Supporting Information

Pd/C-catalyzed facile synthesis of primary aromatic amides by aminocarbonylation of aryl iodides using ammonia surrogates

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General information

Materials and Methods:

All chemicals were purchased from Sigma Aldrich, Alfa Asear and commercial suppliers. The resulting products were purified by column chromatography on silica gel (100-200 mesh; petroleum ether/ethyl acetate). All the products were confirmed by GC (Perkin Elmer Clarrus 400) instrument with FID detector and capillary column (Elite – 1, 30m, 0.32mm ID, 0.25 μm film thickness) using N_2 as carrier gas. GC-MS (Shimadzu QP 2010) instrument with EI detector and capillary column (Elite – 1, 30m, 0.32mm ID, 0.25 μm film thickness) using helium carrier gas. ^1H and ^{13}C NMR spectra were recorded with 400 MHz, 200 MHz and 100 MHz spectrometer respectively and compared with those of authentic data.

General Experimental Procedure for Synthesis of Primary Aromatic Amides:

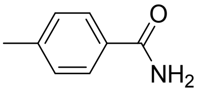
To a 100 mL high-pressure reactor containing, aryl iodide (1 mmol), ammonium carbamate (1.5 mmol), Pd/C (2.5 mol %), KI (0.5 mmol), Acetonitrile (15 mL), and DABCO (2 mmol) were transferred under normal atmosphere. The reactor was closed, then flushed with CO then pressurized with 10 Kg/cm^3 of CO, heated to 90 °C with constant stirring for 8 h. After the completion of reaction, the reactor cooled down to room temperature and degassed carefully. The reaction mixture filtered off by simple filtration and the resulting catalyst reused for next run. The filtrate washed with brine (20 mL) and then aqueous layer extracted with ethyl acetate (3×15 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (100-200 mesh; petroleum ether/ethyl acetate) and the products were confirmed by GC, GC-MS, ^1H (200 and 400 MHz) and ^{13}C NMR (100 MHz) spectroscopy.

A typical procedure for recycling the Pd/C catalyst:

The catalyst was filtered off by simple filtration and it was washed with distilled water (3 x 5 mL) and then with methanol (3 x 5 mL) to remove traces of organic contents. The resulting catalyst was dried under reduced pressure for 5 h and recycled up to four consecutive cycles.

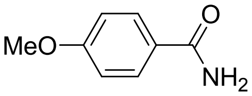
Spectral data for products:

4-Methyl benzamide (3a)



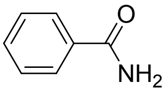
^{1}H NMR ($CDCl_3$, 200 MHz): *δ* = 7.72 (d, 2H, *J* = 8.00 Hz), 7.25 (d, 2H, *J* = 8.00 Hz), 6.06 (bs, 2H), 2.41 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* = 169.46, 142.50, 130.43, 129.25, 127.34, 21.46. **GC-MS** (EI, 70 eV): *m/z* (%) = 135 (63.8) $[M]^+$, 119 (100), 105(2), 91(76), 77(2.5), 65(28), 51(6).

4-Methoxy benzamide (3c)



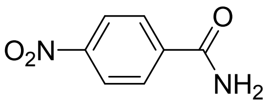
^{1}H NMR ($CDCl_3$, 200 MHz): *δ* = 7.83-7.79 (d, *J* = 8.00 Hz, 2H), 6.96-6.92 (d, *J* = 8.00 Hz, 2H), 6.1 (bs, 2H) 3.86 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* = 162.51, 129.29, 125.29, 113.68, 55.35. **GC-MS** (EI, 70 eV): *m/z* (%) = 151 (57.2) $[M]^+$, 135 (100), 107(20), 92(18), 77(32), 64(12), 50(7).

Benzamide (3e)



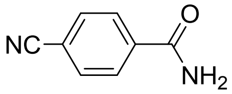
^{1}H NMR (MeOH-d4, 200 MHz): *δ* = 7.85-7.90 (m, 2H), 7.44-7.49 (m, 2H). **^{13}C NMR** ($CDCl_3$, 60 MHz): *δ* = 172.56, 135.06, 133.05, 129.64, 128.76. GC-MS (EI, 70 eV): *m/z* (%) = 121(77) $[M]^+$, 105 (98), 91 (4), 77 (100), 56 (3), 51(42).

4-NO_2 Benzamide (3g)



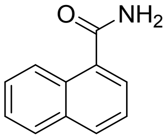
^{1}H NMR ($CDCl_3$, MeOH-d4, 400 MHz): *δ* = 8.30-8.28 (d, 2H), 8.07-8.05 (d, 2H), 7.49 (b, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* = 172.44, 153.66, 143.56, 133.14, 127.28. **GC-MS** (EI, 70 eV): *m/z* (%) = 166 (80) $[M]^+$, 150 (100), 136 (14.9), 120 (31), 104 (36), 92(27), 76 (25,6), 65 (24.5), 50 (21).

4-CN Benzamide (3h)



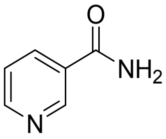
^{1}H NMR (DMSO-d6, 200 MHz): *δ* = 8.21 (s, 1H), 8.04-7.97 (m, 4H), 7.92 (s, 1H). **^{13}C NMR** (DMSO-d6, 100 MHz): *δ* = 176.04, 147.92, 141.98, 137.87, 127.28, 123.24. **GC-MS** (EI, 70 eV): *m/z* (%) = 146 (56) [M]$^{+}$, 130 (100), 102 (64.1), 90 (2), 75 (21.5), 51 (14.2).

1-Naphthamide (3f)



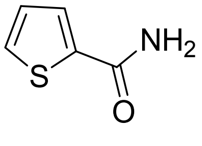
^{1}H NMR (MeOH-d4, 200 MHz): *δ* = 8.33 (m, 1H), 7.68-7.90 (m, 3H), 7.59-7.48 (m, 4H). ^{13}C NMR (MeOH-d4, 100 MHz): *δ* = 176.60, 146.86, 135.35, 131.78, 129.54, 128.78, 128.08, 127.53, 126.54, 126.00. GC-MS (EI, 70 eV): *m/z* (%) = 171(82.7) [M]$^{+}$, 155 (77.7), 127 (100), 63 (17.1), 51 (8.6).

3-Nicotinamide (3j)



^{1}H NMR (CDCl$_3$, 400 MHz): *δ* = 8.03 (s, 1H), 8.68-8.67 (d, 1H), 8.28-8.26 (d, 1H), 7.50-7.46 (dd, 1H). **^{13}C NMR** (CDCl$_3$, 100 MHz): *δ* = 172.16, 155.54, 152.10, 140.13, 133.60, 127.71. GC-MS (EI, 70 eV): *m/z* (%) = 122 (100) [M]$^{+}$, 106 (70), 94 (11), 78 (85), 51 (57).

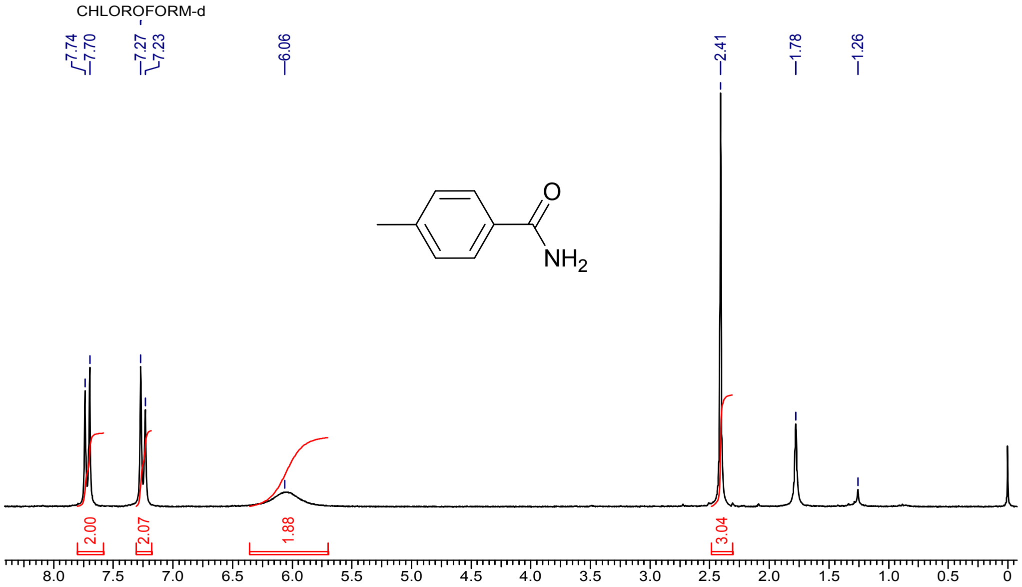
2- Thiophenecarboxamide (3l)

