Electronic Supplementary Information

(ESI)

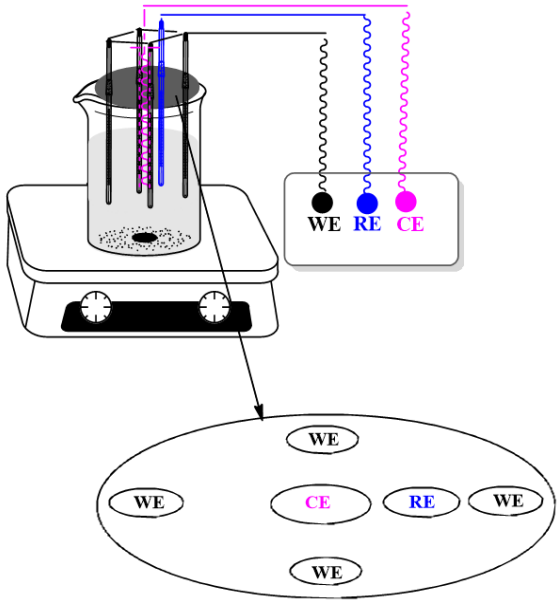
Electrode instead of catalyst and enzyme. A greener protocol for the synthesis of new 2-hydroxyacetamides derivatives containing γ-lactone ring

Abbas Maleki,* Davood Nematollahi,* Fereshteh Rasouli and Azam Zeinodini-Meimand

Table of Contents

Apparatus

Cyclic voltammetry, controlled-potential coulometry and preparative electrolysis were performed using an Autolab model PGSTAT302N potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm^2 area) and platinum wire was used as a counter electrode. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of four carbon rods (6 mm diameter and 4 cm length), placed as single rods in the edges of a square, and large stainless steely gauze constitutes the counter electrode. The working electrode potentials were measured versus Ag/AgCl (all electrodes from AZAR electrode). The electrolysis was performed in a simple cell (a narrow beaker type cell, 100 ml), equipped with a magnetic stirrer.



Arrangement of the electrodes and cell

Reagens

3,5-di-*tert*-butylcatechol, *n*-butylamine, *n*-propylamine, ethylamine, methylamine, benzylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, cyclooctylamine were reagent-grade materials and carbonate salts were of pro-analysis grade, from E. Merck. These chemicals were used without further purification.

Electrochemical synthesis 9a-17a: General procedure

Controlled-potential method

In a typical procedure, four carbon rods as working electrodes, a stainless steely gauze as auxiliary electrode along with an Ag/AgCl reference electrode were immersed into an undivided cell containing a mixture (60 mL) of water (carbonate buffer, *c* = 0.2 M, pH = 11)/acetonitrile (40/60 v/v). This mixture was pre-electrolyzed at the 0.05 V versus Ag/AgCl, then 1 mmol of 3,5-di-*tert*-butylcatechol and 1 mmol of **9-17** were added to the cell and the mixture was stirred until homogeneity was achieved. The electrolysis was terminated when the decay of the current became more than 95% (within about 3-4 hours). The process was interrupted during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. At the end of electrolysis, after evaporation of acetonitrile, the residue was transferred to a separating funnel and extracted with cyclohexane or *n*-hexane. The extracted portion was recrystallized in *n*-hexane or chloroform. After purification, all products were characterized by: IR, ^{1}H NMR, ^{13}C NMR and MS. Moreover, product **9a** was also characterized by single crystal X-ray diffraction.

Constant-current method (Galvanostatic method)

A mixture (60 mL) of water (carbonate buffer, *c* = 0.2 M, pH = 11)/acetonitrile (40/60 v/v) containing 1 mmol of 3,5-di-*tert*-butylcatechol and 1 mmol of **9-17** was electrolyzed in an undivided cell equipped with a carbon anode (an assembly of four rods, with 30 cm^2) and a large stainless steely gauze cathode at 25 °C under a constant-current density of 1.0 mA cm^{-2}. The other steps are similar to those described above in the controlled-potential method.

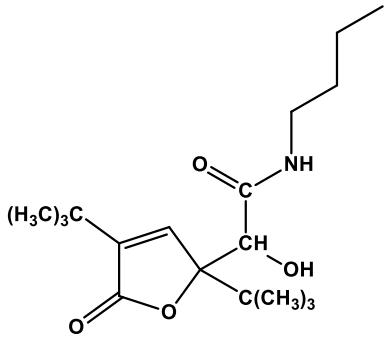
Table S1. Electrochemical synthesis of **9a-17a** at constant current condition[a]

Entry	Product	Yields[b] (%)
1	**9a**	61
2	**10a**	54
3	**11a**	62
4	**12a**	50
5	**13a**	55
6	**14a**	60
7	**15a**	50
8	**16a**	62
9	**17a**	70

[a]General procedure: **1** (1 mmol), **9-17** (1 mmol), acetonitrile (24ml), carbonat buffer (36ml), current density 1 mA cm^{-2}.
[b]Yield of isolated product.

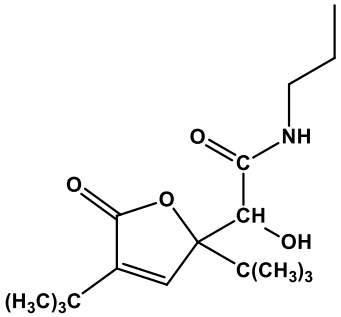
Characterization of Products

9a: *N*-butyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



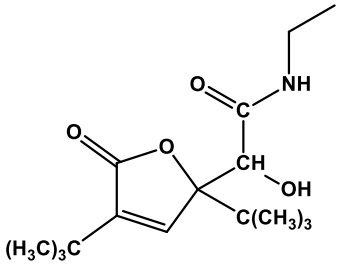
^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 0.88 (t, 3H), 1.06 (s, 9H), 1.21 (s, 9H), 1.32 (m, 2H), 1.44(m, 2H), 3.20 (m, 2H), 4.49 (d, 1H), 4.61 (d, 1H), 7.12 (NH, 1H), 7.31 (ring, 1H); ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 13.2, 19.8, 25.7, 27.4, 31.3, 31.39, 39.3, 37.7, 39.2, 73.6, 89.3, 142.7, 146.5, 169.9, 170.7; IR (KBr): 3371, 3323, 1741, 1658, 1313 cm^{-1}; MS (EI) *m/z* (relative intensity): 326 [M+H^+] (5), 269 (4), 196 (95), 181 (100), 169 (45), 130 (30), 57(18).

10a: *N*-propyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



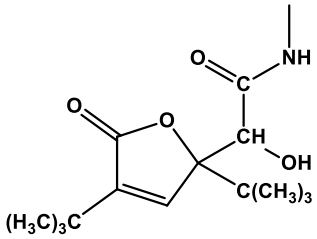
^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 0.86 (t, 3H), 1.05 (s, 9H), 1.20 (s, 9H), 1.46 (t, 2H), 3.07 (m, CH_2), 4.50 (d, 1H), 4.73 (d, 1H), 7.10 (NH, 1H), 7.32 (ring, 1H); ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 10.9, 22.3, 25.6, 27.4, 31.3, 37.7, 41.2, 73.7, 89.4, 142.7, 146.57, 170.0, 170.8; IR (KBr): 3381, 3327, 1743, 1658, 1315 cm^{-1}; MS (EI) *m/z* (relative intensity): 313 [M+2H^{+}] (3), 312 [M+1H^{+}] (10), 196 (55), 181 (63), 169 (42), 116 (42), 57 (100), 43 (98), 41 (90).

11a: *N*-ethyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



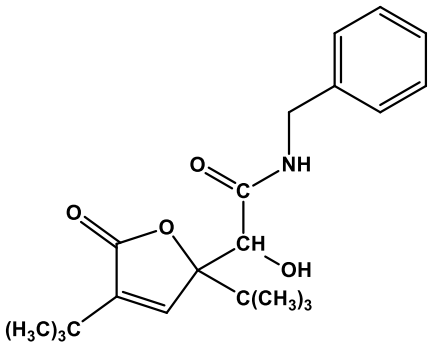
^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 1.07 (s, 12H), 1.21 (s, 9H), 3.19 (t, 2H), 4.50 (q, 2H), 7.13 (NH,1H), 7.31 (ring,1H); ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 13.9, 25.6, 27.4, 31.3, 34.2, 37.6, 73.5, 89.2, 142.8, 146.4, 169.7, 170.7; IR (KBr): 3385, 3321, 1741, 1663, 1317 cm^{-1}; MS (EI) *m/z* (relative intensity): 300 [M+3] (1), 299 [M+2] (4), 298 [M+1] (40), 296 (1), 196 (12), 181(20), 102 (8), 72 (25), 57 (100), 41 (61), 29 (75).

12a: *N*-methyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



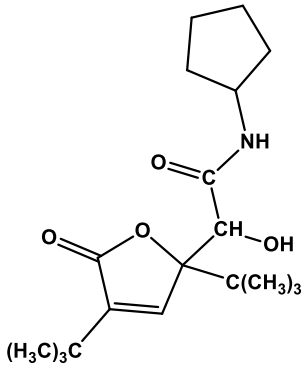
^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 1.07 (s, 9H), 1.21 (s, 9H), 2.70 (d, CH_3), 4.47 (d, 1H), 4.60 (d, 1H), 7.10 (NH, 1H),7.30(ring, 1H); ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 25.5, 25.6, 27.4, 31.2, 37.5, 73.7, 89.3, 142.8, 146.4, 170.4, 170.7; IR(KBr): 3362, 3319, 1740, 1664, 1313 cm^{-1}; MS (EI) *m/z* (relative intensity): 285 [M+2] (1), 284 [M+1] (6), 196 (39), 181 (65), 169 (55), 125 (32), 57 (100), 41 (54), 29 (63).

13a: *N*-benzyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 1.01 (s, 9H), 1.22 (s, 9H), 2.97(s, 2H), 4.28 (d, 1H), 4.40 (d, 1H), 4.60 (d, 1H), 4.74 (d, 1H), 7.27 (m, 6H, aromatic),7.61 (NH, 1H); ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 170.8, 170.2, 146.5, 142.8, 138.6, 128.29, 127.8, 127.0, 89.4, 74.1, 43.20, 37.7, 31.3, 27.4, 25.7; IR (KBr): 3377, 3292, 3086, 2960, 2872, 1739, 1662, 1315 cm^{-1}; MS (EI) *m/z* (relative intensity): 361 [M+2] (2), 360 [M+1] (12), 285 (5), 196 (40), 181 (50), 164 (30), 106 (40), 91 (100), 57 (80), 41 (55), 29 (33).

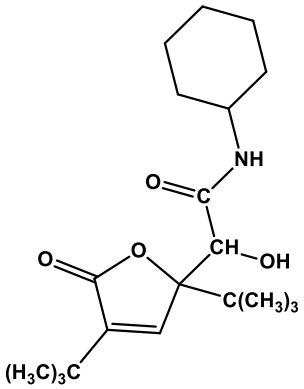
14a: N-cyclopentyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.12 (s, 9H), 125 (s, 9H), 1.40 (m, 2H), 1.57 (m, 2H), 1.69 (m, 2H), 1.94 (m, 2H), 4.11(m, 2H), 4.47 (s, 1H), 5.75 (d, lactone ring, 1H), 7.13 (s, NH, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 24.1, 24.1, 26.6, 28.5, 32.2, 32.9, 33.7, 38.8, 52.4, 73.0, 89.9, 144.6, 146.4, 169.8; IR (KBr): 1636, 1733, 2958, 3309

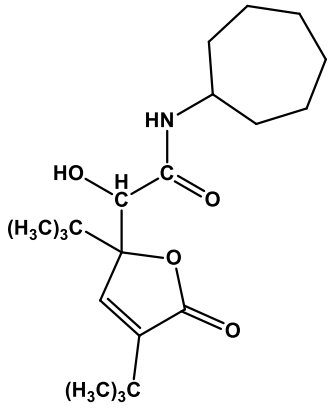
cm^{-1}; MS (EI) *m/z* (relative intensity): 339 [M+2] (20), 338 [M+1] (80), 337 [M] (10), 263 (18), 197 (75), 181 (90), 142 (30), 84 (45).

15a: *N*-cyclohexyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.12 (s, 9H), 1.18 (m, 2H), 1.24 (s, 9H), 1.33 (m, 3H), 1.61 (q, 1H), 1.71 (q, 1H), 1.83, 1.92 (d, 1H), 3.63 (m,1H), 4.47 (s,1H), 5.71 (lactone ring, 1H), 7.14 (NH, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 171.6, 169.4, 146.5, 144.4, 89.9, 73.0, 50.0, 38.8, 33.3, 32.9, 32.2, 32.0, 28.5, 26.6, 25.7, 25.2; IR (KBr): 3439, 3320, 2959, 2937, 2857, 1753, 1649, 1551 cm^{-1}; MS (EI) *m/z* (relative intensity): 352 [M+1] (2), 295 (1), 277 (2), 197 (5), 196 (39), 181 (50), 83 (48), 67 (48), 57(100), 41(77).

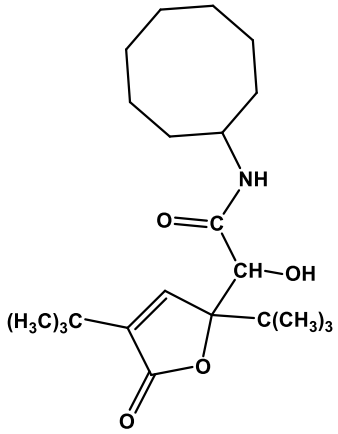
16a: *N*-cycloheptyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide



^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.14 (s, 1H), 5.78 (d, 1H), 4.45 (s, 1H), 4.14 (s, 1H), 3.81 (m, 1H), 1.88 (m, 2H), 1.61 (m, 4H), 1.47 (m, 2H), 1.43 (m, 4H), 1.39 (s, 9H), 1.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 171.6, 169.1, 146.5, 144.4, 89.9, 73.1, 52.2, 38.8, 35.3, 35.0, 32.2, 28.5, 28.4, 28.4, 26.6, 24.4, 24.4; IR (KBr): 3310, 2957,

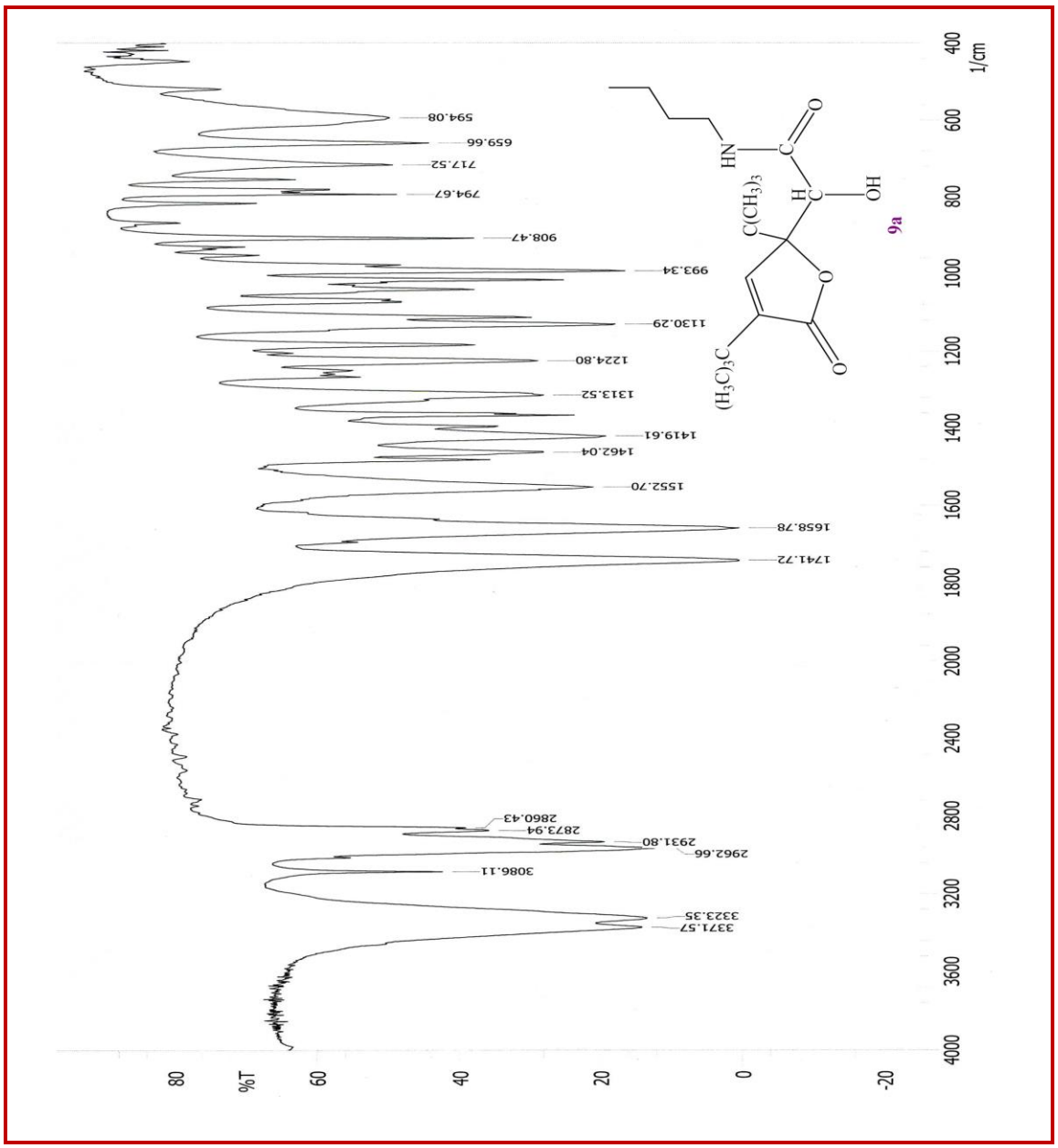
2932, 2866, 1736, 1632 cm^{-1}; MS (EI) *m/z* (relative intensity): 367 [M+2] (1), 366 [M+1] (2), 269 (0.5), 196 (2), 181 (2), 57 (100), 41 (17).

17a: *N*-cyclooctyl-2-(2,4-di-tert-butyl-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyacetamide

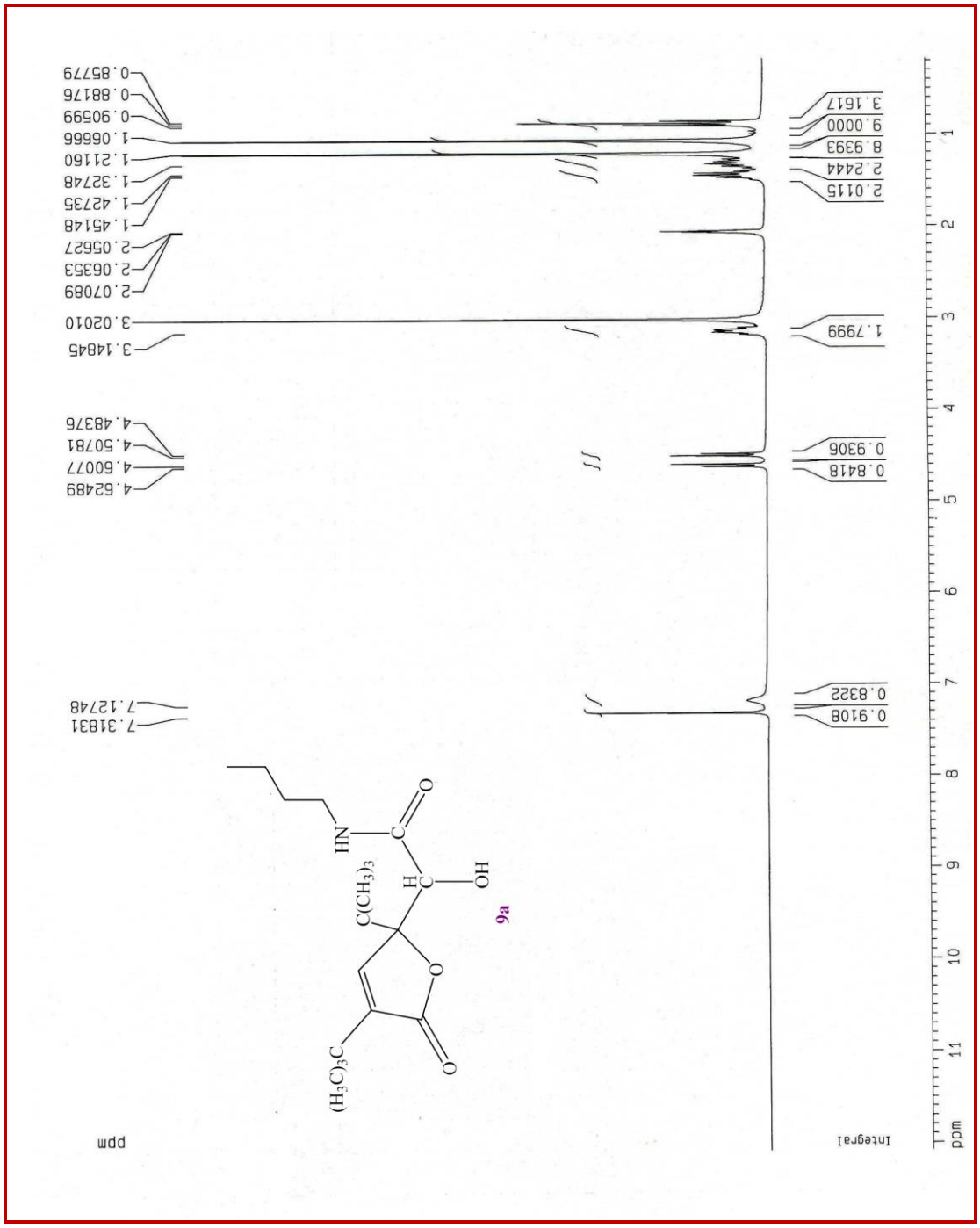


^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.14 (s, 1H), 5.77 (d, 1H), 4.44 (d, 1H), 4.14 (s, 1H), 3.87 (t, 1H), 1.77 (m, 2H), 1.65 (t, 2H), 1.55 (m, 10H), 1.24 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 171.6, 169.1, 146.5, 144.4, 89.9, 73.0, 51.2, 38.9, 32.6, 32.3, 32.2, 28.5, 27.4, 27.3, 26.6, 25.9, 24.0; IR (KBr): 3316, 2926, 1737, 1633, 1533 cm^{-1}; MS (EI) *m/z* (relative intensity):382 [M+3] (1), 380 [M+1] (6), 364 (2), 323 (6), 290 (10), 226 (12), 195 (100), 184 (50), 181 (85), 169 (80), 125 (40), 83 (53), 69 (55), 56 (98), 41 (42).

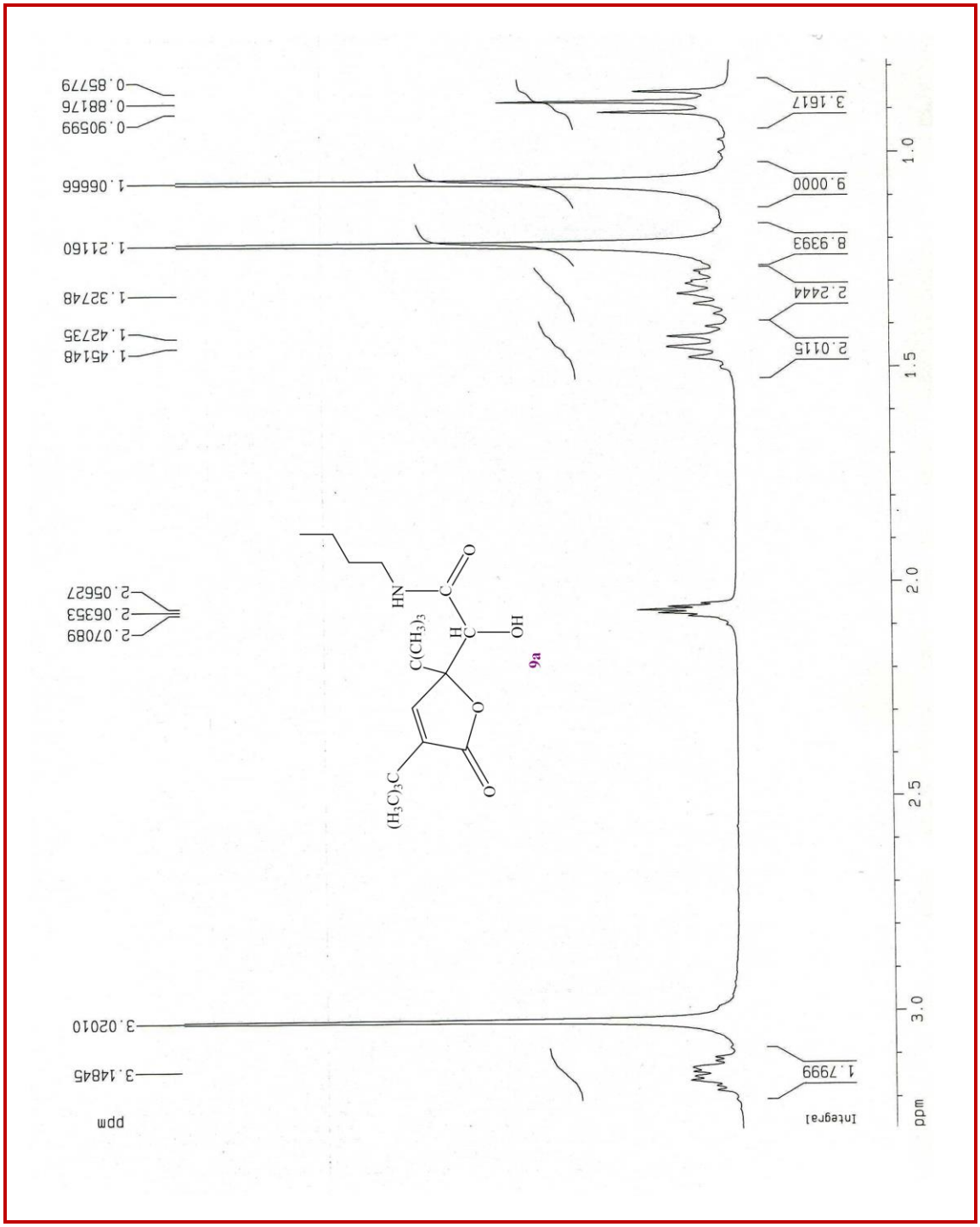
FTIR, ^{1}H NMR, ^{13}C NMR and mass spectra



