

Supporting Information

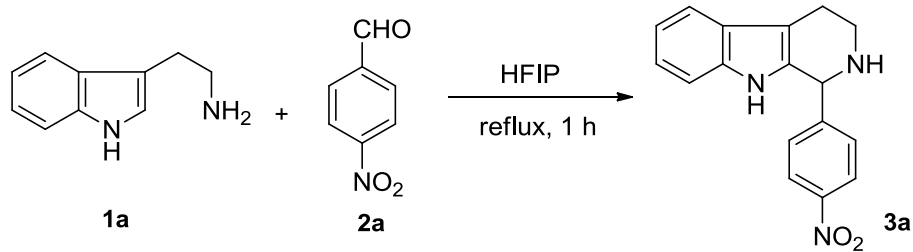
Simple and Efficient Synthesis of Tetrahydro- β -Carbolines via the Pictet–Spengler Reaction in 1,1,1,3,3,3-Hexafluoro-2-Propanol (HFIP)

Li-Na Wang, Su-Li Shen, and Jin Qu*

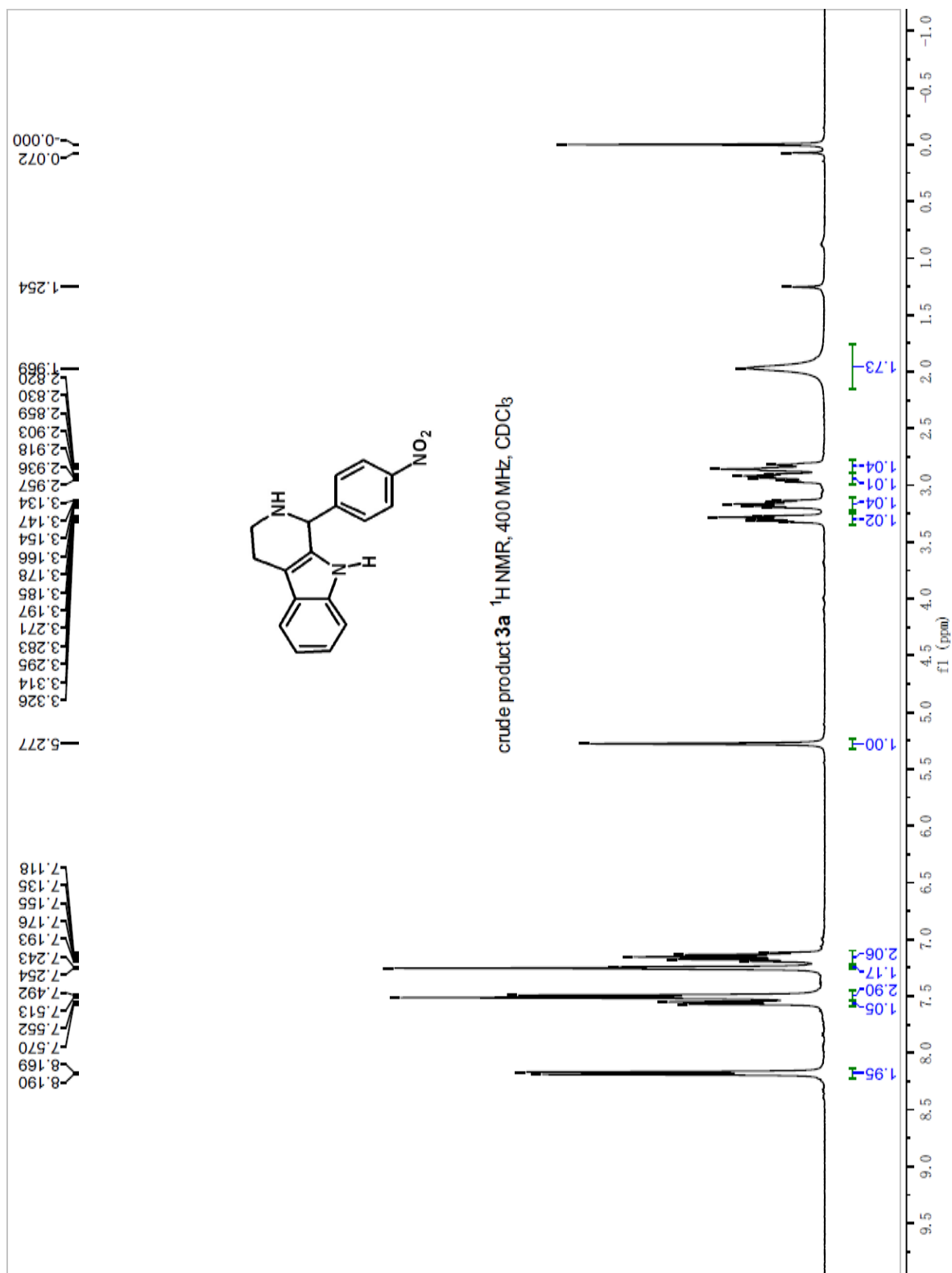
State Key Laboratory of Elemento-Organic Chemistry, Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China.

Fax: +86-(022)-23505521 and E-mail: qujin@nankai.edu.cn

| | |
|-------------------|----|
| NMR spectra..... | 1 |
| HRMS spectra..... | 67 |

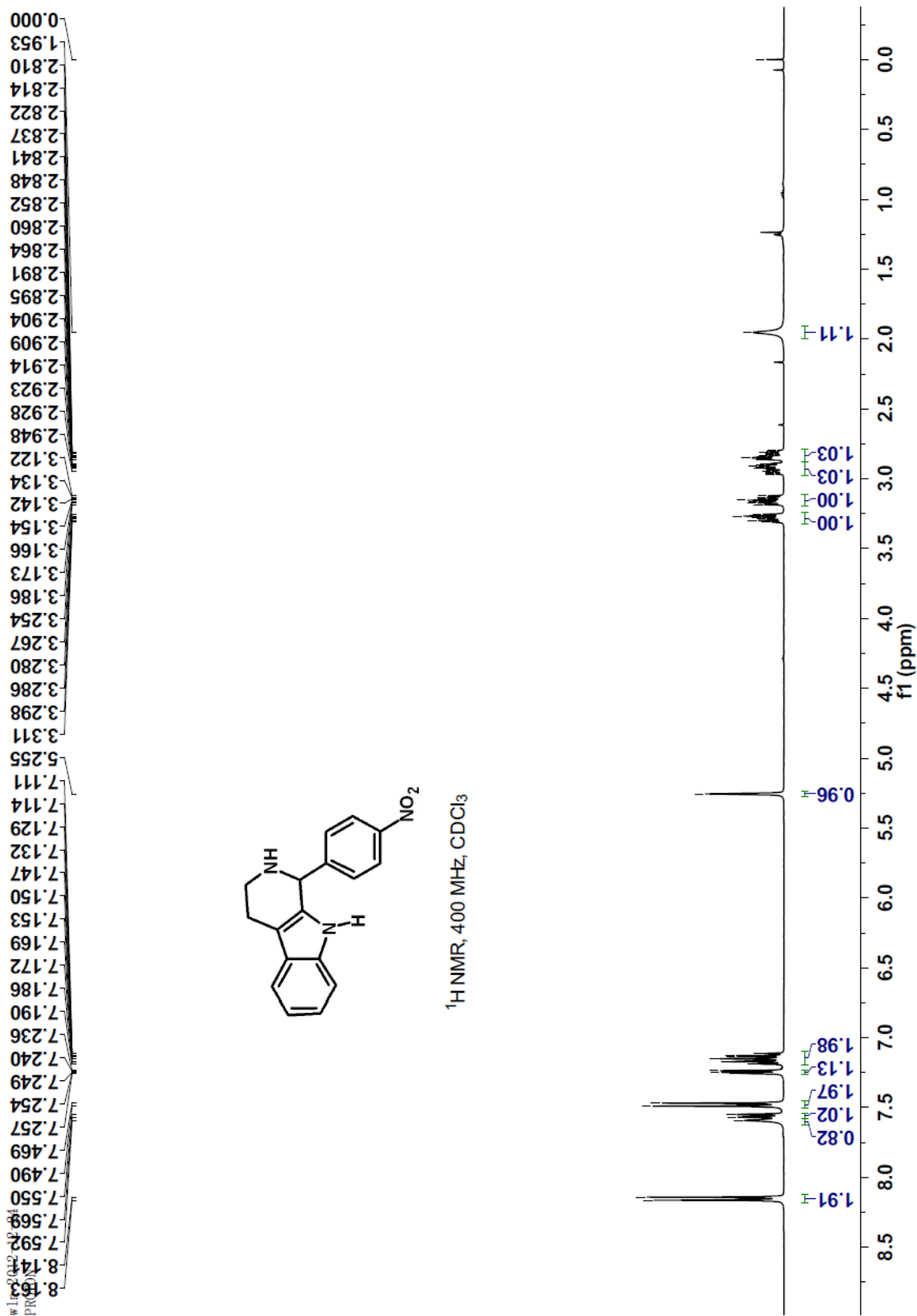


The ^1H NMR spectrum of the crude product after removal of solvent HFIP.

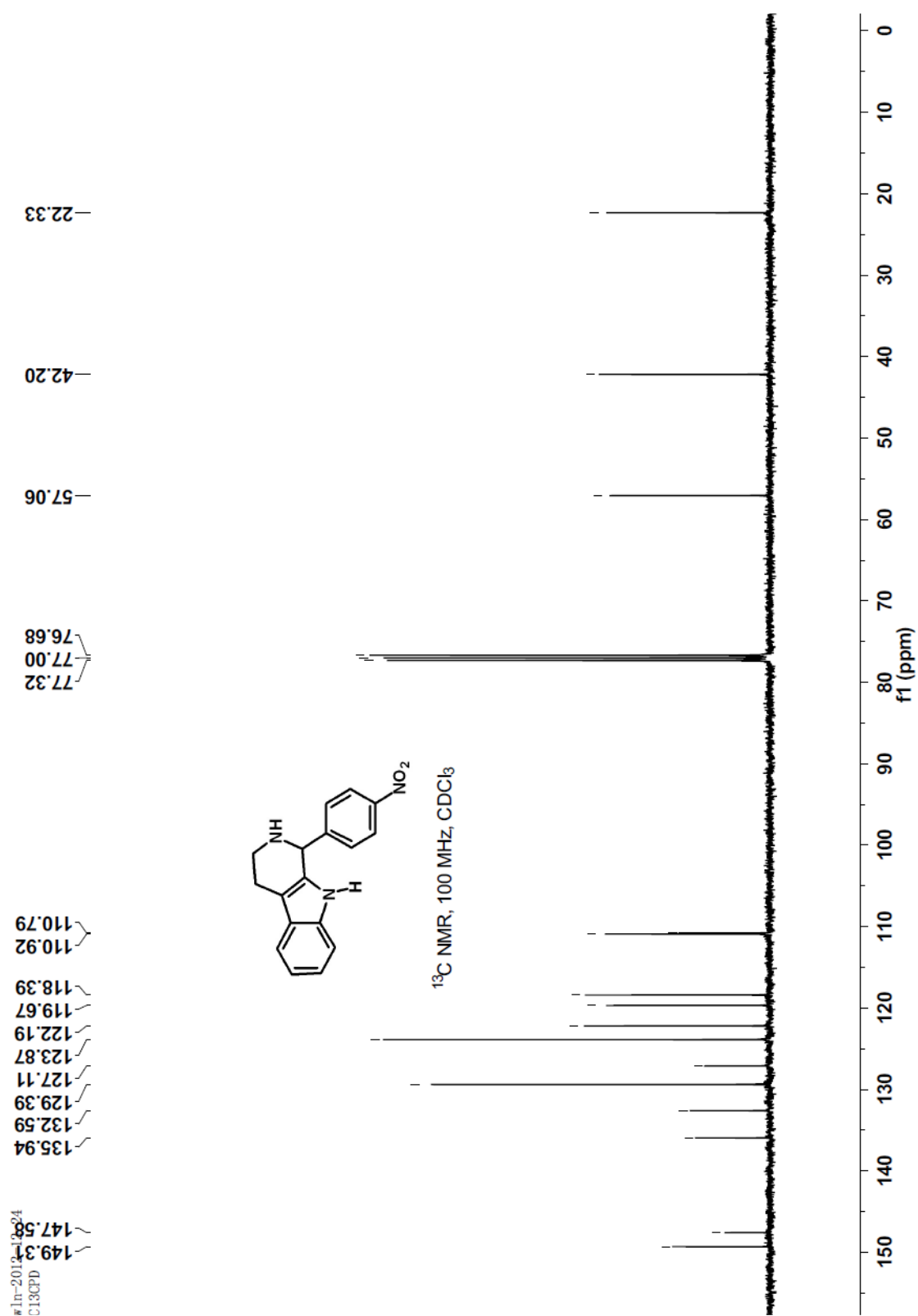


NMR spectra

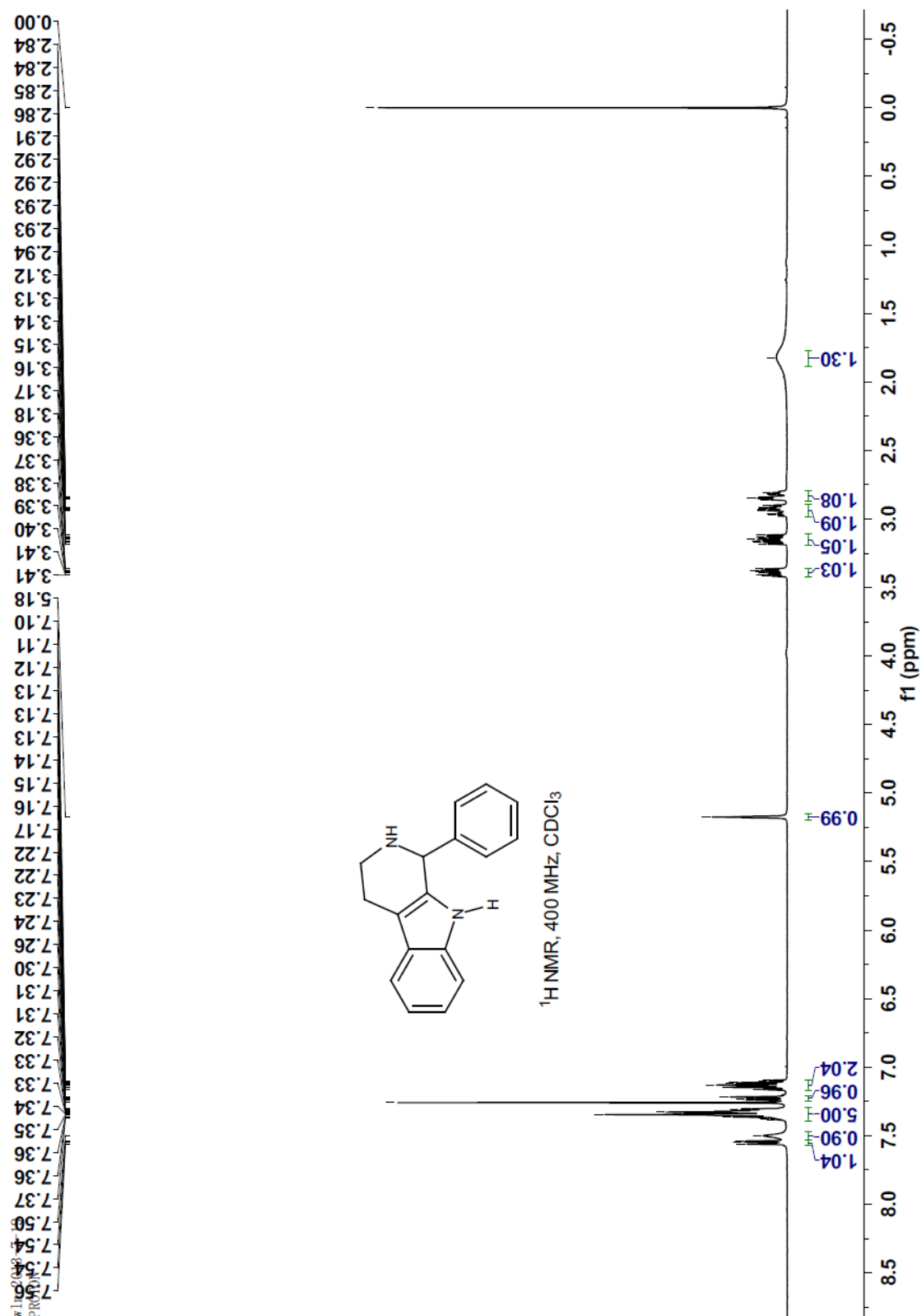
1-(4-Nitrophenyl)-1,2,3,4-tetrahydro- β -carboline (3a): ^1H NMR



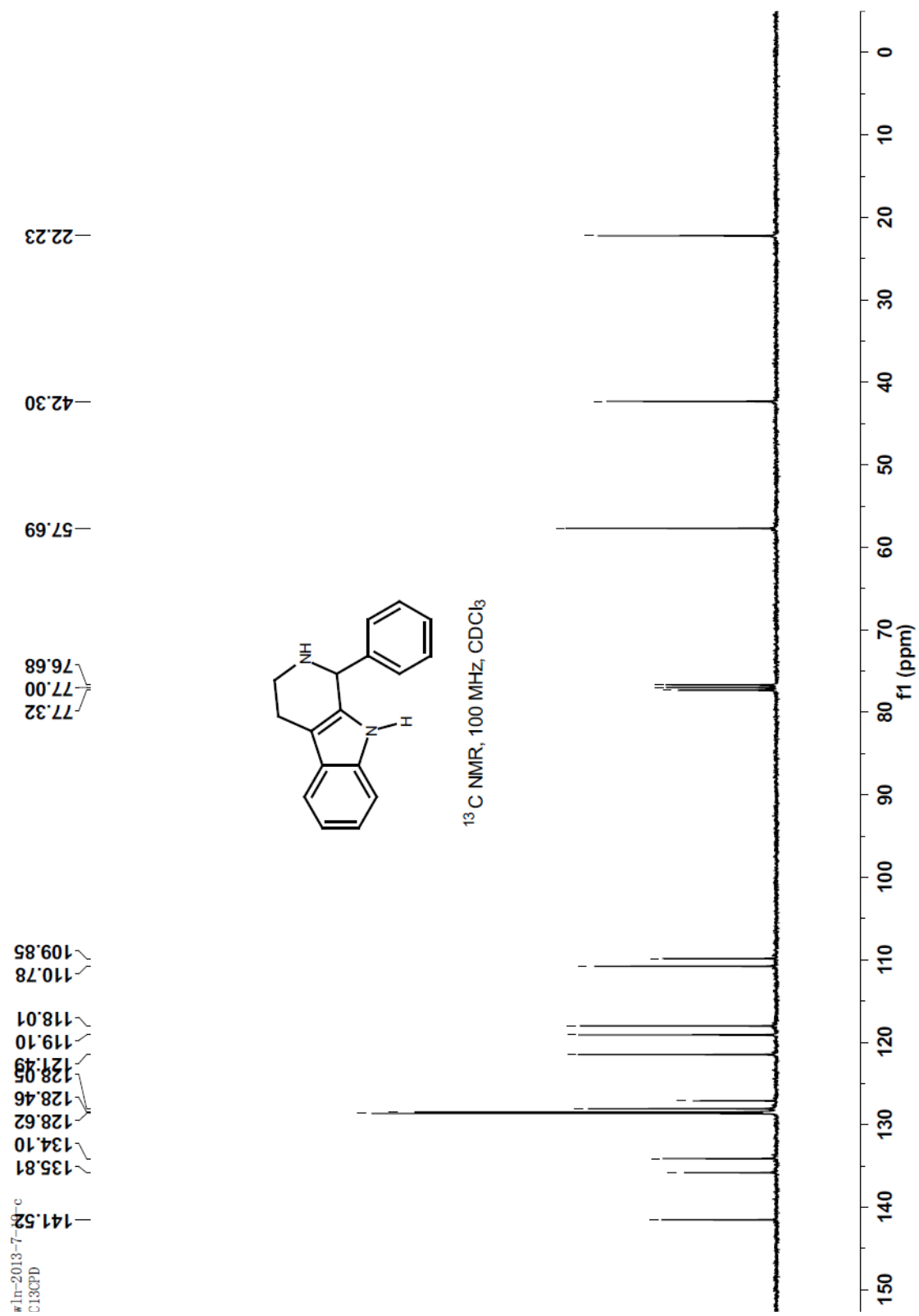
1-(4-Nitrophenyl)-1,2,3,4-tetrahydro-β-carboline (3a): ¹³C NMR



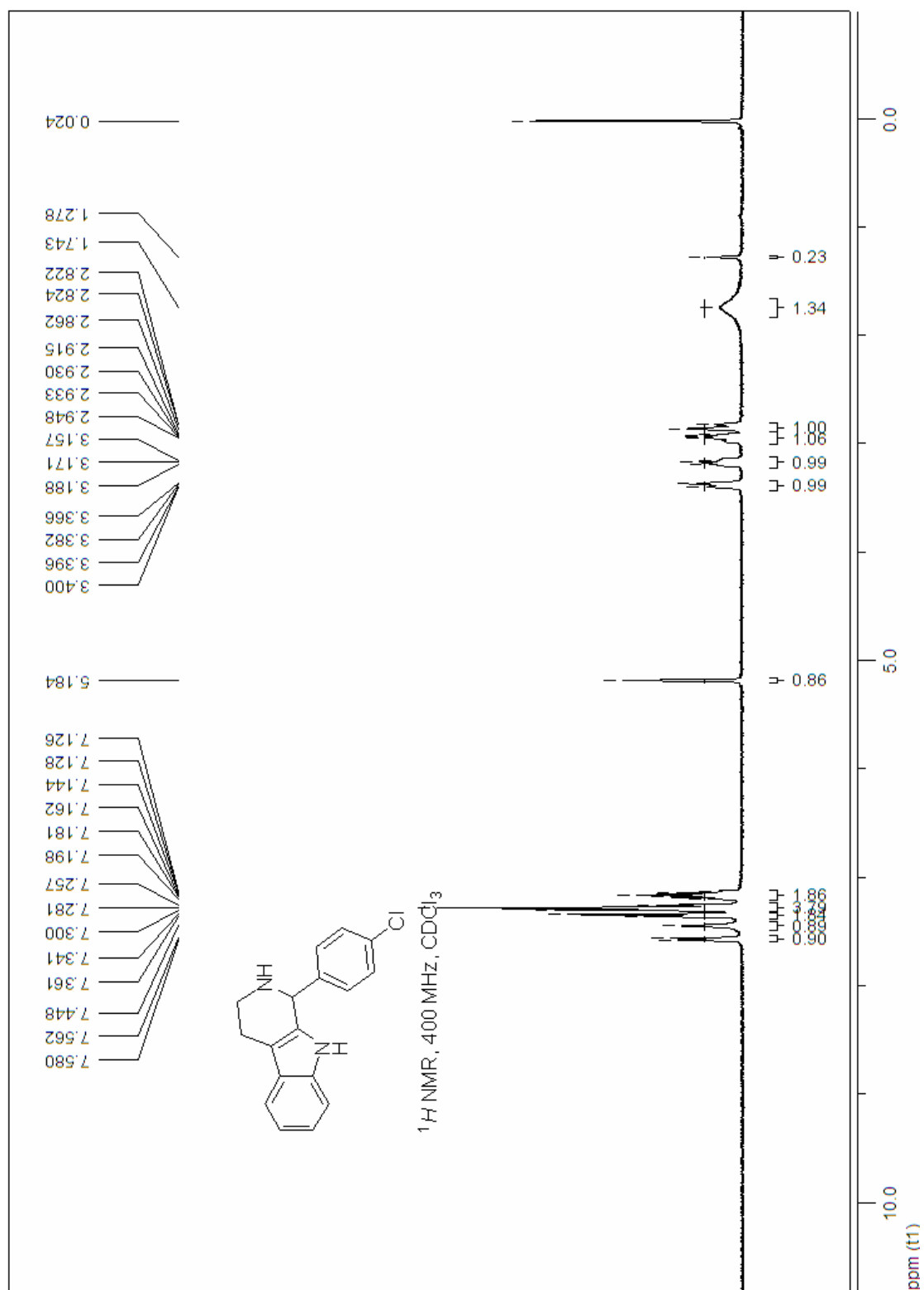
1-Phenyl-1,2,3,4-tetrahydro- β -carboline (3b): ^1H NMR



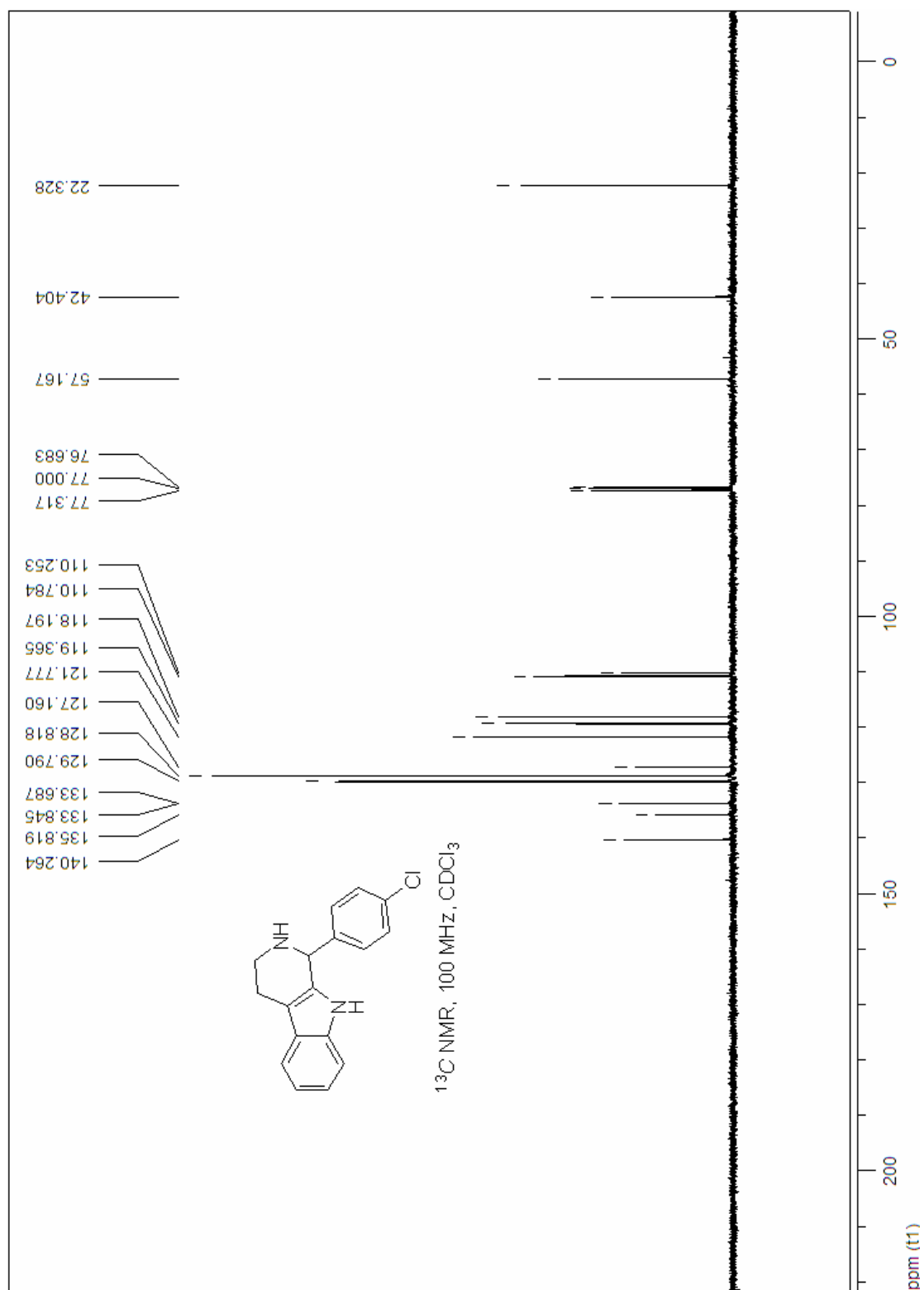
1-Phenyl-1,2,3,4-tetrahydro-β-carboline (3b): ¹³C NMR



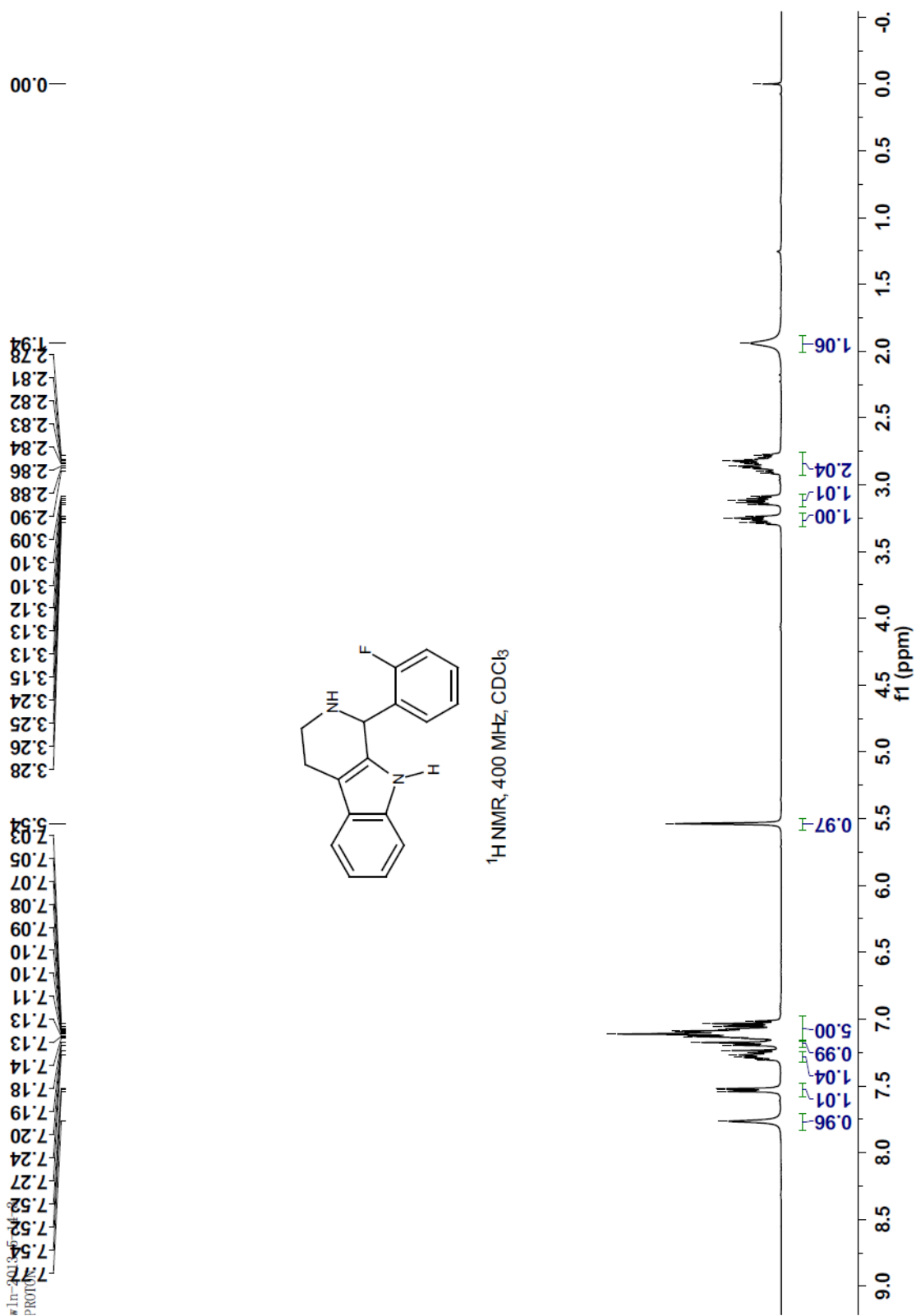
1-(4-Chlorophenyl)-1,2,3,4-tetrahydro-β-carboline (3c): ¹H NMR