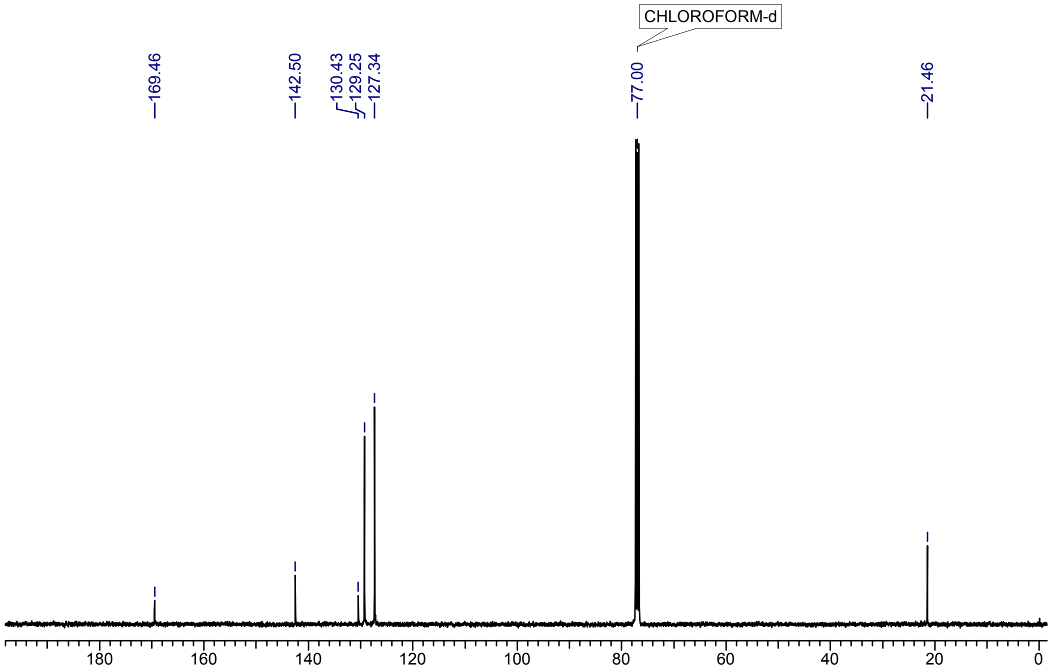


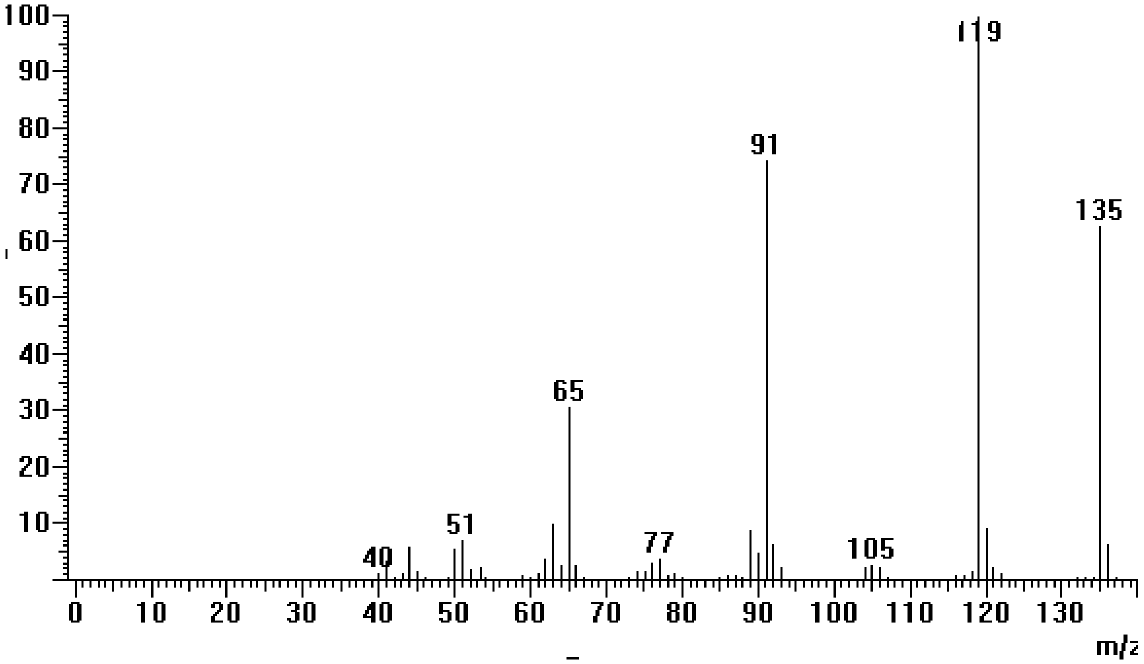
^{1}H NMR (Acetone-d6, 200 MHz): *δ* = 7.67-7.76 (m, 2H), 7.11-7.15 (m, 1H). GC-MS (EI, 70 eV): *m/z* (%) = 127 (72) [M]$^{+}$, 111 (100), 83 (12), 57 (8.2), 45 (11.8).

^{1}H and ^{13}C NMR Spectra of Products:

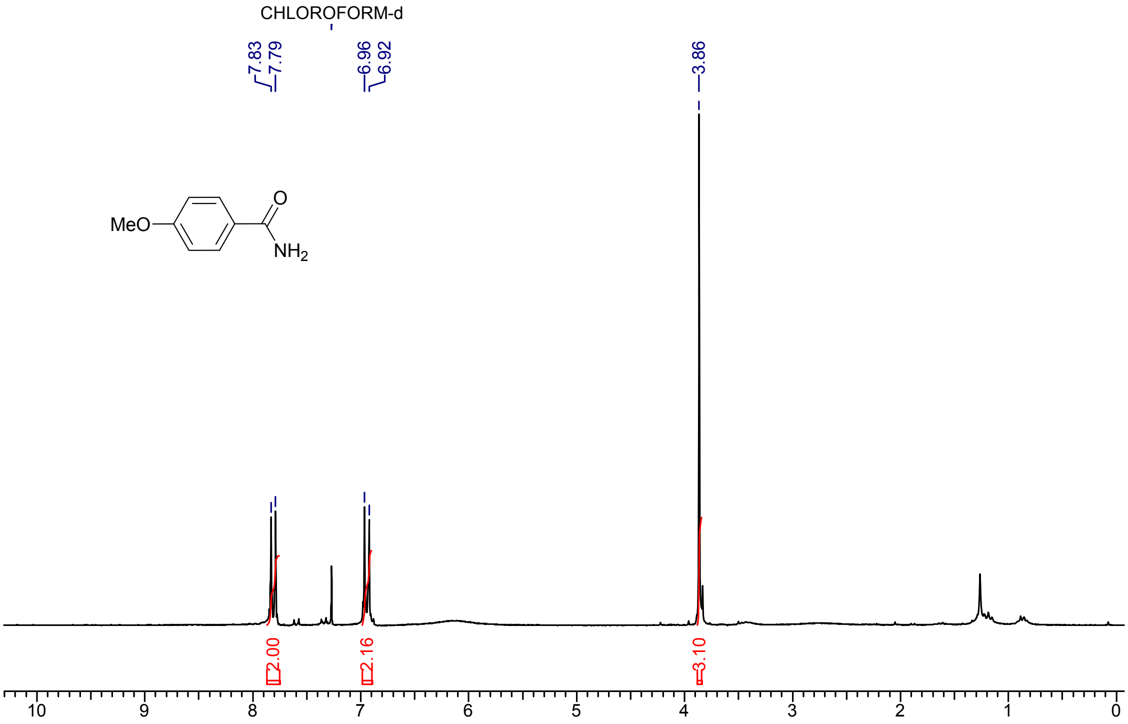
4-Methyl benzamide (3a)

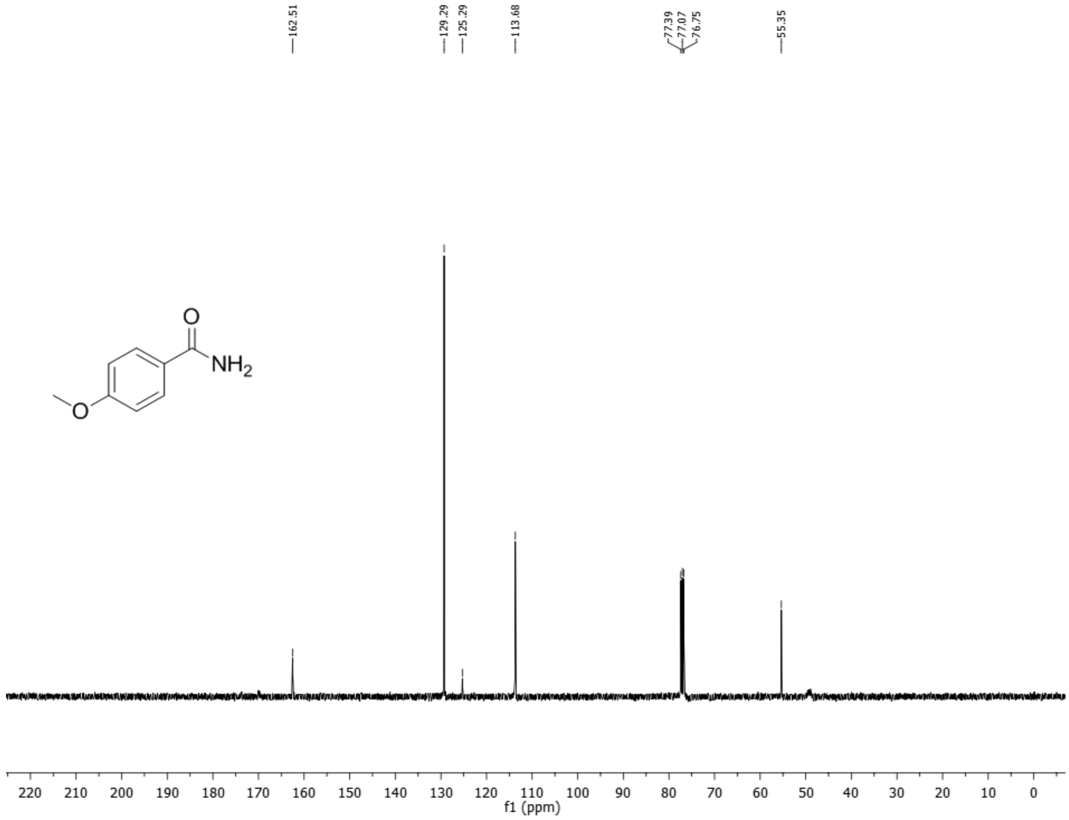






4-Methoxy benzamide (3c)

