

Supporting Information

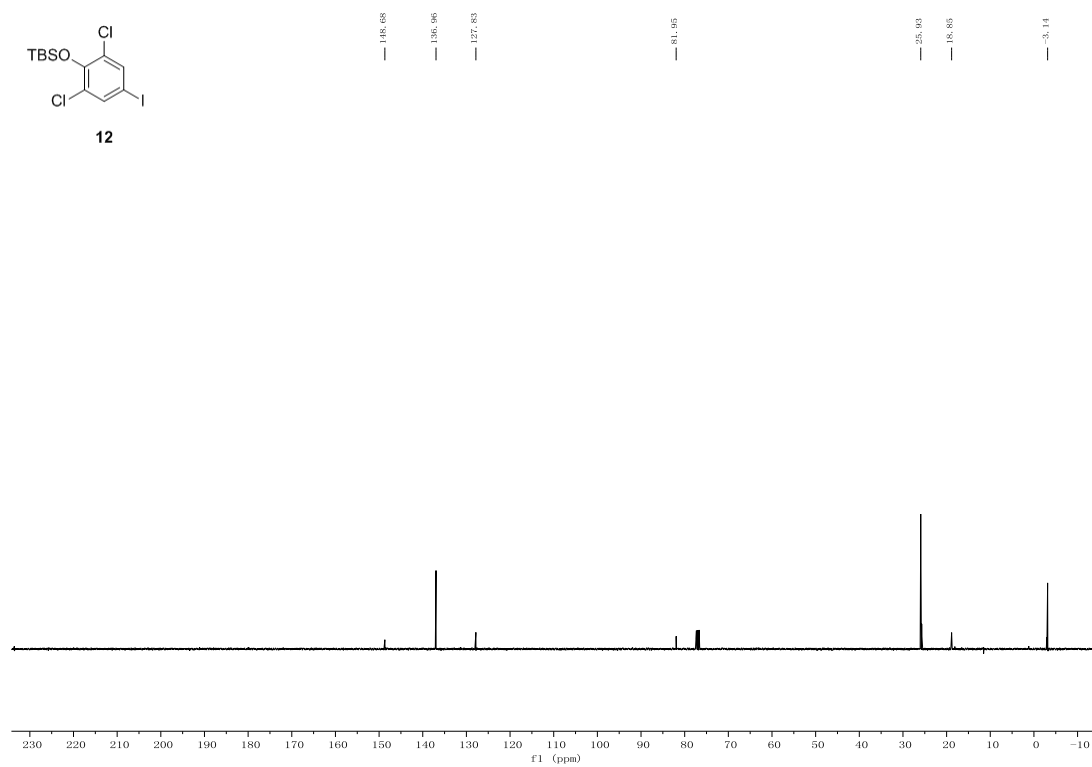
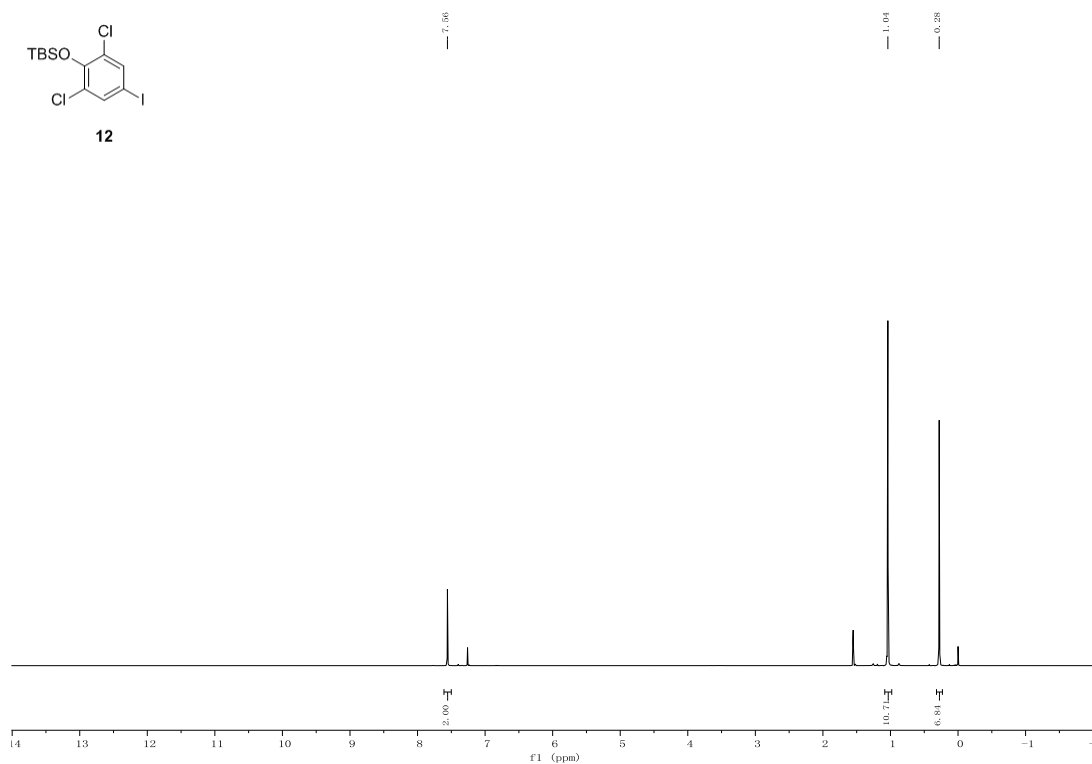
Asymmetric Total Synthesis of Nannocystin A

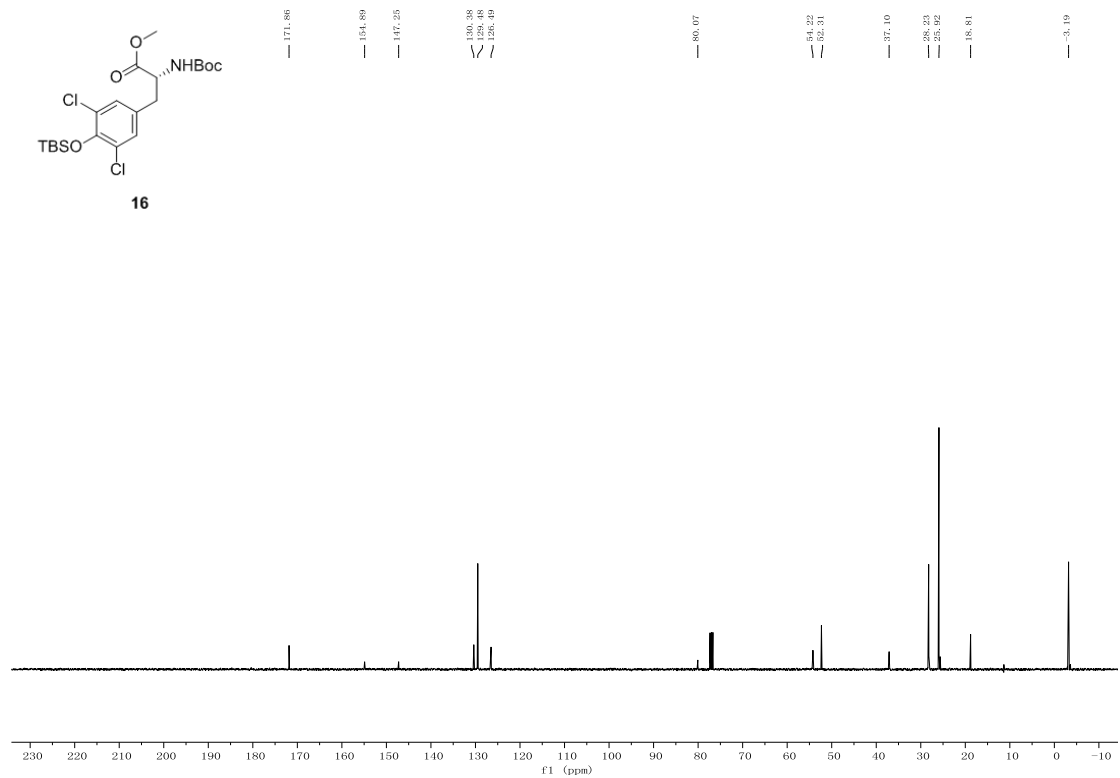
