

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

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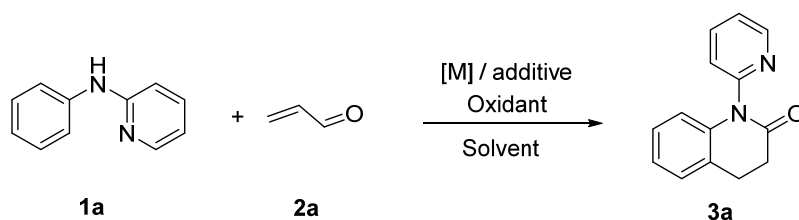
^bLakeside High School, Augusta 30809, United States

Electronic Supplementary Information

Contents

1. Optimization of the Reaction Conditions.....	2
2. X-ray Crystallographic Data of 1-(Pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one 3aa	3
3. Kinetic Isotope Effect Experiment.....	3
4. ¹ H NMR, ¹³ C NMR, HR-MS Spectra of Dihydroquinolinone Derivatives 3	4
5. ¹ H NMR Spectrum of The Mixture of Dihydroquinolinone Derivative 3aa and Deuterated Dihydroquinolinone Derivative 3aa-D₄	58

1. Optimization of the Reaction Conditions



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) ₂ Cl] ₂	-	MeOH	0
5	[(p-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)	dioxane	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 AgSbF₆ (10 mol%) in MeOH (1 mL) was stirred at 50 °C for 3 h under air. ^bIsolated yields. ^cUnder O₂. ^dUnder N₂. ^eT = 25 °C. ^fT = 90 °C, in a sealed tube.

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

Datablock: 160719_wzj_3aa

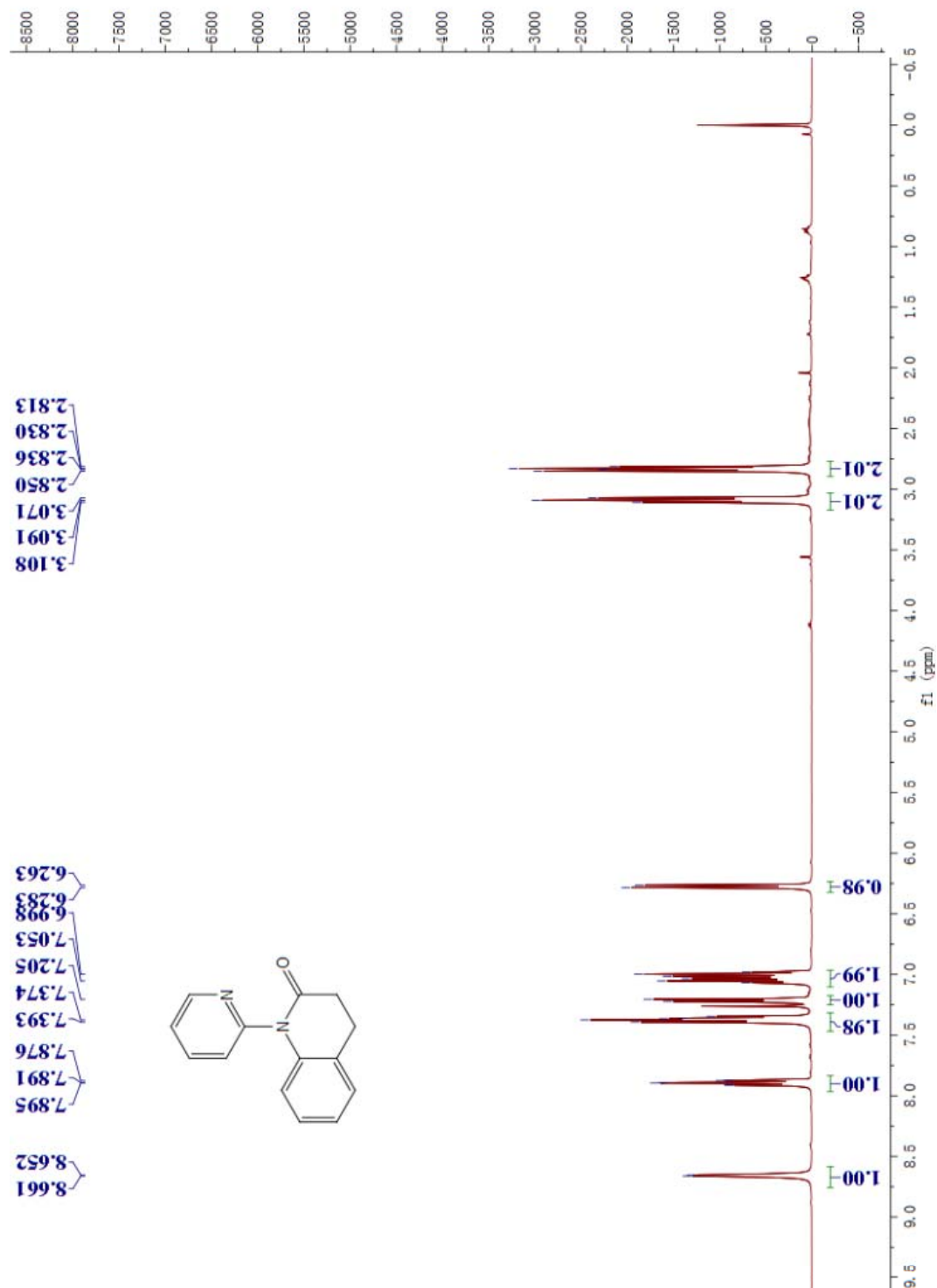
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Cell:	a=14.8634 (9) alpha=90	b=9.0465 (6) beta=90
Temperature:	170 K	c=16.6597 (13) gamma=90
	Calculated	Reported
Volume	2240.1 (3)	2240.1 (3)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C14 H12 N2 O	C14 H12 N2 O
Sum formula	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*Cl₂]₂ (1.5 mg, 2.5 mol %), AgSbF₆ (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-D₄**.

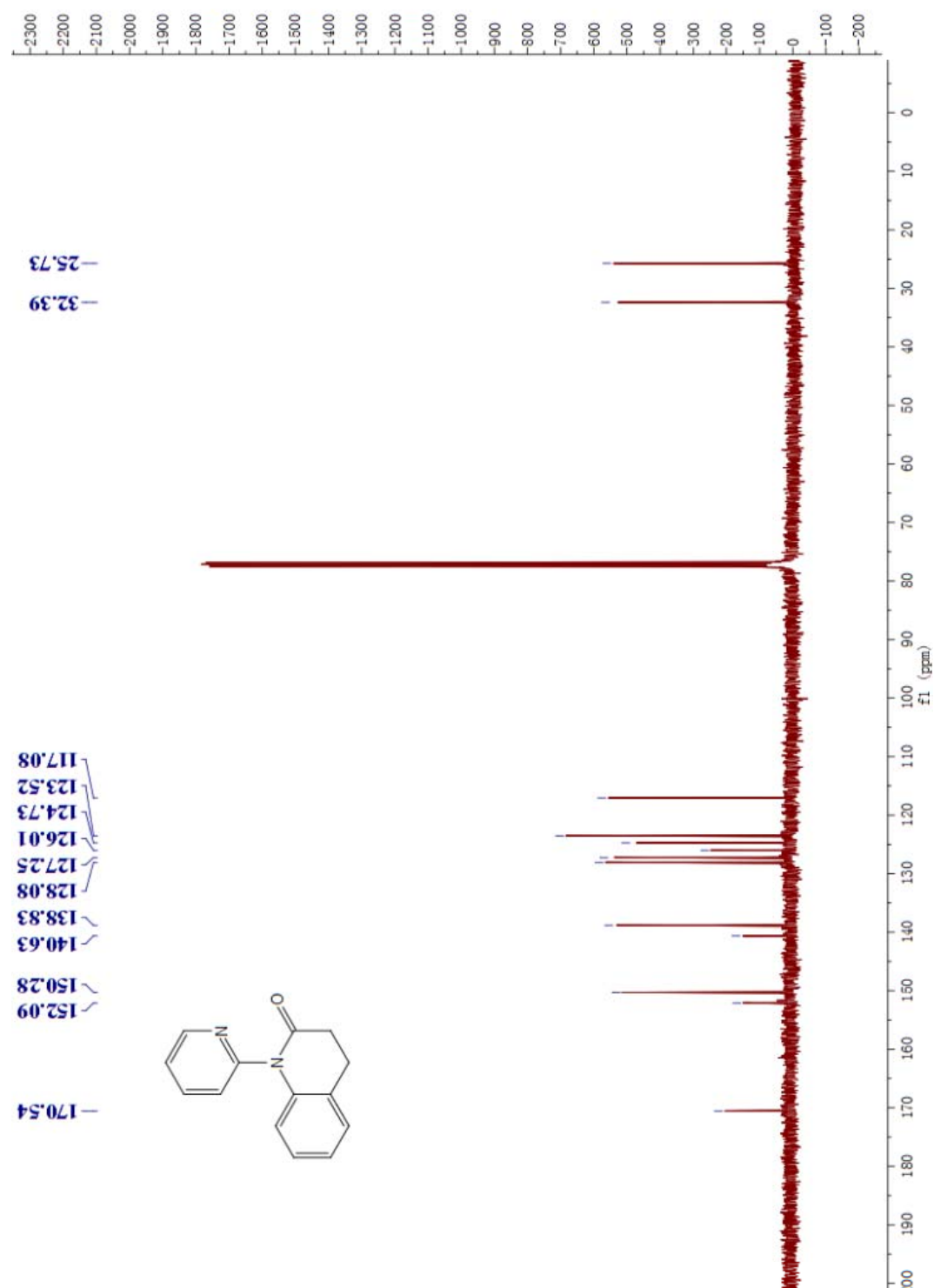
4. ^1H NMR, ^{13}C NMR, HR-MS Spectra of Dihydroquinolinone Derivatives 3

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



¹³C 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**

Tolerance = 0.8 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 67 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

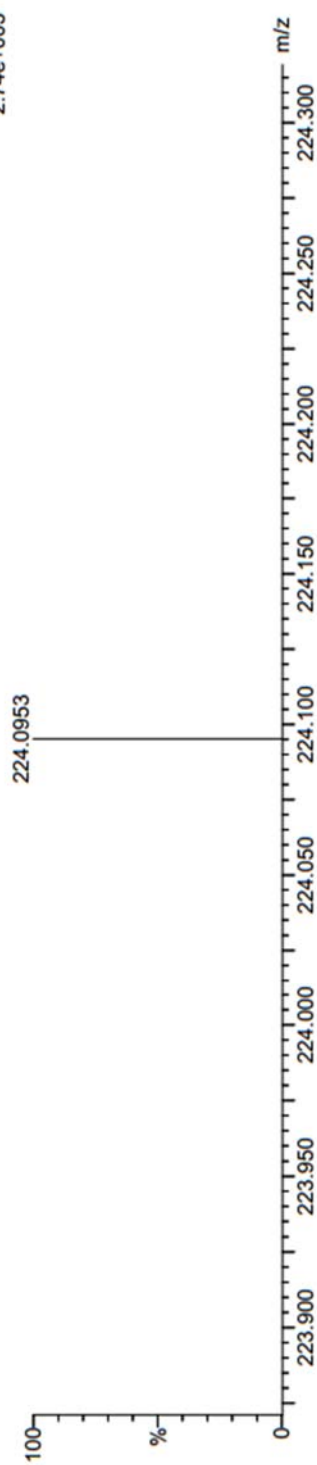
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GCT Premier ZJU

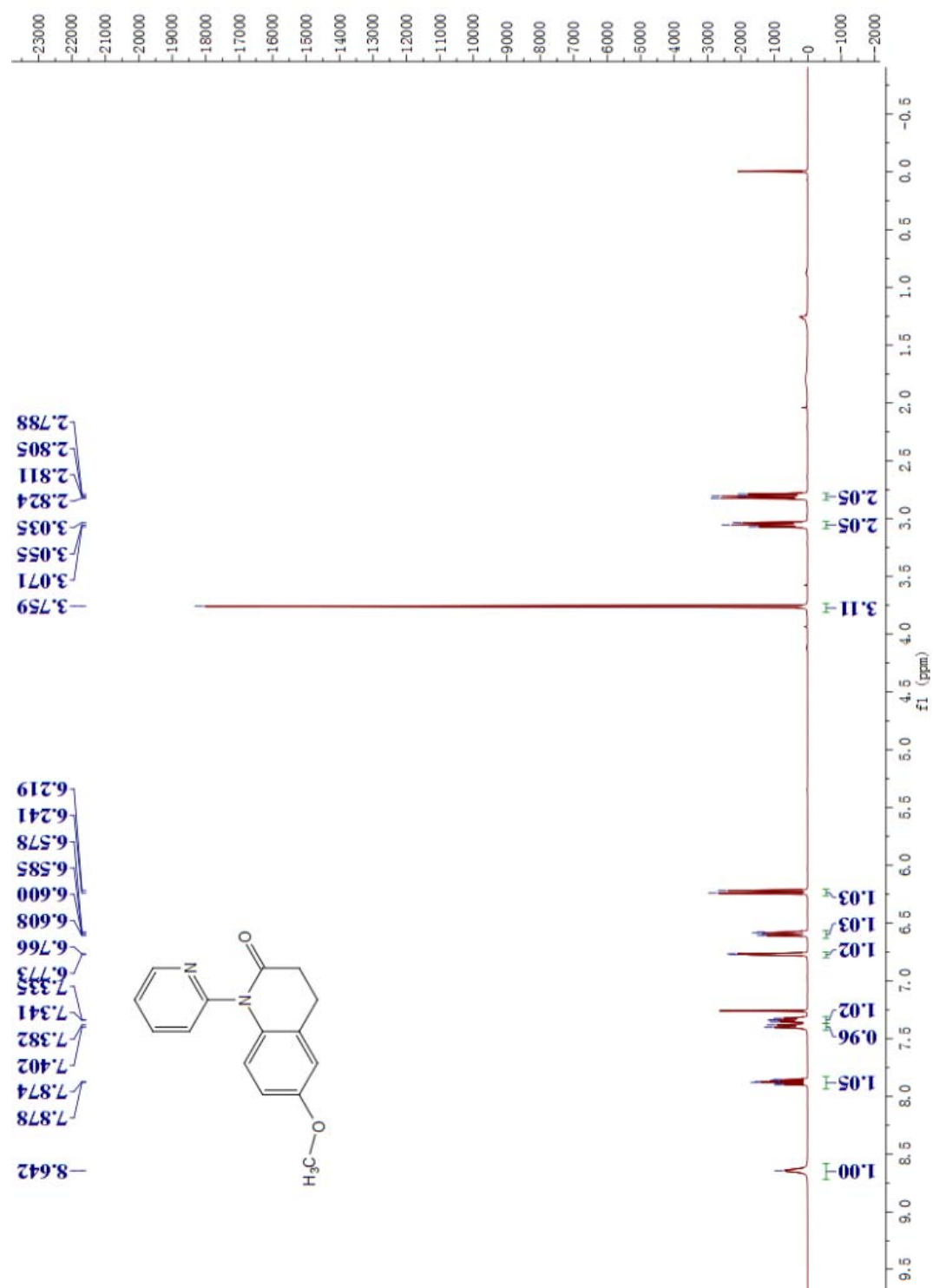
TOF MS EI+

05-May-2016

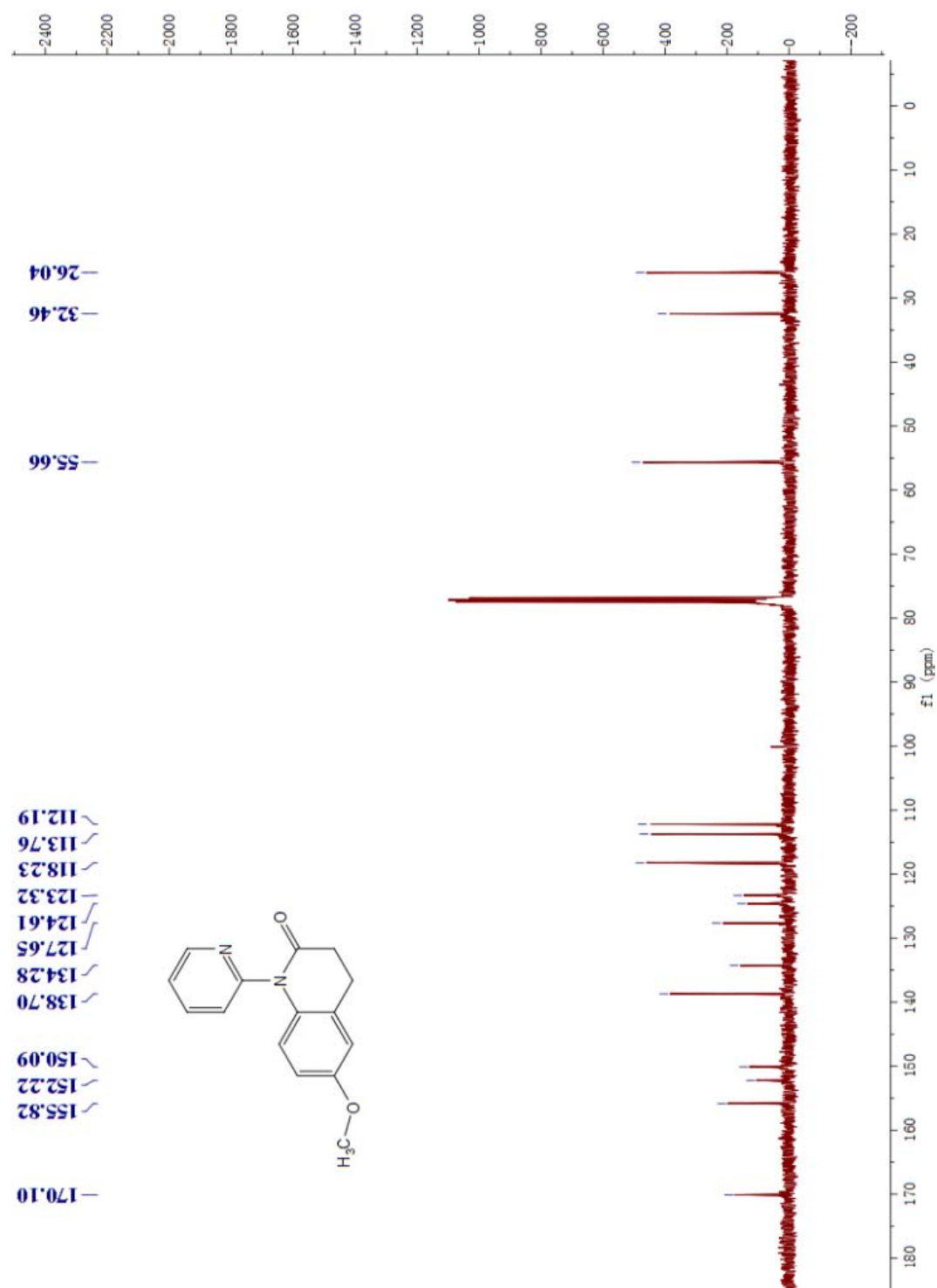


Minimum:				-1.5	
Maximum:				50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
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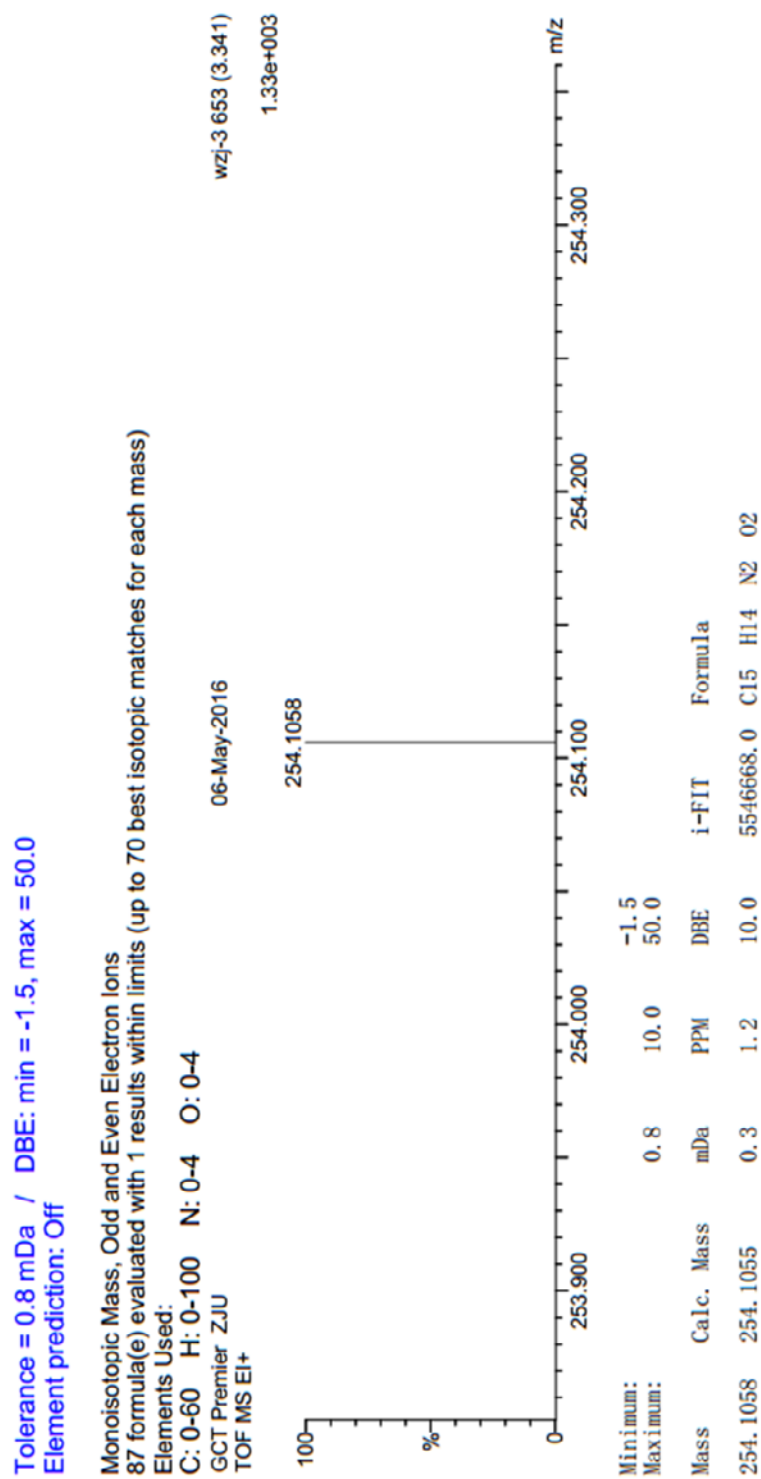
¹H NMR Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



