Supporting Information

Transformylating Amine with DMF to Formamide over CeO_2 Catalyst

Yehong Wang, Feng Wang,* Chaofeng Zhang, Mingrun Li, Jian Zhang, and Jie Xu*

State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (China)

E-mail: wangfeng@dicp.ac.cn; xujie@dicp.ac.cn

Website: www.fwang.dicp.ac.cn

Contents

1. Chemicals and Reagents

All chemicals were of analytical grade and used as purchased without further purification. Most of chemicals were purchased from J&K Chemicals. $(NH_4)_2[Ce(NO_3)_6]$, $Ce(NO_3)_3{\cdot}6H_2O$, benzylamine and other various amines were purchased from Aladdin Chemicals.

2. Catalyst Preparation

The CeO_2 samples were prepared by a precipitation method. Generally, 5.0 g of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in 100 mL of Millipore purified water (18 $m\Omega{\cdot}cm^{-1}$), and the solution was adjusted to pH=11.0 by NH_4OH (3.4 M) under stirring at room temperature. The resulting gel mixture was then washed with water, dried in an oven at 115 ° C for 12 h, then calcined at 500 °C in air for 4 h. Some other catalysts were also obtained for comparison. The MoO_3 sample was prepared according to the reference. [1] Nb_2O_5 was prepared by the calcination of $NH_4[Nb(C_2O_4)_2(H_2O)]{\cdot}6(H_2O)_n$ (provided by CBMM, Brazil) at 500 °C for 3 h. The oxides (TiO_2, WO_3, V_2O_5, ZrO_2, Y_2O_3, Eu_2O_3, MnO_2, Al_2O_3, MgO), zeolites (ZSM-22, H-ZSM-5, Y, HY, H-Beta, H-MOR, SAPO-11), and homogeneous acids [$Sc(CF_3SO_3)_3$, $Yb(CF_3SO_3)_3$], $H_3PO_{40}W_{12}{\cdot}xH_2O$ and $H_4[Si(W_3O_{10})_4]$ were all commercially available (Aladdin and J&K).

3. Catalyst Characterization

The DMF/n-butylamine-adsorption IR method was conducted on a Tensor 27 (Bruker) IR spectrometer. The sample was pressed into a self-supporting disk (13 mm diameter, 25− 27.7 mg) and placed in a homemade IR cell attached to a closed glass-circulation system. Prior to adsorption, the sample disk was pretreated by

heating at 200 ° C for 1 h in vacuum (pressure <5.4×10^{-1}Pa) and then cooled to 30 °C. After a spectrum was collected, the sample disk was exposed to DMF or n-butylamine vapor. IR spectra of the chemisorbed DMF or n-butylamine were recorded after evacuation at 100 °C, 150 °C, 200 °C for 0.5 h to eliminate physically adsorbed DMF or n-butylamine. Spectra were collected after cooling to 30 °C. The surface area and of the samples were measured at -196 ^{o}C by using nitrogen adsorption according to the Brunauer–Emmett–Teller method (BET) by using a Quantachrome QUADRASORB-SI apparatus. The acidity or alkali of the samples was characterized by performing temperature-programmed desorption of ammonia or carbon dioxide (NH_3-TPD, CO_2-TPD) with an automated catalyst characterization system (Autochem 2920, Micromeritics) with a TCD detector. We used a calibration curve to calculate the ammonia or carbon dioxide amount by converting the peak area to concentration.

4. Catalytic Tests

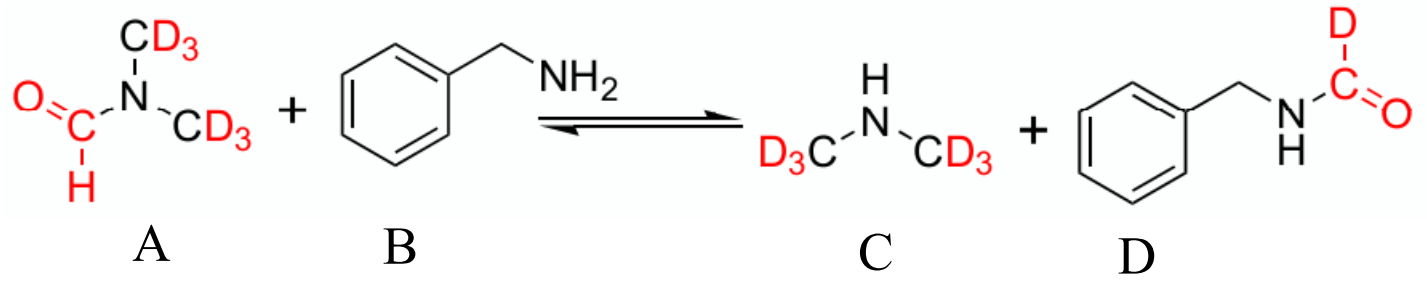
The catalytic reactions were conducted in a glass batch reactor. Typically, benzylamine (1.5 mmol), N, N-dimethylformamide (DMF, 2 mL), catalyst (100 mg) and a stirring bar were placed in a glass pressure reactor (heavy wall, max: 0.6 MPa, Synthware Glass) with a Teflon bushing. The reactor was then immersed in an oil bath preheated at the desired reaction temperature. After the reaction was completed in 0.5 h-12 h, the catalyst was filtered out, washed with acetone for three times, dried at 115 ^{o}C and then calcined at 500 ^{o}C for 4 h prior to further use in recycling experiment. Products were confirmed by a GC-MS (Agilent 7890A-5975C).

The conversion and selectivity were determined by normalizing Gas Chromatography (GC, Agilent 7890A) integration area. Product yields were calculated by multiplying conversion by selectivity.

Table S1. Catalyst screening in the formylation of benzyl amine to benzyl amide.[a]

No.	Catalyst	A–B[b]	S_{BET} (m^2 g^{-1})	Conv (%)	Select (%)
1	–	–	–	0	0
			Zeolites		
2	NaY	MA	17	6	17
3	H-MOR	SA	80	15	80
4	HZSM-5	SA	79	19	79
5	HY	SA	59	22	59
6	ZSM-22	SA	77	22	77
7	SAPO-11	SA	65	23	65
8	H-β	SA	91	43	91
			Metal oxides		
9	Eu_2O_3	WB	23	5	40
10	MgO	SB	32	8	25
11	WO_3	MA	8	8	50
12	Y_2O_3	WB	8	9	33
13	Nb_2O_5	MA	21	14	93
14	V_2O_5	MA	13	82	32
15	α-MnO_2	MA	49	95	5
16	ZrO_2	MA+MB	9	23	52
17	α-Al_2O_3	SA+WB	74	23	65
18	TiO_2[c]	MA+MB	73	25	96
19	CeO_2	MA+SB	67	80	>99
20	CeO_2[d]	MA+SB	67	95	>99
21	CeO_2[e]	MA+SB	67	67	98

[a] Reaction conditions: catalyst 100 mg, BAn 1.5 mmol, DMF 2 mL, 100 °C, 4 h. [b] Classification of metal oxides was from literature.[2] Symbols: Weak (W), Medium (M) and Strong (S); Acid (A) and Base (B). [c] Anatase. [d] 180 °C, 8h. [e] 100 °C, 4 h, 1.9 mL DMF, 0.1 mL H_2O.



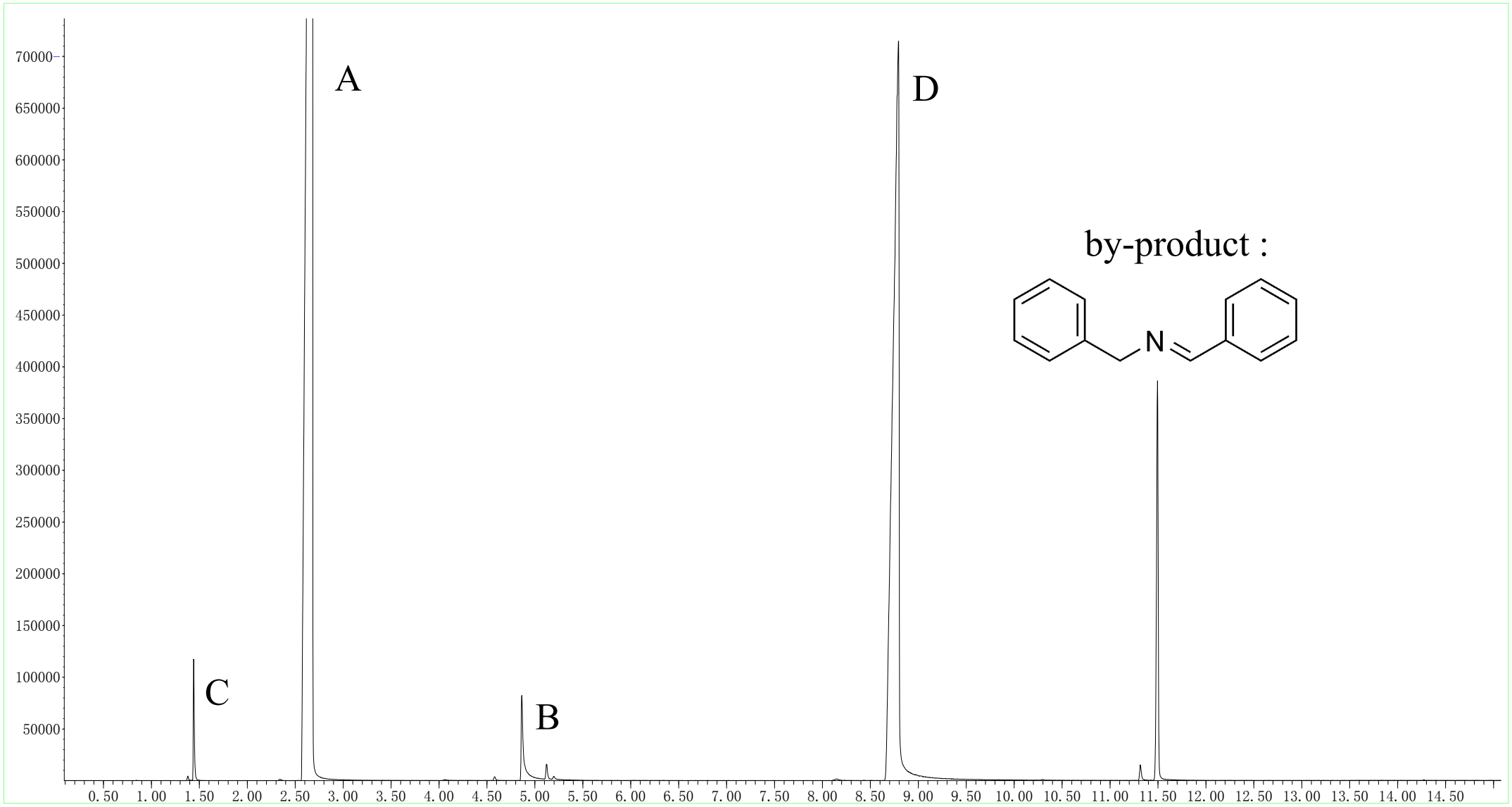
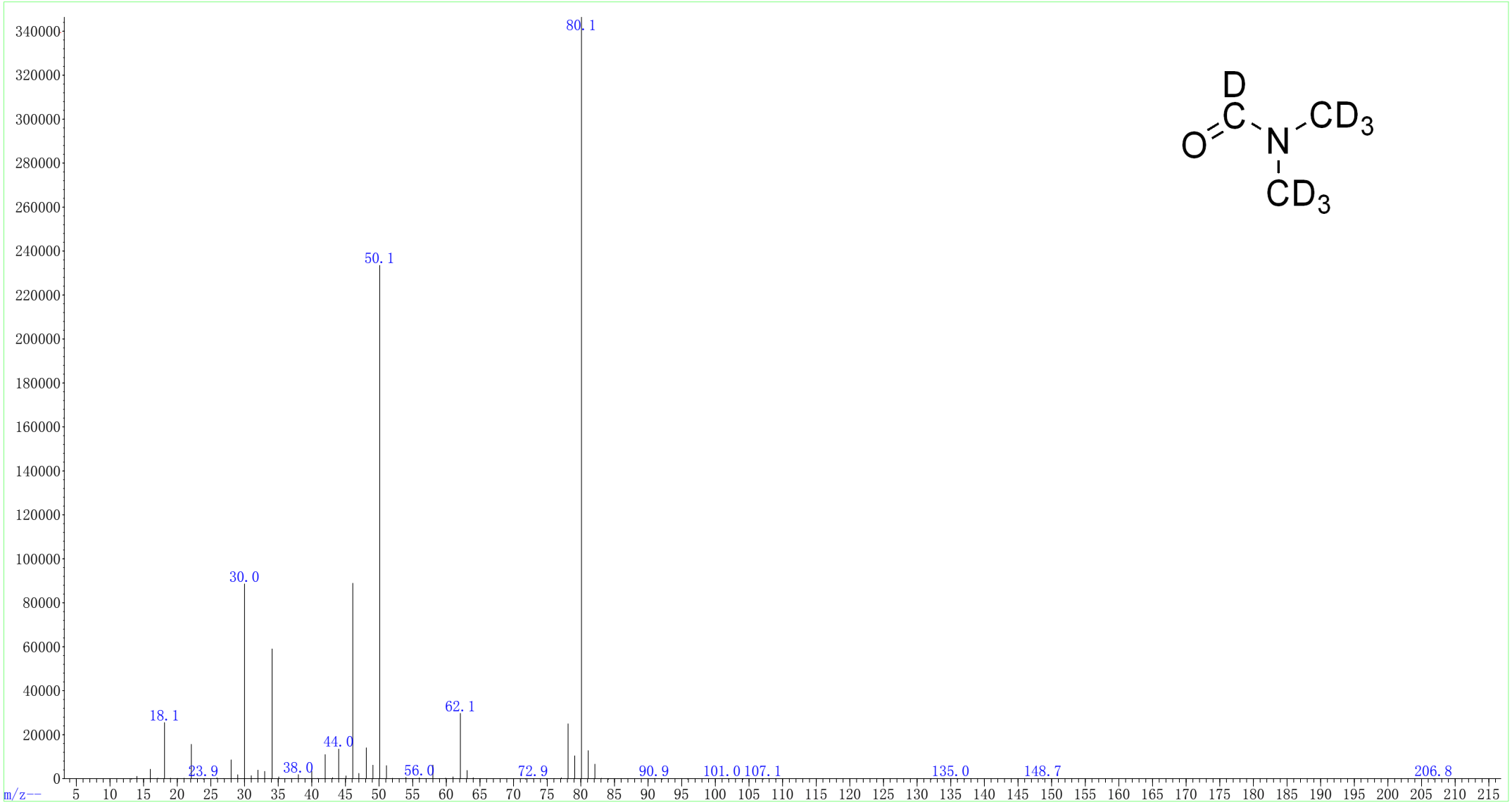


Figure S1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D
C
O
N
CD3
CD3

Figure S1

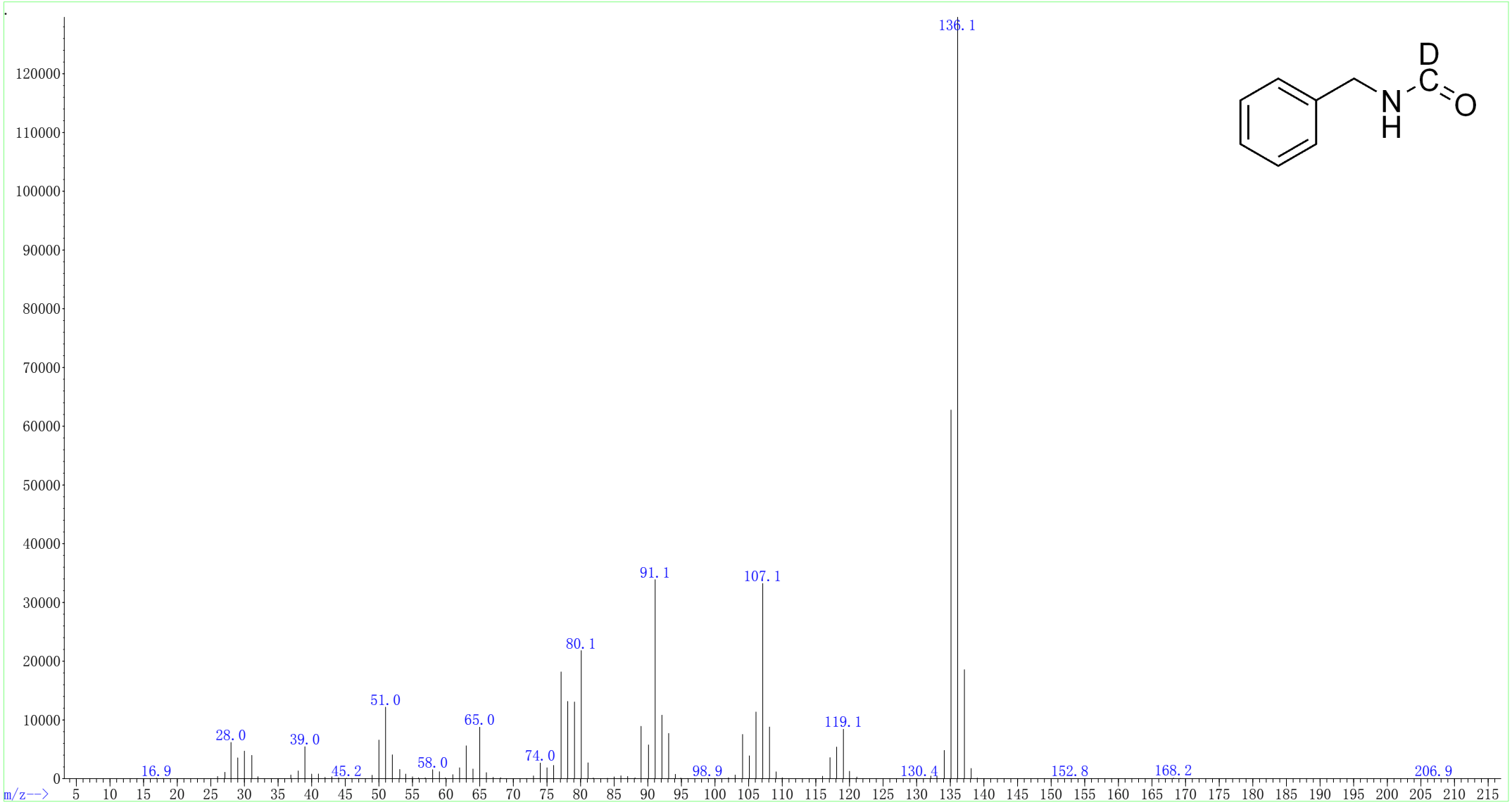
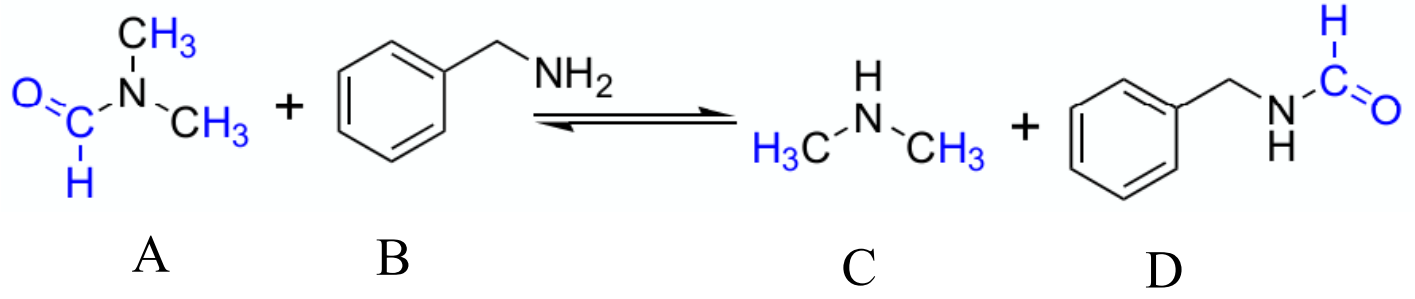


Figure S1

Figure S1



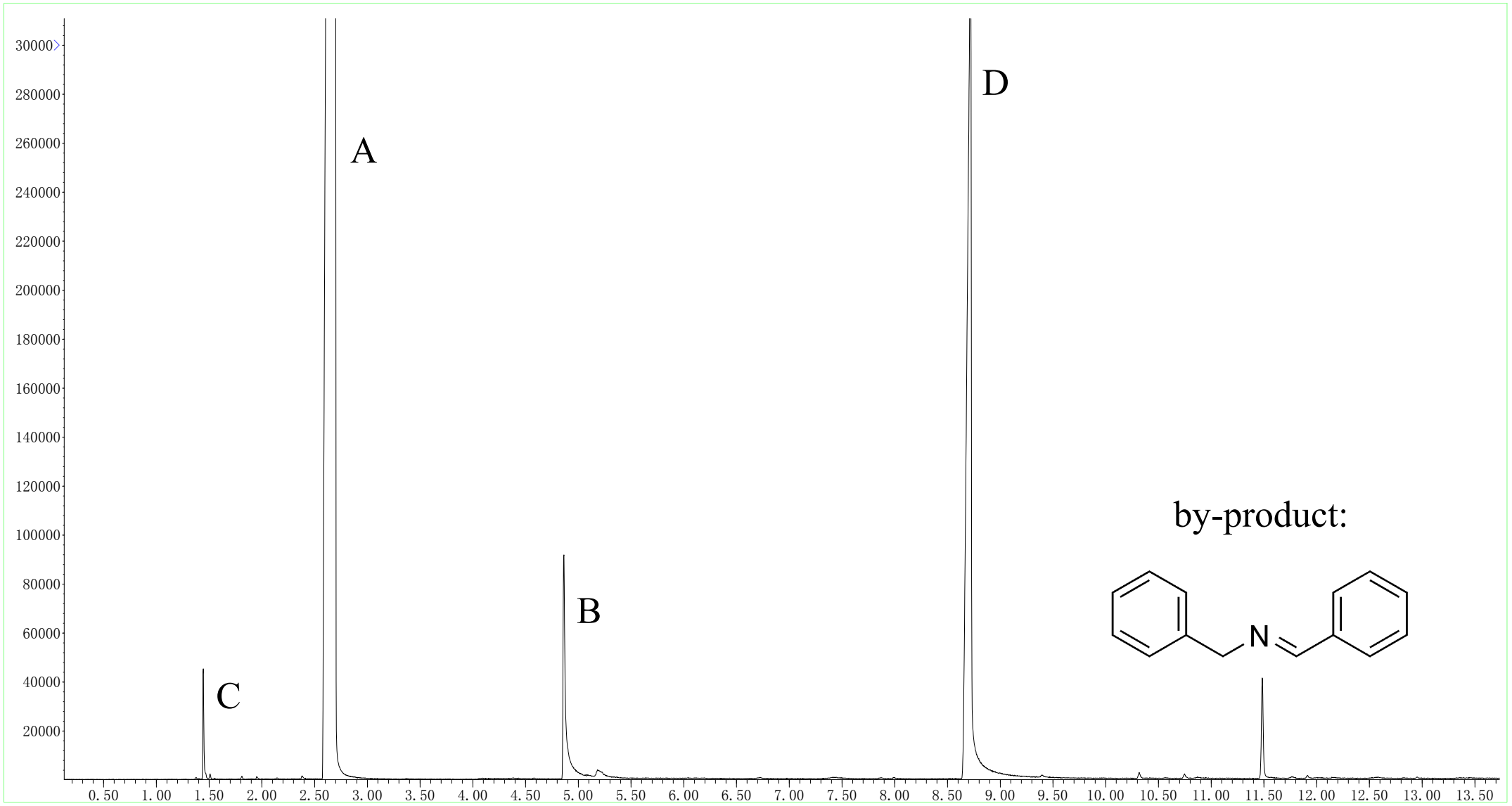


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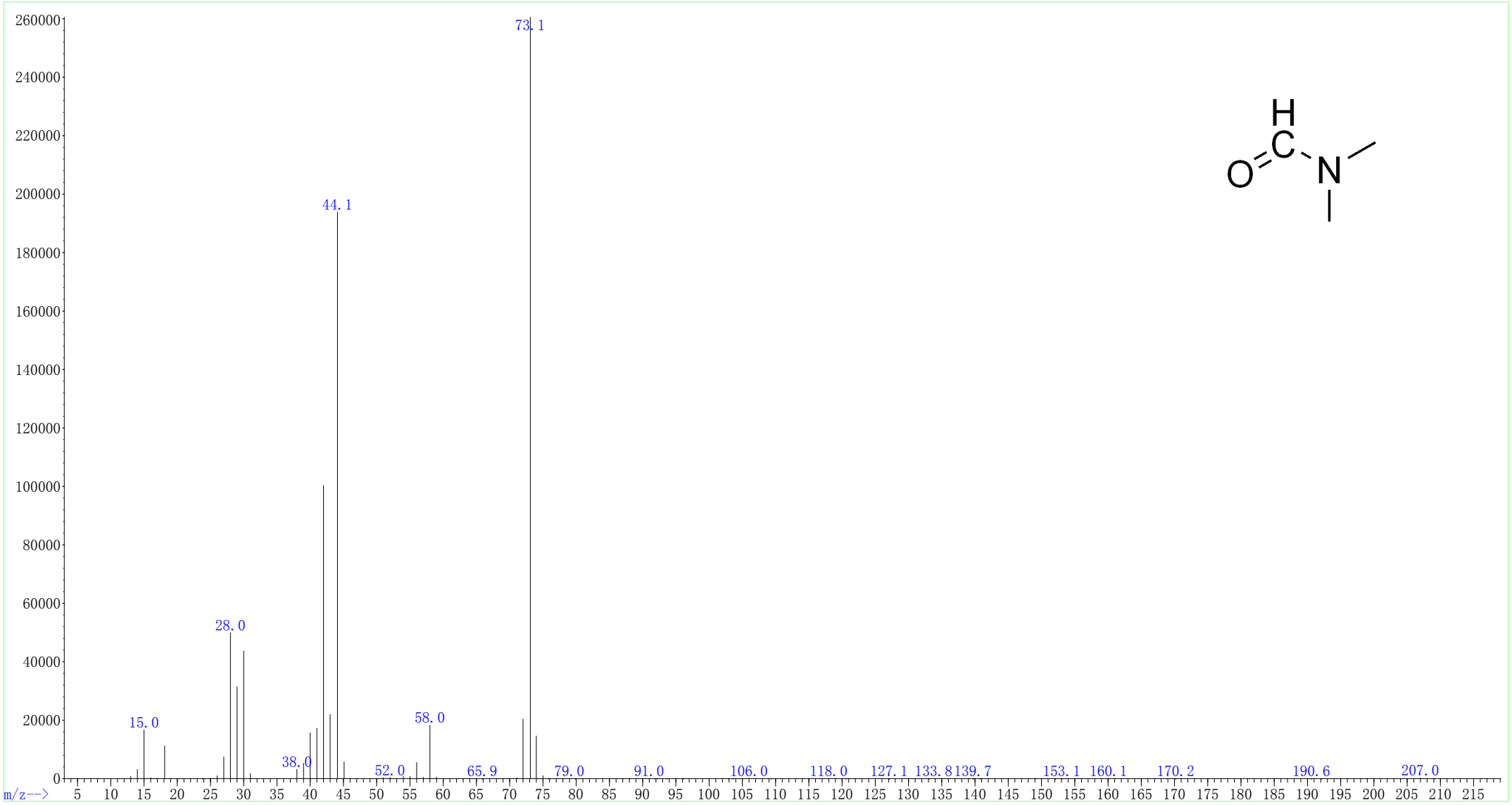
Figure S2



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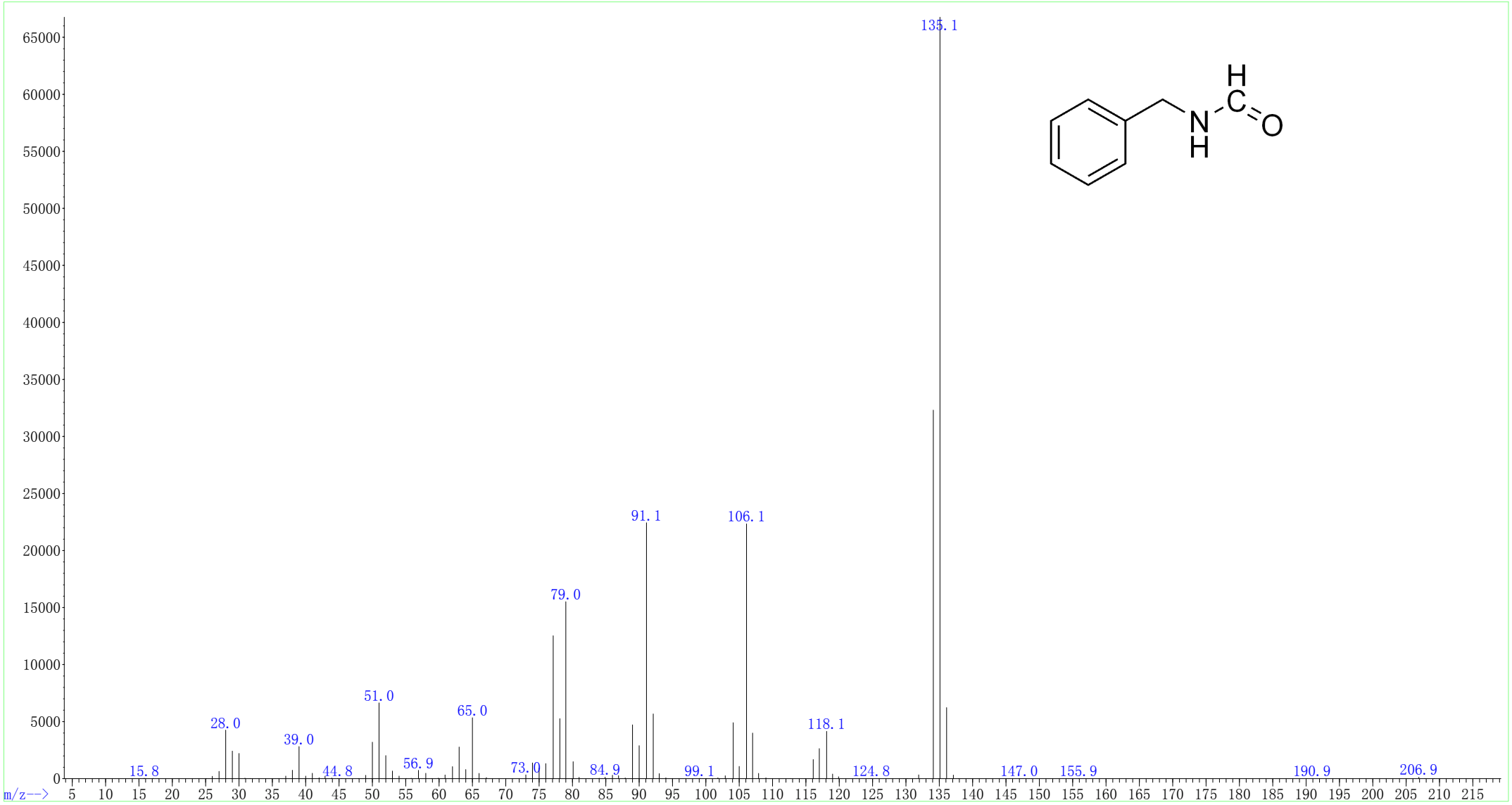


