

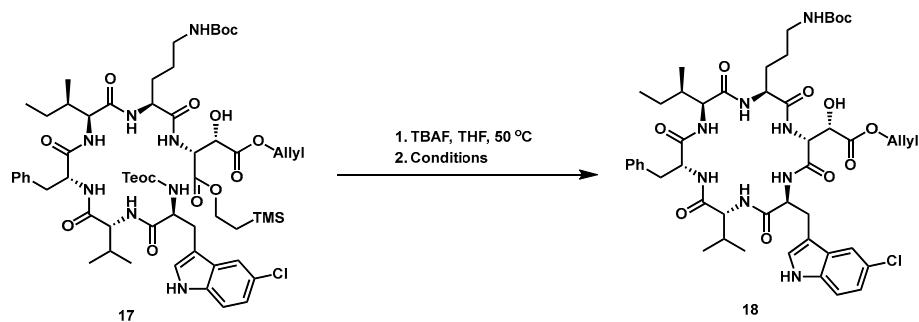
## *Supplementary Information*

### Table of Contents:

1. Optimization of Macrocyclization.	S2
2. Synthetic Schemes of Compounds <b>19</b> , <b>20</b> , <b>22</b> , <b>24</b> .	S3
3. NMR Data Comparison between Natural Noursamycin A and Synthetic Sample <b>1</b> .	S4
4. NMR Data Comparison between Natural Nicrophorusamide A and Synthetic Sample <b>25</b> .	S7
5. NMR Spectra.	S10
6. References.	S30

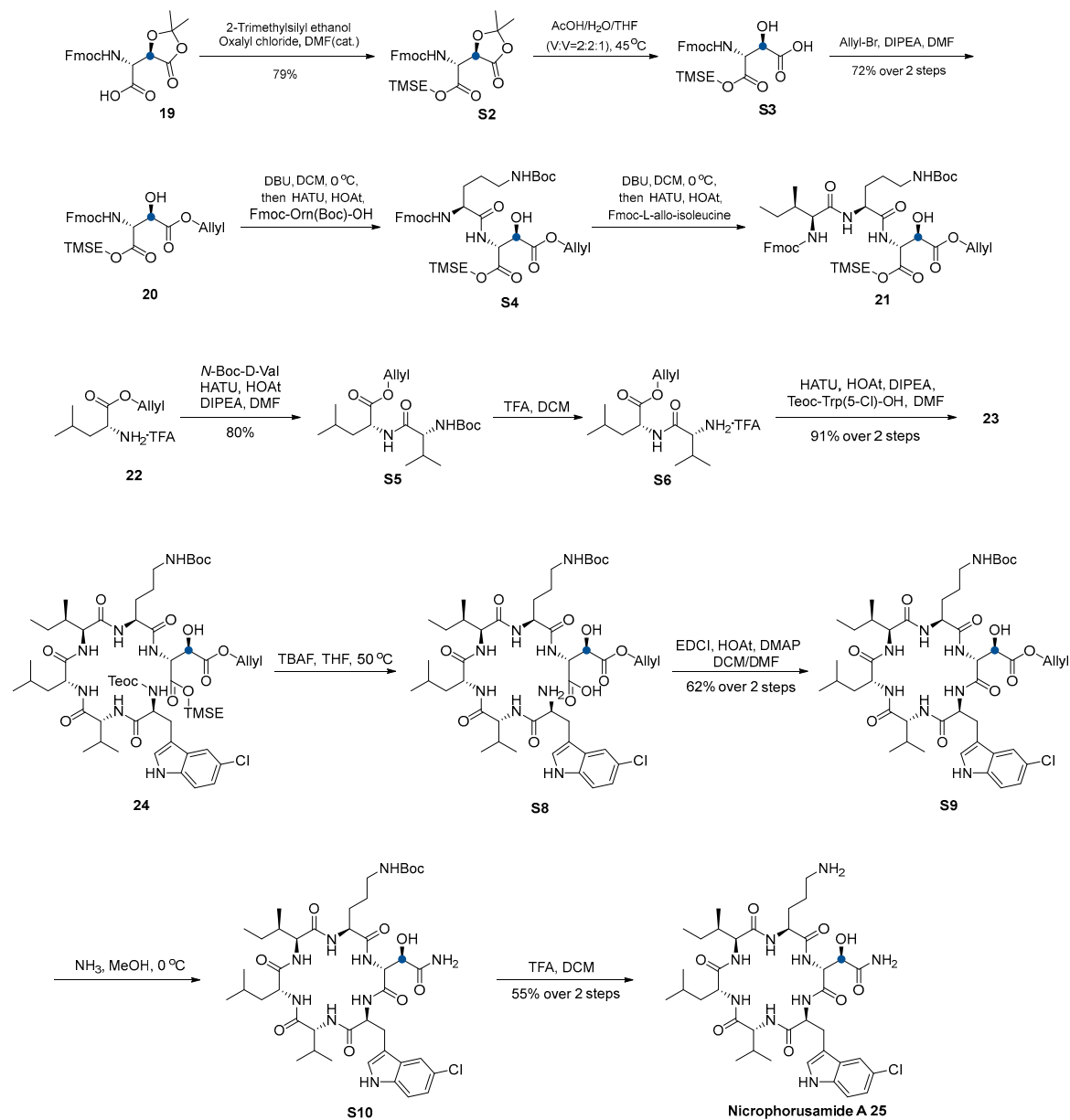
# 1. Optimization of Macrocyclization.

Table S1. Optimization of macrocyclization of linear precursor.



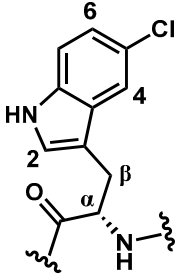
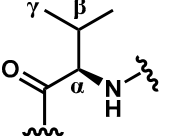
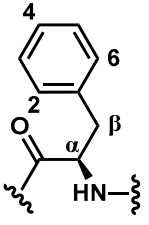
Entry	Conditions (equiv)	Yield (%) over 2 steps
1	HATU (1.5), HOAt (1.5), DIPEA (2.0), DMF	35
2	BEP (3.0), DIPEA (6.0), DCM	24
3	EDCI (2.0), HOAt (2.0), DMAP (0.2), DCM	58
4	PyAOP (3.0), DIPEA (6.0), DCM	42
5	FDPP (3.0), DIPEA (6.0), DCM	trace
6	EDCI (2.0), HOAt (2.0), DMAP (0.2), DCM:DMF=20:1	65

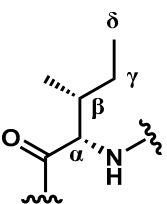
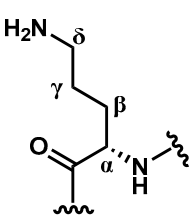
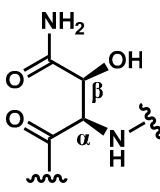
## 2. Synthetic Schemes of Compounds 19, 20, 22, 24.



### 3. NMR Data Comparison between Natural Noursamycin A and Synthetic Sample 1.

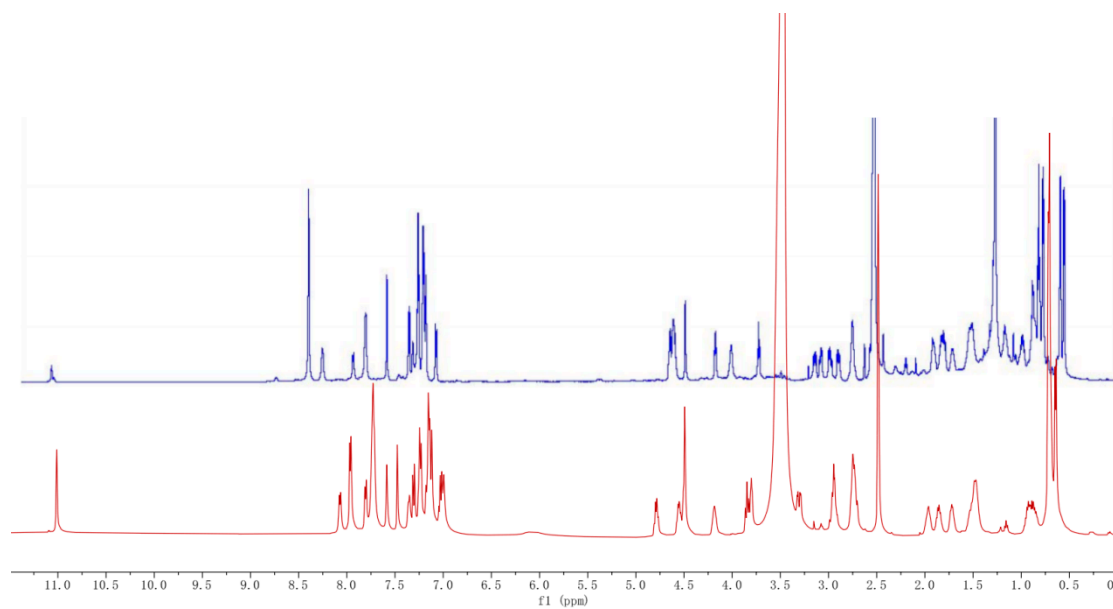
Table S2.  $^{13}\text{C}$  NMR<sup>a</sup> comparison of natural noursamycin A and synthetic sample 1.

Amino acid Residue	Noursamycin A			
	Pos.	Natural ( $\delta_{\text{A1}}$ )	Synthetic Sample <b>1</b> ( $\delta_{\text{A2}}$ )	$\Delta\delta =$ $\delta_{\text{A1}} - \delta_{\text{A2}}$
<b>Trp<sup>1</sup></b> 	$\alpha$	54.1	52.6	1.5
	$\beta$	27.5	27.7	-0.2
	2	126.0	125.6	0.4
	3	110.3	110.1	0.2
	3a	128.8	128.3	0.5
	4	118.0	117.3	0.7
	5	123.4	123.0	0.4
	6	121.2	120.7	0.5
	7	113.2	112.8	0.5
	7a	135.1	134.5	0.6
	COOH	171.7	171.1	0.6
<b>Val<sup>2</sup></b> 	$\alpha$	60.9	60.6	0.3
	$\beta$	29.5	29.7	-0.2
	$\gamma_1$	19.3	19.1	0.2
	$\gamma_2$	19.1	18.8	0.3
	COOH	171.4	170.6	0.8
<b>Phe<sup>3</sup></b> 	$\alpha$	54.9	53.9	1.0
	$\beta$	37.4	38.5	-1.1
	1	138.4	137.2	1.2
	2, 6	129.3	129.3	0.0
	3, 5	128.4	128.1	0.3
	4	126.6	126.3	0.3

	COOH	171.6	170.7	0.9
<b>Ile<sup>4</sup></b> 	$\alpha$	57.5	58.2	-0.7
	$\beta$	36.7	35.8	0.9
	$\gamma$ (methyl)	14.8	14.3	0.5
	$\gamma$	26.0	25.4	0.6
	$\delta$	11.1	11.6	-0.5
	COOH	172.2	171.4	0.8
<b>Orn<sup>5</sup></b> 	NH2	-	-	-
	$\alpha$	53.6	52.4	1.2
	$\beta$	27.5	26.1	1.4
	$\gamma$	25.5	24.2	1.3
	$\delta$	39.5	overlap	-
	COOH	172.5	172.1	0.4
<b>OH-ASN<sup>6</sup></b> 	$\alpha$	56.1	56.6	-0.5
	$\beta$	71.6	70.6	1.0
	CO-	173.8	174.2	-0.4
	COOH	170.0	169.0	1.0

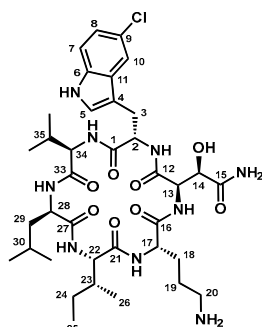
<sup>a</sup>All chemical shifts are reported in ppm. All spectra were measured in DMSO-*d*<sub>6</sub> and referenced to the residual solvent peak at  $\delta_{\text{H}} = 2.50$  ppm and  $\delta_{\text{C}} = 39.52$  ppm as done in the original isolation report.<sup>1</sup> <sup>13</sup>C-NMR spectrum was recorded at 126 MHz.

Figure S1. Comparison of  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz) spectra of synthetic sample **1** (red) and nousamycin A (blue, screenshot from supporting information of nousamycin A's isolation article published in 2019<sup>1</sup>).



#### 4. NMR Data Comparison between Natural Nicrophorusamide A and Synthetic Sample **25**.

Table S3. NMR<sup>a</sup> comparison between natural nicrophorusamide A and synthetic sample **25**.



