Supplementary data

A highly selective turn-off fluorescent probe for Cu(II) based on dansyl derivative and its application in living cell imaging

Jiaguo Huang[a], Min Liu[a], Xiaoqian Ma[b], Qiong Dong[b], Bin Ye[b], Wei Wang[b], Wenbin Zeng[a,*]

[a]School of Pharmaceutical Sciences, Central South University.

[b]The Third Xiangya Hospital, Central South University

Correspondence information: Wenbin Zeng, School of Pharmaceutical Sciences, Central South University, 172 Tongzipo road, Changsha, 410013, P. R. China. Fax: 0086-731-82650459; Tel: 0086-731-82650459; E-mail: wbzeng@hotmail.com.

Contents

1. Optimization of condition for probe 1 measurement

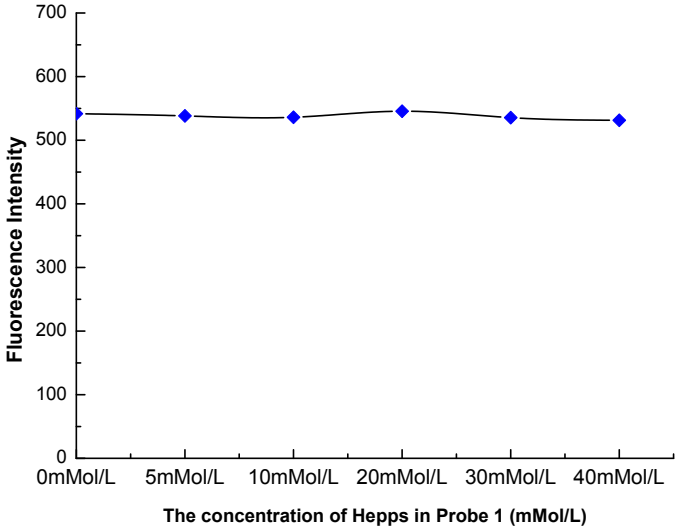


Fig. S1. Influence of the HEPES buffer solution concentration on the fluorescence intensity of 20 μM probe **1**. (pH =7.0, $\lambda_{ex}/\lambda_{em}$ = 348 nm/515 nm).

2. The UV response of 1 to various metal ions

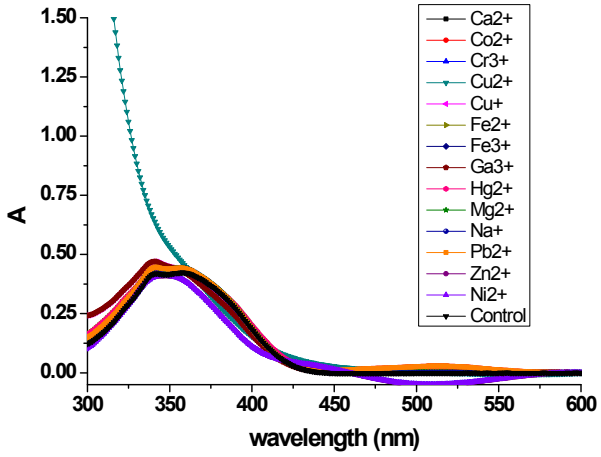
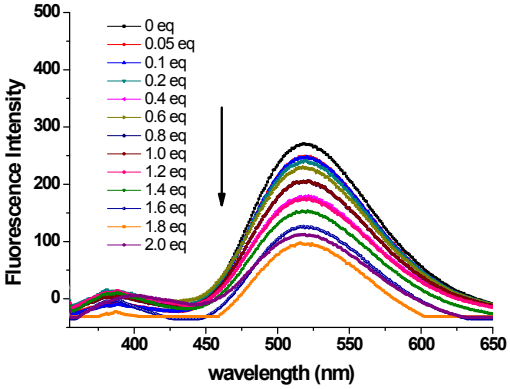


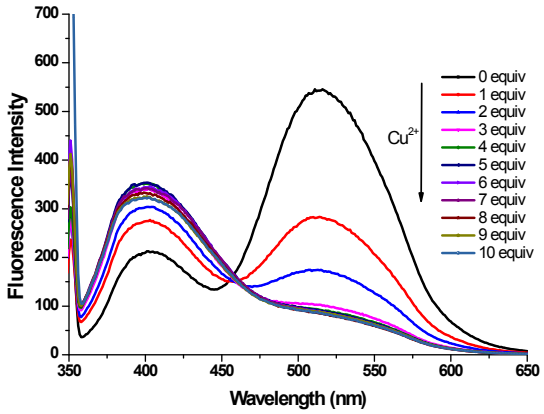
Fig. S2. UV-vis absorption spectra of probe **1** (16 μM) towards various metal ions (800μM) in CH_3CN/HEPES buffer (8/2, v/v, pH =7.0).

3. The titration experiments of probe 1

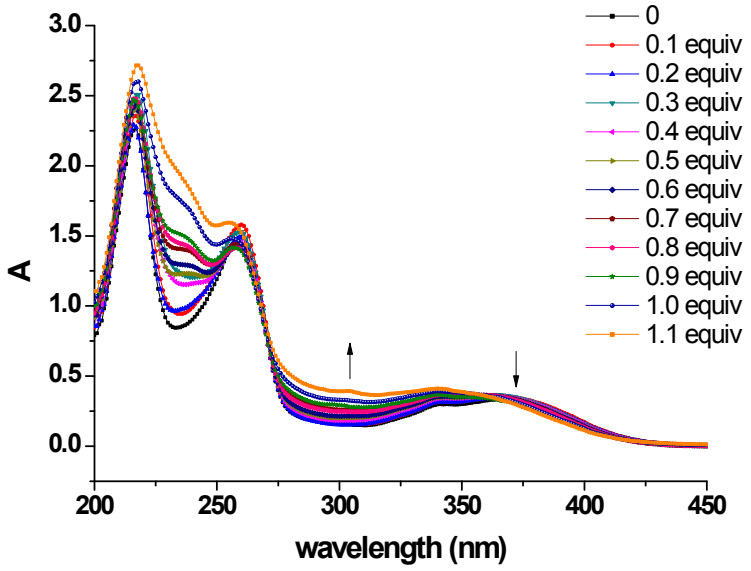
(a)



(b)



(c)



(d)

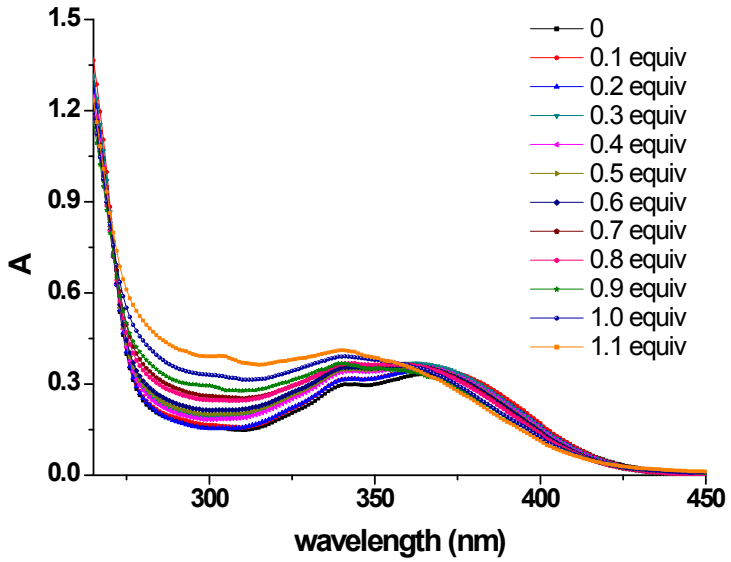


Fig. S3. (a) Fluorescence spectra of 8 μM probe 1 with Cu^{2+} between 0 and 2 equiv (CH_3CN/HEPES buffer = 8/2, v/v, pH=7.0, $\lambda_{ex}/\lambda_{em}$= 348 nm /515 nm); (b) Fluorescence spectra of 20 μM probe 1 with Cu^{2+} between 0 and 10 equiv (only HEPES buffer, pH=7.0, λ_{ex} = 348 nm); (c) UV-vis absorption spectra of probe **1** (16 μM) with Cu^{2+} between 0 and 1.1 equiv ((CH_3CN/HEPES buffer = 8/2, v/v, pH=7.0); (d) spectra of (c) from 260 nm to 450 nm.

