10.1071/CH15115_AC



Australian Journal of Chemistry 2015, 68(11), 1668-1671

# SUPPLEMENTARY MATERIAL

# Formation of Carbanions from Carboxylate Ions Bearing Electron-withdrawing Groups via Photoinduced Decarboxylation: Addition of Generated Carbanions to Benzaldehyde

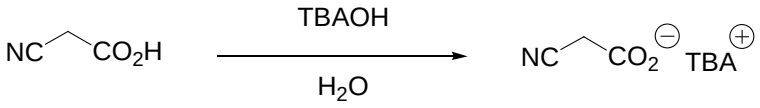
Yuta Kumagai, Takashi Naoe, Keisuke Nishikawa, Kazuyuki Osaka, Toshio Morita, Yasuharu Yoshimi*

*Email: yyoshimi@u-fukui.ac.jp

## General Experimental

$^{1}H$ and $^{13}C$ NMR were recorded on JEOL JNM-AL-300 (300 and 75 MHz) spectrometer and for solution in $CDCl_3$ containing tetramethylsilane as internal standard. GC-MS spectra were obtained using a Shimazu GCMS-QP5000. The light source was RIKO UV-100HA 100-W high-pressure mercury arc. Phen, Biphenyl, DCB, and DCN were recrystallized from hexane and EtOAc. Column chromatography was performed on Wakogel C-300, particle size 45-75 mm.

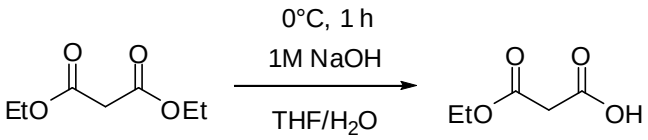
## Preparation of tetra-*n*-butylammonium cyanoacetate 4a




**4a**

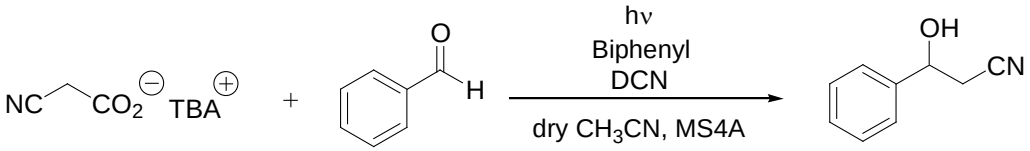
Cyanoacetic acid (5 mmol) and tetra-*n*-butylammonium hydroxide 30-hydrate (TBAOH, 5 mmol) were added to $H_2O$ (50 ml). The mixture was stirred for 2 h at room temperature, and then concentrated under reduced pressure to give **4a**. Other TBA salts **4b**-**e** were also prepared from the corresponding acetic acid derivatives with TBAOH.

**Preparation of malonate acid monoethyl ester**



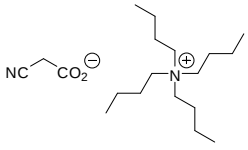

Diethylmalonate (50 mmol) was hydrolyzed by using 1M NaOH in an aqueous THF solution (THF 125 ml, $H_2O$ 125 ml) at 0 ℃. The mixture was stirred for 1 h at 0 ℃, and then was concentrated under reduced pressure. The product was purified by silica gel column chromatography using hexane and EtOAc as eluents to give malonate acid monoethyl ester.

**General procedure for the photoreaction of 4a**

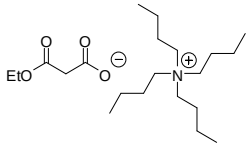



A dry $CH_3CN$ solution (30 ml) containing **4a** (0.15 mmol, 5 mM), benzaldehyde **5a** (0.15 mmol, 5mM), biphenyl (0.6 mmol, 20 mM), 1,4-dicyanonaphthalene (0.6 mmol, 20 mM), and 4A molecular sieves (6g) in two Pyrex vessels (15 mm x 180 mm) was purged with argon for 10 min. The mixture was irradiated with a 100-W high-pressure mercury lamp for 10 h. Then the solvent was evaporated. The product was purified by silica gel column chromatography using hexane, chloroform, and EtOAc as eluents to give adduct **6a**.

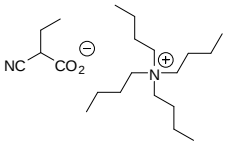
**Characterization date**



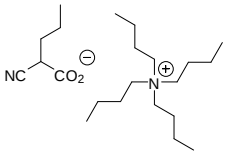

**4a**; Colorless liquid; $^1$H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.2 Hz, 12H), 1.38-1.50 (m, 8H), 1.61-1.71 (m, 8H), 3.24 (s, 2H), 3.29 (t, *J* = 7.2 Hz, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.5, 19.5, 23.8, 58.6, 118.8, 165.1.



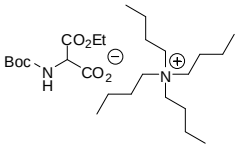

**4b**; Colorless liquid; $^1$H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.2 Hz, 12H), 1.25, (t, *J* = 7.2 Hz, 3H), 1.39-1.51 (m, 8H), 1.61-1.72 (m, 8H), 3.25 (s, 2H), 3.29-3.35 (m, 8H), 4.12 (q, *J* =7.2 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.4, 13.9, 19.4, 23.6, 45.7, 58.3, 59.7, 170.0, 170.4.



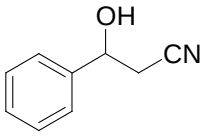
**4c**; Colorless liquid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 0.95-1.12 (m, 15H), 1.38-1.50 (m, 8H), 1.60-1.71 (m, 8H), 1.91-2.01 (m, 2H), 3.22-3.38 (m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 12.1, 13.7, 19.7, 23.9, 24.5, 42.8, 58.7, 122.0, 169.0.



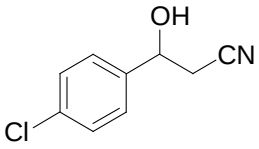
**4d**; Colorless liquid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 0.91-1.07 (m, 15H), 1.38-1.71 (m, 17H), 1.84-1.93 (m, 2H), 3.26-3.32 (m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.6, 19.6, 20.8, 23.8, 32.9, 41.0, 58.6, 122.0, 169.1.



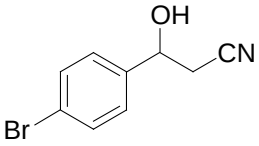
**4e**; Colorless liquid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 0.94-1.07 (t, *J* = 7.2 Hz, 12H), 1.25-1.31 (m, 3H), 1.37-1.47 (m, 17H), 1.49-1.69 (m, 8H), 3.26 (t, *J* = 7.2 Hz, 8H), 3.63 (m, 1H), 4.13-4.22 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.5, 14.0, 19.5, 23.7, 28.2, 58.3, 60.1, 60.4, 155.0, 166.9, 171.0.



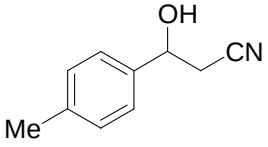
**6a**; Compound has been previously reported.[1] White solid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.79 (d, *J* = 6.9 Hz, 2H), 5.07 (t, *J* = 6.9 Hz, 1H), 7.41-7.43 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.9, 70.2, 117.2, 125.5, 128.9, 129.0, 141.0; GC-MS 147 ($M^+$).



**6b**; Compound has been previously reported.[1] White solid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.76 (d, *J* = 6.9 Hz, 2H), 5.04 (t, *J* = 6.9 Hz, 1H), 7.35-7.40 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 28.0, 69.7, 116.9, 126.9, 129.1, 134.7,139.4; GC-MS 181, 183 ($M^+$).

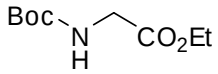


**6c**; Compound has been previously reported.[2] White solid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.77 (d, *J* = 6.3 Hz, 2H), 5.04 (t, *J* = 6.3 Hz, 1H), 7.26-7.31 (m, 2H), 7.53-7.55(m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 28.0, 69.6, 116.8, 122.9, 127.3, 132.1, 139.9; GC-MS 225, 227 ($M^+$).



**6d**; Compound has been previously reported.[1] White solid; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.77 (d, *J* = 6.0 Hz, 2H), 5.02 (t, *J* = 6.0 Hz,

1H), 7.20-7.31 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.2, 27.9, 70.1, 117.3, 125.4, 129.6, 138.1, 138.8; GC-MS 161 ($M^+$).

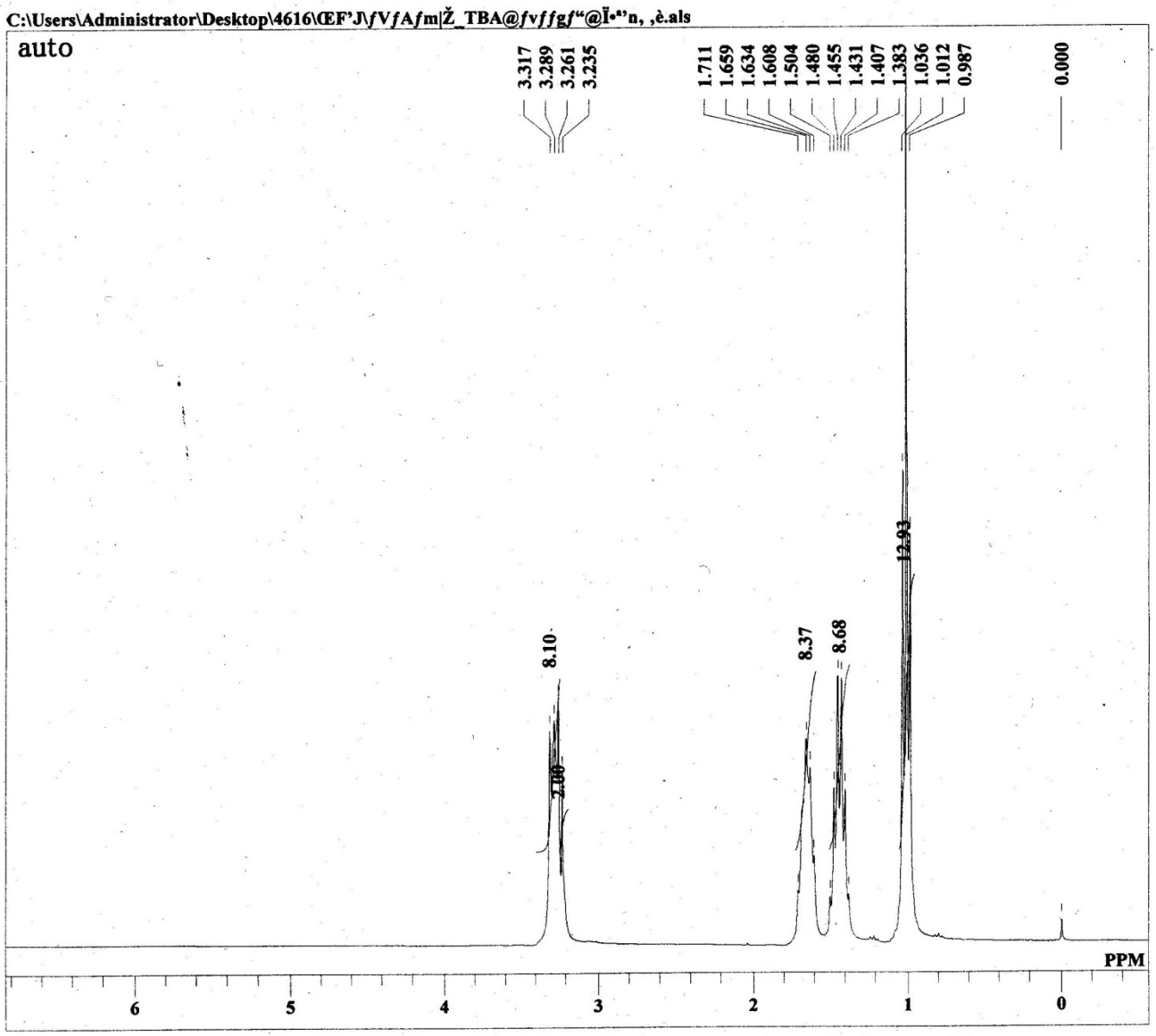


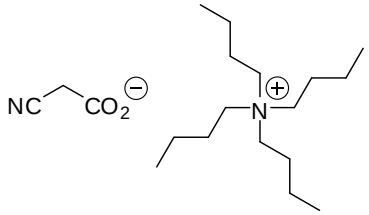

**8**; Compound has been previously reported.[3] White solid; $^1$H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, *J* = 6.9 Hz, 3H), 1.46 (s, 9H), 3.90-3.91 (m, 2H), 4.21 (q, *J* = 6.9 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 14.1, 28.3, 42.4, 61.3, 79.9, 155.7, 170.3; GC-MS 203 ($M^+$).

