Electronic Supplementary Information

Transamidation of Primary Carboxamides, Phthalimide, Urea and Thiourea with Amines Using $Fe(OH)_3@Fe_3O_4$ Magnetic Nanoparticles as an Efficient Recyclable Catalyst

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1. General remarks

All experiments were carried out under argon. All chemicals and solvents were purchased from commercial suppliers and used without further purification. FT-IR spectra were obtained over the region 400–4000 cm^{-1} with a Nicolet IR100 FT-IR with spectroscopic grade KBr. The powder X-ray diffraction spectrum was recorded at room temperature using a Philips X-Pert 1710 diffractometer with Co Kα (α=1.79285 Å) voltage: 40 kV, current: 40 mA and in the range 20°–80° (2θ) with a scan speed of 0.02°/s. The morphology of catalyst was studied with scanning electron microscopy using SEM (Philips XL 30 and S-4160) on gold coated samples. The magnetic properties of $Fe(OH)_3@Fe_3O_4$ were obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran, www.mdk-magnetic.com). Transmission electron microscopy (TEM) were carried out at 120 kV (Philips model CM120). Thermal gravimetric analysis (TGA) was performed on a Thermal Analyzer with a heating rate of 20 °C min^{-1} over a temperature range of 25–1100 °C under flowing compressed N_2. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (DRX 400 MHz and DRX 500 MHz) in pure deuterated $CDCl_3$ solvent with tetramethylsilane (TMS) as internal standard.

2. Experimental procedures

2.1. Preparation of the $Fe(OH)_3@Fe_3O_4$ catalyst

The synthesis of the $Fe(OH)_3@Fe_3O_4$ catalyst was conducted according to the procedure previously reported. In a typical preparation procedure, the mixture of 4.0 mmol $FeCl_3{\cdot}6H_2O$ and 2.0 mmol $FeCl_2{\cdot}4H_2O$ salts in 40.0 mL of deionized water under vigorous stirring. An ammonia solution (25% (w/w)) was added in dropwise manner over 5 min to the stirring mixture to maintain the reaction *p*H about 11. The resulting black dispersion was stirred vigorously for 1h at room temperature and then was refluxed for 1h. Fe_3O_4 nanoparticles were magnetically gathered and the residue was repeatedly washed with water and ethanol. Subsequently, as-prepared Fe_3O_4 nanoparticles and 15.0 mmol of $FeCl_3{\cdot}6H_2O$ were ultrasonically dispersed into 10.0 mL of ethanol. After totally dissolution and dispersion, the nanoparticles were separated from the ethanol solution by magnetic decantation and dried at 80 °C for 4h. $Fe(OH)_3@Fe_3O_4$ nanoparticles were obtained by dropwise addition of aqueous ammonia (25% (w/w), 5 mL) to the dried brown nanoparticles under vigorous stirring. Finally, the products of $Fe(OH)_3@Fe_3O_4$ were magnetically separated, washed with water, and dried in an oven at 373 K overnight for further usage.

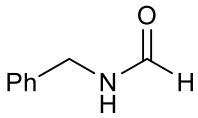
2.2. General Procedure for the transamidation

To a mixture of catalyst (30.0 mg, 2.6 mol%) and amine (1.0 mmol) in *p*-xylene (1.0 mL) were added amide (1.0 mmol) under argon atmosphere, and the mixture was refluxed for 10 h. After

completion of reaction, the reaction mixture was allowed to cool to room temperature. It was then diluted with EtOAc and the catalyst was separated from the reaction mixture by using an external magnet and washing twice with EtOAc, all volatiles were removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford the desired product.

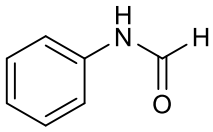
3. Characterization of the corresponding amide

***N*-benzylformamide 3a**



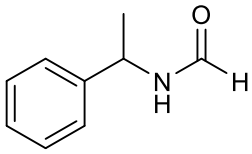
Isolated yield = 92% (87%); IR (KBr): ν (cm^{-1}) = 3277, 3047, 1644, 1534, 1456, 1387, 1230; MS (EI, 70 eV): m/z (%) = 135 (M^+, 80), 118 (10), 106 (73), 91 (100), 79 (57), 77 (51), 67 (27), 57 (8).

***N*-phenylformamide 3b**



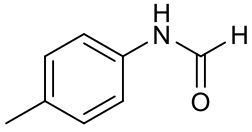
Isolated yield = 88% (81%); IR (KBr): ν (cm^{-1}) = 3267, 3063, 2876, 1684, 1601, 1541, 1439, 1305, 1147; MS (EI, 70 eV): m/z (%) = 121 (M^+, 100), 93 (75), 77 (4), 66 (31).

***N*-(1-phenylethyl)formamide 3c**



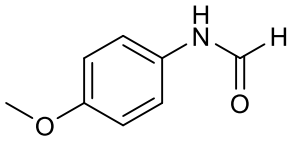
Isolated yield = 82% (80%); IR (KBr): ν (cm^{-1}) = 3279, 3044, 2978, 2865, 1668, 1530, 1382, 1262, 1088; MS (EI, 70 eV): m/z (%) = 149 (M^+, 100), 134 (67), 119 (14), 105 (79), 91 (10), 84 (92), 79 (68), 77 (62), 72 (5).

***N*-p-tolylformamide 3d**



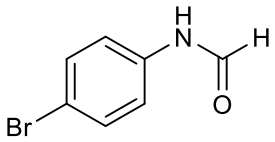
Isolated yield = 91% (84%); IR (KBr): ν (cm^{-1}) = 3190, 3035, 2921, 1684, 1516, 1398, 1300, 1040; MS (EI, 70 eV): m/z (%) = 301 (M^+, 10), 135 (86), 106 (100), 91 (5), 77 (30).

***N*-(4-methoxyphenyl)formamide 3e**



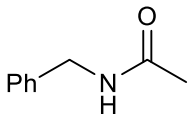
Isolated yield = 89% (88%); IR (KBr): ν (cm^{-1}) = 3243, 3152, 2893, 1656, 1548, 1509, 1386, 1237, 1025; MS (EI, 70 eV): m/z (%) = 151 (M^+, 87), 136 (14), 122 (57), 108 (100), 95 (40), 80 (85).

***N*-(4-bromophenyl)formamide 3f**



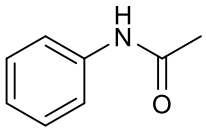
Isolated yield = 80% (75%); IR (KBr): ν (cm^{-1}) = 3258, 3050, 2868, 1671, 1591, 1531, 1390, 1302, 1063; MS (EI, 70 eV): m/z (%) = 199 (M^+, 100), 171 (66), 119 (3), 92 (41), 65 (50).

***N*-benzylacetamide 3i**



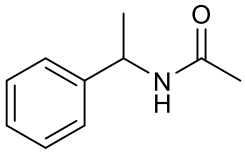
Isolated yield = 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 7.30-7.37 (m, 5H), 5.83 (br s, 1H), 4.45 (s, 2H), 2.05 (s, 3H).; ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C (ppm) = 169.9, 138.2, 128.7, 127.9, 127.6, 43.8, 23.3; IR (KBr): ν (cm^{-1}) = 3290, 3084, 2928, 2854, 1640, 1550, 1441, 1366, 1025; MS (EI, 70 eV): m/z (%) = 149 (M^+, 100), 106 (82), 91 (25), 77 (12).

***N*-phenylacetamide 3j**



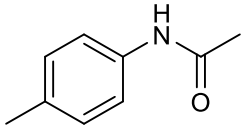
Isolated yield = 70%; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) = 9.92 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 2.03 (s, 6H).; IR (KBr): ν (cm^{-1}) = 3292, 1665, 1606, 1546, 1432, 1029; MS (EI, 70 eV): m/z (%) = 135 (M^+, 85), 119 (3), 93 (100), 77 (12), 65 (60), 57 (4).

***N*-(1-phenylethyl)acetamide 3k**



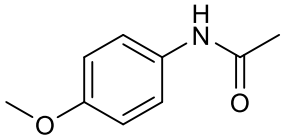
Isolated yield = 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 7.28-7.40 (m, 5H), 5.79 (br s, 1H), 5.16 (q, *J* = 8.0 Hz, 1H), 2.02 (s, 3H), 1.52 (d, *J* = 8.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C (ppm) = 169.1, 143.1, 128.7, 127.4, 126.2, 48.9, 23.5, 21.7; IR (KBr): ν (cm^{-1}) = 3264, 3067, 2925, 1644, 1549, 1445, 1373 1027; MS (EI, 70 eV): m/z (%) = 163 (M^+, 37), 148 (37), 120 (56), 106 (100), 77 (48).

***N*-(p-tolyl)acetamide 3l**



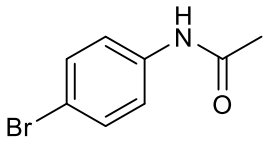
Isolated yield = 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 9.41 (br s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (m, *J* = 8.0 Hz, 2H), 2.91 (s, 3H), 2.08 (s, 3H); IR (KBr): ν (cm^{-1}) = 3284, 3122, 2942, 1662, 1529, 1314, 1027; MS (EI, 70 eV): m/z (%) = 149 (M^+, 70), 107 (100), 106 (97), 91 (3), 77 (17).

***N*-(4-methoxyphenyl)acetamide 3m**



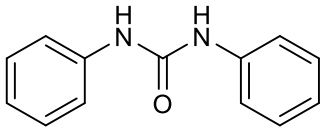
Isolated yield = 79%; IR (KBr): ν (cm^{-1}) = 3247, 3071, 2925, 1653, 1510, 1409, 1240, 1026; MS (EI, 70 eV): m/z (%) = 165 (M^+, 72), 149 (16), 123 (80), 108 (100), 95 (17), 91 (10), 80 (27).

***N*-(4-bromophenyl)acetamide 3n**



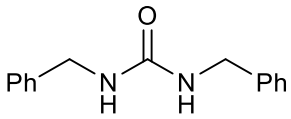
Isolated yield = 64%; IR (KBr): ν (cm^{-1}) = 3297, 3187, 1671, 1595, 1532, 1484, 1388, 1305, 1004; MS (EI, 70 eV): m/z (%) = 213 (M^+, 77), 178 (100), 145 (12), 143 (12), 119 (6), 92 (67), 91 (36), 65 (46).

1,3-diphenylurea 3o



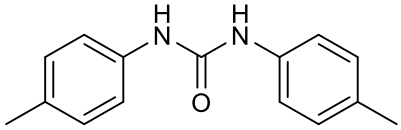
Isolated yield = 64%; IR (KBr): ν (cm^{-1}) = 3323, 1645, 1599, 1549, 1439, 1306, 1230; MS (EI, 70 eV): m/z (%) = 212 (M^+, 82), 119 (5), 93 (100), 92 (15), 77 (14).