Nicrophorusamide A

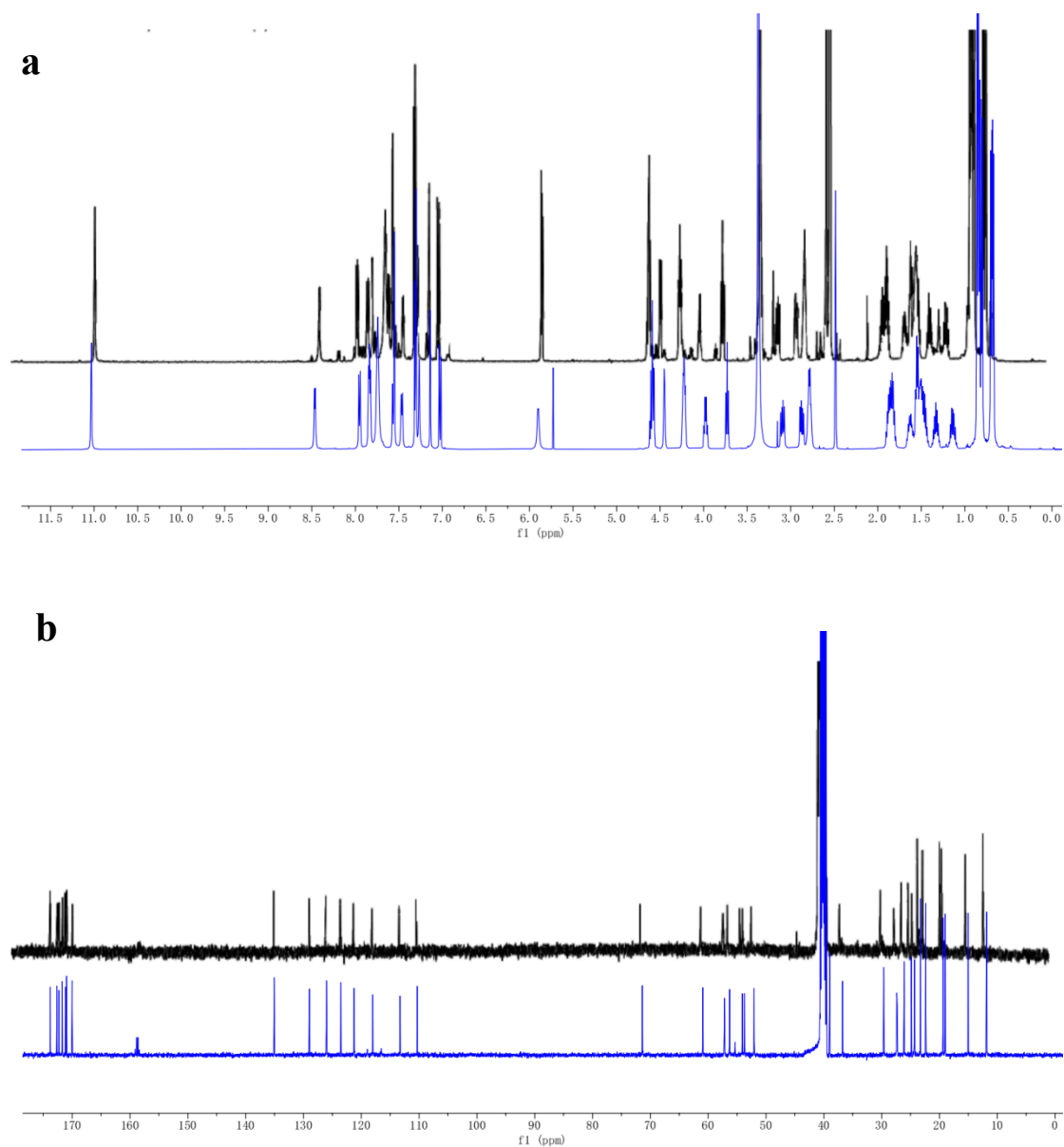
Carbon No.	<sup>13</sup> C NMR		$\Delta\delta^{13}\text{C}$
	natural / $\delta_{A1}$ (ppm)	synthetic / $\delta_{A2}$ (ppm)	$\delta_{A1}-\delta_{A2}$
1	171.1	171.1	0.0
2	53.5	53.5	0.0
3	26.7	26.7	0.0
4	109.8	109.8	0.0
5	125.4	125.5	-0.1
6	134.5	134.5	0.0
7	112.7	112.7	0.0
8	120.7	120.7	0.0
9	122.9	123.0	-0.1
10	117.5	117.5	0.0
11	128.4	128.4	0.0
12	169.4	169.5	-0.1
13	55.8	55.7	0.1
14	70.8	70.8	0.0
15	173.2	173.2	0.0
16	170.6	170.6	0.0

17	53.1	53.2	-0.1
18	26.8	26.8	0.0
19	23.7	23.8	-0.1
20	38.4	38.4	0.0
21	171.7	171.7	0.0
22	56.5	56.6	-0.1
23	36.3	36.2	0.1
24	25.6	25.6	0.0
25	11.3	11.3	0.0
26	14.5	14.5	0.0
27	172.1	172.1	0.0
28	51.5	51.5	0.0
29	39.6	overlap	-
30	24.3	24.3	0.0
31	22.7	22.7	0.0
32	21.8	21.8	0.0
33	170.4	170.4	0.0
34	60.4	60.4	0.0
35	29.1	29.1	0.0
36	18.5	18.4	0.1
37	18.8	18.8	0.0

<sup>a</sup>All chemical shifts are reported in ppm. Coupling constants are given in parentheses and reported in Hz. All spectra were measured in DMSO-*d*<sub>6</sub> and referenced to the residual solvent peak at  $\delta_{\text{H}} = 2.50$  ppm and  $\delta_{\text{C}} = 39.52$  ppm as done in the original isolation report.<sup>2</sup> <sup>1</sup>H-NMR spectrum was recorded at 500 MHz. <sup>13</sup>C-NMR spectrum was recorded at 126 MHz.

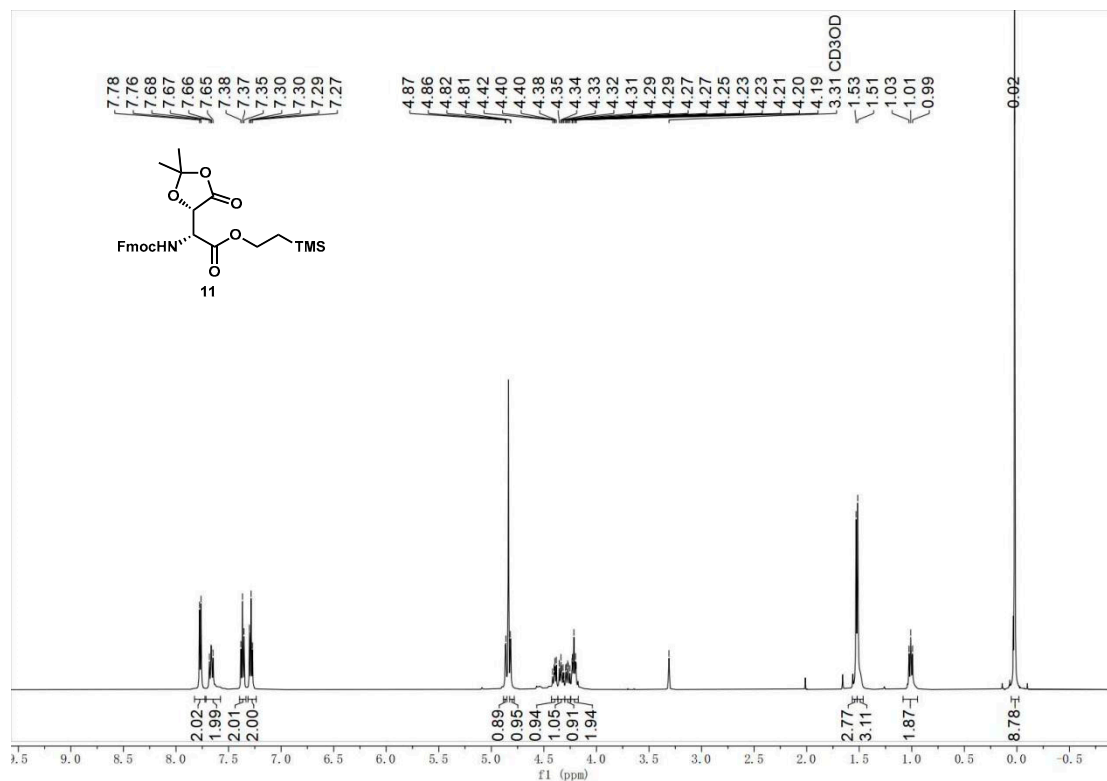


Figure S2. Comparison of (a)  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz), (b)  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz) spectra of synthetic nicrophorusamide A (blue) and nicrophorusamide A (black, screenshot from supporting information of nicrophorusamide A's isolation article published in 2017<sup>2</sup>).

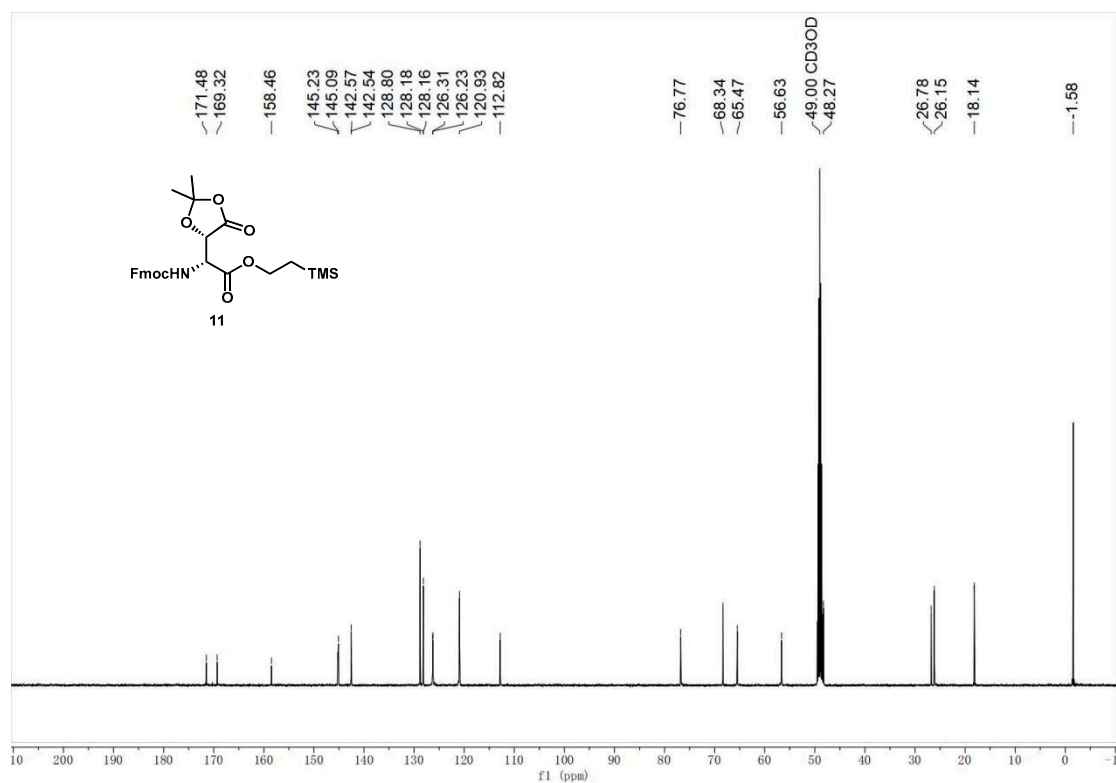


## 5. NMR Spectra.

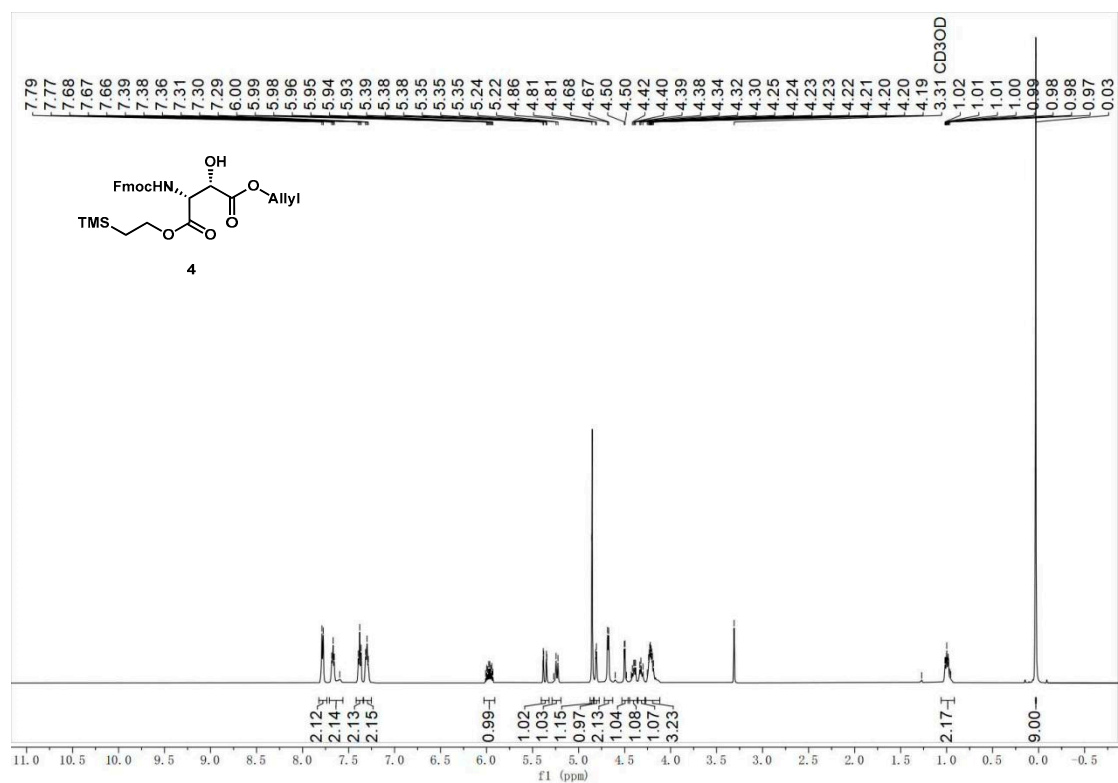
### $^1\text{H}$ NMR spectra for 11 (MeOD)