[1]Sukanta Kamila, Dunming Zhu, Edward R. Biehl, and Ling Hua, *Org. Lett*. **2006**, *20*, 4429-4431.

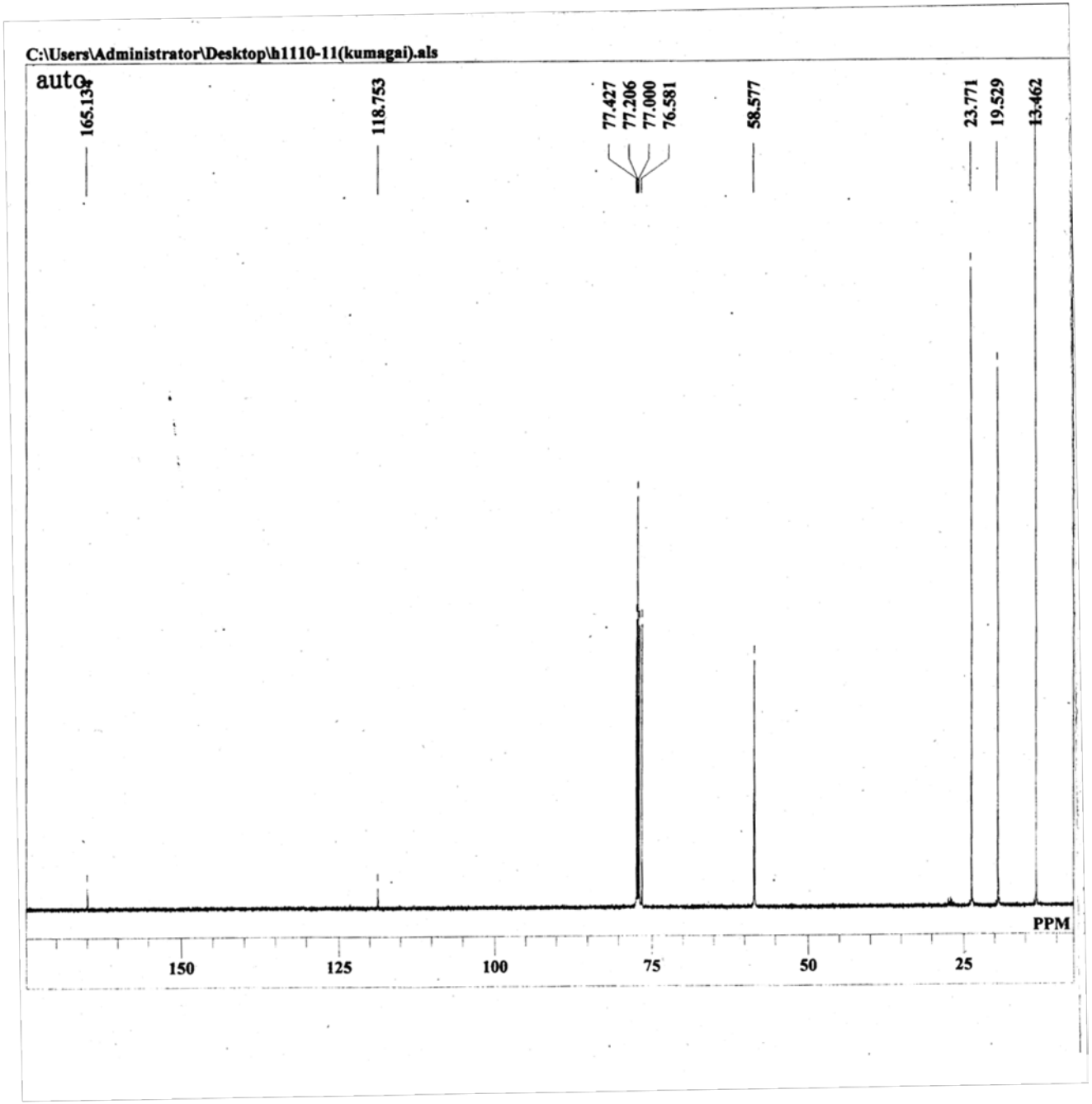
[2]Dunming Zhu, Haribabu Ankati, Chandrani Mukherjee, Yan Yang, Edward R. Biehl, and Ling Hua, *Org. Lett*. **2007**, *13*, 2561-2563.

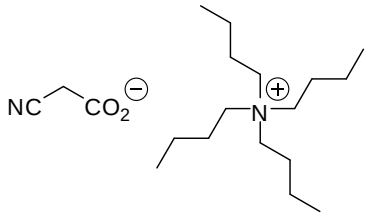
[3]Graham L. Simpson, Andrew H. Gordon, David M. Lindsay, Netnepa Promsawan, Matthew P. Crump, Keith Mulholland, Barry R. Hayter, amd Timothy Gallagher, *J. Am. Chem. Soc.*, **2006**, *128*, 10638-10639.


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒVƒAƒm|Ž_TBA@ƒvƒfƒgƒ"@Ï•"n, ,è.als
auto
3.317
3.289
3.261
3.235
1.711
1.659
1.634
1.608
1.504
1.480
1.455
1.431
1.407
1.383
1.036
1.012
0.987
0.000
8.10
8.37
8.68
12.93
2.00
PPM
6
5
4
3
2
1
0

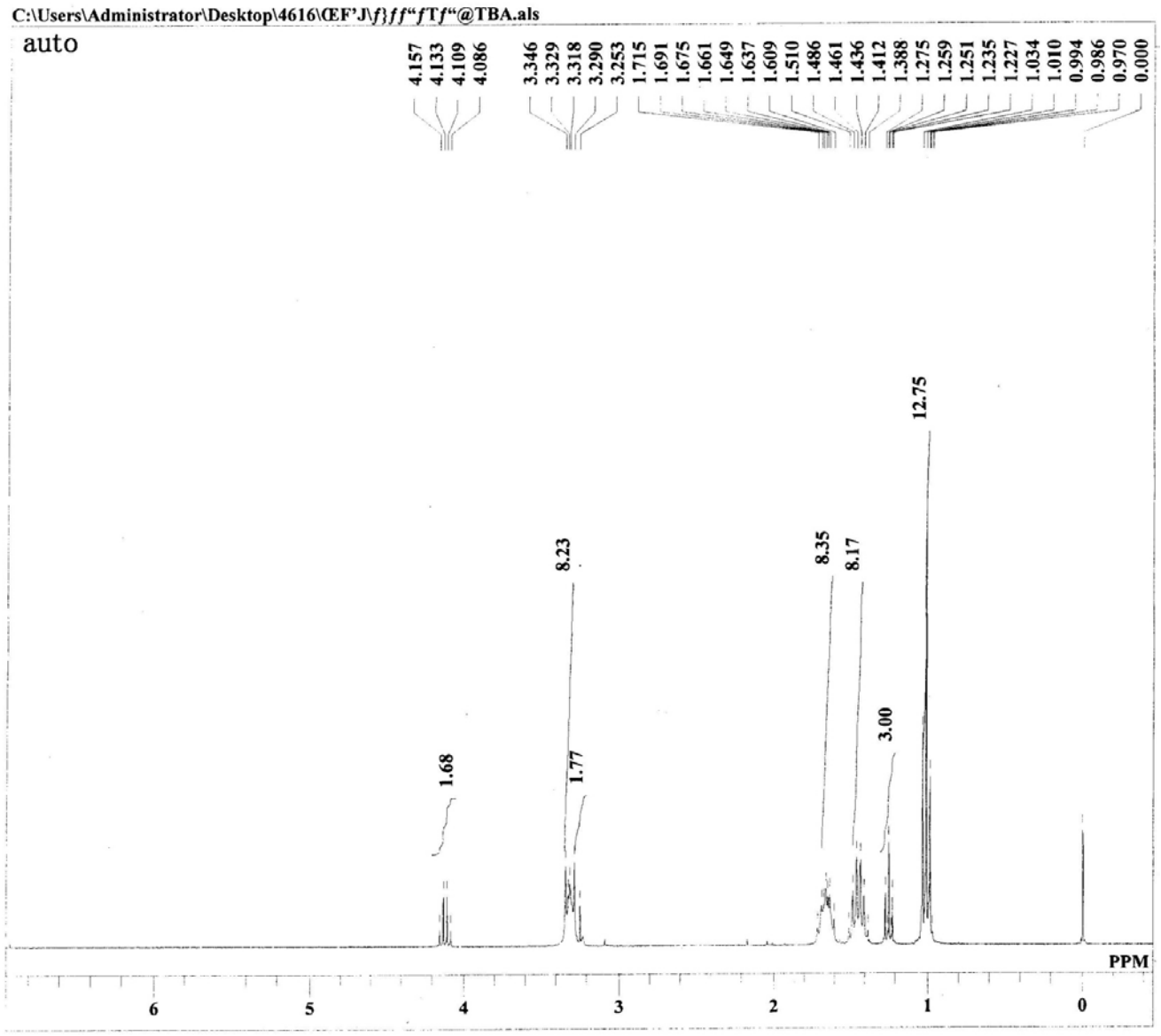

NC
CO2
N

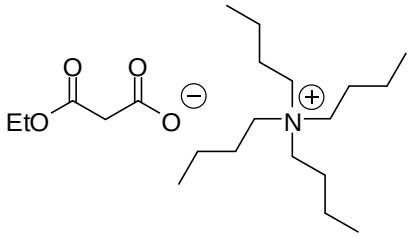
**4a** $^{1}$H NMR


C:\Users\Administrator\Desktop\h1110-11(kumagai).als
auto
165.134
118.753
77.427
77.206
77.000
76.581
58.577
23.771
19.529
13.462
PPM
150
125
100
75
50
25

