

*Supporting information*

**EFFICIENT CONSTRUCTIONS OF THE FOUR DIFFERENT  
THIENOPYRIMIDINONE SKELETONS VIA VARIOUS  
CYCLOCONDENSATION OF *o*-AMINOTHIENONITRILE WITH  
CARBONYL COMPOUNDS**

Junjuan Yang, Daxin Shi, Kai Zhang, Zhangtao Zhao, Fadong Qiu, Yujiao Bi, Qi Zhang, and Jiarong Li\*

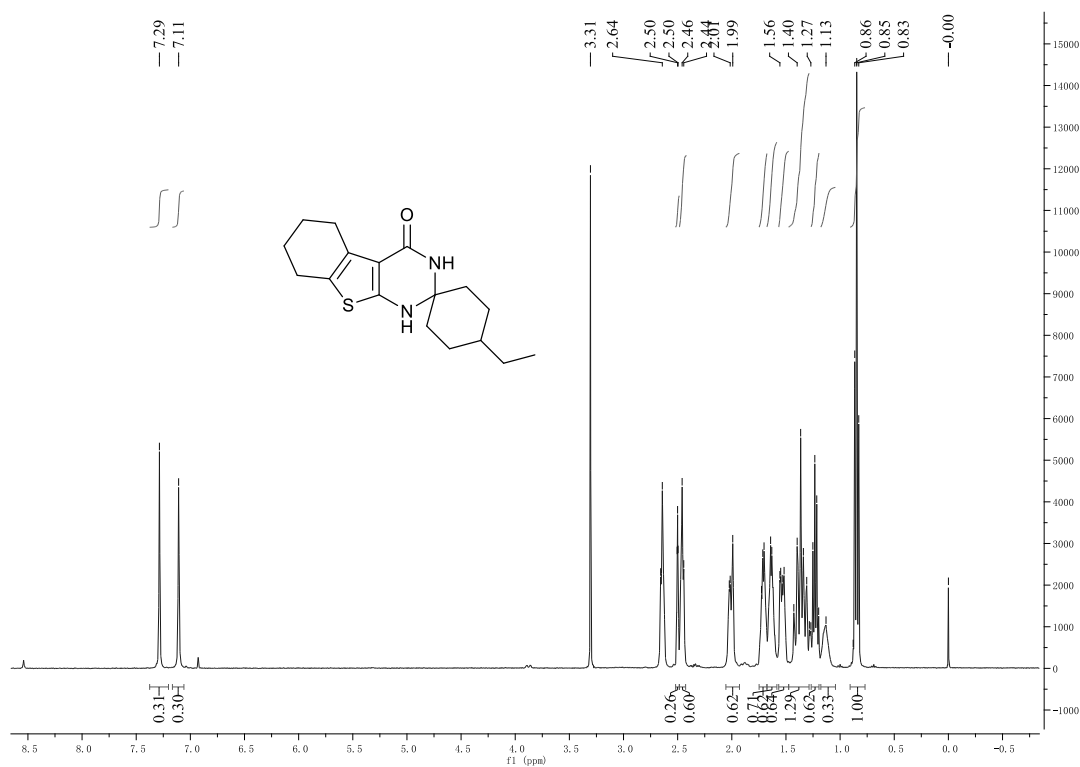
*School of Chemical Engineering and Environment, Beijing Institute of Technology, 100081 Beijing, China; E-mail:  
jrli@bit.edu.cn*

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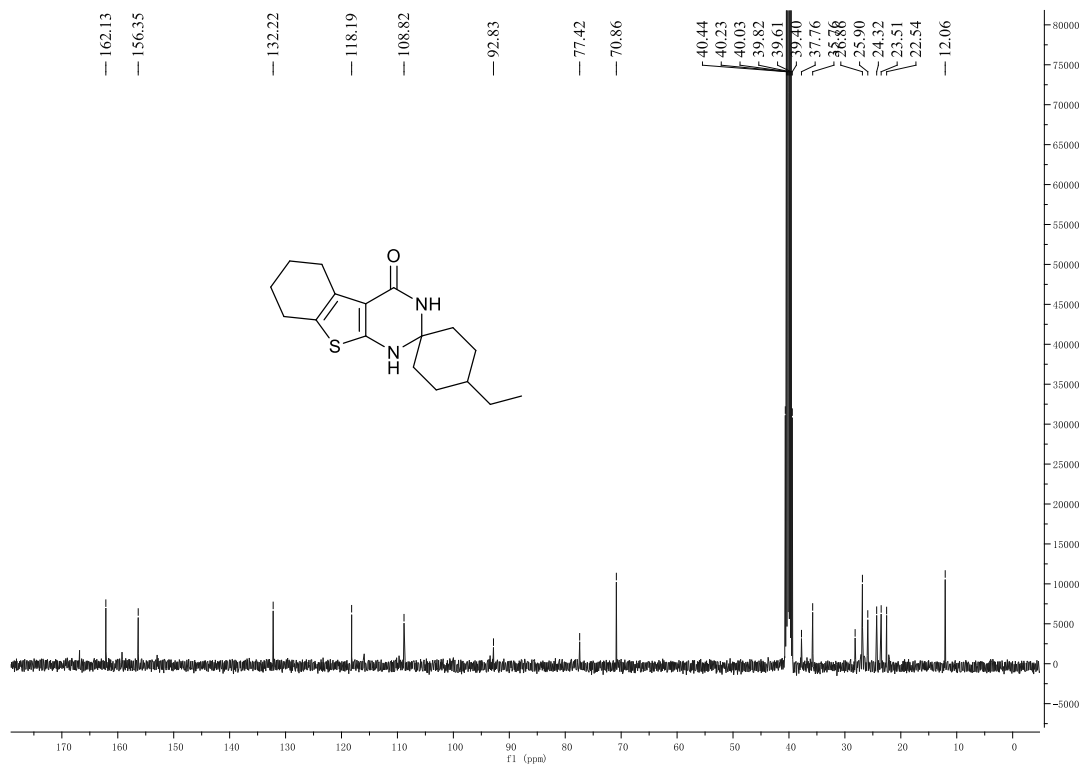
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# 1. Copies of 3 <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra

## <sup>1</sup>H NMR spectrum of 3a



## <sup>13</sup>C NMR spectrum of 3a

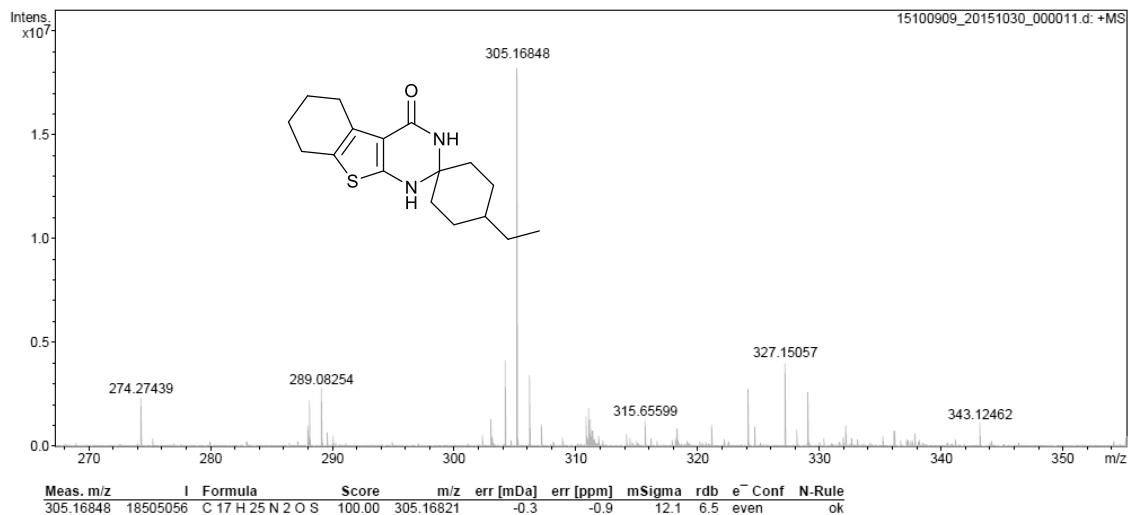


# ESI-HRMS spectrum of **3a**

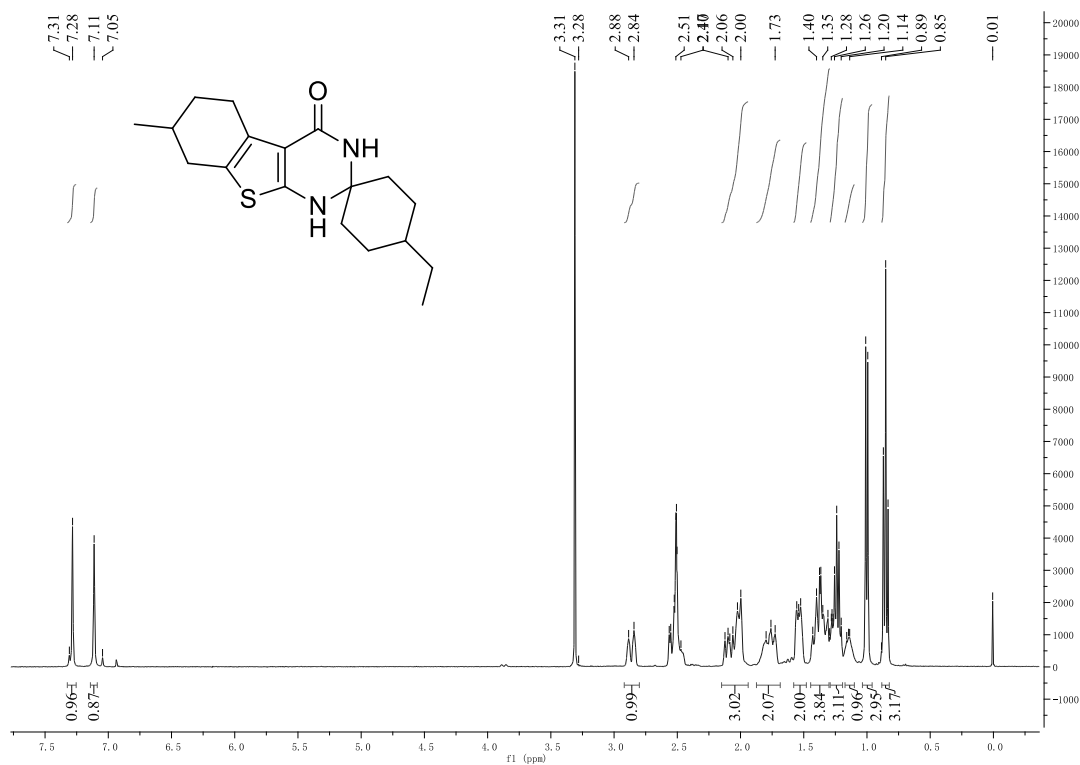
## Peking University Mass Spectrometry Sample Analysis Report

### Analysis Info

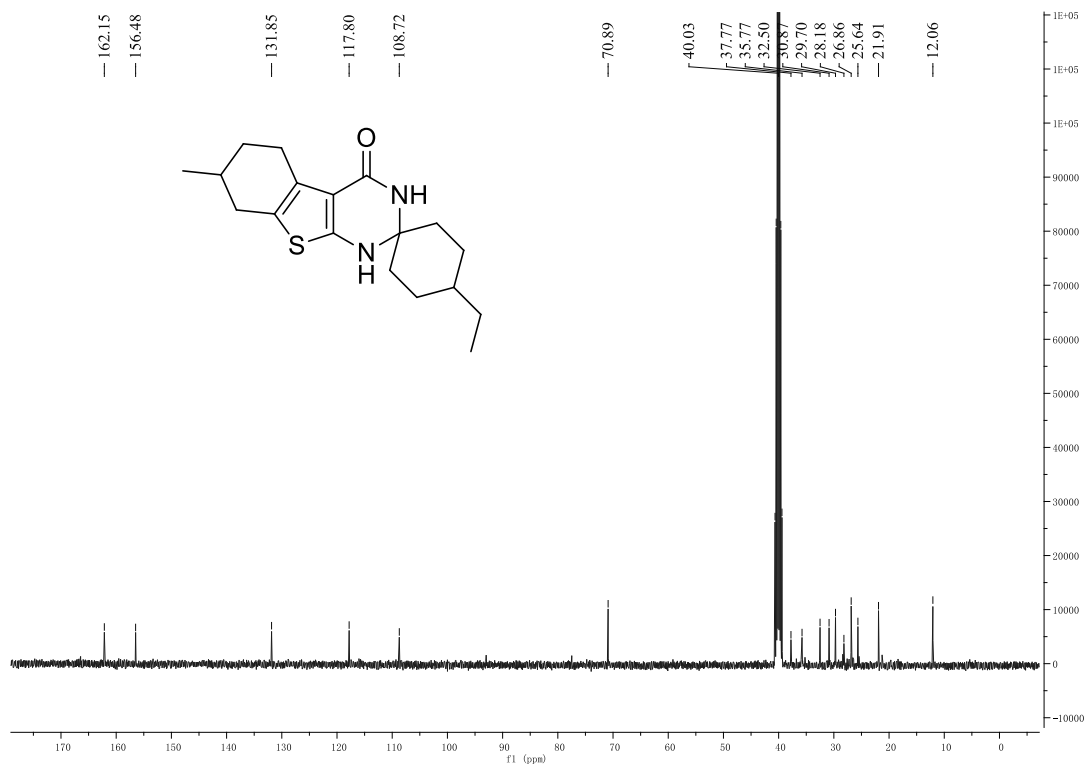
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Sample	YB21-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



<sup>1</sup>H NMR spectrum of **3b**



<sup>13</sup>C NMR spectrum of **3b**

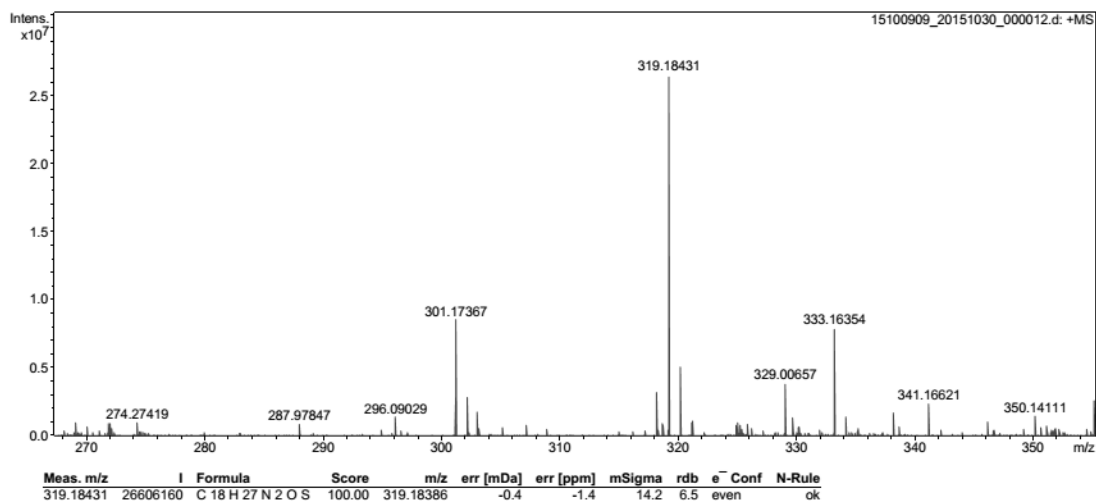


# ESI-HRMS spectrum of **3b**

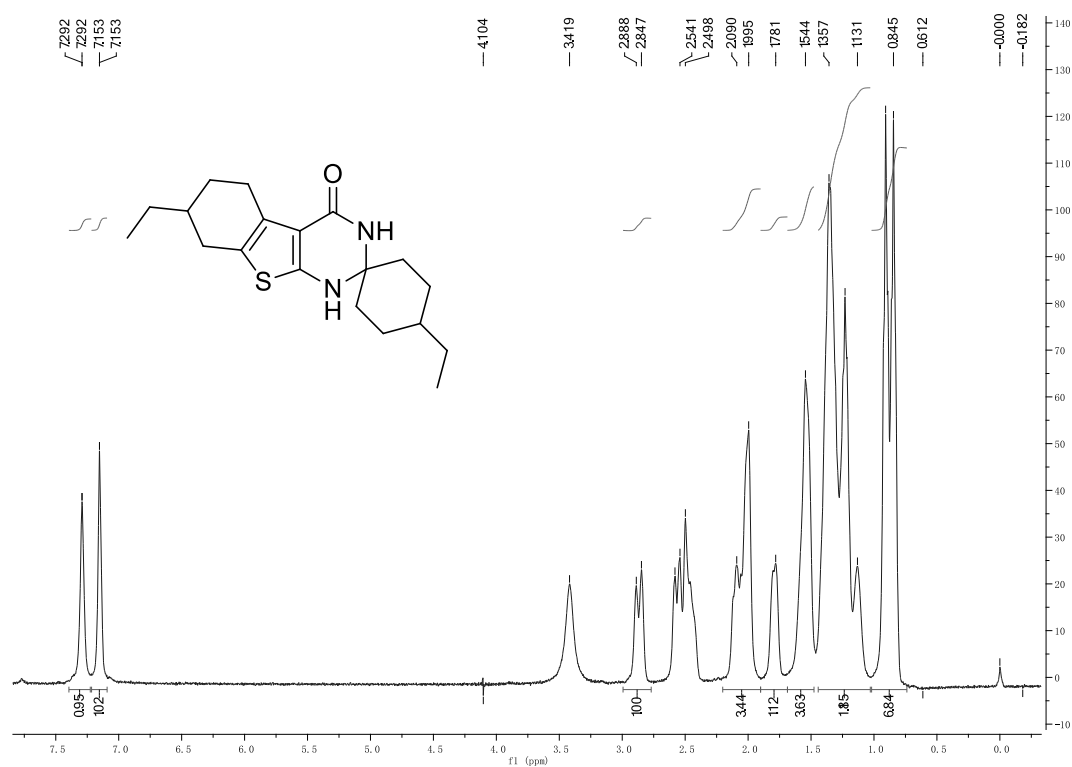
## Peking University Mass Spectrometry Sample Analysis Report

### Analysis Info

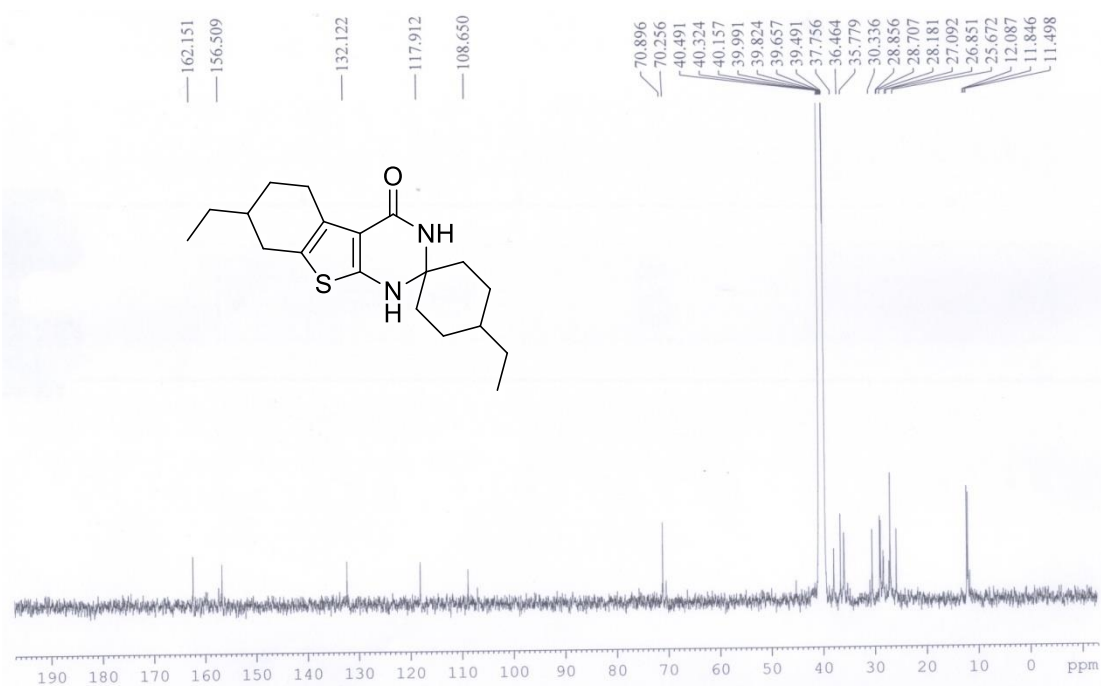
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Sample	YB22	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



### $^1\text{H}$ NMR spectrum of **3c**



### $^{13}\text{C}$ NMR spectrum of **3c**

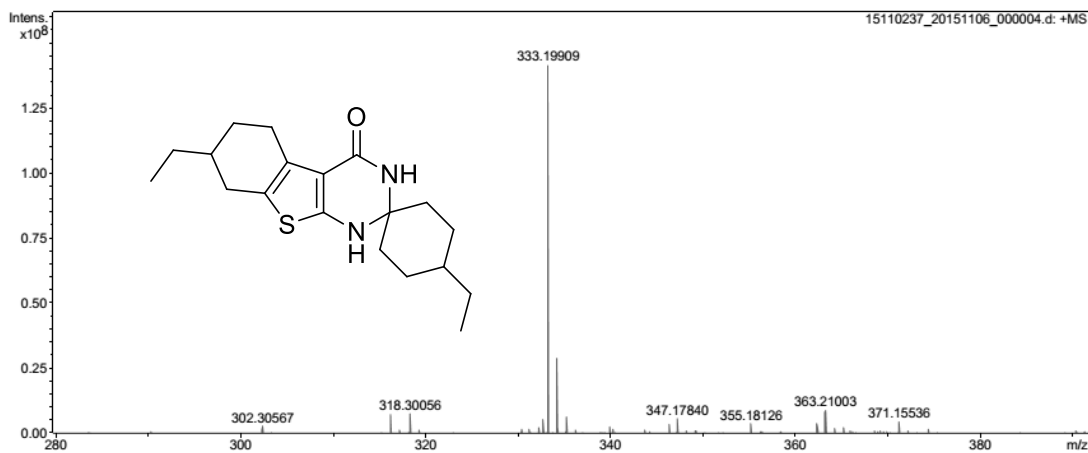


# ESI-HRMS spectrum of **3c**

## Analysis Info

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 Comment ESI Positive

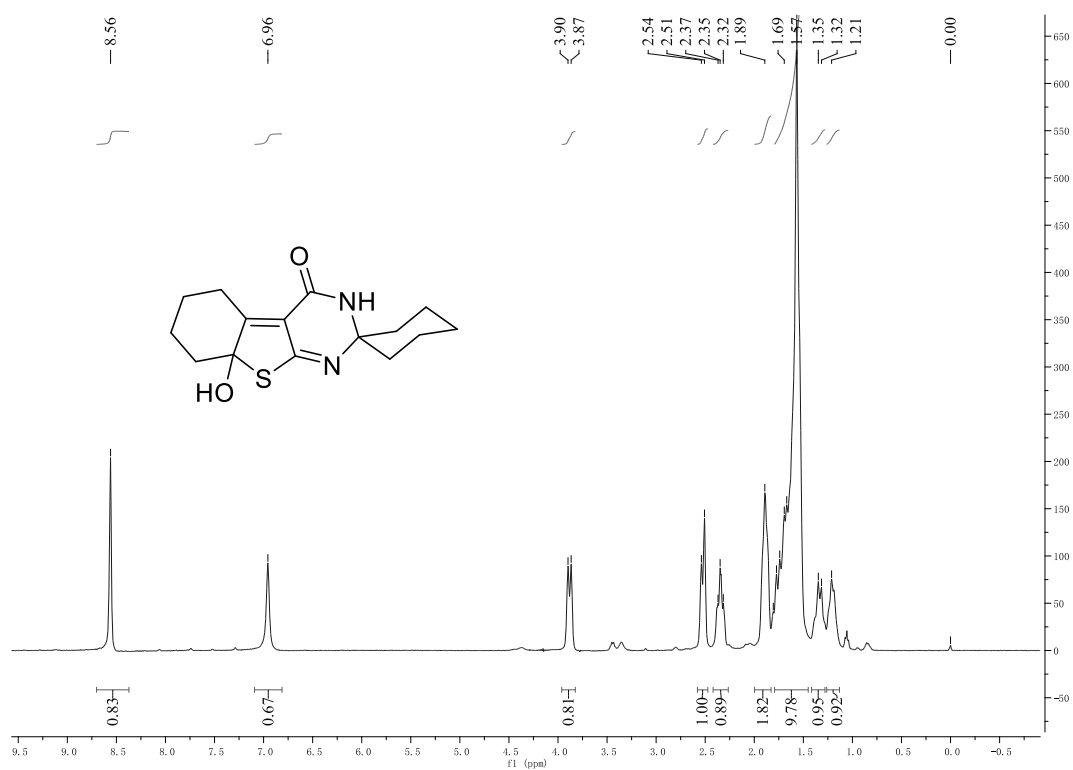
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 Instrument Bruker Apex IV FTMS  
 Operator Peking University



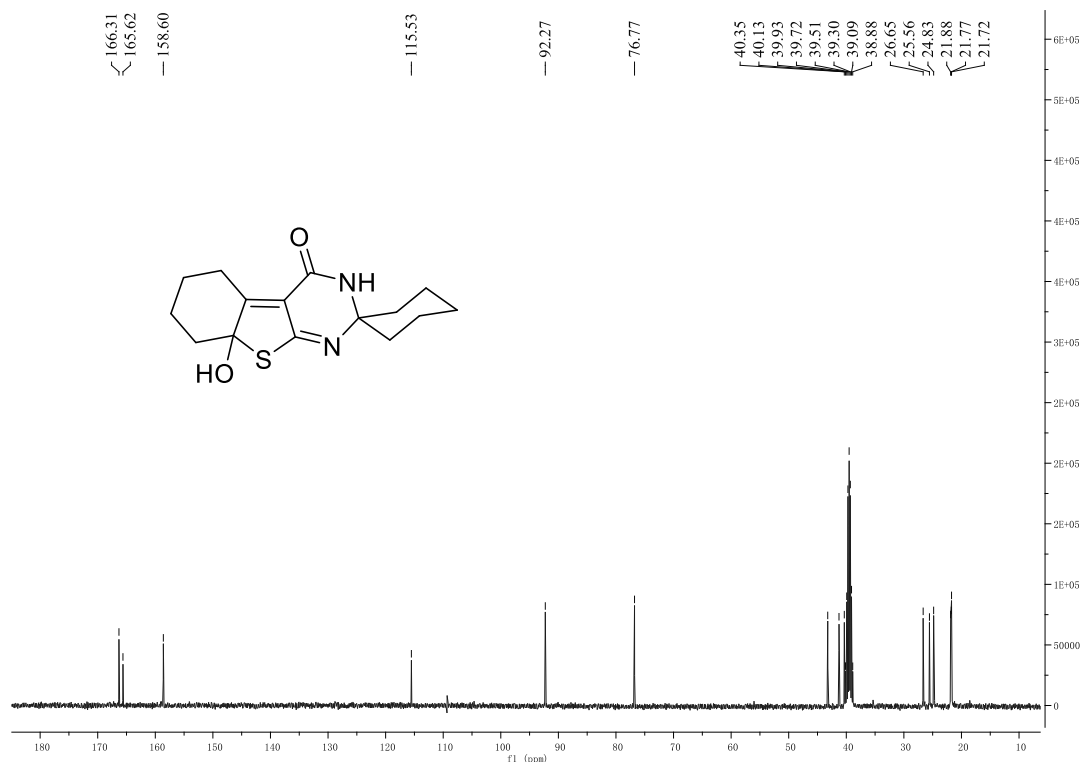
Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup>	Conf	N-Rule
333.19909	142184496	C <sub>19</sub> H <sub>29</sub> N <sub>2</sub> O <sub>2</sub> S	100.00	333.19951	0.4	1.3	13.6	6.5	even		ok
347.17840	5846804	C <sub>19</sub> H <sub>27</sub> N <sub>2</sub> O <sub>2</sub> S	100.00	347.17878	0.4	1.1	24.0	7.5	even		ok

