

Supplementary Material

A new protocol for the synthesis of primary, secondary and tertiary anthranilamides utilizing *N*-(2-aminoarylacyl)benzotriazoles

Nevin Kanişkan, Şule Kökten and İlhami Çelik*

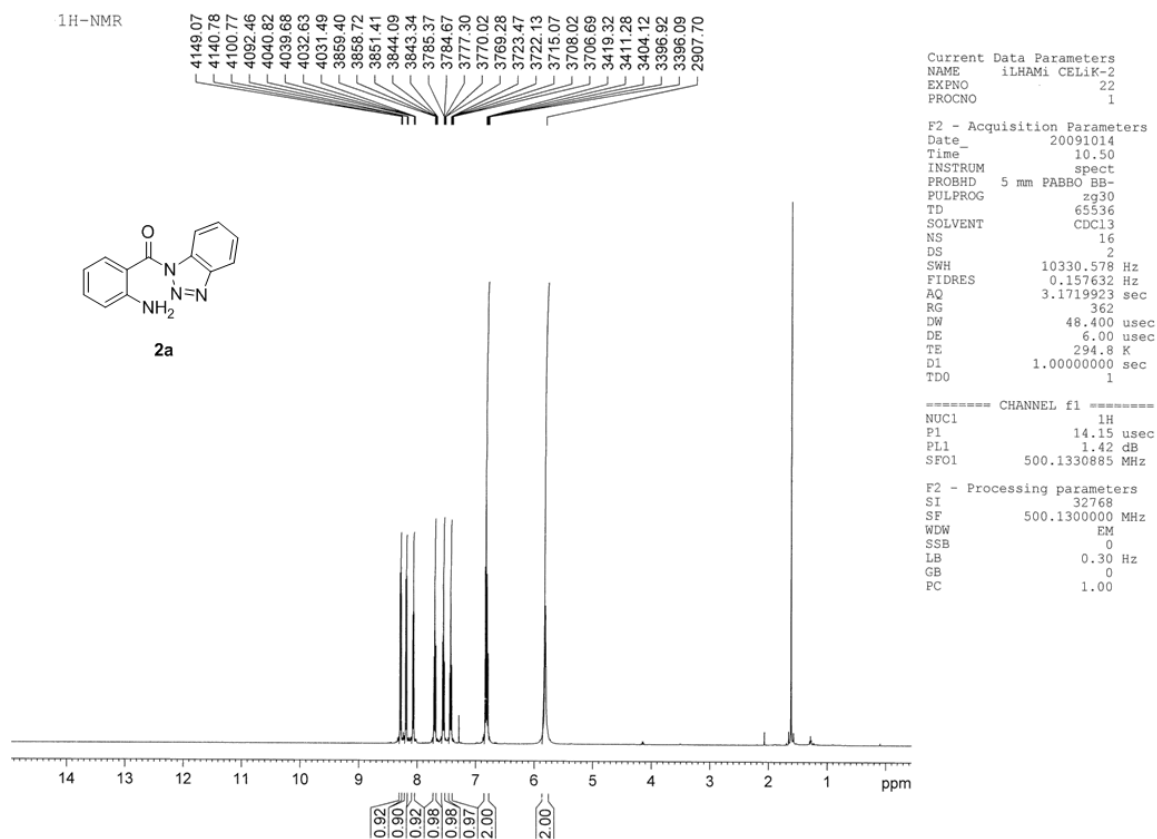
Department of Chemistry, Faculty of Science, Anadolu University, Eskişehir – 26470, Turkey

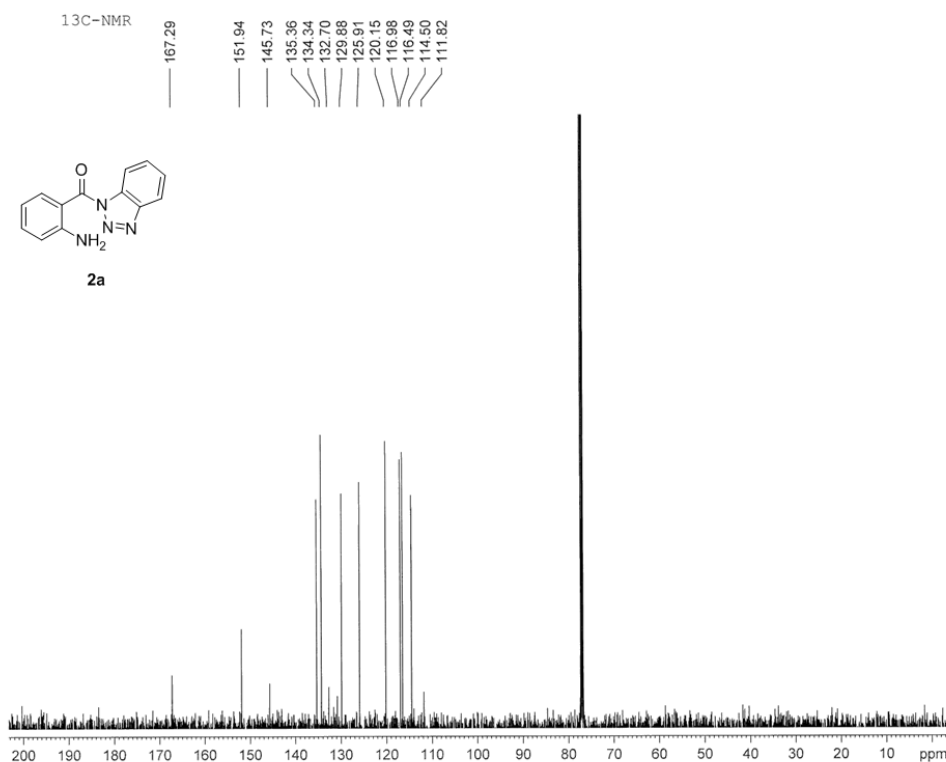
E-mail: ilcelik@anadolu.edu.tr

Table of Contents

1. ¹H, ¹³C NMR and MS spectra of the products and by-products S11. *N*-(2-Aminoarylacyl)benzotriazoles (2a-o)

(2-Aminophenyl) (benzotriazole-1-yl)methanone (2a)





```

Current Data Parameters
NAME      iLHAMI CELiK-2
EXPNO    23
PROCNO   1

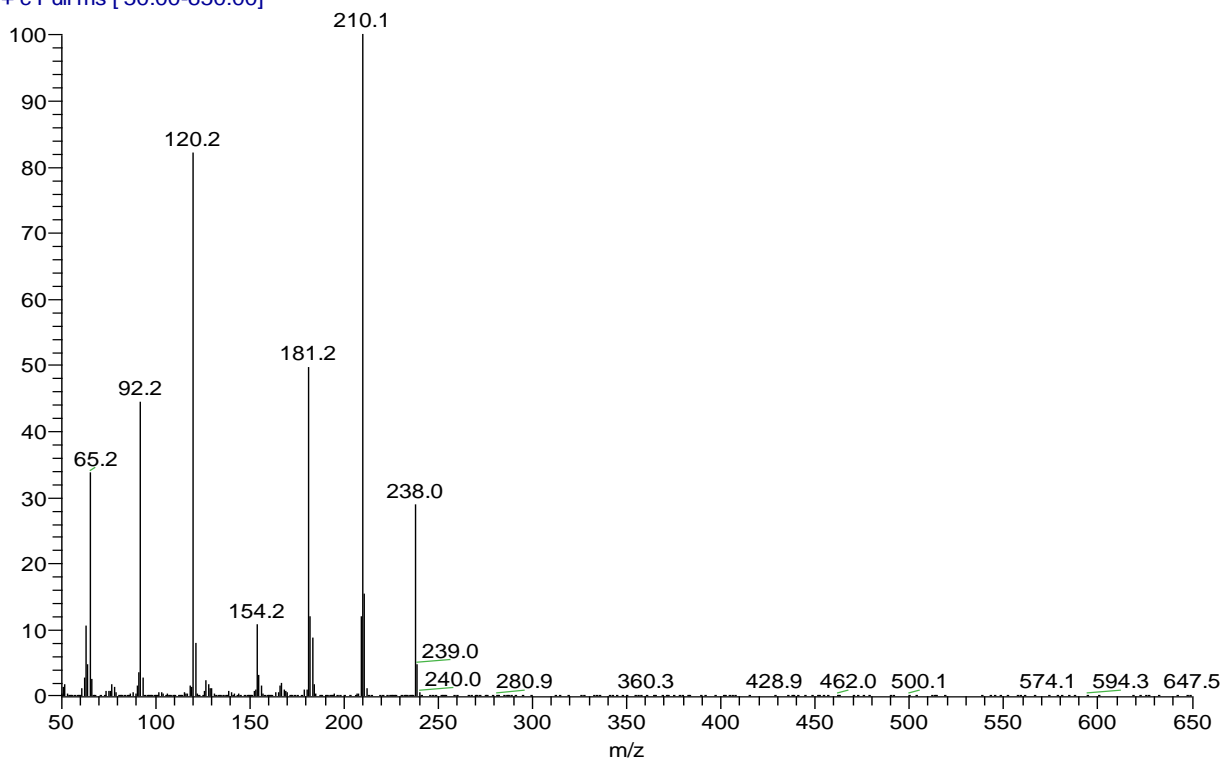
F2 - Acquisition Parameters
Date_    20091014
Time     10.58
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       95
DS       4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ       1.1010548 sec
RG       362
DW       16.800 usec
DE       6.00 usec
TE       297.2 K
D1       2.00000000 sec
d11      0.03000000 sec
DELTA    1.89999998 sec
TDO      1

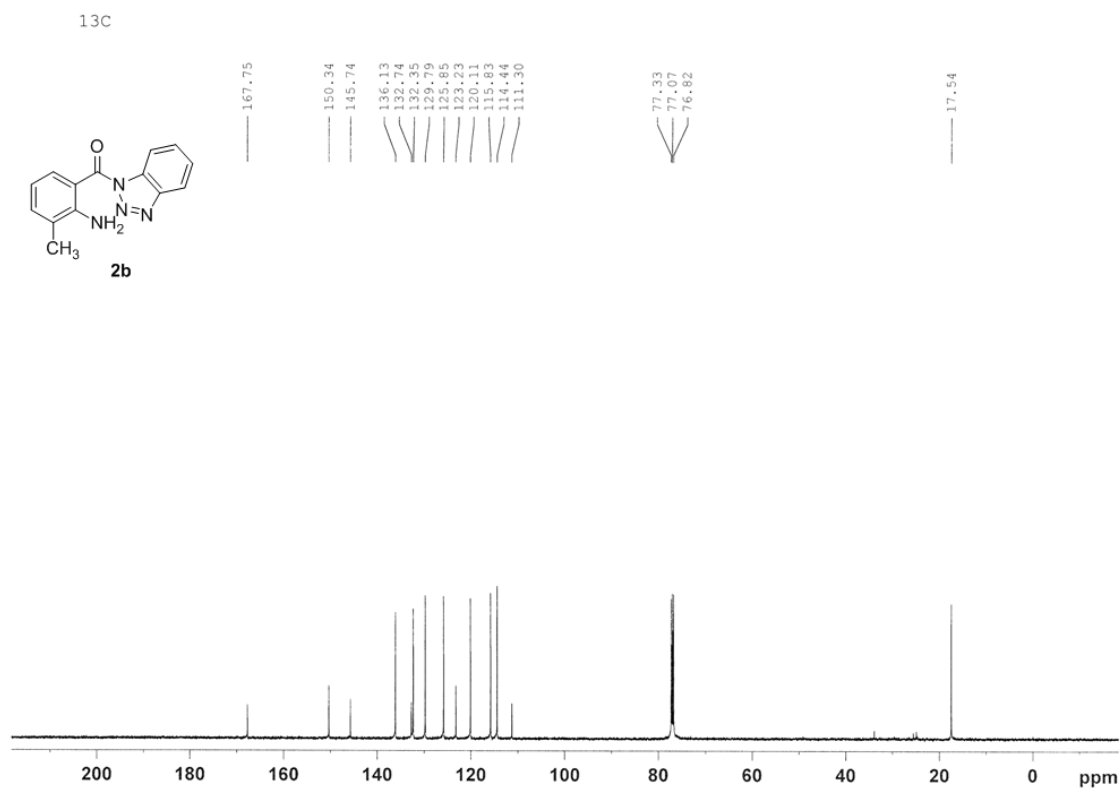
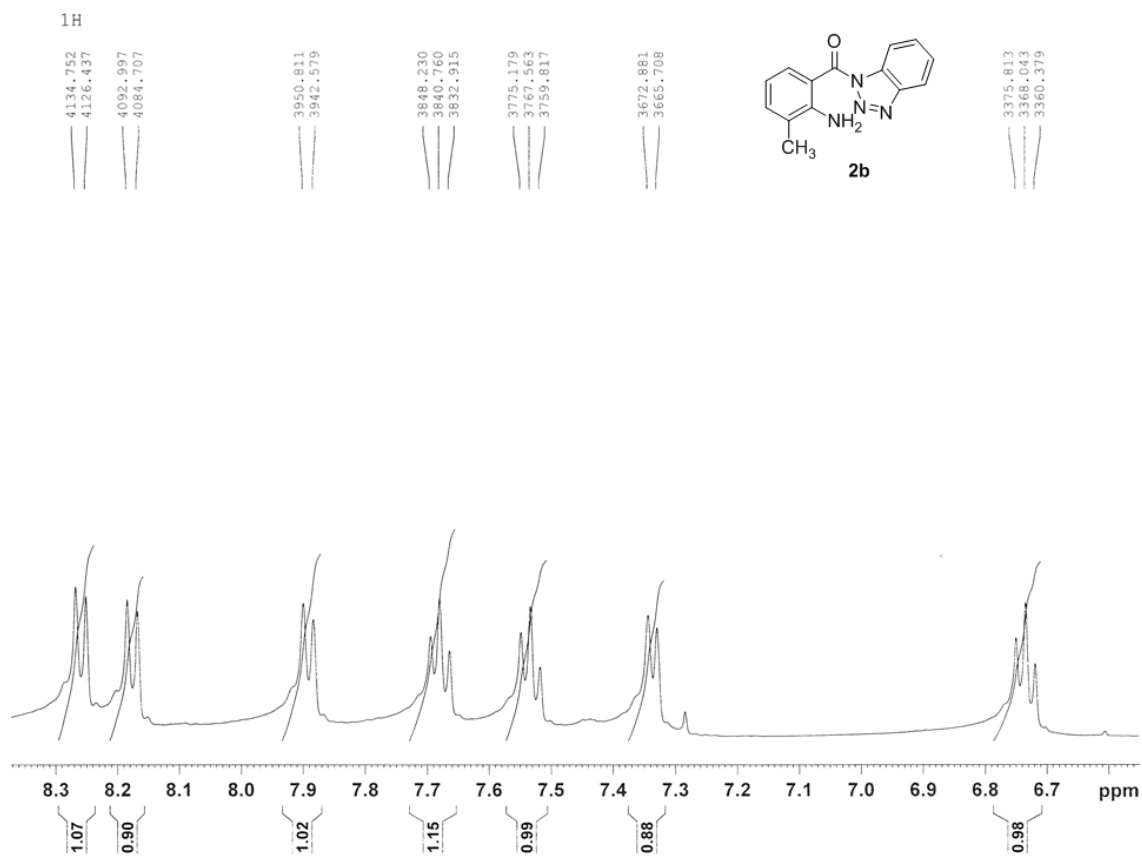
===== CHANNEL f1 =====
NUC1     13C
P1       8.30 usec
PL1      0.00 dB
SFO1     125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.42 dB
PL12     17.00 dB
PL13     17.00 dB
SFO2     500.1320005 MHz

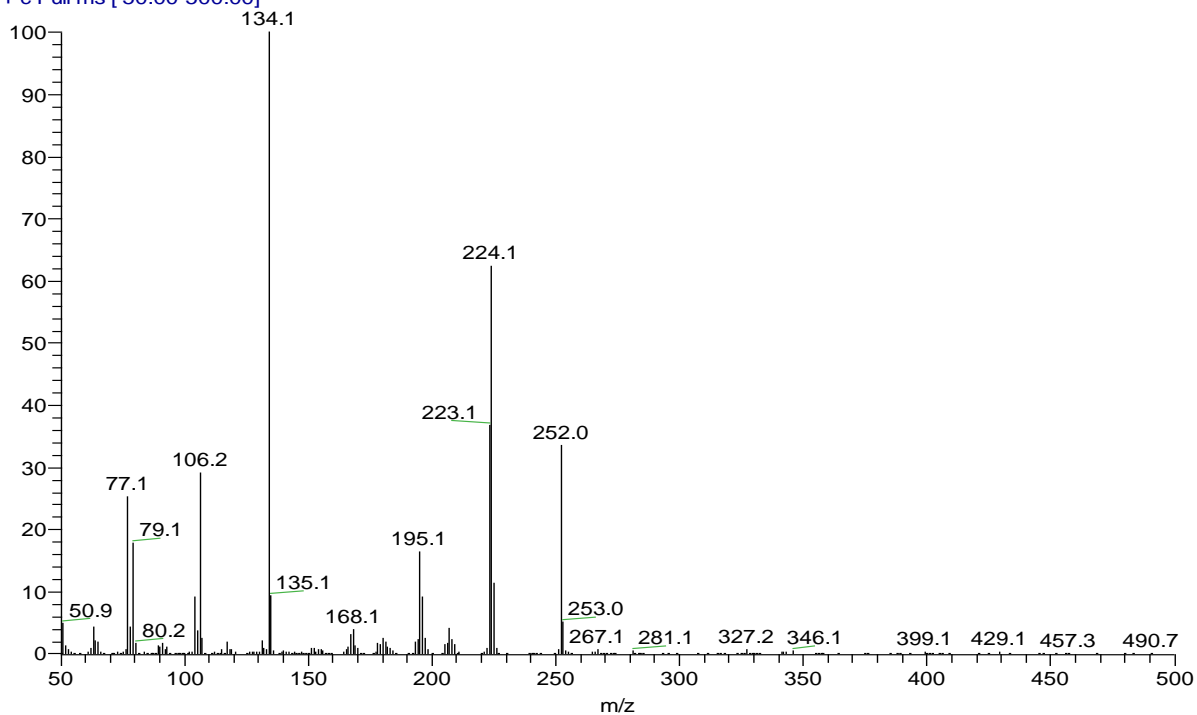
F2 - Processing parameters
SI       32768
SF       125.7577890 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
    
```

S73-1 #1048 RT: 13.22 AV: 1 NL: 1.08E7
T: + c Full ms [50.00-650.00]

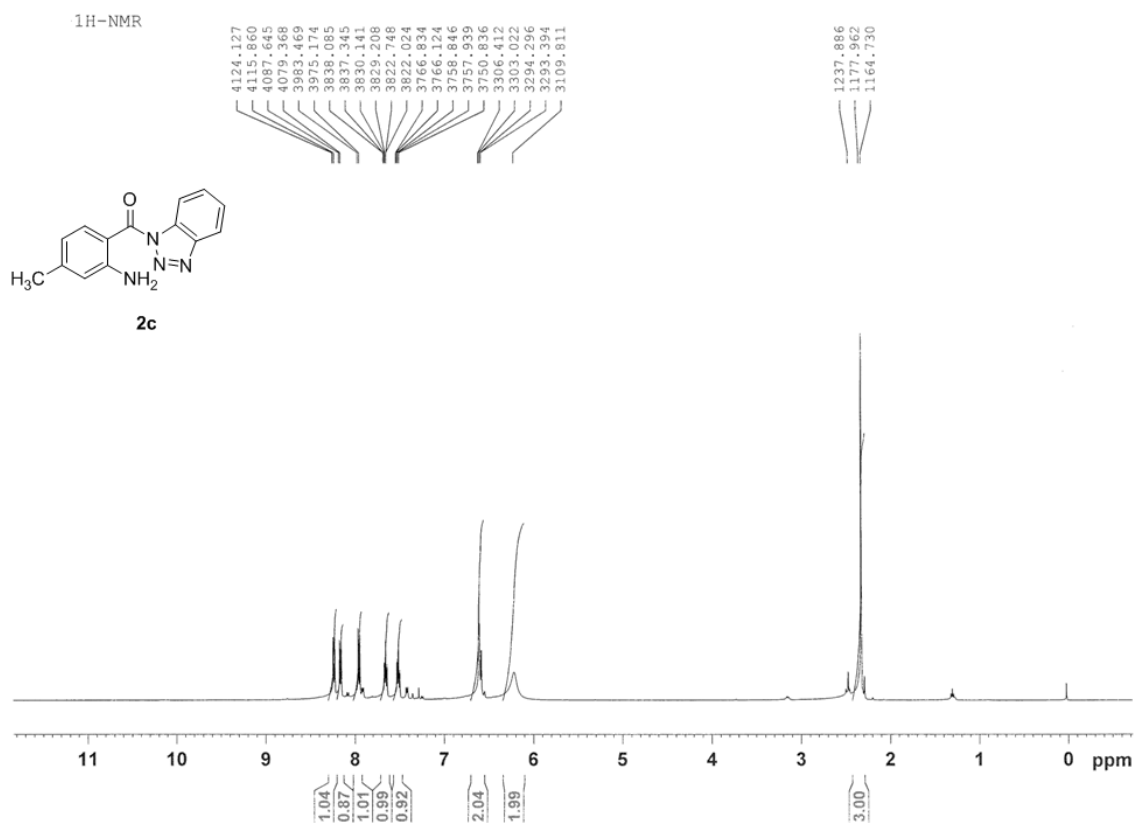


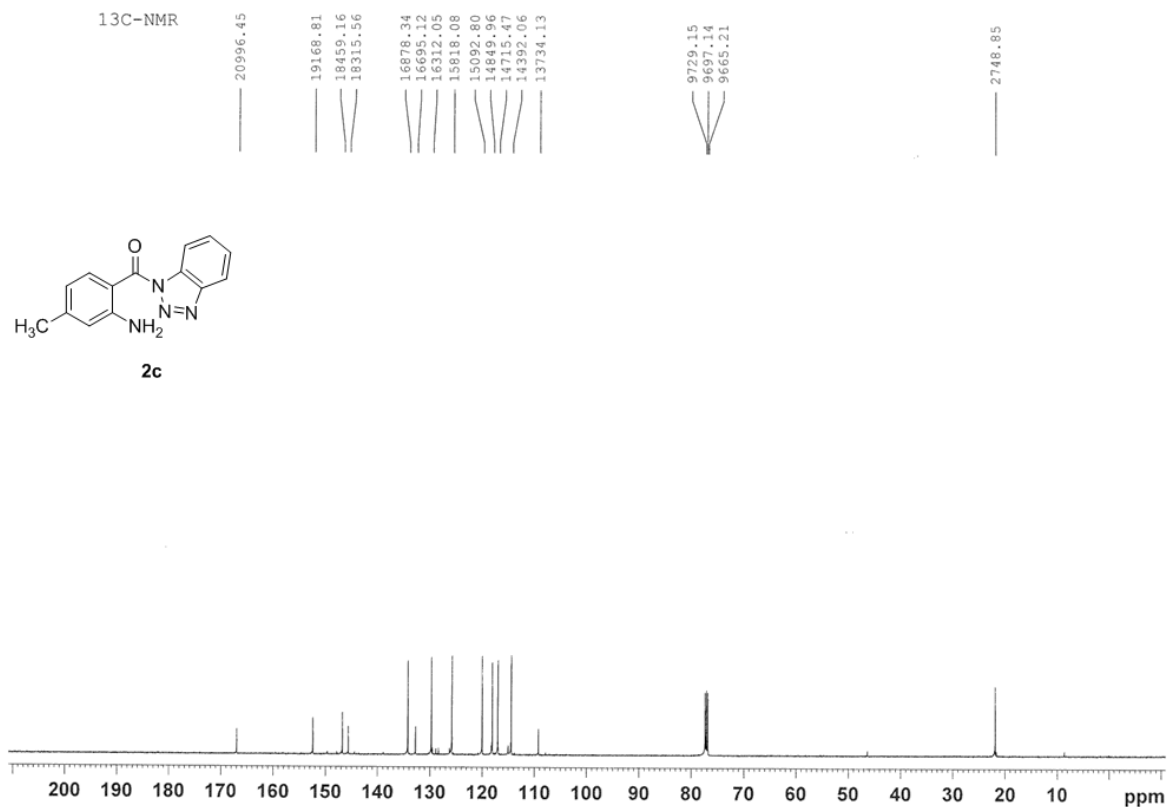
(2-Amino-3-methylphenyl) (benzotriazole-1-yl)methanone (**2b**)

S115 #2420 RT: 23.86 AV: 1 NL: 3.75E6
T: + c Full ms [50.00-500.00]

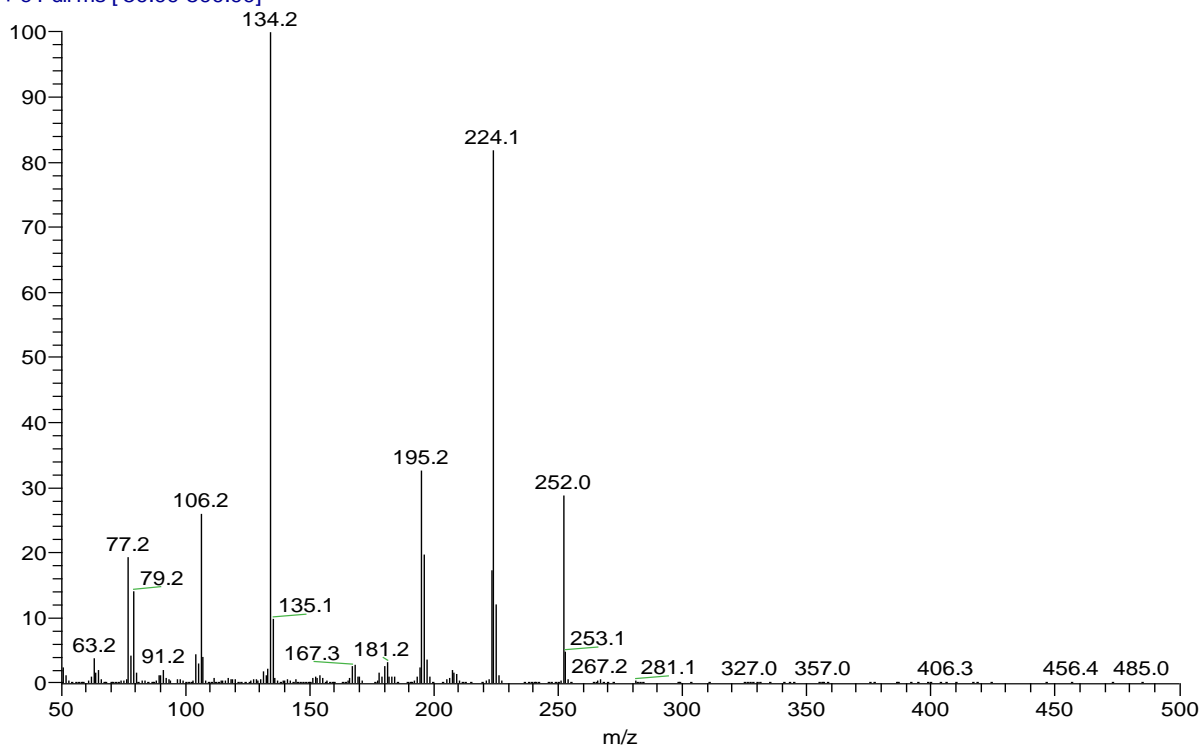


(2-Amino-4-methylphenyl) (benzotriazole-1-yl)methanone (**2c**)

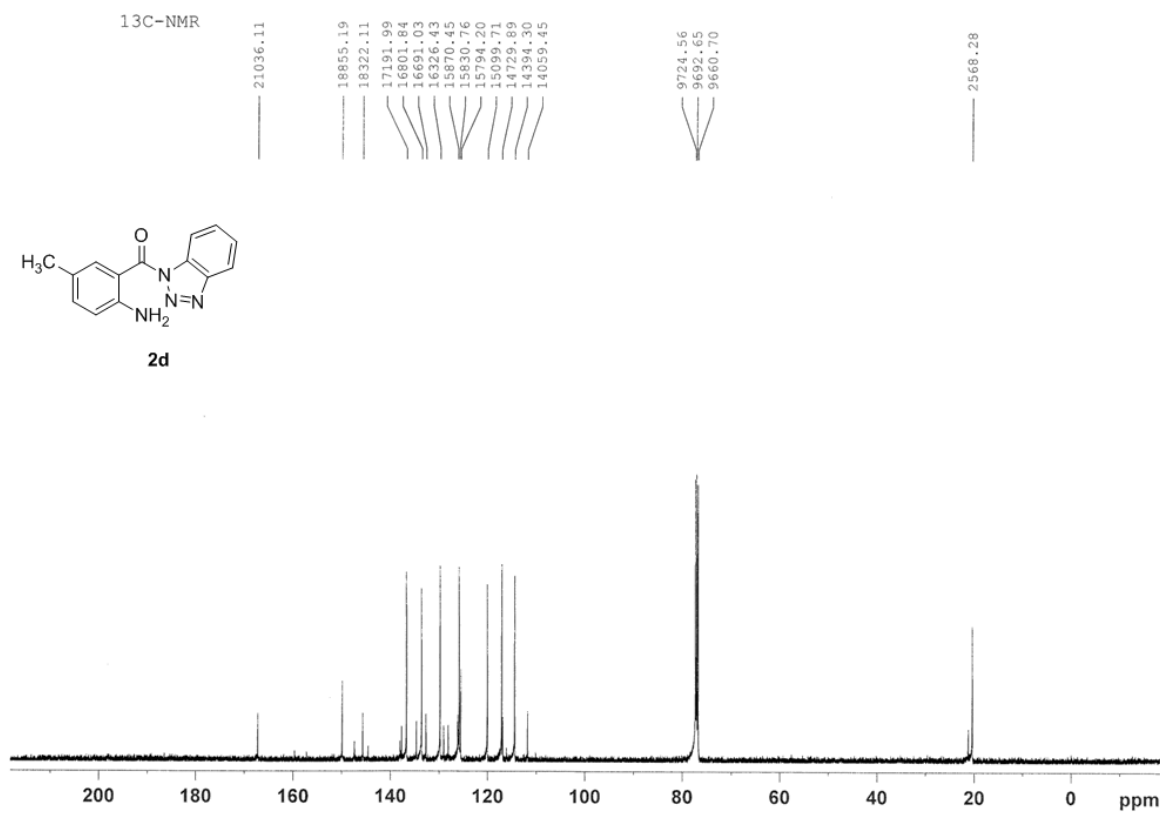
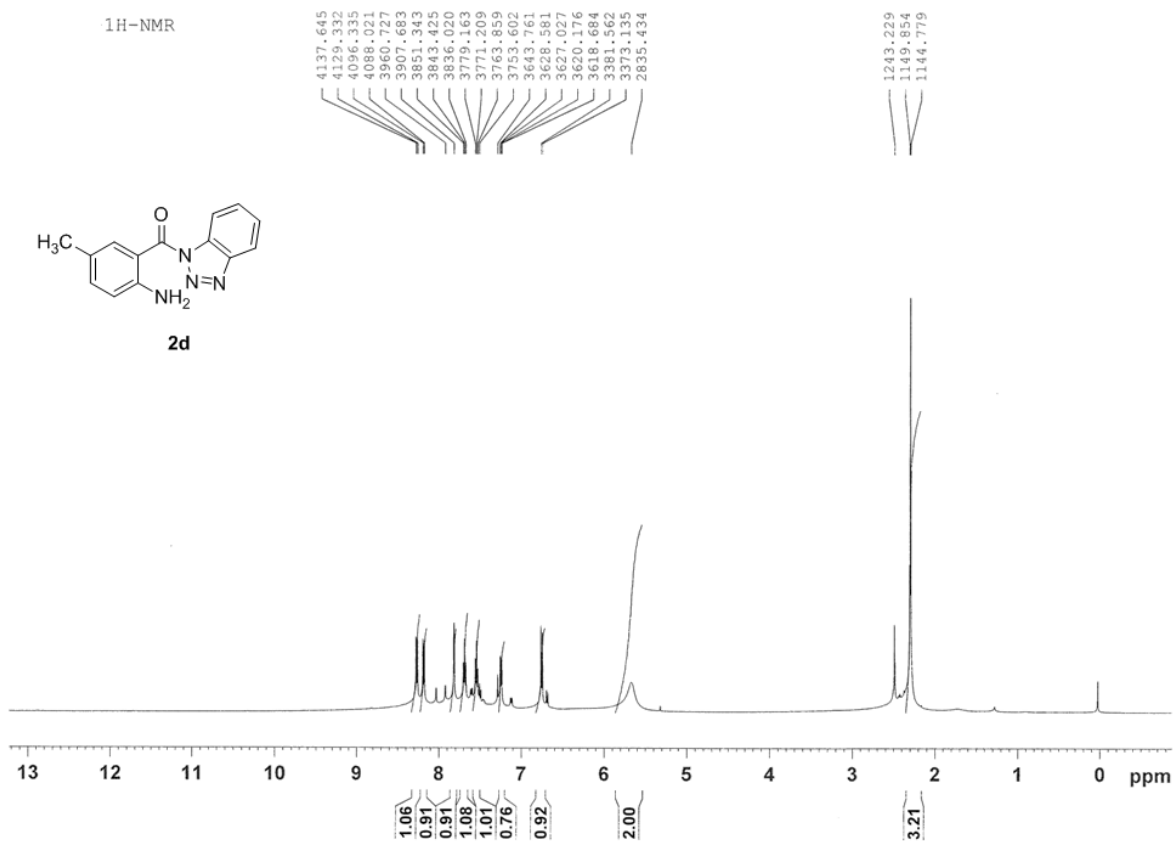




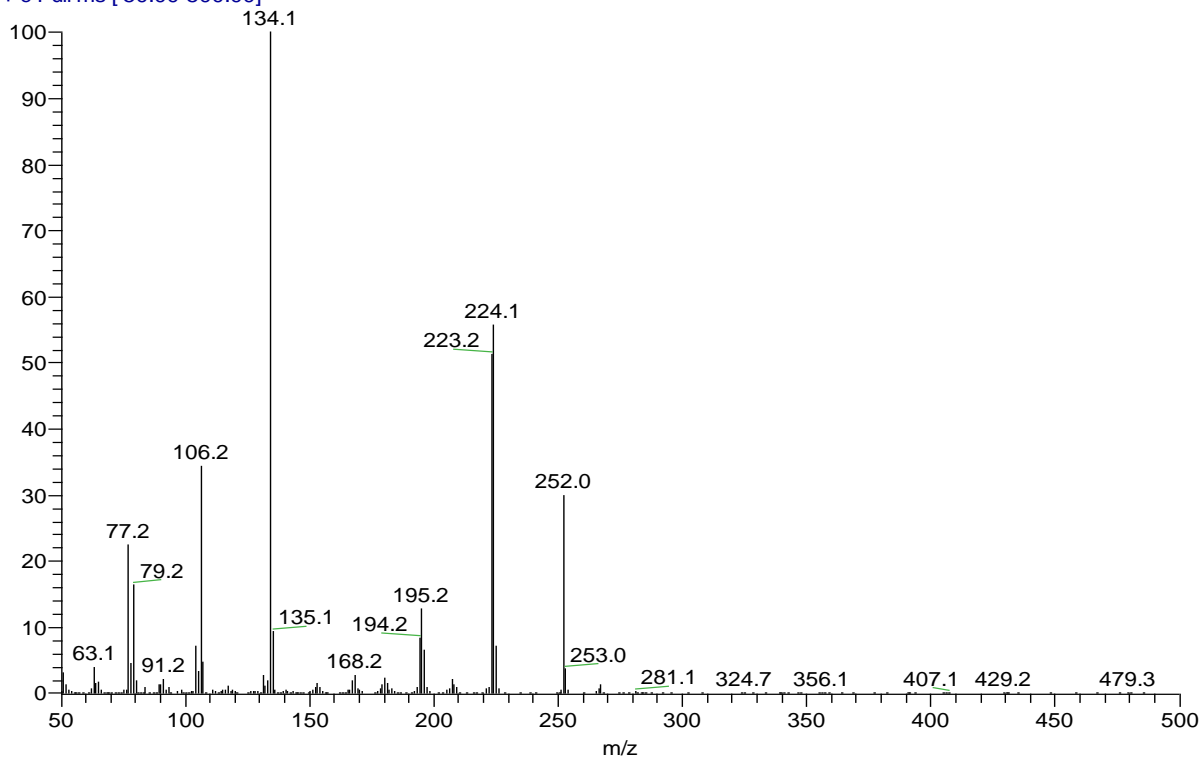
S117 #2454 RT: 24.14 AV: 1 NL: 1.52E7
T: + c Full ms [50.00-500.00]



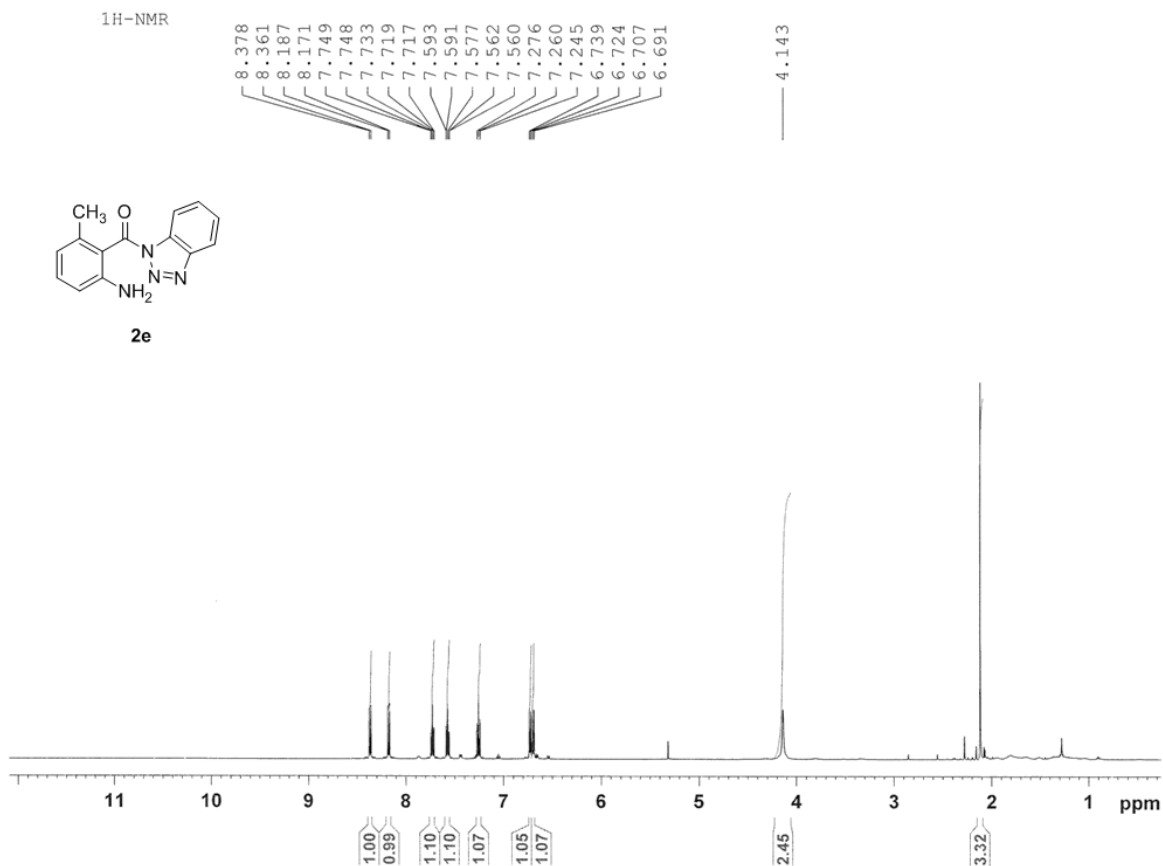
(2-Amino-5-methylphenyl) (1H-benzotriazole-1-yl)methanone (**2d**)



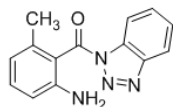
S-81 #2428 RT: 23.73 AV: 1 NL: 1.70E7
T: + c Full ms [50.00-500.00]



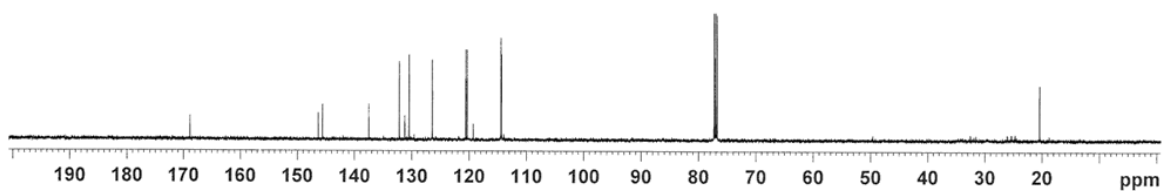
(2-Amino-6-methylphenyl) (benzotriazole-1-yl)methanone (**2e**)



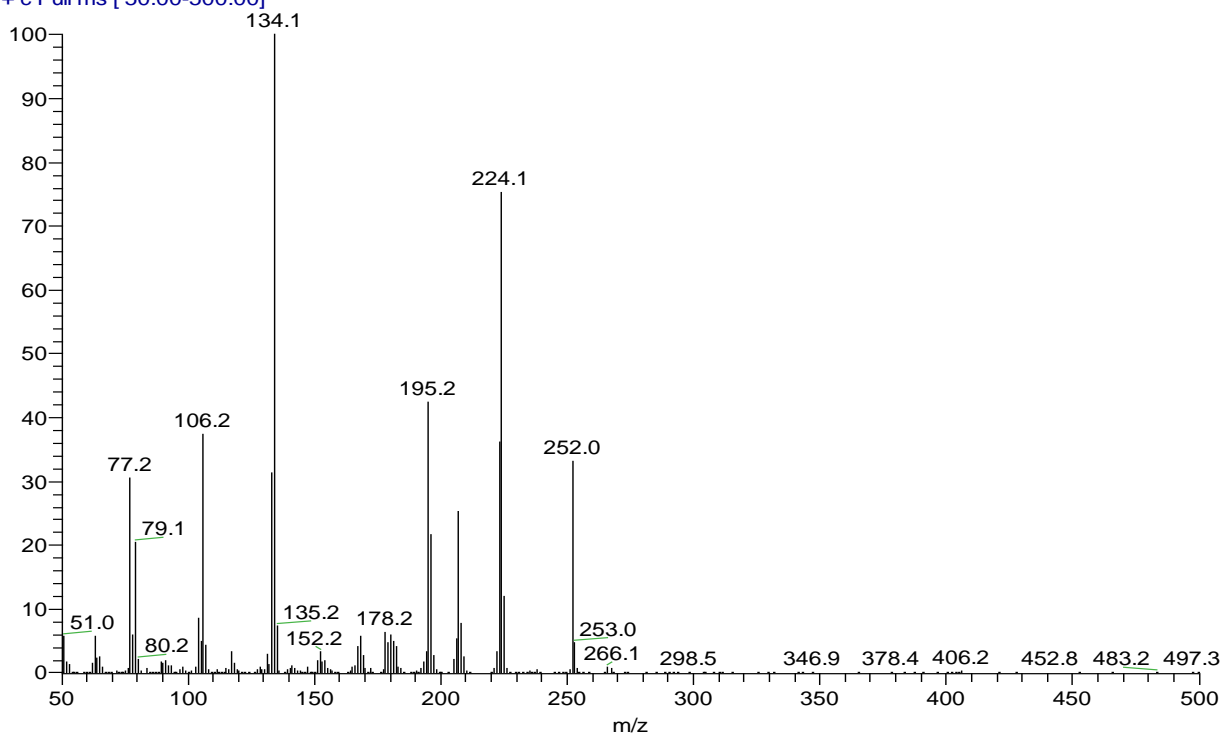
¹³C-NMR



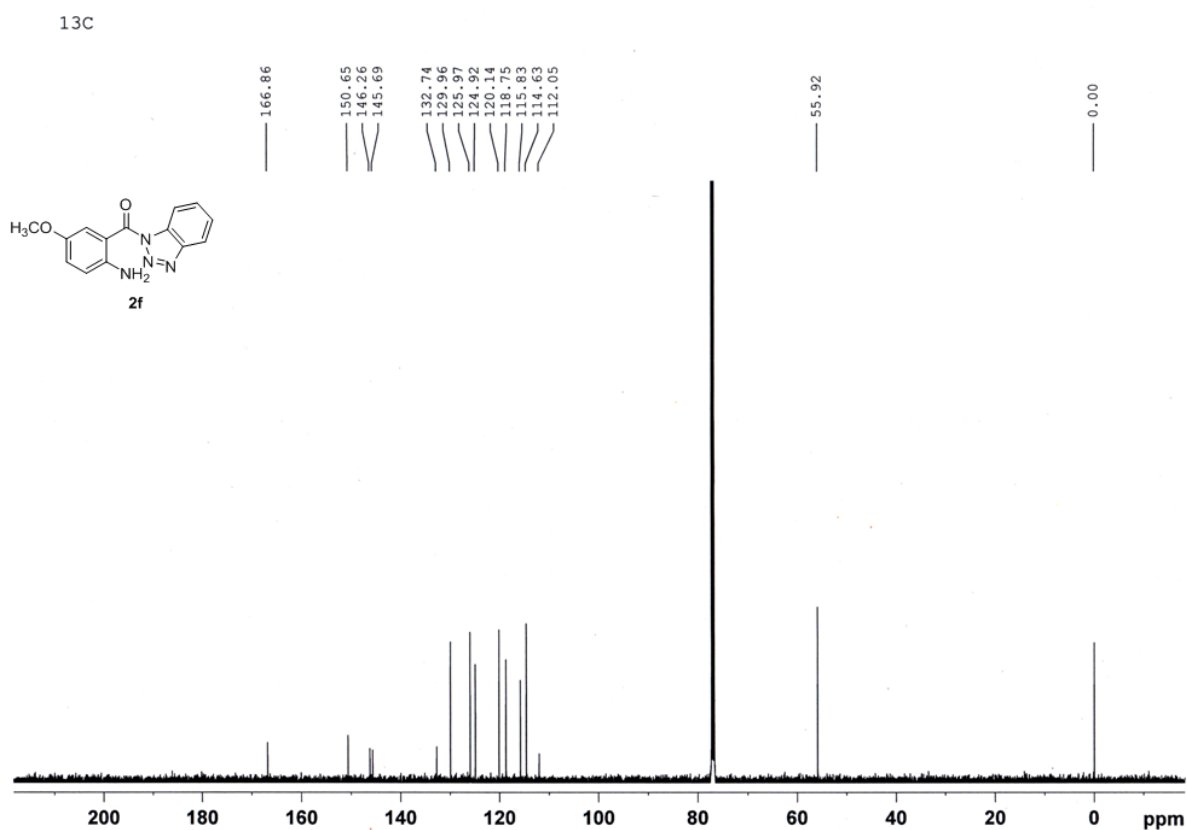
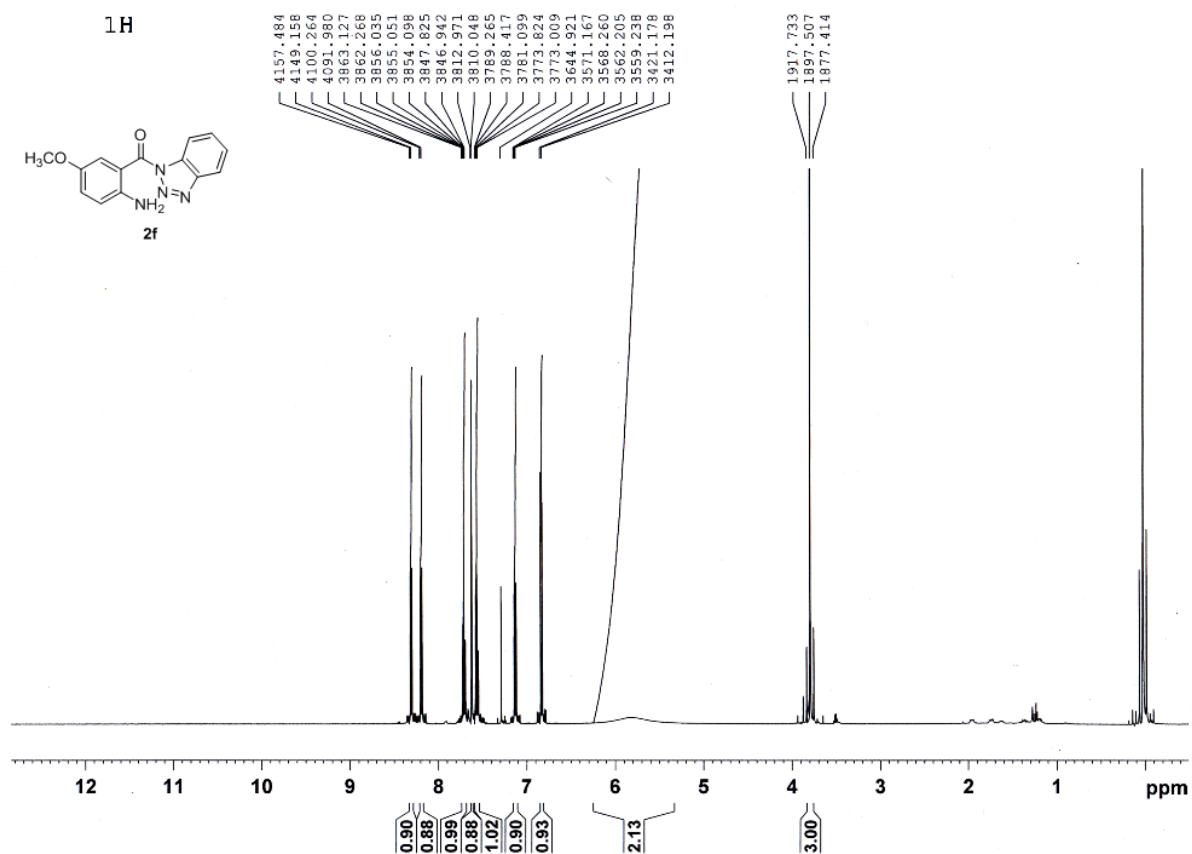
2e



