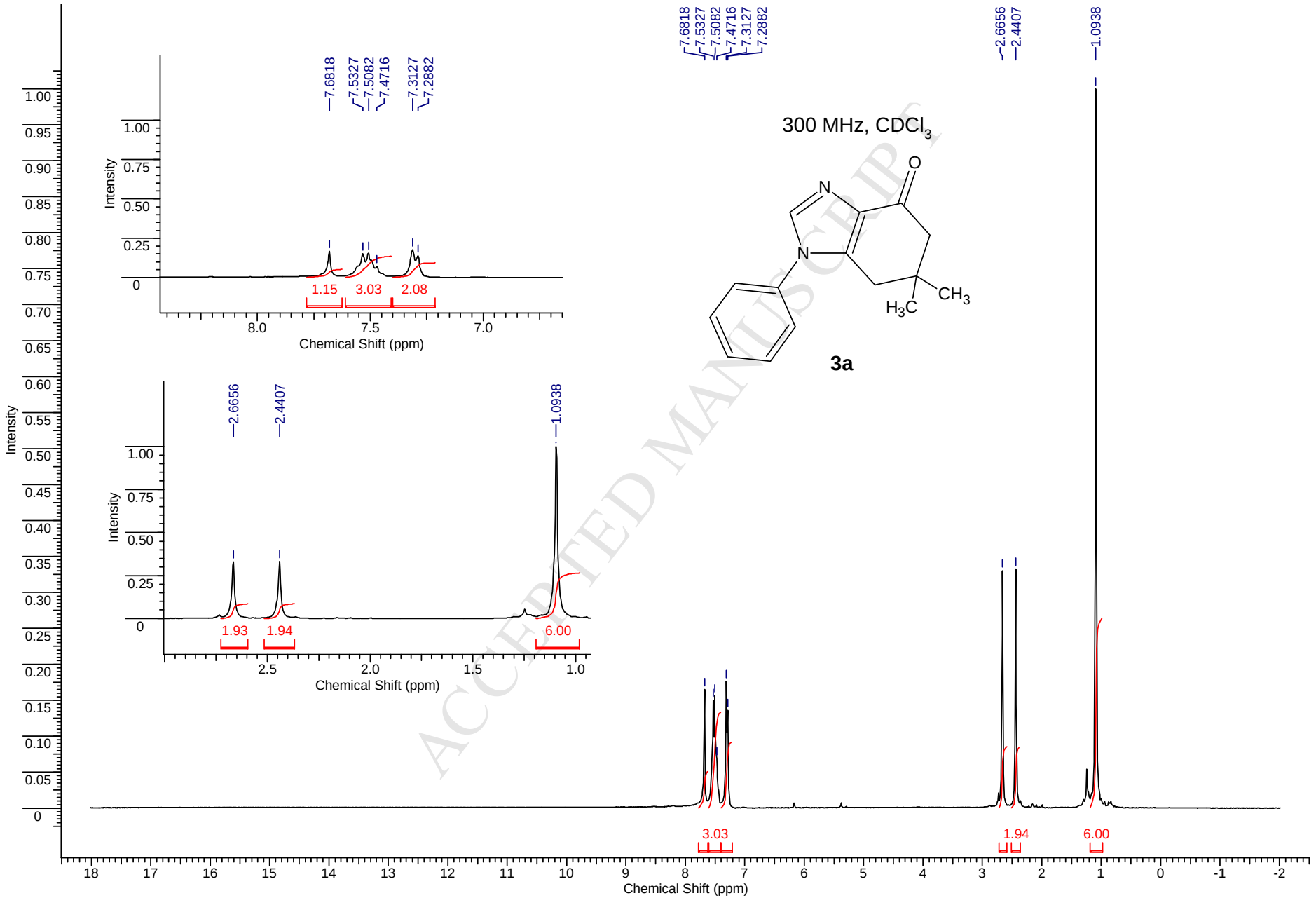


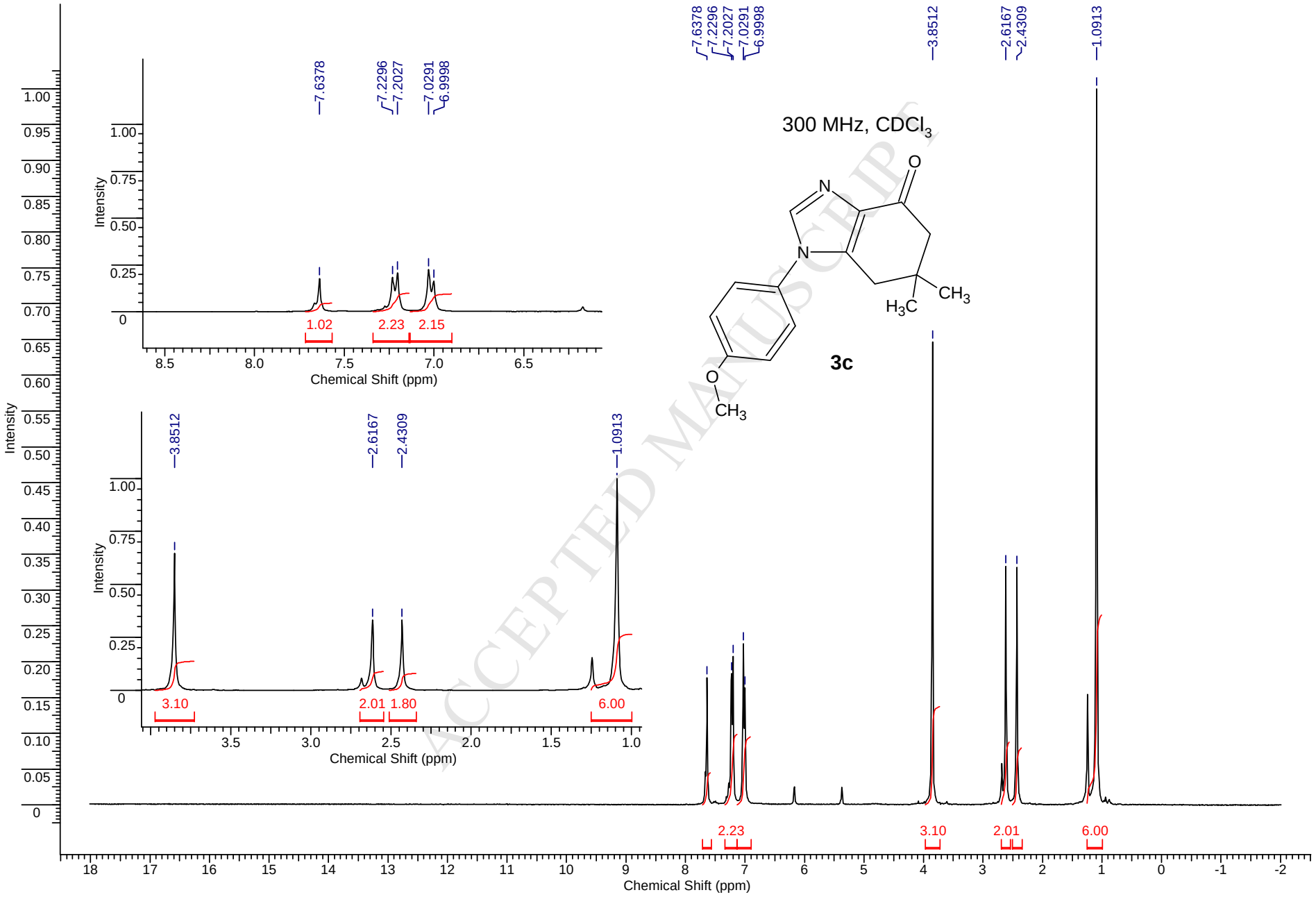


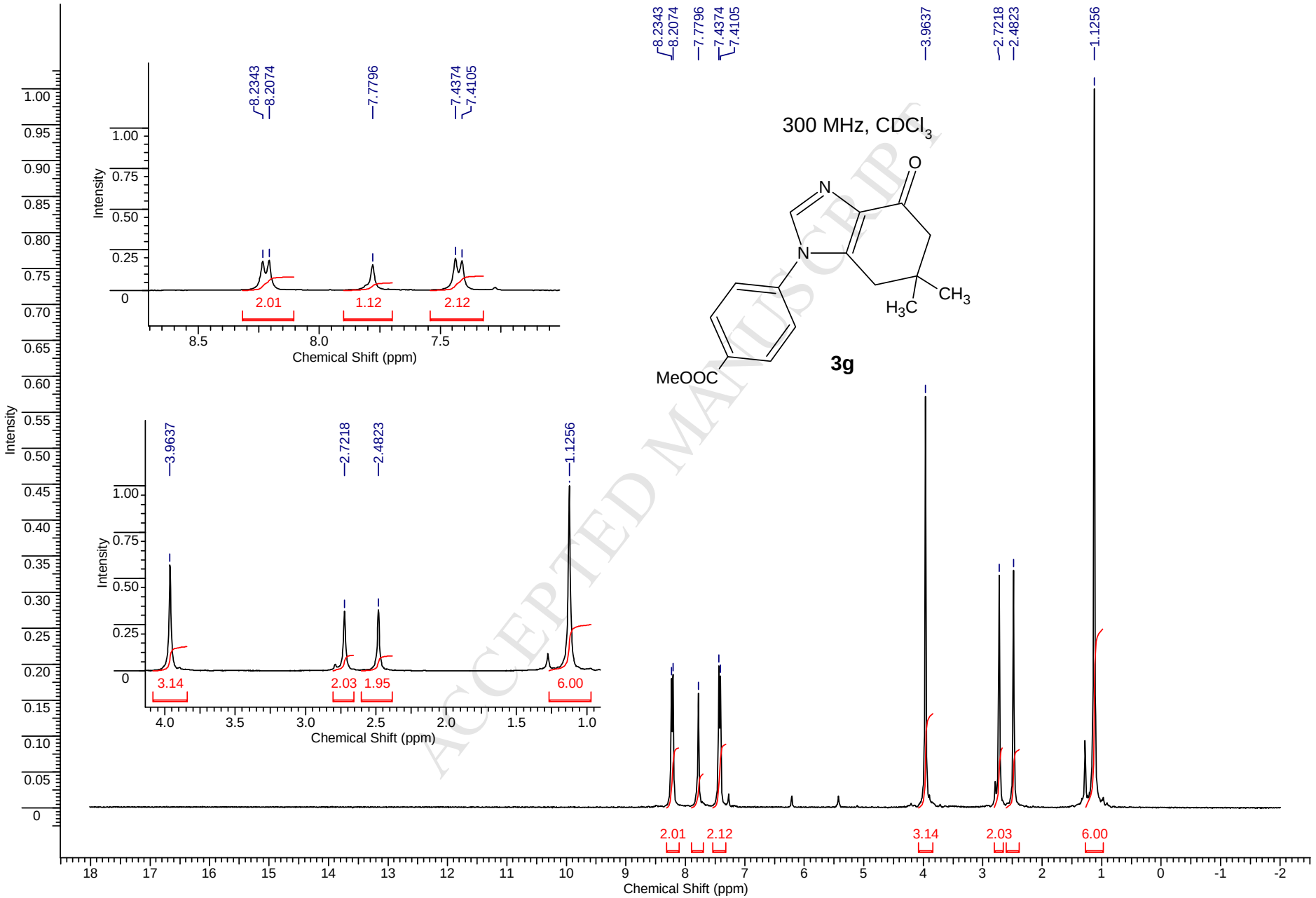


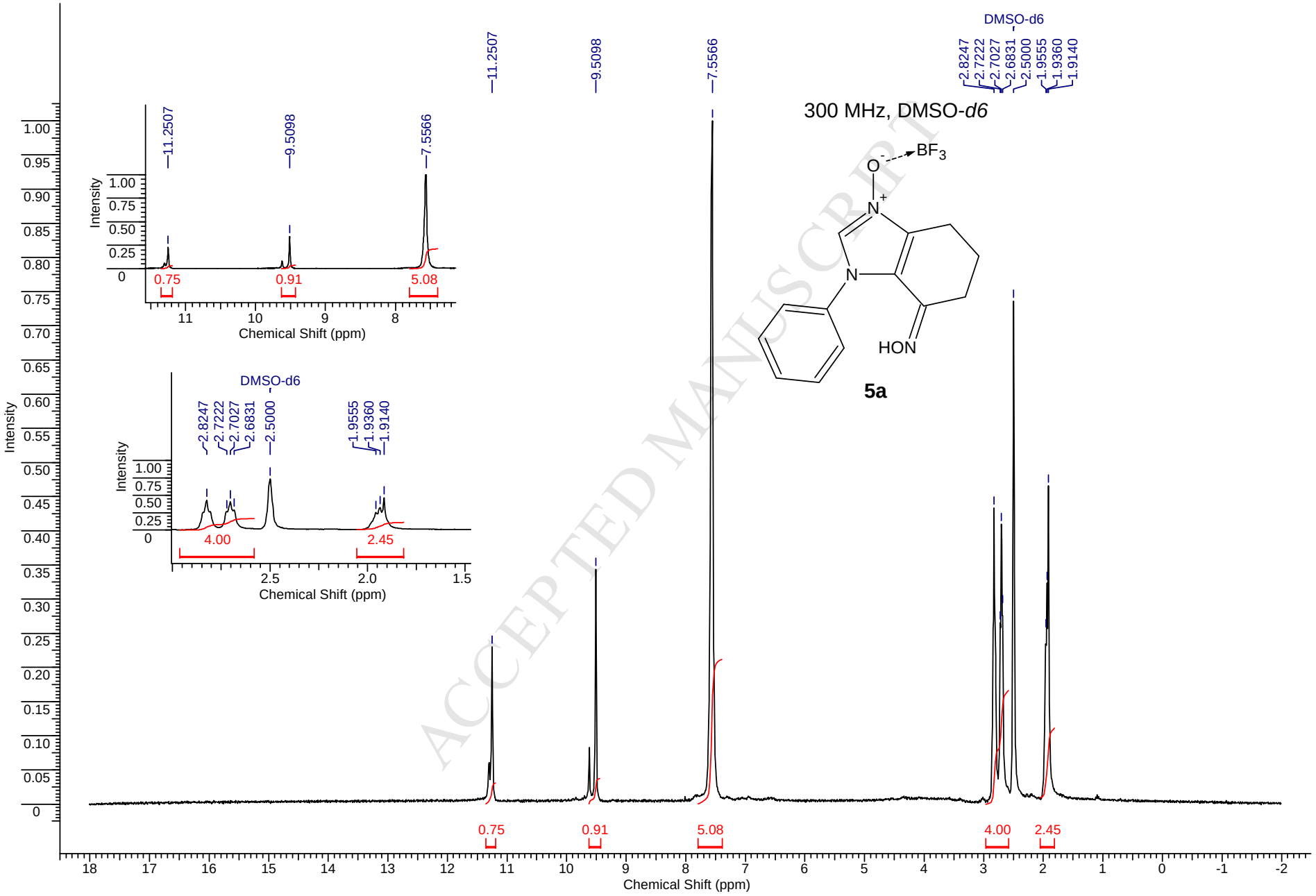


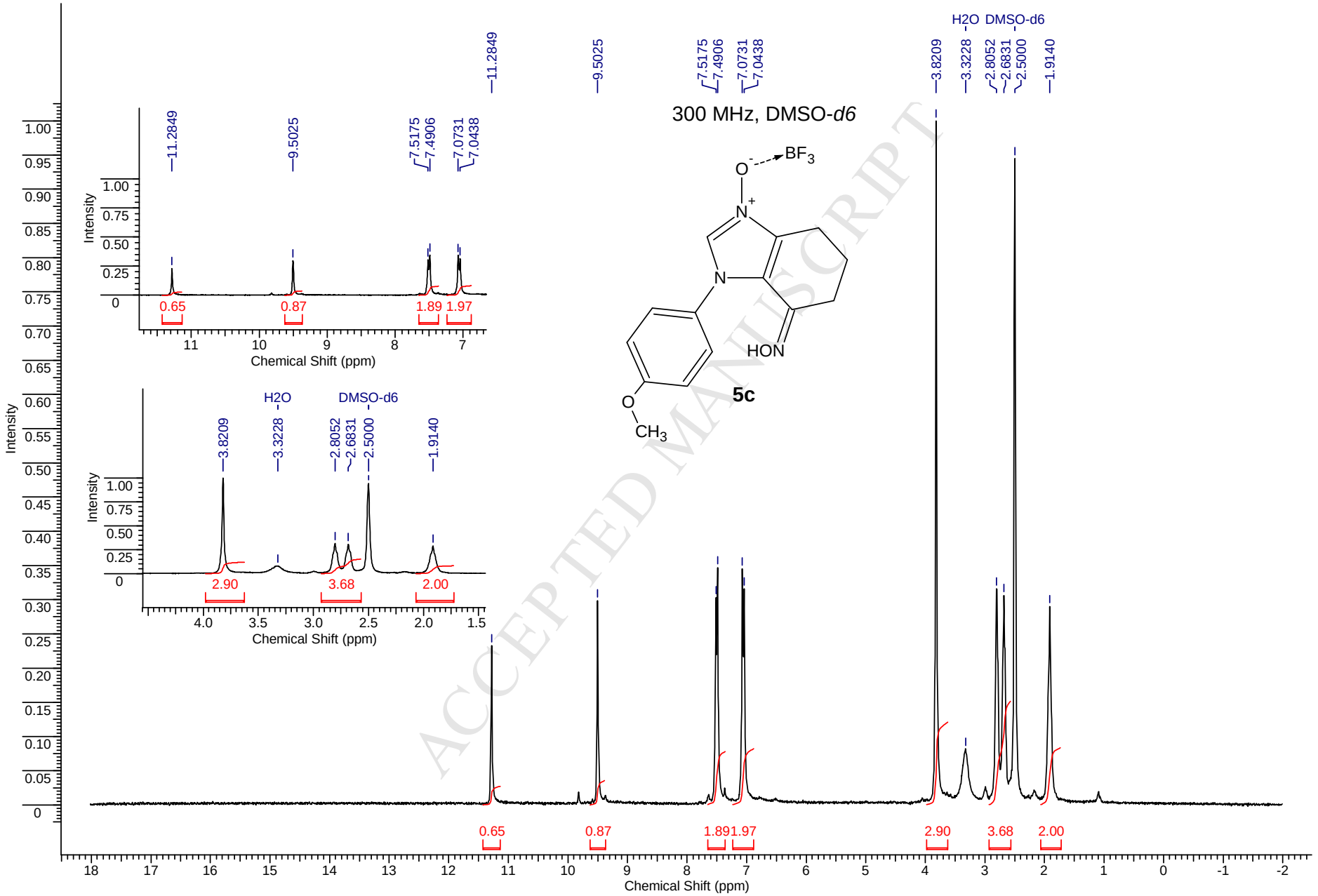


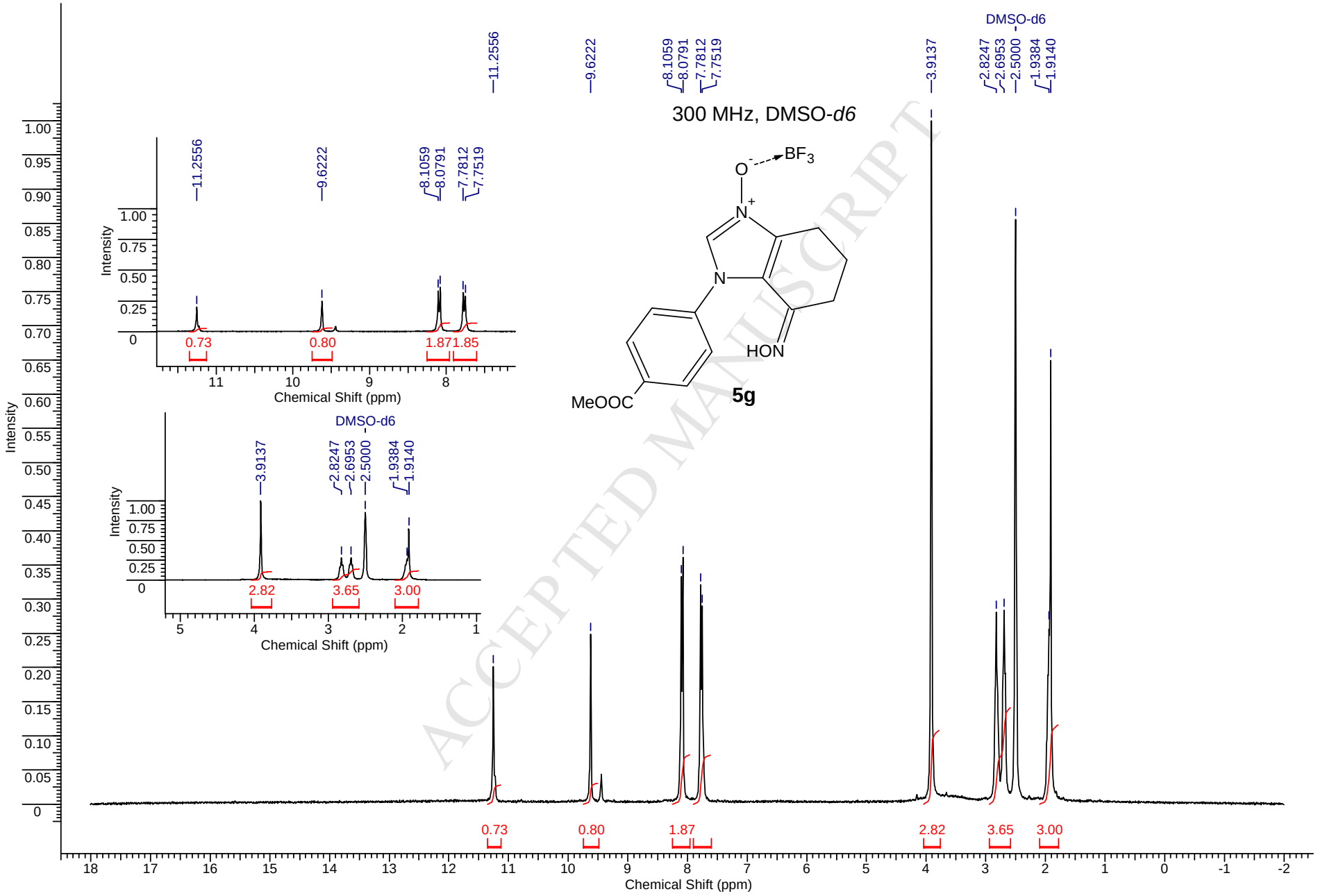


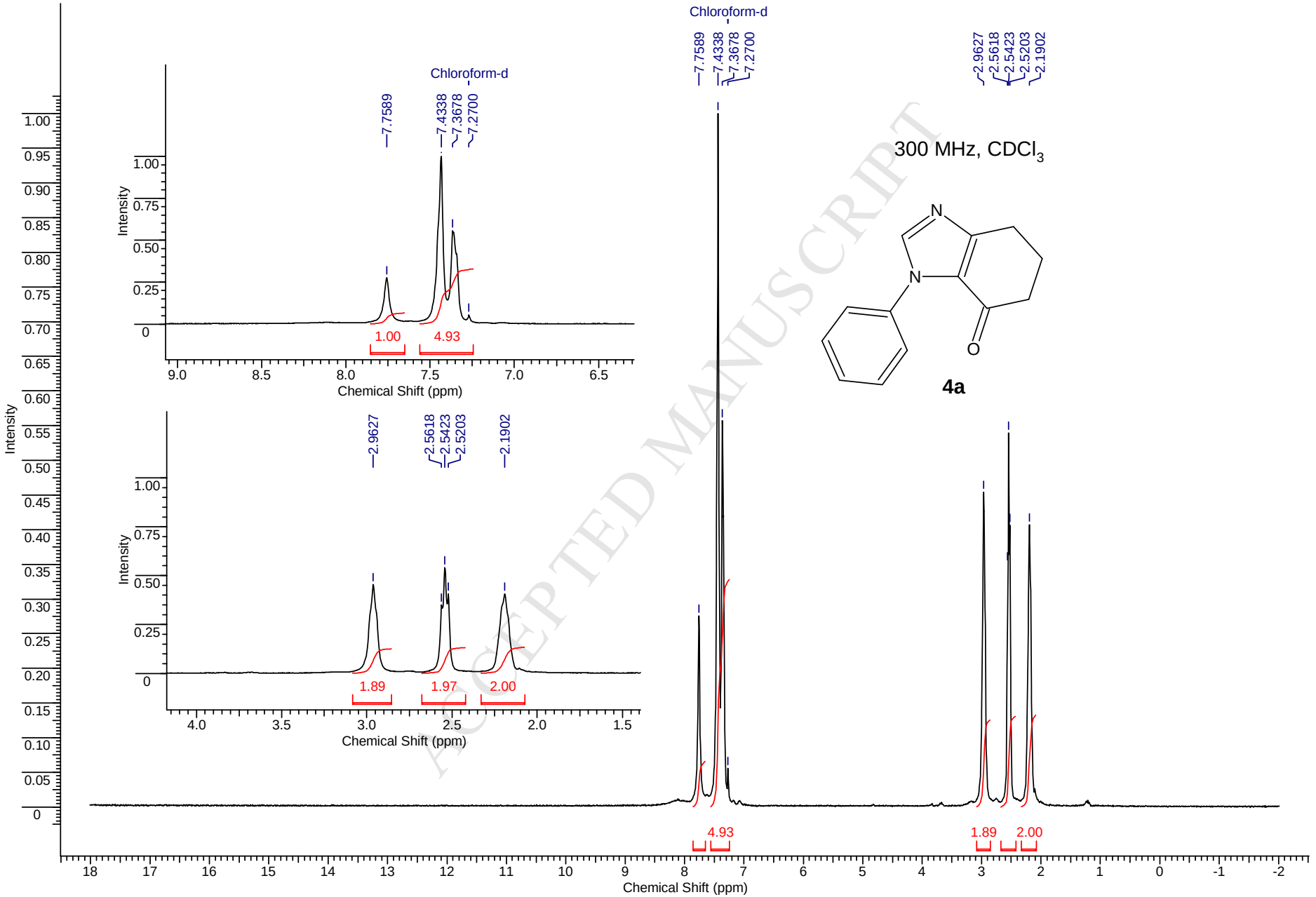


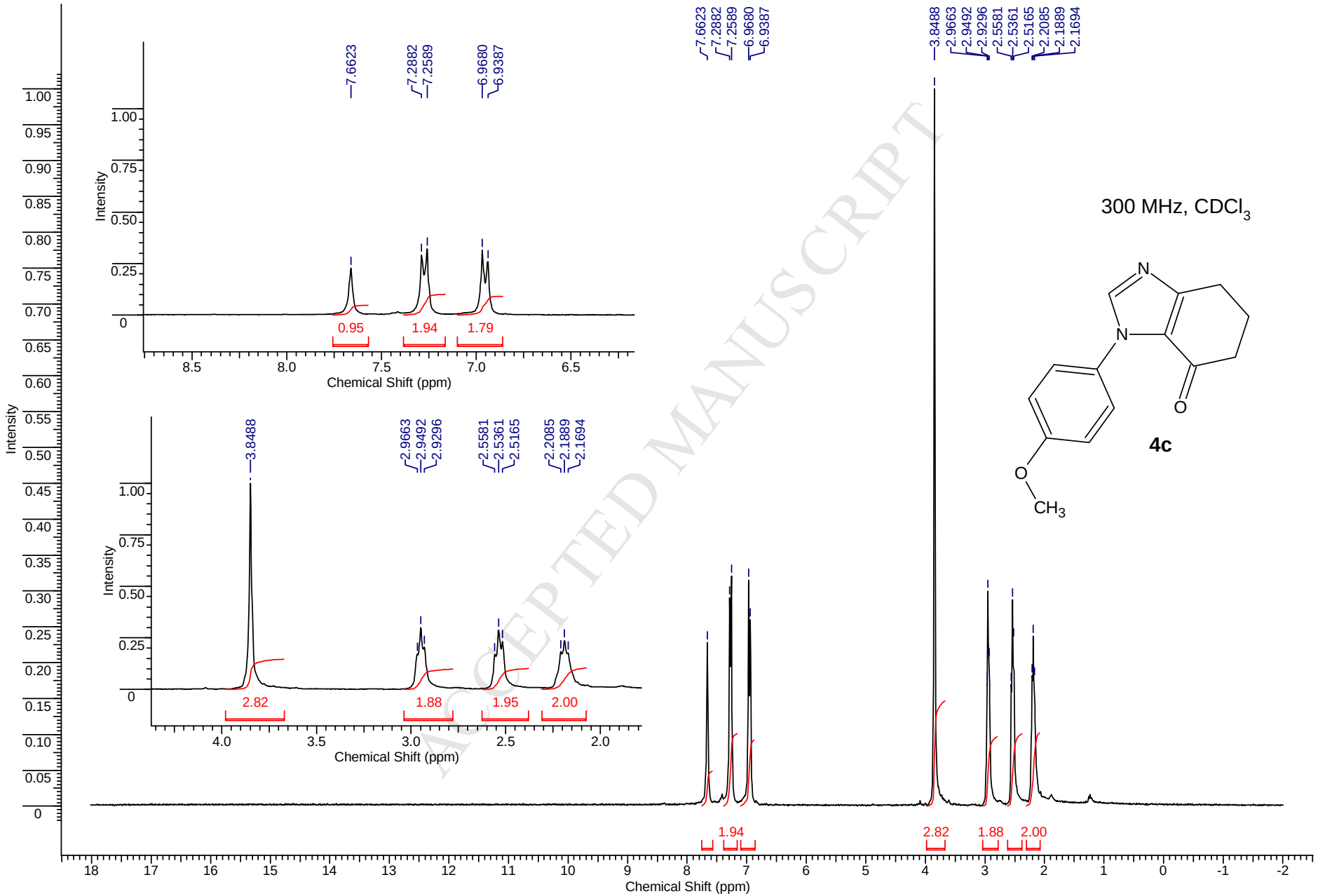


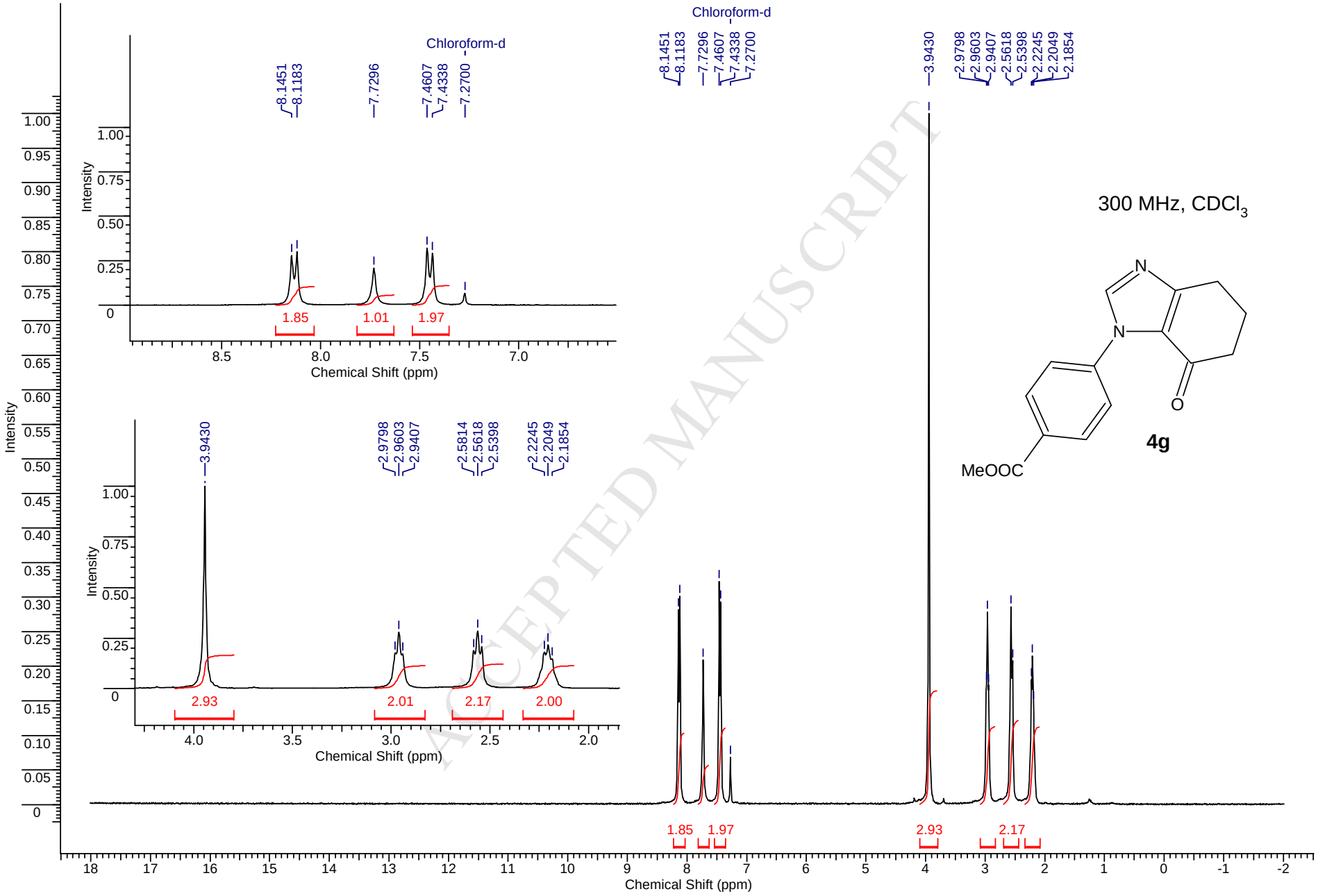


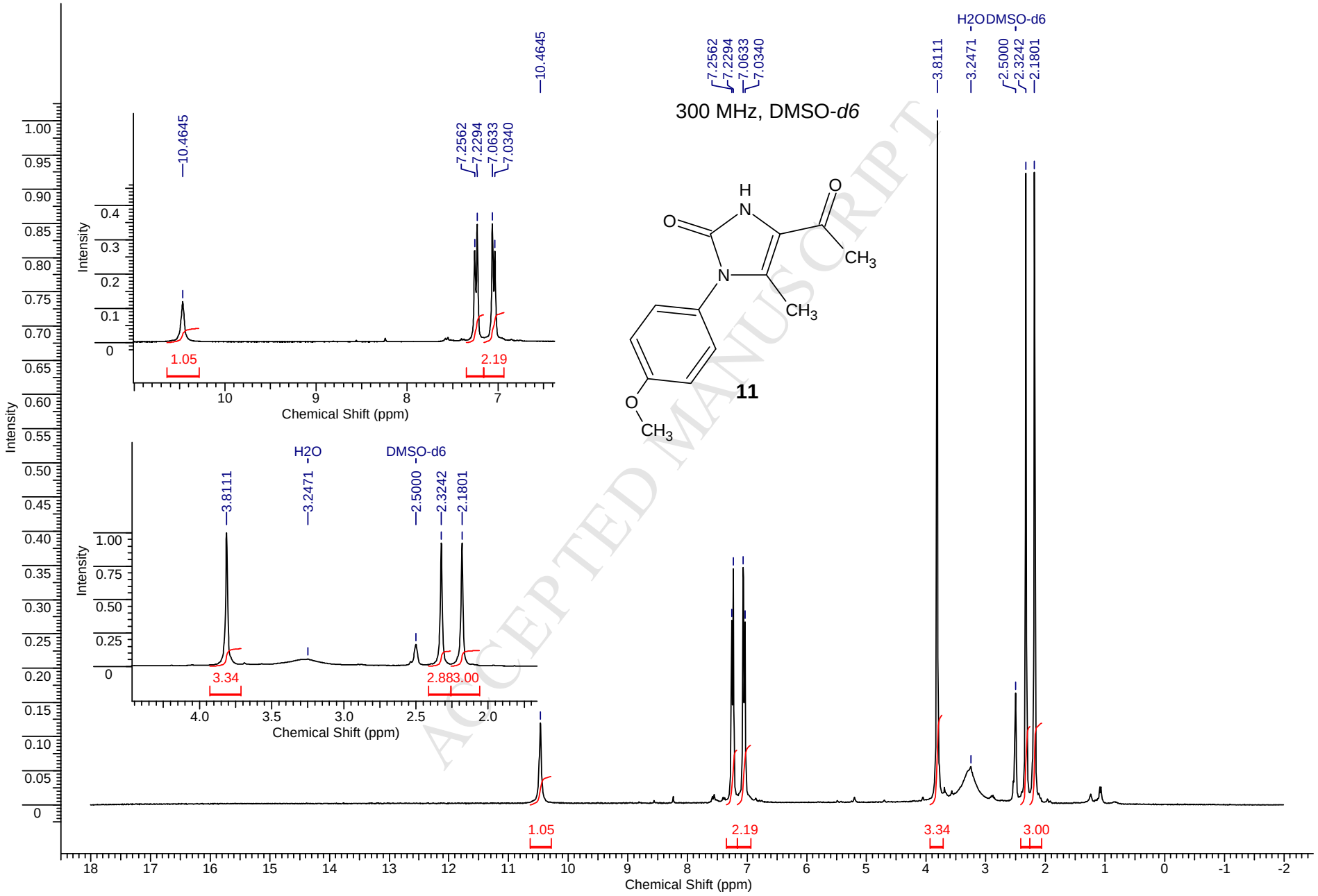


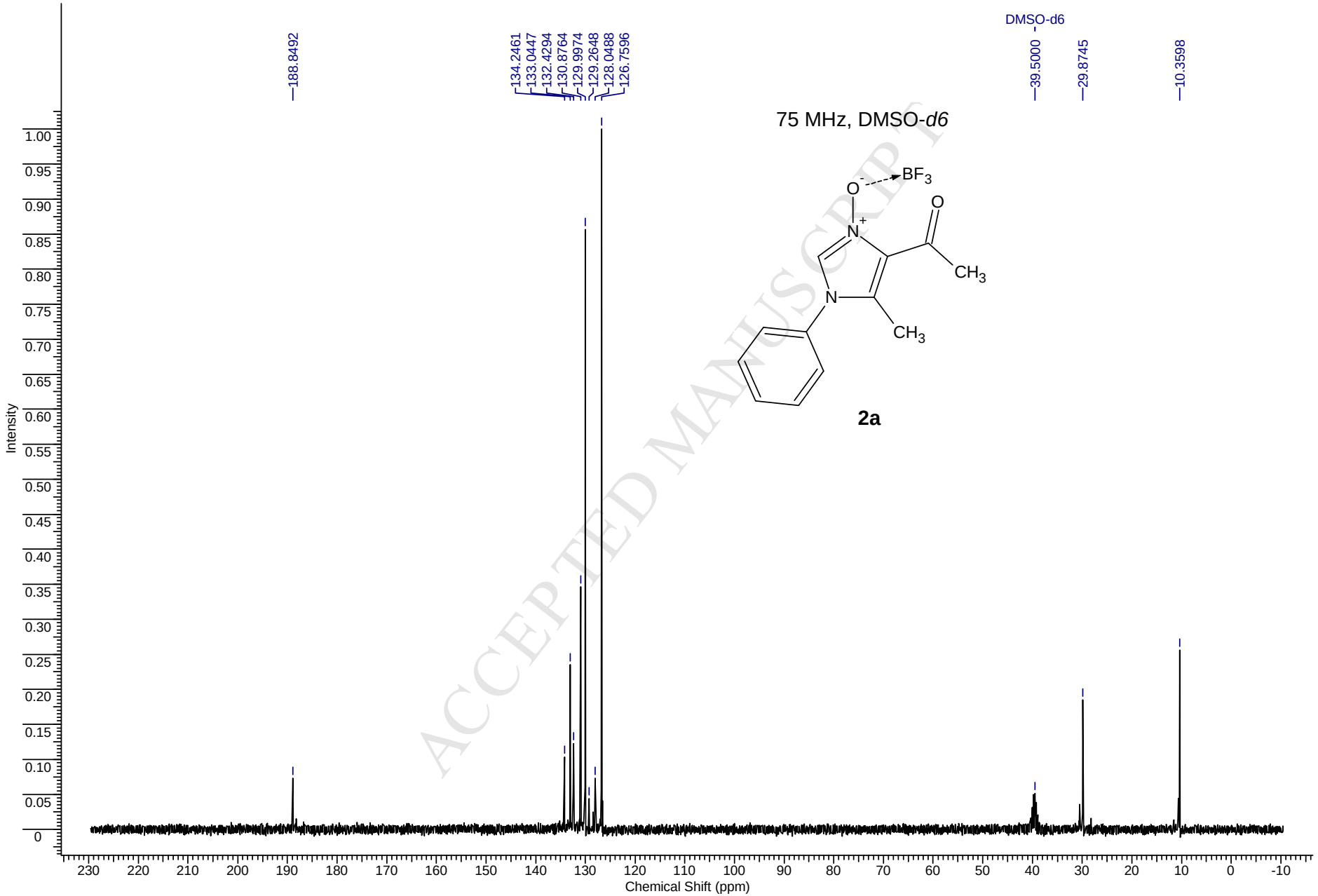


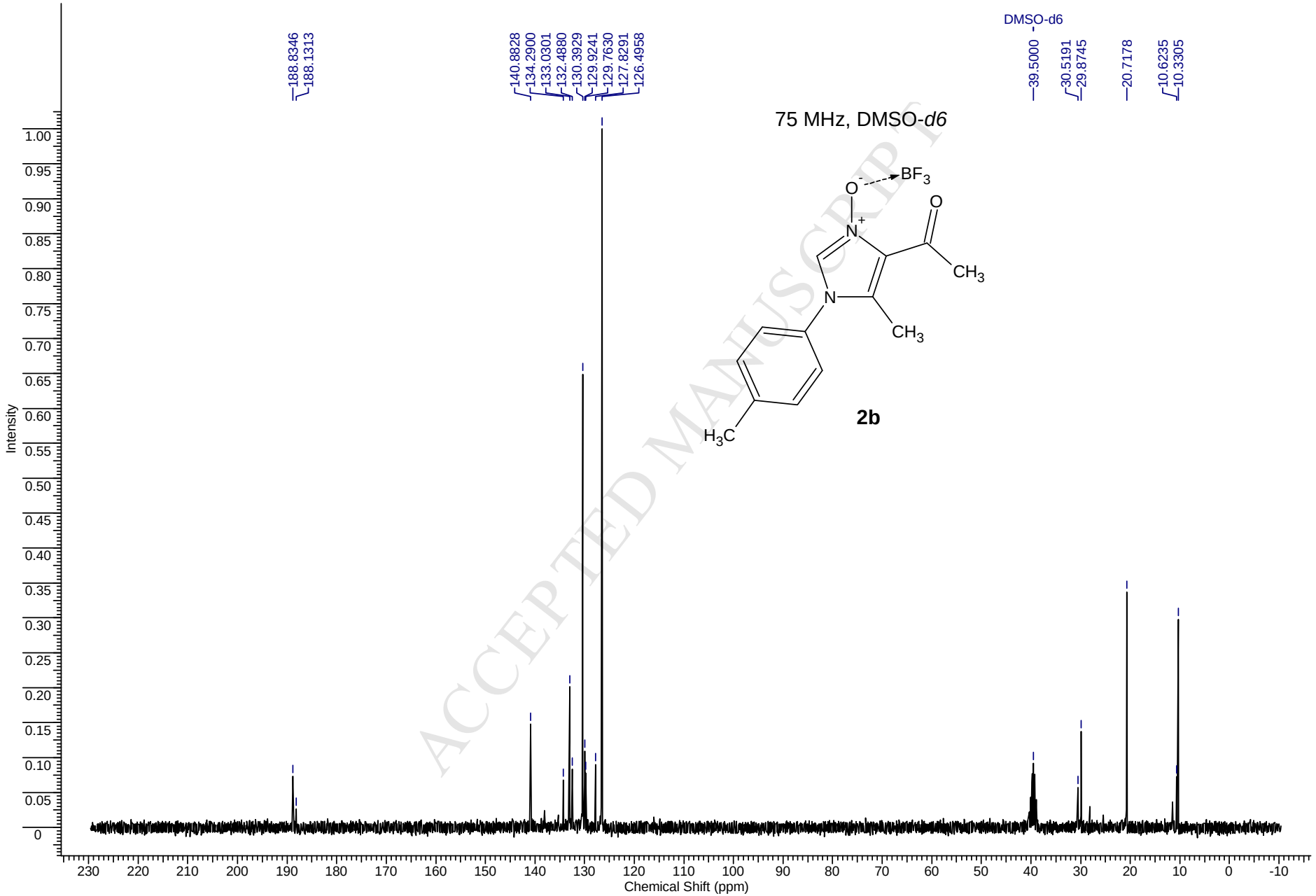


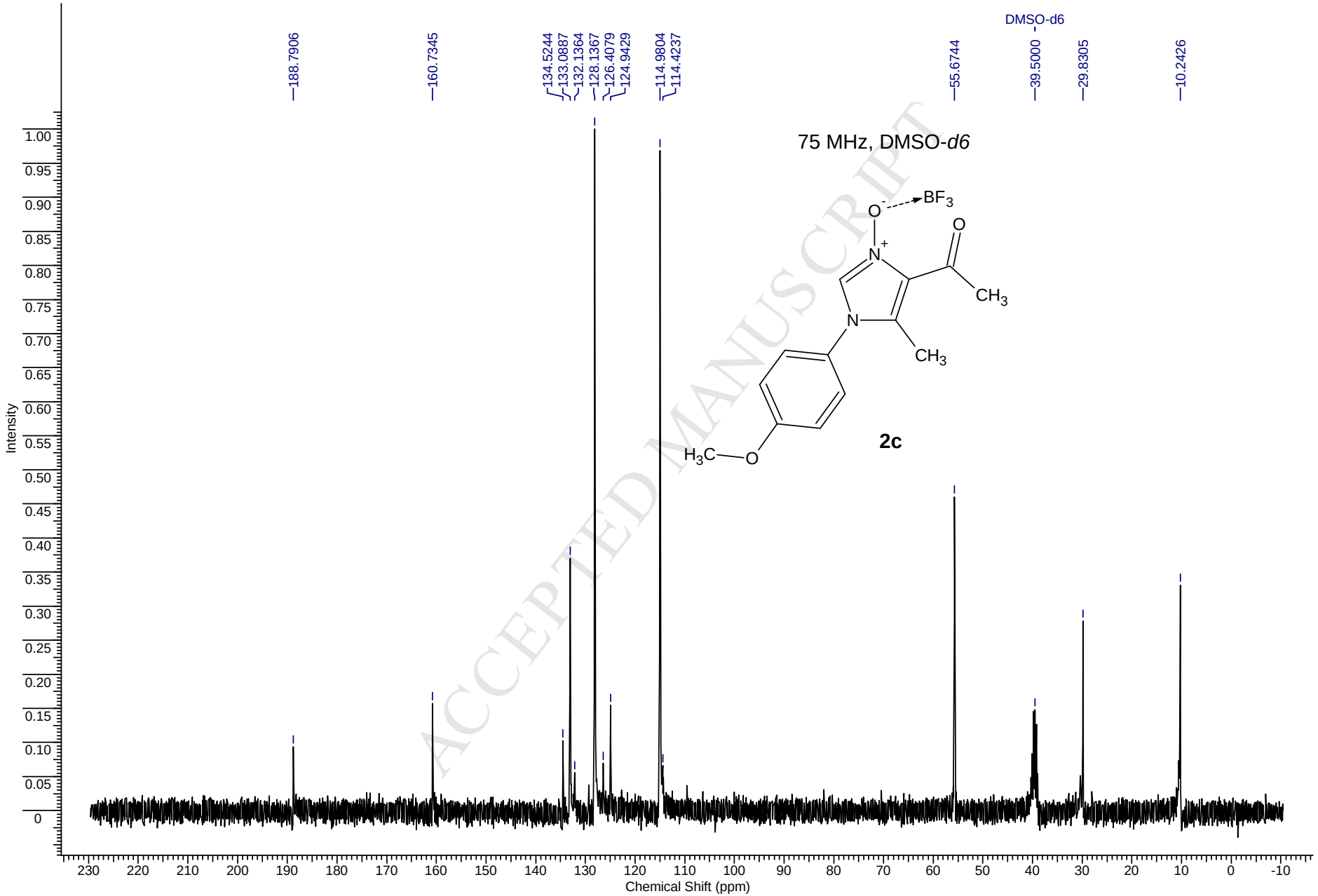


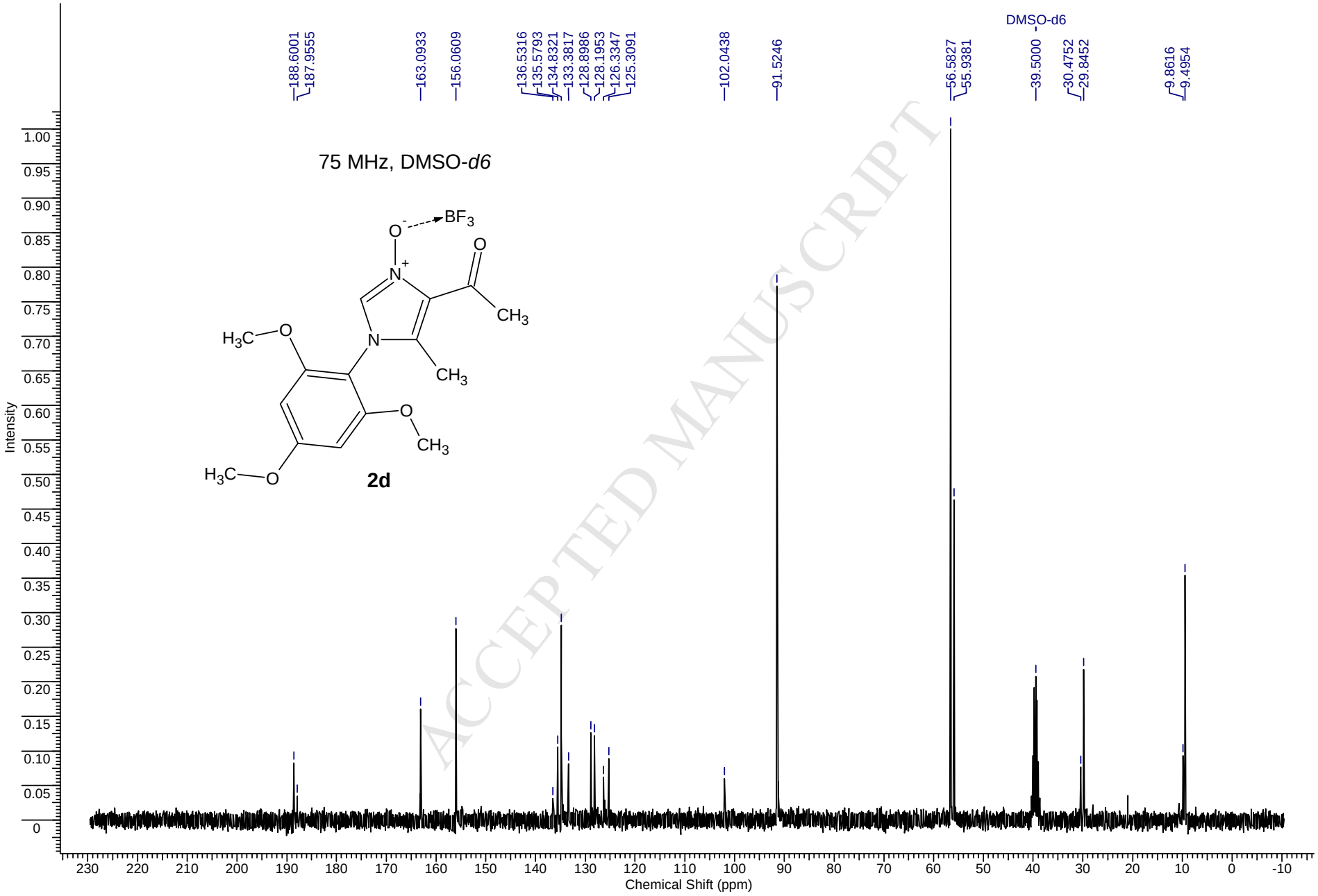


