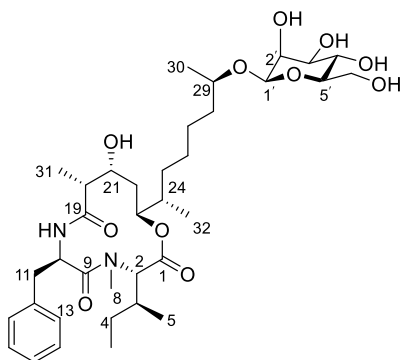


# Supplementary Information

## Table of Contents

1. NMR comparison of natural and synthetic colletotrichamide A and colletopeptide A
2. NMR spectra

1. NMR comparison of natural and synthetic colletotrichamide A and colletopeptide A



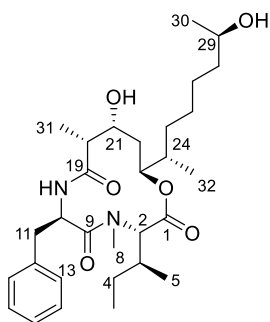
Colletotrichamide A

No.	Colletotrichamide A		
	Natural ( $\delta_3$ )	Synthetic ( $\delta_4$ )	$\Delta\delta=\delta_3-\delta_4$
1	168.6	168.6	0.0
2	59.7	59.8	-0.1
3	29.8	29.8	0.0
4	23.3	23.3	0.0
5	9.8	9.7	0.1
6	15.3	15.3	0.0
7			
8	29.8	29.8	0.0
9	173.0	173.0	0.0
10	49.6	49.6	0.0
11	35.8	35.8	0.0
12	137.7	137.7	0.0
13	129.1	129.1	0.0
14	128.2	128.2	0.0
15	126.4	126.4	0.0
16	128.2	128.2	0.0
17	129.1	129.1	0.0
18			
19	173.5	173.5	0.0
20	46.3	46.3	0.0
21	67.0	67.0	0.0
22	31.4	31.5	-0.1
23	76.0	76.0	0.0
24	33.5	33.5	0.0
25	31.7	31.7	0.0
26	26.1	26.1	0.0
27	25.3	25.3	0.0
28	36.9	36.9	0.0
29	72.3	72.4	-0.1

<b>30</b>	19.2	19.2	0.0
<b>31</b>	7.5	7.5	0.0
<b>32</b>	15.6	15.6	0.0
<b>1'</b>	97.5	97.5	0.0
<b>2'</b>	71.2	71.3	-0.1
<b>3'</b>	73.9	73.9	0.0
<b>4'</b>	67.3	67.3	0.0
<b>5'</b>	77.4	77.4	0.0
<b>6'</b>	61.4	61.5	-0.1

No.	Colletotrichamide A		
	Natural ( $\delta_1$ ) $\delta H$ (mult., <i>J</i> , Hz)	Synthetic ( $\delta_2$ ) $\delta H$ (mult., <i>J</i> , Hz)	$\Delta\delta=\delta_1-\delta_2$ $\delta H$ (mult., <i>J</i> , Hz)
<b>1</b>			
<b>2</b>	4.77(d, 11.5)	4.77(d, 11.6)	0.00
<b>3</b>	1.83 (m)	1.86 (m)	-0.03
<b>4</b>	0.95 (m)	0.95 (m)	0.00
	0.68 (m)	0.67 (m)	0.01
<b>5</b>	0.68(m)	0.67 (m)	0.01
<b>6</b>	0.79 (d, 6.5)	0.79 (d, 6.4)	0.00
<b>7</b>			
<b>8</b>	2.66 (s)	2.66 (s)	0.00
<b>9</b>			
<b>10</b>	5.06 (dt, 9.5, 6.0)	5.06 (dt, <i>J</i> = 9.4, 6.2)	0.00
<b>11</b>	3.08 (dd, 13.0, 9.5)	3.08 (dd, 12.9, 9.4)	0.00
	2.84 (dd, 13.0, 6.0)	2.84 (dd, 12.8, 6.2)	0.00
<b>12</b>			
<b>13</b>	7.22 (d, 7.0)	7.23 (d, 4.0)	-0.01
<b>14</b>	7.24 (d, 7.0)	7.26 (d, 7.1)	-0.02
<b>15</b>	7.19 (m)	7.19 (m)	0.00
<b>16</b>	7.24 (d, 7.0)	7.26 (d, 7.1)	-0.02
<b>17</b>	7.22 (d, 7.0)	7.23 (d, 4.0)	-0.01
<b>18</b>	8.61 (d, 9.5)	8.58 (d, 9.5)	0.03
<b>19</b>			
<b>20</b>	2.57 (dq, 6.5, 3.5)	2.58 (dt, 6.9, 4.0),	-0.01
<b>21</b>	3.87 (ddd, 8.5, 5.5, 3.5)	3.88 (d, 8.9)	-0.01
<b>21-OH</b>	4.51 (d, 5.5)	4.50 (d, 5.1)	0.01
<b>22</b>	1.51 (m)	1.51 (m)	0.00
	1.44 (dd, 15.0, 3.5)	1.44 (d, 17.1)	0.00
<b>23</b>	4.63 (dt, 10.5, 3.0)	4.64 (d, 10.0),	-0.01
<b>24</b>	1.86 (m)	1.86 (m)	0.00
<b>25</b>	1.55 (m)	1.51 (m)	0.04

	0.99 (dd, 10.5, 3.0)	0.98 (s)	0.01
<b>26</b>	1.23 (m)	1.23 (s)	0.00
	1.17 (m)	1.16 (m)	0.01
<b>27</b>	1.26 (m)	1.26 (m)	0.00
<b>28</b>	1.51 (m)	1.51 (m)	0.00
	1.34 (dt, 13.5, 6.5)	1.34 (d, 6.8)	0.00
<b>29</b>	3.77(sextet, 6.0)	3.77 (q, 6.2)	0.00
<b>30</b>	1.05 (d, 6.0)	1.06 (d, 6.1)	-0.01
<b>31</b>	0.84 (d, 6.5)	0.84 (d, 6.8)	0.00
<b>32</b>	0.71 (d, 6.5)	0.71 (d, 6.5)	0.00
<b>1'</b>	4.43 (s)	4.43 (s)	0.00
<b>2'</b>	3.54 (dd, 5.0, 2.0)	3.54 (s)	0.00
<b>2'-OH</b>	4.18 (d, 5.0)	4.17 (d, 4.3)	0.01
<b>3'</b>	3.26 (m)	3.26 (m)	0.00
<b>3'-OH</b>	4.53 (d, 5.0)	4.53 (s)	0.00
<b>4'</b>	3.26 (m)	3.26 (m)	0.00
<b>4'-OH</b>	4.71 (d, 4.5)	4.71 (s)	0.00
<b>5'</b>	3.01 (ddd, 8.5, 5.5, 2.0)	3.01 (dt, 6.5, 3.0)	0.00
<b>6'</b>	3.67 (ddd, 11.5, 5.5, 2.0)	3.67 (ddd, 11.5, 5.3, 2.2)	0.00
	3.44 (dt, 11.5, 5.5)	3.45 (m)	-0.01
<b>6'-OH</b>	4.37 (t, 5.5)	4.35 (t, 5.5)	0.02

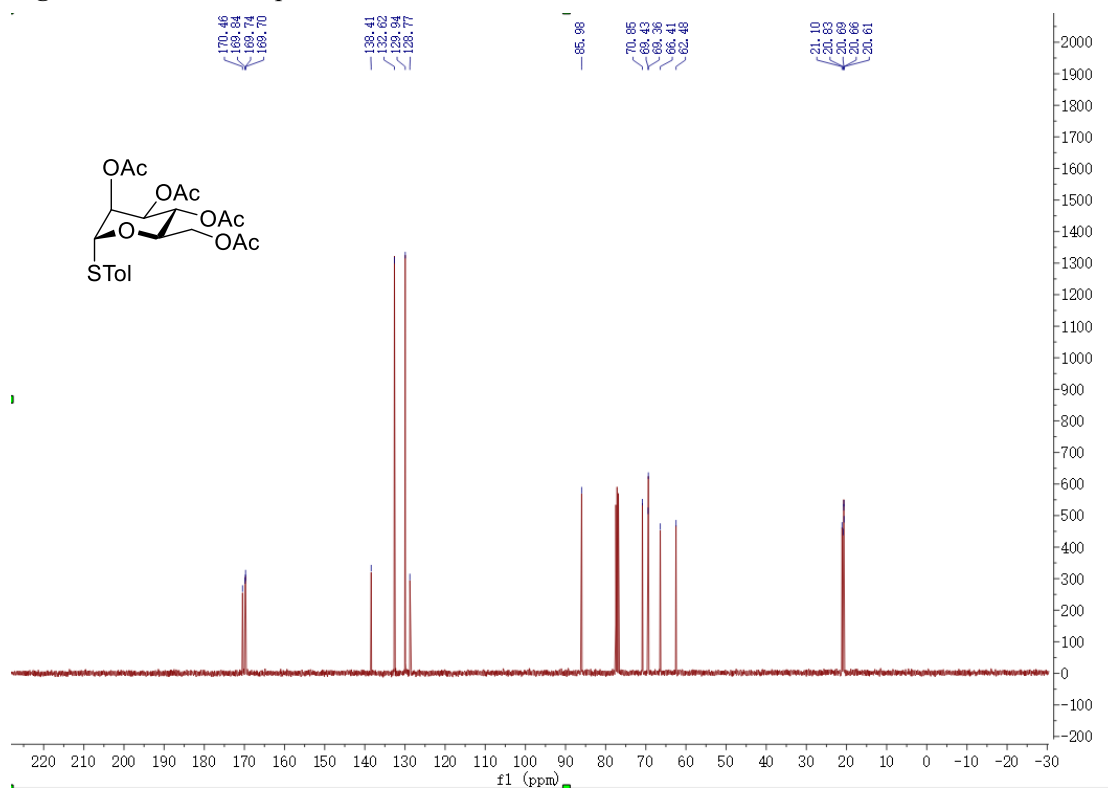


Colleteopeptide A

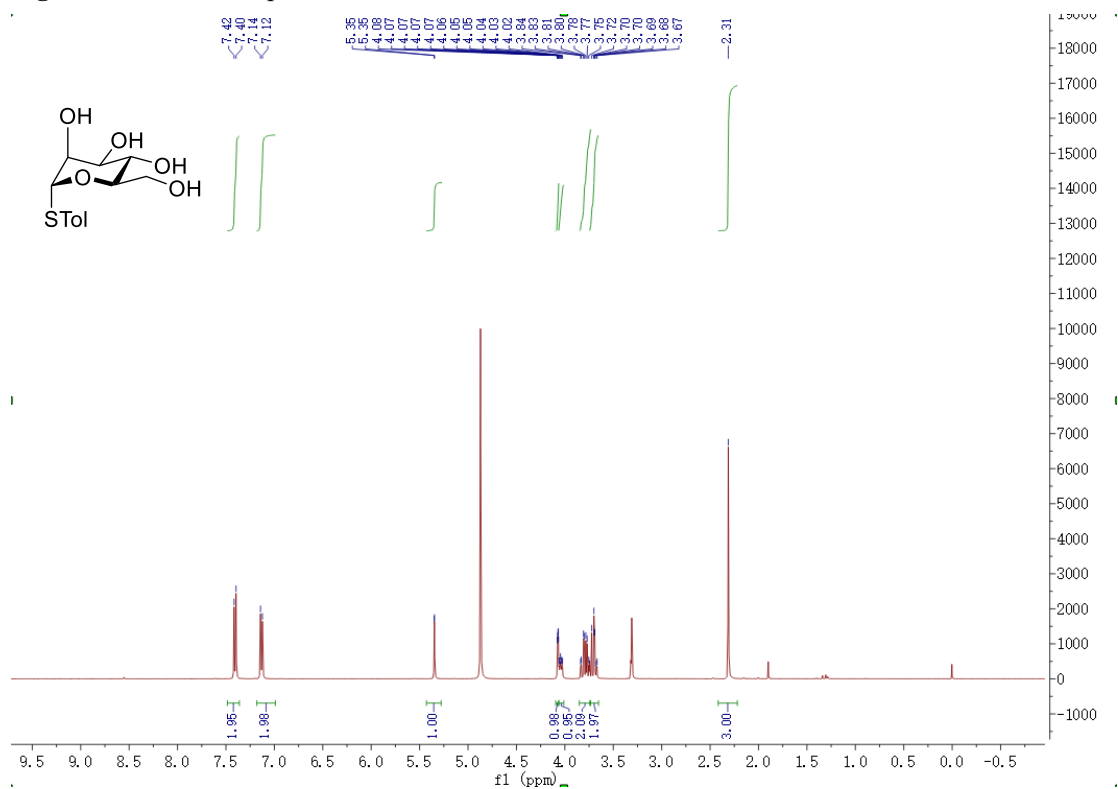
No.	Colleteopeptide A		
	Natural ( $\delta_3$ )	Synthetic ( $\delta_4$ )	$\Delta\delta=\delta_3-\delta_4$
1	170.1	170.1	0.0
2	62.1	62.1	0.0
3	31.7	31.7	0.0
4	24.9	24.9	0.0
5	10.3	10.3	0.0
6	15.9	15.9	0.0
7			
8	30.8	30.9	-0.1
9	175.2	175.2	0.0
10	51.8	51.8	0.0
11	37.4	37.4	0.0
12	138.4	138.4	0.0
13	130.3	130.3	0.0
14	129.6	129.6	0.0
15	127.9	127.9	0.0
16	129.6	129.6	0.0
17	130.3	130.3	0.0
18			
19	176.4	176.4	0.0
20	48.7	48.7	0.0
21	69.1	69.1	0.0
22	32.7	32.7	0.0
23	77.8	77.9	-0.1
24	35.3	35.3	0.0
25	33.3	33.3	0.0
26	27.6	27.6	0.0
27	27.1	27.1	0.0
28	40.2	40.2	0.0
29	68.5	68.6	-0.1
30	23.5	23.5	0.0
31	7.8	7.8	0.0
32	16.3	16.3	0.0