4. The fluorescent intensity change of 1 to various anions

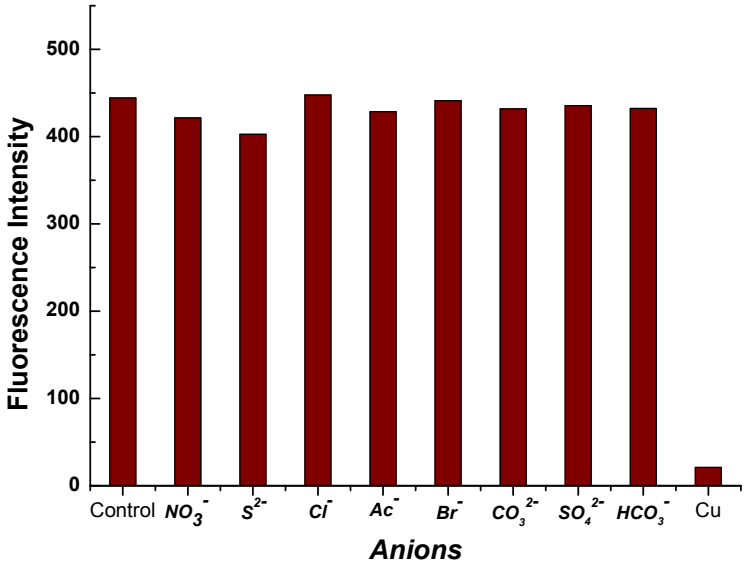


Fig. S4. The fluorescence variation of probe 1 (16 μM) to various anions at 800 μM concentration in CH3CN/HEPES buffer (8/2, v/v, pH=7.0, $\lambda_{ex}/\lambda_{em}$= 348 nm /515 nm).

5. Binding Constant[1]

The binding constant was calculated from the emission intensity - titration curves. According to the equation:

$(F-F_0) / F_0 = f /[1+(1/K_s [Cu^{2+}])]$,

where F_0 is the emission intensity of probe **1** at 515 nm, F is the emission intensity of **1**at 515 nm upon the addition of different concentration of Cu (II) , f is the fraction of the initial fluorescence which is accessible to the sensor, $[Cu^{2+}]$ is the concentration of Cu^{2+} .

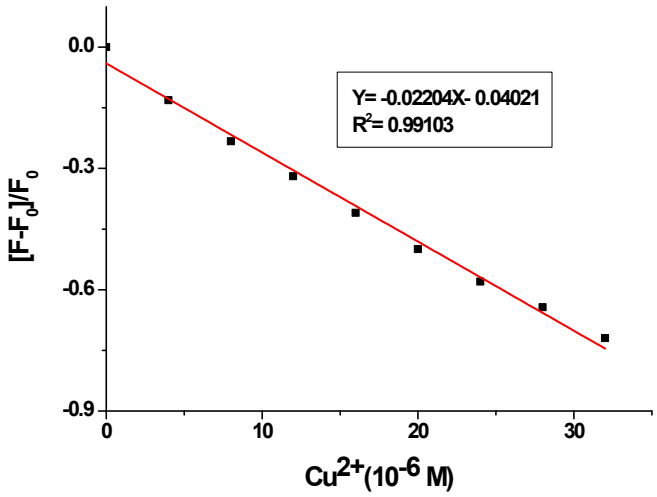


Fig. S5. Fitting of Fluorescence titration curve of **1** in CH_3CN/HEPES (8: 2, v/v, pH =7.0). The binding constant is Ks = $5.08x10^4$ M^{-1}.

6. Job plot of the complexation between the probe 1 and Cu^{2+}

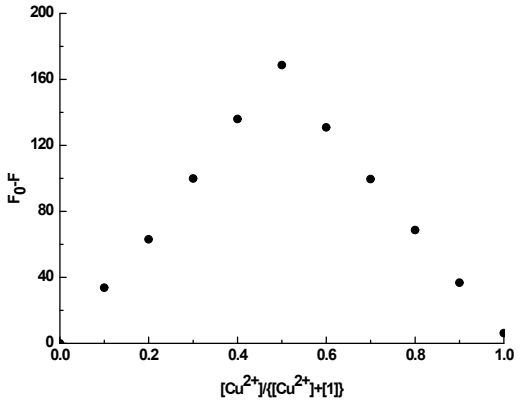


Fig. S6. Job plot of the complexation between the probe **1** and Cu^{2+} (CH_3CN/HEPES buffer = 8/2, v/v, pH=7.0, $\lambda_{ex}/\lambda_{em}$= 348 nm /515 nm). The total molar concentration of **1** and Cu^{2+} is 10μM;

7. The effect of pH

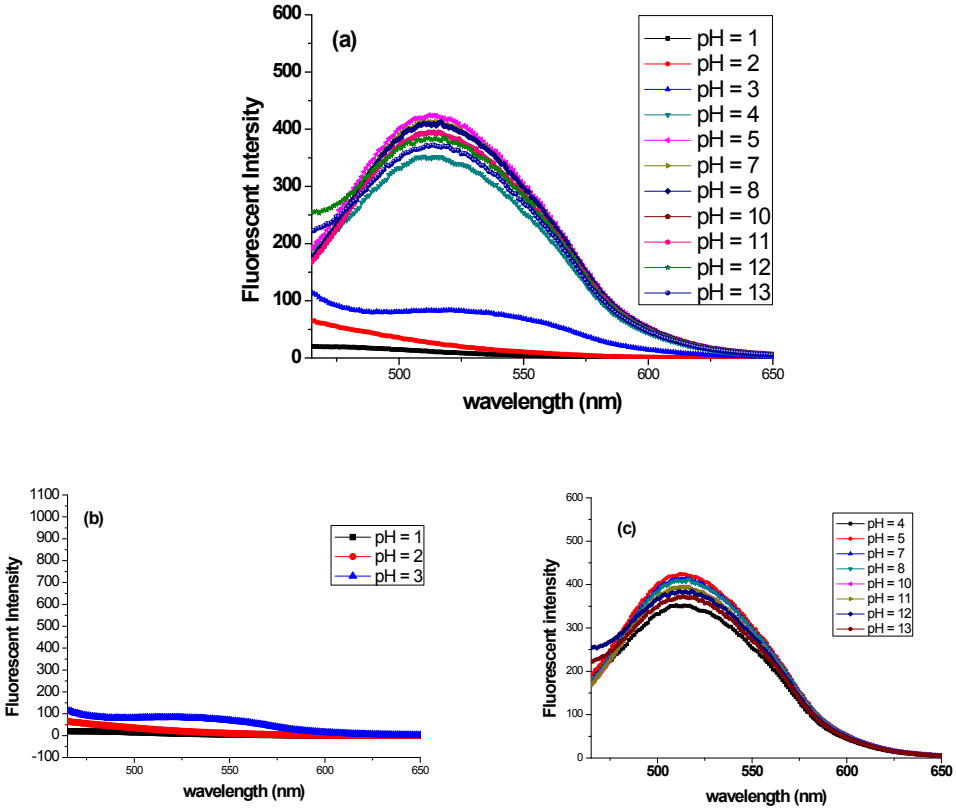


Fig. S7. (a) Influence of pH on fluorescence spectra of free **1** (16 μM) in CH_3CN/H_2O solution (8/2, v/v); (b) Influence of pH from 1.0 to 3.0; (c) Influence of pH 4.0 to 13.0.

