Supporting Information

Copper Catalyzed Efficient Synthesis of 2-Benzimidazolone Scaffold from 2-Nitroaniline and Dimethyl Carbonate *via* Hydrosilylation Reaction

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I. Table 5 Effects of different carbonate sources for the synthesis of **2a**.[a]

Sr. No.	Carbonate source	Conversion (%)[b]	Yield (%)[b]
1	DMC	100	96[c]
2	DEC	-	ND, ND[d]
3	DPC	-	ND
4	Di-*tert*-butyl di-carbonate	-	ND
5	Phenyl Carbamate	-	ND
6	*N*,*N*'-disuccinimidyl carbonate	-	ND

[a] Reaction conditions: **1a** (1 mmol), $Cu(OAc)_2 \cdot H_2O$ (5.0 mol%), Carbonate source (2.5 eq), PMHS (2.0 eq), 20 h at 100 °C.

[b] Based on GC-GC/MS analysis of corresponding products.

ND – not detected.

DMC-dimethylcarbonate

DEC – diethyl carbonate

DPC – diphenyl carbonate

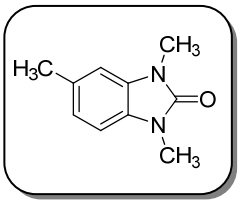
PMHS – polymethylhydrosiloxane.

[c] Isolated Yield.

[d] 150 °C.

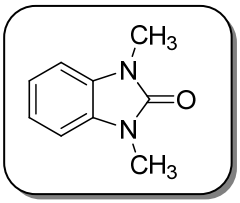
II. Characterization data of compounds:[1,2]

1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2a):



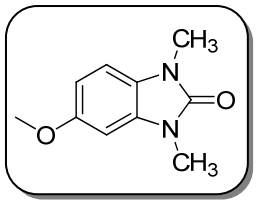
Whitish solid; yield: 96%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS): δ = 6.89–6.87 (d, J = 8 Hz, 1H), 6.83–6.81 (d, J = 8 Hz, 1H), 6.77 (s, 1H), 3.37 (s, 6H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 27 °C, TMS): δ = 154.86, 131.06, 130.19, 127.95, 121.74, 108.11, 107.09, 27.24, 27.17, 21.60. GC-MS (EI) (% relative intensity): *m/z* = 176 (100) $[M]^+$, 161 (10), 147 (8), 133 (14), 91 (9), 88 (8), 77 (8), 65 (10), 51 (5), 42 (4). IR (neat) ν_{max}/cm^{-1} = 2918, 2850, 1693, 1498, 1446, 1390, 1265, 1124, 1012, 910, 721, 586.

1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2b):



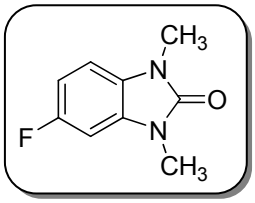
Yellowish solid; yield: 90%; GC-MS (EI) (% relative intensity): *m/z* = 162 (100) $[M]^+$, 161 (53), 147 (10), 133 (16), 119 (19), 92 (16), 77 (11), 65 (10), 51 (10). IR (neat) ν_{max}/cm^{-1}: 2916, 2849, 1691, 1500, 1390, 1267, 1120, 1012, 910, 717, 586.

5-methoxy-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2c):



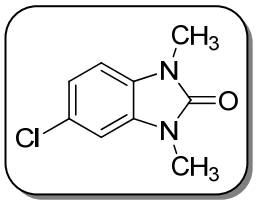
Yellowish solid; yield: 95%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS) δ = 6.85-6.83 (d, J = 8 Hz, 1H), 6.66-6.64 (d, J = 8 Hz, 1H), 6.57 (s, 1H), 3.83 (s, 3H), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 27 °C, TMS) δ = 156.12, 154.10, 134.76, 124.78, 124.05, 108.00, 106.83, 56.41, 30.09. GC-MS (EI) (% relative intensity): *m/z* = 193 (12) $[M+1]^+$, 192 (100) $[M]^+$, 177 (90), 149 (51), 106 (7), 65 (8), 51 (5). IR (neat) ν_{max}/cm^{-1}: 2932, 2363, 1688, 1508, 1396, 1223, 1134, 1035, 956, 852, 785, 734, 464.

5-fluoro-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2d):



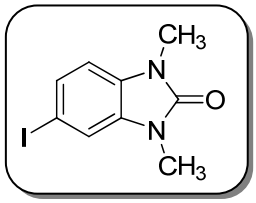
Yellowish solid; yield: 90%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS) δ = 8.02 (s, 1H), 7.73–7.71 (d, J = 8 Hz, 1H), 7.53–7.51 (d, J = 8 Hz, 1H), 3.05 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, 27 °C, TMS) δ = 167.81, 154.49 (d, JC–F = 239.5 Hz), 152.11, 141.54, 124.61 (d, JC–F = 24.3 Hz), 119.99 (d, JC–F = 6.9 Hz), 111.24 (d, JC–F = 25.8 Hz), 29.68, 29.64 ppm. GC-MS (EI) (% relative intensity): *m/z* = 180 (100) $[M]^+$, 179 (46), 165 (14), 151 (18), 150 (17), 149 (11), 137 (28), 110 (18), 95 (9), 83 (11), 44 (10).

5-chloro-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2e):



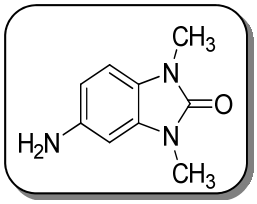
Yellowish solid; yield: 82%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS) δ = 6.91–6.89 (d, J = 8 Hz, 1H), 6.85–6.83 (d, J = 8 Hz, 1H), 6.78 (s, 1H), 3.39 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 27 °C, TMS) δ = 154.60, 130.86, 130.01, 127.78, 121.52, 107.87, 106.84, 29.47, 26.89. GC-MS (EI) (% relative intensity): *m/z* = 196 (100) $[M]^+$,177 (8), 161 (90), 149 (49), 92 (7).

5-iodo-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2f):



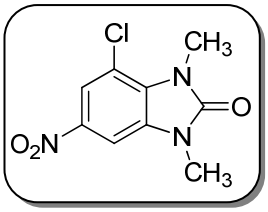
Brownish solid; yield: 71%; GC-MS (EI) (% relative intensity): *m/z* = 242 (20) $[M]^+$, 154 (17), 140 (55), 127 (57), 112 (42), 98 (62), 84 (28), 70 (53), 58 (35), 44 (100), 41 (49).

5-amino-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2g):



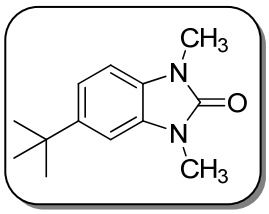
Brownish solid; yield: 85%; GC-MS (EI) (% relative intensity): *m/z* = 177 (100) $[M]^+$, 176 (64), 162 (14), 149 (14), 135 (15), 95 (9), 42 (5).

4-chloro-1,3-dimethyl-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2h):



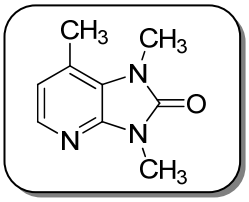
Brownish solid; yield: 75%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS) δ = 8.04 (s, 1H), 7.76 (s, 1H), 3.79 (s, 3H), 3.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 27 °C, TMS) δ = 154.99, 145.24, 135.57, 131.26, 129.88, 119.53, 114.29, 29.51, 27.60. GC-MS (EI) (% relative intensity): *m/z* = 241 (100) $[M]^+$, 211 (29), 195 (42), 152 (15), 126 (25), 76 (10), 40 (5). IR (neat) ν_{max}/cm^{-1}: 2972, 1707, 1495, 1333, 1064, 1029, 883, 740, 661.

5-tert-butyl-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2i):



Off-white solid; yield: 81%; ^{1}H NMR ($CDCl_3$, 400 MHz, 27 °C, TMS) δ = 8.15 (s, 1H), 7.75–7.73 (d, *J* = 8 Hz, 1H), 6.8–6.79 (d, *J* = 8 Hz, 1H), 3.02 (s, 6H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 27 °C, TMS) δ = 154.41, 149.59, 144.44, 138.30, 134.32, 122.32, 113.16, 33.66, 30.80, 29.79, 29.45. GC-MS (EI) (% relative intensity): *m/z* = 218 (45) $[M]^+$, 204 (14), 203 (100), 188 (11), 175 (17), 162 (12), 87 (6), 77 (5). IR (neat) ν_{max}/cm^{-1}: 2962, 1697, 1508, 1454, 1392, 1259, 1141, 948, 893, 794, 732, 650, 586.

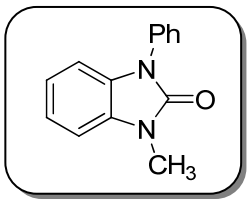
1,3,7-trimethyl-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (2j):



Yellowish solid; yield: 45%; ^{1}H NMR ($CDCl_3$, 400 MHz, 26 °C, TMS) δ = 8.08 (d, *J* = 5.09 Hz, 1H), 6.58 (d, *J* = 4.7 Hz, 1H), 3.46 (s, 6H), 2.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 26 °C, TMS) δ = 158.25, 153.60, 152.25, 146.53, 131.23, 117.36, 31.47, 28.12, 21.47. GC-MS (EI) (% relative intensity): *m/z* =

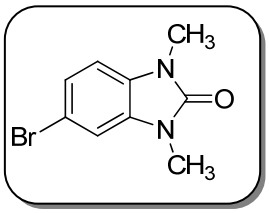
178 (11) $[M+1]^+$, 177 (100) $[M]^+$, 176 (26), 148 (53), 134 (14), 92 (12), 65 (11), 42 (13).

1-methyl-3-phenyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2l):



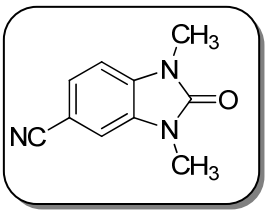
Yellowish solid; yield: 71%; ^{1}H NMR ($CDCl_3$, 400 MHz, 26 °C, TMS) δ = 7.54–7.52 (m, 3H), 7.41–7.40 (m, 1H), 7.26 (s, 1H), 7.17–7.04 (m, 4H), 3.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 26 °C, TMS) δ = 153.89, 142.10, 135.12, 130.80, 129.49, 128.85, 127.57, 126.95, 125.96, 121.96, 121.43, 108.64, 107.63, 29.70. GC-MS (EI) (% relative intensity): *m/z* = 225 (16) $[M+1]^+$, 224 (100) $[M]^+$, 223 (23), 195 (15), 167 (7), 77 (17), 51 (11).

5-bromo-1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2n):



Brownish solid; Yield: 87%; ^{1}H NMR ($CDCl_3$, 400 MHz, 26 °C, TMS) δ = 8.47 (d, J = 2.3 Hz, 1H), 7.42 (dd, J = 8, 2.3 Hz, 1H), 6.73 (d, J = 8 Hz, 1H), 3.46 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 26 °C, TMS) δ = 154.51, 143.59, 138.48, 132.85, 128.28, 120.33, 107.80, 30.85, 30.70. GC-MS (EI) (% relative intensity): *m/z* = 242 (11) $[M+2]^+$, 241 (98) $[M+1]^+$ 240 (100) $[M]^+$, 238 (29), 225 (13), 132 (15), 120 (9), 118 (35), 91 (7), 77 (10), 65 (6), 51 (5).

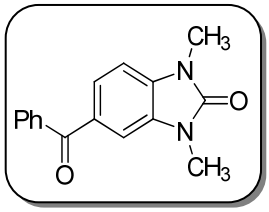
1,3-dimethyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carbonitrile (2o):



Yellowish solid; Yield: 81%; ^{1}H NMR ($CDCl_3$, 400 MHz, 26 °C, TMS) δ = 8.15 (s, 1H), 7.75–7.73 (d, J = 8 Hz, 1H), 6.8–6.79 (d, J = 8 Hz, 1H), 3.02 (s, 6H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 26 °C, TMS) δ = 153.95, 146.92, 137.13, 131.88, 126.23, 119.67, 117.69, 104.91, 30.91, 30.88. GC-MS

(EI) (% relative intensity): *m/z* = 188 (12) $[M+1]^+$, 187 (100) $[M]^+$, 158 (15), 144 (17), 117 (17), 91 (10), 77 (6), 44 (9).