1,3-dibenzylurea 3p



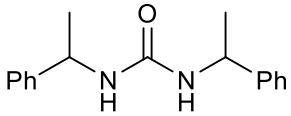
Isolated yield = 71%; IR (KBr): ν (cm^{-1}) = 3328, 3029, 2922, 2870, 1620, 1450, 1252, 1099; MS (EI, 70 eV): m/z (%) = 240 (M^+, 37), 149 (29), 106 (100), 91 (67), 79 (22), 77 (17).

1,3-di-p-tolylurea 3q



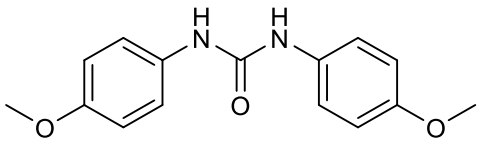
Isolated yield = 85%; IR (KBr): ν (cm^{-1}) = 3308, 2924, 1641, 1564, 1409, 1241; MS (EI, 70 eV): m/z (%) = 240 (M^+, 85), 150 (10), 133 (20), 107 (100), 106 (97), 91 (32), 77 (61).

1,3-bis(1-phenylethyl)urea 3r



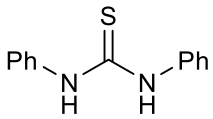
Isolated yield = 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 7.27-7.31 (m, 10H), 5.99 (br s, 2H), 4.79 (q, *J* =8.0 Hz, 2H), 1.43 (d, *J* =8.0 Hz, 6H); IR (KBr): ν (cm^{-1}) = 3329, 2969, 1626, 1575, 1447, 1248, 1115; MS (EI, 70 eV): m/z (%) = 268 (M^+, 91), 253 (5), 163 (20), 149 (7), 120 (100), 106 (100), 105 (96), 91 (10), 77 (60).

1,3-bis(4-methoxyphenyl)urea 3s



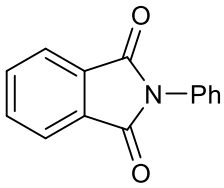
Isolated yield = 58%; IR (KBr): ν (cm^{-1}) = 3449, 2927, 1716, 1613, 1516, 1387, 1254, 1104; MS (EI, 70 eV): m/z (%) = 272 (M^+, 1), 253 (100), 238 (80), 210 (21), 130 (22), 106 (21), 76 (42).

1,3-diphenylthiourea 3v



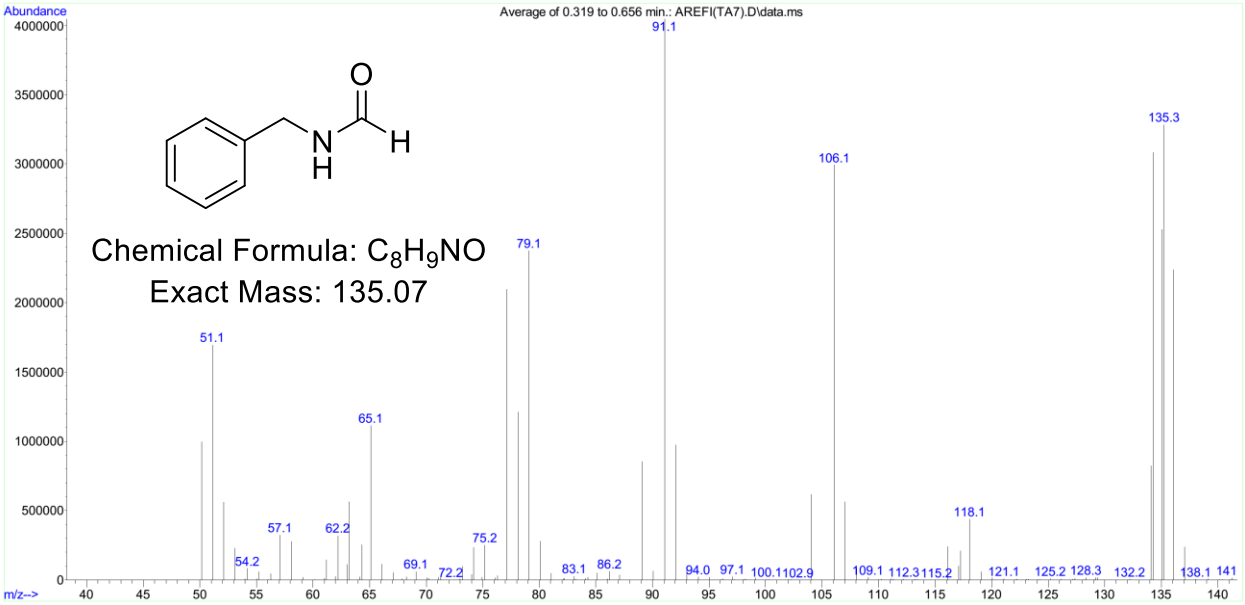
Isolated yield = 58%; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) = 9.79 (s, 2H), 7.47 (t, *J* =7.5 Hz, 2H), 7.32 (t, *J* =7.5, 2H), 7.11 (t, *J* =7.5, 1H); IR (KBr): ν (cm^{-1}) = 3204, 3020, 1545, 1449, 1339, 1234, 1068.

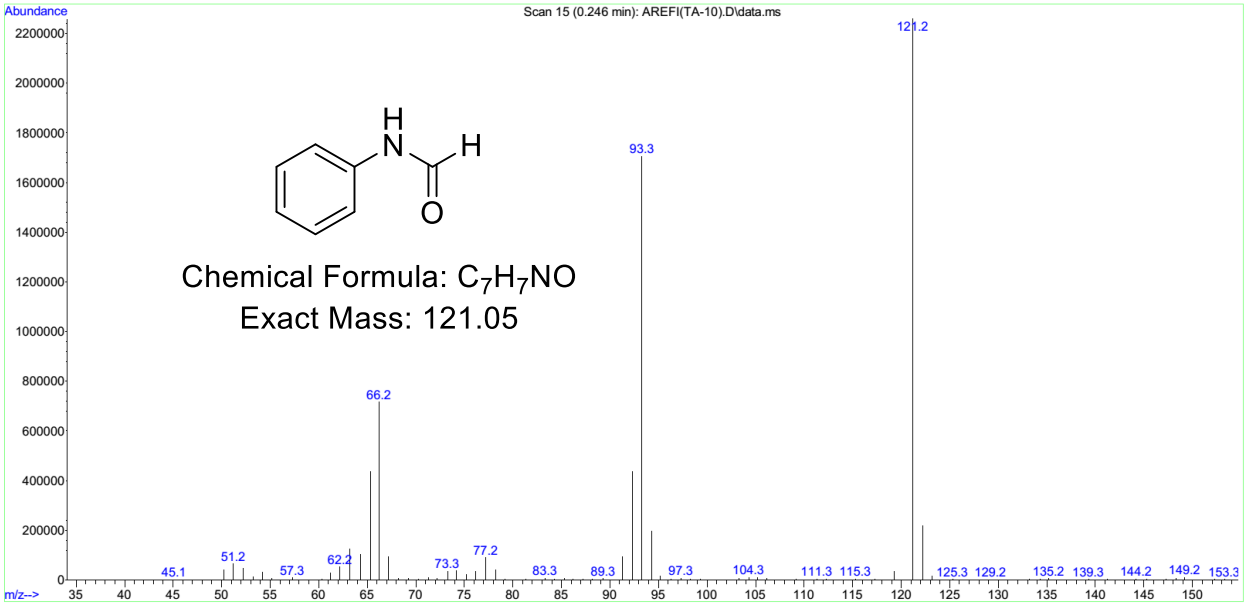
2-phenyl isoindoline-1,3-dione 3w



Isolated yield = 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 7.99-8.01 (m, 2H), 7.82-7.84 (m, 2H), 7.47-7.55 (m, 5H); IR (KBr): ν (cm^{-1}) = 3457, 1709, 1497, 1384, 1112; MS (EI, 70 eV): m/z (%) = 223 (M^+, 85), 209 (20), 179 (100), 152 (31), 130 (22), 104 (79), 91 (46), 77 (77).

4. Copy of ^{1}H NMR, ^{13}C NMR and mass spectra of amide derivatives

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93.3
66.2
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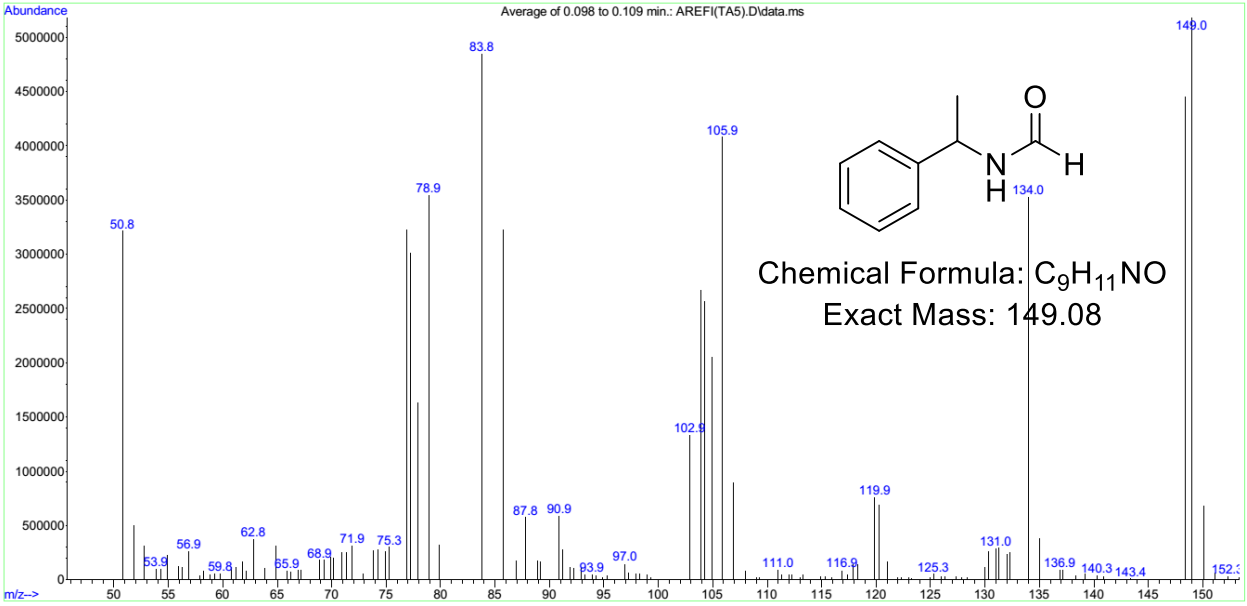
Exact Mass: 121.05
m/z-->


