# Supplementary Material

# A new, simple and efficient method for the synthesis of tricyclic [1,3]oxazolo[3,2-*d*][1,4]benzoxazepine, [1,3]oxazino[3,2-*d*][1,4]benzoxazepine, pyrimido[1,2-*d*][1,4]benzoxazepine and their derivatives

**Muhammad Ashram[a*], Firas F. Awwadi[b]**

*[a]Chemistry Department, Mutah university, Al-Karak, Jordan*
*[b]Chemistry Department, The University of Jordan, Amman, Jordan, 11942*
*E-mail: ashram_1961@yahoo.com*

## Table of Contents

**Table S1.** Crystal data and structure refinement for Compound **7**.

| | | |
|---|---|---|
| Empirical formula | $C_{11}H_{13}NO_2$ | |
| Formula weight | 191.22 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 6.1750(4) Å | a= 90°. |
| | b = 7.4084(5) Å | b= 90°. |
| | c = 21.3275(14) Å | g = 90°. |
| Volume | 975.67(11) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.302 $Mg/m^3$ | |
| Absorption coefficient | 0.090 $mm^{-1}$ | |
| F(000) | 408 | |
| Crystal size | 0.5 x 0.4 x 0.4 $mm^3$ | |
| Theta range for data collection | 3.35 to 26.30°. | |
| Index ranges | -7<=h<=5, -9<=k<=9, -26<=l<=24 | |
| Reflections collected | 4696 | |
| Independent reflections | 1689 [R(int) = 0.0201] | |
| Completeness to theta = 26.30° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.87701 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1689 / 0 / 128 | |
| Goodness-of-fit on $F^2$ | 1.032 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0338, wR2 = 0.0776 | |
| R indices (all data) | R1 = 0.0434, wR2 = 0.0821 | |
| Absolute structure parameter | 2.5(15) | |
| Extinction coefficient | 0.038(3) | |
| Largest diff. peak and hole | 0.105 and -0.106 e.$Å^{-3}$ | |

**Table S2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **7**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(5) | 4495(2) | 9300(2) | 9688(1) | 55(1) |
| N(1) | 5548(2) | 7219(2) | 8504(1) | 48(1) |
| C(2) | 3211(3) | 7377(2) | 8586(1) | 45(1) |
| O(10) | 2298(2) | 6731(2) | 8022(1) | 71(1) |
| C(3) | 2459(3) | 9274(2) | 8721(1) | 40(1) |
| C(7) | 6731(3) | 7174(3) | 9093(1) | 56(1) |
| C(13) | 894(3) | 12690(3) | 9026(1) | 63(1) |
| C(14) | 2306(3) | 11815(2) | 9425(1) | 57(1) |
| C(12) | 283(3) | 11878(3) | 8471(1) | 60(1) |
| C(4) | 3099(3) | 10132(2) | 9270(1) | 44(1) |
| C(11) | 1046(3) | 10176(3) | 8326(1) | 51(1) |
| C(6) | 6615(3) | 8920(3) | 9446(1) | 61(1) |
| C(8) | 5746(4) | 5524(3) | 8158(1) | 66(1) |
| C(9) | 3883(4) | 5652(3) | 7710(1) | 77(1) |

**Table S3.** Bond lengths [Å] and angles [°] for **7**.

| | |
|---|---|
| O(5)-C(4) | 1.3847(19) |
| O(5)-C(6) | 1.435(2) |
| N(1)-C(7) | 1.454(2) |
| N(1)-C(2) | 1.458(2) |
| N(1)-C(8) | 1.462(2) |
| C(2)-O(10) | 1.412(2) |
| C(2)-C(3) | 1.508(2) |
| C(2)-H(2) | 0.9800 |
| O(10)-C(9) | 1.428(2) |
| C(3)-C(11) | 1.384(2) |
| C(3)-C(4) | 1.390(2) |
| C(7)-C(6) | 1.499(3) |
| C(7)-H(7A) | 0.9700 |
| C(7)-H(7B) | 0.9700 |

| | |
|---|---|
| C(13)-C(12) | 1.380(3) |
| C(13)-C(14) | 1.380(3) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(4) | 1.380(2) |
| C(14)-H(14) | 0.9300 |
| C(12)-C(11) | 1.381(3) |
| C(12)-H(12) | 0.9300 |
| C(11)-H(11) | 0.9300 |
| C(6)-H(6A) | 0.9700 |
| C(6)-H(6B) | 0.9700 |
| C(8)-C(9) | 1.499(3) |
| C(8)-H(8A) | 0.9700 |
| C(8)-H(8B) | 0.9700 |
| C(9)-H(9A) | 0.9700 |
| C(9)-H(9B) | 0.9700 |
| C(4)-O(5)-C(6) | 115.04(13) |
| C(7)-N(1)-C(2) | 113.35(14) |
| C(7)-N(1)-C(8) | 112.00(14) |
| C(2)-N(1)-C(8) | 102.23(15) |
| O(10)-C(2)-N(1) | 105.45(14) |
| O(10)-C(2)-C(3) | 110.85(14) |
| N(1)-C(2)-C(3) | 113.70(15) |
| O(10)-C(2)-H(2) | 108.9 |
| N(1)-C(2)-H(2) | 108.9 |
| C(3)-C(2)-H(2) | 108.9 |
| C(2)-O(10)-C(9) | 108.23(14) |
| C(11)-C(3)-C(4) | 118.11(16) |
| C(11)-C(3)-C(2) | 121.83(16) |
| C(4)-C(3)-C(2) | 119.98(15) |
| N(1)-C(7)-C(6) | 112.96(15) |
| N(1)-C(7)-H(7A) | 109.0 |
| C(6)-C(7)-H(7A) | 109.0 |
| N(1)-C(7)-H(7B) | 109.0 |
| C(6)-C(7)-H(7B) | 109.0 |
| H(7A)-C(7)-H(7B) | 107.8 |
| C(12)-C(13)-C(14) | 119.80(17) |
| C(12)-C(13)-H(13) | 120.1 |
| C(14)-C(13)-H(13) | 120.1 |
| C(13)-C(14)-C(4) | 120.11(18) |

| | |
|---|---|
| C(13)-C(14)-H(14) | 119.9 |
| C(4)-C(14)-H(14) | 119.9 |
| C(13)-C(12)-C(11) | 119.74(18) |
| C(13)-C(12)-H(12) | 120.1 |
| C(11)-C(12)-H(12) | 120.1 |
| C(14)-C(4)-O(5) | 118.01(16) |
| C(14)-C(4)-C(3) | 120.87(17) |
| O(5)-C(4)-C(3) | 121.09(15) |
| C(12)-C(11)-C(3) | 121.34(18) |
| C(12)-C(11)-H(11) | 119.3 |
| C(3)-C(11)-H(11) | 119.3 |
| O(5)-C(6)-C(7) | 113.21(16) |
| O(5)-C(6)-H(6A) | 108.9 |
| C(7)-C(6)-H(6A) | 108.9 |
| O(5)-C(6)-H(6B) | 108.9 |
| C(7)-C(6)-H(6B) | 108.9 |
| H(6A)-C(6)-H(6B) | 107.7 |
| N(1)-C(8)-C(9) | 101.75(15) |
| N(1)-C(8)-H(8A) | 111.4 |
| C(9)-C(8)-H(8A) | 111.4 |
| N(1)-C(8)-H(8B) | 111.4 |
| C(9)-C(8)-H(8B) | 111.4 |
| H(8A)-C(8)-H(8B) | 109.3 |
| O(10)-C(9)-C(8) | 105.32(15) |
| O(10)-C(9)-H(9A) | 110.7 |
| C(8)-C(9)-H(9A) | 110.7 |
| O(10)-C(9)-H(9B) | 110.7 |
| C(8)-C(9)-H(9B) | 110.7 |
| H(9A)-C(9)-H(9B) | 108.8 |

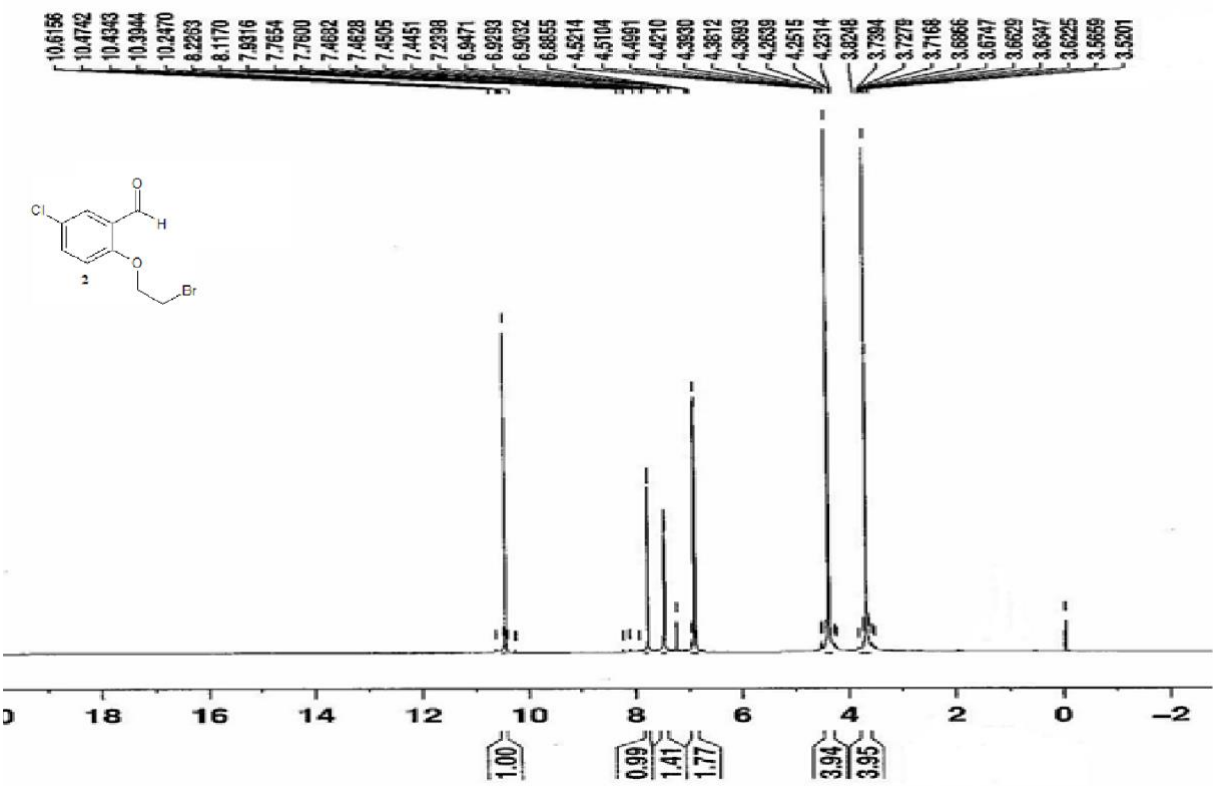
Symmetry transformations used to generate equivalent atoms:

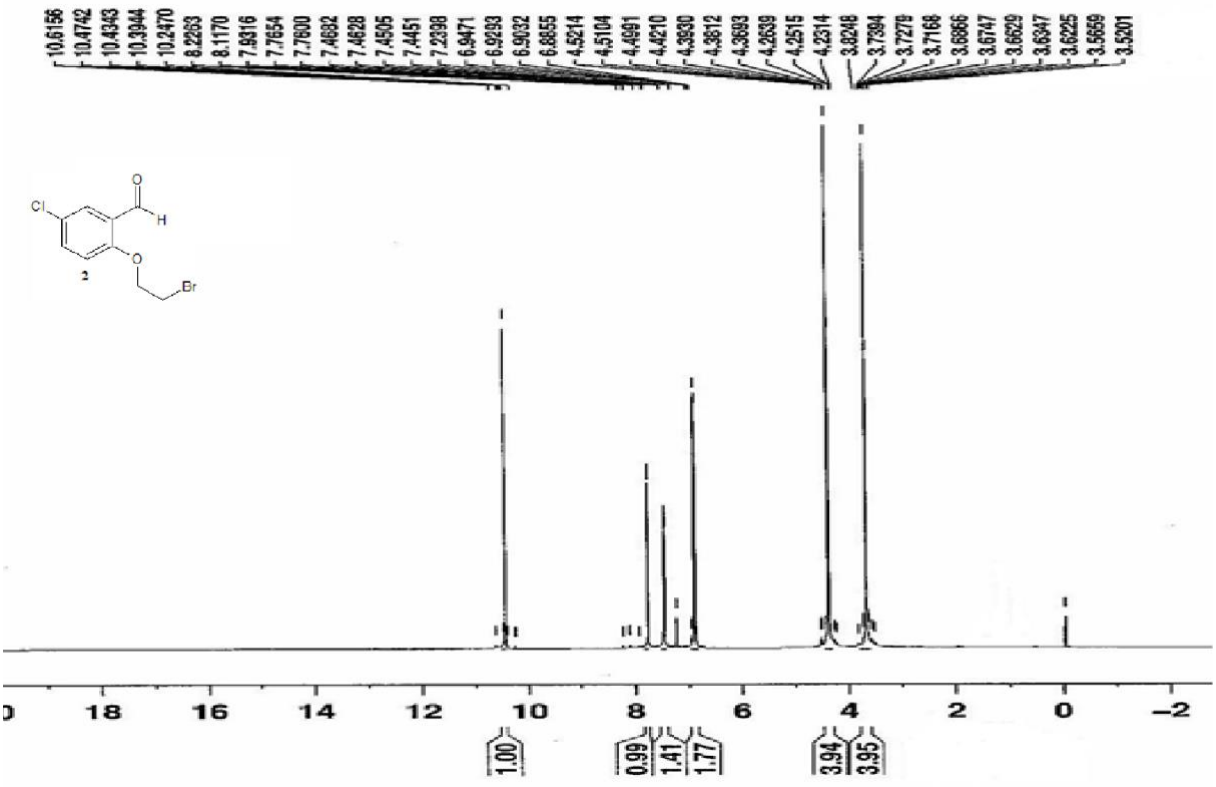
**Table S4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(5) | 62(1) | 62(1) | 41(1) | 4(1) | -3(1) | 2(1) |
| N(1) | 46(1) | 51(1) | 46(1) | 4(1) | 6(1) | 12(1) |
| C(2) | 46(1) | 47(1) | 42(1) | -3(1) | 2(1) | 4(1) |
| O(10) | 71(1) | 75(1) | 66(1) | -31(1) | -18(1) | 23(1) |
| C(3) | 40(1) | 43(1) | 38(1) | 3(1) | 8(1) | 1(1) |
| C(7) | 45(1) | 64(1) | 60(1) | 11(1) | -2(1) | 10(1) |
| C(13) | 66(1) | 41(1) | 84(1) | -2(1) | 13(1) | 8(1) |
| C(14) | 68(1) | 45(1) | 59(1) | -11(1) | 6(1) | -2(1) |
| C(12) | 59(1) | 54(1) | 67(1) | 12(1) | 4(1) | 16(1) |
| C(4) | 47(1) | 44(1) | 40(1) | 5(1) | 6(1) | -3(1) |
| C(11) | 50(1) | 58(1) | 45(1) | 2(1) | 4(1) | 10(1) |
| C(6) | 53(1) | 70(1) | 59(1) | 4(1) | -11(1) | 0(1) |
| C(8) | 75(1) | 65(1) | 59(1) | -5(1) | 6(1) | 28(1) |
| C(9) | 96(2) | 69(1) | 65(1) | -22(1) | -2(1) | 27(1) |

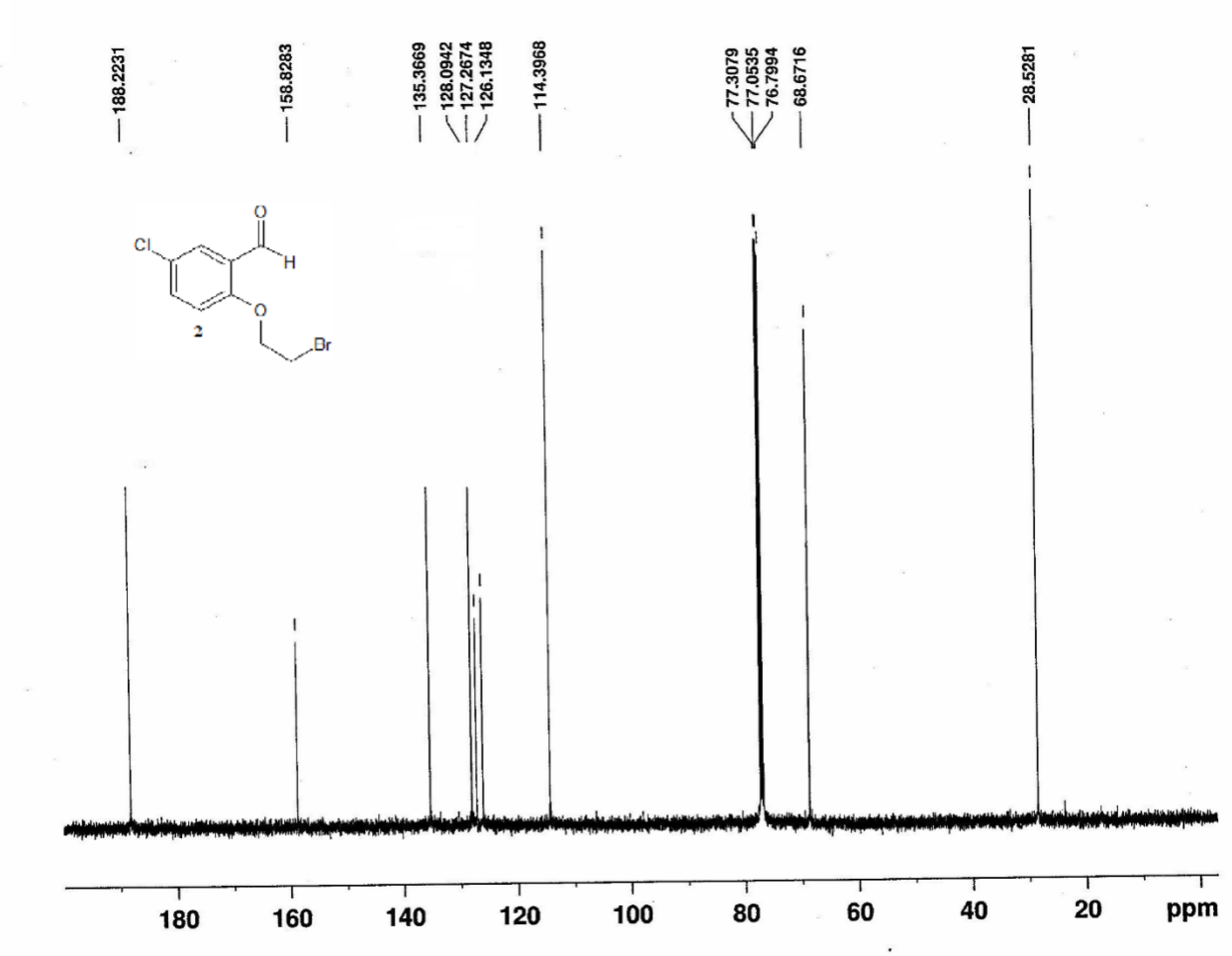
**Table S5.** Hydrogen coordinates ( $x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **7**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 2758 | 6589 | 8931 | 54 |
| H(7A) | 8237 | 6893 | 9008 | 68 |
| H(7B) | 6149 | 6217 | 9354 | 68 |
| H(13) | 356 | 13823 | 9130 | 76 |
| H(14) | 2724 | 12362 | 9798 | 69 |
| H(12) | -639 | 12475 | 8195 | 72 |
| H(11) | 602 | 9625 | 7956 | 61 |
| H(6A) | 7634 | 8881 | 9792 | 73 |
| H(6B) | 7048 | 9895 | 9170 | 73 |
| H(8A) | 5600 | 4489 | 8433 | 80 |
| H(8B) | 7118 | 5451 | 7938 | 80 |
| H(9A) | 4333 | 6217 | 7321 | 92 |
| H(9B) | 3309 | 4463 | 7617 | 92 |

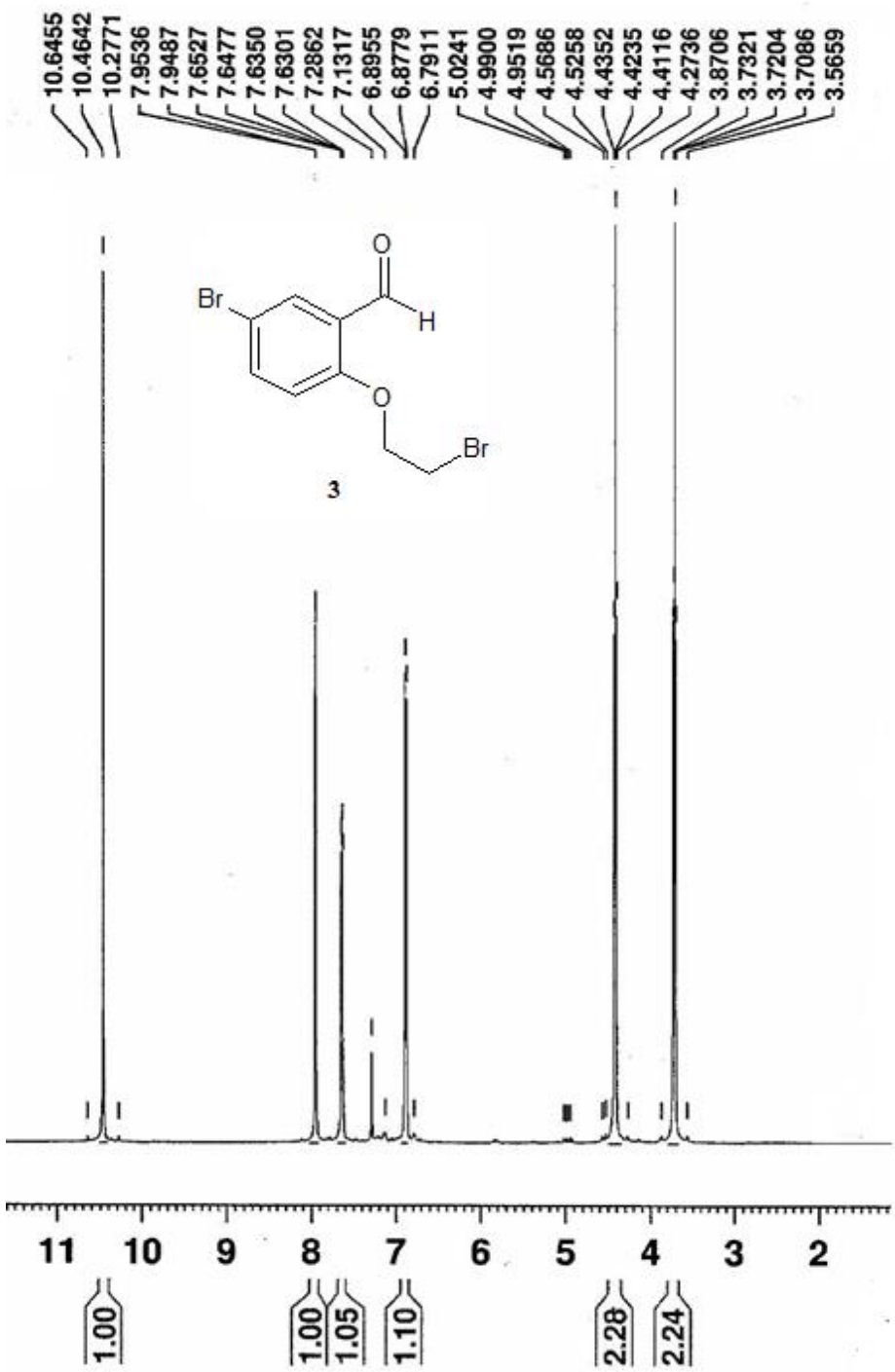


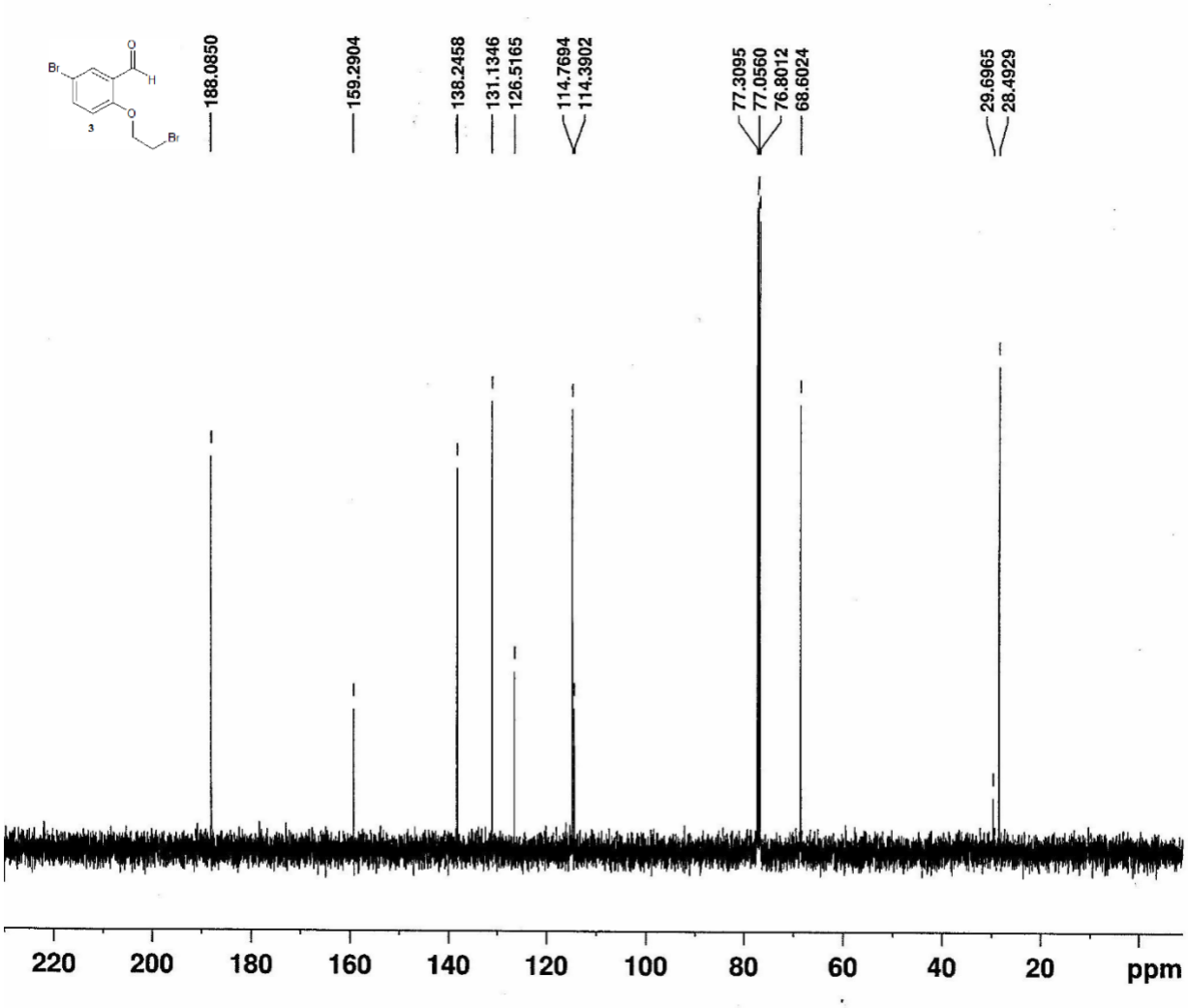

 

