

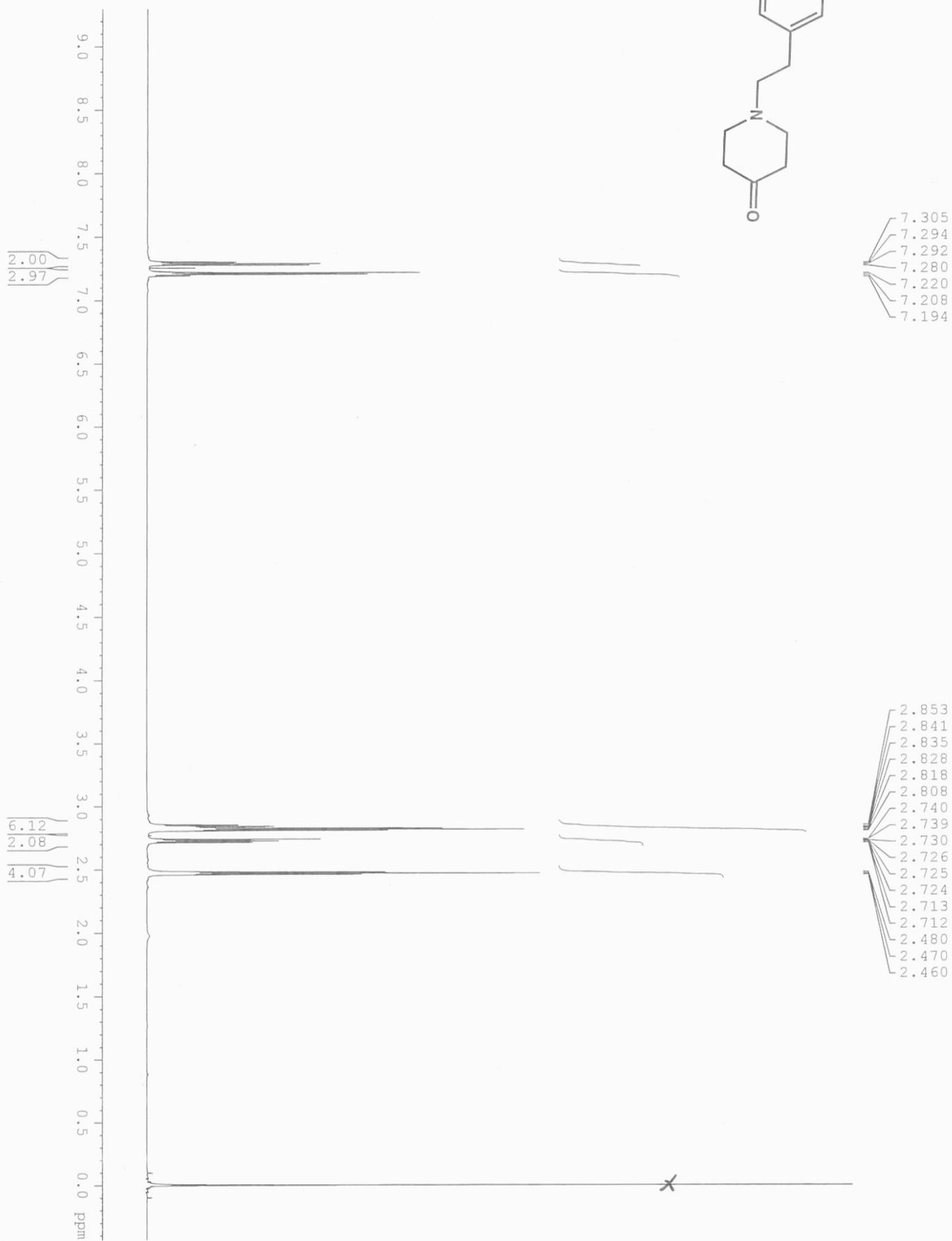
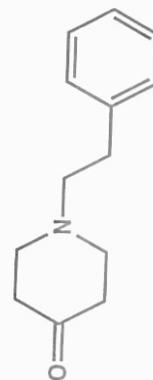
An efficient, optimized synthesis of fentanyl and related analogs

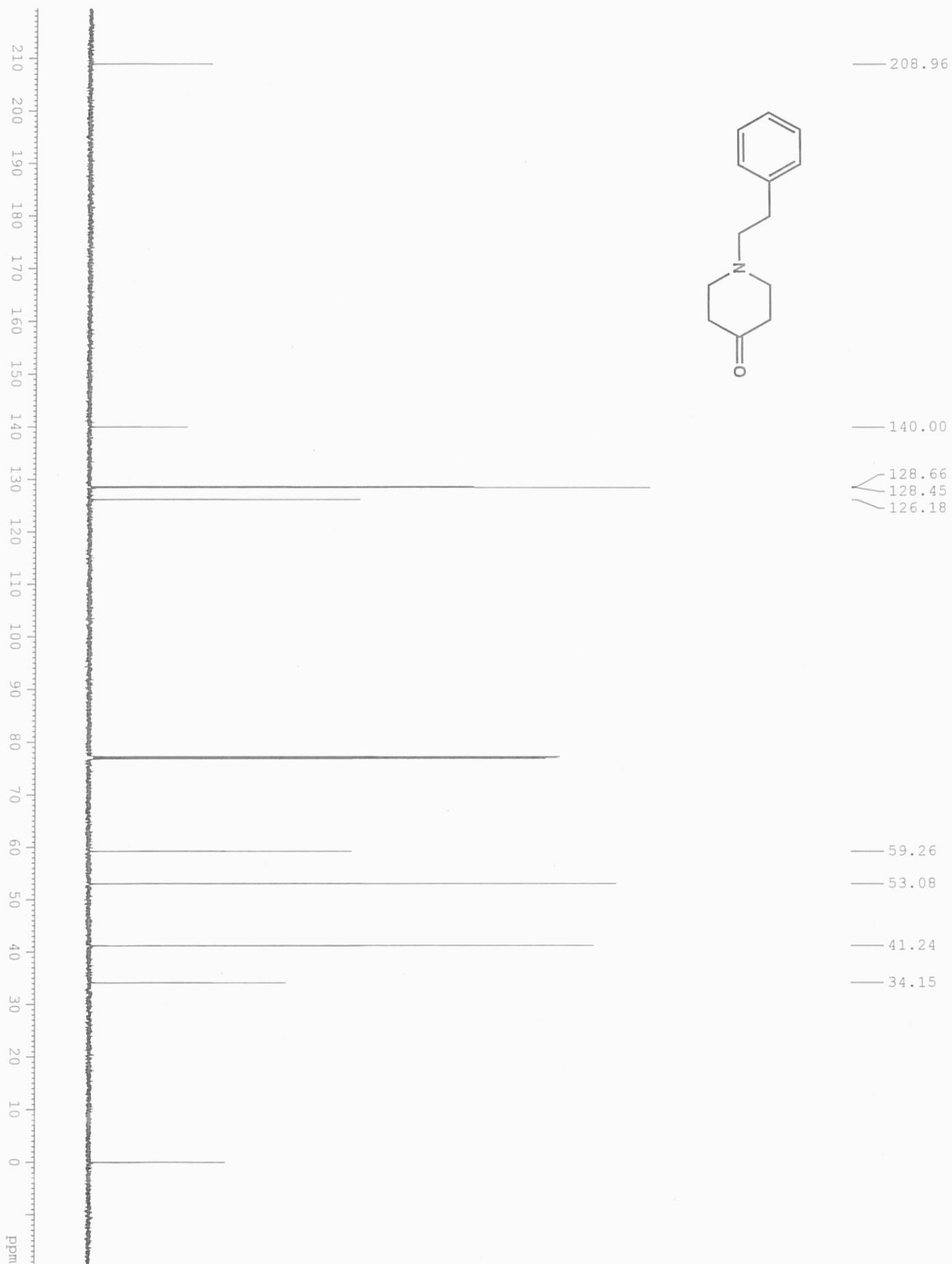
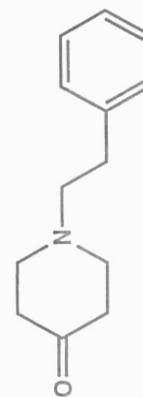
Carlos A. Valdez, Roald N. Leif and Brian P. Mayer*

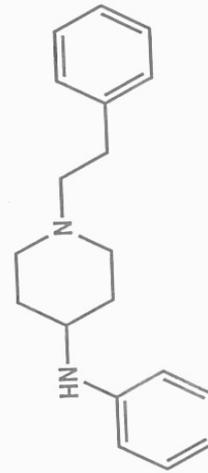
*Forensic Science Center, Lawrence Livermore National Laboratory
Livermore, CA 94550 USA*

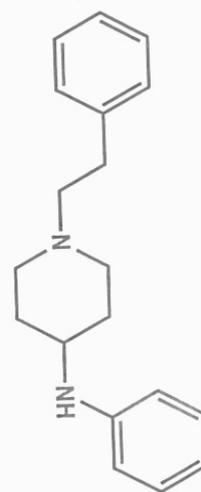
- Supporting Information -

Content	Page
¹ H NMR of N-phenylethylpiperidin-4-one (13)	S2
¹³ C NMR of N-phenylethylpiperidin-4-one (13)	S3
¹ H NMR of N-[1-(2-phenylethyl)-4-piperidinyl]aniline (14)	S4
¹³ C NMR of N-[1-(2-phenylethyl)-4-piperidinyl]aniline (14)	S5
¹ H NMR of Fentanyl (4)	S6
¹³ C NMR of Fentanyl (4)	S7
¹ H NMR of Fentanyl hydrochloride (15)	S8
¹³ C NMR of Fentanyl hydrochloride (15)	S9
¹ H NMR of Fentanyl citrate (16)	S10
¹³ C NMR of Fentanyl citrate (16)	S11
¹ H NMR of Acetylfentanyl (9)	S12
¹³ C NMR of Acetylfentanyl (9)	S13
¹ H NMR of Acetylfentanyl hydrochloride (17)	S14
¹³ C NMR of Acetylfentanyl hydrochloride (17)	S15
¹ H NMR of Acetylfentanyl citrate (18)	S16
¹³ C NMR of Acetylfentanyl citrate (18)	S17
¹ H NMR of 2-(Thiophen-2-yl)ethyl methanesulfonate (19)	S18
¹³ C NMR of 2-(Thiophen-2-yl)ethyl methanesulfonate (19)	S19
¹ H NMR of N-[2-(2-thienyl)ethyl]-4-piperidinone (20)	S20
¹³ C NMR of N-[2-(2-thienyl)ethyl]-4-piperidinone (20)	S21
¹ H NMR of N-phenyl-1-(2-(thiophen-2-yl)ethyl)piperidin-4-amine (21)	S22
¹³ C NMR of N-phenyl-1-(2-(thiophen-2-yl)ethyl)piperidin-4-amine (21)	S23
¹ H NMR of Thiofentanyl (10)	S24
¹³ C NMR of Thiofentanyl (10)	S25
¹ H NMR of Thiofentanyl hydrochloride (23)	S26
¹³ C NMR of Thiofentanyl hydrochloride (23)	S27
¹ H NMR of Thiofentanyl citrate (24)	S28
¹³ C NMR of Thiofentanyl citrate (24)	S29
¹ H NMR of Acetylthiofentanyl (11)	S30
¹³ C NMR of Acetylthiofentanyl (11)	S31
¹ H NMR of Acetylthiofentanyl hydrochloride (25)	S32
¹³ C NMR of Acetylthiofentanyl hydrochloride (25)	S33
¹ H NMR of Acetylthiofentanyl citrate (26)	S34
¹³ C NMR of Acetylthiofentanyl citrate (26)	S35