Abundance
Average of 0.098 to 0.109 min.: AREFI(TA5).D\data.ms
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83.8
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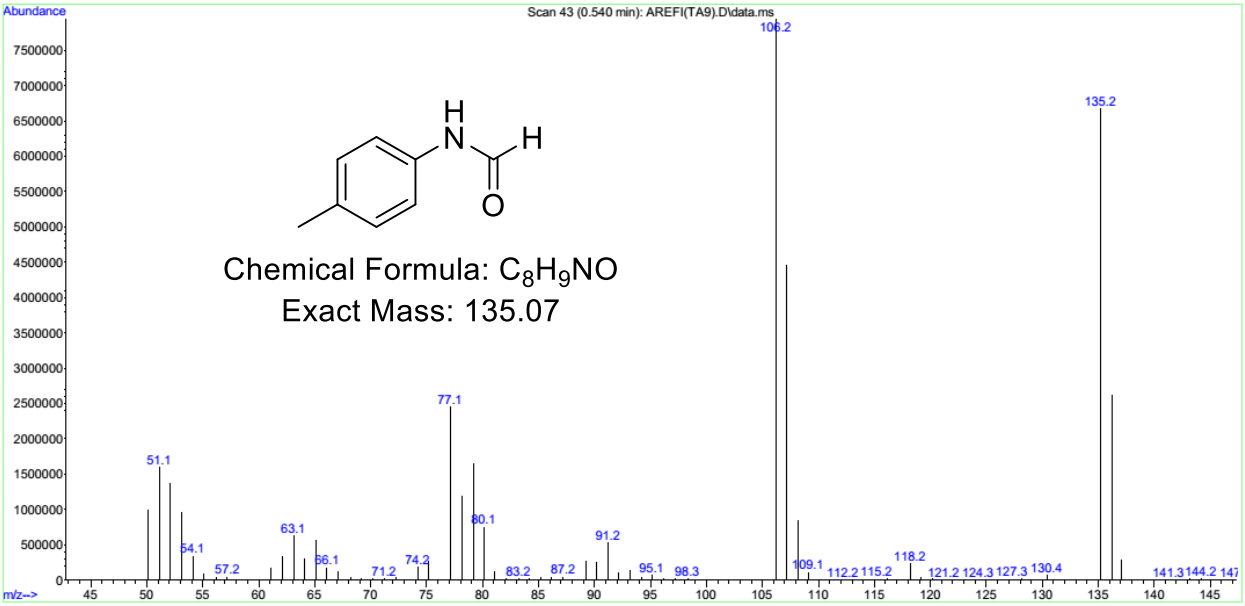
78.9
134.0
50.8
Chemical Formula: C9H11NO
Exact Mass: 149.08
m/z-->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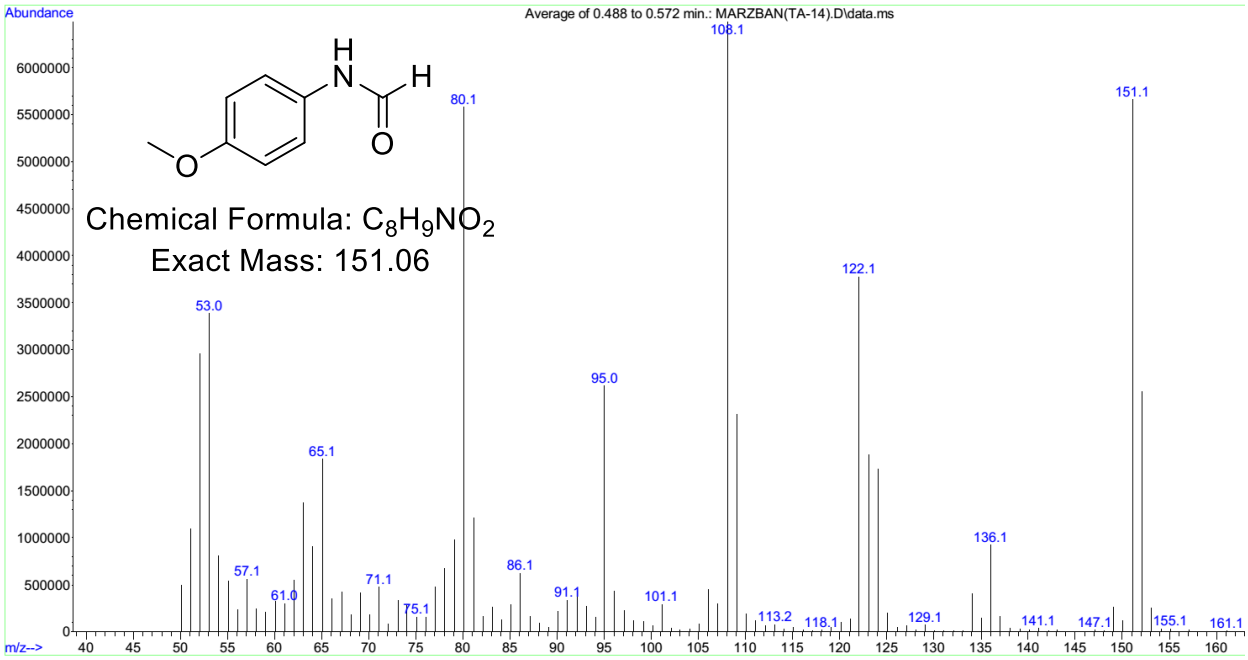
Exact Mass: 135.07
m/z-->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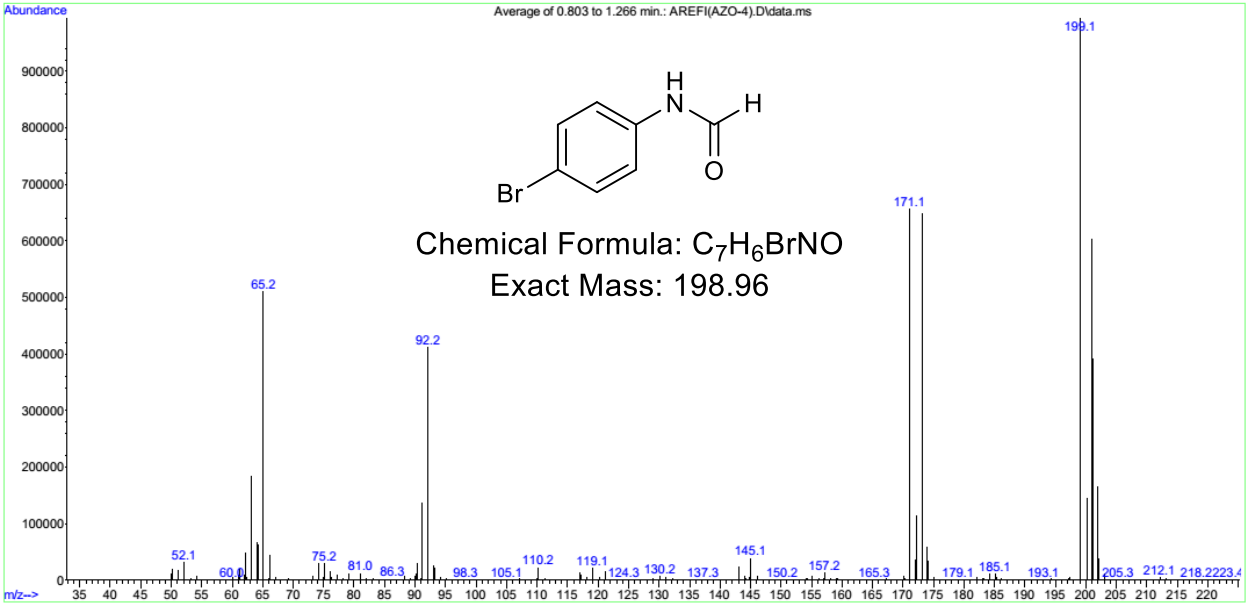
Chemical Formula: C8H9NO2
Exact Mass: 151.06
m/z-->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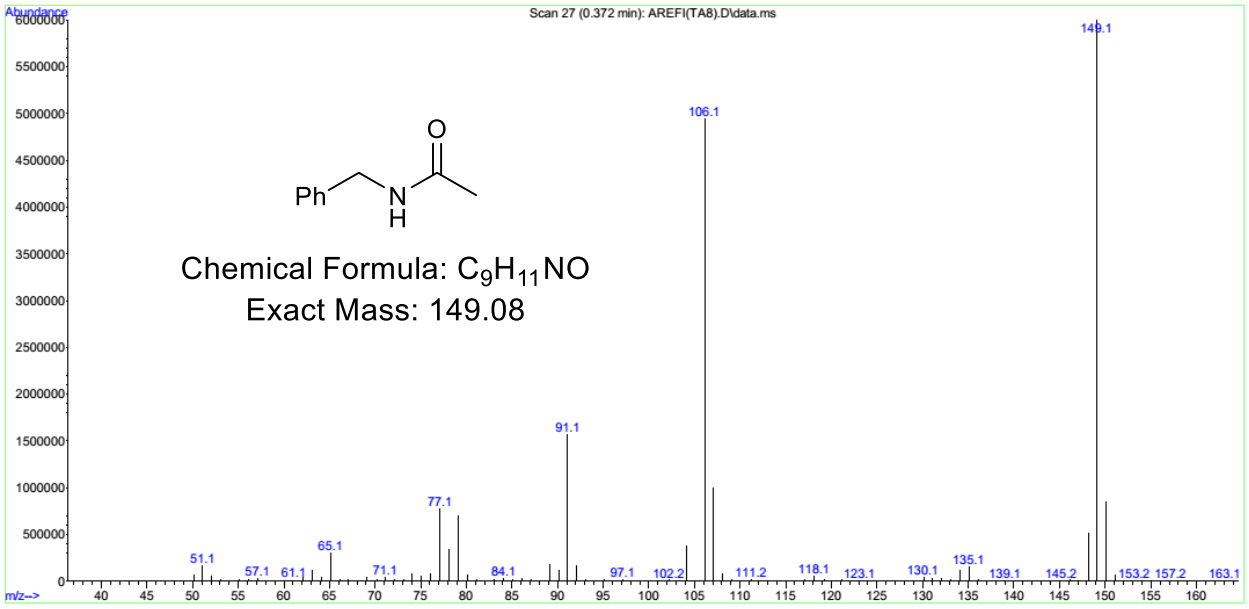
Br
H
N
H
O
Chemical Formula: C7H6BrNO
Exact Mass: 198.96
199.1
171.1
65.2
92.2
m/z-->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Ph
N
H
O
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Exact Mass: 149.08
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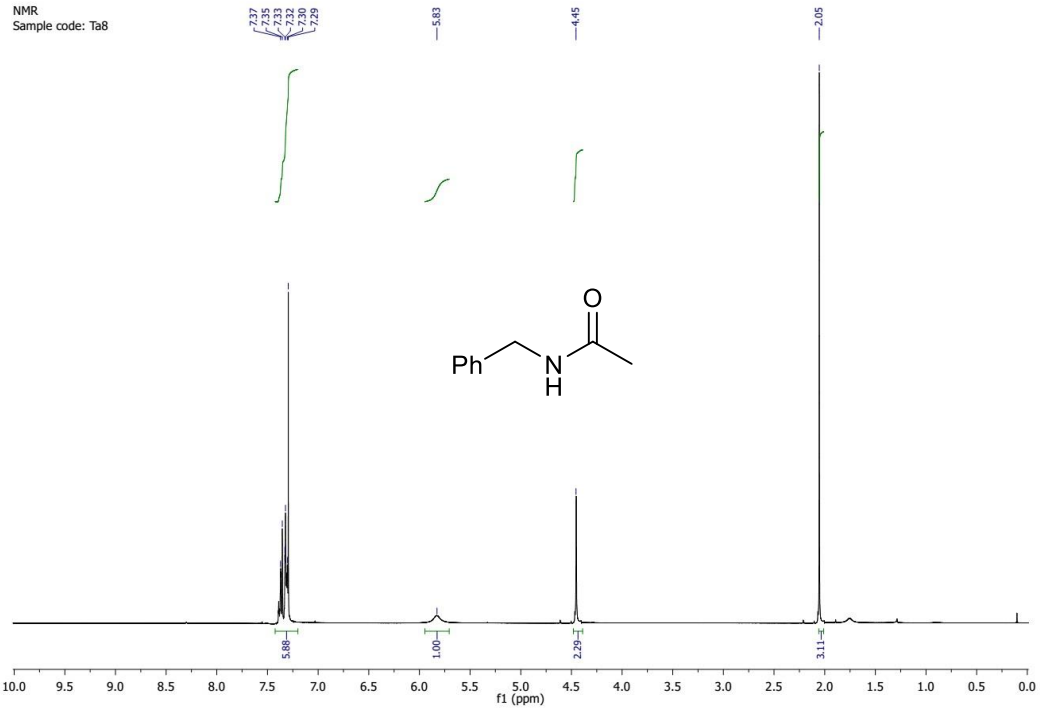
106.1
91.1
77.1
65.1
m/z-->