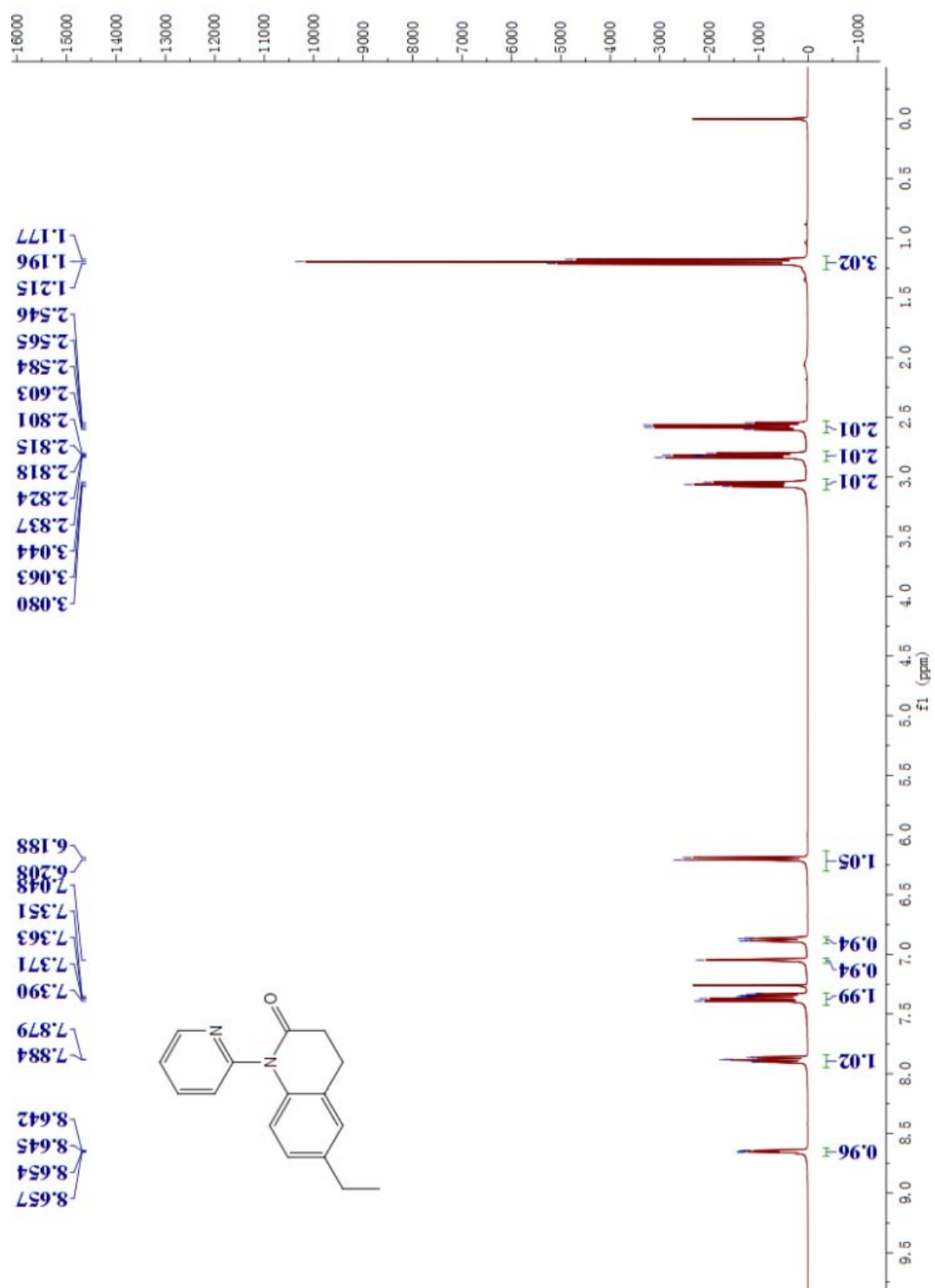
¹³C NMR Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



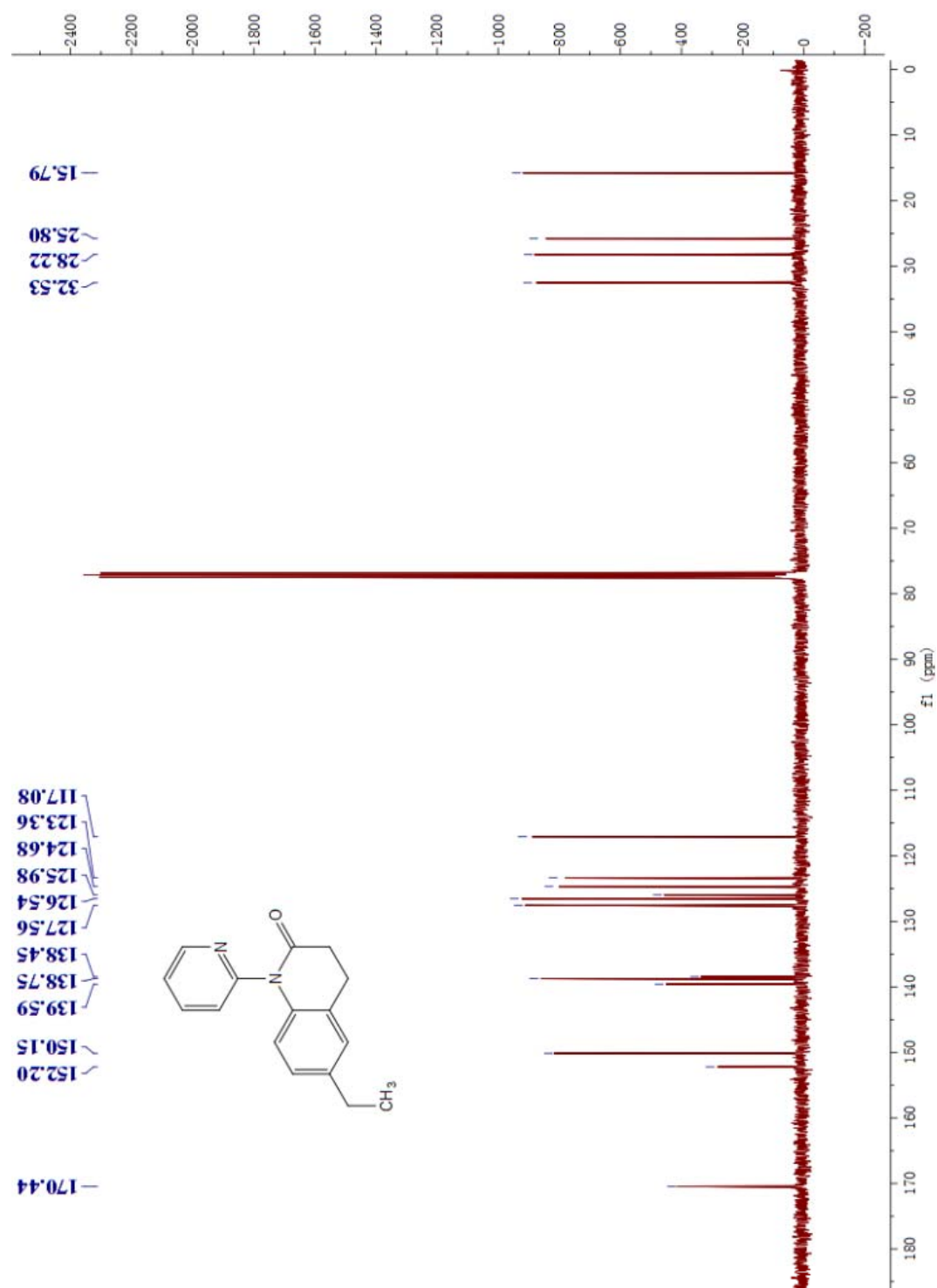
HR-MS Spectrum of 6-methoxy-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ba**



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



¹³C 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**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

59 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

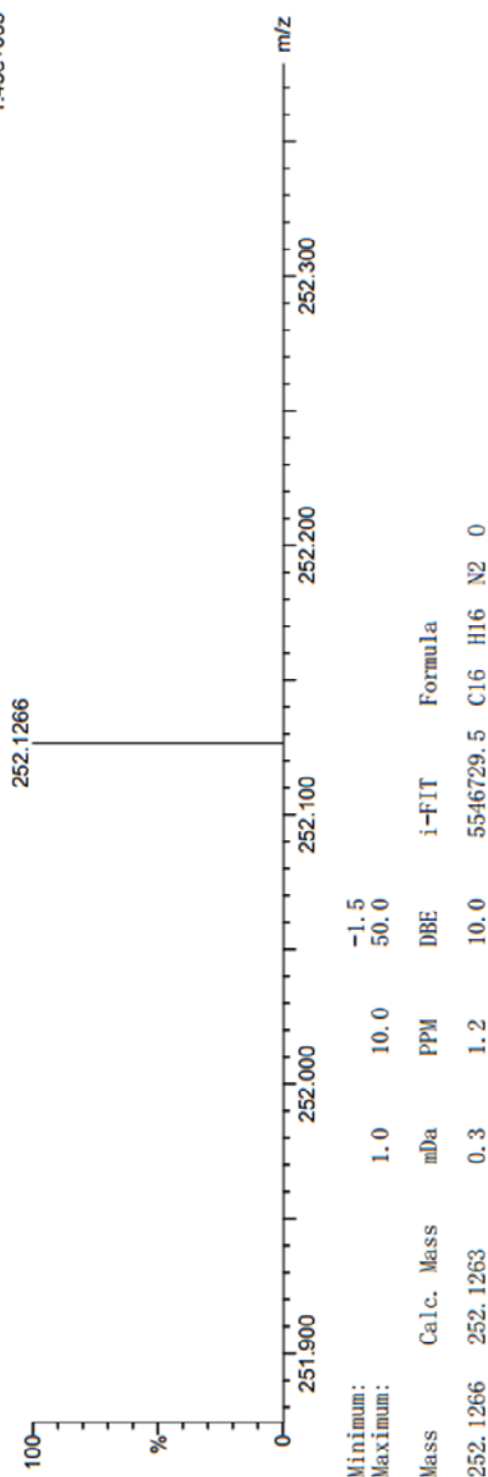
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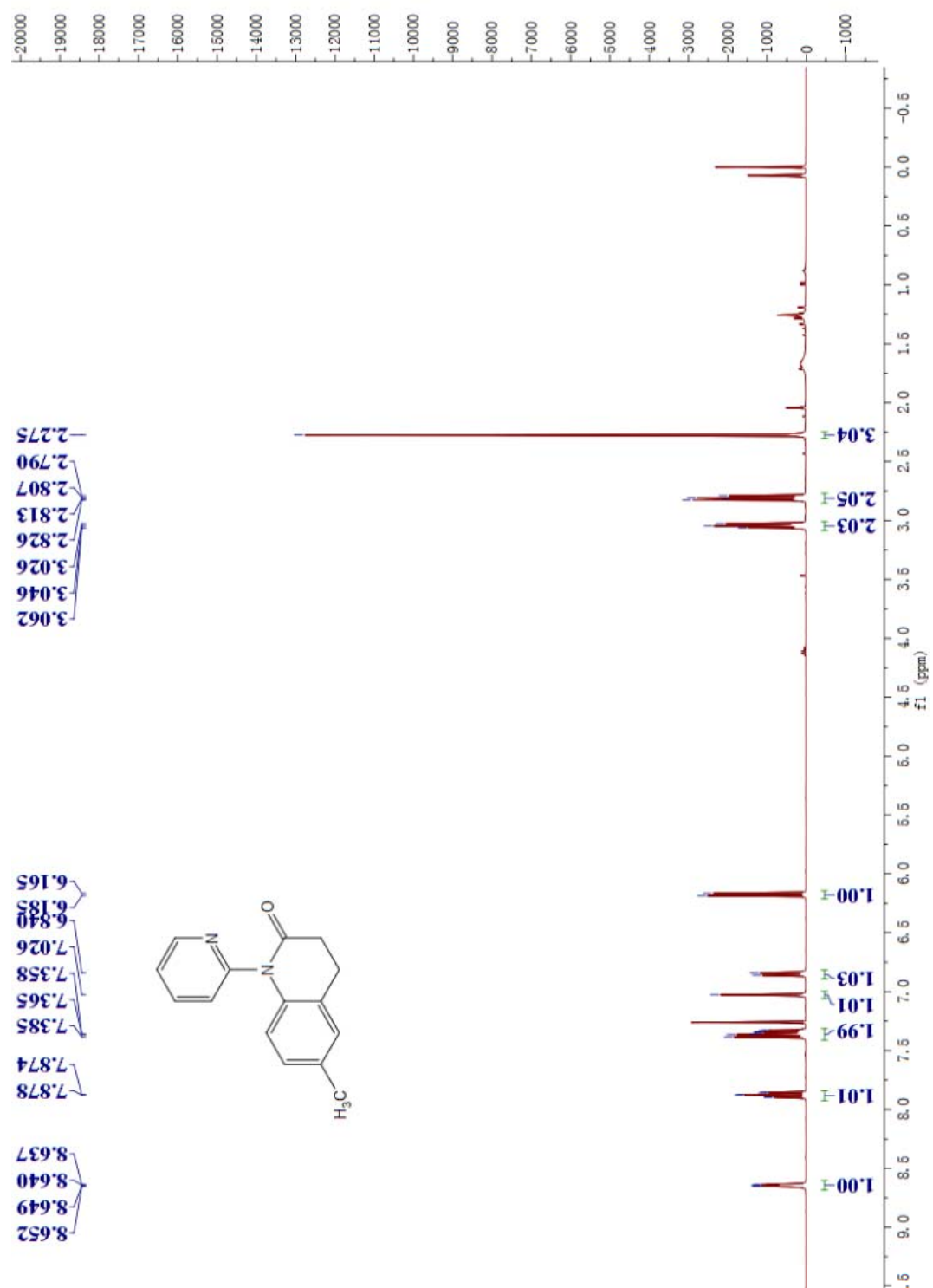
GCT Premier ZJU

TOF MS EI+

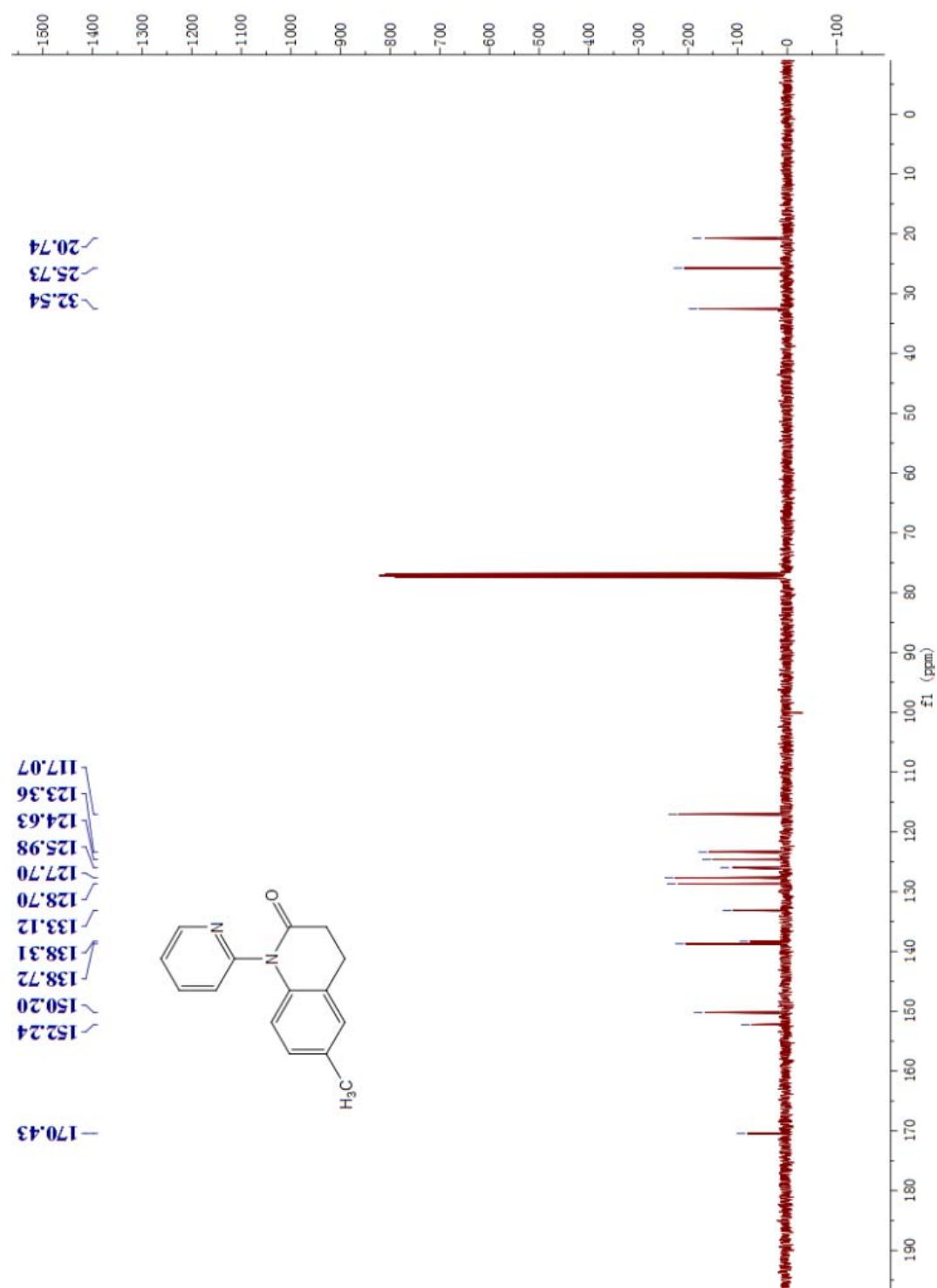
06-Jul-2016



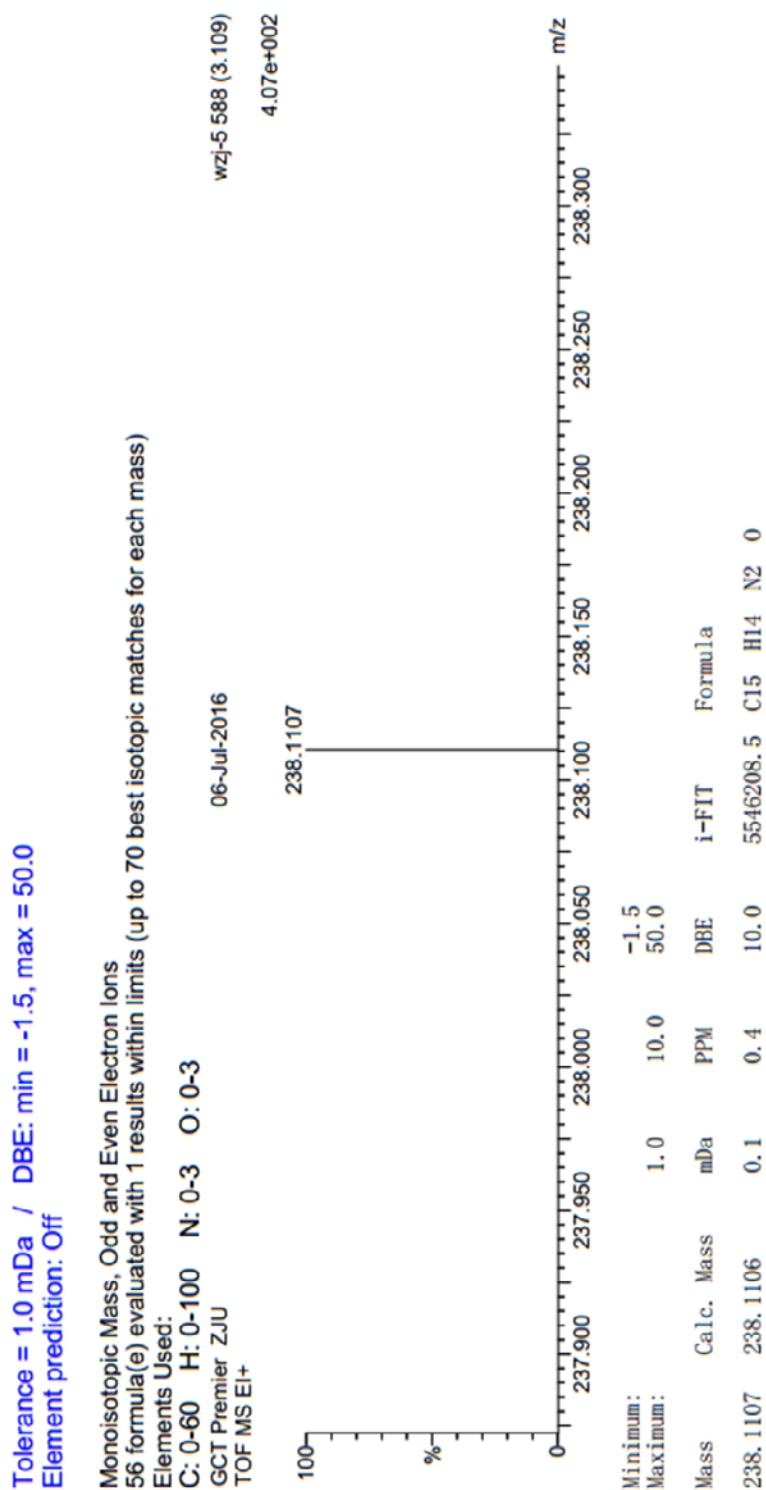
¹H NMR Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



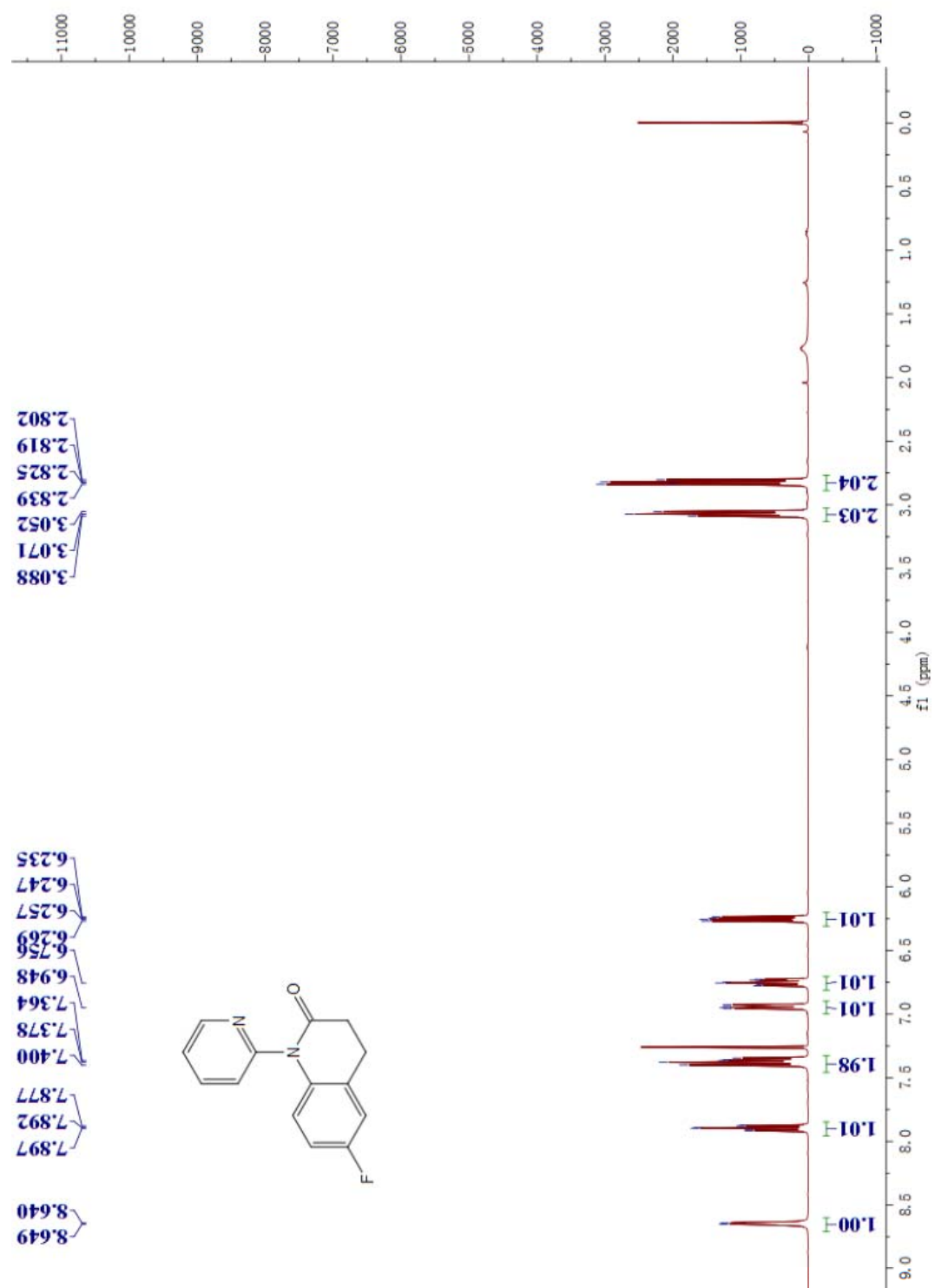
^{13}C NMR Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