No.	Colletopeptide A		
	Natural ( $\delta_1$ ) $\delta H$ (mult., J, Hz)	Synthetic ( $\delta_2$ ) $\delta H$ (mult., J, Hz)	$\Delta\delta=\delta_1-\delta_2$ $\delta H$ (mult., J, Hz)
1			
2	4.84 (d, 11.6)	4.85 (s)	-0.01
3	1.89 (m)	1.89 (m)	0.00
4	0.95 (m)	0.95 (m)	0.00
	0.75 (m)	0.74 (m)	0.01
5	0.74 (d, 3.8)	0.74 (d, 3.5)	0.00
6	0.86 (d, 6.5)	0.86 (d, 6.5)	0.00
7			
8	2.71 (s)	2.71 (s)	0.00
9			
10	5.26 (dd, 10.8, 5.3)	5.26 (dd, J = 10.7, 5.3)	0.00
11	3.22 (dd, 12.8, 10.8)	3.22 (dd, 12.8, 10.7)	0.00
	2.91 (dd, 12.8, 5.3)	2.91 (dd, 12.8, 5.3)	0.00
12			
13	7.26 (overlap)	7.26 (m)	0.00
14	7.26 (overlap)	7.26 (m)	0.00
15	7.21 (m)	7.21 (m)	0.00
16	7.26 (overlap)	7.26 (m)	0.00
17	7.26 (overlap)	7.26 (m)	0.00
18			
19			
20	2.65 (m)	2.66 (m)	-0.01
21	4.03 (dd, 8.4, 3.9)	4.04 (dd, 8.3, 3.6)	-0.01
21-OH		4.55 (s)	
22	1.69 (ddd, 15.7, 8.4, 2.0)	1.69 (ddd, 15.8, 8.4, 2.2)	0.00
	1.59 (dd, 15.7, 3.9)	1.59 (m)	0.00
23	4.76 (d-like, 10.4)	4.76 (ddd, 10.6, 4.3, 2.2)	0.00
24	1.98 (m)	1.99 (m)	-0.01
25	1.62 (m)	1.63 (m)	-0.01
	1.05 (m)	1.05 (m)	0.00
26	1.29 (m)	1.30 (m)	-0.01
27	1.36 (overlap)	1.37 (m)	-0.01
28	1.46 (m)	1.47 (m)	-0.01
	1.36 (overlap)	1.37 (m)	-0.01
29	3.70 (m)	3.71 (m)	-0.01
30	1.14 (d, 6.2)	1.14 (d, 6.1)	0.00
31	1.00 (d, 6.8)	1.01 (d, 6.9)	-0.01
32	0.80 (d, 6.6)	0.80 (d, 6.6)	0.00

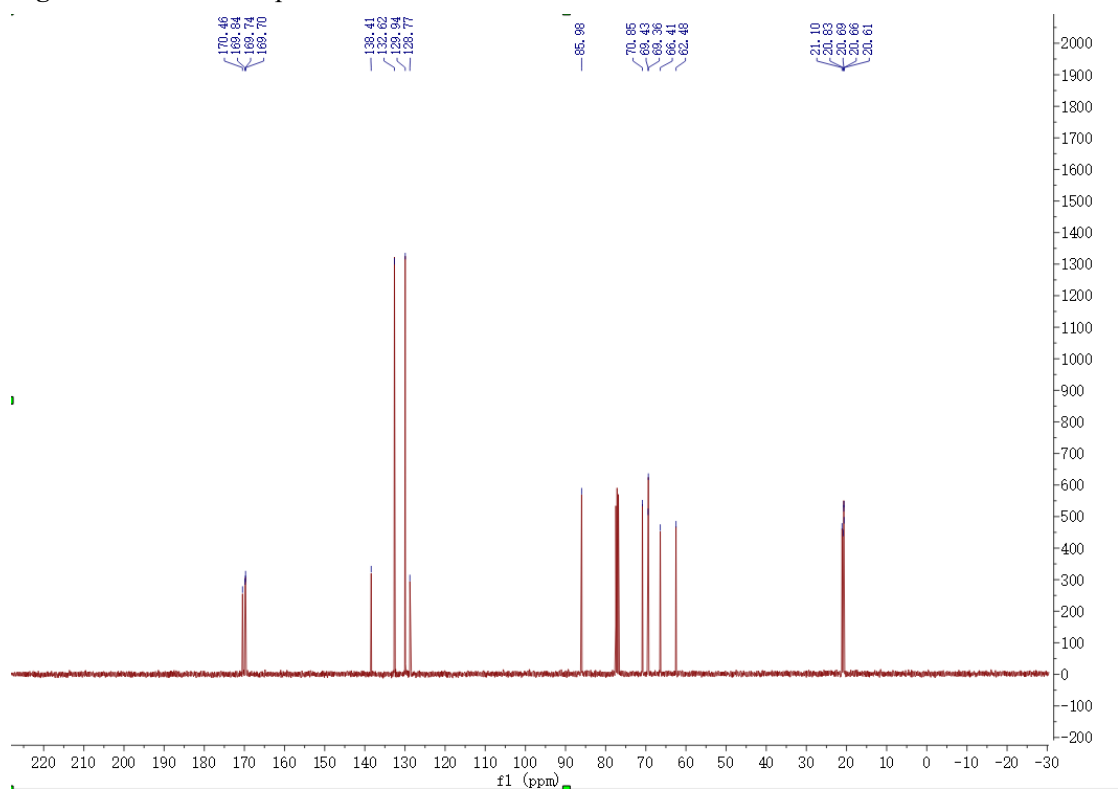
**Figures S1**  $^1\text{H}$  NMR Spectrum of **9**