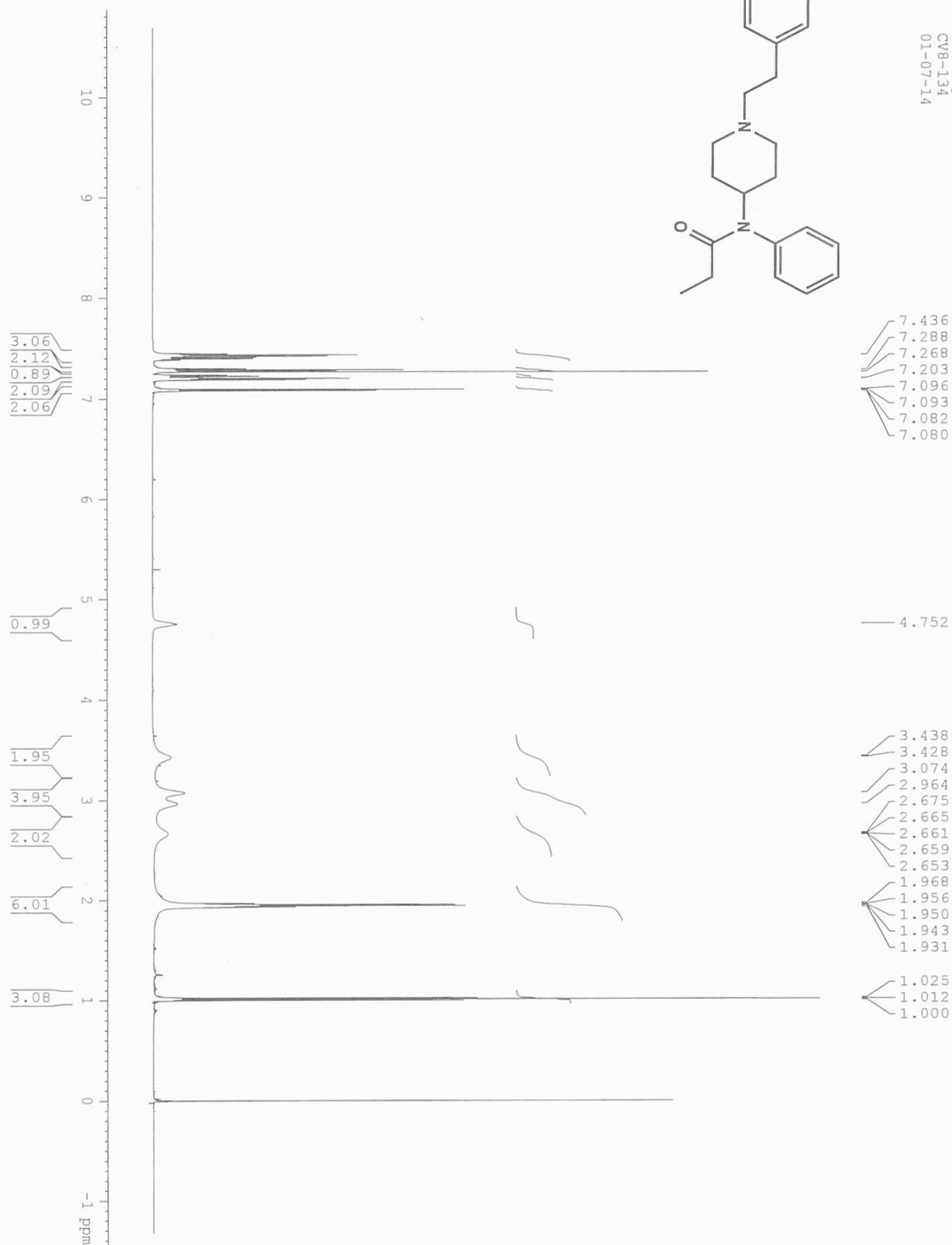
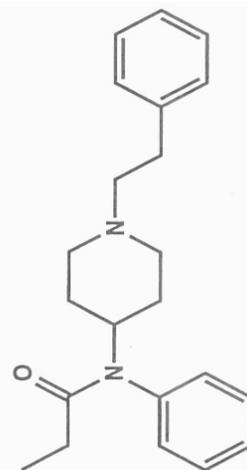




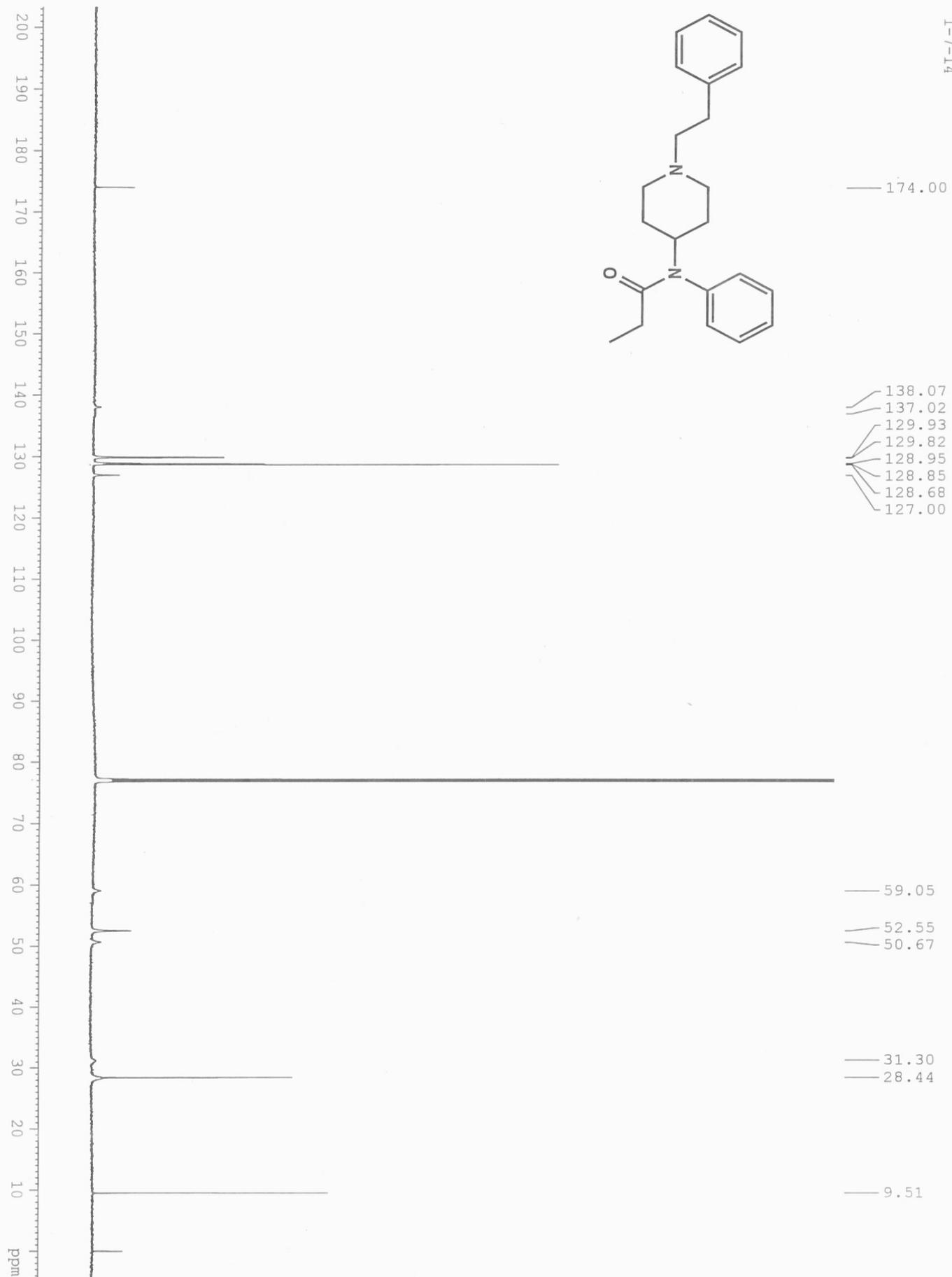
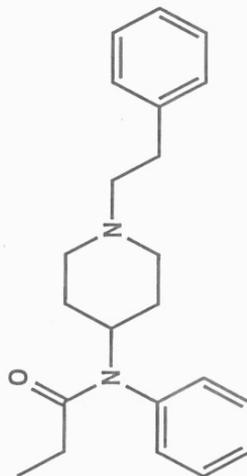




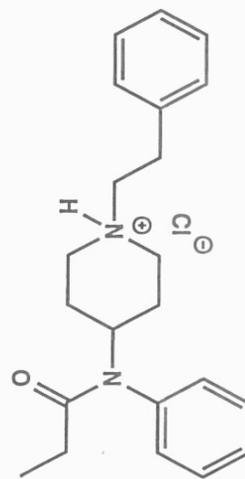
Fentanyl (Free base)
CV8-134
01-07-14



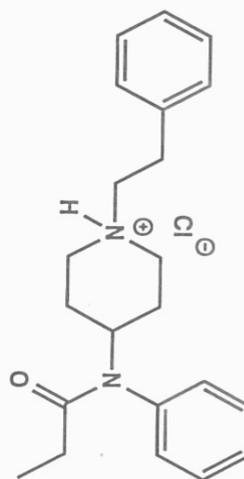
Fentanyl (Free base)
CV8-134
1-7-14



Fentanyl1 (HCl salt)
CV8-148
1-23-14



Fentanyl (HCl salt)
CV8-148
1-23-14



— 177.49

137.19
136.26
129.80
129.28
129.09
128.76
127.38

— 57.58

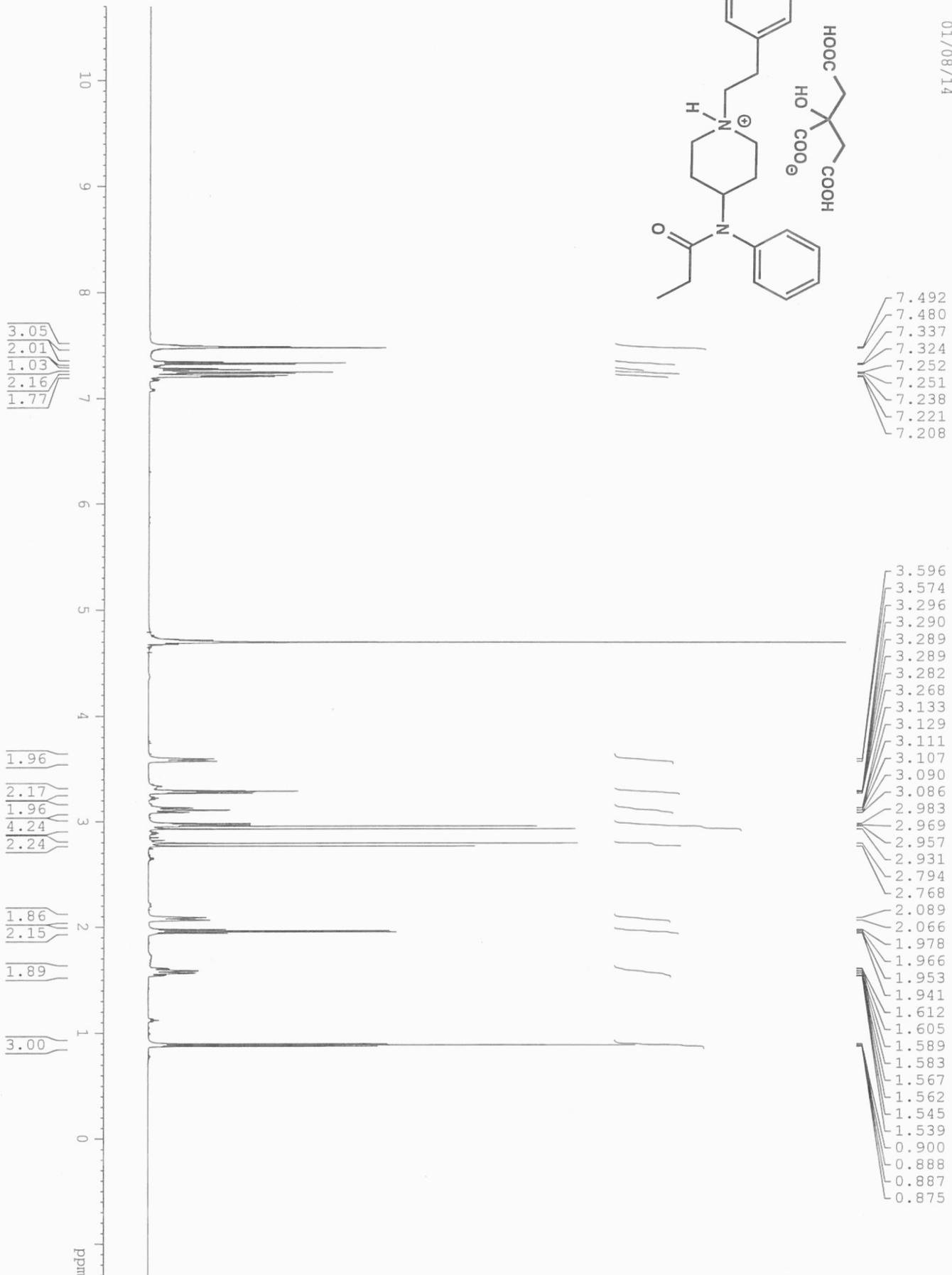
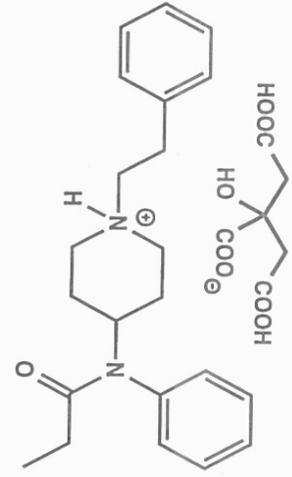
52.10
50.00