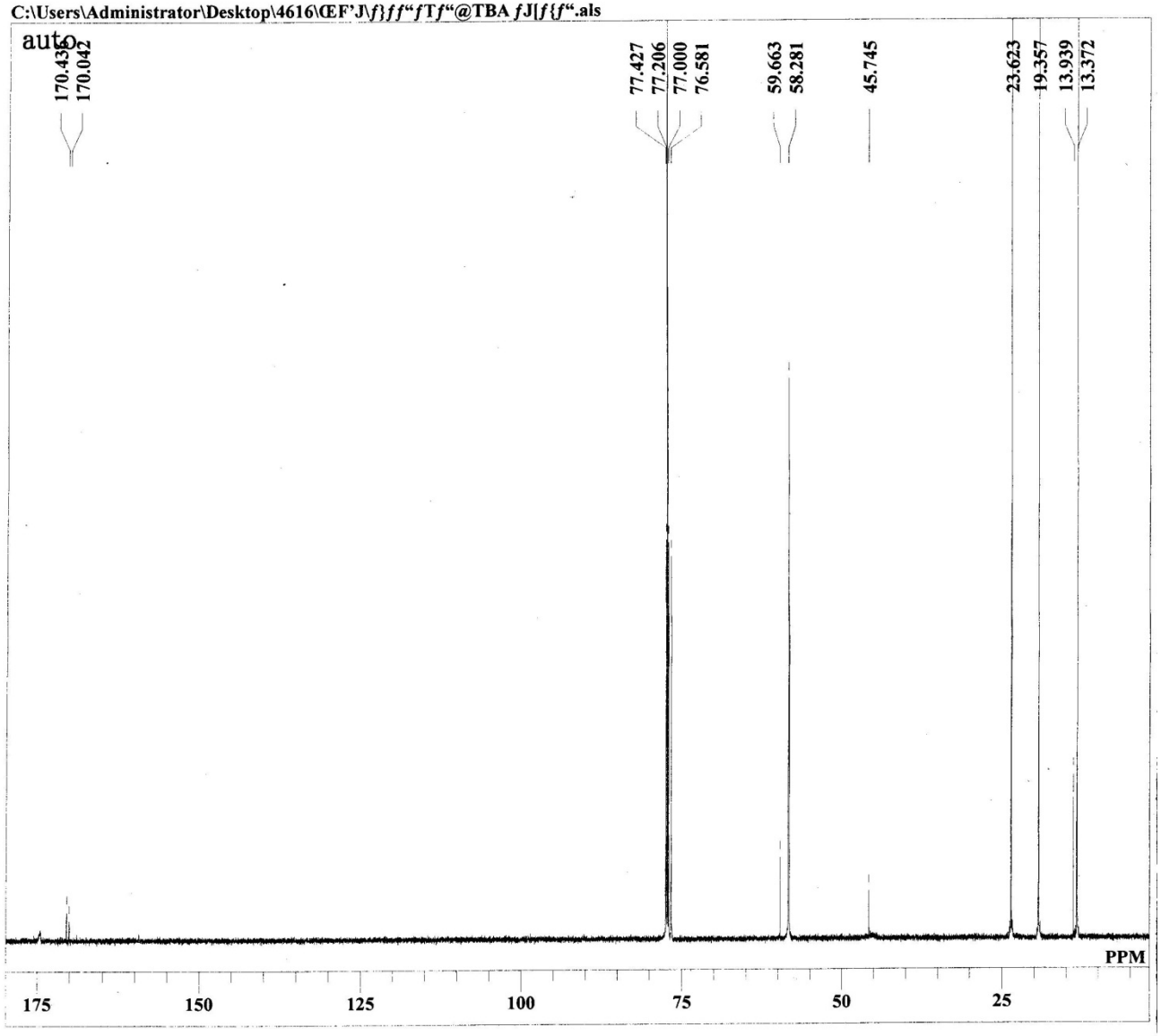

NC
CO2
N

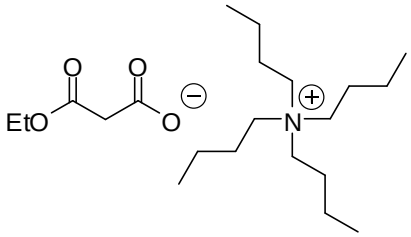
**4a** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒ}ƒƒ"ƒTƒ"@TBA.als
auto
4.157
4.133
4.109
4.086
3.346
3.329
3.318
3.290
3.253
1.715
1.691
1.675
1.661
1.649
1.637
1.609
1.510
1.486
1.461
1.436
1.412
1.388
1.275
1.259
1.251
1.235
1.227
1.034
1.010
0.994
0.986
0.970
0.000
1.68
8.23
1.77
8.35
8.17
3.00
12.75
PPM
6
5
4
3
2
1
0

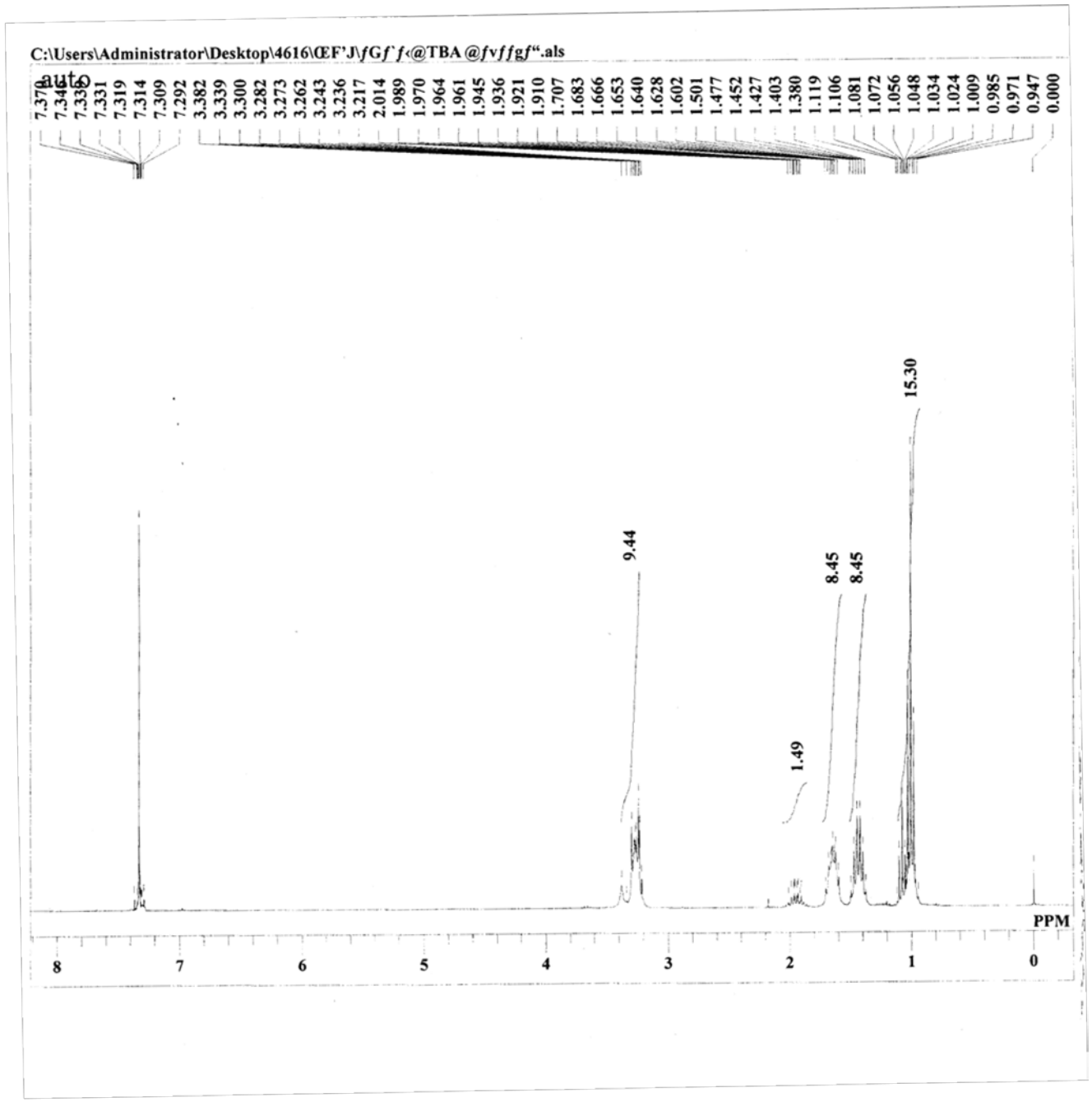

O
O
EtO
O
N

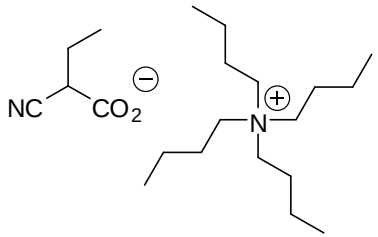
**4b** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒ}ƒƒ"ƒTƒ"@TBA ƒJ[ƒ{ƒ".als
auto
170.436
170.042
77.427
77.206
77.000
76.581
59.663
58.281
45.745
23.623
19.357
13.939
13.372
PPM
175
150
125
100
75
50
25

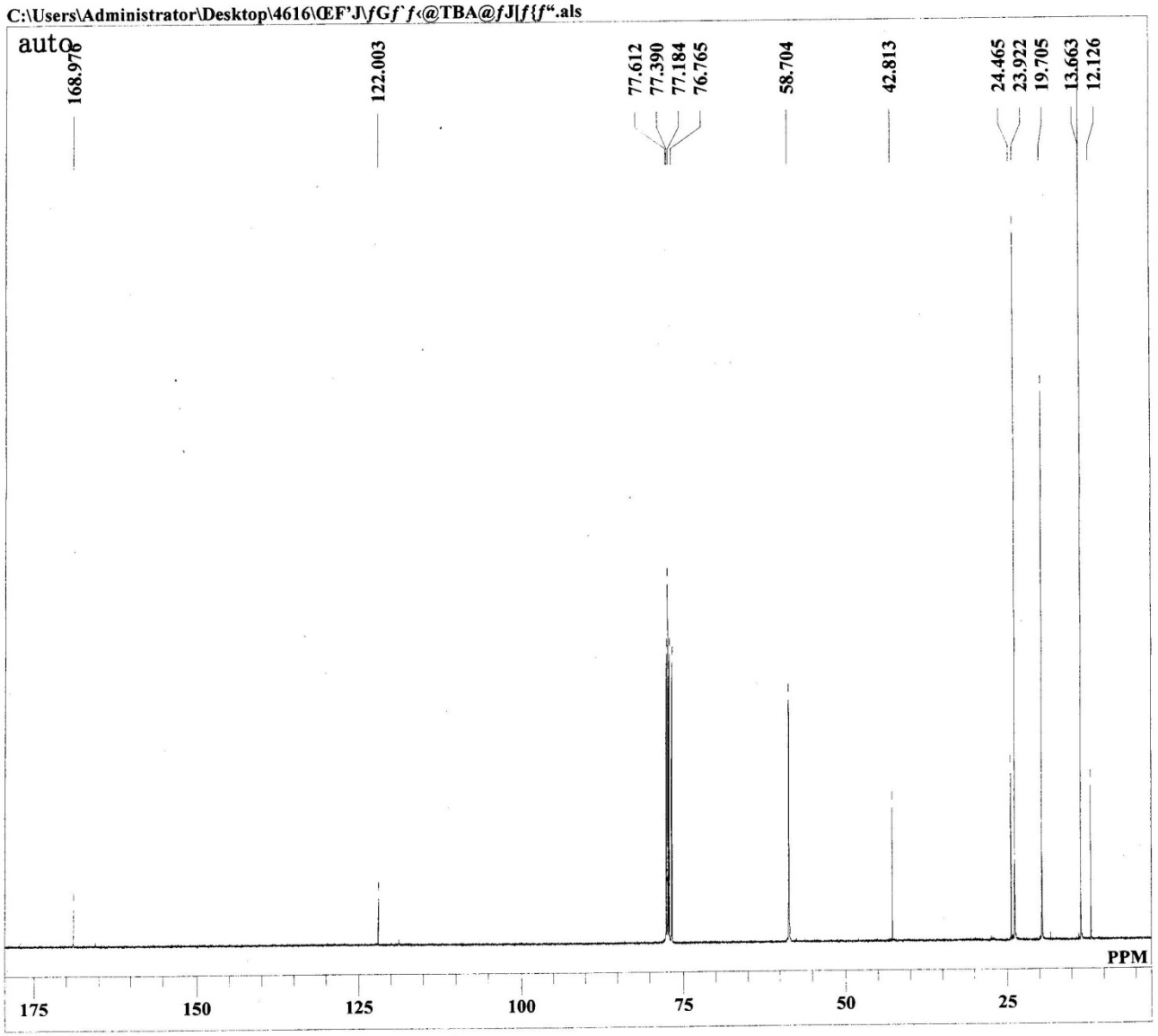

O
O
EtO
O
N

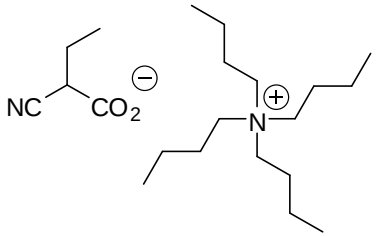
**4b** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\fGf`f‹@TBA @fvffgf".als
auto
7.378 7.346 7.338 7.331 7.319 7.314 7.309 7.292 3.382 3.339 3.300 3.282 3.273 3.262 3.243 3.236 3.217 2.014 1.989 1.970 1.964 1.961 1.945 1.936 1.921 1.910 1.707 1.683 1.666 1.653 1.640 1.628 1.602 1.501 1.477 1.452 1.427 1.403 1.380 1.119 1.106 1.081 1.072 1.056 1.048 1.034 1.024 1.009 0.985 0.971 0.947 0.000
9.44
8.45
8.45
1.49
15.30
PPM
8
7
6
5
4
3
2
1
0