## 2. Copies of 4 <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra

<sup>1</sup>H NMR spectrum of **4a**



<sup>13</sup>C NMR spectrum of **4a**



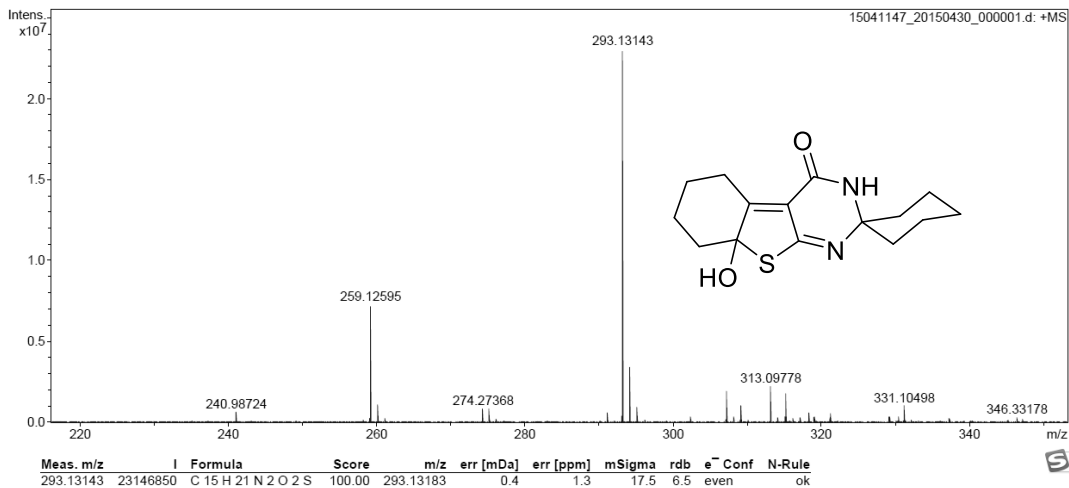
# ESI-MS spectrum of 4a

## Peking University Mass Spectrometry Sample Analysis Report

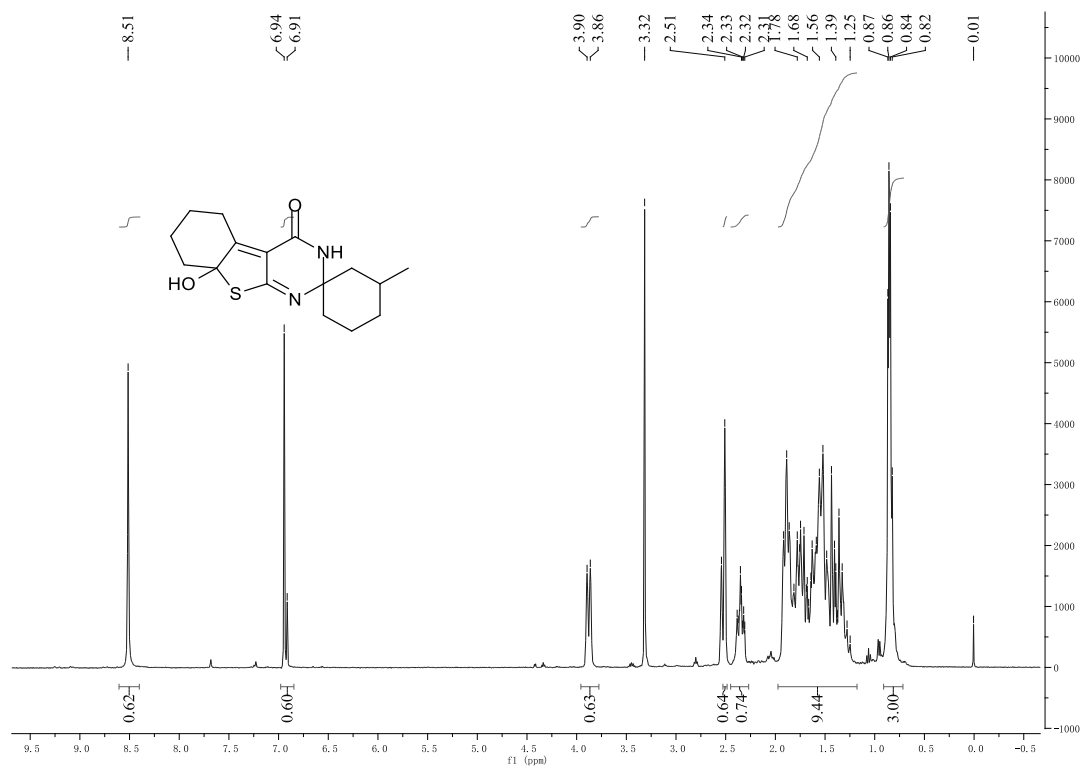
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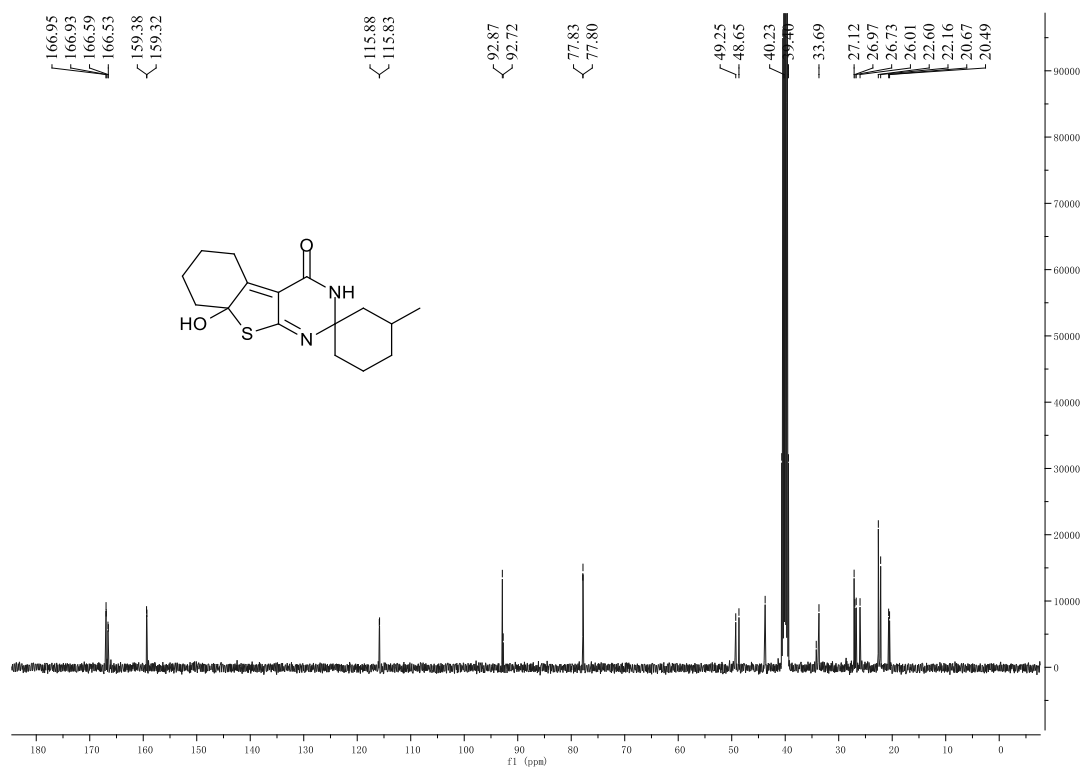
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 Instrument Bruker Apex IV FTMS  
 Operator Peking University



# <sup>1</sup>H NMR spectrum of **4b**



# <sup>13</sup>C NMR spectrum of **4b**



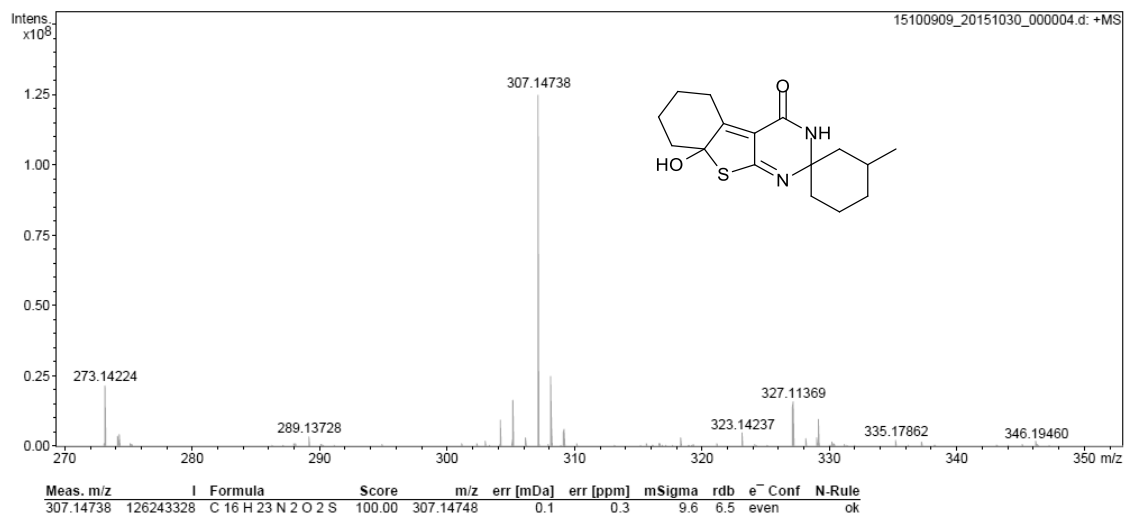
ESI-MS spectrum of **4b**

## Peking University Mass Spectrometry Sample Analysis Report

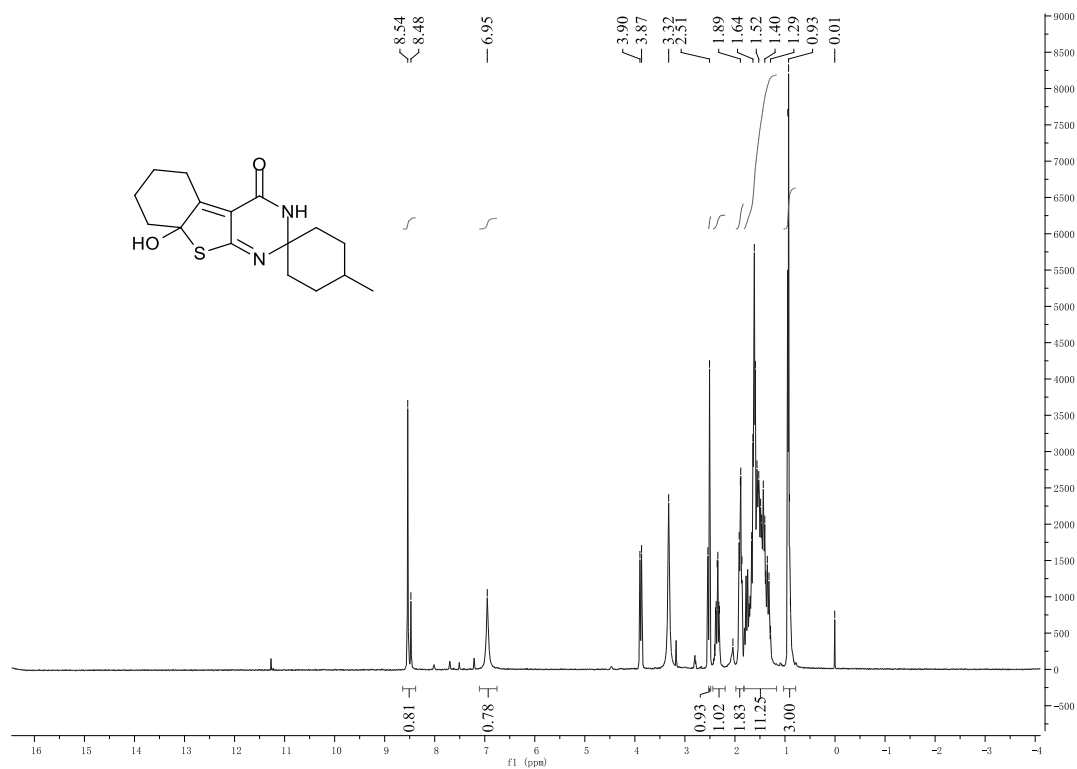
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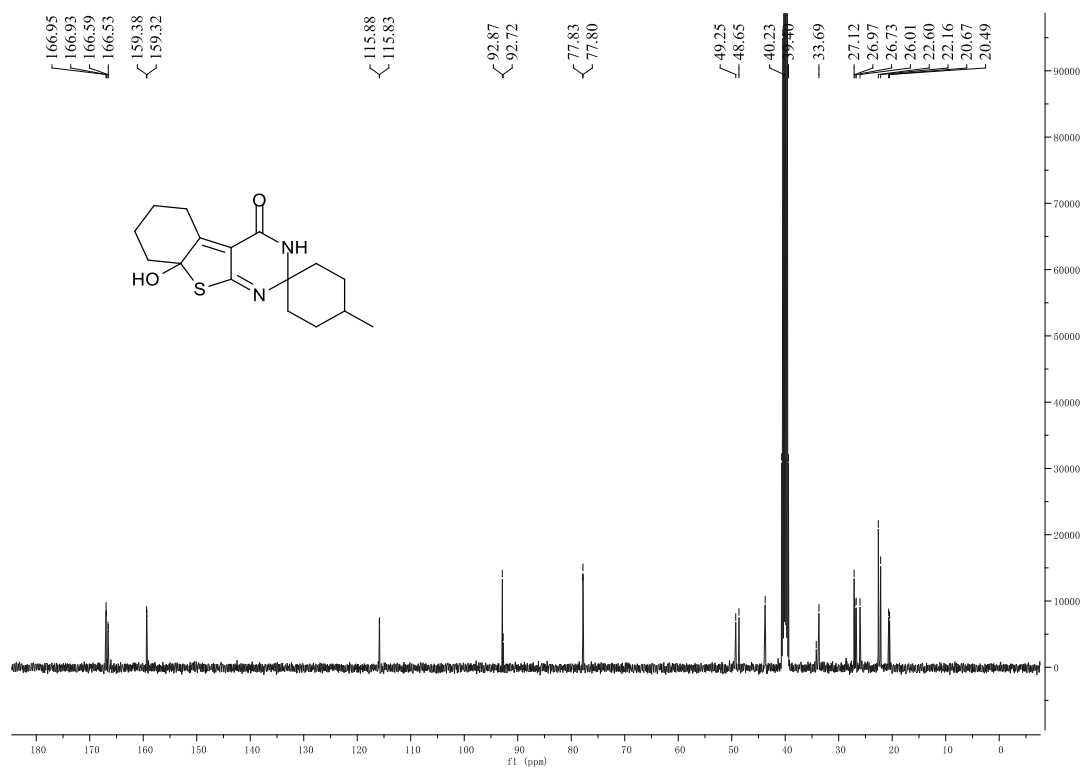
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Instrument Bruker Apex IV FTMS  
Operator Peking University



# <sup>1</sup>H NMR spectrum of 4c



# <sup>13</sup>C NMR spectrum of 4c



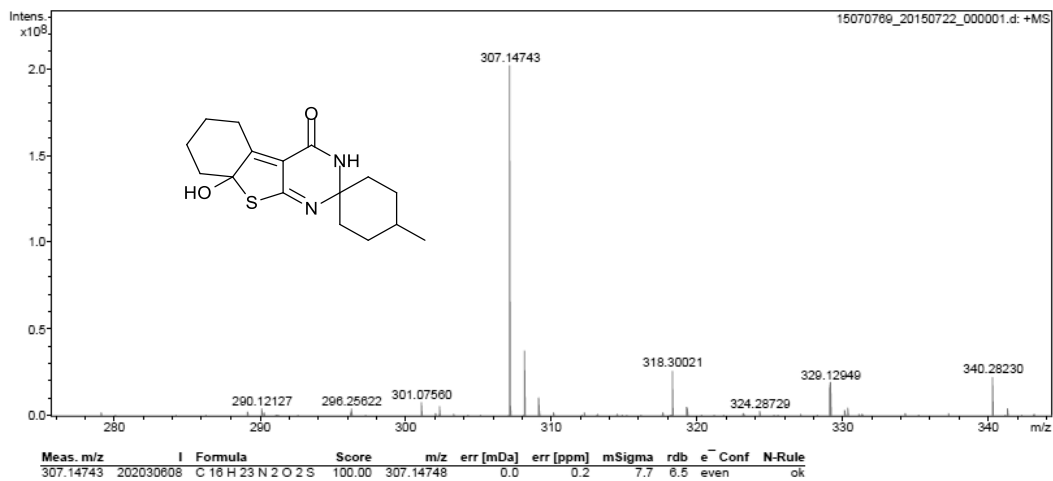
ESI-MS spectrum of **4c**

## Peking University Mass Spectrometry Sample Analysis Report

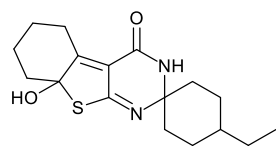
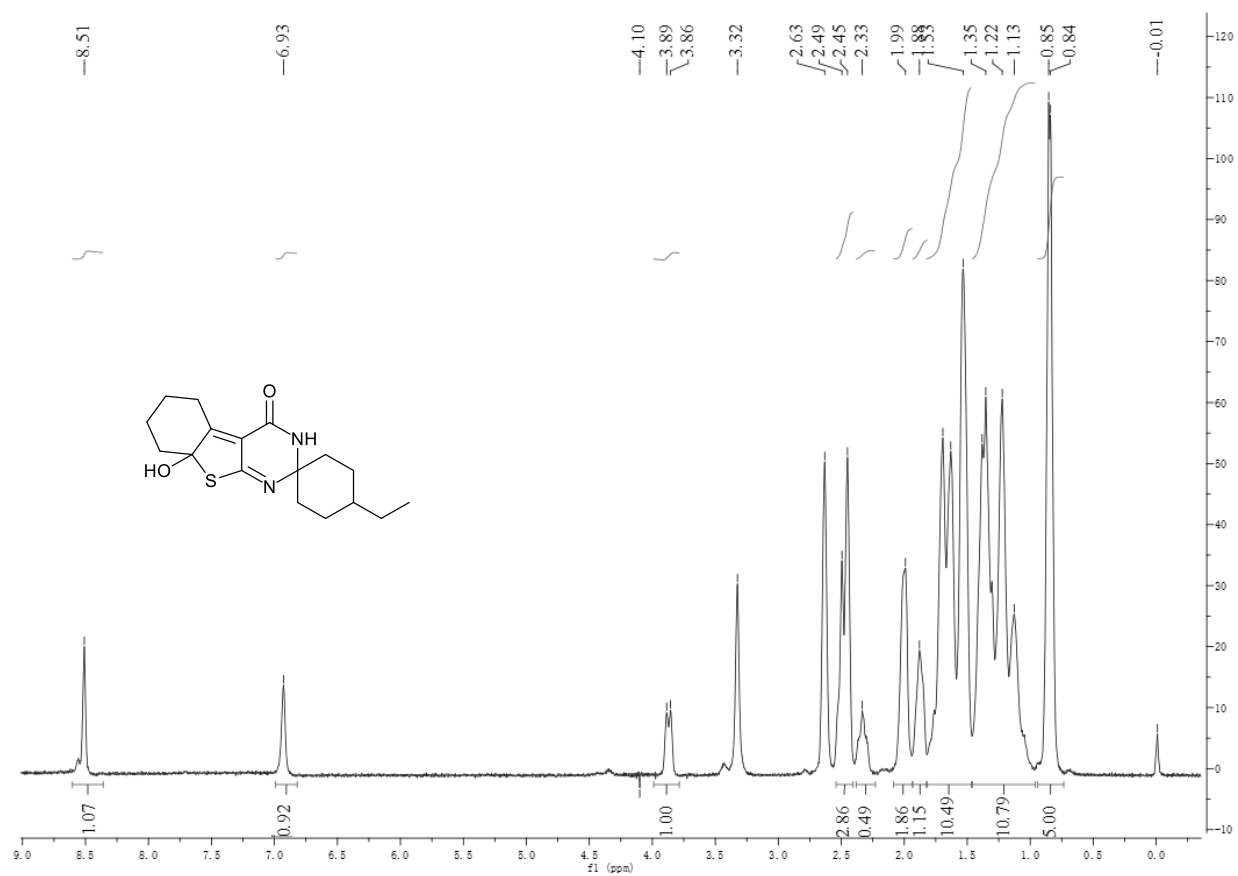
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Comment ESI Positive

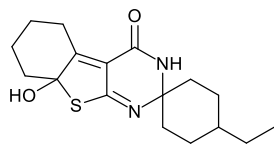
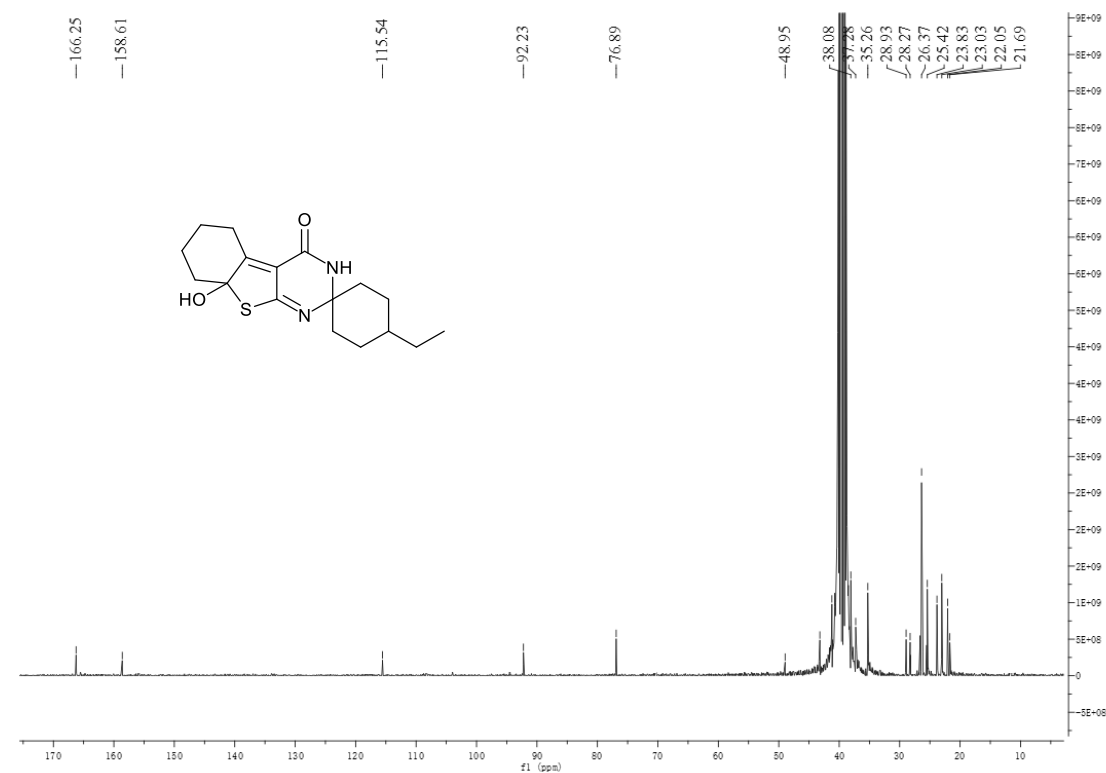
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Instrument Bruker Apex IV FTMS  
Operator Peking University



### <sup>1</sup>H NMR spectrum of **4d**



### <sup>13</sup>C NMR spectrum of **4d**



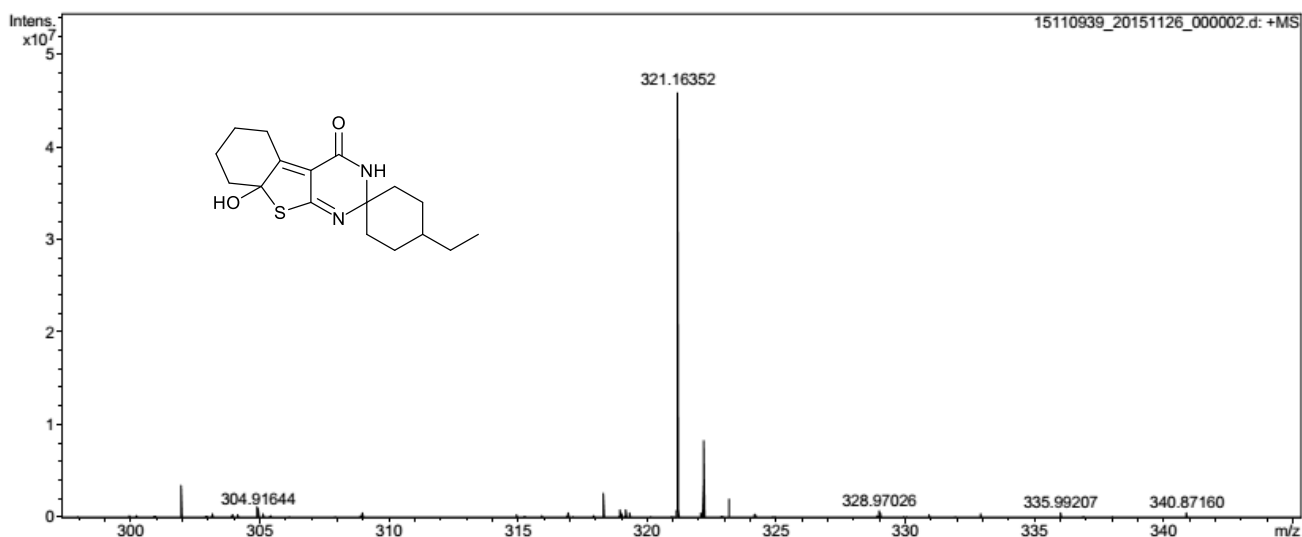
ESI-MS spectrum of **4d**

## Peking University Mass Spectrometry Sample Analysis Report

## Analysis Info

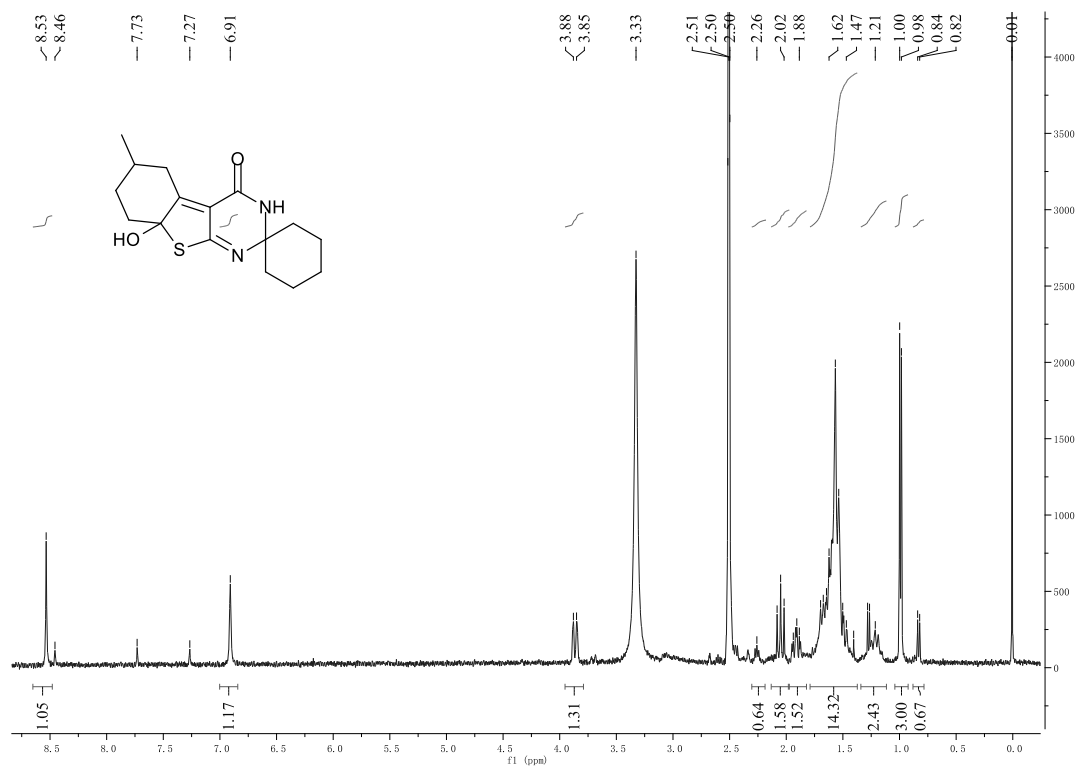
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Comment ESI Positive