**Figures S3**  $^1\text{H}$  NMR Spectrum of **10**

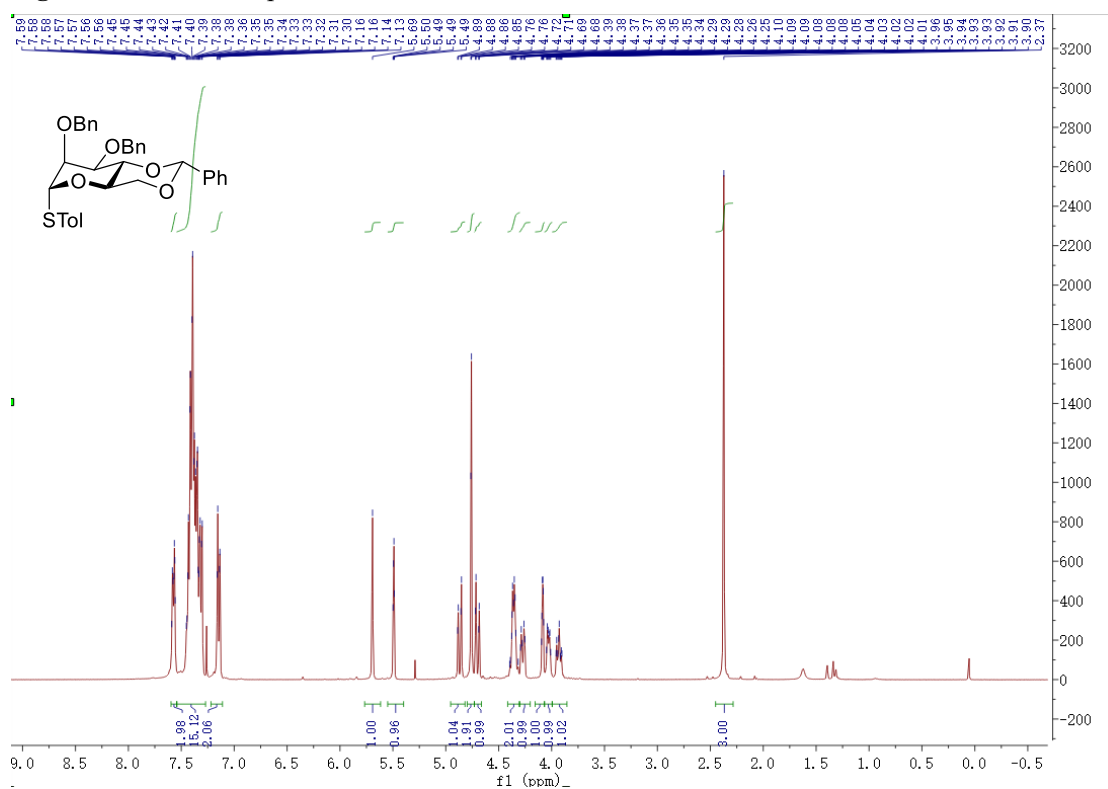


**Figures S4**  $^{13}\text{C}$  NMR Spectrum of **10**

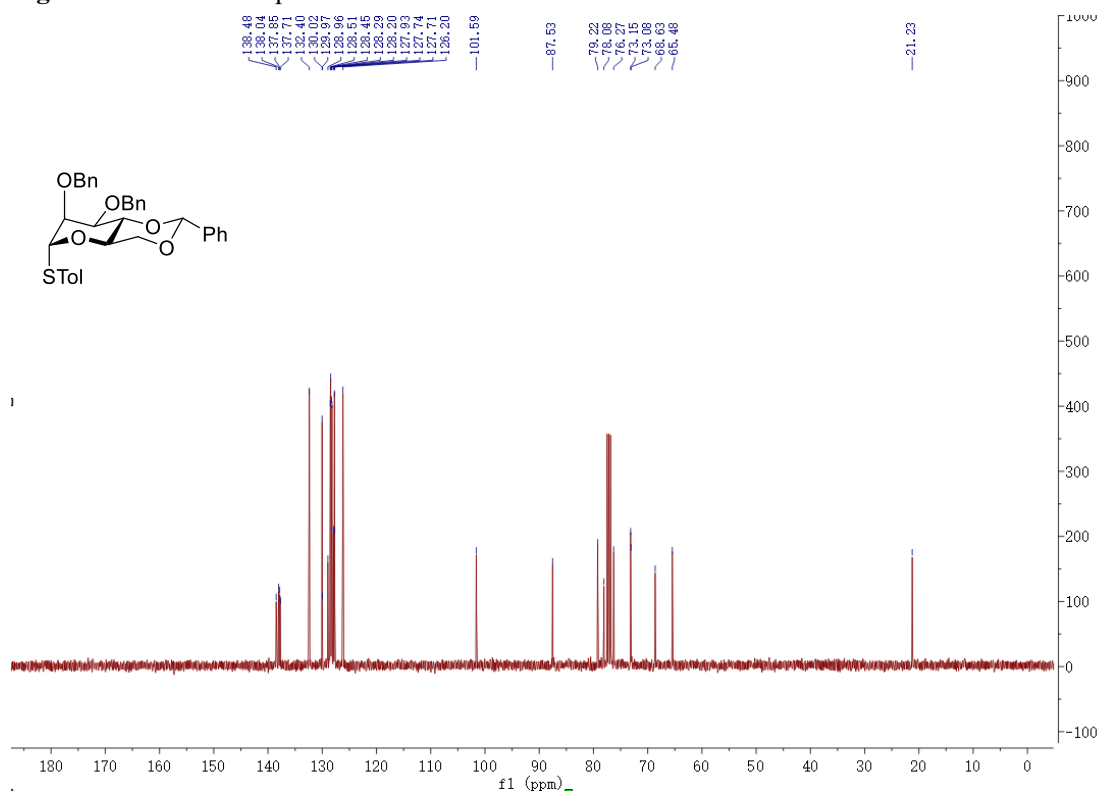




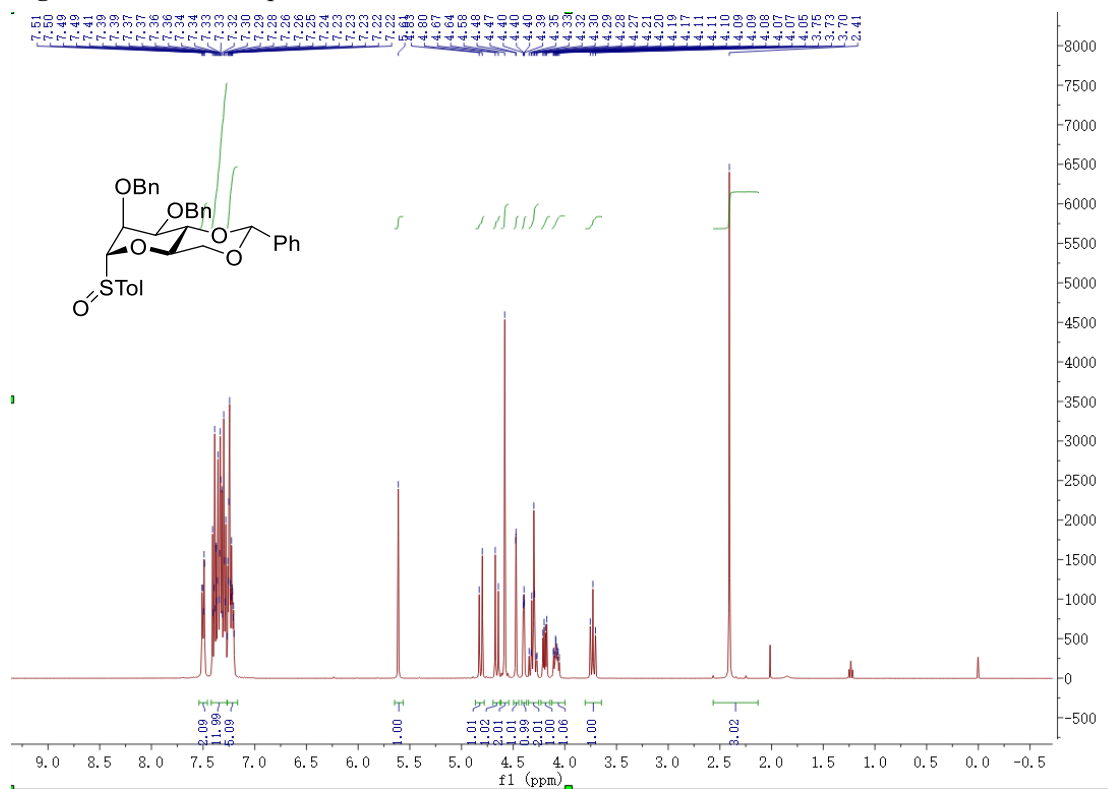
**Figures S5**  $^1\text{H}$  NMR Spectrum of **12**



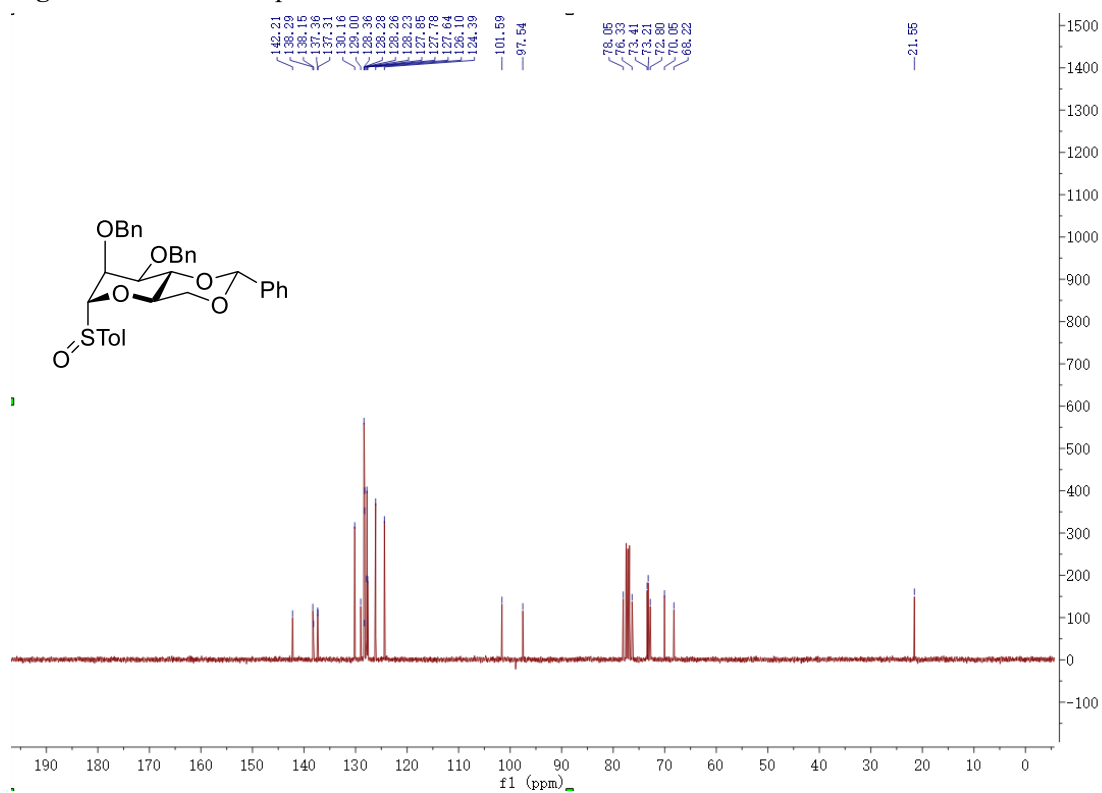
**Figures S6**  $^{13}\text{C}$  NMR Spectrum of **12**



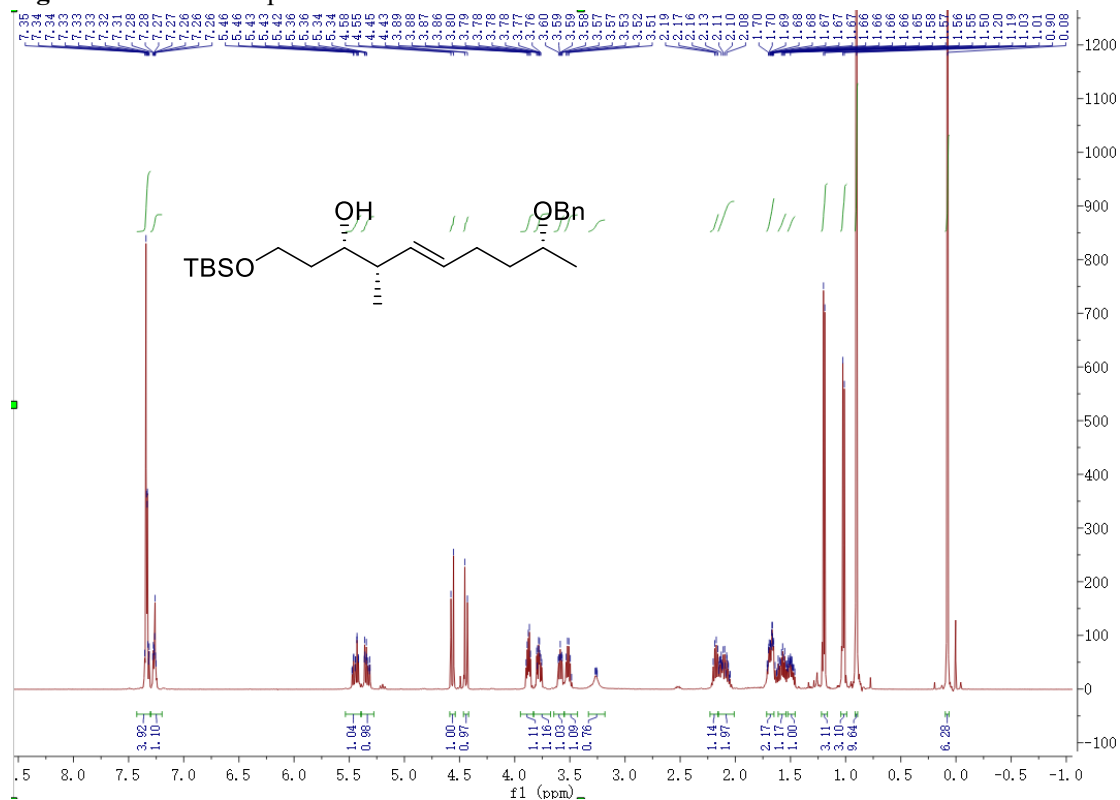
**Figures S7**  $^1\text{H}$  NMR Spectrum of **3**



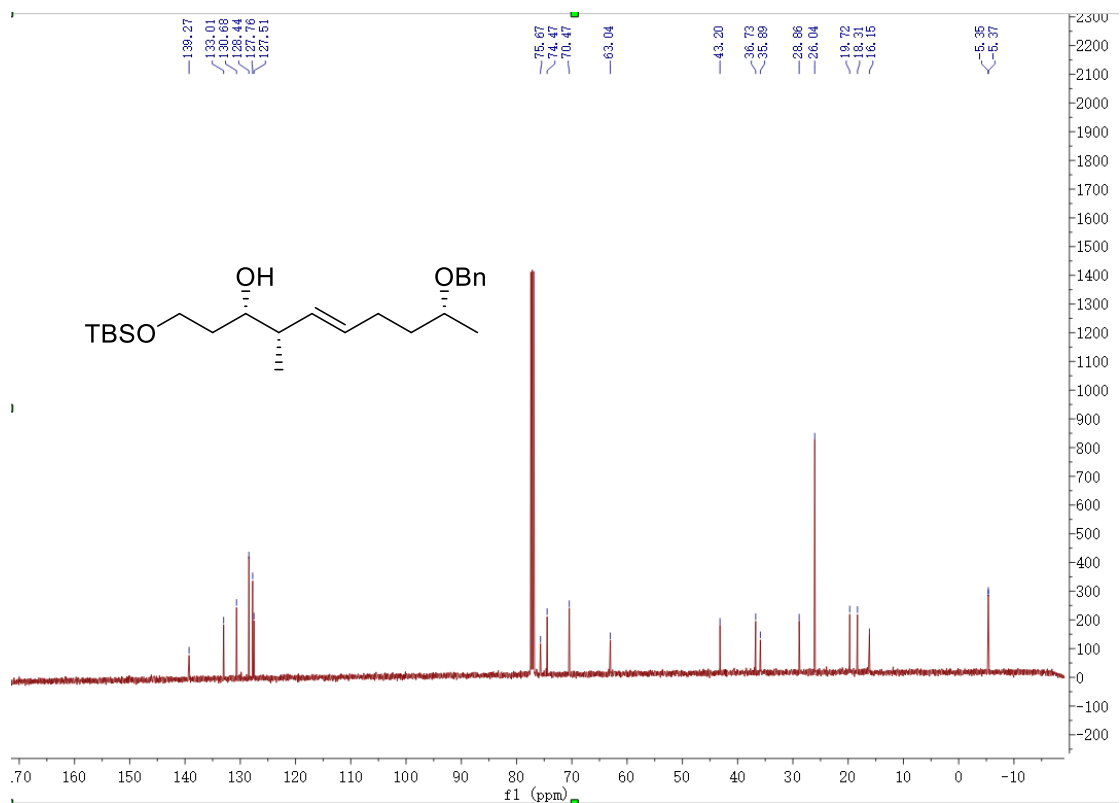
**Figures S8**  $^{13}\text{C}$  NMR Spectrum of **3**