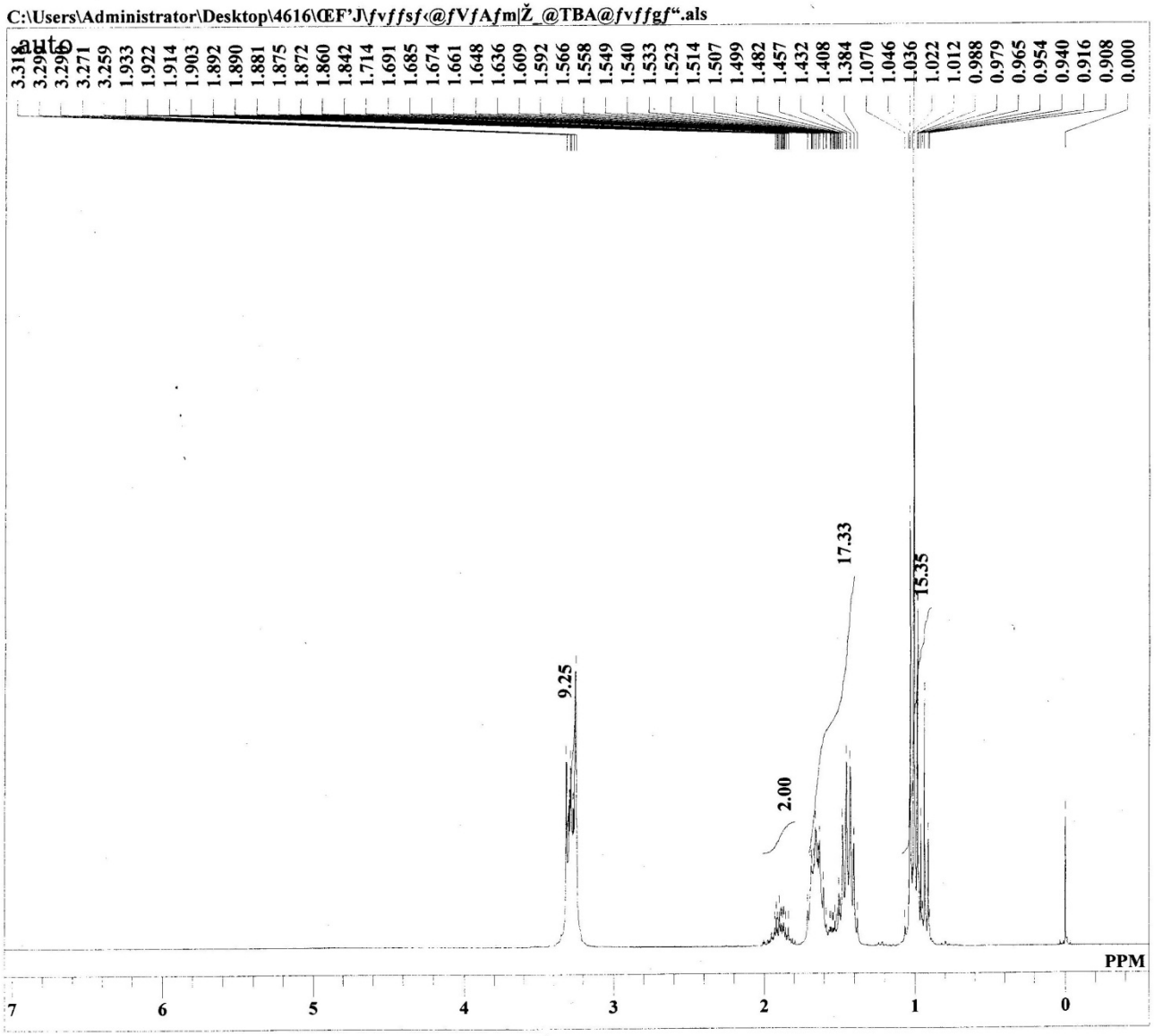

NC
CO2
N

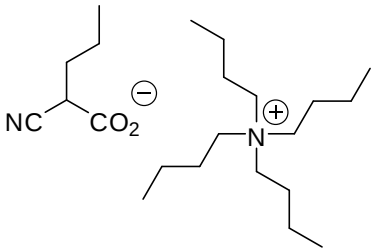
**4c** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒGƒ`ƒ‹@TBA@ƒJ[ƒfƒ“.als
auto
168.978
122.003
77.612
77.390
77.184
76.765
58.704
42.813
24.465
23.922
19.705
13.663
12.126
PPM
175
150
125
100
75
50
25

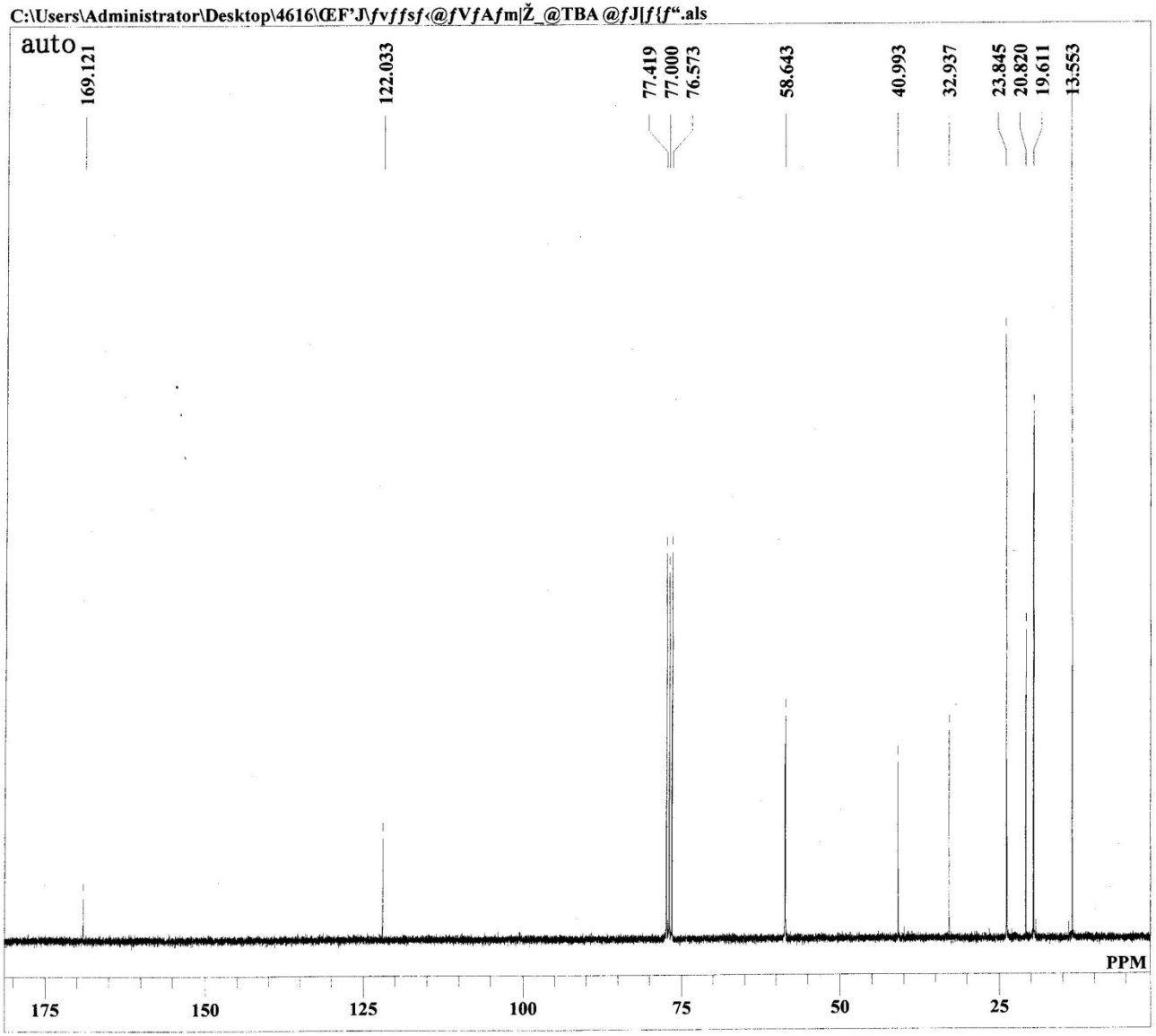

NC
CO2
N

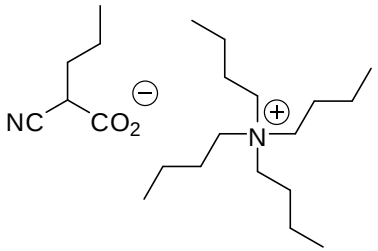
**4c** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒvƒƒsƒ‹@ƒVƒAƒm|Ž_@TBA@ƒvƒƒgf“.als
auto
3.318
3.296
3.271
3.259
1.933
1.922
1.914
1.903
1.892
1.890
1.881
1.875
1.872
1.860
1.842
1.714
1.691
1.685
1.674
1.661
1.648
1.636
1.609
1.592
1.566
1.558
1.549
1.540
1.533
1.523
1.514
1.507
1.499
1.482
1.457
1.432
1.408
1.384
1.070
1.046
1.036
1.022
1.012
0.988
0.979
0.965
0.954
0.940
0.916
0.908
0.000
9.25
2.00
17.33
15.35
PPM
7
6
5
4
3
2
1
0

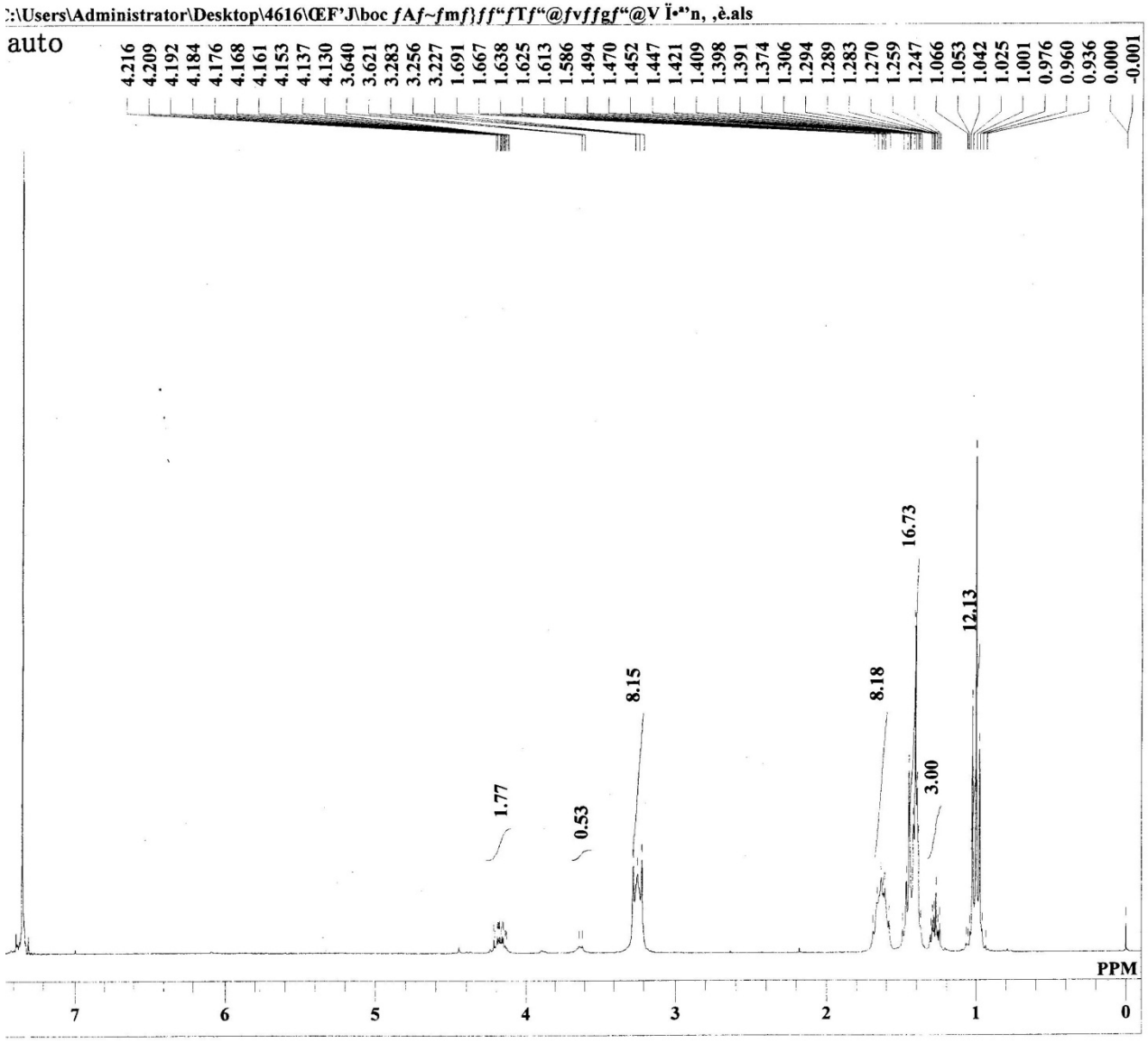

NC
CO2
N

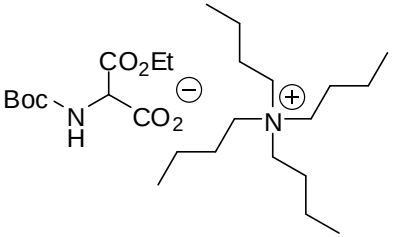
**4d** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒvƒfsf‹@fVfAfm|Ž_@TBA @fJ[f{f".als
auto
169.121
122.033
77.419
77.000
76.573
58.643
40.993
32.937
23.845
20.820
19.611
13.553
PPM
175
150
125
100
75
50
25