Figure S2

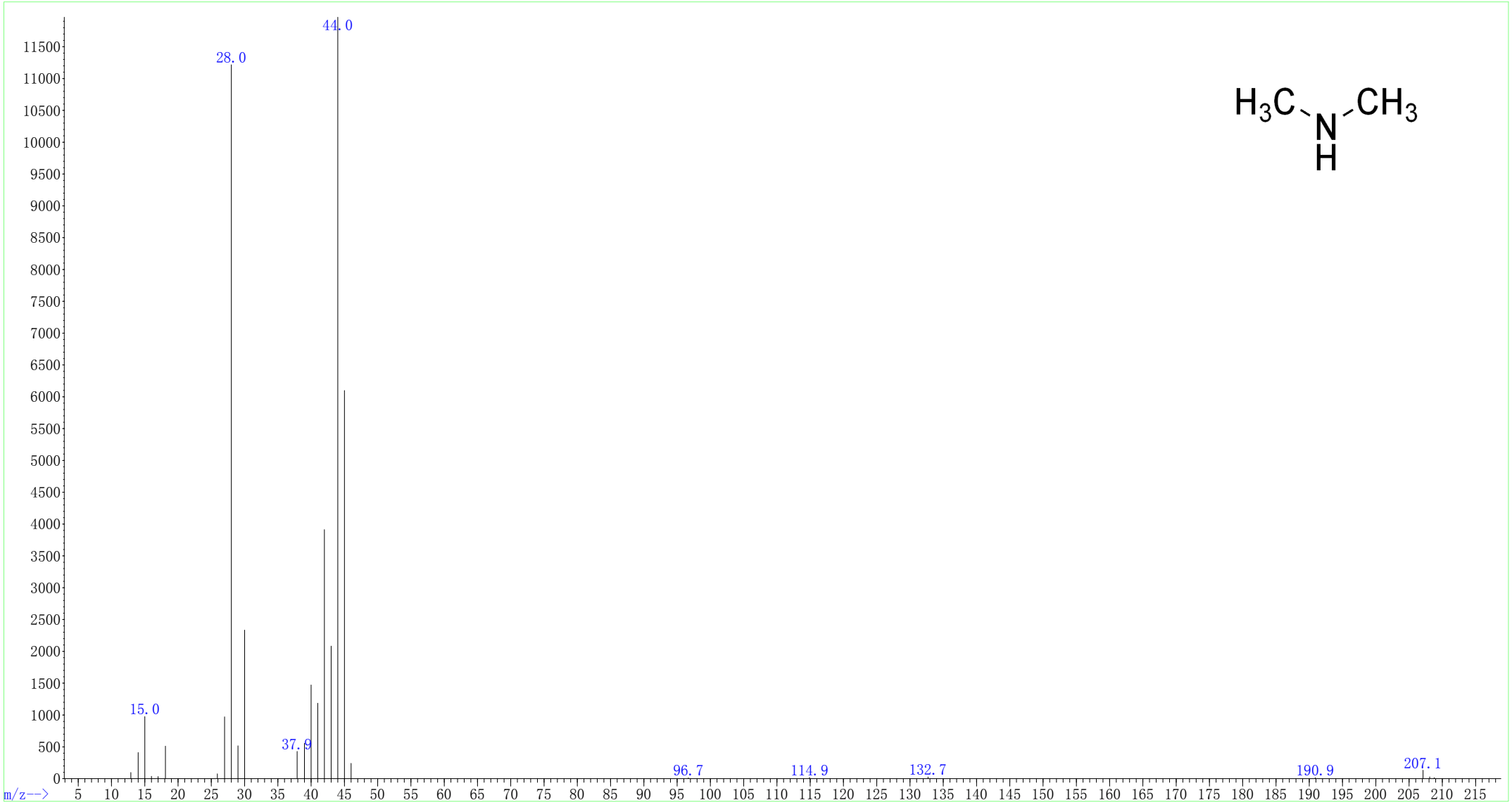


Figure S2

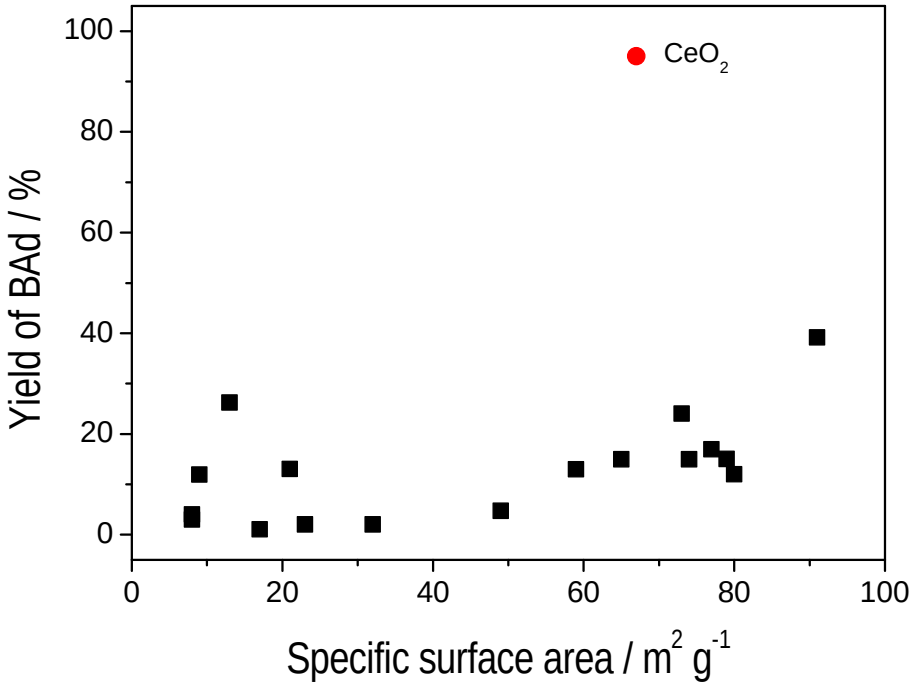


Figure S3 The relationship of the specific surface of zeolites and metal oxides against the yield of BAd. No clear dependence of surface area was observed. The data were from Table S1.

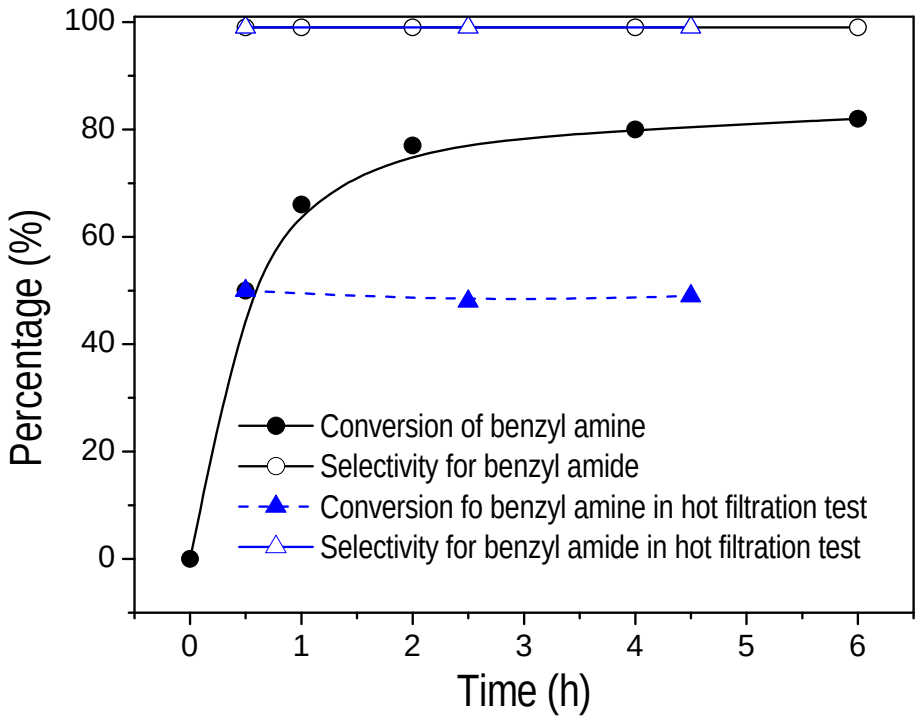


Figure S4 Catalyst hot filtration test. Reaction condition: catalyst 100 mg, benzyl amine 1.5 mmol, DMF 2 mL. The catalyst was filtered out in 30 min and the filtrate was further reacted under the same reaction condition at 100 ^{o}C.

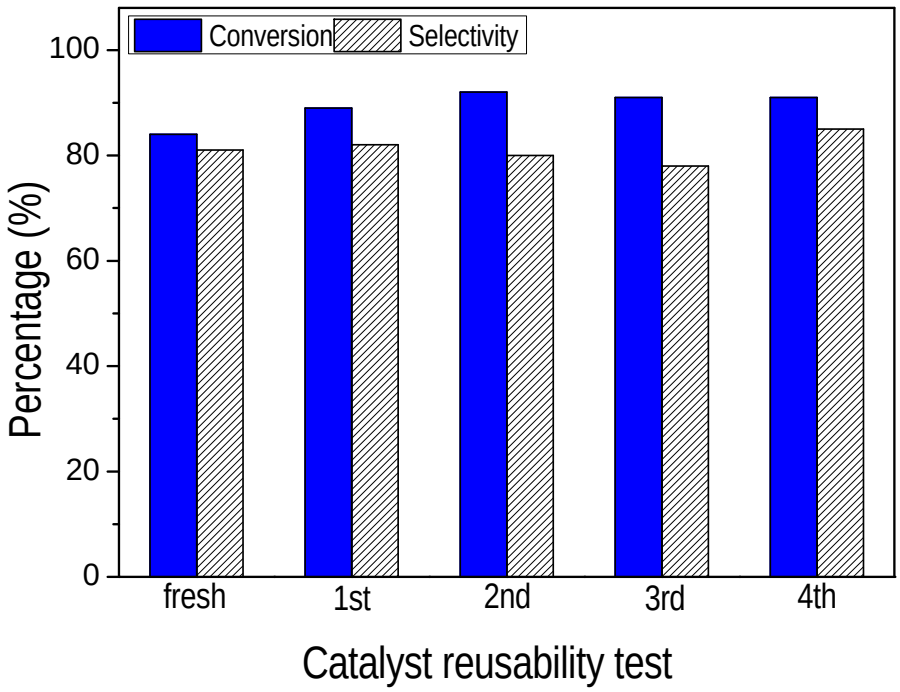


Figure S5 Reusability of ceria in the transformylation of benzyl amine to benzyl amide.

Reaction conditions: Catalyst 100 mg, benzy amine 1.5 mmol, DMF 2mL, 160 ^{o}C, 5h.

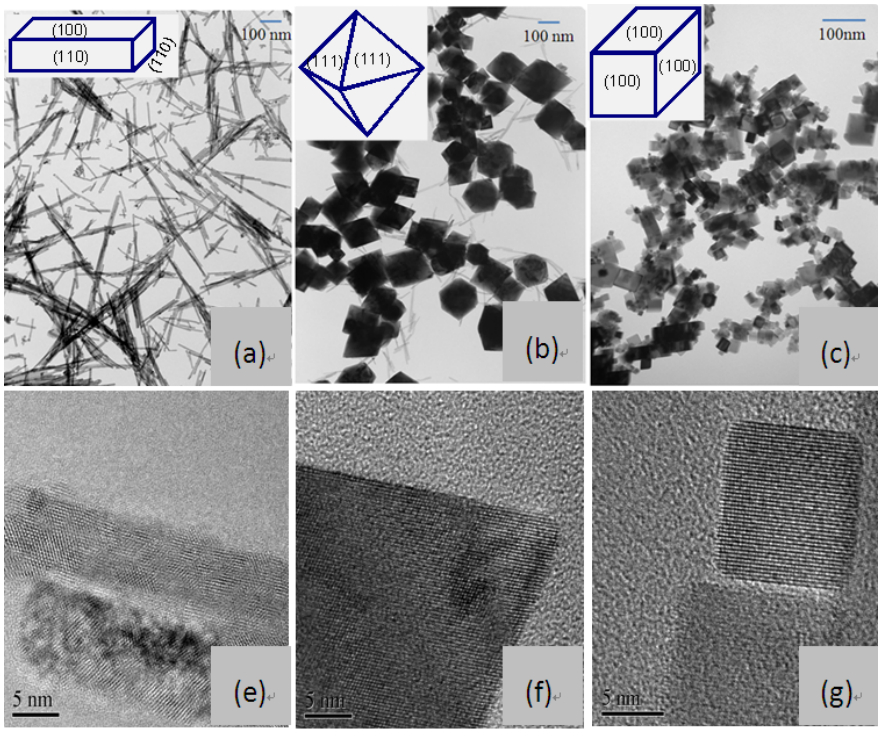


Figure S6 TEM of (a) nano-rod, (b) nano-octahedral, and (c) nano-cube and HETEM of (e) nano-rod, (f) nano-octahedral, and (g) nano-cube.

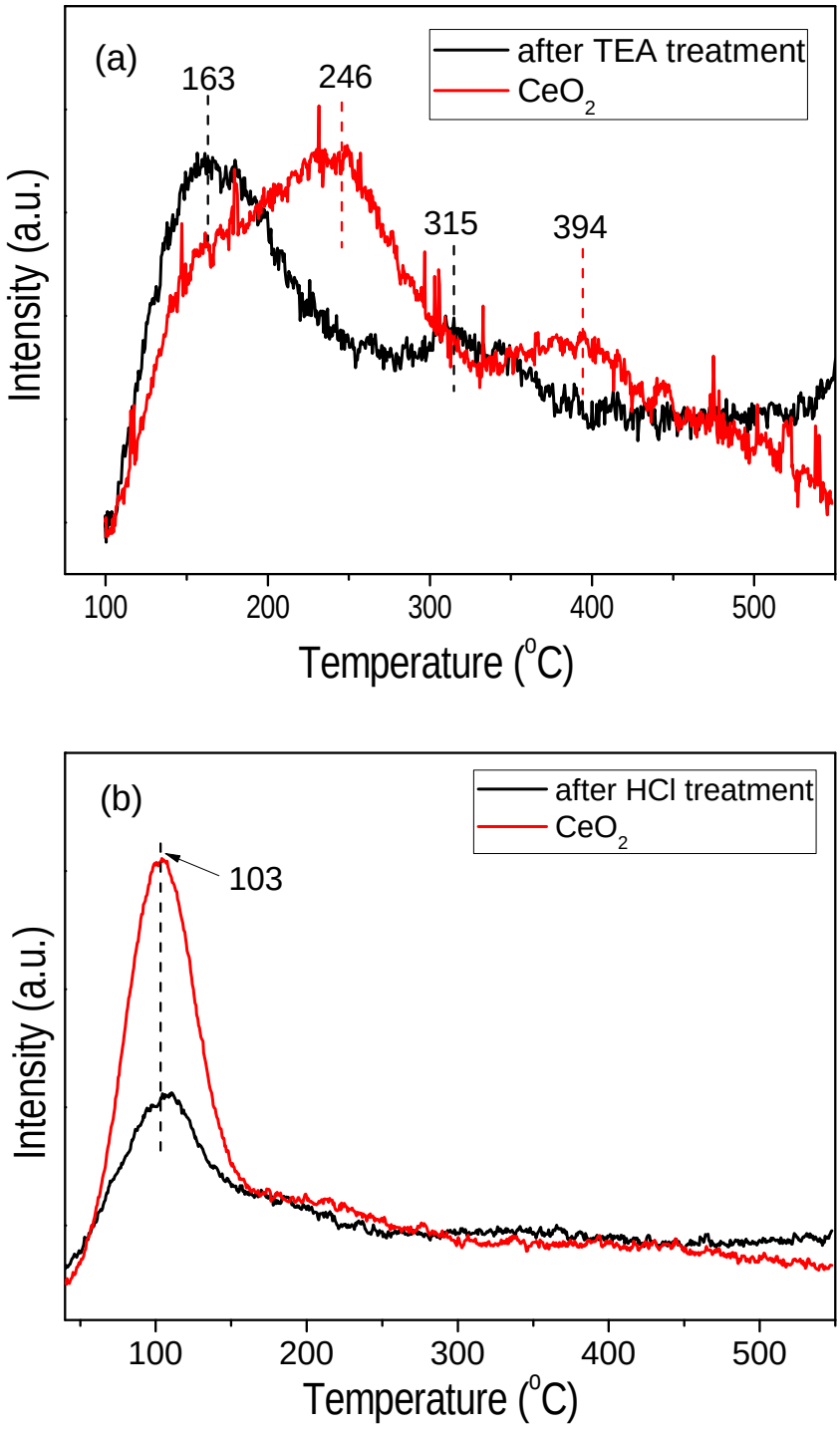


Figure S7 (a) NH_3-TPD of ceria and ceria after TEA treatment (b) CO_2-TPD of ceria and ceria after HCl treatment

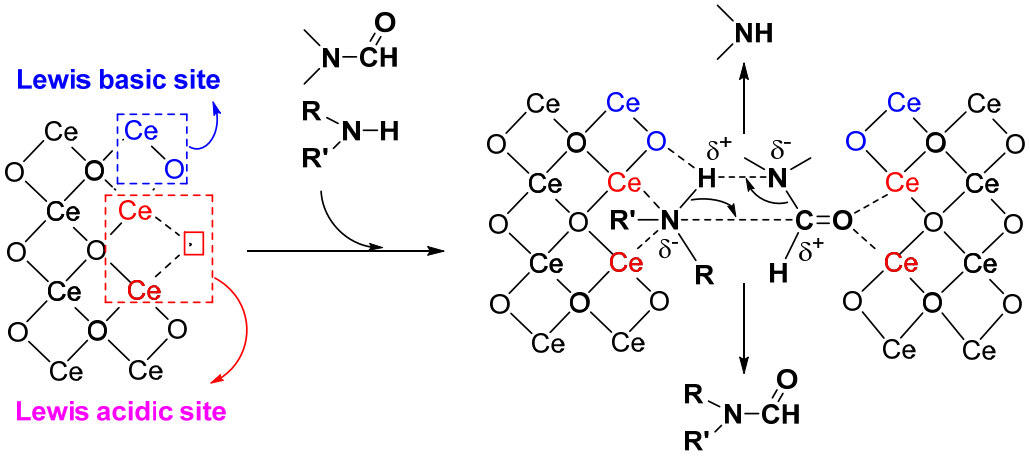


Figure S8. Tentative reaction mechanism.

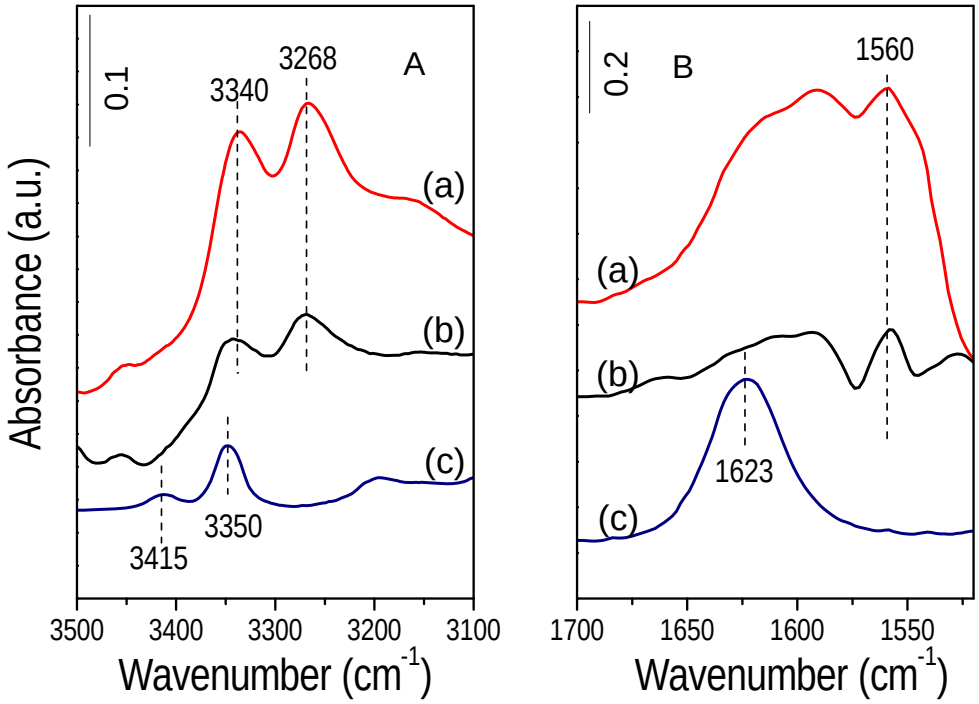


Figure S9 In situ FT-IR of n-butylamine absorbed on CeO_2 and desorption at (a) 100 ^oC and (b) 150 ^oC (c) FT-IR of liquid n-butylamine

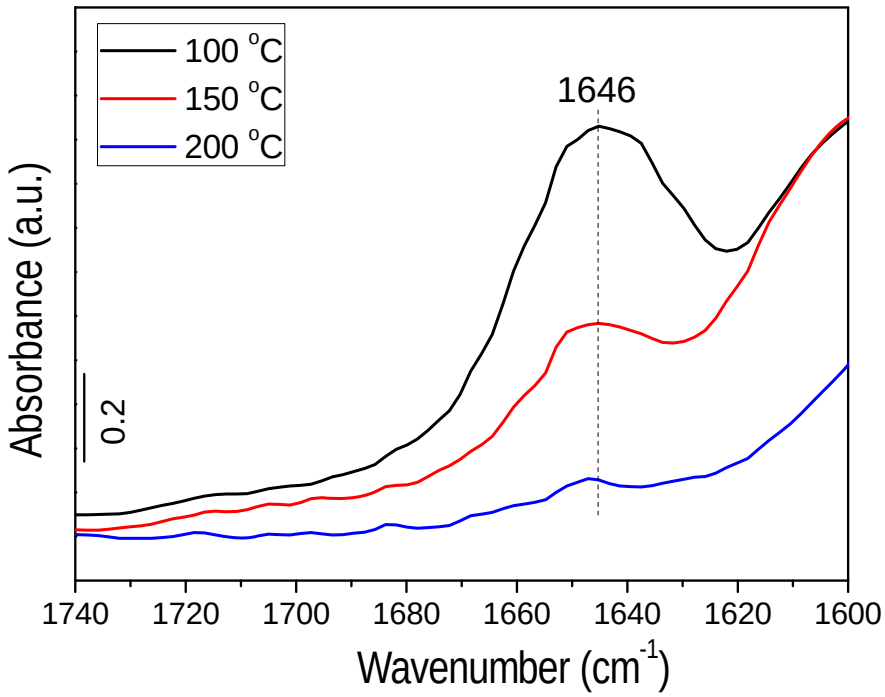
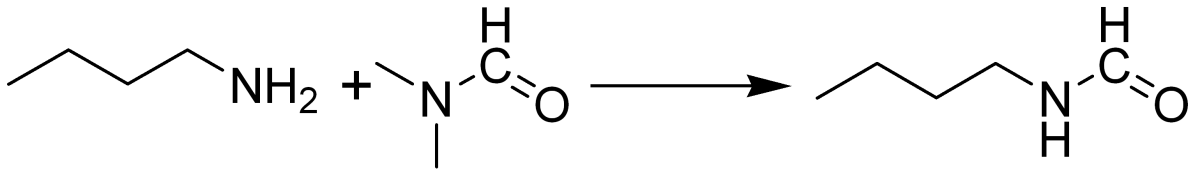


Figure S10 In situ absorbing FT-IR of DMF absorbed on CeO_2 pretreated at 500 °C.

Reference

[1] F. Wang, W. Ueda, *Chemical Communications* **2008**, 3196-3198.
[2] G. Busca, *Phys. Chem. Chem. Phys.* **1999**, *1*, 723-736.



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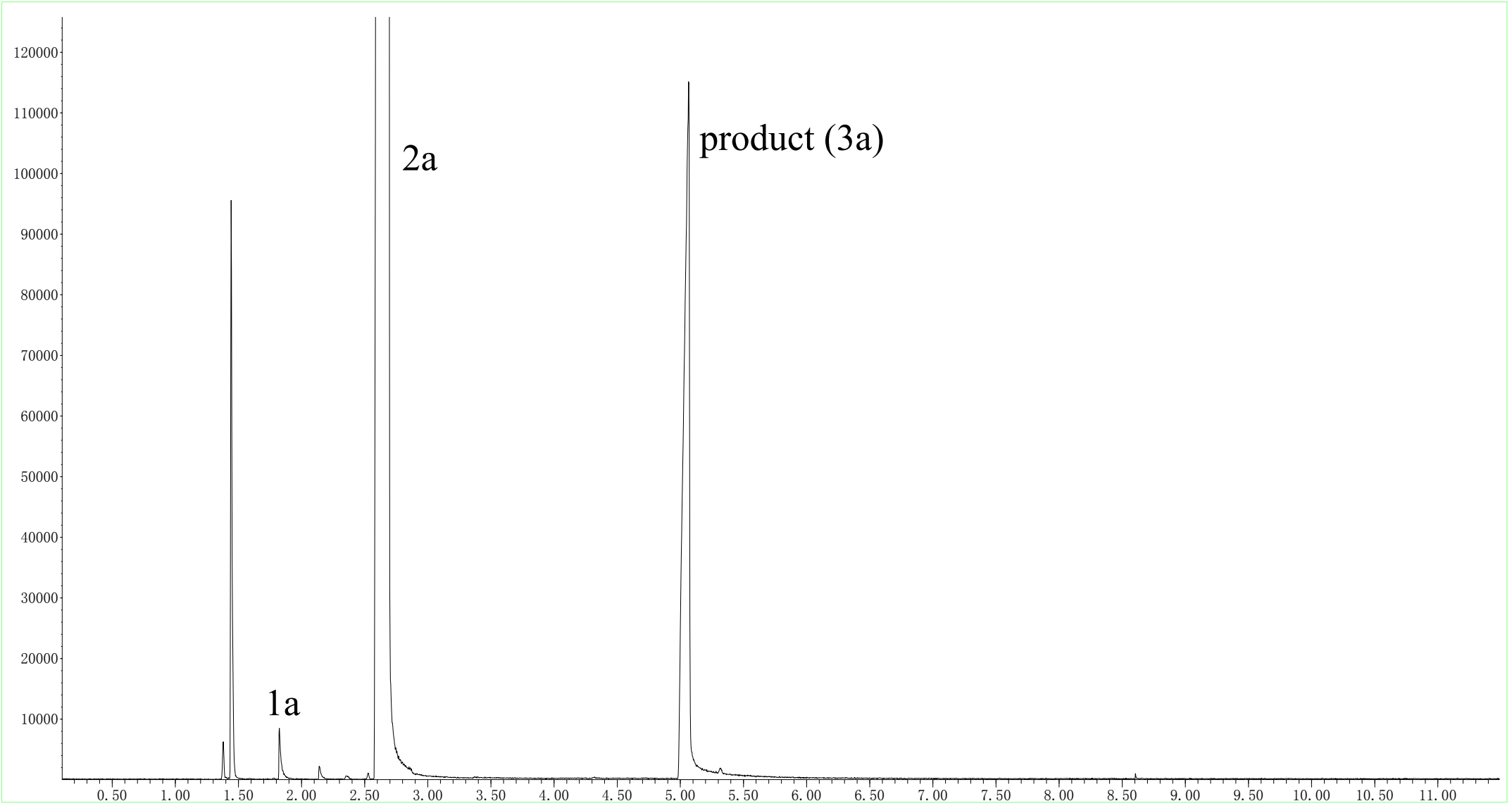

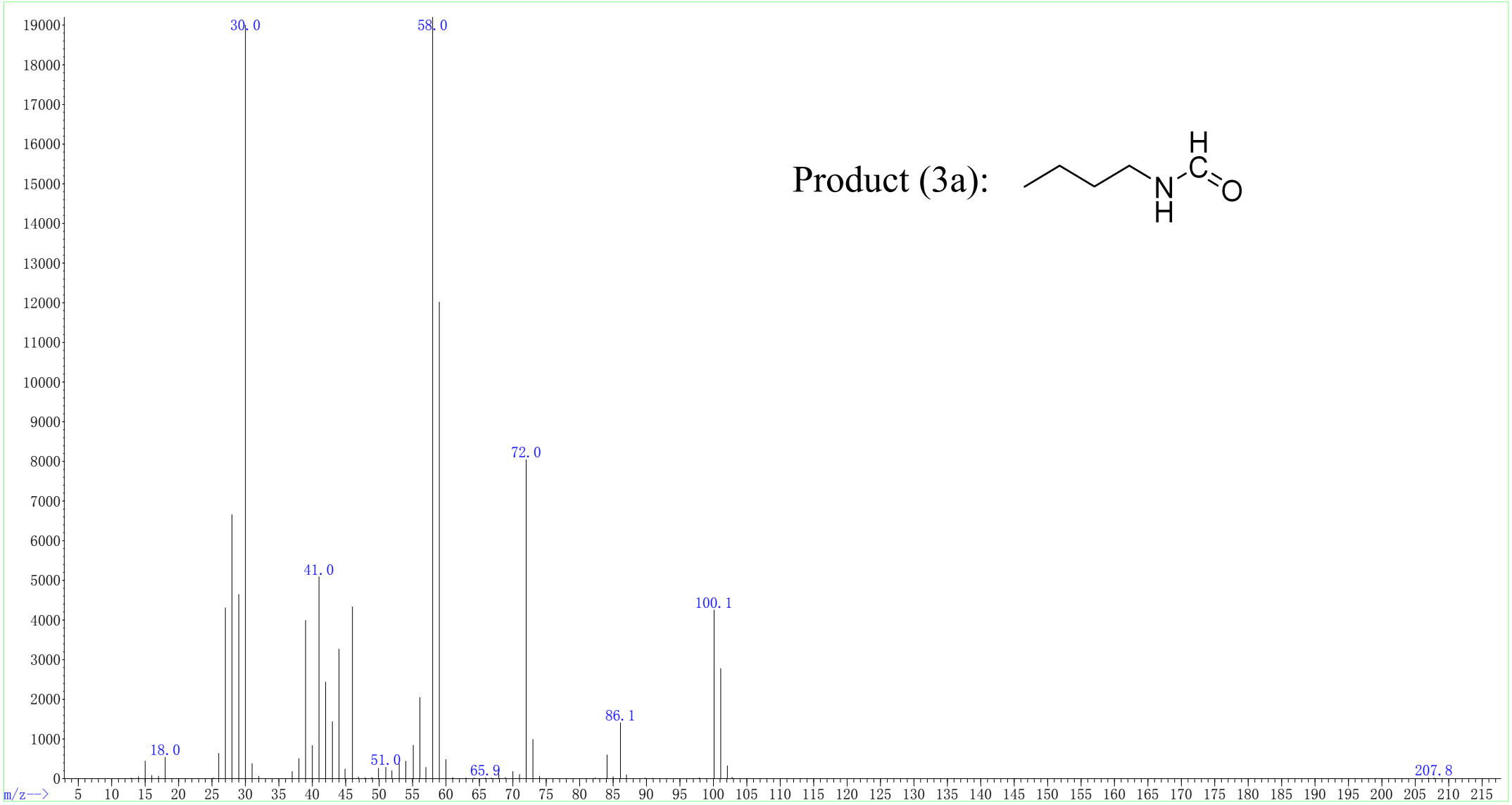

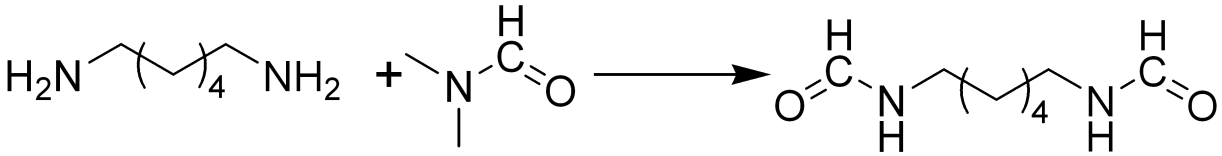
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H
C
O
O
C
H
N
H
4
N
C
H
O