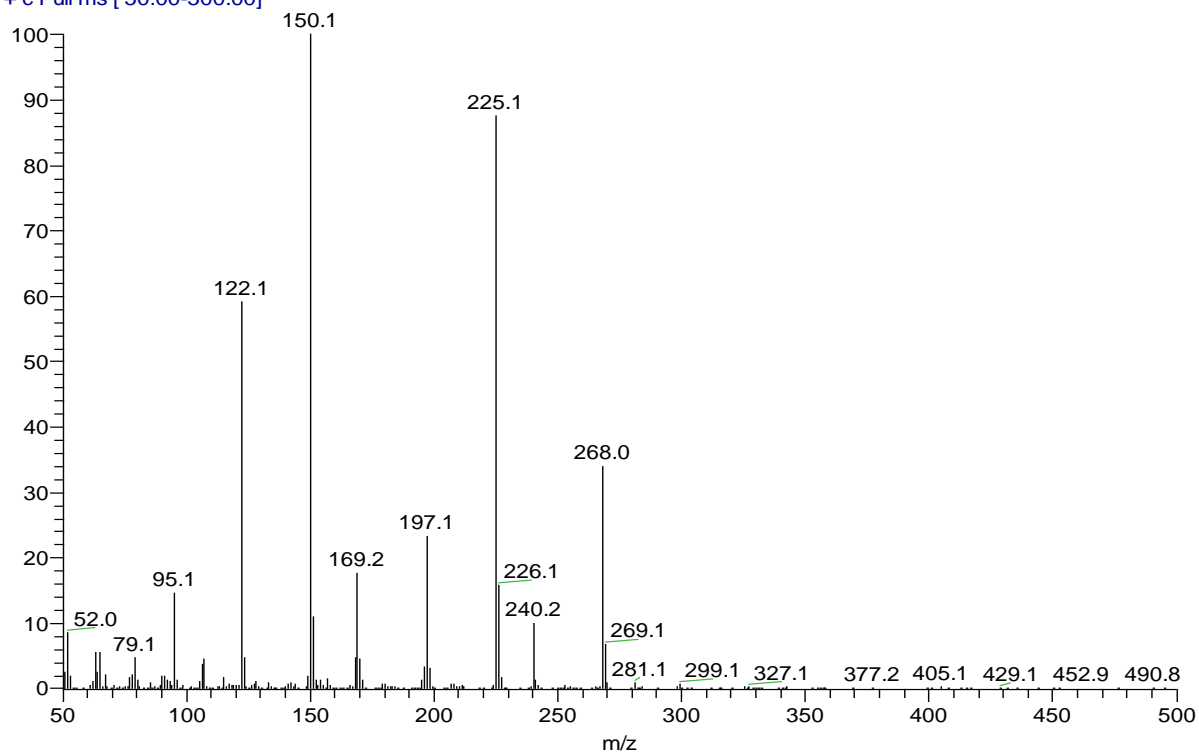
S-94 #2297 RT: 22.55 AV: 1 NL: 1.31E7
 T: + c Full ms [50.00-500.00]



(2-Amino-5-methoxyphenyl) (benzotriazole-1-yl)methanone (**2f**)

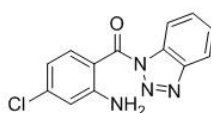
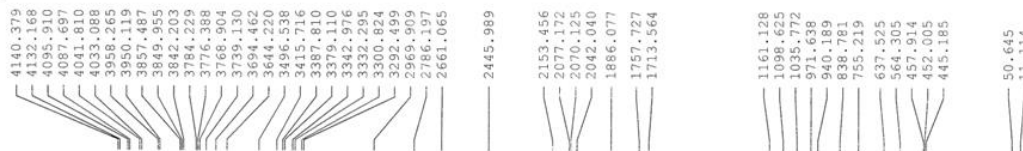


S91-2 #2511 RT: 24.62 AV: 1 NL: 7.52E6
 T: + c Full ms [50.00-500.00]

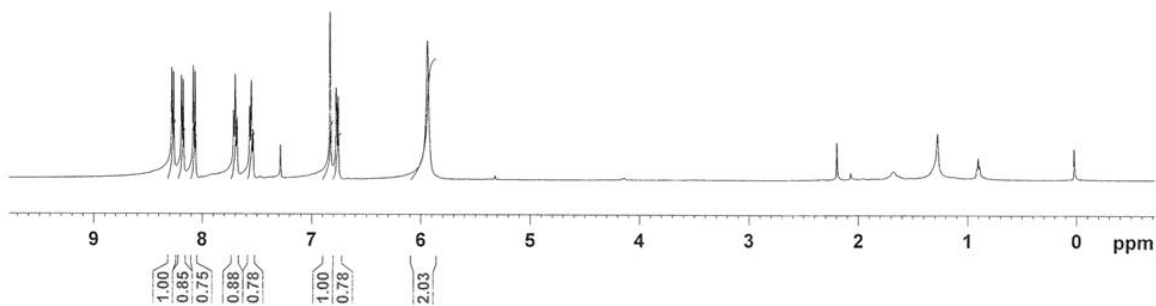


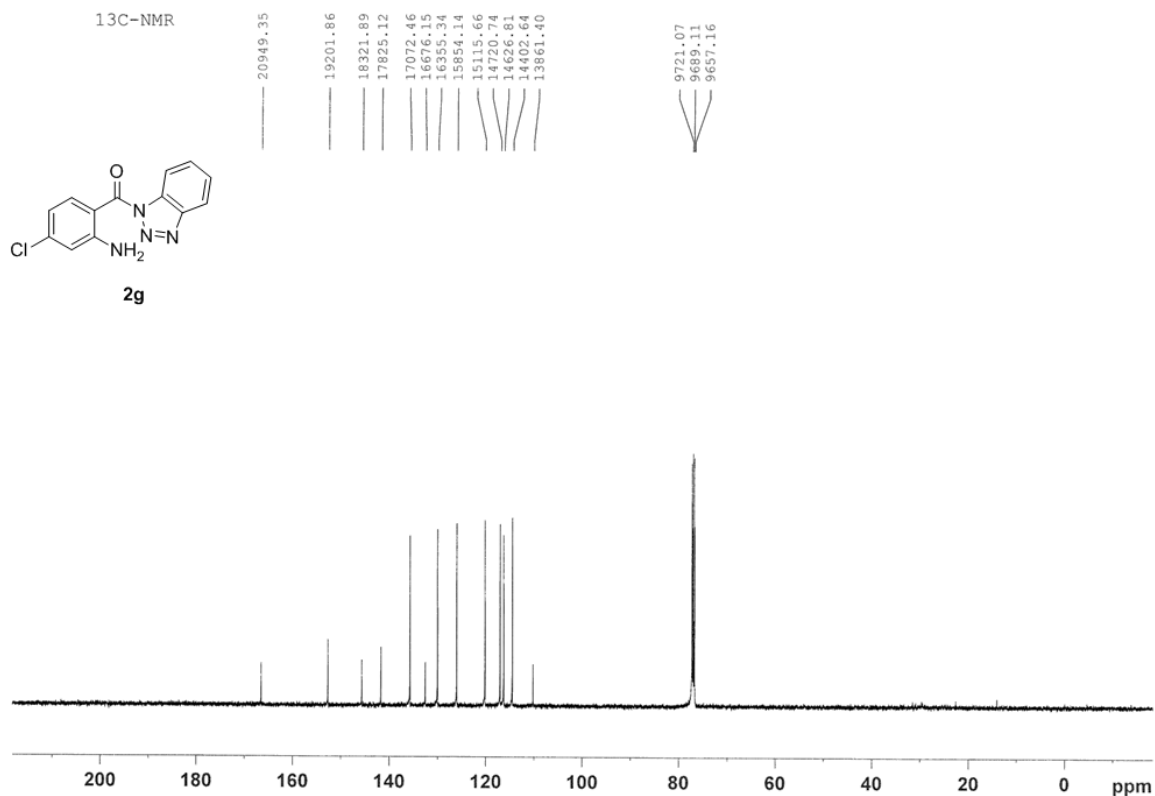
(2-Amino-4-chlorophenyl) (benzotriazole-1-yl)methanone (**2g**)

¹H-NMR

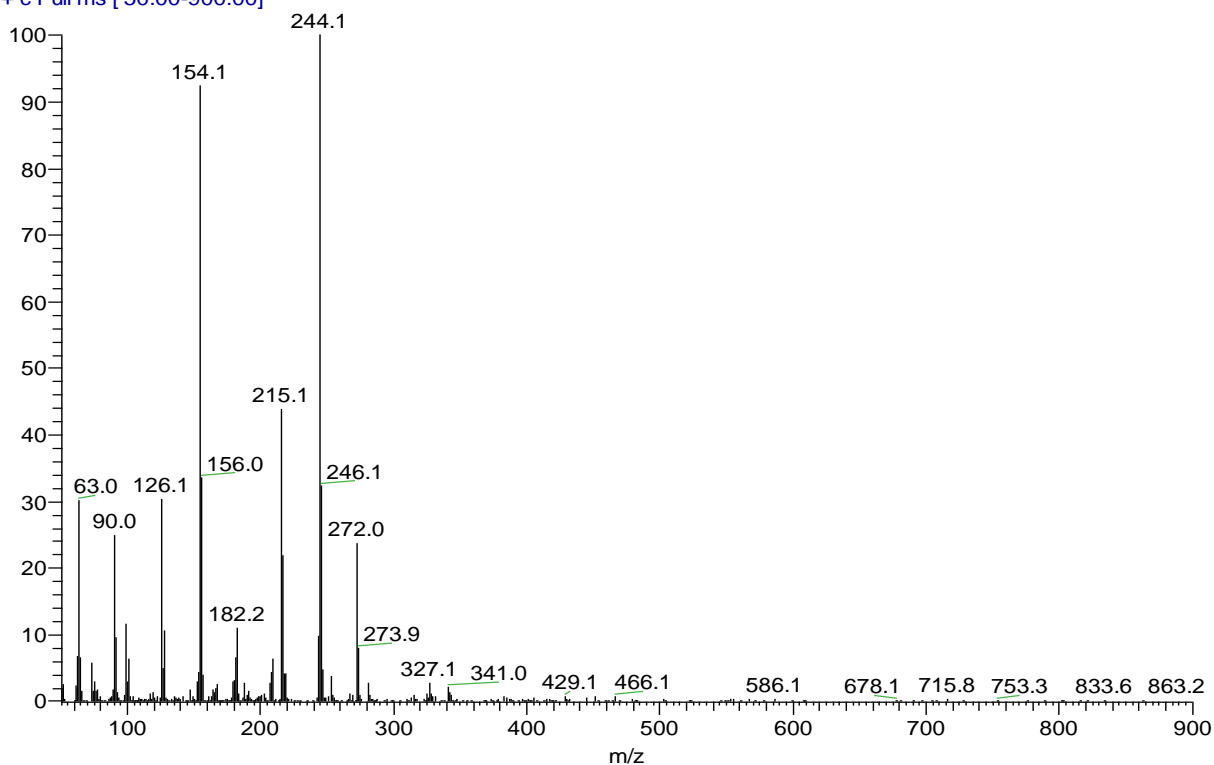


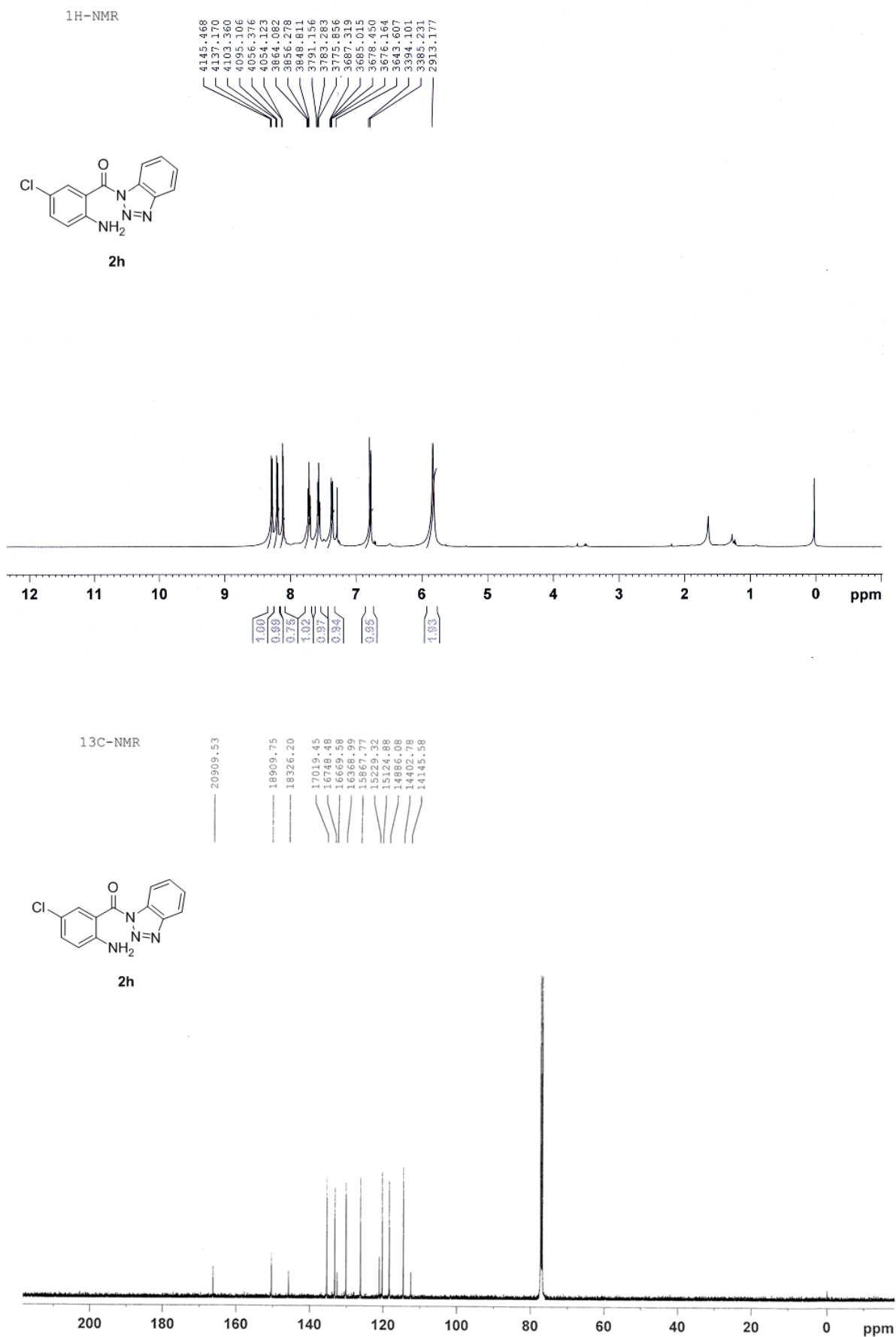
2g



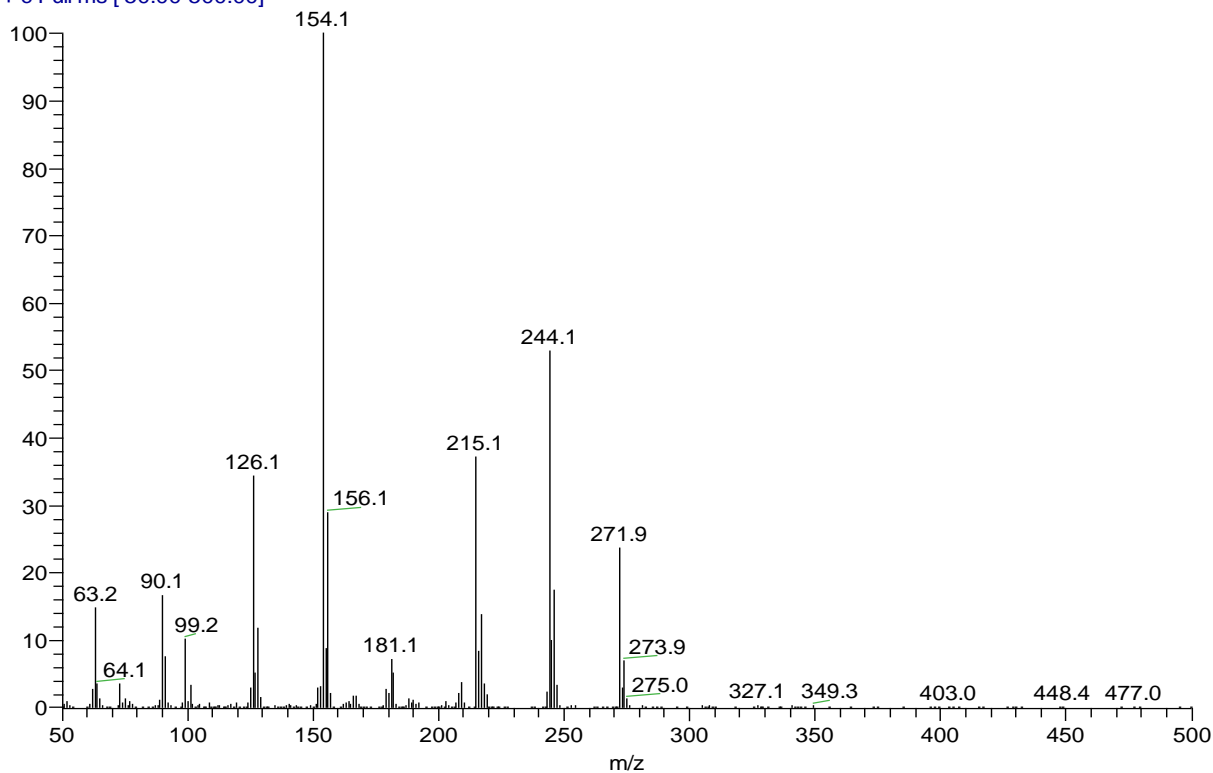


S83-2 #1079 RT: 15.75 AV: 1 NL: 7.19E5
T: + c Full ms [50.00-900.00]



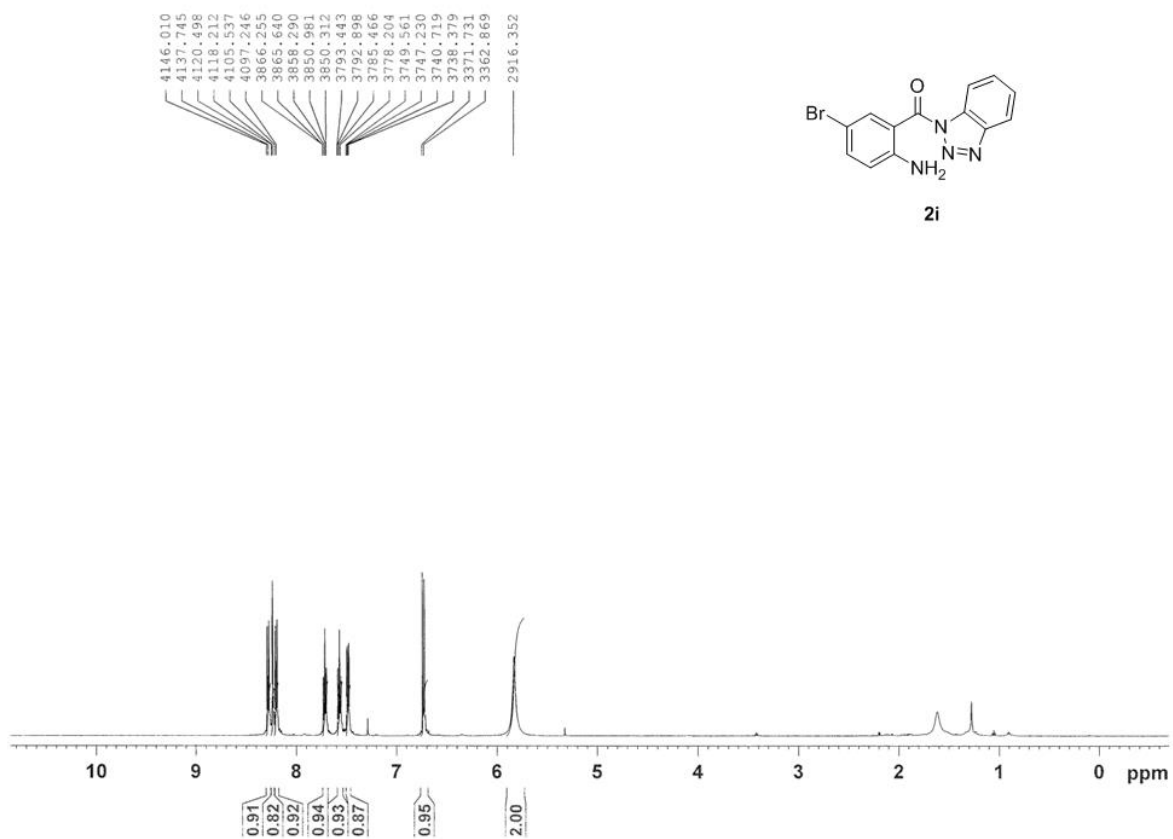
(2-Amino-5-chlorophenyl) (benzotriazole-1-yl)methanone (**2h**)

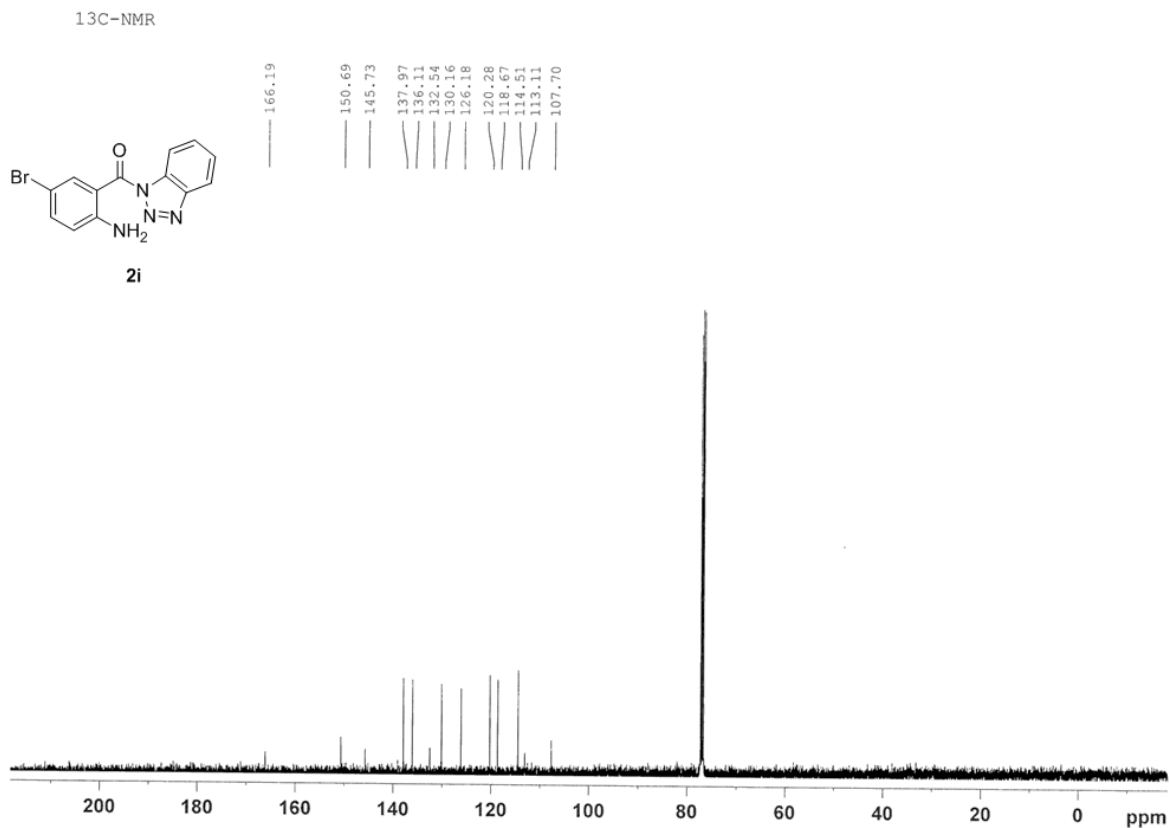
S-85-2 #2553 RT: 24.83 AV: 1 NL: 8.33E6
T: + c Full ms [50.00-500.00]



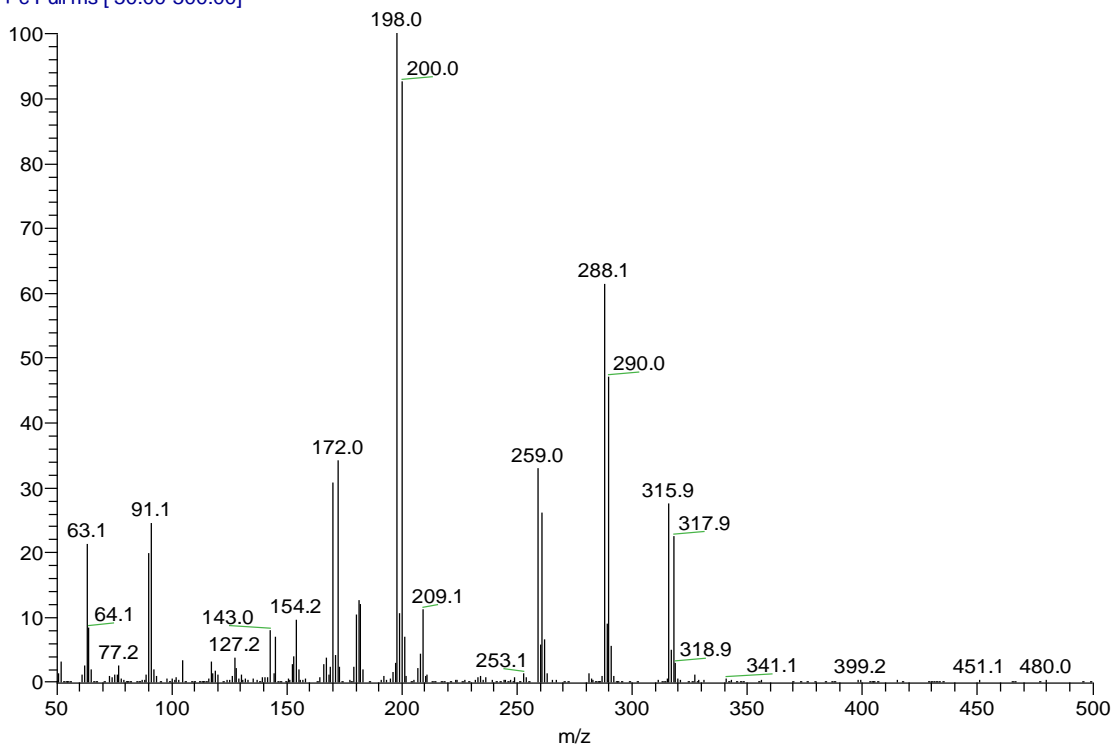
(2-Amino-5-bromophenyl) (benzotriazole-1-yl)methanone (**2i**)

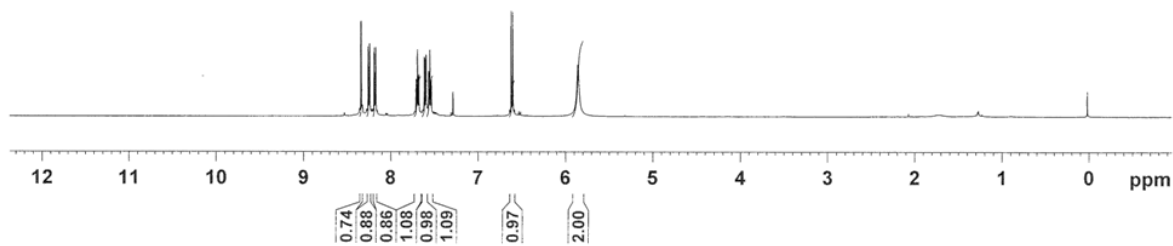
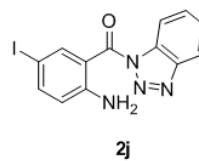
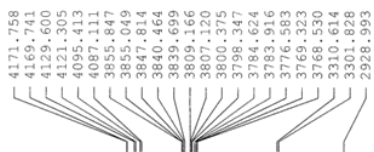
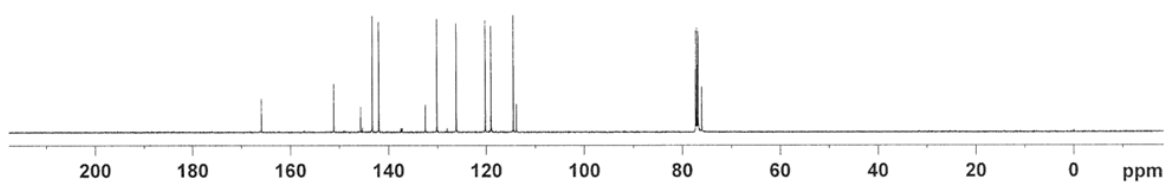
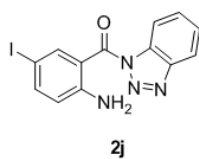
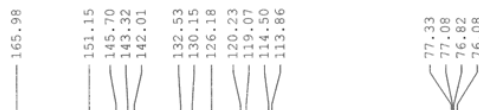
¹H-NMR



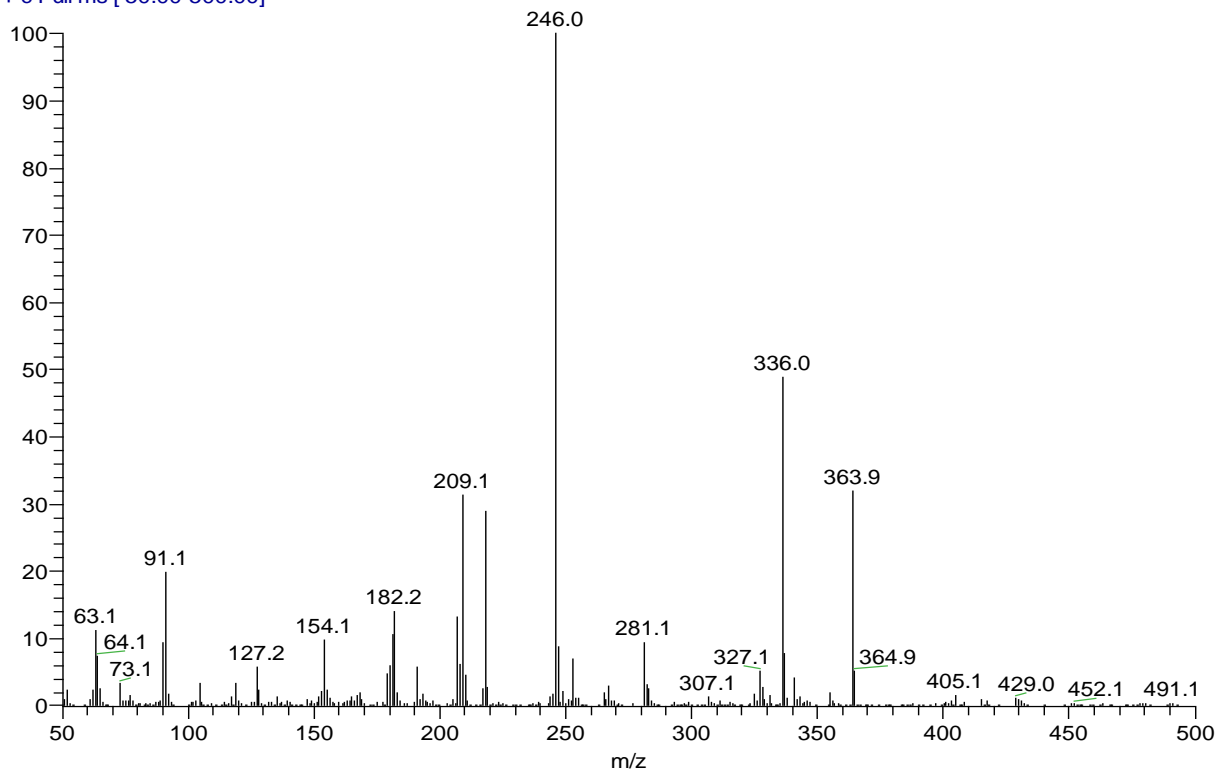


S112 #2682 RT: 25.95 AV: 1 NL: 3.59E6
T: + c Full ms [50.00-500.00]



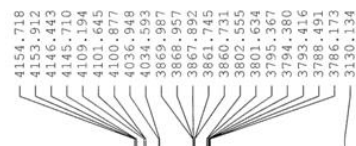
(2-Amino-5-iodophenyl) (benzotriazole-1-yl)methanone (**2j**)¹H-NMR¹³C-NMR

S-2 #2893 RT: 27.61 AV: 1 NL: 5.96E5
 T: + c Full ms [50.00-500.00]

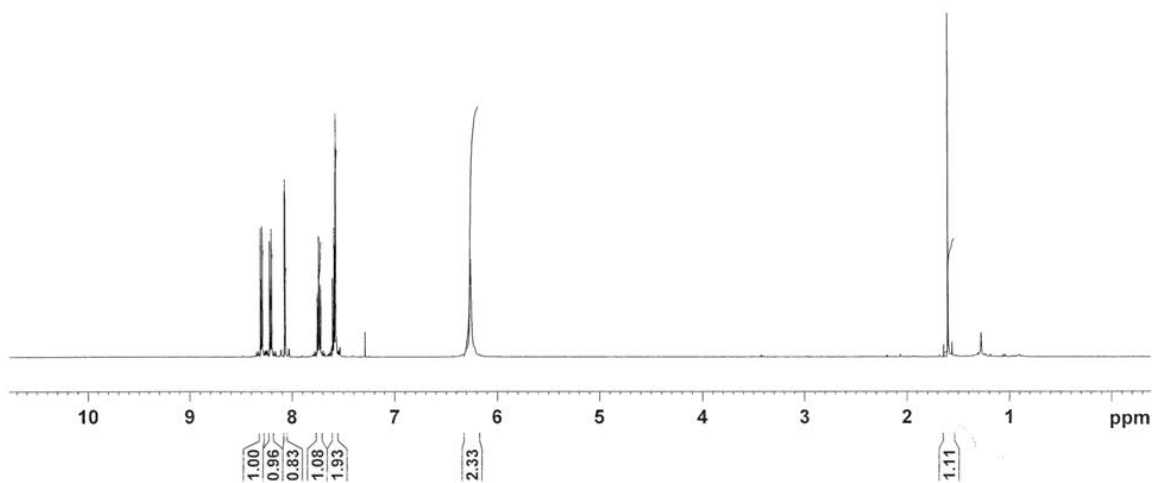
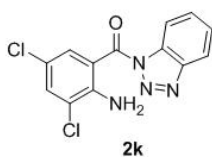


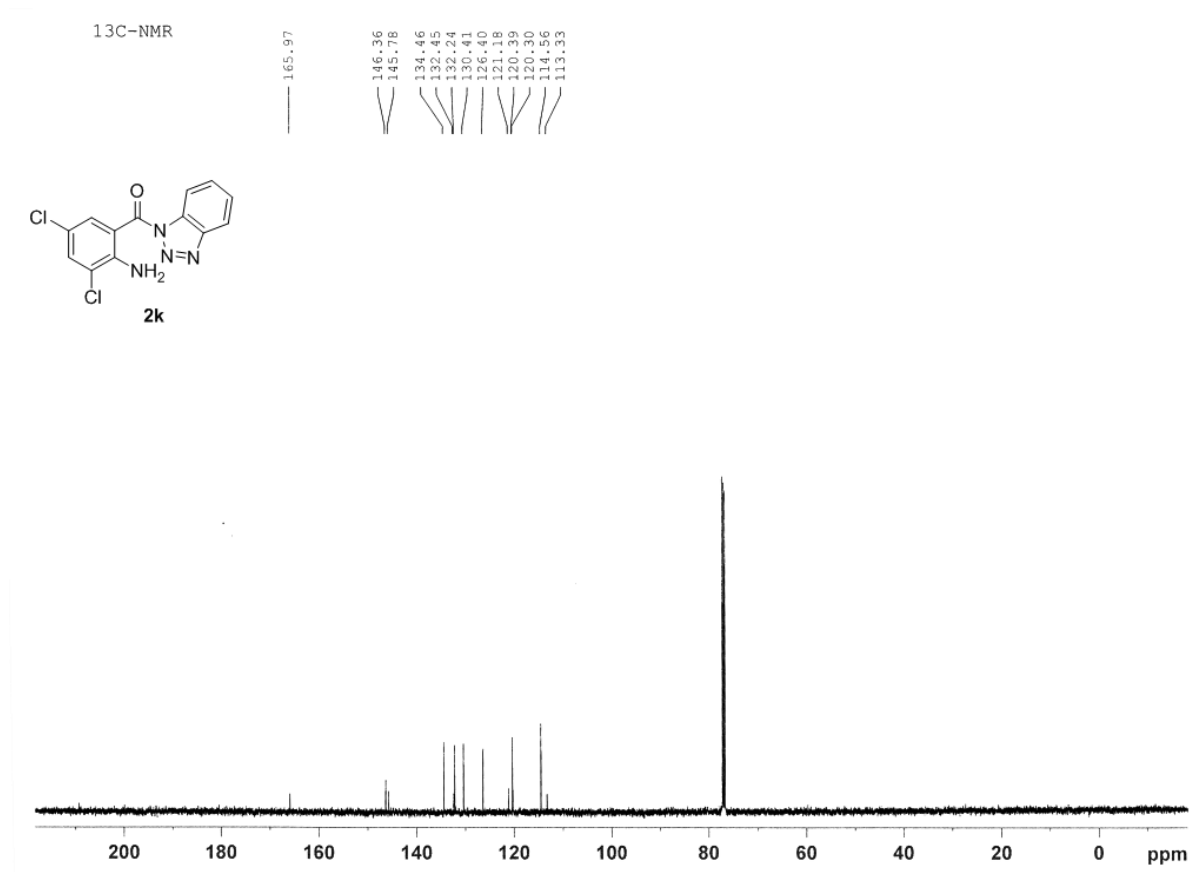
(2-Amino-3, 5-dichlorophenyl) (benzotriazole-1-yl)methanone (**2k**)

¹H-NMR

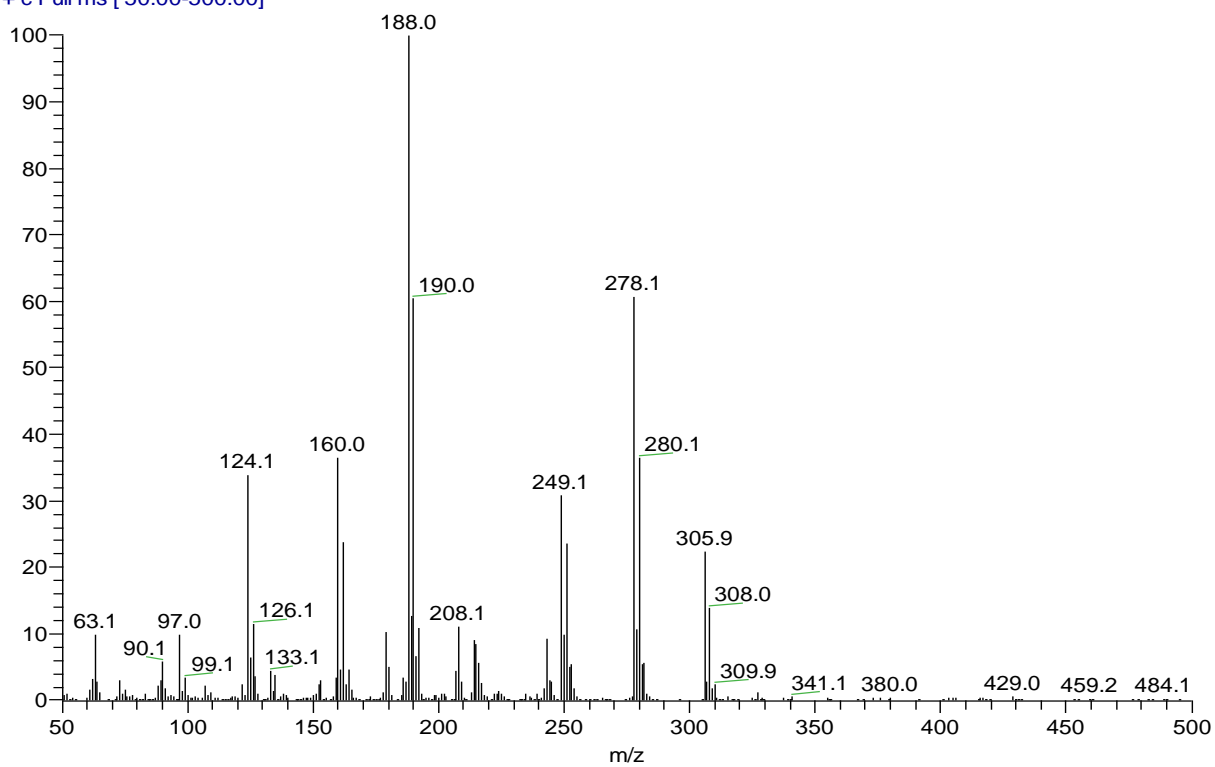


800.925



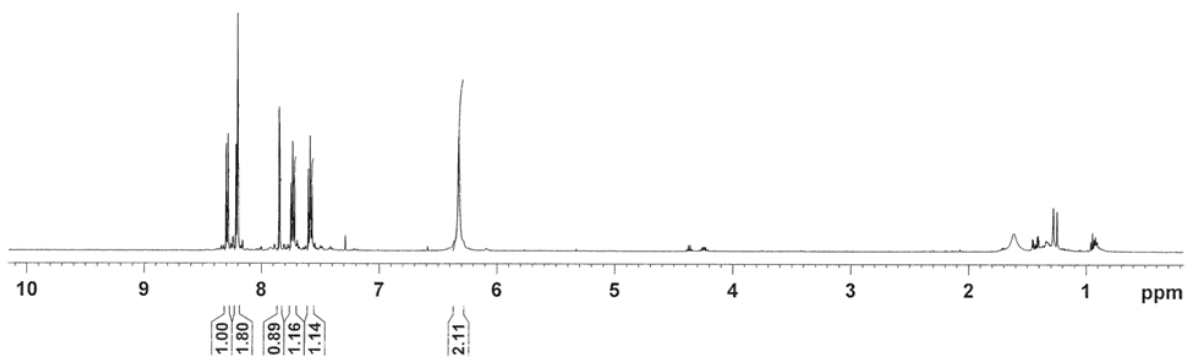
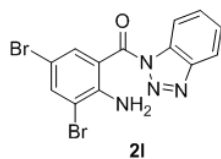
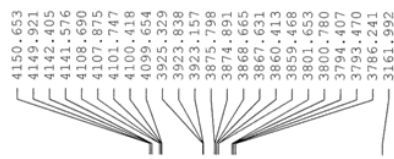