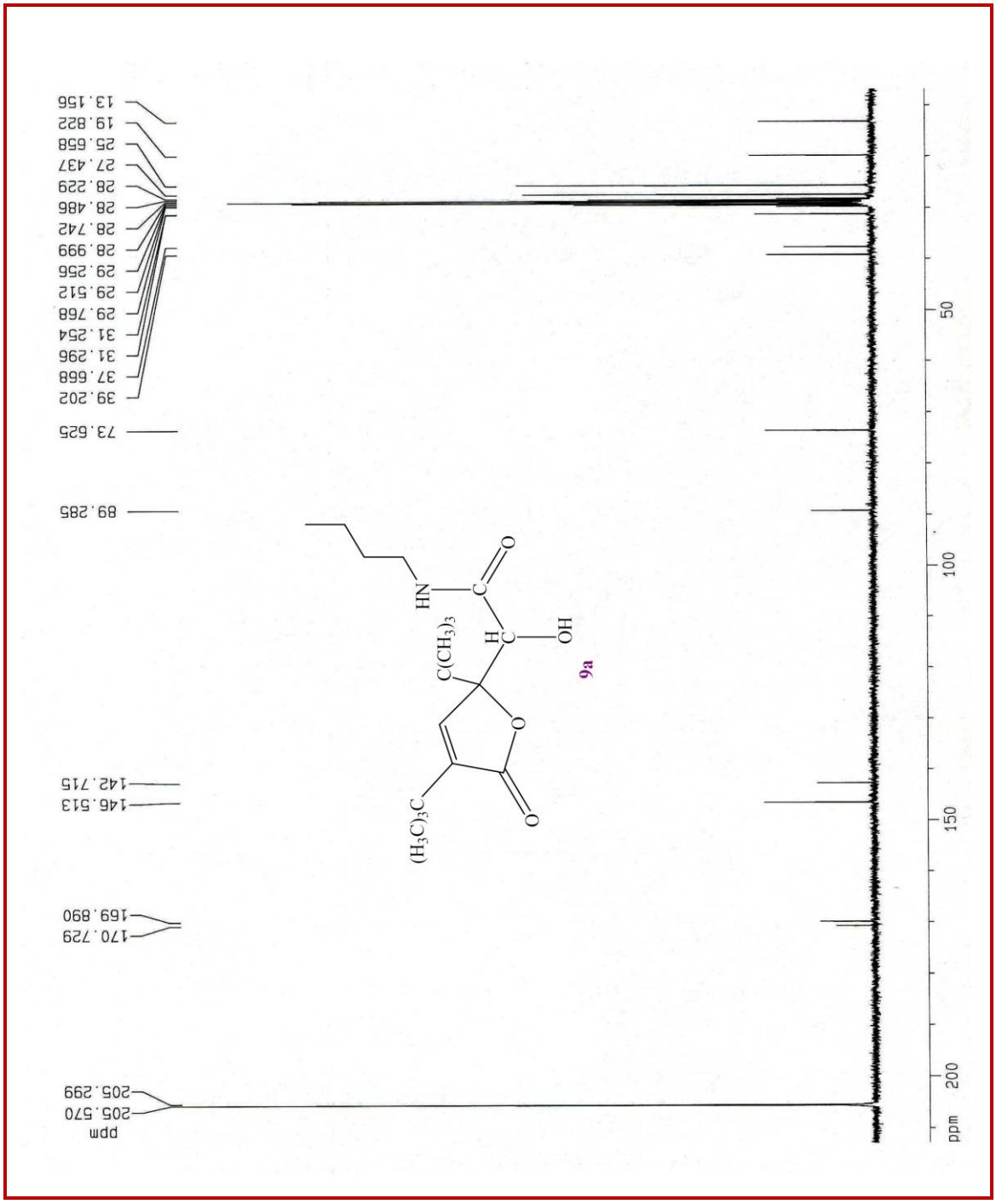
FTIR of 9a



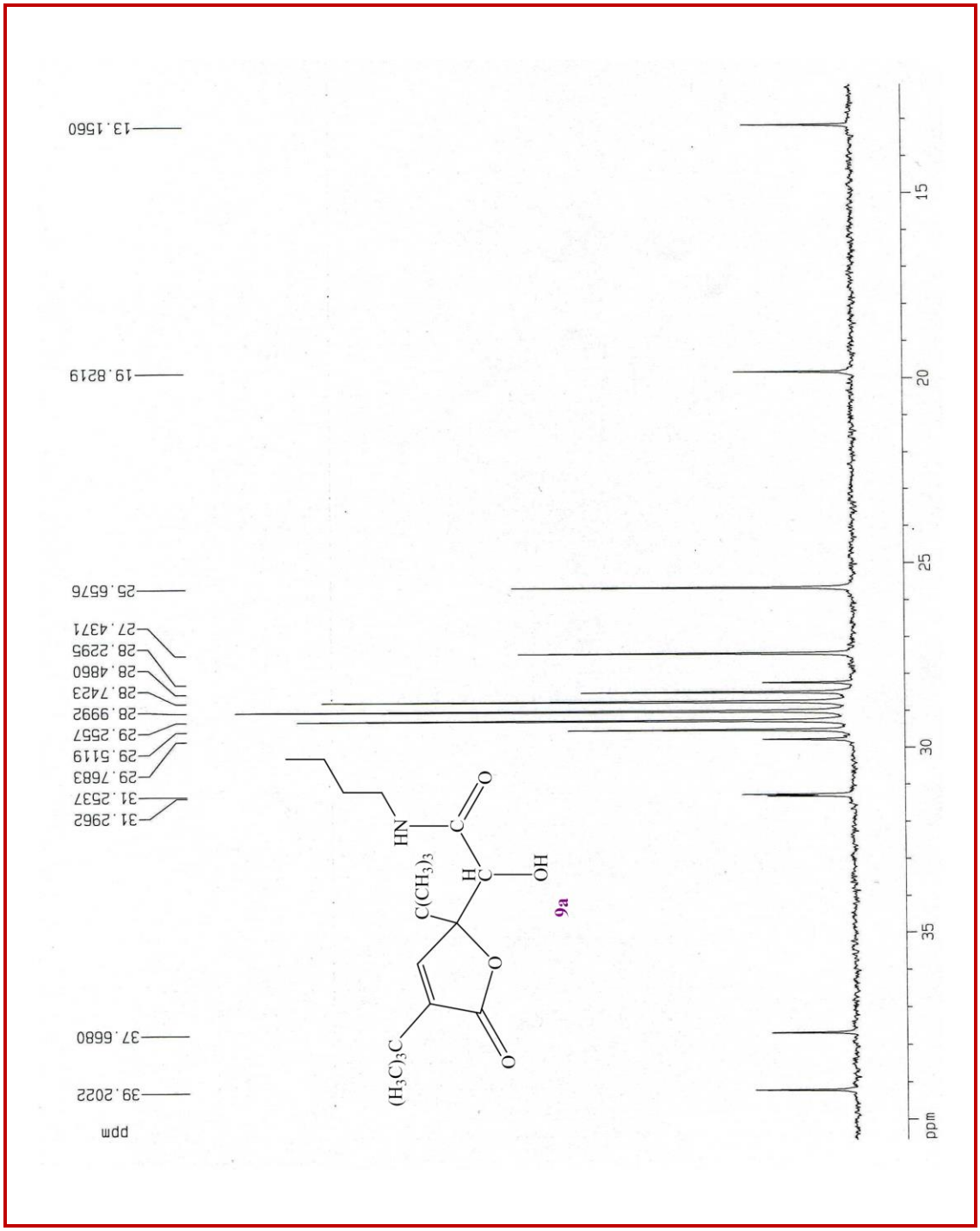
^{1}H NMR of 9a



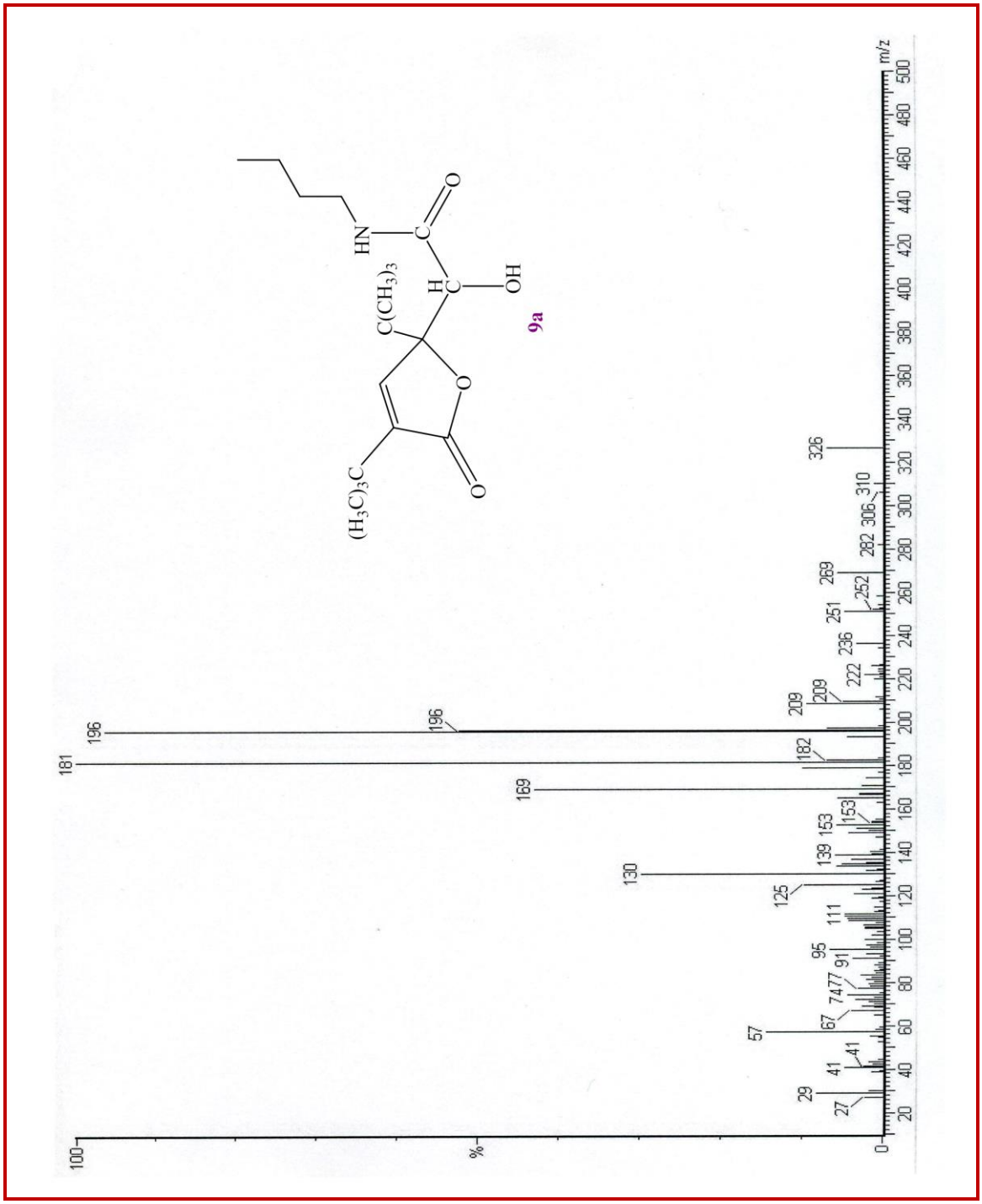
Expanded ^{1}H NMR of 9a


13.156
19.822
25.658
27.437
28.229
28.486
28.742
28.999
29.256
29.512
29.768
31.254
31.296
37.668
39.202
73.625
89.285
142.715
146.513
169.890
170.729
205.299
205.570
ppm
50
100
150
200
HN
C
O
H
C
OH
C(CH3)3
O
O
(H3C)3C
9a

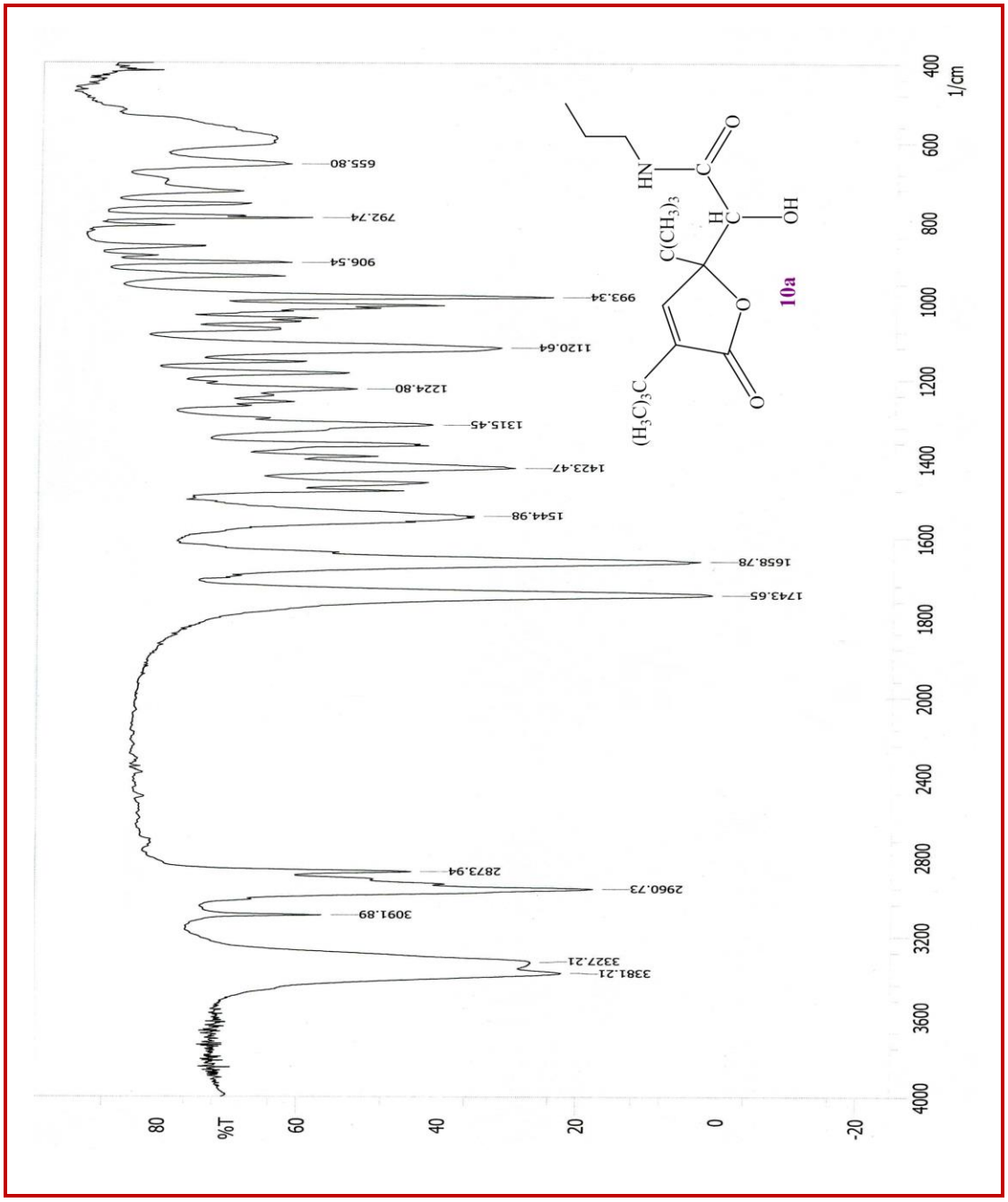
^{13}C NMR of 9a



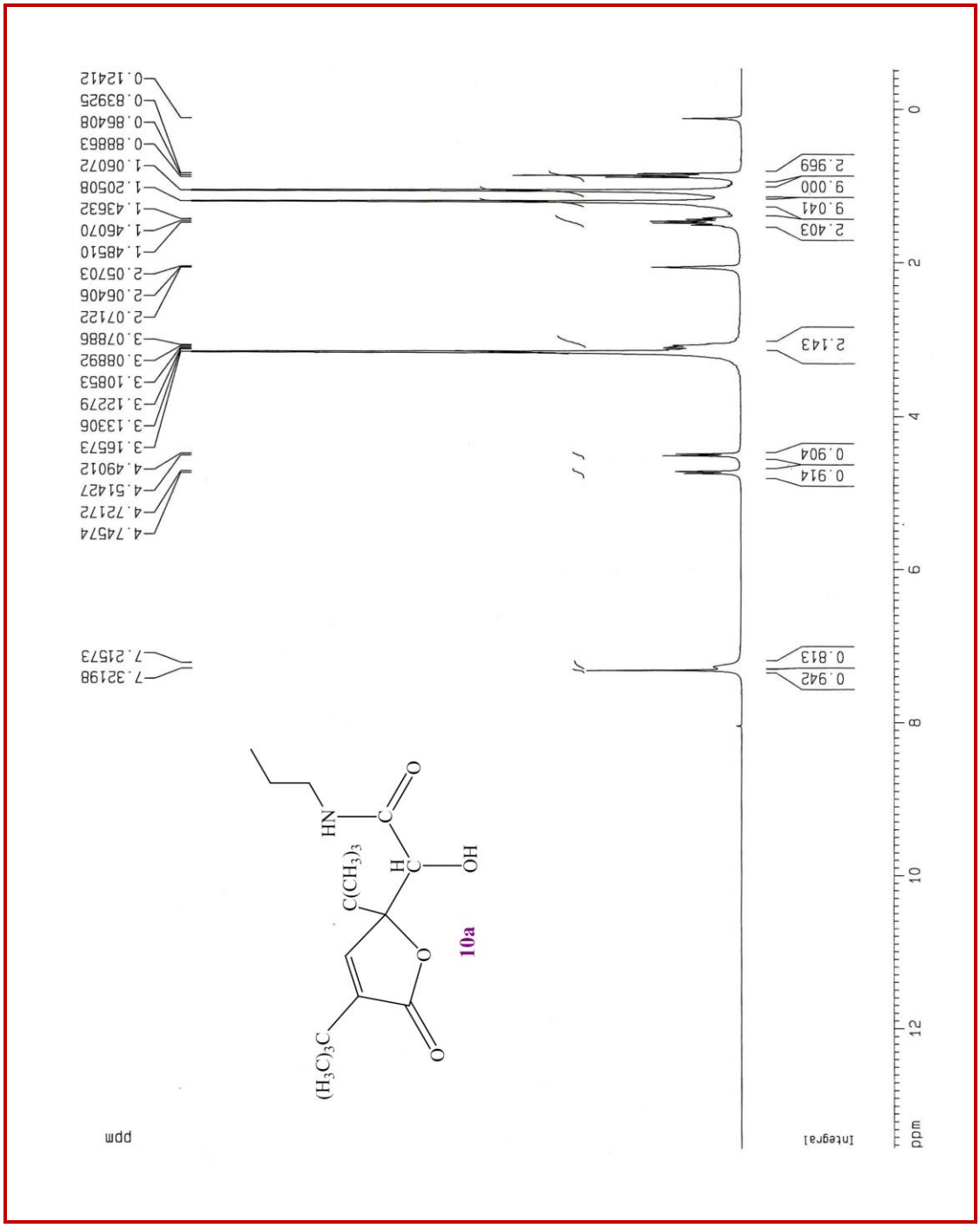
Expanded ^{13}C NMR of 9a


HN
C
O
H
C
OH
C(CH3)3
O
O
(H3C)3C
9a
m/z
%
100
0
326
310
306
282
289
252
251
236
222
209
209
196
196
182
181
169
153
153
139
130
125
111
95
91
77
74
67
57
41
41
29
27

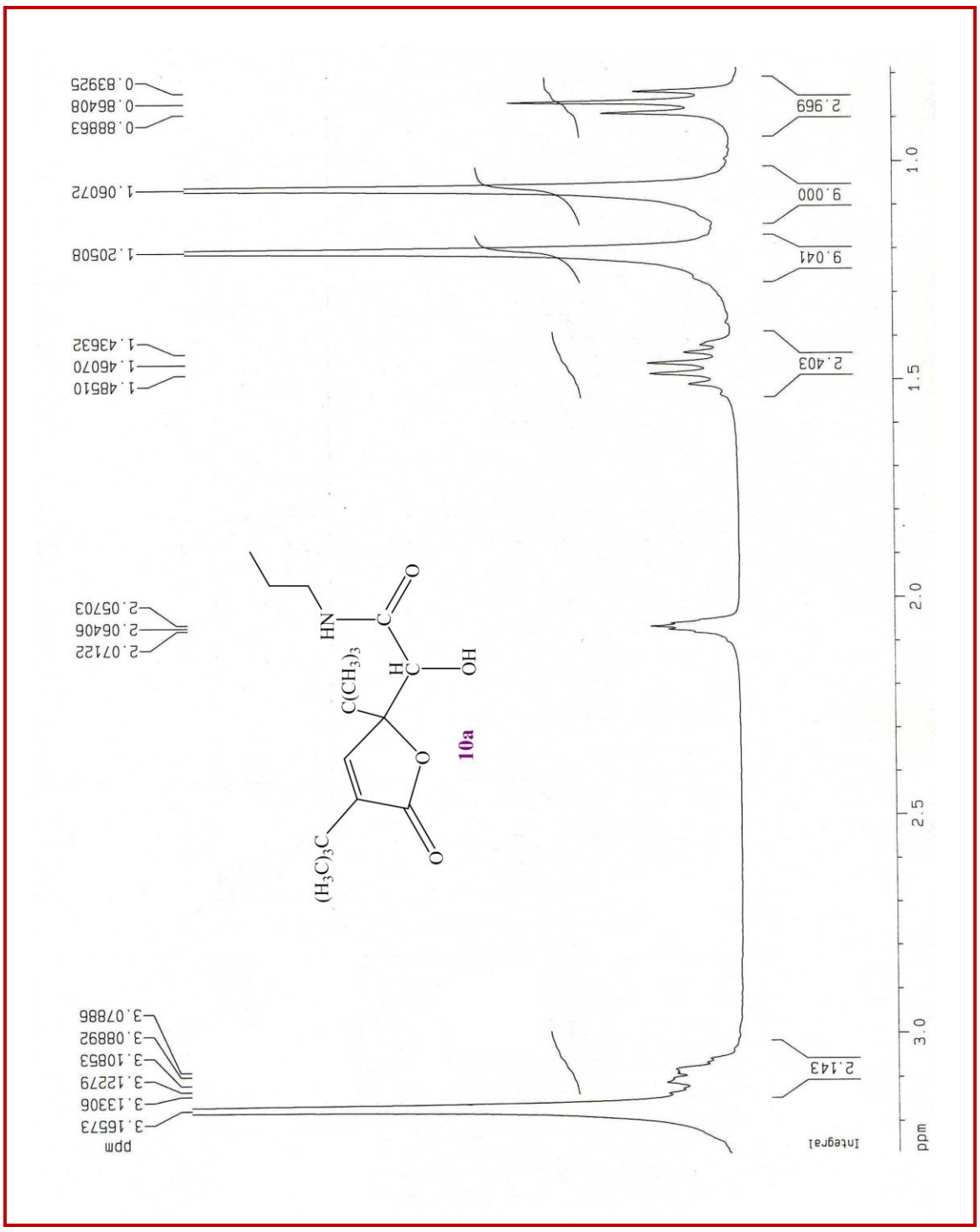
MS of 9a


3381.21
3327.21
3091.89
2960.73
2873.94
1743.65
1658.78
1544.98
1423.47
1315.45
1224.80
1120.64
993.34
906.54
792.74
655.80
10a
%T
1/cm

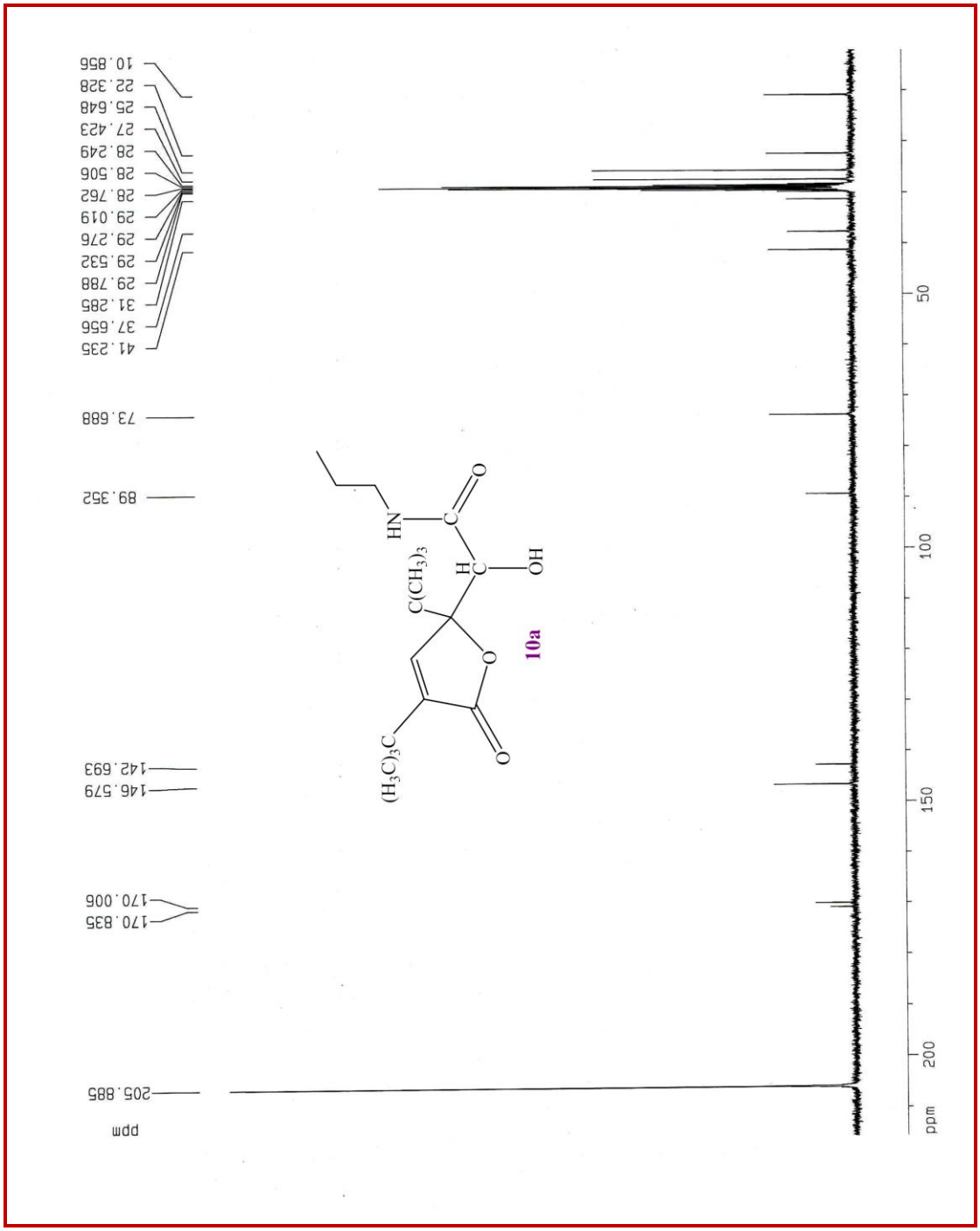
FTIR of 10a


ppm
Integral
0.942
0.813
7.32198
7.21573
0.914
0.904
2.143
2.403
9.041
9.000
2.969
10a