NMR
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2.05
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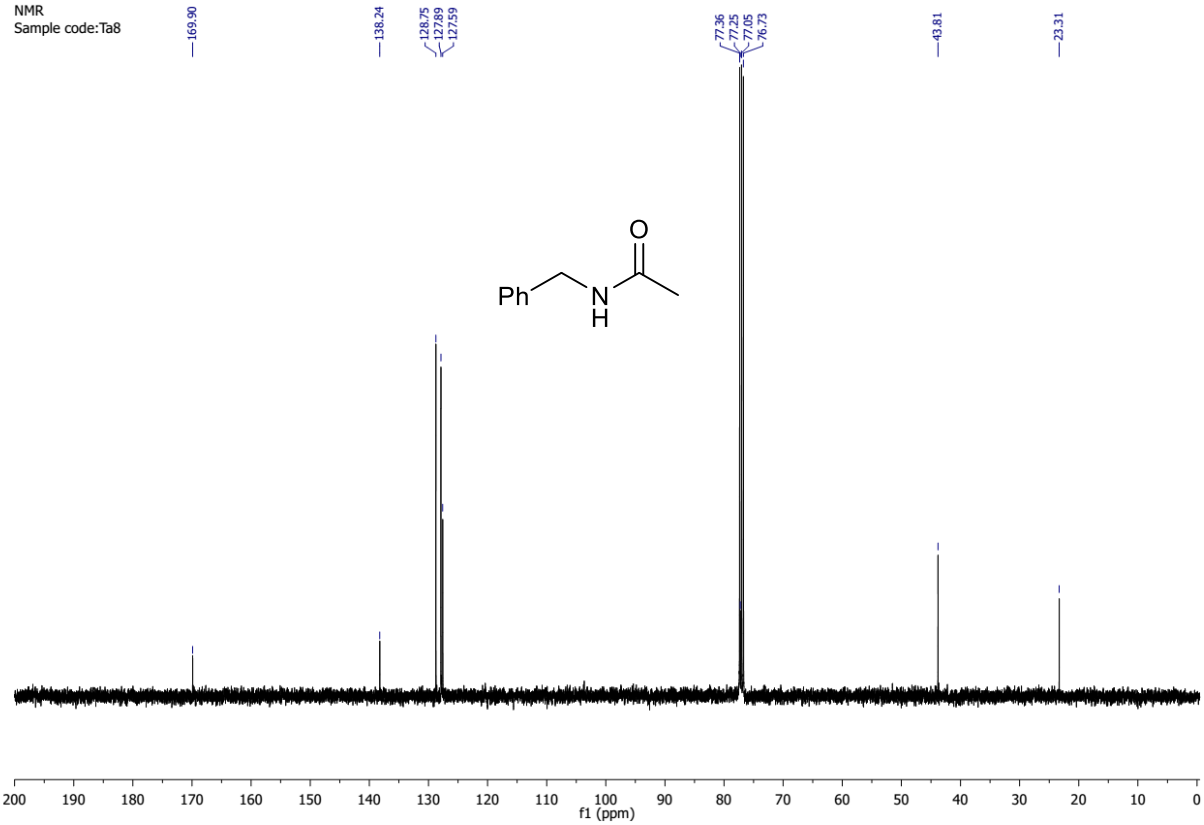
N
H
5.88
1.00
2.29
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NMR
Sample code:Ta8
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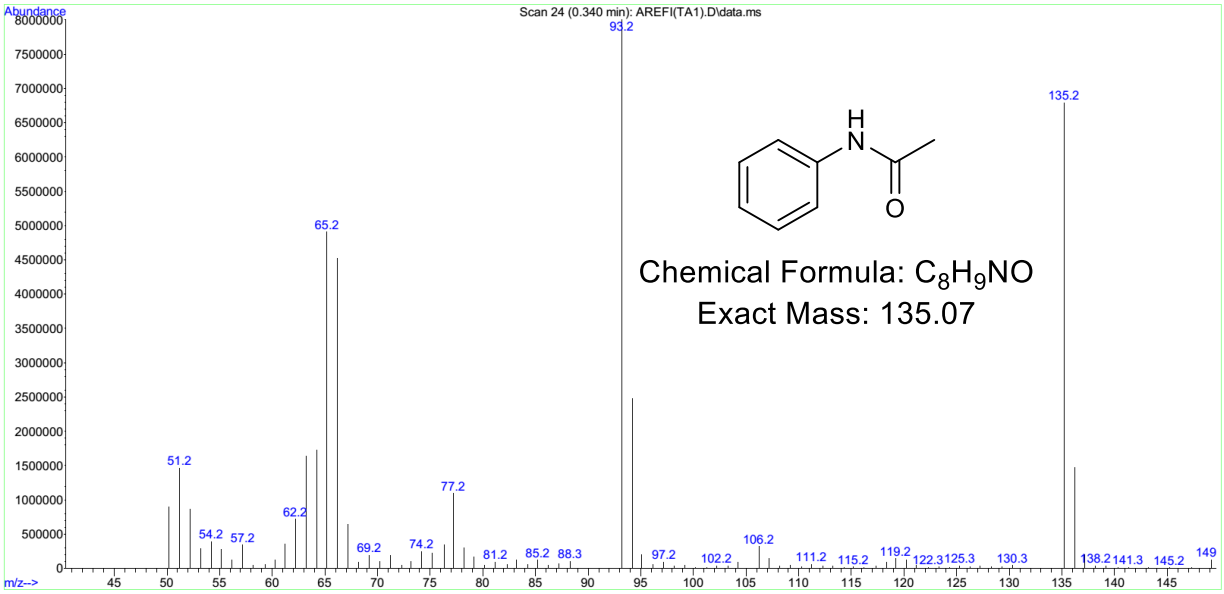
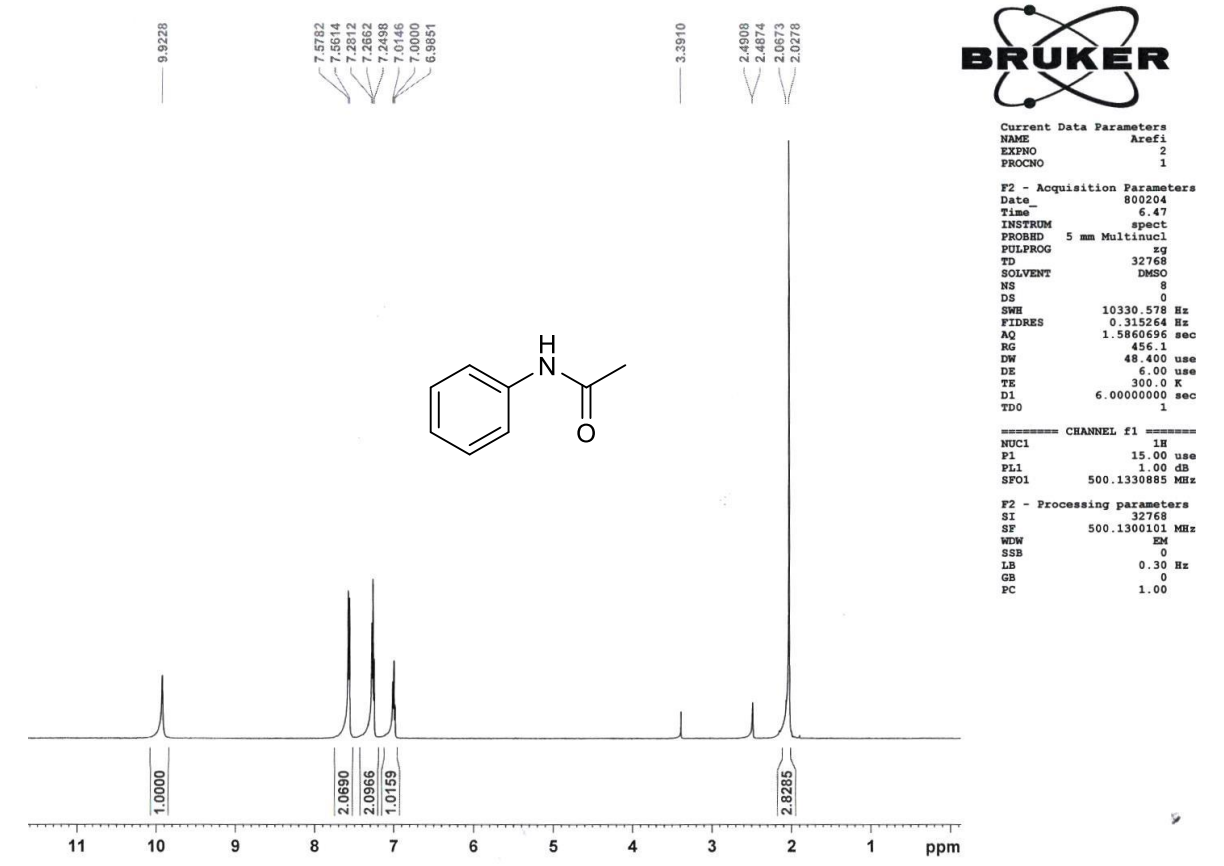
77.36
77.25
77.05
76.73
43.81
23.31
O
Ph
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