S110 #2654 RT: 25.33 AV: 1 NL: 3.56E6
 T: + c Full ms [50.00-500.00]

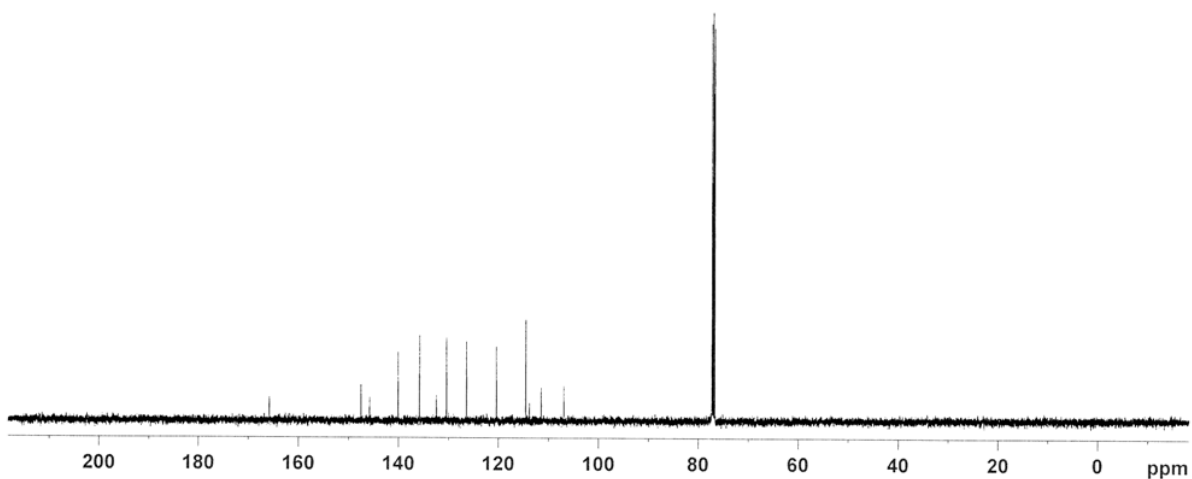
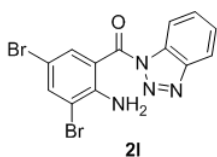


(2-Amino-3, 5-dibromophenyl) (benzotriazole-1-yl)methanone (**21**)

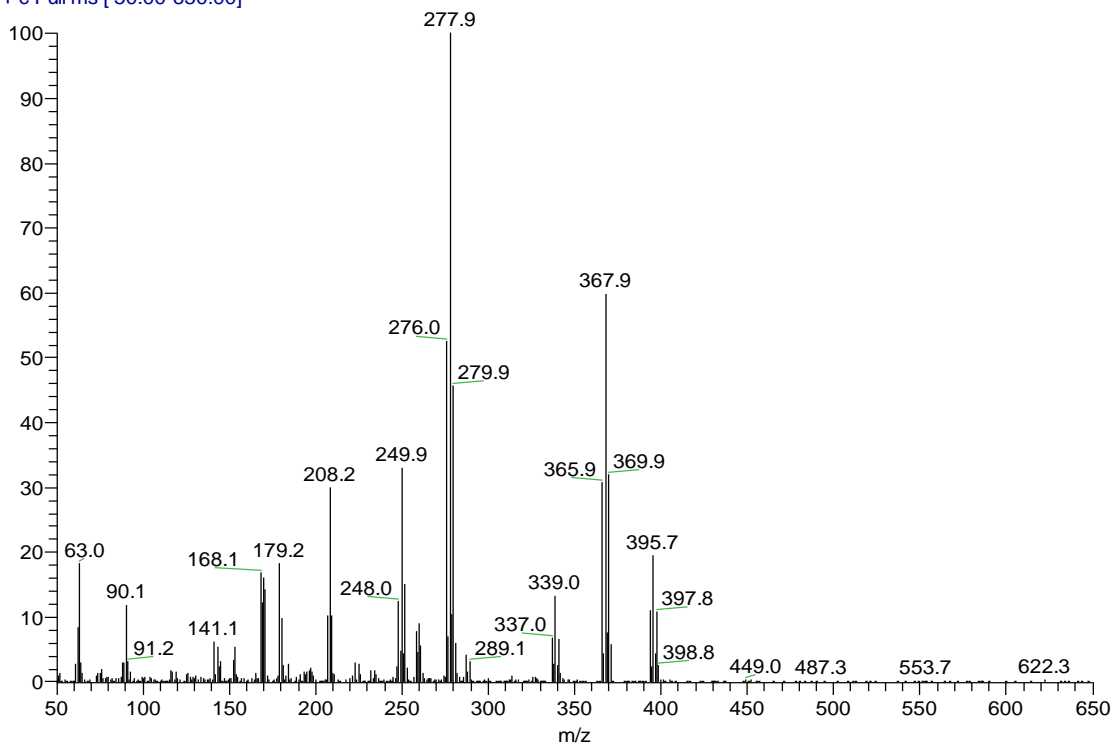
¹H-NMR



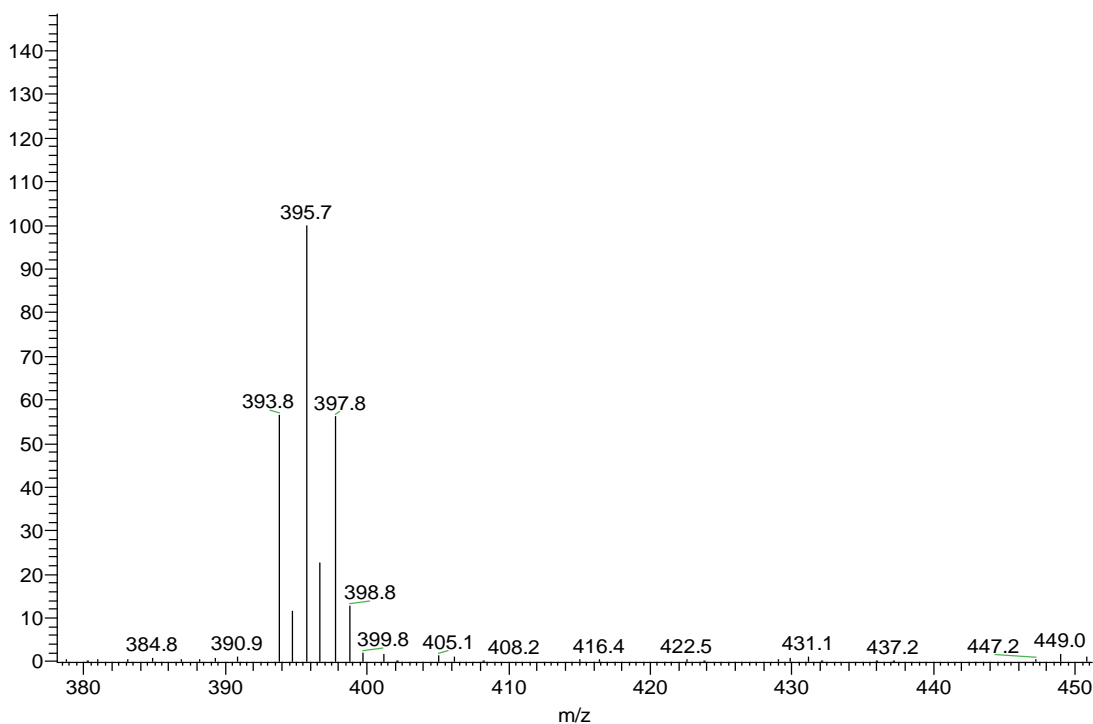
¹³C-NMR

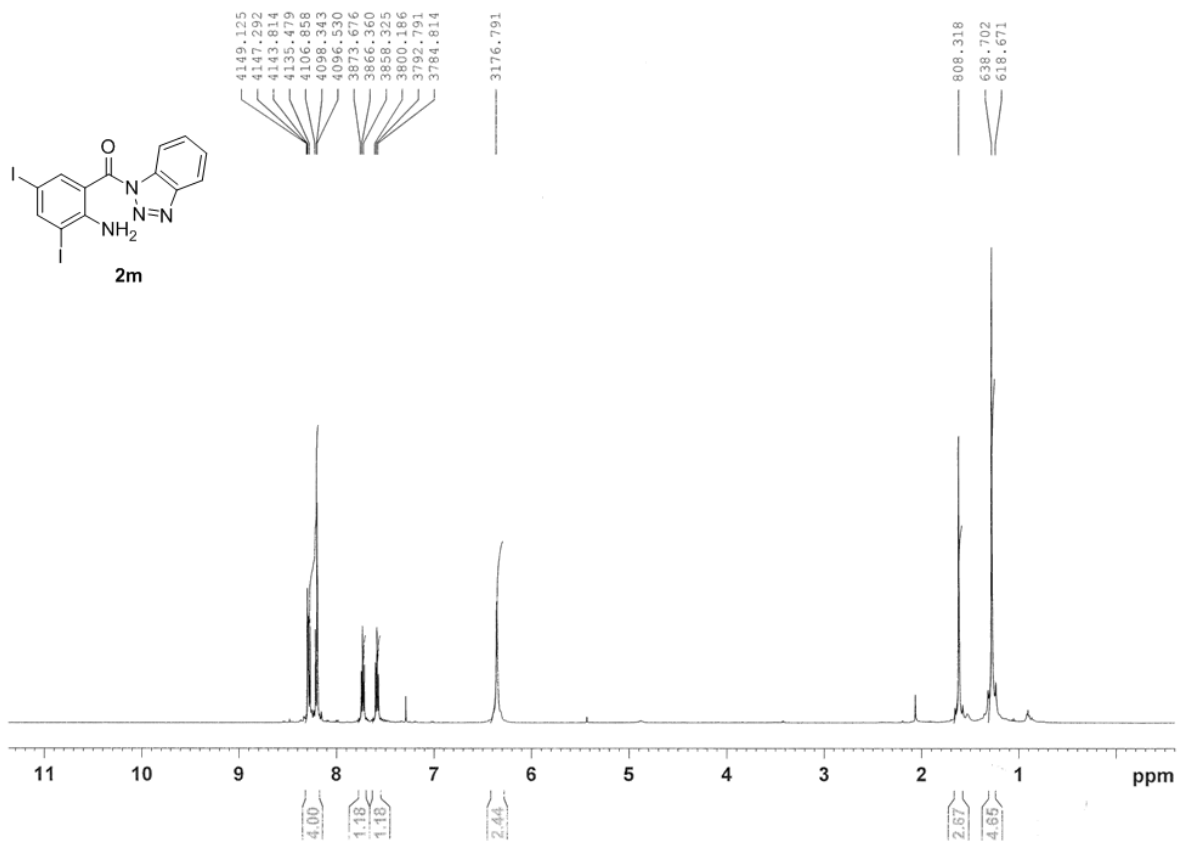
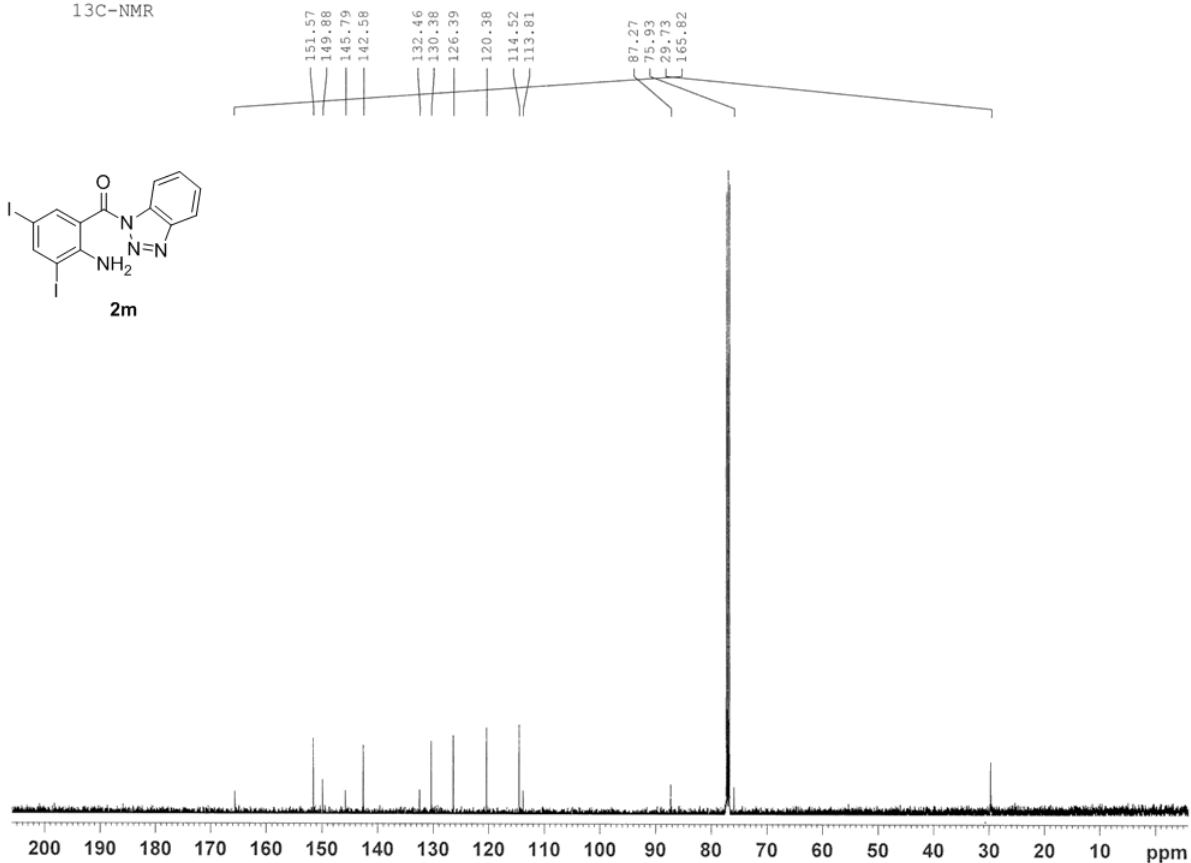


S-107-1 #1253 RT: 15.57 AV: 1 NL: 1.54E6
 T: + c Full ms [50.00-650.00]

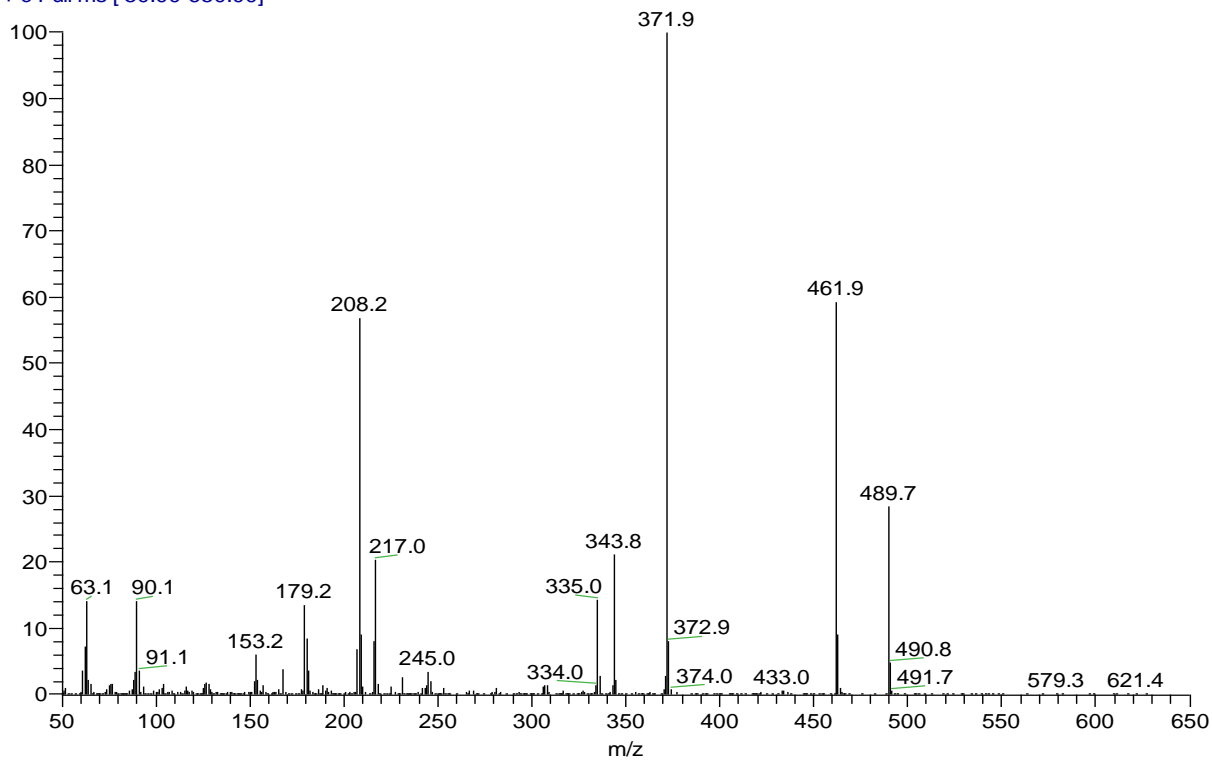


S-107-1 #1253 RT: 15.57 AV: 1 NL: 2.98E5
 T: + c Full ms [50.00-650.00]



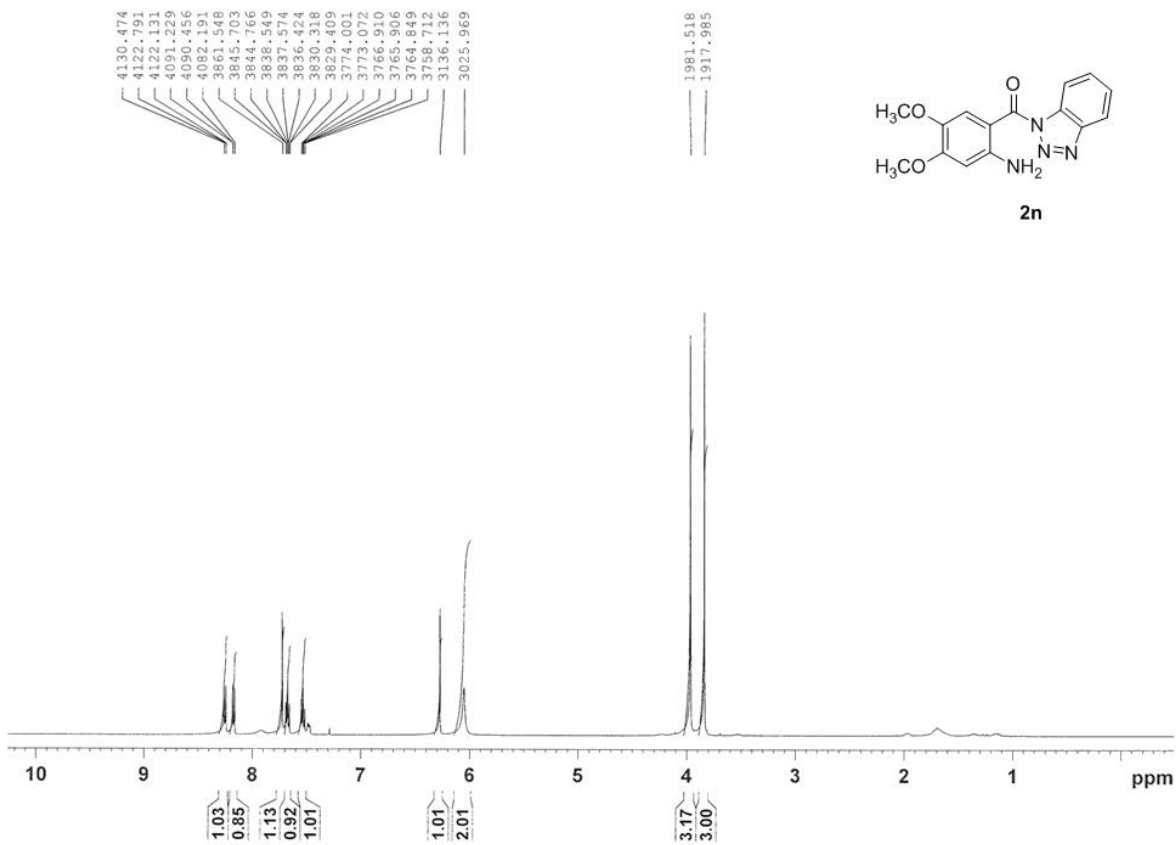
(2-Amino-3, 5-diiodophenyl) (benzotriazole-1-yl)methanone (**2m**)¹H-NMR¹³C-NMR

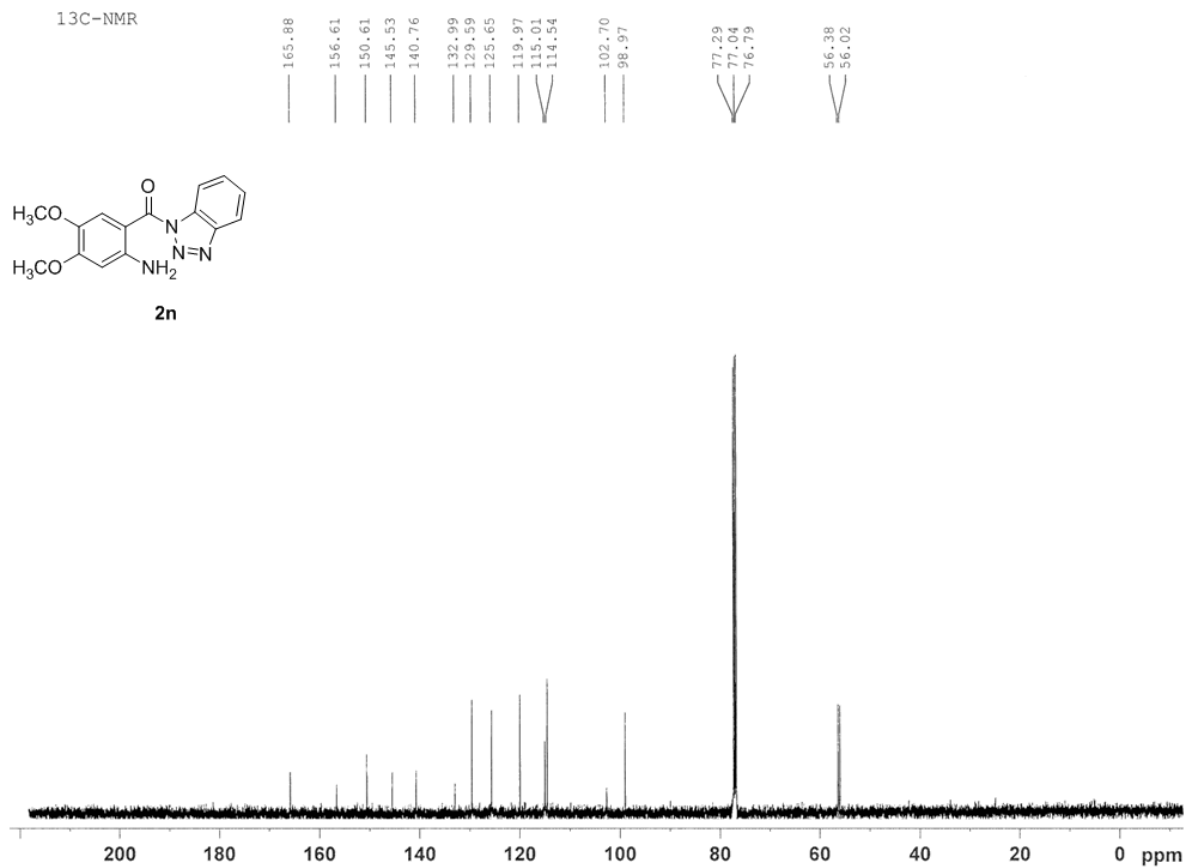
Di-I-02 #1382 RT: 17.91 AV: 1 NL: 2.96E6
 T: + c Full ms [50.00-650.00]



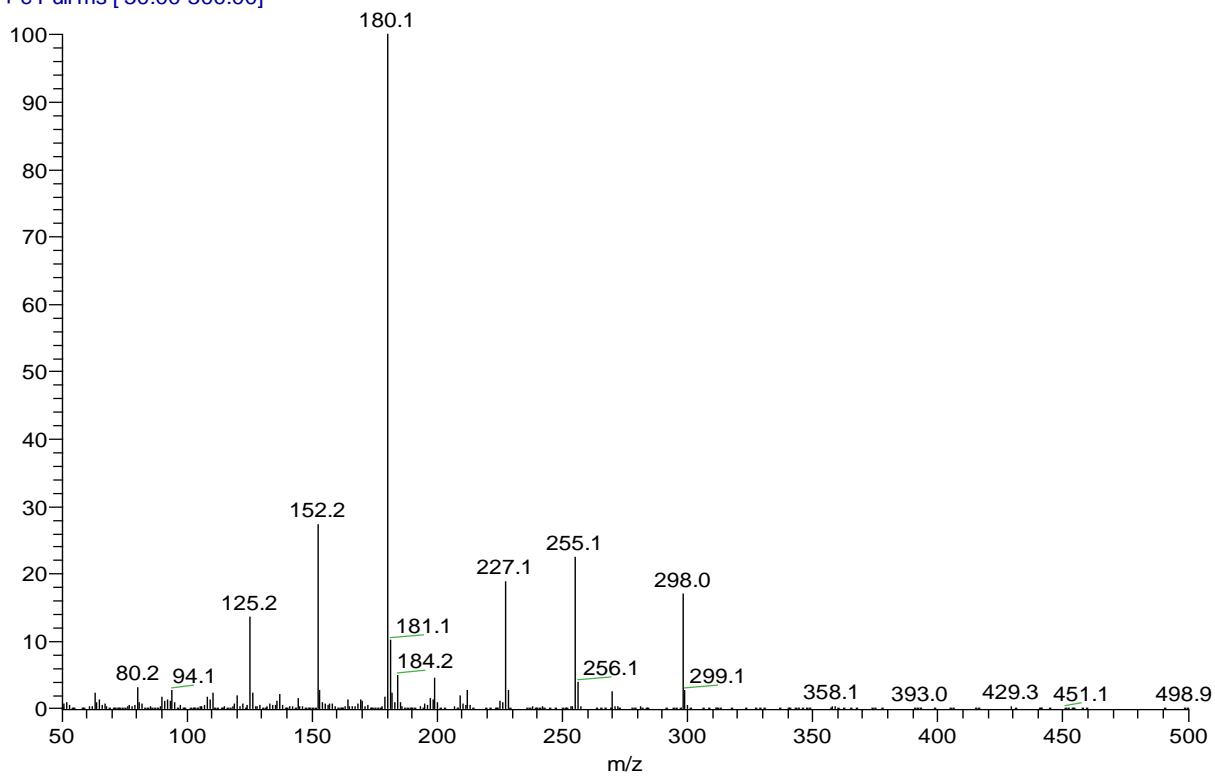
(2-Amino-4, 5-dimethoxyphenyl) (benzotriazole-1-yl)methanone (**2n**)

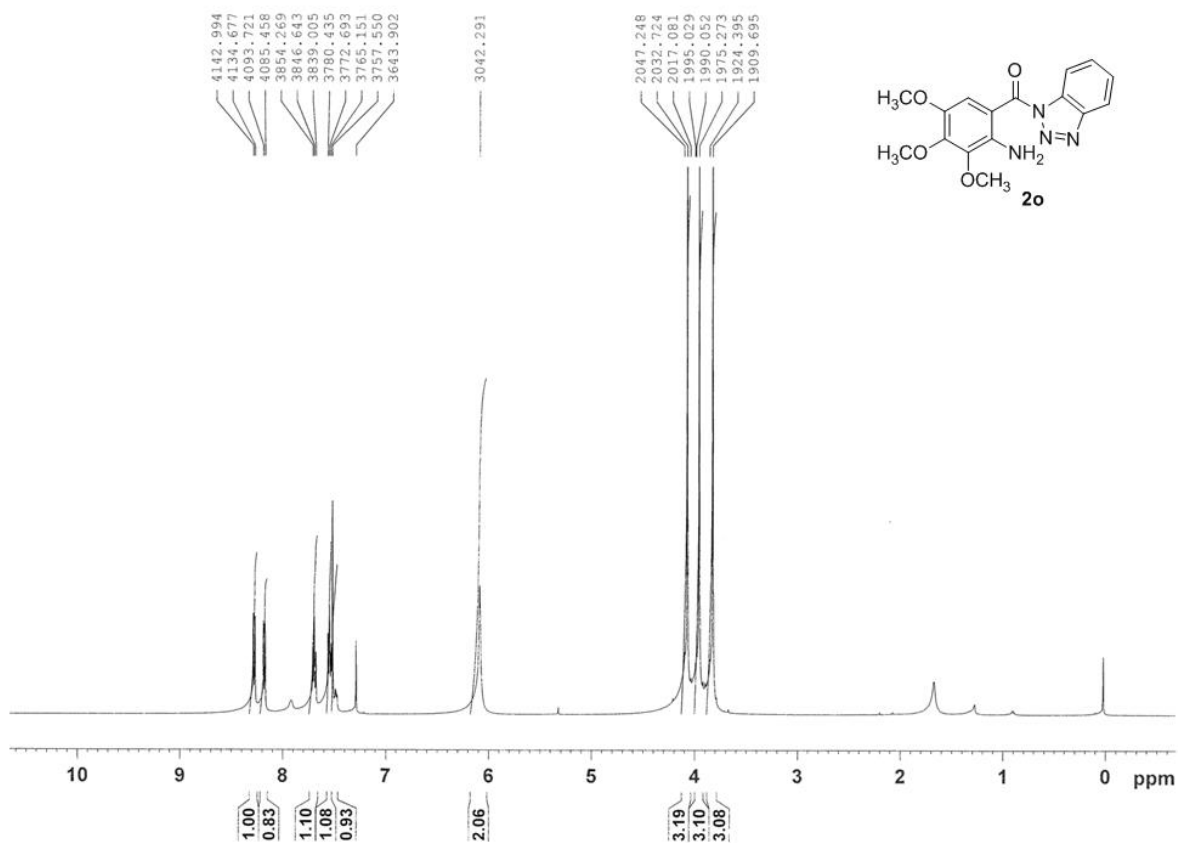
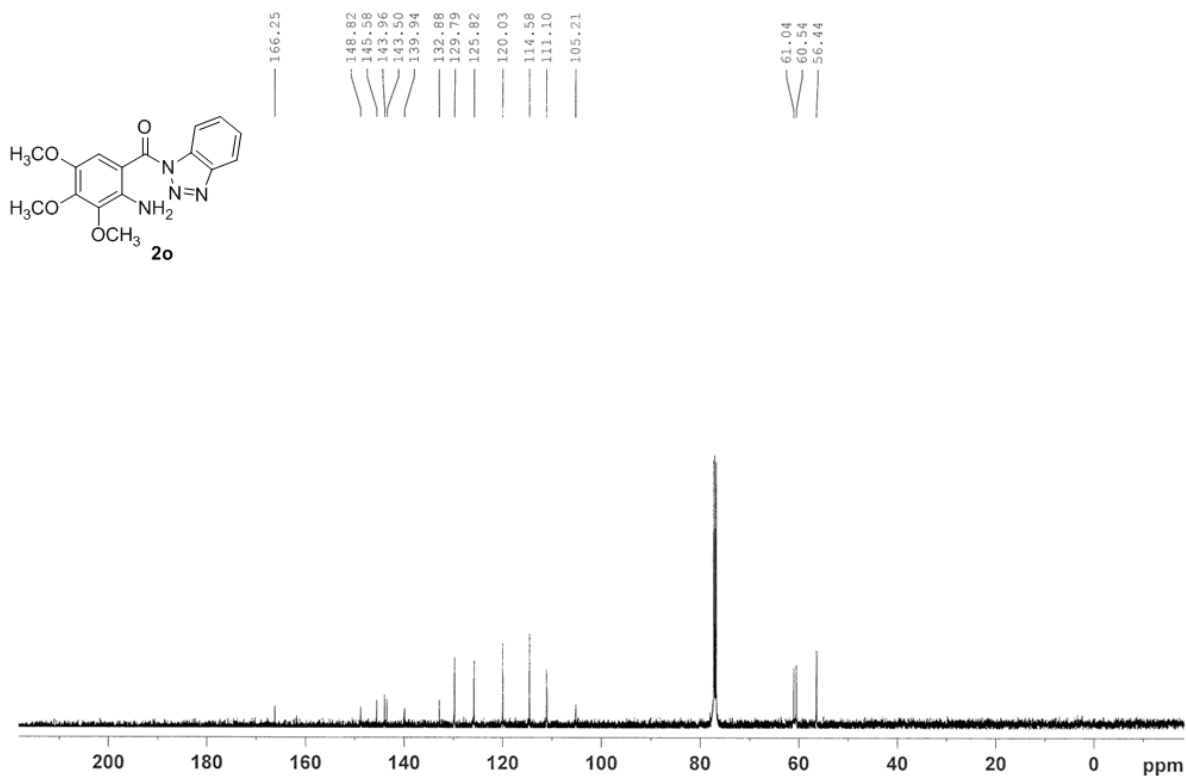
¹H-NMR





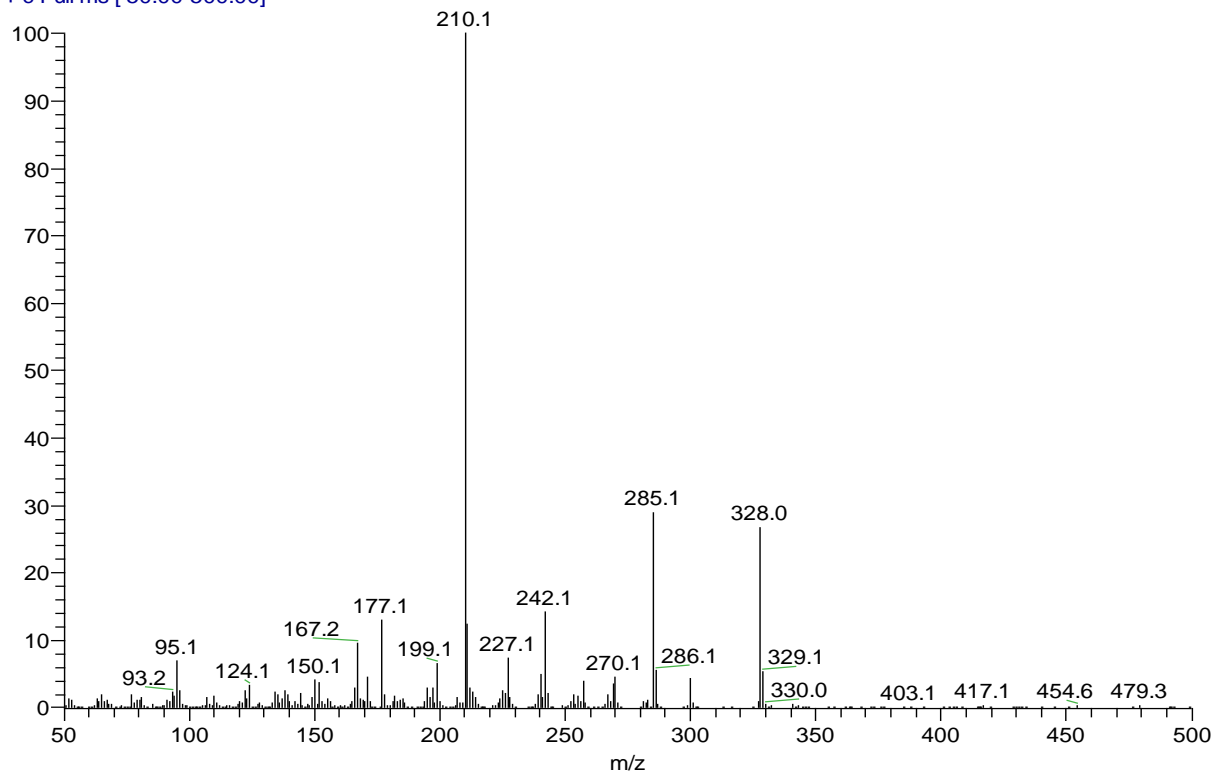
s108-2 #3037 RT: 28.12 AV: 1 NL: 2.18E7
T: + c Full ms [50.00-500.00]



(2-Amino-3, 4, 5-trimethoxyphenyl) (benzotriazole-1-yl)methanone (**2o**)¹H-NMR¹³C-NMR

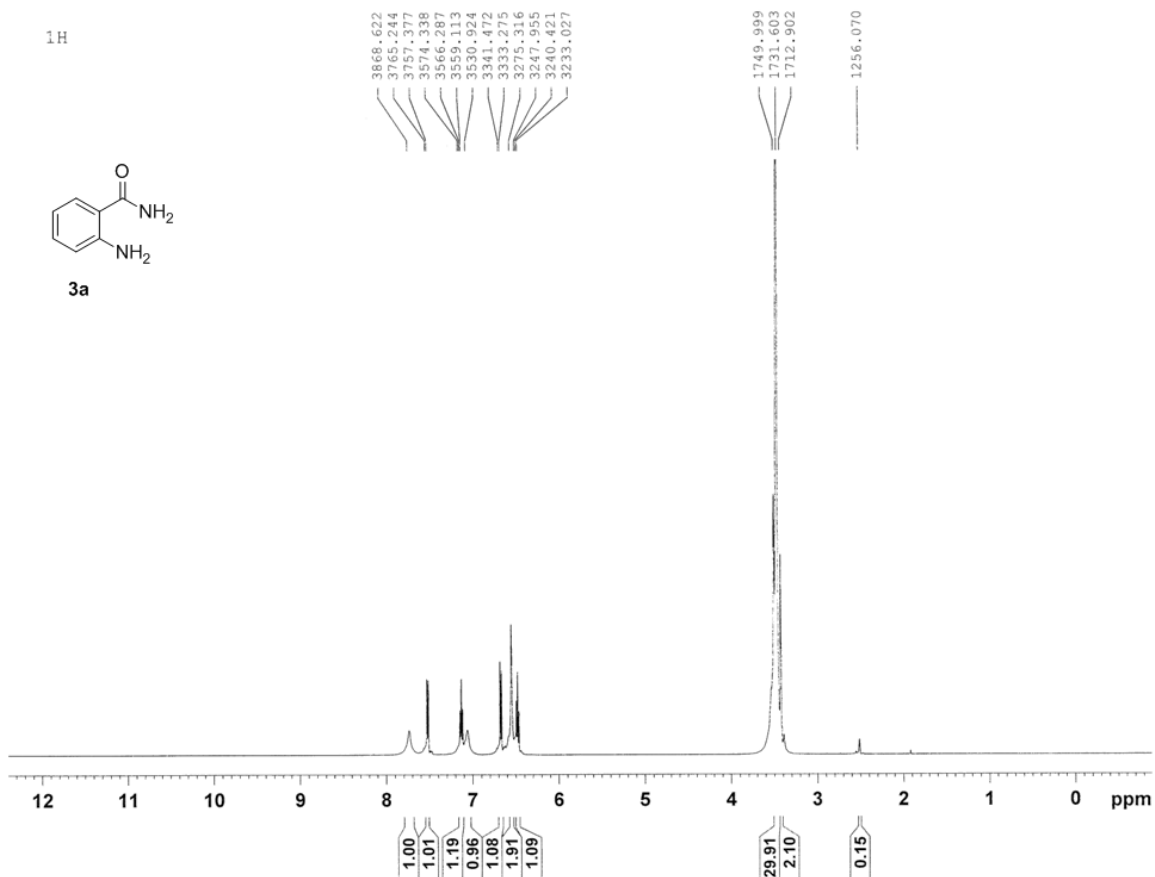
S113 #2880 RT: 27.50 AV: 1 NL: 4.29E6

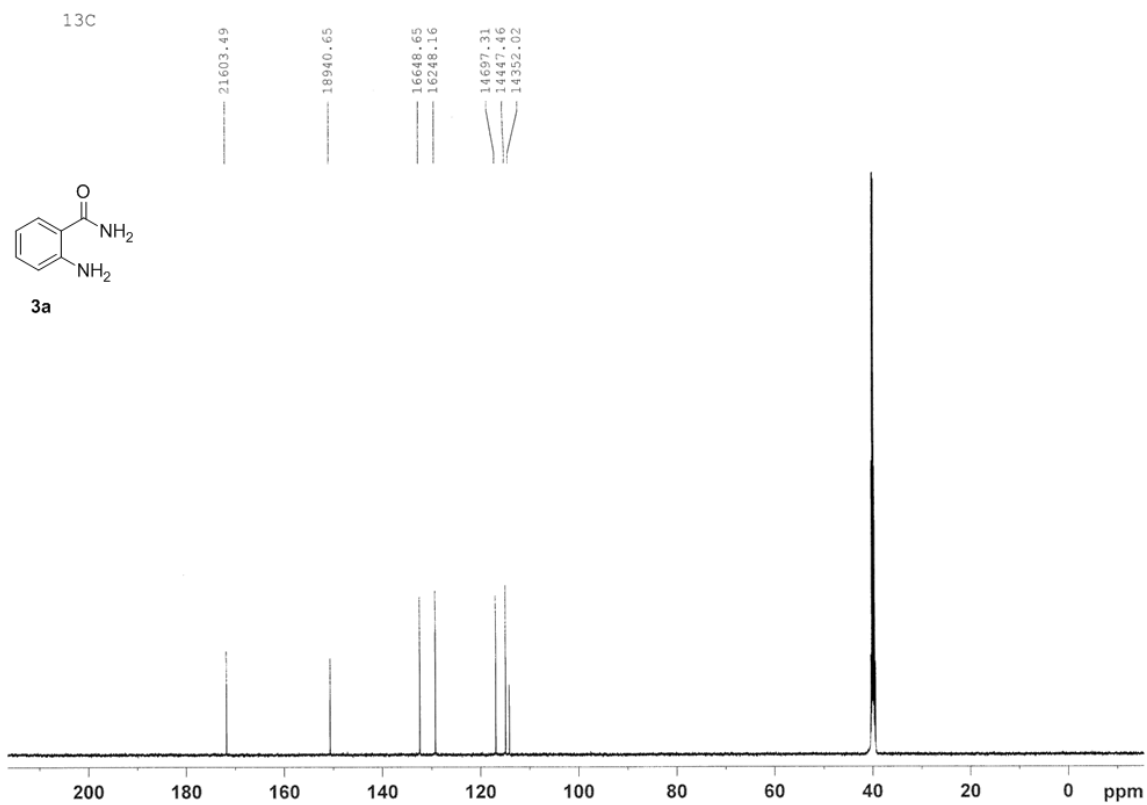
T: + c Full ms [50.00-500.00]