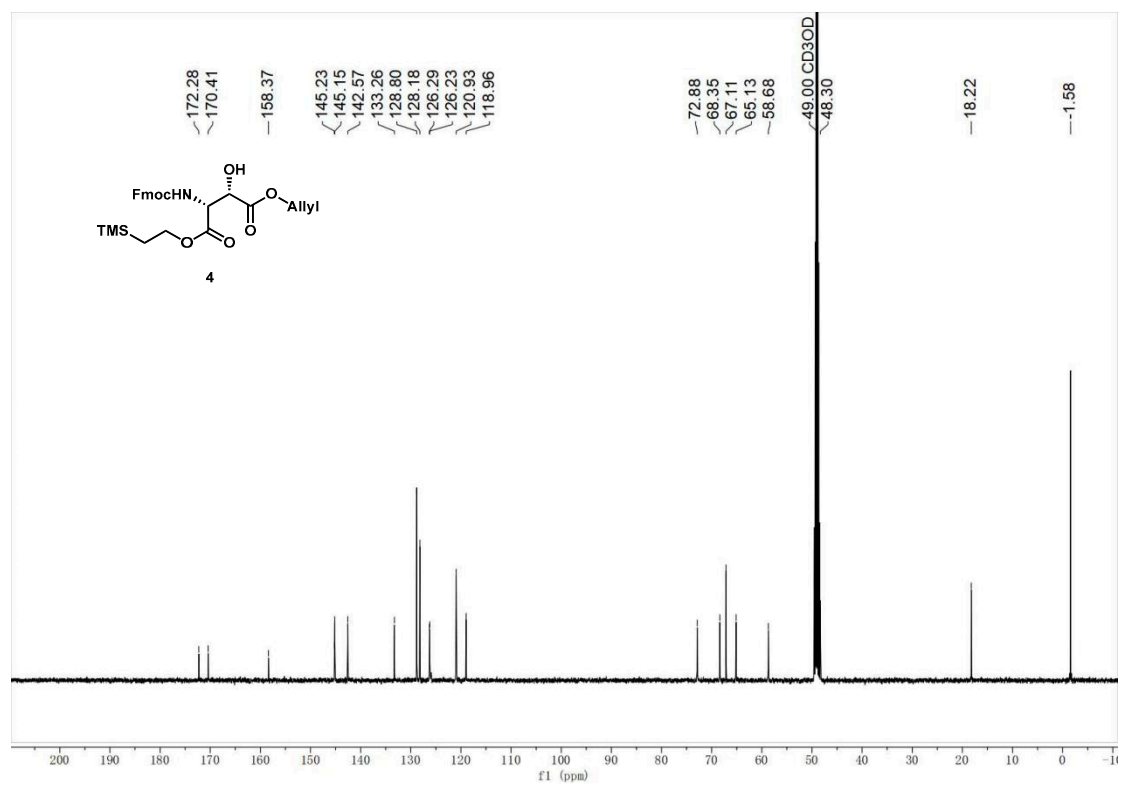
### $^{13}\text{C}$ NMR spectra for 11 (MeOD)



**<sup>1</sup>H NMR spectra for 4 (MeOD)**



**<sup>13</sup>C NMR spectra for 4 (MeOD)**



CC(C)(C)COC(=O)[C@H](O)[C@@H](NC(=O)C[C@H](Nc1ccc(C(C)(C)C)cc1)C(=O)OCCN(C)C)C(=O)OCCN(C)C

**13**

<sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD) of compound **13**. The spectrum displays peaks corresponding to the structure, with integration values indicated below the baseline.

Chemical Shift (ppm)	Integration
7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.	

[illegible]

CC[C@H](C)[C@@H](C(=O)N[C@@H](CCCCNC(=O)OC(C)(C)C)C(=O)N[C@@H](C[C@H](O)C(=O)OCCOC(C)(C)C)C(=O)OCCOC(C)(C)C

2

7.80  
7.79  
7.70  
7.68  
7.66  
7.41  
7.39  
7.37  
7.33  
7.31  
7.29  
7.29  
5.40  
5.40  
5.36  
5.35  
5.26  
5.26  
5.24  
5.23  
5.03  
5.02  
4.70  
4.69  
4.68  
4.68  
4.48  
4.47  
4.41  
4.40  
4.39  
4.38  
4.24  
4.18  
4.17  
4.16  
4.15  
4.14  
3.31 CD3OD  
3.04  
3.02  
1.53  
1.51  
1.44  
1.42  
1.40  
1.00  
0.99  
0.98  
0.95  
0.93  
0.92  
0.90  
0.02  
0.02  
0.01  
0.01

1.97  
1.84  
1.96  
2.00  
0.99  
1.06  
1.08  
1.10  
2.22  
1.06  
0.97  
2.03  
1.03  
2.86  
1.96  
2.11  
1.11  
2.74  
8.95  
1.09  
8.16  
8.97

f1 (ppm)

Chemical structure of compound **2** is shown above the spectrum. The structure is a complex molecule featuring a central carbon atom bonded to a hydroxyl group, a carboxylate group, and two amide groups. The amide groups are further substituted with a TMS group and an allyl group, respectively. The chemical structure is labeled with **2**.

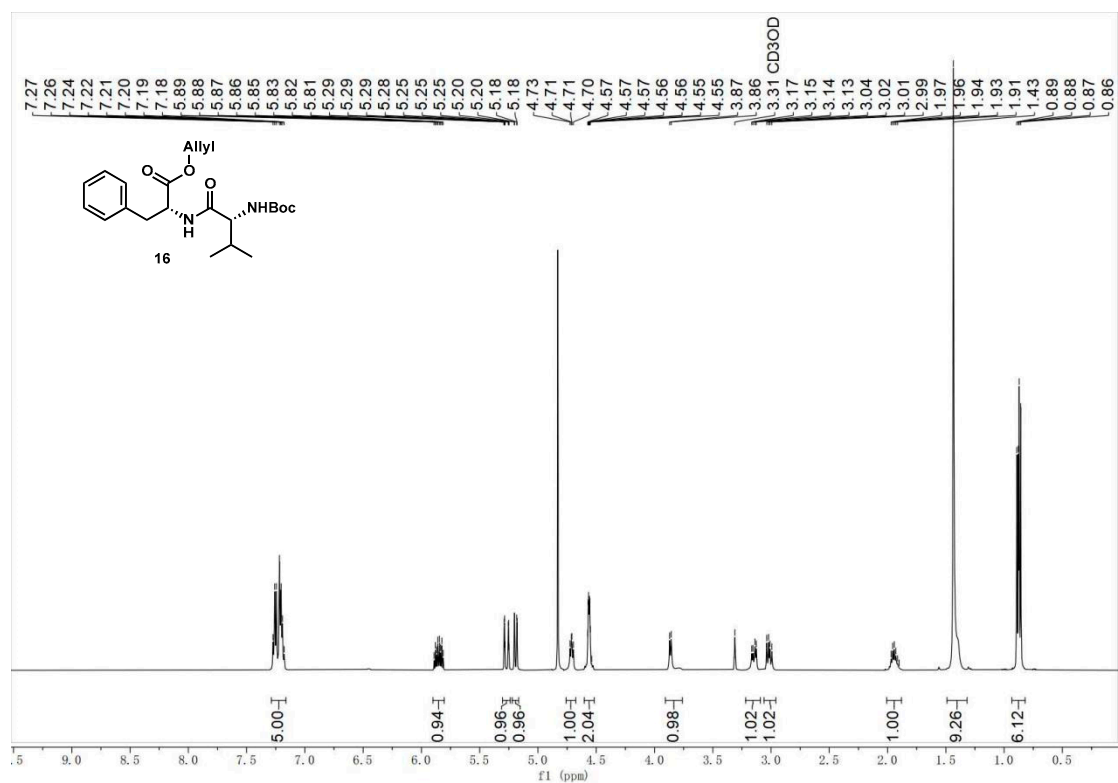
The <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) shows the following chemical shifts (ppm):

- 174.59, 173.76, 172.16, 169.74, 158.76, 158.50
- 145.35, 145.08, 142.55, 133.21, 128.73, 128.14, 128.12, 126.22, 120.87, 118.92
- 79.89, 72.52, 68.01, 67.07, 65.14, 60.36, 56.78, 54.05
- 49.00 CDCl<sub>3</sub>, 48.39
- 40.70, 38.22, 30.19, 28.72, 27.25, 18.19, 15.00, 11.94
- 1.68

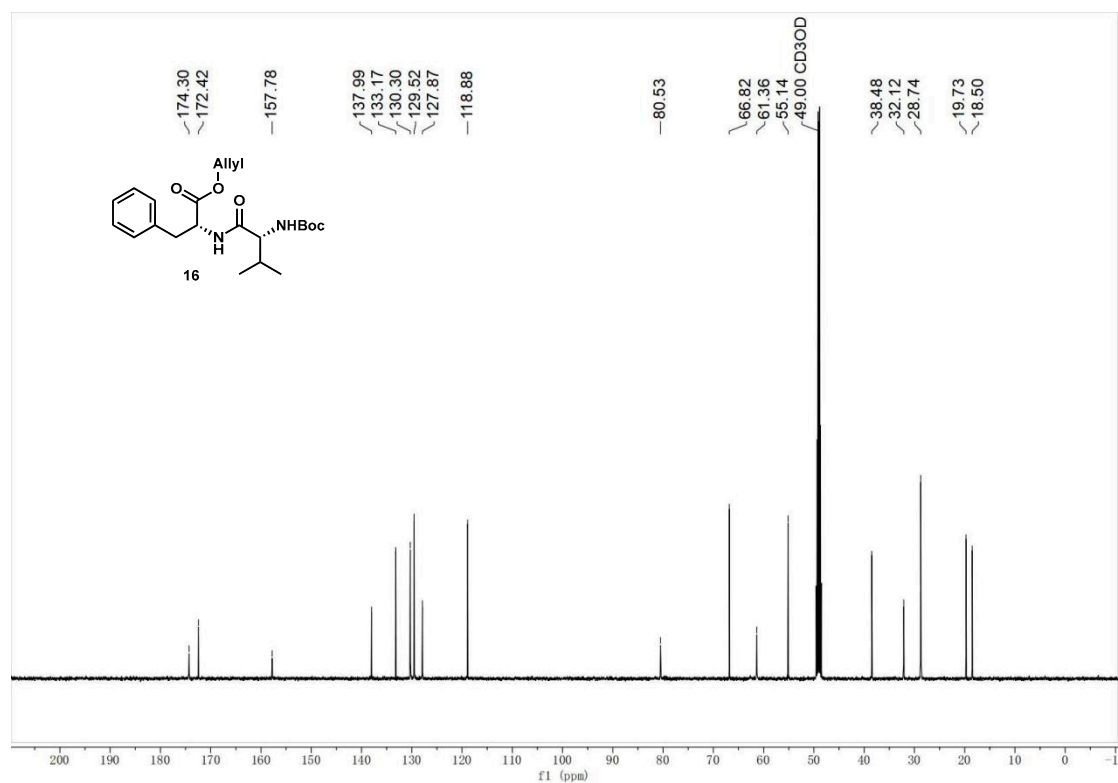
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

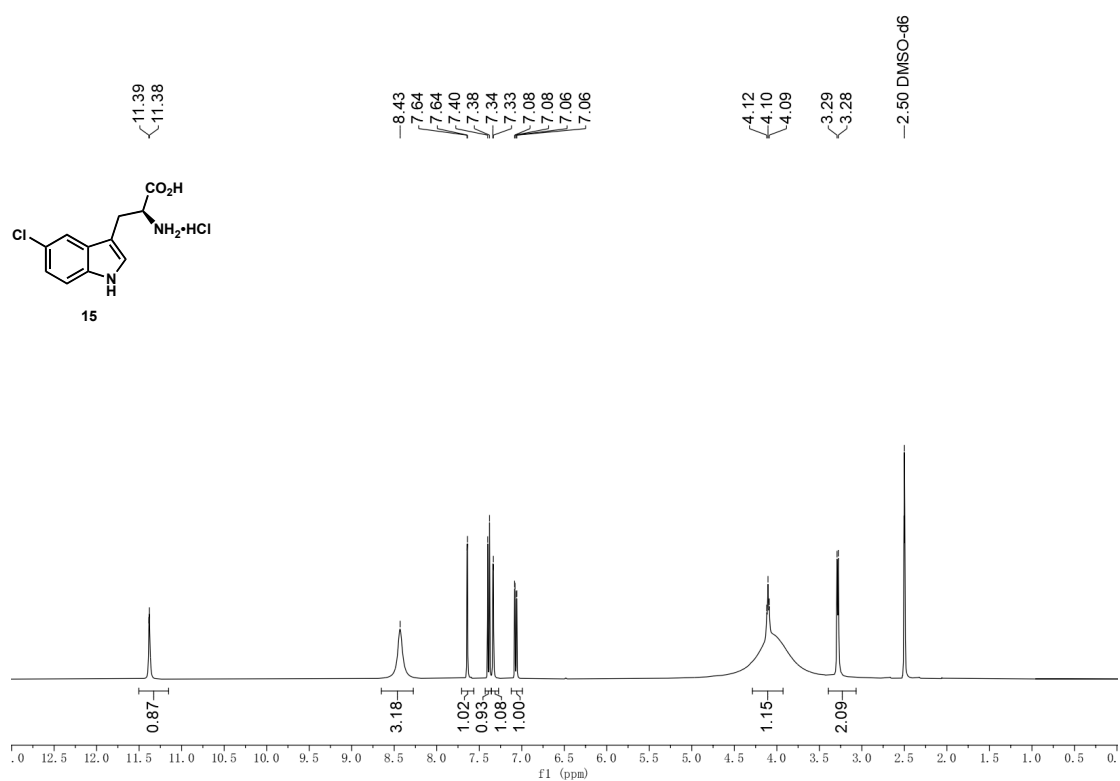
**<sup>1</sup>H NMR spectra for 16 (MeOD)**