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129.29
125.29
113.68
77.39
77.07
76.75
55.35
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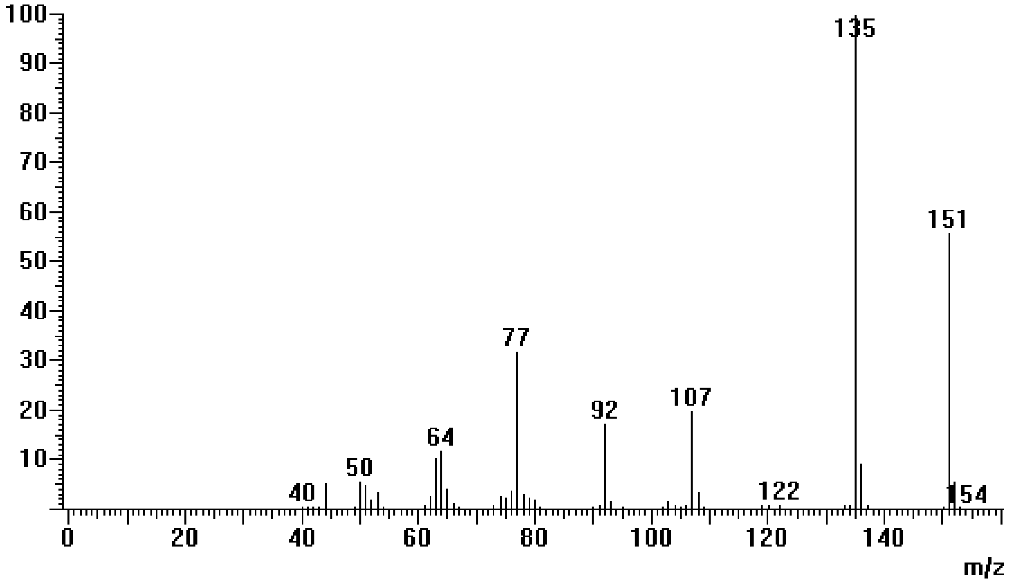
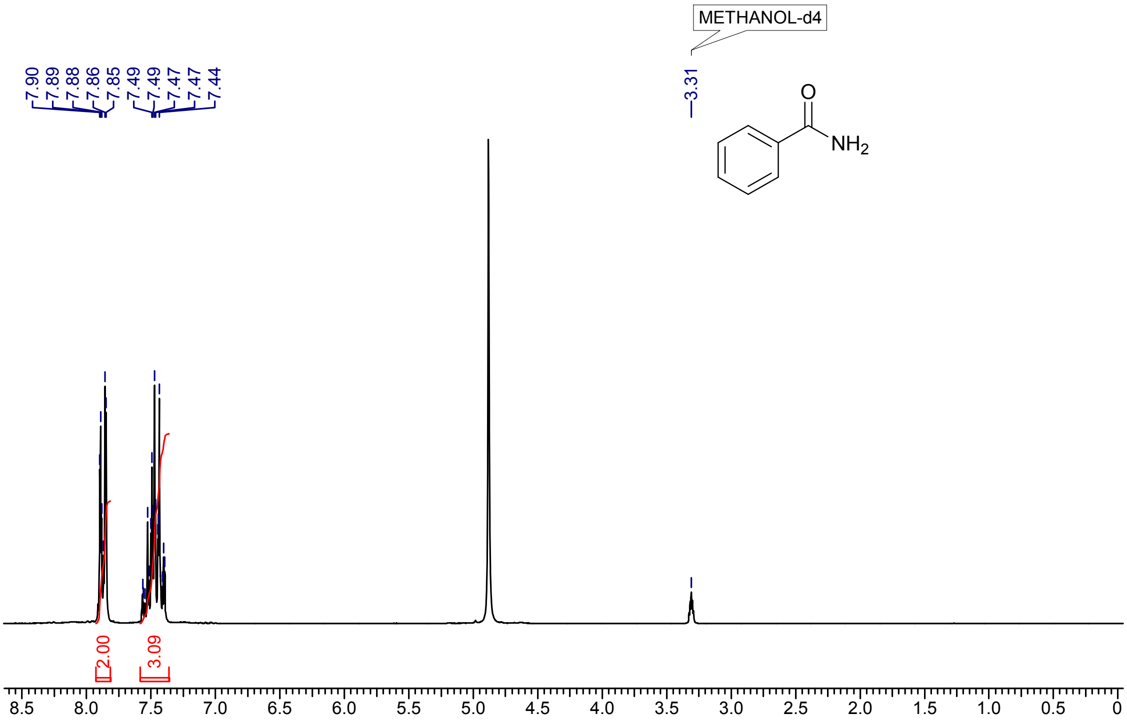
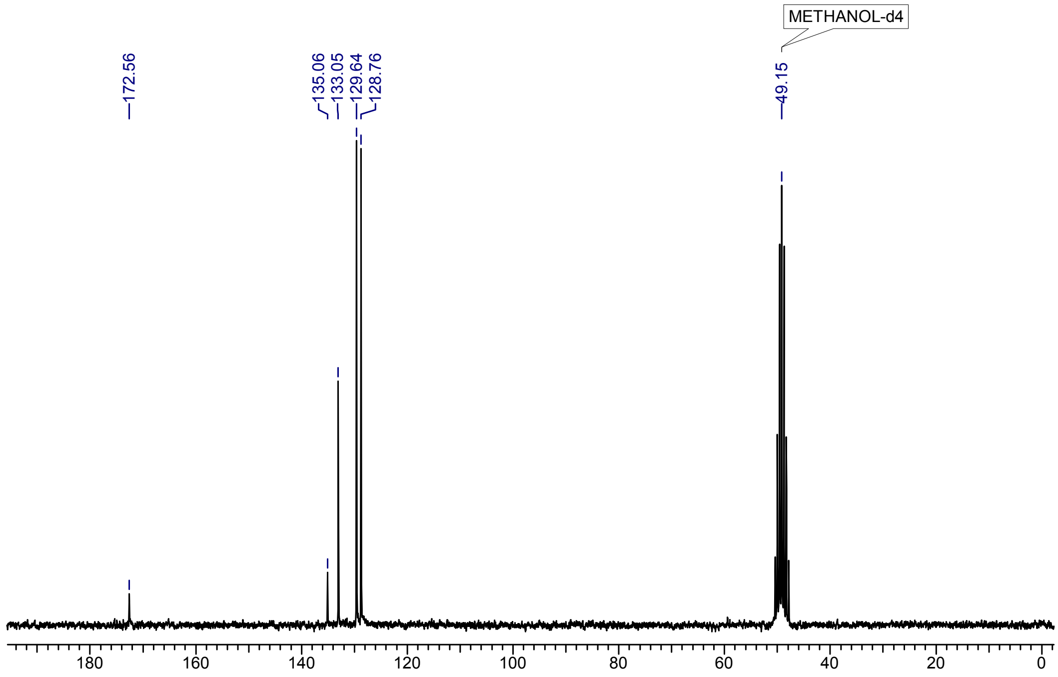
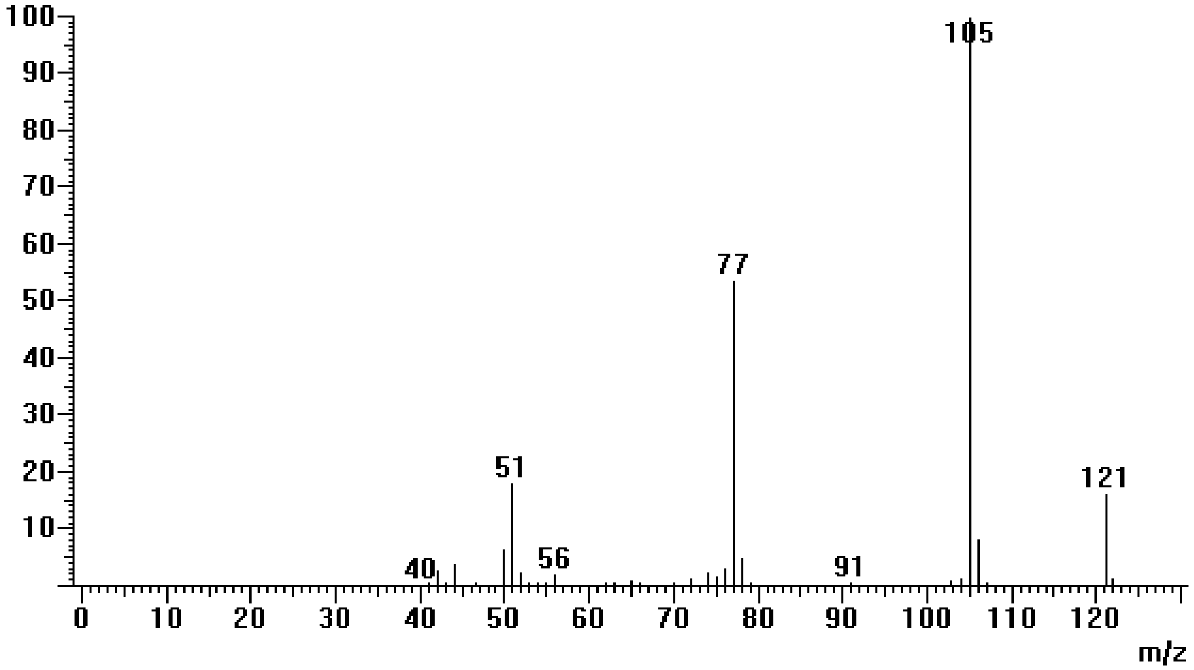
NH2
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


