Supporting Information

Effect of solvent ratio and counter ions on the morphology of copper nanoparticles: Its catalytic application in β-enaminones synthesis

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Contents

1. XRD pattern of CuO NPs, Cu_2O NPs and $Cu(OH)_2$

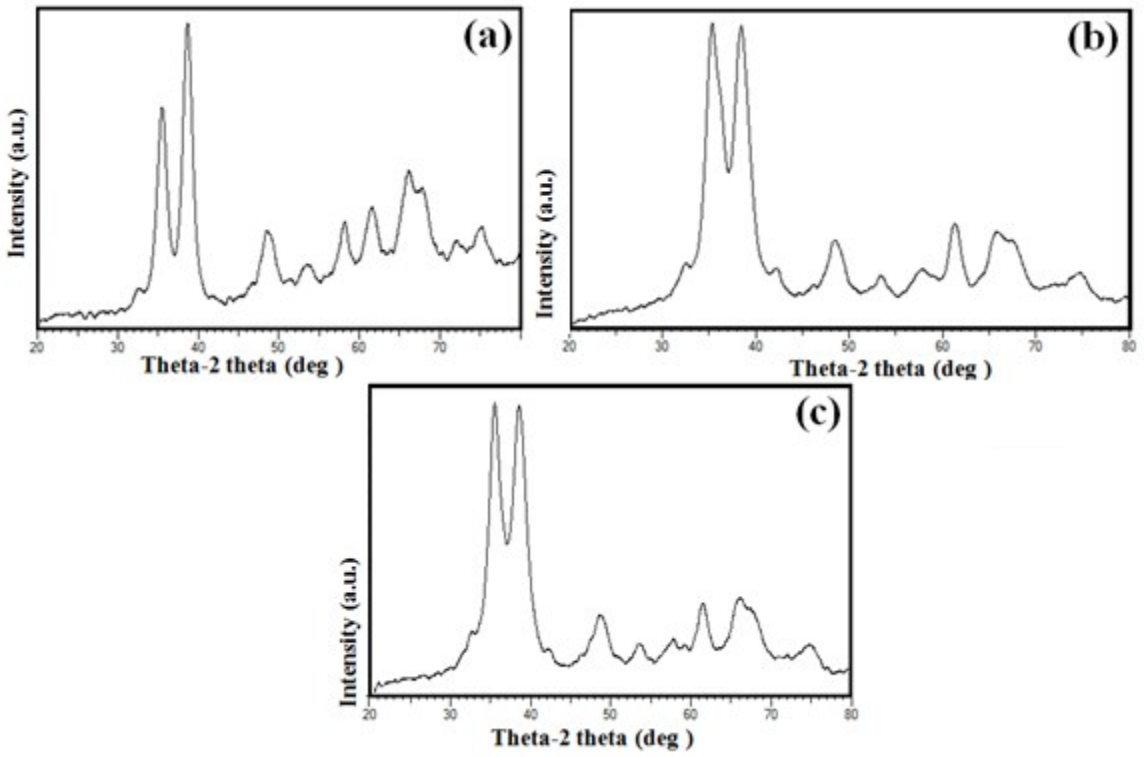


Fig. 1 XRD pattern of CuO NPs prepared at (a) 1:9 (b) 5:5 (i) 9:1 of EG/water

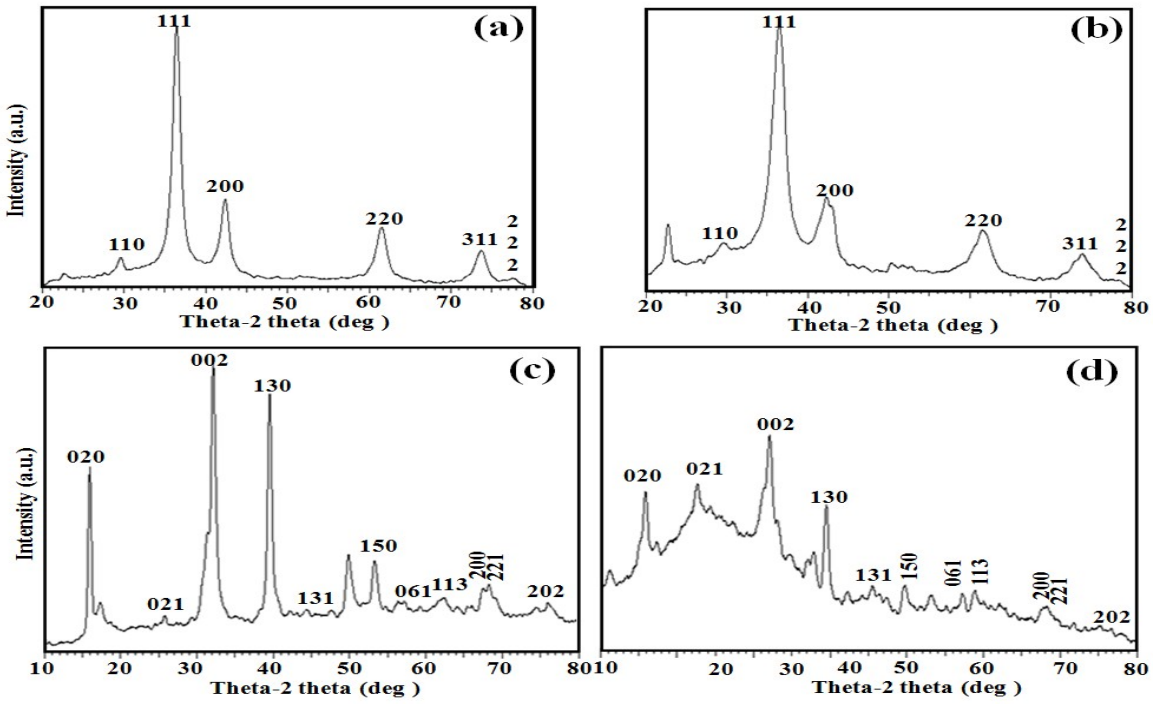


Fig. 2 XRD pattern: (a,b) Cu_2O NPs, (c,d) $Cu(OH)_2$ prepared at 3:7 and 7:3 of EG/ water at 600 W for 4 min.

2. Typical procedure for synthesis β-enaminoes and β-enamino esters

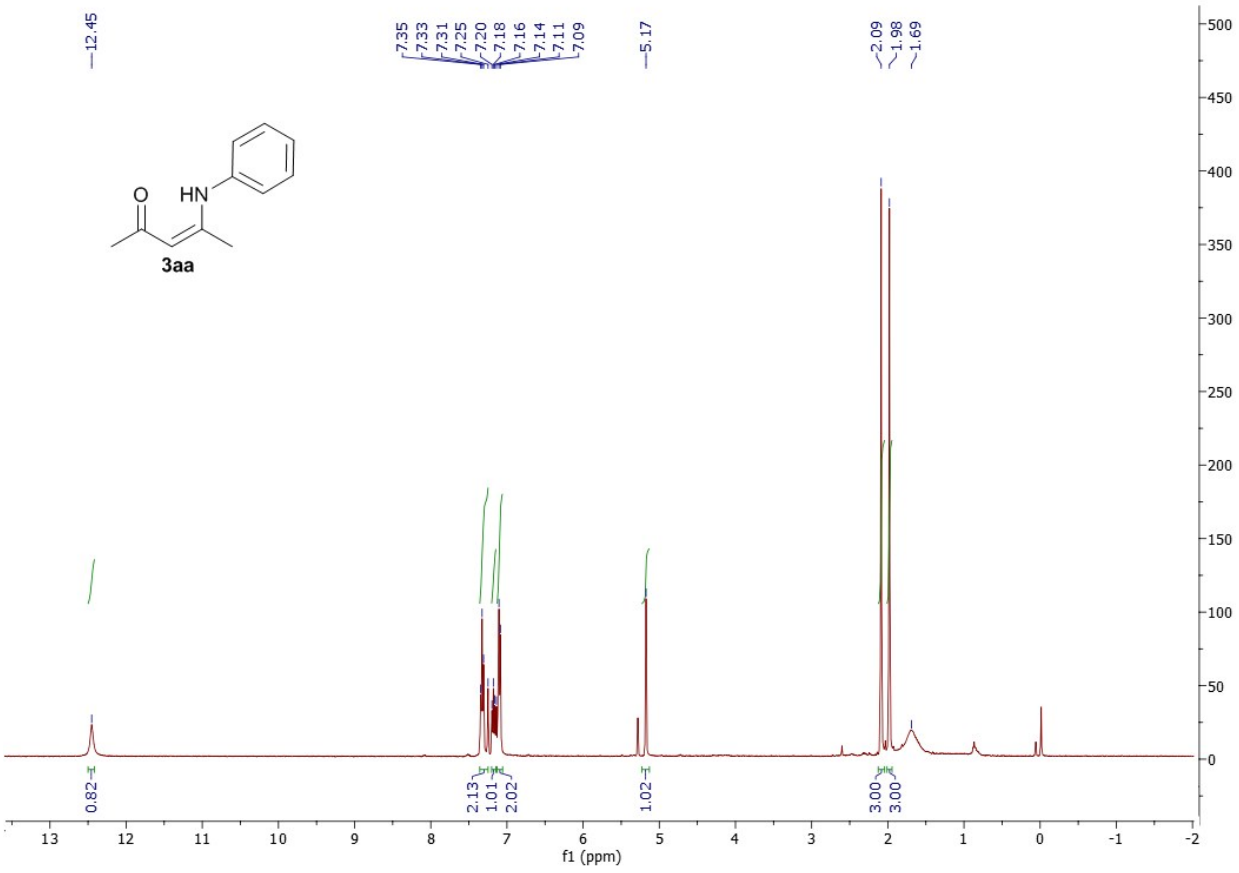
The experiment was carried out in 25 mL reaction vial, in a typical reaction procedure; the CuO NPs as catalyst was introduced into a reaction vial containing acetylacetone (1 mmol) and an amine (1 mmol). The reaction mixture was stirred at 60 °C temperature for 9 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was recovered by filtration. The mixture was concentrated under vacuum. The residue was purified by chromatography to afford the desired compound. All products are well known in