Figures S9  $^1\text{H}$  NMR Spectrum of **5**

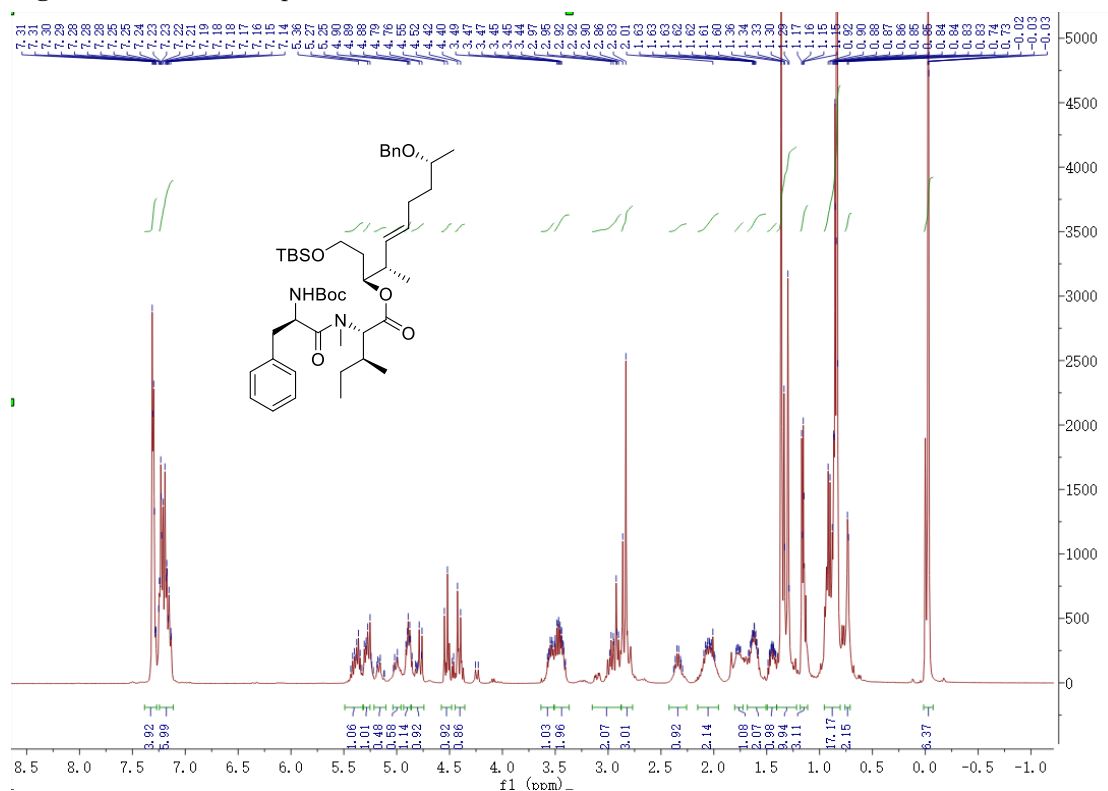


Figures S10  $^{13}\text{C}$  NMR Spectrum of **5**

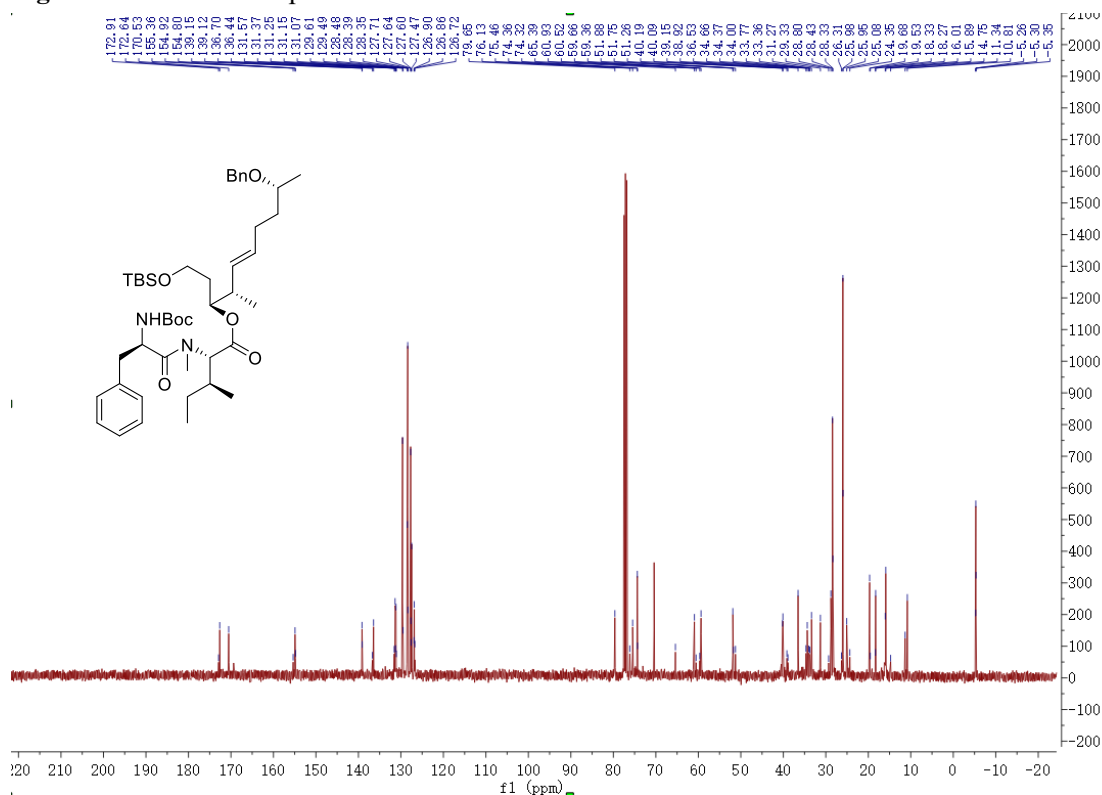


Chemical structure of compound 10 is shown. The <sup>13</sup>C NMR spectrum (f1 (ppm)) displays peaks corresponding to the structure, with labeled chemical shifts (ppm): 171.10, 170.63, 156.07, 155.63, 139.19, 137.48, 136.45, 131.19, 128.37, 127.69, 127.62, 127.45, 80.10, 78.88, 78.37, 74.37, 70.42, 63.47, 62.26, 60.83, 59.54, 58.99, 40.39, 36.58, 34.71, 34.60, 33.27, 32.17, 30.22, 29.56, 28.79, 28.46, 26.02, 24.88, 23.46, 19.68, 19.54, 18.33, 18.29, 16.28, 15.99, 10.77, 10.32, 5.24, and -5.24.

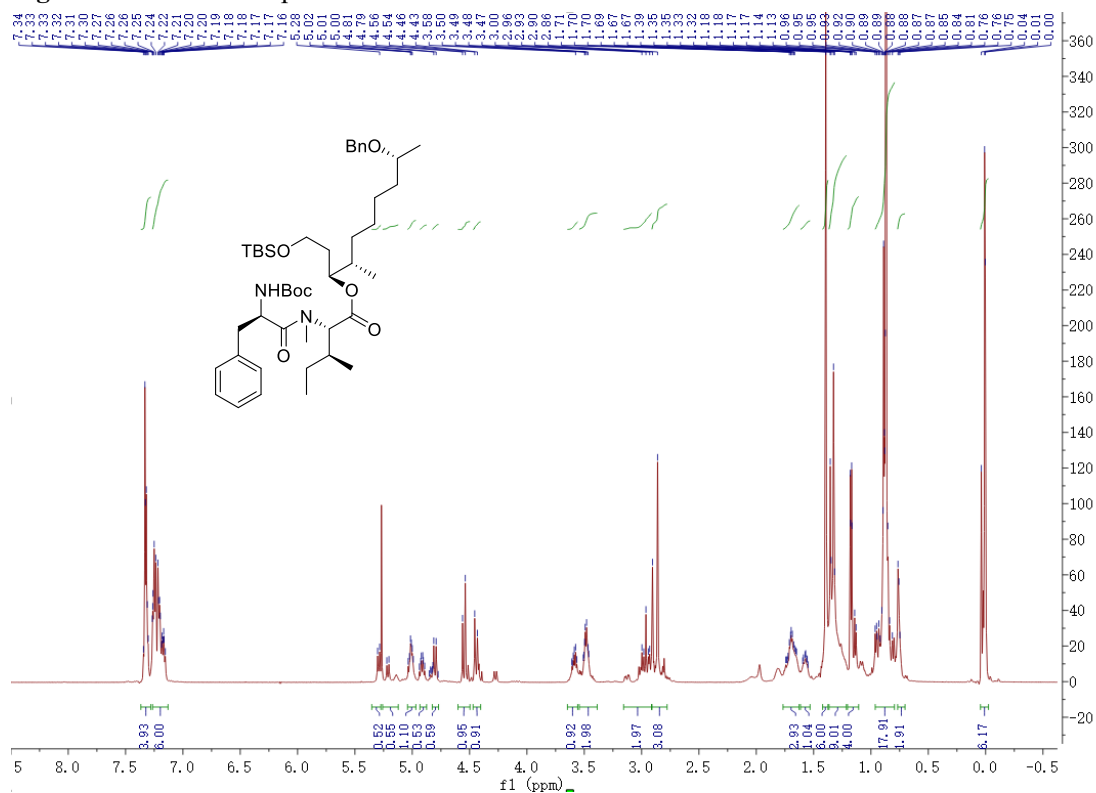
**Figures S13**  $^1\text{H}$  NMR Spectrum of **18**



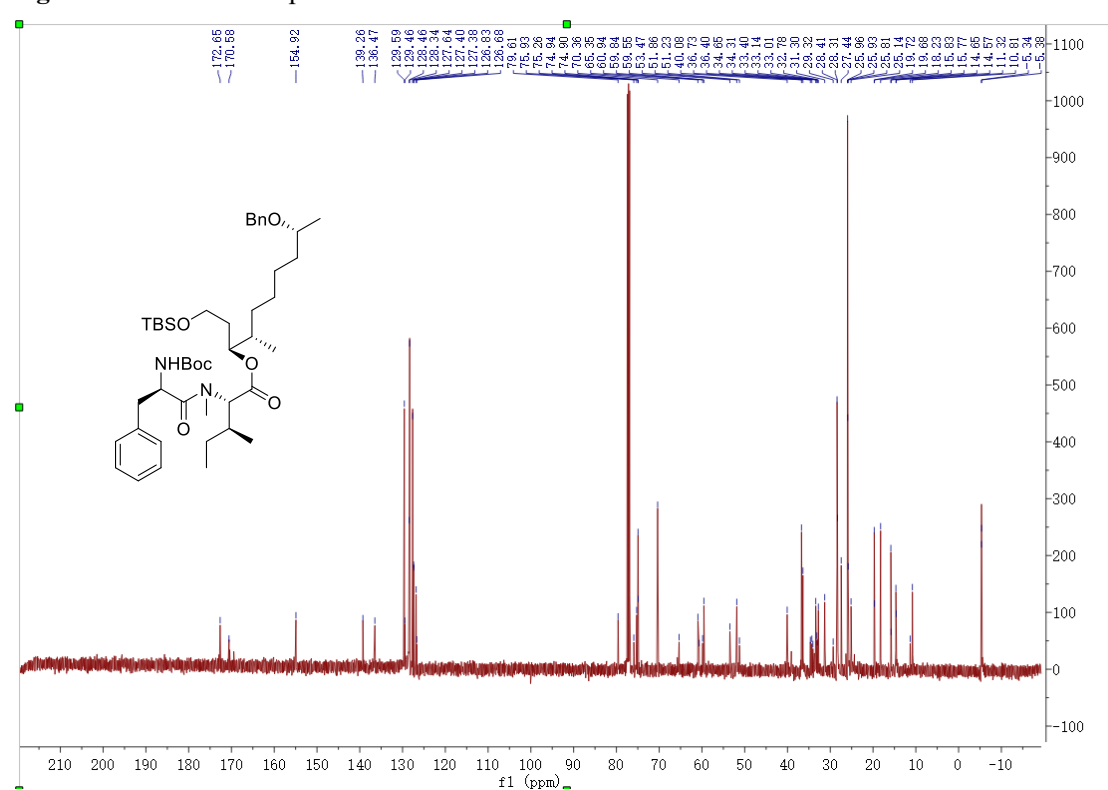
**Figures S14**  $^{13}\text{C}$  NMR Spectrum of **18**