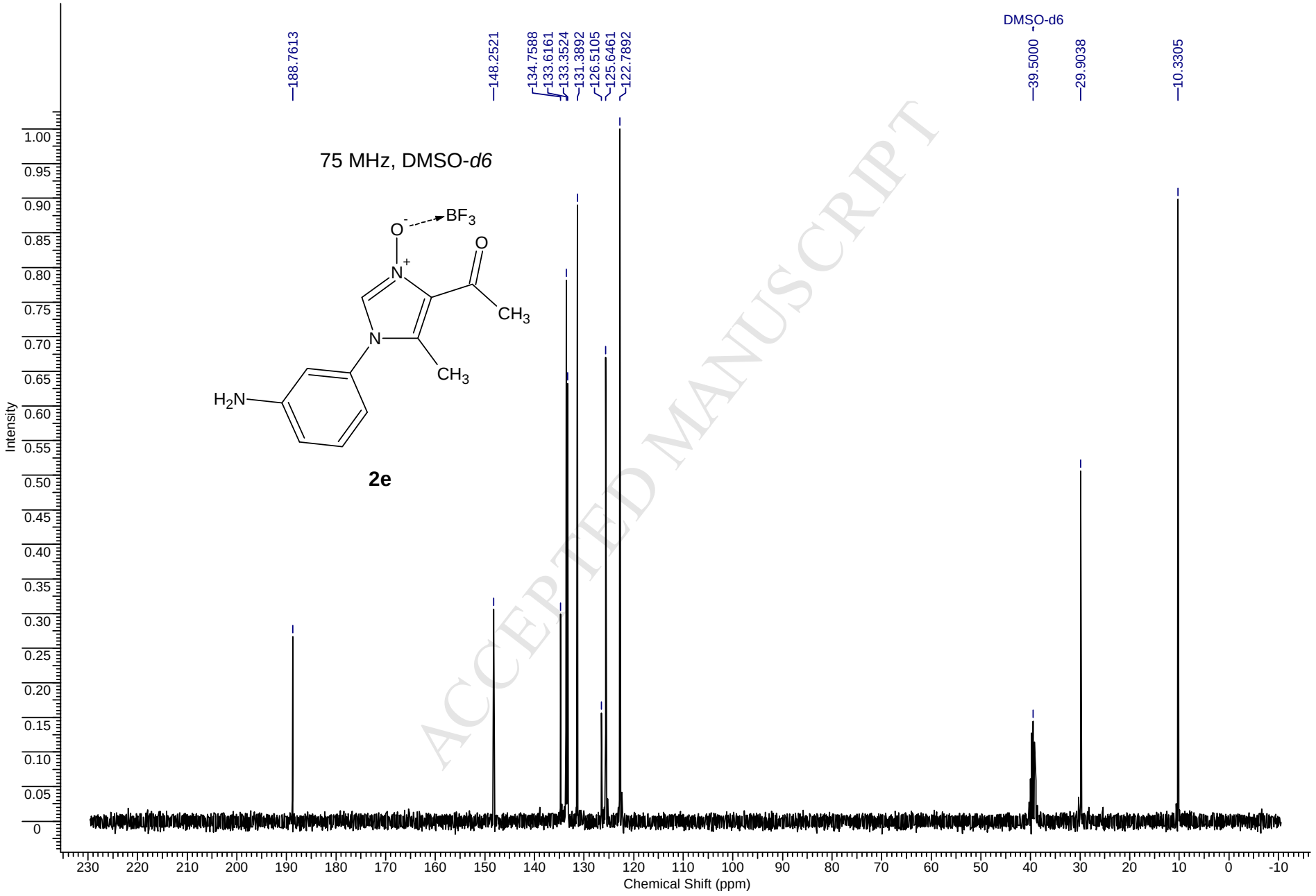


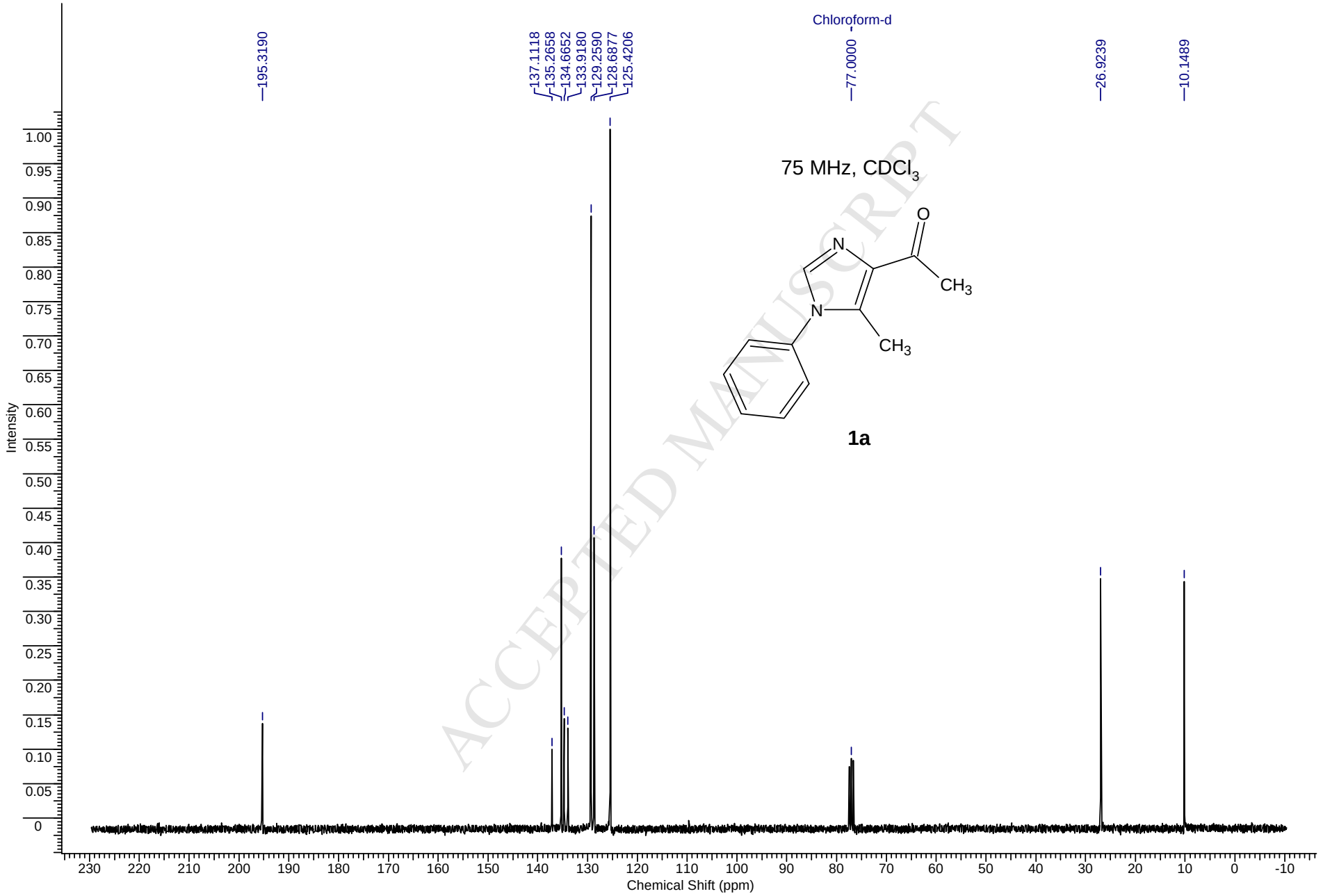


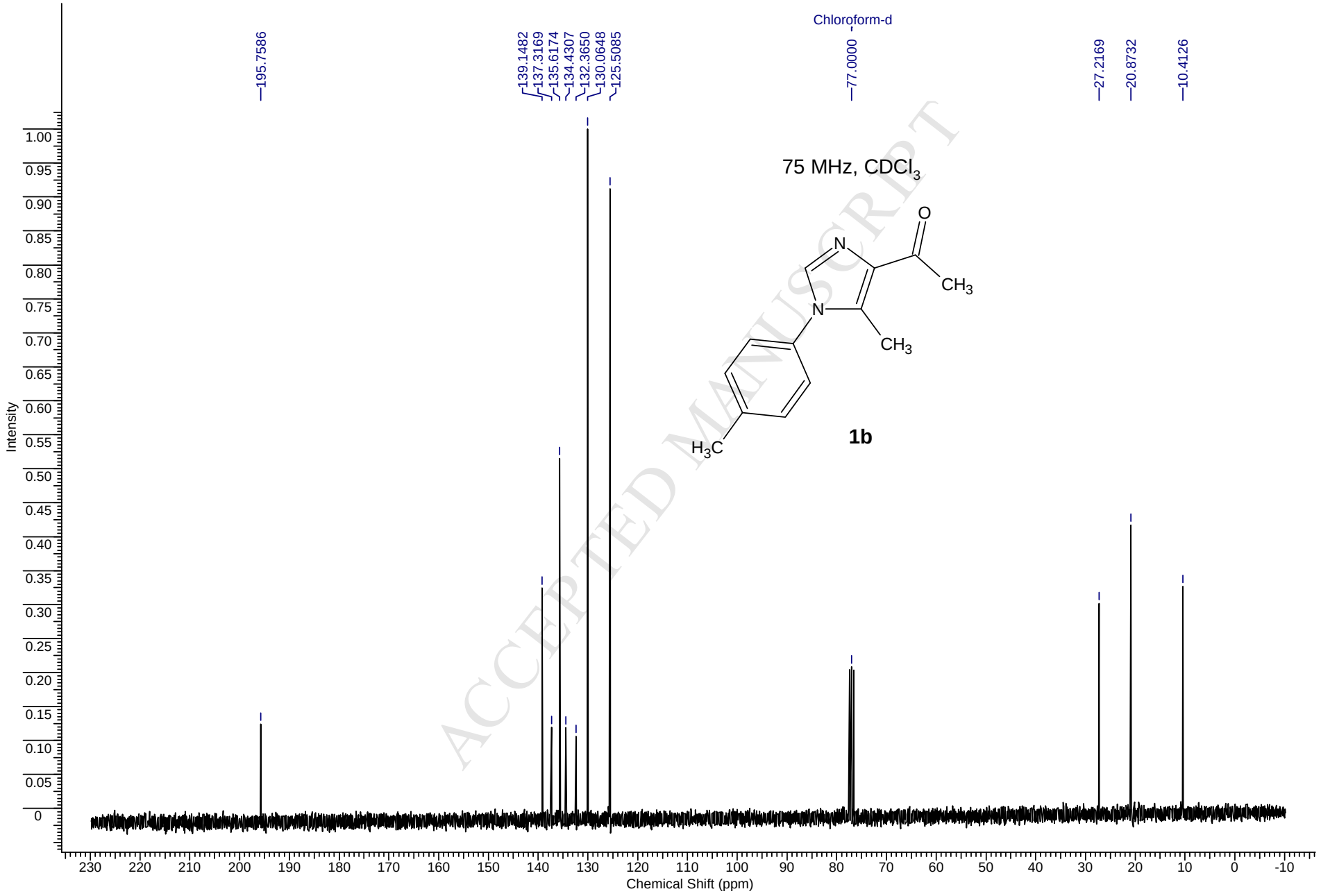


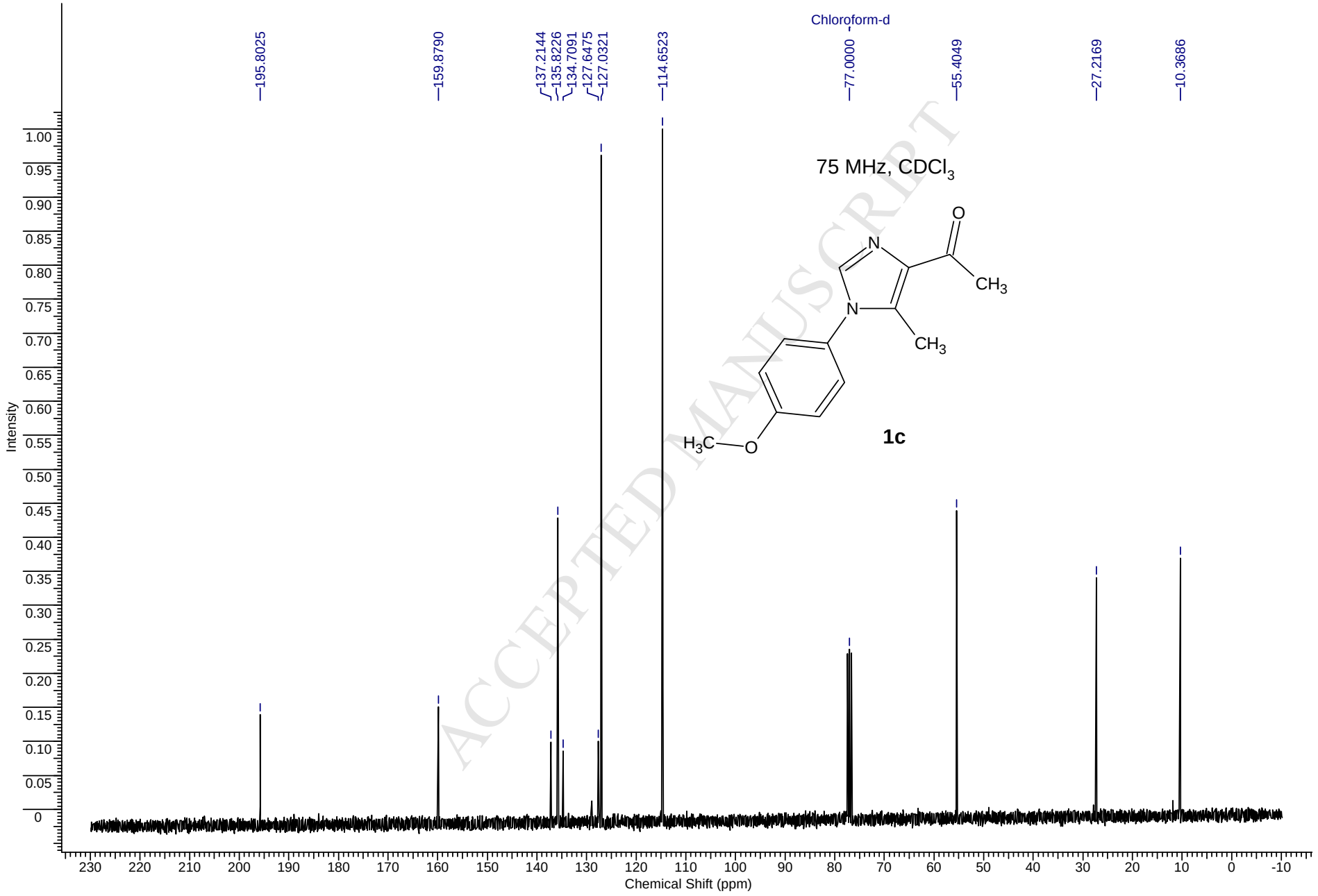


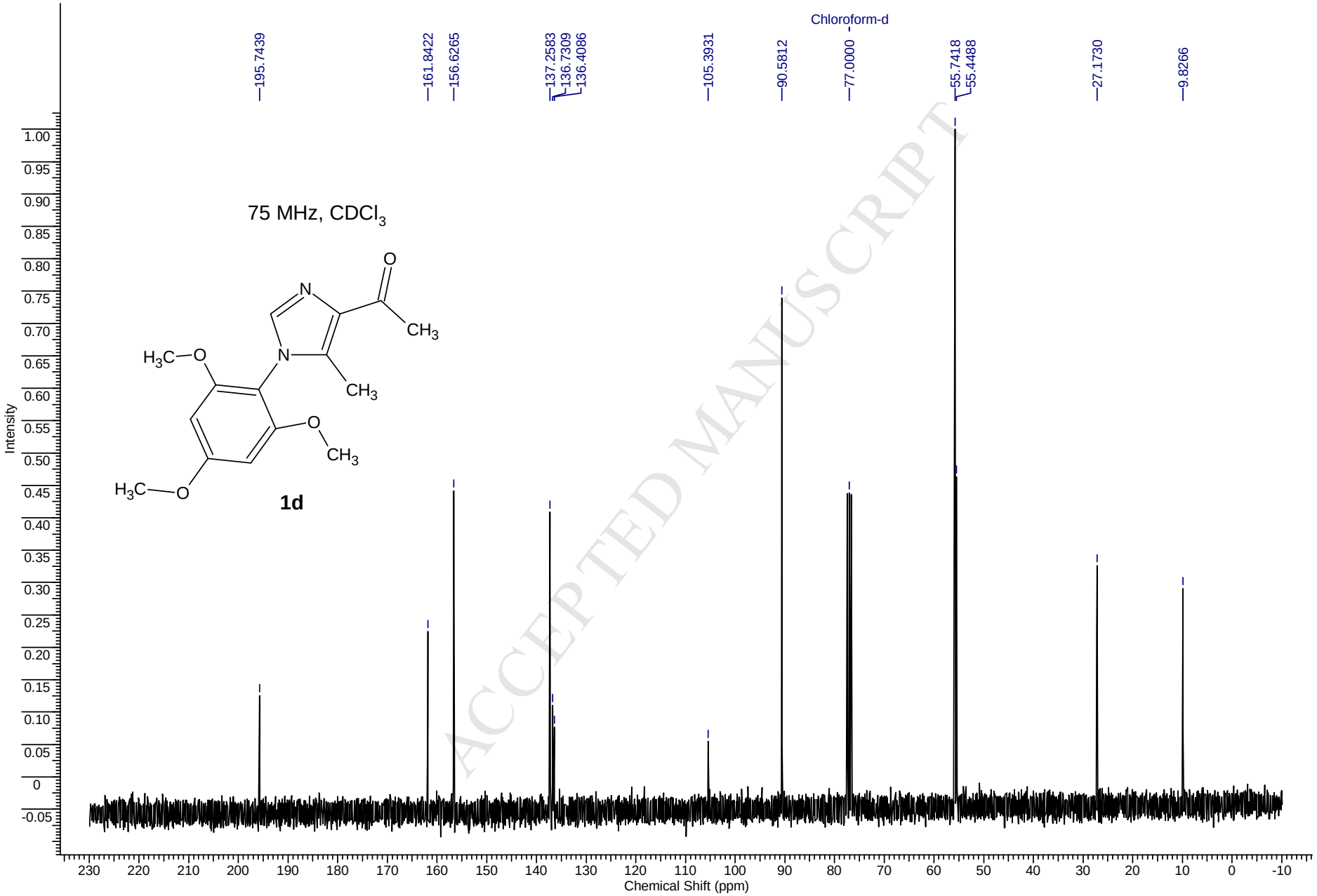


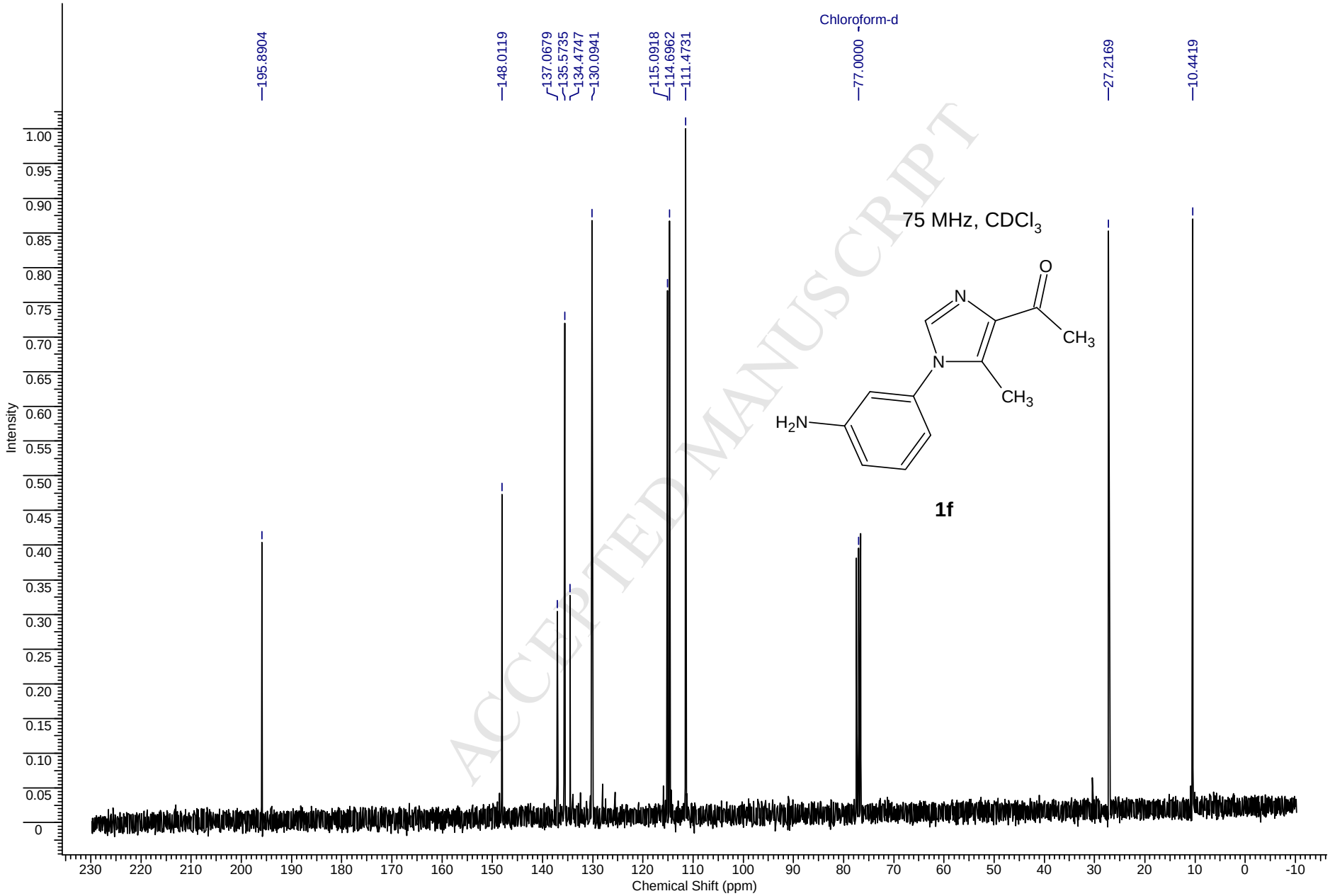


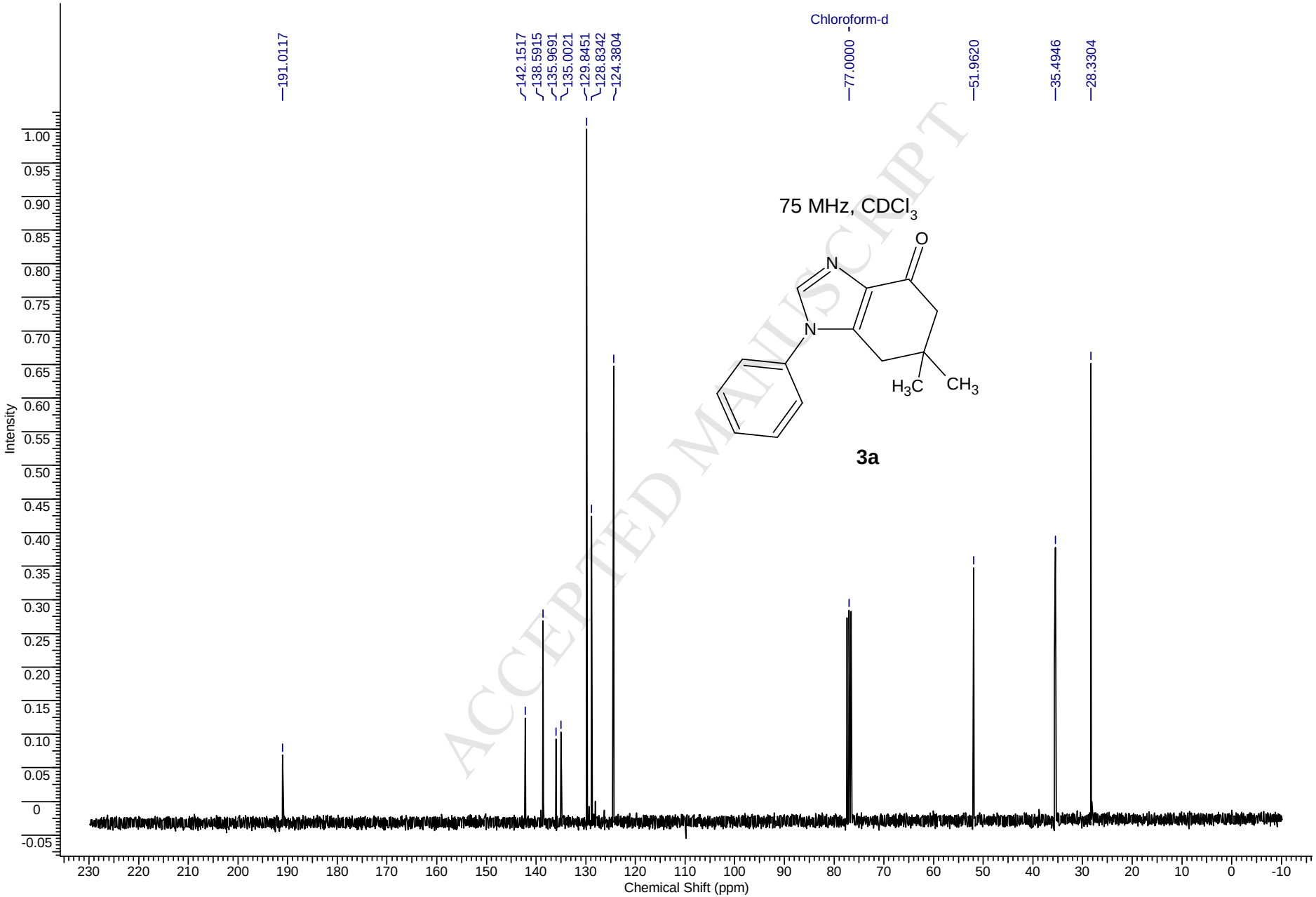


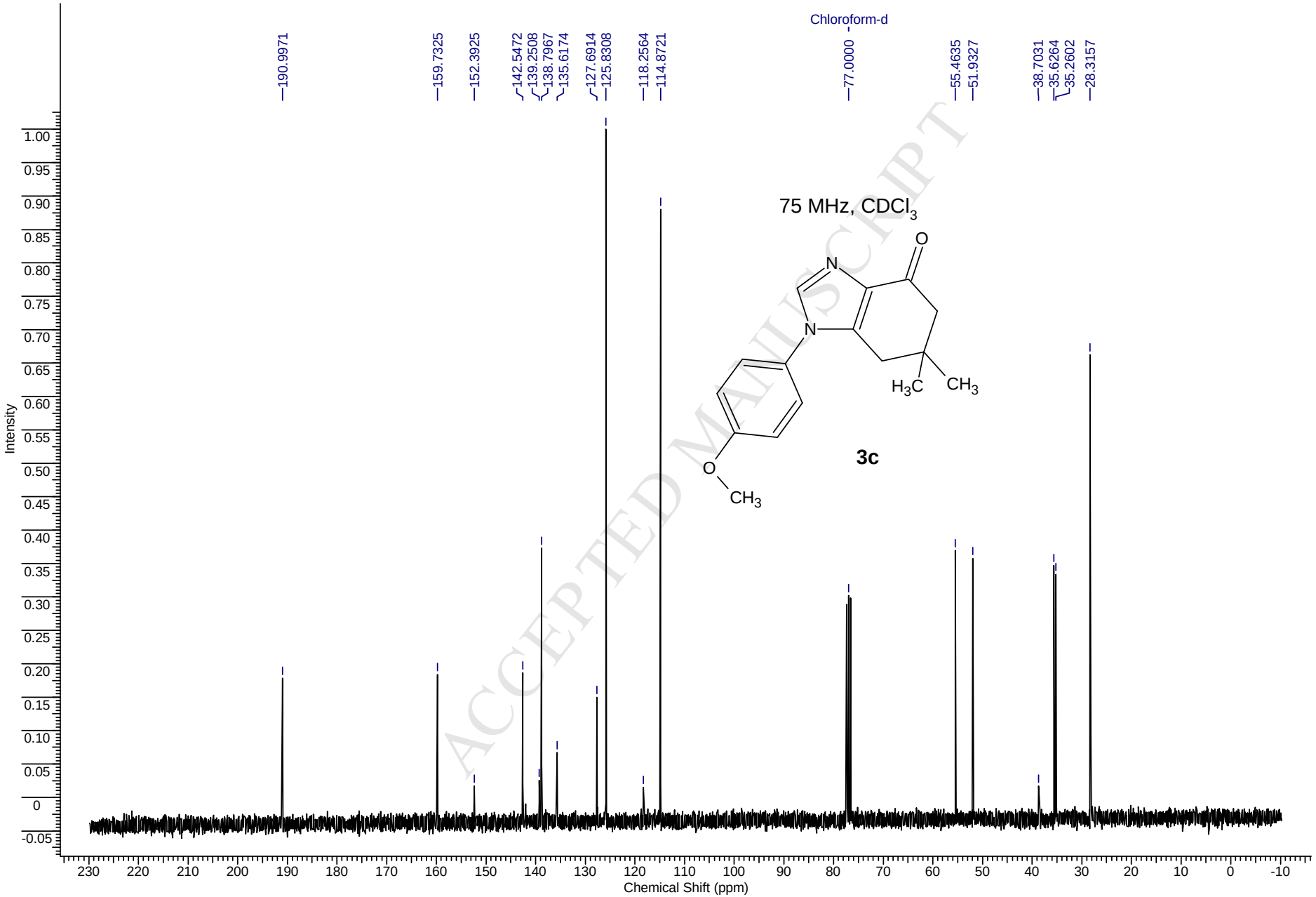


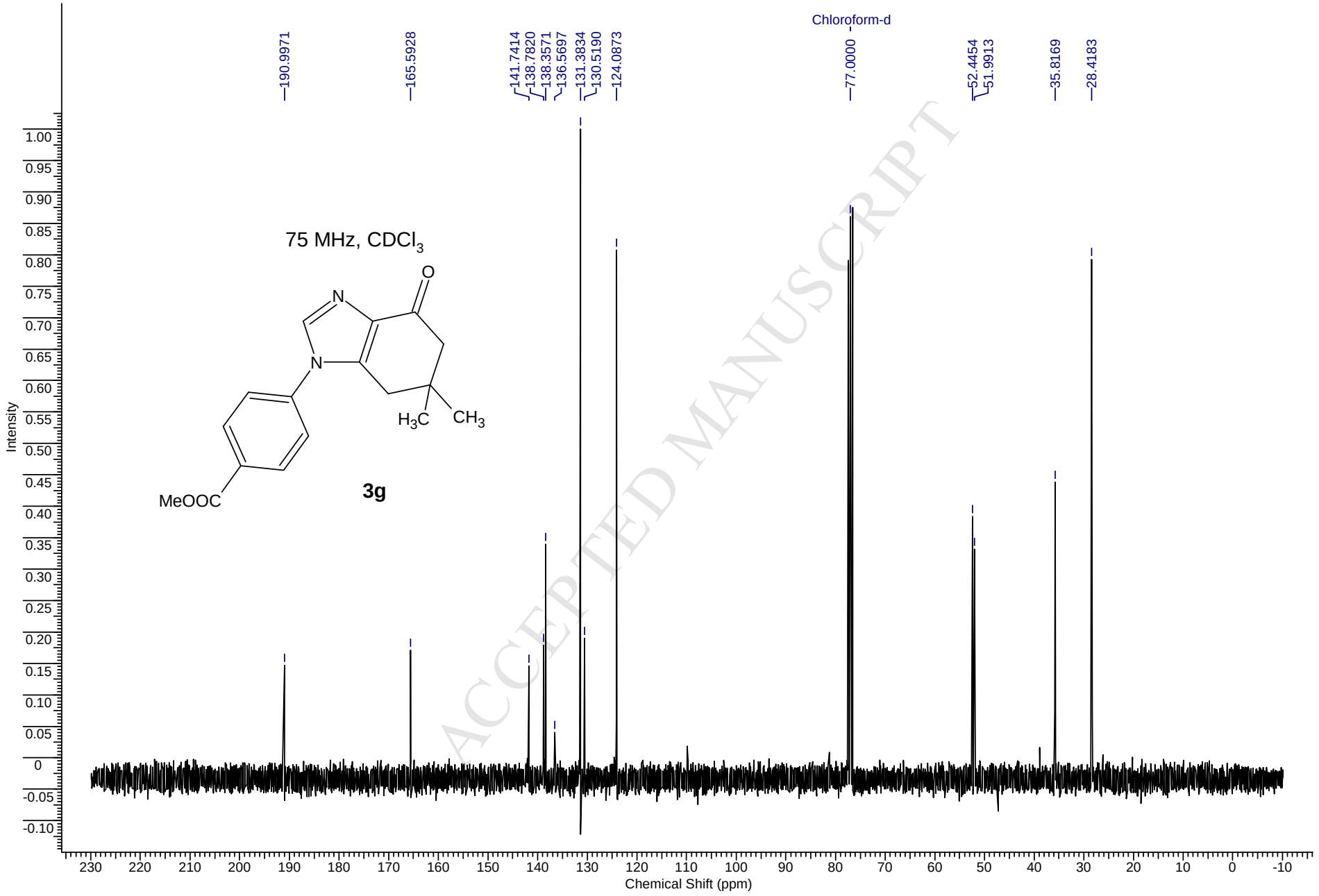


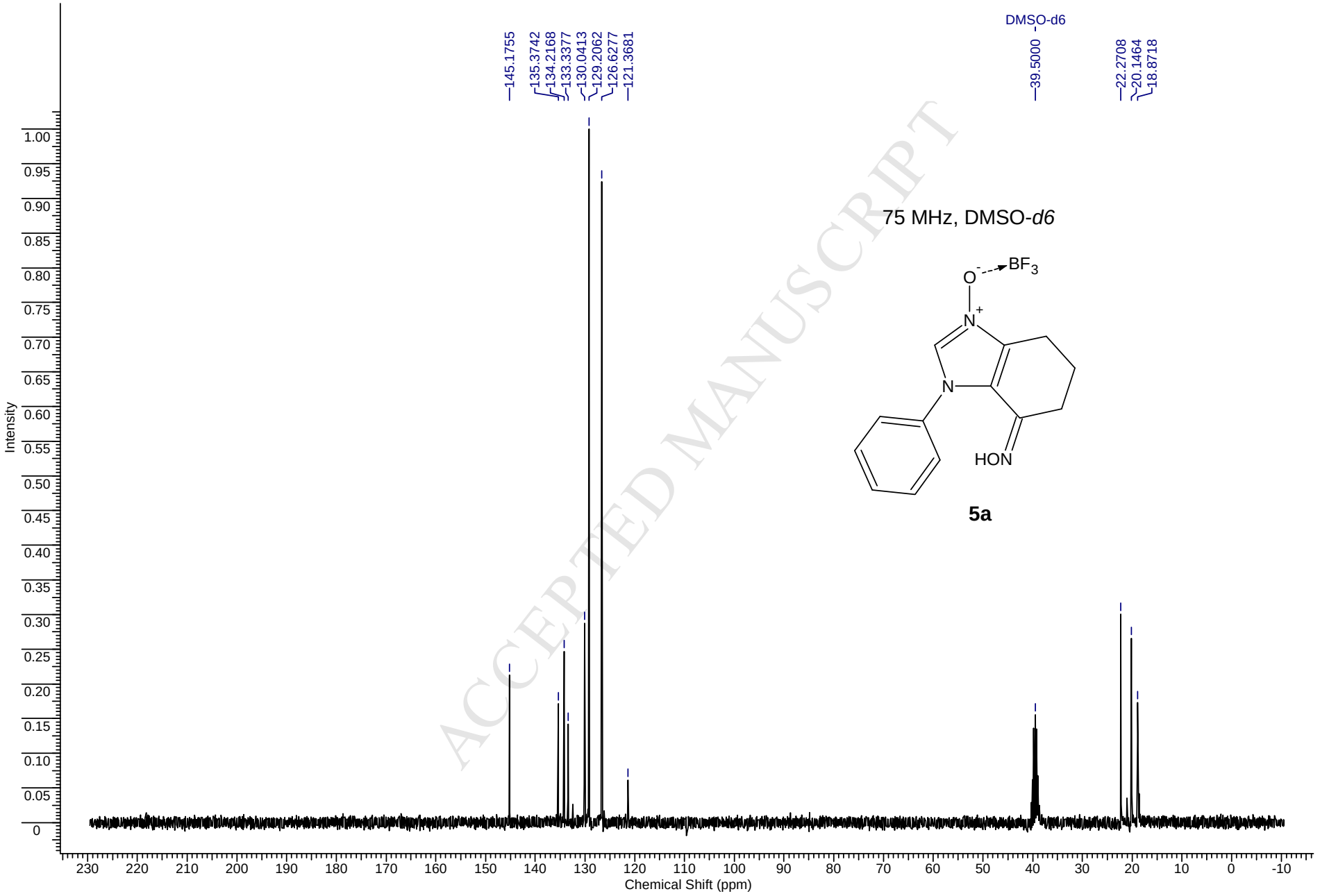


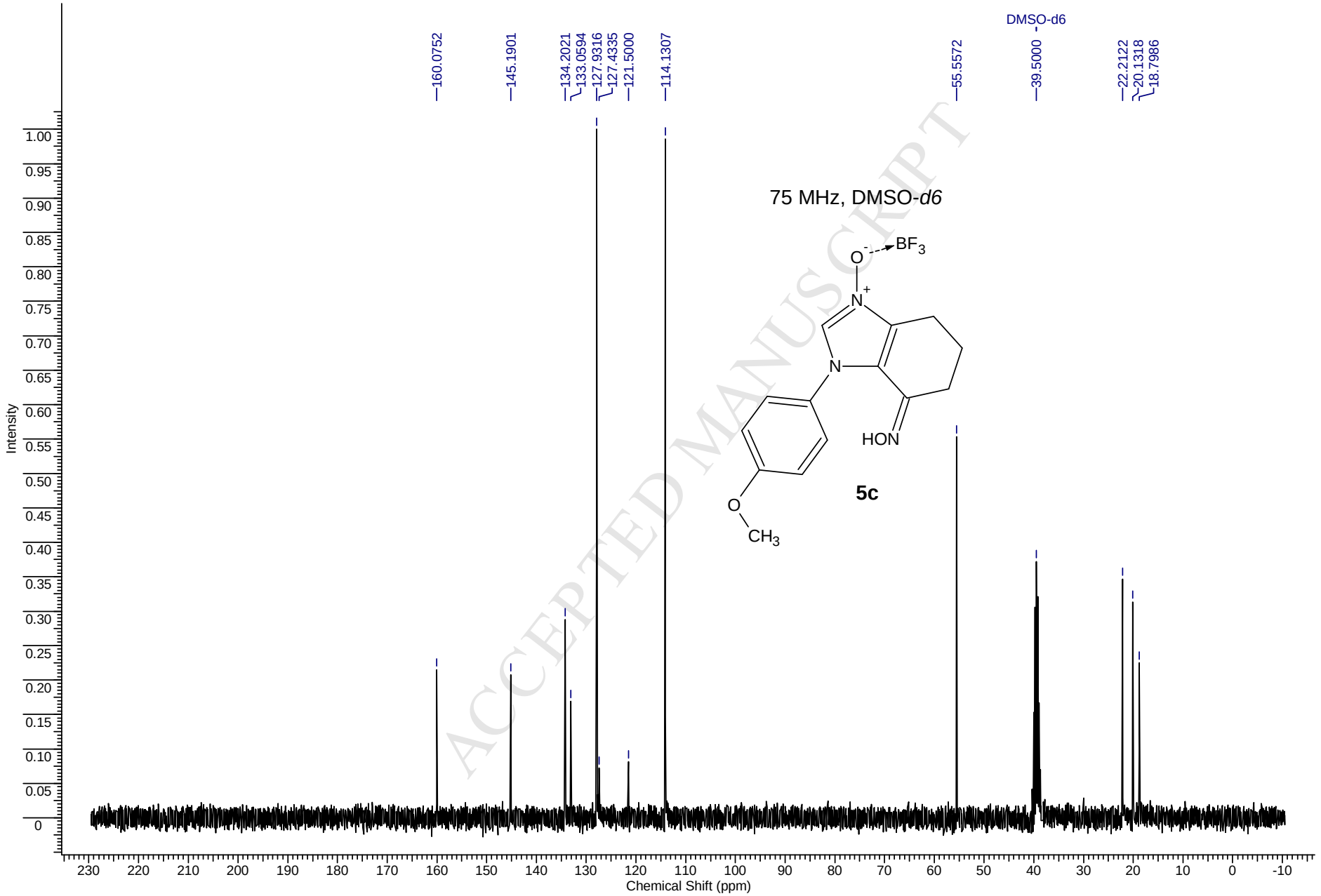


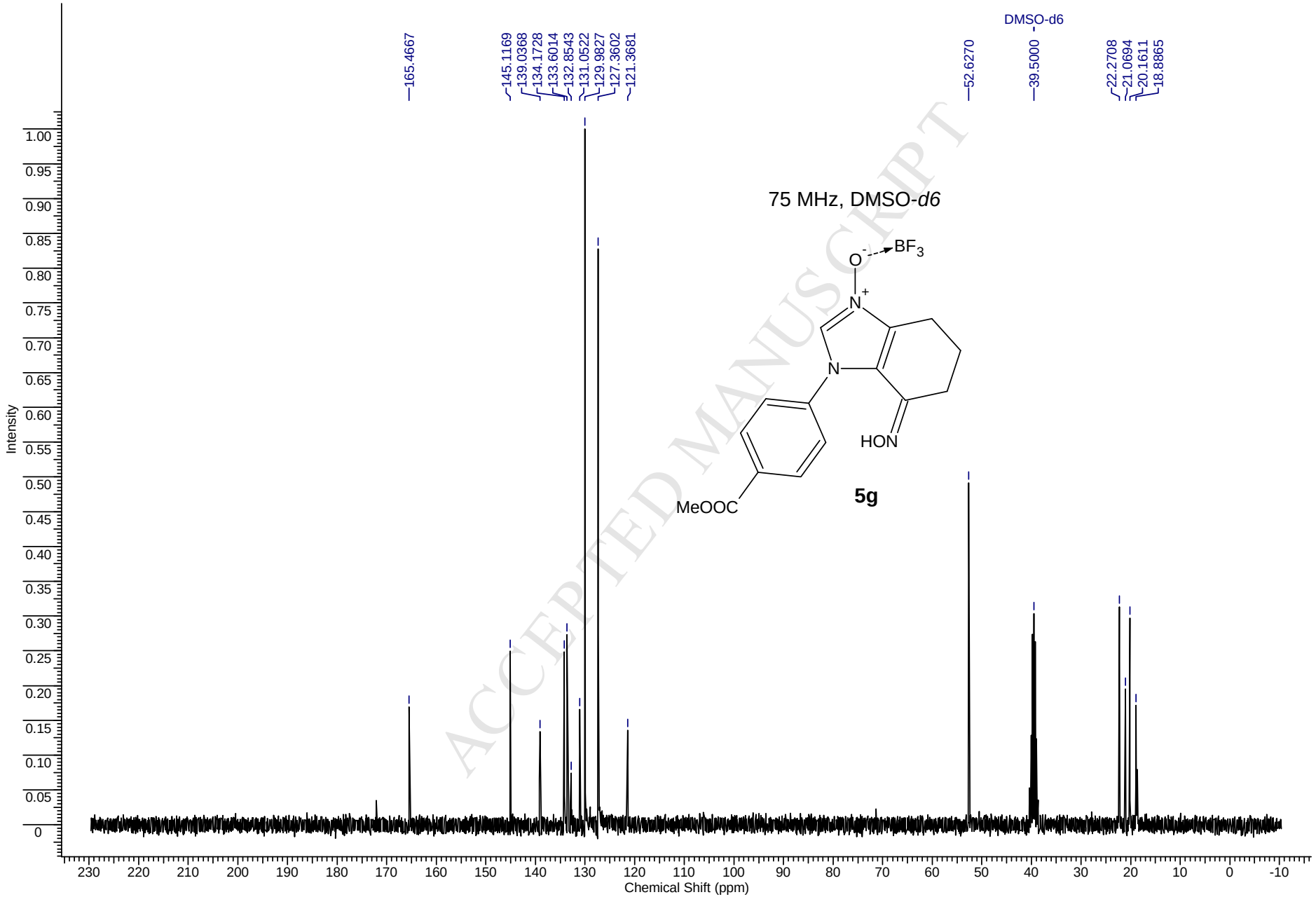


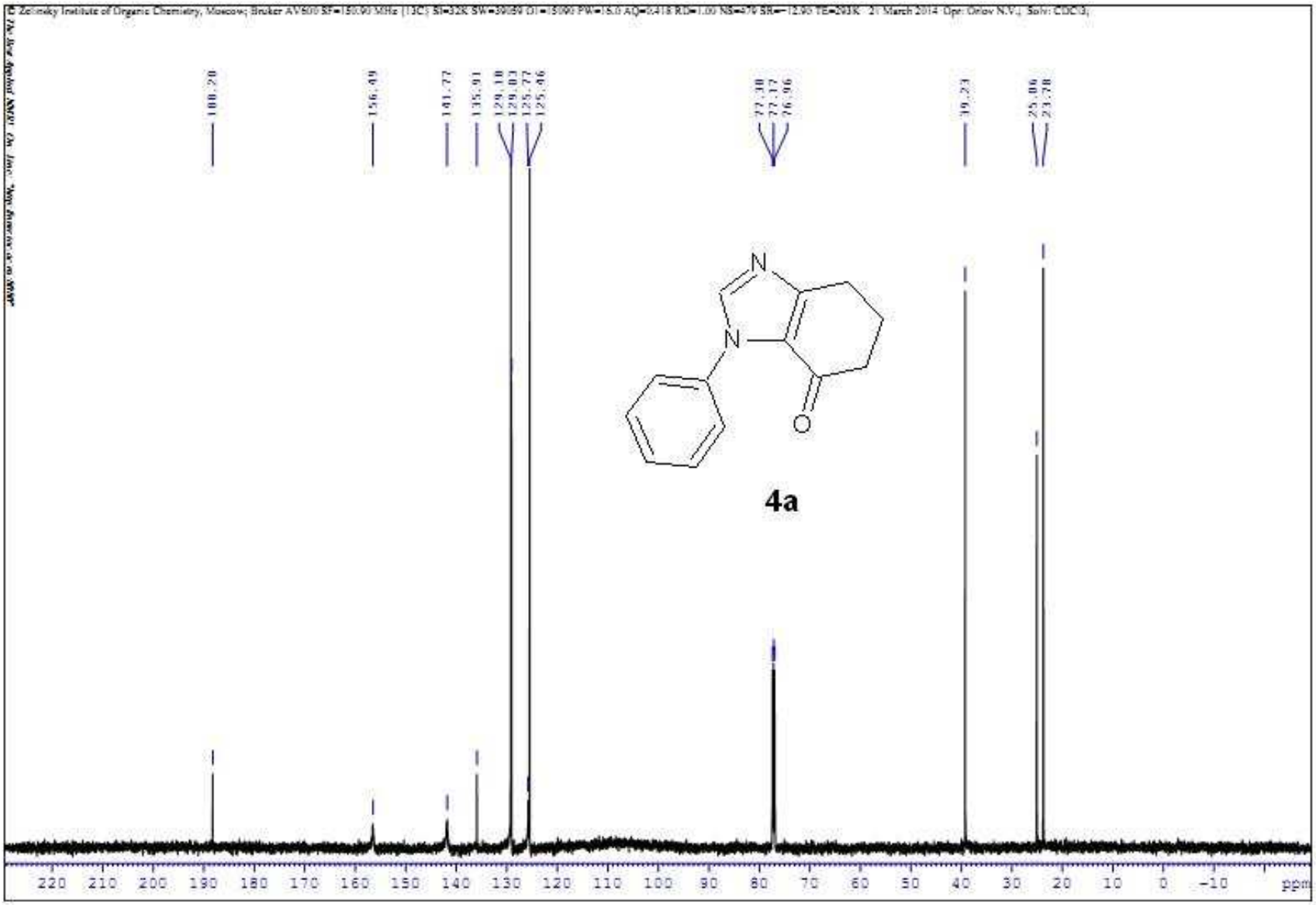