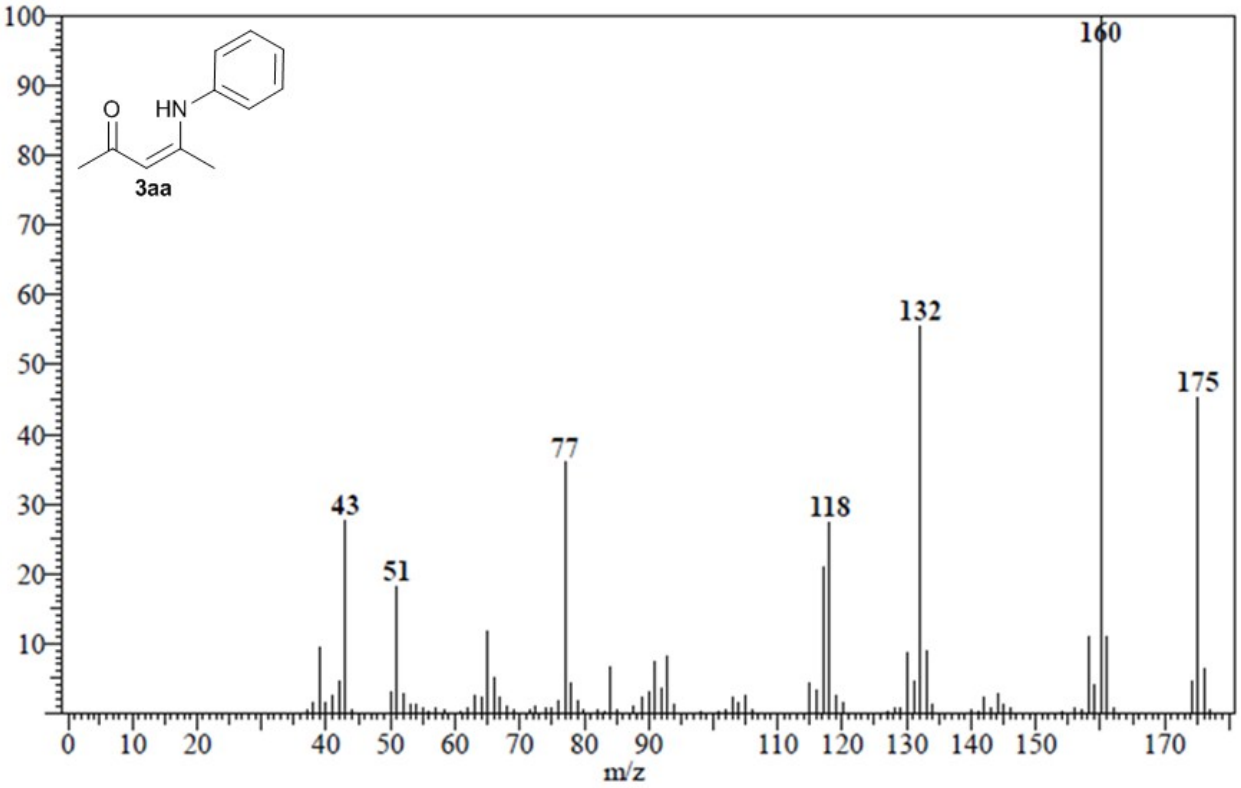
the literature and were characterized using GC-MS (Shimadzu QP 2010) and were also compared with authentic samples.

Characterisation data

1) 4-(phenylamino)pent-3-en-2-one (3aa)

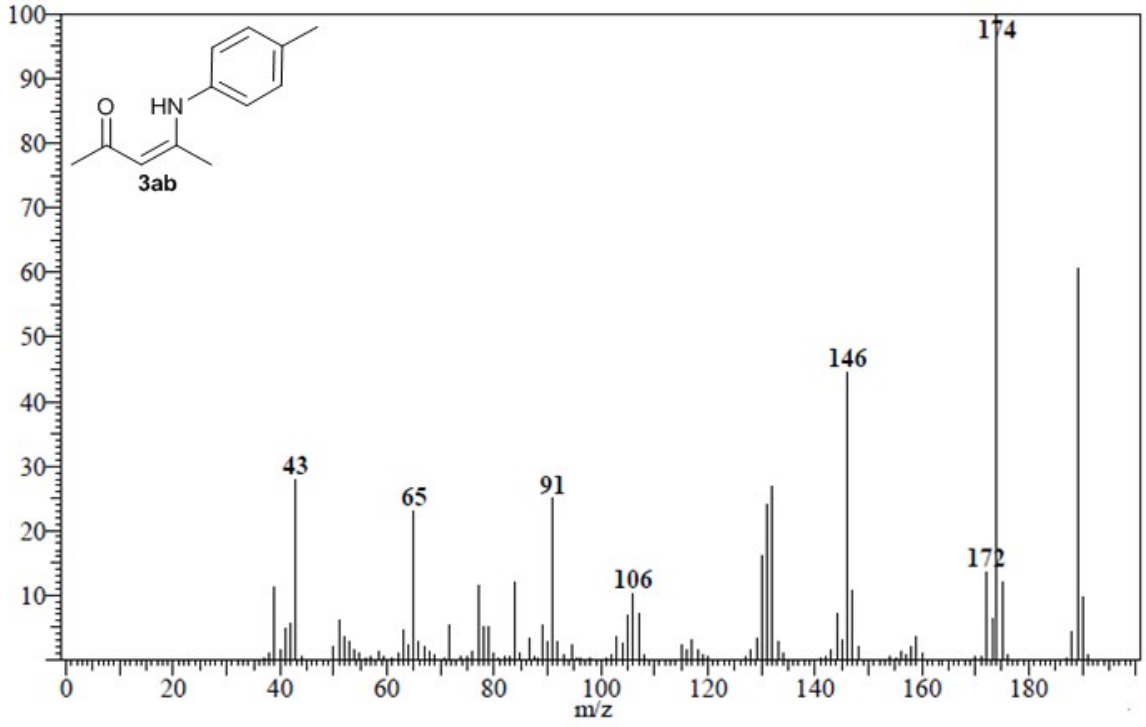
Yellow solid, m.p (46 °C), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.45 (s, 1H), 7.31 (m, 2H), 7.17 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 5.17 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H). **GC-MS** (EI, 70 eV): m/z (%) = 176 (6) [M+], 175 (45), 160 (100), 132 (56), 118 (38), 77 (35), 51 (19), 44 (39).




O
HN
3aa
100
90
80
70
60
50
40
30
20
10
0
10
20
40
50
60
70
80
90
110
120
130
140
150
170
m/z
160
132
175
77
43
118
51

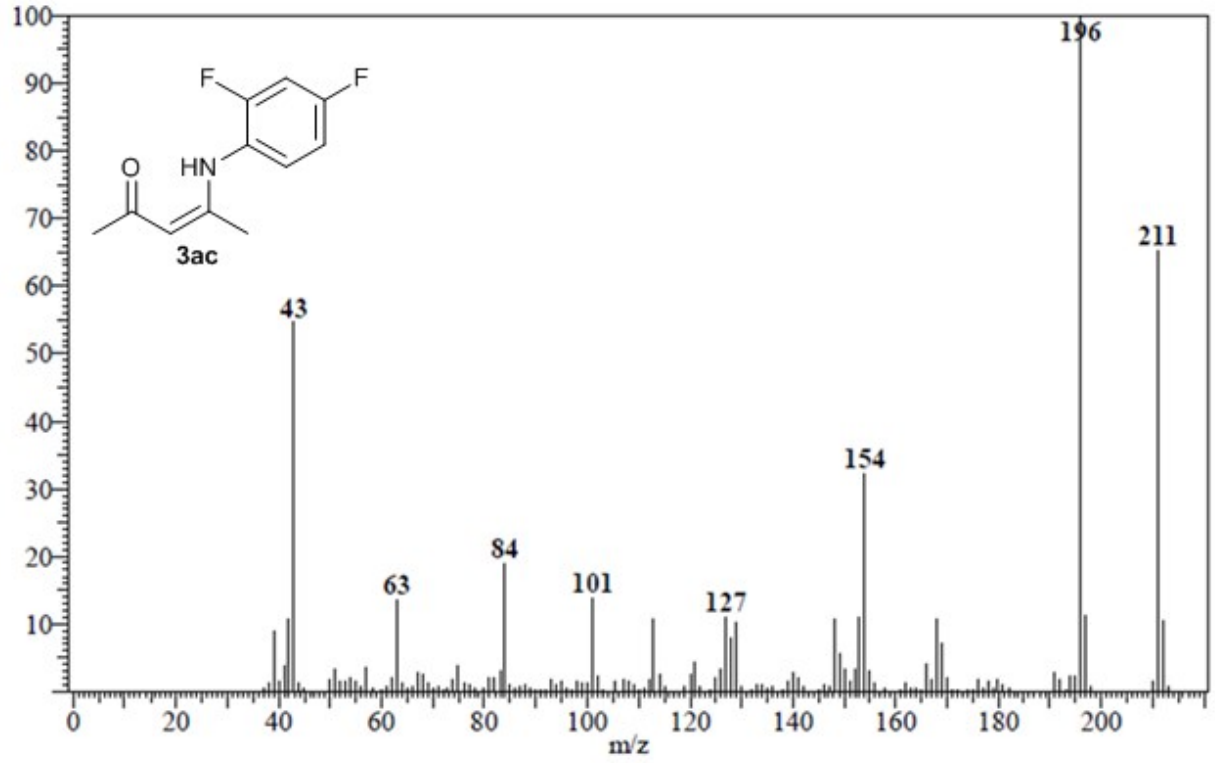
2) 4-(p-tolylamino)pent-3-en-2-one (3ab)