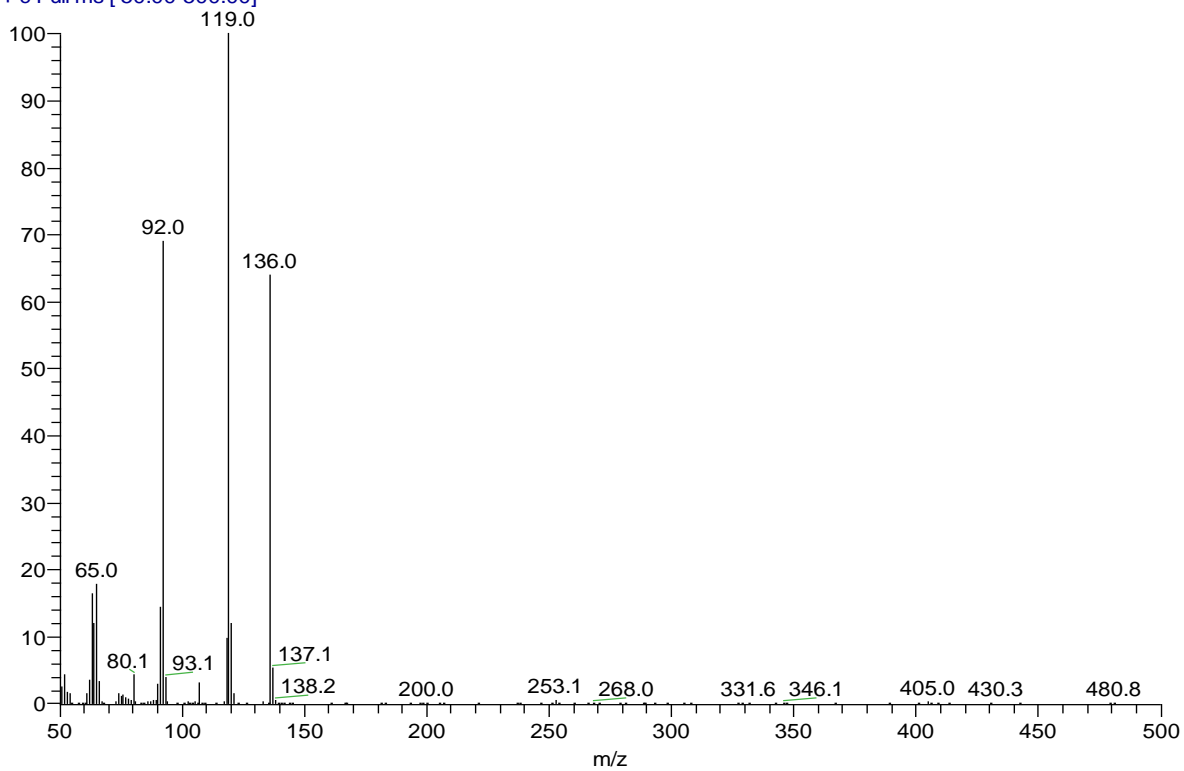
2. Primary Amides (3a-g)

2-Aminobenzamide (3a)

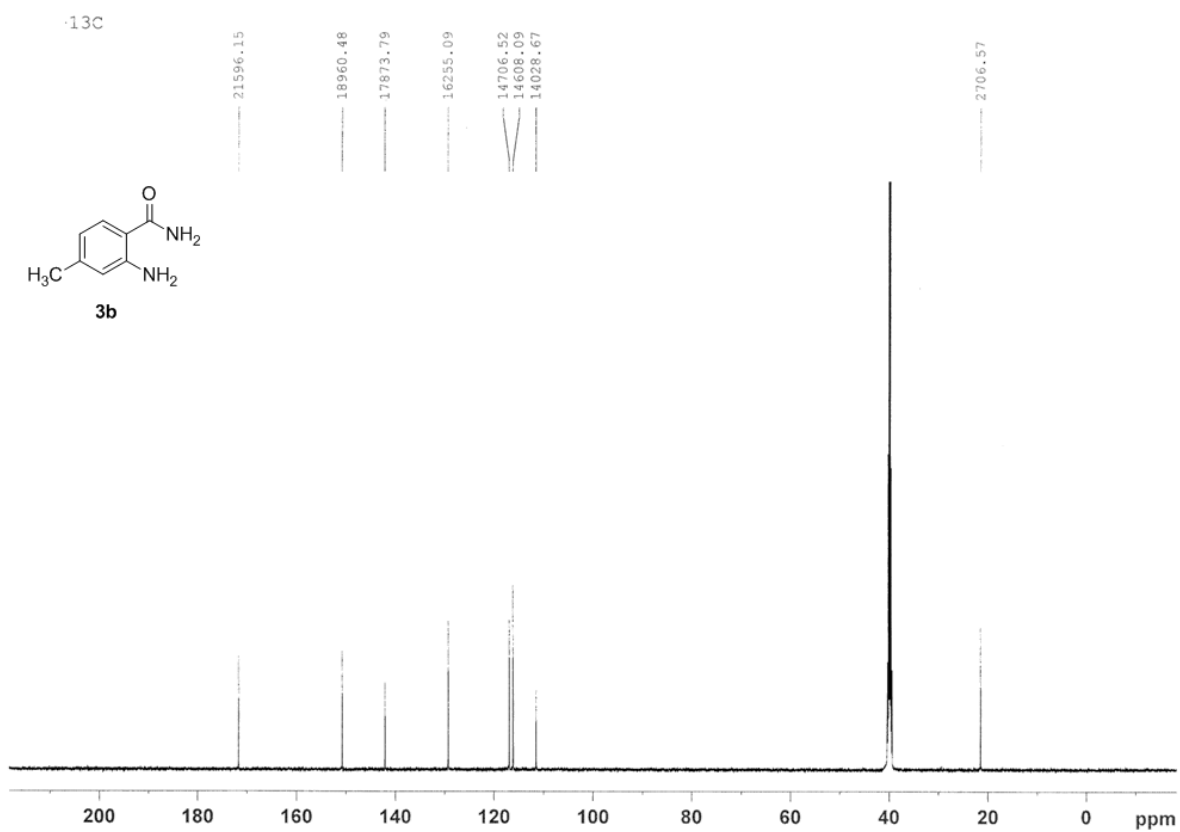
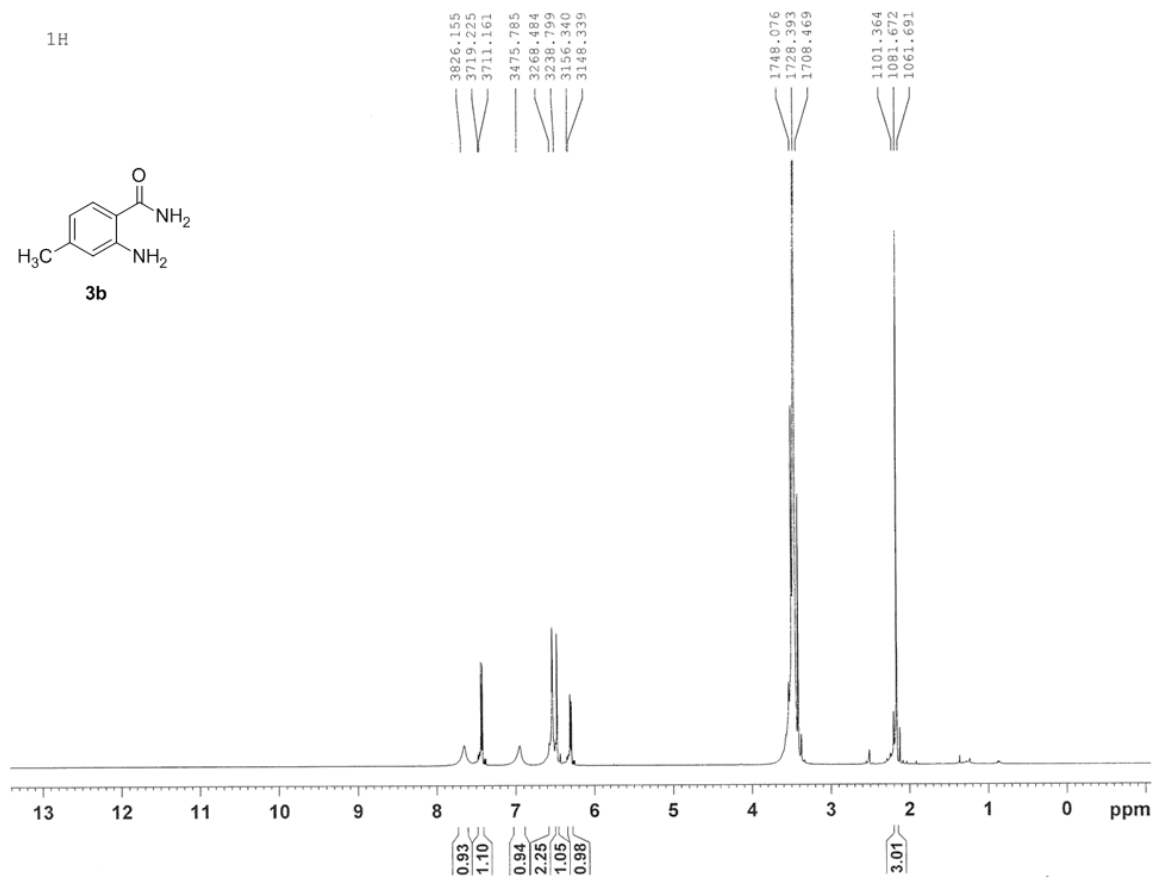




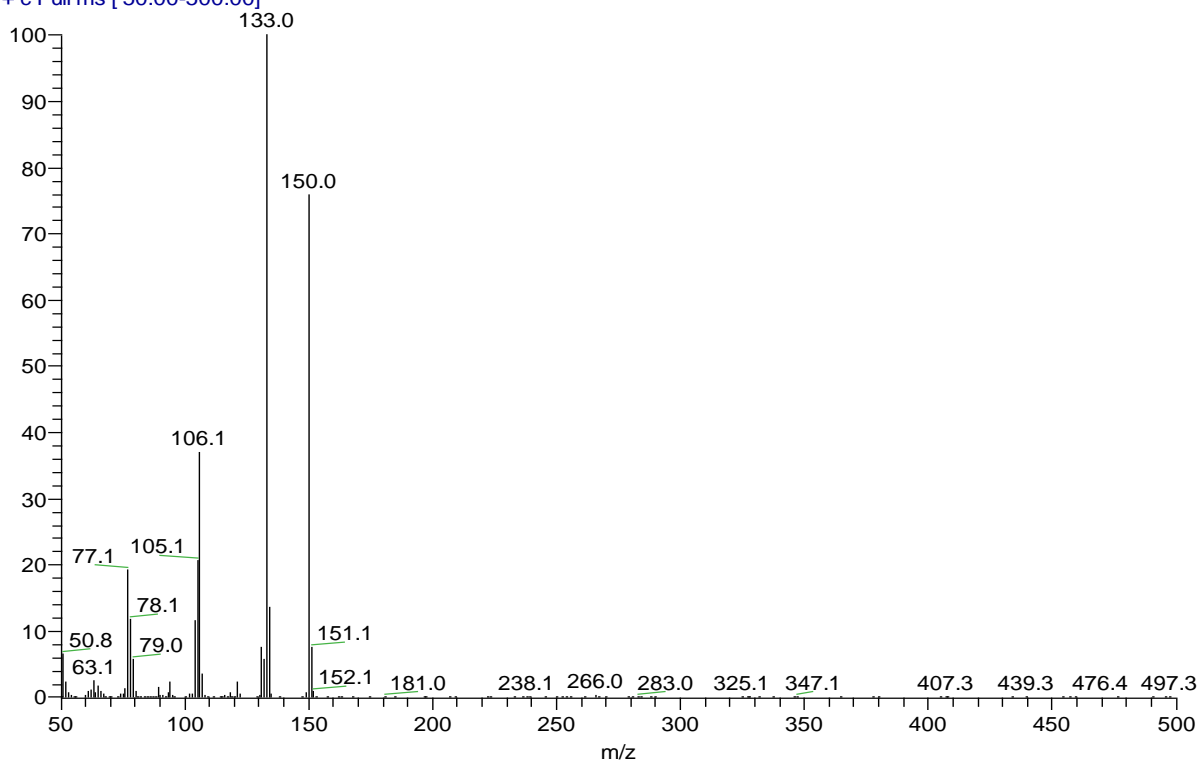
S142-136 #1381 RT: 14.73 AV: 1 NL: 4.35E5
T: + c Full ms [50.00-500.00]



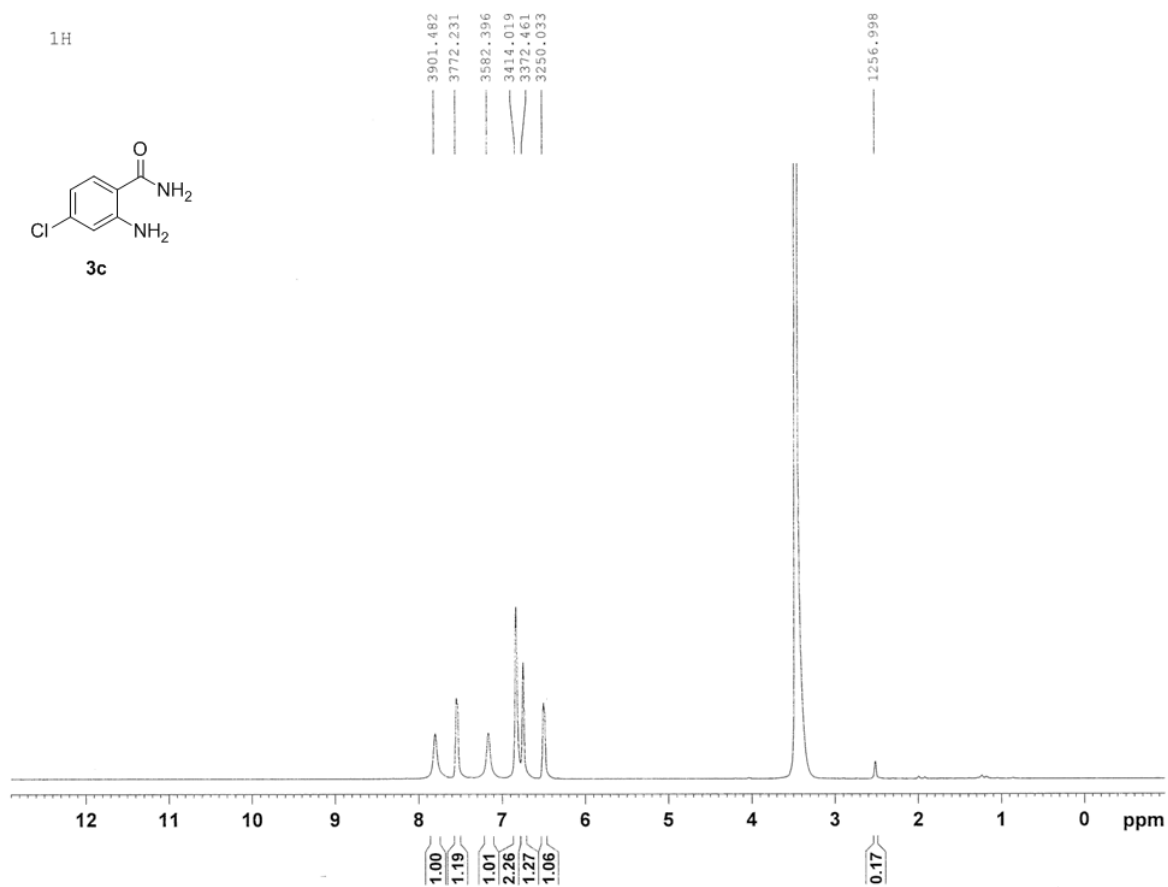
2-Amino-4-methylbenzamide (3b)

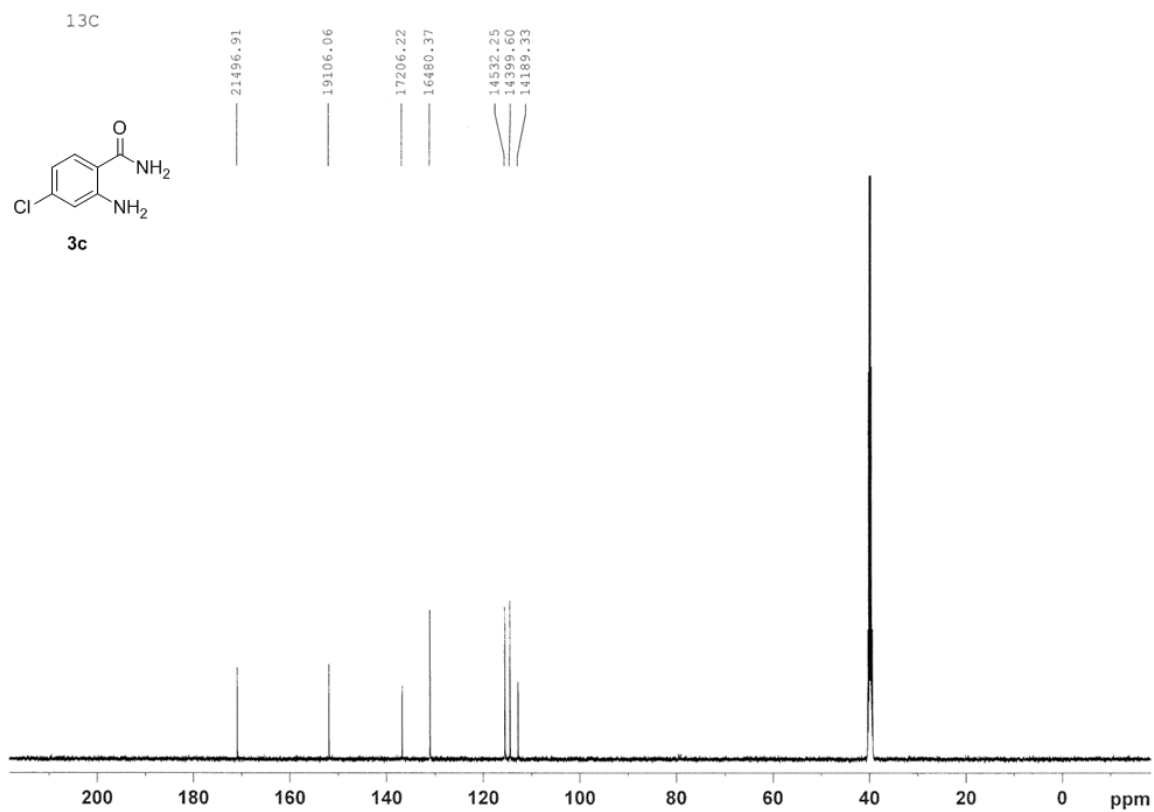


S143 #1495 RT: 16.06 AV: 1 NL: 4.23E6
T: + c Full ms [50.00-500.00]

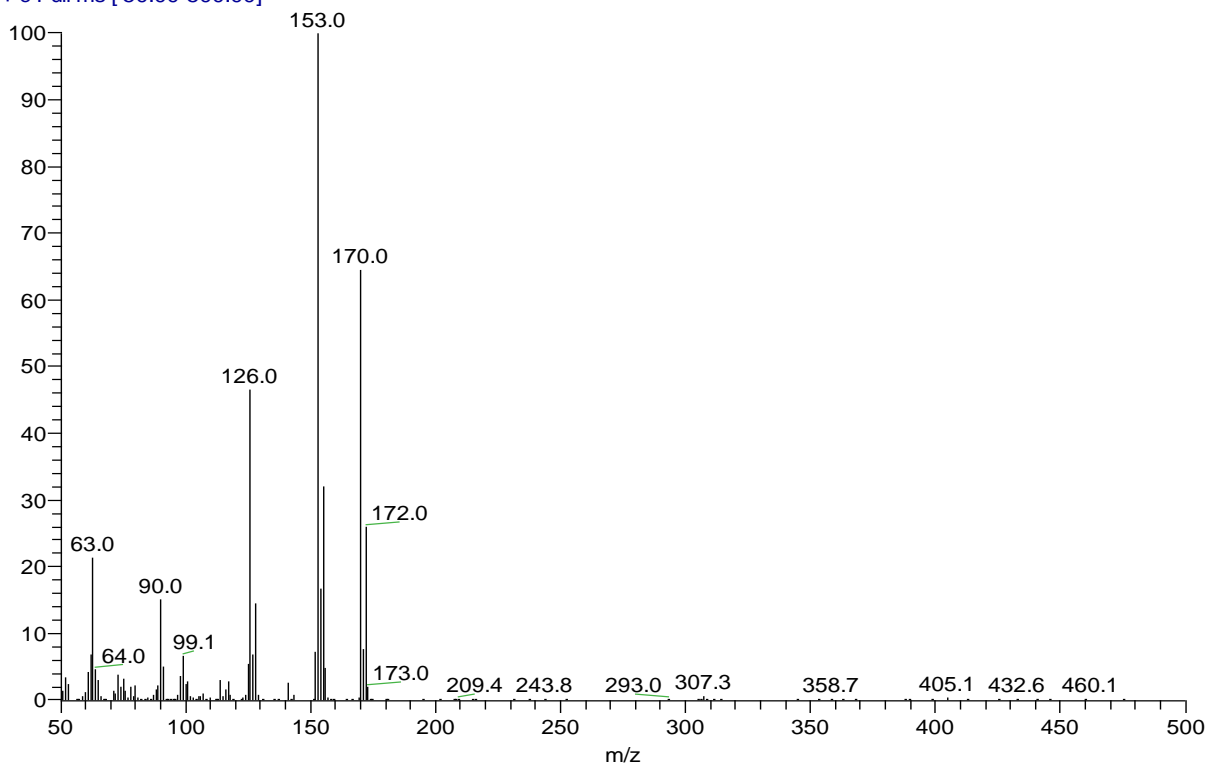


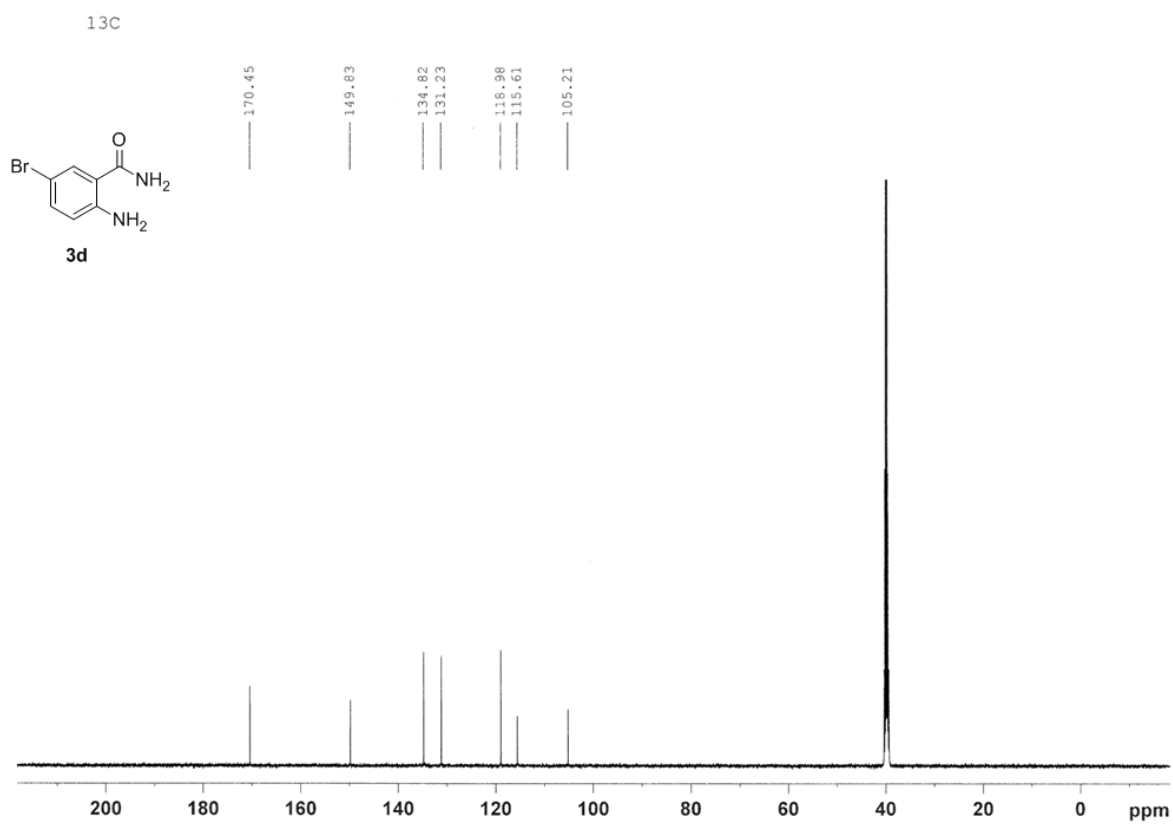
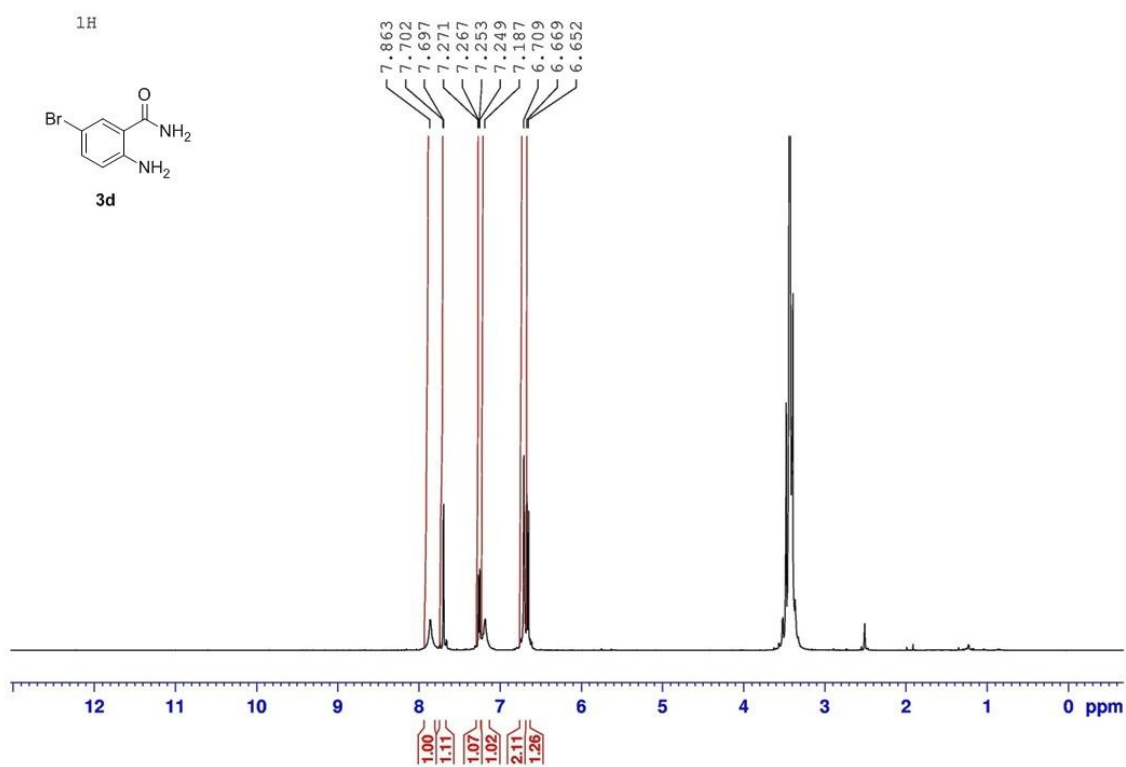
2-Amino-4-chlorobenzamide (**3c**)



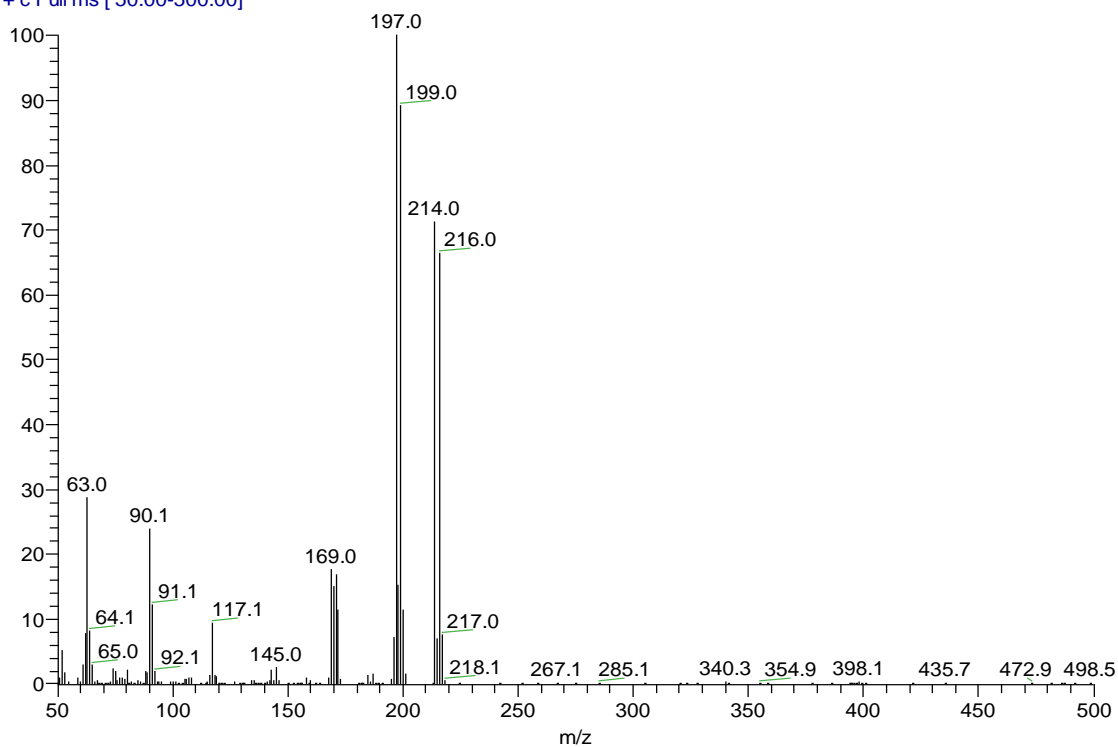


S144-170 #1686 RT: 17.25 AV: 1 NL: 1.52E6
 T: + c Full ms [50.00-500.00]

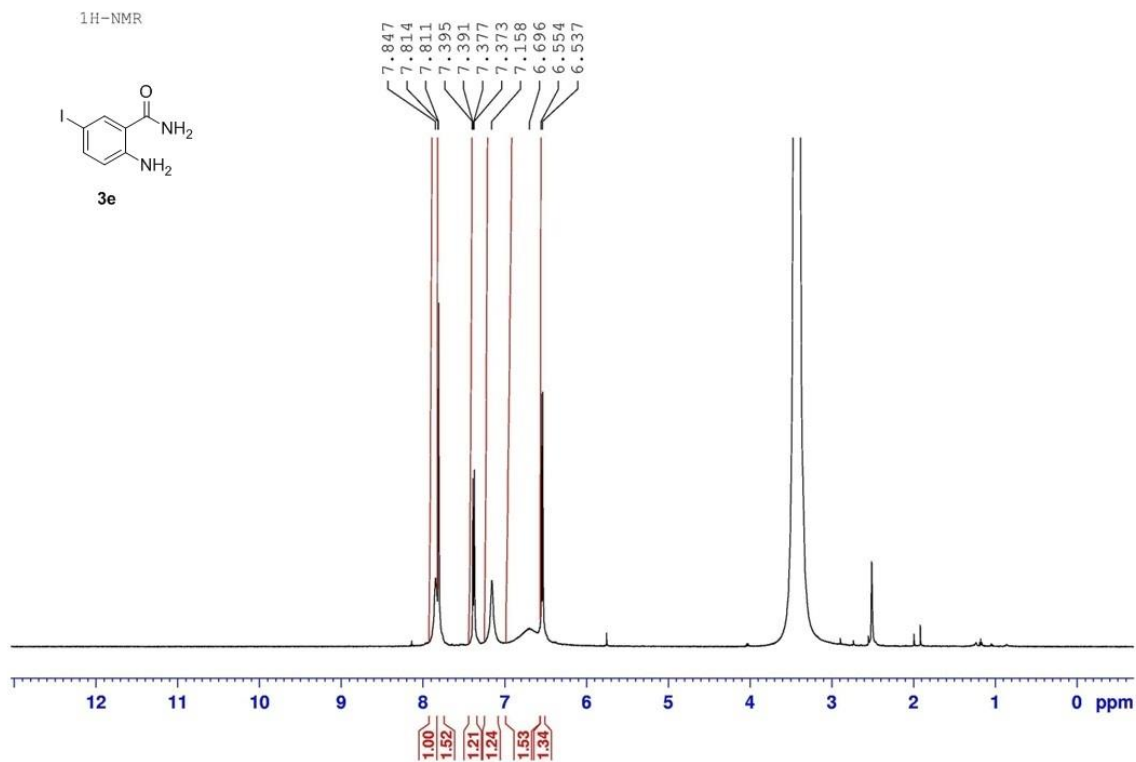


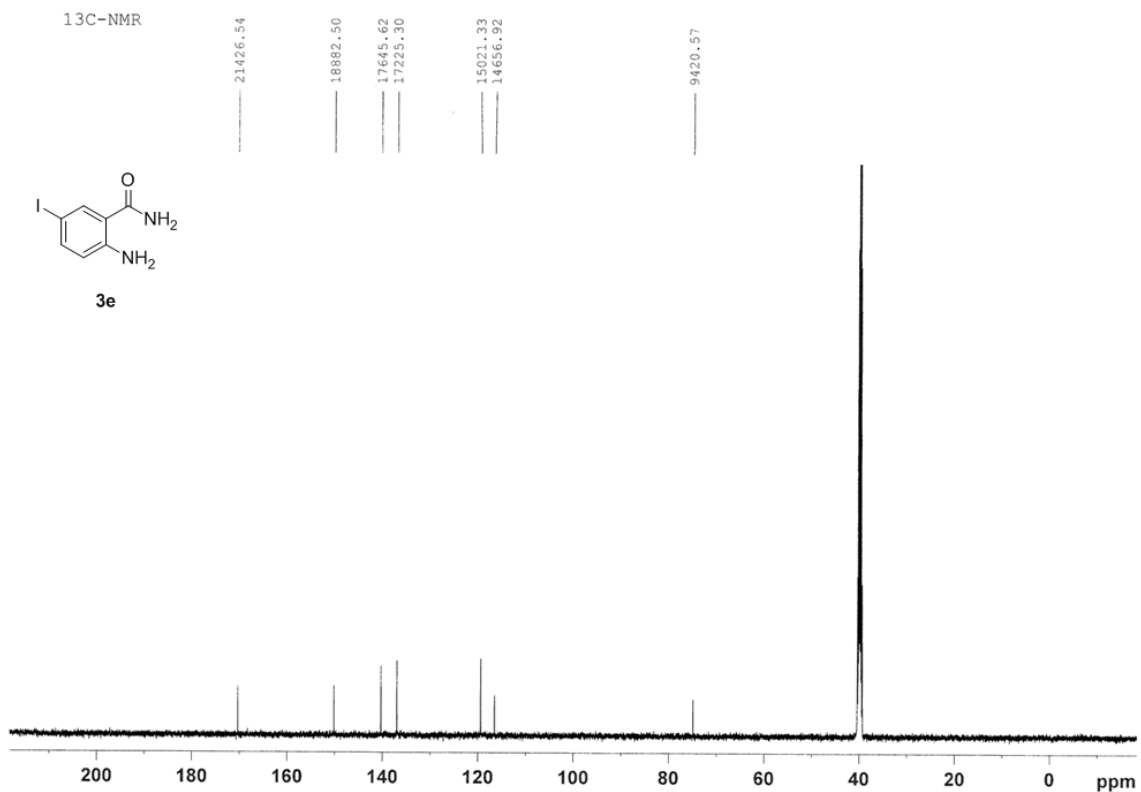
2-Amino-5-bromobenzamide (**3d**)

S147-215 #1794 RT: 18.25 AV: 1 NL: 1.46E6
T: + c Full ms [50.00-500.00]

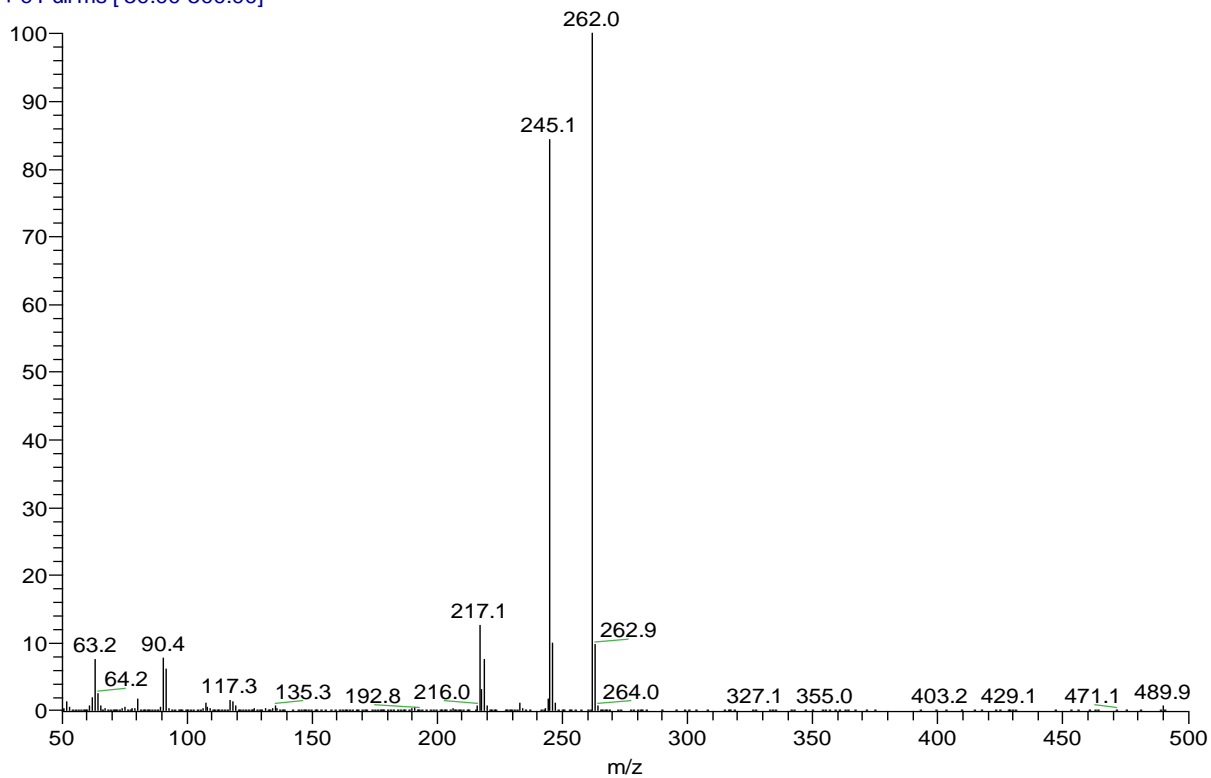


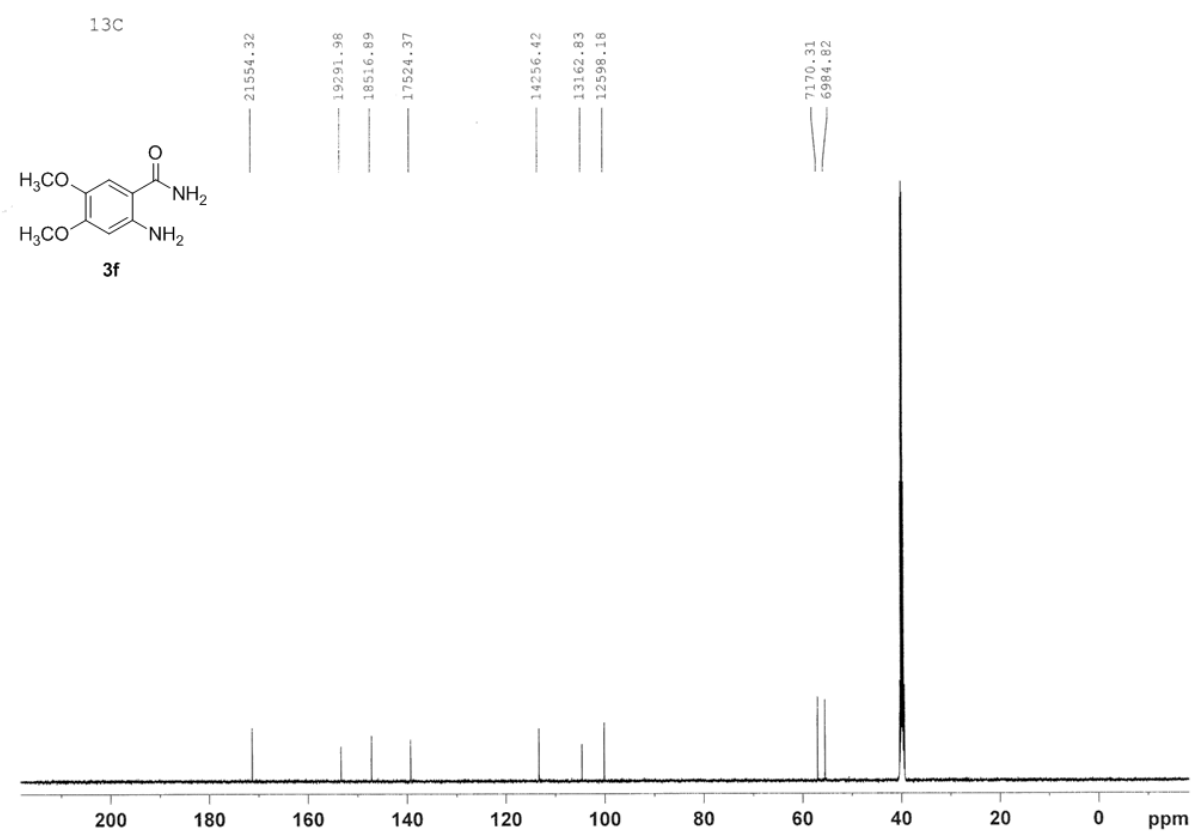
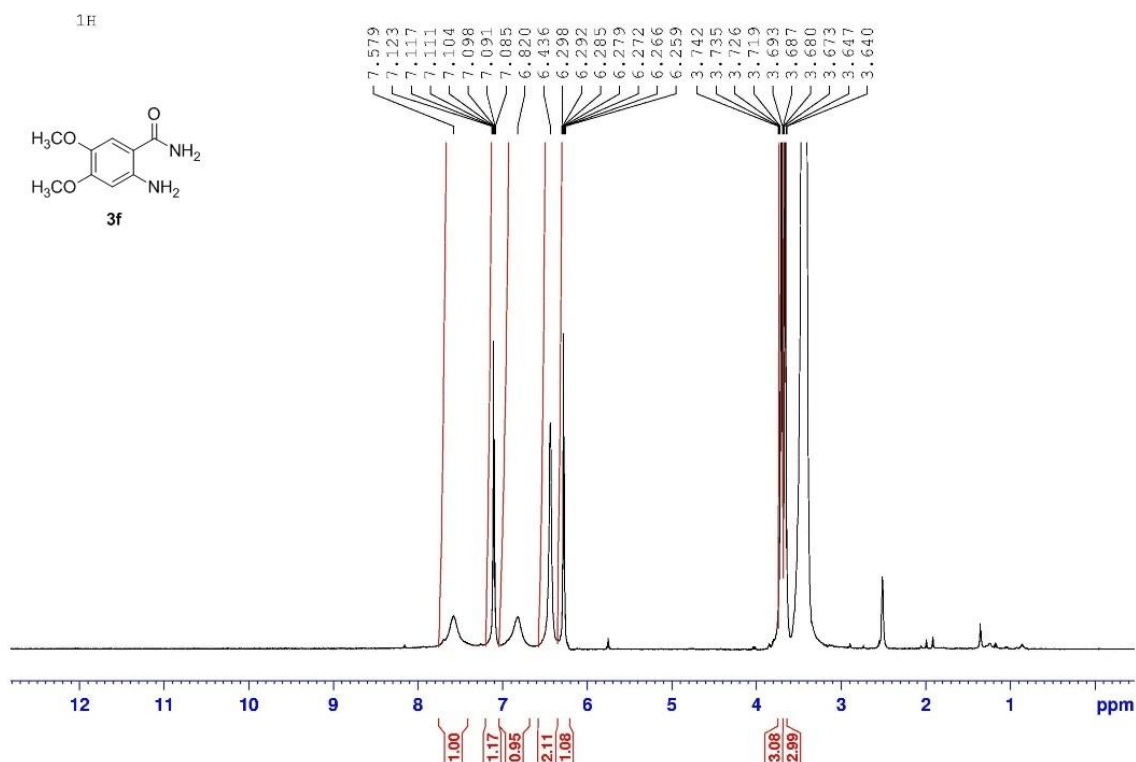
2-Amino-5-iodobenzamide (**3e**)



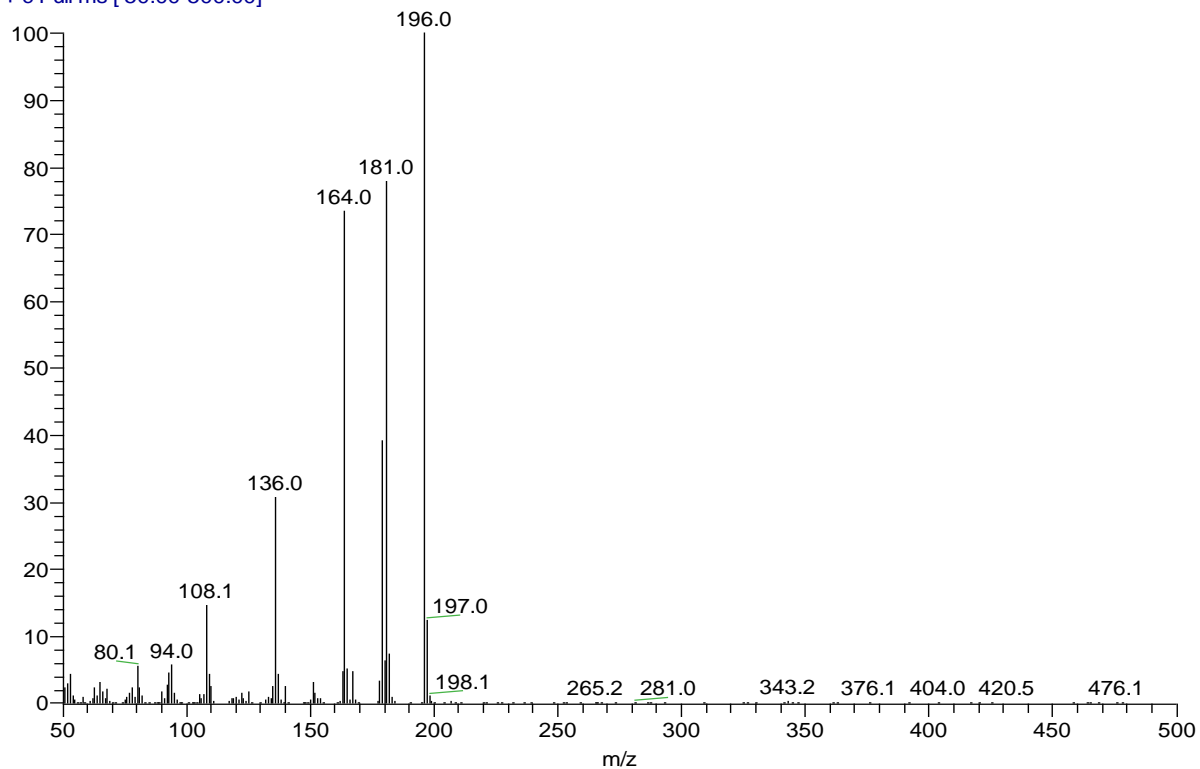


S125 #1950 RT: 19.56 AV: 1 NL: 2.81E7
T: + c Full ms [50.00-500.00]