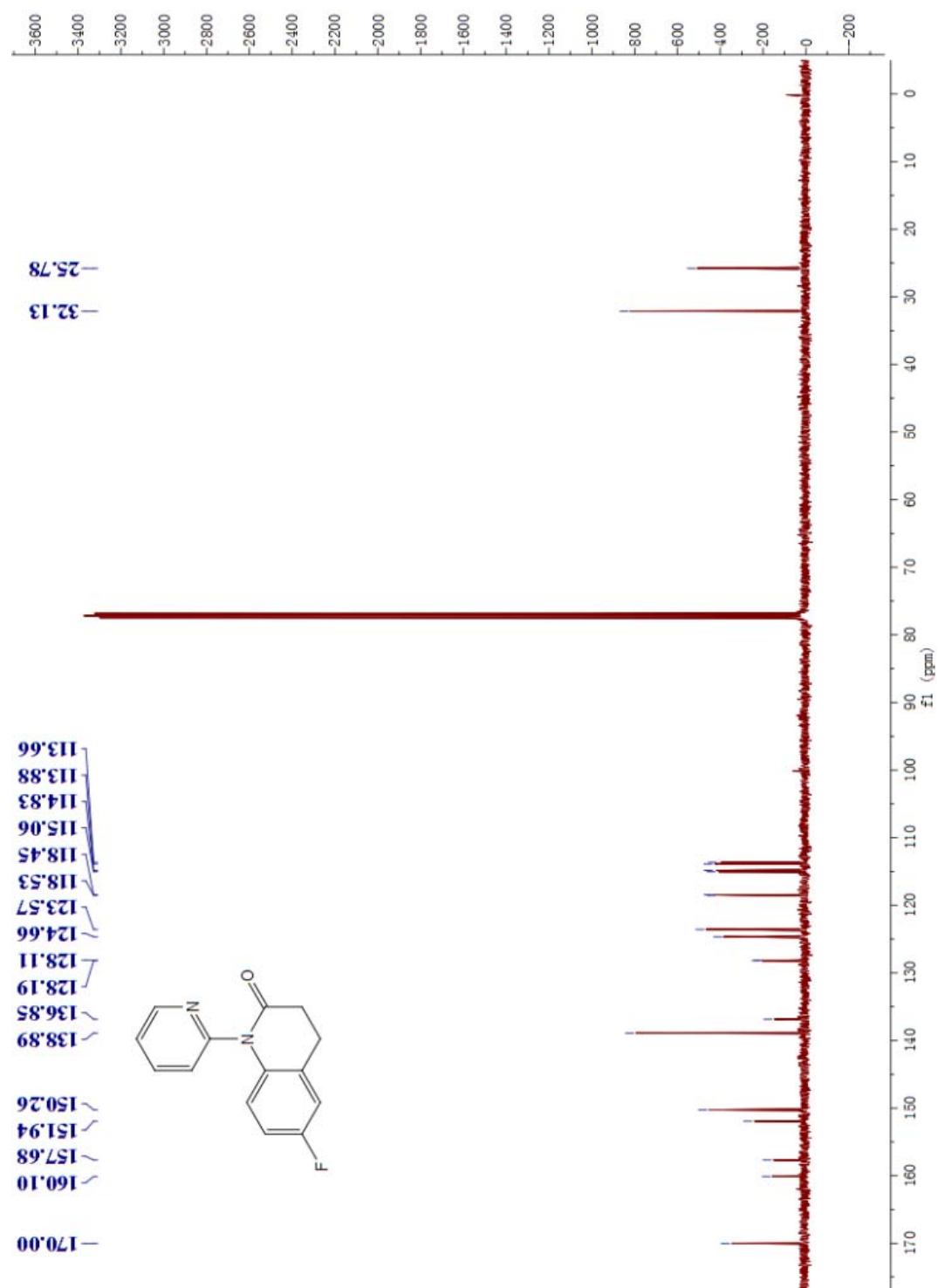
HR-MS Spectrum of 6-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3da**



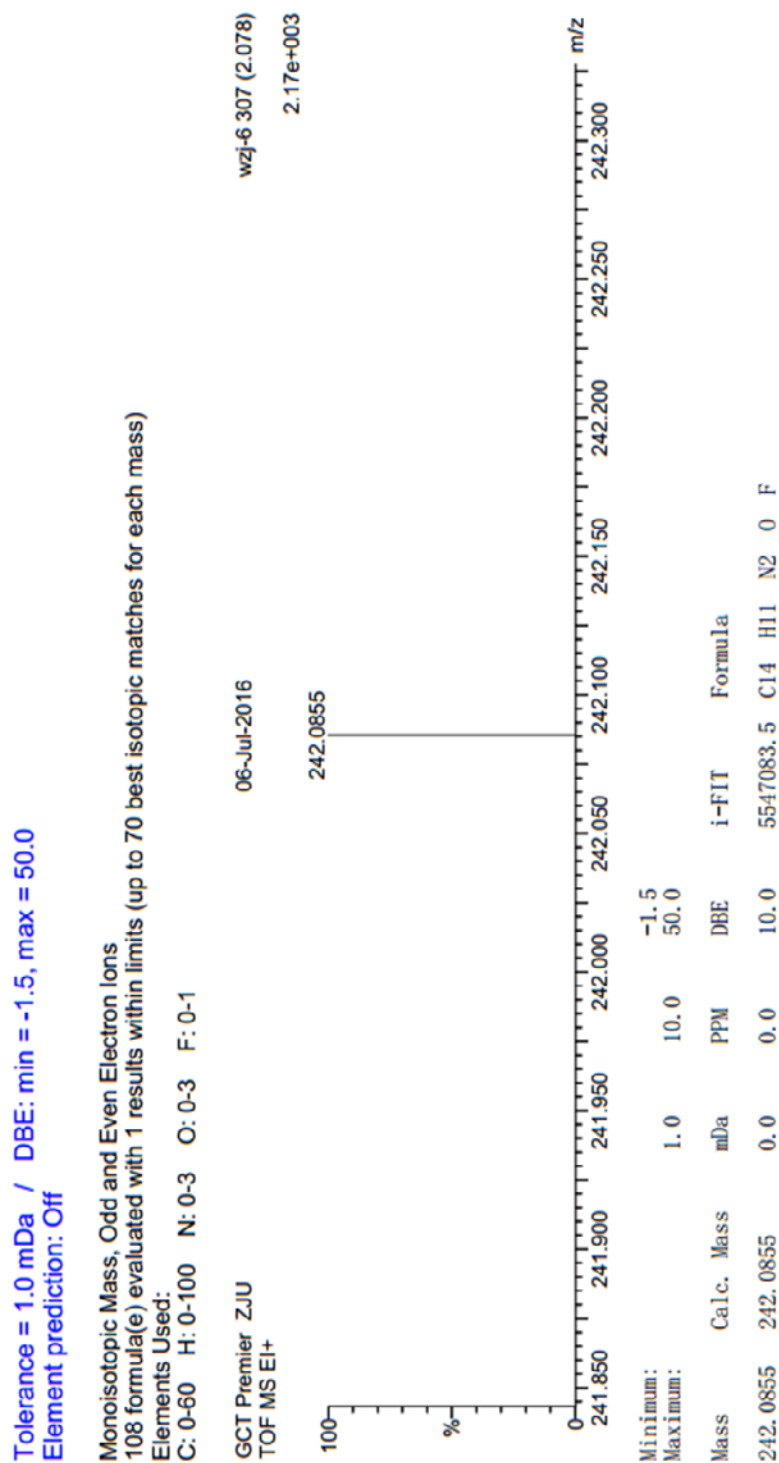
¹H NMR Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



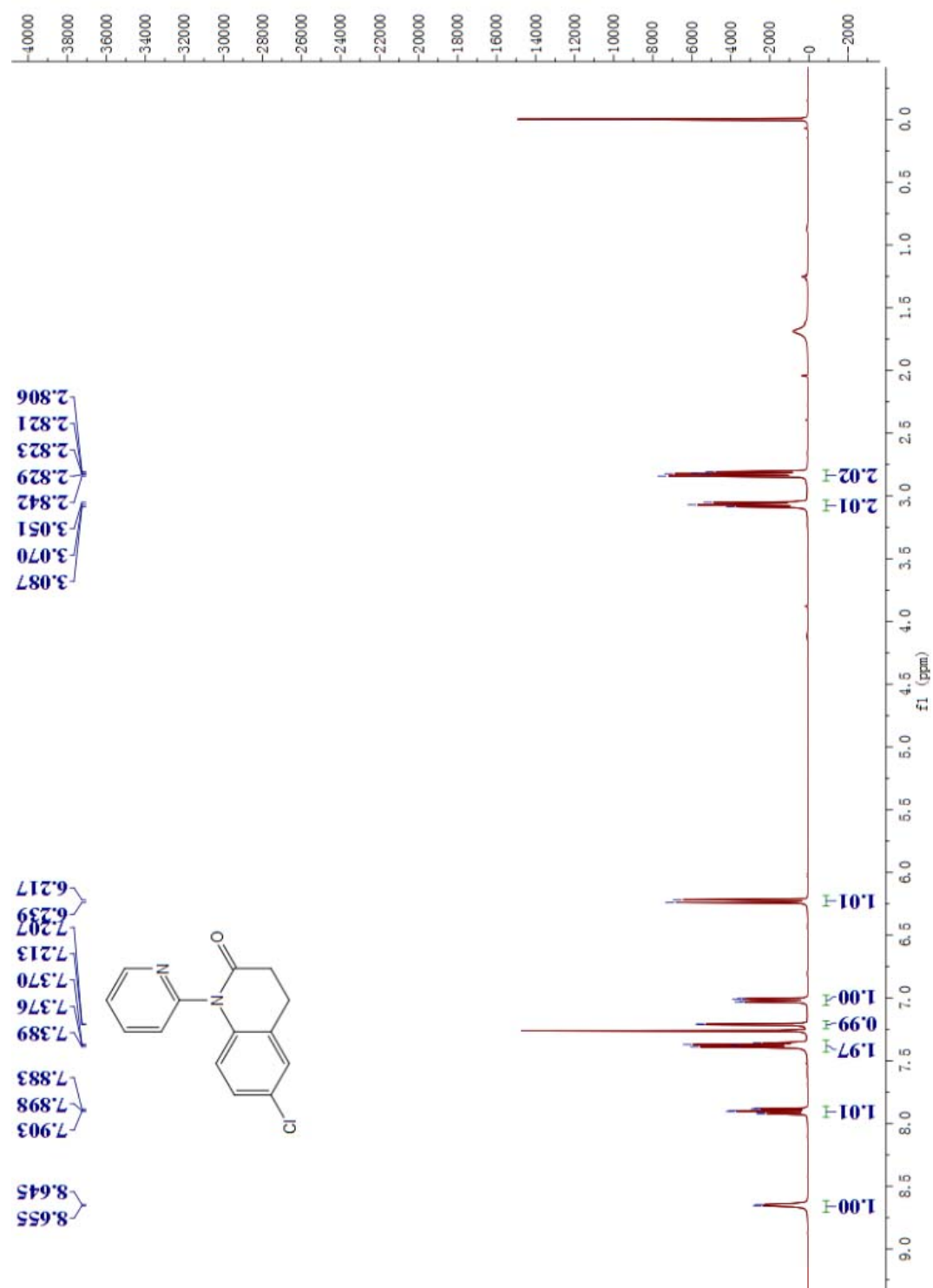
^{13}C NMR Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



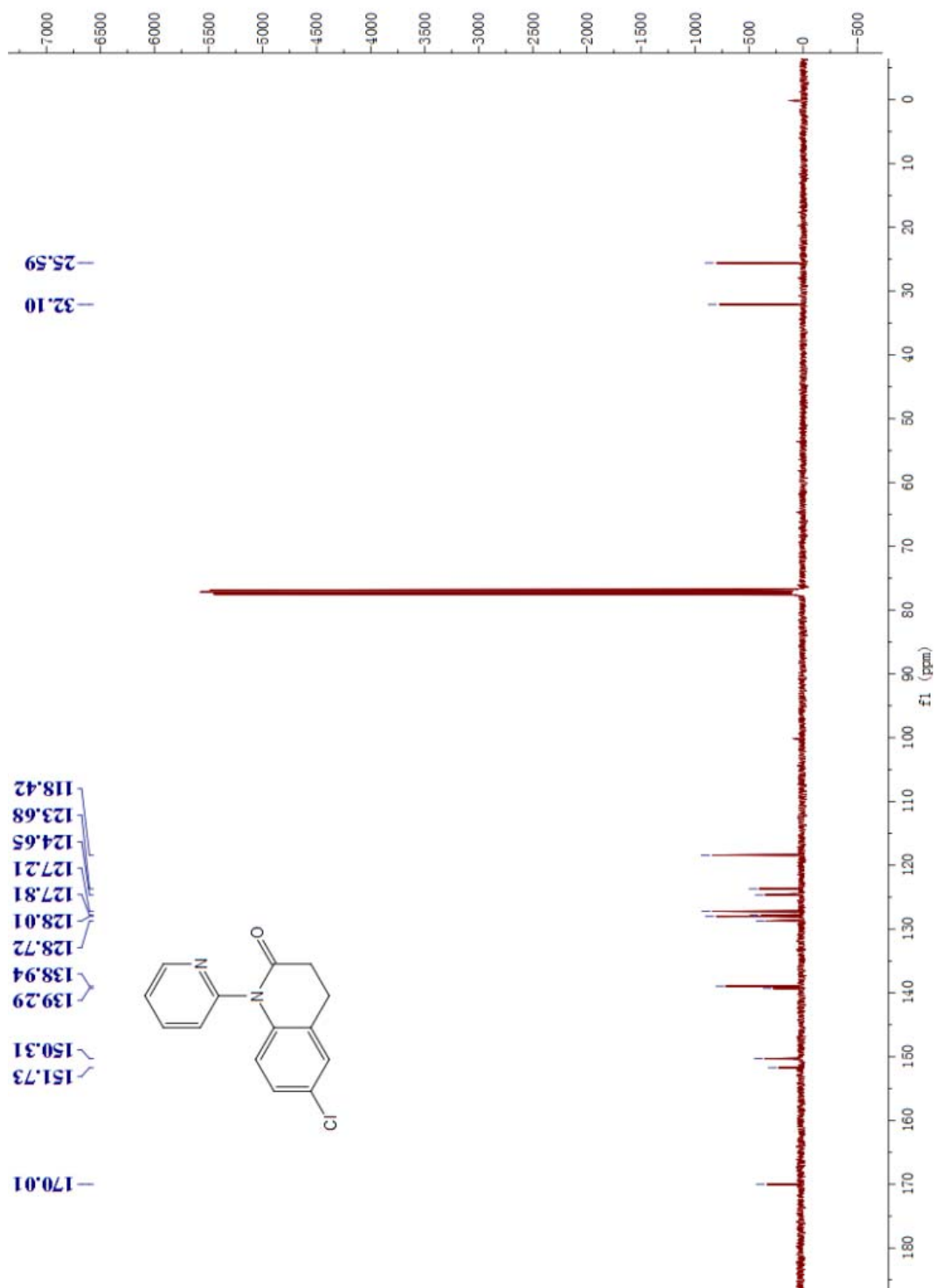
HR-MS Spectrum of 6-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ea**



¹H 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**

Tolerance = 0.8 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
80 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

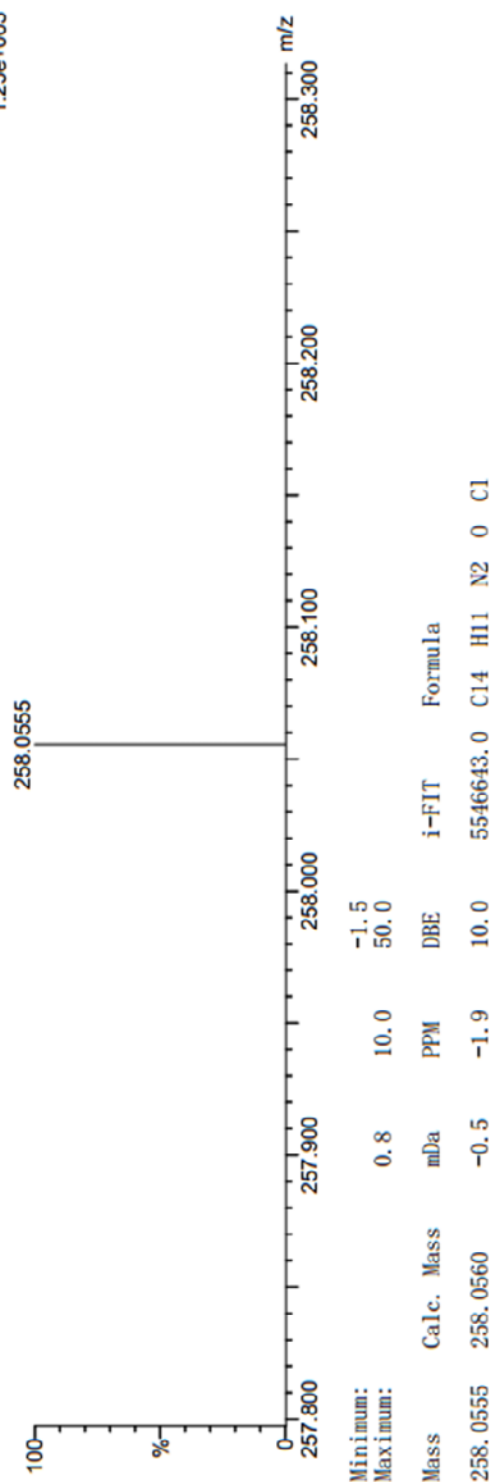
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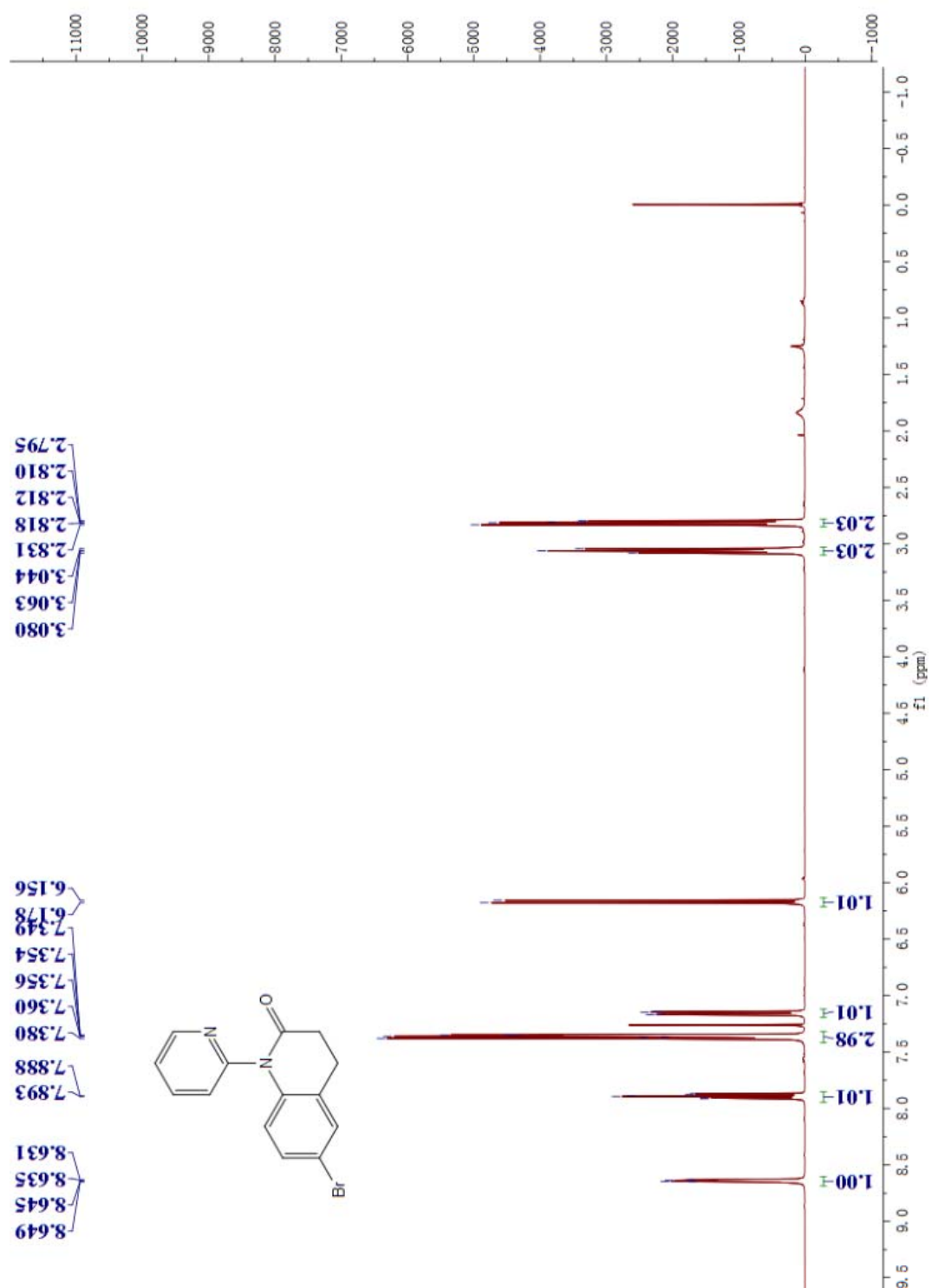
GCT Premier ZJU

TOF MS EI+

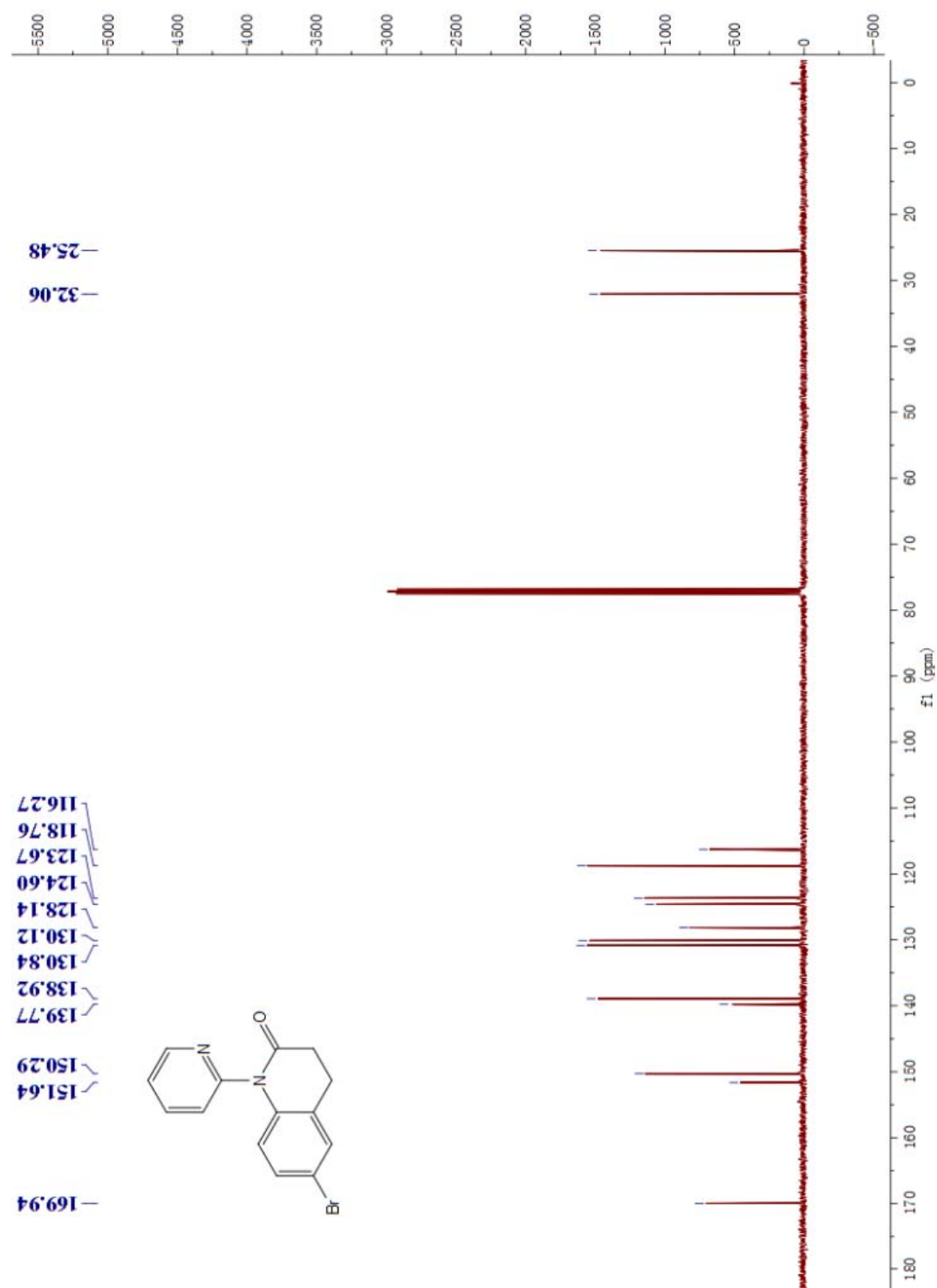
06-May-2016



¹H 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**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

