General procedure for γ-oxyamination of unsaturated aldehydes under metal-organocatalytic conditions (A)

A mixture of an unsaturated aldehyde (0.75 mmol), TEMPO (0.25 mmol, 39 mg), CuBr (0.025 mmol, 3.7 mg, 2 -NO_2PhCO_2H (0.025 mmol, 4.2 mg) and (S)-α,α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (0.025 m mol, 8.6 mg) in toluene (0.25 M, 1mL) was added in a vial and stirred at 25^0C for overnight. The solvent was re moved under reduced pressure to produce a residue which was purifed by column chromatography on a silica ge l eluting with hexane and ether (99:1 v/v) to afford the oxyamination product.

General procedure for one-pot γ-oxyamination of allylic alcohols under metal-organocatalytic conditions (B)

A mixture of an allylic alcohol (0.75mmol), TEMPO (0.25 mmol, 39 mg), CuBr (0.025 mmol, 3.7 mg), 2-NO_2P hCO_2H (0.025 mmol, 4.2 mg) and (S)-α,α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (0.025 mmol, 8. 6 mg) in toluene (1M, 0.25mL) was added in a vial and stirred at 25^0C for overnight. The solvent was removed under reduced pressure to produce a residue which was purifed by column chromatography on a silica gel elutin g with hexane and ether (99:1 v/v) to afford the oxyamination product.

General procedure for sequential γ-oxyamination of allylic alcohols under metal-organocatalytic conditio ns (C)

A mixture of an allylic alcohol (0.75mmol), TEMPO (0.025 mmol, 3.9 mg), CuBr (0.025 mmol, 3.7mg) in DMF (1M, 0.25mL) was added in a vial and oxygen was purged through it for a minute. Then, the reaction mixture w as stirred at 25^0C for overnight. 2-NO_2PhCO_2H (0.025 mmol, 4.2 mg), TEMPO (0.225 mmol, 35.1 mg) and (S)- α,α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (0.025 mmol, 8.6 mg) were added into the reaction mix ture and kept stirring at 25^0C for overnight. The reaction mixture was quenched with HCl solution and extracted with diethyl ether. The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The resulted re sidue was purifed by column chromatography on a silica gel eluting with hexane and ether (99:1 v/v) to afford t he oxyamination product.

Synthesis of (E)-methyl 4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-2-enoate (2c)

In a 100 ml round bottom flask equipped with magnetic stir bar, compound (E)-4-(2,2,6,6-tetramethylpiperidin- 1-yloxy)hex-2-enal **2b** (390 mg, 1.54 mmol) was dissolved in a mixture of MeOH (8.0 mL), CH_3CN (8.0 mL), water (8.0 mL) and cooled to 0 ^{O}C. KH_2PO_4 (580 mg, 4.26 mmol) and $NaClO_2$ (366 mg, 3.23 mmol) were adde d subsequently to the ice cooled solution of the reaction mixture. H_2O_2 (35% solution, 4.6 mL) was injected slo wly to the reaction mixture at the same temperature. After the completion of the addition the reaction mixture w as warmed up to RT. After 2 h the pH of the reaction mixture was adjusted to 3 with dilute HCl and saturated N a_2SO_3 solution (30 mL) was added. The resulting mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. Th e organic layer was concentrated in vacuum and the residue was dissolved in 5.0 mL dry CH_2Cl_2. Methanol (213 mg, 4.62 mmol), N,N-dimethylaminopyridine (9.4 mg, 0.08 mmol) and Diisopropylcarbodiimide (195 mg, 1.54 mmol) were subsequently added to the reaction mixture and stirred for 2 h at rt. After completion of the reaction solvents were evaporated under vacuum and the crude product was subjected to FC on silica gel using 1% dieth ylether in hexane as eluent. Yield: 76 % (331.6 mg).

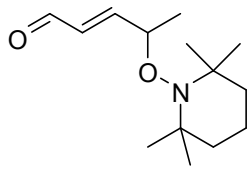
Synthesis of (E)-methyl 4-hydroxyhex-2-enoate (2d)

Compound **2c** (175mg, 0.62 mmol) were dissolved in 20 ml THF: H_2O: AcOH (1:1:3) solution. Zinc powder (1. 6 g, 24.7 mmol) was added to the mixture and stirred at 65^{o}C for 4 hrs. After cooling to room temperature the re action mixture was diluted with ethyl acetate, filtered through celite and evaporated to dryness. The crude produ ct was purified by silica gel flash chromatography. Yield: 43 % (38.2 mg).

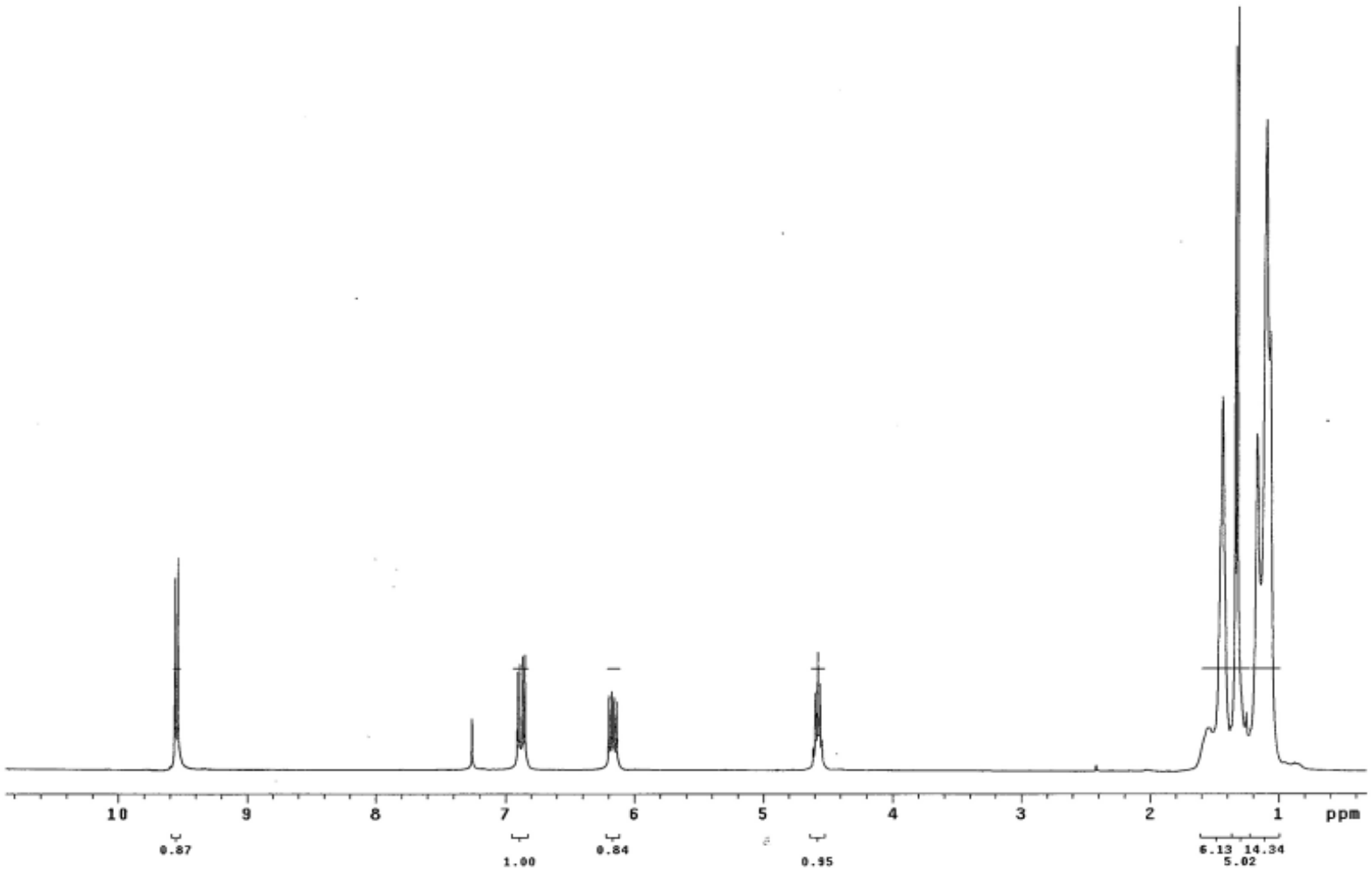
Synthesis of (E)-methyl 4-oxohex-2-enoate (2e)

To a stirred solution of (E)-methyl 4-hydroxyhex-2-enoate **2d** (35 mg, 0.24 mmol) in 2.4 ml toluene, TEMPO (1.9 mg, 0.072 mmol), $Fe(NO_3)_3.9H_2O$ (4.8 mg, 0.012 mmol) and NaCl (0.7 mg, 0.012 mmol) were added subsequently. Then the reaction mixture was placed under oxygen through a balloon and stirred for 2 h. After completion of the reaction the resulting mixture was evaporated and purified by silica gel column chromatography (2 % diethylether in hexane). Yield: 51 % (17.6 mg).[i]

To a stirred solution of (E)-methyl 4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-2-enoate **2c** (70 mg, 0.25 mmol) in 1.2 ml CH_2Cl_2, *m*CPBA (60 mg, 0.35 mmol) was added portion wise at 0°C. After 2 h the reaction mixture was treated with aqueous Na_2SO_3 solution, extracted with CH_2Cl_2 and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (2 % diethylether in hexane). Yield: 57 % (20.1 mg).[ii]



(E)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)pent-2-enal (1b) R_f = 0.44 in 1:5 v/v ether/hexane; colorless oil; yield 40.7 mg (0.17 mmol, 68 %). IR (KBr): 2932, 1695, 1376, 1133, 976 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ: 1.07-1.44 (21H, m), 4.58 (1H, m), 6.16 (1H, dd, *J* = 7.6, 16 Hz), 6.87 (1H, dd, *J* = 6.8, 15.8 Hz), 9.54 (1H, d, *J* =9.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 17.6, 20.5, 20.7, 20.8, 34.6, 34.9, 40.5, 79.5, 130.8, 160.1, 194.0 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{14}H_{25}NO_2$: 240.1964; found: 240.1961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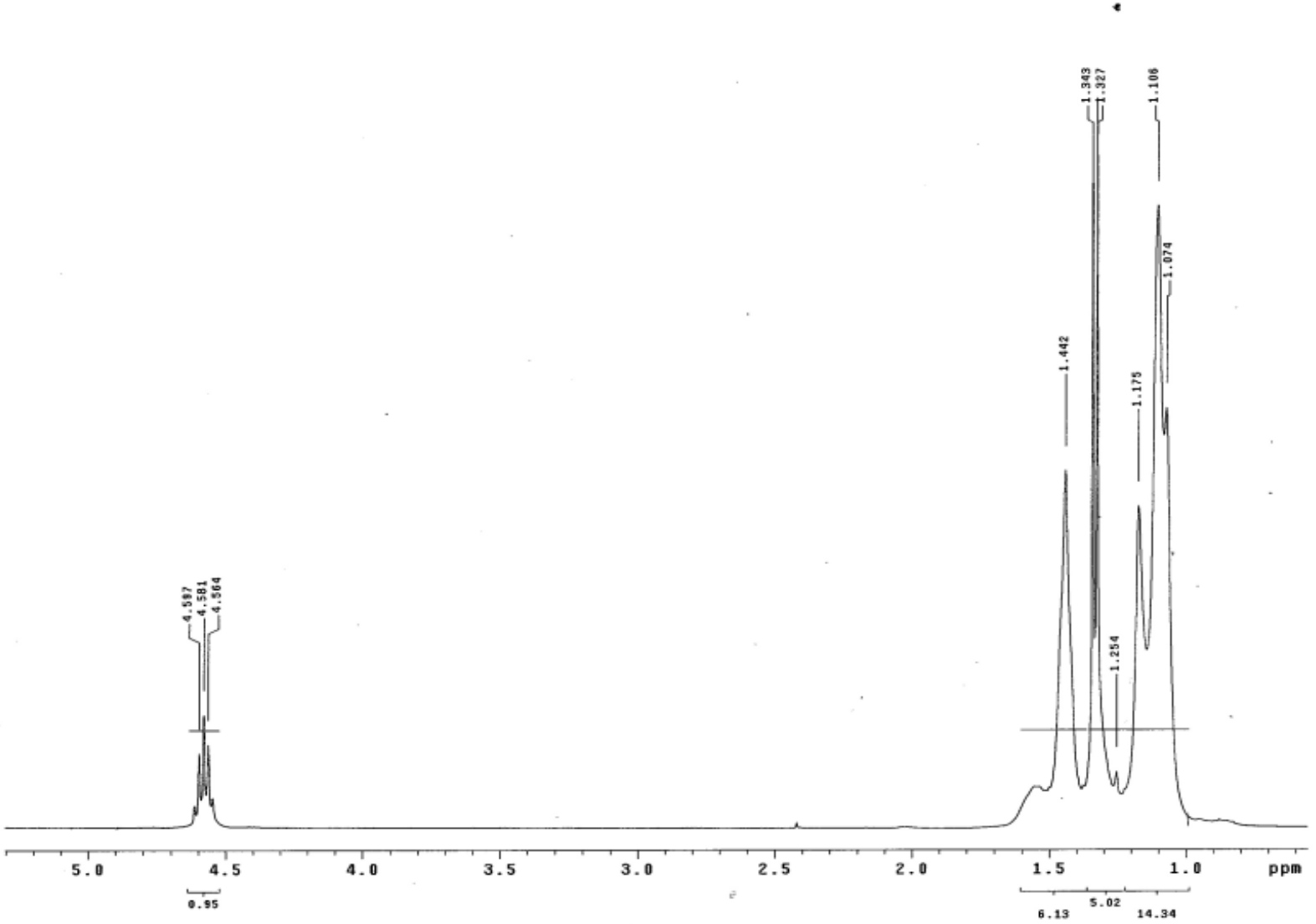
5.02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ppm
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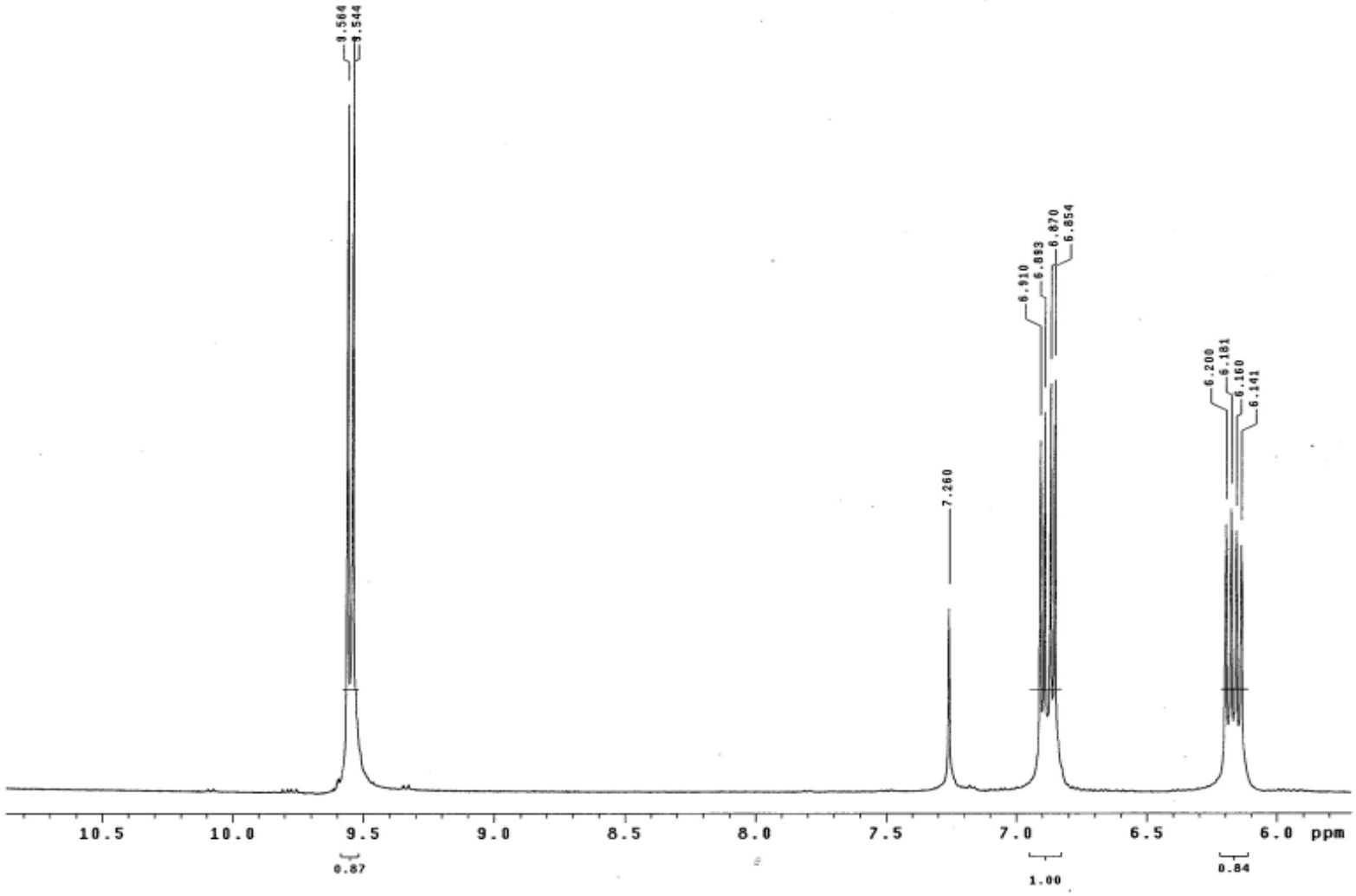
6.13
5.02
14.34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8.0
7.5
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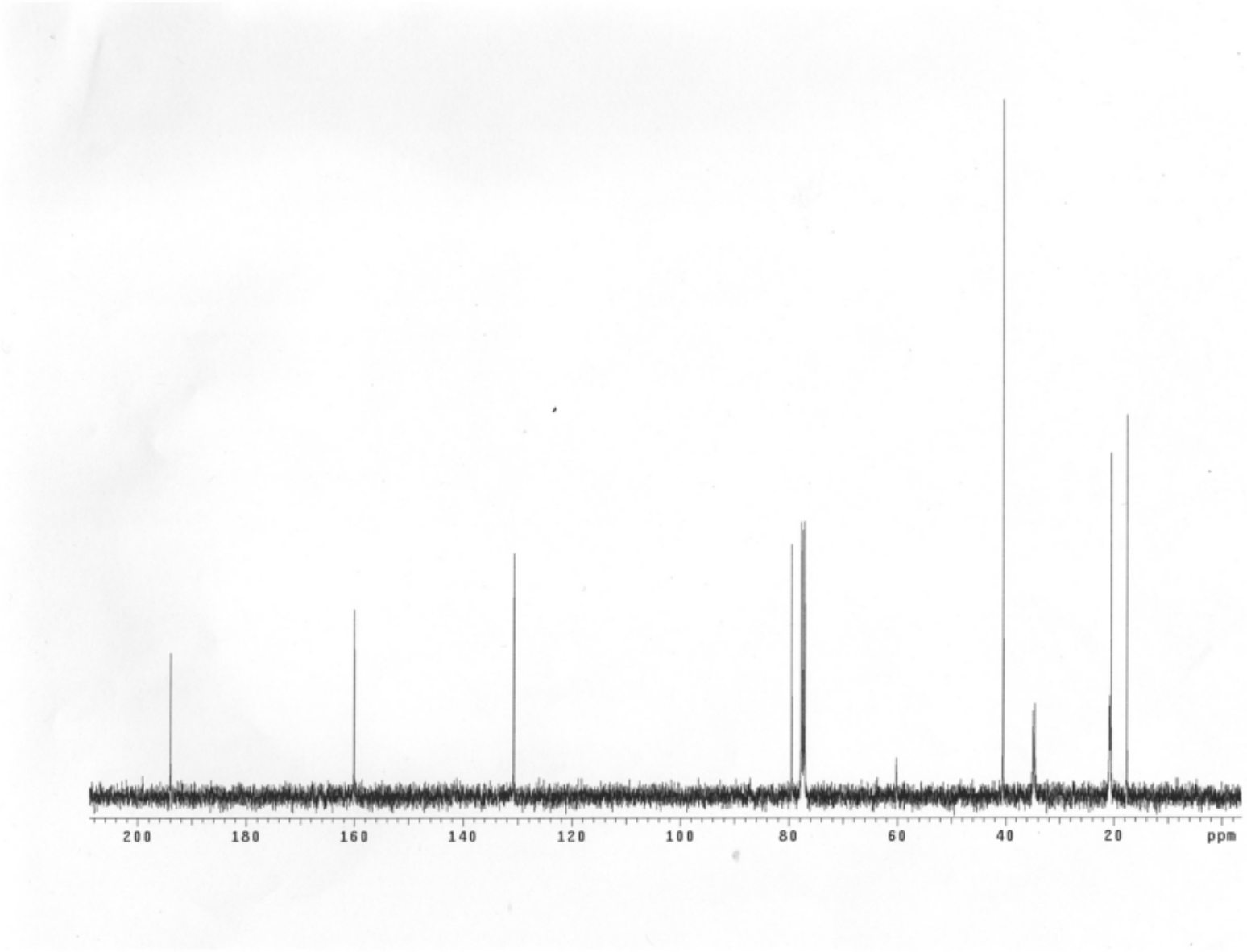
6.0 ppm
0.87
1.00
0.84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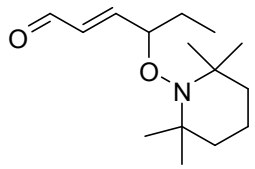
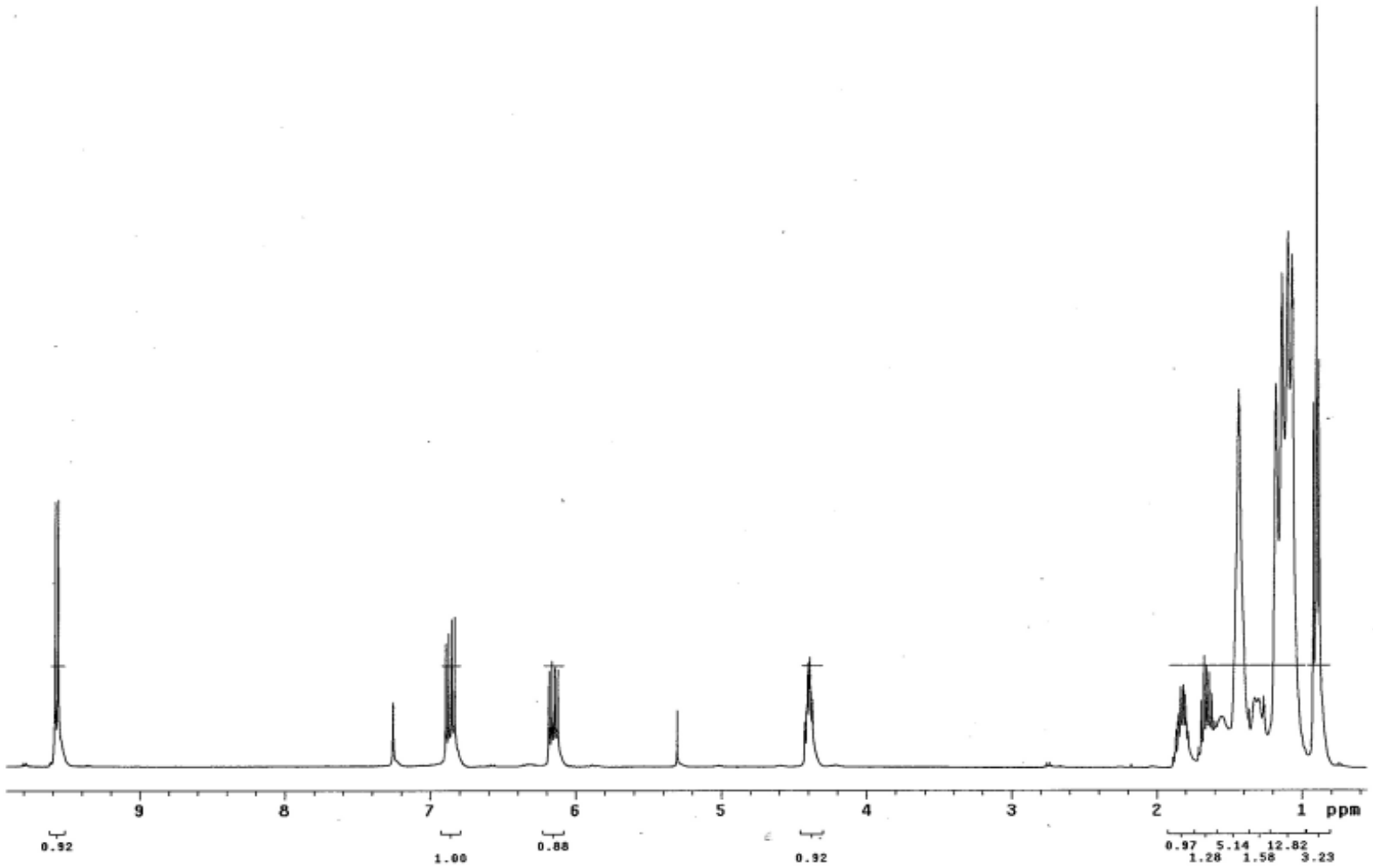
20
ppm