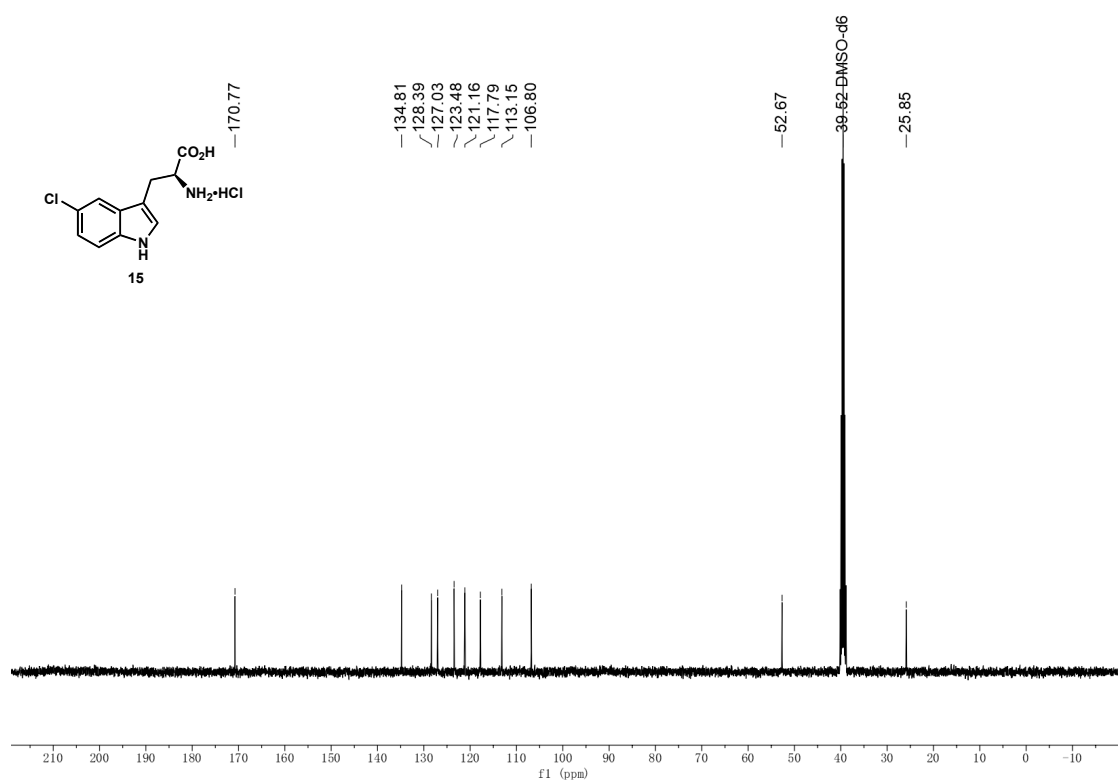
**<sup>13</sup>C NMR spectra for 16 (MeOD)**



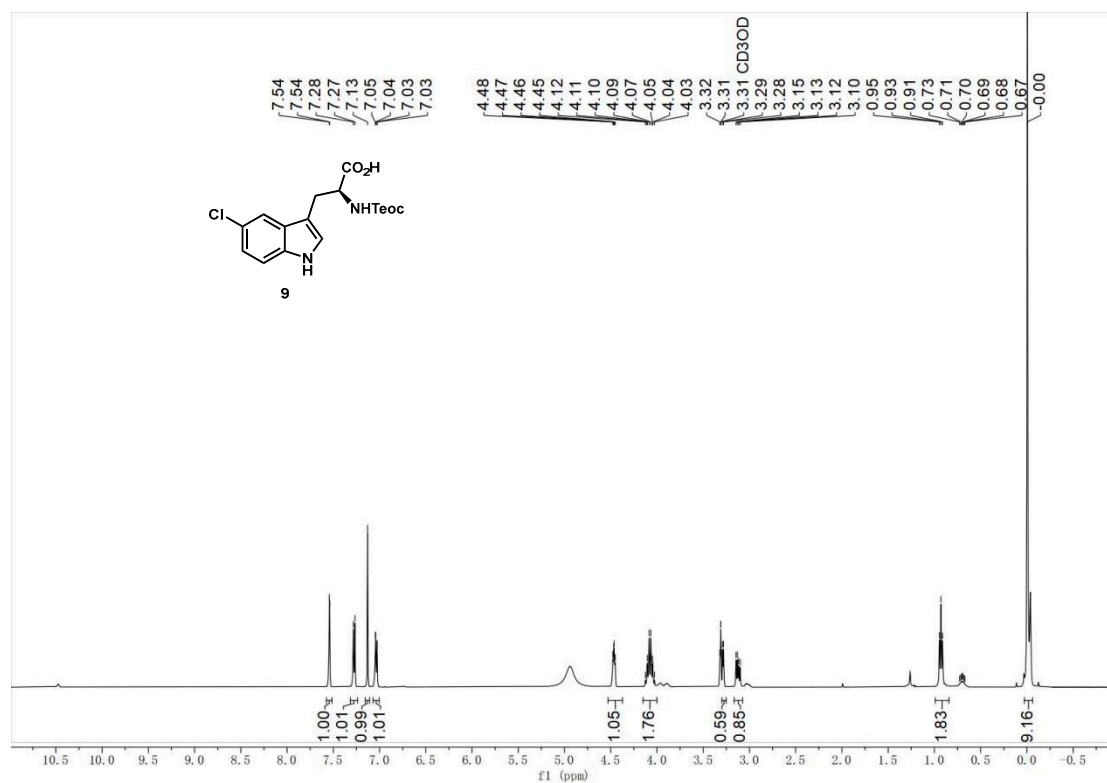
**<sup>1</sup>H NMR spectra for 15 (DMSO-*d*<sub>6</sub>)**



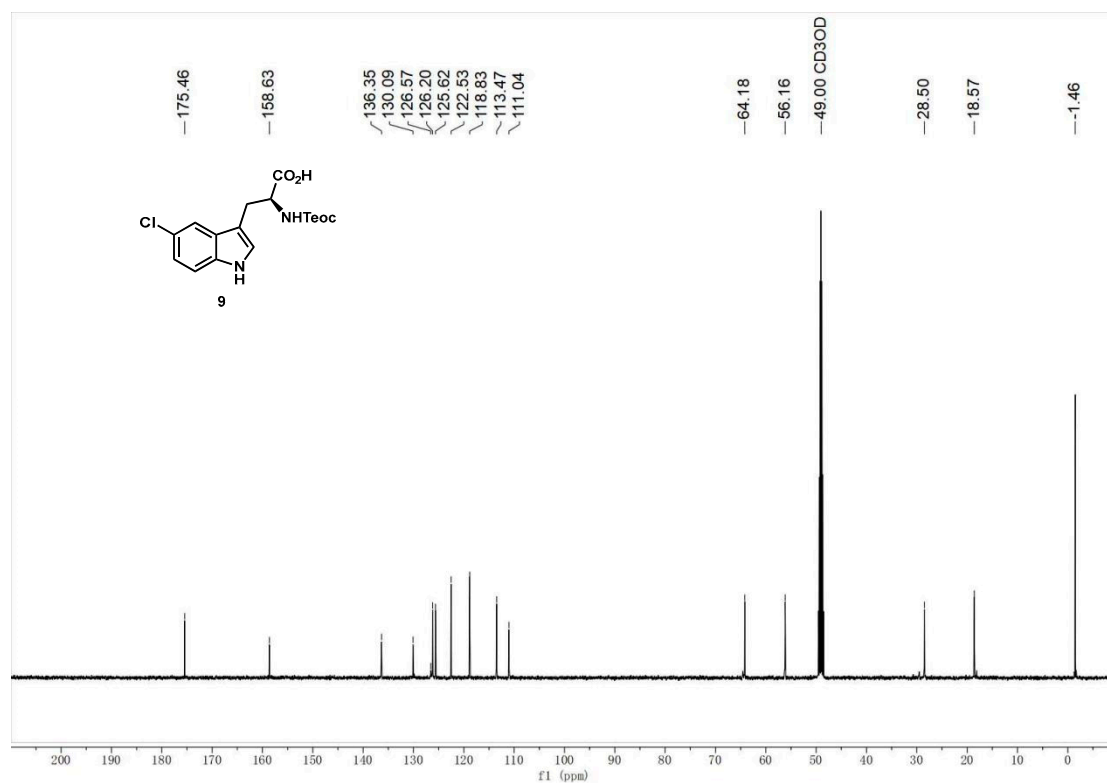
**<sup>13</sup>C NMR spectra for 15 (DMSO-*d*<sub>6</sub>)**



**<sup>1</sup>H NMR spectra for 9 (MeOD)**

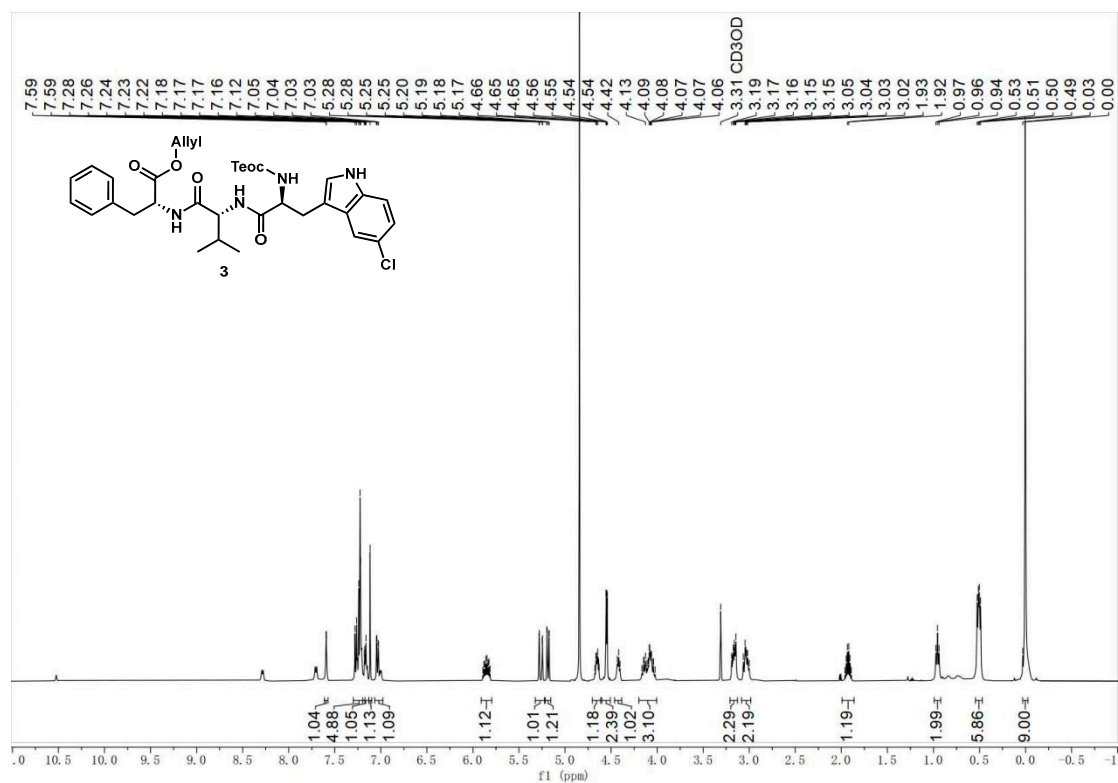


**<sup>13</sup>C NMR spectra for 9 (MeOD)**

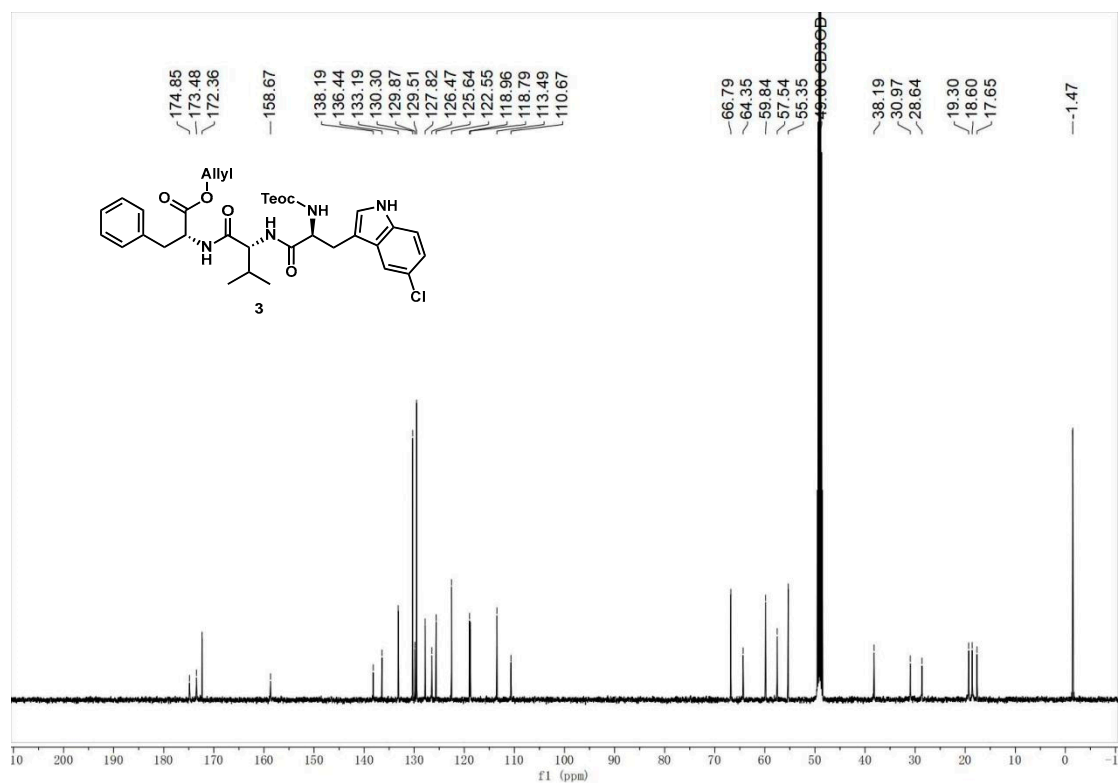




### <sup>1</sup>H NMR spectra for 3 (MeOD)



**$^{13}\text{C}$  NMR spectra for 3 (MeOD)**



Chemical structure of compound 17 is shown above the spectrum. The structure is a complex molecule featuring a central core with various functional groups, including a Boc-protected amine, a Teoc-protected amine, a TMS-protected alcohol, and a chlorophenyl group.

**1H NMR Spectrum (DMSO-d6):**

**Chemical Shifts (ppm):** 11.00, 10.99, 8.17, 7.99, 7.70, 7.33, 7.31, 7.25, 7.23, 7.22, 7.20, 7.19, 7.14, 7.12, 7.04, 7.03, 7.02, 7.02, 5.33, 5.33, 5.24, 5.21, 4.61, 4.61, 4.60, 4.60, 4.36, 4.35, 4.34, 4.27, 4.27, 4.09, 4.06, 3.94, 3.90, 2.90, 2.89, 2.87, 2.50 (DMSO-d6), 1.38, 1.36, 1.22, 1.02, 0.92, 0.92, 0.90, 0.89, 0.85, 0.84, 0.83, 0.82, 0.78, 0.77, 0.75, 0.70, 0.69, 0.68, 0.68, 0.66, 0.00, -0.05.

