A Cascade C–H Functionalization/Cyclization Reaction of *N*-Arylpyridin-2-amines with *α,β*-Unsaturated Aldehydes for The Synthesis of Dihydroquinolinone Derivatives under Rhodium Catalysis

Zi-Jun Wu,[a] Kenneth L. Huang[b] and Zhi-Zhen Huang*[,a]

[a]Department of Chemistry, Zhejiang University, Hangzhou, 310028, P. R. China

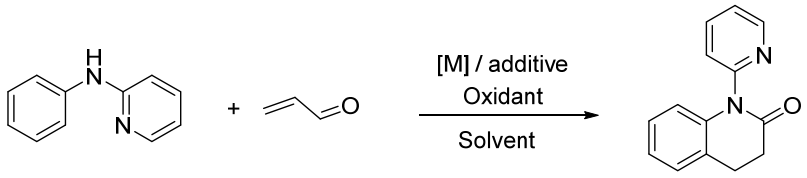
[b]Lakeside High School, Augusta 30809, United States

Electronic Supplementary Information

.

Contents

1. Optimization of the Reaction Conditions



1a **2a** **3a**

Entry	[M]	Additive (equiv)	Solvent	Yield[a,b]
1	$Co(acac)_2$	-	MeOH	0
2	$Pd(OAc)_2$	-	MeOH	0
3	$[Cp^*IrCl_2]_2$	-	MeOH	0
4	$[Rh(COD)_2Cl]_2$	-	MeOH	0
5	$[(p\text{-cymene})RuCl_2]_2$	-	MeOH	Trace
6	$[Cp^*RhCl_2]_2$	-	MeOH	72
7	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1)	MeOH	86
8	$[Cp^*RhCl_2]_2$	$AgNTf_2$ (0.1)	MeOH	75
9	$[Cp^*RhCl_2]_2$	AgOAc(0.1)	MeOH	72
10	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1), HOAc(2.0)	MeOH	88
11	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1), PivOH(2.0)	MeOH	92
12	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	MeOH	93[c]
13	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	MeOH	0[d]
14	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	EtOAc	90
15	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	dixoane	83
16	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	MeCN	89
17	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	MeOH	56[e]
18	$[Cp^*RhCl_2]_2$	$AgSbF_6$(0.1),PivOH(2.0)	MeOH	65[f]
19	-	$AgSbF_6$(0.1),PivOH(2.0)	MeOH	0

[a] The mixture of **1a** (0.10 mmol), **2a** (0.20 mmol), [M] (2.5 mol%) and $AgSbF_6$ (10 mol%) in MeOH (1 mL) was stirred at 50 °C for 3 h under air. [b]Isolated yields. [c]Under O_2. [d]Under N_2. [e]T = 25 °C. [f] T = 90 °C, in a sealed tube.

2. X-ray Crystallographic Data of 1-(Pyridin-2-yl)-3,4-Dihydro-quinolin-2(1H)-one 3aa

Datablock: 160719_wzj_3aa

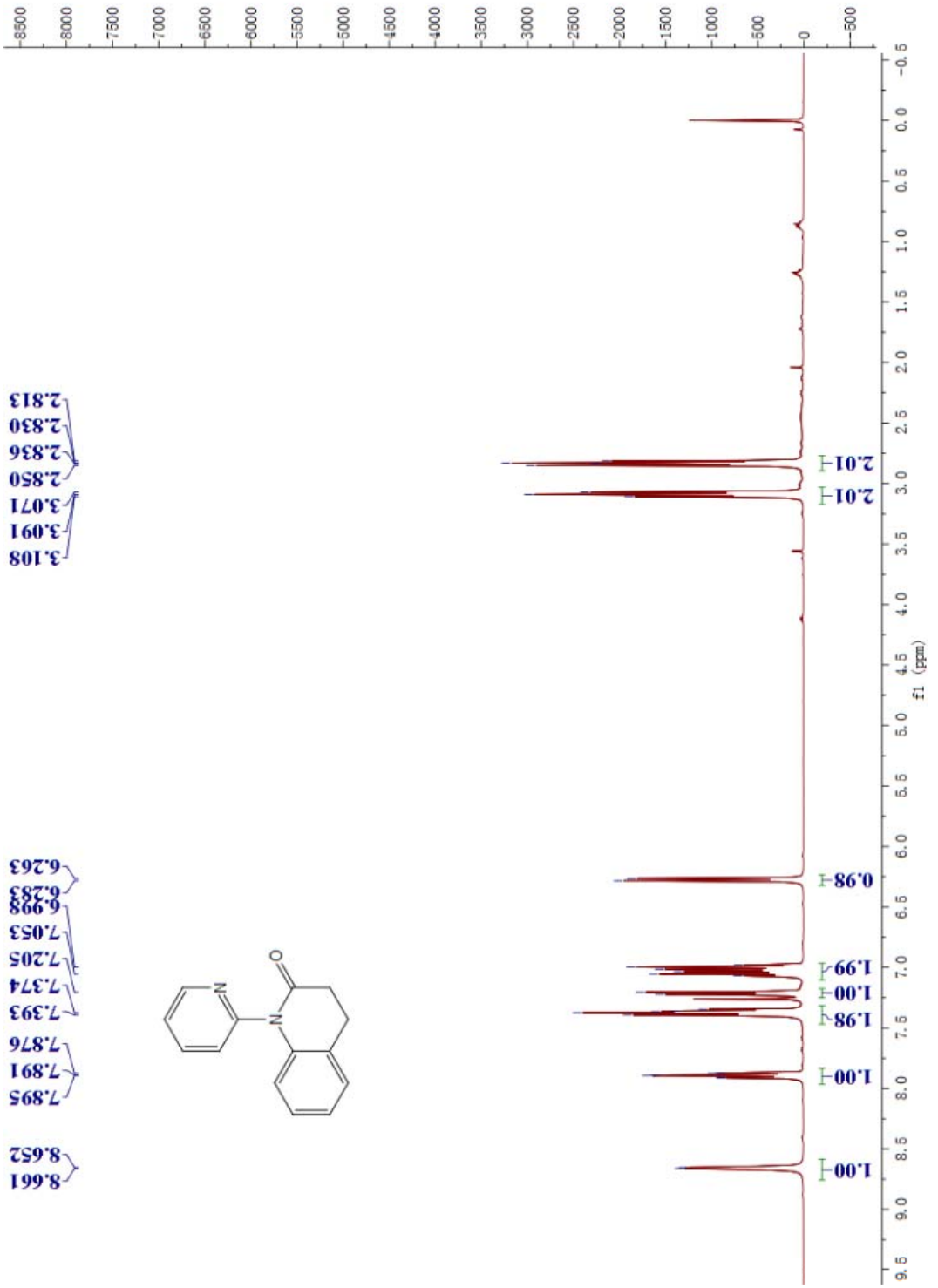
```
Bond precision:  C-C = 0.0041 A          Wavelength=0.71073

Cell:            a=14.8634(9)     b=9.0465(6)     c=16.6597(13)
                 alpha=90         beta=90         gamma=90
Temperature:     170 K

                Calculated                Reported
Volume          2240.1(3)                 2240.1(3)
Space group     P n a 21                  P n a 21
Hall group      P 2c -2n                  P 2c -2n
Moiety formula  C14 H12 N2 O              C14 H12 N2 O
Sum formula     C14 H12 N2 O              C14 H12 N2 O
Mr              224.26                    224.26
Dx,g cm-3       1.330                     1.330
Z               8                         8
Mu (mm-1)       0.086                     0.086
F000            944.0                     944.0
F000'           944.37
h,k,lmax        17,10,20                  17,10,20
Nref            4089[ 2120]               2113
Tmin,Tmax       0.966,0.975               0.905,1.000
Tmin'           0.966

Correction method= # Reported T Limits: Tmin=0.905 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.00/0.52      Theta(max)= 25.350

R(reflections)= 0.0391( 1803)     wR2(reflections)= 0.0969( 2113)

S = 1.035                 Npar= 308
```

3. Kinetic Isotope Effect Experiment

A mixture of *N*-phenylpyridin-2-amine **1a** (0.05 mmol), deuterio-**1a** (0.05 mmol), **2** (0.20 mmol), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $AgSbF_6$ (3.4 mg, 0.01 mmol), PivOH (20.4 mg, 0.20 mmol, 2.0 equiv) in MeOH (1.0 mL) was stirred for 1h at 50 °C. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether / ethyl acetate as an eluent) to give a mixture of dihydroquinolinone **3aa** and deuterated dihydroquinolinone **3aa**-D_4.

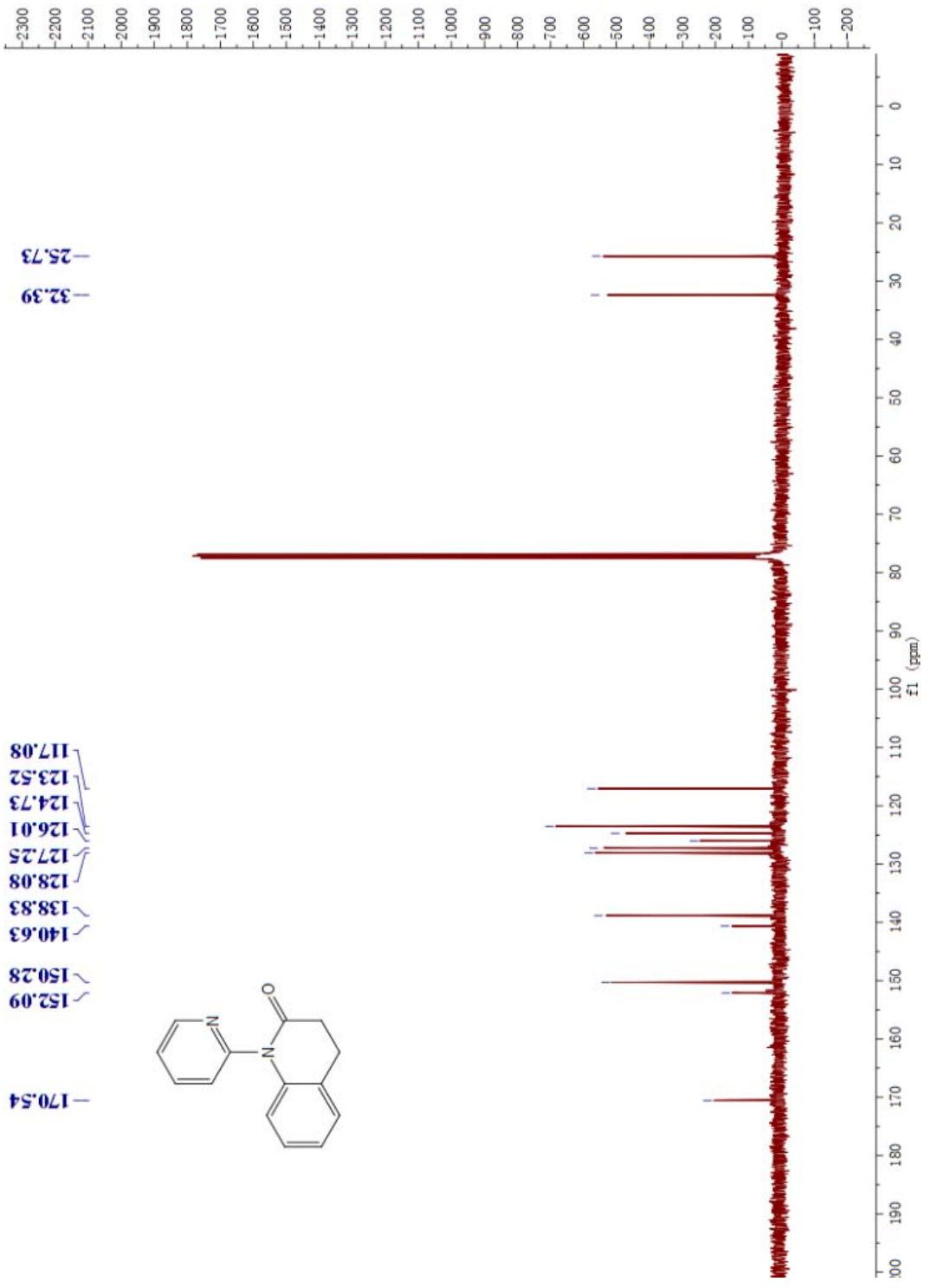
4. ^{1}H NMR, ^{13}C NMR, HR-MS Spectra of Dihydroquinolinone Derivatives 3

^{1}H NMR Spectrum of 1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3aa**

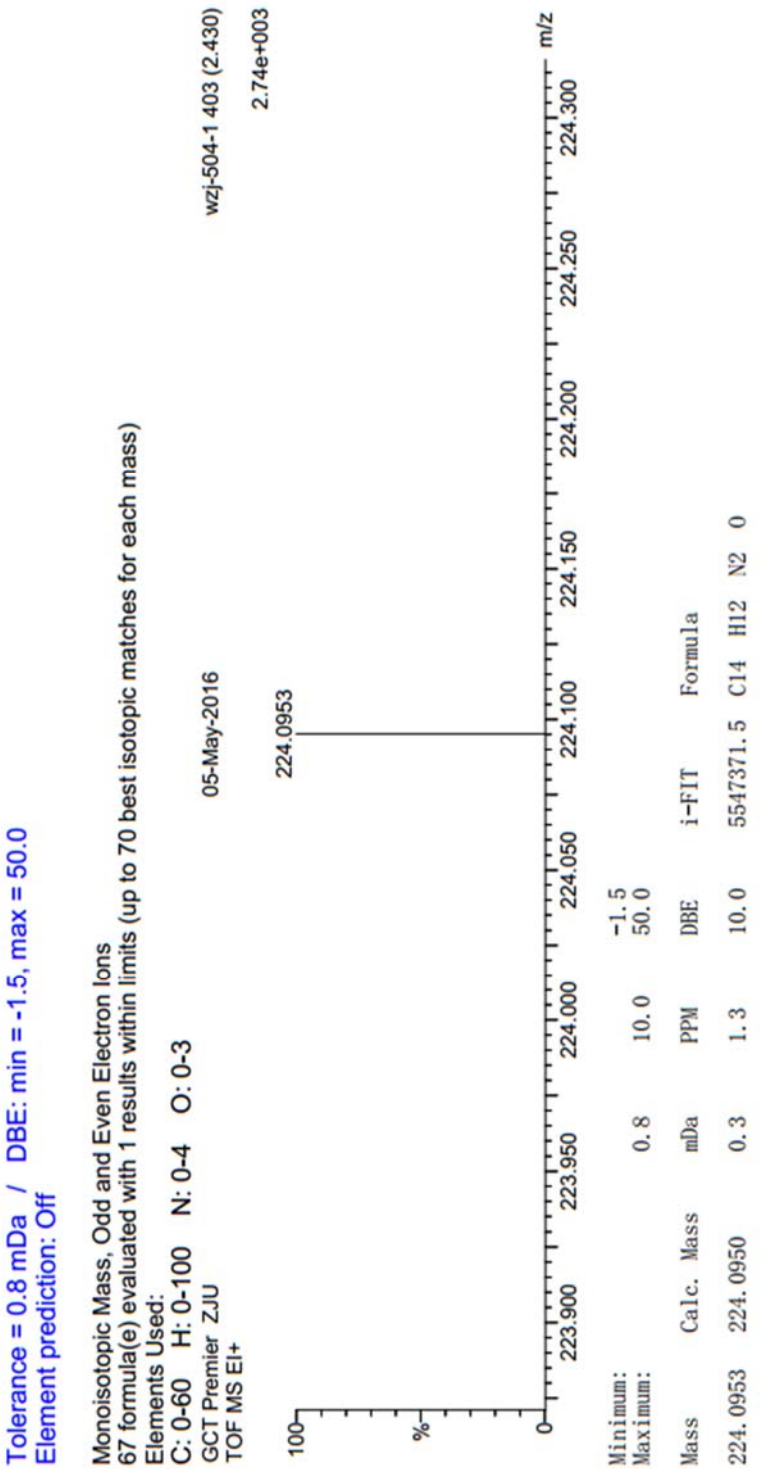


^{13}C NMR Spectrum of 1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one

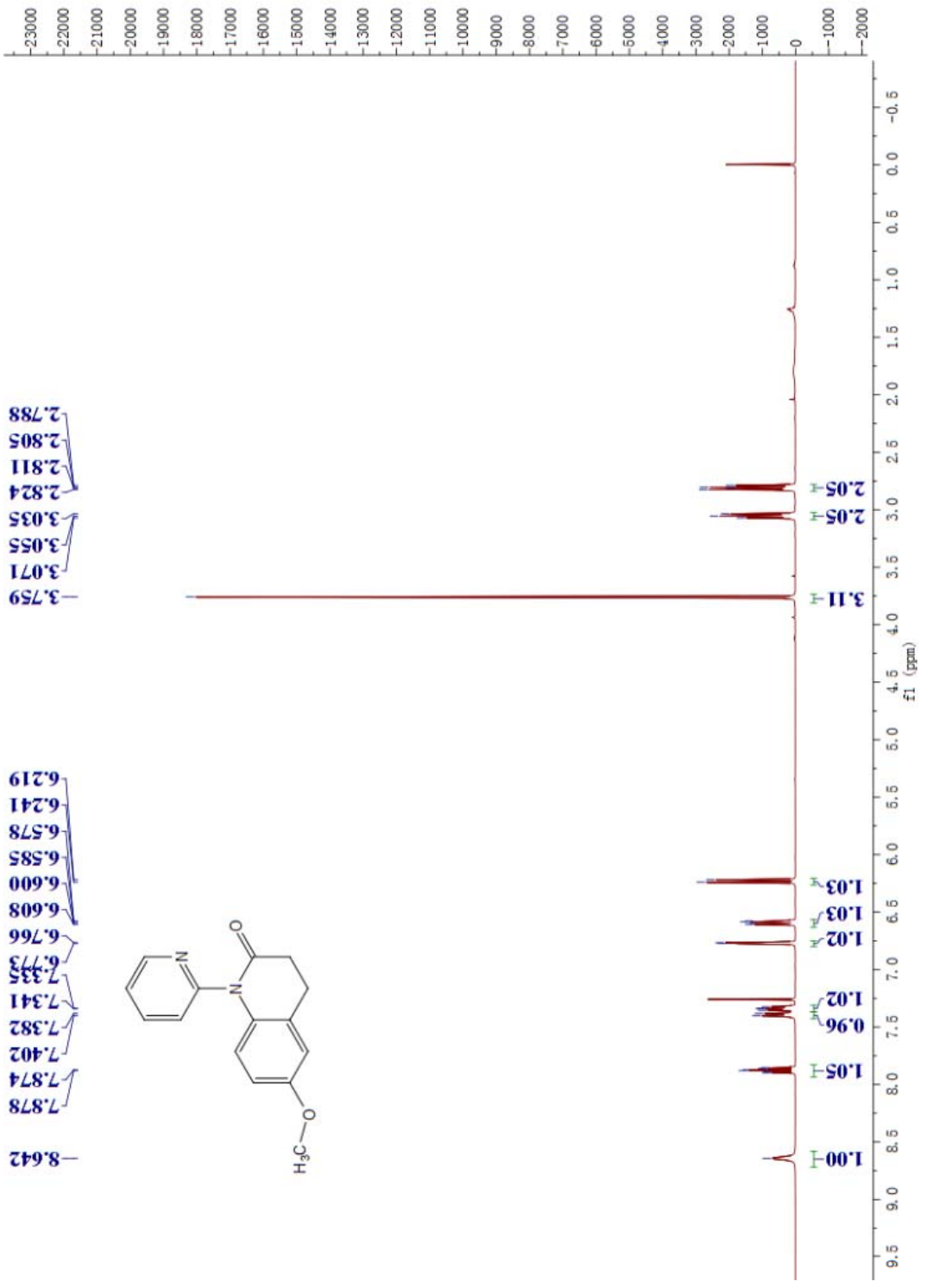
3aa



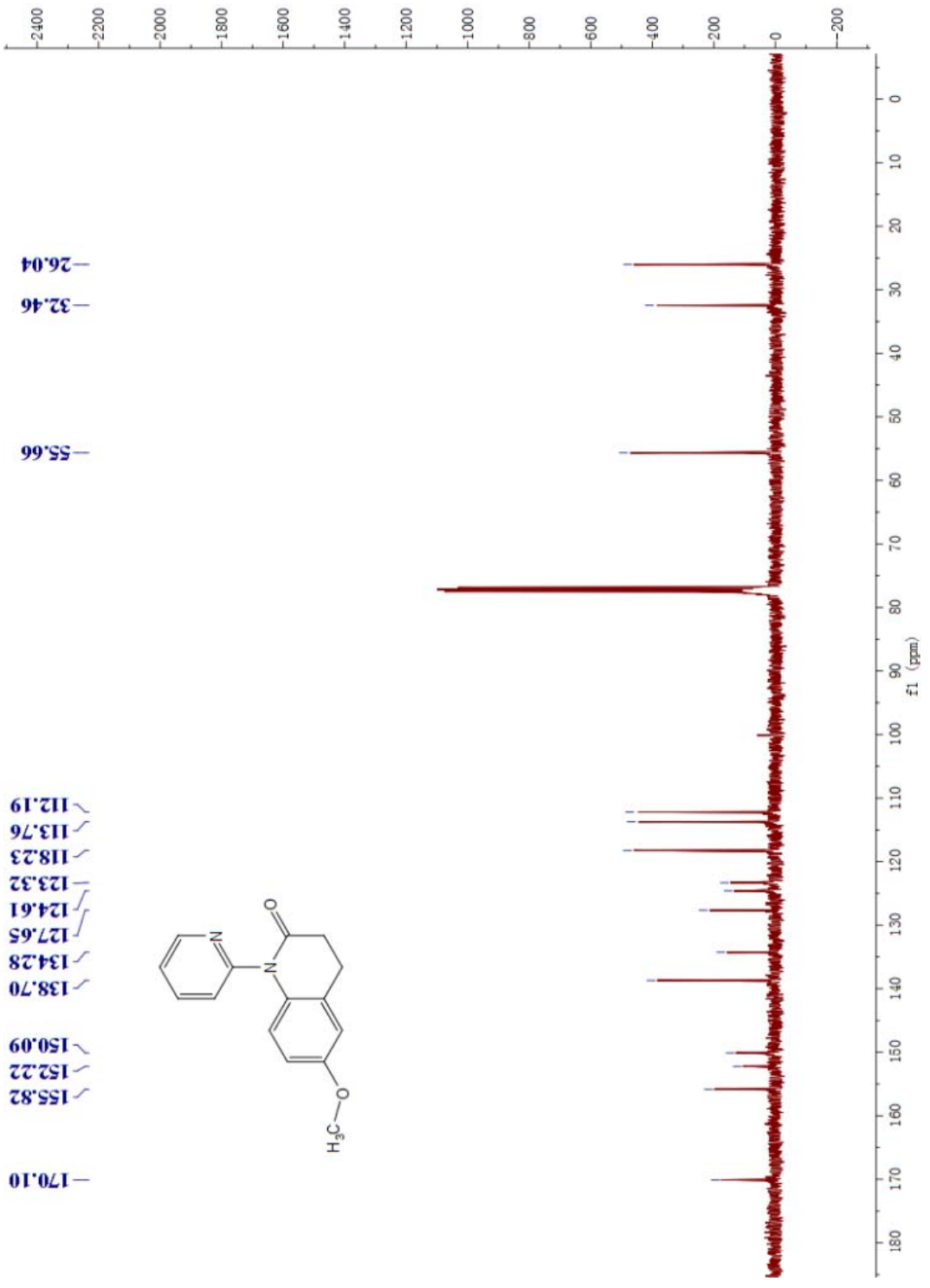
HR-MS Spectrum of 1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3aa**



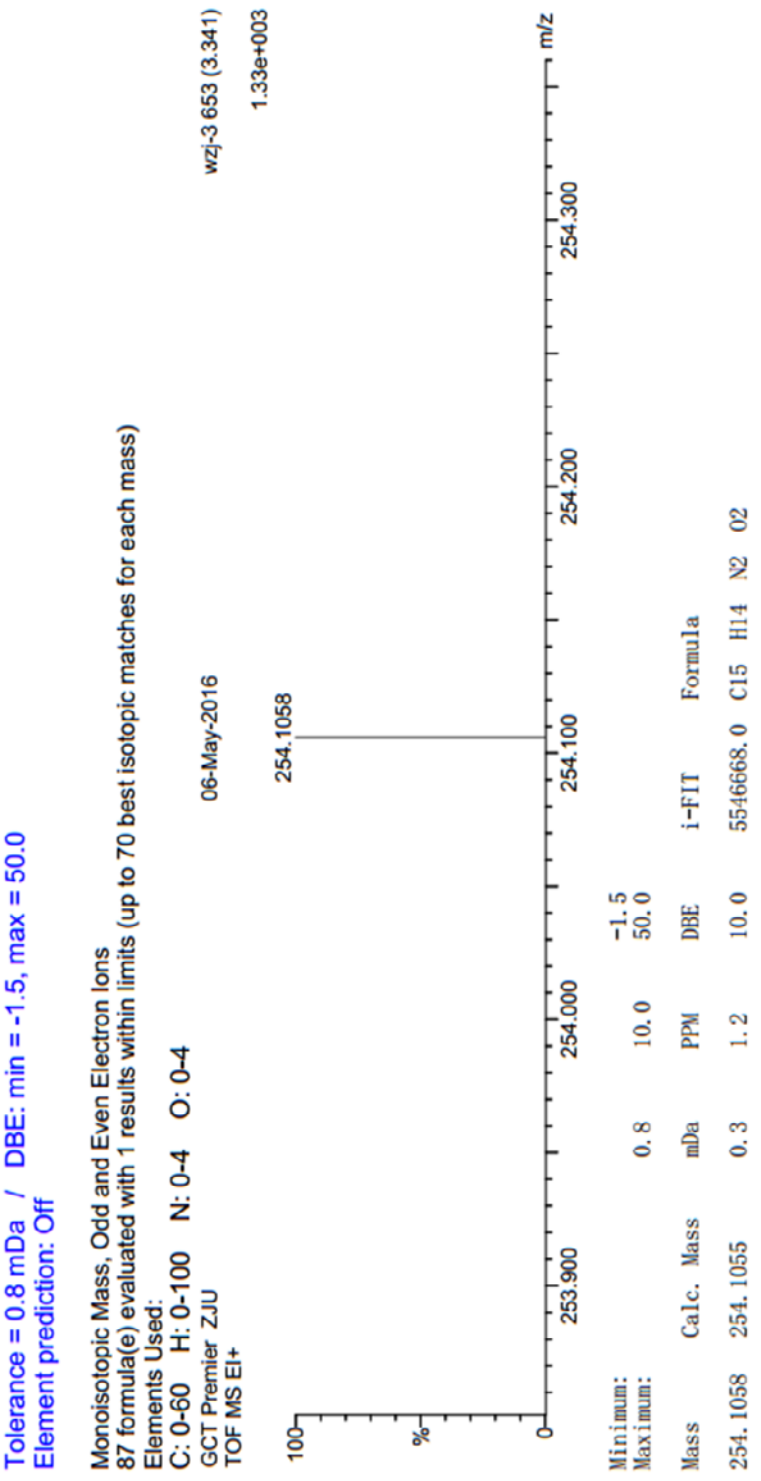
^{1}H NMR Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