(E)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-2-enal (2b) R_f = 0.44 in 1:5 v/v ether/hexane; colorless oil; y ield 50.6 mg (0.2000 mmol, 80 %). IR (KBr): 2935, 1695, 1377, 1258, 977 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ: 0.89-1.87 (23H, m), 4.40 (1H, m), 6.15 (1H, dd, *J* = 7.6, 16 Hz), 6.87 (1H, dd, *J* = 7.6, 16 Hz), 9.58 (1H, d, *J* = 7.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 9.8, 17.6, 20.7, 20.8, 27.1, 34.4, 35.0, 40.6, 84.7, 132.3, 159.3, 193.9 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{15}H_{27}NO_2$:254.2120; found: 254.2118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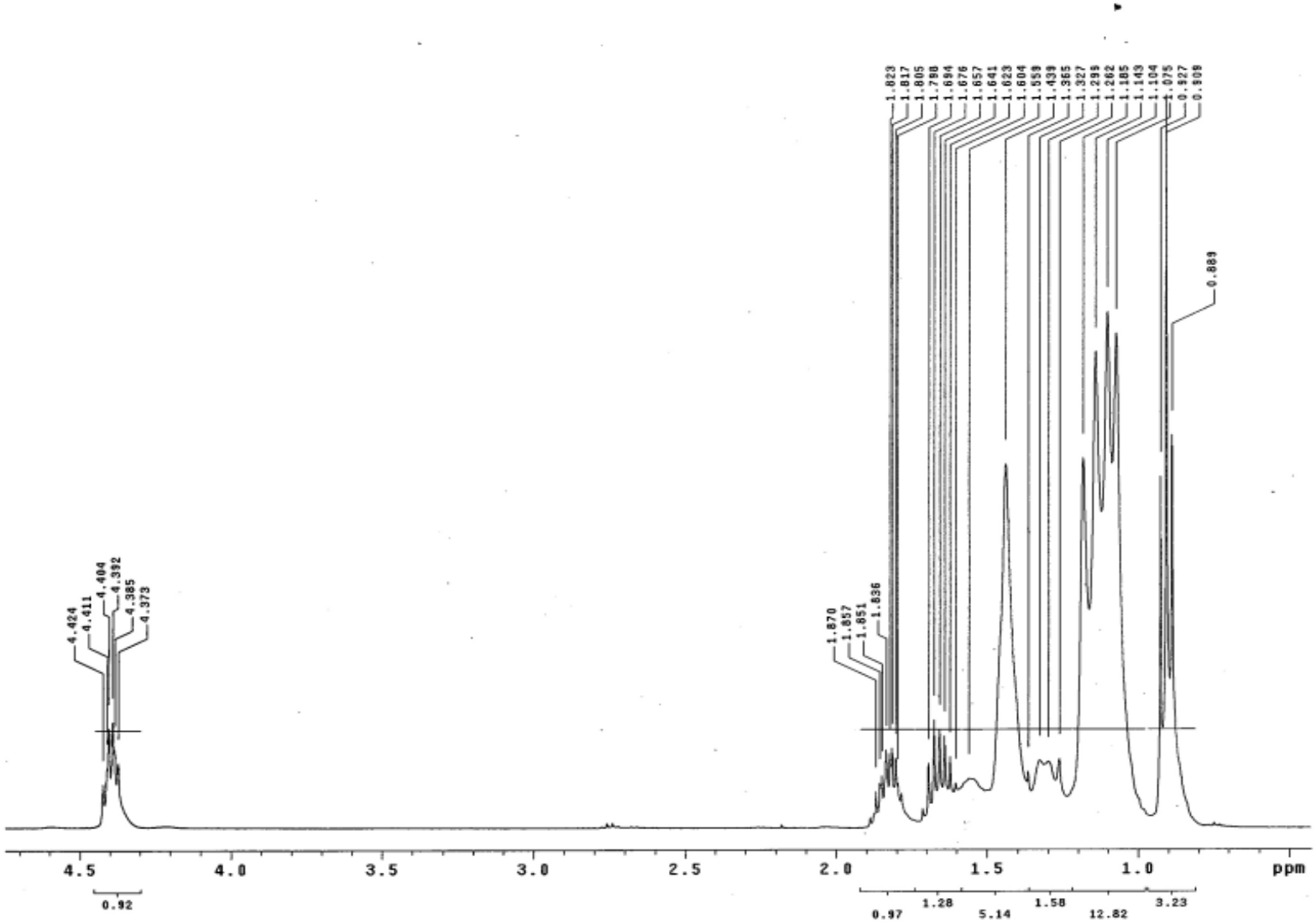
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1.694
1.676
1.657
1.641
1.623
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1.559
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1.365
1.327
1.235
1.202
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0.908
0.883
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4.0
3.5
3.0
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ppm
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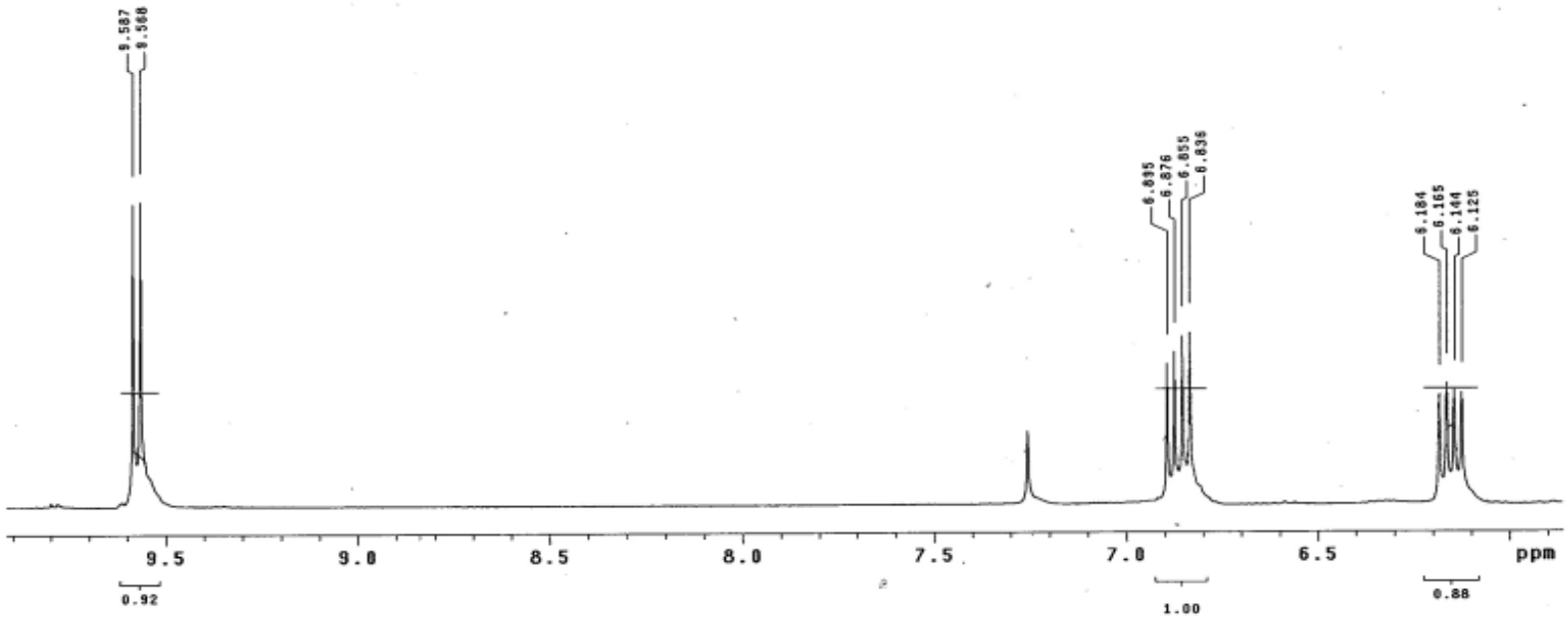
12.82
3.23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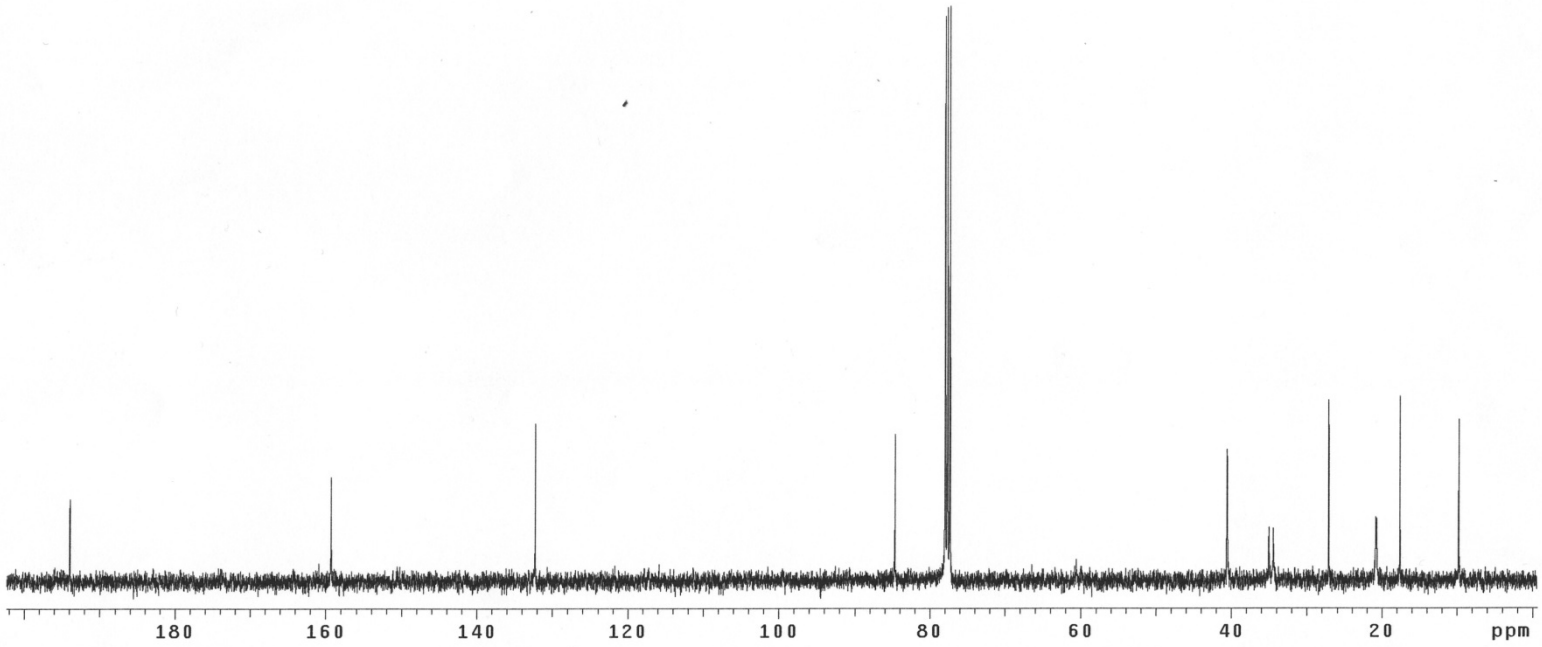
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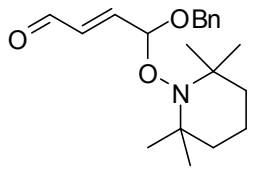
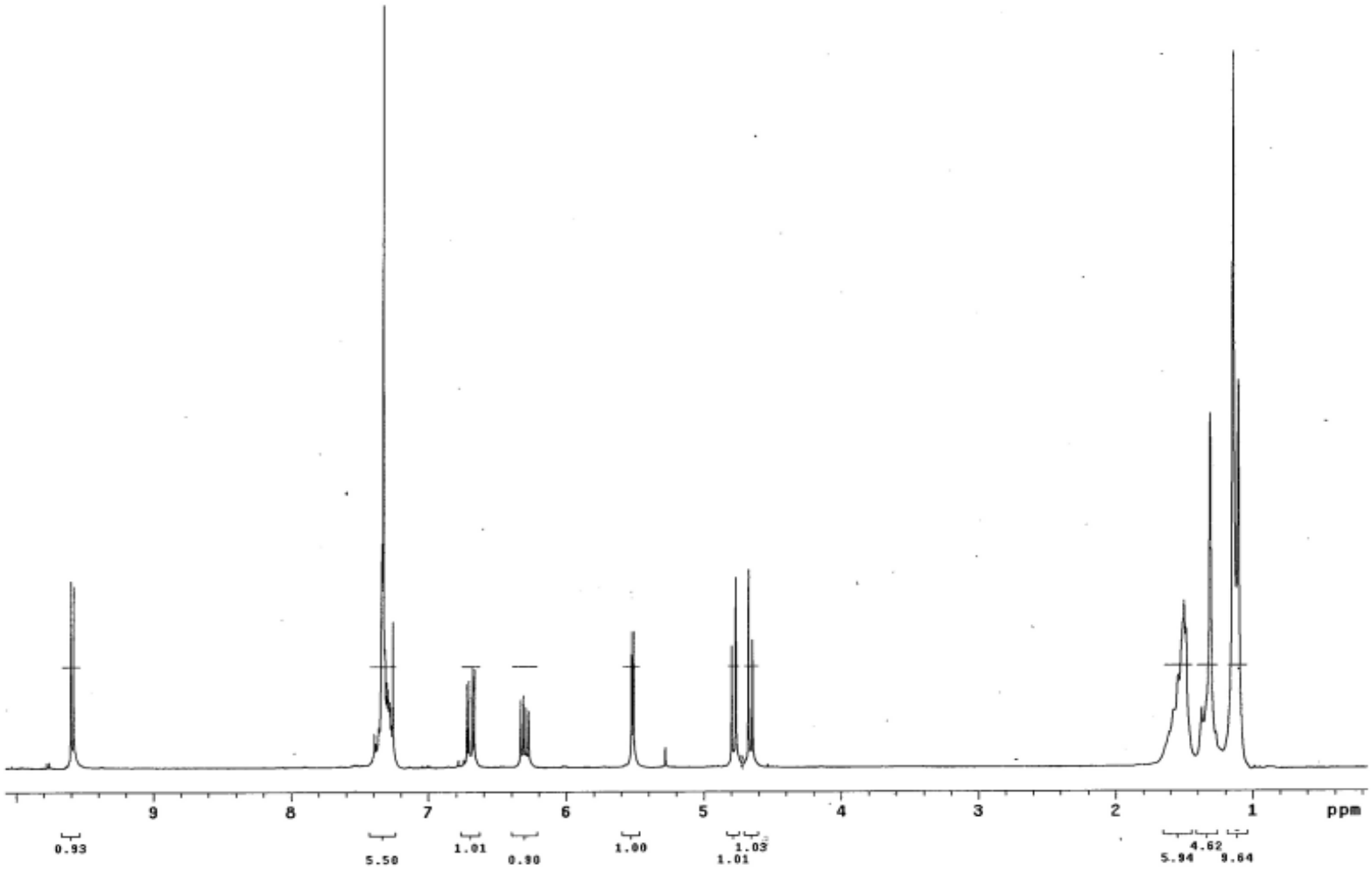
40
20
ppm