100
90
80
70
60
50
40
30
20
10
135
151
77
107
92
64
50
40
122
154
0
20
40
60
80
100
120
140
m/z

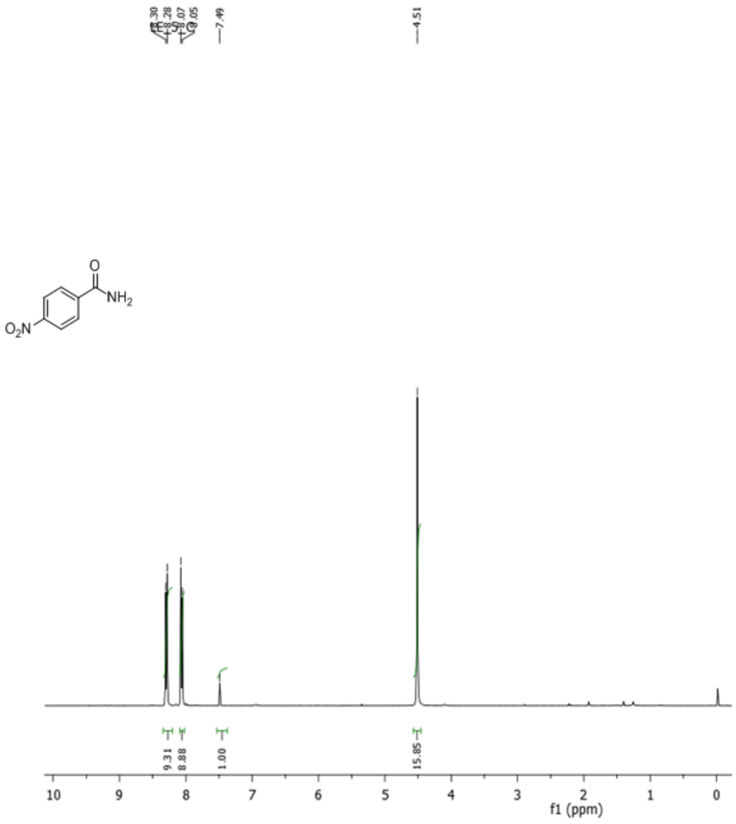
Benzamide (3e)

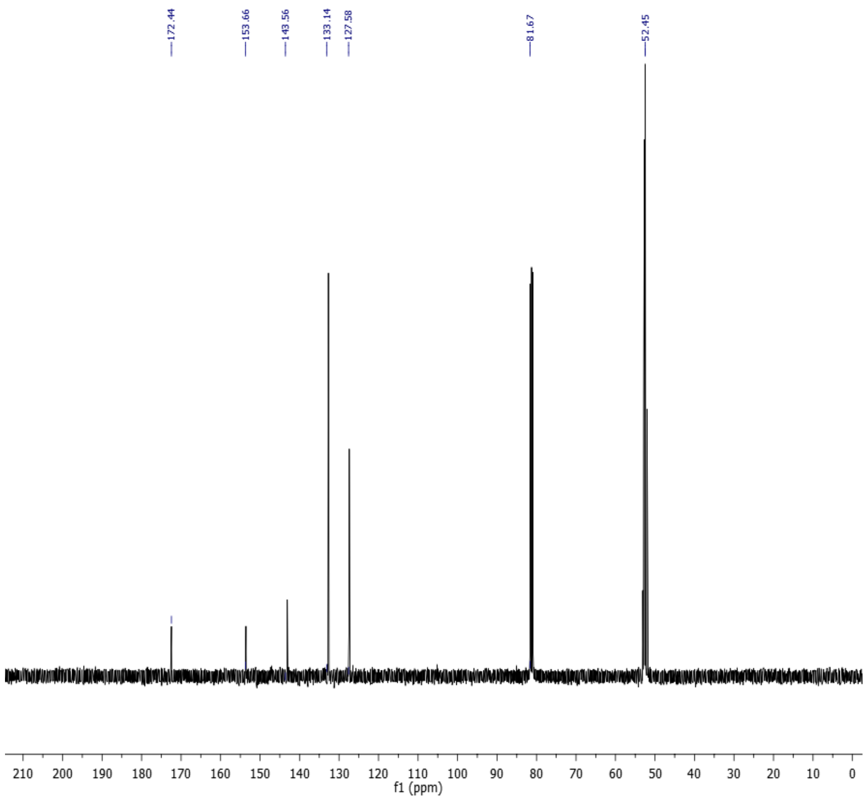






4-Nitro benzamide (3g)




172.44
153.66
143.56
133.14
127.58
81.67
52.45
210
200
190
180
170
160
150
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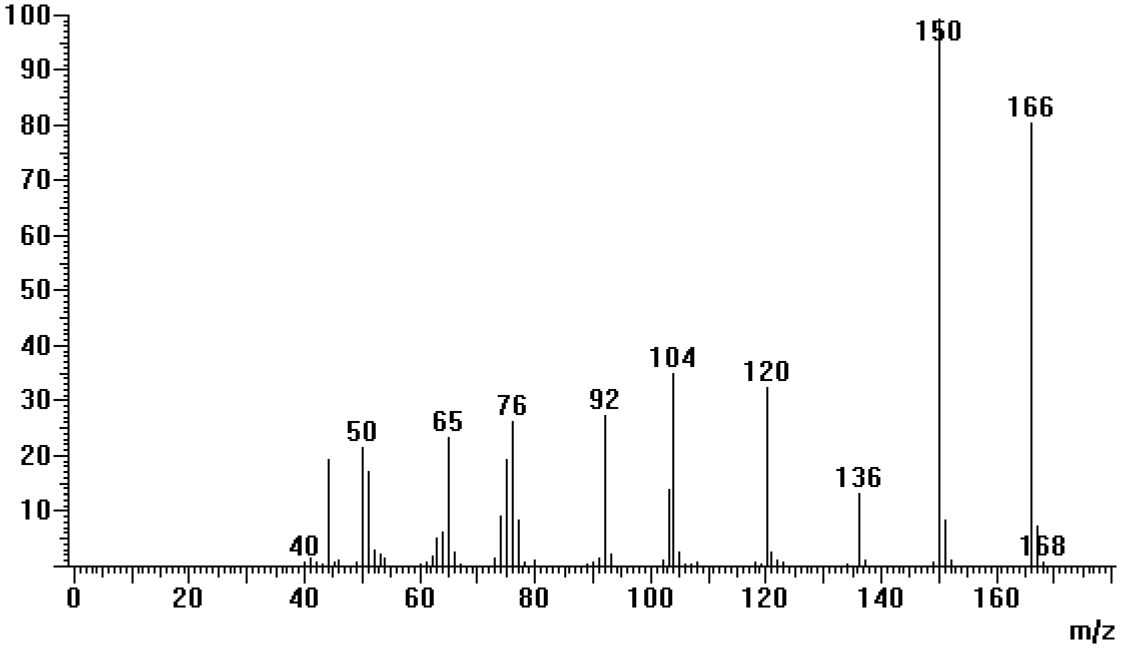
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


