HETEROGENEOUS CATALYTIC HYDROGENATION OF UNPROTECTED INDOLES IN WATER: A GREEN SOLUTION TO A LONG-STANDING CHALLENGE

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MATERIALS: All the indoles and acid additives were purchased from Aldrich and used without any purification. Pt/C was purchased from Acros Organics and Pt/Al_2O_3 was purchased from Engelhard. $CDCl_3$ used as a solvent (99.8%) for NMR studies was an Aldrich product. Other solvents used in synthesis with minimum purity of 99.5% were Fisher products. Water used as a solvent in the synthesis was deionized water.

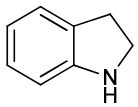
NMR ANALYSIS: The ^{1}H and ^{13}C spectra were obtained on a 300 MHz Varian NMR spectrometer, in $CDCl_3$ with tetramethylsilane as internal standards or the residual solvent signals. The temperature was 25 °C (accuracy ±1 °C) and controlled by the Varian control unit.

GC-MS ANALYSIS: The mass spectrometric identification of the products have been carried out by an Agilent 6850 gas chromatograph- 5973 mass spectrometer system (70 eV electron impact ionization) using a 30m long DB-5 type column (J&W Scientific).

MELTING POINTS: All the melting points are uncorrected and recorded on a MEL-TEMP apparatus.

Representative procedure for the hydrogenation of indoles to indolines: The hydrogenations were performed in a Berghof HR-100 autoclave using a Teflon liner at room temperature (25°C). Pt/C (30 mg), *p*-TSA·H_2O (228 mg, 1.2 mmol), indole (117 mg, 1 mmol) and deionized water (5 mL) were charged to the Teflon liner. Then the autoclave was flushed with hydrogen three times, filled to a pressure of 30 bar and stirred (1000 rpm) for 3 h. After the completion of the reaction, the catalyst was removed by filtration. The filtrate was quenched with 1 mol % aqueous NaOH solution by adjusting the pH to 8. The aqueous layer was extracted with two portions of 15 mL CH_2Cl_2. The CH_2Cl_2 extracts were combined and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography.

4. Indoline



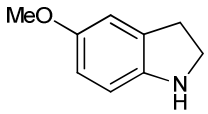
Colorless oil, R_f = 0.30 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.21 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.59 (t, *J* = 8.4 Hz, 2H), 3.10 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 151.4, 129.1, 126.9, 124.4, 118.4, 109.2, 47.1, 29.6.

MS-C_8H_9N (119) m/z (%): 119 (M^+, 100), 91 (21), 77 (2), 65 (6), 58 (7).

10. 5-Methoxyindoline



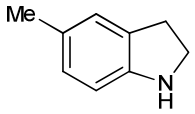
Light brown oil, R_f = 0.25 (30 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 6.78 (s, 1H), 6.60 (m, 2H), 3.75 (s, 3H), 3.50 (t, *J* = 8.4 Hz, 2H), 3.00 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 153.6, 145.5, 131.3, 112.2, 111.6, 110.2, 56.0, 47.9, 30.6.

MS-$C_9H_{11}NO$ (149) m/z (%): 149 (M^+, 54), 134 (100), 117 (3), 104 (9), 77 (7).

11. 5-Methylindoline



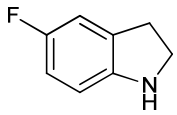
Light brown oil, R_f = 0.25 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 6.93 (s, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 3.47 (t, *J* = 8.1 Hz, 2H), 2.95 (t, *J* = 8.1 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 149.4, 129.9, 128.2, 127.7, 125.6, 109.6, 47.8, 30.2, 21.0.

MS-$C_9H_{11}N$ (133) m/z (%): 133 (M^+, 100), 117 (28), 103 (5), 77 (9), 65 (7).

12. 5-Fluoroindoline



Colorless oil, R_f = 0.25 (20 % EtOAc in hexane)

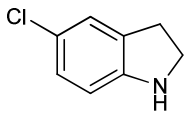
^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 6.84 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.70 (dt, *J* = 9.0, 2.7 Hz, 1H), 6.54 (dd, *J* = 8.1, 4.2 Hz, 1H), 3.64 (bs, 1H), 3.55 (t, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 158.5, 155.3, 147.4, 113.1, 112.8, 112.1, 111.8, 109.5, 109.4, 47.8, 30.1.

^{19}F NMR (282.4 MHz, $CDCl_3$), δ(ppm) −126.4

MS-C_8H_8FN (137) m/z (%): 137 (M^+, 100), 116 (3), 109 (33), 83 (8), 67 (7).

13. 5-Chloroindoline



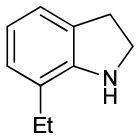
Light brown oil, R_f = 0.27 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.04 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.72 (bs, 1H), 3.54 (t, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 150.1, 131.2, 126.8, 124.7, 122.9, 109.8, 47.5, 29.6.

MS-C_8H_8ClN (153) m/z (%): 153 (M^+, 100), 125 (7), 117 (77), 89 (23), 58 (9).

14. 7-Ethylindoline



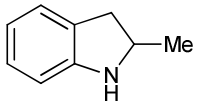
Brown oil, R_f = 0.33 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.90 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 3.63 (t, *J* = 8.1 Hz, 2H), 3.55 (bs, 1H), 3.12 (t, *J* = 8.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 149.3, 128.7, 125.9, 124.8, 122.0, 118.8, 47.1, 29.9, 24.0, 13.1.

MS-$C_{10}H_{13}N$ (147) m/z (%): 147 (M^+, 63), 132 (100), 117 (24), 105 (7), 91 (6).

15. 2-Methylindoline



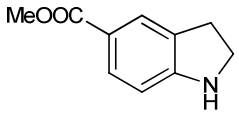
Light brown oil, R_f = 0.40 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.12 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.02 (m, 1H), 3.60 (bs, 1H), 3.18 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.67 (dd, *J* = 15.3, 7.8 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 151.1, 129.1, 127.4, 124.9, 118.7, 109.3, 55.4, 37.9, 22.4.

MS-$C_9H_{11}N$ (133) m/z (%): 133 (M^+, 33), 118 (100), 91 (17), 77 (4), 65 (3).

16. Methyl indoline-5-carboxylate



Light orange solid, R_f = 0.20 (20 % EtOAc in hexane)

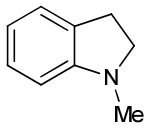
M.P.: 67-69 °C

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.76 (m, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 3.65 (t, *J* = 8.4 Hz, 2H), 3.07 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 199.6, 157.4, 130.8, 129.1, 126.3, 107.5, 100.2, 51.7, 47.4, 28.9.

MS-$C_{10}H_{11}NO_2$ (177) m/z (%): 177 (M^+, 82), 146 (100), 118 (27), 89 (12), 72 (6).

17. 1-methylindoline



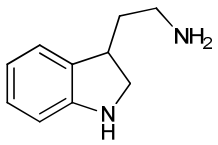
Brown oil, R_f = 0.25 (10 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.07 (m, 2H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 3.27 (t, *J* = 8.4 Hz, 2H), 2.92 (t, *J* = 8.4 Hz, 2H), 2.74 (s, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 153.3, 130.2, 127.2, 124.1, 117.6, 107.1, 56.0, 36.2, 28.6.

MS-$C_9H_{11}N$ (133) m/z (%): 133 (M^+, 100), 117 (41), 103 (4), 91 (10), 77 (6).

18. 2-(Indolin-3-yl)ethanamine



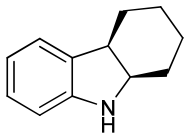
Light brown oil, R_f = 0.50 (5 % MeOH in DCM)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.08 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.67 (t, *J* = 8.7 Hz, 1H), 3.32 (m, 1H), 3.20 (t, *J* = 8.4 Hz, 1H), 2.80 (bs, 2H), 1.96 (m, 2H), 1.70 (m, 2H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 151.4, 132.8, 127.6, 123.9, 118.8, 109.7, 53.6, 40.4, 39.9, 38.4.

MS-$C_{10}H_{14}N_2$ (162) m/z (%): 162 (M^+, 30), 145 (19), 130 (50), 117 (100), 91 (20).

19. (±)-*cis*-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole



White solid, R_f = 0.38 (20 % EtOAc in hexane)

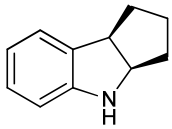
M.P. : 93-94°C

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.09 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 3.73 (q, *J* = 6.6 Hz, 1H), 3.65 (bs, 1H), 3.10 (q, *J* = 6.6 Hz, 1H), 1.76 (m, 2H), 1.56 (m, 3H), 1.39 (m, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 150.7, 133.4, 126.9, 123.1, 118.7, 110.1, 59.6, 40.8, 29.1, 26.9, 22.4, 21.6.

MS-$C_{12}H_{15}N$ (173) m/z (%): 173 (M^+, 30), 144 (9), 130 (100), 117 (14), 90 (5).

20. (±)-*cis*-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole



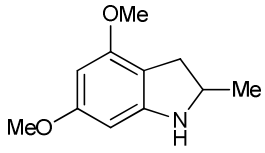
Colorless oil, R_f = 0.25 (10 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.03 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.66 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 4.34 (m, 1H), 3.76 (dt, *J* = 6.6, 2.1 Hz, 1H), 1.94 (m, 2H), 1.70 (m, 4H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 151.3, 133.3, 127.2, 124.4, 118.2, 108.3, 63.2, 47.1,36.8, 34.8, 24.3.

MS-$C_{11}H_{13}N$ (159) m/z (%): 159 (M^+, 28), 130 (100), 117 (10), 89 (5), 77 (4).

21. 4,6-dimethoxy-2-methylindoline



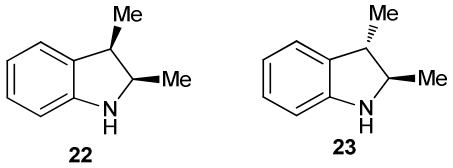
Light brown oil, R_f = 0.25 (20 % EtOAc in hexane)

^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 5.90 (m, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.38 (m, 1H), 3.14 (dd, *J* = 8.7, 5.1, 1H), 1.26 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 161.2, 157.0, 153.1, 112.8, 89.3, 88.6, 55.5, 55.3, 55.0, 34.5, 19.0.

MS-$C_{11}H_{15}NO_2$ (193) m/z (%): 193 (M^+, 38), 178 (100), 163 (18), 147 (20), 132 (7).

22, 23. (±)-2,3-dimethylindoline



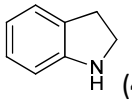
22:23 = 6:1

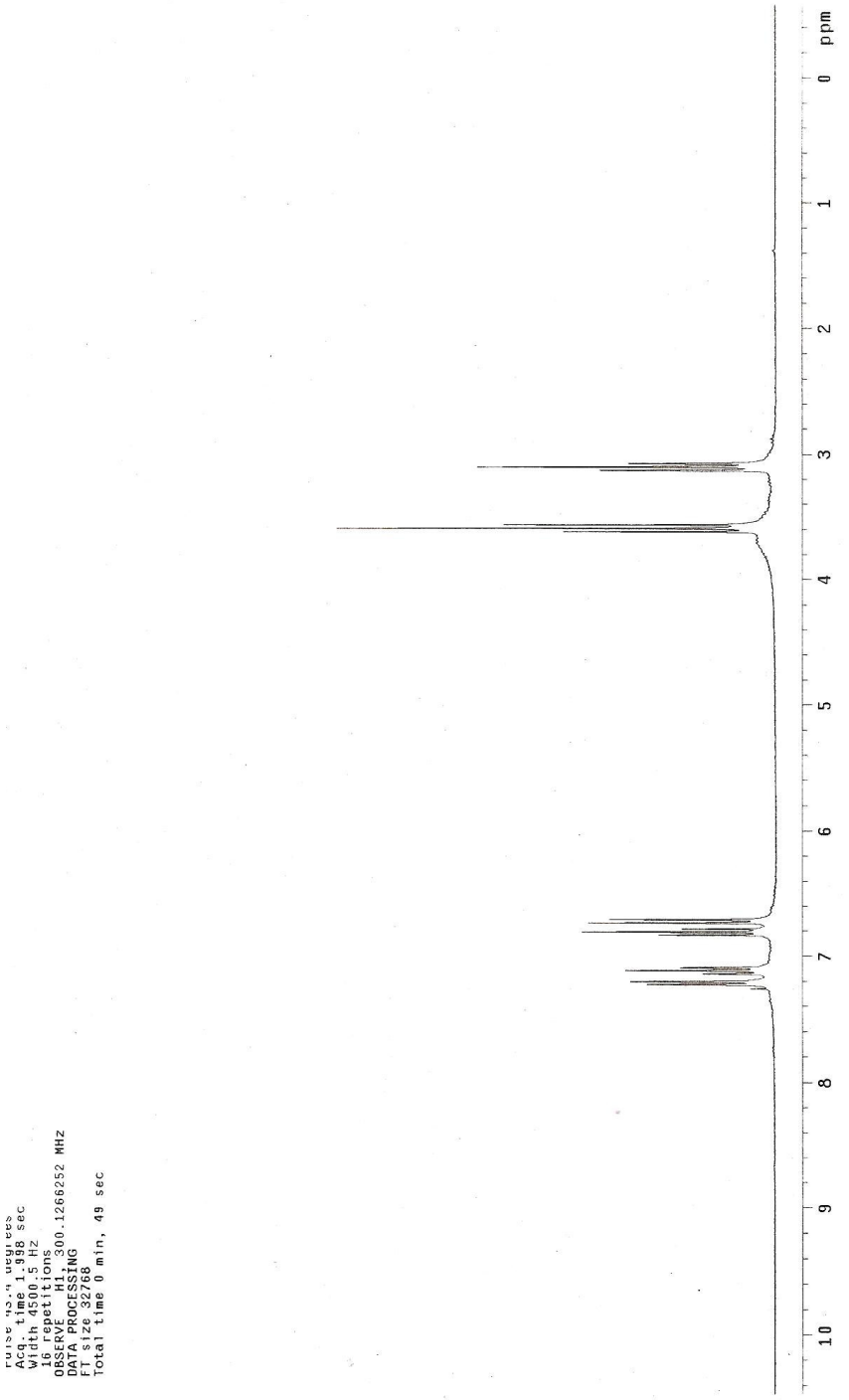
Brown oil, R_f = 0.40 (20 % EtOAc in hexane)

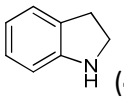
^{1}H NMR (300.128 MHz, $CDCl_3$), δ (ppm) 7.12 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.97 (m, 1H), 3.66 (bs, 1H), 3.50 (m, 1H, minor isomer), 3.31 (quin, *J* = 7.5 Hz, 1H), 2.86 (quin, *J* = 6.9 Hz, minor isomer), 1.36 (d, *J* = 2.1 Hz, 3H, minor isomer), 1.34 (d, *J* = 3.0 Hz, 3H, minor isomer), 1.22 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 1H).