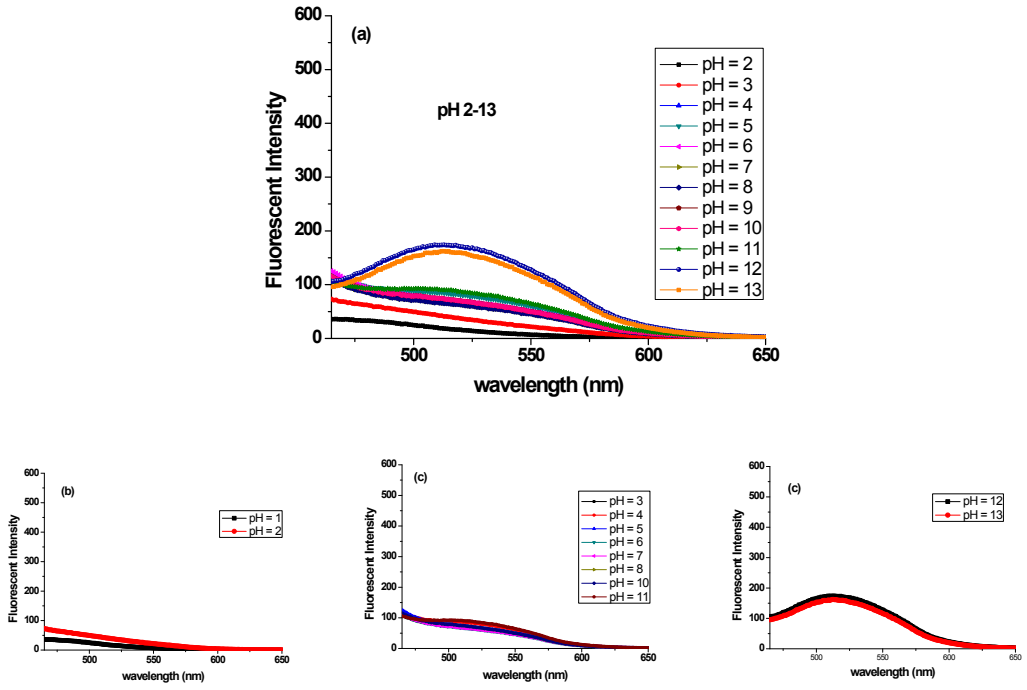


Fig. S8. (a) Influence of pH on fluorescence spectra of **1**/Cu^{2+} adduct (16 μM **1** and 80 μM Cu^{2+}) in CH_3CN/H_2O solution (8/2, v/v); (b) Influence of pH from 1.0 to 2.0; (c) Influence of pH from 3.0 to 11.0; (d) Influence of pH from 12.0 to 13.0.

8. Fluorescence quantum yield

Table S1. Photophysical Data[a]

Sample	F_{515}	Φ_f (%)
1	178.03	8.2
1 + Cu^{2+}	9.23	0.42

[a]F_{515} : Fluorescence intensity at 515nm. Φ_f: Fluorescence quantum yield.

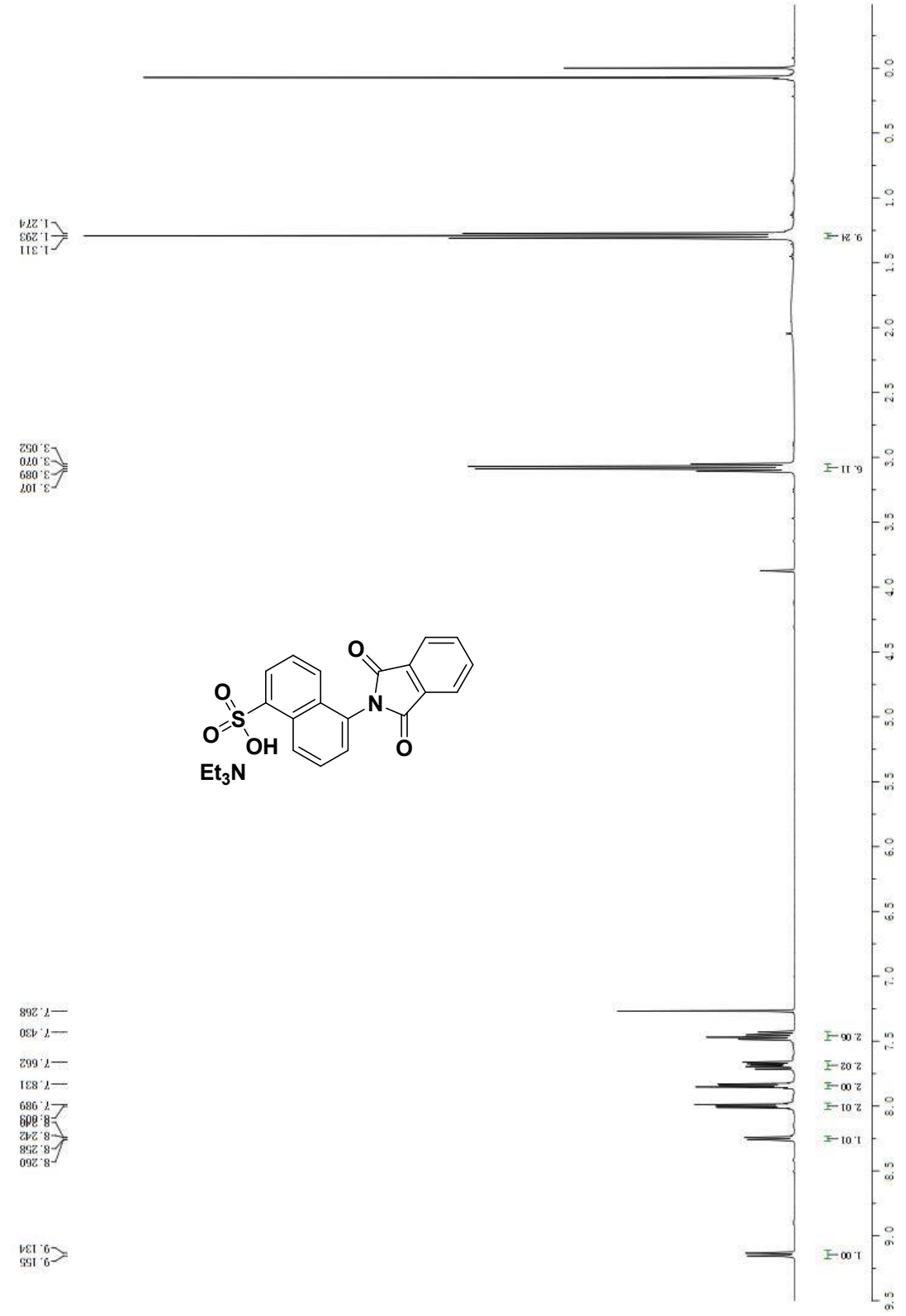
9. Reference

1. Hou, F.P.; Huang, L.; Xi, P.X.; Cheng, J.; Zhao, X. F.; Xie, G.Q.; Shi, Y.J.; Cheng, F.J.; Yao, X.J.; Bai, D.C.; Zeng, Z. Z. *Inorg. Chem.* 2012, **51**, 2454.
2. Melhuish, W. H. *J. Phys. Chem.* 1961, **65**, 229.

10. ^{1}H NMR, ^{13}C NMR, ESI-MS or HRMS spectra

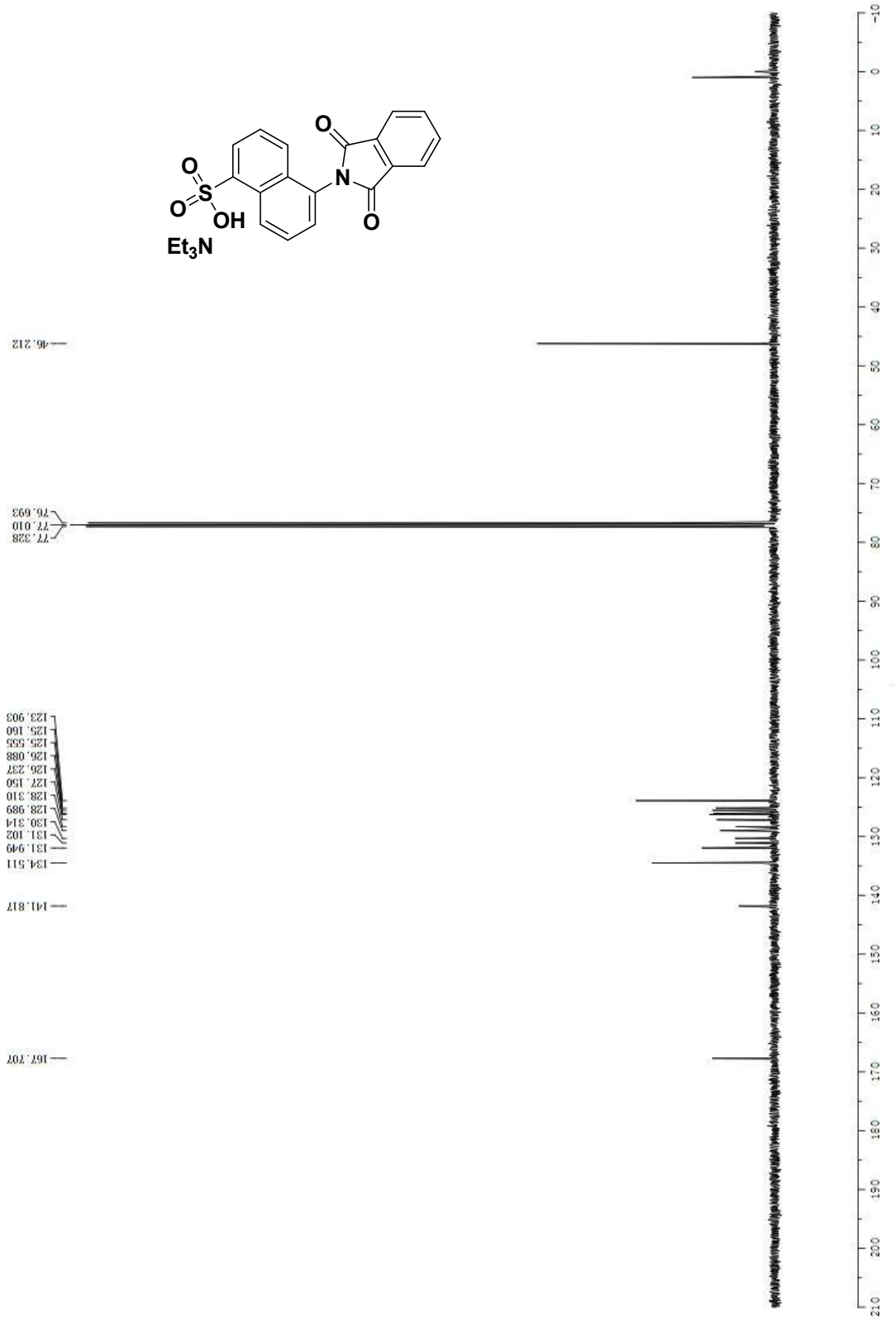
5-(1, 3-dioxoisoindolin-2-yl)naphthalene-1-sulfonic acid (3)