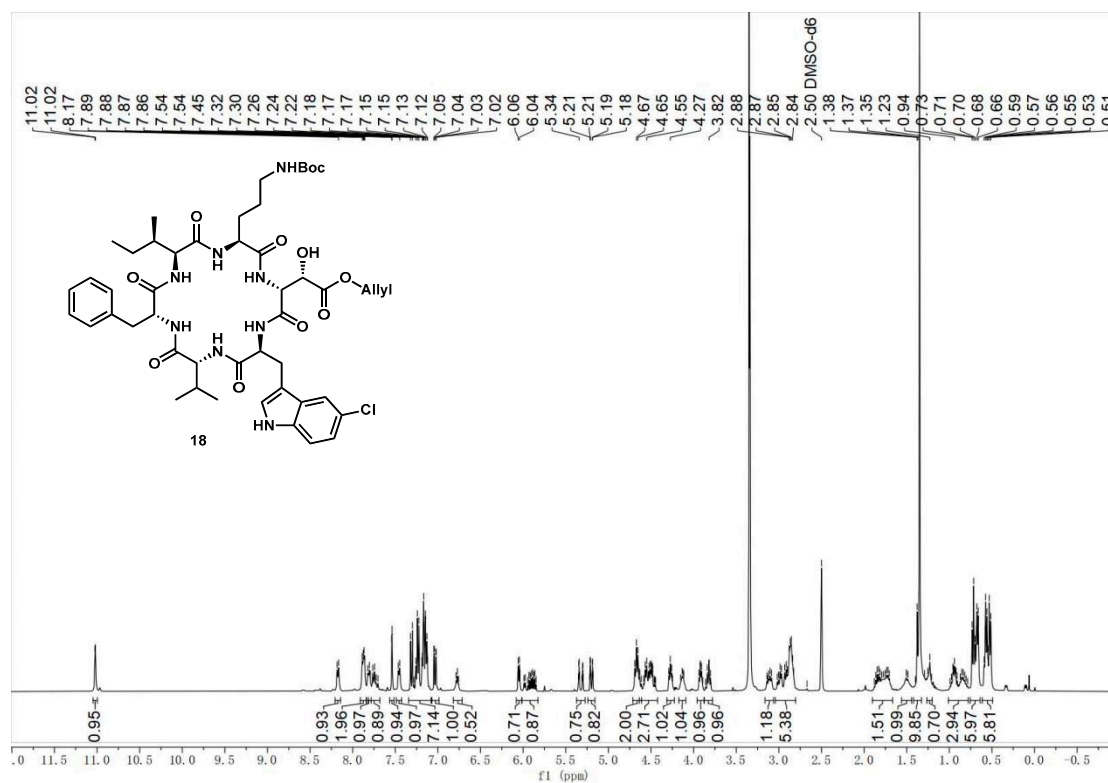
**Integrations:** 0.95, 1.63, 1.86, 0.93, 0.78, 0.88, 5.04, 1.98, 1.24, 0.81, 1.10, 0.89, 0.81, 0.81, 0.77, 0.91, 1.84, 0.89, 1.96, 1.08, 0.79, 2.00, 1.61, 0.91, 1.01, 3.91, 0.86, 0.90, 0.97, 1.19, 10.83, 1.14, 2.98, 2.01, 3.25, 11.47, 18.49.

Chemical structure of compound 17 is shown above the spectrum. The structure is a complex molecule featuring a central core with various functional groups, including amides, esters, and a TMS-protected alcohol. The spectrum displays peaks corresponding to these functional groups, with the following chemical shifts (ppm) labeled above the peaks:

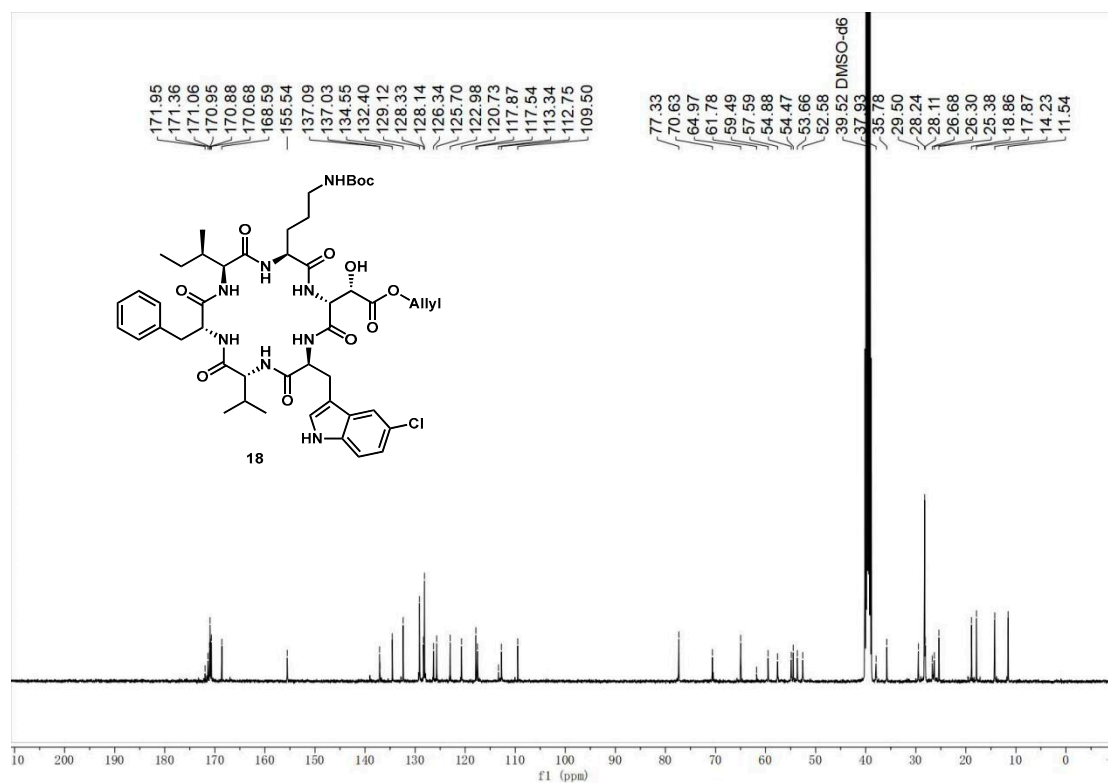
171.97, 171.62, 170.85, 170.76, 170.63, 170.44, 168.53, 156.09, 155.57, 137.54, 134.53, 132.33, 129.13, 128.46, 127.98, 126.13, 125.91, 123.01, 120.66, 118.04, 117.94, 112.68, 110.10, 77.38, 71.27, 65.04, 62.99, 61.79, 57.42, 55.47, 54.85, 54.16, 52.00, 39.52, 37.88, 36.99, 31.27, 30.27, 28.89, 28.98, 28.25, 27.85, 25.92, 25.56, 19.08, 17.58, 17.27, 16.80, 14.18, 11.60, 1.56, 1.64.

The spectrum shows a series of peaks in the aromatic region (110-172 ppm), a cluster of peaks in the aliphatic region (14-31 ppm), and a small peak at 1.64 ppm. The solvent peak for DMSO-d6 is visible at 40 ppm.

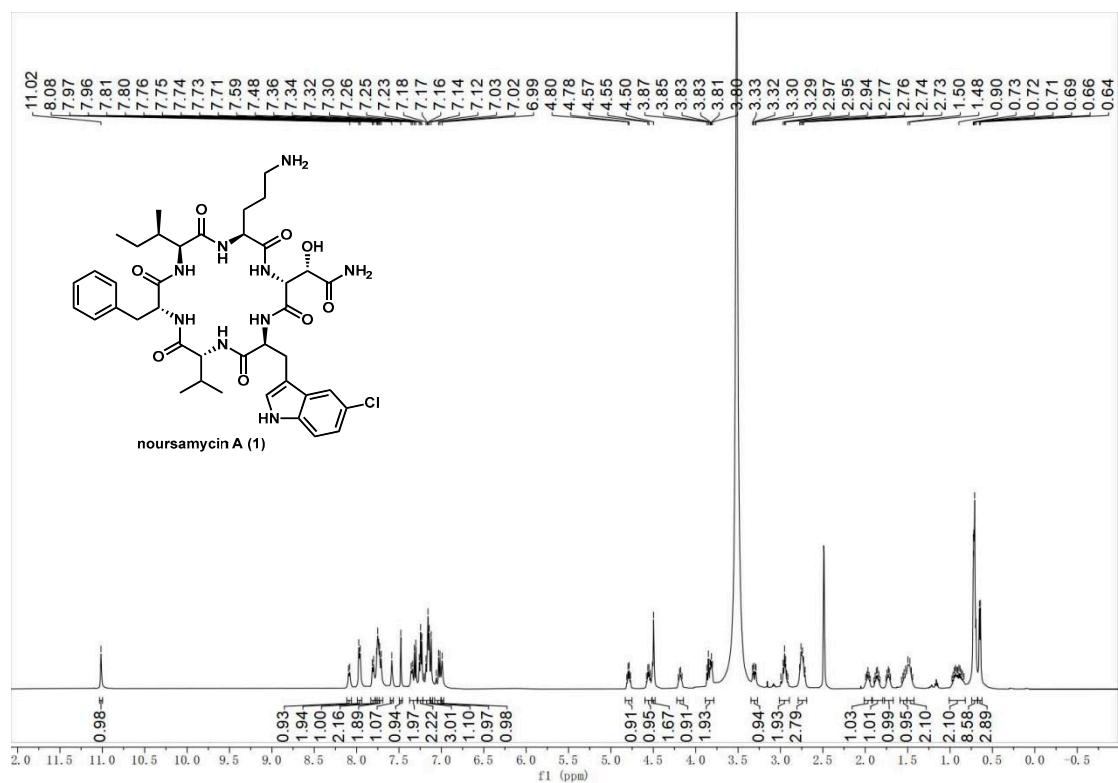
**<sup>1</sup>H NMR spectra for 18 (DMSO-*d*<sub>6</sub>)**



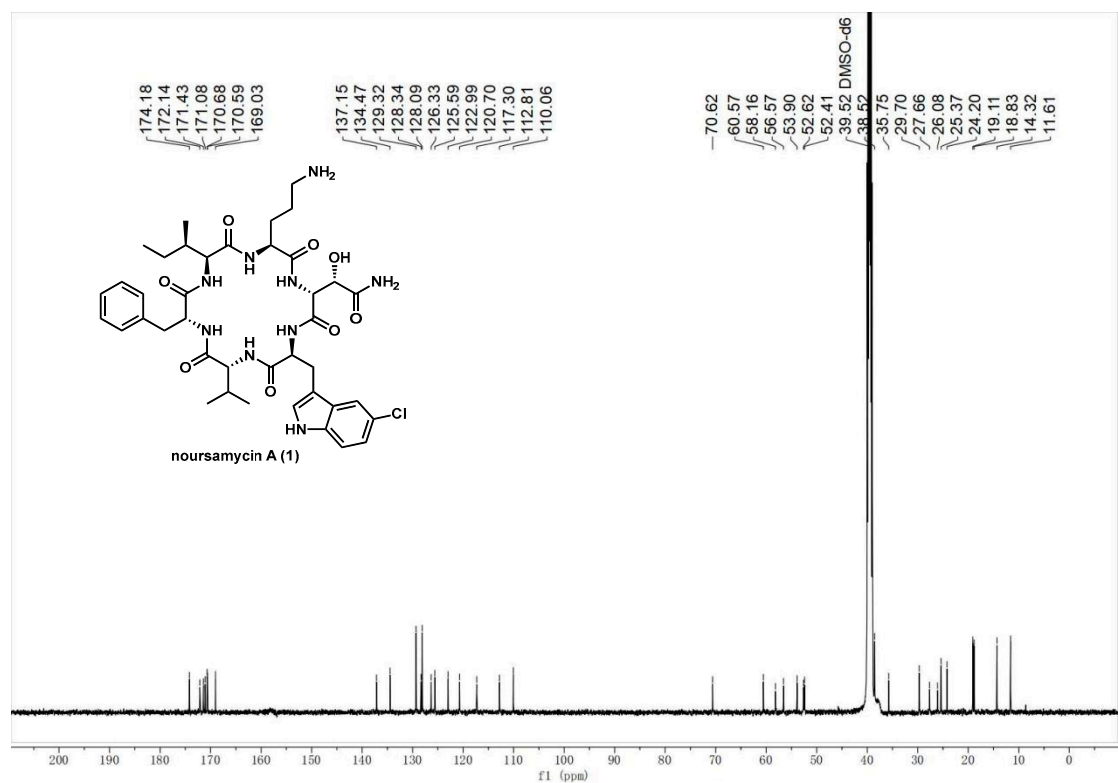
**<sup>13</sup>C NMR spectra for 18 (DMSO-*d*<sub>6</sub>)**