29.84
28.22
27.46

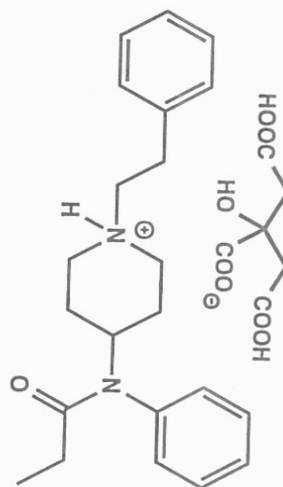
— 9.02



fentanyl (citrate salt)
CV8-139
01/08/14



Fentanyl citrate
CV8-139
01/08/14



177.48
177.07
173.60

137.19
136.27
129.80
129.29
129.10
128.77
127.38

73.38

57.58

52.10

49.99

43.34

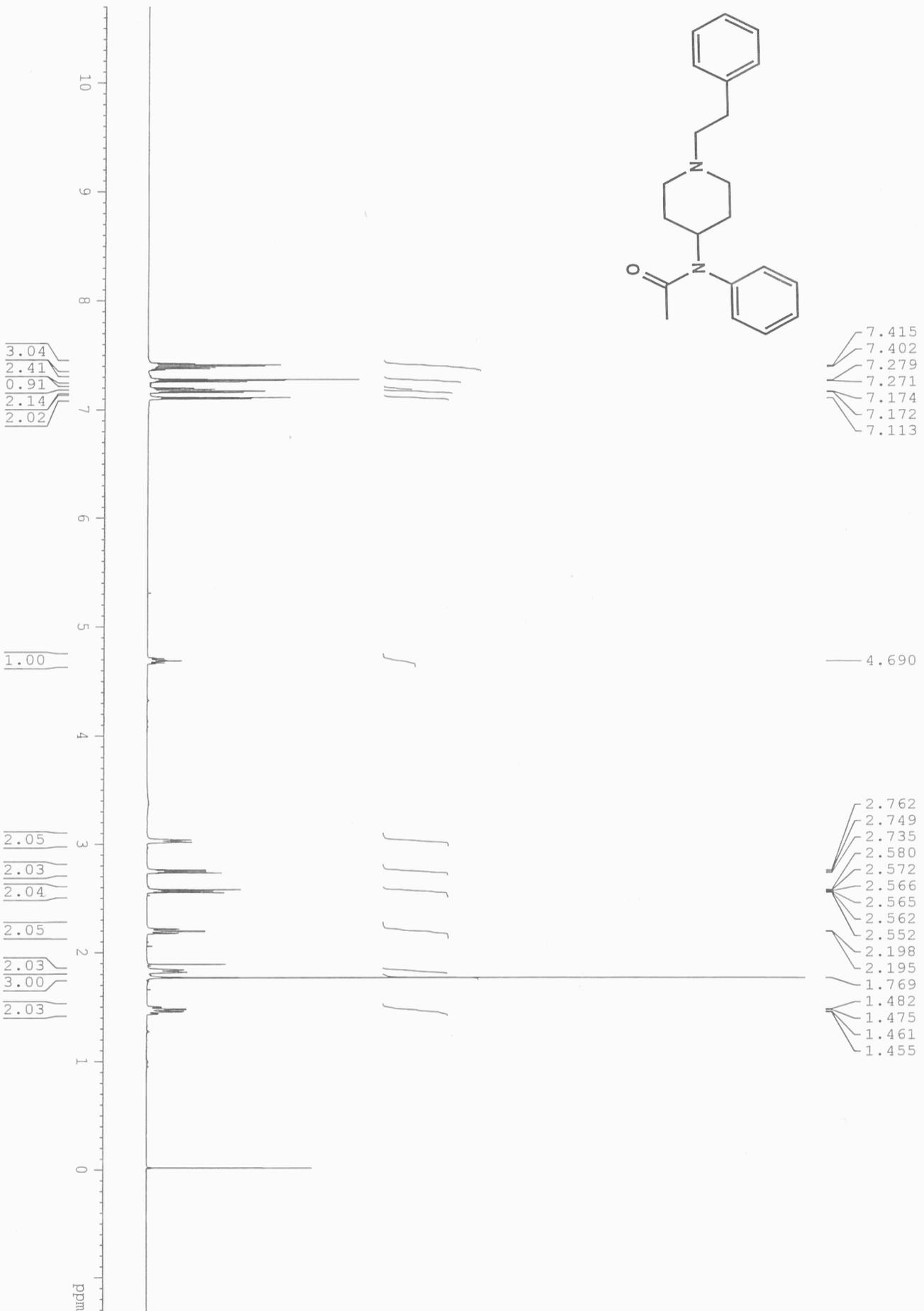
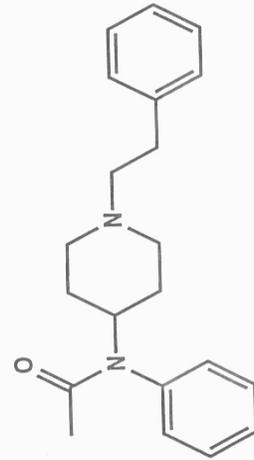
29.85

28.23

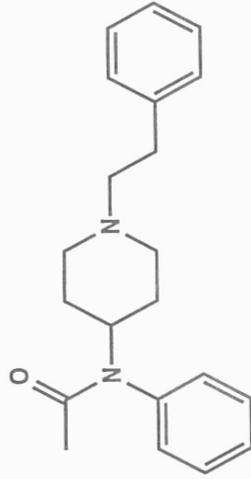
27.46

9.03

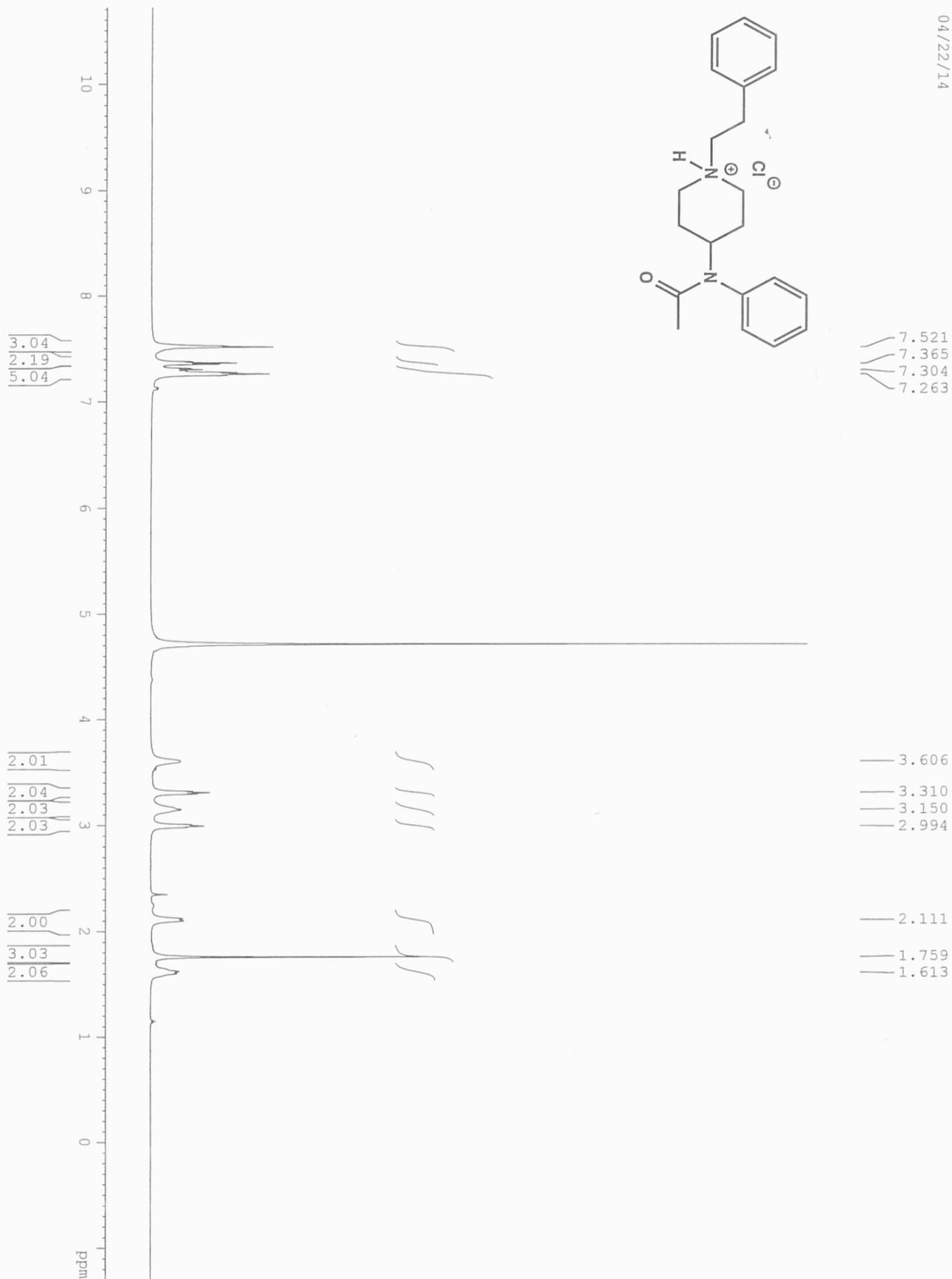
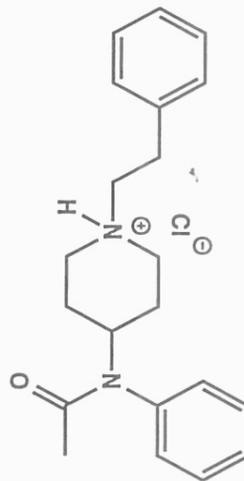




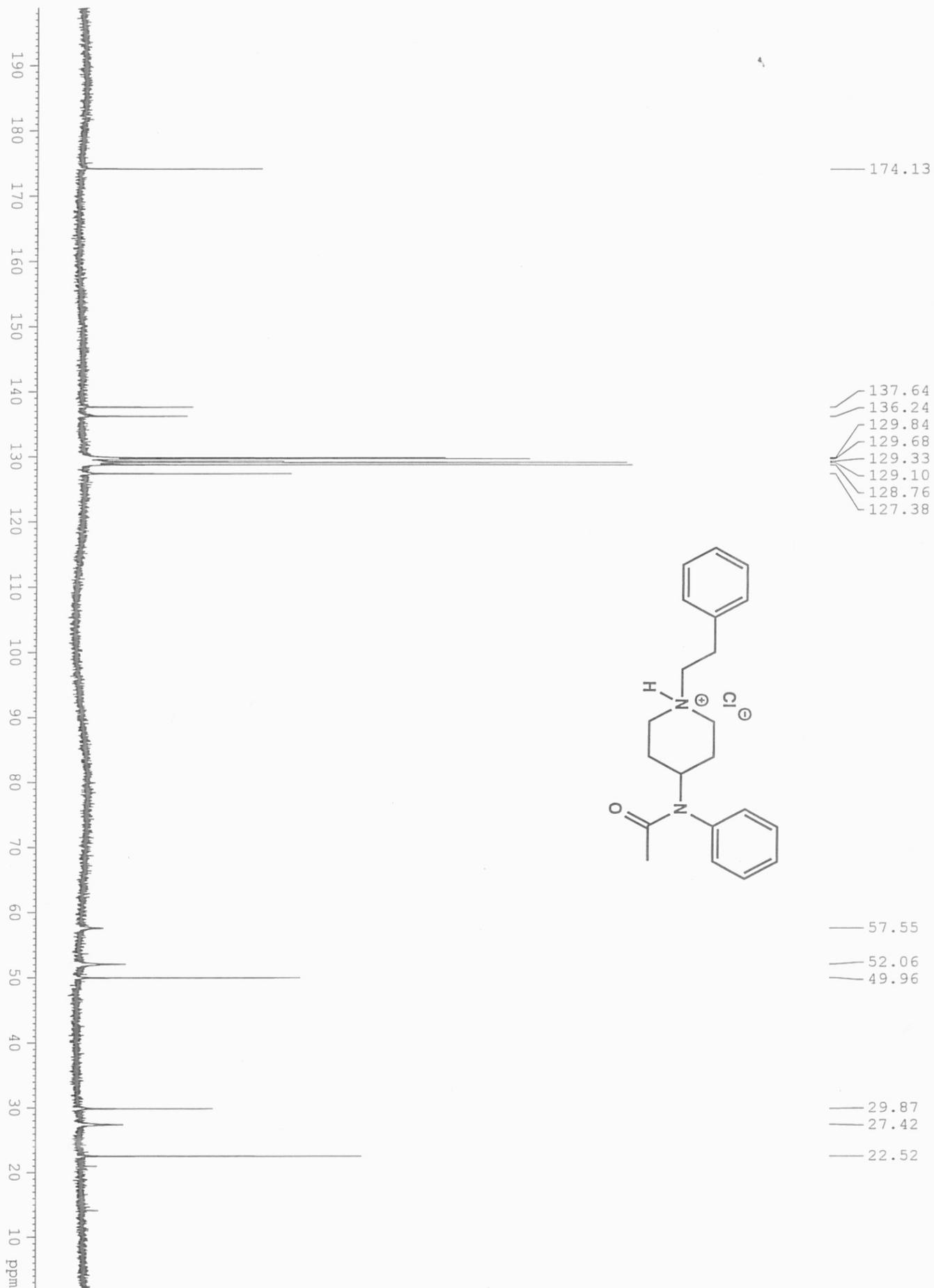
Acetyl[fentanyl] (Free base)
CV8-144
04/23/14