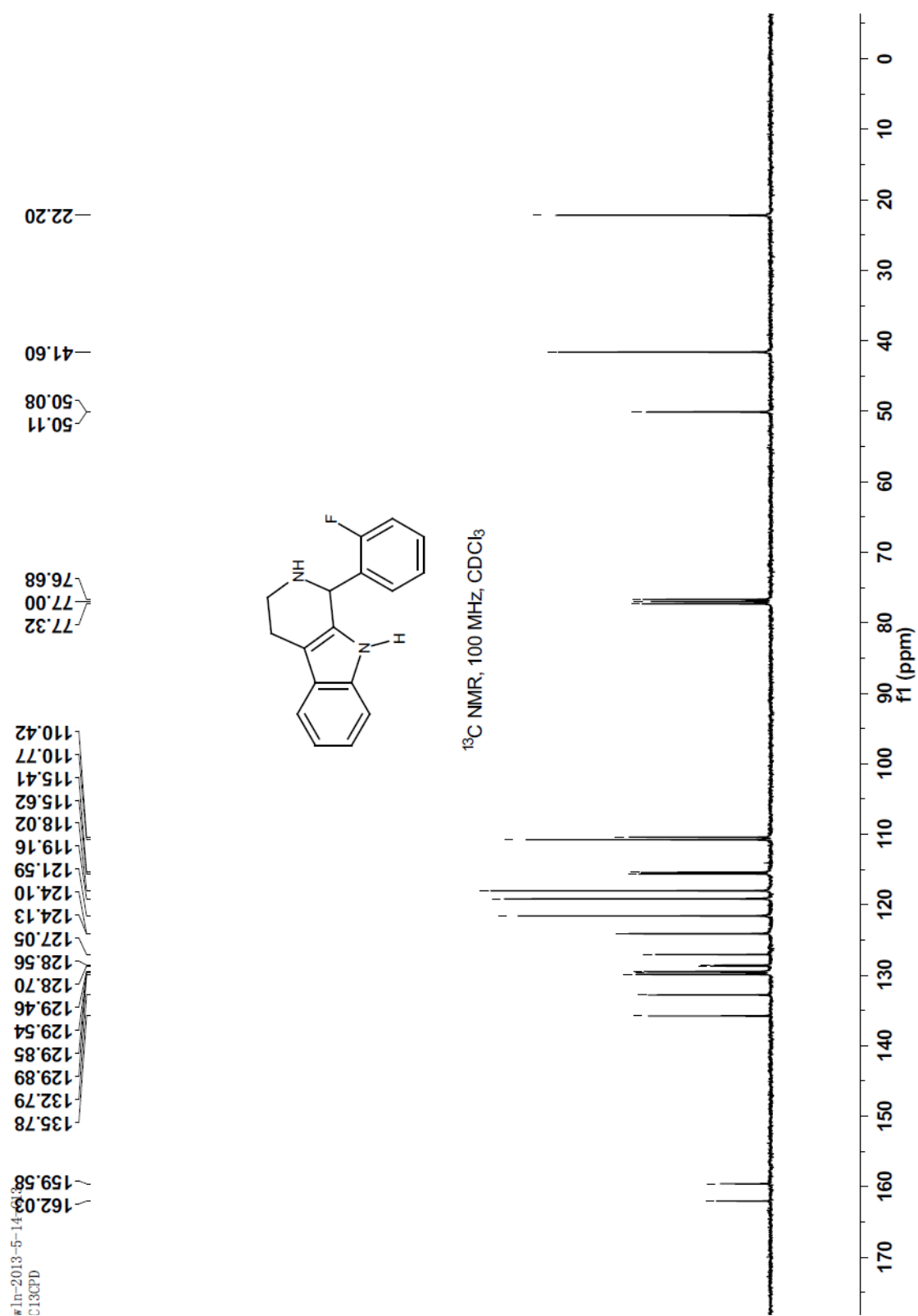
1-(4-Chlorophenyl)-1,2,3,4-tetrahydro-β-carboline (3c): ¹³C NMR



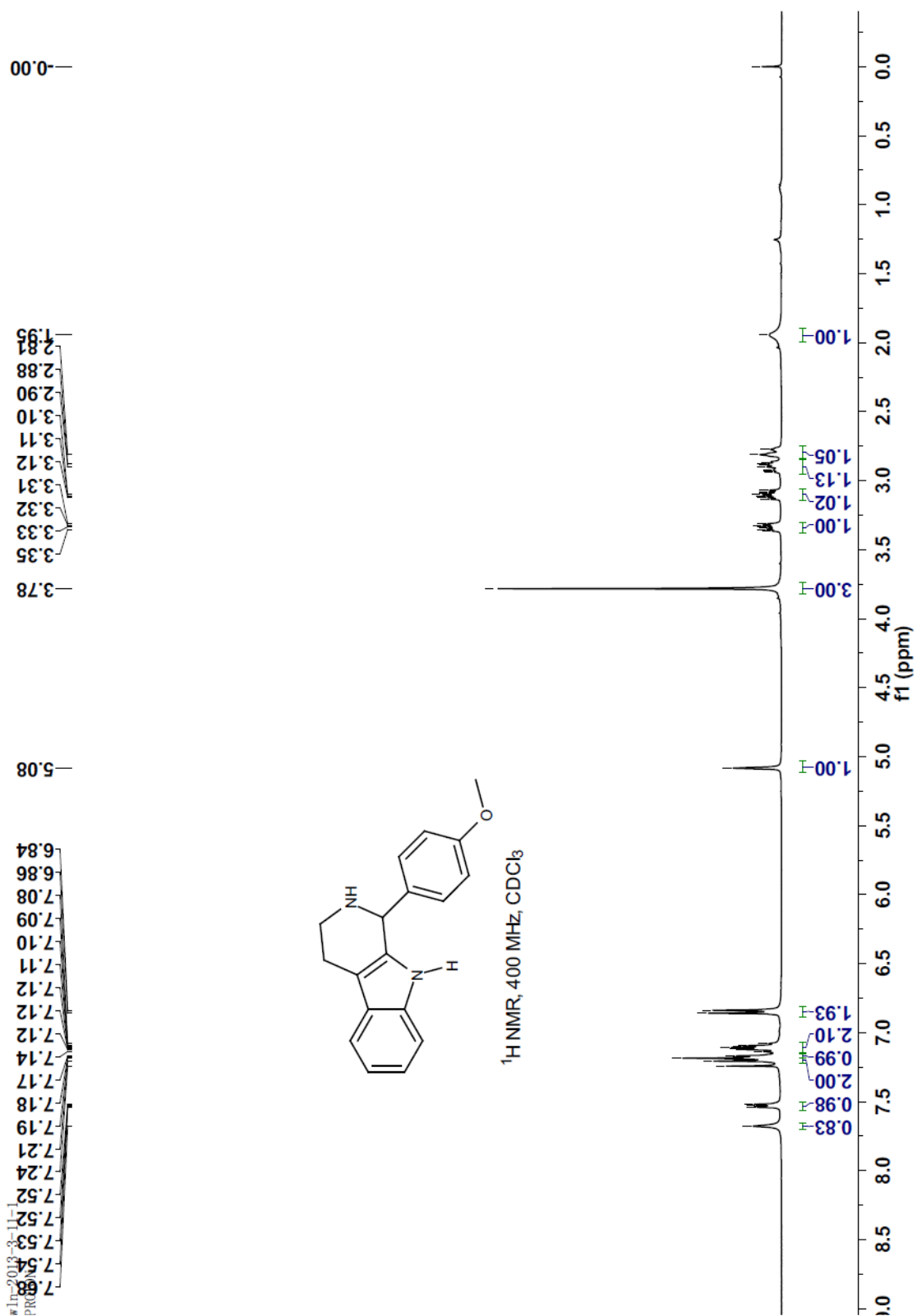
1-(2-Fluorophenyl)-1,2,3,4-tetrahydro- β -carboline (3d): ^1H NMR



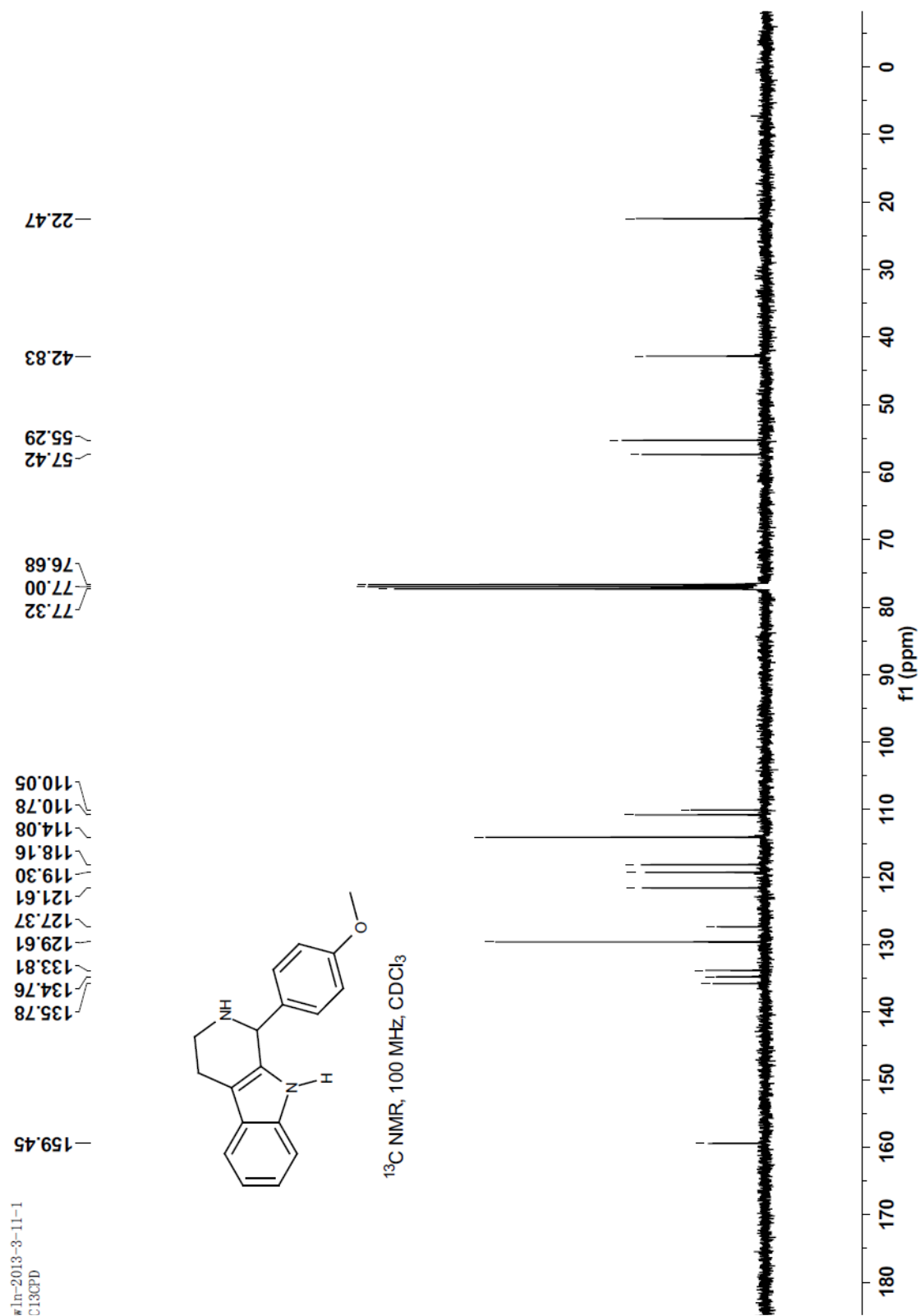
1-(2-Fluorophenyl)-1,2,3,4-tetrahydro- β -carboline (3d): ^{13}C NMR



1-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro- β -carboline (3e): ^1H NMR

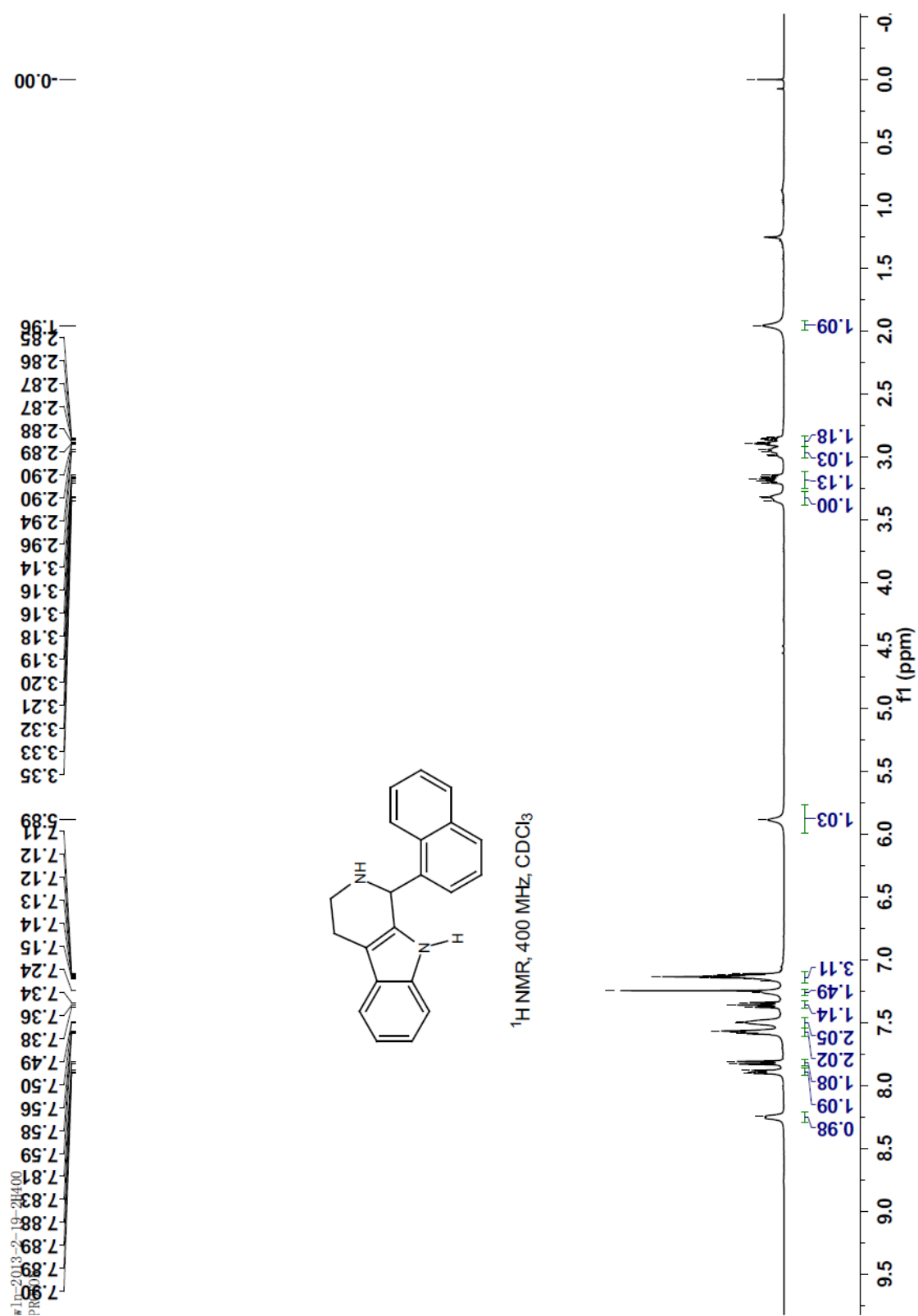


1-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro- β -carboline (3e): ^{13}C NMR

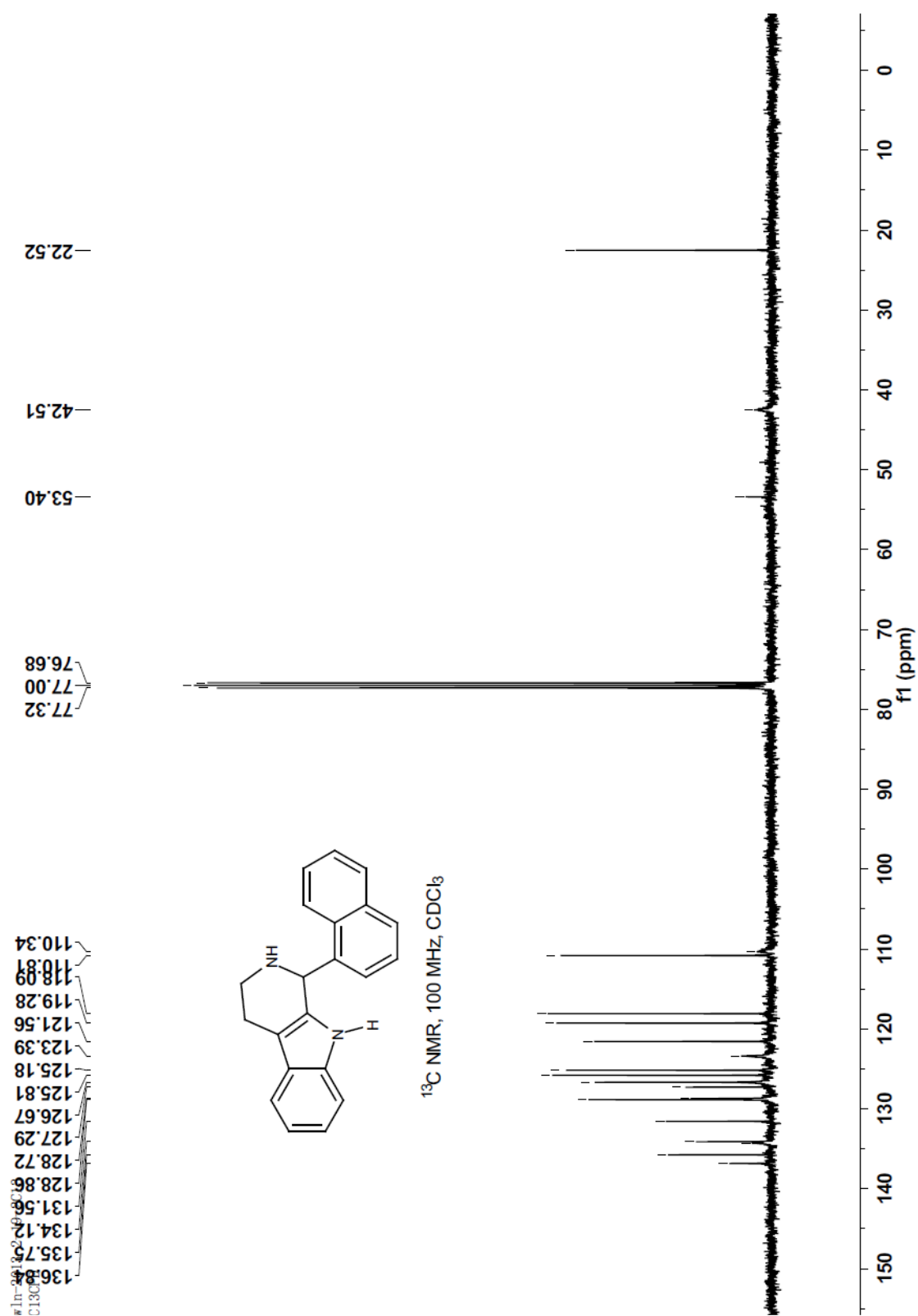


WIn-2013-3-11-1
C13CPD

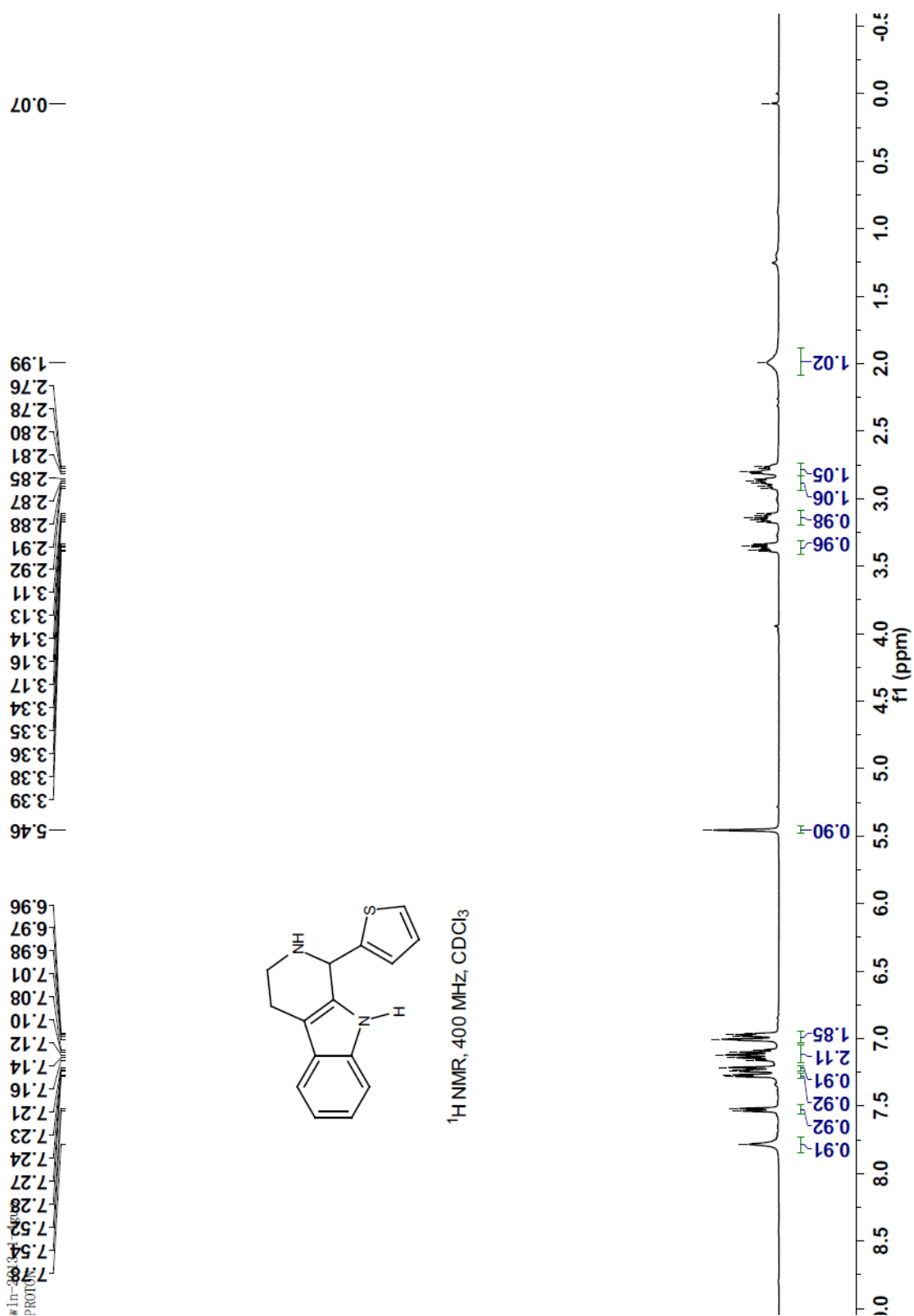
1-(Naphthyl)-1,2,3,4-tetrahydro- β -carboline (3f): ^1H NMR



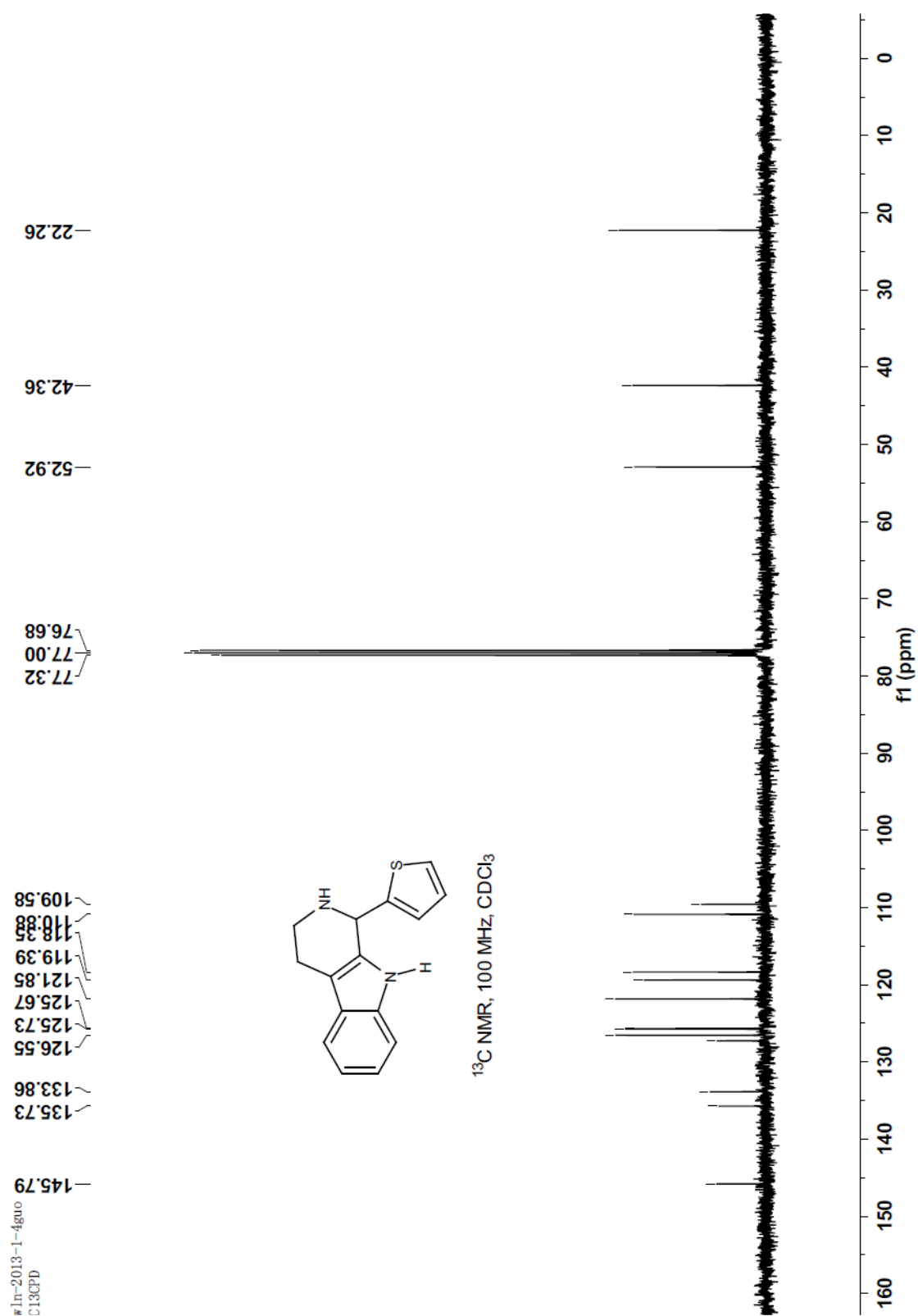
1-(Naphthyl)-1,2,3,4-tetrahydro-β-carboline (3f): ¹³C NMR



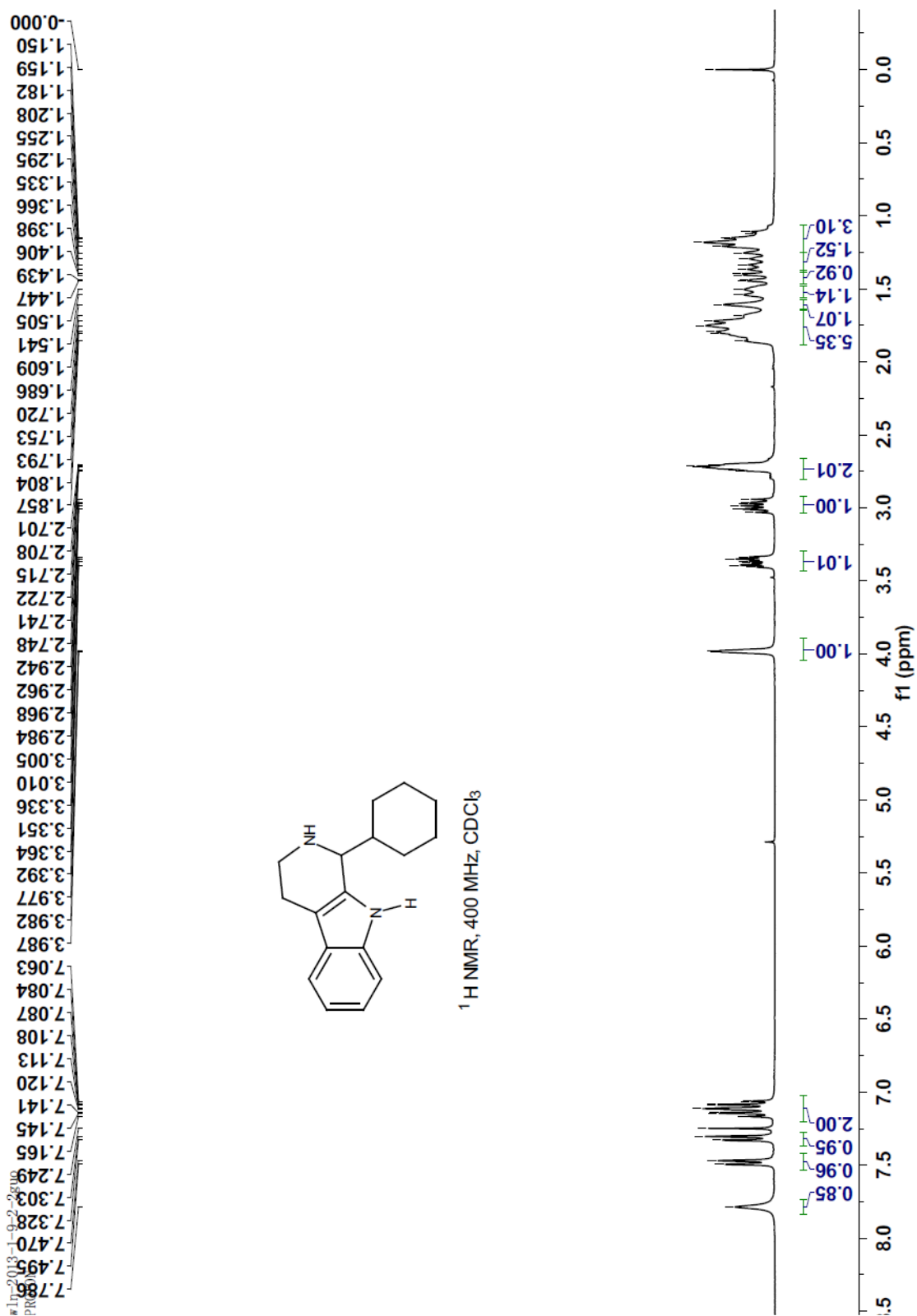
1-(2-Thienyl)-1,2,3,4-tetrahydro-β-carboline (3g): ¹H NMR