^{1}H NMR (400 MHz, $CDCl_3$)



5-(1, 3-dioxoisoindolin-2-yl)naphthalene-1-sulfonic acid (3)

^{13}C NMR (400 MHz, $CDCl_3$)

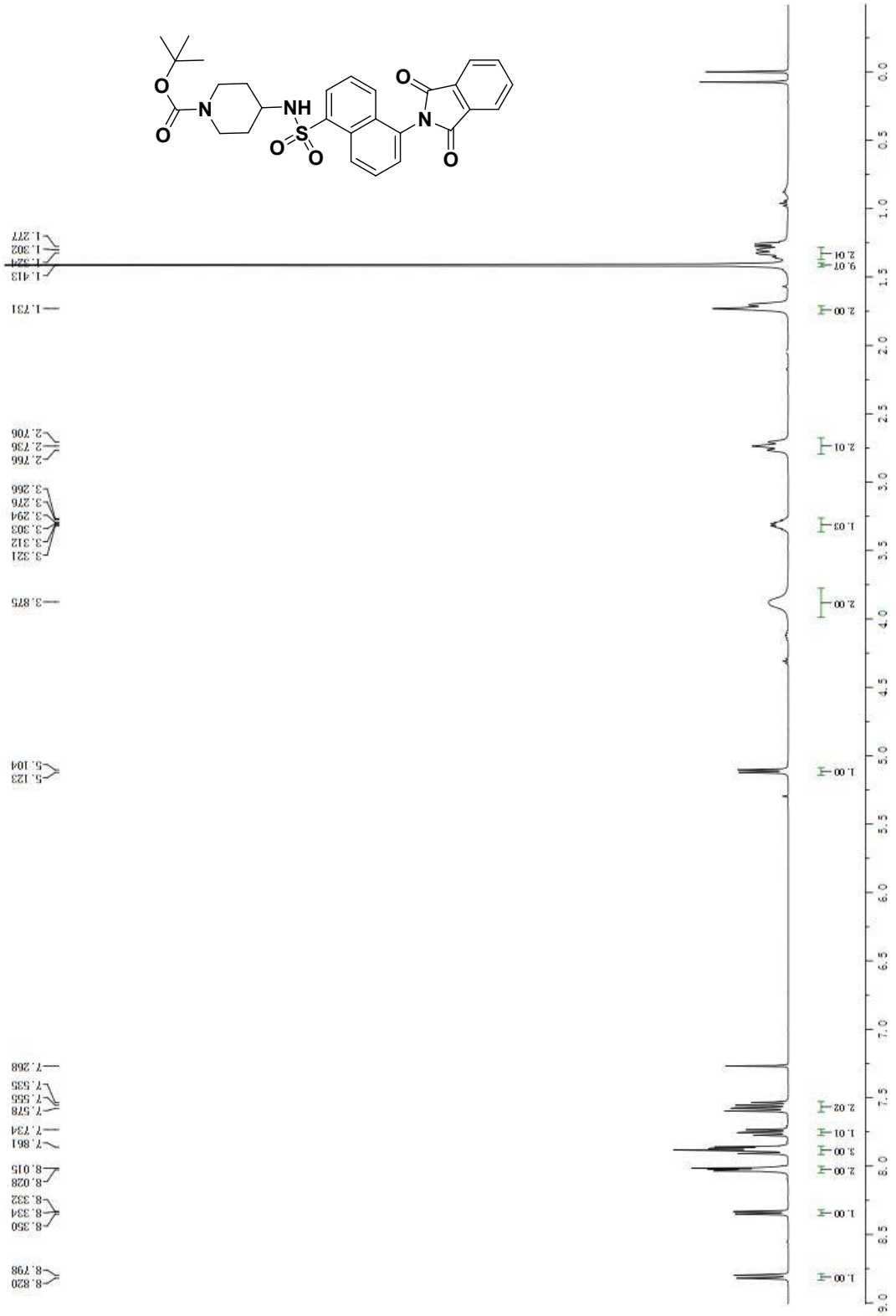


5-(1, 3-dioxoisoindolin-2-yl)naphthalene-1-sulfonic acid (3)

HRMS

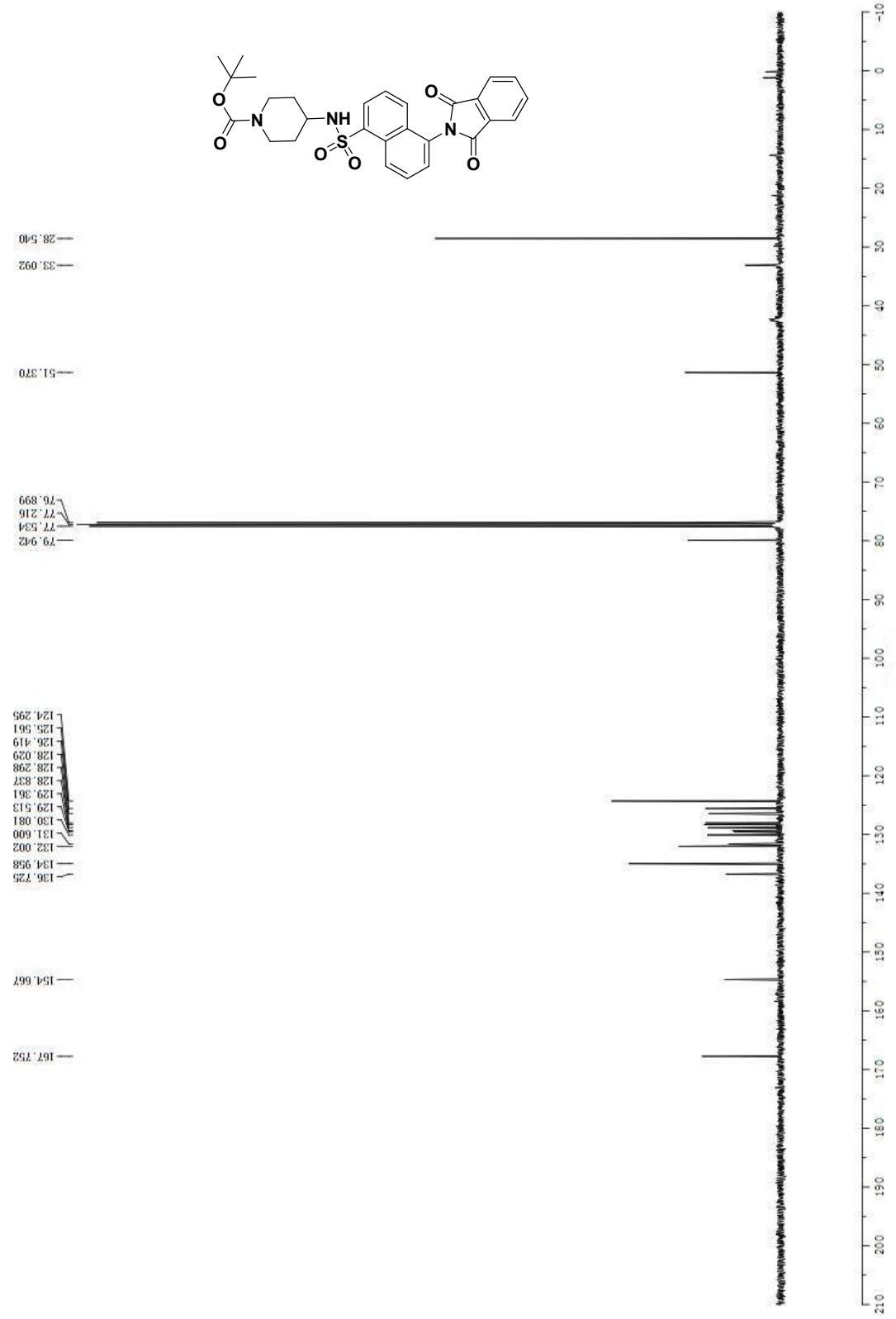
Tert-butyl4-(5-(1,3-dioxoisoindolin-2-yl)naphthalene-1-sulfonamido)piperidine-1-carboxylate (5)