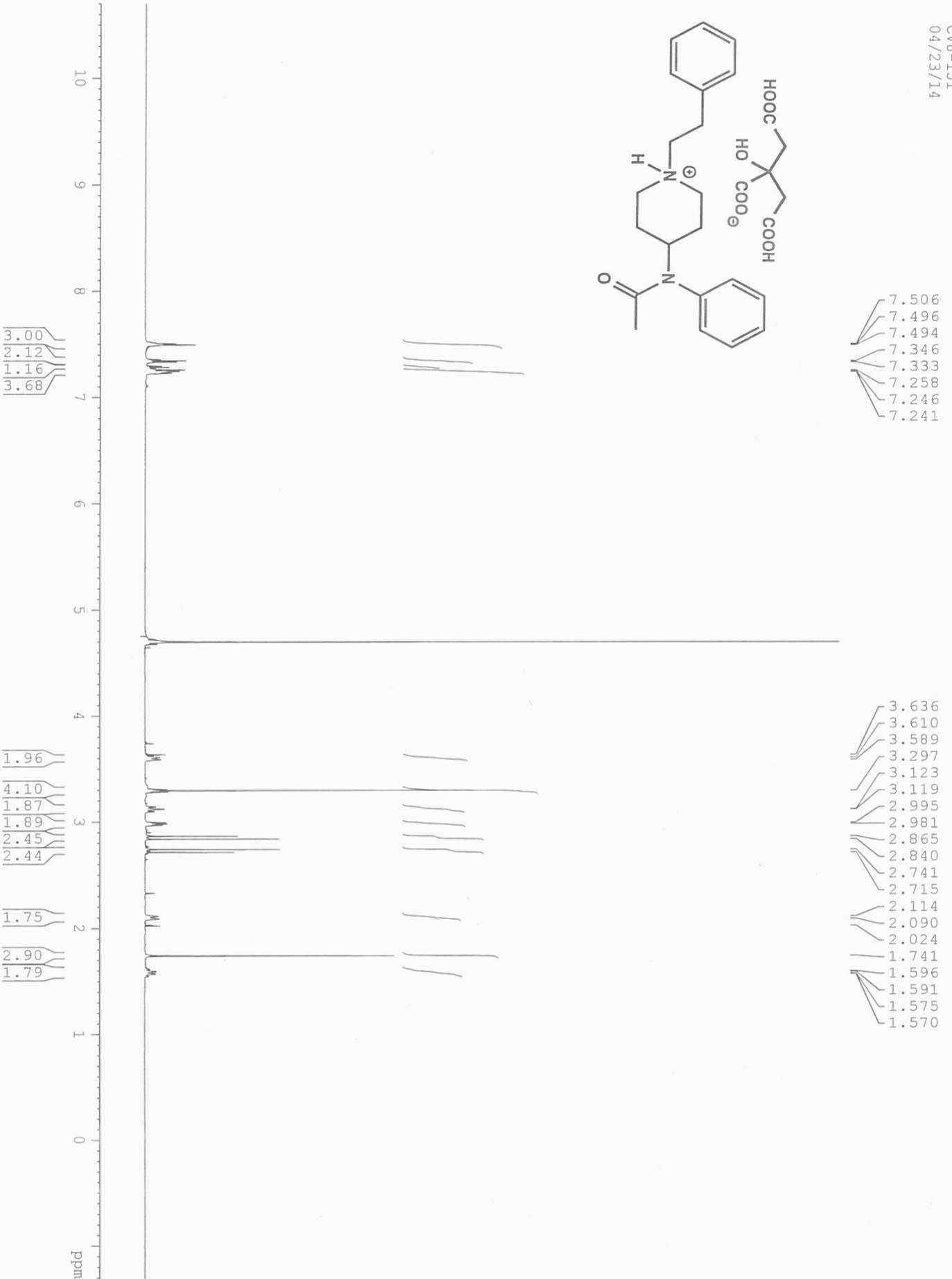
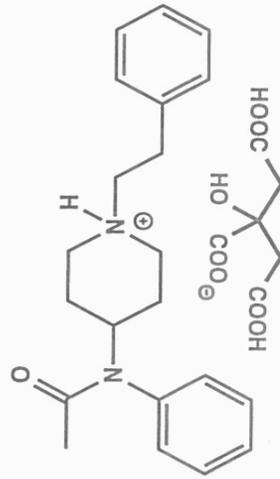
AcetylFentanyl1 (HCl salt)
CV8-150
04/22/14



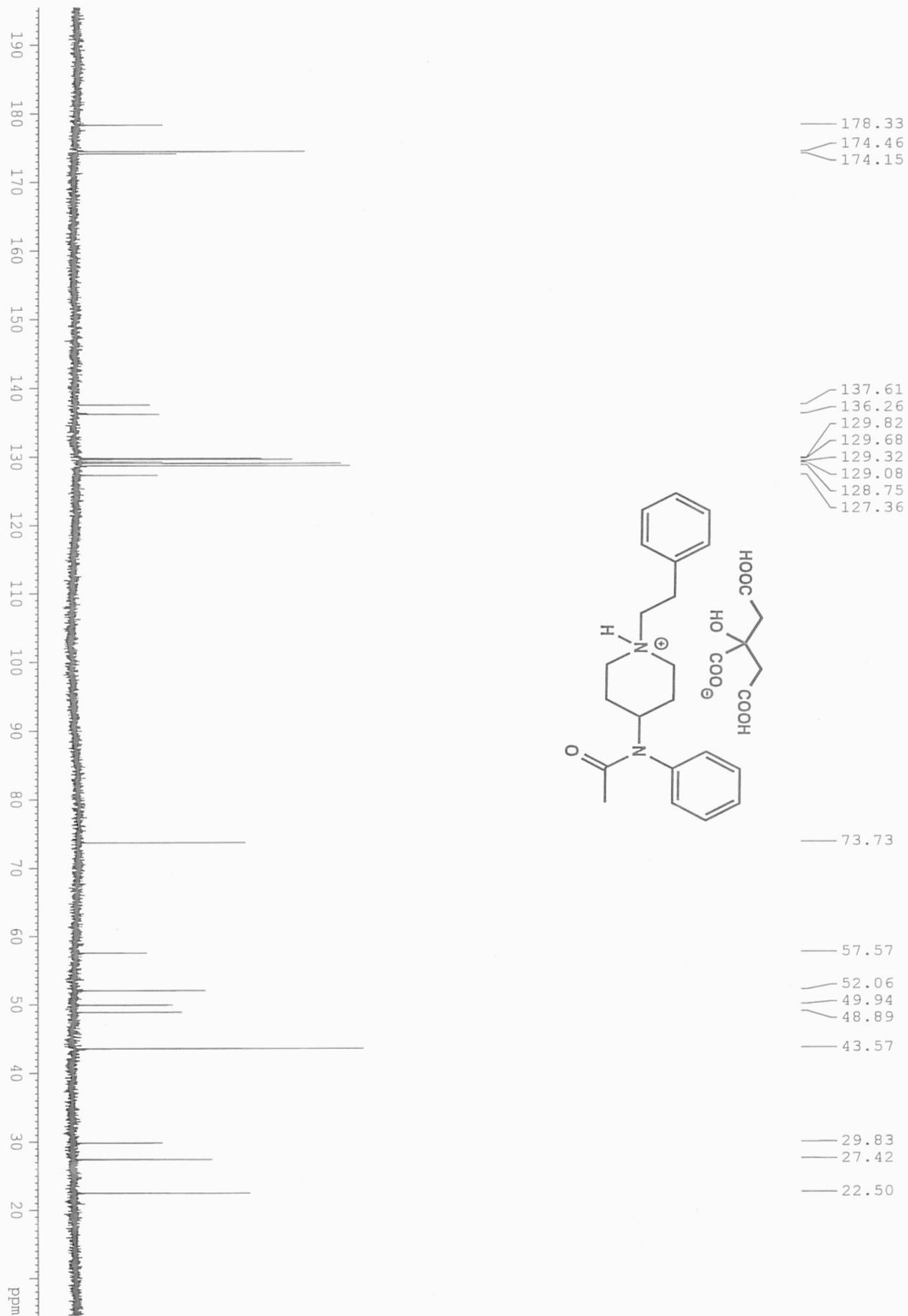
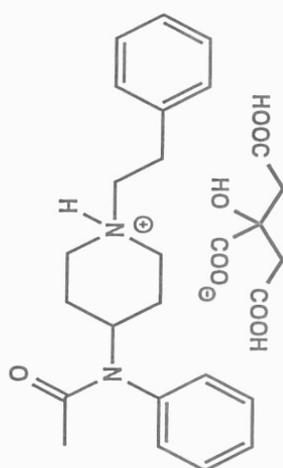
AcetylFentanyl1 (HCl salt)
CV8-150
04/22/14



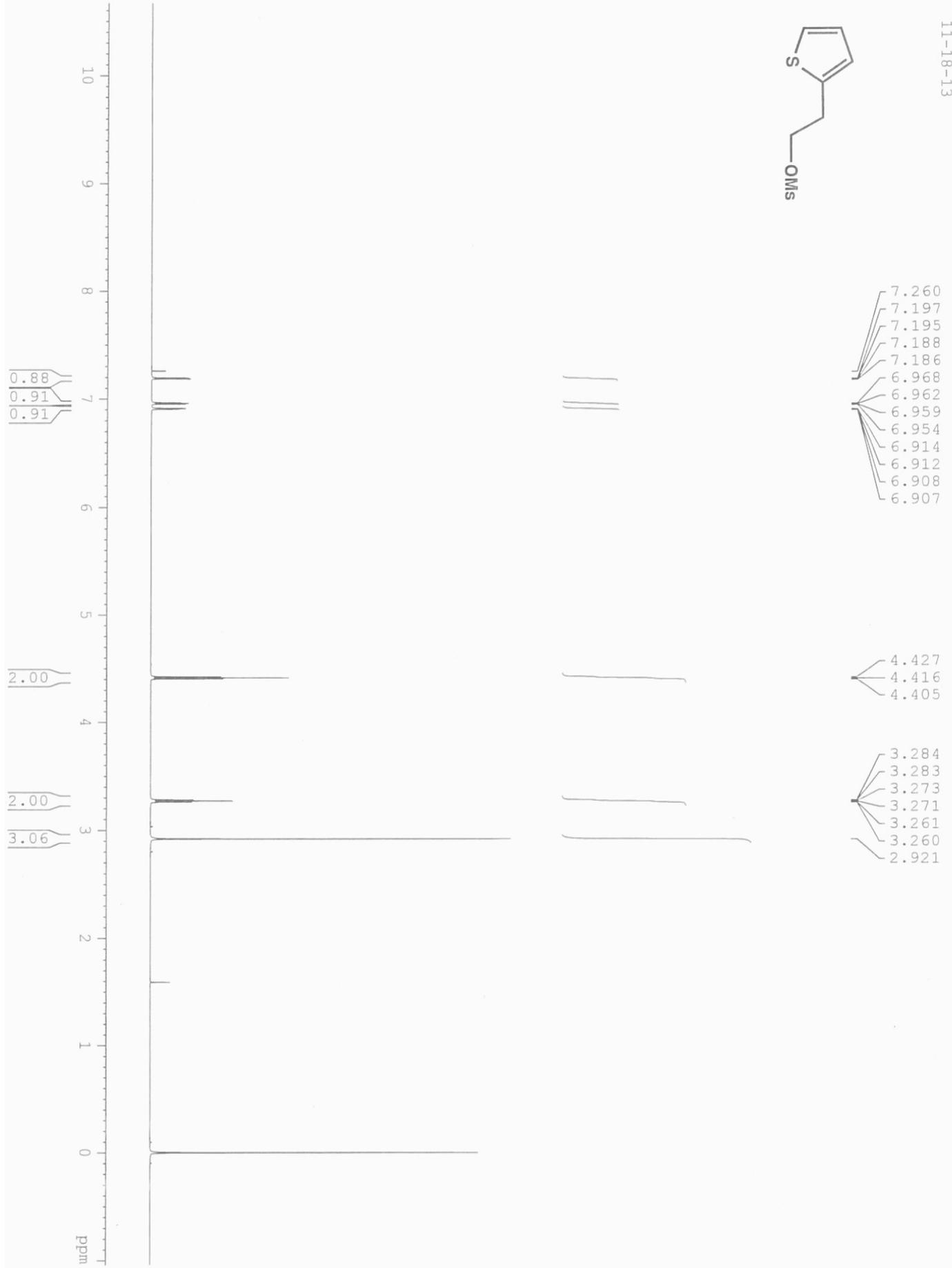
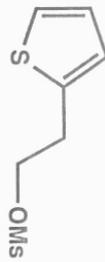
Acetyl[fentanyl] (citrate salt)
CV8-151
04/23/14