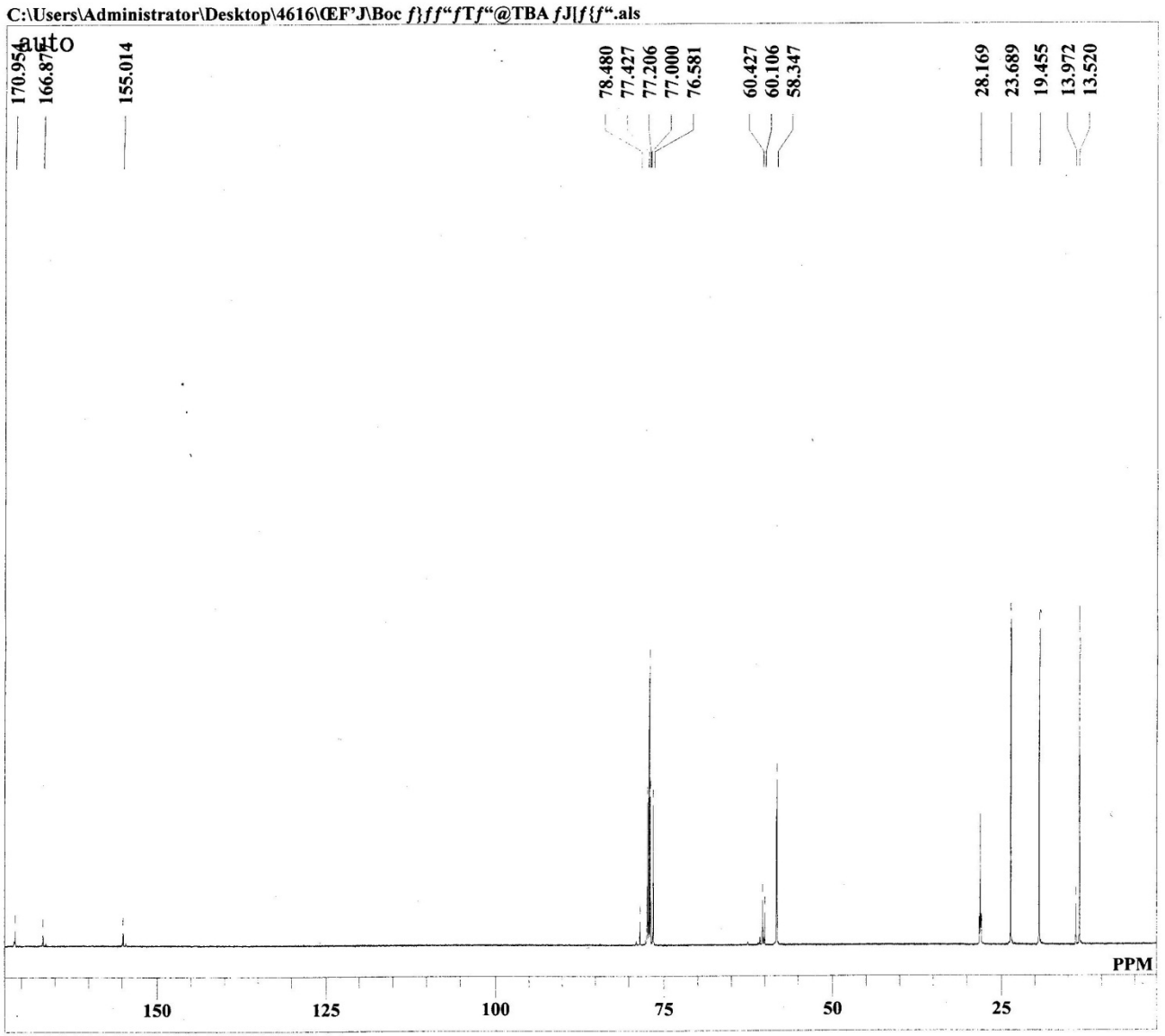

NC
CO2
N

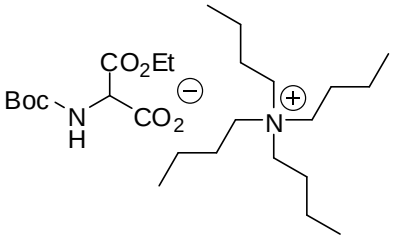
**4d** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\boc ƒAƒ~ƒmƒ}ƒƒ"ƒTƒ"@ƒvƒƒgƒ"@V Ï•"n, ,è.als
auto
4.216
4.209
4.192
4.184
4.176
4.168
4.161
4.153
4.137
4.130
3.640
3.621
3.283
3.256
3.227
1.691
1.667
1.638
1.625
1.613
1.586
1.494
1.470
1.452
1.447
1.421
1.409
1.398
1.391
1.374
1.306
1.294
1.289
1.283
1.270
1.259
1.247
1.066
1.053
1.042
1.025
1.001
0.976
0.960
0.936
0.000
-0.001
1.77
0.53
8.15
8.18
16.73
3.00
12.13
PPM
7
6
5
4
3
2
1
0

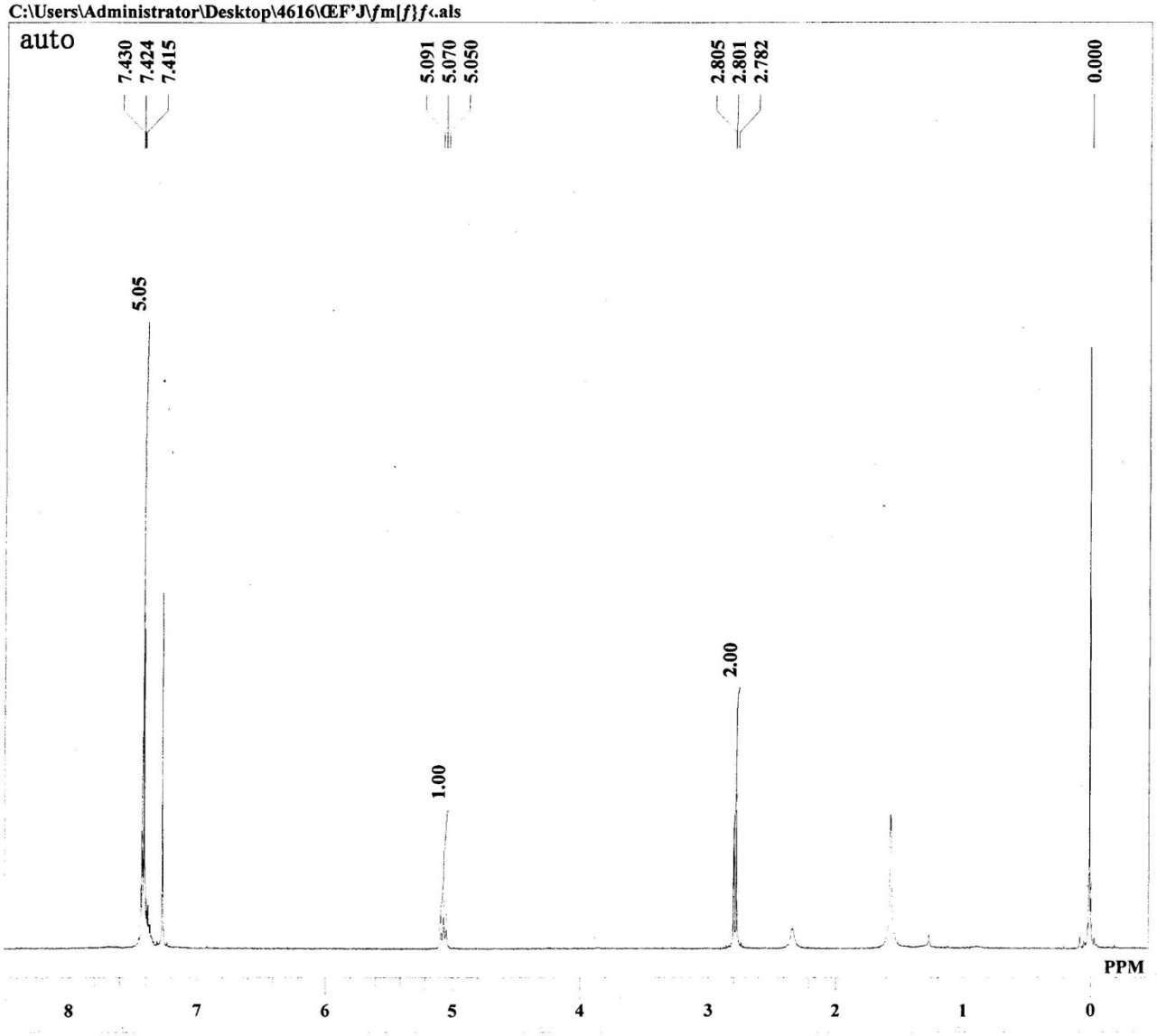

CO2Et
Boc
N
H
CO2
N

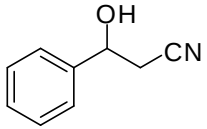
**4e** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\Boc ƒ}ƒƒ"ƒTƒ"@TBA ƒJ|ƒ{ƒ".als
auto
170.954
166.877
155.014
78.480
77.427
77.206
77.000
76.581
60.427
60.106
58.347
28.169
23.689
19.455
13.972
13.520
PPM
150
125
100
75
50
25