(E)-4-(benzyloxy)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)but-2-enal (3b) R_f = 0.73 in 1:4 v/v ethyl acetate/ hexane; white solid; yield 25.7 mg (0.0776 mmol, 31%); mp 68-70^{0}C. IR (KBr): 2932, 1696, 1378, 1095, 698 c m^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ: 1.11-1.55 (18H, m), 4.66 (1H, d, *J* = 11.6 Hz), 4.78 (1H, d, *J* = 11.6Hz), 5.5 2 (1H, d, *J* = 4.8 Hz), 6.27 (1H, dd, *J* = 8, 16 Hz), 6.67 (1H, dd, *J* = 5.2, 15.6 Hz) 7.30 (m, 5H), 9.59 (1H, d, *J* = 8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 17.5, 20.6, 21.0, 33.9, 34.0, 40.4, 40.8, 60.1, 61.2, 70.2, 105.3, 127.8, 127.9, 128.6, 133.1, 137.9, 150.8, 193.6 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{20}H_{29}NO_3$:332.2226; foun d: 332.2224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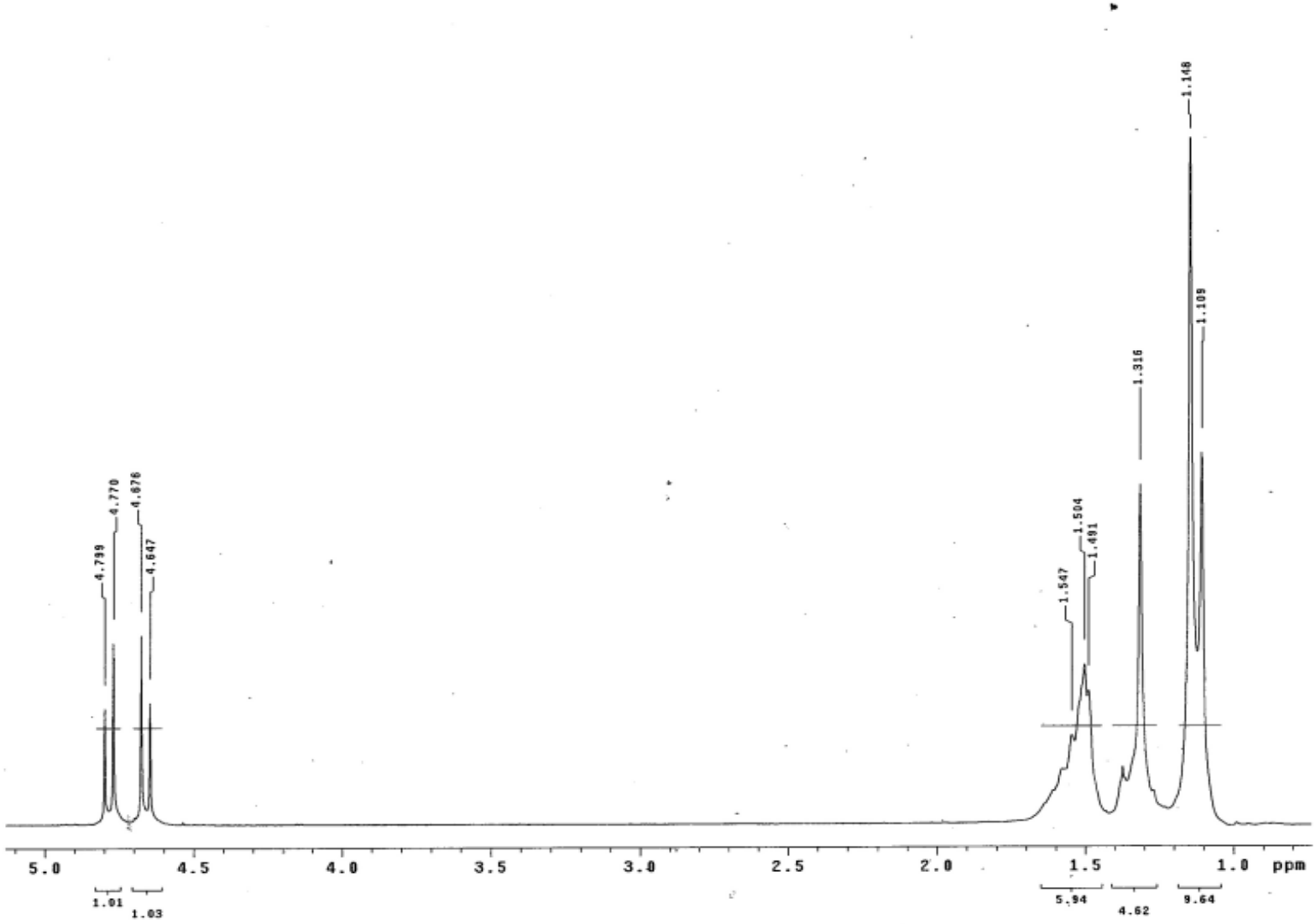
9.64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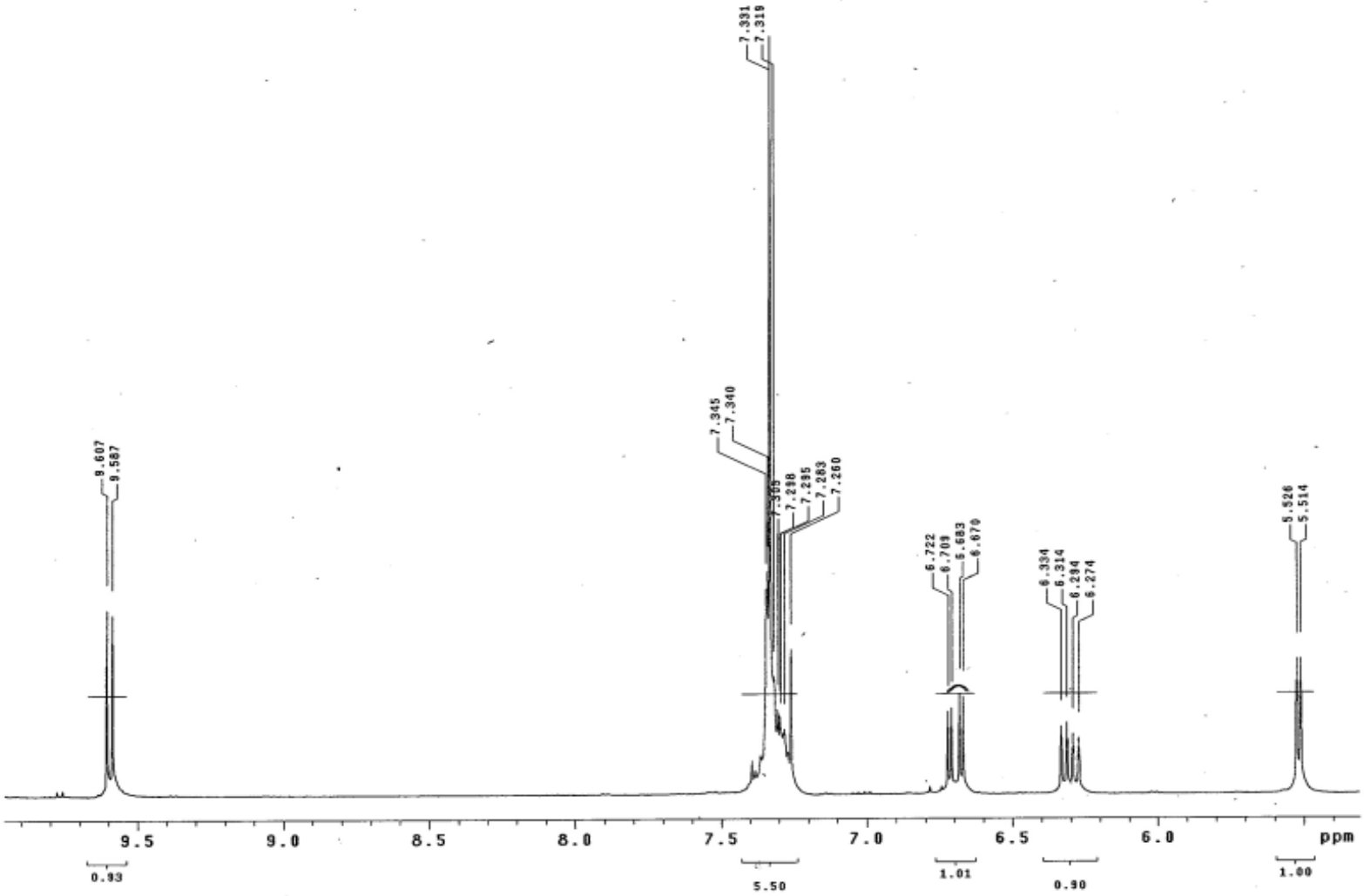
4.62
9.64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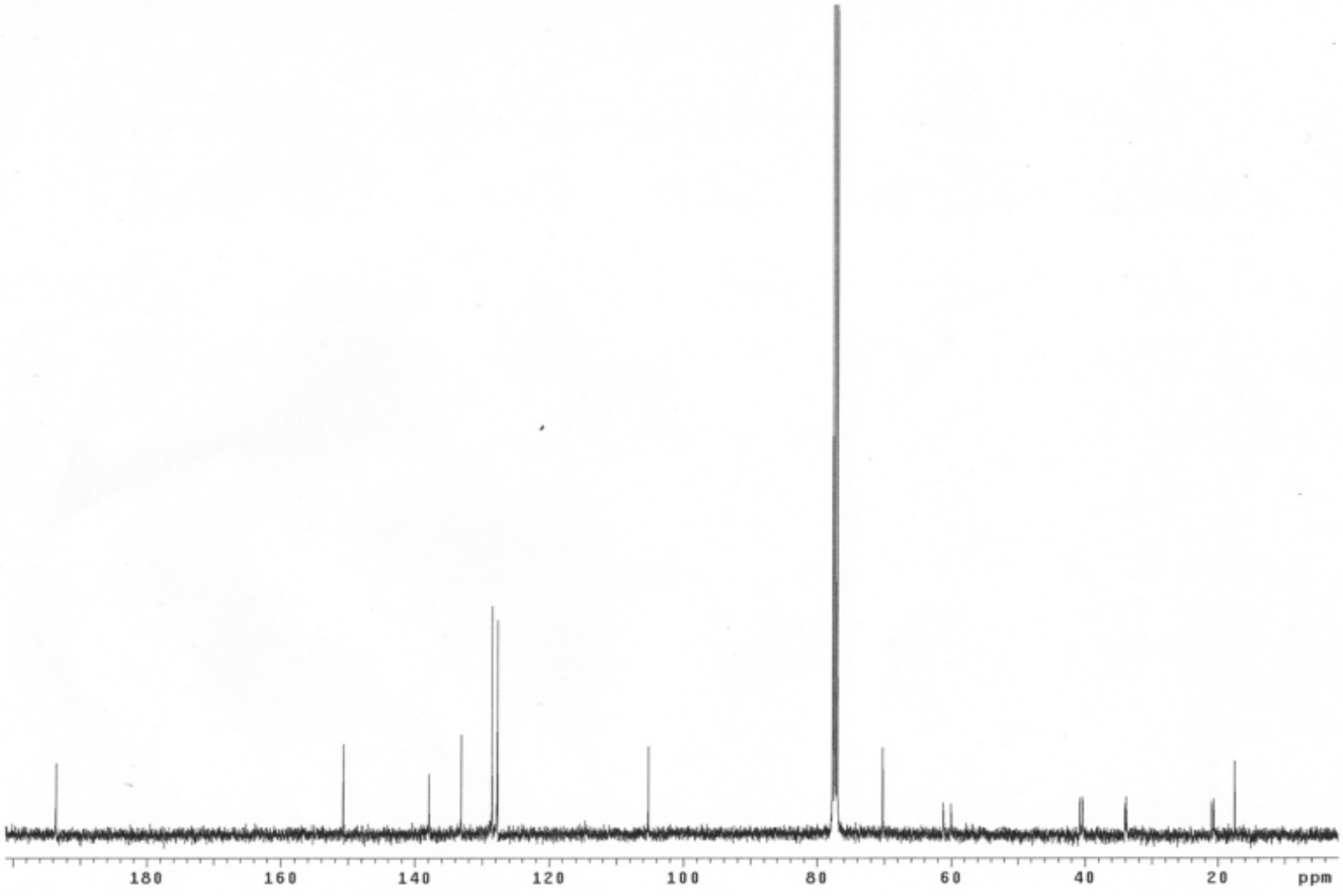
0.90
1.00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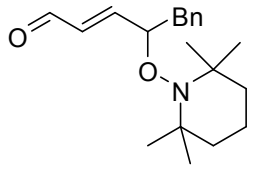
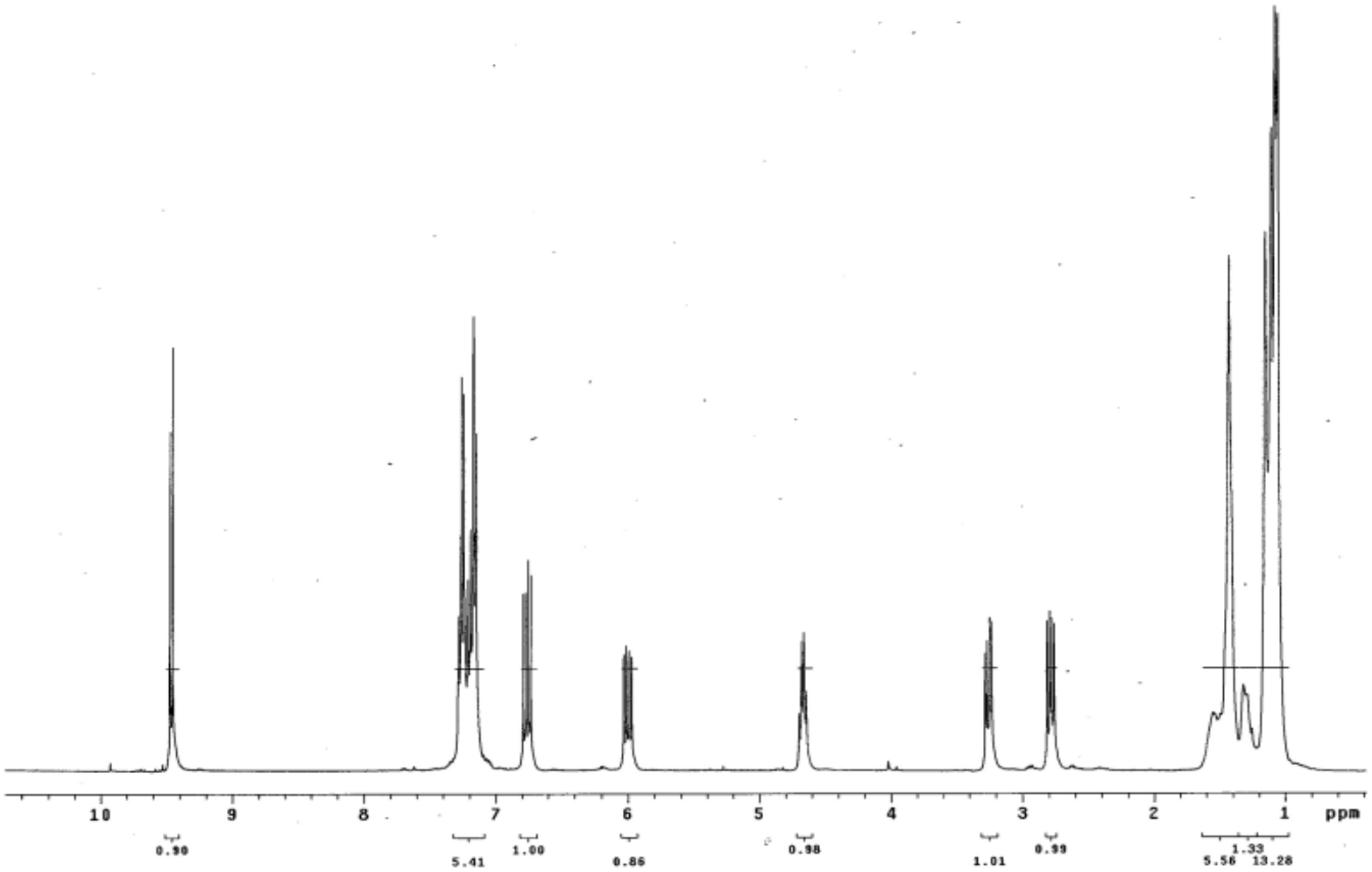
80
60
40
20
ppm



(E)-5-phenyl-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)pent-2-enal (4b) R_f = 0.37 in 1:5 v/v ether/hexane; col orless oil; yield 35.5 mg (0.1126 mmol, 45%). IR (KBr): 2972, 1725, 1385, 1132, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 4 00MHz) δ: 1.07-1.55 (18H, m), 2.80 (1H, dd, *J* = 8.4, 13.2 Hz), 3.26 (1H, dd, *J* = 5.6,13.2 Hz), 4.67 (1H, m), 6. 00 (1H, dd, *J* = 6.8, 15.8 Hz), 6.77 (1H, dd, *J* = 7.2, 15.8 Hz), 7.22 (5H, m), 9.47 (1H, d, *J*=7.6 Hz) ppm pm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 17.6, 20.8, 21.0, 34.5, 35.2, 40.6, 41.2, 84.1, 126.7, 128.5, 129.8, 132.3, 137.2, 158. 1, 193.7 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{20}H_{29}NO_2$:316.2277; found: 326.2279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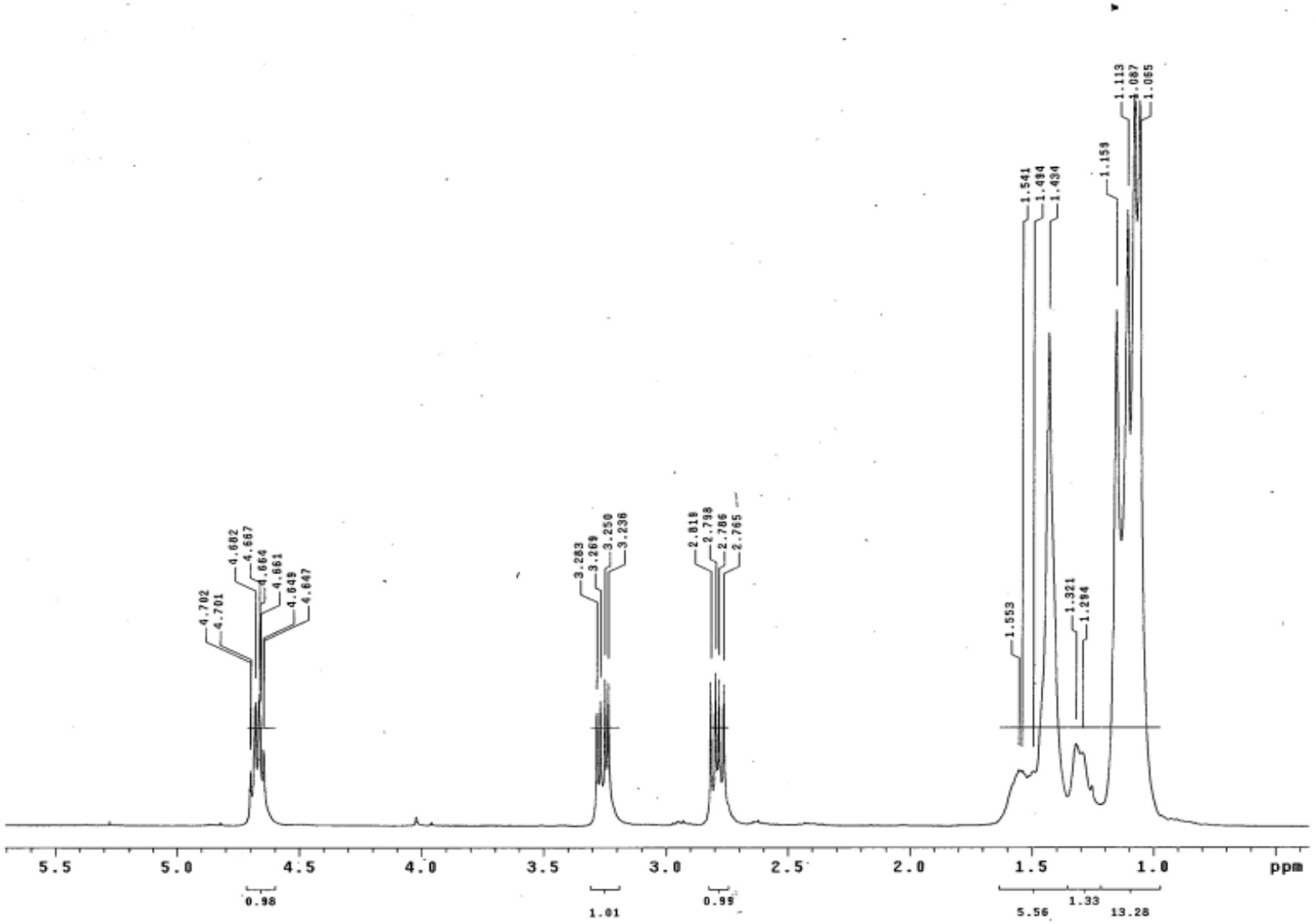
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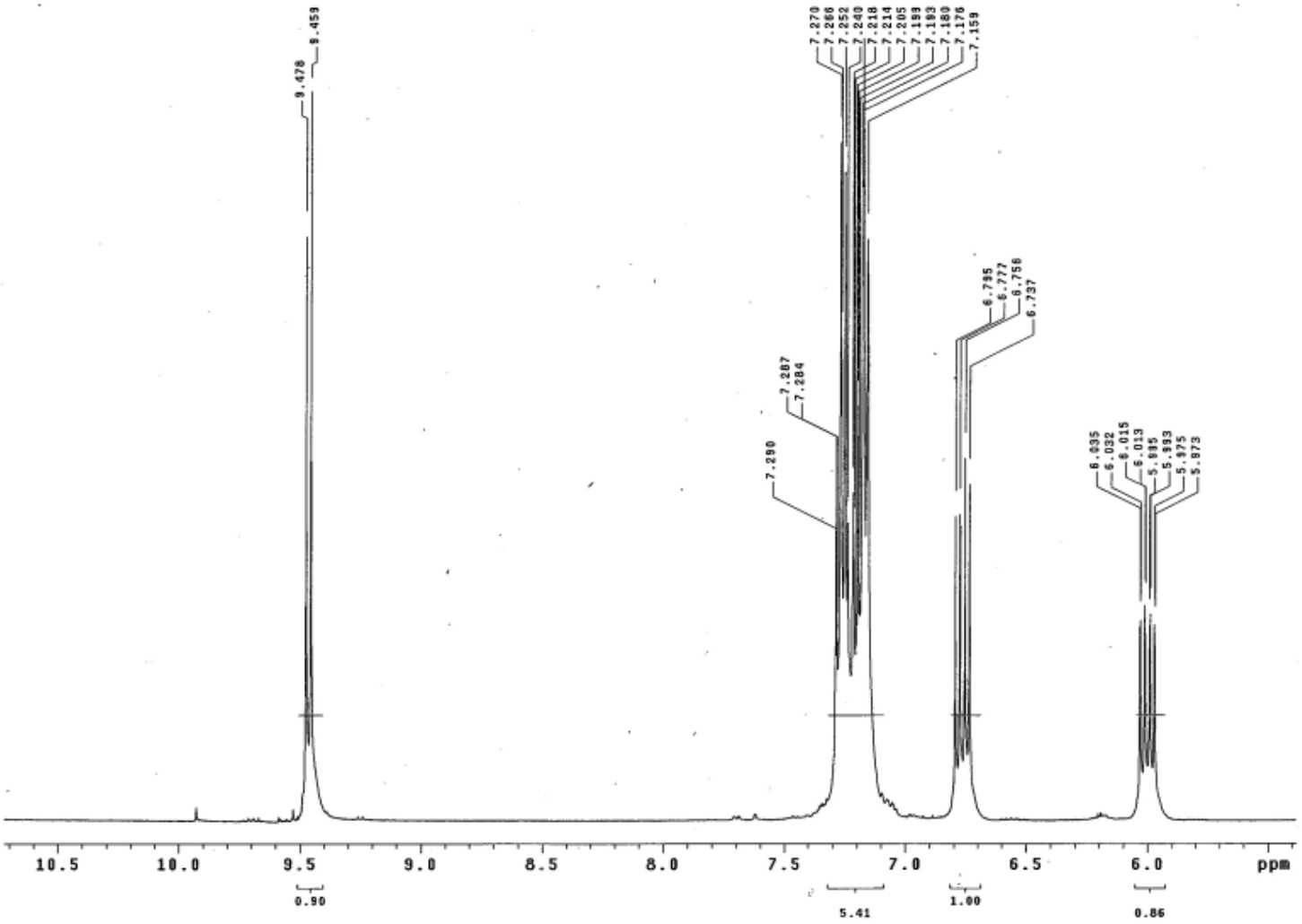
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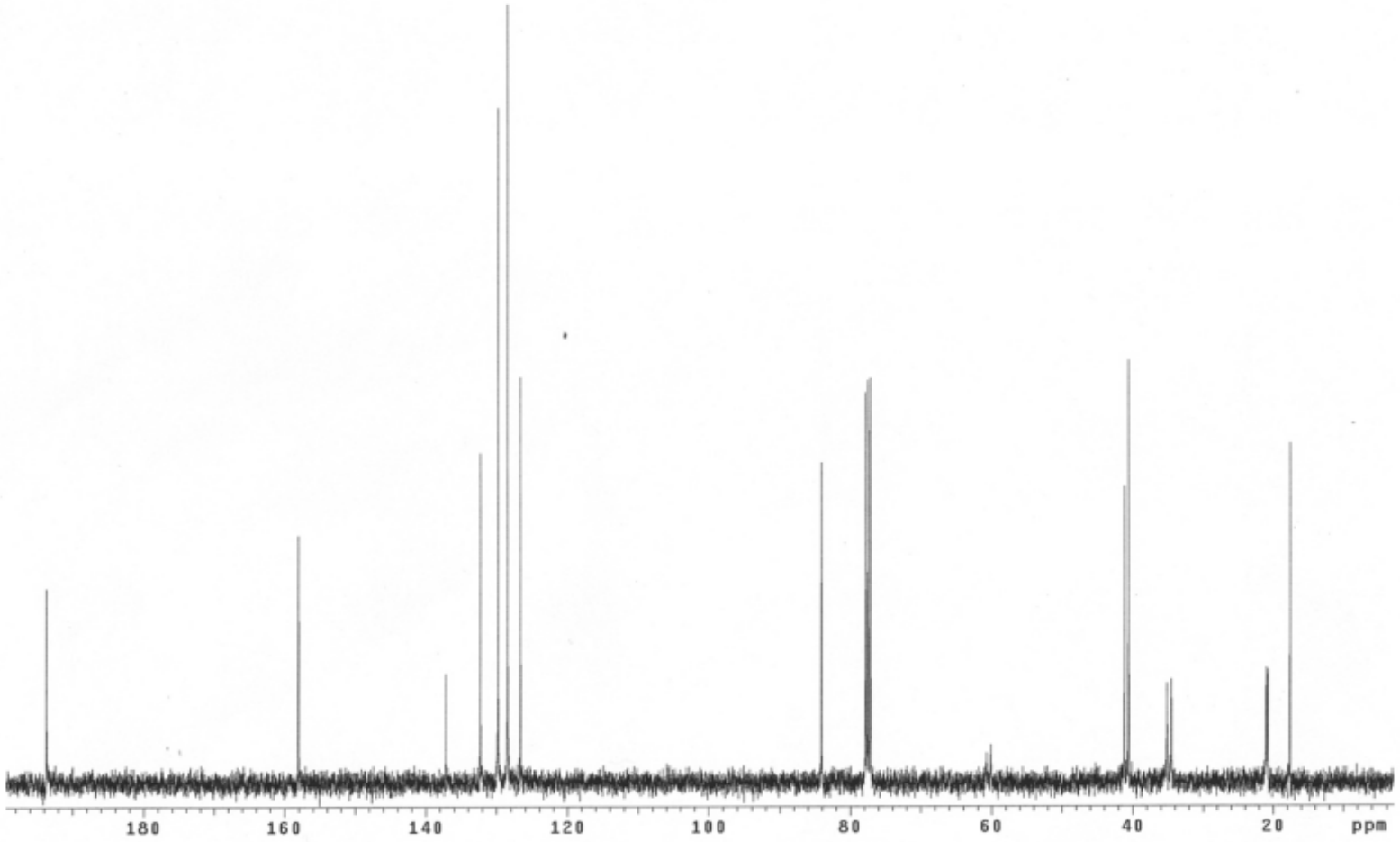
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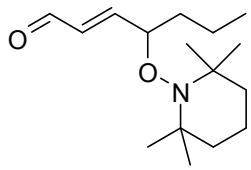
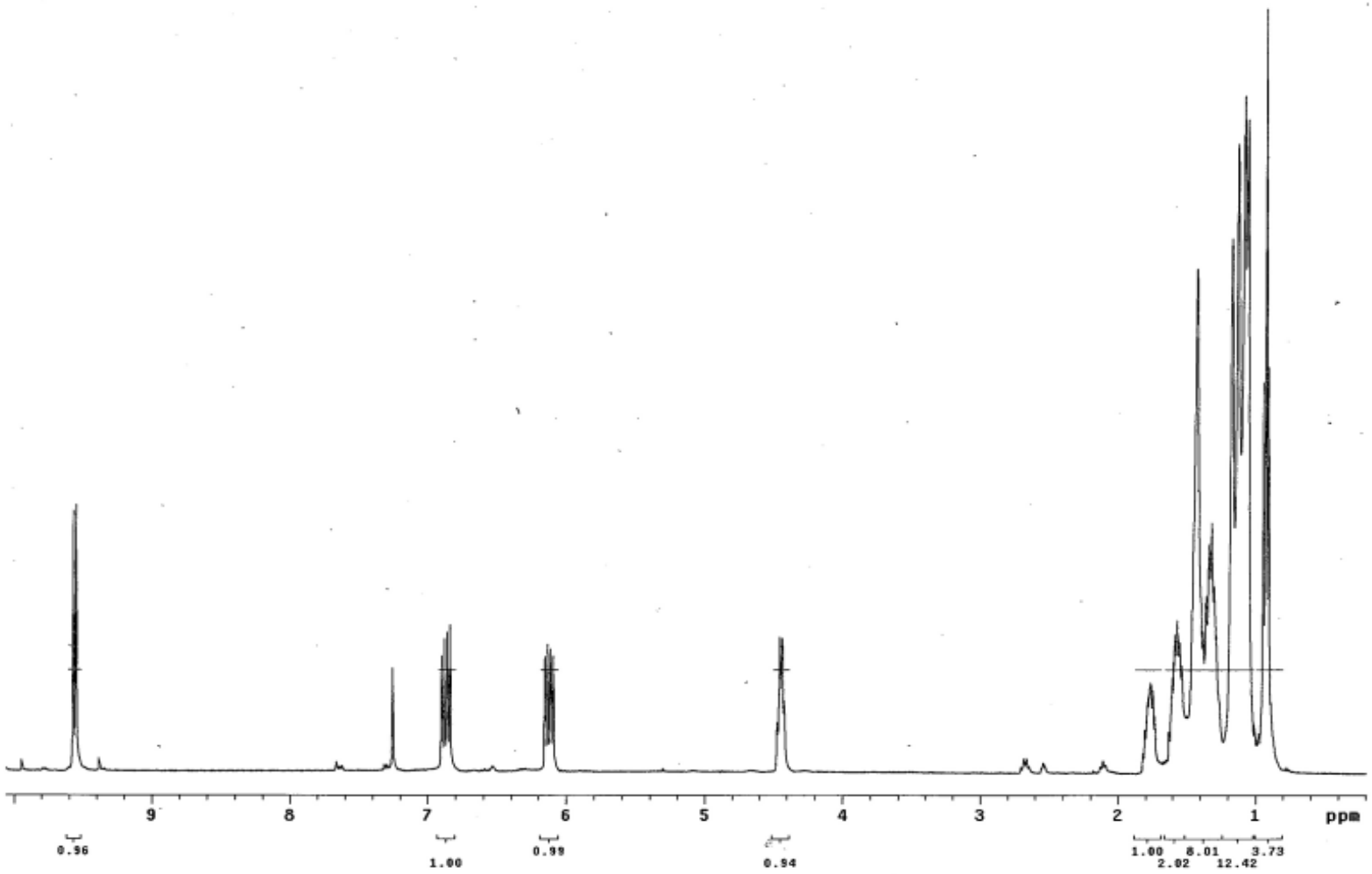
40
20
ppm