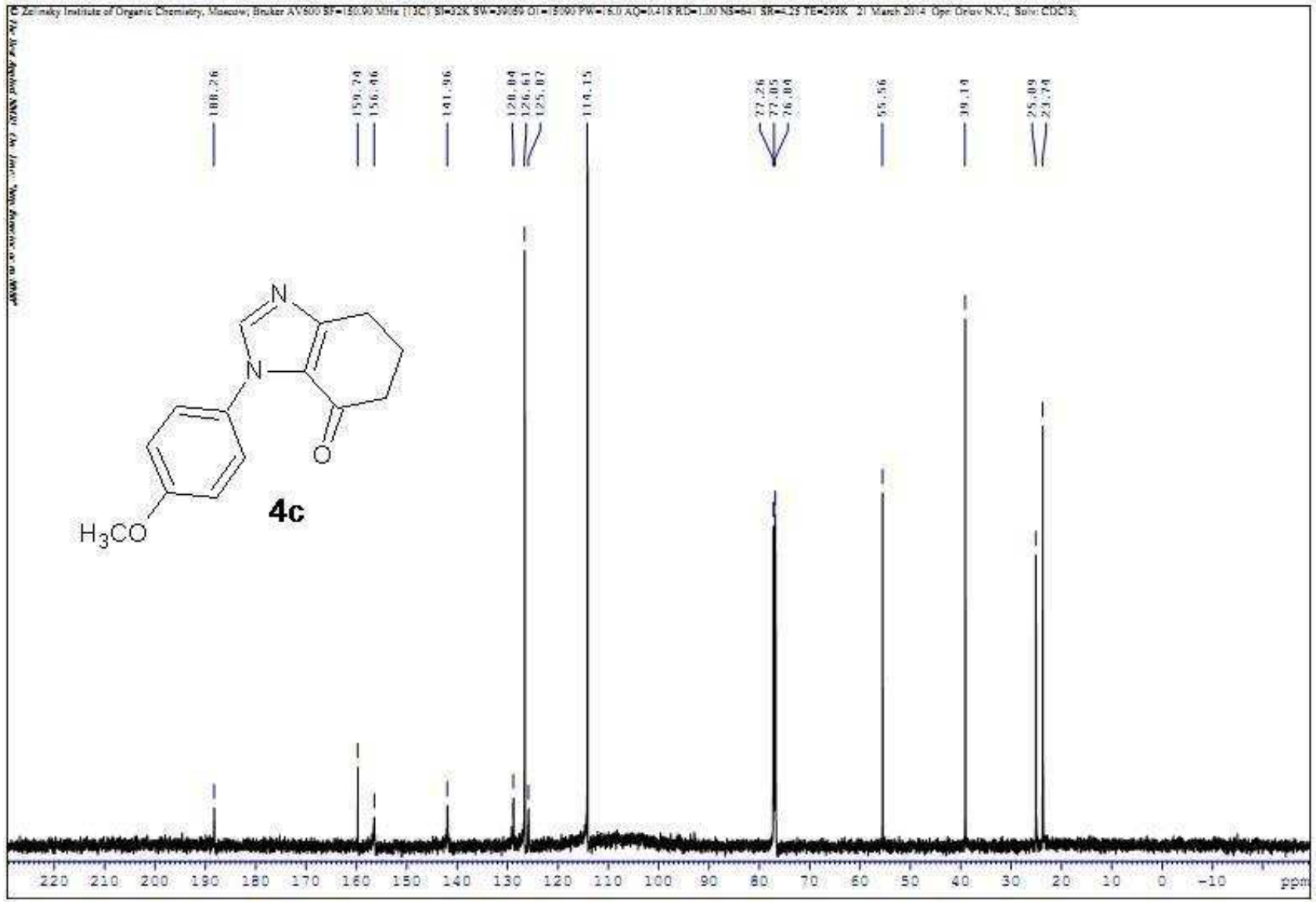


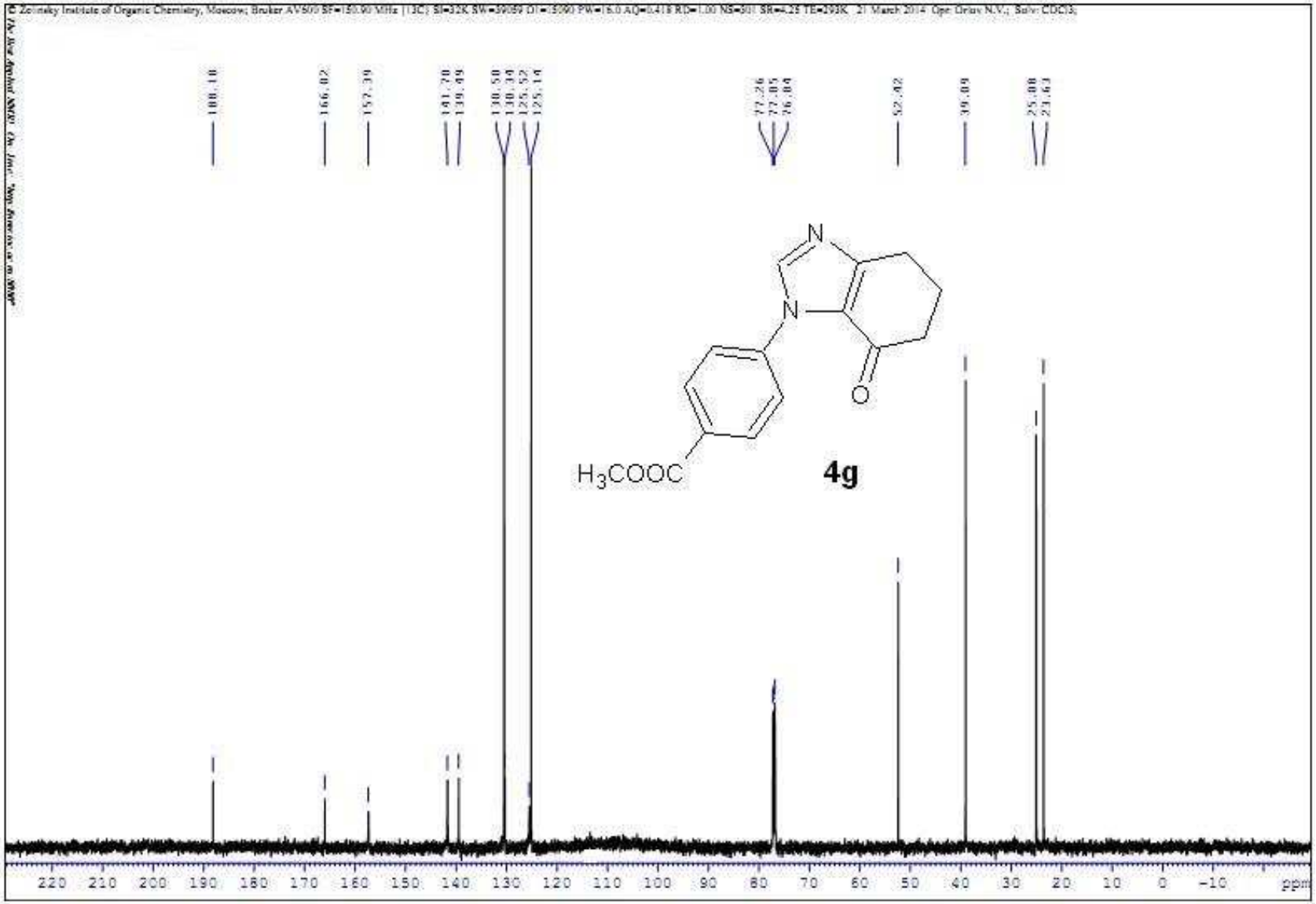


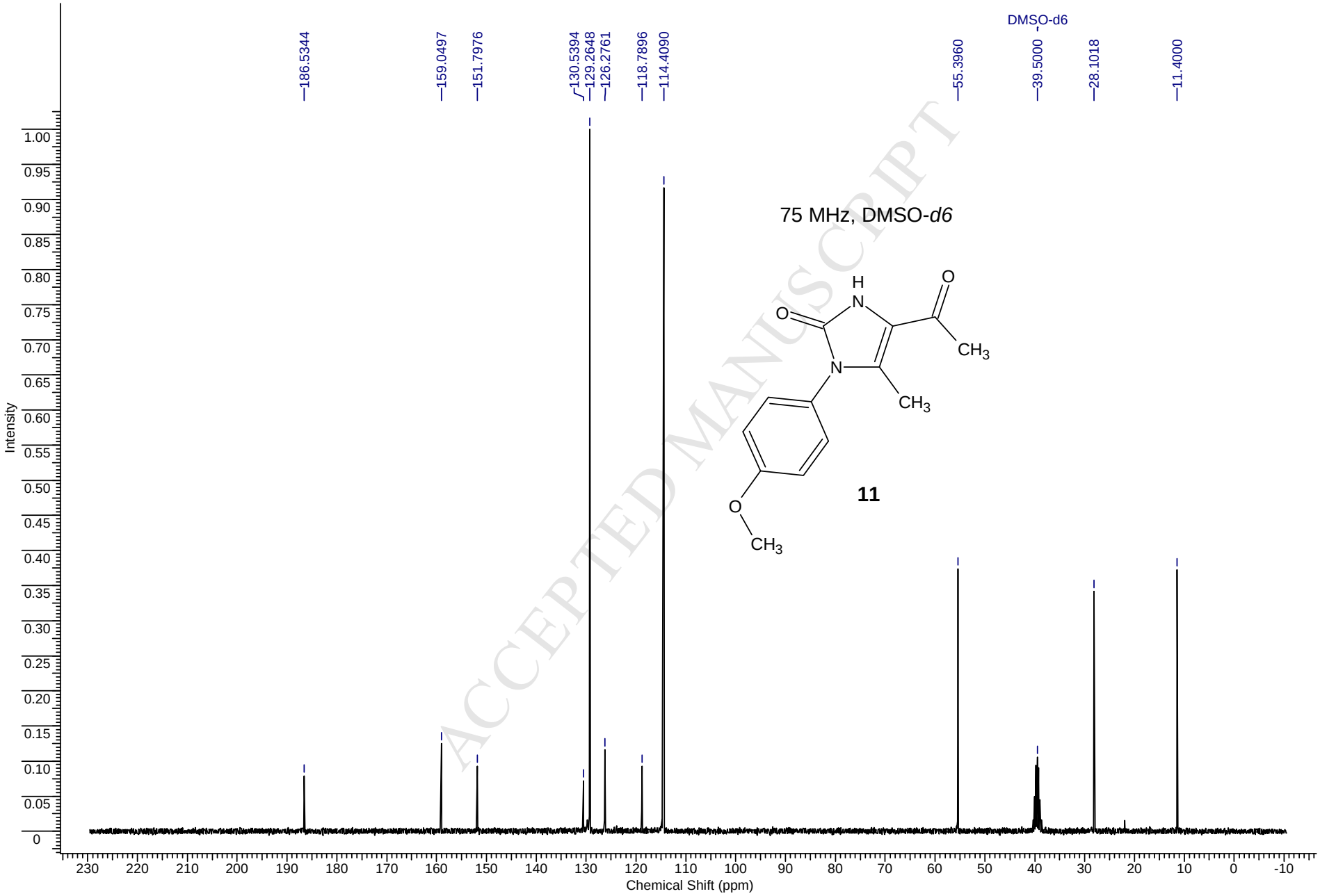


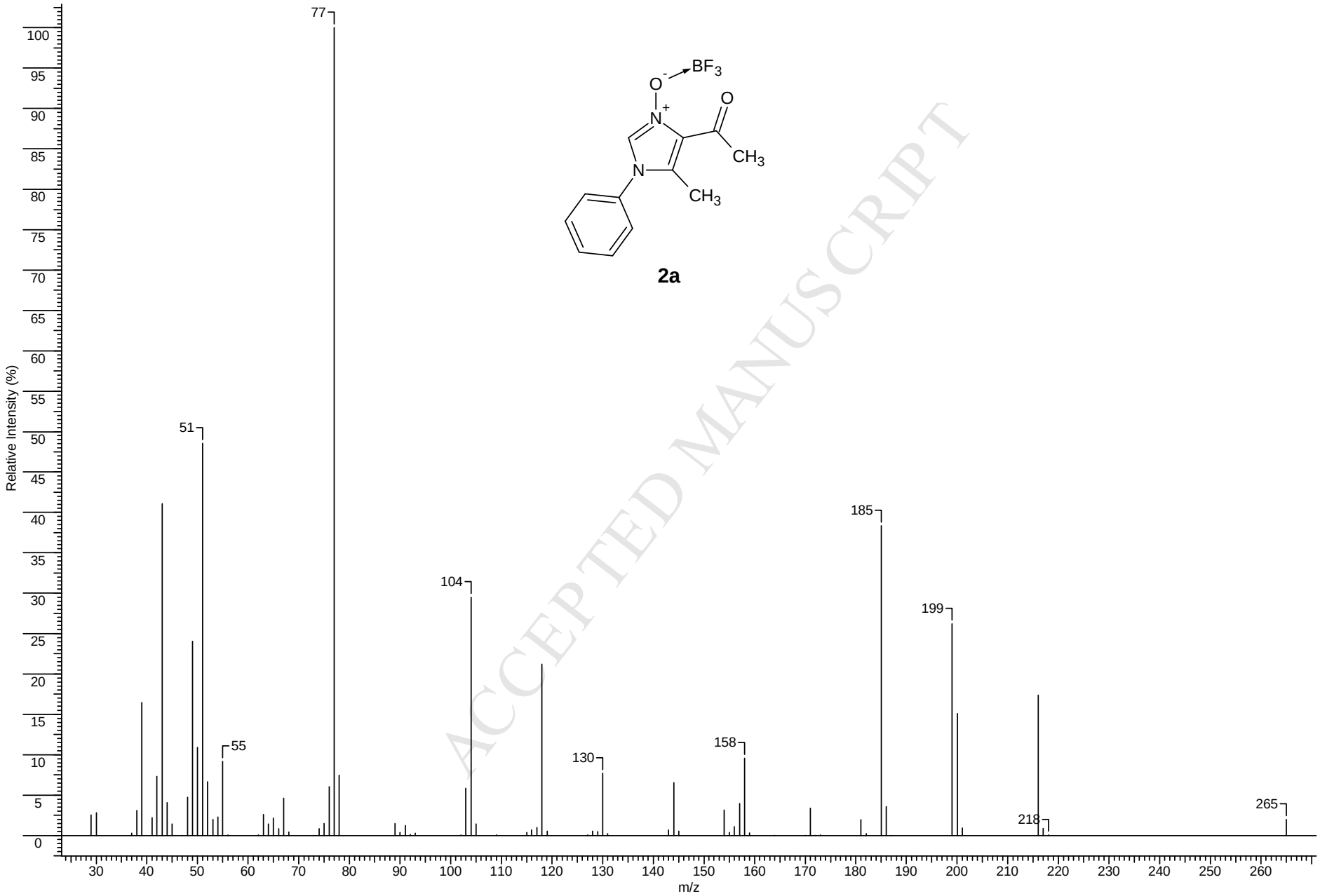



© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AV600 SF=150.90 MHz (13C) SI=32K SW=39682.01=15000 PW=15.0 AQ=0.418 RD=1.00 NS=479 SR=-12.90 TE=293K 21 March 2014 Opr: Orlov N.V.; Solv: CDCl3;
188.20
156.49
141.77
135.91
129.18
129.03
125.77
125.46
77.38
77.17
76.96
19.23
25.86
23.78
N
N
O
4a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

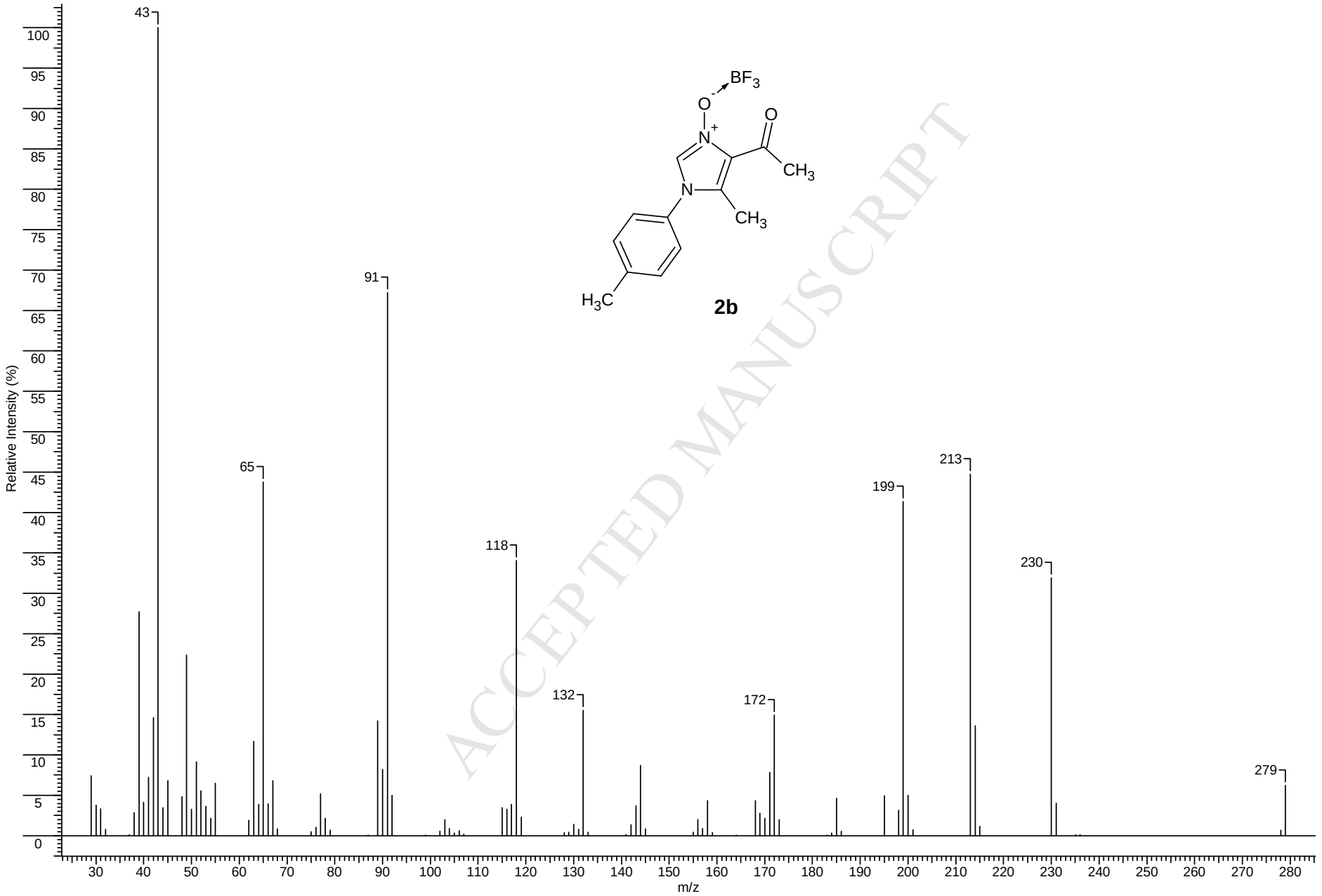

188.26
159.79
156.46
141.96
128.84
126.61