BRUKER

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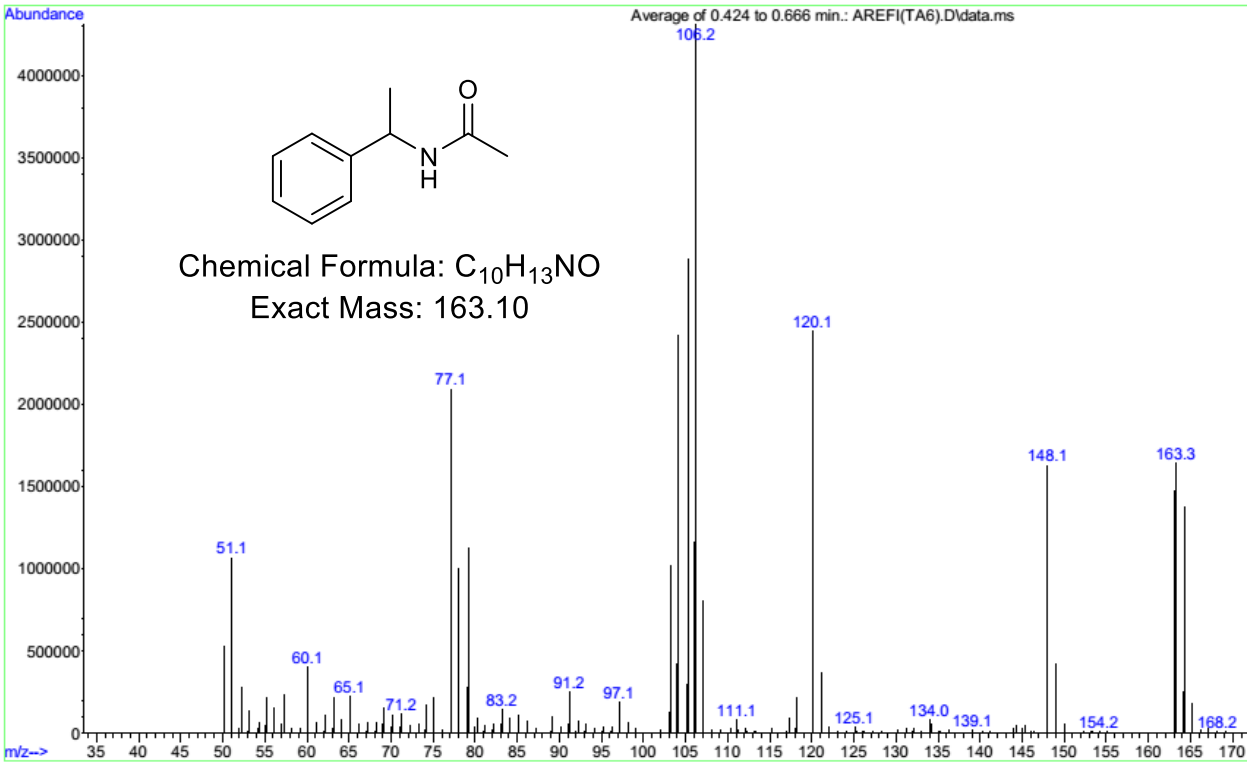
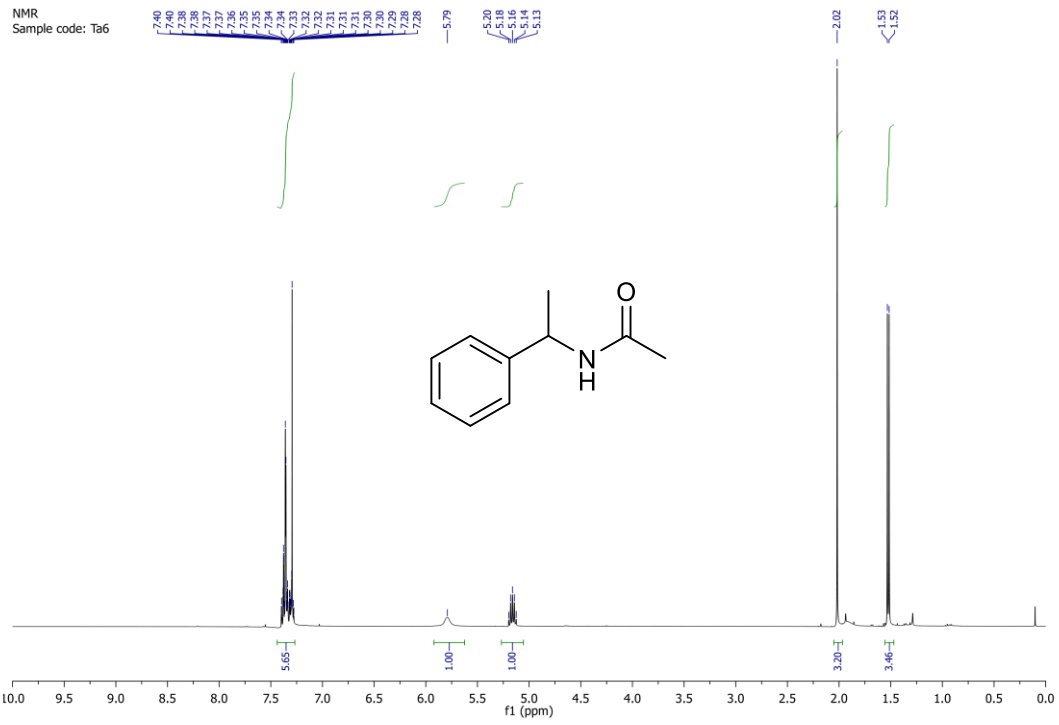
Current Data Parameters
NAME                  Arefi
EXPNO                     2
PROCNO                    1

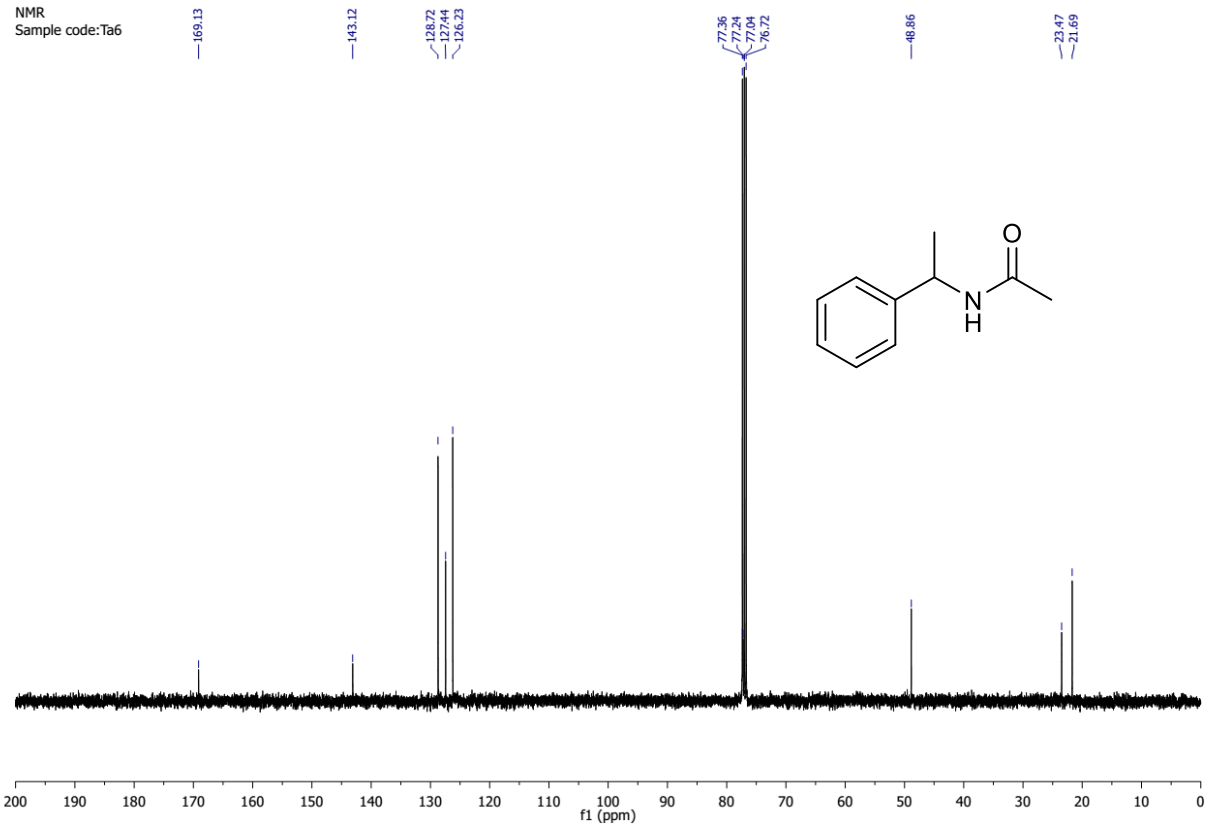
F2 - Acquisition Parameters
Date_                800204
Time                   6.47
INSTRUM               spect
PROBHD   5 mm Multinucl
PULPROG                zg
TD                     32768
SOLVENT                DMSO
NS                     8
DS                     0
SWH                10330.578 Hz
FIDRES             0.315264 Hz
AQ                 1.5860696 sec
RG                     456.1
DW                    48.400 use
DE                     6.00 use
TE                    300.0 K
D1                 6.00000000 sec
TD0                    1