(E)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hept-2-enal (5b) R_f = 0.70 in 1:4 v/v ether/hexane; colorless oil; yield 34.1 mg (0.1276 mmol, 45%). IR (KBr): 2962, 1696, 1375, 1133, 985 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ: 0.89-1.79 (25H, m), 4.44 (1H, m), 6.13 (1H, dd, *J* = 7.6, 15.6 Hz), 6.88 (1H, dd, *J* = 7.6, 15.6 Hz), 9.57 (1H, d, *J* = 8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.6, 17.6, 18.7, 20.7, 34.4, 35.1, 36.4, 40.5, 83.4, 132.1, 159.6, 194.0 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{16}H_{29}NO_2$:268.2277; found: 268.2273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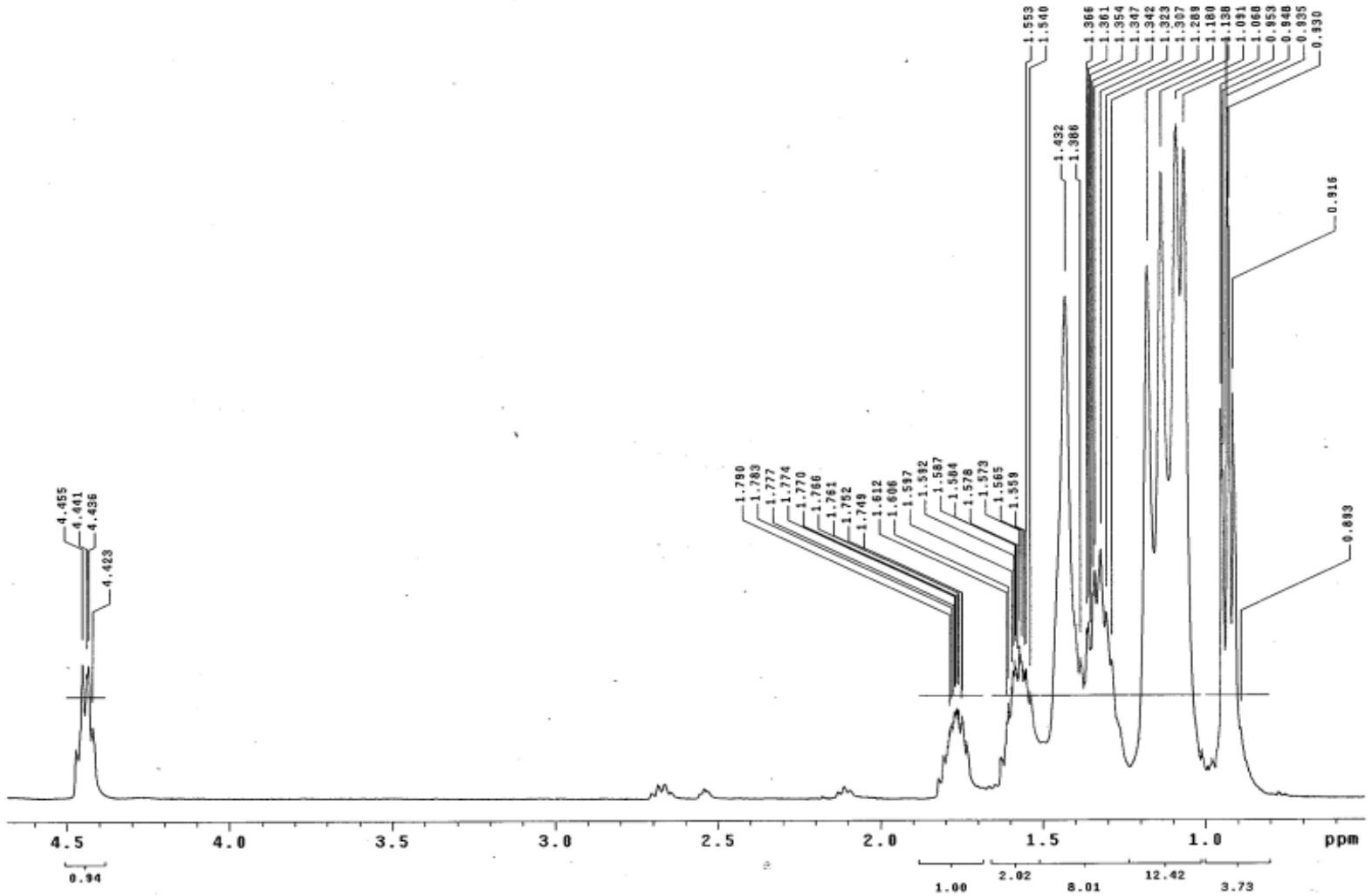
3.73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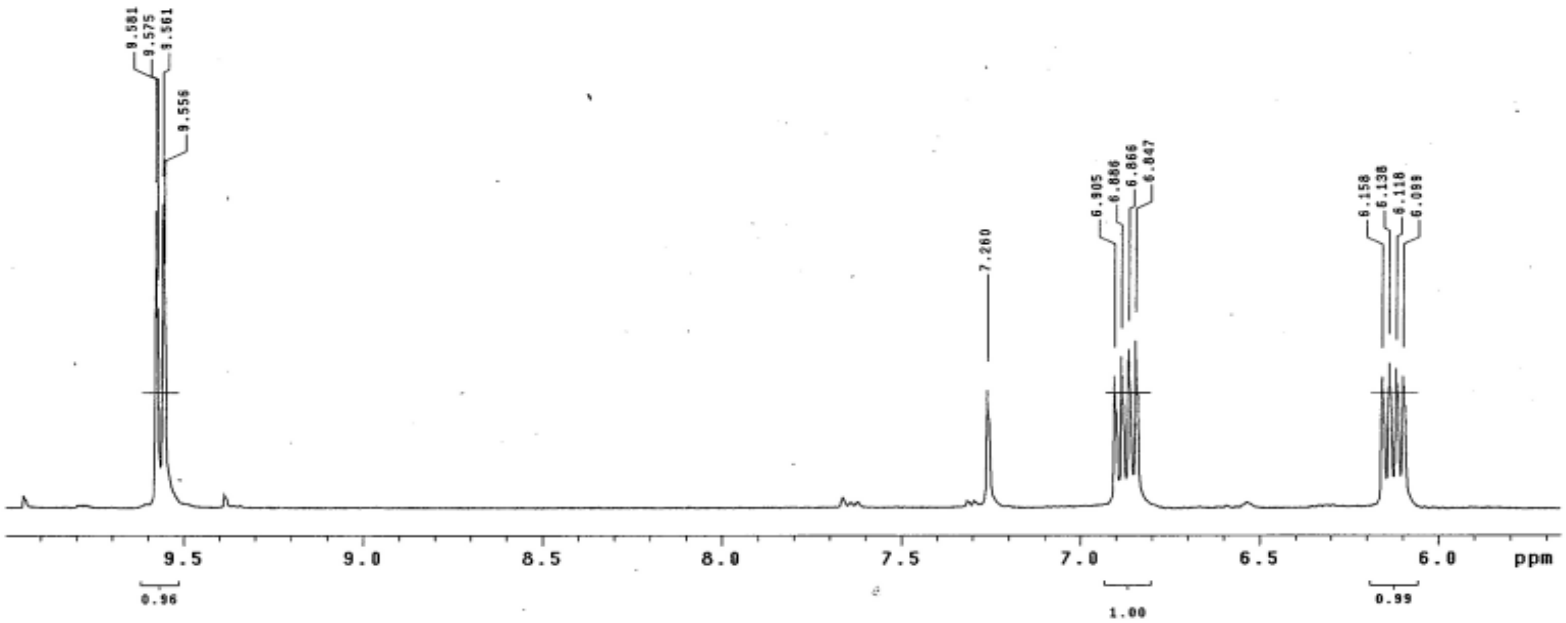
1.770
1.766
1.761
1.752
1.749
1.612
1.606
1.597
1.592
1.587
1.584
1.578
1.573
1.565
1.559
1.553
1.540
1.432
1.386
1.366
1.361
1.354
1.347
1.342
1.323
1.307
1.289
1.180
1.138
1.091
1.068
0.953
0.948
0.935
0.930
0.916
0.893
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.94
1.00
2.02
8.01
12.42
3.73


9.581
9.575
9.561
9.556
7.260
6.905
6.886
6.866
6.847
6.158
6.138
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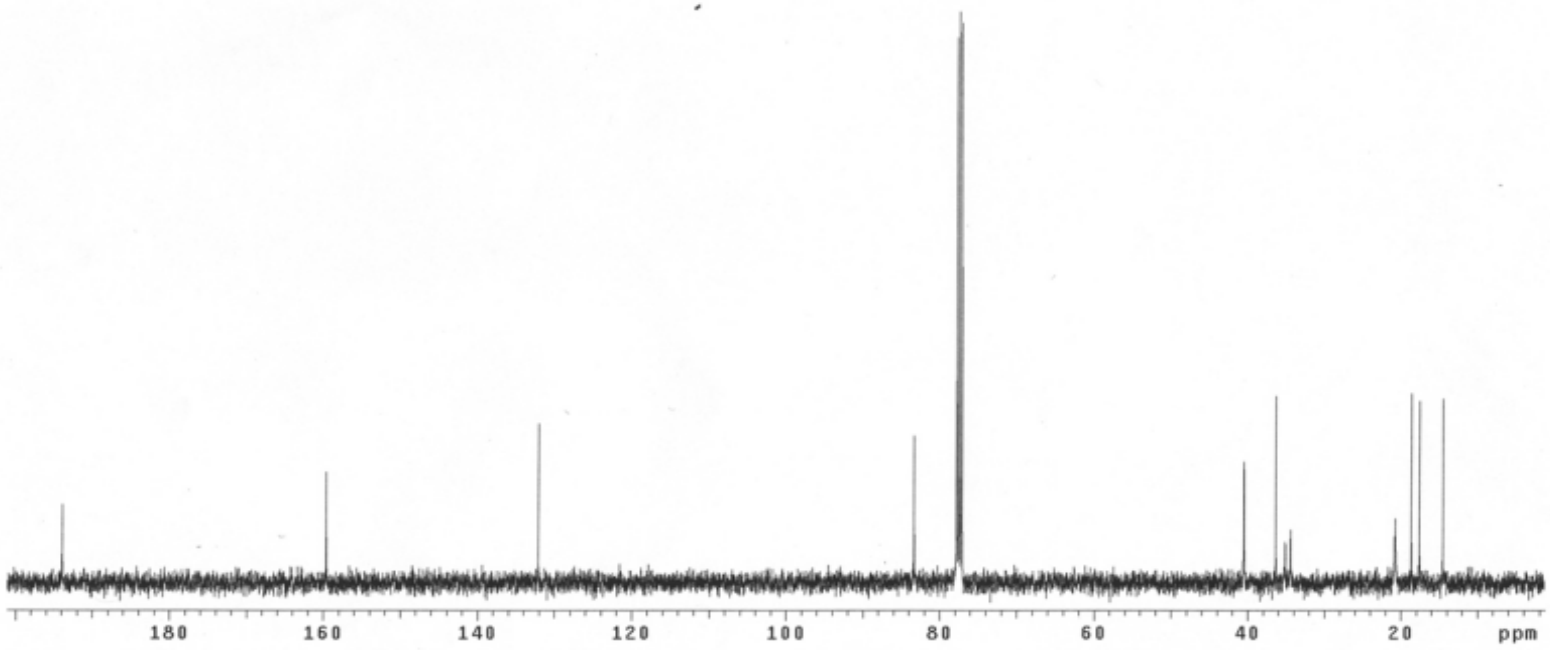
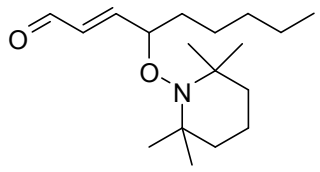
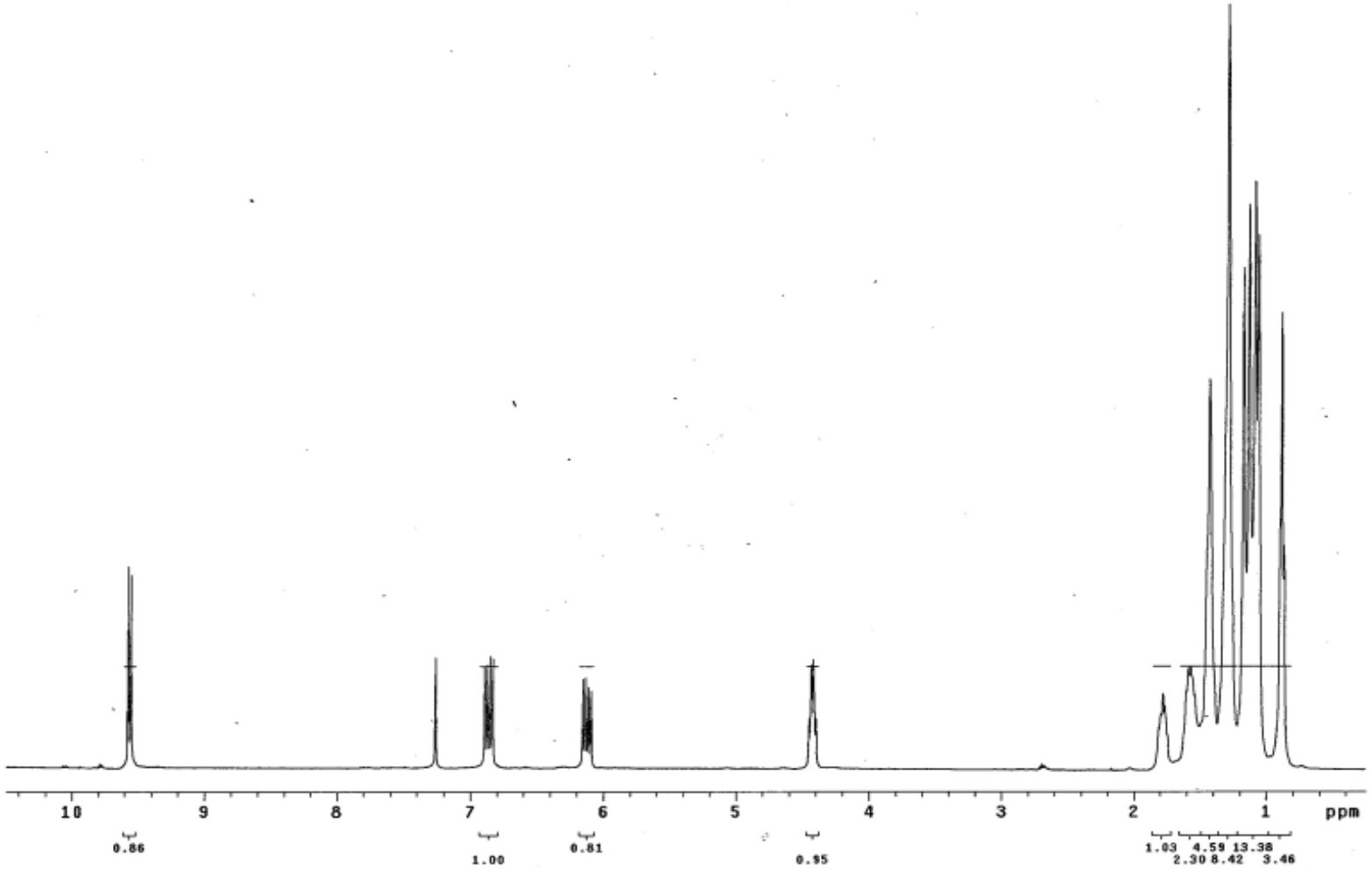
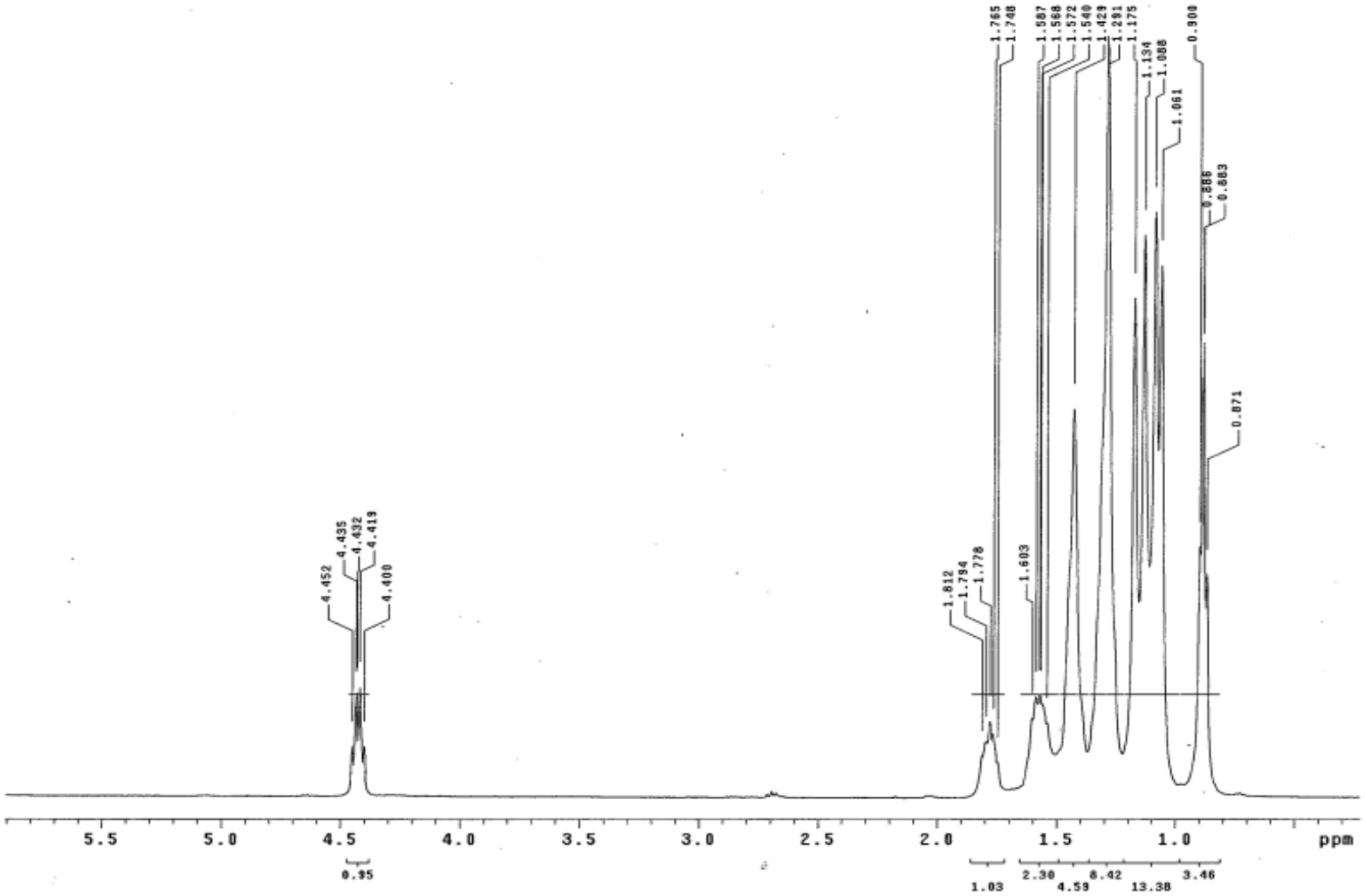
6.099
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm
0.96
1.00
0.99