125.87
114.15
77.26
77.05
76.84
55.56
39.19
25.89
23.74
N
N
O
H3CO
4c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


188.18
166.82
152.39
141.70
139.49
130.50
130.35
125.52
125.14
77.26
77.05
76.84
52.42
39.09
25.88
23.63
N
N
O
H3COOC
4g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

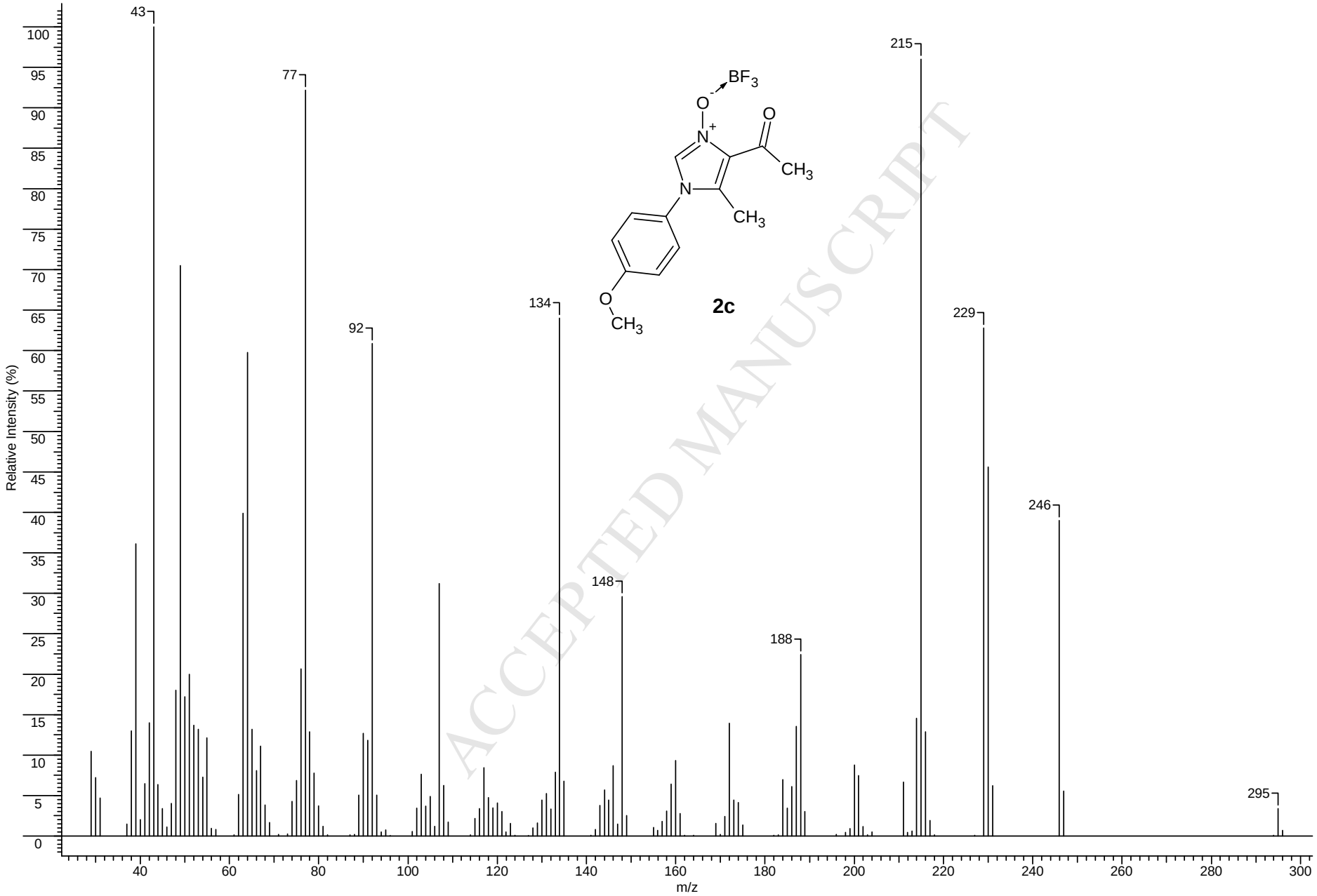


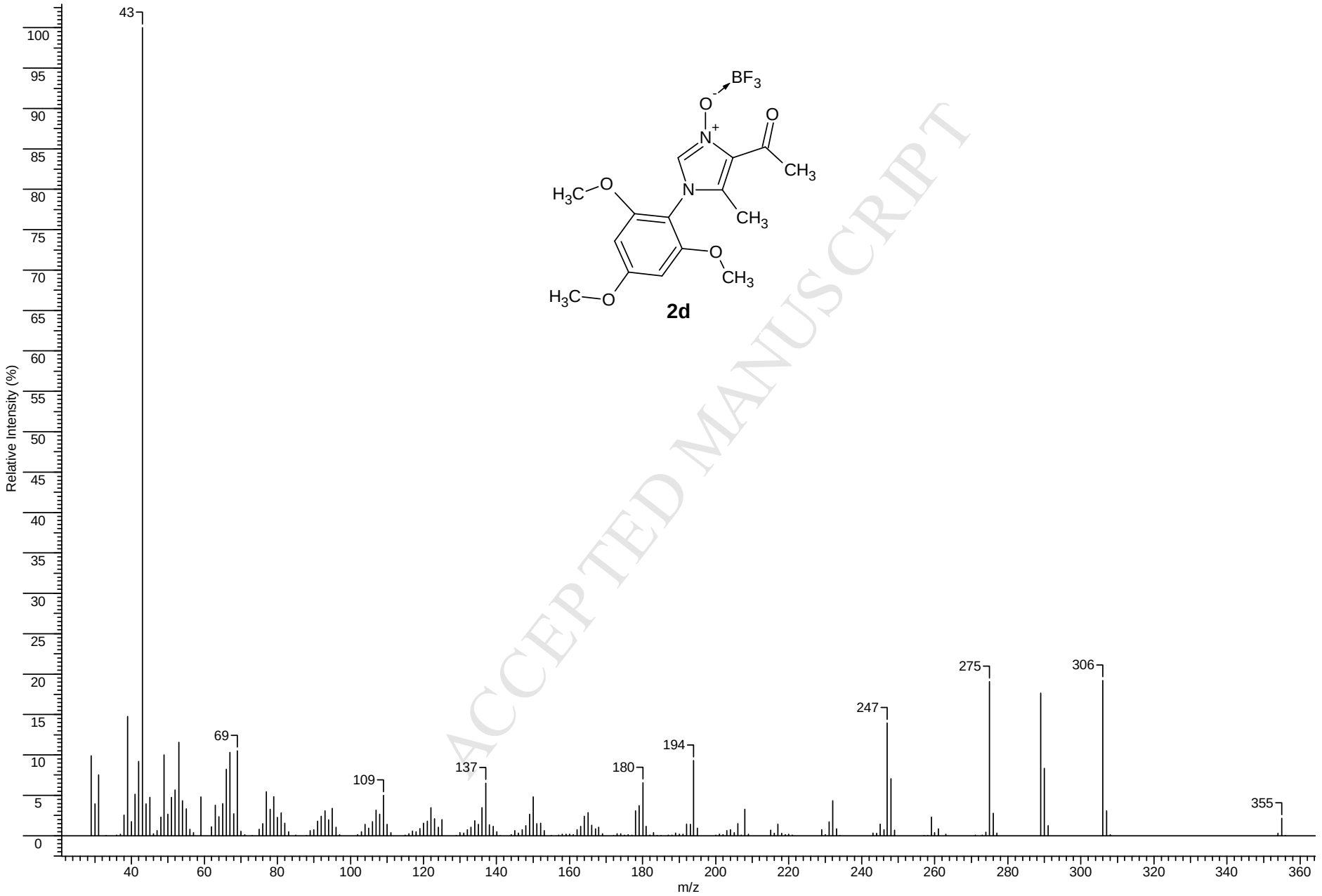


2a



2b





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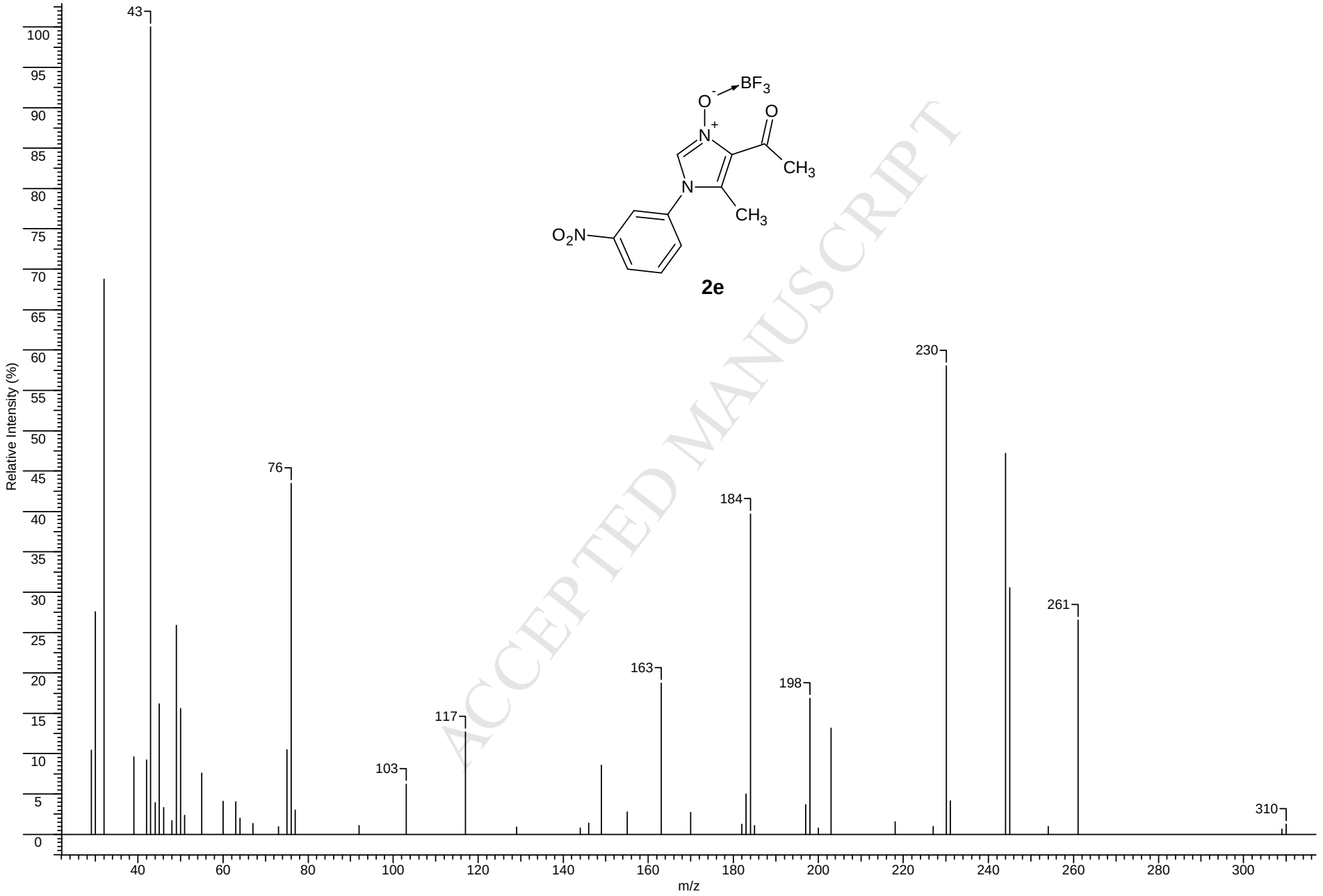

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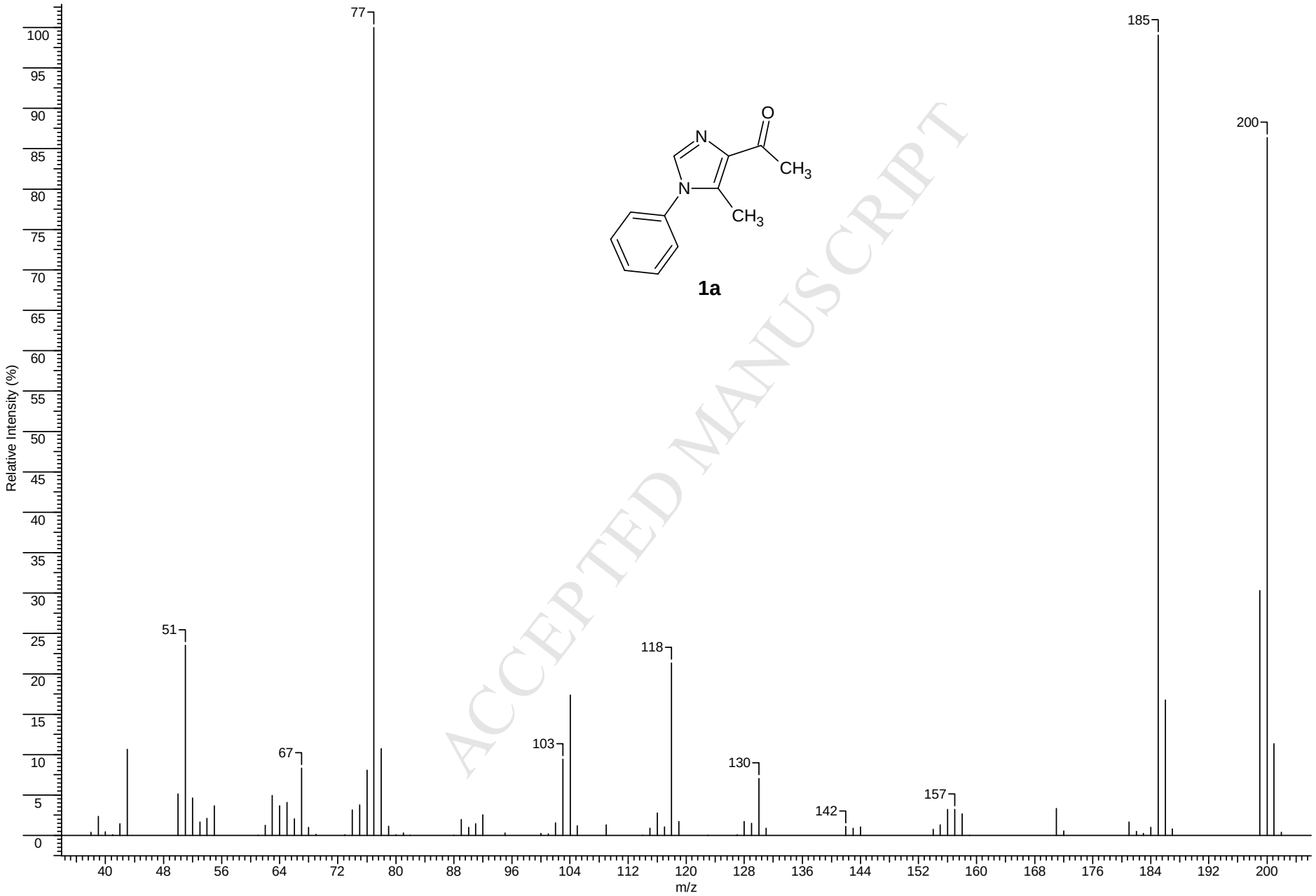