1b 2b 3b


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110000
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95000
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85000
80000
75000
70000
65000
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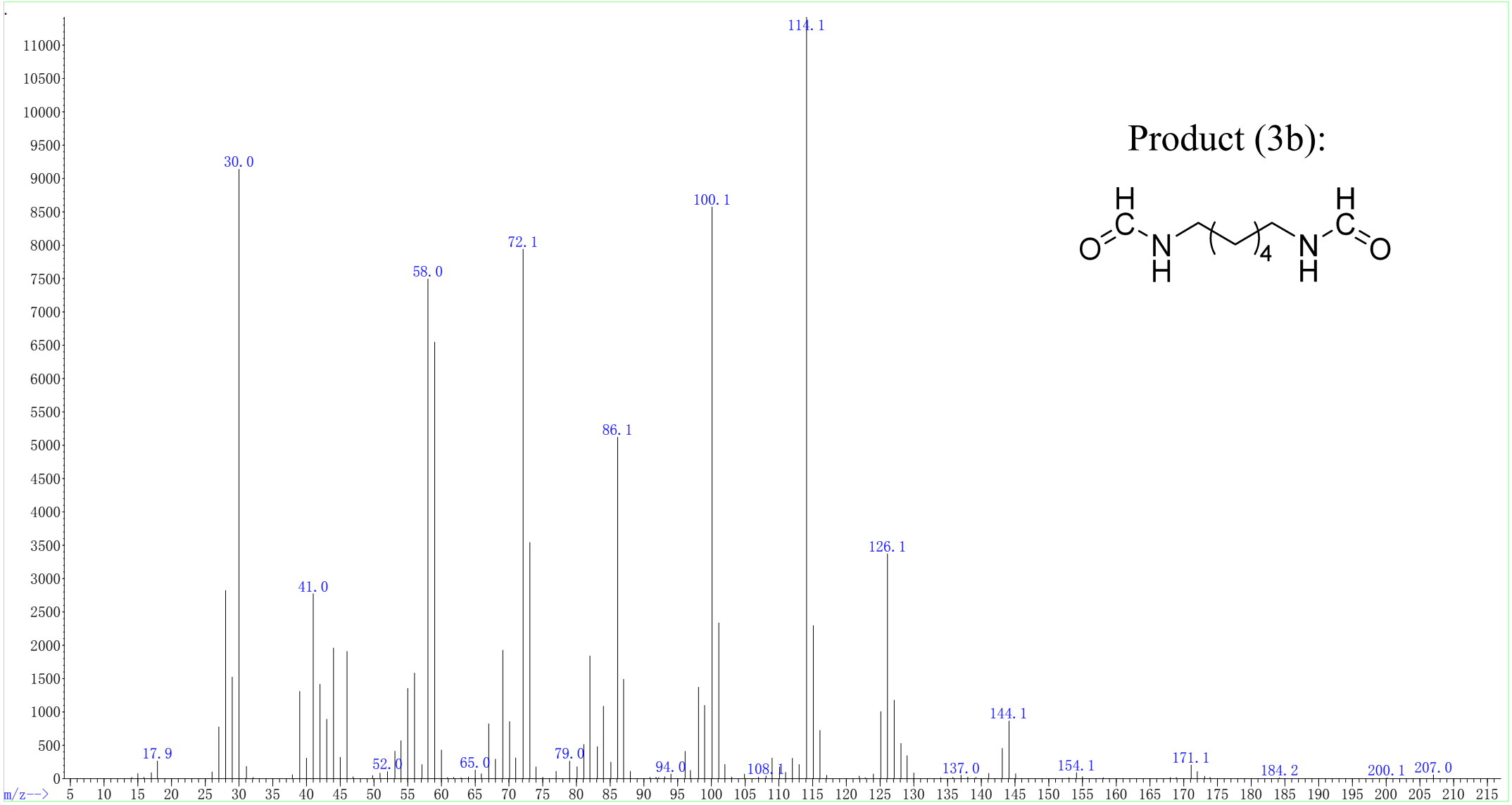

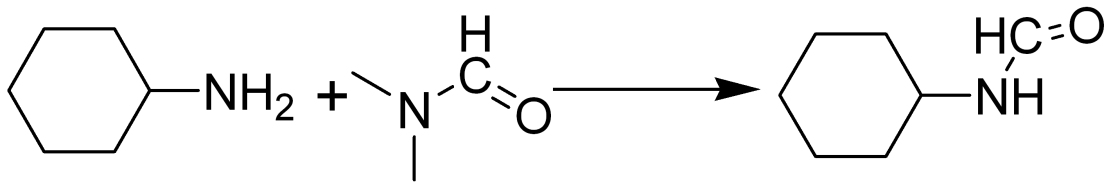

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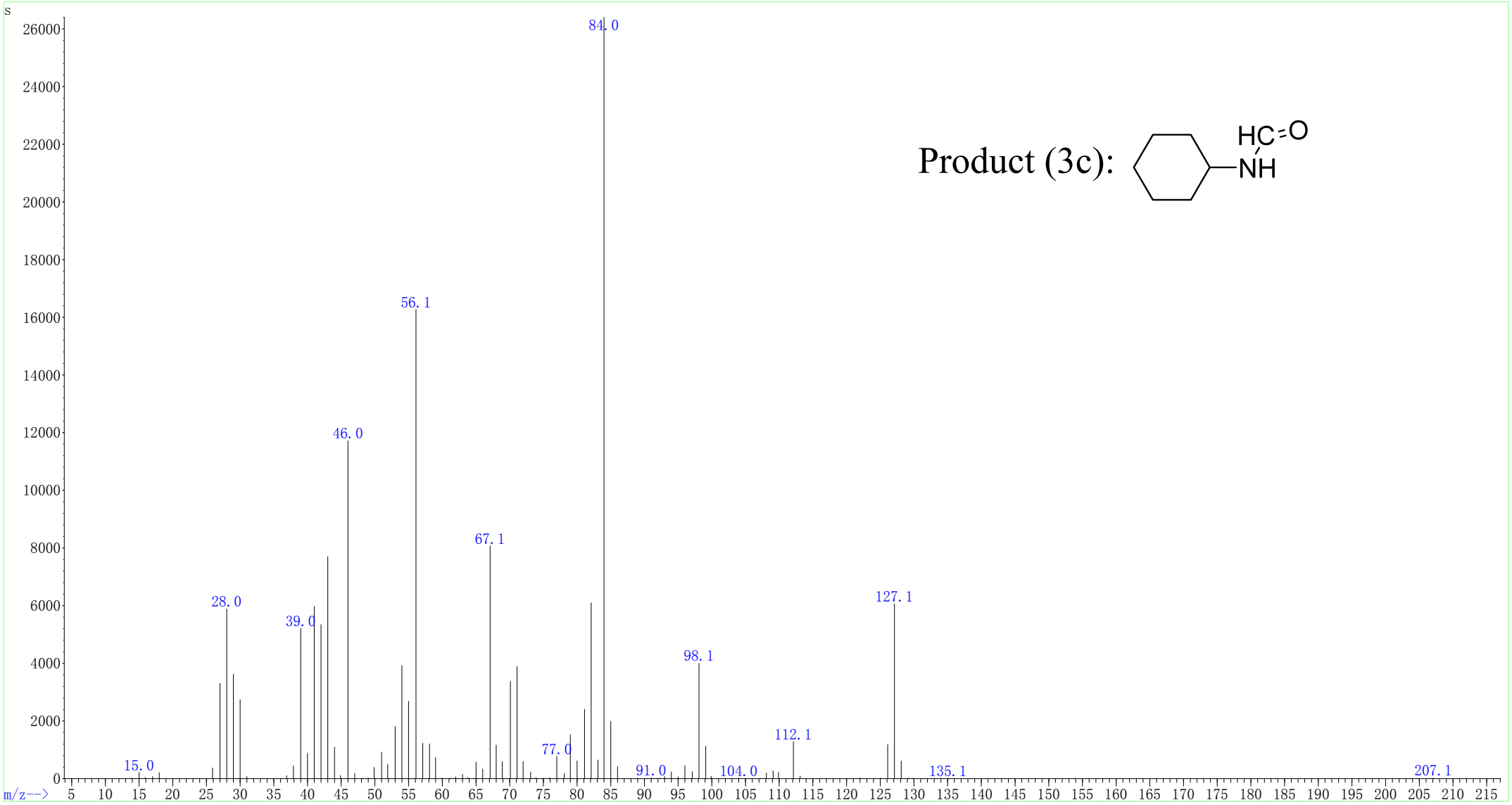
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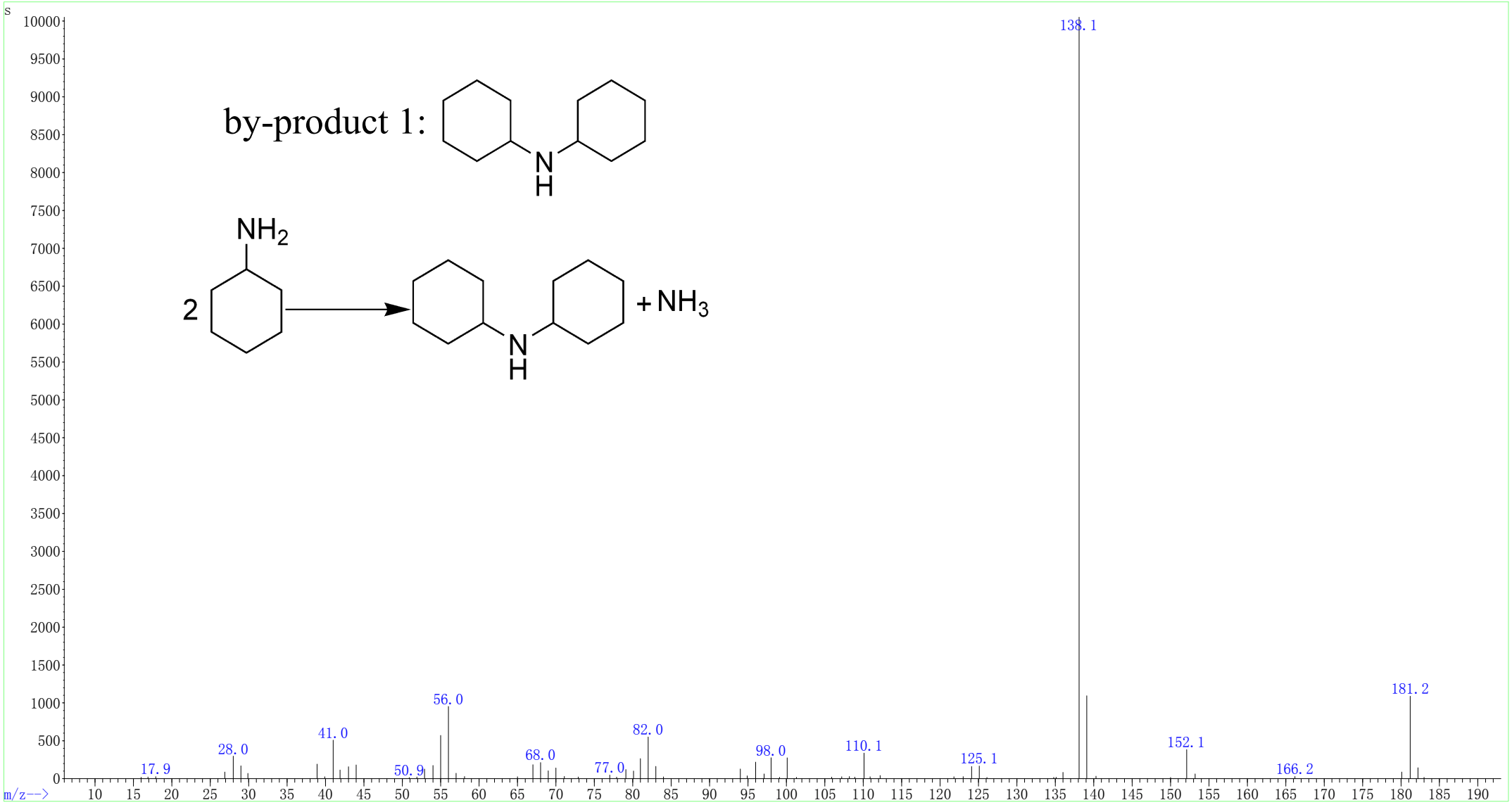
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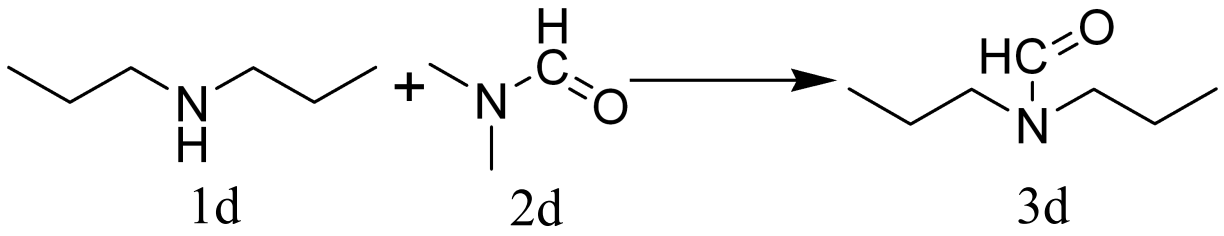

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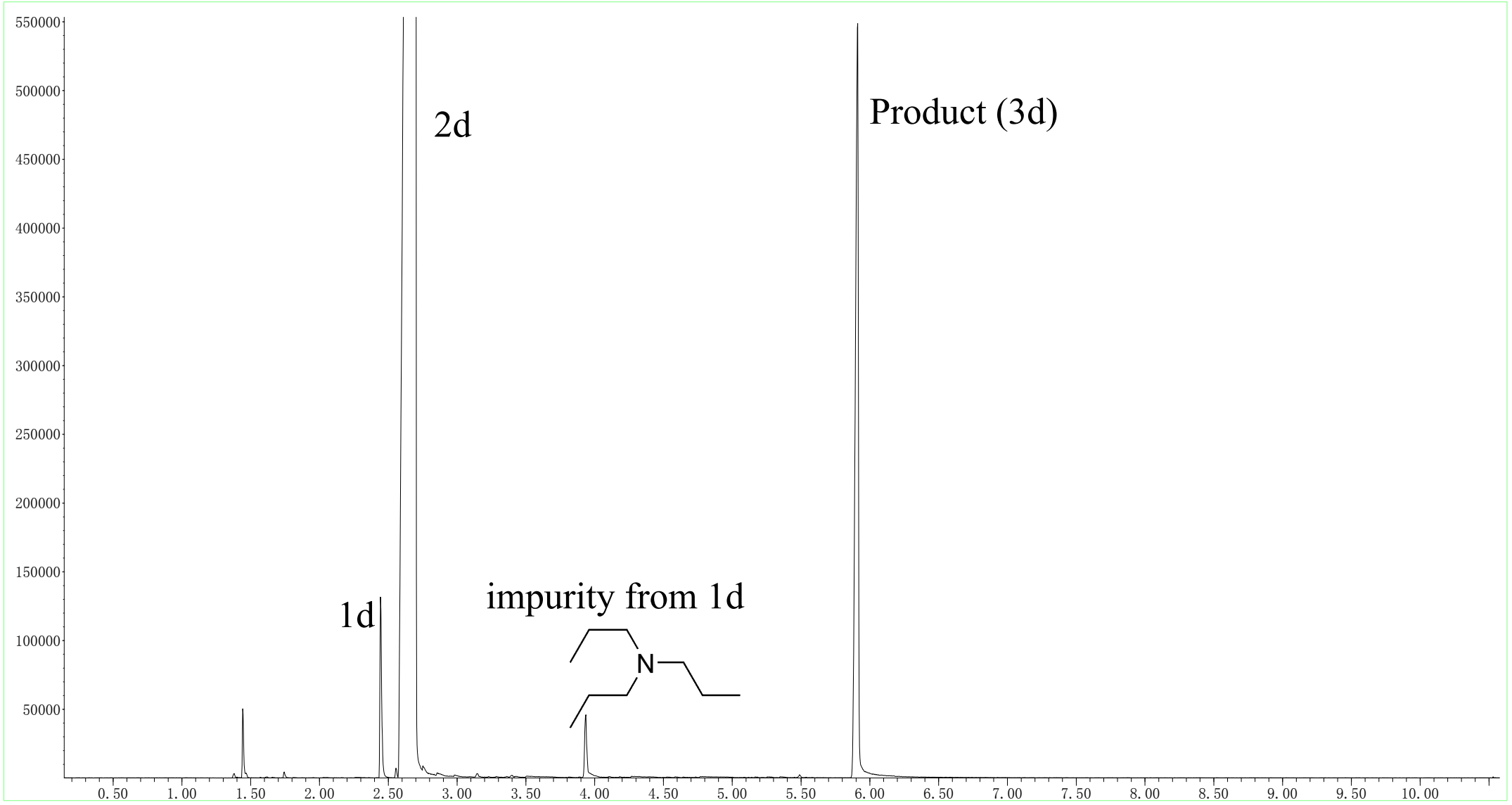

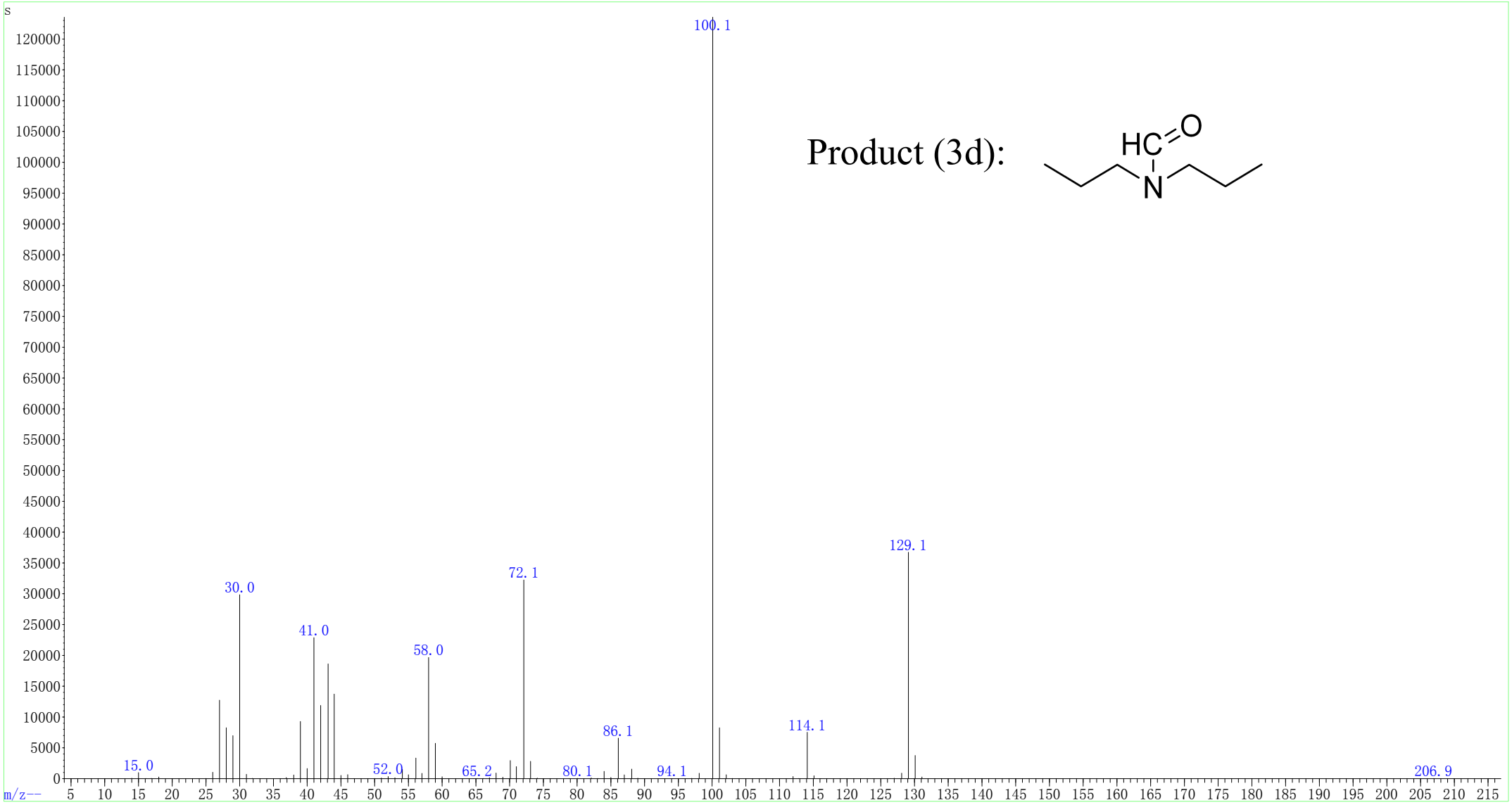
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m/z--

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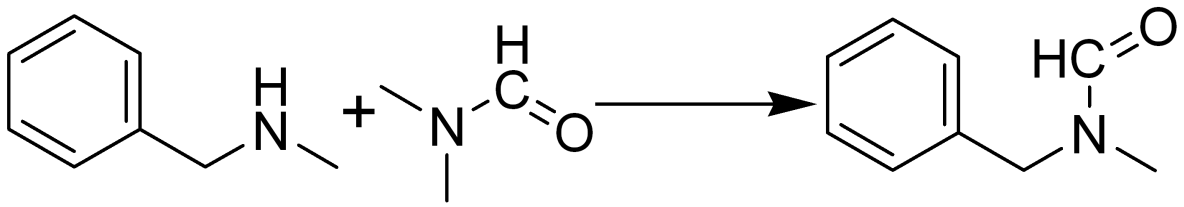

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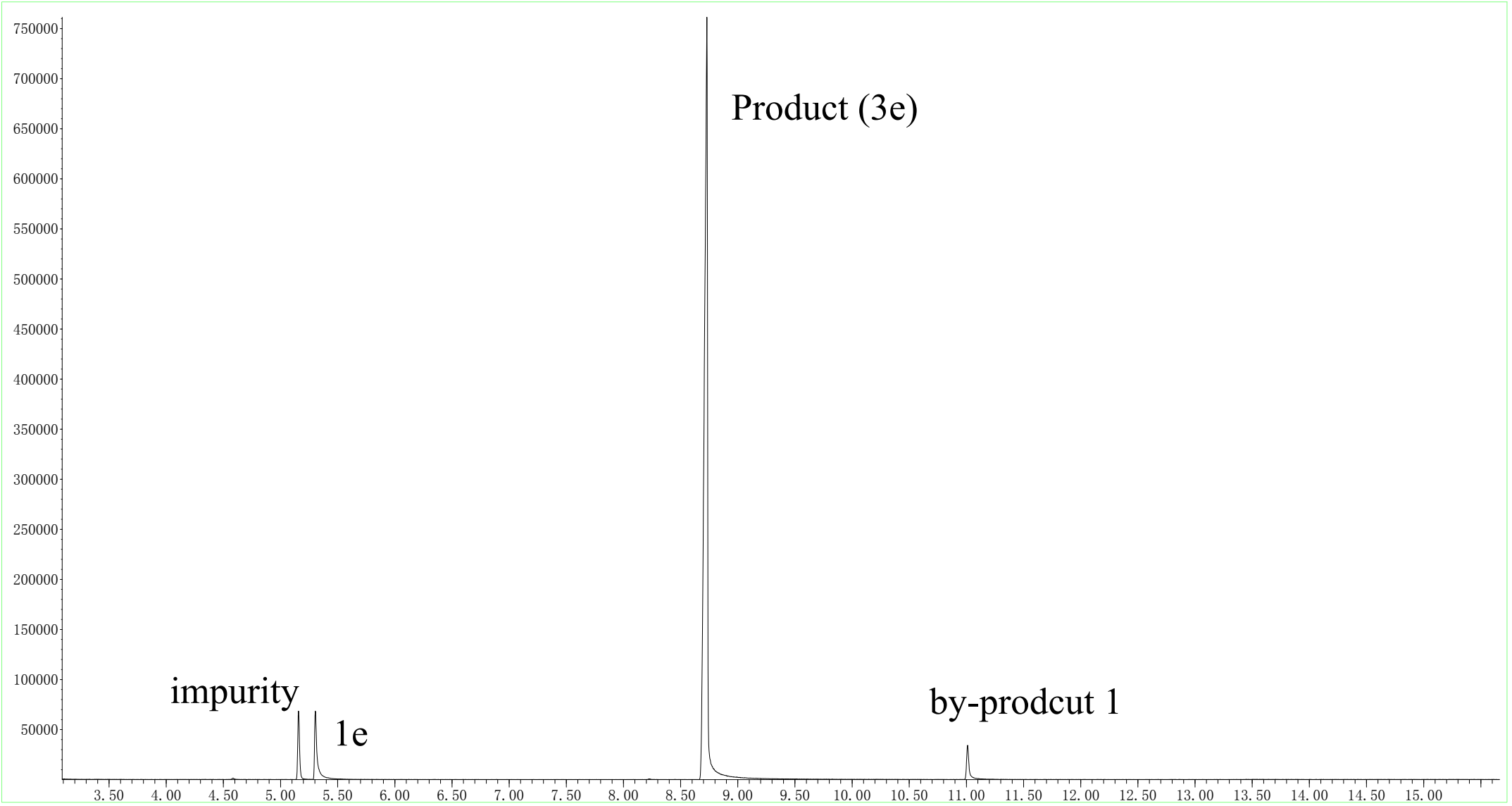