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Instrument Bruker Apex IV FTMS  
Operator Peking University

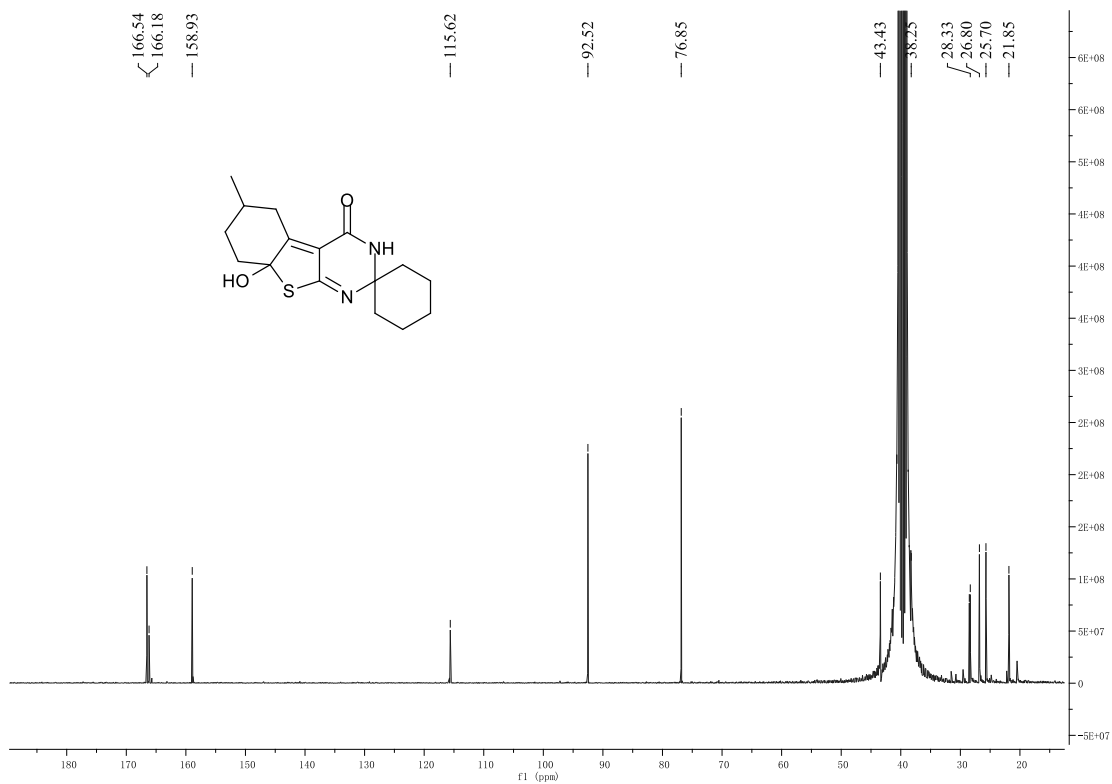


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321.16352	46277404	C 17 H 25 N 2 O 2 S	100.00	321.16313	-0.4	-1.2	14.5	6.5	even	ok

# <sup>1</sup>H NMR spectrum of 4e



# <sup>13</sup>C NMR spectrum of 4e



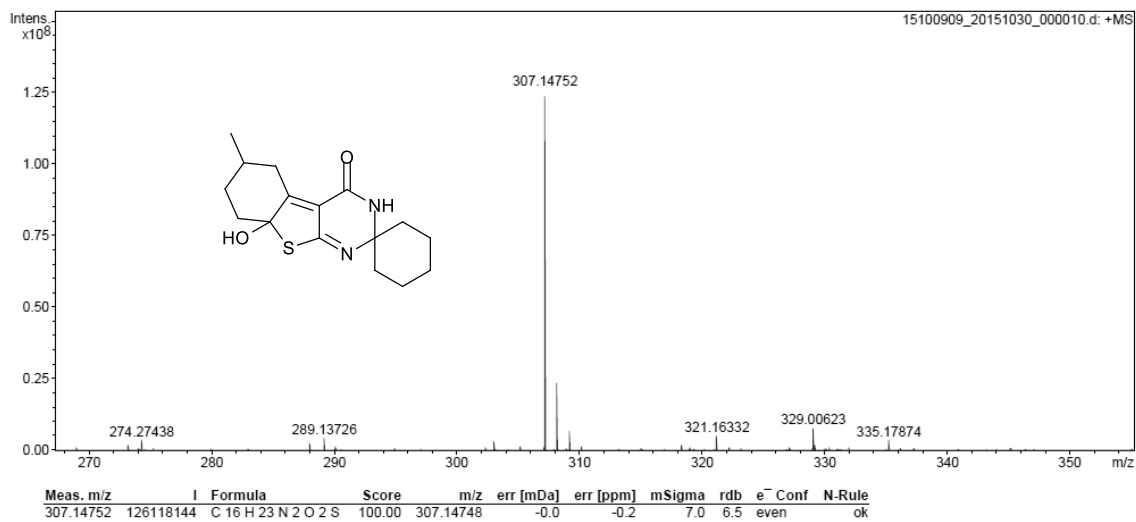
ESI-MS spectrum of **4e**

## Peking University Mass Spectrometry Sample Analysis Report

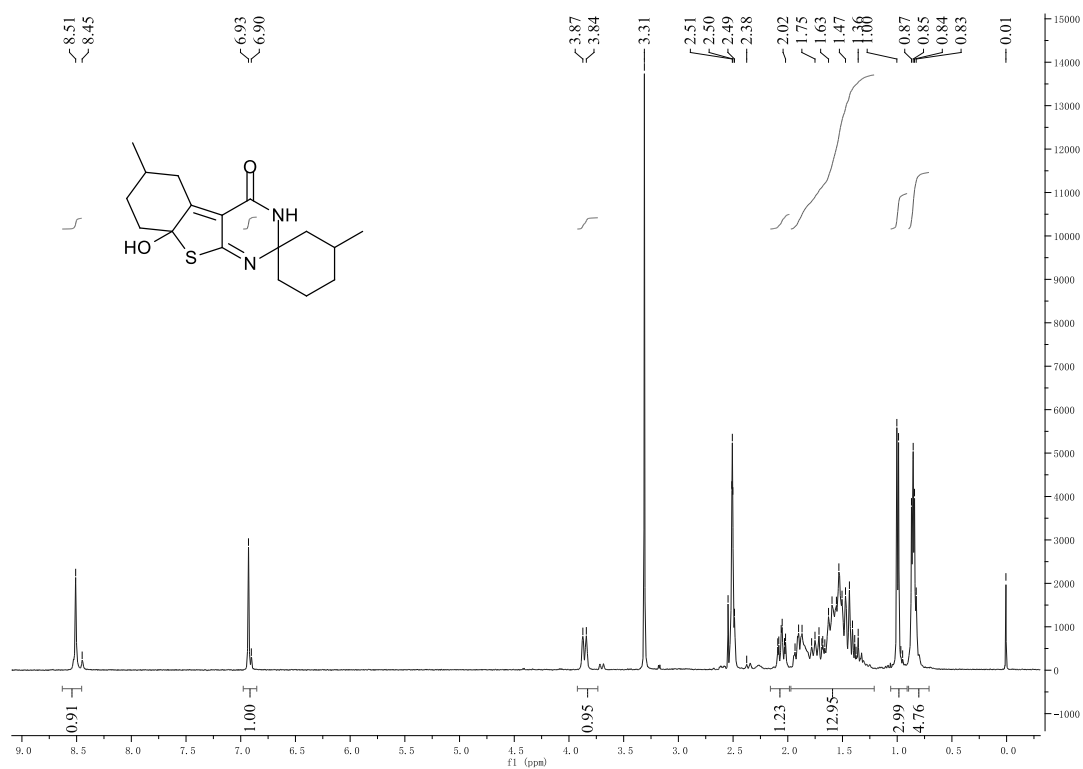
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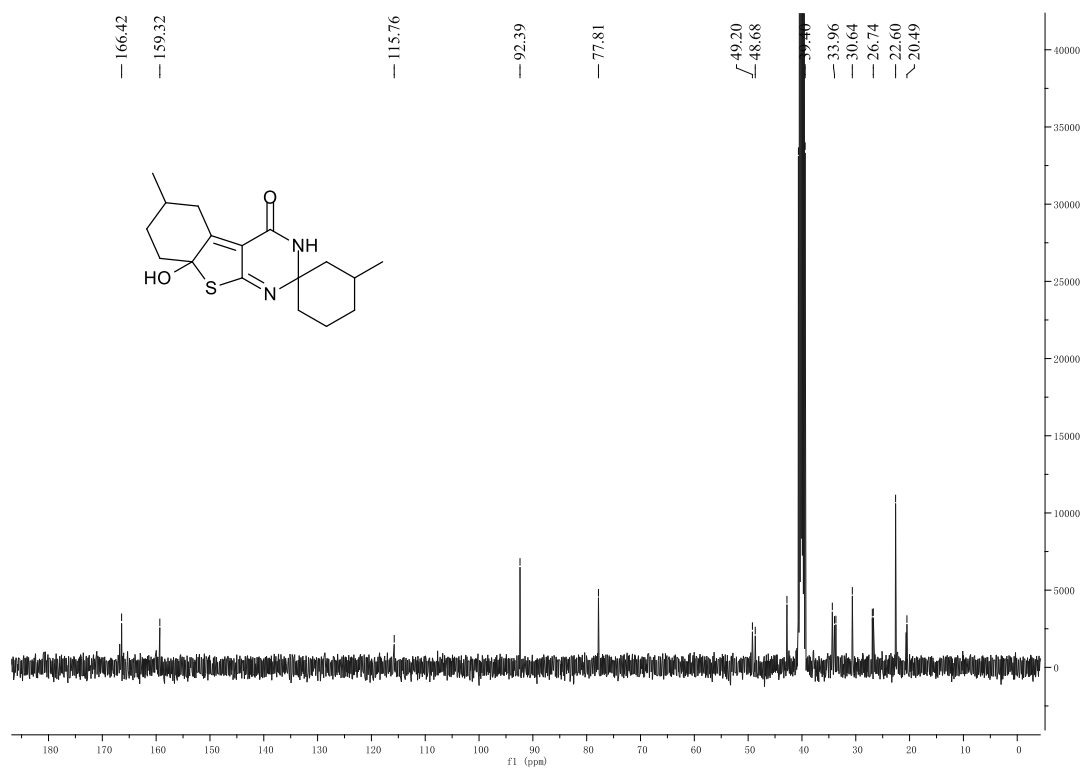
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Operator Peking University



# <sup>1</sup>H NMR spectrum of 4f



# <sup>13</sup>C NMR spectrum of 4f



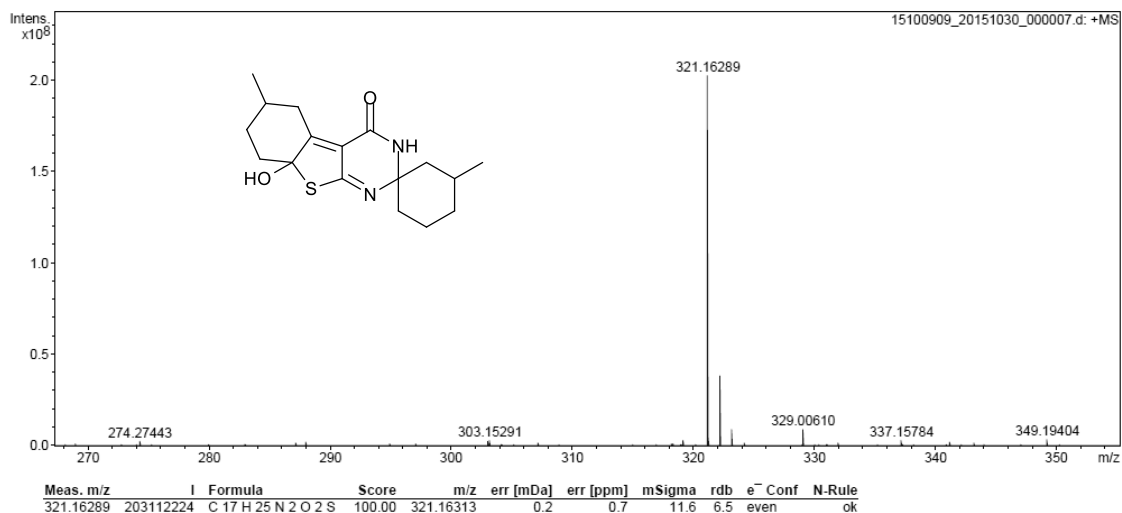
# ESI-MS spectrum of 4f

## Peking University Mass Spectrometry Sample Analysis Report

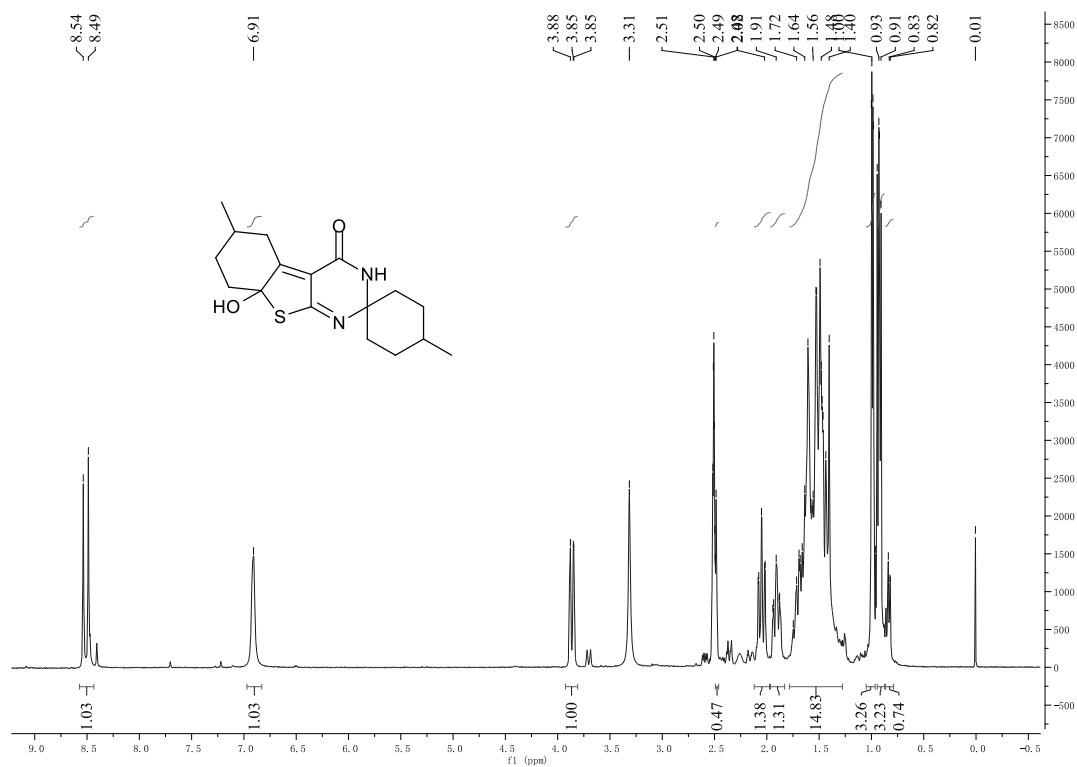
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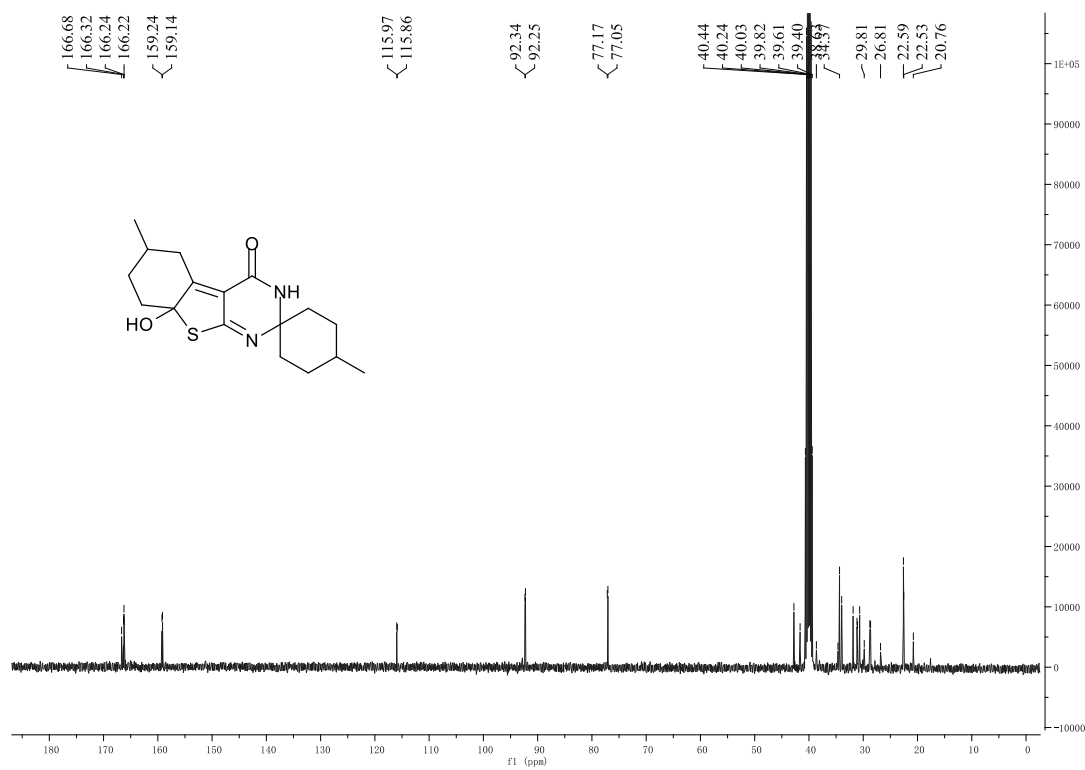
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 Instrument Bruker Apex IV FTMS  
 Operator Peking University



<sup>1</sup>H NMR spectrum of **4g**



<sup>13</sup>C NMR spectrum of **4g**



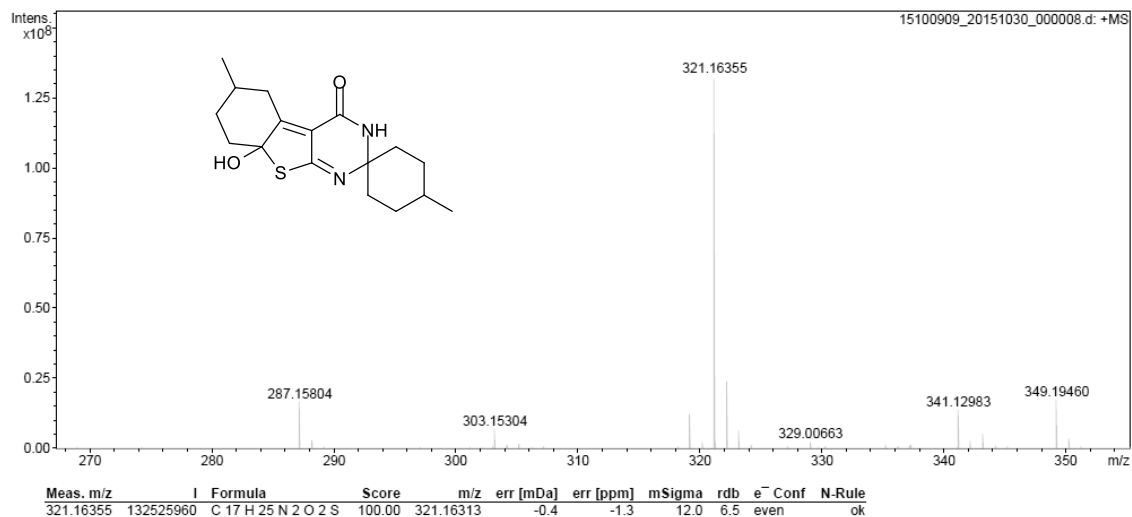
ESI-MS spectrum of **4g**

## Peking University Mass Spectrometry Sample Analysis Report

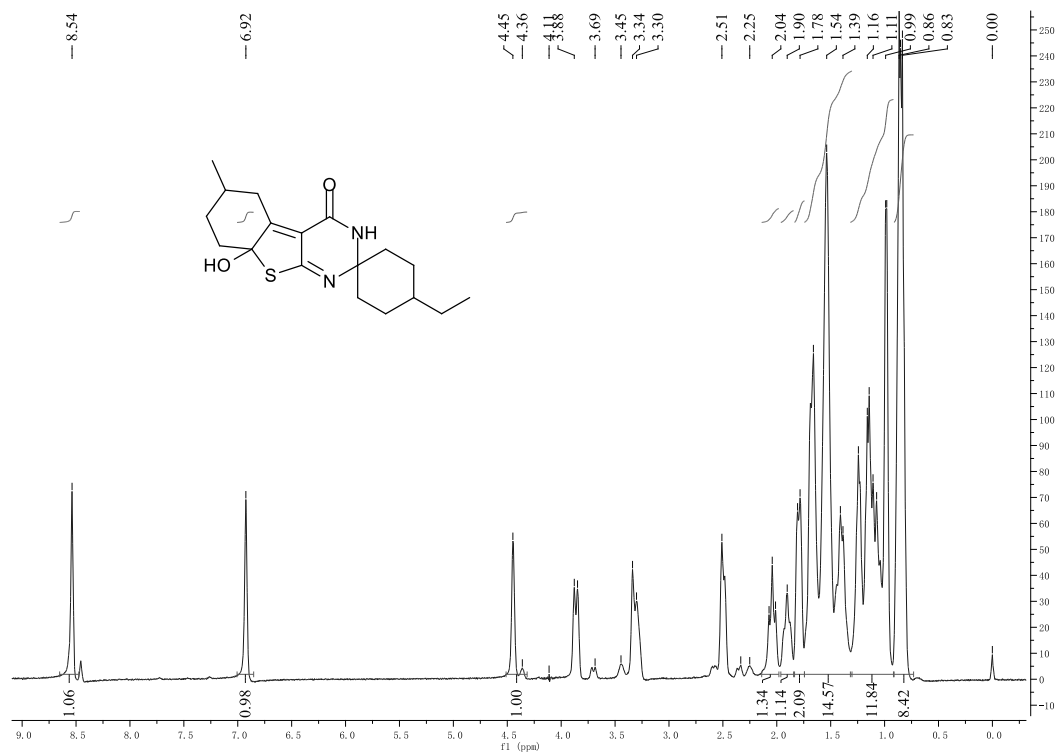
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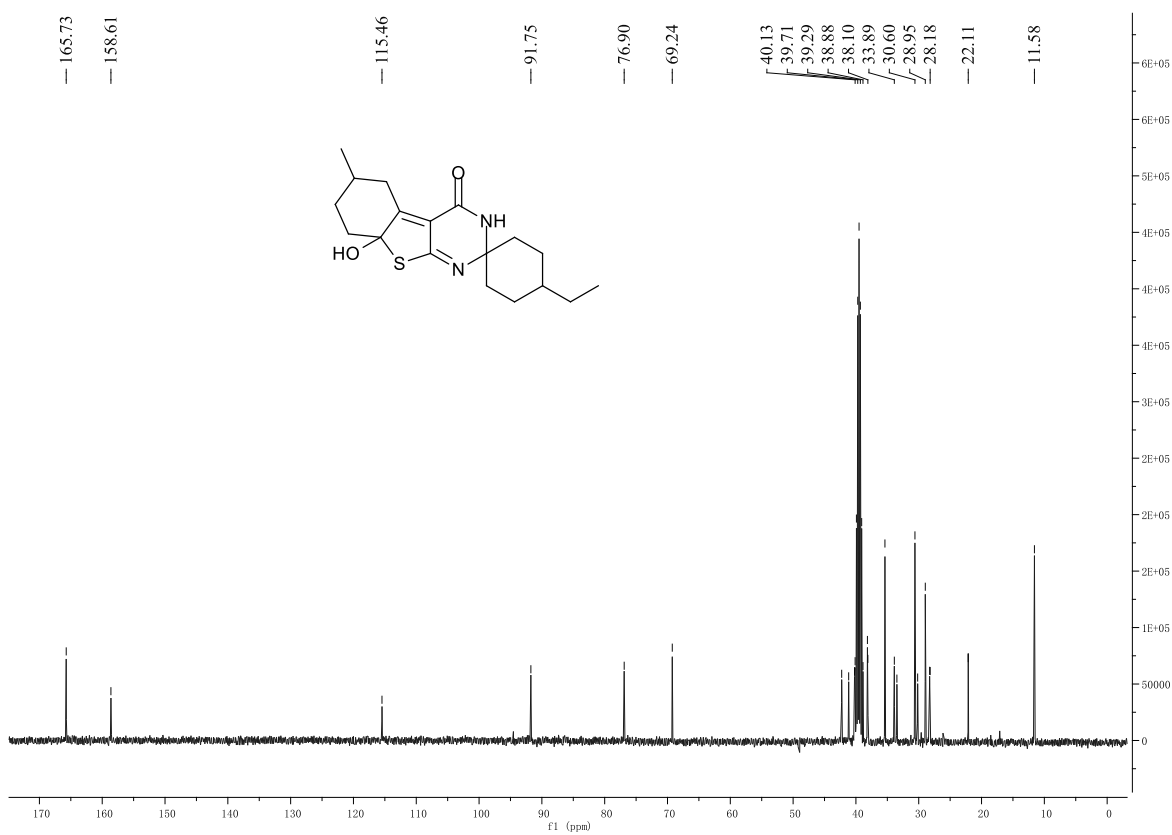
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Instrument Bruker Apex IV FTMS  
Operator Peking University