^{1}H NMR (400 MHz, $CDCl_3$)



Tert-butyl4-(5-(1,3-dioxoisoindolin-2-yl)naphthalene-1-sulfonamido) piperidine -1-carboxylate (5)

^{13}C NMR (400 MHz, $CDCl_3$)

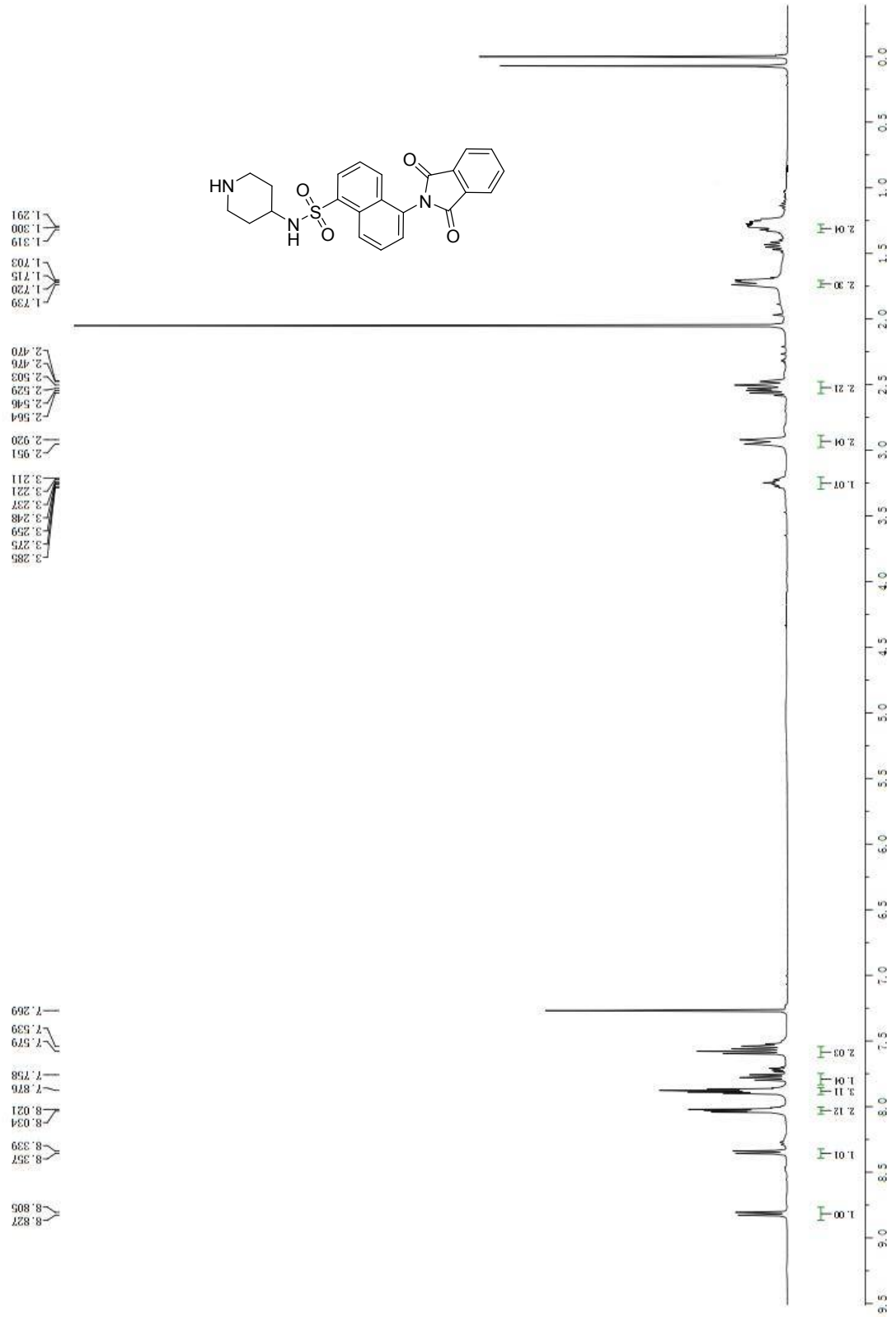


Tert-butyl4-(5-(1,3-dioxoisoindolin-2-yl)naphthalene-1-sulfonamido) piperidine -1-carboxylate (5)

HRMS

5-(1,3-dioxoisoindolin-2-yl)-N-(piperidin-4-yl)naphthalene-1-sulfonamide (6)

^{1}H NMR (400 MHz, $CDCl_3$)



5-(1,3-dioxoisoindolin-2-yl)-N-(piperidin-4-yl)naphthalene-1-sulfonamide (6)

ESI-MS

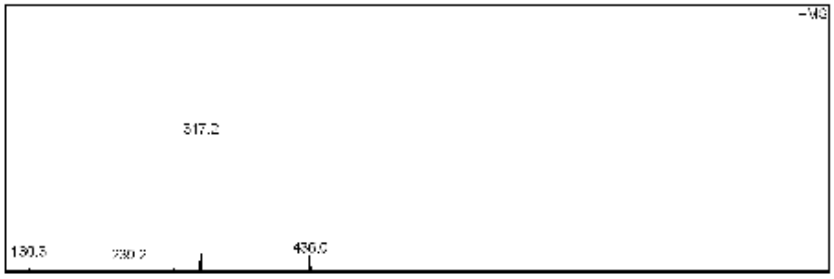
Mass Spectrum Deconvolution Report

Analysis Info

Analysis Name	D:\Data\20120329-Jack-09.d	Acquisition Date	3/29/2012 6:38:57 PM
Method	20111121-TEA.m	Operator	YLJ
Sample Name	20120329-Jack-09	Instrument	esquire6000
Comment	20120329-Jack-09		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	105 m/z	Scan End	1000 m/z
Capillary Exit	113.5 Volt	Skimmer	40.0 Volt	Trap Drive	29.9
Accumulation Time	1162 µs	Averages	2 Spectra	Auto MS/MS	off