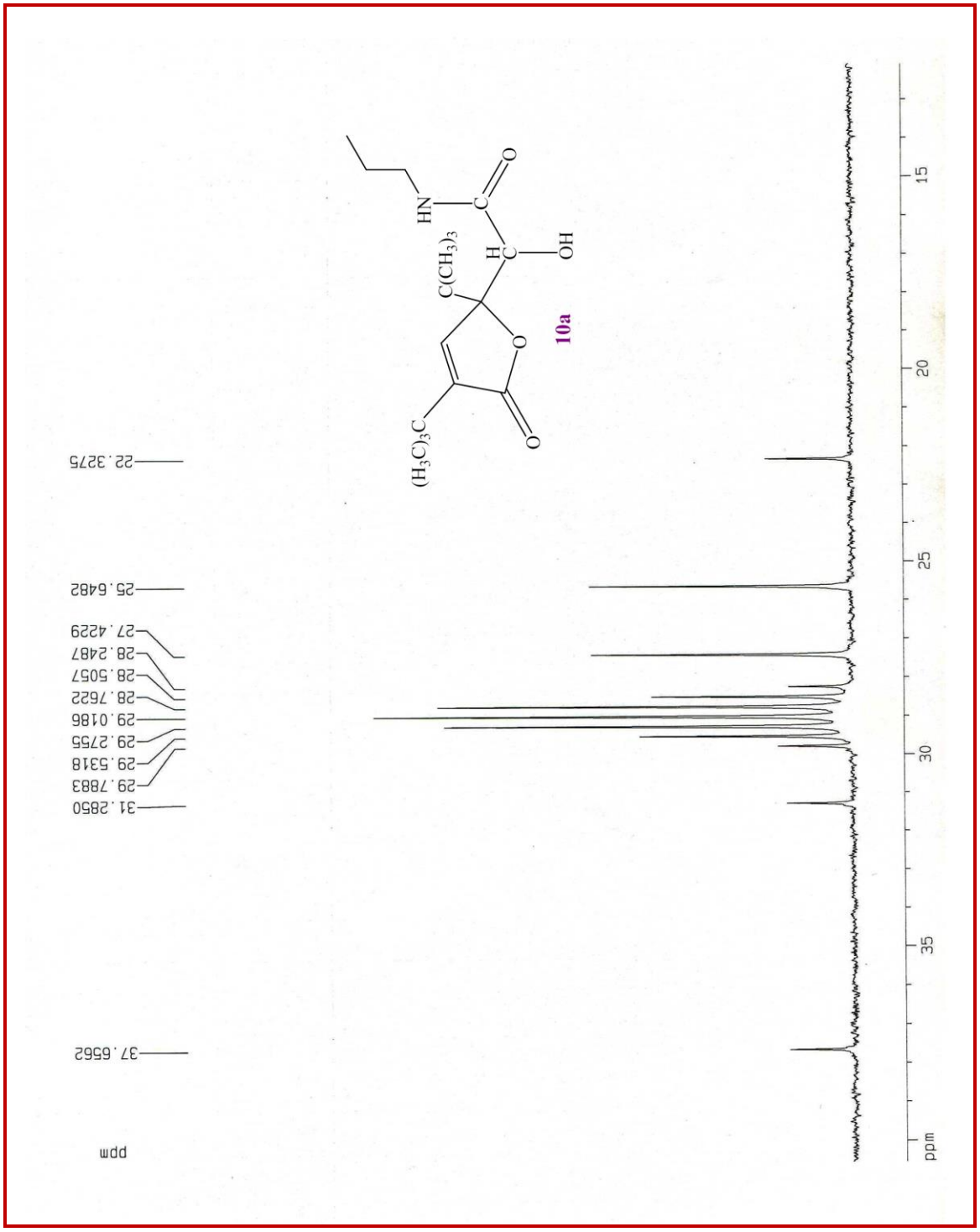
^{1}H NMR of 10a



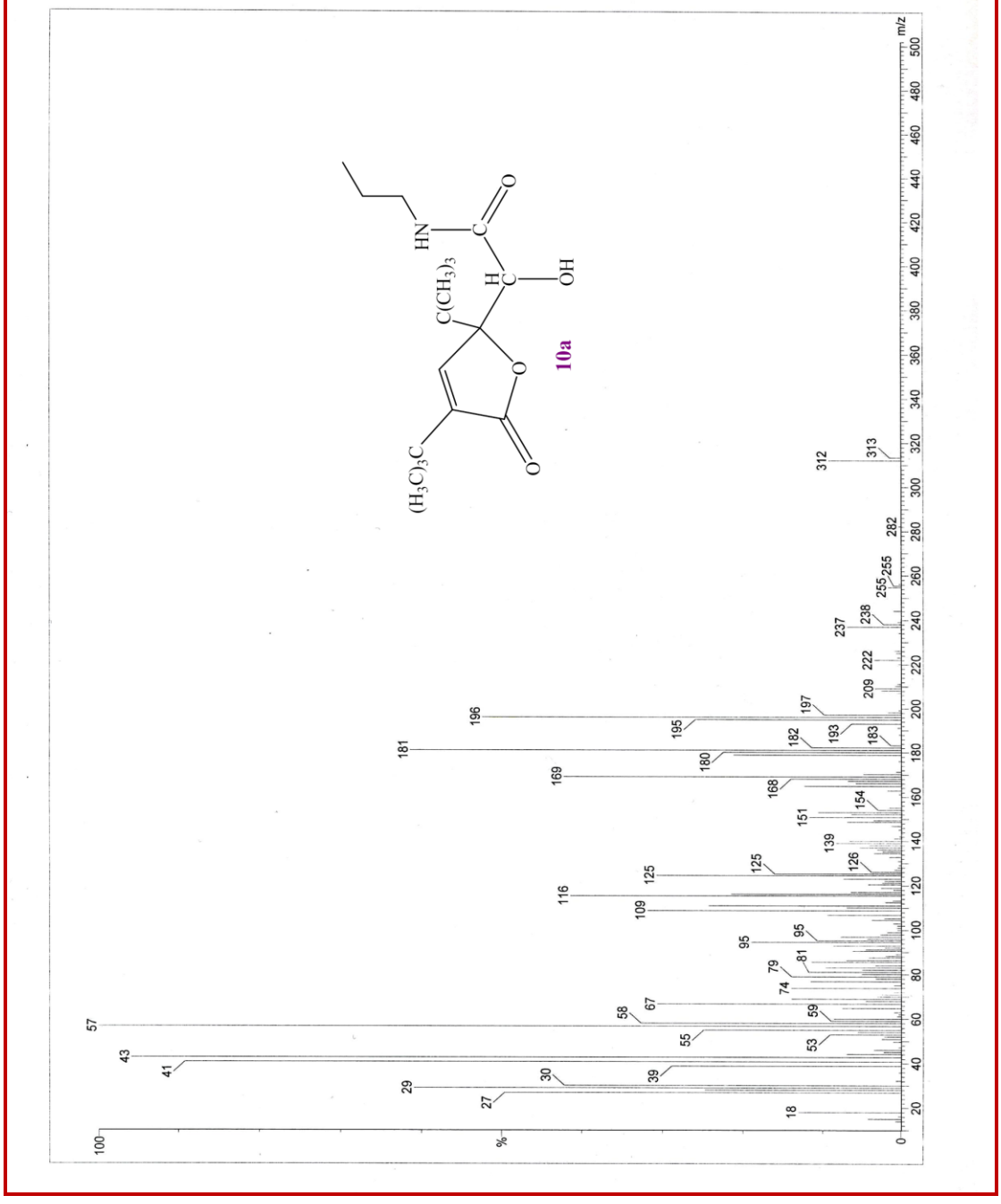
Expanded ^{1}H NMR of 10a



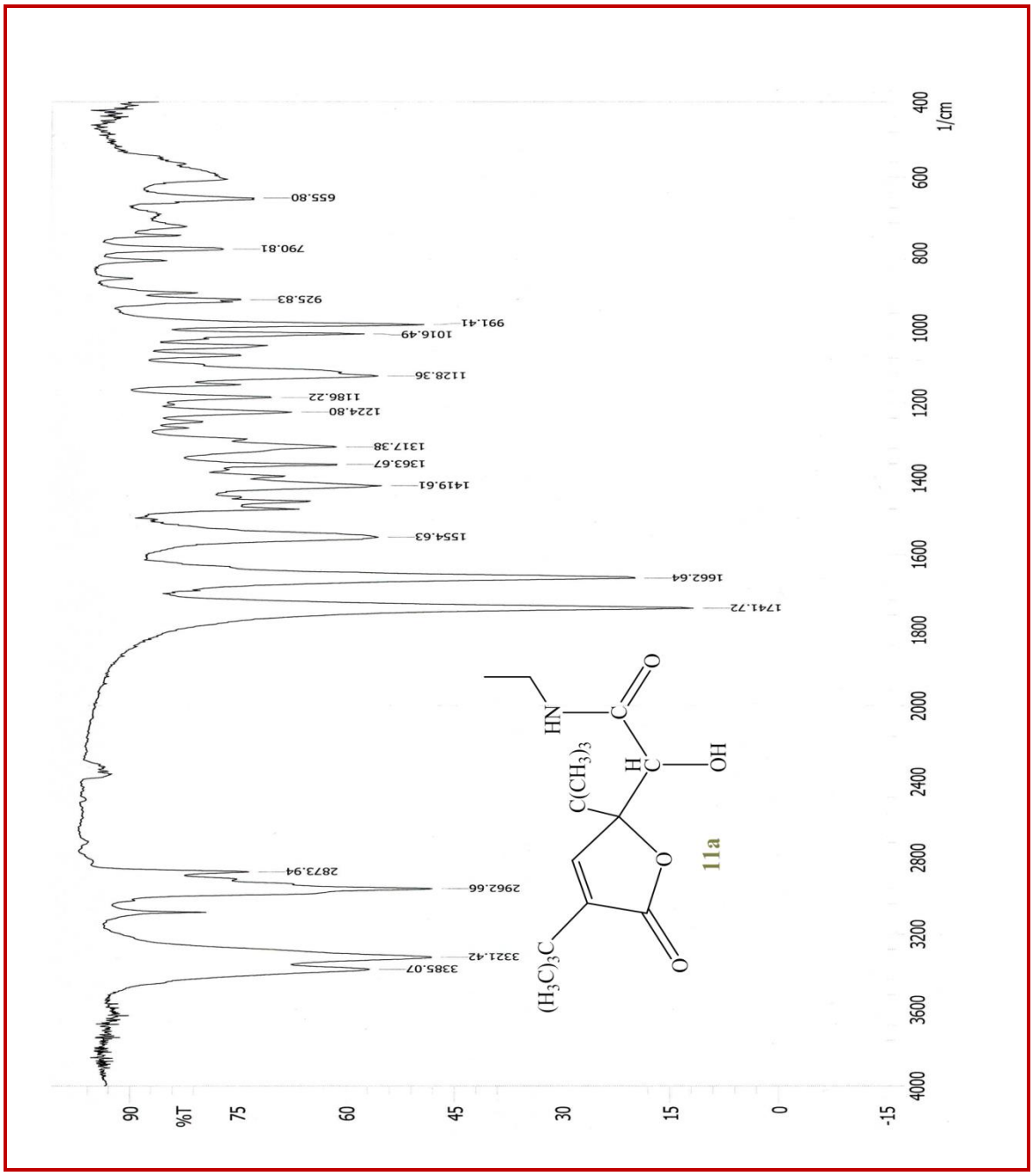
^{13}C NMR of 10a



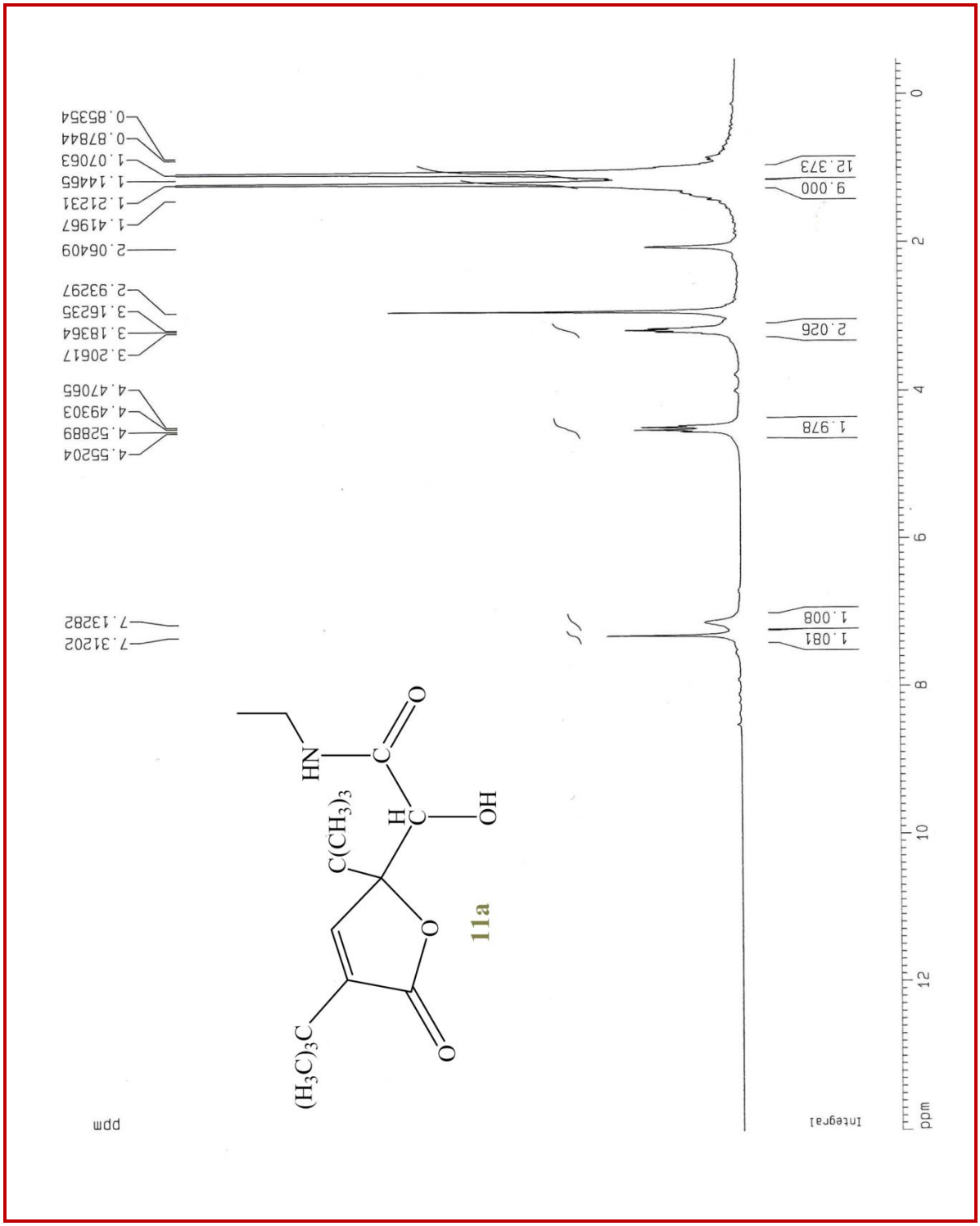
Expanded ^{13}C NMR of 10a


HN
C
O
H
C
OH
C(CH3)3
O
O
(H3C)3C
10a
m/z
%
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
57
43
41
29
27
18
30
39
55
53
58
67
59
74
79
81
95
95
109
116
125
125
126
139
151
154
168
169
180
181
182
193
183
195
196
197
209
222
237
238
255
255
282
312
313

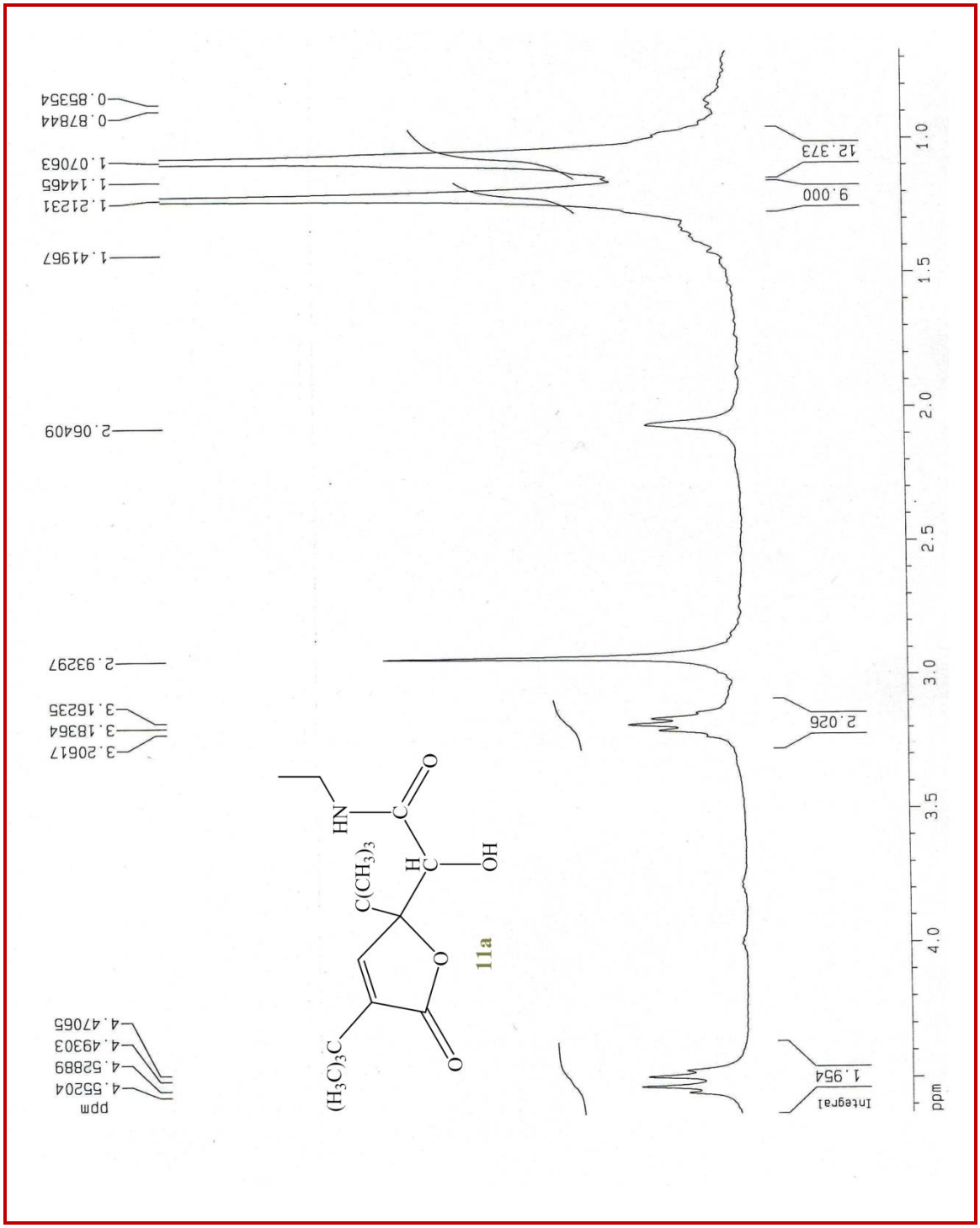
MS of 10a


%T
1/cm
655.80
790.81
925.83
991.41
1016.49
1128.36
1186.22
1224.80
1317.38
1363.67
1419.61
1554.63
1662.64
1741.72
2873.94
2962.66
3321.42
3385.07
HN
C
O
C(CH3)3
H
C
OH
O
O
(H3C)3C
11a

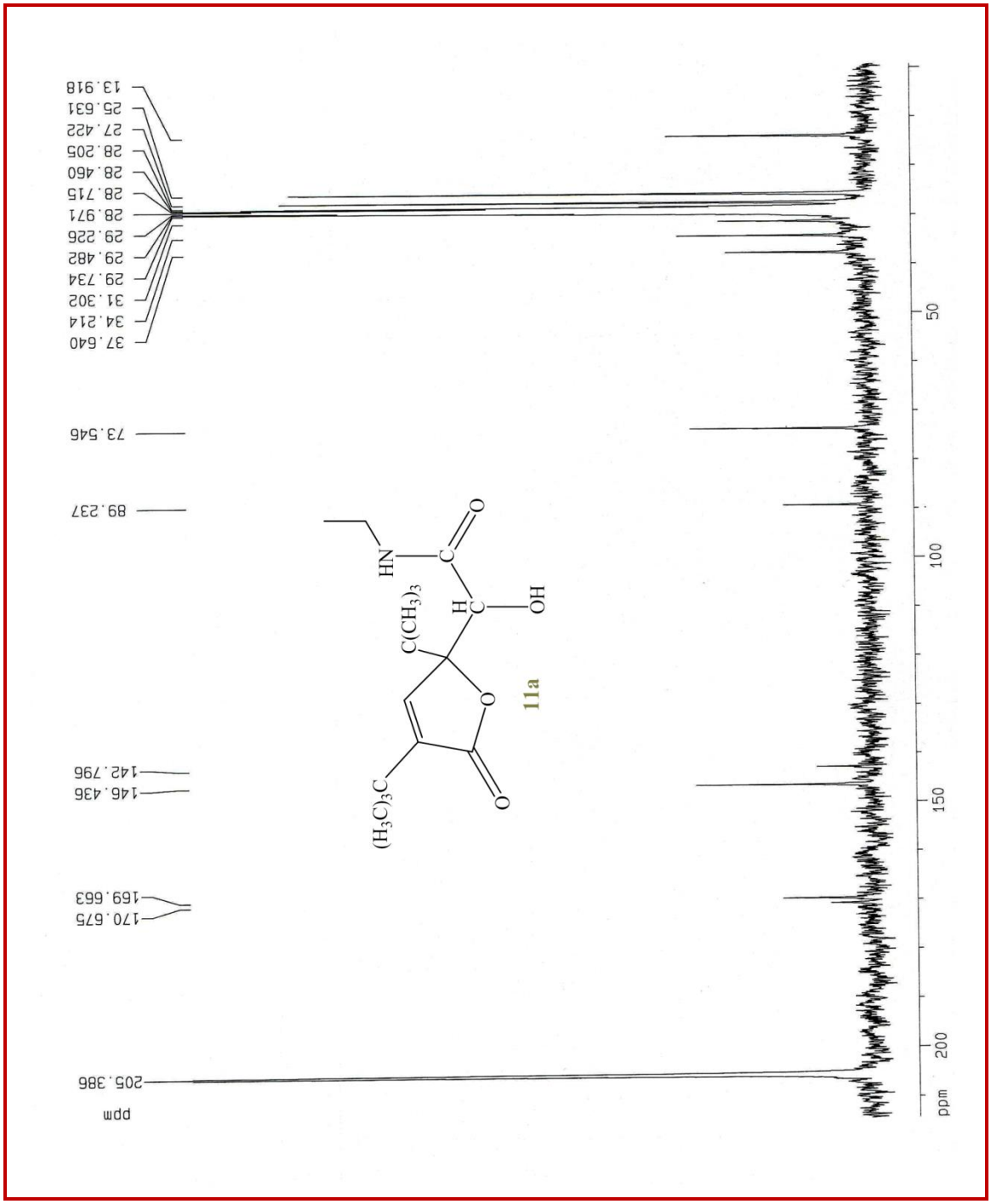
IR of 11a



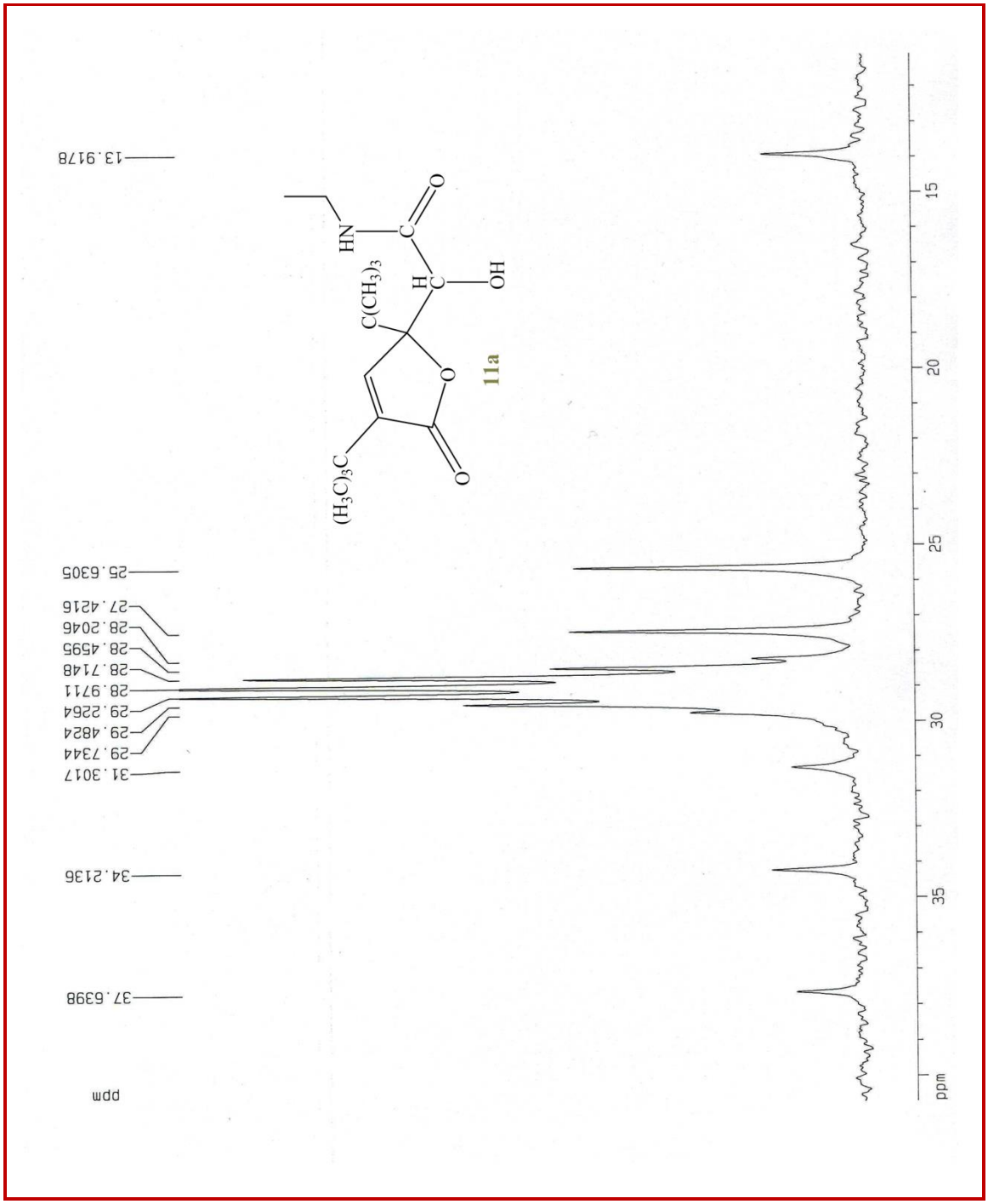
^{1}H NMR of 11a



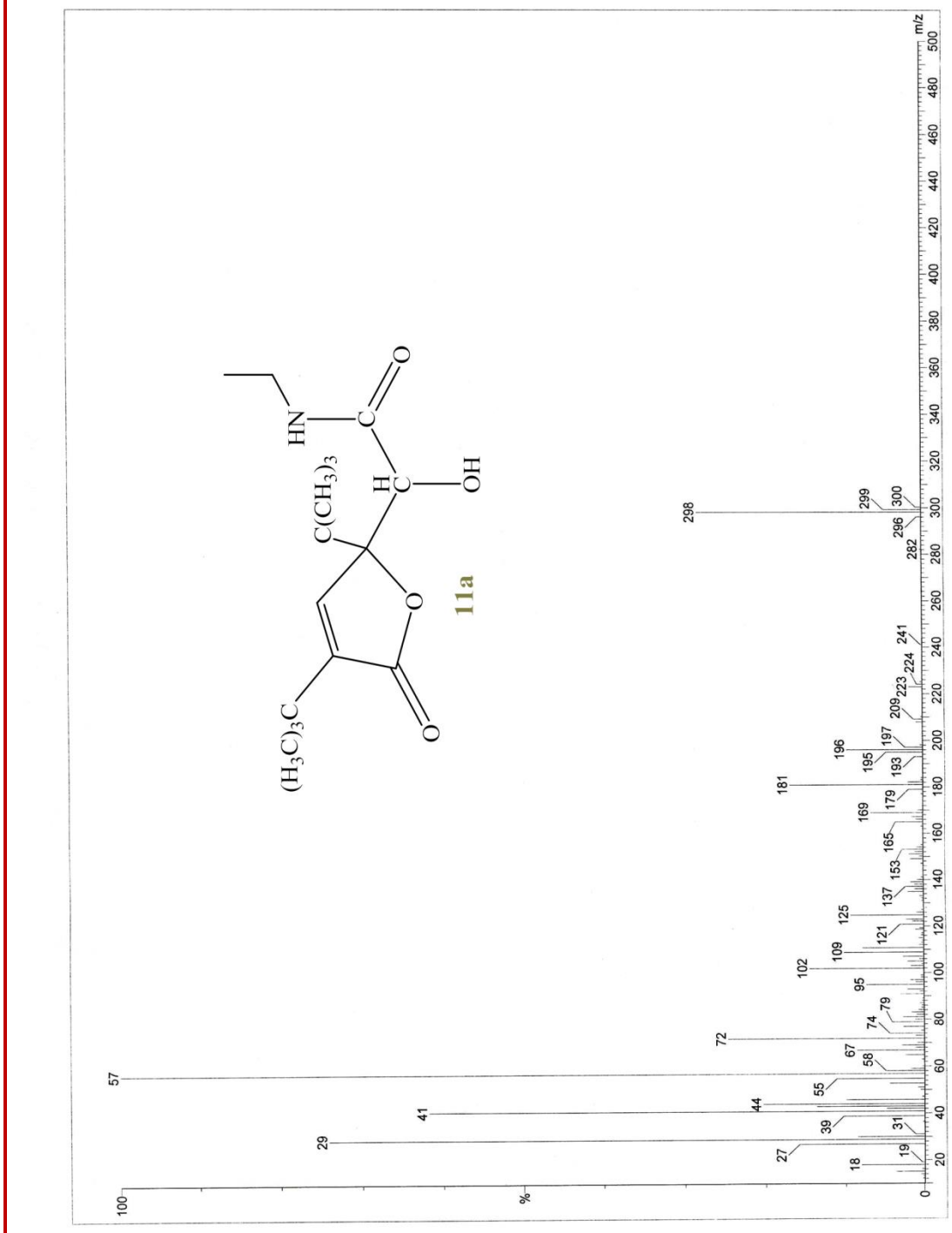
Expanded ^{1}H NMR of 11a



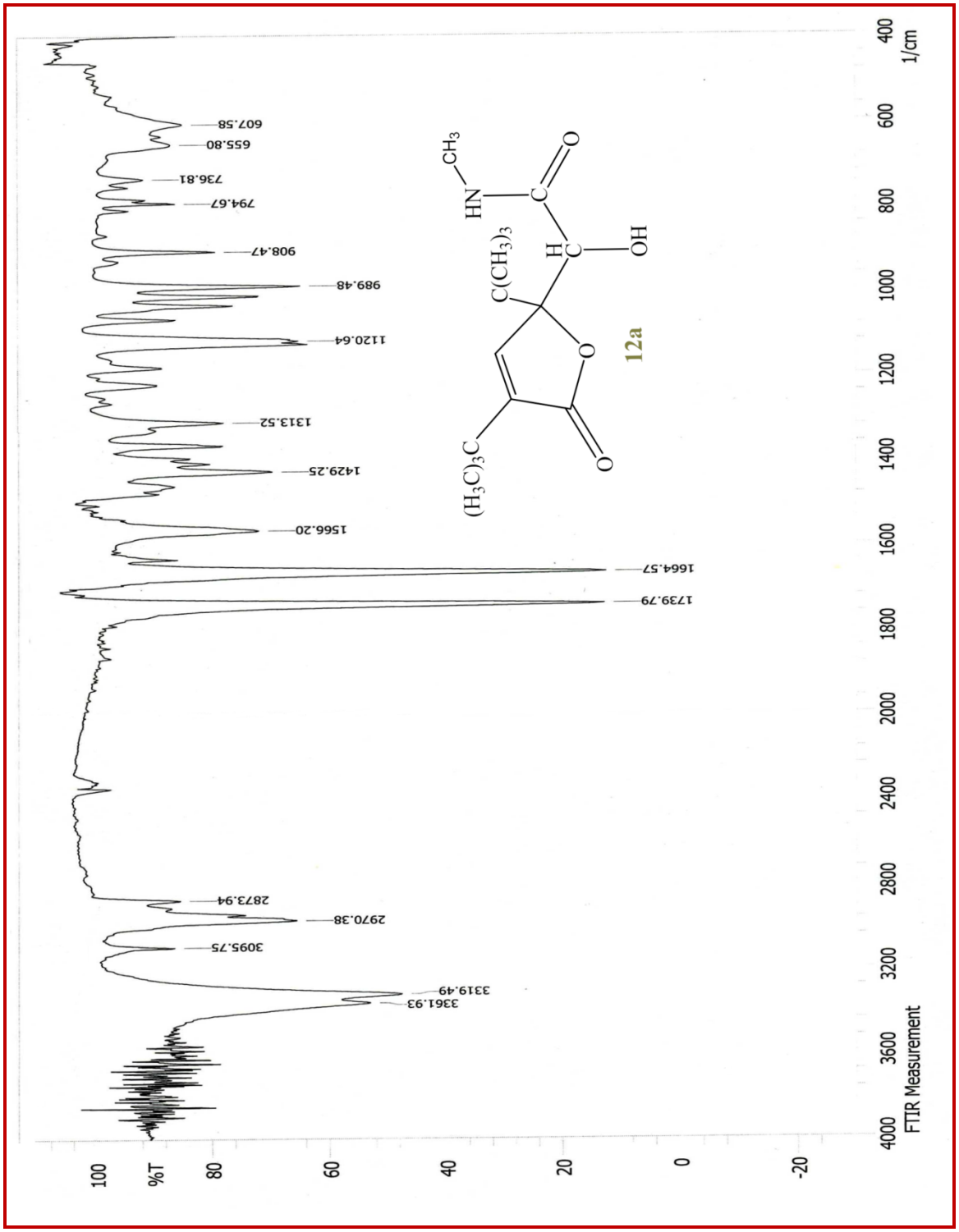
^{13}C NMR of 11a



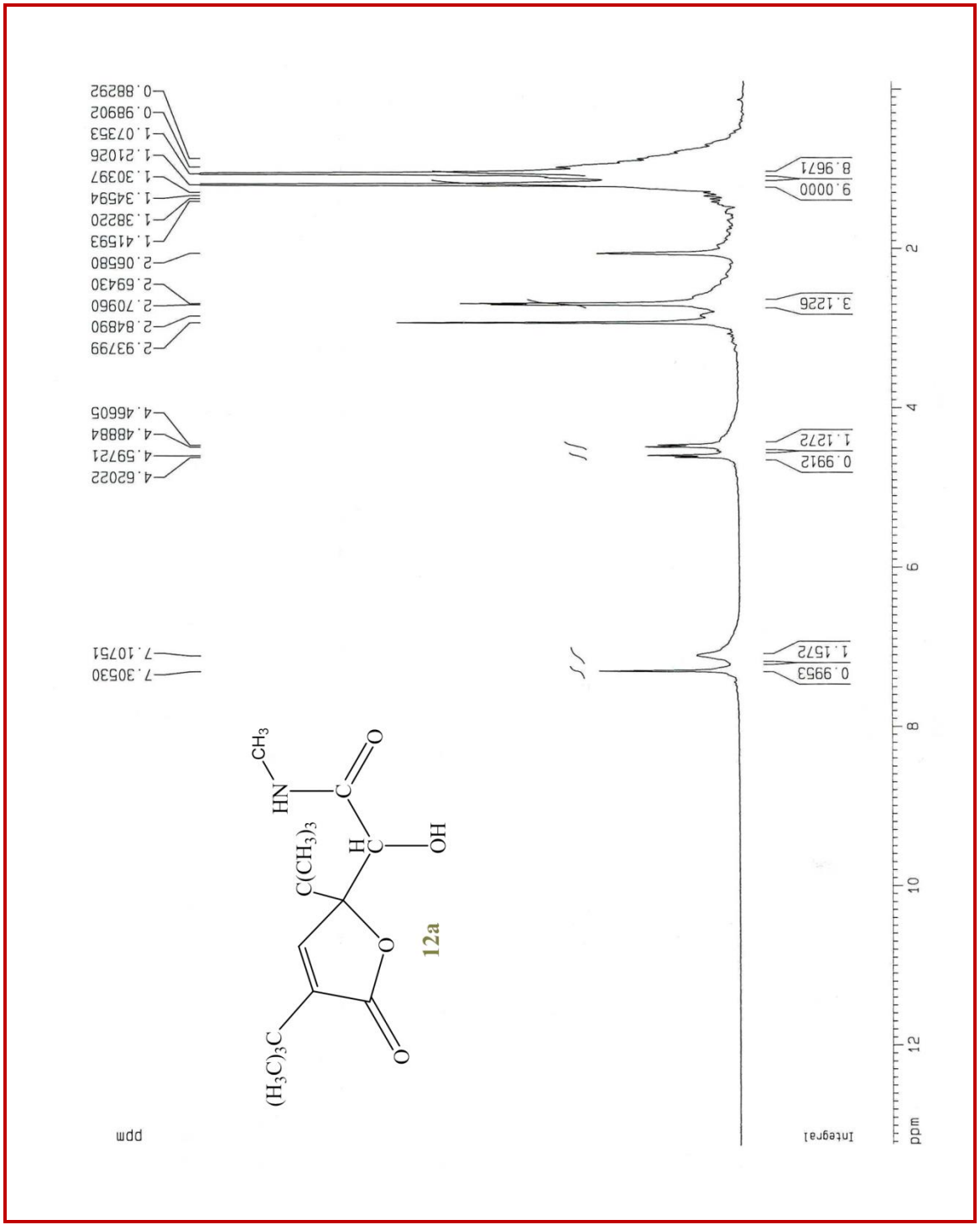
Expanded ^{13}C NMR of 11a


HN
C
O
H
C
OH
C(CH3)3
O
O
(H3C)3C
11a
m/z
%
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
57
41
29
27
18
19
39
31
44
55
58
67
72
74
79
95
102
109
121
125
137
153
165
169
179
181
193
195
196
197
209
223
224
241
282
296
298
299
300