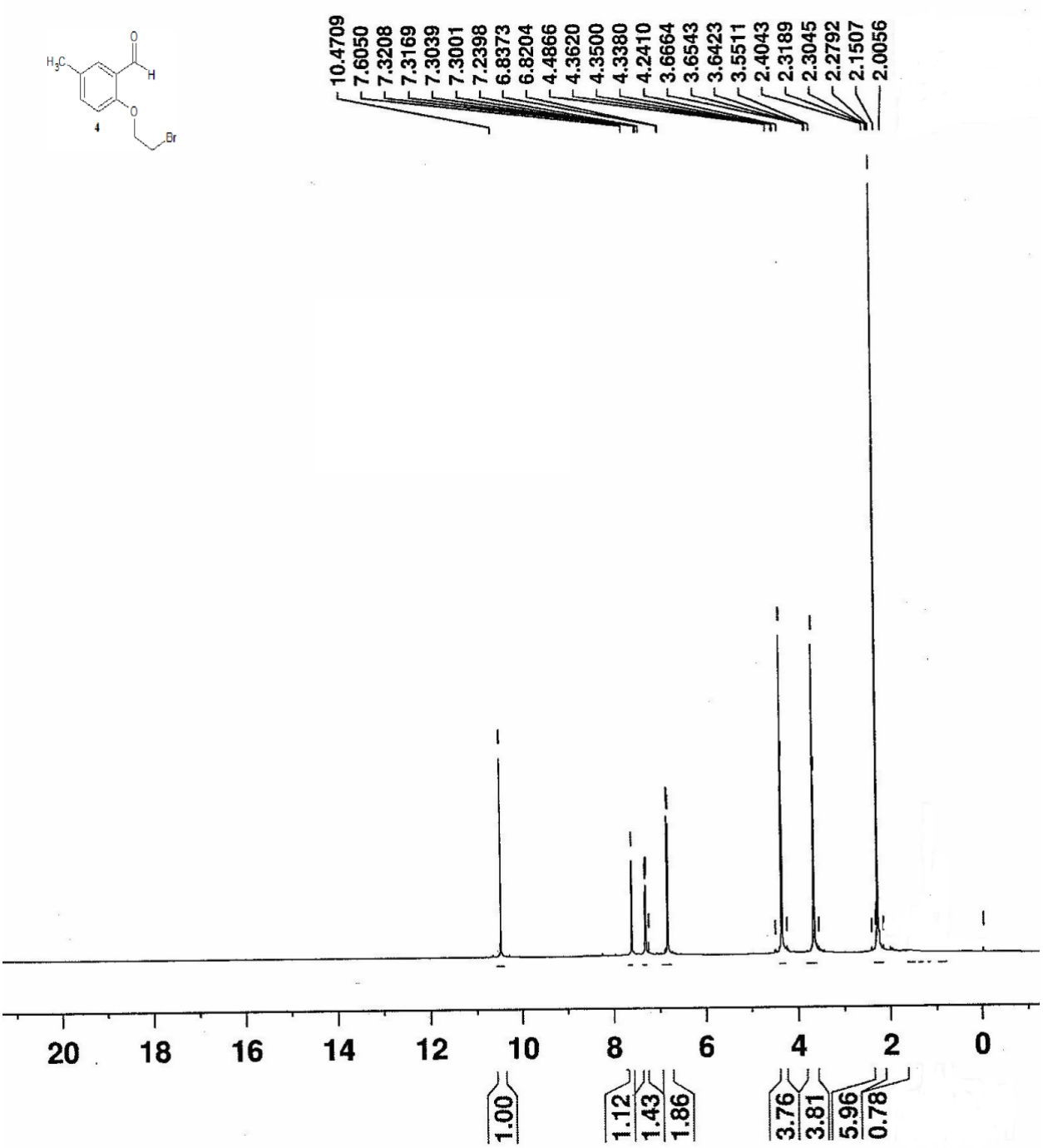


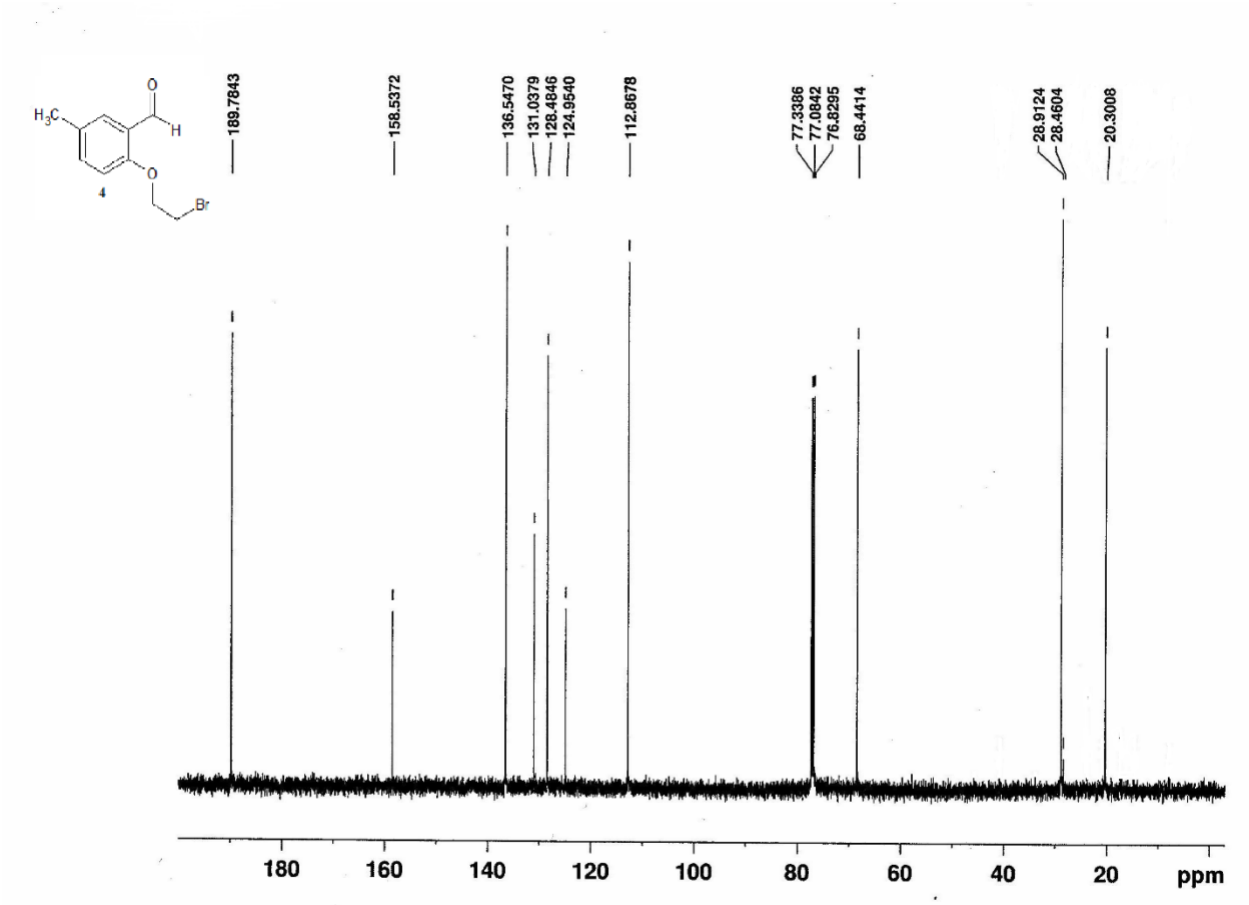

 

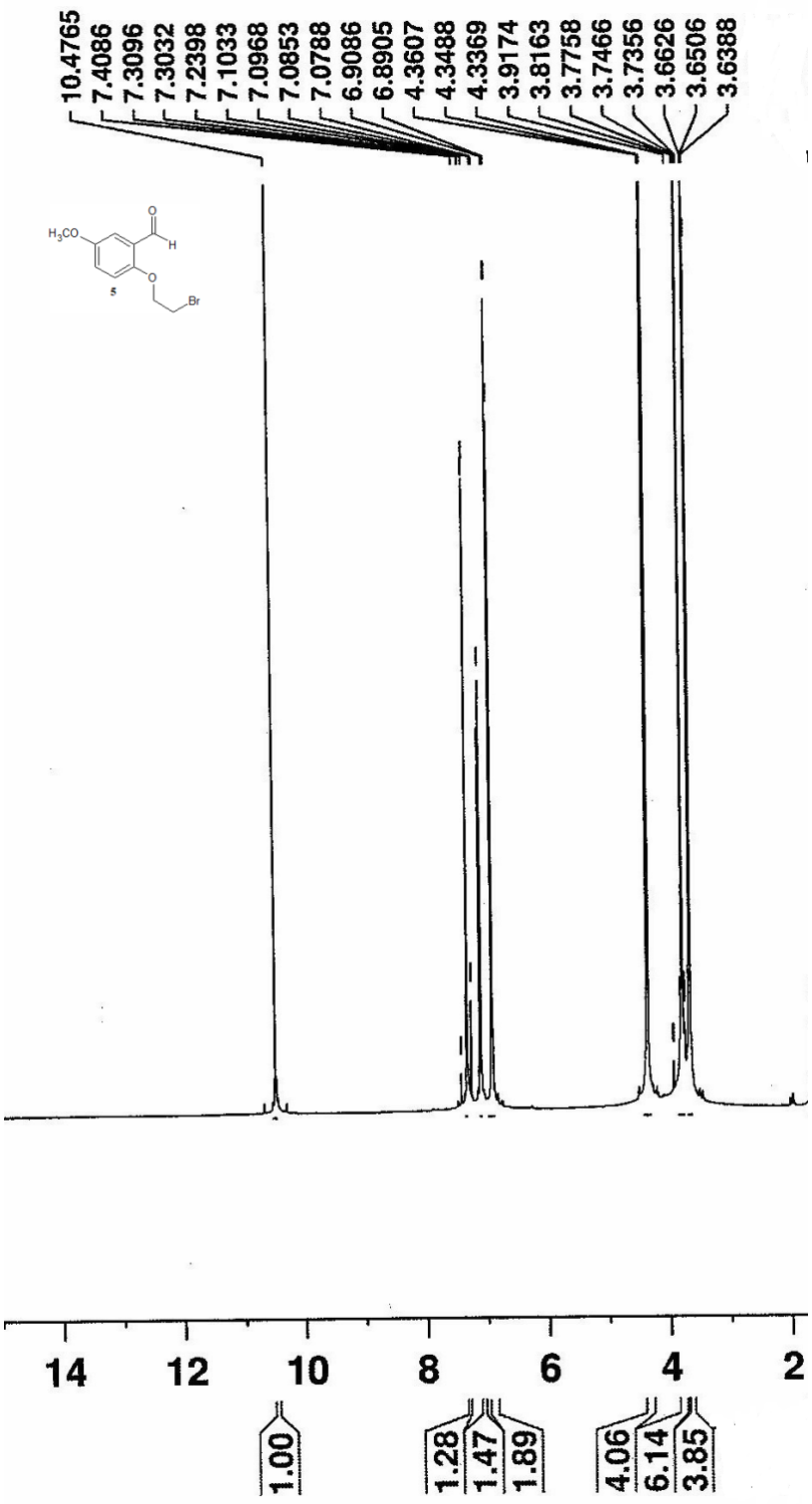


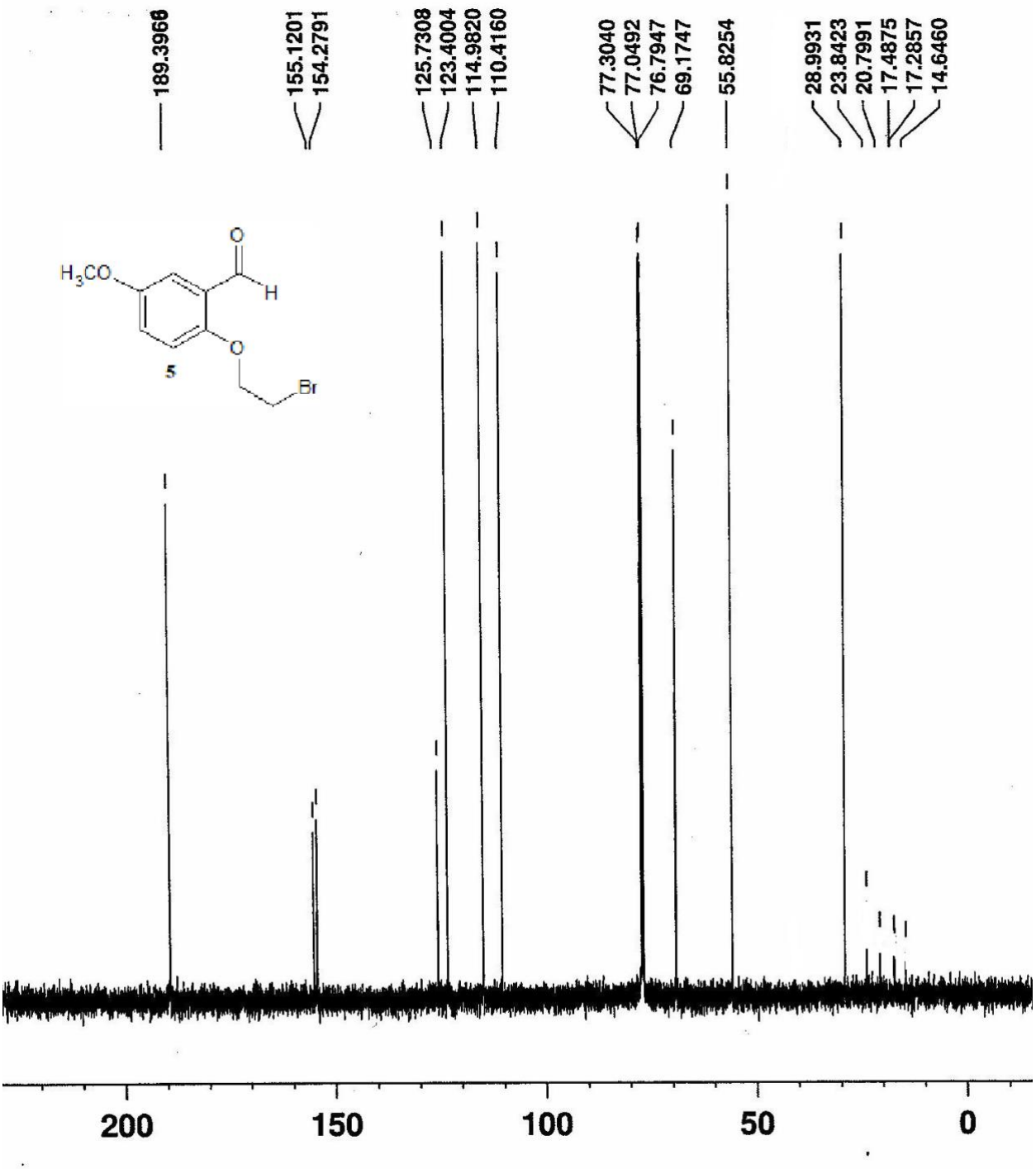




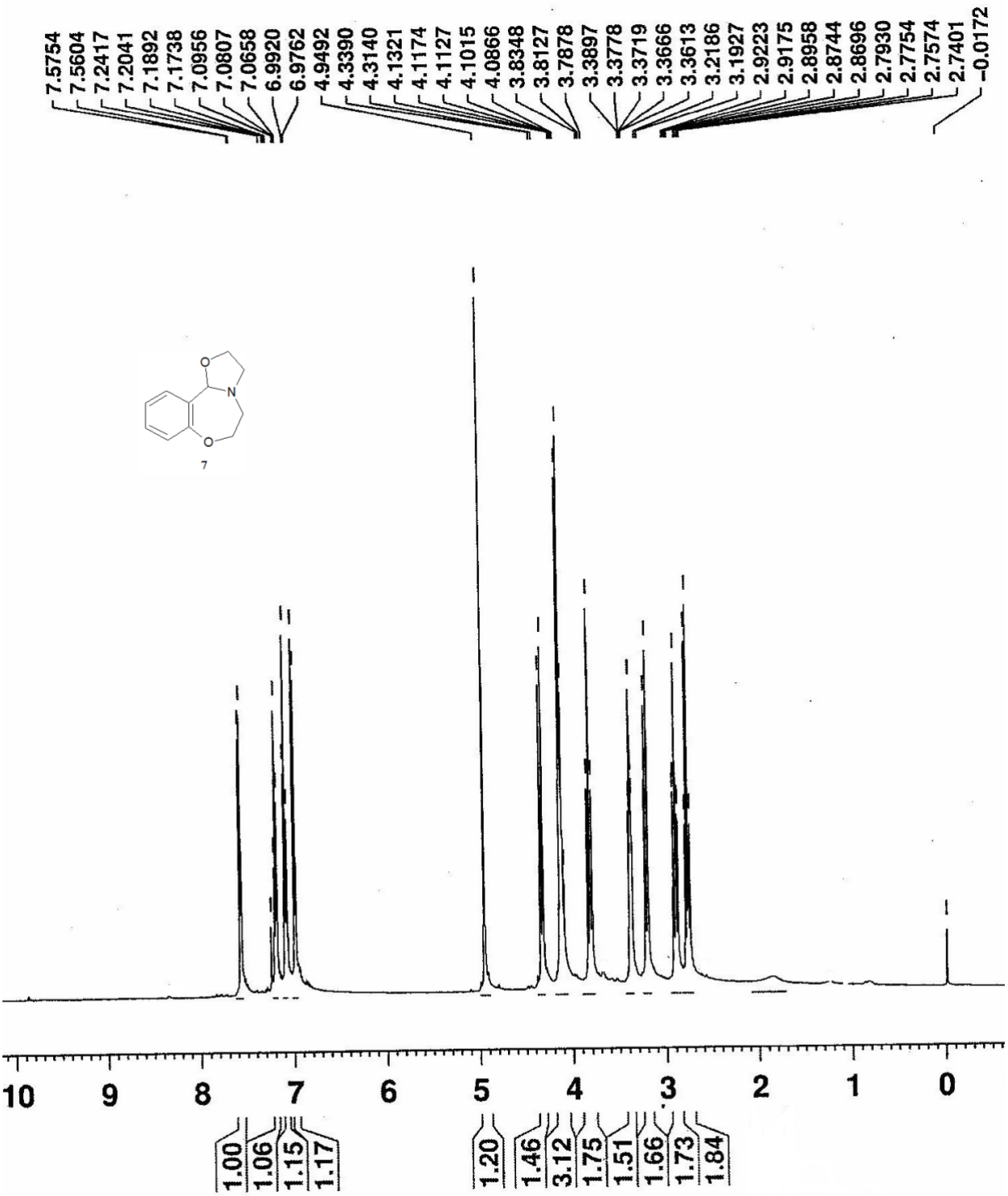


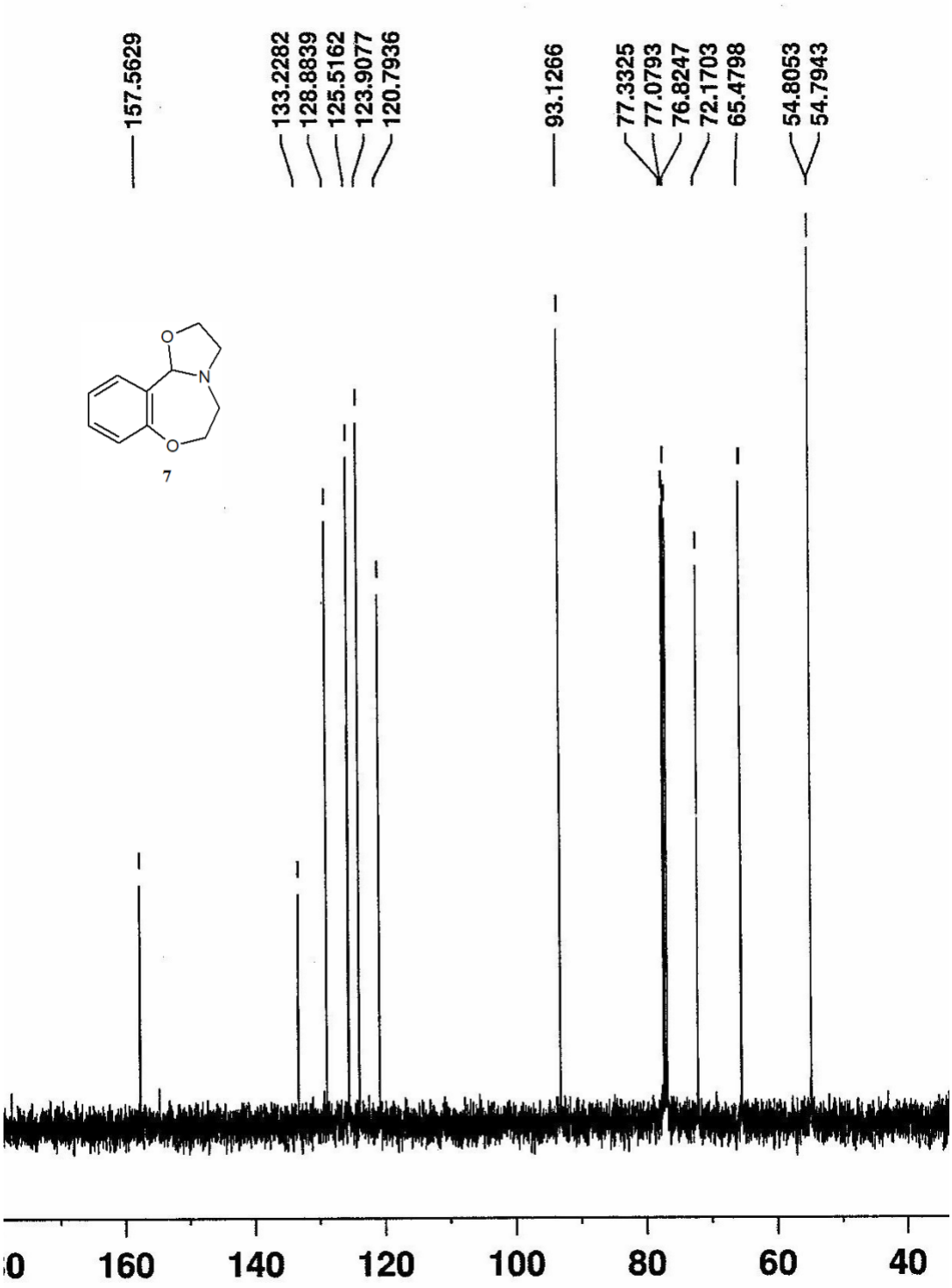


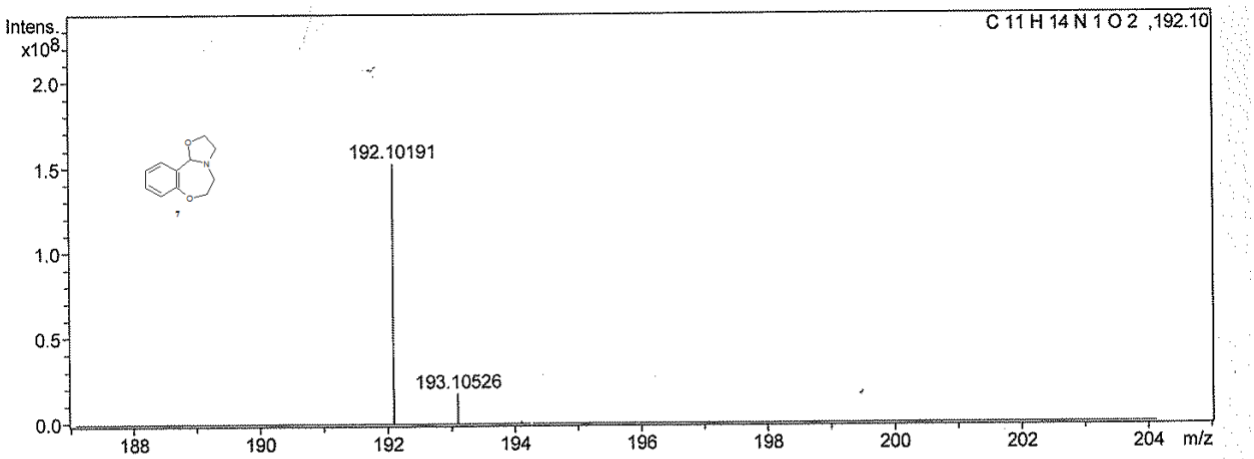

 