# <sup>1</sup>H NMR spectrum of **4h**



# <sup>13</sup>C NMR spectrum of **4h**



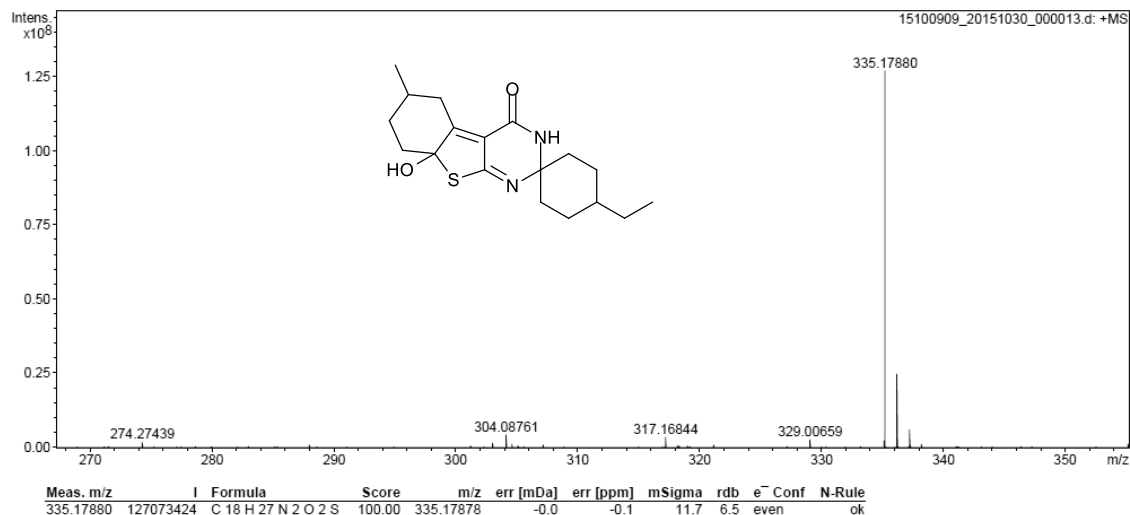
ESI-MS spectrum of **4h**

## Peking University Mass Spectrometry Sample Analysis Report

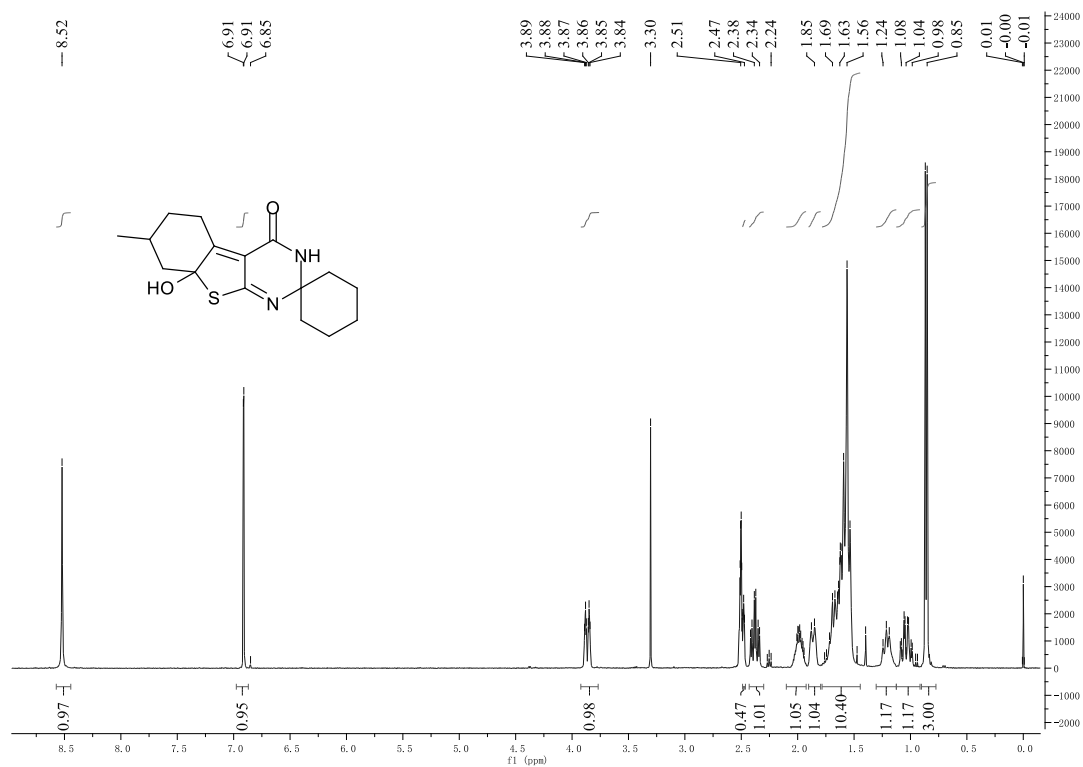
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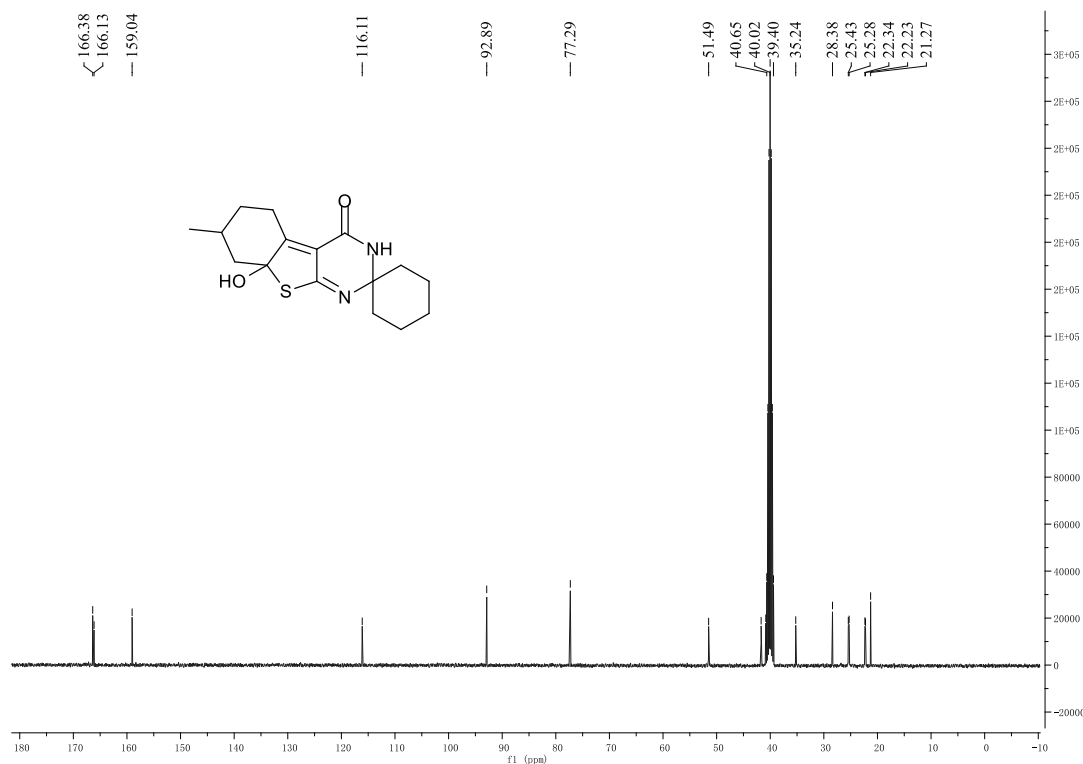
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Operator Peking University



# <sup>1</sup>H NMR spectrum of **4i**



# <sup>13</sup>C NMR spectrum of **4i**



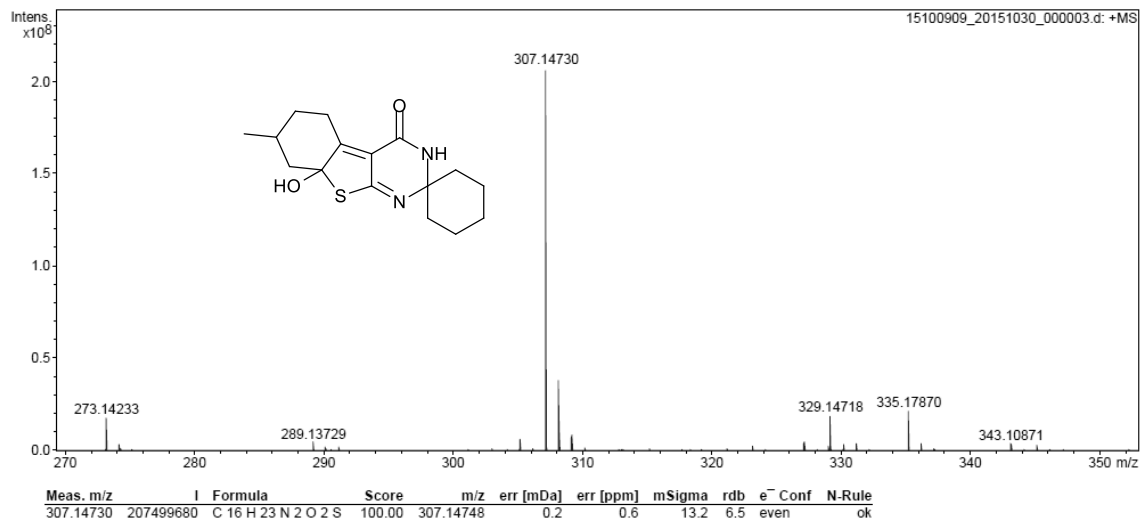
ESI-MS spectrum of **4i**

## Peking University Mass Spectrometry Sample Analysis Report

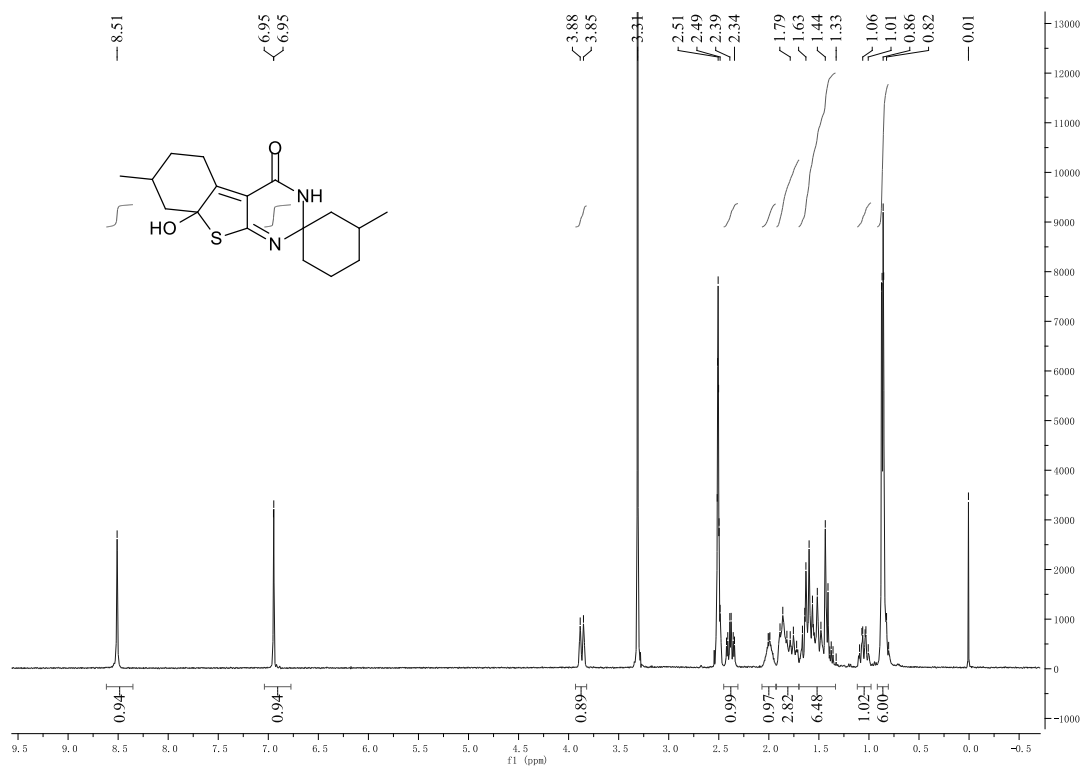
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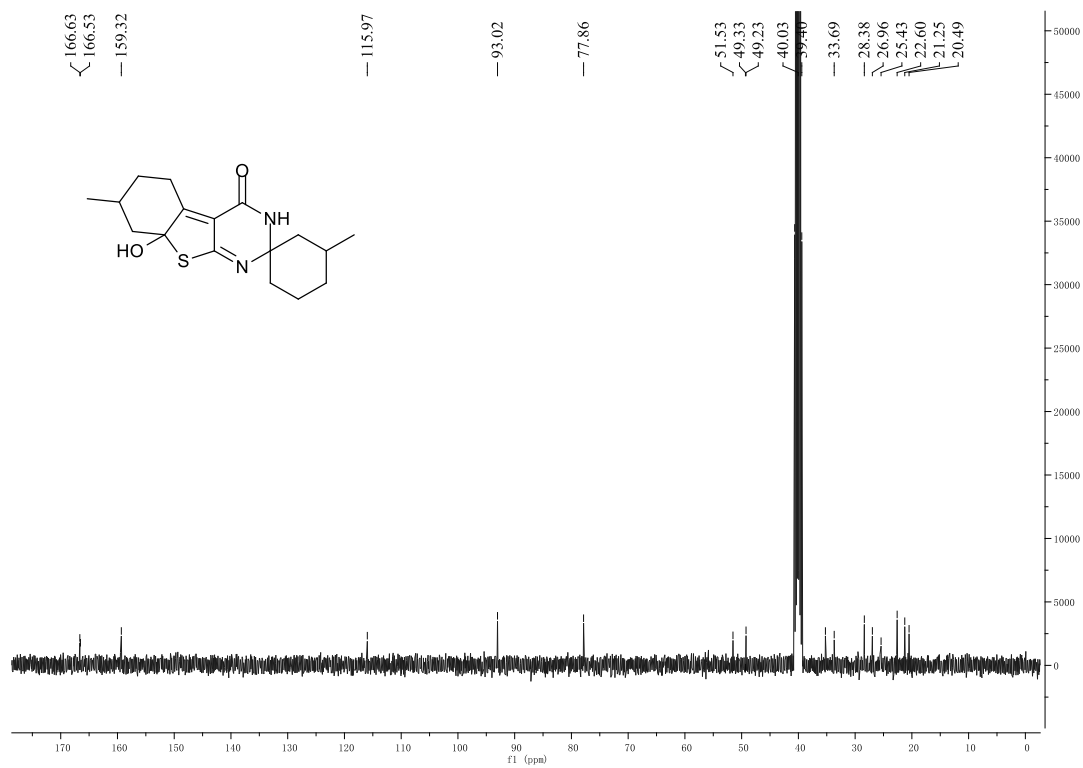
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Operator Peking University



# <sup>1</sup>H NMR spectrum of 4j



# <sup>13</sup>C NMR spectrum of 4j



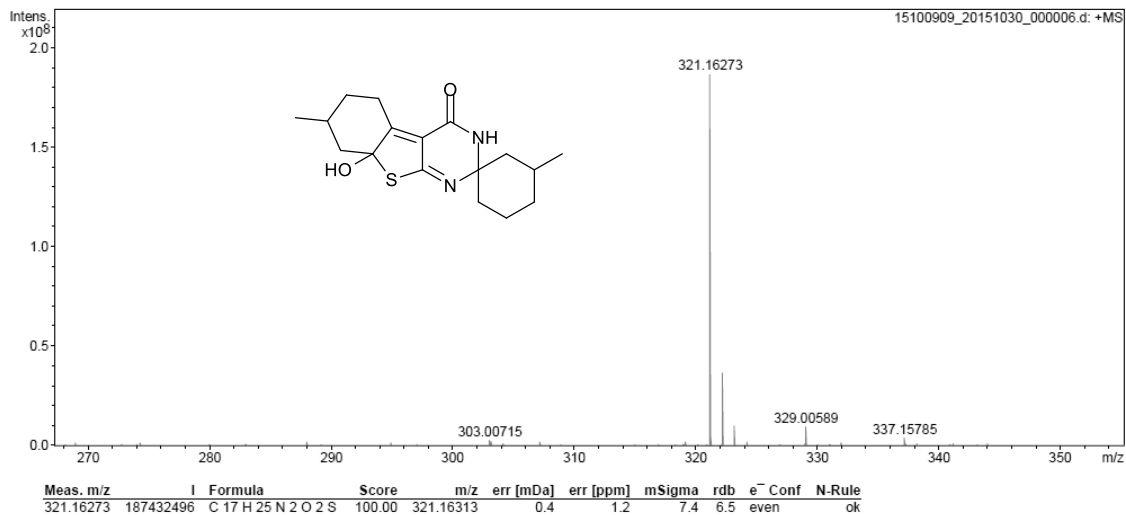
## ESI-MS spectrum of 4j

## Peking University Mass Spectrometry Sample Analysis Report

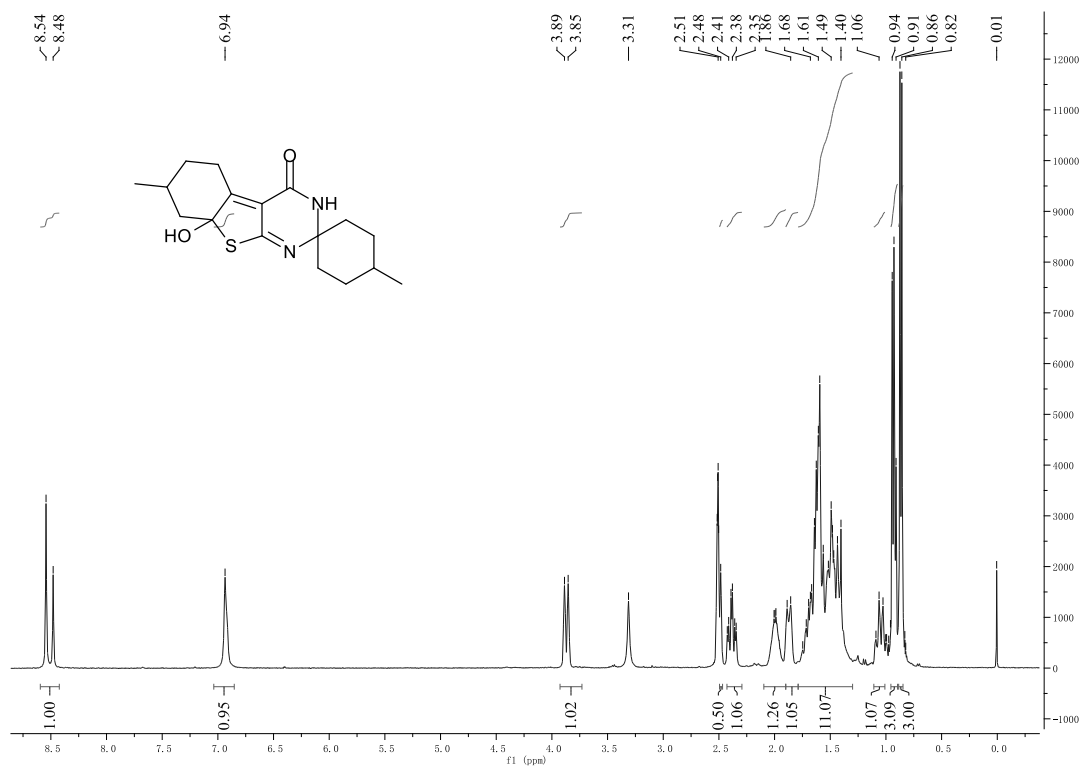
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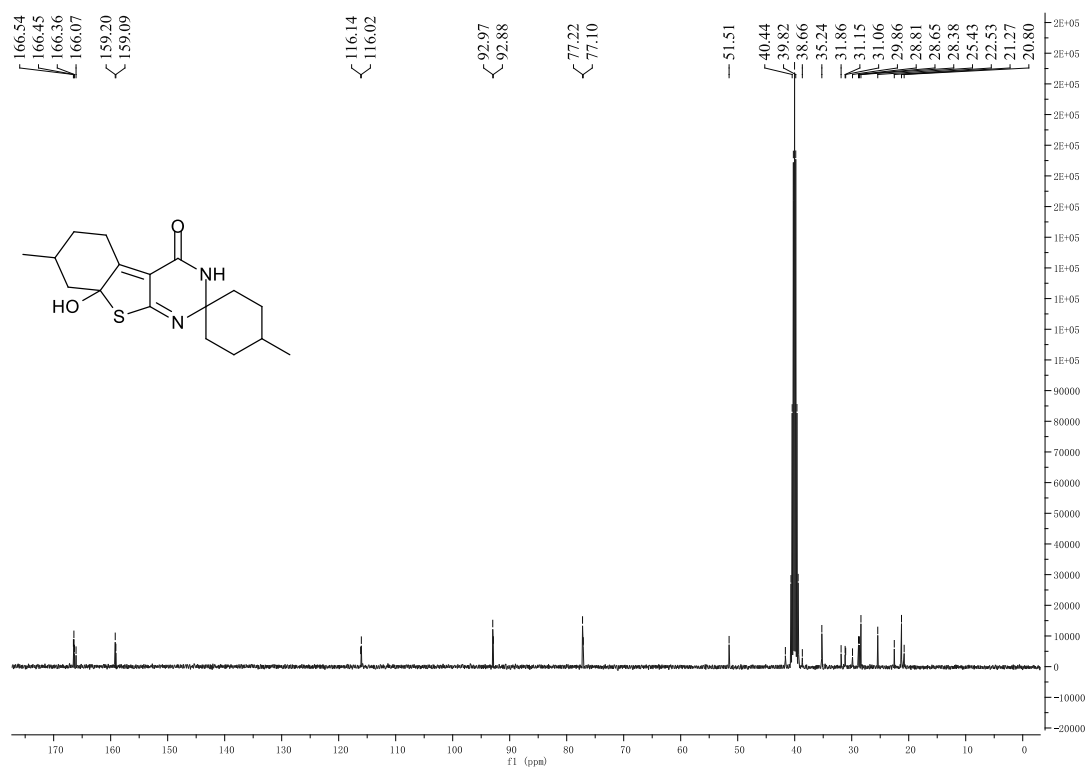
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Operator Peking University



### <sup>1</sup>H NMR spectrum of **4k**



### <sup>13</sup>C NMR spectrum of **4k**



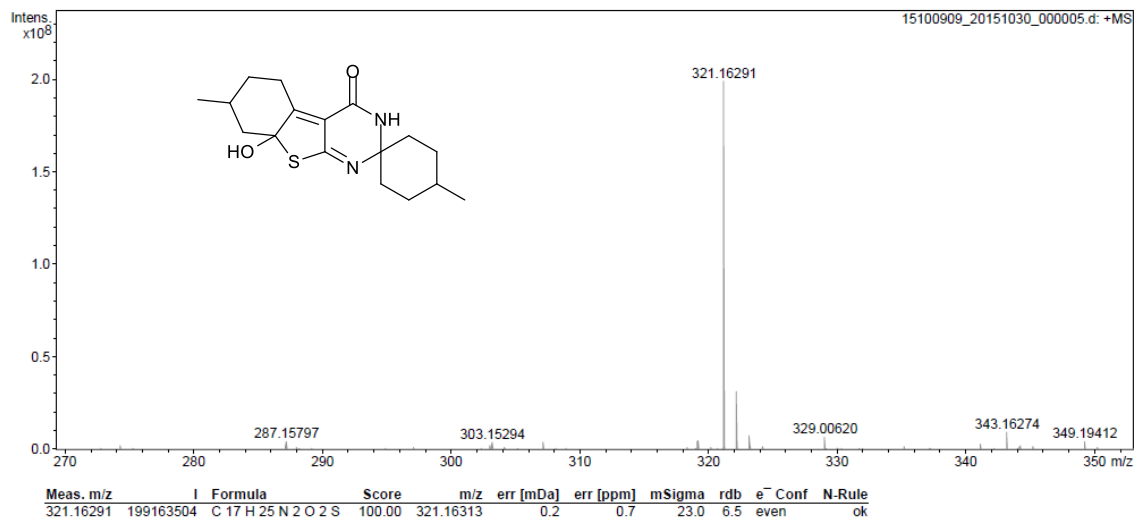
ESI-MS spectrum of **4k**

## Peking University Mass Spectrometry Sample Analysis Report

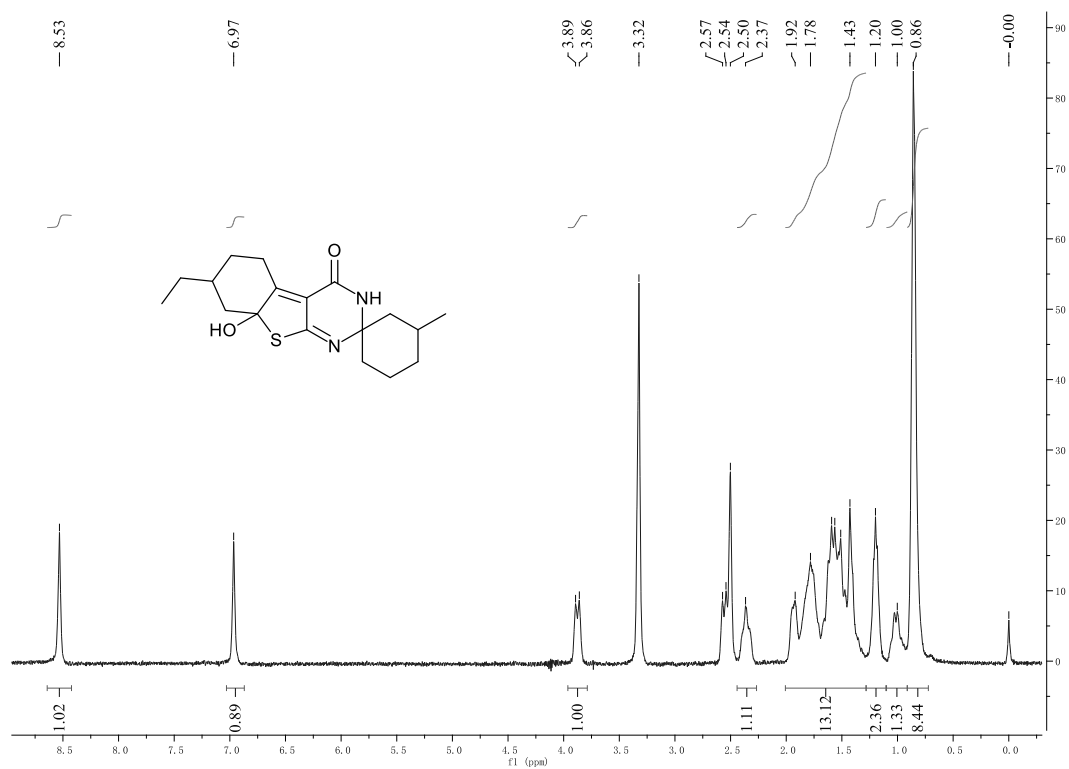
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Comment ESI Positive

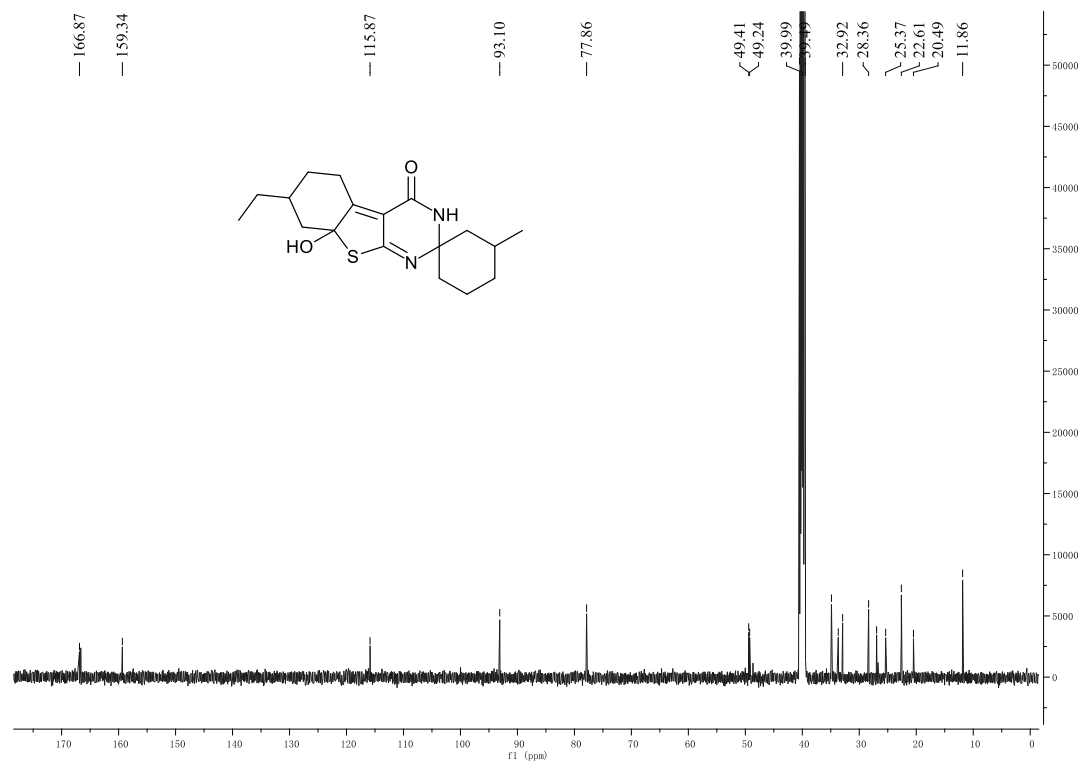
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Instrument Bruker Apex IV FTMS  
Operator Peking University