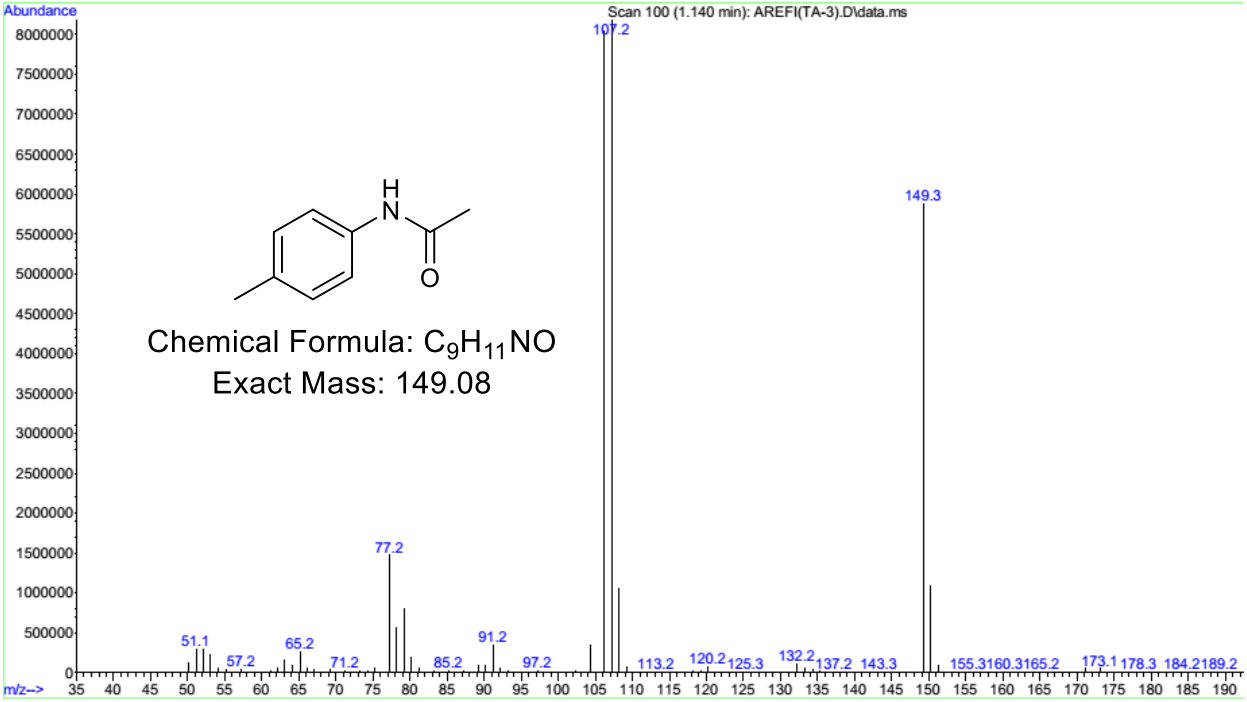
======== CHANNEL f1 =======
NUC1                      1H
P1                    15.00 use
PL1                    1.00 dB
SFO1           500.1330885 MHz