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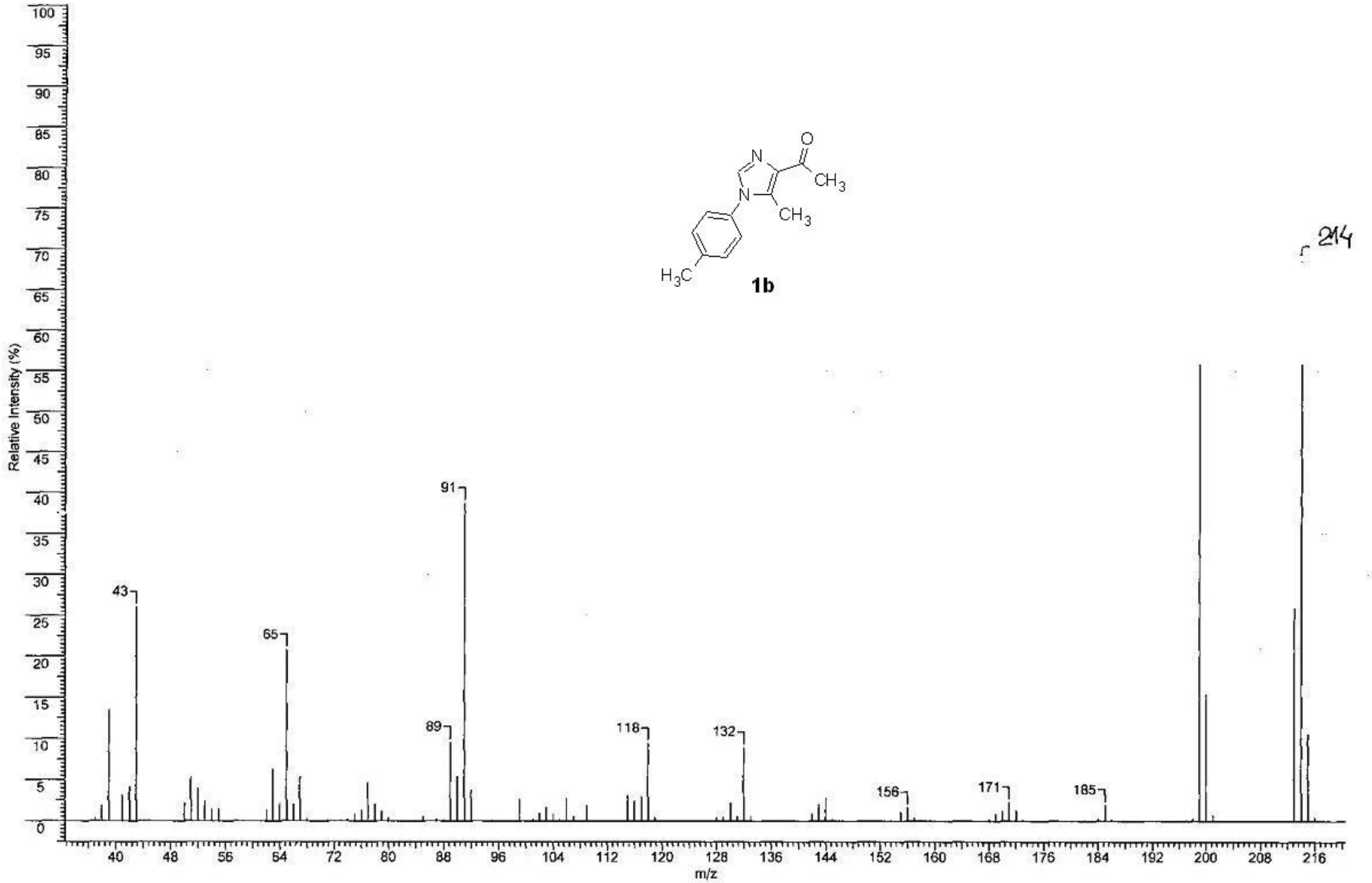
214
1b
Relative Intensity (%)
m/z
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89
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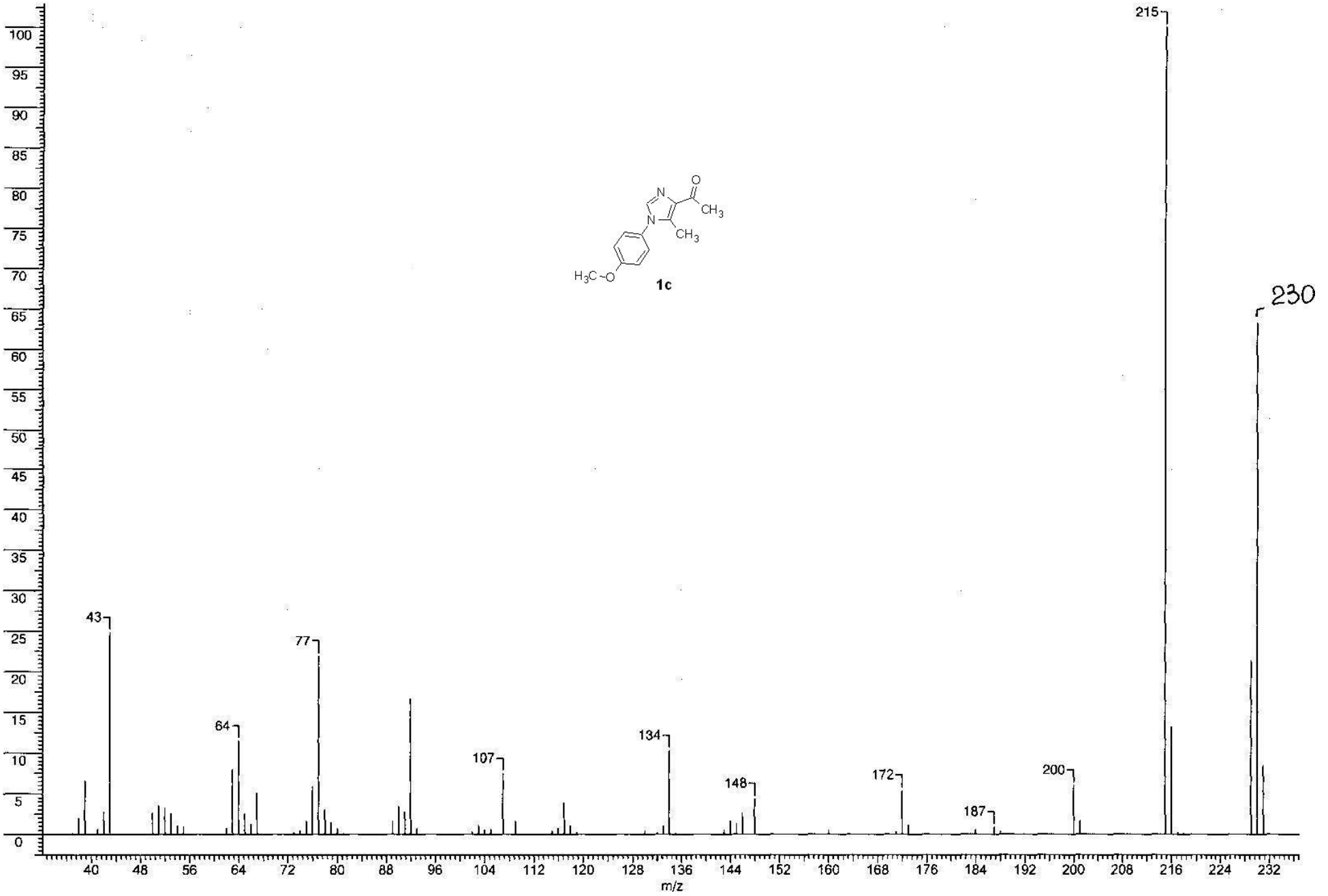
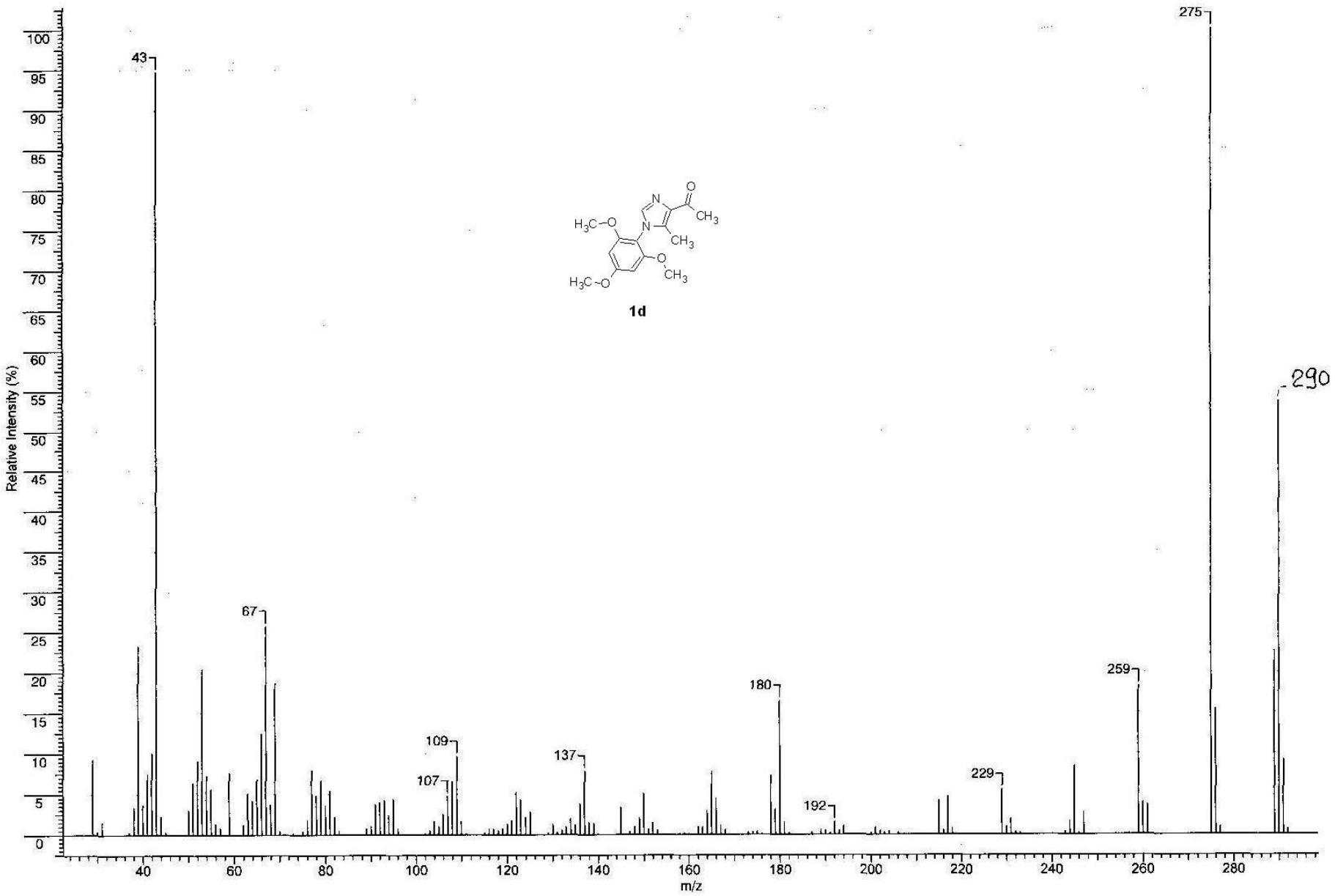
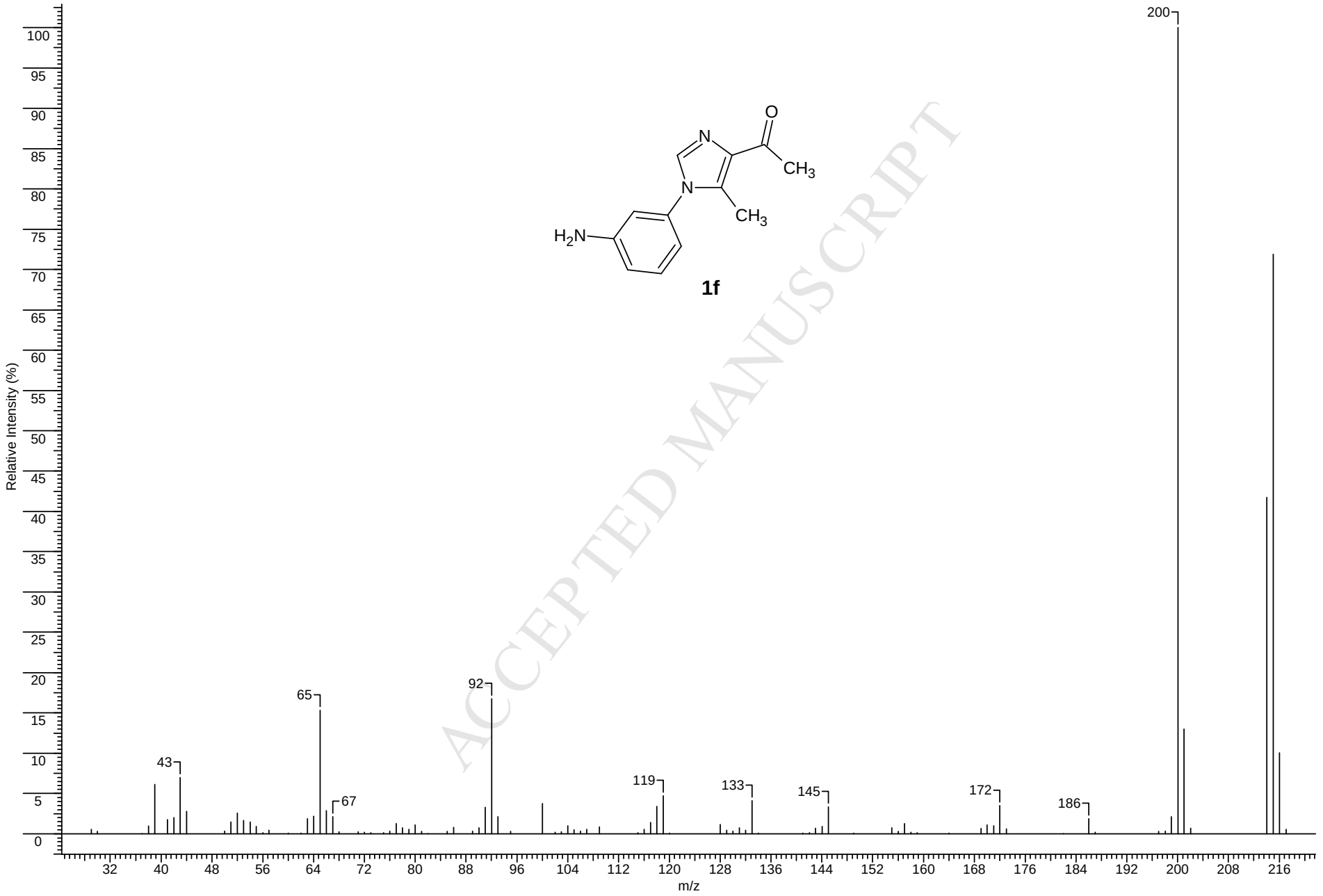
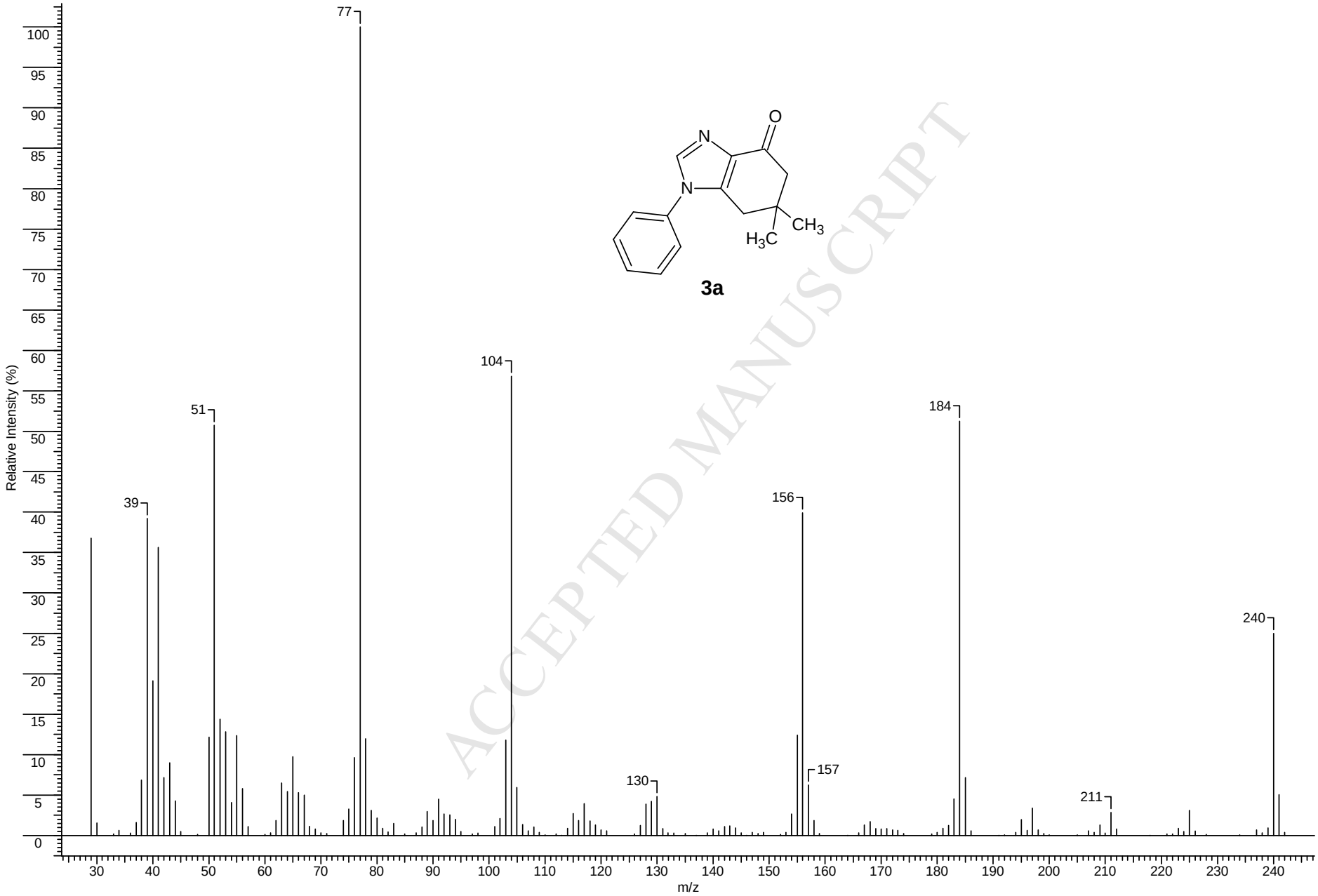