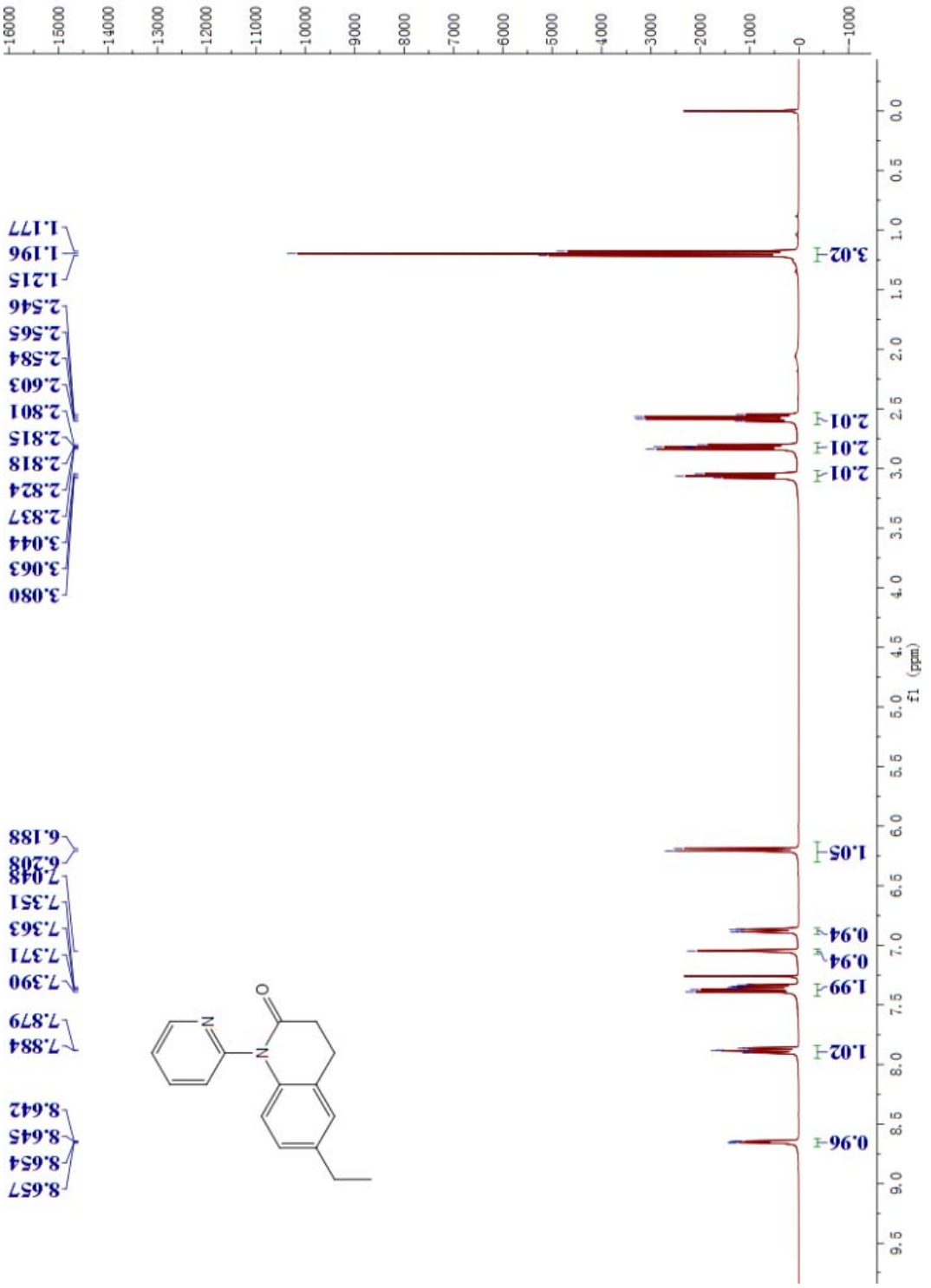
^{13}C NMR Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



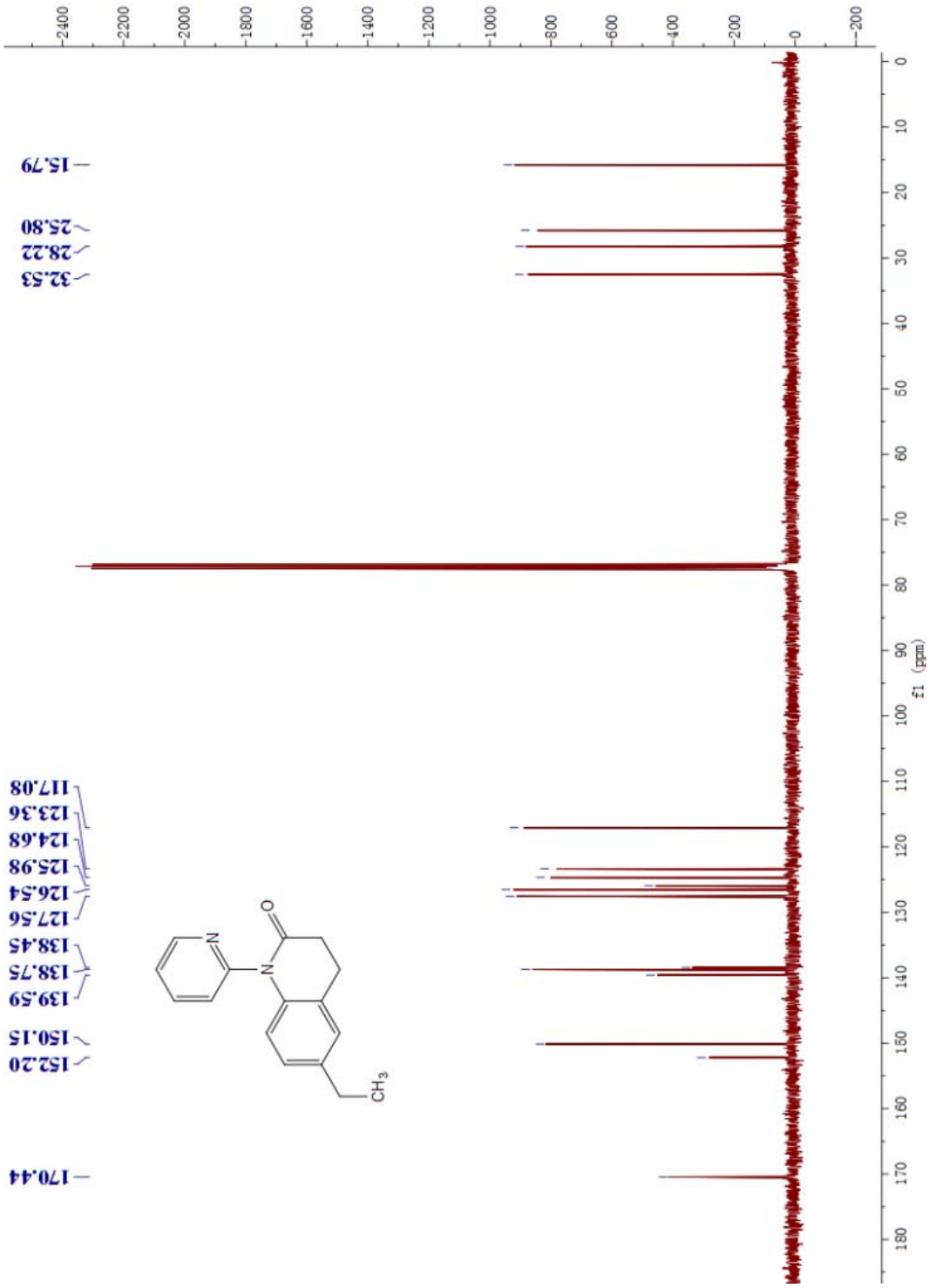
HR-MS Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



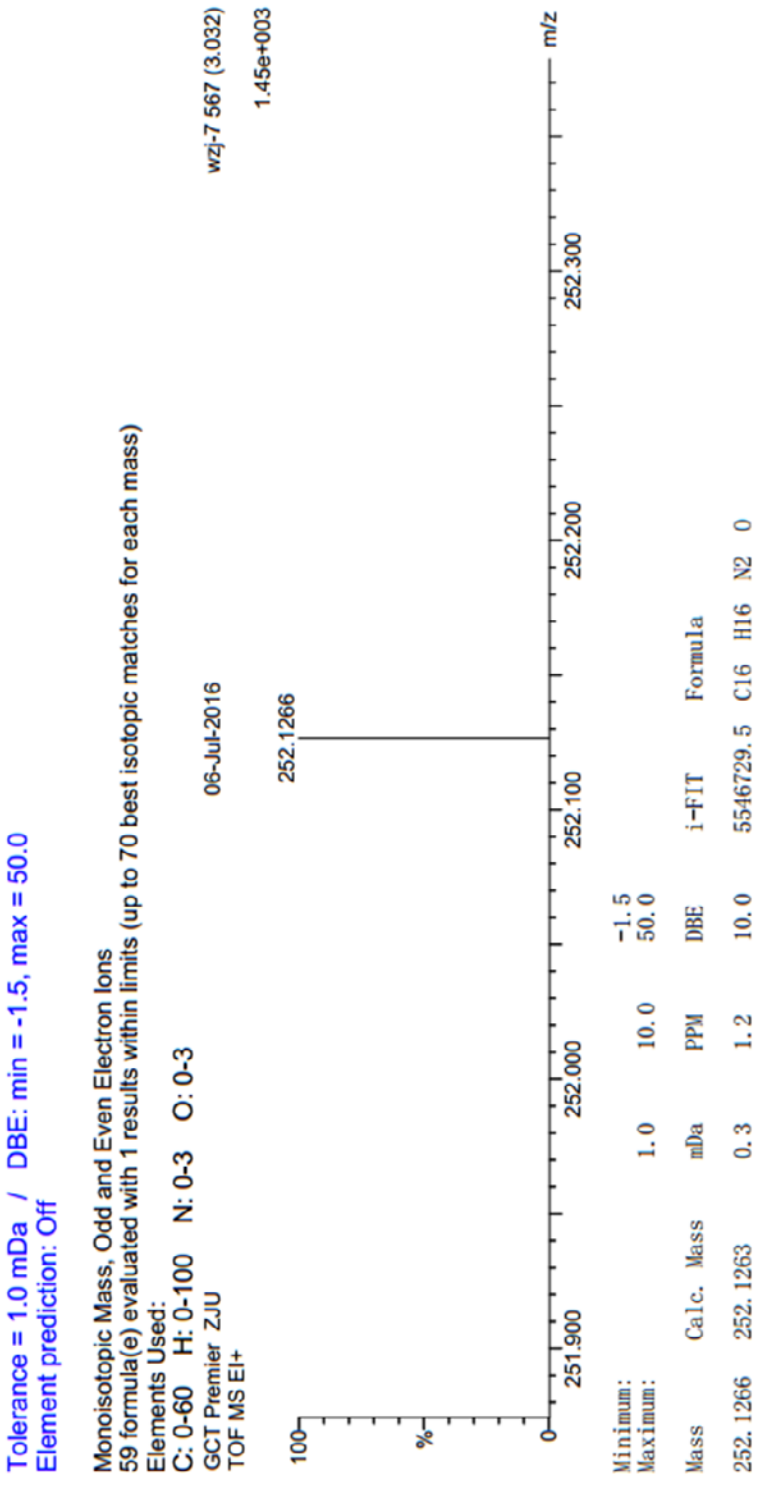
^{1}H NMR Spectrum of 6-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ca**



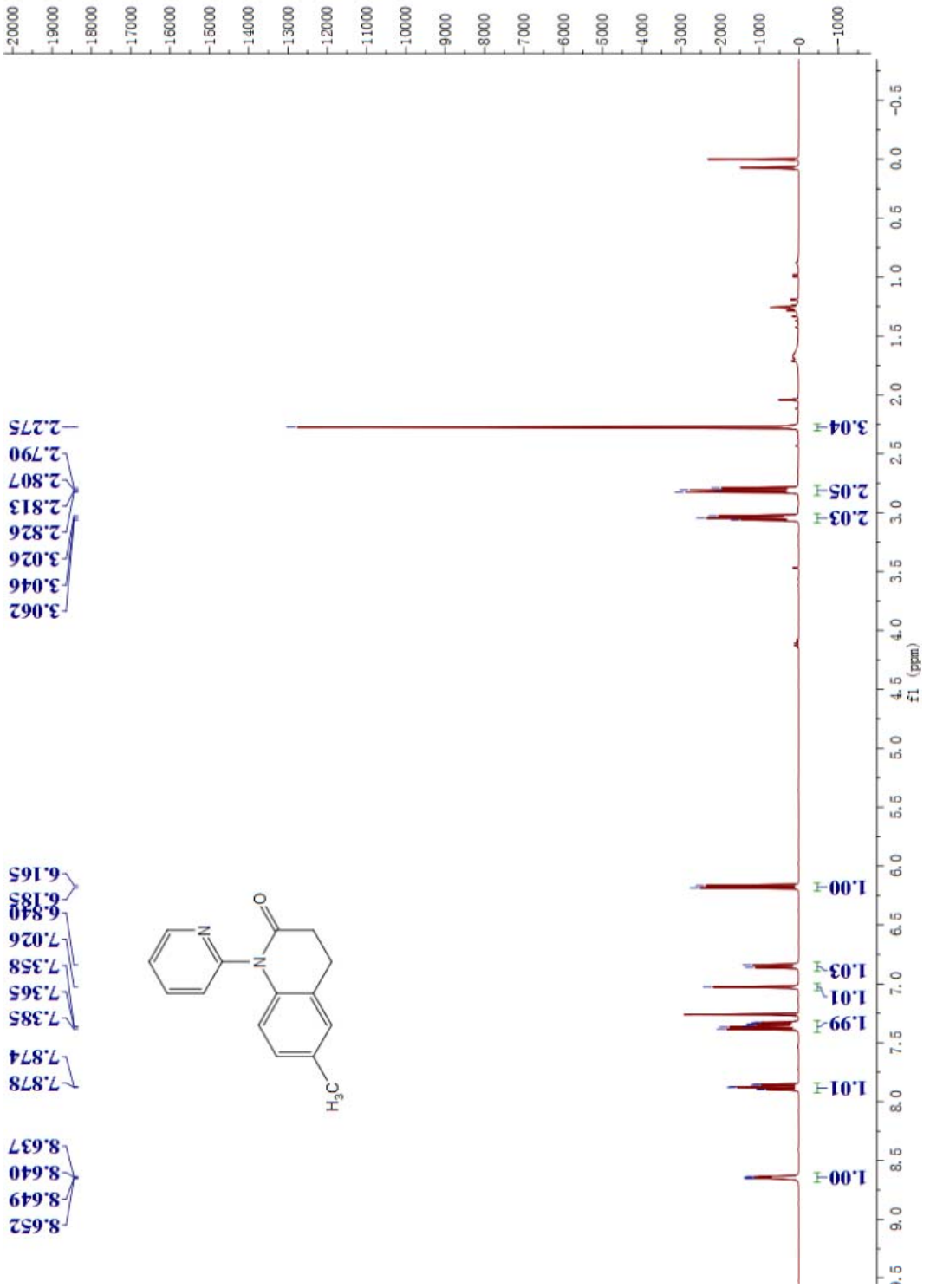
^{13}C NMR Spectrum of 6-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ca**



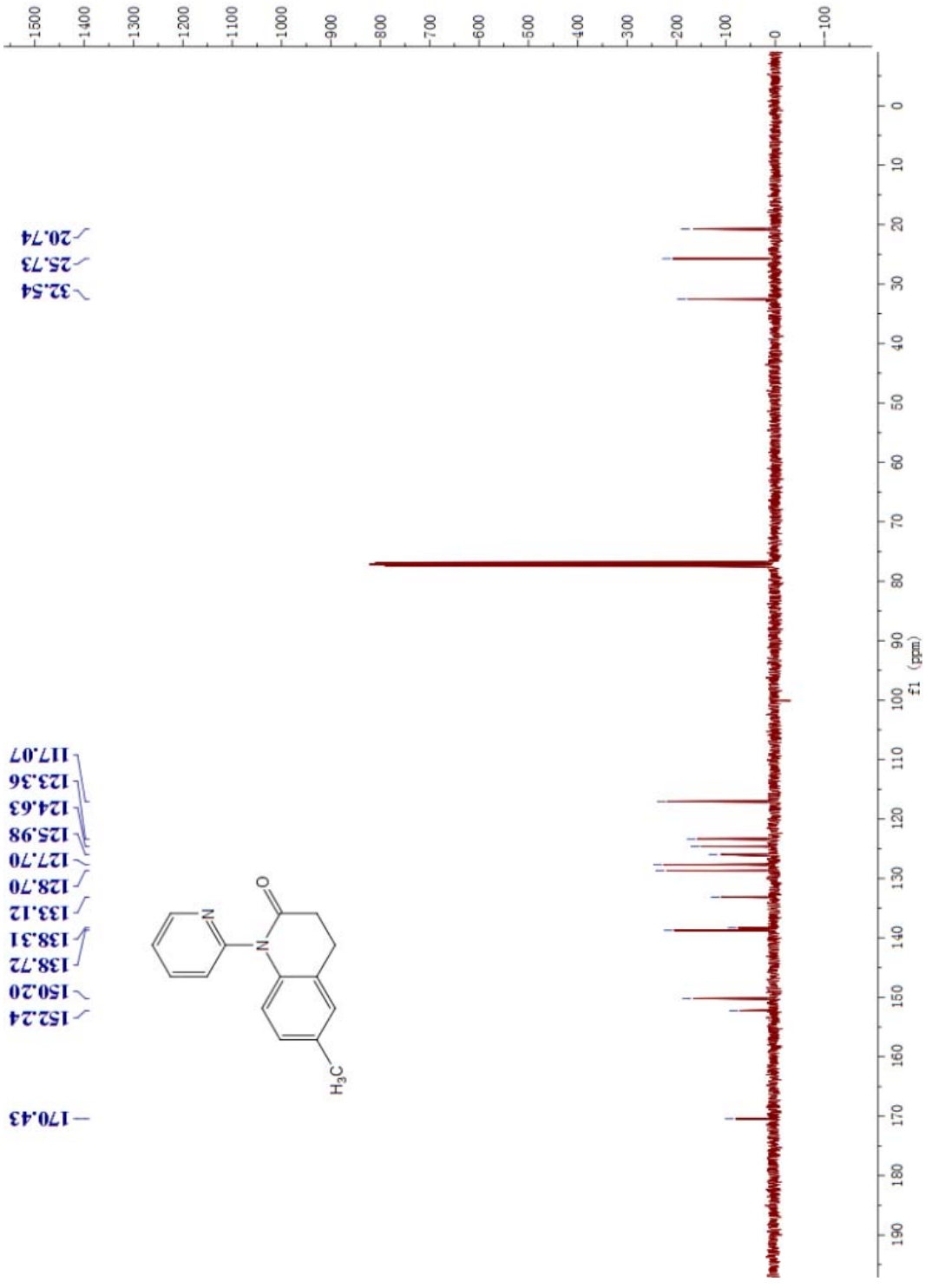
HR-MS Spectrum of 6-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ca**



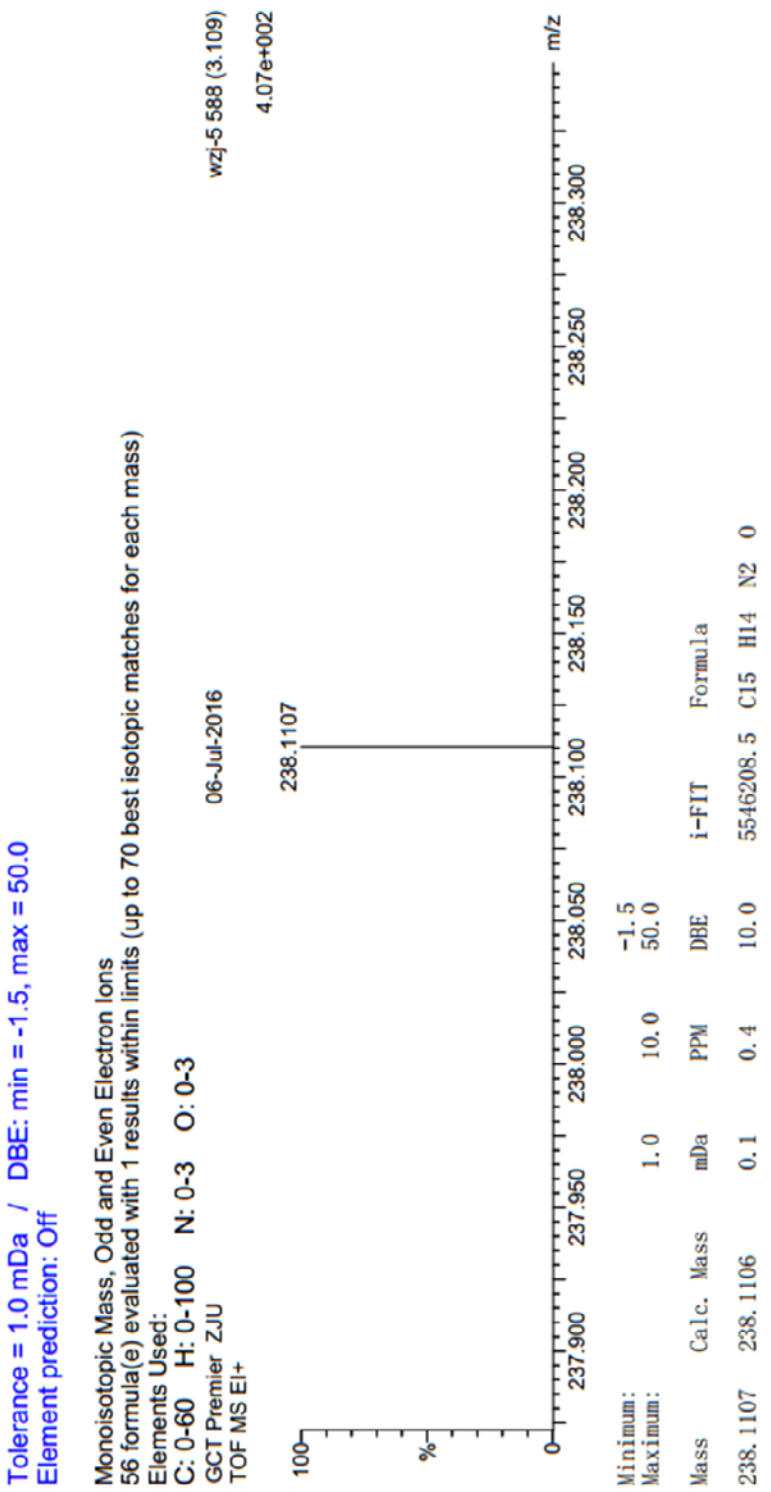
^{1}H NMR Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



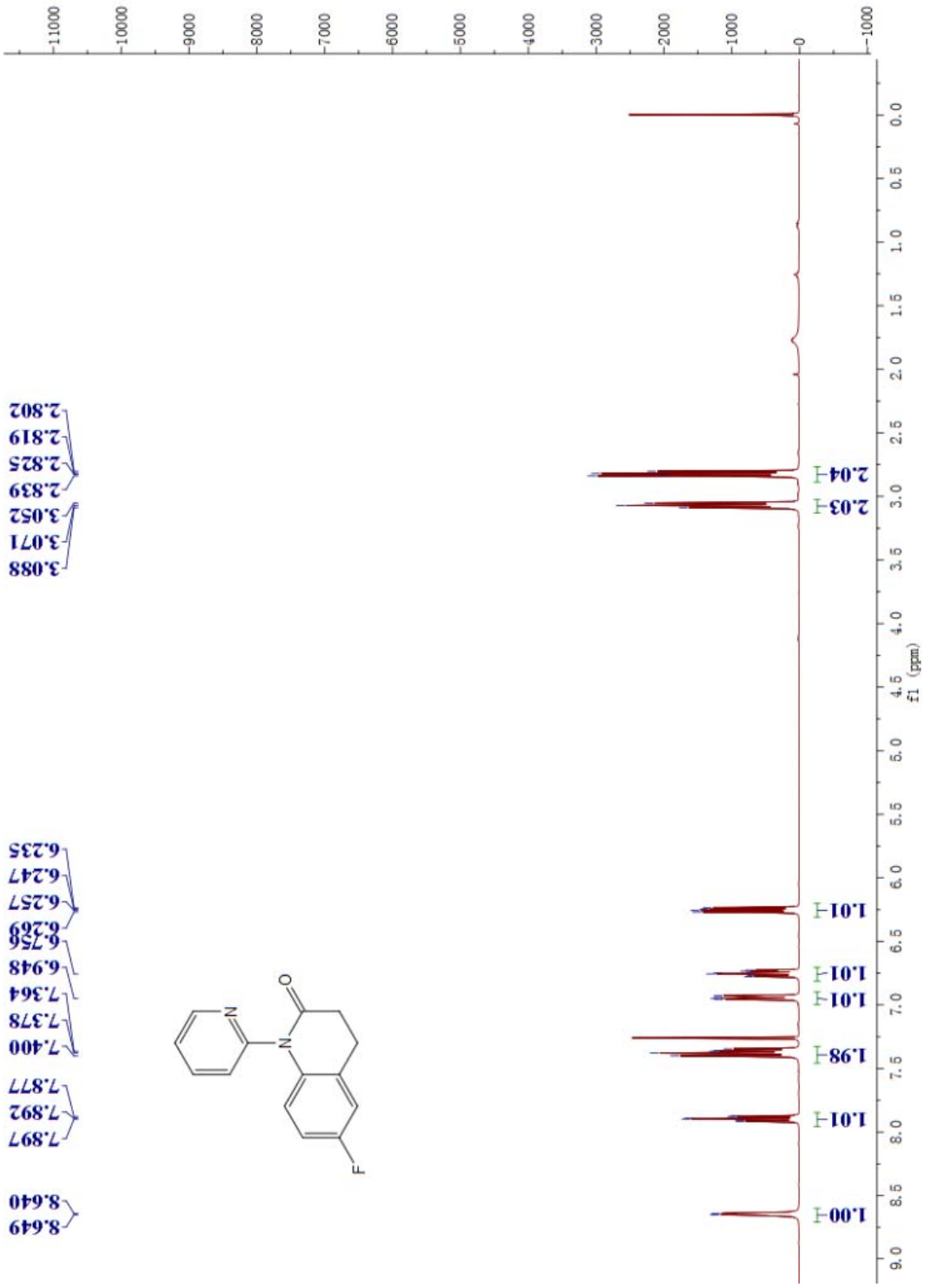
^{13}C NMR Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