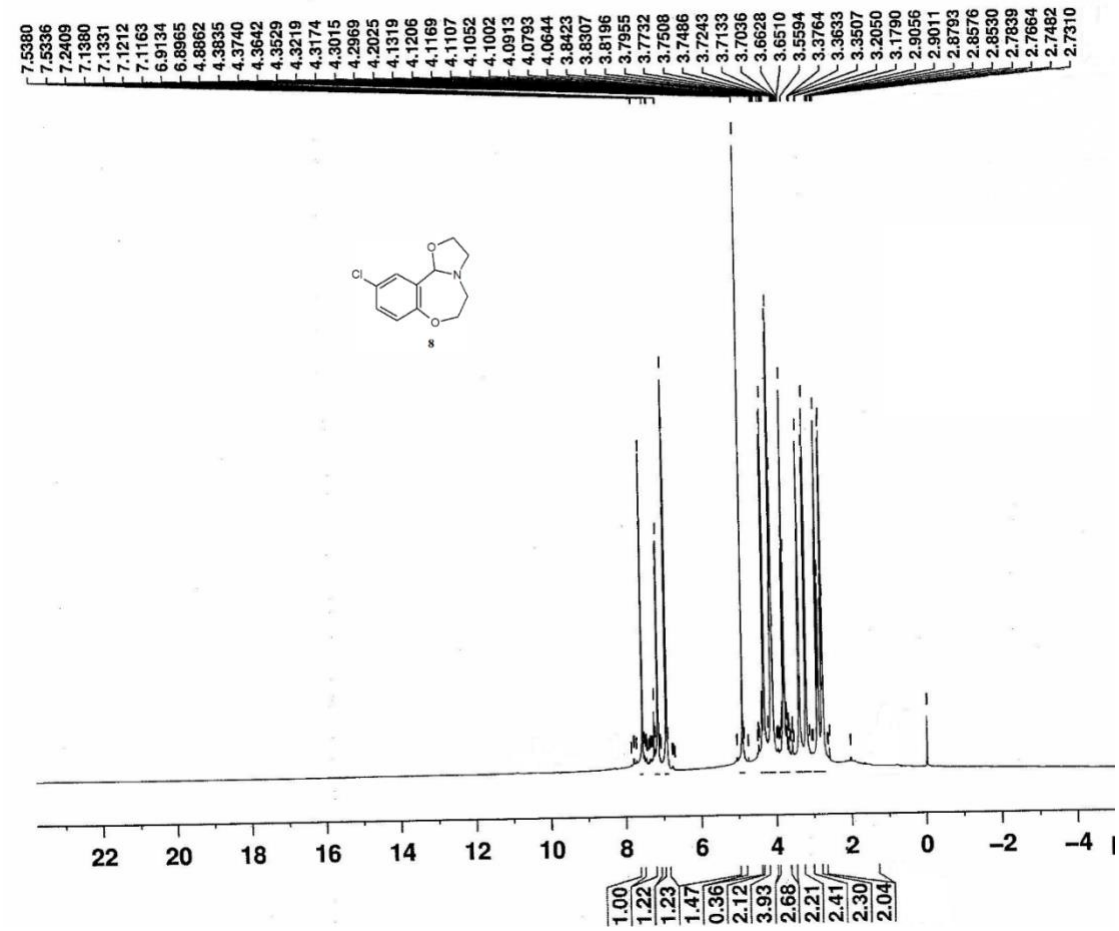

 

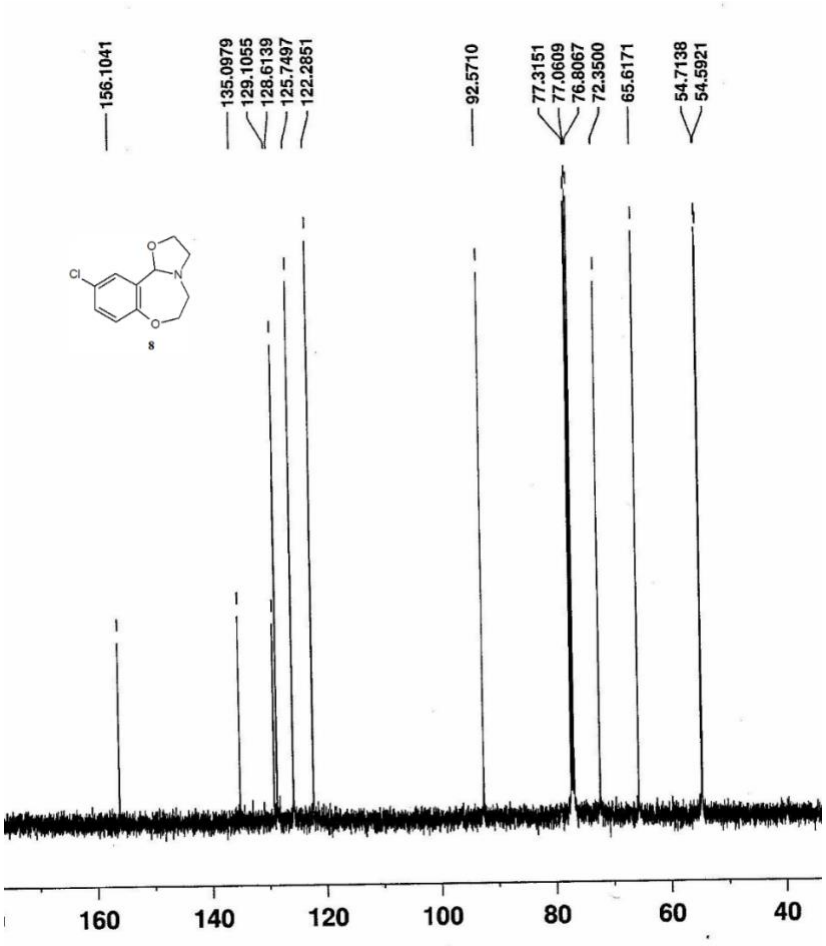


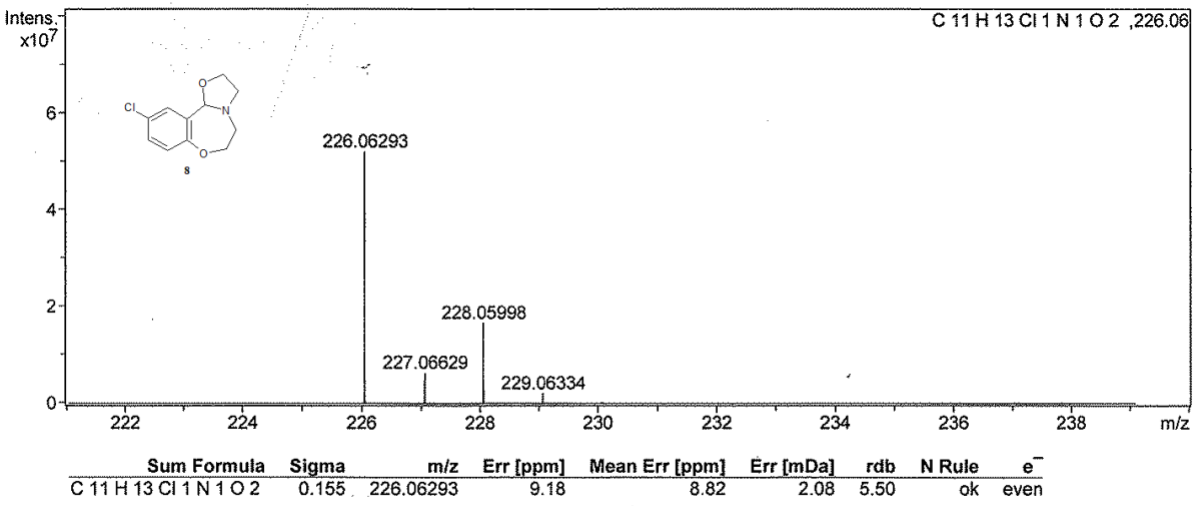




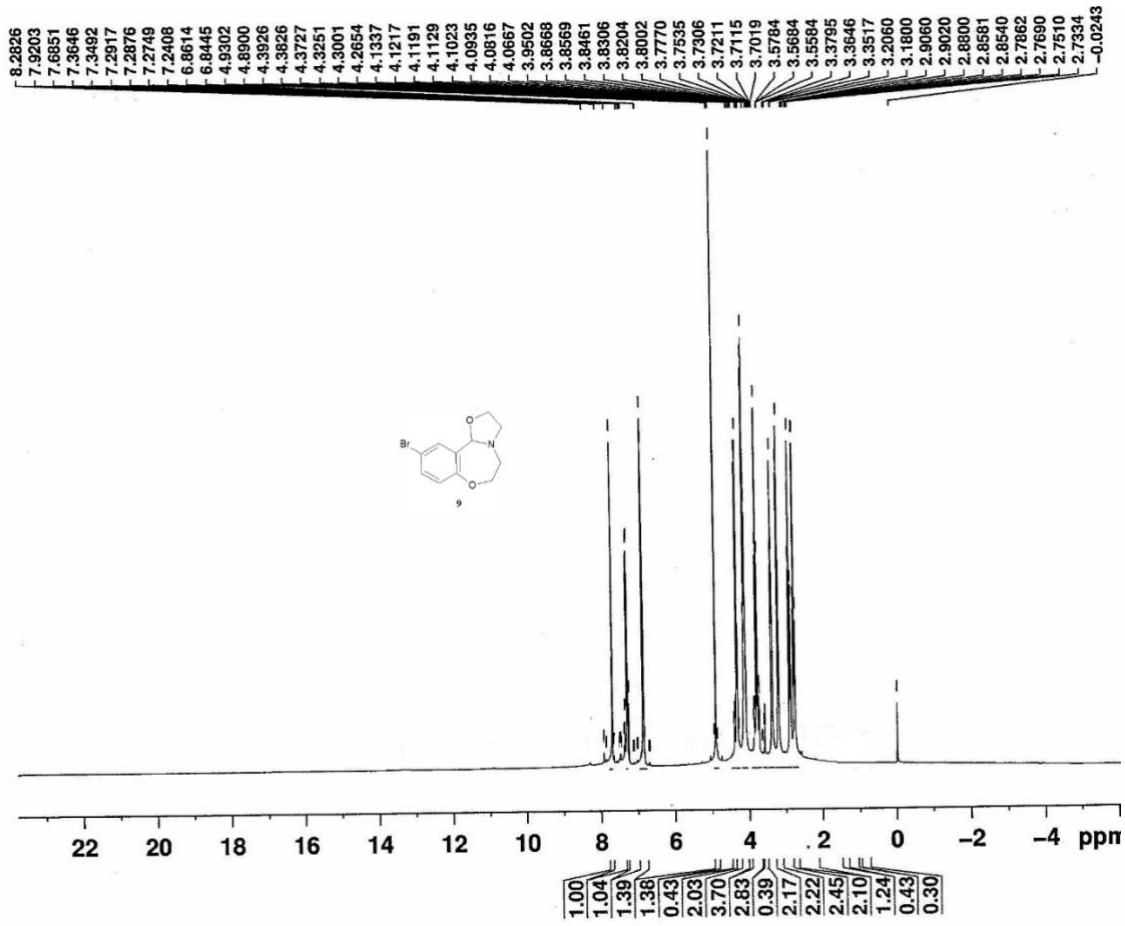

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 11 H 14 N 1 O 2 | 0.004 | 192.10191 | 6.52 | 6.30 | 1.25 | 5.50 | ok | even |



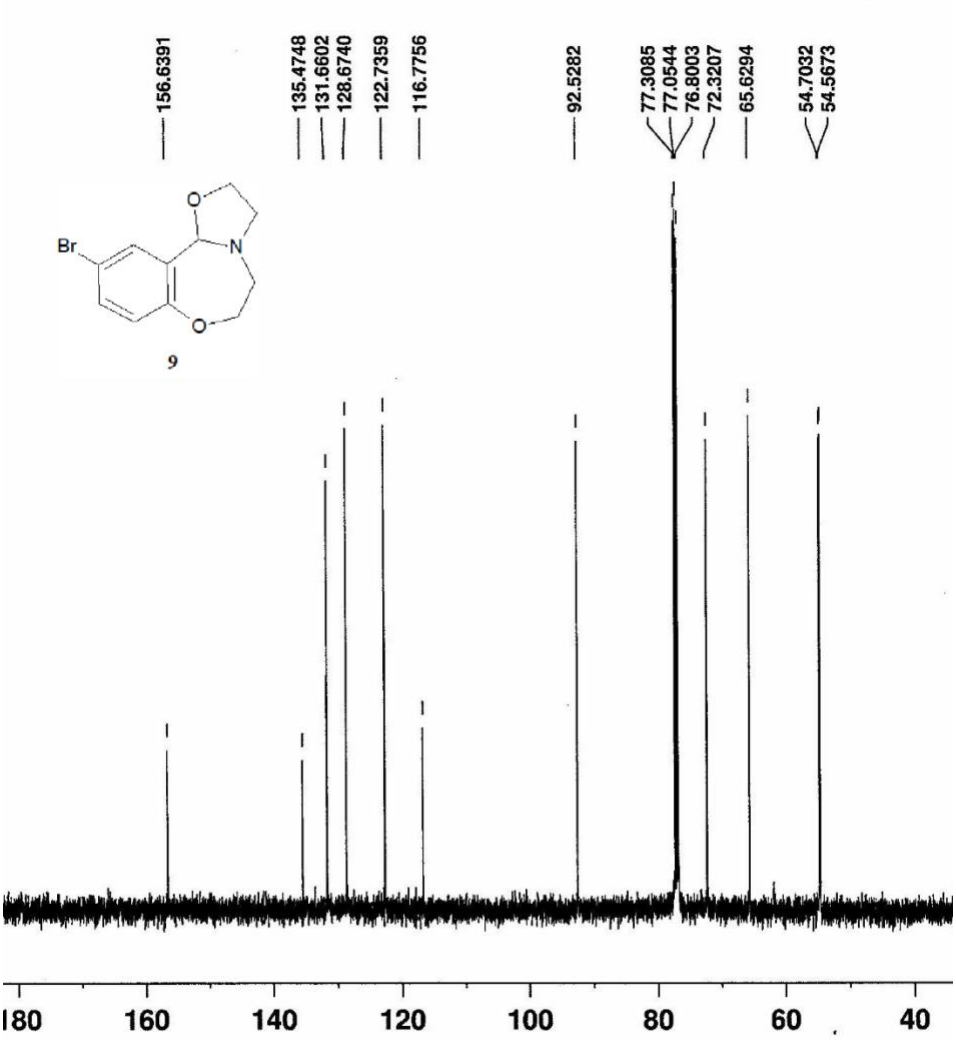


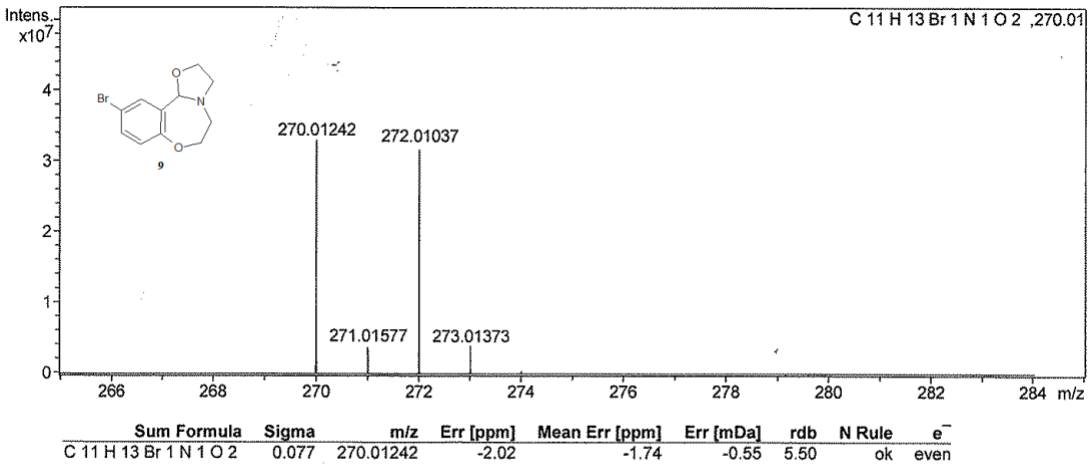




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 11 H 13 Cl 1 N 1 O 2 | 0.155 | 226.06293 | 9.18 | 8.82 | 2.08 | 5.50 | ok | even |

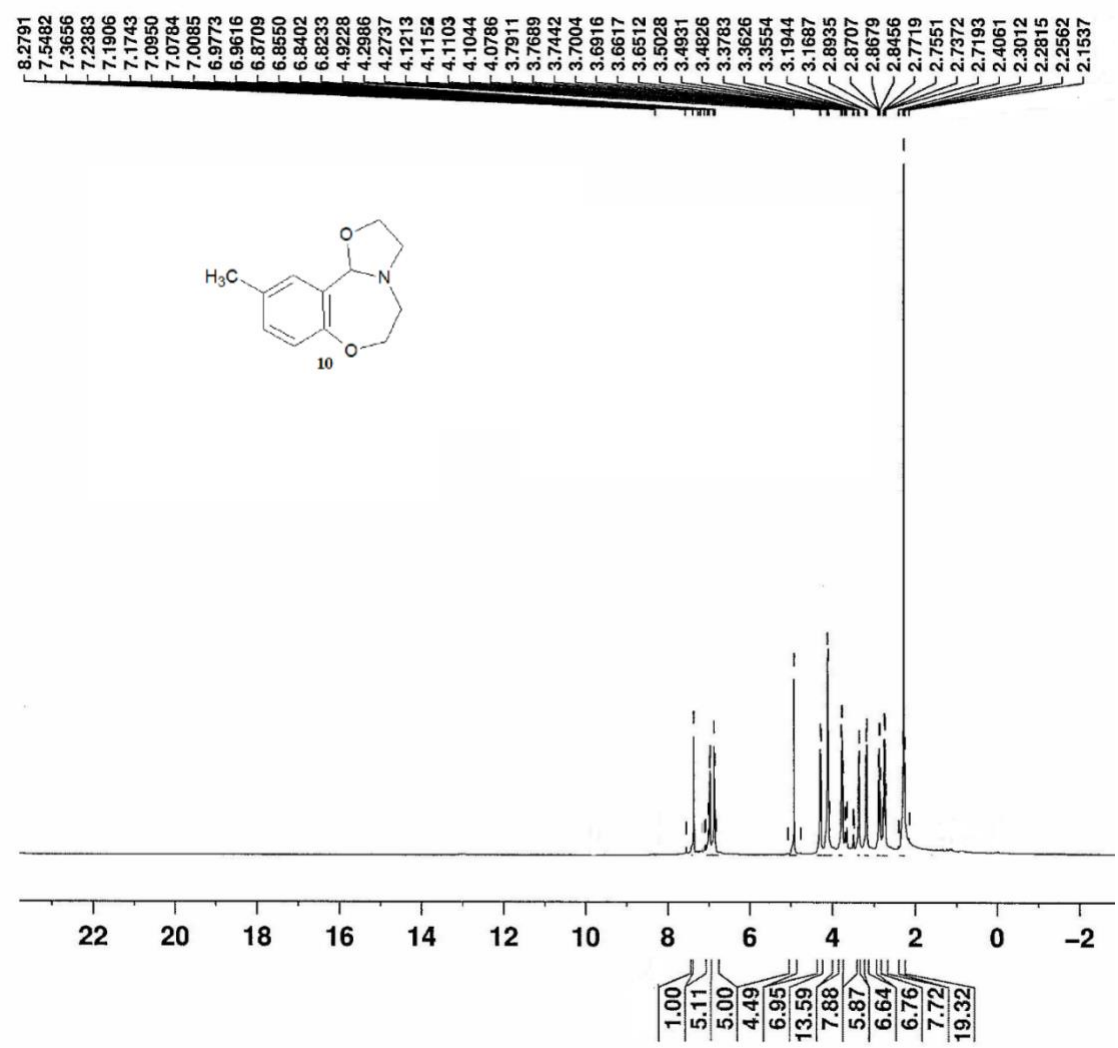


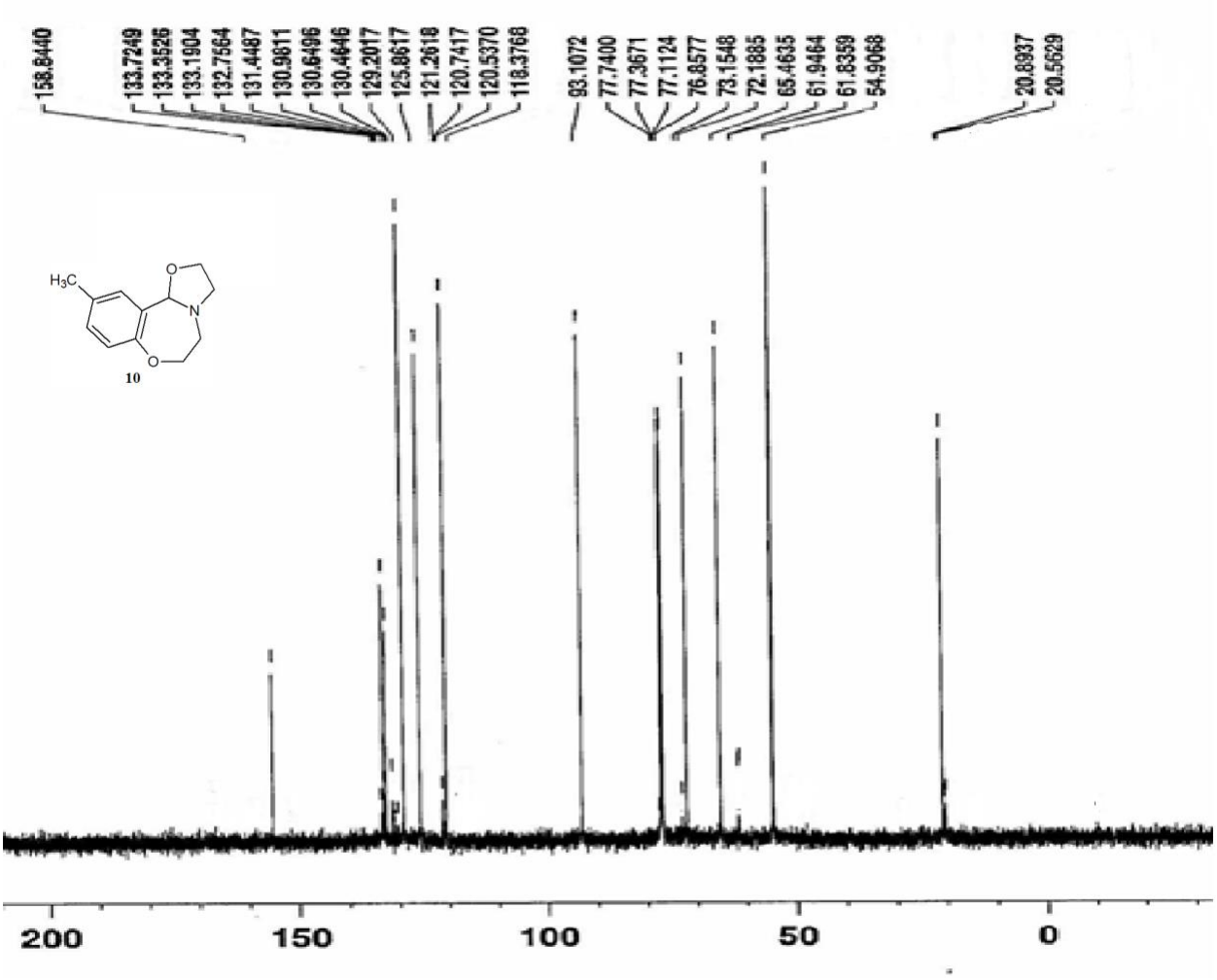


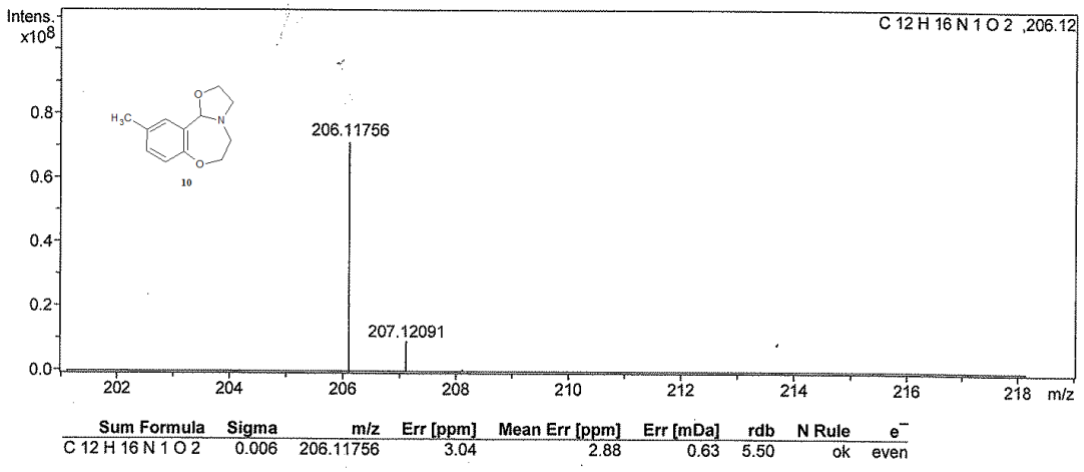




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 11 H 13 Br 1 N 1 O 2 | 0.077 | 270.01242 | -2.02 | -1.74 | -0.55 | 5.50 | ok | even |