54 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

Elements Used:

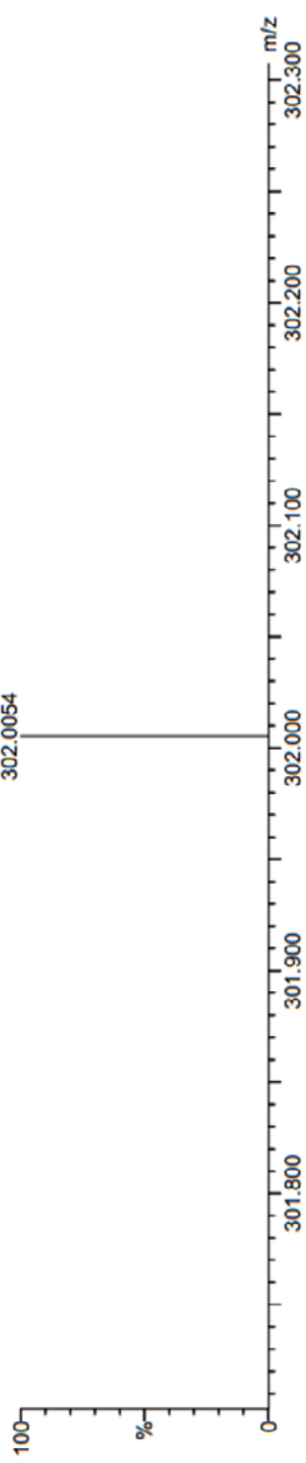
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GCT Premier ZJU

06-Jul-2016

wzj-8 565 (3.018)

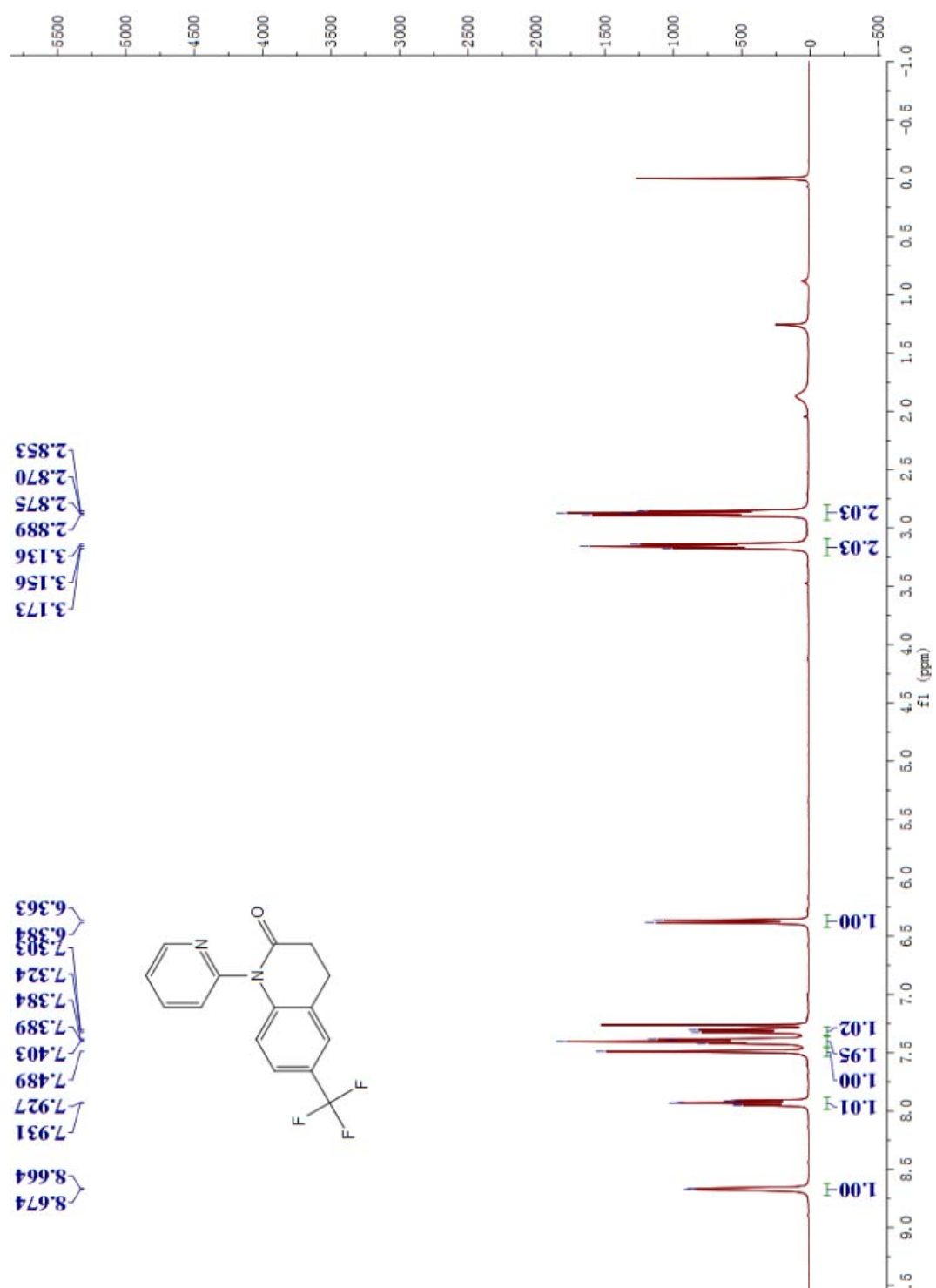
2.14e+003



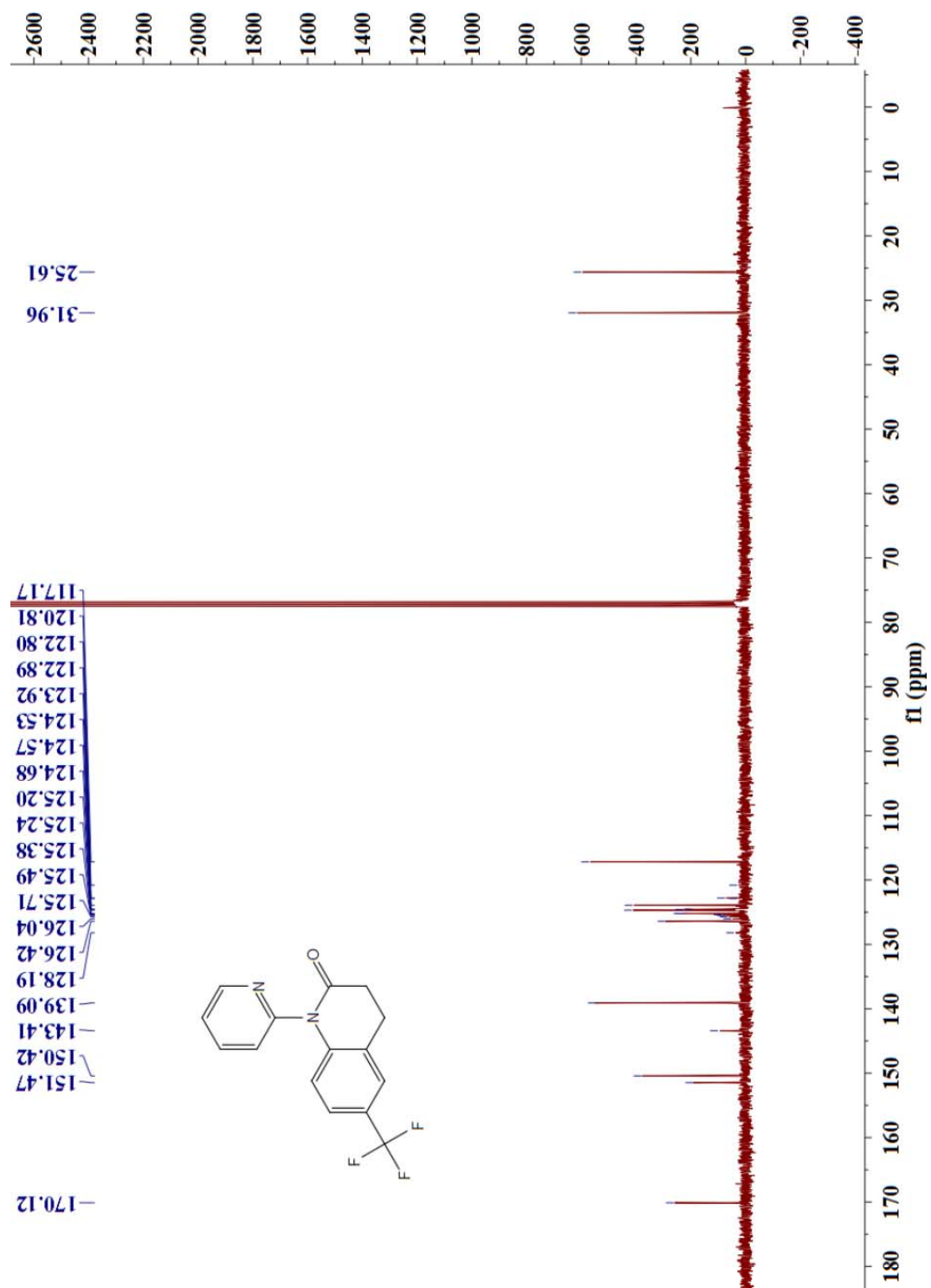
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Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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¹H NMR Spectrum of 1-(pyridin-2-yl)-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one **3ha**



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



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

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

Elements Used:

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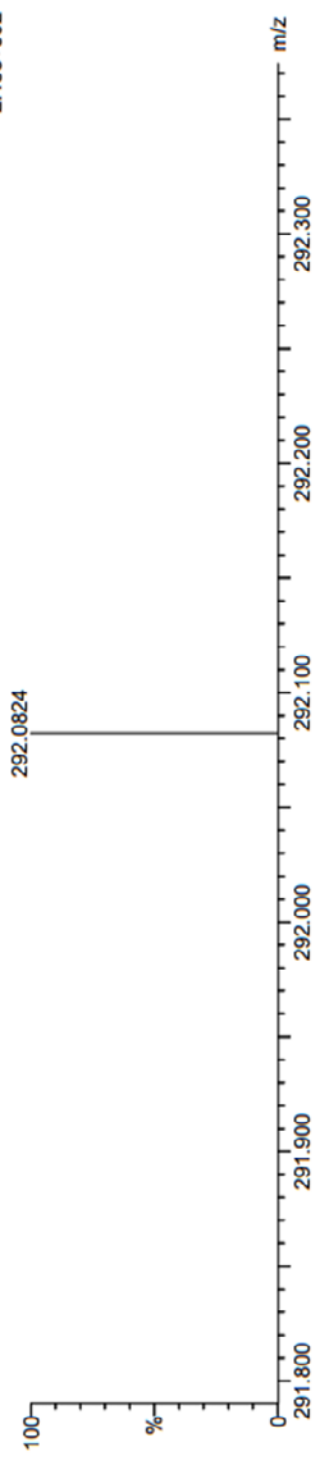
GCT Premier ZJU

TOF MS EI+

06-Jul-2016

wzj-13 486 (2.735)

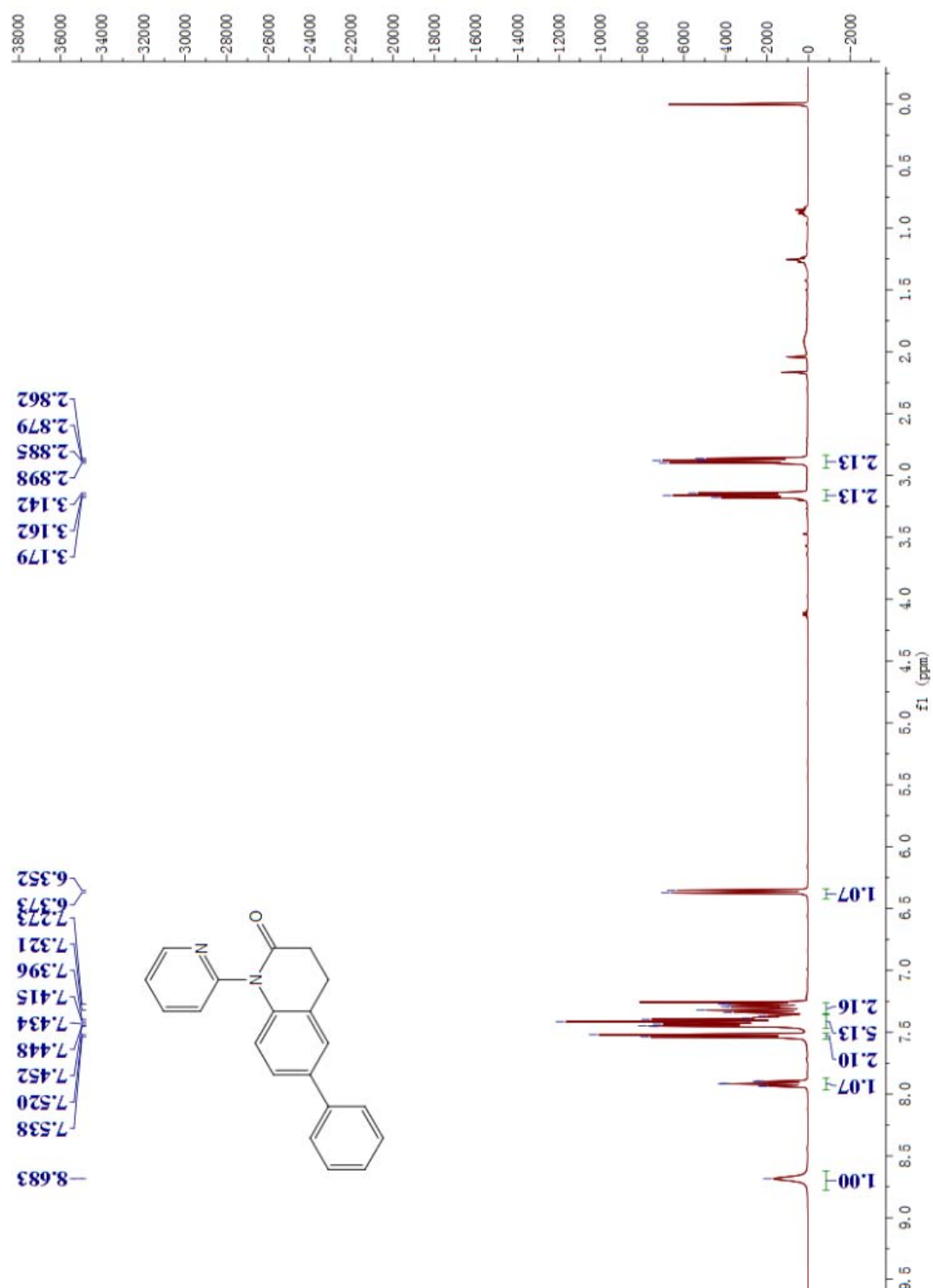
2.46e+002



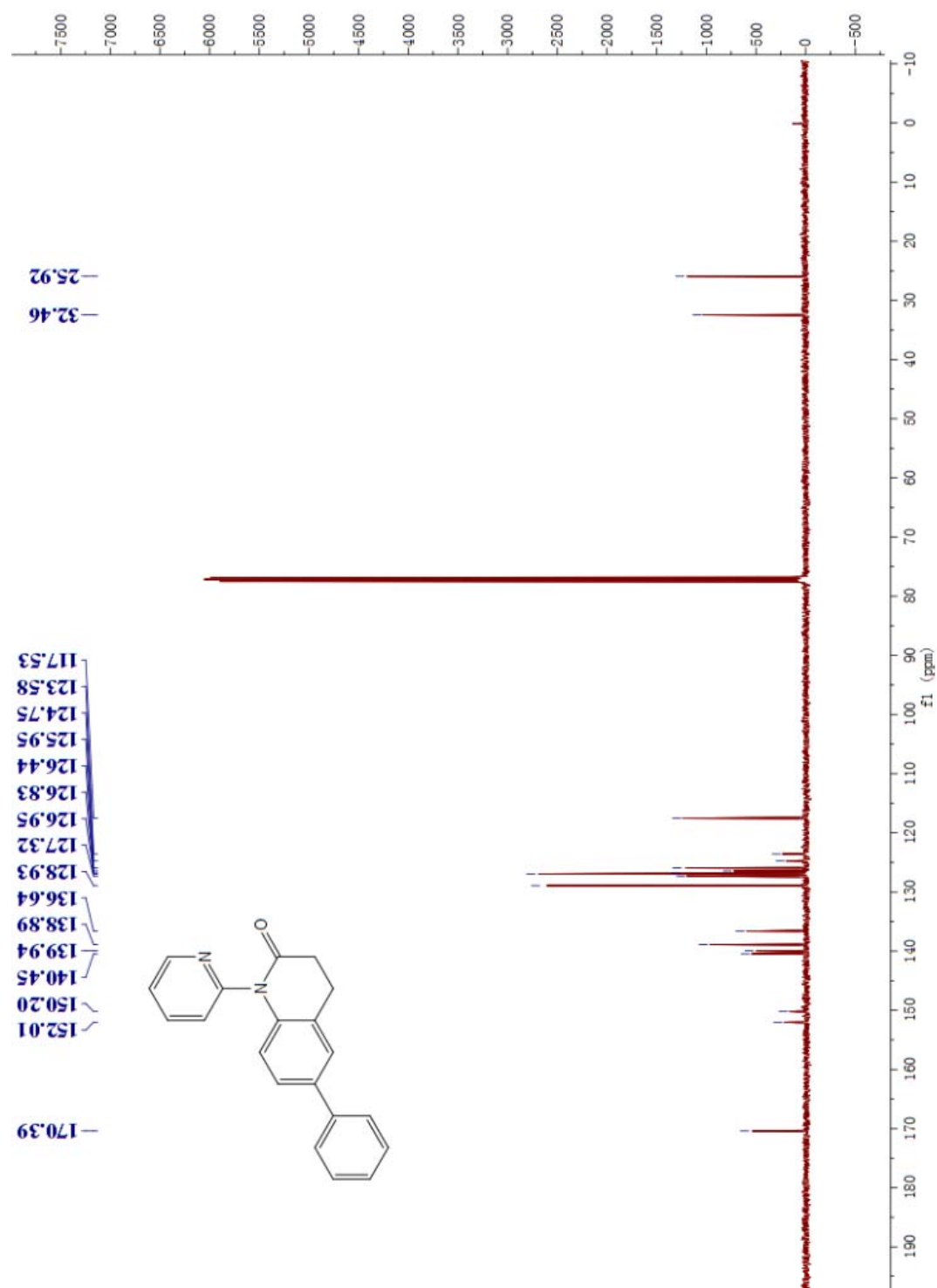
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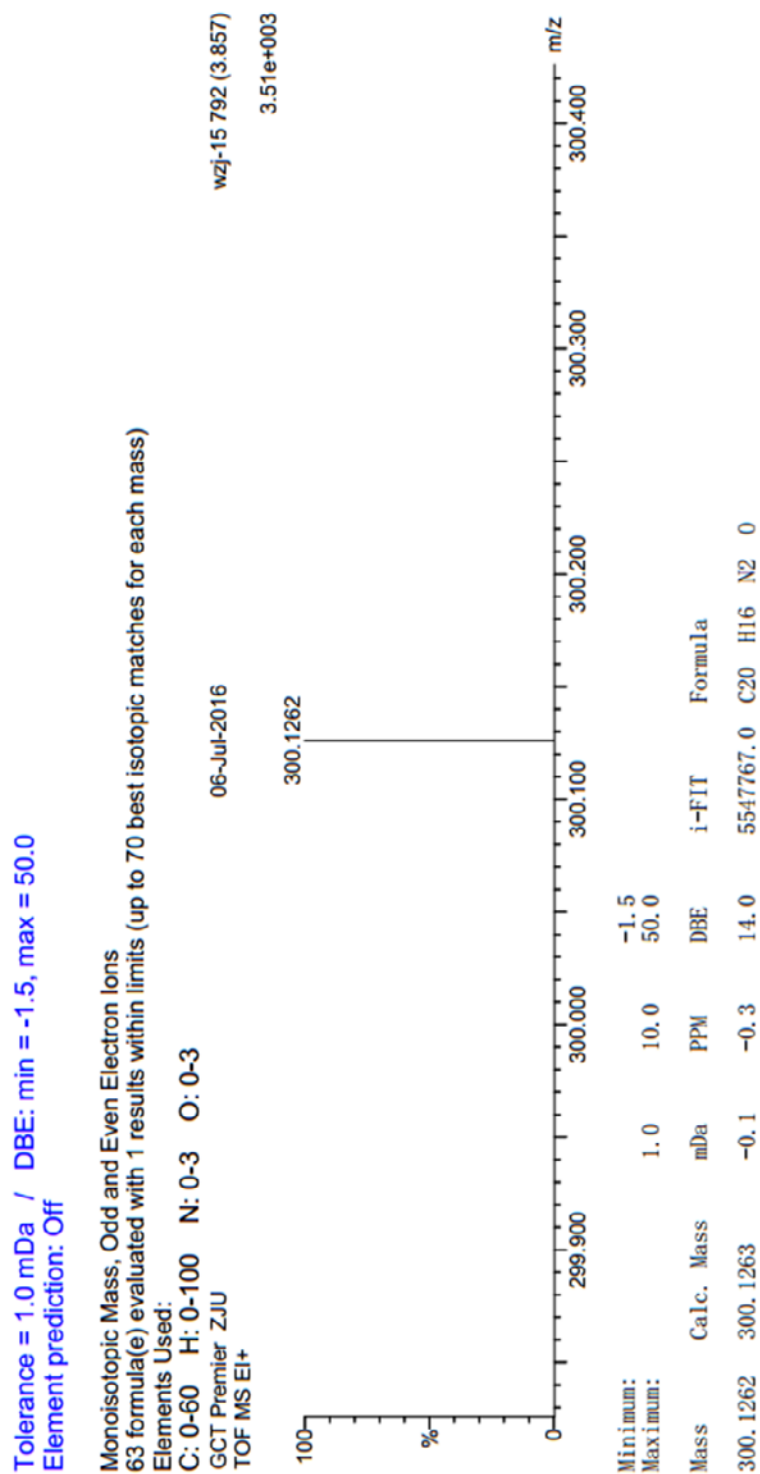
¹H NMR Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