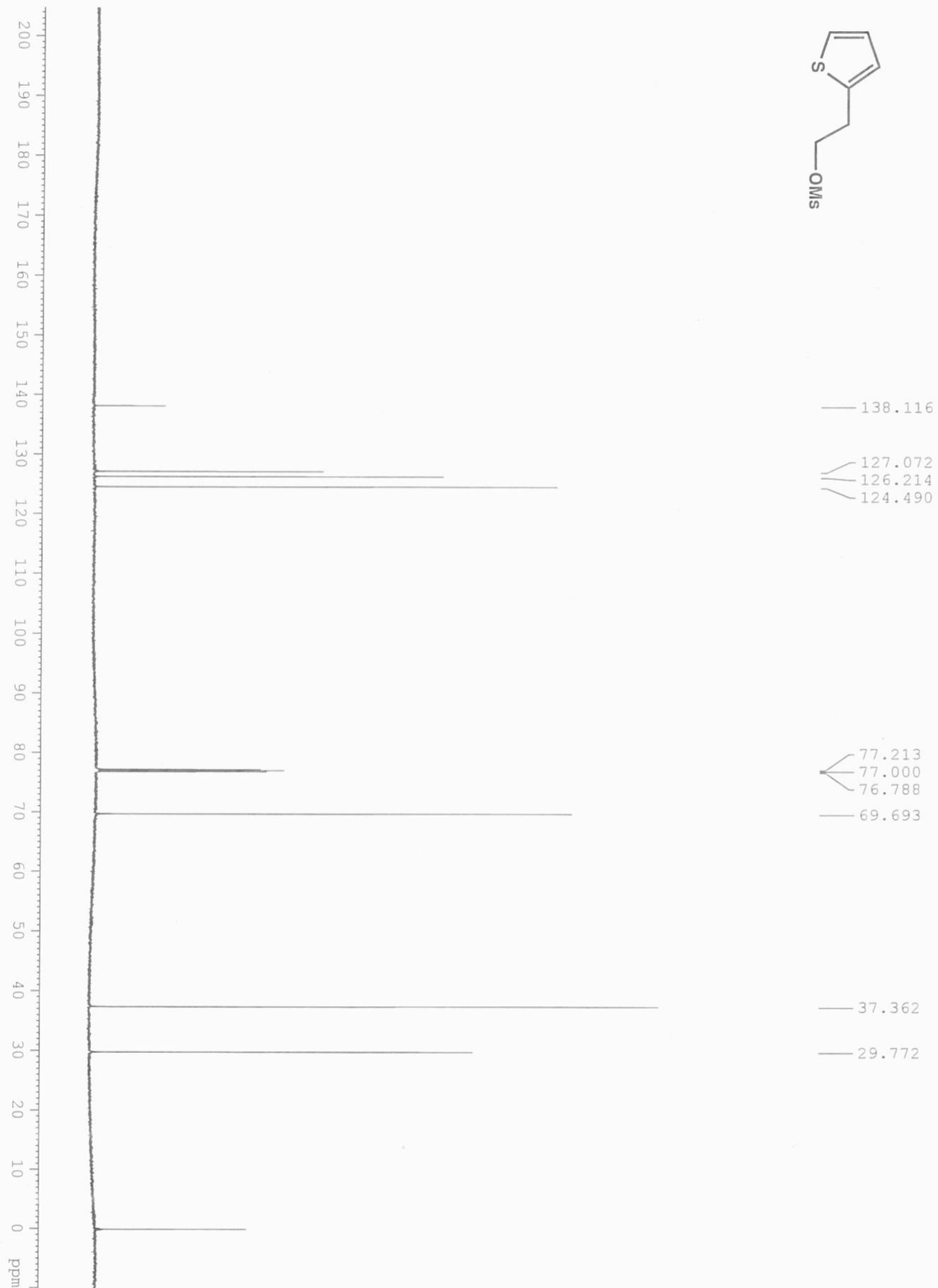
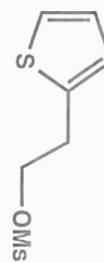
Acetyl1fentanyl] (citrate salt)
CV8-151
04/23/14

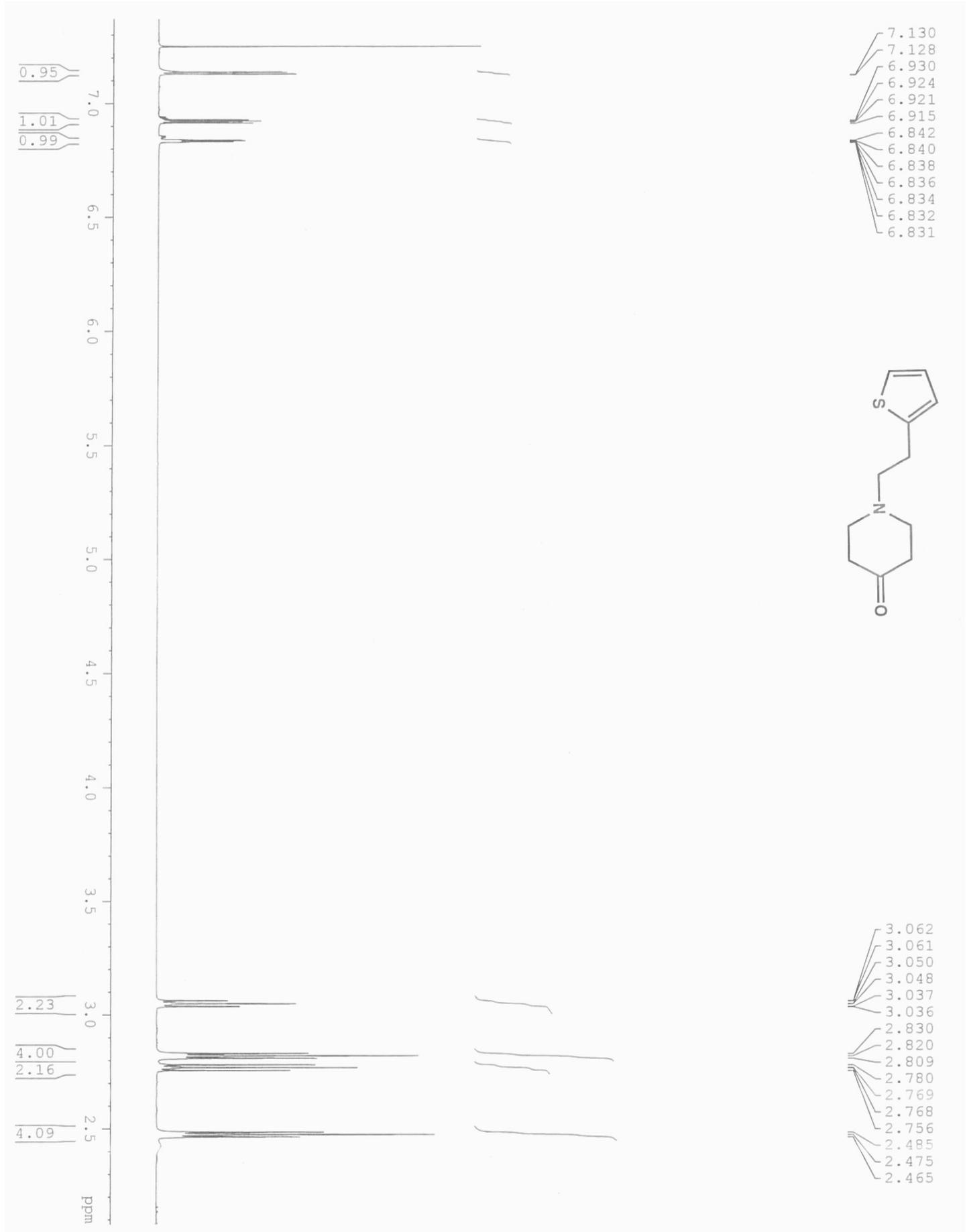


CV8-108
Thiophene ethanol mesylate
11-18-13

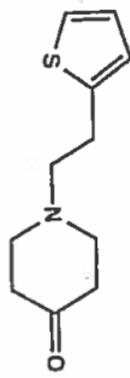


CV8-108
Thiophene ethanol mesylate
11-18-13





210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



— 209.005

— 142.442

— 126.609
— 124.745
— 123.705

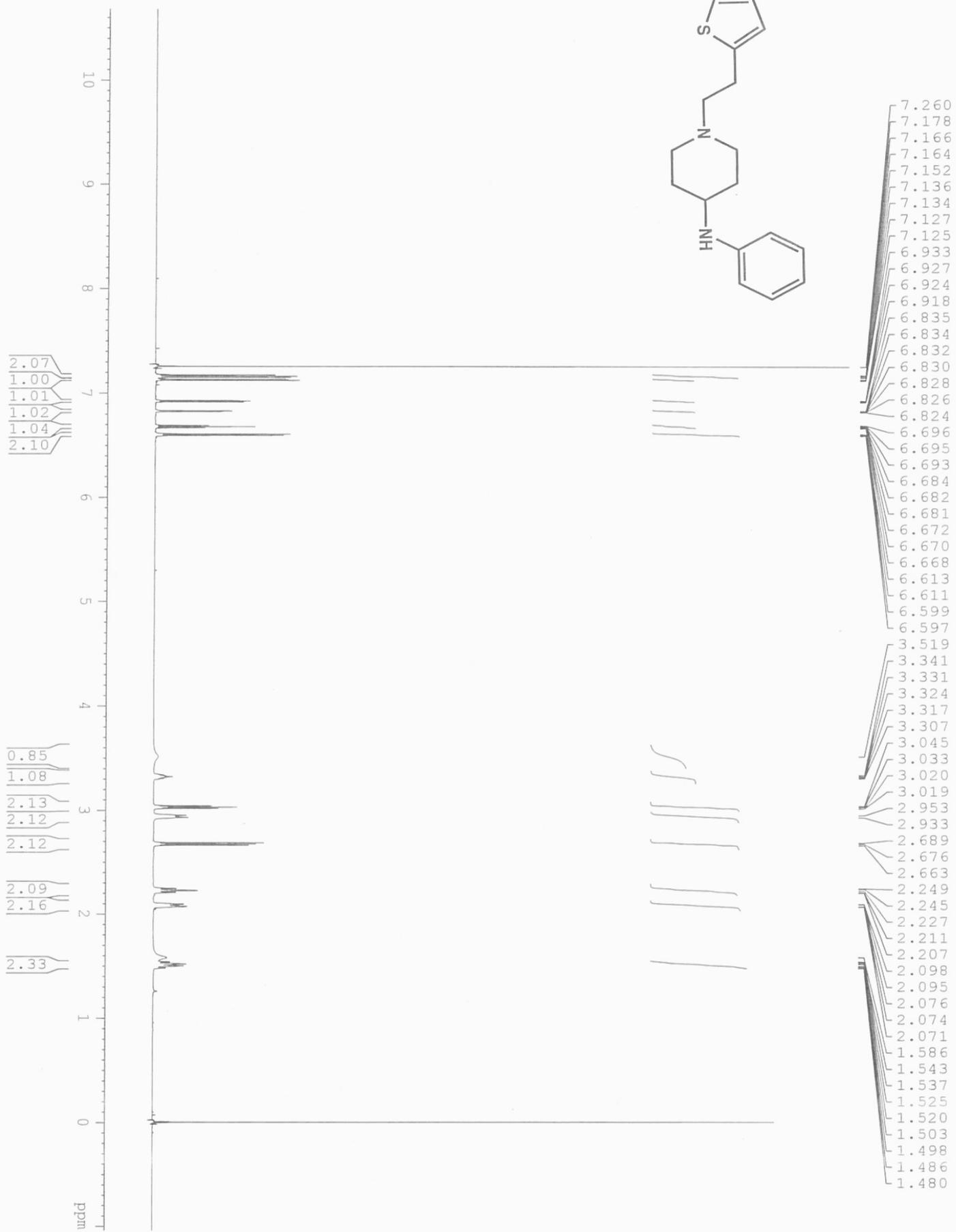
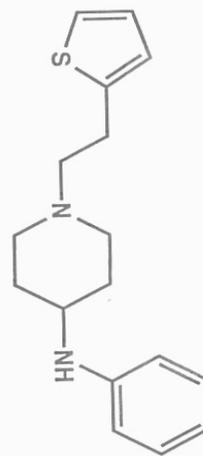
— 77.239
— 77.026
— 76.816

