Electronic Supplementary Information

Oxidative Functionalization of Aliphatic and Aromatic Amino Acid Derivatives with H_2O_2 Catalyzed by a Nonheme Imine Based Iron Complex

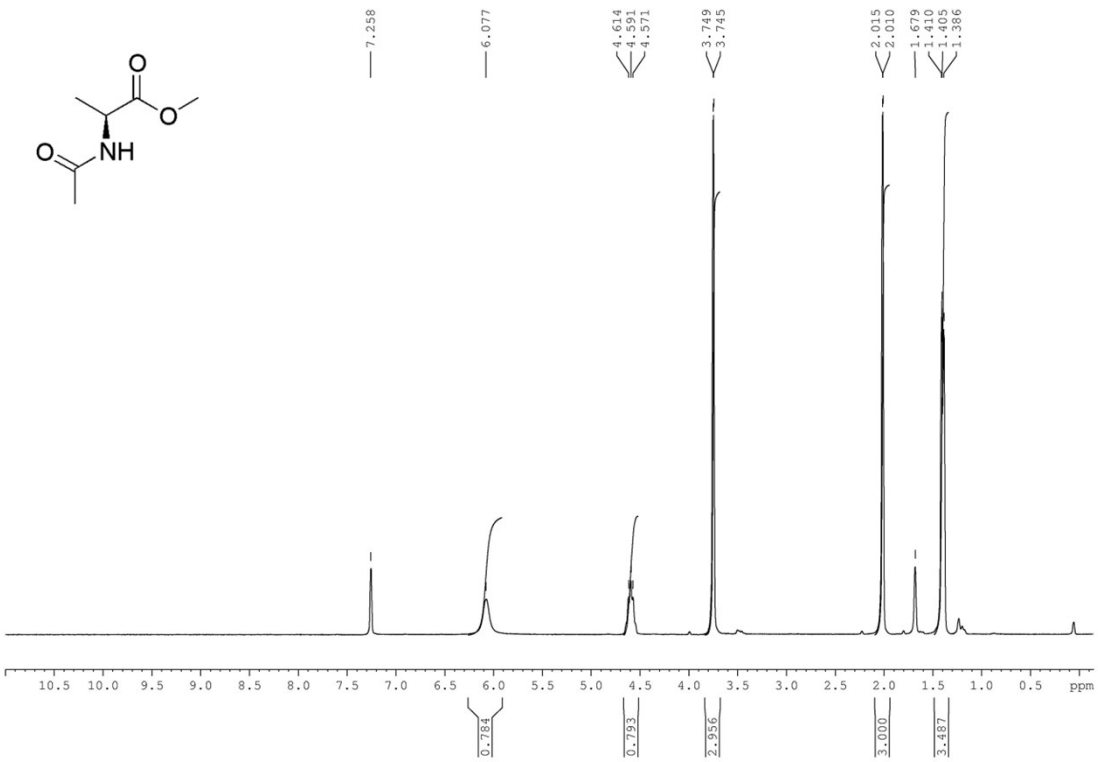
Barbara Ticconi,[a] Arianna Colcerasa,[a] Stefano Di Stefano,[a] Osvaldo Lanzalunga,[a]* Andrea Lapi,[a] Marco Mazzonna[a] and Giorgio Olivo[b]

[a] Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza" and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, I-00185 Rome, Italy; Phone: +390649913711; Fax: +390649913629; Email: osvaldo.lanzalunga@uniroma1.it

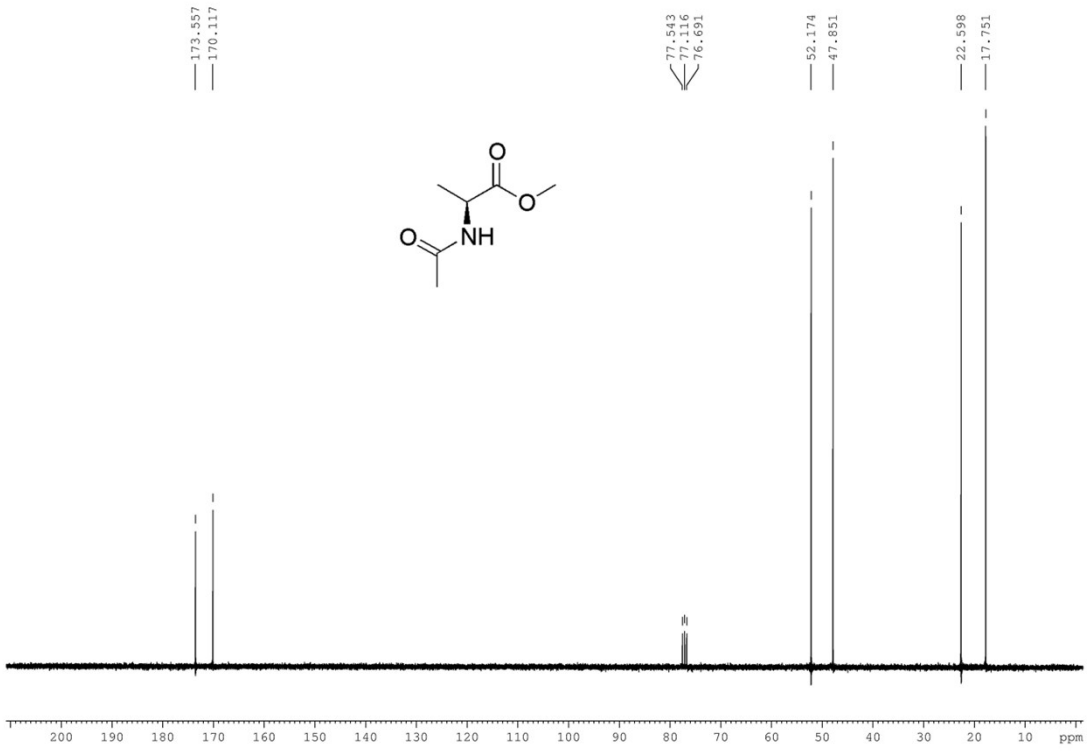
[b] Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain.

Content

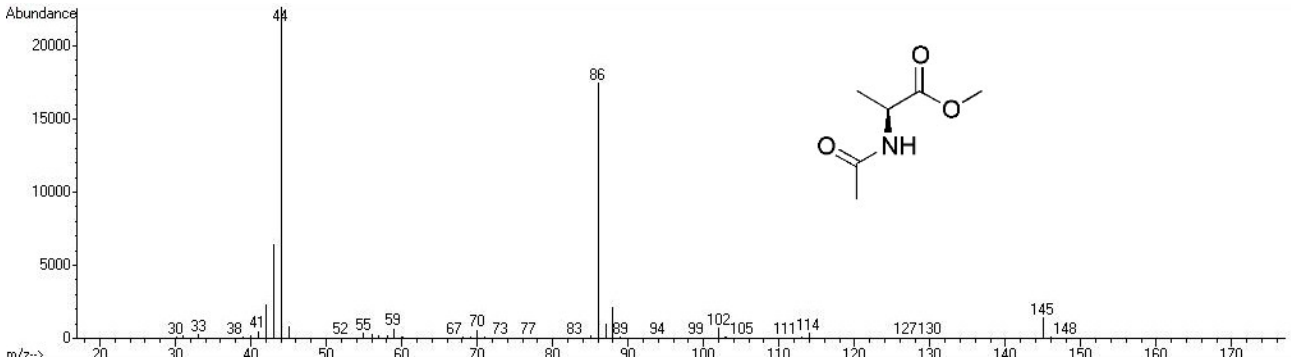
N-AcAlaOMe (**2**)[1]



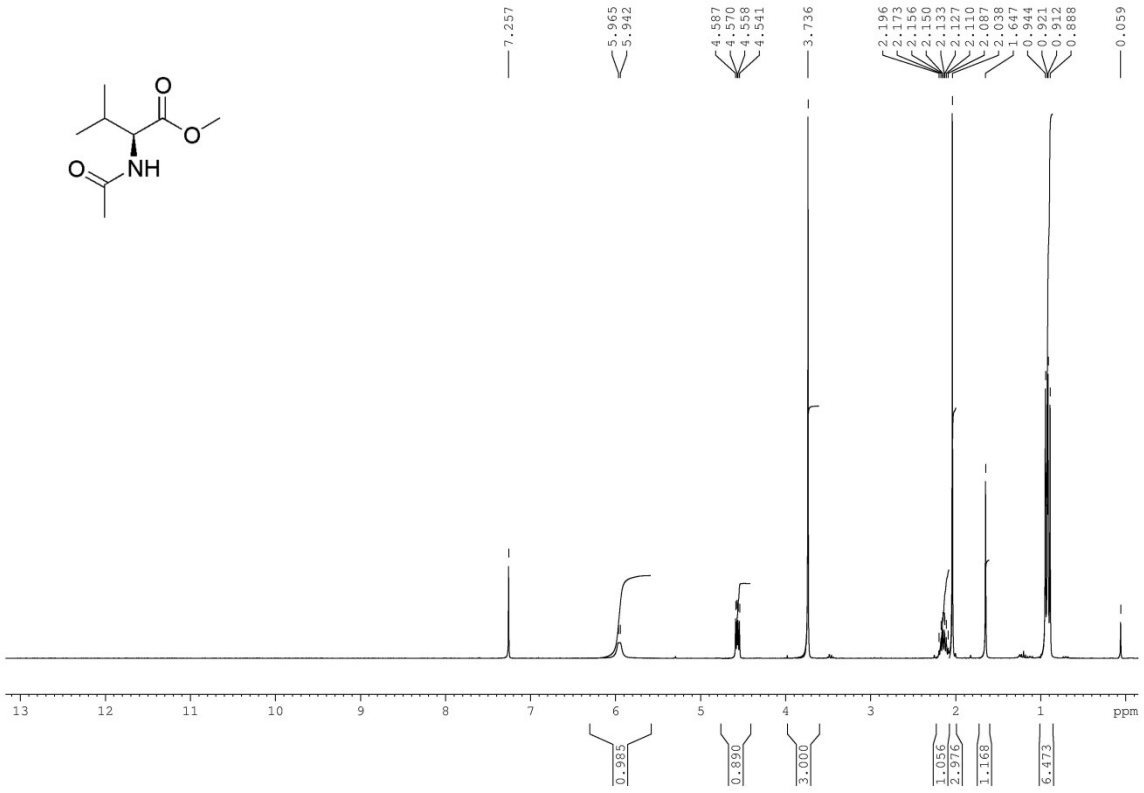
$CDCl_3$ (300 MHz)



$CDCl_3$ (75 MHz)



N-AcValOMe (**3**)[1]



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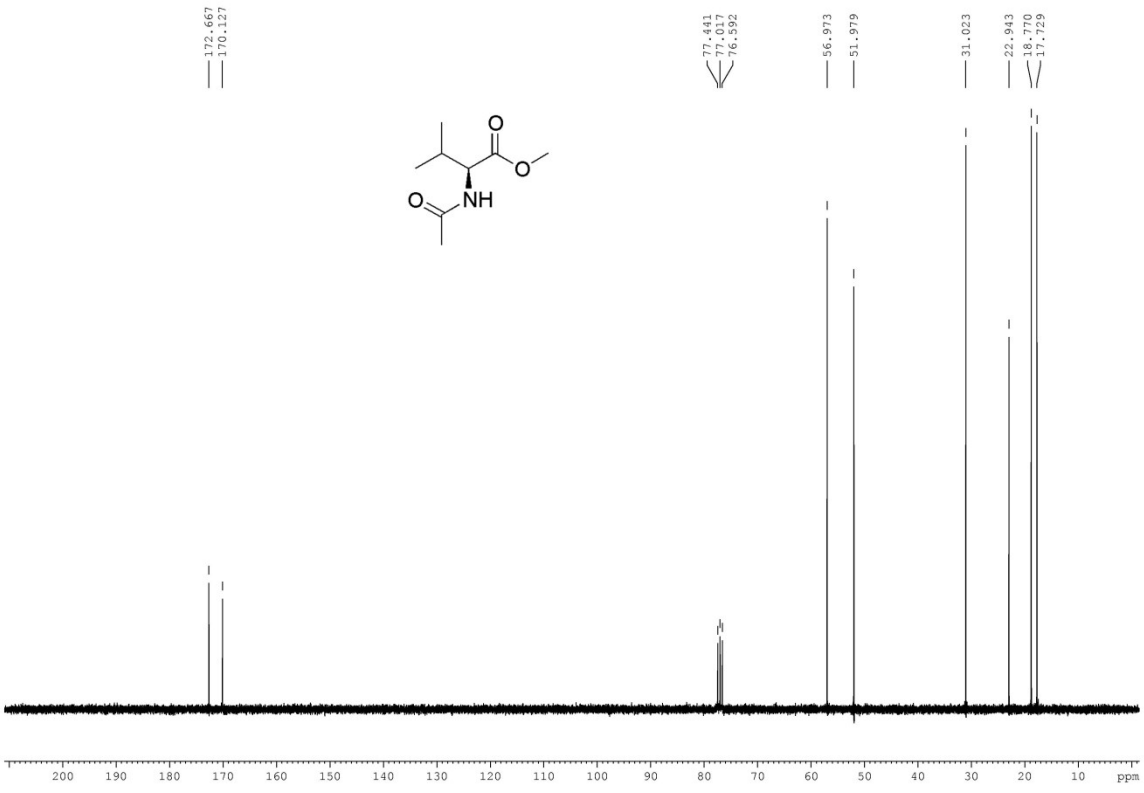
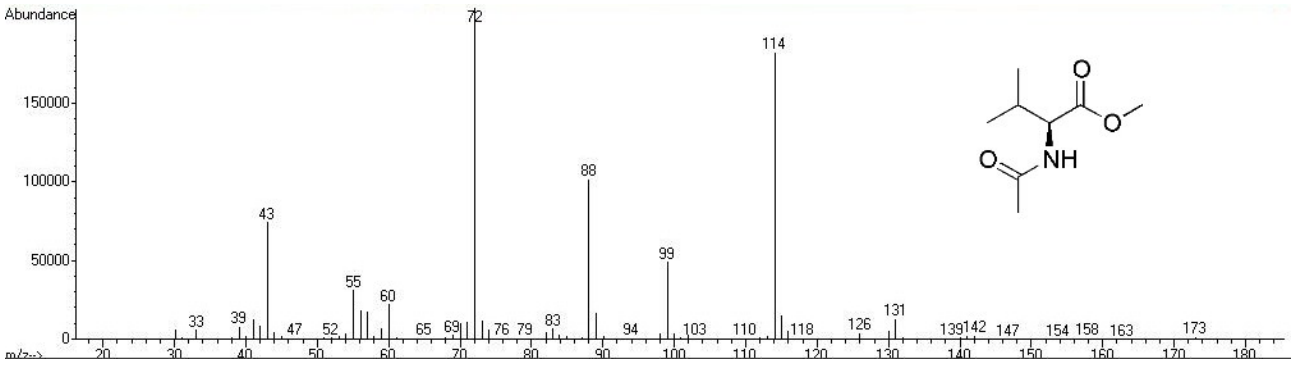
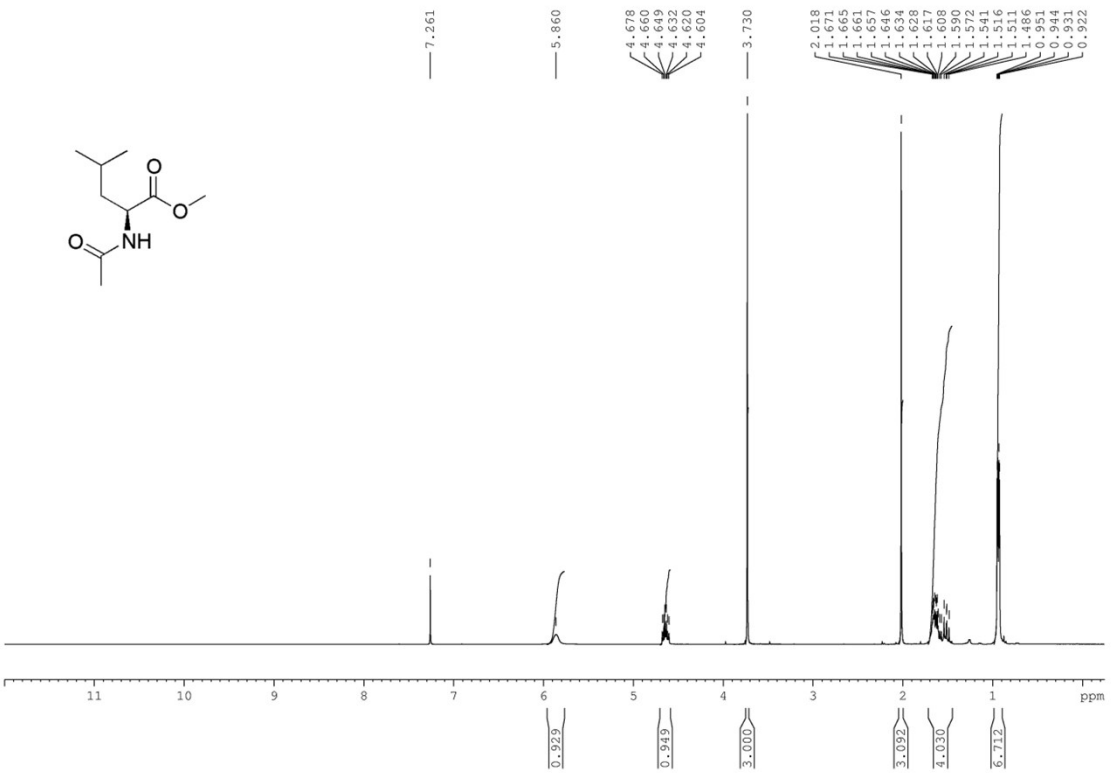

