Analysis and Characterization of Designer Tryptamines using Electrospray Ionization Mass Spectrometry (ESI-MS)

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ABSTRACT: The analysis and characterization of 12 "designer" tryptamines by electrospray ionization mass spectrometry (ESI-MS) are presented. Molecular weights were confirmed based on the experimental observation of protonated and deprotonated pseudo-molecular ions in the positive and negative ion modes, respectively. Standard tandem mass spectrometry (MS^2) experiments were also performed, and the results provided for the characterization of various fragmentation signatures, useful for the future analysis of currently unknown, similar compounds. The fragmentation spectra obtained from collision-induced dissociation (CID) experiments (35 eV) were also compiled as part of an in-house mass spectral library. Results from selected MS^3 experiments are presented and their use in structural elucidation is discussed. For comparison, the gas chromatography/mass spectrometry (GC/MS) data for the tryptamines are also included and discussed.

KEYWORDS: Tryptamines, Analogues, Designer Drugs, Electrospray Ionization-Mass Spectrometry, ESI-MS, Pseudo-molecular Ion, Fragmentation, Tandem Mass Spectrometry, Collision-Induced Dissociation, GC/MS, Forensic Chemistry.

Introduction

"Designer drugs" are compounds with structures that are very similar to controlled substances, but that are not specifically controlled. Also known as "analogues," most of these compounds have never been previously encountered or characterized, and so are not present in commercial spectral libraries; therefore, they can represent unusual challenges for forensic laboratories. Definitive identification of such drugs usually requires in-depth analysis using multiple and complementary techniques, including infrared spectroscopy (IR), gas chromatography/mass spectrometry (GC/MS), and nuclear magnetic resonance (NMR).

For decades, the use of electron ionization (EI) mass spectrometry as a detector for gas chromatography (GC) instruments has been a main step in the structure elucidation process used by analytical and synthetic chemists [1]. Electron ionization mass spectra of many thousands of compounds, normally collected under 70 eV of energy, are readily available from reference databases [2] and instrument manufacturers [3]. The capabilities of mass spectrometry, however, have greatly expanded with the more recent development of specialized ionization techniques like electrospray ionization (ESI) [4] and atmospheric pressure chemical ionization (APCI) [5], making possible the analysis of many polar and thermally labile compounds that were not amenable to GC/MS analyses. Through the ESI process, ions in solution are transported into the gas phase by a series of solvent evaporation and Coulomb explosion steps, preserving the original intact ions and introducing them into the

vacuum-housed mass analyzer without significant fragmentation. As a result, this process produces singly and/or multiply charged ions which, upon mass spectrometric analysis, provide direct molecular weight information - a critical step in identification.

In addition, the interface of an ESI source to an ion-trap mass spectrometer provides for not only molecular weight determinations, but also for tandem and MS^n fragmentation analysis of intact gas-phase ions via collision-induced dissociation (CID) experiments using a target gas [5]. By performing these experiments under controlled conditions, further structural elucidation can be accomplished, and the additional spectra generated can be collected and stored as part of a laboratory-generated library.

Certain synthetic tryptamines produce hallucinogenic effects in humans [6,7]. These properties can be expected based on the structural similarities between these tryptamines and some naturally occurring hallucinogenic tryptamines such as psilocybin, psilocin, dimethyltryptamine, bufotenine, and ibogaine. By slightly modifying the structures of these latter substances, synthetic chemists have developed novel "designer" tryptamines with very similar, new, modified, unusual, and/or otherwise desirable psychedelic properties. Synthetic details for the preparation of some designer tryptamines have been available to the public for many years [8]. However, the scientific literature provides only very limited information regarding their analysis and characterization [9-13]. Most of the available literature focuses on the extraction of the naturally available tryptamines from their source [14], or the analysis and detection of their metabolites in animal biological fluids [15-18].

This paper presents the analysis of various designer tryptamines using ESI-MS. Figure 1 illustrates the core structure of a tryptamine-type molecule, while Table 1 lists the 12 compounds investigated in this work, along with details of their structure. Some of these compounds were recently acquired during a law enforcement investigation targeting their open sale on the internet. Initially, these compounds were identified at this laboratory using IR and NMR spectroscopy, GC, and GC/MS techniques. Analysis by ESI-MS provides complementary information that is valuable for the full characterization of these compounds. For most of the compounds, the generation of pseudo-molecular ions via ESI provides molecular weight information that is not available via GC/MS analysis. MS^n fragmentation experiments further complement the structural information obtained from GC/MS, and allow the additional characterization of thermally labile compounds.

Experimental

Solutions for each of the analogues were prepared by dissolving the appropriate amount in methanol to obtain a final concentration of approximately 10 μg/mL. Solutions were introduced into the mass spectrometer using a ThermoFinnigan Surveyor autosampler. Sample injections (10 μL) were loaded into a methanol constant flow (200 μL/min) provided by a ThermoFinnigan Surveyor solvent pump.

Mass spectra were collected using a ThermoFinnigan LCQ Advantage MAX ion-trap mass spectrometer equipped with an ESI source and operated using the Xcalibur software (Version 1.4) provided by the manufacturer. The ESI voltage needle was kept at 5.0 kV, generating a spray current of approximately 0.3 μA. The sheath and auxiliary sweep gas flows (nitrogen) were operated at 40 and 10 units, respectively. Conditions inside the source were as follows: Capillary temperature 300 ^{O}C; capillary voltage ±30 V; and tube lens voltage ±15 V. Negative and positive mass spectra were collected in the centroid mode for the *m/z* range of 50 to 550. Each scan collected was composed of three microscans using a maximum ion injection time of 50 milliseconds. During ion storage, the trap was operated with the automatic gain control (AGC) set point at 5×10^7 ions and Helium (99.999% purity) was used as the trapping gas. After sequential ejection from the trap, ions were detected using a conversion dynode (±14.7 kV) and electron multiplier (-750 V) assembly. The pressure within the mass analyzer region was kept at 6.7×10^{-6} Torr by using a turbomolecular pump. MS^n experiments were performed by isolating the desired precursor ions using an isolation window of 3.0 *m/z* units. The isolated ions were then subjected to normalized collision energies between 25 and 35 eV (%) in order to generate characteristic fragmentation.

Helium (99.999% purity) was used as the collision gas, and ions were activated during 30 milliseconds using an activation q value of 0.25.

Experimental data were analyzed using the qualitative analysis program provided within the Xcalibur software suite. In addition, all MS^2 fragmentation data were incorporated into an in-house spectral library.

For the GC/MS data (displayed in the Appendices), solutions of the 12 analogues were prepared in methanol at a concentration of 1 mg/mL. Samples were introduced into the gas chromatograph using 1.0 μL injections. The GC oven program used was: initial temperature: 90 ^{O}C (1 minute hold), ramp to 300 ^{O}C (20 ^{O}C/minute); final temperature: 300 ^{O}C (5 minute hold). Helium was used as the carrier gas at a constant flow of 1 mL/minute. Mass spectra were obtained using a ThermoFinnigan PolarisQ ion-trap mass spectrometer controlled by the Xcalibur software.

Results and Discussion

ESI-MS Experiments

Figures 2a and 2b present the positive and negative ion mode full-scan electrospray mass spectra obtained for 4-acetoxy-*N,N*-diisopropyltryptamine (**9**). The singly protonated and singly deprotonated pseudo-molecular ions are clearly represented at *m/z* 303 and 301, respectively, indicating a molecular weight of 302 for this compound. Similar spectra were obtained for the other 11 analogues. The molecular weights determined from all of these experiments are included in Table 1. Under the experimental conditions utilized, the signal intensity for the negative ion spectra was observed to be somewhat dependent on the structure of the compounds, specifically the presence of methoxy, acetoxy, or hydroxy groups. Molecules containing such functionalities were observed to produce more intense deprotonated pseudo-molecular ions.

Full-scan electrospray analysis was especially useful for the identification and differentiation of 4-hydroxy-*N,N*-diisopropyltryptamine (**7**) and 4-acetoxy-*N,N*-diisopropyltryptamine (**9**). The latter compound is thermally unstable, and standard GC/MS analyses gave highly similar spectra (see Appendices). However, ESI-MS provided accurate molecular weight information, allowing a easy identification.

ESI-MS^2 Experiments

In addition to collecting full-scan ESI spectra for these molecules, ESI-MS/MS (ESI-MS^2) fragmentation experiments were also performed in order to obtain structural information that would complement the information previously obtained via GC/MS experiments. ESI-MS^2 fragmentation experiments were performed in the positive ion mode at various normalized collision energies. The spectra generated at 35 eV were considered to be the most useful, and so were exported and compiled into an in-house library for future use in the identification of unknowns.

The Appendices contain the ESI-MS^2 spectra obtained for each of the tryptamines investigated using a normalized collision energy of 35 eV (top panels) . After isolation of the singly protonated pseudo-molecular or parent species, the ions were subjected to collisions with the target gas Helium, producing fragments that partially characterize the original molecule. For all the tryptamines investigated, major fragments observed correspond to two types of dissociations, both due to cleavages on the aliphatic side chain of the molecule. The first cleavage is between the nitrogen and the *alpha* carbon, with the second cleavage occurring between the *alpha* and *beta* carbons (see Figure 1). The former process results in the production of ammonia or a neutral primary or secondary amine (depending on the amine substituents), with the charge being transferred to the indole-containing fragment. The latter fragmentation process produces a charged amine, along with a neutral indole-containing fragment. Both of these fragmentation processes are illustrated in Figure 3 for the case of 5-methoxy-*N,N*-methylisopropyltryptamine (**11**).

For compounds with the same molecular weights, the fragmentation patterns obtained from the ESI-MS^2 experiments were useful for elucidating structures. For example, 4-acetoxy-*N,N*-methylisopropyltryptamine (**8**) and 5-methoxy-*N,N*-diisopropyltryptamine (**10**) have the same molecular weight of 274. In both cases, the protonated and deprotonated pseudo-molecular ions are observed at *m/z* 275 and 273, respectively, not allowing for their distinction. However, ESI-MS^2 analysis produced different fragmentation patterns for these compounds (see Appendices 8 and 10). For 4-acetoxy-*N,N*-methylisopropyltryptamine (**8**), the major fragment is observed at *m/z* 202, with additional fragments at *m/z* 160 and 86. Whereas for 5-methoxy-*N,N*-diisopropyl-tryptamine (**10**), the major fragment is observed at *m/z* 114, with additional fragments at *m/z* 102 and 174.

The usefulness of ESI-MS^2 analyses can also be illustrated by again comparing 4-hydroxy-*N,N*-diisopropyl-tryptamine (**7**) and 4-acetoxy-*N,N*-diisopropyltryptamine (**9**). As mentioned before, these compounds are virtually undistinguishable by GC/MS analysis, due to the thermal instability of the 4-acetoxy group. In addition to providing direct molecular weight information, ESI-MS^2 analysis produces distinctive fragments that allow their specific characterization. For 4-acetoxy-*N,N*-diisopropyltryptamine (**9**), fragments are produced at *m/z* 202, 160, 114, and 102. Whereas for 4-hydroxy-*N,N*-diisopropyltryptamine (**7**), fragments are produced at *m/z* 160, 114, and 102. While the fragment at *m/z* 202 is the predominant fragment produced from the former compound, it is absent from the latter, providing a marker ion for differentiation.