Yellow solid, m.p (58 °C), **GC-MS** (EI, 70 eV): m/z (%) = 190 (10) [M+], 189 (60), 174 (100), 146 (44), 106 (10), 91 (25), 65 (19), 43 (37).



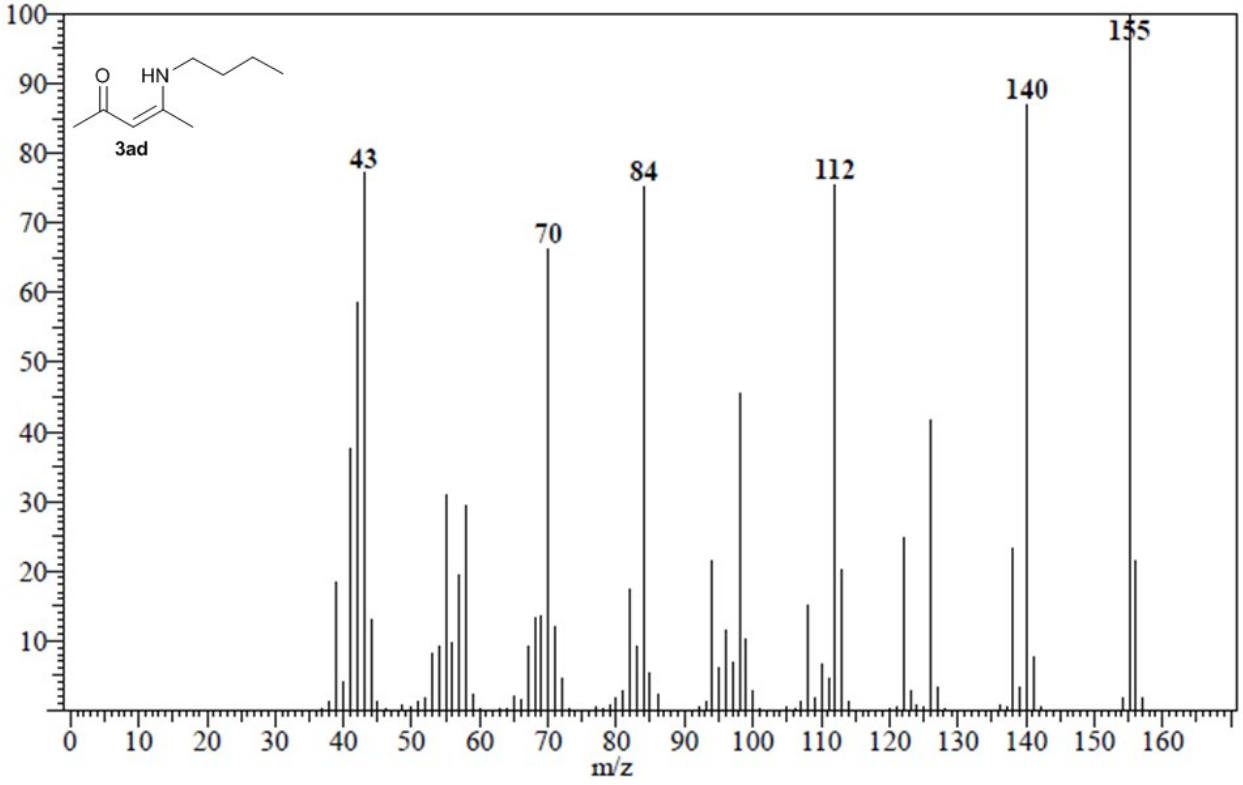
3) 4-((2,4-difluorophenyl)amino)pent-3-en-2-one (3ac)

Yellow solid, m.p (46 °C), **GC-MS** (EI, 70 eV): m/z (%) = 212 (10) [M+], 211 (66), 196 (100), 154 (32), 127 (11), 101 (14), 84 (19), 63 (14), 43 (55).



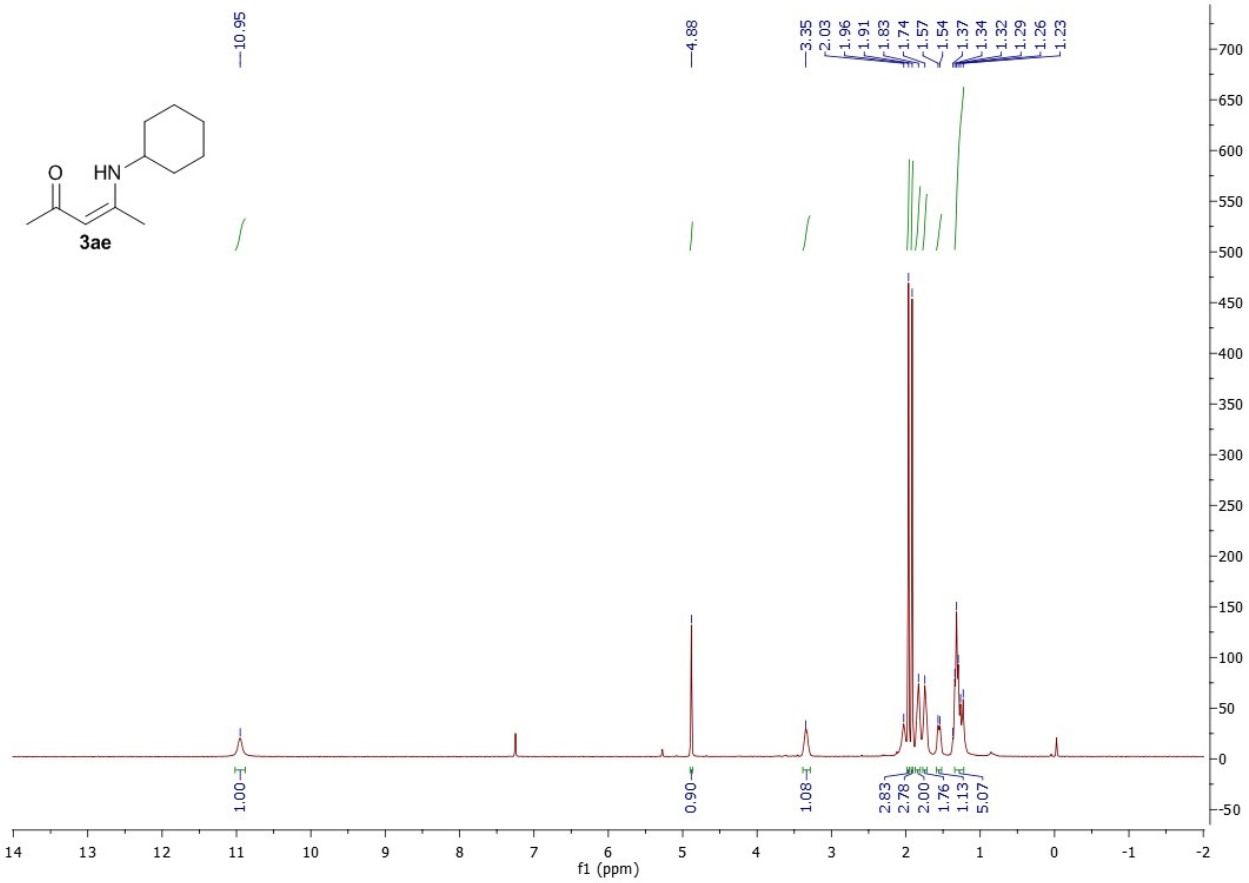
4) 4-(butylamino)pent-3-en-2-one (3ad)