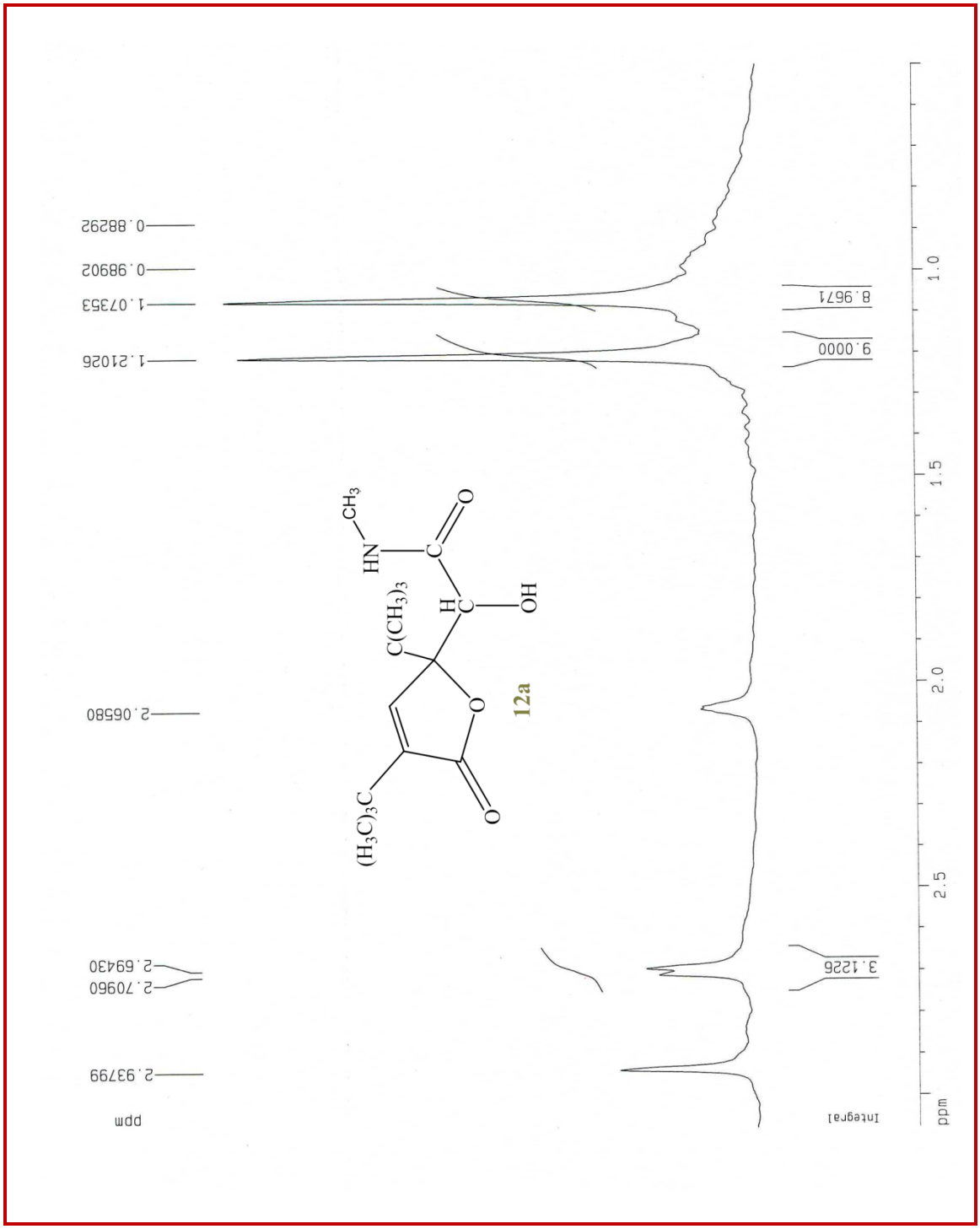
MS of 11a


FTIR Measurement
%T
1/cm
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
100
80
60
40
20
0
-20
3361.93
3319.49
3095.75
2970.38
2873.94
1739.79
1664.57
1566.20
1429.25
1313.52
1120.64
989.48
908.47
794.67
736.81
655.80
607.58
12a

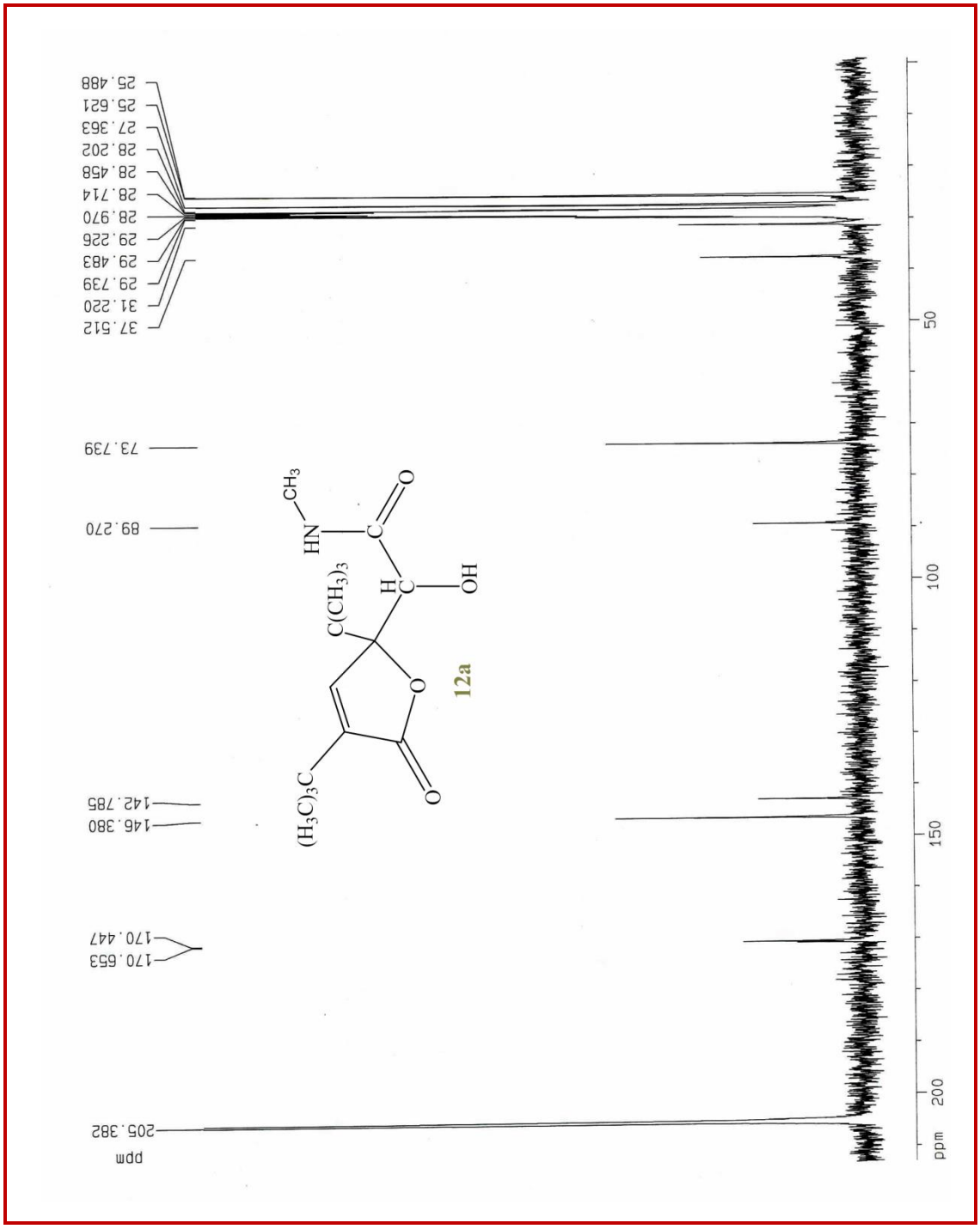
IR of 12a



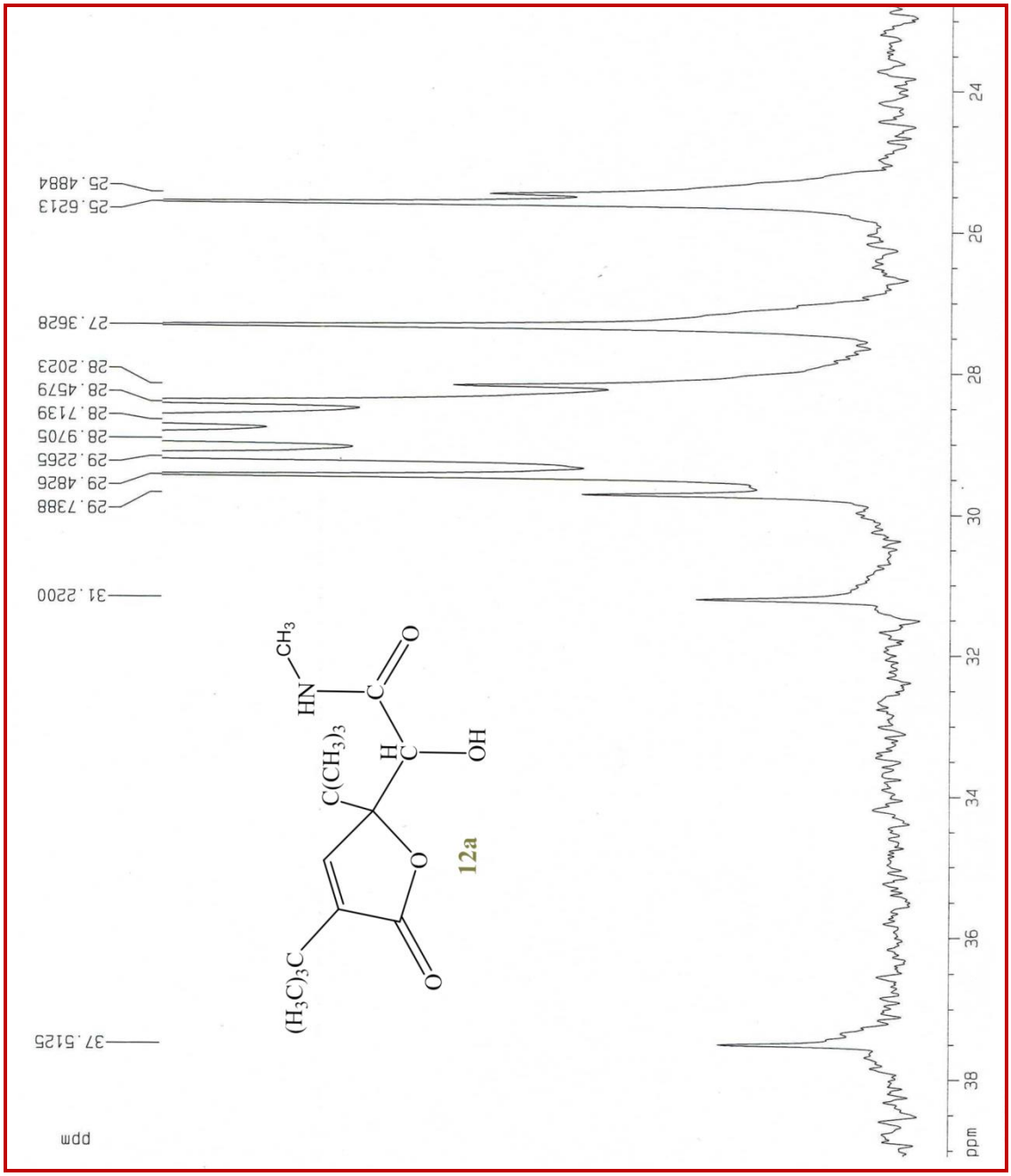
^{1}H NMR of 12a



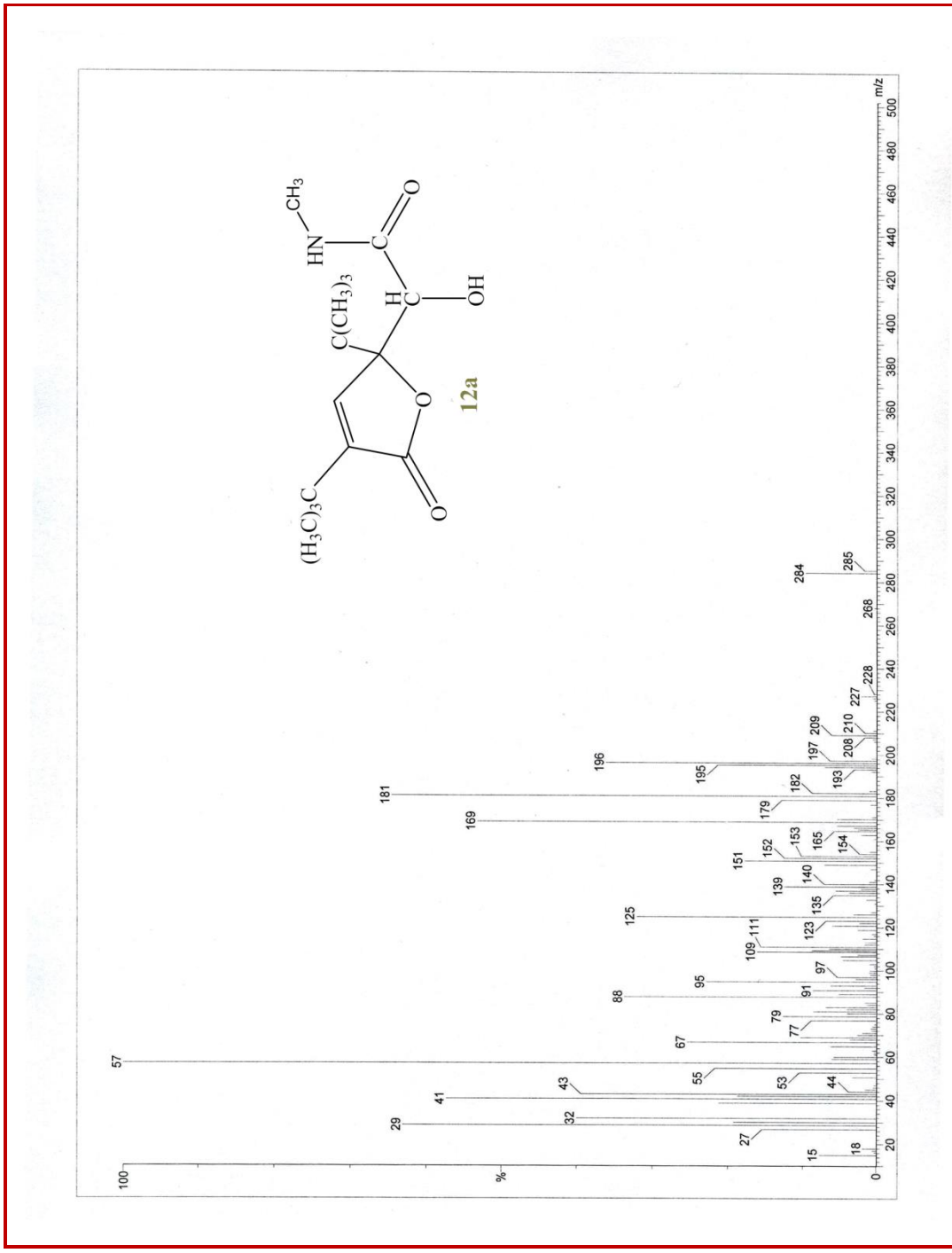
Expanded ^{1}H NMR of 12a



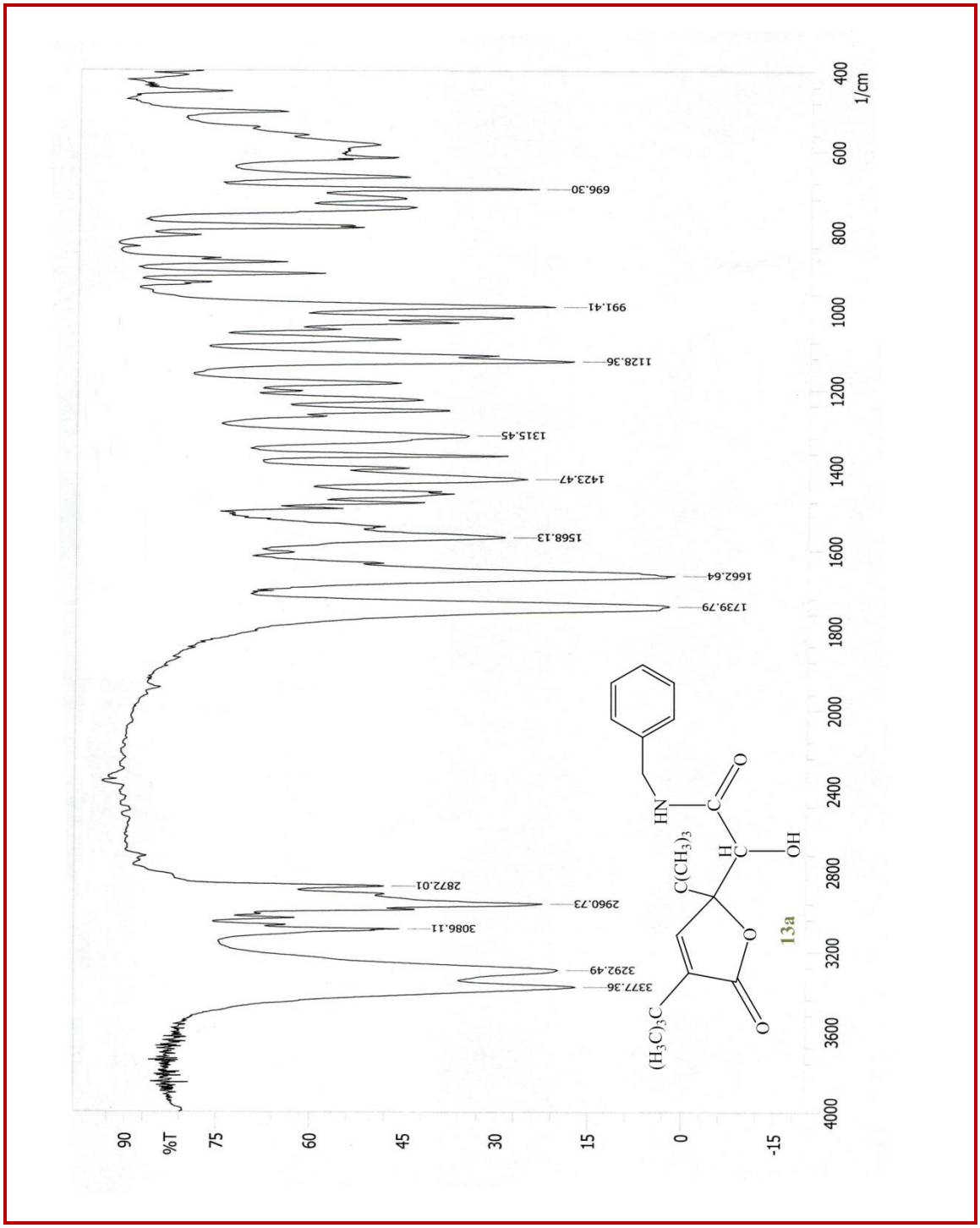
^{13}C NMR of 12a



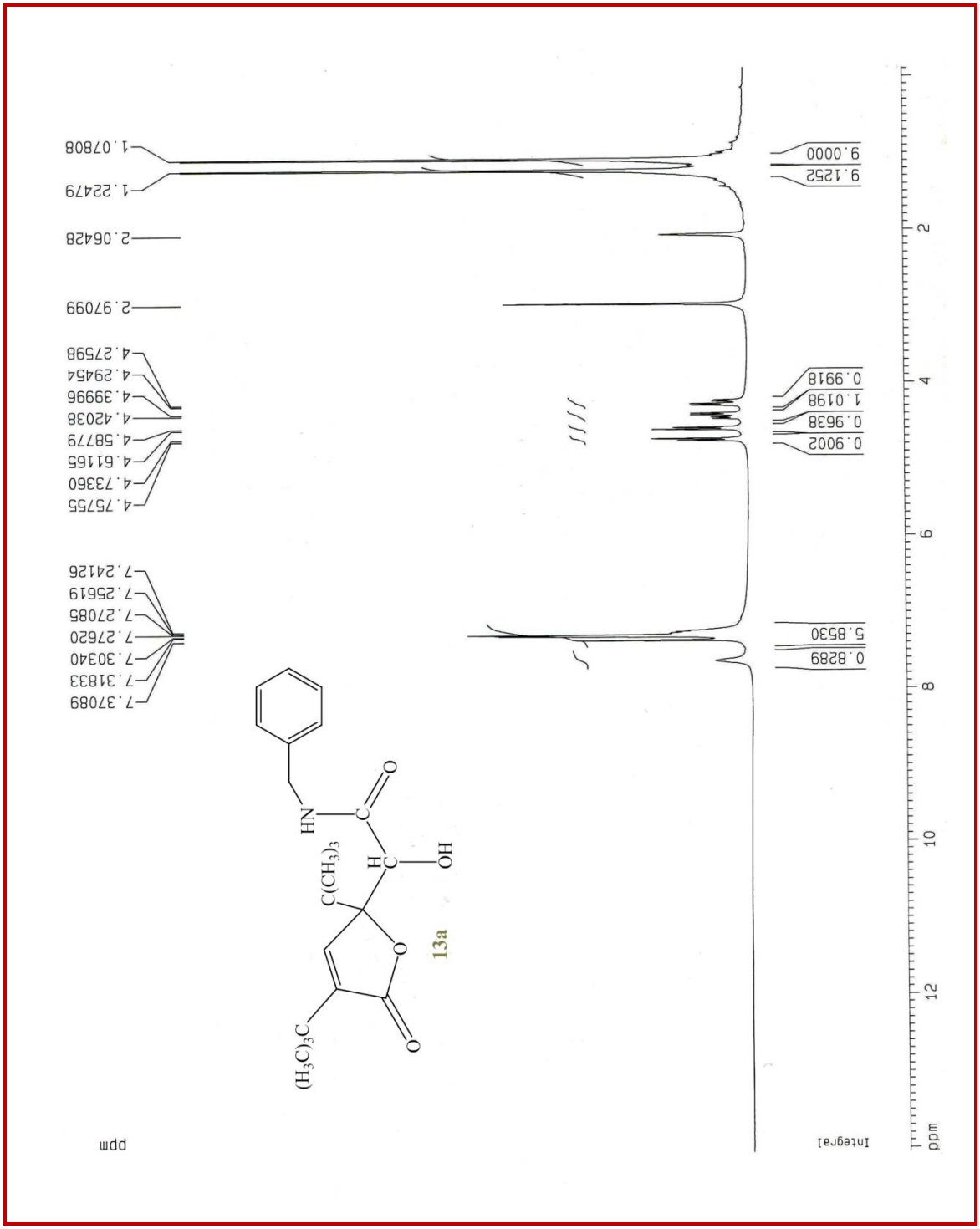
Expanded ^{13}C NMR of 12a



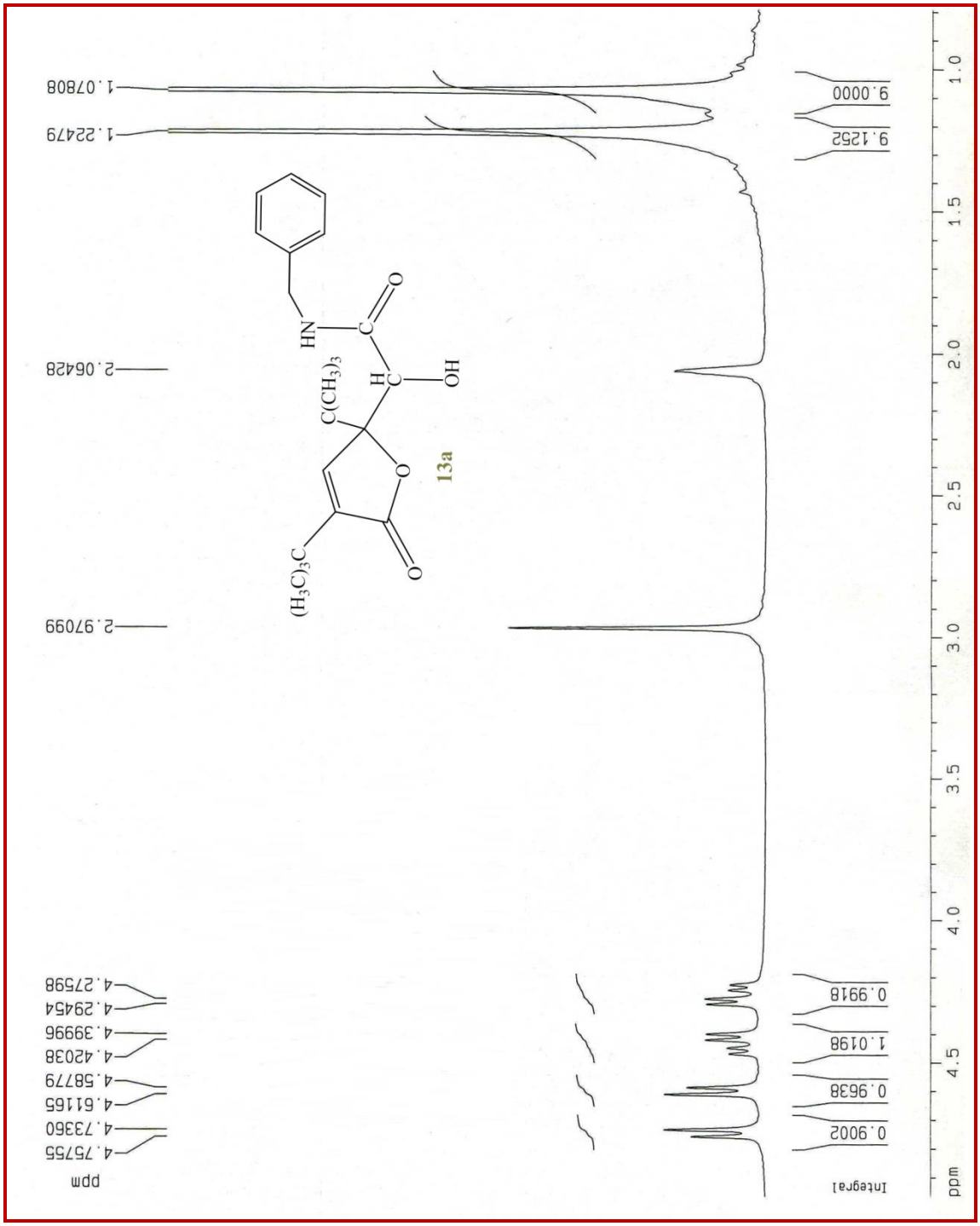
MS of 12a


%T
90
75
60
45
30
15
0
-15
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
1/cm
3377.36
3292.49
3086.11
2960.73
2872.01
1739.79
1662.64
1568.13
1423.47
1315.45
1128.36
991.41
696.30
HN
C(CH3)3
H
C
OH
O
O
O
O
(H3C)3C
13a