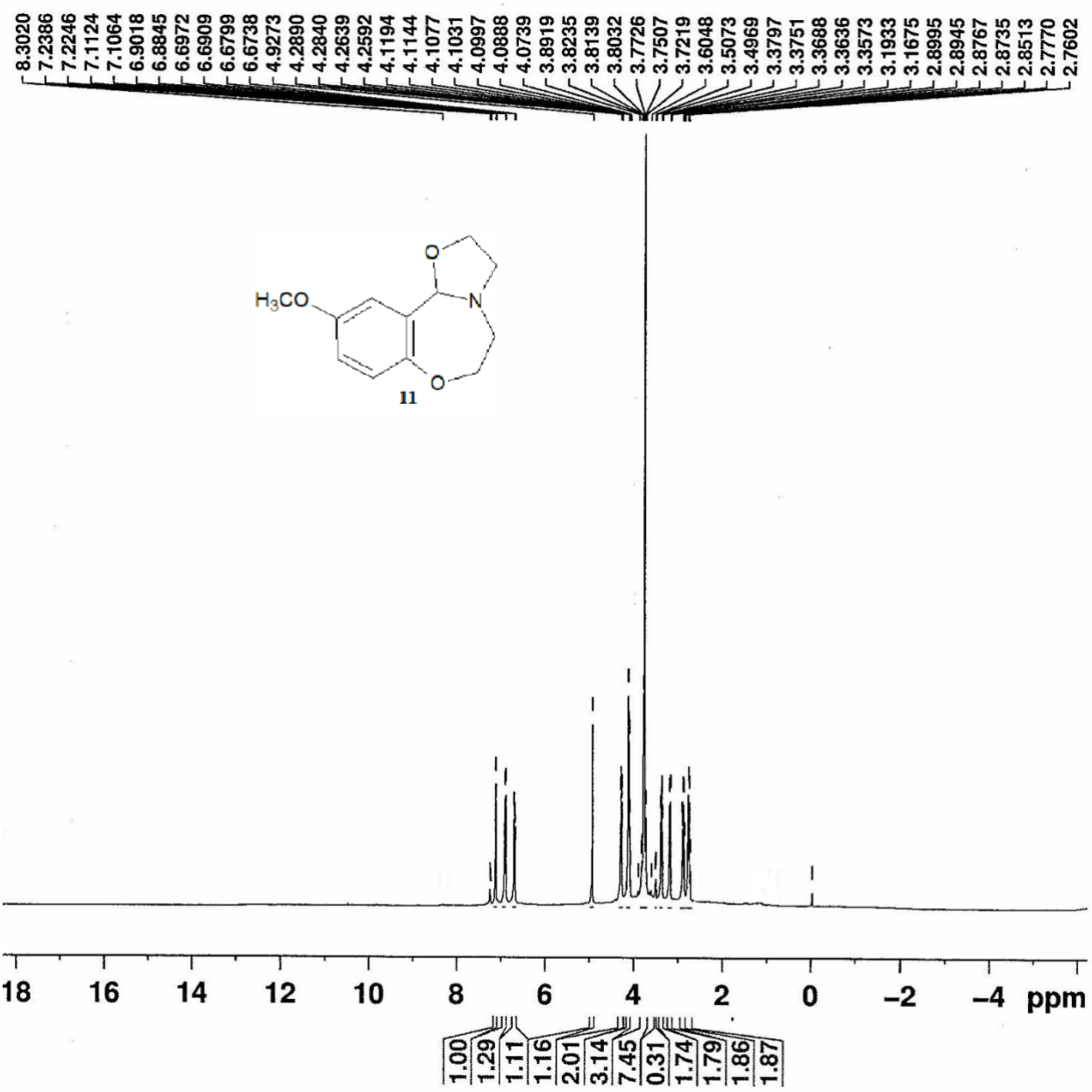


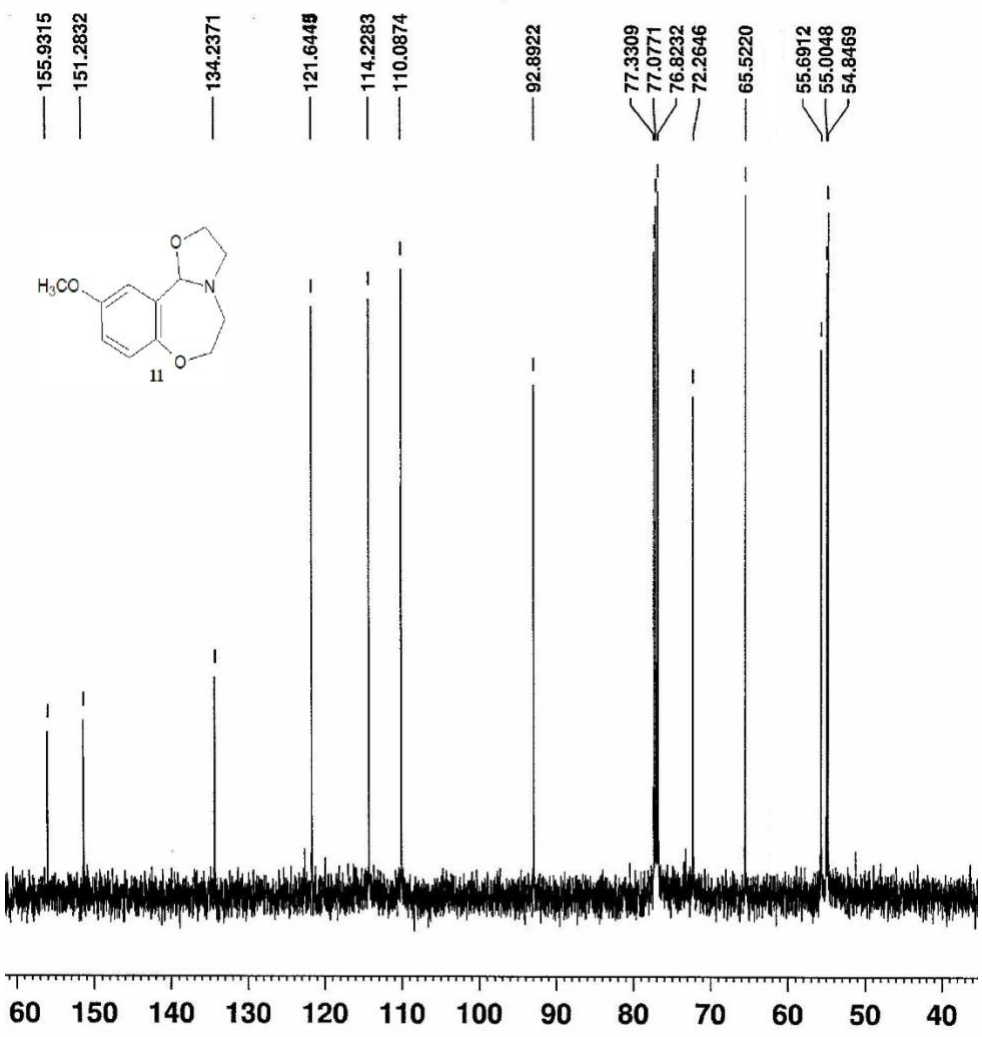

 

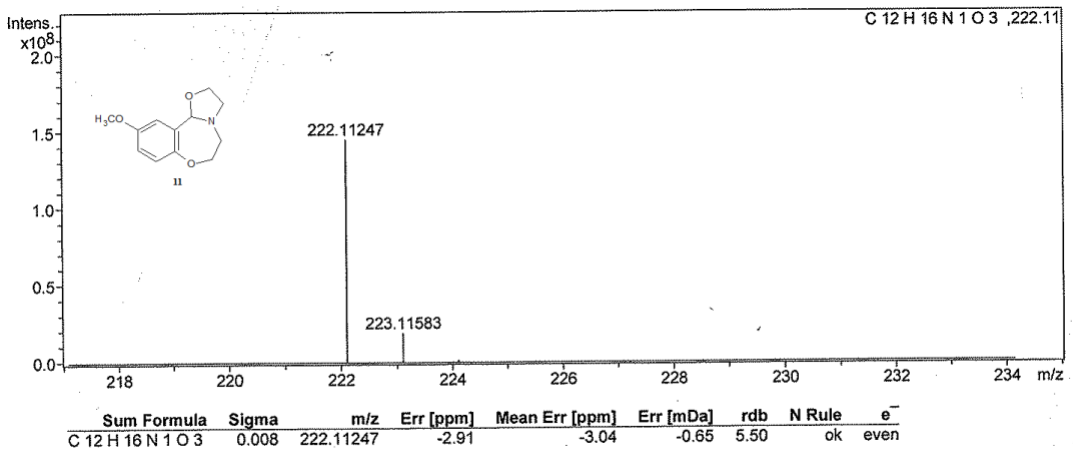


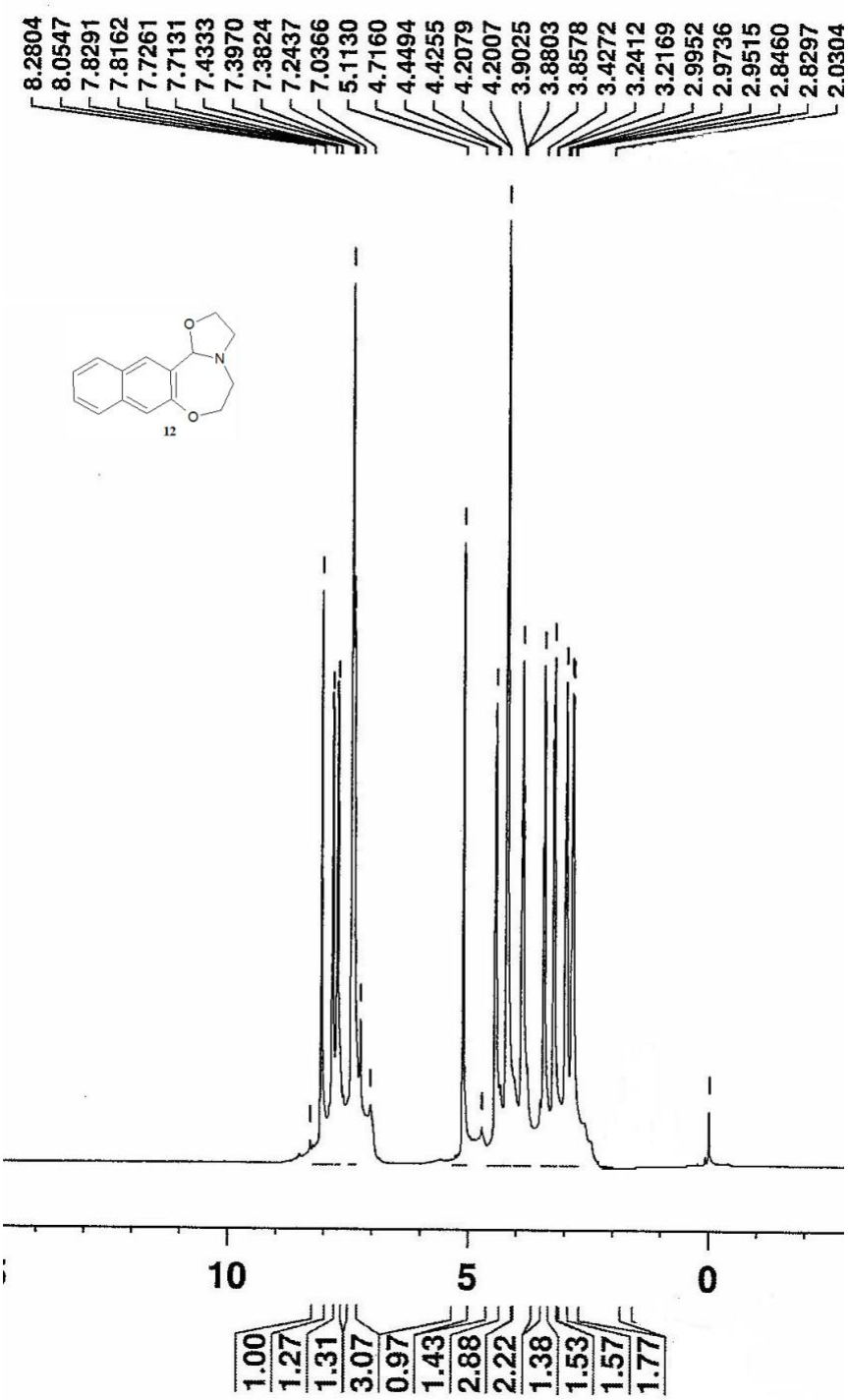

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 16 N 1 O 2 | 0.006 | 206.11756 | 3.04 | 2.88 | 0.63 | 5.50 | ok | even |



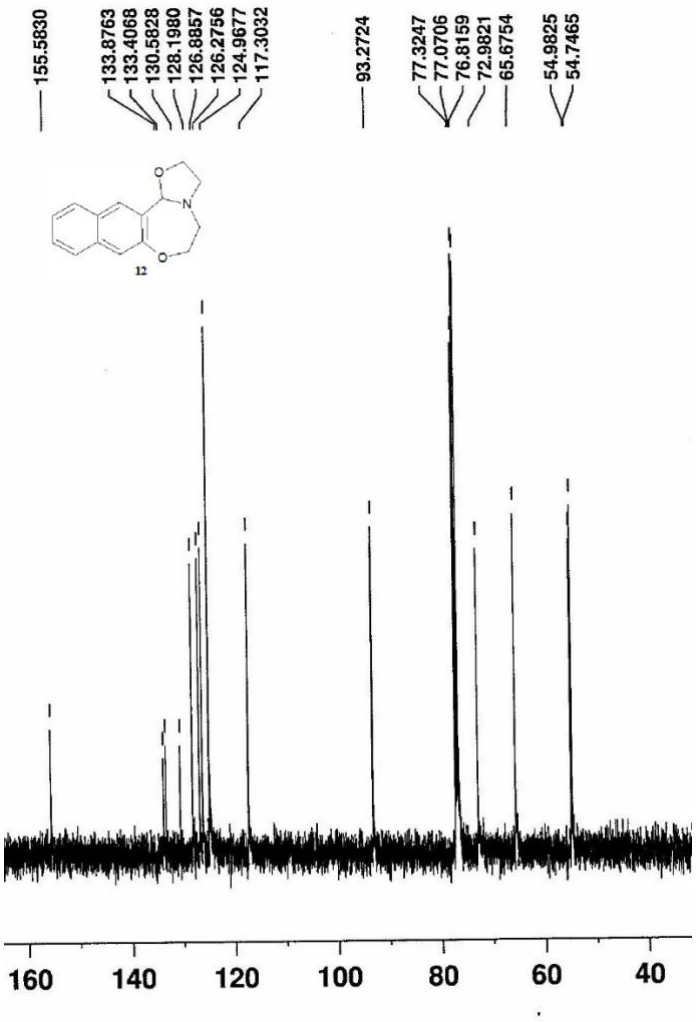


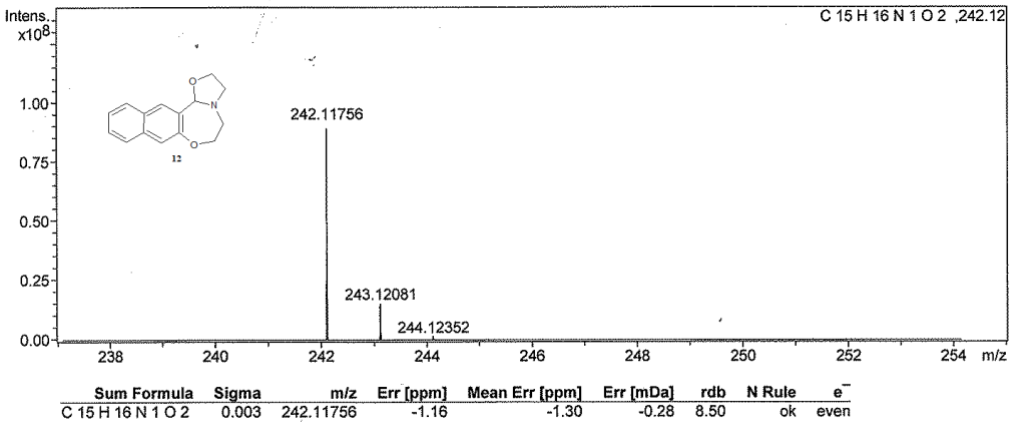




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 16 N 1 O 3 | 0.008 | 222.11247 | -2.91 | -3.04 | -0.65 | 5.50 | ok | even |

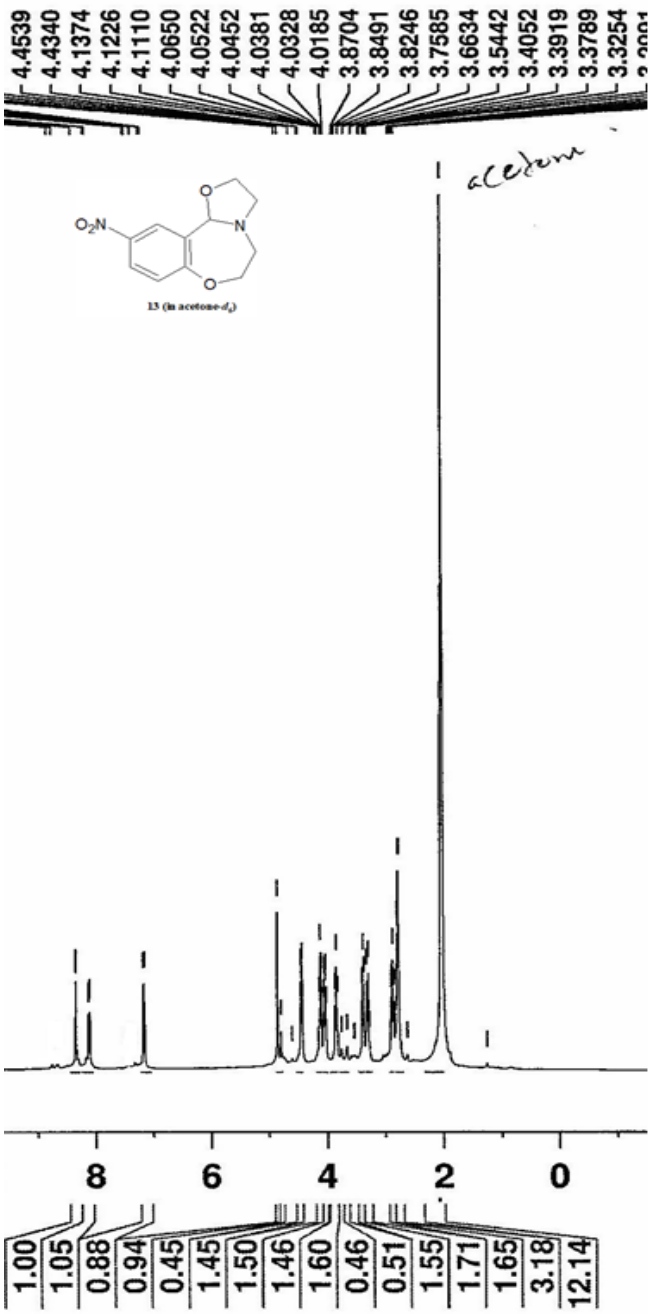


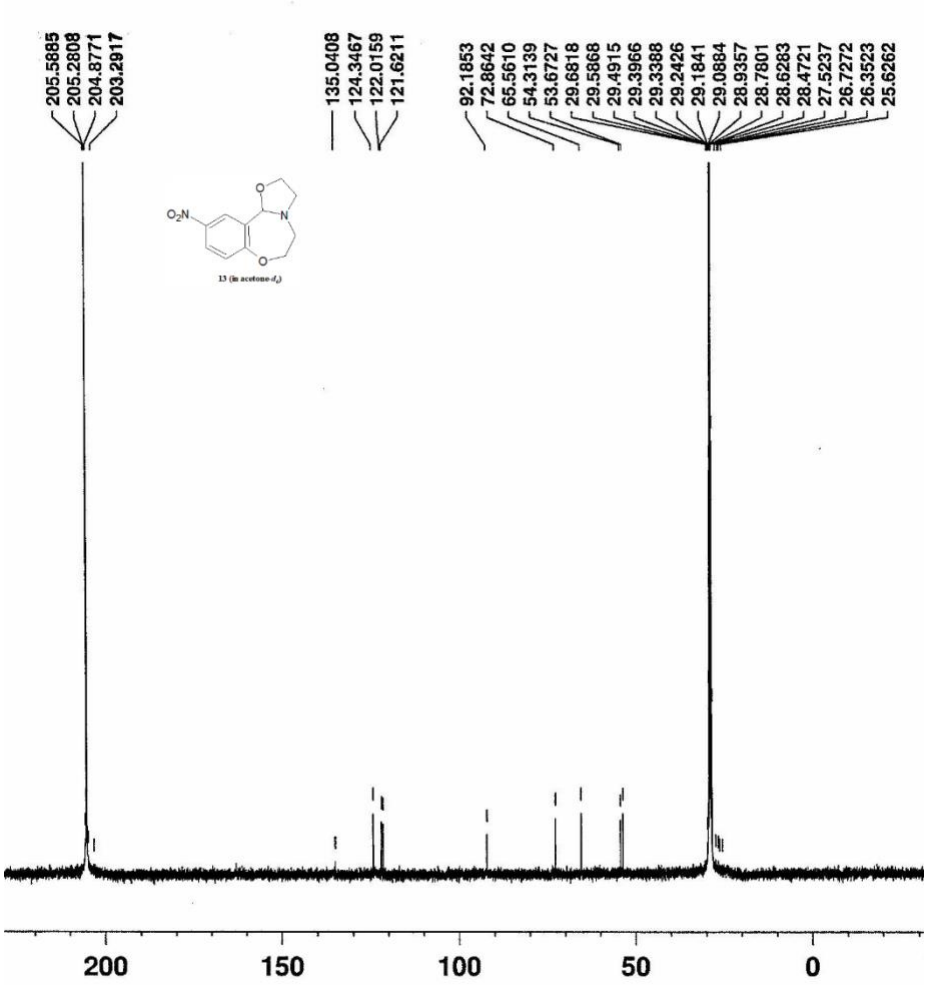

 

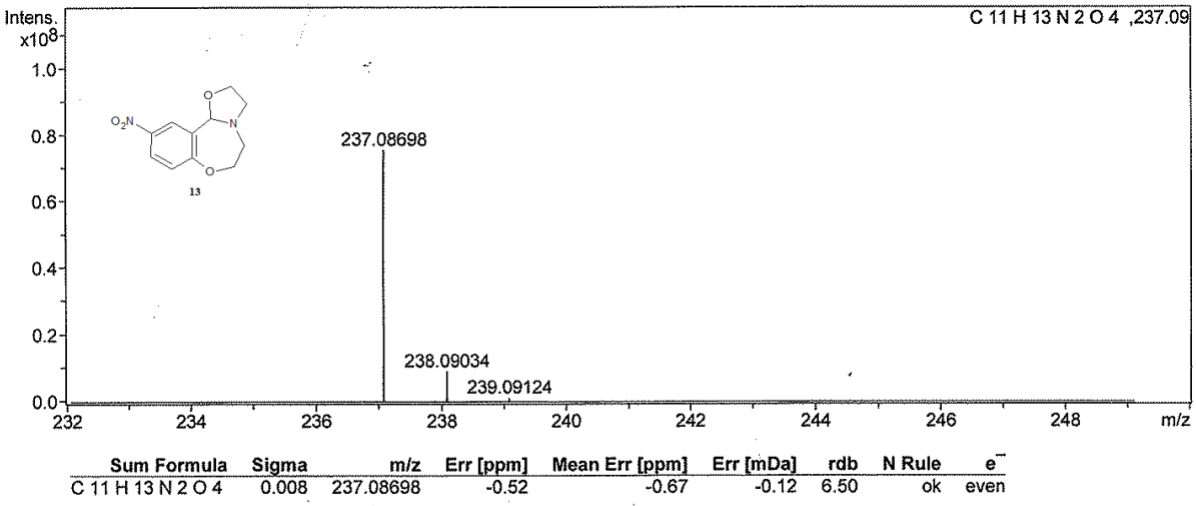


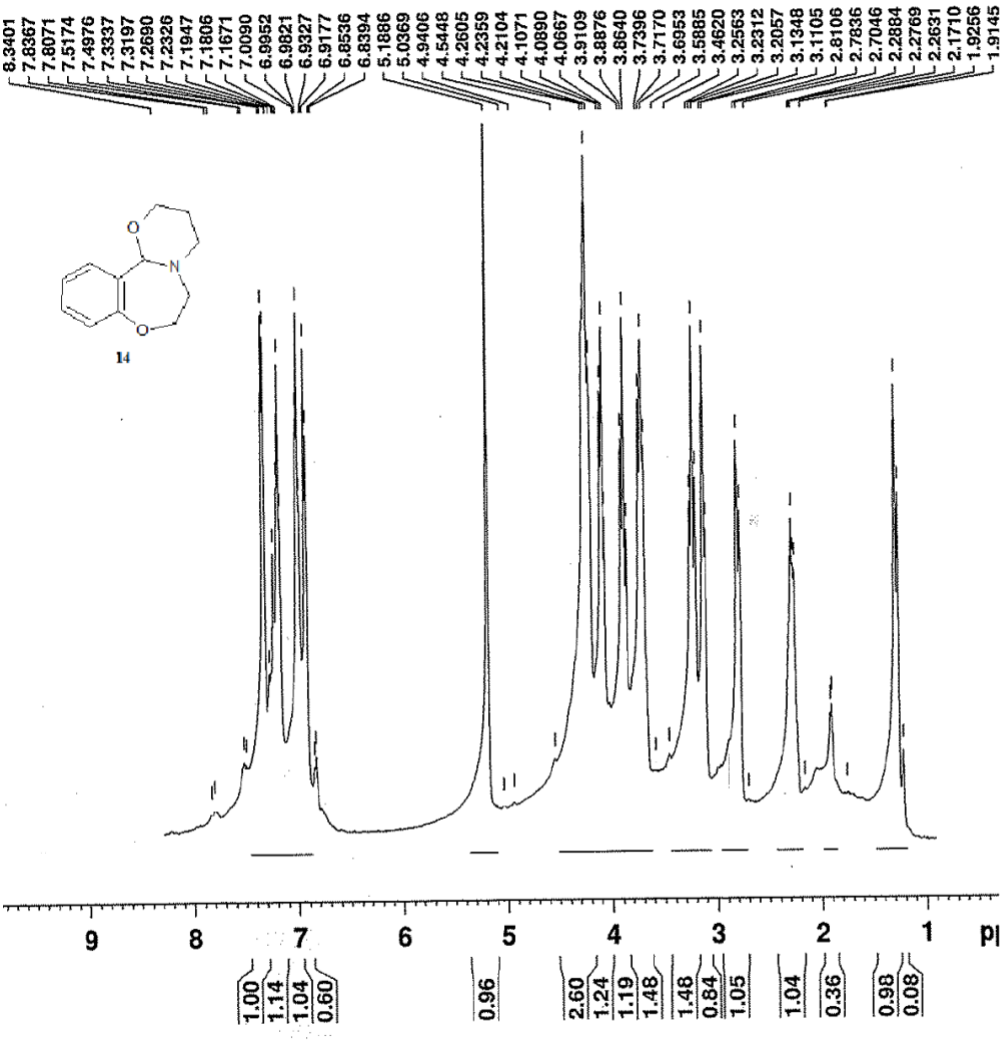

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 15 H 16 N 1 O 2 | 0.003 | 242.11756 | -1.16 | -1.30 | -0.28 | 8.50 | ok | even |