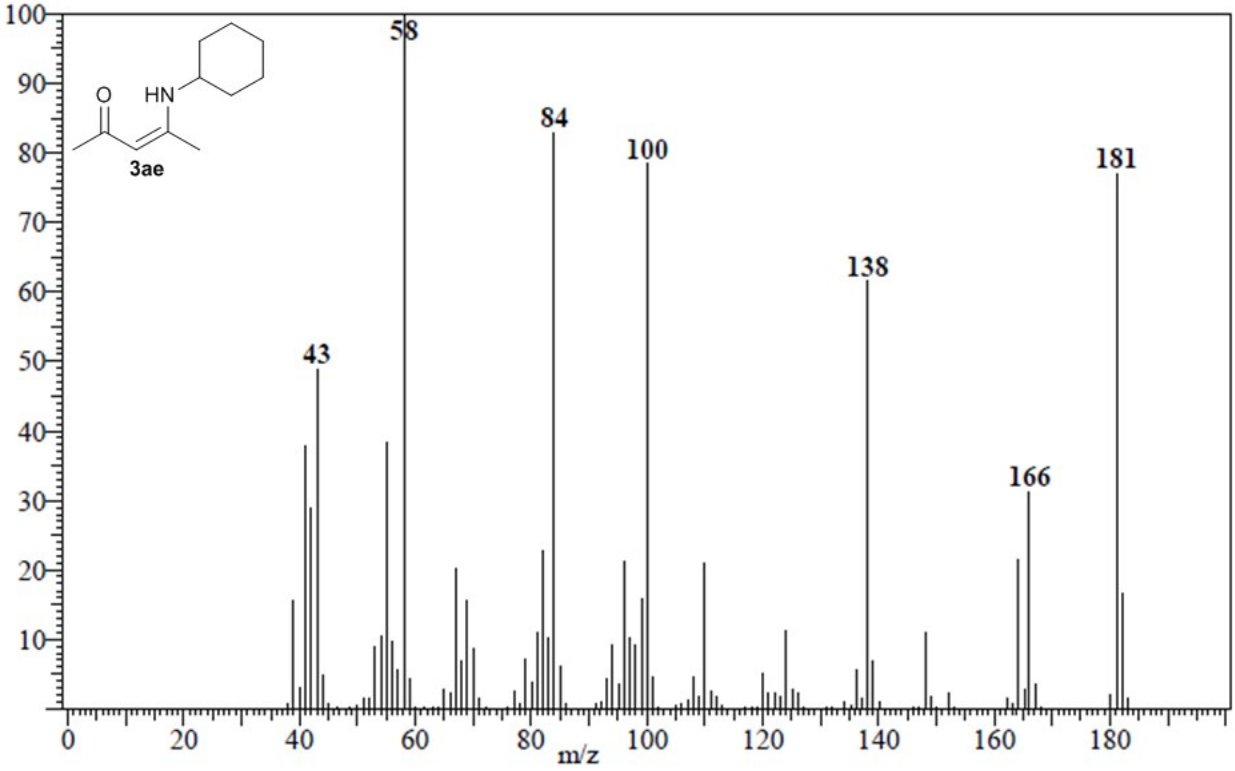
Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 156 (22) [M+], 155 (100), 140 (86), 112 (75), 84 (86), 70 (66), 43 (77).



5) 4-(cyclohexylamino)pent-3-en-2-one (3ae)

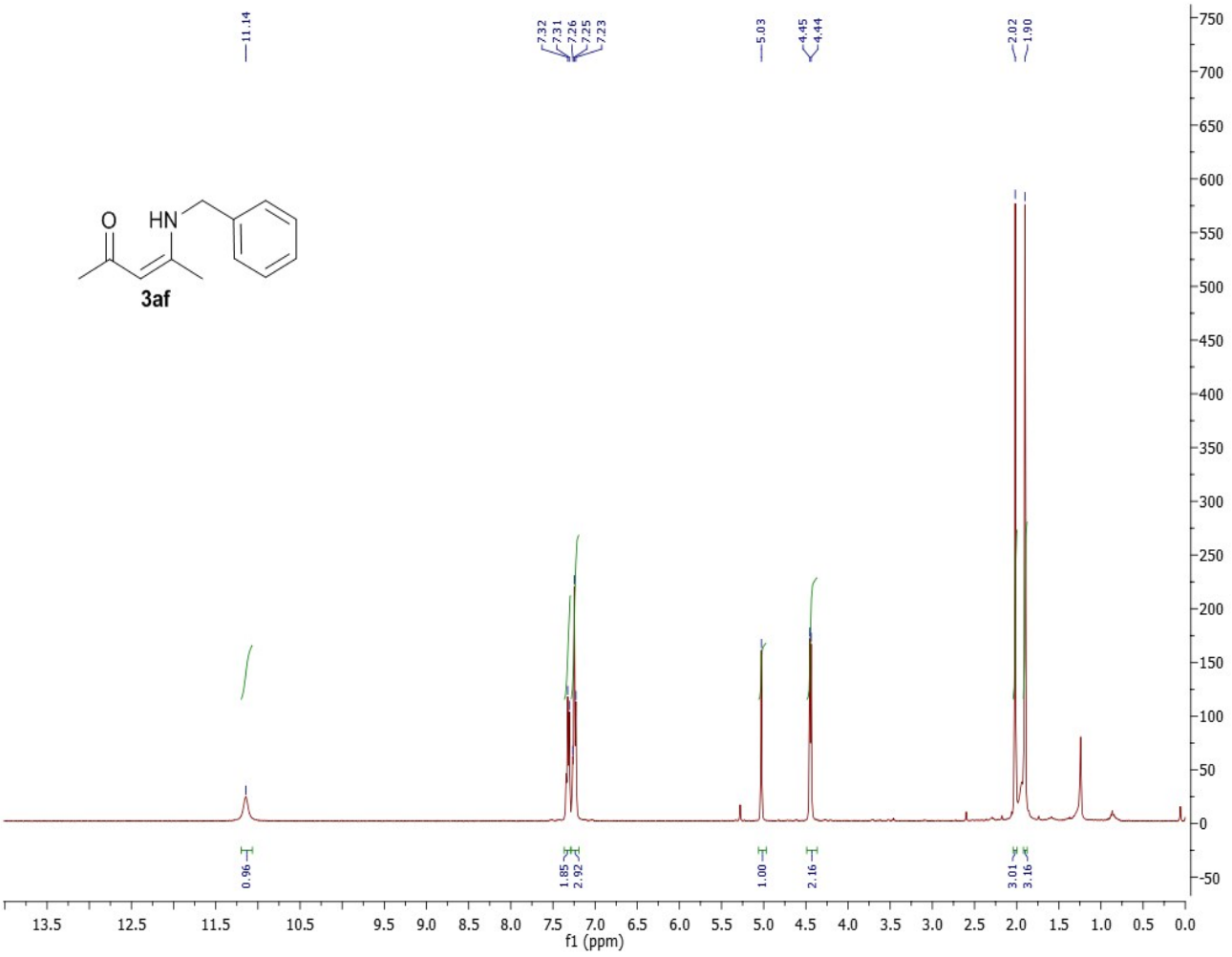
Yellow liquid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 4.88 (s, 1H), 3.35 (s,1H), 1.96 (s, 3H), 1.91 (s, 3H), 1.83 (s, 2H), 1.74 (s, 2H), 1.55 (d, J = 9.6 Hz, 1H), 1.36 – 1.21 (m, 5H). **GC-MS** (EI, 70 eV): m/z (%) = 182 (16) [M+], 181 (76), 166 (30), 138 (61), 100 (78), 84 (83), 58 (100), 43 (49).