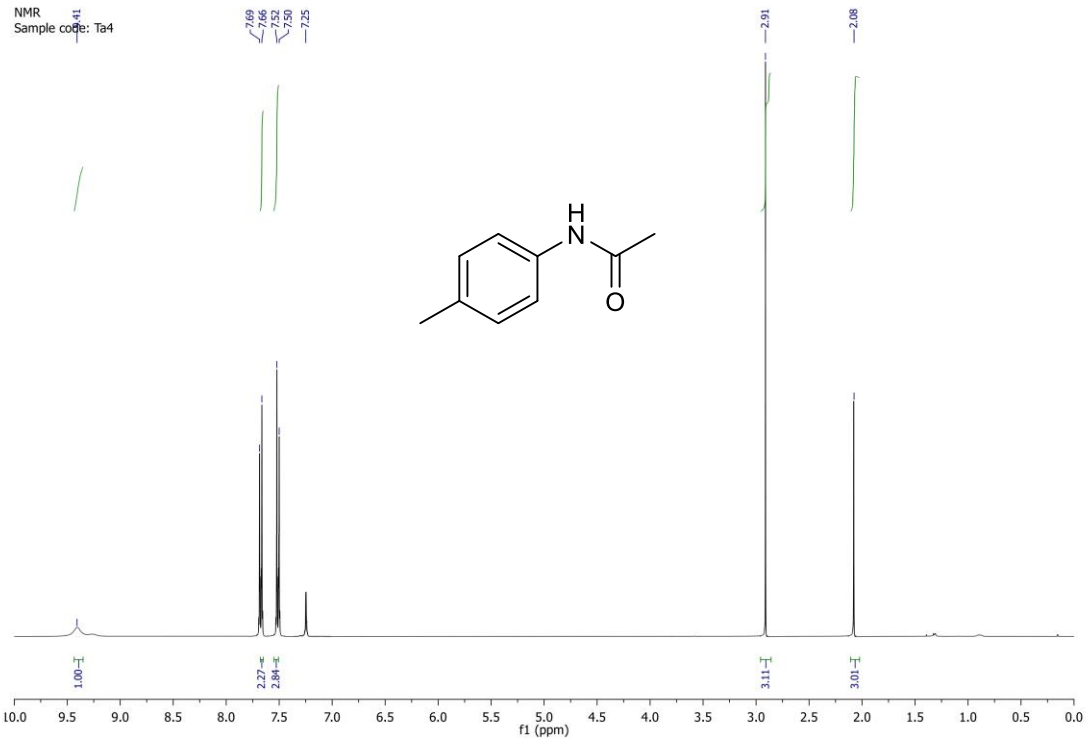
F2 - Processing parameters
SI                     32768
SF             500.1300101 MHz
WDW                       EM
SSB                    0
LB                    0.30 Hz
GB                     0
PC                     1.00
```

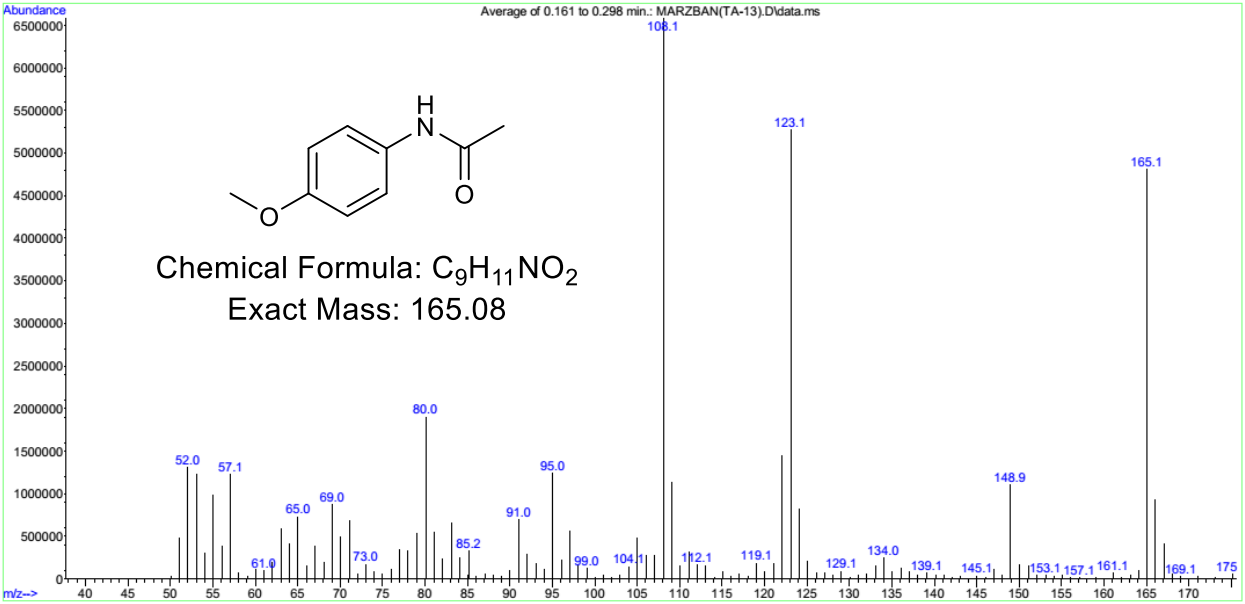

Abundance
Average of 0.424 to 0.666 min.: AREFI(TA6).D\data.ms
106.2
120.1
77.1
148.1
163.3
51.1
60.1
65.1
71.2
83.2
91.2
97.1
111.1
125.1
134.0
139.1
154.2
168.2
m/z-->
Chemical Formula: C10H13NO
Exact Mass: 163.10

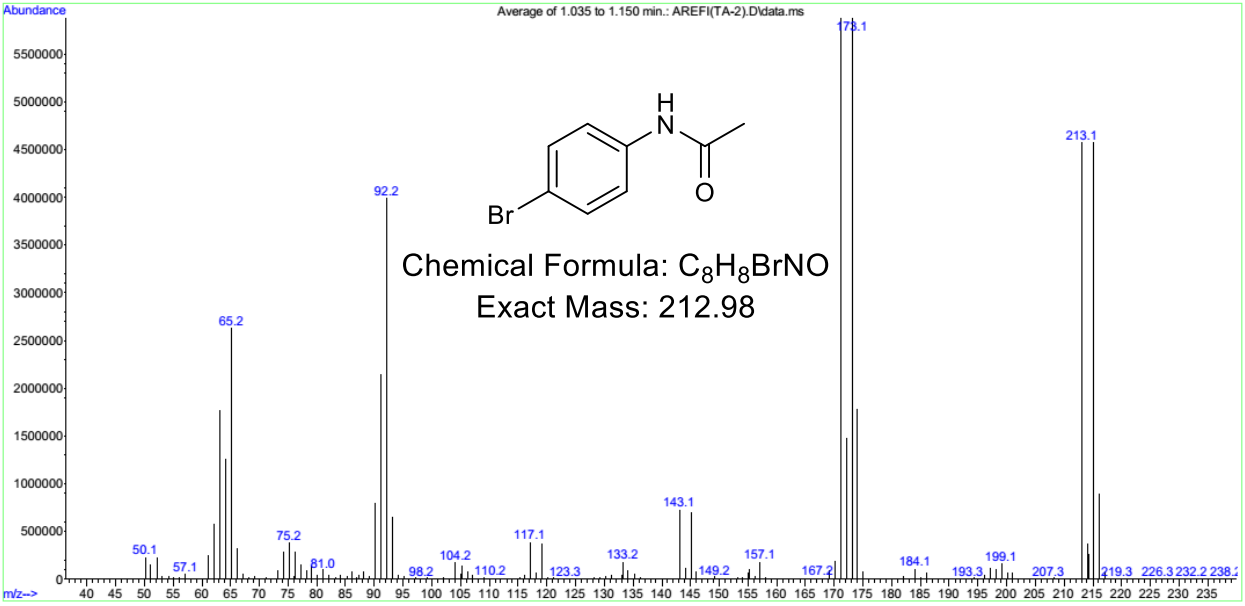

NMR
Sample code: Ta6
f1 (ppm)

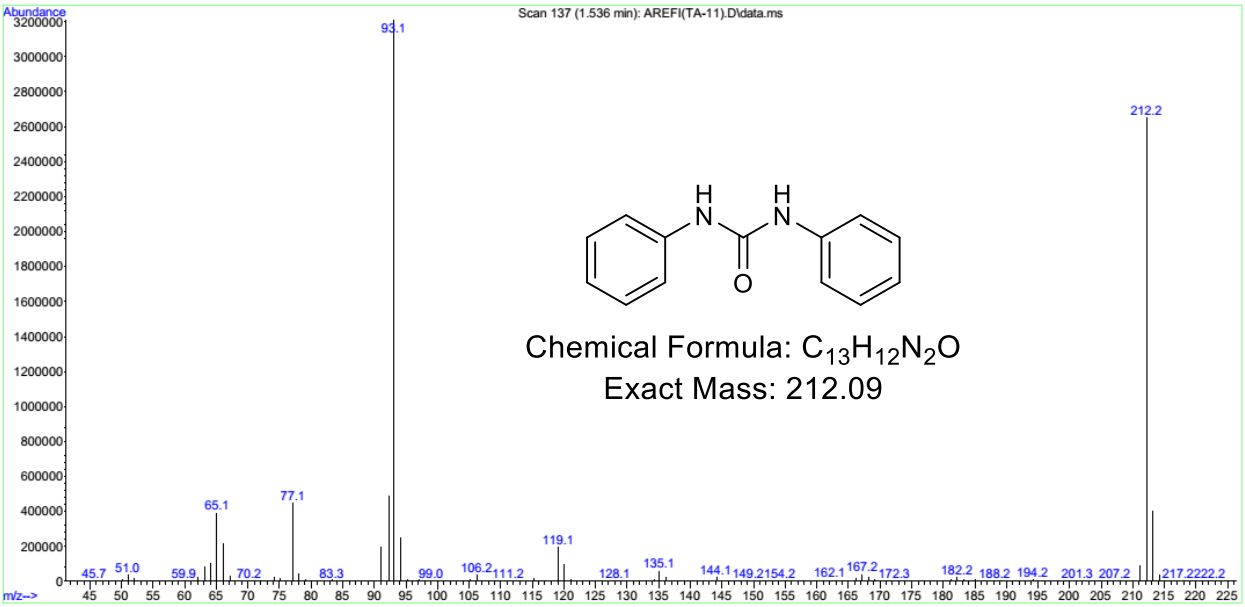

NMR
Sample code:Ta6
169.13
143.12
128.72
127.44
126.23
77.36
77.24
77.04
76.72
48.86
23.47
21.69
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

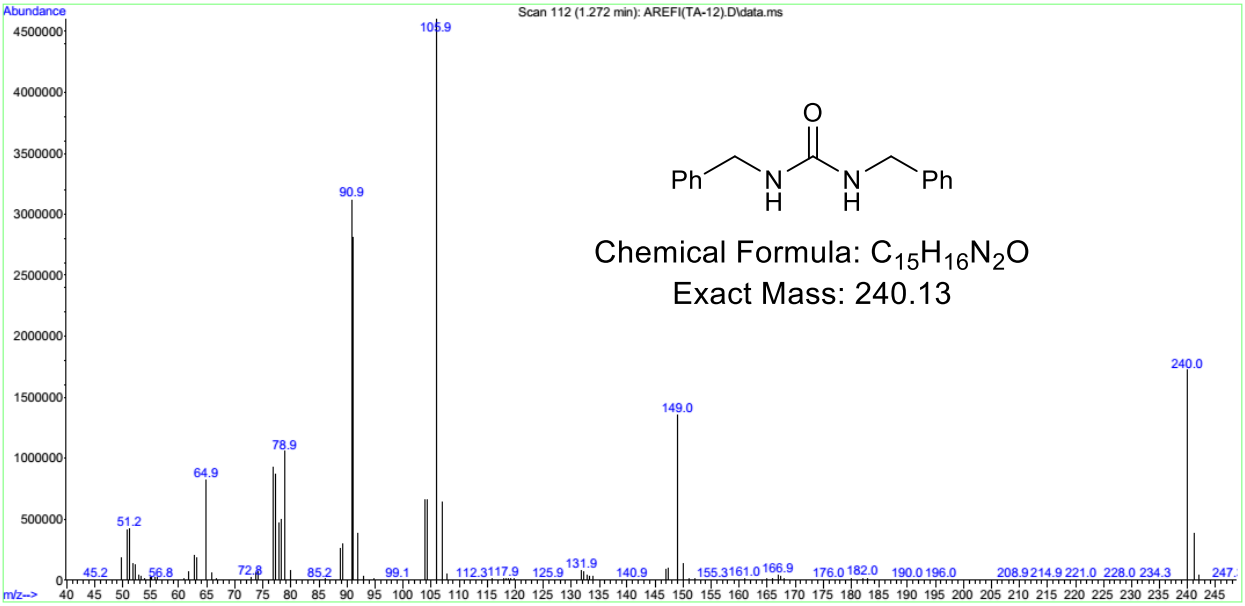

Abundance
Scan 100 (1.140 min): AREFI(TA-3).D\data.ms
107.2
149.3
77.2
51.1
57.2
65.2
71.2
85.2
91.2
97.2
113.2
120.2
125.3
132.2
137.2
143.3
155.3
160.3
165.2
173.1
178.3
184.2
189.2
m/z-->
H
N
O
Chemical Formula: C9H11NO
Exact Mass: 149.08


NMR
Sample code: Ta4
9.41
7.69
7.66
7.52
7.50
7.25
2.91
2.08
1.00
2.27
2.84
3.11
3.01
f1 (ppm)

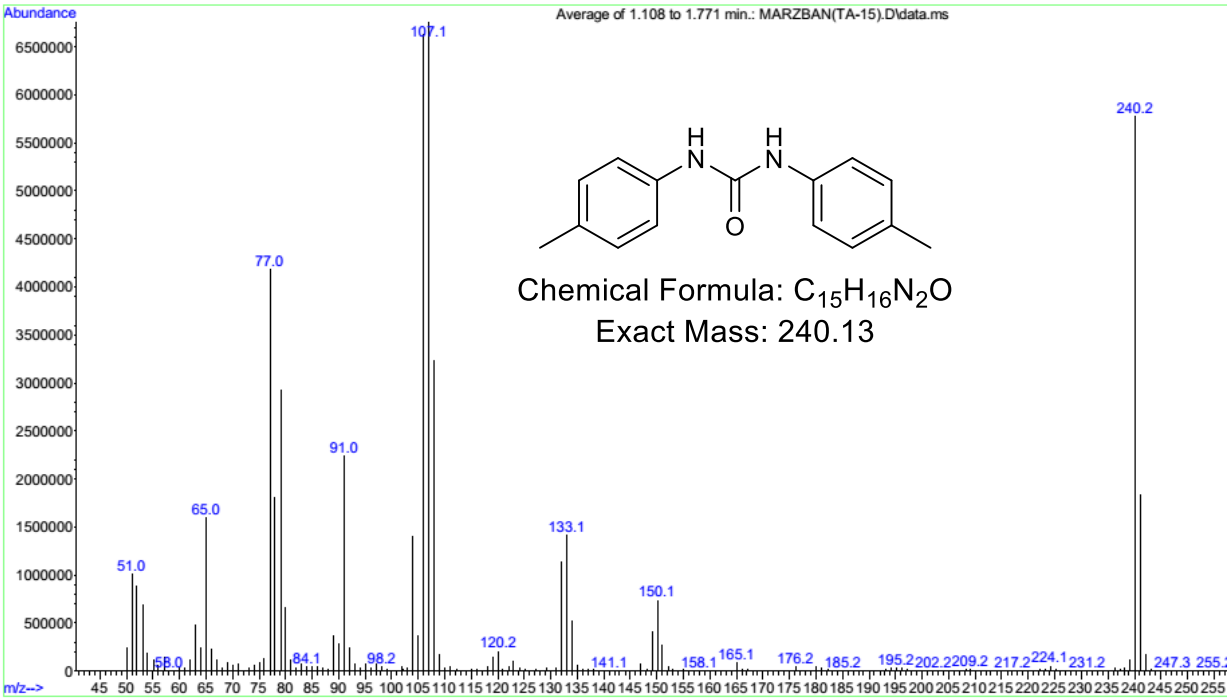

Abundance