100
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70
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30
20
10
150
166
104
120
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76
65
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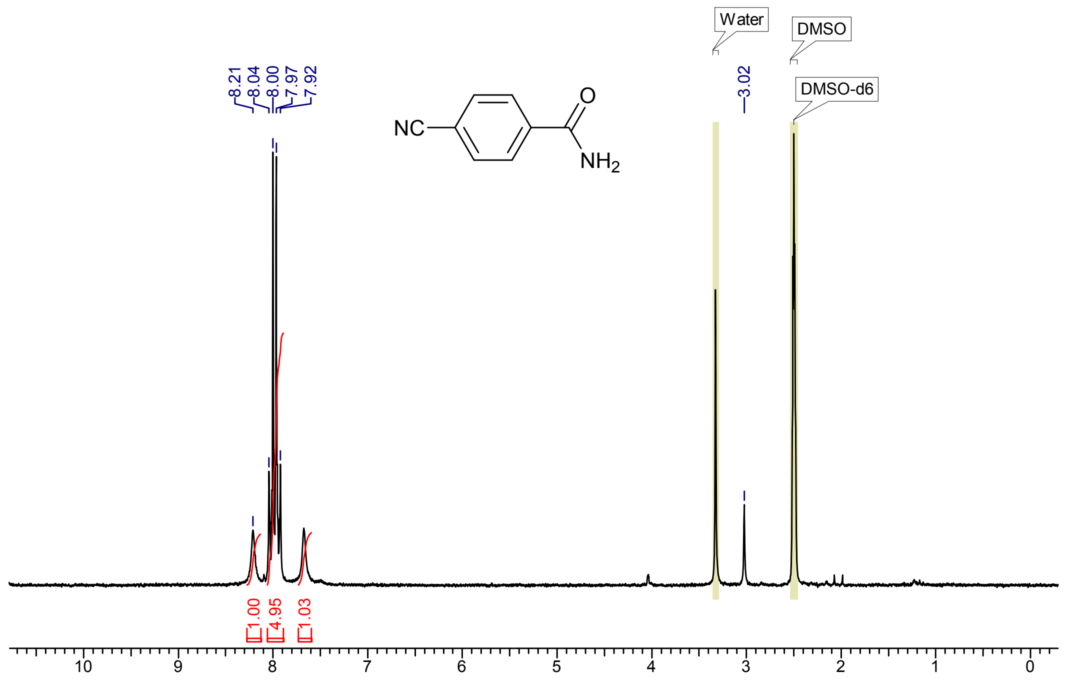
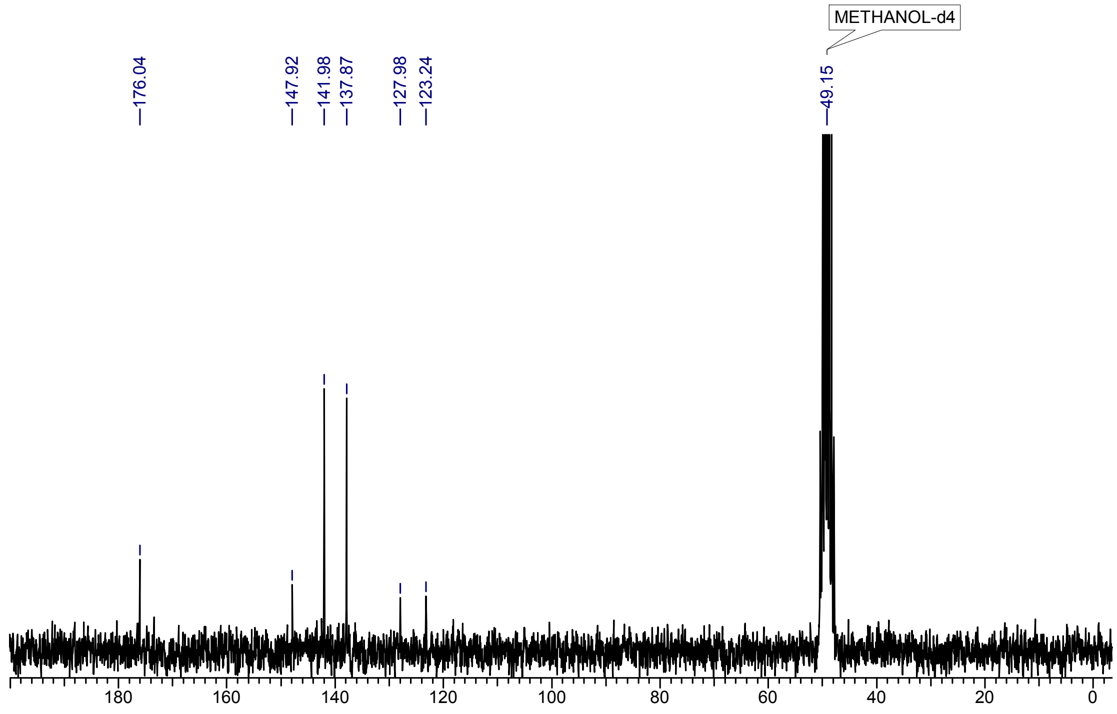
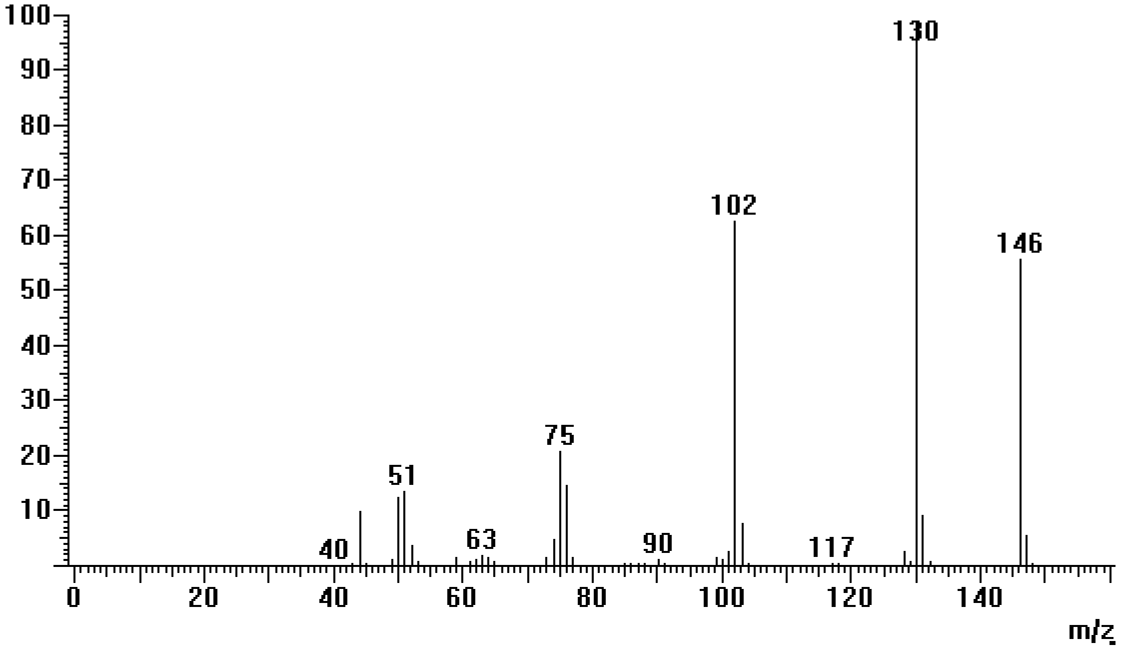
168
0
20
40
60
80
100
120
140
160
m/z

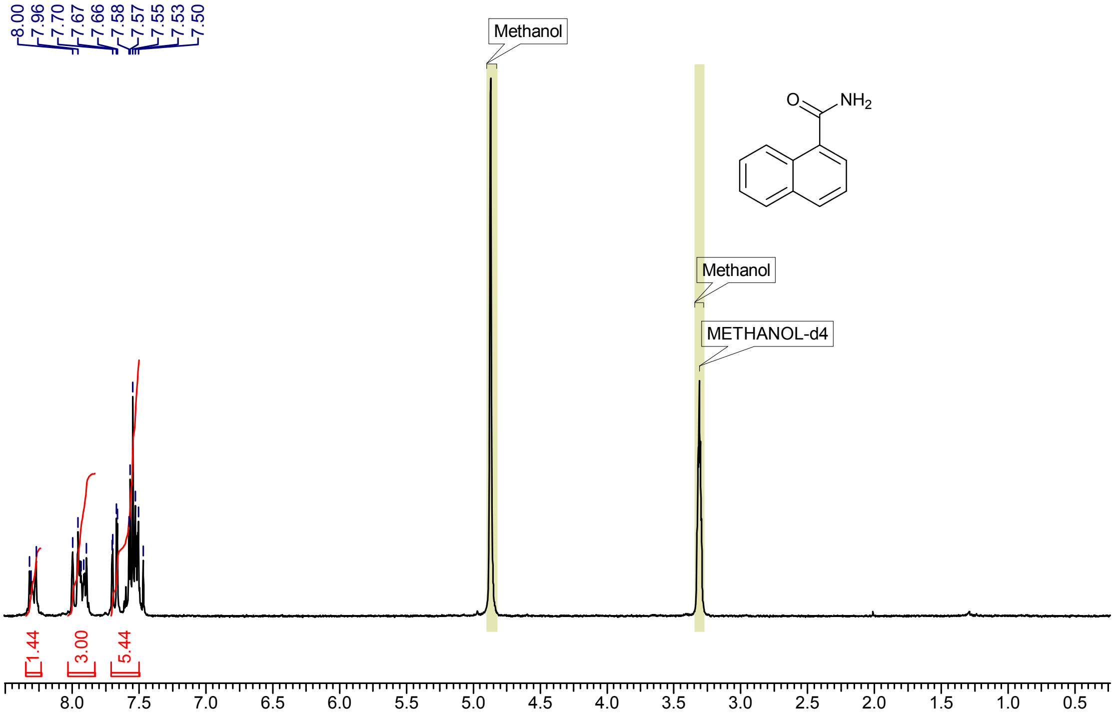
4-Cyano benzamide (3h)