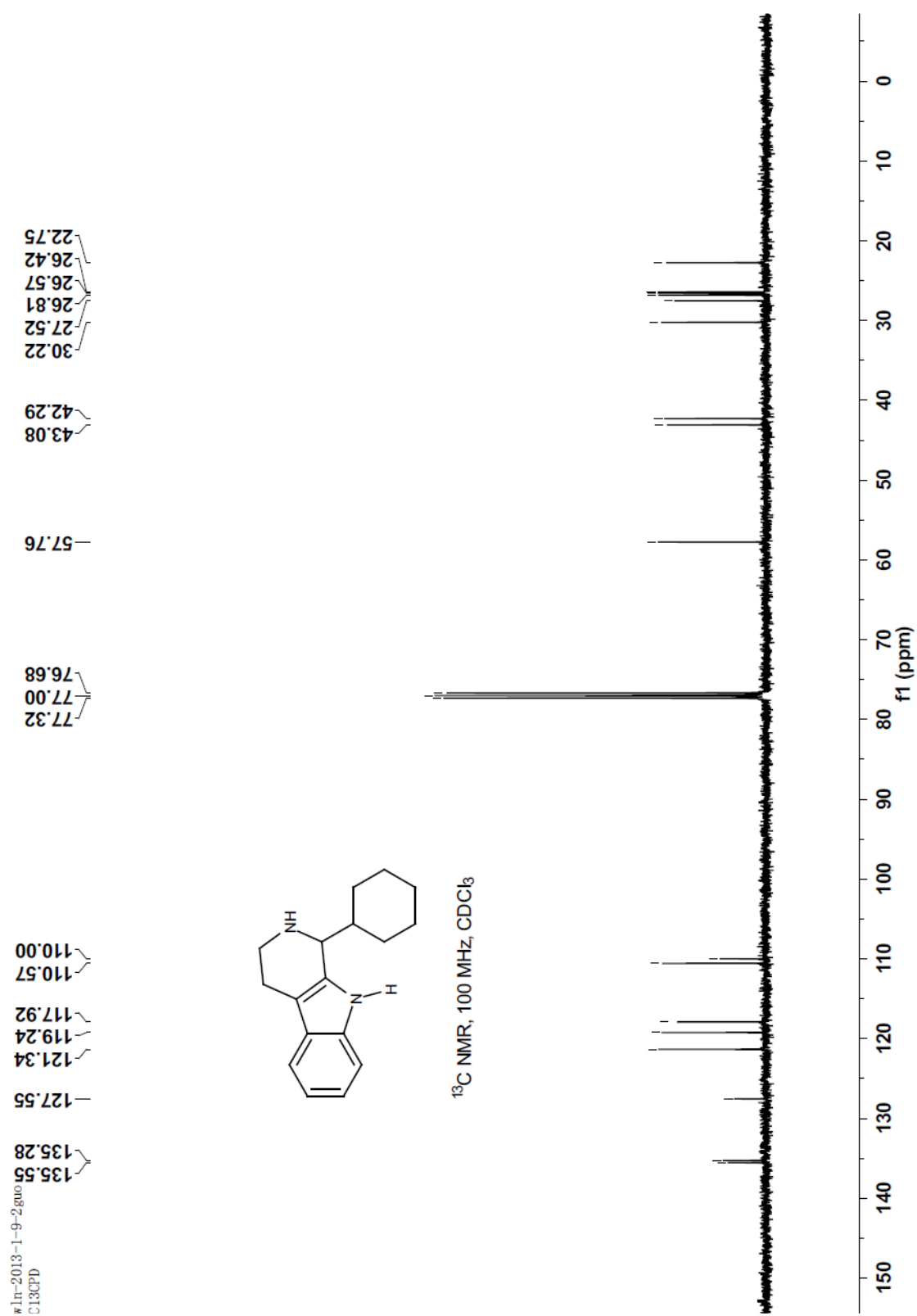
1-(2-Thienyl)-1,2,3,4-tetrahydro- β -carboline (3g): ^{13}C NMR



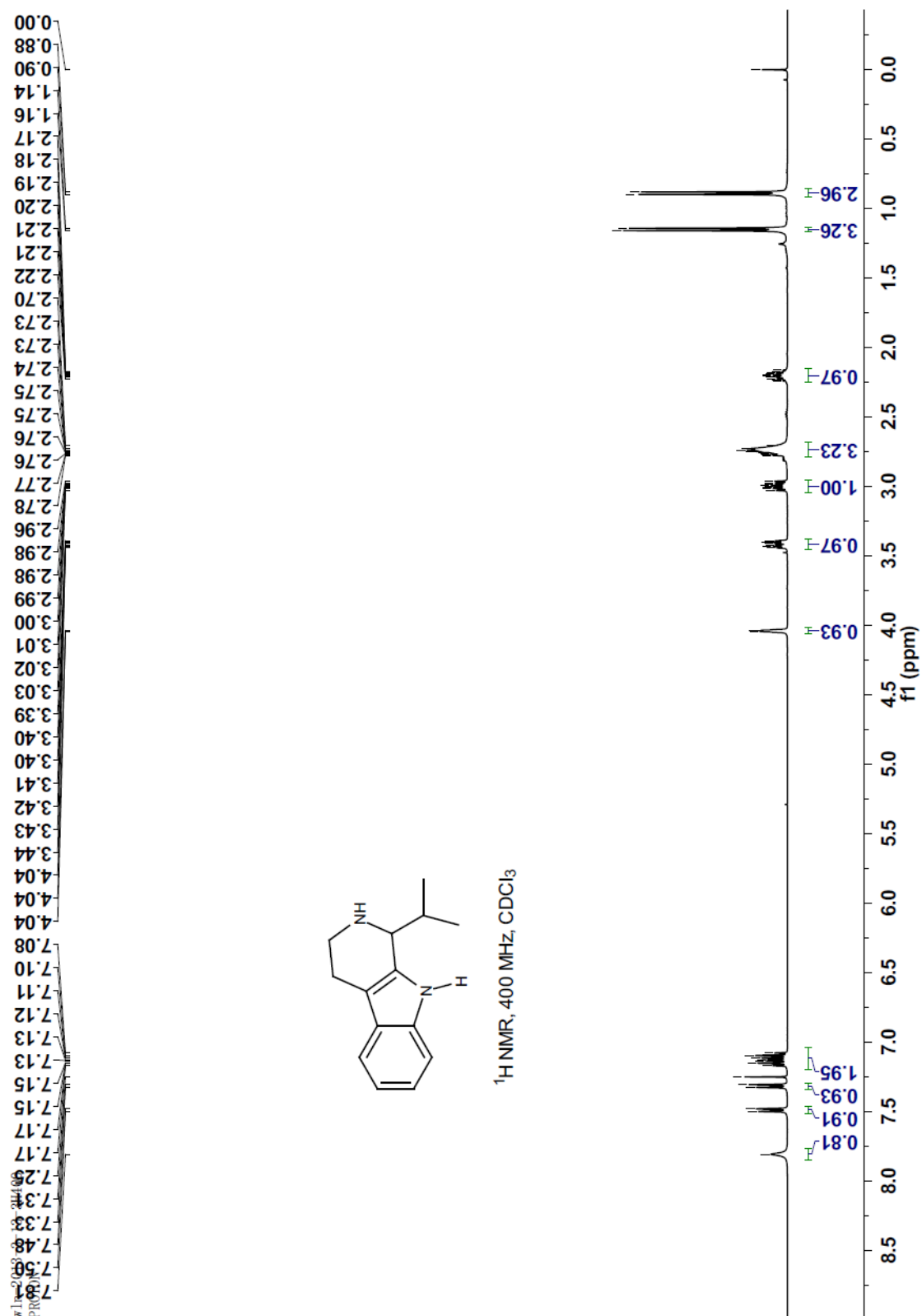
1-Cyclohexyl-1,2,3,4-tetrahydro-β-carboline (3h): ¹H NMR



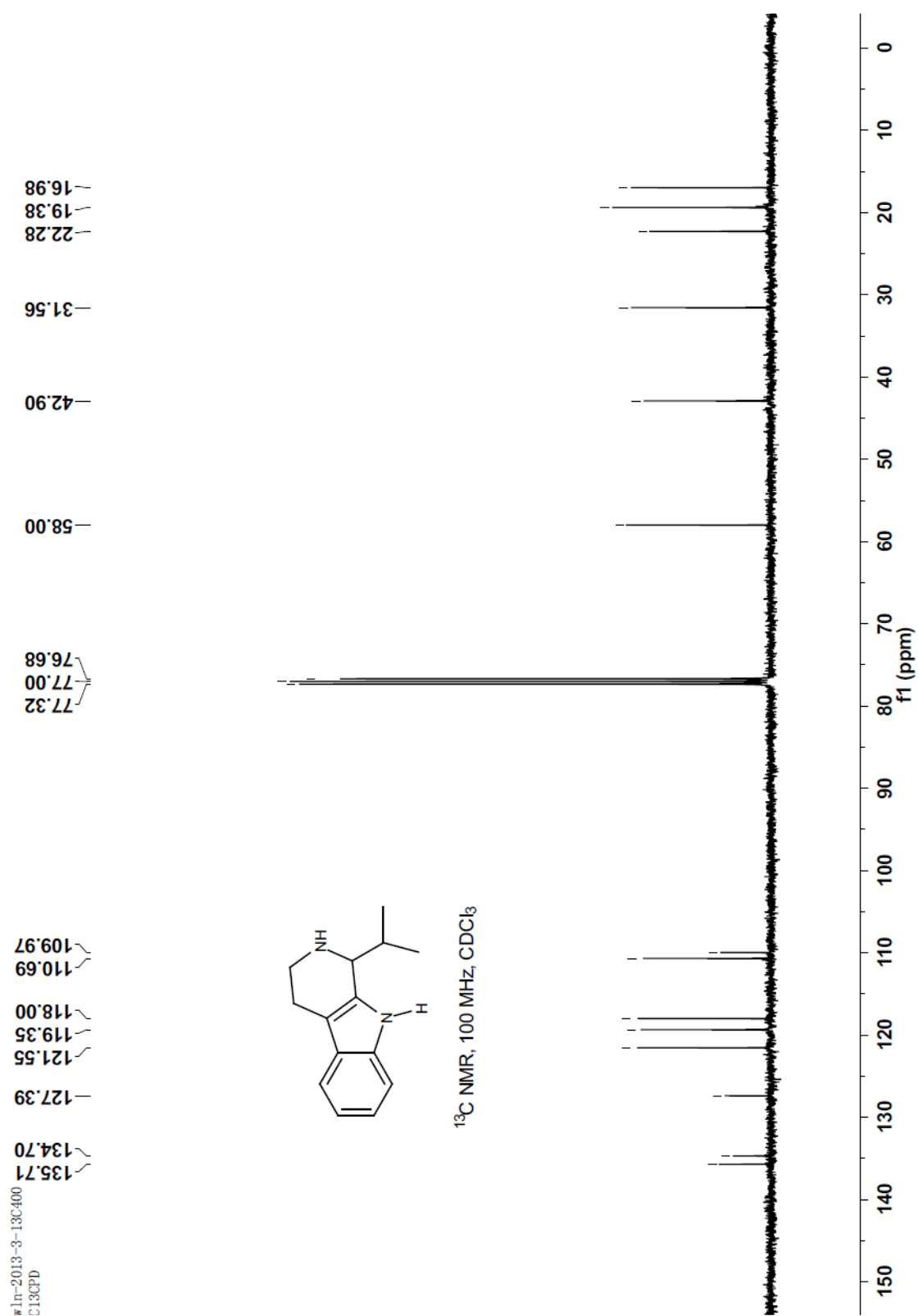
1-Cyclohexyl-1,2,3,4-tetrahydro- β -carboline (3h): ^{13}C NMR



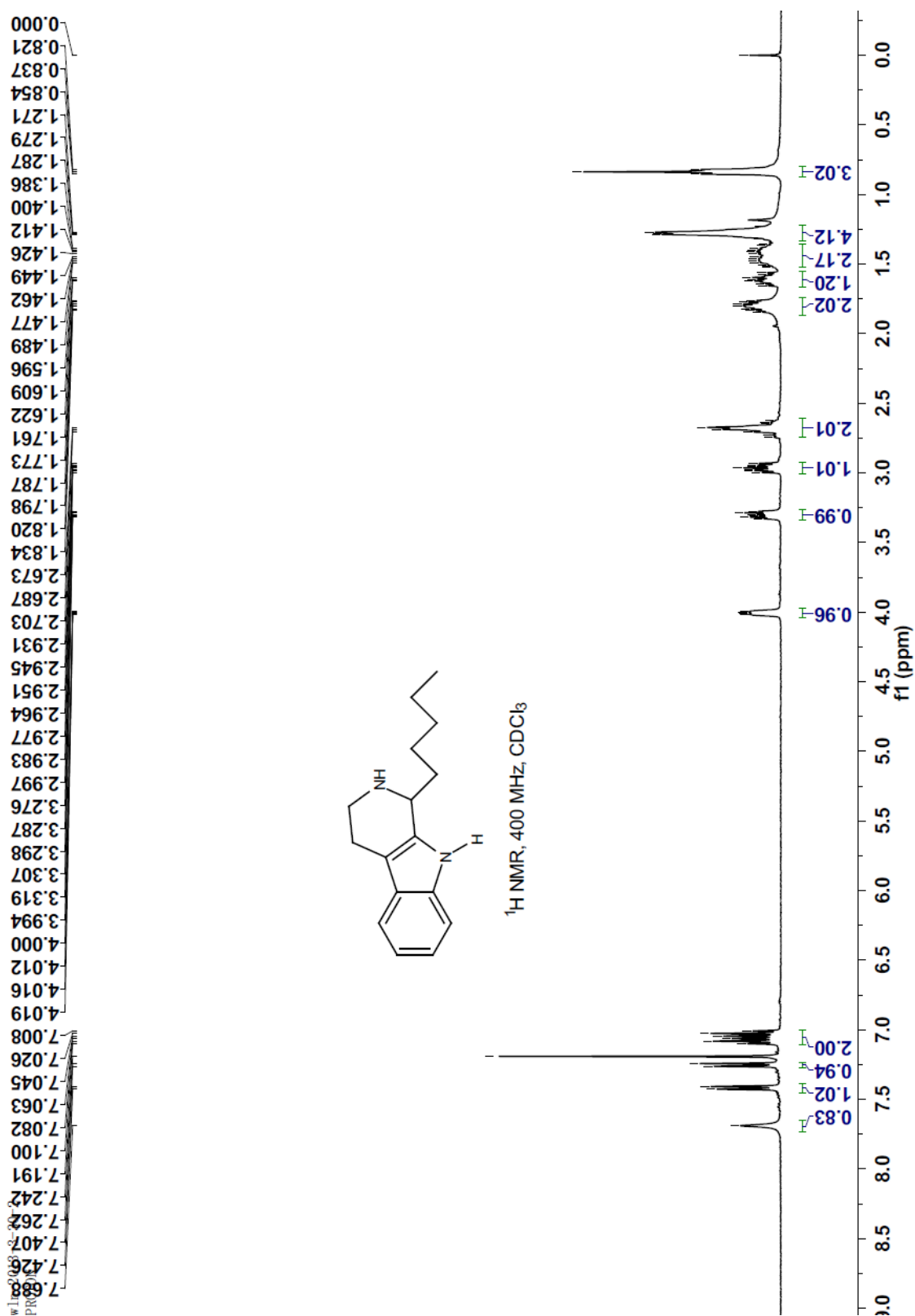
1-Isopropyl-1,2,3,4-tetrahydro-β-carboline (3i): ¹H NMR



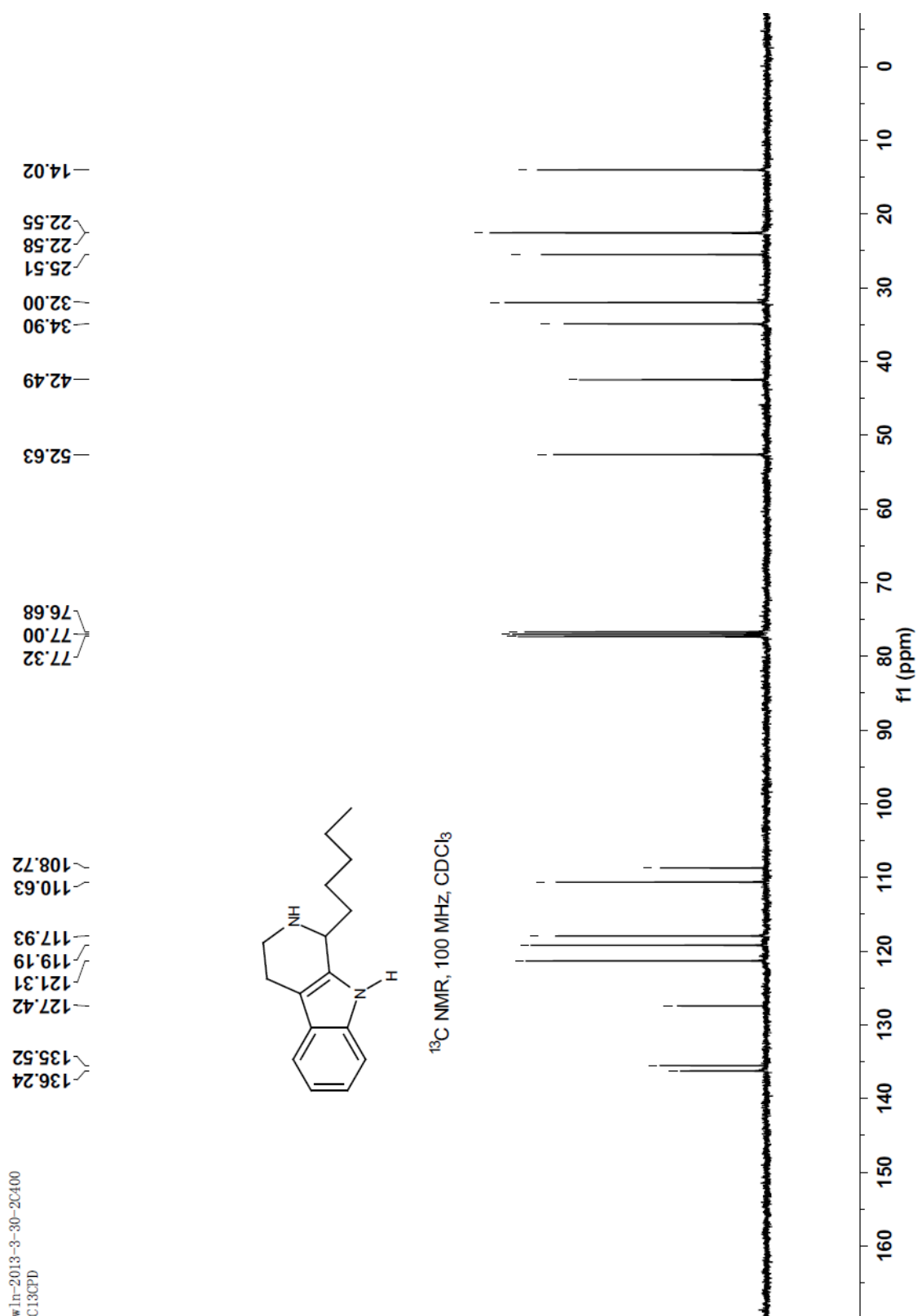
1-Isopropyl-1,2,3,4-tetrahydro-β-carboline (3i): ¹³C NMR



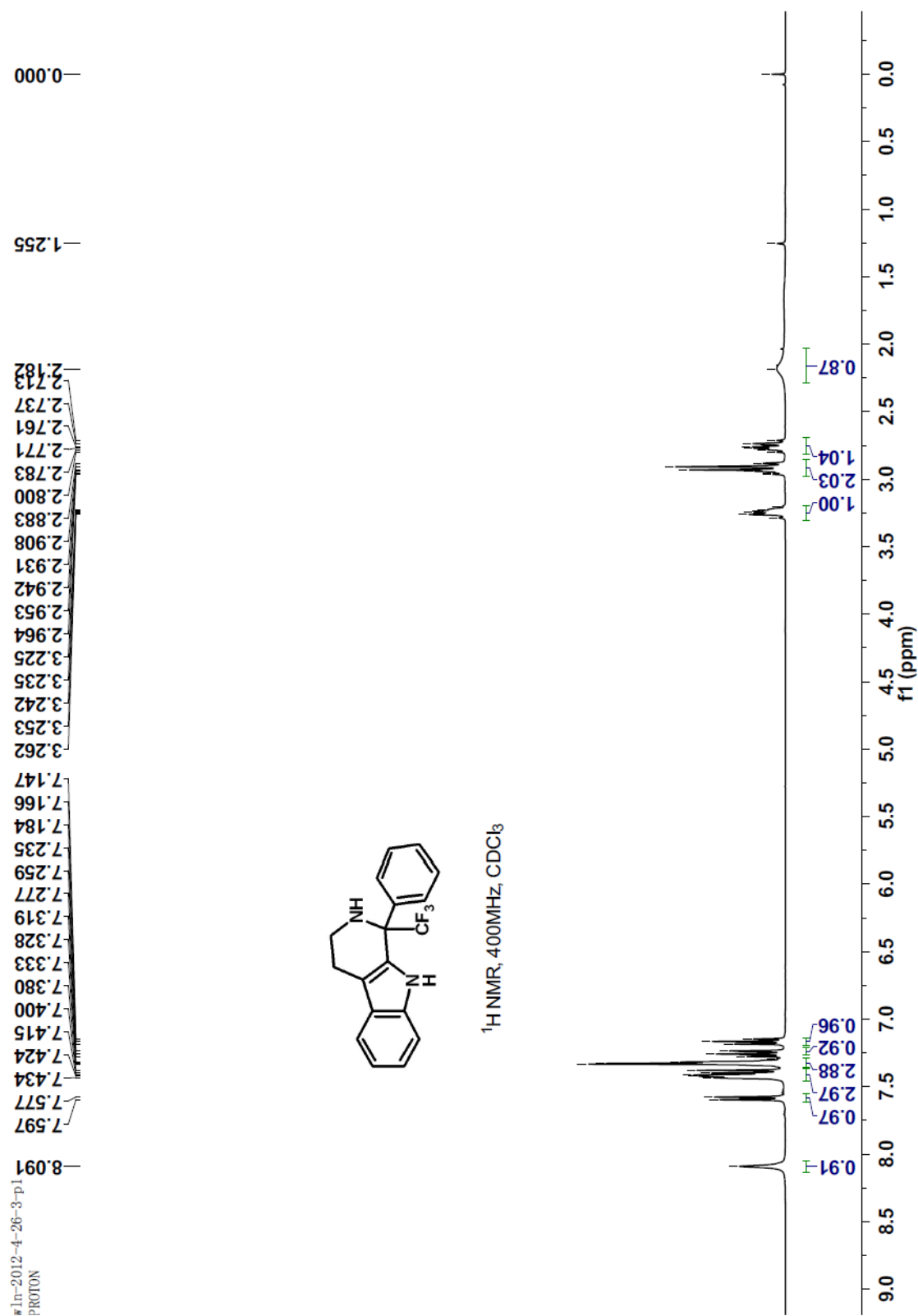
1-Pentyl-1,2,3,4-tetrahydro- β -carboline (3j): ^1H NMR



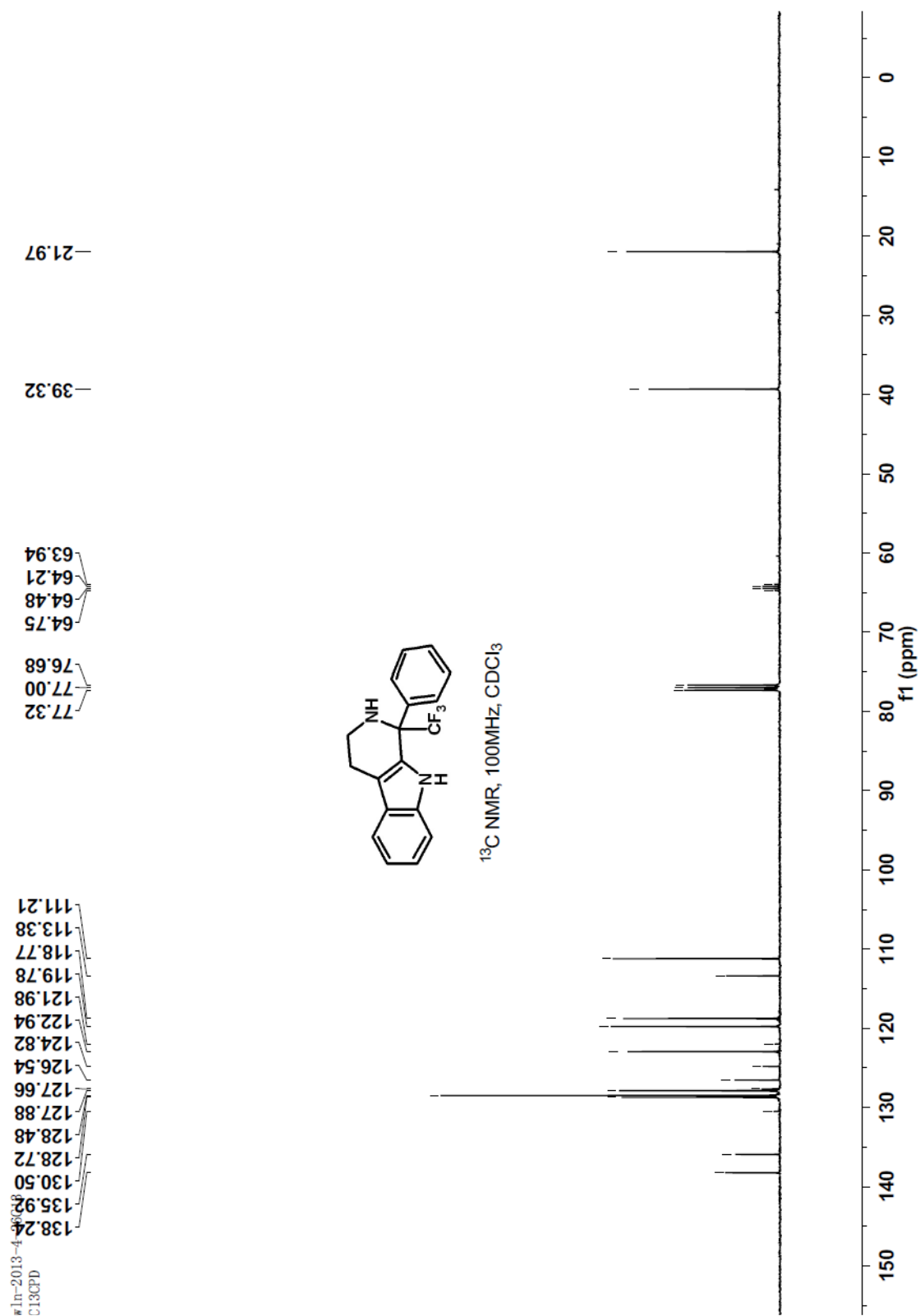
1-Pentyl-1,2,3,4-tetrahydro- β -carboline (3j): ^{13}C NMR



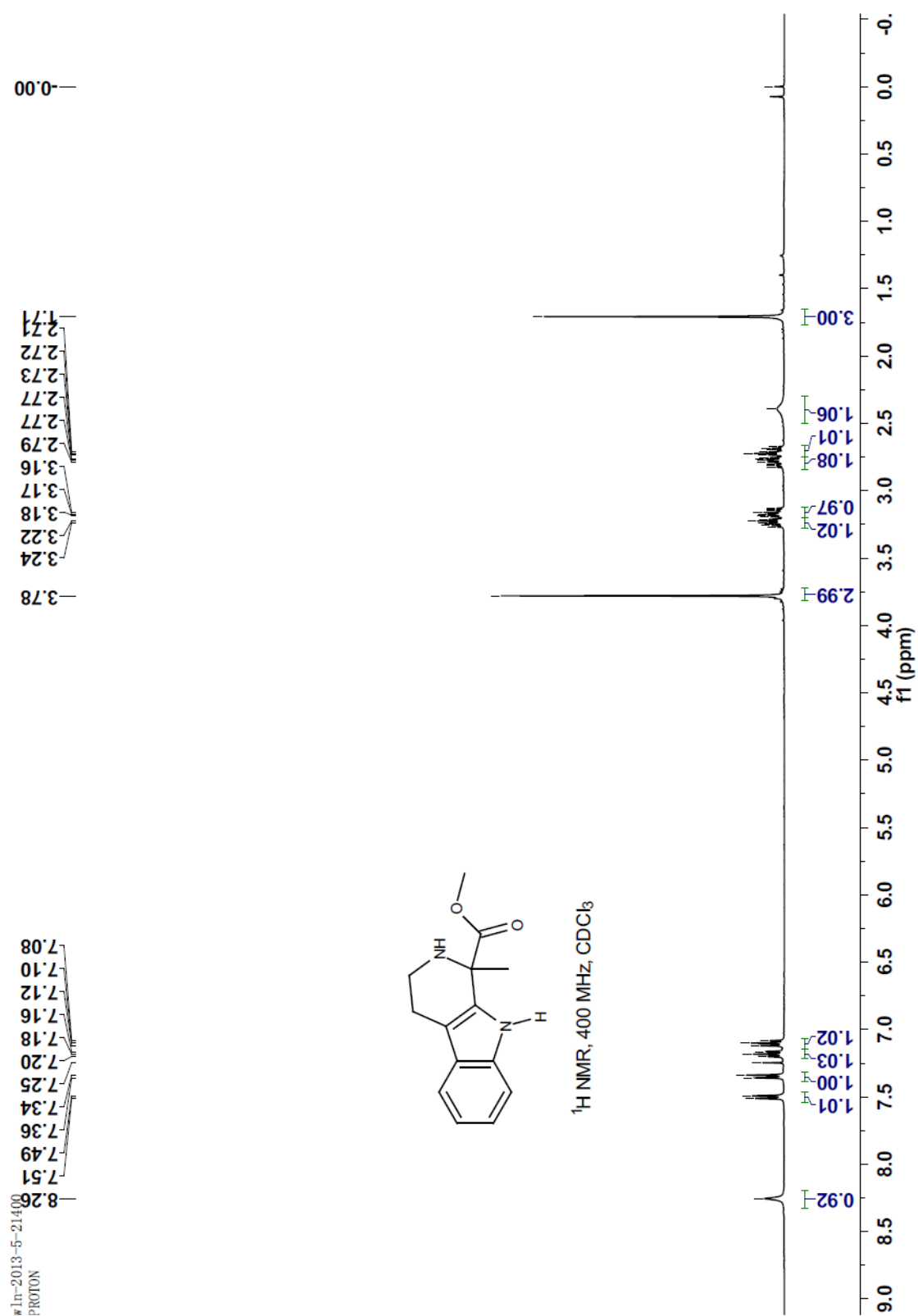
1-Phenyl-1-trifluoromethyl-1,2,3,4-tetrahydro-β-carboline (3k): ¹H NMR



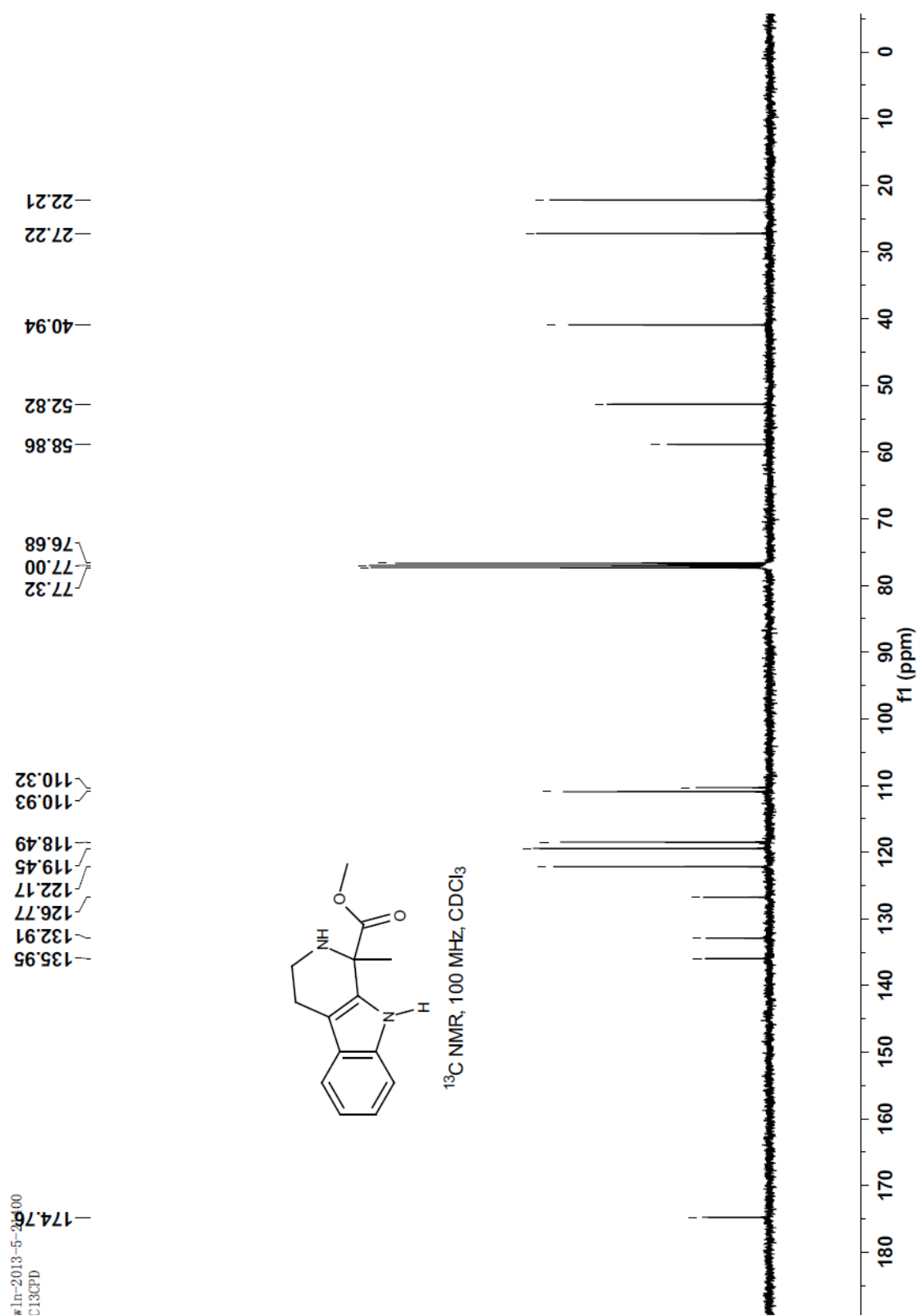
1-Phenyl-1-trifluoromethyl-1,2,3,4-tetrahydro-β-carboline (3k): ¹³C NMR