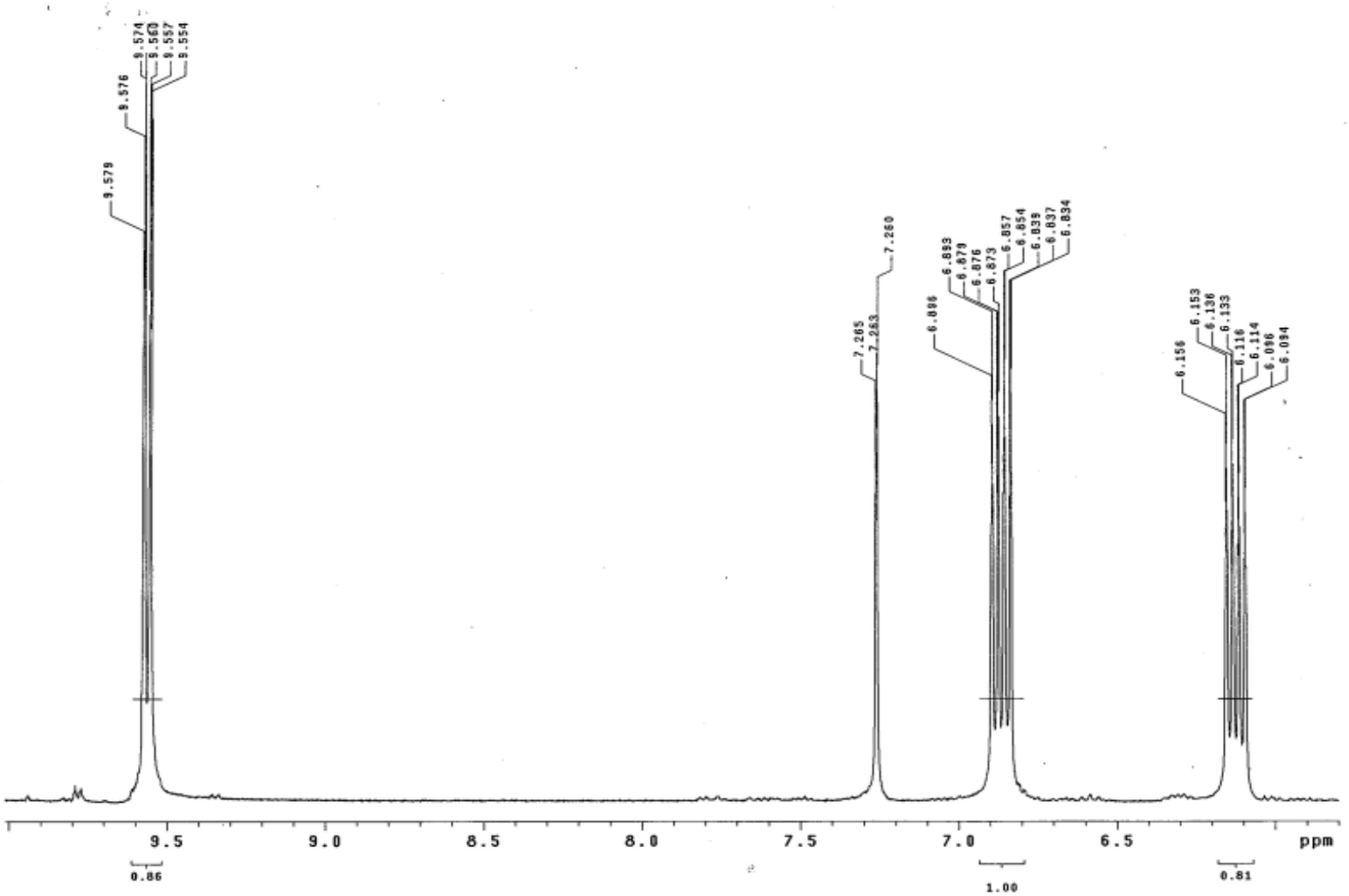

180
160
140
120
100
80
60
40
20
ppm

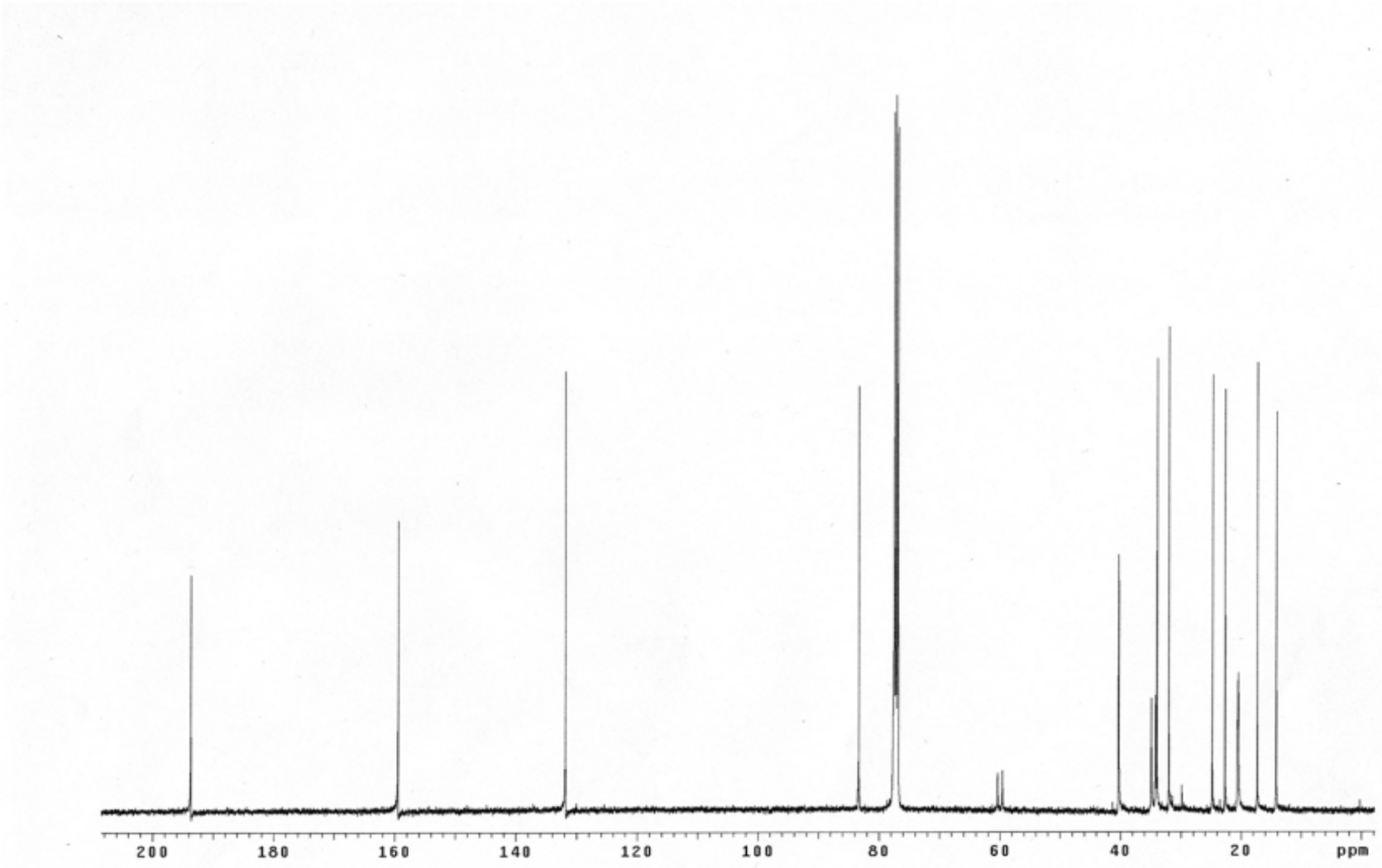


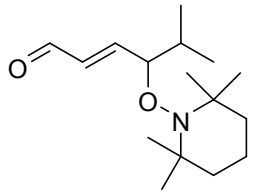
(E)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)non-2-enal (6b) R_f = 0.63 in 1:4 v/v ether/hexane; colorless oil; yield 39.9 mg (0.135 mmol, 54%). IR (KBr): 2931, 1696, 1375, 1132, 976 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ: 0.87-1.81 (27H, m), 4.43 (1H, m), 6.13 (1H, dd, *J* = 8, 15.6 Hz), 6.87 (1H, dd, *J* = 8, 15.6 Hz), 9.57 (1H, d, *J* = 8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.2, 17.4, 20.5, 20.6, 22.7, 24.8, 32.0, 34.0, 34.2, 34.9, 40.3, 83.3, 131.8, 159.5, 193.7 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{18}H_{33}NO_2$:296.2590; found: 296.2590


10
9
8
7
6
5
4
3
2
1
ppm
0.86
1.00
0.81
0.95
1.03
4.59
13.38
2.30
8.42
3.46

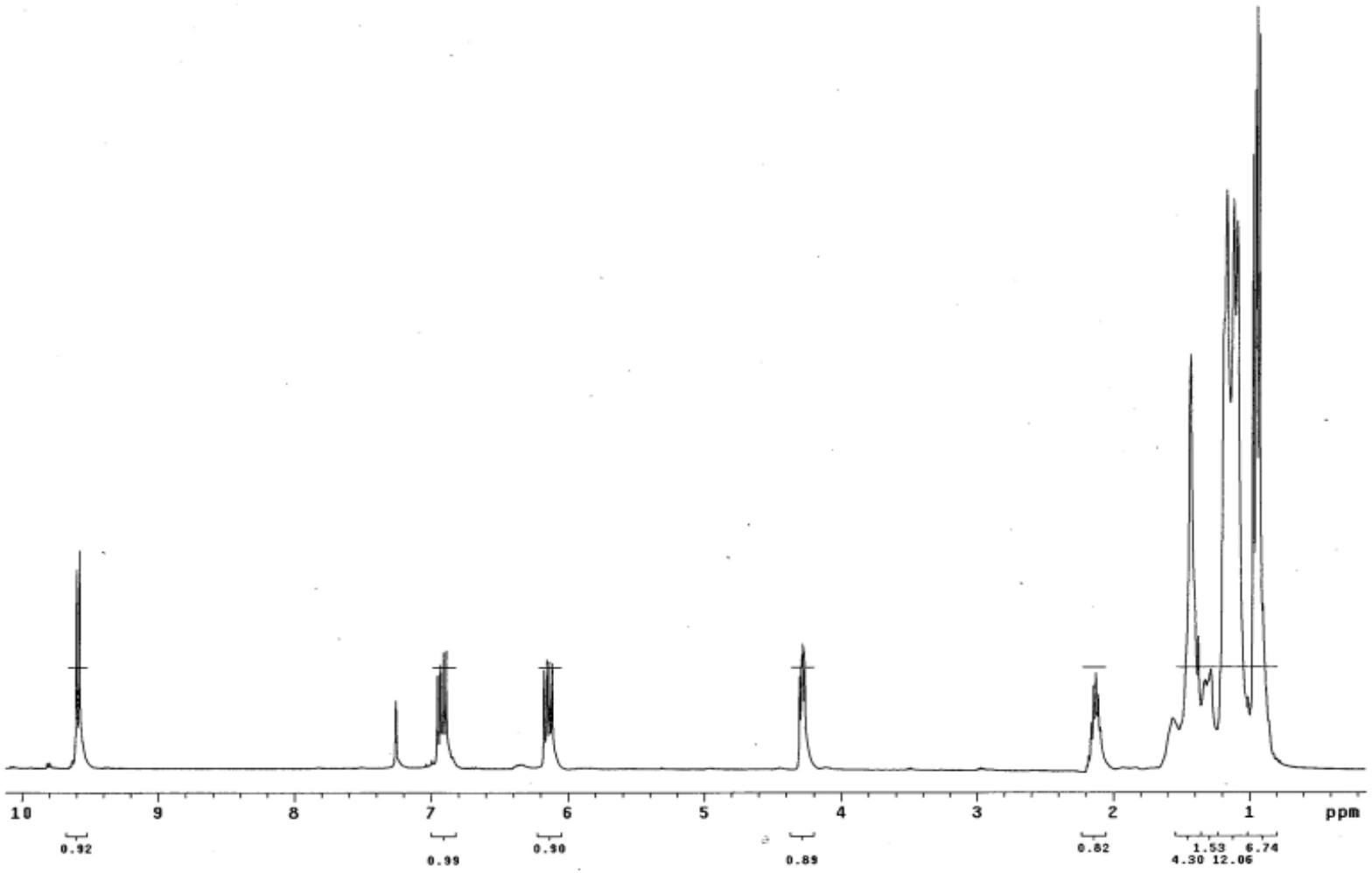

4.452
4.435
4.432
4.419
4.400
1.812
1.794
1.778
1.603
1.765
1.740
1.587
1.568
1.572
1.540
1.429
1.291
1.175
1.134
1.088
1.061
0.900
0.886
0.883
0.871
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
1.03
2.30
4.59
8.42
13.38
3.46

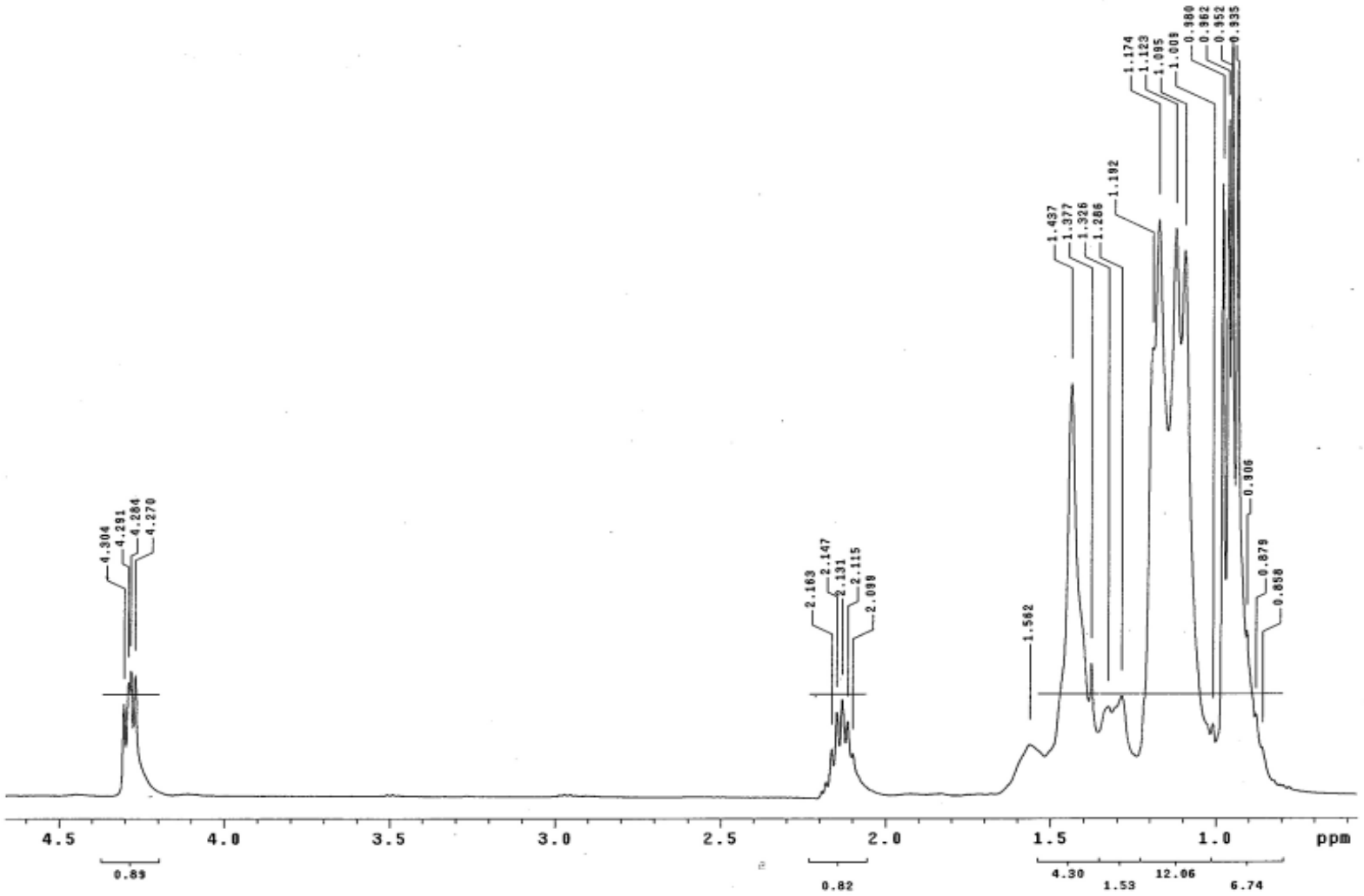

9.579
9.576
9.574
9.560
9.557
9.554
7.265
7.260
6.886
6.883
6.879
6.876
6.873
6.857
6.854
6.839
6.837
6.834
6.156
6.153
6.136
6.133
6.116
6.114
6.096
6.094
9.5
9.0
8.5
8.0
7.5
7.0
6.5
ppm
0.86
1.00
0.81

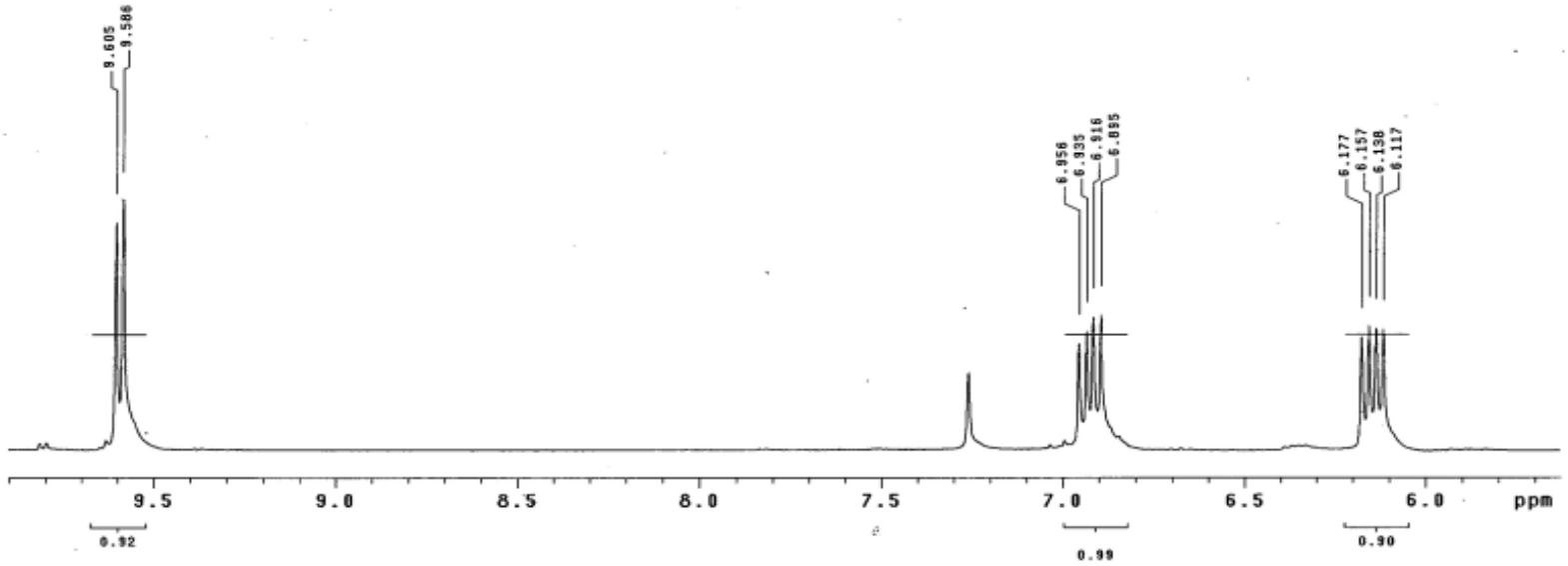

200
180
160
140
120
100
80
60
40
20
ppm

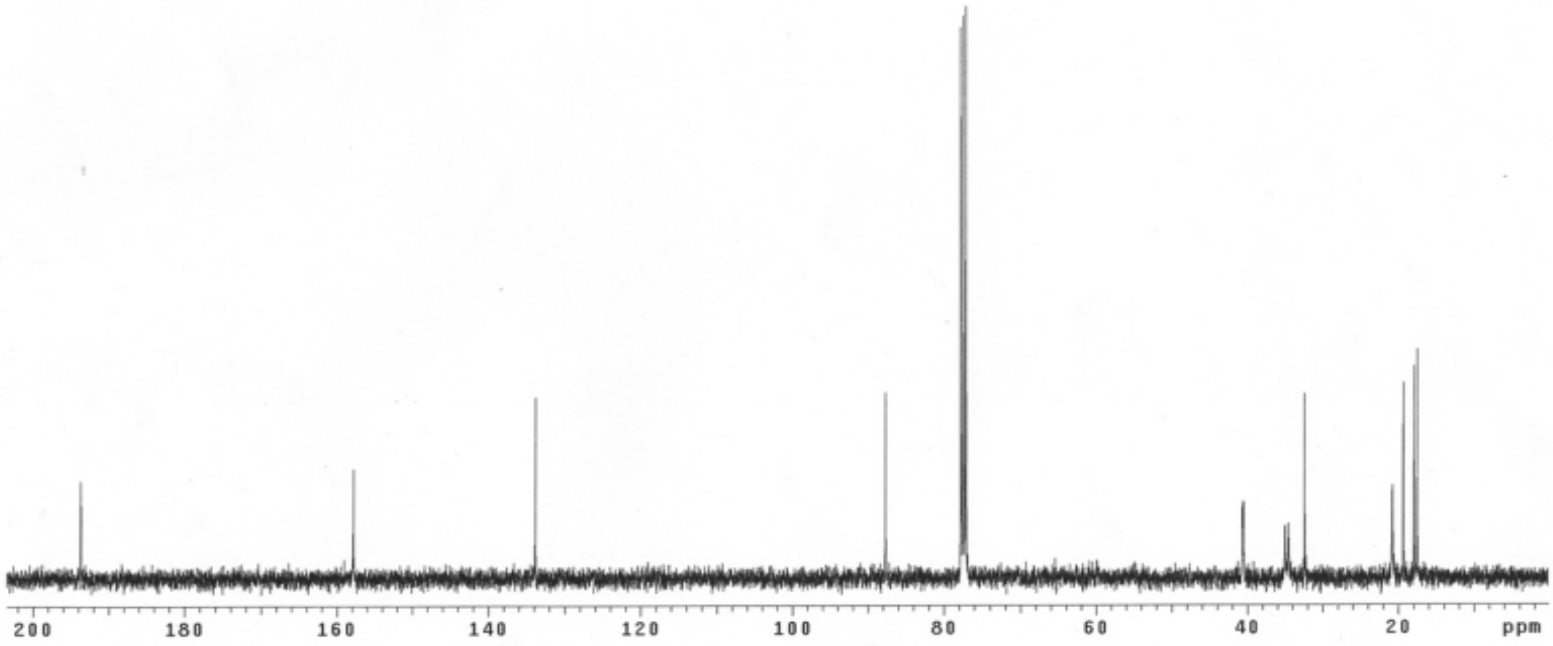


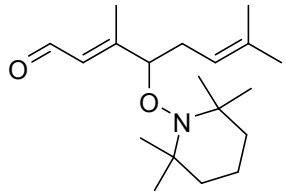
(E)-5-methyl-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-2-enal (7b) R_f = 0.63 in 1:4 v/v ether/hexane; colo rless oil; yield 30.7 mg (0.1149 mmol, 46%). IR (KBr): 2969, 1695, 1375, 1133, 986 cm^{-1}. ^1H NMR ($CDCl_3$, 40 0MHz) δ: 0.86-1.44 (24H, m), 2.13 (1H, m), 4.29 (1H, m), 6.15 (1H, dd, *J* = 8, 15.8 Hz), 6.93 (1H, dd, *J* = 8.4, 1 6 Hz), 9.60 (1H, d, *J* = 7.6 Hz)ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 17.6, 18.0, 19.4, 20.8, 32.4, 34.6, 35.0, 40.5, 40.7, 87.7, 133.8, 157.8, 193.8 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{16}H_{29}NO_2$:268.2277; found: 268.22 79


10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.99
0.90
0.89
0.82
1.53
6.74
4.30
12.06