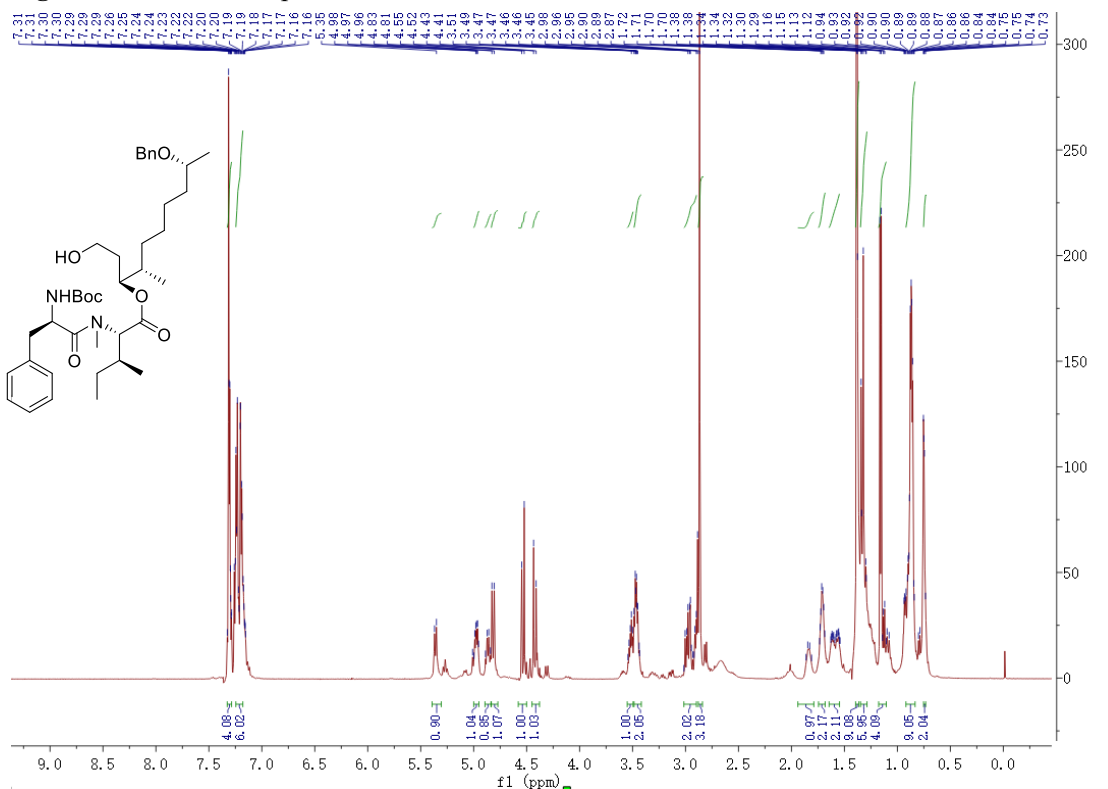
Figures S15  $^1\text{H}$  NMR Spectrum of 19



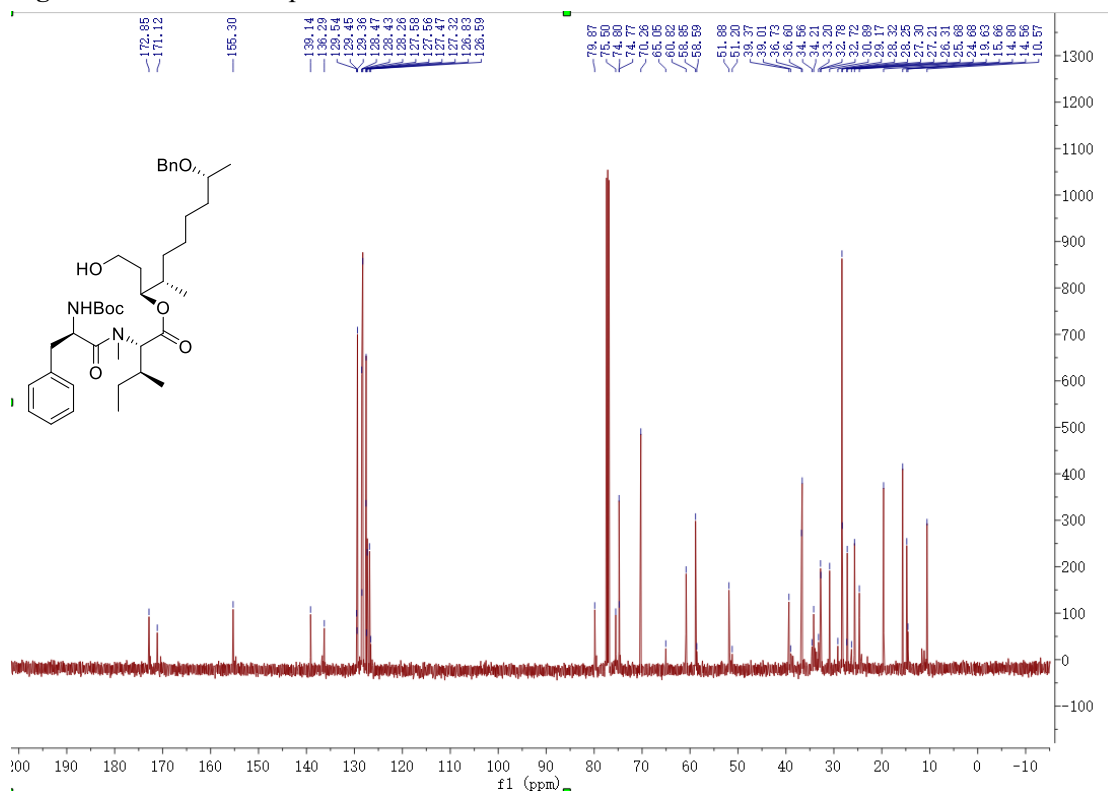
Figures S16  $^{13}\text{C}$  NMR Spectrum of 19



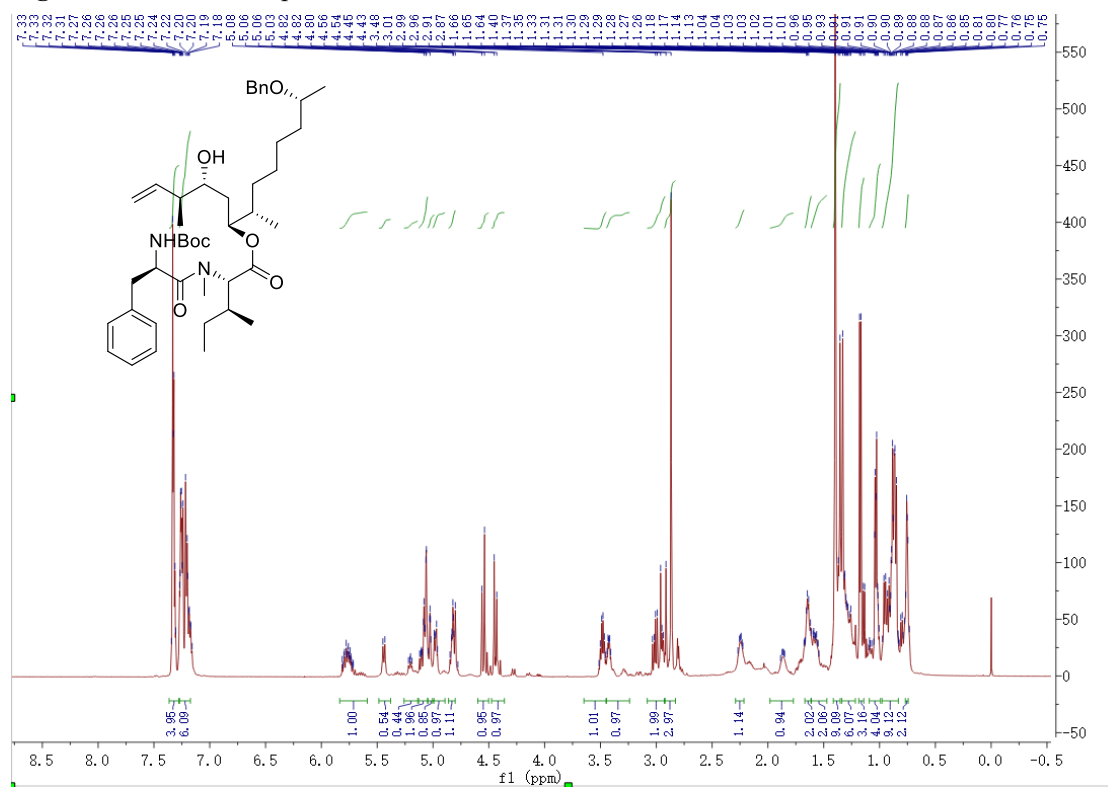
**Figures S17**  $^1\text{H}$  NMR Spectrum of **20**



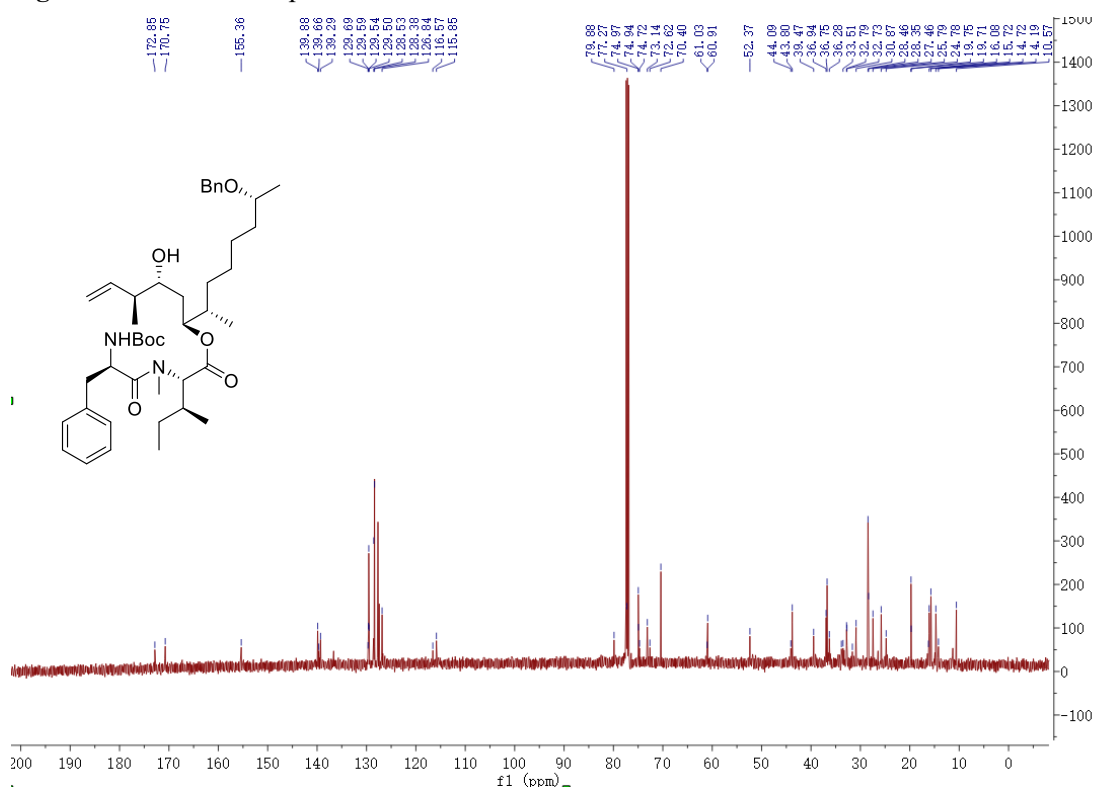
**Figures S18**  $^{13}\text{C}$  NMR Spectrum of **20**