5-benzoyl-1,3-dimethyl-1*H*-benzo[d]imidazol-2(3*H*)-one (2p):



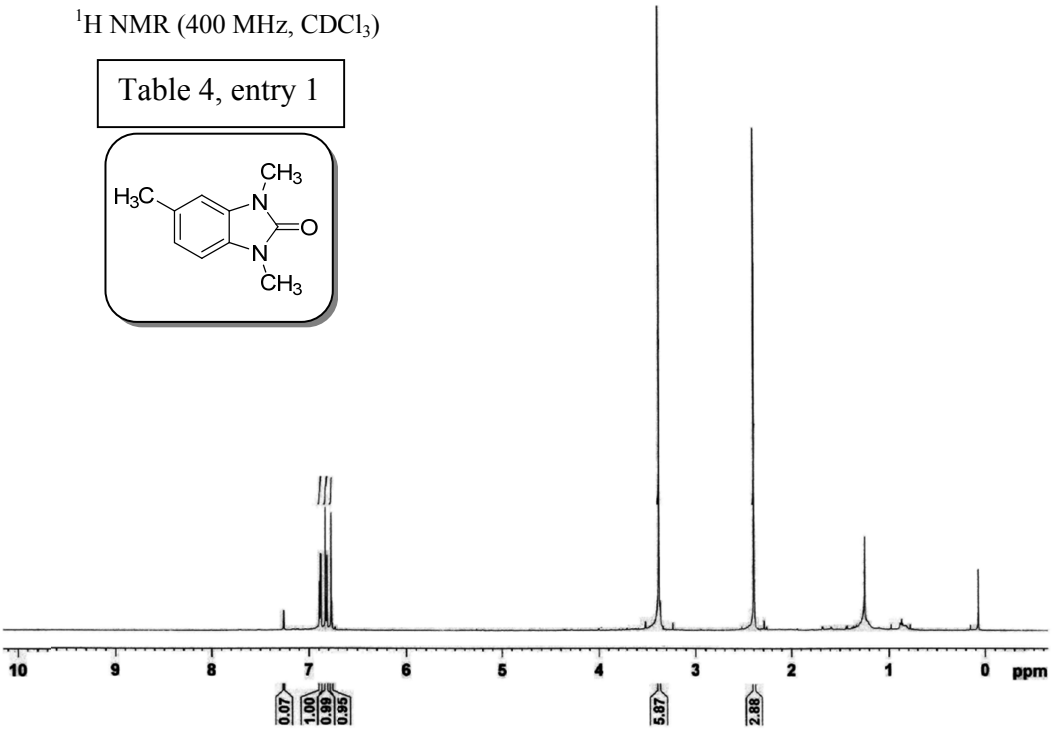
Whitish solid; Yield: 79%; ^{1}H NMR ($CDCl_3$, 400 MHz, 26 °C, TMS) δ = 7.78 (m, 7H), 7.0 (d, J = 8 Hz, 1H), 3.48-3.47 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 26 °C, TMS) δ = 196.03, 154.84, 139.26, 138.26, 133.77, 132.90, 132.0, 130.92, 130.10, 129.80, 128.23, 125.67, 108.88, 106.25, 29.67, 27.43. GC-MS (EI) (% relative intensity): *m/z* = 267 (10) $[M+1]^+$, 266 (65) $[M]^+$, 204 (10), 176 (18), 175 (100), 163 (12), 132 (6), 91 (4), 77 (5), 42 (14).

III. Copies of ^{1}HNMR and ^{13}CNMR Spectra:

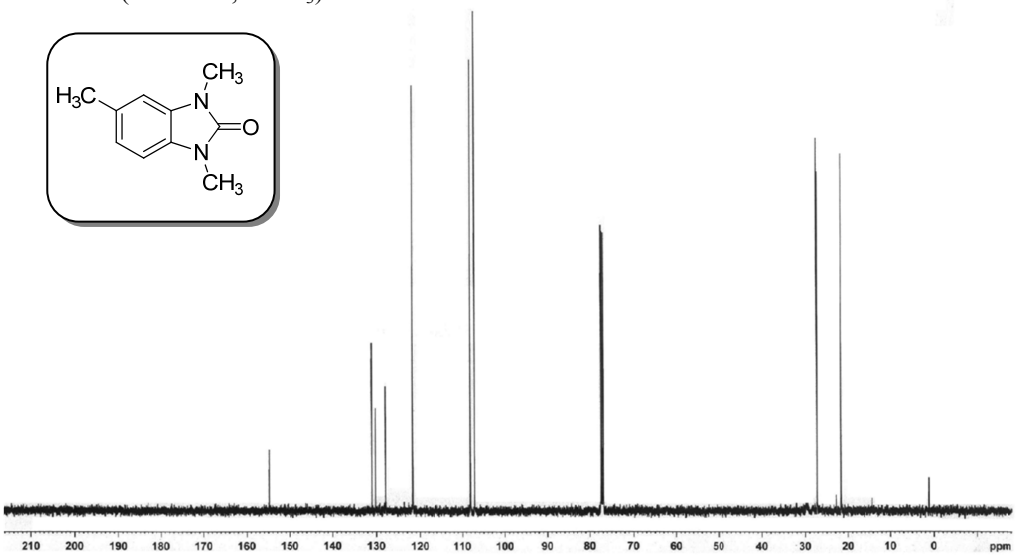
1,3,5-trimethyl-1H-benzo[d]imidazol-2(3H)-one (2a)

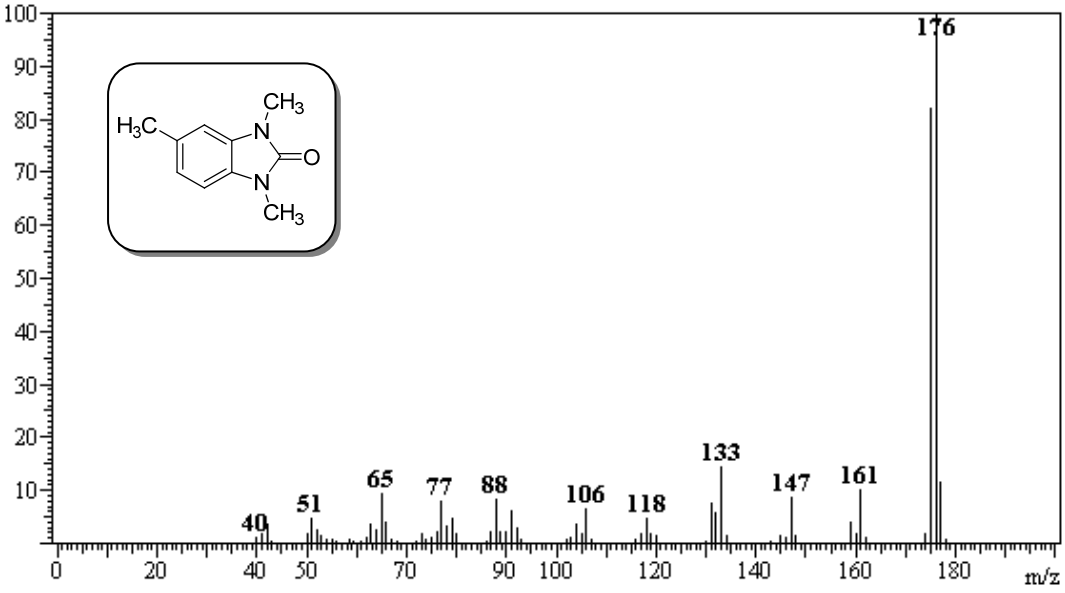
^{1}H NMR (400 MHz, $CDCl_3$)

Table 4, entry 1

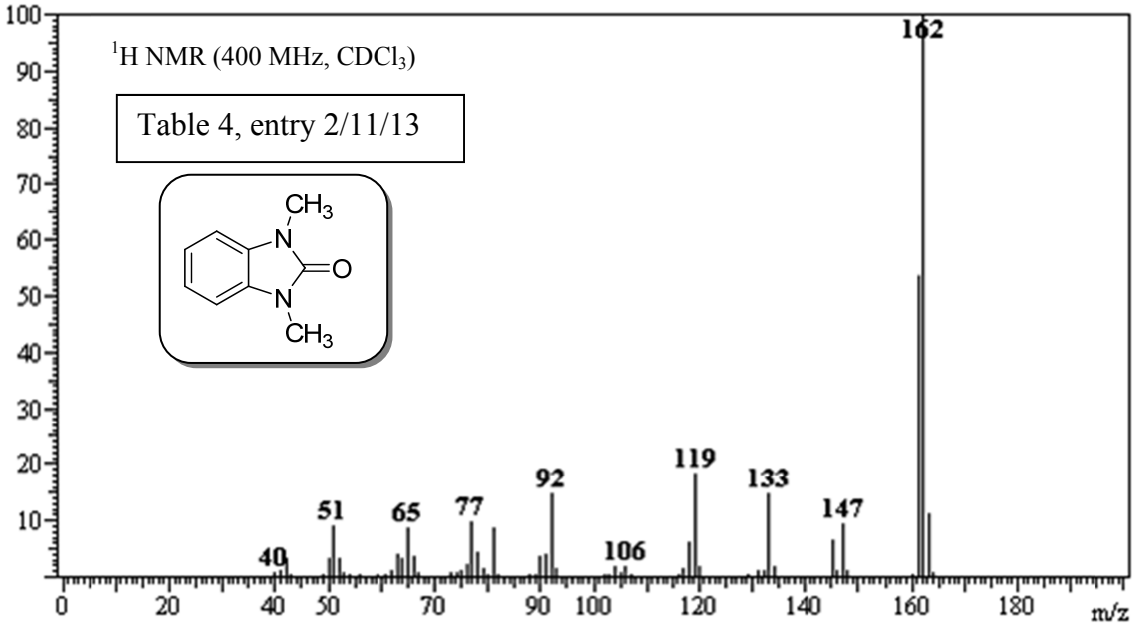


^{13}C NMR (100 MHz, $CDCl_3$)