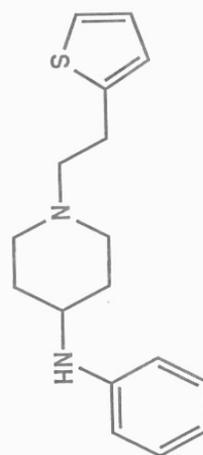
— 60.386

— 53.005

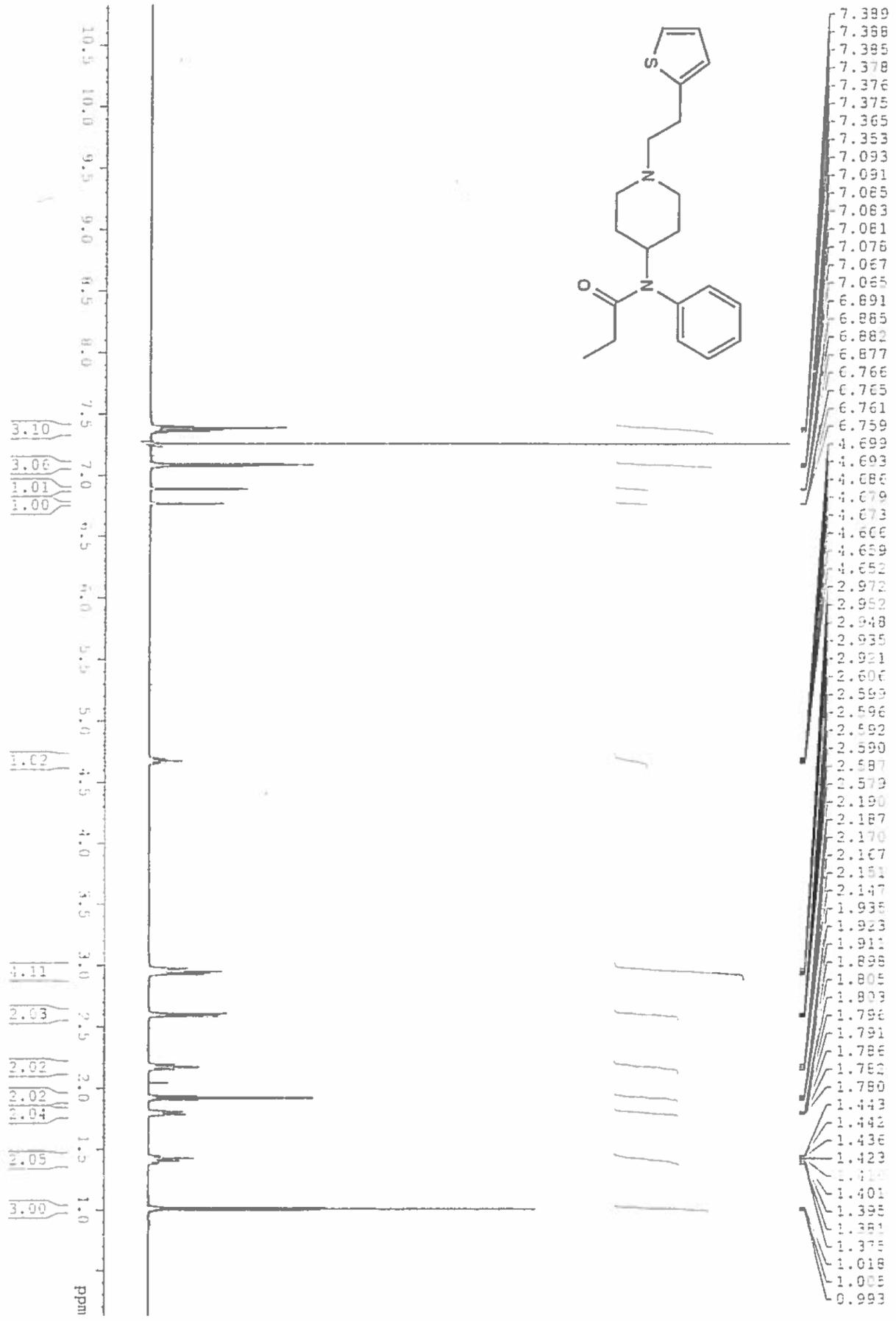
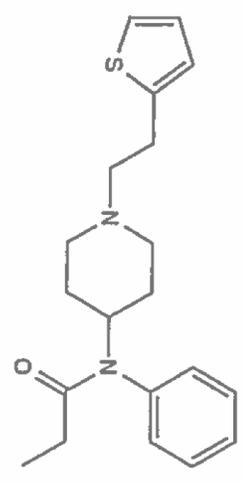
— 41.263

— 28.306

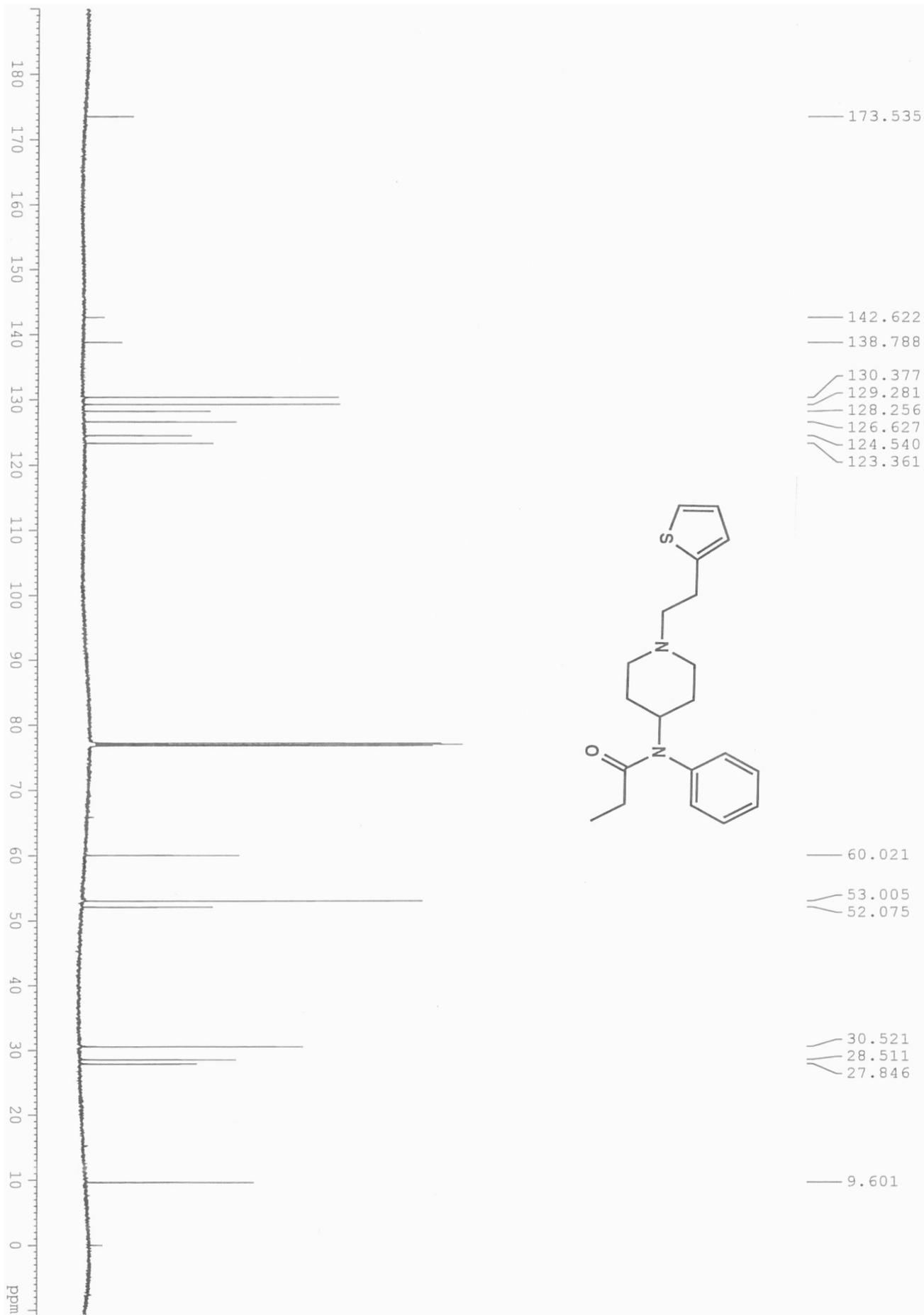
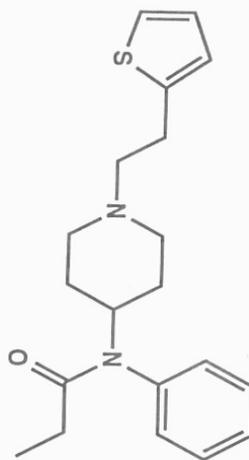


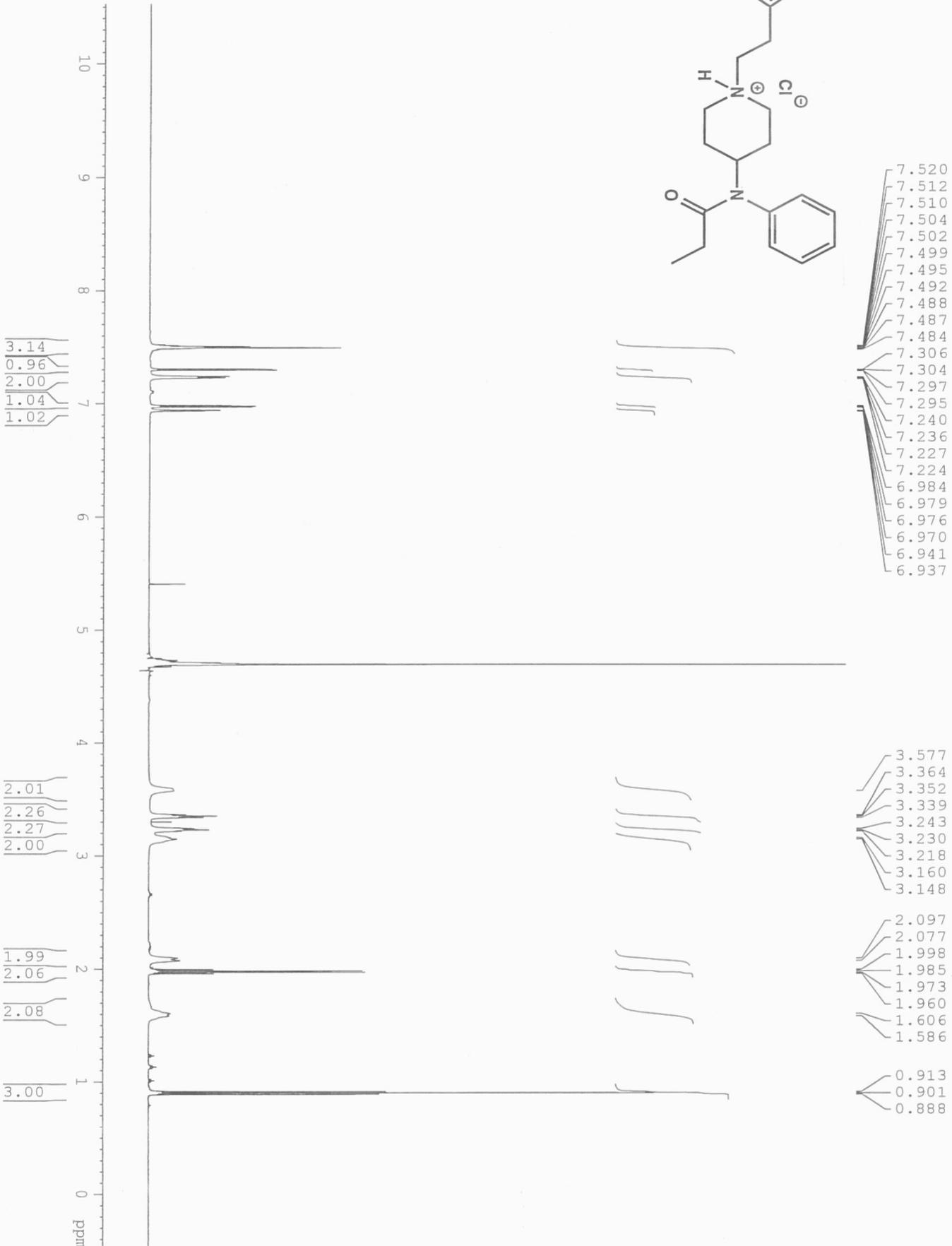
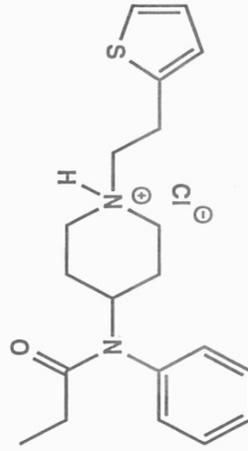