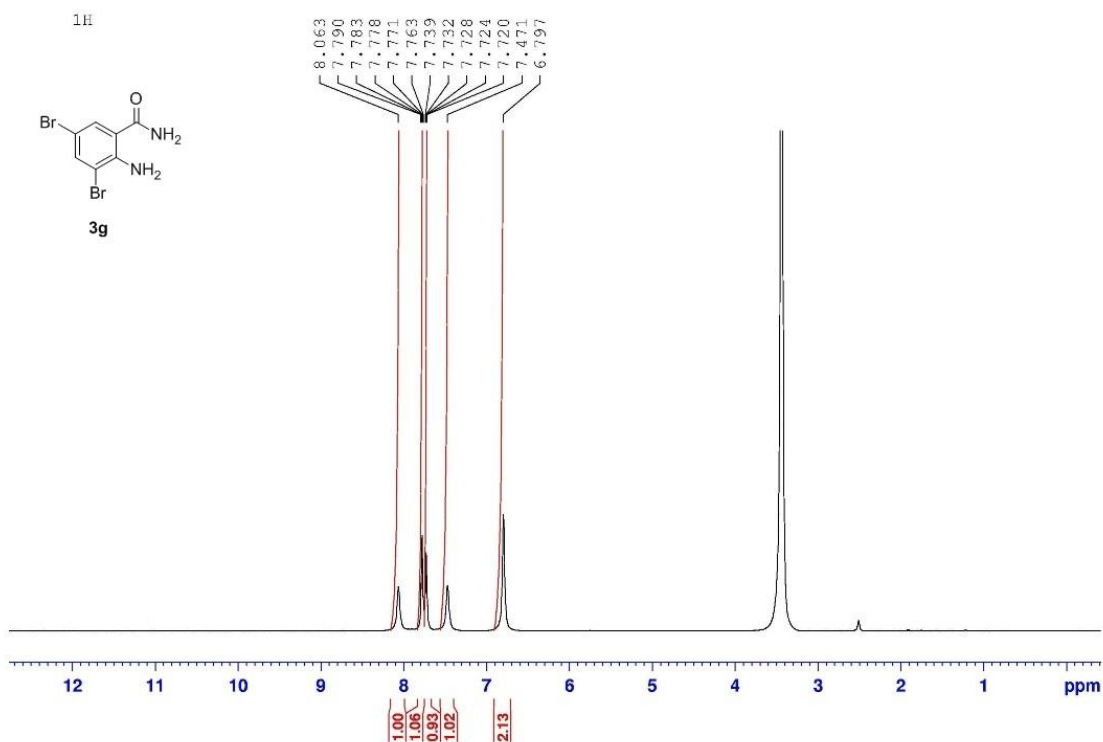


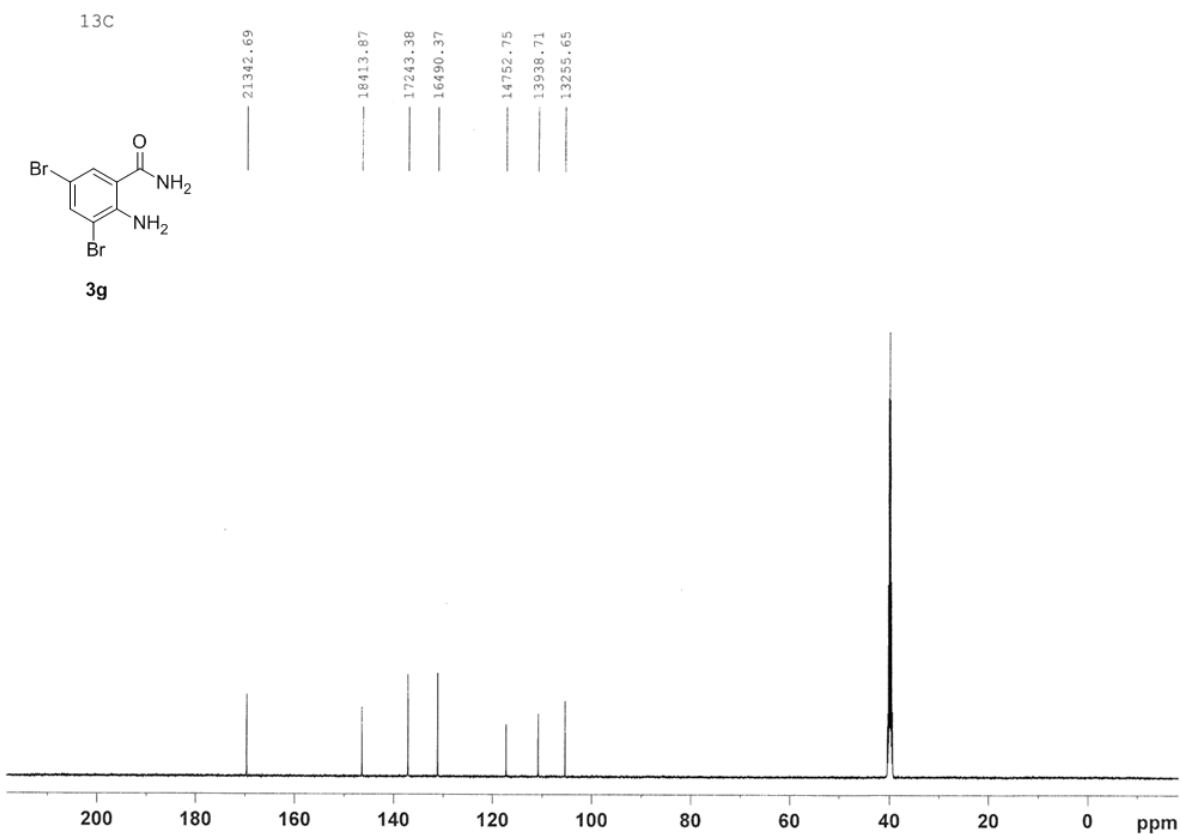
2-Amino-4,5-dimethoxybenzamide (**3f**)

S146 #1966 RT: 19.95 AV: 1 NL: 2.46E6
T: + c Full ms [50.00-500.00]

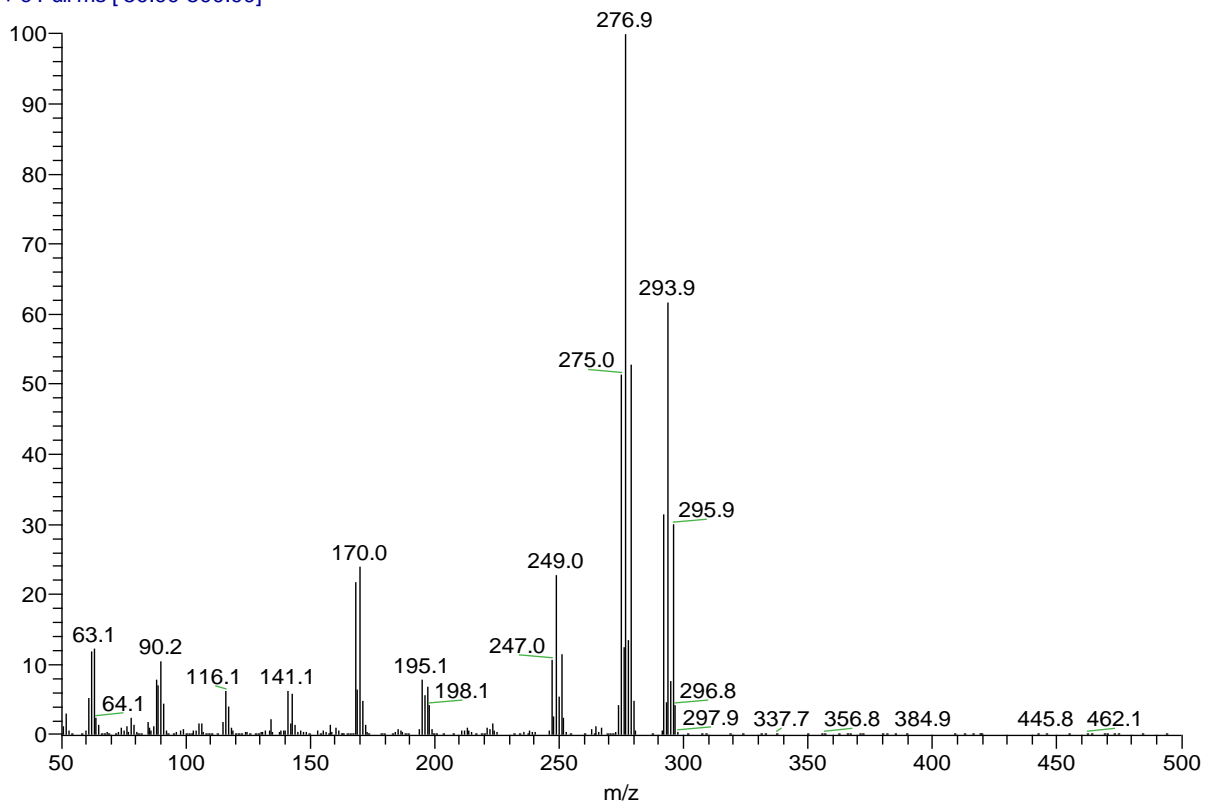


2-Amino-3,5-dibromobenzamide (**3g**)

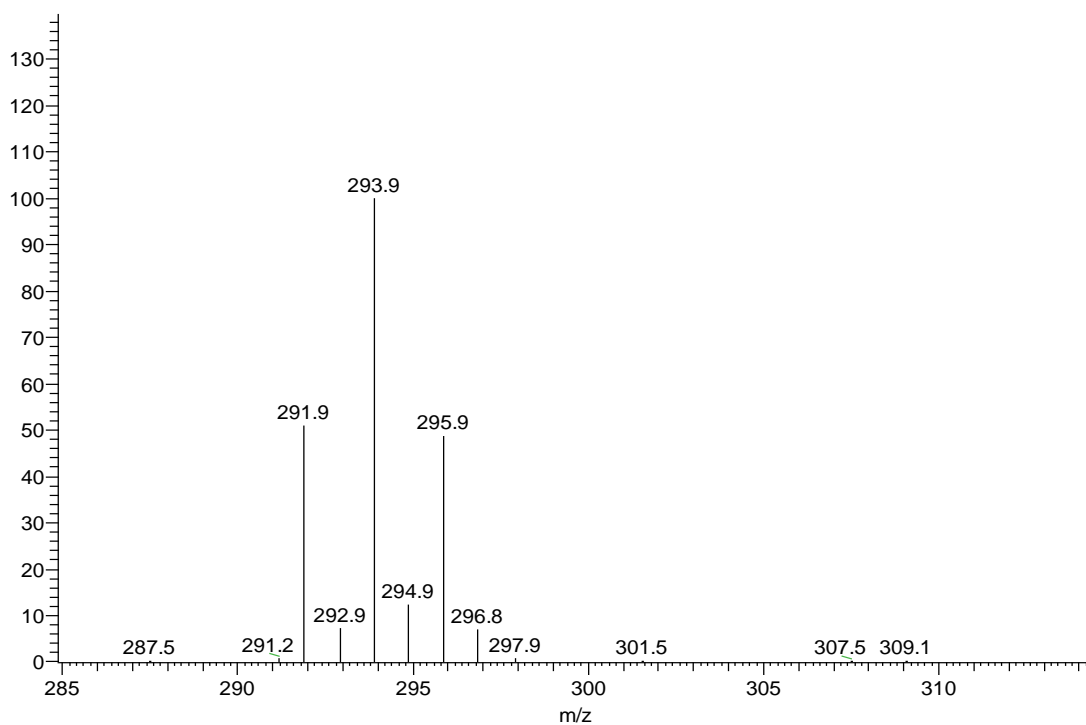




S145-294 #2042 RT: 20.40 AV: 1 NL: 7.07E6
T: + c Full ms [50.00-500.00]

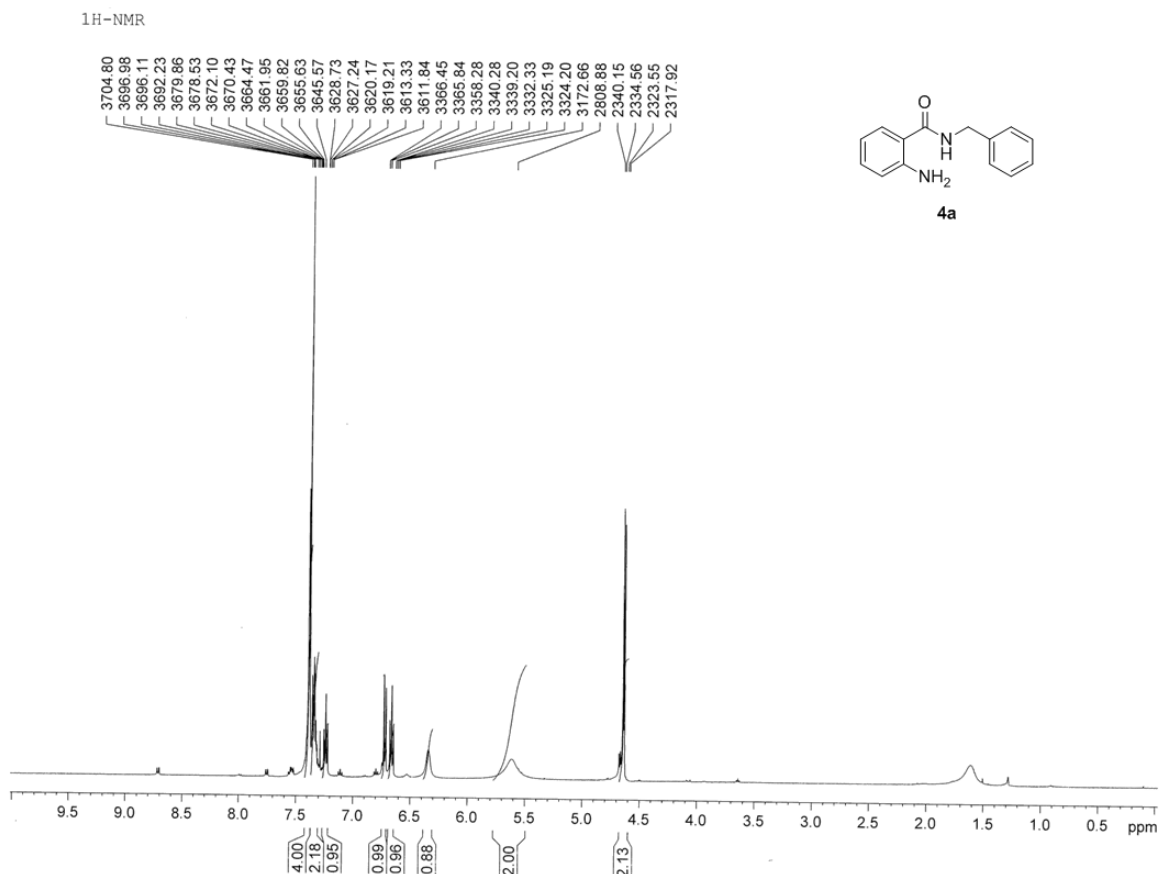


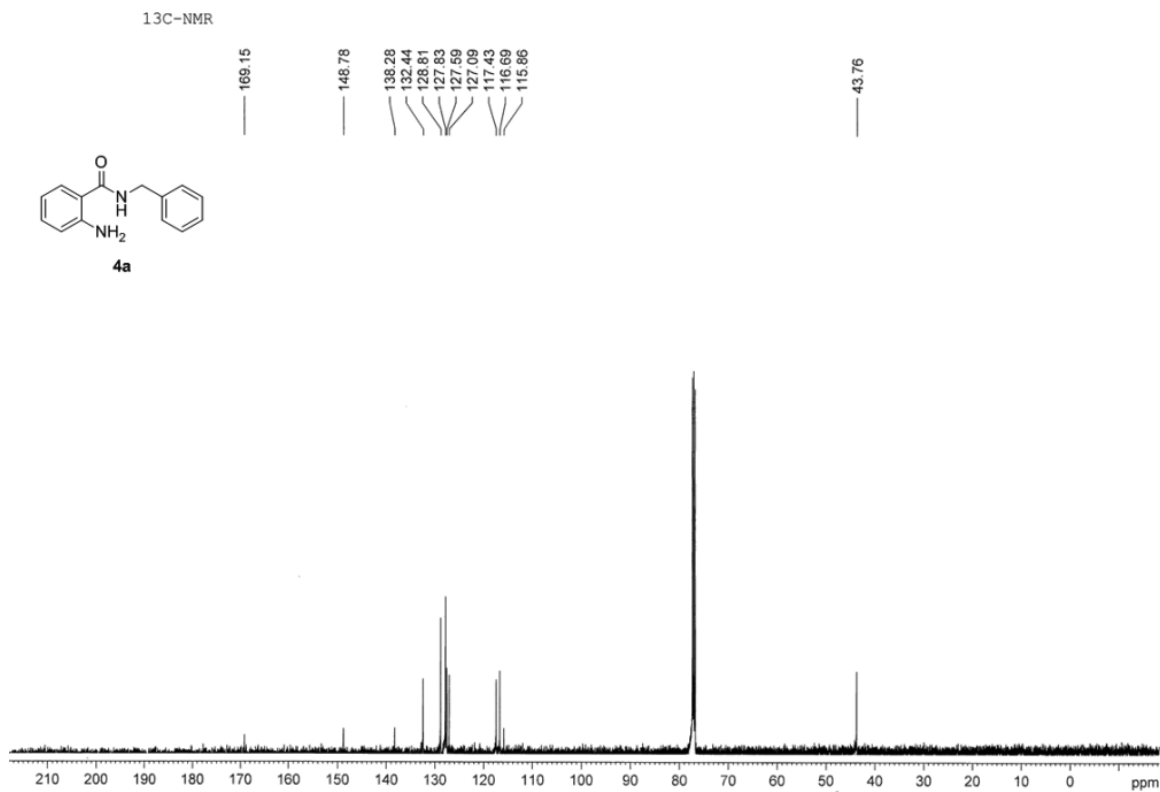
S145-294 #2042 RT: 20.40 AV: 1 NL: 4.36E6
 T: + c Full ms [50.00-500.00]



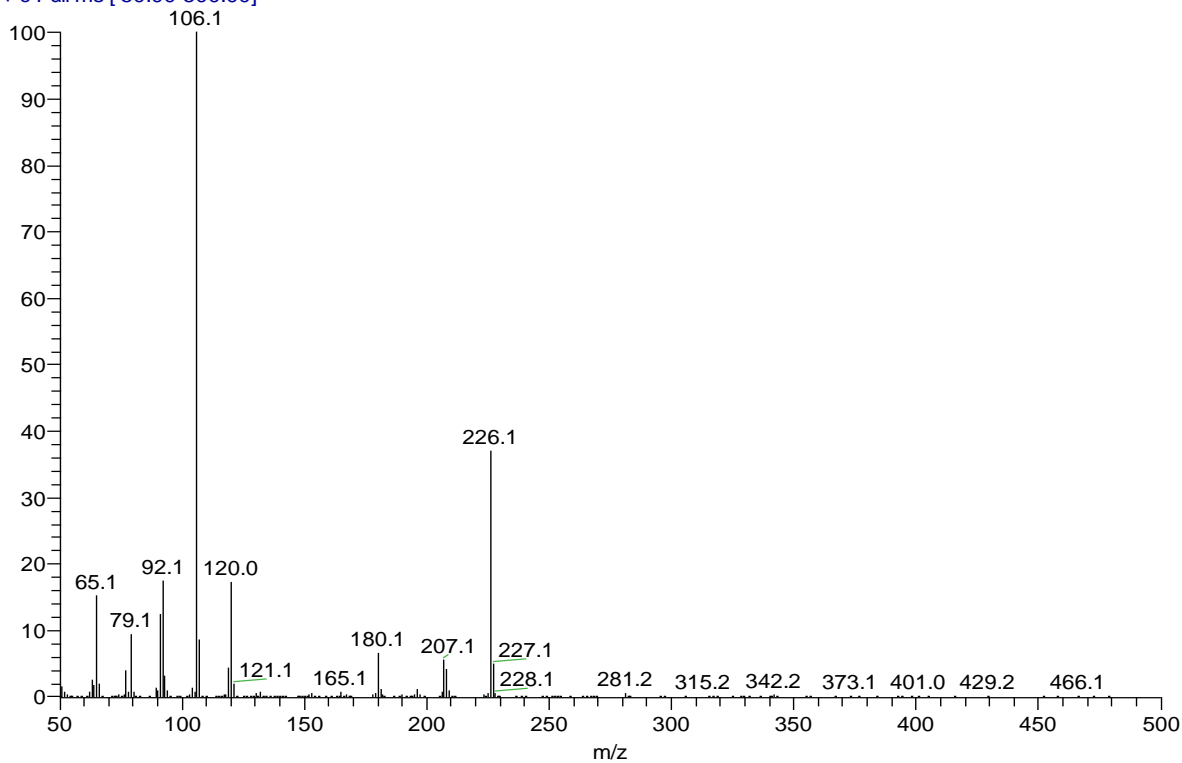
3. Secondary Antranilamides (4a-i)

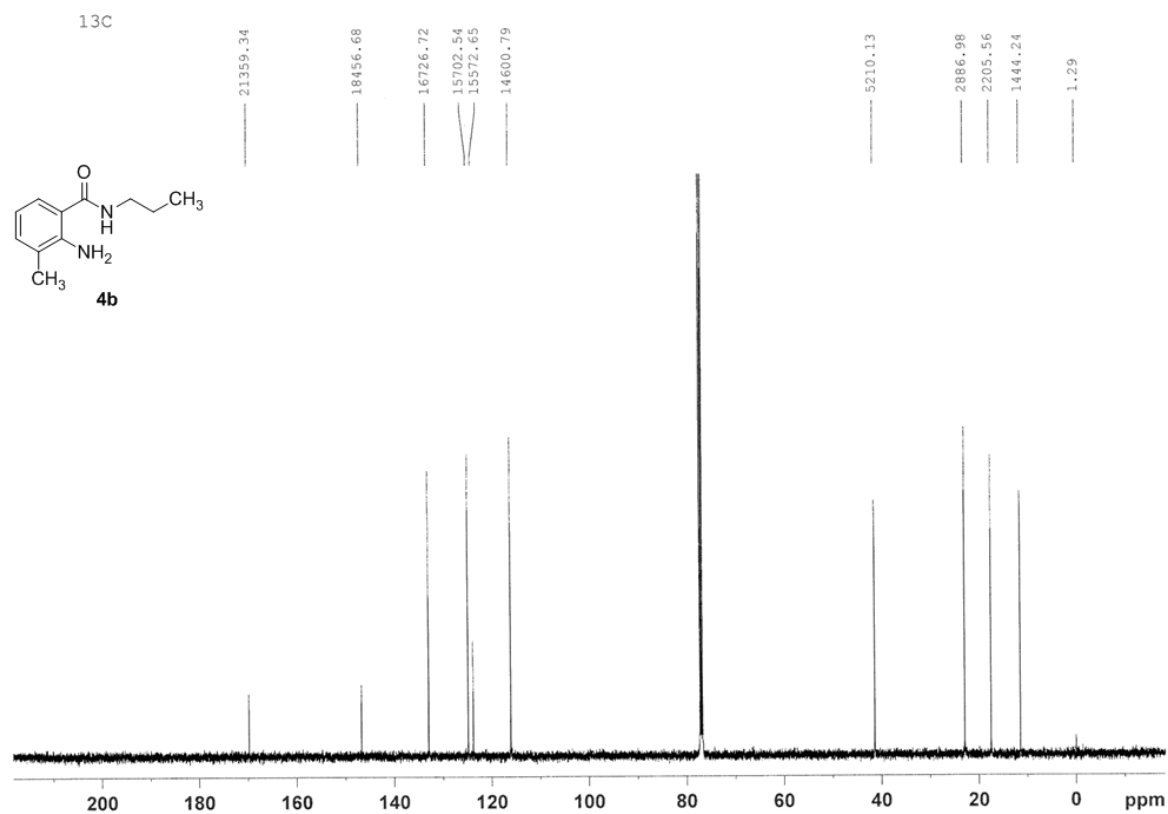
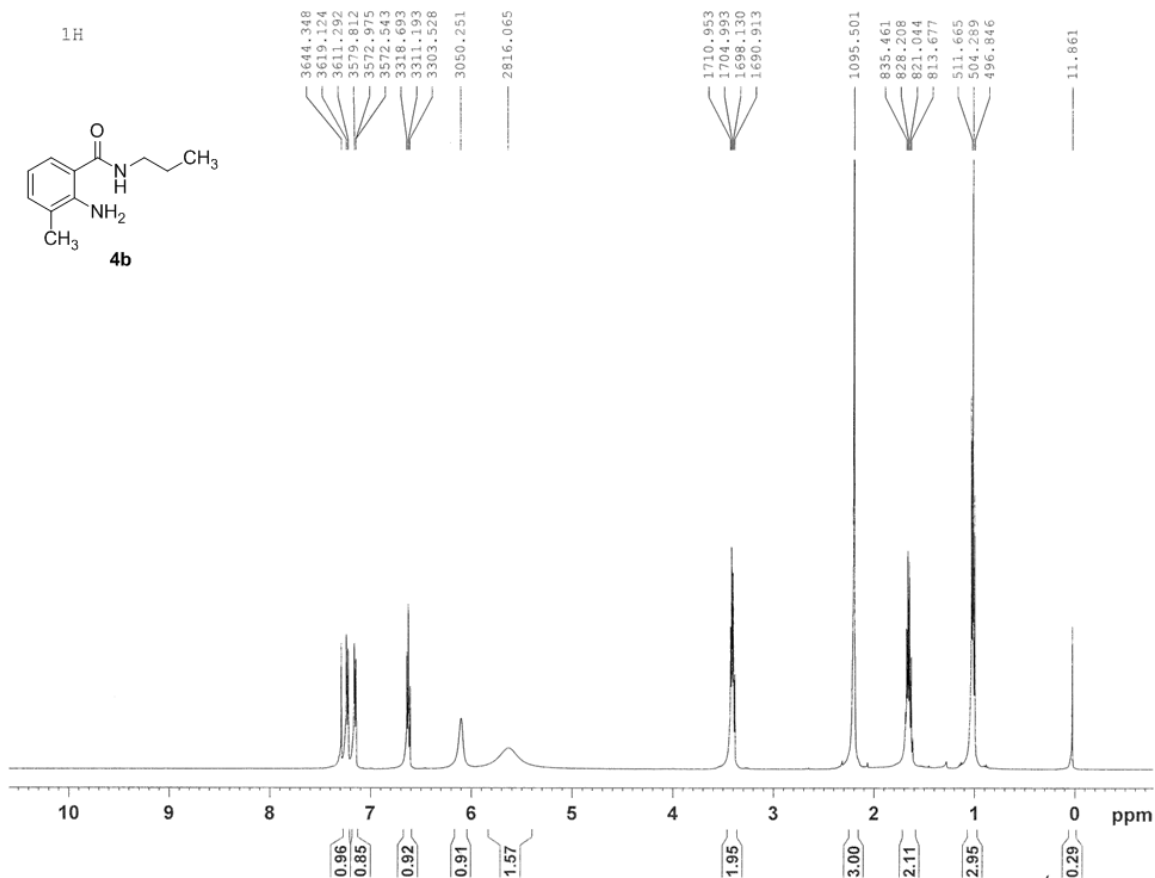
2-Amino-N-benzylbenzamide (4a)



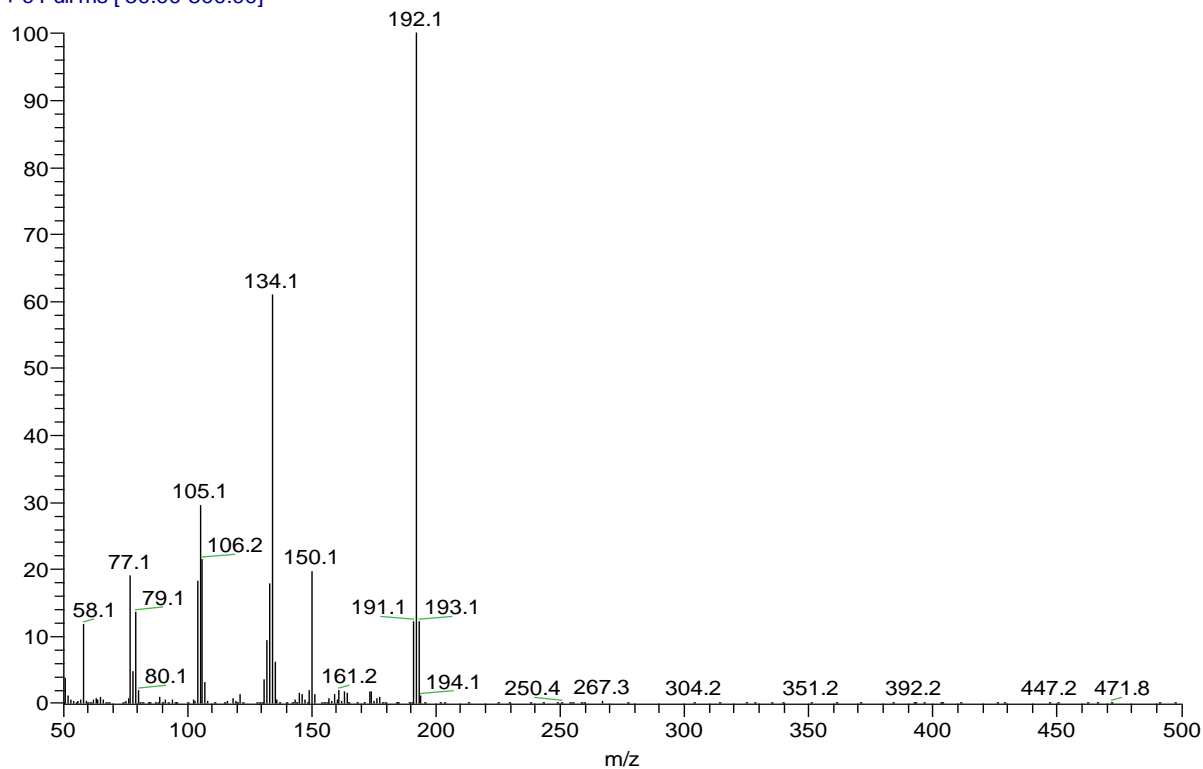


S76-212 #2209 RT: 22.04 AV: 1 NL: 3.30E6
 T: + c Full ms [50.00-500.00]



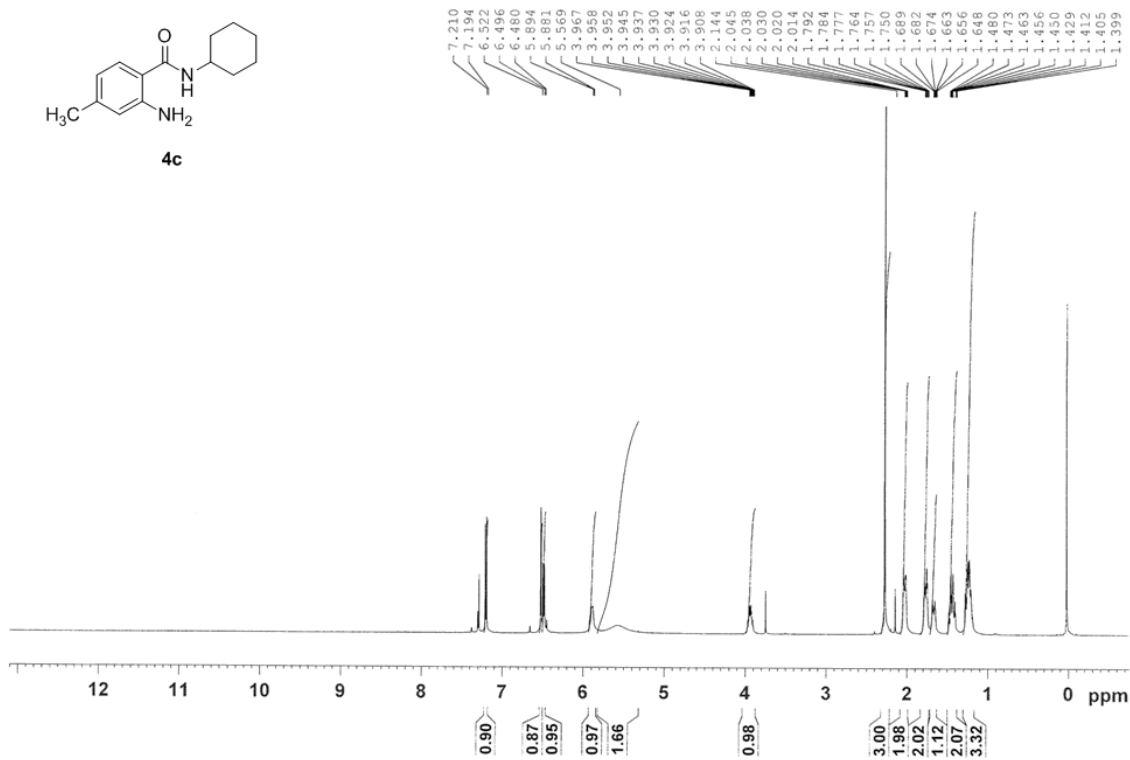
2-Amino-3-methyl-N-propylbenzamide (**4b**)

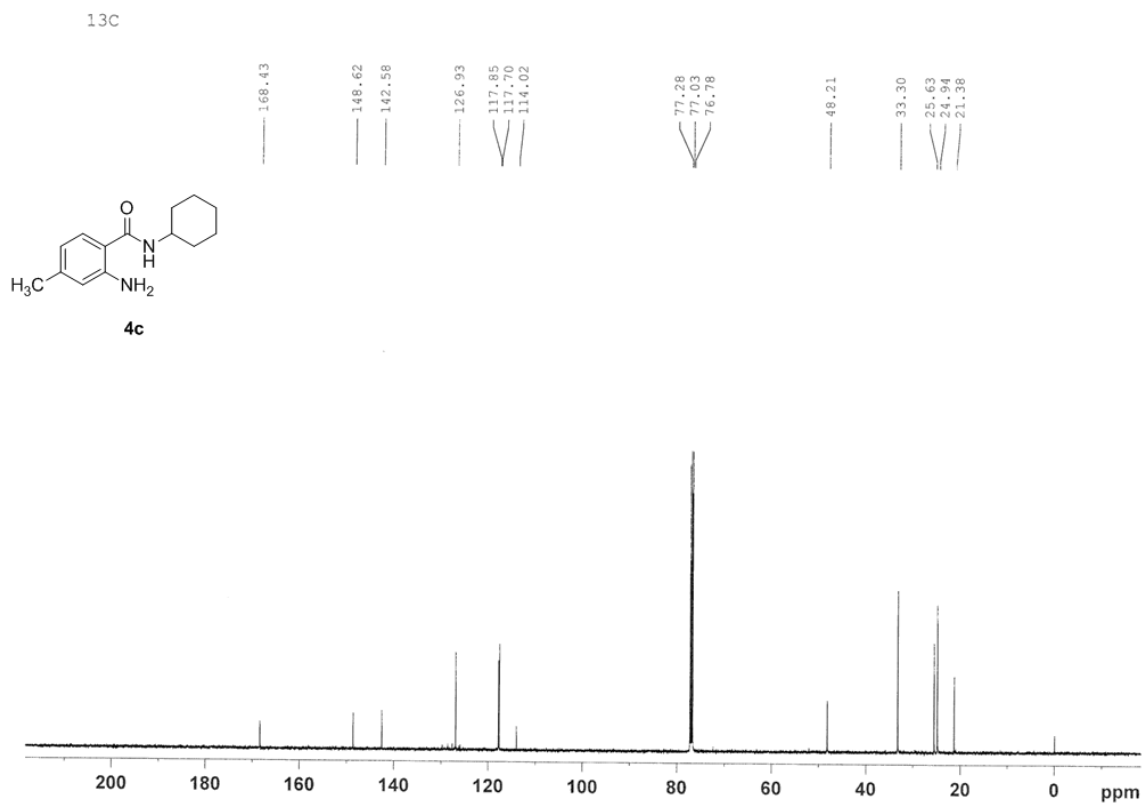
S124-192 #1739 RT: 17.85 AV: 1 NL: 3.84E6
 T: + c Full ms [50.00-500.00]



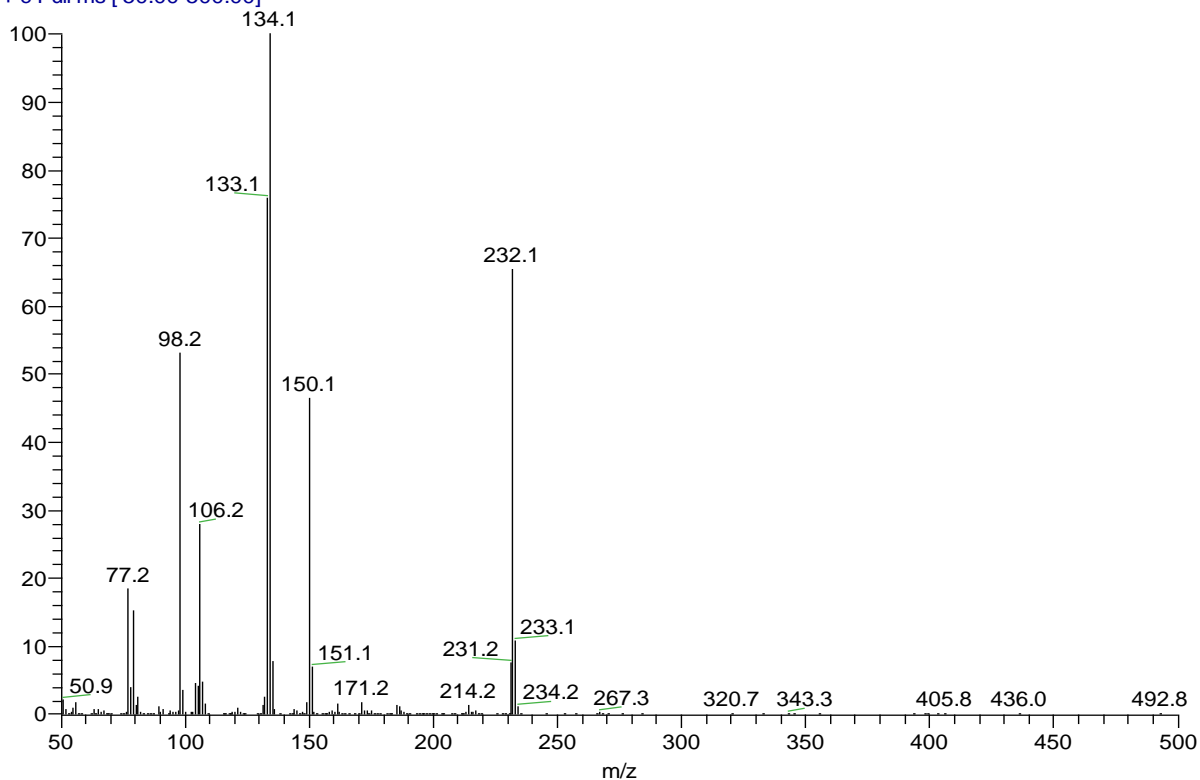
2-Amino-N-cyclohexyl-4-methylbenzamide (**4c**)

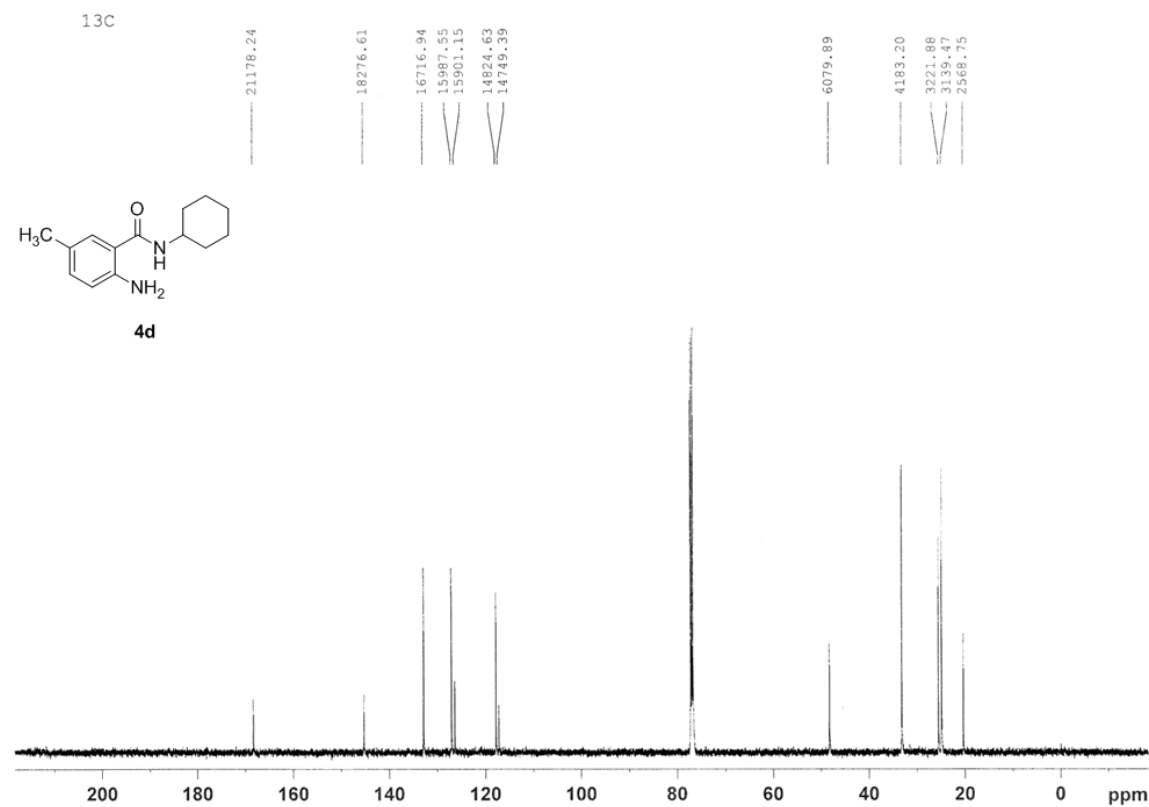
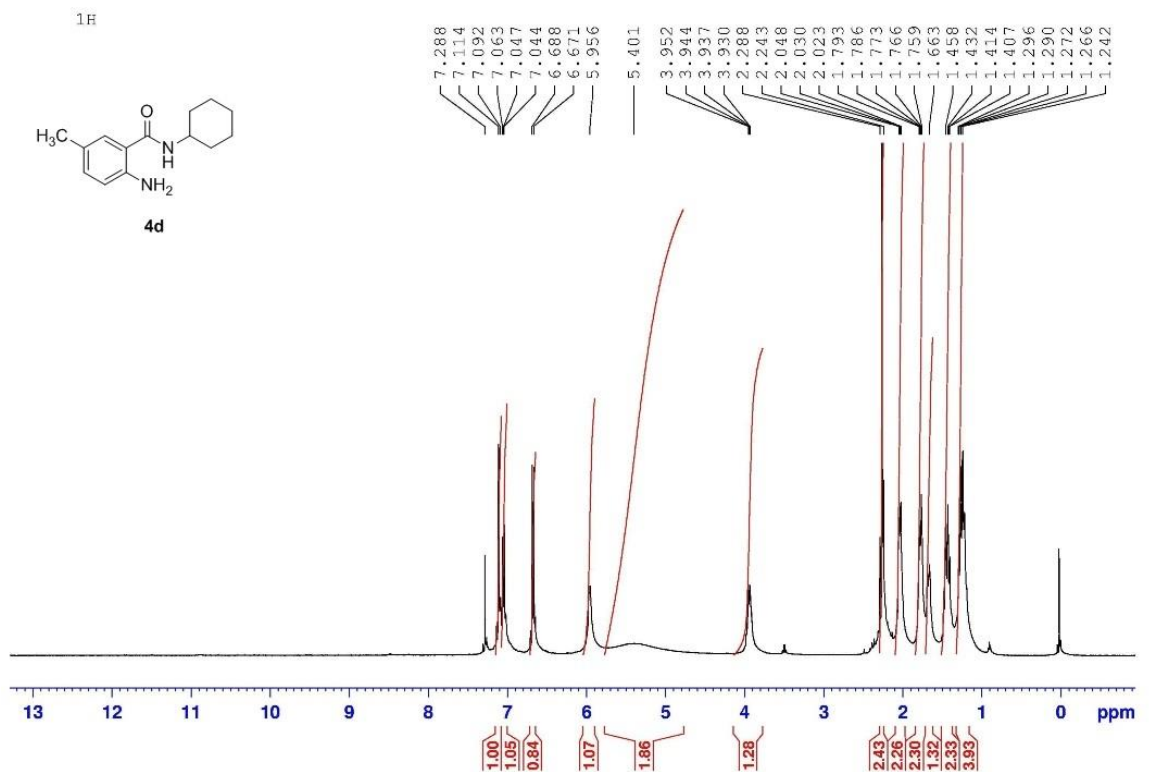
¹H