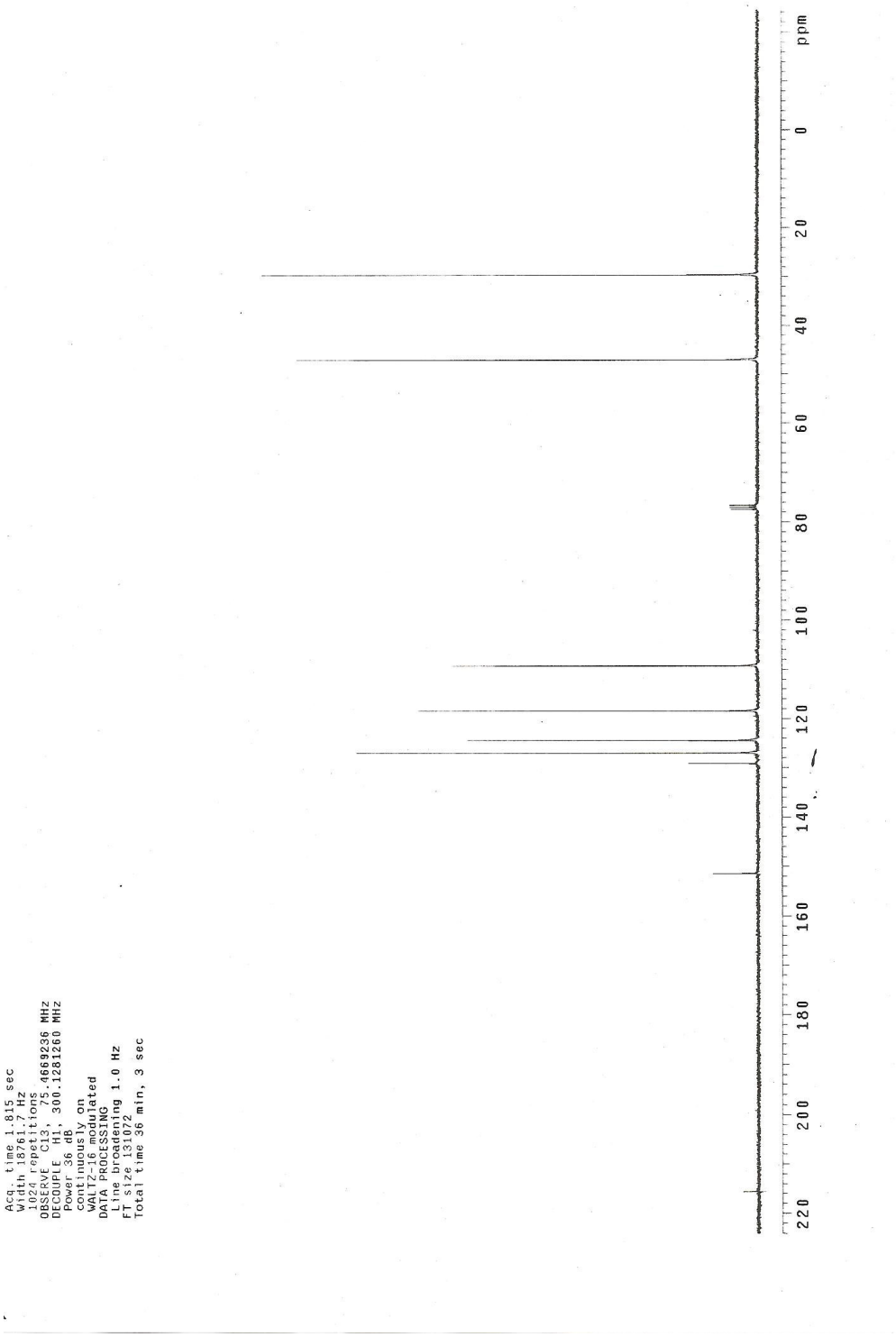
^{13}C NMR (75.474 MHz, $CDCl_3$), δ (ppm) 149.9, 134.1, 127.1, 127.1 (minor isomer), 123.6, 123.1 (minor isomer), 118.5, 118.4 (minor isomer), 109.2, 109.0 (minor isomer), 63.7 (minor isomer), 58.2, 44.1, (minor isomer), 39.3, 20.3 (minor isomer), 17.0 (minor isomer), 16.1, 13.5.

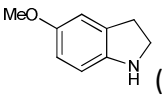
MS-$C_{10}H_{13}N$ (147) m/z (%): 147 (M^+, 38), 132 (100), 117 (39), 103 (4), 77 (8).

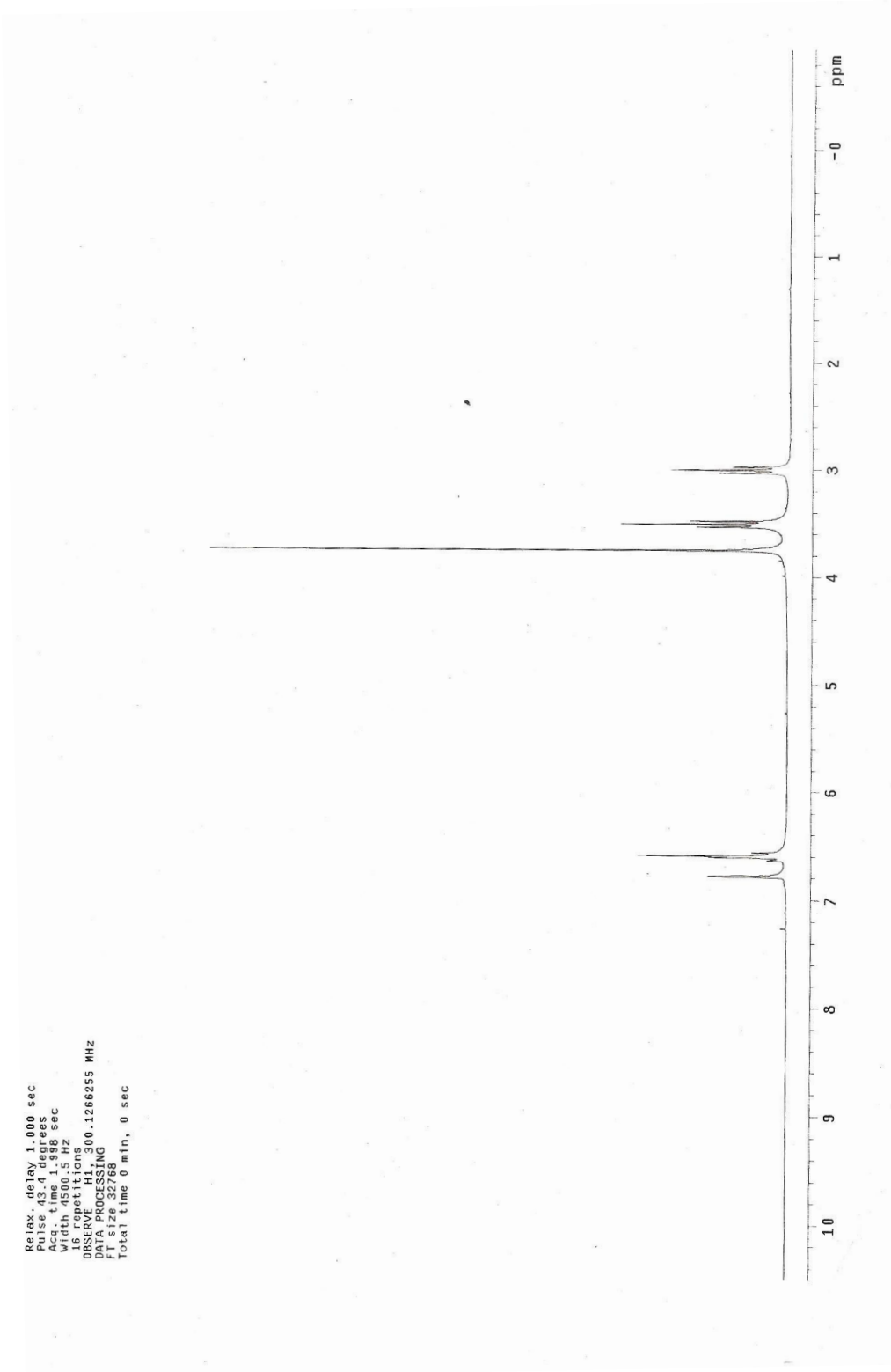
^{1}H NMR of  **(4)**

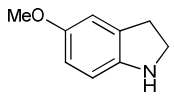

Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266252 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
ppm
0
1
2
3
4
5
6
7
8
9
10

^{13}C NMR of  **(4)**

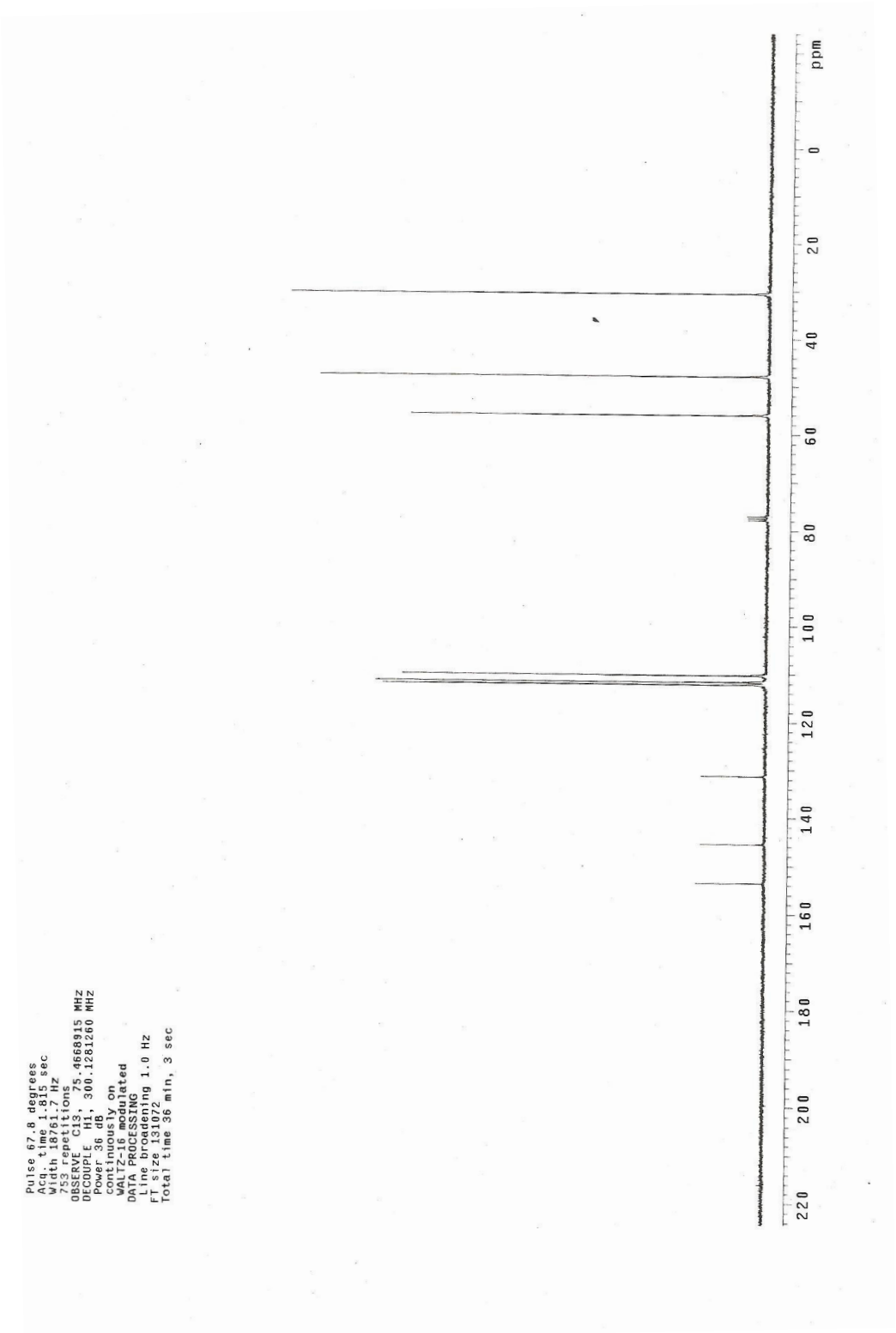

Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669236 MHz
DECOUPLE H1, 300.1281200 MHz
Power 56 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

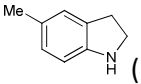
^{1}H NMR of  **(10)**


Relax. delay 1.000 sec
Pulse 43.1 degrees
Acq. time 1.998 sec
Width 4500.5 HZ
16 repetitions
OBSERVE H1, 300.1266255 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
10
9
8
7
6
5
4
3
2
1
-0