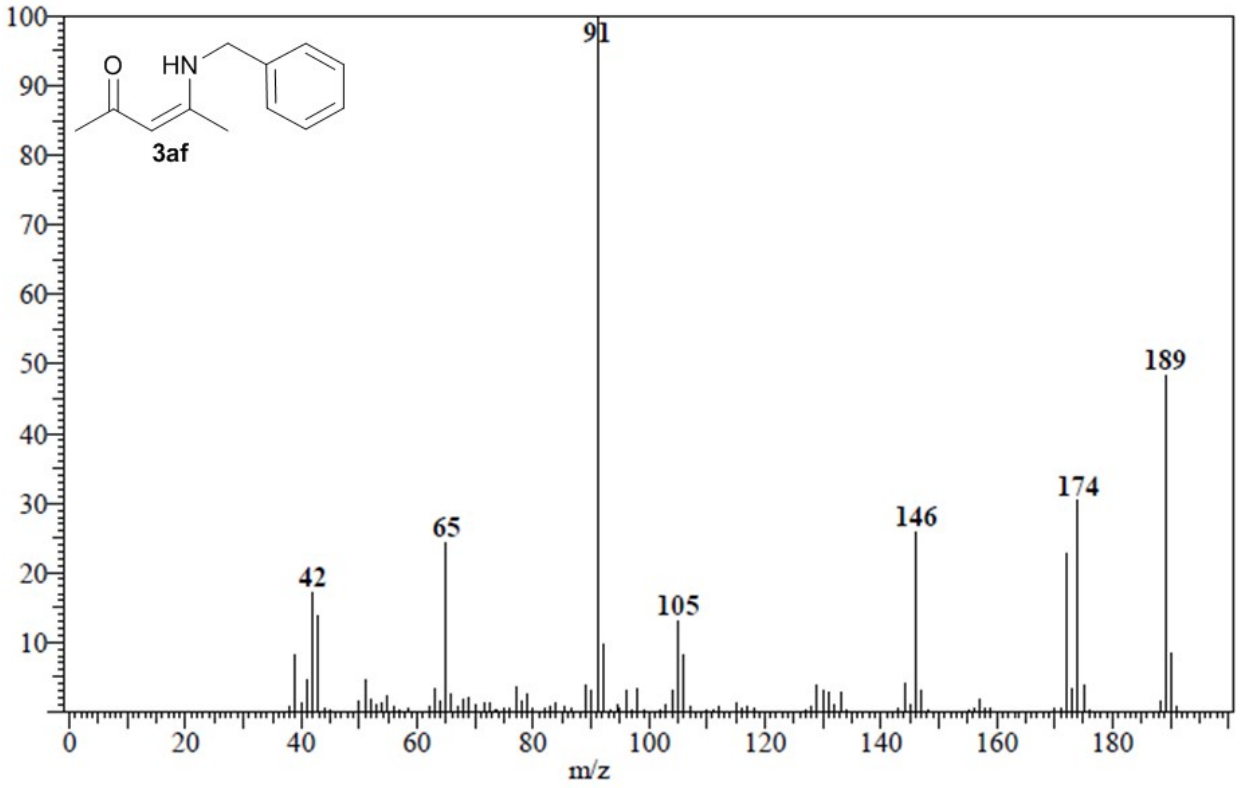



3ae
58
84
100
181
138
43
166
m/z

6) 4-(benzylamino)pent-3-en-2-one (3af)

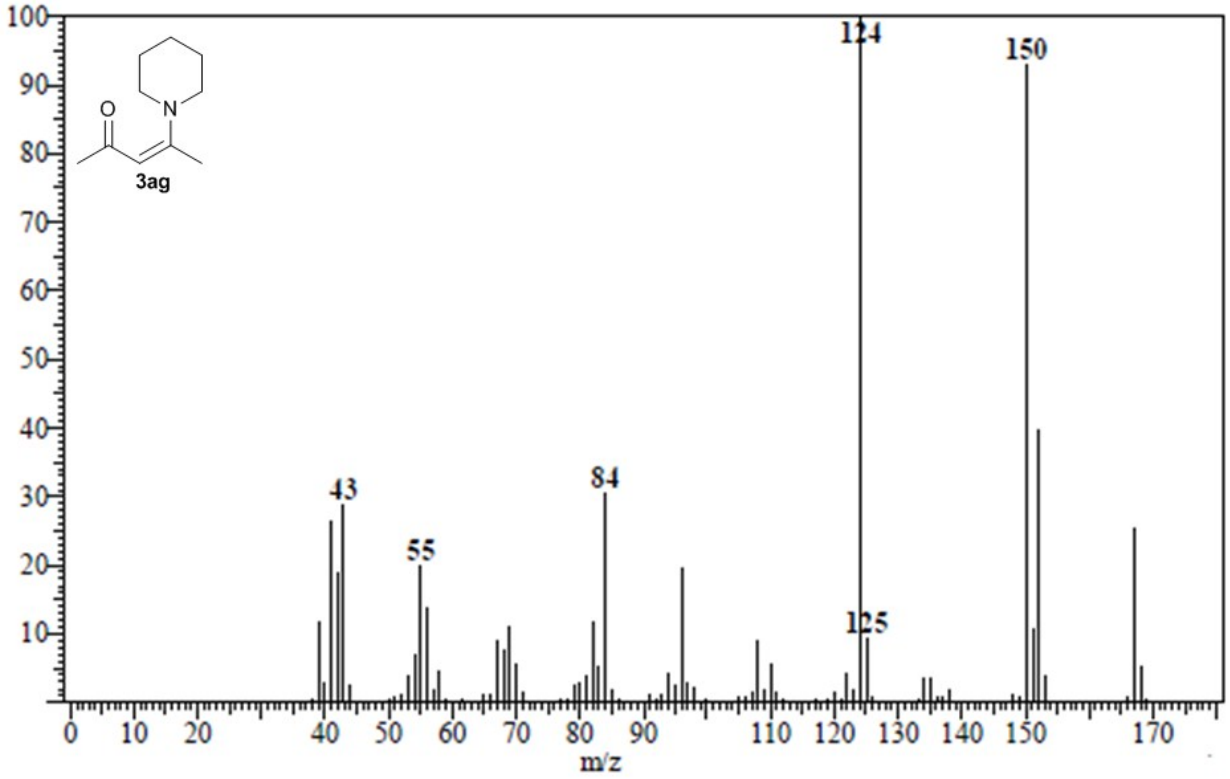
Yellow liquid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.14 (s, 1H), 7.32 (d, J = 7.1 Hz, 2H), 7.25 (t, J = 7.5 Hz, 3H), 5.03 (s, 1H), 4.44 (d, J = 6.3 Hz, 2H), 2.02 (s, 3H), 1.90 (s, 3H). **GC-MS** (EI, 70 eV): m/z (%) = 190 (9) [M+], 189 (48), 174 (33), 146 (26), 105 (12), 91 (100), 65 (19), 42 (17).




O
HN
3af
91
189
174
146
65
42
105
m/z

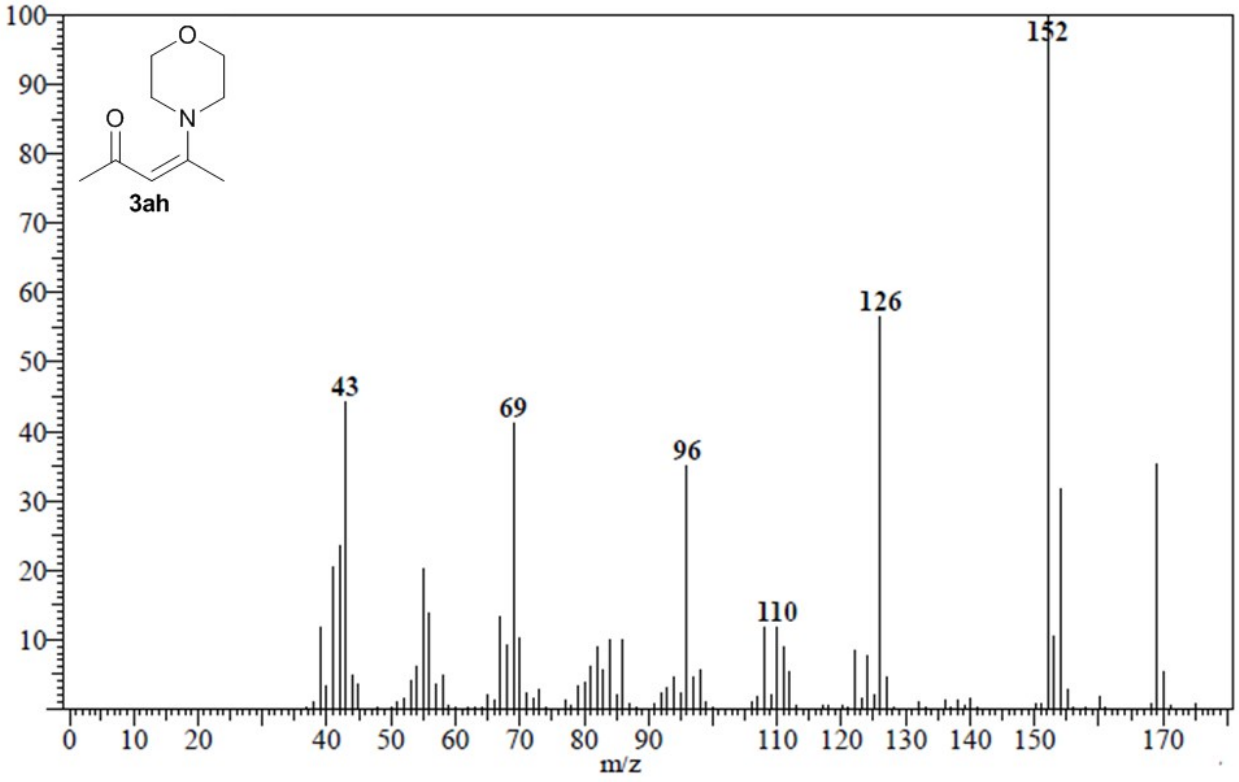
7) 4-(piperidin-1-yl)pent-3-en-2-one (3ag)

Yellow solid, m.p (49 °C), **GC-MS** (EI, 70 eV): m/z (%) = 168 (5) [M+], 167 (25), 150 (94), 125 (9), 124 (100), 84 (30), 55 (20), 43 (29).