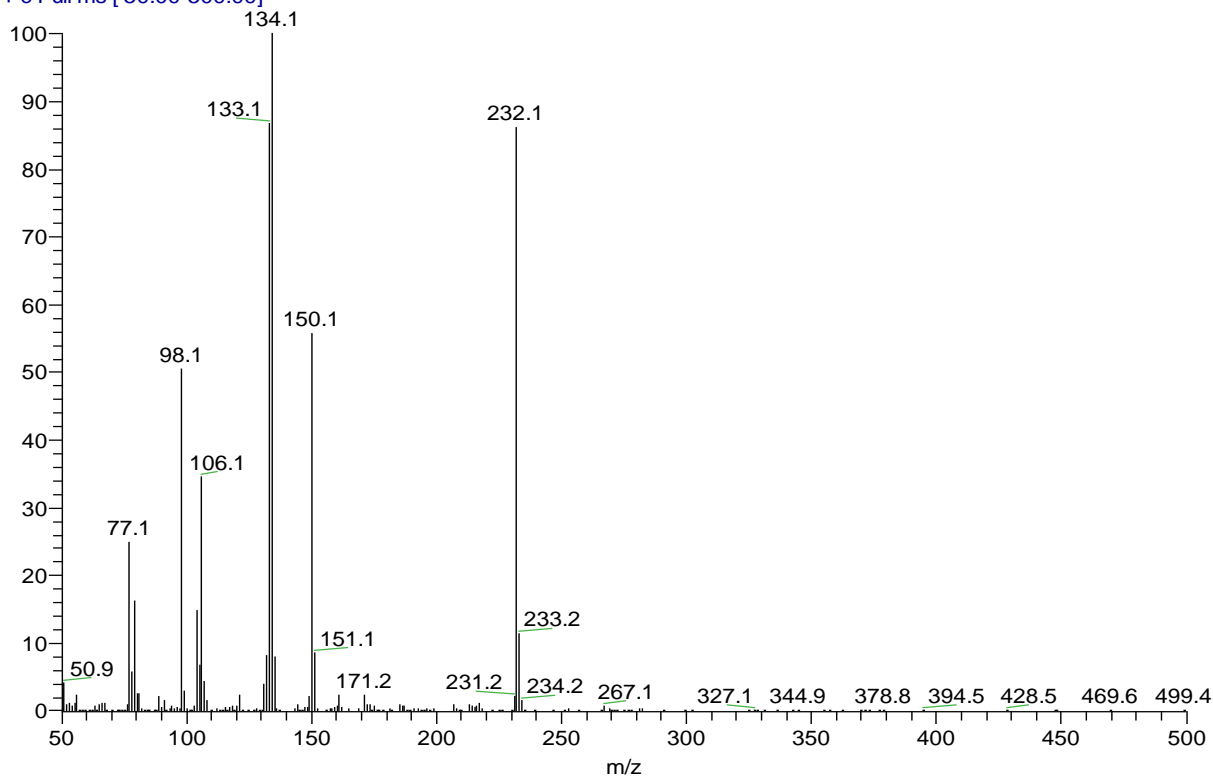


S119 #2189 RT: 21.70 AV: 1 NL: 1.11E7
T: + c Full ms [50.00-500.00]

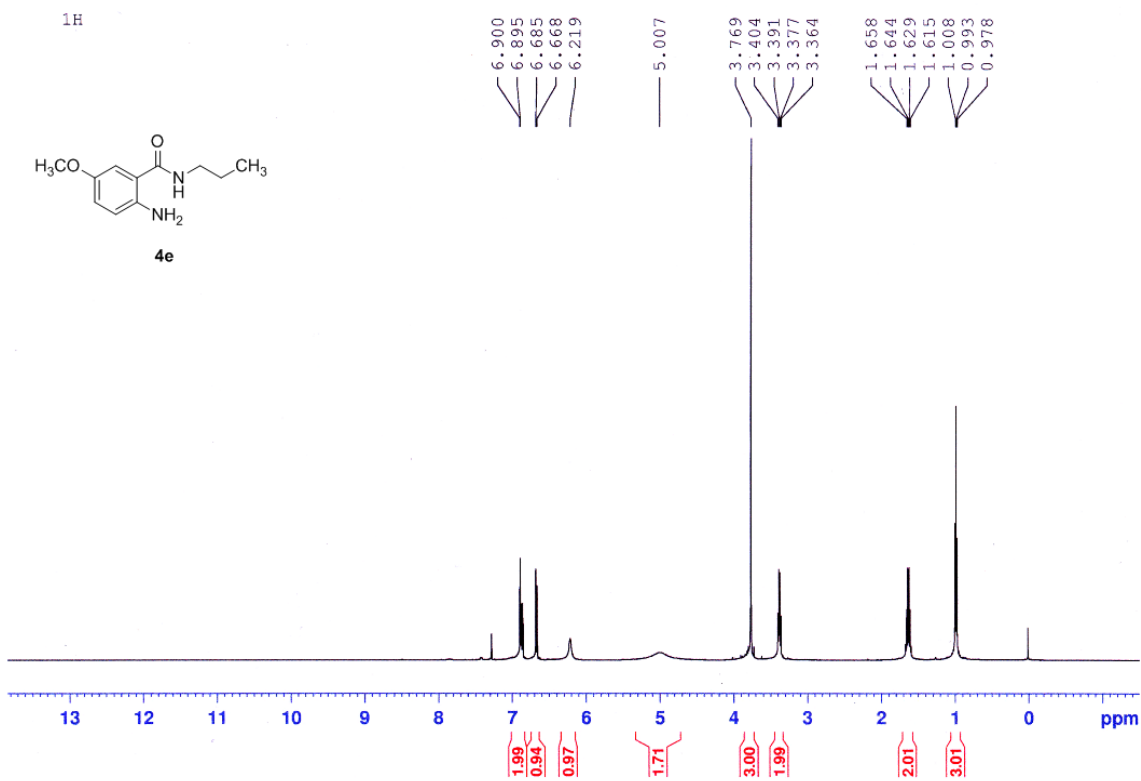


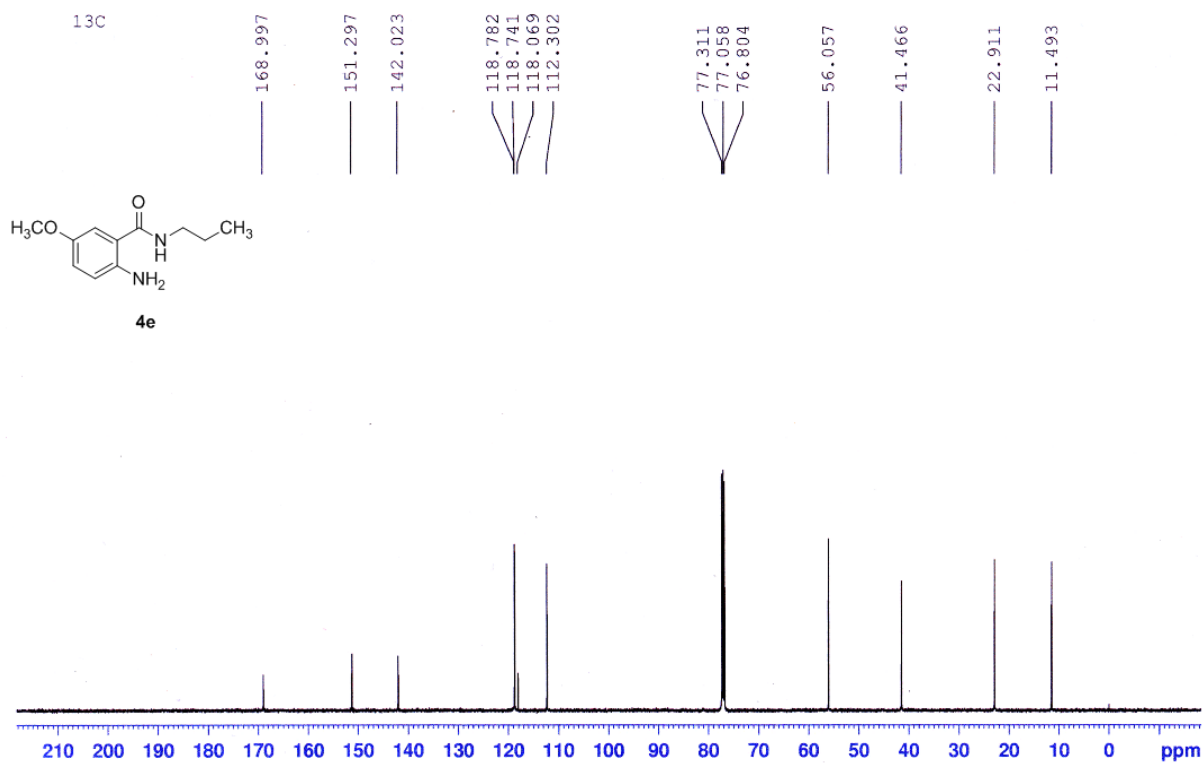
2-Amino-N-cyclohexyl-5-methylbenzamide (**4d**)

S86-232 #2158 RT: 21.46 AV: 1 NL: 6.24E5
T: + c Full ms [50.00-500.00]

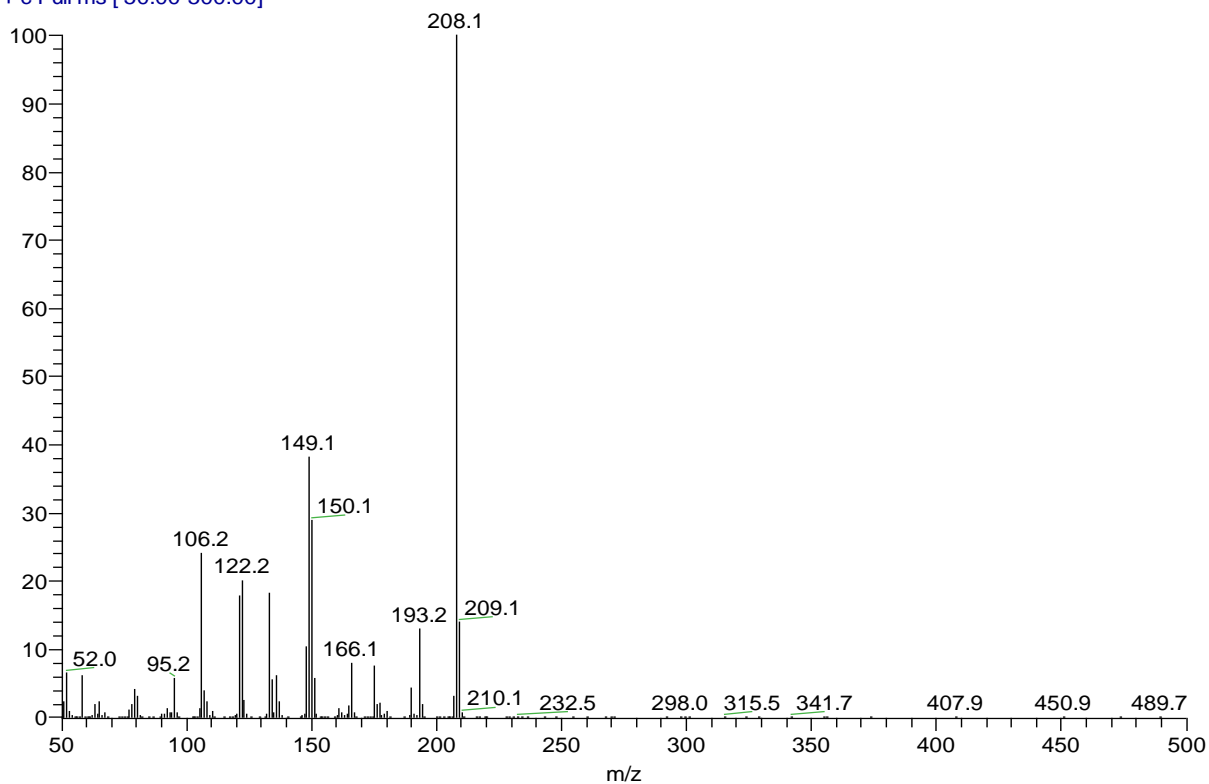


2-Amino-5-methoxy-N-propylbenzamide (**4e**)

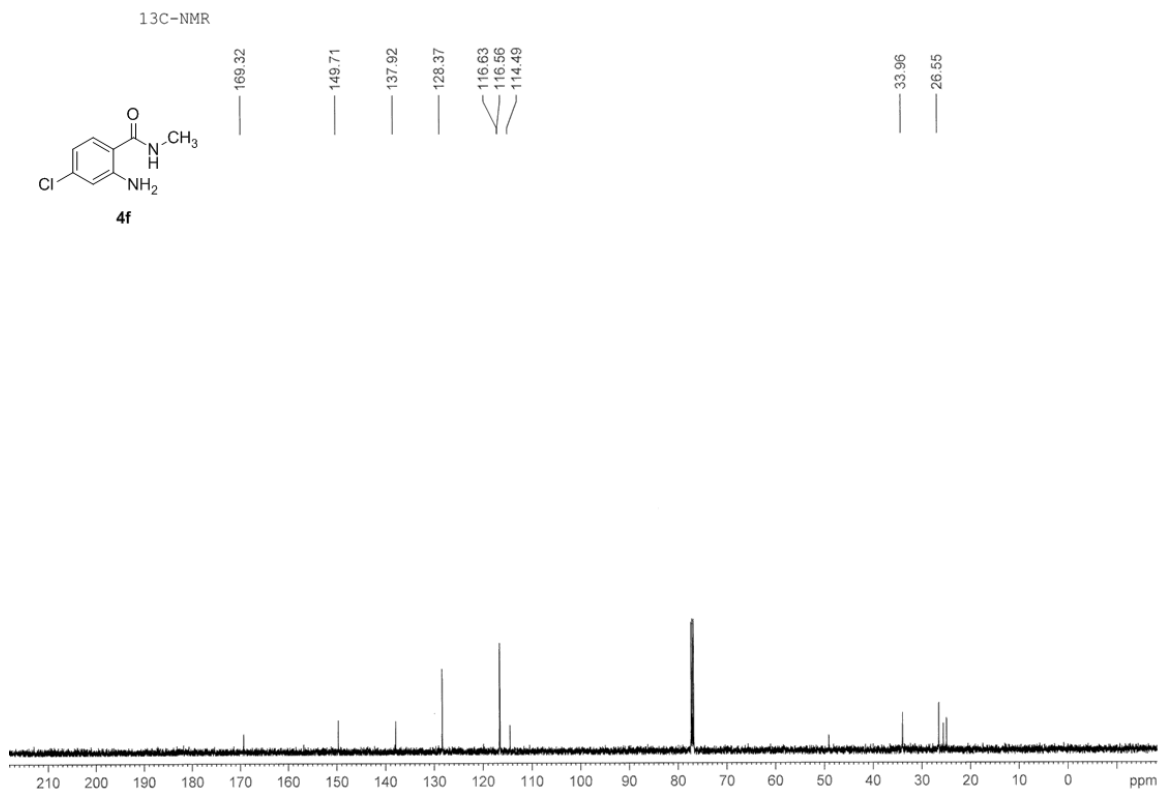
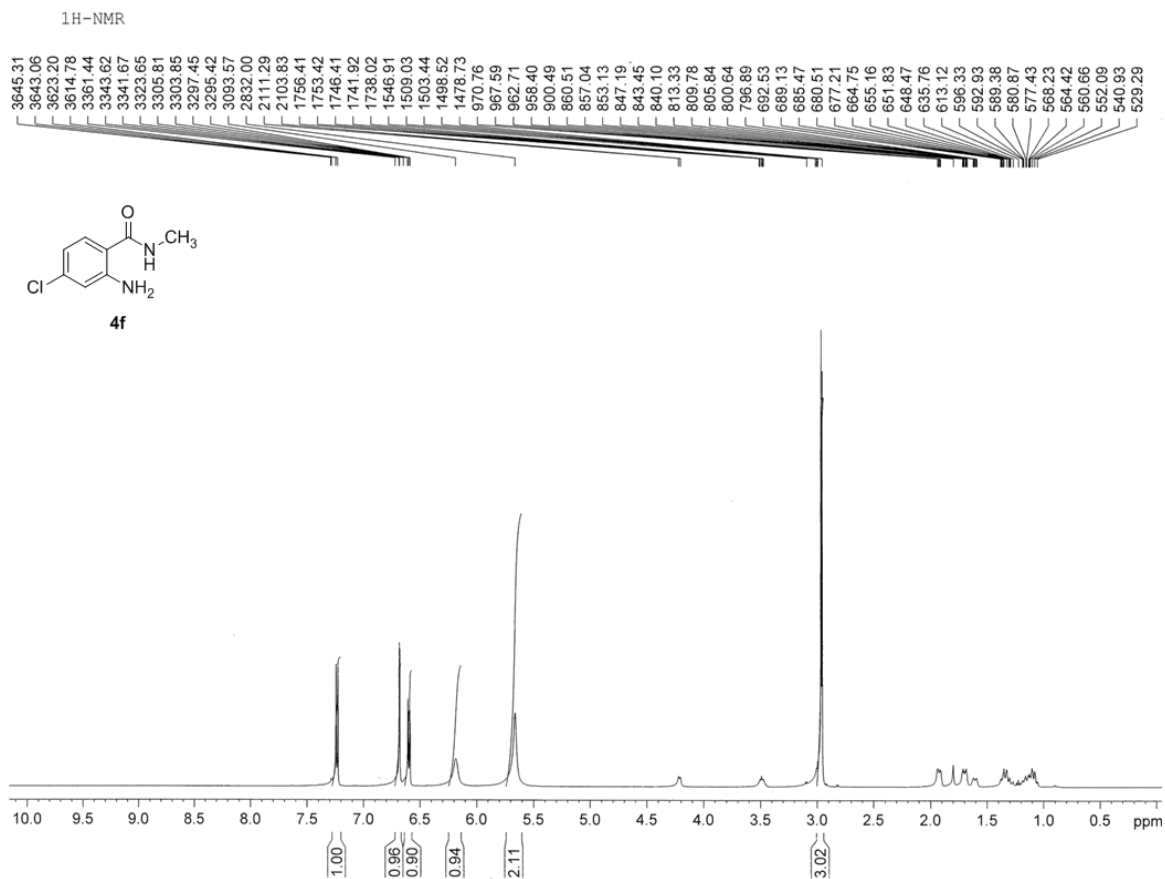




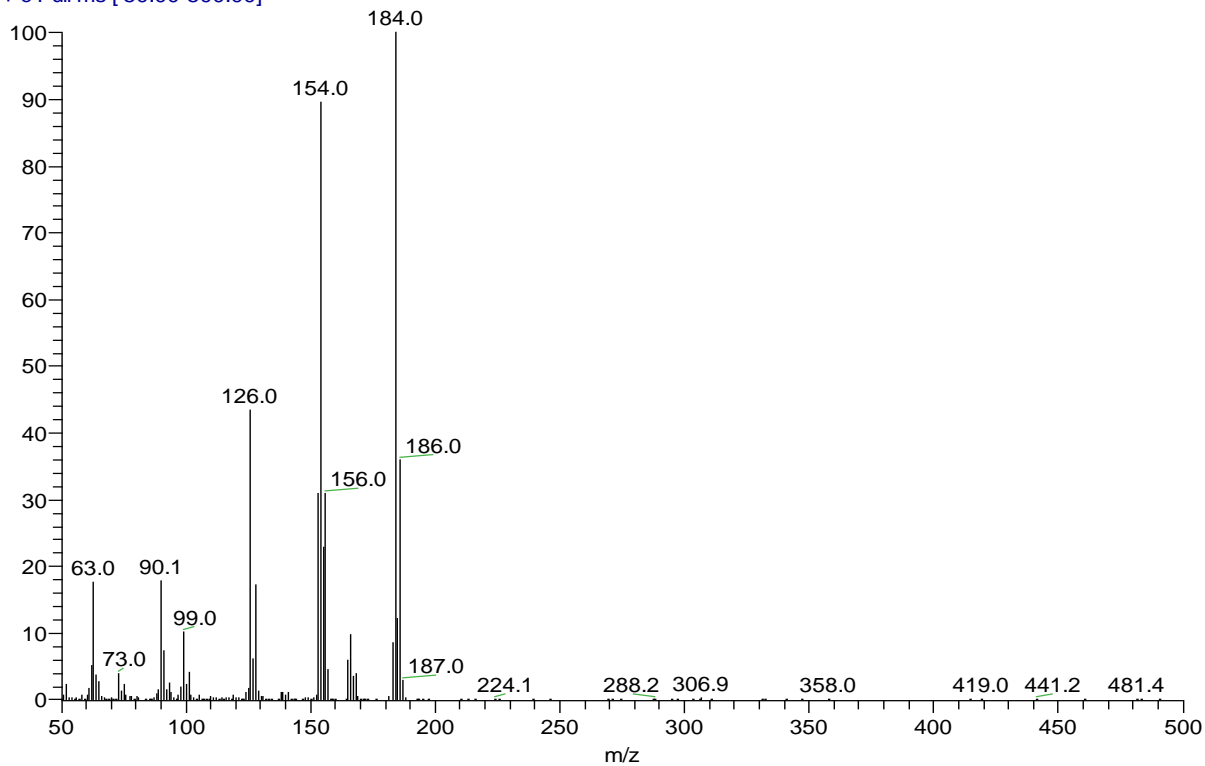
S156-208 #2054 RT: 20.89 AV: 1 NL: 1.35E7
T: + c Full ms [50.00-500.00]



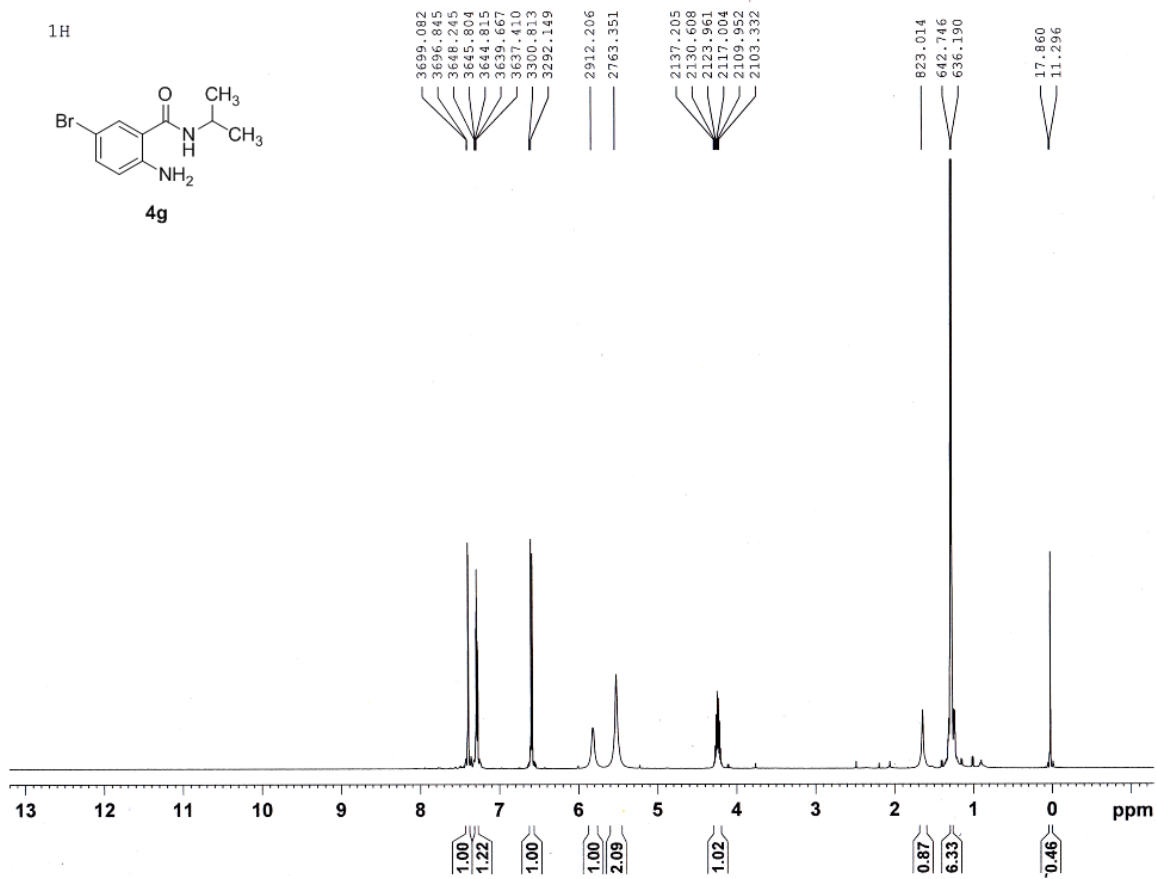
2-Amino-4-chloro-N-methylbenzamide (4f)

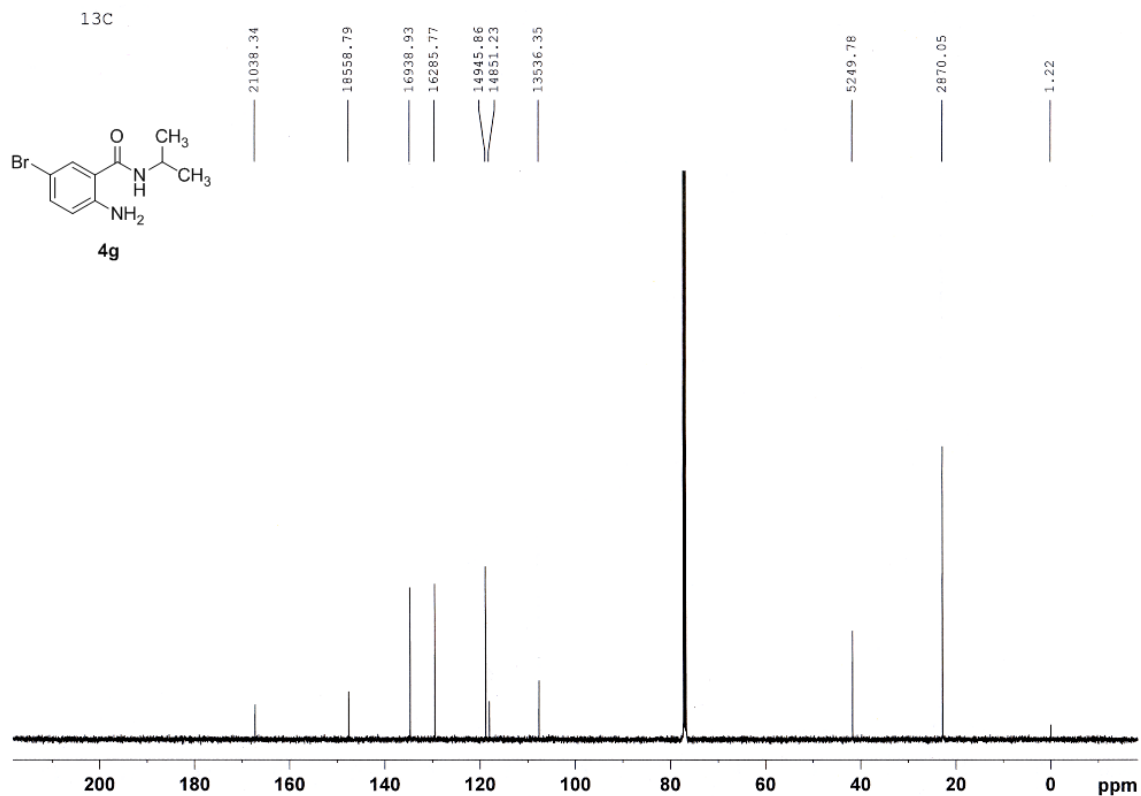


S88-184 #1723 RT: 17.65 AV: 1 NL: 3.60E6
 T: + c Full ms [50.00-500.00]

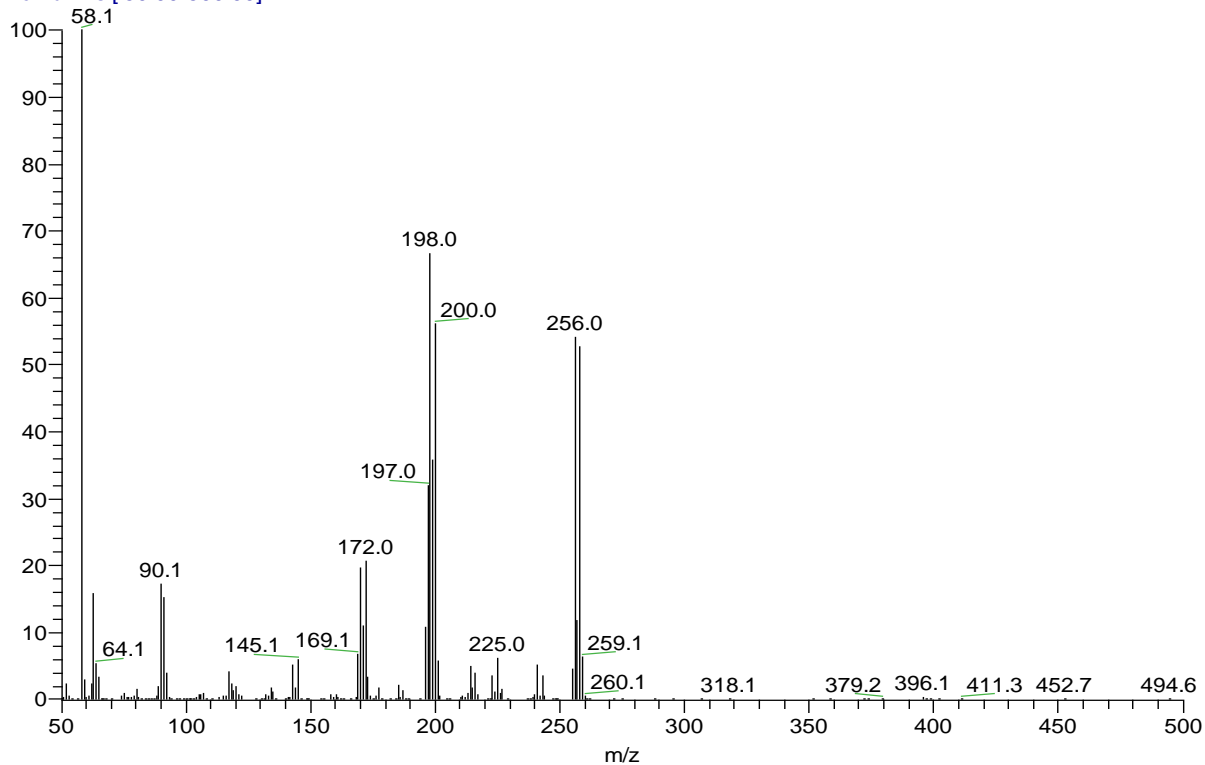


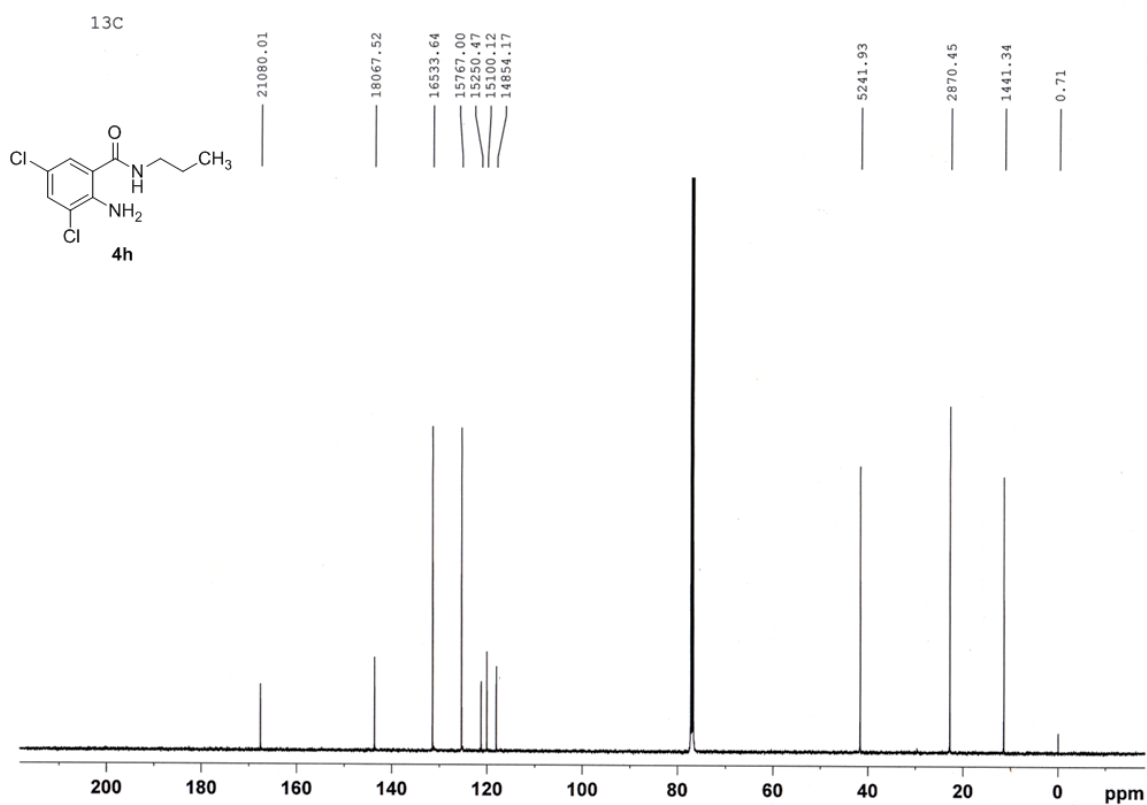
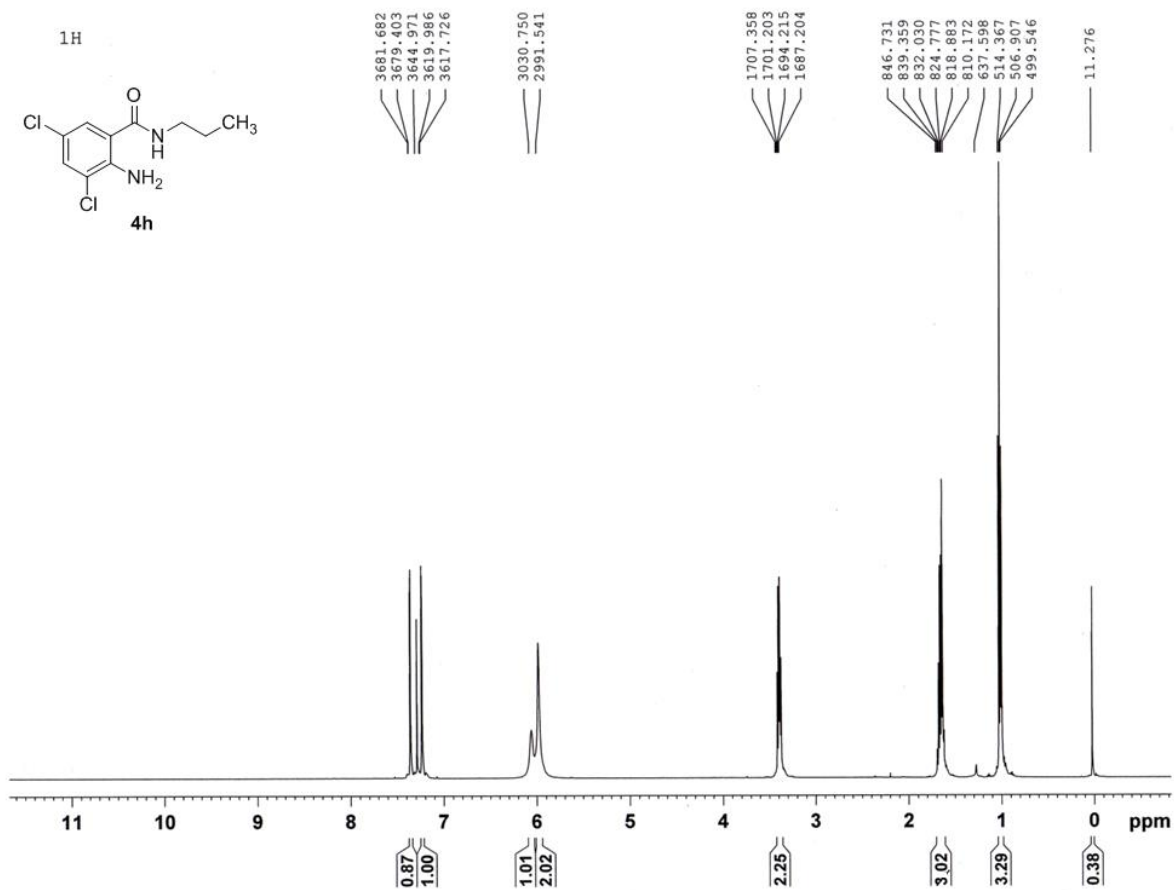
2-Amino-5-bromo-N-isopropylbenzamide (4g)



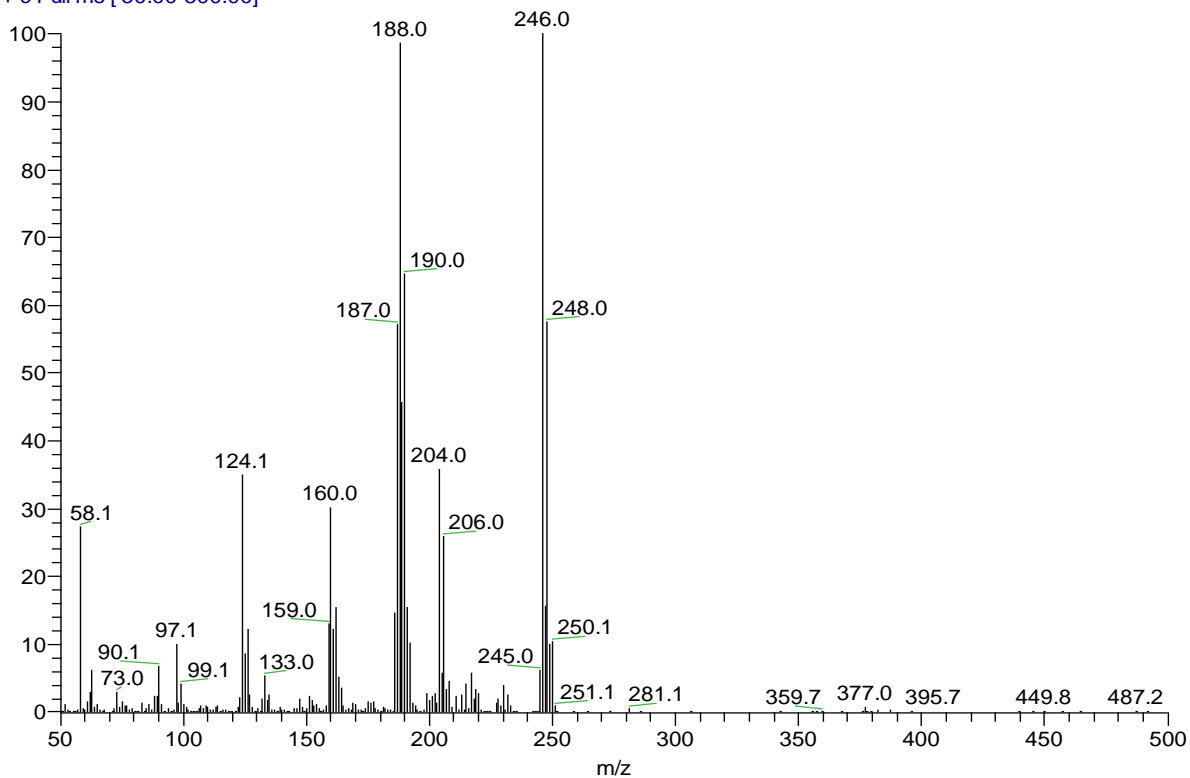


S127-257 #1871 RT: 18.91 AV: 1 NL: 3.85E6
T: + c Full ms [50.00-500.00]



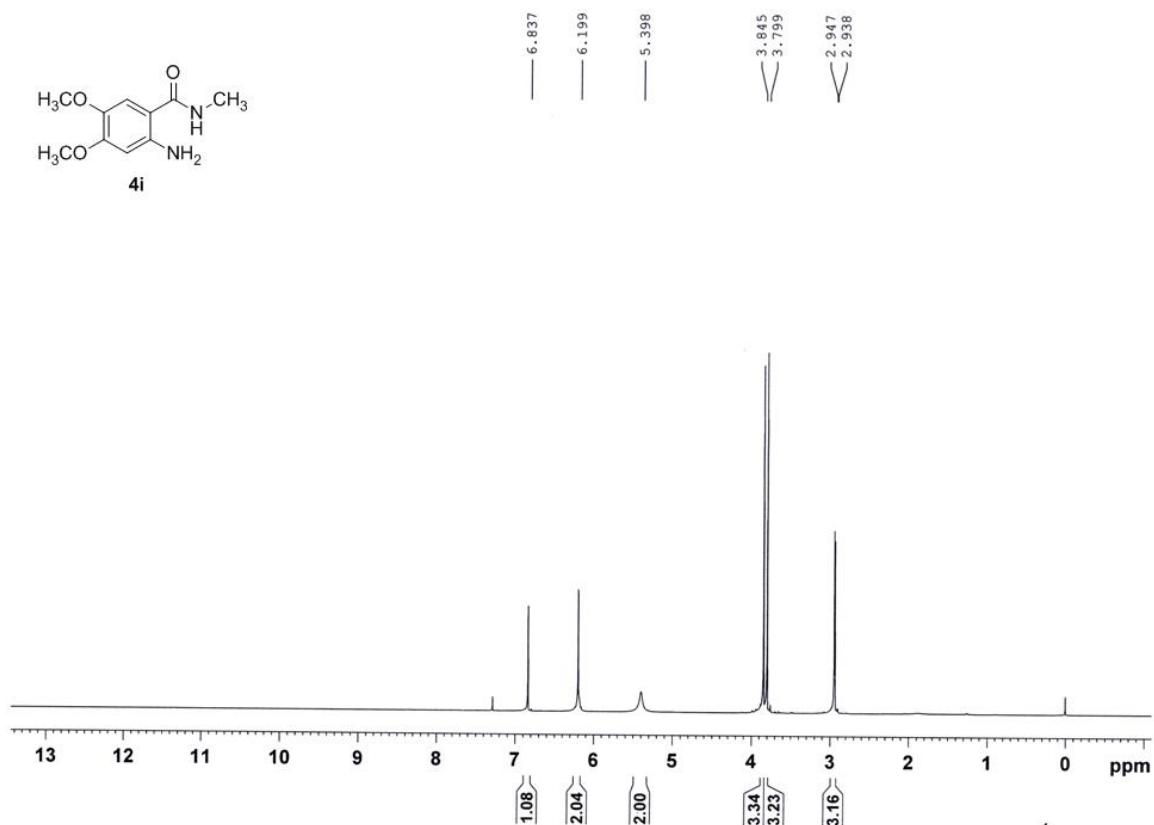
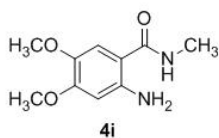
2-Amino-3,5-dichloro-N-propylbenzamide (**4h**)

S123-247 #1983 RT: 19.83 AV: 1 NL: 2.86E6
T: + c Full ms [50.00-500.00]

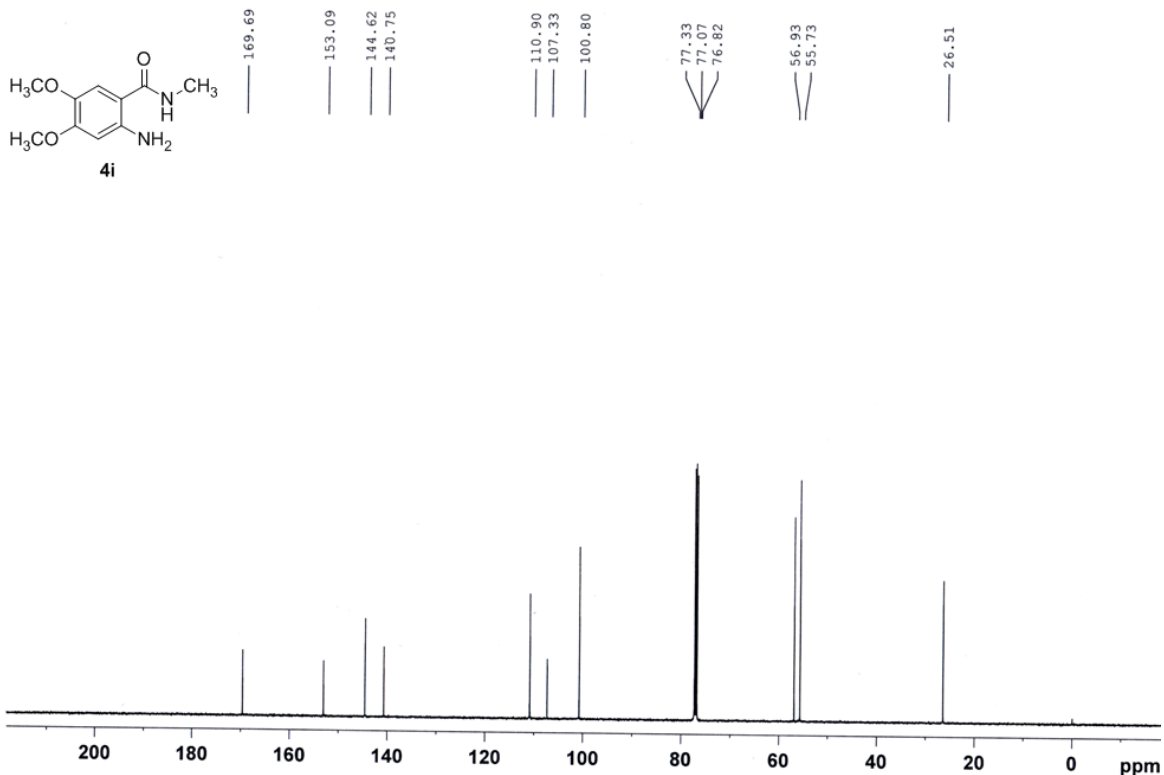


2-Amino-4,5-dimethoxy-N-methylbenzamide (**4i**)