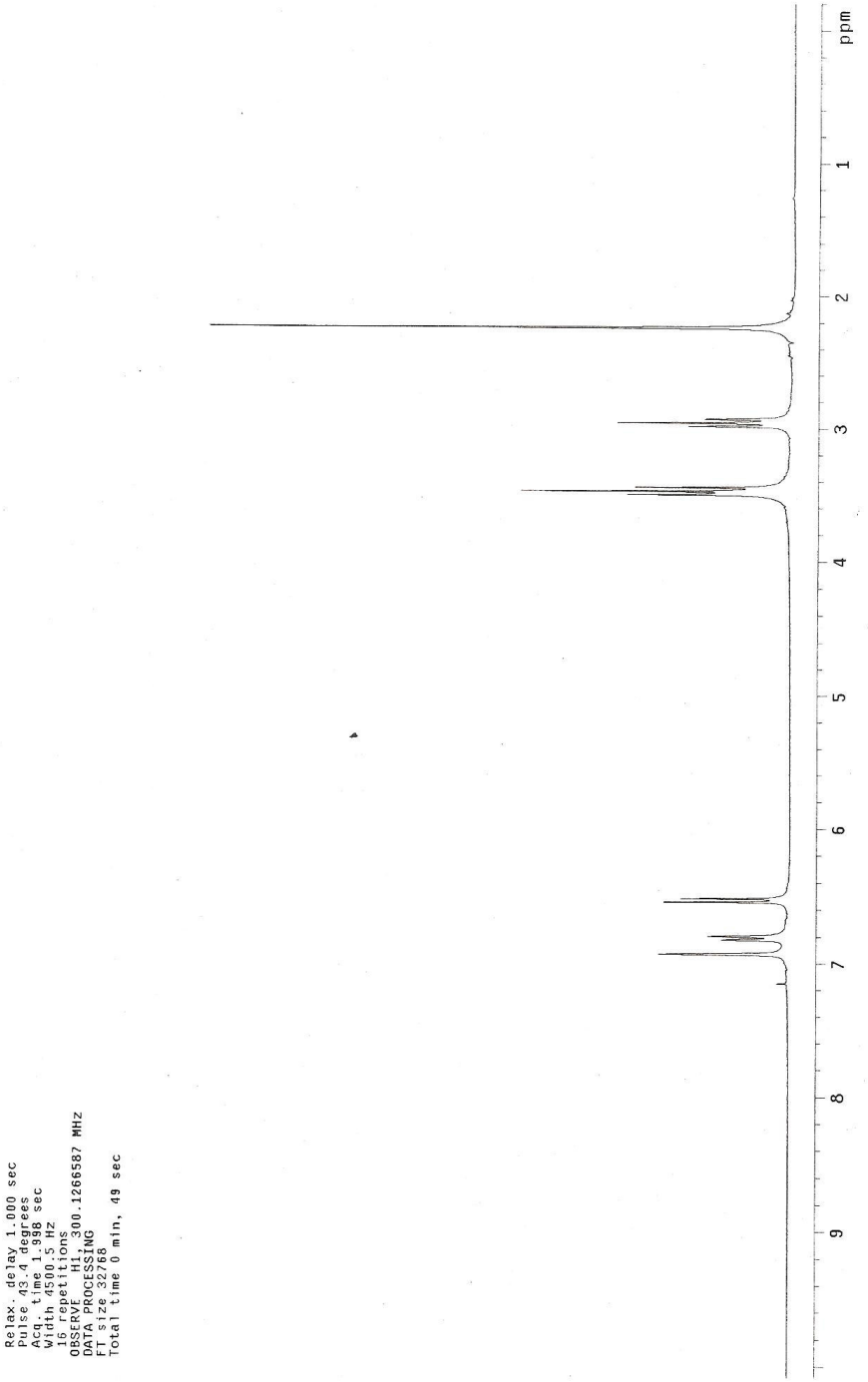
^{13}C NMR of  (**10**)

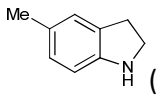
MeO
N
H


Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
753 repetitions
OBSERVE C13, 75.4668915 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

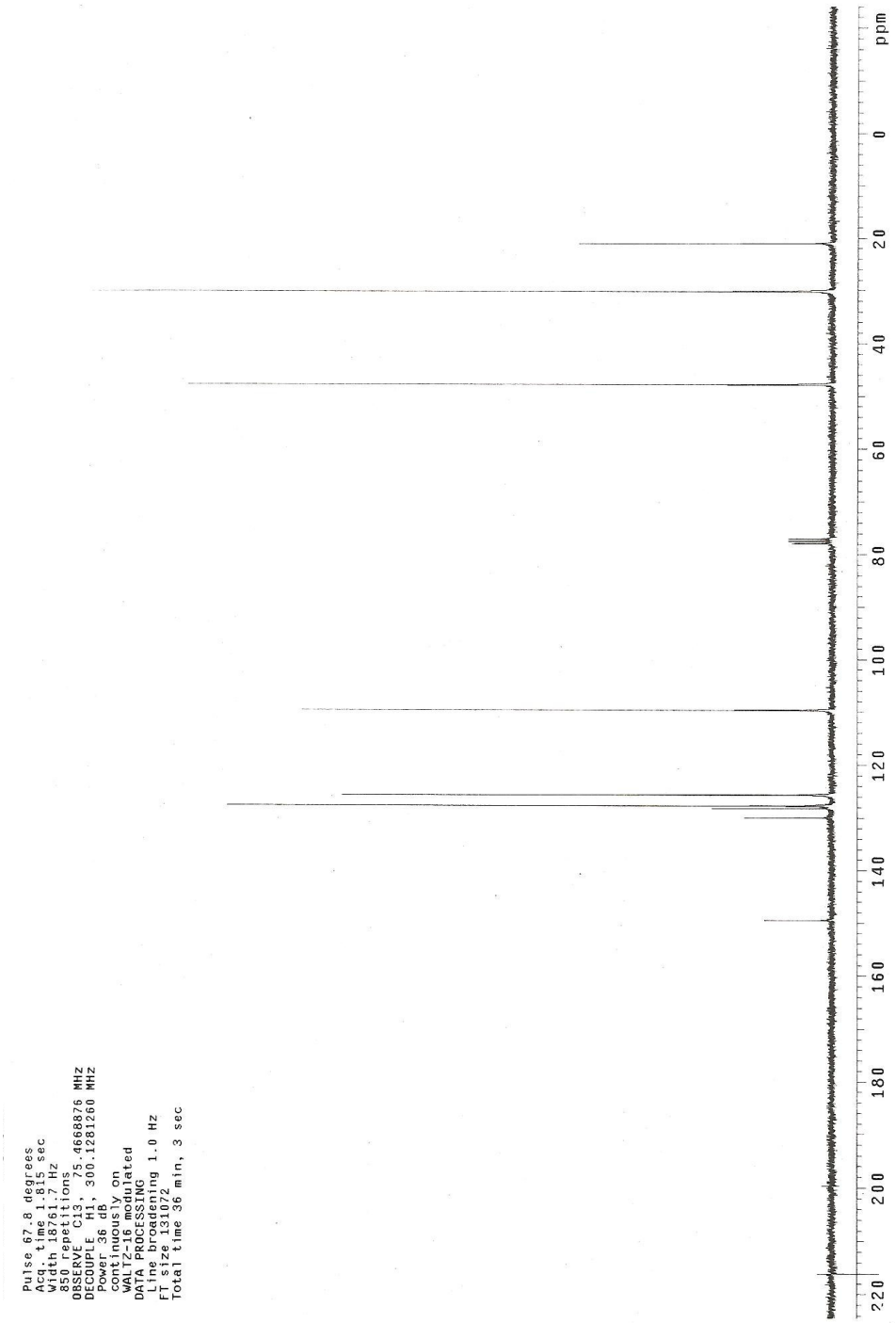
^{1}H NMR of  **(11)**

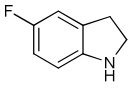
Me
N
H

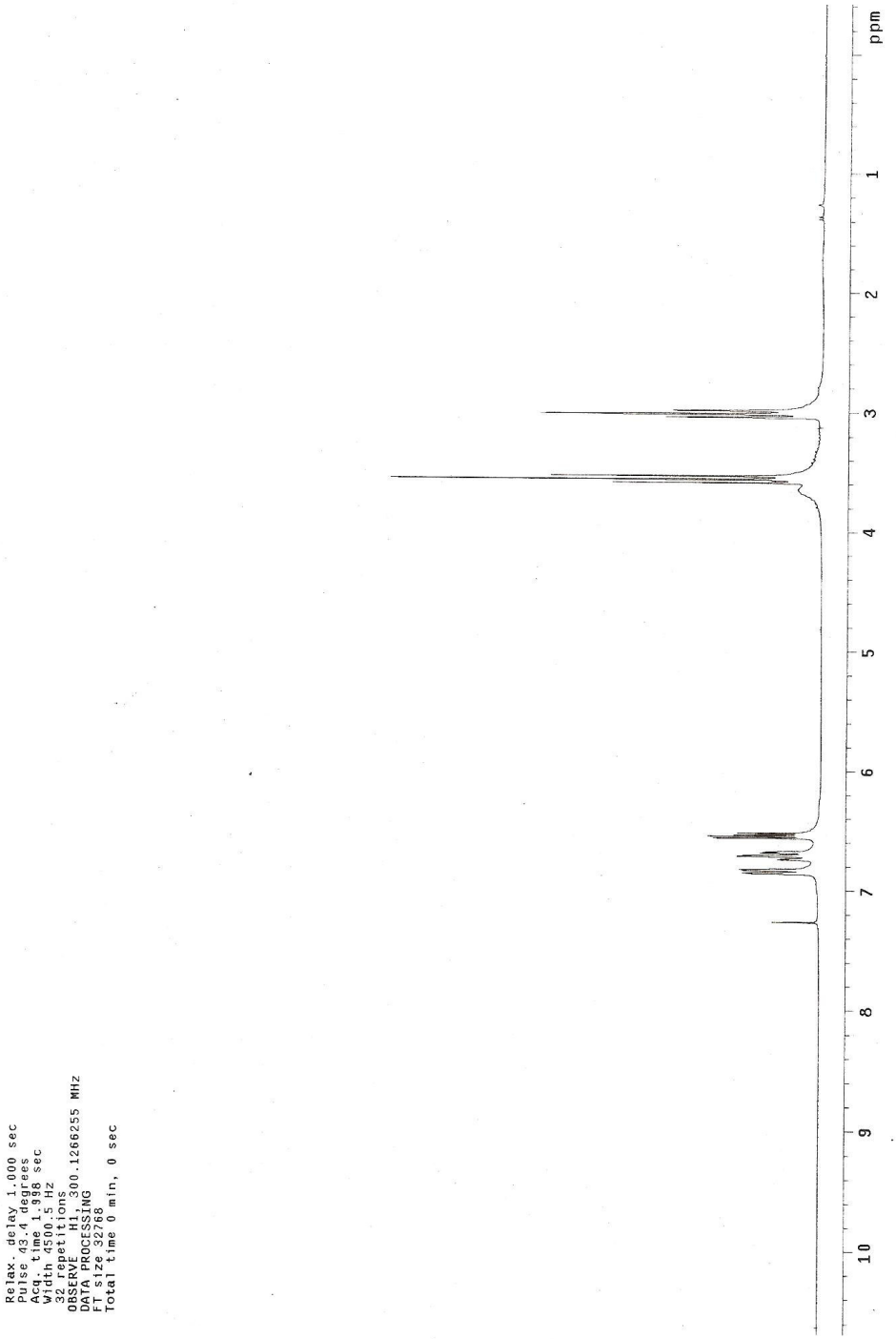

ppm
1
2
3
4
5
6
7
8
9
Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.988 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266587 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

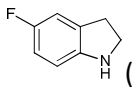
^{13}C NMR of  **(11)**

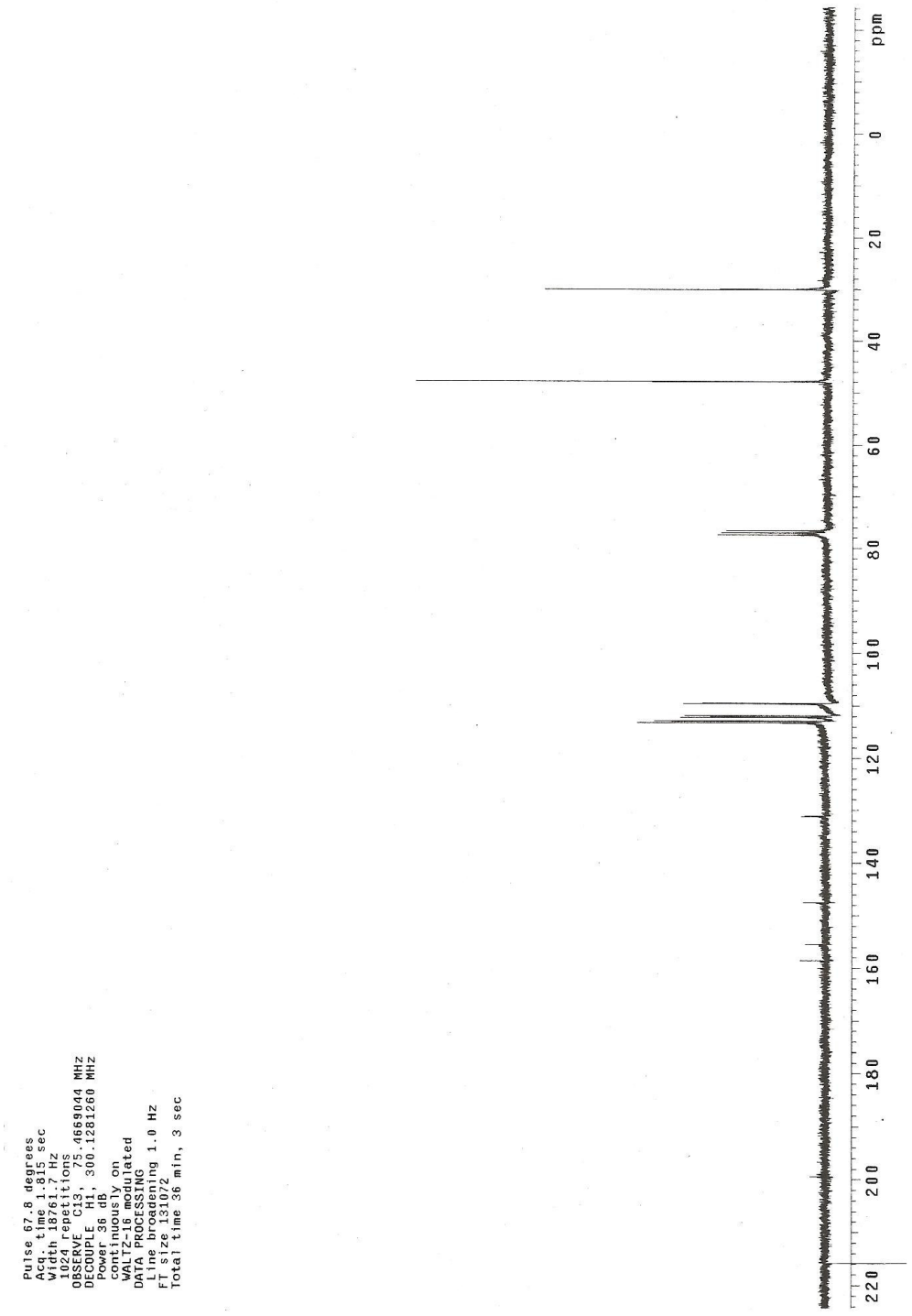
Me
N
H

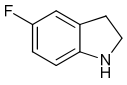

Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
850 repetitions
OBSERVE C13, 75.4668876 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

^{1}H NMR of  (**12**)

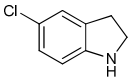

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4510.5 Hz
32 repetitions
OBSERVE H1, 300.1266255 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
1
2
3
4
5
6
7
8
9
10