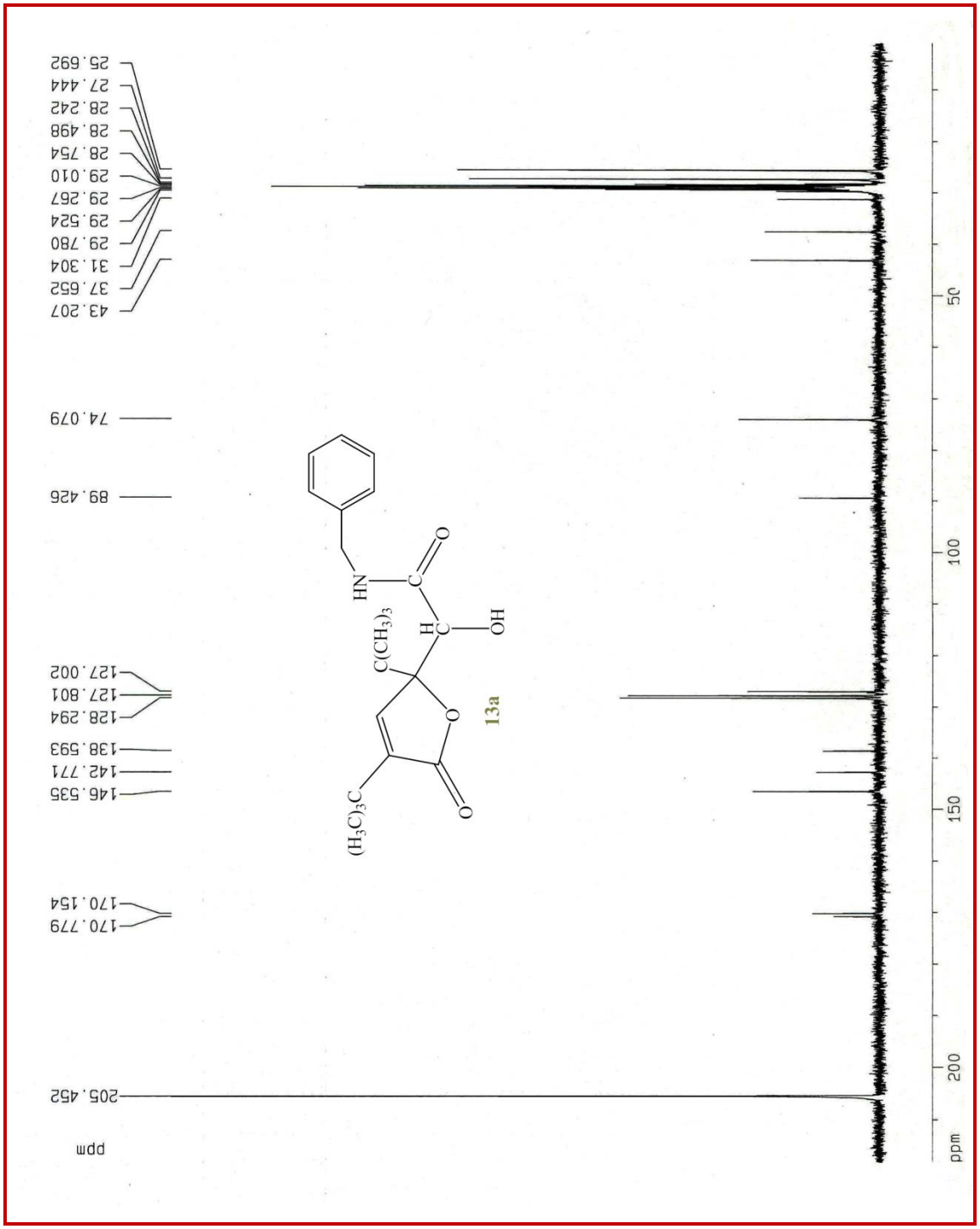
IR of 13a



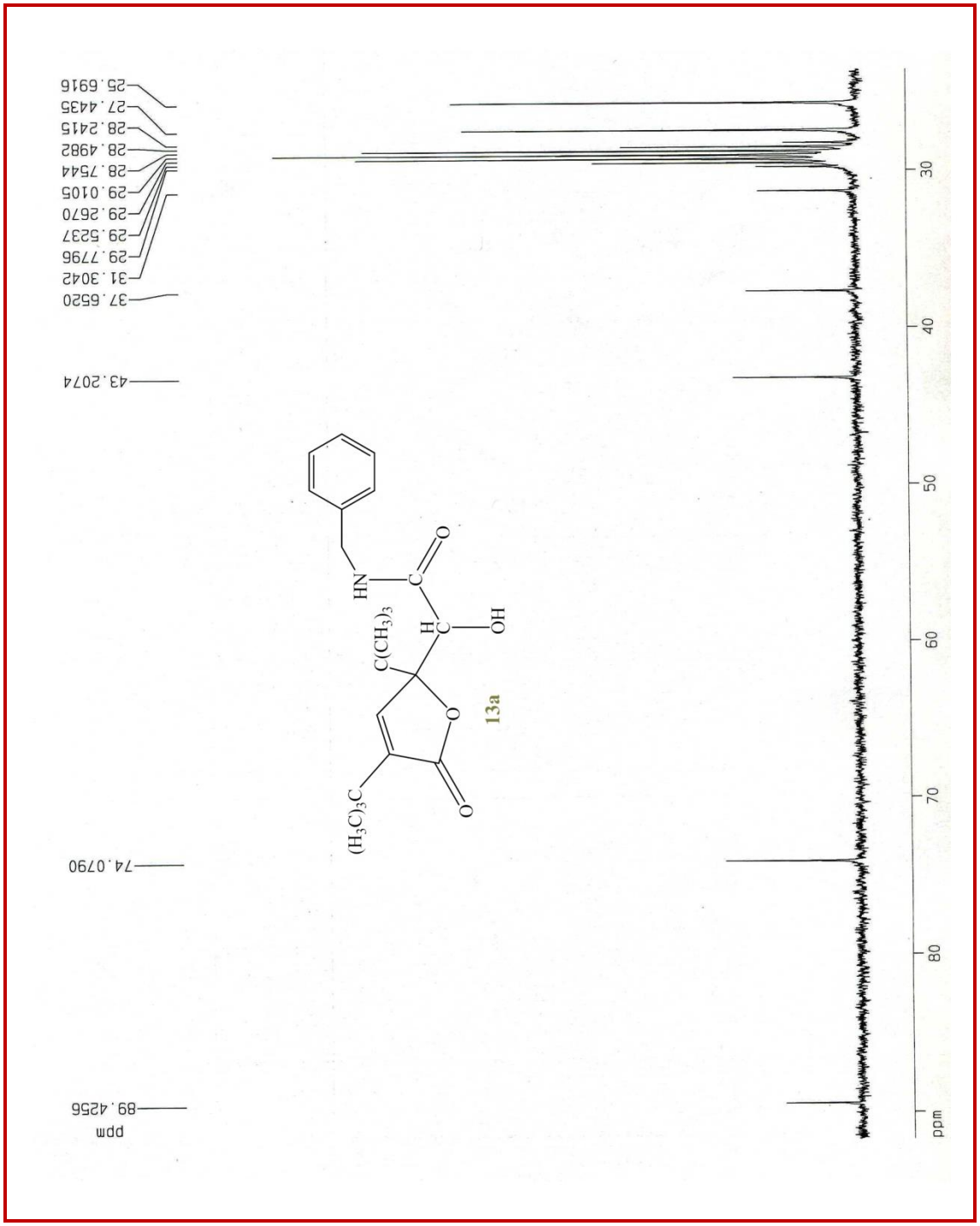
^{1}H NMR of 13a



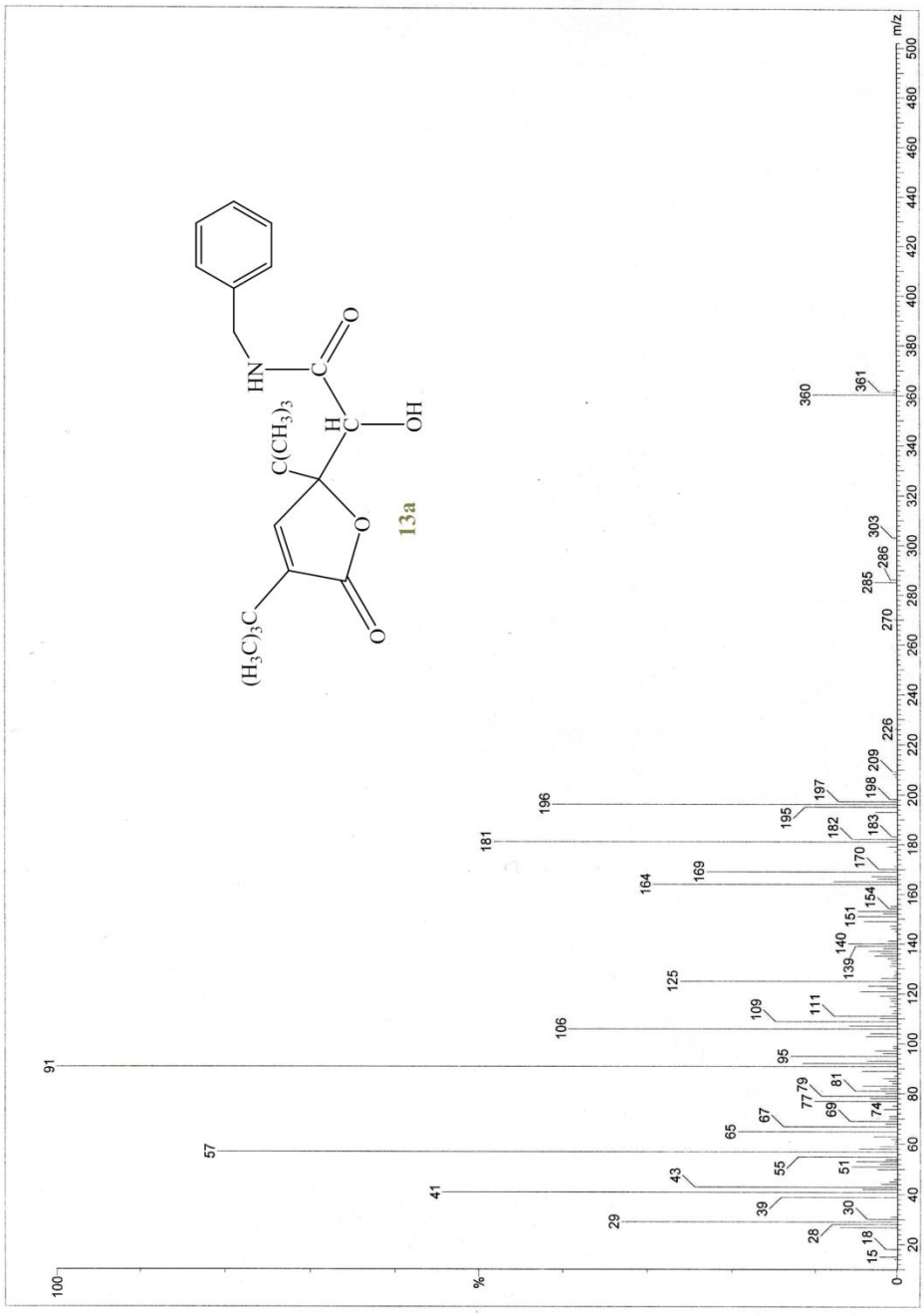
Expanded ^{1}H NMR of 13a



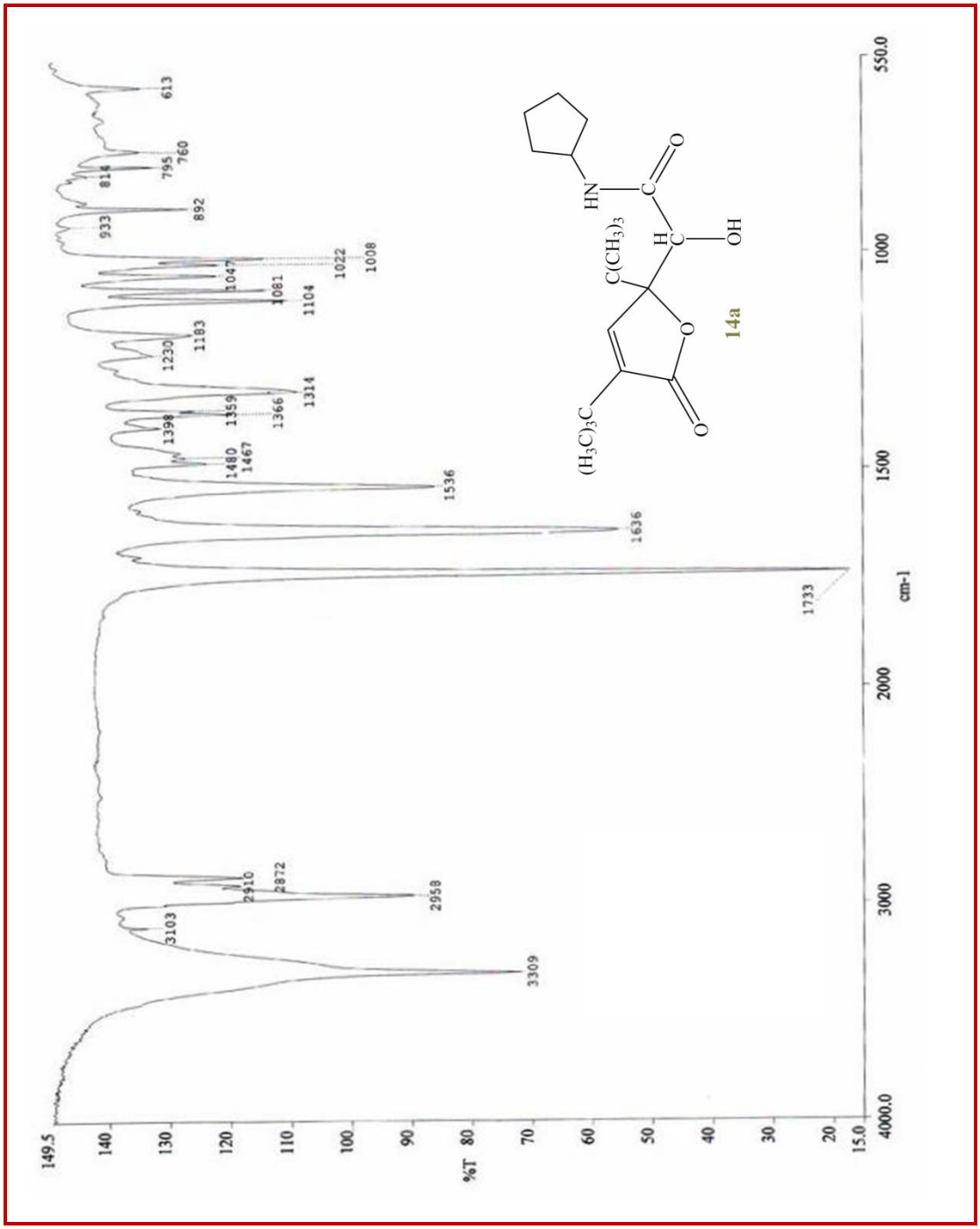
^{13}C NMR of 13a



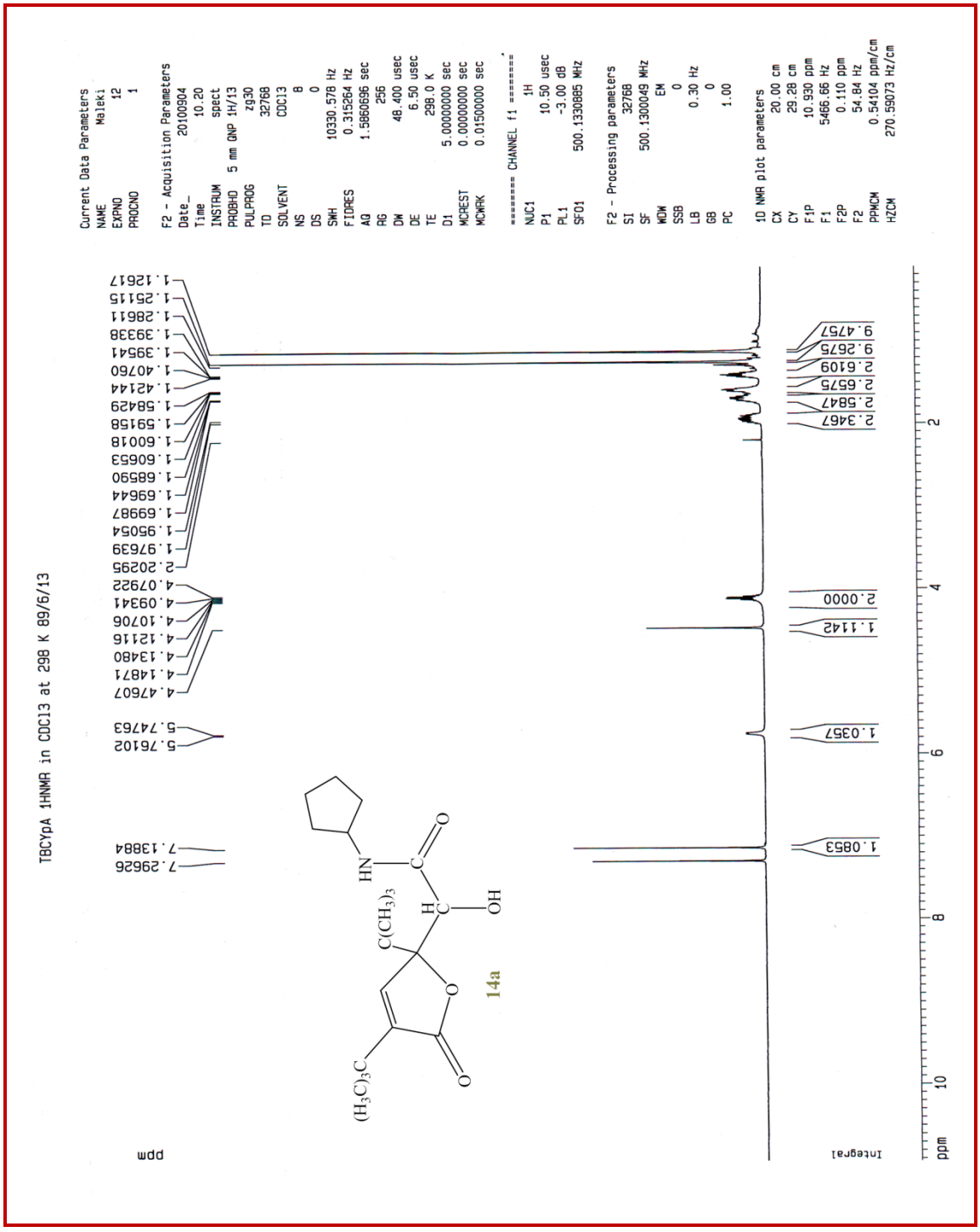
Expanded ^{13}C NMR of 13a


HN
C
O
H
C
OH
C(CH3)3
O
O
(H3C)3C
13a
%
m/z
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
270
280
300
320
340
360
380
400
420
440
460
480
500
91
57
41
29
43
39
30
28
18
15
65
67
55
51
77
79
69
74
81
95
106
109
111
125
139
140
151
154
164
169
170
181
182
183
195
196
197
198
209
226
285
286
303
360
361

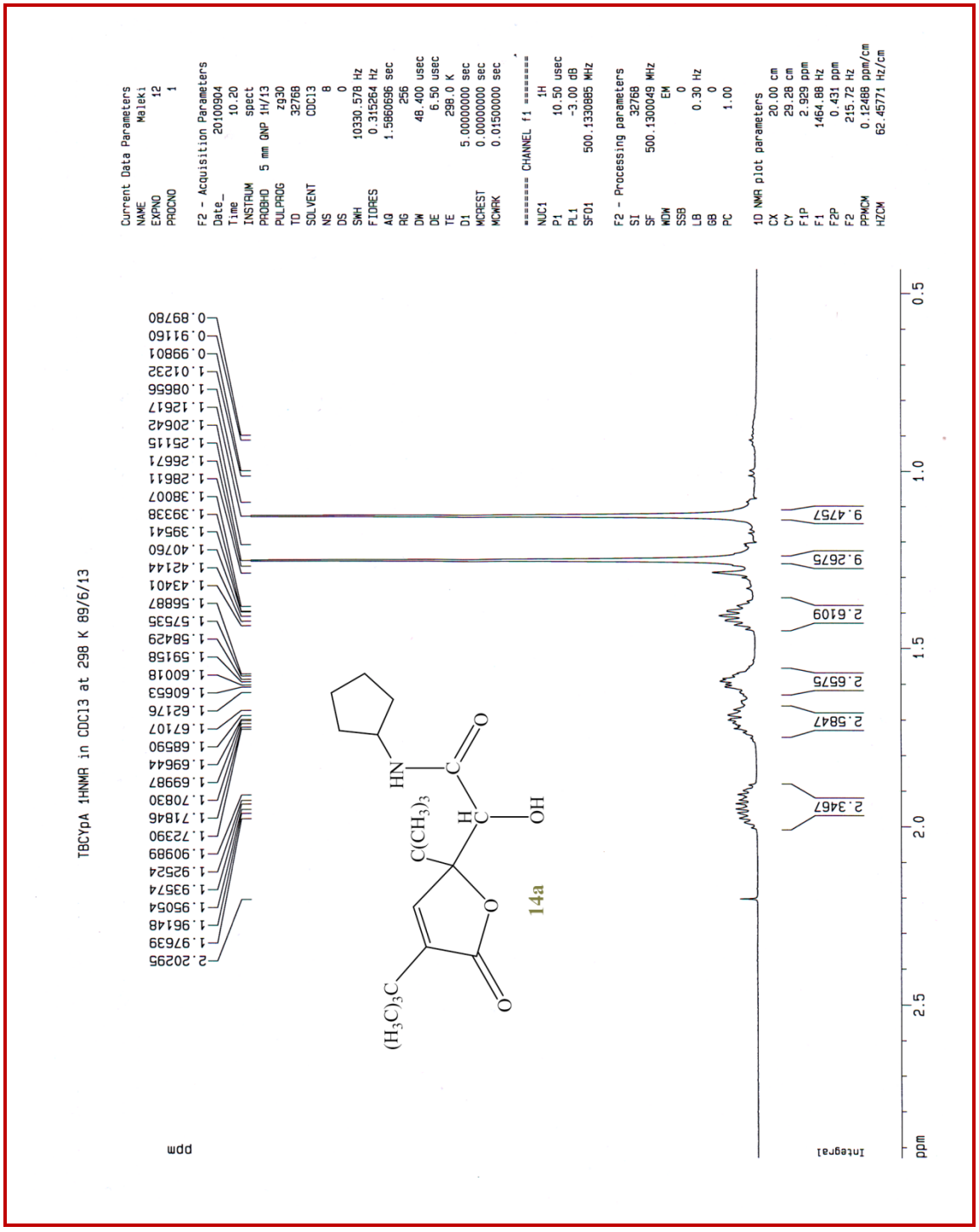
MS of 13a


149.5
140
130
120
110
100
90
%T 80
70
60
50
40
30
20
15.0
4000.0
3000
2000
1500
1000
550.0
cm-1
3309
3103
2958
2910
2872
1733
1636
1536
1480
1467
1398
1359
1366
1314
1230
1183
1104
1081
1047
1022
1008
933
892
818
795
760
613
HN
C
O
C(CH3)3
H
C
OH
O
O
(H3C)3C
14a

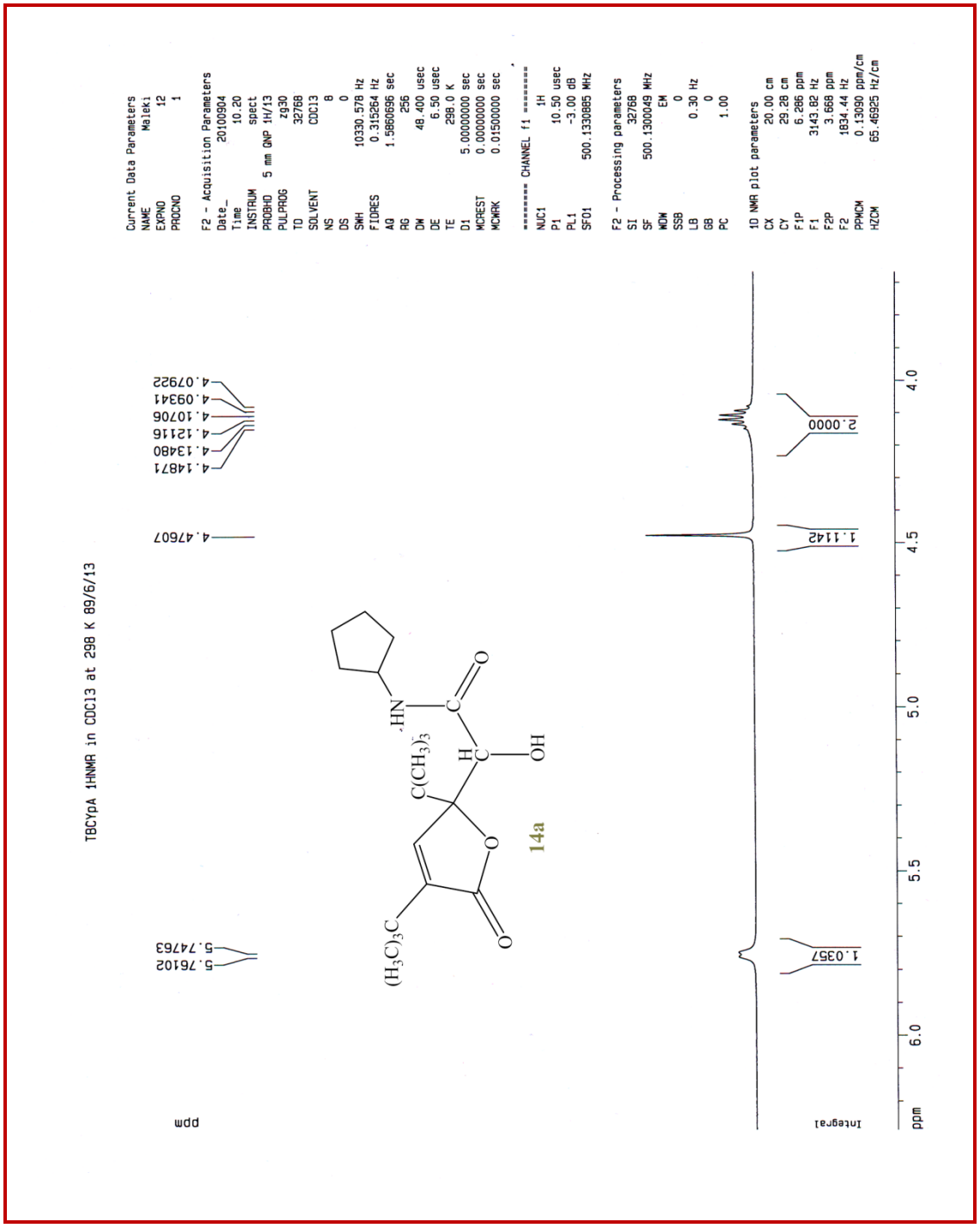
IR of 14a


TBCYpA 1HNMR in CDCl3 at 298 K 89/6/13
Current Data Parameters
NAME Maleki
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100904
Time 10.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 256
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 29.28 cm
F1P 10.930 ppm
F1 5466.66 Hz
F2P 0.110 ppm
F2 54.84 Hz
PPMCM 0.54104 ppm/cm
HZCM 270.59073 Hz/cm
1.12617
1.25115
1.28611
1.39338
1.39541
1.40760
1.42144
1.58429
1.59158
1.60018
1.60653
1.68590
1.69644
1.69987
1.95054
1.97639
2.02295
4.07922
4.09341
4.10706
4.12116
4.13480
4.14871
4.47607
5.74763
5.76102
7.13884
7.29626
9.4757
9.2675
2.6109
2.6575
2.5847
2.3467
2.0000
1.1142
1.0357
1.0853
HN
C(CH3)3
O
H
C
OH
O
O
(H3C)3C
14a
ppm
Integral