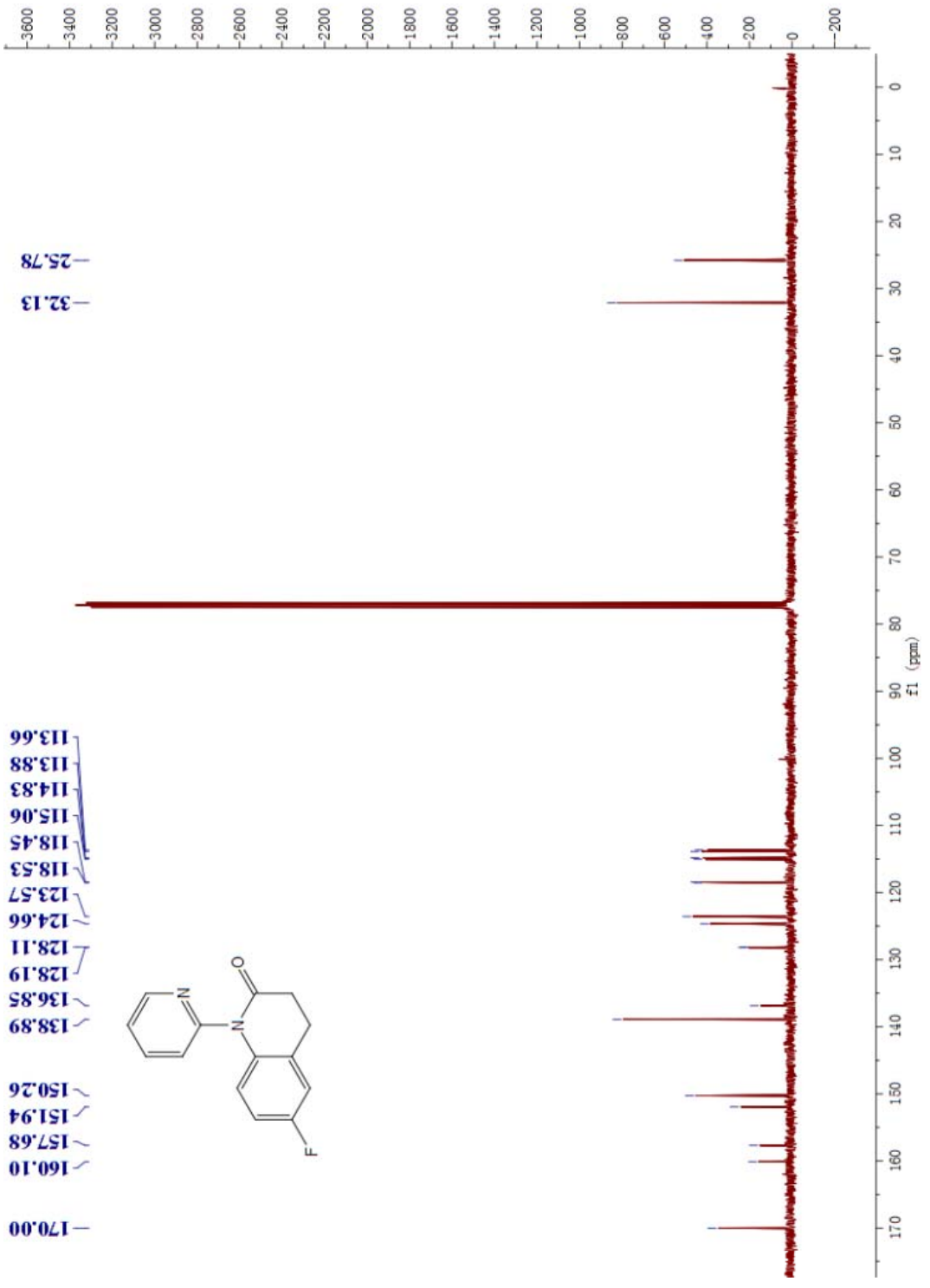
HR-MS Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



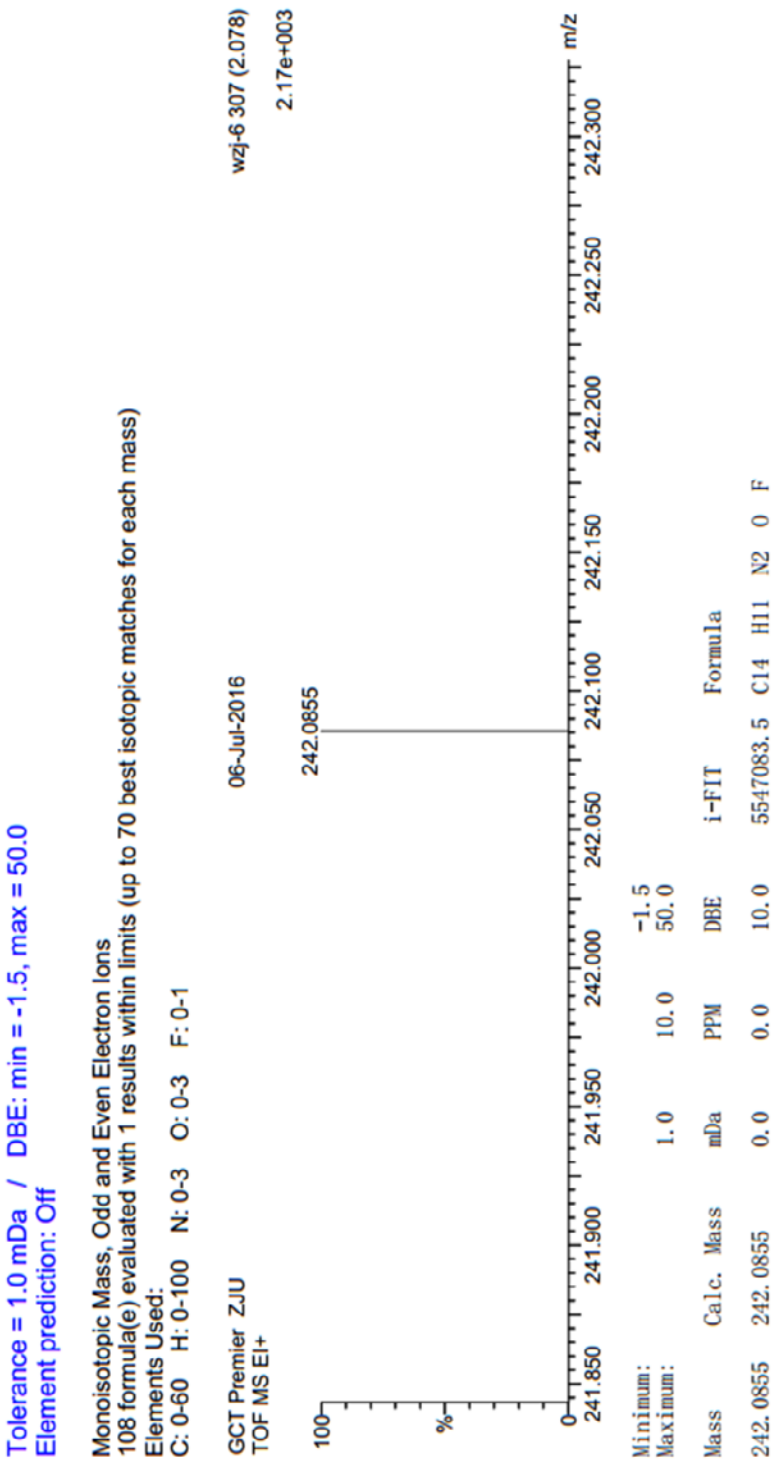
^{1}H NMR Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



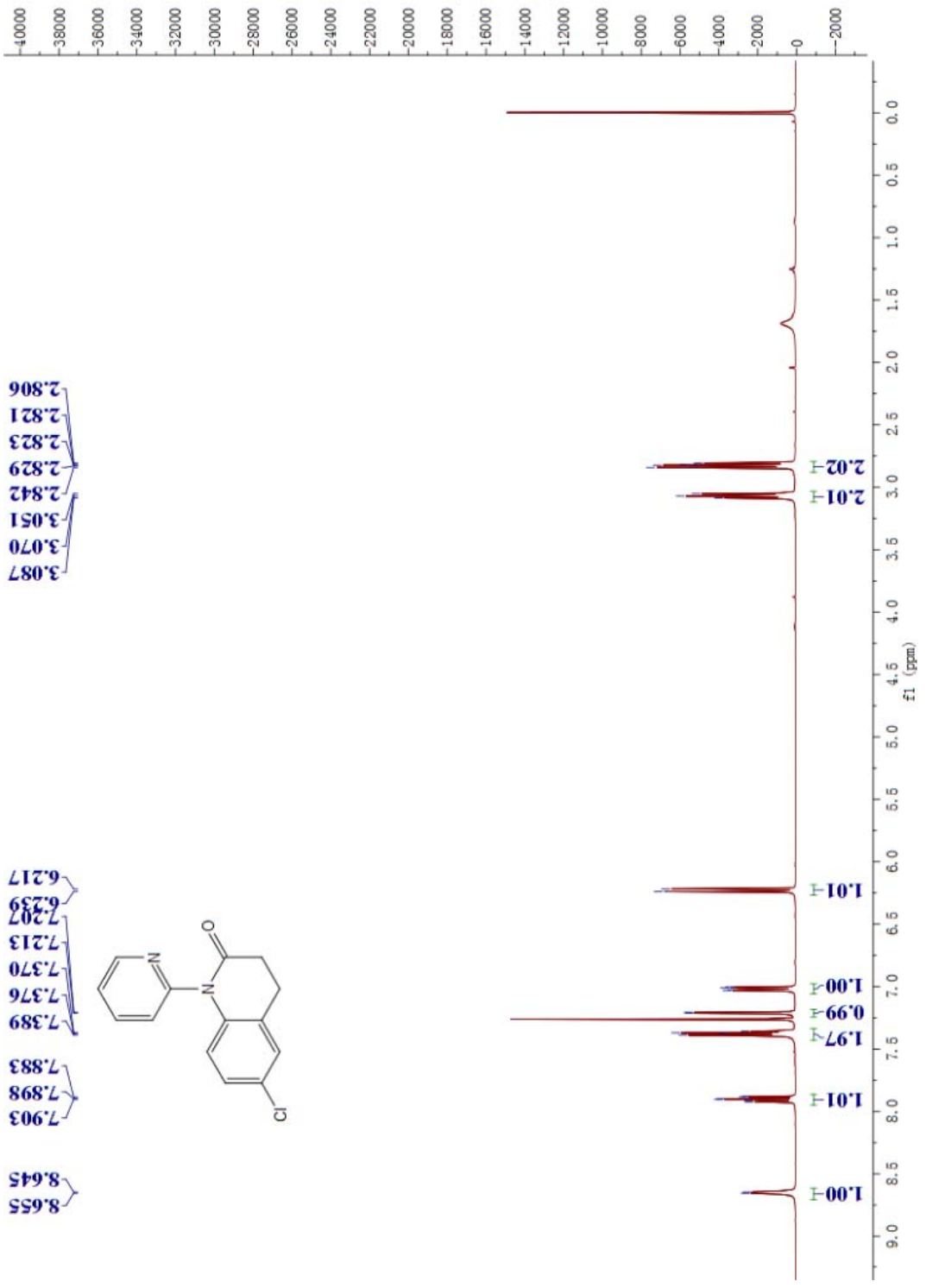
^{13}C NMR Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



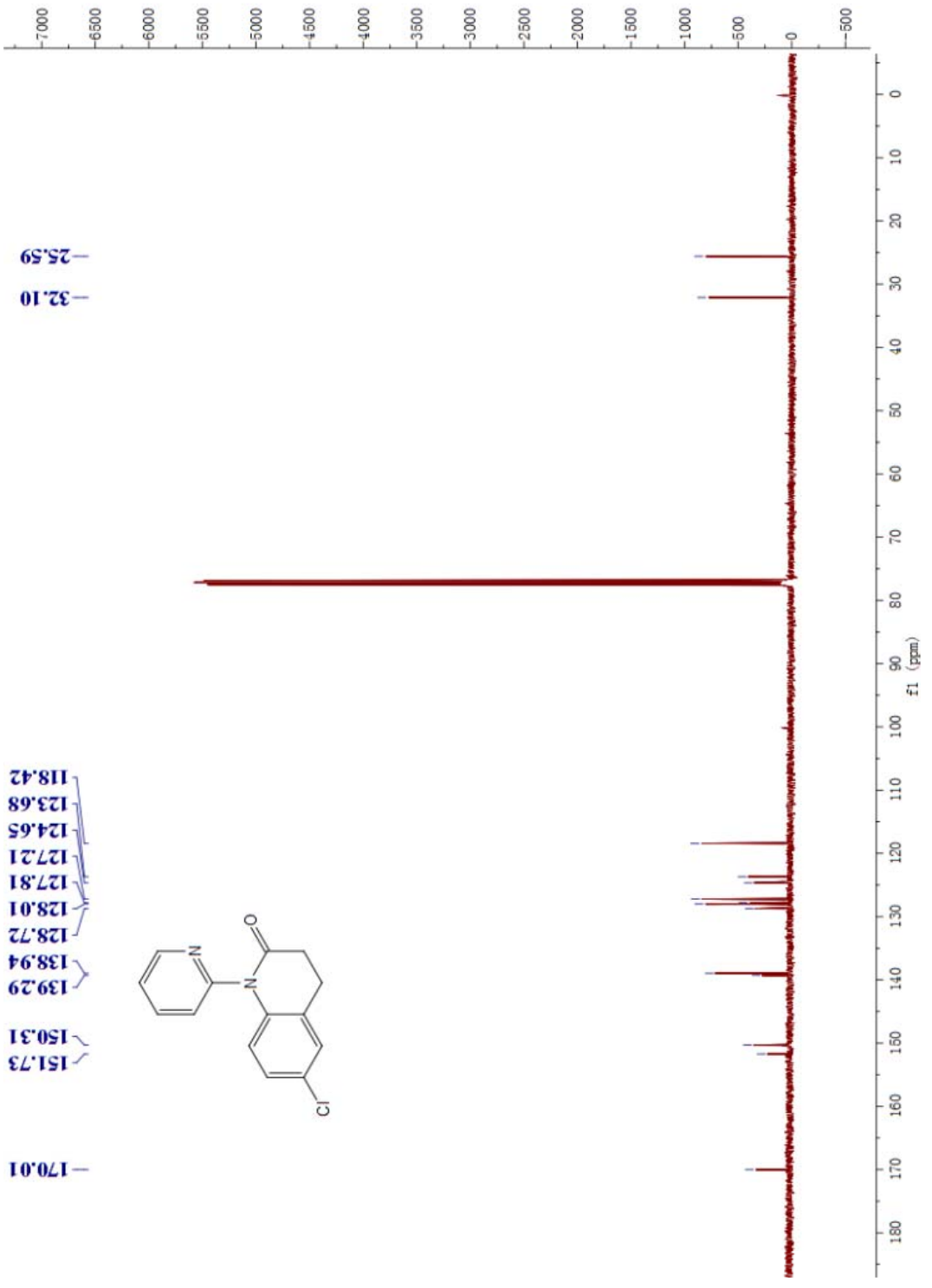
HR-MS Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



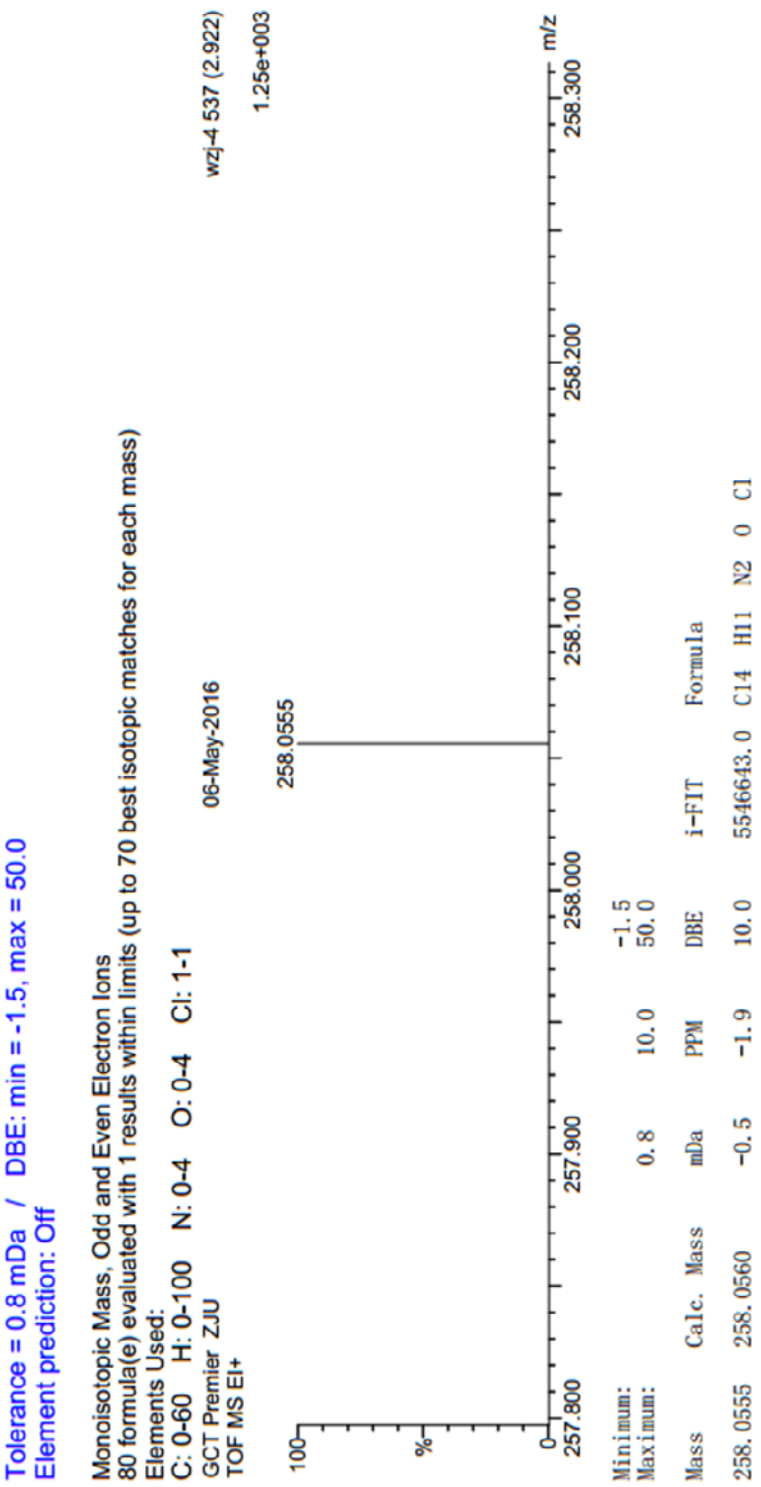
^{1}H NMR Spectrum of 6-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3fa**



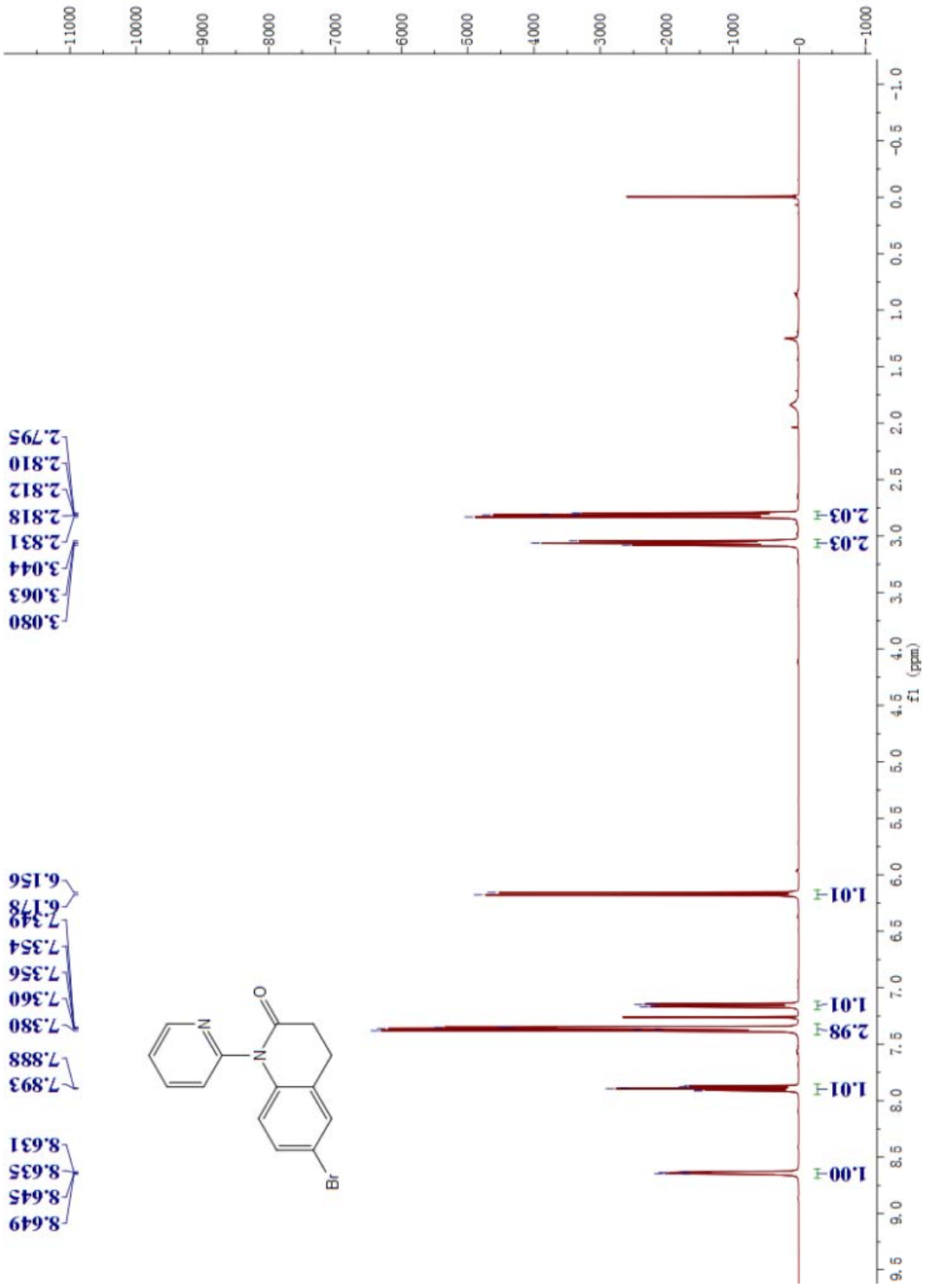
^{13}C NMR Spectrum of 6-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3fa**



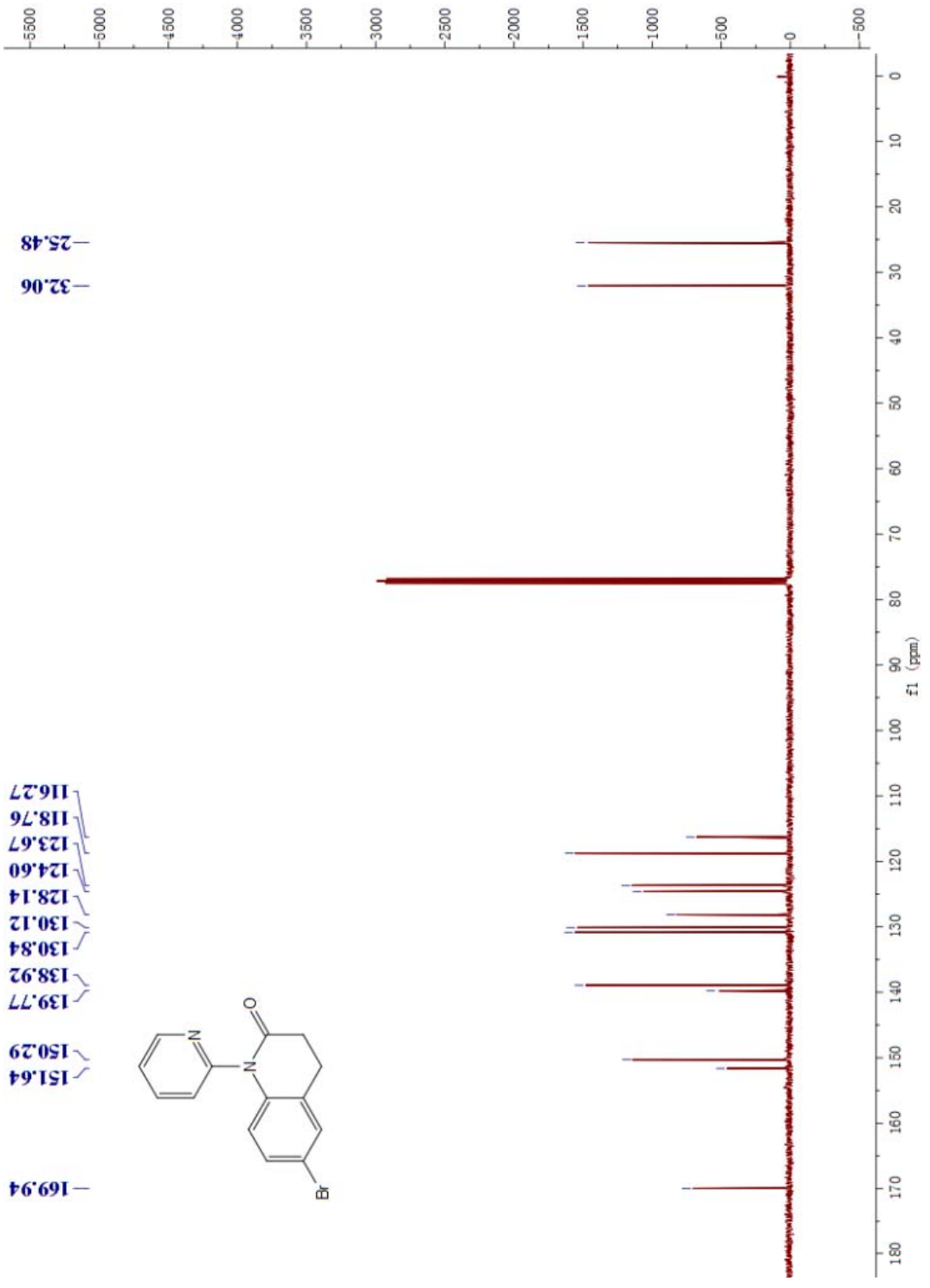
HR-MS Spectrum of 6-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3fa**