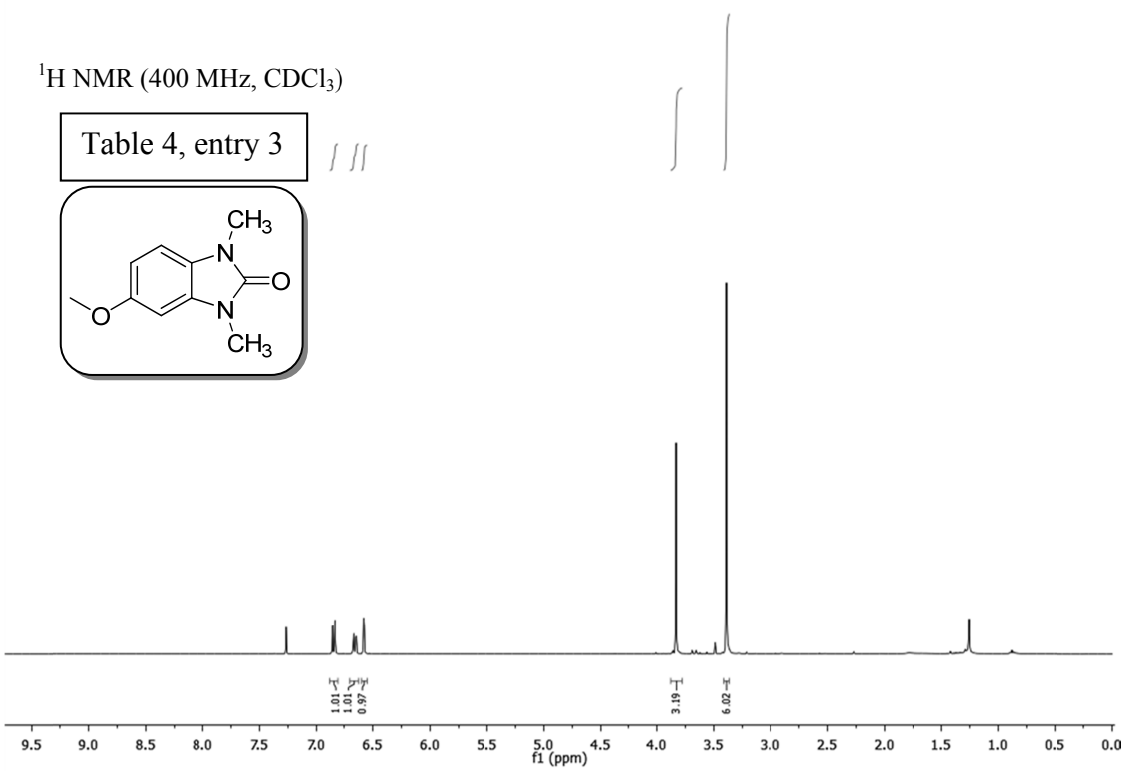


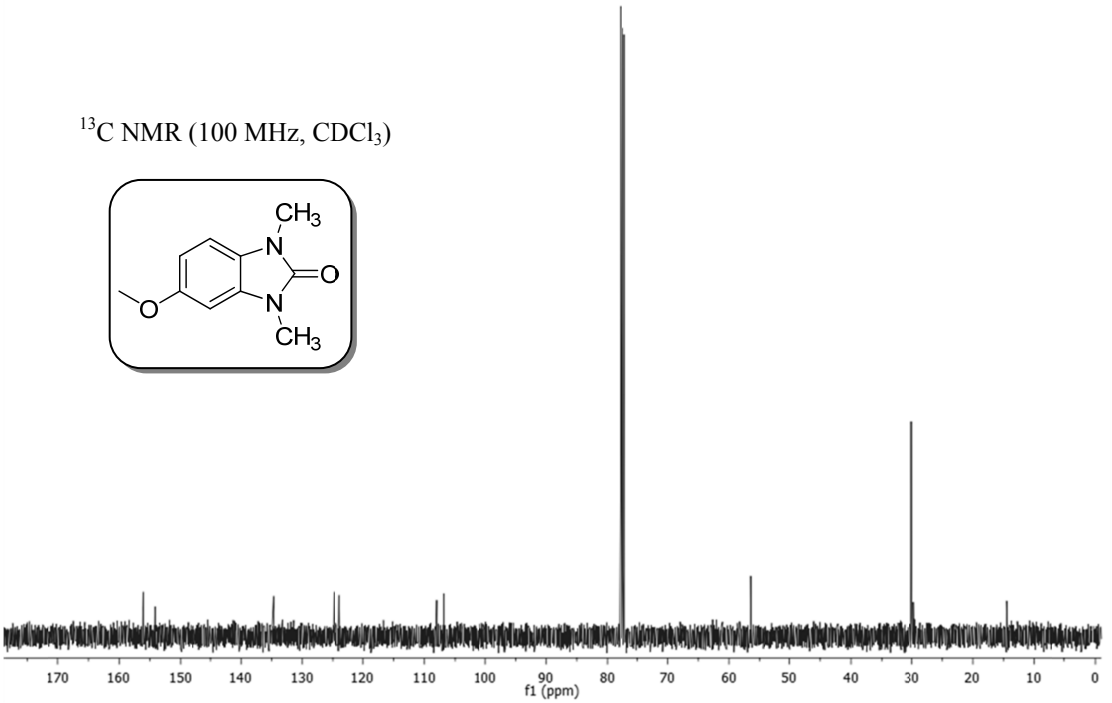

176
133
147
161
65
77
88
106
118
51
40
m/z

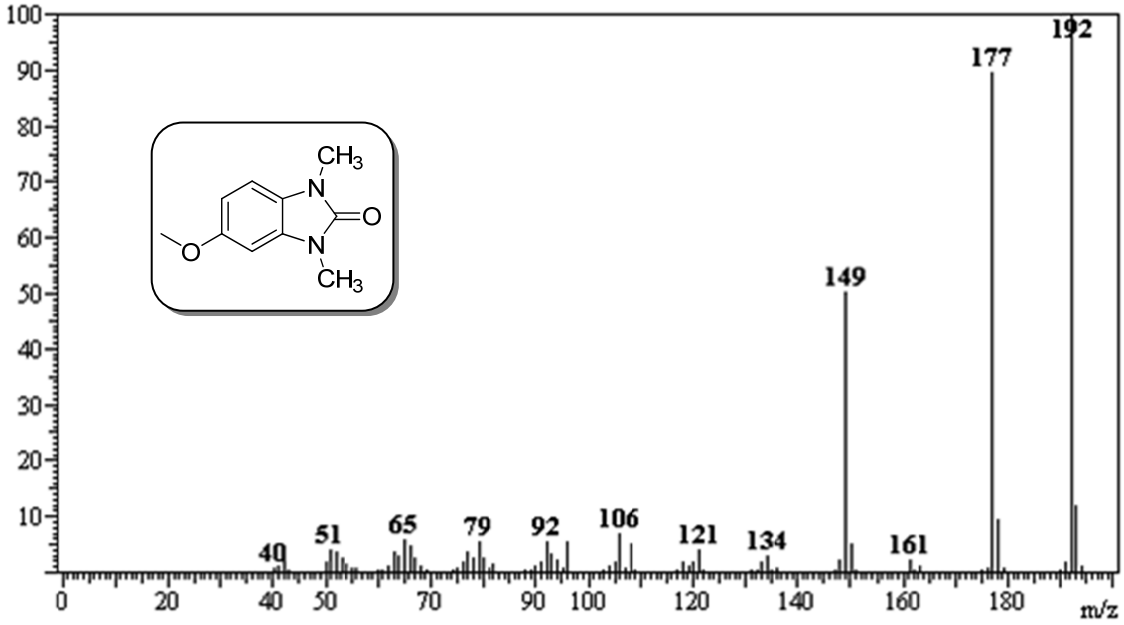
1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2b)



5-methoxy-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2c)






100
90
80
70
60
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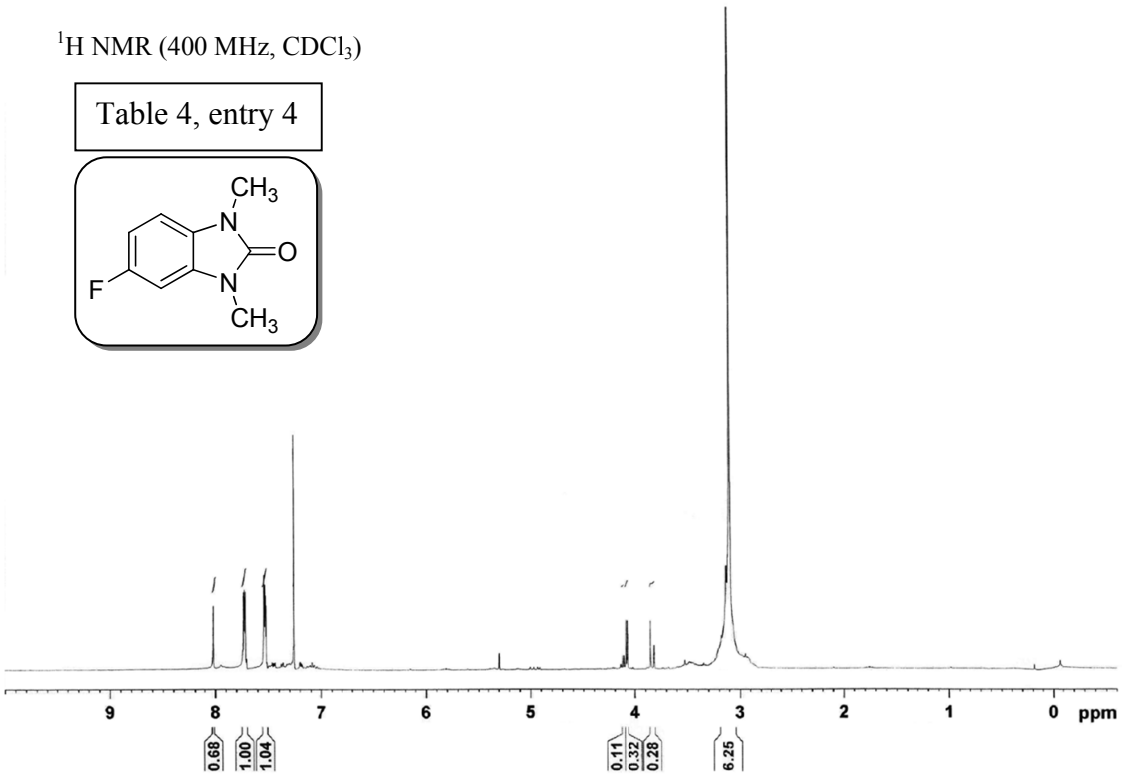
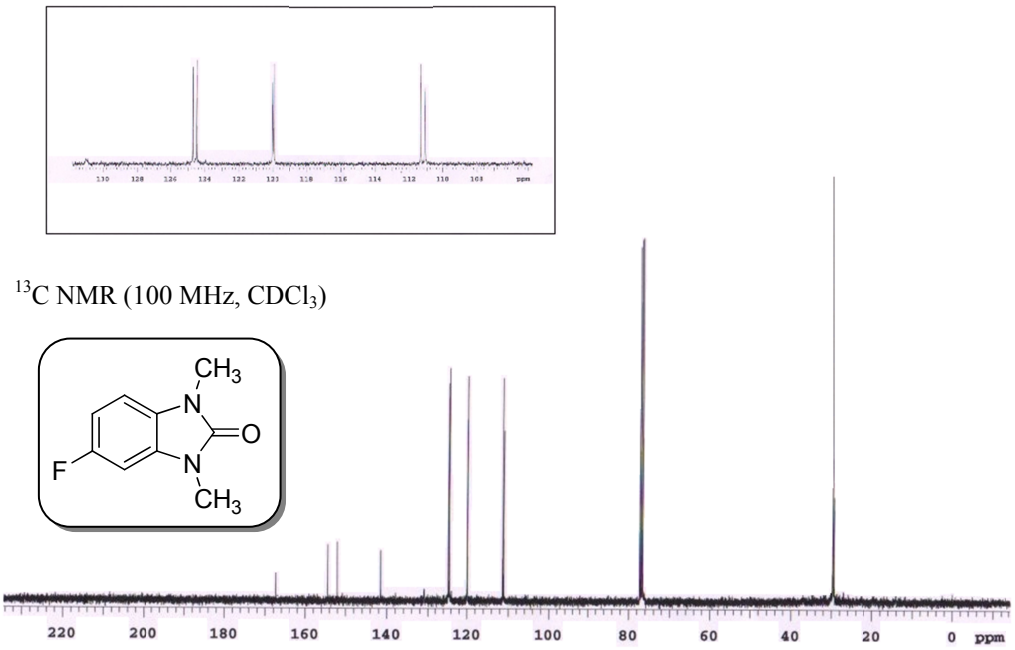
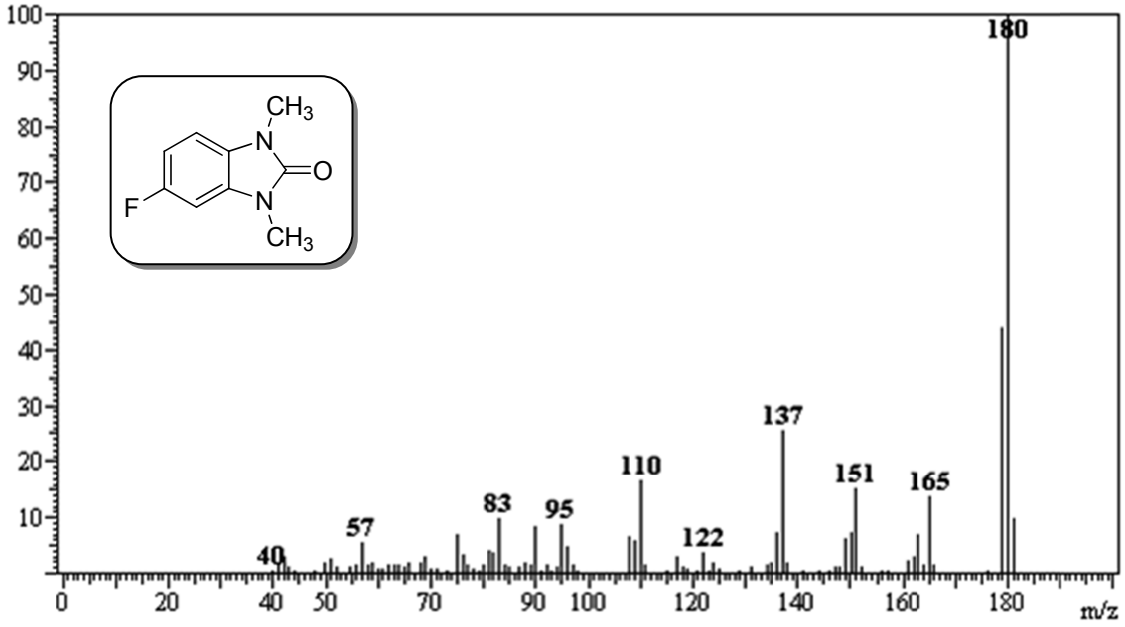
40
30
20
10
192
177
149
40
51
65
79
92
106
121
134
161
0
20
40
50
70
90
100
120
140
160
180
m/z
CH3
N
O
N
CH3
O