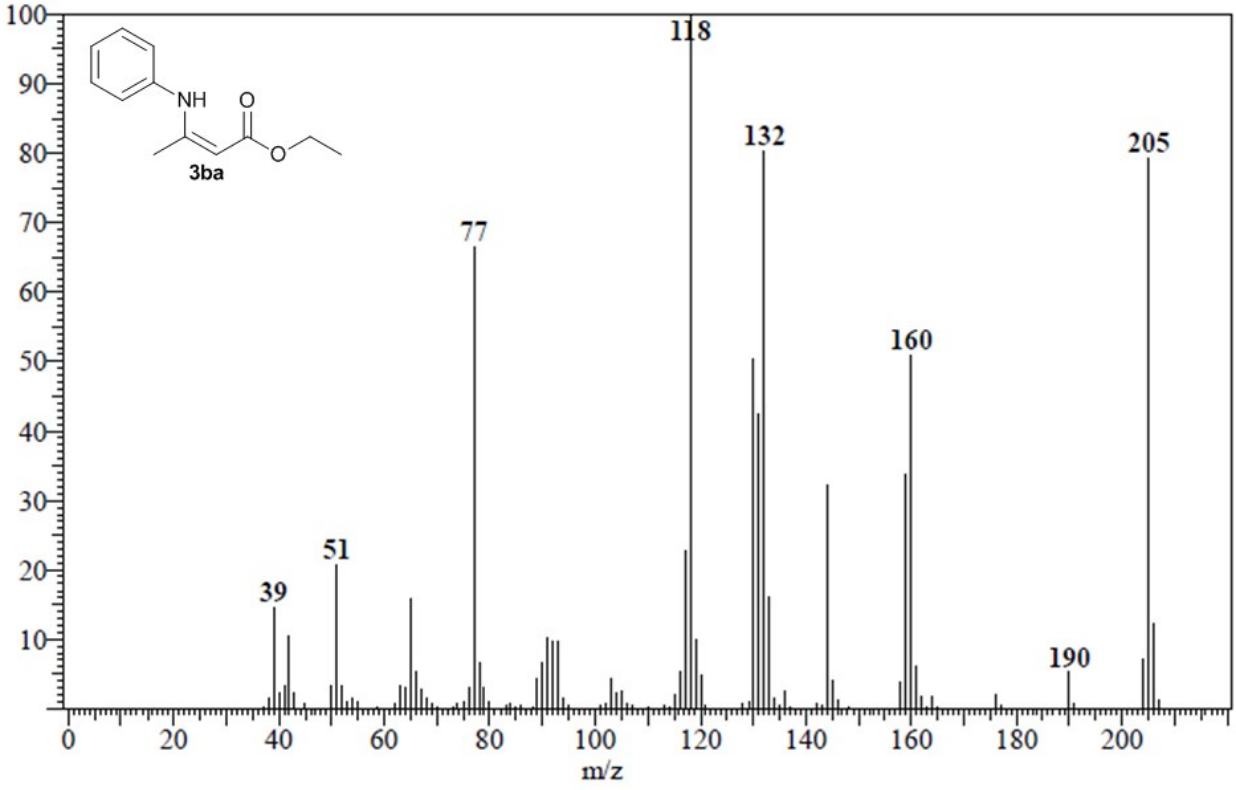
8) 4-morpholinopent-3-en-2-one (3ah)

Yellow oily liquid **, GC-MS** (EI, 70 eV): m/z (%) = 170 (5) [M+], 169 (35), 152 (100), 126 (56), 110 (12), 96 (34), 69 (42), 43 (44).



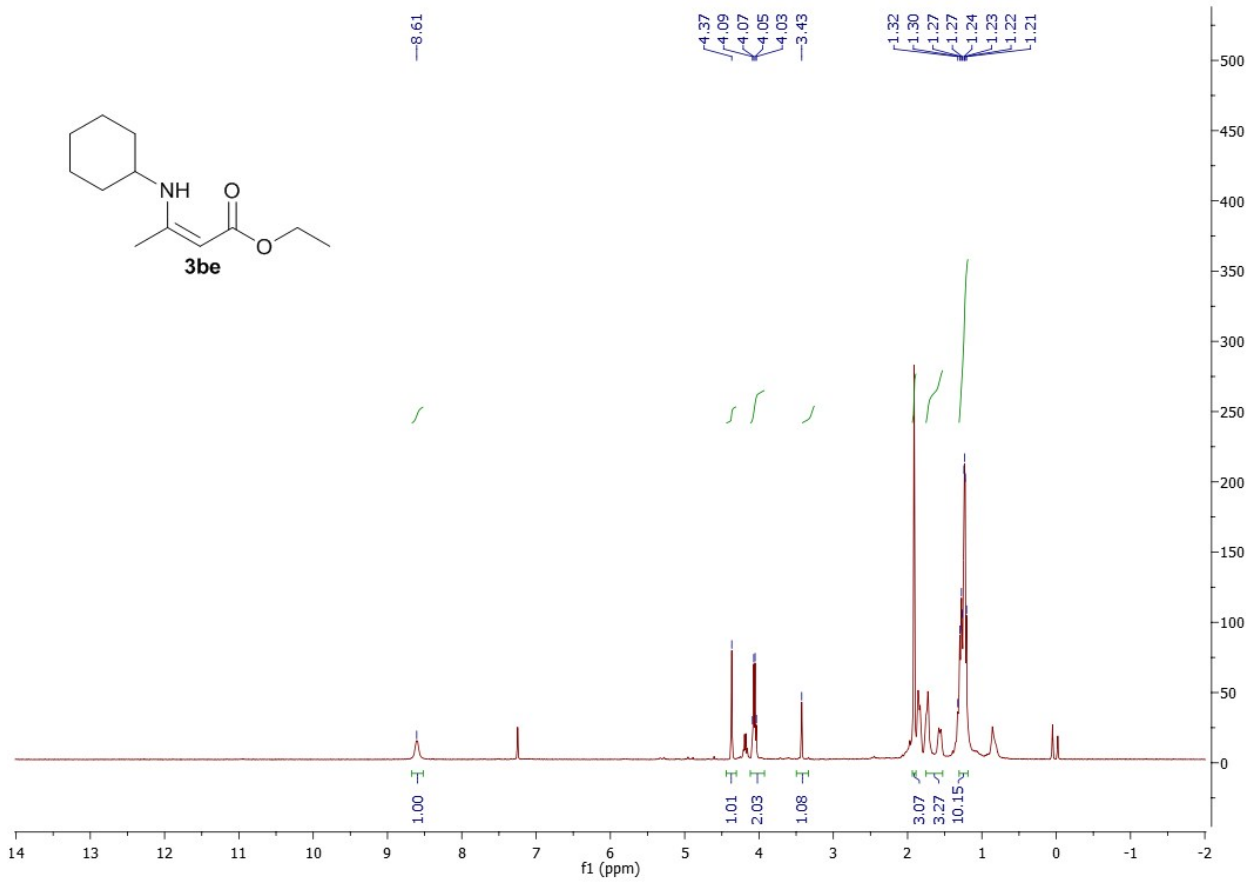
9) Ethyl 3-(phenylamino)but-2-enoate (3ba)

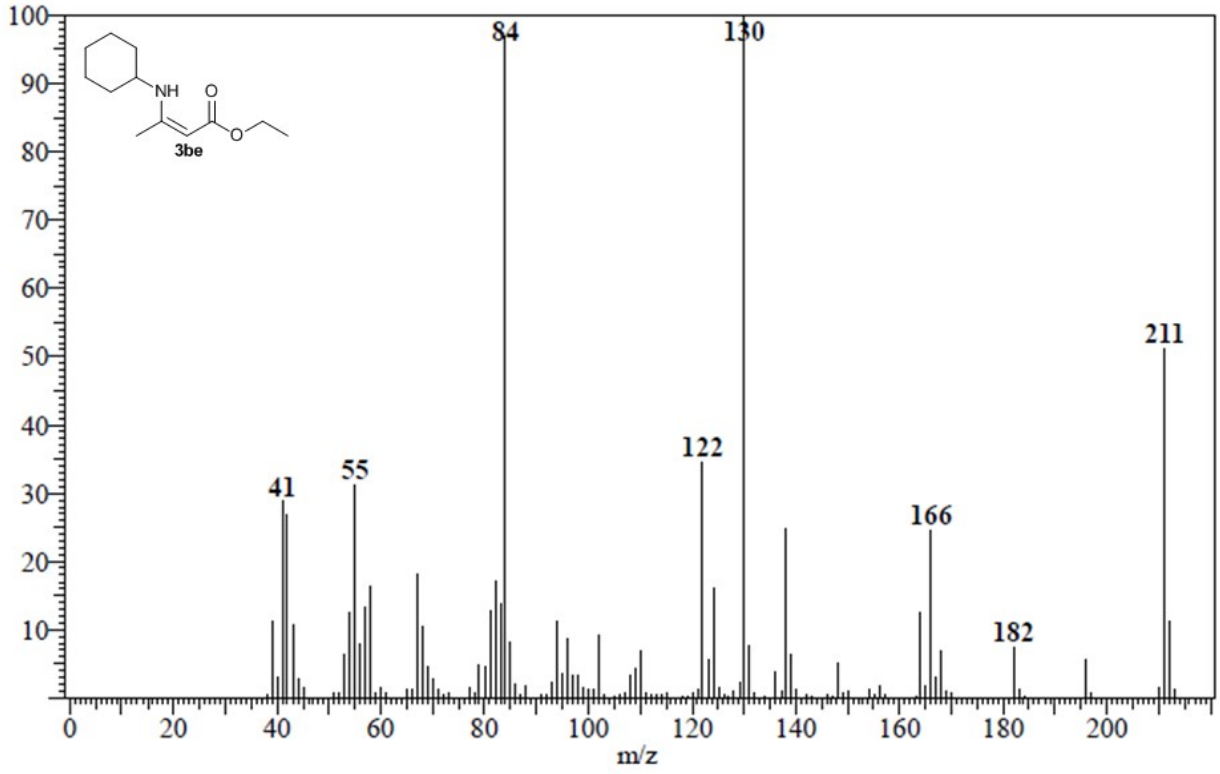
Yellow oily liquid, **GC-MS** (EI, 70 eV): m/z (%) = 206 (12) [M+], 205 (80), 190 (5), 160 (52), 132 (80), 118 (100), 77 (66), 51 (21), 39 (17).