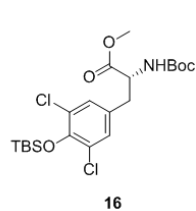
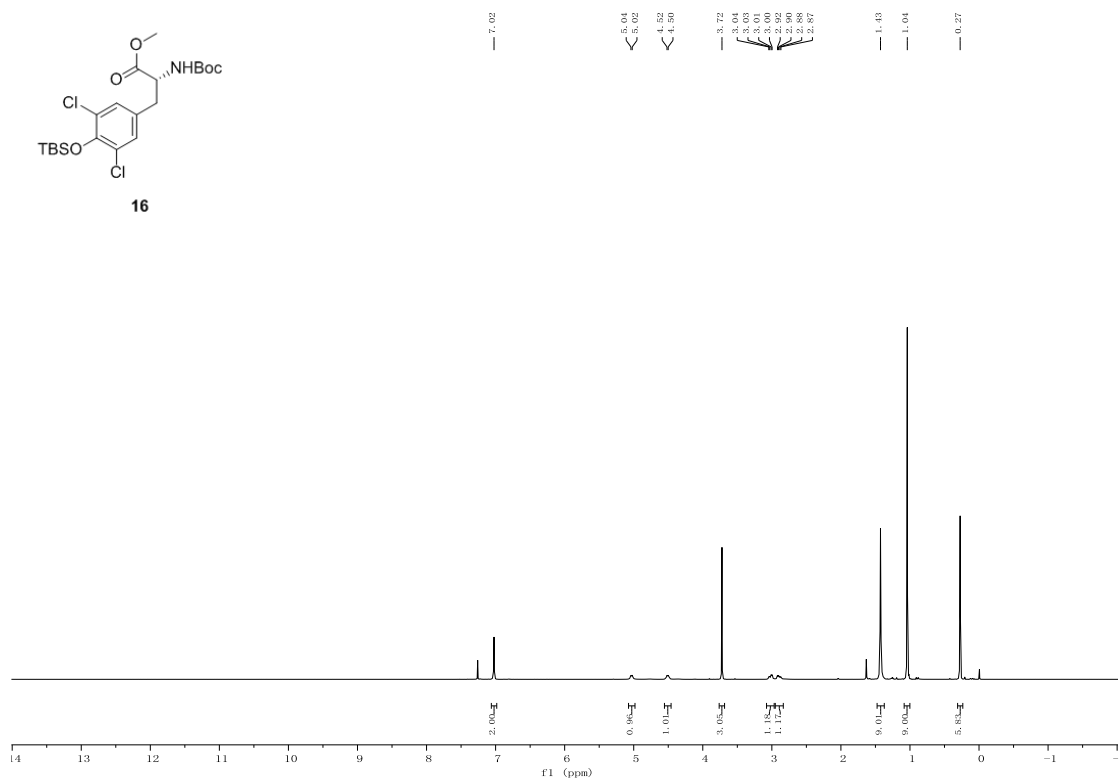
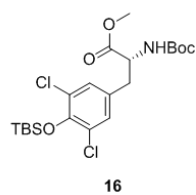
Qiang Liu, Ping Hu* and Yun He*