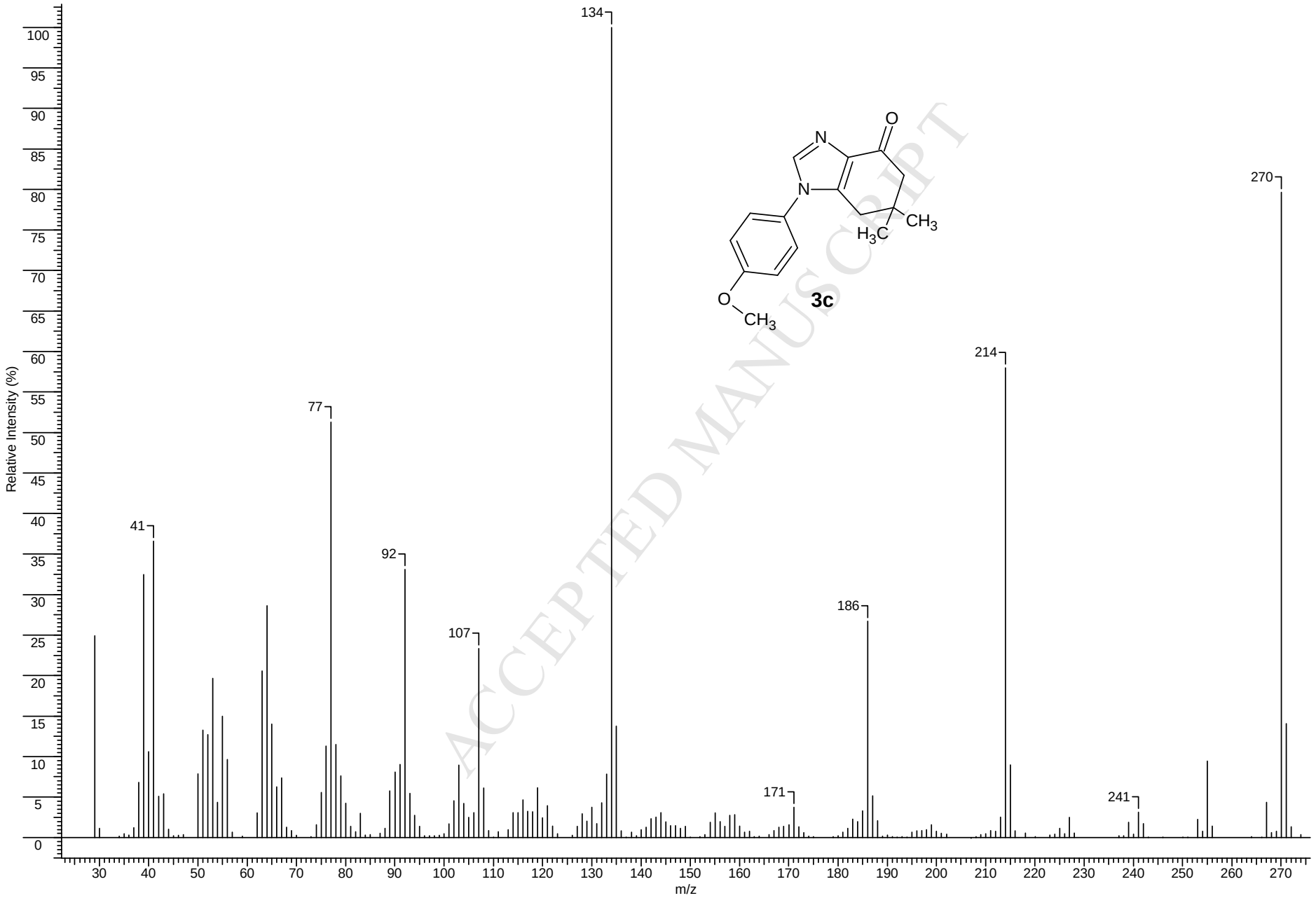


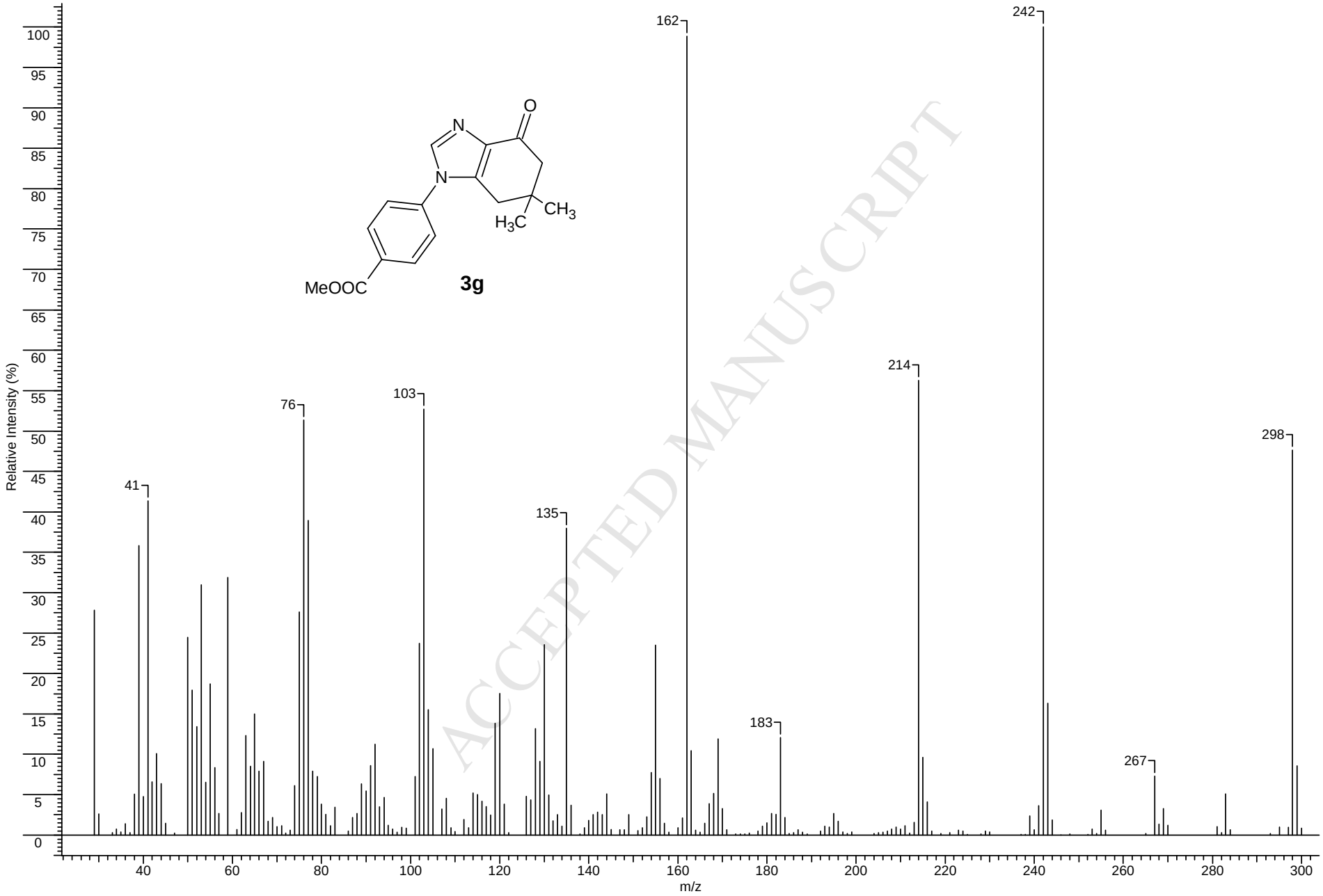


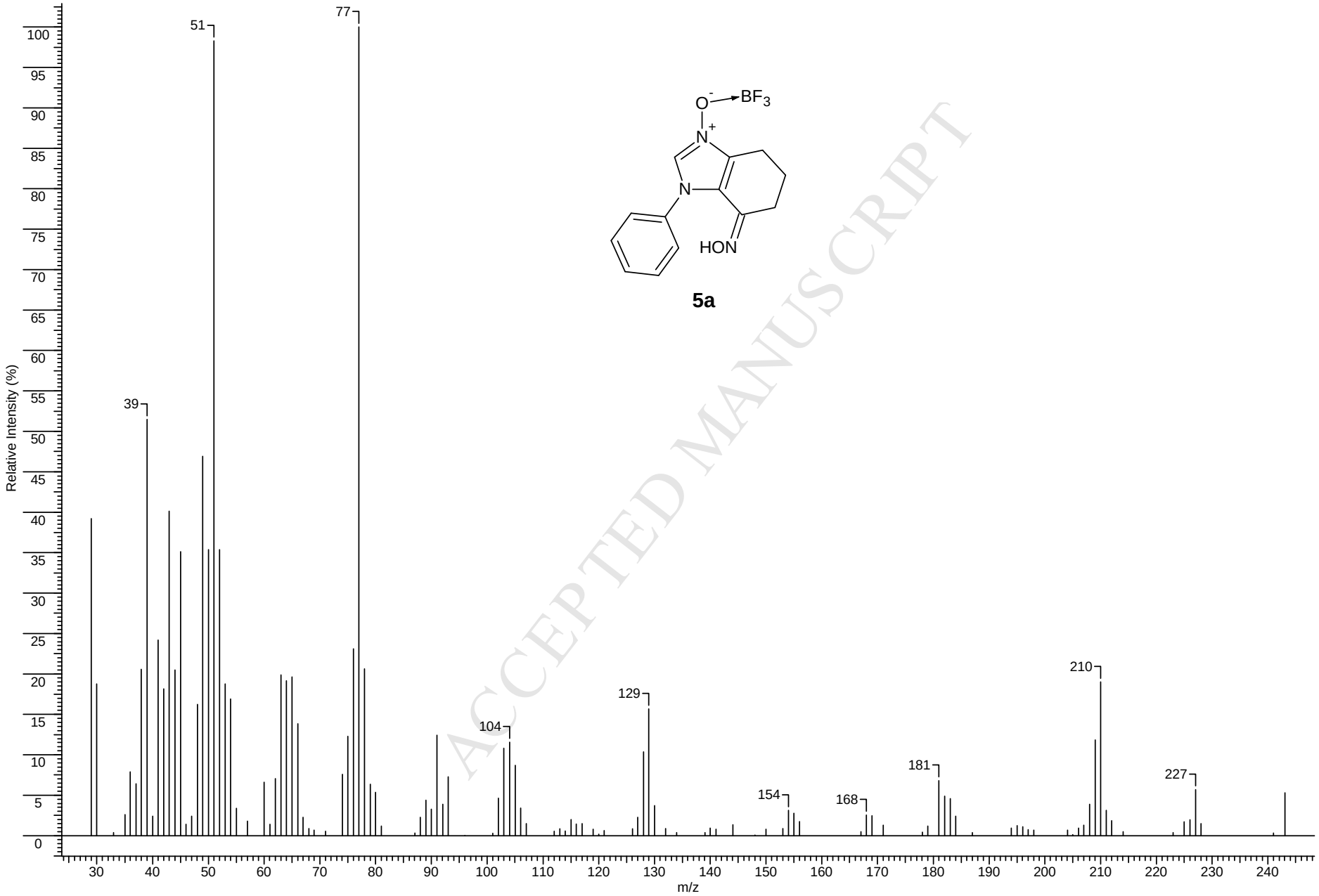
1f



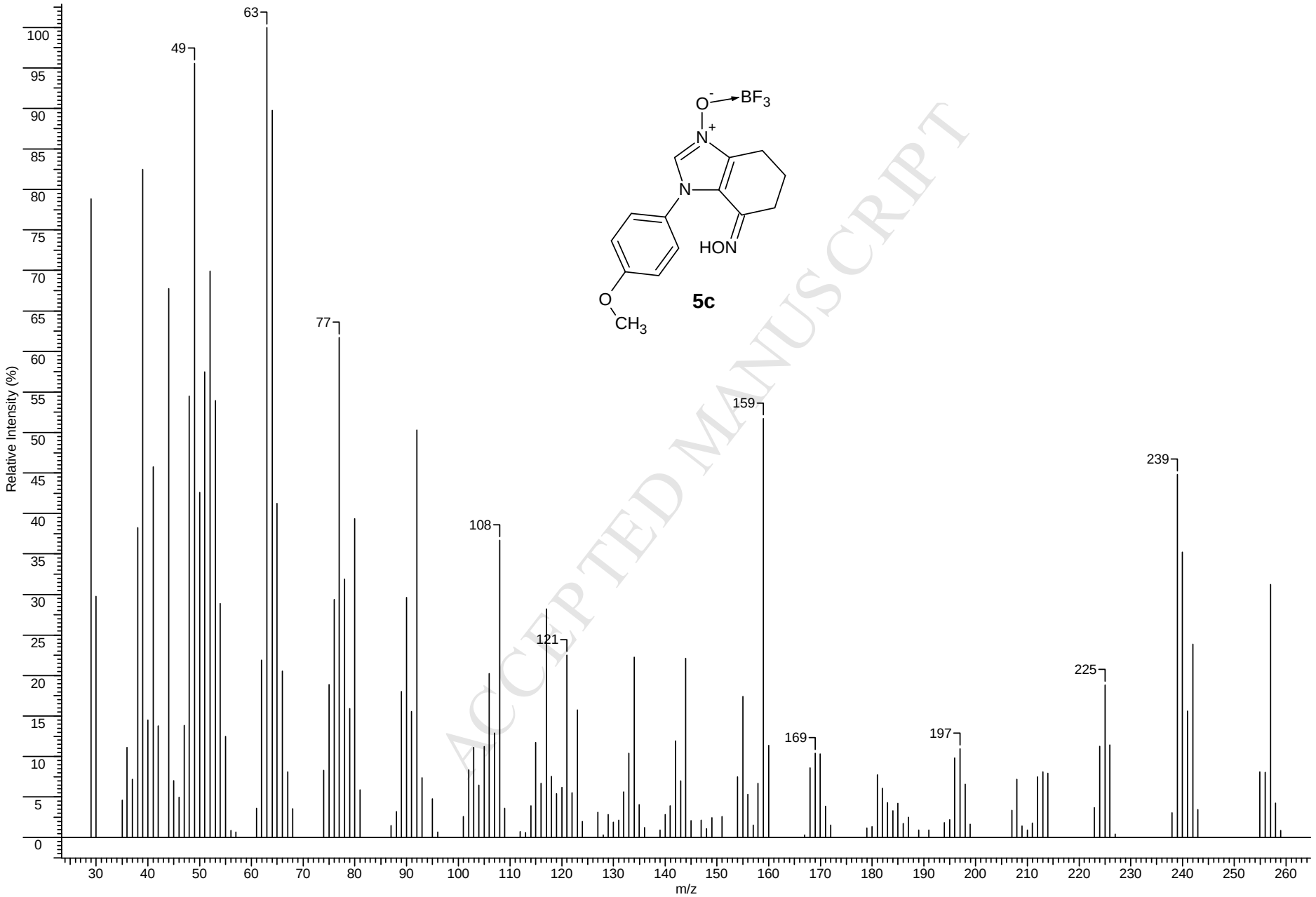
3a

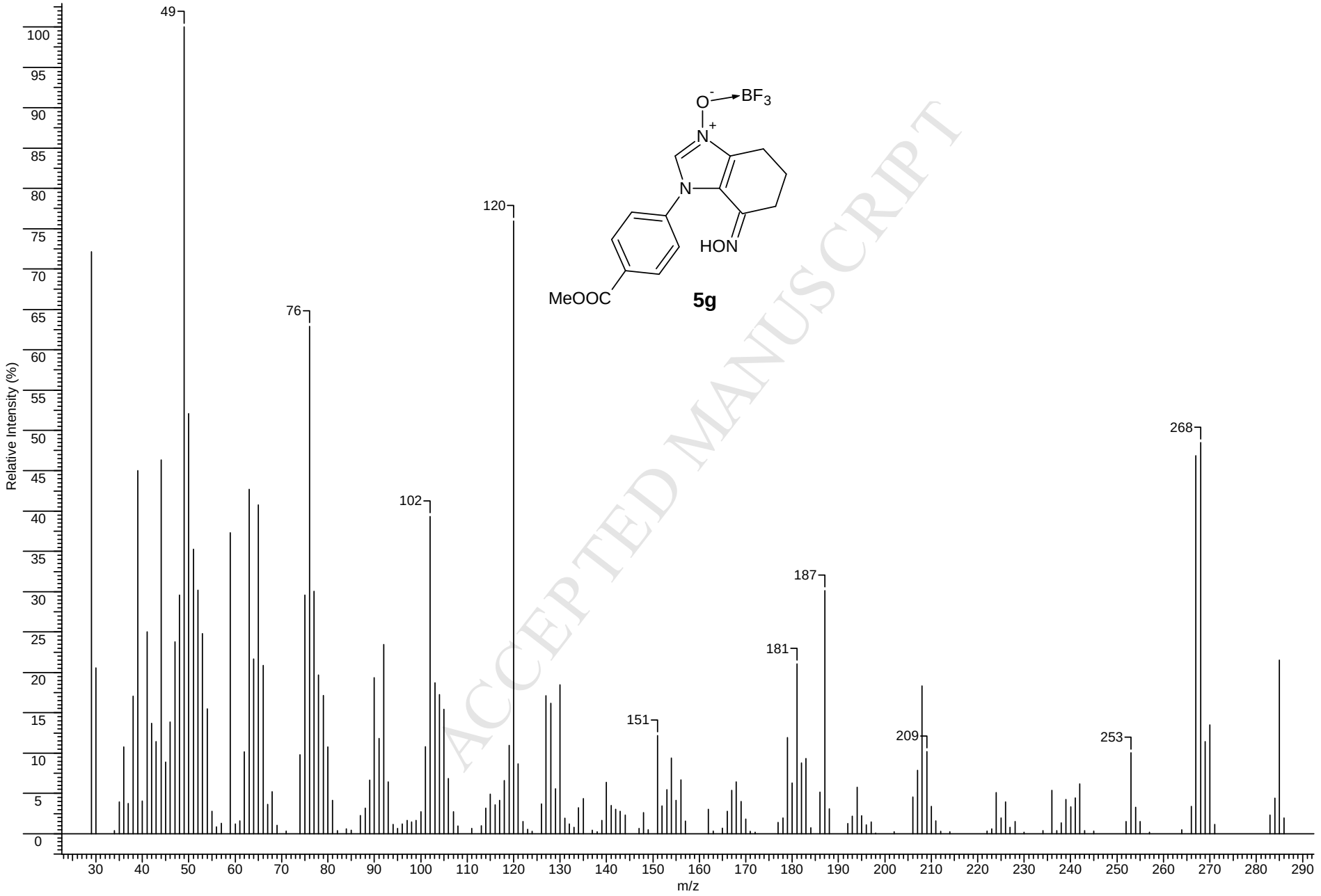


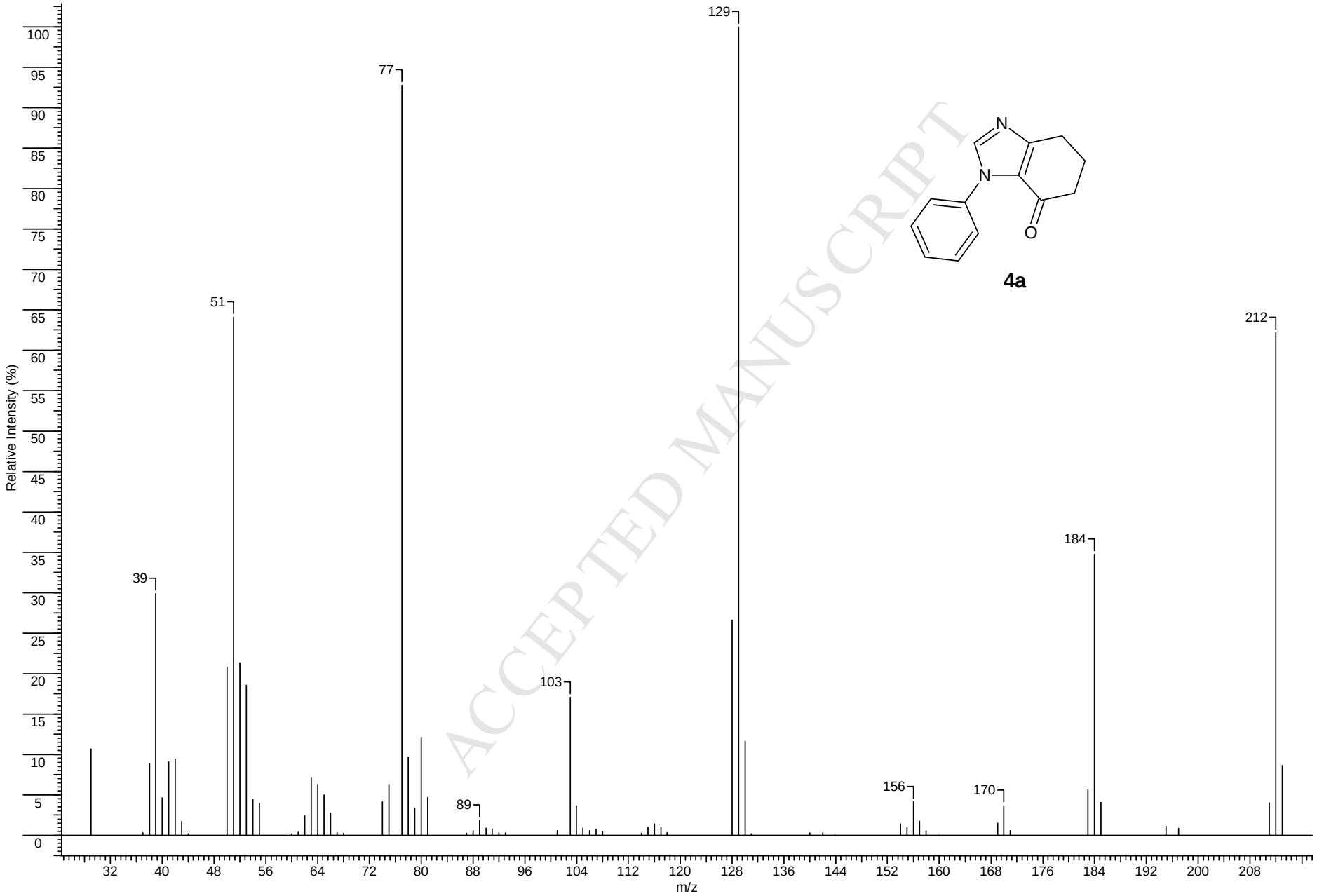


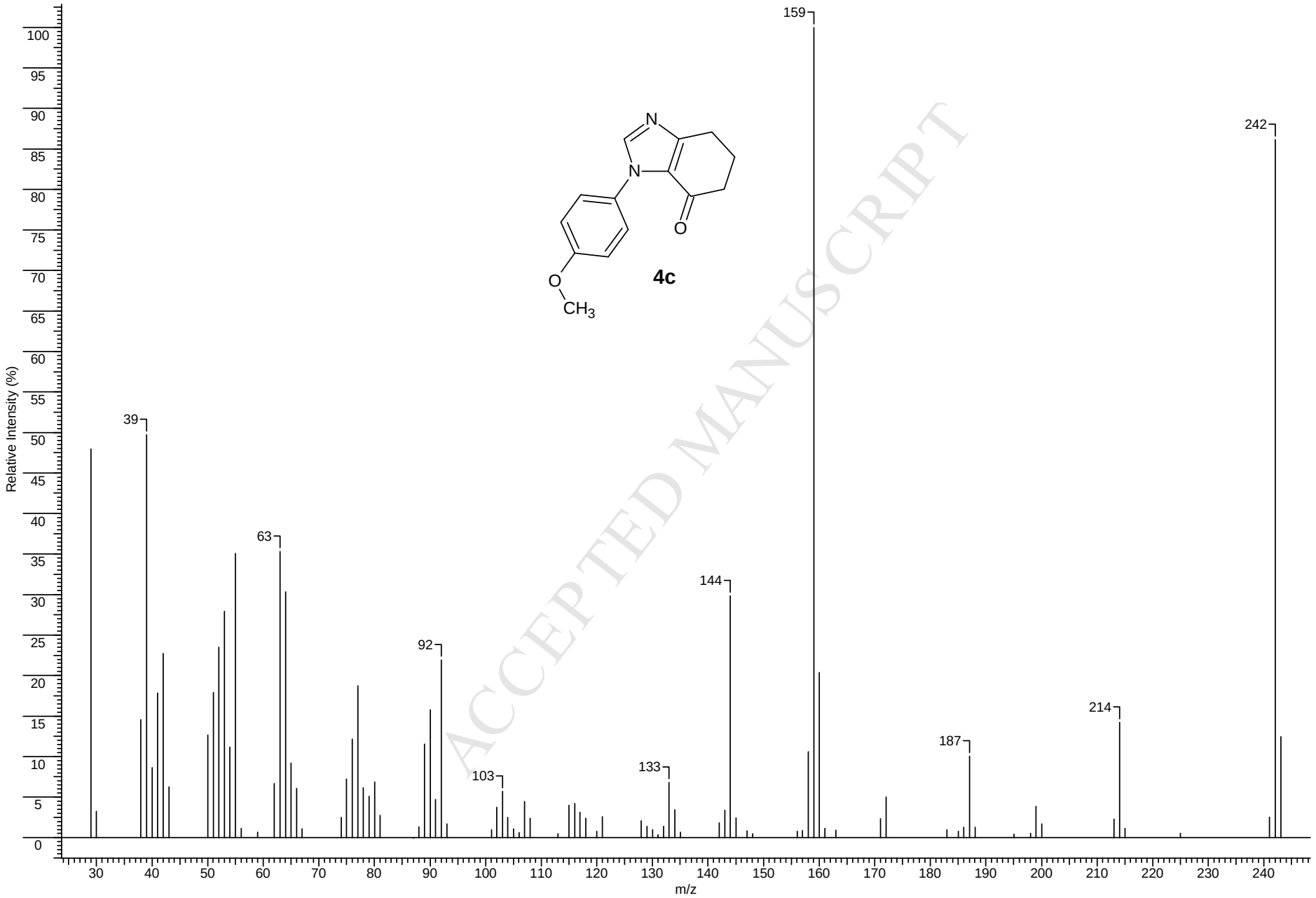


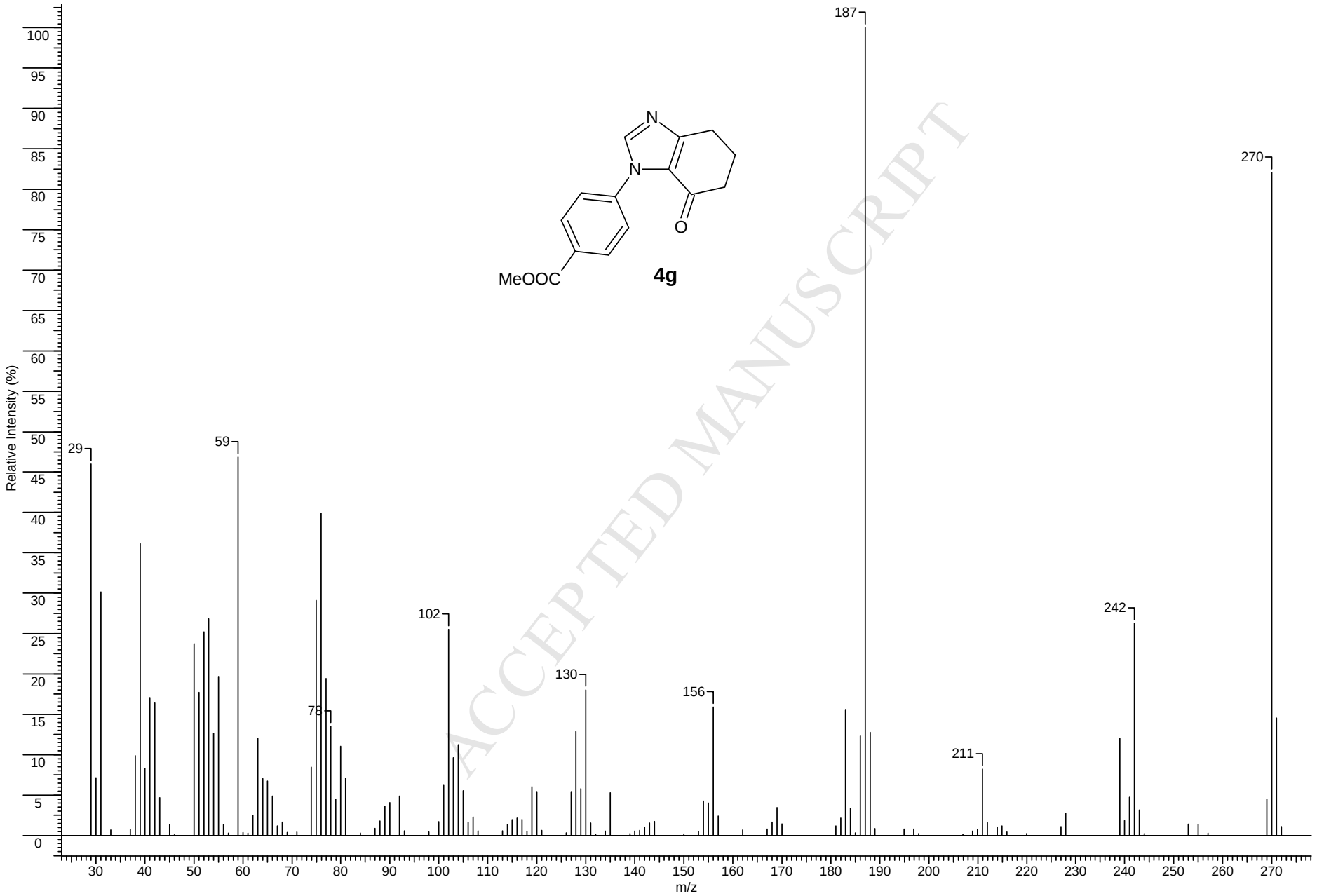
5a

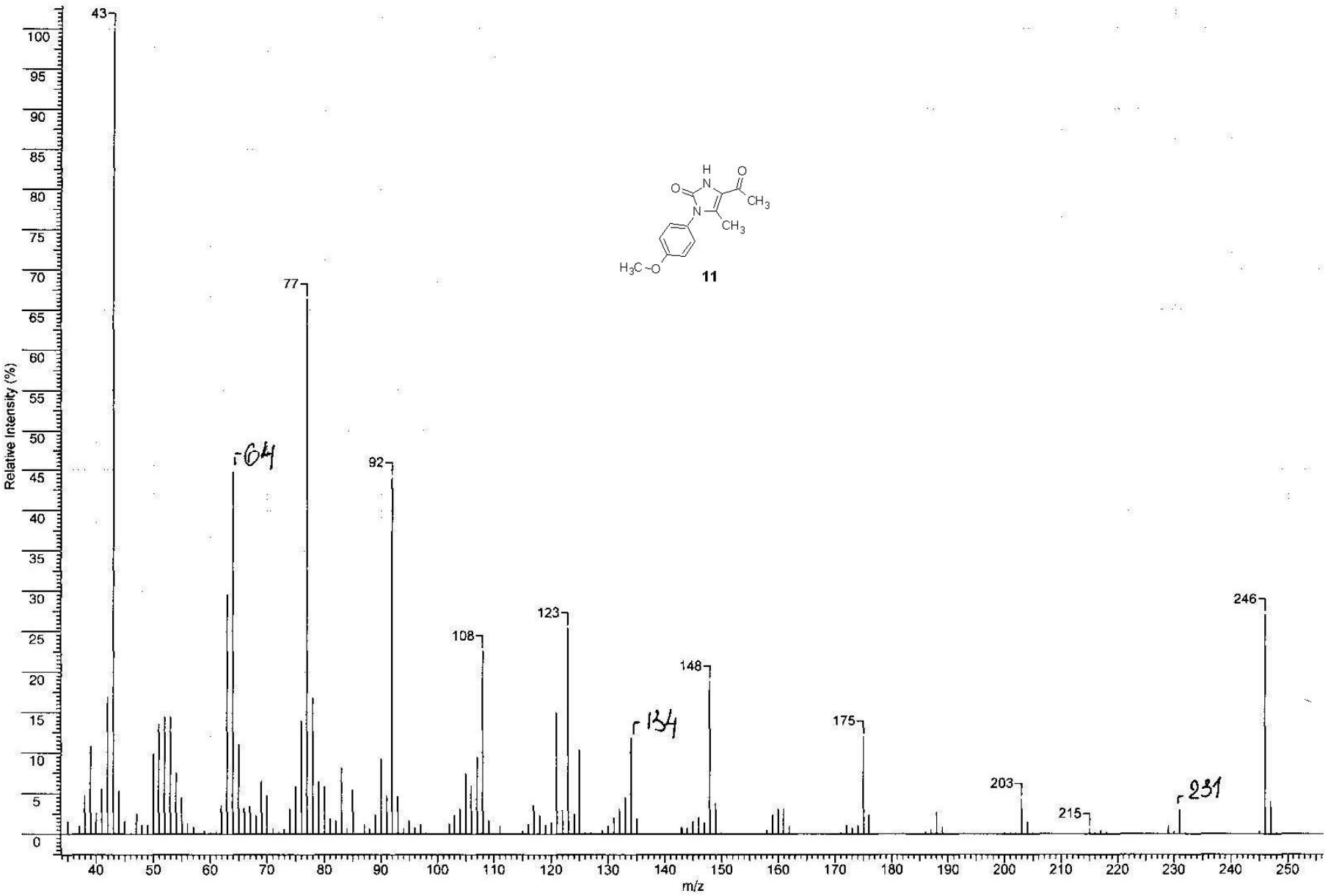











Relative Intensity (%)
m/z
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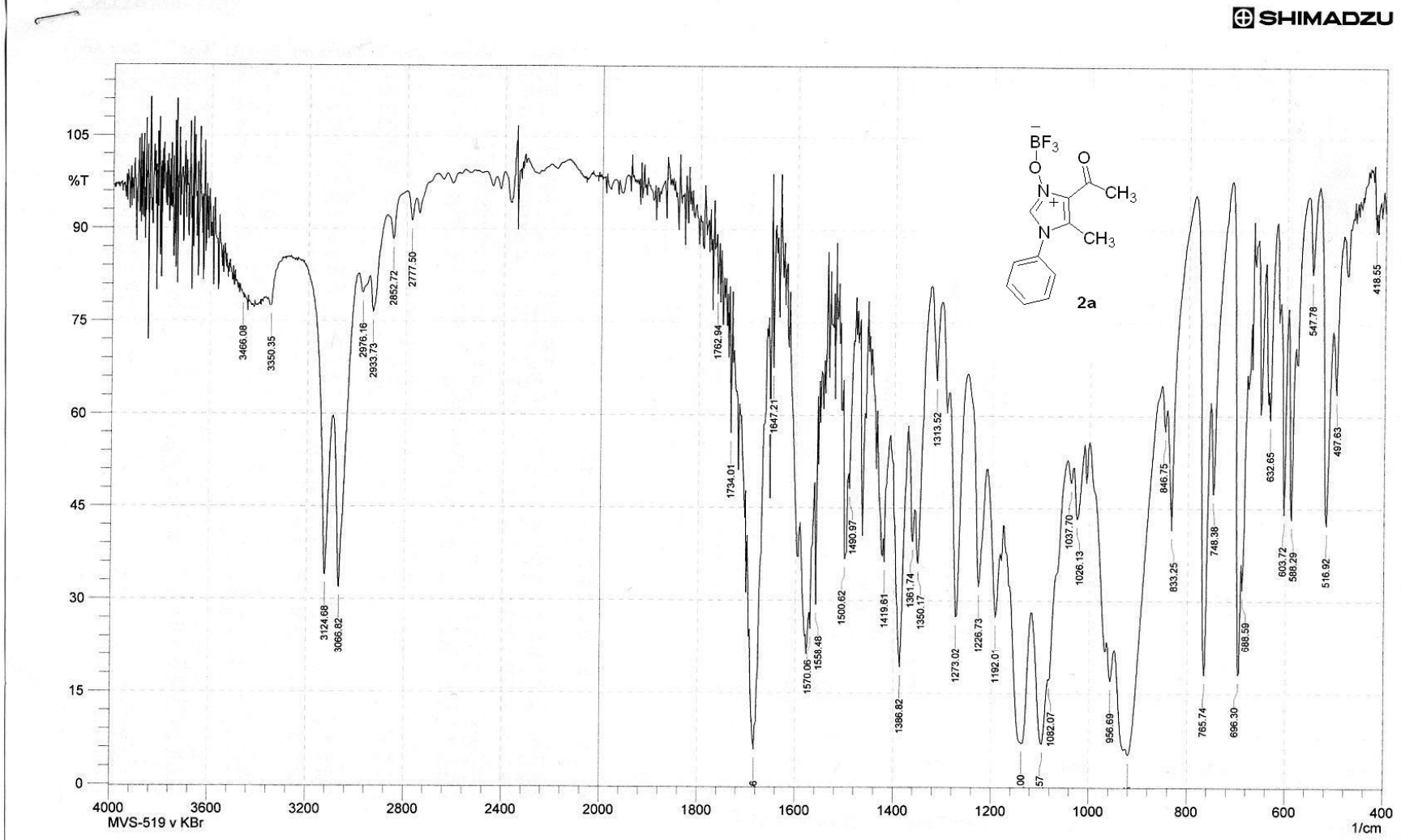

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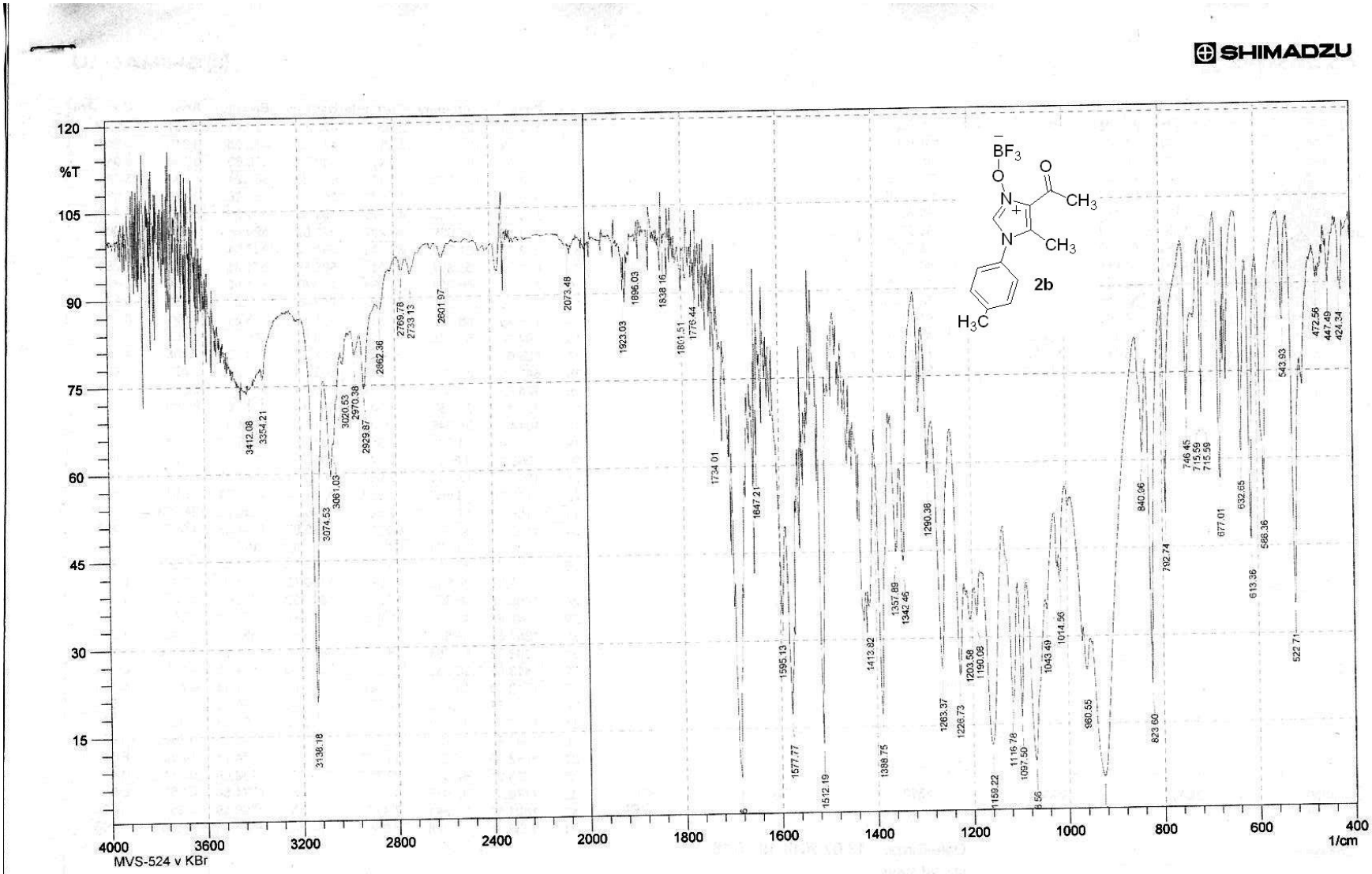
User; Krasitel



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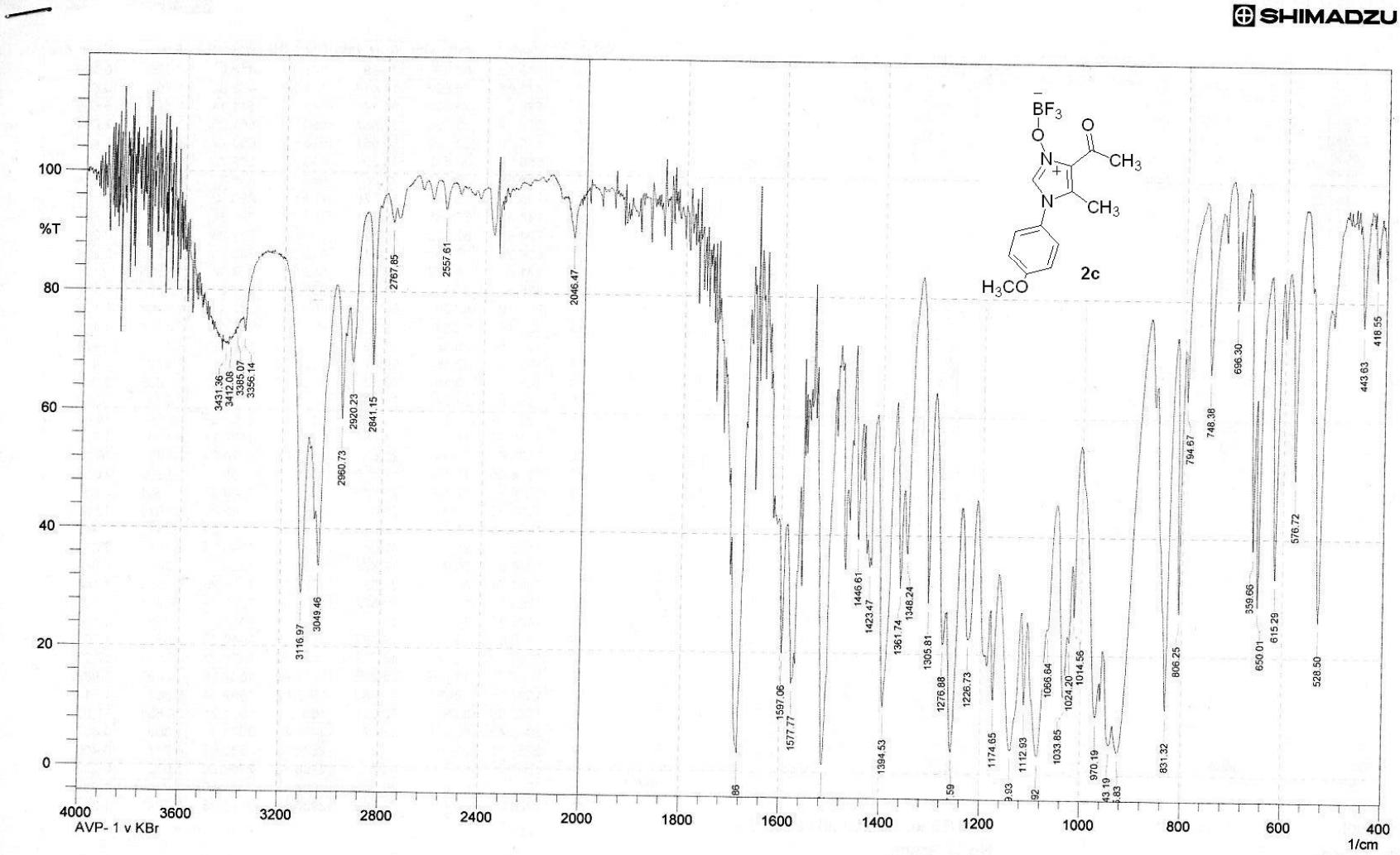
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1200
1000
800
600
400
1/cm
AVP- 1 v KBr
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3412.06
3365.07
3356.14
3116.97
3049.46
2960.73
2920.23
2841.15
2767.85
2557.61
2046.47
1597.06
1577.77
1446.61
1423.47
1394.53
1361.74
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1112.93
1066.64
1033.85
1024.20
1014.56
970.19
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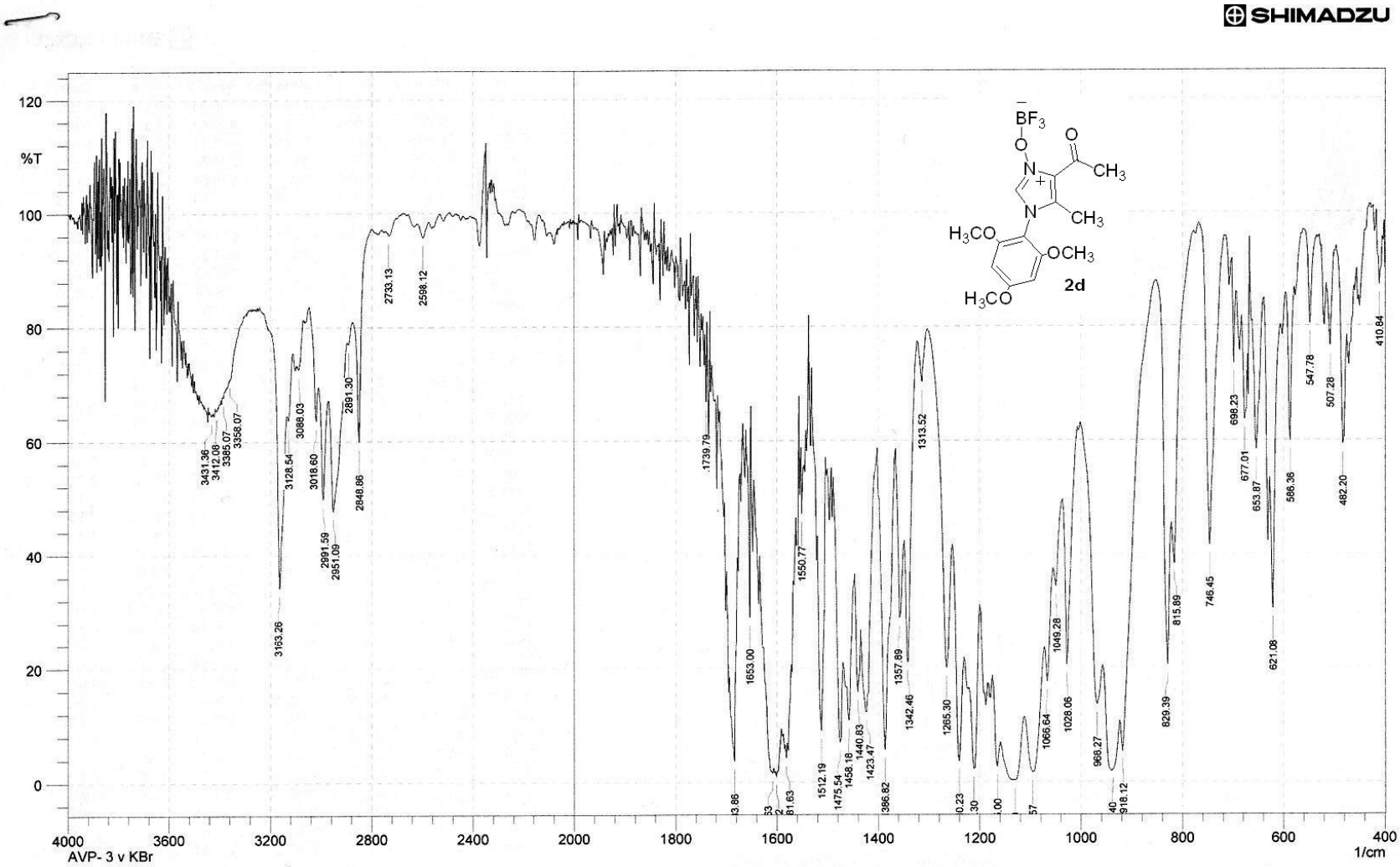
Date/Time; 17.02.2014 18:20:38
User; Krasitel