GC/MS Experiments

The Appendices also include the standard EI spectra obtained using a GC/MS system (bottom panels). Not surprisingly, most of the spectra are characterized by the presence of one major peak (base peak) corresponding to fragmentation of the *sigma* bond between the *alpha* and *beta* carbons. For 10 of the compounds (tryptamines 2 - 11), *alpha* cleavage [19] results in retention of the charge by the amine group. For *alpha*-methyltryptamine (**1**) and 5-methoxy-*alpha*-methyltryptamine (**12**), the most favorable fragmentation, inductive cleavage [19], results in charge migration to the indole-containing fragment, producing peaks at *m/z* 130 and 160, respectively. An additional hydrogen rearrangement process is also involved, resulting in major peaks at *m/z* 131 and 161, respectively. GC/MS experiments also produce characteristic signatures for the different amine substituents. For example, *m/z* 86 is characteristic of the *N,N*-methylisopropyl and *N,N*-diethyl groups, while *m/z* 114 is characteristic of the *N,N*-dipropyl or *N,N*-diisopropyl functionalities. For these two latter isomeric species, the additional presence of ions at *m/z* 72 and 86, respectively, provides a useful distinguishing factor.

Additional bond cleavages in the tryptamine molecule result in the generation of specific fragmentation signatures. These can be of great use when interpreting data generated by either GC/MS or ESI-MS^2 techniques. For example, the presence of an ion at *m/z* 144 is indicative of a non-substituted indole moiety, after cleavage of the *sigma* bond between the amine nitrogen and the *alpha* carbon. The same type of cleavage leads to the generation of peaks at *m/z* 174 and 202 for compounds where the indole contains a methoxy or acetoxy functionality, respectively. As previously mentioned, cleavage between the *alpha* and *beta* carbons produces a high-intensity peak at *m/z* 86, due to the generation of the $C_4H_{10}{}^+N{=}CH_2$ fragment, which can be produced from the diethylamine or methylisopropylamine group. Through the same process, the generation of *m/z* 114 is indicative of the $C_6H_{14}{}^+N{=}CH_2$ fragment, consistent with either dipropylamine or diisopropylamine. For dimethyltrypamine compounds, the analogous peak will appear at *m/z* 58 due to $C_2H_6{}^+N{=}CH_2$. As observed for *alpha*-methyltryptamine (**1**) and 5-methoxy-*alpha*-methyltryptamine (**12**), cleavage between the *alpha* and *beta* carbons also produces signature ions at *m/z* 130 and 160, characteristic of an unsubstituted and a methoxy-substituted indole, respectively.

ESI-MS^n Experiments

The use of ESI combined with a quadrupole ion trap as the mass analyzer provides the enhanced capabilities of MS^n experiments. To illustrate the usefulness of this type of analysis, ESI-MS^3 experiments were performed on *N,N*-dipropyltryptamine (**5**) and *N,N*-diisopropyltryptamine (**6**). As illustrated in the Appendices, the fragments

generated during MS^2 analysis do not allow for the unambiguous differentiation of these two compounds, although the presence of *m/z* 86 (5 % intensity) for *N,N*-dipropyltryptamine (**5**) does suggests that they are in fact different. By isolation and fragmentation of the singly protonated pseudo-molecular ions at *m/z* 245 using a collision energy of 25 eV (%), major ions at *m/z* 144 and 114 are generated for both compounds. However, further isolation and fragmentation of the *m/z* 114 ion, using a collision energy of 30 eV, leads to significantly different MS^3 spectra (see Figures 4 and 5). Fragmentation of the *m/z* 114 ion produces a fragment at *m/z* 86 for *N,N*-dipropyltryptamine and a fragment at *m/z* 72 for *N,N*-diisopropyltryptamine. These ions correspond to the loss of the neutral fragments $CH_2{=}CH_2$ and $CH_2{=}CHCH_3$, respectively. These losses are characteristics of the dipropyl and diisopropyl groups, respectively, providing a tool for differentiation. In fact, further fragmentation (MS^4) of the *m/z* 86 ion, produced from the fragmentation of *N,N*-dipropyltryptamine, generates a peak at *m/z* 58, consistent with the loss of a second $CH_2{=}CH_2$ molecule from the remaining dipropyl chain (data not shown). Similar MS^4 analysis of the *m/z* 72 ion from *N,N*-diisopropyltryptamine would produce additional information regarding the second diisopropyl group; however, the additional loss of 42 would produce an ion at *m/z* 30, which is below the observable low-mass limit of 50 for this instrument. These ESI-MS^3 results are in agreement with the GC/MS data obtained for *N,N*-dipropyltryptamine and *N,N*-diisopropyltryptamine, where the presence of *m/z* 86 and 72 is a basis for differentiation.

The complementary value of the GC/MS and ESI-MS data can be better illustrated using *alpha*-methyltryptamine (**1**). The GC/MS spectrum does not provide molecular weight information, but it does indicate the presence of a non-substituted indole (*m/z* 130), with the presence of a phenyl group further confirmed by *m/z* 77. Although the ion at *m/z* 44 is indicative of C_2H_6N, no confirmation of the $-NH_2$ group is obtained. By direct observation of the pseudo-molecular ion, the ESI-MS data provide a direct determination of molecular weight at 174. The ESI-MS^2 spectrum, while simple and only containing one major ion at *m/z* 158, provides a signature indicating the loss of ammonia from the protonated intact molecule, confirming the presence of a $-NH_2$ substituent.

Conclusions

The analysis of 12 tryptamine analogues using ESI-MS has been presented. Full scan analysis in the positive and negative ionization modes allowed the observation of singly protonated and singly deprotonated ions, providing molecular weight information. MS^2 experiments allowed the fragmentation of pseudo-molecular ions to be investigated under controlled experimental conditions, providing structural information for each one of the compounds, and making possible the observation of fragmentation signatures. Particularly useful was the generation of ESI full-scan and MS^2 spectra for the thermally-labile compound 4-acetoxy-*N,N*-diisopropyl-tryptamine, which provided a distinction from 4-hydroxy-*N,N*-diisopropyltryptamine. MS^3 experiments were also performed and results provided an additional technique for the differentiation of compounds with the same molecular weight and similar MS^2 spectra. The results presented are in agreement with those obtained using standard GC/MS techniques, and show the utility of ESI-MS as a complementary analytical technique that can be used in conjunction with GC/MS, NMR, and IR spectroscopy in the structural characterization of tryptamines.

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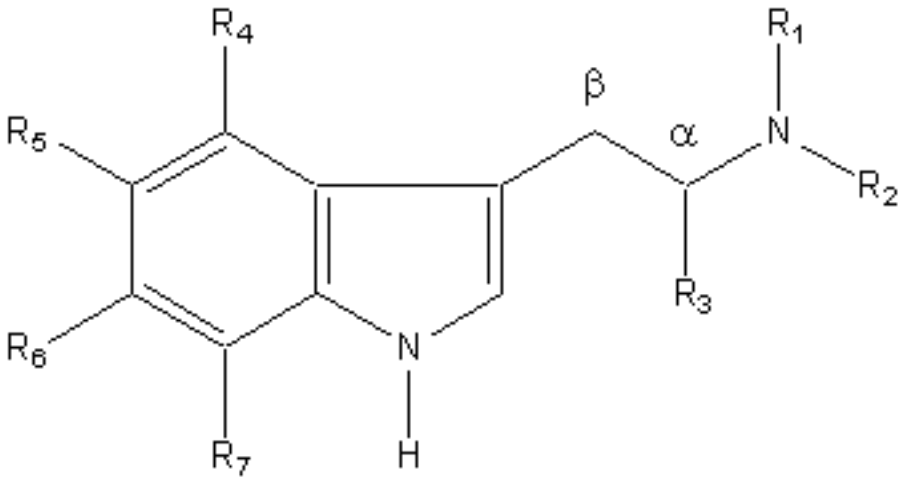
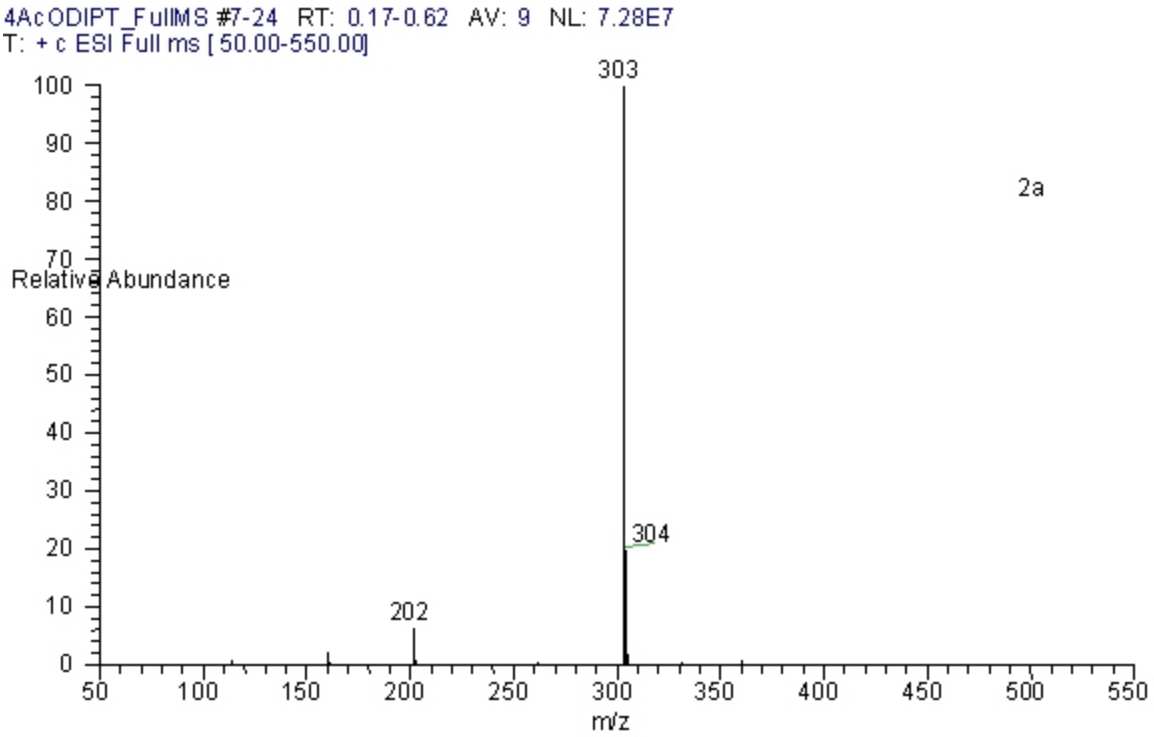


Figure 1. Core Structure of the Tryptamines

Table 1. Designer Tryptamines Investigated (Refer to Figure 1 for Substituent Positions).