172.667
170.127
77.441
77.017
76.592
56.973
51.979
31.023
22.943
18.770
17.729
O
O
O
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

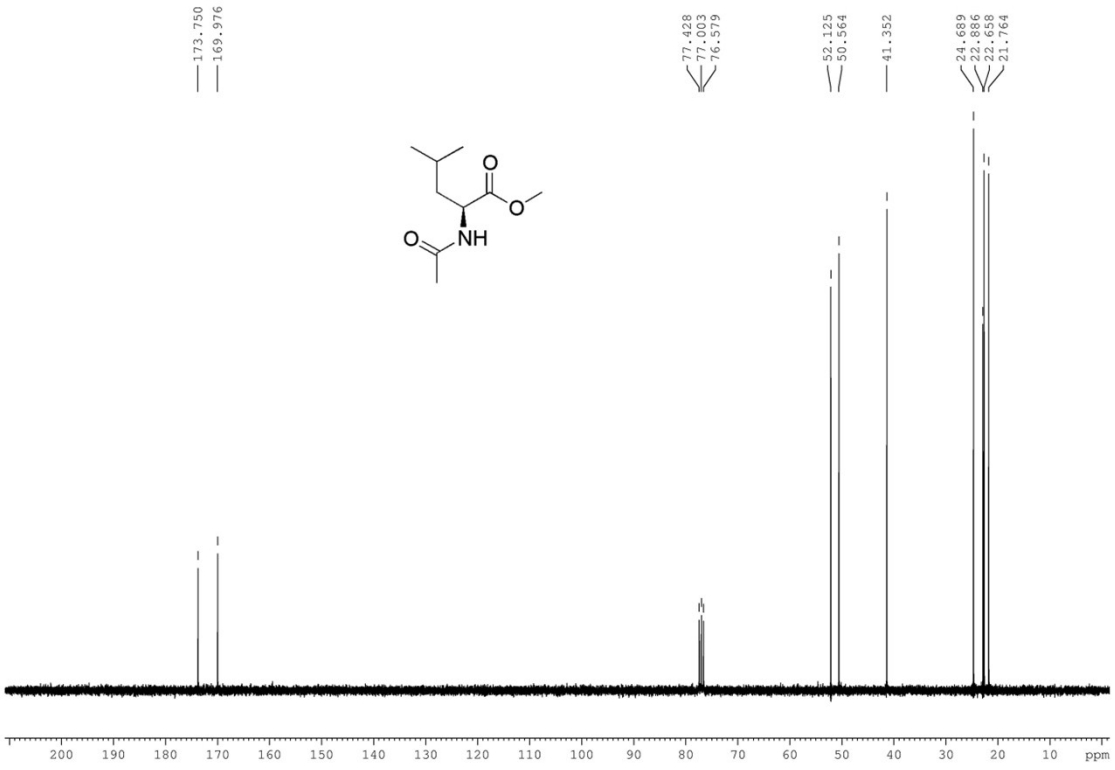
$CDCl_3$ (75 MHz)


Abundance
150000
100000
50000
0
72
114
88
43
99
55
60
33
39
47
52
65
69
76
79
83
94
103
110
118
126
131
139
142
147
154
158
163
173
O
O
O
NH

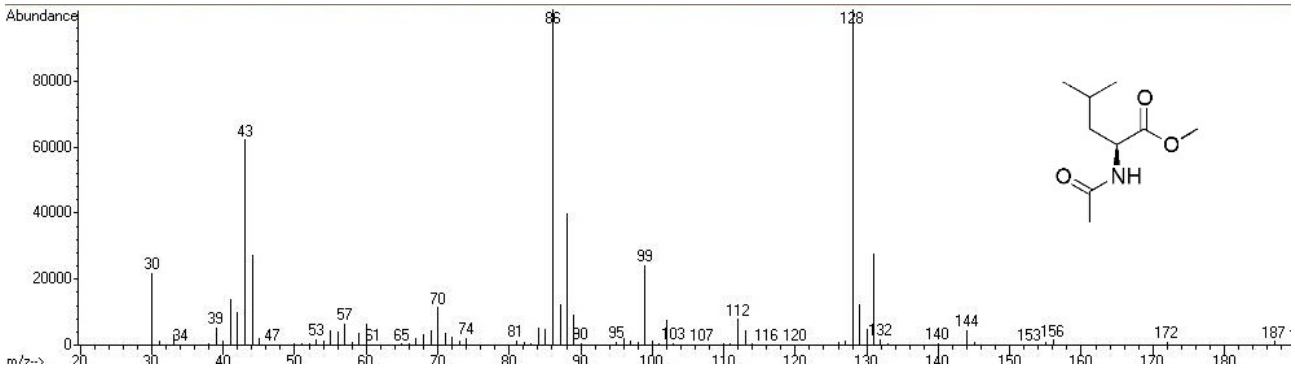
N-AcLeuOMe (**4**)[1]



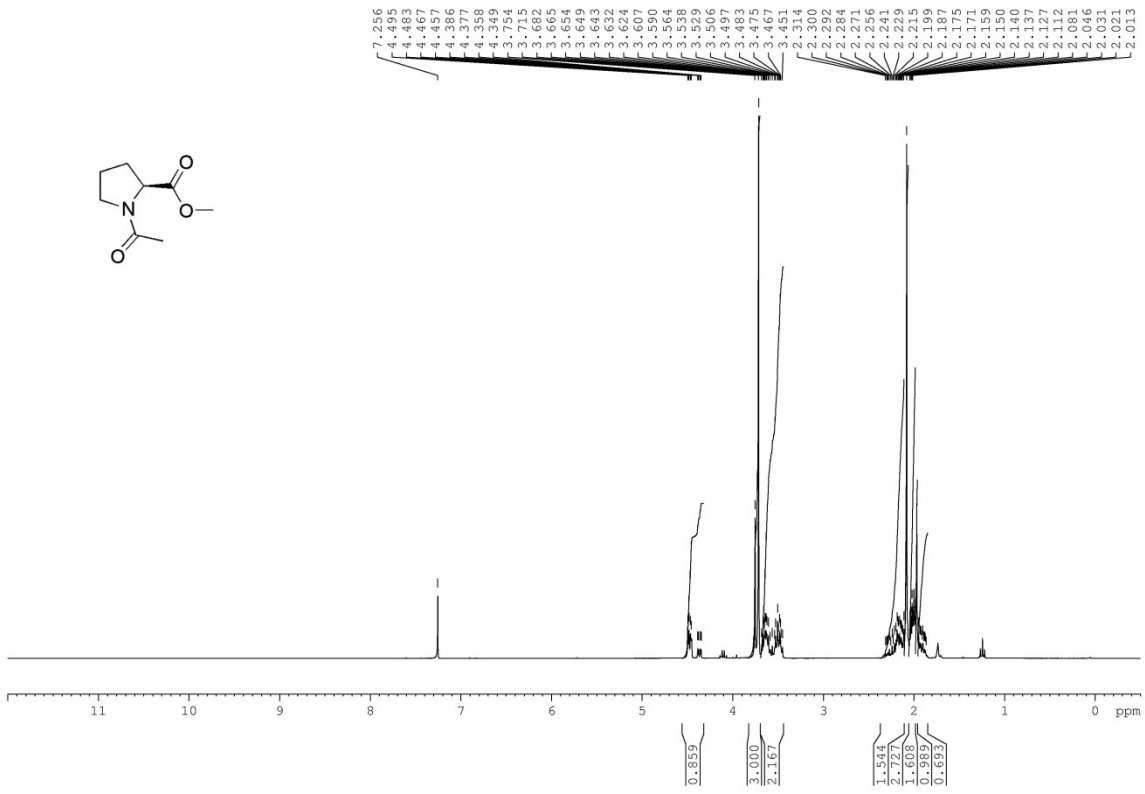
$CDCl_3$ (300 MHz)



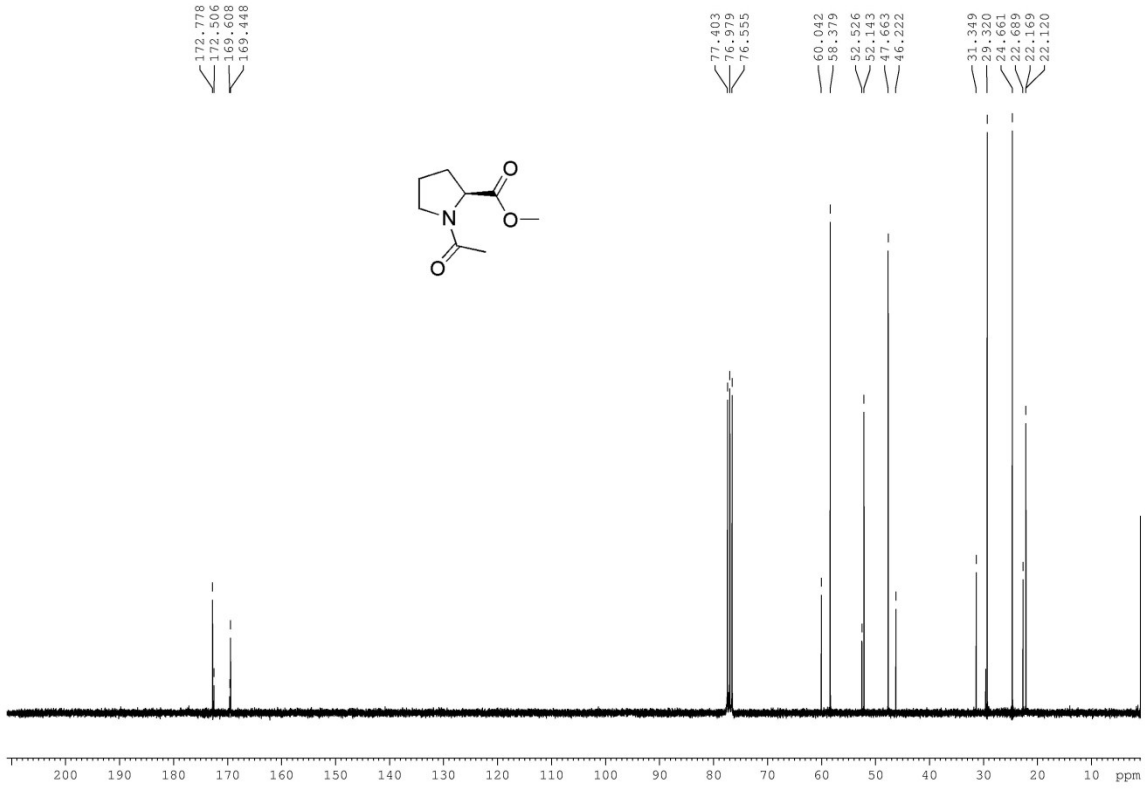
$CDCl_3$ (75 MHz)



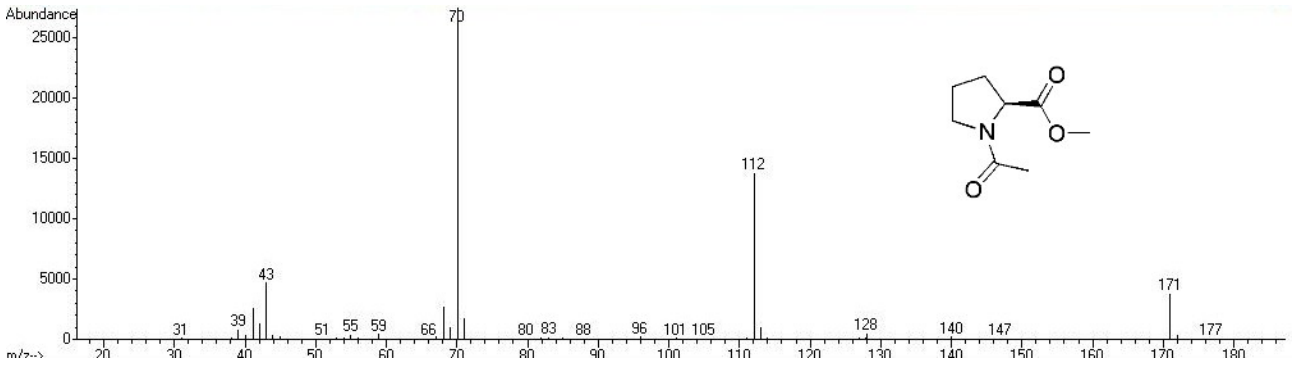
N-AcProOMe (**5**)[2,3]