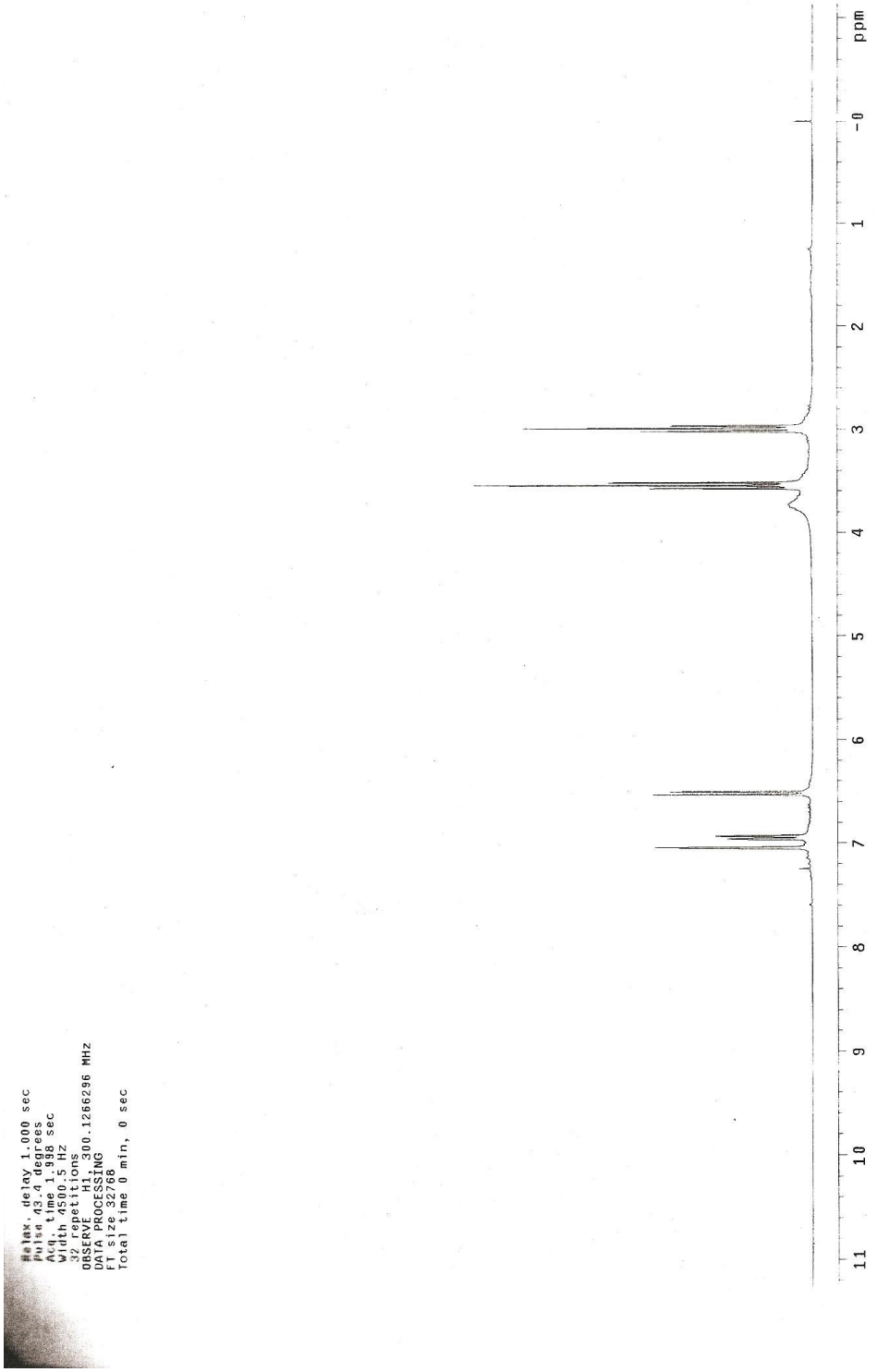
^{13}C NMR of  (**12**)

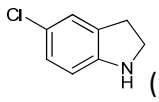

Pulse 67.8 degrees
Acq. time 1.915 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669044 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

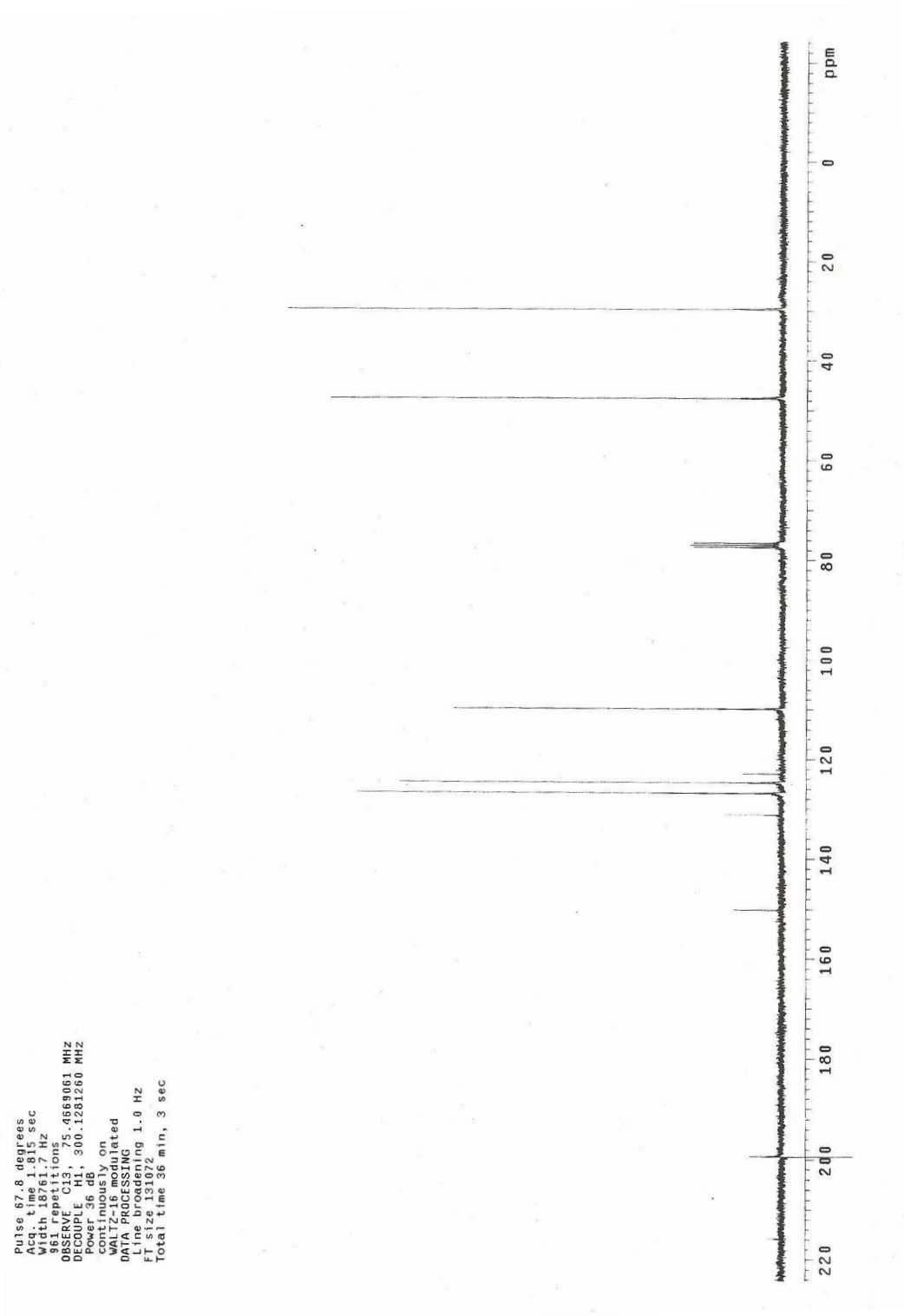
^{19}F NMR of  (**12**)

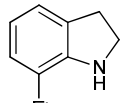

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "Mighty300"
Relax. delay 4.000 sec
Pulse 5.0 usec
Acq. time 0.300 sec
Width 70000.0 Hz
16 repetitions
OBSERVE F19, 282.4011453 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 11 sec
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

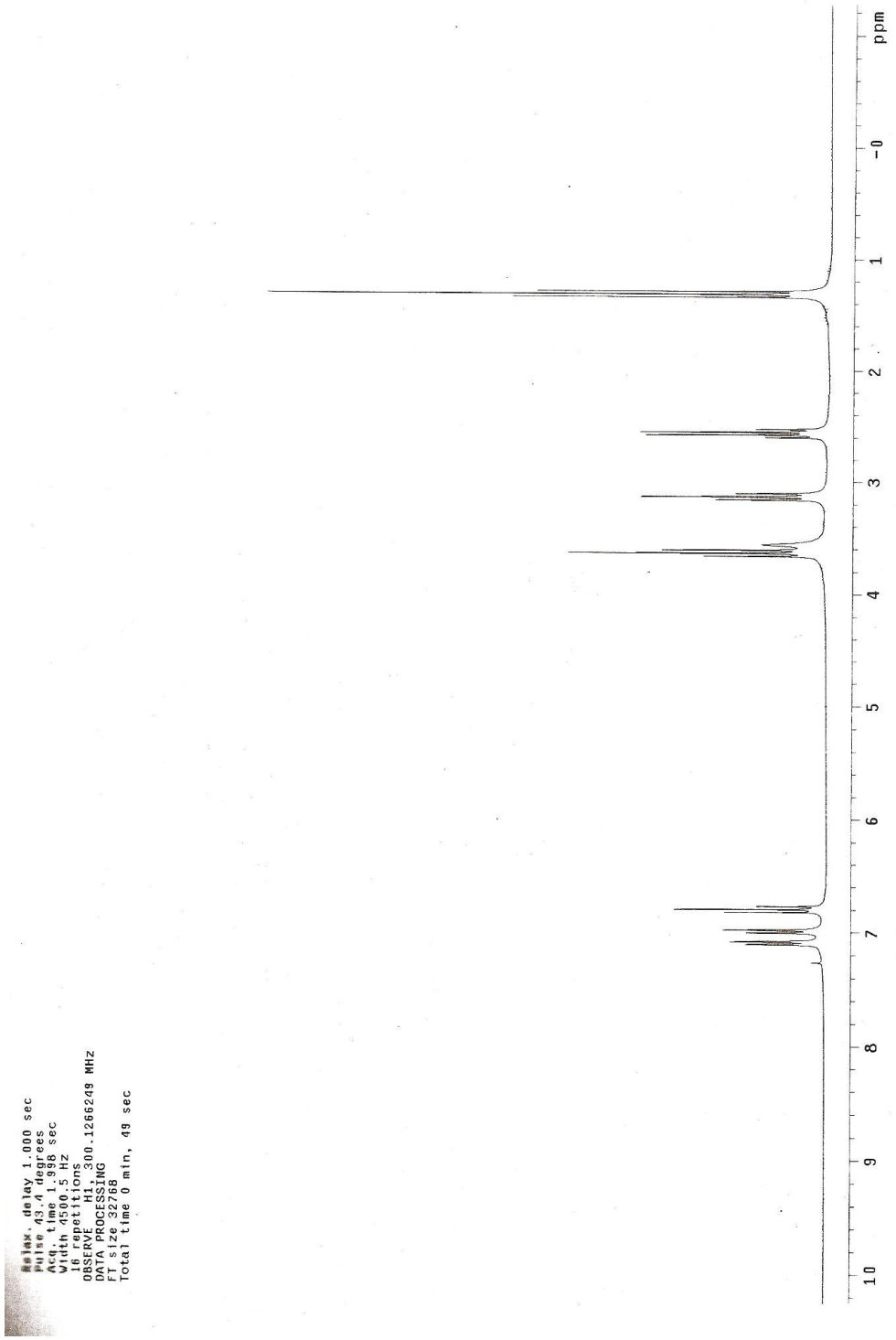
^{1}H NMR of  (**13**)

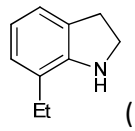

delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
32 repetitions
OBSERVE H1, 300.1266296 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
11
10
9
8
7
6
5
4
3
2
1
-0

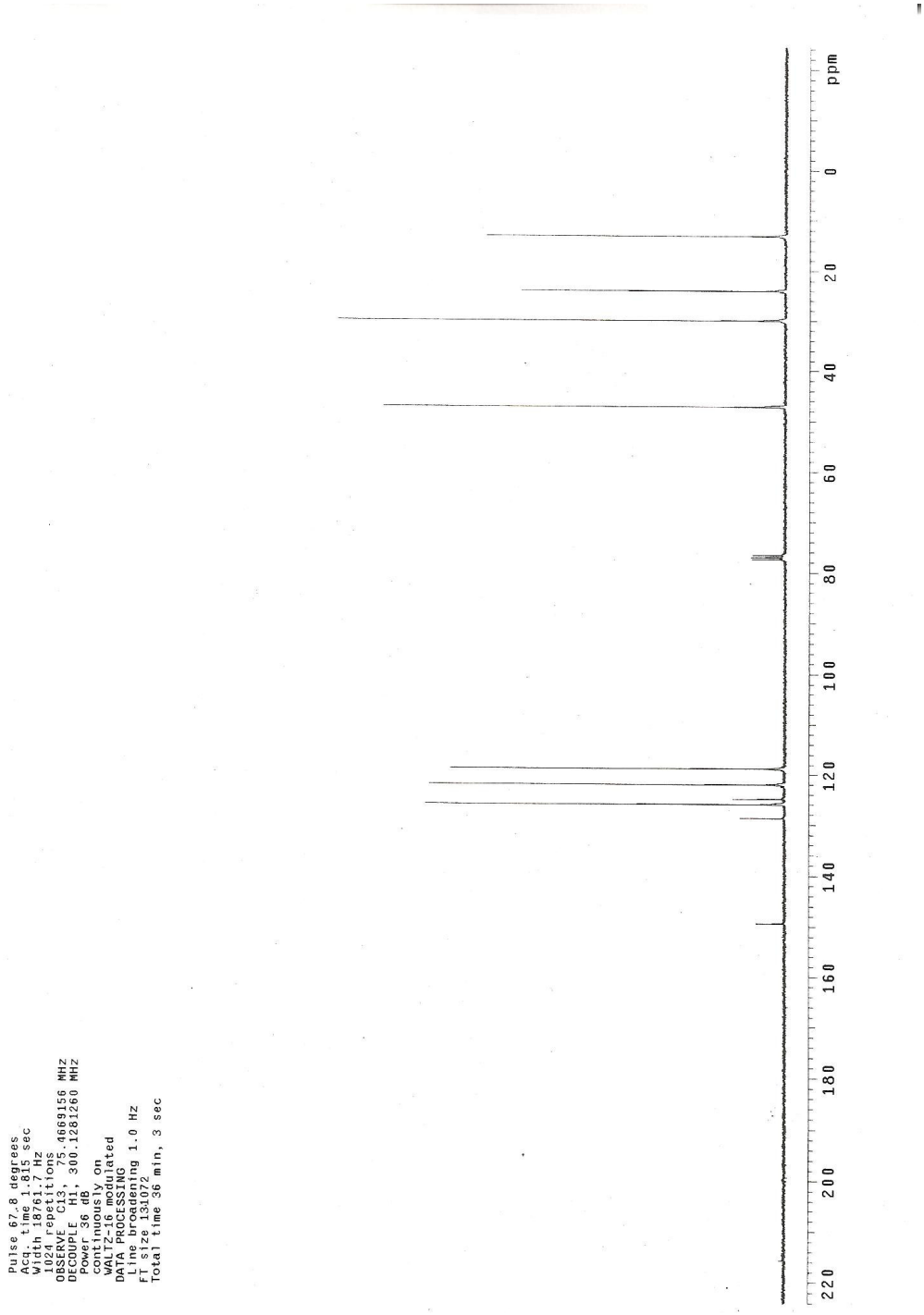
^{13}C NMR of  **(13)**

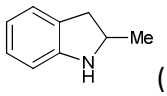

Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
961 repetitions
OBSERVE C13, 75.4669061 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
0
20
40
60
80
100
120
140
160
180
200
220