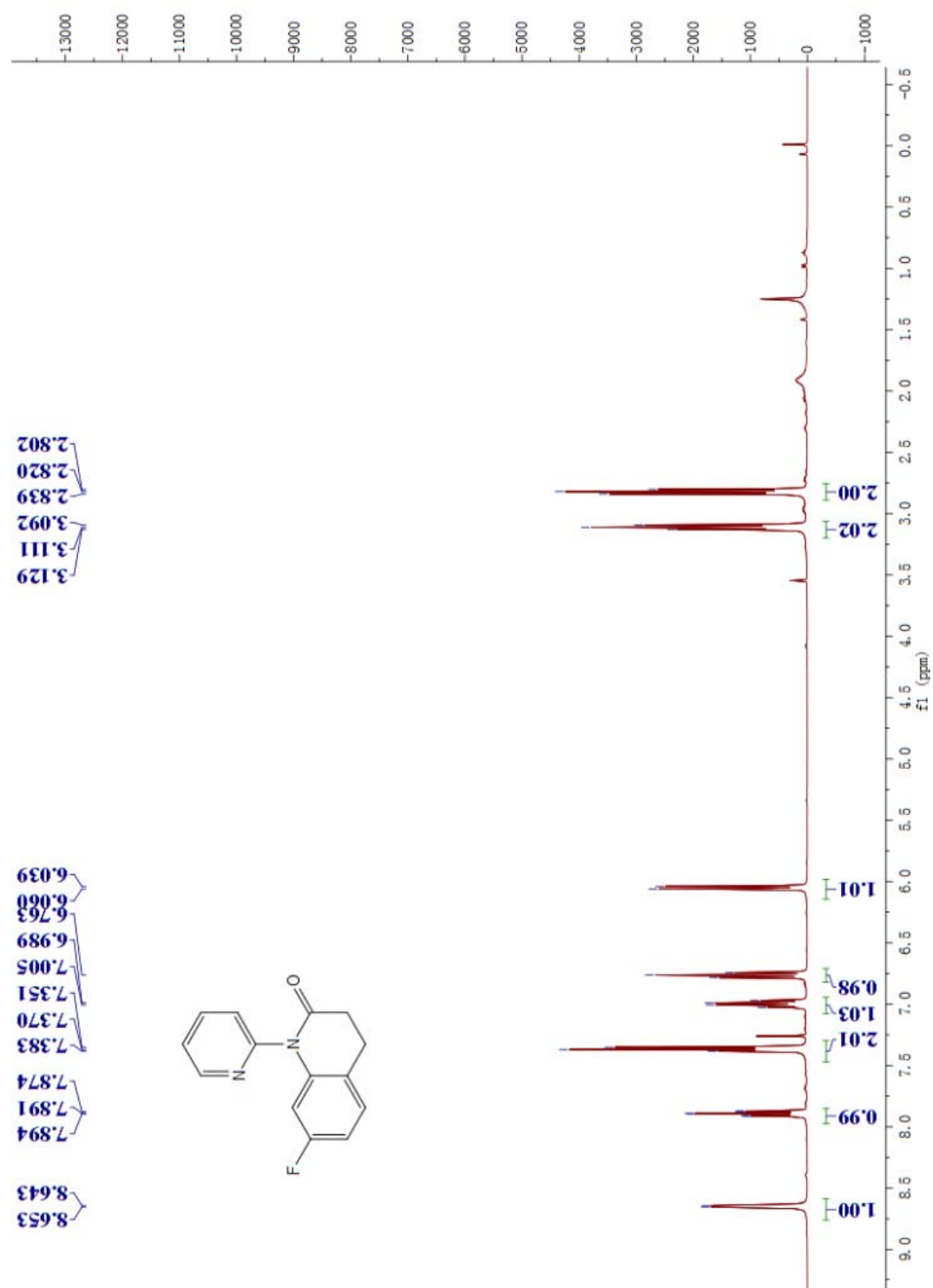
^{13}C NMR Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



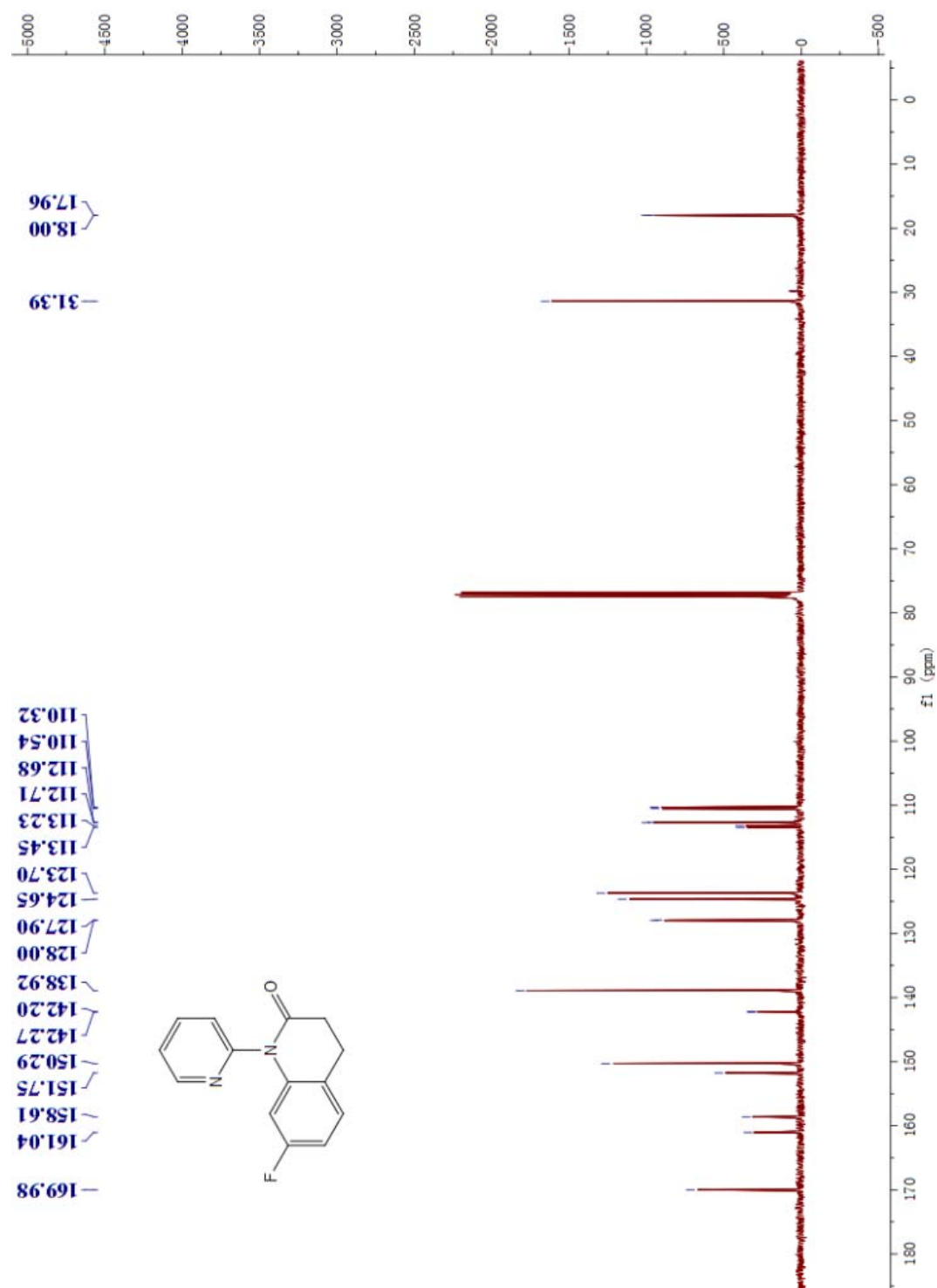
HR-MS Spectrum of 6-phenyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ia**



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



¹³C 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**

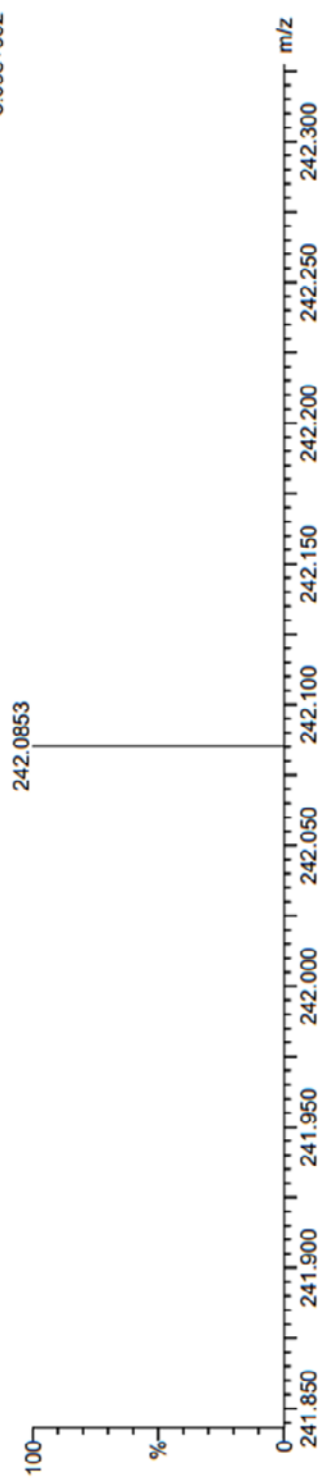
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
139 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-60 H: 0-100 N: 0-3 O: 0-3 F: 1-3

GCT Premier ZJU
TOF MS EI+

06-Jul-2016

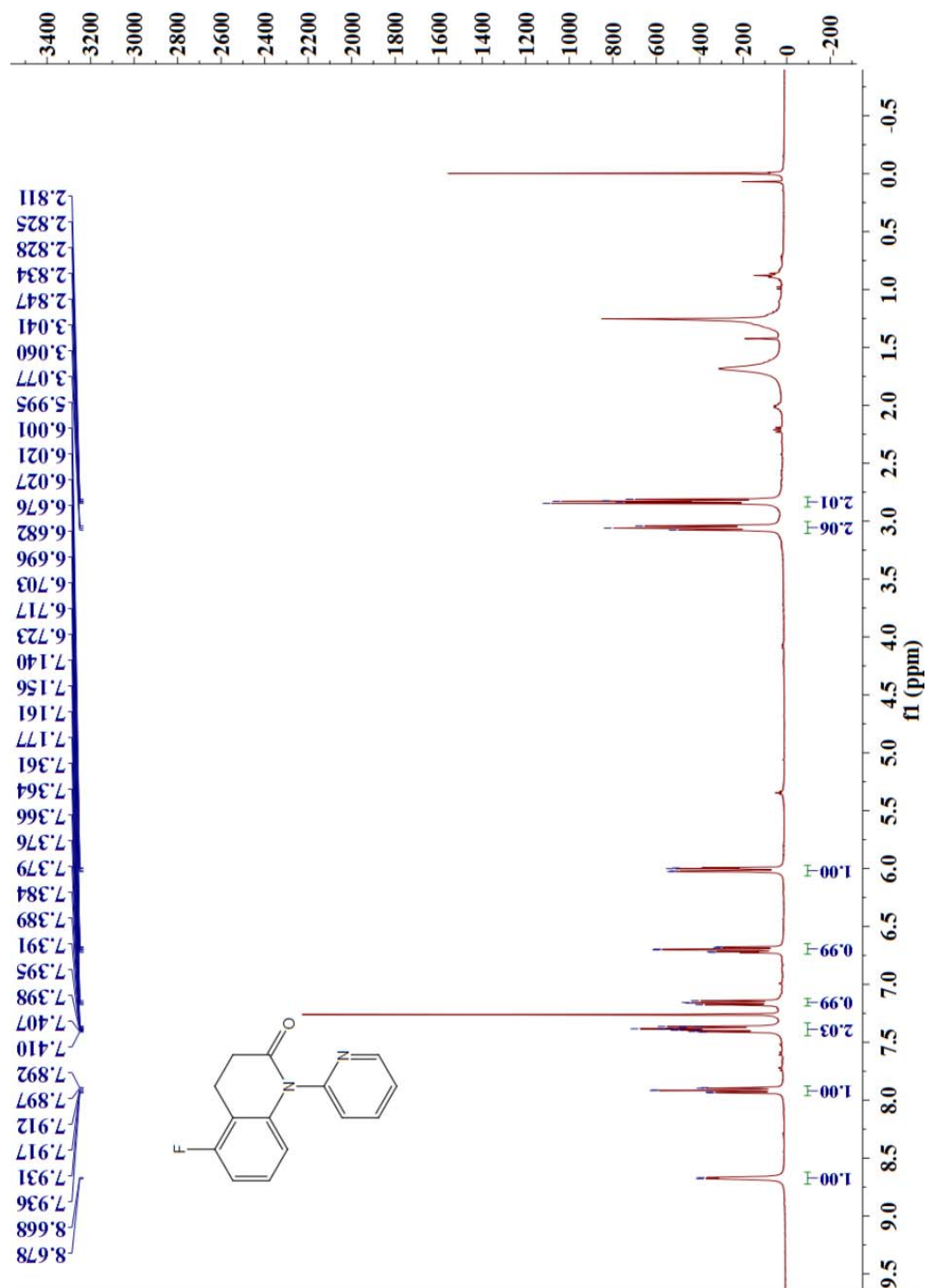
wzj-16-1 505 (2.805)
8.09e+002



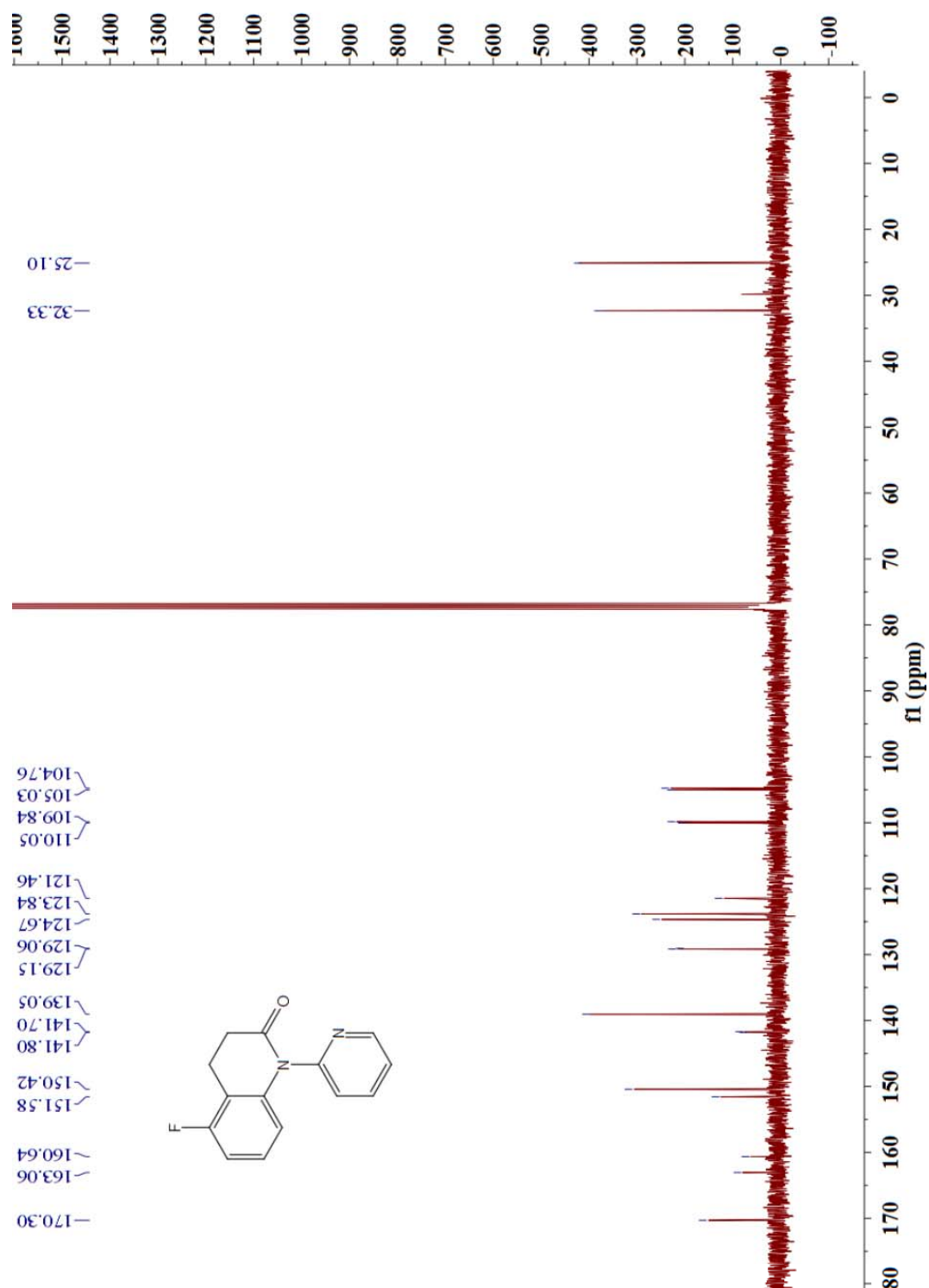
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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¹H NMR Spectrum of 5-fluoro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ja'**



¹³C 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**'

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 54 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

Elements Used:

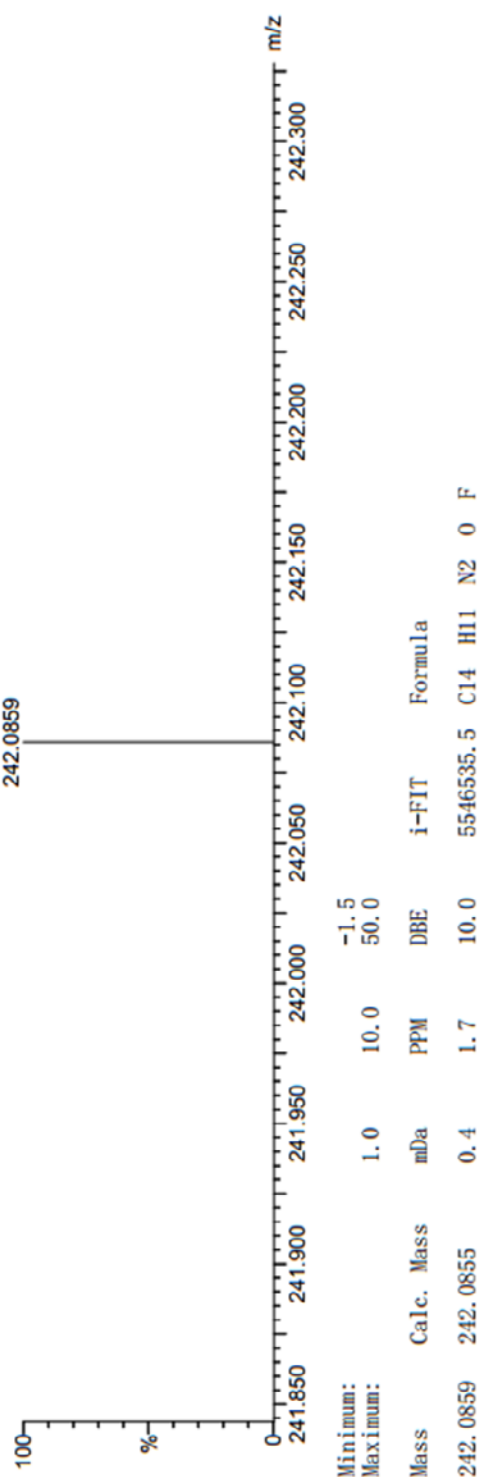
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GCT Premier ZJU