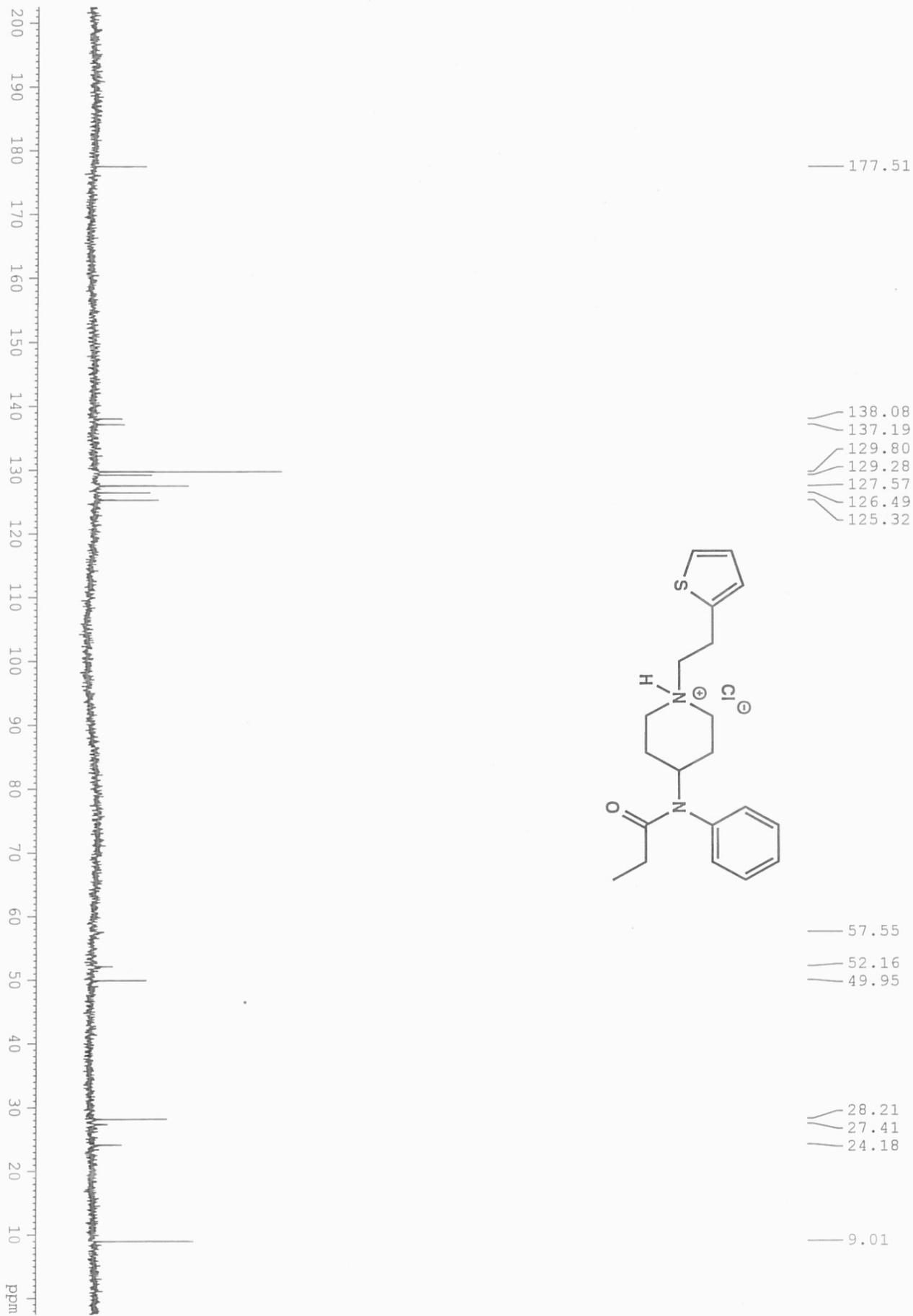
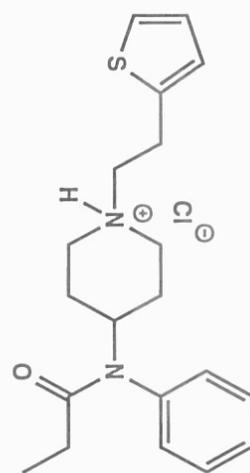
CV8-102
 Thioencanyl (free base)
 3-7-14

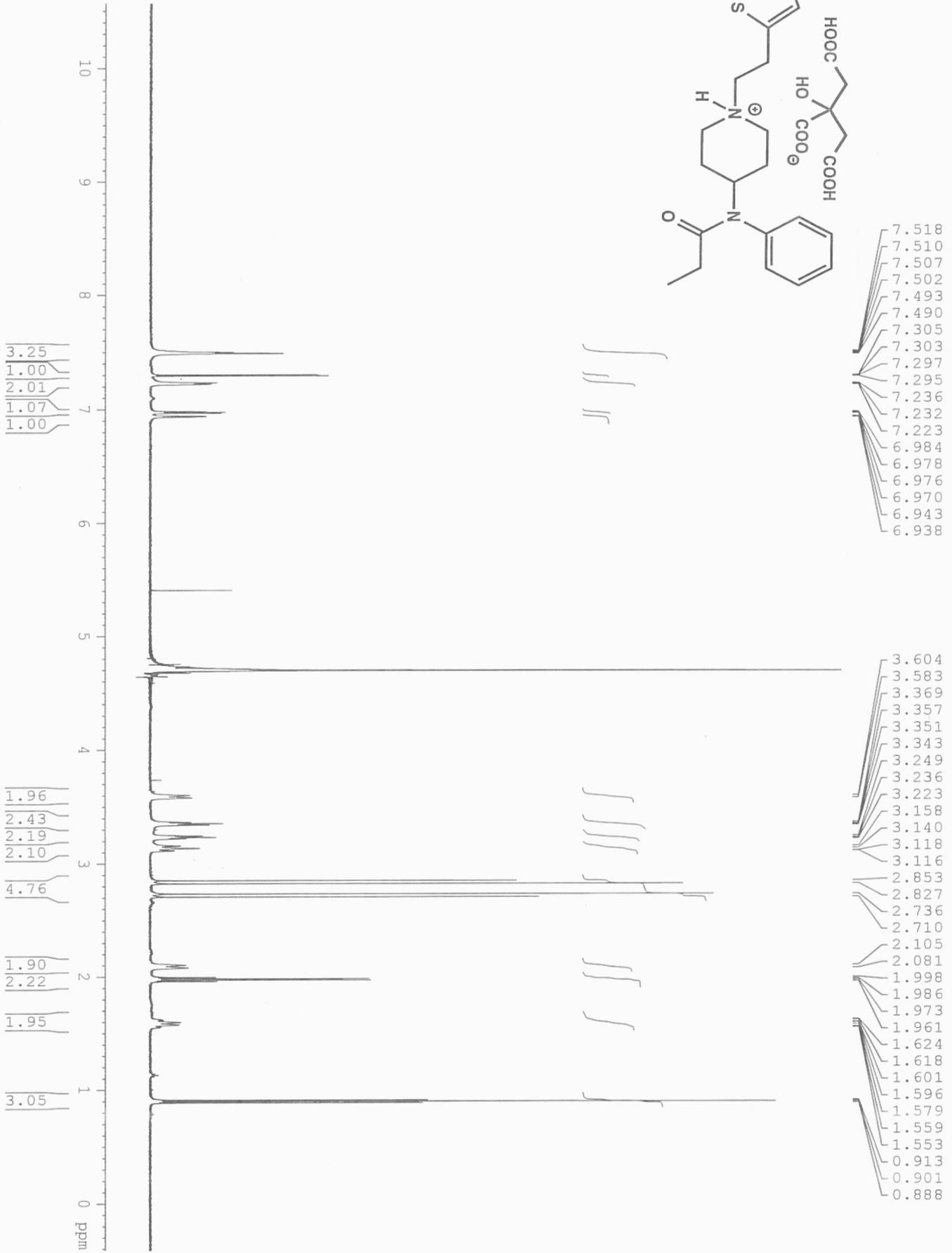
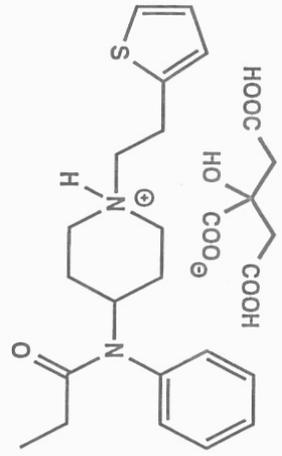


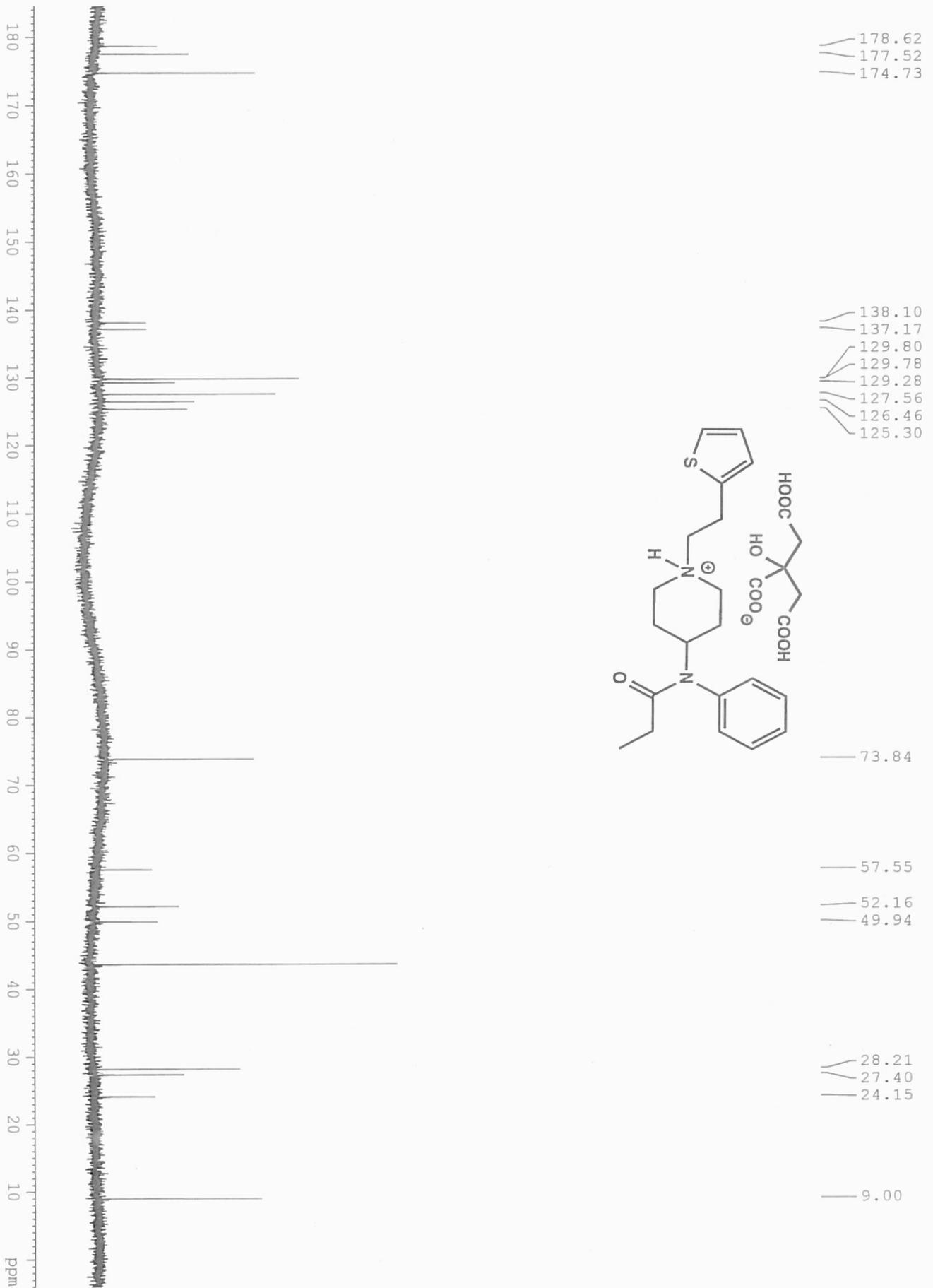
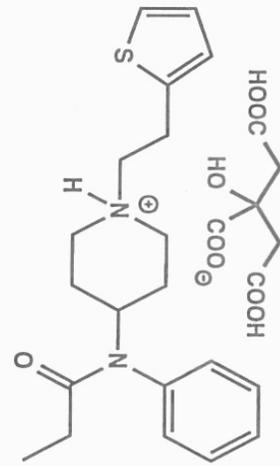
CV8-162
Thiofentanyl (Free base)
3-7-14