No.	Compound	R1	R2	R3	R4	R5	MW
1	*alpha*-Methyltryptamine	H	H	-Me	H	H	174
2	*N,N*-Dimethyltryptamine	-Me	-Me	H	H	H	188
3	*N,N*-Diethyltryptamine	-Et	-Et	H	H	H	216
4	*N,N*-Methylisopropyltryptamine	-Me	-iPr	H	H	H	216
5	*N,N*-Dipropyltryptamine	-Pr	-Pr	H	H	H	244
6	*N,N*-Diisopropyltryptamine	-iPr	-iPr	H	H	H	244
7	4-Hydroxy-*N,N*-diisopropyltryptamine	-iPr	-iPr	H	-OH	H	260
8	4-Acetoxy-*N,N*-methylisopropyltryptamine	-Me	-iPr	H	-OAc	H	274
9	4-Acetoxy-*N,N*-diisopropyltryptamine	-iPr	-iPr	H	-OAc	H	302
10	5-Methoxy-*N,N*-diisopropyltryptamine	-iPr	-iPr	H	H	-OMe	274
11	5-Methoxy-*N,N*-methylisopropyltryptamine	-Me	-iPr	H	H	-OMe	246
12	5-Methoxy-*alpha*-methyltryptamine	H	H	-Me	H	-OMe	204



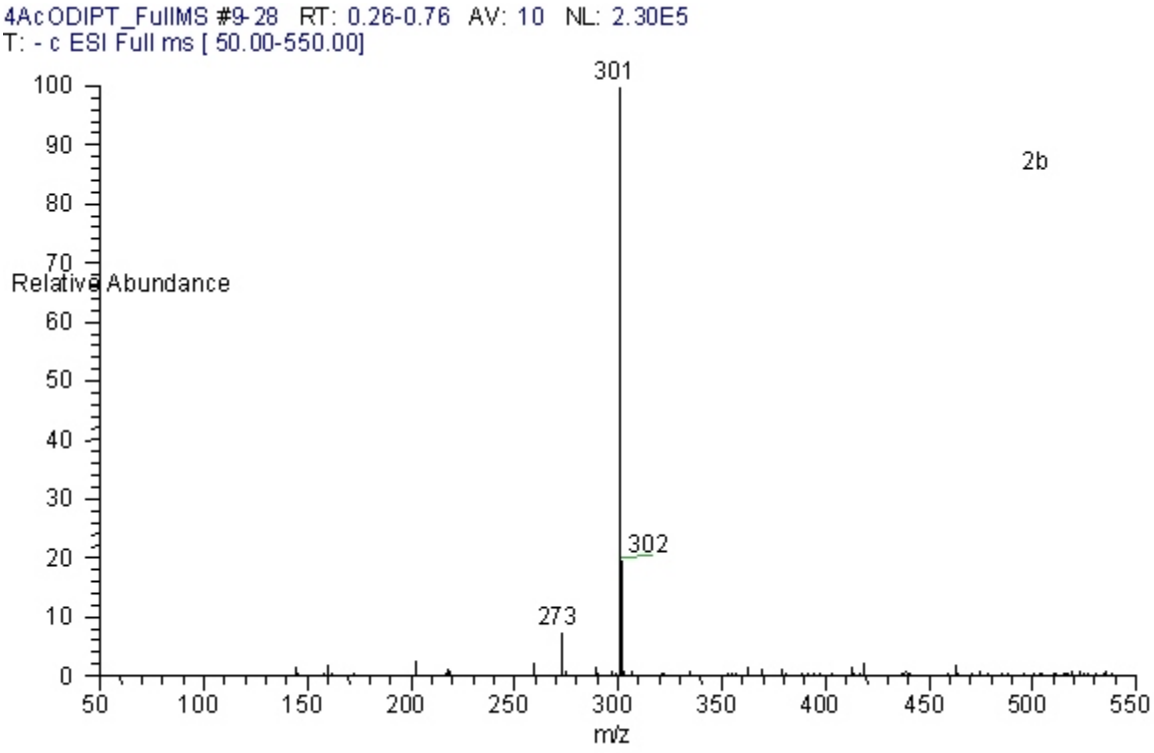


Figure 2. (a) Positive and (B) Negative Ion Mode Electrospray Ionization Mass Spectra for 4-Acetoxy-*N,N*-diisopropyltryptamine (**6**).

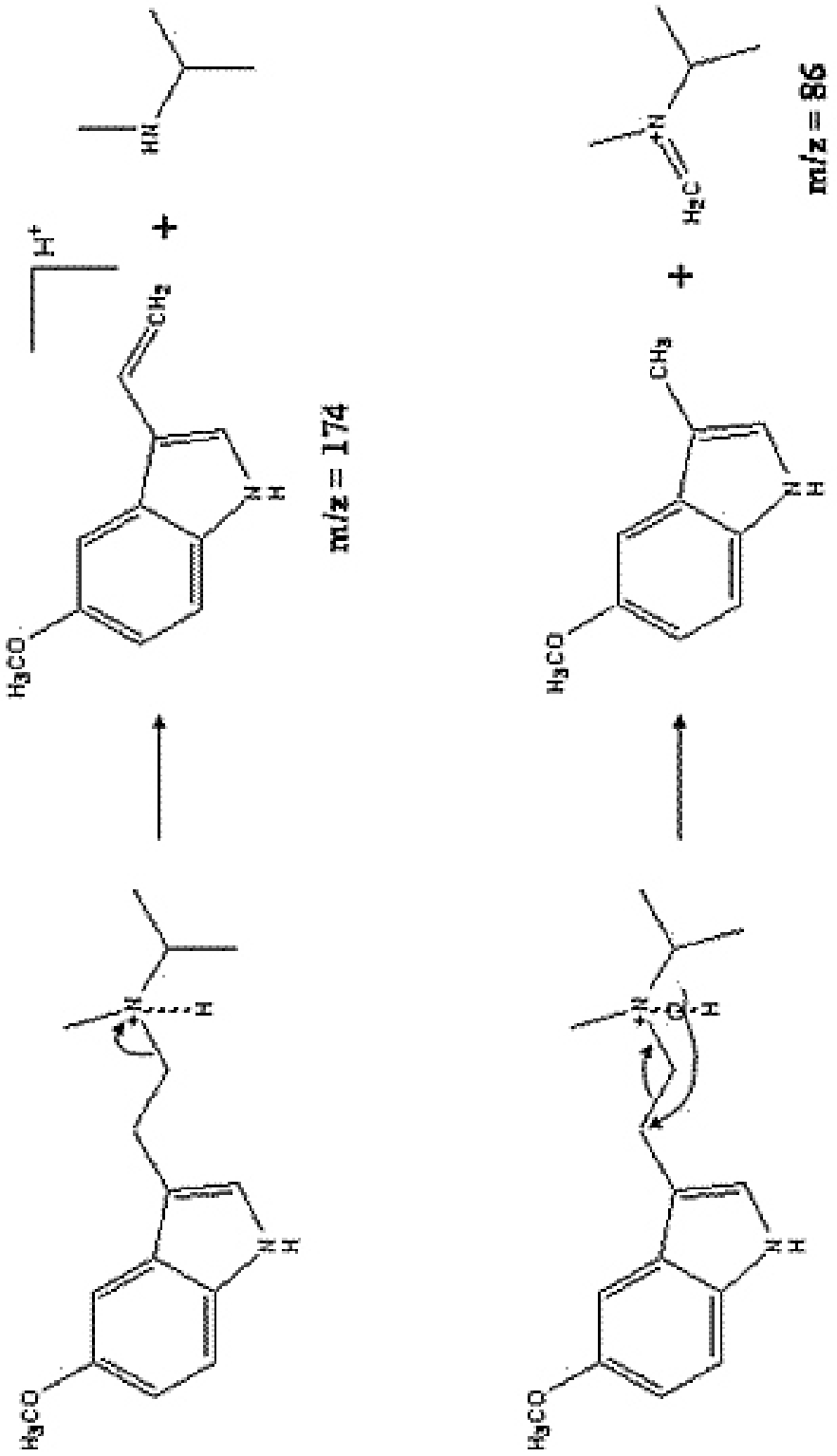


Figure 3. Chemical Diagram Illustrating the Two Main Fragmentation Processes Observed During the MS^2 Analysis of Tryptamines.

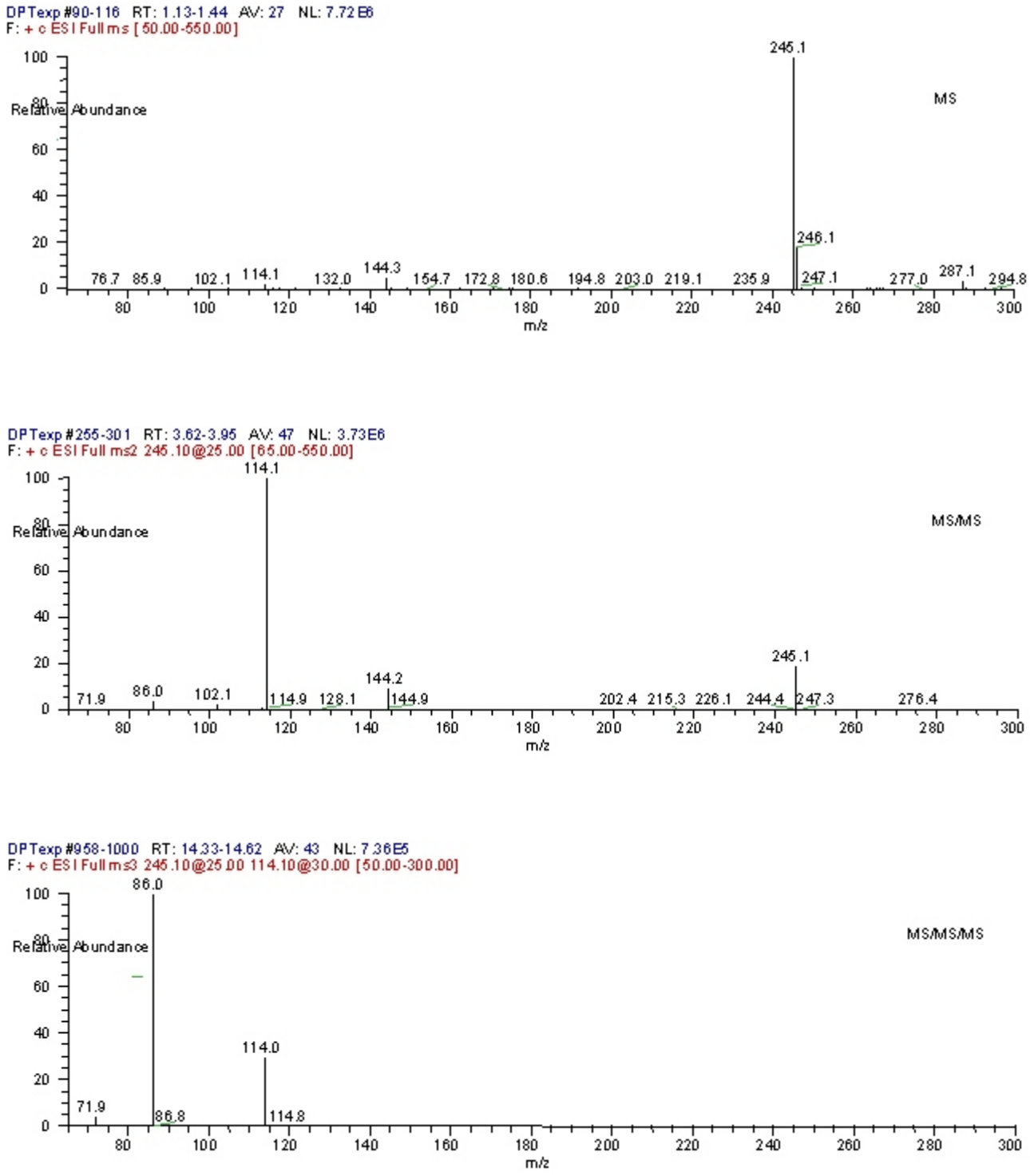


Figure 4. Full Mass, MS^2 and MS^3 Spectra Obtained for *N,N*-Dipropyltryptamine (**5**).