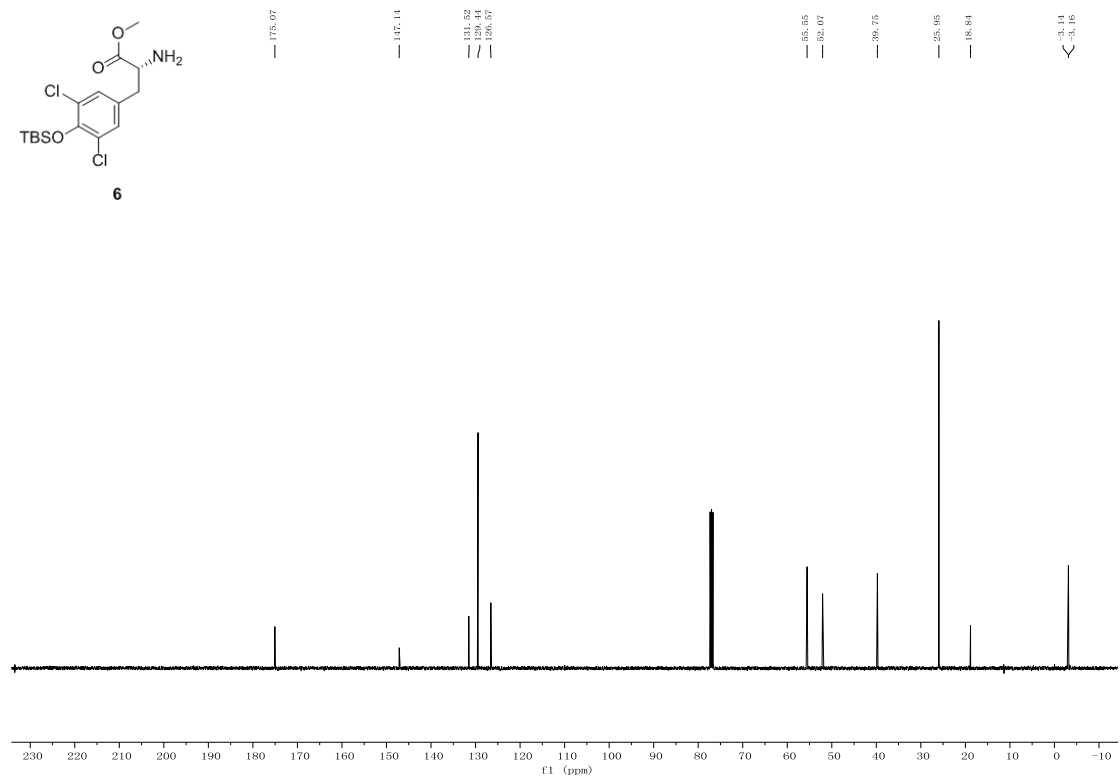
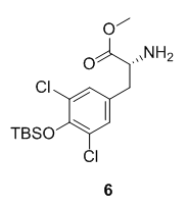
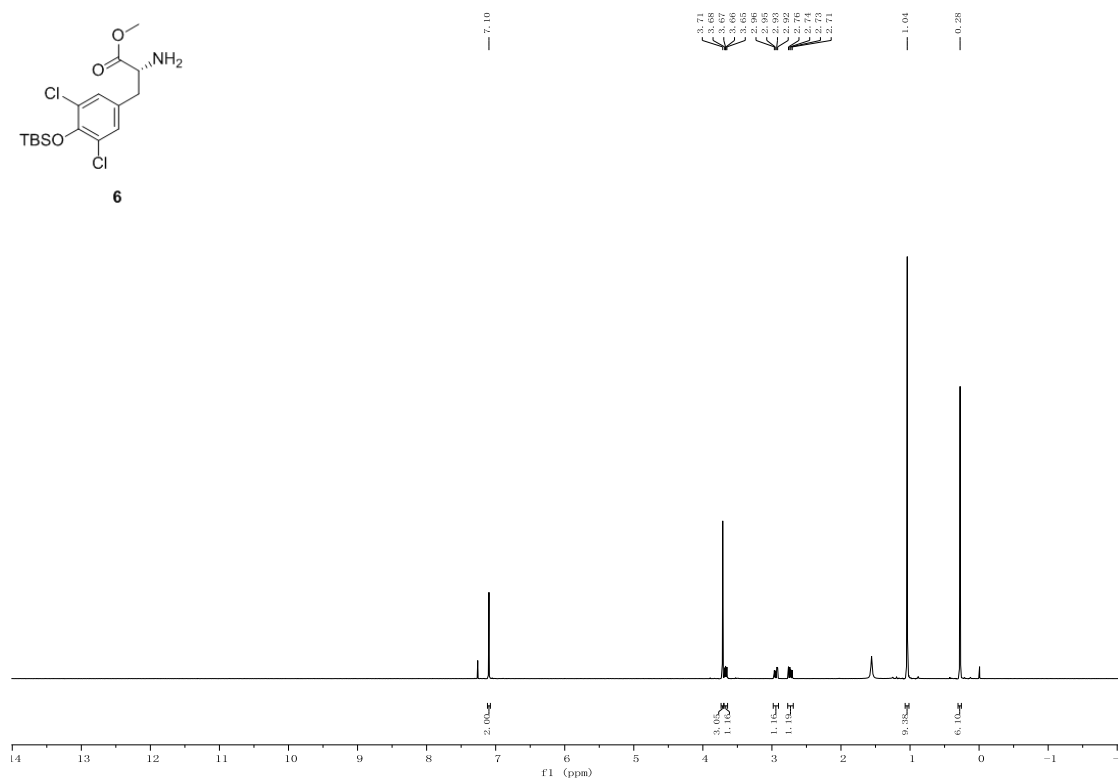
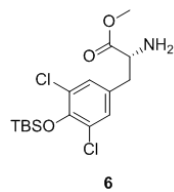
Table of Contents

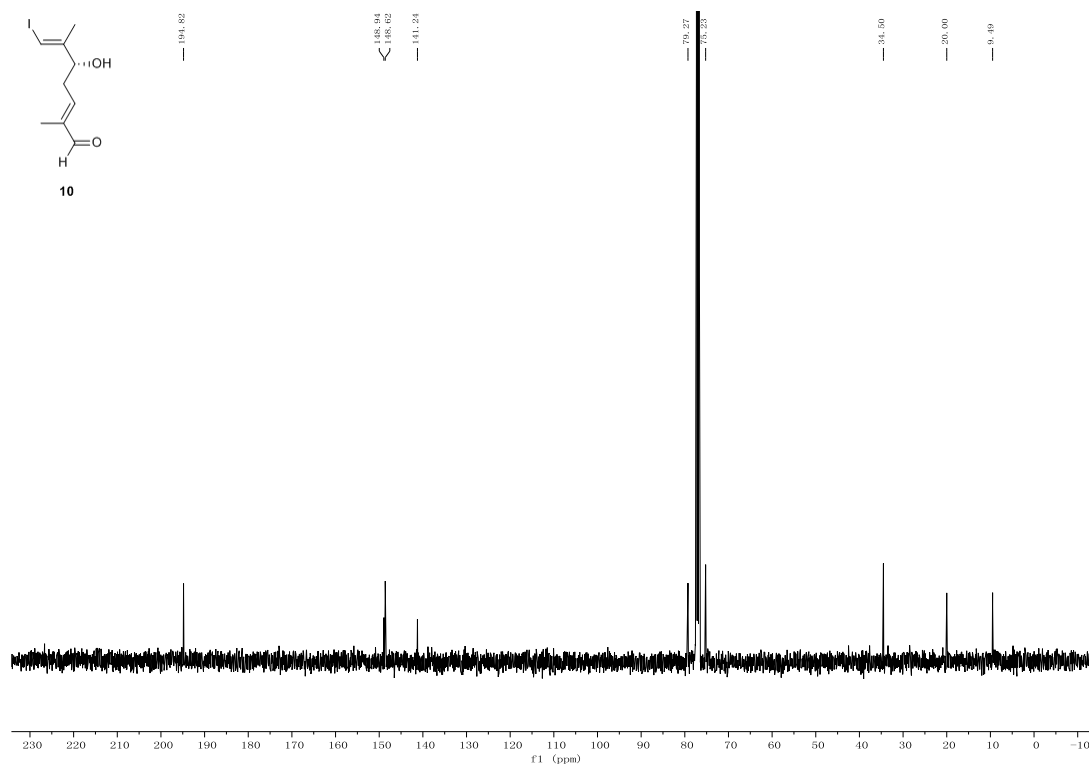