5-fluoro-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2d)



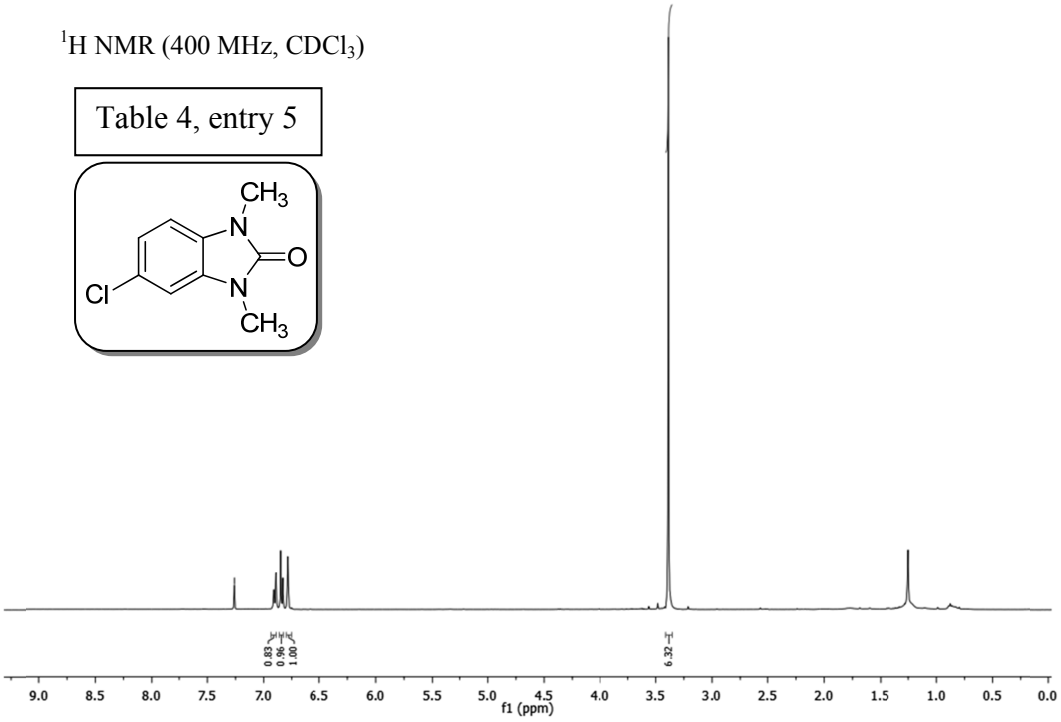



CH3
N
O
F
N
CH3
180
137
110
151
165
83
95
57
122
40
m/z

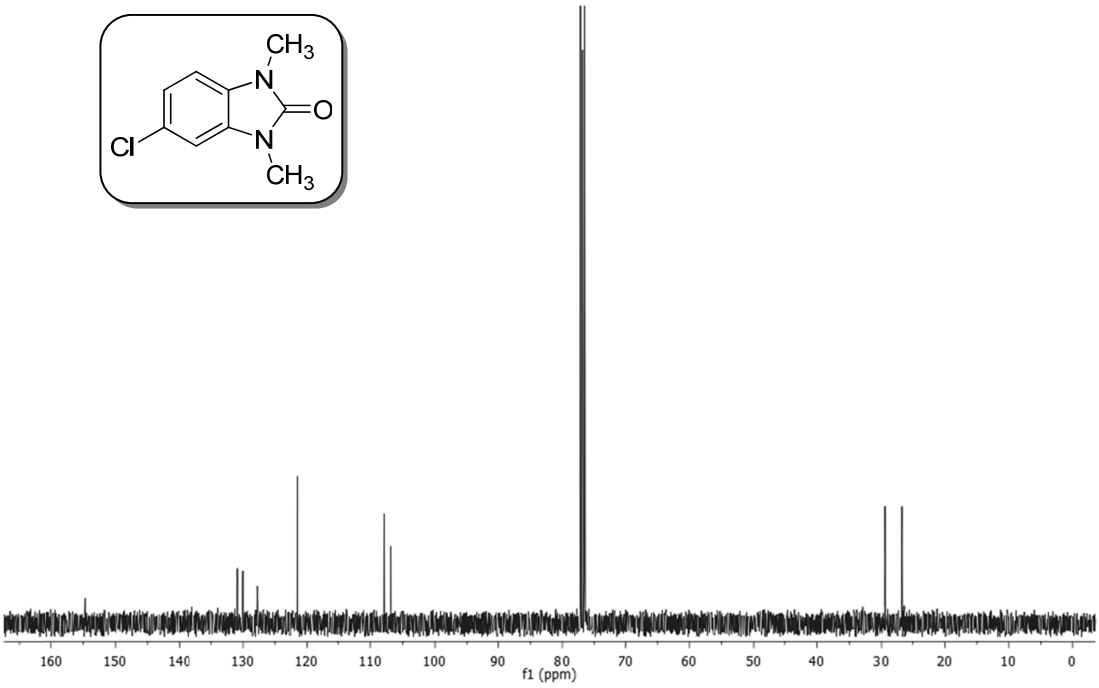
5-chloro-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2e)

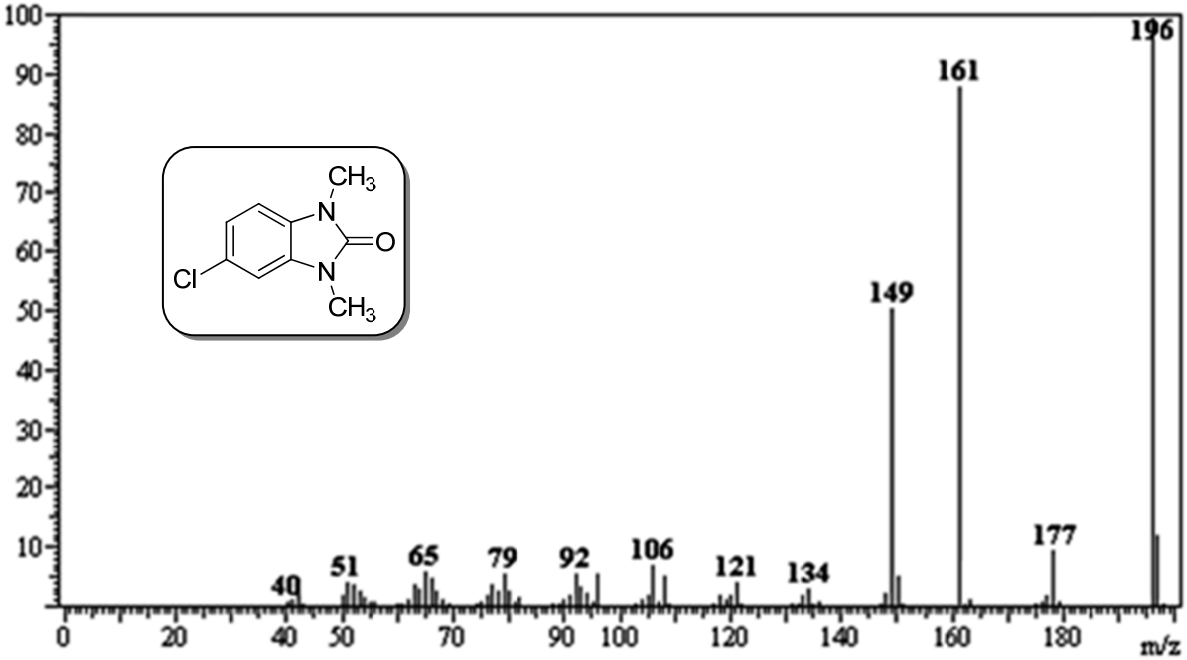
^{1}H NMR (400 MHz, $CDCl_3$)

Table 4, entry 5



^{13}C NMR (100 MHz, $CDCl_3$)




100
90
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40
30
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120
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160
180
m/z
196
161
149
177
40
51
65
79
92
106
121
134
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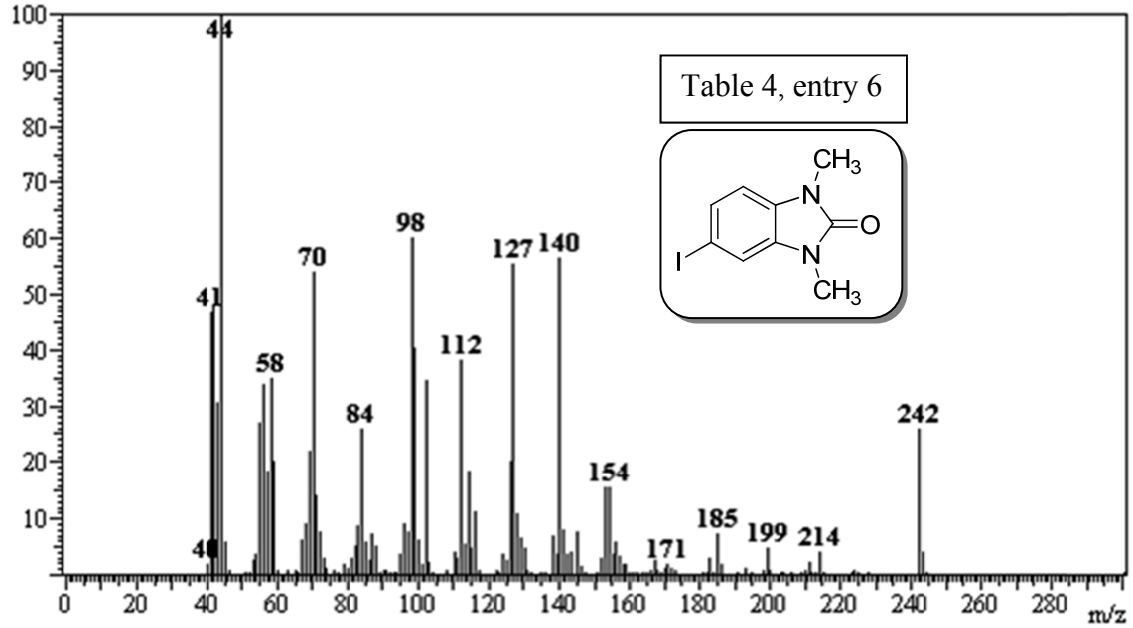
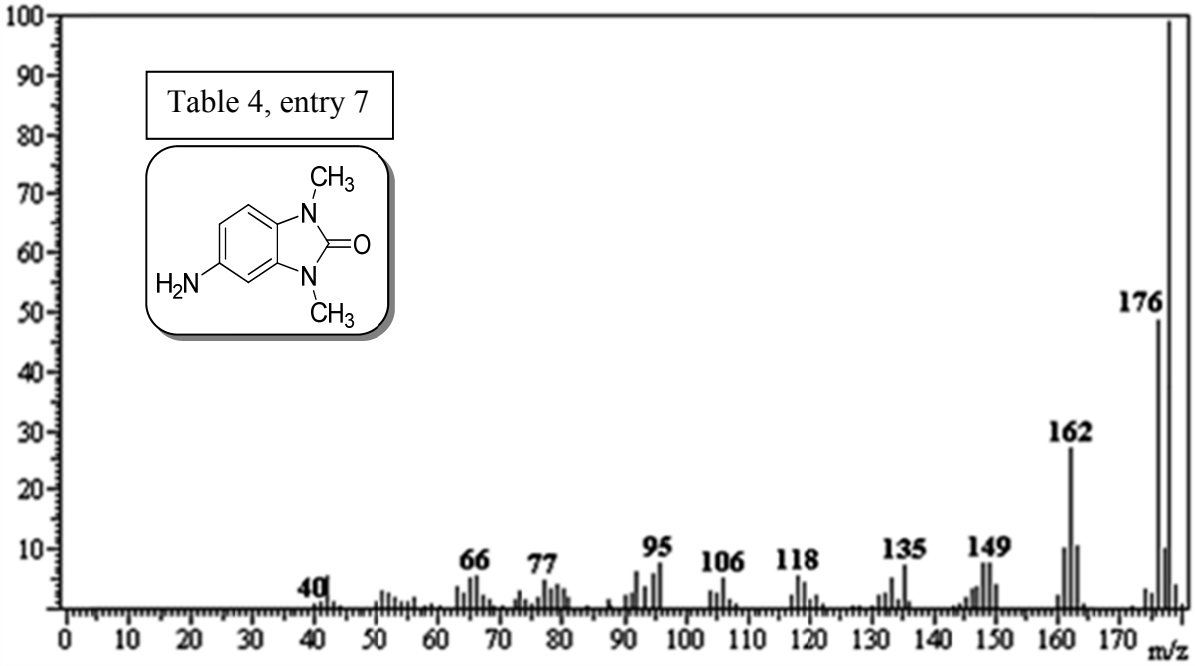
N
O
Cl
N
CH3