^{1}H NMR of  (**14**)

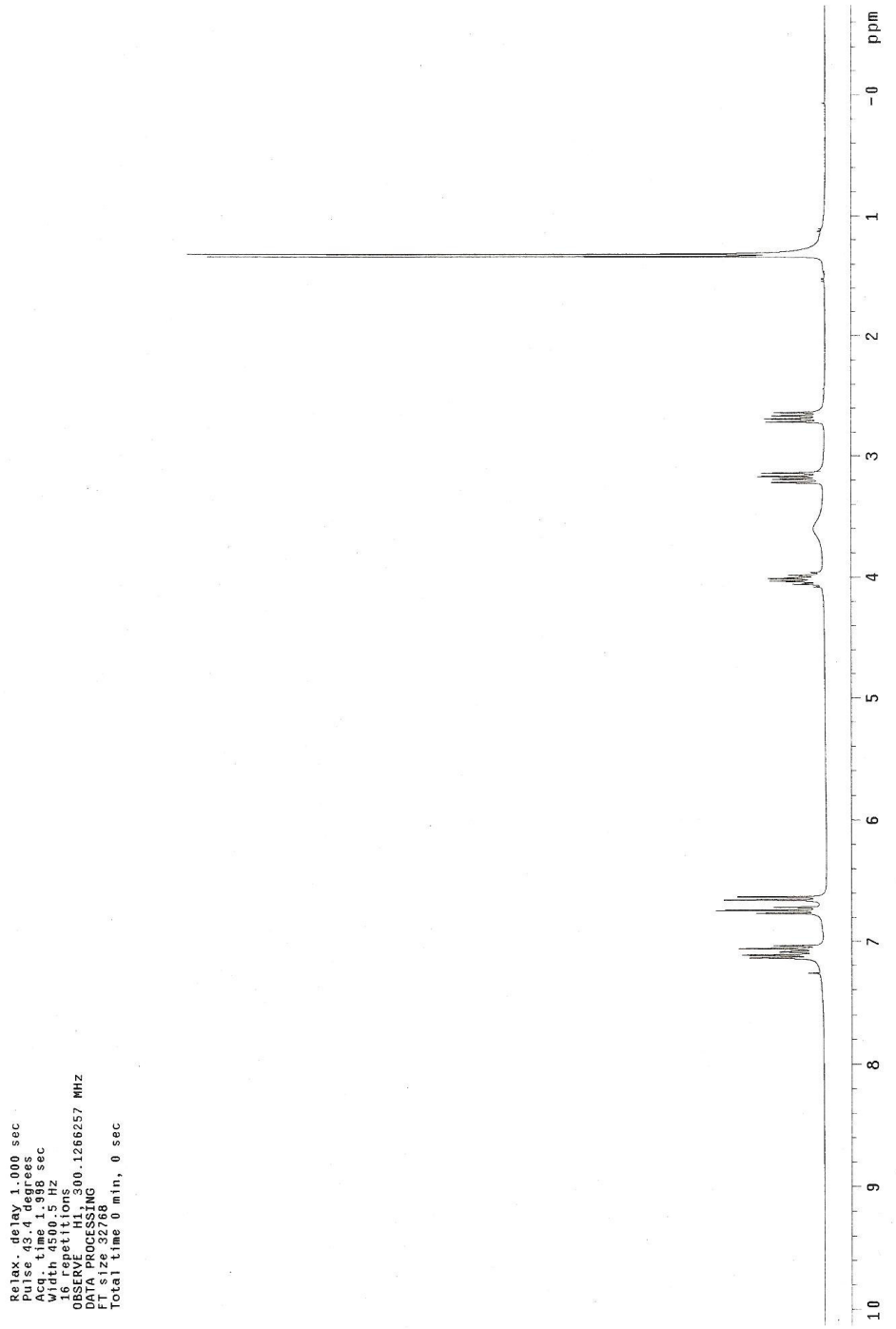

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4501.5 Hz
16 repetitions
OBSERVE H1, 300.1266249 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
ppm
10
9
8
7
6
5
4
3
2
1
-0

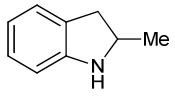
^{13}C NMR of  (**14**)


Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669156 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

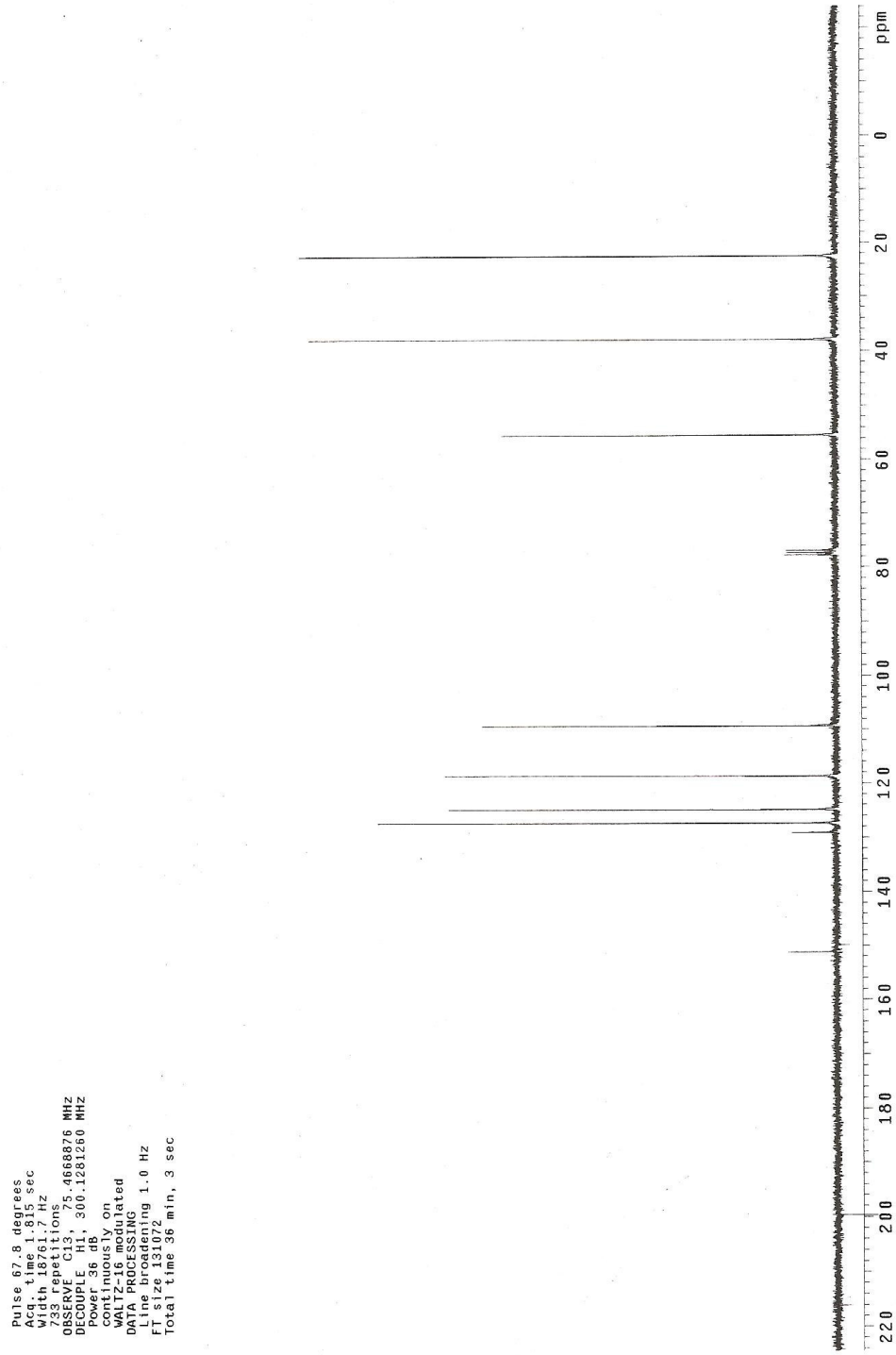
^{1}H NMR of  **(15)**

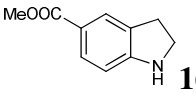
Me
N
H


Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.498 sec
Width 4800.5 Hz
16 repetitions
OBSERVE H1, 300.1266257 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
10
9
8
7
6
5
4
3
2
1
0

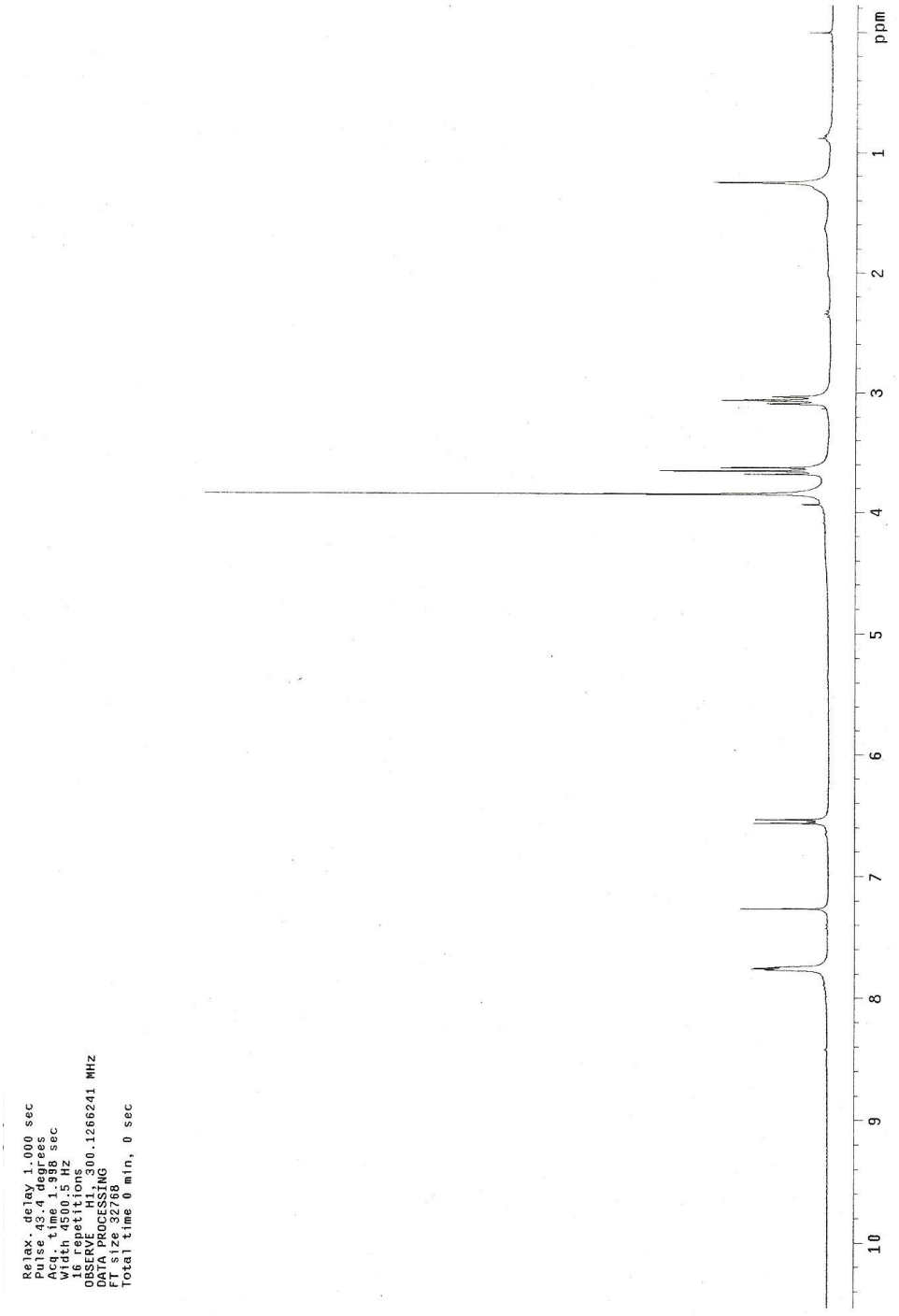
^{13}C NMR of  (**15**)

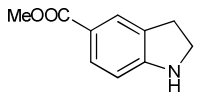
Me
N
H


Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
733 repetitions
OBSERVE C13, 75.4668876 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