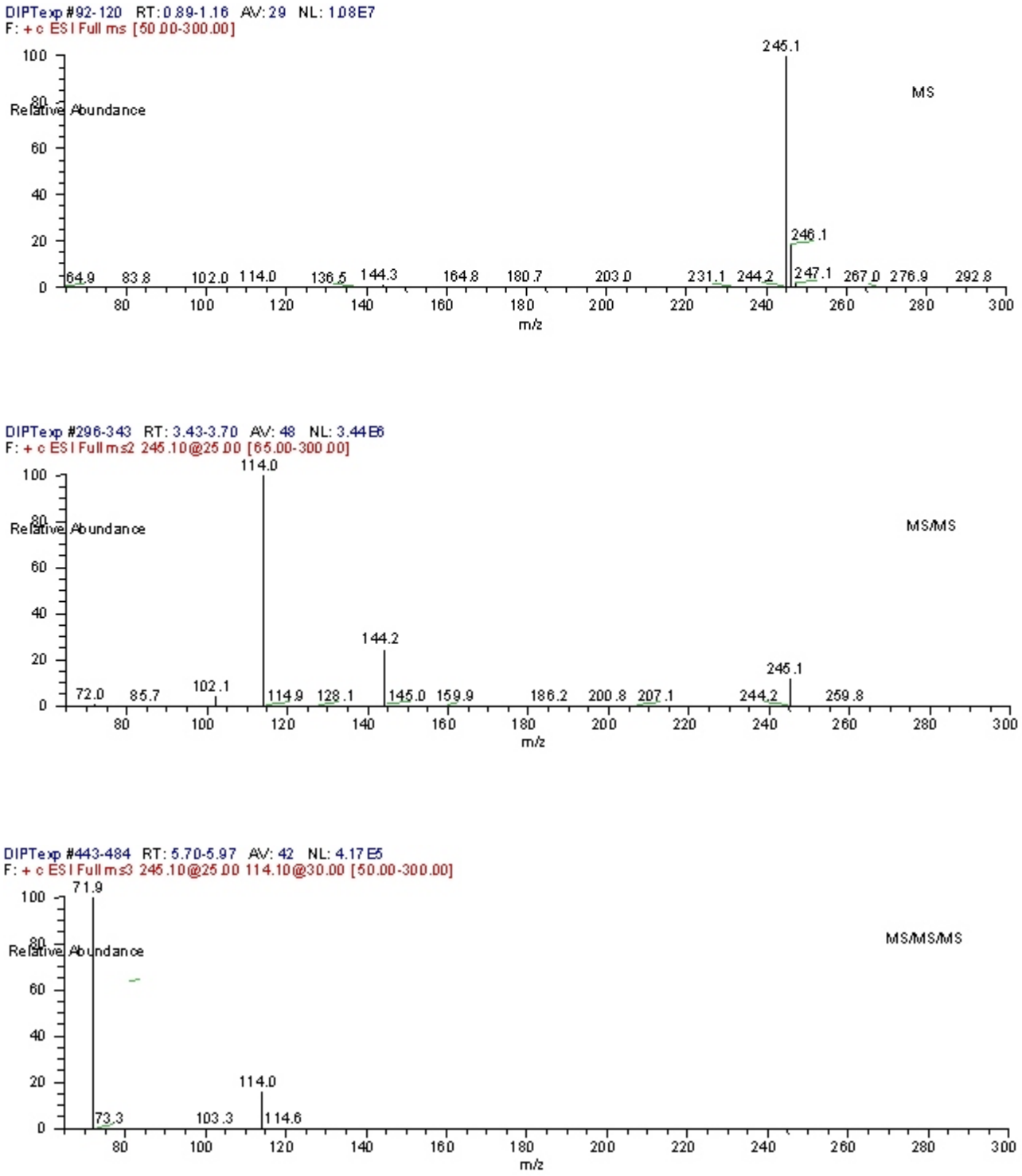
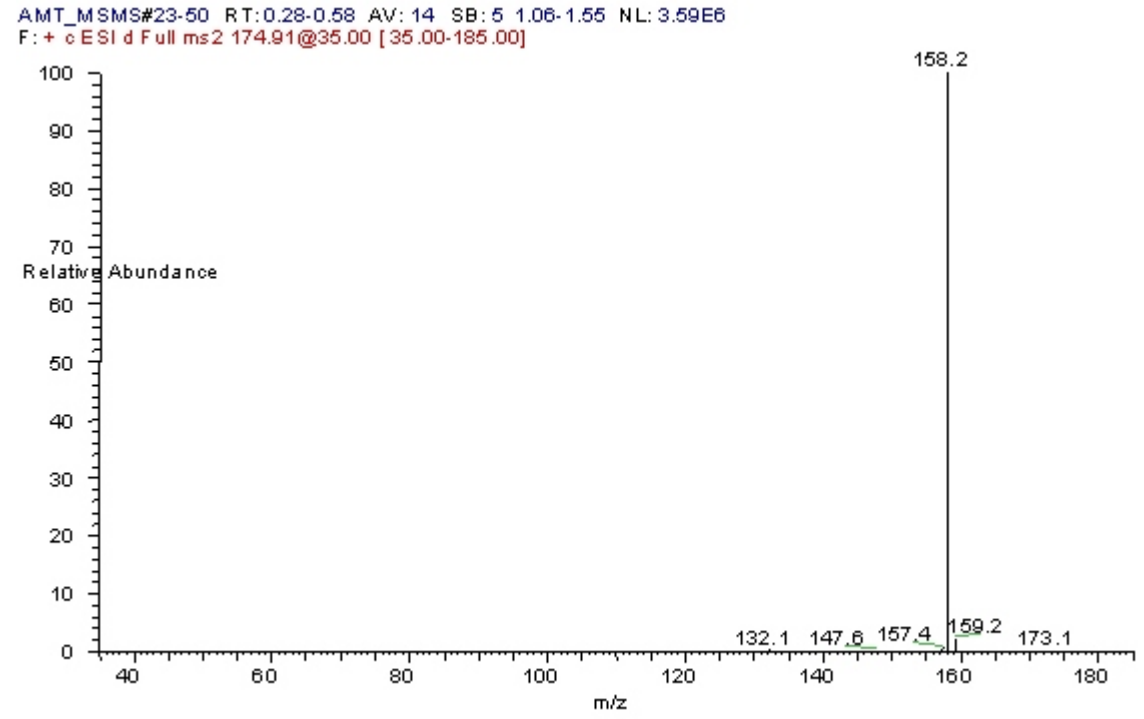
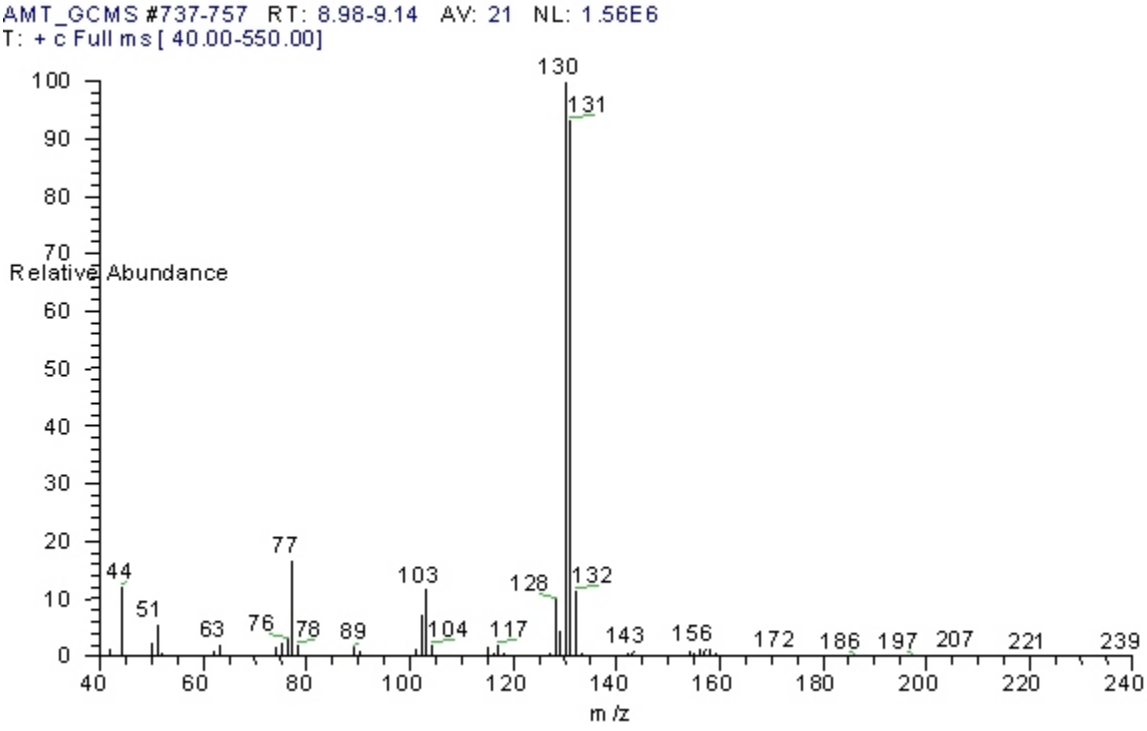
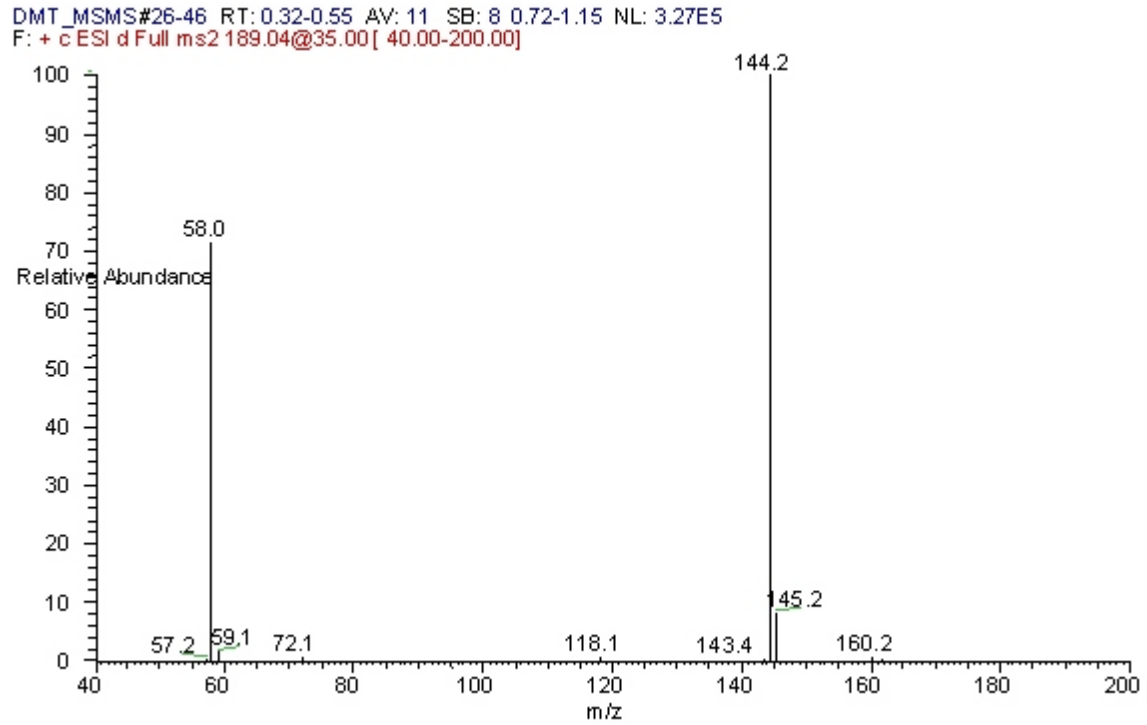