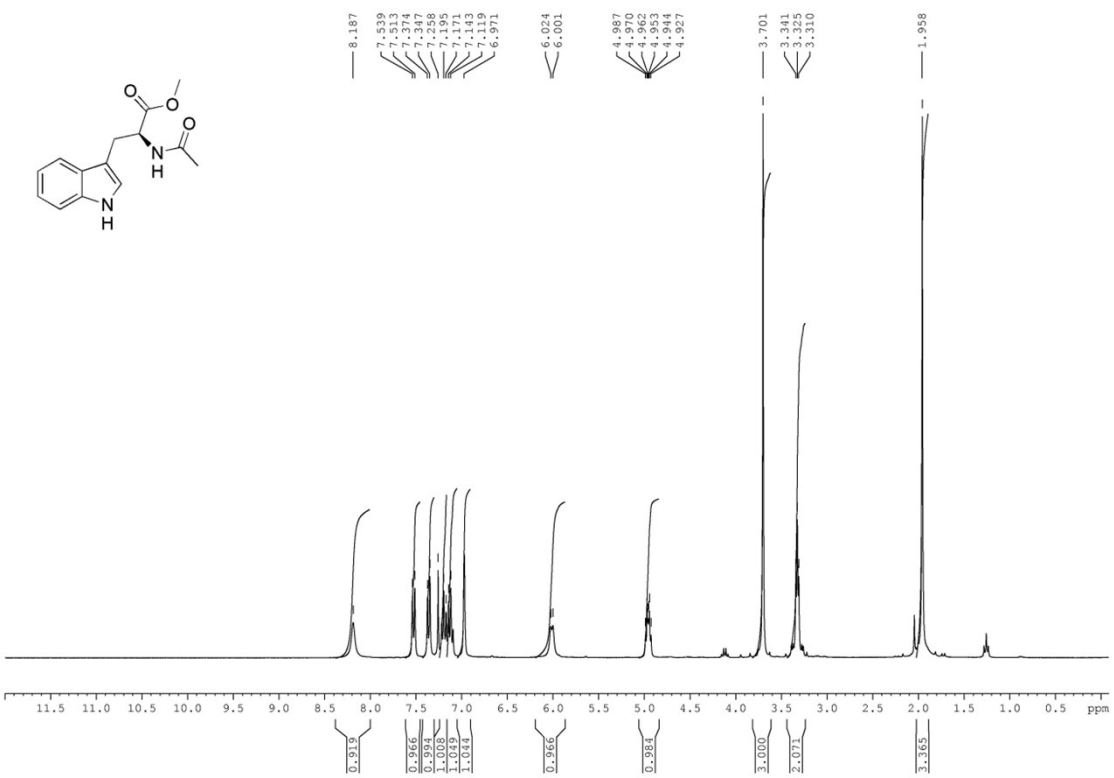
$CDCl_3$ (300 MHz)


172.778
172.506
169.608
169.448
77.403
76.979
76.555
60.042
58.379
52.526
52.143
47.663
46.222
31.349
29.320
24.661
22.689
22.169
22.120
O
N
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

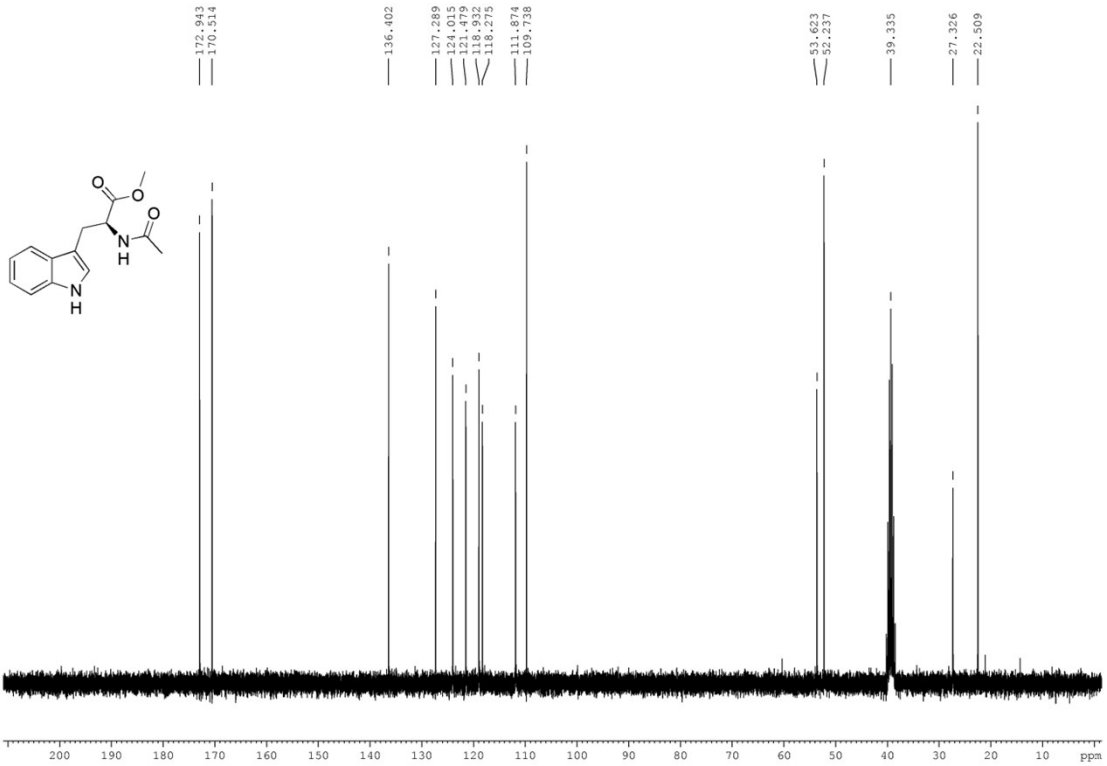
$CDCl_3$ (75 MHz)


Abundance
25000
20000
15000
10000
5000
0
70
112
43
171
31
39
51
55
59
66
80
83
88
96
101
105
128
140
147
177
O
N
O
O

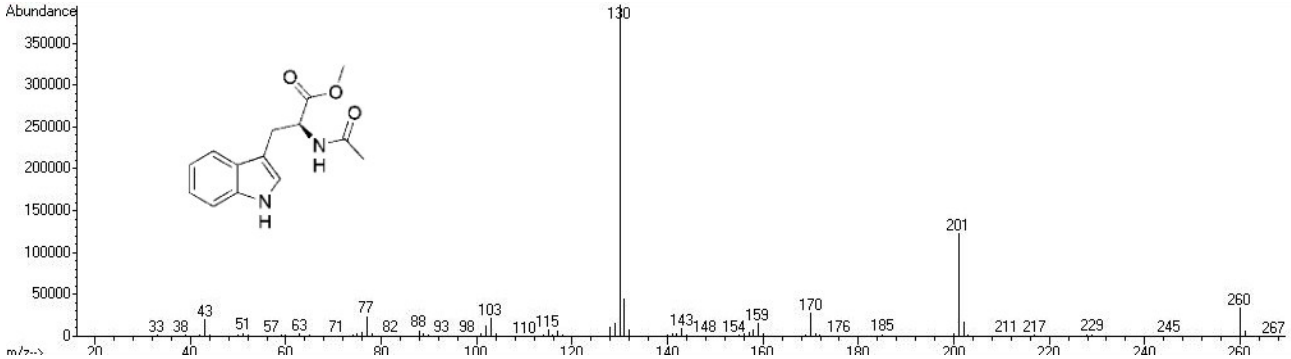
N-AcTrpOMe (**6**)[4-6]



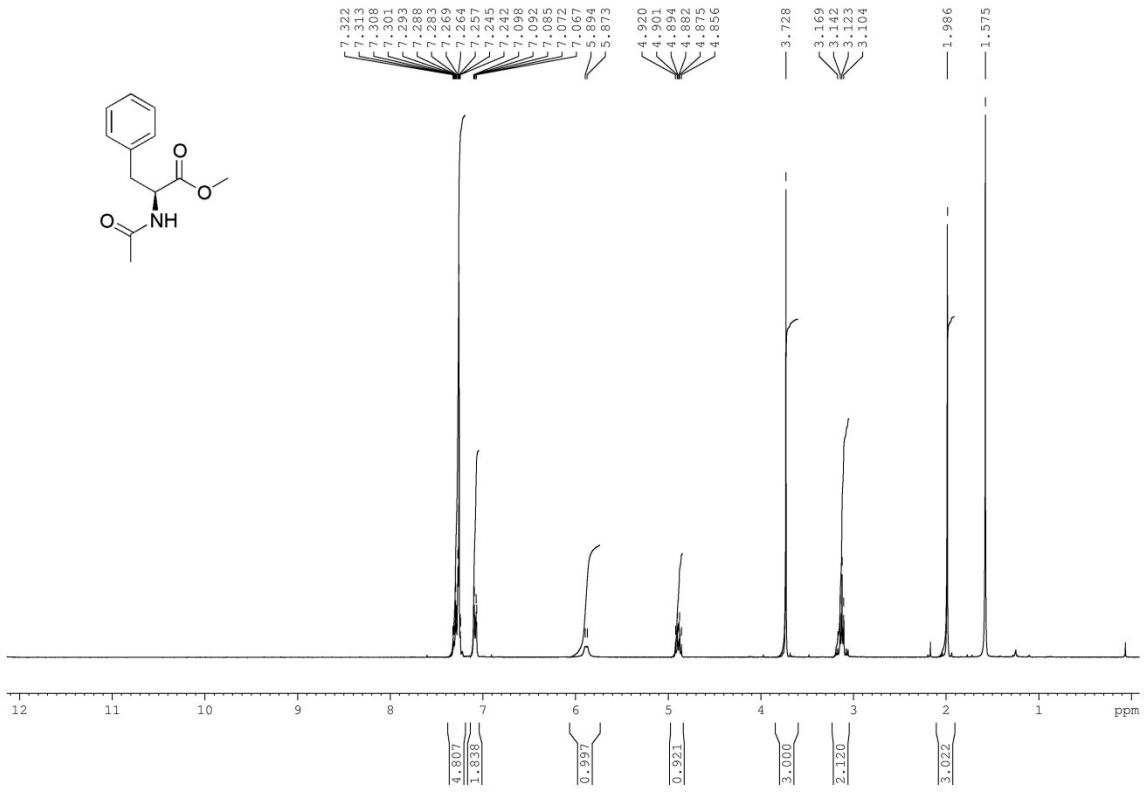
$CDCl_3$ (300 MHz)



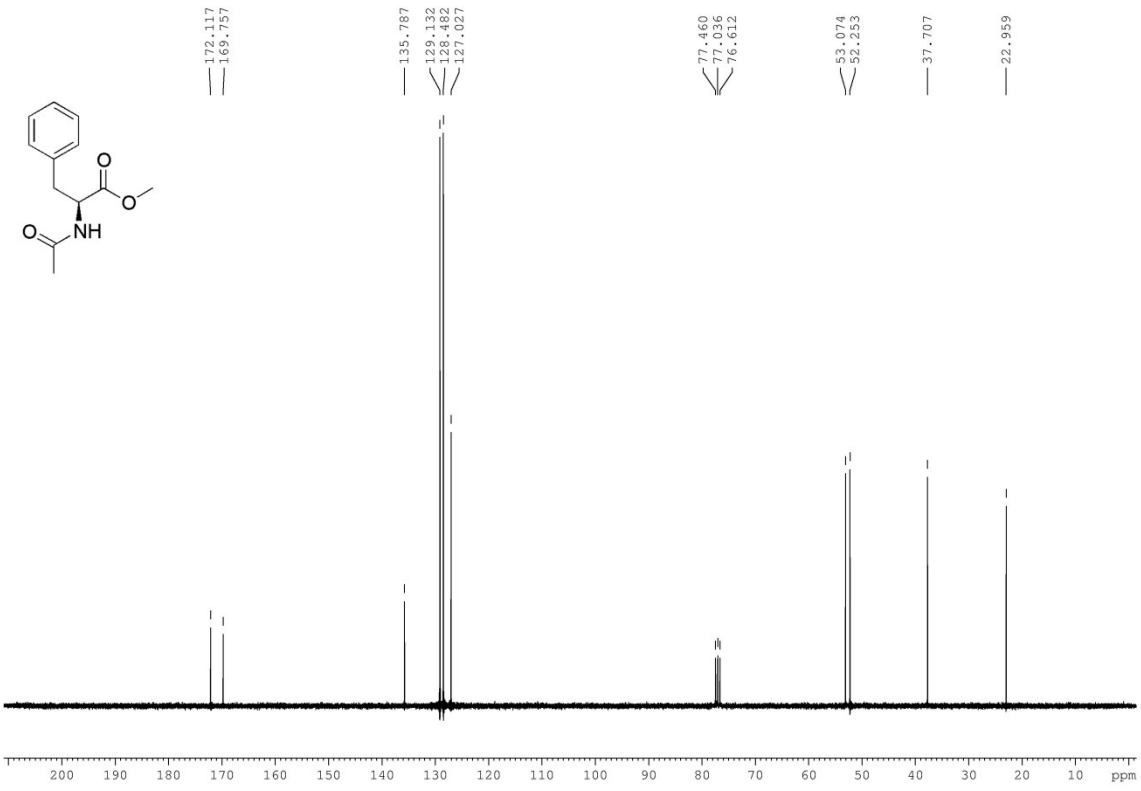
DMSO-d_6 (75 MHz)



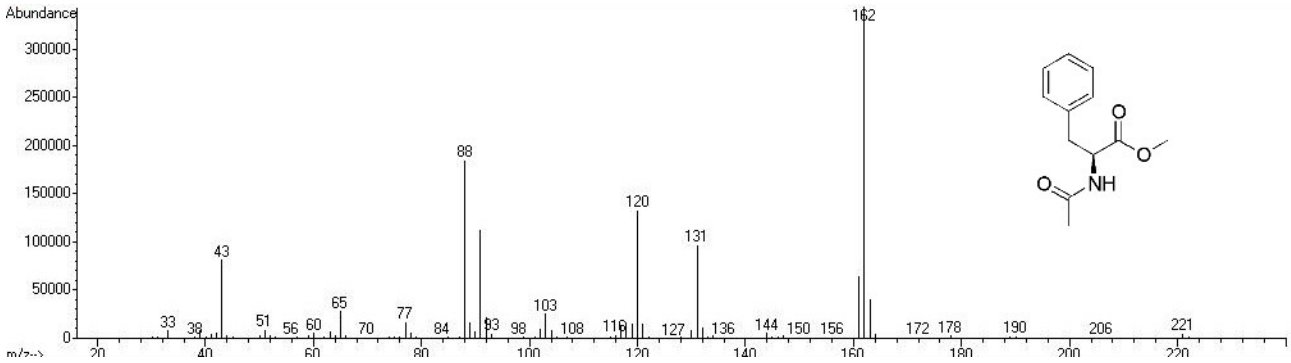
N-AcPheOMe (**7**)[1]