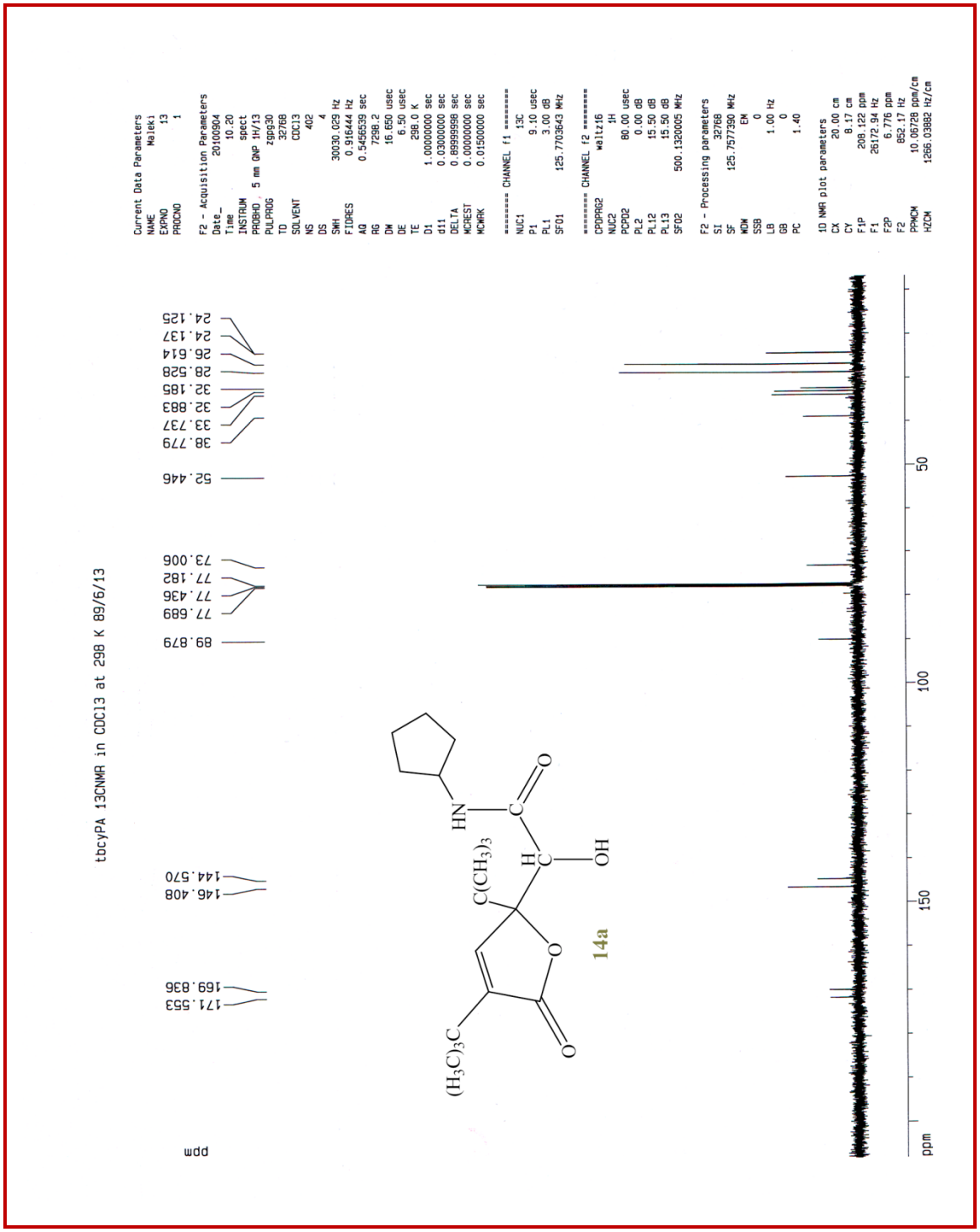
^{1}H NMR of 14a



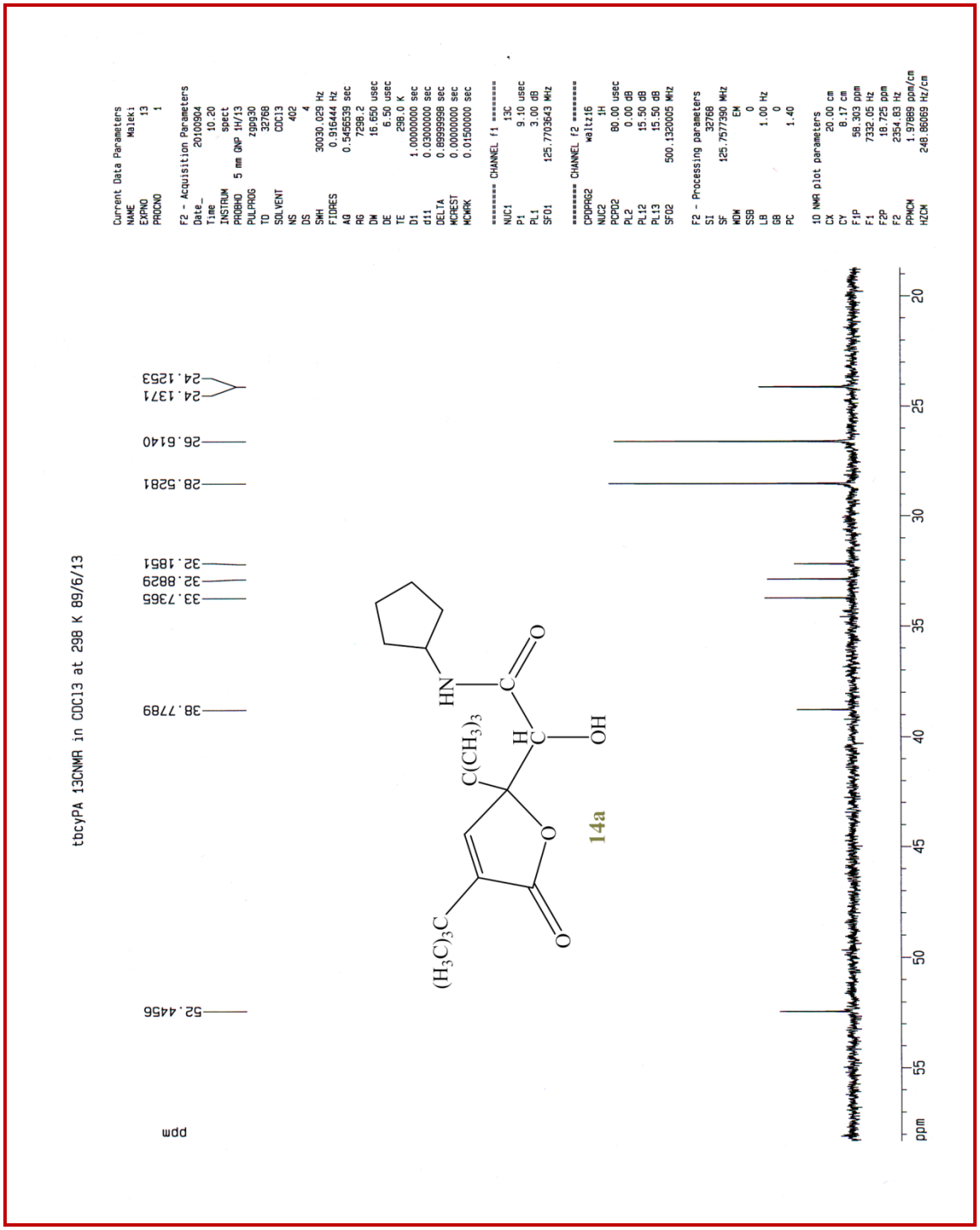
Expanded ^{1}H NMR of 14a



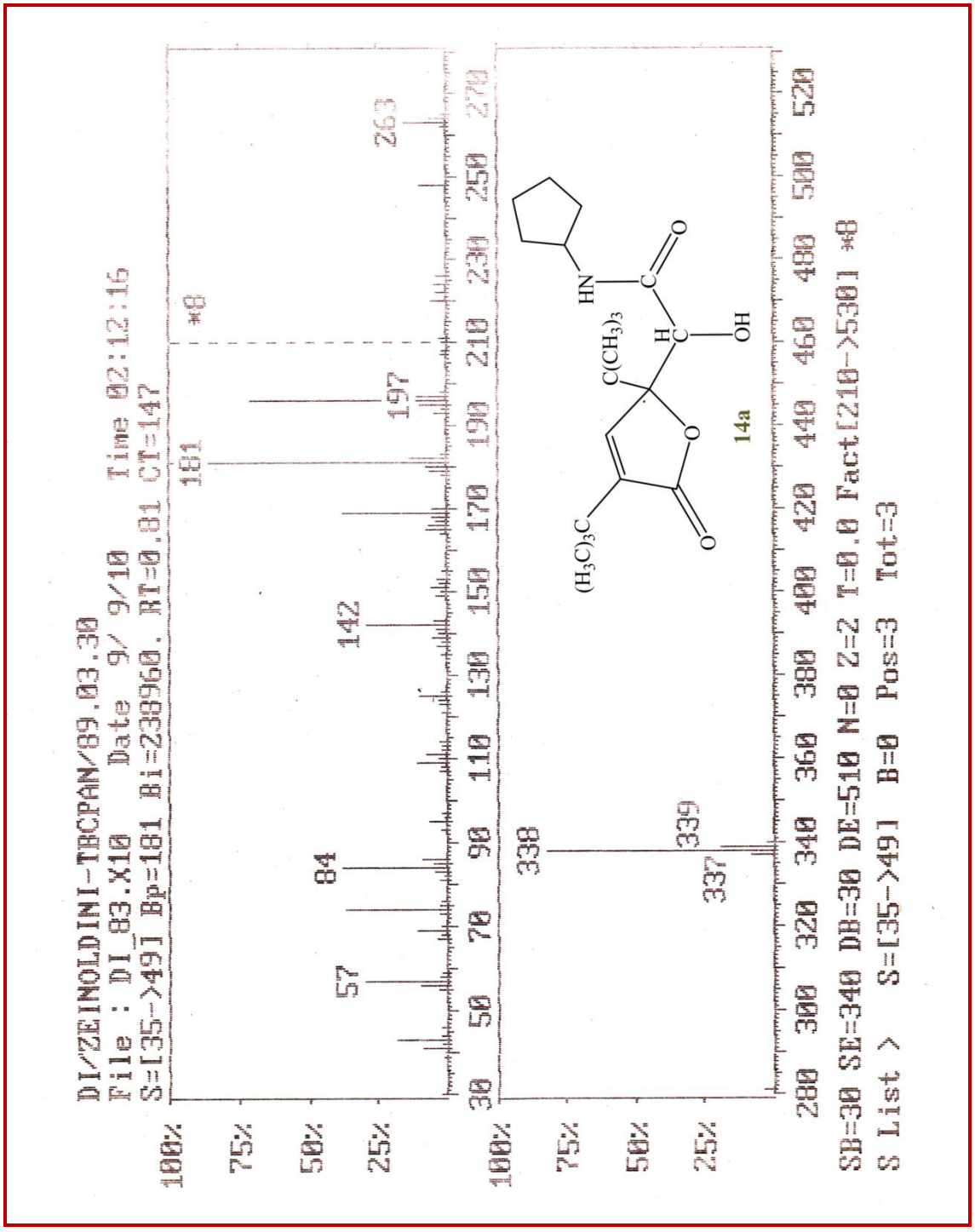
Expanded ^{1}H NMR of 14a



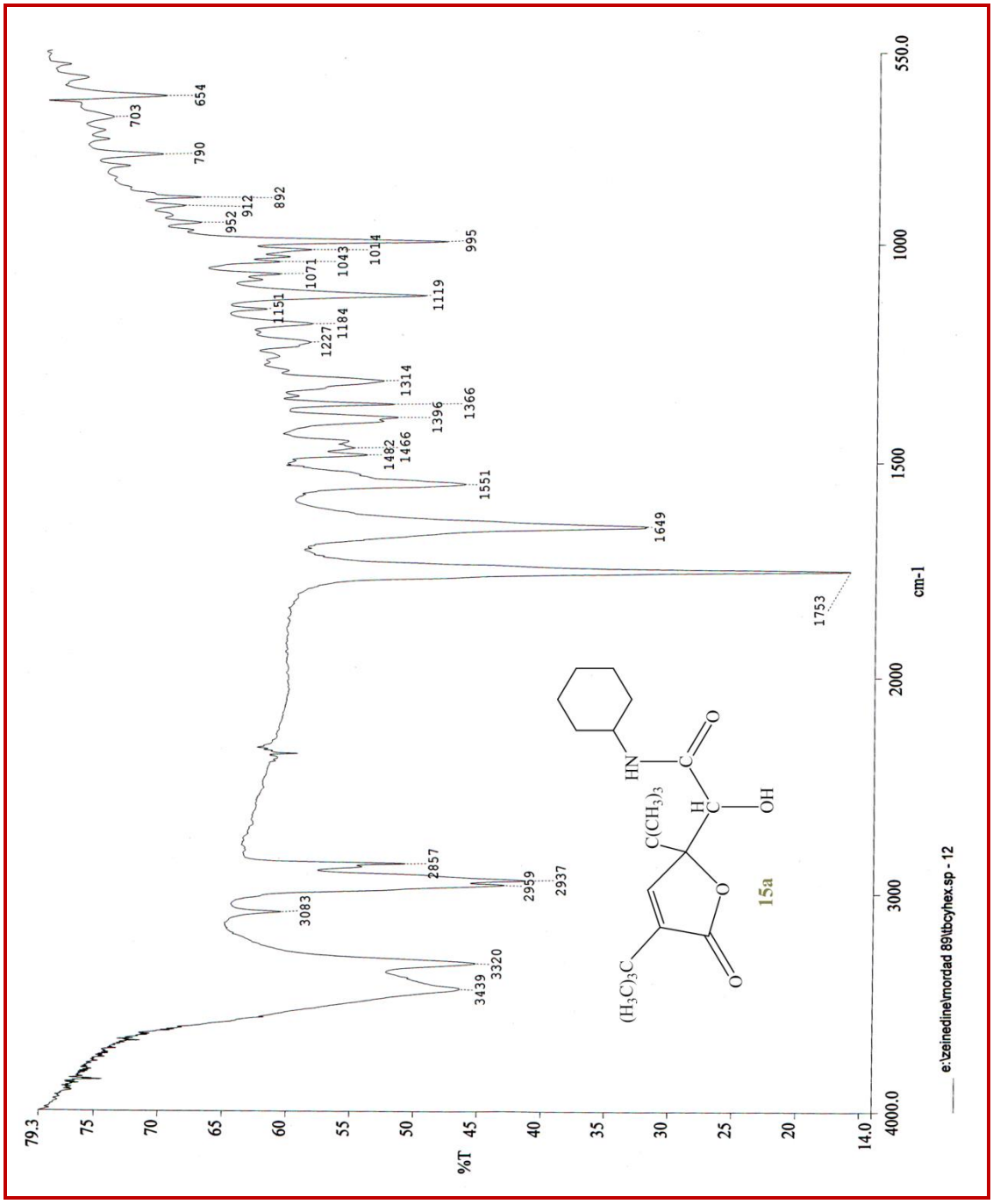
^{13}C NMR of 14a



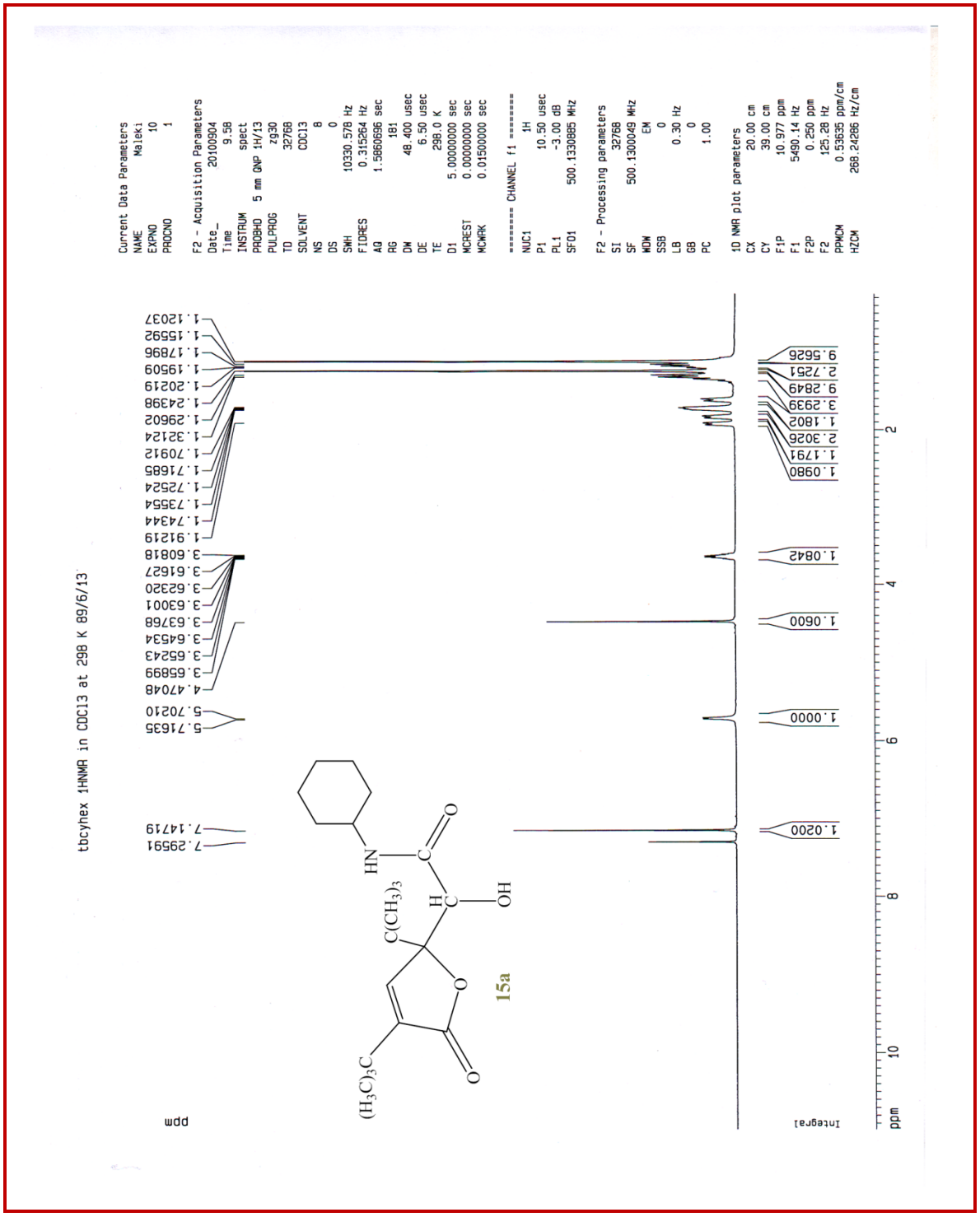
Expanded ^{13}C NMR of 14a


DI/ZEINOLDINI-TBCPAN/89.03.30
File : DI_83.X10 Date 9/ 9/10 Time 02:12:15
S=[35-->49] Bp=181 Bi=238960. RT=0.81 CT=147
SB=30 SE=340 DB=30 DE=510 N=0 Z=2 T=0.0 Fact[210-->530] *8
S List > S=[35-->49] B=0 Pos=3 Tot=3
14a

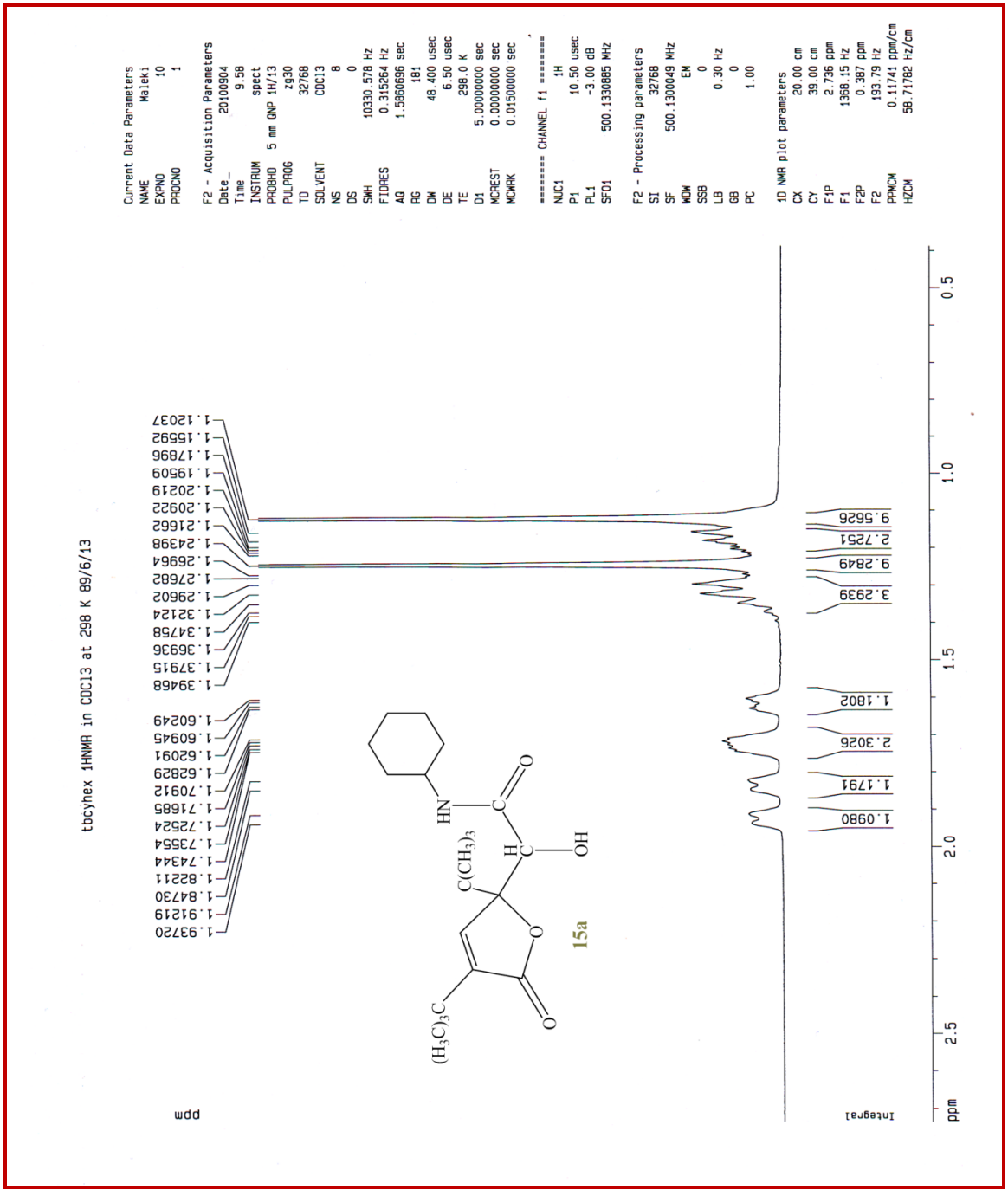
MS of 14a


79.3
75
70
65
60
55
50
45
40
35
30
25
20
14.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
3439
3320
3083
2959
2937
2857
1753
1649
1551
1482
1466
1396
1366
1314
1227
1184
1151
1119
1071
1043
1014
995
952
912
892
790
703
654
HN
C(CH3)3
H
C
OH
O
O
O
(H3C)3C
15a
e:\zeinedine\mordad 89\tbcyhex.sp - 12

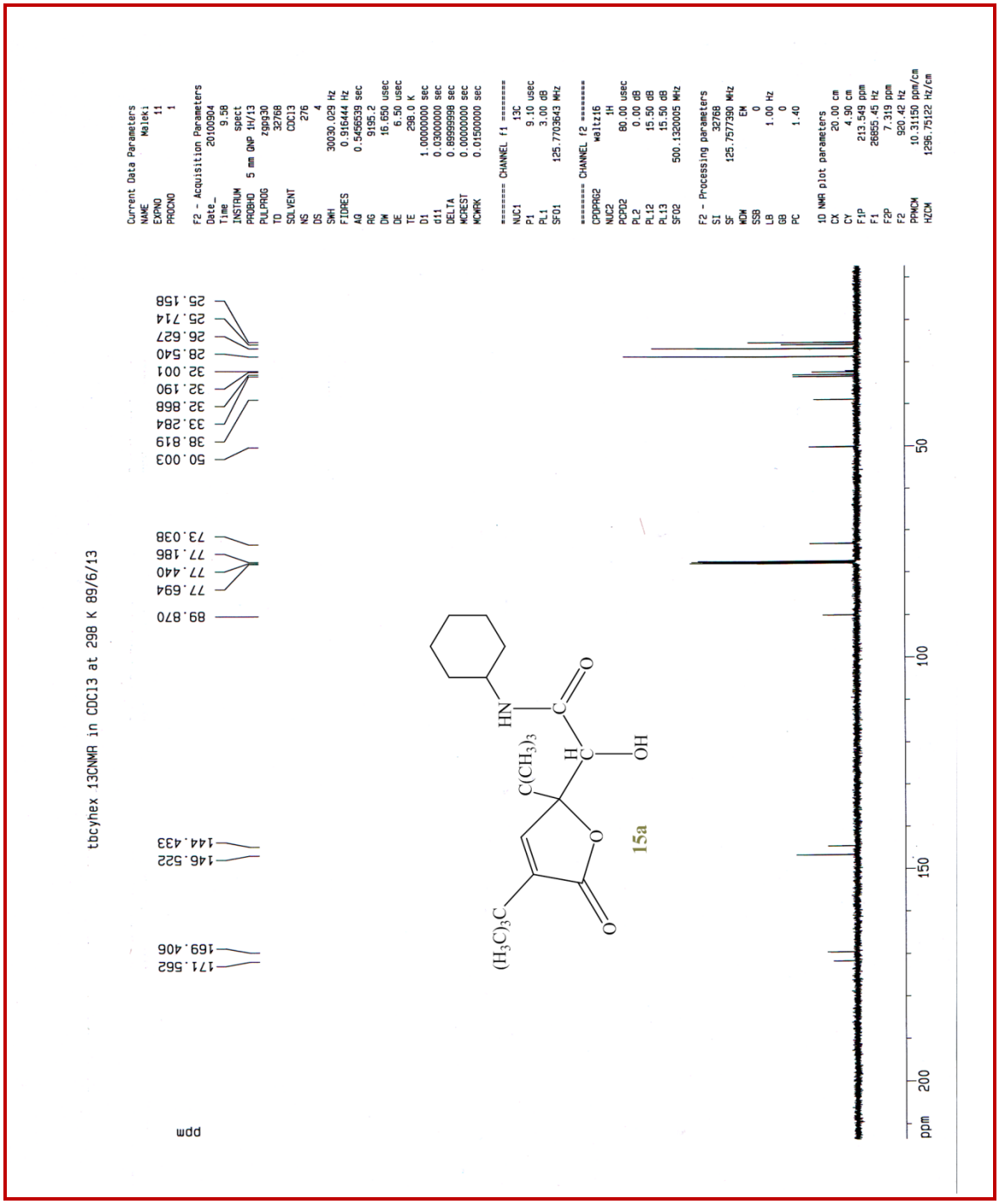
FTIR of 15a


tbcyhex 1HNMR in CDCl3 at 298 K 89/6/13
Current Data Parameters
NAME Maleki
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100904
Time 9.58
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 39.00 cm
F1P 10.977 ppm
F1 5490.14 Hz
F2P 0.250 ppm
F2 125.28 Hz
PPMCM 0.53635 ppm/cm
HZCM 268.24286 Hz/cm
7.29591
7.14719
5.71635
5.70210
4.47048
3.65899
3.65243
3.64534
3.63768
3.63001
3.62320
3.61627
3.60818
1.91219
1.74344
1.73554
1.72524
1.71685
1.70912
1.32124
1.29602
1.24398
1.20219
1.19509
1.17896
1.15592
1.12037
9.5626
2.7251
2.2849
3.2939
1.1802
2.3026
1.1791
1.0980
1.0842
1.0600
1.0000
1.0200
15a
ppm
Integral