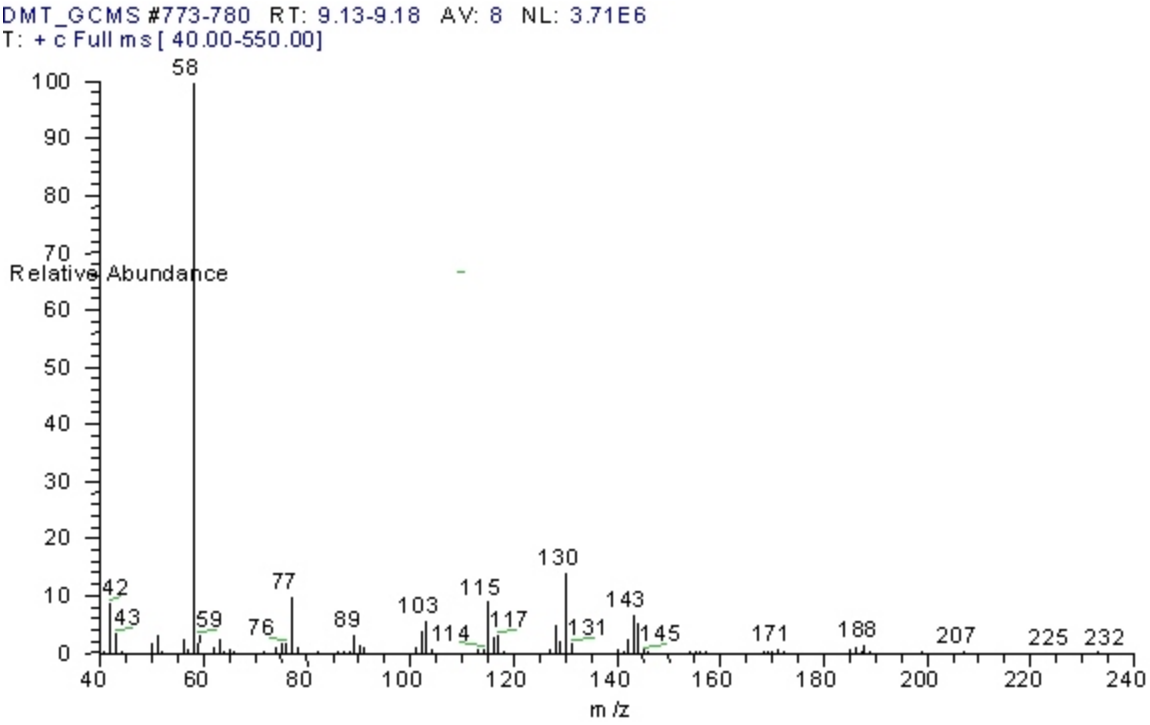
Figure 5. Full Mass, MS^2 and MS^3 Spectra Obtained for *N,N*-Diisopropyltryptamine (**6**).



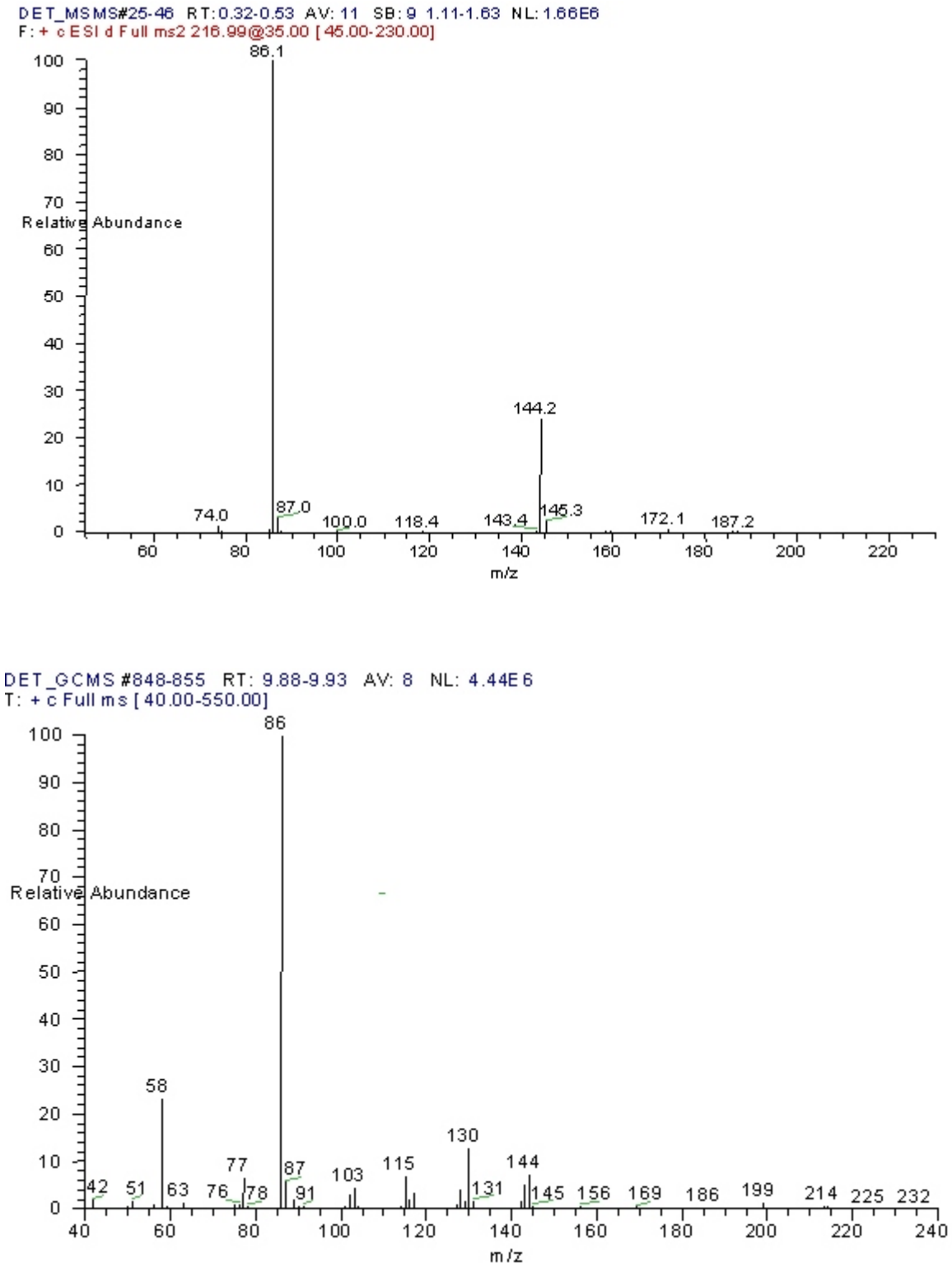


Appendix 1. *alpha*-Methyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).