5-iodo-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2f)



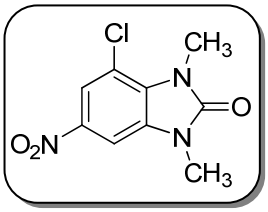
5-amino-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2g)

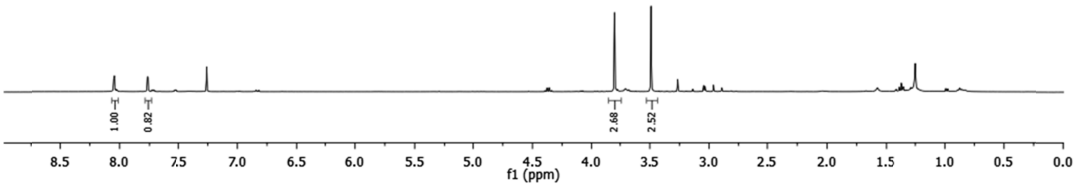


4-chloro-1,3-dimethyl-6-nitro-1H-benzo[d]imidazol-2(3H)-one (2h)

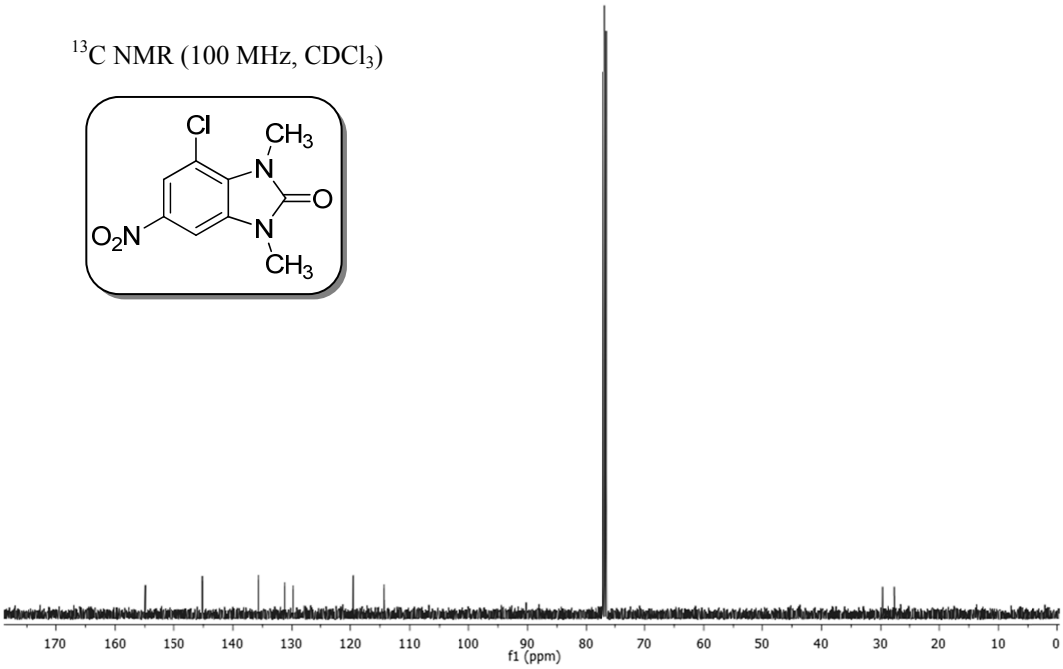
^{1}H NMR (400 MHz, $CDCl_3$)

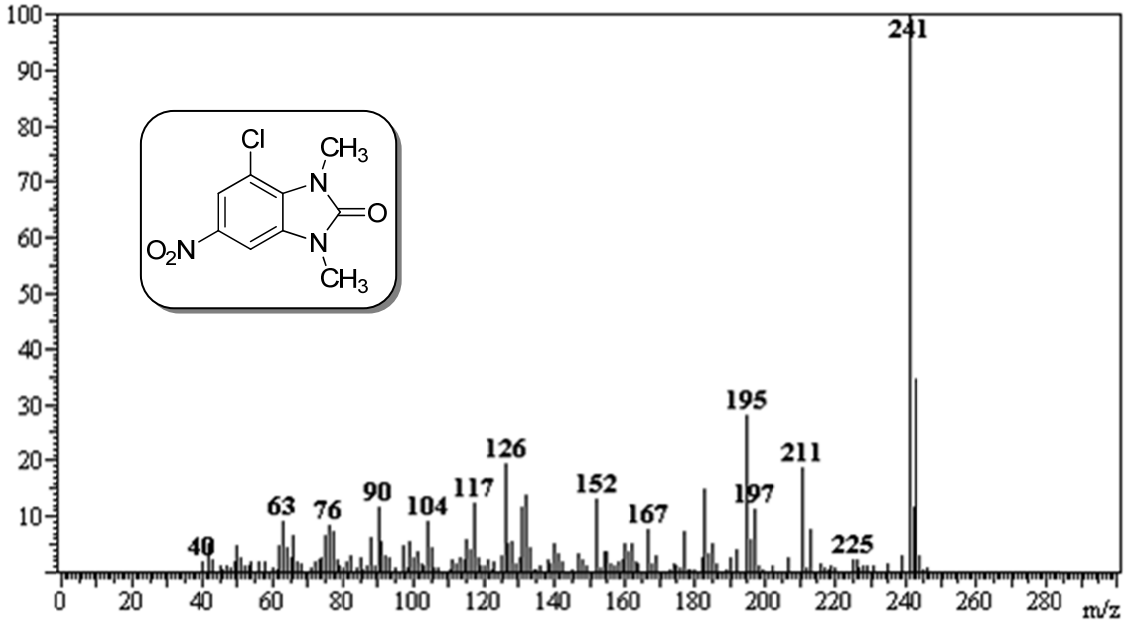
Table 4, entry 8



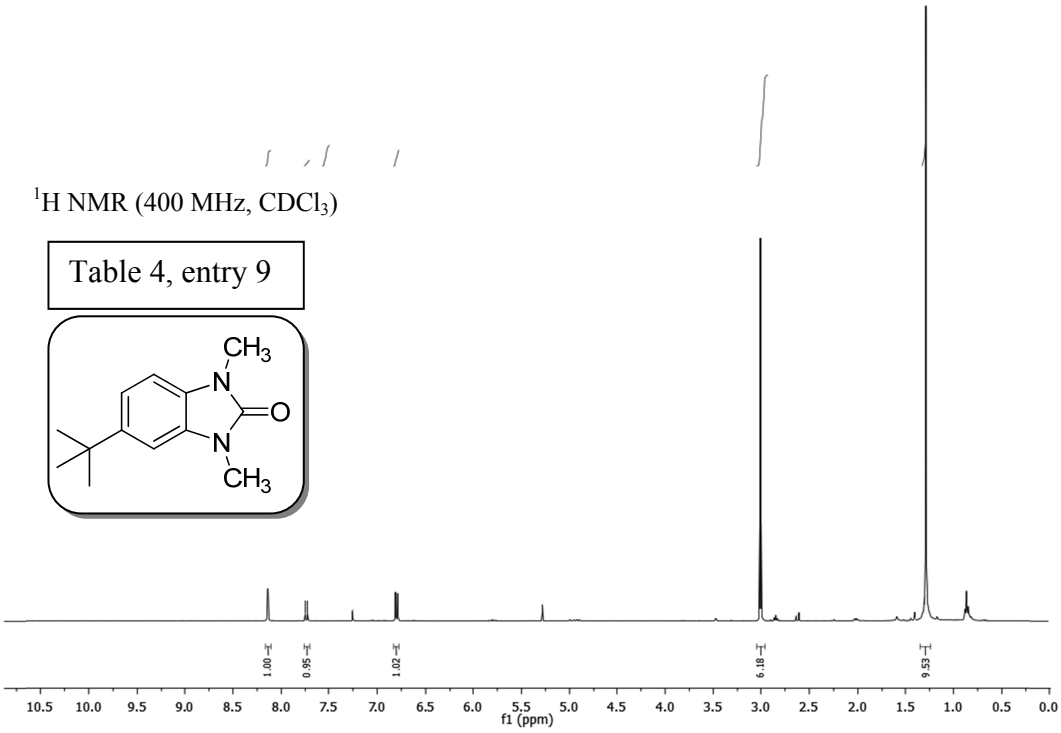


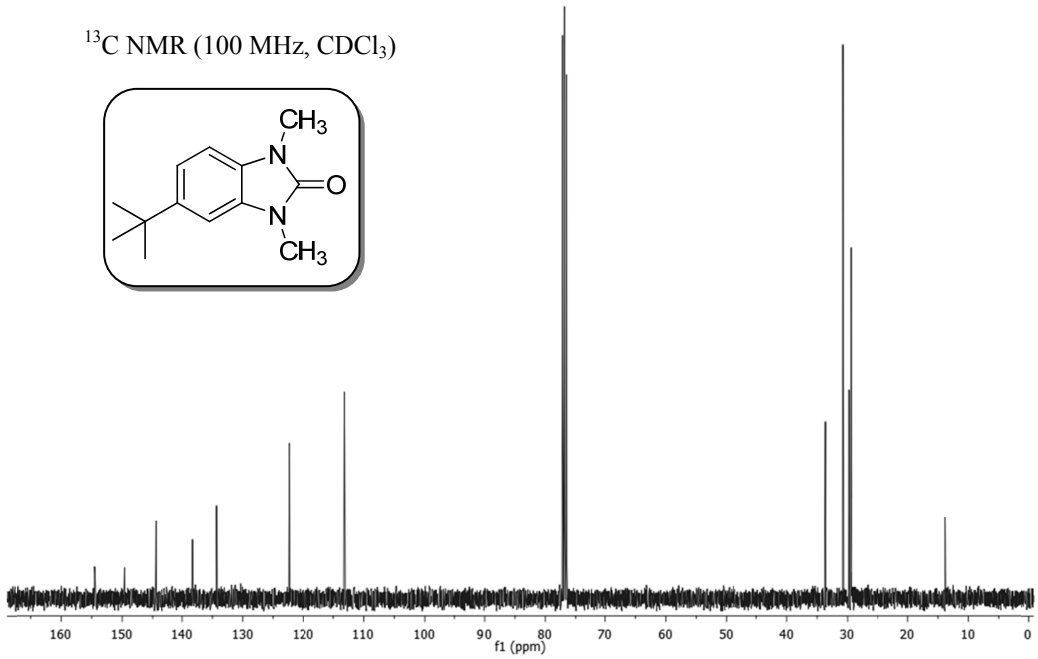
^{13}C NMR (100 MHz, $CDCl_3$)