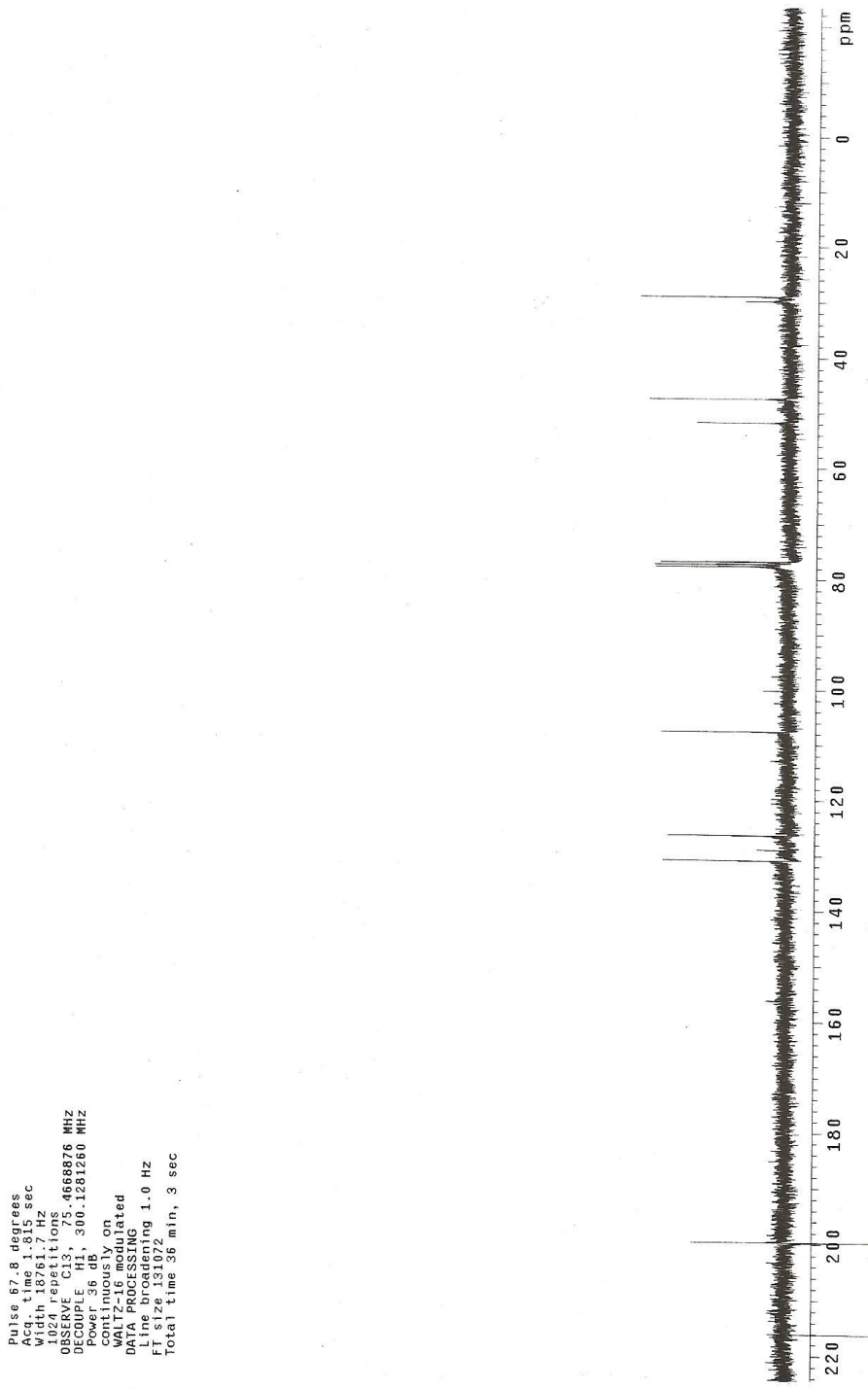
^{1}H NMR of  **16**

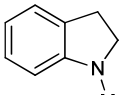
MeOOC
N
H

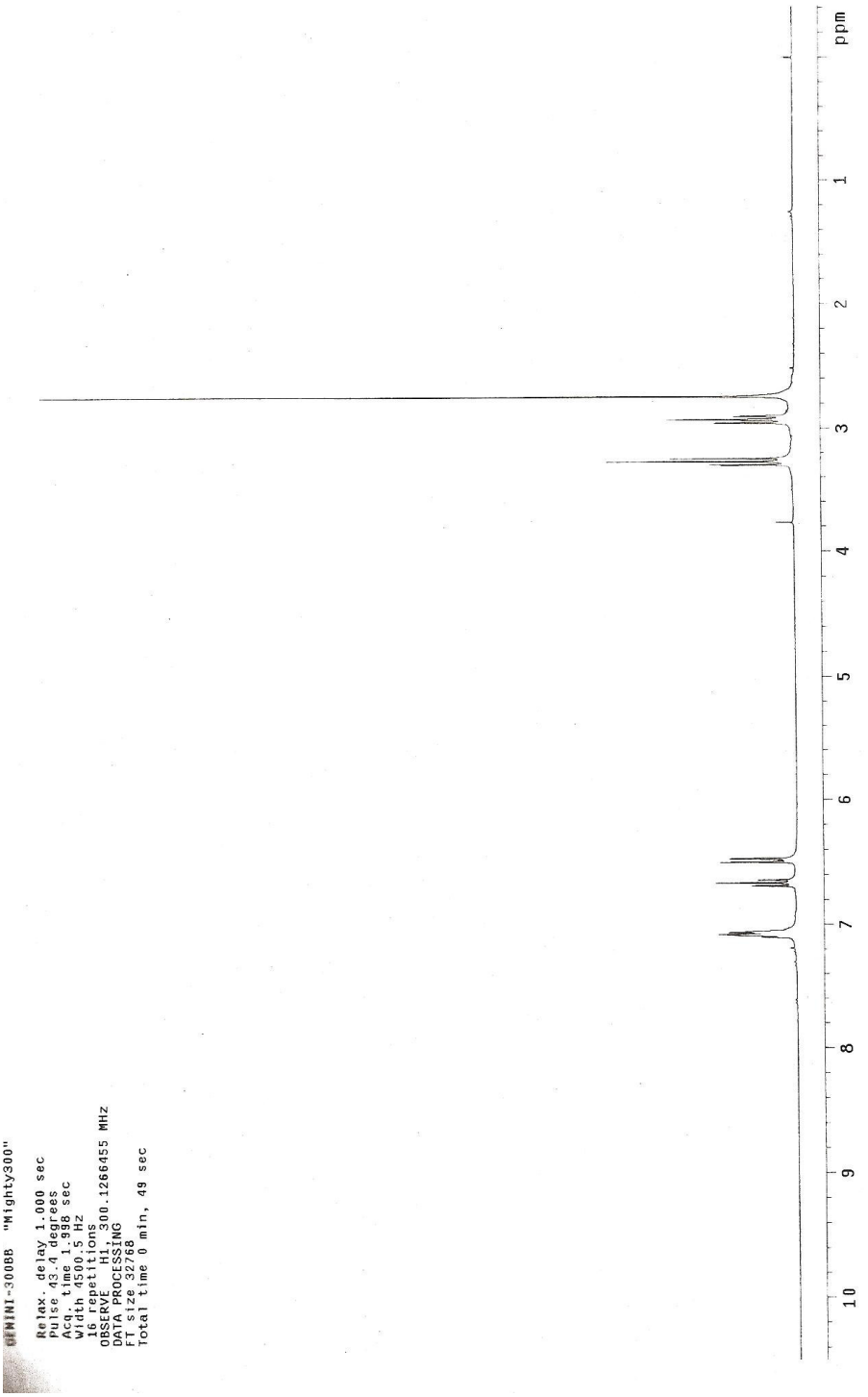

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266241 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
1
2
3
4
5
6
7
8
9
10

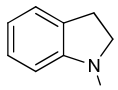
^{13}C NMR of  (**16**)

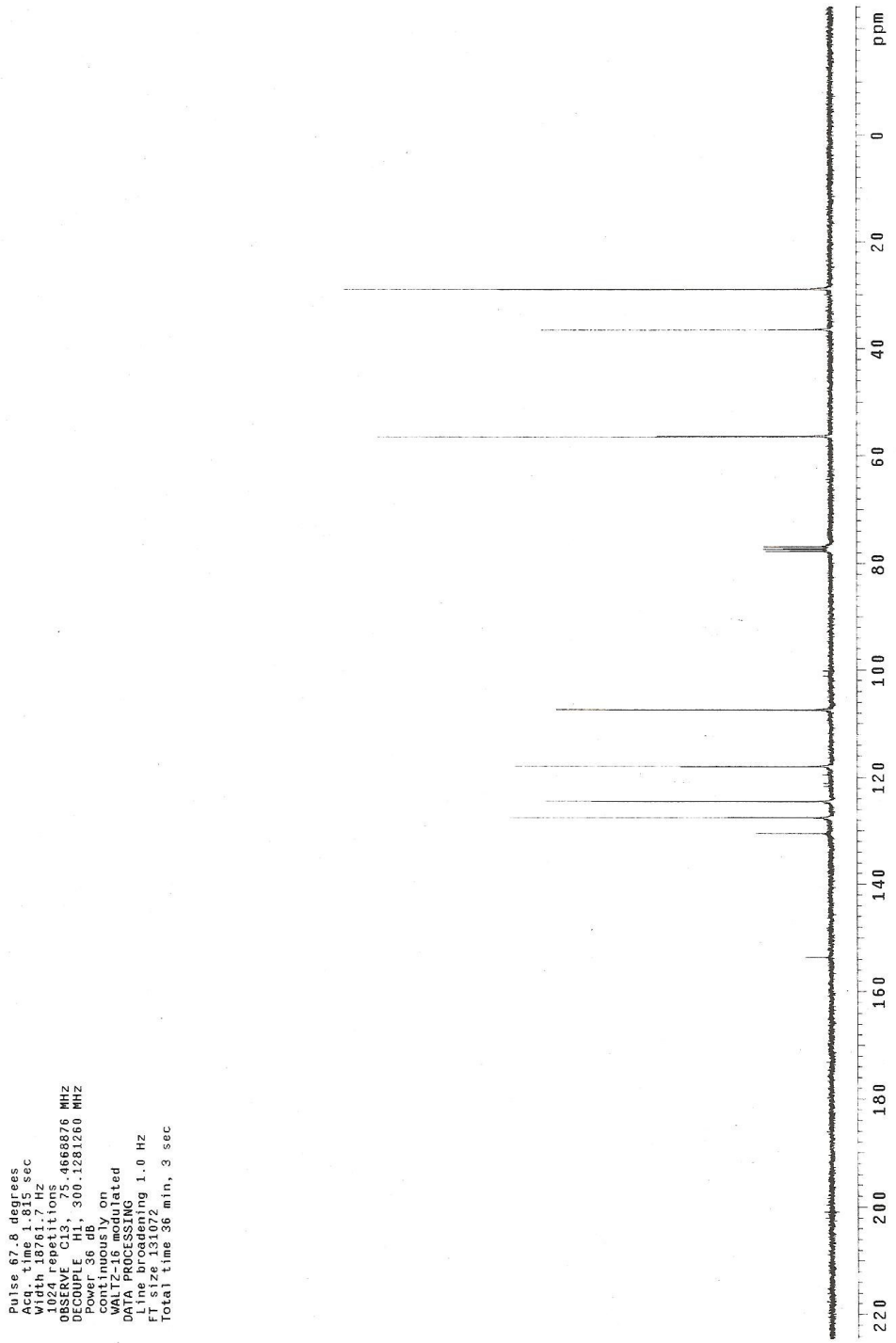
MeOOC
N
H

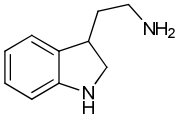

Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4668876 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

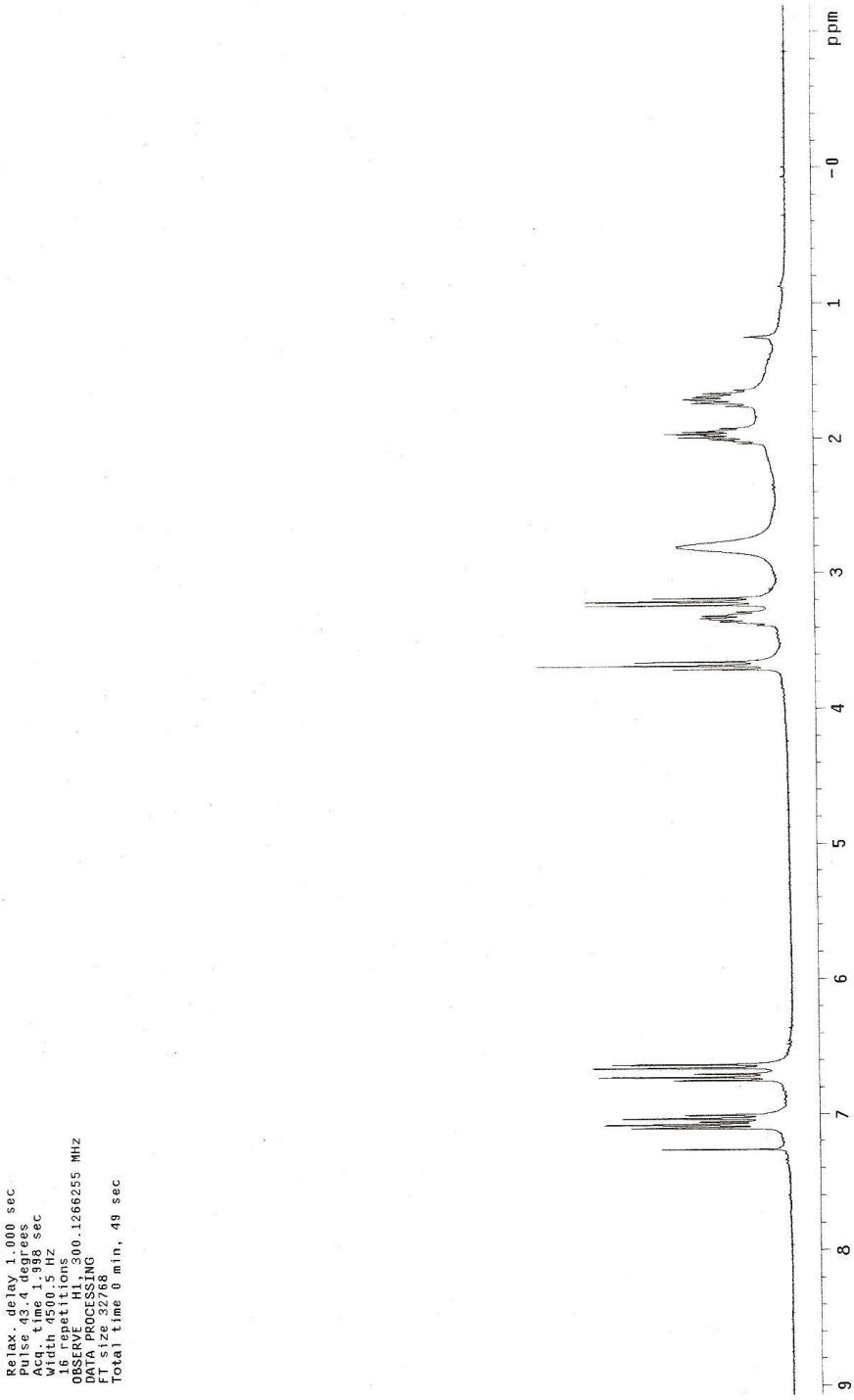
^{1}H NMR of  (**17**)