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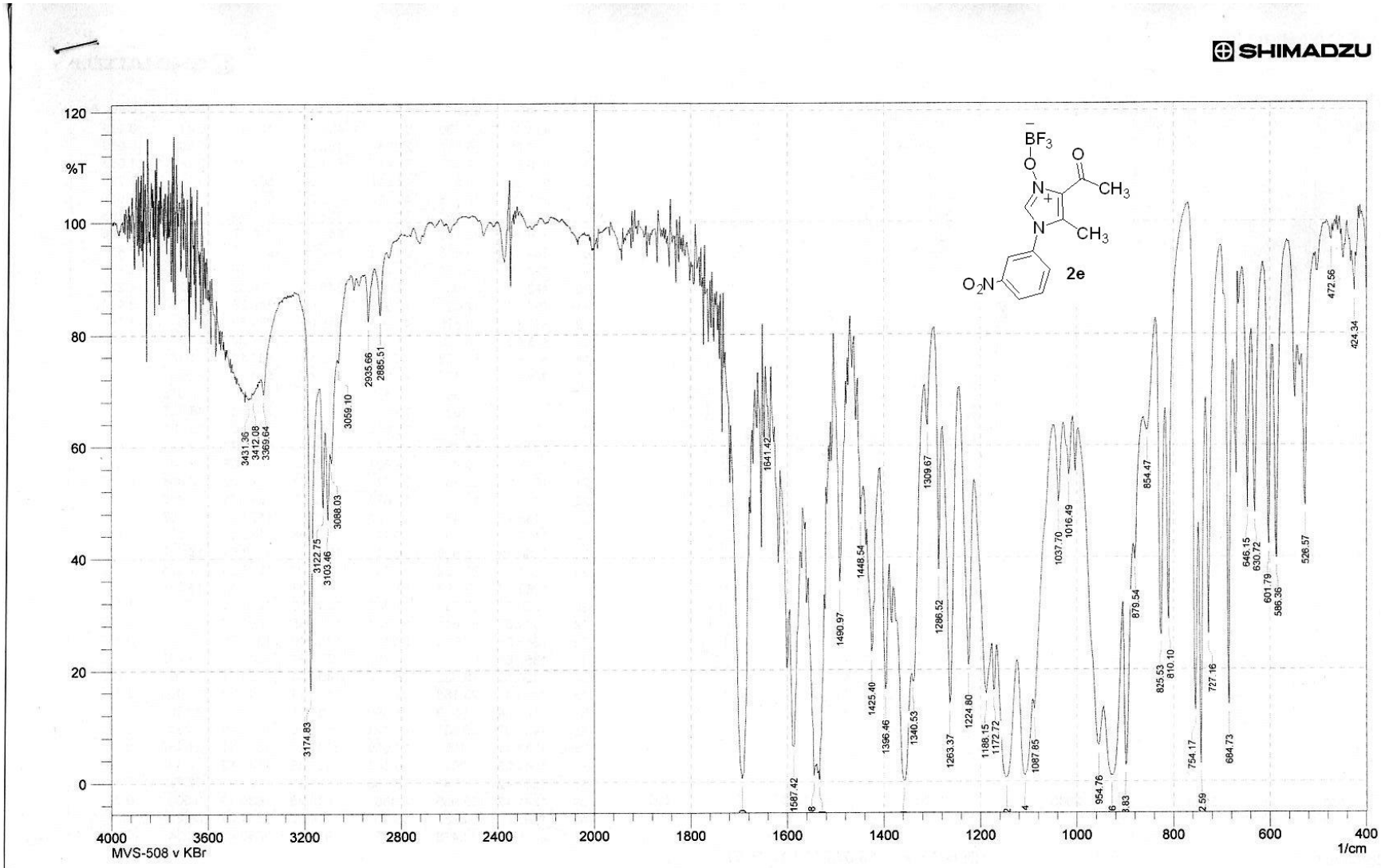
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1/cm
MVS-508 v KBr
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Date/Time; 13.02.2014 17:16:29
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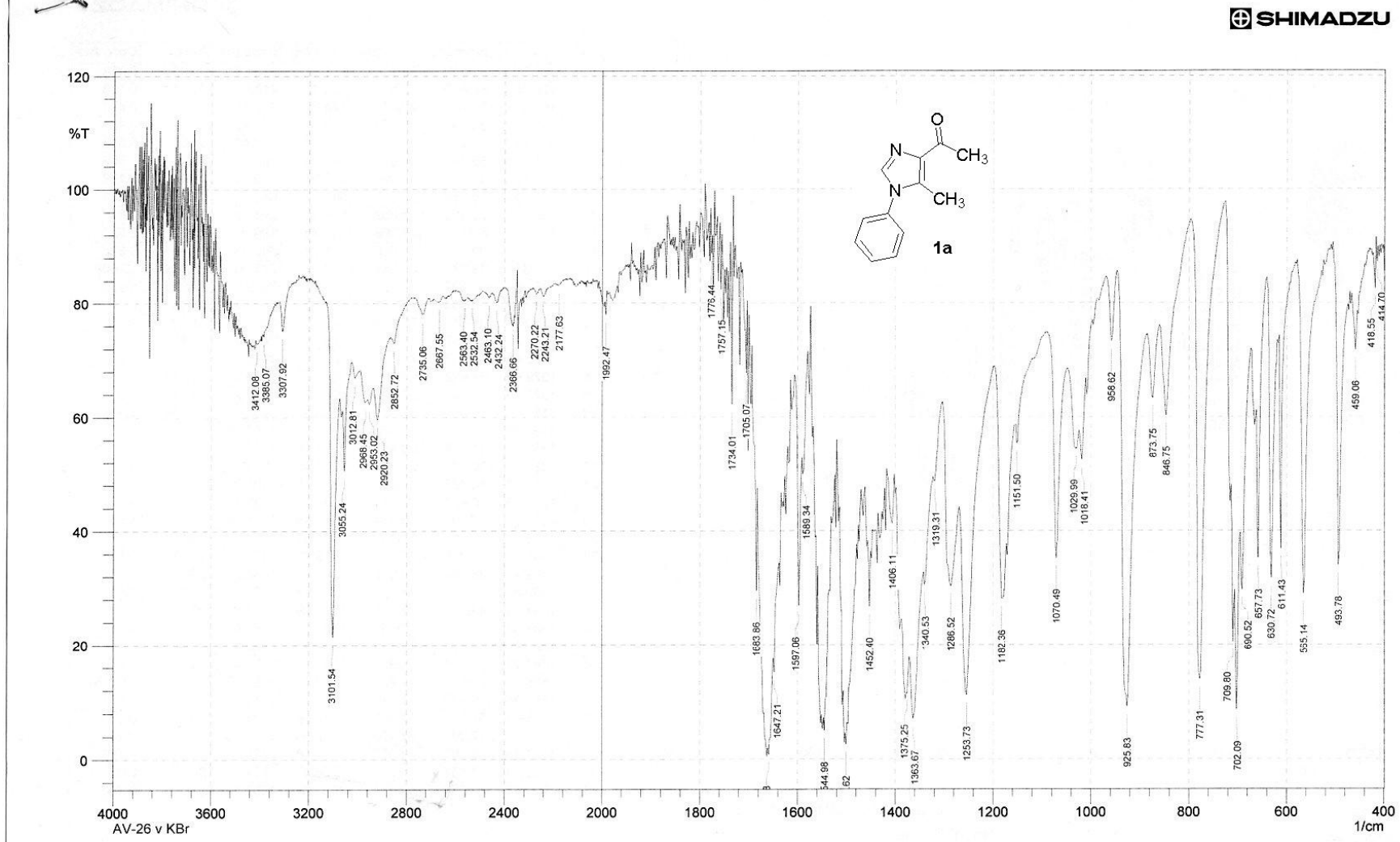

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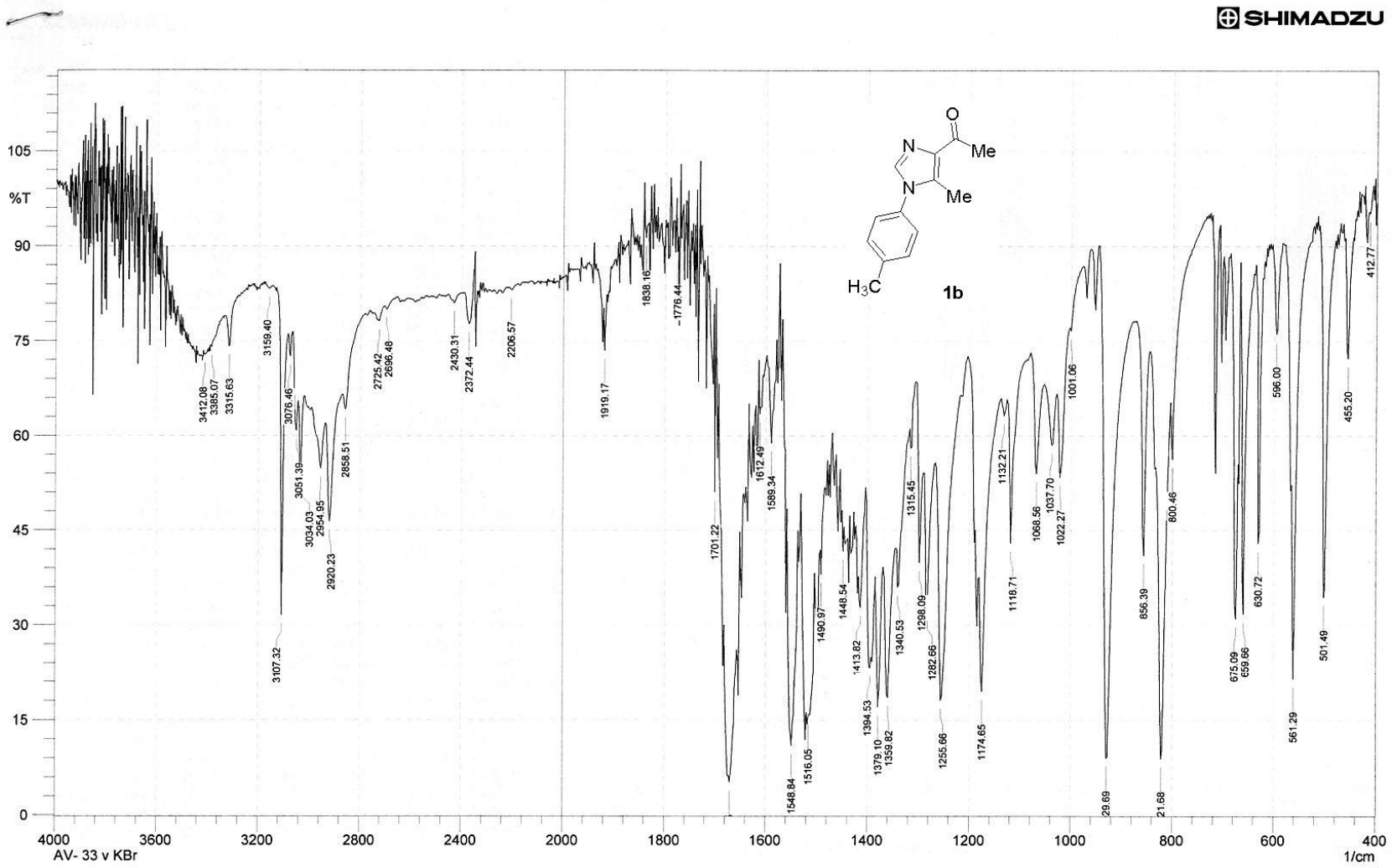

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AV- 33 v KBr

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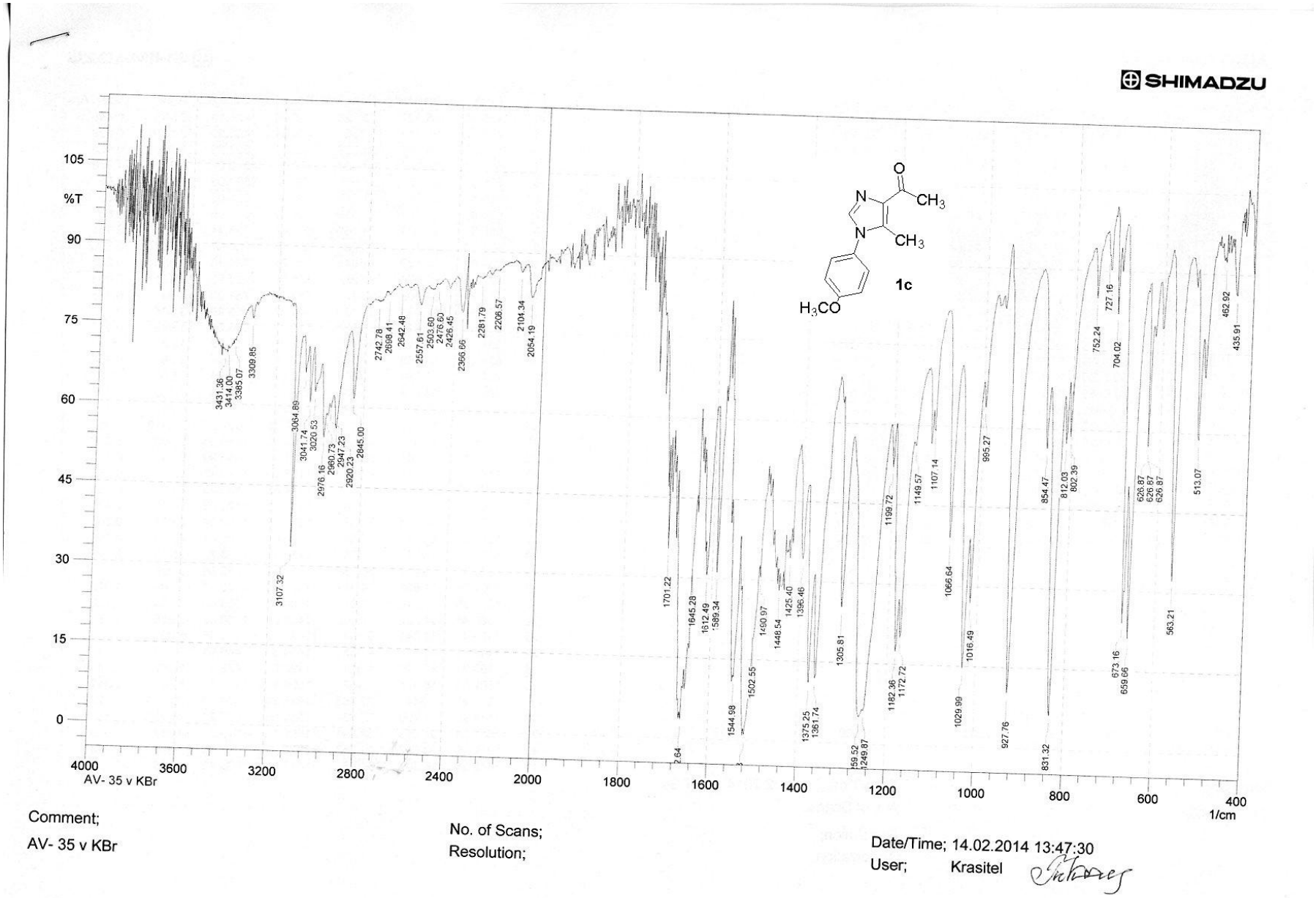
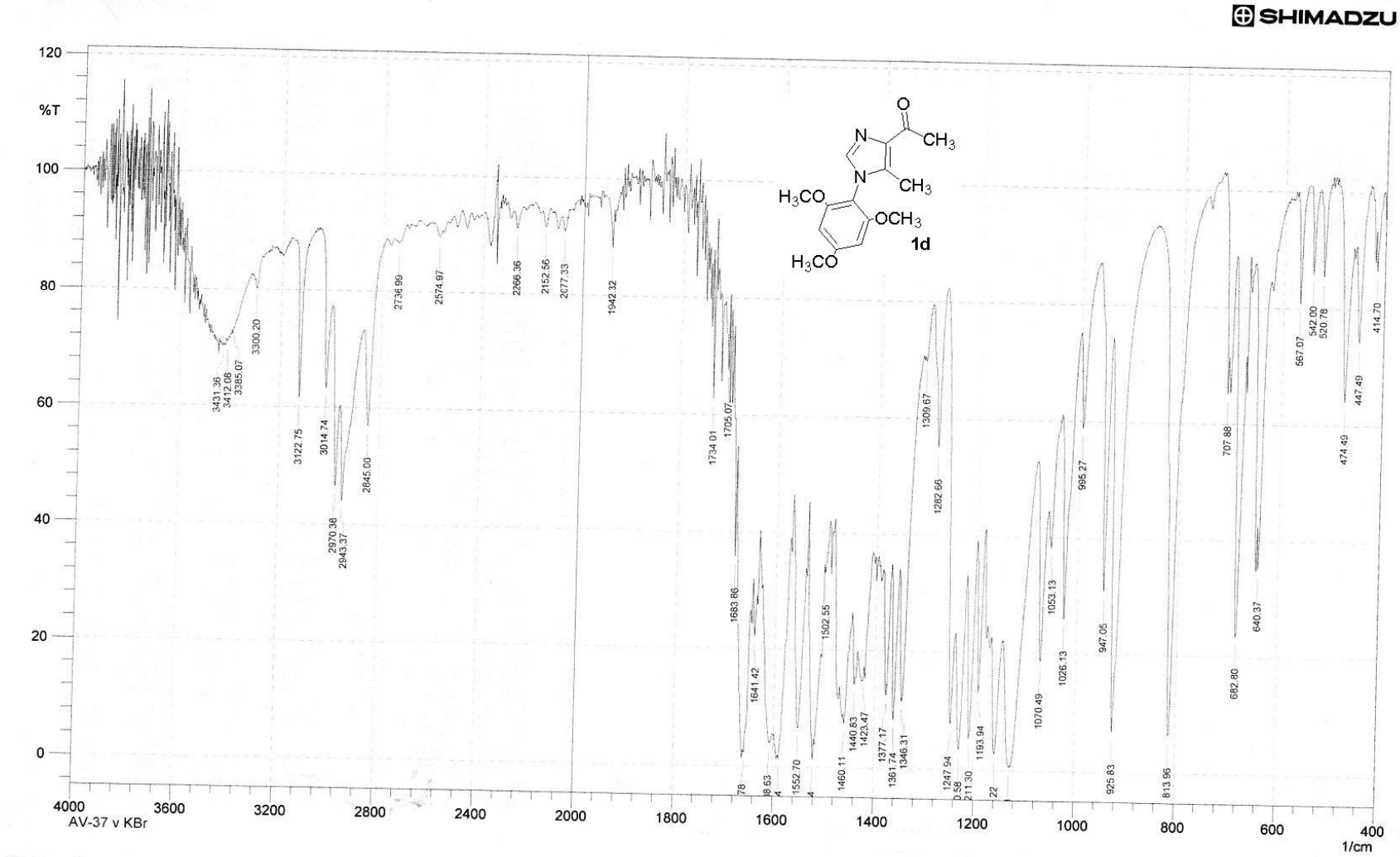
Date/Time; 17.02.2014 18:57:28
User; Krasitel

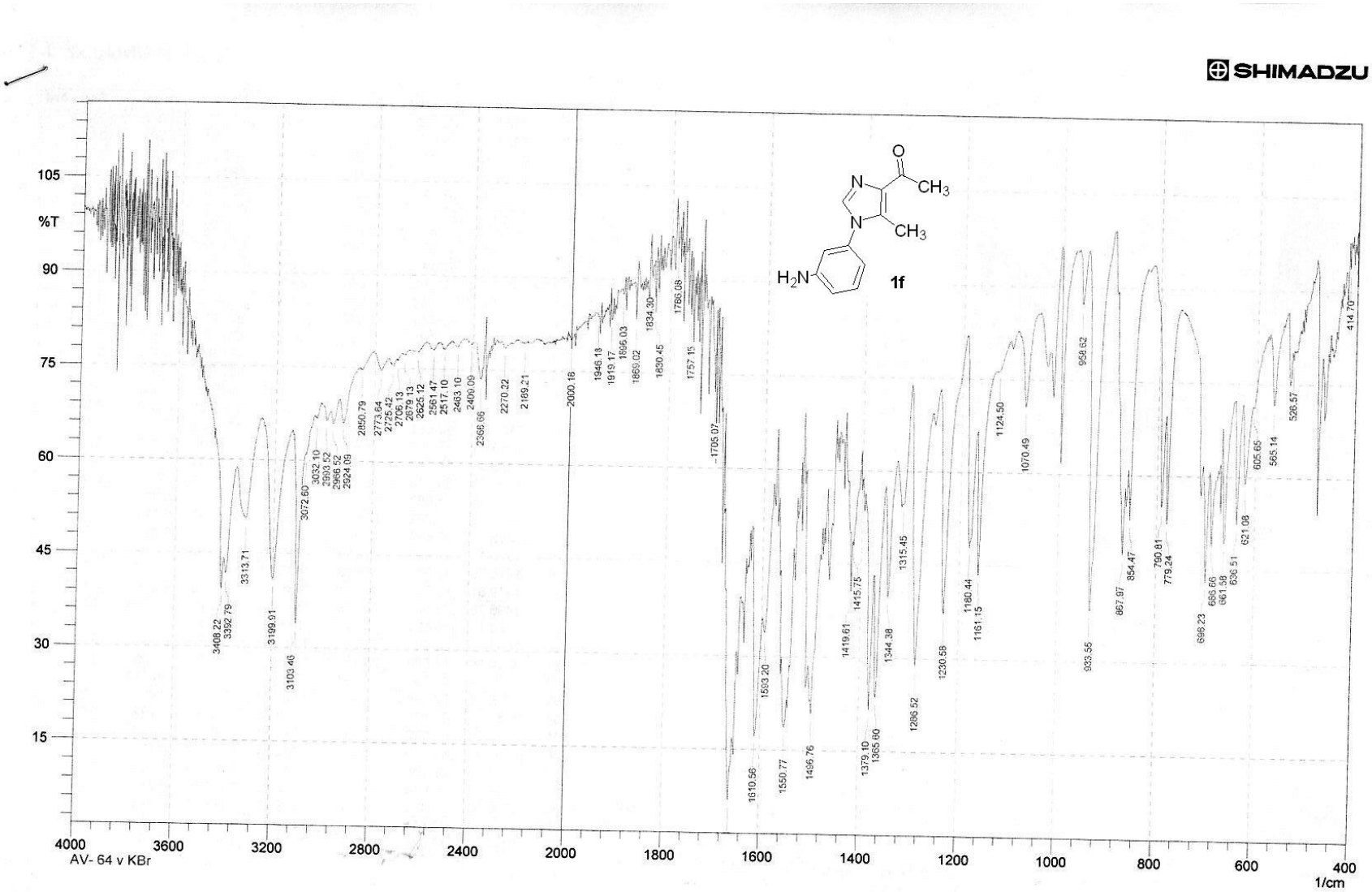

SHIMADZU
%T
105
90
75
60
45
30
15
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
1/cm
AV- 35 v KBr
3431.36
3414.00
3385.07
3309.85
3107.32
3064.89
3041.74
3020.53
2976.16
2960.73
2947.23
2920.23
2845.00
2742.78
2698.41
2642.48
2557.61
2503.60
2476.60
2426.45
2356.66
2281.79
2206.57
2104.34
2054.19
1701.22
1645.28
1612.49
1589.34
1544.98
1502.55
1490.97
1448.54
1425.40
1396.46
1375.25
1361.74
1305.81
1259.52
1249.87
1199.72
1182.36
1172.72
1149.57
1107.14
1066.64
1029.99
1016.49
995.27
927.76
854.47
831.32
812.03
802.39
752.24
727.16
704.02
673.16
659.66
626.87
626.67
626.87
563.21
513.07
462.92
435.91
O
CH3
N
N
CH3
H3CO
1c
Comment;
AV- 35 v KBr
No. of Scans;
Resolution;
Date/Time; 14.02.2014 13:47:30
User; Krasitel



Comment;
AV-37 v KBr

No. of Scans;
Resolution;

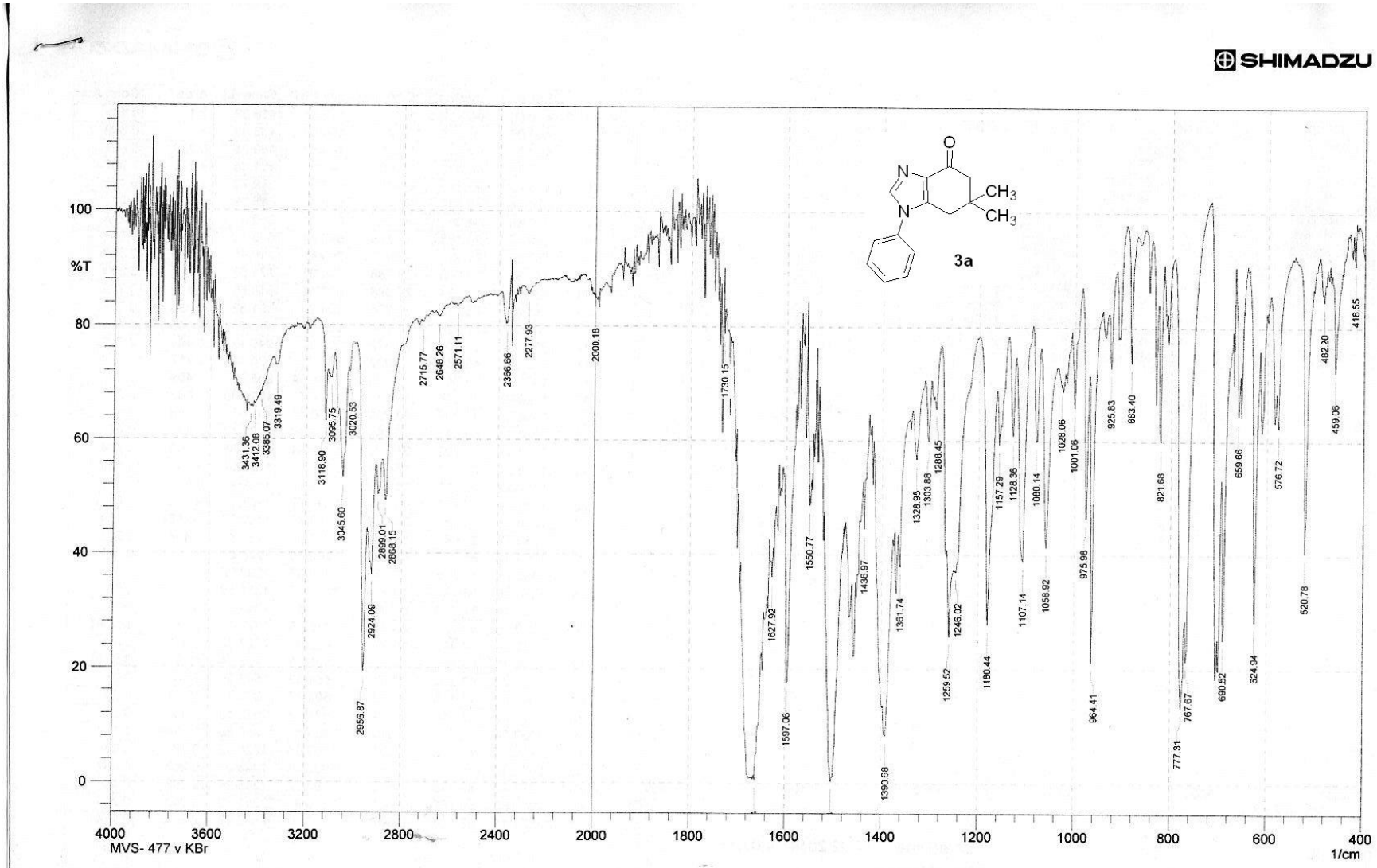
Date/Time; 13.02.2014 18:21:07
User; Krasitel



Comment;
AV- 64 v KBr

No. of Scans;
Resolution;

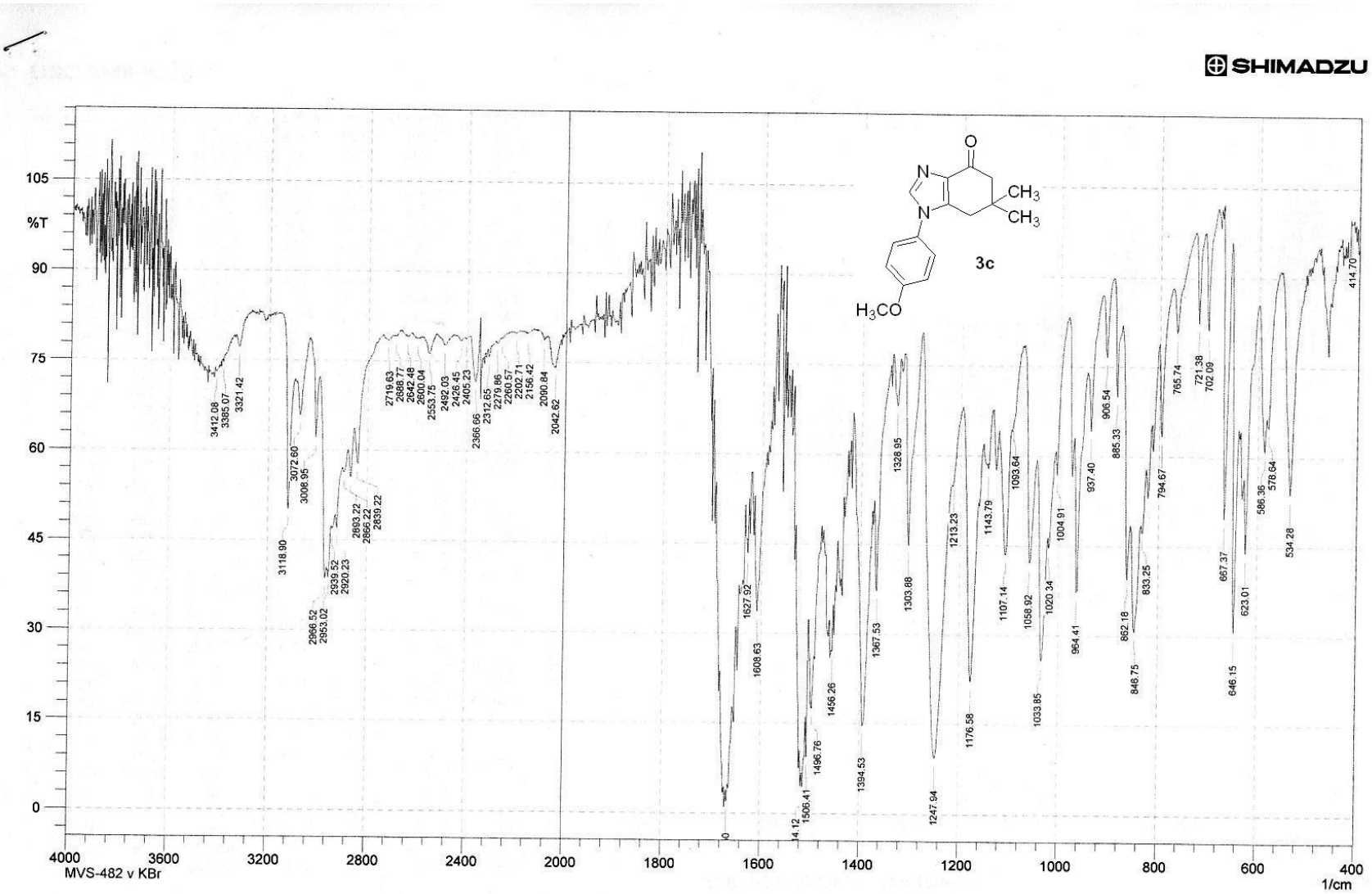
Date/Time; 14.02.2014 14:44:40
User; Krasitel