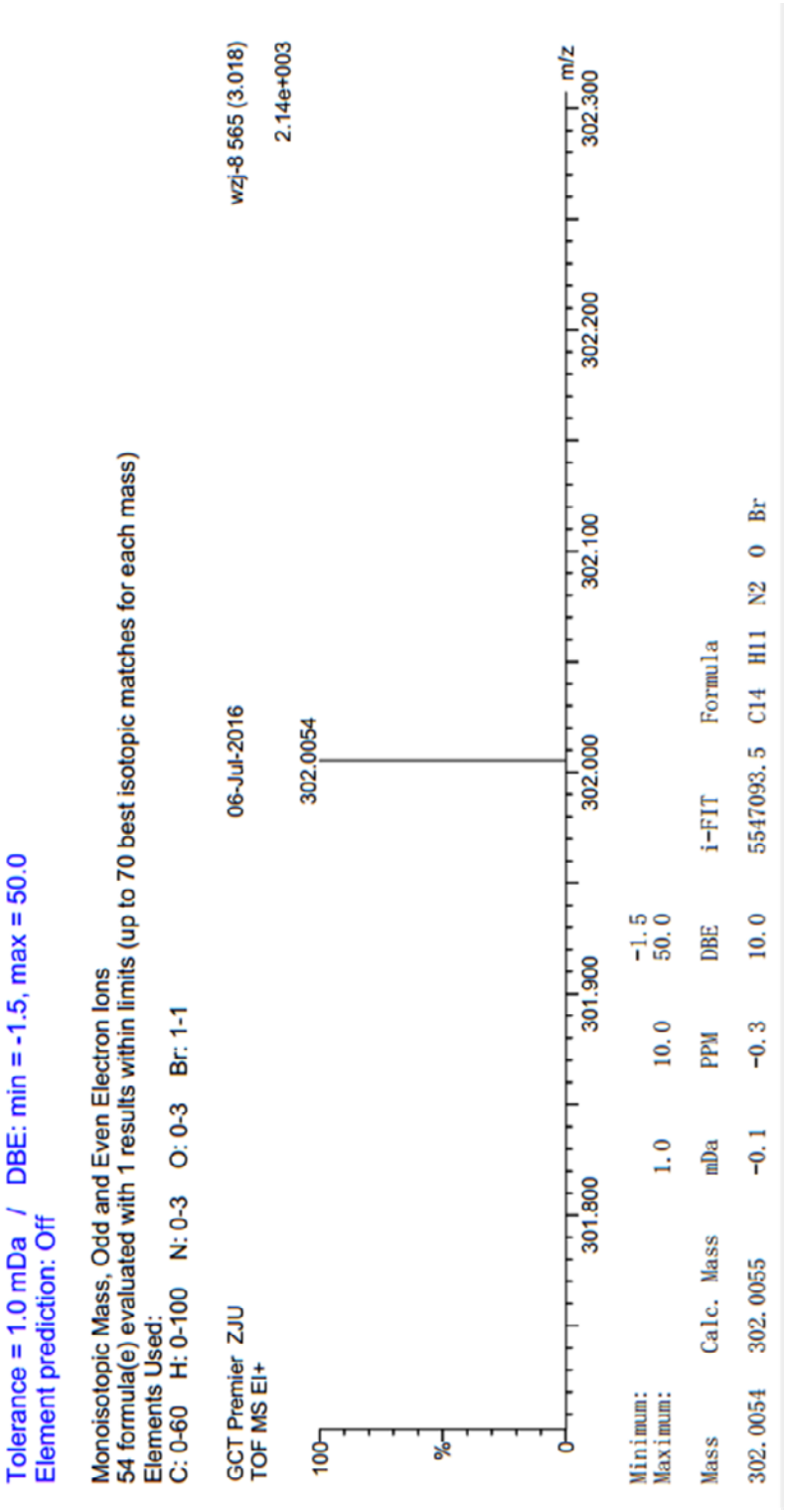
^{1}H NMR Spectrum of 6-bromo-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ga**



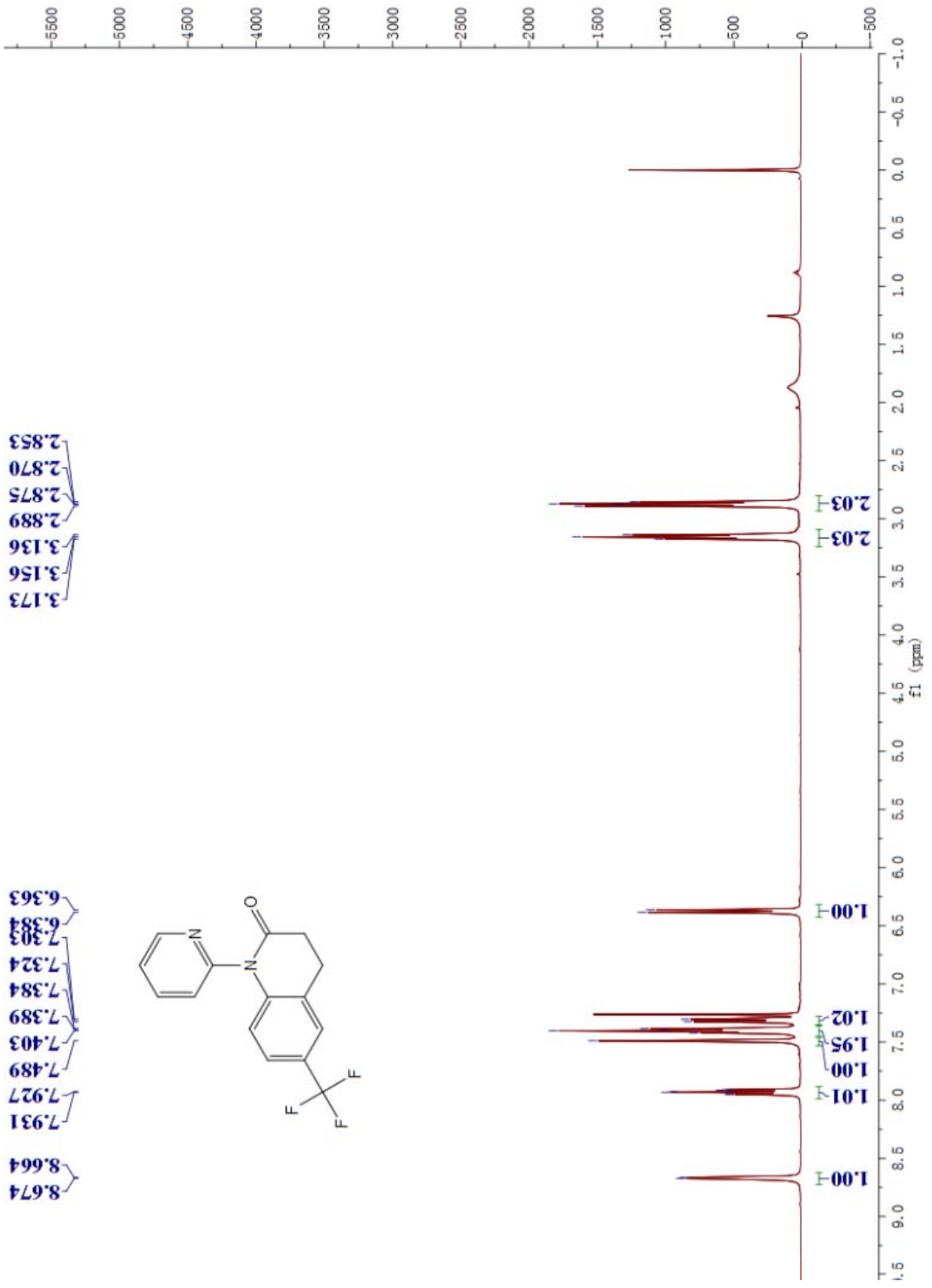
^{13}C NMR Spectrum of 6-bromo-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ga**



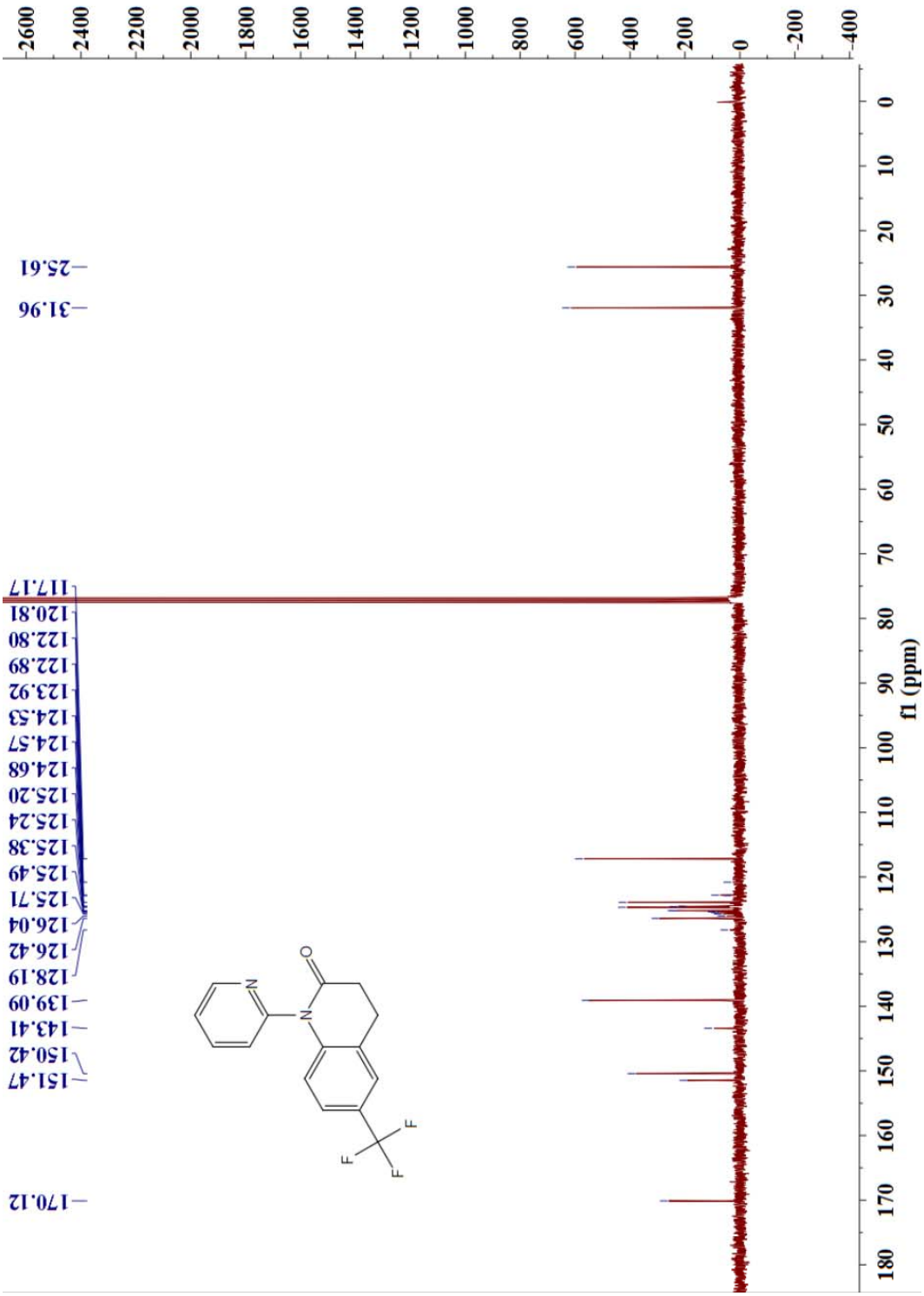
HR-MS Spectrum of 6-bromo-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ga**



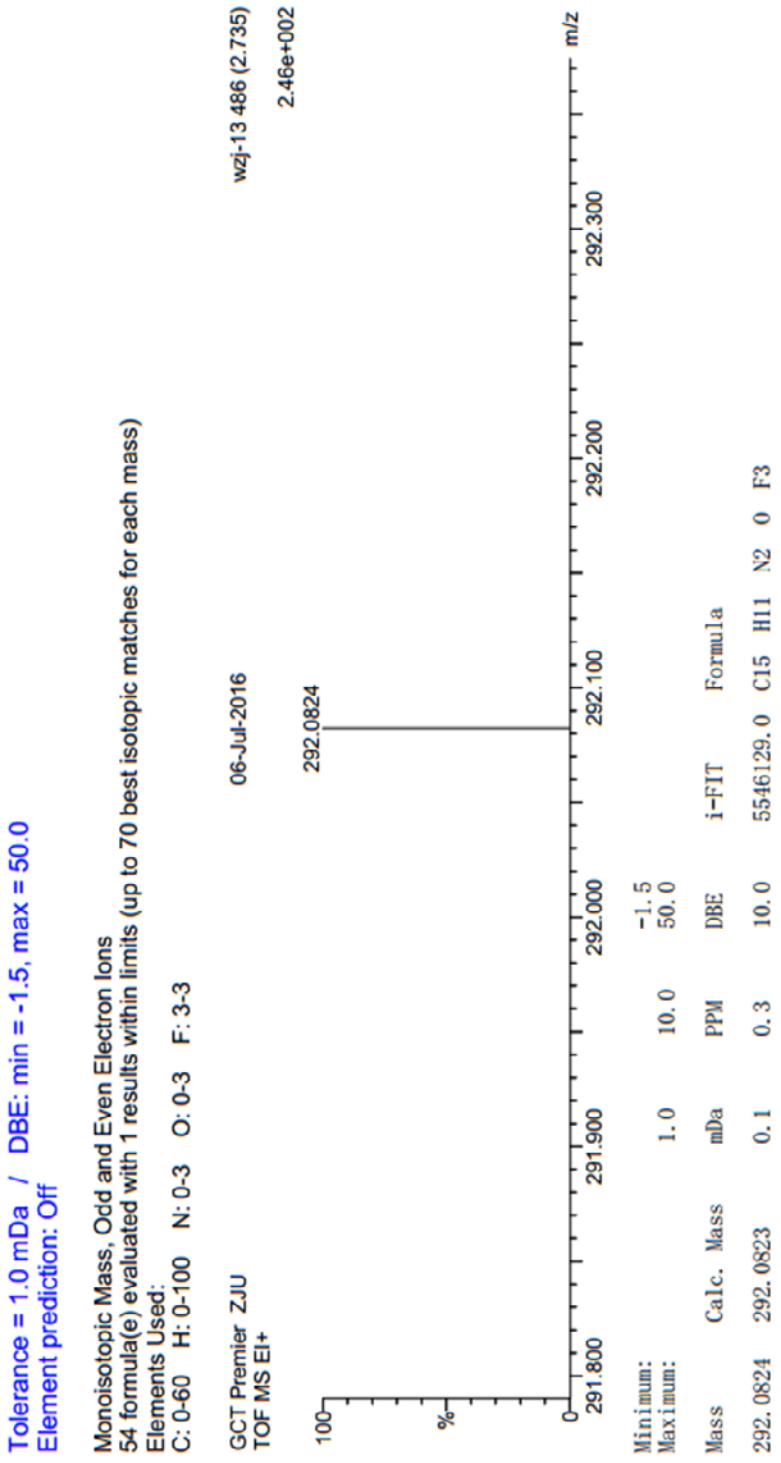
^{1}H NMR Spectrum of 1-(pyridin-2-yl)-6-(trifluoromethyl)-3,4-dihydro-quinolin-2(1H)-one **3ha**



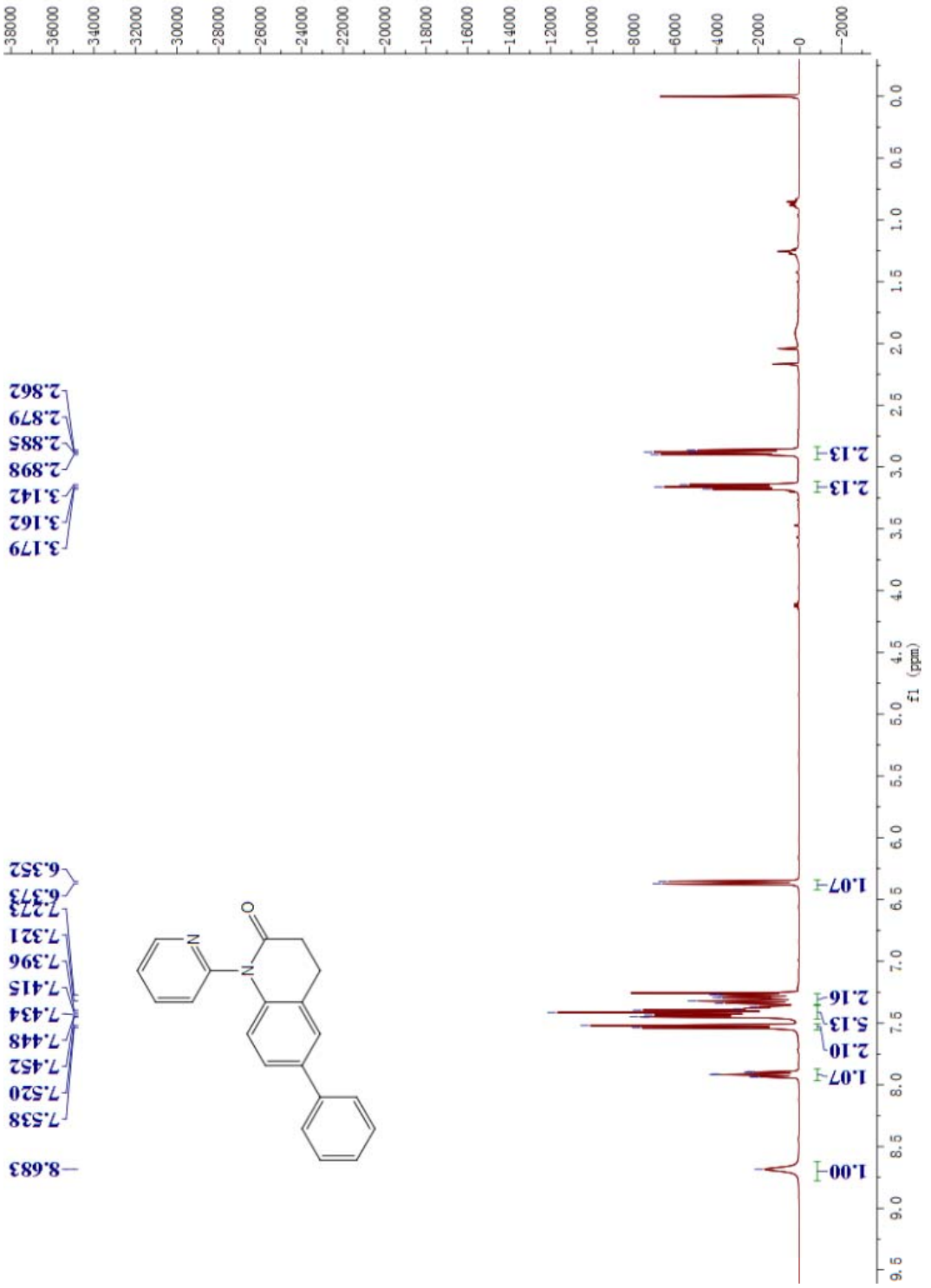
^{13}C NMR Spectrum of 1-(pyridin-2-yl)-6-(trifluoromethyl)-3,4-dihydro-quinolin-2(1H)-one **3ha**



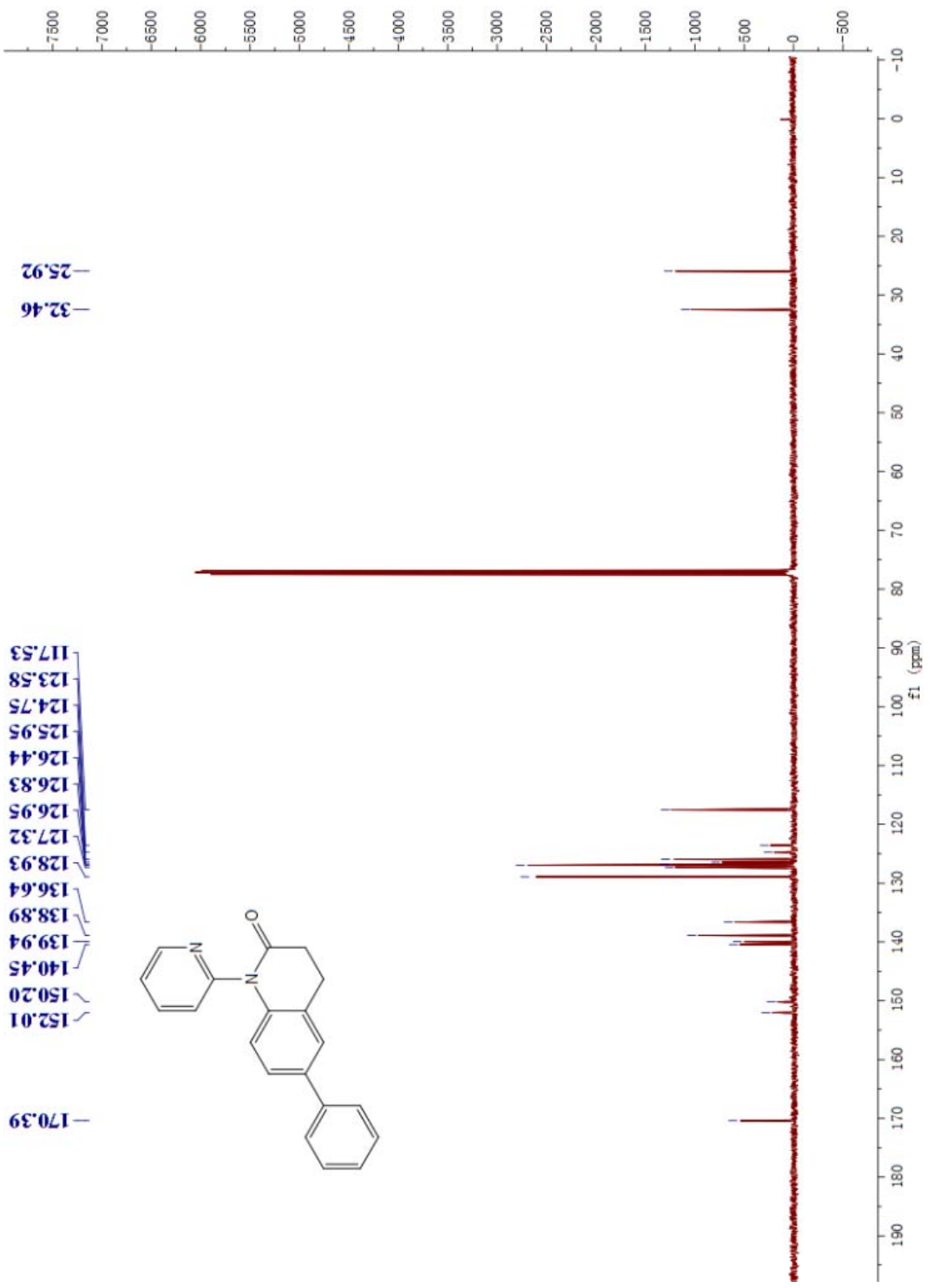
HR-MS Spectrum of 1-(pyridin-2-yl)-6-(trifluoromethyl)-3,4-dihydro-quinolin-2(1H)-one **3ha**