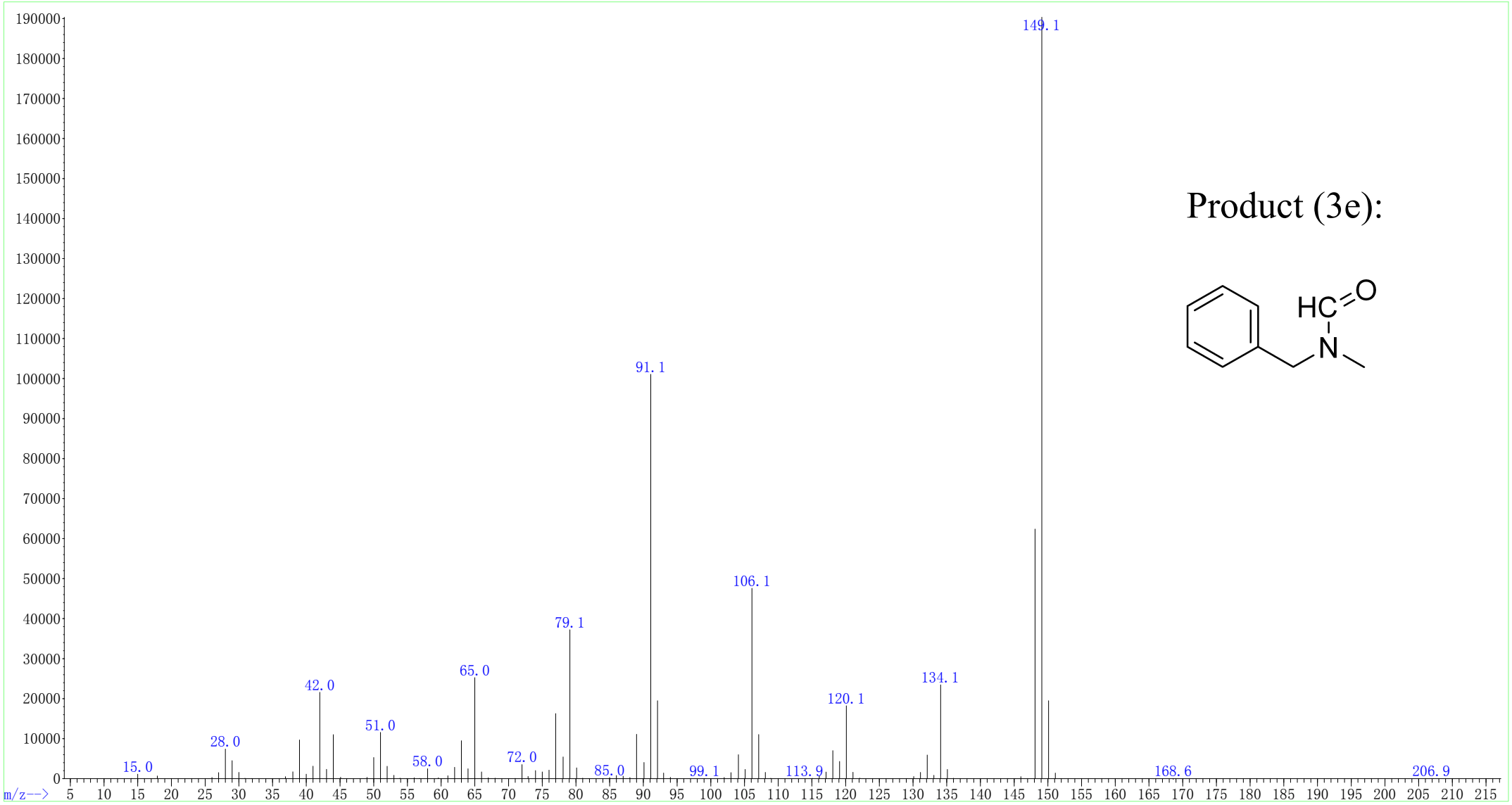
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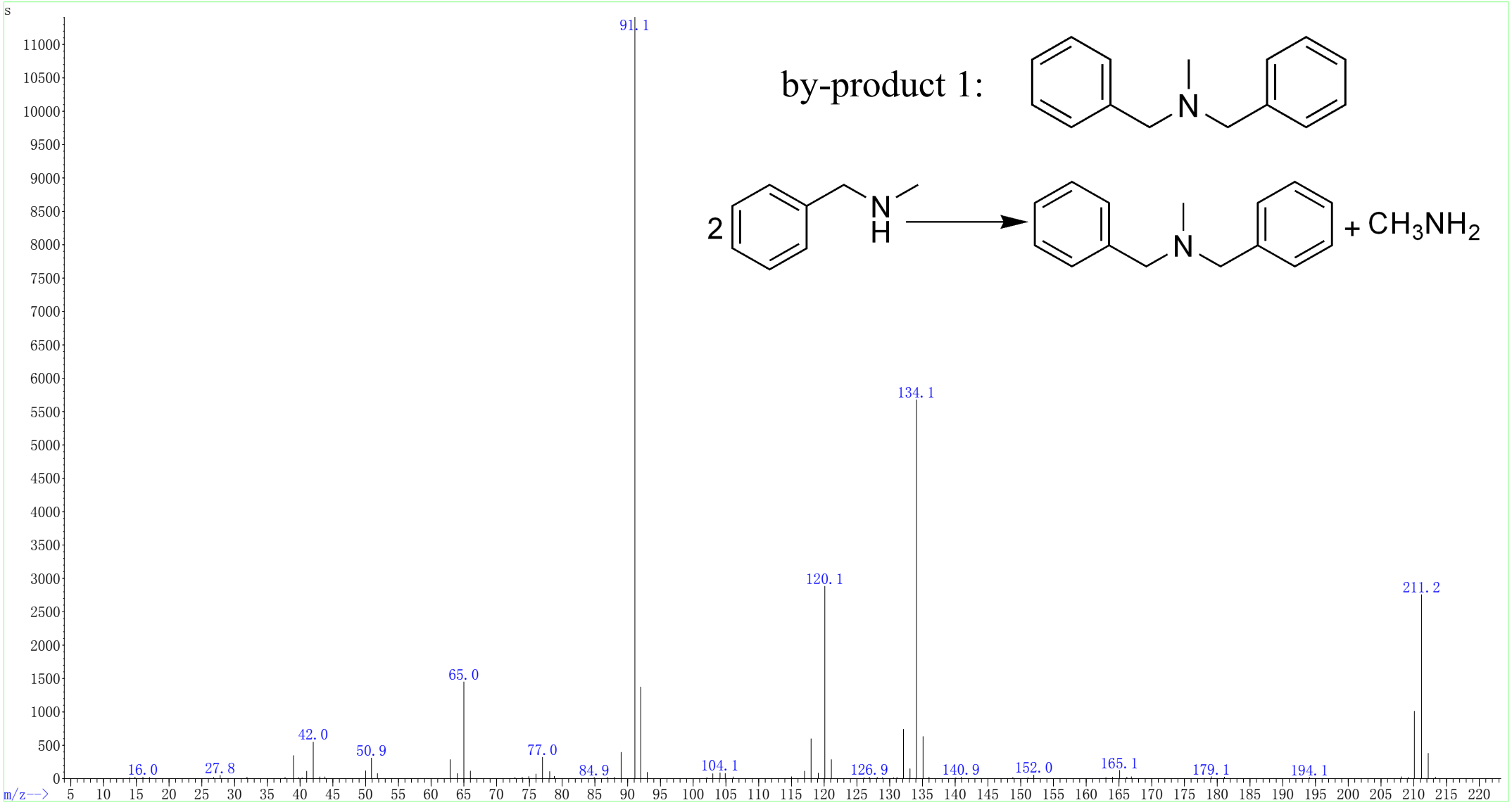
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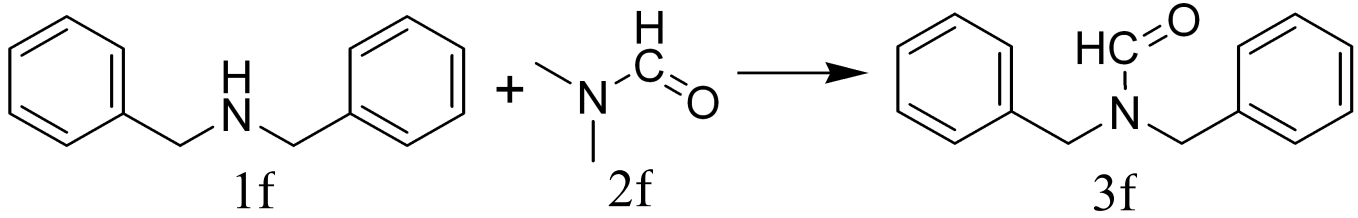

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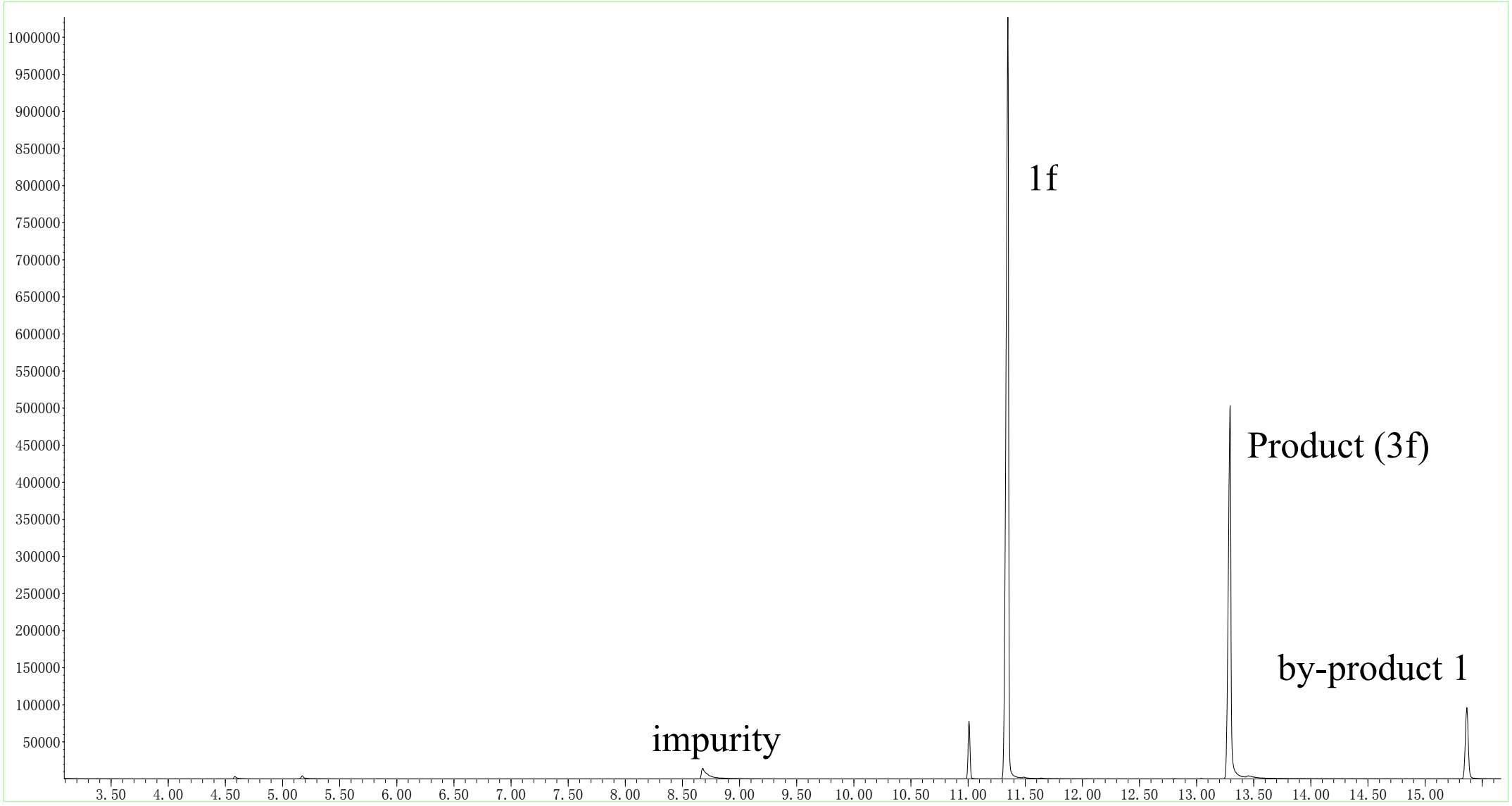

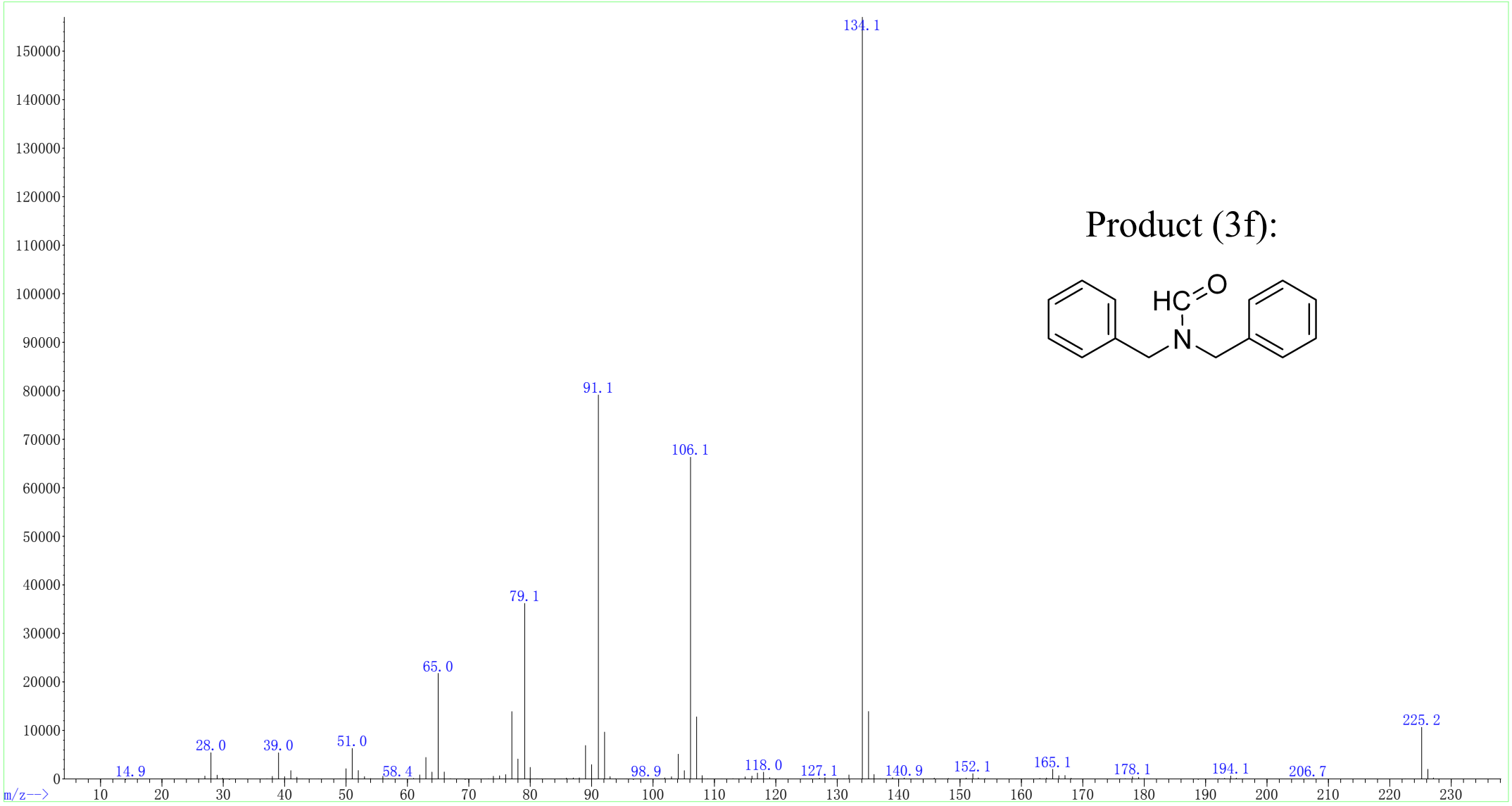
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m/z-->
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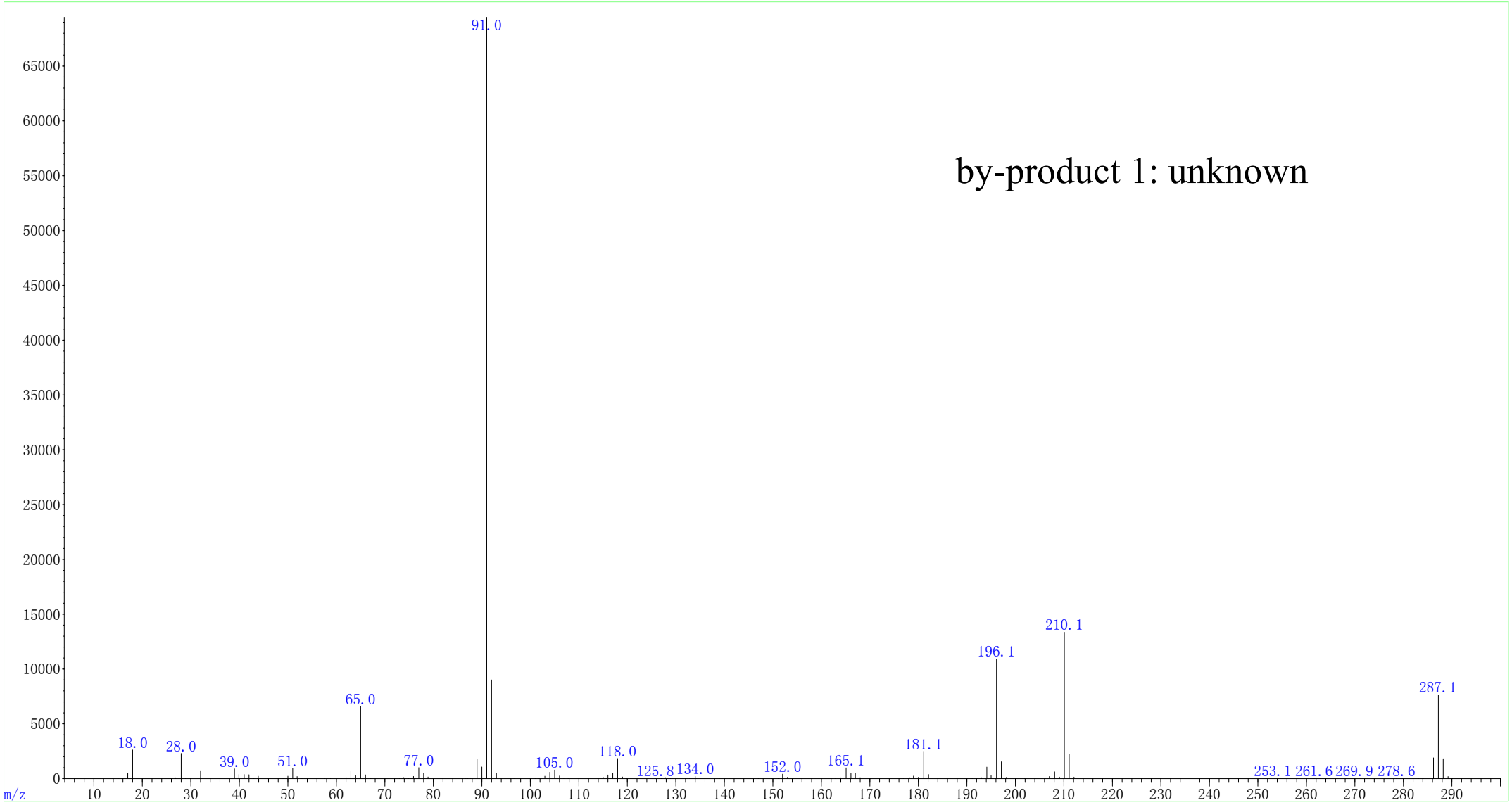
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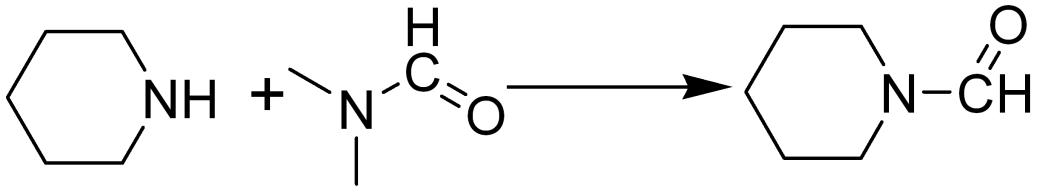
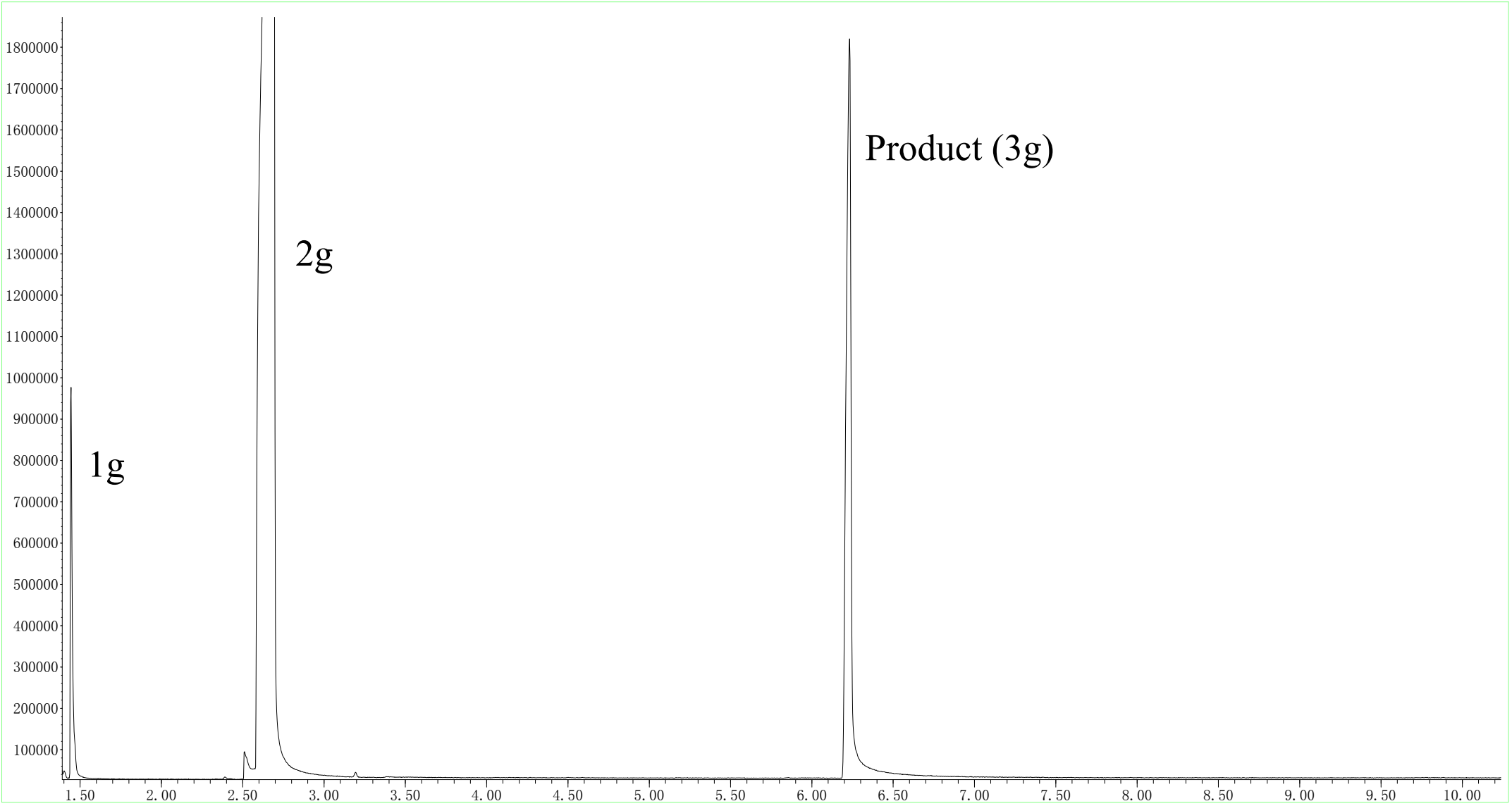
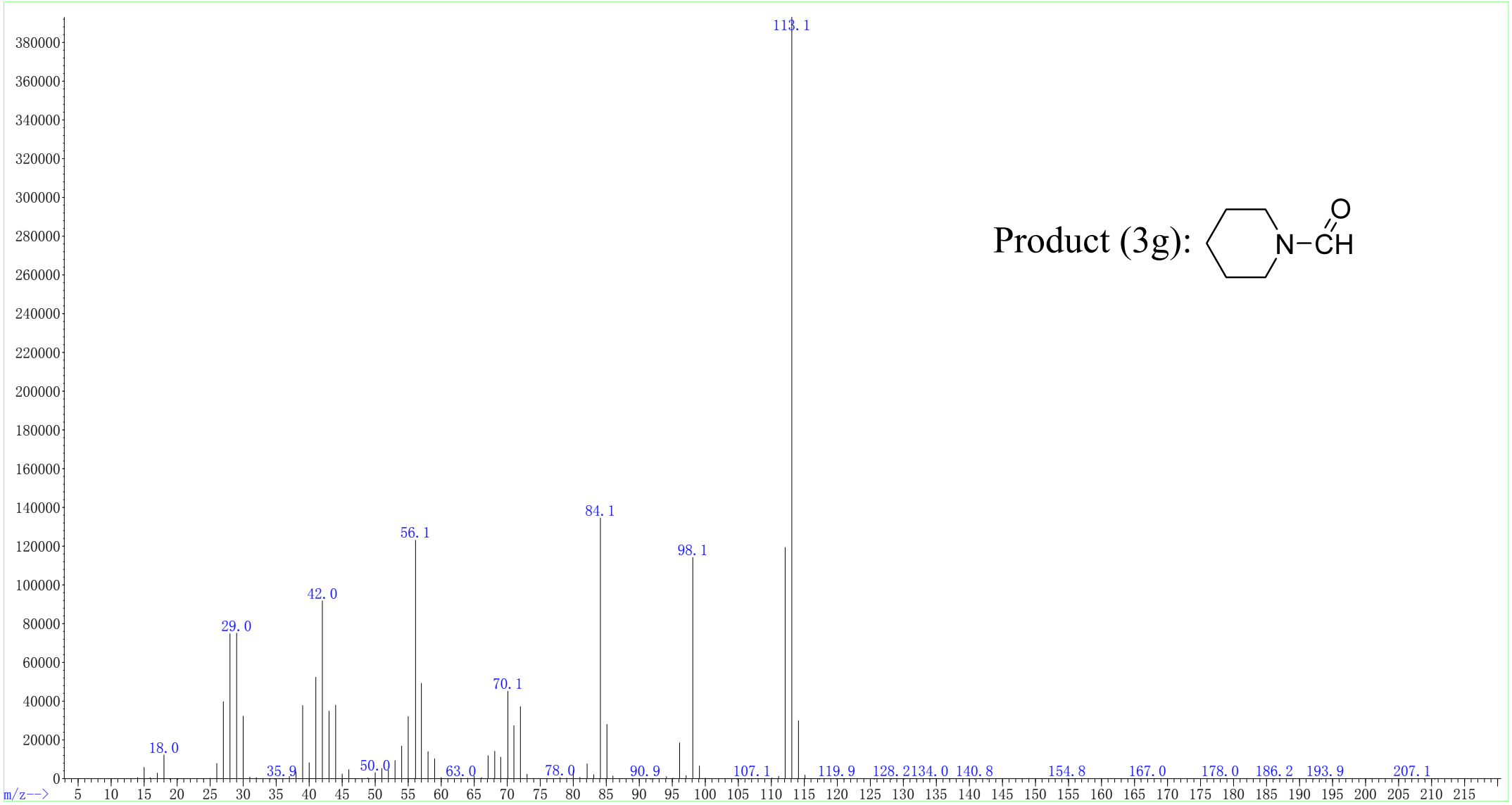
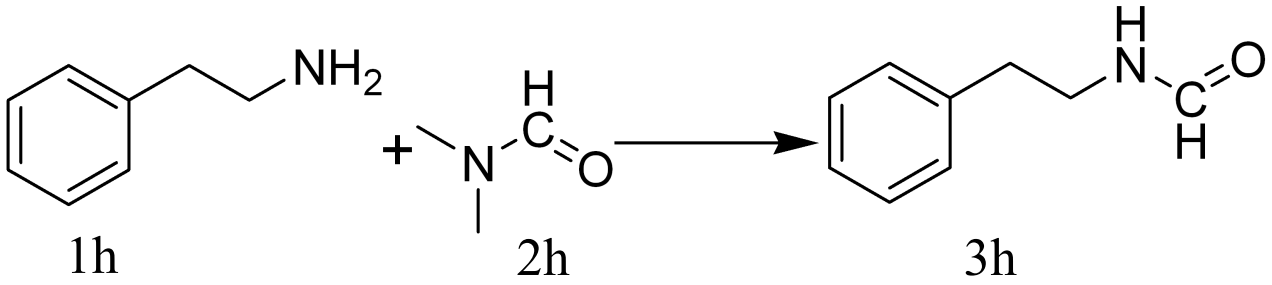
287.1
m/z--