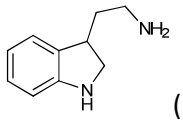

GEMINI-300BB "Mighty300"
Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266455 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
ppm
10
9
8
7
6
5
4
3
2
1

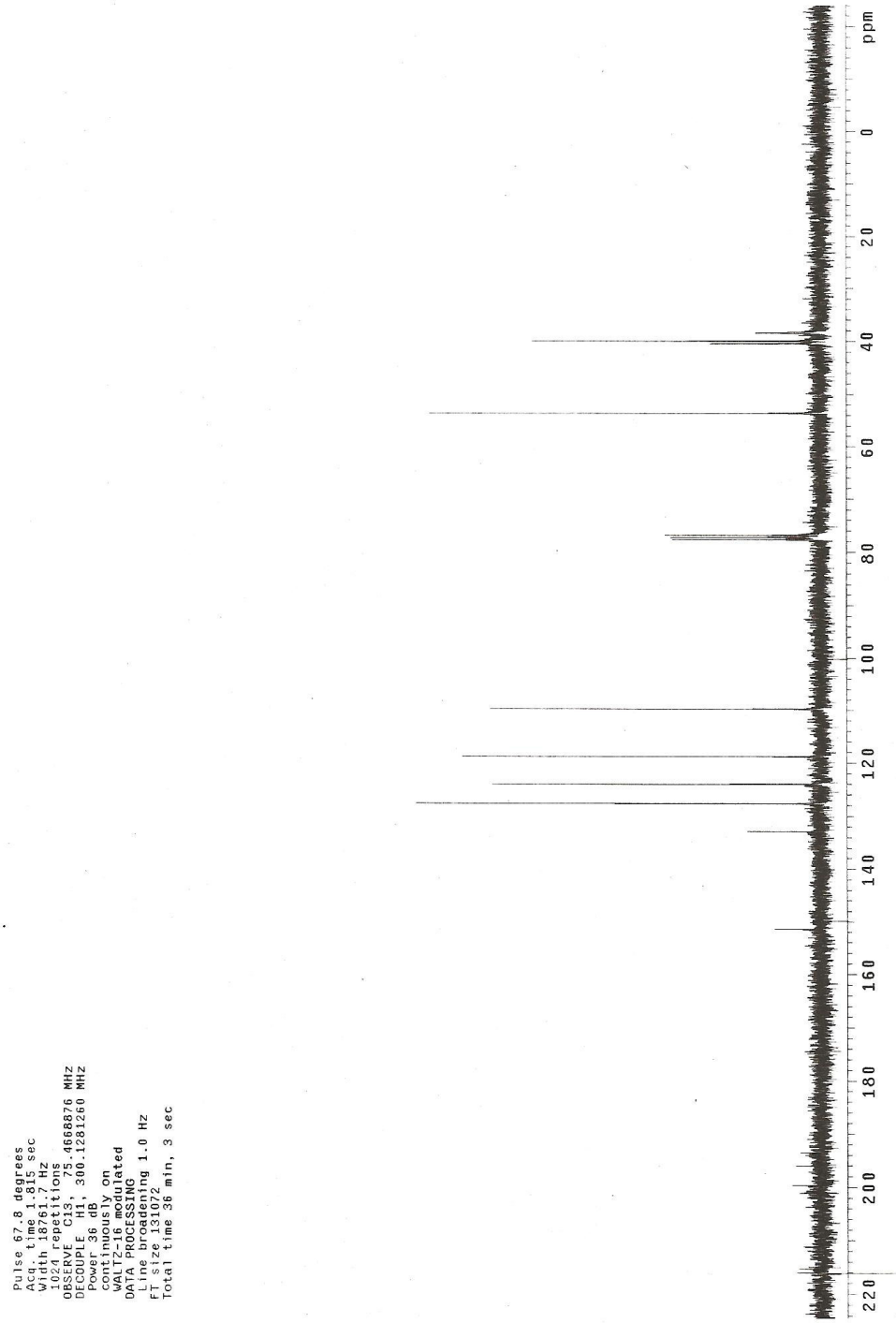
^{13}C NMR of  (**17**)

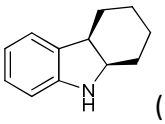

Pulse 67.8 degrees
Acq. time 1.915 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4668876 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously ON
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

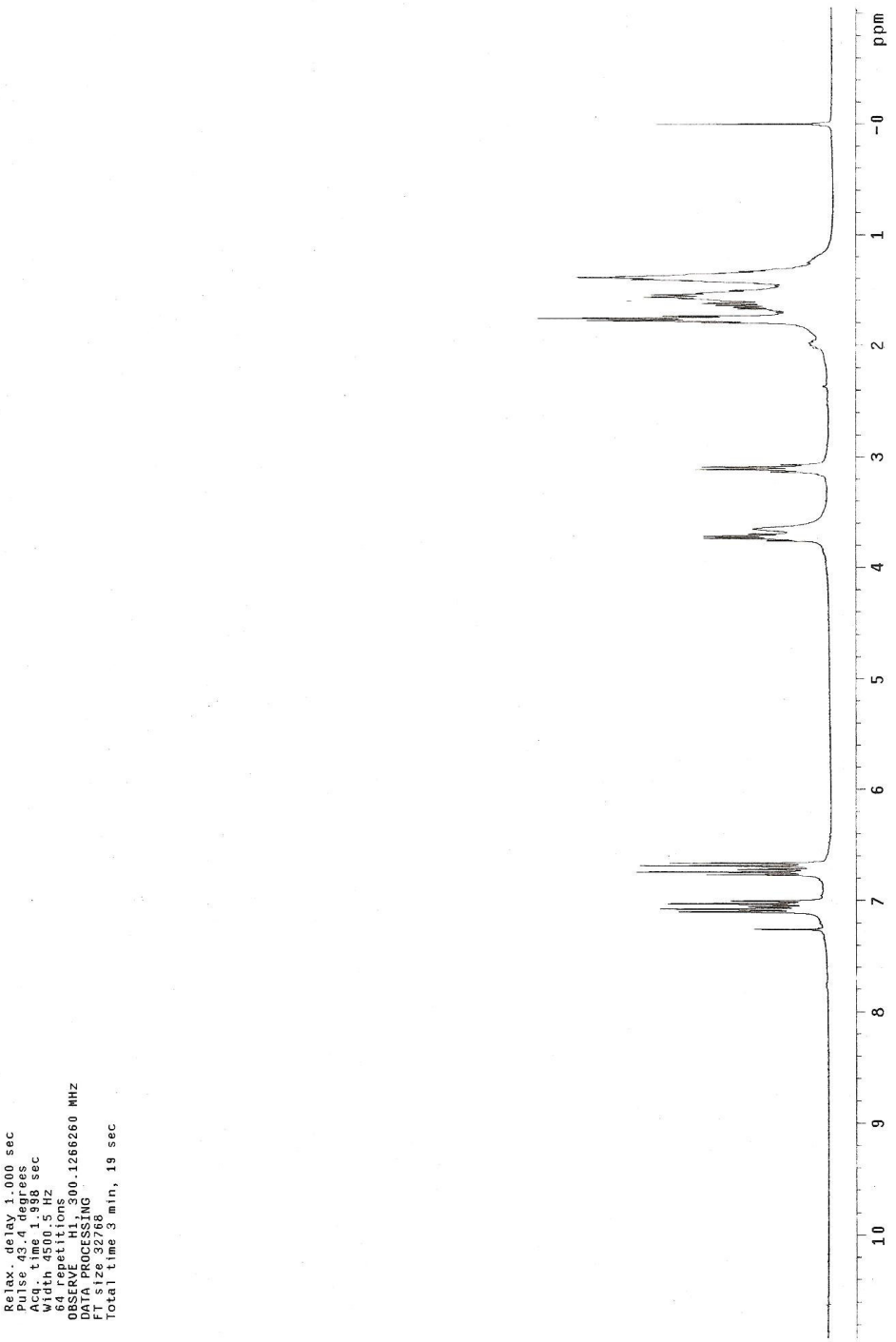
^{1}H NMR of  **(18)**

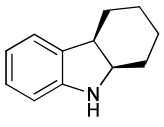

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266255 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
ppm
9
8
7
6
5
4
3
2
1
-0

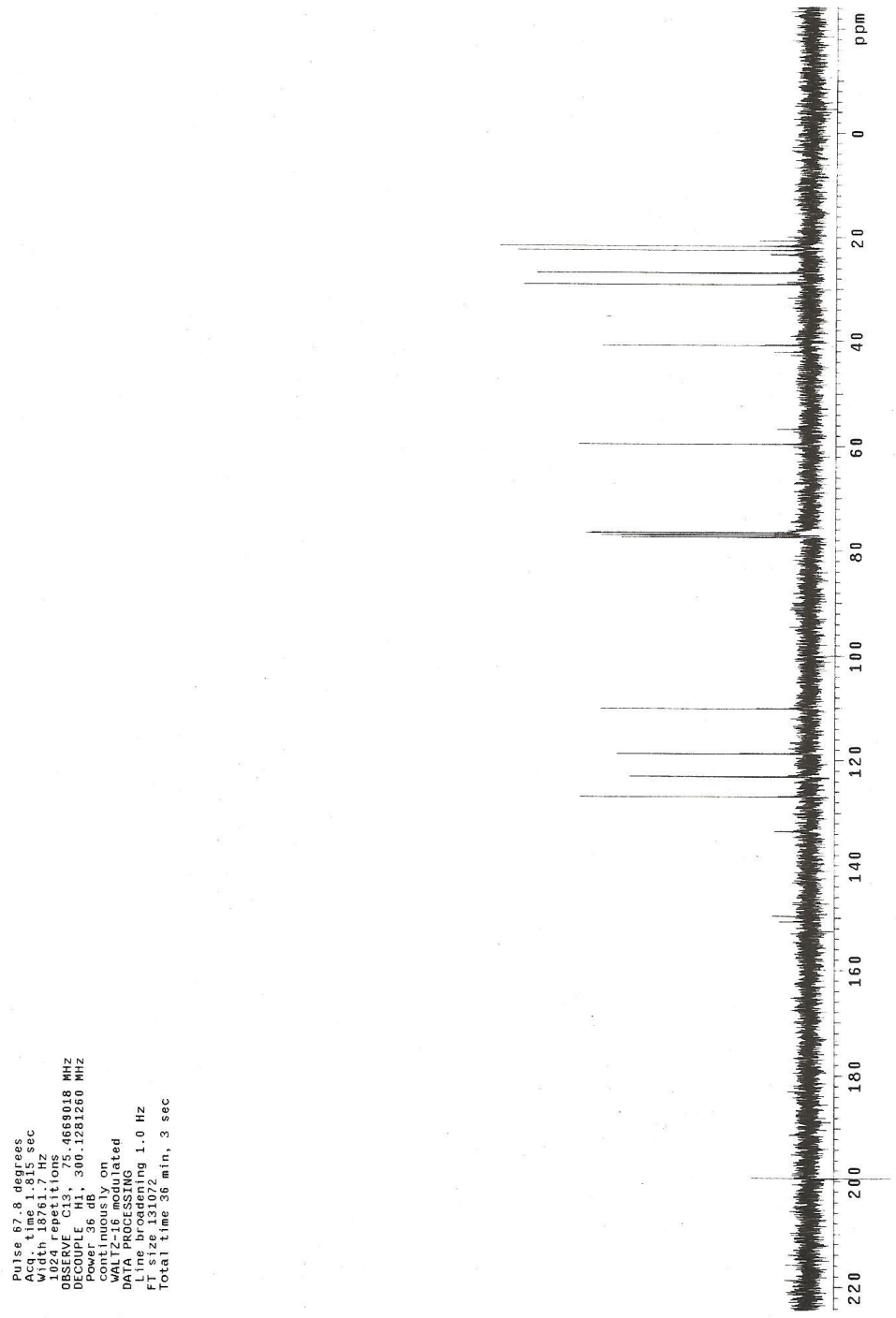
^{13}C NMR of  (**18**)

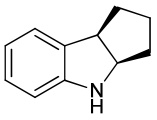

Pulse 67.8 degrees
Acq. time 1.185 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4668876 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

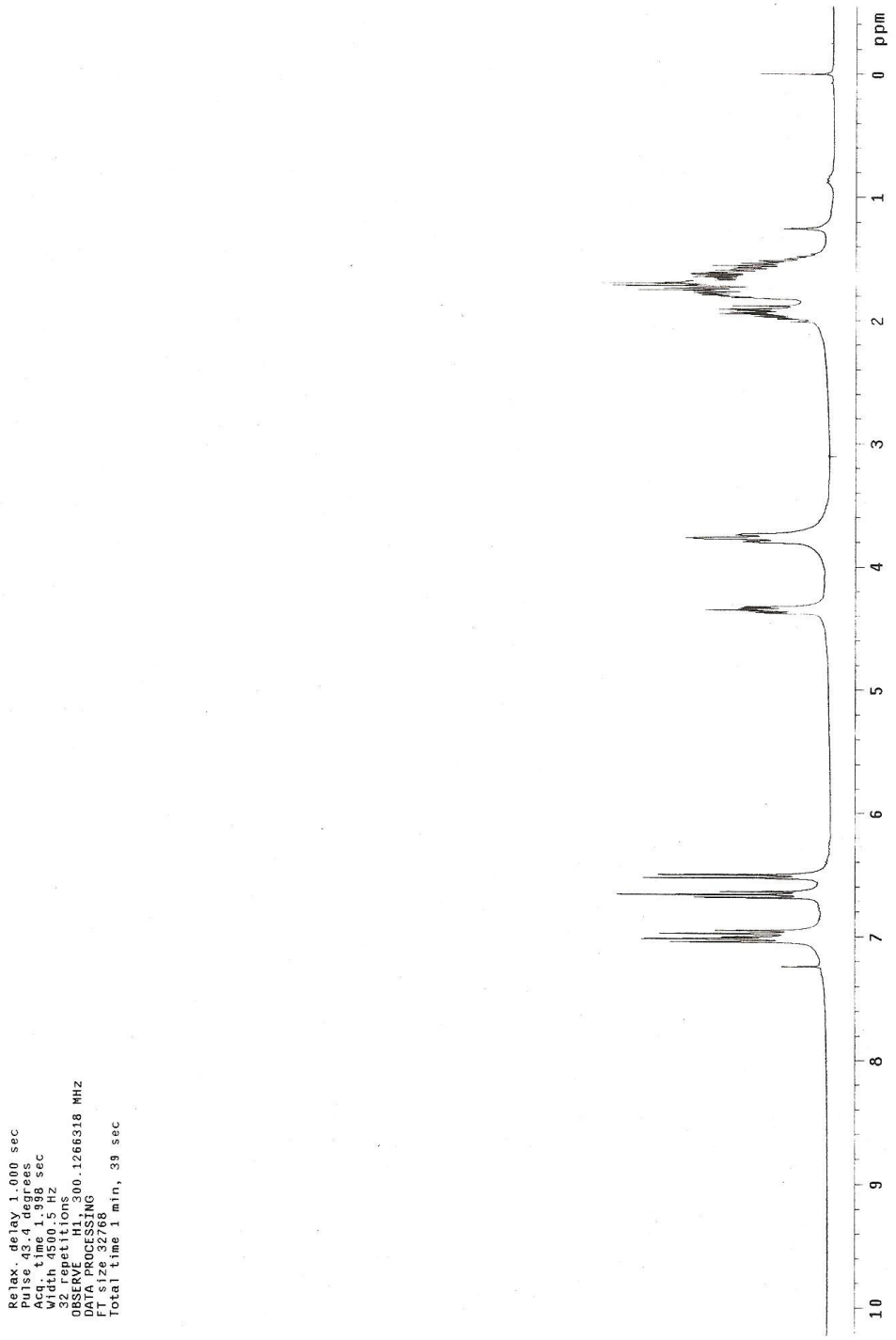
^{1}H NMR of  **(19)**

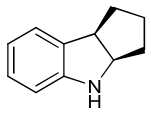

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.1266260 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 19 sec
ppm
10
9
8
7
6
5
4
3
2
1
-0