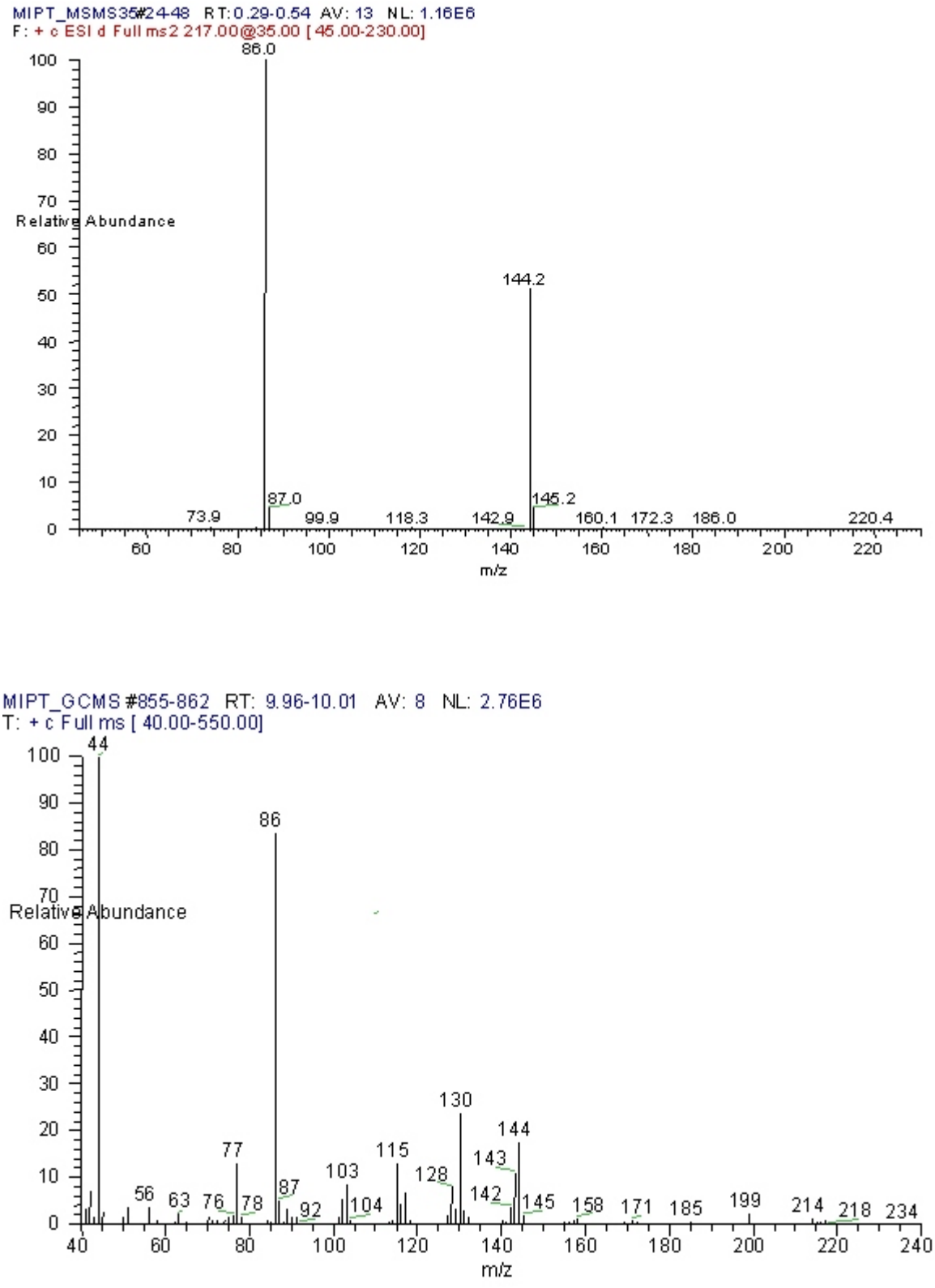




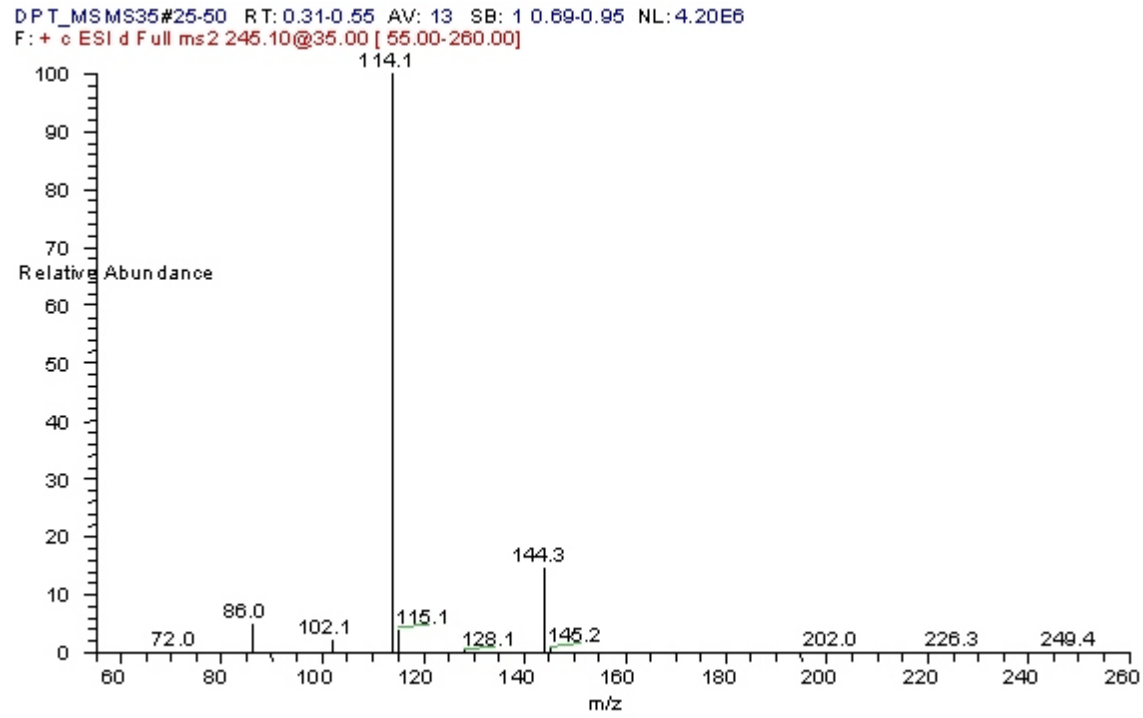
Appendix 2. *N,N*-Dimethyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).

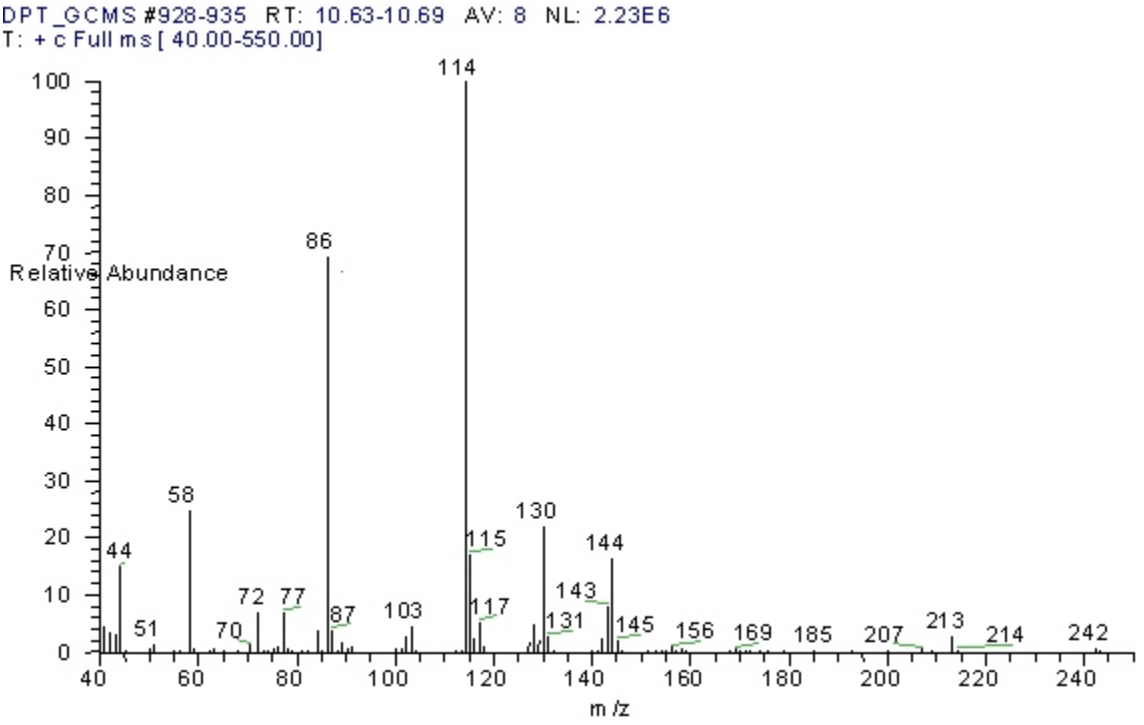


Appendix 3. *N,N*-Diethyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).

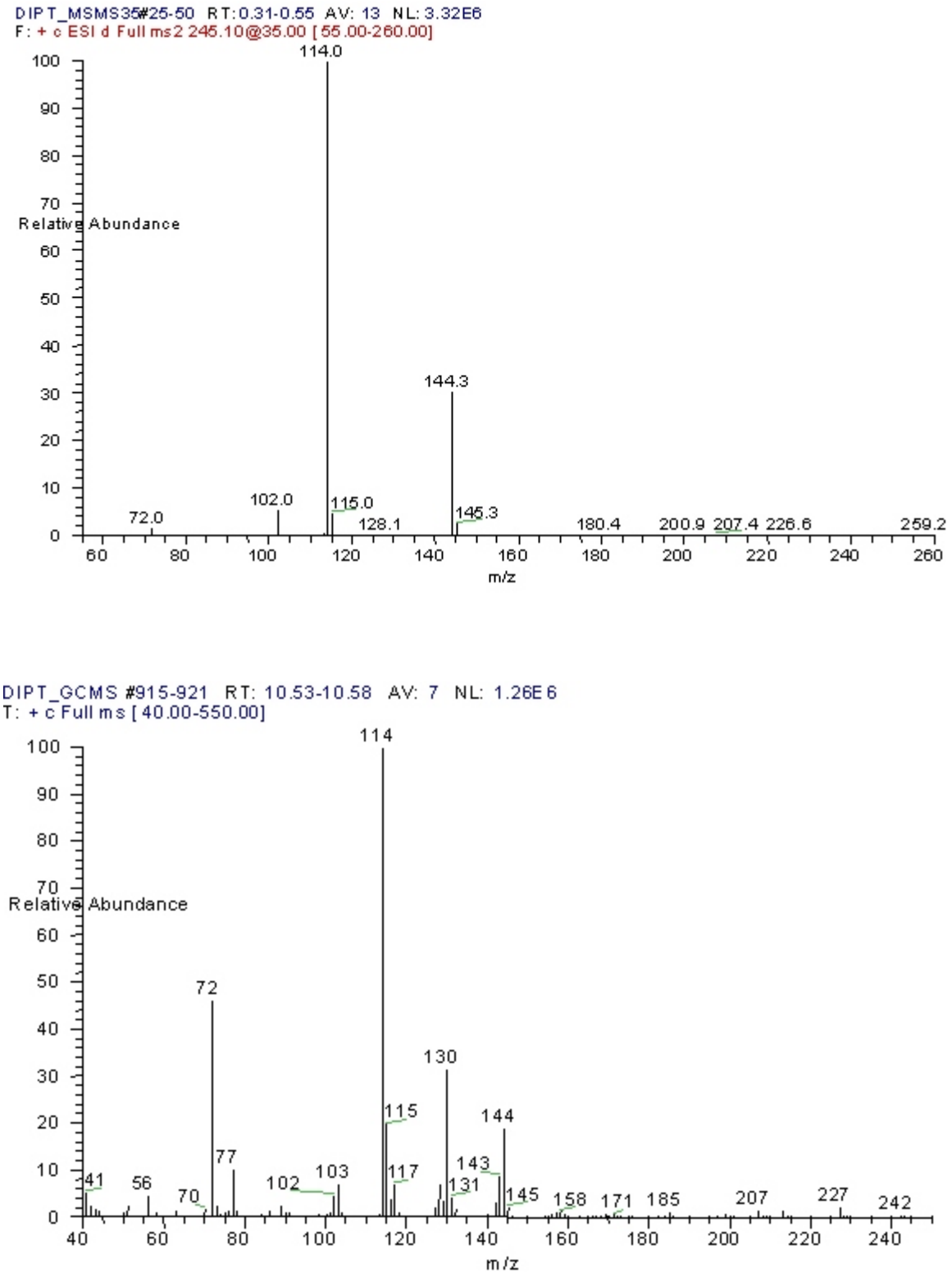


Appendix 4. *N,N*-Methylisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).