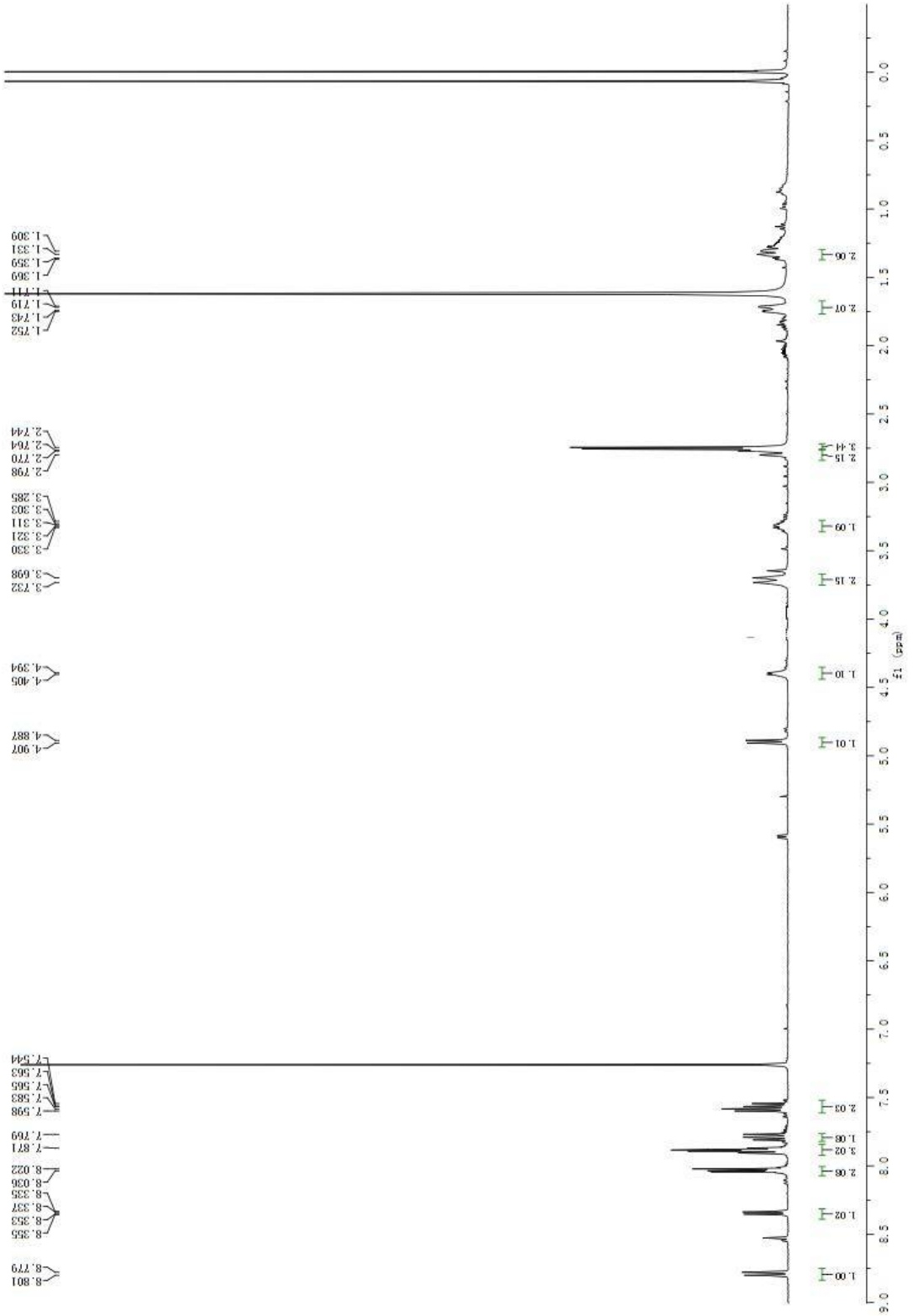


#	m/z	I
1	116.3	11708
2	130.3	19035
3	239.2	13555
4	241.2	3001
5	288.4	4146
6	317.2	240331
7	318.0	32527
8	319.2	3411
9	436.0	26177
10	437.0	7170

4-(5-(1,3-dioxoisoindolin-2-yl)naphthalene-1-sulfonamido)-N-methylpiperidine-

1-carboxamide (7)

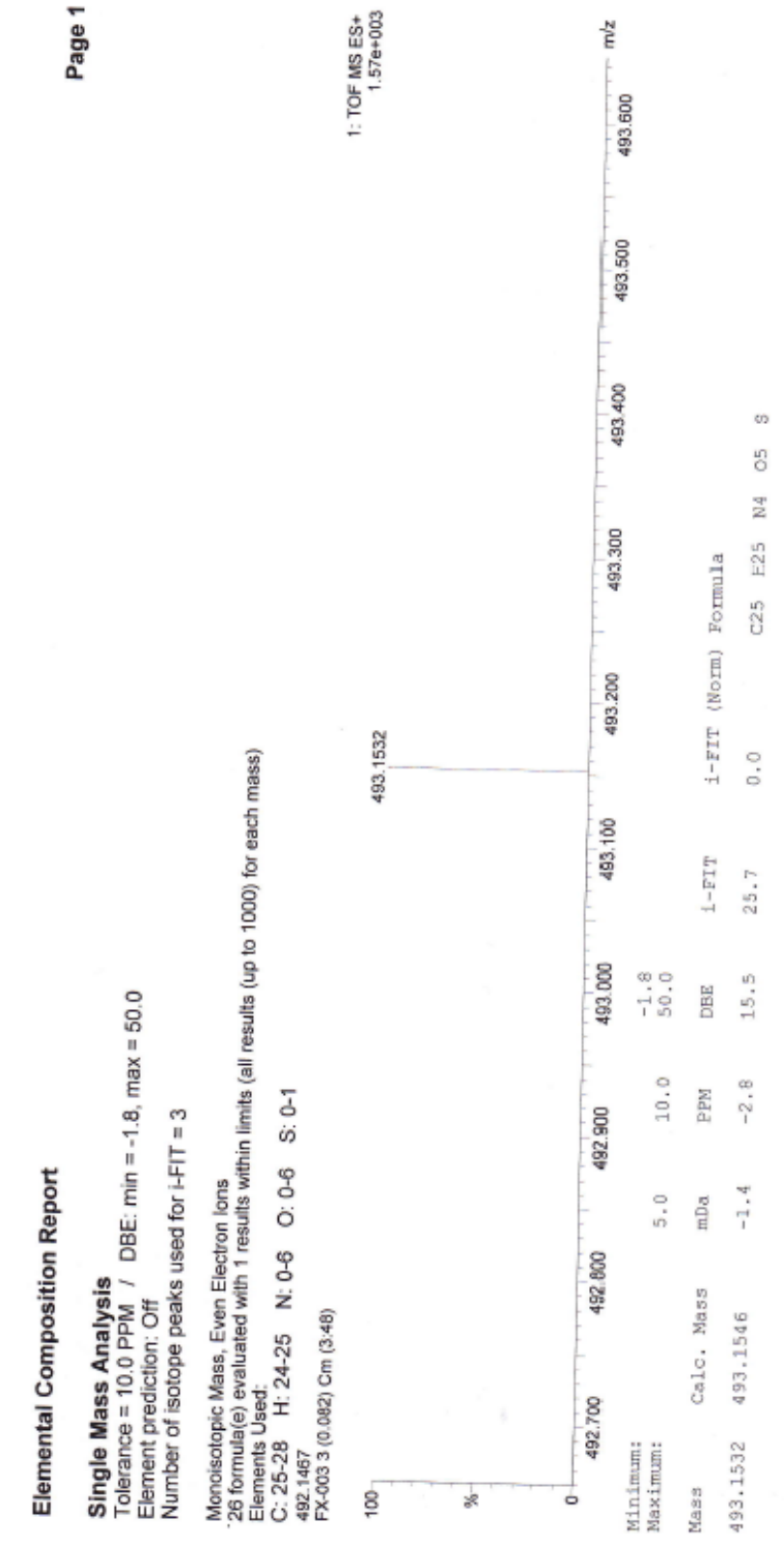
^{1}H NMR (400 MHz, $CDCl_3$)