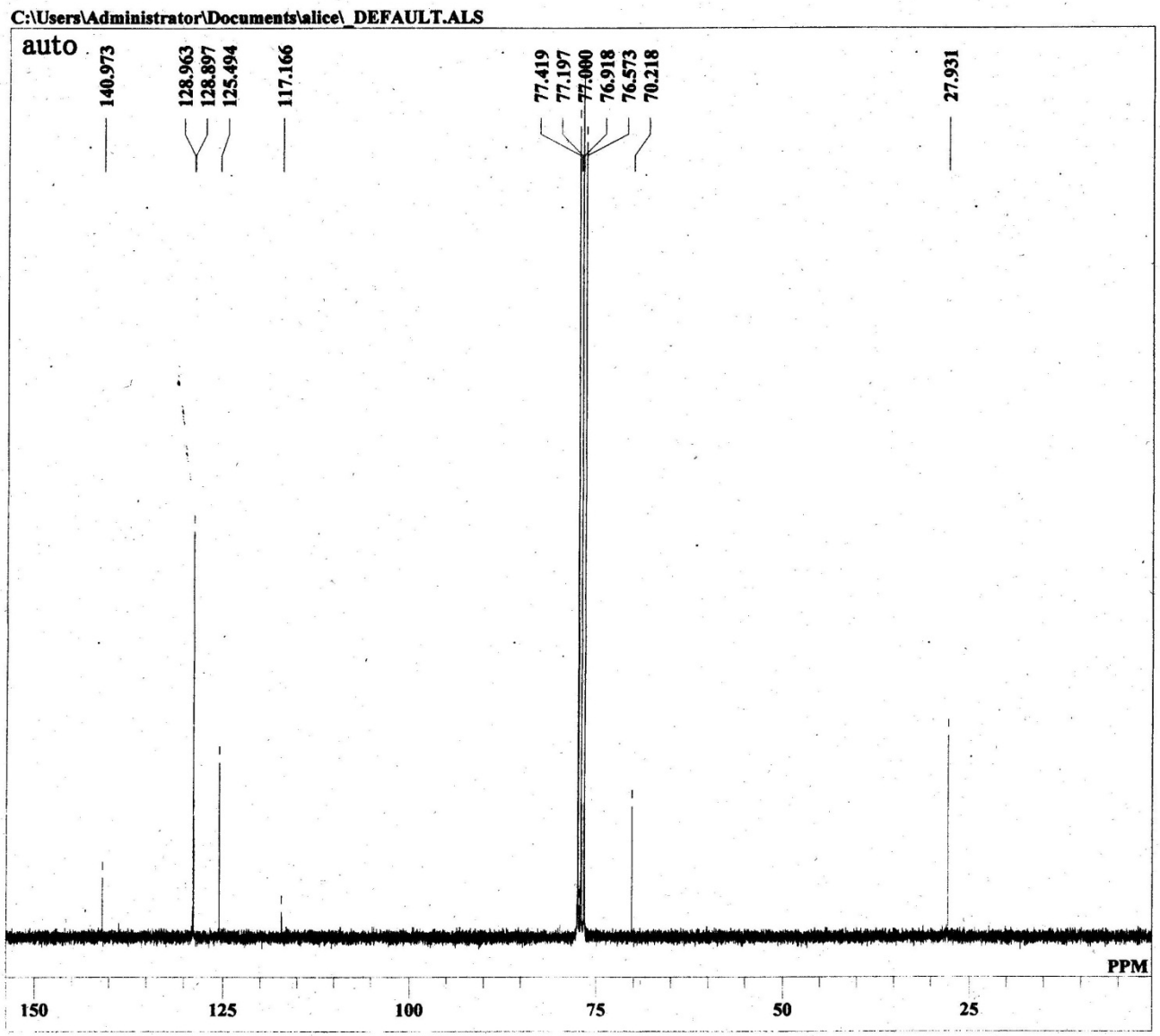

CO2Et
Boc
N
H
CO2
N

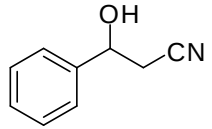
**4e** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\fm[f}fc.als
auto
7.430
7.424
7.415
5.091
5.070
5.050
2.805
2.801
2.782
0.000
5.05
1.00
2.00
PPM
8
7
6
5
4
3
2
1
0

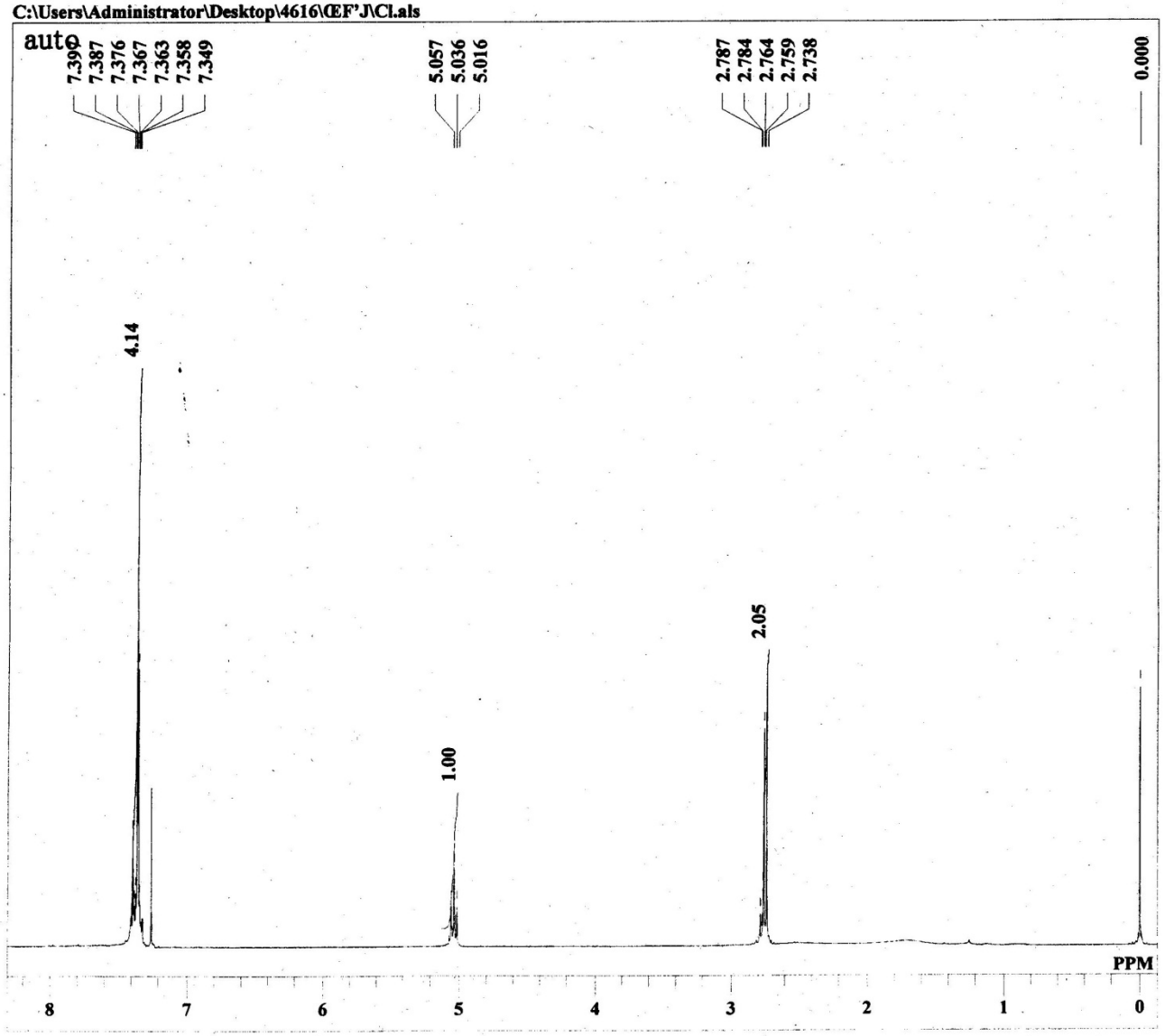

OH
CN

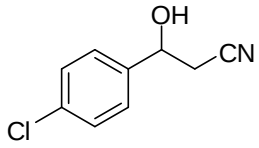
**6a** $^{1}$H NMR


C:\Users\Administrator\Documents\alice_DEFAULT.ALS
auto
140.973
128.963
128.897
125.494
117.166
77.419
77.197
77.000
76.918
76.573
70.218
27.931
PPM
150
125
100
75
50
25

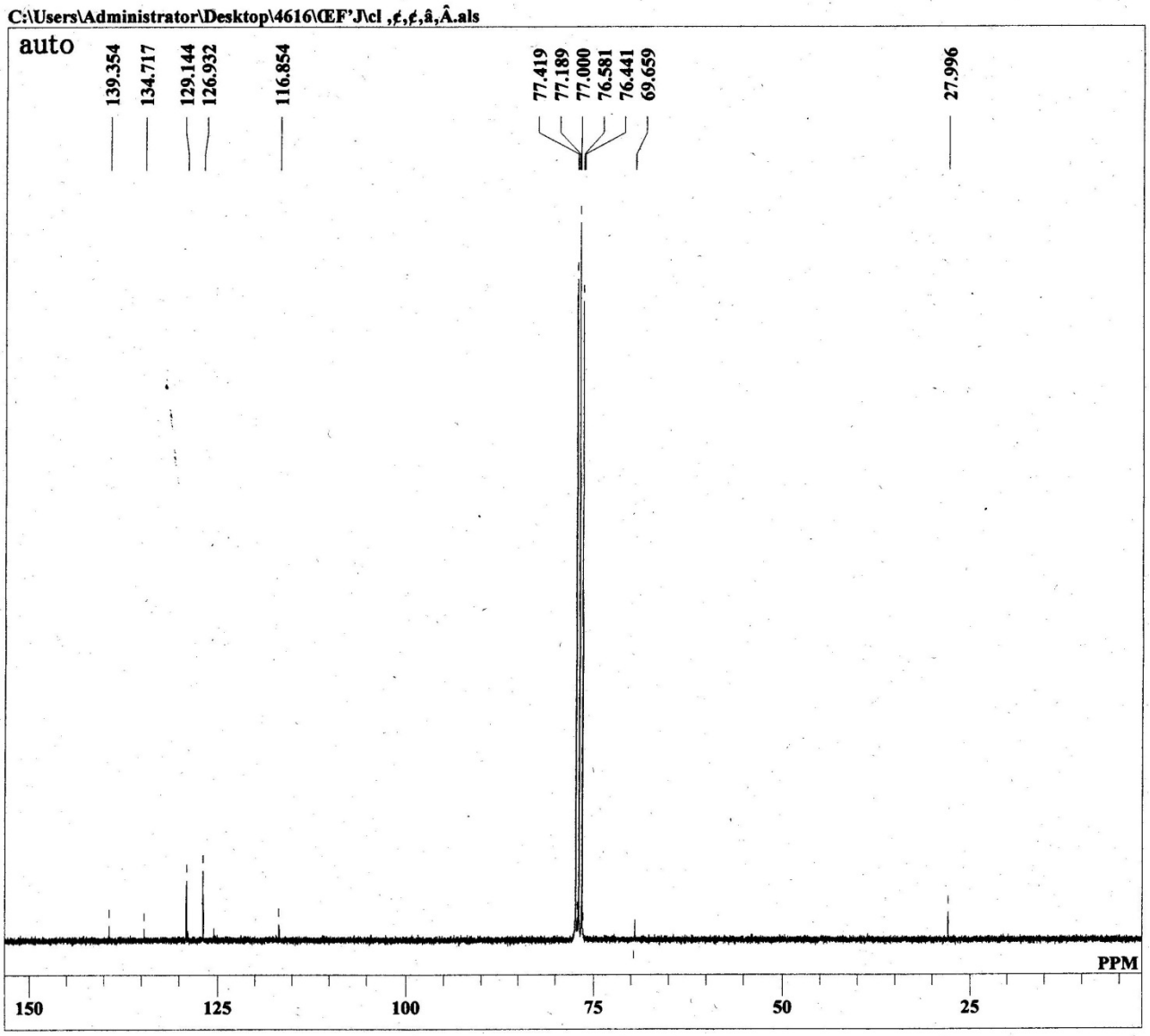

OH
CN

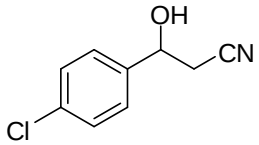
**6a** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\Cl.als
auto
7.390
7.387
7.376
7.367
7.363
7.358
7.349
5.057
5.036
5.016
2.787
2.784
2.764
2.759
2.738
0.000
4.14
1.00
2.05
PPM
8
7
6
5
4
3
2
1
0