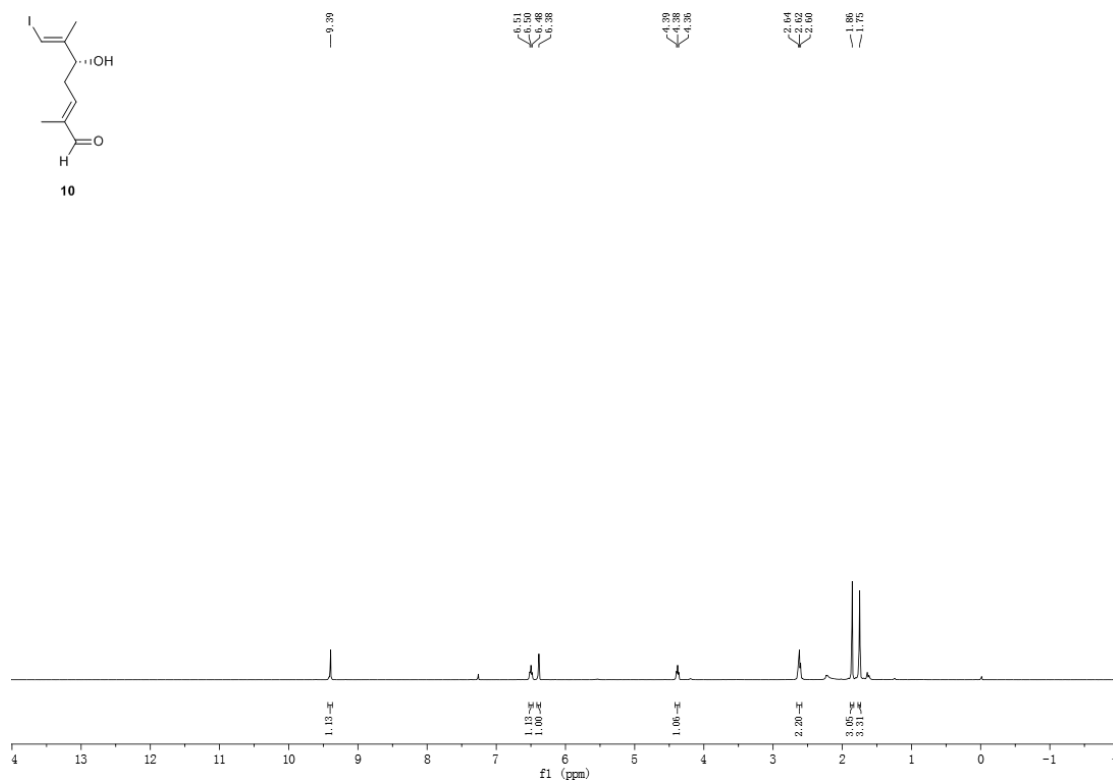
1. Experimental Spectra.....	S2
2. Comparison of ^1H NMR Data of Natural and Synthetic Nannocystin A (Table S1).....	S22