Comment;
MVS- 477 v KBr

No. of Scans;
Resolution;

Date/Time; 14.02.2014 14:07:18
User; Krasitel



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MVS-482 v KBr

No. of Scans;
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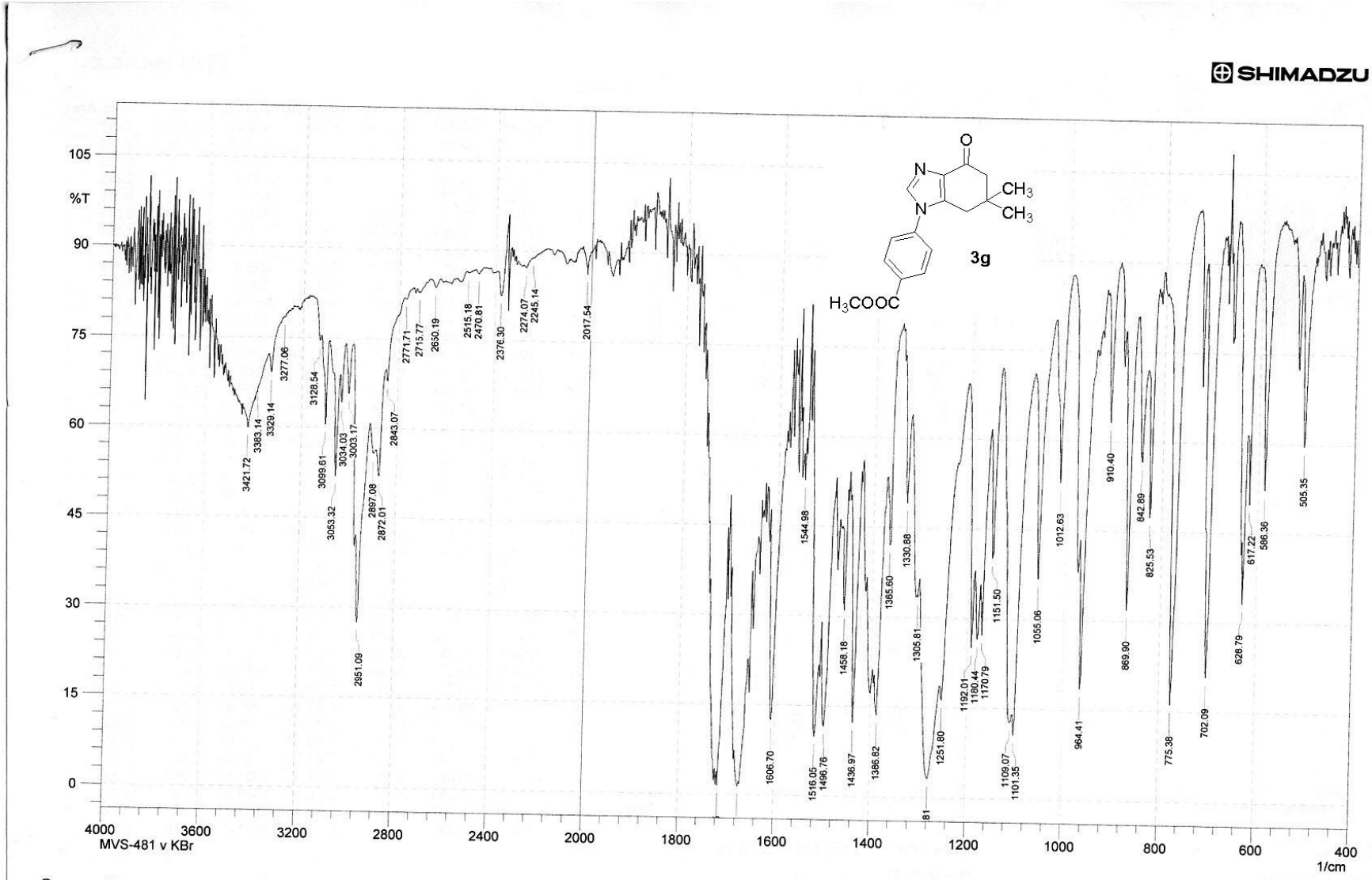
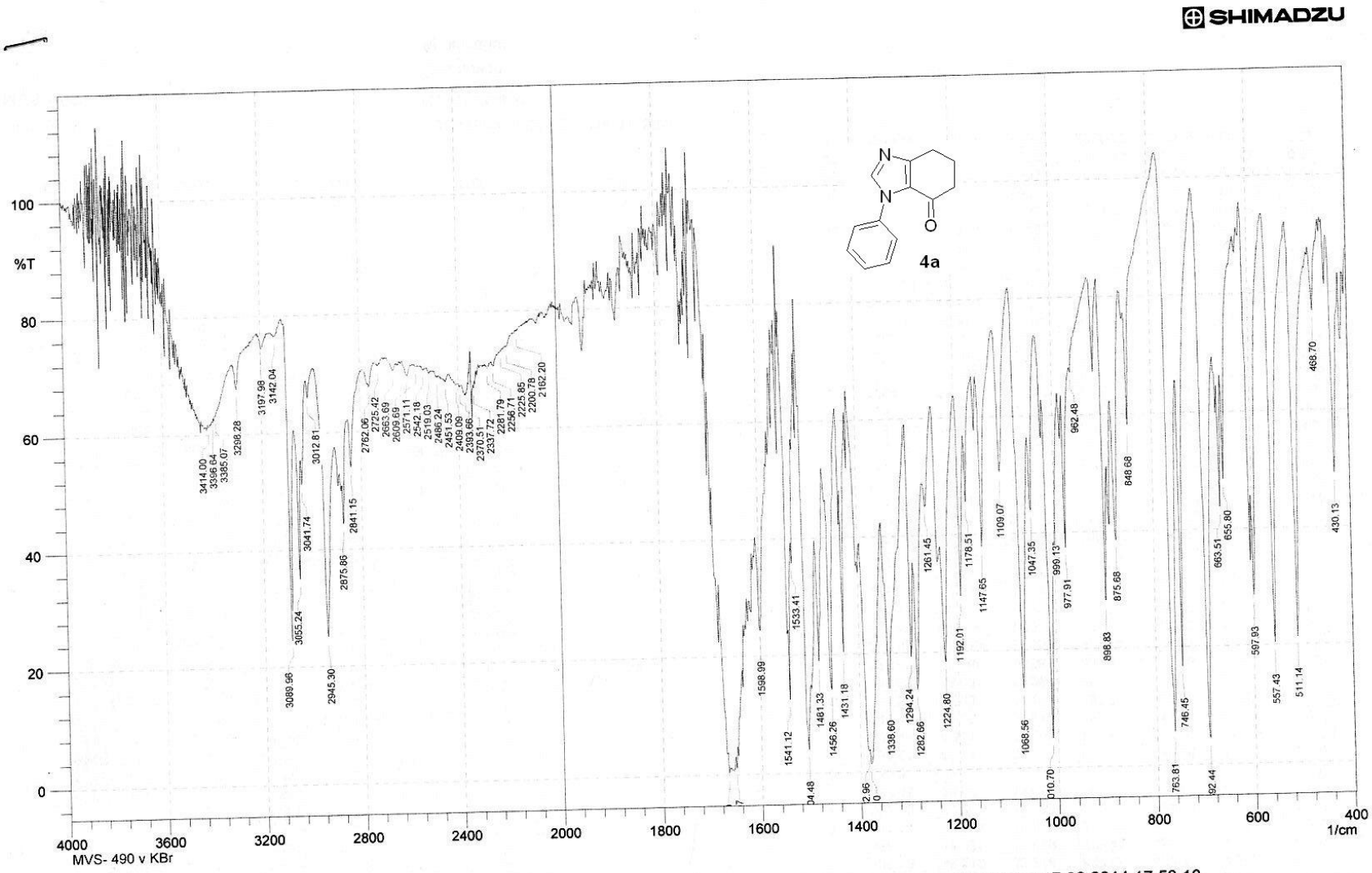
Date/Time; 13.02.2014 20:58:38
User; Krasitel



Comment;
MVS-481 v KBr

No. of Scans;
Resolution;

Date/Time; 12.02.2014 19:16:23
User; Krasitel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100
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20
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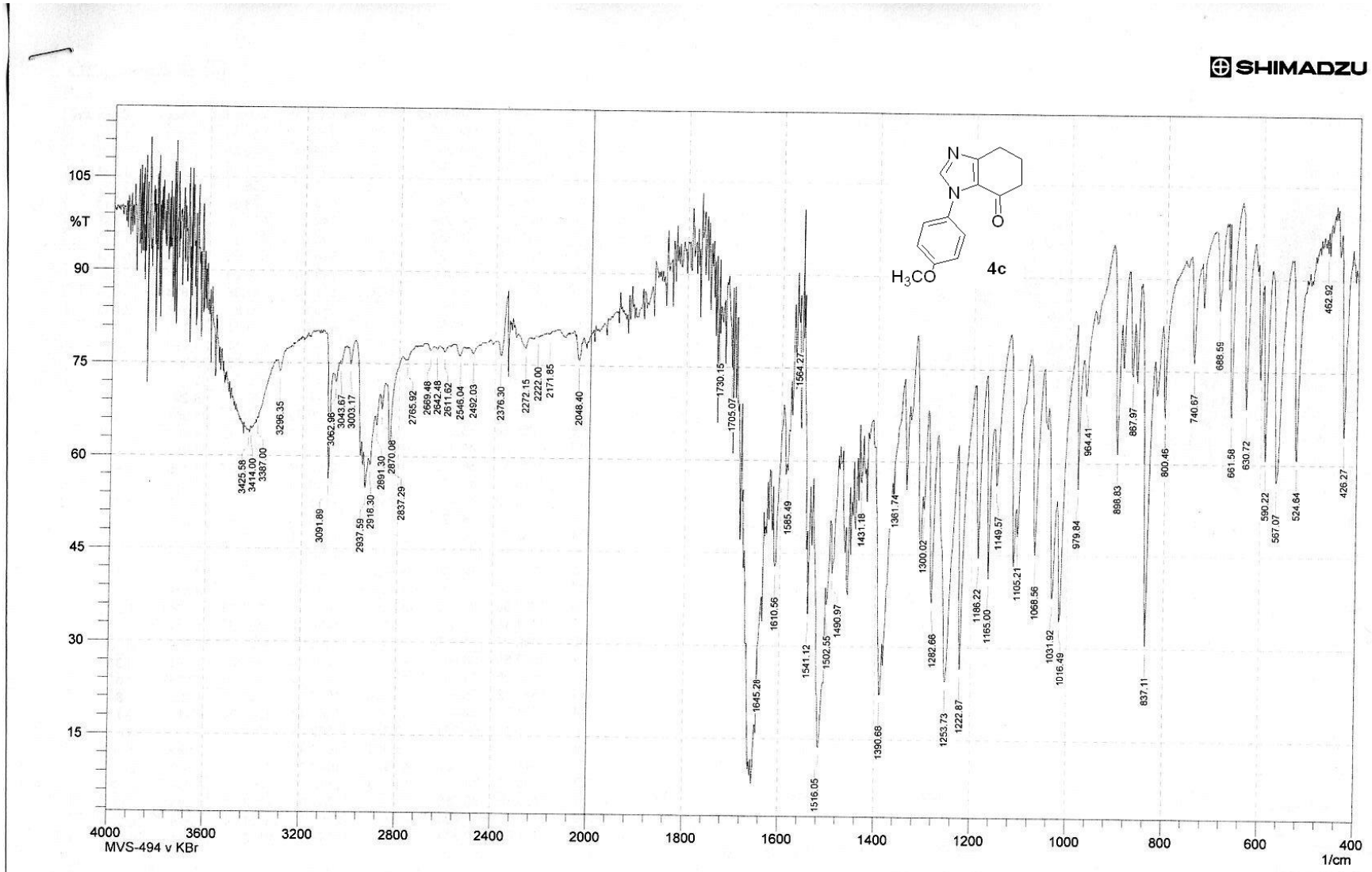
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
1/cm
MVS- 490 v KBr
3414.00
3396.64
3385.07
3298.28
3197.98
3142.04
3089.96
3055.24
3041.74
3012.81
2945.30
2875.86
2841.15
2762.06
2725.42
2663.69
2609.69
2571.11
2542.18
2519.03
2486.24
2451.53
2408.09
2393.66
2370.51
2337.72
2281.79
2256.71
2225.85
2200.78
2162.20
1598.99
1541.12
1533.41
1481.33
1456.26
1431.18
1338.60
1294.24
1282.66
1261.45
1224.80
1192.01
1178.51
1147.65
1109.07
1068.56
1047.35
999.13
977.91
962.48
898.83
875.68
848.68
763.81
746.45
663.51
655.80
597.93
557.43
511.14
468.70
430.13
Comment;
MVS- 490 v KBr
No. of Scans;
Resolution;
Date/Time; 17.02.2014 17:53:13
User; Krasitel



Comment;
MVS-494 v KBr

No. of Scans;
Resolution;

Date/Time; 13.02.2014 17:39:50
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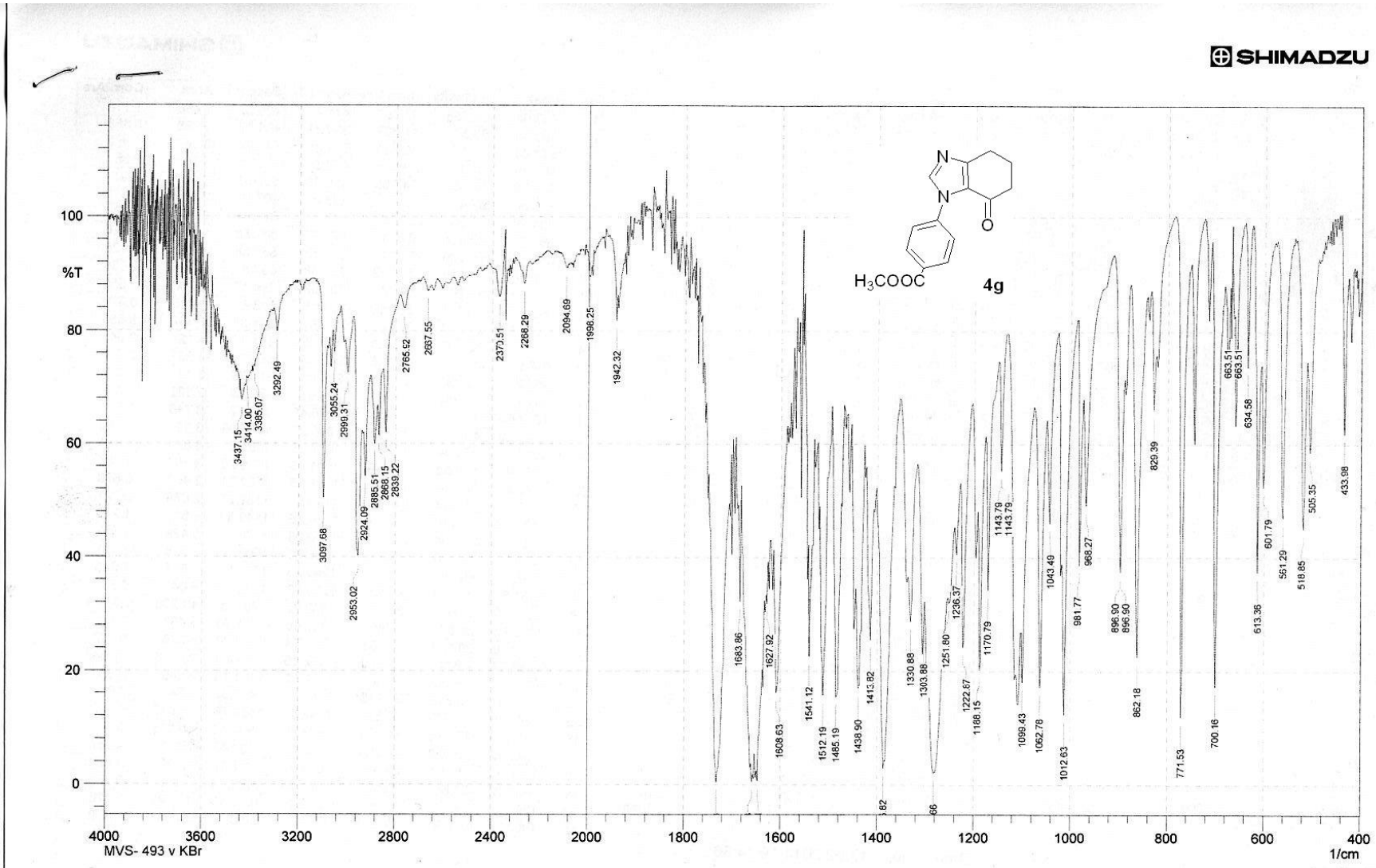
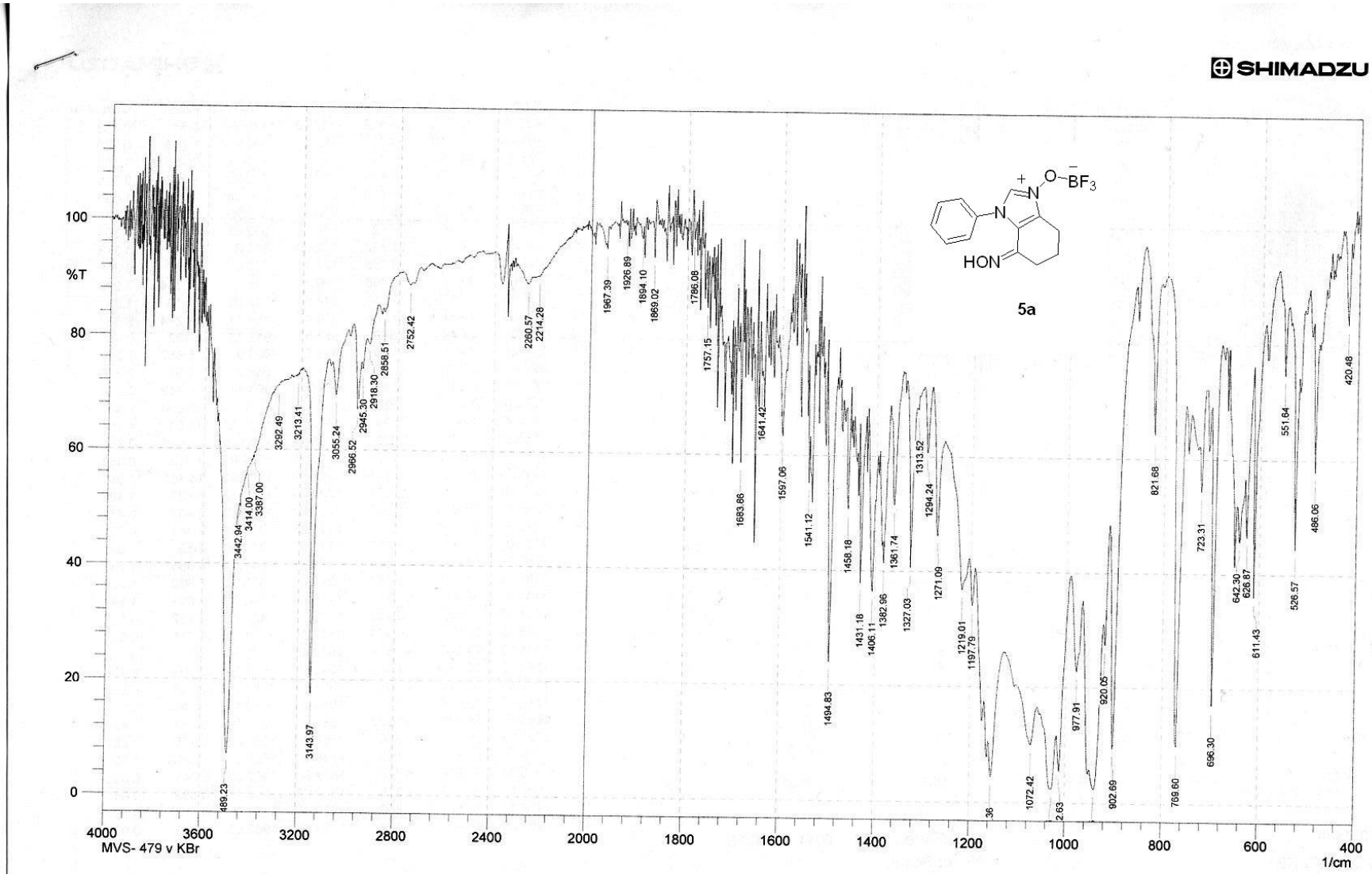


Comment;
MVS- 493 v KBr

No. of Scans;
Resolution;

Date/Time; 17.02.2014 19:14:36
User; Krasitel


SHIMADZU
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40
20
0
4000
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3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
1/cm
MVS- 479 v KBr
3442.94
3414.00
3387.00
3292.49
3213.41
3143.97
3055.24
2966.52
2945.30
2918.30
2858.51
2752.42
2260.57
2214.28
1967.39
1926.89
1894.10
1869.02
1786.09
1757.15
1683.86
1641.42
1597.06
1541.12
1494.83
1458.18
1431.18
1406.11
1382.96
1361.74
1327.03
1313.52
1294.24
1271.09
1219.01
1197.79
1072.42
977.91
920.05
902.69
821.68
769.60
723.31
696.30
642.30
626.87
611.43
551.64
526.57
496.06
489.23
420.48
HON
BF3
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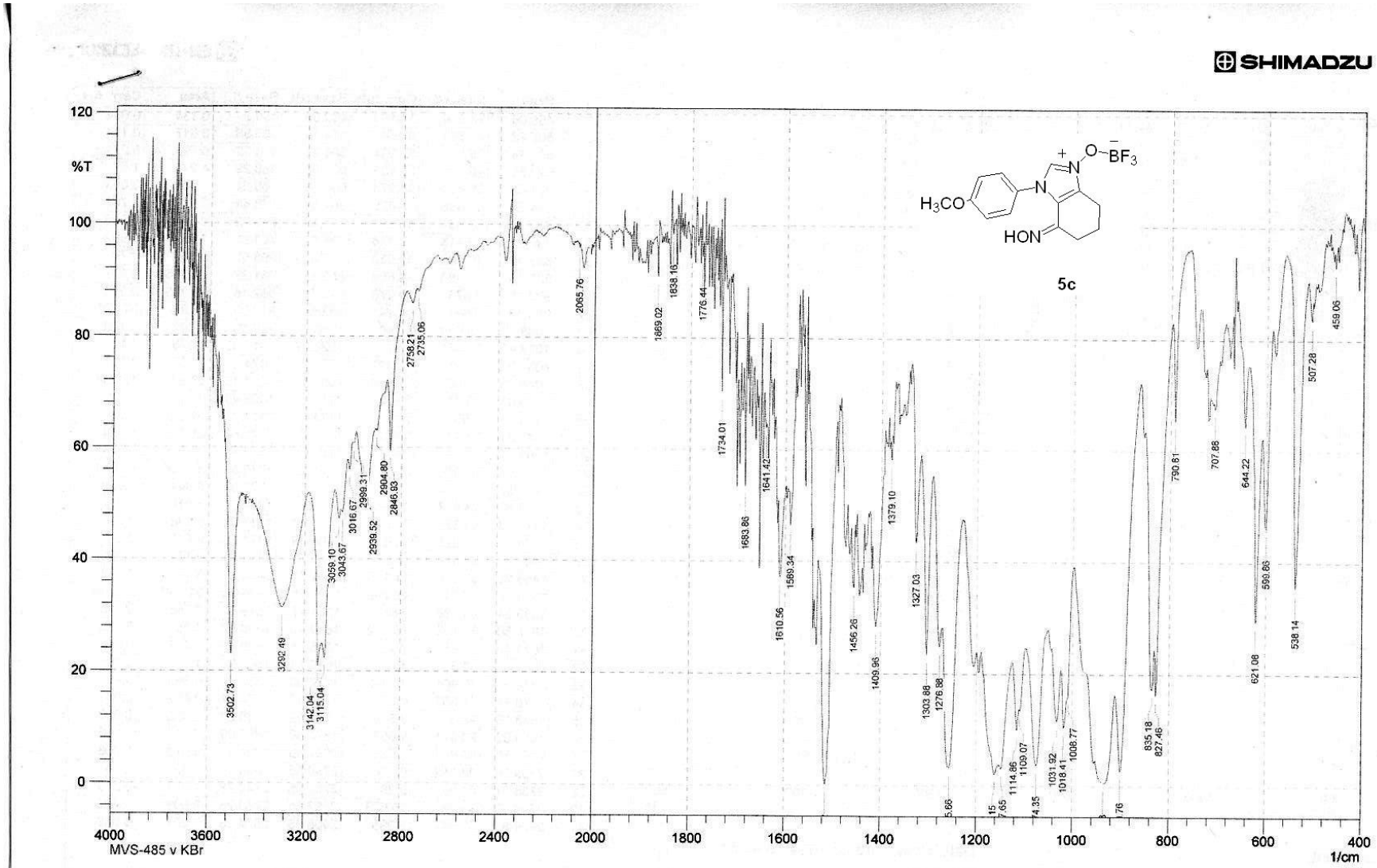
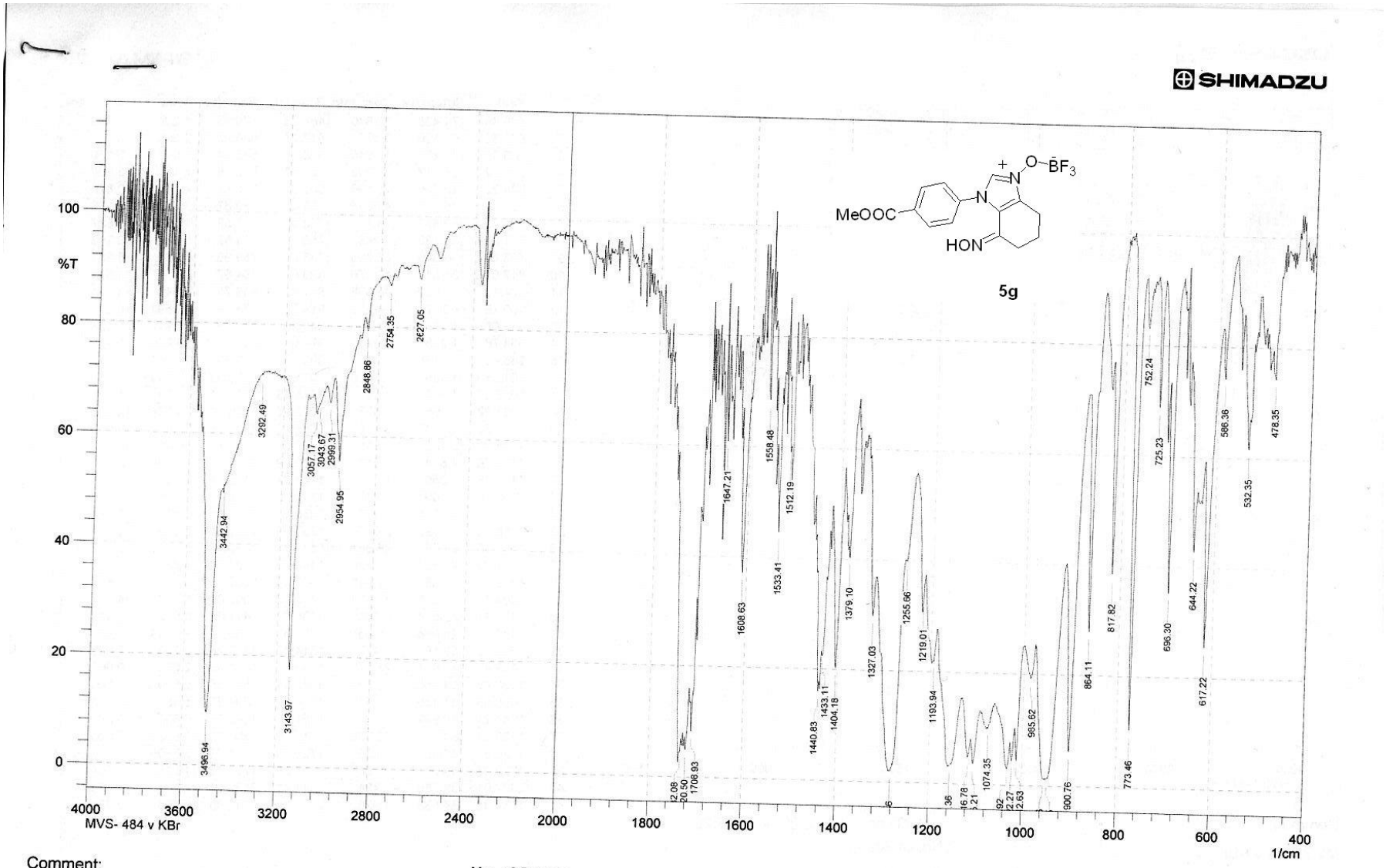
Comment;
MVS- 479 v KBr
No. of Scans;
Resolution;
Date/Time; 14.02.2014 14:26:38
User; Krasitel



Comment;
MVS-485 v KBr

No. of Scans;
Resolution;

Date/Time; 13.02.2014 18:41:54
User; Krasitel

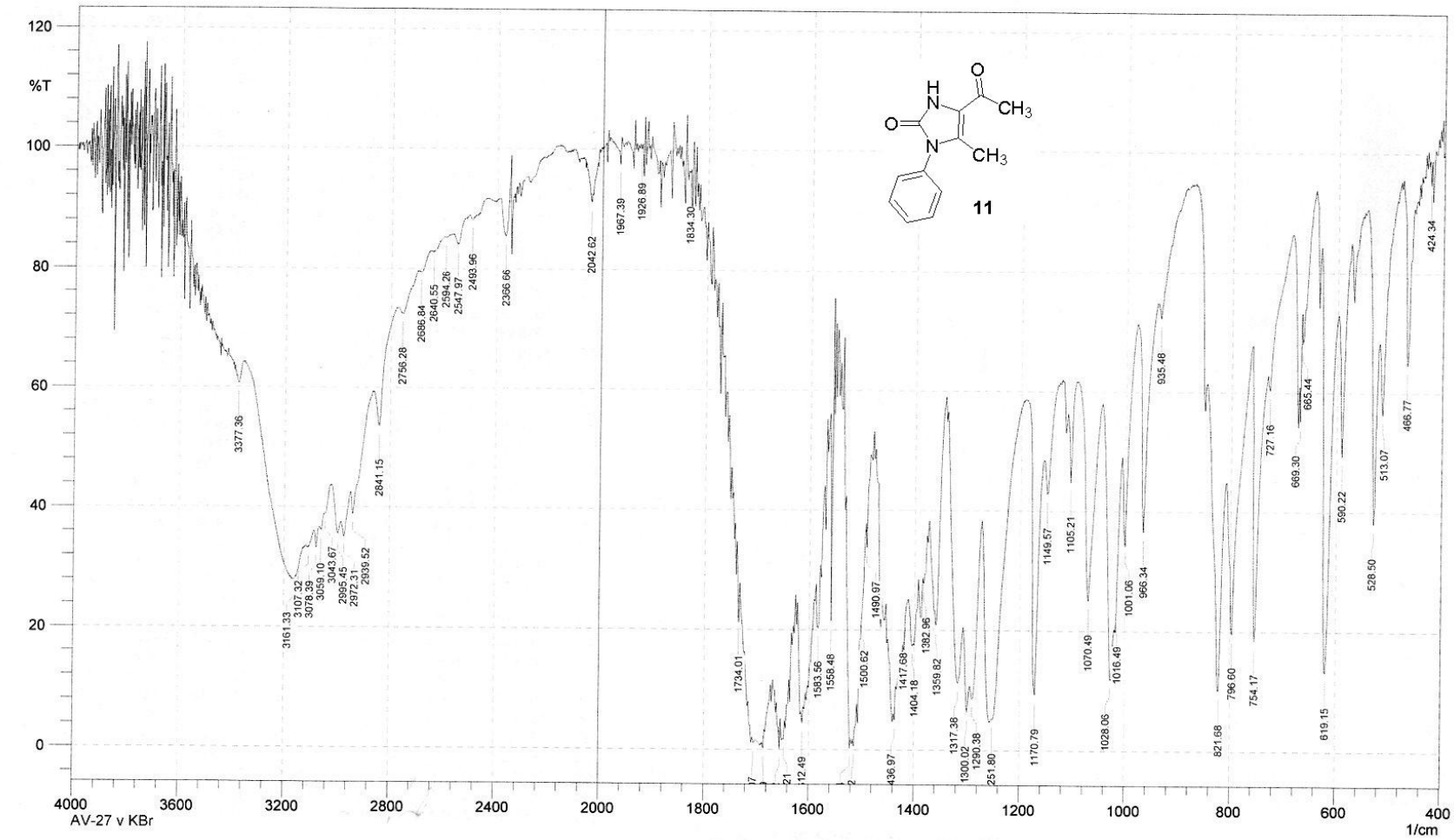


Comment;
MVS- 484 v KBr

No. of Scans;
Resolution;

Date/Time; 17.02.2014 17:15:26
User; Krasitel

SHIMADZU



Comment;
AV-27 v KBr

No. of Scans;
Resolution;

Date/Time; 13.02.2014 20:35:14
User; Krasitel