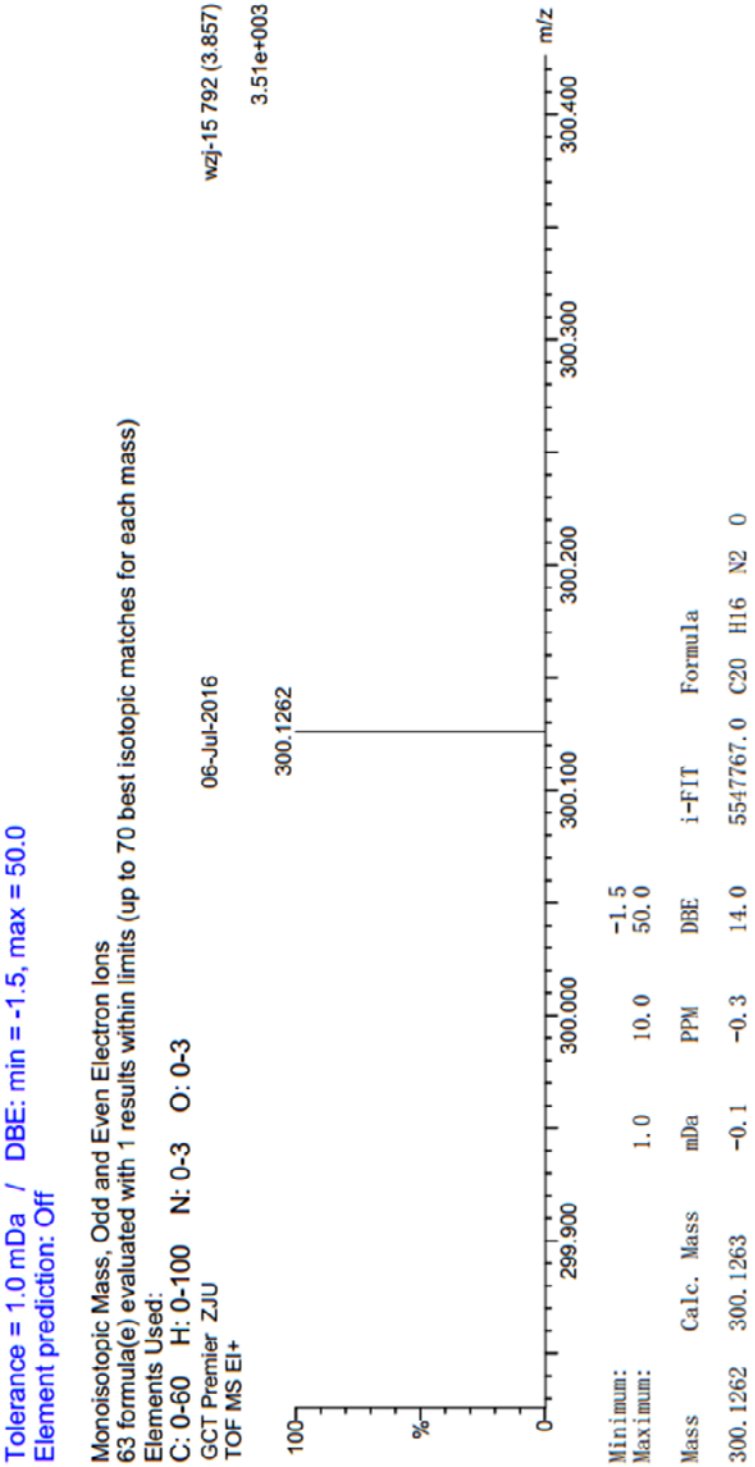
^{1}H NMR Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



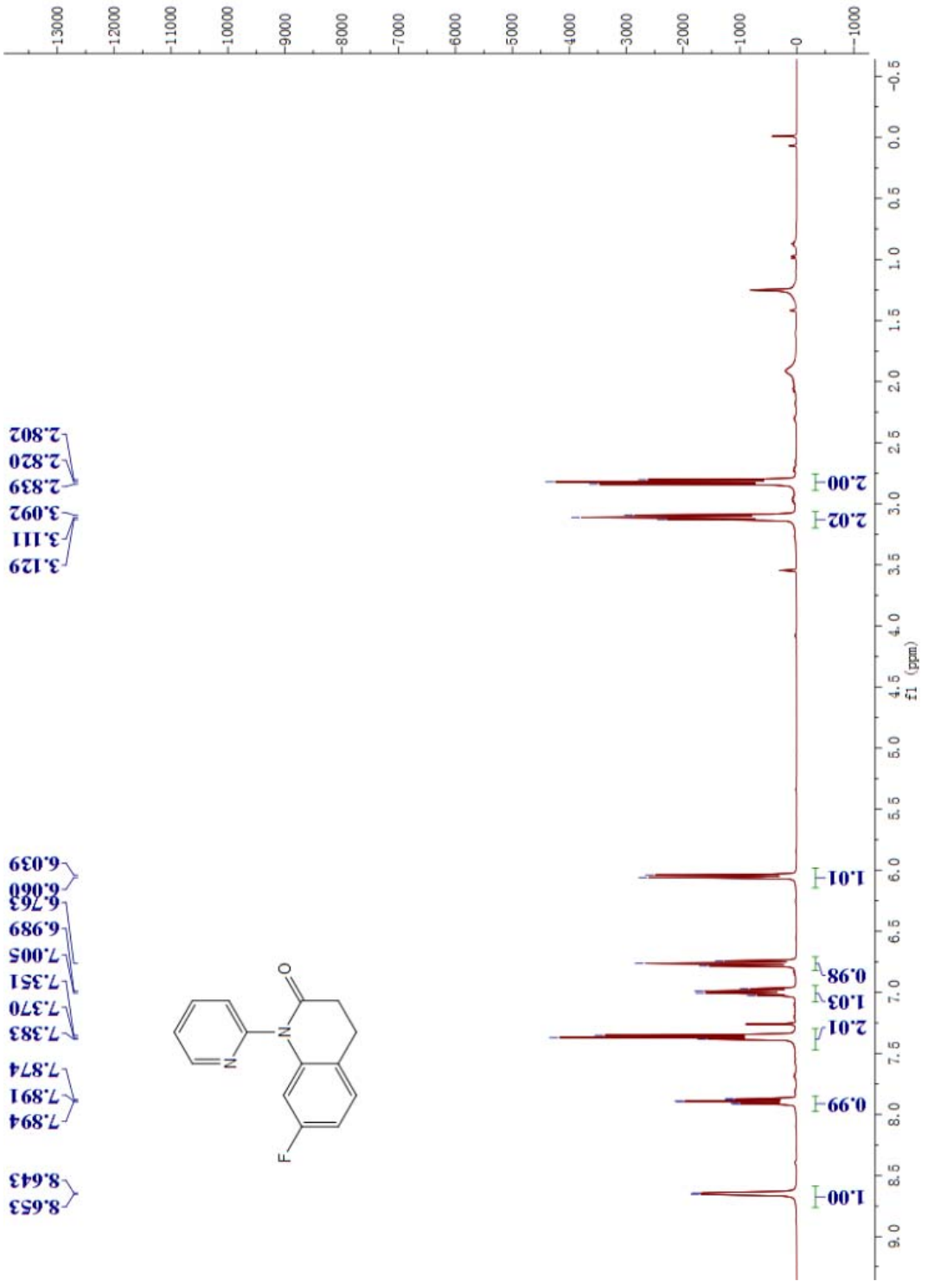
^{13}C NMR Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



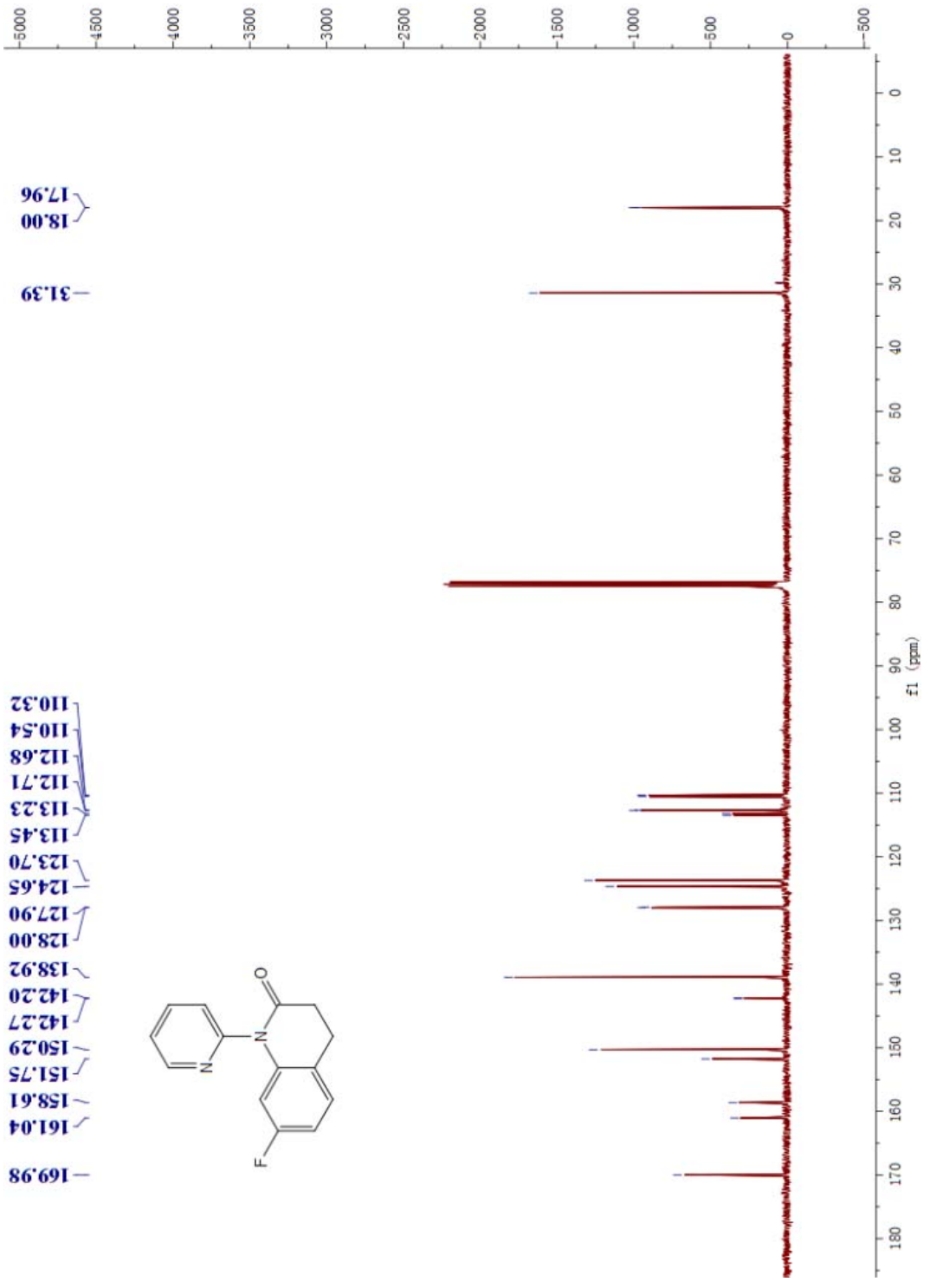
HR-MS Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



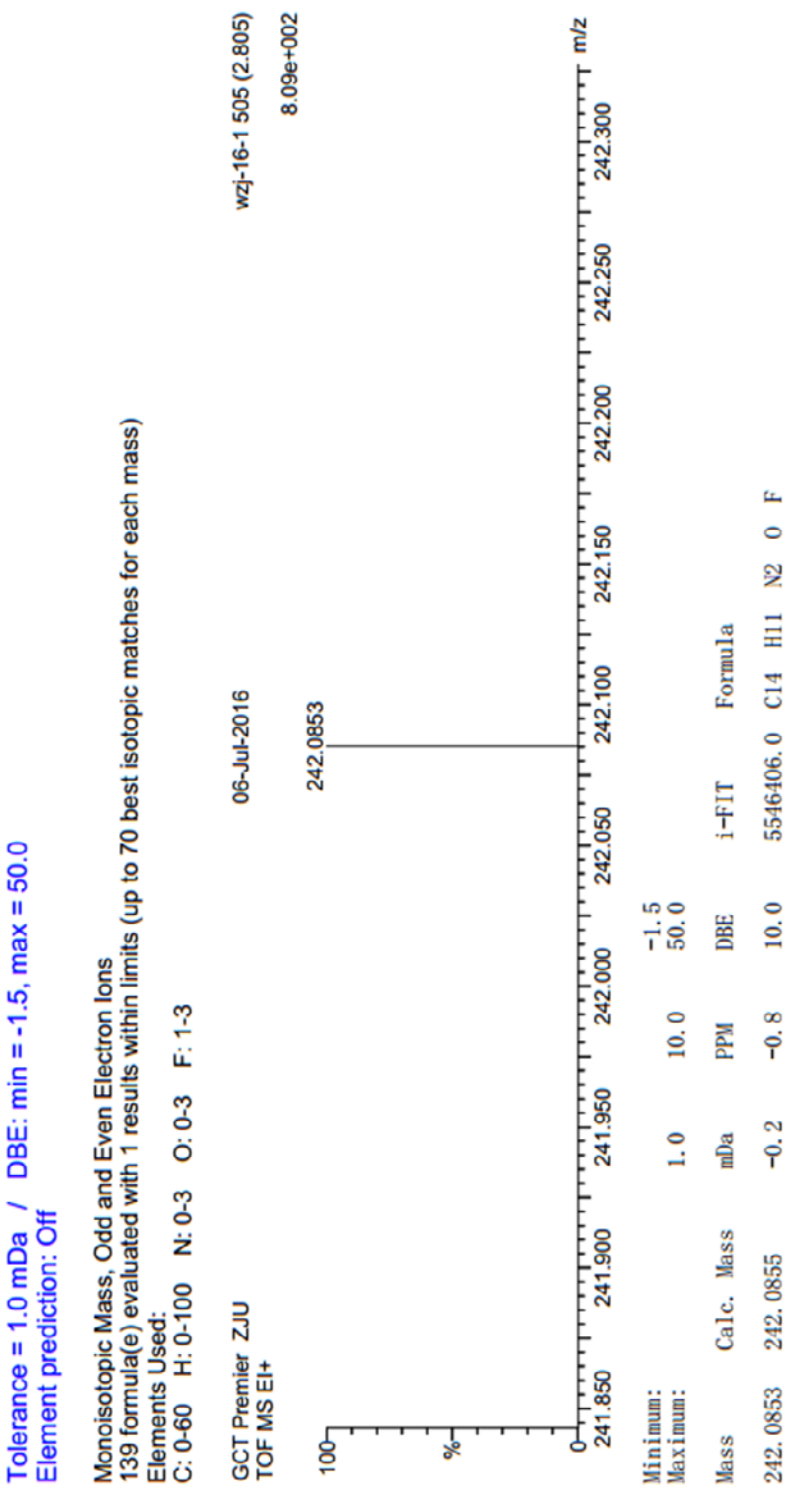
^{1}H NMR Spectrum of 7-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja**



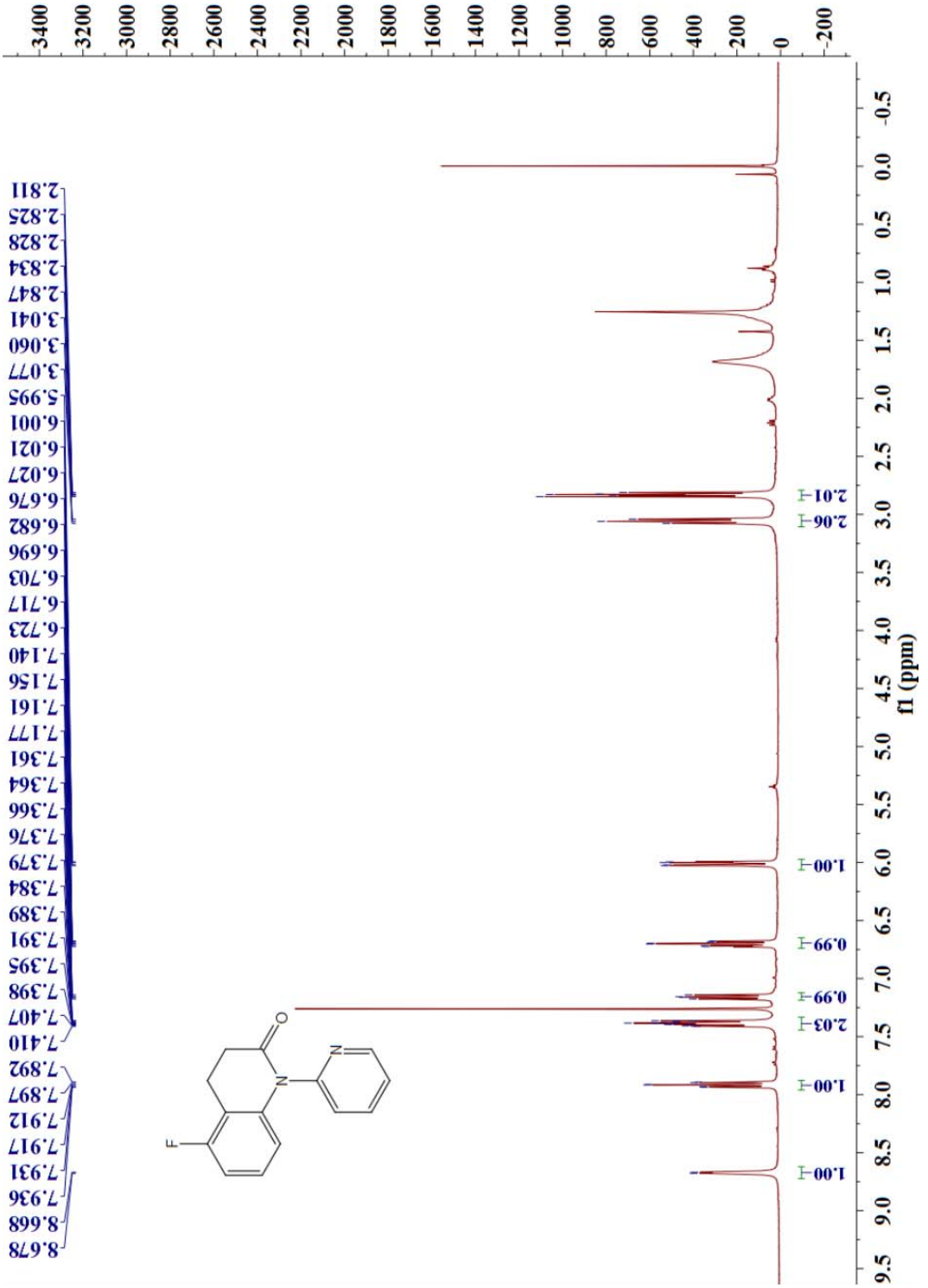
^{13}C NMR Spectrum of 7-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja**



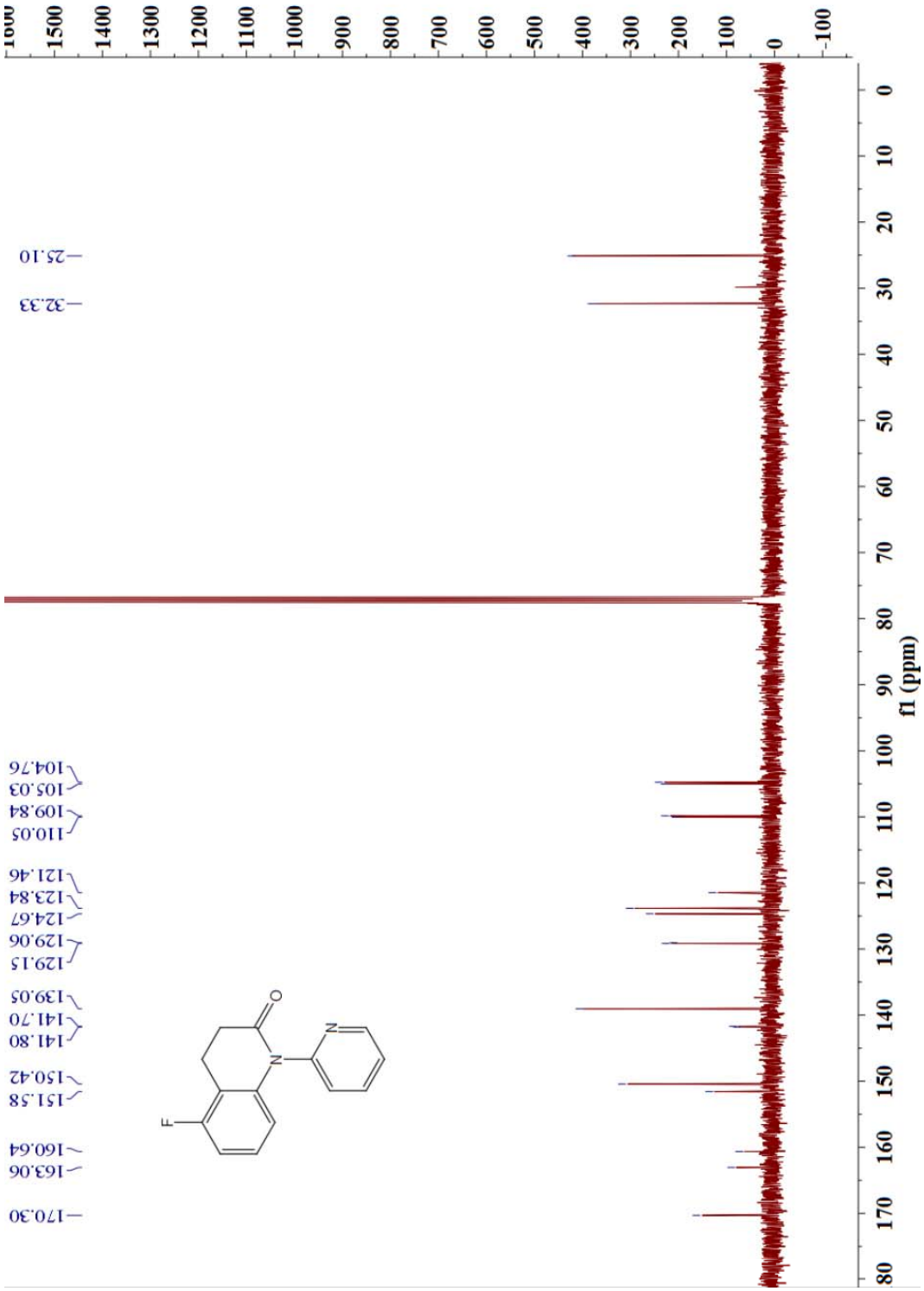
HR-MS Spectrum of 7-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja**



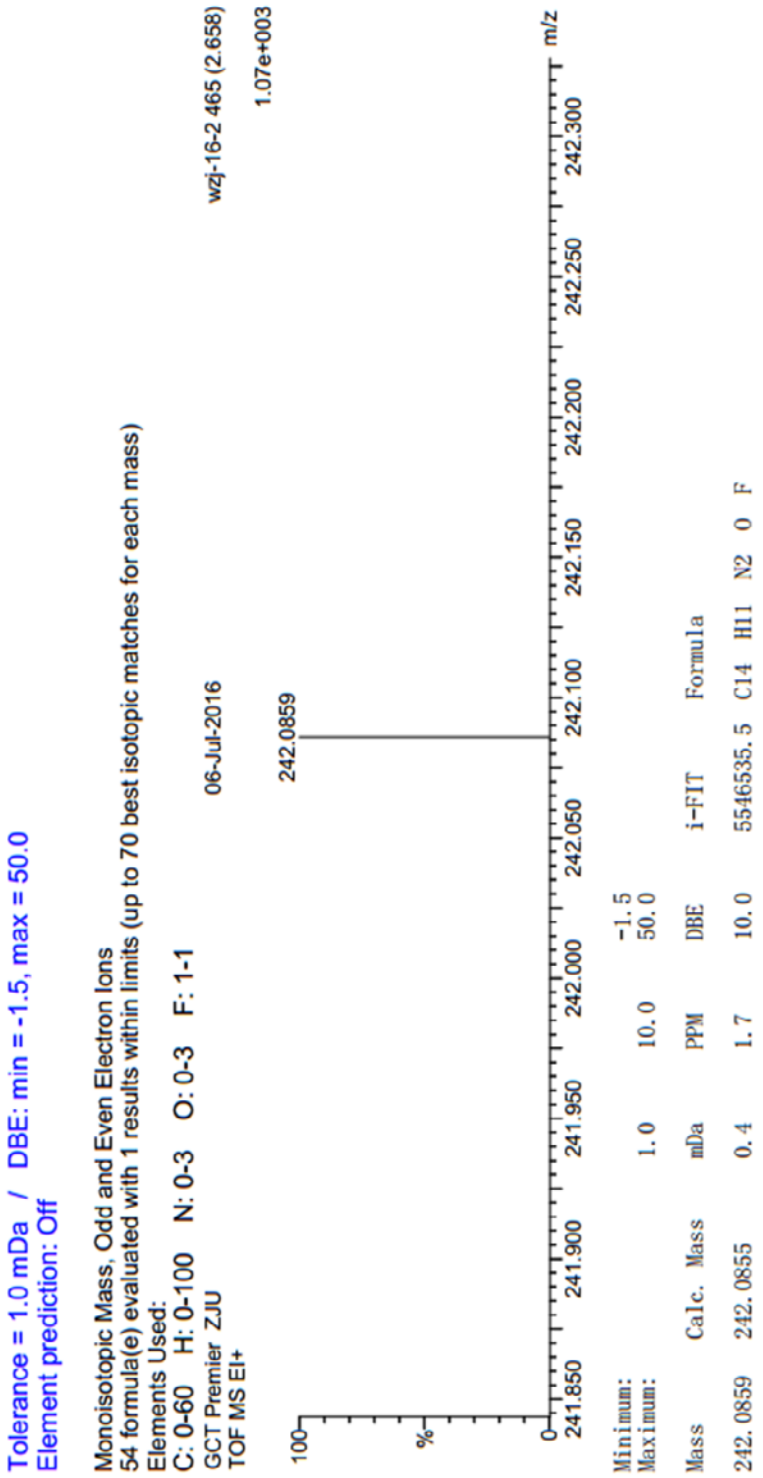
^{1}H NMR Spectrum of 5-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja'**