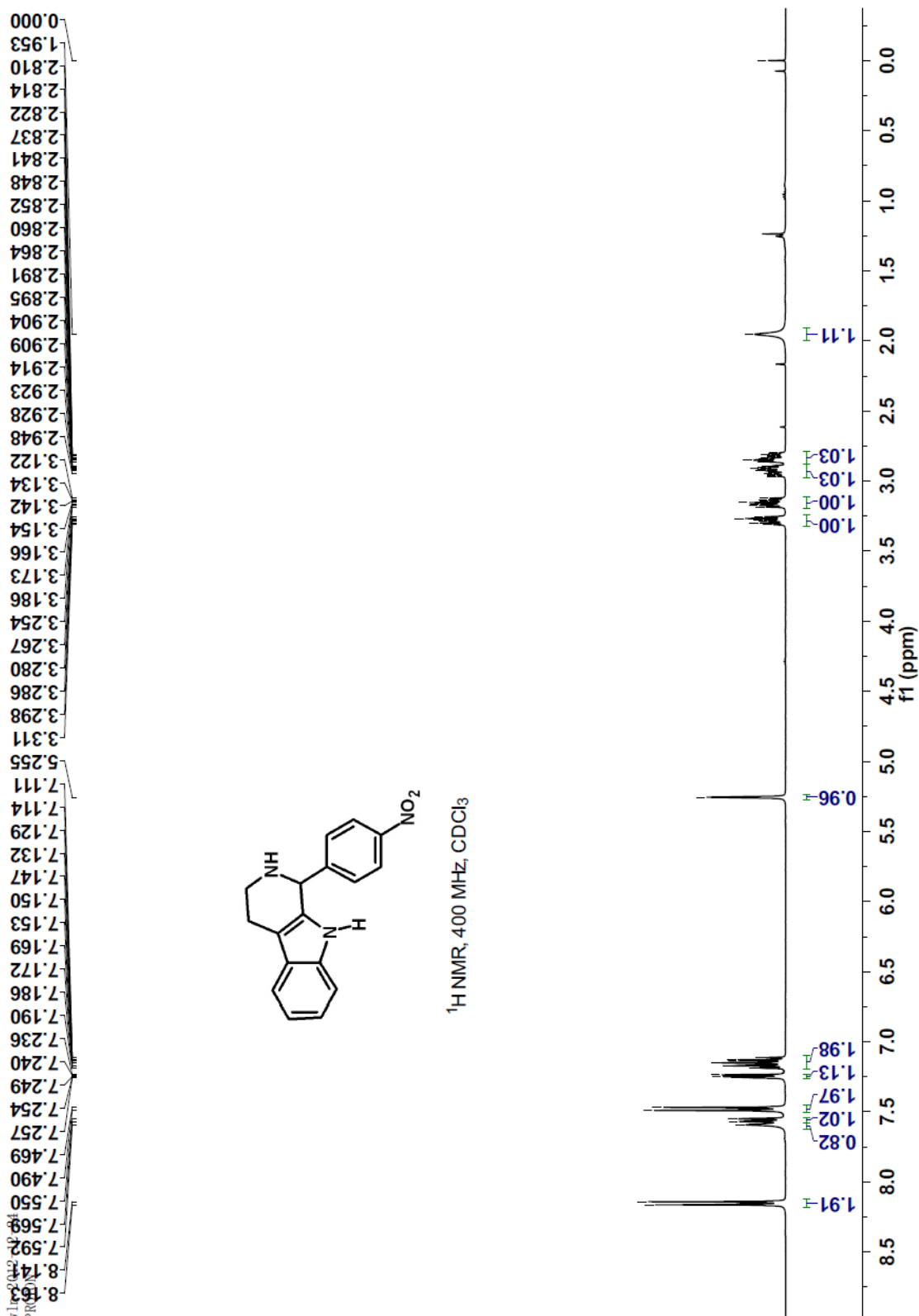
Methyl-(1-methyl-1,2,3,4-tetrahydro-β-carboline-1-yl) carboxylate (3l): ¹H NMR



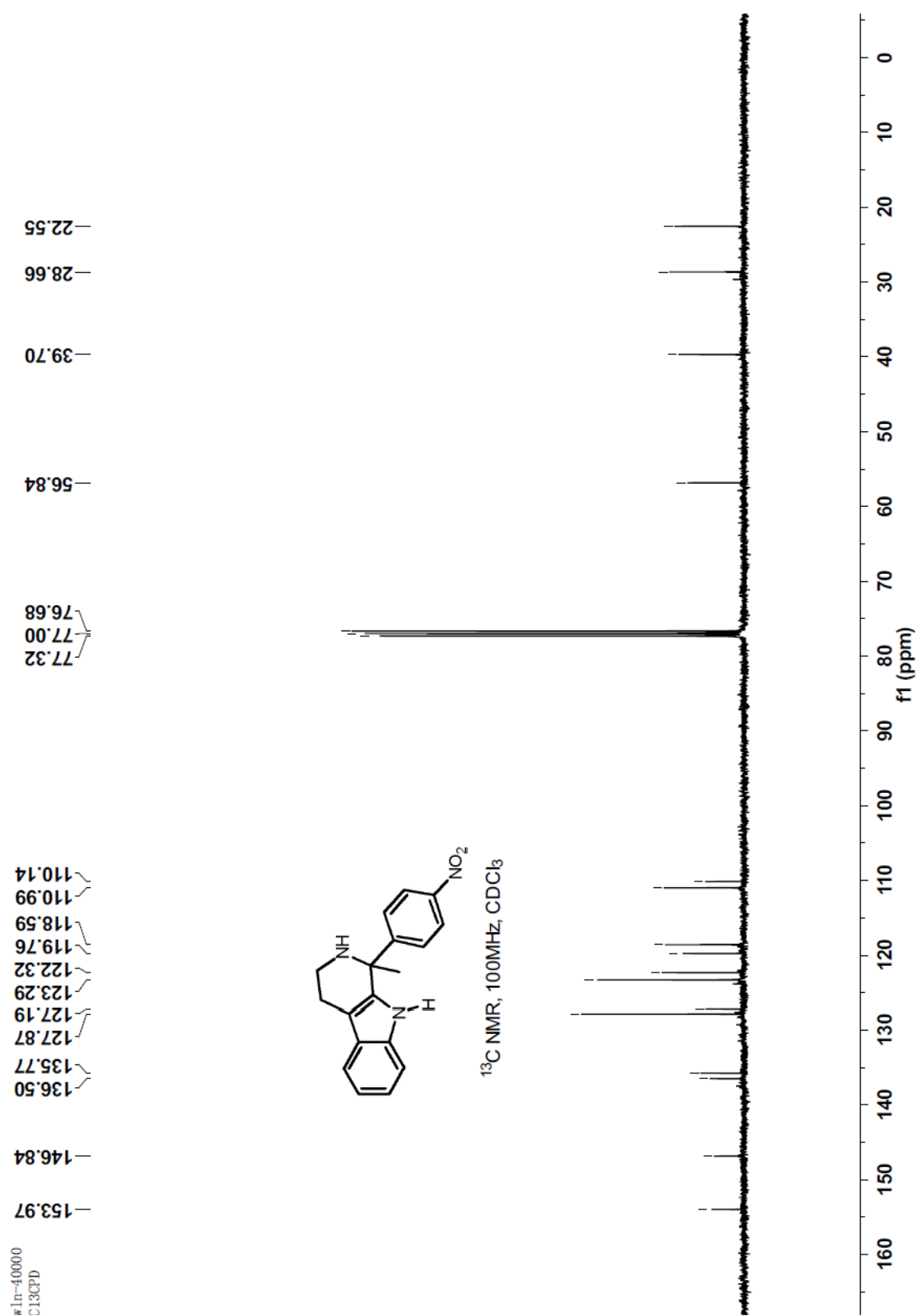
Methyl-(1-methyl-1,2,3,4-tetrahydro-β-carboline-1-yl) carboxylate (3l): ¹³C NMR



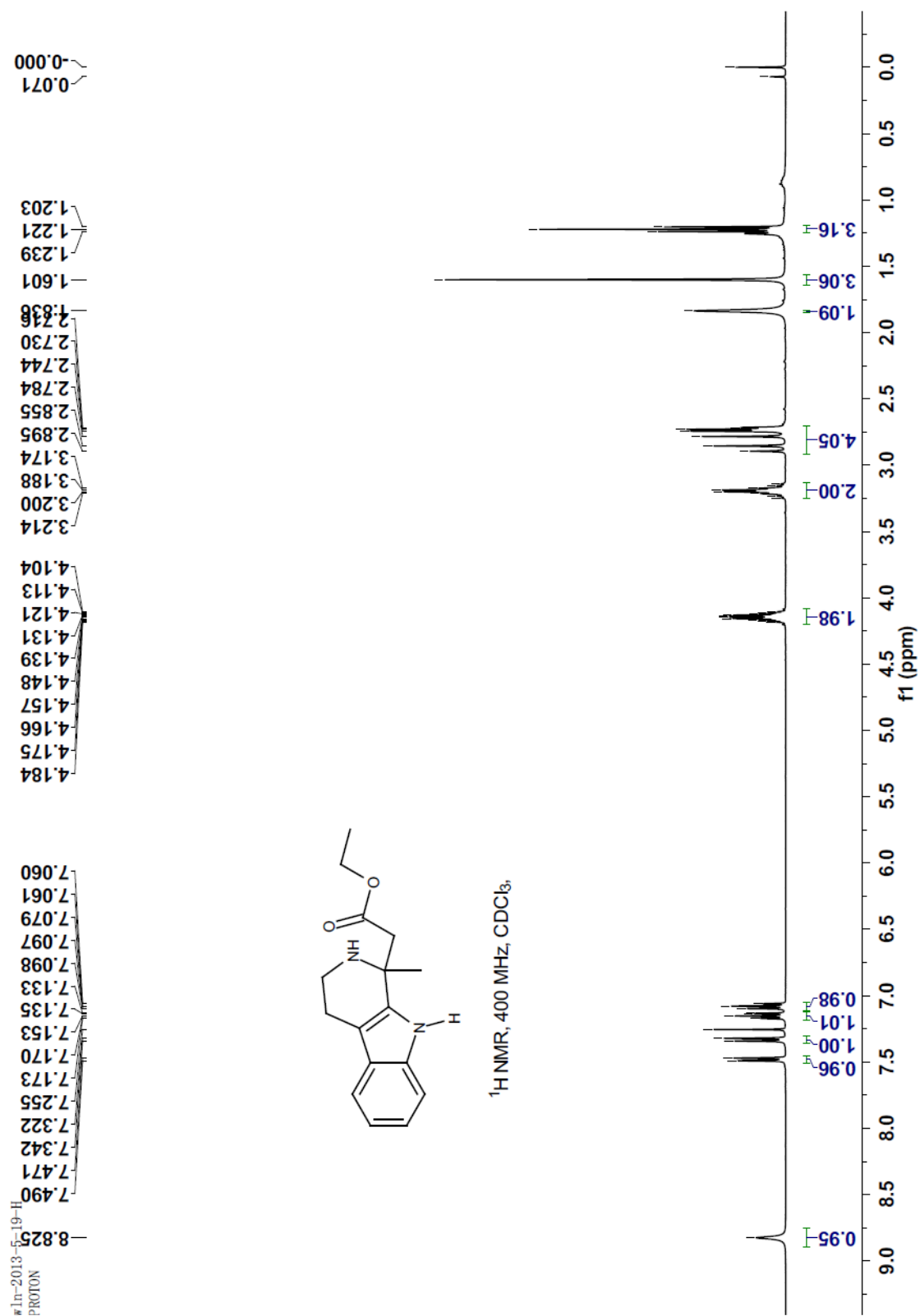
1-Methyl-1-(4-nitrophenyl)-1,2,3,4-tetrahydro-β-carboline (3m): ¹H NMR



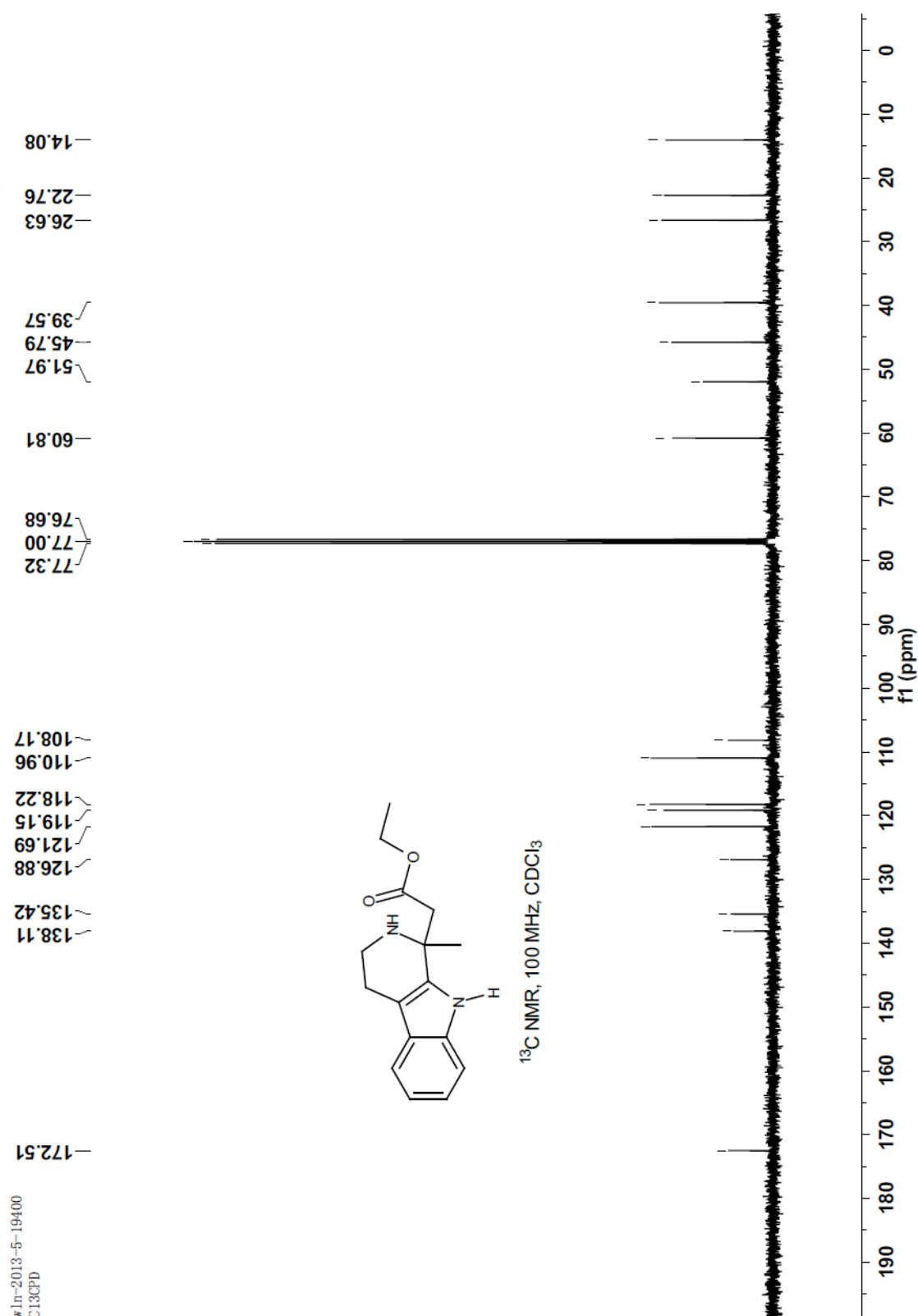
1-Methyl-1-(4-nitrophenyl)-1,2,3,4-tetrahydro-β-carboline (3m): ¹³C NMR



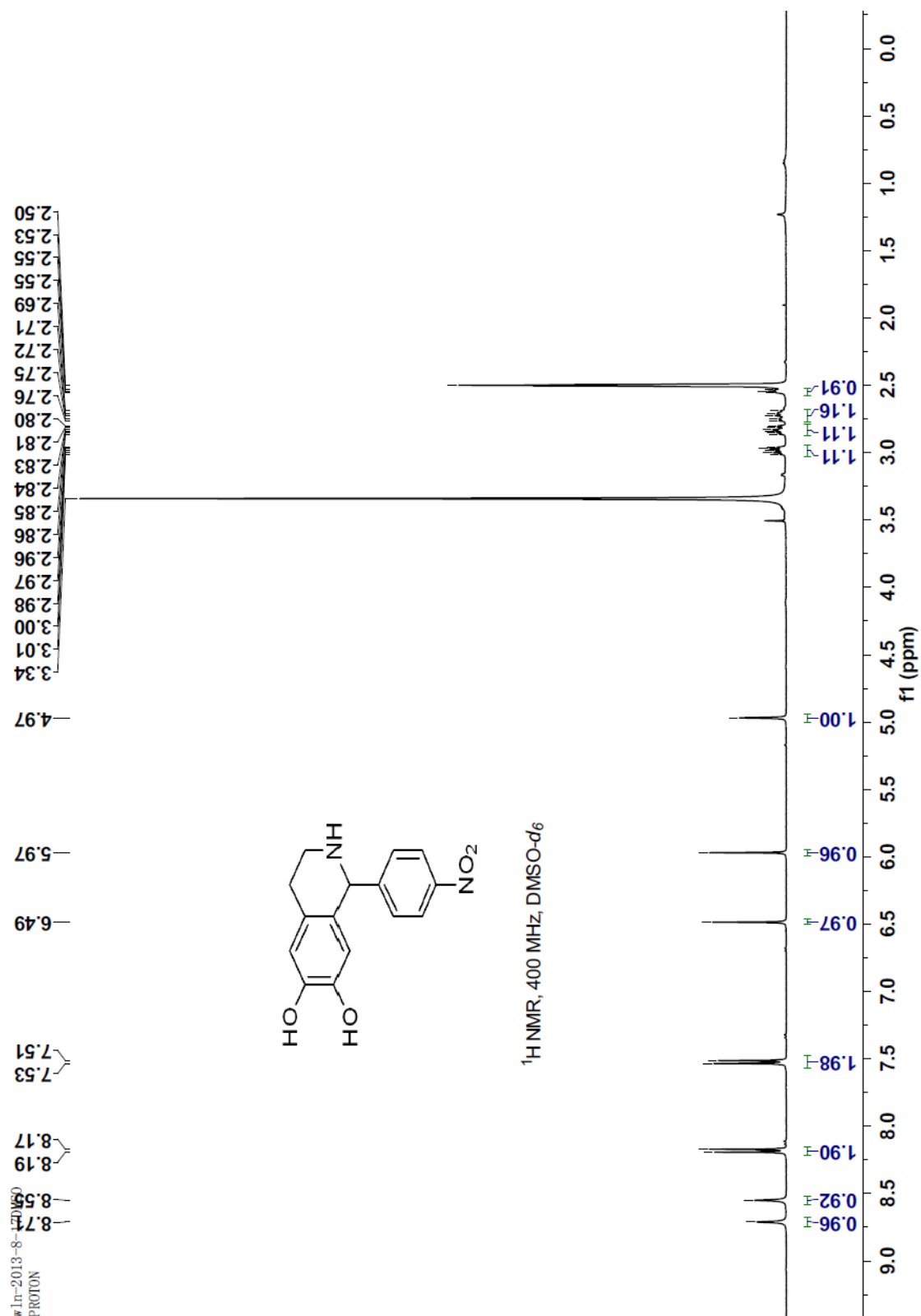
Ethyl-2-(1-methyl-1,2,3,4-tetrahydro-β-carboline-1-yl) acetate (3n): ¹H NMR



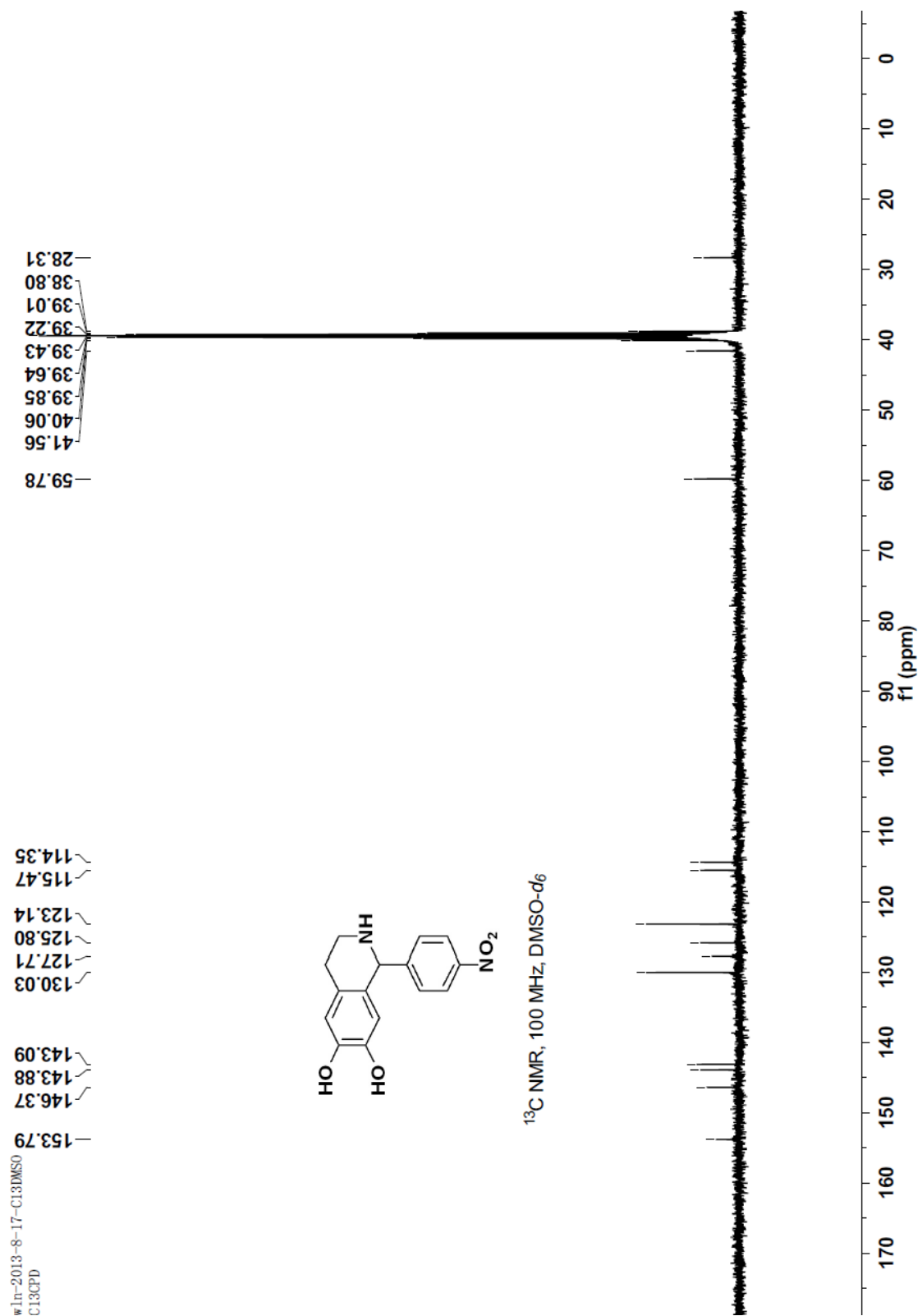
Ethyl-2-(1-methyl-1,2,3,4-tetrahydro-β-carboline-1-yl) acetate (3n): ¹³C NMR



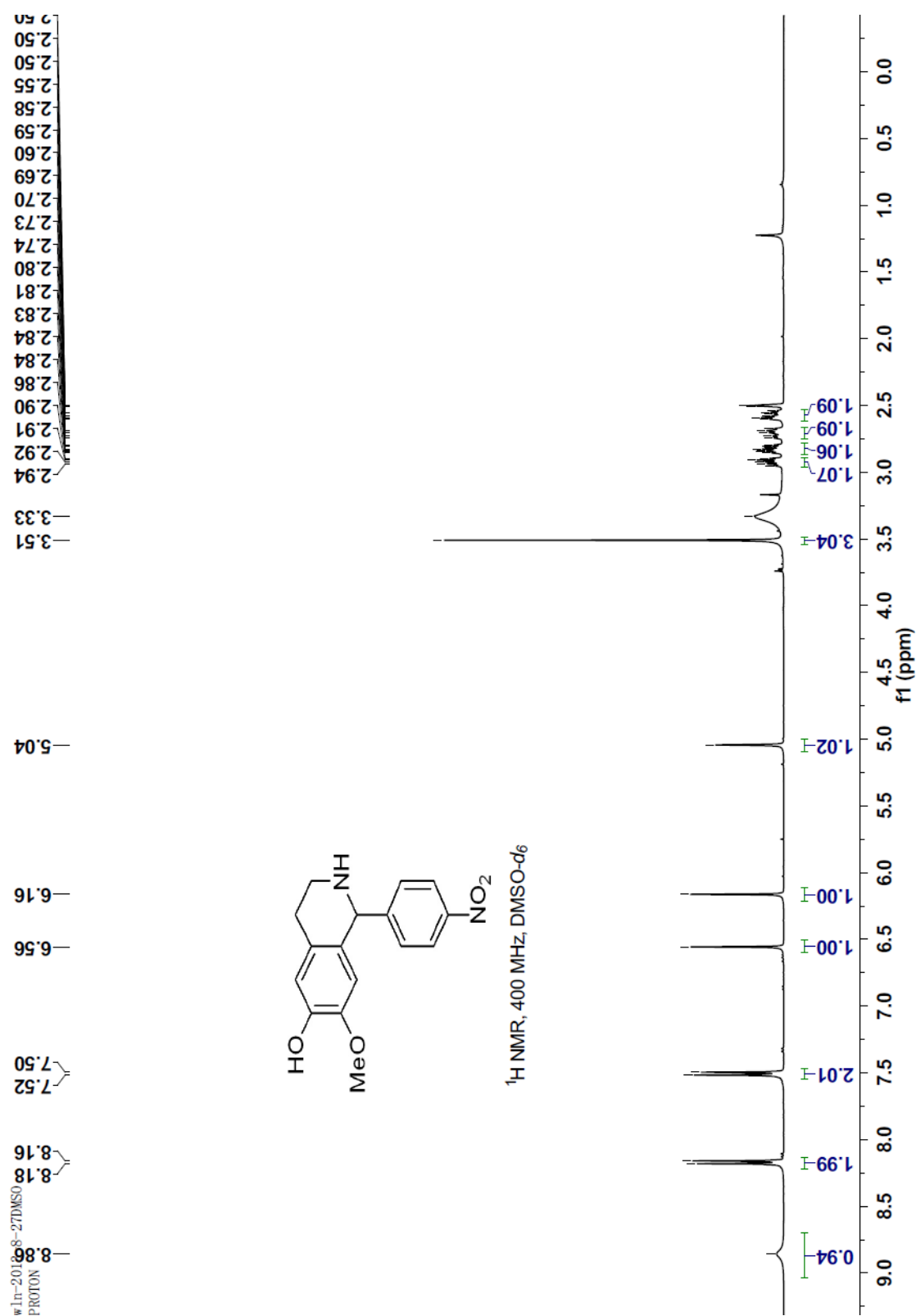
1-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline-6,7-diol (3o): ¹H NMR



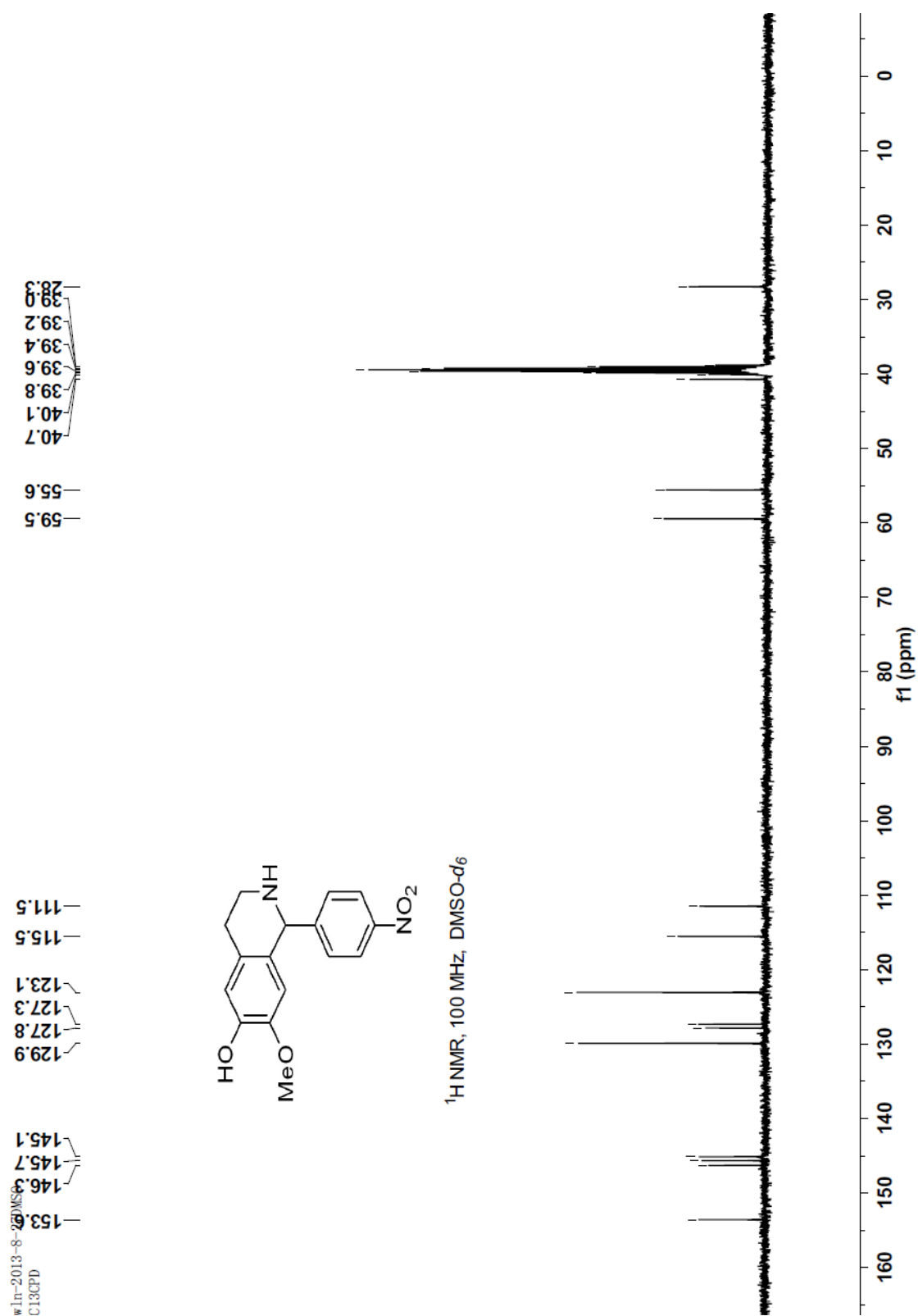
1-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline-6,7-diol (3o) : ^{13}C NMR



1-(4-Nitrophenyl)-6-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline (3p): ¹H NMR