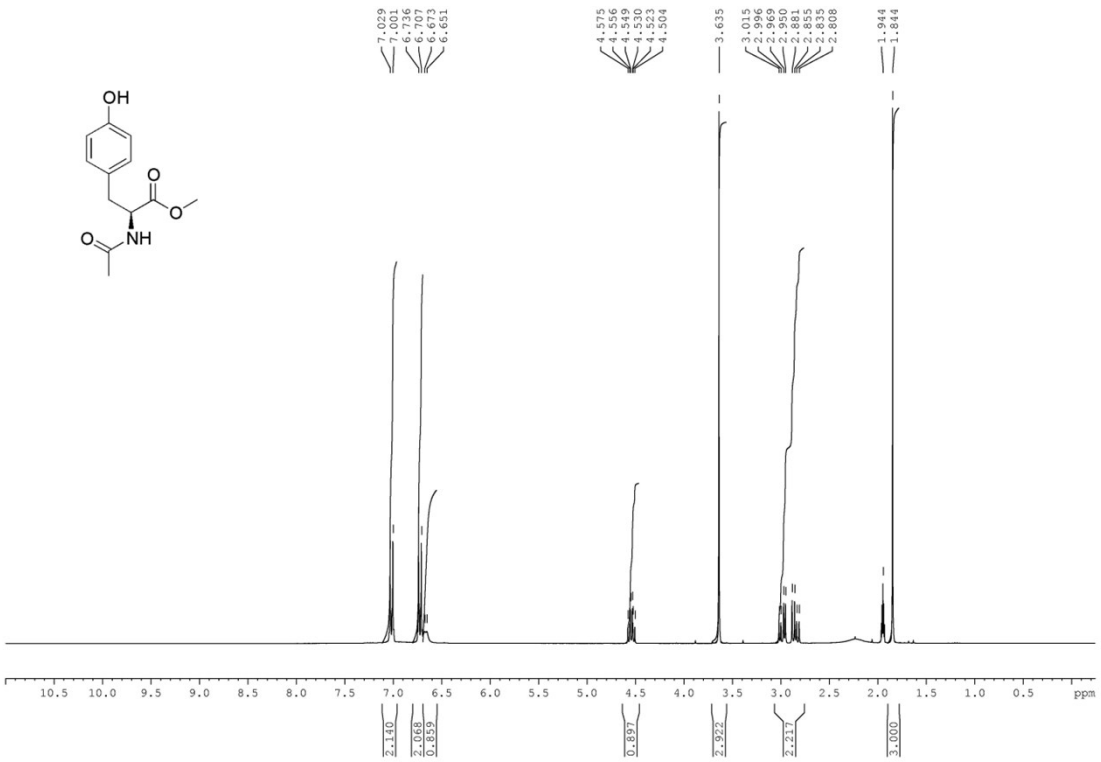
$CDCl_3$ (300 MHz)


172.117
169.757
135.787
129.132
128.482
127.027
77.460
77.036
76.612
53.074
52.253
37.707
22.959
O
O
NH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

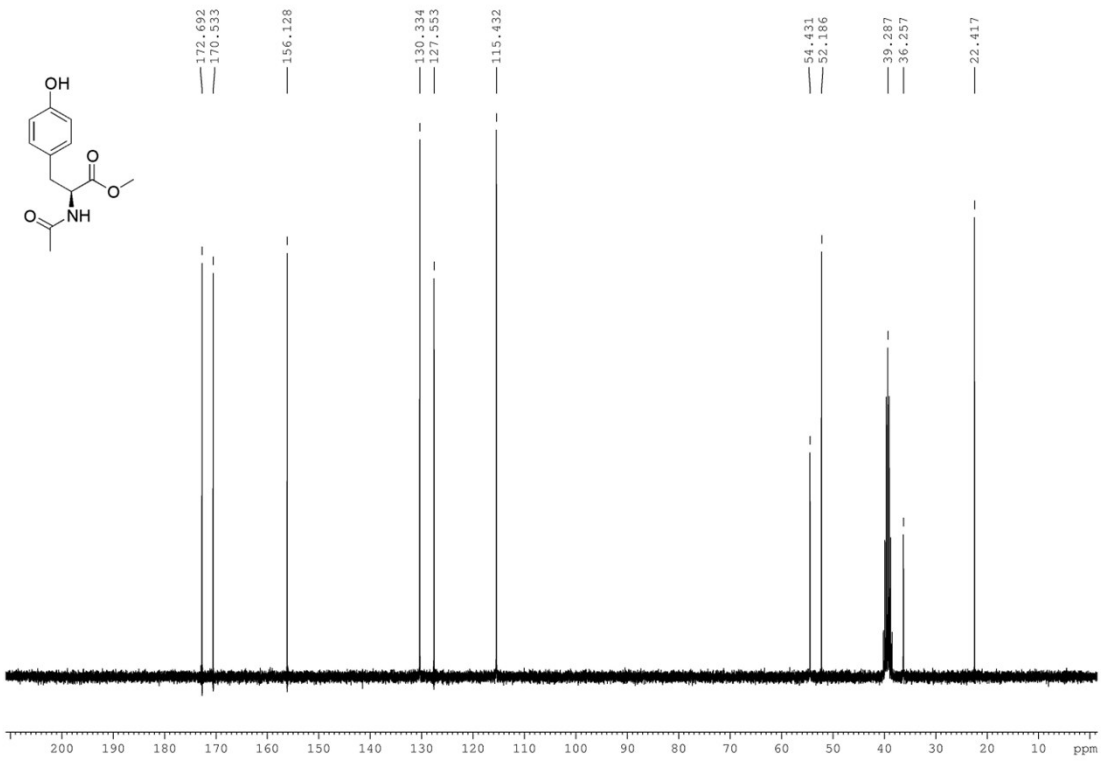
$CDCl_3$ (75 MHz)


Abundance
300000
250000
200000
150000
100000
50000
0
162
88
120
131
43
65
77
103
33 39 51 56 60 70 84 93 98 108 116 127 136 144 150 156 172 178 190 206 221
O
O
NH

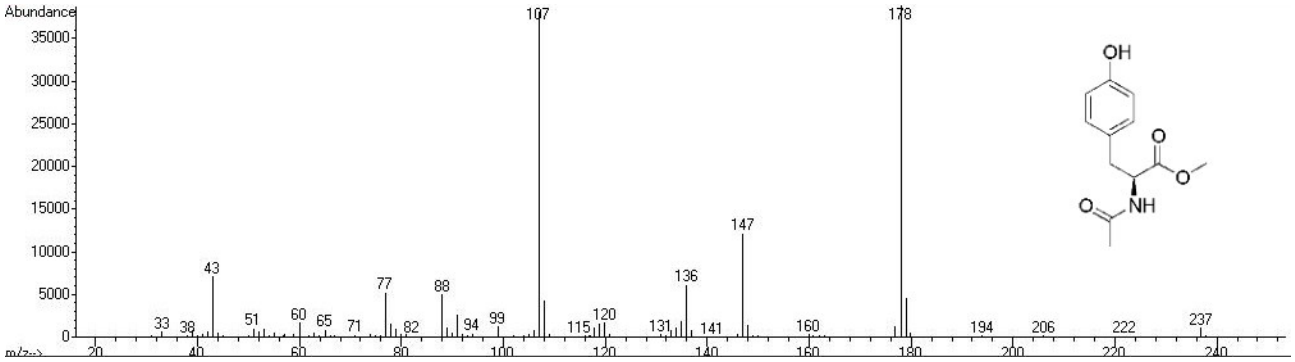
N-AcTyrOMe (**8**)[7]



CD_3CN (300 MHz)

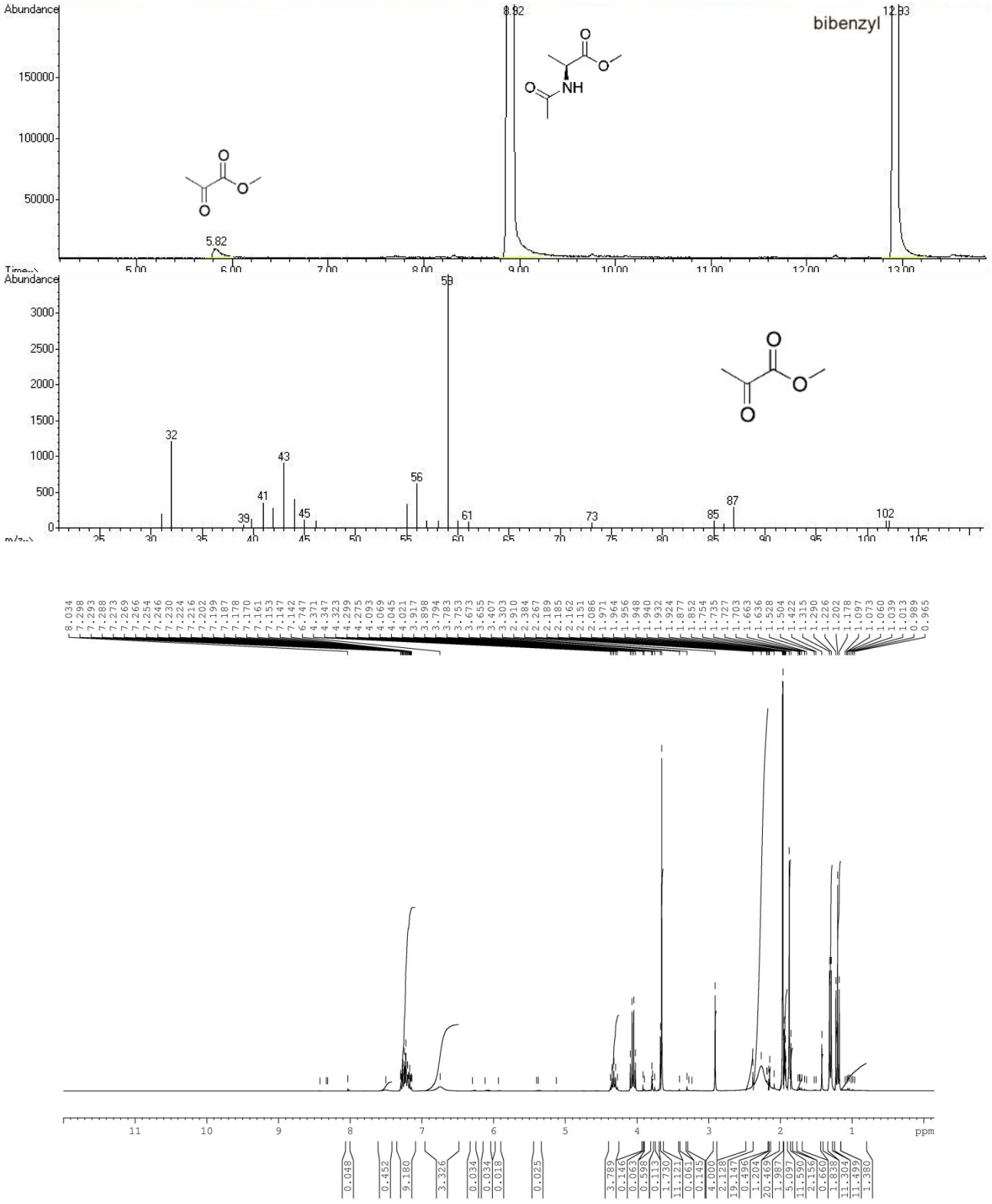


DMSO-d_6 (75 MHz)

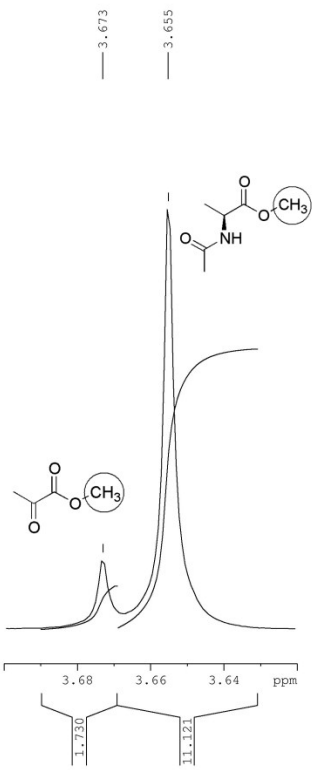

Abundance
35000
30000
25000
20000
15000
10000
5000
0
107
178
147
136
43
77
88
33
38
51
60
65
71
82
94
99
115
120
131
141
160
194
206
222
237
20
40
60
80
100
120
140
160
180
200
220
240
OH
O
O
NH
O