**Figures S19**  $^1\text{H}$  NMR Spectrum of **21**



**Figures S20**  $^{13}\text{C}$  NMR Spectrum of **21**

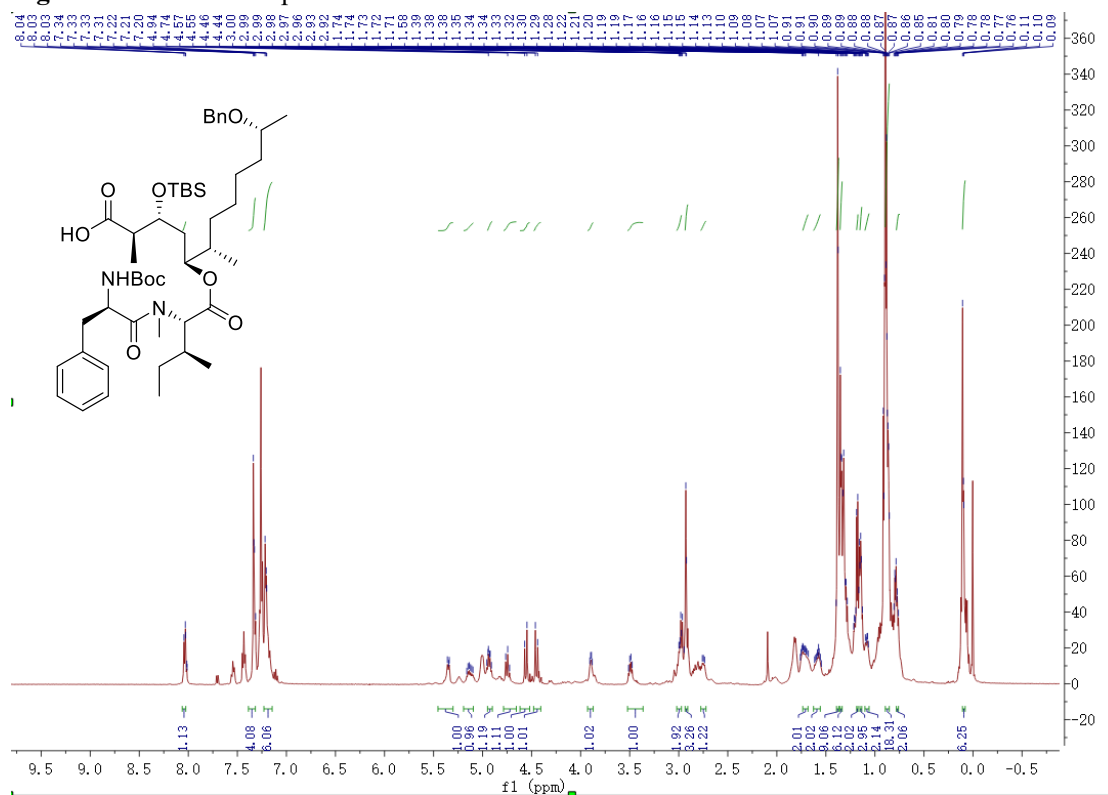




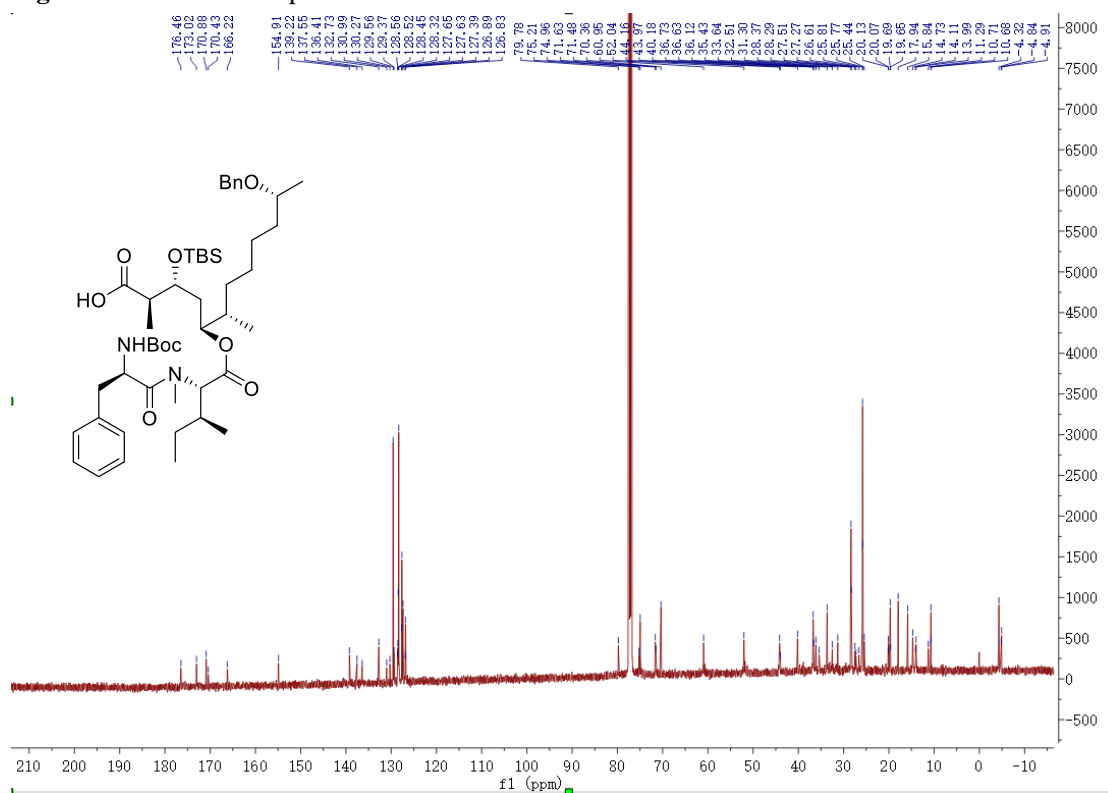
[illegible]

Chemical structure of compound 10 is shown in the top left. The  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>) is displayed below the structure, showing peaks from -10 to 210 ppm. The x-axis is labeled f1 (ppm) and the y-axis represents intensity from 0 to 2100.

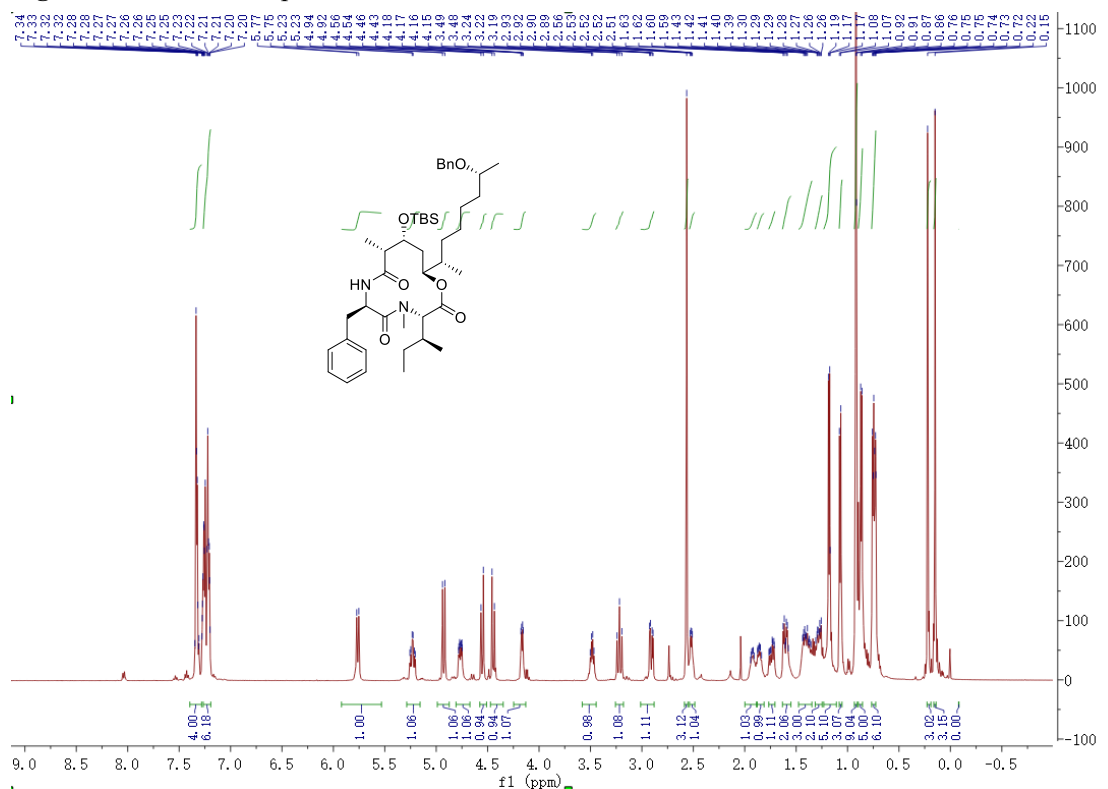
**Figures S23**  $^1\text{H}$  NMR Spectrum of **23**



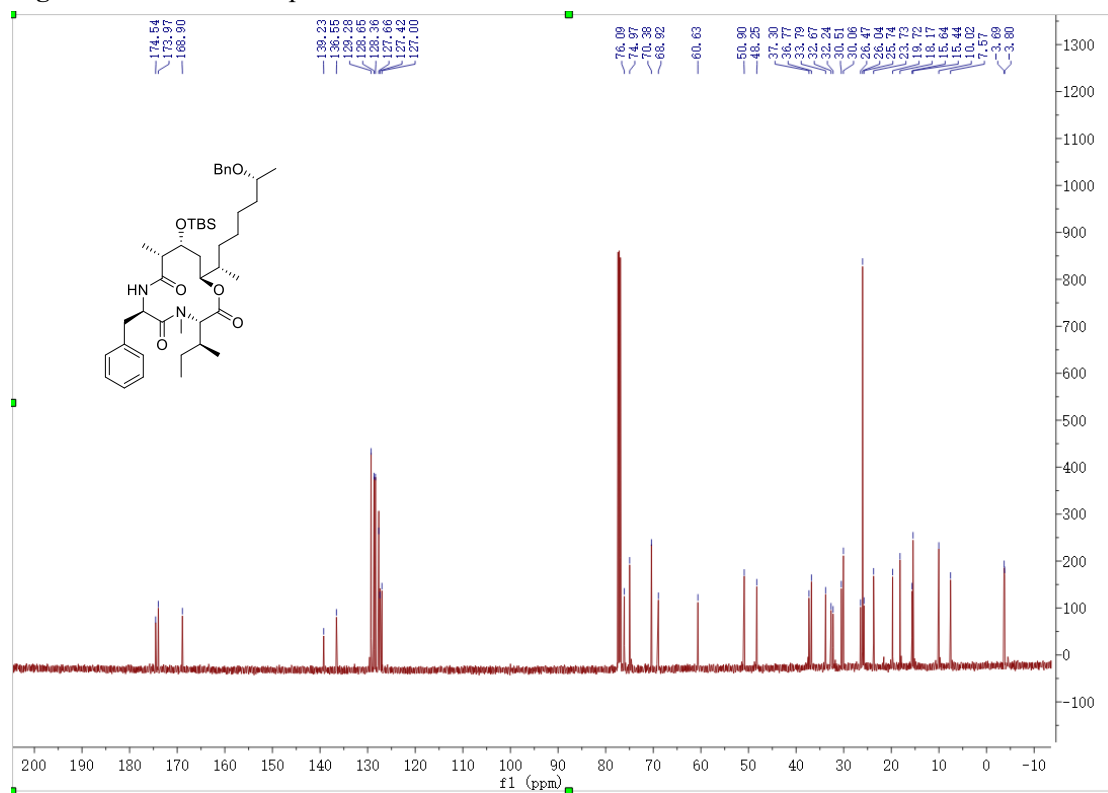
**Figures S24**  $^{13}\text{C}$  NMR Spectrum of **23**