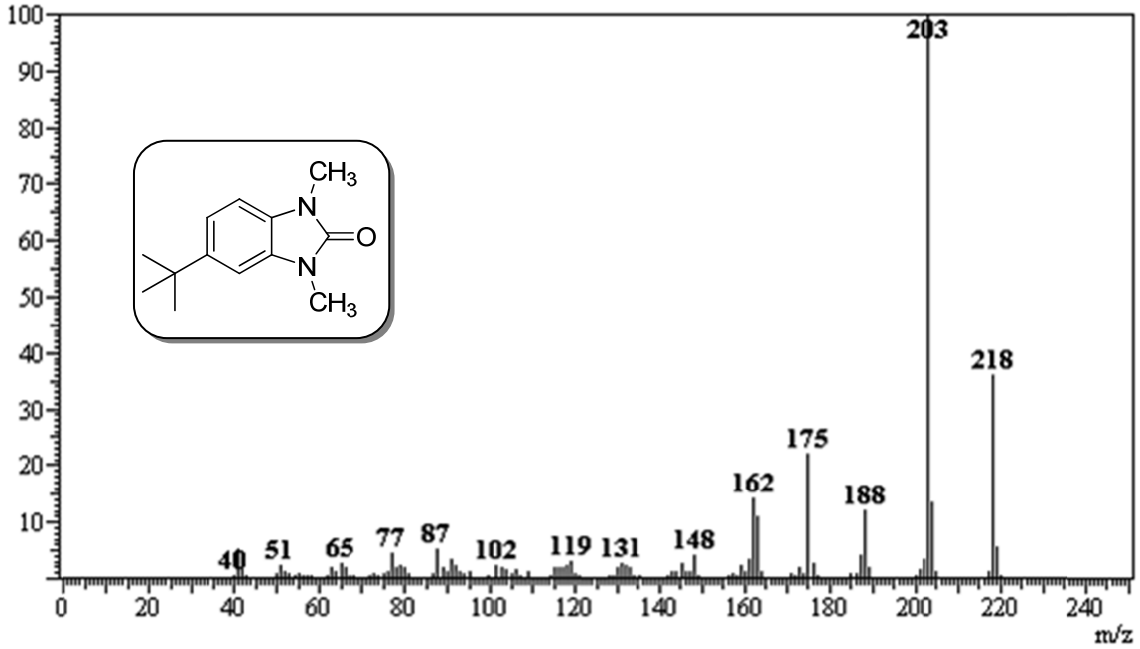



241
195
211
126
152
117
104
90
76
63
40
197
167
225
m/z
Cl
CH3
N
O
O2N
N
CH3

5-tert-butyl-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2i)



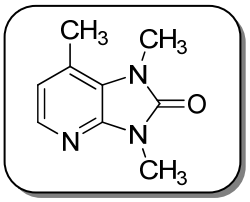


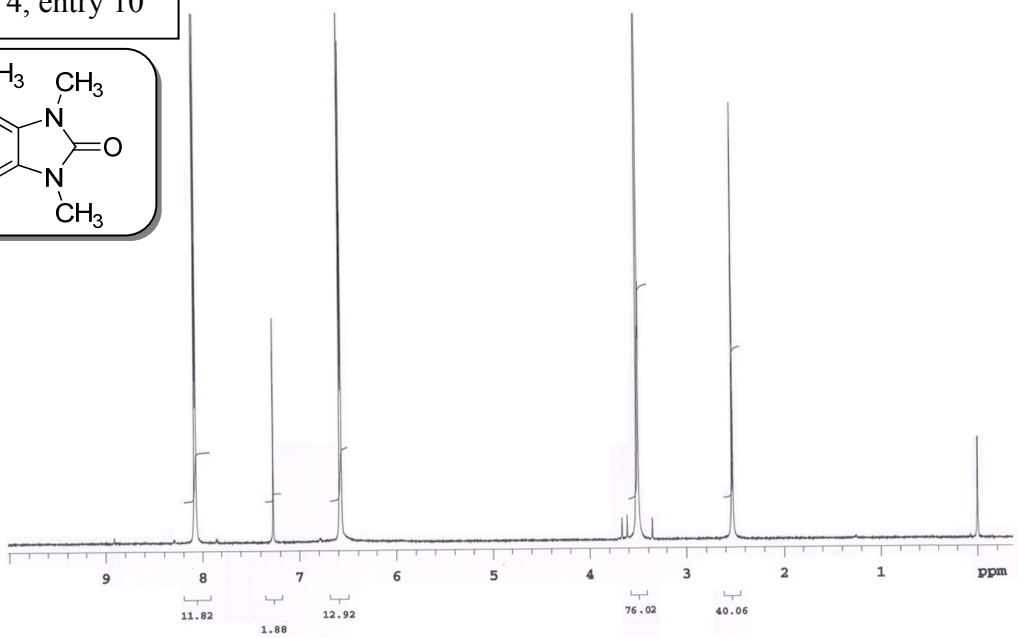

203
218
175
162
188
40
51
65
77
87
102
119
131
148
m/z

1,3,7-trimethyl-1H-imidazo[4,5-b]pyridin-2(3H)-one (2j)

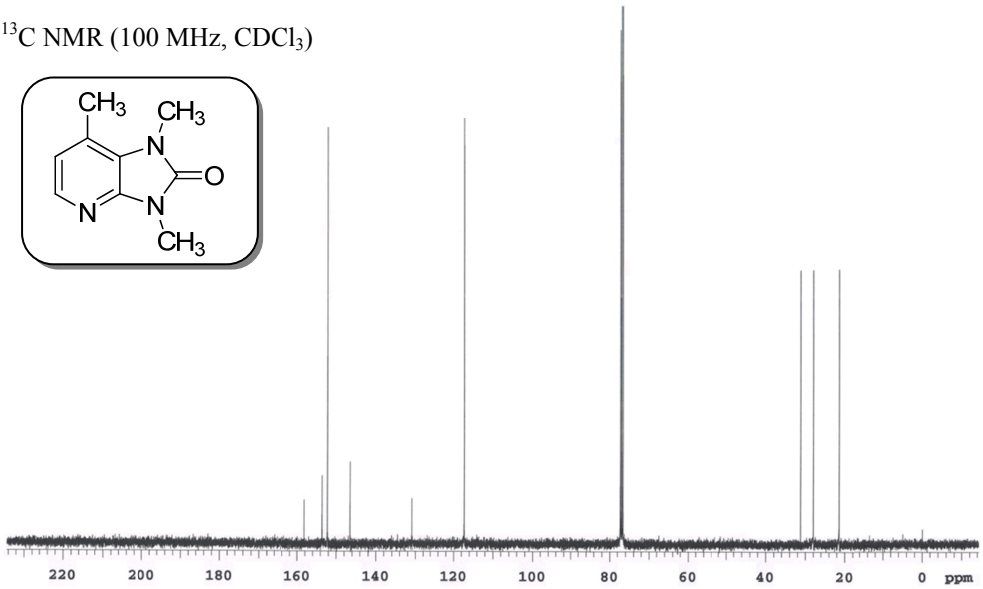
^{1}H NMR (400 MHz, $CDCl_3$)

Table 4, entry 10





^{13}C NMR (100 MHz, $CDCl_3$)



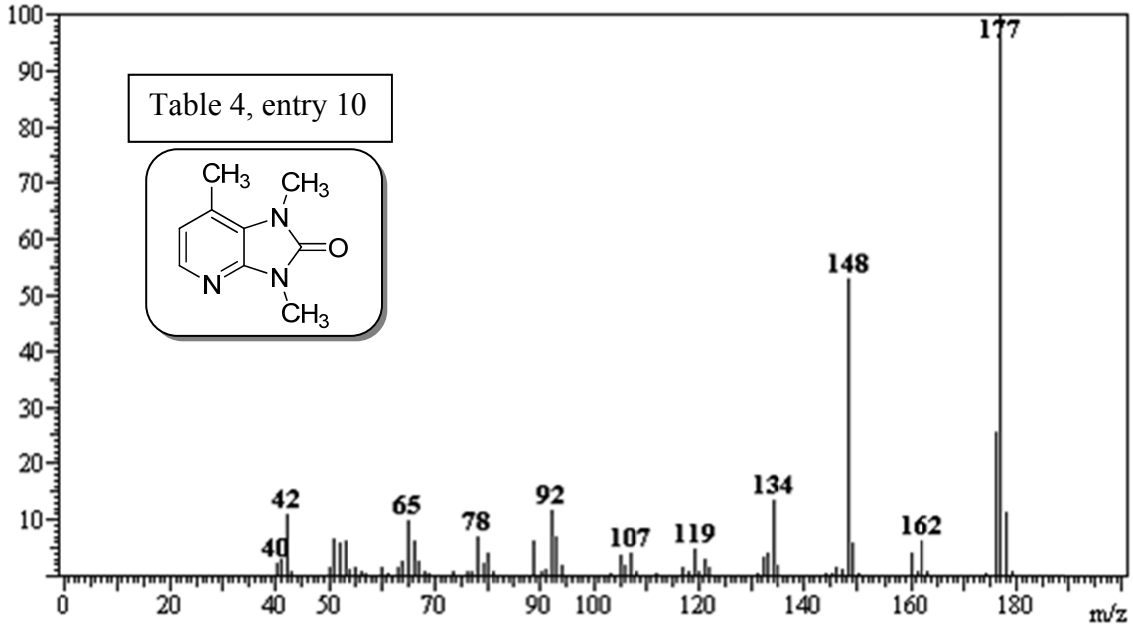
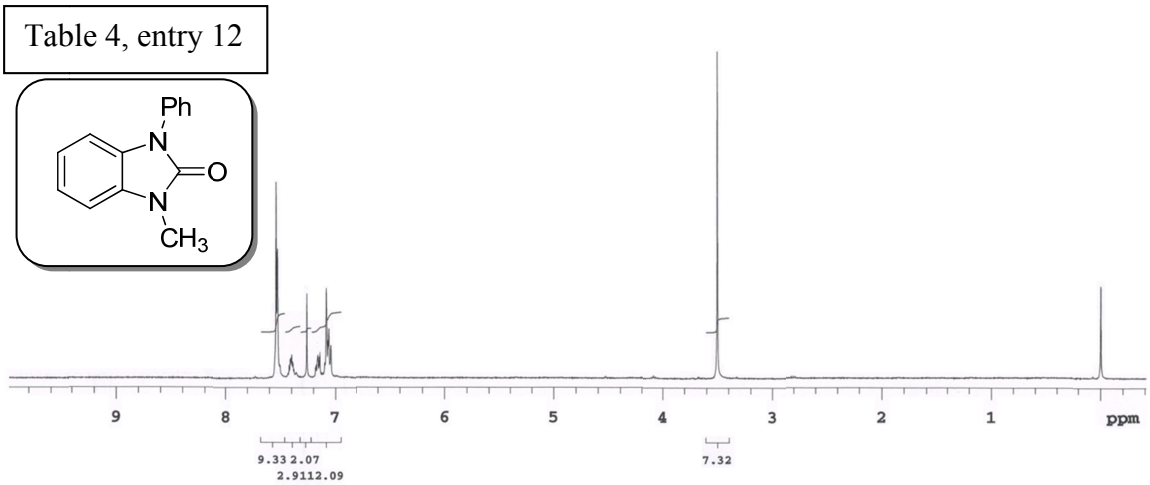