3. Comparison of ^{13}C NMR Data of Natural and Synthetic Nannocystin A (Table S2).....	S23

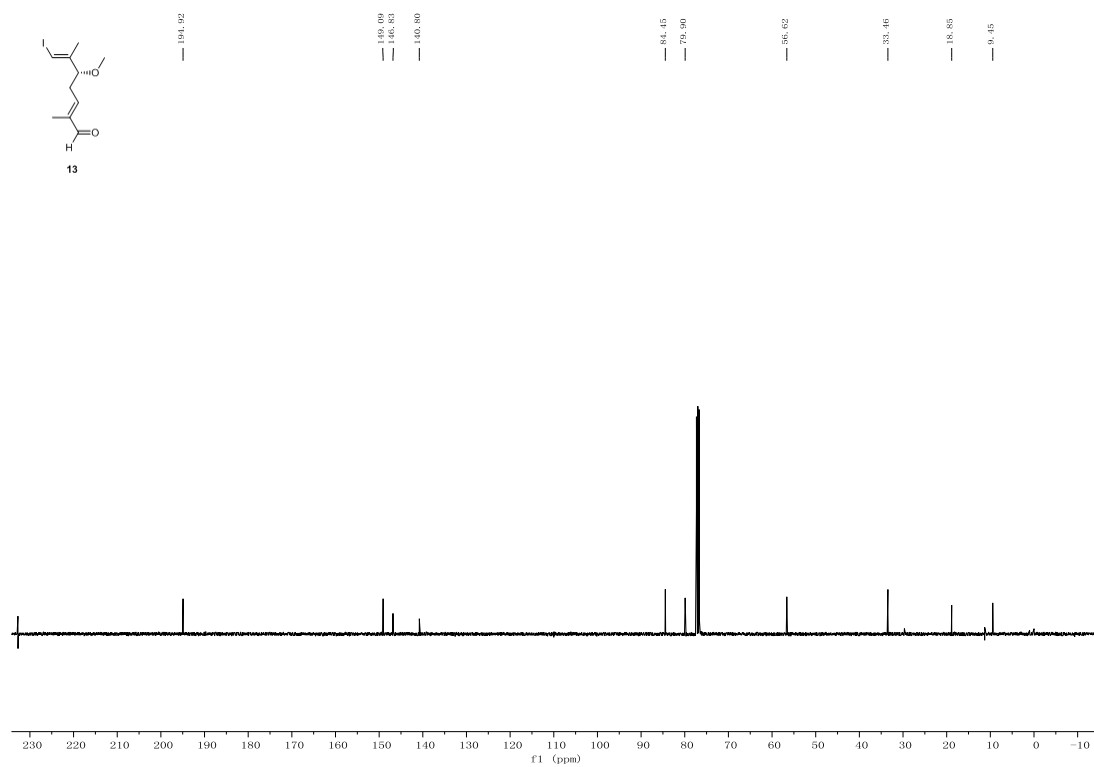
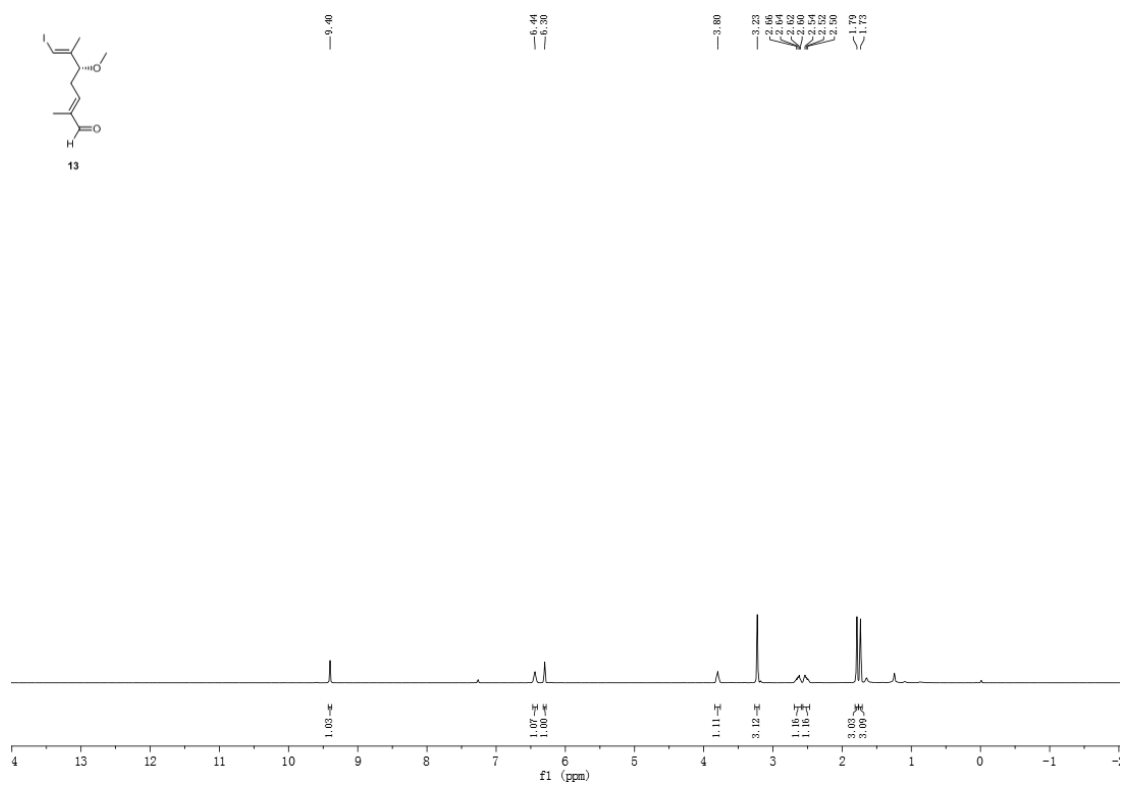