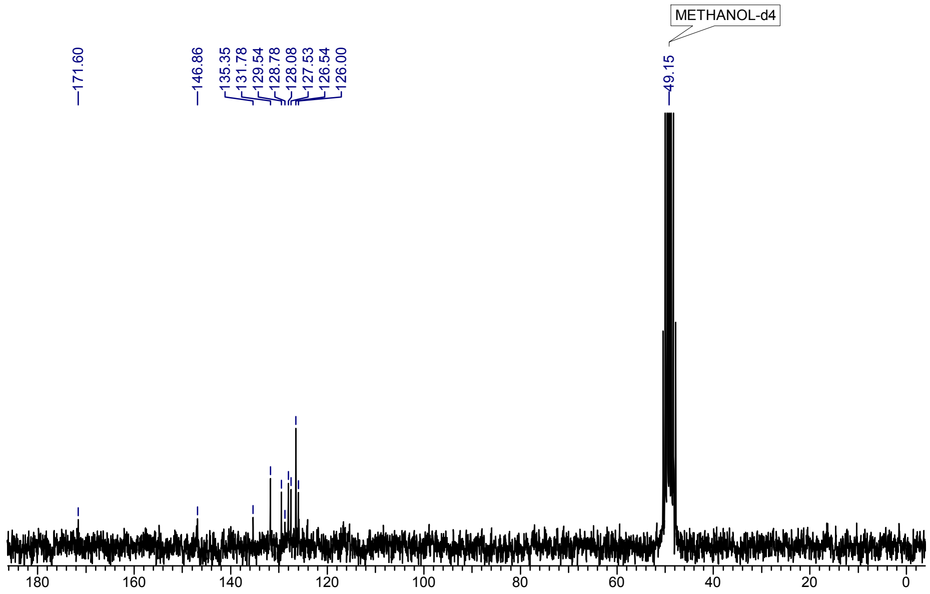


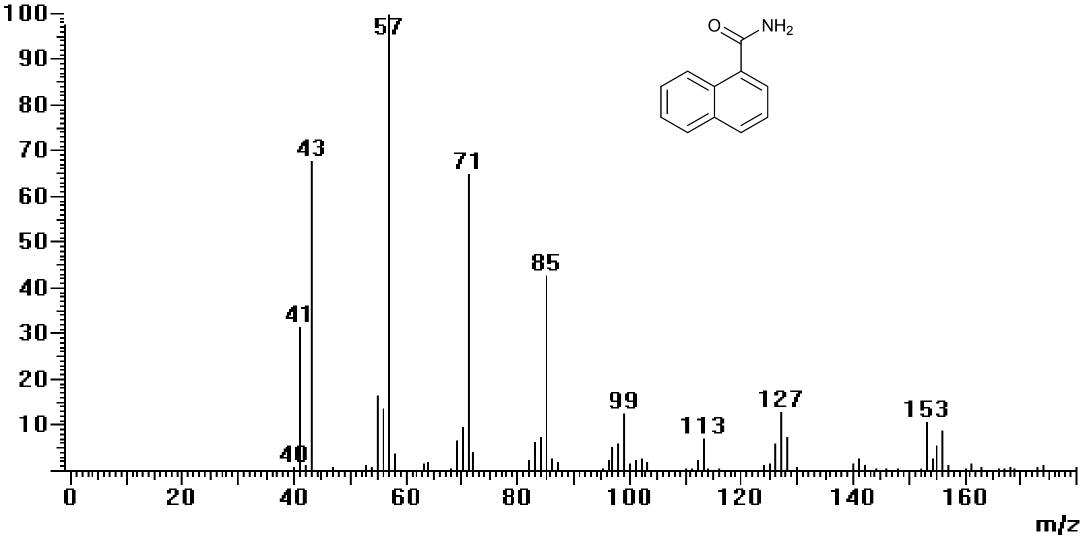




1-Naphthamide (3f)




METHANOL-d4
171.60
146.86
135.35
131.78
129.54
128.78
128.08
127.53
126.54
126.00
49.15
180
160
140
120
100
80
60
40
20
0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70
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43
71
85
41
40
99
113
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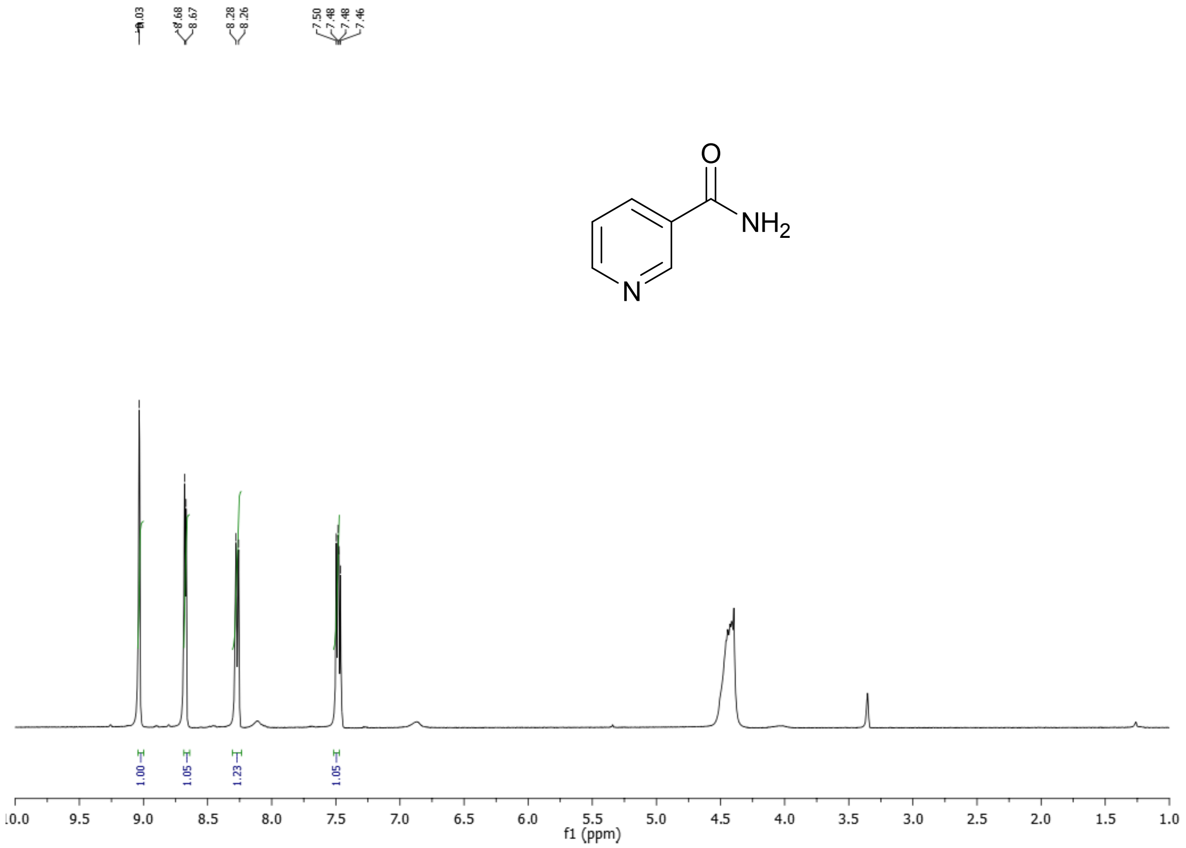
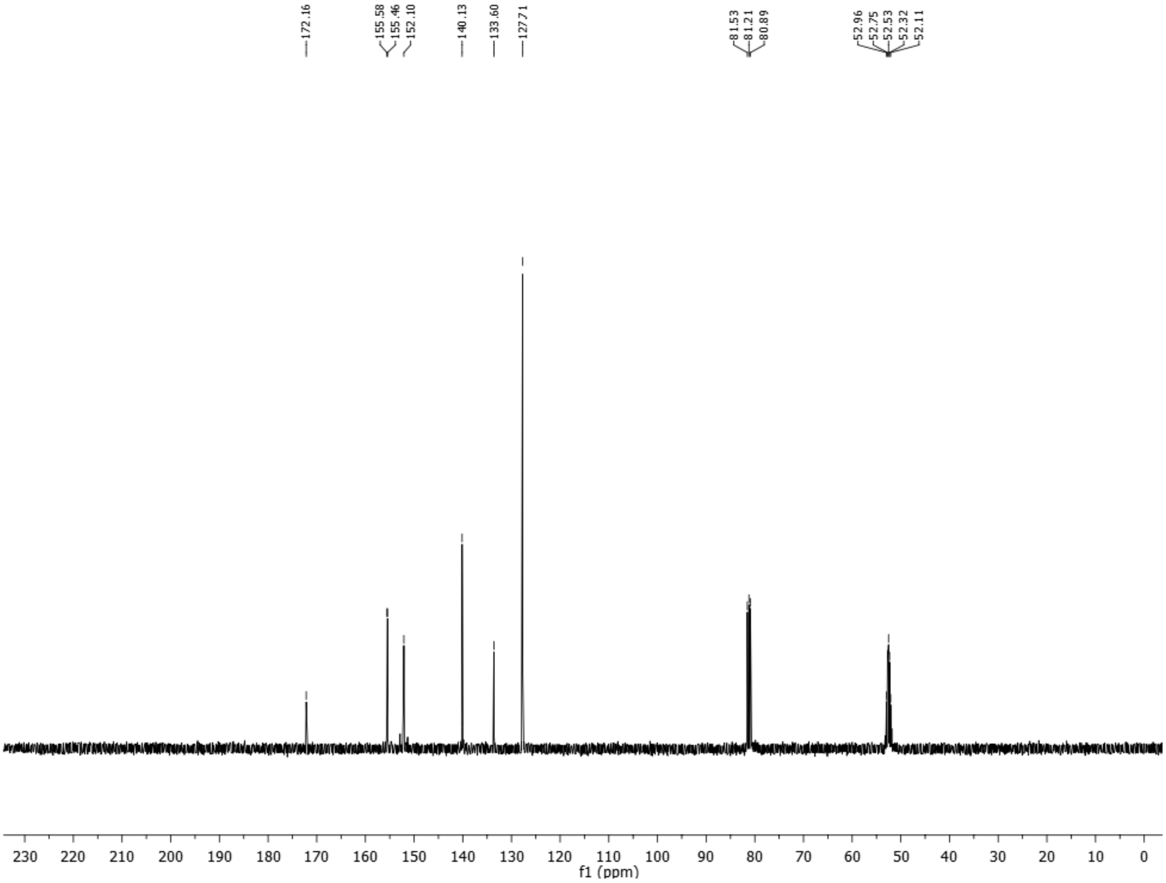
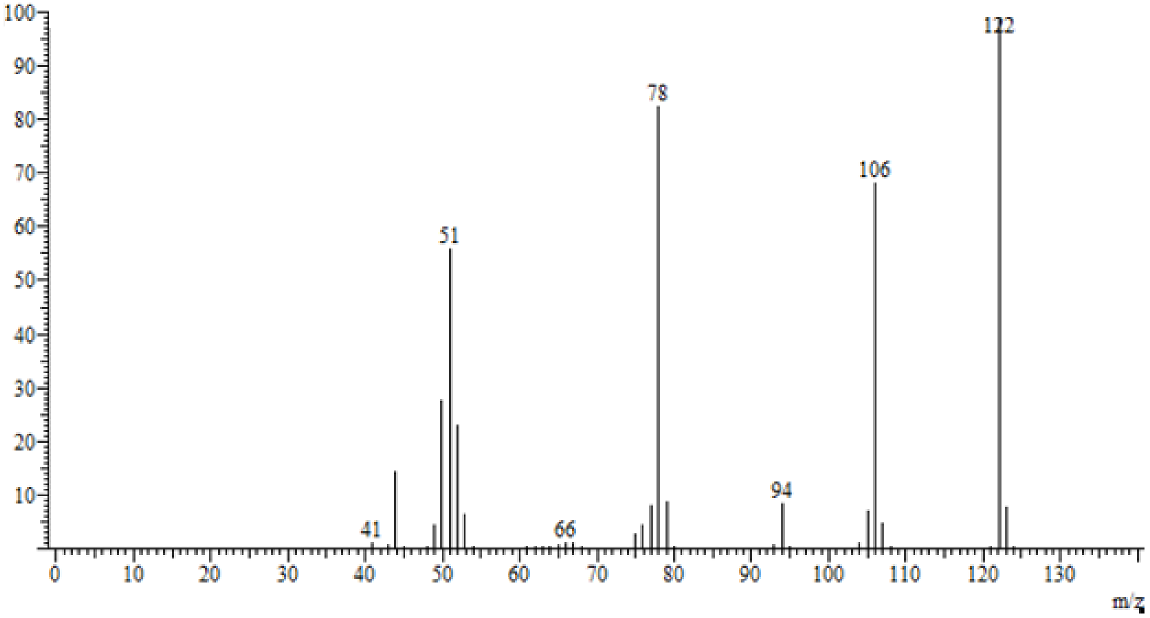
O
NH2
0
20
40
60
80
100
120
140
160
m/z