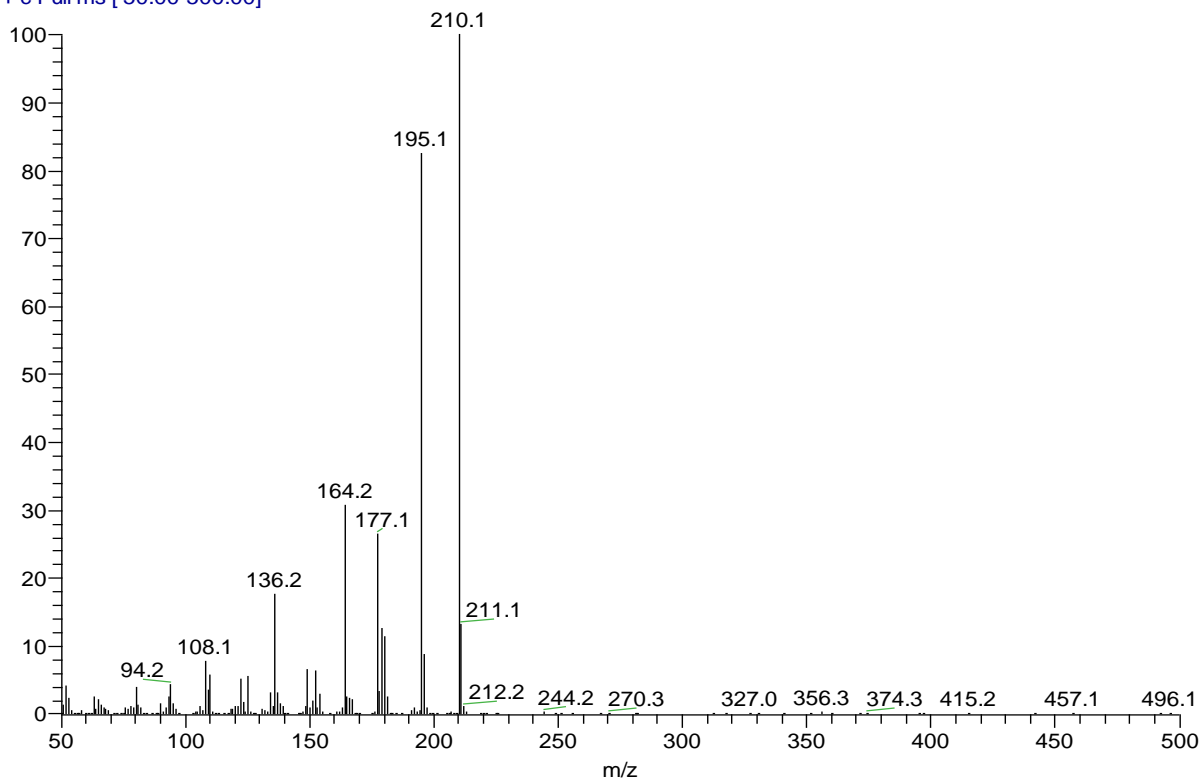
¹H



13C

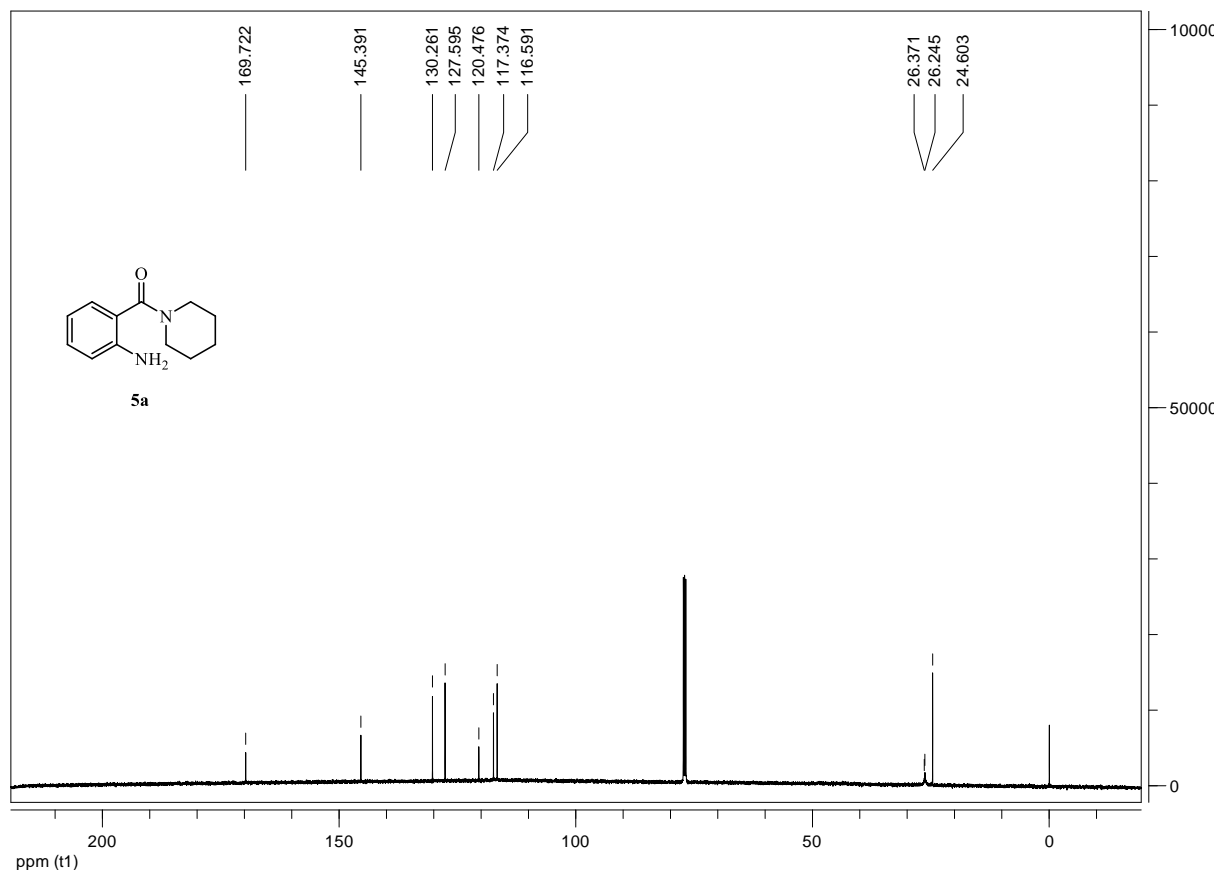
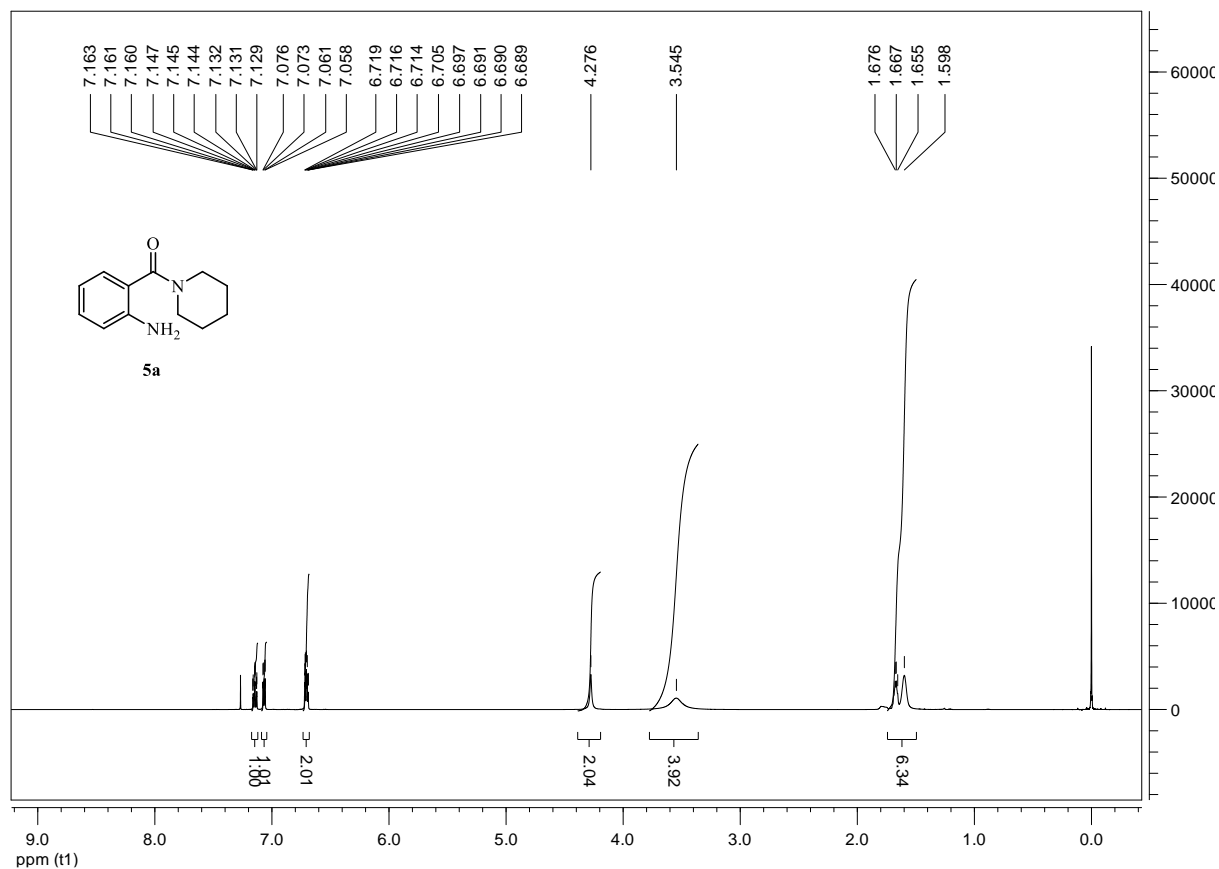


S152-211 #2148 RT: 21.78 AV: 1 NL: 3.75E6
T: + c Full ms [50.00-500.00]

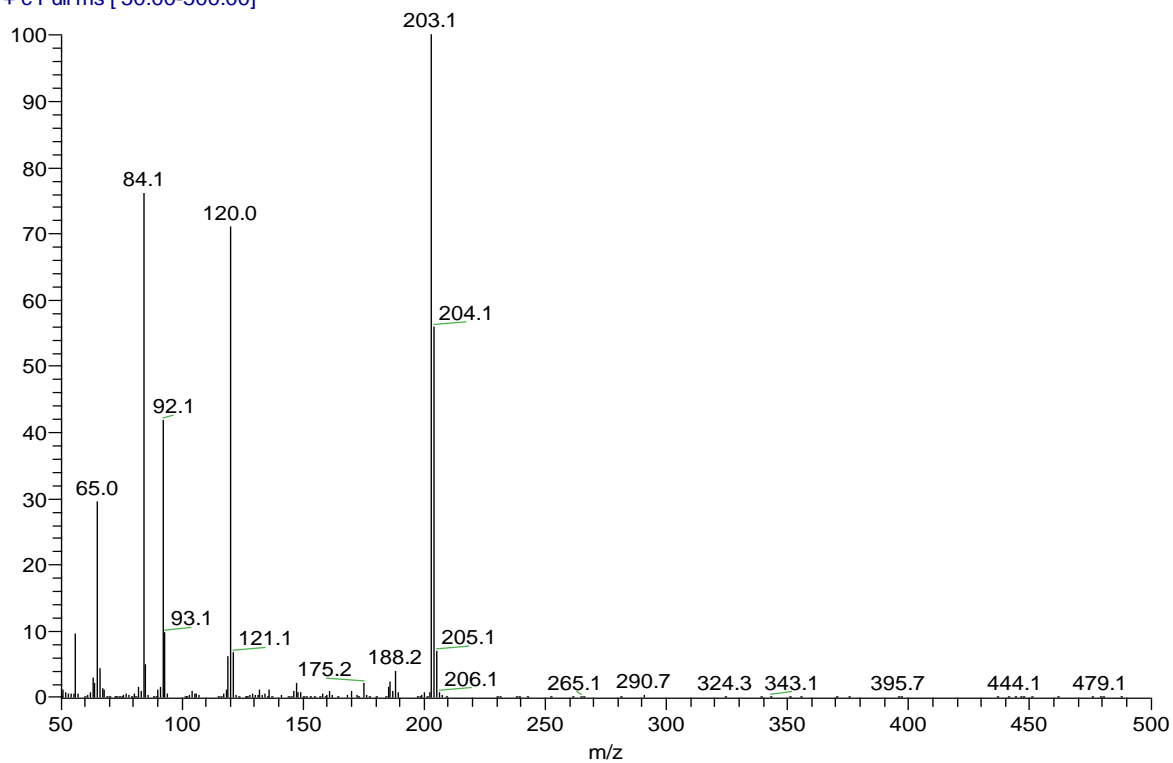


4. Tertiary Amides (5a-5h):

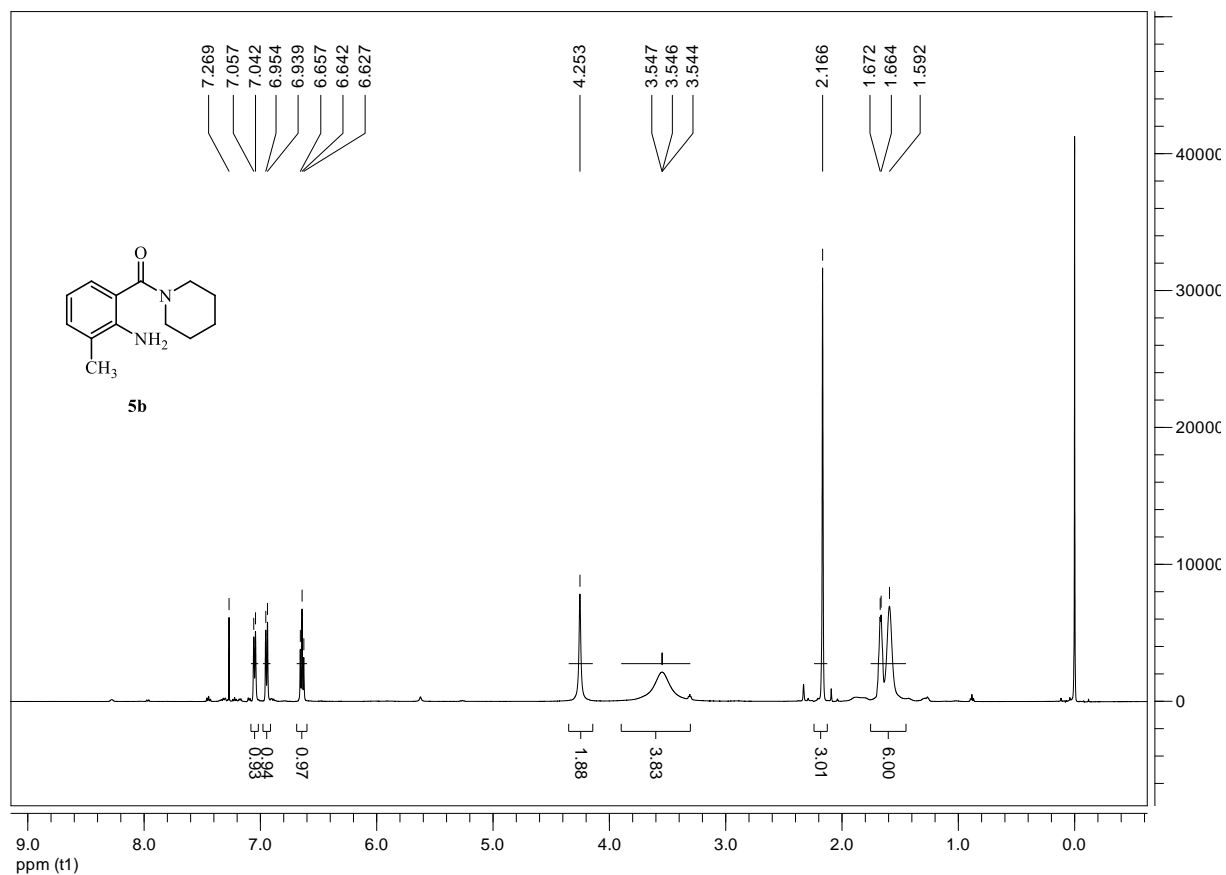
(2-Aminophenyl)(piperidin-1-yl)methanone (5a)

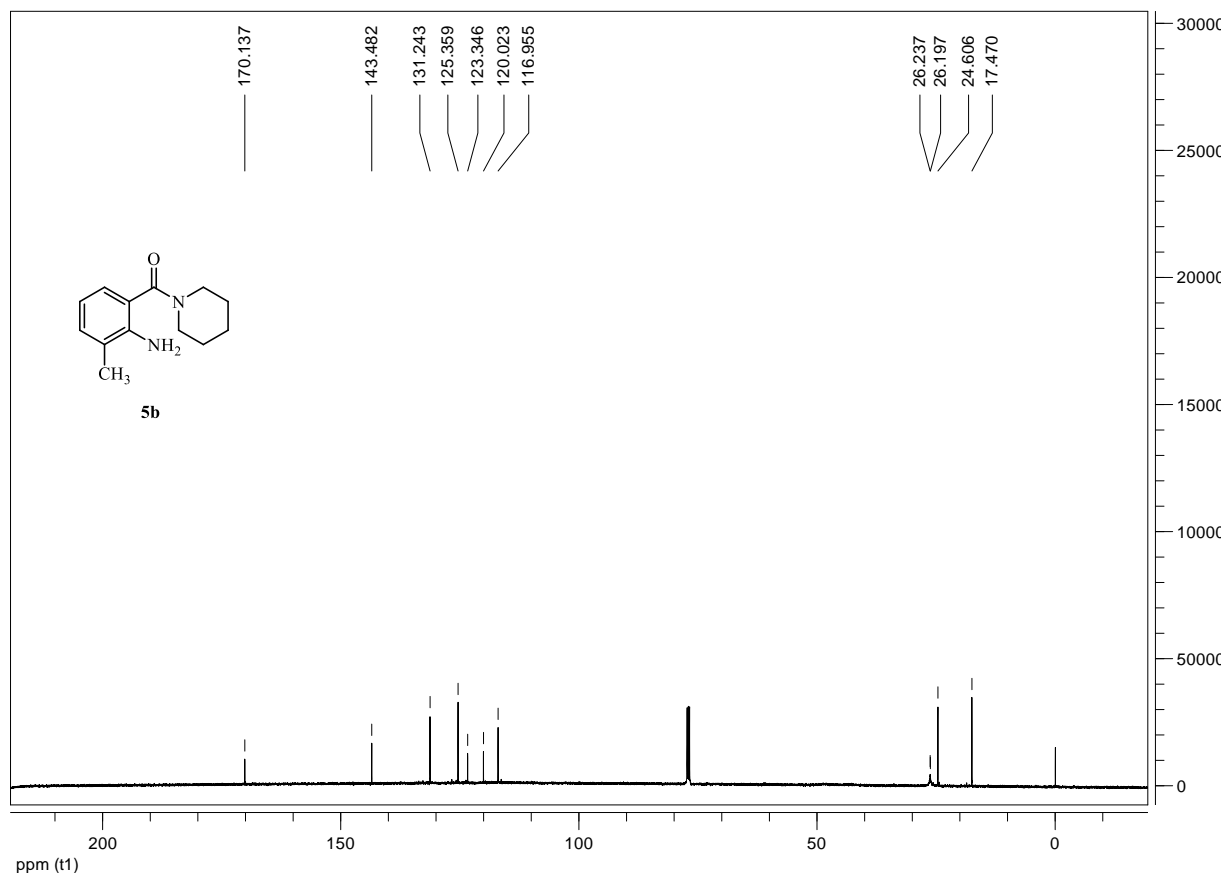


S148-204 #1879 RT: 18.95 AV: 1 NL: 1.83E6
T: + c Full ms [50.00-500.00]

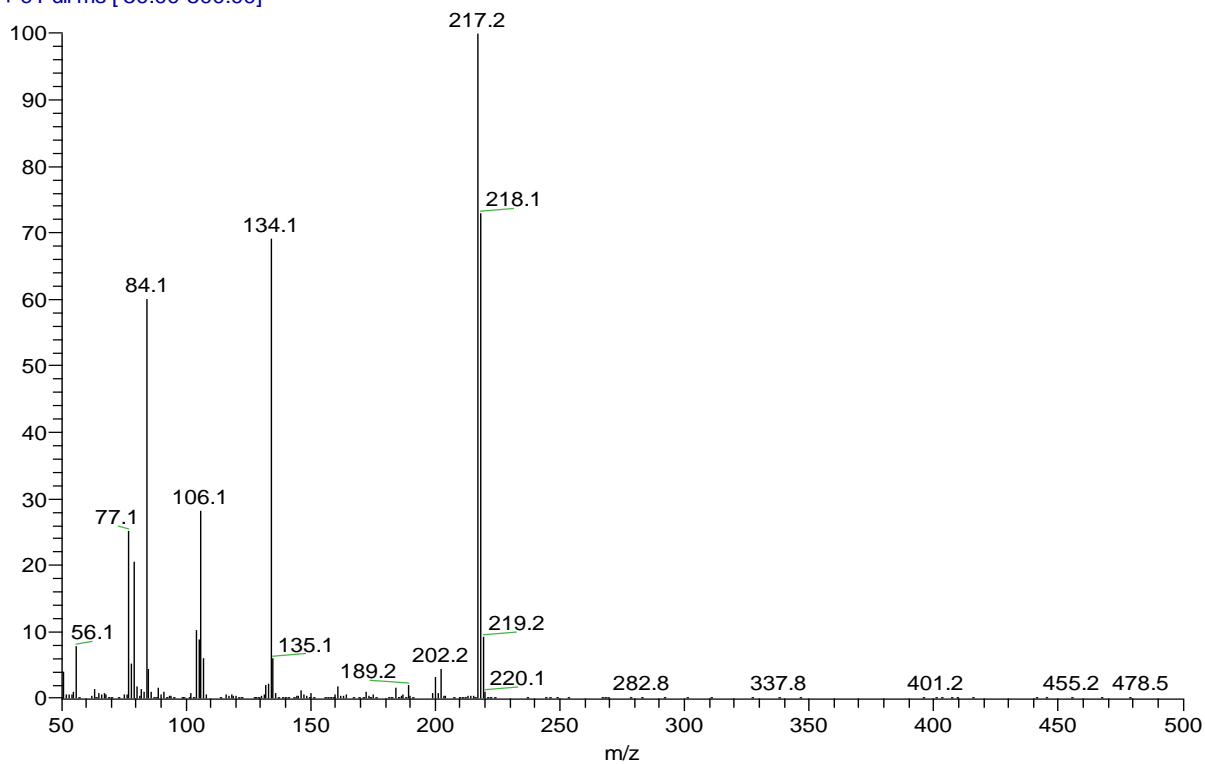


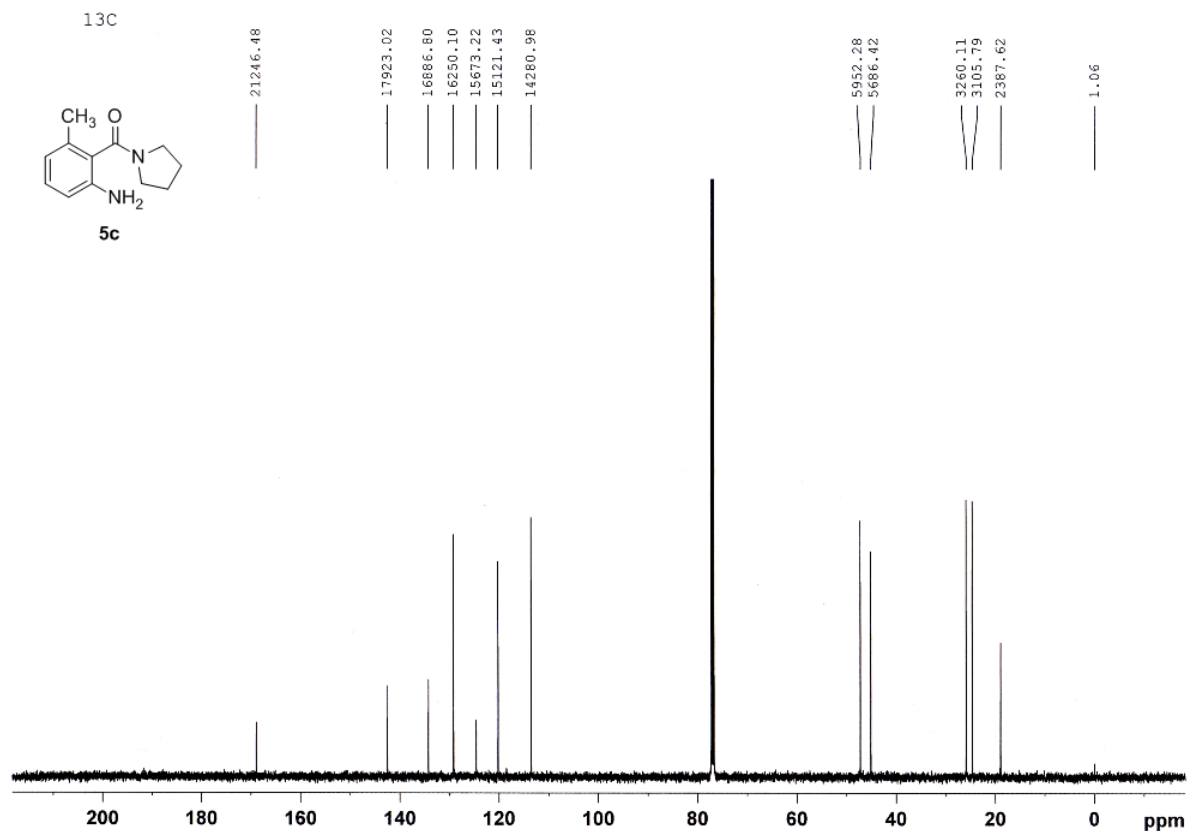
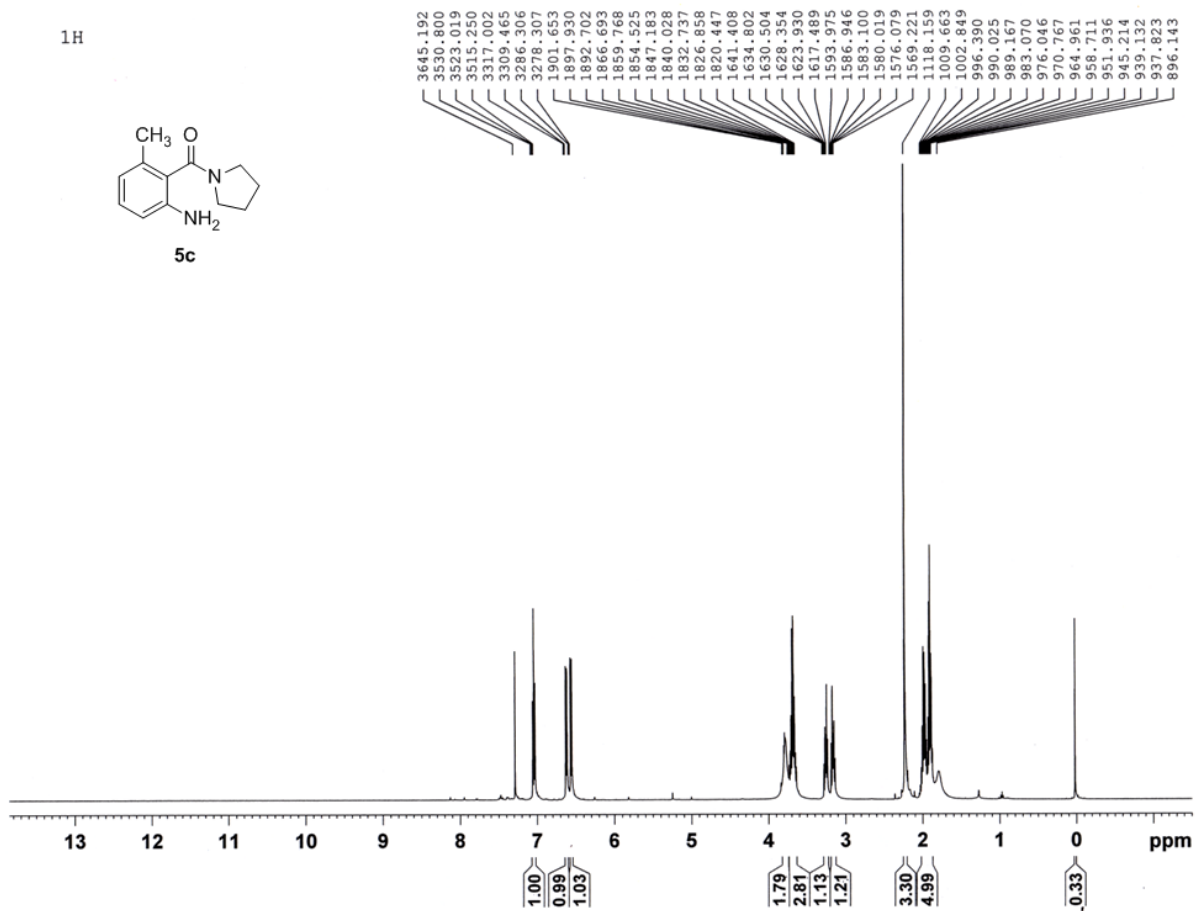
(2-Amino-3-methylphenyl)(piperidin-1-yl)methanone (**5b**)



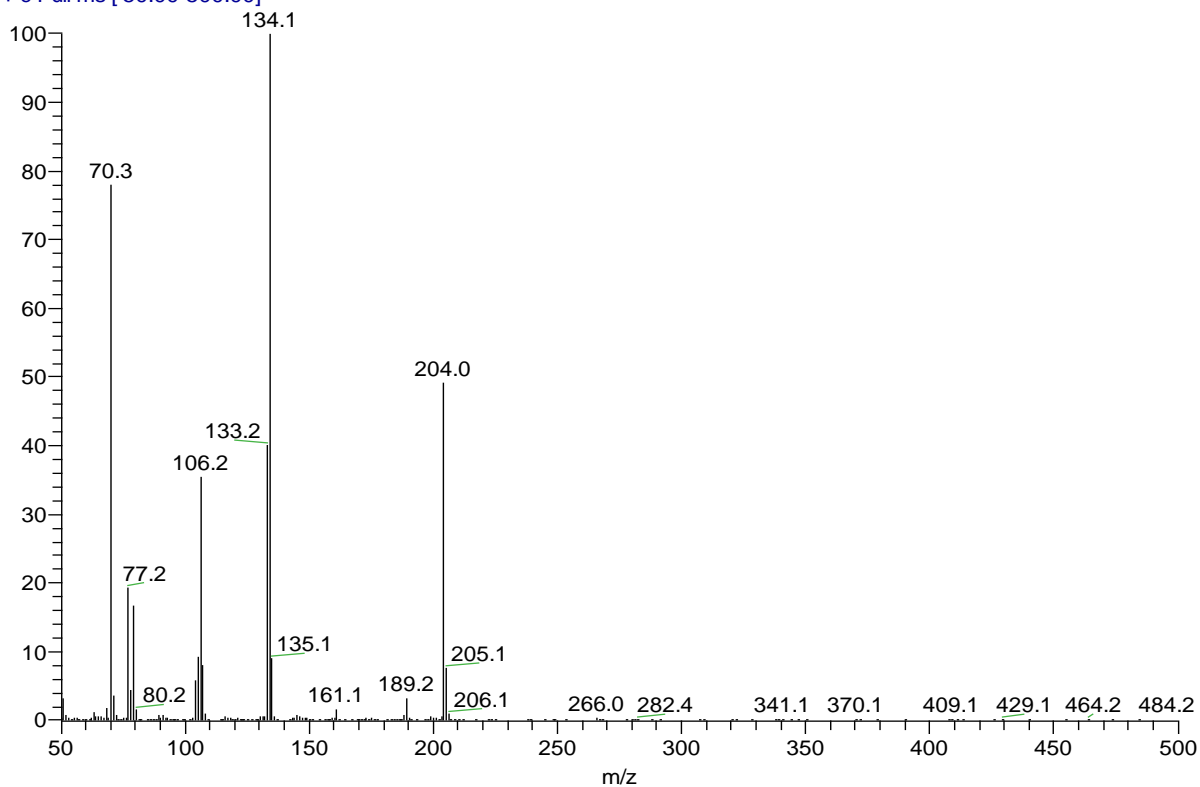


S149-218 #1973 RT: 19.86 AV: 1 NL: 3.65E6
 T: + c Full ms [50.00-500.00]



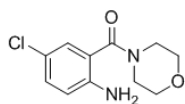
(2-Amino-6-methylphenyl)(pyrrolidin-1-yl)methanone (**5c**)

S133 #1804 RT: 18.80 AV: 1 NL: 1.34E7
T: + c Full ms [50.00-500.00]

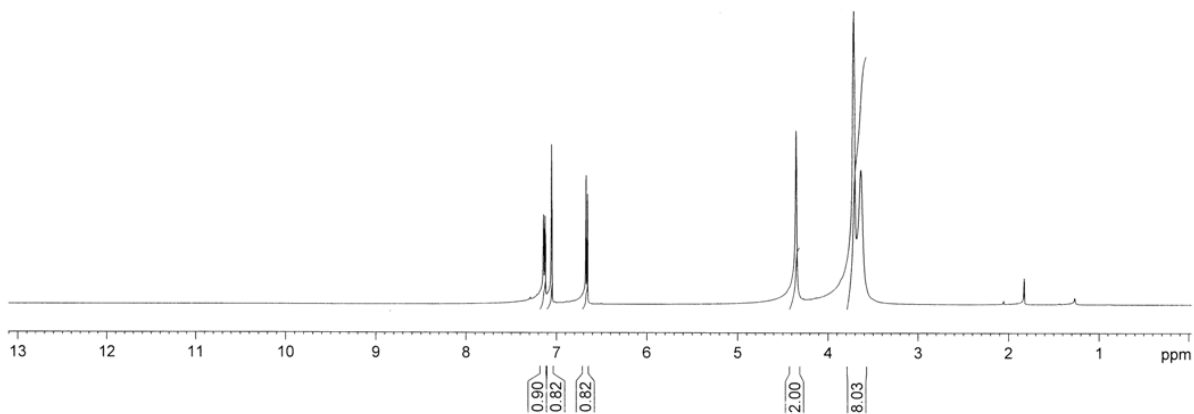


(2-Amino-5-chlorophenyl) (morpholino) methanone (**5d**)

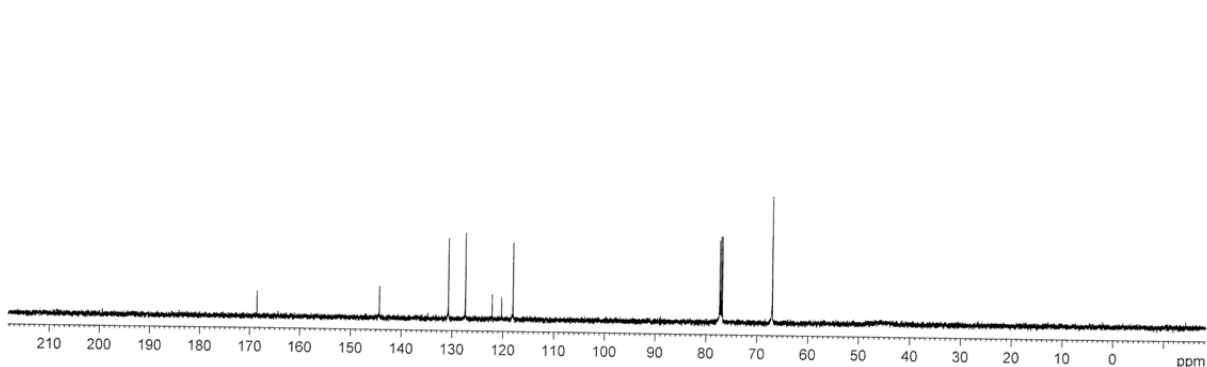
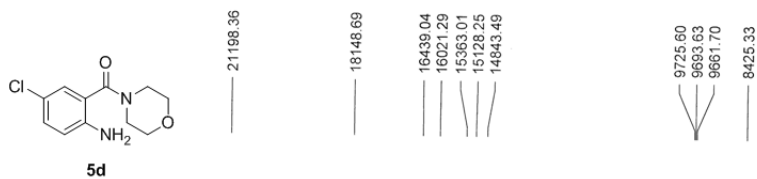
¹H-NMR



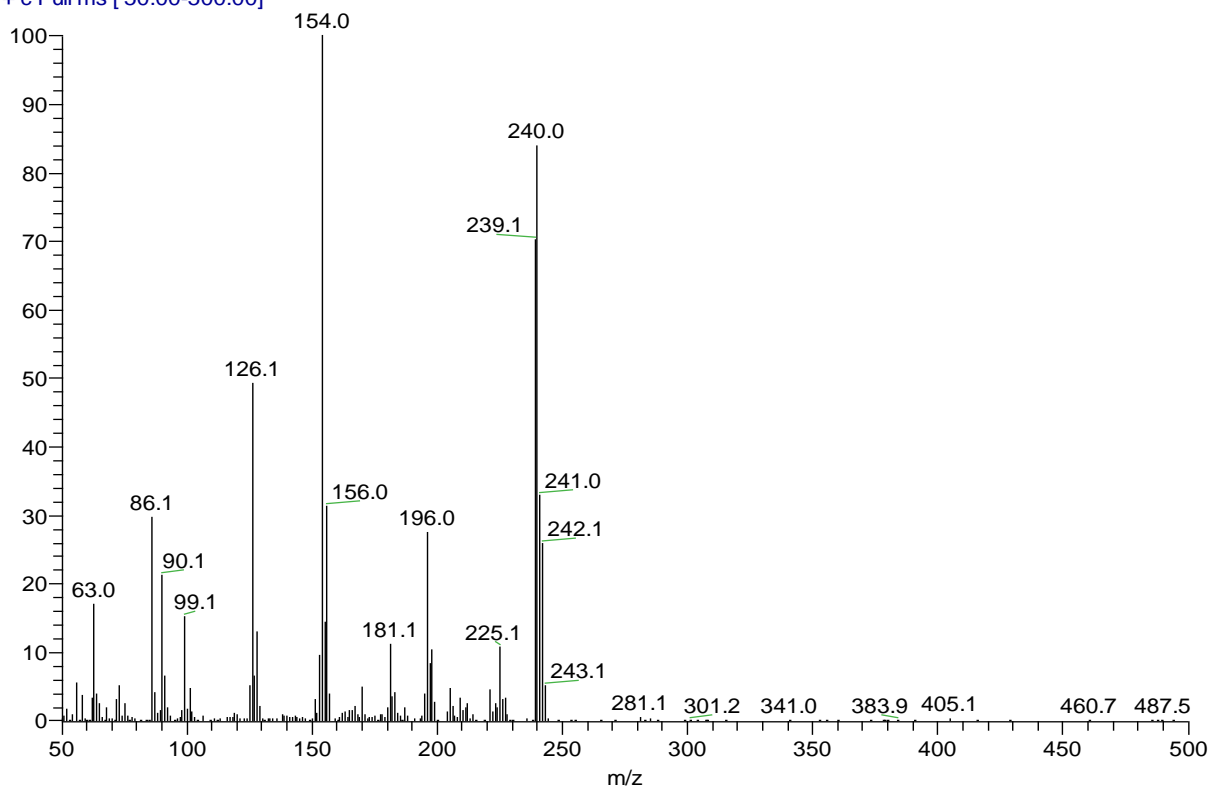
5d

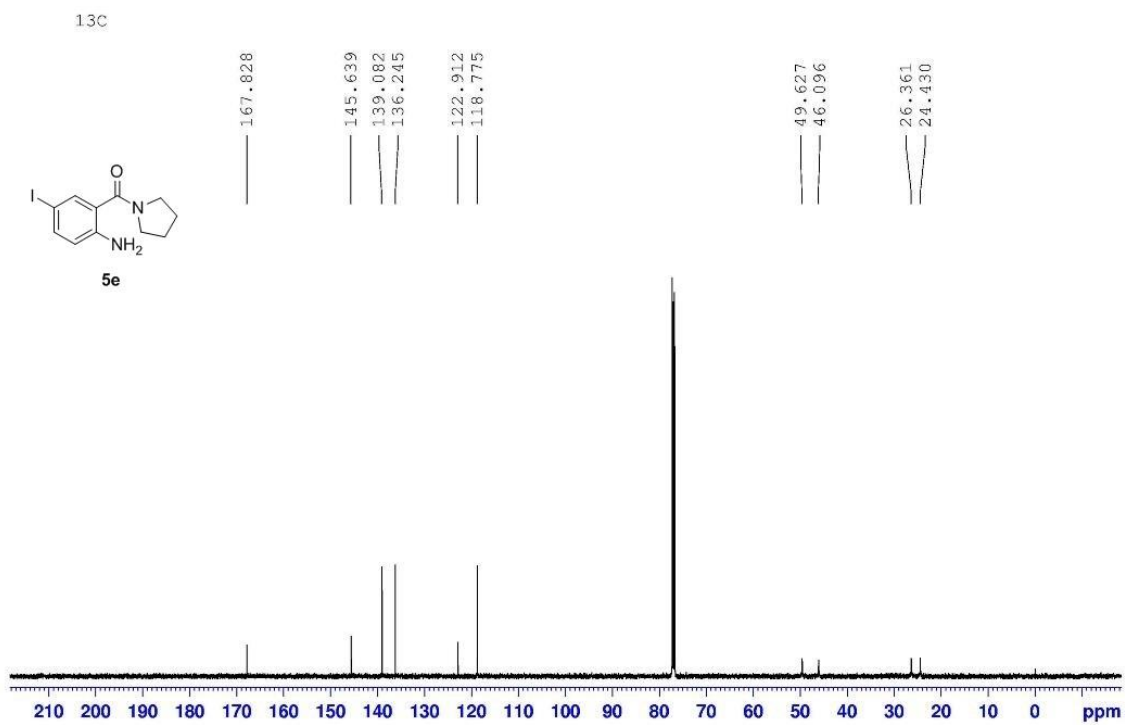
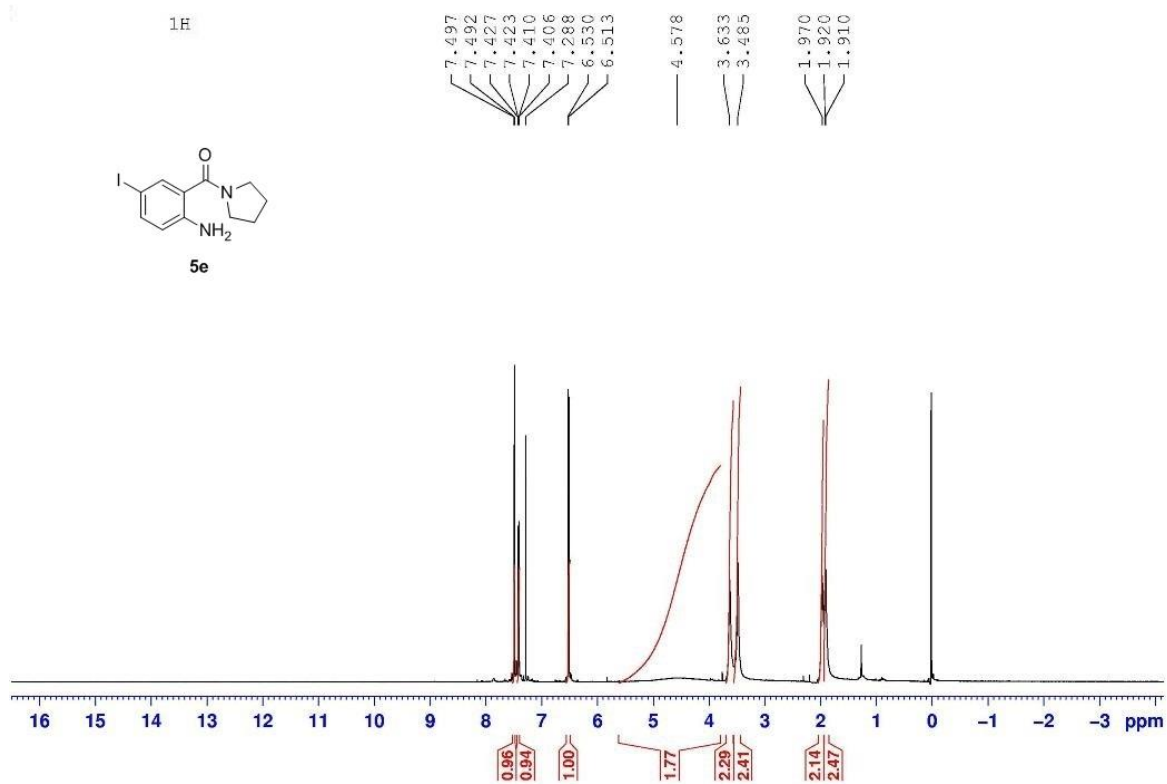