1. Experimental Spectra

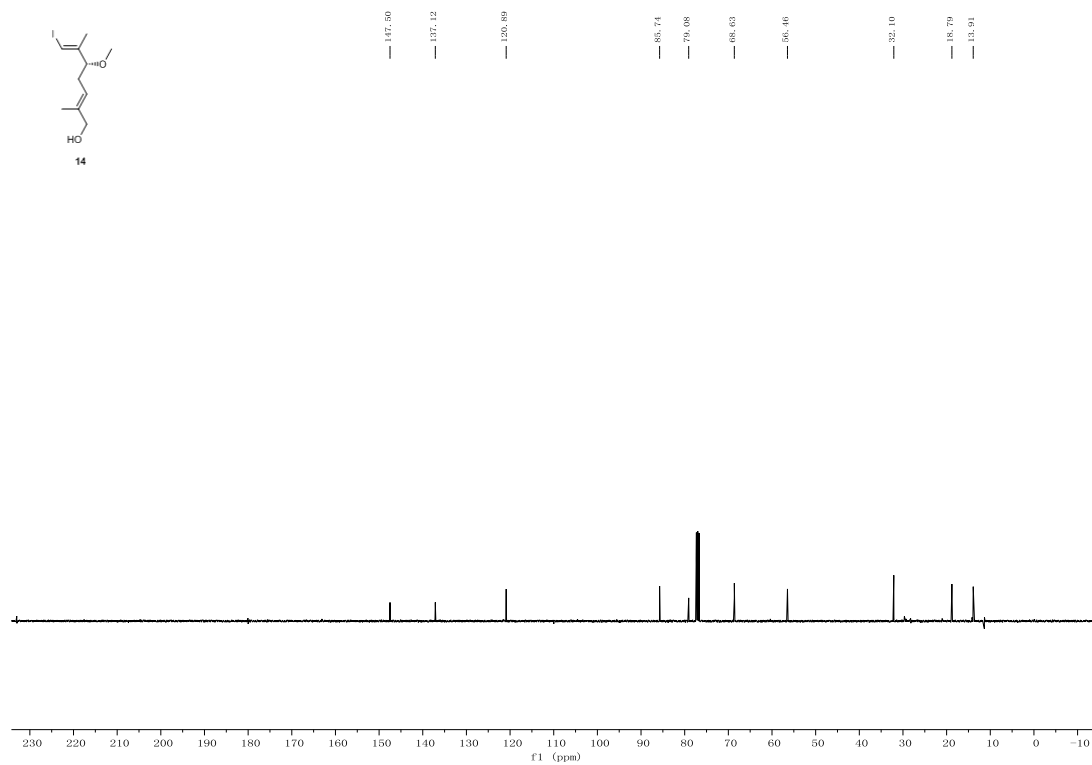
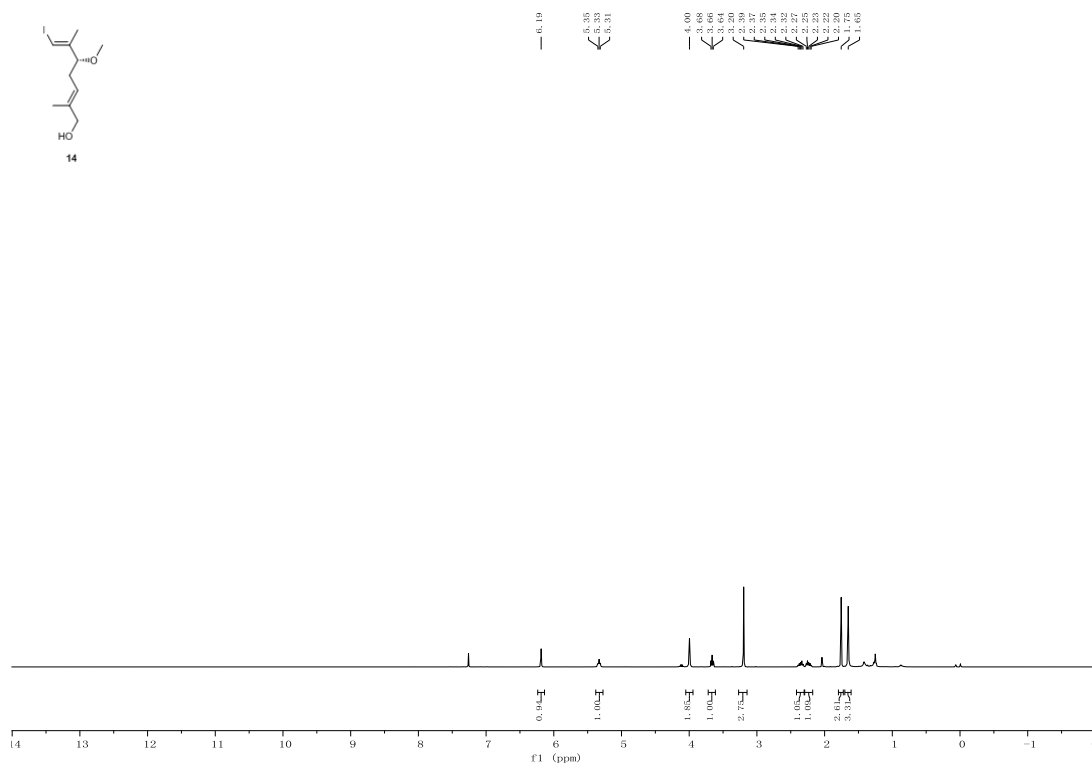


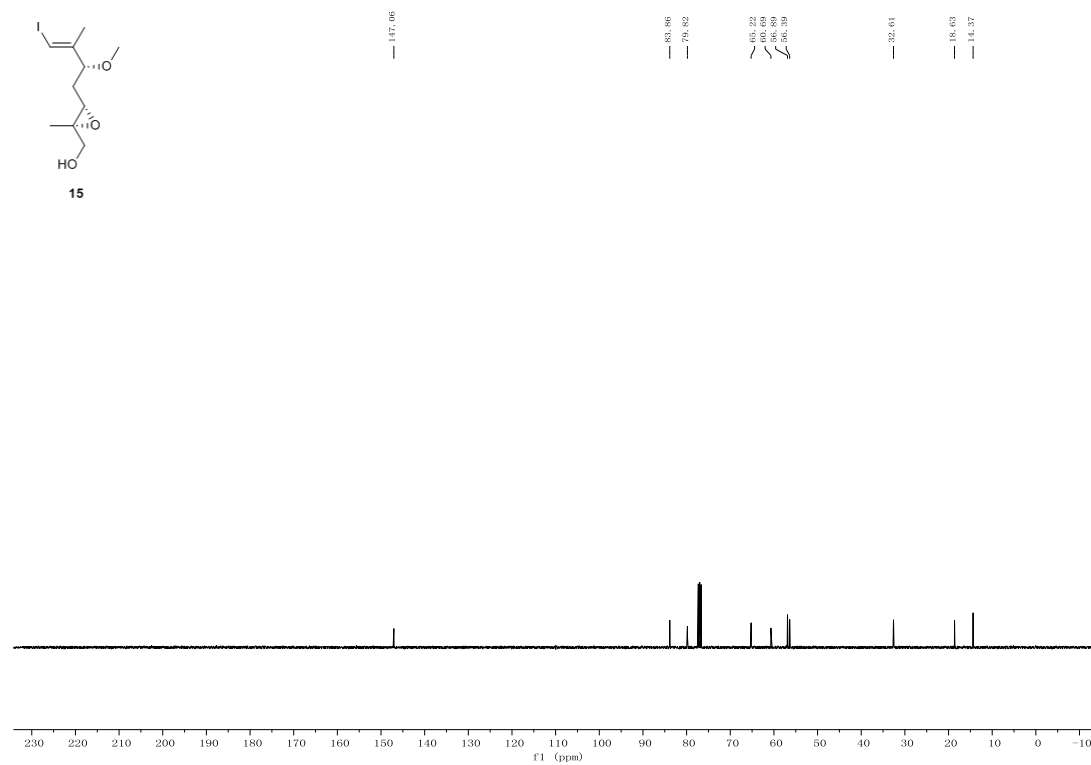
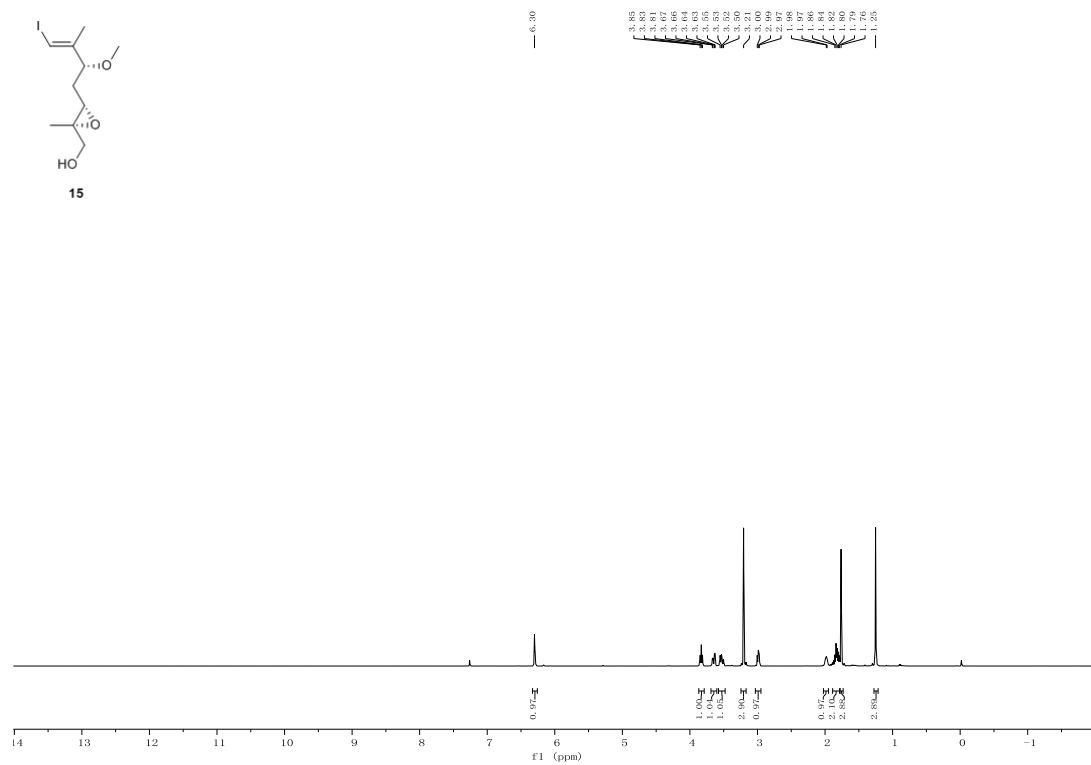