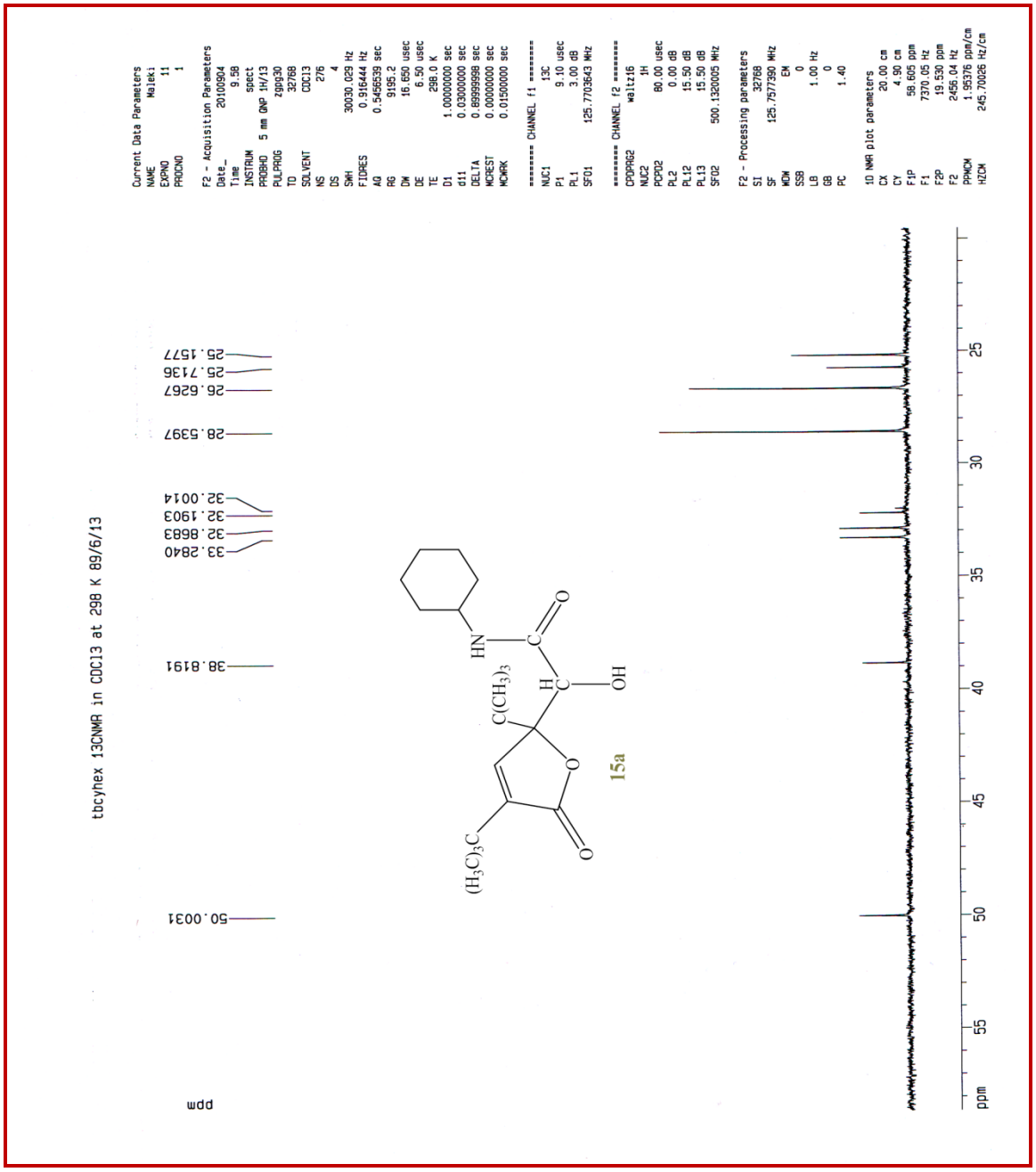
[1]HNMR of **15a**



Expanded ^{1}H NMR of 15a



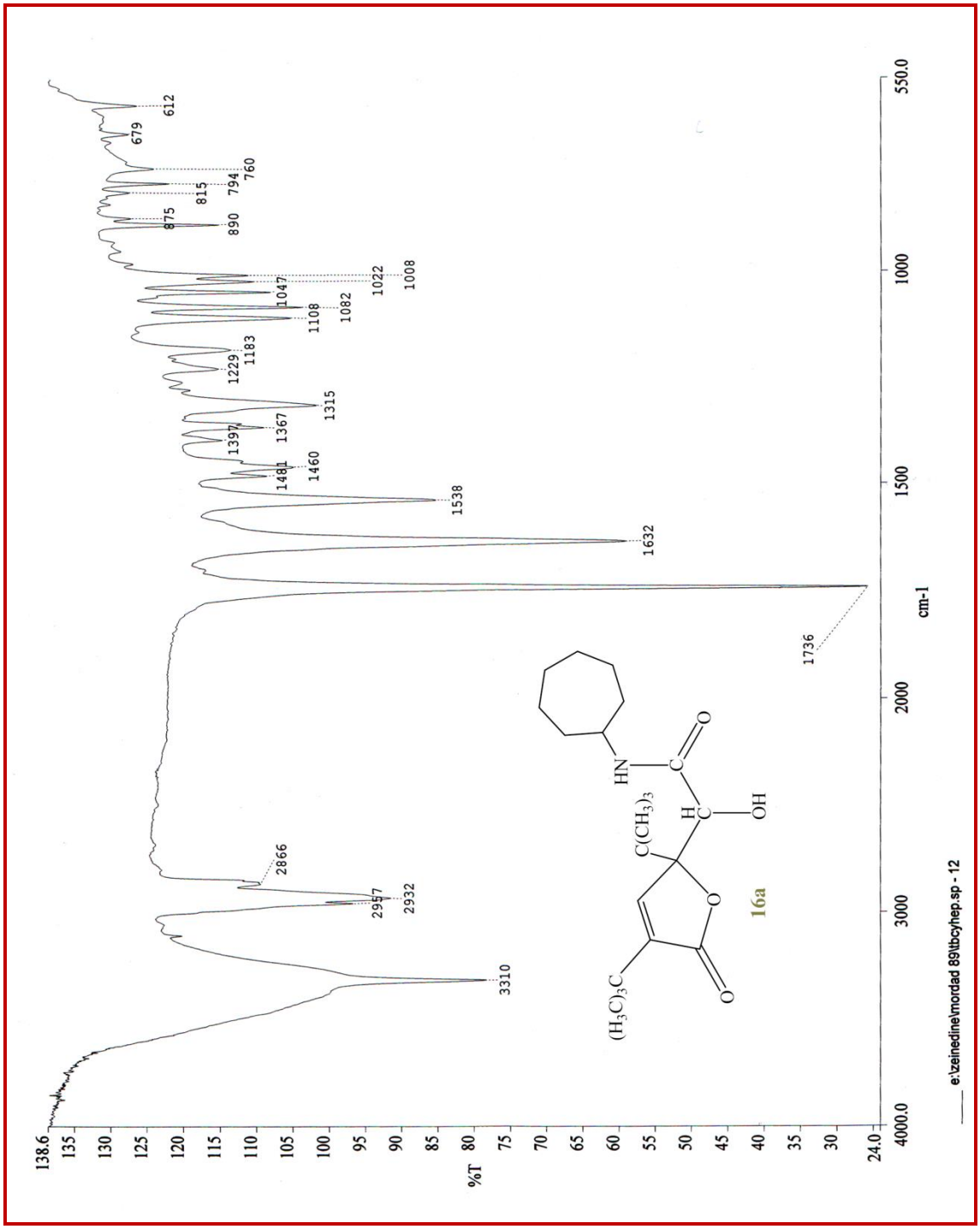
^{13}C NMR of 15a



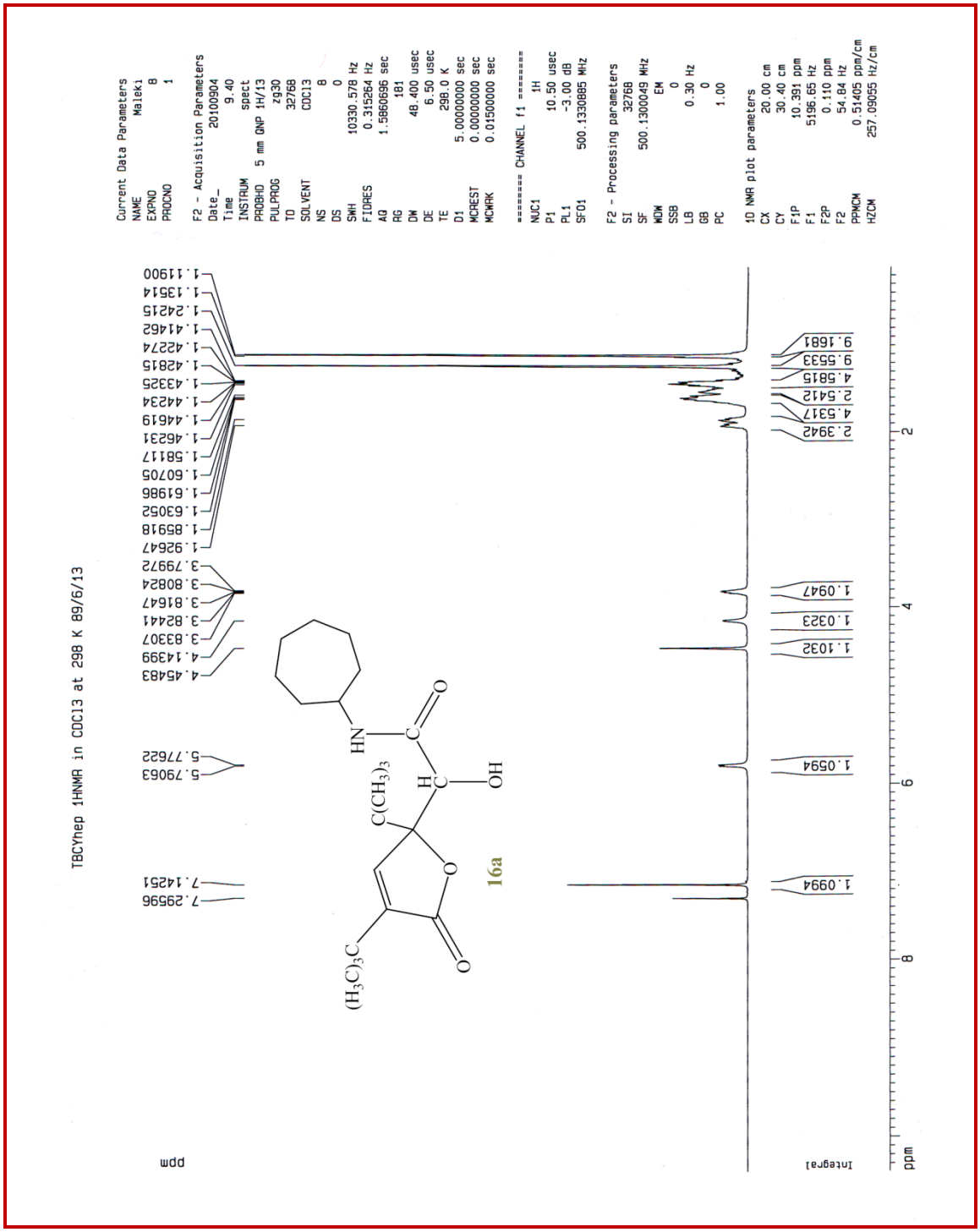
Expanded ^{13}C NMR of 15a


Solid Probe
Scan EI+
9.05e6
TBHEXYL 17 (0.280)
100
%
0
m/z
HN
C(CH3)3
H
C
OH
O
O
O
(H3C)3C
15a

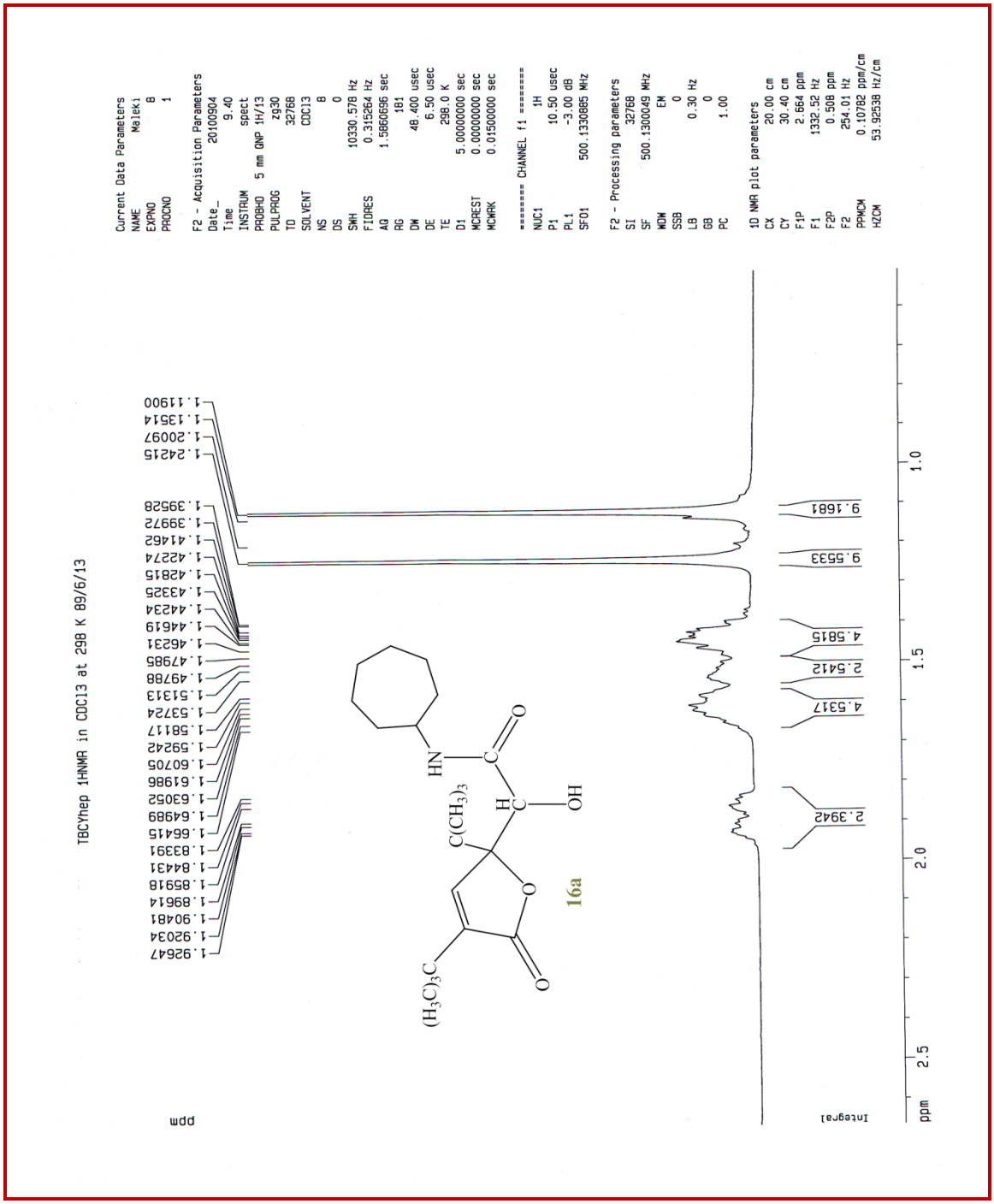
MS of 15a


138.6
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
3310
2957
2932
2866
1736
1632
1538
1481
1460
1397
1367
1315
1229
1183
1108
1082
1047
1022
1008
890
875
815
794
760
679
612
HN
C(CH3)3
H
C
OH
O
(H3C)3C
16a
e:\zeinedine\mordad 89\tbcyhep.sp - 12

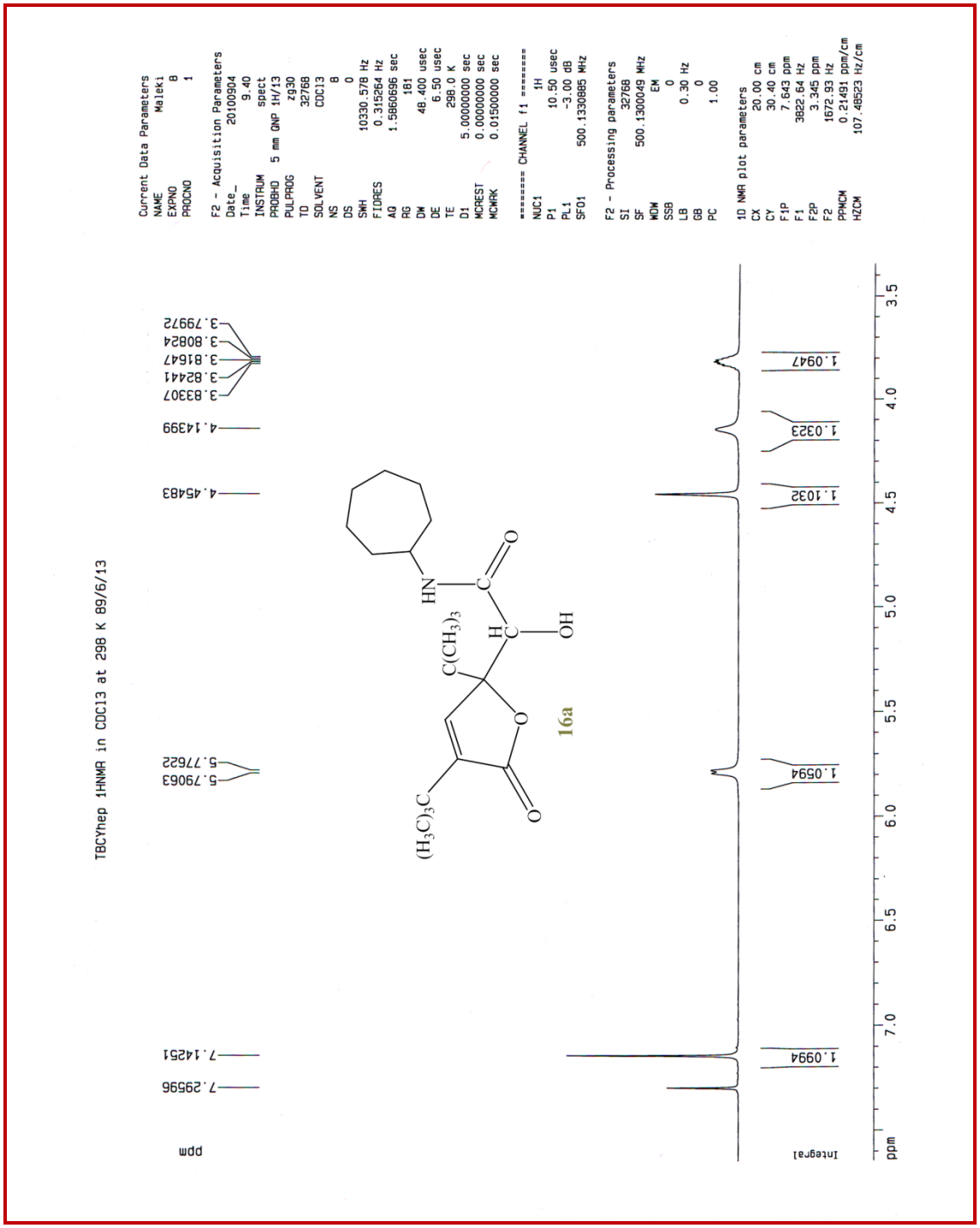
IR of 16a



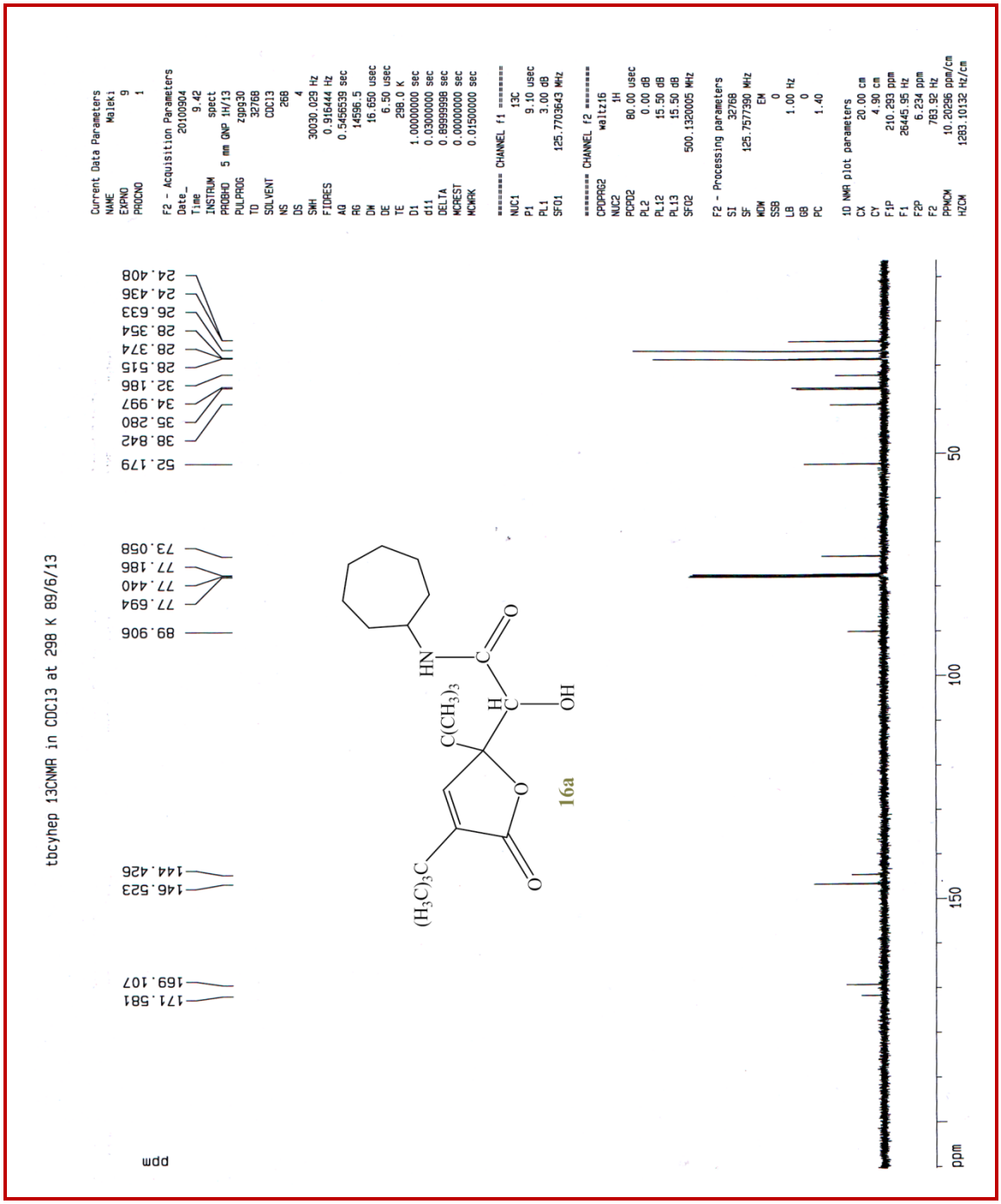
Expanded ^{1}H NMR of 16a



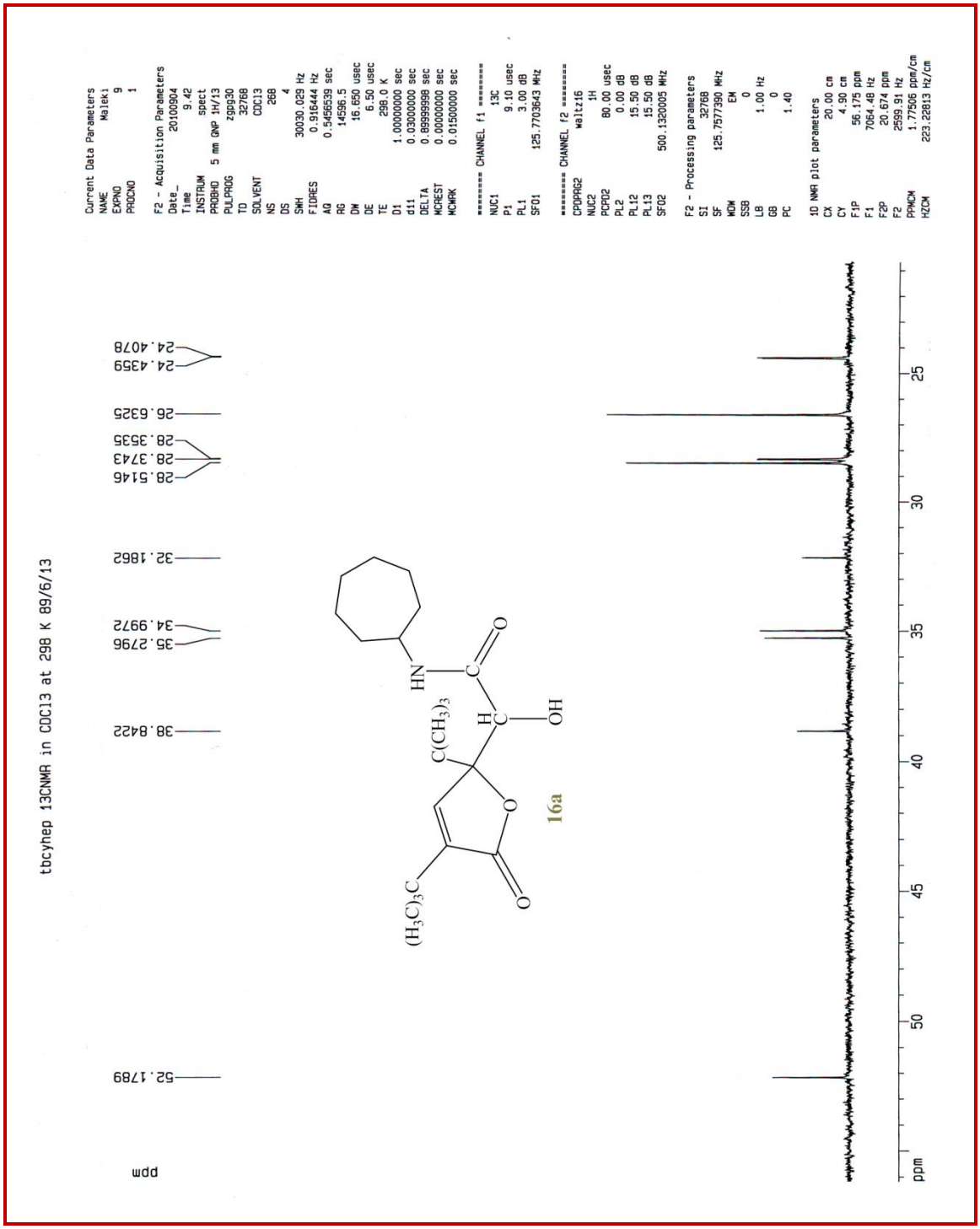
Expanded ^{1}H NMR of 16a



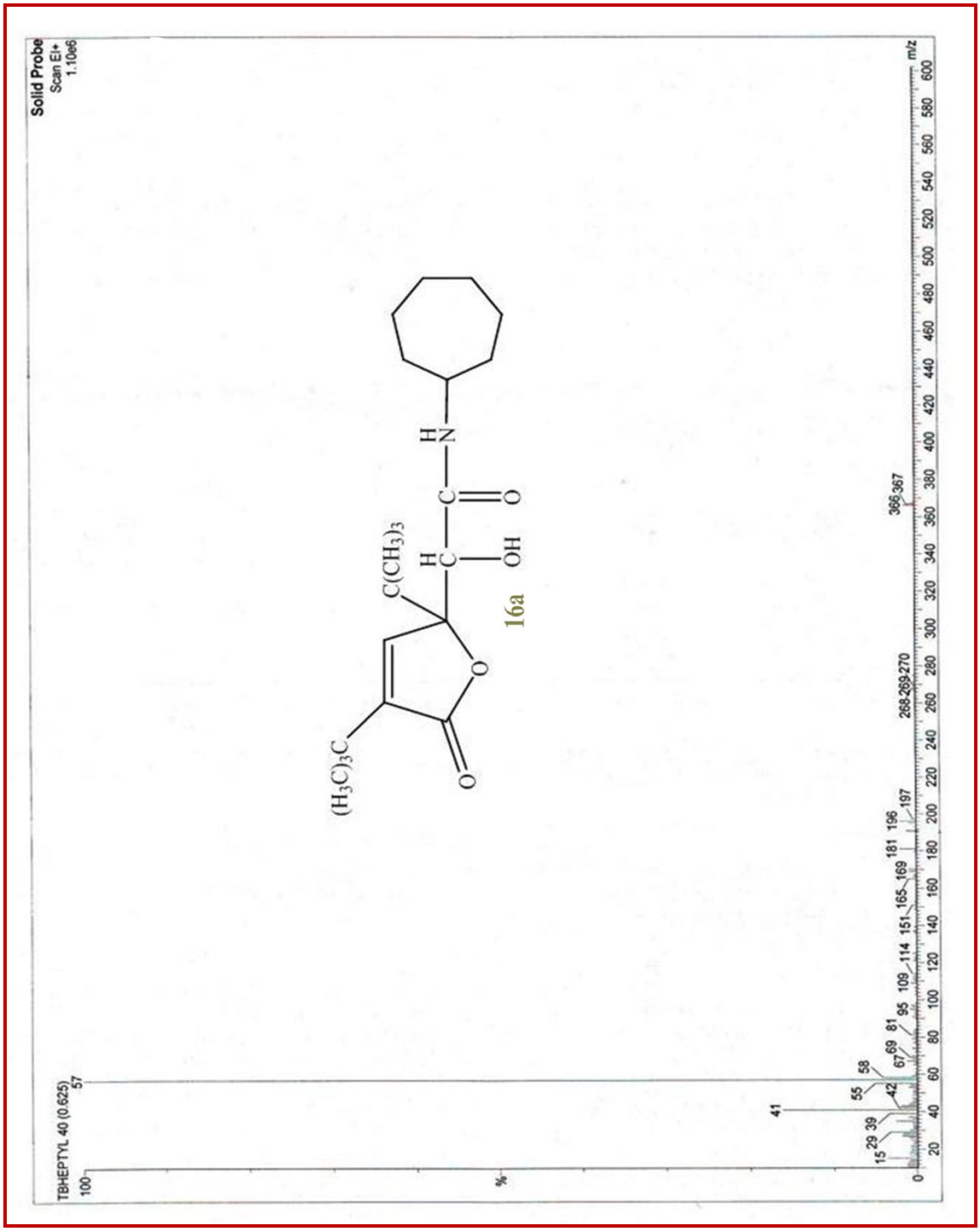
Expanded ^{1}H NMR of 16a



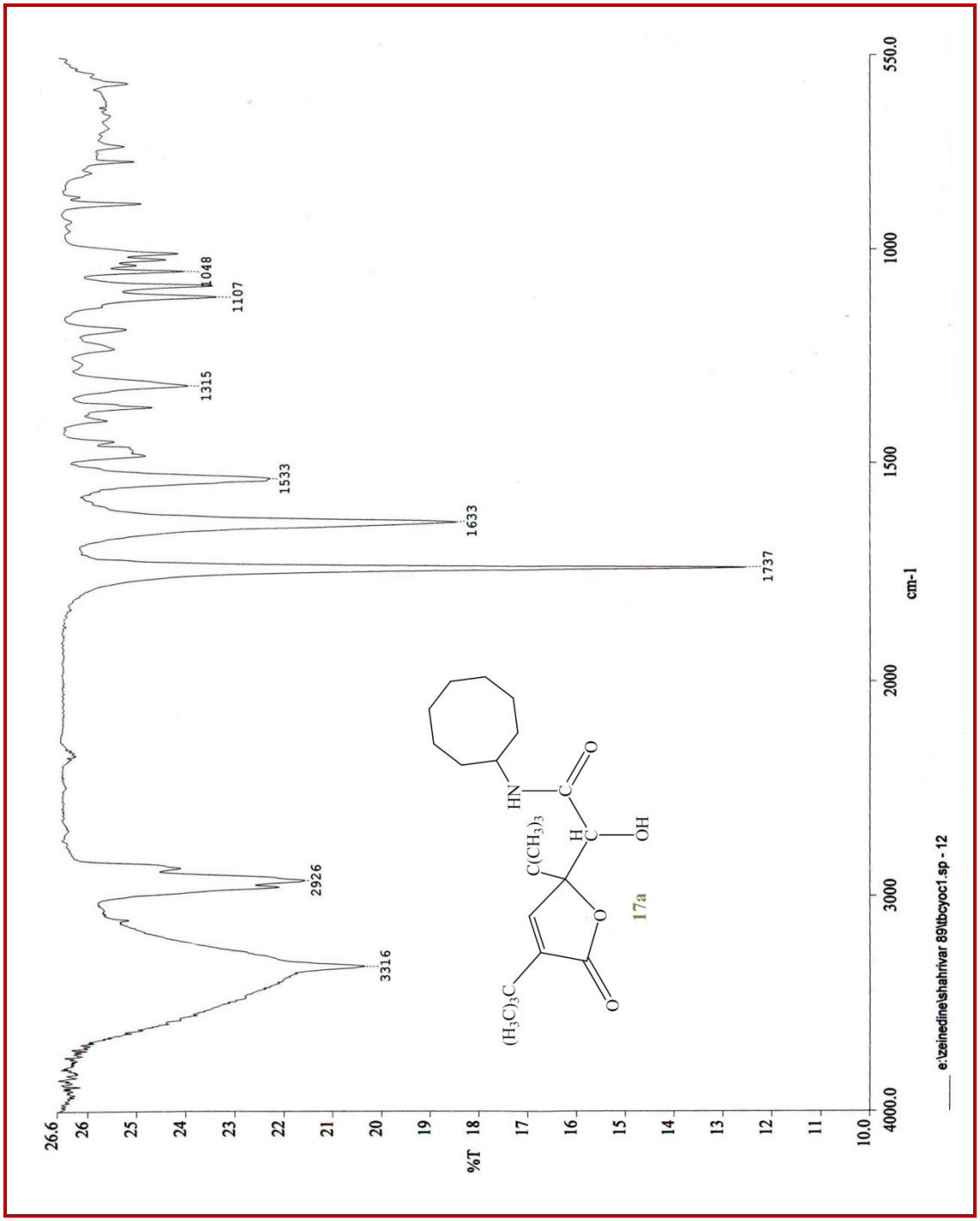
^{13}C NMR of 16a



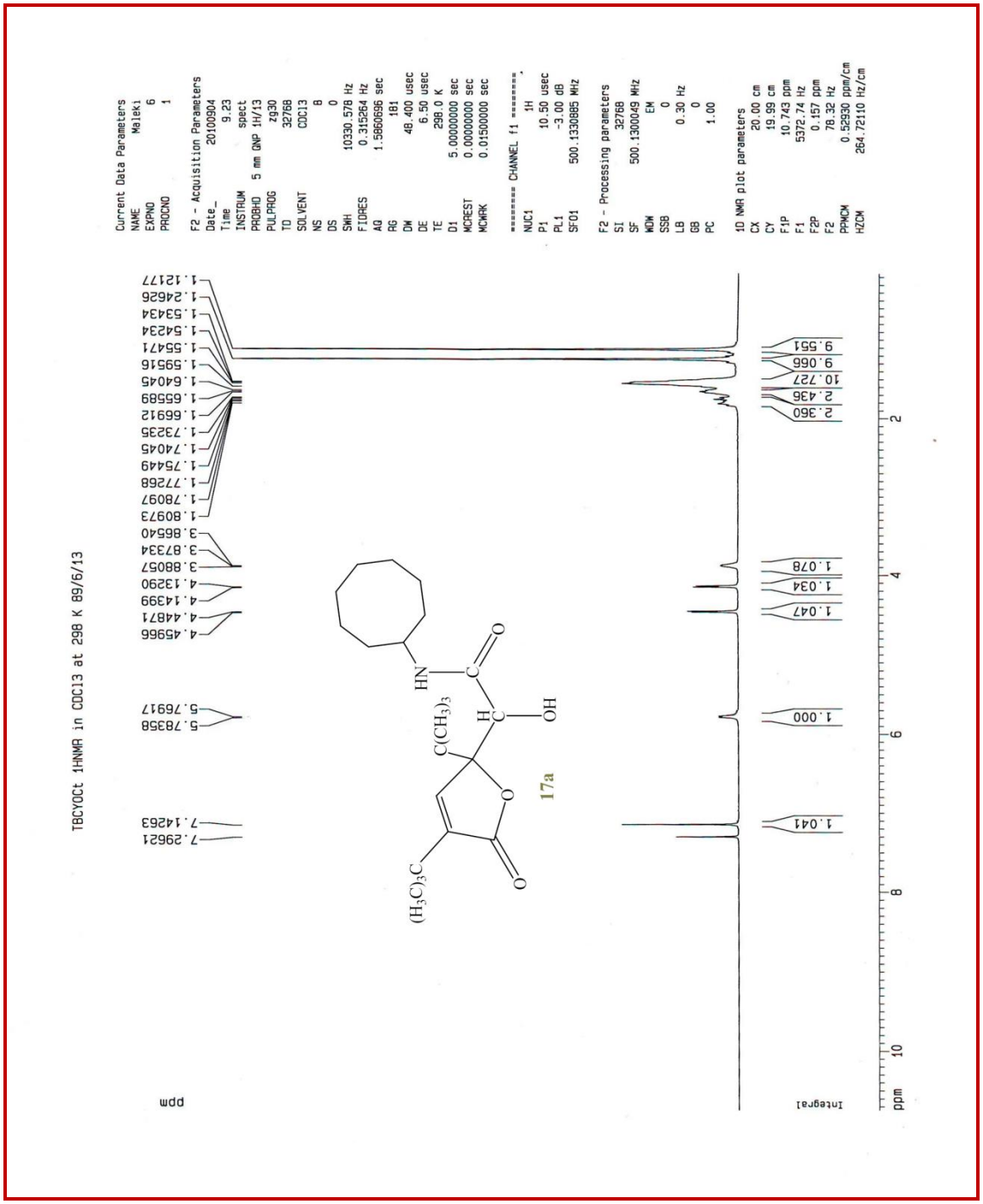
Expanded ^{13}C NMR of 16a


Solid Probe
Scan EI+
1.10e6
TBHEPTYL 40 (0.625)
100
%
0
m/z
16a
$(H_3C)_3C$
$C(CH_3)_3$
H
C
C
O
O
H
N
H
C
OH
O
O
57
41
58
55
42
69
67
81
95
109
114
151
165
169
181
196
197
268
269
270
366
367