Average of 0.161 to 0.298 min.: MARZBAN(TA-13).D\data.ms
Chemical Formula: C9H11NO2
Exact Mass: 165.08
m/z-->


Abundance
Average of 1.035 to 1.150 min.: AREFI(TA-2).D\data.ms
m/z-->
Br
H
N
O
Chemical Formula: C8H8BrNO
Exact Mass: 212.98

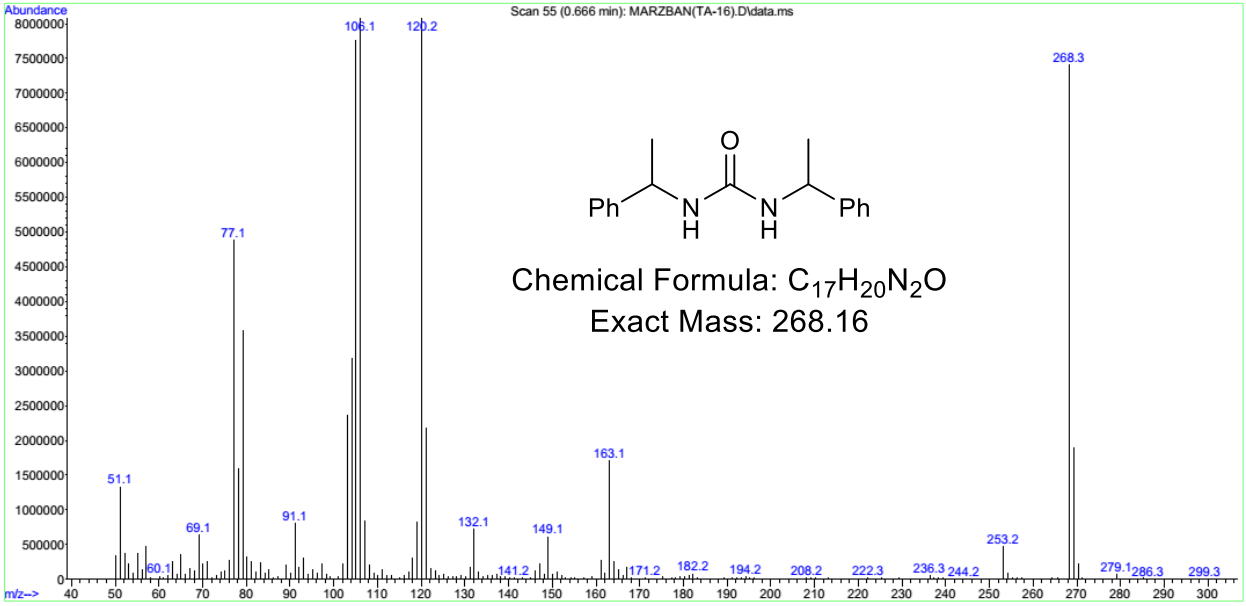

Abundance
Scan 137 (1.536 min): AREFI(TA-11).D\data.ms
m/z-->
H
N
H
N
O
Chemical Formula: C13H12N2O
Exact Mass: 212.09



Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.13

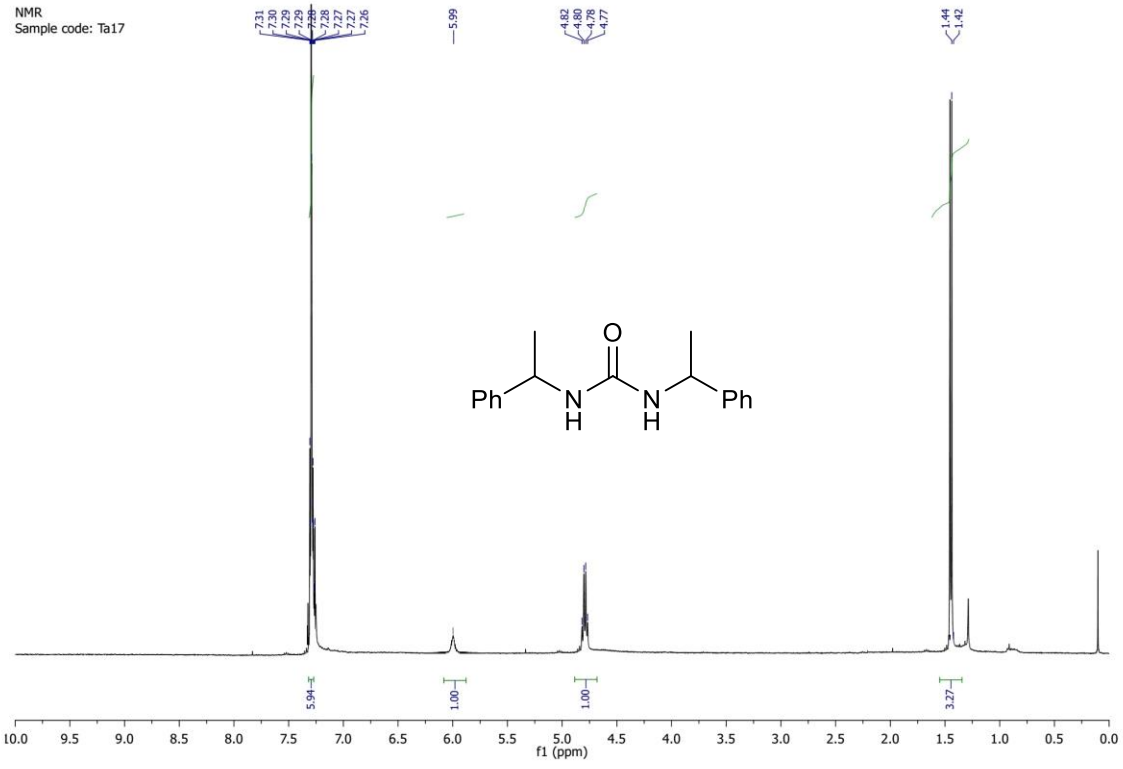


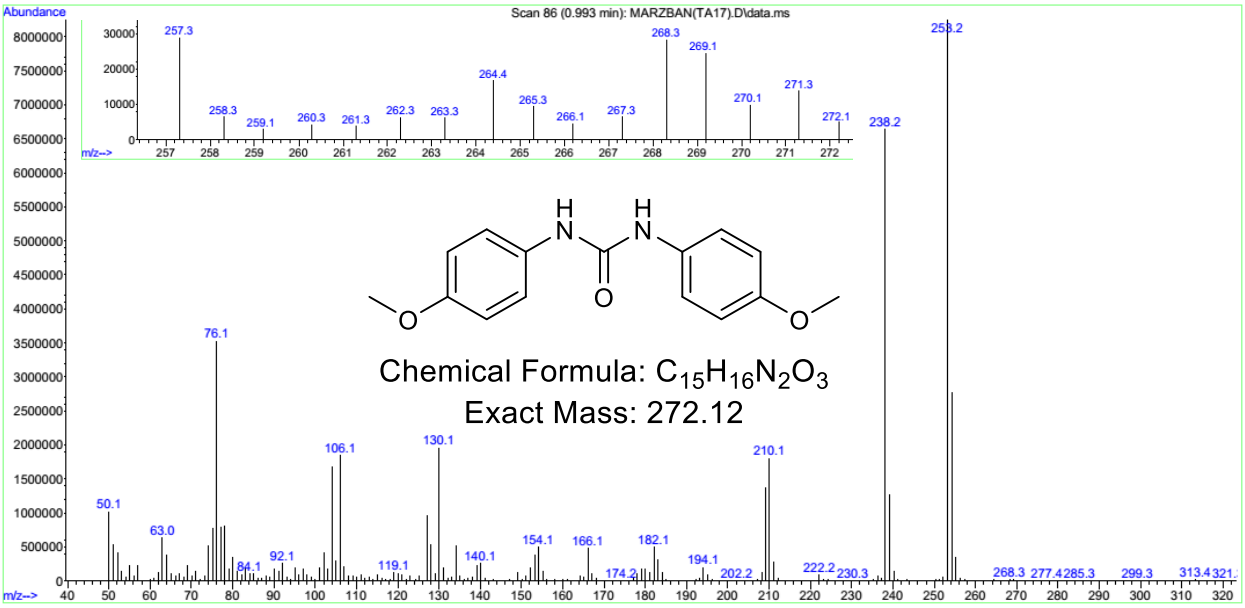
Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.13

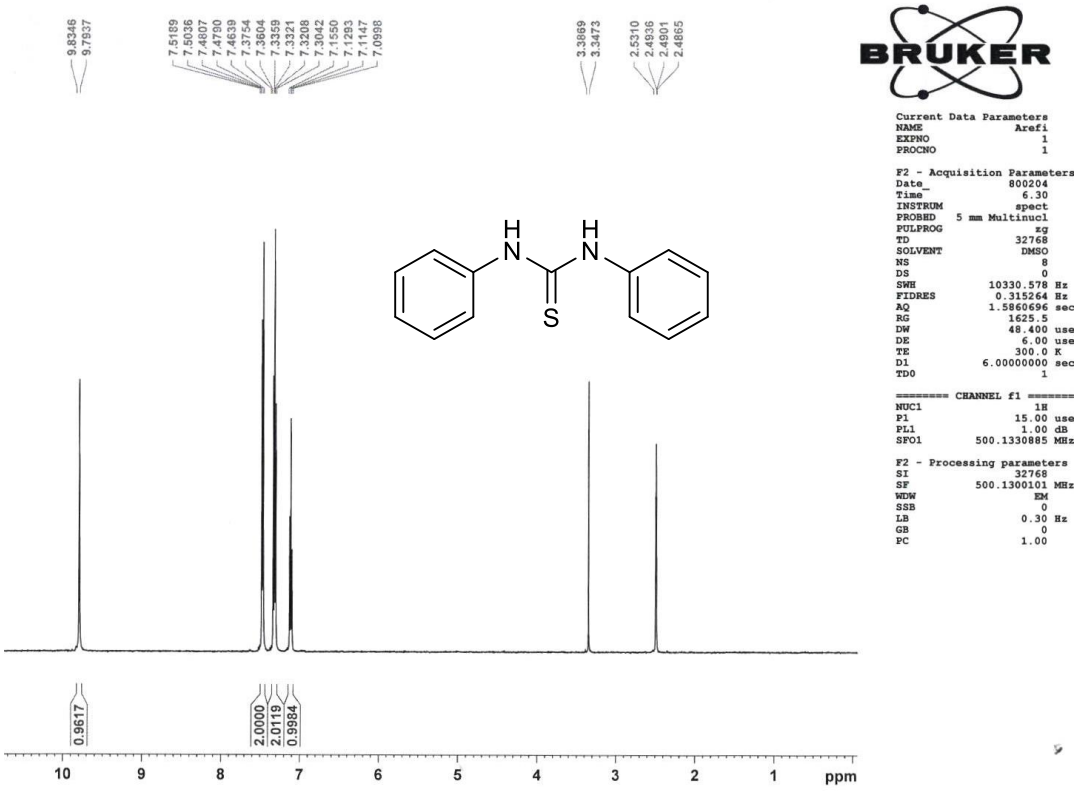


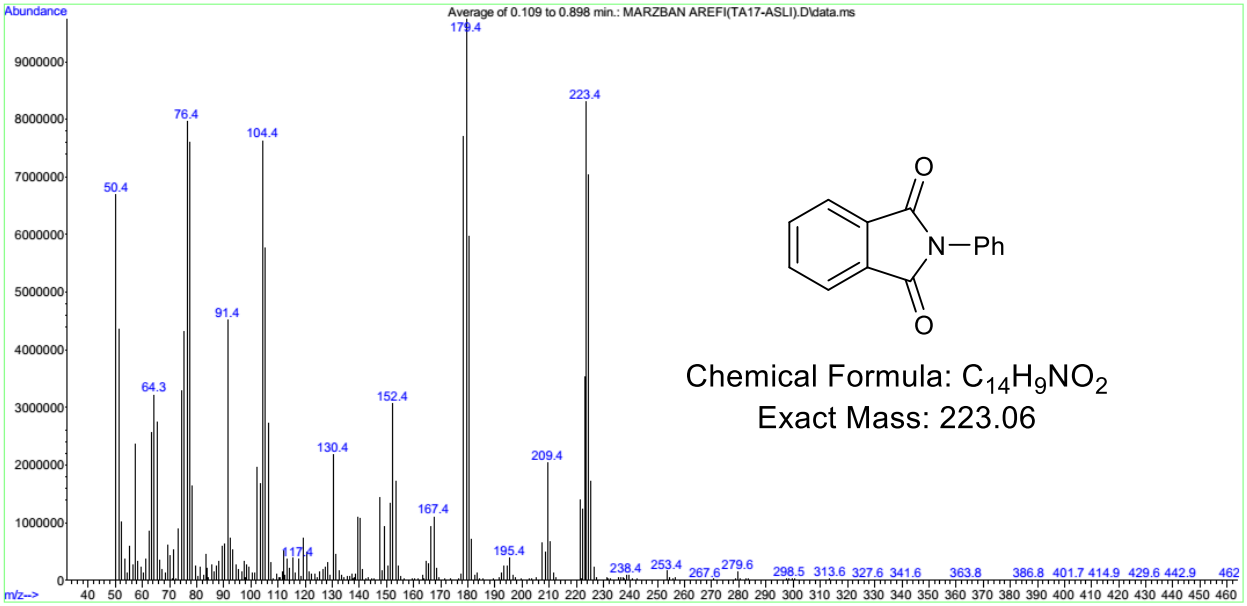
Chemical Formula: $C_{17}H_{20}N_2O$

Exact Mass: 268.16




Abundance
Scan 86 (0.993 min): MARZBAN(TA17).D\data.ms
m/z-->
Chemical Formula: C15H16N2O3
Exact Mass: 272.12


BRUKER
Current Data Parameters
NAME Arefi
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 800204
Time 6.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 1625.5
DW 48.400 use
DE 6.00 use
TE 300.0 K
D1 6.00000000 sec
TD0 1
======== CHANNEL f1 =======
NUC1 1H
P1 15.00 use
PL1 1.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm



Chemical Formula: $C_{14}H_9NO_2$

Exact Mass: 223.06