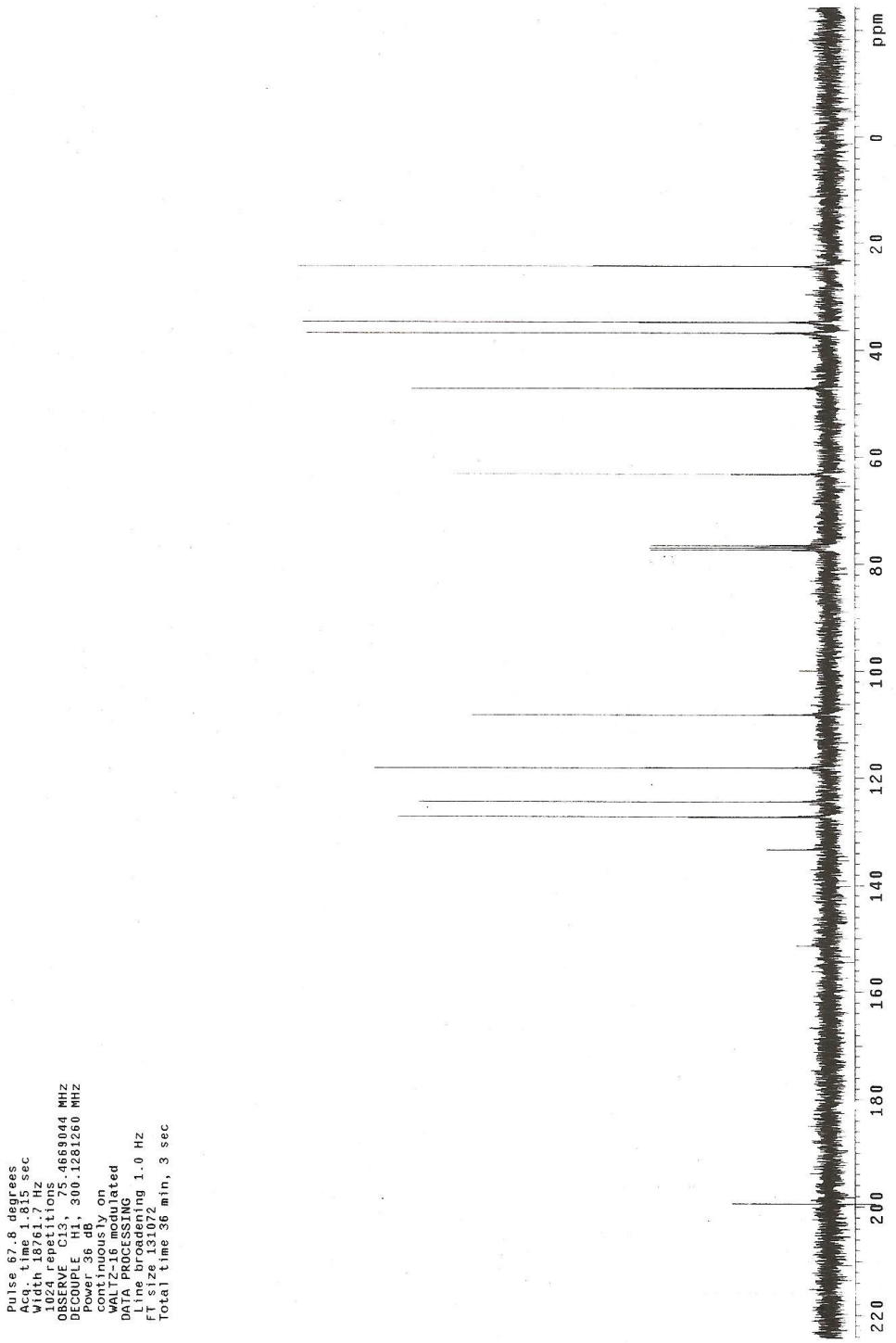
^{13}C NMR of  (**19**)

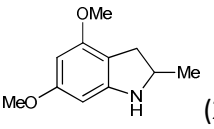

Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669018 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

^{1}H NMR of  **20**

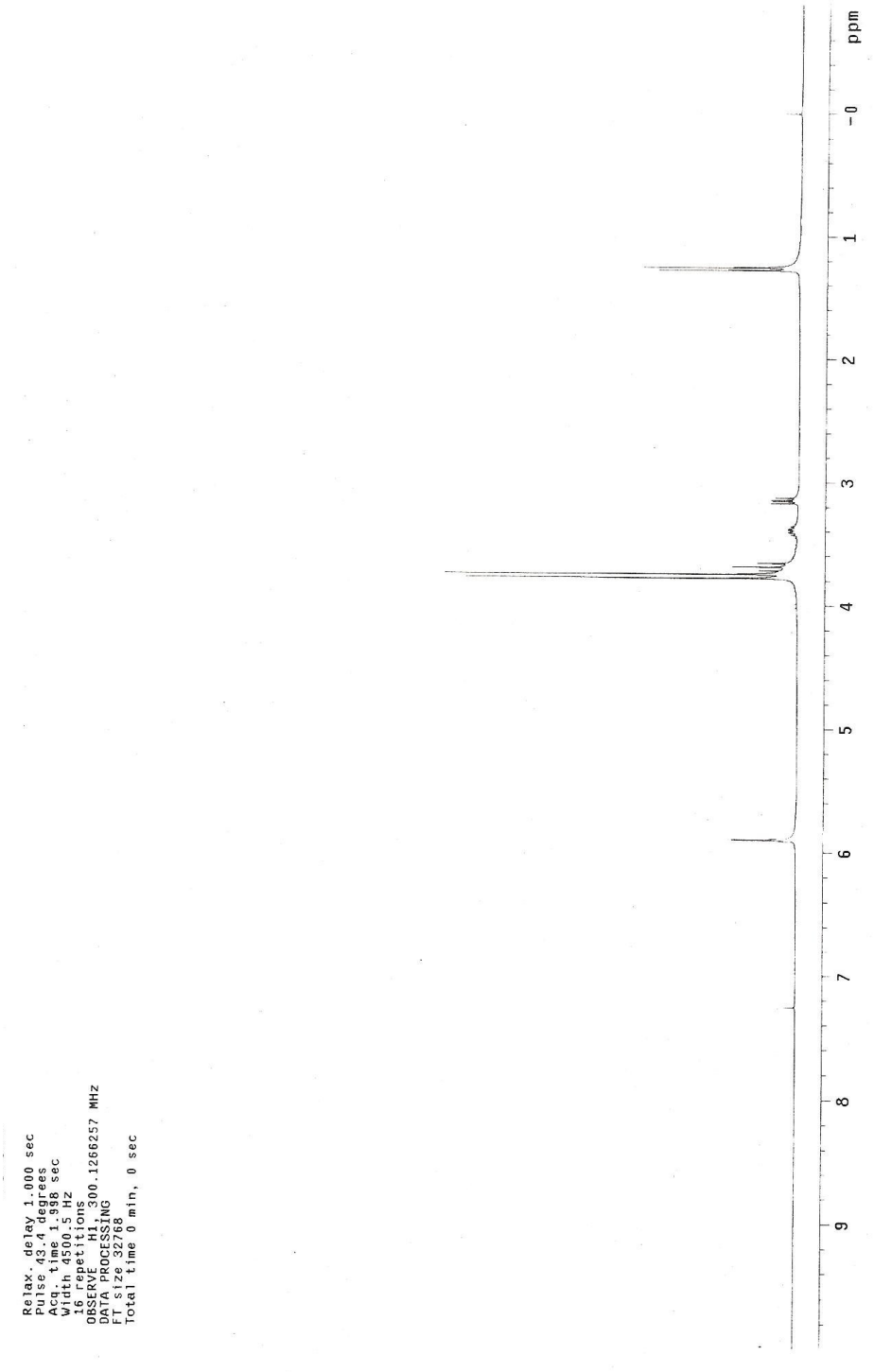

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
32 repetitions
OBSERVE H1, 300.1266318 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 39 sec
10
9
8
7
6
5
4
3
2
1
0 ppm

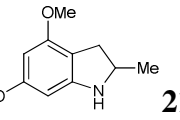
^{13}C NMR of  (**20**)


Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669044 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

^{1}H NMR of  (**21**)

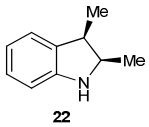
OMe
Me
MeO
N
H


Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266257 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
ppm
9
8
7
6
5
4
3
2
1
-0

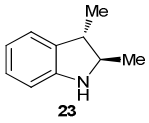
^{13}C NMR of  **21**

OMe
Me
MeO
N
H


Pulse 67.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1024 repetitions
OBSERVE C13, 75.4669024 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec
ppm
220
200
180
160
140
120
100
80
60
40
20
0

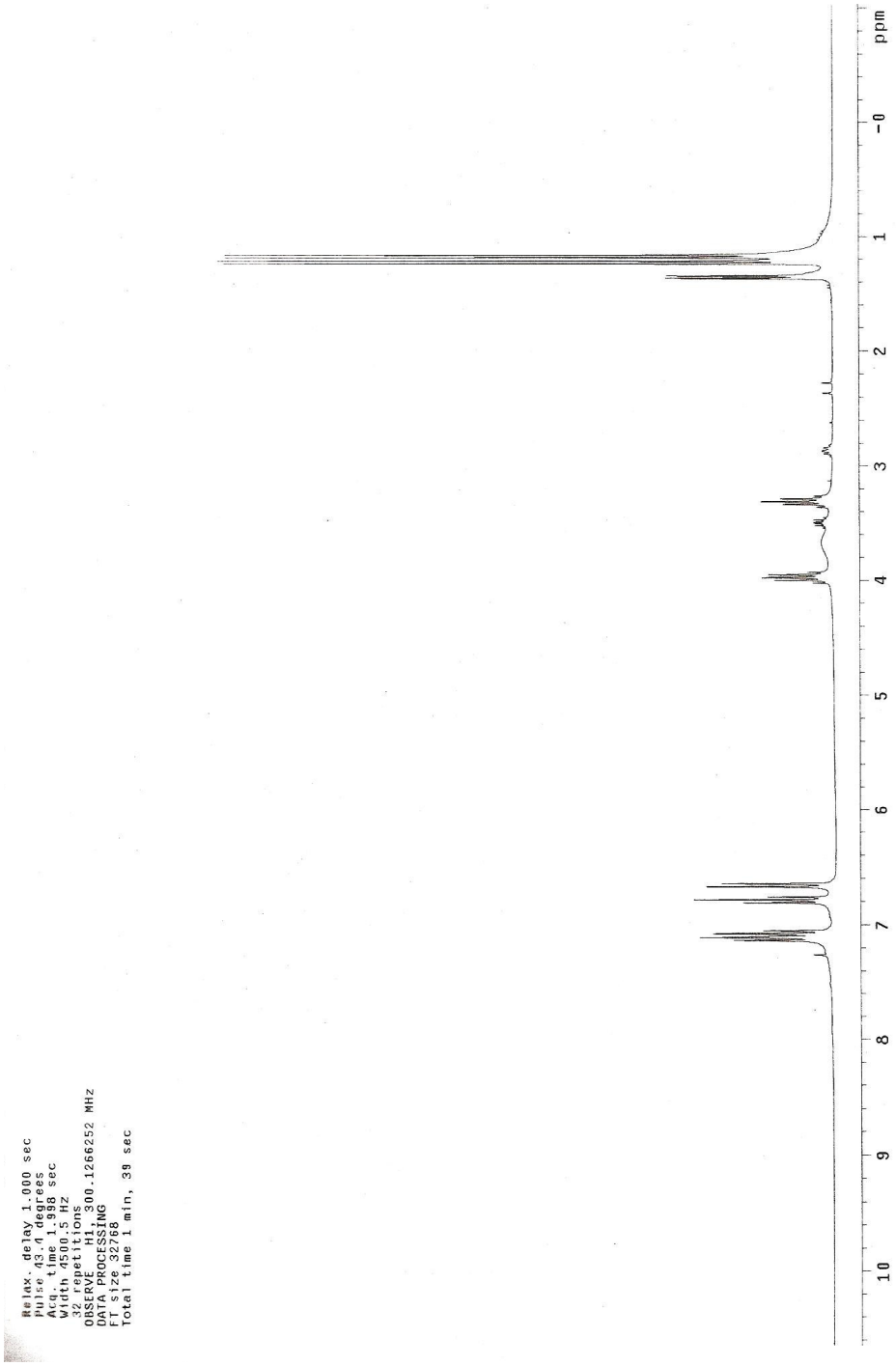


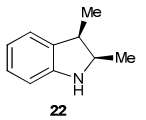
22



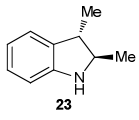
23

^{1}H NMR of **22:23** = 6:1 (**22** and **23**)





22



23

^{13}C NMR of **22:23** = 6:1 (**22** and **23**)