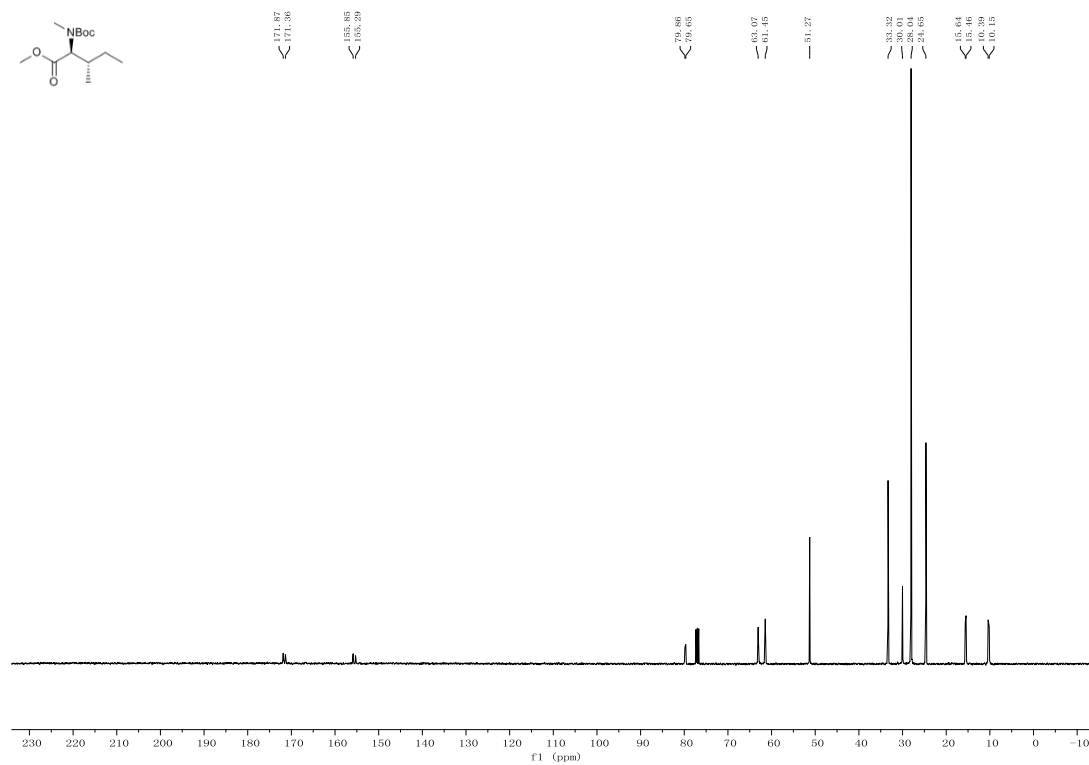
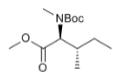
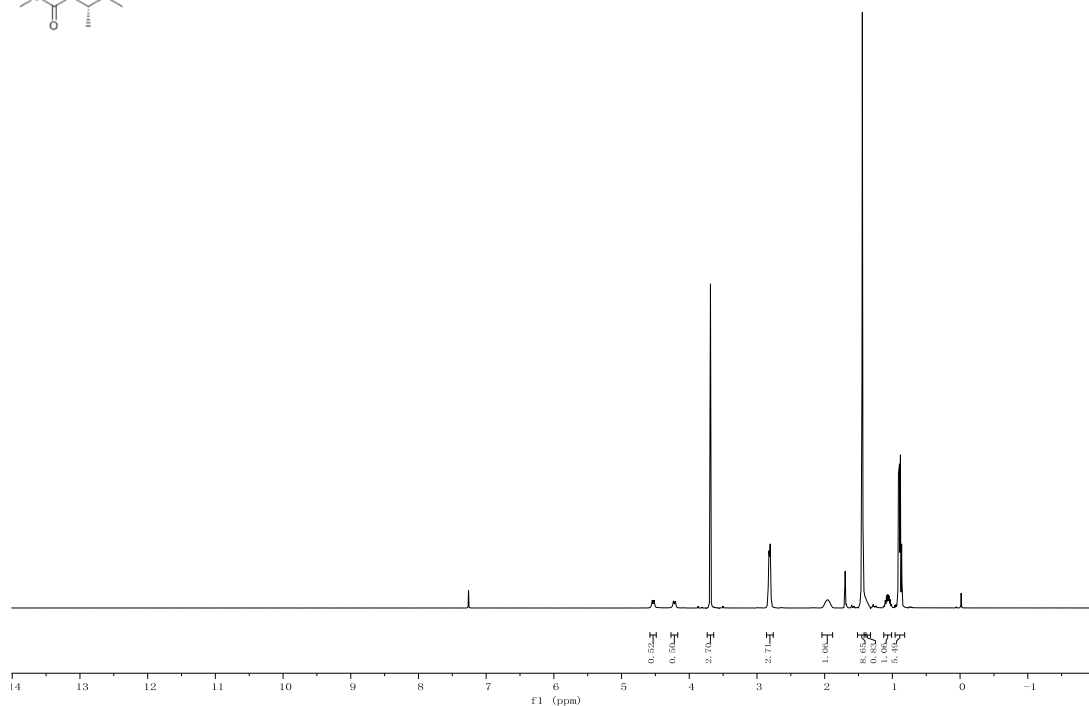
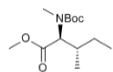


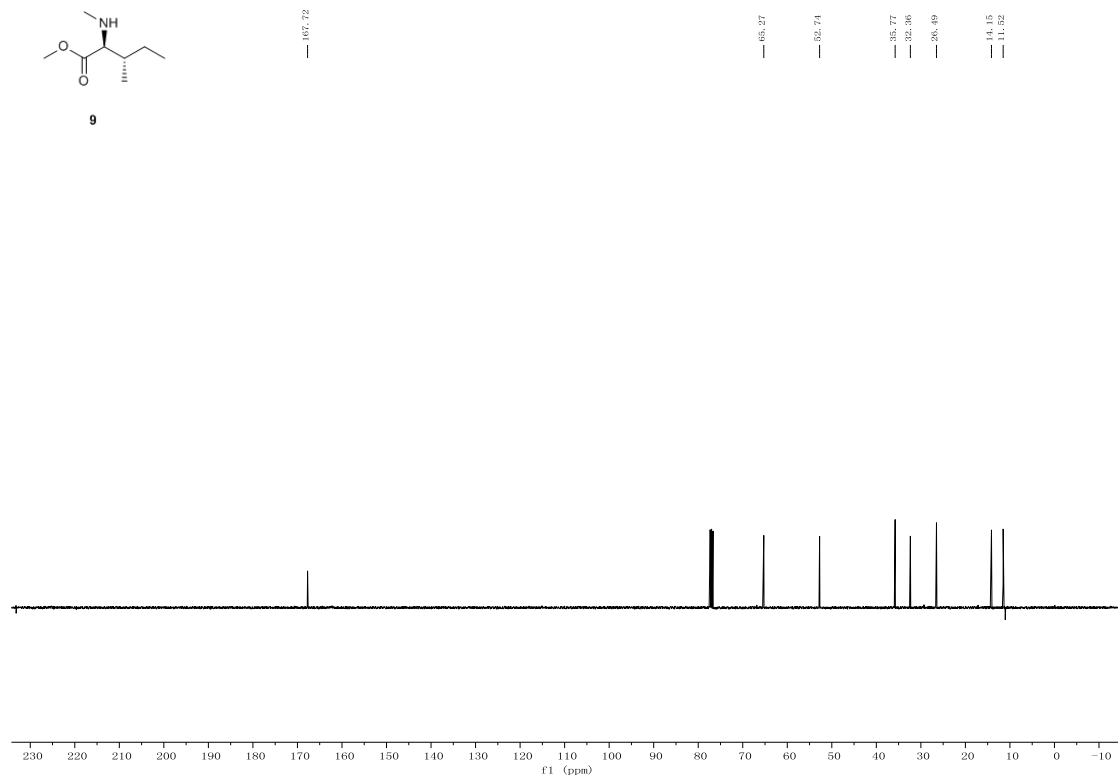