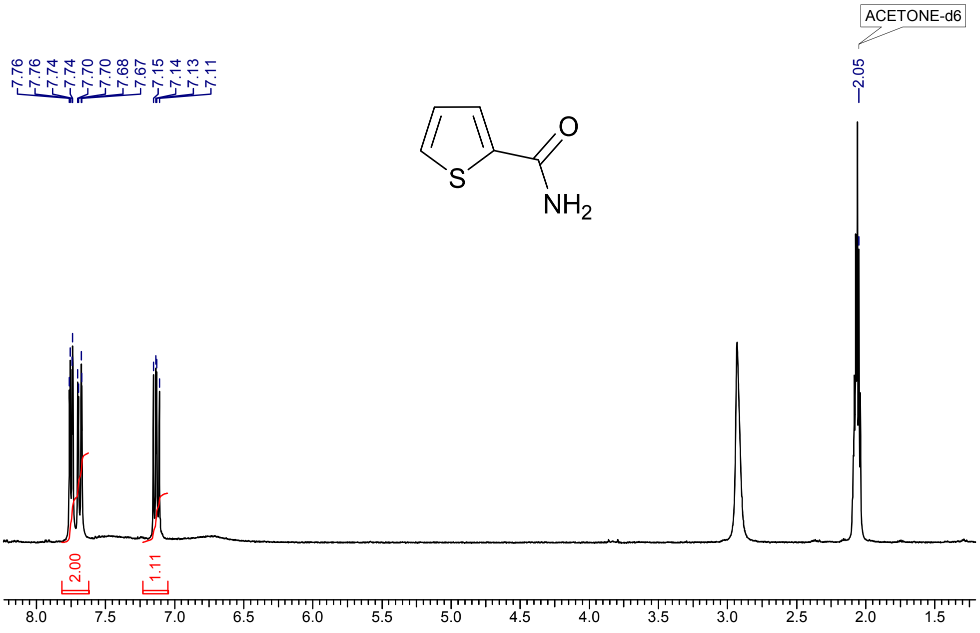
3-Nicotinamide (3j)

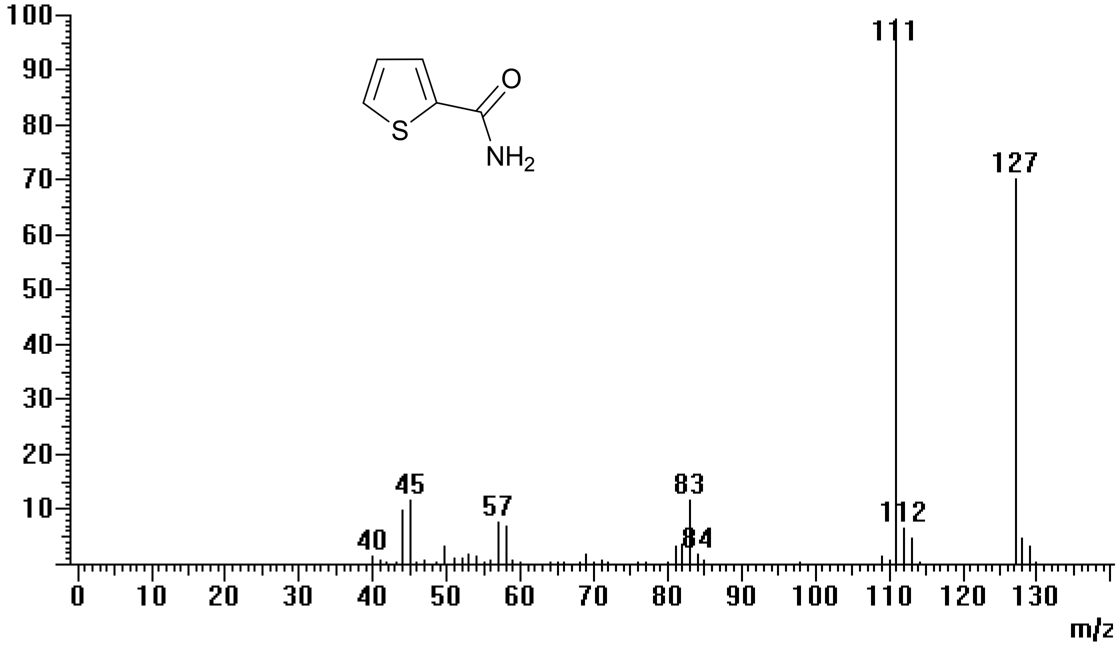






2-Thiophene carboxamide (3l)