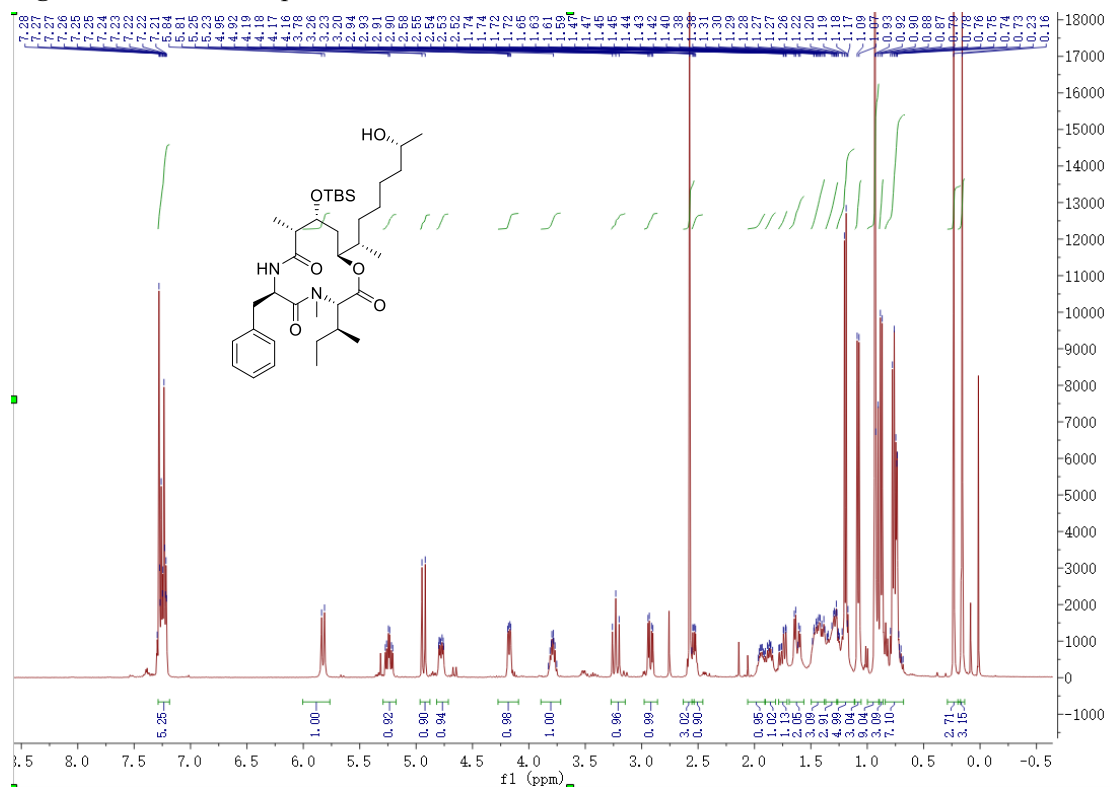
**Figures S25**  $^1\text{H}$  NMR Spectrum of **24**



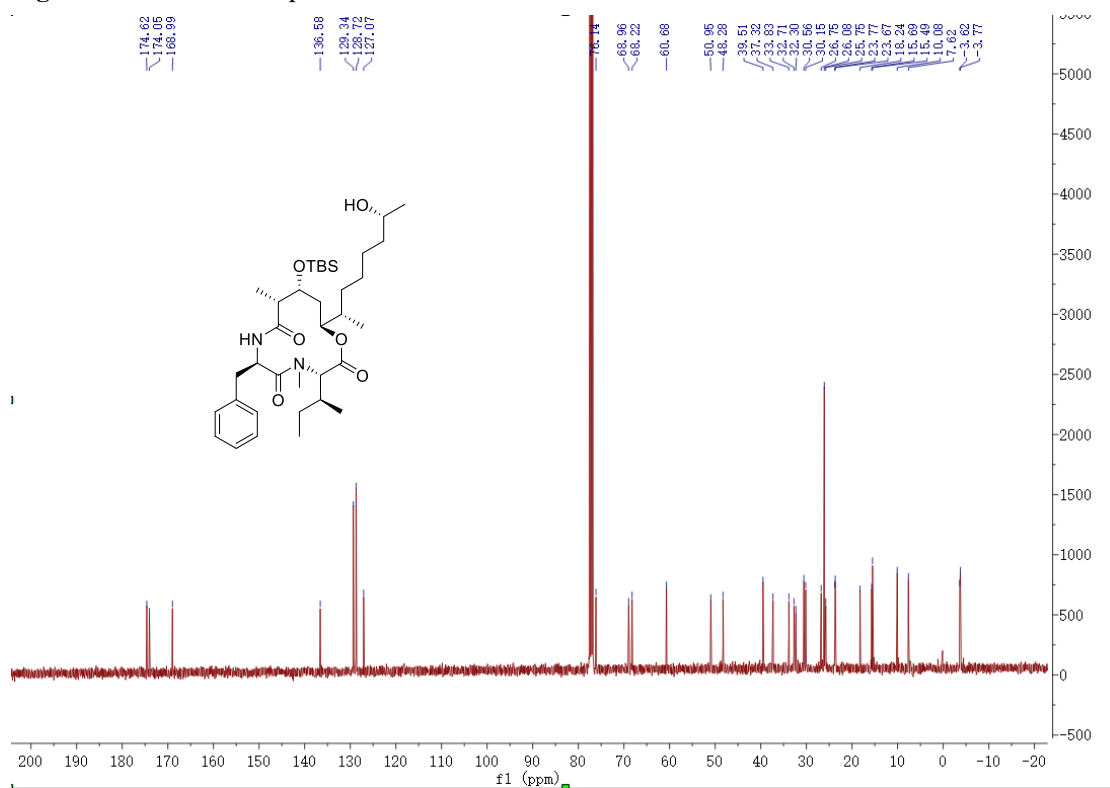
**Figures S26**  $^{13}\text{C}$  NMR Spectrum of **24**



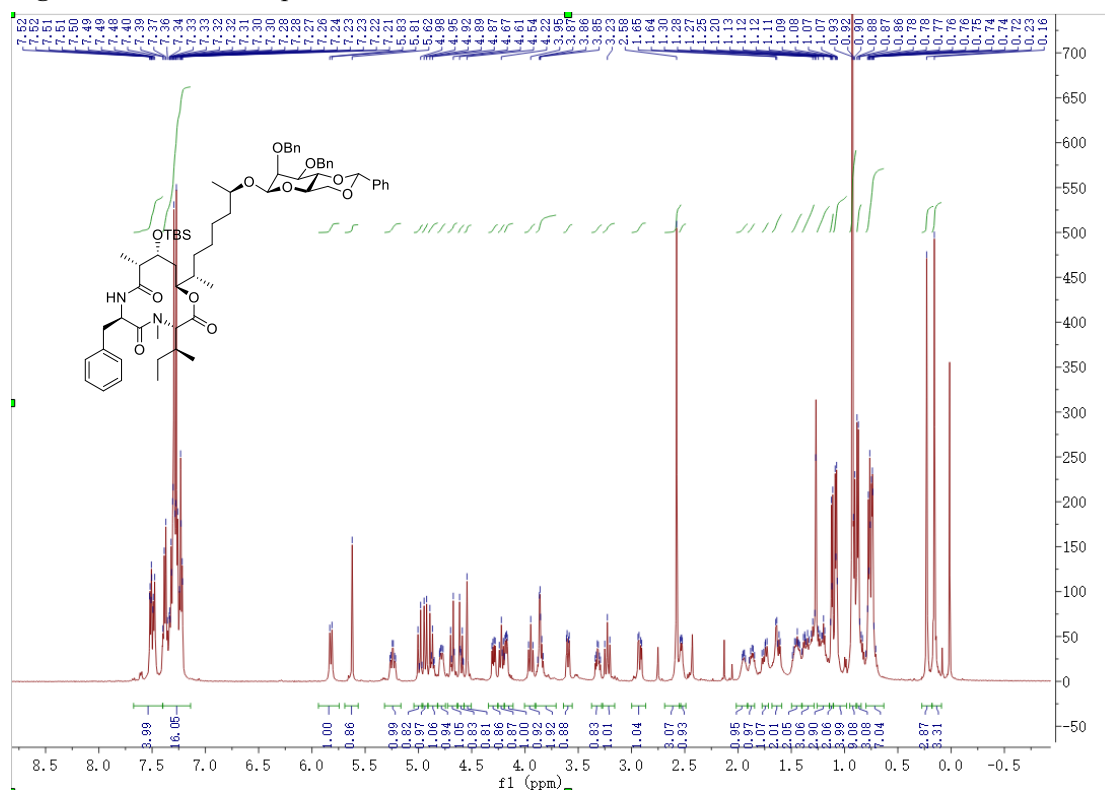
Figures S27  $^1\text{H}$  NMR Spectrum of 4



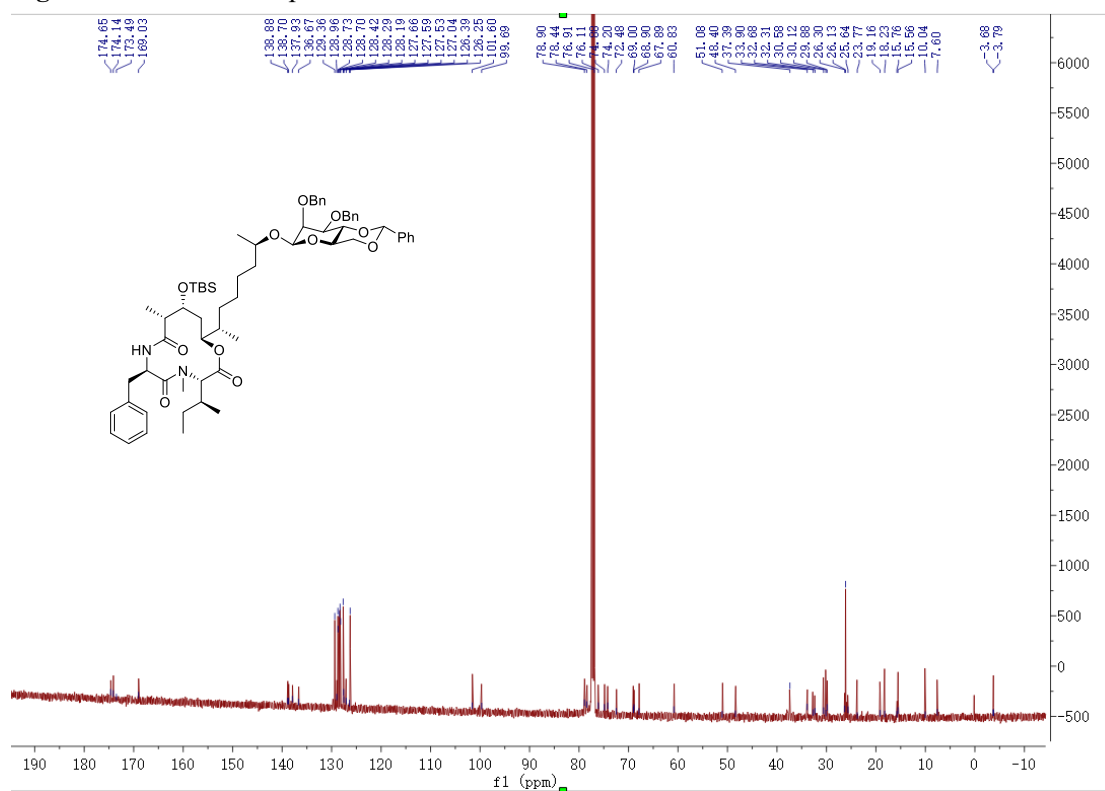
Figures S28  $^{13}\text{C}$  NMR Spectrum of 4