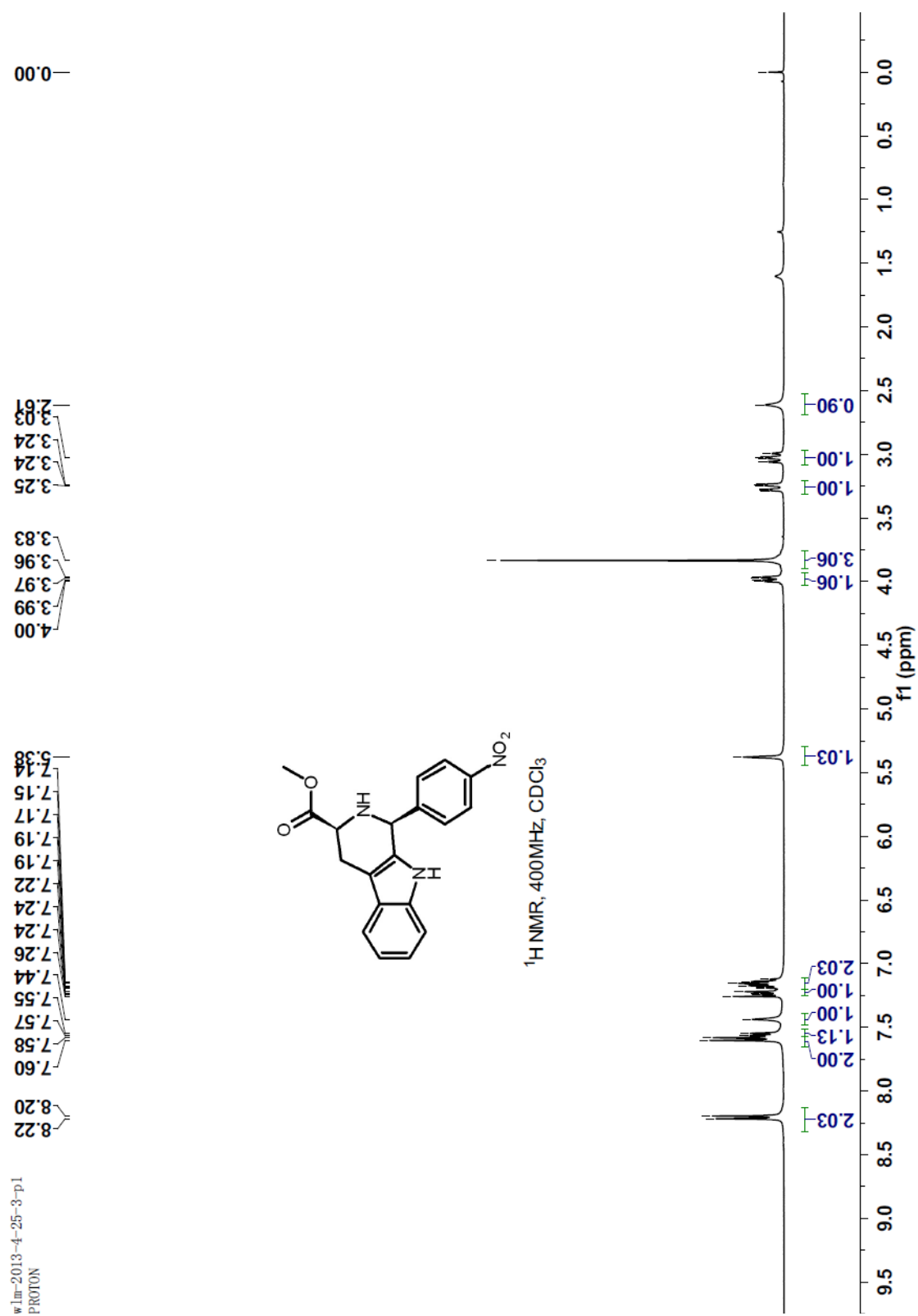


1-(4-Nitrophenyl)-6-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline (3p): ^{13}C NMR

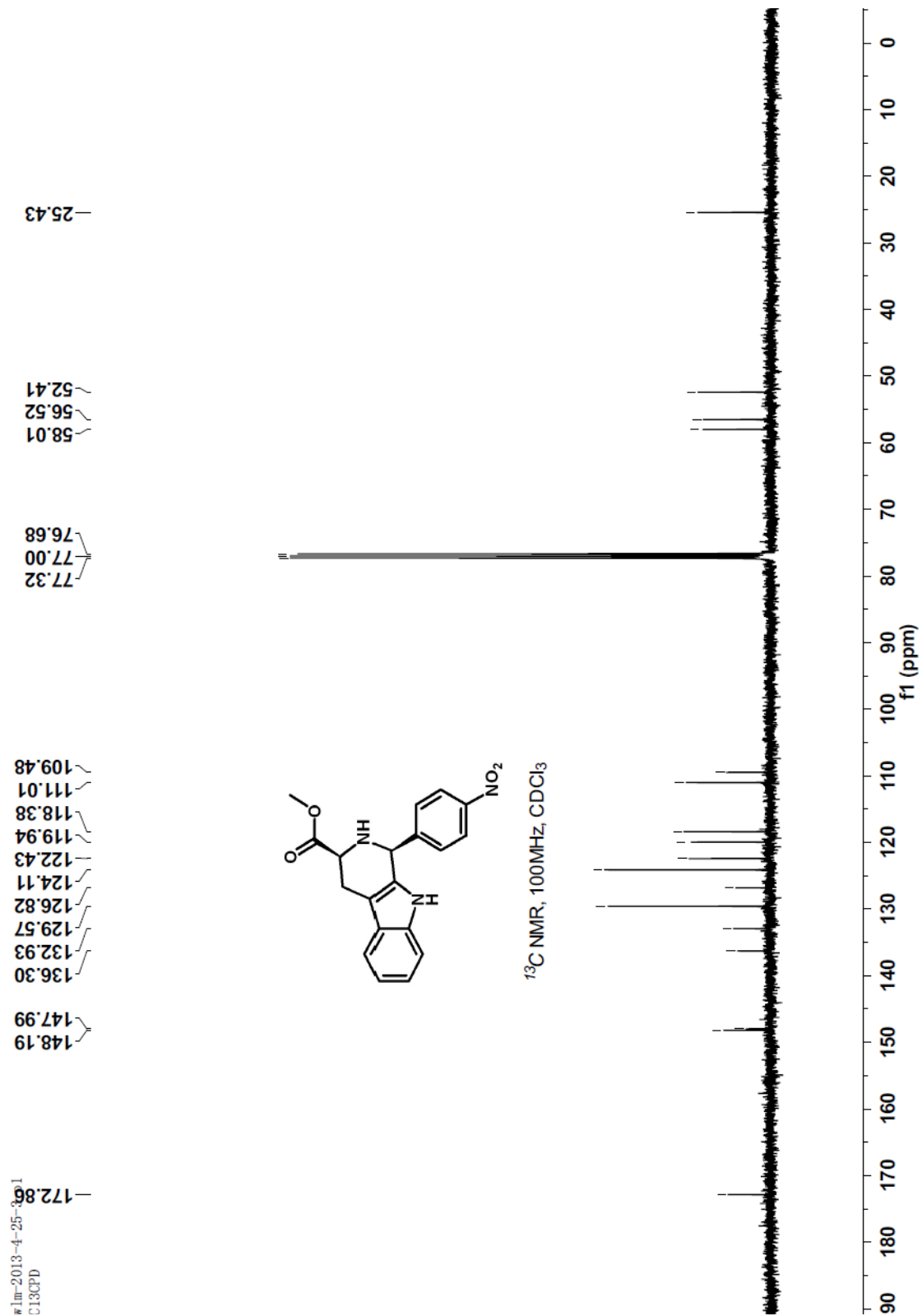


1-(*p*-Nitrophenyl)-3-methoxycarbonyl-1,2,3,4-tetrahydro- β -carboline (3q):

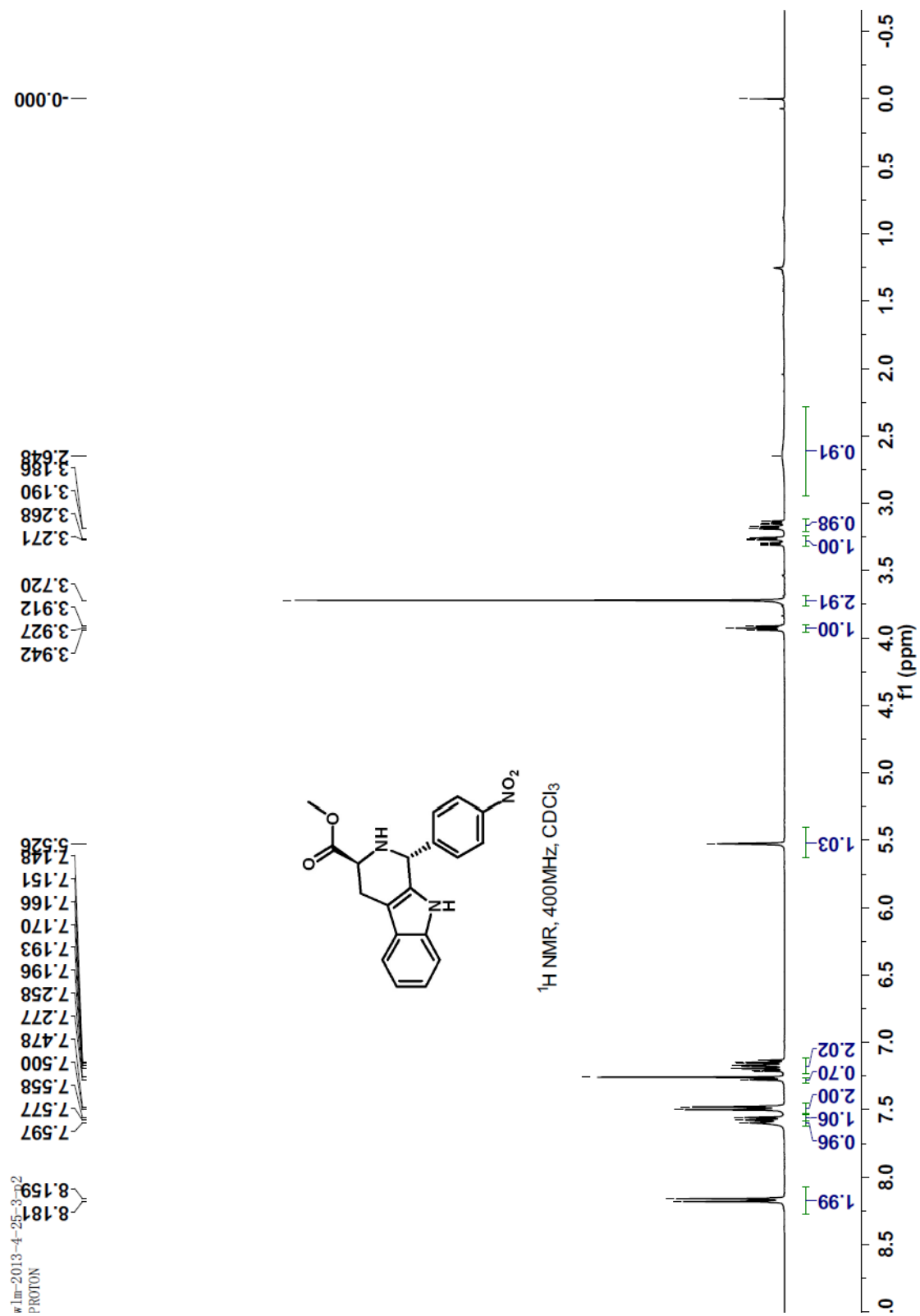
cis-3q: ^1H NMR



cis-3q: ^{13}C NMR

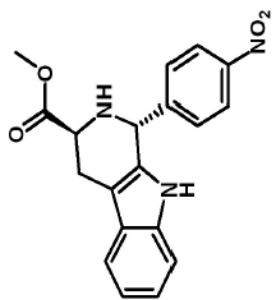


trans-3q: ¹H NMR

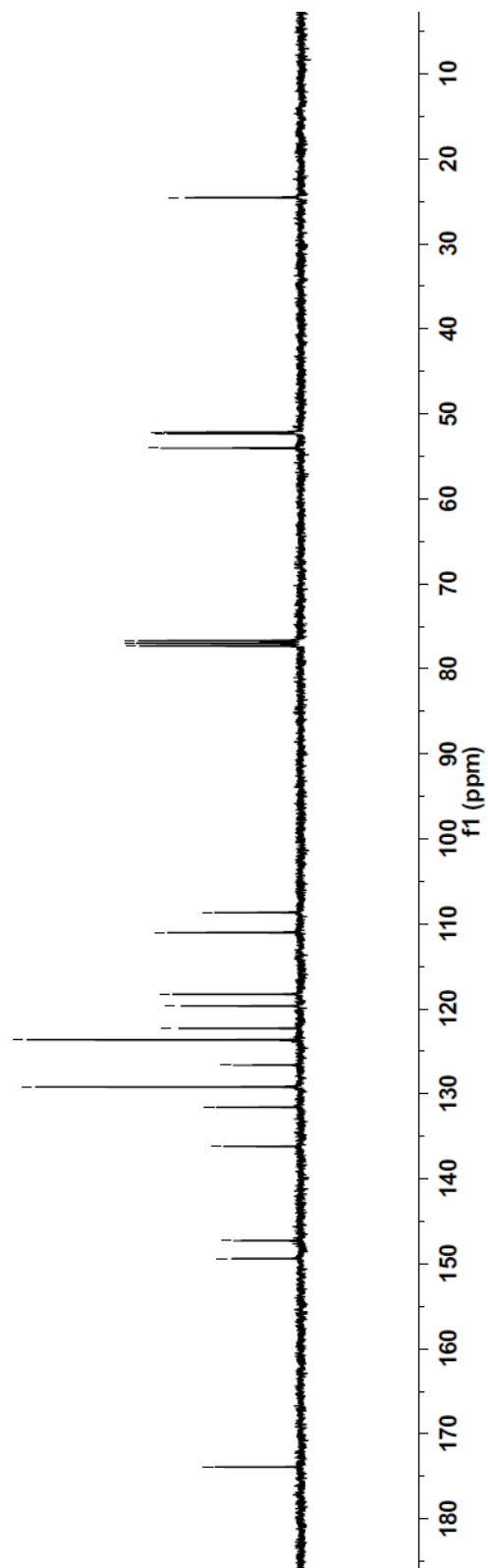


trans-3q: ^{13}C NMR

#1n-2013-4-5p2e13
C13CPD

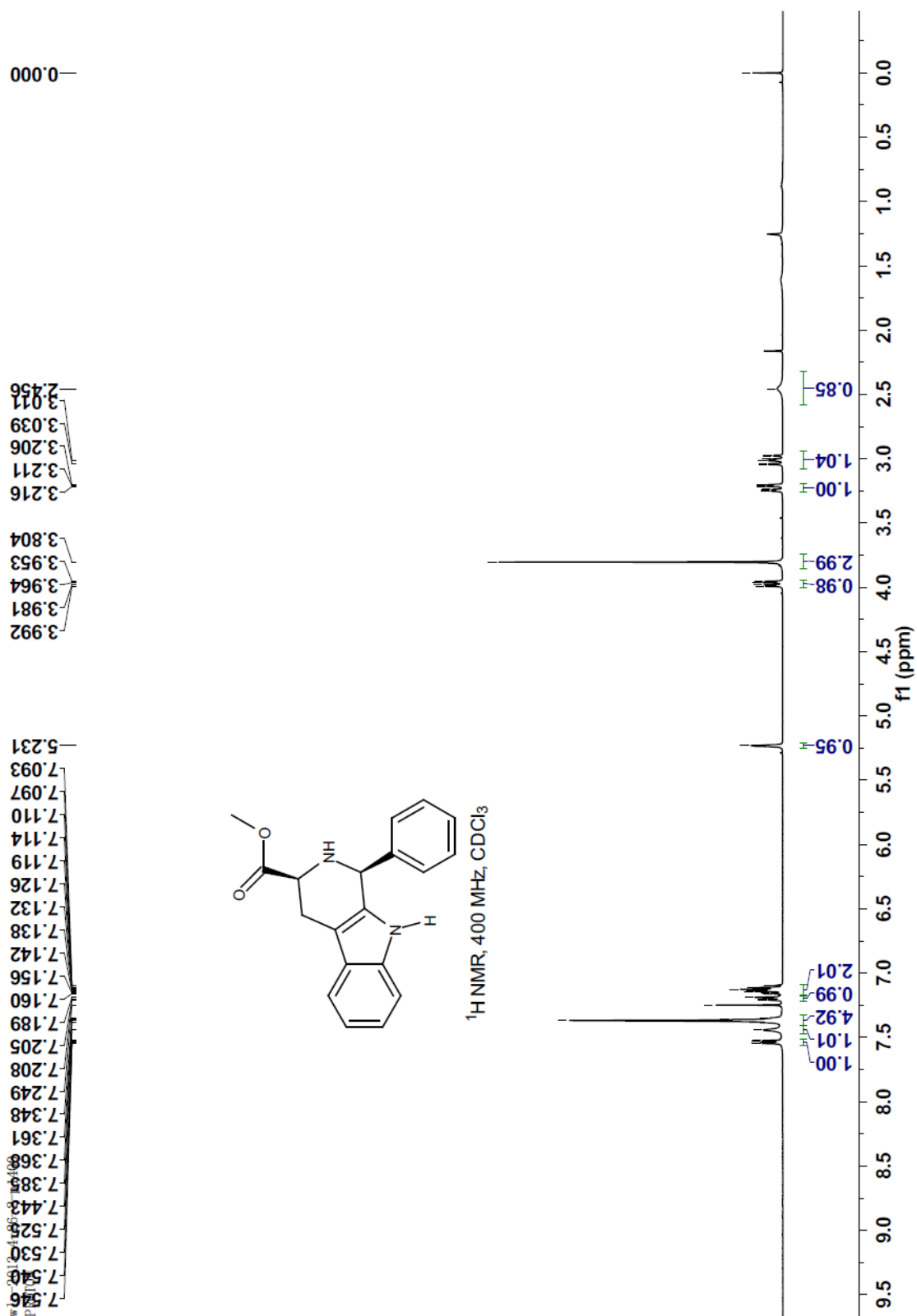


^{13}C NMR, 400MHz, CDCl_3



1-Phenyl-3-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (3r):

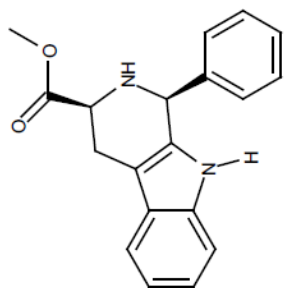
cis-3r: ^1H NMR



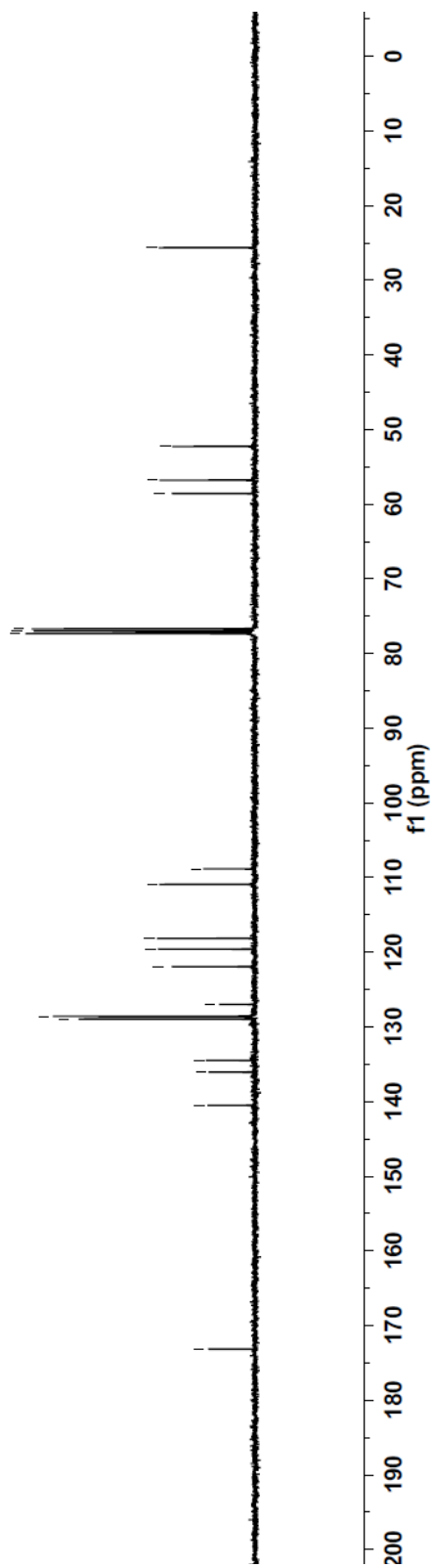
cis-3r: ^{13}C NMR

#1n-2013-4-26pic
C13CPD

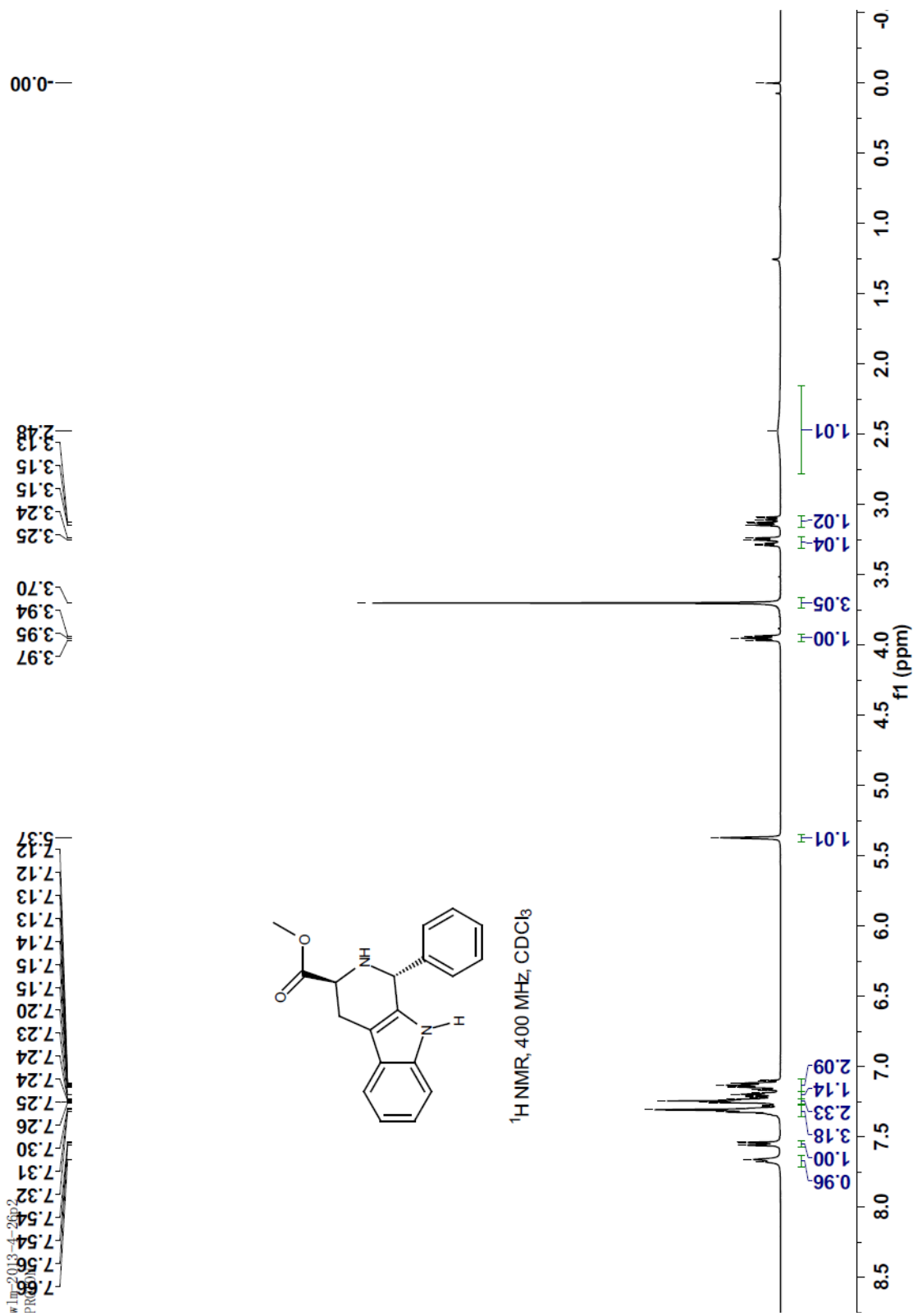
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134.48
128.94
128.59
126.99
121.93
119.59
118.15
110.90
108.83
77.32
77.00
76.68
58.56
56.77
52.25
25.63



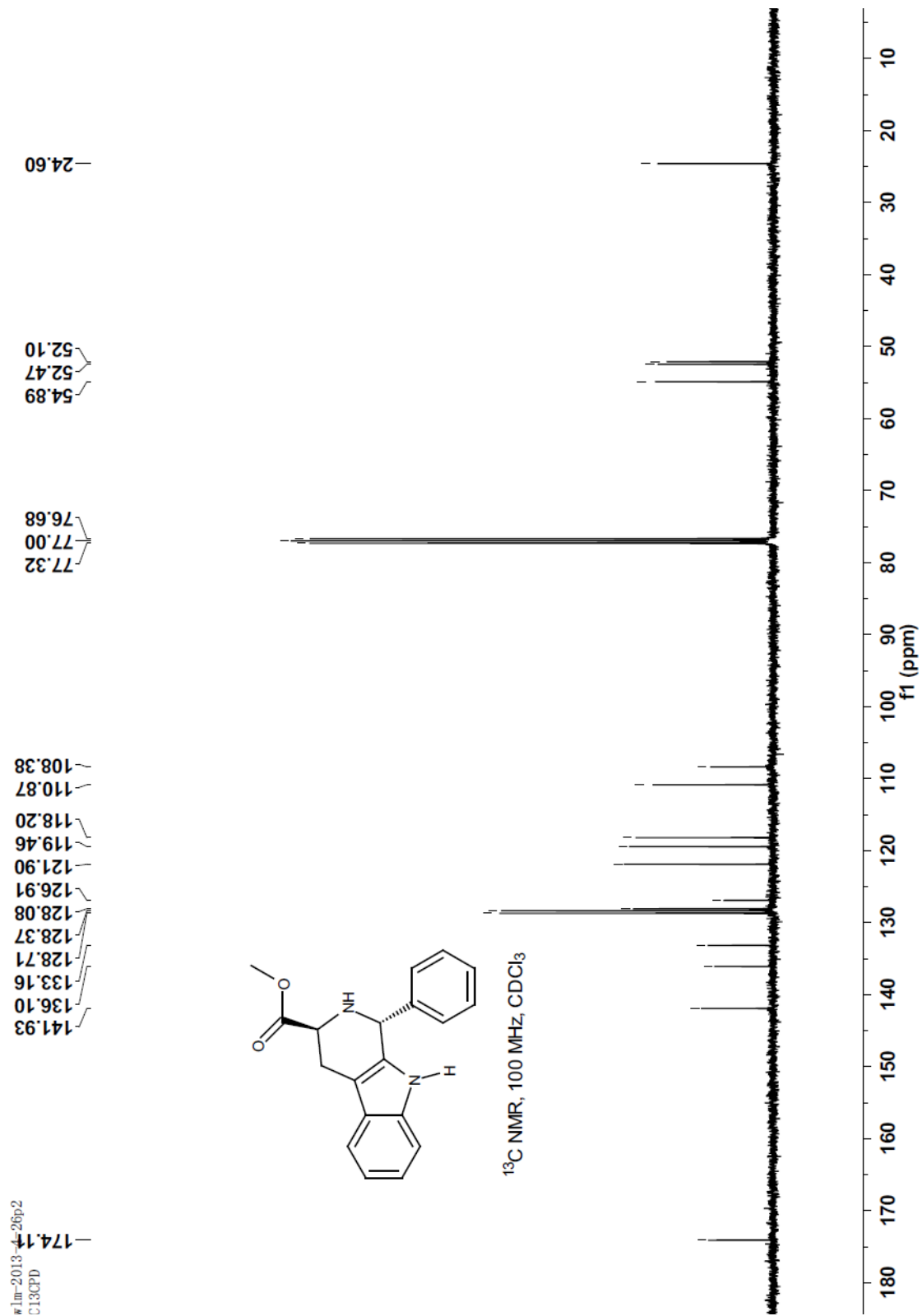
^1H NMR, 100 MHz, CDCl_3



trans-**3r**: ^{13}C NMR

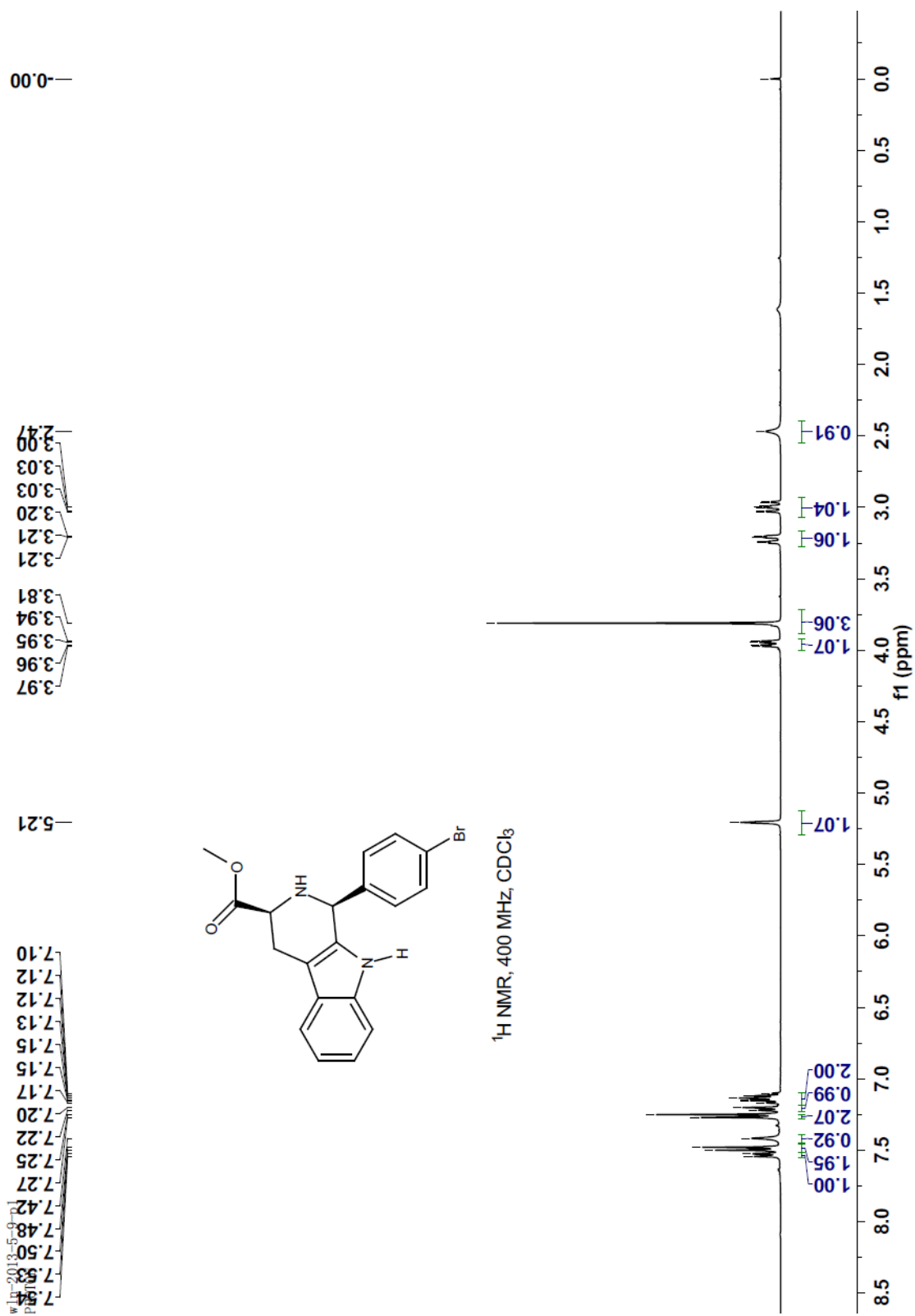


trans-3r: ^{13}C NMR



1-(*p*-Bromophenyl)-3-methoxycarbonyl-1,2,3,4-tetrahydro- β -carboline (3s):

cis-3s: ^1H NMR



cis-3s: ^{13}C NMR

#1n-2013-5-9-d1
C13CPD

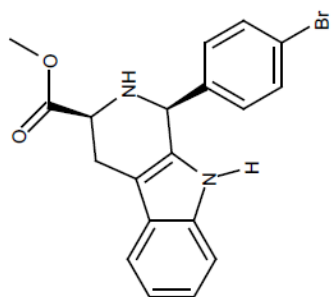
173.04

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132.06
130.30
126.96
122.53
122.12
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110.93
109.08