4-(5-(1,3-dioxoisoindolin-2-yl)naphthalene-1-sulfonamido)-N-methylpiperidine-

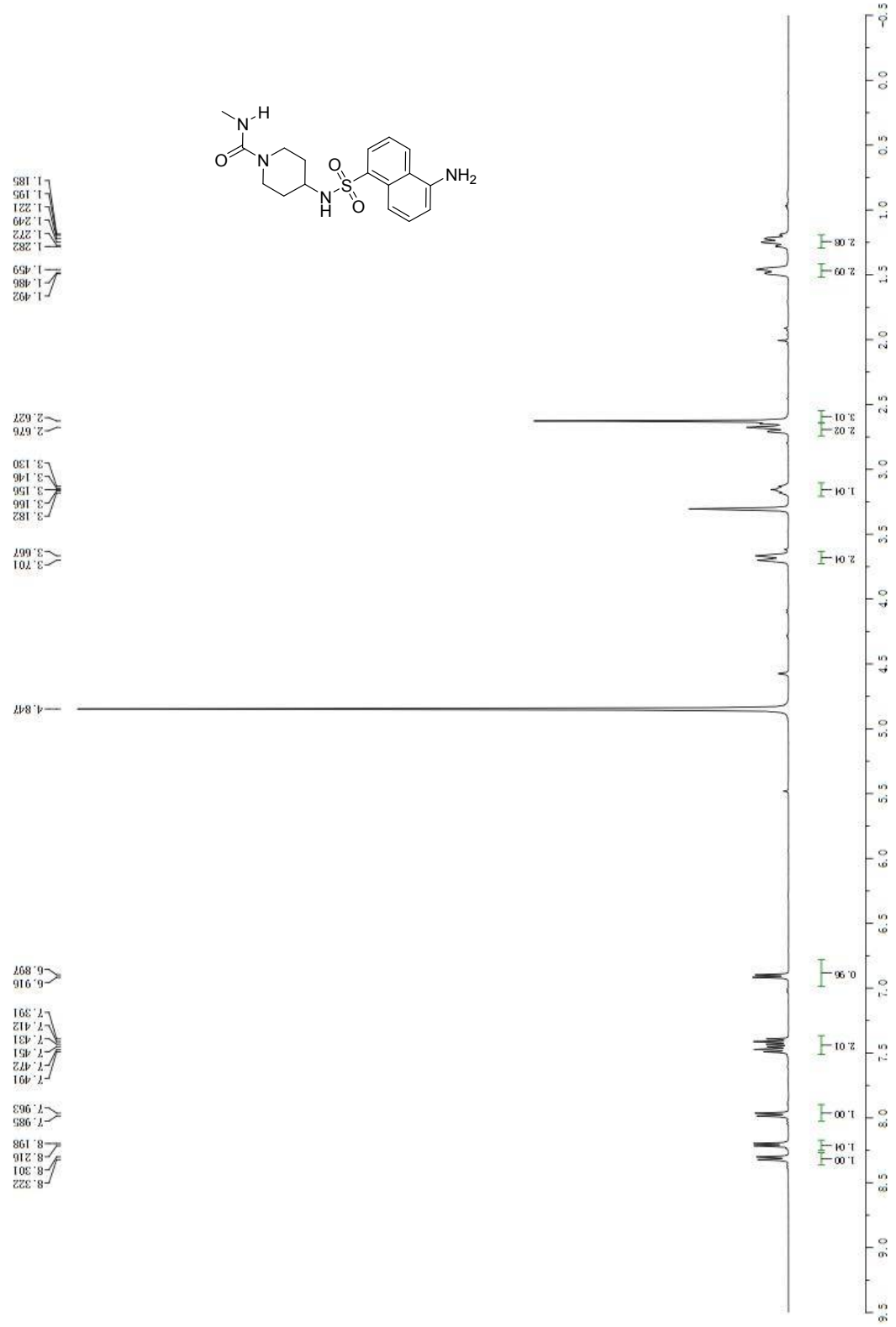
1-carboxamide (7)

HRMS



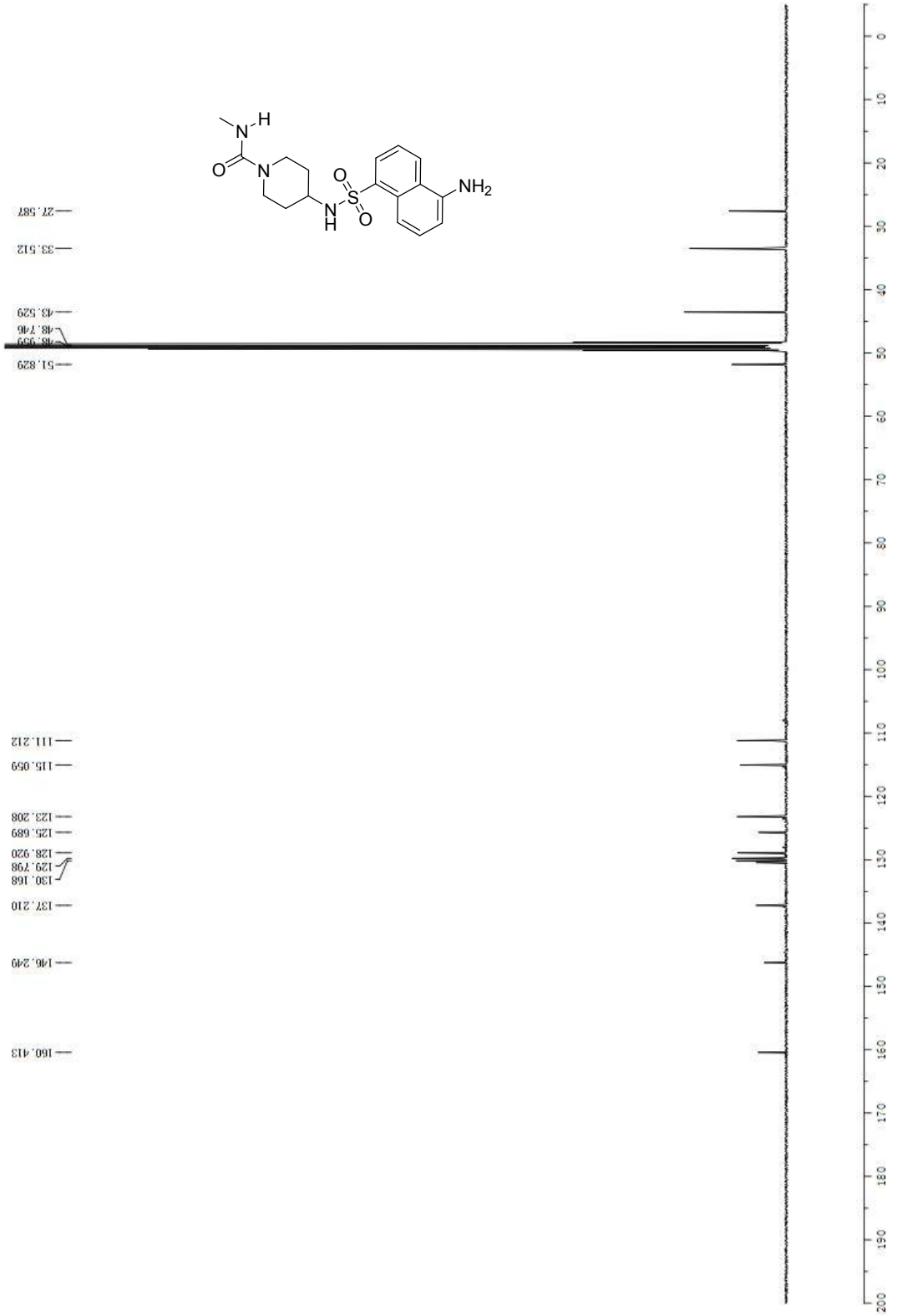
4-(5-aminonaphthalene-1-sulfonamido)-N-methylpiperidine-1-carboxamide (8)

^{1}H NMR (400 MHz, CD_3OD)



4-(5-aminonaphthalene-1-sulfonamido)-N-methylpiperidine-1-carboxamide (8)

^{13}C NMR (400 MHz, CD_3OD)