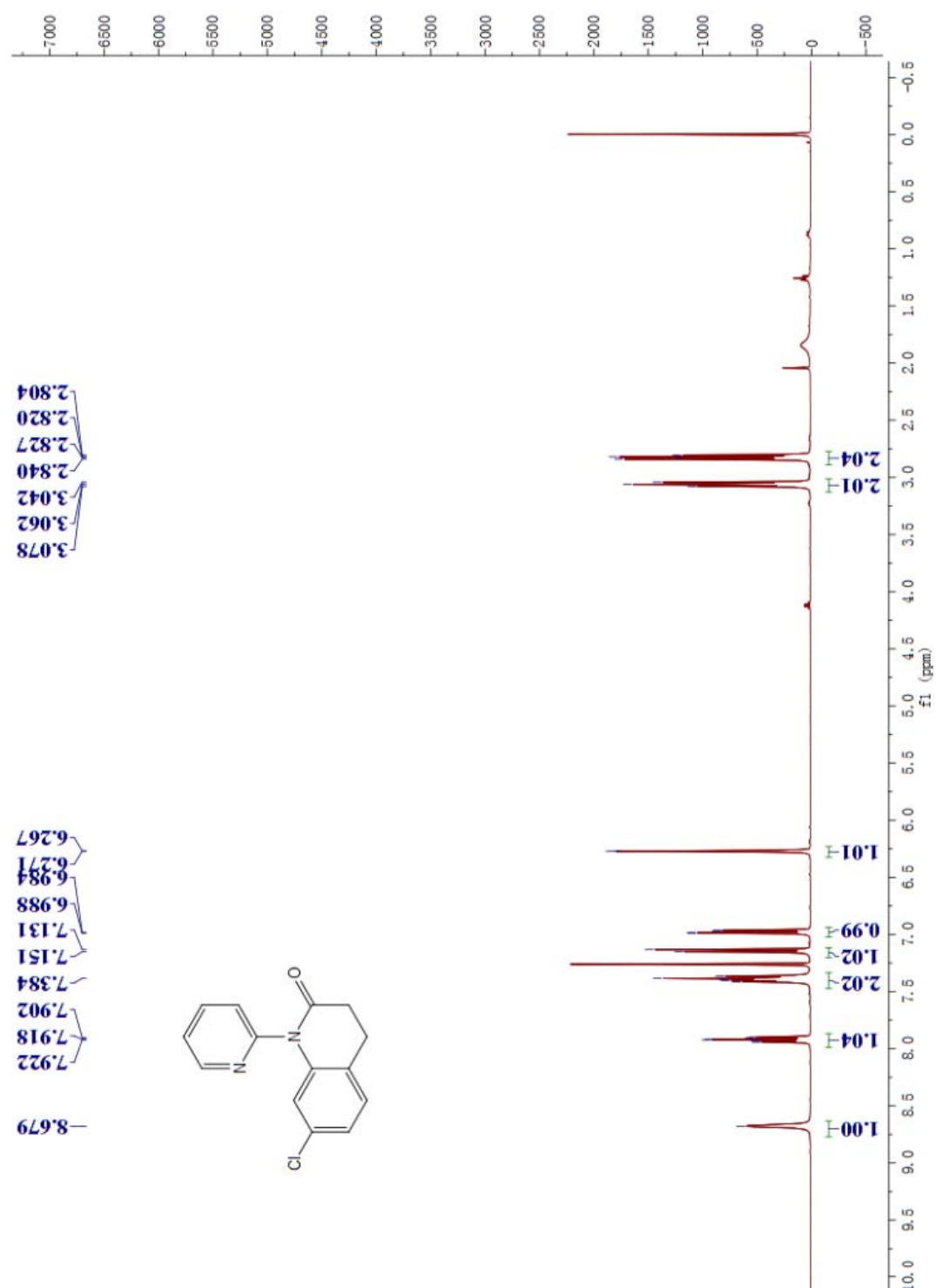
TOF MS EI+

06-Jul-2016

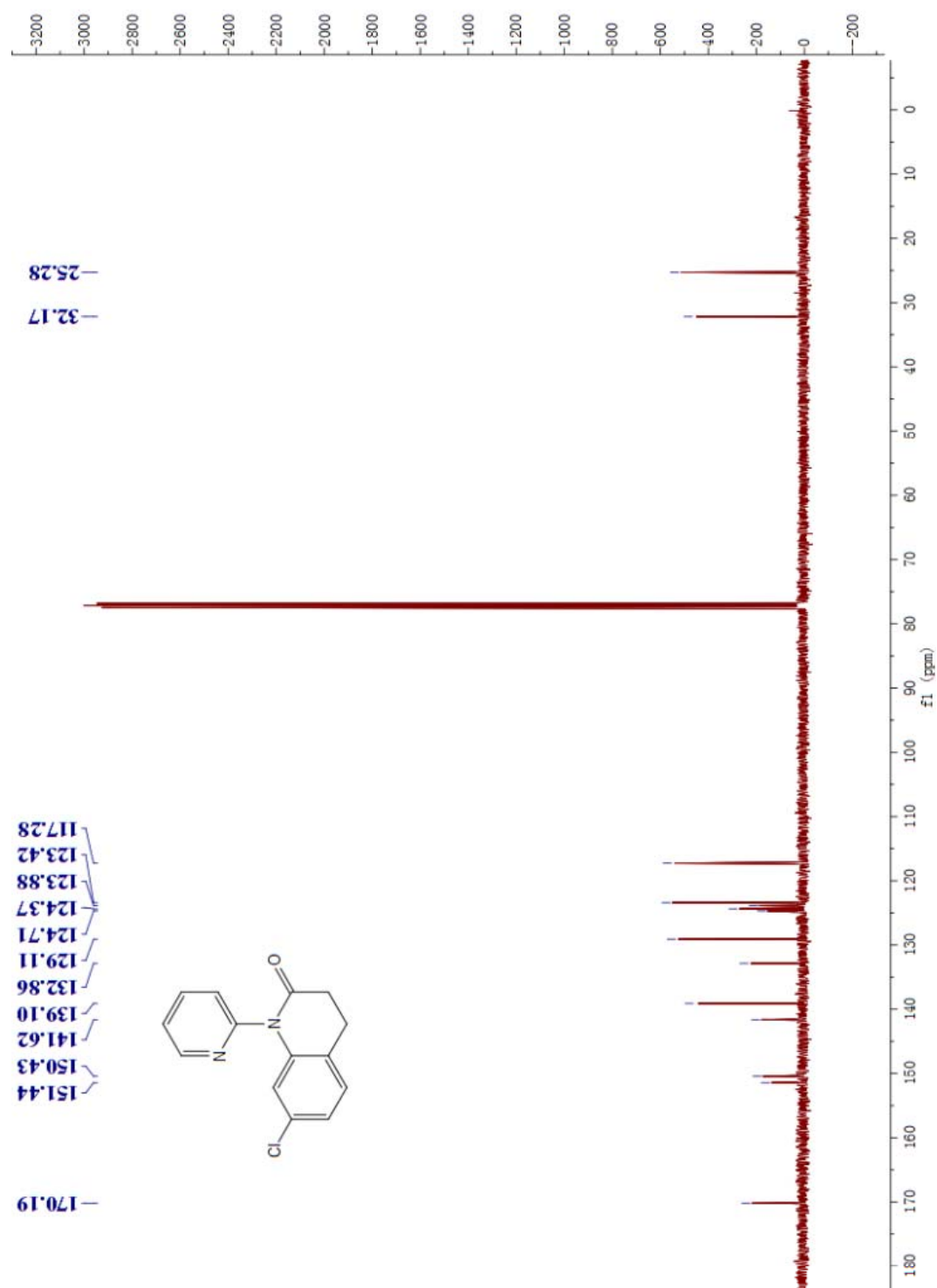
wzj-16-2 465 (2.658)
 1.07e+003



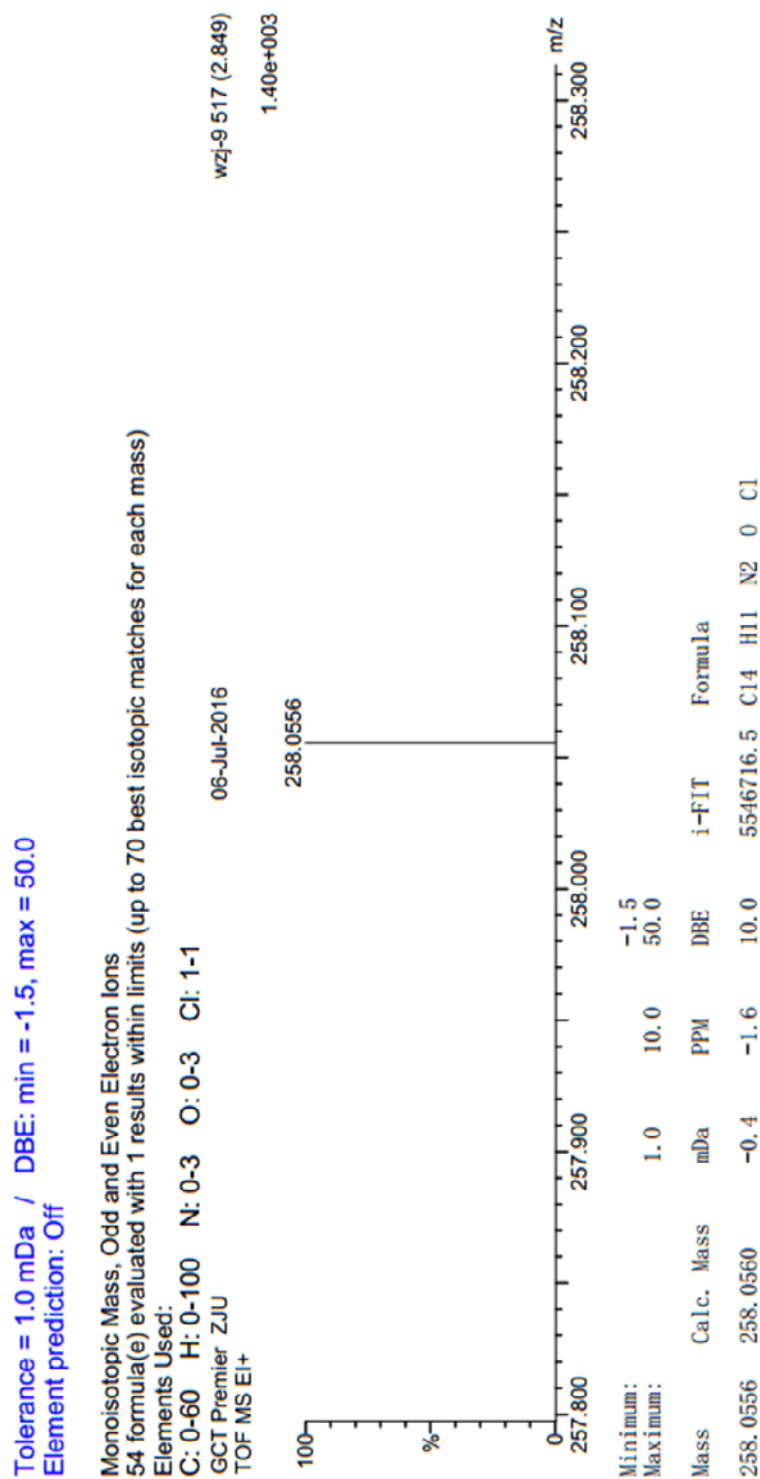
¹H NMR Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



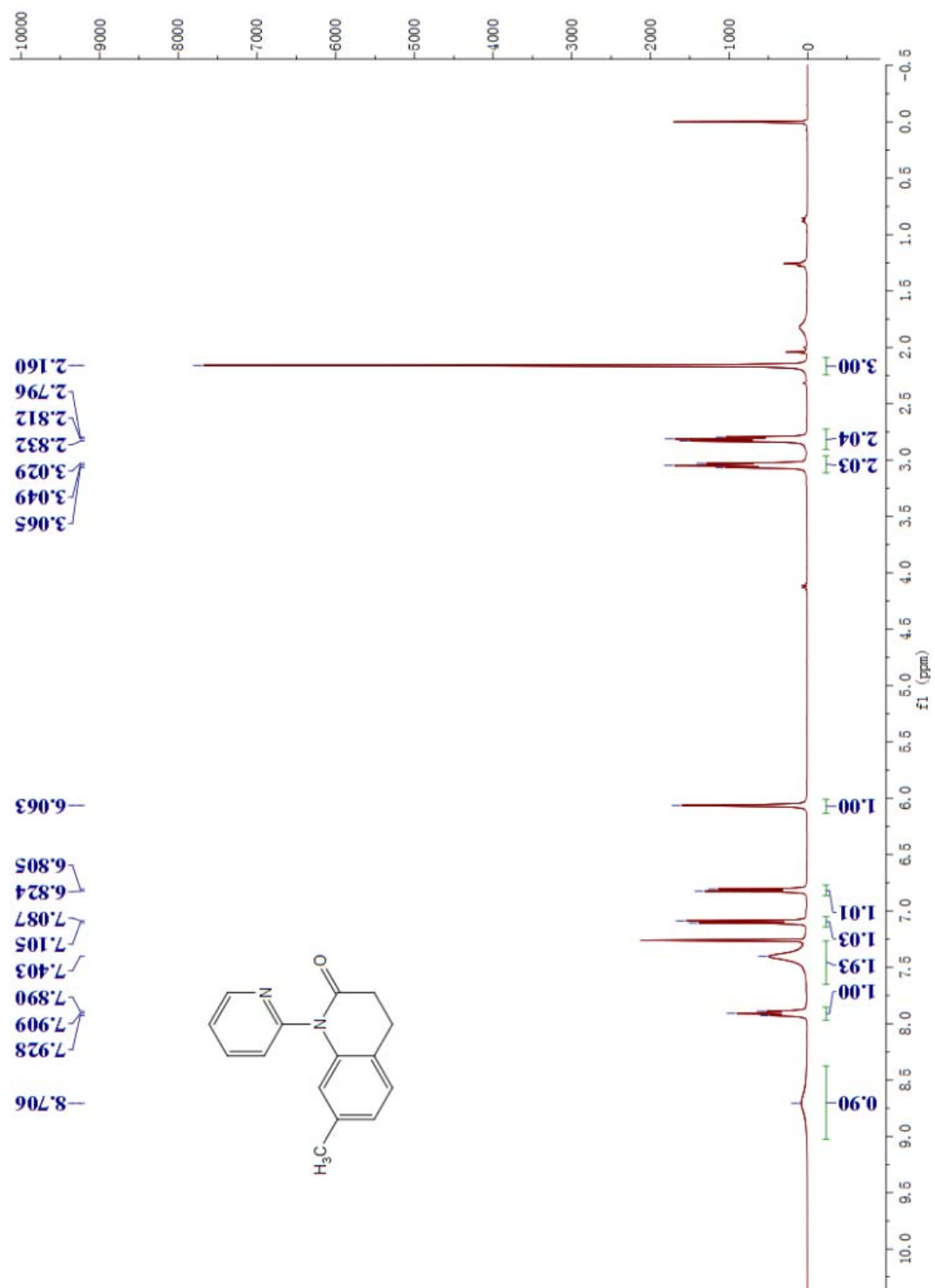
^{13}C NMR Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



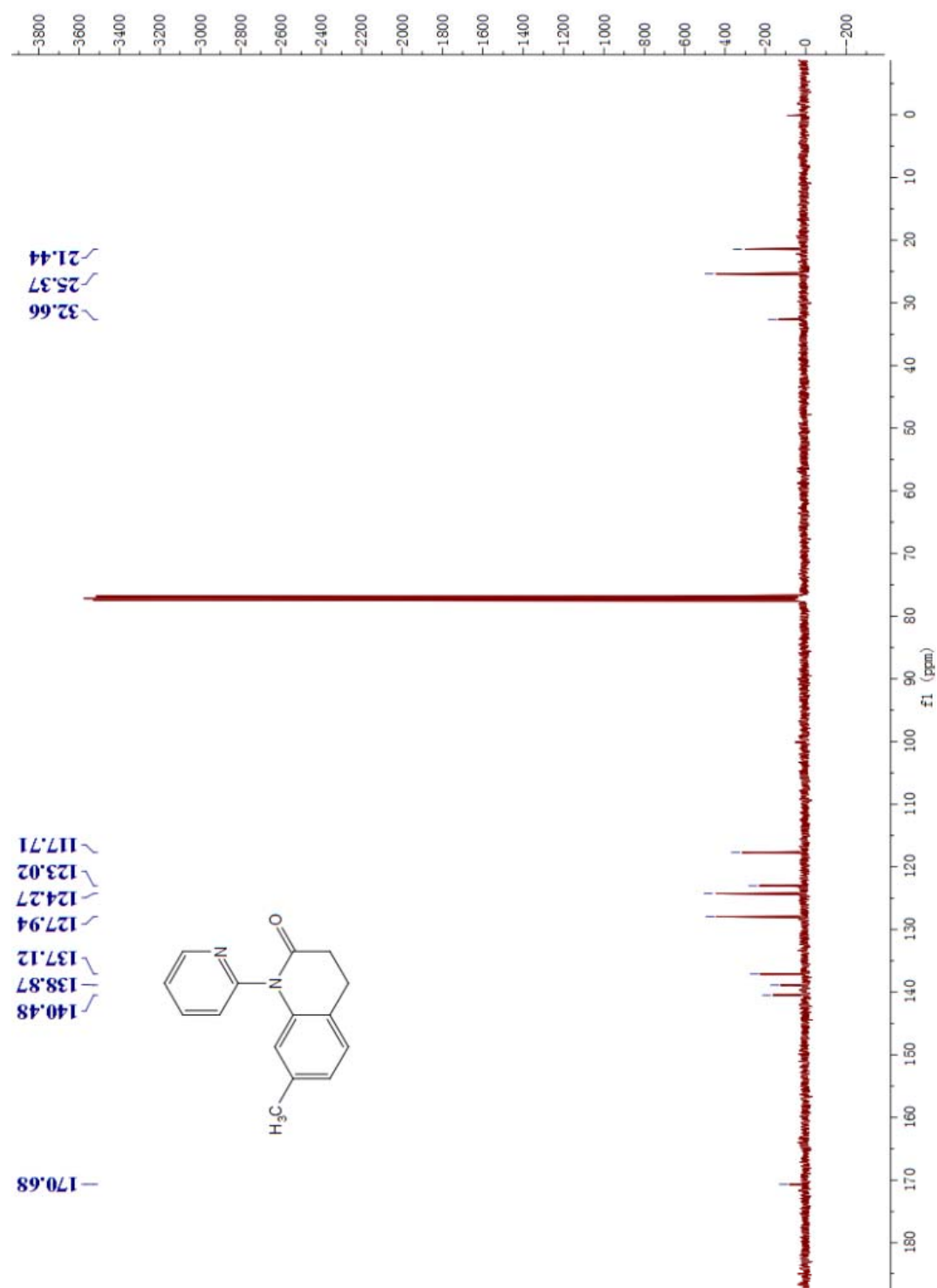
HR-MS Spectrum of 7-chloro-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ka**



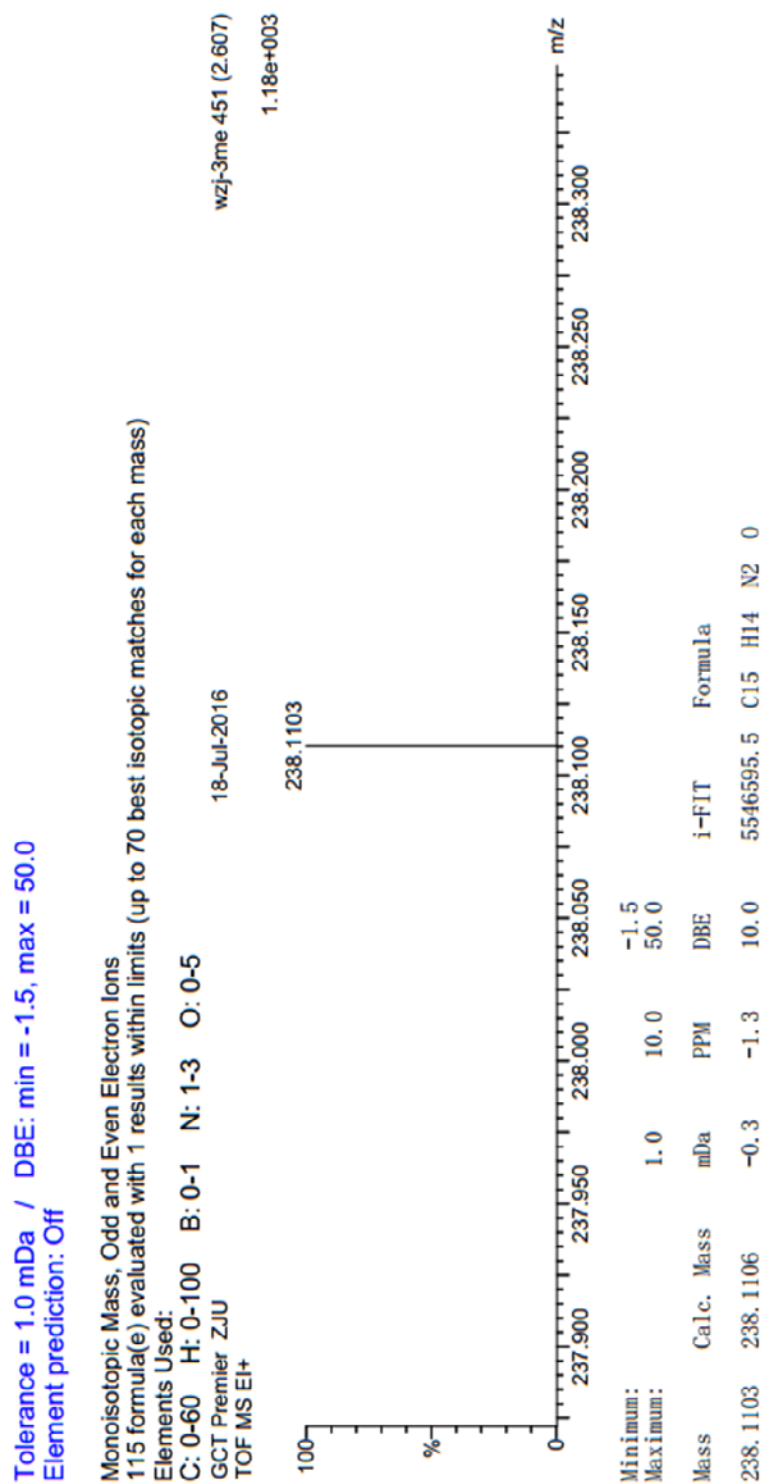
¹H NMR Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



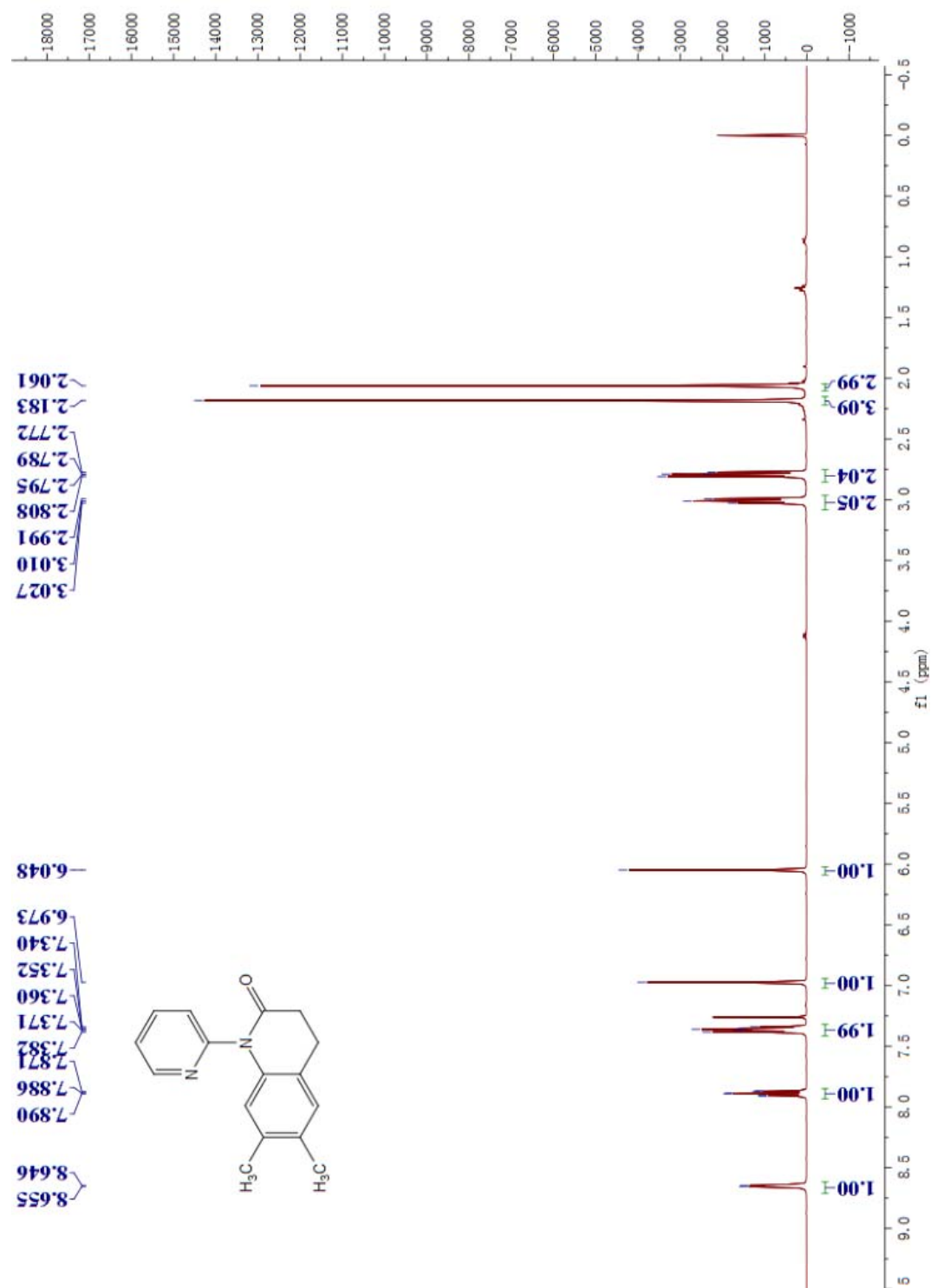
¹³C NMR Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



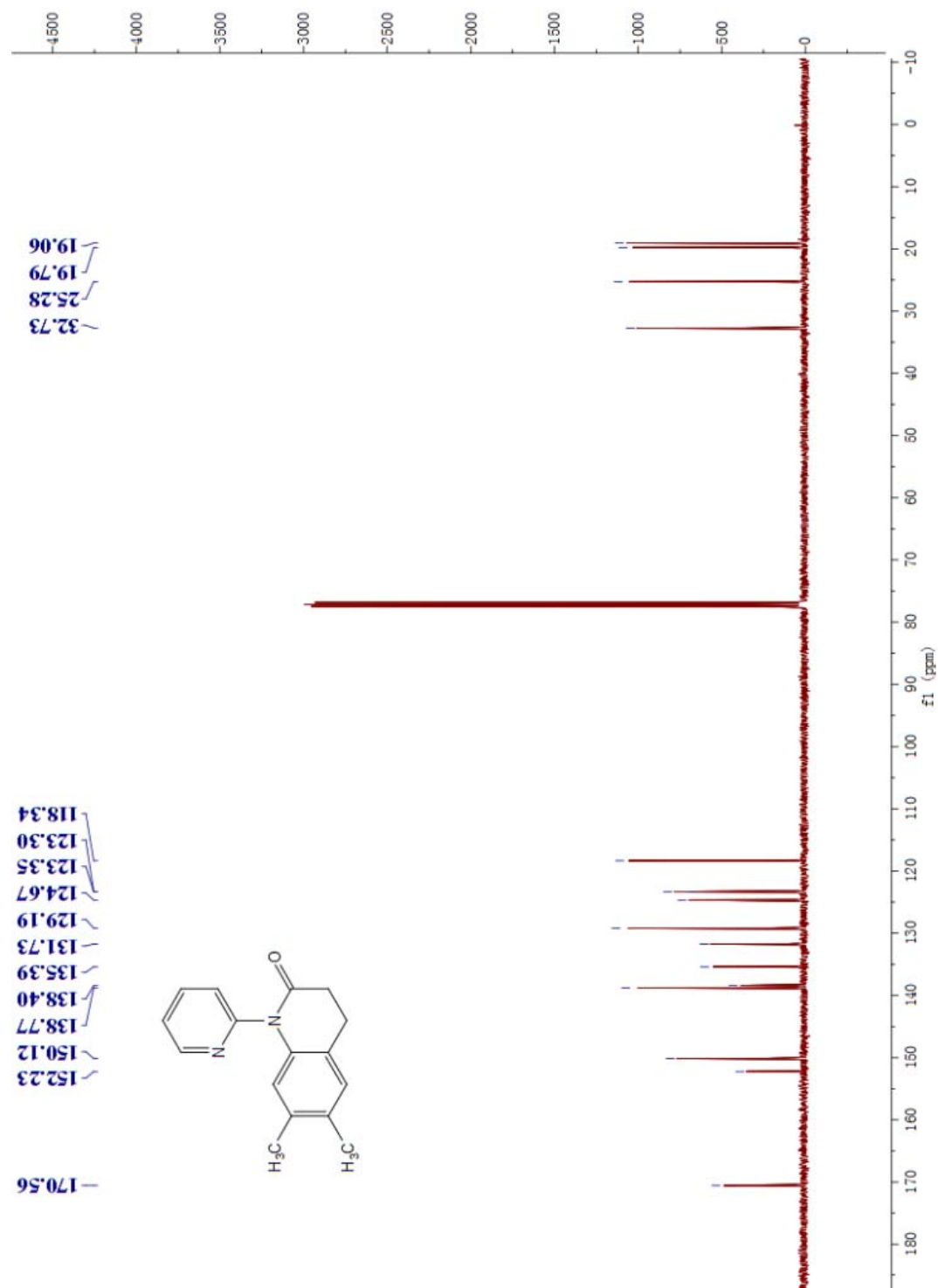
HR-MS Spectrum of 7-methyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3la**