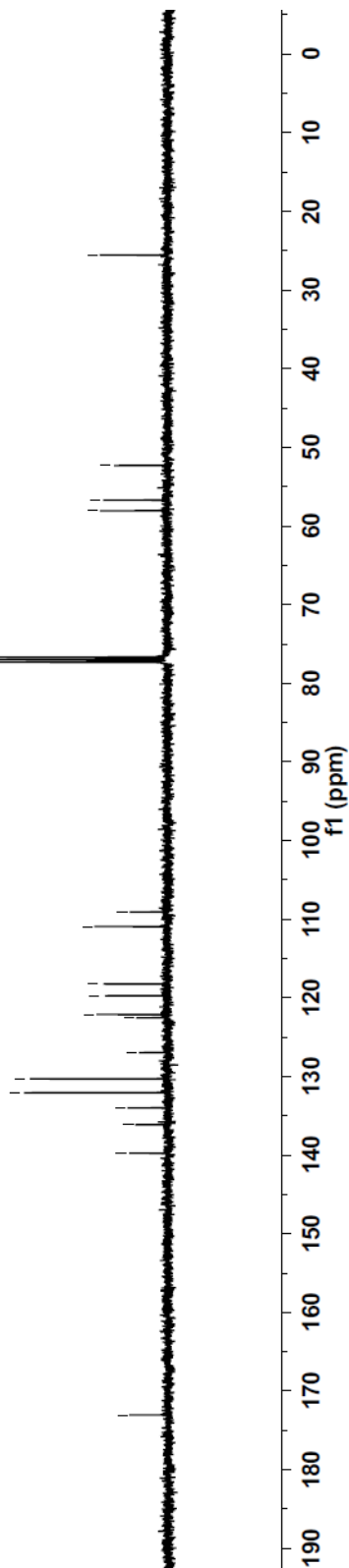
77.32
77.00
76.68

58.07
56.71
52.31

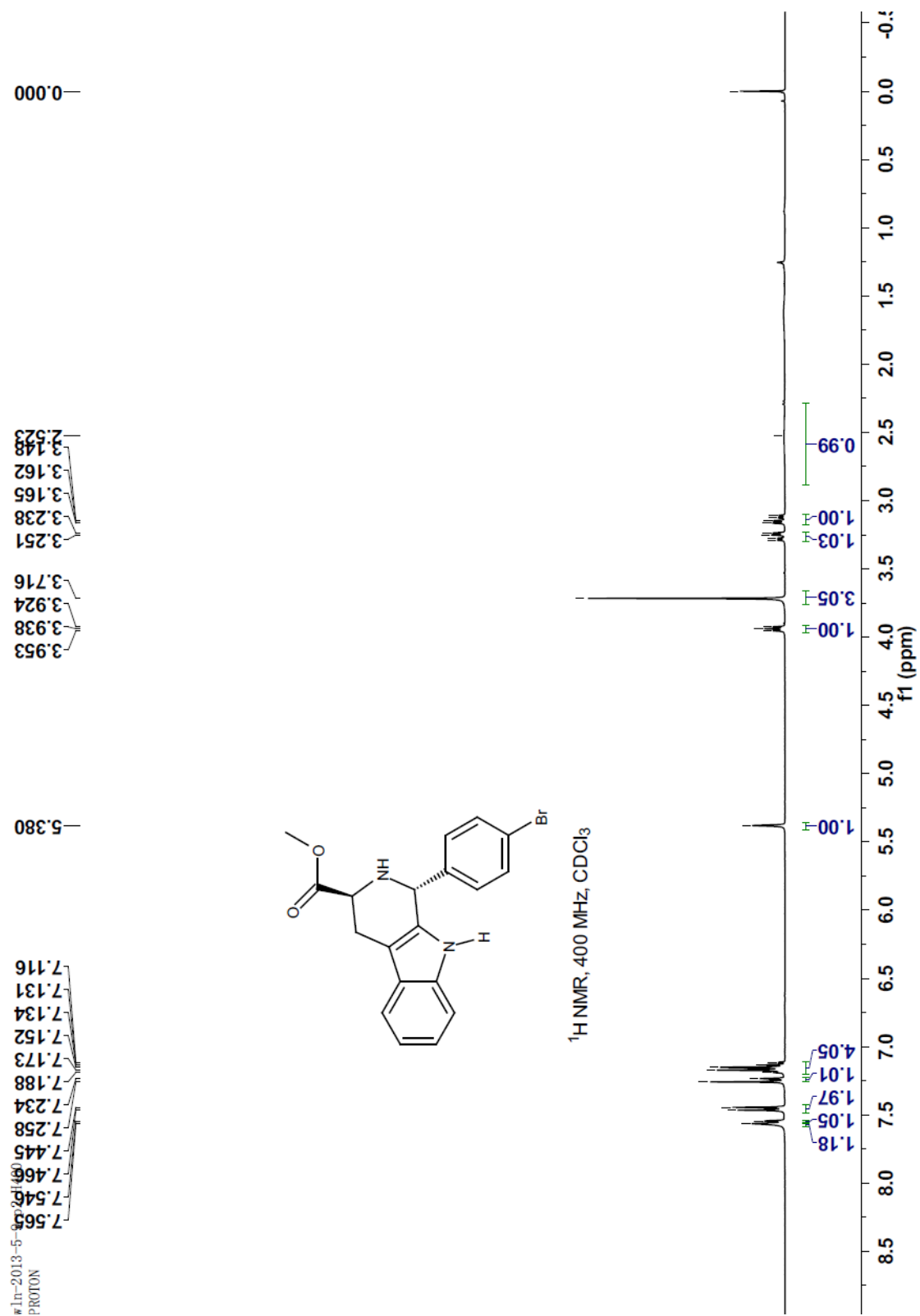
25.55



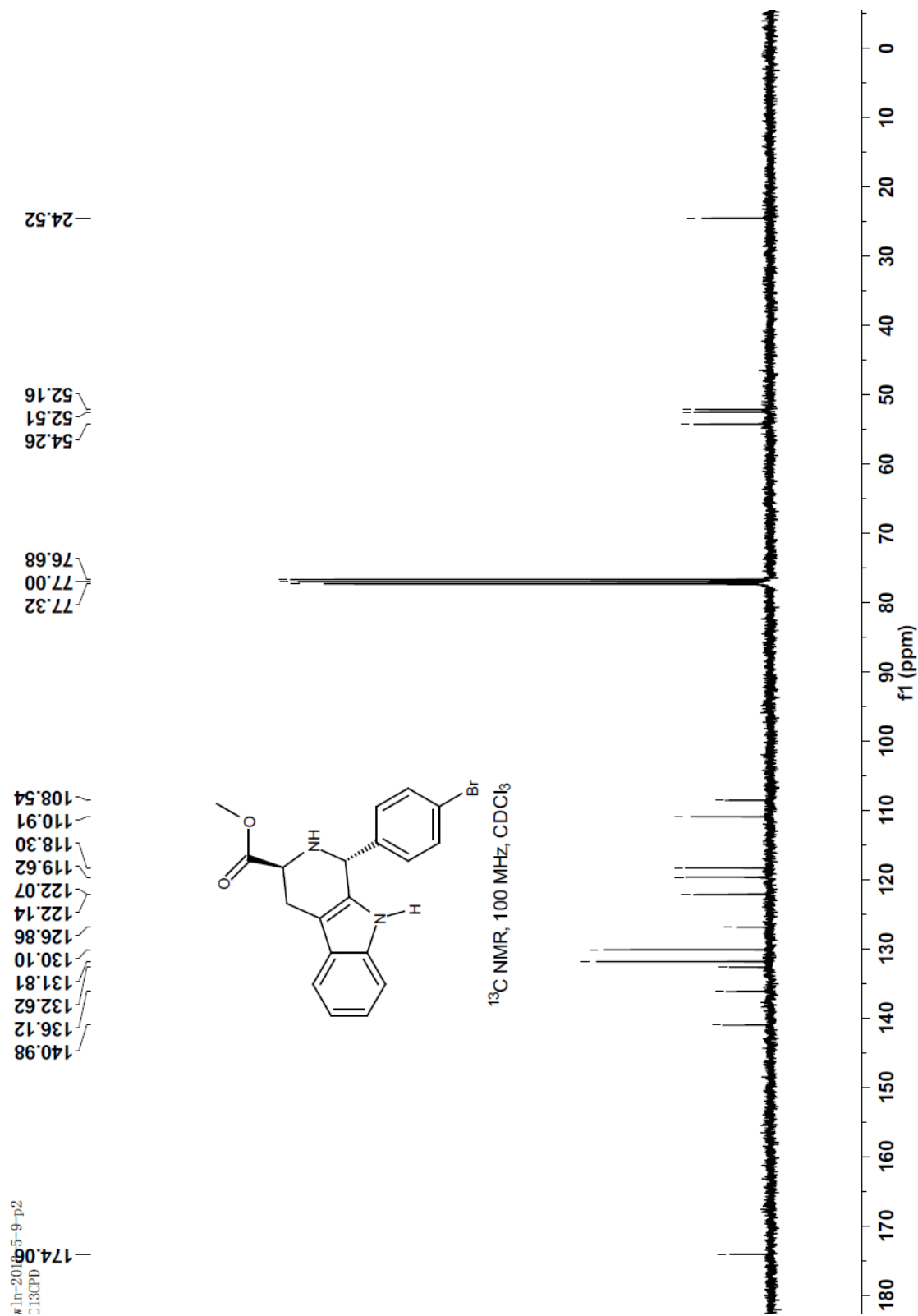
^{13}C NMR, 100 MHz, CDCl_3



trans-3s: ^1H NMR

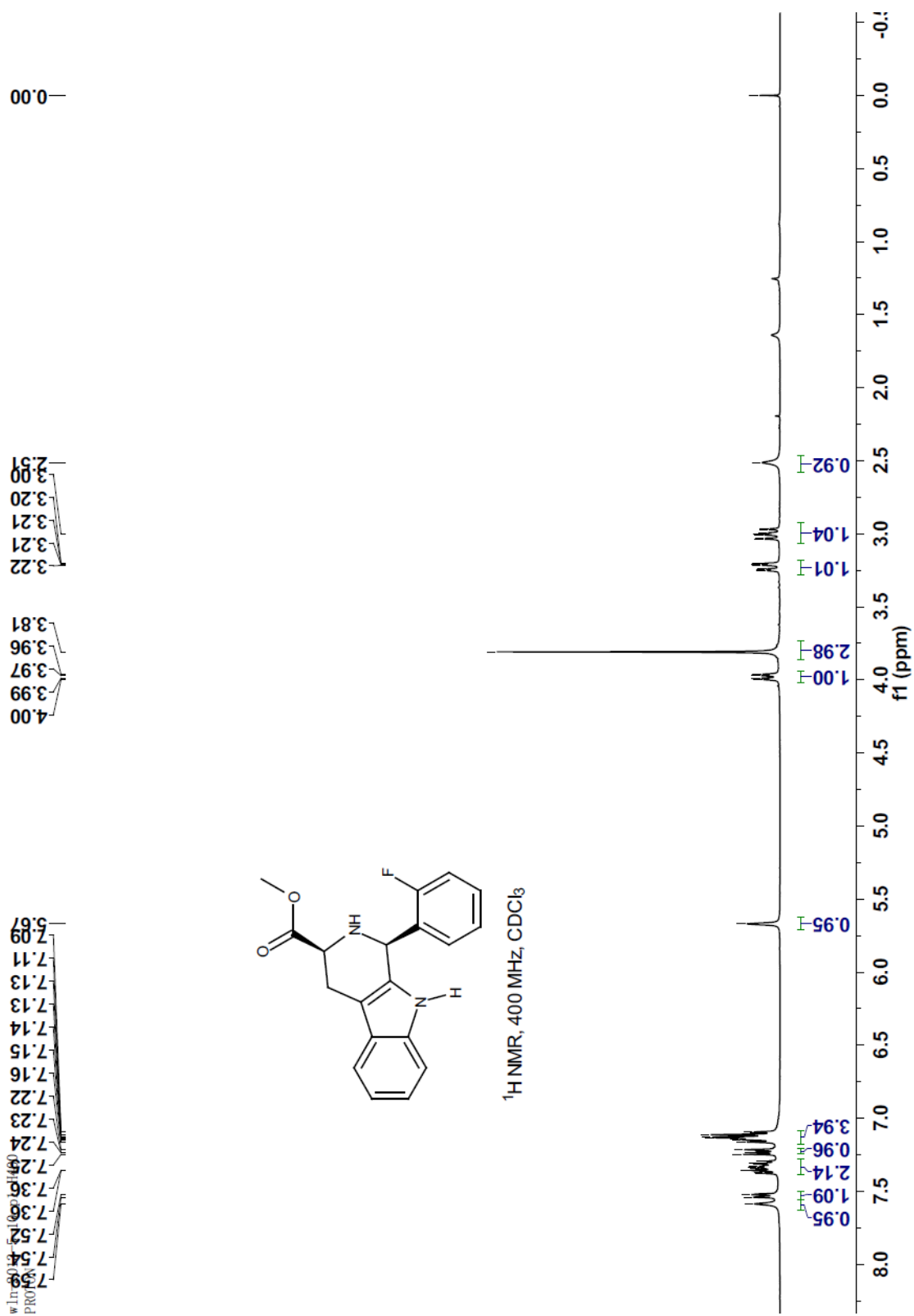


trans-3s: ^{13}C NMR



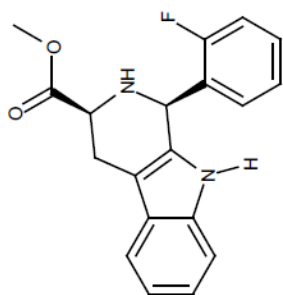
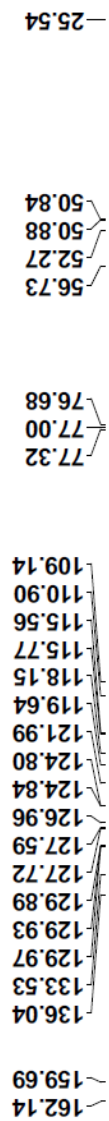
1-(2-Fluorophenyl)-3-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (3t):

cis-3t: ^1H NMR

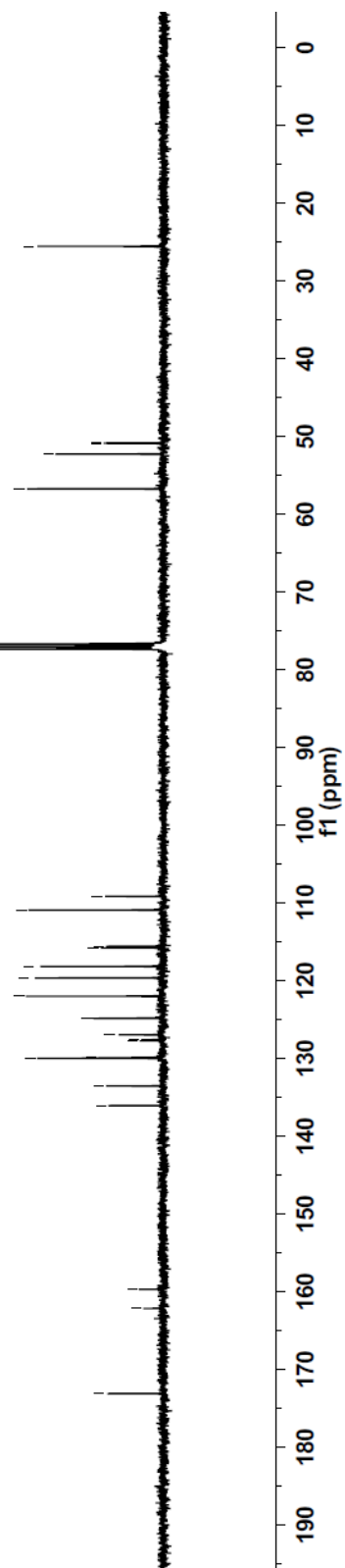


cis-3t: ^{13}C NMR

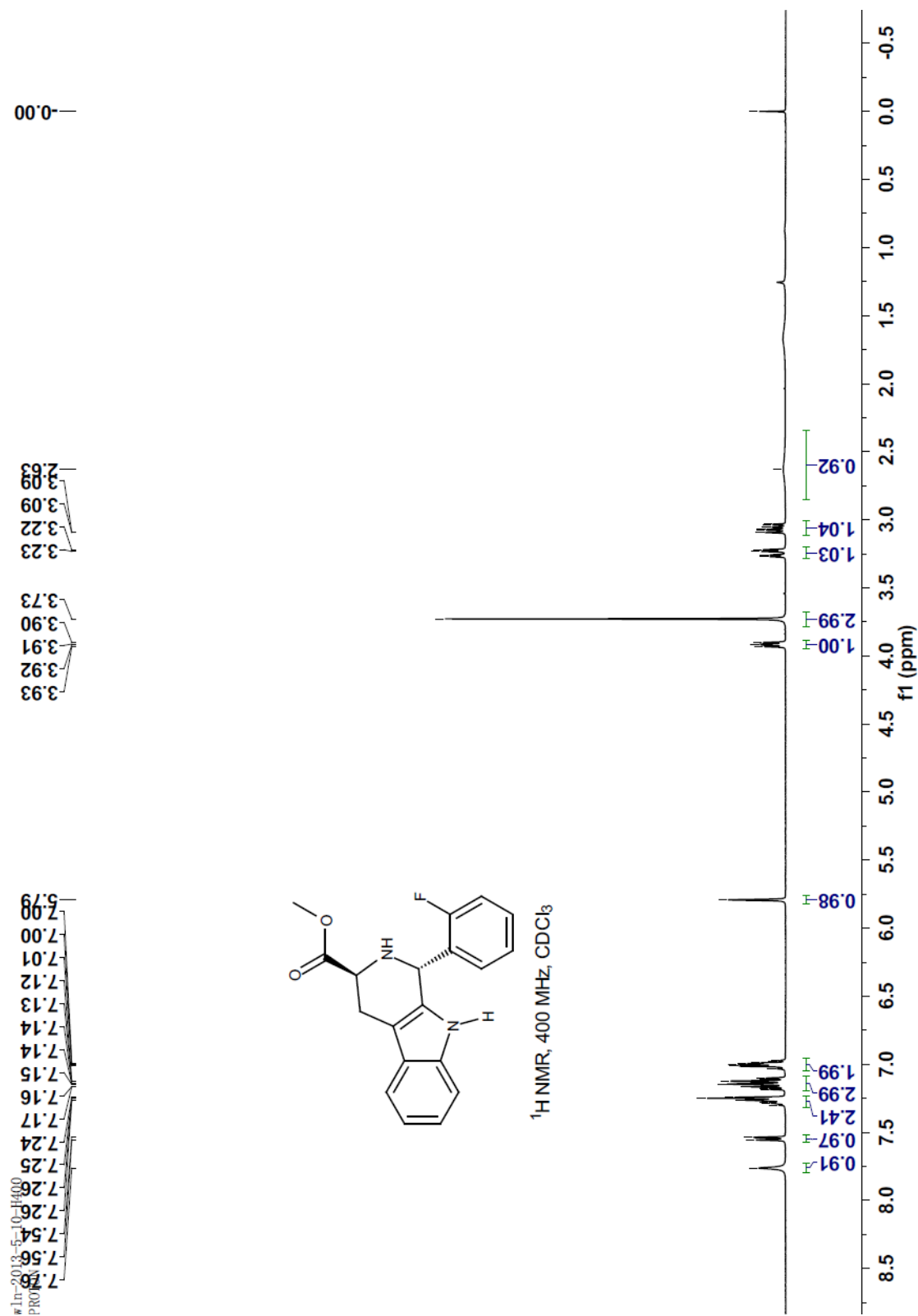
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C13CPD



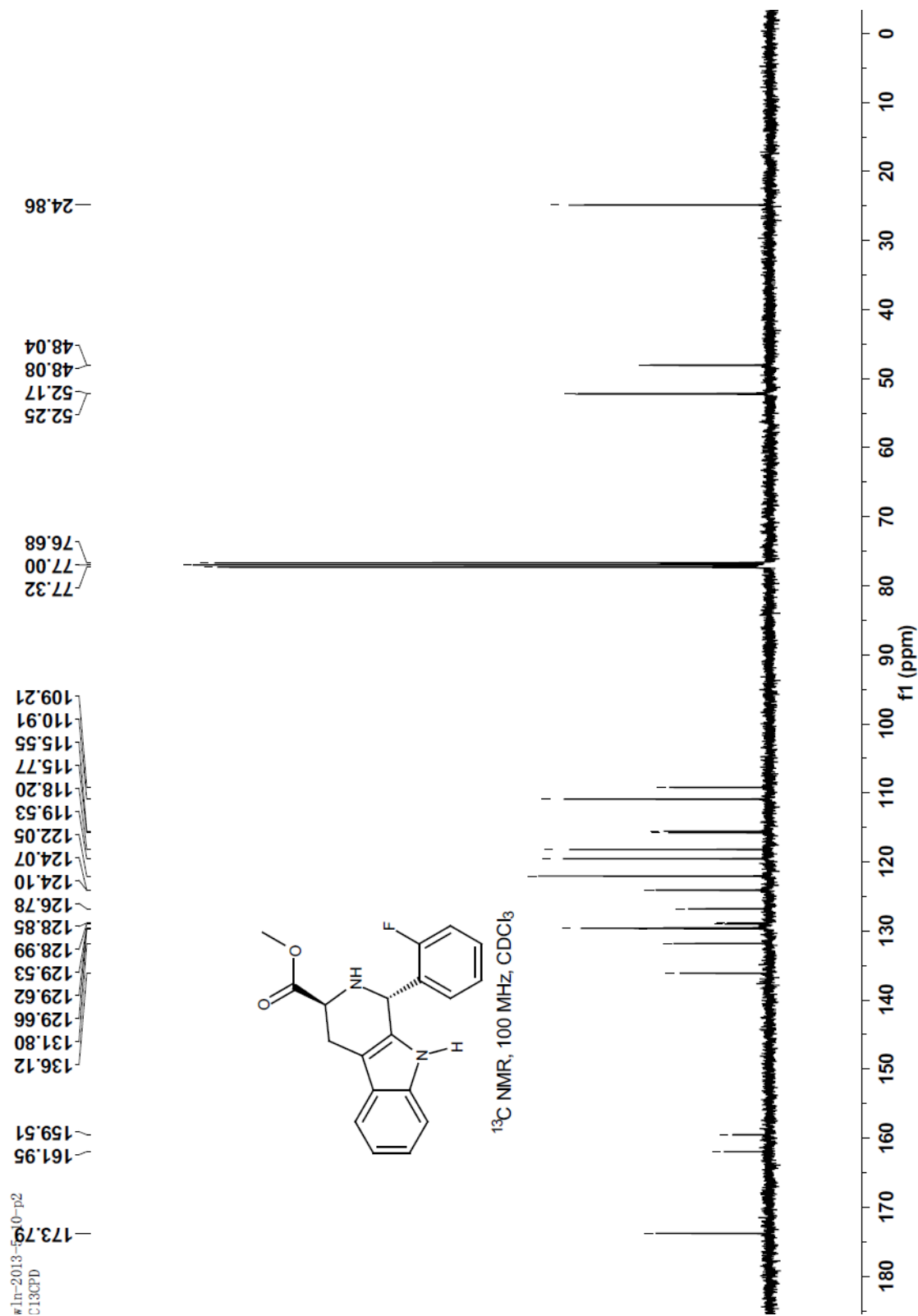
^{13}C NMR, 100 MHz, CDCl_3



trans-3t: ^1H NMR

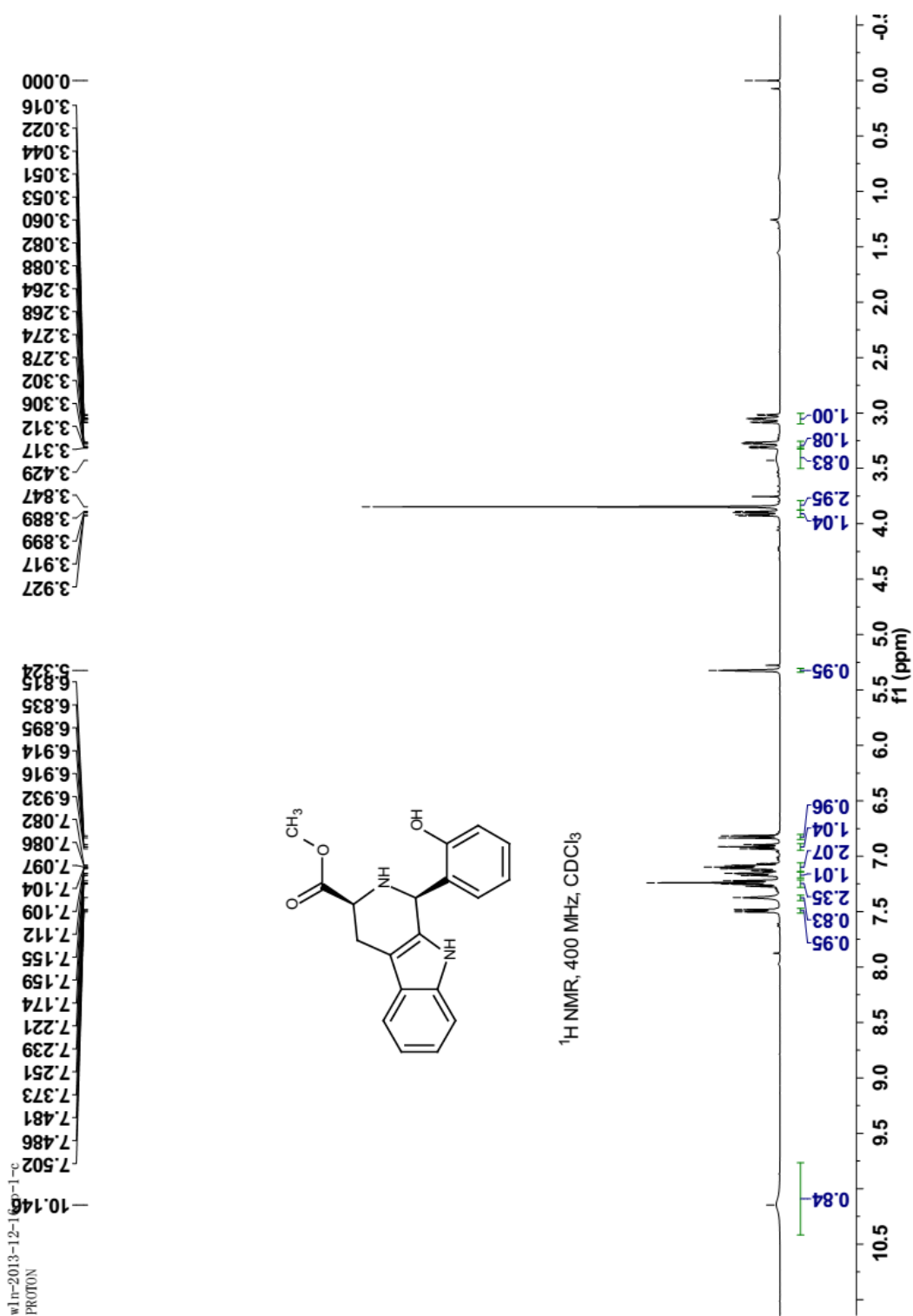


trans-3t: ¹³C NMR

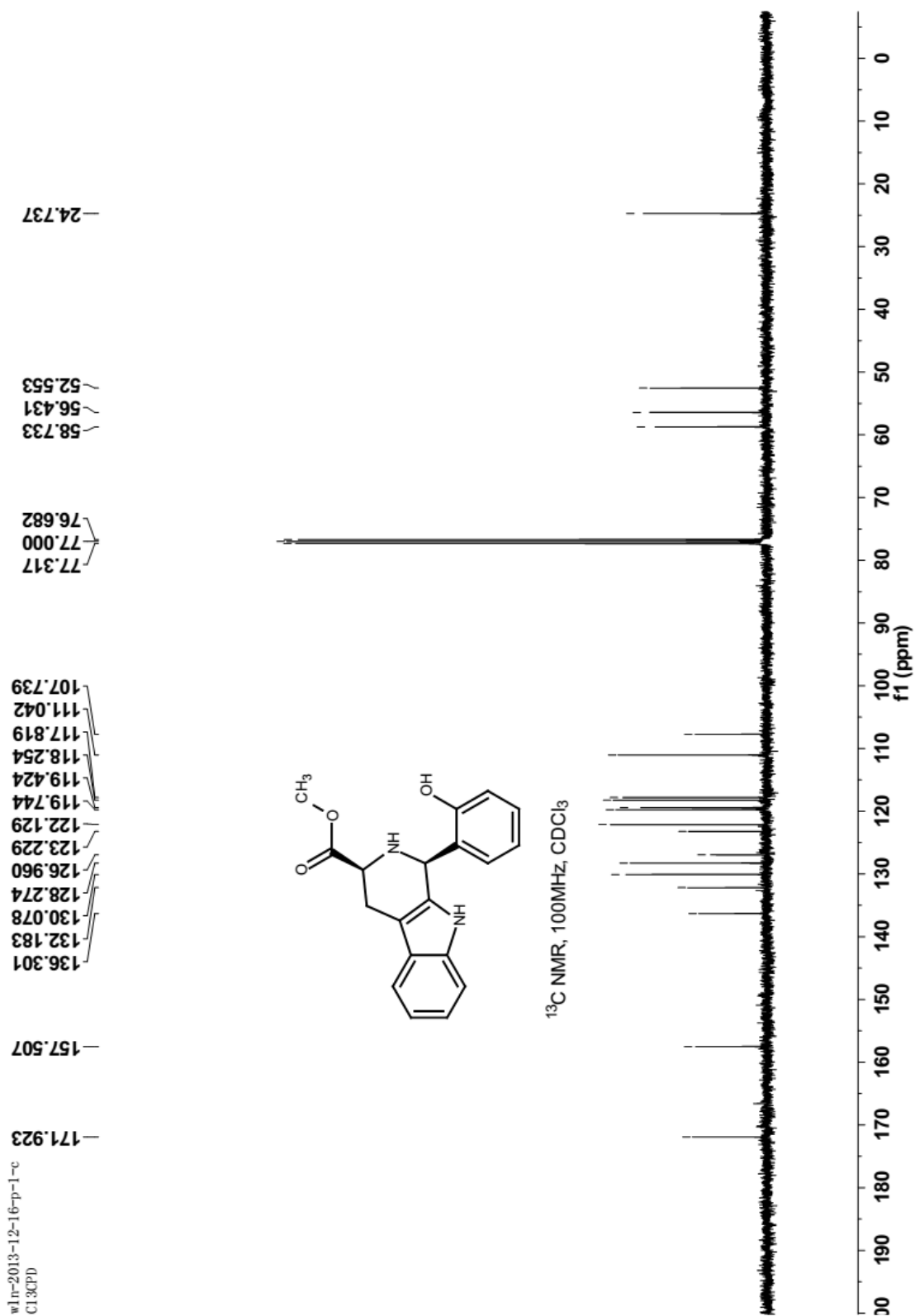


1-(2-Hydroxyphenyl)-3-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (3u)