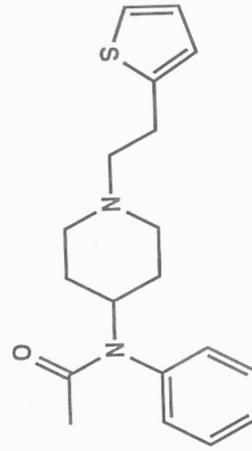




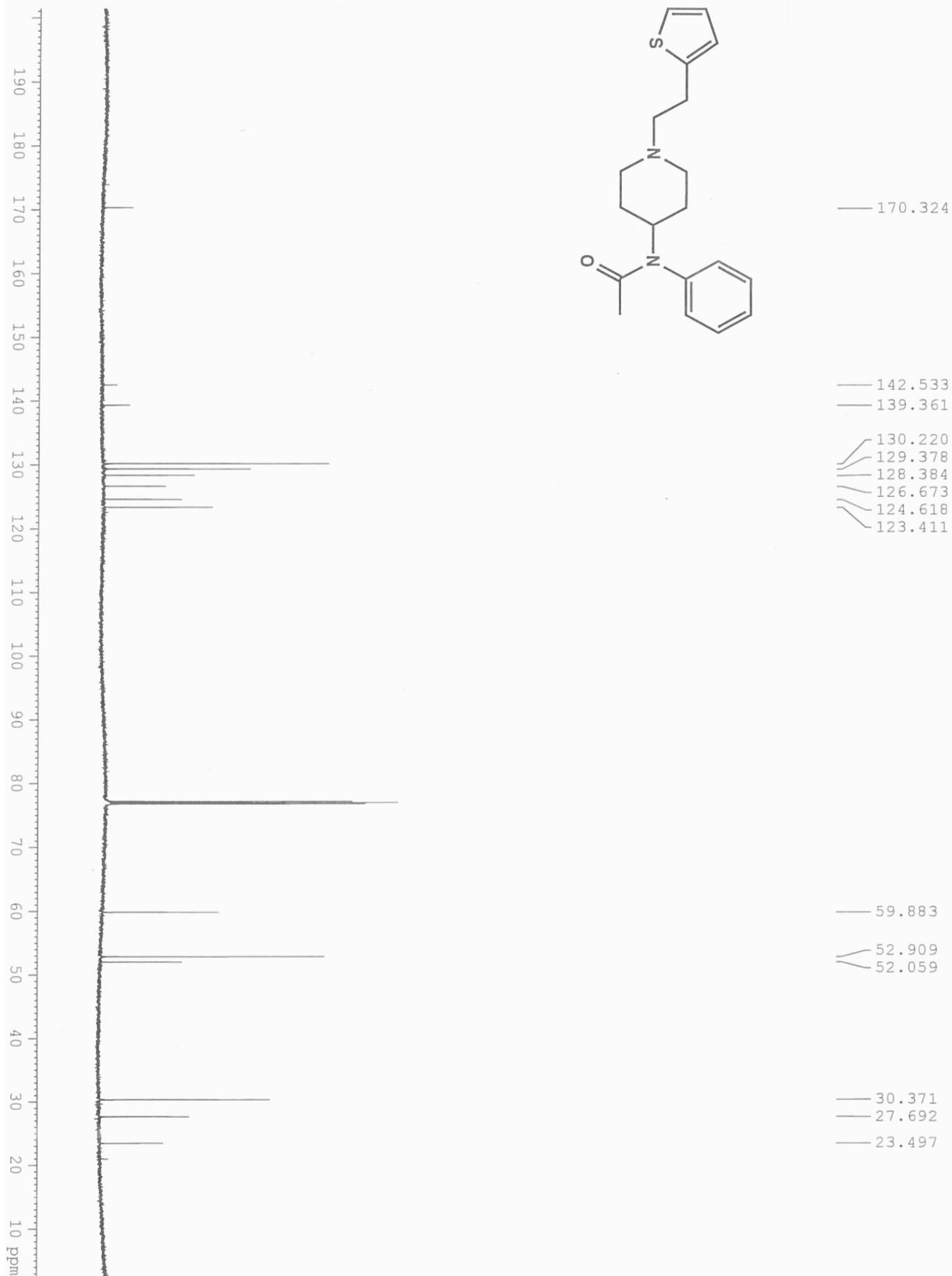
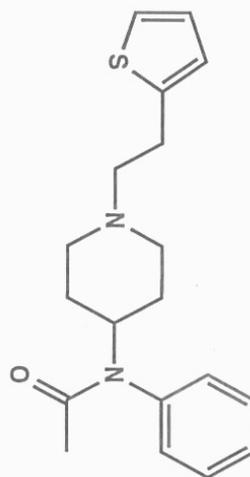




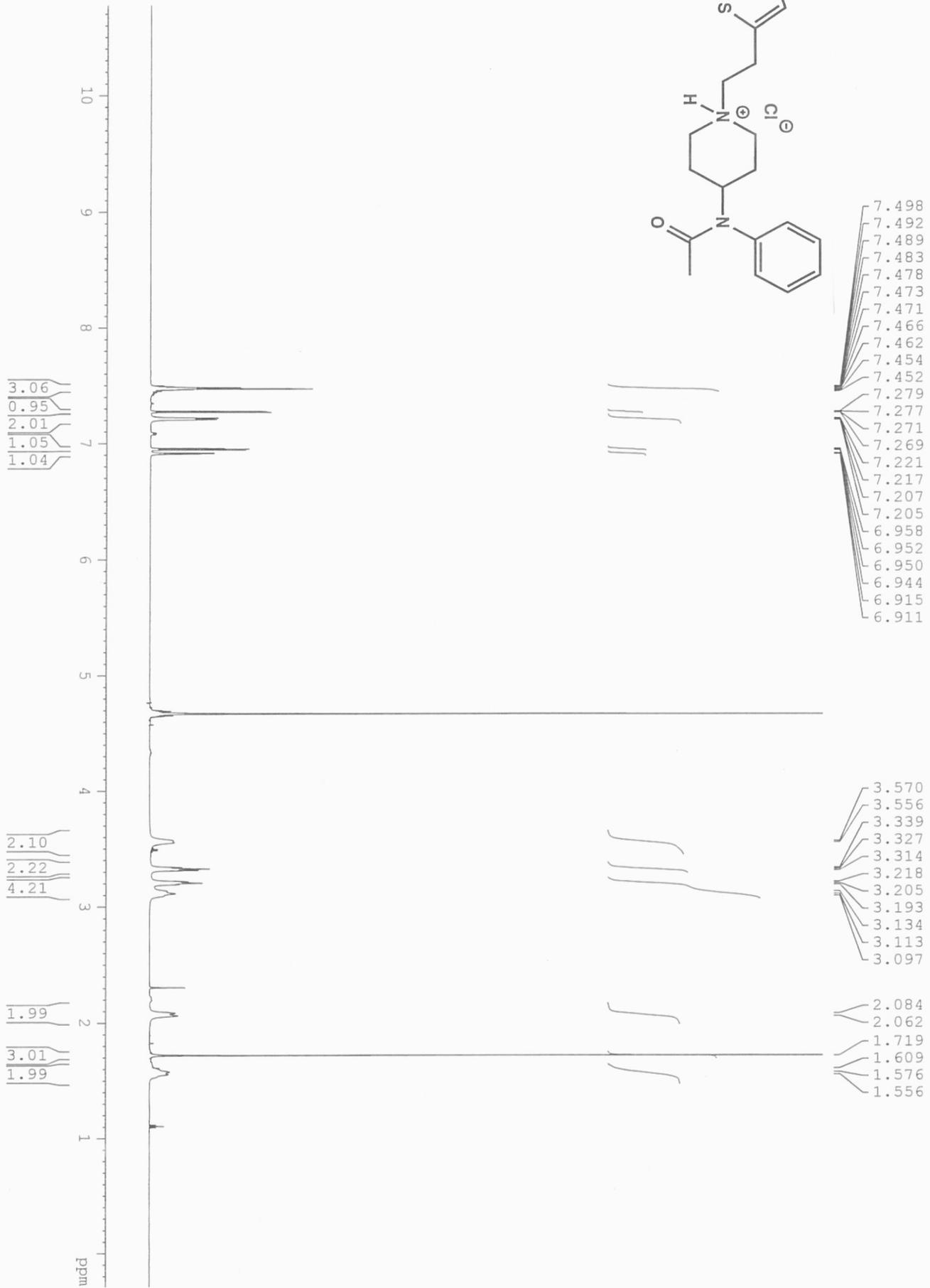
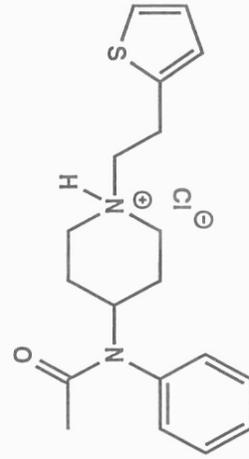
Acetyl[thiofentanyl] (free base)
5-6-14

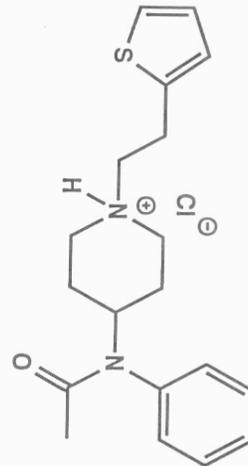


Acetylthiofentanyl 1 (Free base)
CV8-154
5-6-14



Acetylthiofentanyl (HCl salt)
CV8-180
5-7-14





174.096

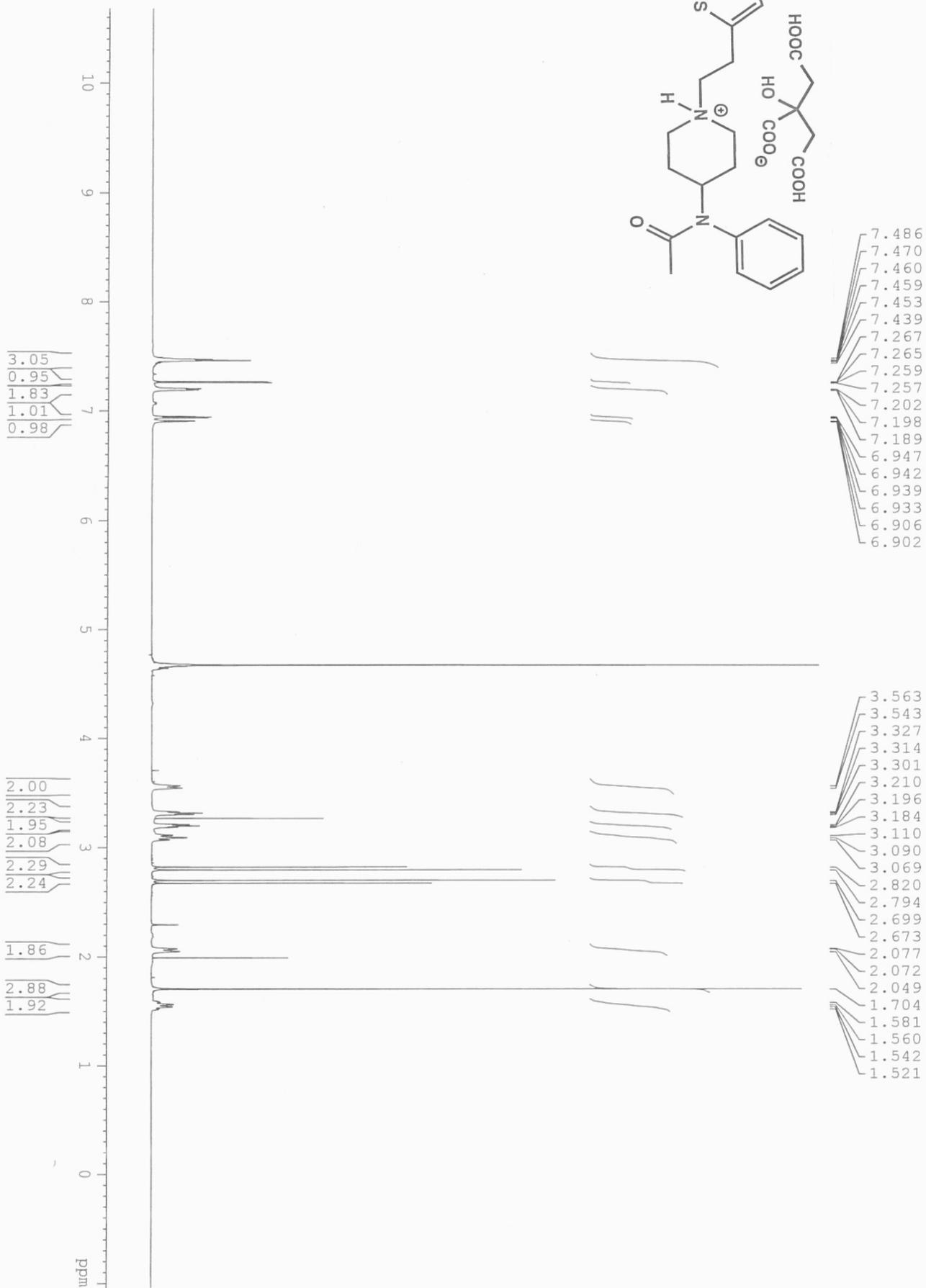
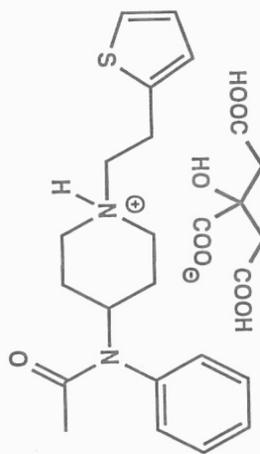
138.020
137.580
129.771
129.621
129.268
127.507
126.427
125.262

57.496

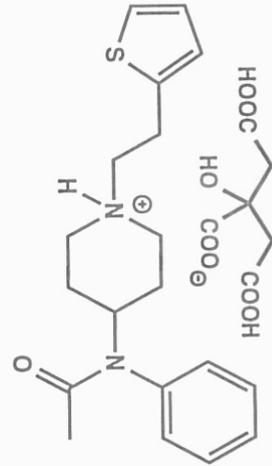
52.071
49.850

27.310
24.114
22.440

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



CV8-181
Acetylthiofentanyl citrate
5-7-14



178.277
174.417
174.055

138.053
137.536
129.764
129.613
129.267
127.509
126.407
125.230

73.654

57.471

52.054

49.826

43.515

27.298

24.081

22.442