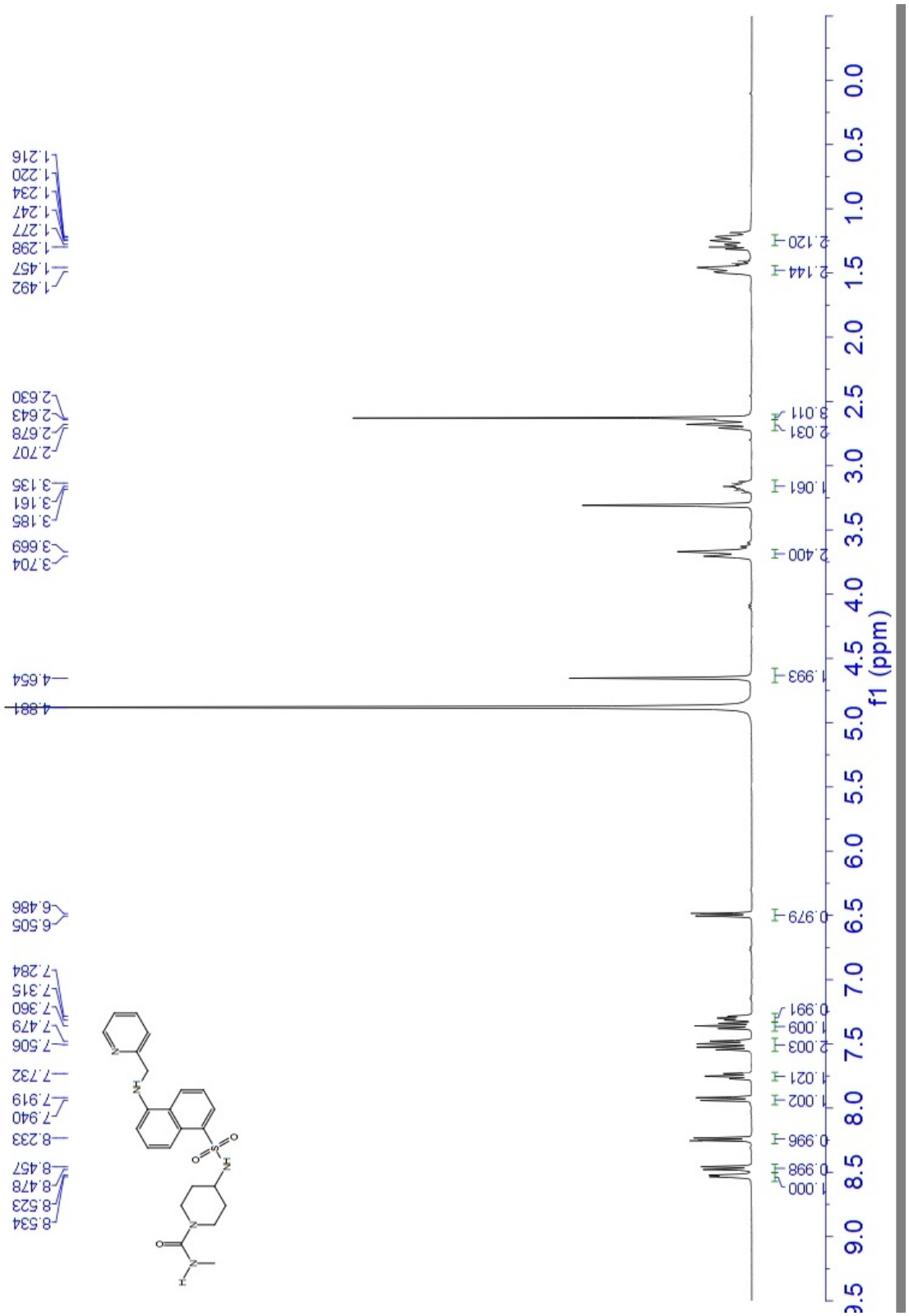
4-(5-aminonaphthalene-1-sulfonamido)-N-methylpiperidine-1-carboxamide (8)

HRMS

N-methyl-4-(5-(pyridin-2-ylmethylamino)naphthalene-1-sulfonamido)piperidine-

1-carboxamide (1)

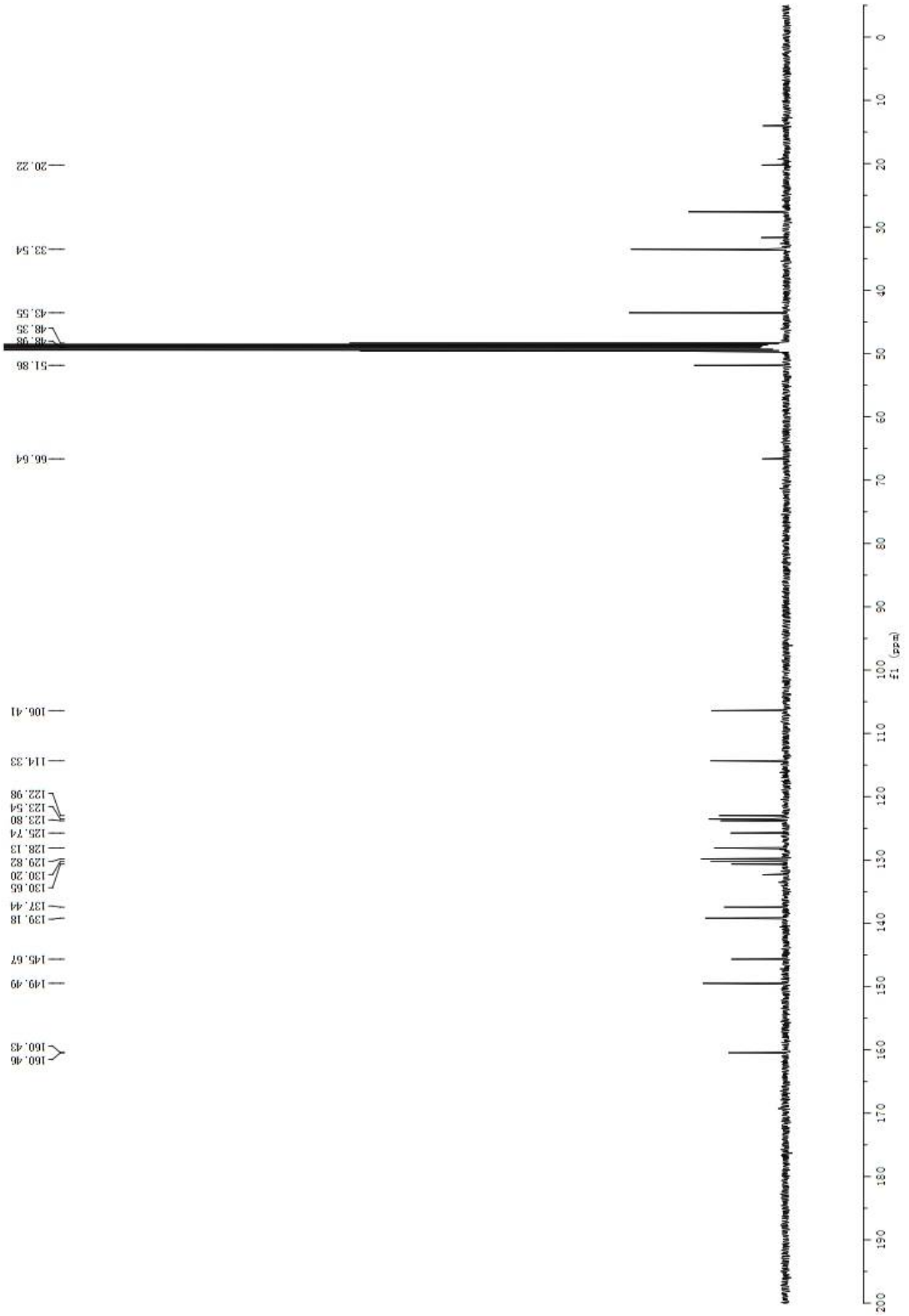
^{1}H NMR (400 MHz, CD_3OD)



N-methyl-4-(5-(pyridin-2-ylmethylamino)naphthalene-1-sulfonamido)piperidine-

1-carboxamide (1)

^{13}C NMR (400 MHz, CD_3OD)



N-methyl-4-(5-(pyridin-2-ylmethylamino)naphthalene-1-sulfonamido)piperidine-

1-carboxamide (1)

HRMS

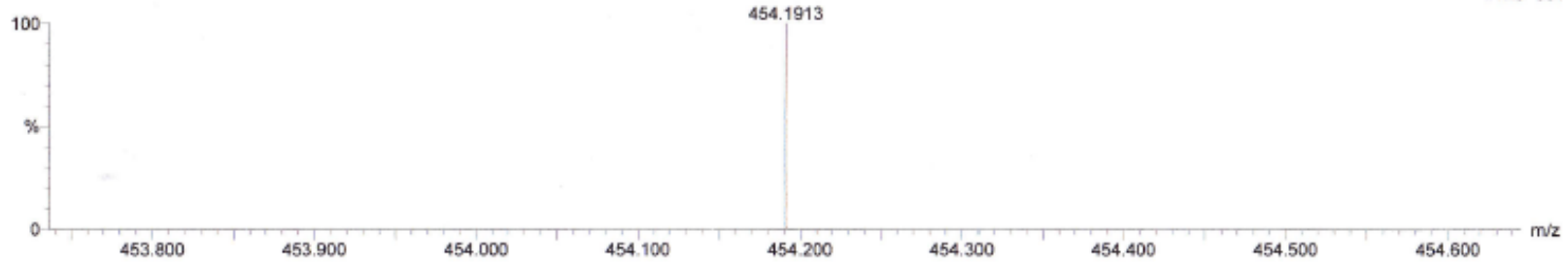
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.8, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
53 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 19-24 H: 24-30 N: 0-6 O: 0-6 S: 0-1

453.1835
FX-008 9 (0.220)

1: TOF MS ES+
1.72e+001



Minimum:				-1.8						
Maximum:		5.0	10.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
454.1913	454.1913	0.0	0.0	12.5	13.4	0.0	C23	H28	N5	O3 S