# <sup>1</sup>H NMR spectrum of **41**



# <sup>13</sup>C NMR spectrum of **41**

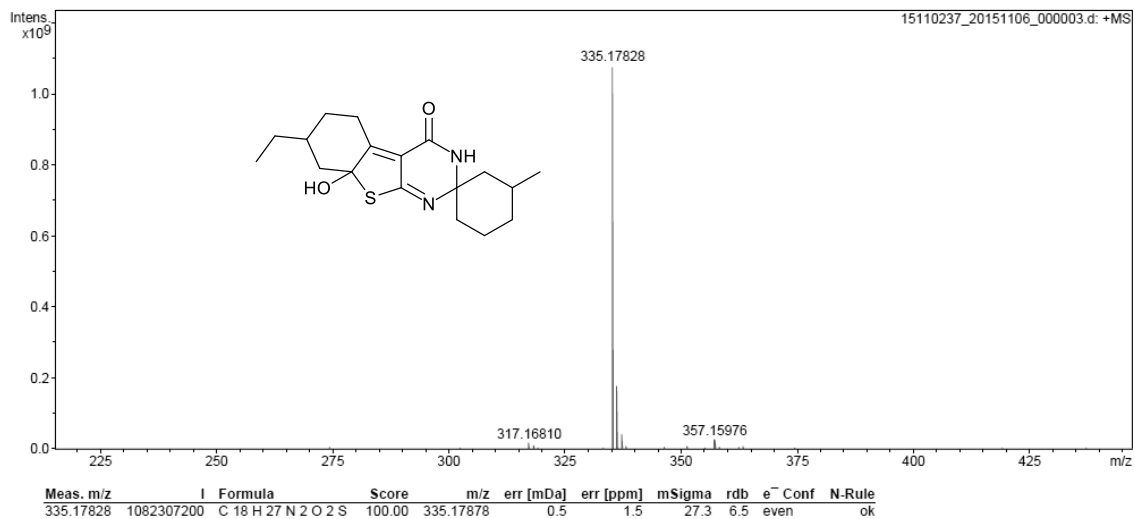


ESI-MS spectrum of **41**

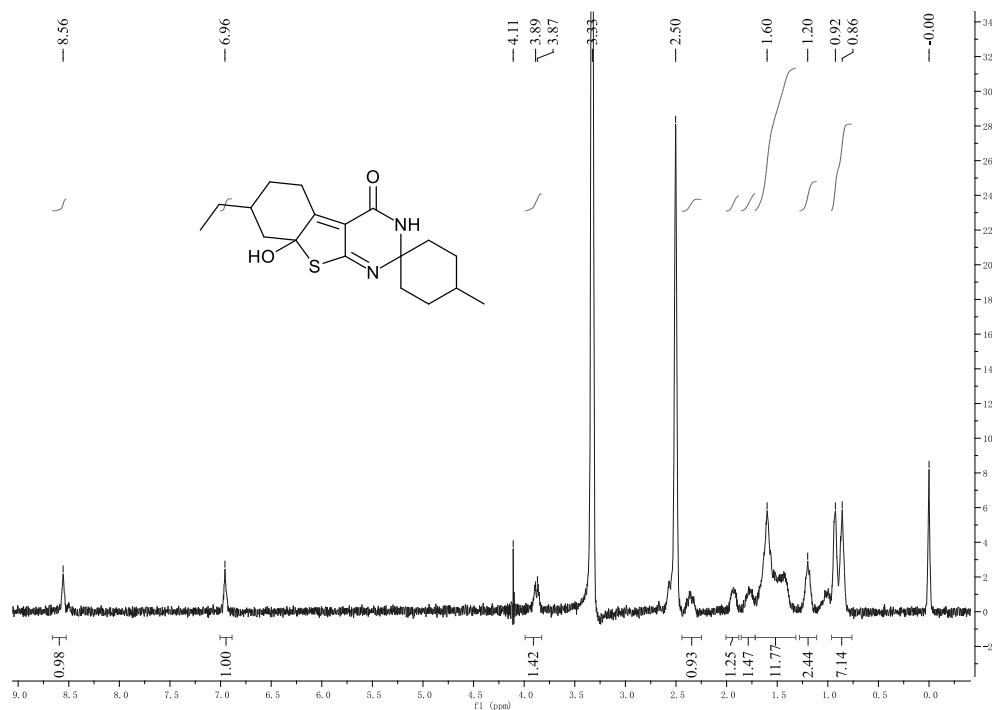
## Peking University Mass Spectrometry Sample Analysis Report

## Analysis Info

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Sample	YB26	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

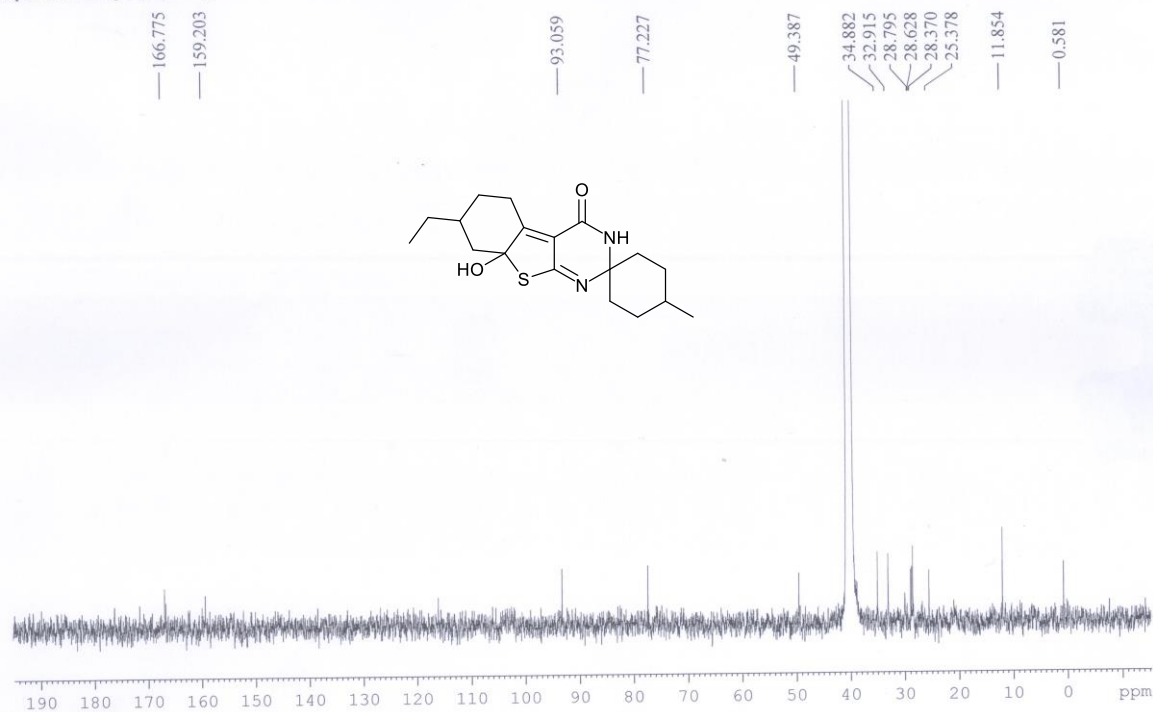


# <sup>1</sup>H NMR spectrum of 4m



# <sup>13</sup>C NMR spectrum of 4m

AVANCE III 500 BRUKER A&T Center BNU  
Sample:BY25 Solvent:DMSO  
Spectrum:beiligong-lijiarong 1109-4 13C



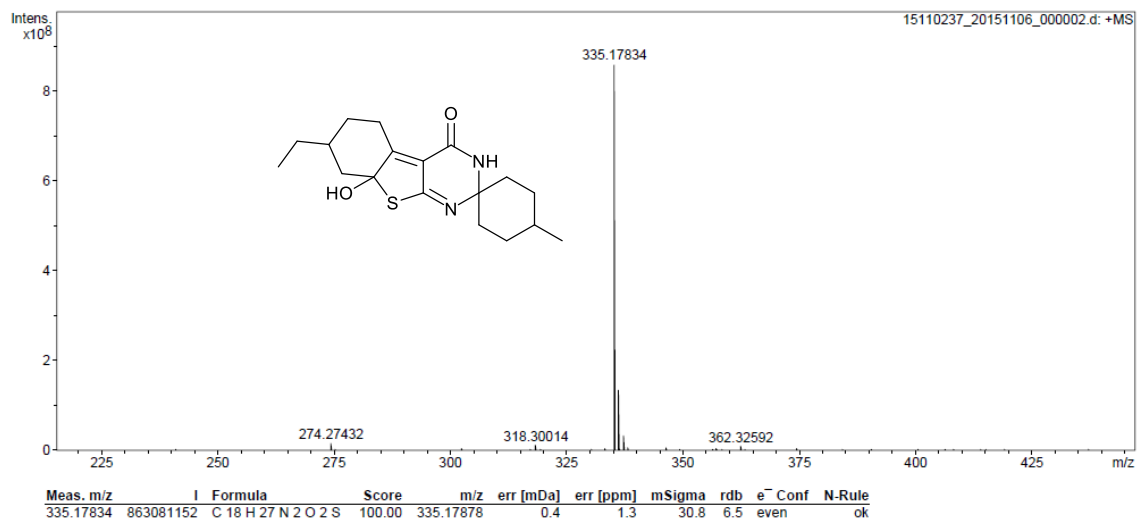
ESI-MS spectrum of **4m**

## Peking University Mass Spectrometry Sample Analysis Report

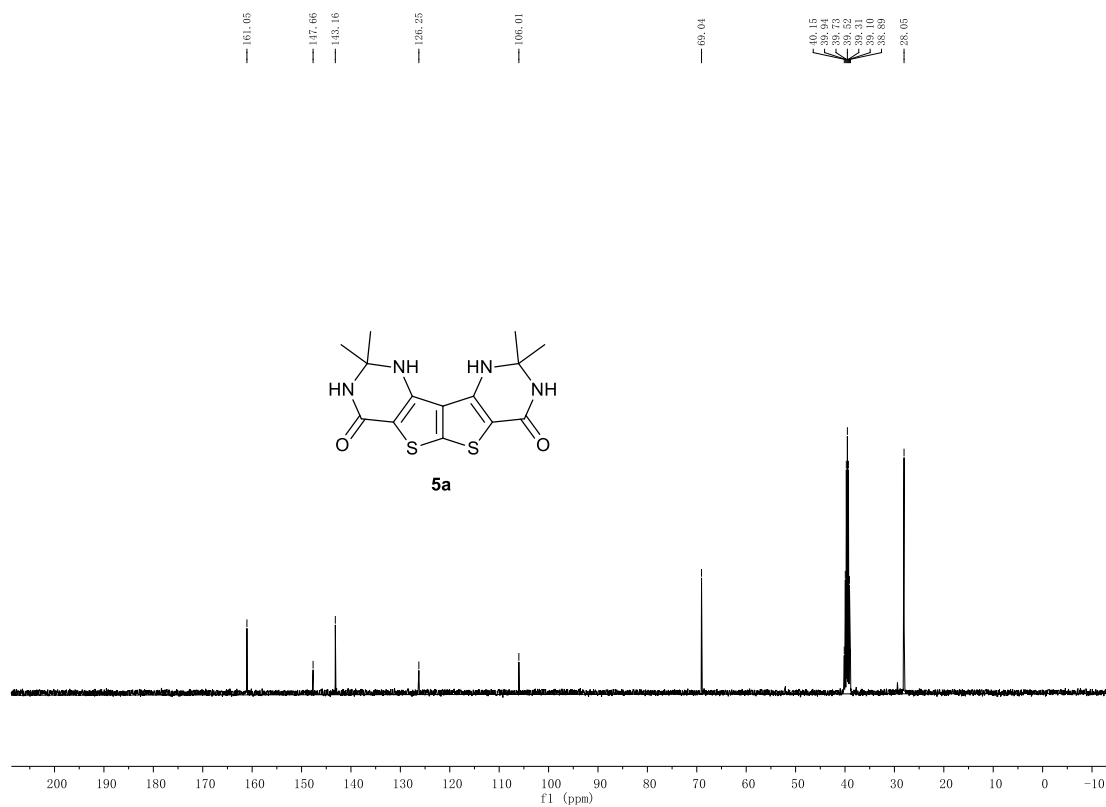
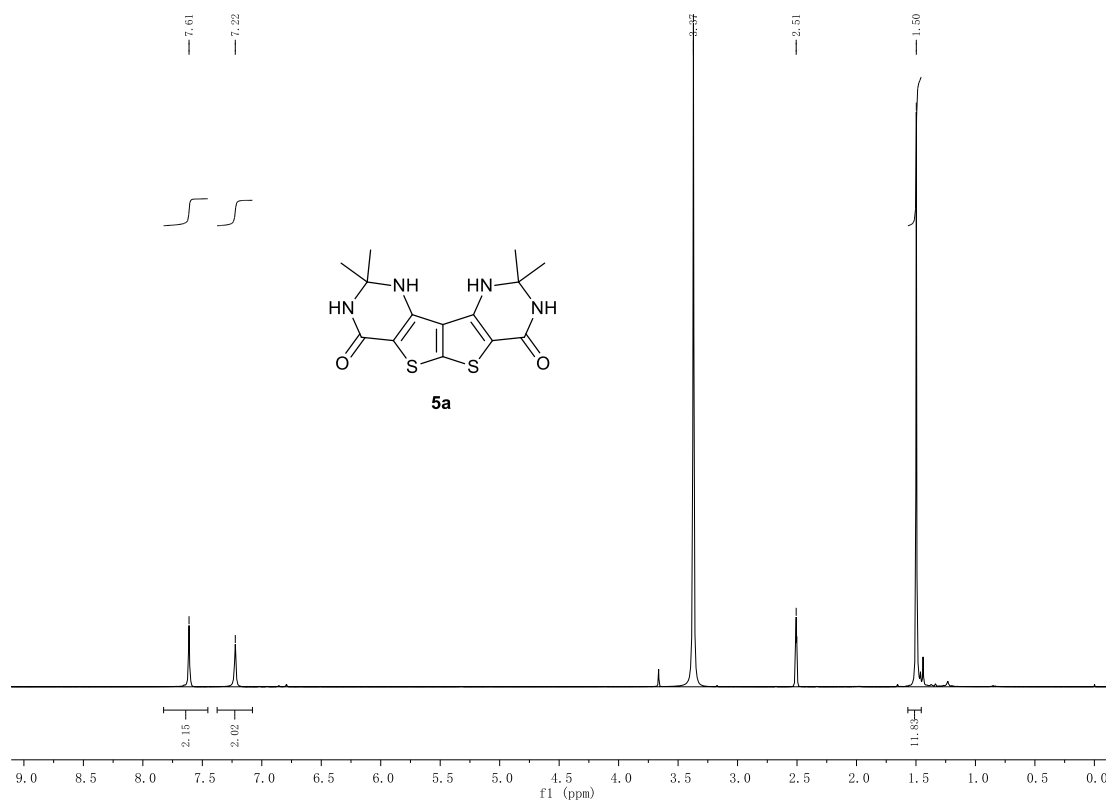
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Sample YB25  
Comment ESI Positive

Acquisition Date 11/6/2015 6:53:45 PM  
Instrument Bruker Apex IV FTMS  
Operator Peking University



### 3. Copies of 5 <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra

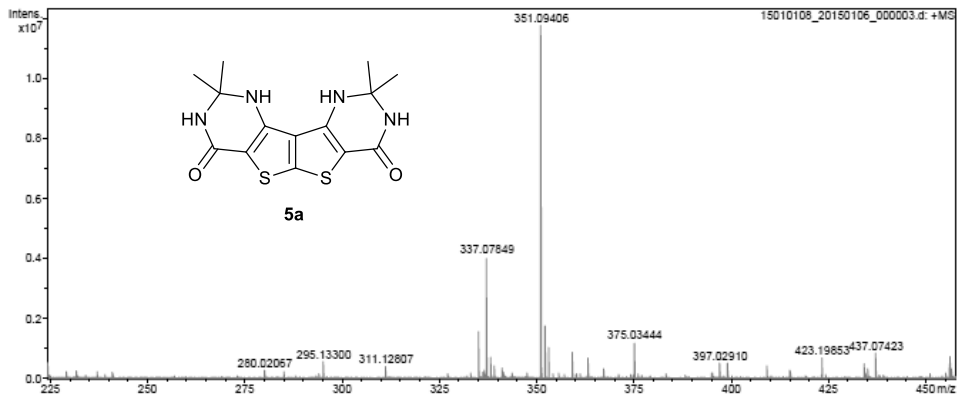


## Peking University Mass Spectrometry Sample Analysis Report

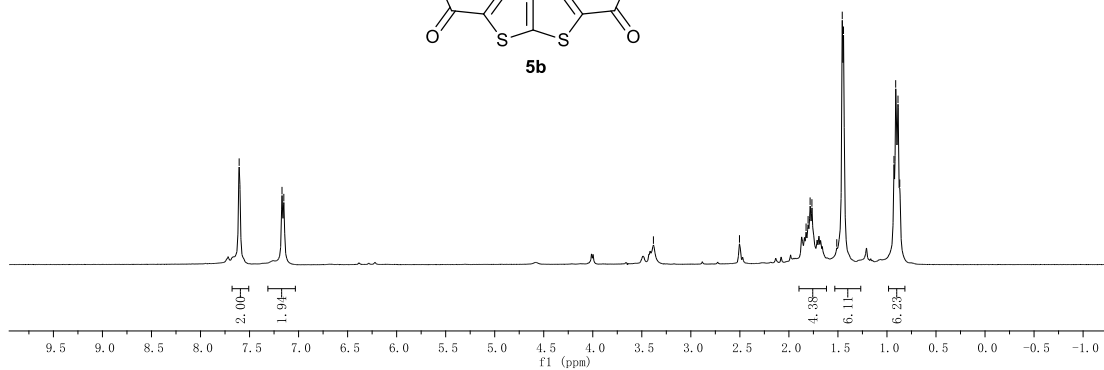
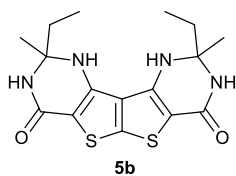
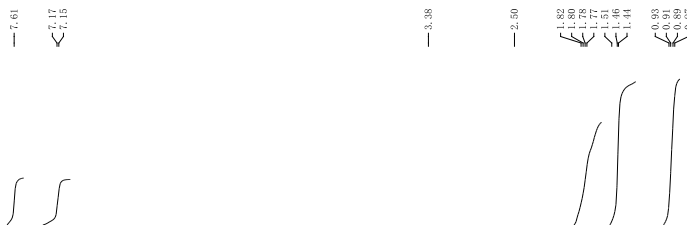
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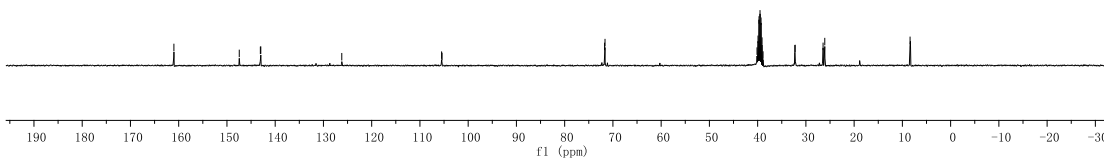
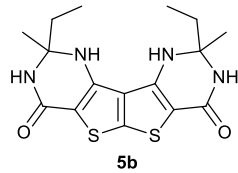
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 Instrument: Bruker Apex IV FTMS  
 Operator: Peking University



Meas. m/z	I	Formula	Score	m/z	err (mDa)	err (ppm)	mSigma	rdB	e <sup>-</sup> Conf	N-Rule
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351.09406	11760174	C 15 H 19 N 4 O 2 S 2	100.00	351.09439	0.3	1.0	23.5	8.5	even	ok



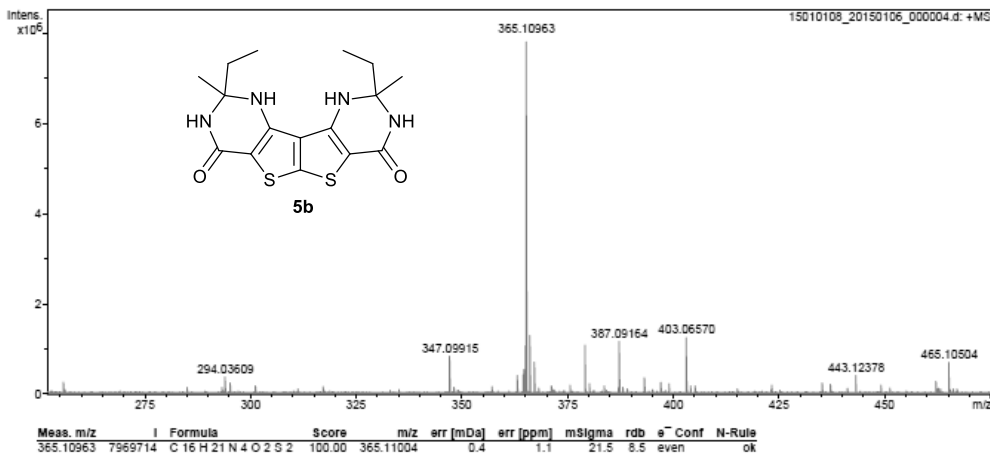
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 39.72  
 39.72  
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 8.41  
 8.34

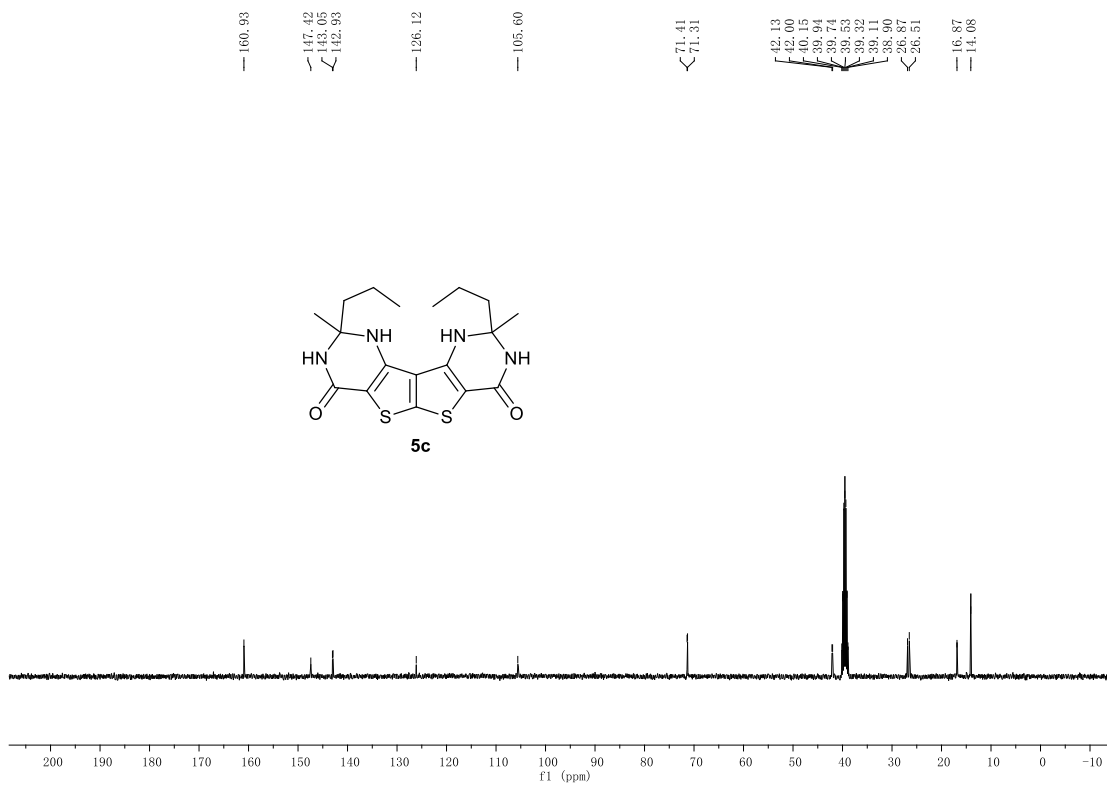
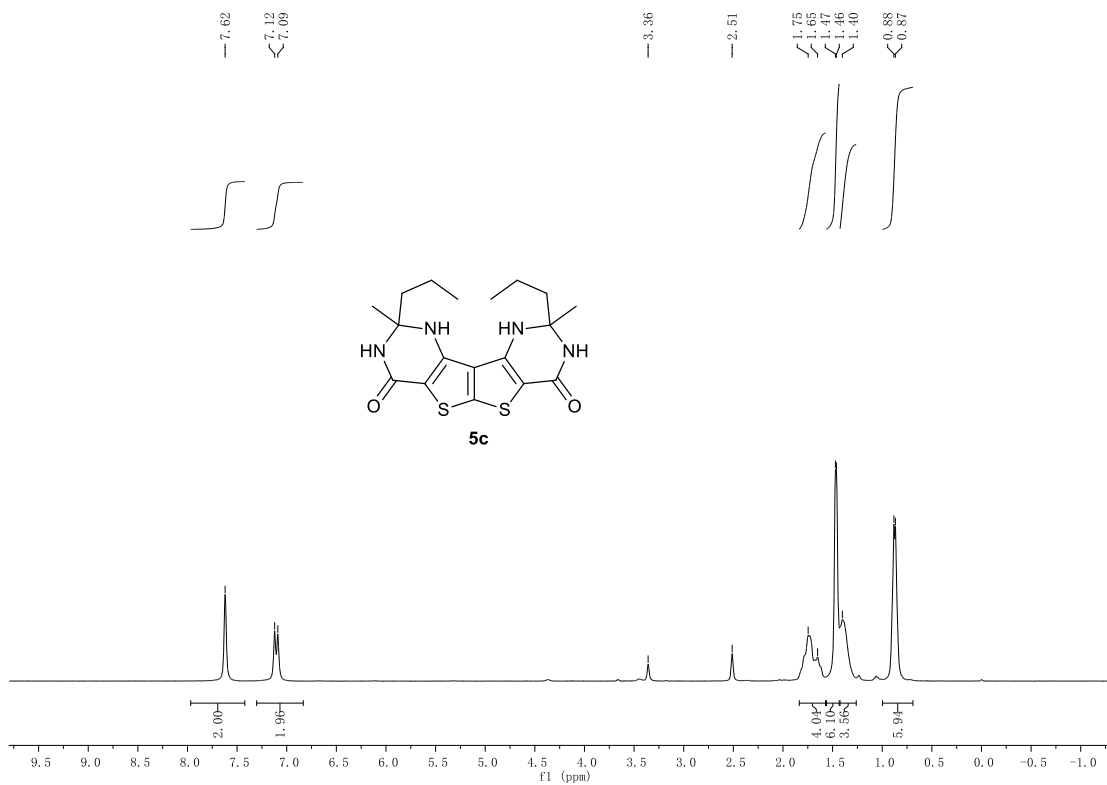


### Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

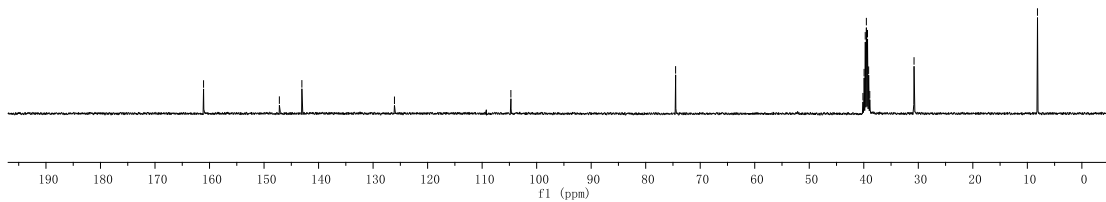
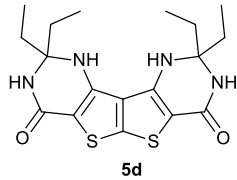
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Sample	027-dt-s-qfd	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University







161.10  
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143.06  
126.08  
104.73  
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30.78  
8.15

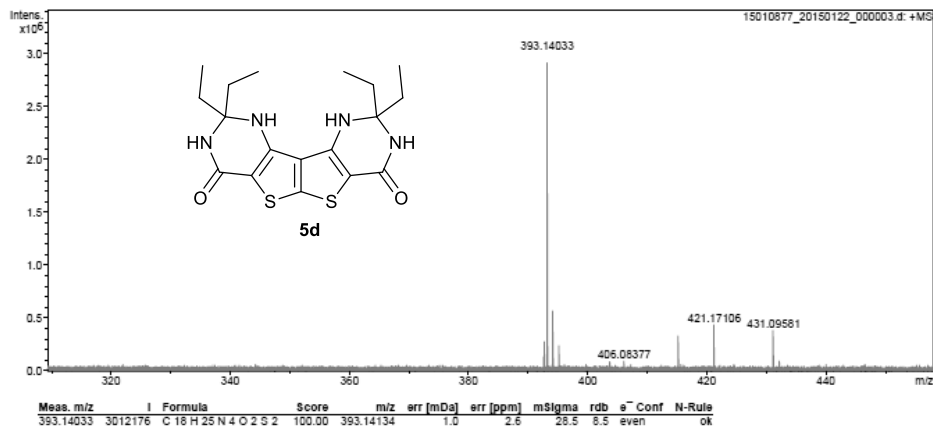


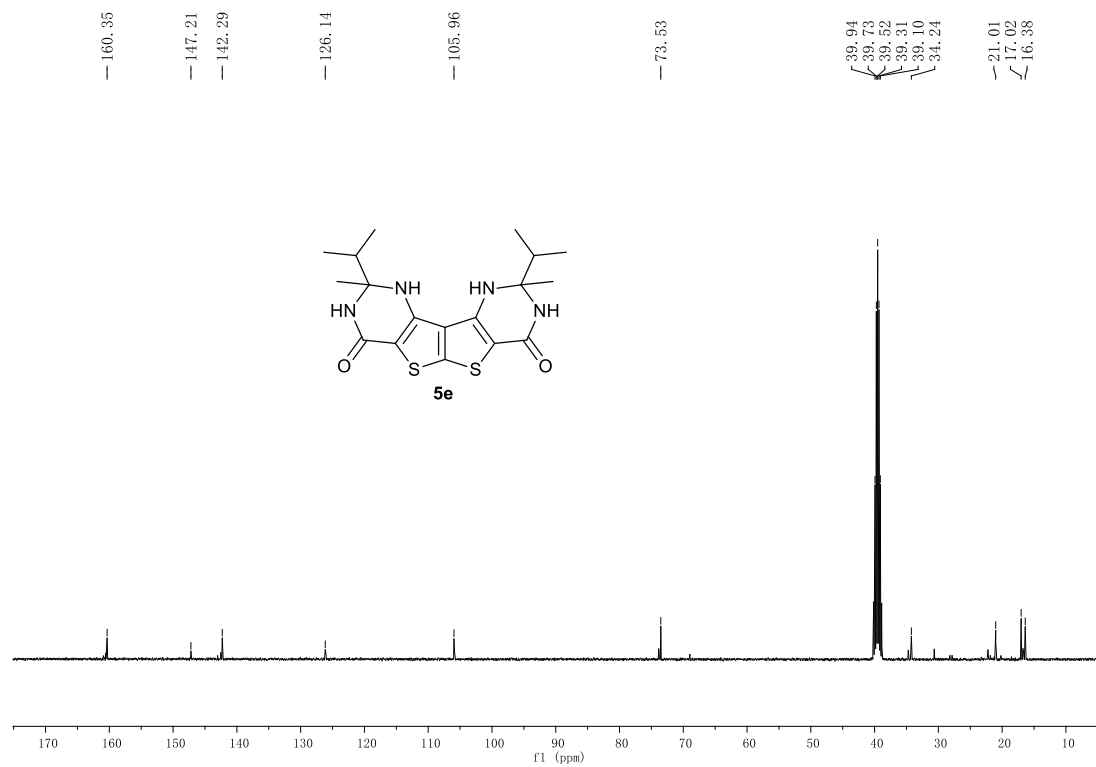
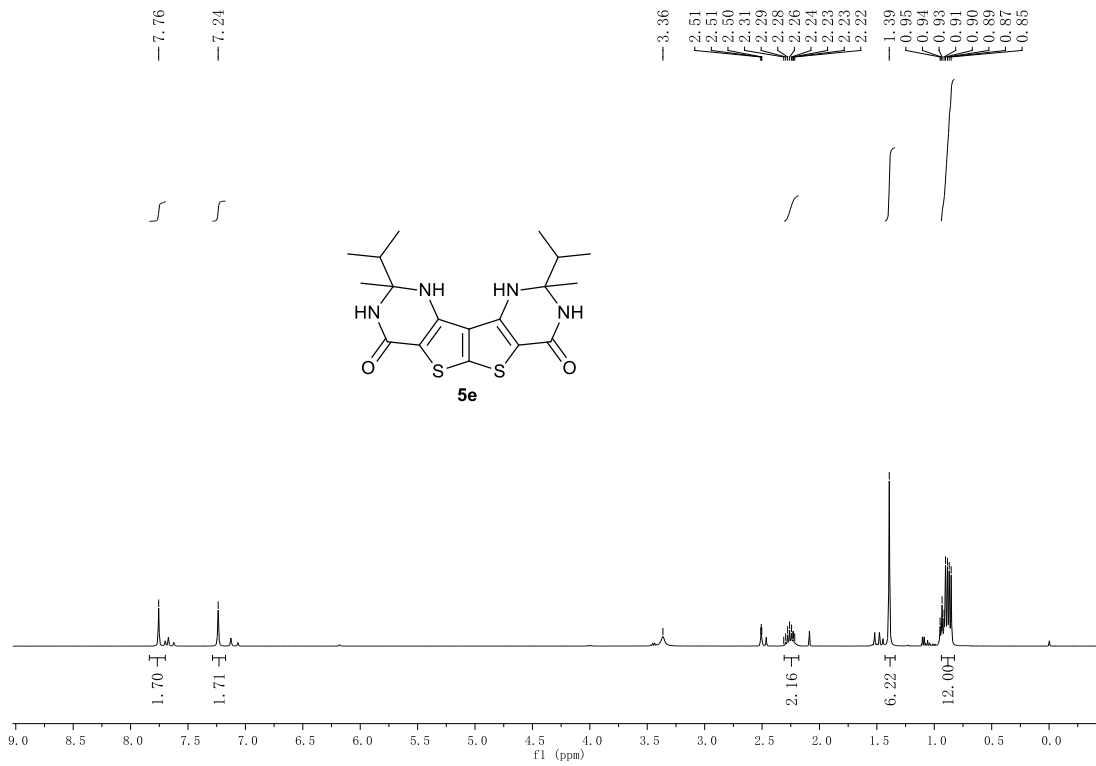
### Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

Analysis Name 15010877\_20150122\_000003.d  
Sample 027-3-wutong-qfd  
Comment ESI Positive

Acquisition Date 1/22/2015 5:03:52 PM  
Instrument Bruker Apex IV FTMS  
Operator Peking University



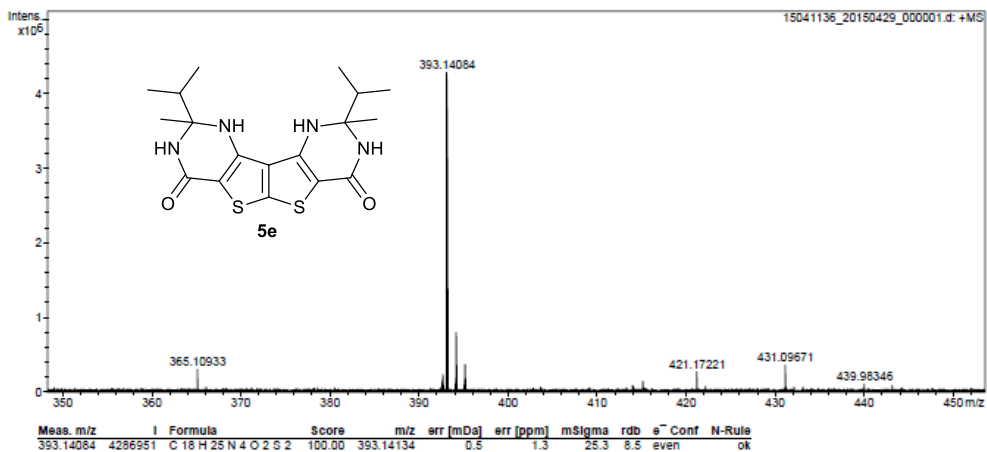


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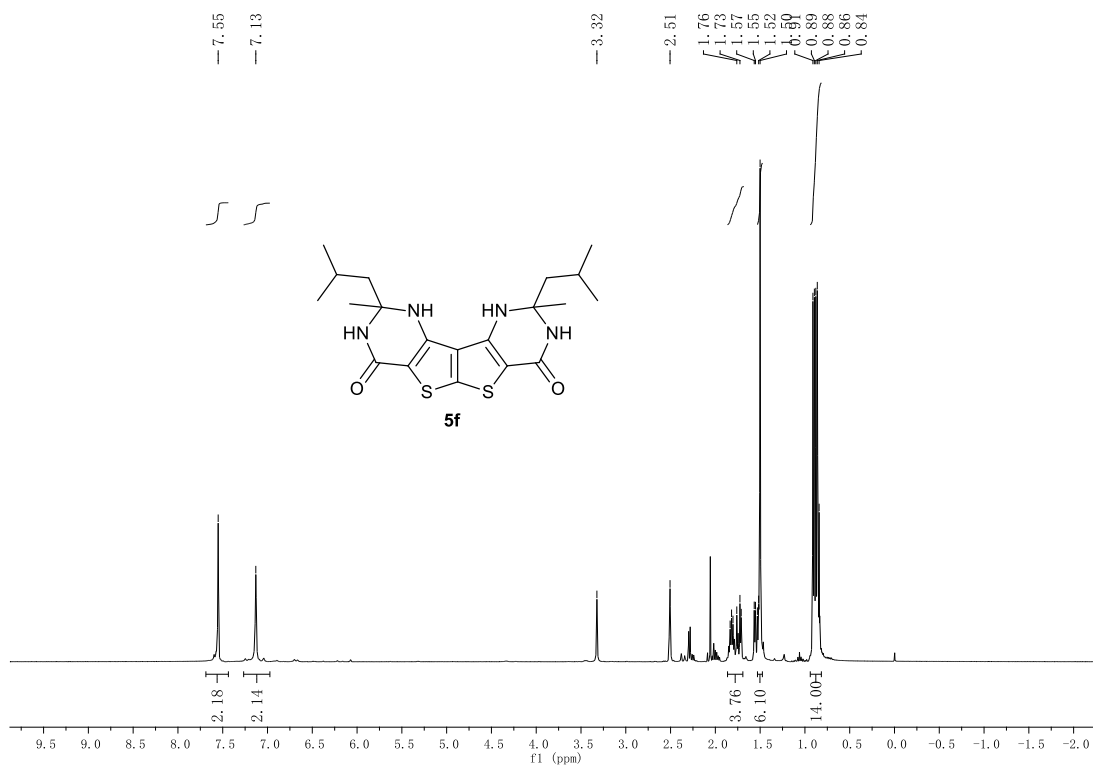
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 Operator: Peking University



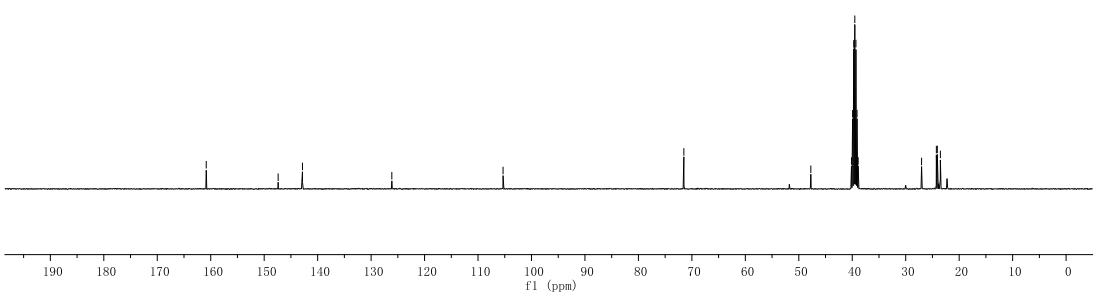
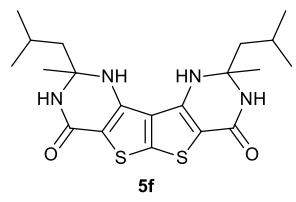
Bruker Compass DataAnalysis 4.0

printed: 4/28/2015 10:40:22 AM

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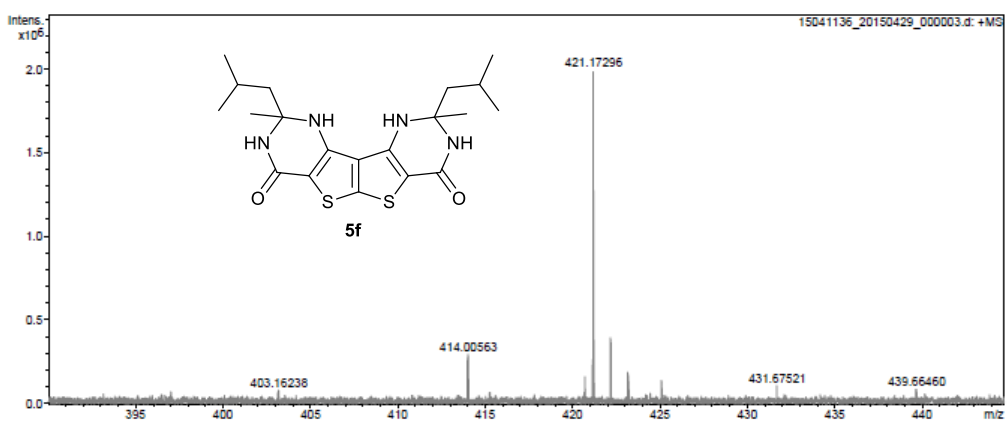


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 — 142.84  
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 — 105.32  
 — 71.50  
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 — 39.52  
 — 39.31  
 — 39.10  
 — 37.03  
 — 24.27  
 — 24.09  
 — 23.52

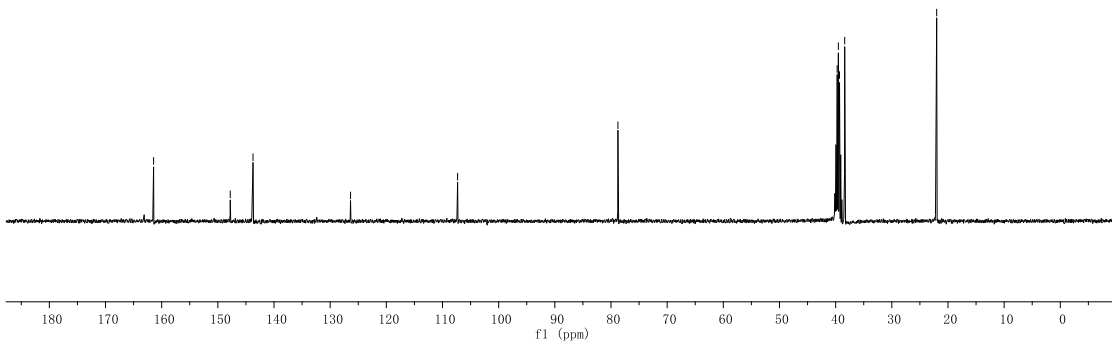
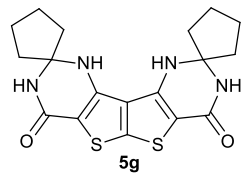
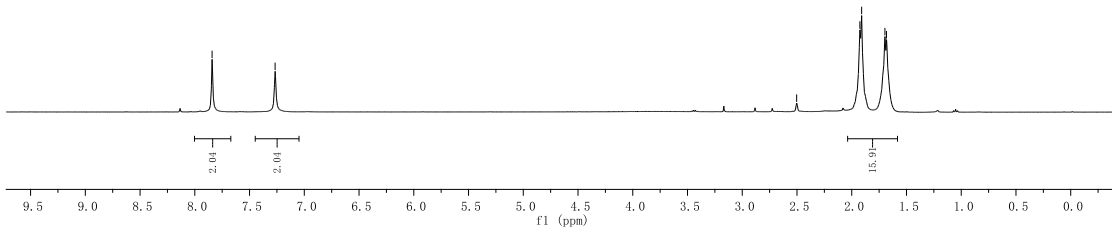
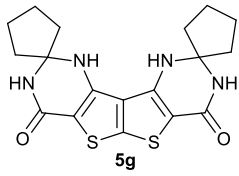


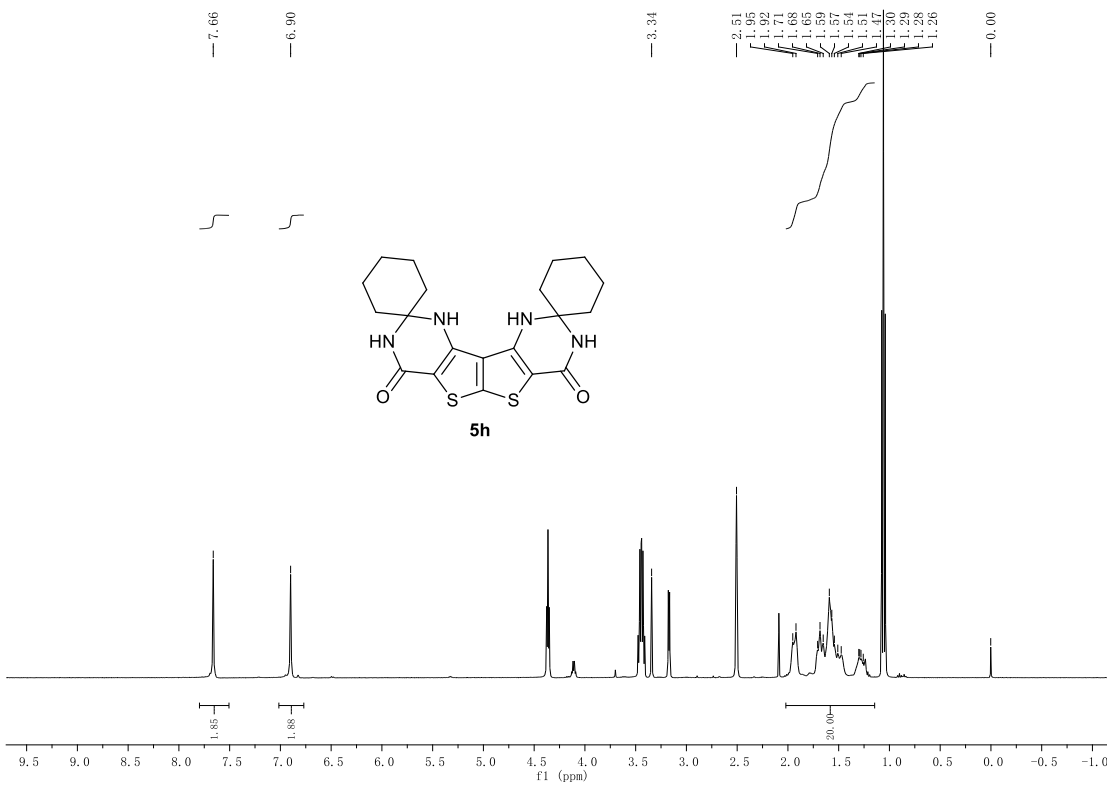
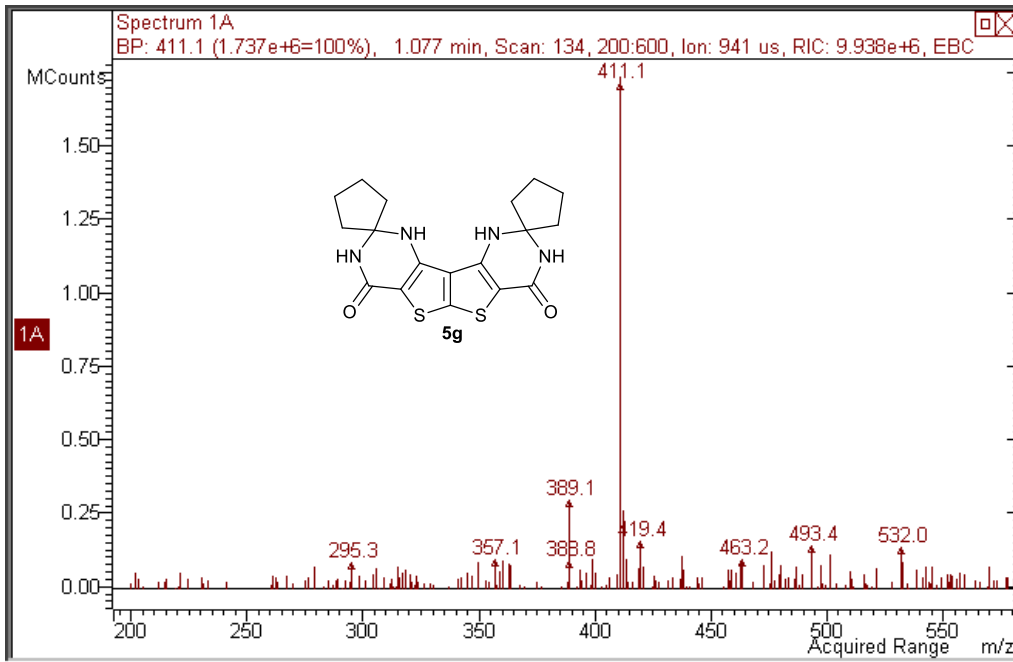
### Peking University Mass Spectrometry Sample Analysis Report

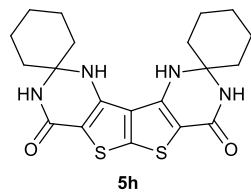
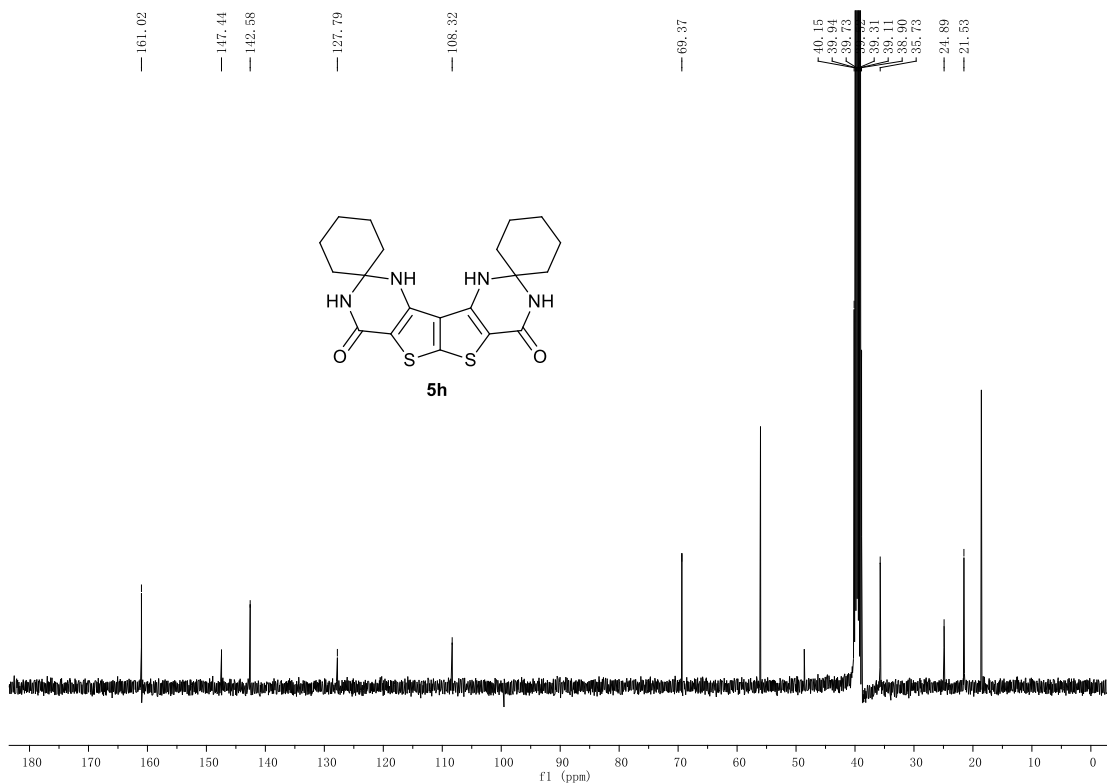
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Analysis Name: 15041136_20150429_000003.d	4/29/2015 10:43:31 AM
Sample: C20H28N4O2S2	Instrument: Bruker Apex IV FTMS
Comment: ESI Positive	Operator: Peking University



Meas. m/z	I	Formula	Score	m/z	err (mDa)	err (ppm)	mSigma	rdB	e <sup>-</sup>	Conf	N-Rule
421.17296	1992481	C <sub>20</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	100.00	421.17264	-0.3	-0.7	29.5	6.5	even		ok