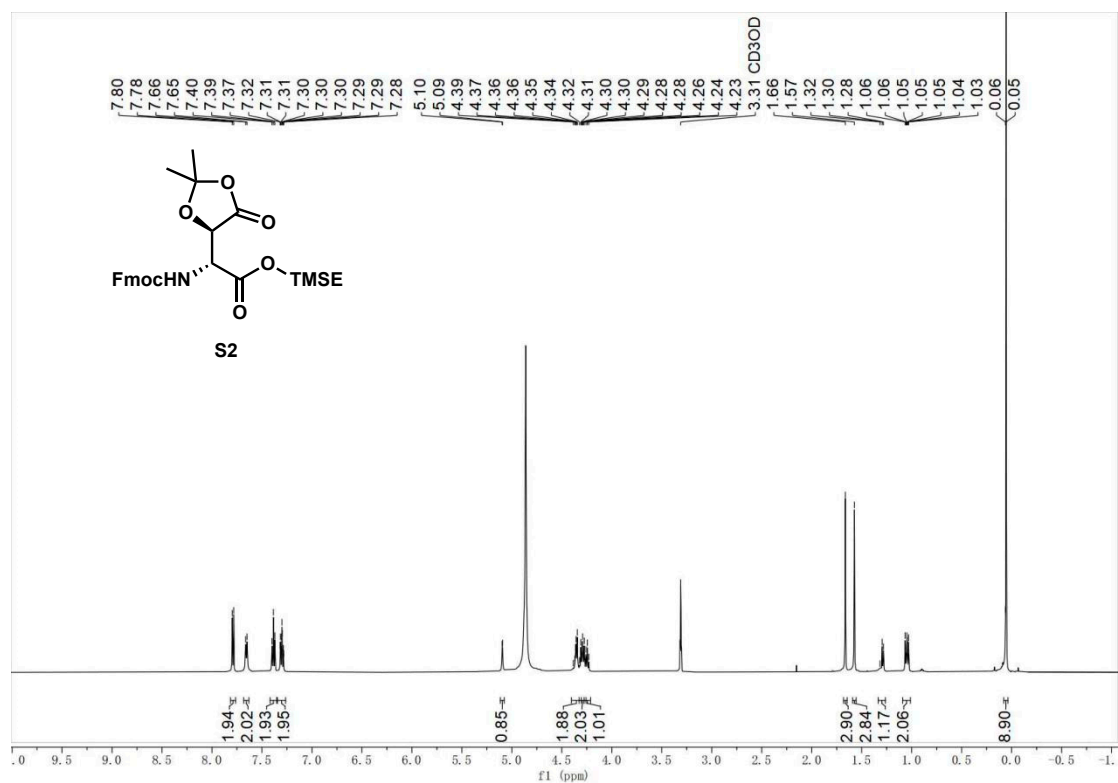
**<sup>1</sup>H NMR spectra for noursamycin A (1) (DMSO-*d*<sub>6</sub>)**



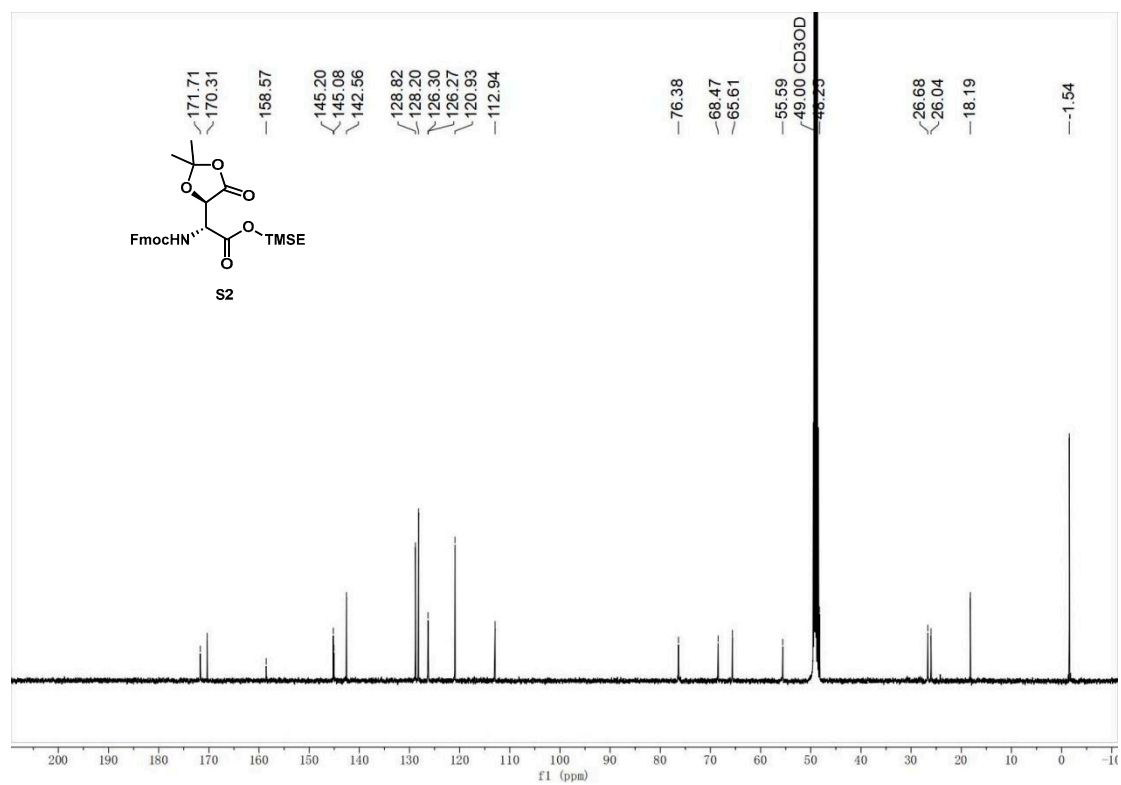
**$^{13}\text{C}$  NMR spectra for nousamycin A (1) ( $\text{DMSO-}d_6$ )**



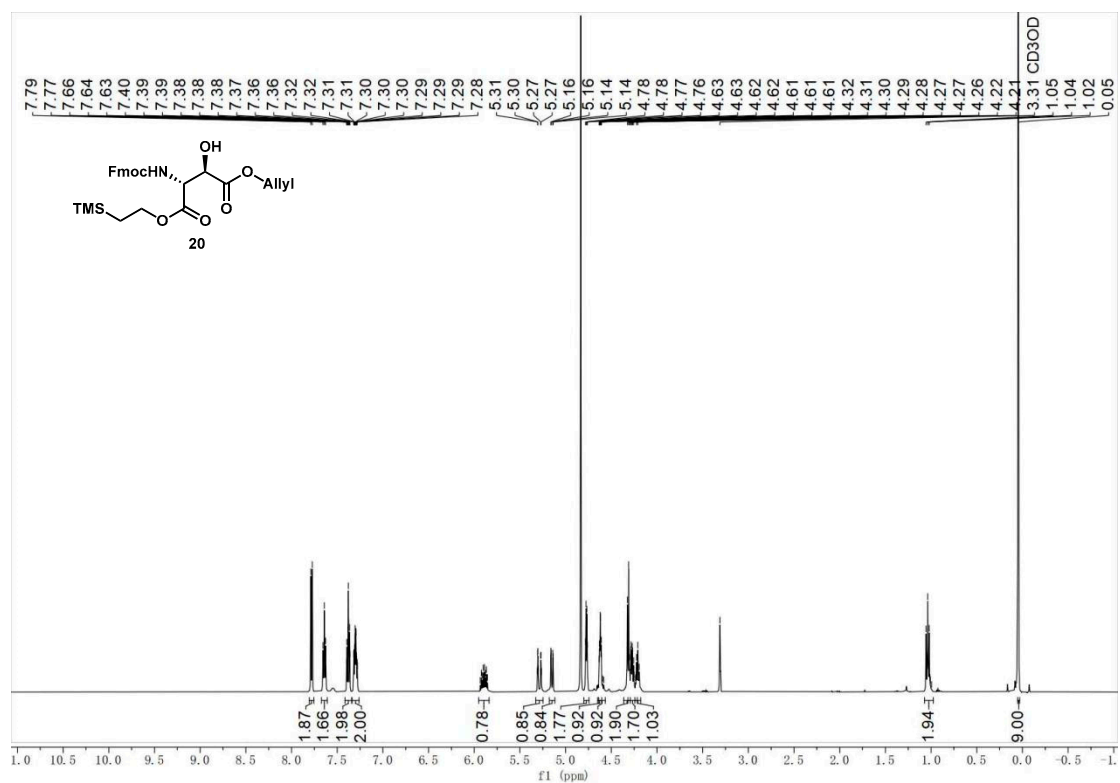
**<sup>1</sup>H NMR spectra for S2 (MeOD)**



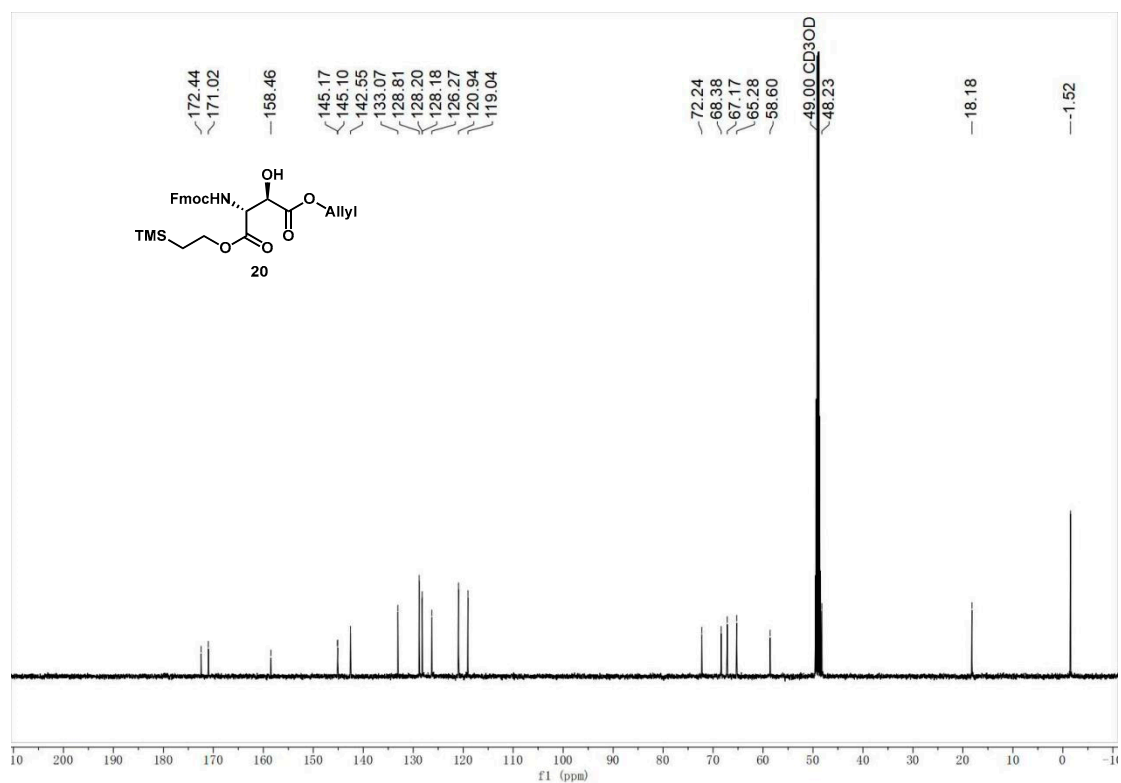
**<sup>13</sup>C NMR spectra for S2 (MeOD)**



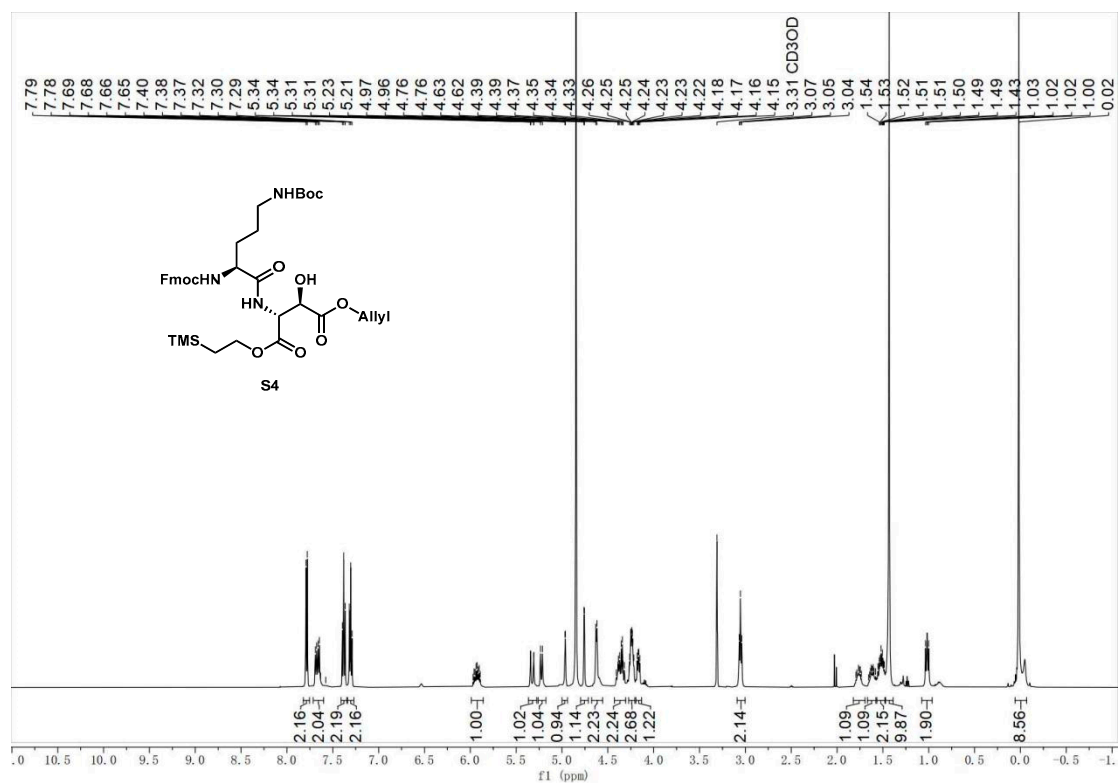
**<sup>1</sup>H NMR spectra for 20 (MeOD)**