¹H 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-dihydroquinolin-2(1H)-one **3ma**



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

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 59 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

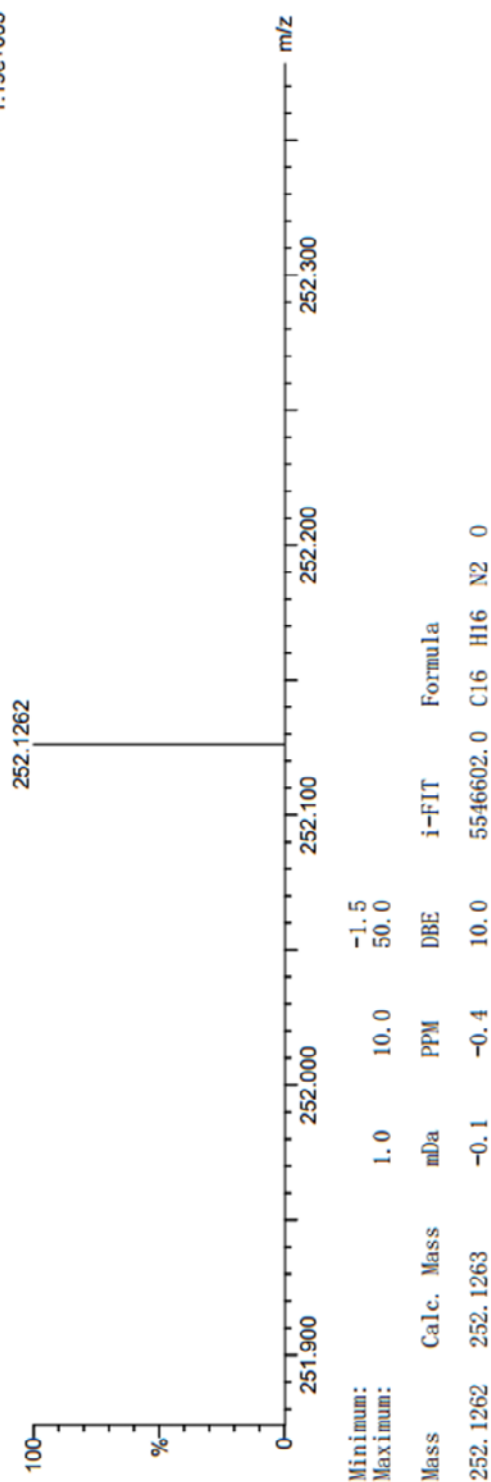
Elements Used:

C: 0-60 H: 0-100 N: 0-3 O: 0-3

GCT Premier ZJU

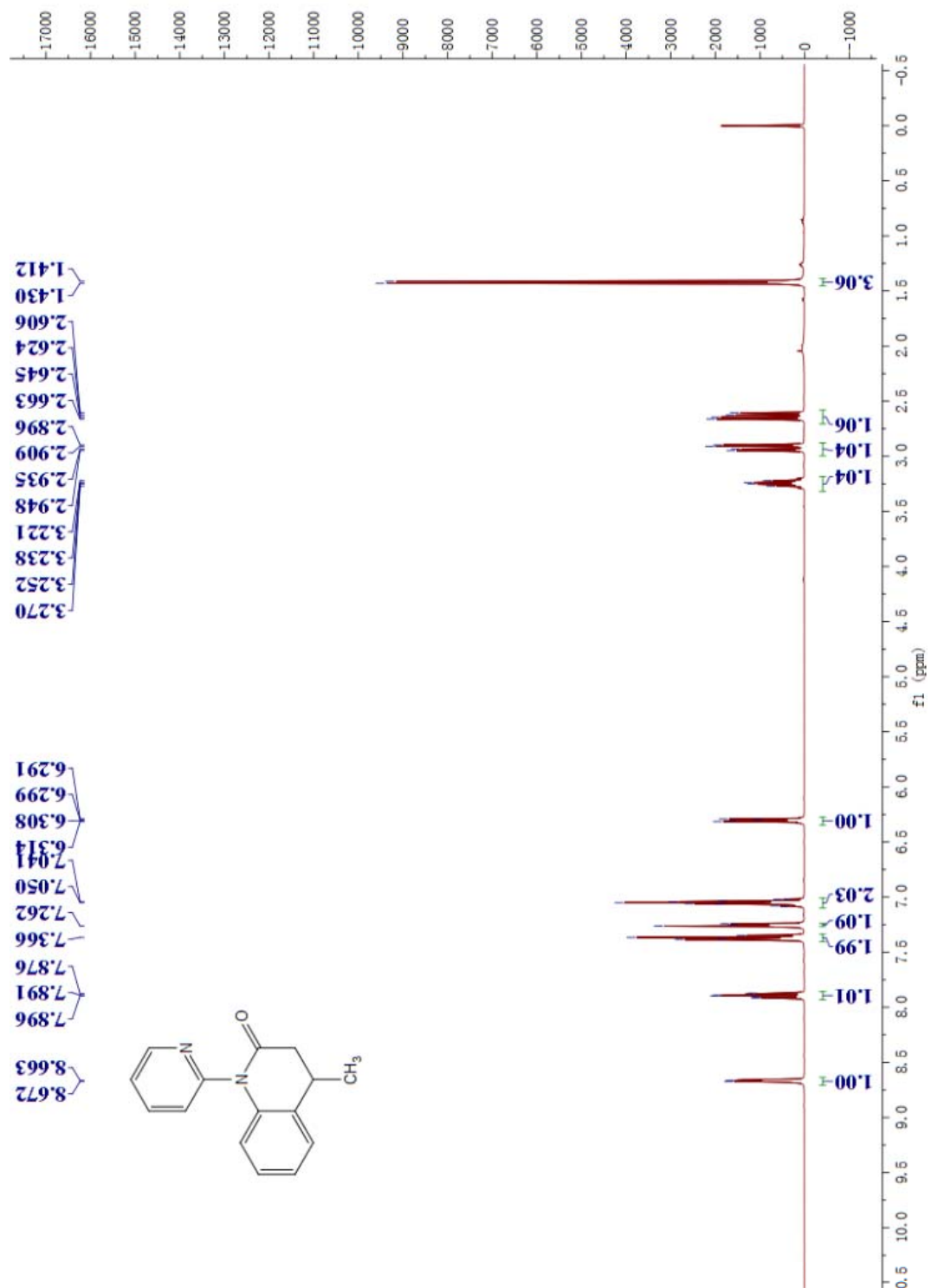
TOF MS EI+

06-Jul-2016

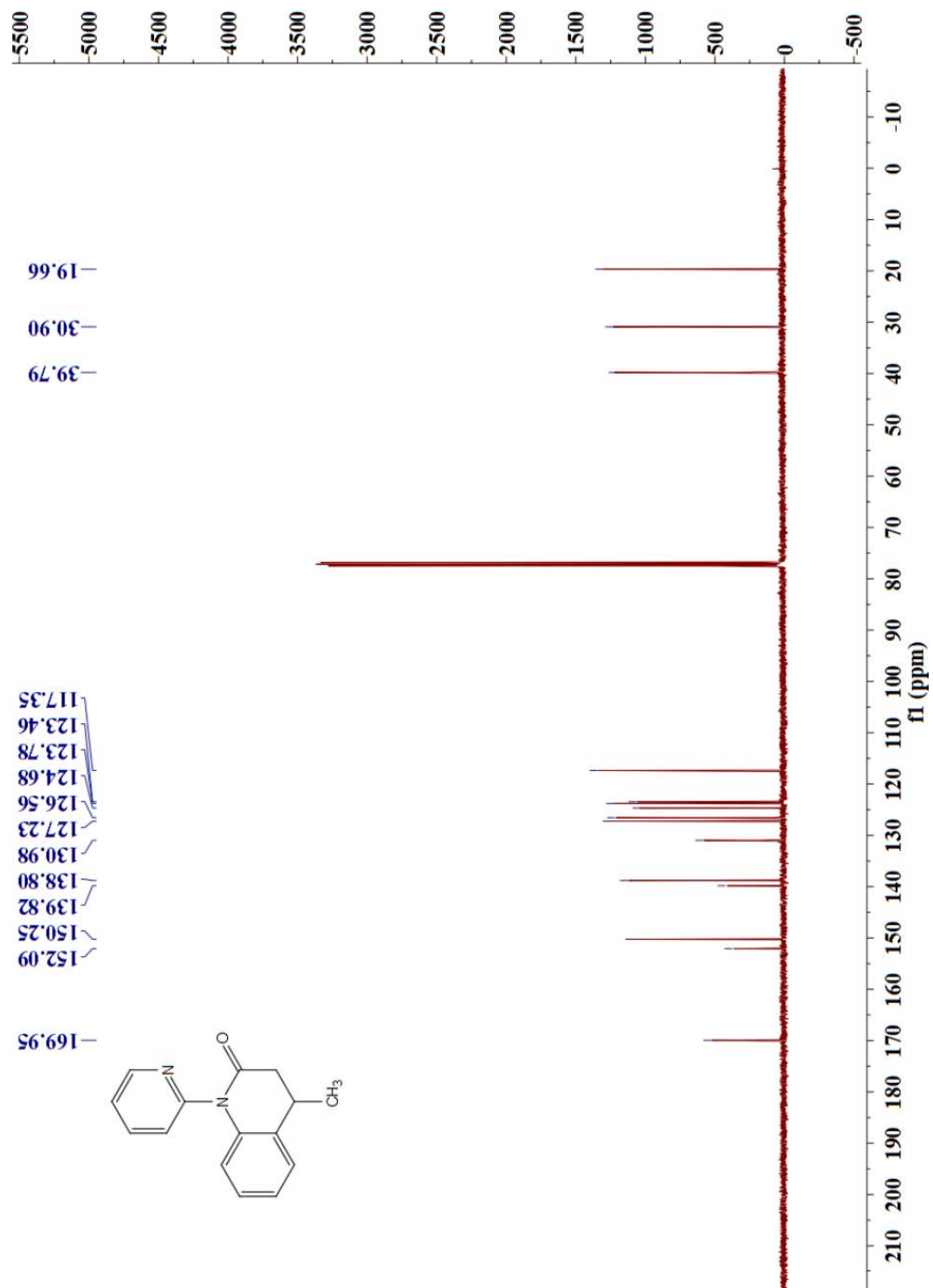


Minimum: -1.5
 Maximum: 50.0

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



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



2(1H)-one **3ab**



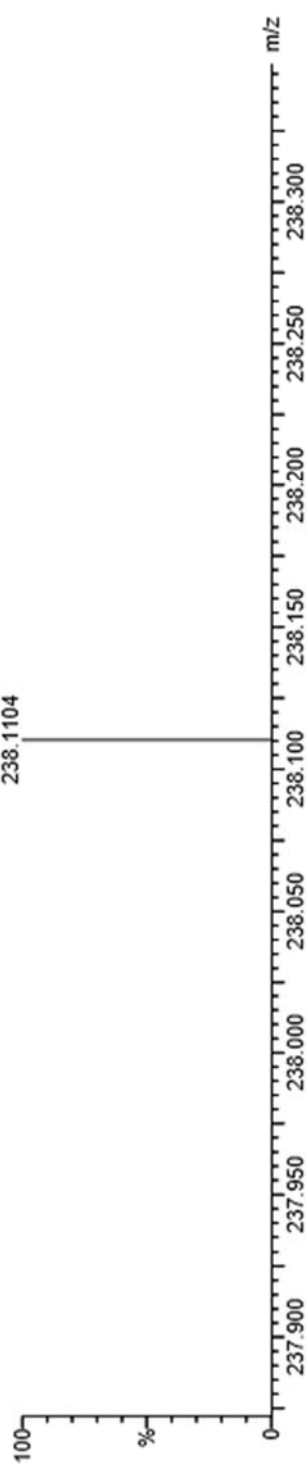
Monoisotopic Mass, Odd and Even Electron Ions
56 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

C: 0-60 H: 0-100 N: 0-3 O: 0-3

GCT Premier ZJU

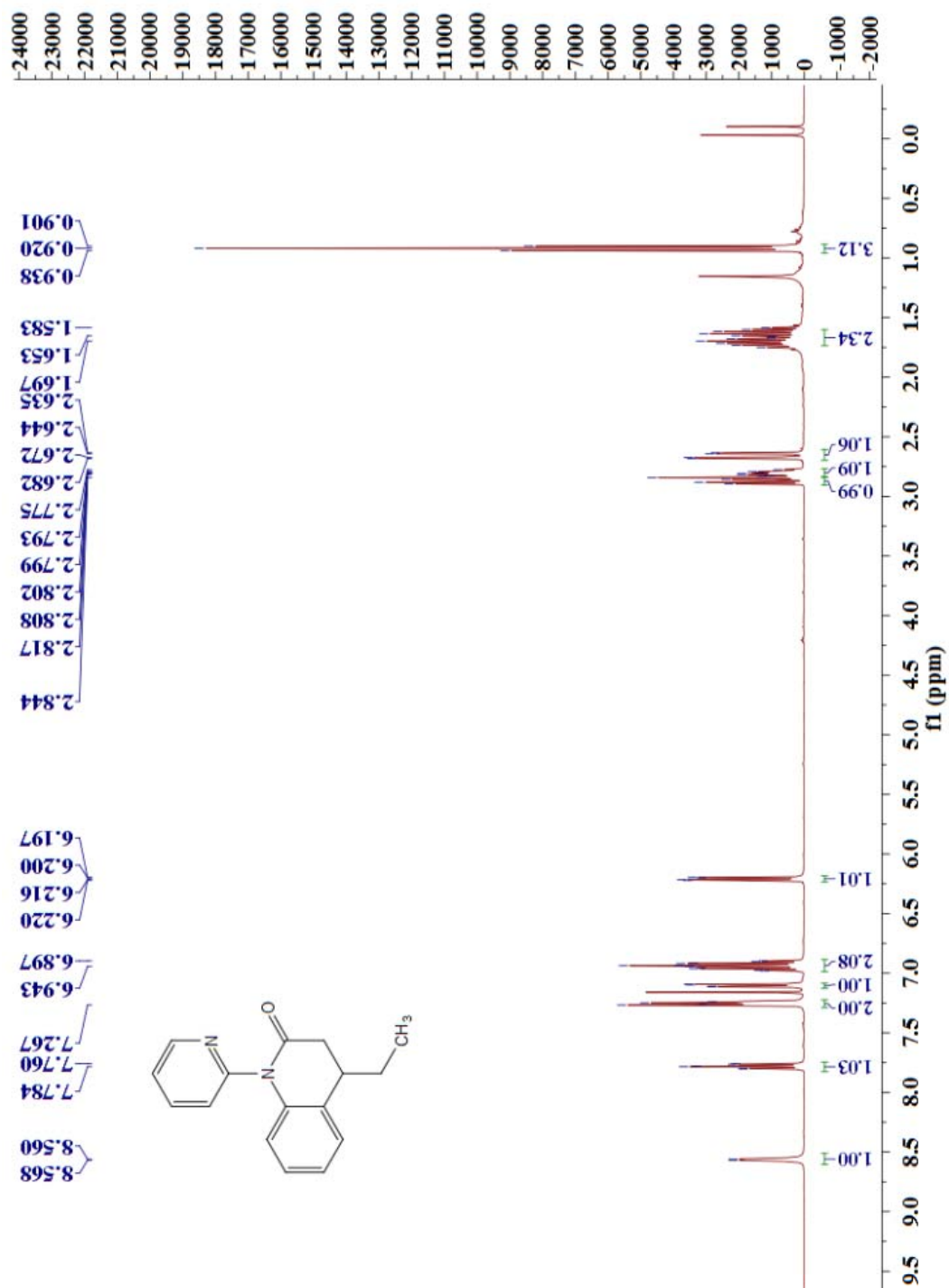
06-Jul-2016

1.93e+003

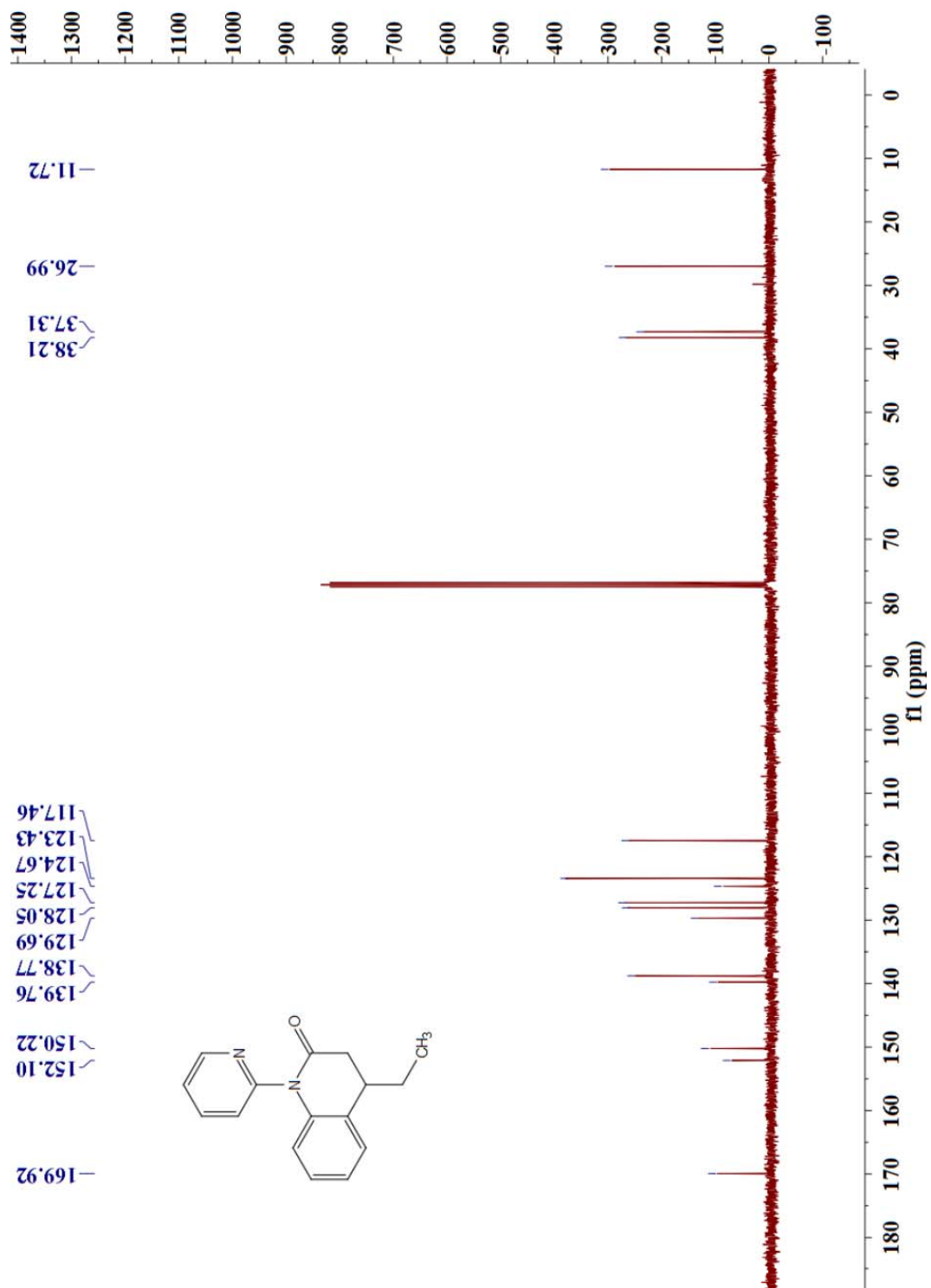


Minimum:					-1.5	
Maximum:		1.0	10.0		50.0	
Mass	Calc. Mass	mDa	PPM	DEE	i-FIT	Formula
238.1104	238.1106	-0.2	-0.8	10.0	5546869.0	C15 H14 N2 O

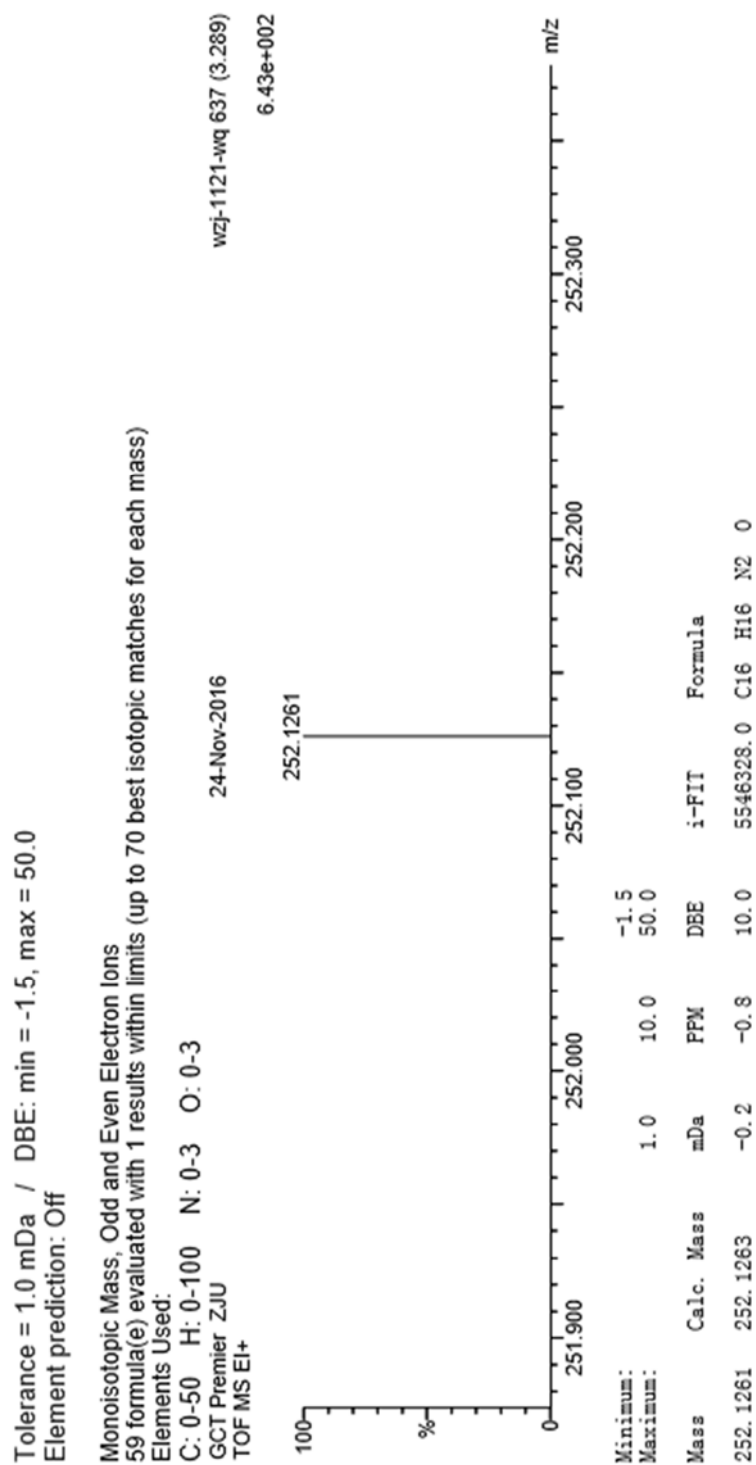
¹H NMR Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