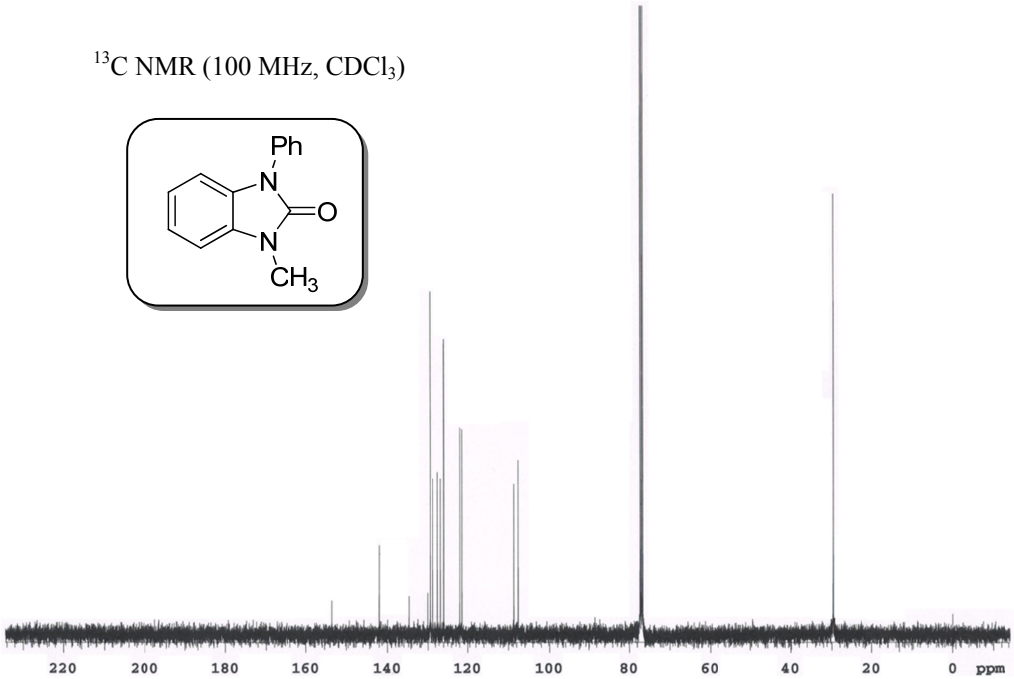
Table 4, entry 10
CH3
CH3
N
O
N
N
CH3
177
148
42
65
78
92
134
40
107
119
162
m/z

1-methyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (2l)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



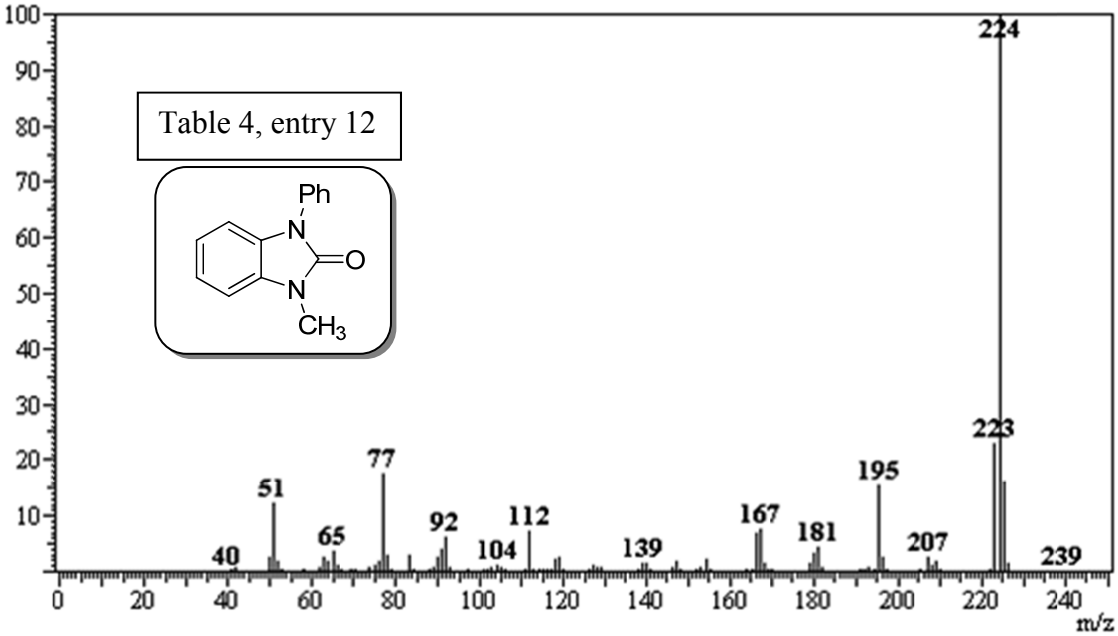
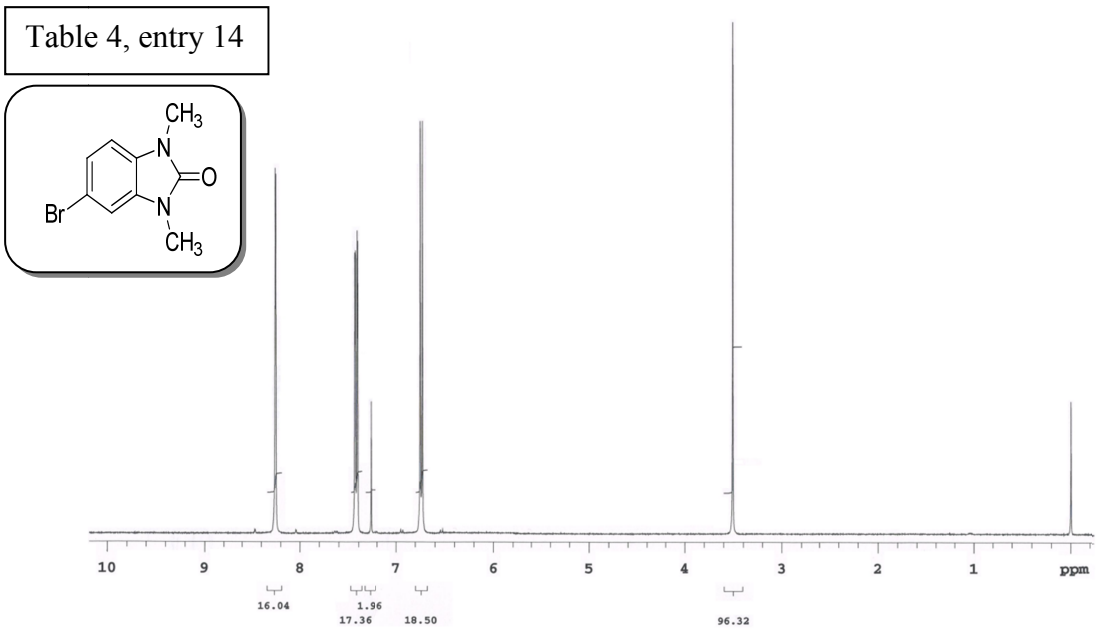


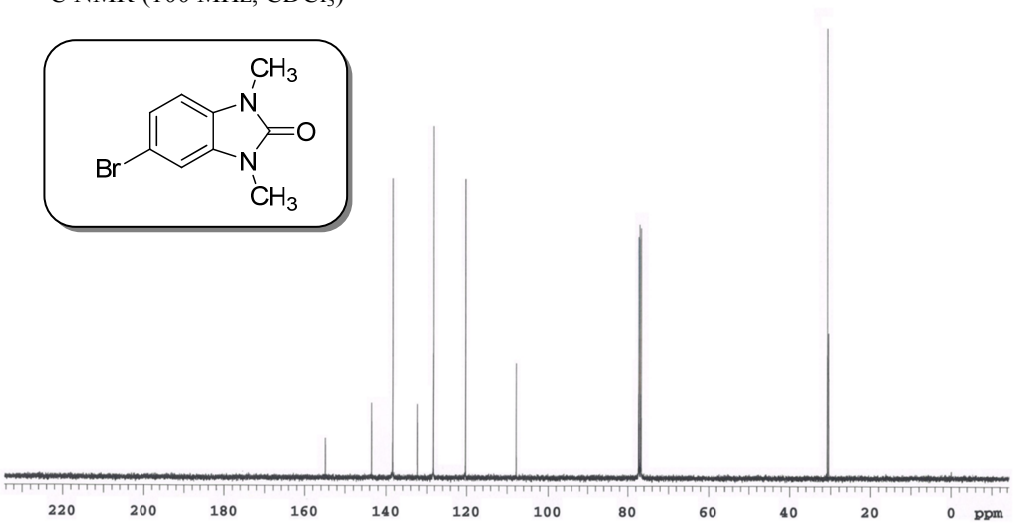
Table 4, entry 12
Ph
N
O
N
CH3
224
223
195
77
51
65
92
112
104
139
167
181
207
239
40
m/z

5-bromo-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2n)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



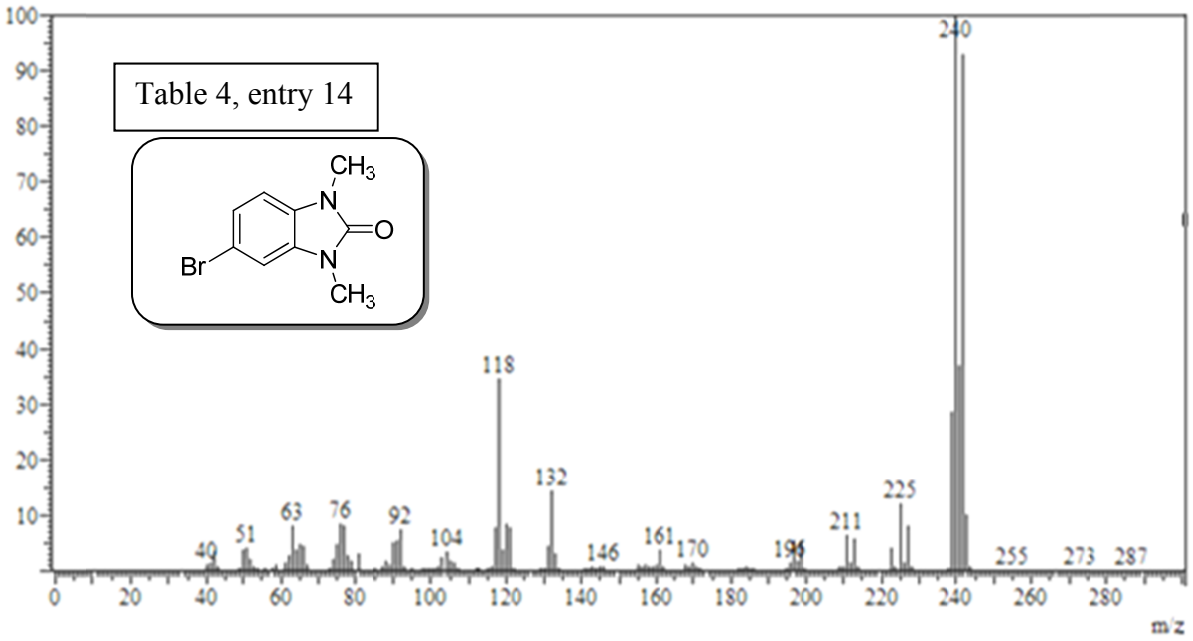
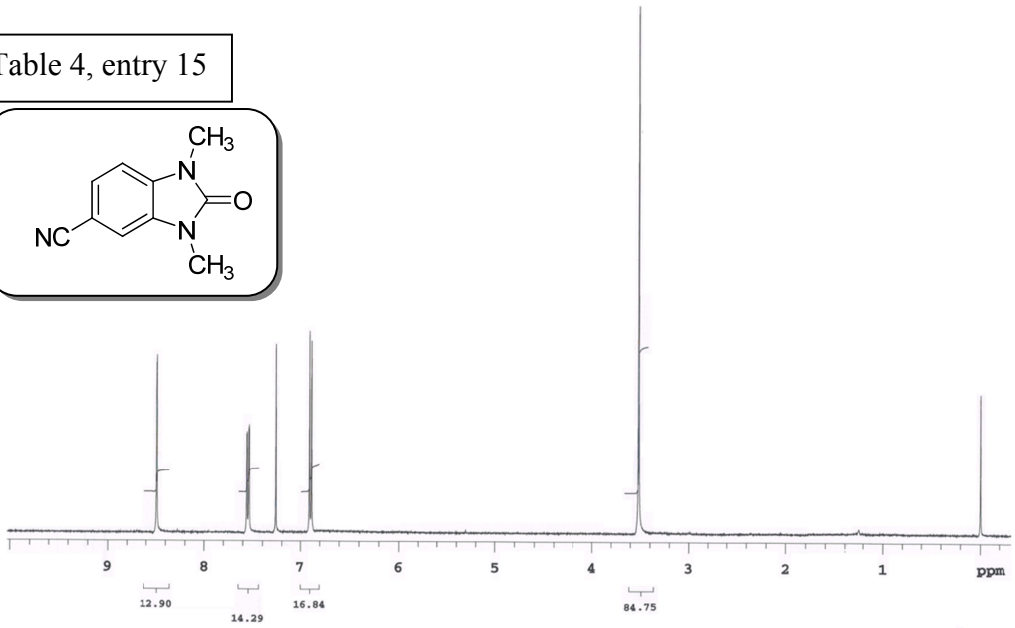