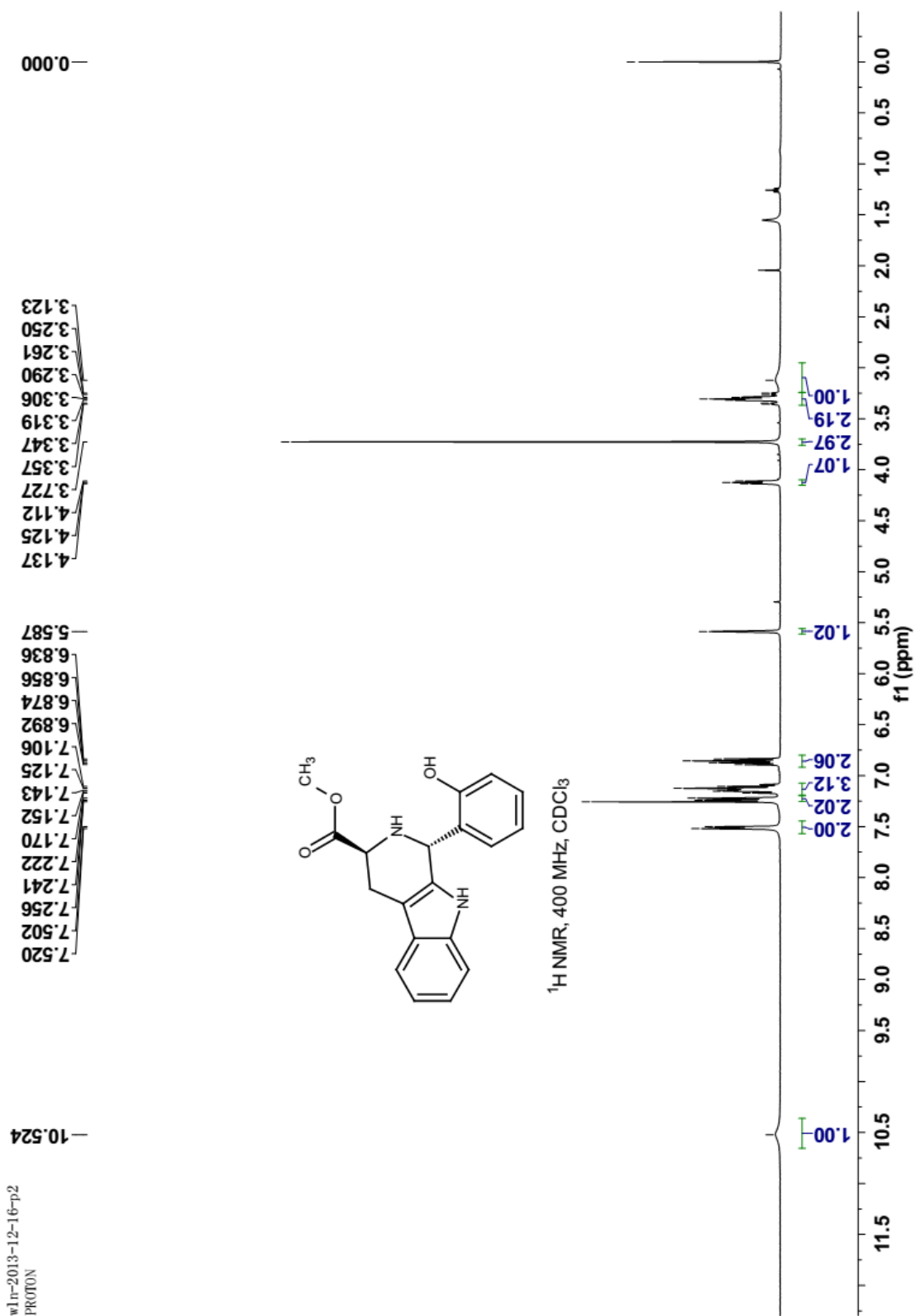
cis-3u: ¹H NMR



cis-3u: ^{13}C NMR

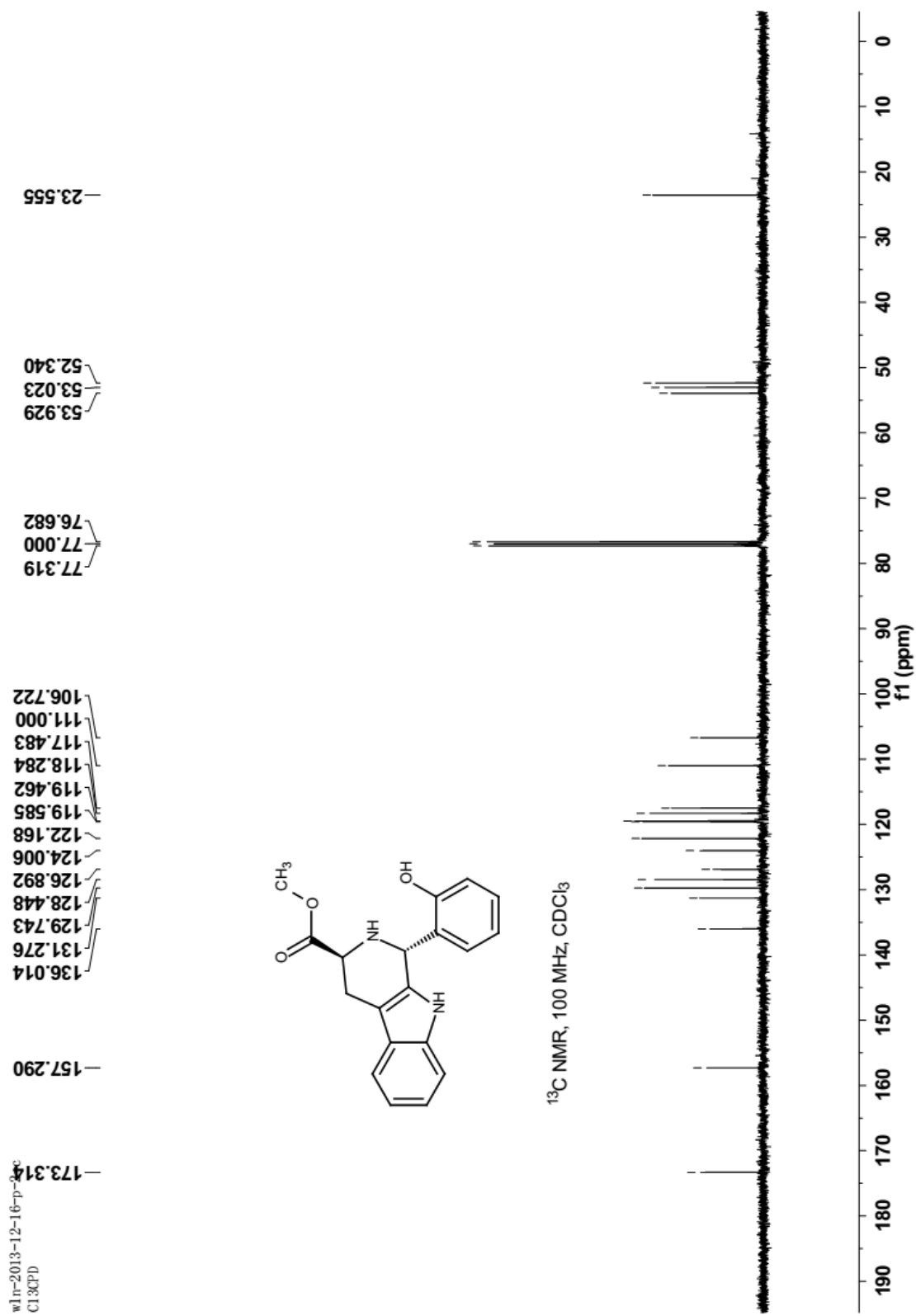


trans-3u: ^1H NMR



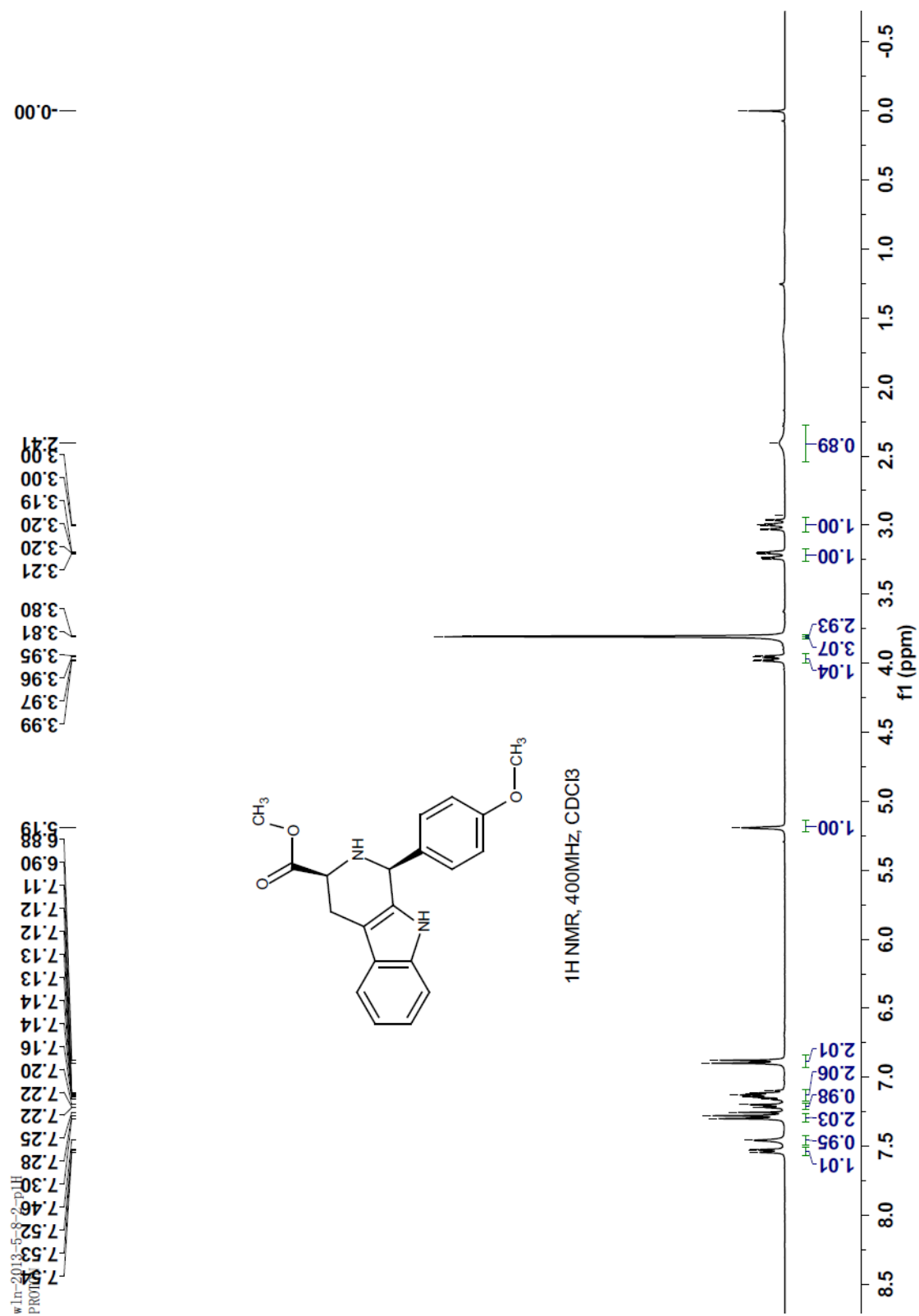
w1r-2013-12-16-p2
PROTON

trans-3u: ^{13}C NMR



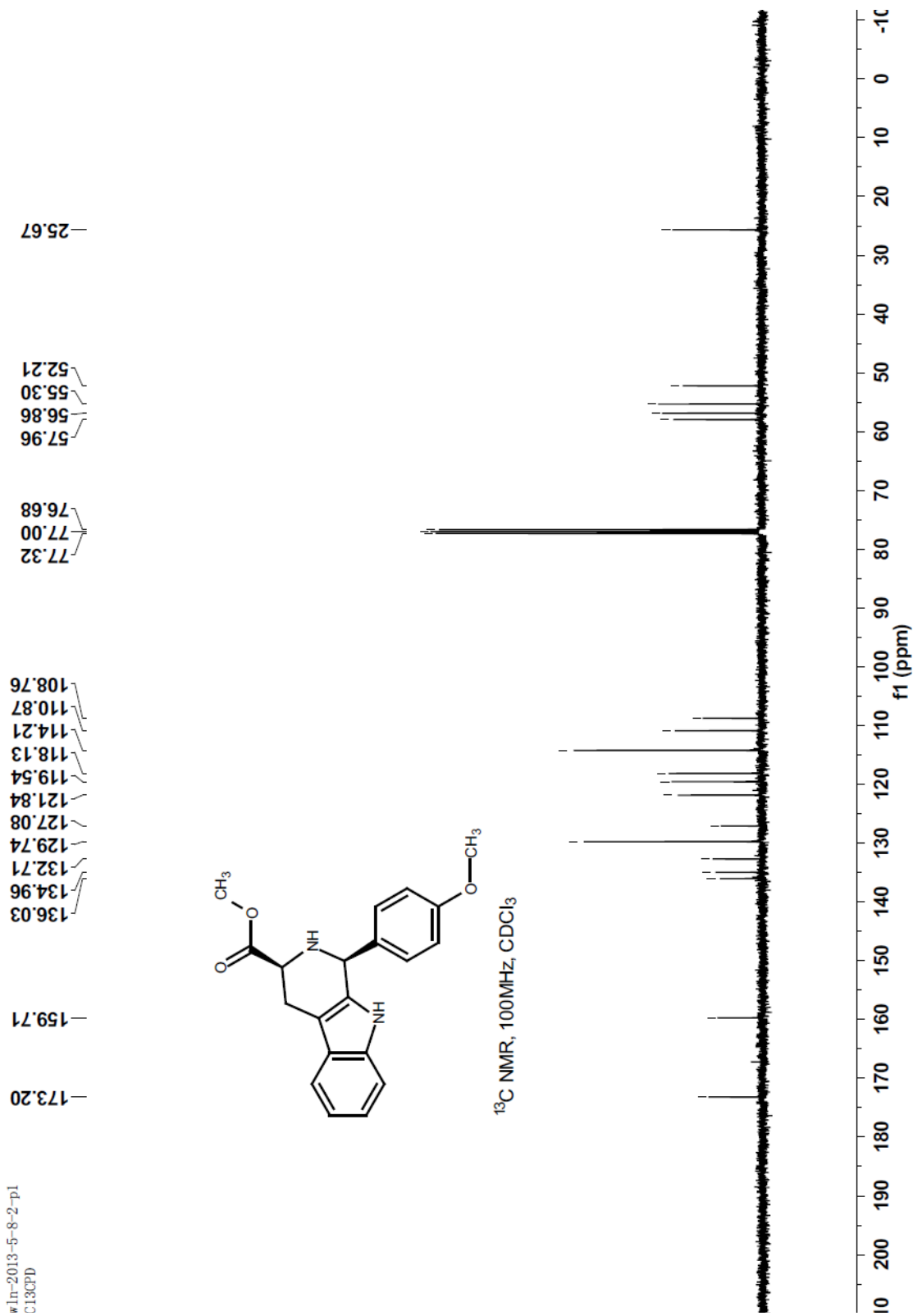
1-(4-Methoxyphenyl)-3-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (3v):

cis-3v: ¹H NMR



cis-3v: ^{13}C NMR

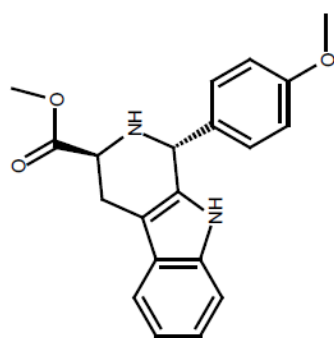
#11-2013-5-8-2-p1
C13CPD



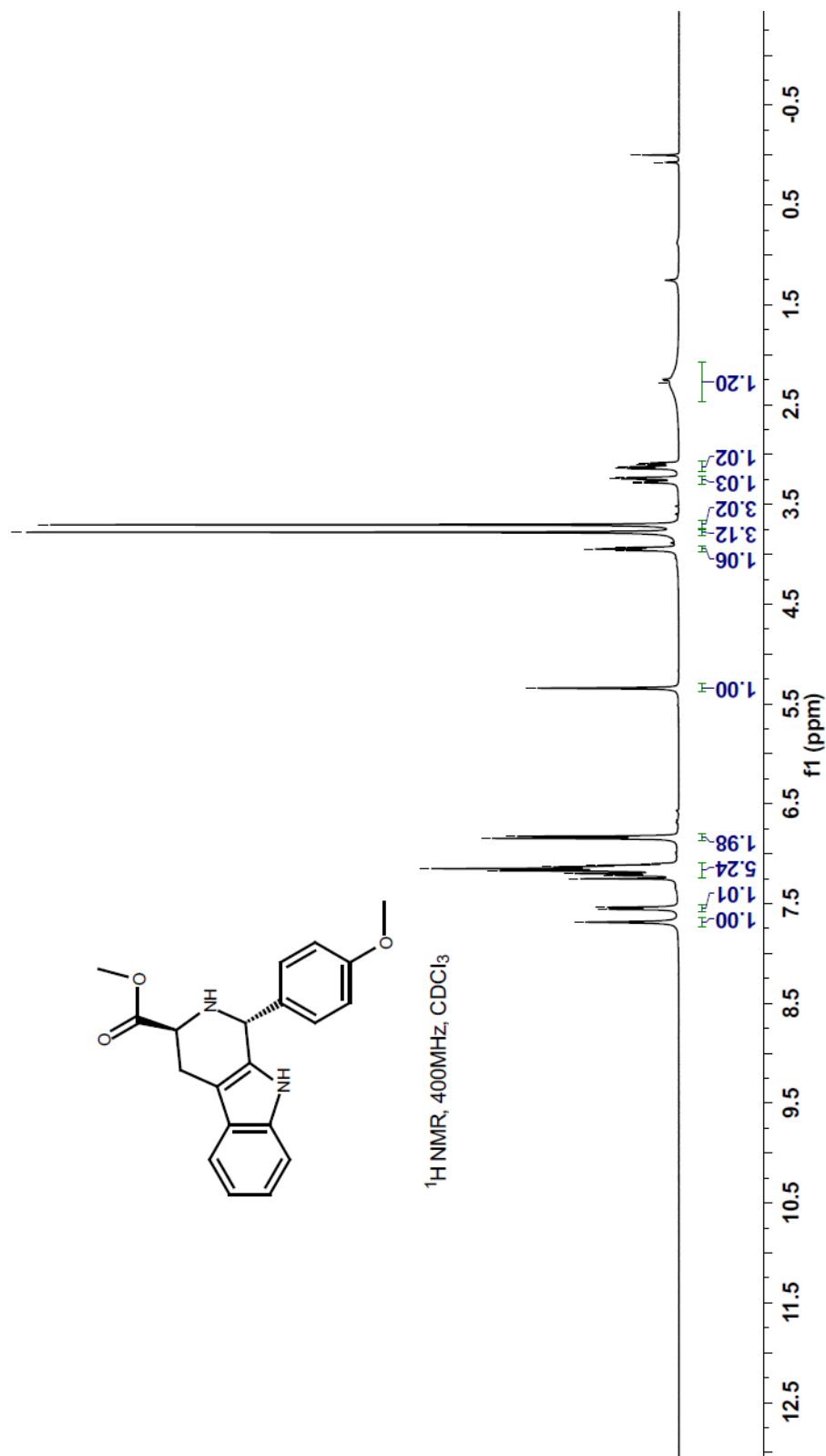
trans-3v: ^1H NMR

#1n-2013-5-8-h-400
PROTON

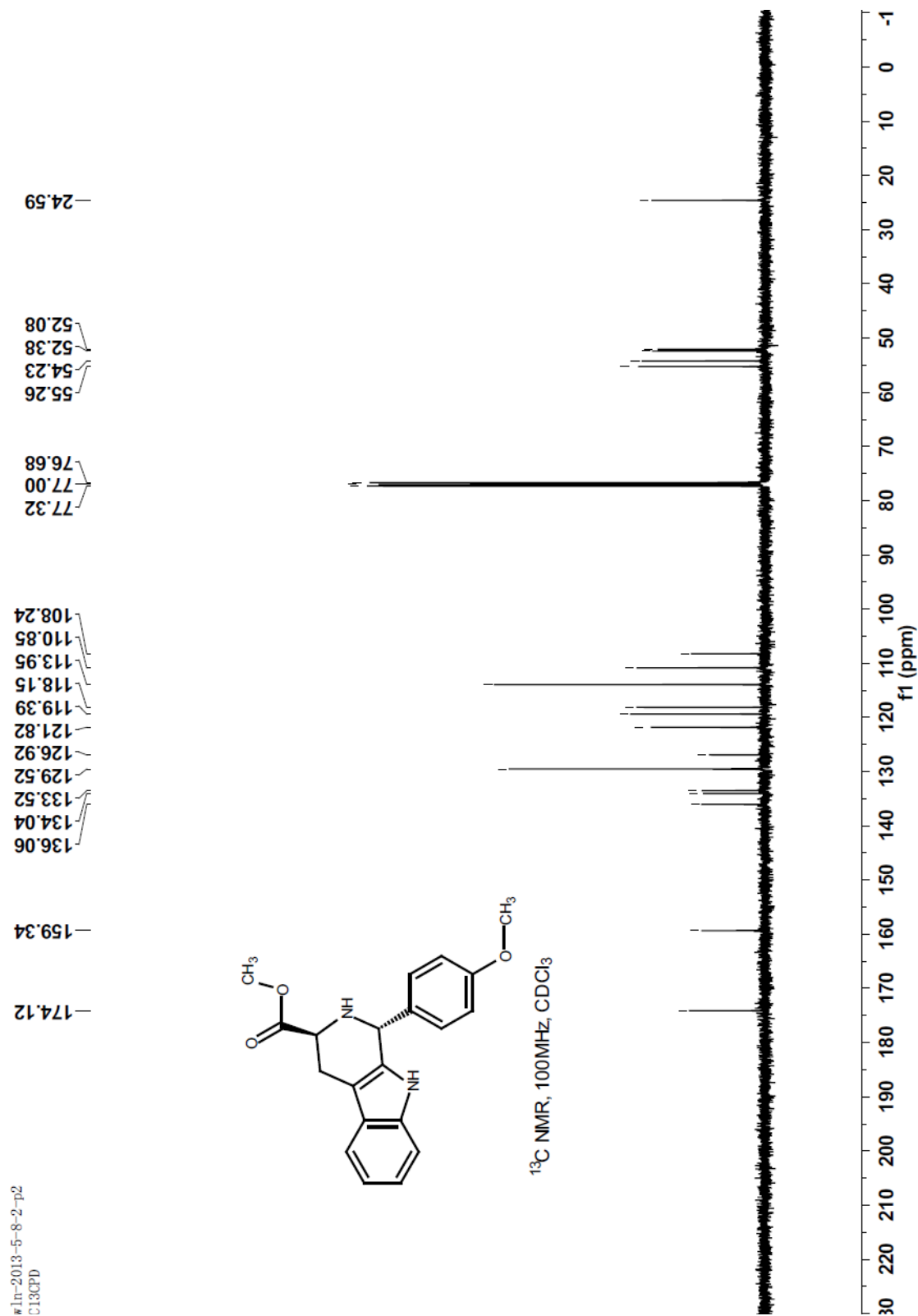
7.69
7.56
7.54
7.25
7.22
7.20
7.17
7.15
7.14
7.13
7.12
7.10
6.85
6.83
5.34
3.96
3.95
3.93
3.78
3.70
3.28
3.24
3.23
3.14
3.12
2.28
0.07
0.00



^1H NMR, 400MHz, CDCl_3

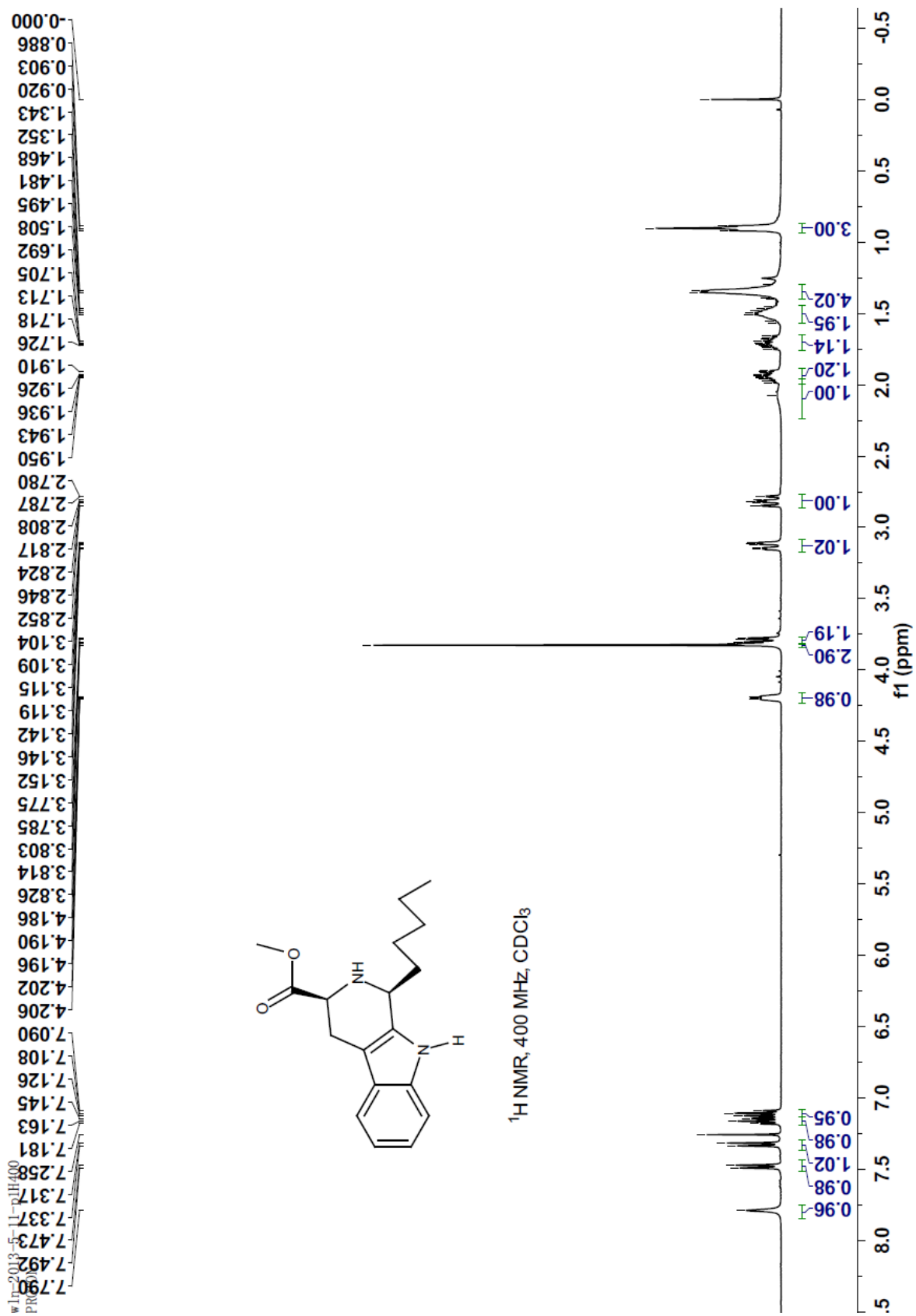


trans-3v: ^{13}C NMR



1-Pentyl-3-methoxycarbonyl-1,2,3,4-tetrahydro- β -carboline (3w):

cis-3w: ¹H NMR



cis-3w: ^{13}C NMR

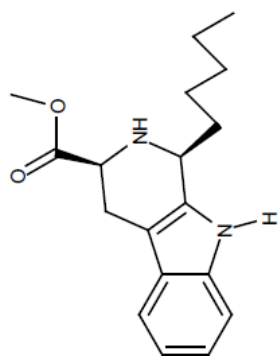
wIn-2013-5-14.d1
C13CPD

173.74
135.87
135.66
127.21
121.69
119.56
117.97
110.77
108.07

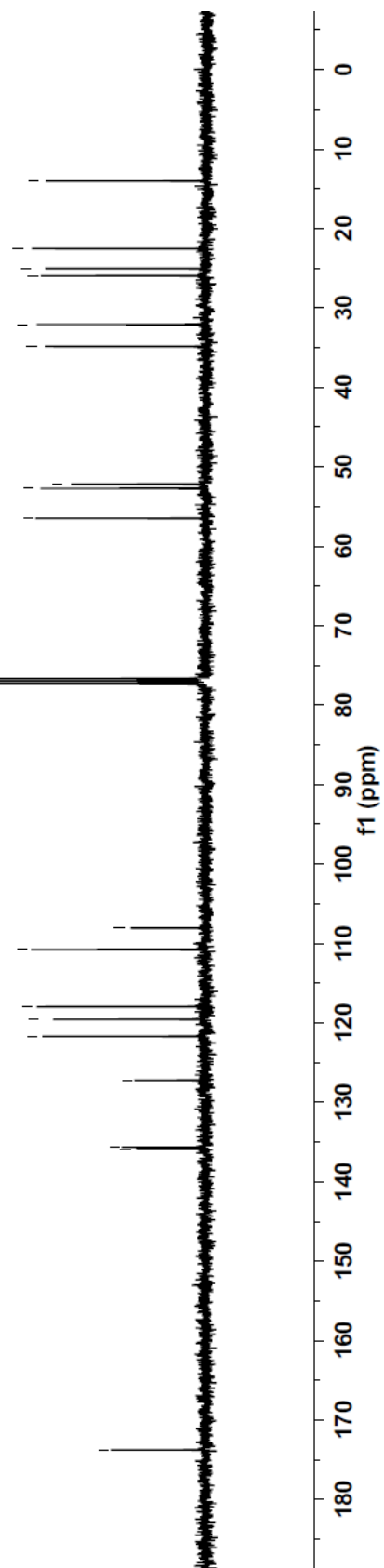
77.32
77.00
76.68

56.48
52.73
52.18

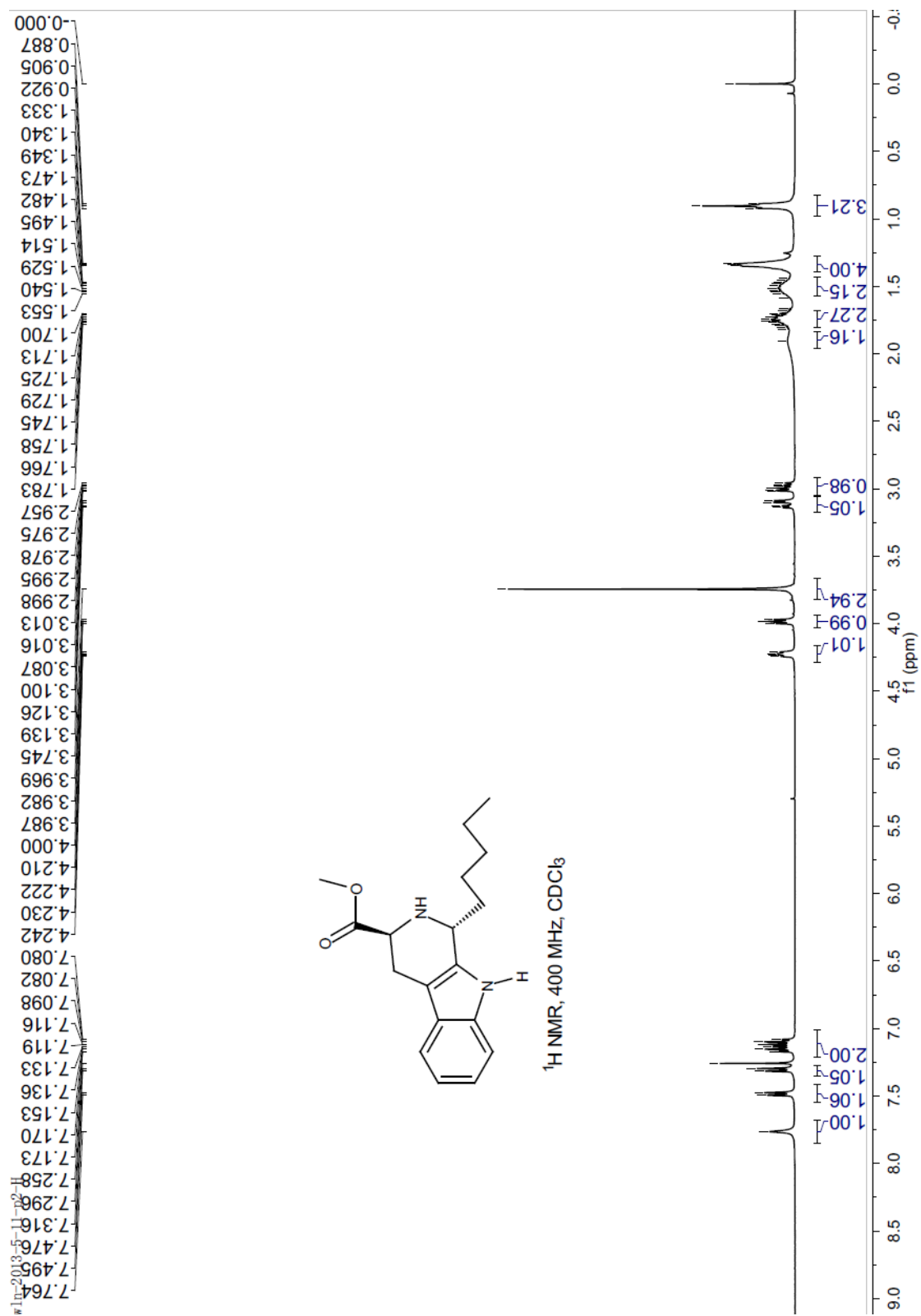
34.85
32.08
25.96
25.04
22.55
14.06



^{13}C NMR, 100 MHz, CDCl_3



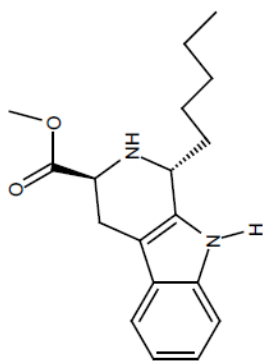
trans-3w: ^1H NMR



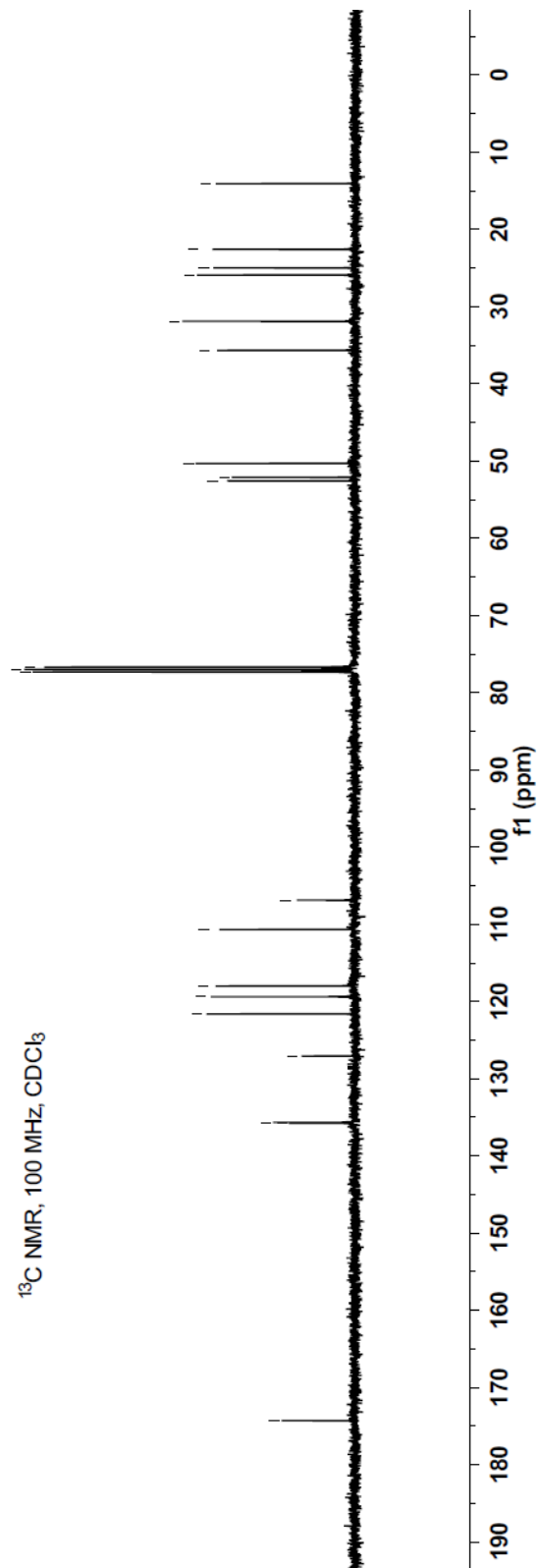
trans-3w: ^{13}C NMR

#11n-2013-5-11-12
C13CPD

- 174.30
- 135.78
- 135.66
- 127.06
- 121.61
- 119.39
- 117.99
- 110.68
- 106.88
- 77.32
- 77.00
- 76.68
- 52.57
- 52.10
- 50.30
- 35.65
- 31.90
- 25.90
- 24.99
- 22.59
- 14.07