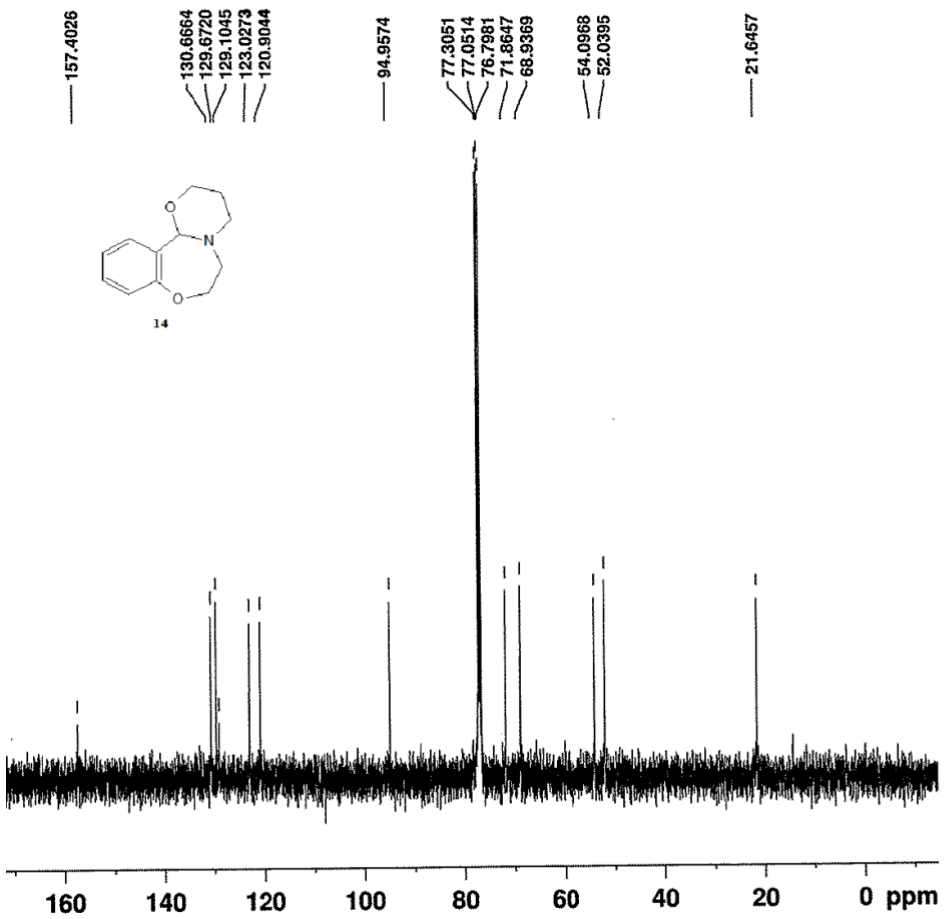


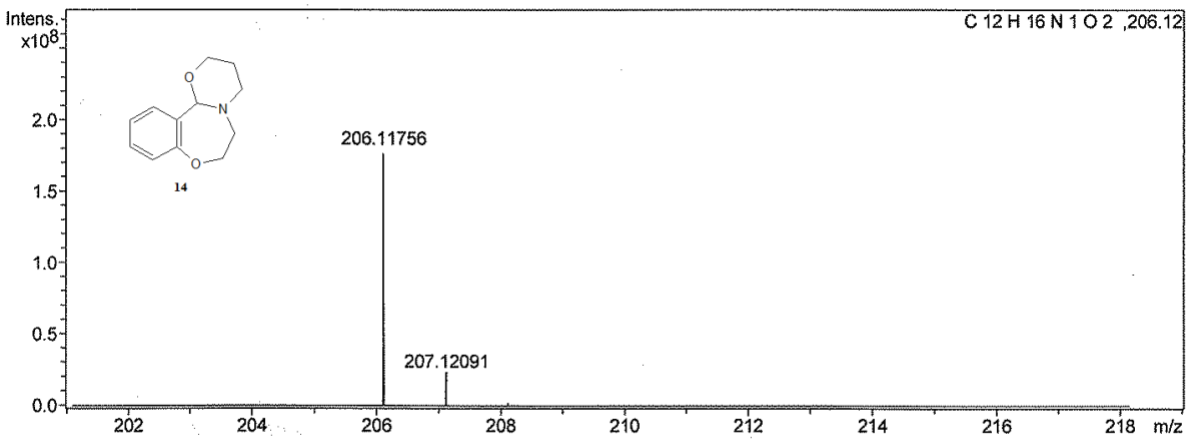




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 11 H 13 N 2 O 4 | 0.008 | 237.08698 | -0.52 | -0.67 | -0.12 | 6.50 | ok | even |

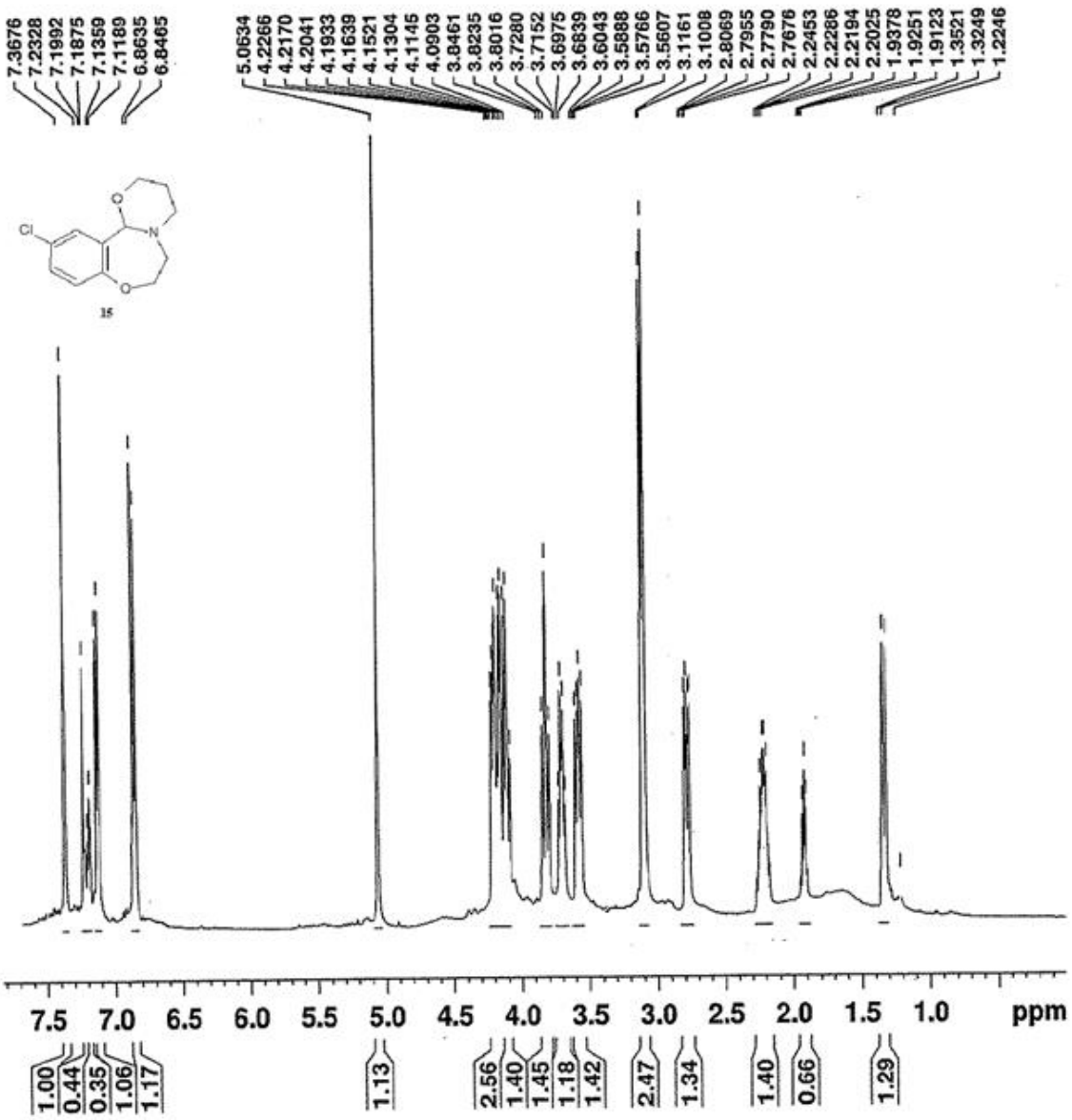


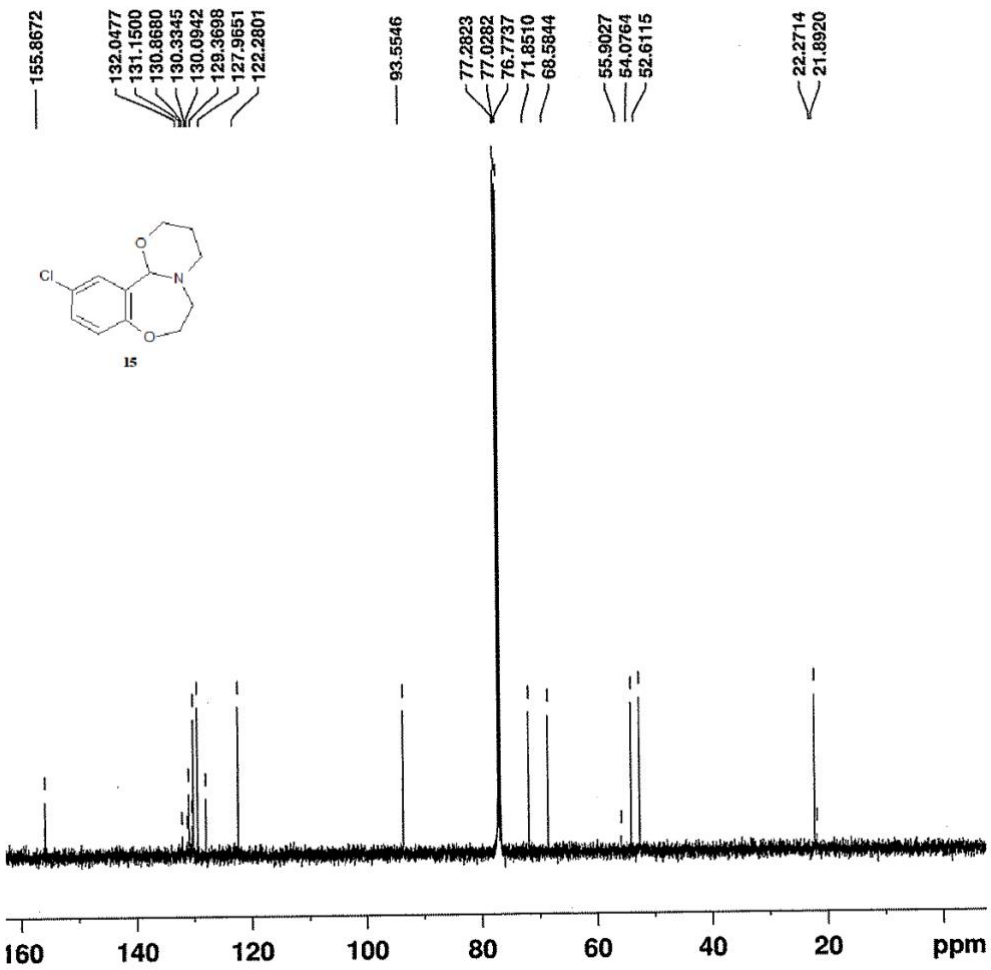


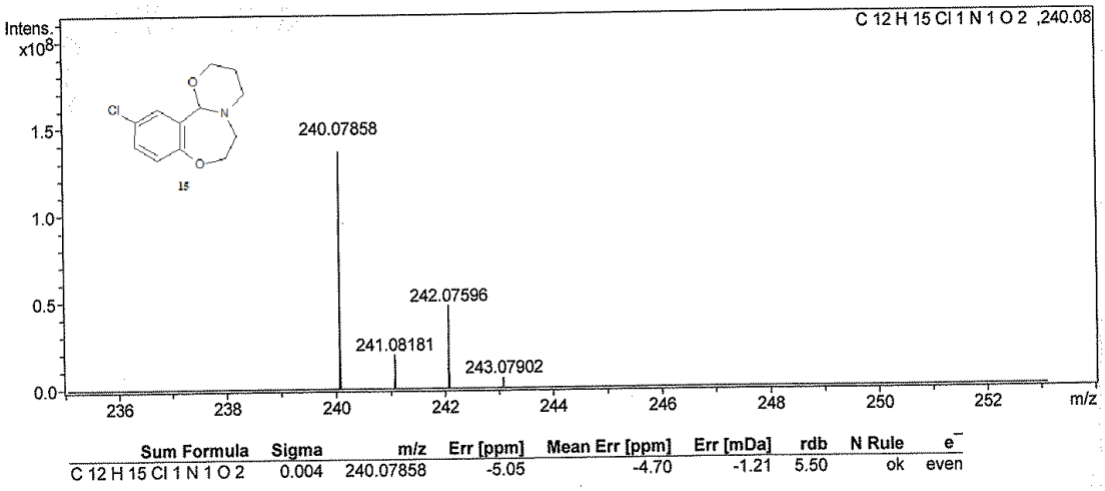




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 16 N 1 O 2 | 0.004 | 206.11756 | 1.40 | 1.23 | 0.29 | 5.50 | ok | even |

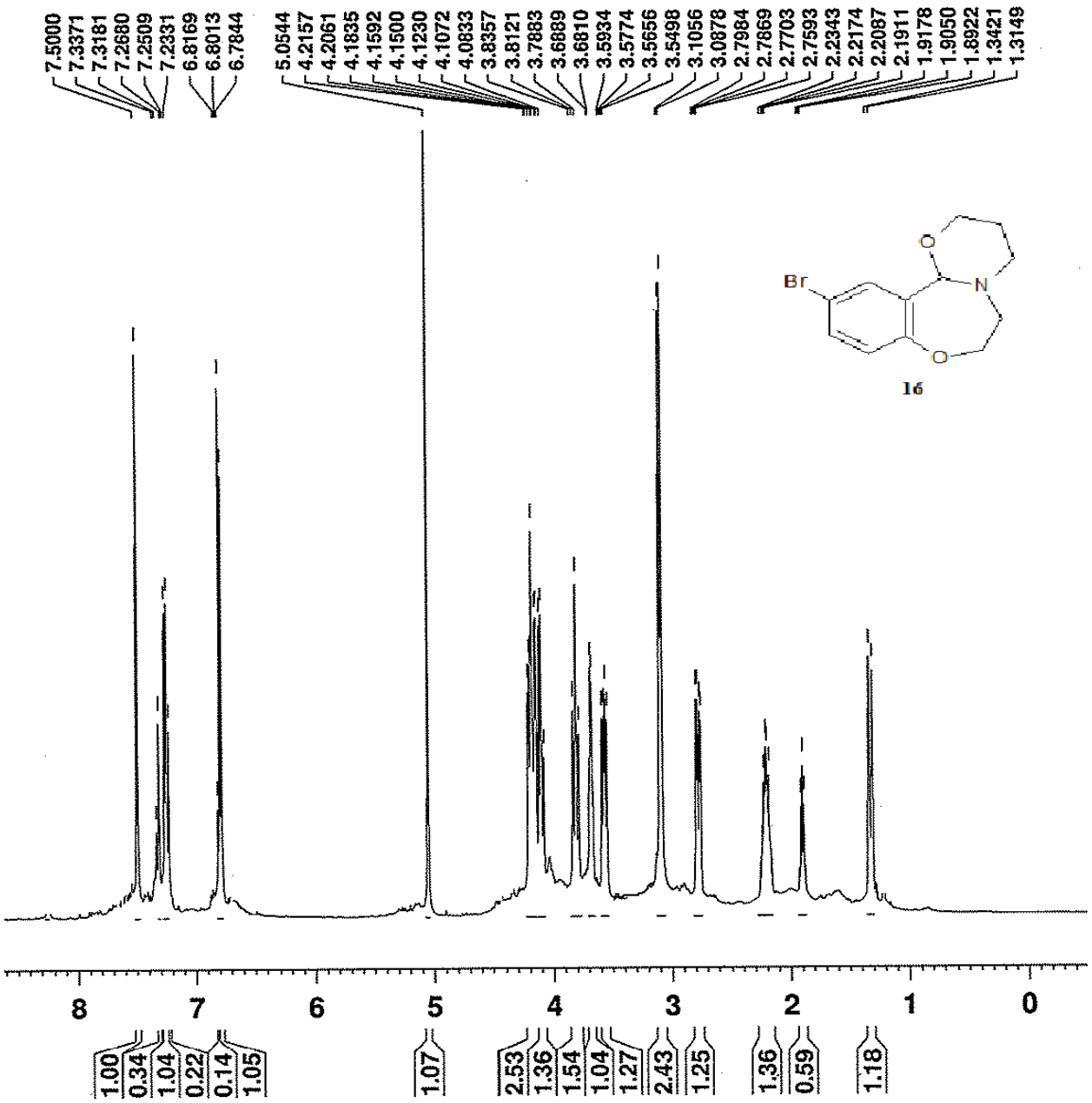


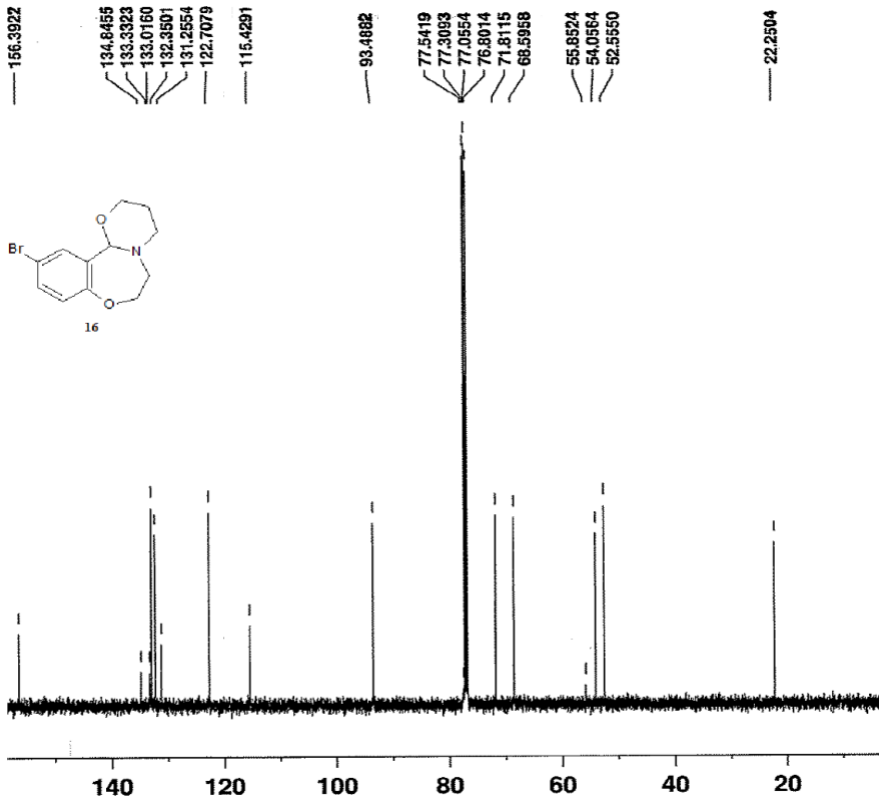

 

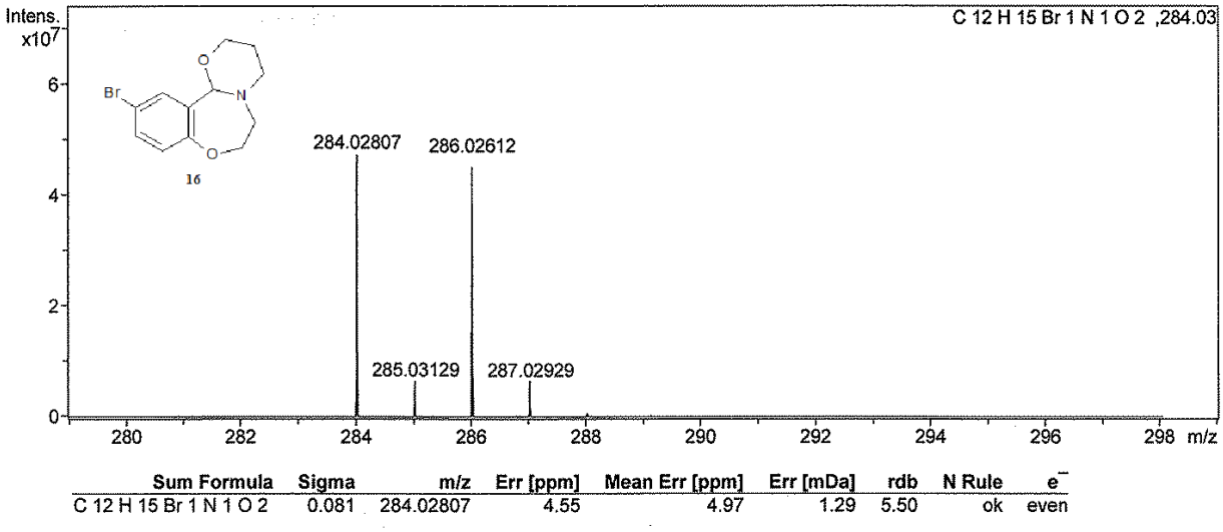


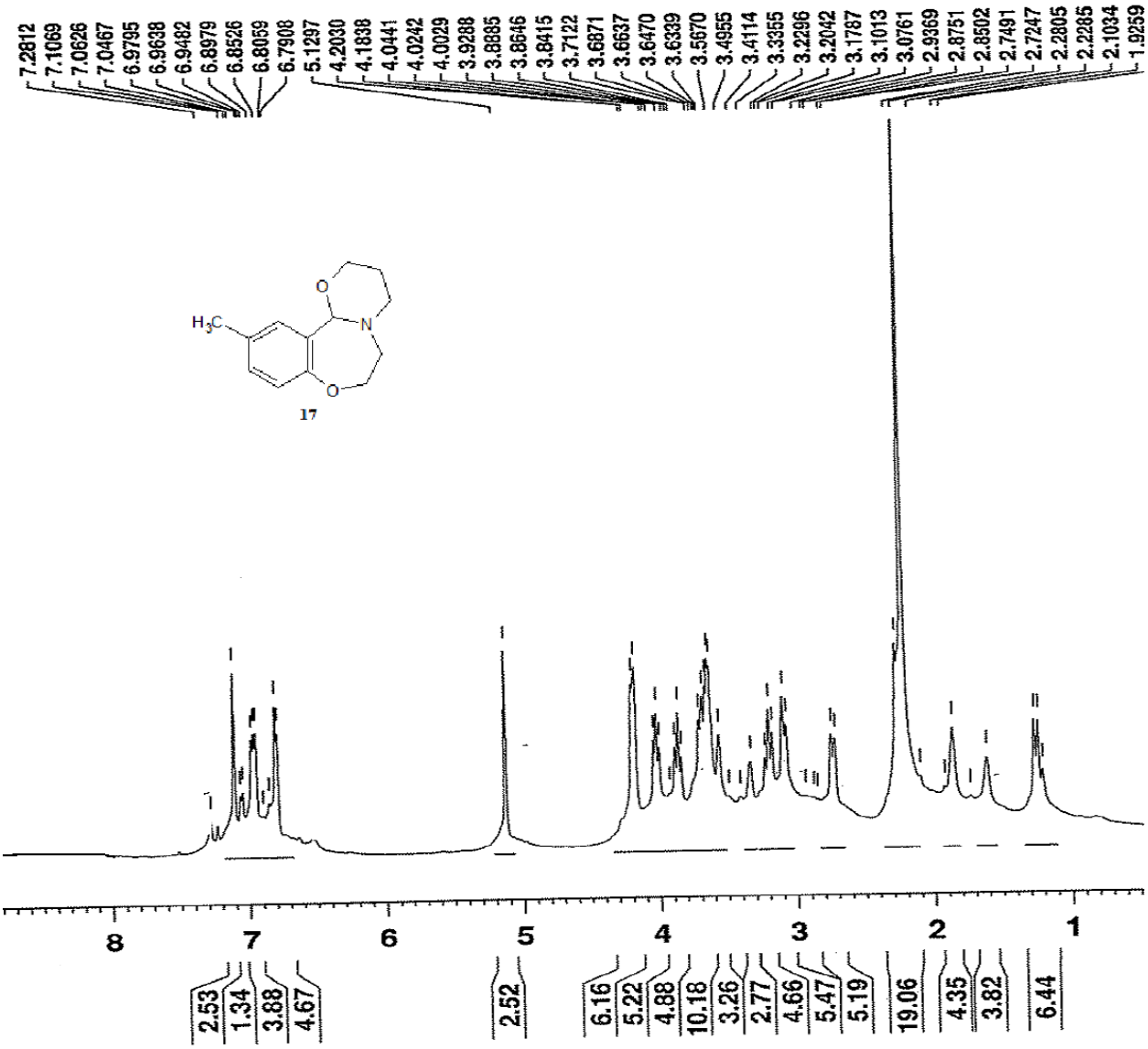

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 15 Cl 1 N 1 O 2 | 0.004 | 240.07858 | -5.05 | -4.70 | -1.21 | 5.50 | ok | even |