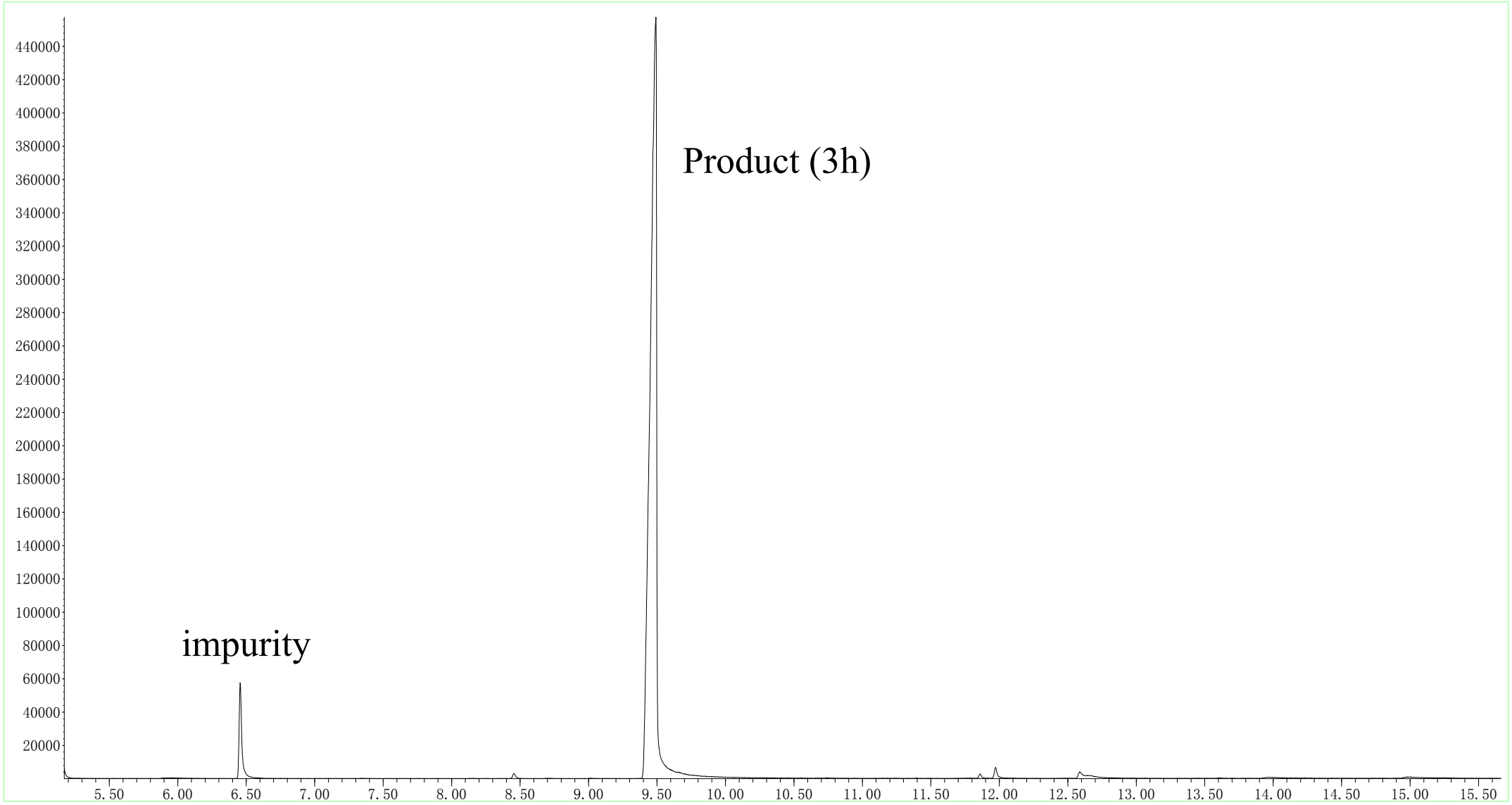
1g 2g 3g

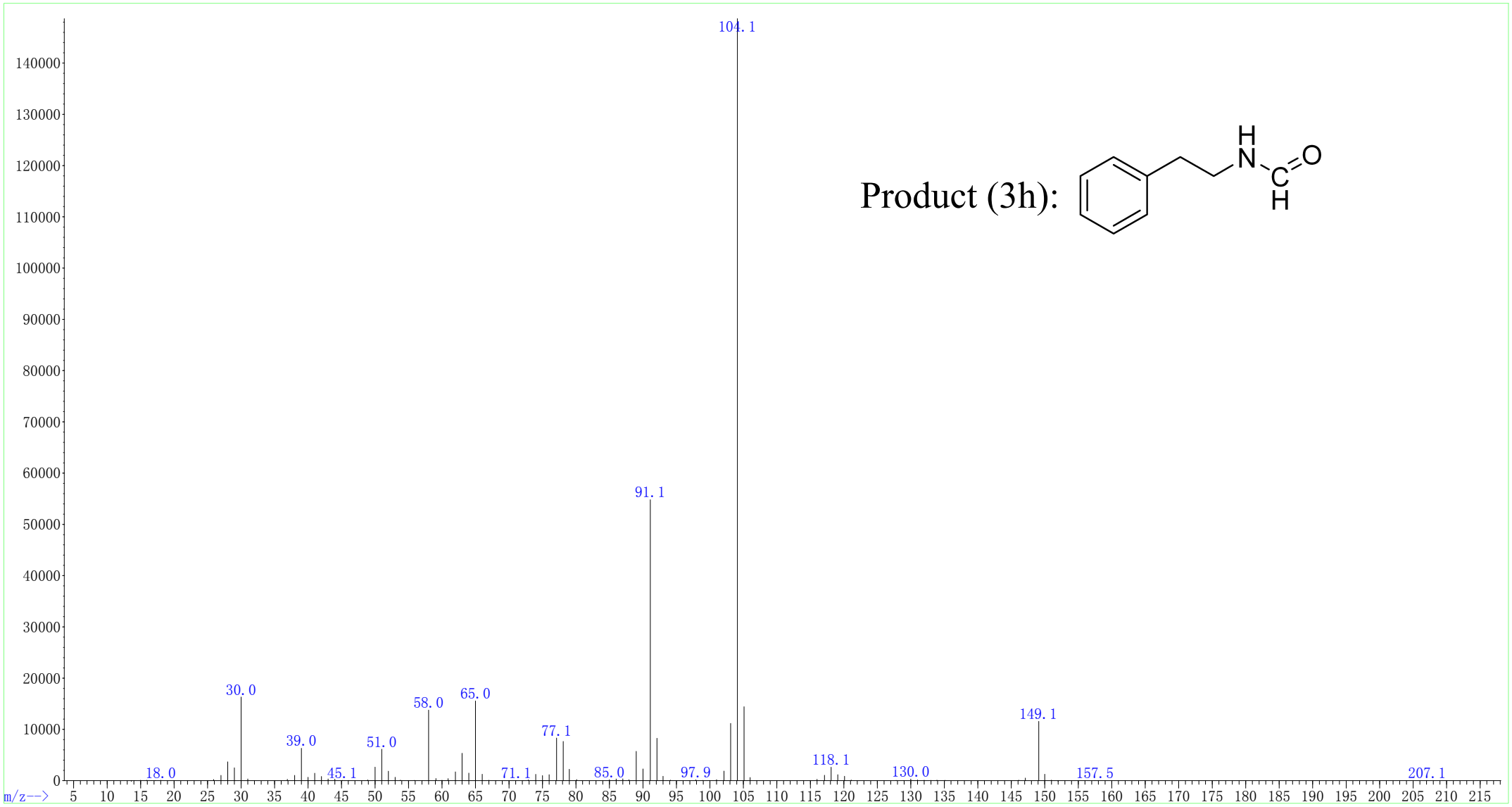


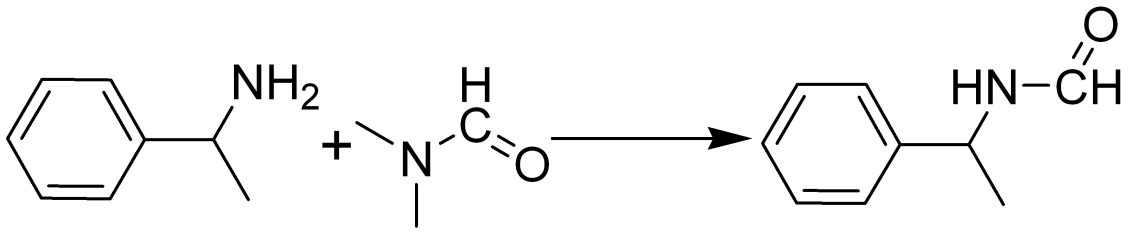




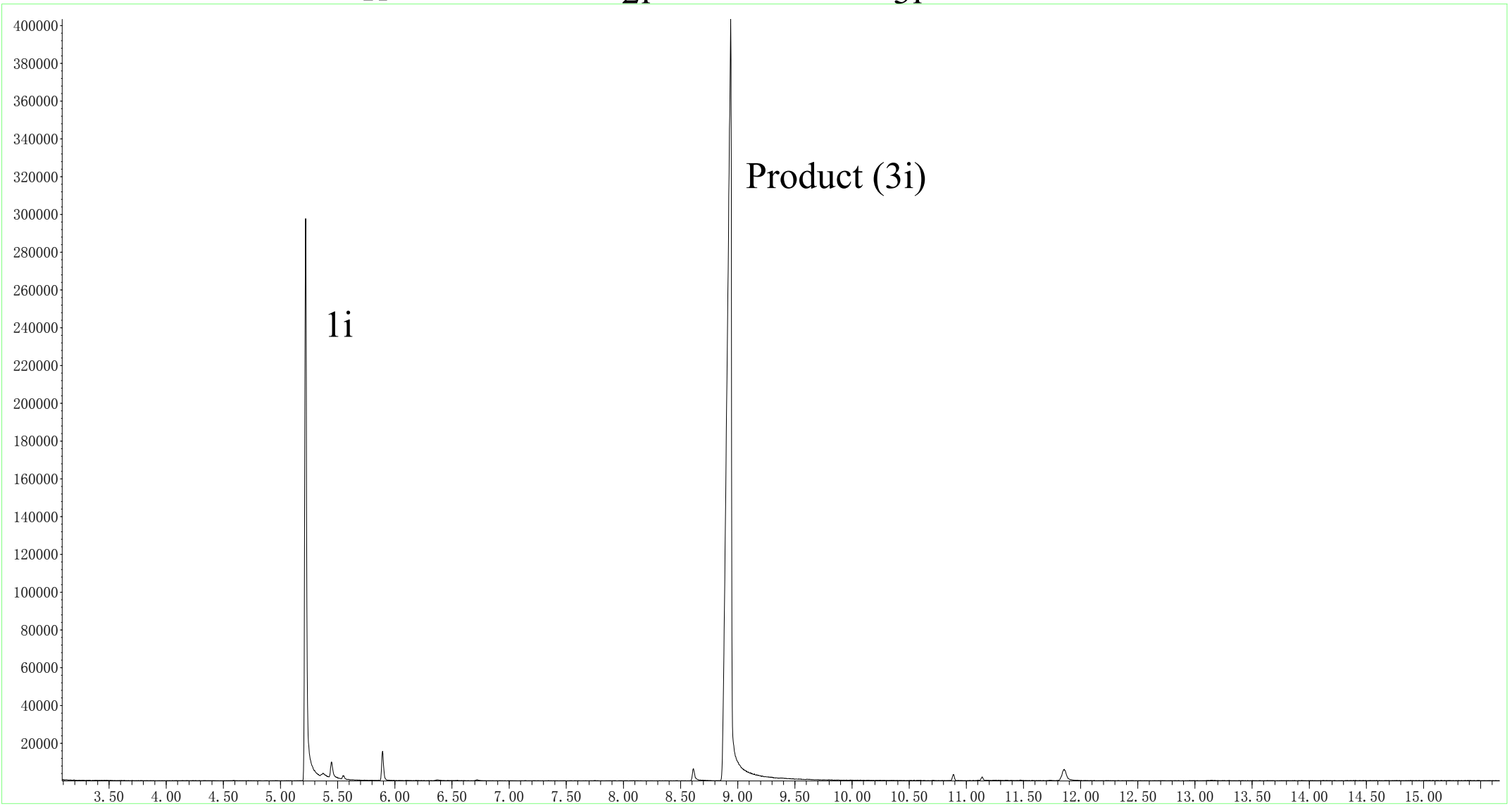
1h 2h 3h

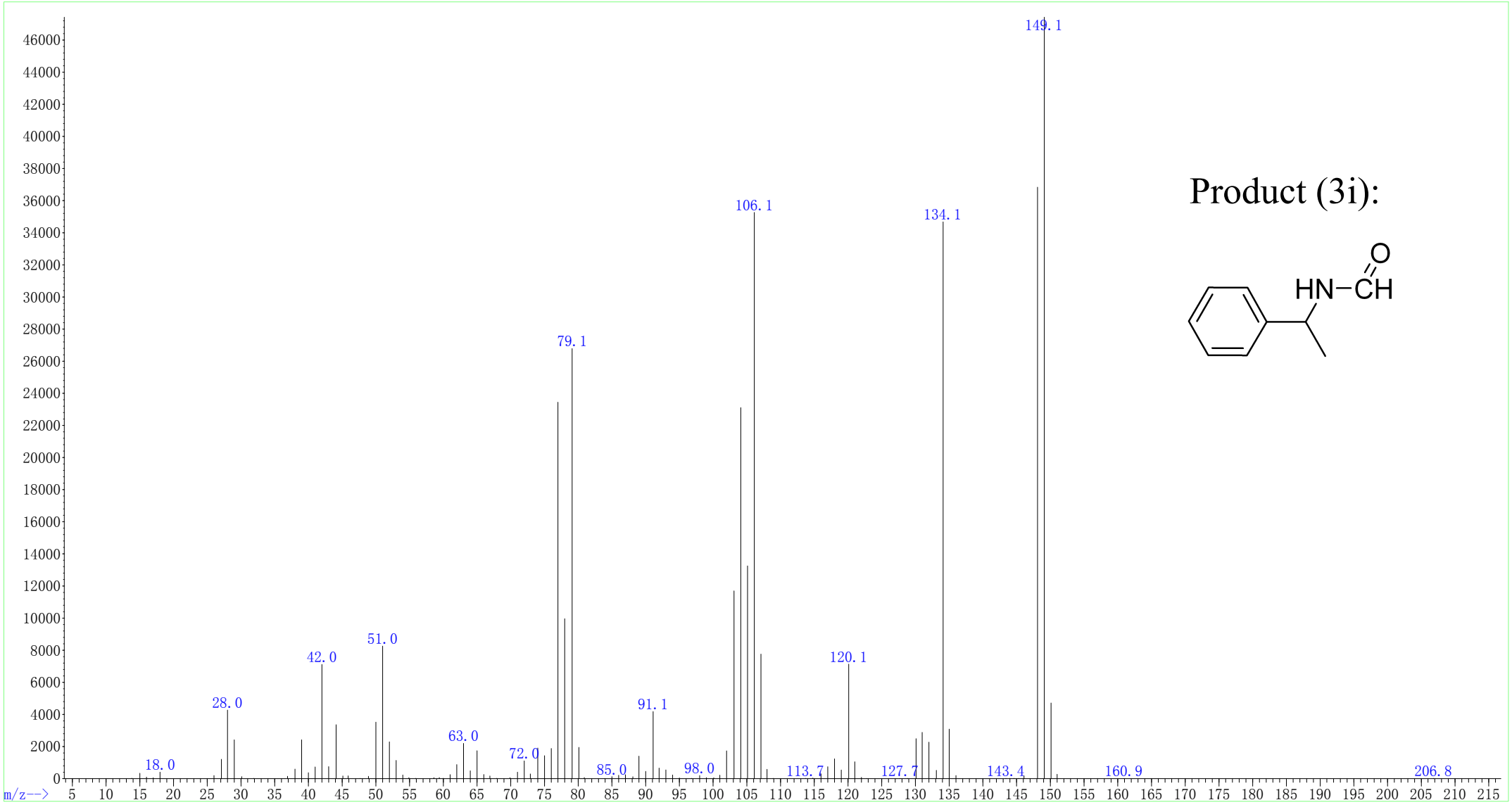


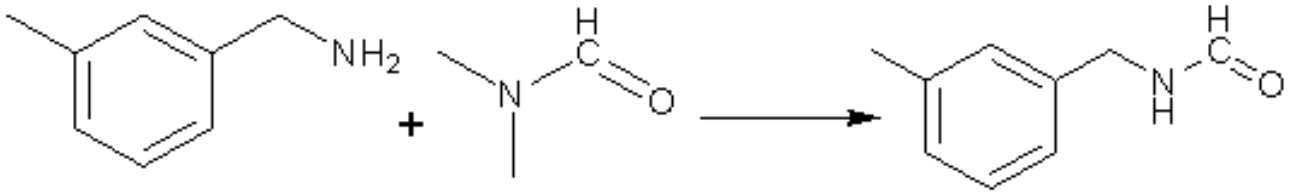




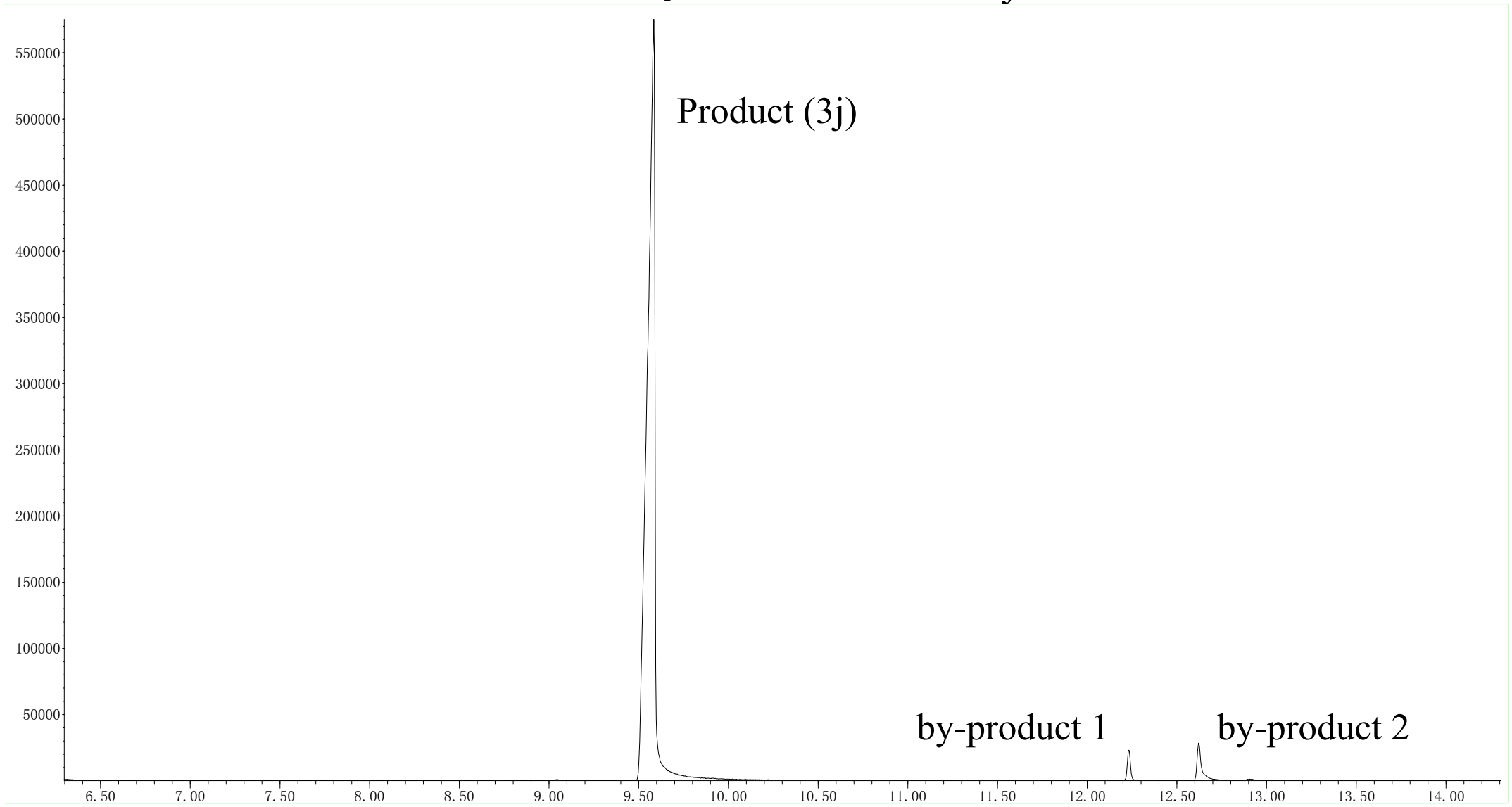
1i 2i 3i

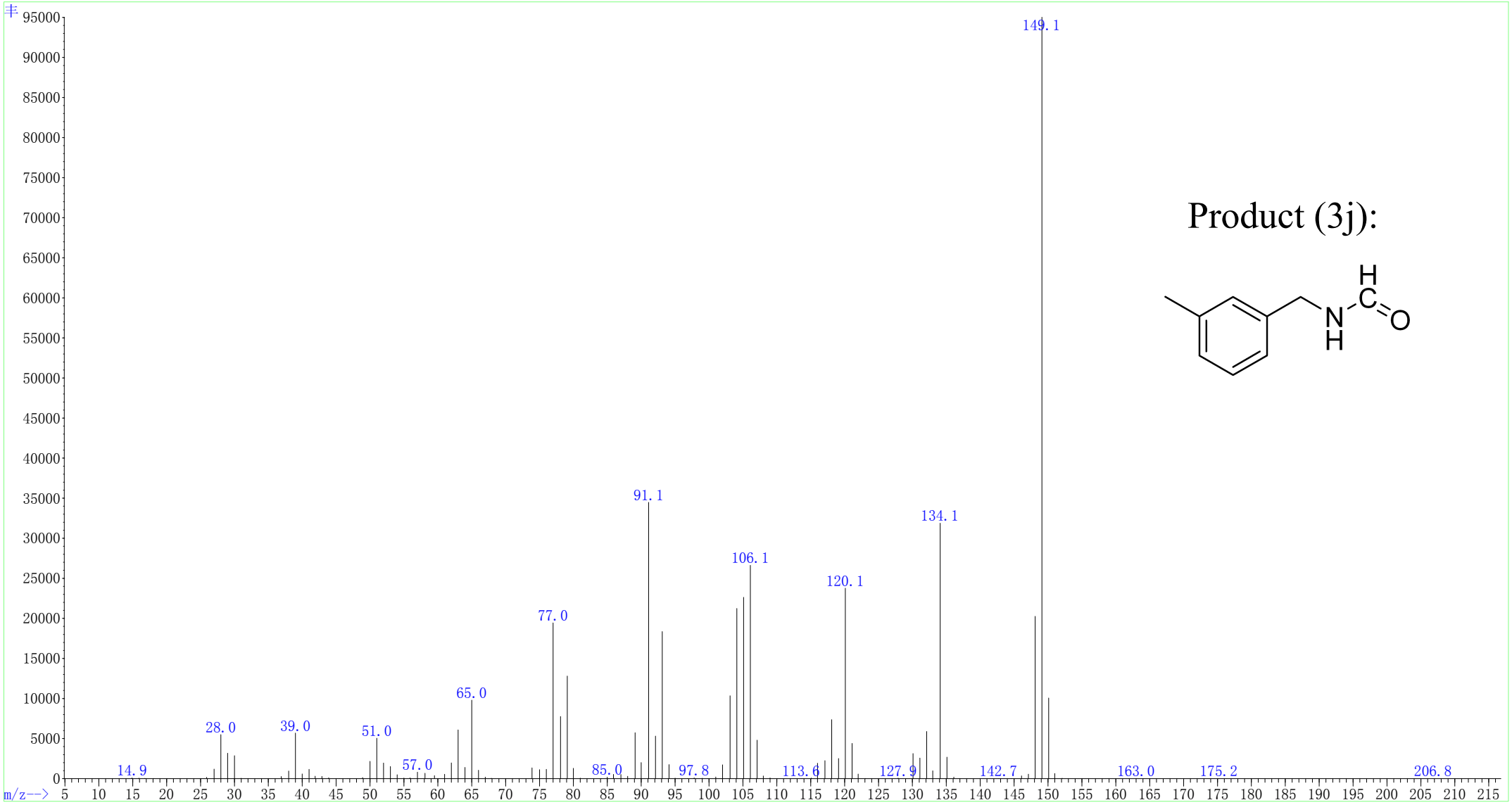


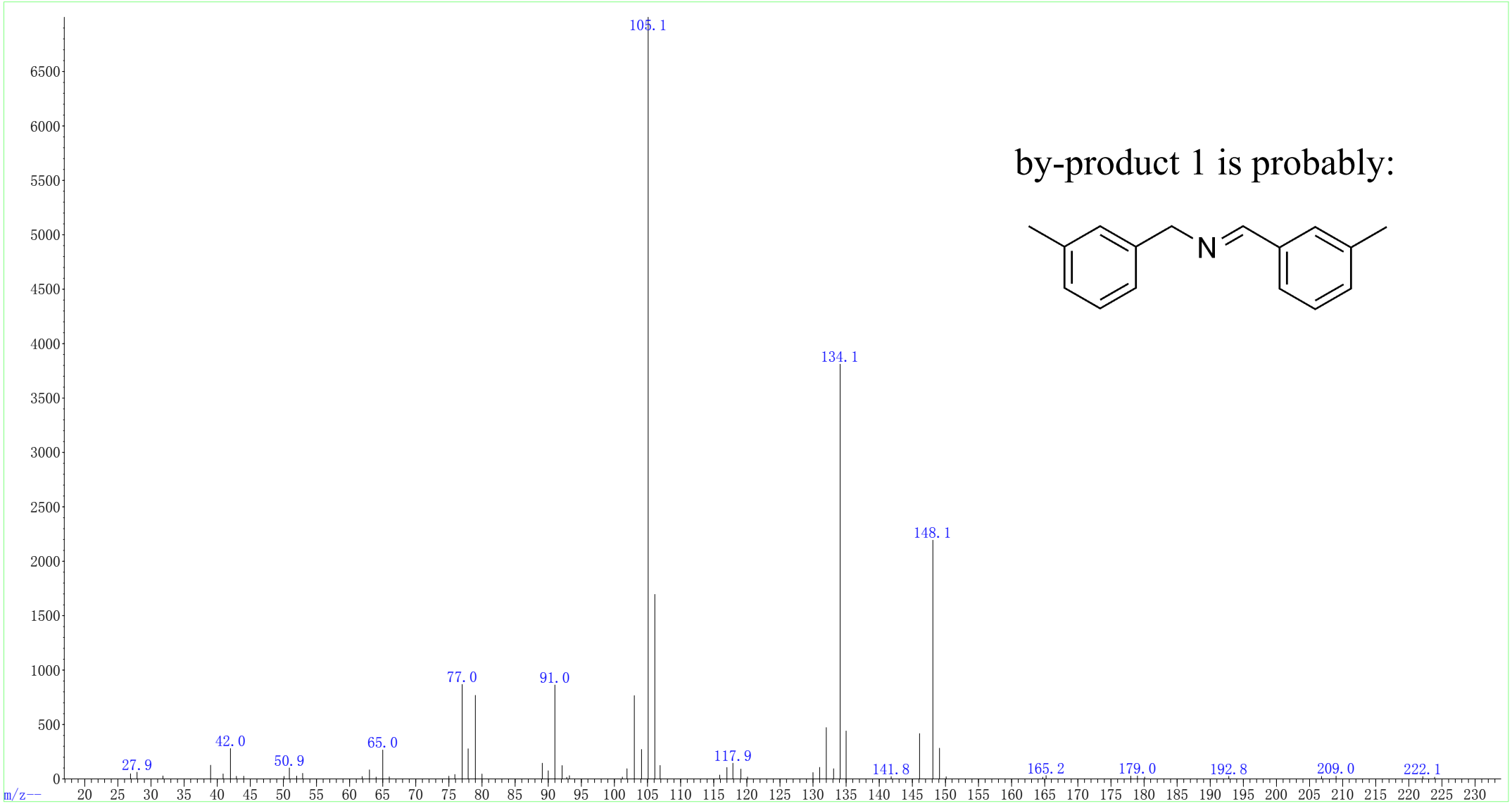

Product (3i):
HN−CH
O
149.1
106.1
134.1
79.1
51.0
42.0
28.0
120.1
91.1
63.0
72.0
18.0
85.0
98.0
113.7
127.7
143.4
160.9
206.8
m/z-->