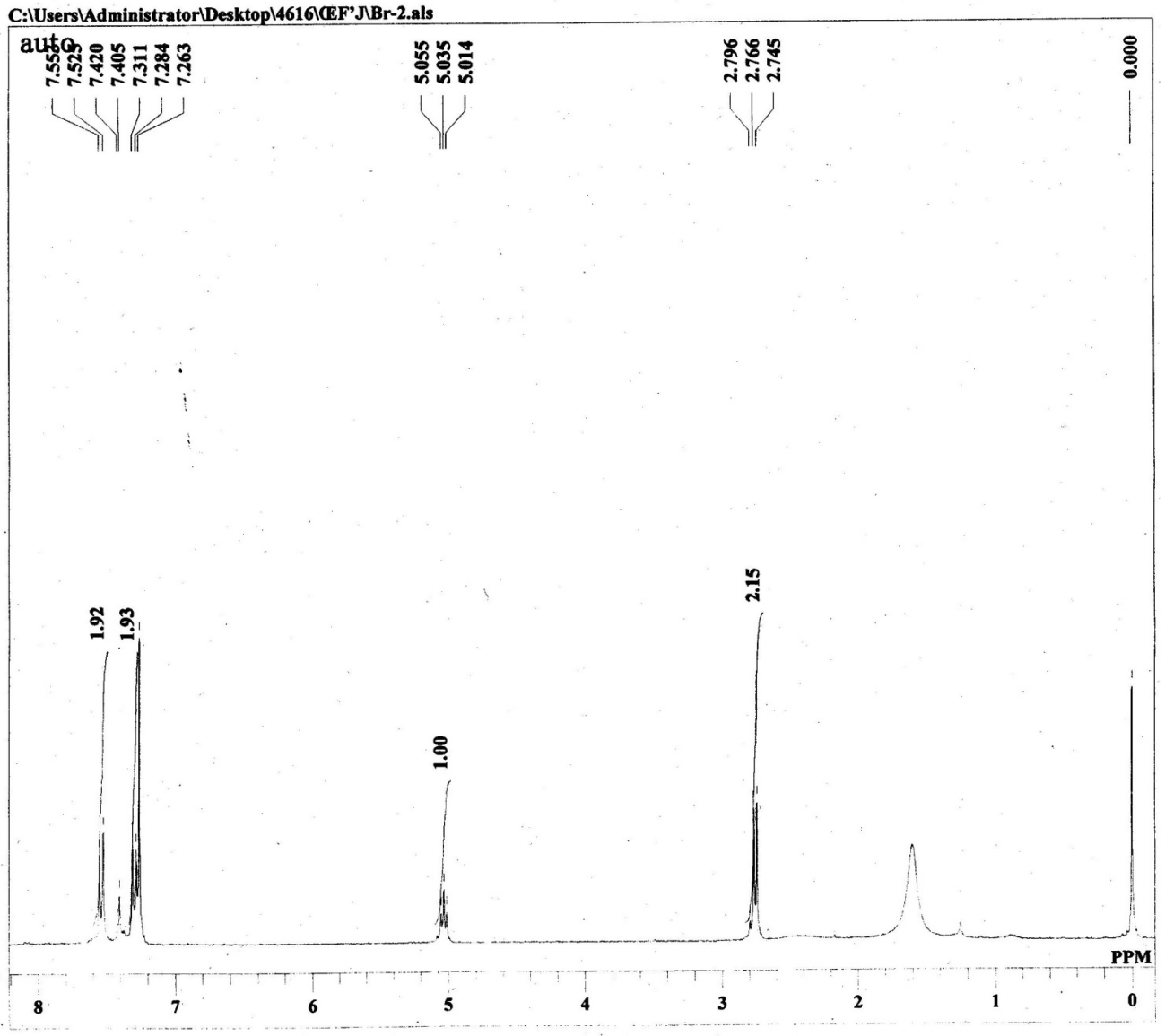

OH
CN
Cl

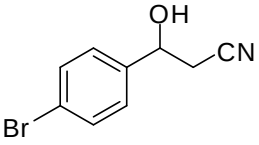
**6b** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\cl ,¢,¢,â,Â.als
auto
139.354
134.717
129.144
126.932
116.854
77.419
77.189
77.000
76.581
76.441
69.659
27.996
PPM
150
125
100
75
50
25

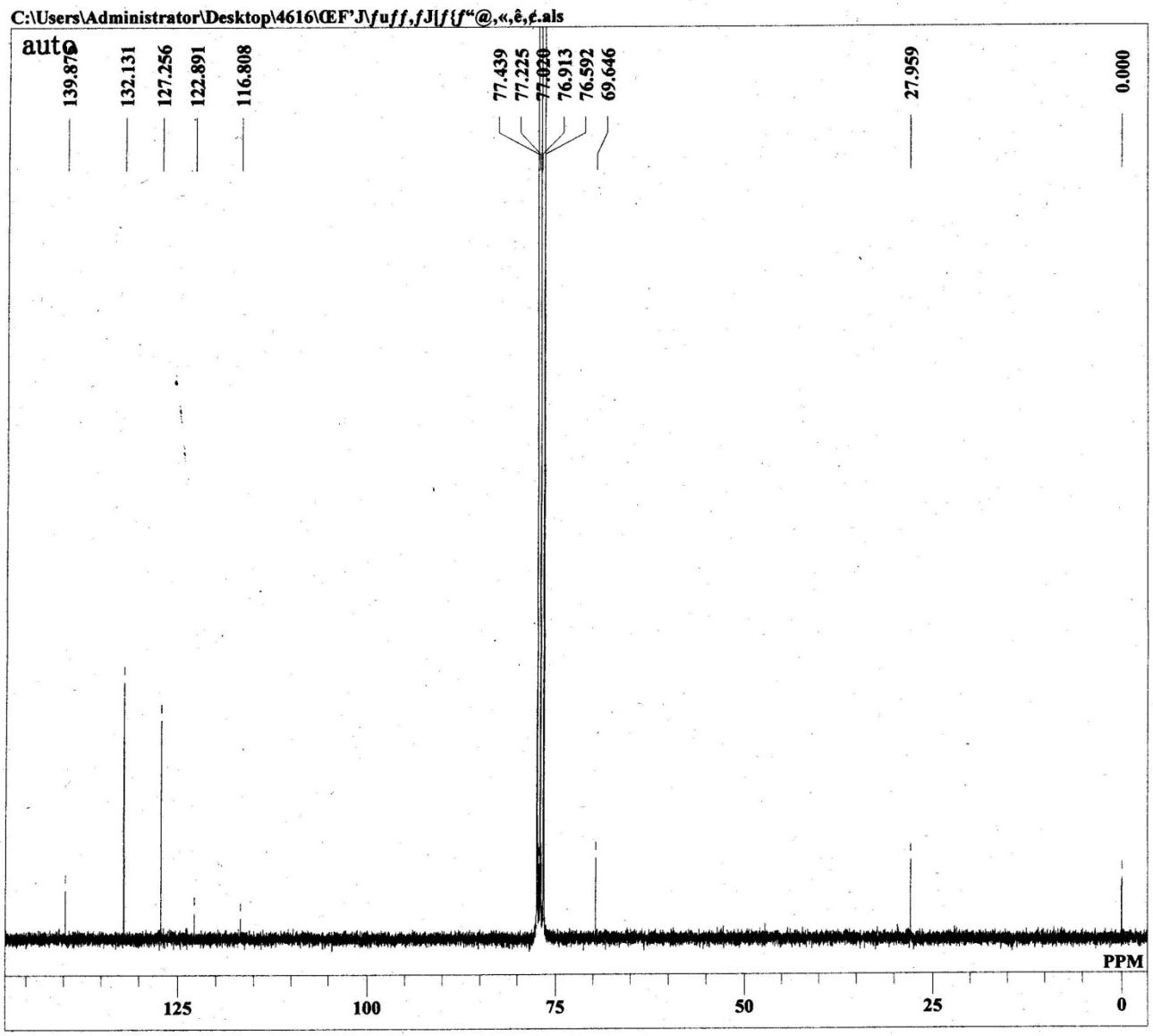

OH
CN
Cl

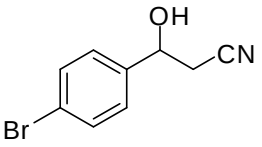
**6b** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\Br-2.als
auto
7.550
7.529
7.420
7.405
7.311
7.284
7.263
5.055
5.035
5.014
2.796
2.766
2.745
0.000
1.92
1.93
1.00
2.15
PPM
8
7
6
5
4
3
2
1
0

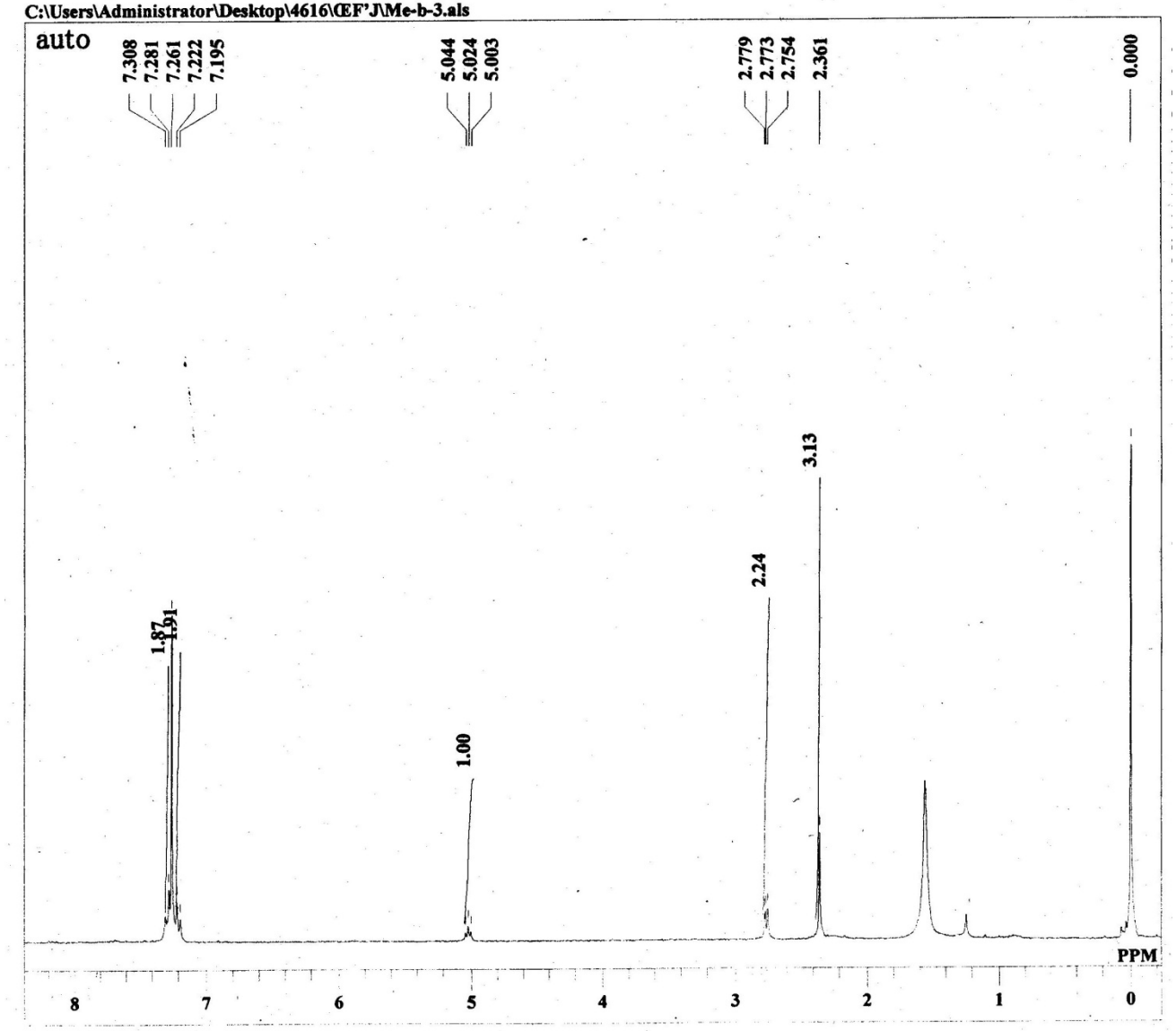

OH
CN
Br

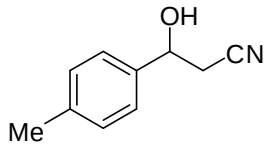
**6c** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\ƒuƒƒ,ƒJ|ƒƒƒ"@,«,ê,¢.als
auto
139.876
132.131
127.256
122.891
116.808
77.439
77.225
77.020
76.913
76.592
69.646
27.959
0.000
PPM
125
100
75
50
25
0