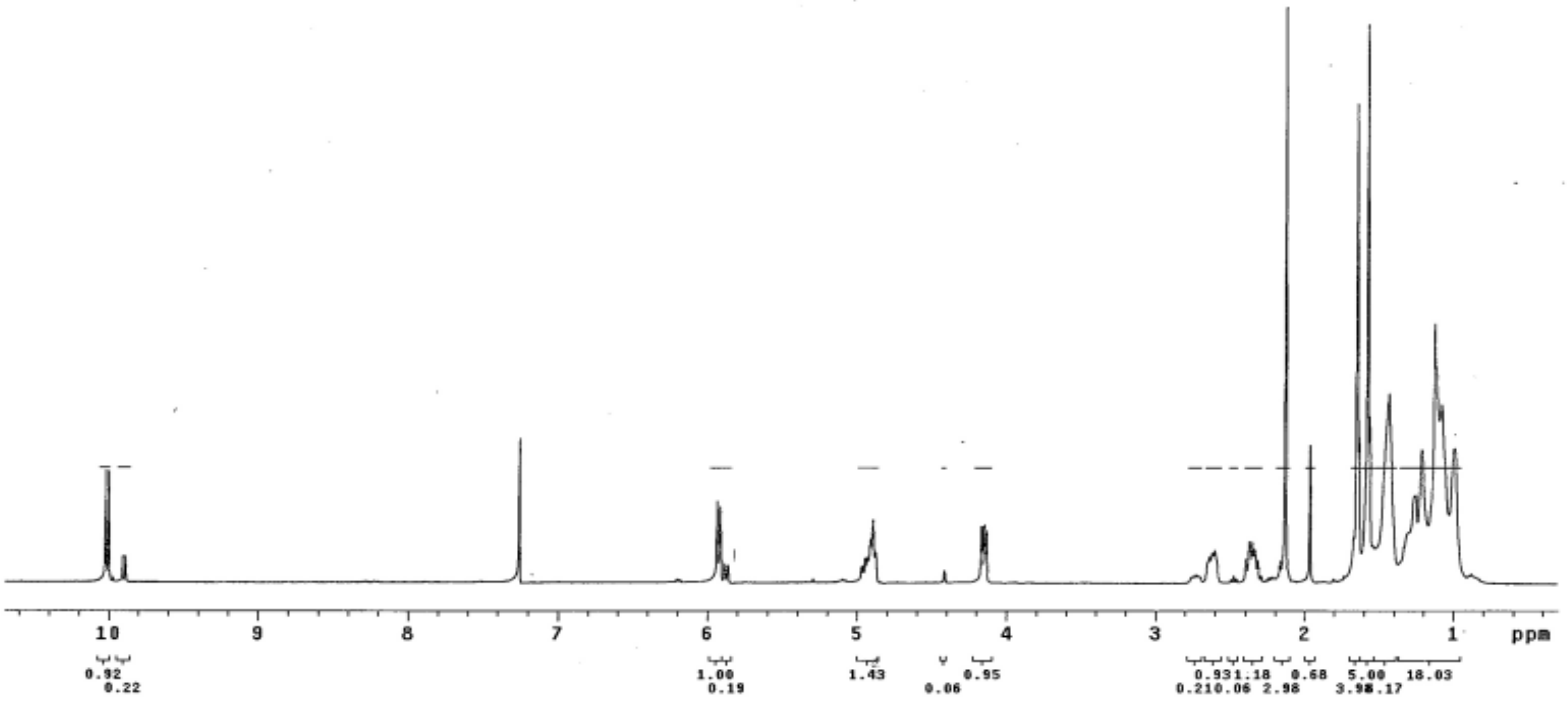

4.304
4.291
4.284
4.270
2.163
2.147
2.131
2.115
2.099
1.562
1.437
1.377
1.326
1.286
1.192
1.174
1.123
1.095
1.009
0.380
0.362
0.352
0.335
0.306
0.879
0.858
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.89
0.82
4.30
1.53
12.06
6.74

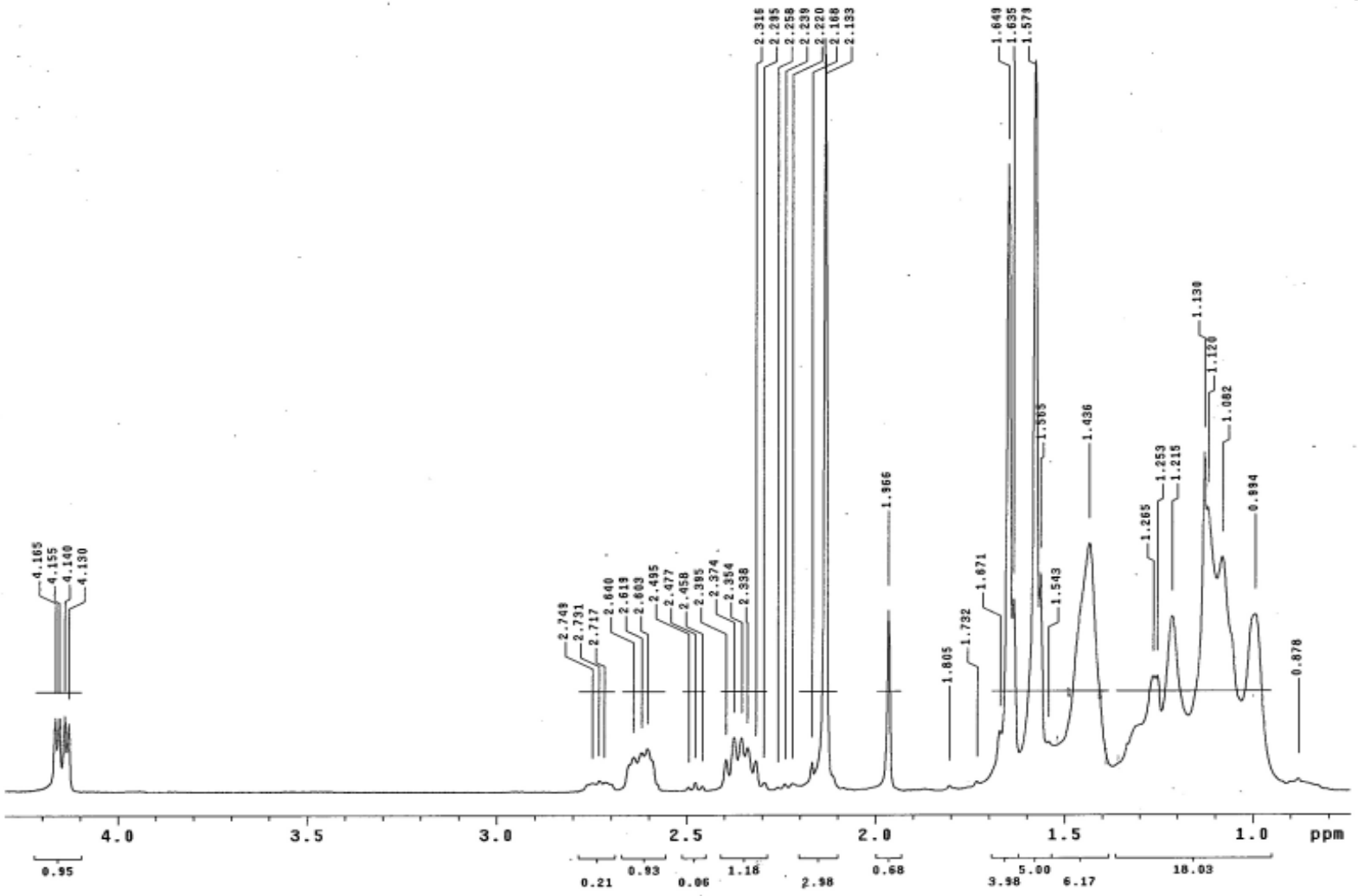

9.605
9.586
6.956
6.935
6.916
6.895
6.177
6.157
6.138
6.117
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm
0.92
0.99
0.90


200
180
160
140
120
100
80
60
40
20
ppm



(E)-3,7-dimethyl-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)octa-2,6-dienal (9b) R_f = 0.51 in 1:4 v/v ether/hexane; isolated as an inseperable mixture with di-isomers (major/minor 81:19); colorless oil; yield 27.6 mg (0.0898 mmol, 36%). IR (KBr): 2931, 1678, 1377, 1132, 974 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ: 0.99-1.65 (major + minor, 24H), 1.97 (3H, s, minor), 2.13 (3H, s, major), (1H, m, major + minor), 2.62 (1H, m, major), 2.73 (1H, m , minor), 4.15 (dd, 1H, *J* = 4, 10 Hz), 4.92 (1H, m, major +minor), 5.87 (1H, d, *J* = 8Hz, minor), 5.92 (1H, d, *J* = 8Hz, major), 9.90 (1H, d, *J* = 8.4 Hz, minor), 10.01 (1H, d, *J* = 8 Hz, major) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.2, 17.5, 18.4, 20.6, 26.2, 31.5, 34.4, 40.7, 40.8, 83.6 (minor), 89.6 (major), 118.9, 128.5 (major), 130.0 (minor), 134.2 (major), 162.0 (minor), 162.6 (major), 191.4 (minor), 191.6 (major). HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{19}H_{33}NO_2$:308.2590; found: 308.2593


10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.22
1.00
0.19
1.43
0.06
0.95
0.93
0.21
1.18
0.06
0.68
2.98
5.00
3.98
18.03
17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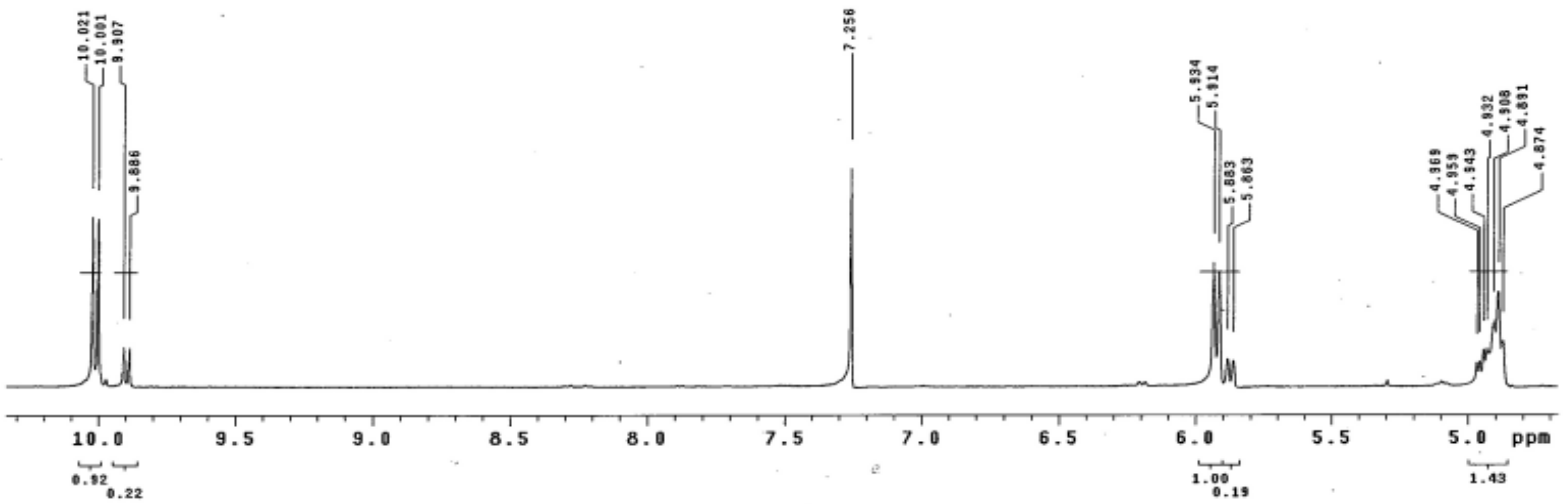
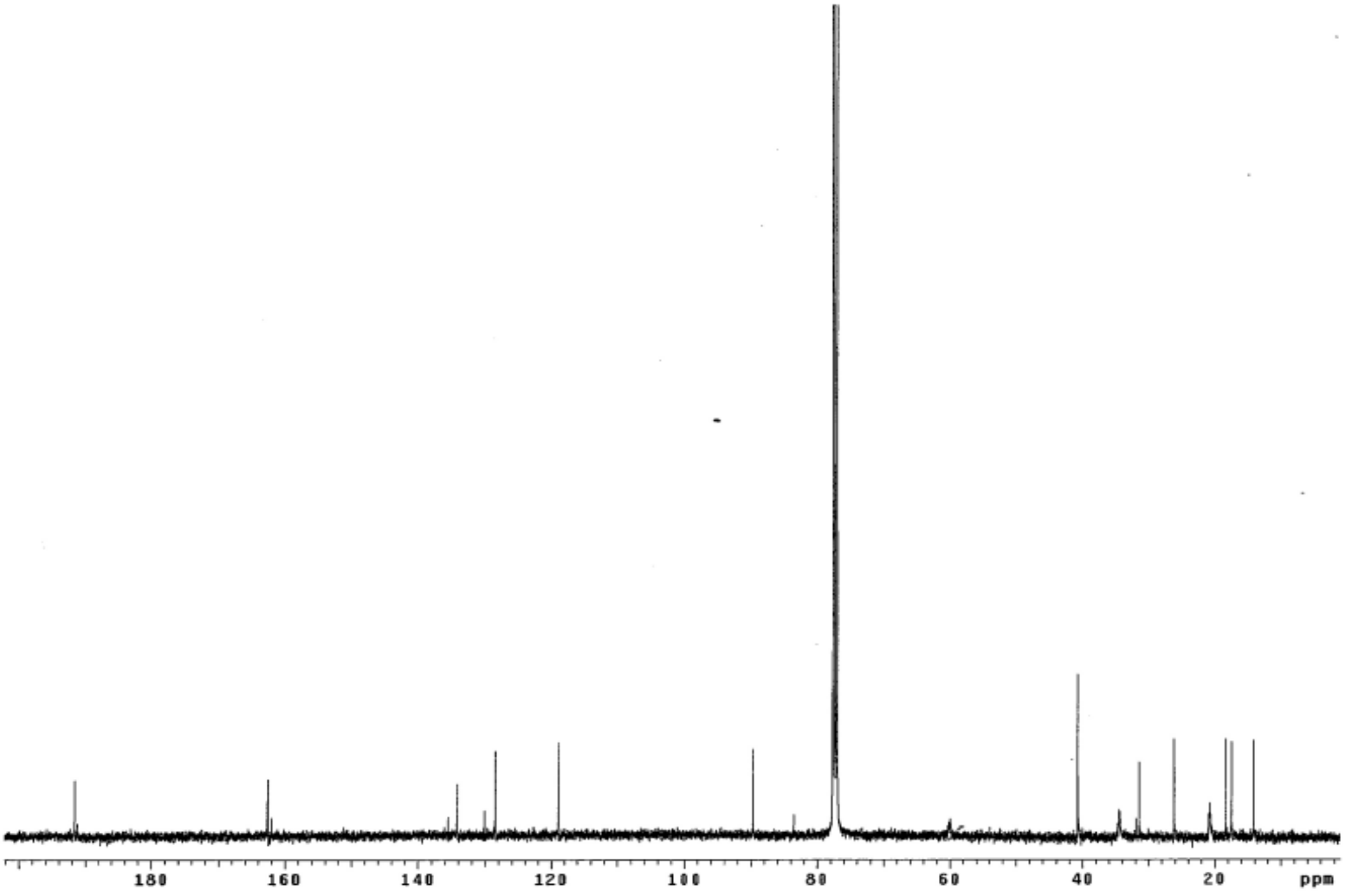
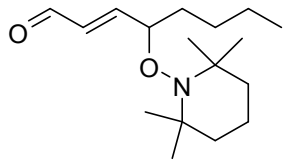
4.155
4.140
4.130
2.748
2.731
2.717
2.640
2.613
2.603
2.495
2.477
2.458
2.395
2.374
2.354
2.338
2.318
2.295
2.258
2.239
2.220
2.168
2.133
1.966
1.805
1.732
1.671
1.649
1.635
1.573
1.543
1.436
1.265
1.253
1.215
1.138
1.120
1.082
0.994
0.878
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
0.21
0.93
0.06
1.18
2.98
0.68
3.98
5.00
6.17
18.03

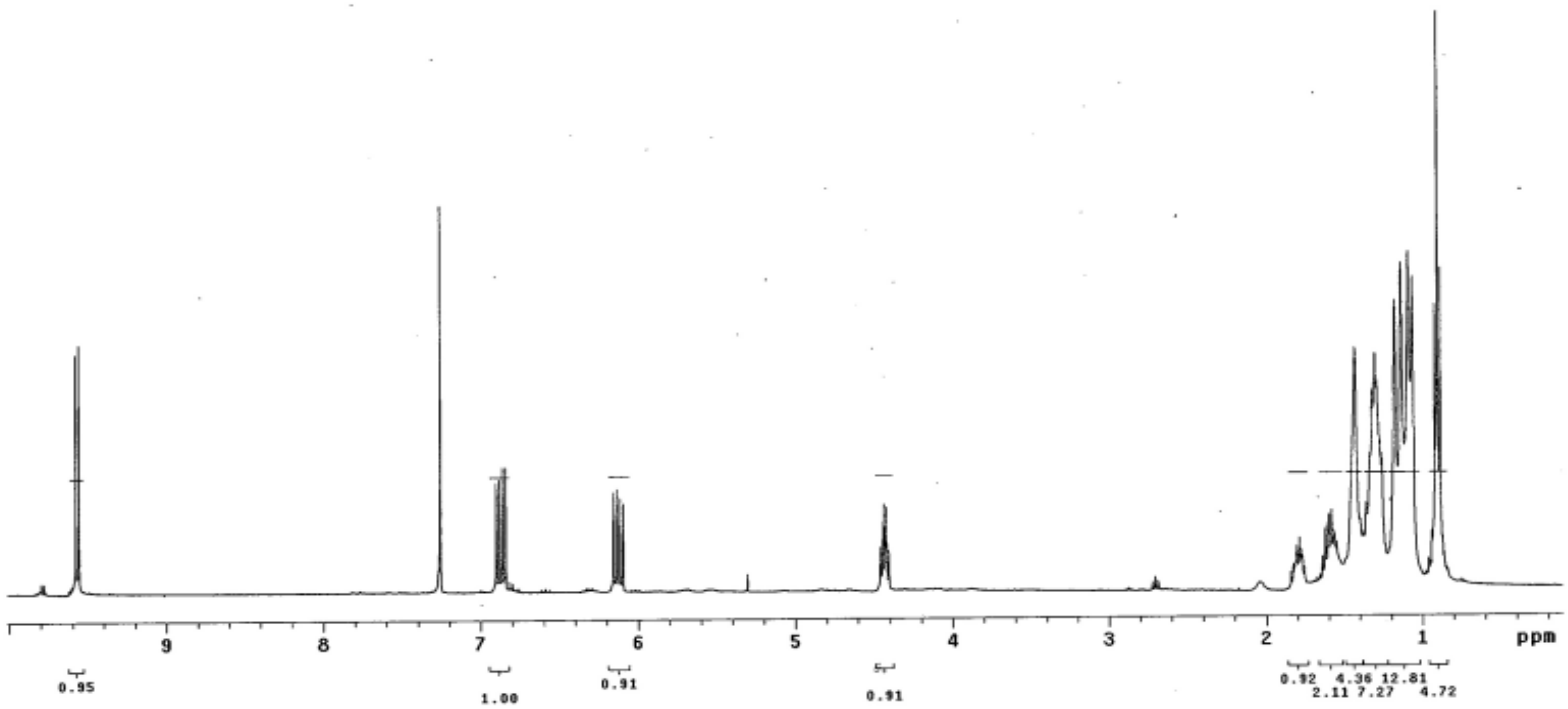

10.021
10.001
9.907
9.886
7.256
5.934
5.914
5.883
5.863
4.969
4.959
4.943
4.932
4.908
4.891
4.874
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
0.92
0.22
1.00
0.19
1.43

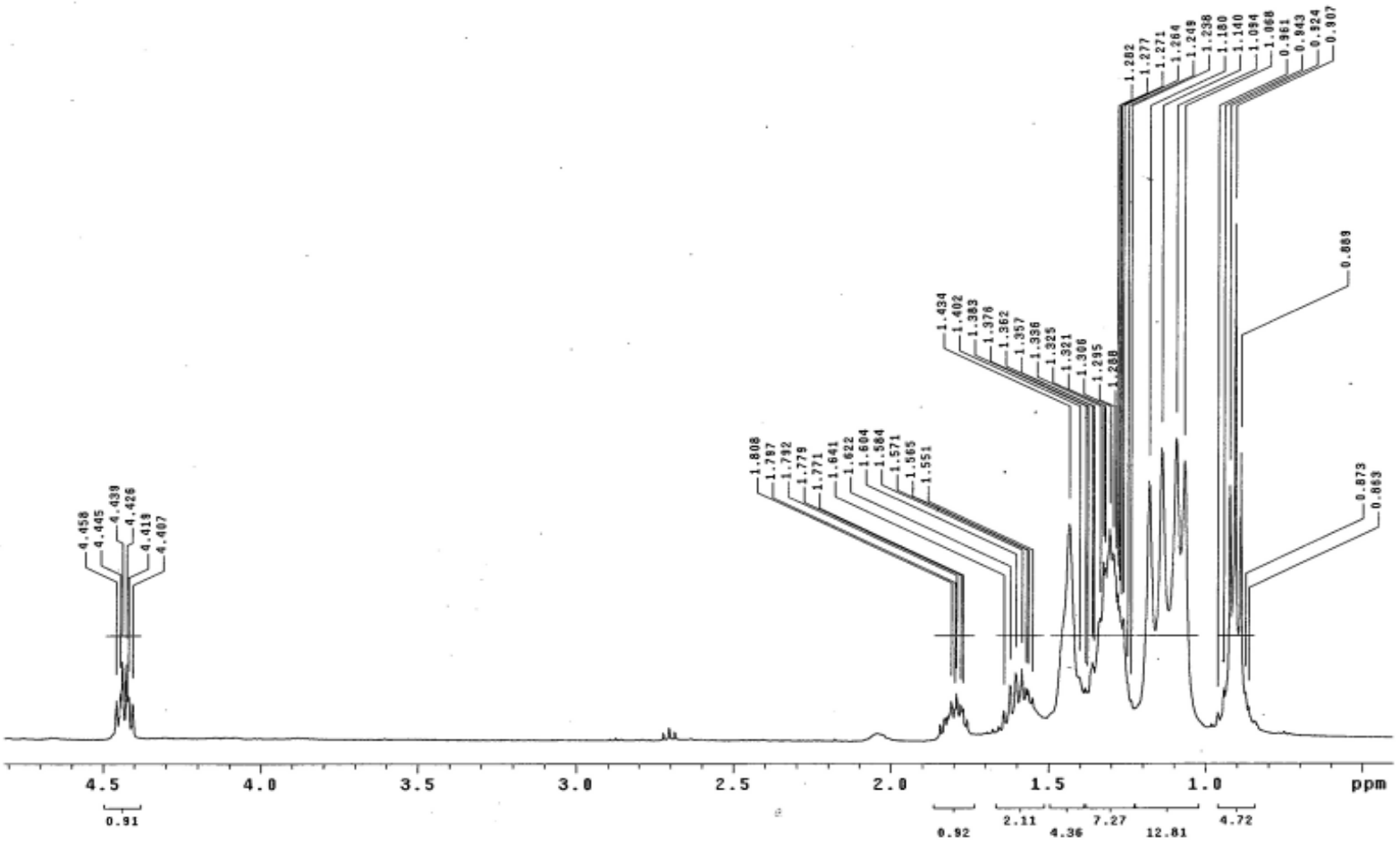

180
160
140
120
100
80
60
40
20
ppm

c



(E)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)oct-2-enal (10b) R_f = 0.67 in 1:4 v/v ether/hexane; colorless oil; yield 18.9 mg (0.0067 mmol, 27%). IR (KBr): 2932, 1695, 1376, 1132, 983 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) (major): 0.89-1.81 (27H, m), 4.43 (1H, m), 6.13 (1H, dd, *J* = 7.6, 16 Hz), 6.87 (1H, dd, *J* = 8, 16 Hz), 9.57 (1H, d, *J* = 7.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ:14.4, 17.6, 20.7, 23.2, 27.6, 34.0, 34.4, 35.1, 40.5, 83.6, 132.1, 159.7, 193.9 ppm. HRMS *m/z* (FAB, $[M+H]^+$): cacld for $C_{17}H_{31}NO_2$:282.2433; found: 282.2430