Table 4, entry 14
CH3
N
O
Br
N
CH3
240
118
132
225
211
63
76
92
51
40
104
146
161
170
255
273
287
m/z

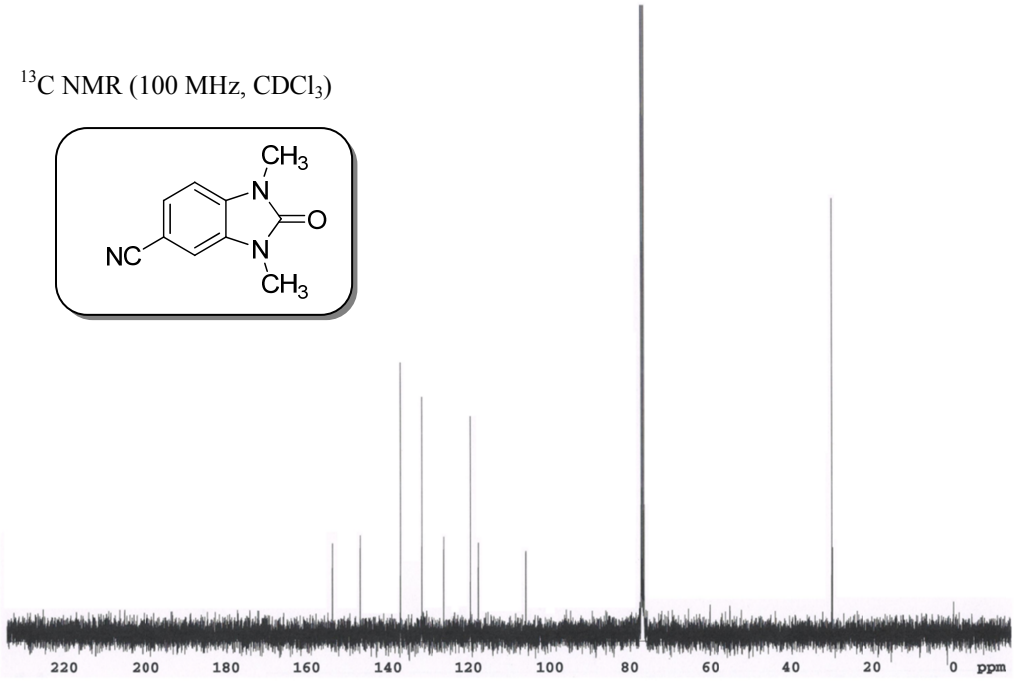
1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[d]imidazole-5-carbonitrile (2o):

^{1}H NMR (400 MHz, $CDCl_3$)

Table 4, entry 15



^{13}C NMR (100 MHz, $CDCl_3$)



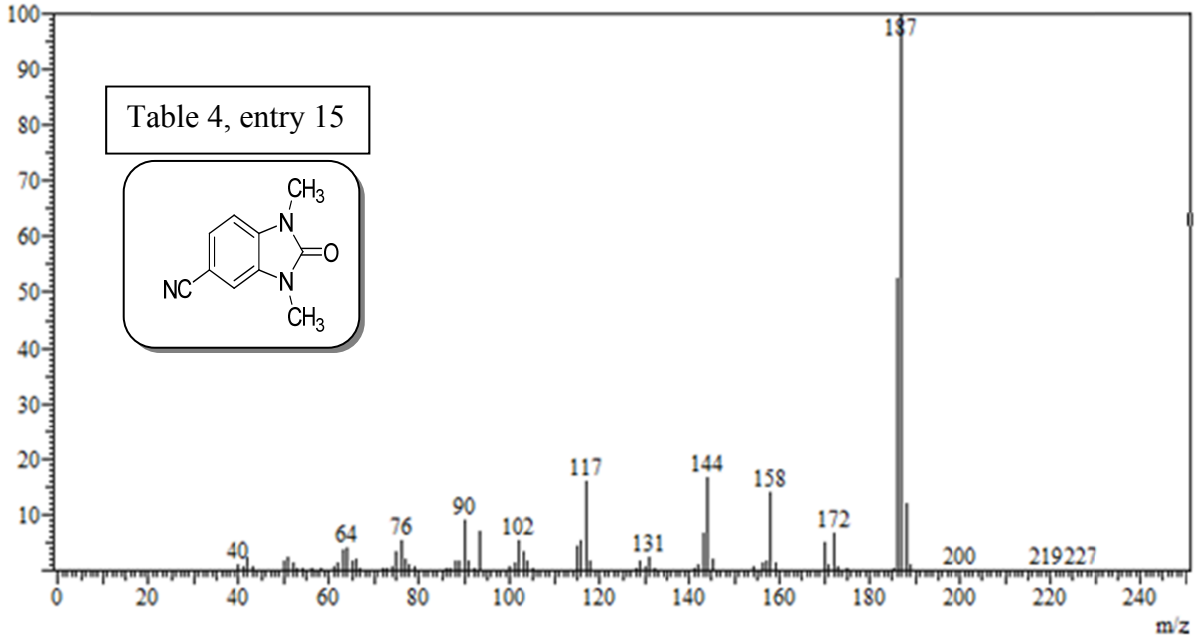
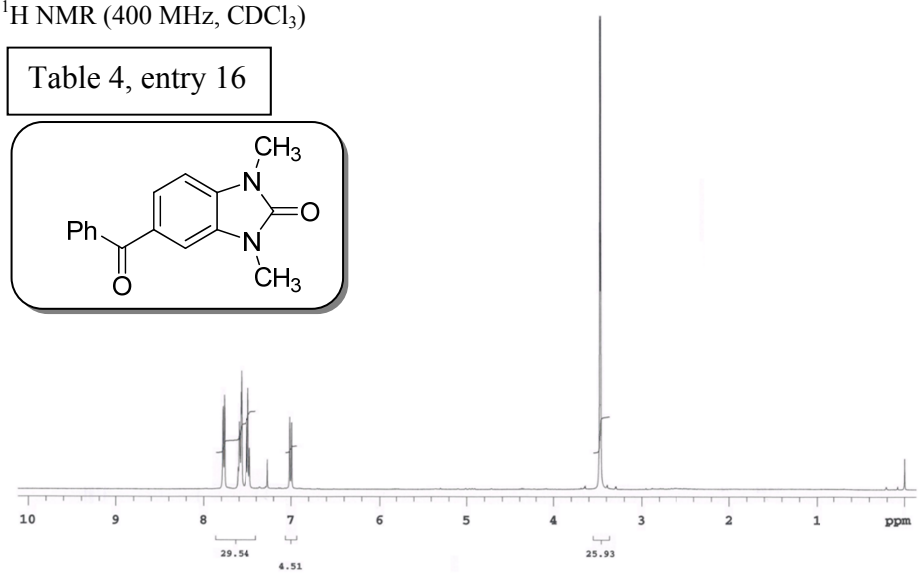


Table 4, entry 15
CH3
N
O
NC
N
CH3
100
90
80
70
60
50
40
30
20
10
187
117
144
158
90
102
64
76
40
131
172
200
219
227
0
20
40
60
80
100
120
140
160
180
200
220
240
m/z

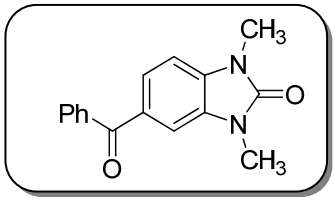
5-benzoyl-1,3-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2p):

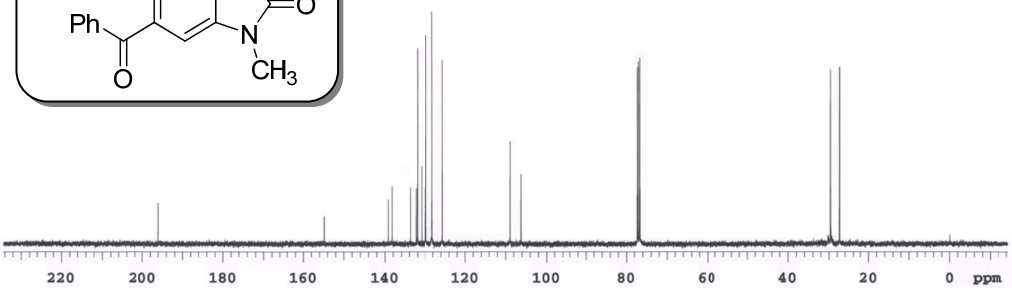
^{1}H NMR (400 MHz, $CDCl_3$)

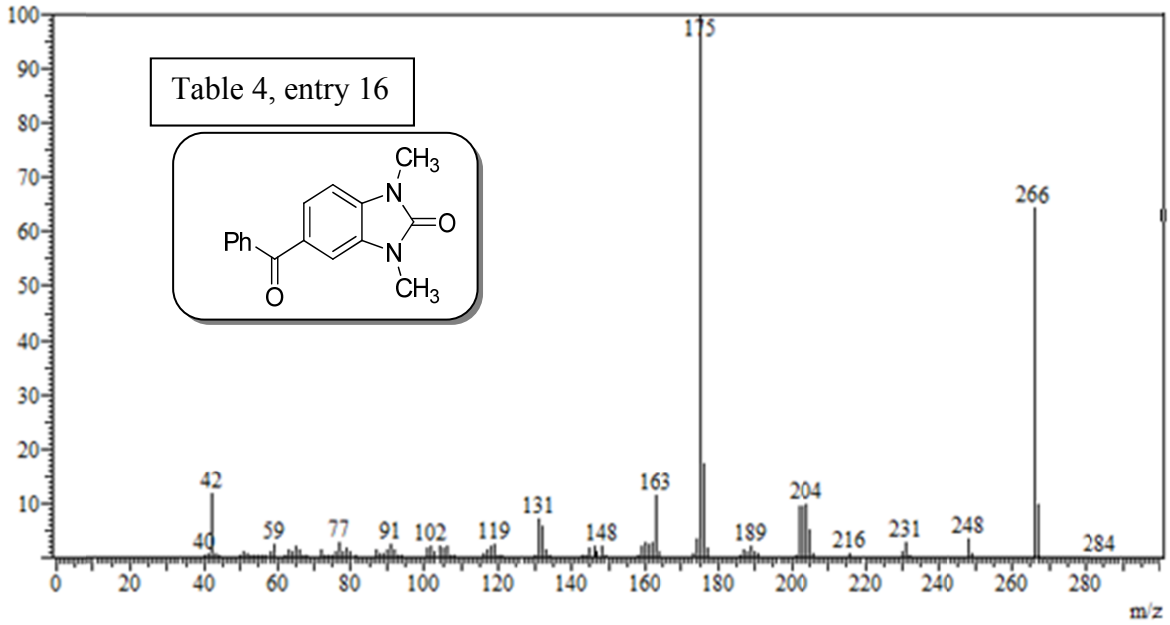
Table 4, entry 16



^{13}C NMR (100 MHz, $CDCl_3$)







IV. References:

1. R. L. Clark and A. A. Pessolano, *Contribution from the Merck sharp and Dohme research laboratories*, 1958, **80**, 1662–1664;
2. T. Kimura, K. Kamata, N. Mizuno, *Angew. Chem., Int. Ed*. 2012, **51**, 6700−6703.