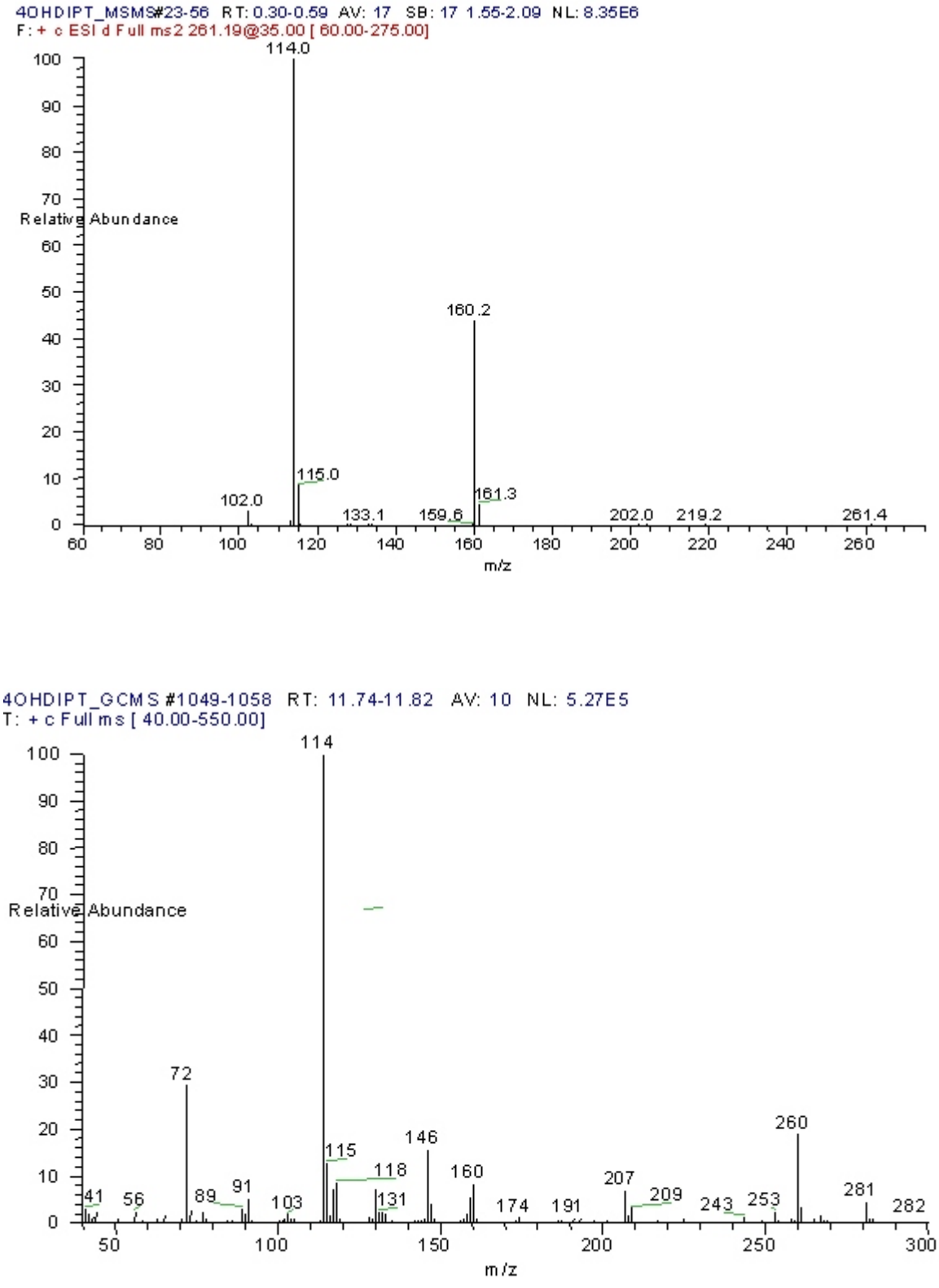




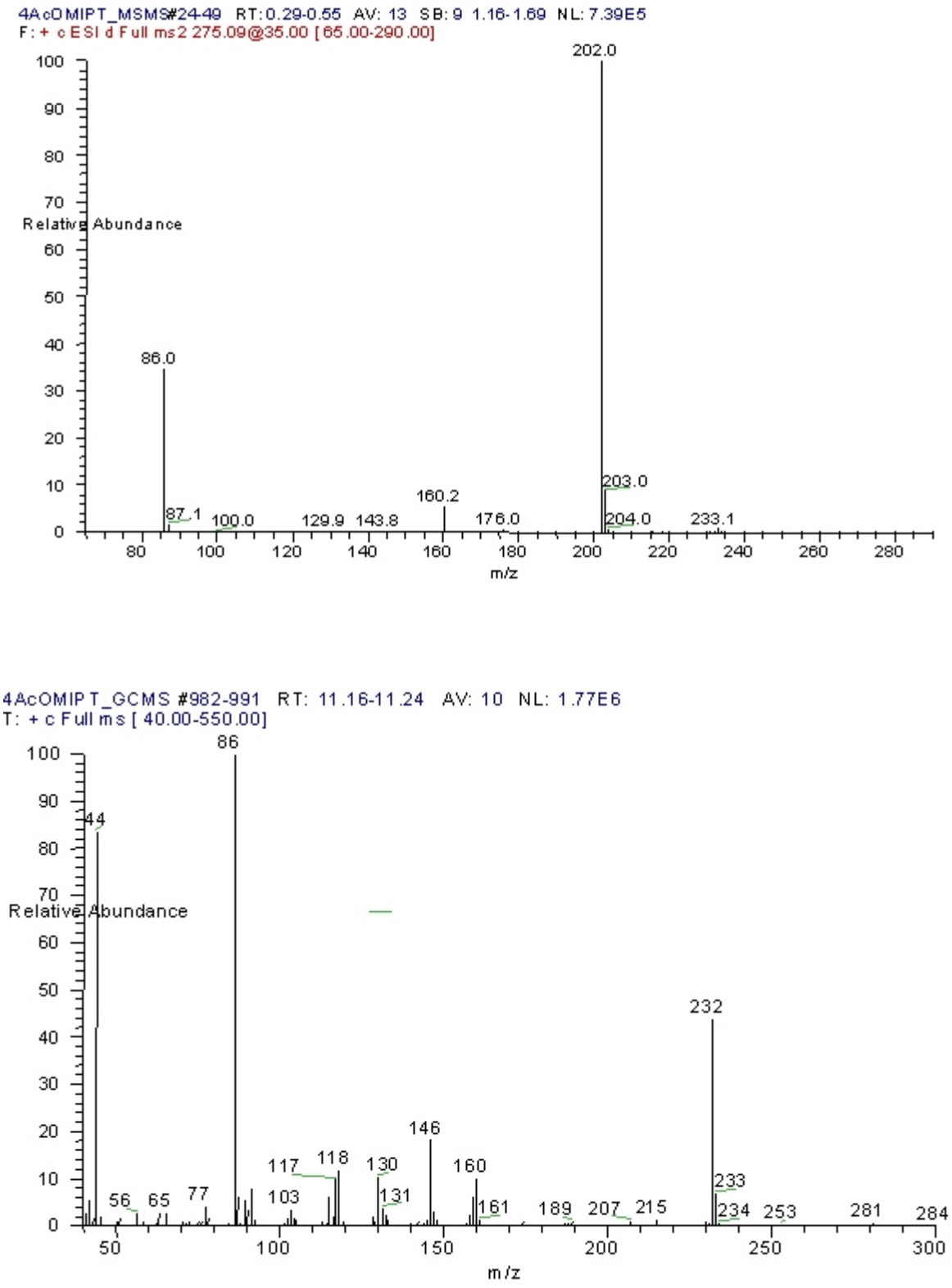
Appendix 5. *N,N*-Dipropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



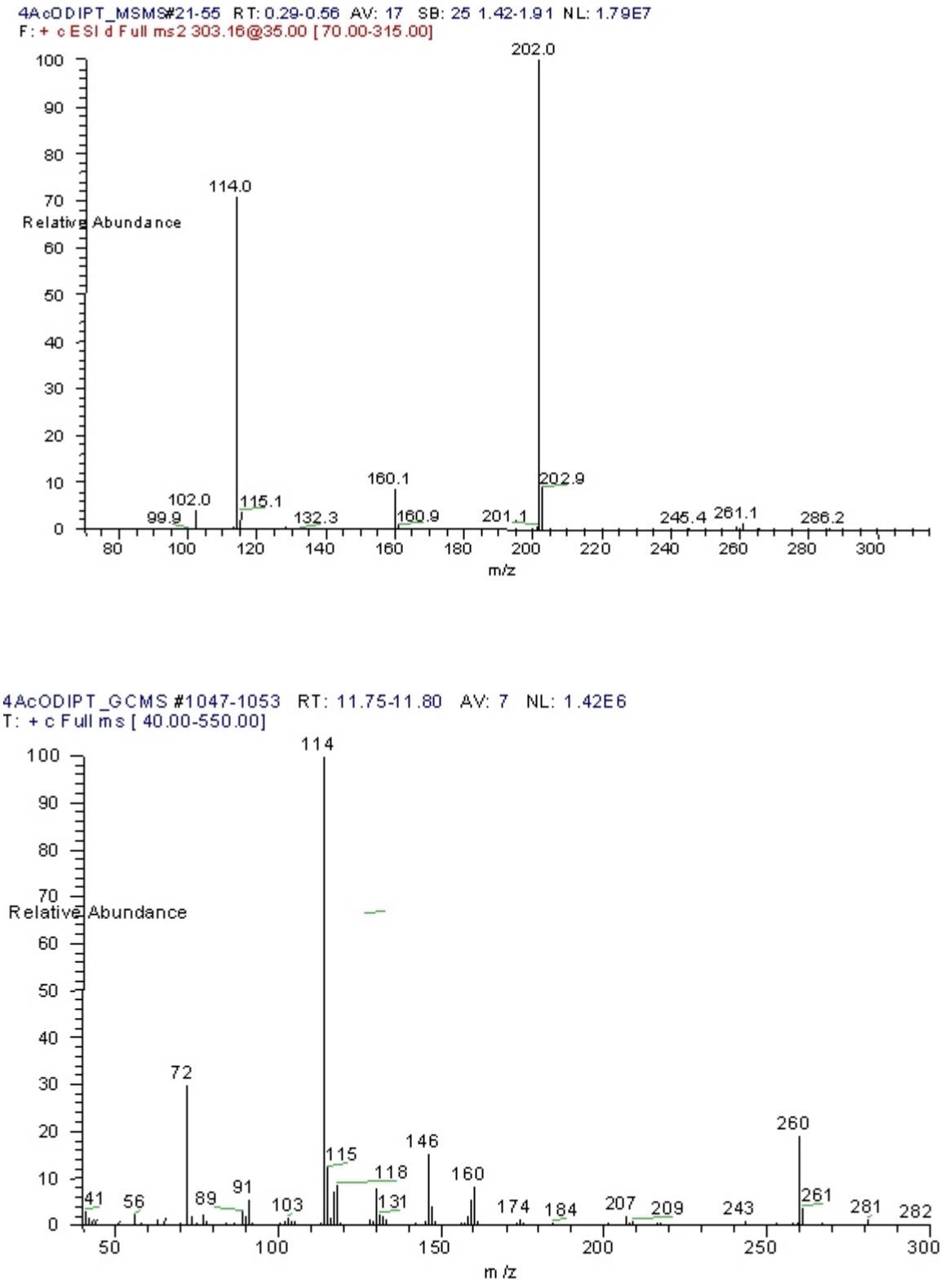
Appendix 6. *N,N*-Diisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