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O
NH2
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20
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10
20
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40
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70
80
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120
130
m/z
111
127
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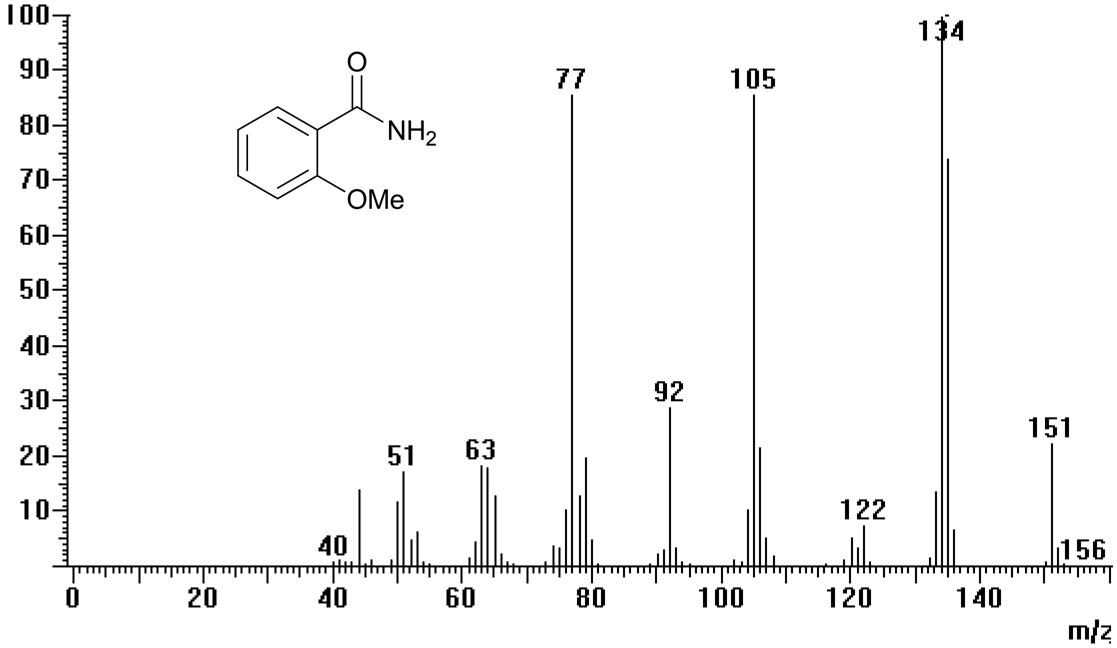
40
57
83
84
112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NH2
OMe
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m/z
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105
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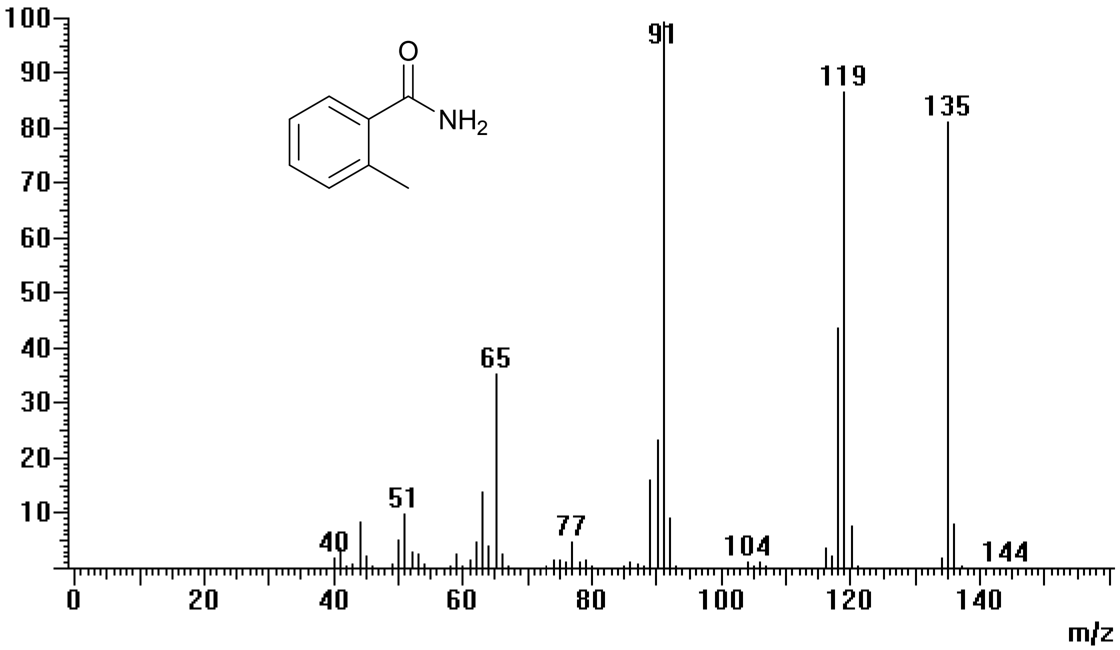
40
156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NH2
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m/z
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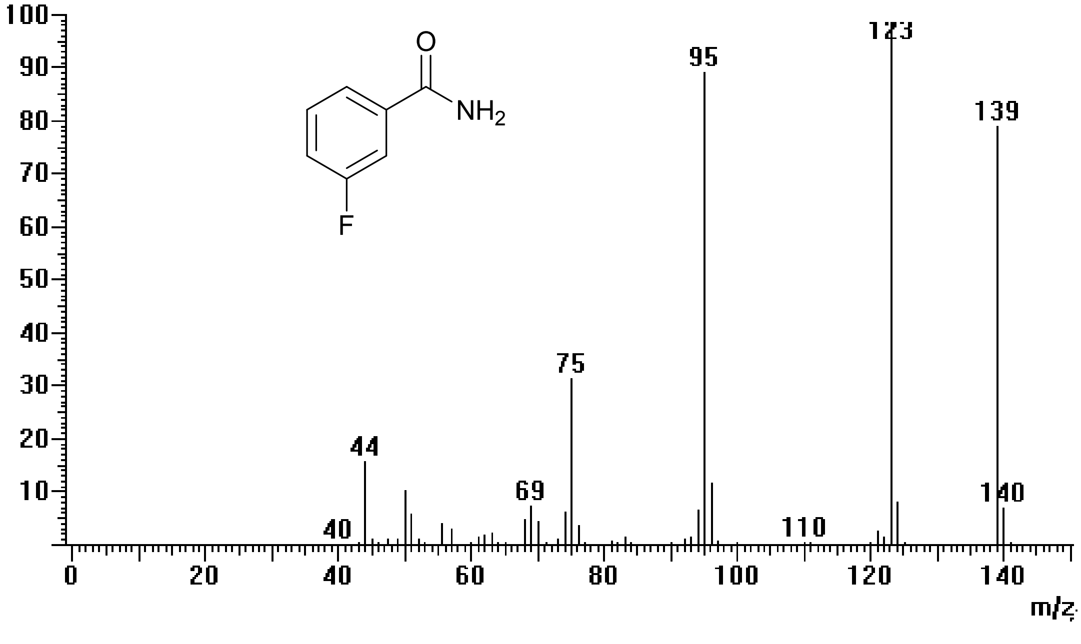
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NH2
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m/z
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139
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40
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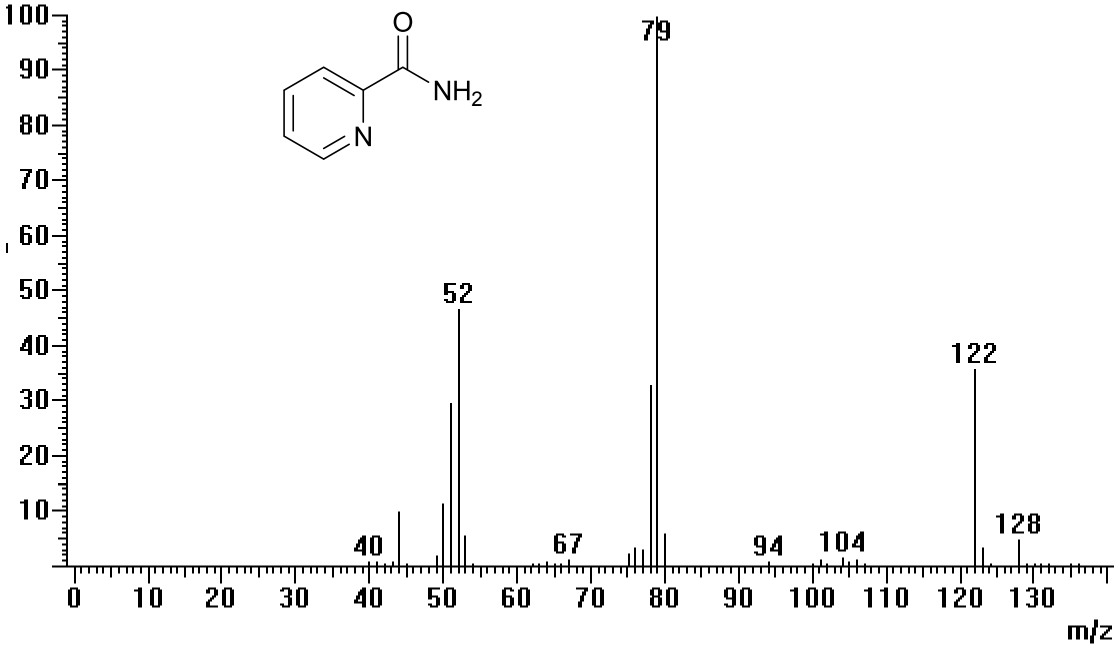

References:

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2. Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Asian J.* **2010**, *5*, 2168.
3. Wu, X.-F.; Bheeter, C. B.; Neumann, H.; Dixneuf, P. H.; Beller, M. *Chem. Commun.* **2012**, *48*, 12237.
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5. Ghosh, S.C.; Ngiam, J. S.; Seayad, A. M. et al; *J. Org. Chem.,* **2012**, *77*, 8007.
6. Owston, N. A.; Parker A. J. and Williams J. M. J. *Org. Lett.*, **2007**, *9,* 3599.