9
8
7
6
5
4
3
2
1
ppm
0.95
1.00
0.91
0.91
0.92
2.11
4.36
7.27
12.81
4.72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4.439
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4.419
4.407
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1.787
1.792
1.779
1.771
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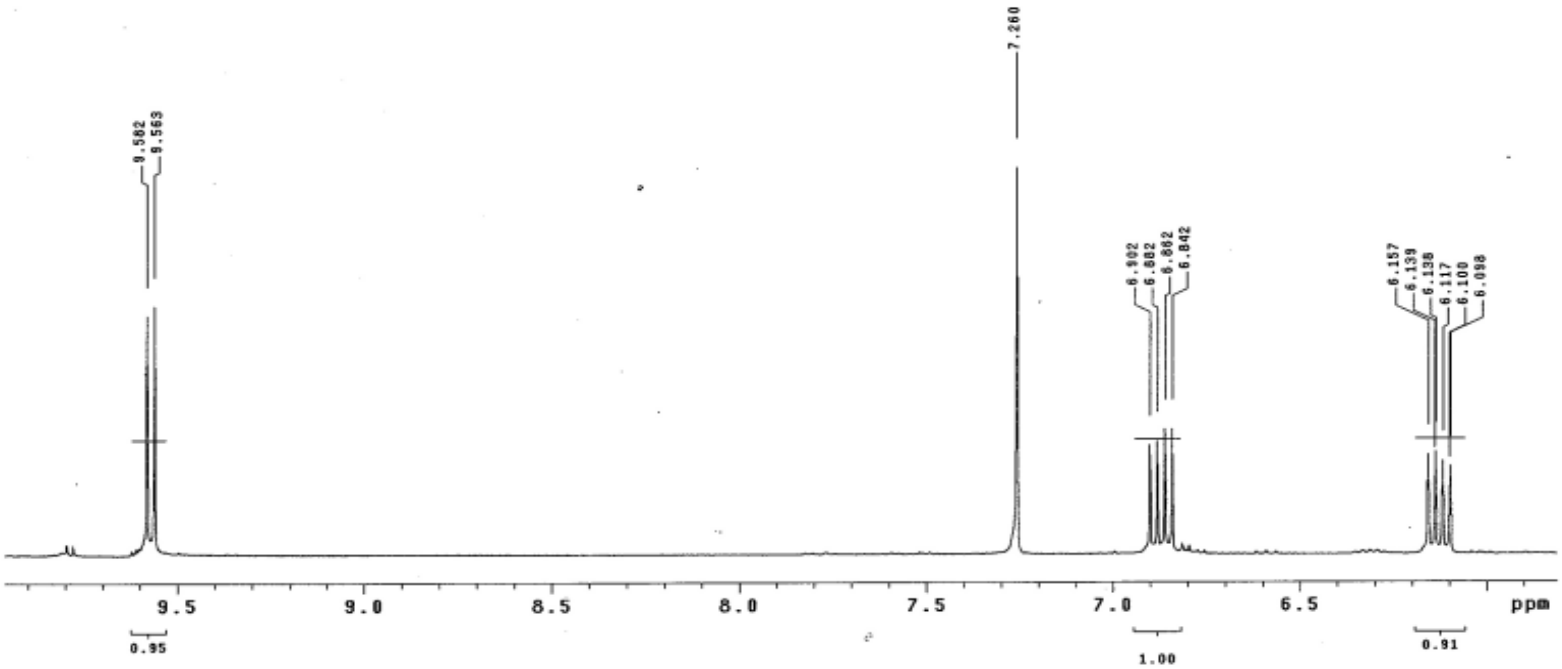
1.622
1.604
1.584
1.571
1.565
1.551
1.434
1.402
1.383
1.376
1.362
1.357
1.336
1.325
1.321
1.306
1.295
1.288
1.282
1.277
1.271
1.264
1.249
1.238
1.180
1.140
1.094
1.068
0.961
0.943
0.924
0.907
0.869
0.873
0.863
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.91
0.92
2.11
4.36
7.27
12.81
4.72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9.563
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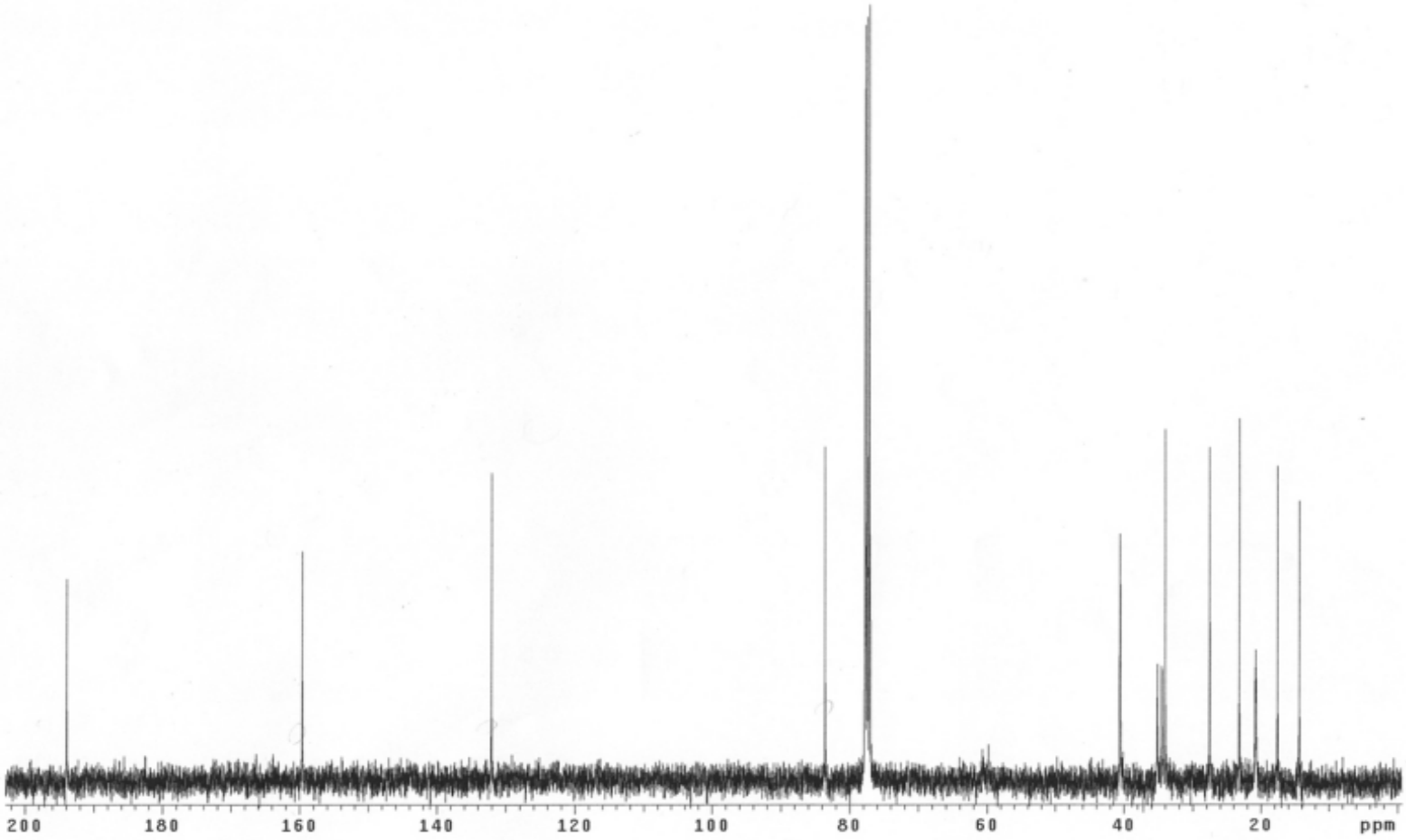
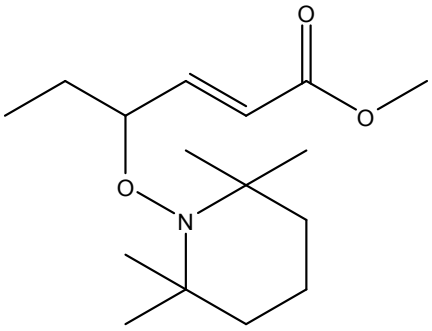
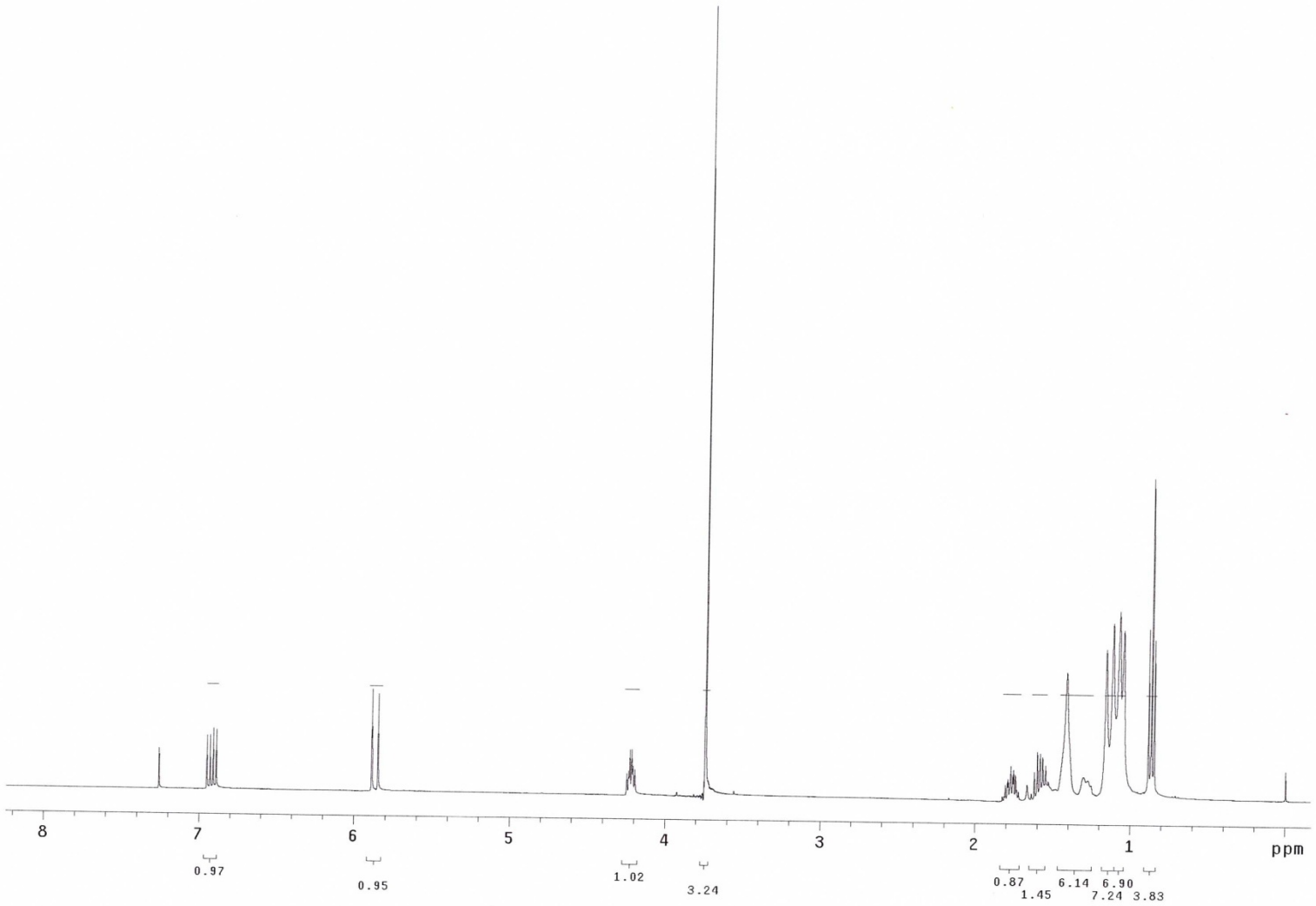
6.902
6.882
6.862
6.842
6.157
6.139
6.138
6.117
6.100
6.098
9.5
9.0
8.5
8.0
7.5
7.0
6.5
ppm
0.95
1.00
0.91

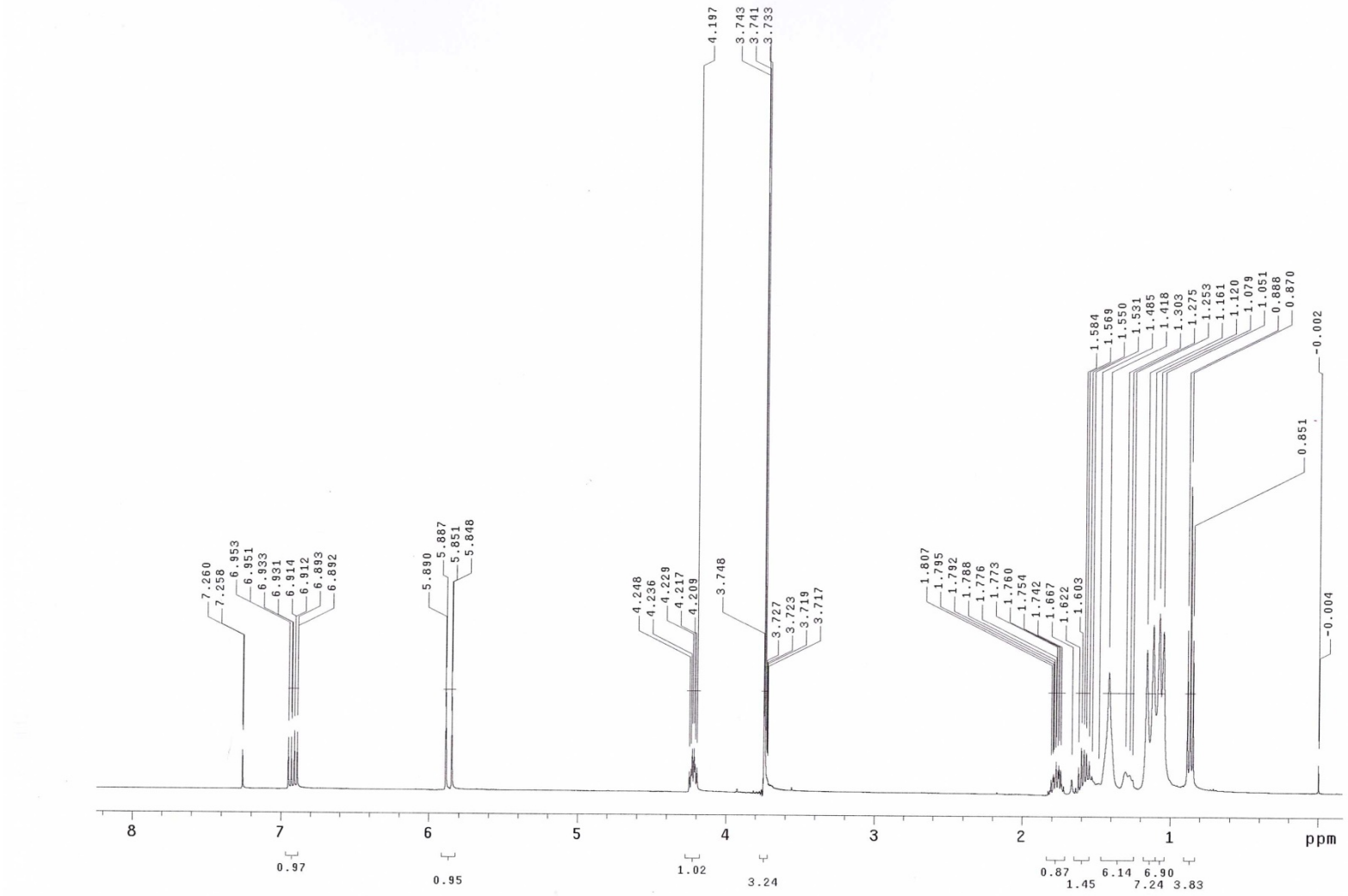

200
180
160
140
120
100
80
60
40
20
ppm



(E)-methyl 4-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-2-enoate (2c)

IR (KBr): ν_{max} = 2972, 2934, 1730, 1463, 1375, 1173 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, *J* = 7.6 Hz), 1.05-1.42 (m, 18 H), 1.53-1.62 (m, 1 H), 1.74-1.81 (m, 1 H), 3.73 (s, 3 H), 4.20 (dt, 1 H, *J* = 8.0, 4.8 Hz), 5.85 (dd, 1 H, *J* = 15.6, 1.2 Hz), 6.89 (ddd, 1 H, *J* = 15.6, 8.0, 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 17.2, 20.3, 20.4, 26.7, 34.0, 34.6, 40.2, 51.4 , 59.5, 60.1, 84.3, 120.6, 150.2, 166.6. HRMS *m/z* (FAB, $[M+H]^+$): calcd for $C_{16}H_{29}NO_3$:284. 2226; found:284.2224.


8
7
6
5
4
3
2
1
ppm
0.97
0.95
1.02
3.24
0.87
1.45
6.14
6.90
7.24
3.83


7.260
7.258
6.953
6.951
6.933
6.931
6.914
6.912
6.893
6.892
5.890
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5.851
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4.248
4.236
4.229
4.217
4.209
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3.748
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3.741
3.733
3.727
3.723
3.719
3.717
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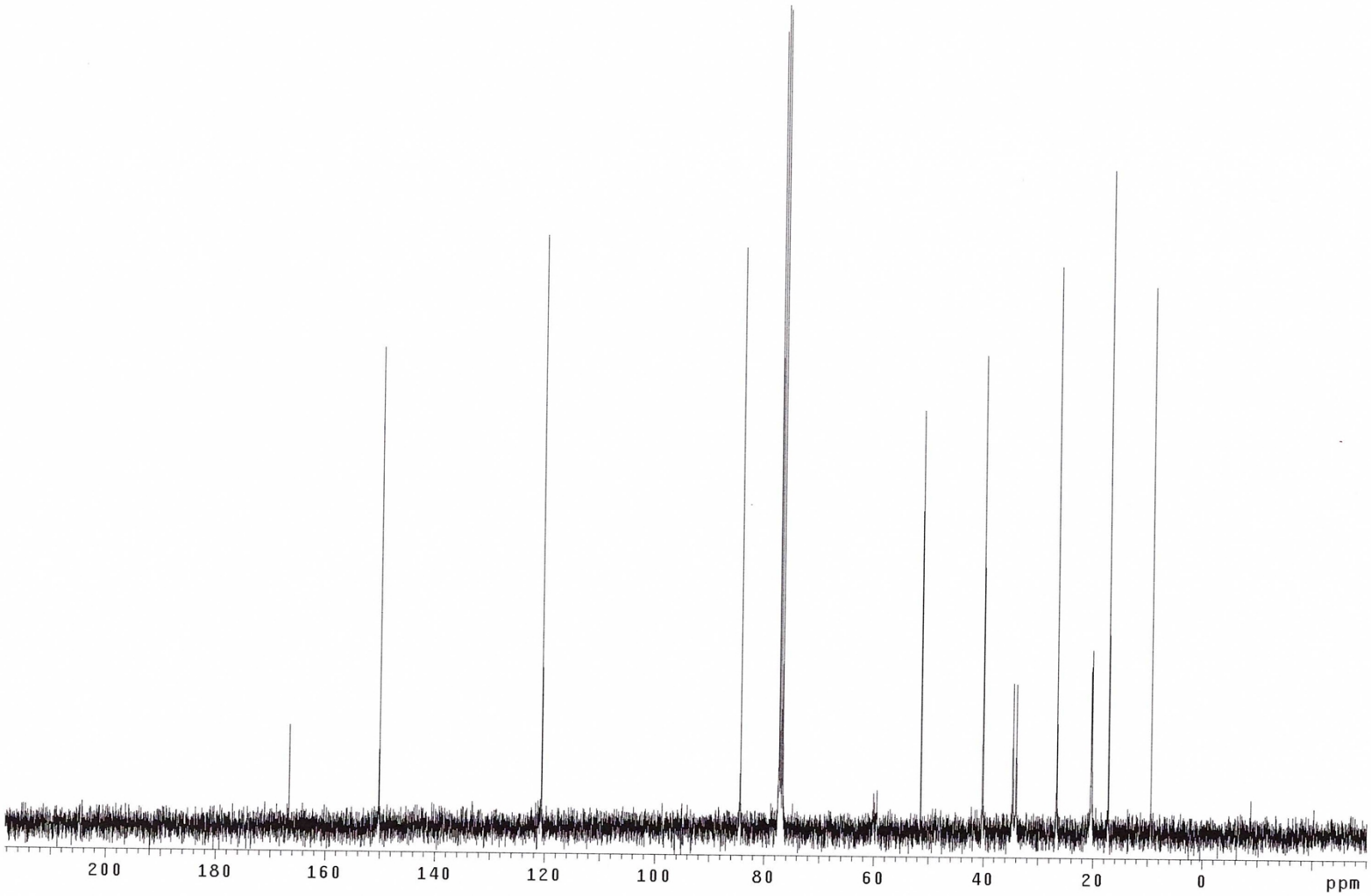
1.795
1.792
1.788
1.776
1.773
1.760
1.754
1.742
1.667
1.622
1.603
1.584
1.569
1.550
1.531
1.485
1.418
1.303
1.275
1.253
1.161
1.120
1.079
1.051
0.888
0.870
0.851
-0.002
-0.004
8
7
6
5
4
3
2
1
ppm
0.97
0.95
1.02
3.24
0.87
1.45
6.14
6.90
7.24
3.83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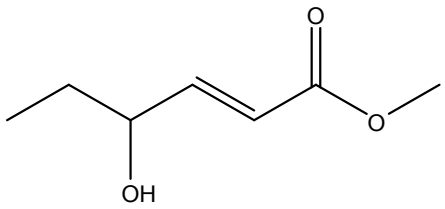
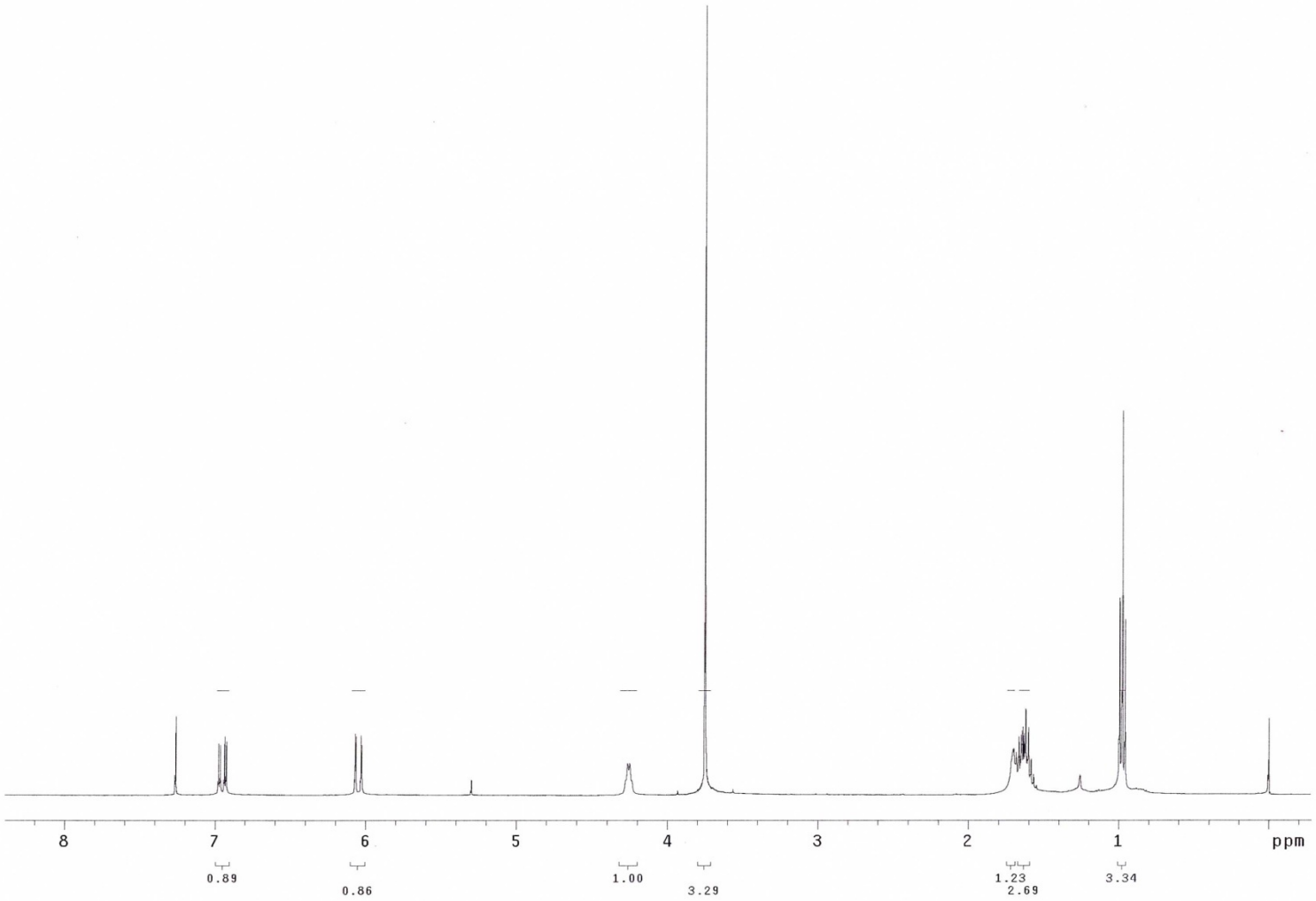
ppm