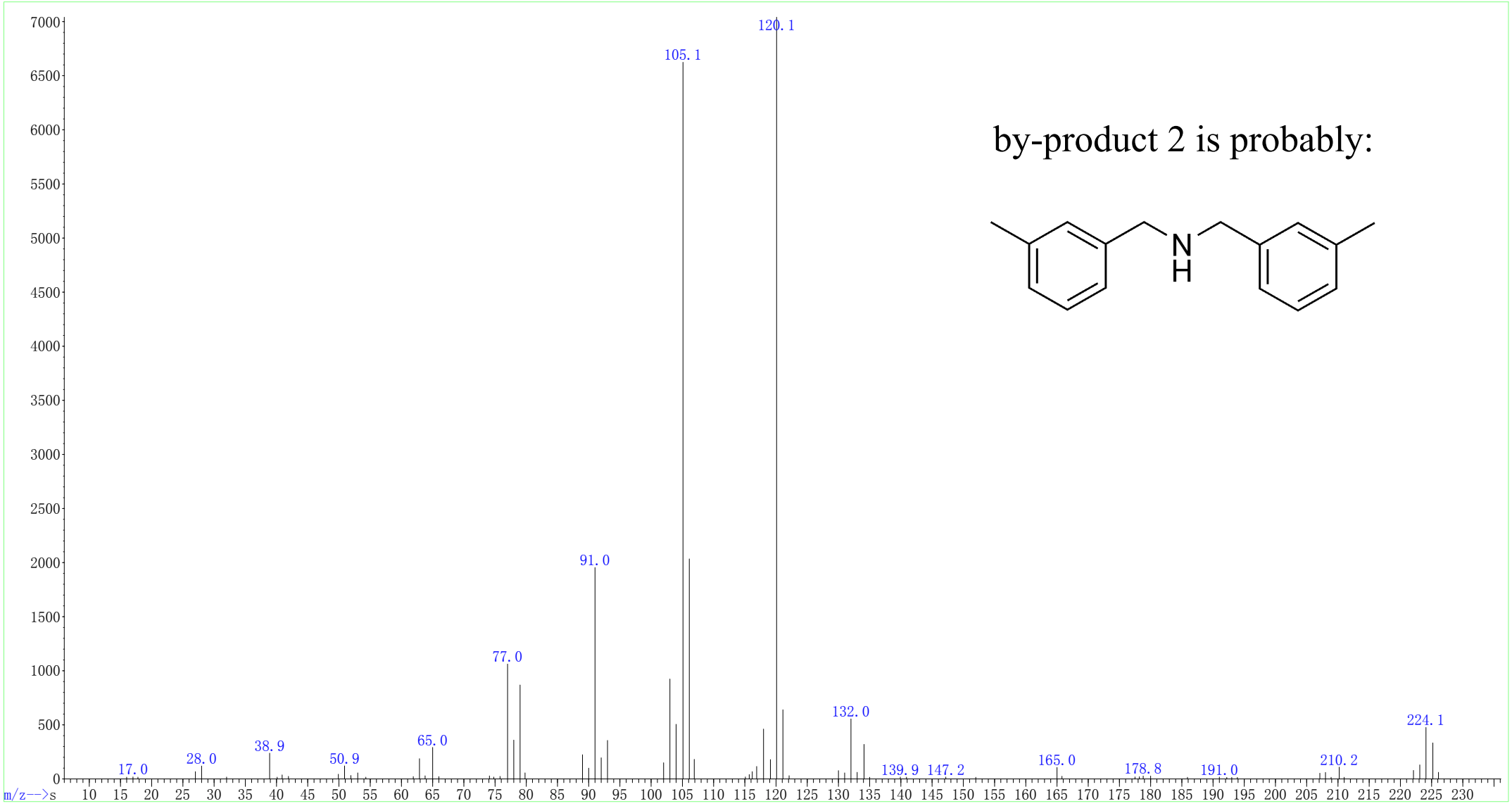


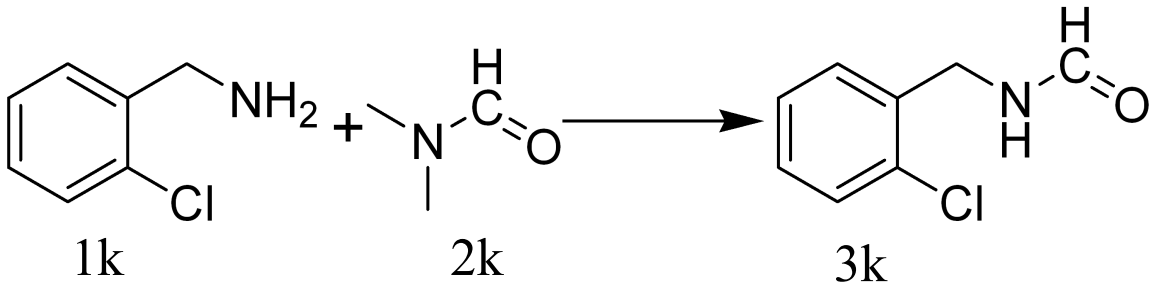
1j 2j 3j

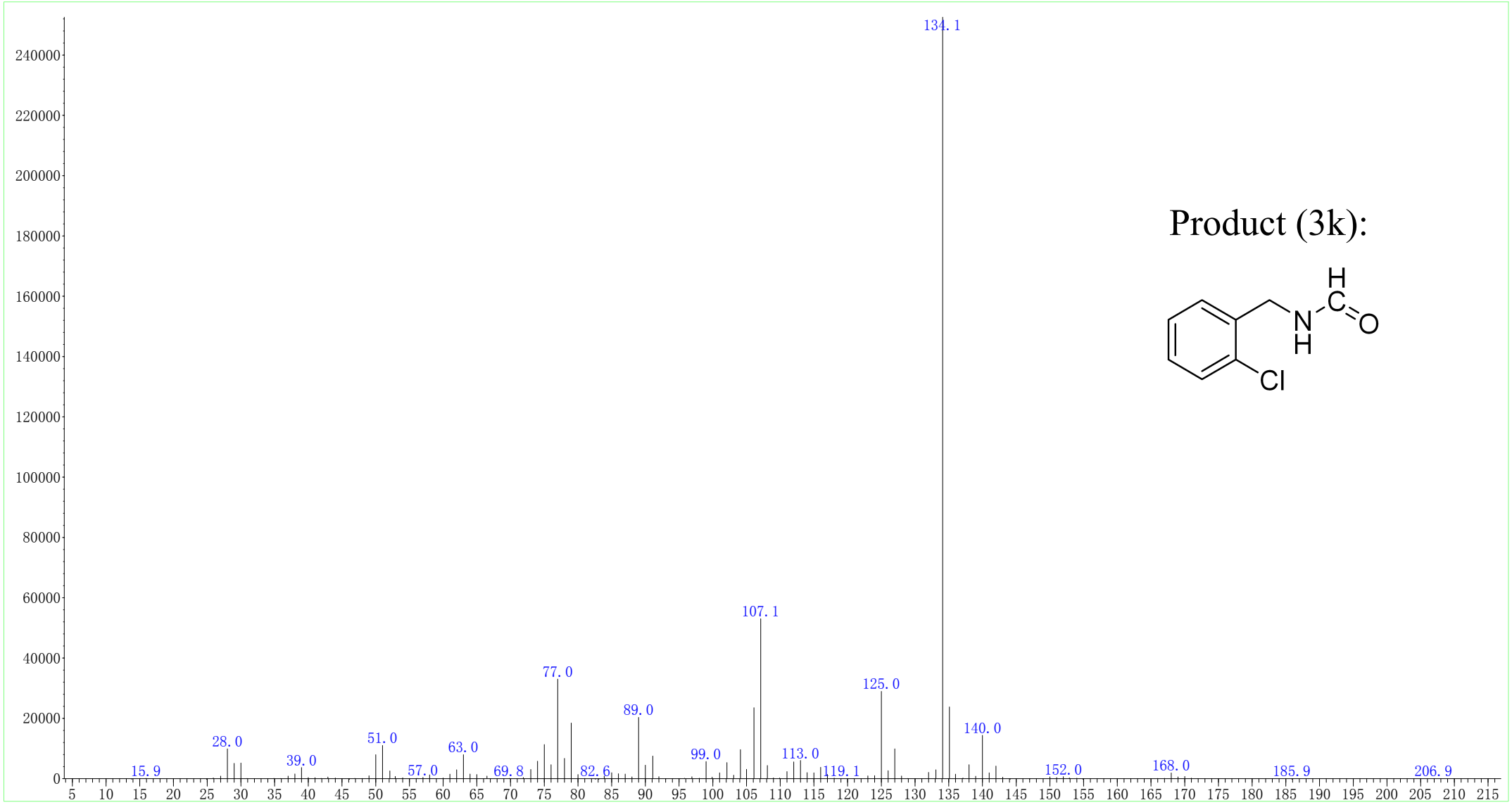


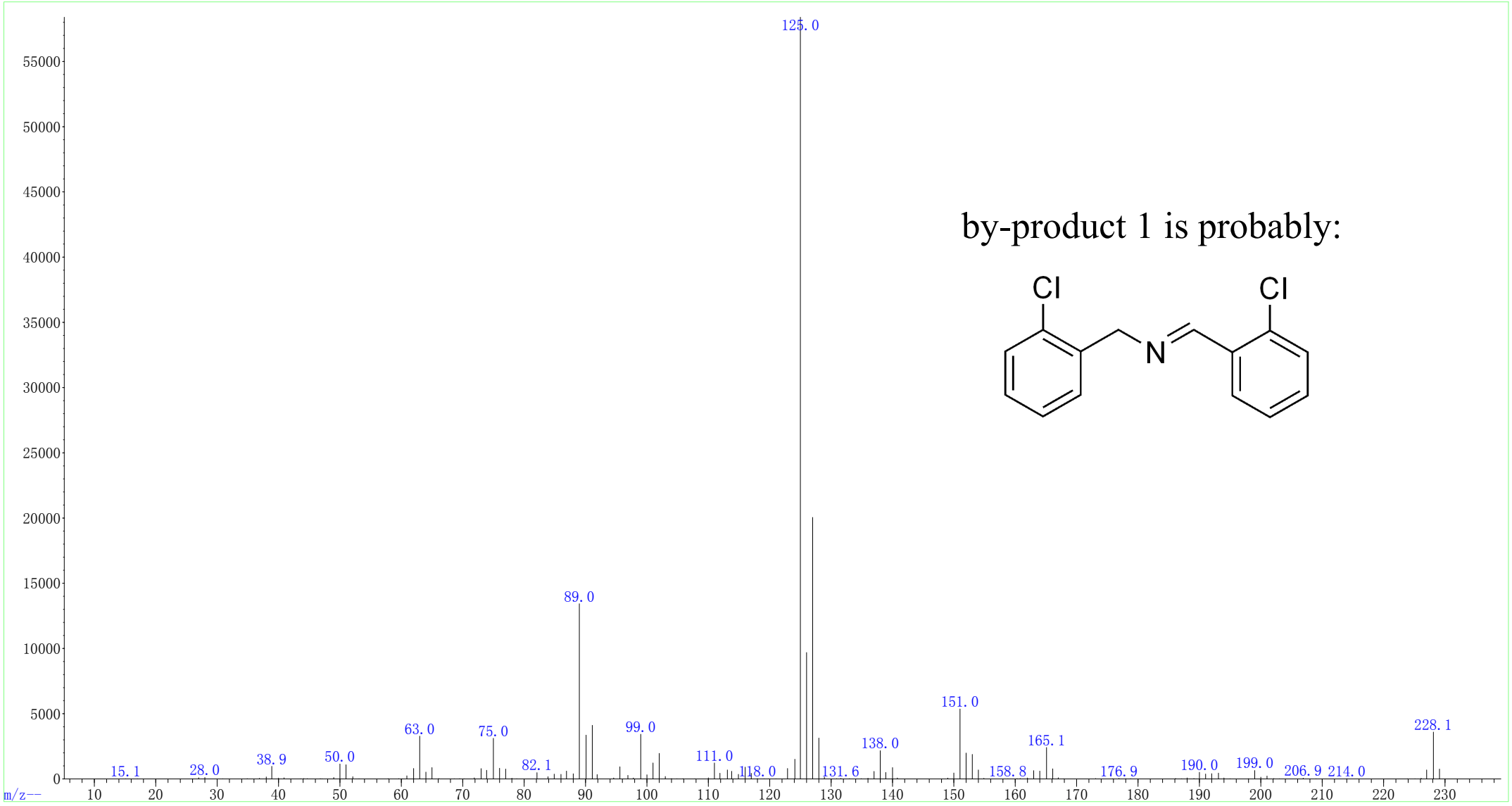


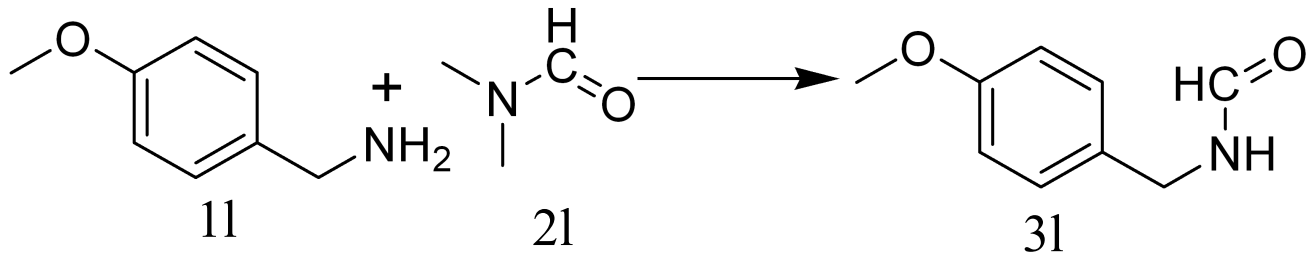

105.1
134.1
148.1
77.0
91.0
42.0
65.0
27.9
50.9
117.9
141.8
165.2
179.0
192.8
209.0
222.1
m/z--
by-product 1 is probably:
N



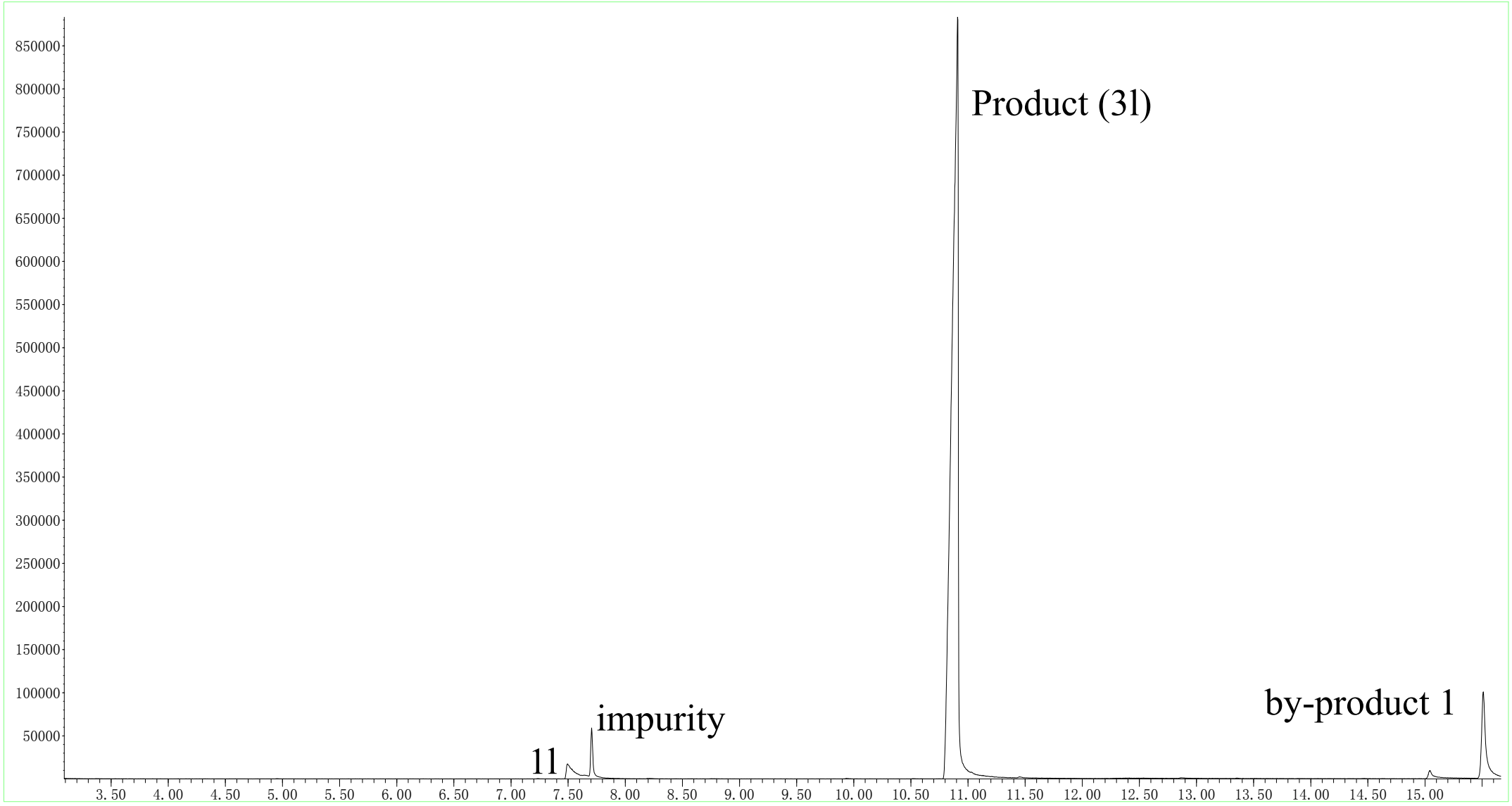



Product (3k):
134.1
107.1
77.0
125.0
89.0
140.0
28.0
51.0
63.0
39.0
99.0
113.0
15.9
57.0
69.8
82.6
119.1
152.0
168.0
185.9
206.9
H
C
O
N
H
Cl


125.0
89.0
151.0
138.0
99.0
63.0
75.0
165.1
228.1
38.9
50.0
82.1
111.0
118.0
131.6
158.8
176.9
190.0
199.0
206.9
214.0
15.1
28.0
m/z--
by-product 1 is probably:
Cl
Cl
N


O
NH2
H
C
N
O
O
HC
O
NH

11 21 31


Product (31)
impurity
11
by-product 1
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
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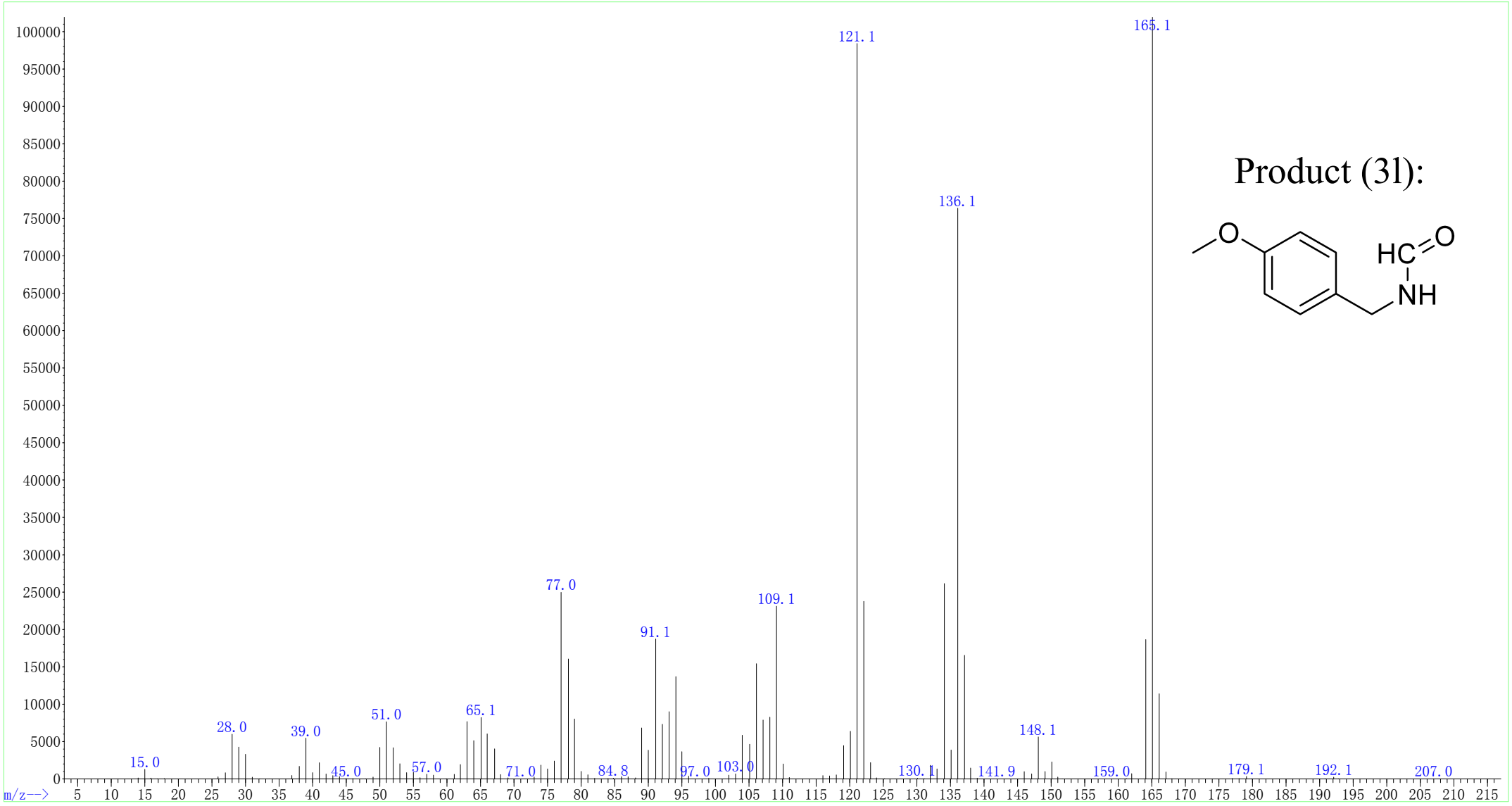
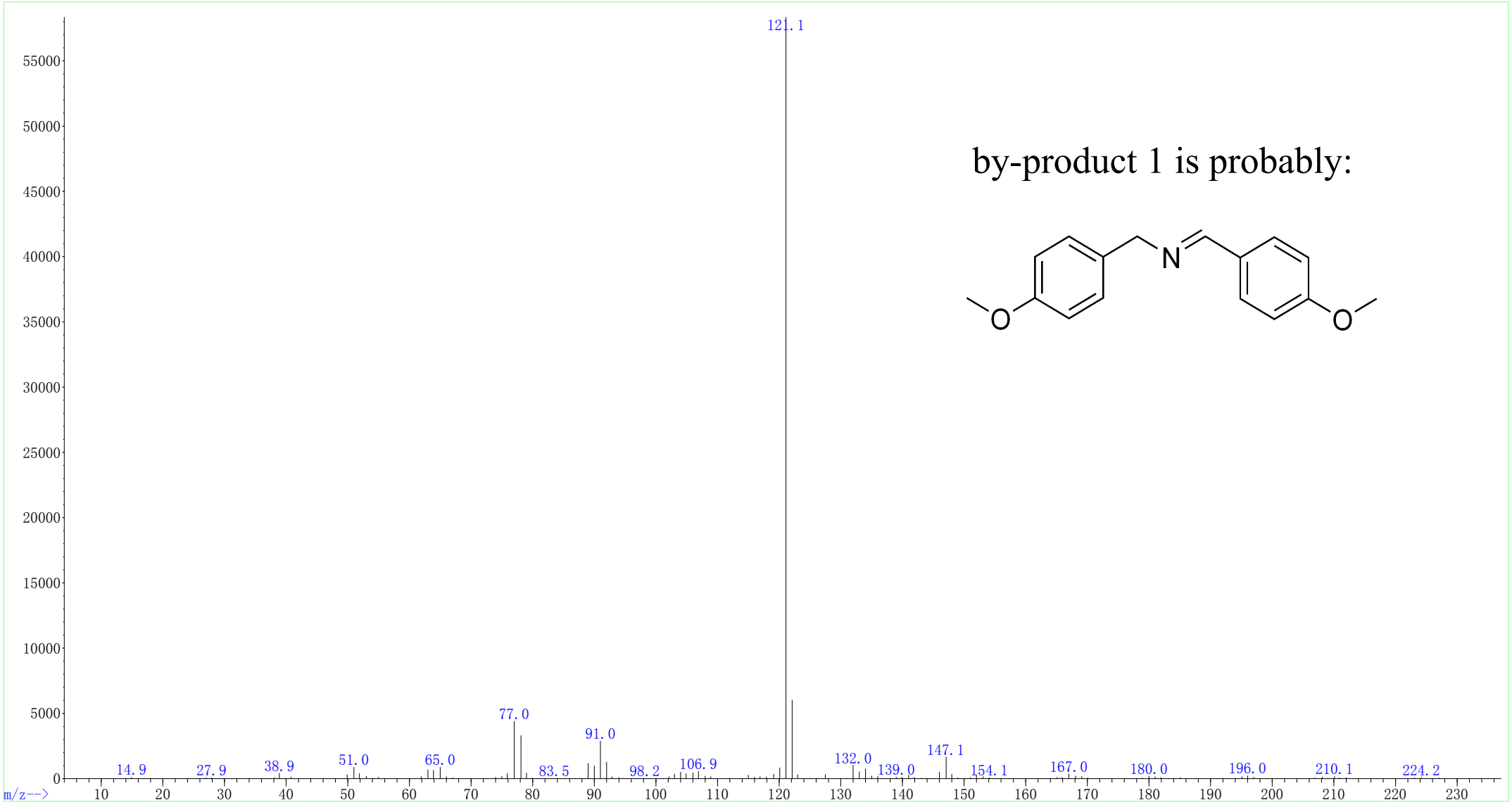
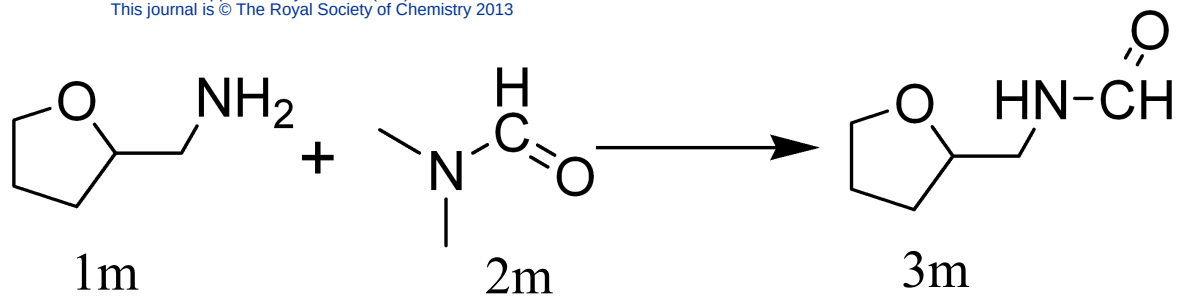
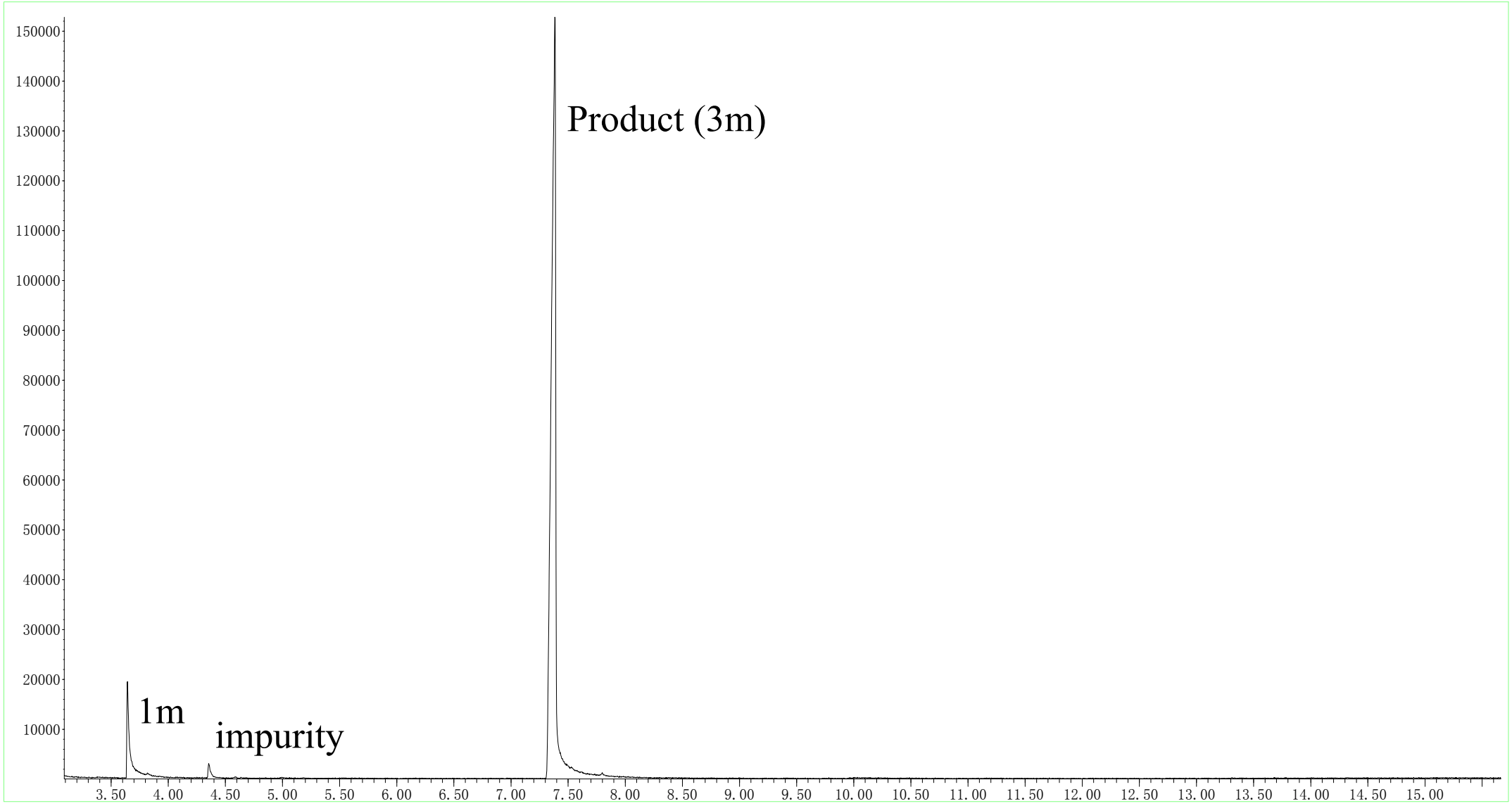
12.50
13.00
13.50
14.00
14.50
15.00




121.1
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
14.9
27.9
38.9
51.0
65.0
77.0
83.5
91.0
98.2
106.9
132.0
139.0
147.1
154.1
167.0
180.0
196.0
210.1
224.2
by-product 1 is probably:
N
O
O


O
NH2
H
C
N
O
O
HN−CH
O

1m 2m 3m


Product (3m)
1m
impurity
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
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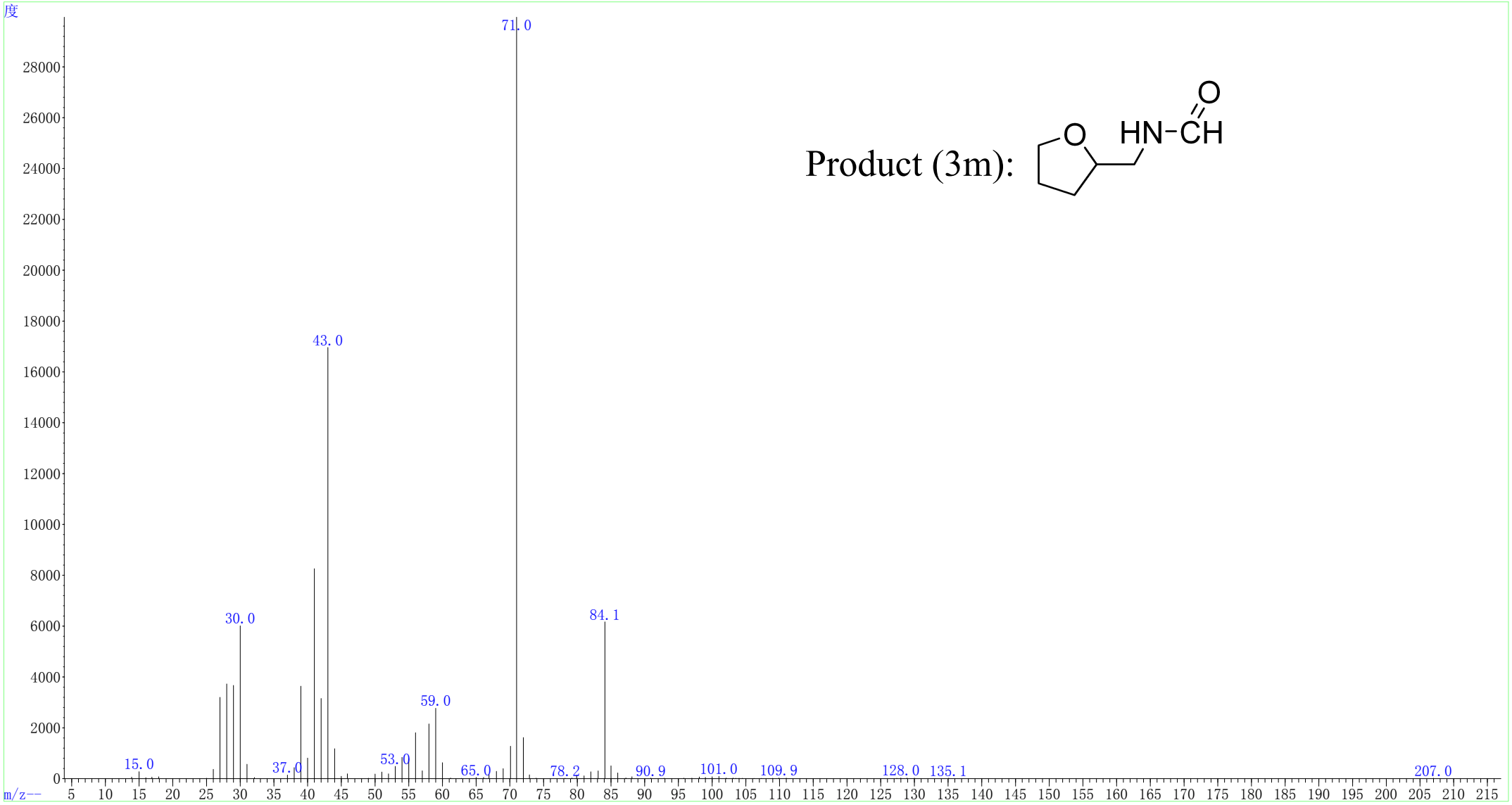
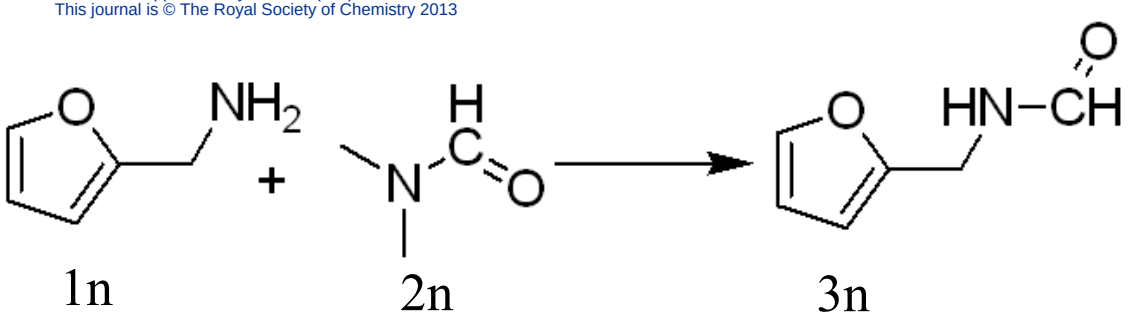
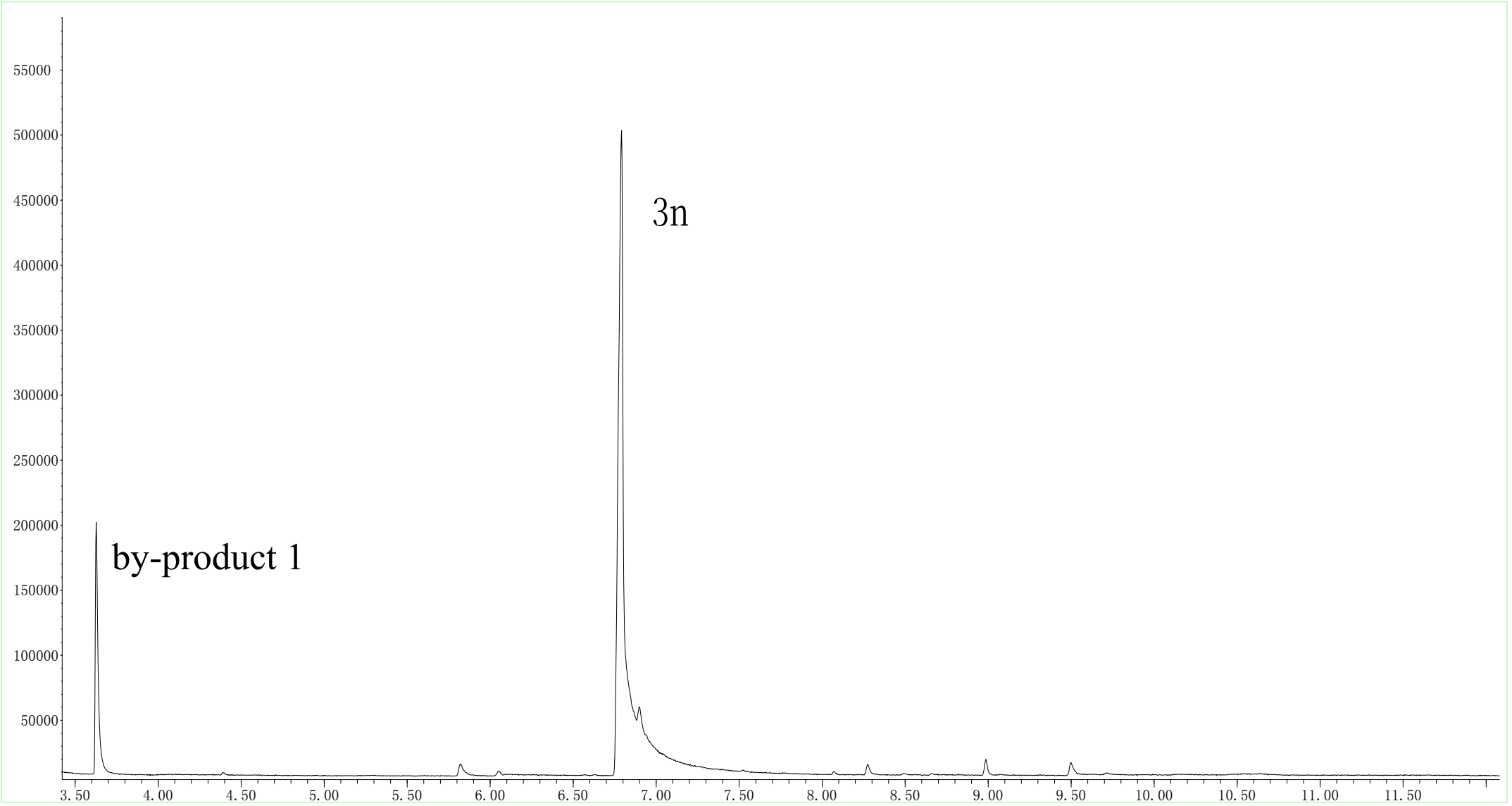
12.50
13.00
13.50
14.00
14.50
15.00