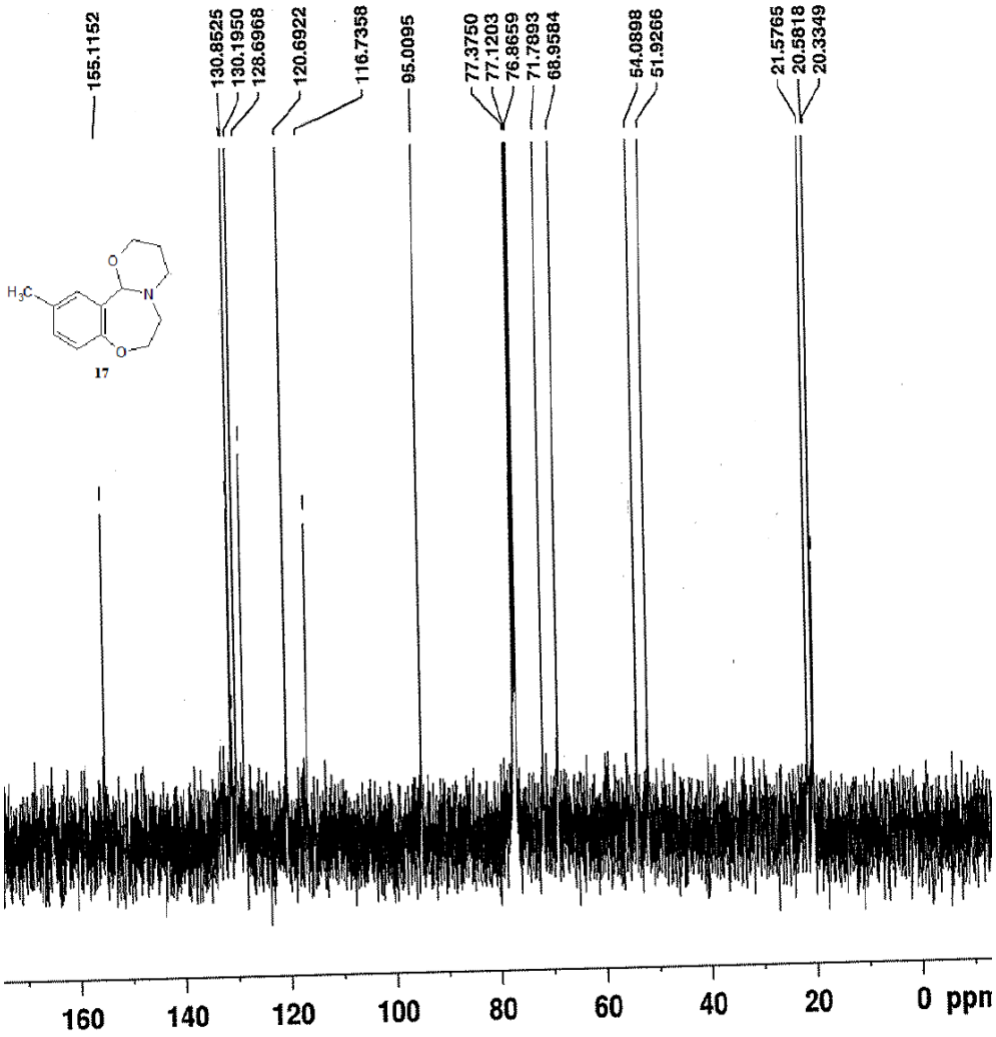


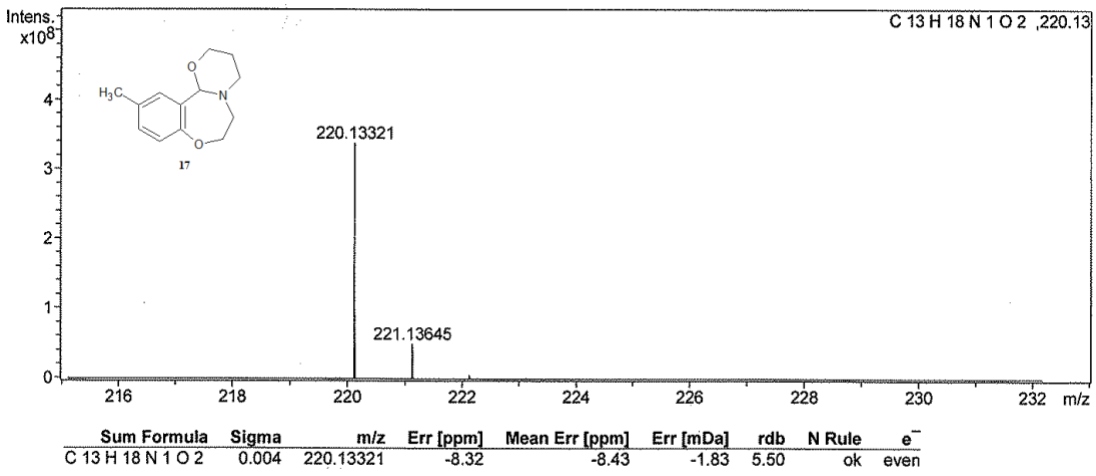




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 15 Br 1 N 1 O 2 | 0.081 | 284.02807 | 4.55 | 4.97 | 1.29 | 5.50 | ok | even |

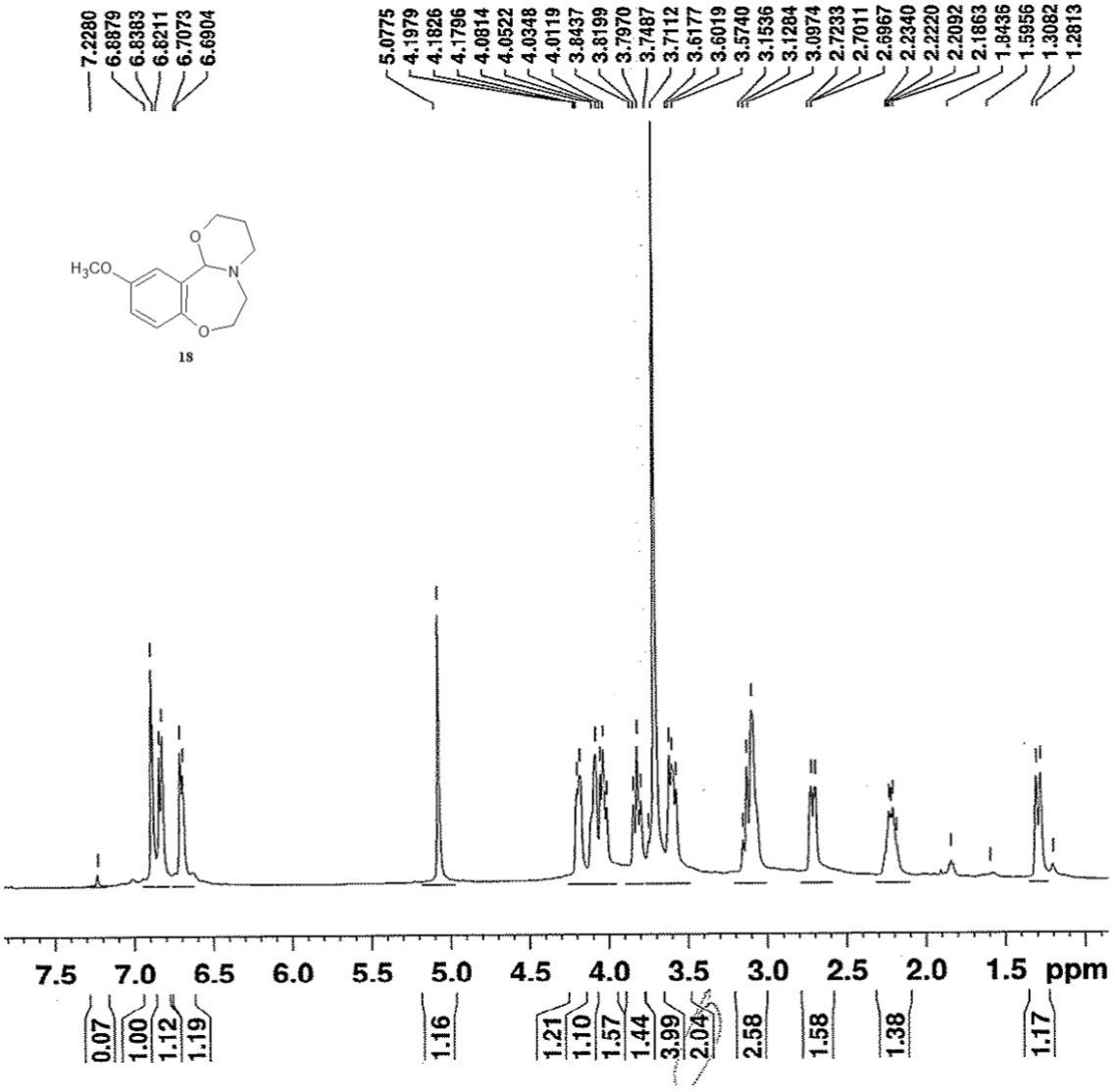


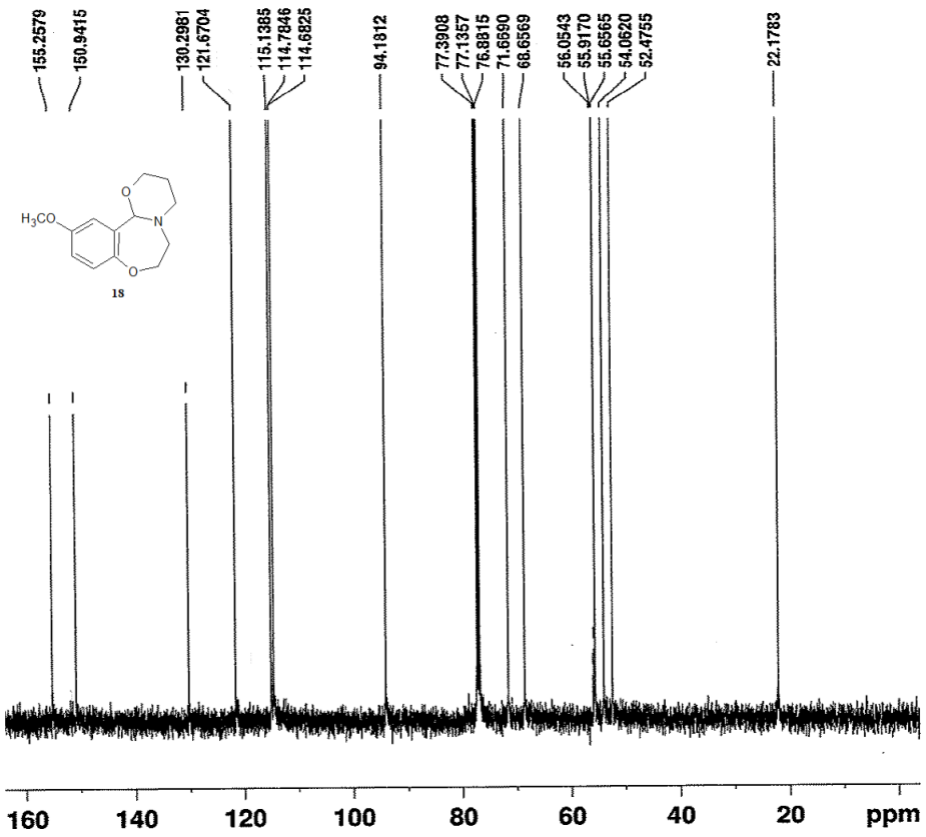


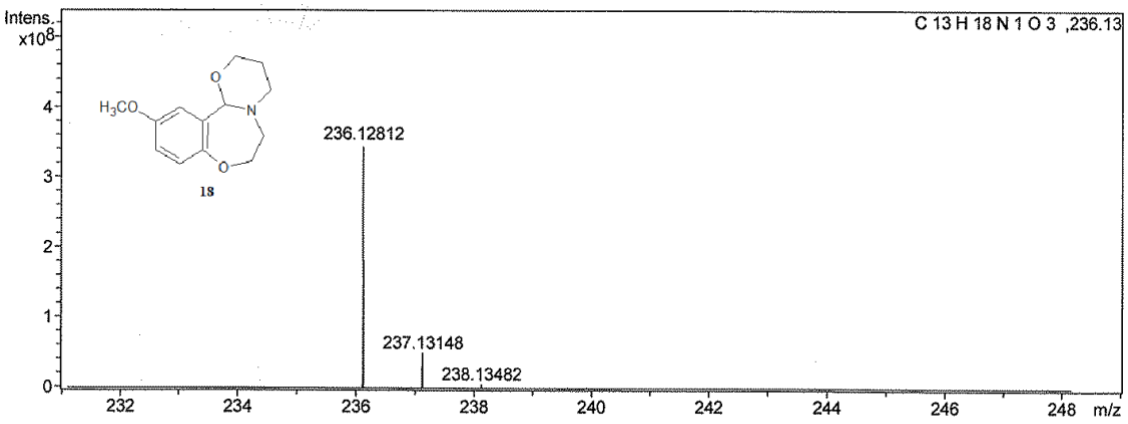




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 13 H 18 N 1 O 2 | 0.004 | 220.13321 | -8.32 | -8.43 | -1.83 | 5.50 | ok | even |

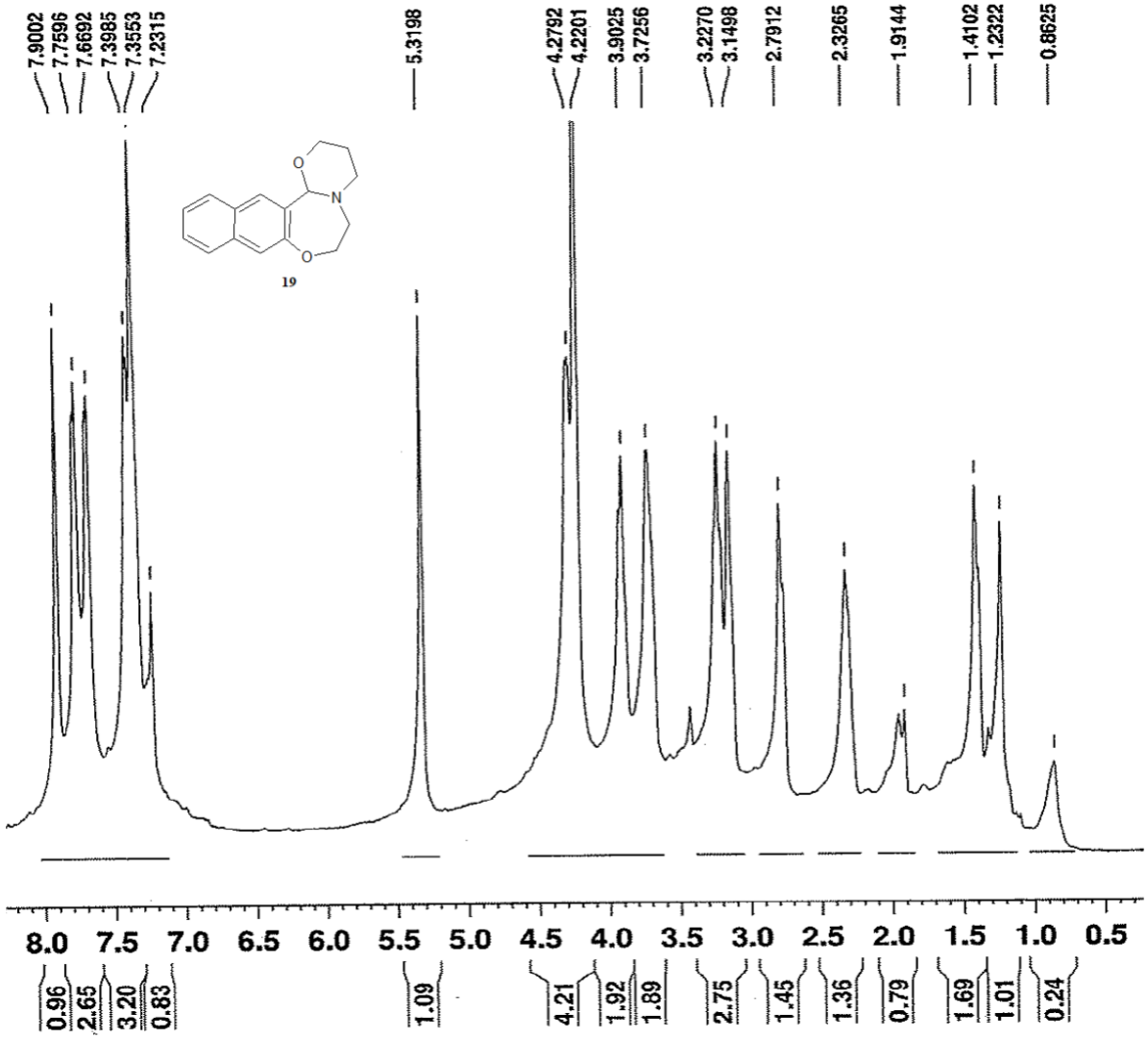


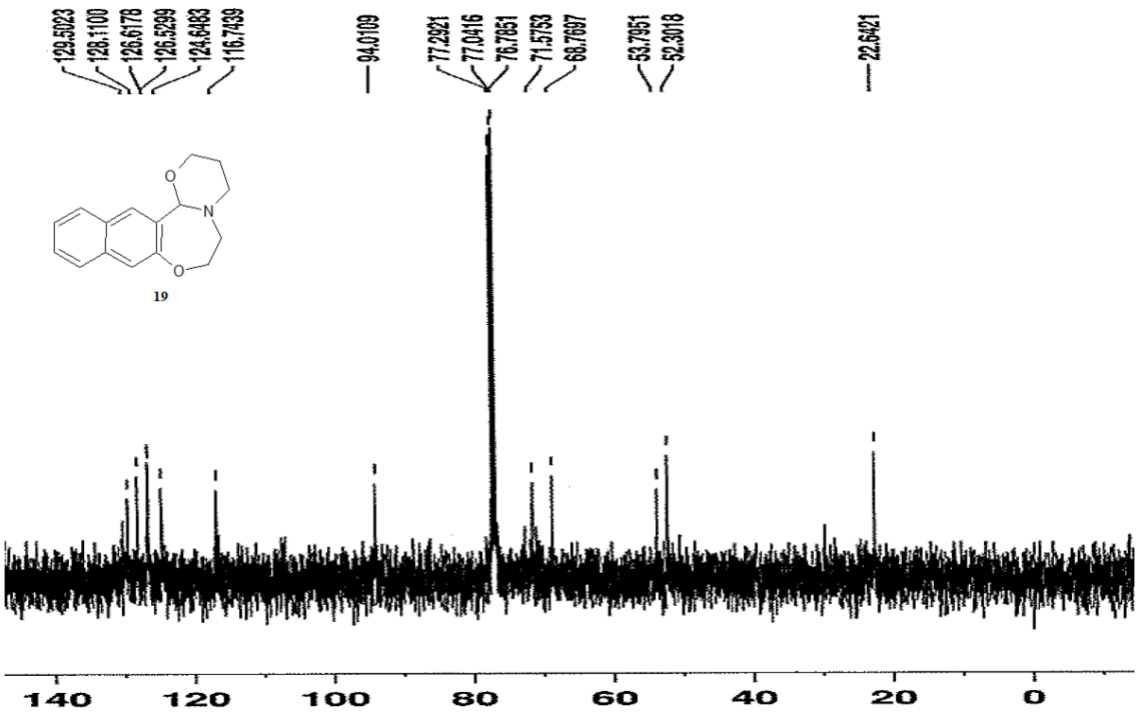


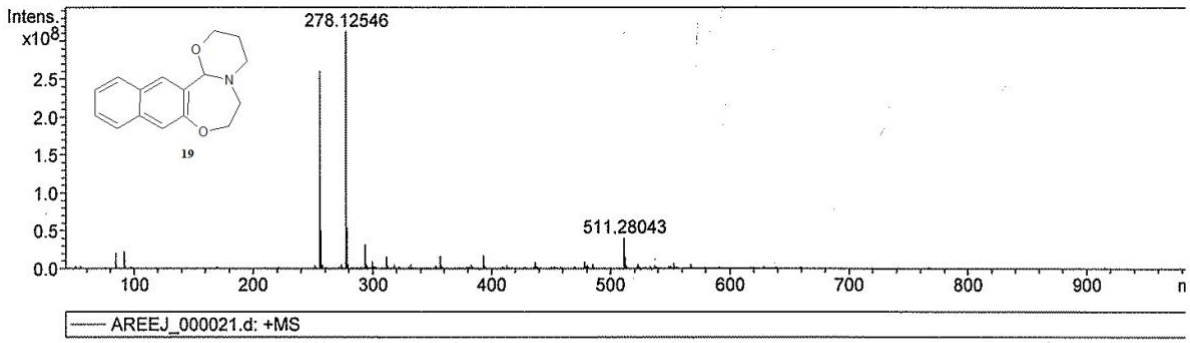




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 13 H 18 N 1 O 3 | 0.007 | 236.12812 | 8.79 | 8.14 | 2.08 | 5.50 | ok | even |



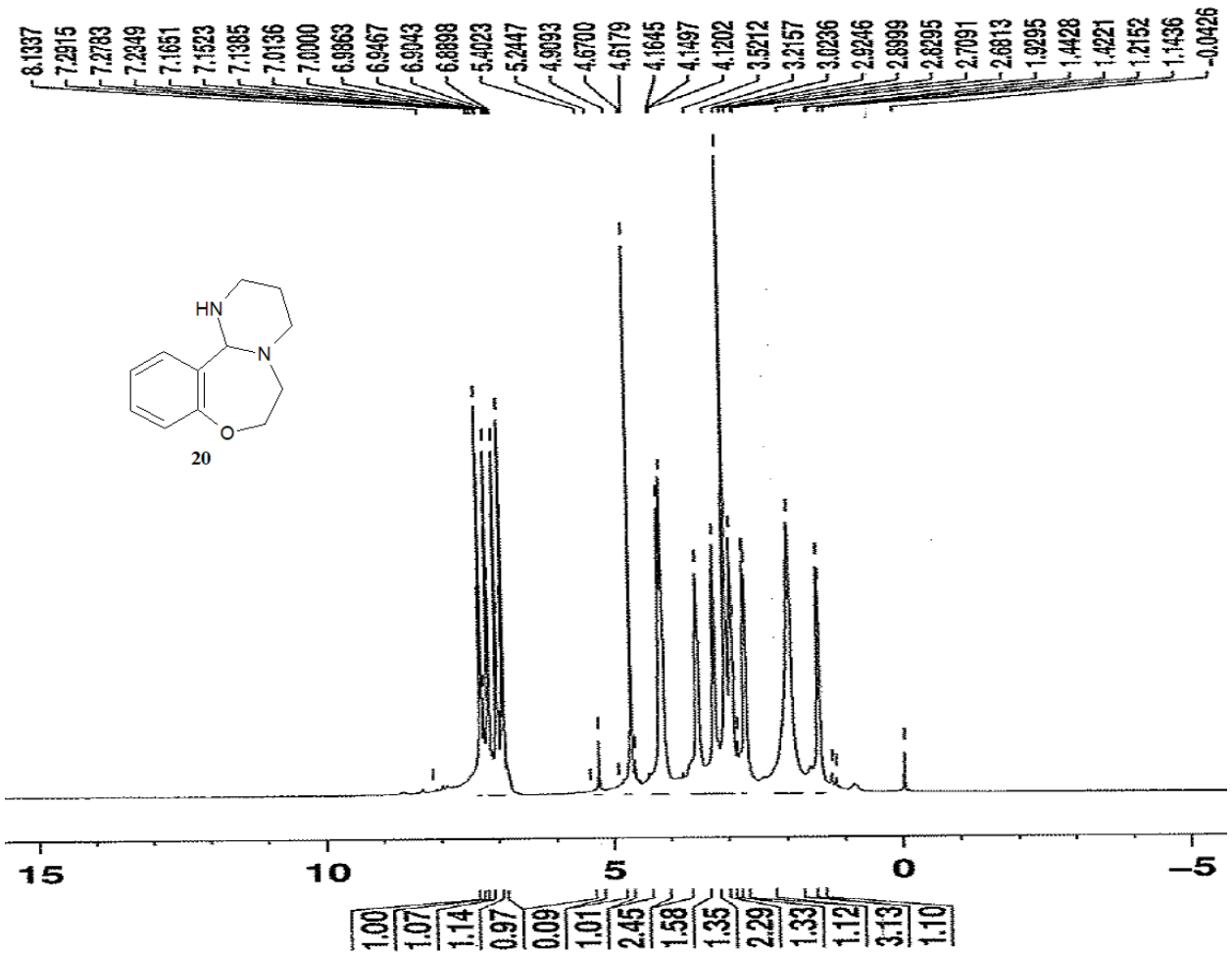

 