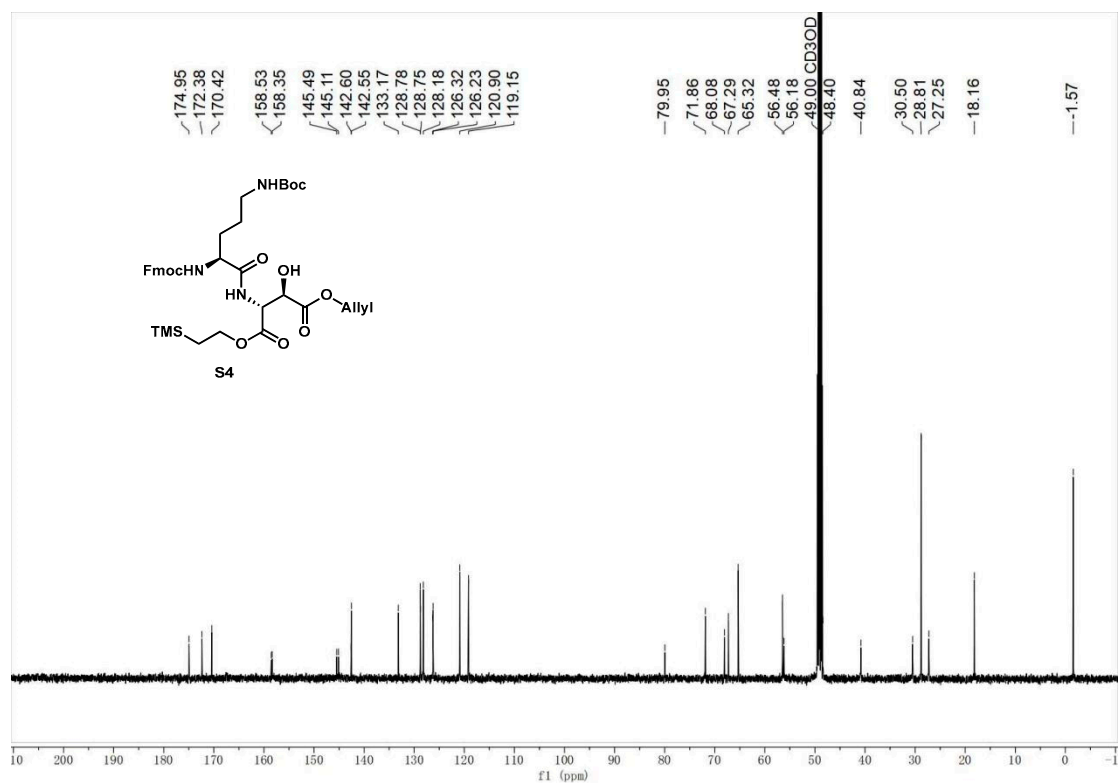
**<sup>13</sup>C NMR spectra for 20 (MeOD)**



**<sup>1</sup>H NMR spectra for S4 (MeOD)**



**<sup>13</sup>C NMR spectra for S4 (MeOD)**



CC[C@H](C)[C@@H](C(=O)N[C@@H](CCCCNC(=O)OC(C)(C)C)C(=O)N[C@@H](COCCOC(=O)C(C)(C)C)C(=O)OCCOC(=O)C(C)(C)C

21

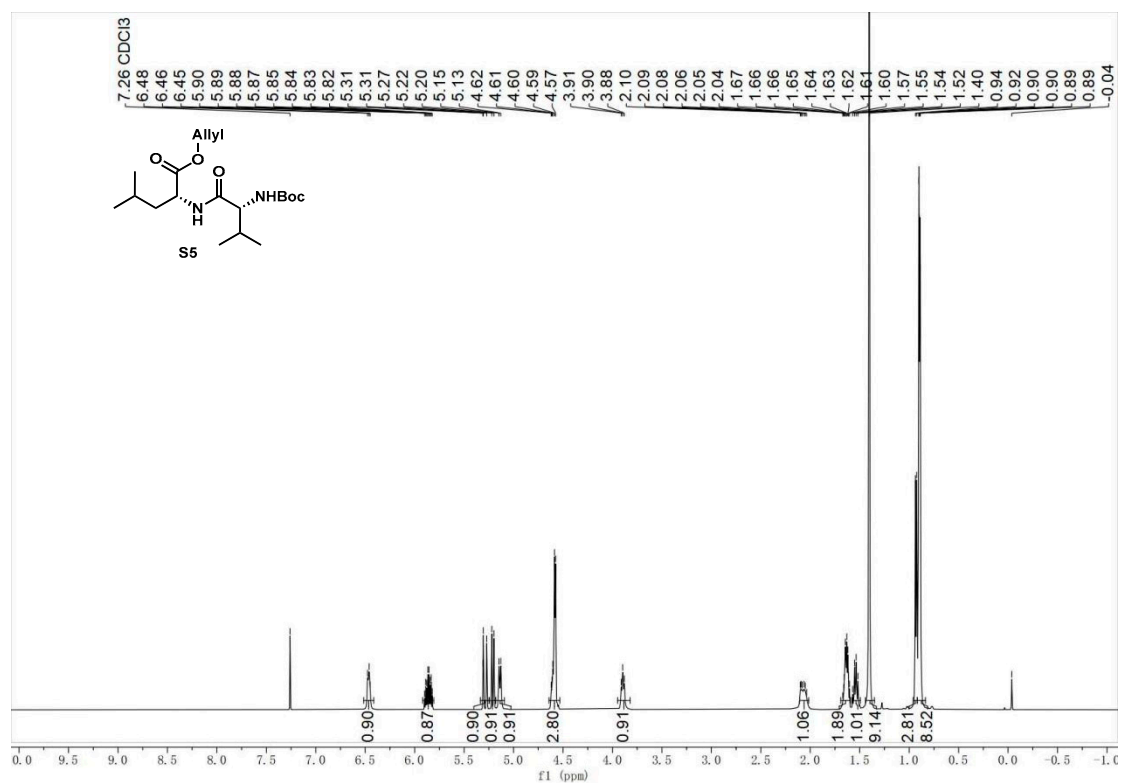
<sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD) of compound 21. The spectrum shows peaks from 0.89 to 7.80 ppm. Integration values are provided below the peaks: 1.99, 1.81, 2.00, 2.00, 0.96, 0.96, 1.07, 1.14, 2.29, 0.70, 1.13, 1.97, 2.83, 1.07, 2.02, 0.95, 1.12, 1.15, 2.03, 9.11, 1.05, 2.02, 6.12, 9.05.

Chemical structure of compound 21 is shown above the spectrum. The structure is a complex molecule featuring a central chiral center with a hydroxyl group, an allyl ester, and a TMS-protected ether. It also includes a Boc-protected amine and a Fmoc-protected amine. The spectrum displays the following chemical shifts (ppm):

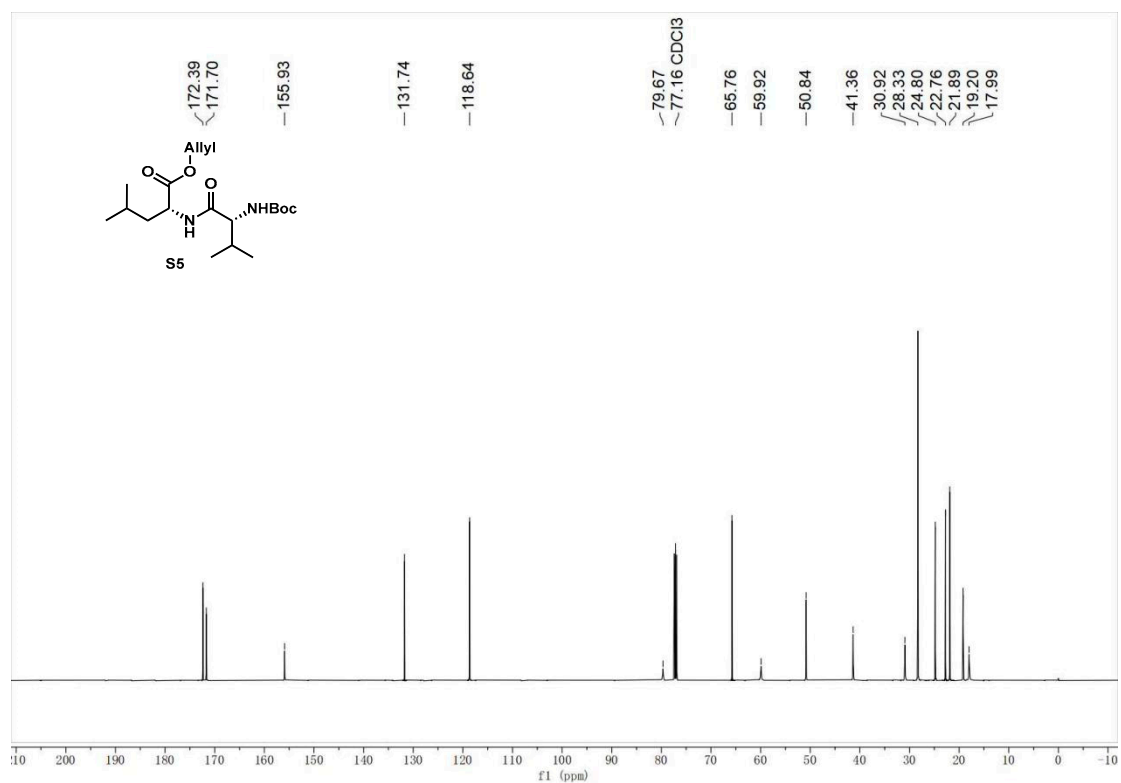
Chemical Shift (ppm)
174.35
173.96
172.36
170.44
158.86
158.50
145.39
145.11
142.60
133.15
128.79
128.19
128.17
126.25
120.92
119.15
79.93
71.96
68.11
67.27
65.33
60.43
56.55
54.01
49.99
48.44
40.79
38.21
30.52
28.79
27.29
27.17
18.18
15.05
12.00
-1.55



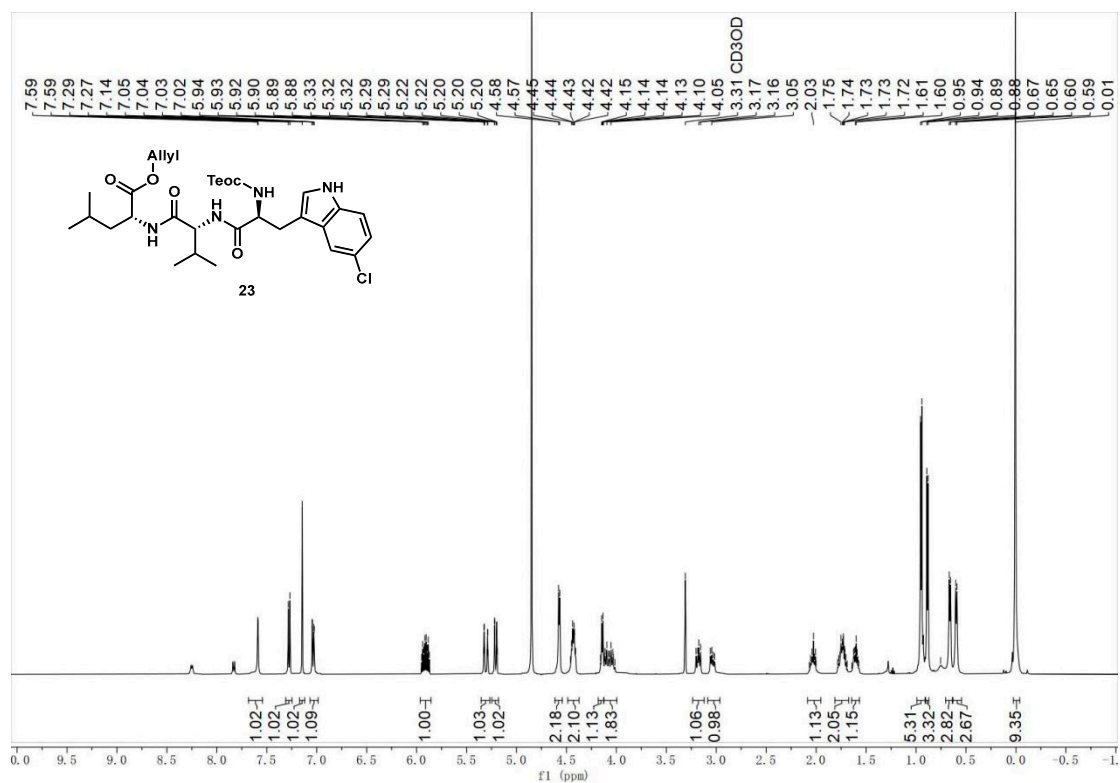
**<sup>1</sup>H NMR spectra for S5 (CDCl<sub>3</sub>)**



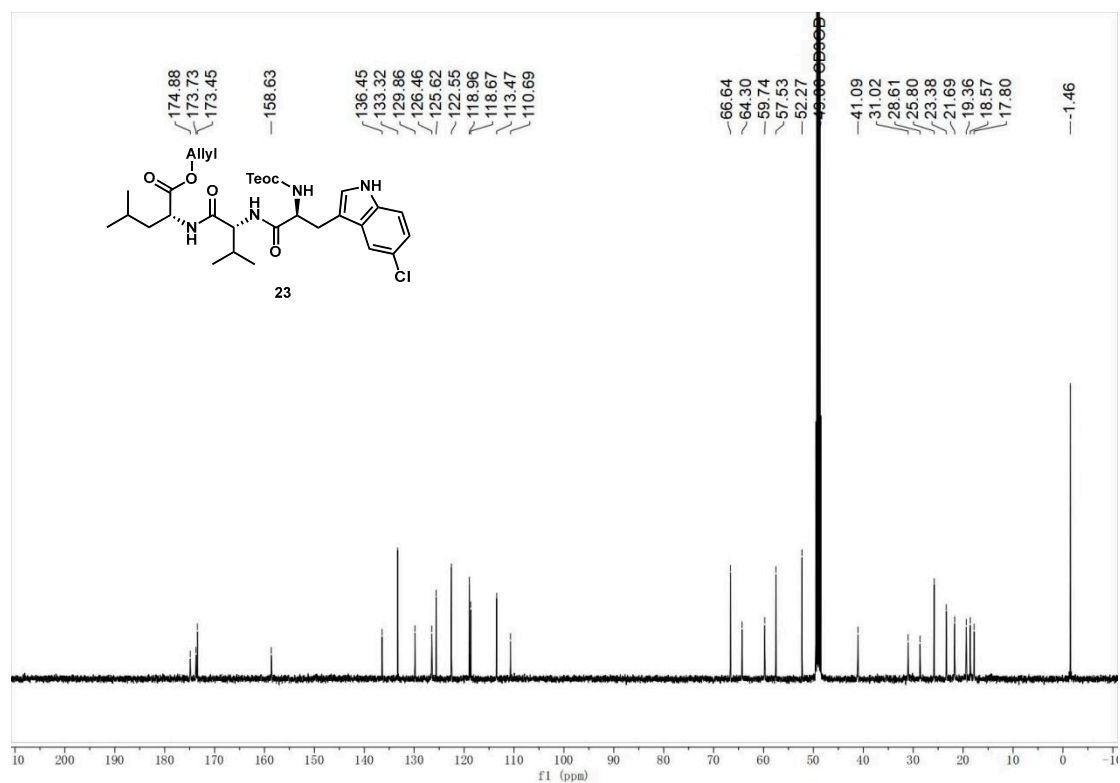
**<sup>13</sup>C NMR spectra for S5 (CDCl<sub>3</sub>)**