Oxidation of *N*-AcAlaOMe (2) with the 1/H_2O_2 system

See ref. [8] for product identification

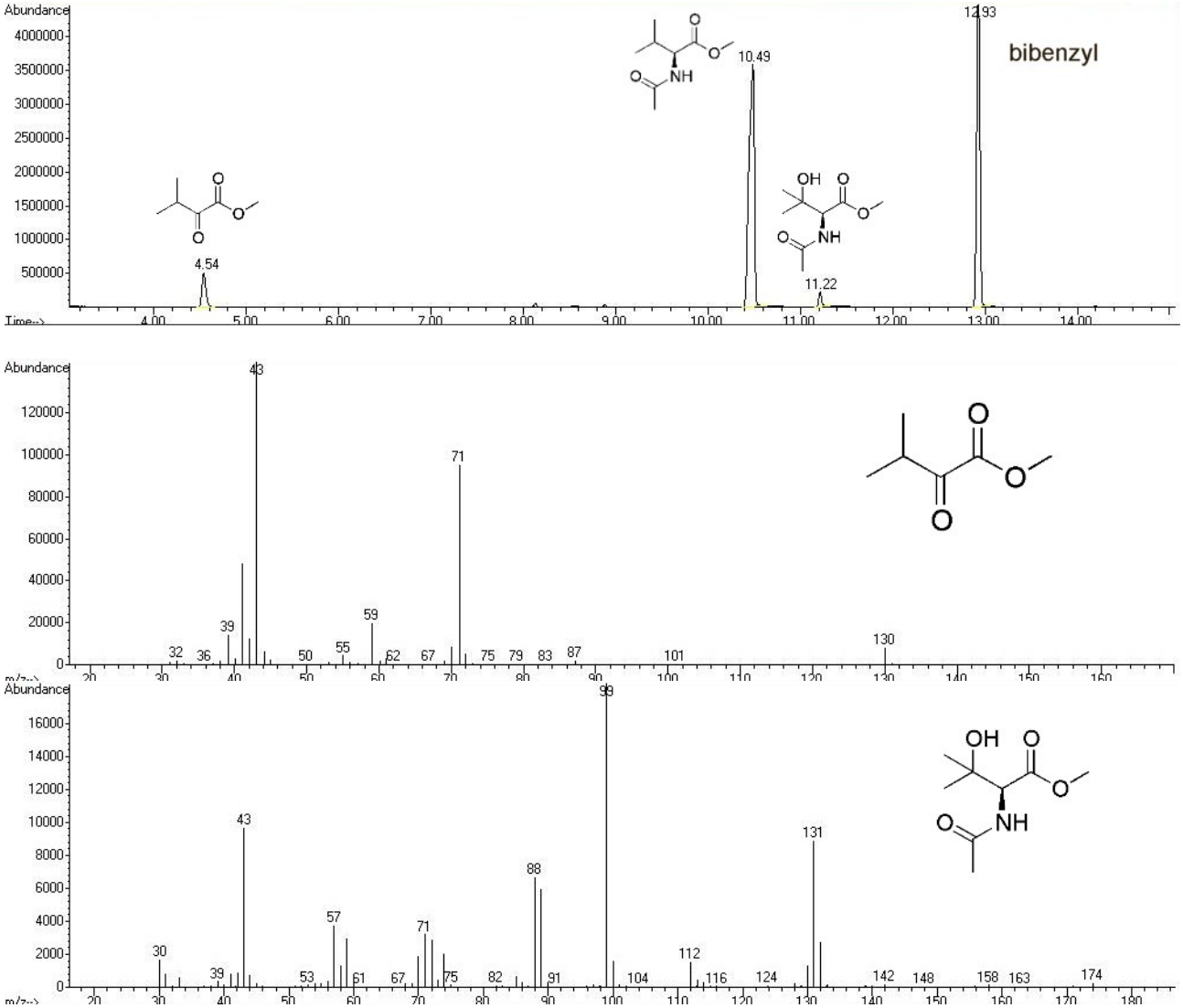


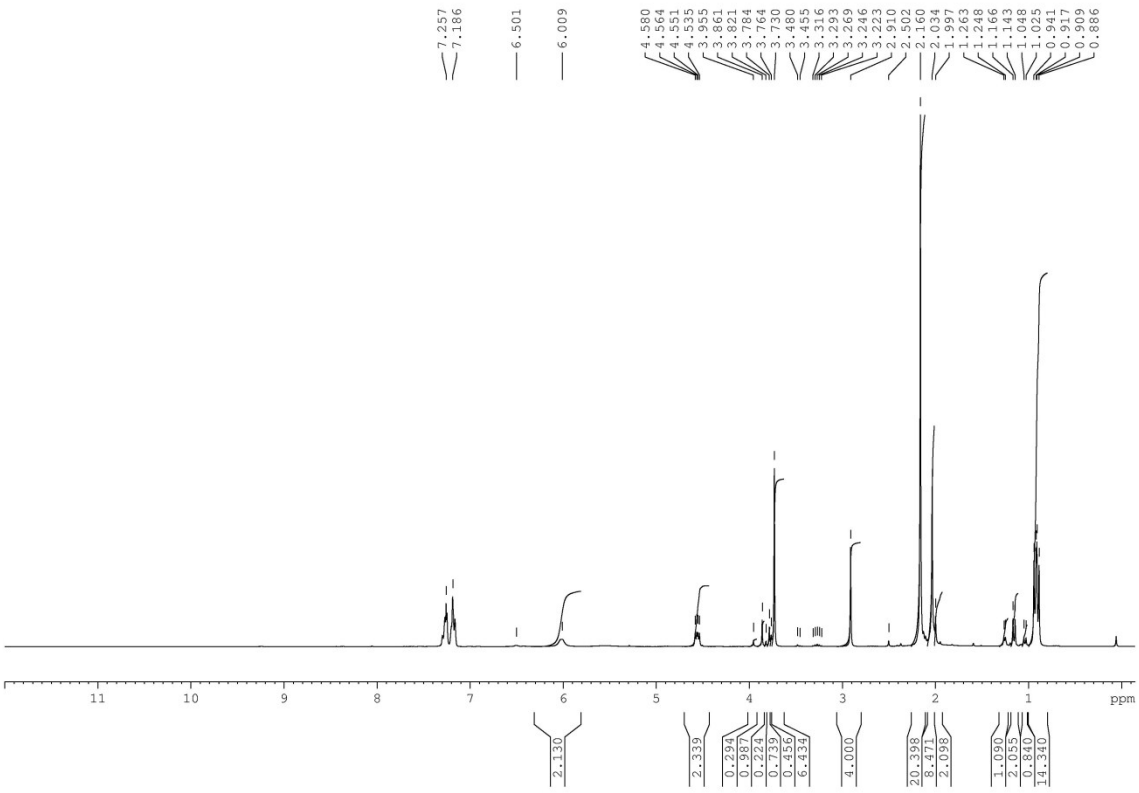
$CDCl_3$ (300 MHz)


3.673
3.655
O
O
CH3
NH
O
O
O
CH3
3.68
3.66
3.64
ppm
1.730
11.121

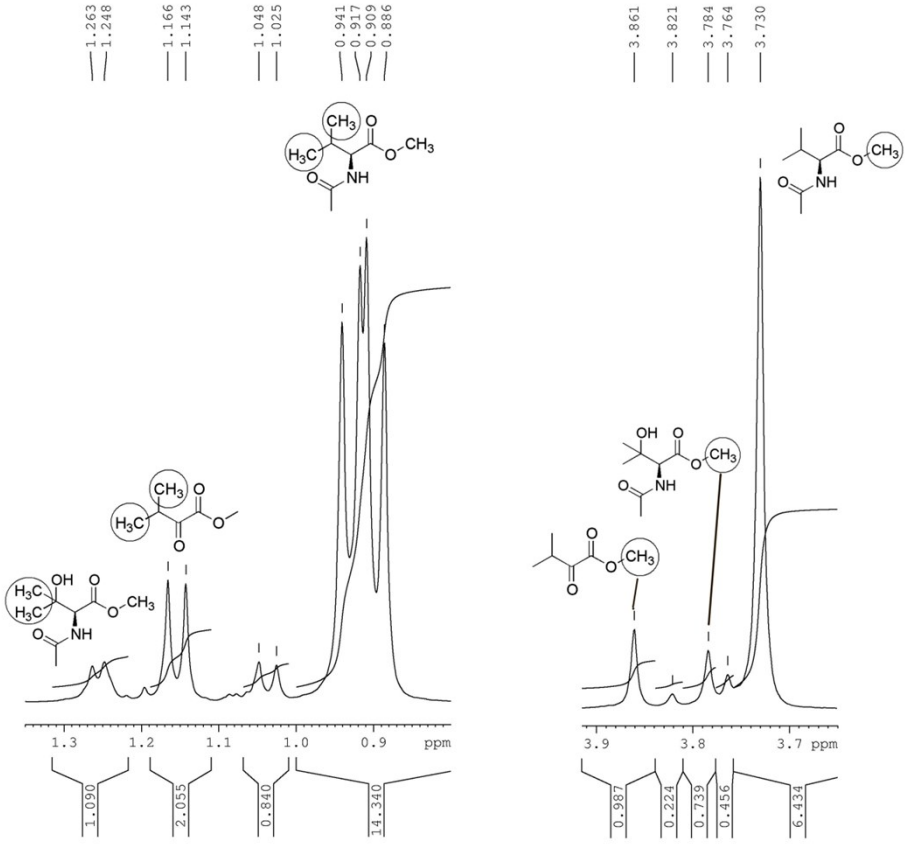
Oxidation of *N*-AcValOMe (3) with the 1/H_2O_2 system

See ref. [9] for products identification



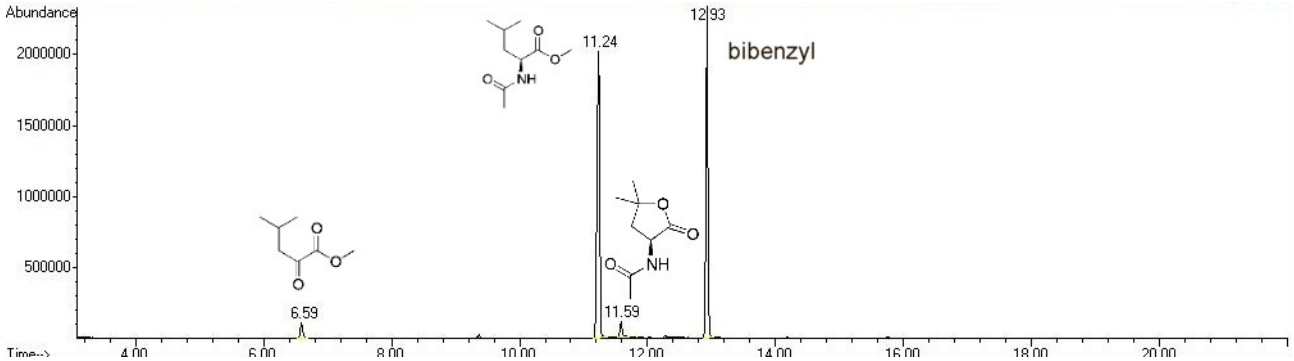


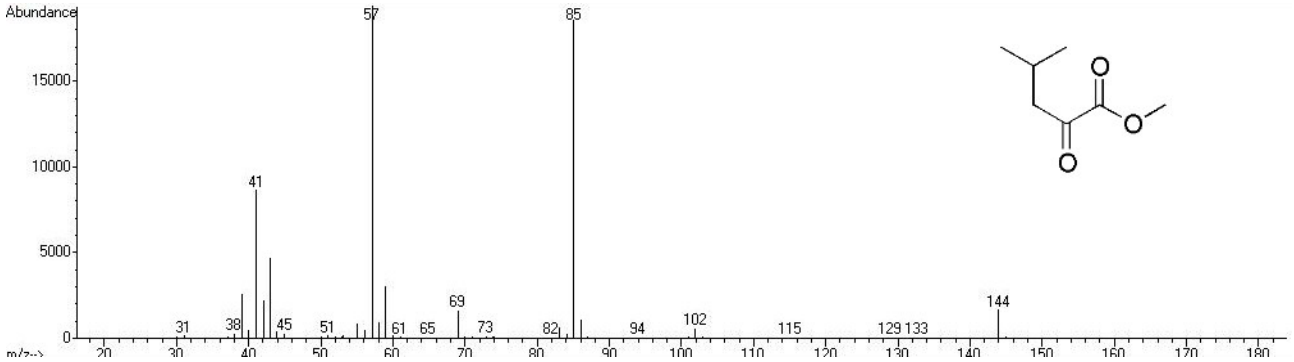
$CDCl_3$ (300 MHz)

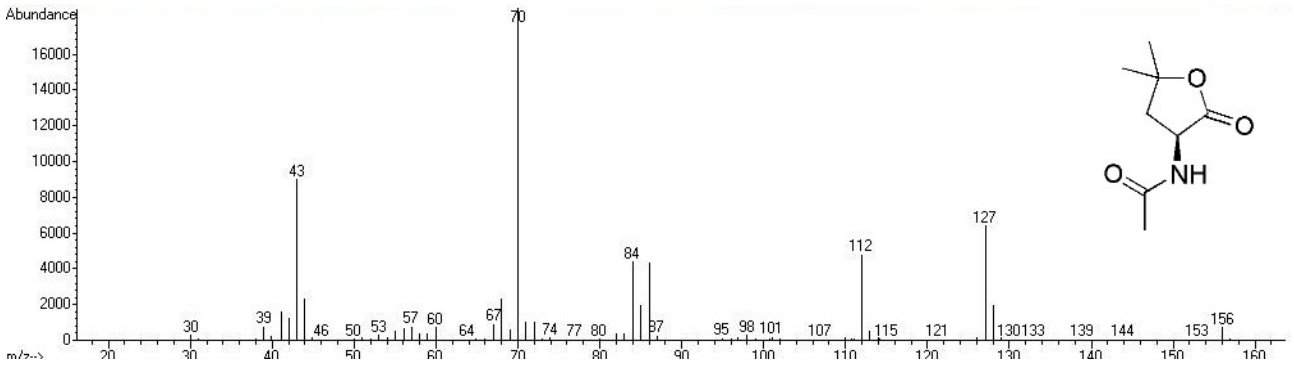


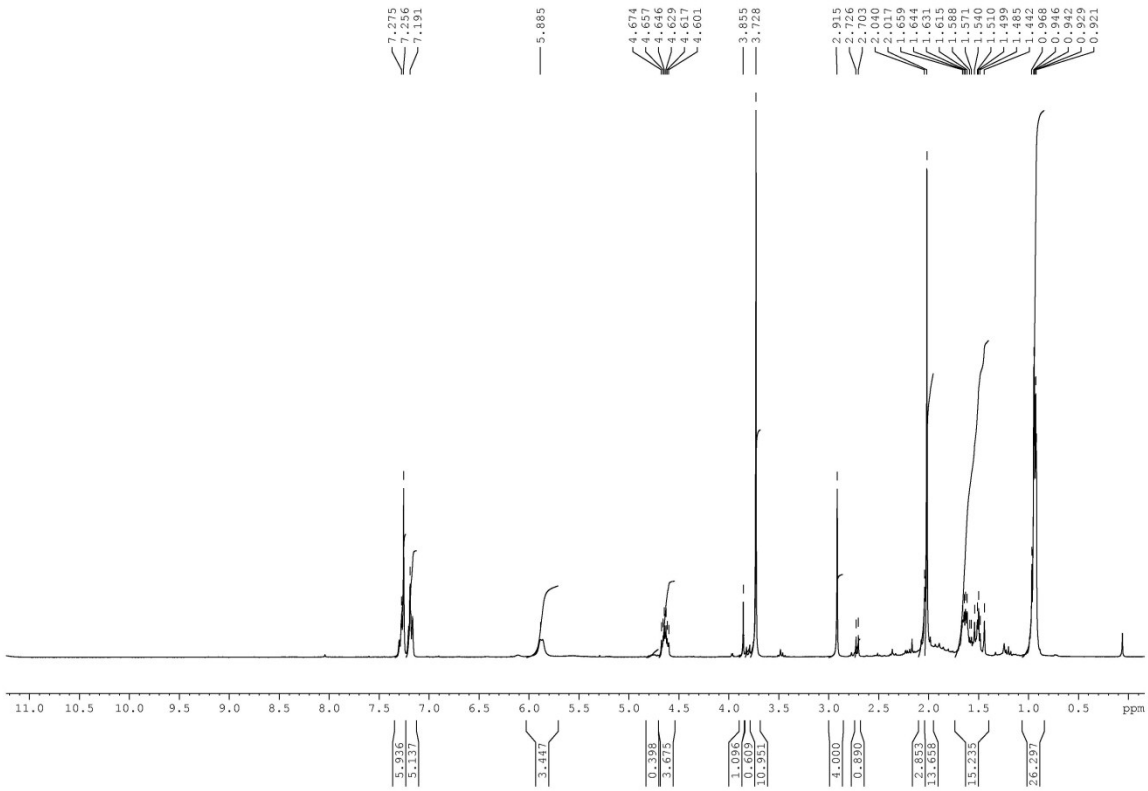
Oxidation of *N*-AcLeuOMe (4) with the 1/H_2O_2 system