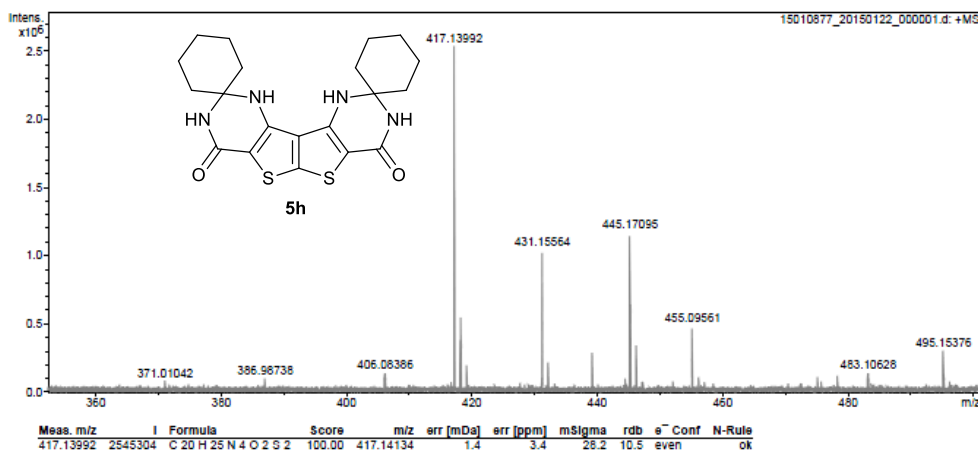


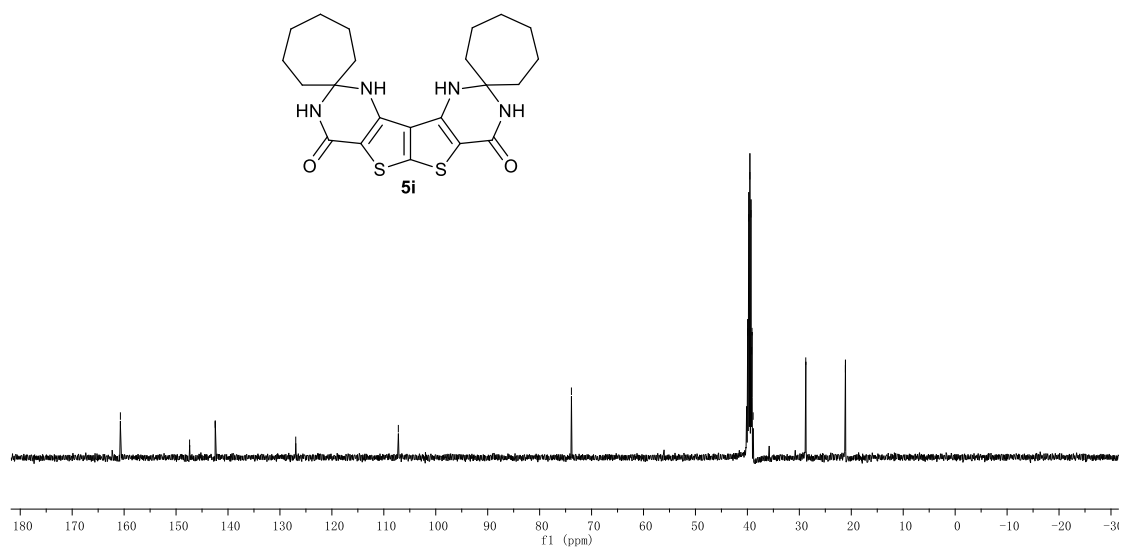
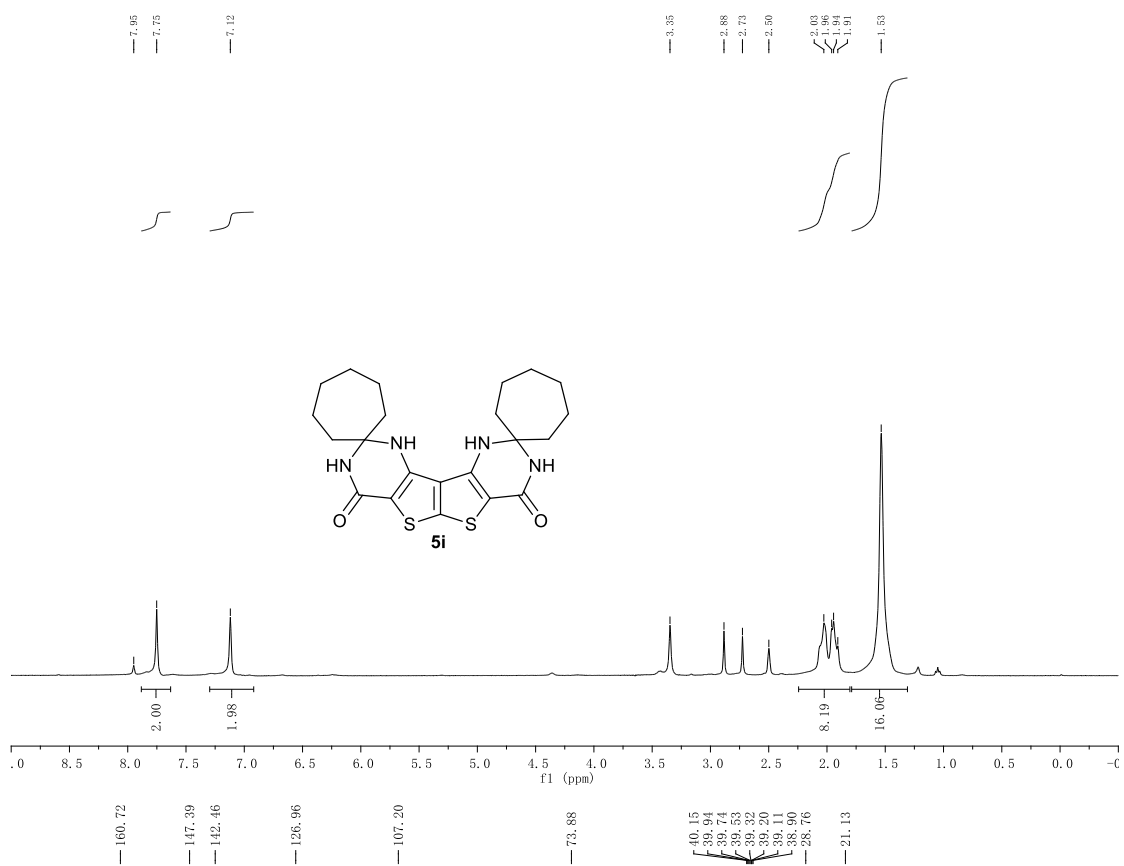
### Peking University Mass Spectrometry Sample Analysis Report

#### Analysis Info

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 Comment: ESI Positive

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 Instrument: Bruker Apex IV FTMS  
 Operator: Peking University



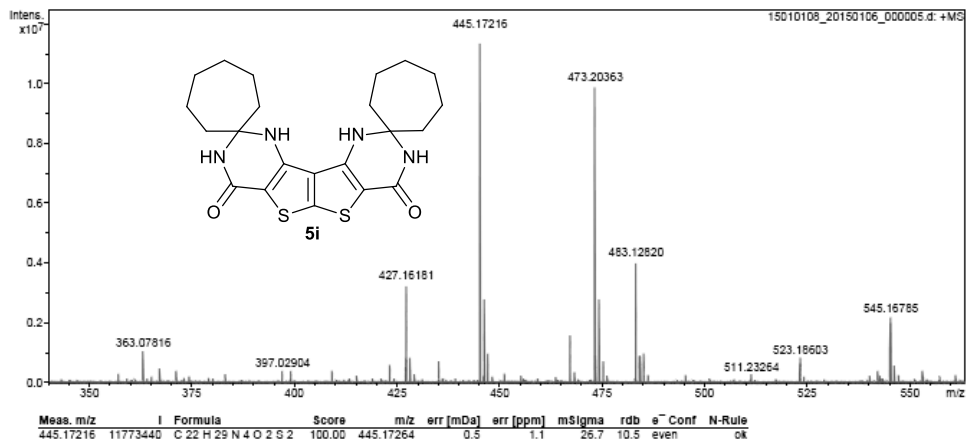


## Peking University Mass Spectrometry Sample Analysis Report

### Analysis Info

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 Comment: ESI Positive

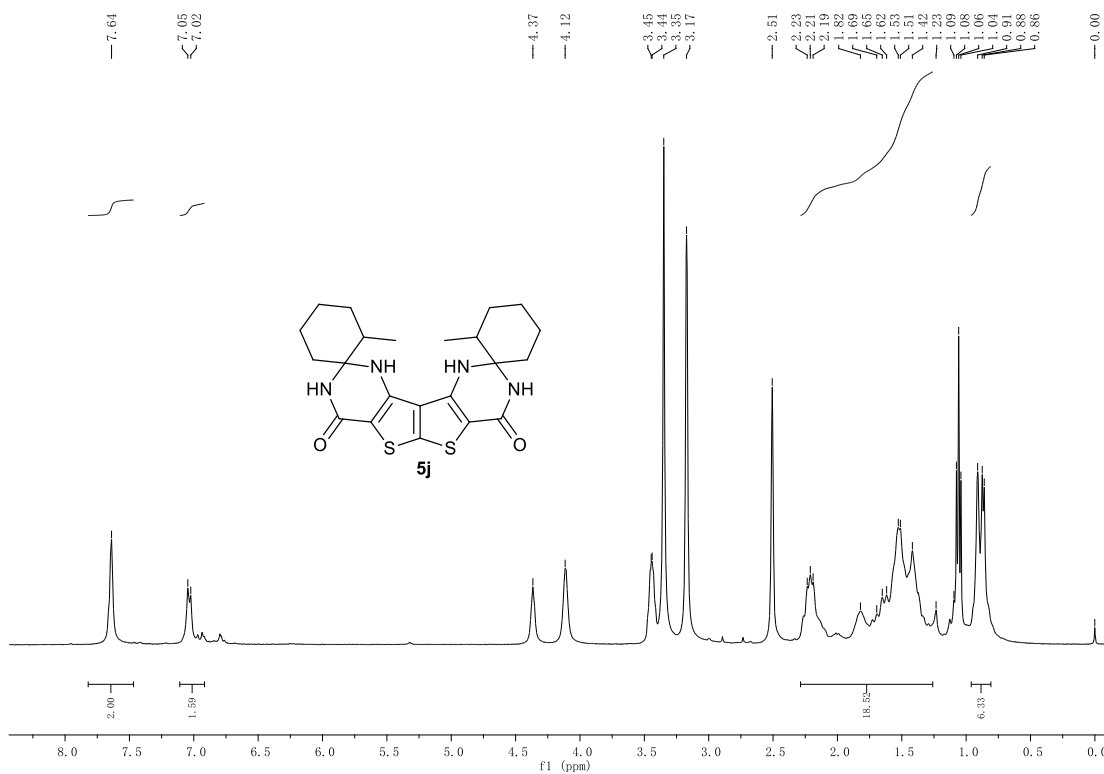
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 Operator: Peking University

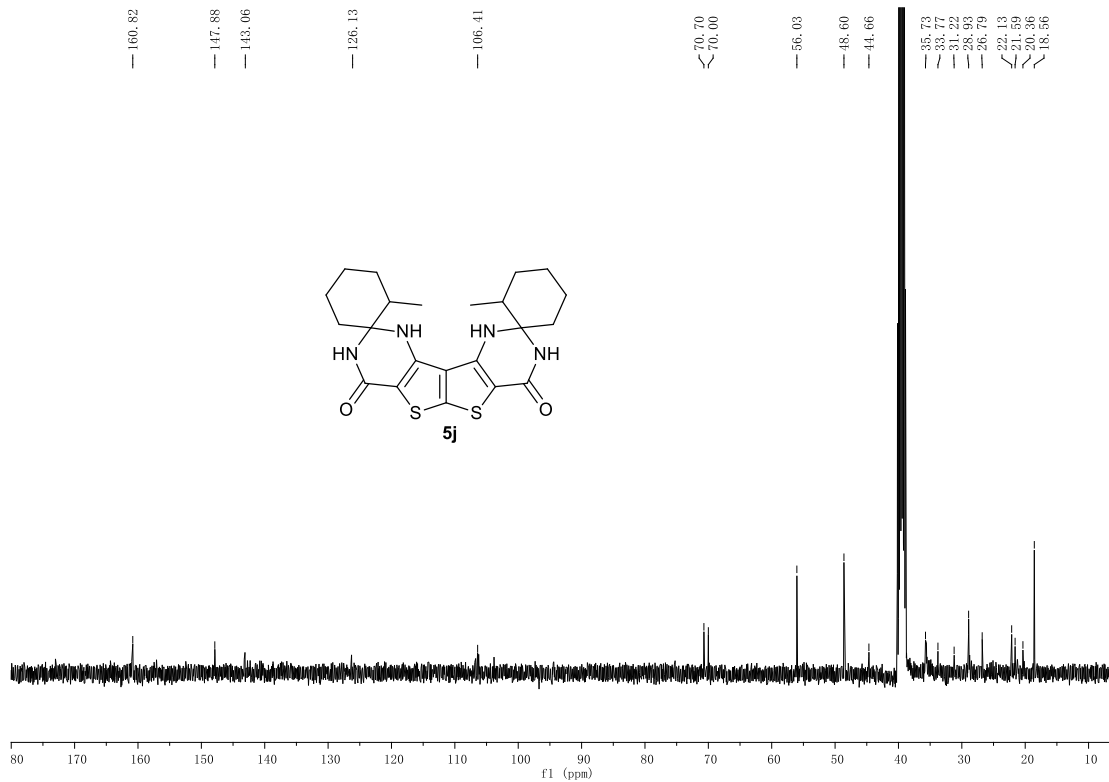


Bruker Compass DataAnalysis 4.0

printed: 1/6/2015 9:54:43 AM

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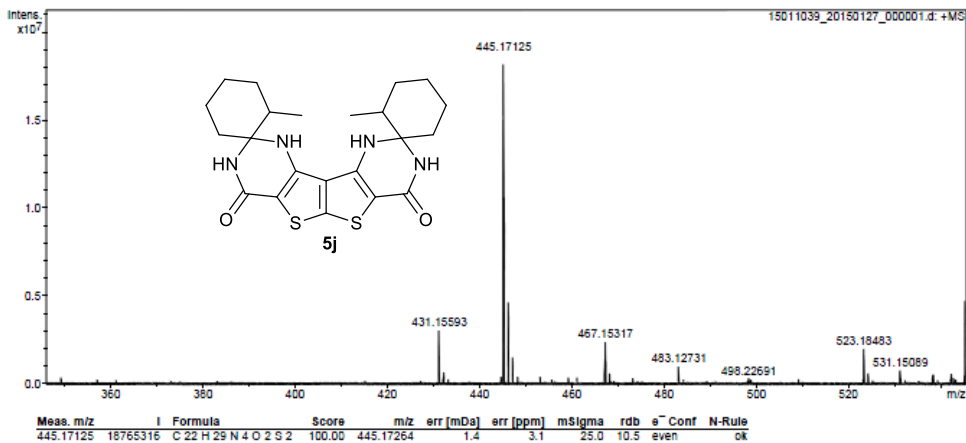


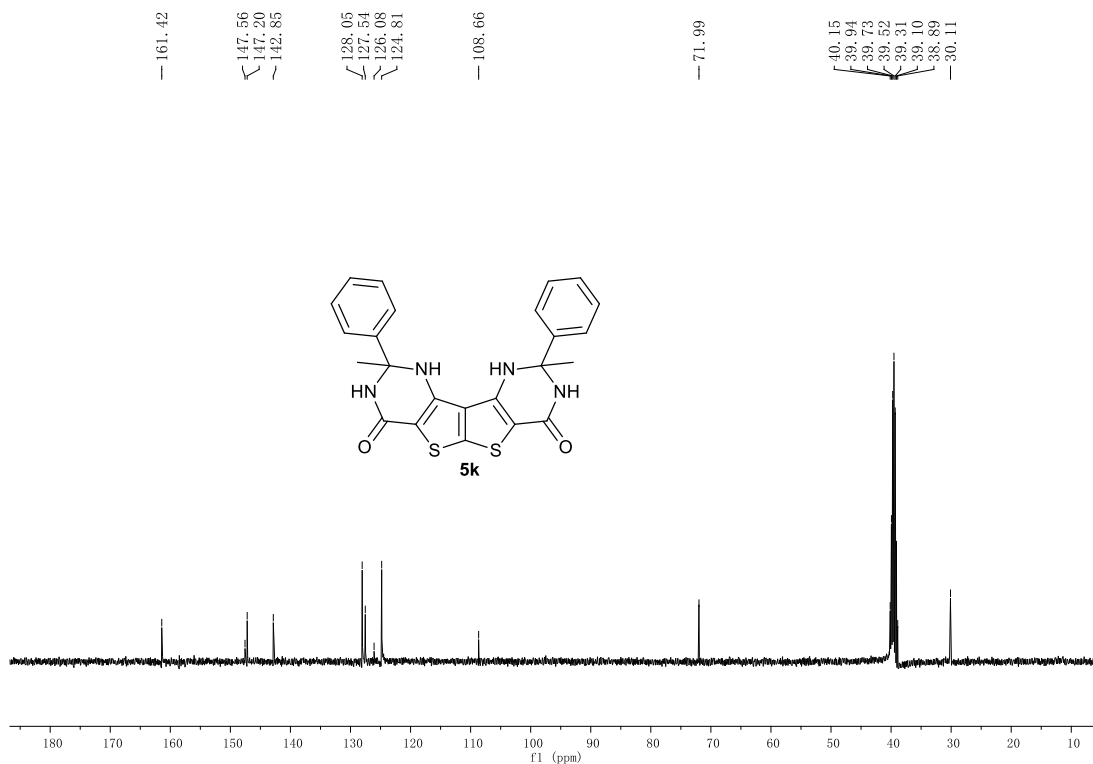
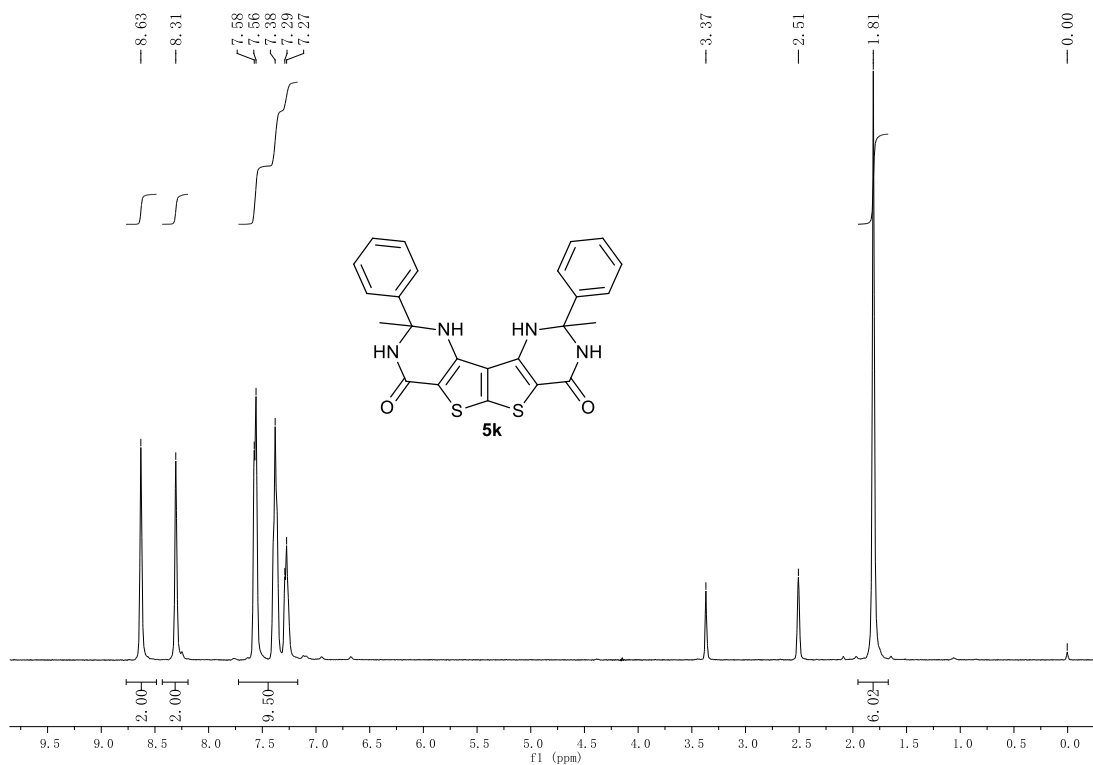
### Peking University Mass Spectrometry Sample Analysis Report

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Acquisition Date: 1/27/2015 4:39:04 PM  
 Instrument: Bruker Apex IV FTMS  
 Operator: Peking University



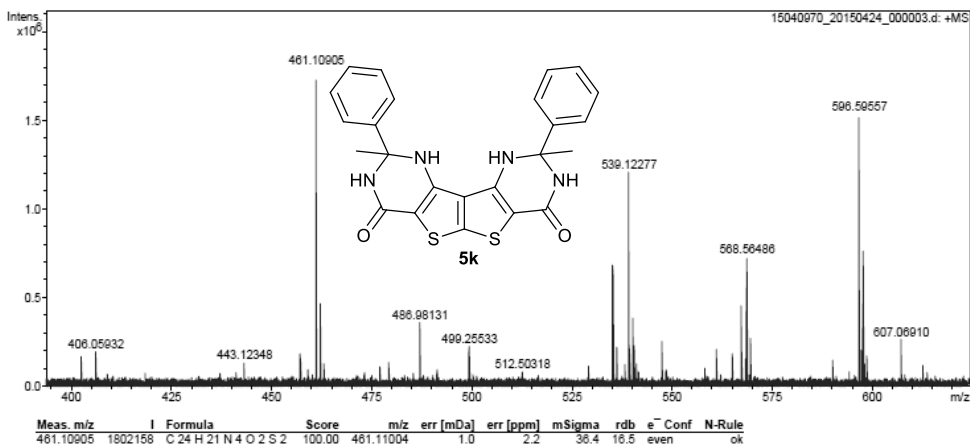


## Peking University Mass Spectrometry Sample Analysis Report

### Analysis Info

Analysis Name: 15040970\_20150424\_000003.d  
 Sample: C24H20N4O2S2  
 Comment: ESI Positive

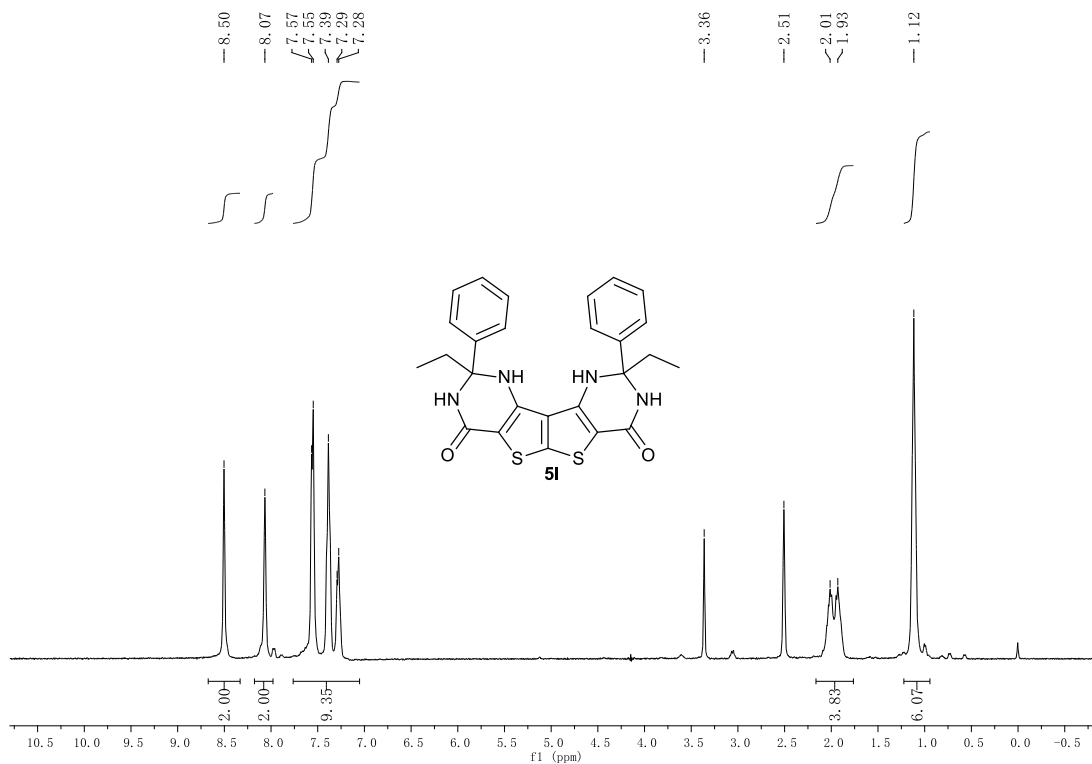
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 Instrument: Bruker Apex IV FTMS  
 Operator: Peking University



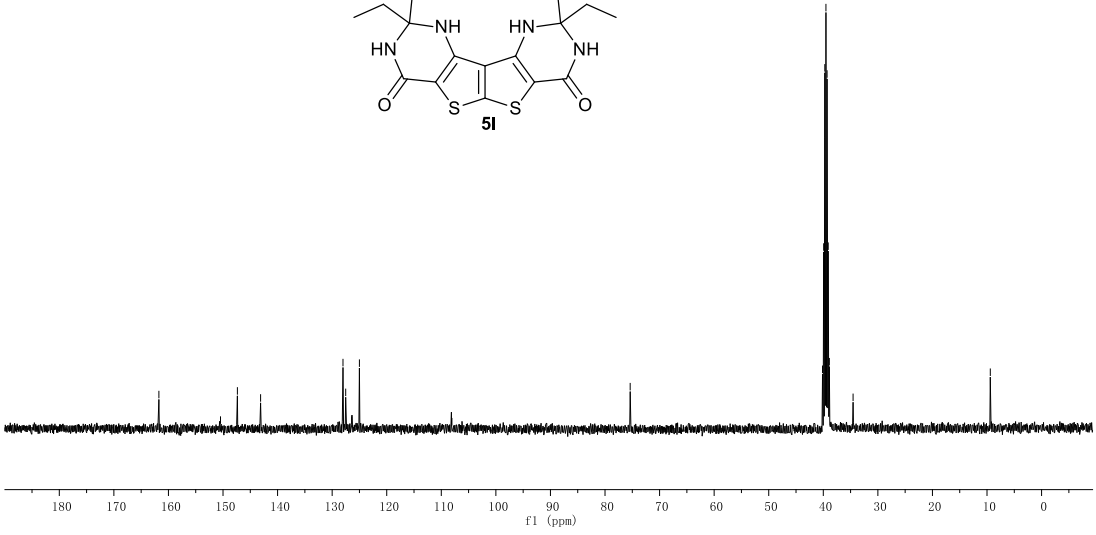
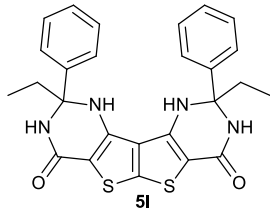
Bruker Compass DataAnalysis 4.0

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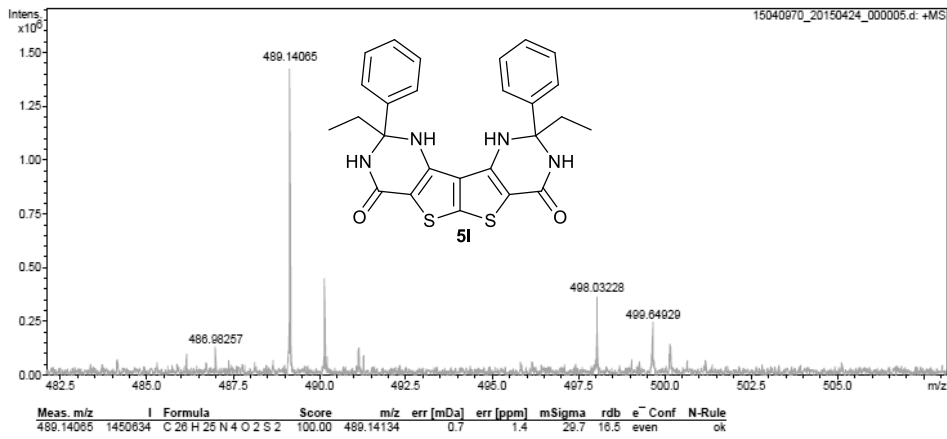
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 ~ 125.01  
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 — 75.39  
 ~ 40.14  
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 ~ 38.89  
 ~ 34.54  
 — 9.10