¹³C-NMR

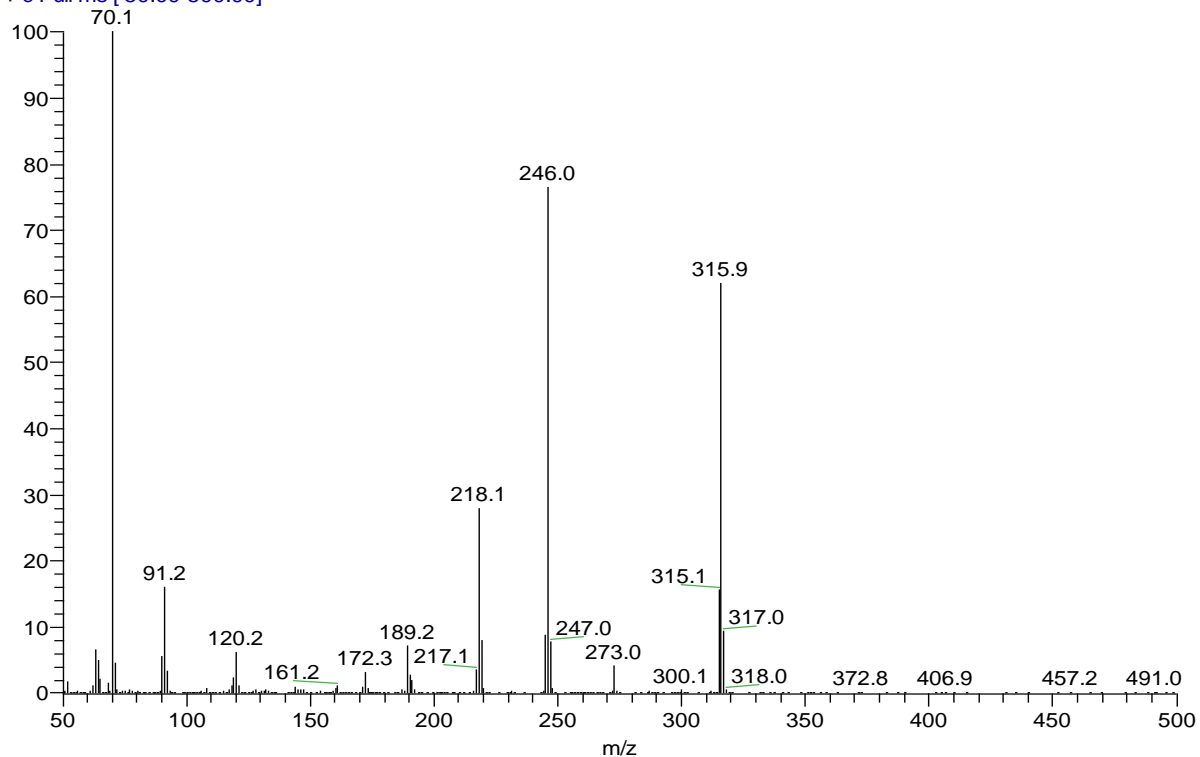


S89-240 #2071 RT: 20.67 AV: 1 NL: 8.16E5
T: + c Full ms [50.00-500.00]

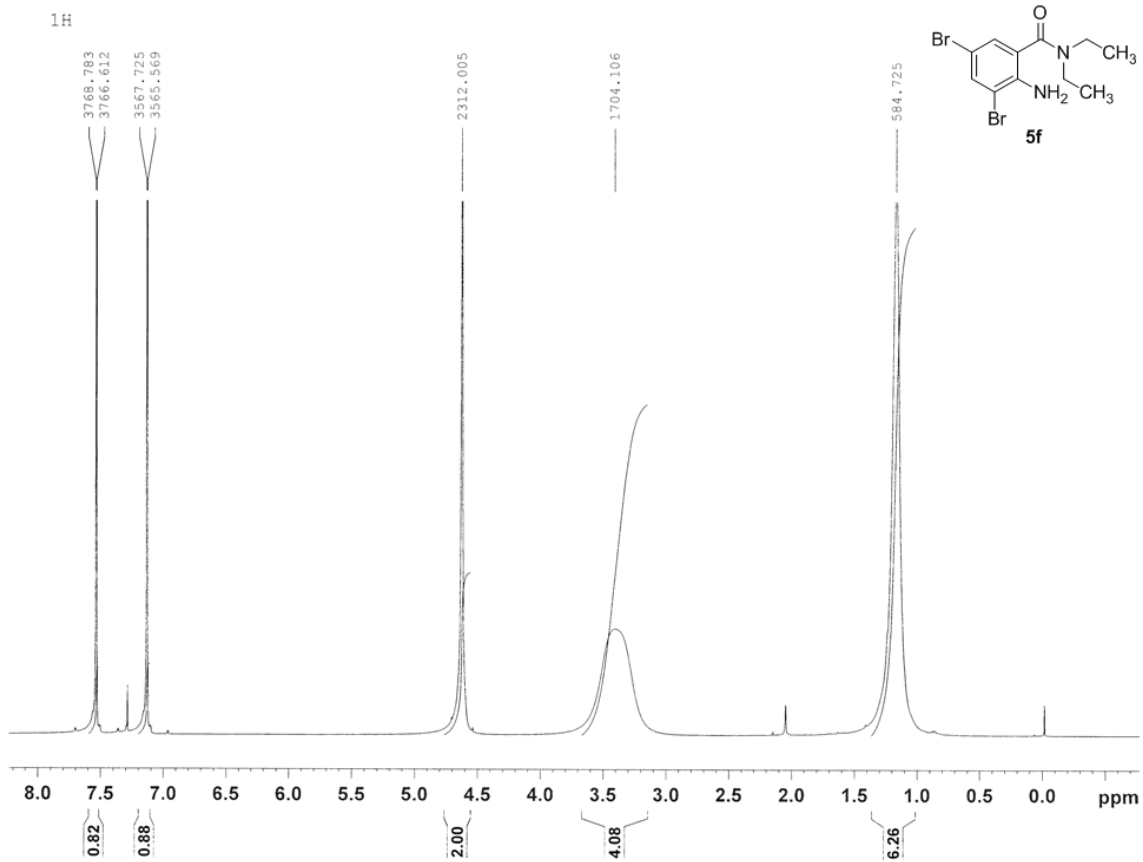


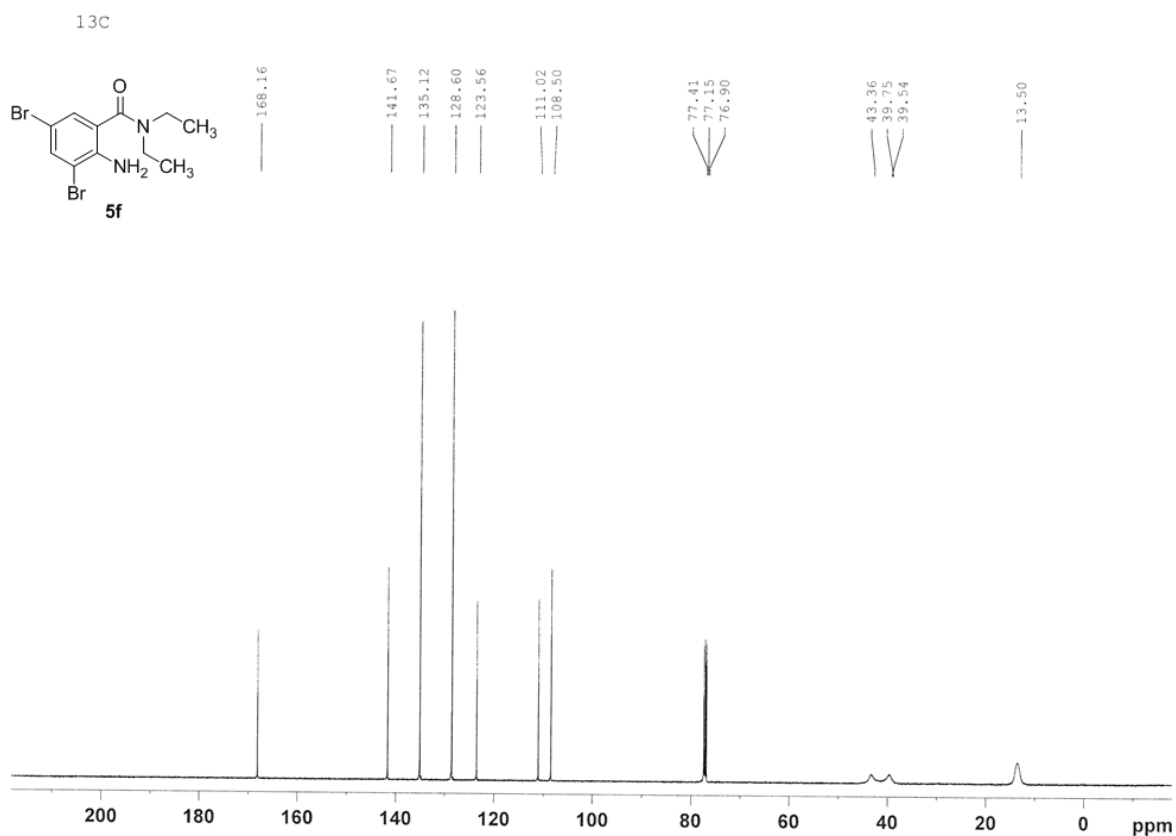
(2-Amino-5-iodophenyl)(pyrrolidin-1-yl)methanone (**5e**)

S118-2 #2224 RT: 22.46 AV: 1 NL: 1.14E7
T: + c Full ms [50.00-500.00]

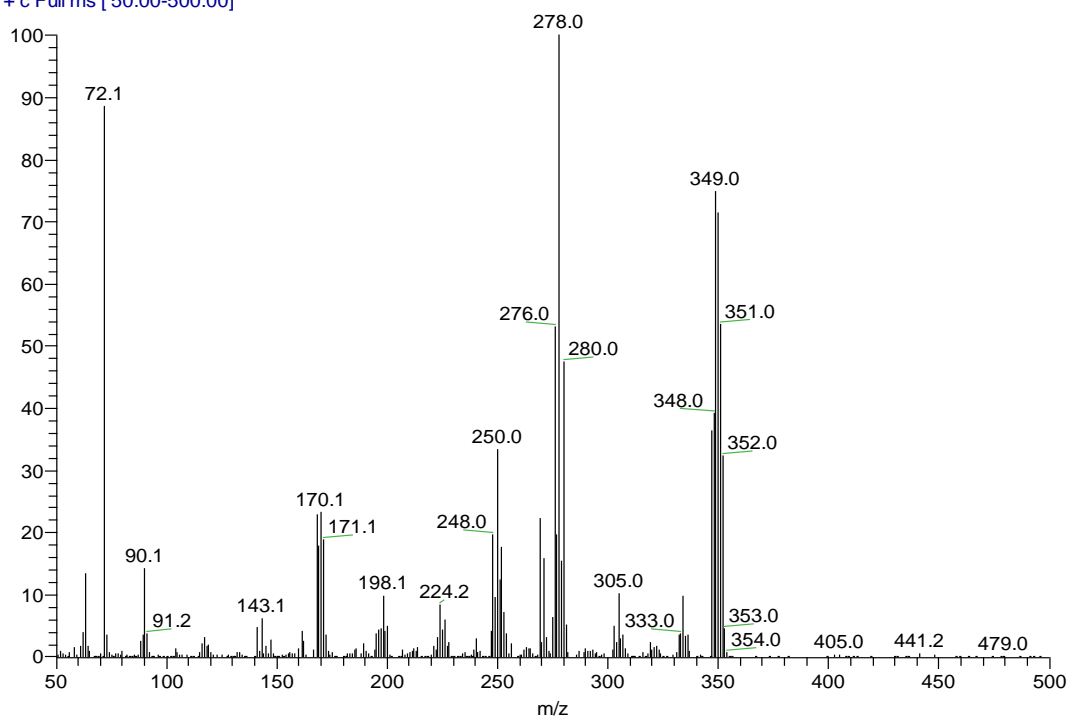


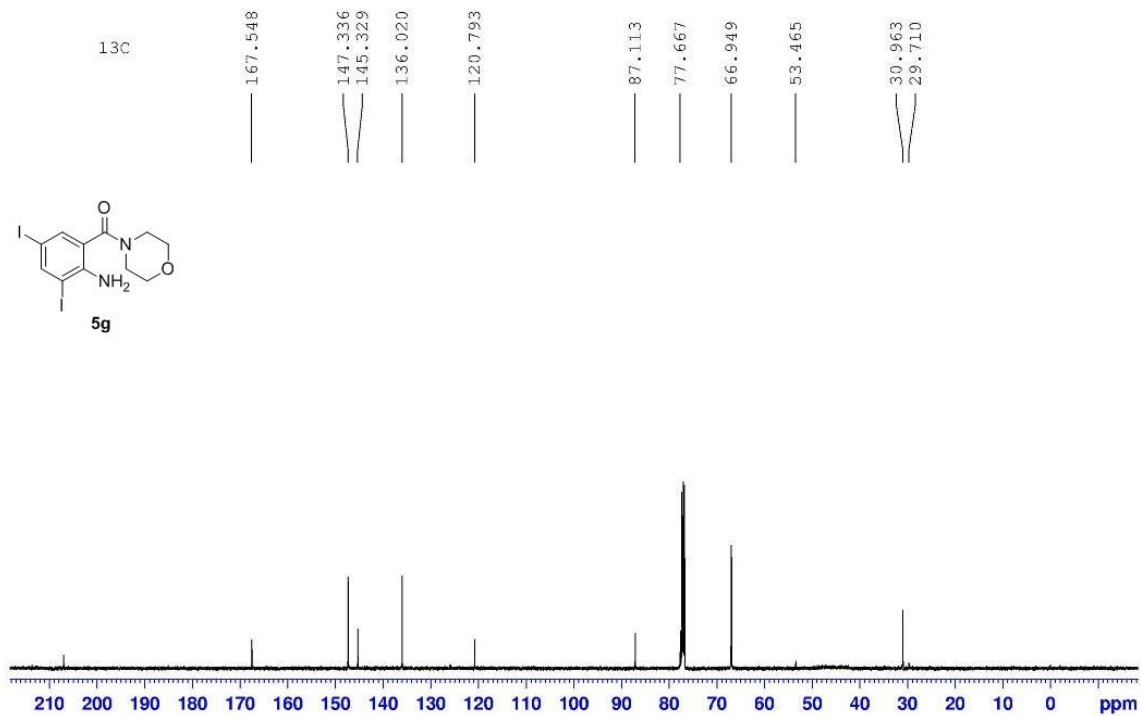
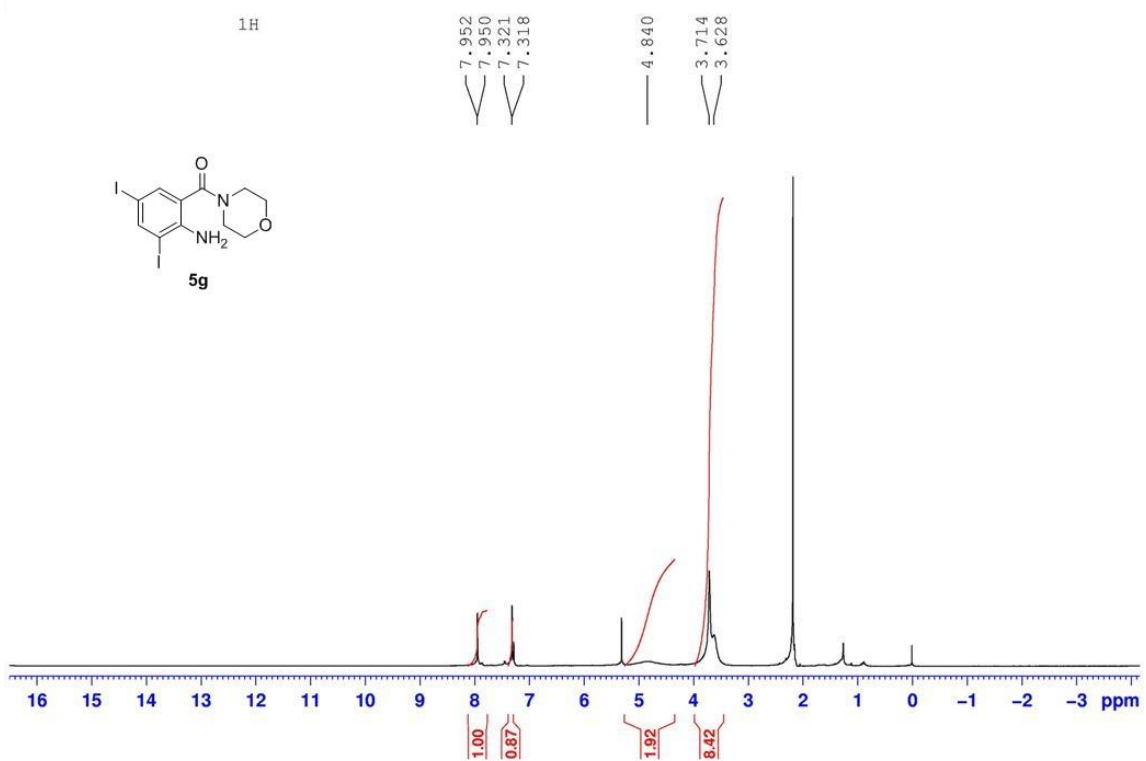
2-Amino-3,5-dibromo-N,N-diethylbenzamide (**5f**)



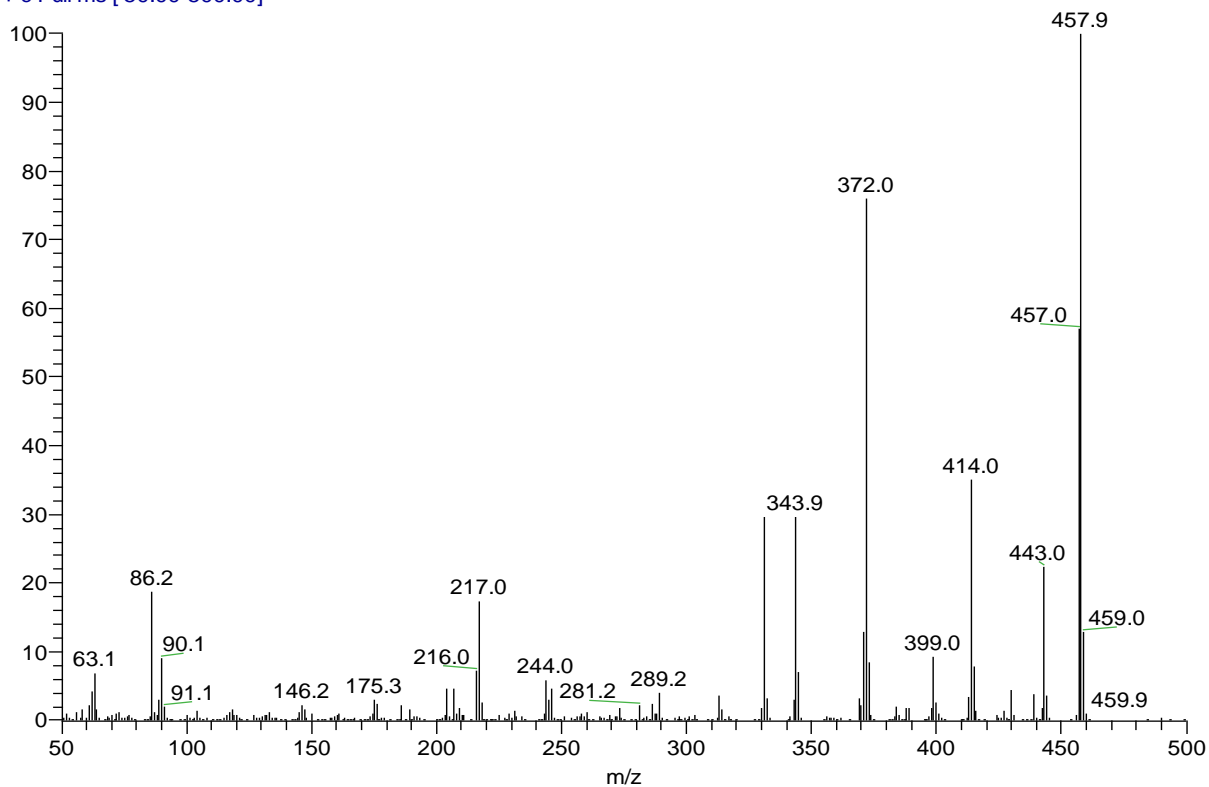


S120 #2056 RT: 21.11 AV: 1 NL: 2.13E6
T: + c Full ms [50.00-500.00]

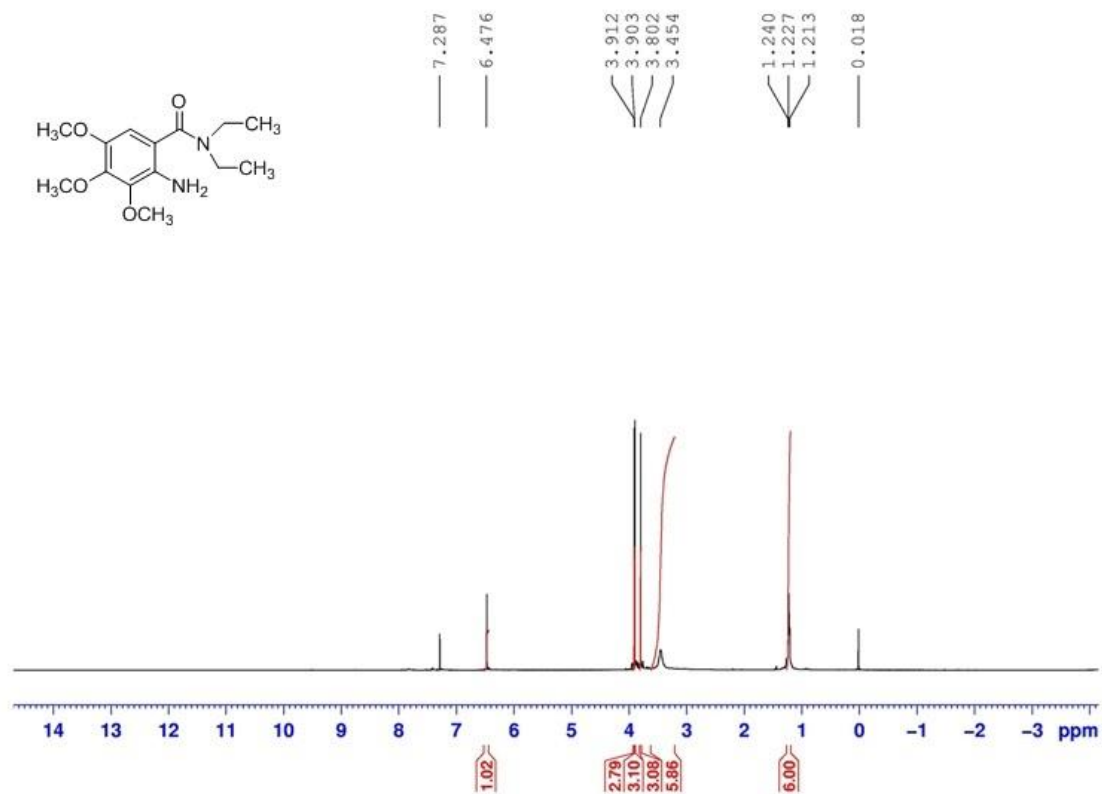


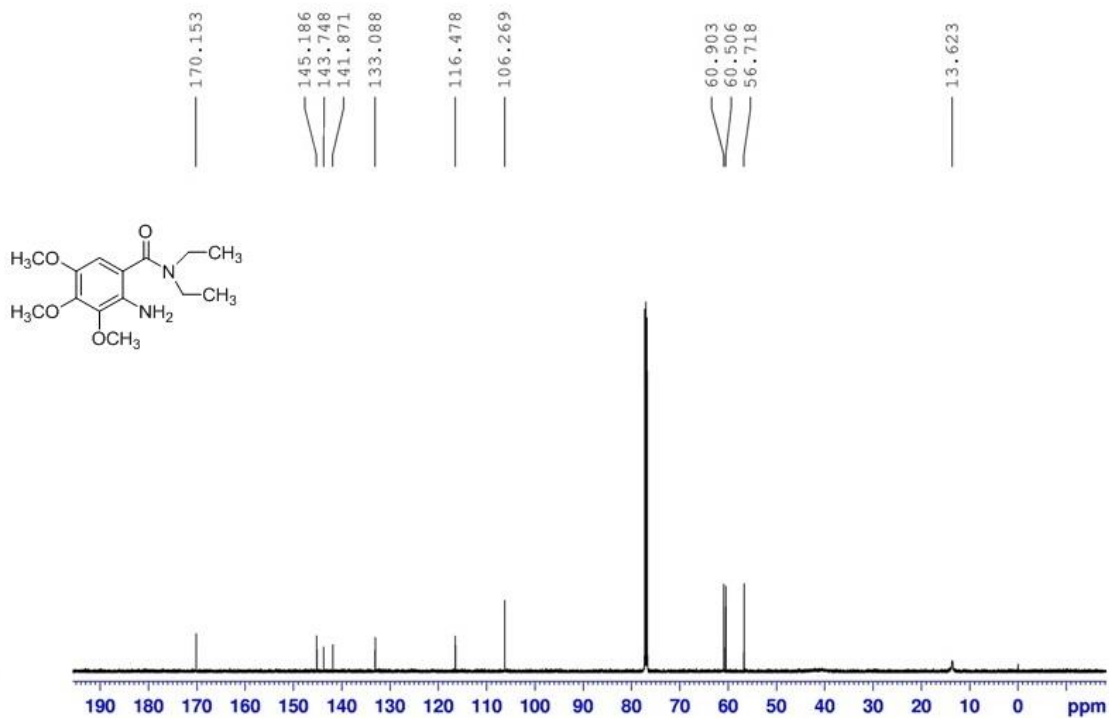
(2-Amino-3,5-diiodophenyl) (morpholino) methanone (**5g**)

S150-458 #2820 RT: 27.42 AV: 1 NL: 2.25E6
T: + c Full ms [50.00-500.00]

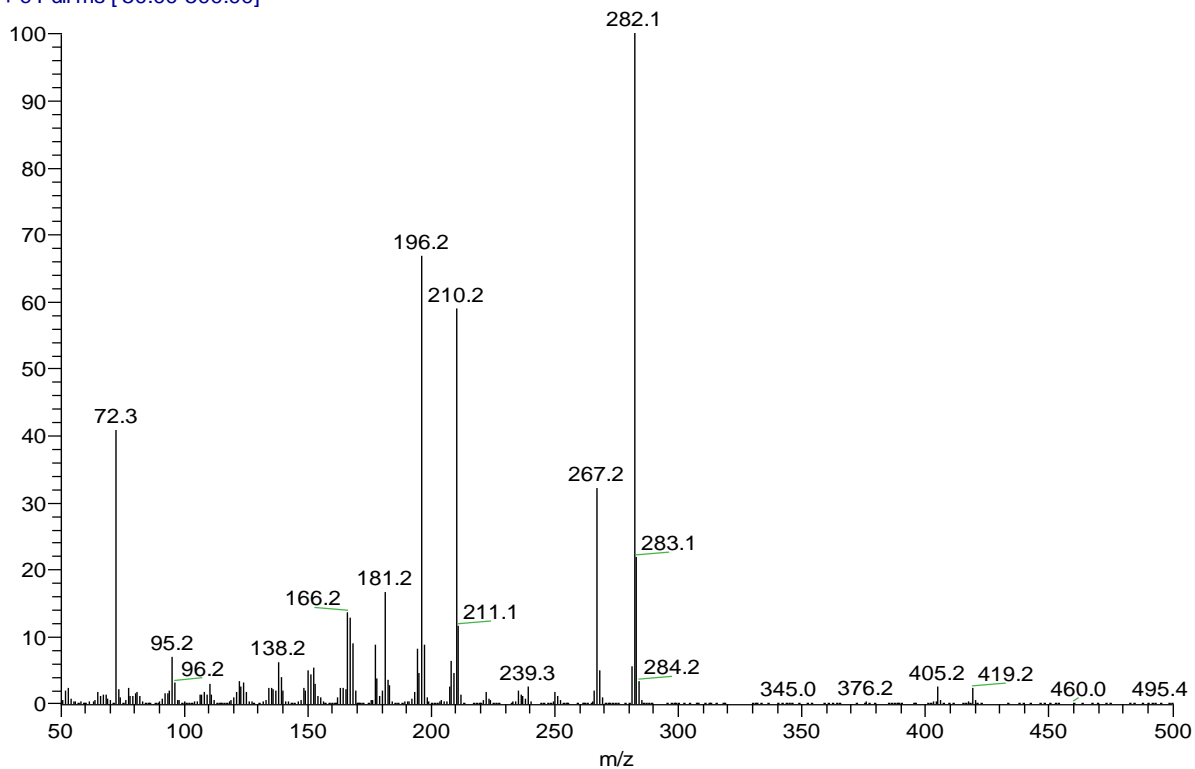


2-Amino-N,N-diethyl-3,4,5-trimethoxybenzamide (**5h**)



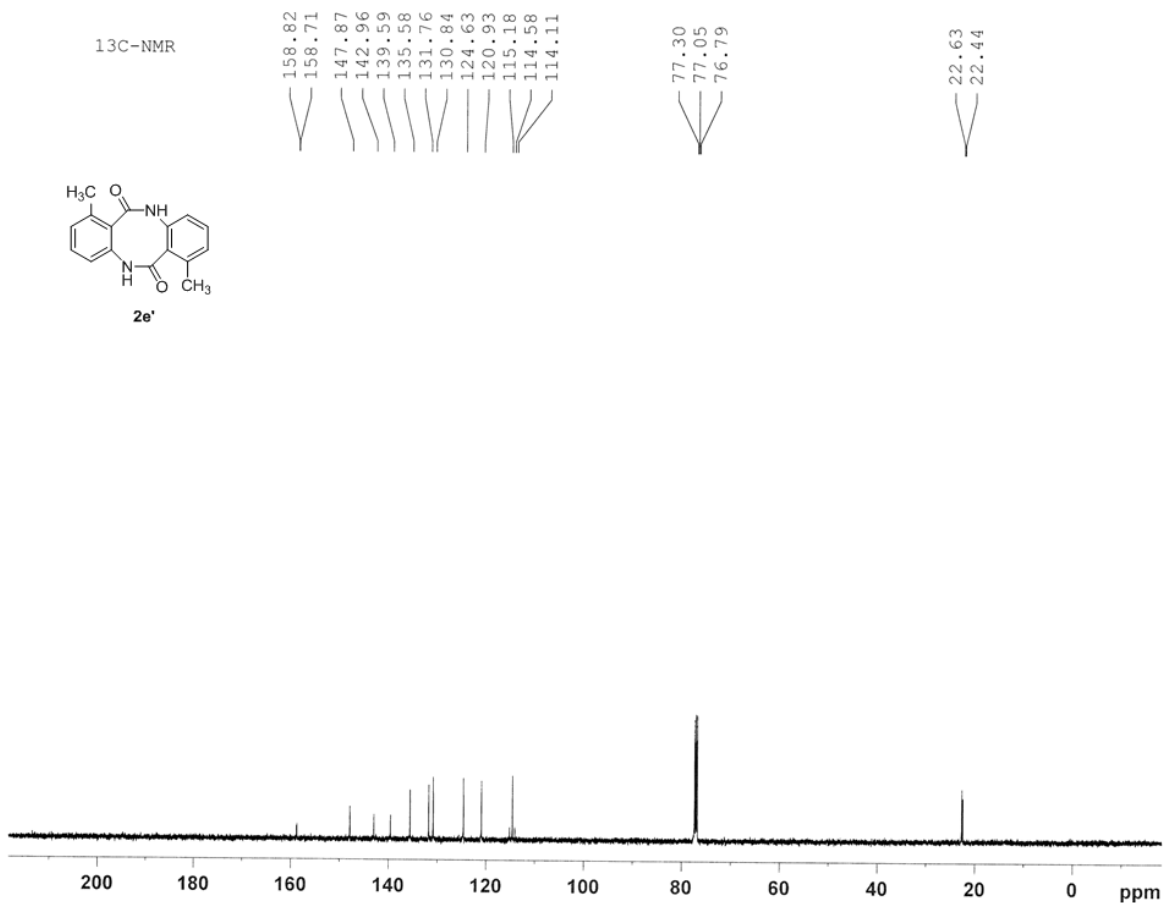
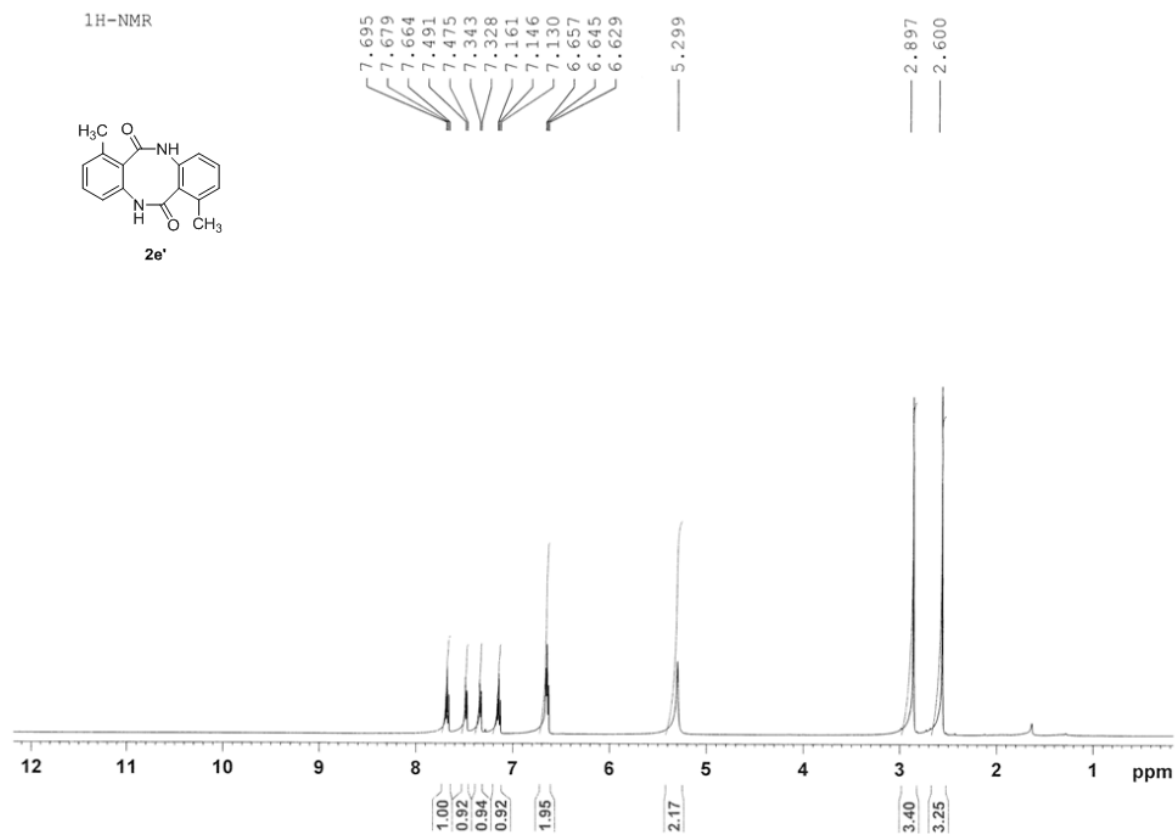


S122 #2072 RT: 20.84 AV: 1 NL: 3.15E7
T: + c Full ms [50.00-500.00]

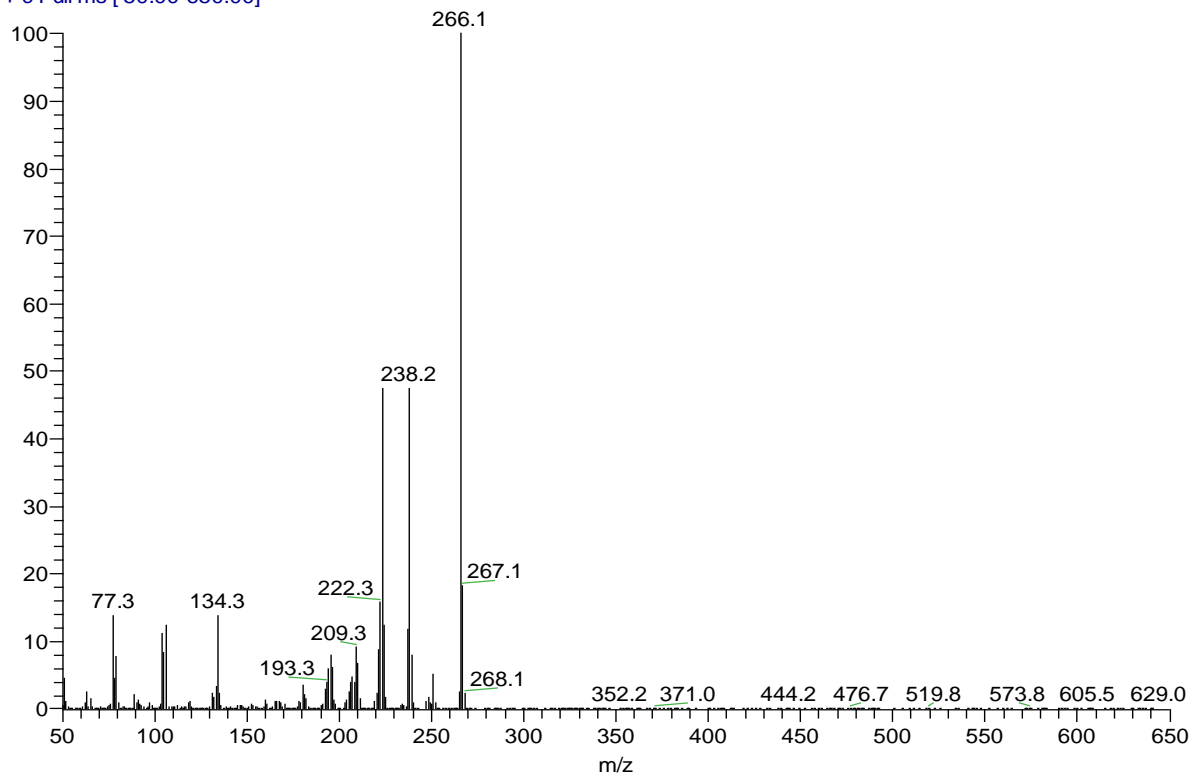


5. By- Products (2e' and 2f')

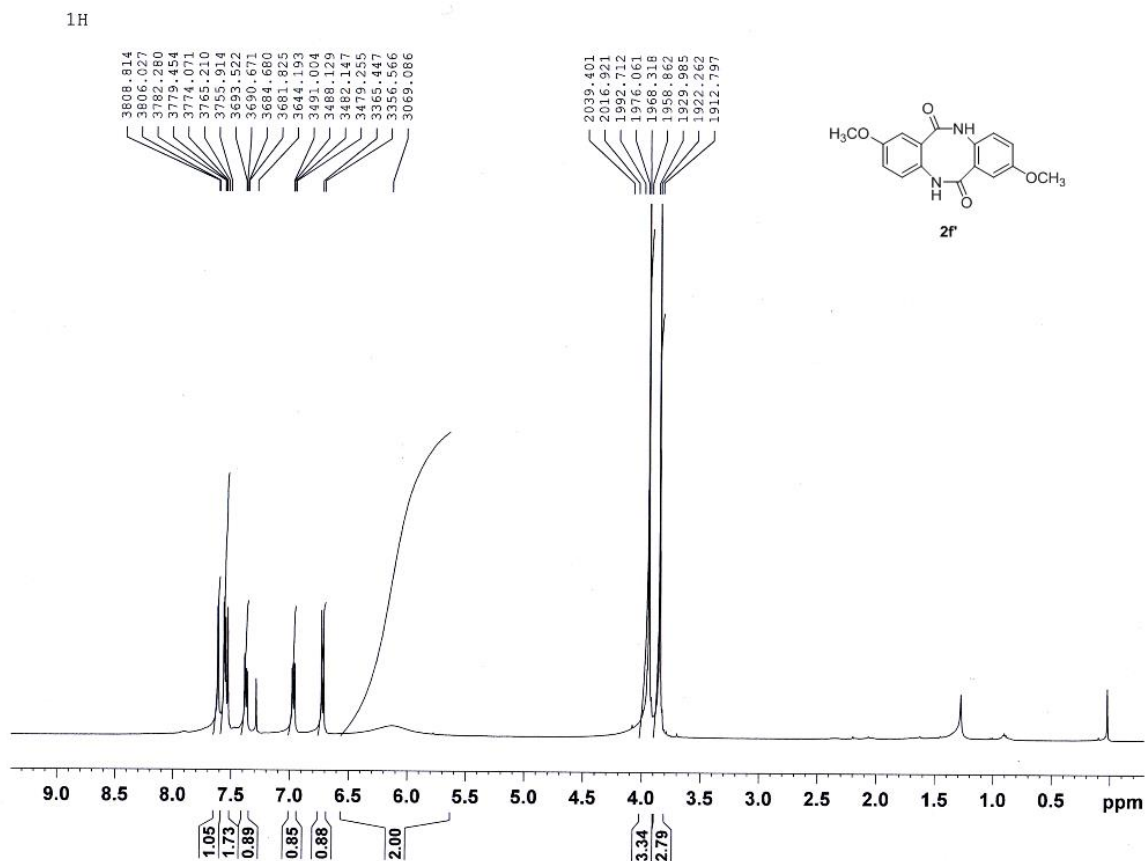
1,7-dimethyldibenzo[b,f][1,5]diazocine-6,12(5H,11H)-dione (2e')

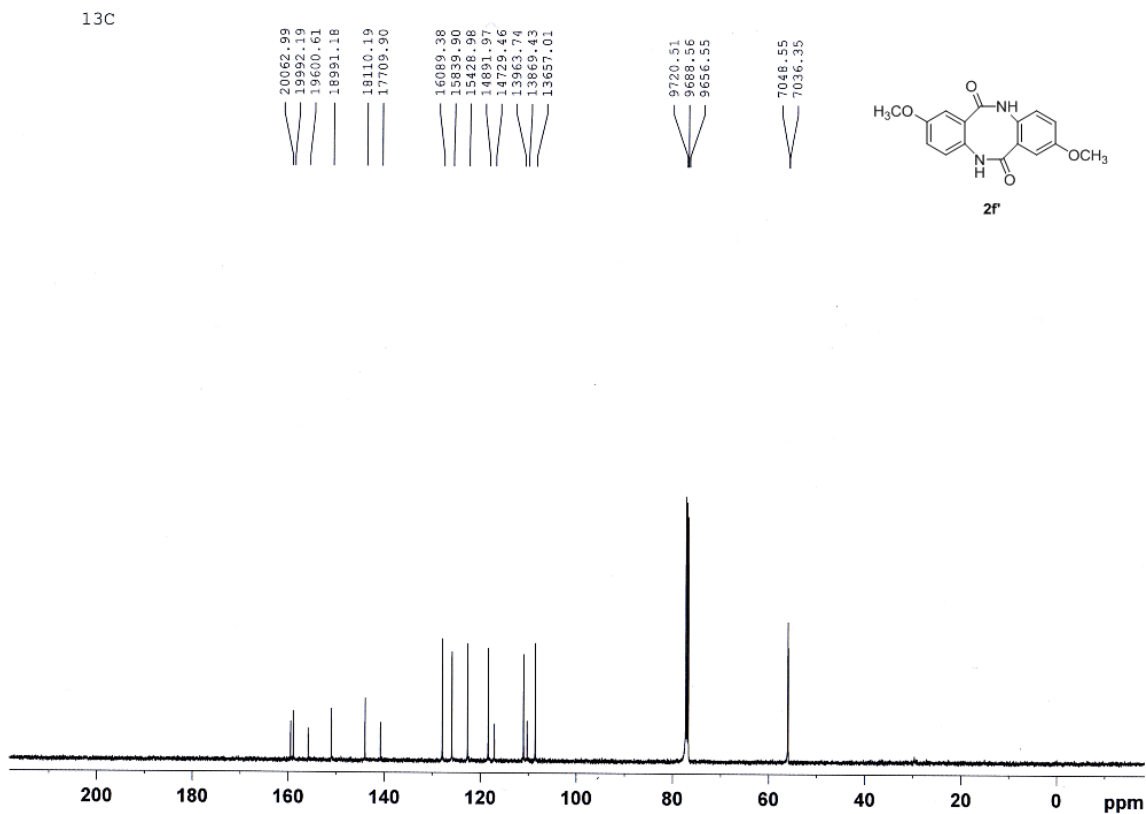


S94Y-1 #1097 RT: 13.84 AV: 1 NL: 2.00E7
T: + c Full ms [50.00-650.00]



1,7-dimethoxydibenzo[b,f][1,5]diazocine-6,12(5H,11H)-dione (**2f'**)





S91 #2885 RT: 27.40 AV: 1 NL: 9.72E6
 T: + c Full ms [50.00-500.00]