See refs. [9a,9c,10] for products identification









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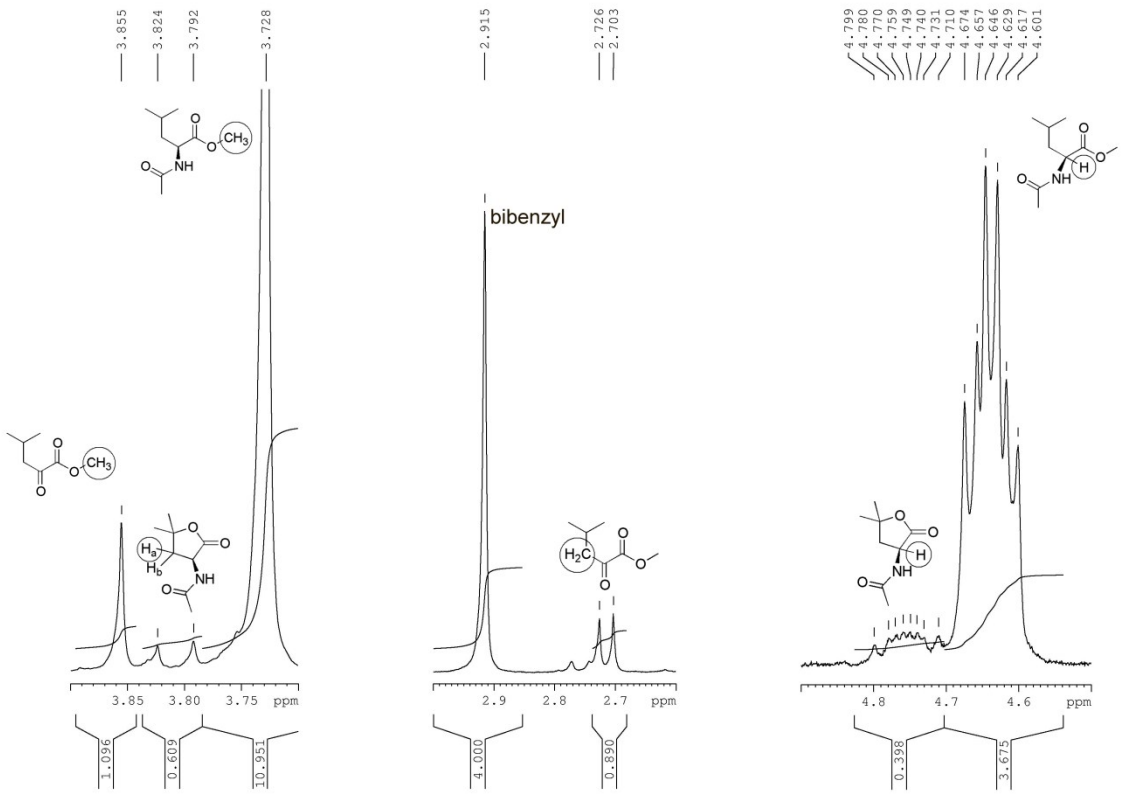
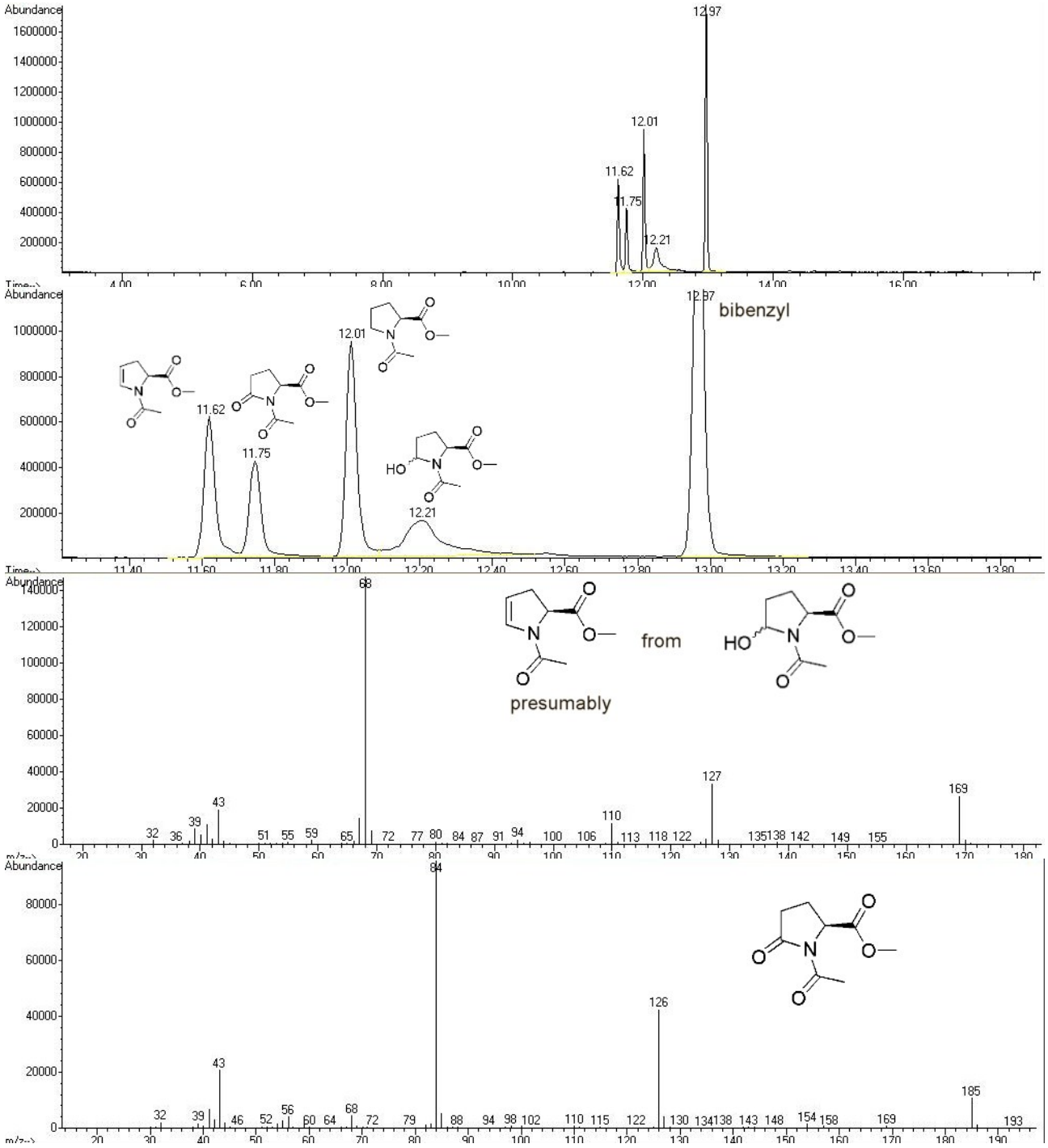
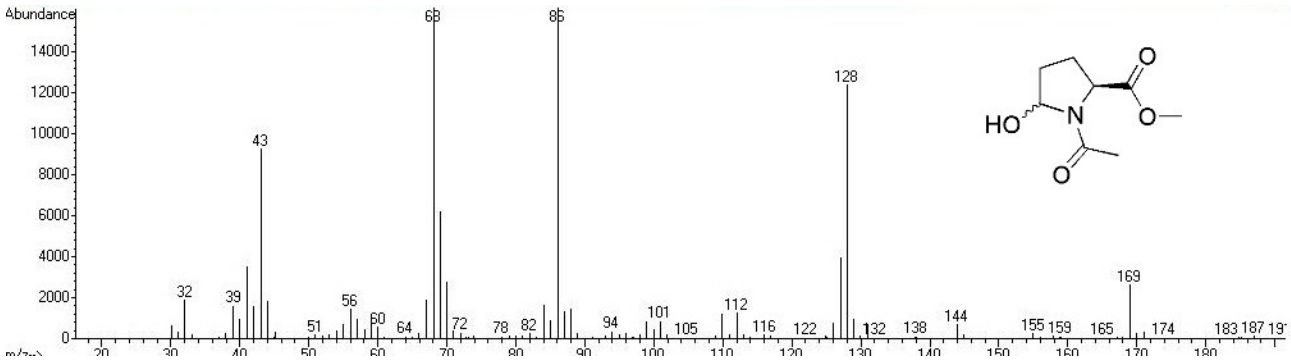
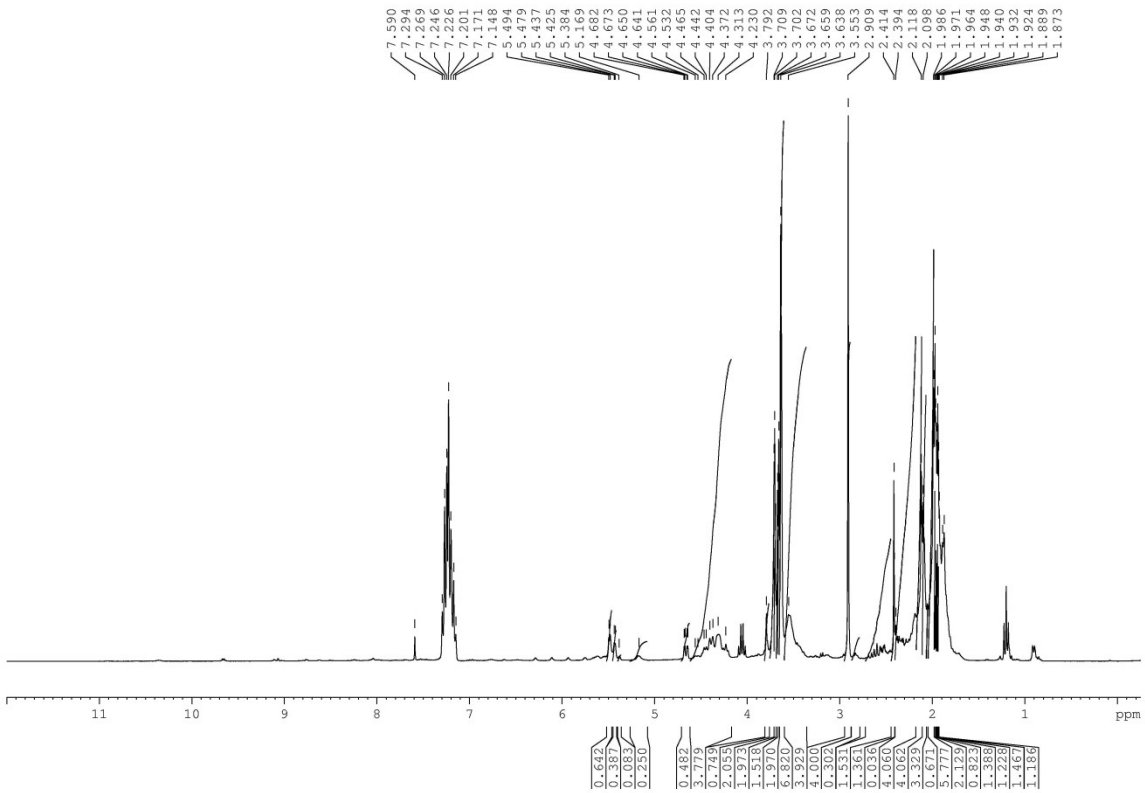


Oxidation of *N*-AcProOMe (5) with the 1/H_2O_2 system

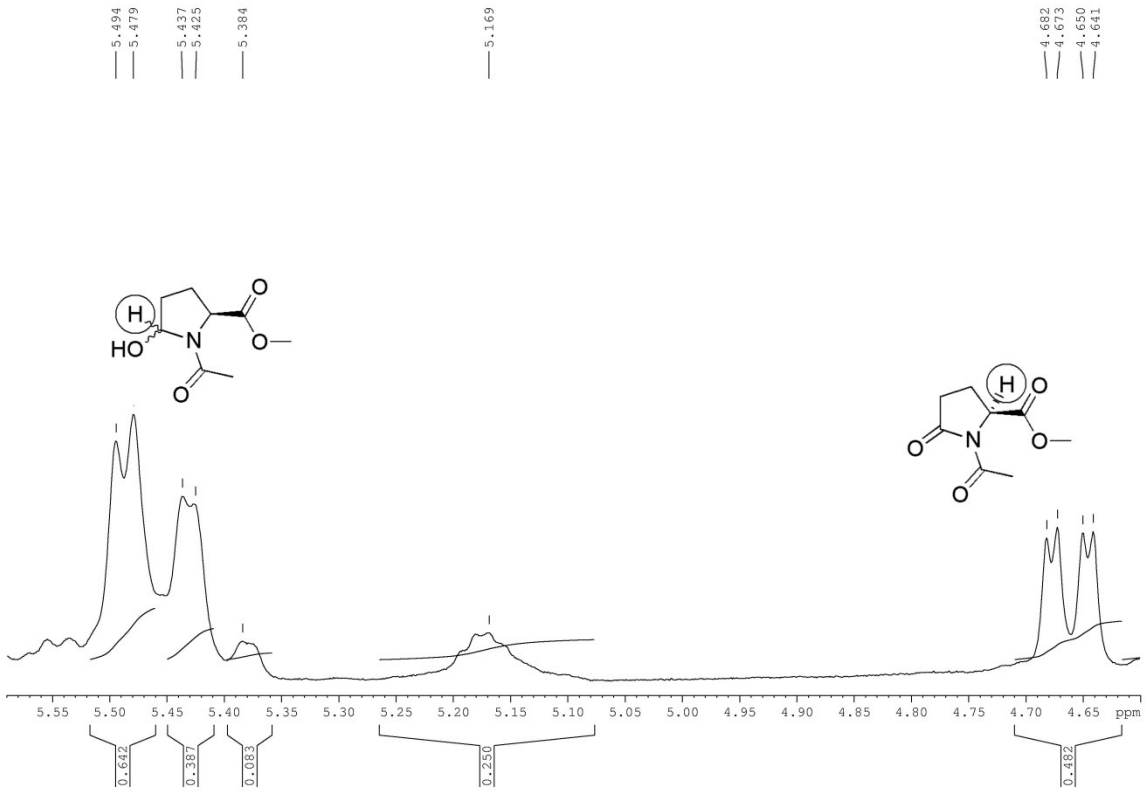
See ref. [11] and [3] for products identification