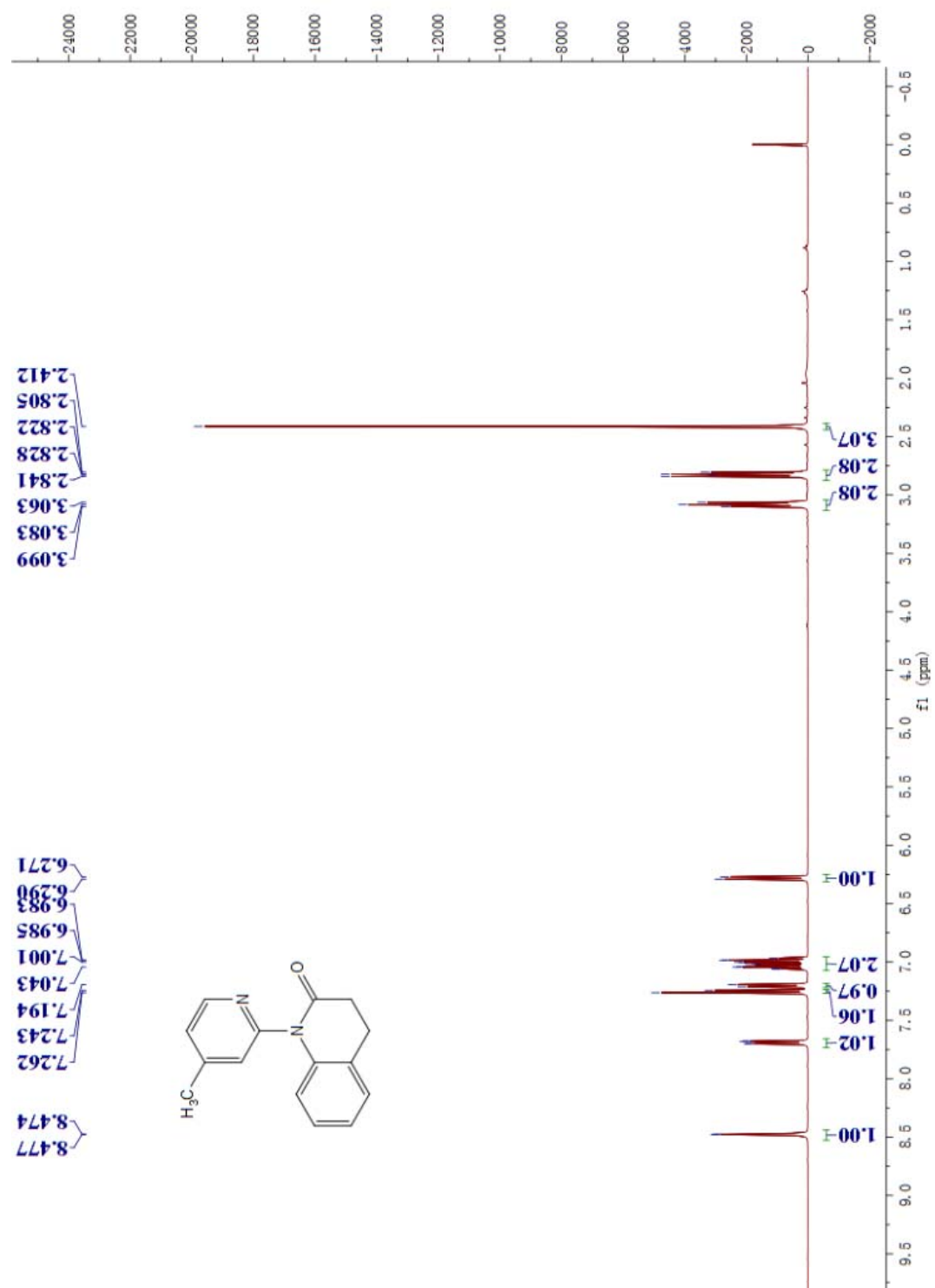
^{13}C NMR Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



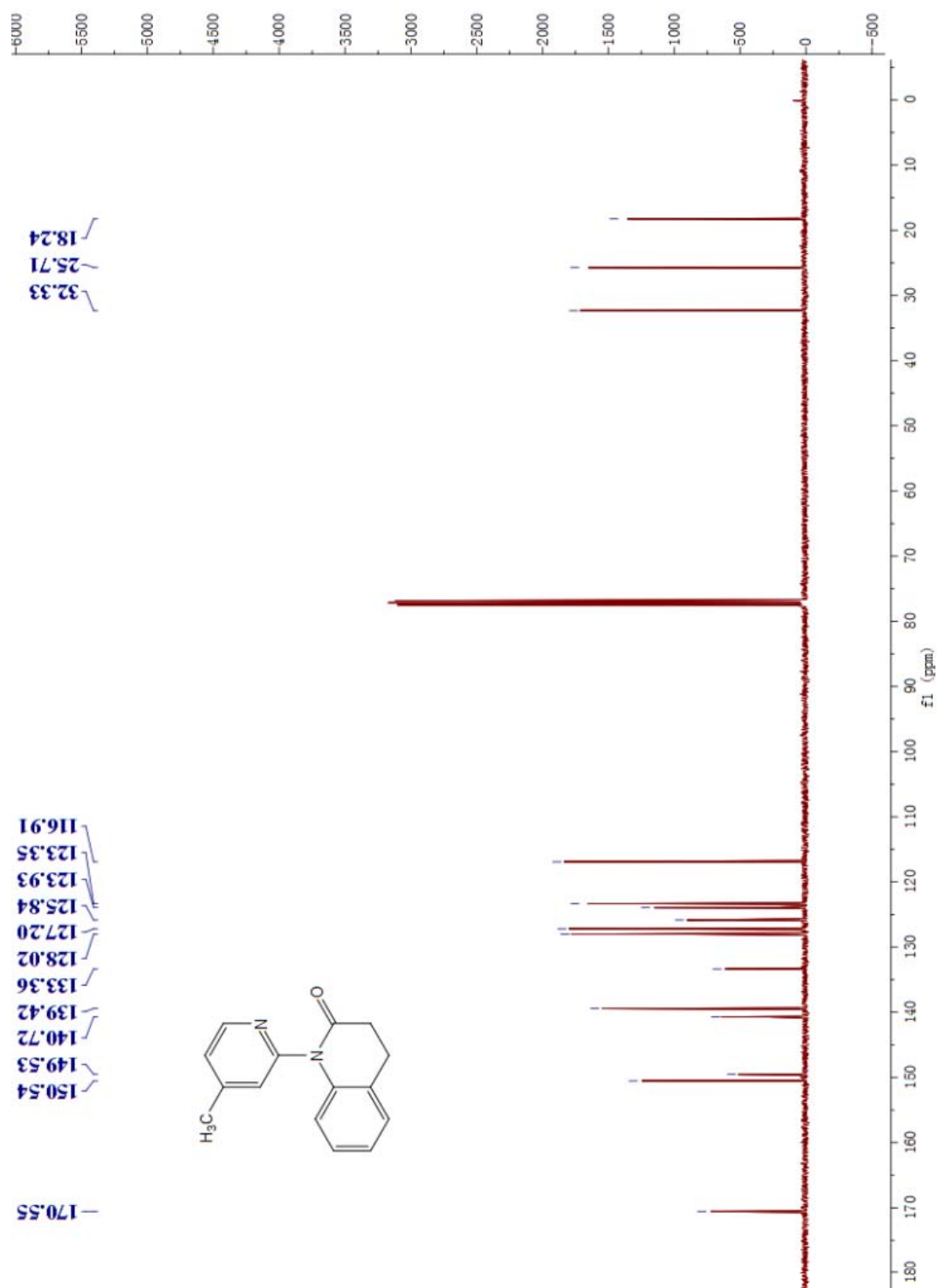
HR-MS Spectrum of 4-ethyl-1-(pyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3ac**



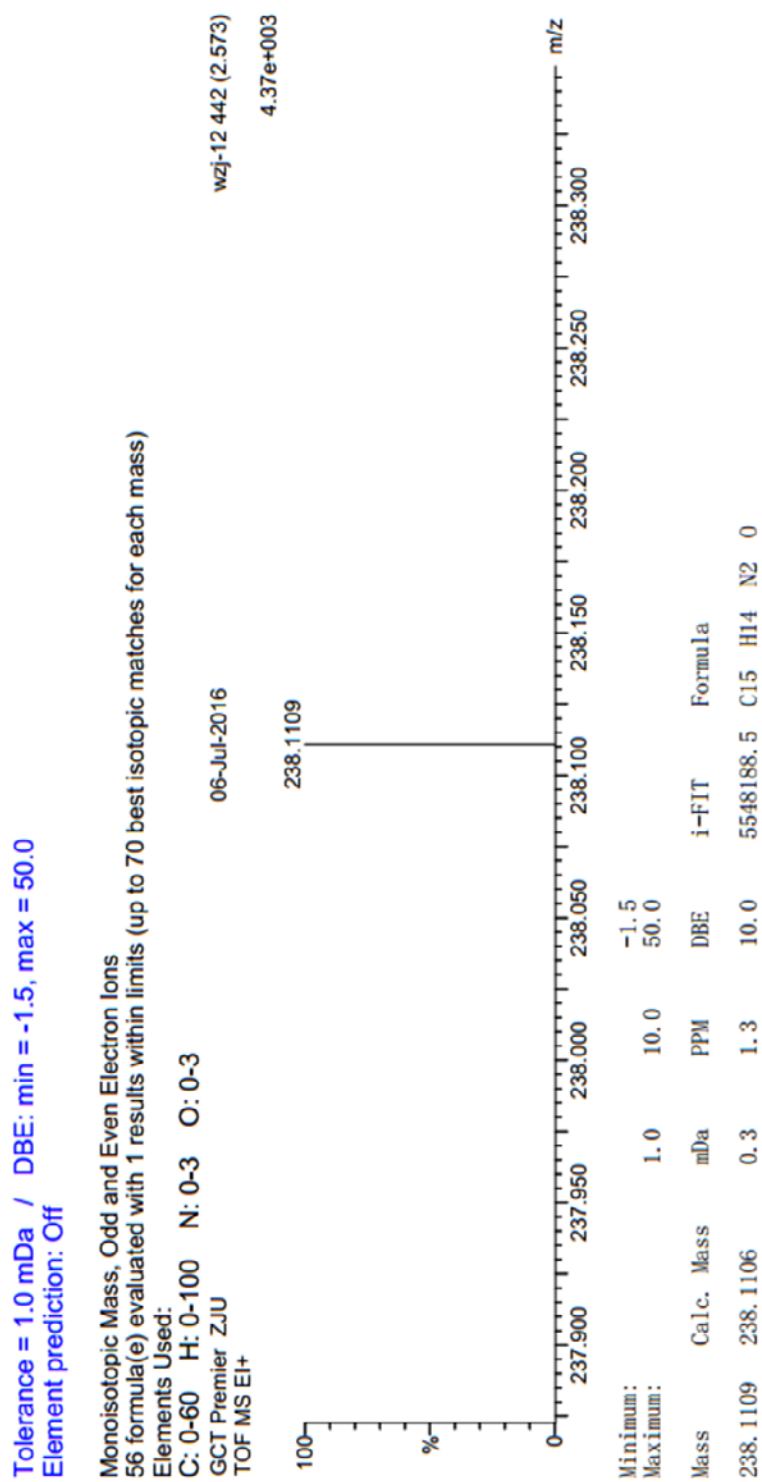
¹H NMR Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3na**



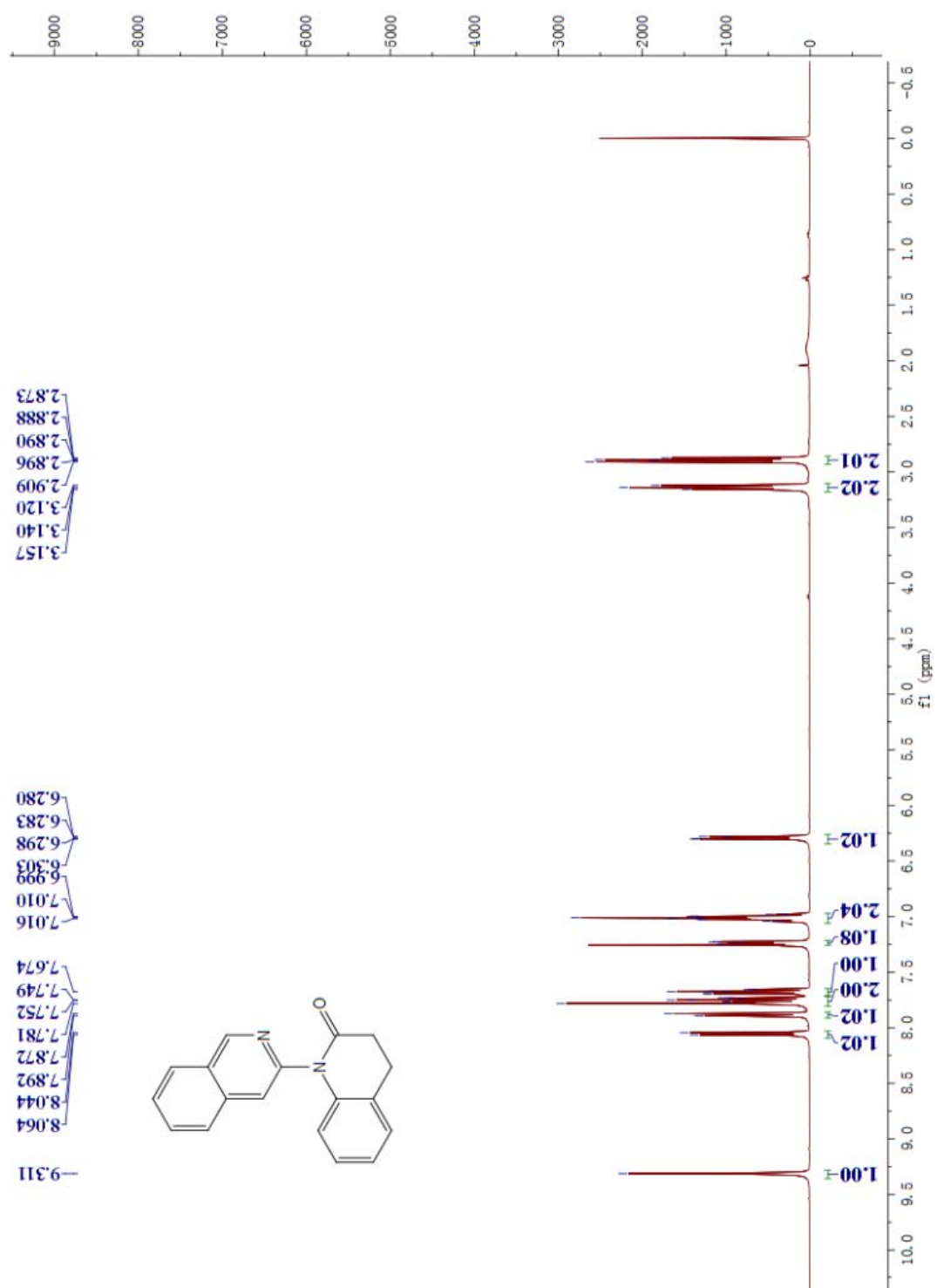
¹³C NMR Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3na**



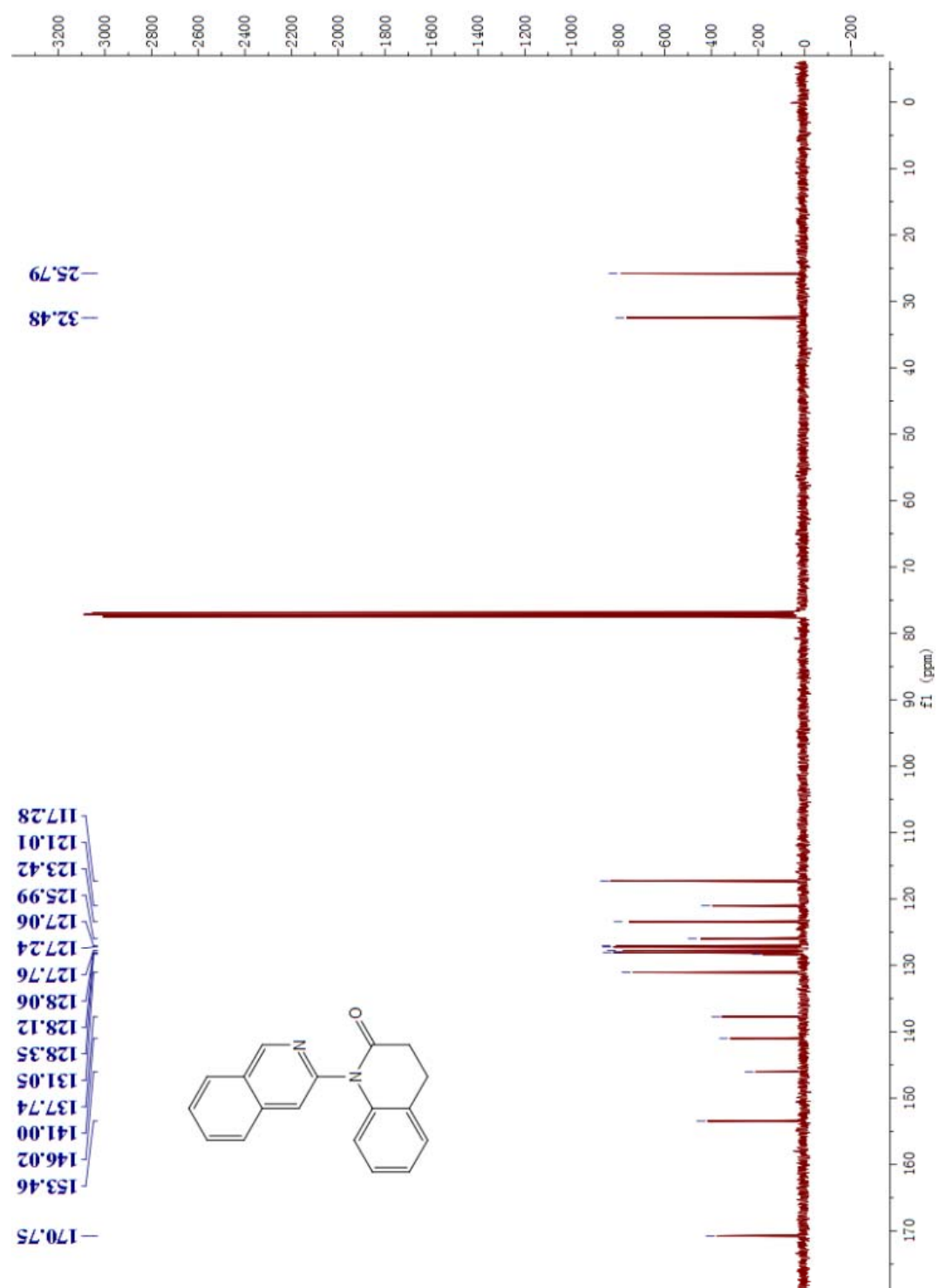
HR-MS Spectrum of 1-(4-methylpyridin-2-yl)-3,4-dihydroquinolin-2(1H)-one **3na**



¹H NMR Spectrum of 1-(isoquinolin-3-yl)-3,4-dihydroquinolin-2(1H)-one **30a**

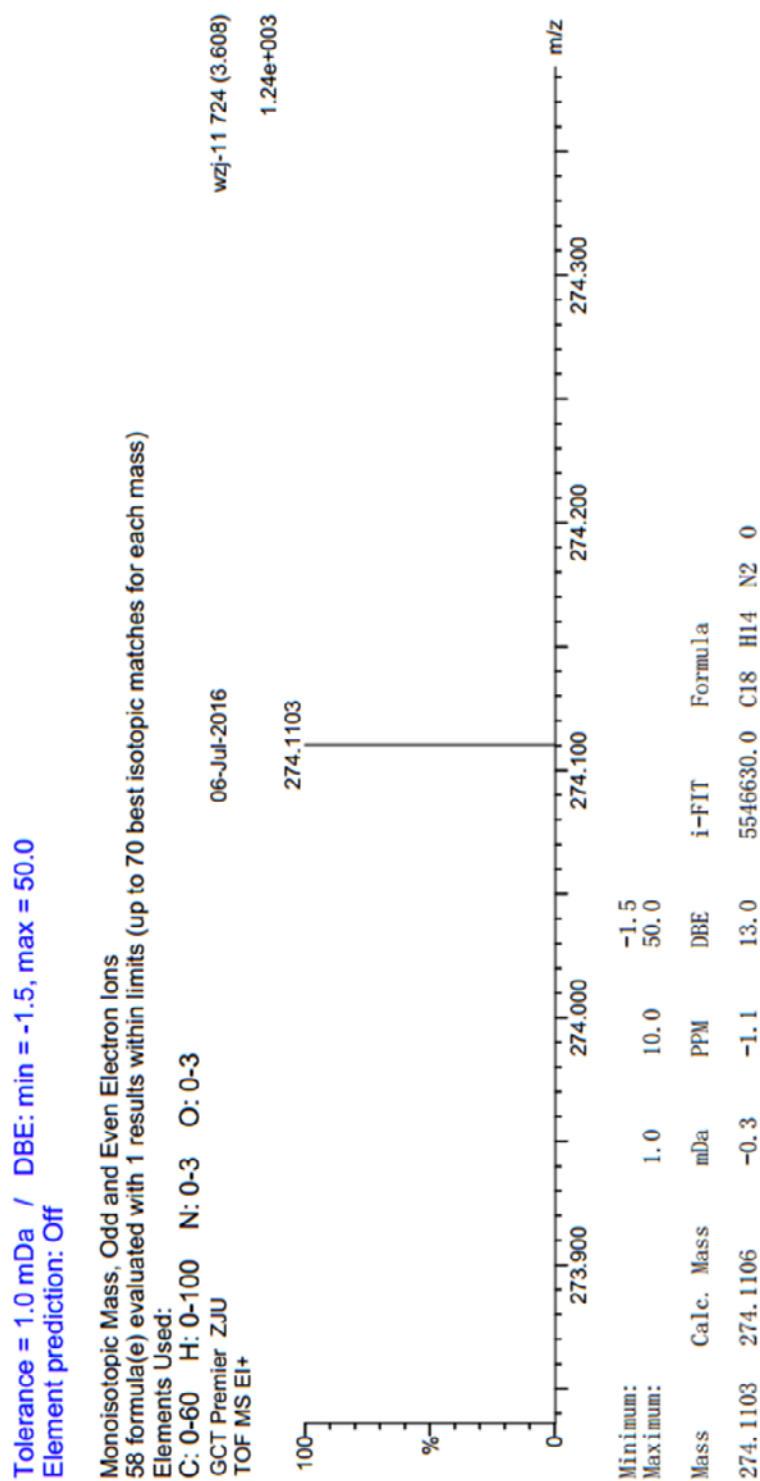


^{13}C NMR Spectrum of 1-(isoquinolin-3-yl)-3,4-dihydroquinolin-2(1H)-one **30a**



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

30a



5. ^1H NMR Spectrum of the mixture of dihydroquinolinone derivative **3aa** and deuterated dihydroquinolinone derivative **3aa-D₄**