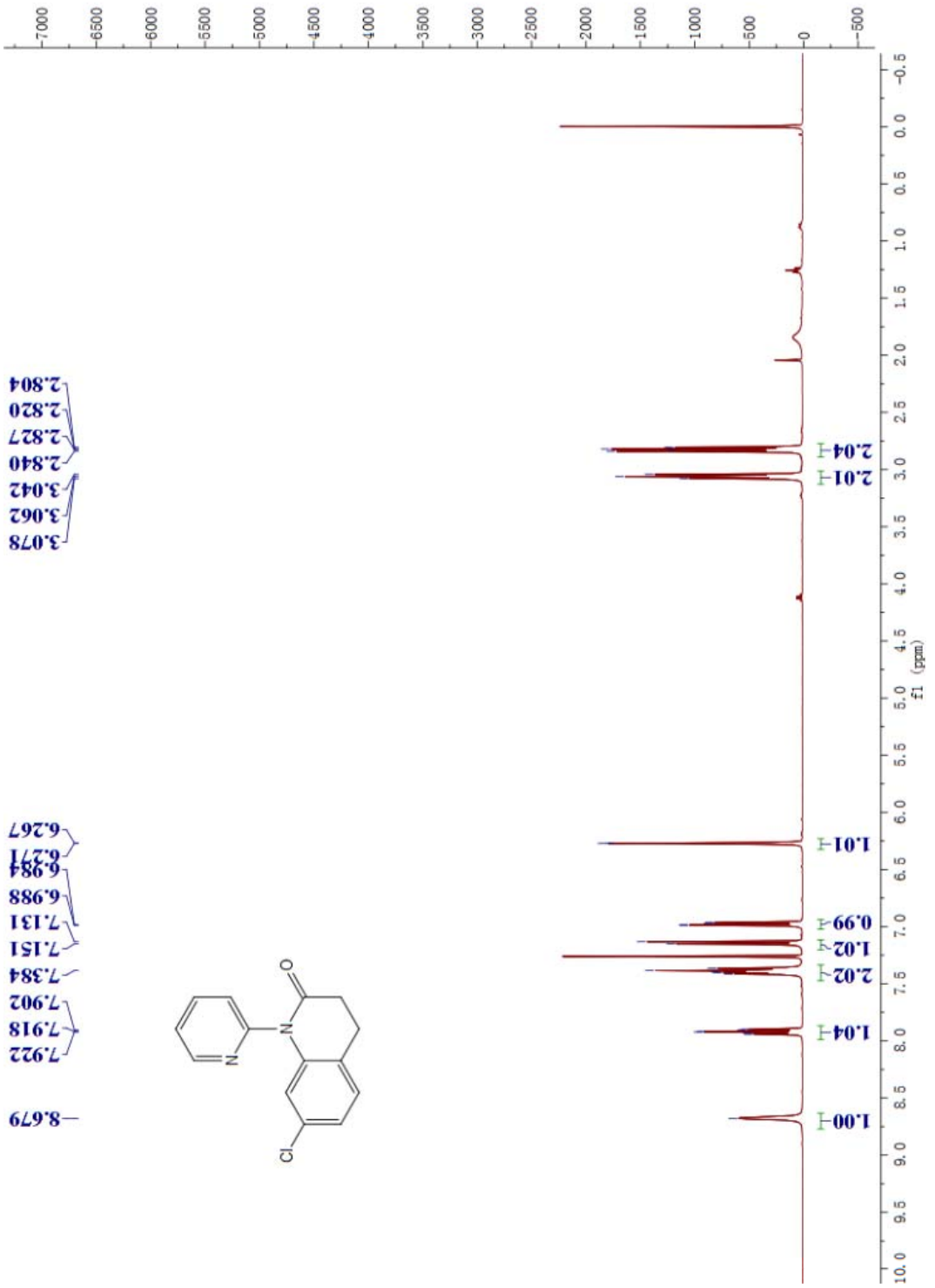
^{13}C NMR Spectrum of 5-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja'**



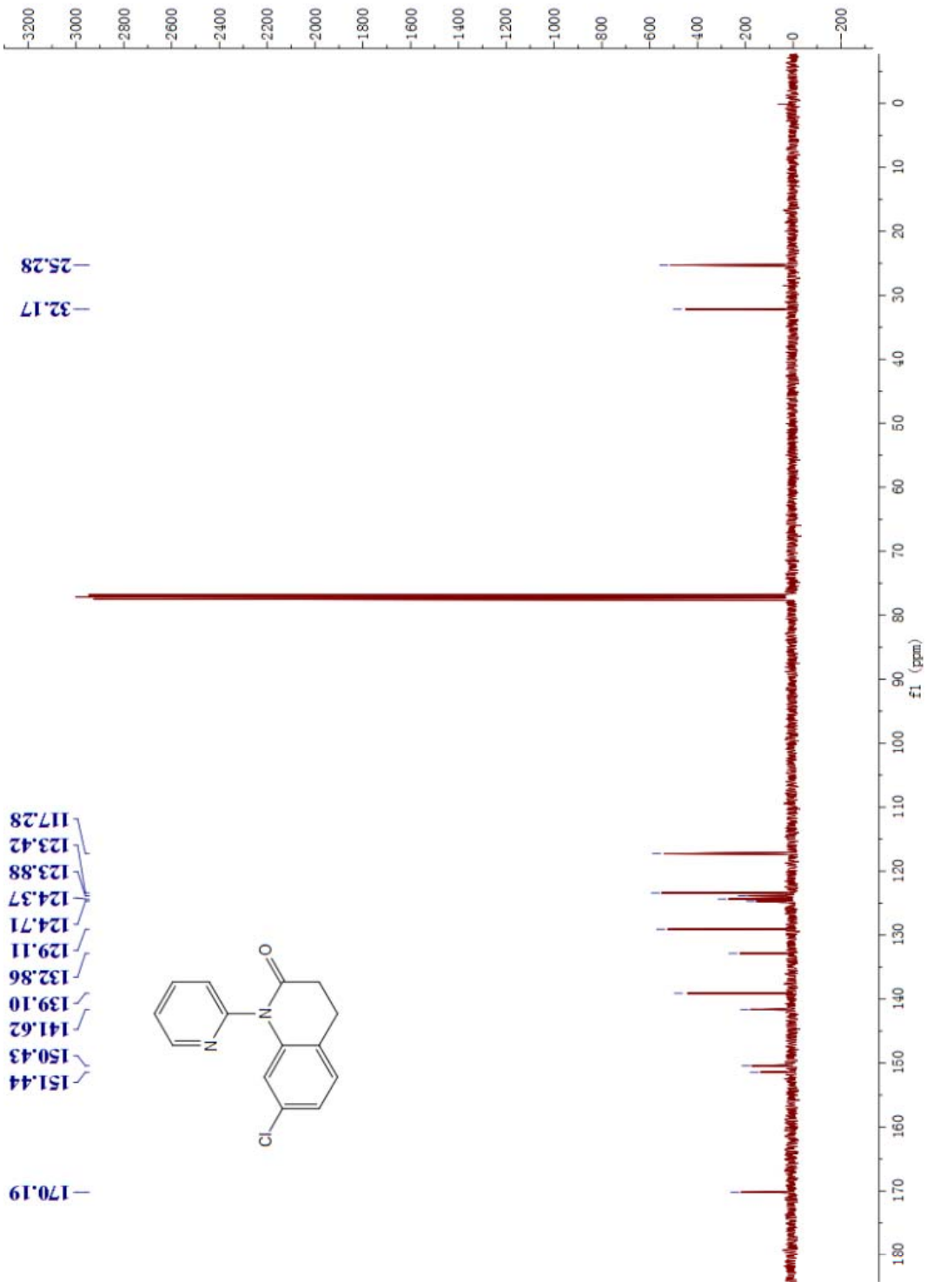
HR-MS Spectrum of 5-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja'**



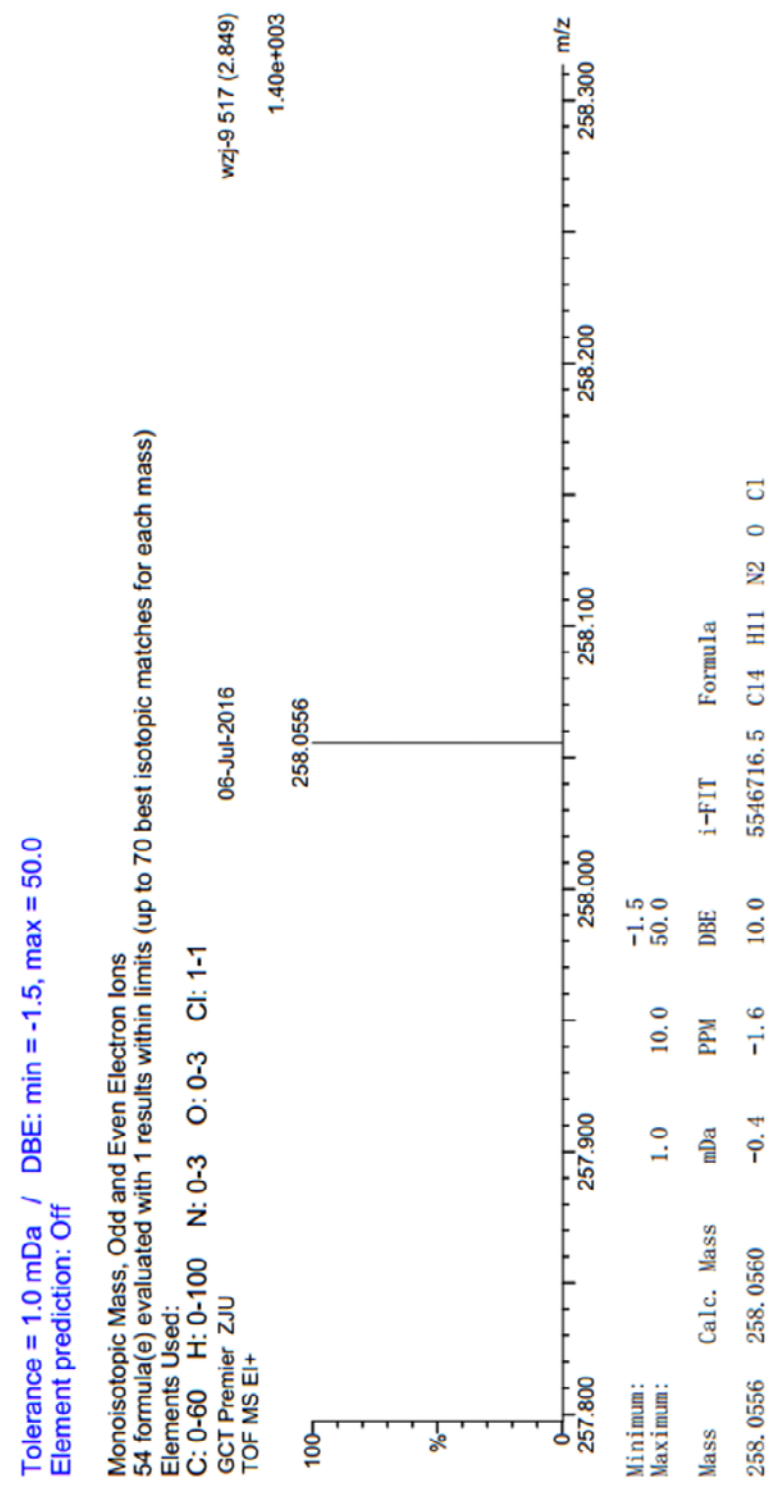
^{1}H NMR Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



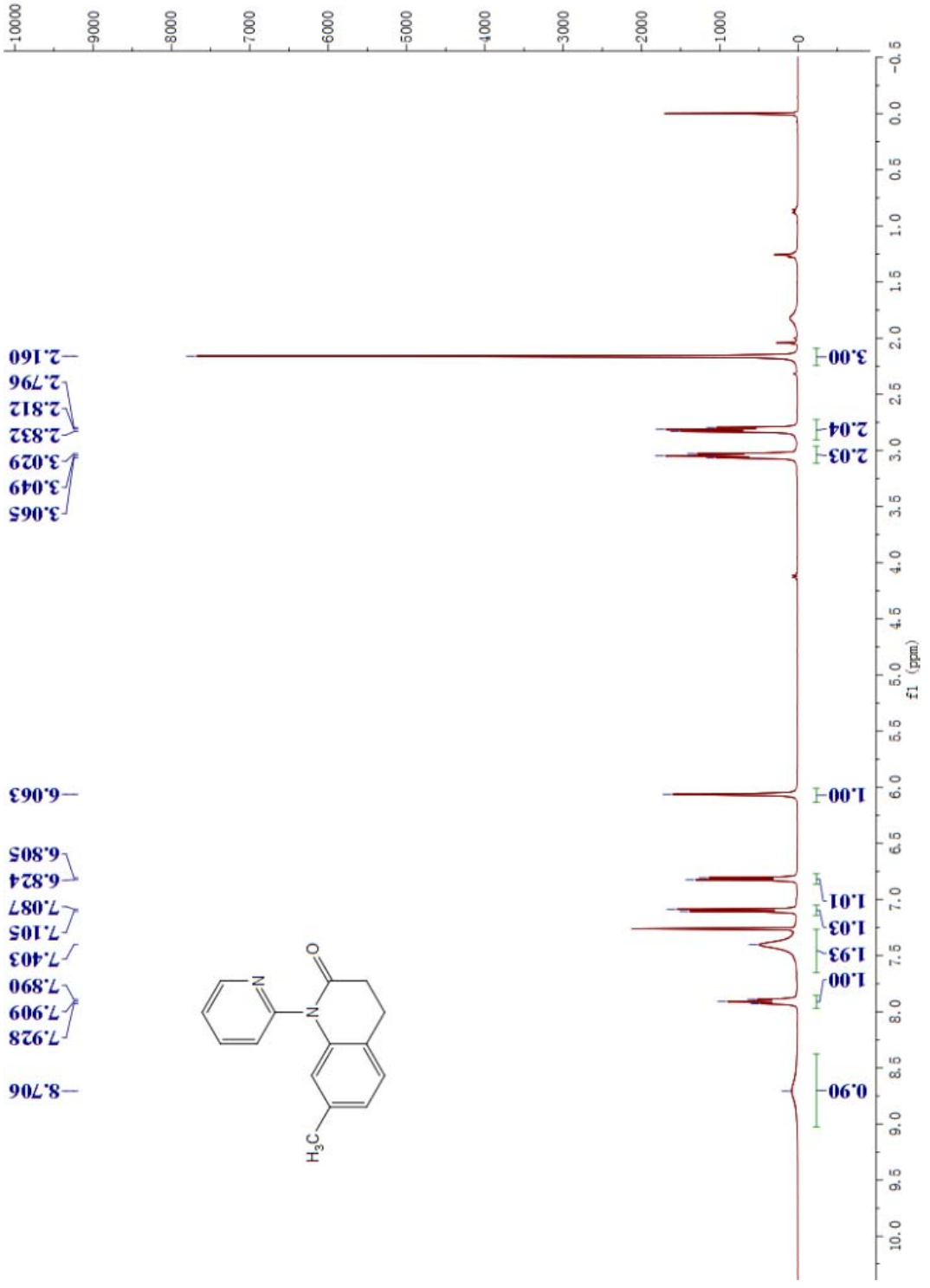
^{13}C NMR Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



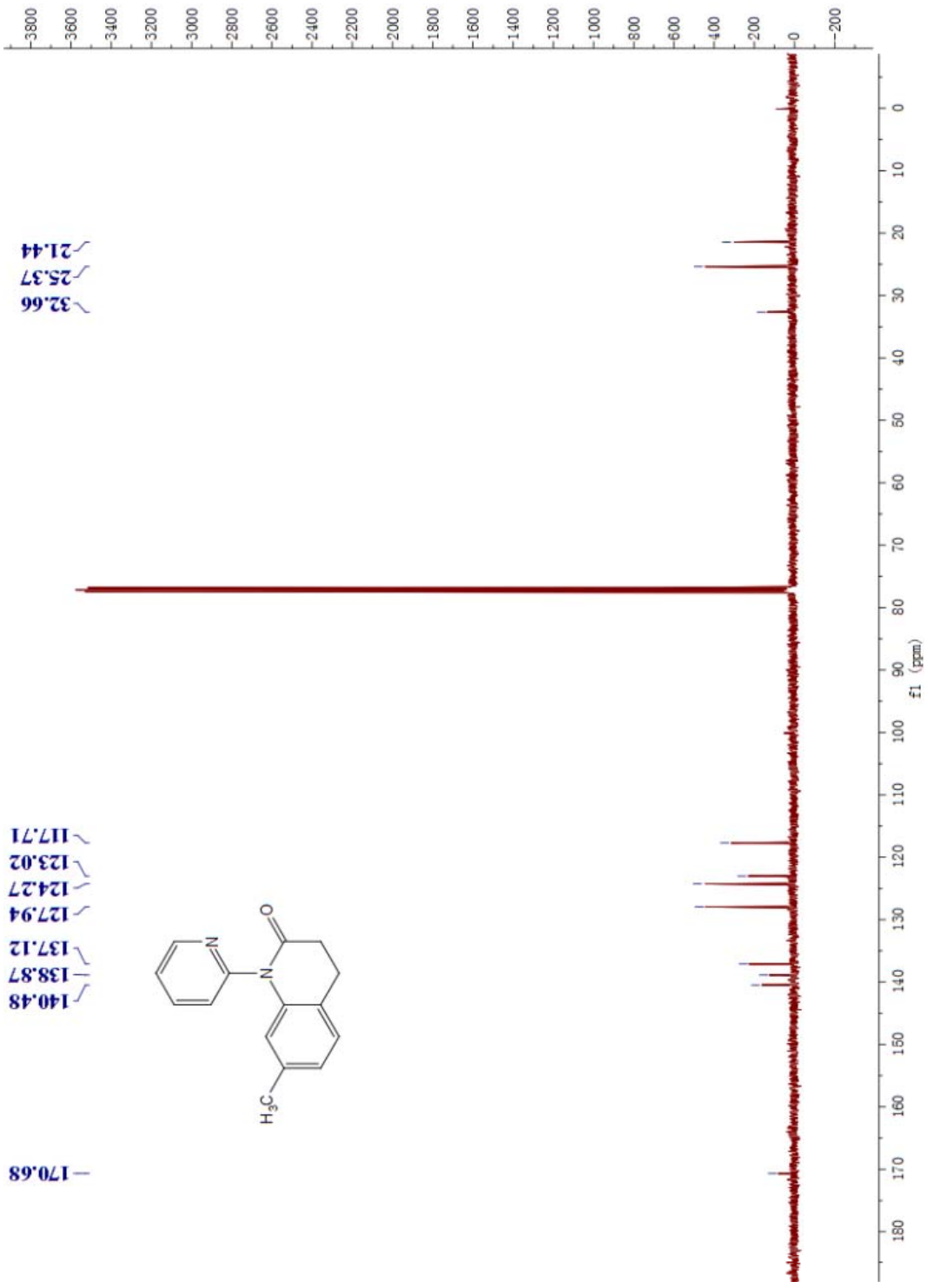
HR-MS Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



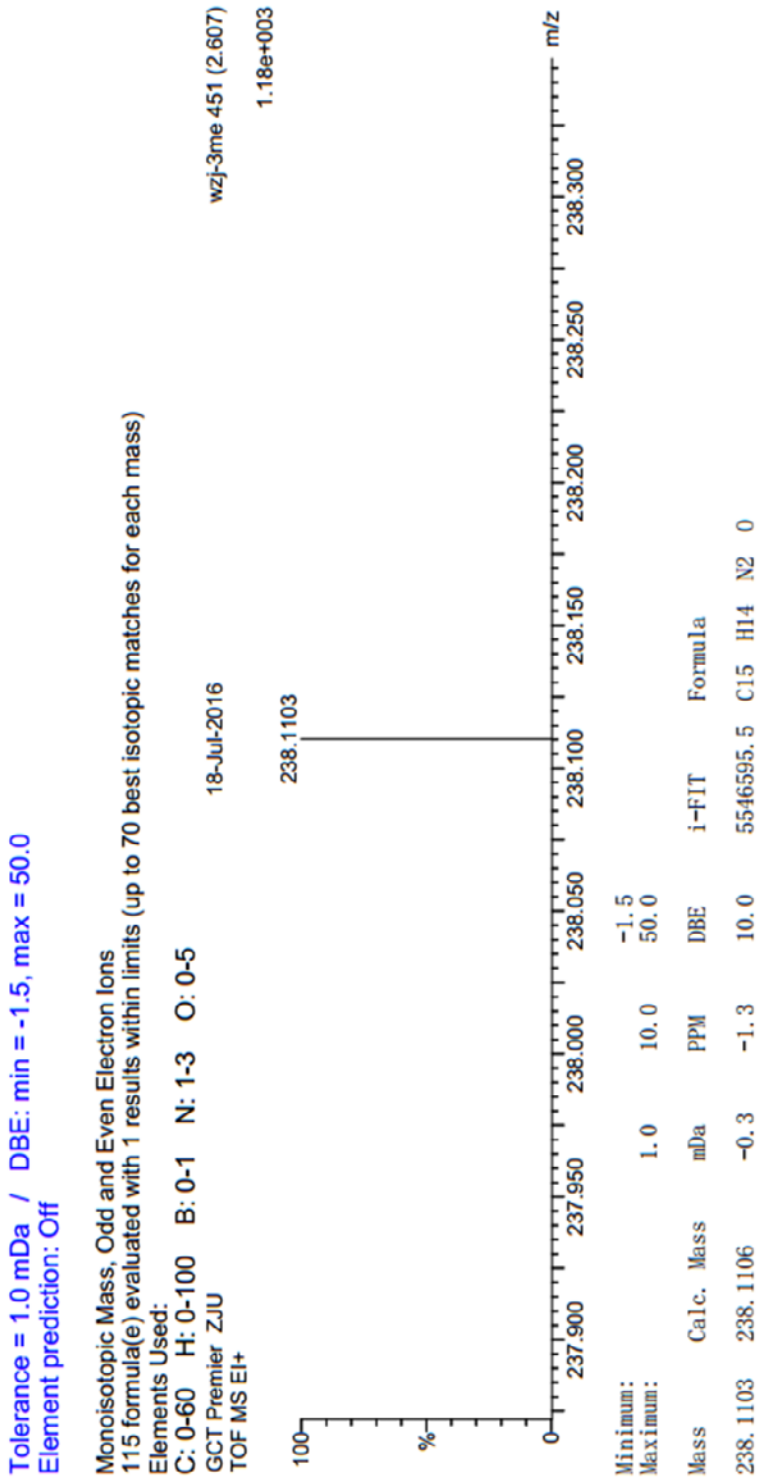
[1]H NMR Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



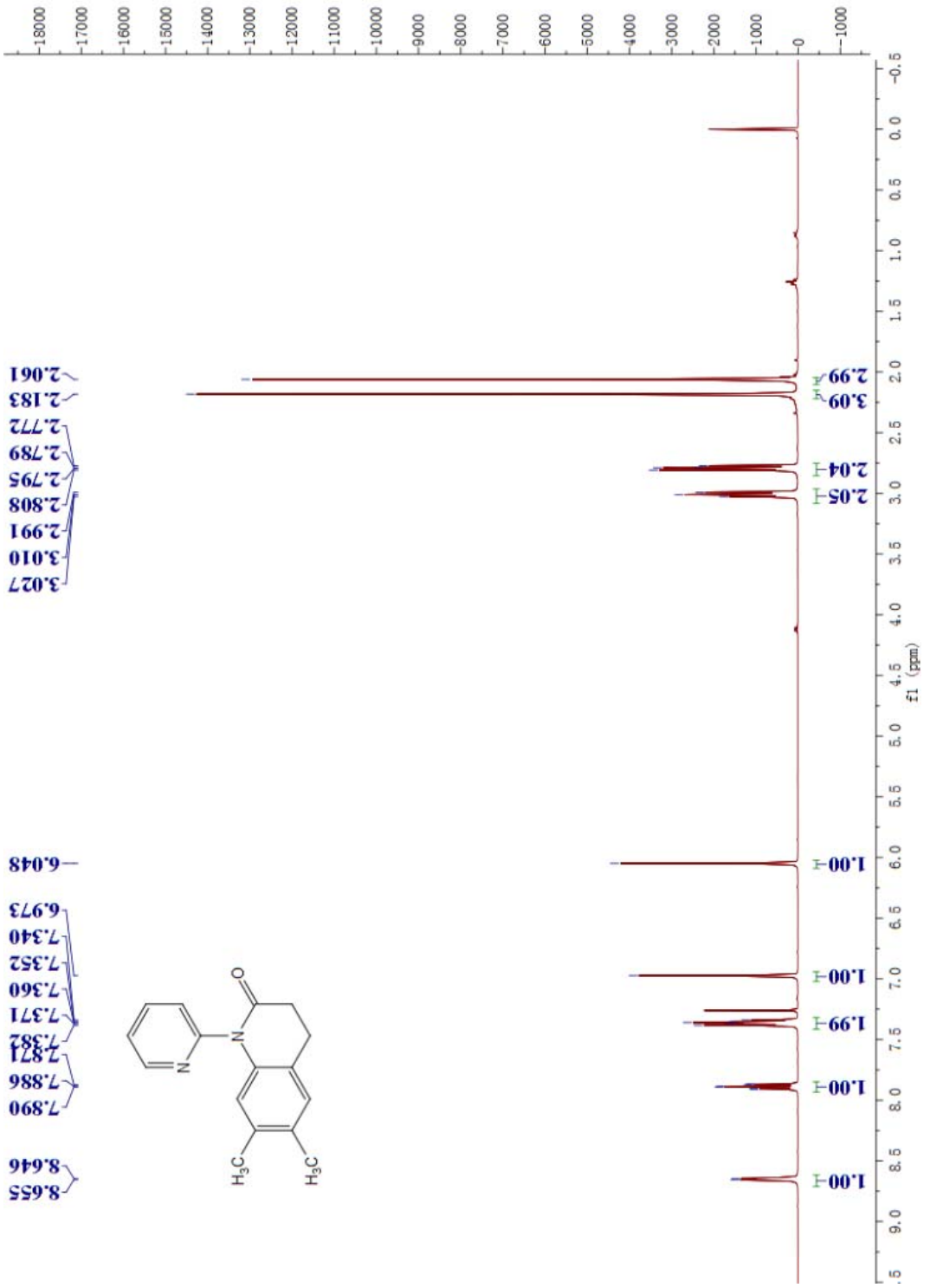
^{13}C NMR Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