度
71.0
43.0
30.0
84.1
59.0
15.0
37.0
53.0
65.0
78.2
90.9
101.0
109.9
128.0
135.1
207.0
m/z--
Product (3m):
O
HN-CH
O


O
NH2
+
H
C
N
O
O
HN−CH
O

1n 2n 3n


55000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
3n
by-product 1
3.50
4.00
4.50
5.00
5.50
6.00
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7.50
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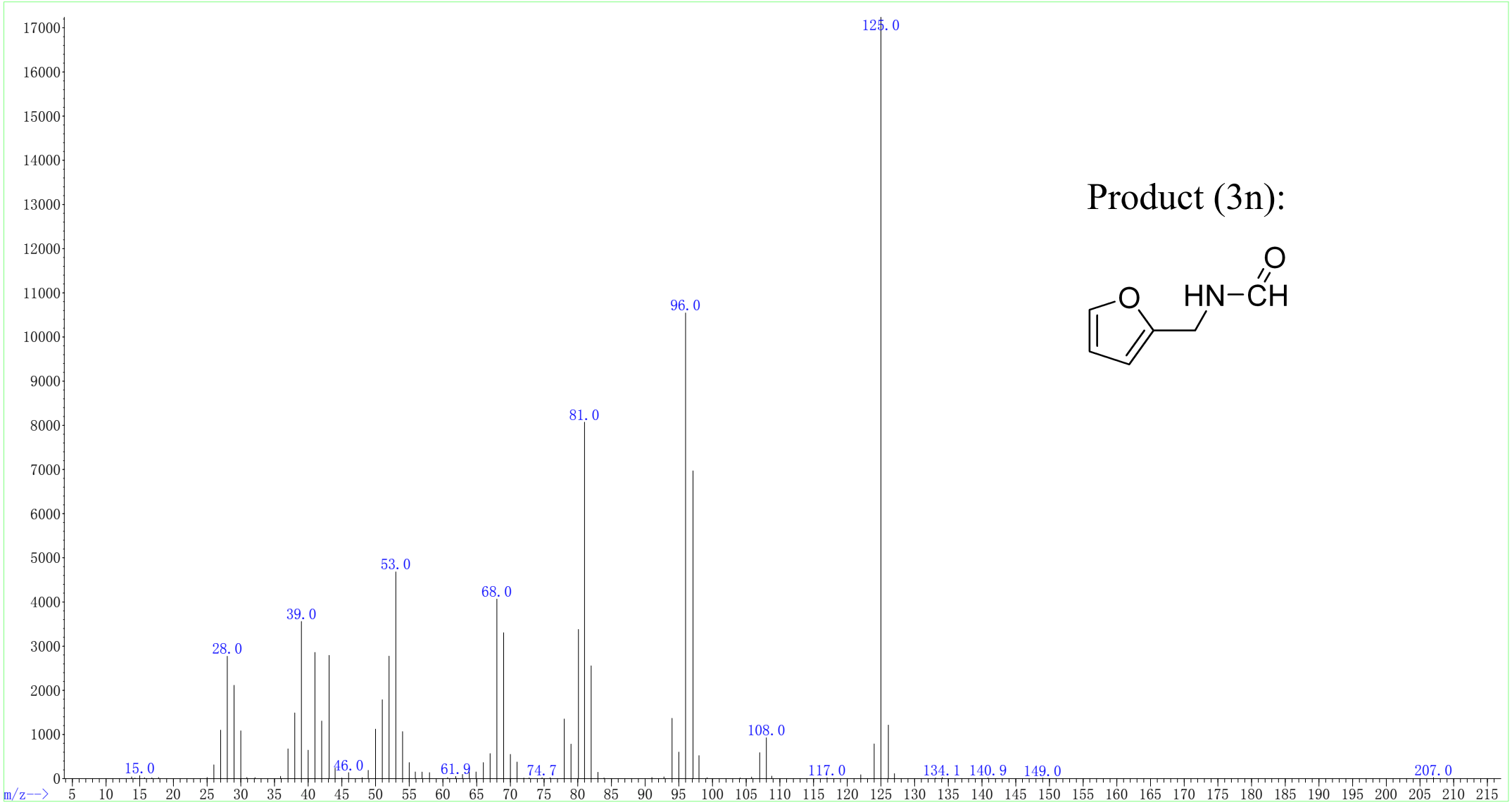
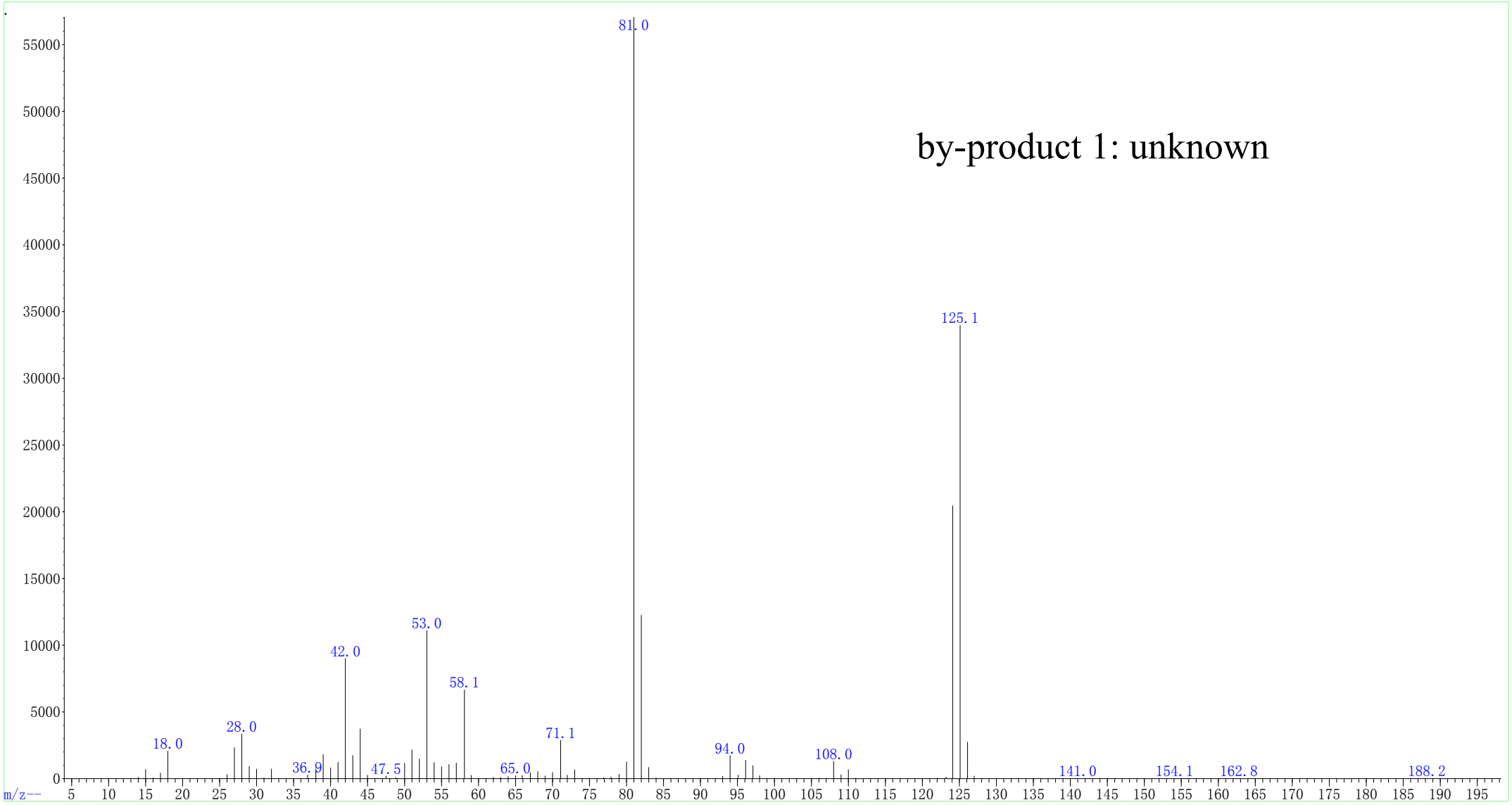
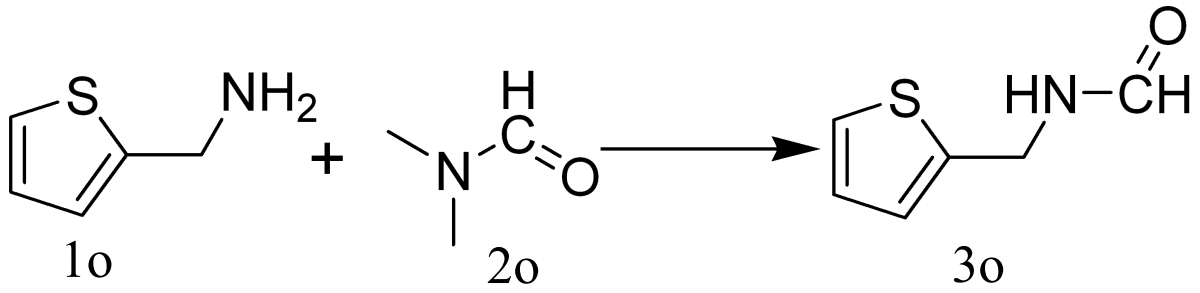
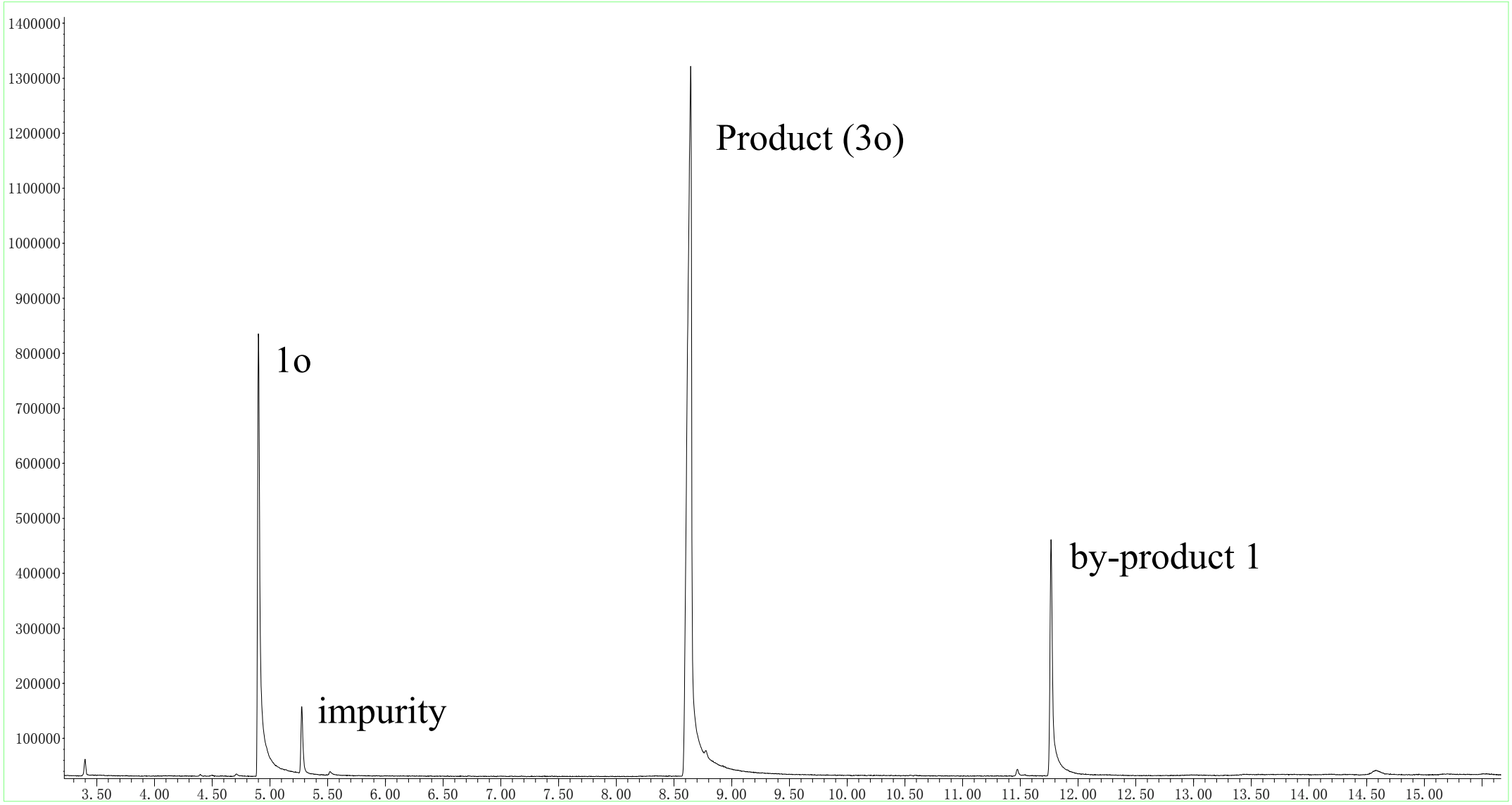
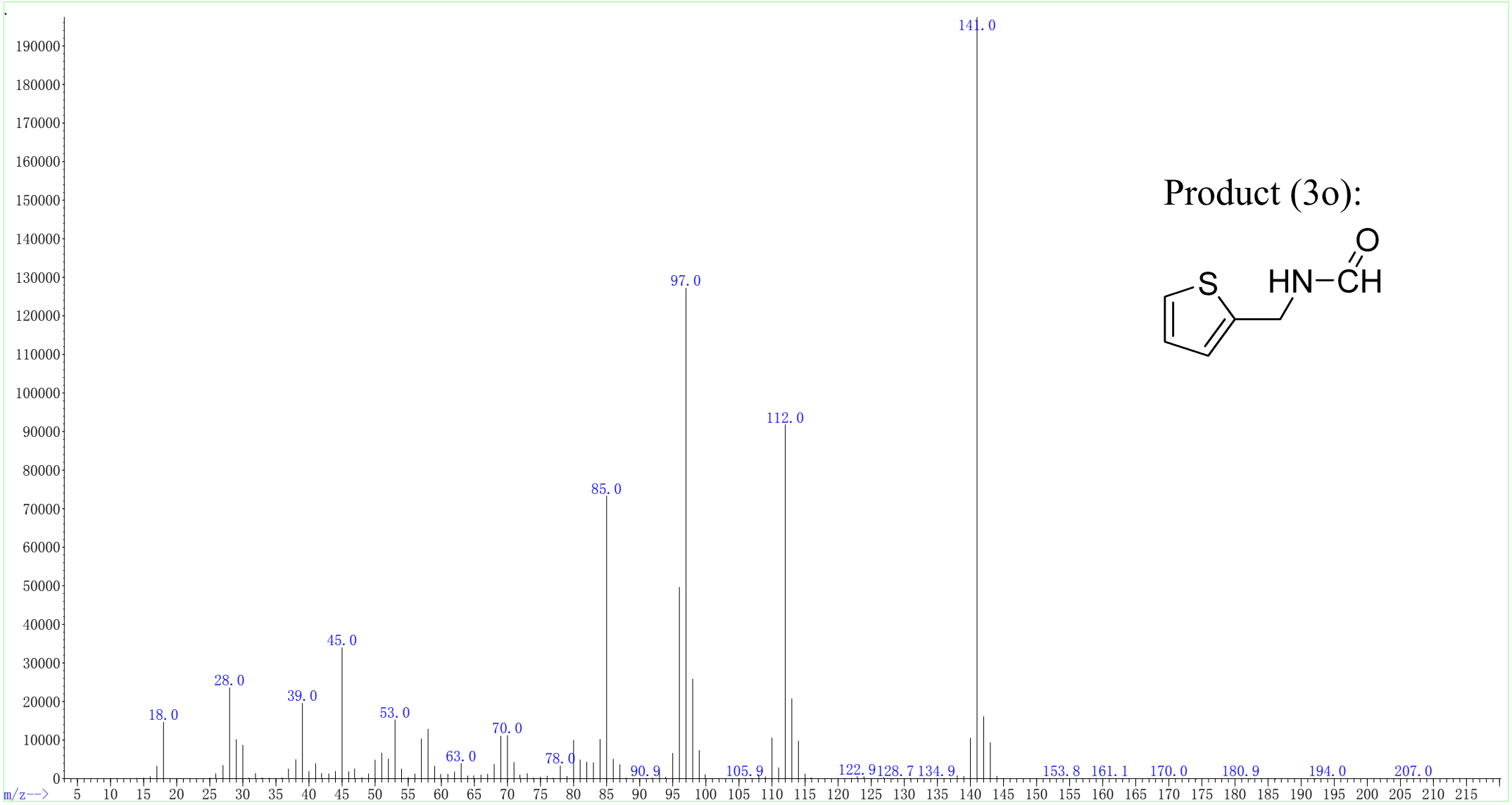
9.00
9.50
10.00
10.50
11.00
11.50

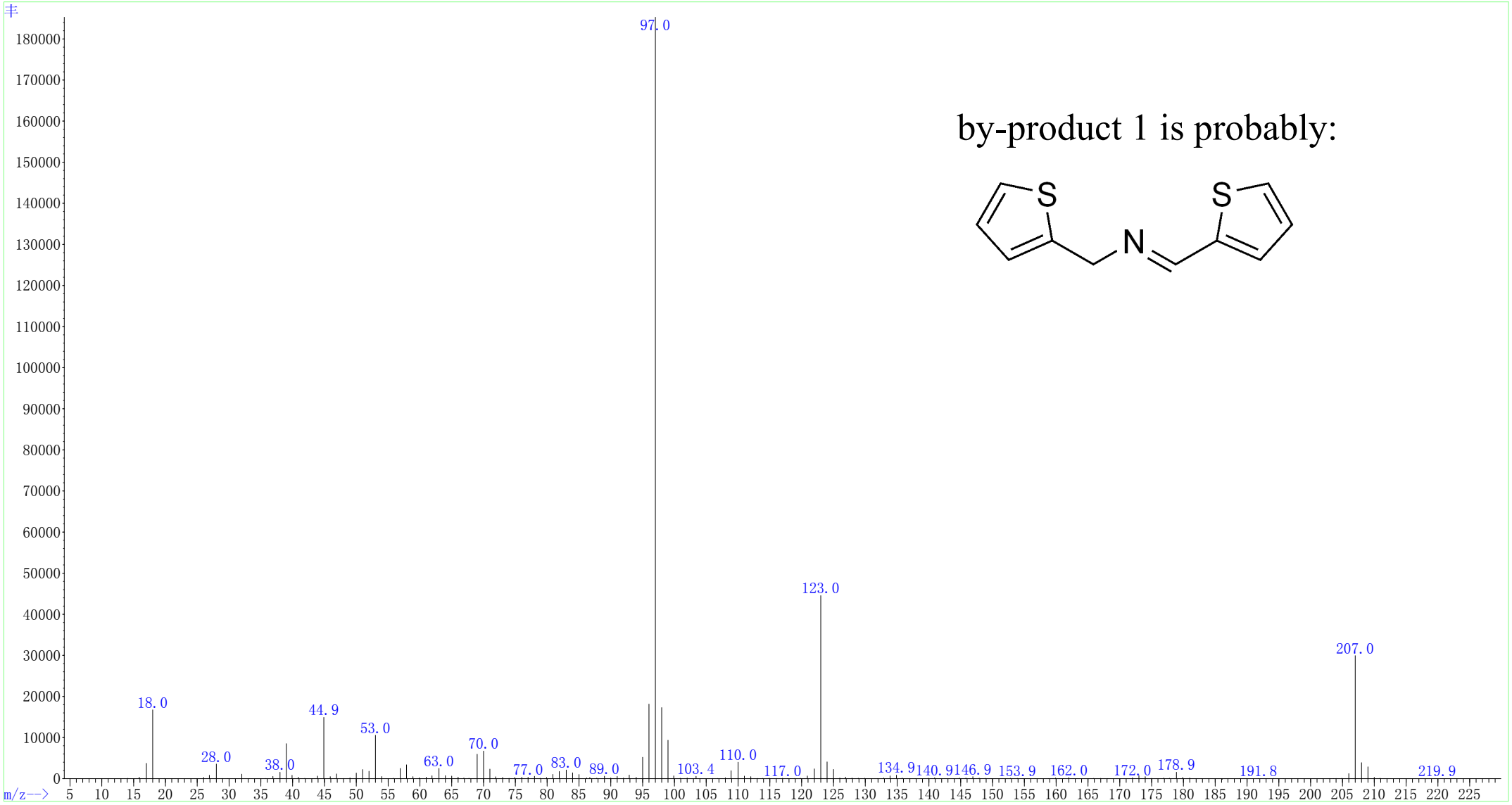

125.0
96.0
81.0
53.0
68.0
39.0
28.0
15.0
46.0
61.9
74.7
108.0
117.0
134.1
140.9
149.0
207.0
m/z-->
Product (3n):
O
HN−CH
O



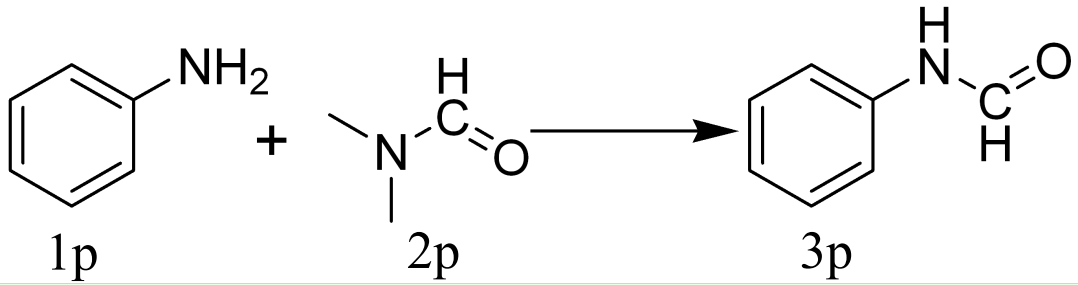




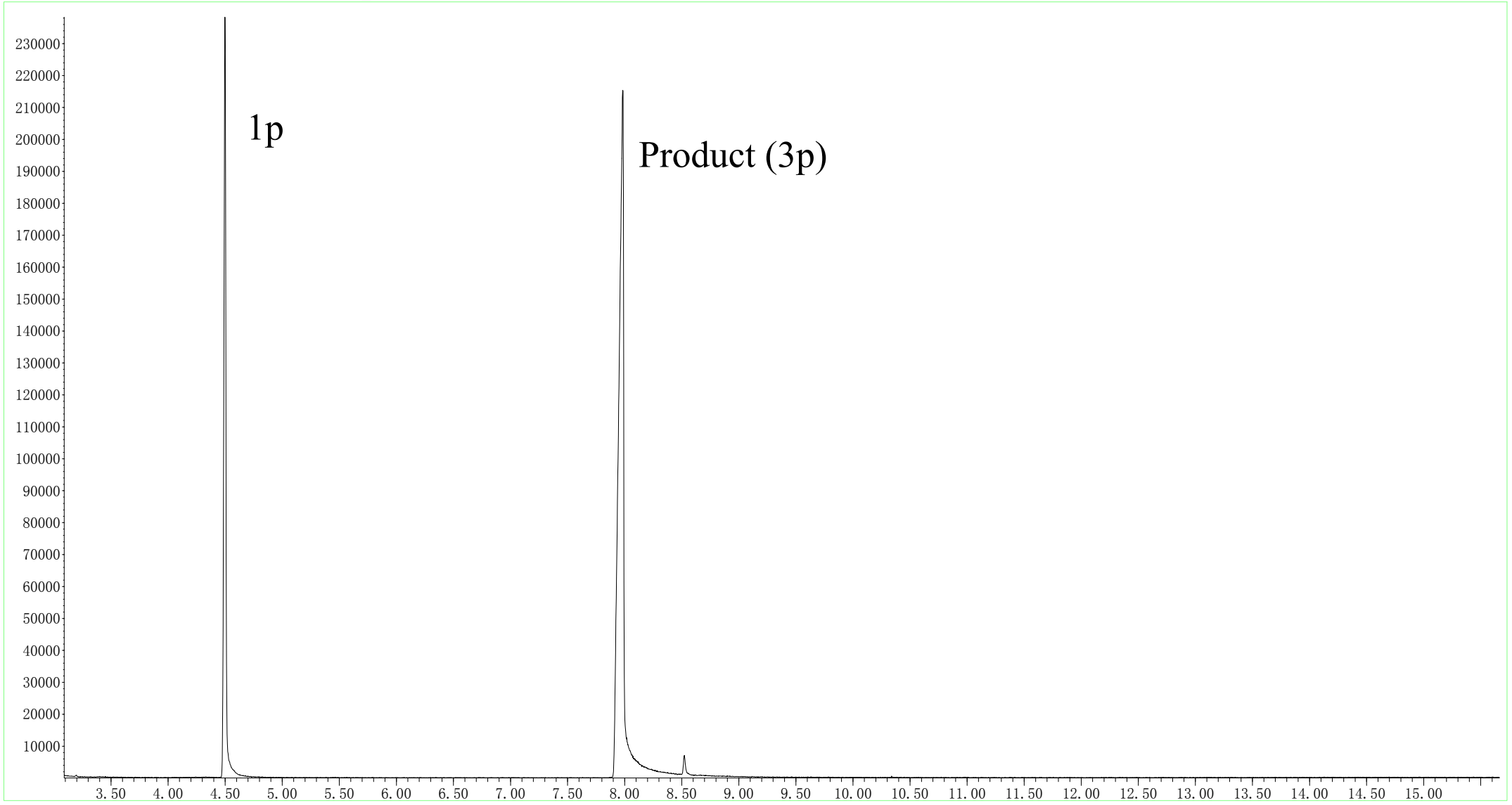




by-product 1 is probably:


NH2
H
C
N
O
H
N
C
O
H

1p + 2p → 3p


1p
Product (3p)
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
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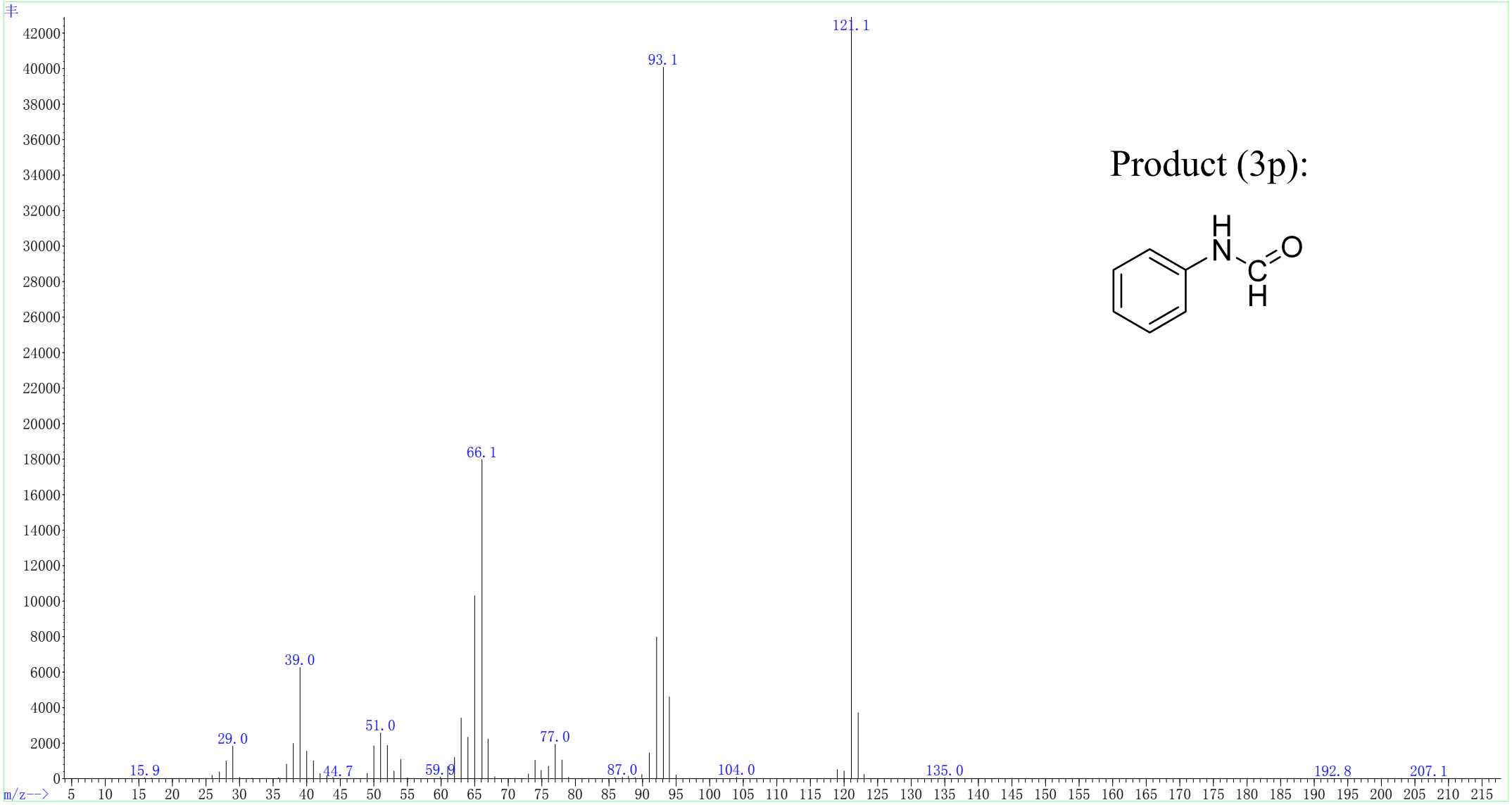
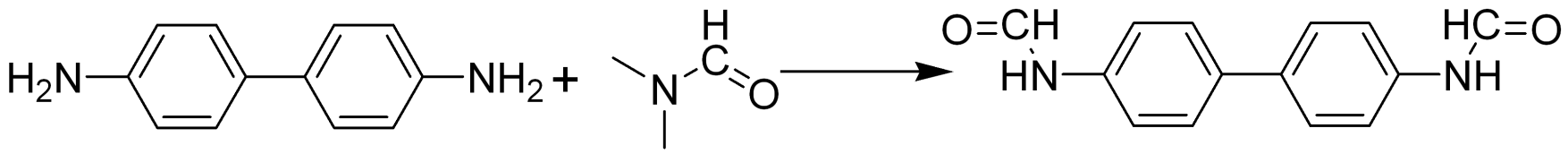
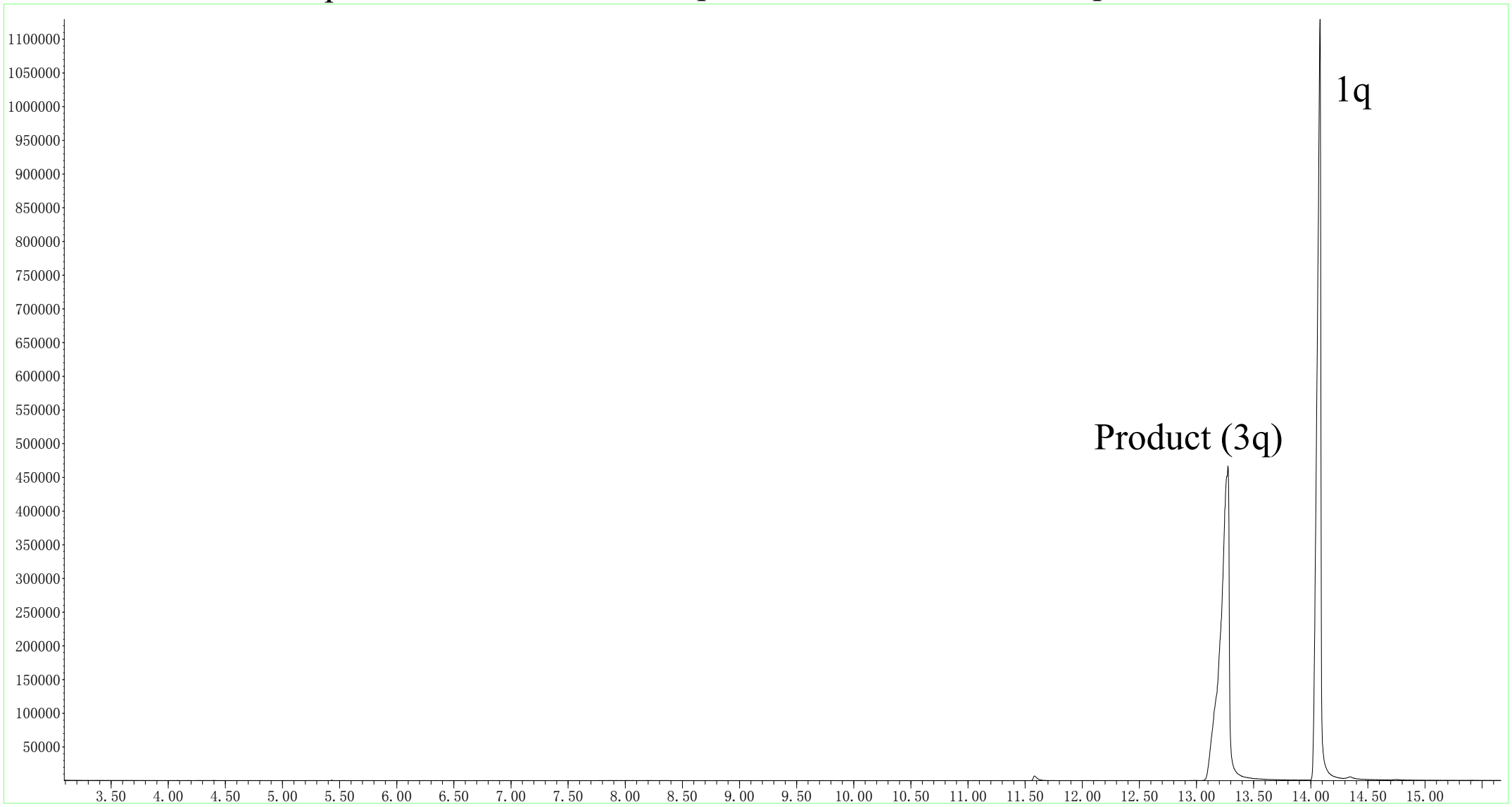
12.50
13.00
13.50
14.00
14.50
15.00


121.1
93.1
66.1
39.0
29.0
51.0
77.0
15.9
44.7
59.9
87.0
104.0
135.0
192.8
207.1
m/z-->
Product (3p):
H
N
C
O
H


H2N
NH2 +
H
C
N
O
O=CH
HN
HC=O
NH

1q 2q 3q


1100000
1050000
1000000
950000
900000
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
1q
Product (3q)
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
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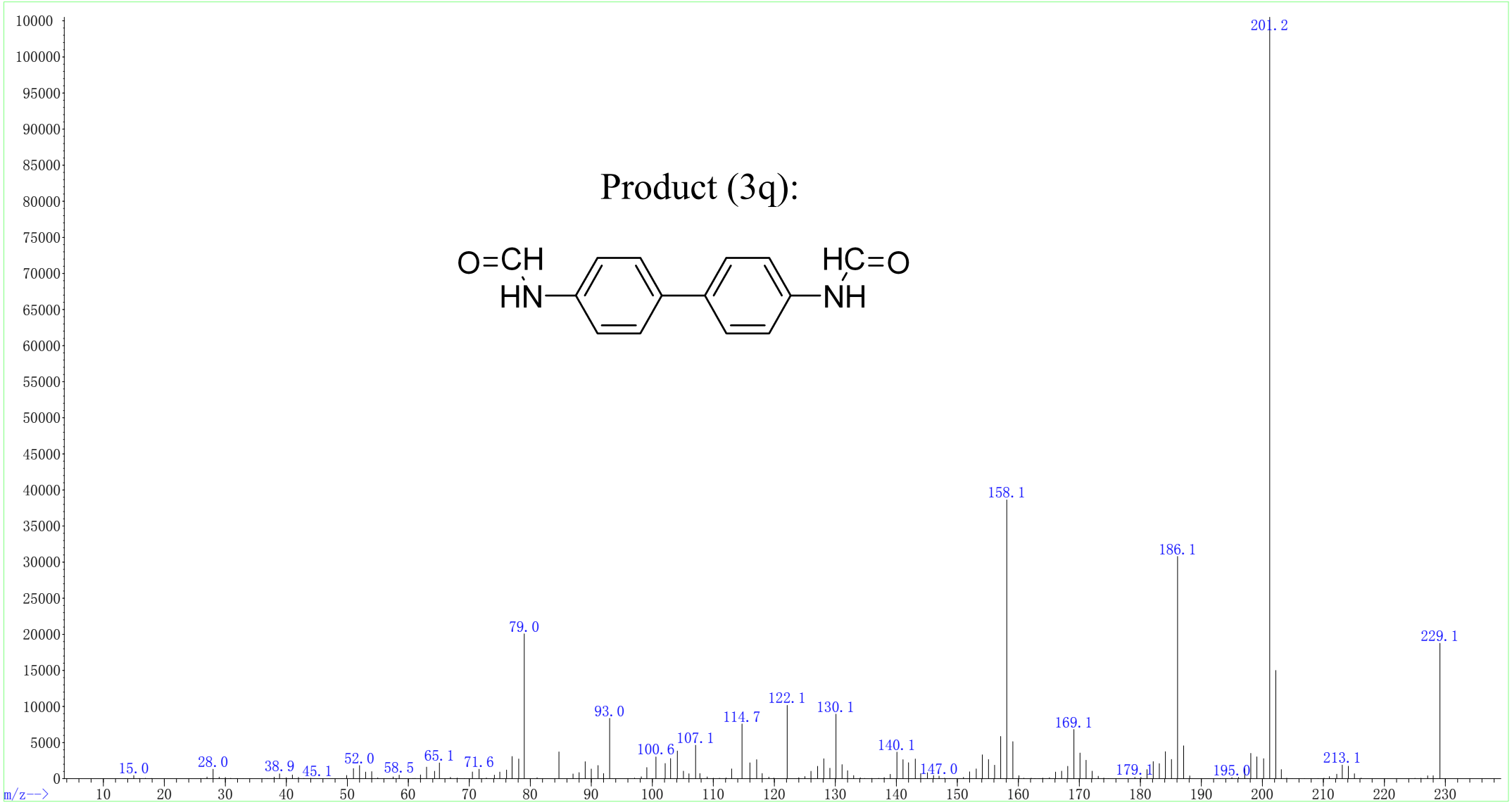
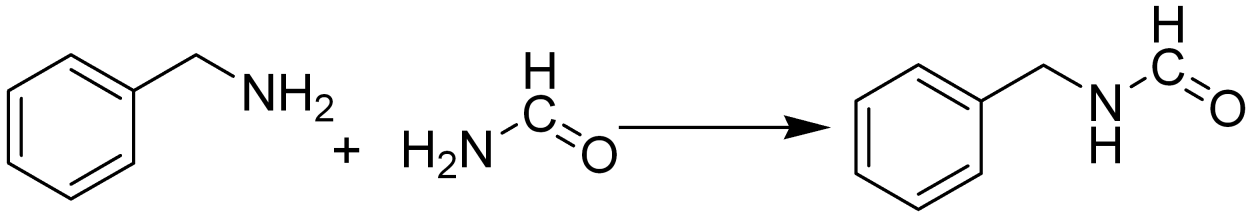
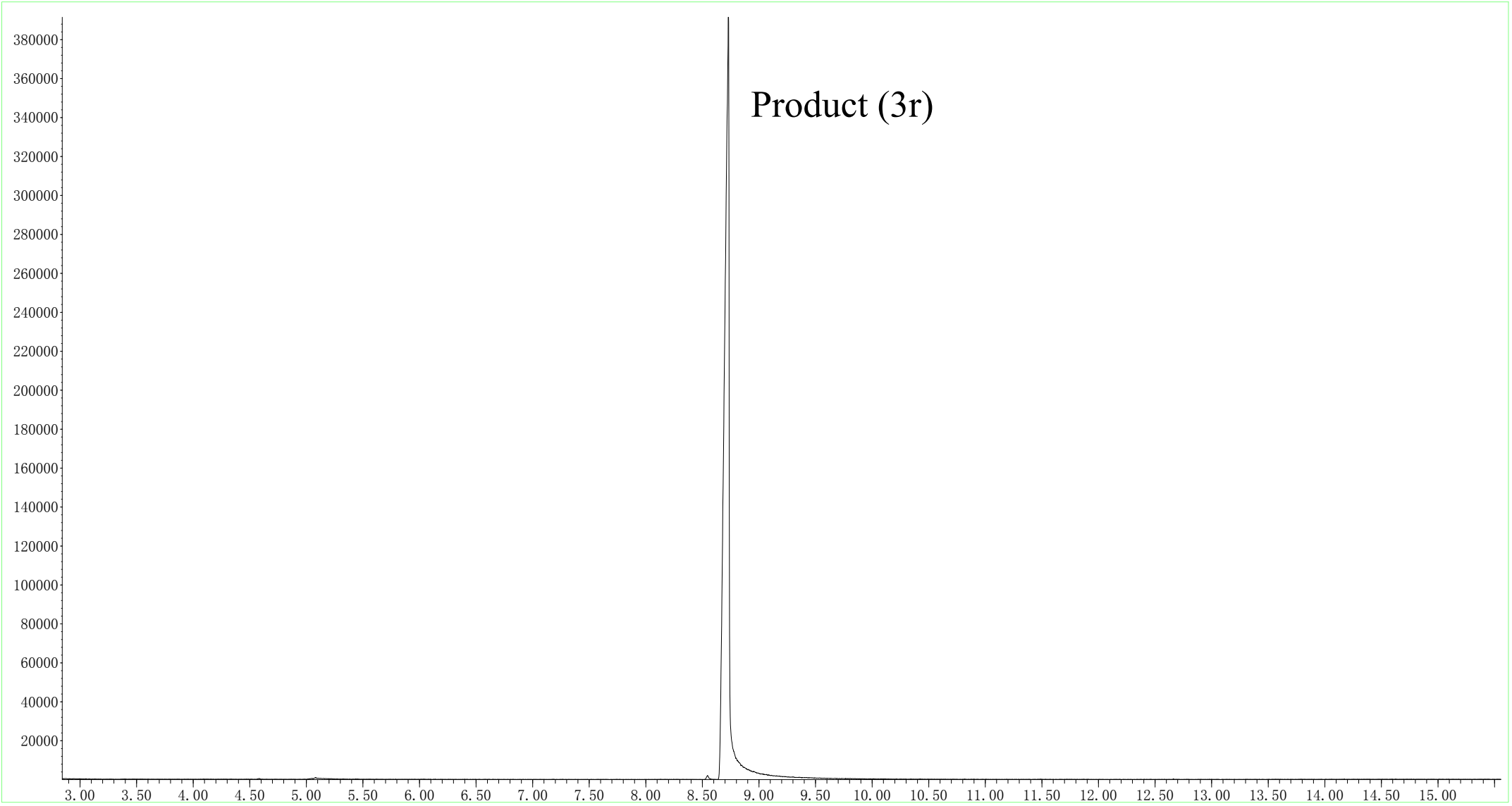
12.50
13.00
13.50
14.00
14.50
15.00

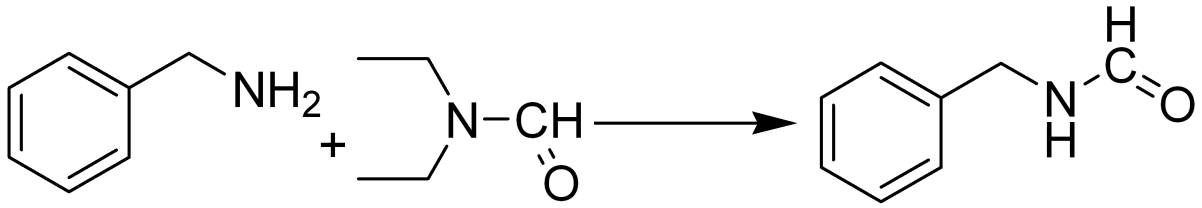

Product (3q):
O=CH
HN
HC=O
NH
201.2
158.1
186.1
79.0
229.1
93.0
122.1
130.1
114.7
169.1
107.1
100.6
140.1
65.1
71.6
52.0
58.5
38.9
45.1
28.0
15.0
147.0
179.1
195.0
213.1
m/z-->


NH2
+
H2N
H
C
O
N
H
H
C
O

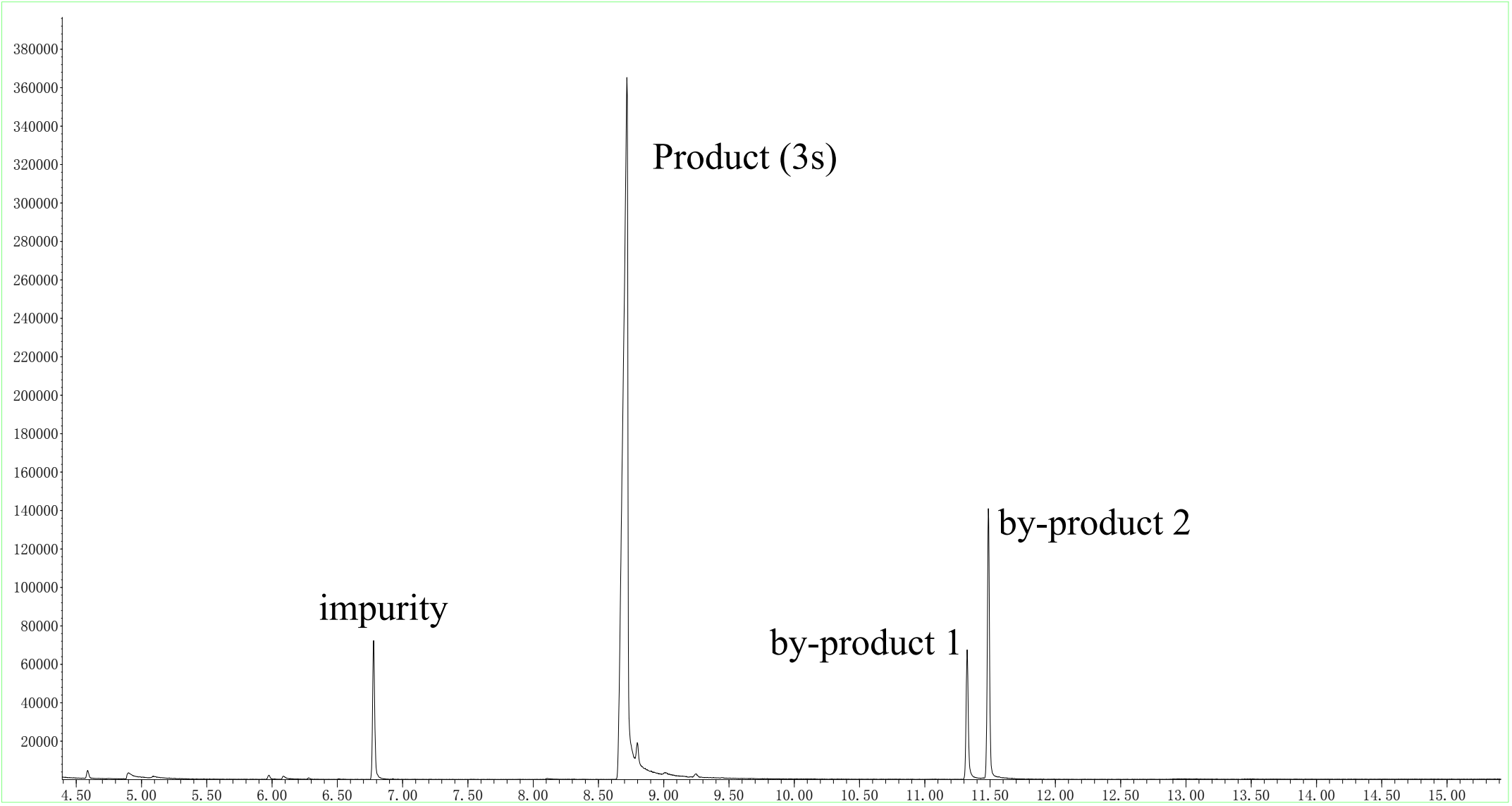
1r 2r 3r


Product (3r)
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
10.00
10.50
11.00
11.50
12.00
12.50
13.00
13.50
14.00
14.50
15.00


Product (3r):
135.1
91.1
106.1
79.1
51.0
28.0
65.0
39.0
118.1
16.0
45.1
57.0
73.0
85.0
98.9
149.0
157.1
207.1
m/z-->


NH2
N
CH
O
H
C
O
N
H

1s 2s 3s


Product (3s)
impurity
by-product 1
by-product 2
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
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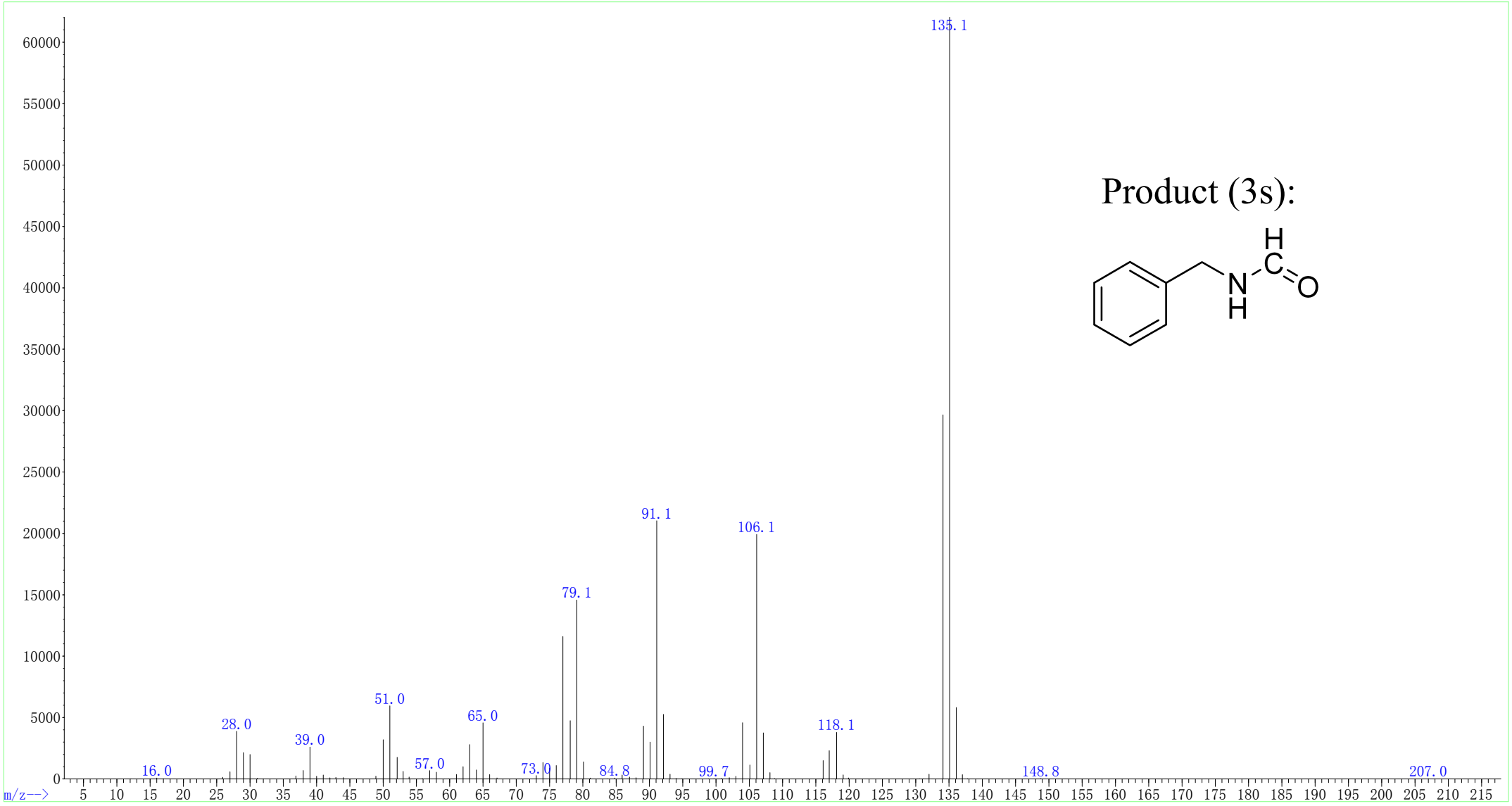
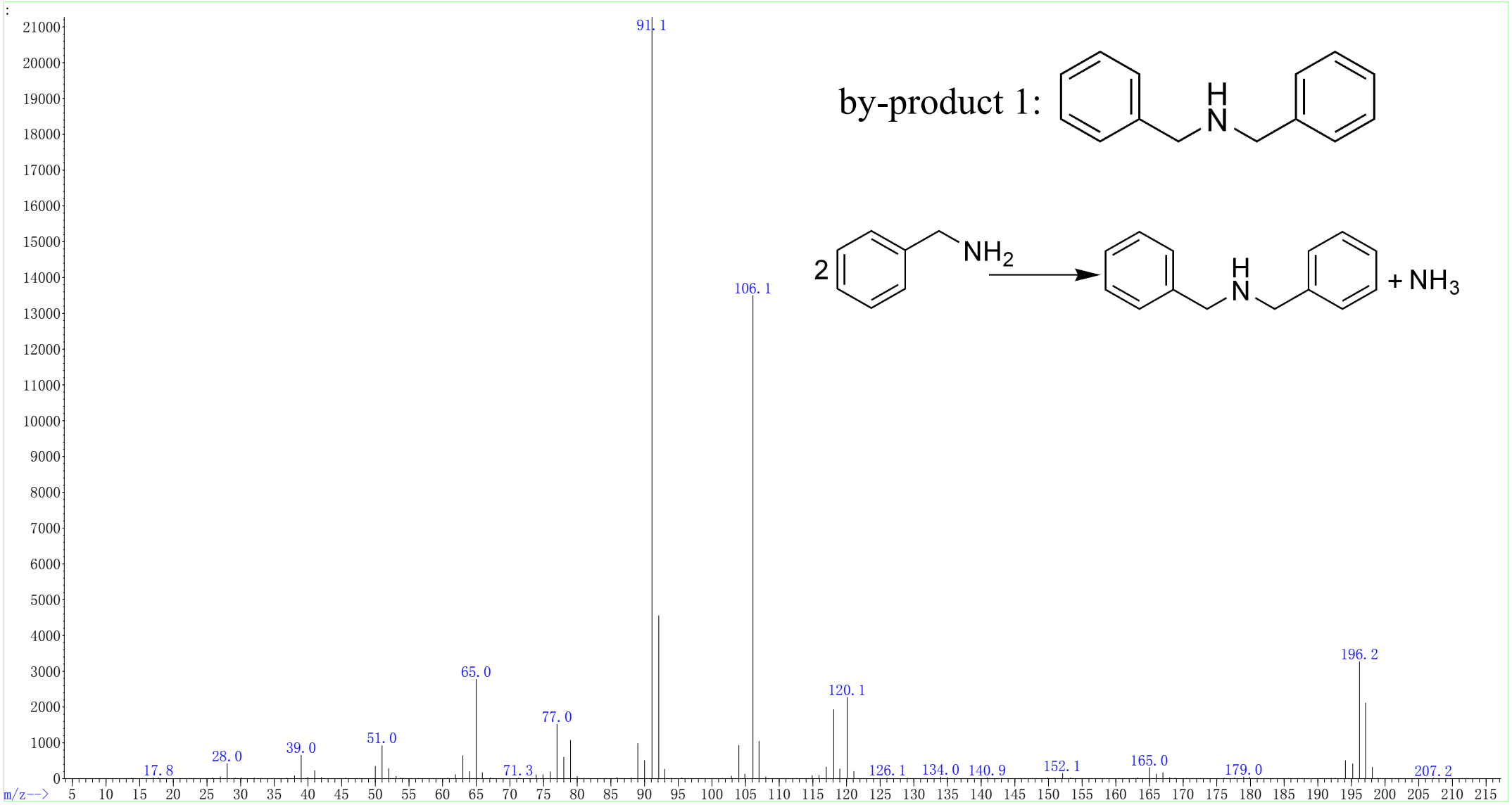
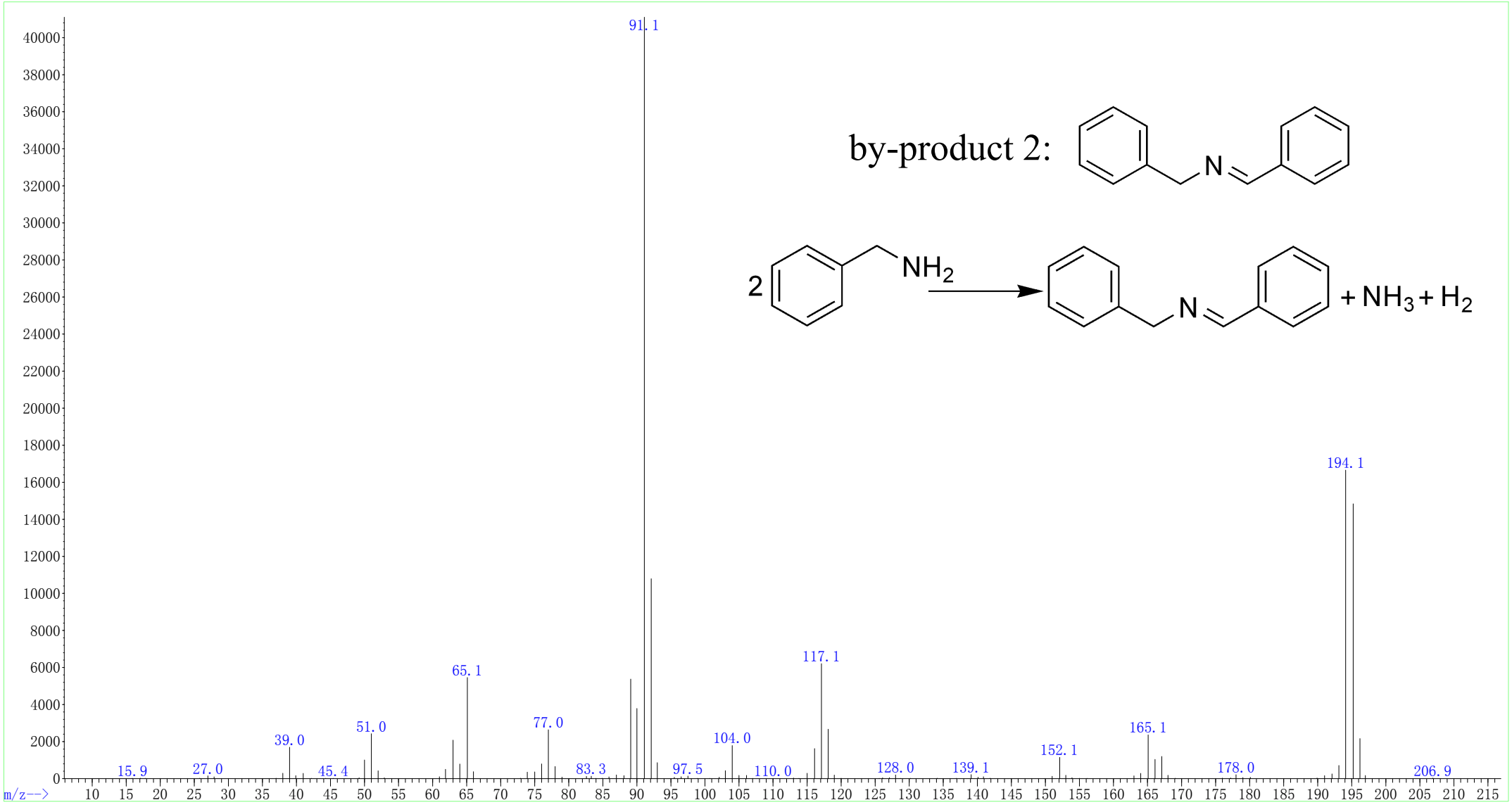
12.50
13.00
13.50
14.00
14.50
15.00


Product (3s):
H
C
O
N
H
135.1
91.1
106.1
79.1
51.0
65.0
28.0
39.0
57.0
16.0
73.0
84.8
99.7
118.1
148.8
207.0
m/z-->




91.1
194.1
117.1
65.1
77.0
39.0
51.0
104.0
165.1
152.1
15.9
27.0
45.4
83.3
97.5
110.0
128.0
139.1
178.0
206.9
m/z-->
by-product 2:
2
NH2
N
+ NH3 + H2