10) Ethyl 3-(cyclohexylamino)but-2-enoate (3be)

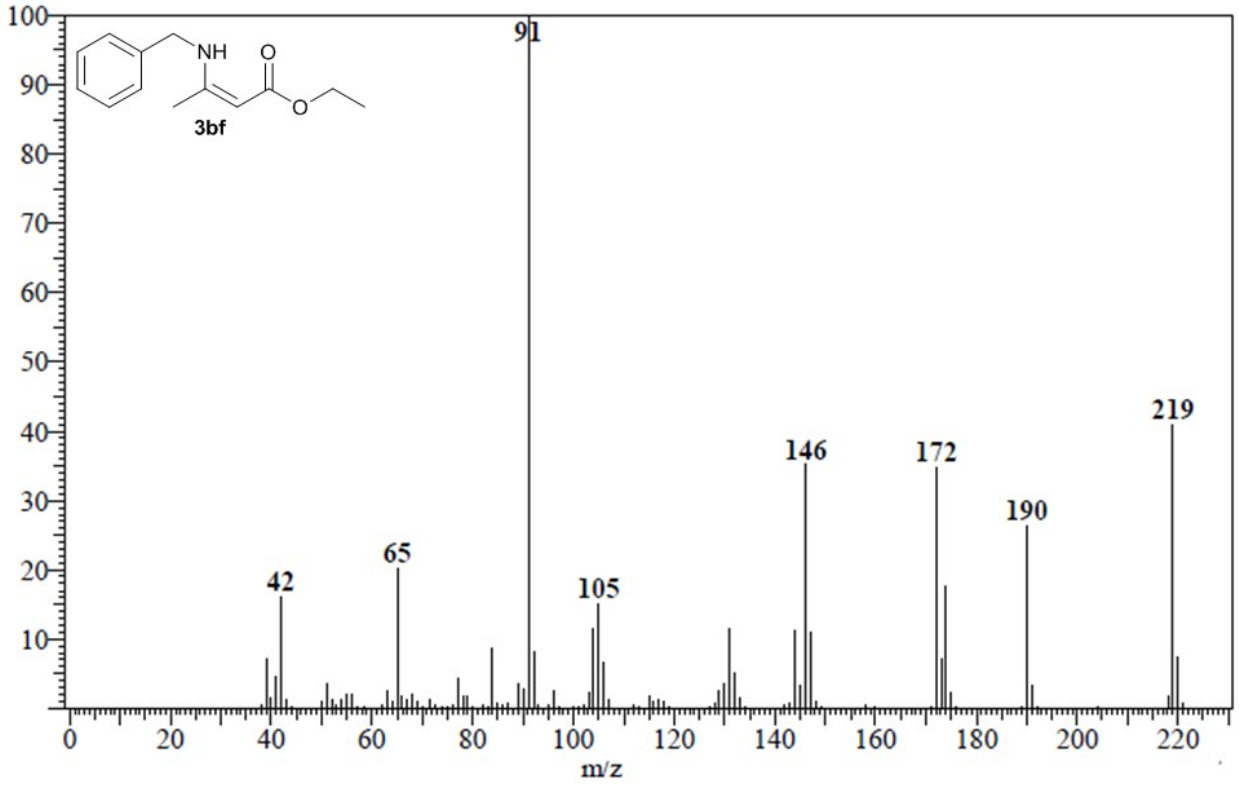
Yellow oily liquid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 4.37 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.29 (d, J = 5.3 Hz, 1H), 1.91 (s, 3H), 1.75 – 1.53 (m, 3H), 1.31 – 1.19 (m, 10H). **GC-MS** (EI, 70 eV): m/z (%) = 212 (11) [M+], 211 (31), 182 (7), 166 (25), 130 (100), 122 (35), 84 (96), 55 (31), 41 (39)




84
130
211
122
55
41
166
182
NH
O
O
3be
m/z

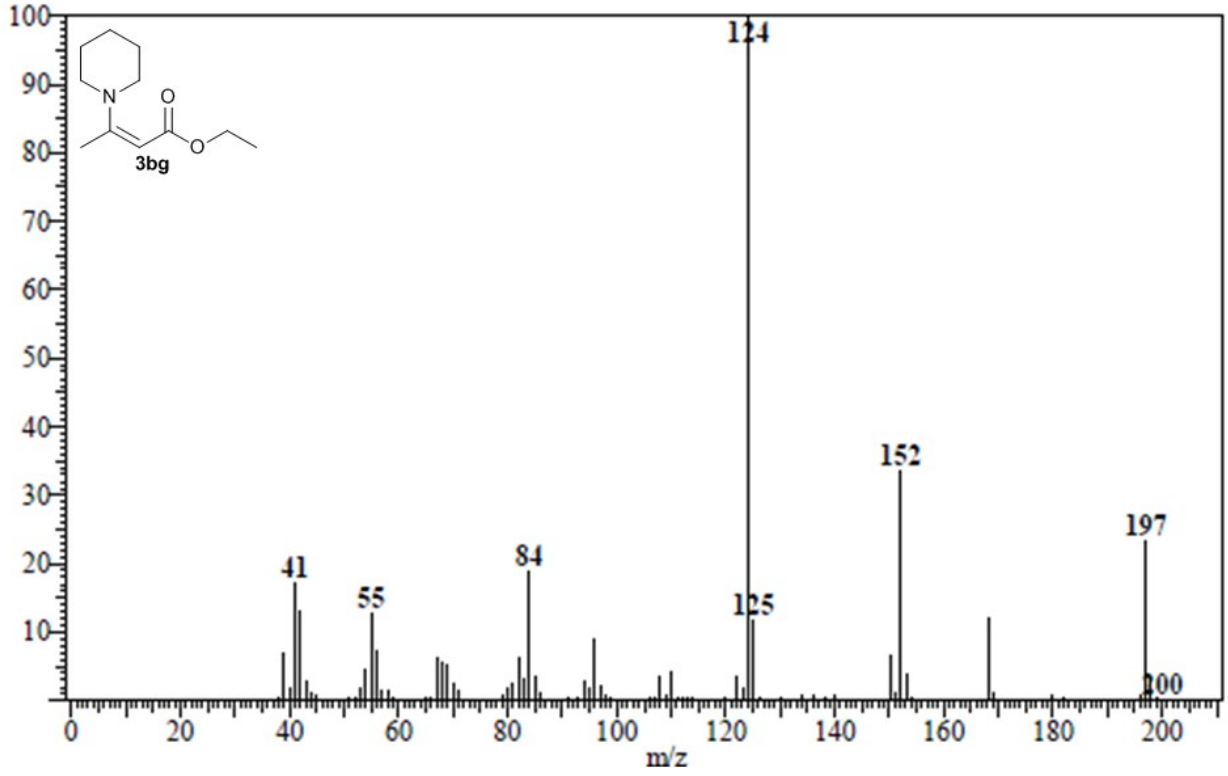
11) Ethyl 3-(benzylamino)but-2-enoate (3bf)

Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 220 (7) [M+], 219 (42), 172 (35), 146 (45), 105 (15), 91 (100), 65 (21), 42 (16).