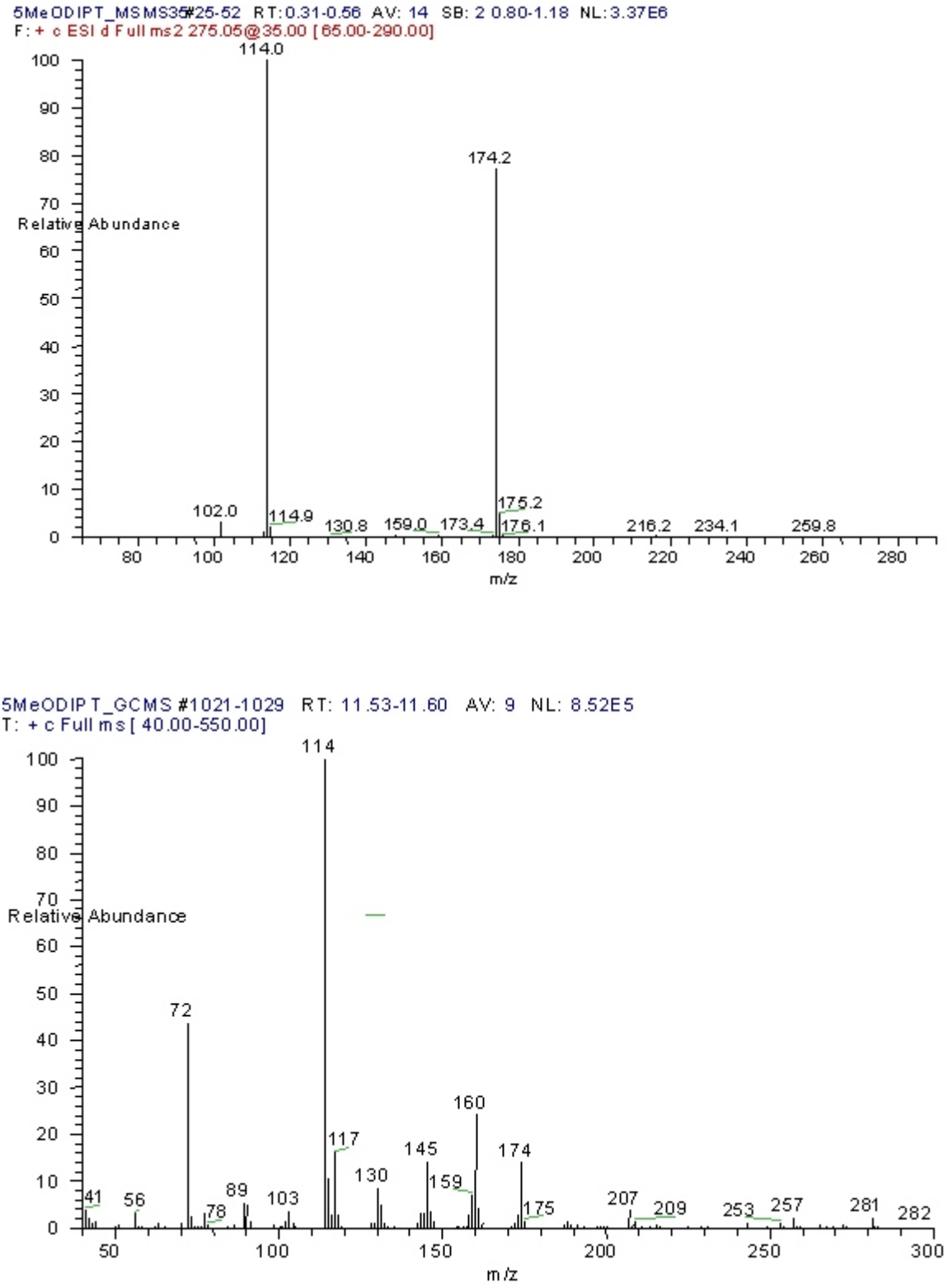
Appendix 7. 4-Hydroxy-*N,N*-diisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



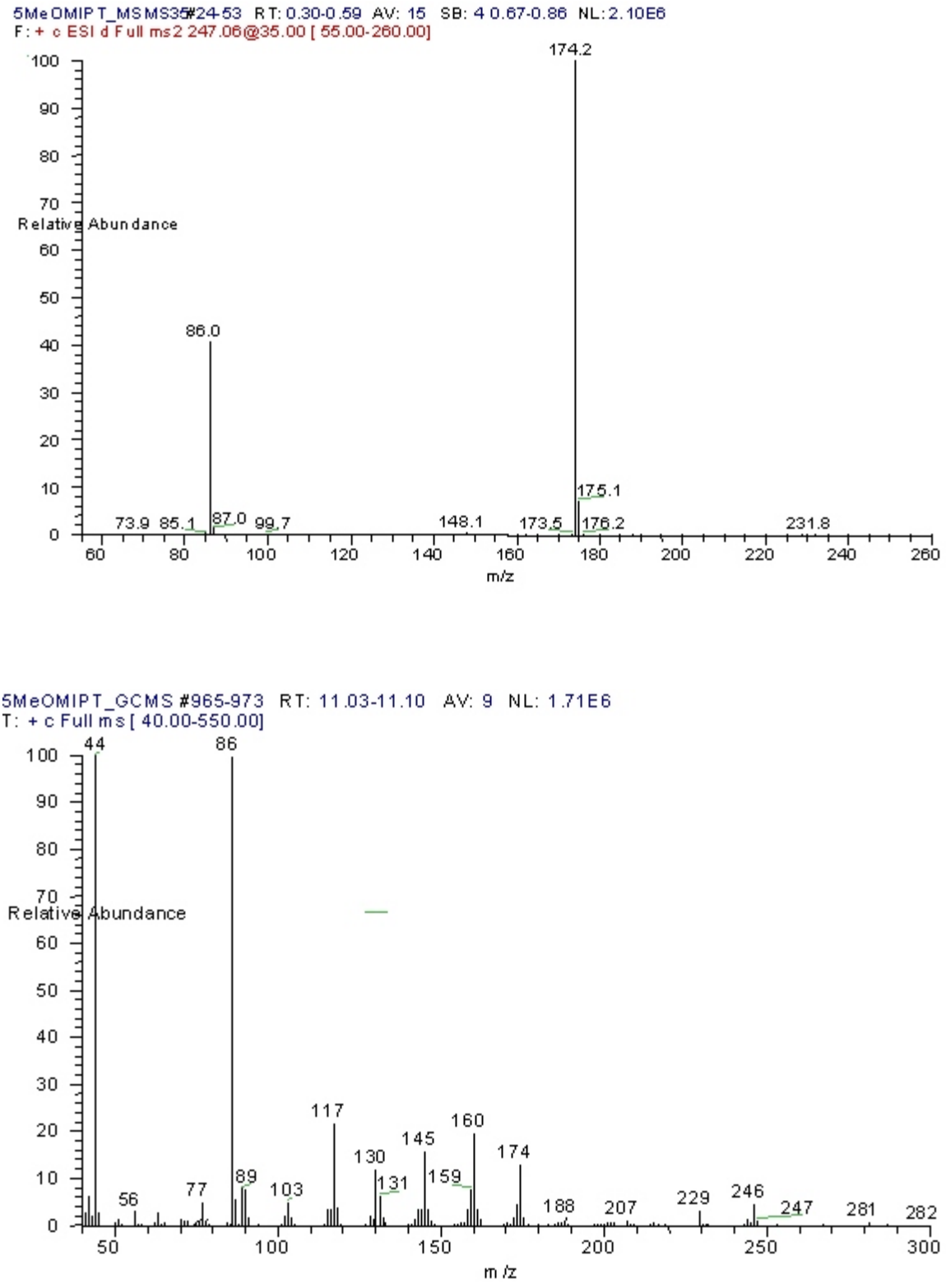
Appendix 8. 4-Acetoxy-*N,N*-methylisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom)



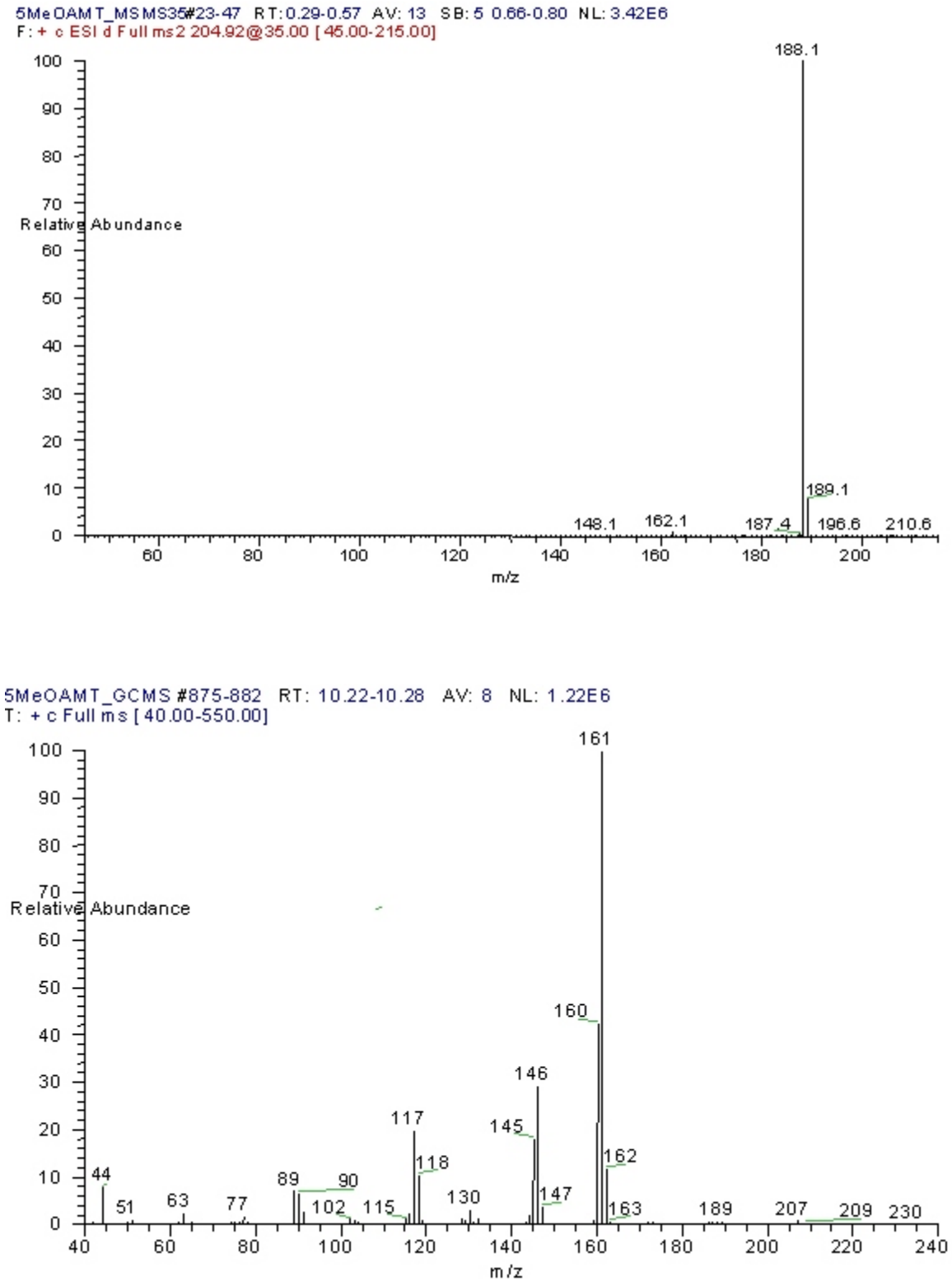
Appendix 9. 4-Acetoxy-*N,N*-diisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



Appendix 10. 5-Methoxy-*N,N*-diisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



Appendix 11. 5-Methoxy-*N,N*-methylisopropyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).



Appendix 12. 5-Methoxy-*alpha*-methyltryptamine: ESI-MS^2 (top) and GC/MS (bottom).