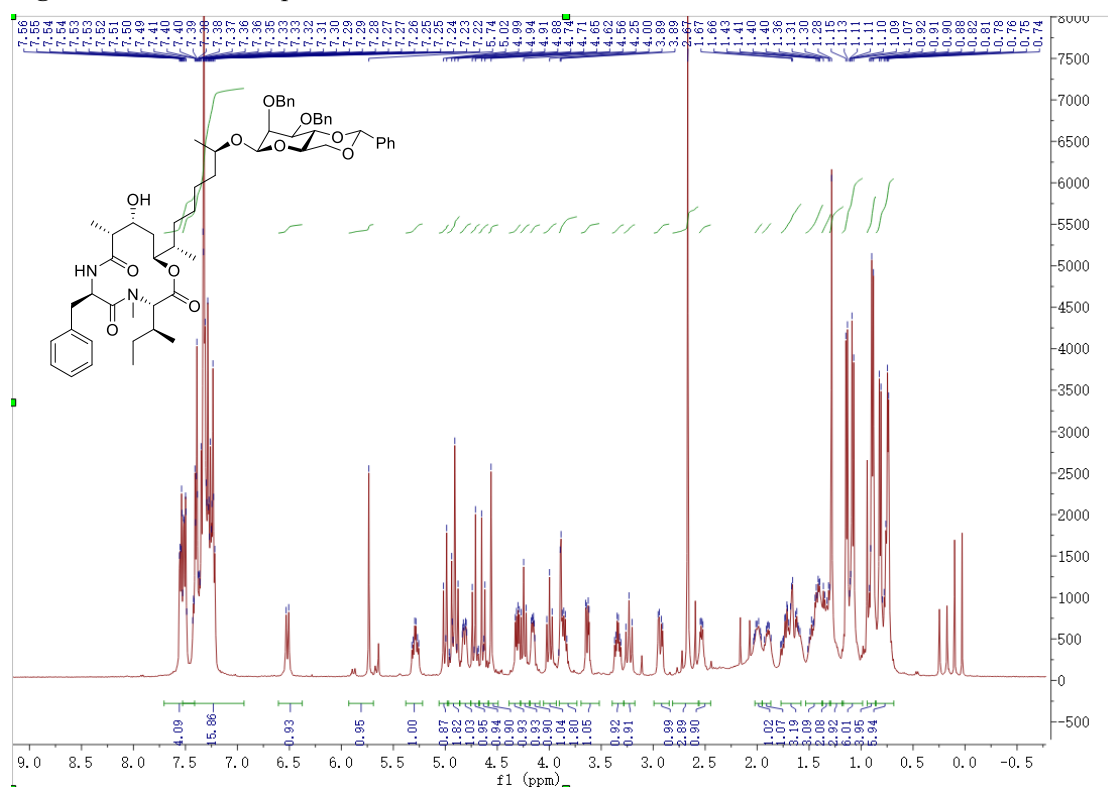
**Figures S29**  $^1\text{H}$  NMR Spectrum of **25**



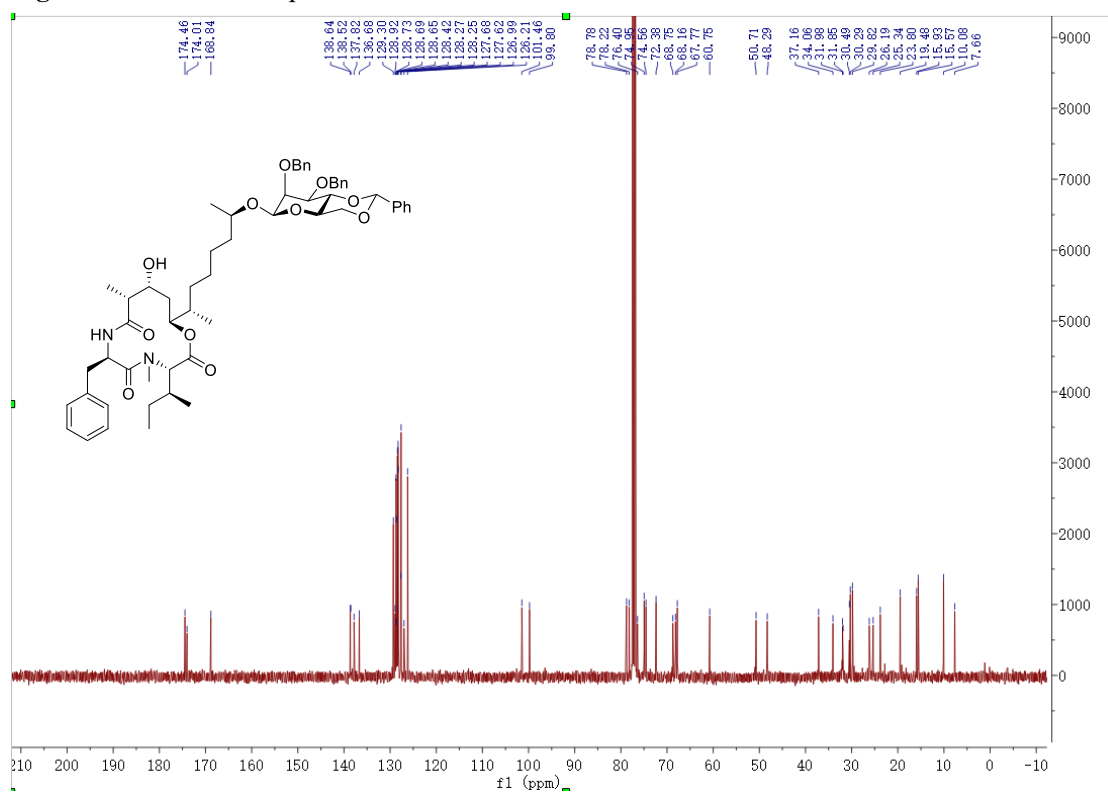
**Figures S30**  $^{13}\text{C}$  NMR Spectrum of **25**



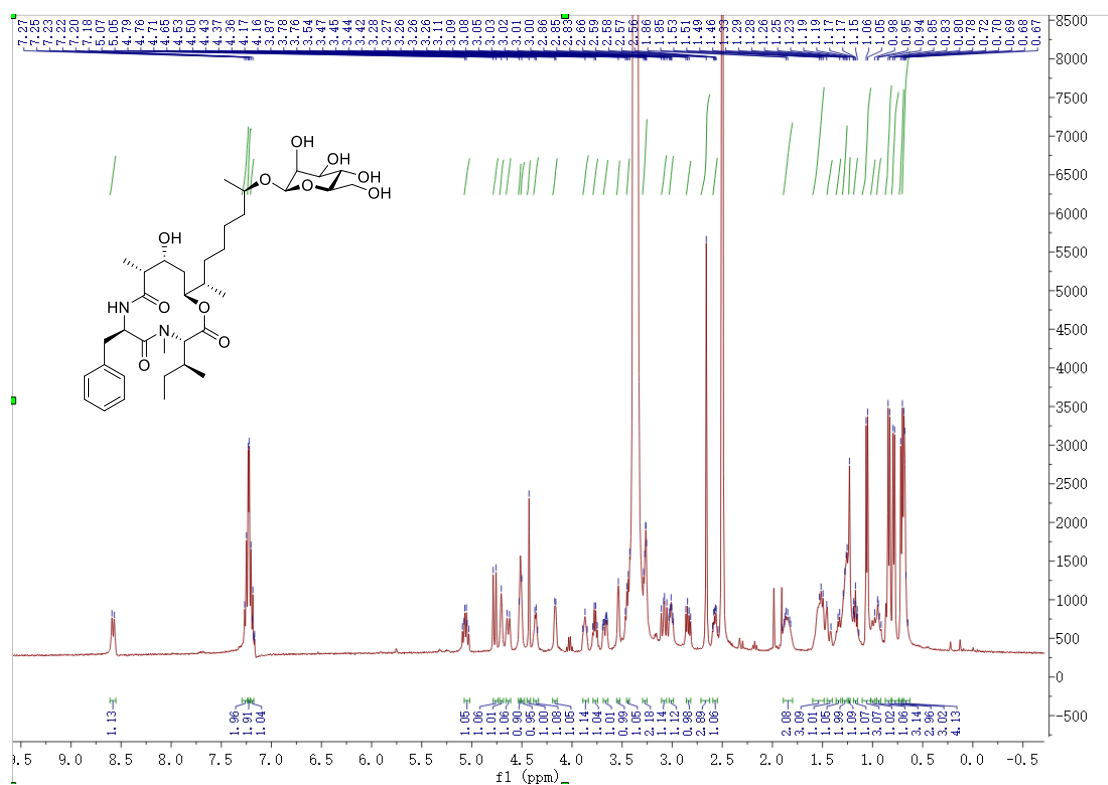
**Figures S31**  $^1\text{H}$  NMR Spectrum of **26**



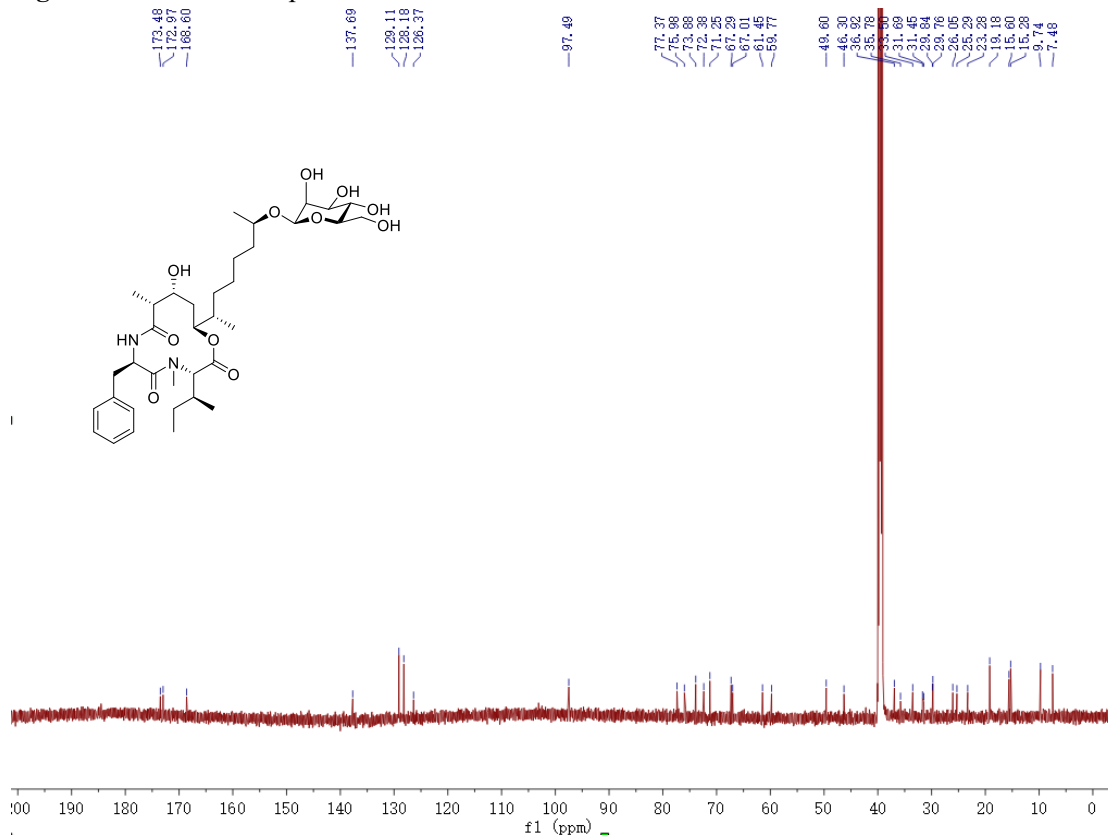
**Figures S32**  $^{13}\text{C}$  NMR Spectrum of **26**



**Figures S33**  $^1\text{H}$  NMR Spectrum of colletotrichamide A



**Figures S34**  $^{13}\text{C}$  NMR Spectrum of colletotrichamide A



**Figures S35**  $^1\text{H}$  NMR Spectrum of colletopeptide A