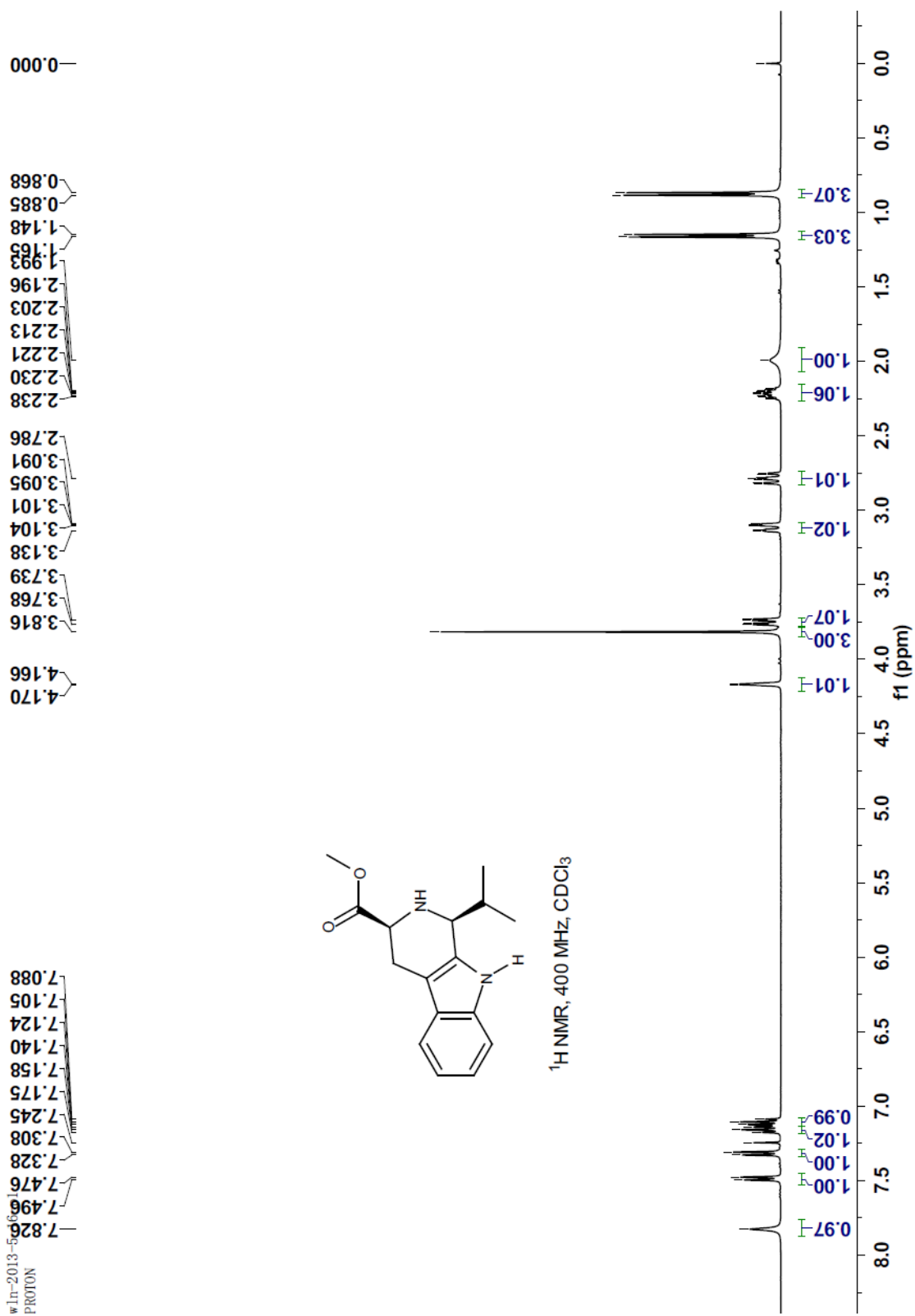


^{13}C NMR, 100 MHz, CDCl_3



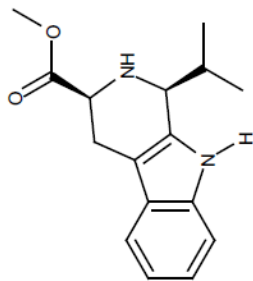
1-Isopropyl-3-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (3x):

cis-3x: ^1H NMR

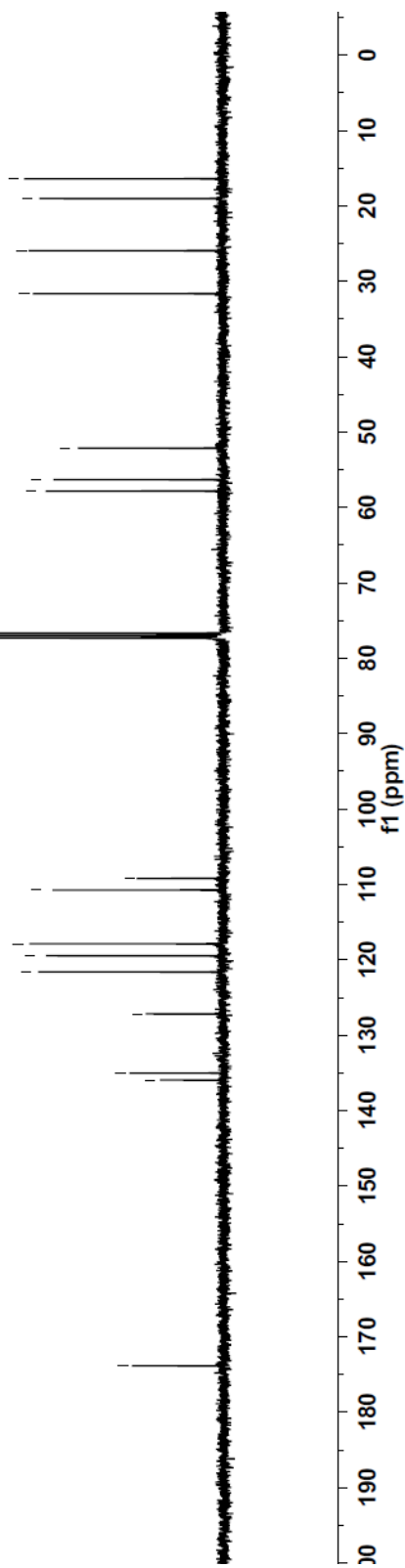


cis-3x: ^{13}C NMR

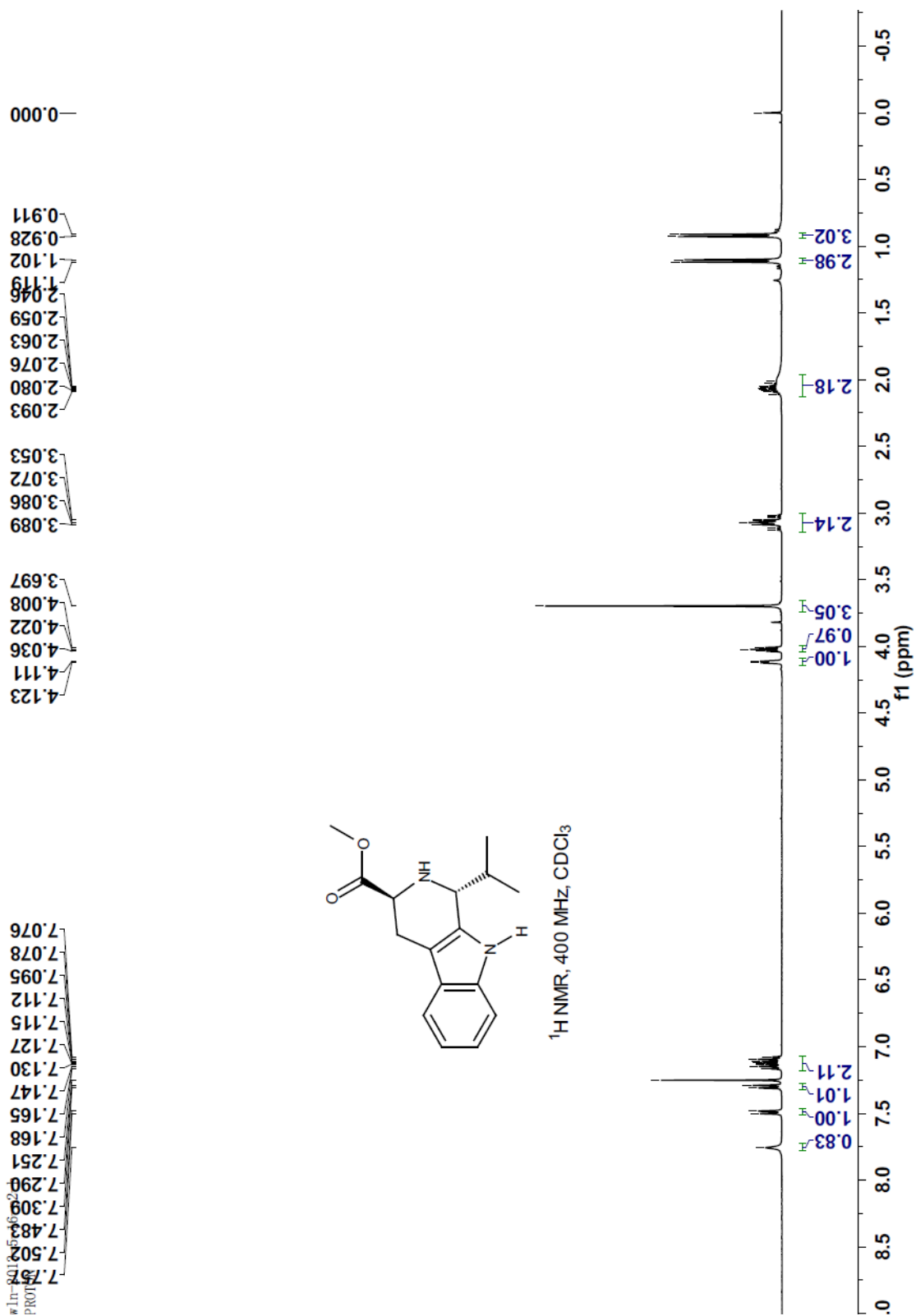
#In-2013-5-16-pl
C13CPD



^{13}C NMR, 100 MHz, CDCl_3



trans-3x: ^1H NMR



trans-3x: ^{13}C NMR

#111-2013-5-16-12
C13CPD

174.63

135.81

134.58

127.06

121.53

119.29

117.96

110.61

107.86

77.32
77.00
76.68

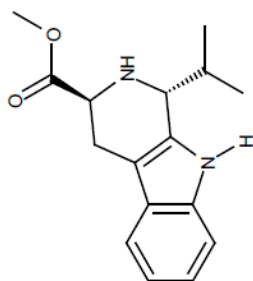
55.26
53.52
52.02

32.90

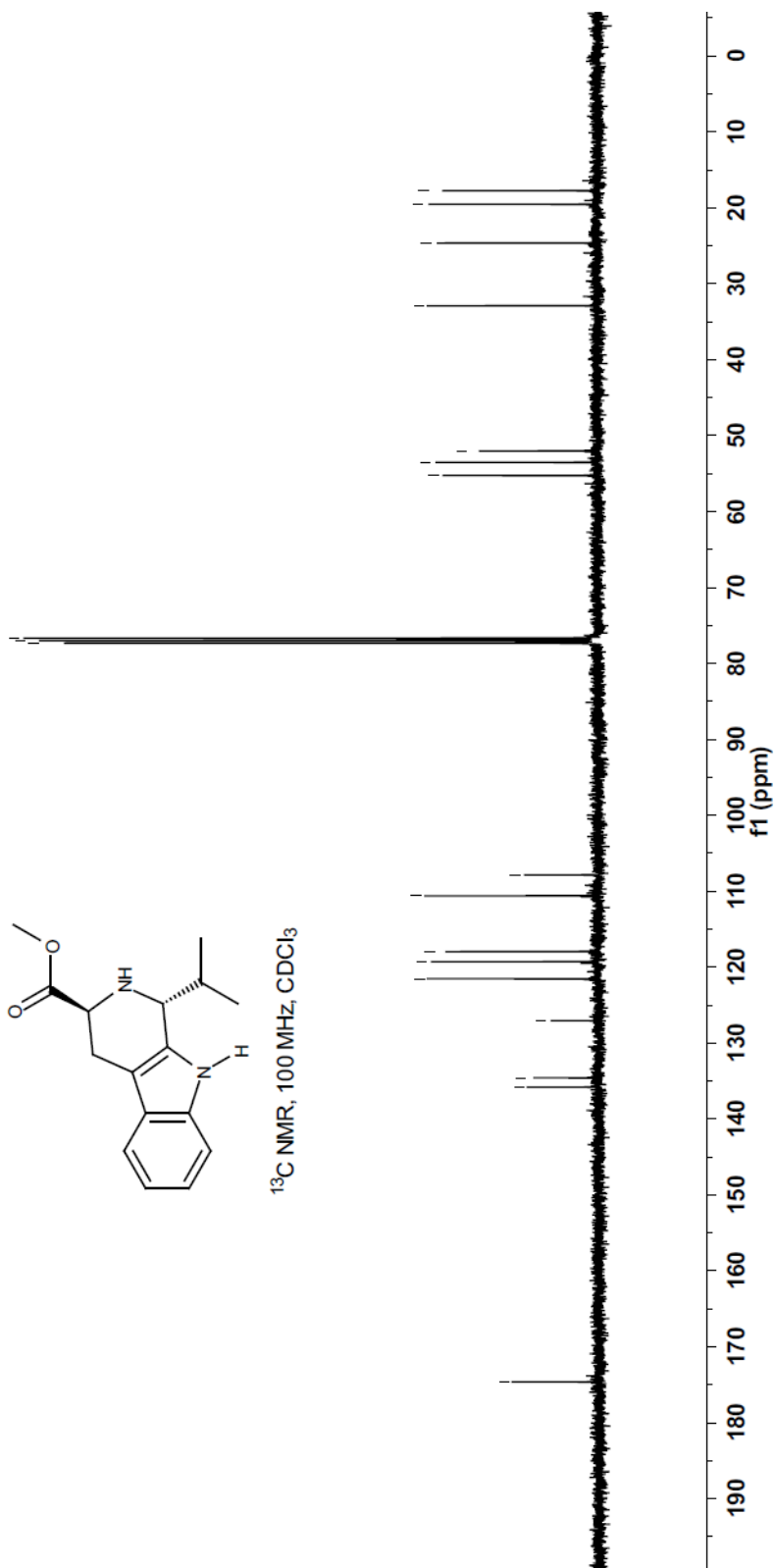
24.64

19.54

17.75



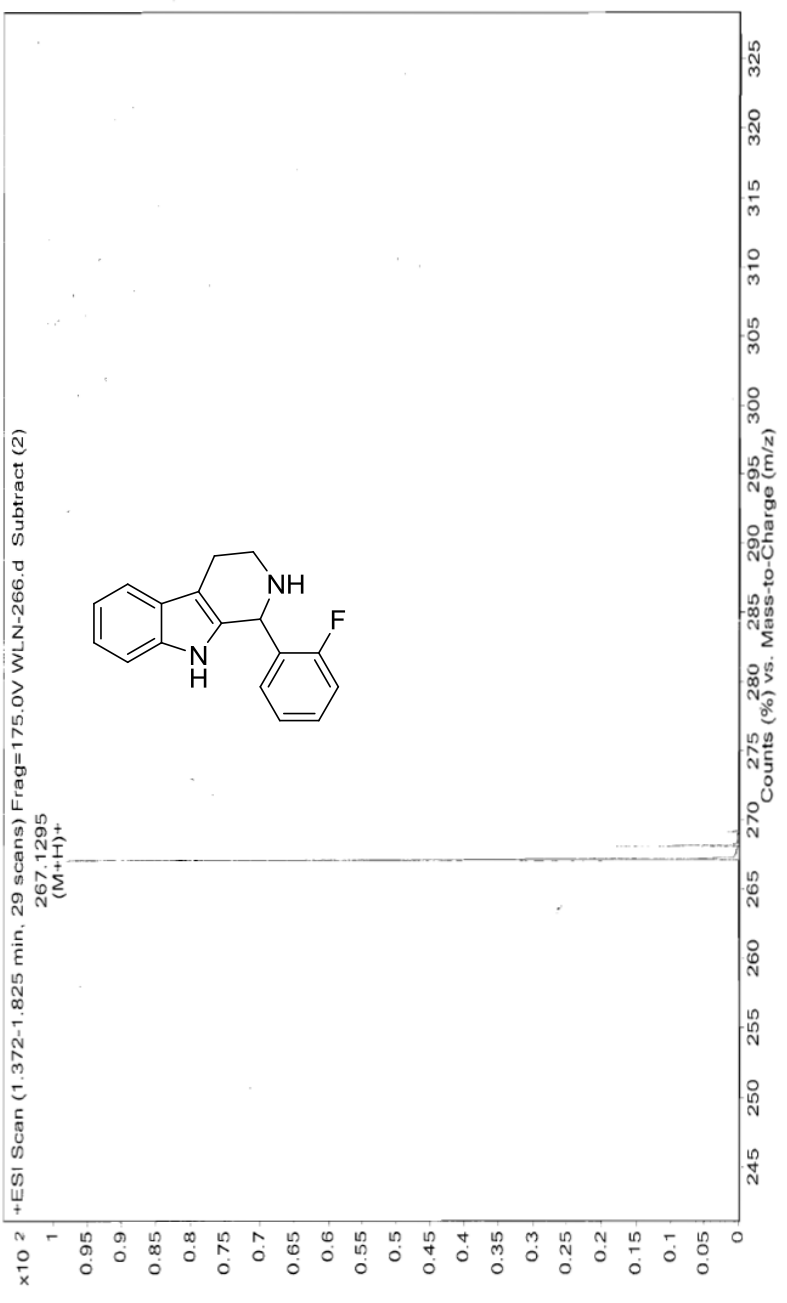
^{13}C NMR, 100 MHz, CDCl_3



1-(2-Fluorophenyl)-1,2,3,4-tetrahydro-β-carboline (3d): HRMS

Z-6 / 12 | 2

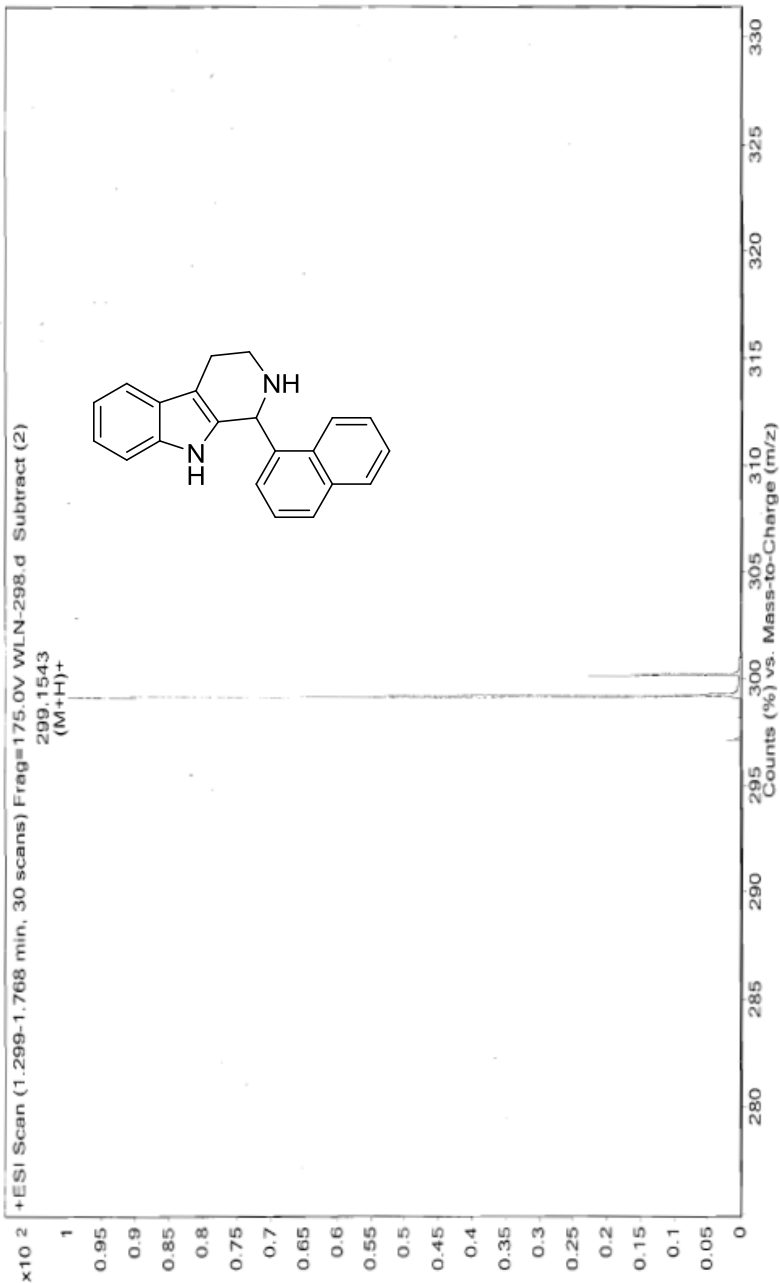
Sample Name: IC/ms
 Inj Vol: 1
 Data Filename: WLN-266.d
 Position: InjPosition
 ACQ Method: chen-ms.m
 Instrument Name: Instrument 1
 Sample Type: Sample
 Comment:
 User Name:
 IRM Calibration Status:
 Acquired Time: 7/9/2013 9:36:29 AM
 Some Ions Missed



1-(Naphthyl)-1,2,3,4-tetrahydro-β-carboline (3f): HRMS

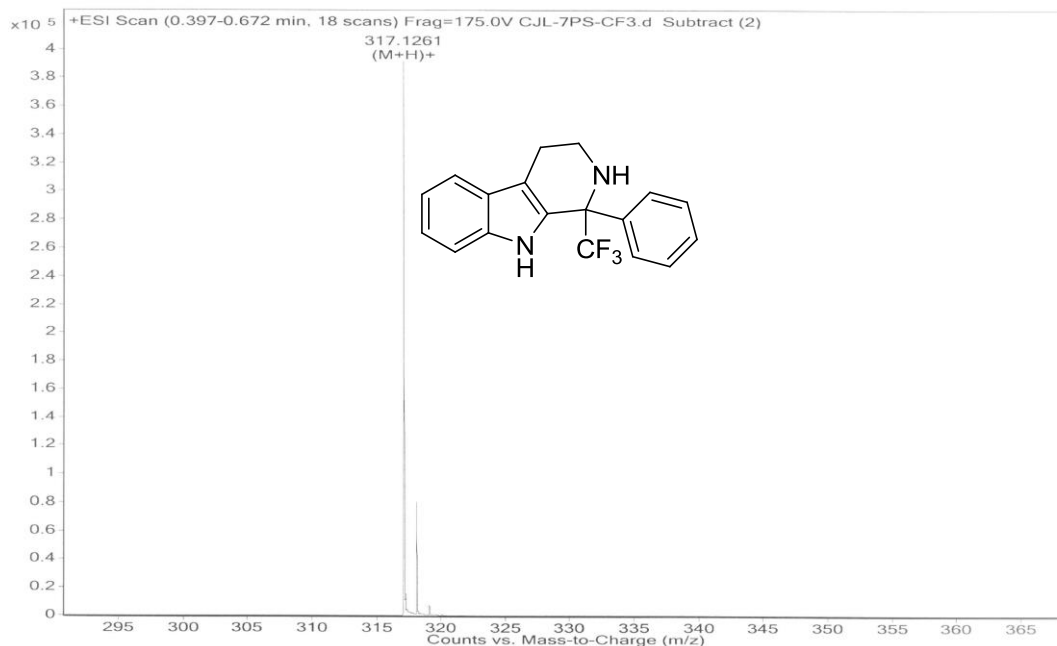
297.1343

Sample Name: Iq/ms
 Inj Vol: 1
 Data Filename: WLN-298.d
 Position: P1-A2
 InjPosition: chen-ms.m
 ACQ Method:
 Instrument Name: P1-A2
 SampleType: chen-ms.m
 Instrument 1: Sample
 User Name: IRM Calibration Status
 Acquired Time: 7/9/2013 9:40:11 AM
 Some Ions Missed



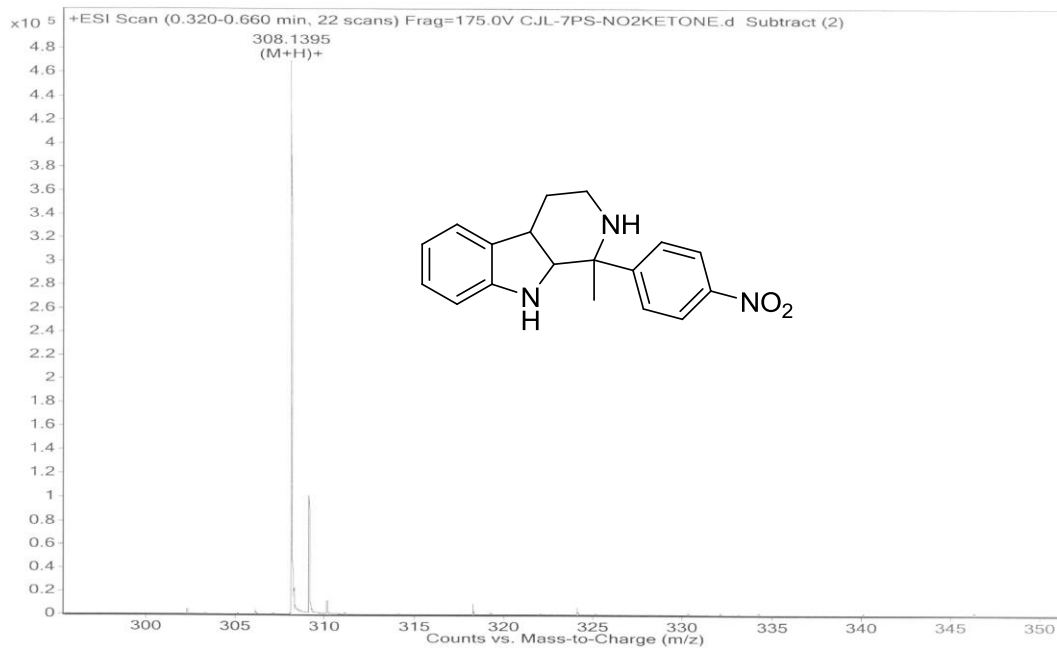
1-Phenyl-1-trifluoromethyl-1,2,3,4-tetrahydro-β-carboline (3k): HRMS

| | | | | | | | |
|---------------|---------------|-------------|--------|-----------------|-------------|------------------------|---------------------|
| Sample Name | LC/MS | Position | Vial 3 | Instrument Name | QTOF | User Name | |
| Inj Vol | -1 | InjPosition | | SampleType | Sample | IRM Calibration Status | Some Ions Missed |
| Data Filename | CJL-7PS-CF3.d | ACQ Method | | Comment | No:20110414 | Acquired Time | 4/19/2011 3:04:52 F |



1-Methyl-1-(4-nitrophenyl)-1,2,3,4-tetrahydro-β-carboline (3m): HRMS

| | | | | | | | |
|---------------|---------------------|-------------|--------|-----------------|-------------|------------------------|---------------------|
| Sample Name | LC/MS | Position | Vial 3 | Instrument Name | QTOF | User Name | |
| Inj Vol | -1 | InjPosition | | SampleType | Sample | IRM Calibration Status | Some Ions Missed |
| Data Filename | CJL-7PS-NO2KETONE.d | ACQ Method | | Comment | No:20110414 | Acquired Time | 4/19/2011 3:00:38 F |



Ethyl-2-(1-methyl-1,2,3,4-tetrahydro- β -carboline-1-yl) acetate (3n): HRMS

| | | | | | | | |
|---------------|---------------------|-------------|--------|-----------------|--------|------------------------|---------------------|
| Sample Name | LC/MS | Position | Vial 3 | Instrument Name | QTOF | User Name | |
| Inj Vol | -1 | InjPosition | | SampleType | Sample | IRM Calibration Status | Some Ions Missed |
| Data Filename | CJL-7-PS-CH2CO2ET.d | ACQ Method | | Comment | | Acquired Time | 4/19/2011 3:13:48 P |