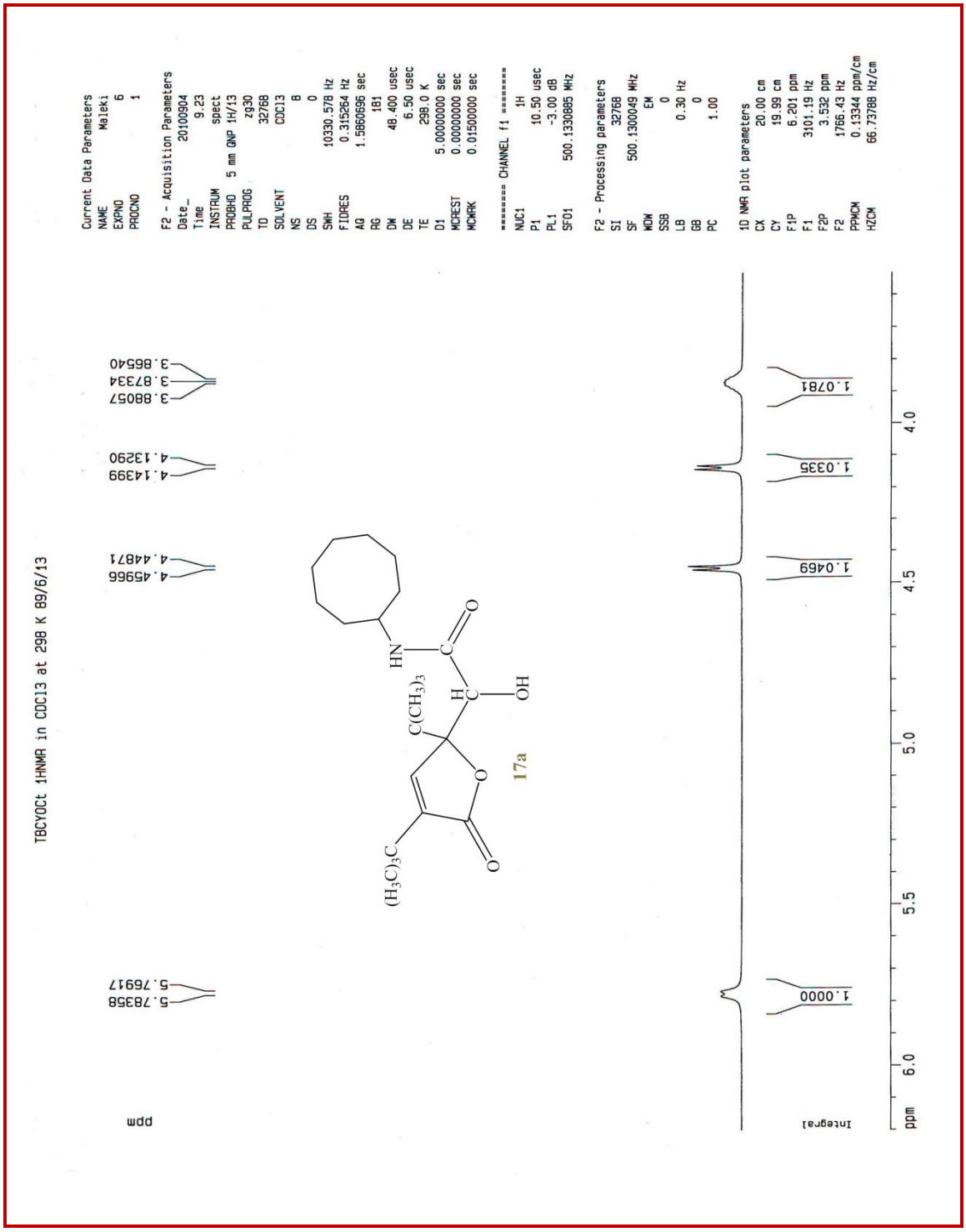
MS of 16a


3316
2926
1737
1633
1533
1315
1107
1048
%T
cm-1
4000.0
3000
2000
1500
1000
550.0
26.6
10.0
17a
HN
C(CH3)3
OH
(H3C)3C
e:\zeinedine\shahrivar 89\tbcyoc1.sp - 12

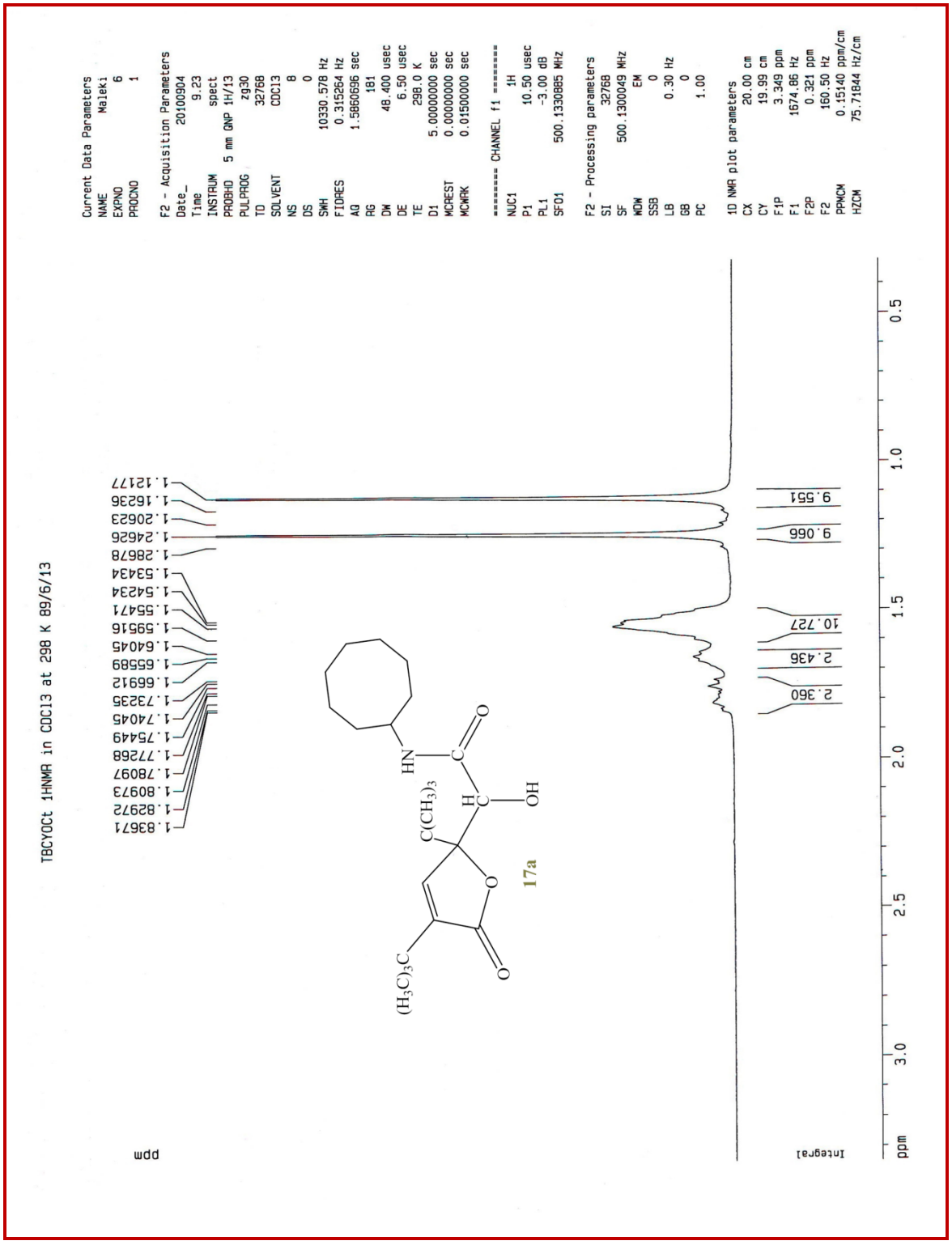
FTIR of 17a



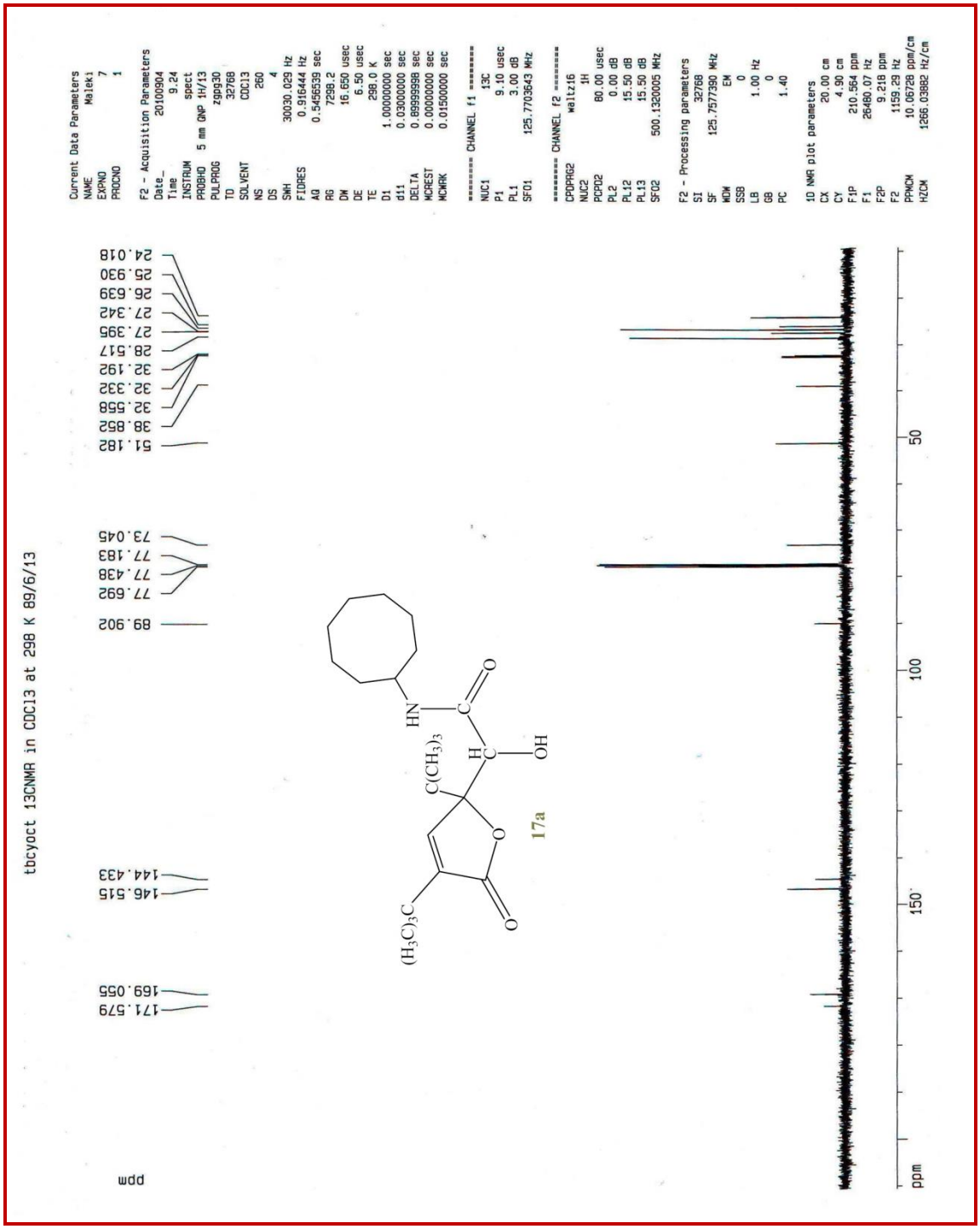
^{1}H NMR of 17a



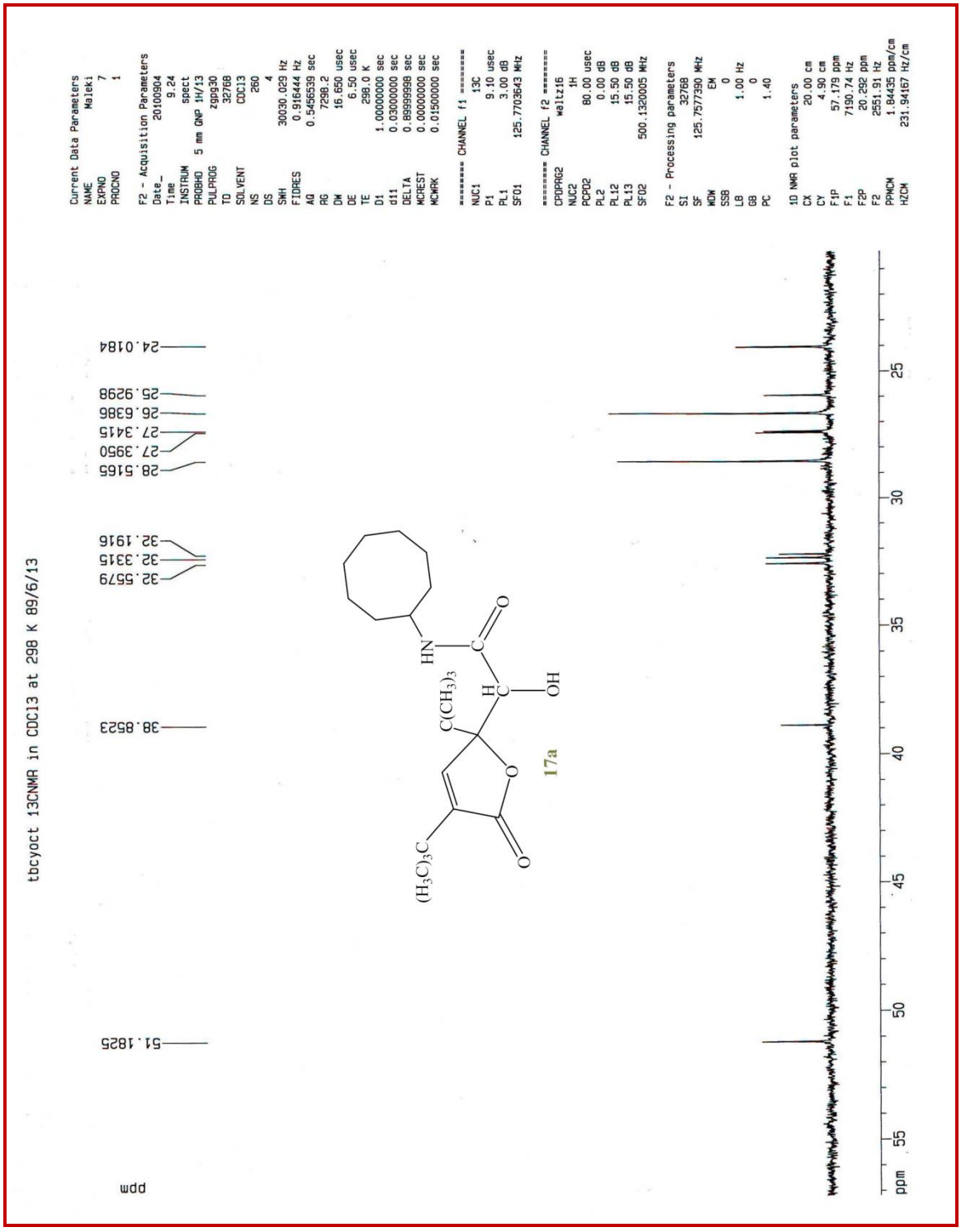
Expanded ^{1}H NMR of 17a



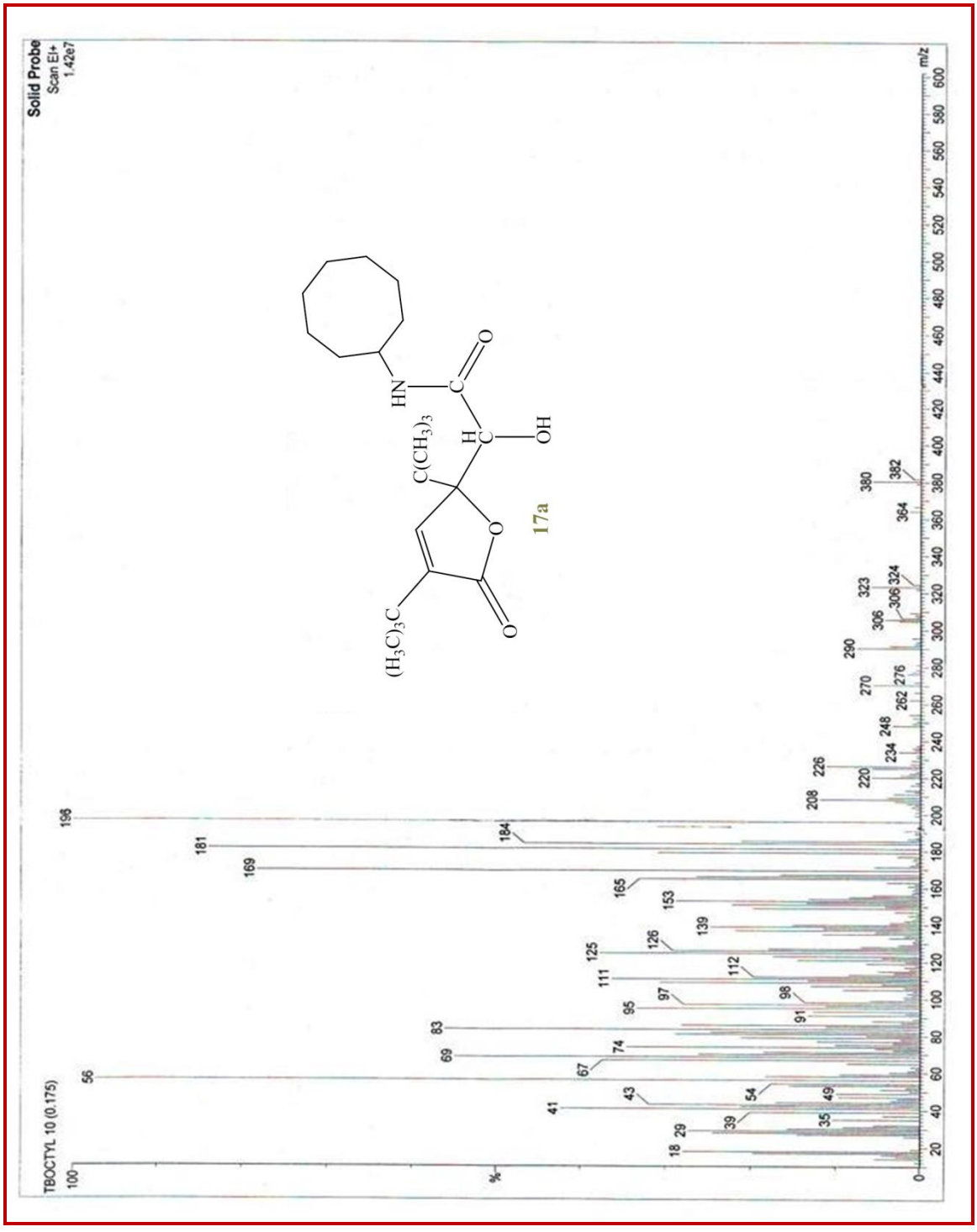
Expanded ^{1}H NMR of 17a



^{13}C NMR of 17a



Expanded ^{13}C NMR of 17a



MS of 17a

VI. Crystallography of 9a

Table S2. Selected bond lengths (Å) and bond Angles (º) of compound **9a**

Bond lengths	
C(2)–C(7)	1.326(3)
C(7)–C(8)	1.498(2)
C(8)–O(2)	1.459(2)
C(1)–O(2)	1.353(2)
C(1)–O(1)	1.205(2)
C(13)–C(14)	1.520(3)
C(8)–C(13)	1.565(3)
C(14)–N(1)	1.330(3)
C(14)–O(4)	1.233(2)
C(15)–N(1)	1.459(3)
Bond angles	
O(3)–C(13)–C(8)	112.89(16)
O(3)–C(13)–C(14)	109.89(16)
C(14)–C(13)–C(8)	110.50(16)
O(4)–C(14)–N(1)	122.7(2)
O(4)–C(14)–C(13)	120.16(19)
N(1)–C(14)–C(13)	117.11(17)
N(1)–C(15)–C(16)	112.5(2)
C(14)–N(1)–C(15)	122.57(19)
C(1)–O(2)–C(8)	109.69(13)
O(1)–C(1)–C(2)	130.32(19)

Table S3: Crystal data and structure refinement for compound **9a**

Empirical formula	$C_{18}H_{31}NO_4$
Formula weight	326
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
a (Å)	9.384(2)
b (Å)	10.484(2)
c (Å)	11.281(2)
α (°)	102.829(17)
β (°)	94.191(18)
γ (°)	113.456(18)
Volume ($Å^3$)	976.4(4)
Z	2
Density(Mg/m^3)	1.107
Crystal size (mm^3)	0.50×0.17×0.15
Absorption coefficient (mm^{-1})	0.077
θ range for data collection (°)	1.88 to 29.31
Index ranges	$-10 \le h \le 12$ $-14 \le k \le 14$ $-15 \le l \le 15$
Reflections collected	11380
Independent reflections	5246 [R_{int} = 0.0611]
Absorption correction	None
Max. and min. transmission	0.5263 and 0.2964
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.127
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0744, wR_2 = 0.1880
R indices (all data)	R_1 = 0.1106, wR_2 = 0.2092
Largest diff. peak and hole ($e.Å^{-3}$)	0.401 and -0.392

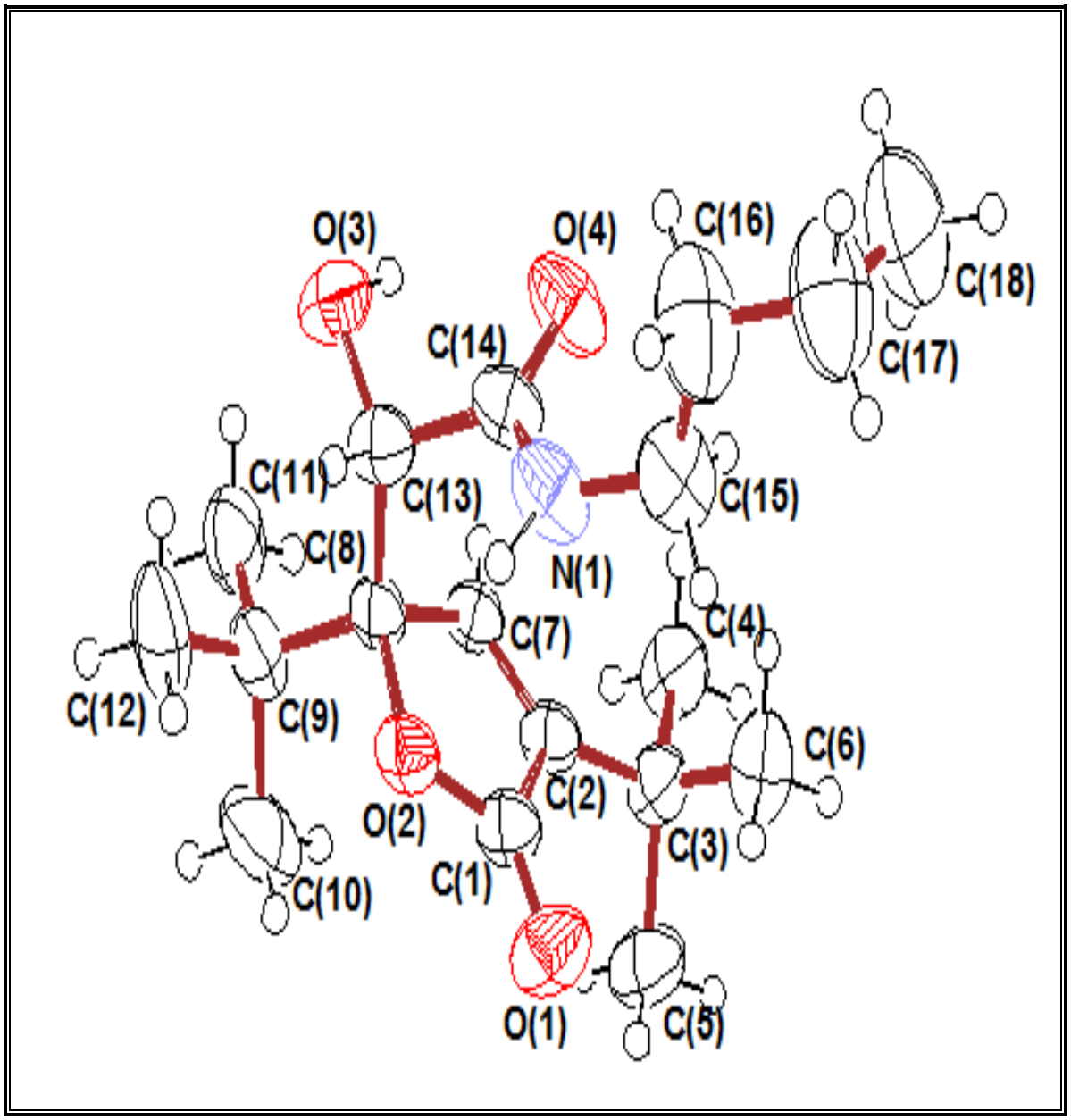


Figure S1. X-ray crystal structure of compound **9a**.

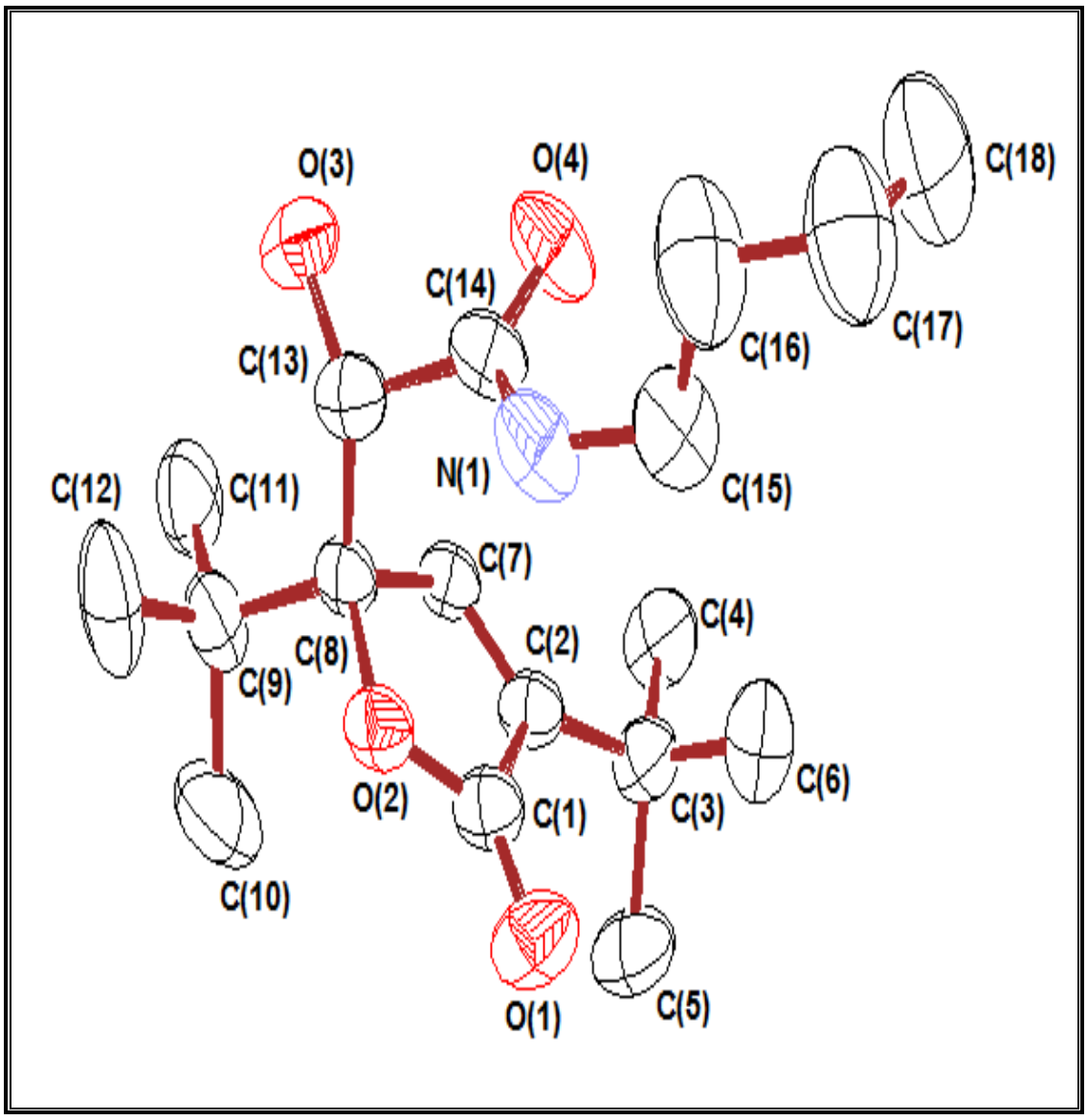


Figure S2. X-ray crystal structure of compound **9a**. The hydrogen atoms are omitted for the reason of clarity.