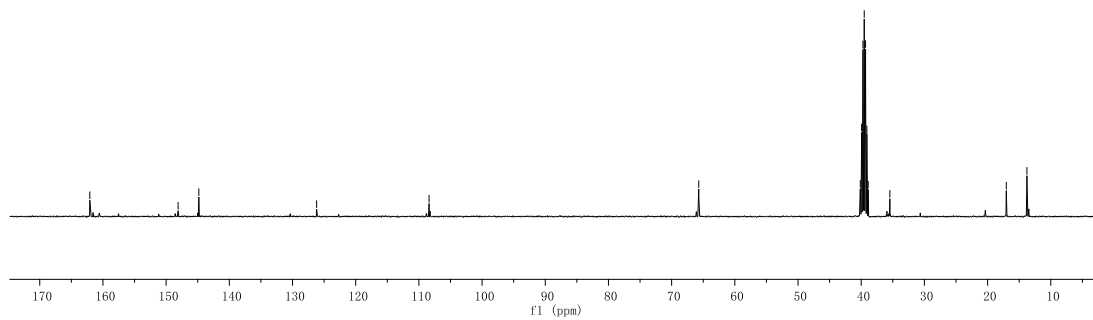
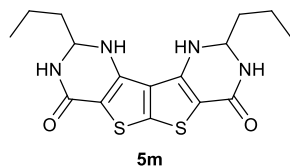
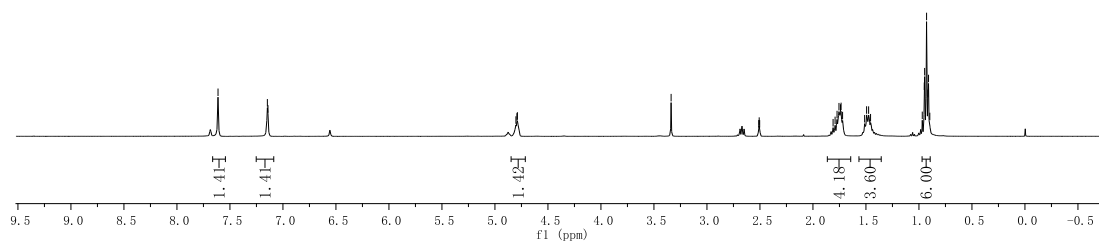
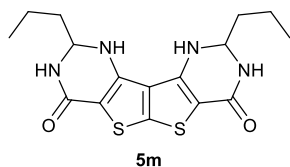
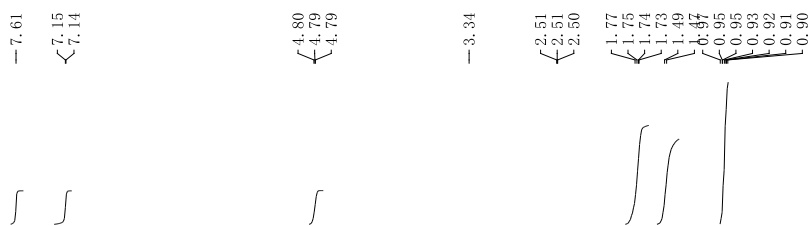


### Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

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Sample	C26H24N4O2S2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



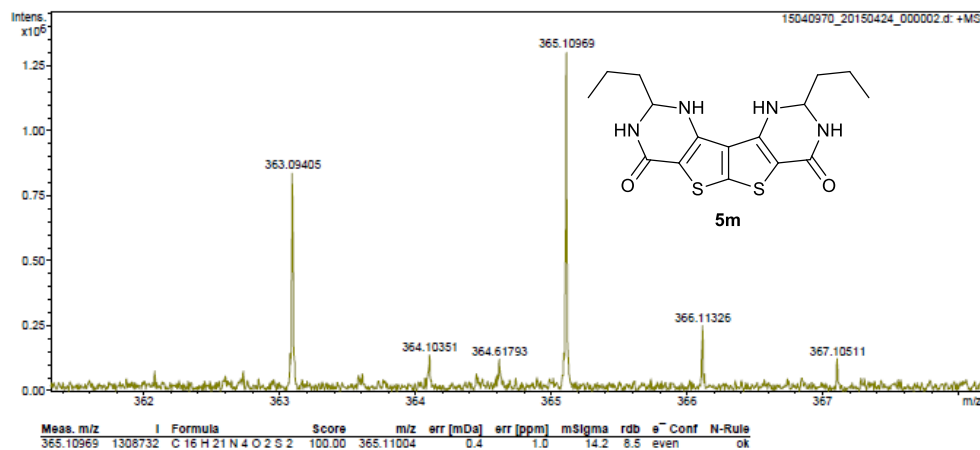


## Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

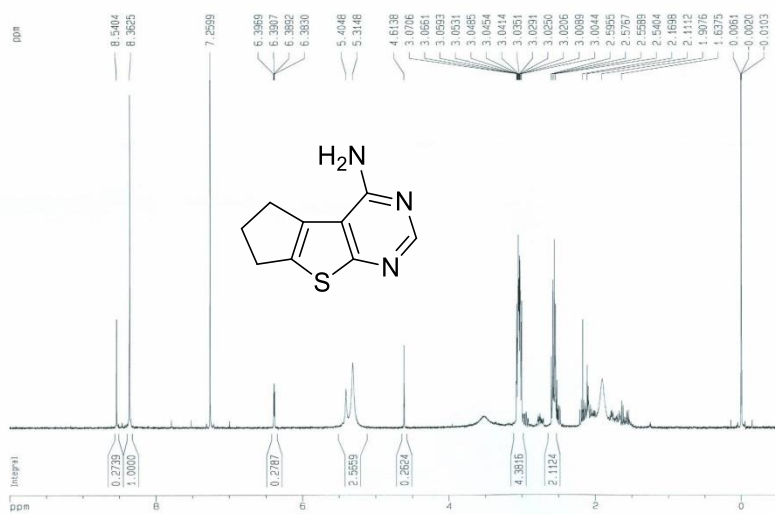
Analysis Name 15040970\_20150424\_000002.d  
 Sample C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>  
 Comment ESI Positive

Acquisition Date 4/24/2015 1:08:02 PM  
 Instrument Bruker Apex IV FTMS  
 Operator Peking University

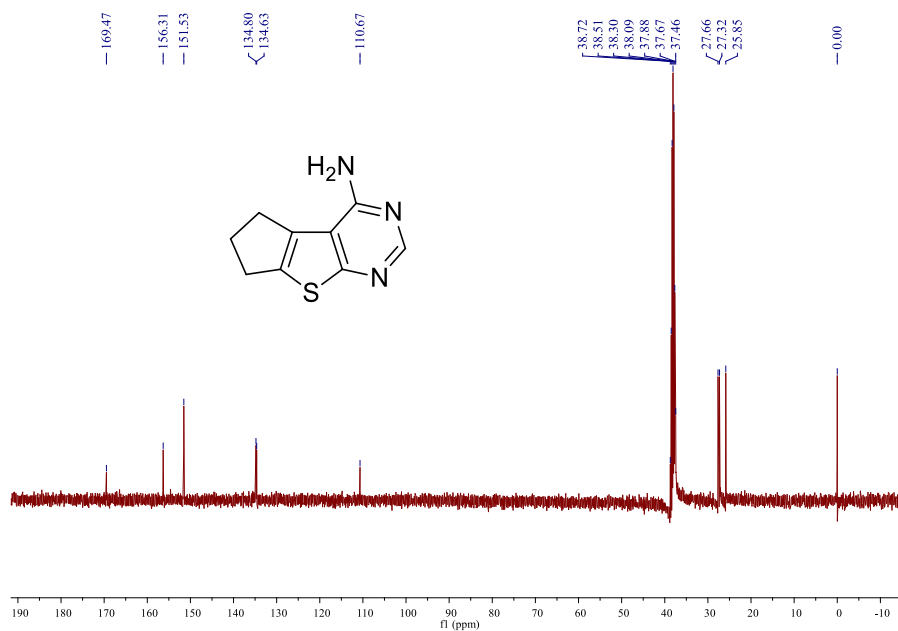


## 4. Copies of 6 spectra

### <sup>1</sup>H NMR spectrum of 6a



### <sup>13</sup>C NMR spectrum of 6a

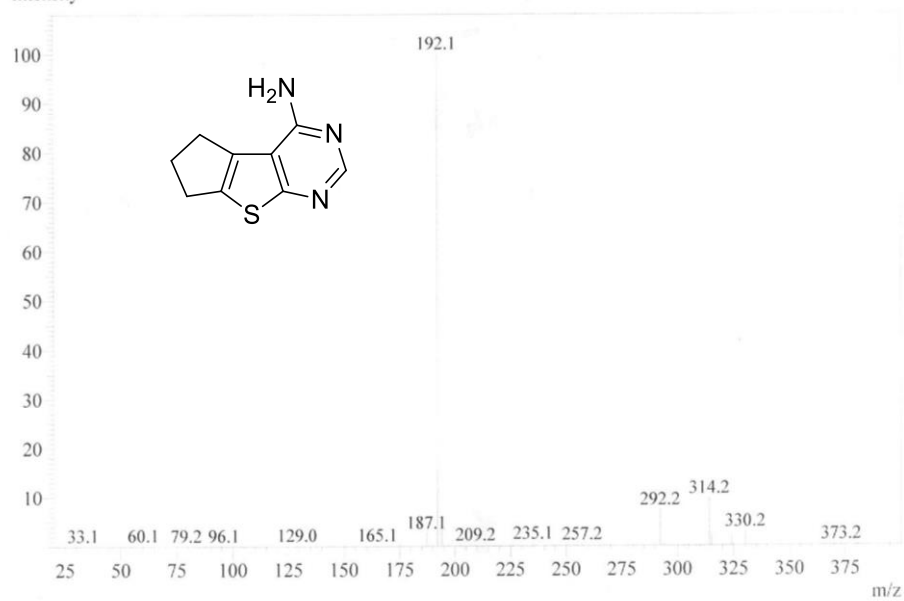


## ESI-MS spectrum of **6a**

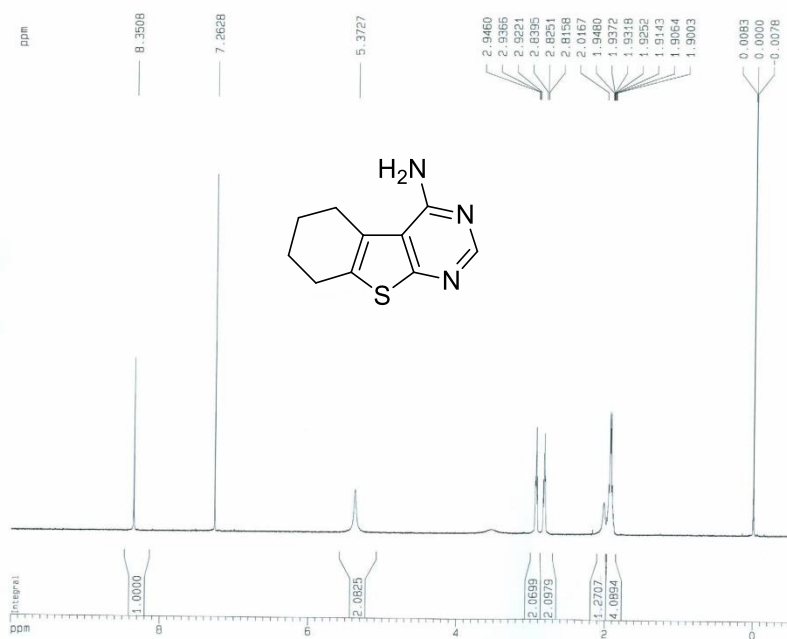
#:1 Ret.Time:Single 2.693(Scan#:102)

Mass Peaks:252 Base Peak:192.10(9633293) Polarity:Pos Segment1 - Event1

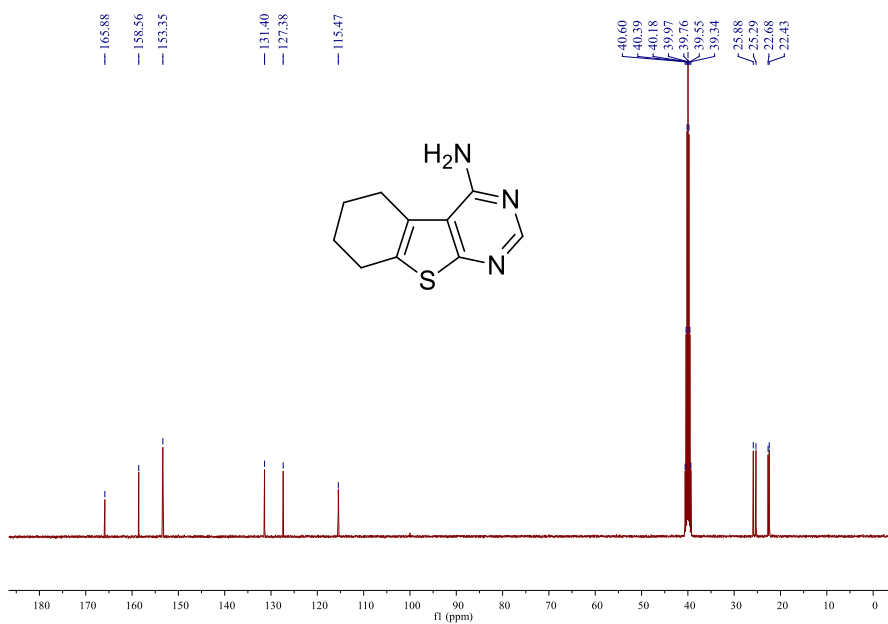
Intensity



### $^1\text{H}$ NMR spectrum of **6b**

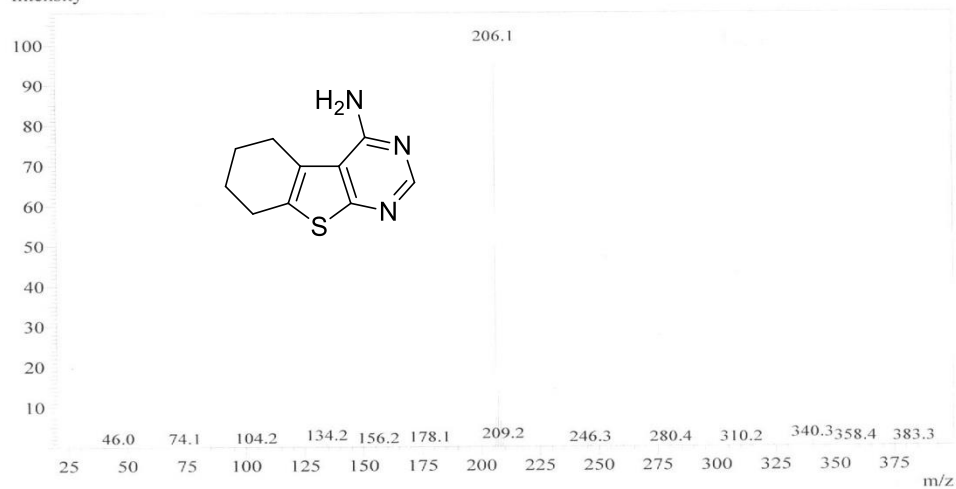


### $^{13}\text{C}$ NMR spectrum of **6b**

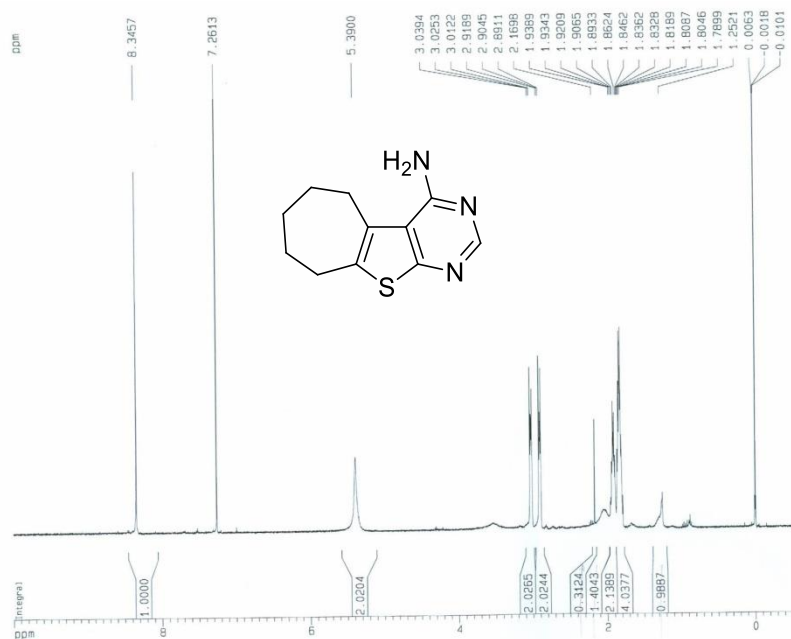


# ESI-MS spectrum of **6b**

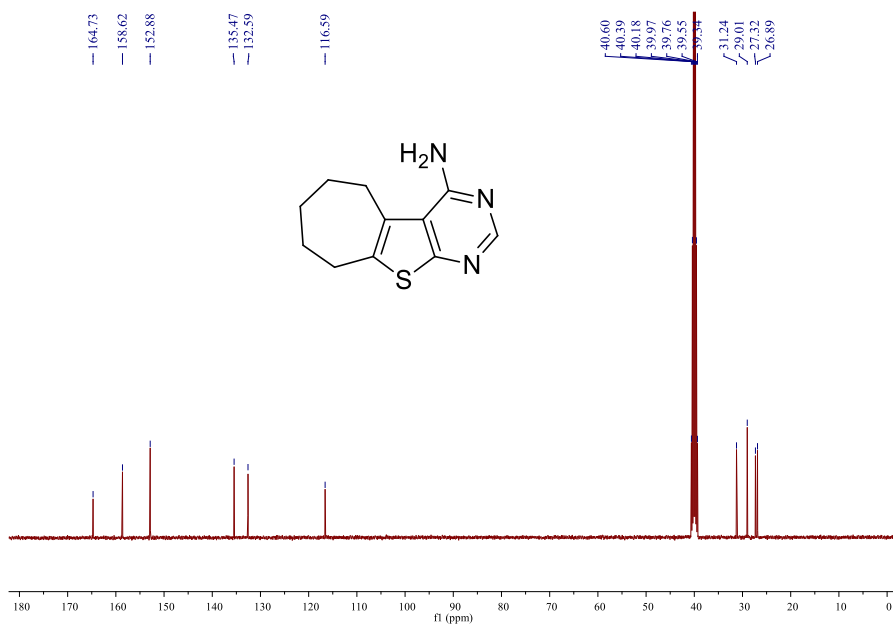
#1 Ret.Time:Single 2.853(Scan#:108)  
Mass Peaks:161 Base Peak:206.05(8325170) Polarity:Pos Segment1 - Event1  
Intensity



$^1\text{H}$  NMR spectrum of **6c**

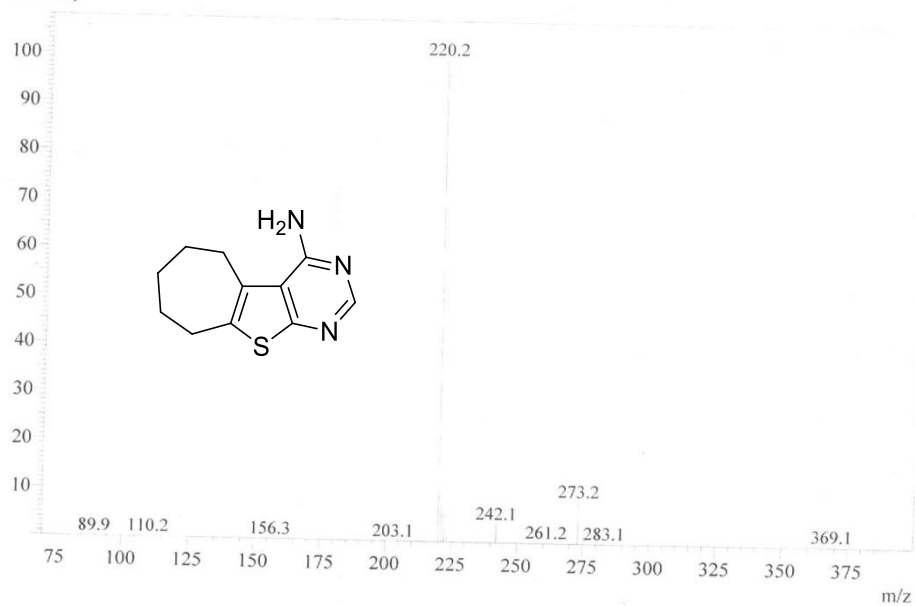


$^{13}\text{C}$  NMR spectrum of **6c**



# ESI-MS spectrum of **6c**

#1 Ret.Time:Single 23.787(Scan#:893)  
Mass Peaks:50 Base Peak:220.15(5179268) Polarity:Pos Segment1 - Event1  
Intensity



## 5. Crystal data and structure refinement

The crystal structure of **4a**, **5a** and **5h** were assigned. Single crystals were mounted with glue on glass fiber and crystal data were collected on the Rigaku AFC10 Saturn724 + (2×2 bin mode) diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.710747 \text{ \AA}$ ). Empirical absorption correction was applied using the SADABS program<sup>S1</sup>. The structures were solved by direct methods<sup>S2</sup> and refined by full-matrix least squares on  $F^2$  using the SHELXL-97 program<sup>S3</sup>. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC 1432663(**4a**), 1408503 (**5a**), 1408466 (**5h**). Copies of the data can be obtained, free of charge, on application to CCDC,12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail:

[deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Table S1**

Crystallographic Data and Structure Refinement for compound **4a**

Identification code	<b>4a</b>
Empirical formula	C <sub>16</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	324.43
CCDC	1432663
Temperature / K	101.8
Crystal system	triclinic
Space group	$P\bar{1}$
$a / \text{\AA}$ , $b / \text{\AA}$ , $c / \text{\AA}$	6.7812(7), 10.3733(10), 12.2852(13)
$\alpha / ^\circ$ , $\beta / ^\circ$ , $\gamma / ^\circ$	88.398(8), 74.952(9), 81.195(9)
Volume / $\text{\AA}^3$	824.65(15)
$Z$	2
$\rho_{\text{calc}} / \text{mg mm}^{-3}$	1.307
$\mu / \text{mm}^{-1}$	0.21
F(000)	348
Crystal size / $\text{mm}^3$	0.40 × 0.35 × 0.35
2 $\Theta$ range for data collection	6.3 to 52°
Index ranges	-5 ≤ $h$ ≤ 8, -12 ≤ $k$ ≤ 12, -13 ≤ $l$ ≤ 15
Reflections collected	7110
Independent reflections	3246[R(int) = 0.0238 (inf-0.9 $\text{\AA}$ )]

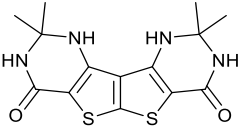
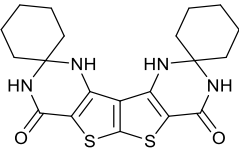
Data/restraints/parameters	3246/0/202
Goodness-of-fit on $F^2$	1.051
Final R indexes [ $I > 2\sigma(I)$ i.e. $F_o > 4\sigma(F_o)$ ]	$R_1 = 0.0355$ , $wR_2 = 0.0799$
Final R indexes [all data]	$R_1 = 0.0423$ , $wR_2 = 0.0847$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.277/-0.211
Flack Parameters	N
Completeness	0.998

**Table S2**

Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ )

Bond	Dist.	Bond	Dist.
S1-C1	1.758(15)	C5-C4	1.528(2)
S1-C4	1.865(16)	C5-C6	1.535(2)
O1-C4	1.402(18)	C4-C3	1.522(2)
O2-C9	1.240(18)	C8-C3	1.496(2)
N1-C1	1.276(19)	C8-C7	1.537(2)
N1-C10	1.465(18)	C13-C14	1.527(2)
C2-C9	1.480(2)	C13-C12	1.527(2)
C2-C1	1.464(2)	C6-C7	1.534(2)
C2-C3	1.337(2)	C15-C10	1.537(2)
N2-C9	1.341(19)	C15-C14	1.532(2)
N2-C10	1.479(19)	C11-C10	1.538(2)
O3-C16	1.423(2)	C11-C12	1.531(2)
Angle	( $^\circ$ )	Angle	( $^\circ$ )
C1-S1-C4	92.66(7)	C3-C4-C5	108.38(12)
C1-N1-C10	119.82(12)	C3-C8-C7	109.14(13)
C1-C2-C9	116.42(13)	C2-C3-C4	115.76(13)
C3-C2-C9	128.39(14)	C2-C3-C8	130.13(14)
C3-C2-C1	115.12(13)	C8-C3-C4	113.81(13)
C9-N2-C10	128.39(12)	C14-C13-C12	111.28(13)
O2-C9-C2	122.36(14)	C7-C6-C5	111.06(13)
O2-C9-N2	122.83(13)	C14-C15-C10	112.60(12)
N2-C9-C2	114.80(13)	C12-C11-C10	112.69(12)
N1-C1-S1	121.96(11)	N1-C10-N2	113.08(12)
N1-C1-C2	126.97(13)	N1-C10-C15	108.23(12)
C2-C1-S1	111.06(11)	N1-C10-C11	106.87(11)
C4-C5-C6	109.85(13)	N2-C10-C15	109.09(11)
O1-C4-S1	111.22(10)	N2-C10-C11	109.74(12)
O1-C4-C5	107.81(12)	C15-C10-C11	109.79(12)
O1-C4-C3	112.83(12)	C13-C14-C15	111.32(13)
C5-C4-S1	111.47(11)	C6-C7-C8	111.92(13)
C3-C4-S1	105.14(10)	C13-C12-C11	110.66(13)

Table S3 Crystallographic data and structure refinement for compound **5a** and **5h**

Identification code	<b>5a</b>	<b>5h</b>
		
Empirical formula	C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> ·CH <sub>3</sub> OH·H <sub>2</sub> O	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>
CCDC	1408503	1408466
Formula weight	386.49	381.03
Temperature / K	101 K	101.2K
λ	0.71070 Å	0.71070 Å
Crystal system	<i>P</i> <sup>-1</sup>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a / Å, b / Å, c / Å	a = 9.9898(7) Å b = 10.1850(8) Å c = 10.5633(8) Å	a=10.6570(7) Å b=19.7811(11) Å c=20.2381(9) Å
α/°, β/°, γ/°	α = 82.133(6)° β = 65.181(7)° γ = 68.473(7)°	α = 90.00° β = 90.00° γ = 90.00°
Volume / Å <sup>3</sup>	907.27(12) Å <sup>3</sup>	4266.4(4) Å <sup>3</sup>
Z	2	8
ρ <sub>calc</sub> / mg mm <sup>-3</sup>	1.415 mg mm <sup>-3</sup>	1.379 mg mm <sup>-3</sup>
μ / mm <sup>-1</sup>	0.322 mm <sup>-1</sup>	0.280 mm <sup>-1</sup>
F(000)	408	1873
Crystal size / mm <sup>3</sup>	0.25 × 0.20 × 0.13 mm <sup>3</sup>	0.55 × 0.50 × 0.50 mm <sup>3</sup>
2θ range for data collection	5.98 to 52°	6.92 to 52°
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 12, -13 ≤ l ≤ 13	-13 ≤ h ≤ 13, -23 ≤ k ≤ 24, -24 ≤ l ≤ 24
Data/parameters	6571 / 3568 [R(int) = 0.0293 (inf-0.9Å)]	26368 / 8372 [R(int) = 0.0676 (inf-0.9Å)]
Independent reflections		
Goodness-of-fit on F <sup>2</sup>	1.052	1.041
Completeness	0.998	0.996
Final R indexes [all data]	R <sub>1</sub> = 0.0379	R <sub>1</sub> = 0.0597

## 6. References

- (S1) Goettingen, Germany, **1997**.
- (S2) Sheldrick, G. M. SHELEX-97, Acta Crystallogr., Sect. A. **1990**; 46: 467-473.
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