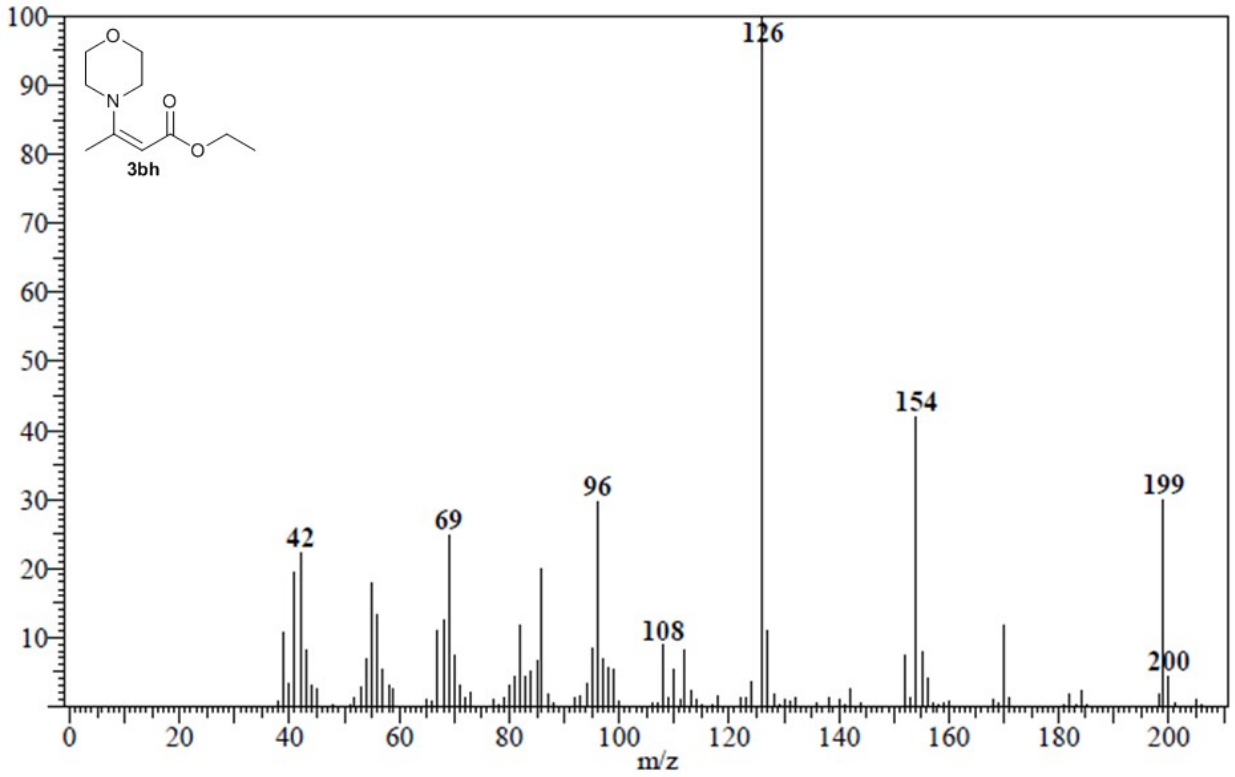
12) Ethyl 3-(piperidin-1-yl)but-2-enoate (3bg)

Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 198 (2) [M+], 197 (23), 152 (33), 124 (100), 84 (19), 55 (14), 41 (17).



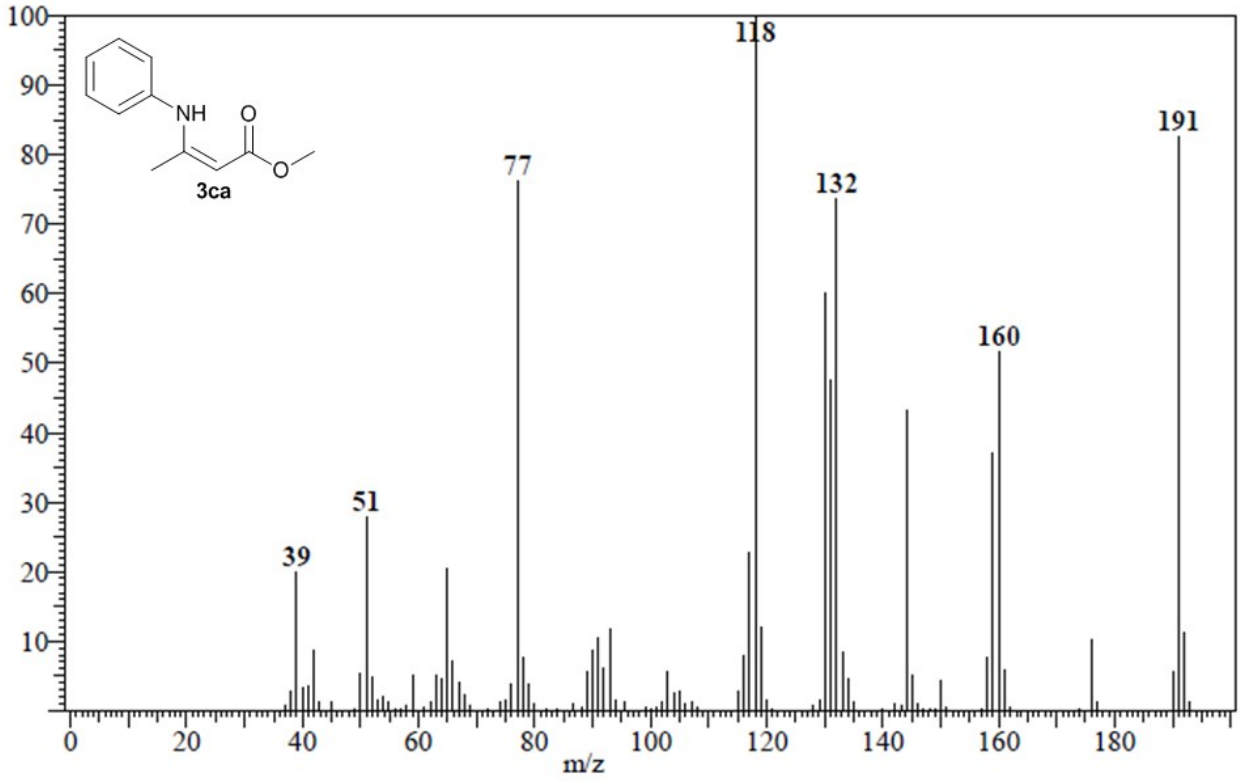
13) Ethyl 3-morpholinobut-2-enoate (3bh)

Yellow solid, m.p (56 °C), **GC-MS** (EI, 70 eV): m/z (%) = 200 (4) [M+], 199 (30), 154 (42), 126 (100), 108 (9), 96 (30), 69 (24), 42 (23).



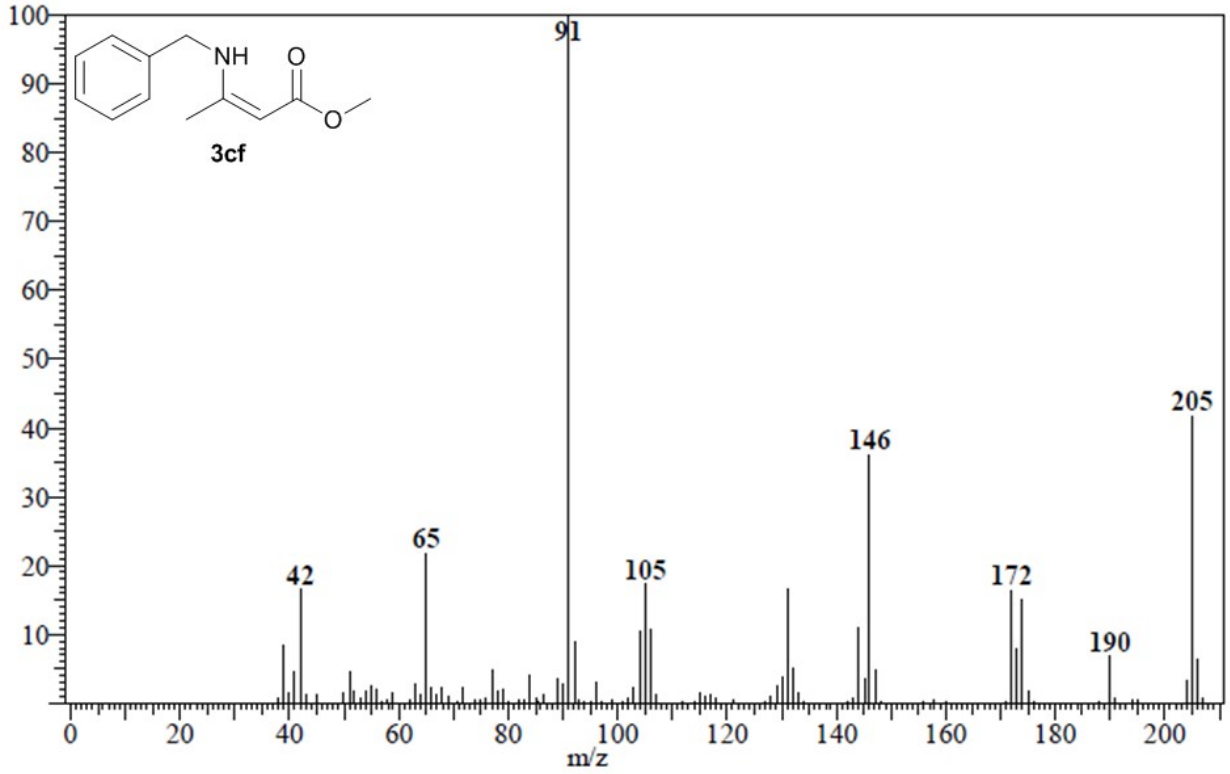
14) Methyl 3-(phenylamino)but-2-enoate (3ch)

Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 193 (1) [M+], 192 (10), 191 (82), 160 (51), 132 (73), 118 (100), 77 (76), 51 (27), 39 (20).



15) Methyl 3-(benzylamino)but-2-enoate (3ch)

Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 206 (4) [M+], 205 (41), 190 (6), 146 (35), 105 (16), 91 (100), 65 (21), 42 (16).



16) Methyl 3-morpholinobut-2-enoate (3ch)

Yellow liquid, **GC-MS** (EI, 70 eV): m/z (%) = 186 (5) [M+], 185 (31), 154 (36), 126 (100), 108 (9), 96 (34), 69 (22), 42 (23).