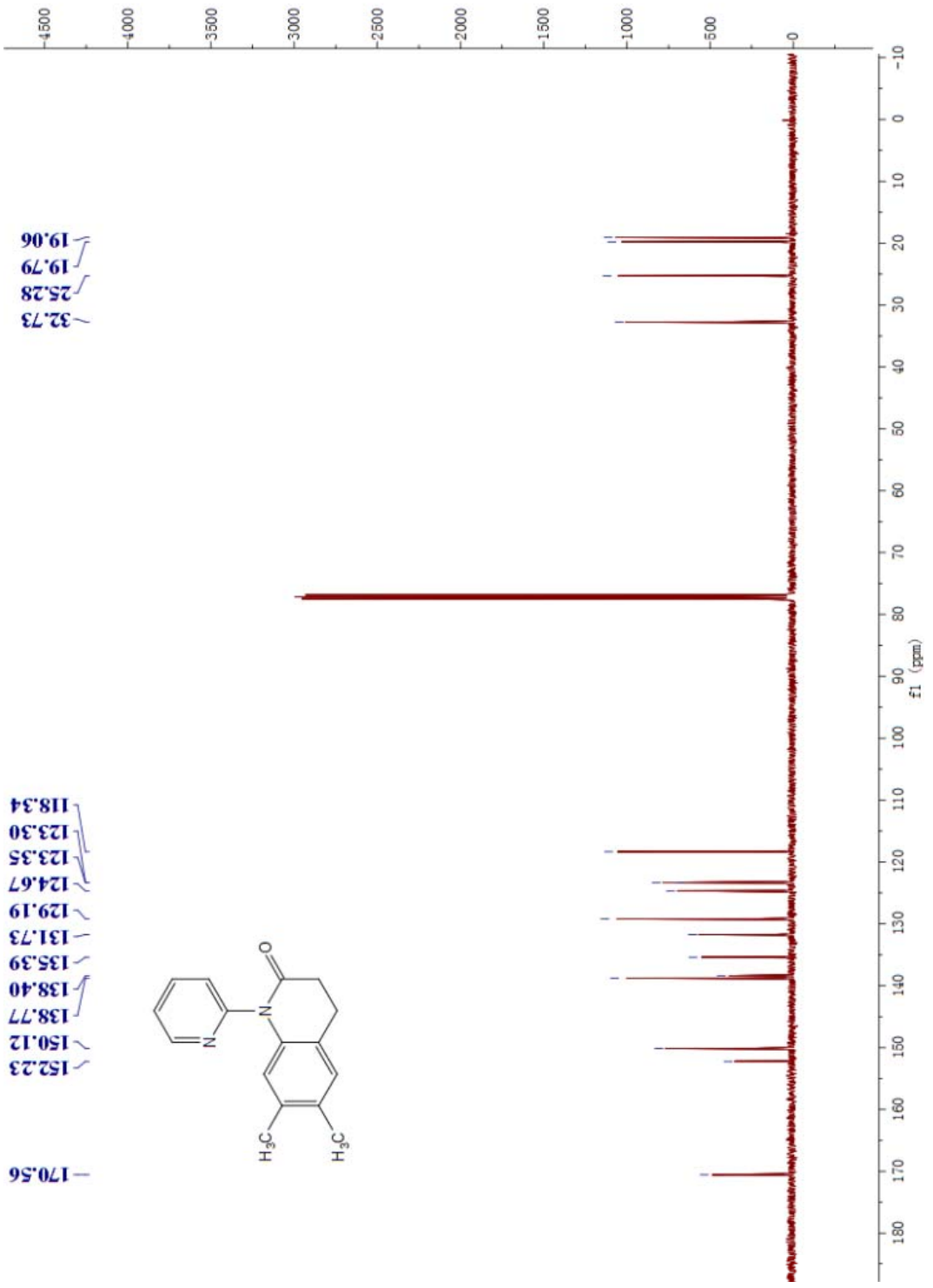
HR-MS Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



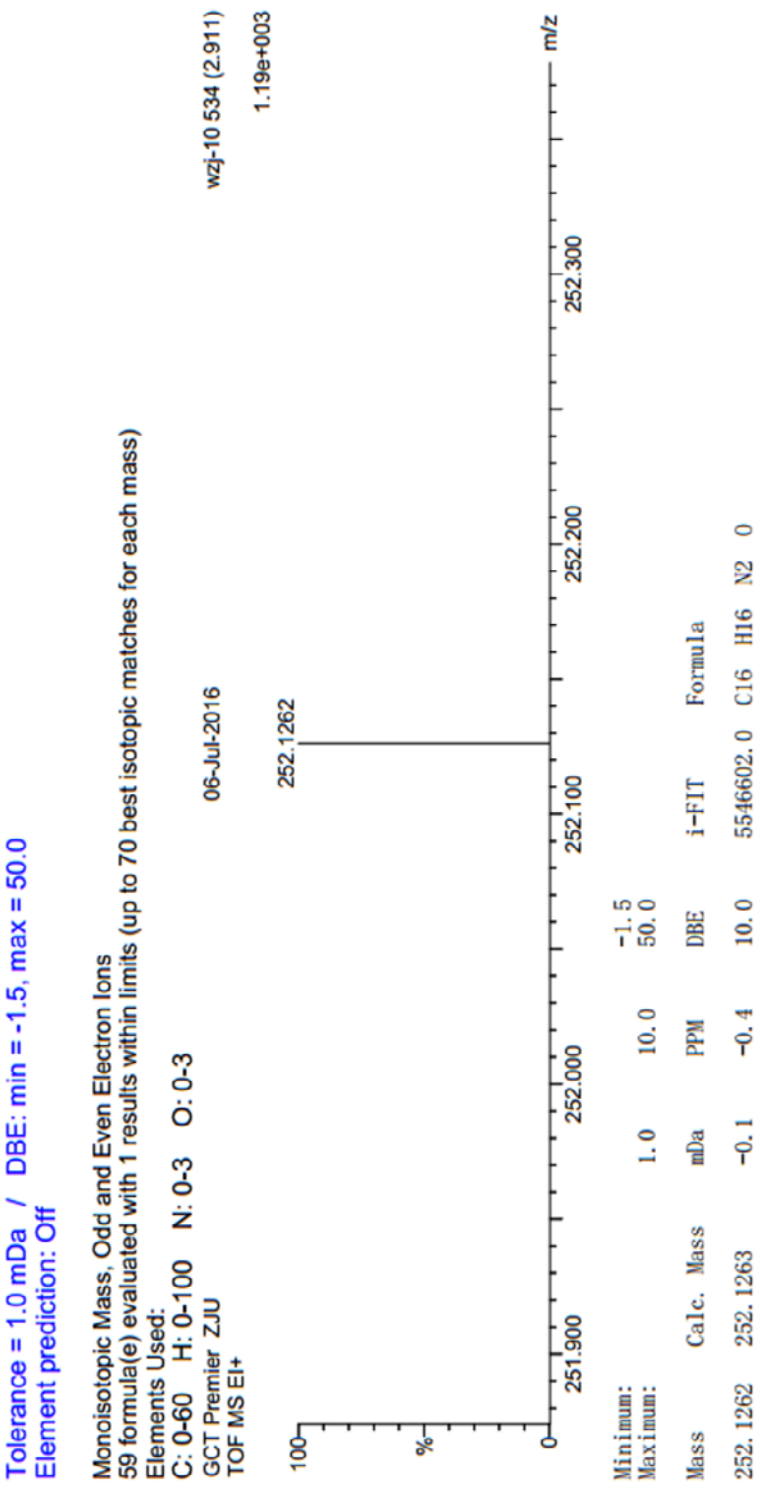
^{1}H NMR Spectrum of 6,7-dimethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ma**



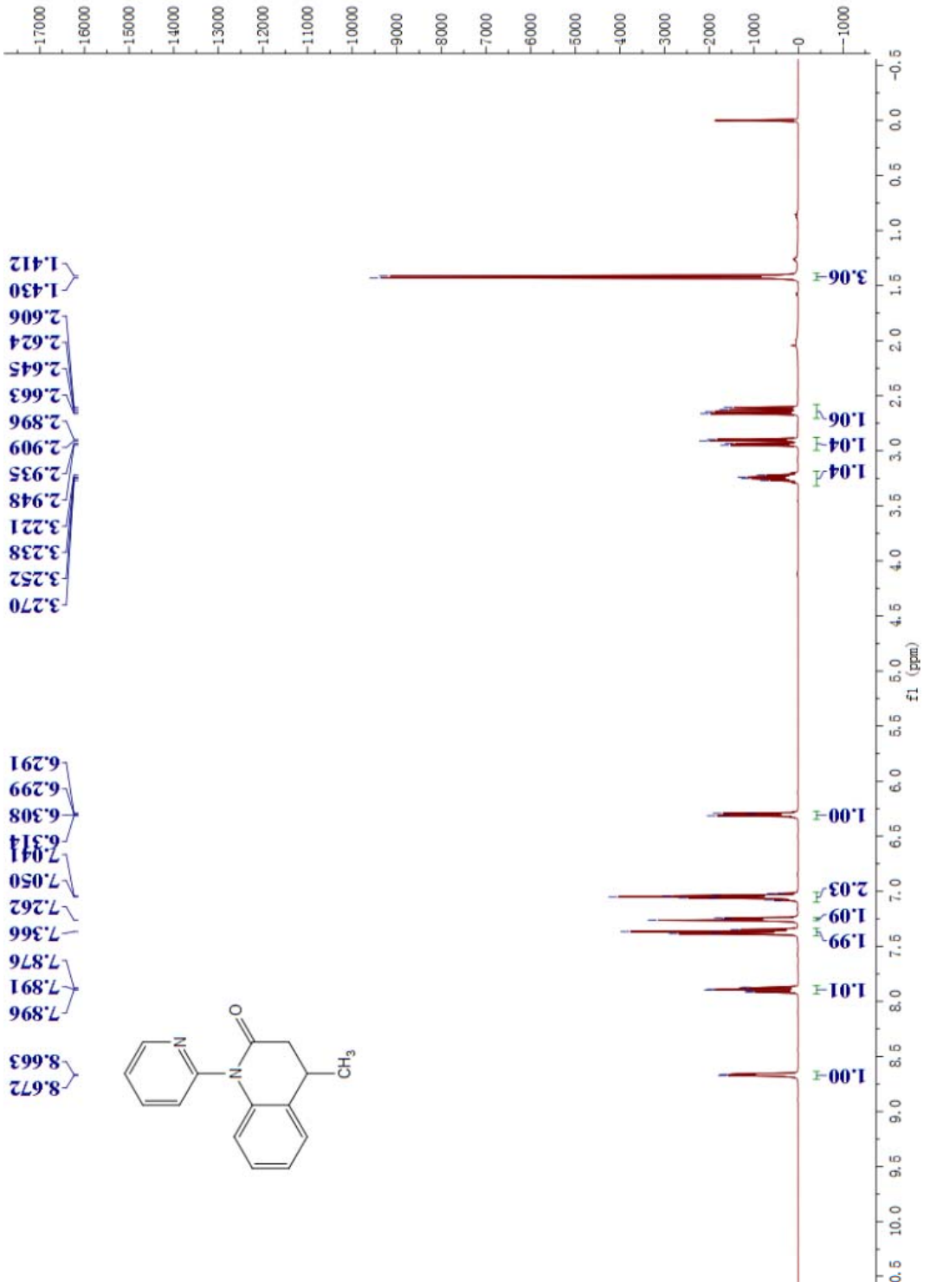
^{13}C NMR Spectrum of 6,7-dimethyl-1-(pyridin-2-yl)-3,4-dihydro-quinolin-2(1H)-one **3ma**



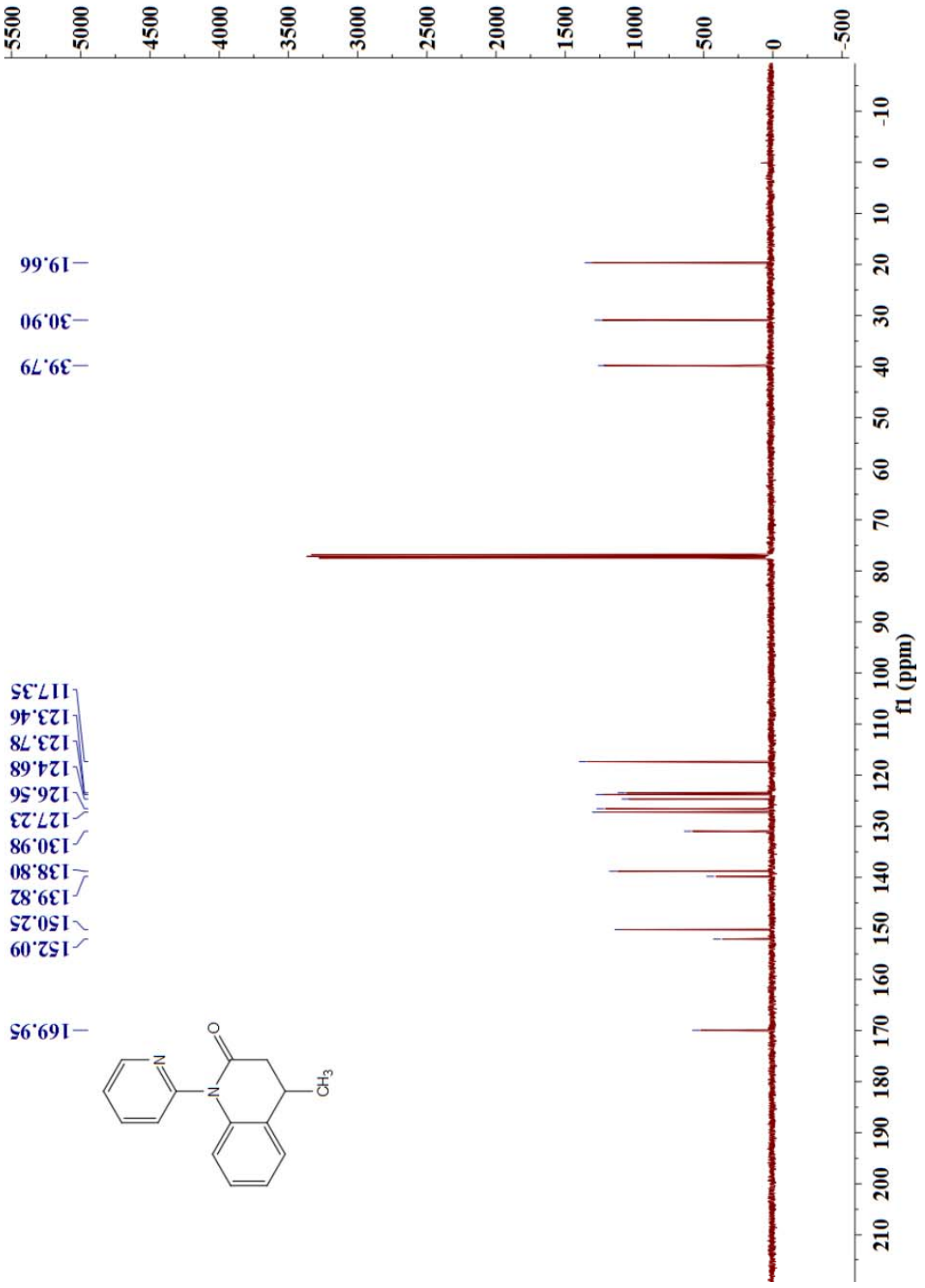
HR-MS Spectrum of 6,7-dimethyl-1-(pyridin-2-yl)-3,4-dihydr-oquinolin-2(1H)-one **3ma**



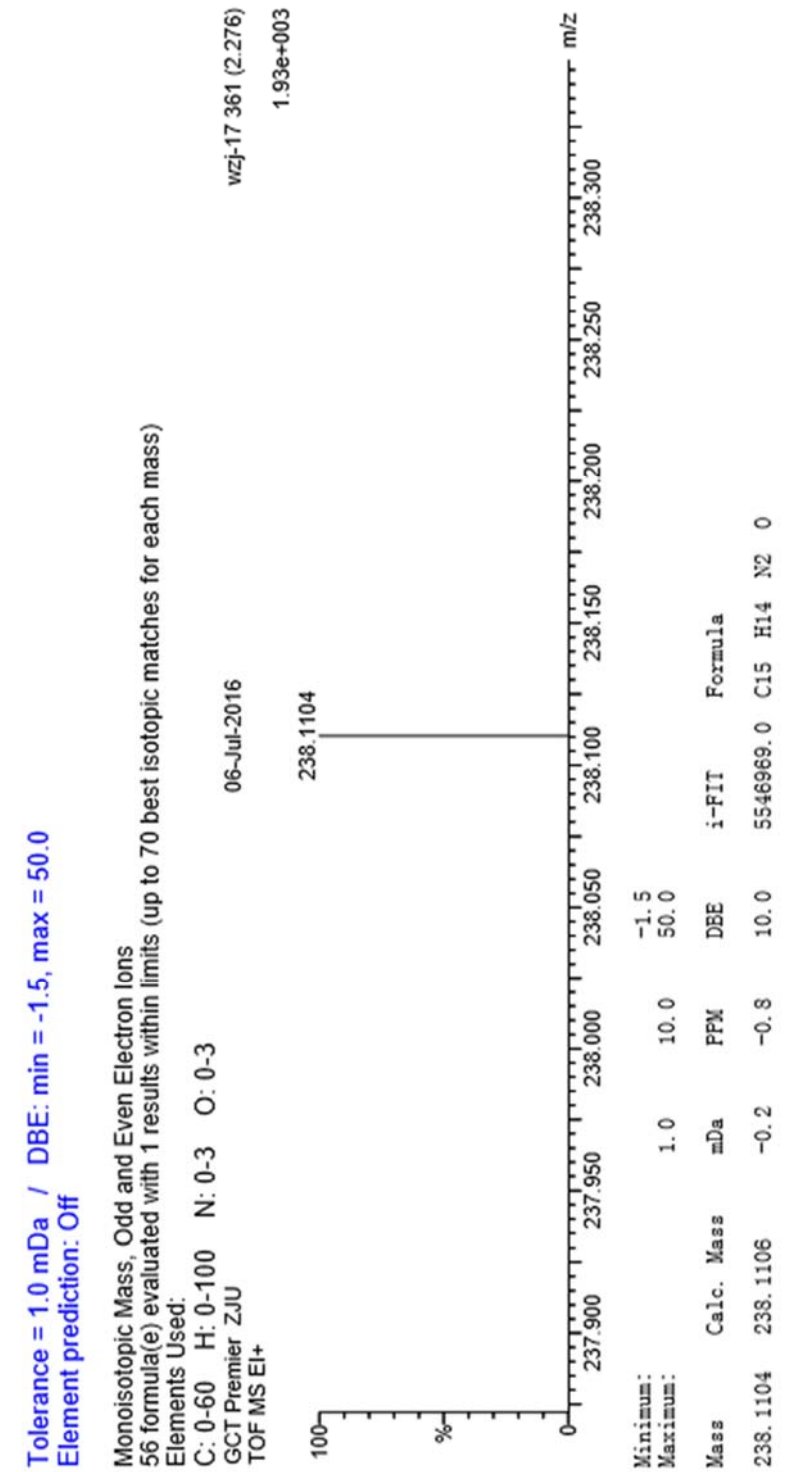
^{1}H NMR Spectrum of 4-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ab**



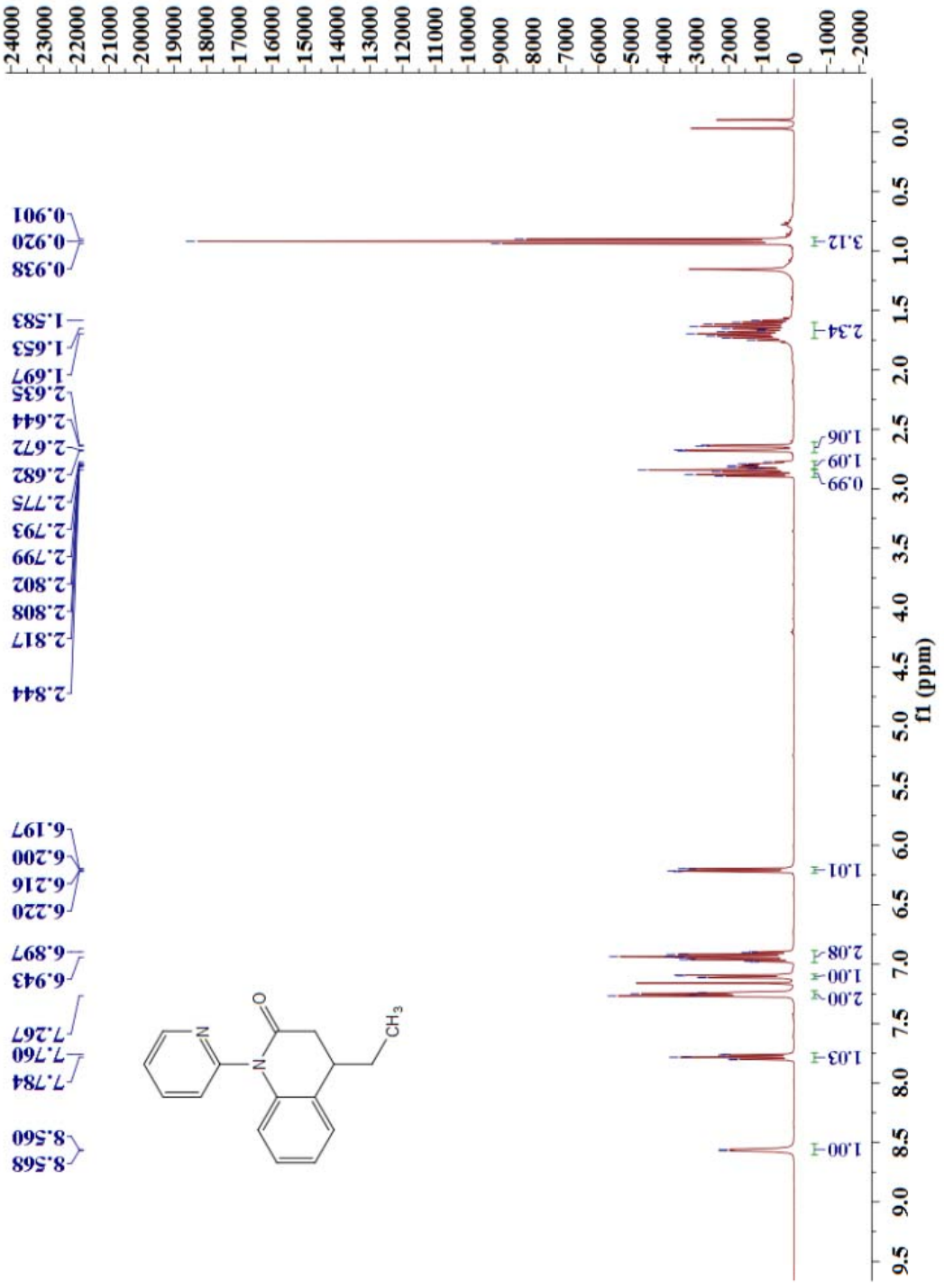
^{13}C NMR Spectrum of 4-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ab**



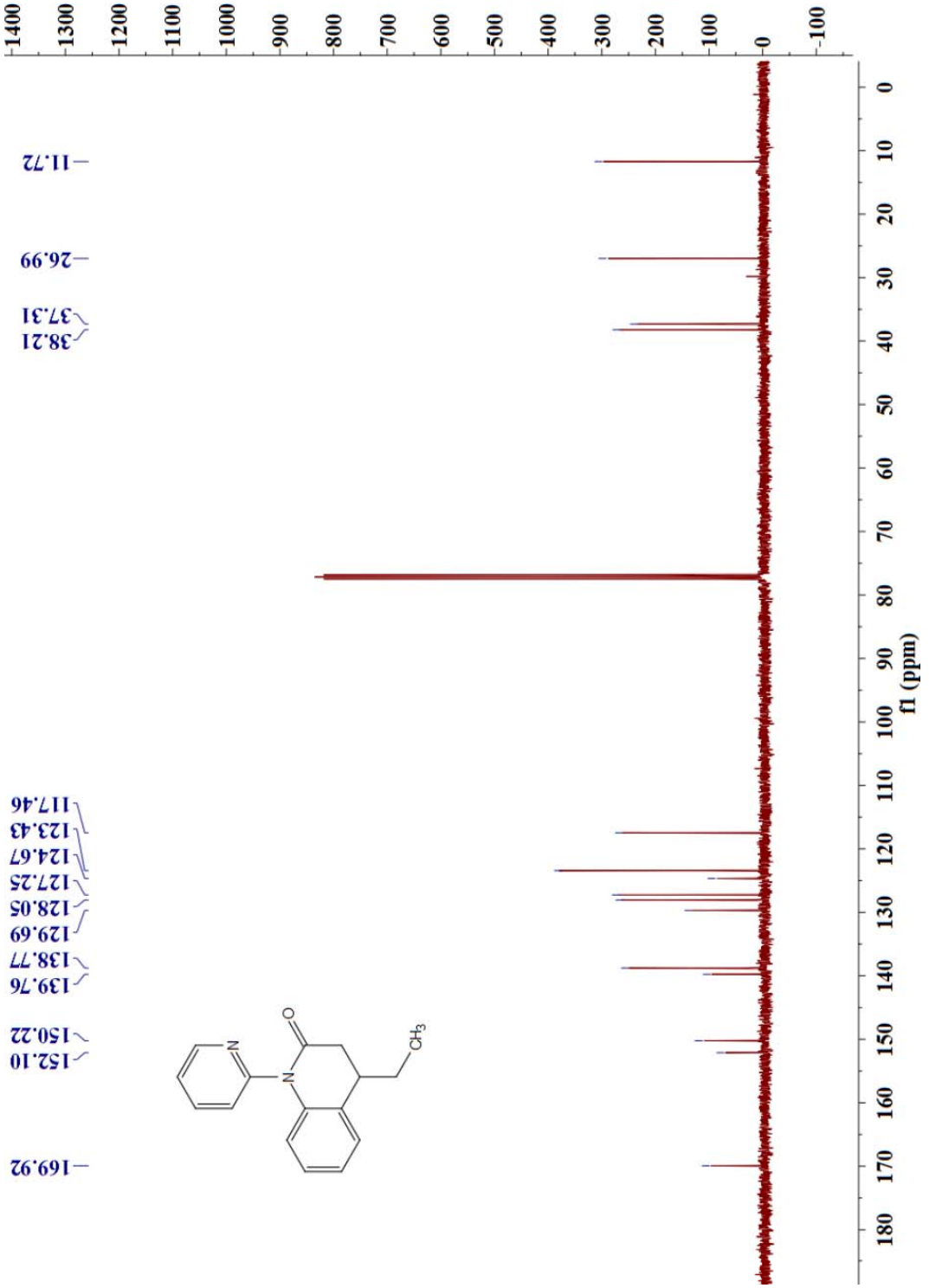
HR-MS Spectrum of 4-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ab**