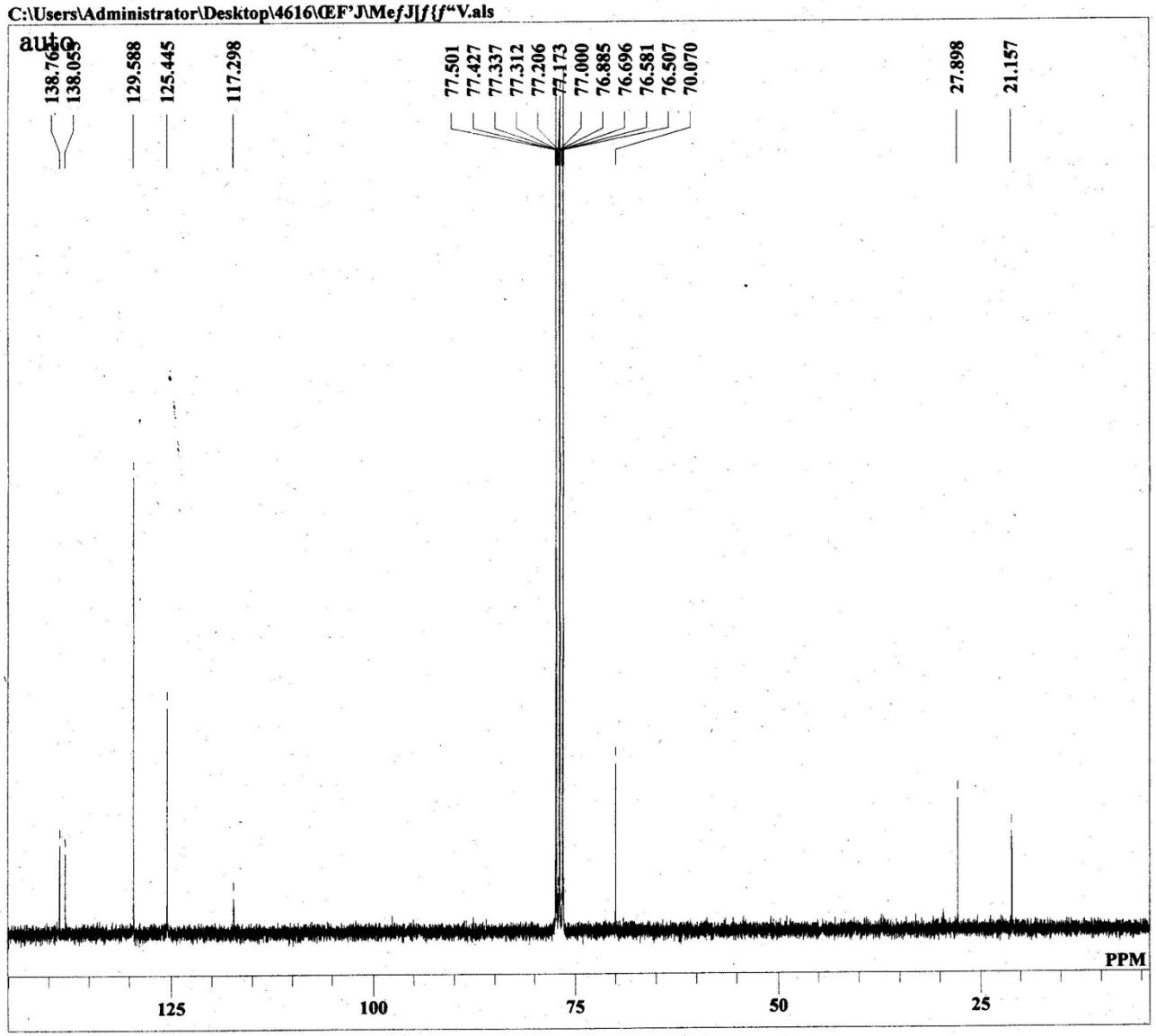

OH
CN
Br

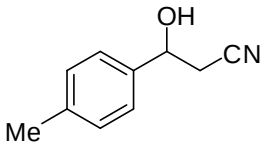
**6c** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\Me-b-3.als
auto
7.308
7.281
7.261
7.222
7.195
5.044
5.024
5.003
2.779
2.773
2.754
2.361
0.000
1.87
1.91
1.00
2.24
3.13
PPM
8
7
6
5
4
3
2
1
0

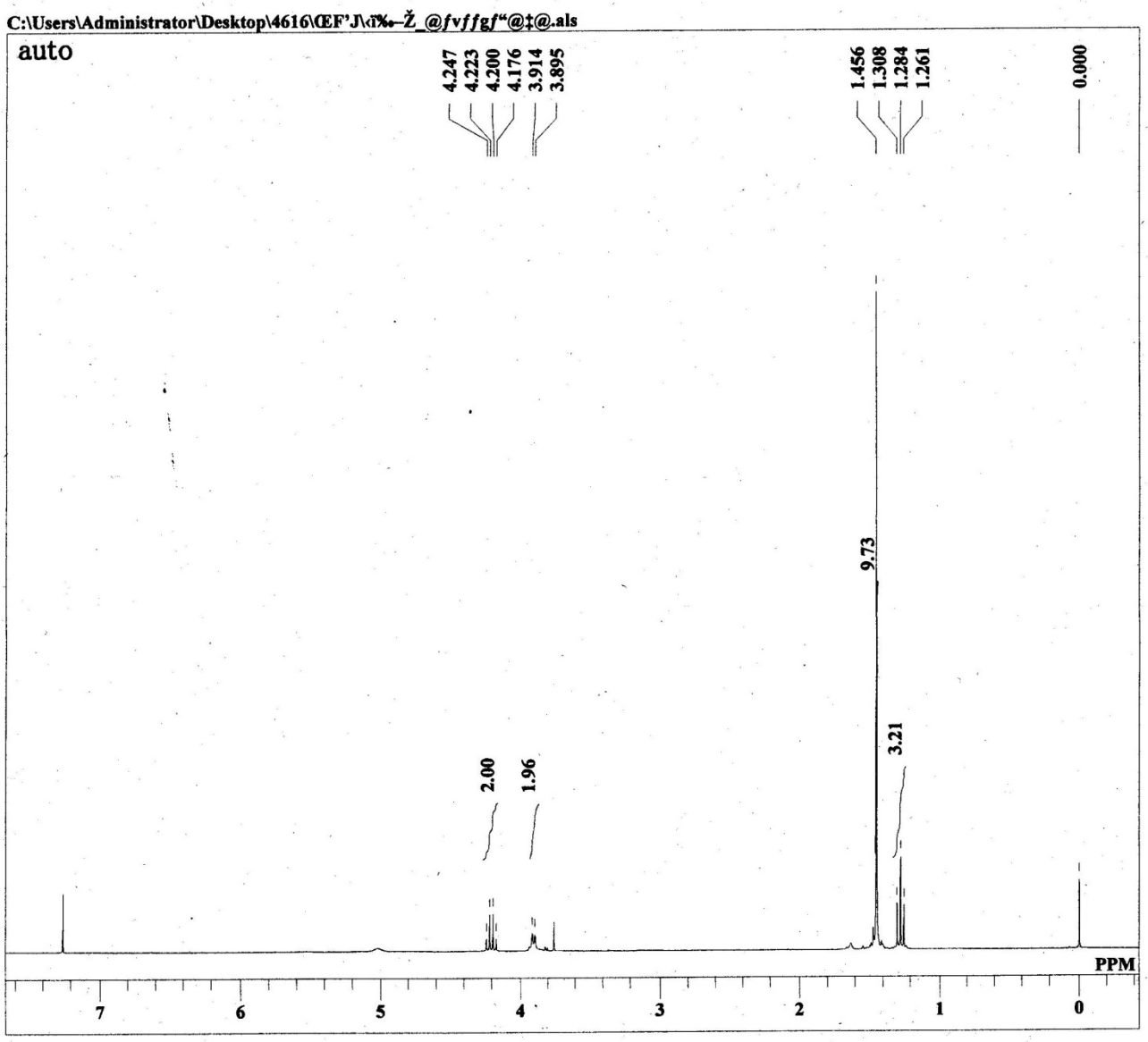

OH
CN
Me

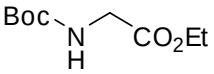
**6d** $^{1}$H NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\MefJ]ƒ{ƒ"V.als
auto
138.766
138.059
129.588
125.445
117.298
77.501
77.427
77.337
77.312
77.206
77.173
77.000
76.885
76.696
76.581
76.507
70.070
27.898
21.157
PPM
125
100
75
50
25

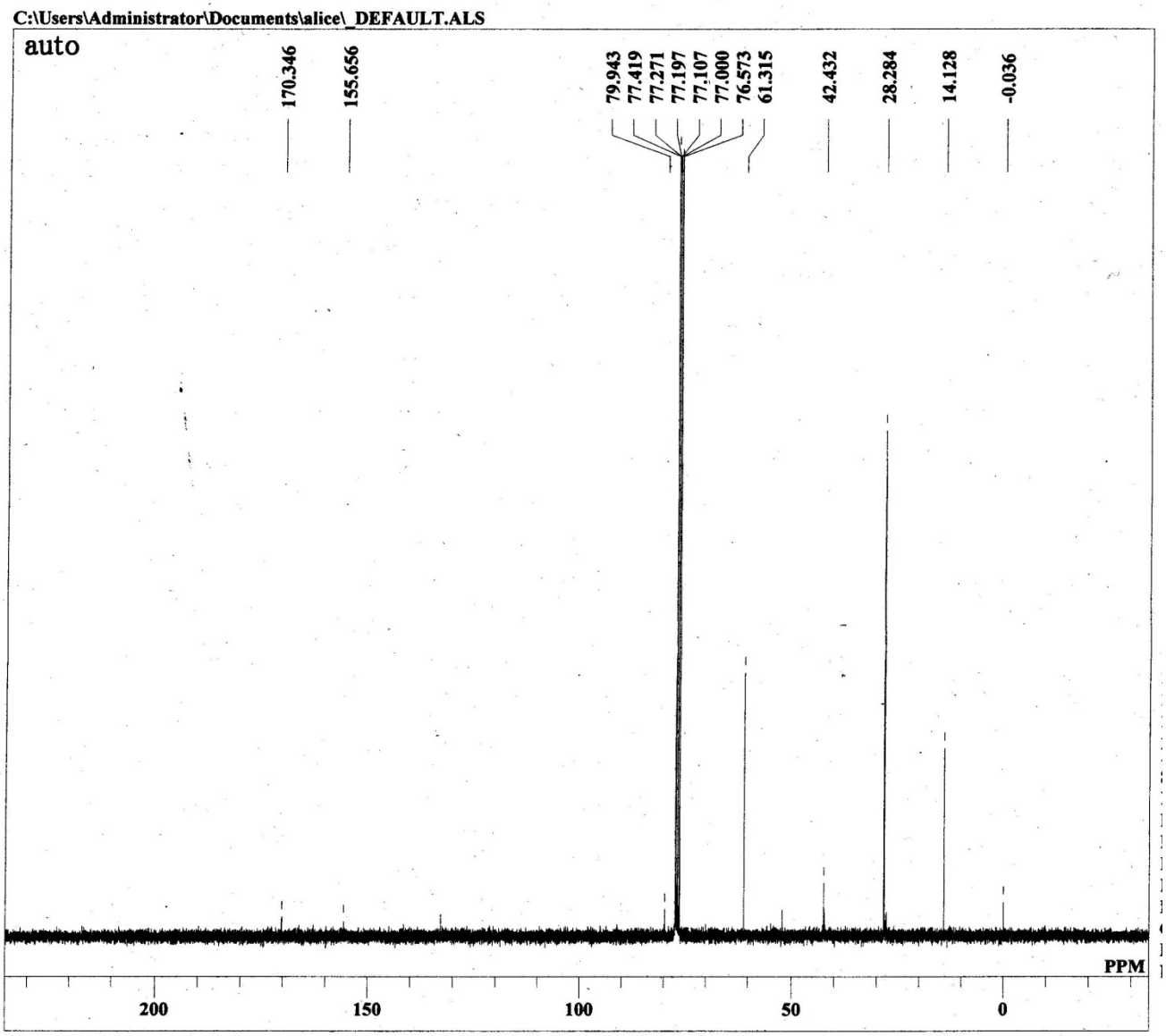

OH
CN
Me

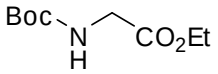
**6d** $^{13}$C NMR


C:\Users\Administrator\Desktop\4616\ŒF'J\‹ï‰–Ž_@ƒvƒfgƒ"@‡@.als
auto
4.247
4.223
4.200
4.176
3.914
3.895
1.456
1.308
1.284
1.261
0.000
9.73
3.21
2.00
1.96
PPM
7
6
5
4
3
2
1
0


Boc
N
H
CO2Et

**8** $^{1}$H NMR


C:\Users\Administrator\Documents\alice_DEFAULT.ALS
auto
170.346
155.656
79.943
77.419
77.271
77.197
77.107
77.000
76.573
61.315
42.432
28.284
14.128
-0.036
PPM
200
150
100
50
0


Boc
N
H
CO2Et

**8** $^{13}$C NMR