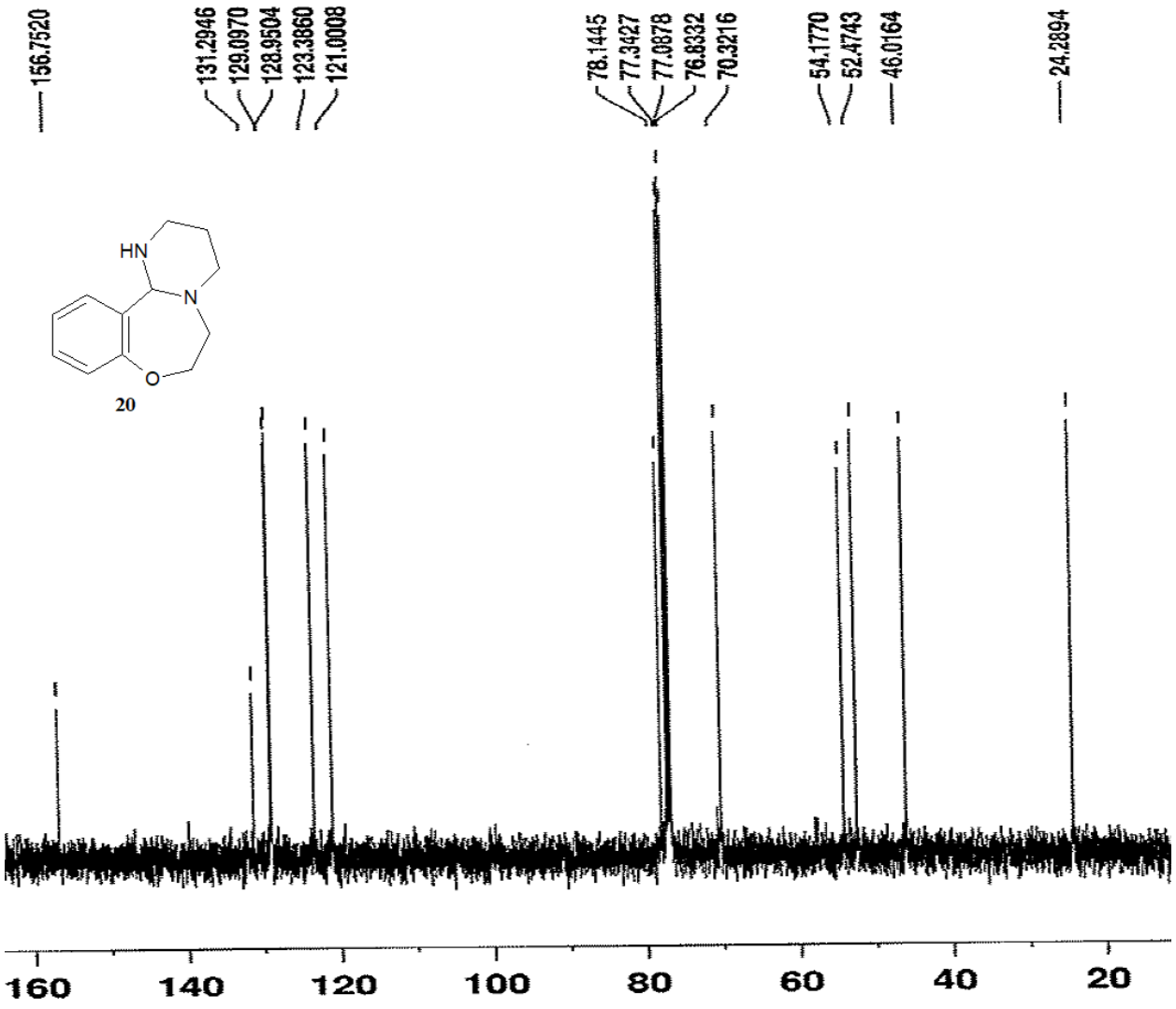


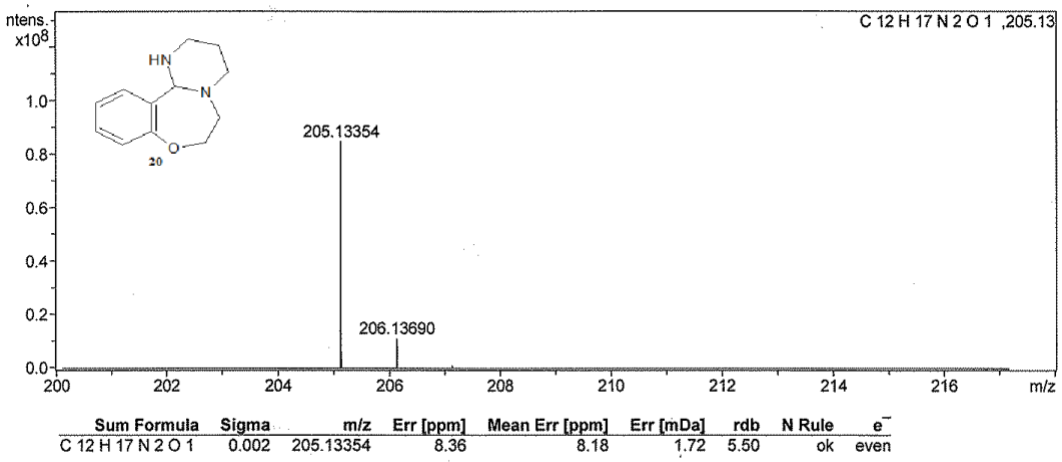




| # | m/z | I | I % |
|---|---|---|---|
| 1 | 256.14266 | 271562658 | 86.7 |
| 2 | 257.14602 | 50335963 | 16.1 |
| 3 | 258.14981 | 4283828 | 1.4 |
| 4 | 274.28414 | 4731094 | 1.5 |
| 5 | 278.09866 | 4711266 | 1.5 |

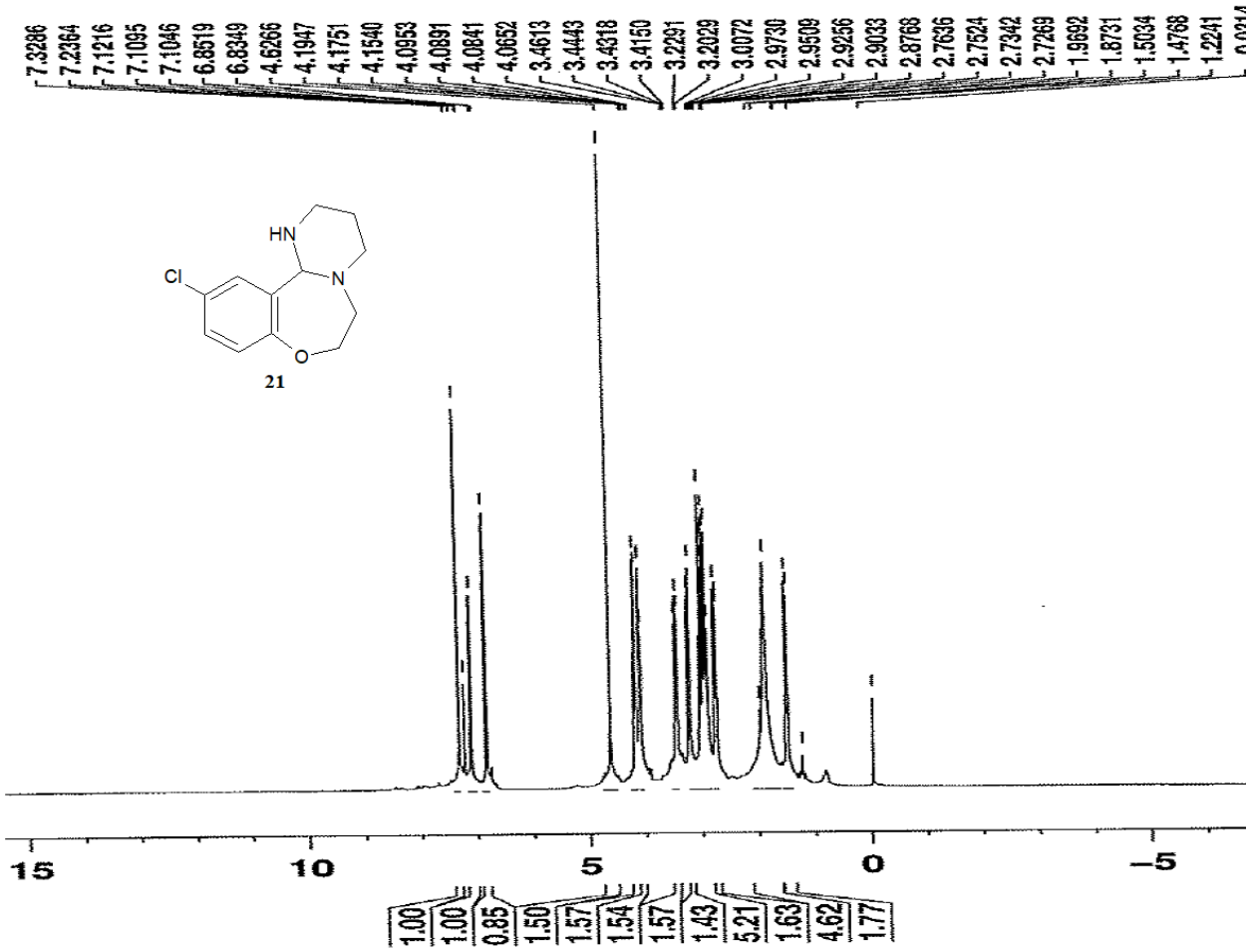
M⁺+H⁺



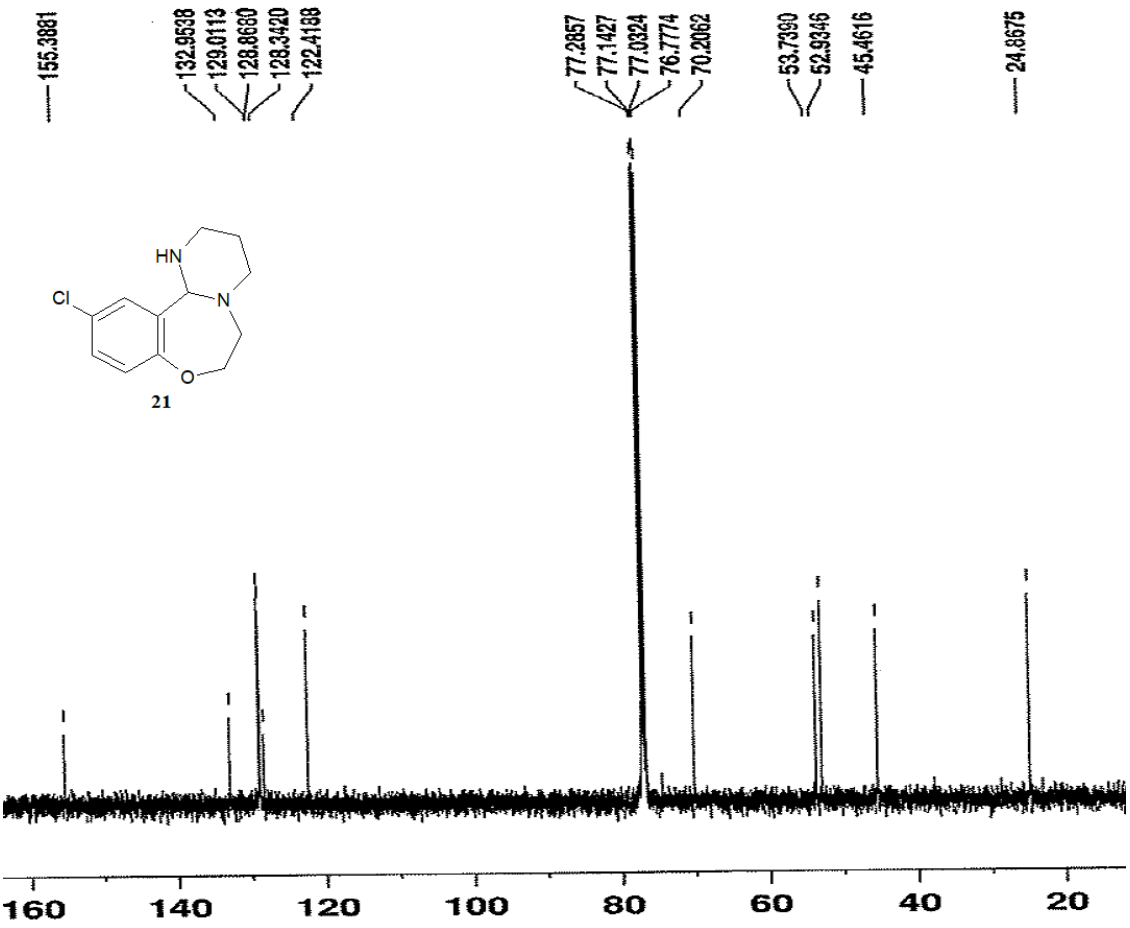


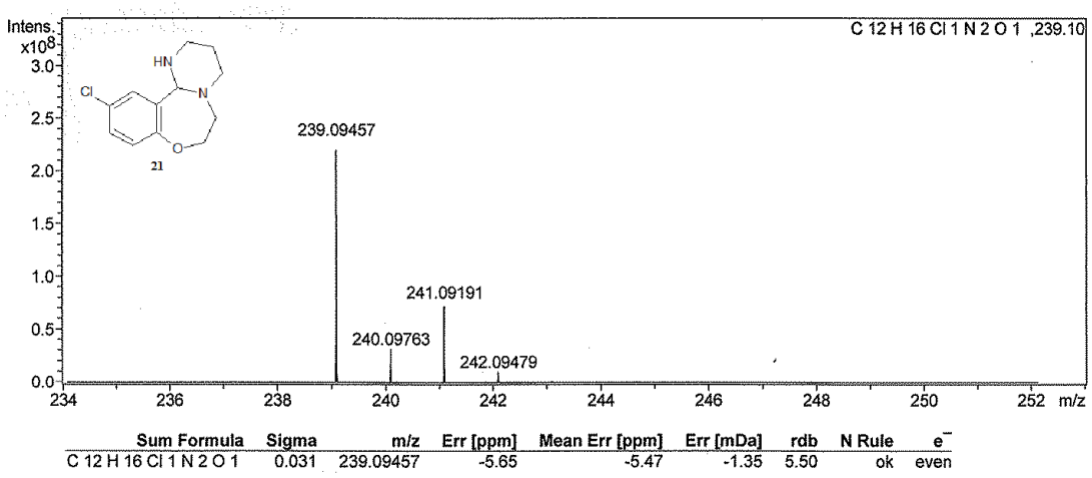




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 17 N 2 O 1 | 0.002 | 205.13354 | 8.36 | 8.18 | 1.72 | 5.50 | ok | even |

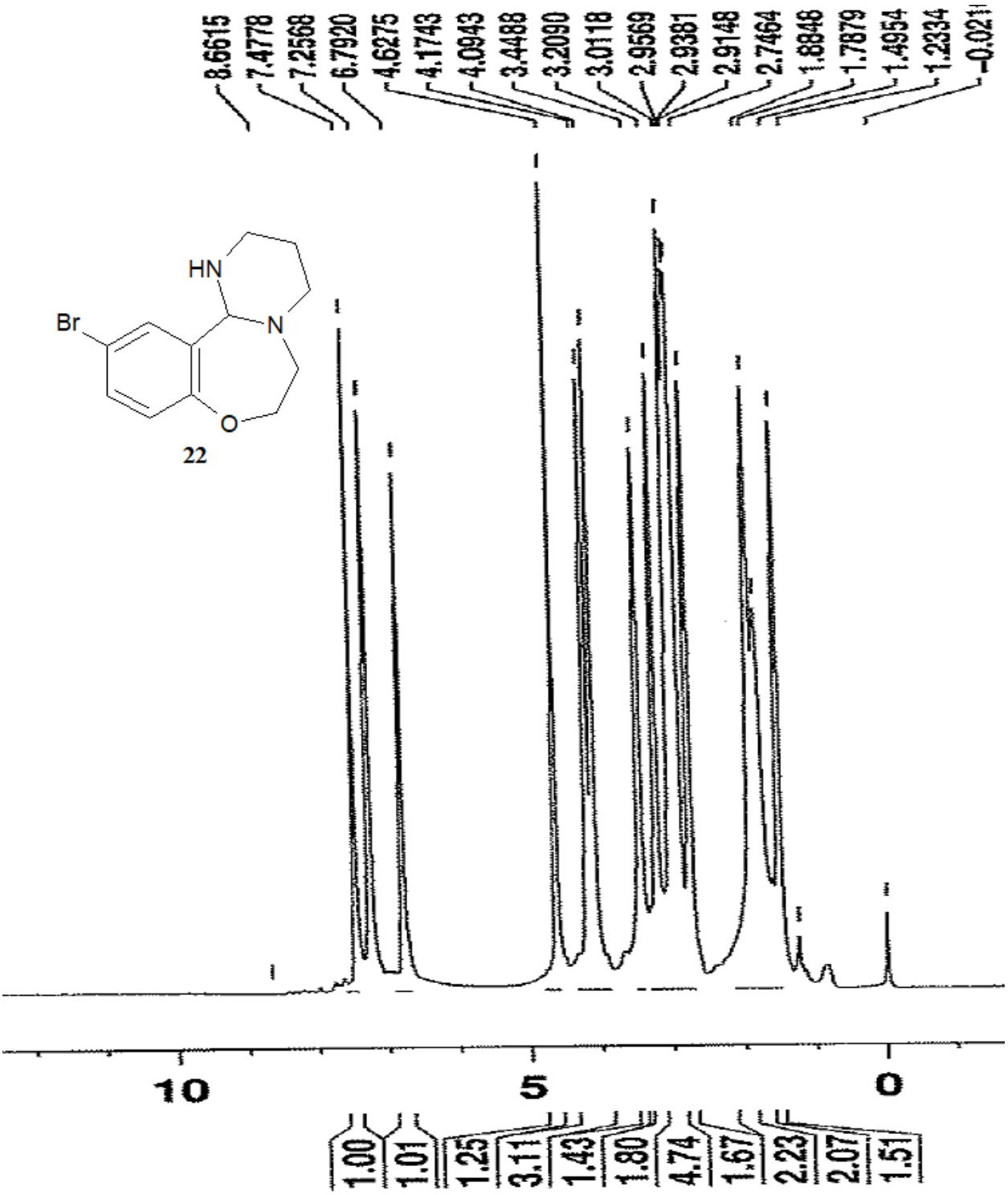


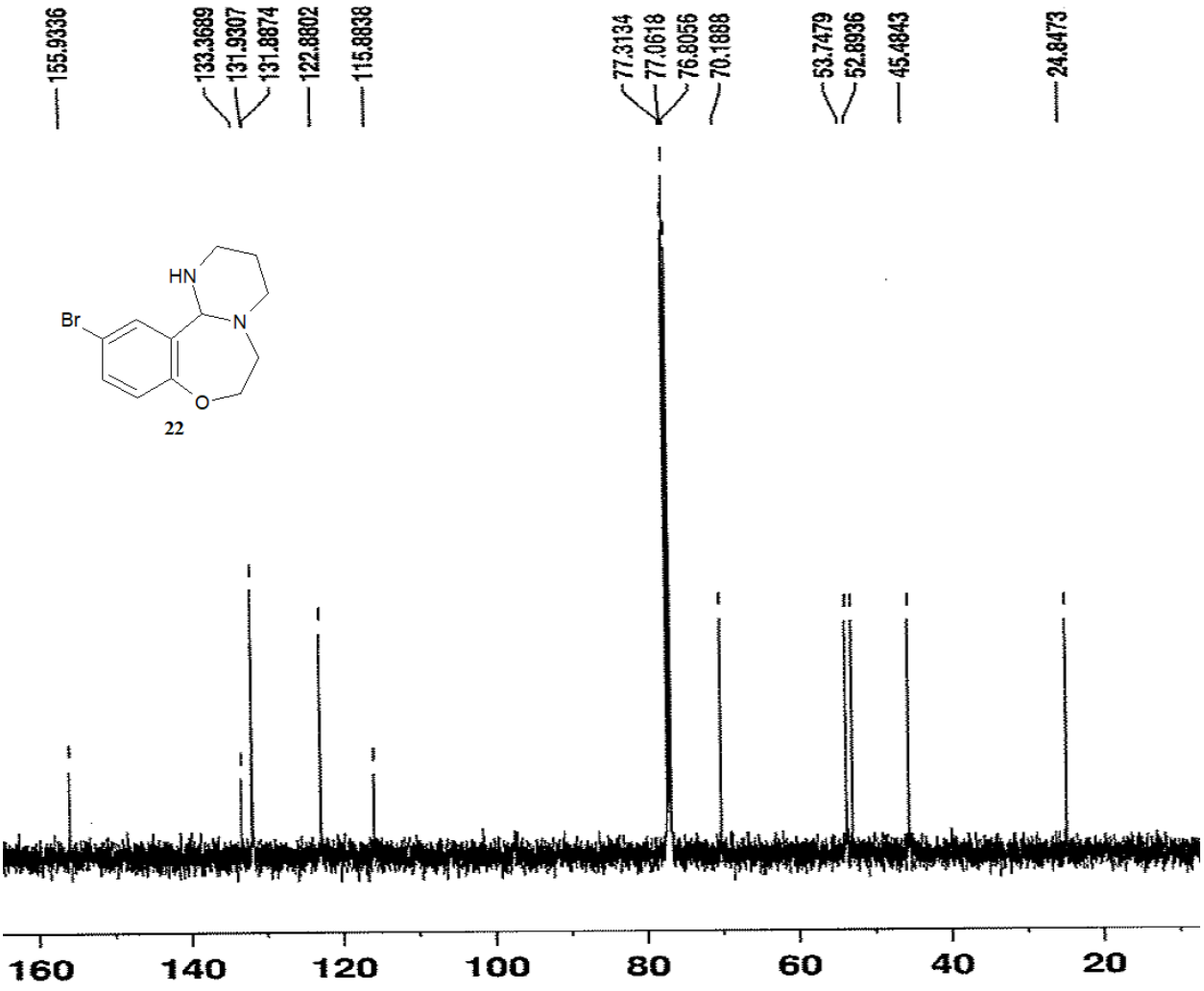

 

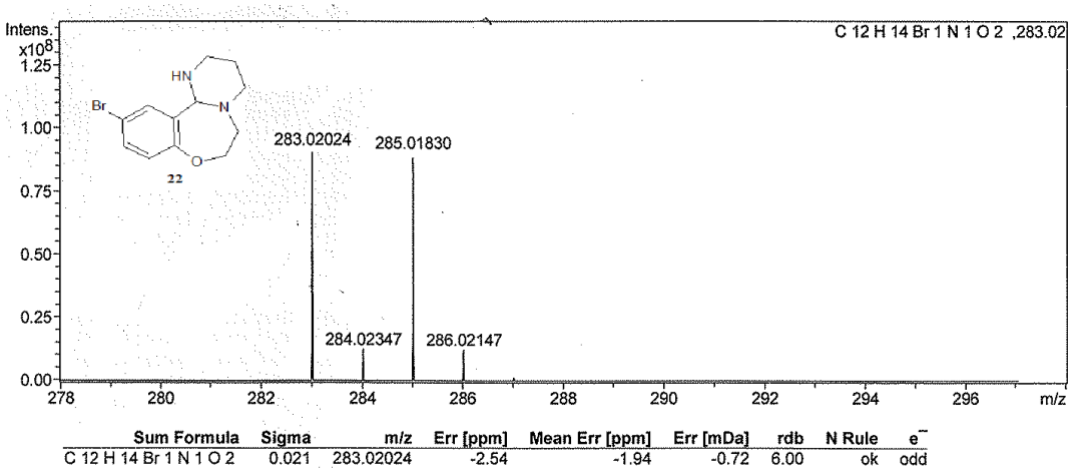


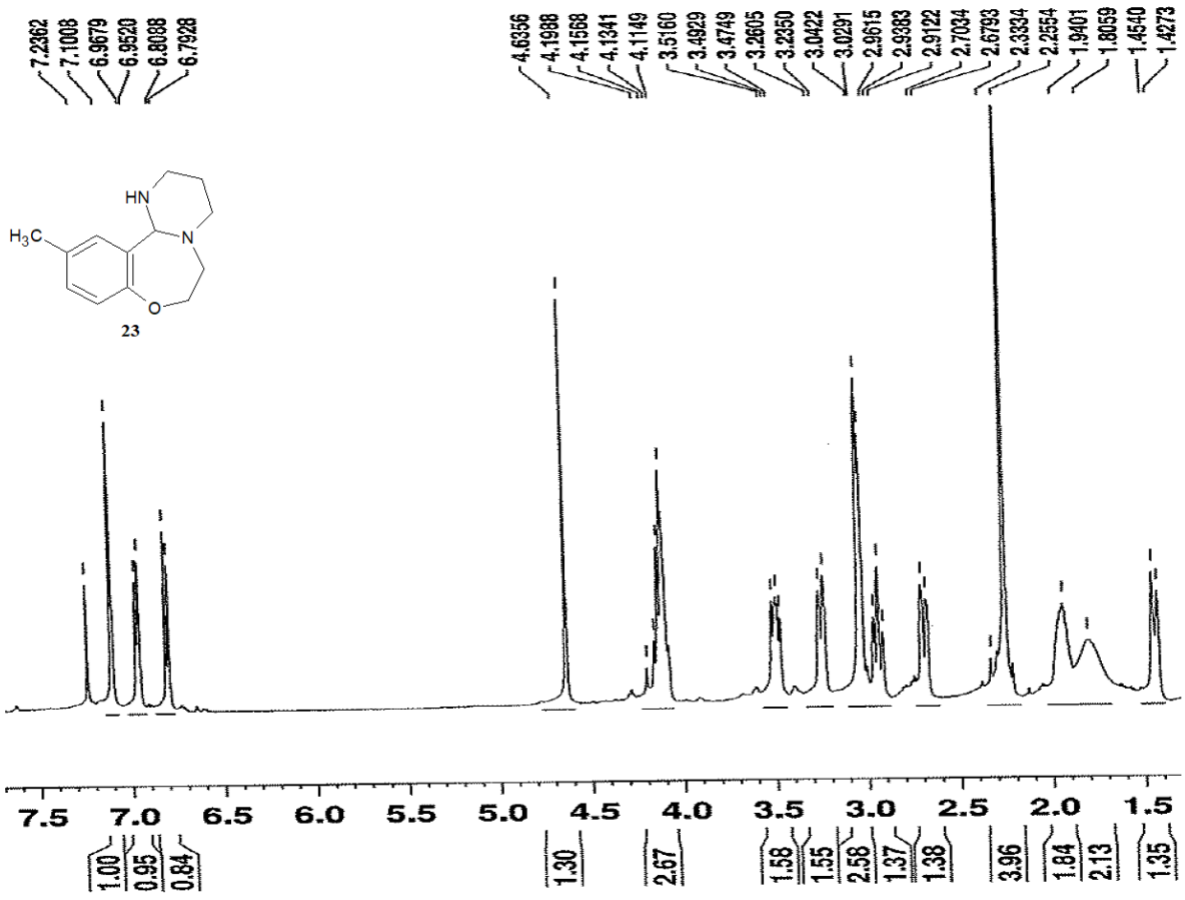

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 16 Cl 1 N 2 O 1 | 0.031 | 239.09457 | -5.65 | -5.47 | -1.35 | 5.50 | ok | even |