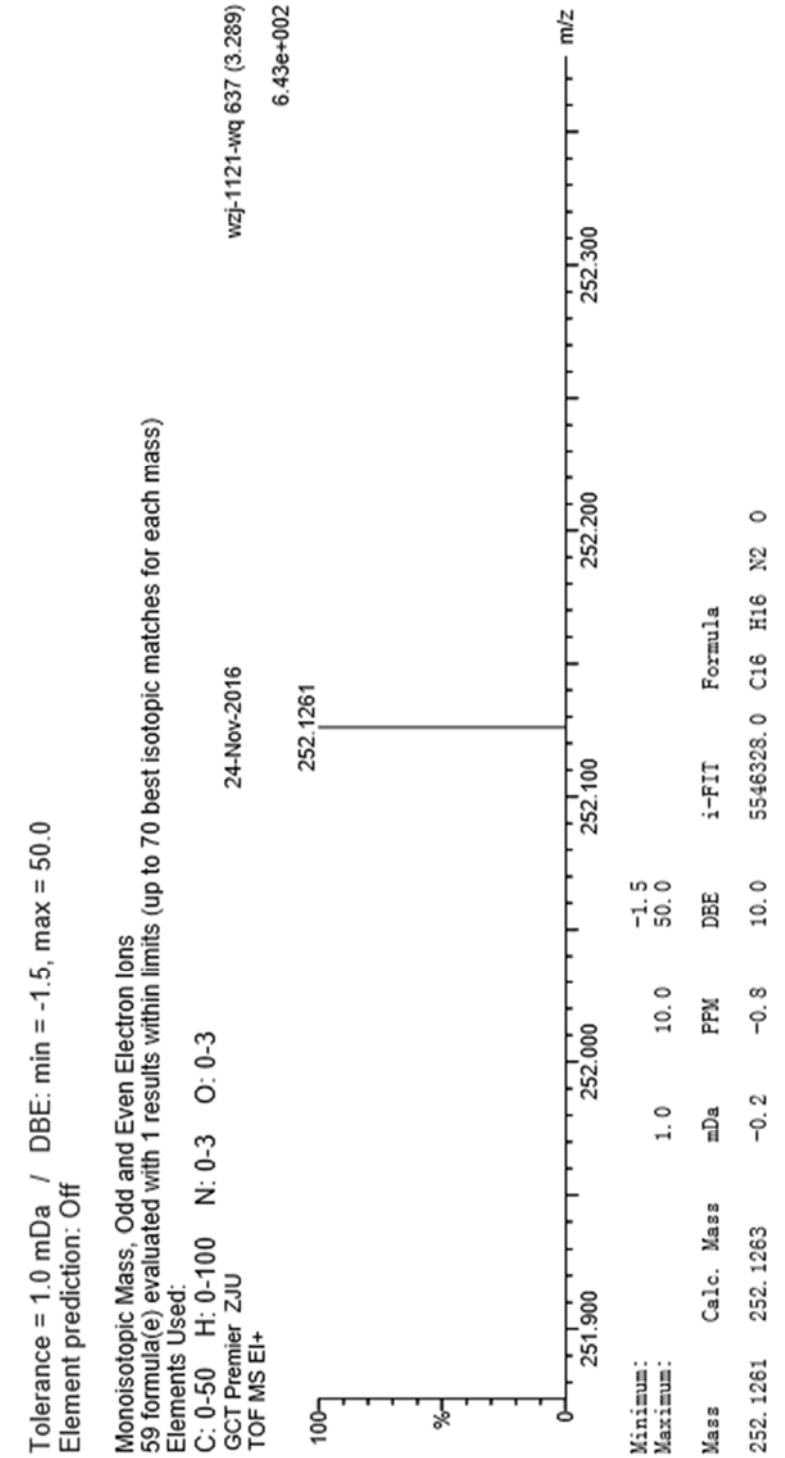
[1]H NMR Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



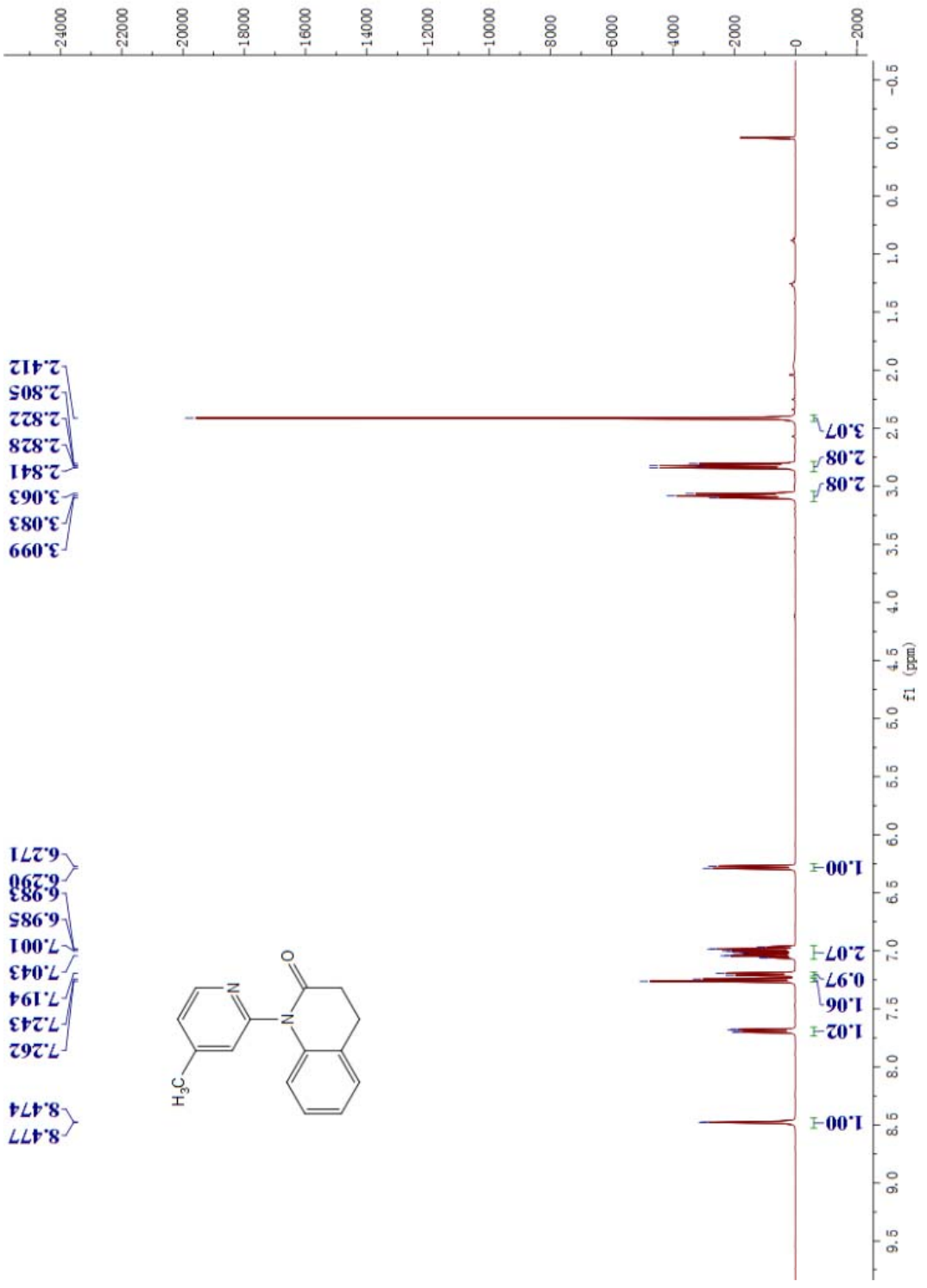
^{13}C NMR Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



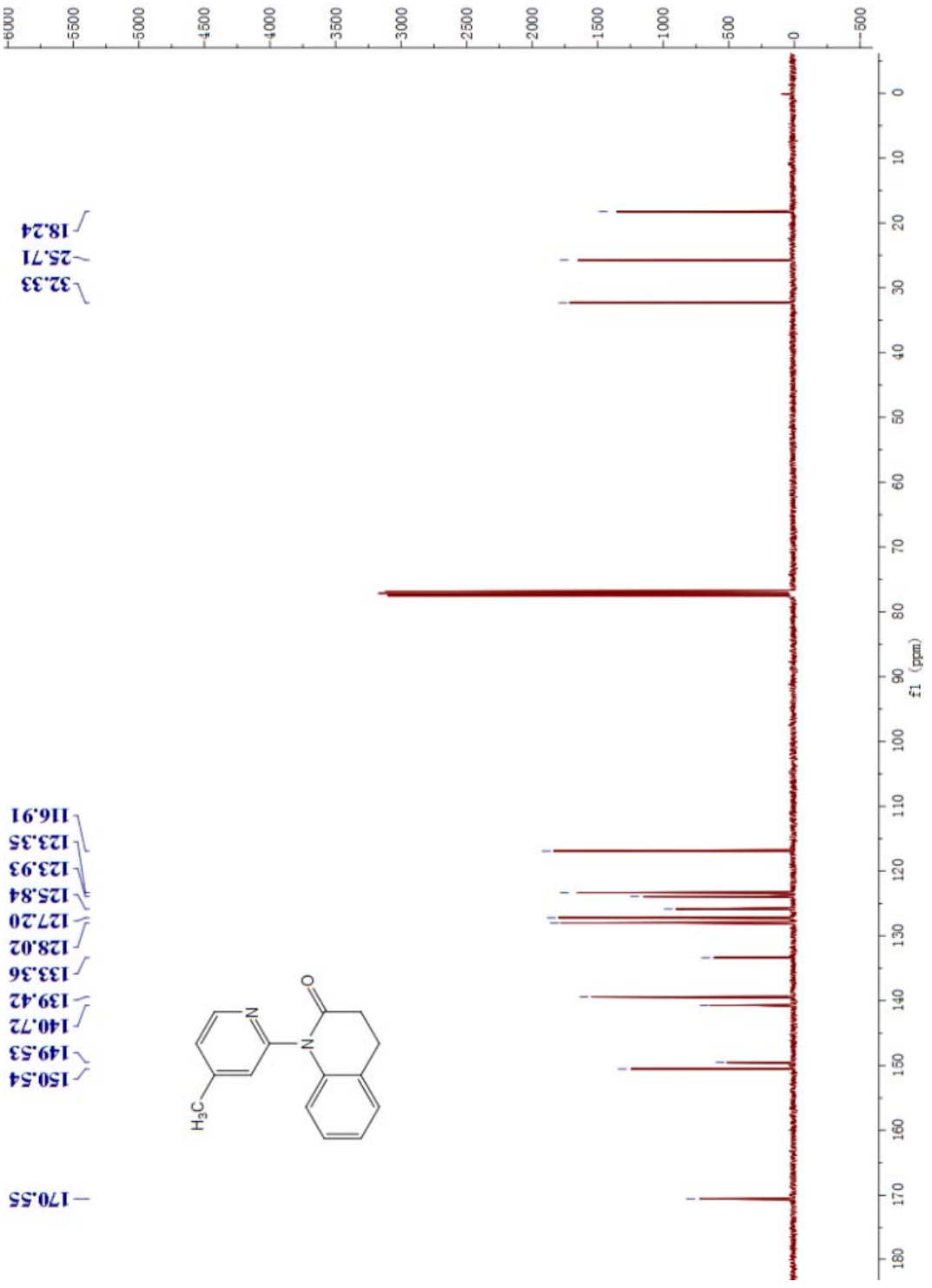
HR-MS Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



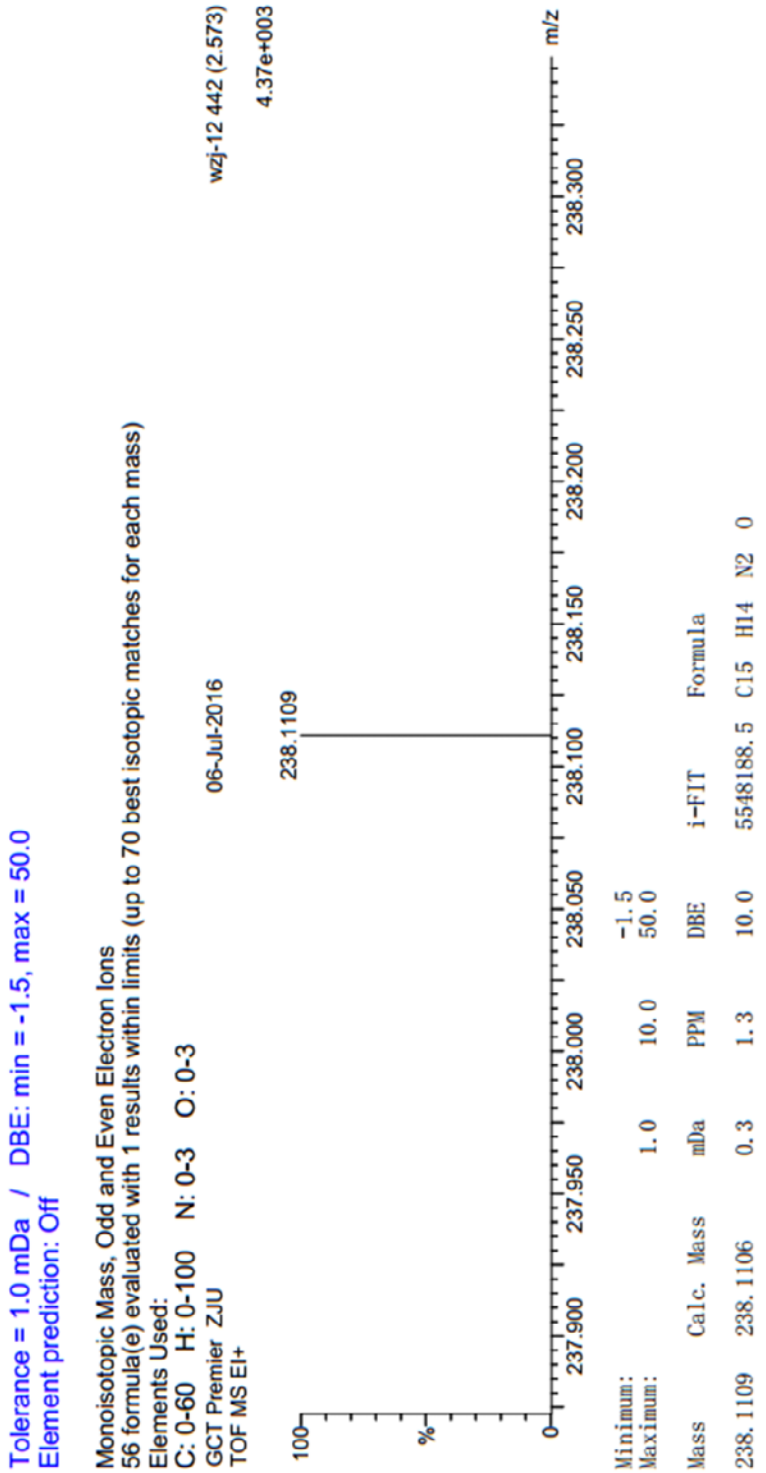
^{1}H NMR Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H) -one **3na**



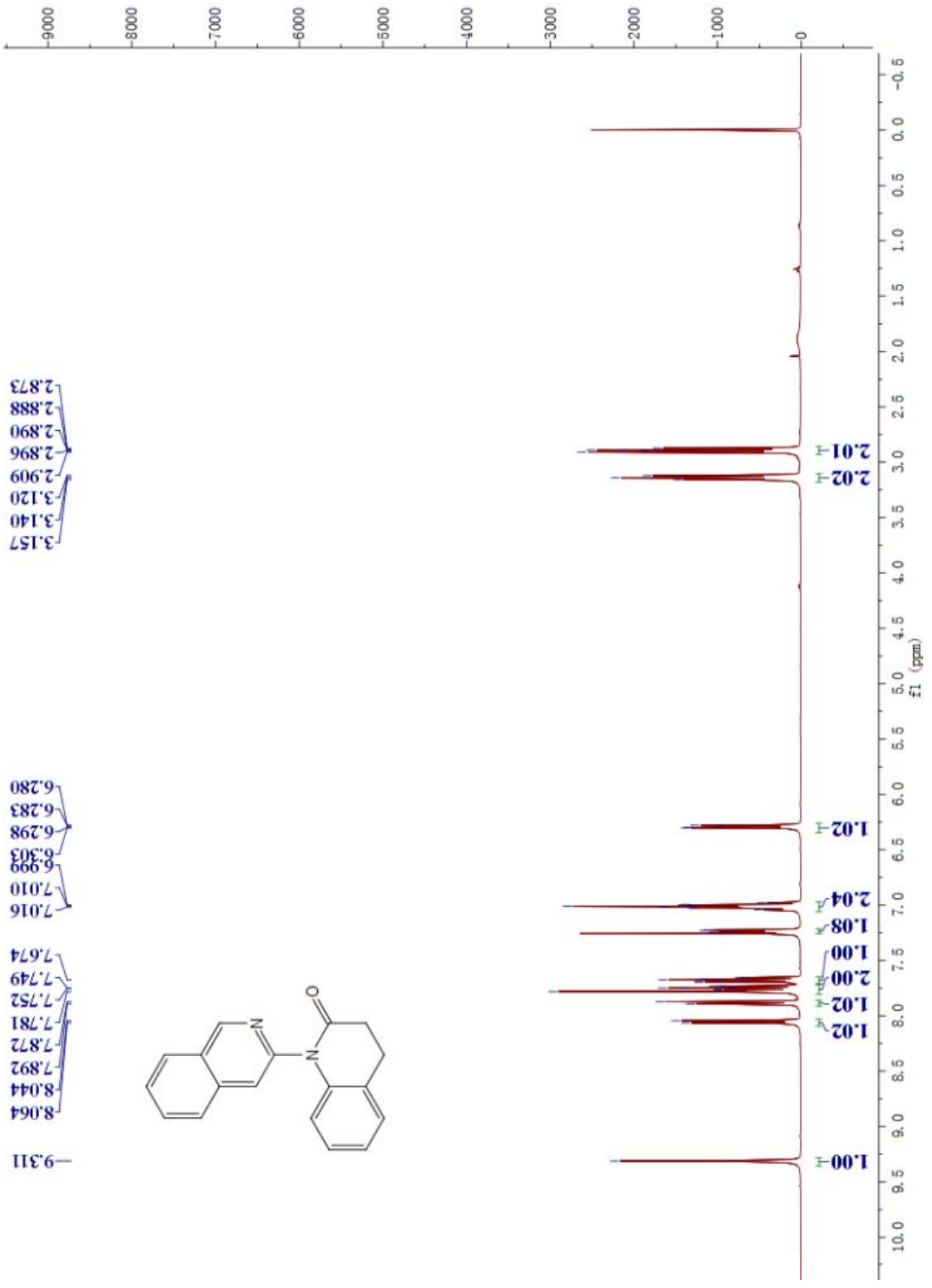
^{13}C NMR Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H) -one **3na**



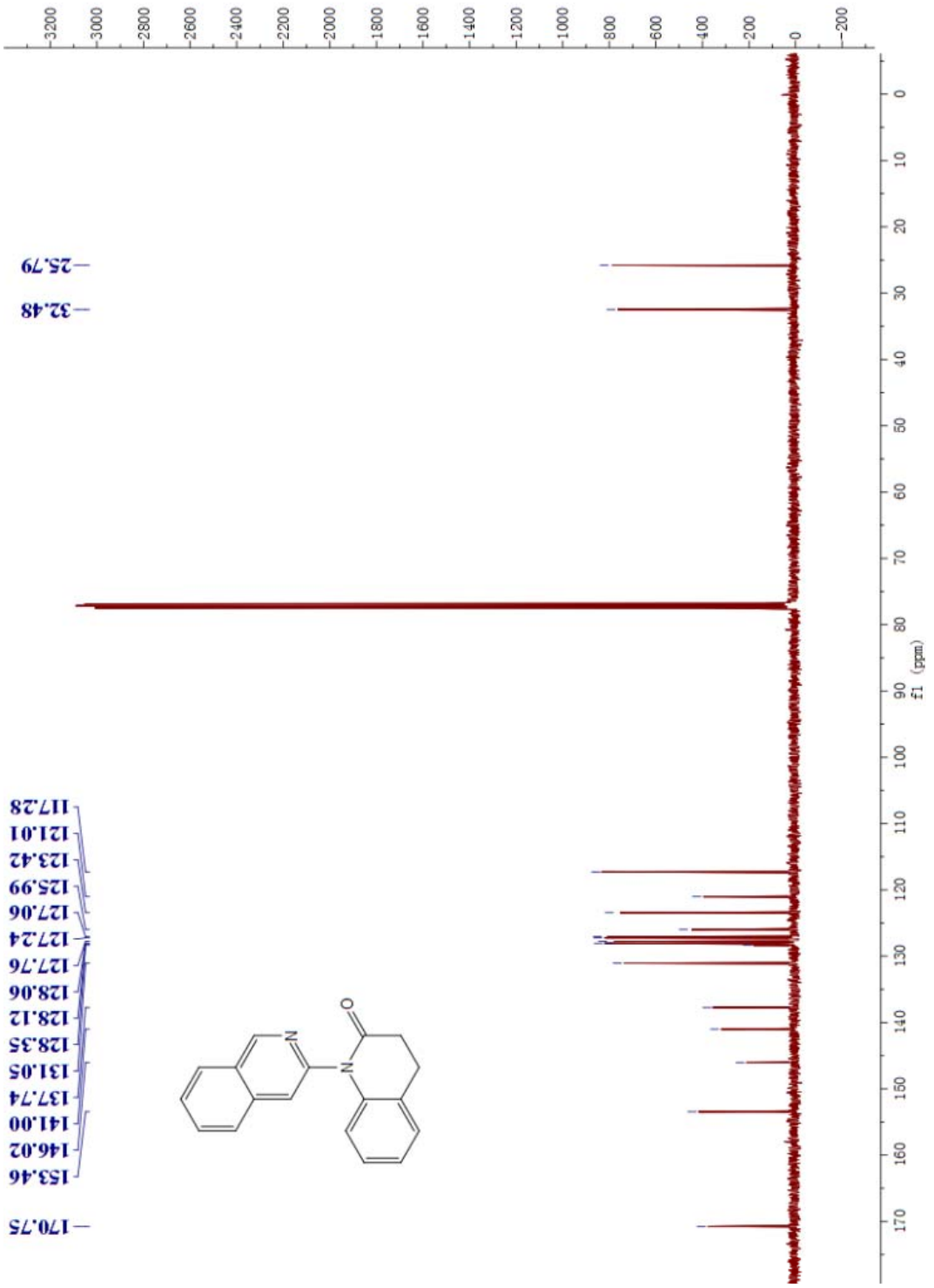
HR-MS Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3na**



^{1}H NMR Spectrum of 1-(isoquinolin-3-yl)-3,4-dihydroquinolin-2(1H)-one **3oa**

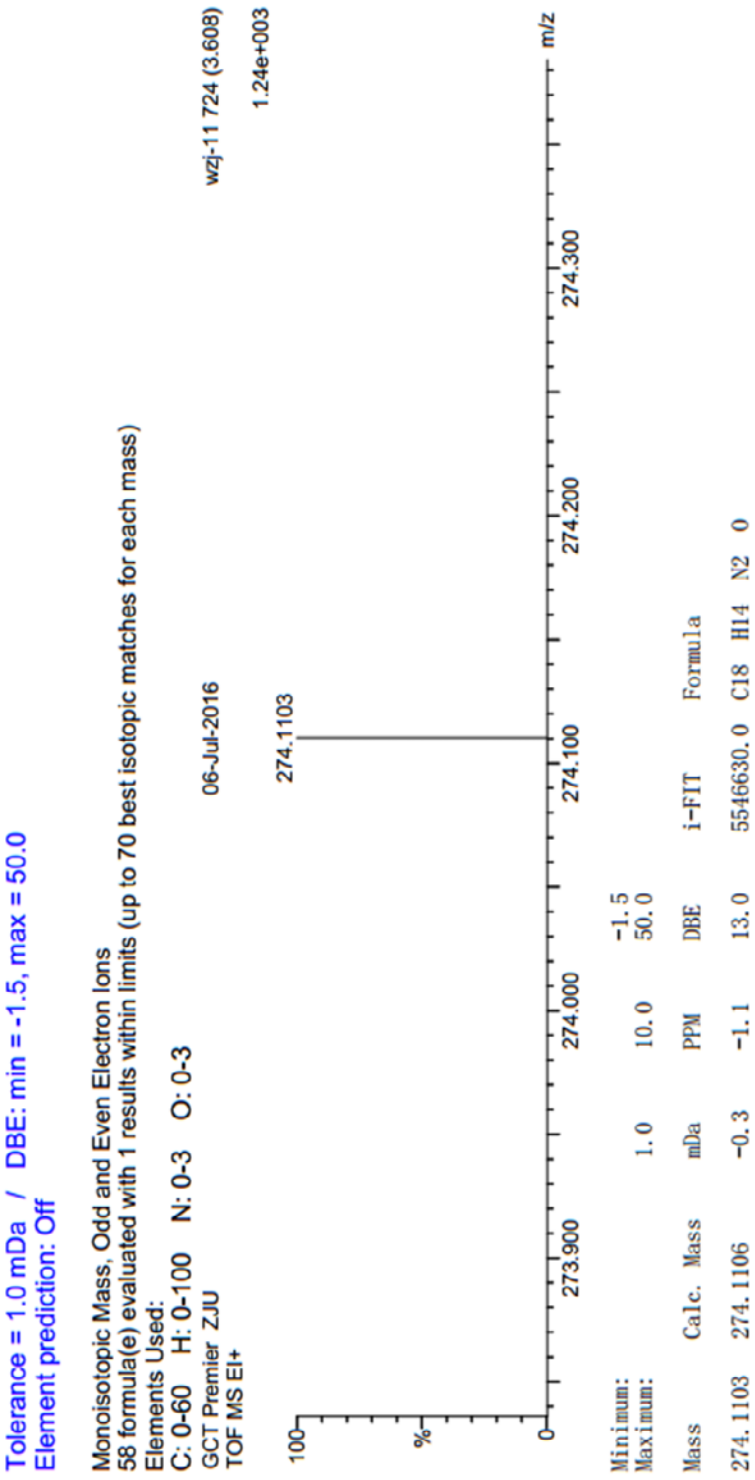


^{13}C NMR Spectrum of 1-(isoquinolin-3-yl)-3,4-dihydroquinolin-2(1H)-one **3oa**



HR-MS Spectrum of 1-(isoquinolin-3-yl)-3,4-dihydroquinolin-2(1H)-one

3oa



5. ^{1}H NMR Spectrum of the mixture of dihydroquinolinone derivative **3aa** and deuterated dihydroquinolinone derivative **3aa**-D_4