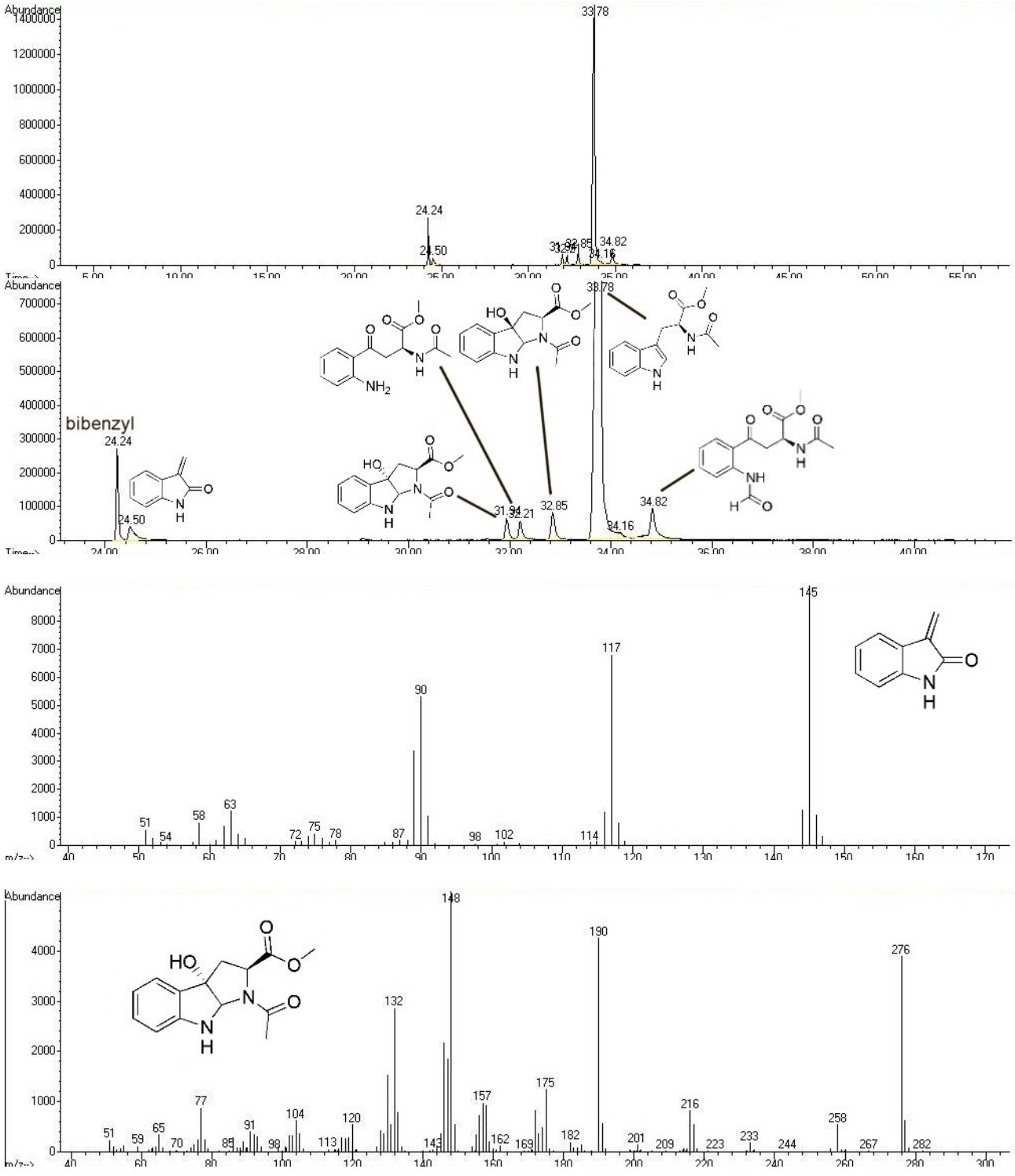


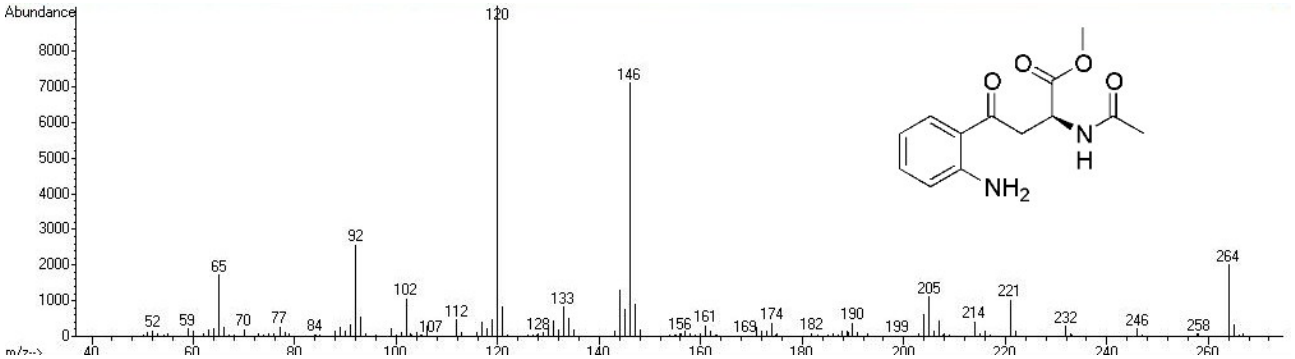
$CDCl_3$ (300 MHz)

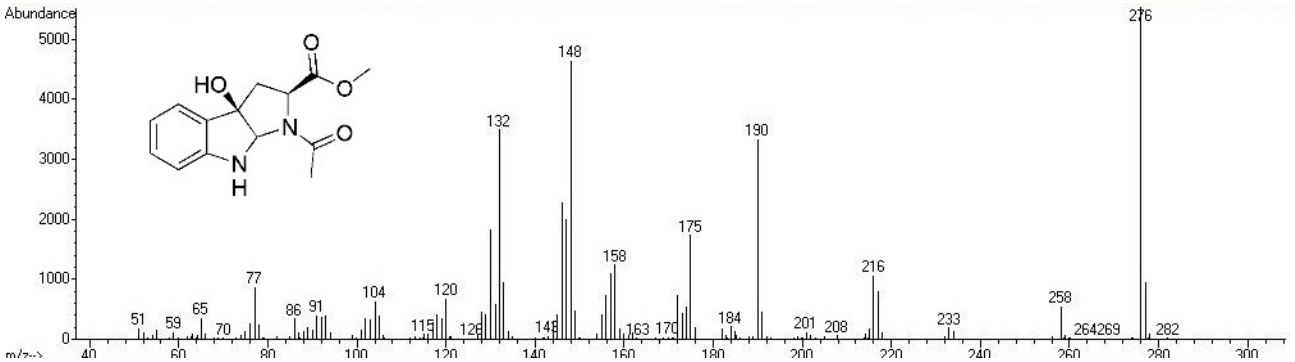

5.494
5.479
5.437
5.425
5.384
5.169
4.682
4.673
4.650
4.641
H
HO
N
O
O
O
H
O
O
N
O
O
5.55
5.50
5.45
5.40
5.35
5.30
5.25
5.20
5.15
5.10
5.05
5.00
4.95
4.90
4.85
4.80
4.75
4.70
4.65
ppm
0.642
0.387
0.083
0.250
0.482

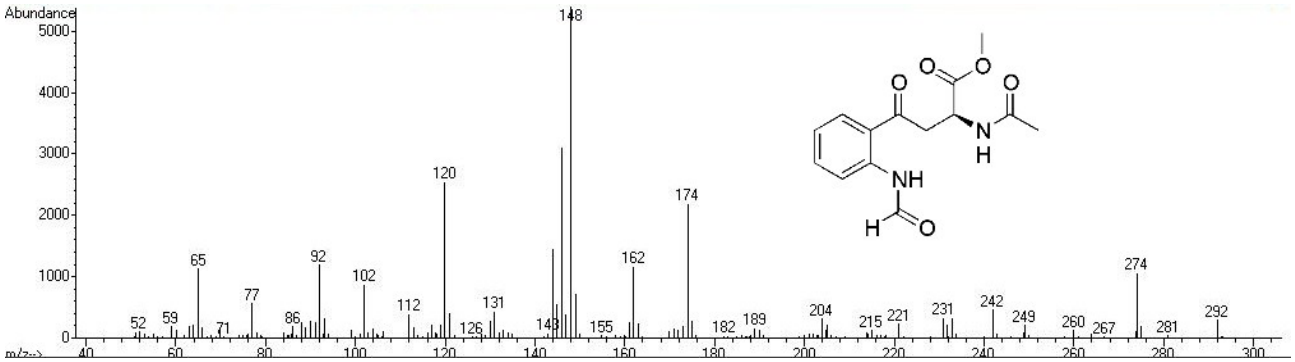
Oxidation of *N*-AcTrpOMe (6) with the $1/H_2O_2$ system

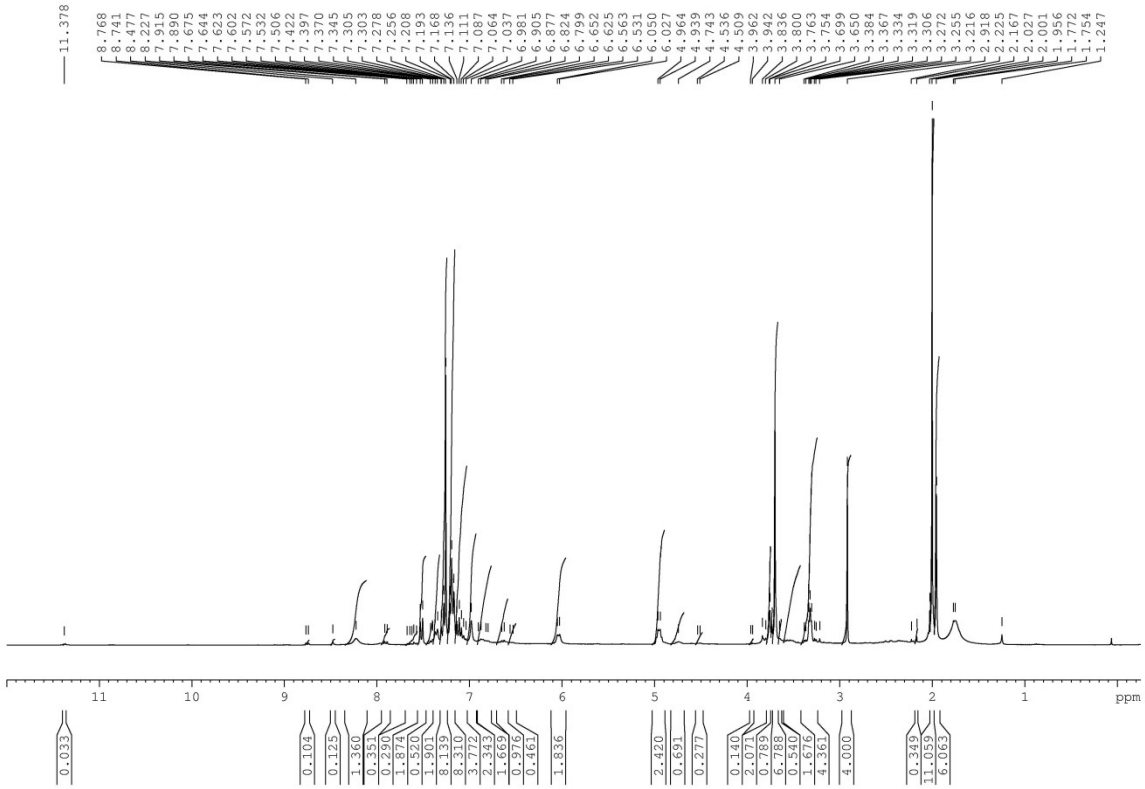
See ref. [12] for products identification