(E)-methyl 4-hydroxyhex-2-enoate (2d)

IR (KBr): ν_{max} = 3446, 2934, 1726, 1377, 1173 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (dt, 3 H, *J* = 7.2, 2.4 Hz), 1.60-1.70 (m, 3 H), 3.75 (s, 3 H), 4.23-4.26 (m, 1 H), 6.03 (dd, 1 H, *J* = 16.0, 1.6 Hz), 6.92 (dd, 1 H, *J* = 15.6, 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 29. 7, 51.7, 72.3, 119.8, 149.9, 166.7. HRMS *m/z* (EI, $[M]^+$): calcd for $C_7H_{12}O_3$:144.0786; found: 144.0783.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1.00
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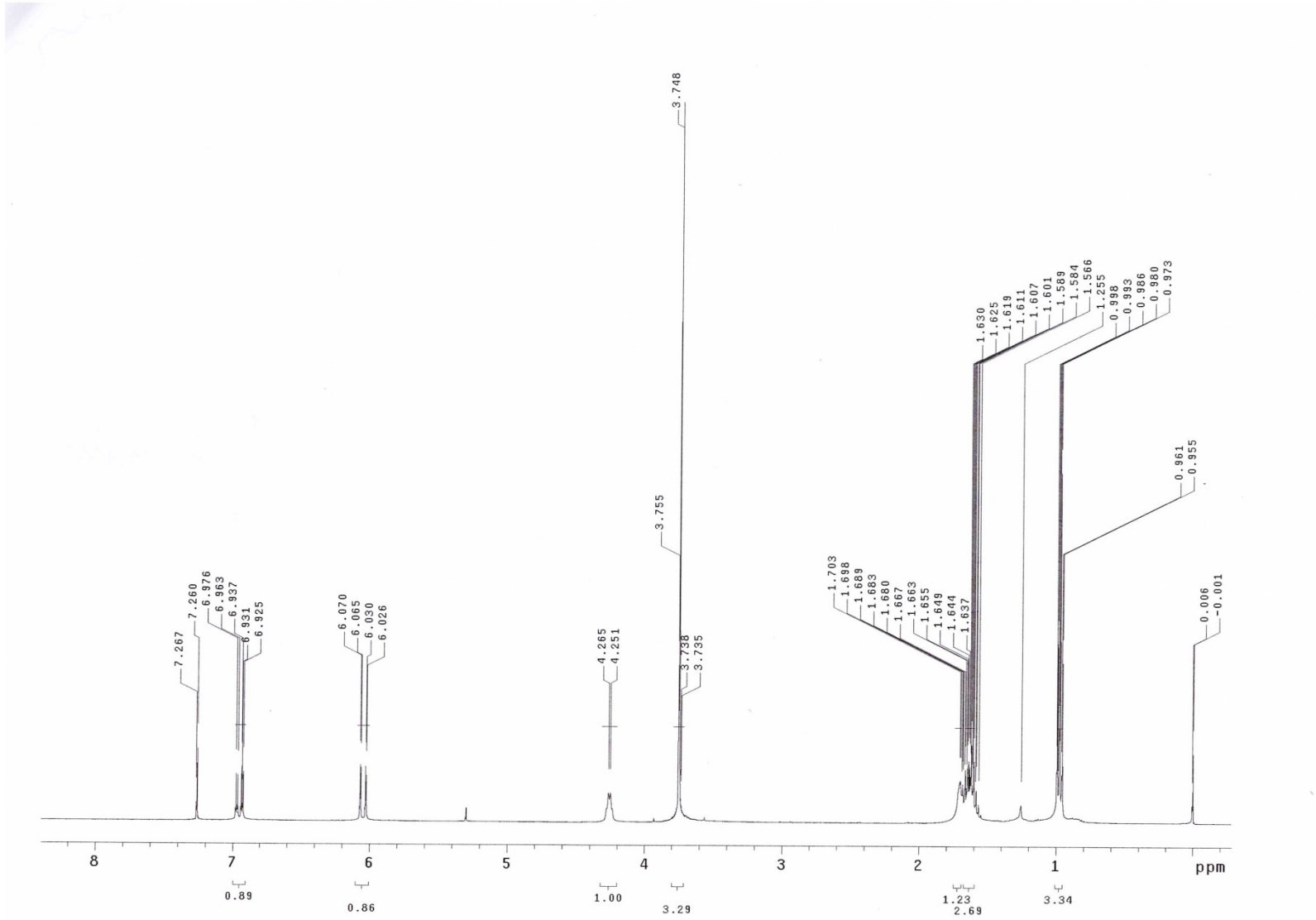
1.23
2.69
3.34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7.260
6.976
6.963
6.937
6.931
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6.026
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4.251
3.748
3.738
3.735
3.755
1.703
1.698
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1.683
1.680
1.667
1.663
1.655
1.649
1.644
1.637
1.630
1.625
1.619
1.611
1.607
1.601
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1.566
1.255
0.998
0.993
0.986
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0.006
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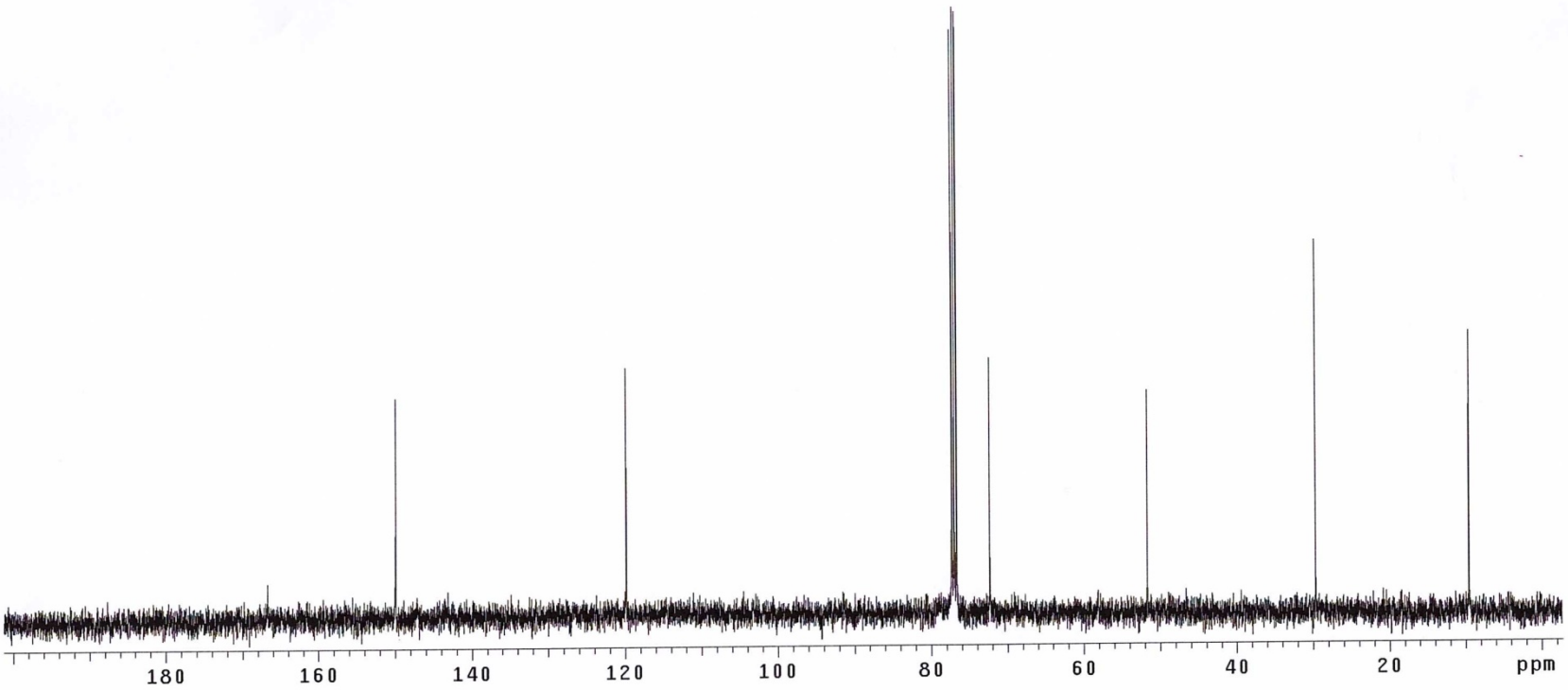
3.34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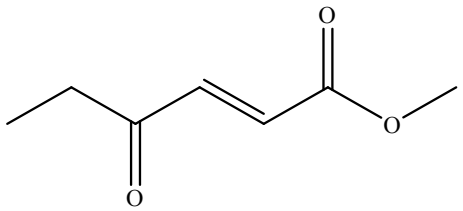
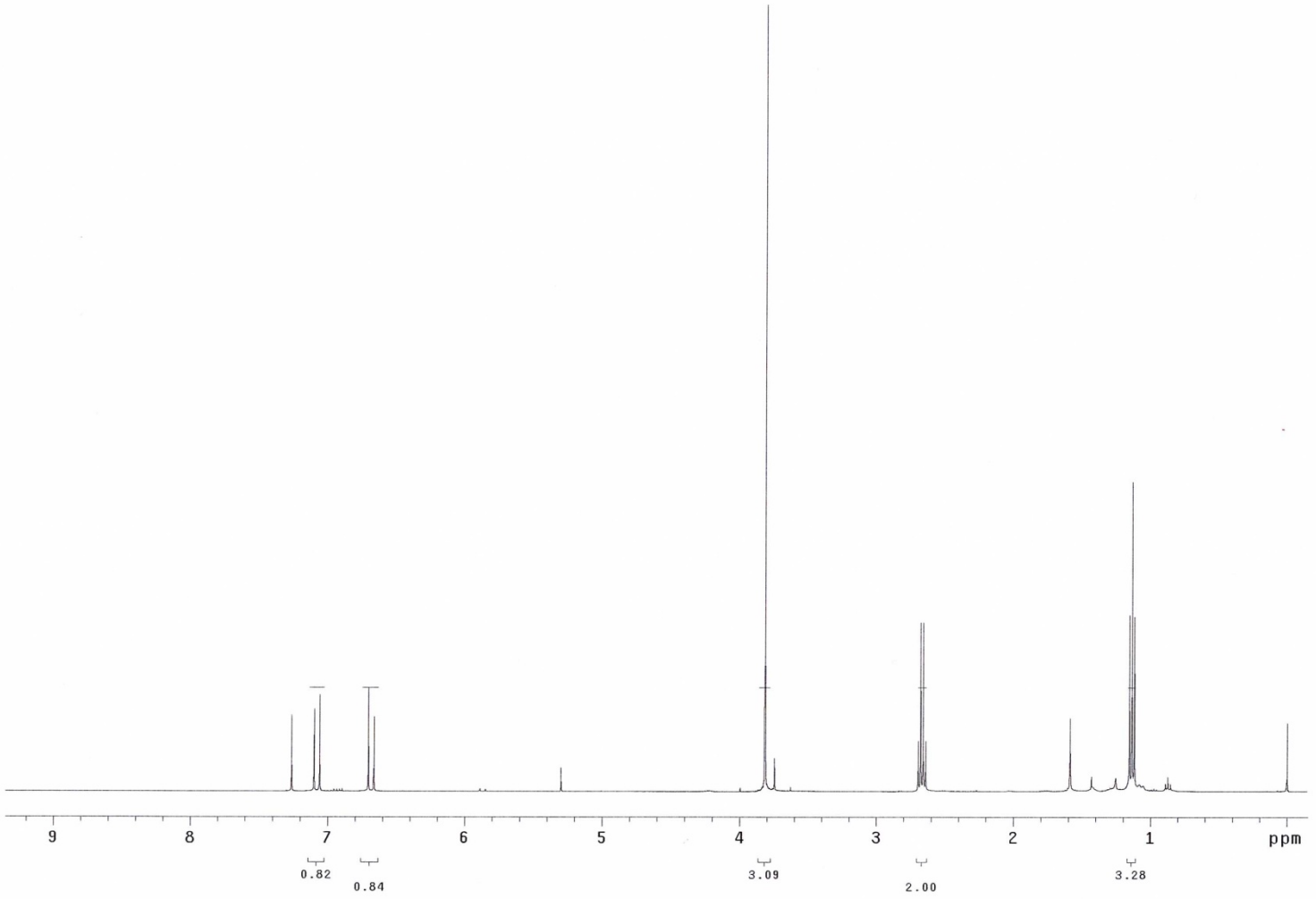
ppm



(E)-methyl 4-oxohex-2-enoate (2e)

IR (KBr): ν_{max} = 2976, 1730, 1669, 1317, 1288, 1180 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, 3 H, *J* = 7.2 Hz), 2.64 (q, 2 H, *J* = 7.2 Hz), 3.81 (s, 3 H), 6.66 (d, 1 H, *J* = 16.0 Hz), 7.06 (d, 1 H, *J* = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.7, 35.0, 52.4, 129.9, 139.2, 165.8, 199.7. HRMS *m/z* (EI, $[M]^+$): calcd for $C_7H_{10}O_3$:142.0630; found:142.0630.


9
8
7
6
5
4
3
2
1
ppm
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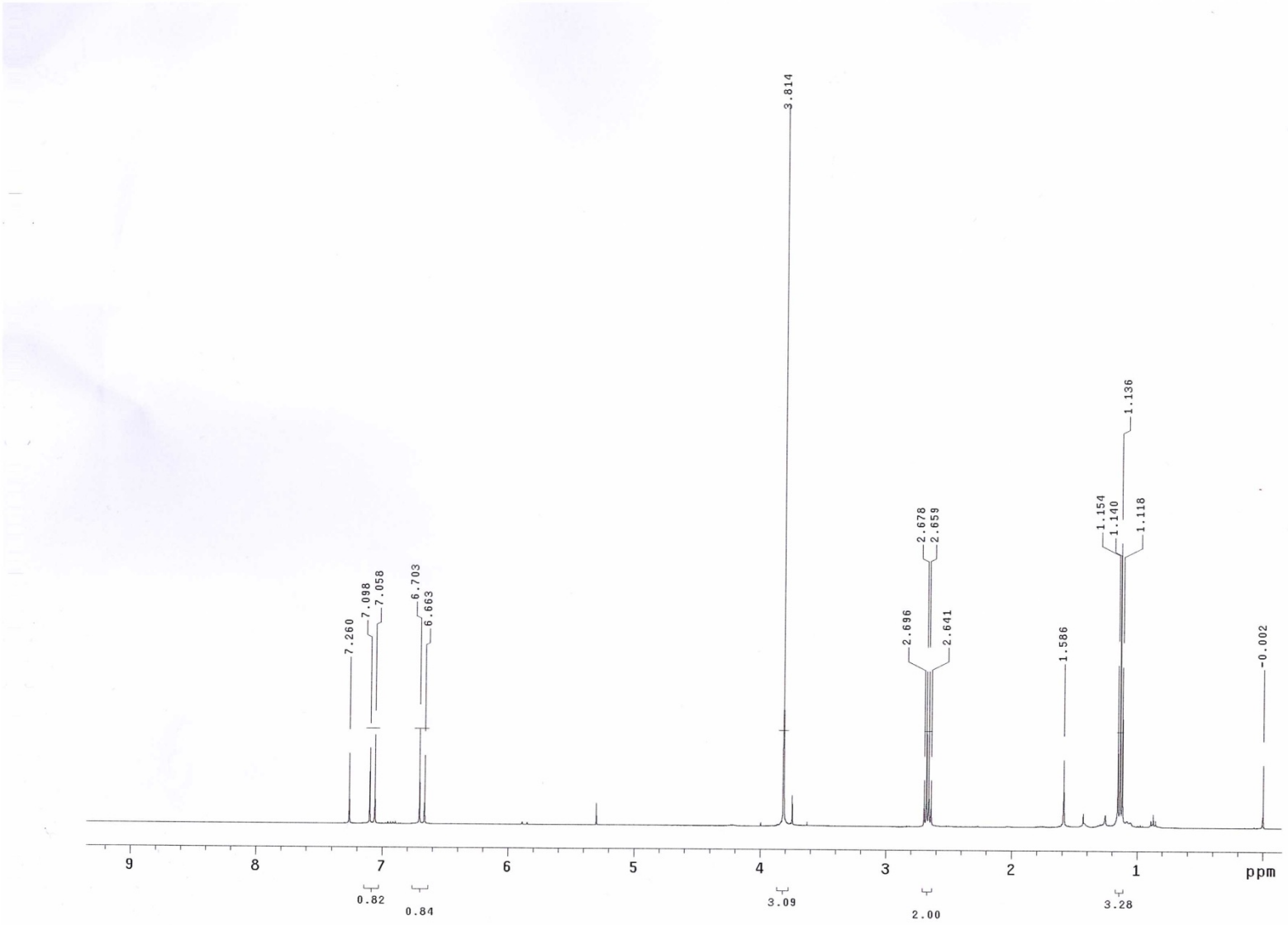
0.84
3.09
2.00
3.28


7.260
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7.058
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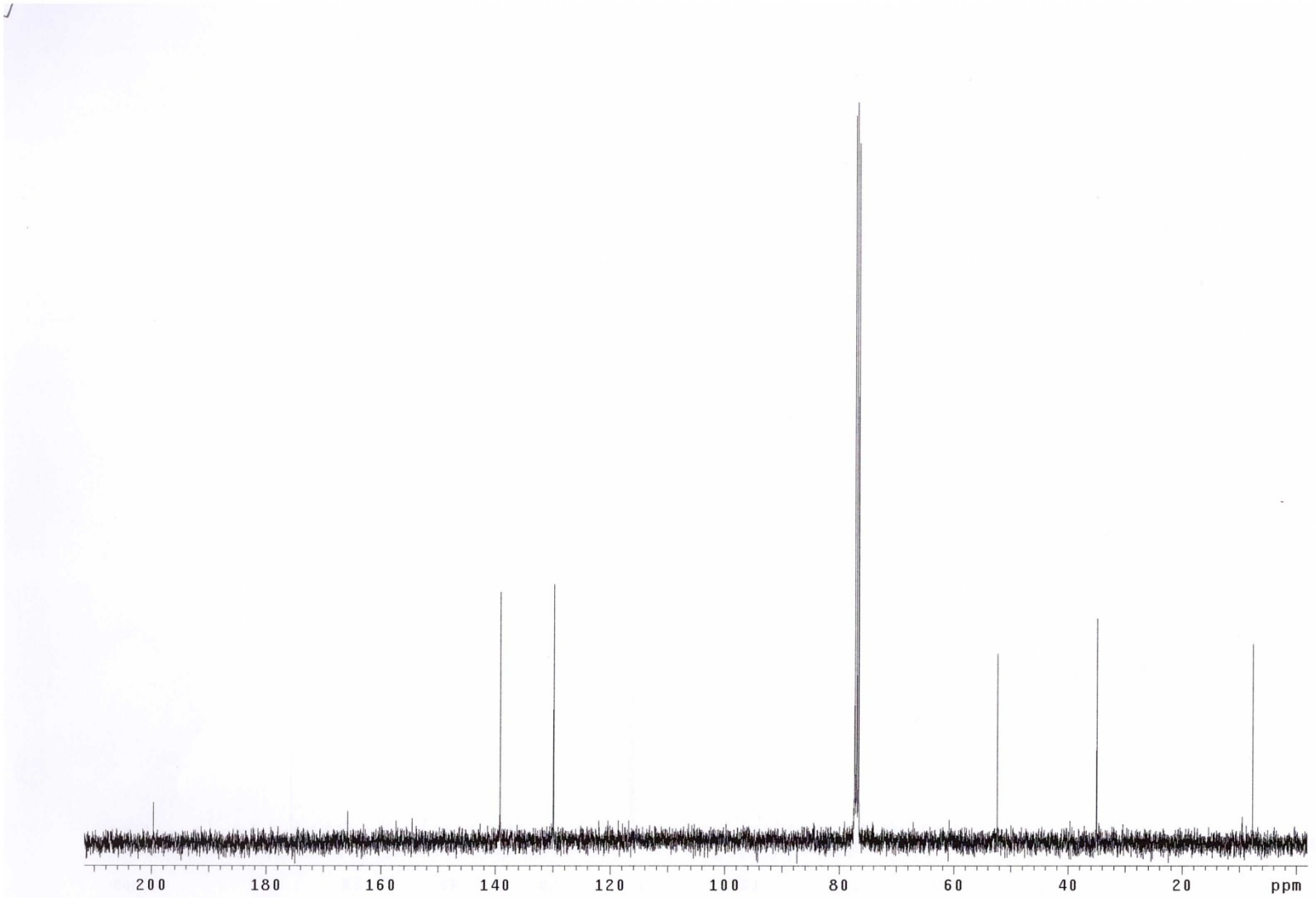
3.814
2.696
2.678
2.659
2.641
1.586
1.154
1.140
1.136
1.118
-0.002
9
8
7
6
5
4
3
2
1
ppm
0.82
0.84
3.09
2.00
3.28


200
180
160
140
120
100
80
60
40
20
ppm

[i] J. Liu, X. Xie, S. Ma, *Synthesis*, **2012**, 1569-1576.

[ii] P. H. Fuller, J.-W. Kim, S. R. Chemler, *J. Am. Chem. Soc*. 2008, **130**, 17638-17639.