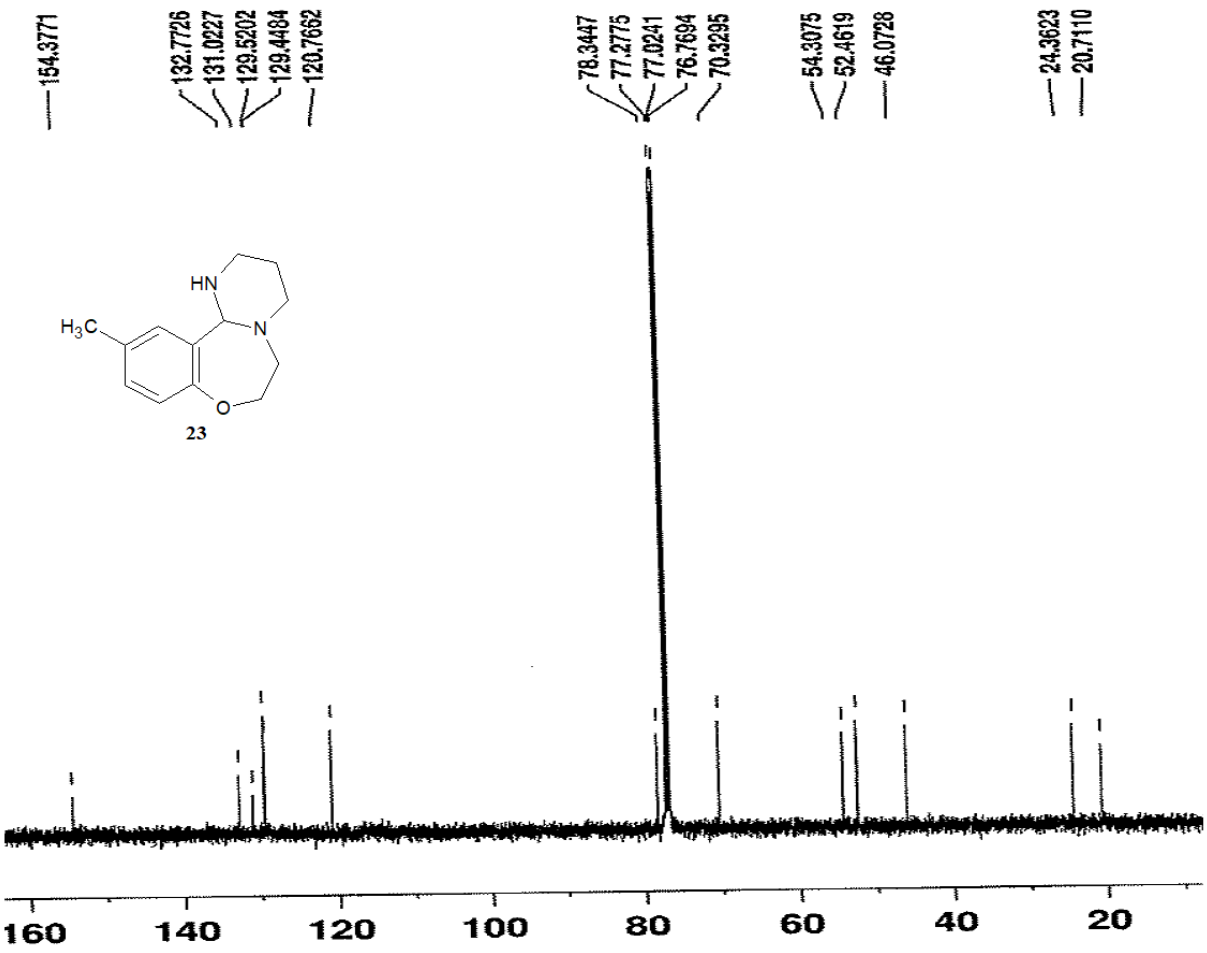


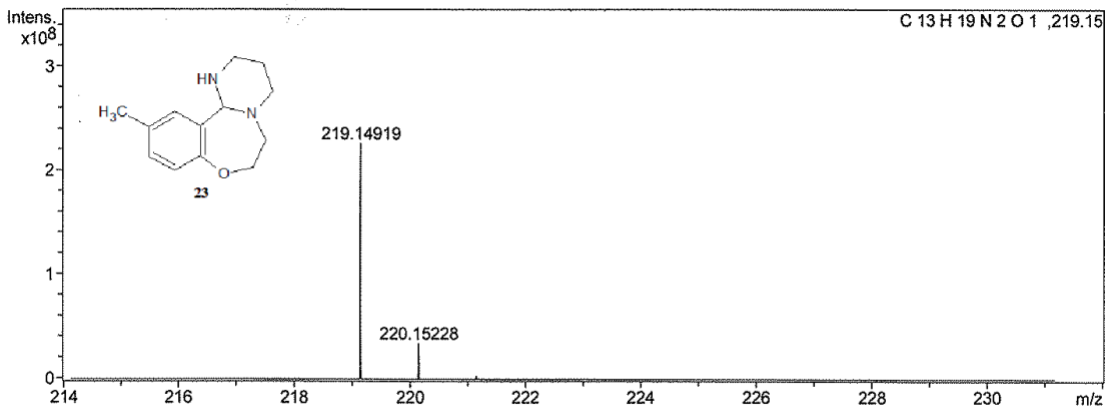




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 12 H 14 Br 1 N 1 O 2 | 0.021 | 283.02024 | -2.54 | -1.94 | -0.72 | 6.00 | ok | odd |

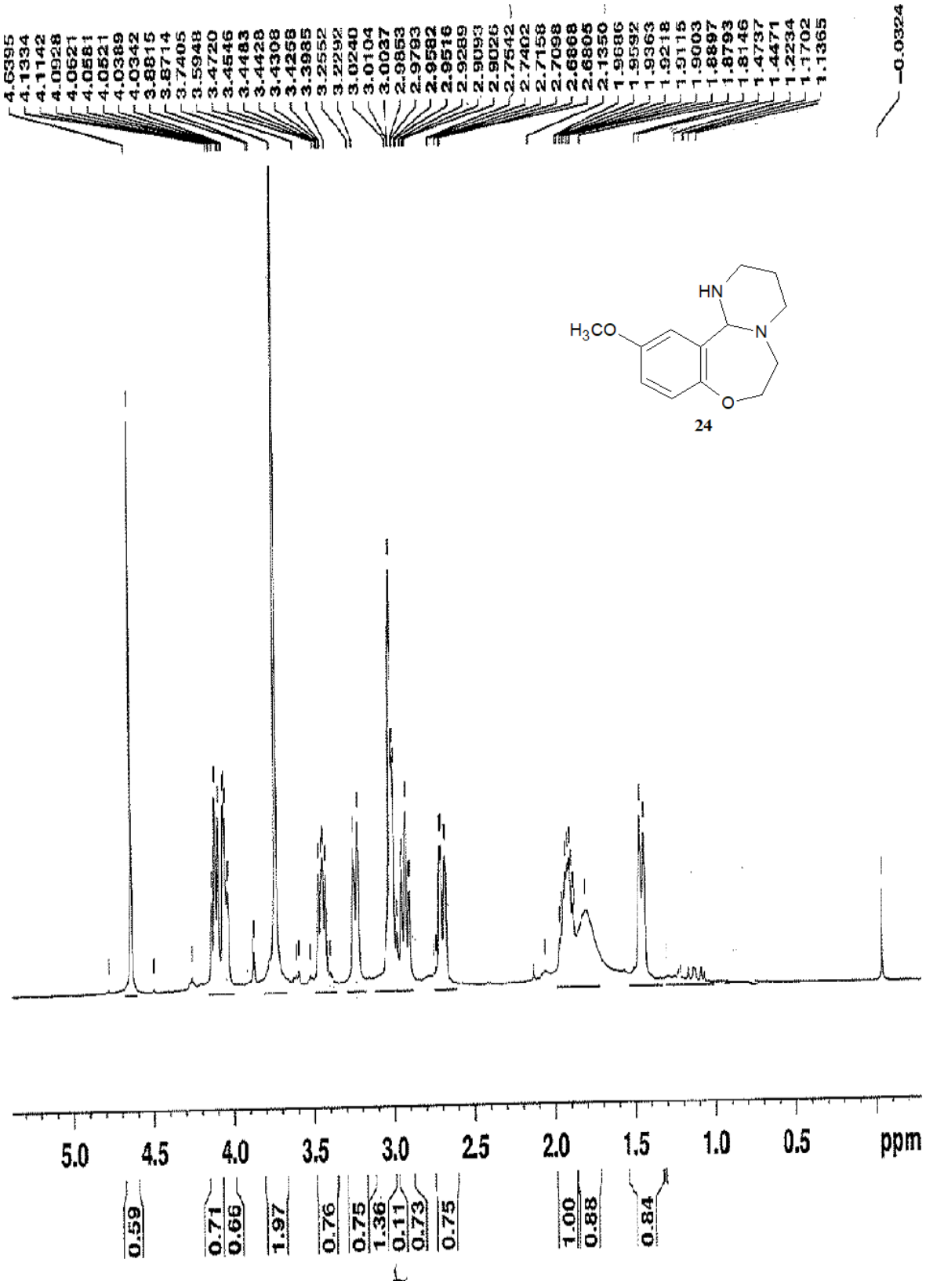


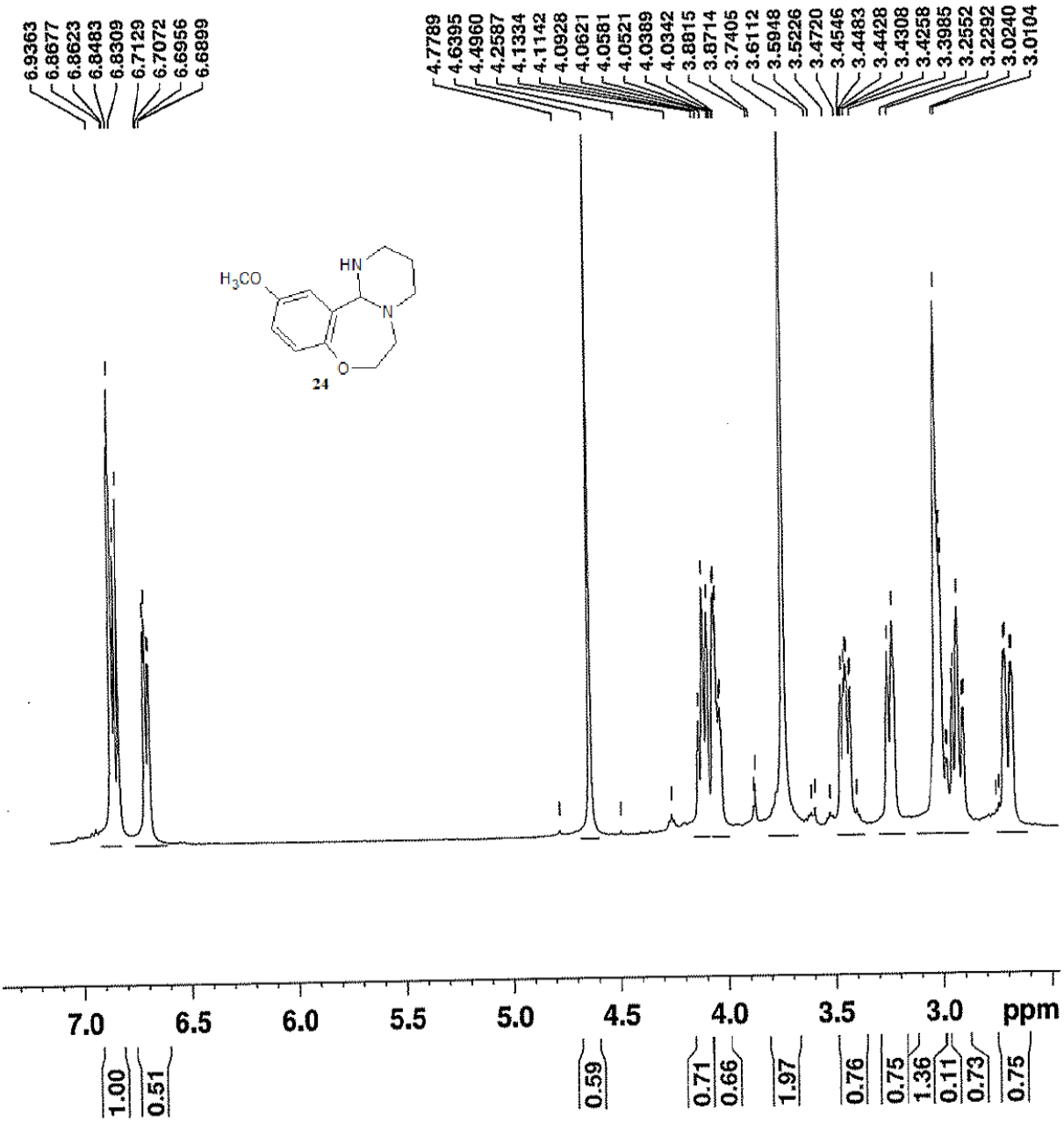


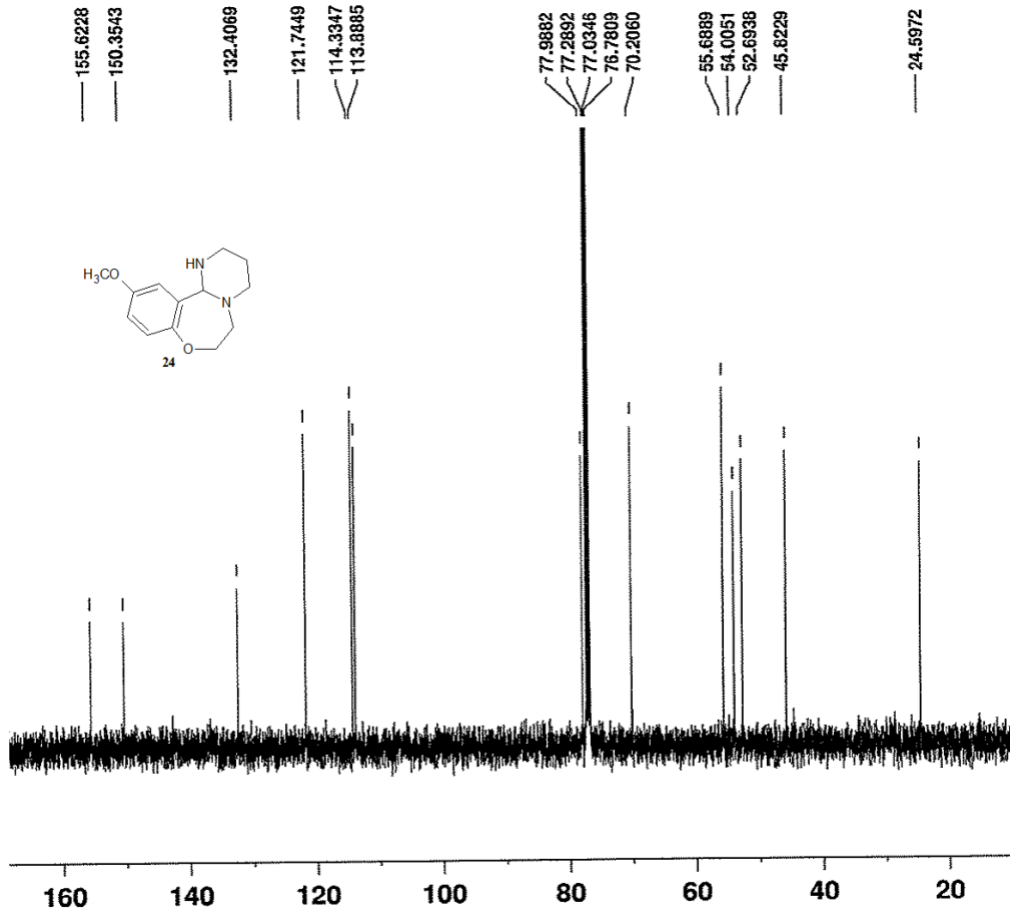



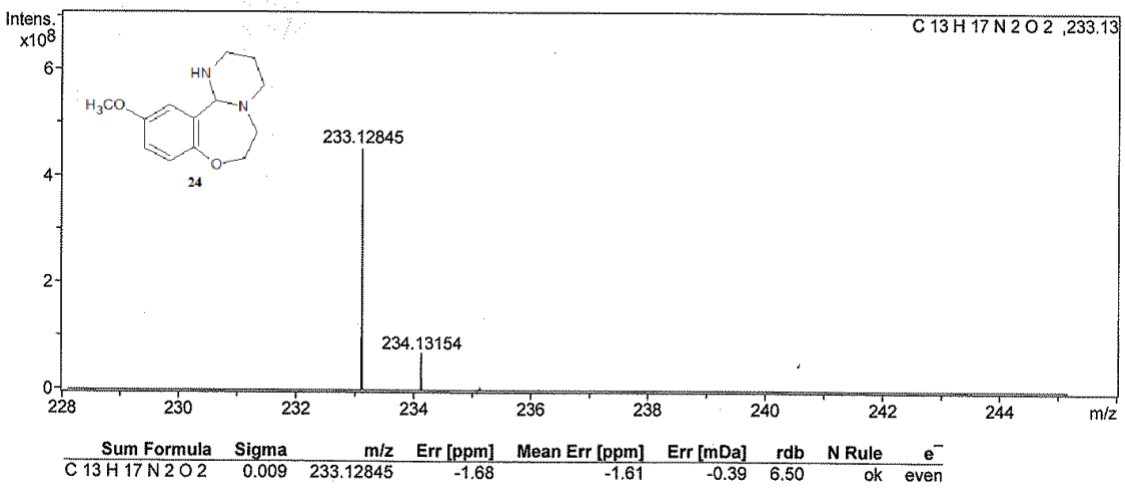

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 13 H 19 N 2 O 1 | 0.005 | 219.14919 | 0.47 | 0.32 | 0.10 | 5.50 | ok | even |



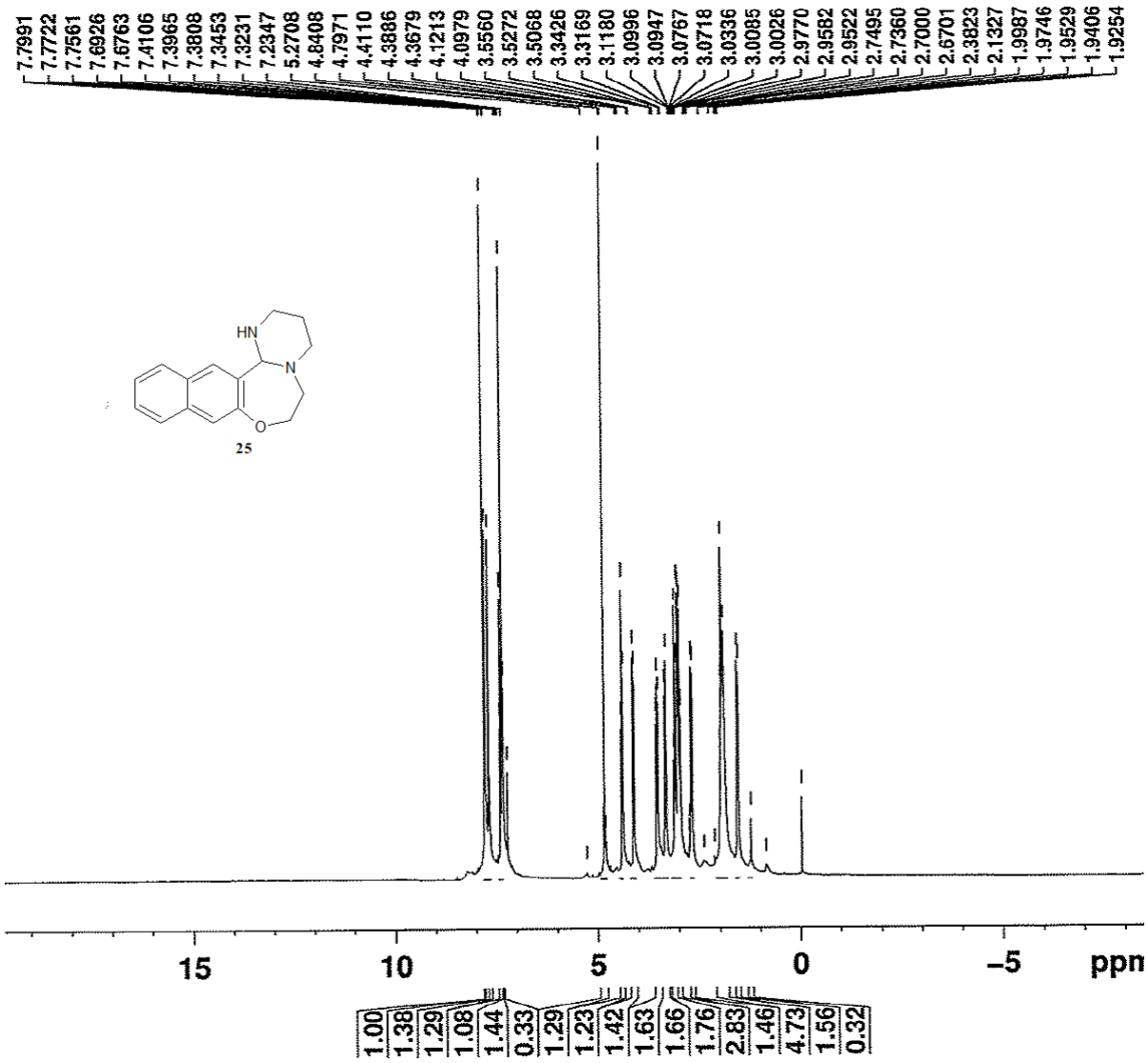

Page S51



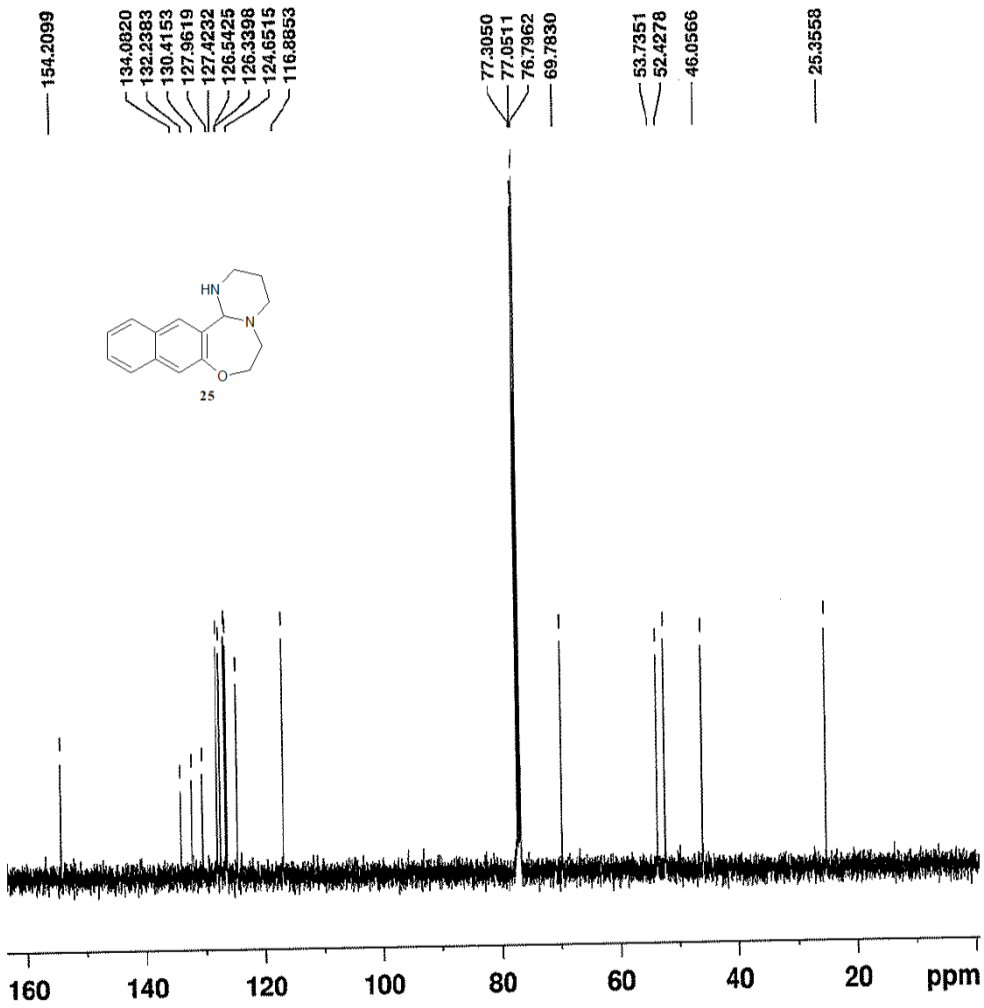


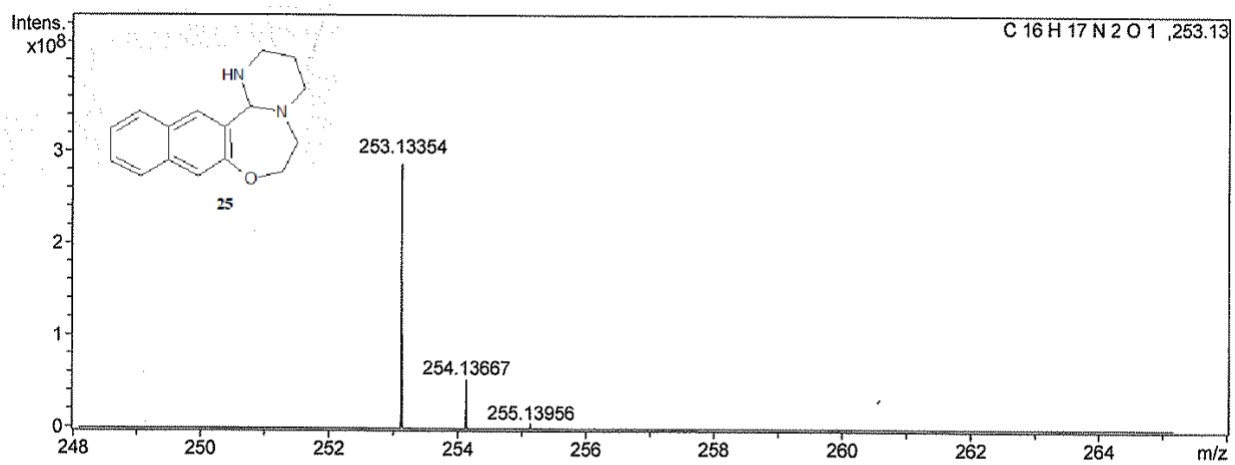




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 13 H 17 N 2 O 2 | 0.009 | 233.12845 | -1.68 | -1.61 | -0.39 | 6.50 | ok | even |






| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 16 H 17 N 2 O 1 | 0.004 | 253.13354 | -2.56 | -2.86 | -0.65 | 9.50 | ok | even |