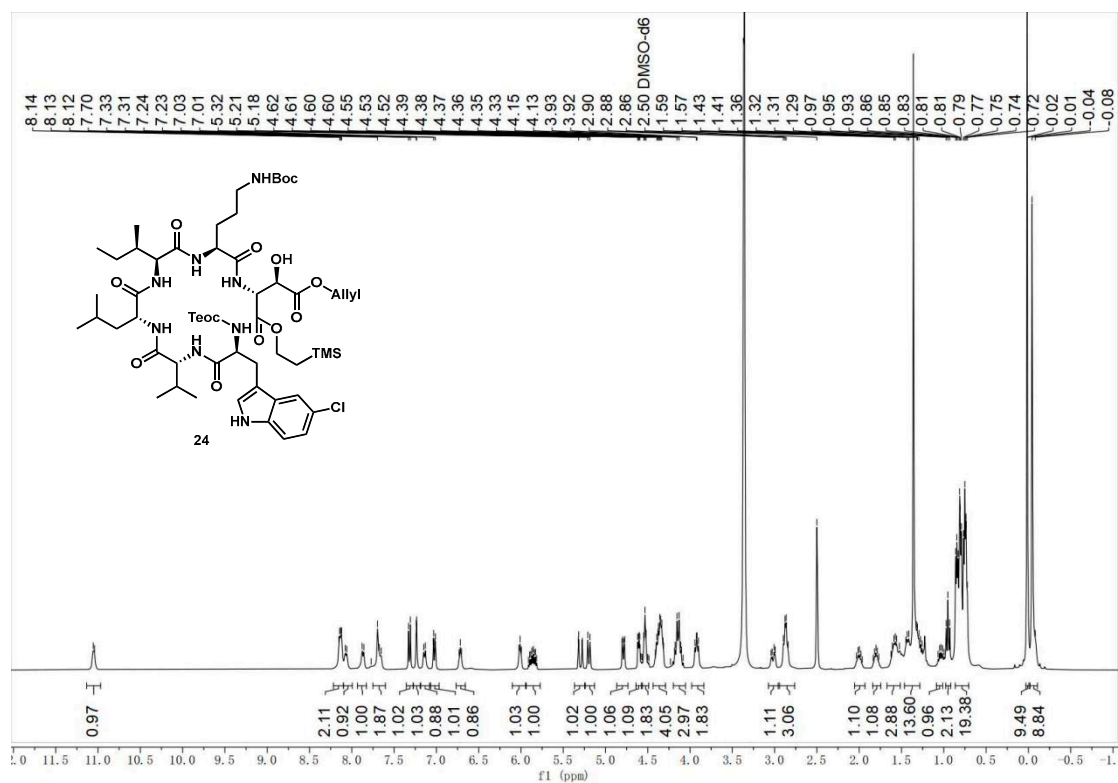
**<sup>1</sup>H NMR spectra for 23 (MeOD)**



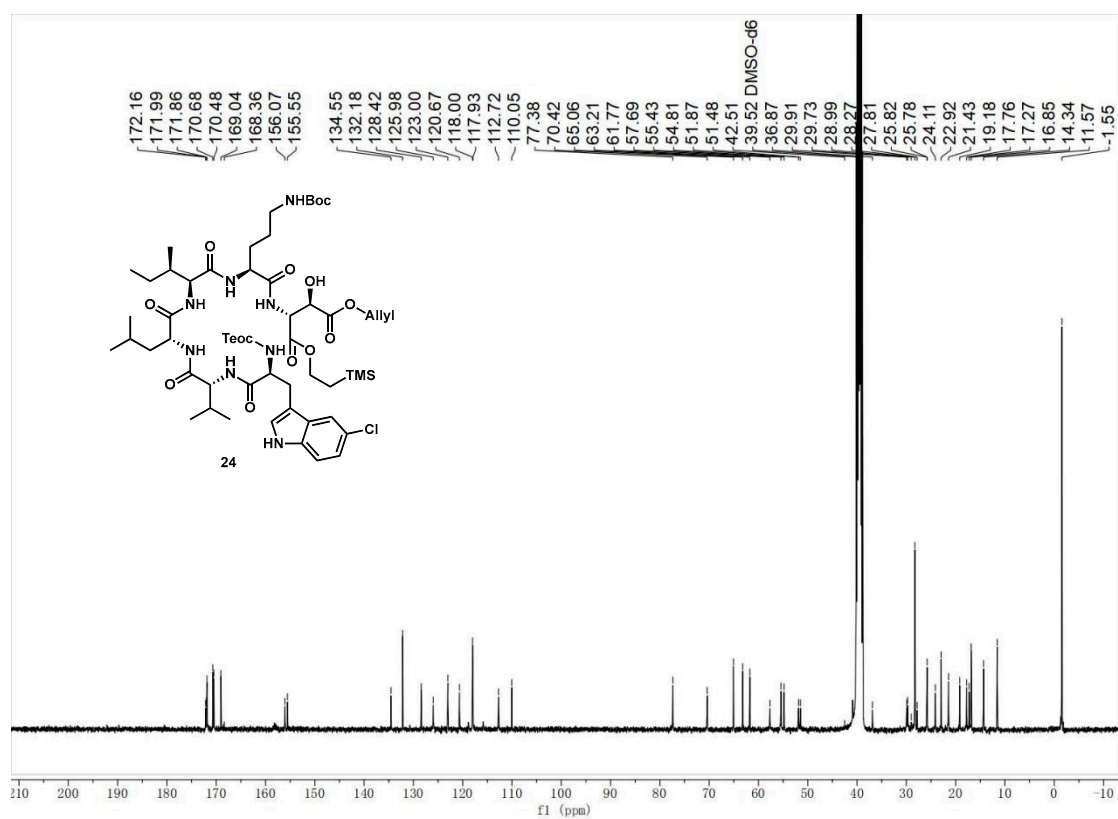
**<sup>13</sup>C NMR spectra for 23 (MeOD)**



**<sup>1</sup>H NMR spectra for 24 (DMSO-*d*<sub>6</sub>)**



**<sup>13</sup>C NMR spectra for 24 (DMSO-*d*<sub>6</sub>)**



Chemical structure of compound S9 is shown above the spectrum. The structure features a 5-chloro-1H-indole-3-yl group, a 2-hydroxy-3-allyloxypropanamide moiety, and a complex amide chain including a Boc-protected amine and a 2-methyl-4-ethylbutanamide derivative.

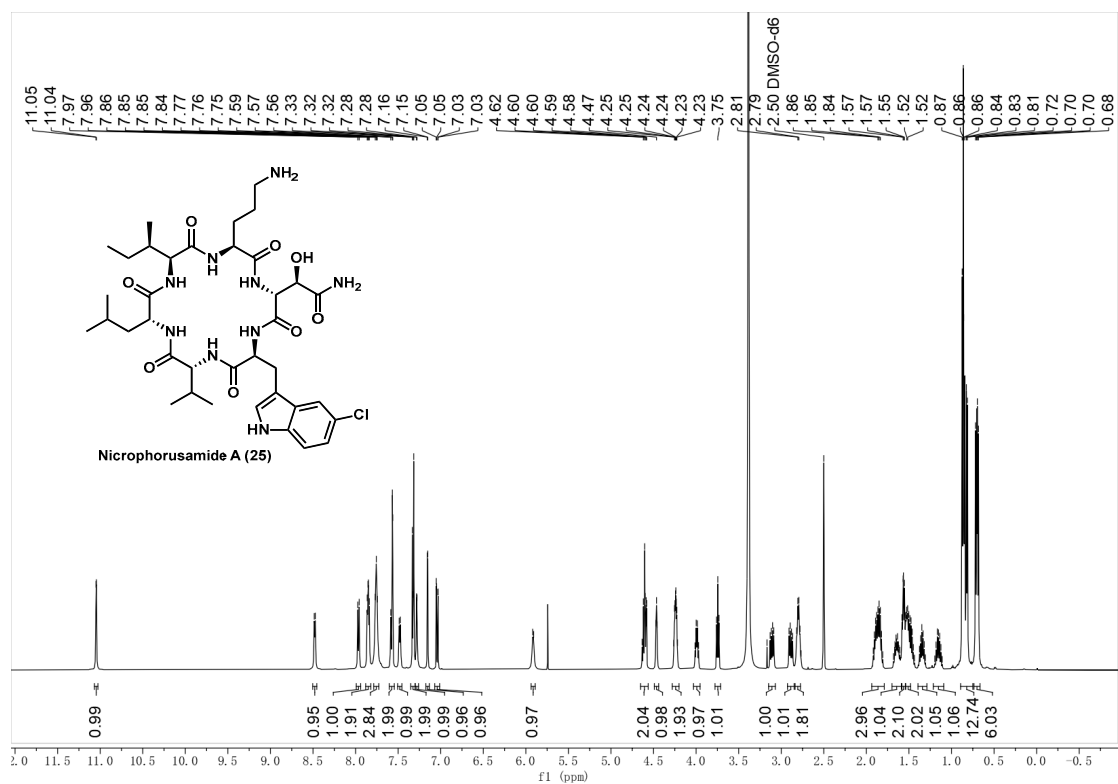
<sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>) of compound S9. The x-axis represents the chemical shift in ppm, ranging from 11.04 to -0.62. The spectrum shows several peaks, with integration values provided below the baseline.

Integration values (from left to right): 1.03, 0.94, 0.99, 0.97, 0.98, 0.97, 0.99, 0.85, 1.00, 0.98, 1.01, 0.91, 1.15, 1.00, 0.99, 1.00, 4.03, 1.98, 1.01, 1.00, 1.04, 3.08, 2.03, 1.01, 3.01, 1.24, 10.00, 2.02, 1.13, 12.07, 5.80.

Chemical shift values (from left to right): 11.04, 11.03, 8.15, 8.13, 7.57, 7.57, 7.32, 7.31, 7.17, 7.16, 7.05, 7.05, 7.03, 7.03, 5.31, 5.28, 5.27, 5.19, 5.18, 5.17, 4.60, 4.59, 4.56, 4.56, 4.54, 4.54, 4.53, 4.53, 4.52, 4.51, 4.23, 3.79, 2.90, 2.89, 2.50 (DMSO-d<sub>6</sub>), 1.89, 1.88, 1.57, 1.56, 1.55, 1.55, 1.53, 1.38, 1.36, 1.30, 1.05, 0.88, 0.87, 0.86, 0.84, 0.83, 0.82, 0.81, 0.65, 0.63, 0.62.

Chemical structure of compound **S9** is shown above the corresponding <sup>13</sup>C NMR spectrum. The structure is a complex molecule featuring a central amide linkage connecting a substituted benzamide derivative (with a 4-chlorophenyl group) to a substituted amide derivative (with a 4-chlorophenyl group). The molecule also contains a 4-chlorophenyl group, a 4-chlorophenyl group, and a 4-chlorophenyl group. The <sup>13</sup>C NMR spectrum (400 MHz, DMSO-d<sub>6</sub>) displays peaks corresponding to the structure, with chemical shifts ranging from approximately 10 to 180 ppm. The spectrum is divided into two main regions: the aromatic/amide region (10-180 ppm) and the aliphatic region (10-40 ppm). The aromatic/amide region shows peaks at 171.97, 171.33, 171.25, 171.16, 171.07, 170.52, 168.65, 155.58, 134.56, 132.36, 128.38, 125.56, 123.00, 120.76, 117.80, 117.59, 112.77, 109.61, 77.35, 70.05, 64.89, 59.71, 56.50, 56.03, 55.33, 53.98, 53.25, and 51.72 ppm. The aliphatic region shows peaks at 39.52, 36.26, 29.15, 28.25, 27.52, 26.81, 26.22, 25.67, 24.27, 22.67, 22.12, 18.84, 17.97, 14.47, and 11.37 ppm. The solvent peak for DMSO-d<sub>6</sub> is observed at 39.52 ppm.

**<sup>1</sup>H NMR spectra for nicrophorusamide A (25) (DMSO-*d*<sub>6</sub>)**



**<sup>13</sup>C NMR spectra for nicrophorusamide A (25) (DMSO-*d*<sub>6</sub>)**



## 6. References.

- (1) Mudalungu, C. M.; von Torne, W. J.; Voigt, K.; Ruckert, C.; Schmitz, S.; Sekurova, O. N.; Zotchev, S. B.; Sussmuth, R. D. Noursamycins, Chlorinated Cyclohexapeptides Identified from Molecular Networking of *Streptomyces noursei* NTR-SR4. *J Nat Prod* **2019**, *82* (6), 1478-1486. DOI: 10.1021/acs.jnatprod.8b00967.
- (2) Shin, Y. H.; Bae, S.; Sim, J.; Hur, J.; Jo, S. I.; Shin, J.; Suh, Y. G.; Oh, K. B.; Oh, D. C. Nicrophorusamides A and B, Antibacterial Chlorinated Cyclic Peptides from a Gut Bacterium of the Carrion Beetle *Nicrophorus concolor*. *J Nat Prod* **2017**, *80* (11), 2962-2968. DOI: 10.1021/acs.jnatprod.7b00506.