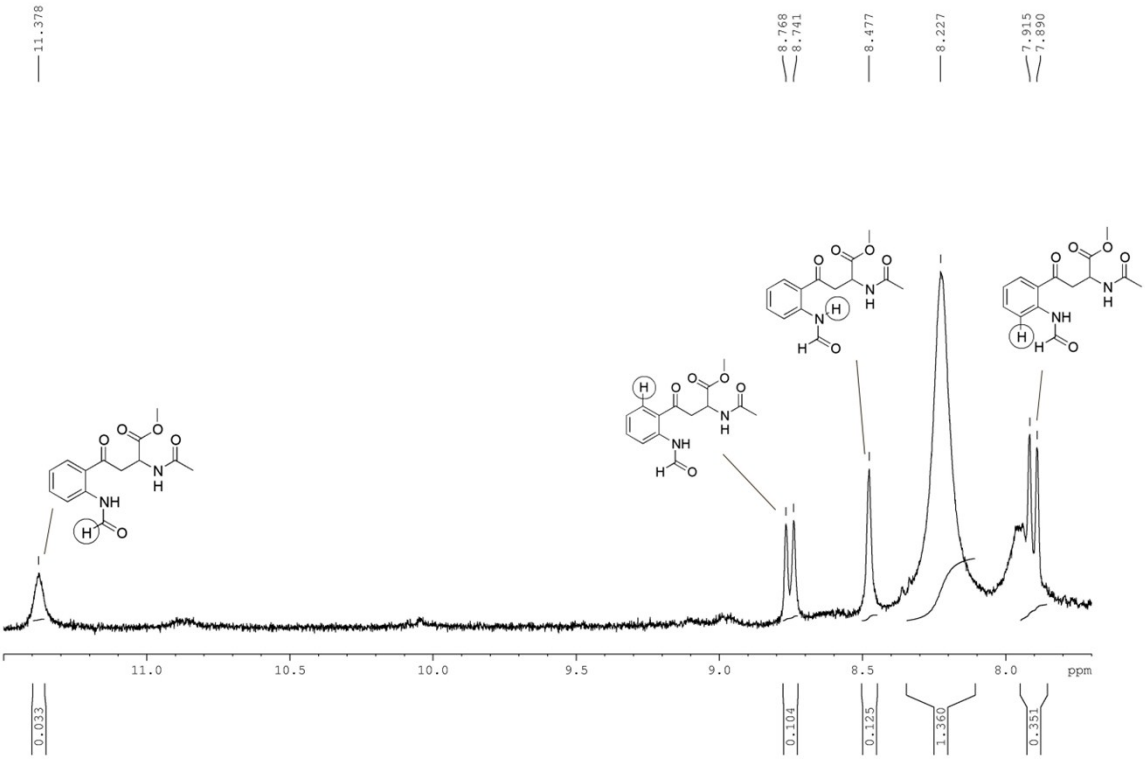

Abundance
120
146
92
65
102
112
133
264
205
221
214
232
246
258
NH2


Abundance
276
148
132
190
175
158
216
77
104
120
258
HO

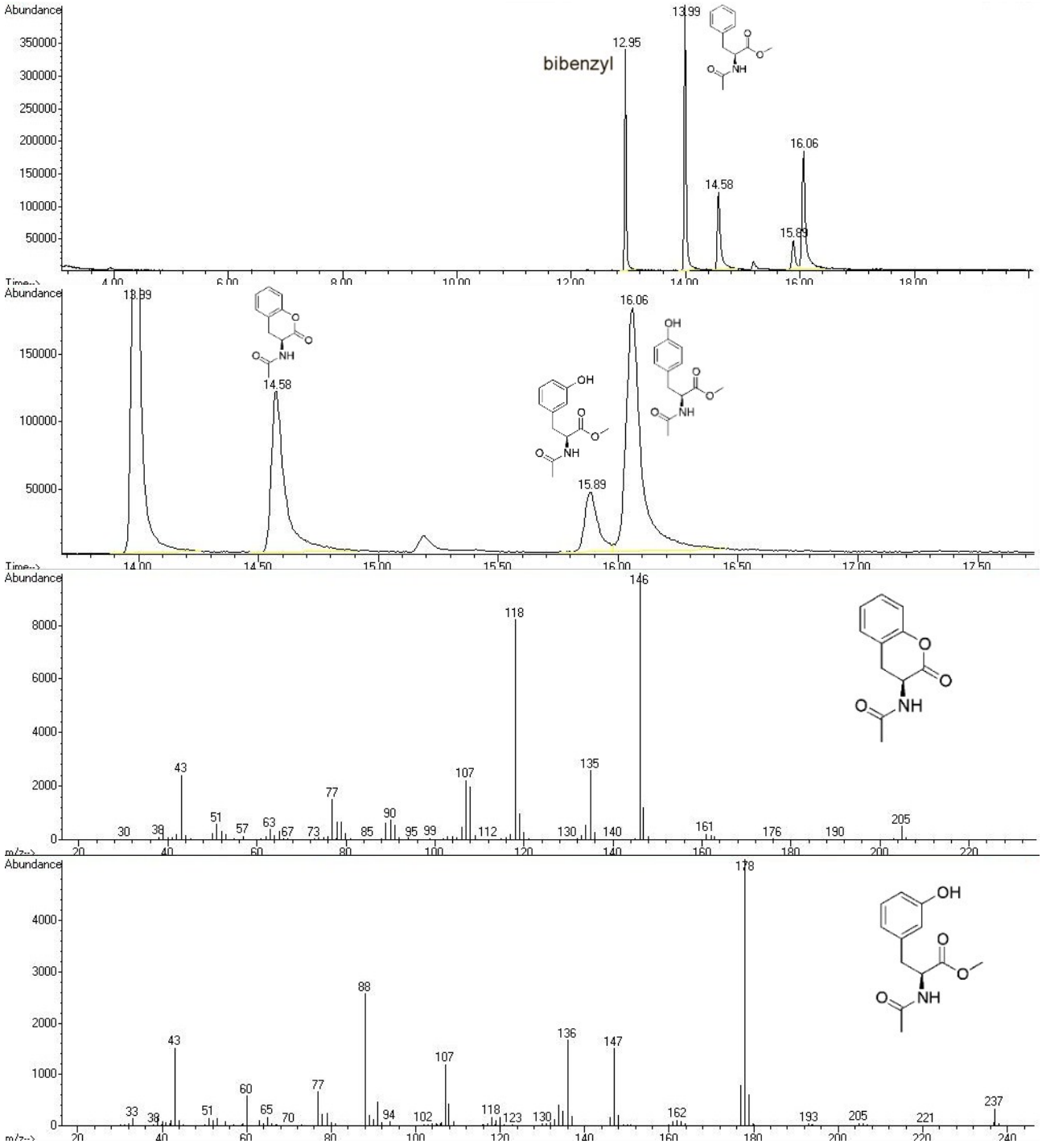

Abundance
148
120
174
65
92
102
162
274
77
112
131
292
NH

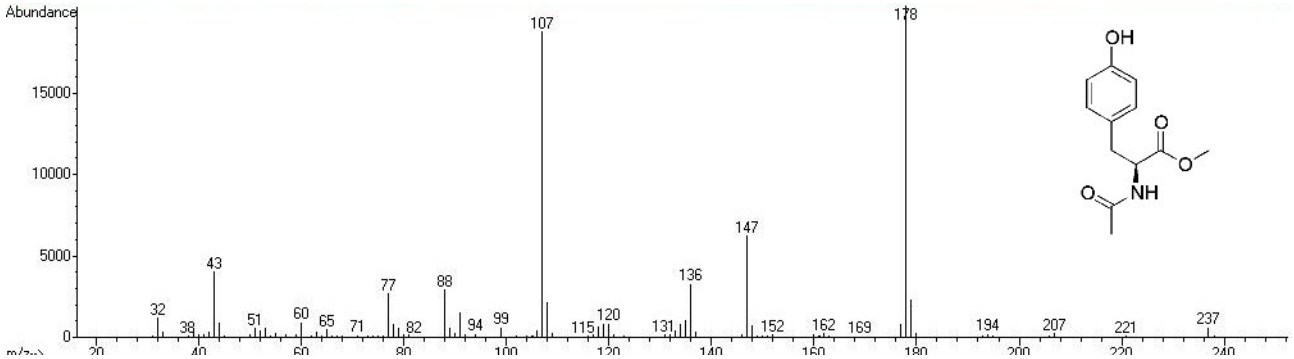


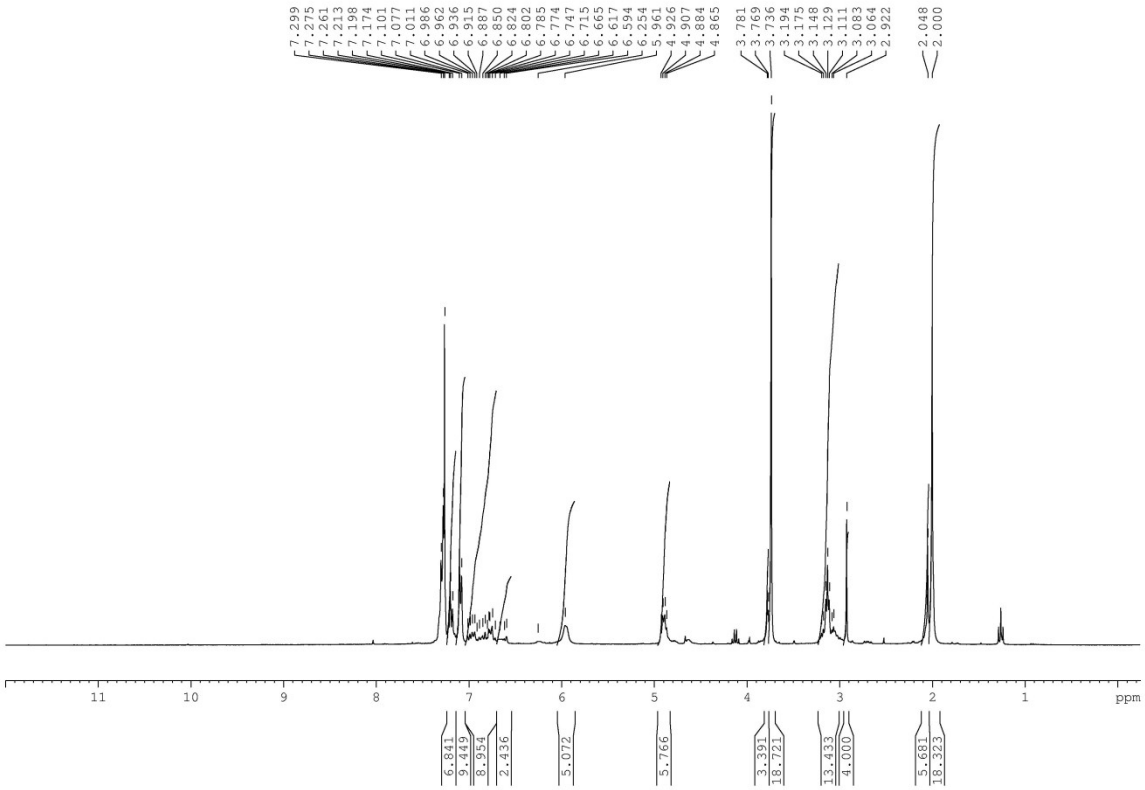
$CDCl_3$ (300 MHz)



Oxidation of *N*-AcPheOMe (7) with the $1/H_2O_2$ system

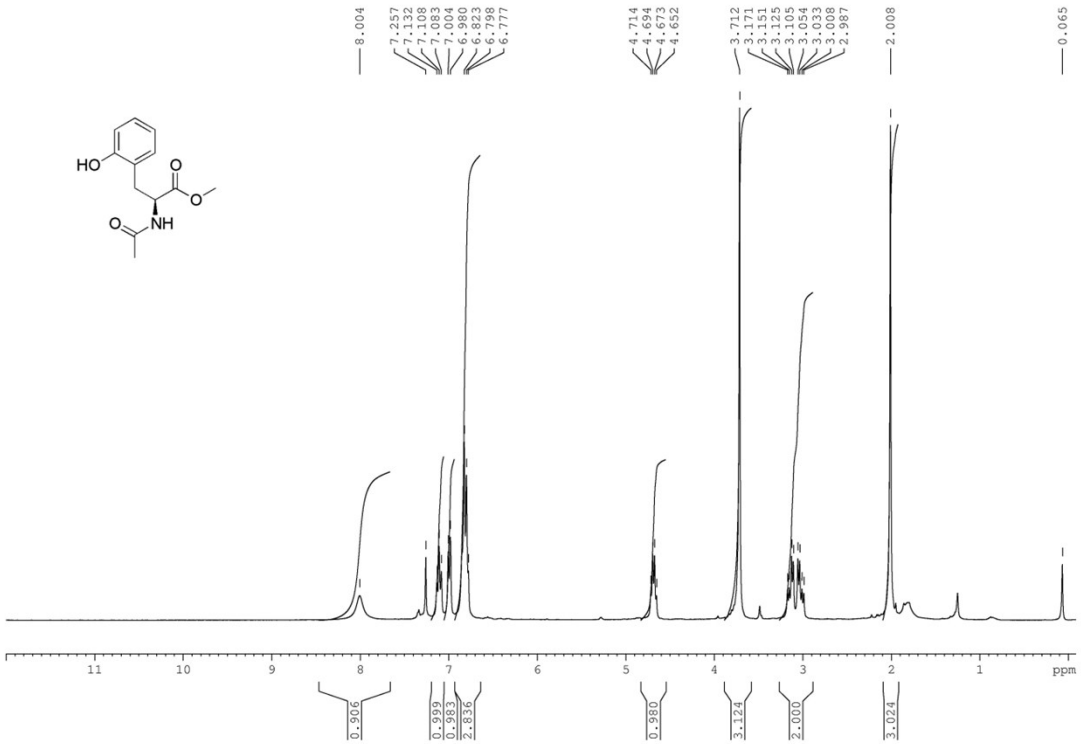




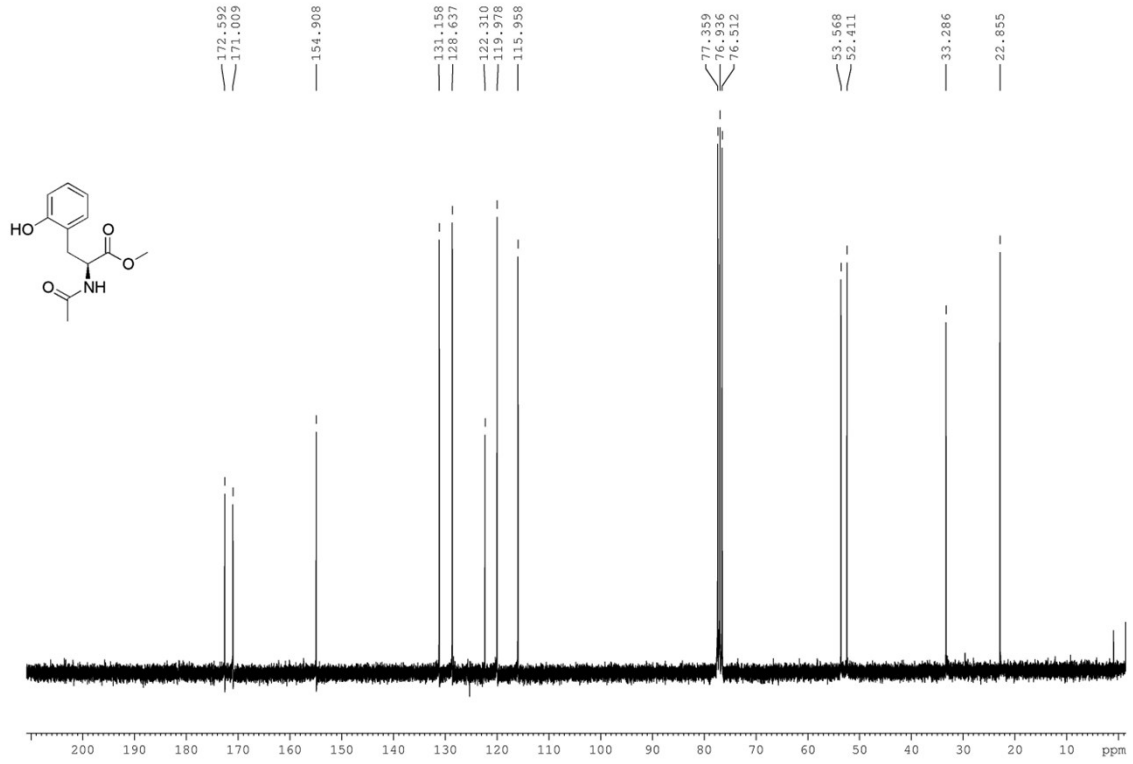


$CDCl_3$ (300 MHz)

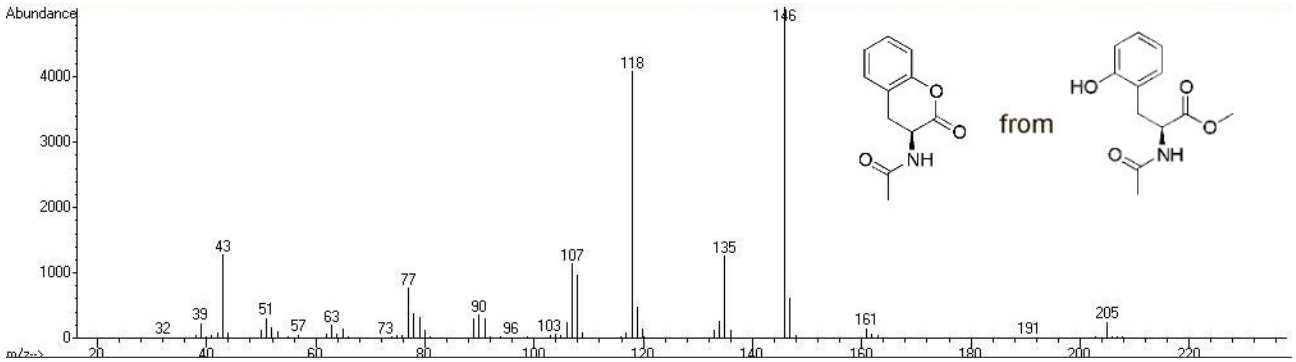
(2*S*)-*N*-acetyl-*o*-hydroxyphenylalanine methyl ester



$CDCl_3$ (300 MHz)



$CDCl_3$ (75 MHz)



GC-MS (70 eV): *m/z* (rel. intensity) = 43(23); 77(14); 107(22), 108(19); 118(79); 135(24); 146(100); 147 (11), 205(M^+, 5).

References

1 R. De Marco, M. L. Di Gioia, A. Leggio, A. Liguori, M. C. Viscomi, *Eur. J. Org. Chem.* 2009, **22**, 3795-3800.

2 I. Duttagupta, D. Misra, S. Bhunya, A. Paul, S. Sinha, *J. Org. Chem.* 2015, **80**, 10585-10604.

3 K. Irie, A. Ishida, T. Nakamura, T. Oh-Ishi, *Chem. Pharm. Bull.* 1984, **32**, 2126-2139.

4 A. J. Reay, T. J. Williams, I. J. S. Fairlamb, *Org. Biomol. Chem.* 2015, **13**, 8298-8309.

5 C.-X. Gu, Q.–W.Bi, C.–K. Gao, J. Wen, Z.-G. Zhao, Z. Chen, *Org. Biomol. Chem.* 2017, **15**, 3396-3400.

6 J. P. J. Marais, I. Mueller-Harvey, E. V. Brandt, D. Ferreira, *J. Agric. Food Chem*. 2000, **48**, 3440–3447.

7 A. J. Pearson, P. R.Bruhn, *J. Org. Chem.* 1991, **56**, 7092-7097.

8 Y.-G. Si, J. Chen, F. Li, J.-H. Li, Y.-J. Qin, B. Jiang, *Adv. Synth. Catal.* 2006, **348**, 898–904.

9 a) S. Tahara, J. Mizutani, *Agr. Biol. Chem.* 1975, **39**, 71-76. b) Y. Endo, K. Shudo, a. Itai, M. Hasegawa, S. I. Sakai, *Tetrahedron*, 1986, **42**, 5905-5924. c) M. R. Rella, P. G. Williard *J. Org. Chem.* 2007, **72**, 525-531.

10 S. Thiede, P. R. Wosniok, D. Herkommer, T. Debnar, M. Tian, T. Wang, M. Schrempp, D. Menche, *Chem. Eur. J.* 2017, **23**, 3300-3320.

11 a) S. Yoshifuji, K. I. Tanaka, T. Kawai, V. Nitta, *Chem. Pharm. Bull.* 1985, **33**, 5515-5521. b) K. Drauz, A. Kleemann, J. Martens, P. Scherberich, *J. Org. Chem.* 1986, **51**, 3494-3498.

12 a) S. E. V. Bell, R. F. C. Brown, F. W. Eastwood, J. M. Horvath, *Aust. J. Chem.* 2000, **53**, 183-190. b) M. Nakagava, S. Kato, S. Kataoka, S. Kodato, H. Watanabe, H. Okajima, B. Witkop, B. *Chem. Pharm. Bull.* 1981, **29**, 1013-1026. c) C. Goeschen, N. Wibowo, J. M. White, U. Wille, *Org. Biomol. Chem.* 2011, **9**, 3380-3385.