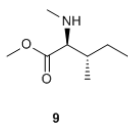
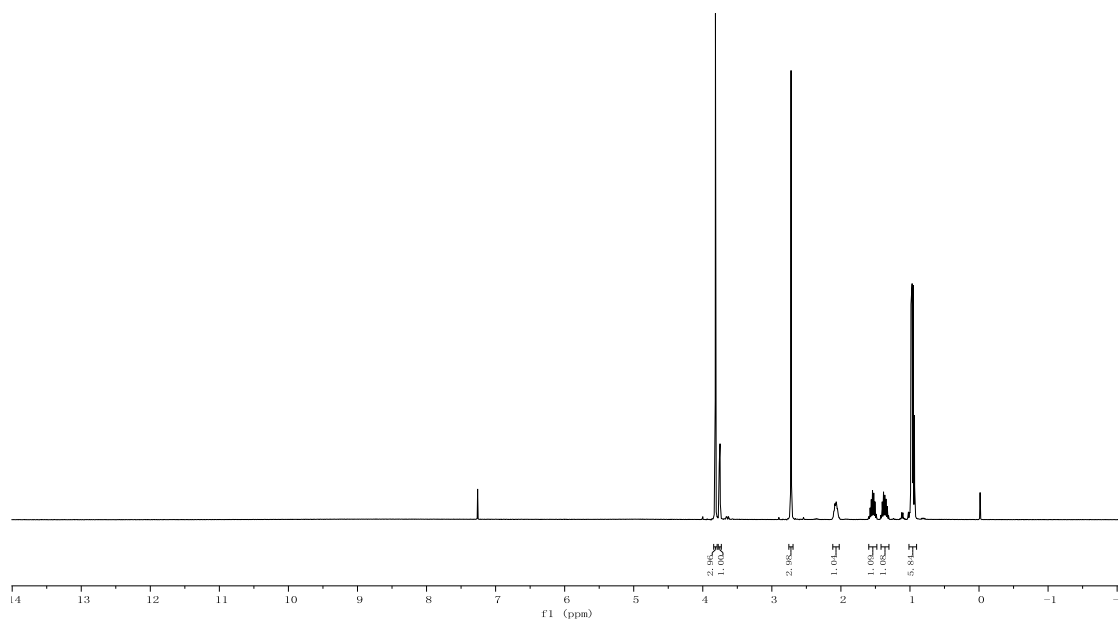
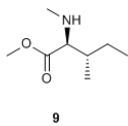


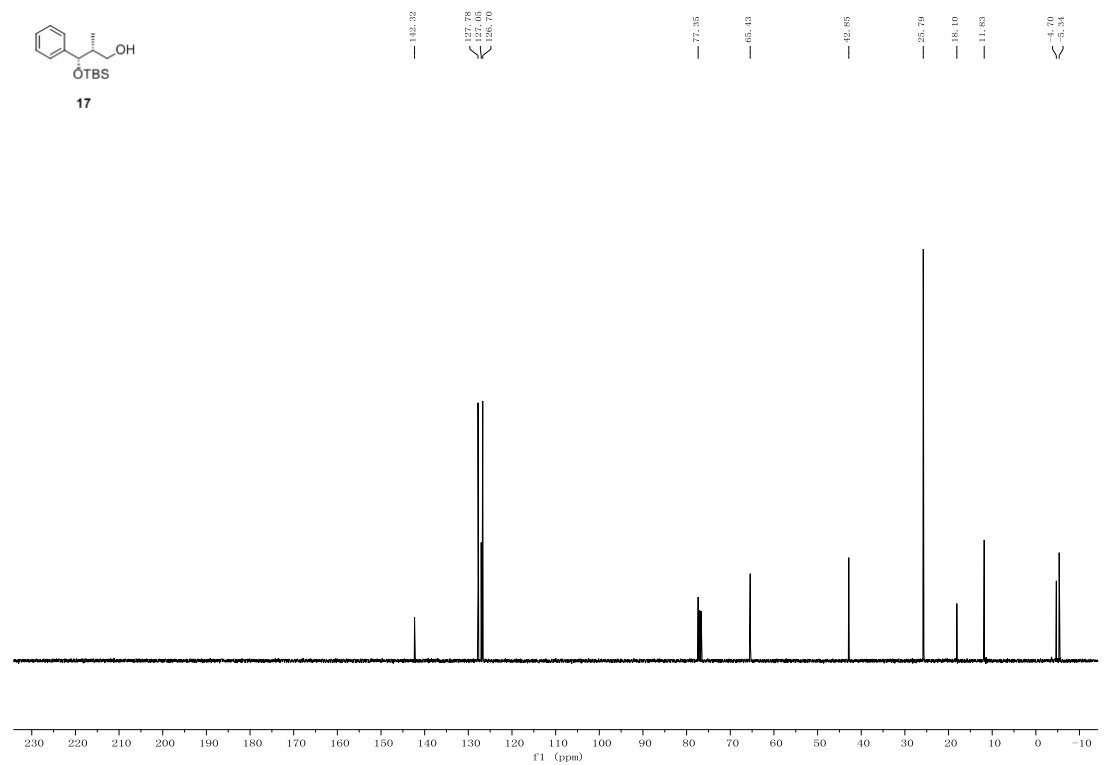
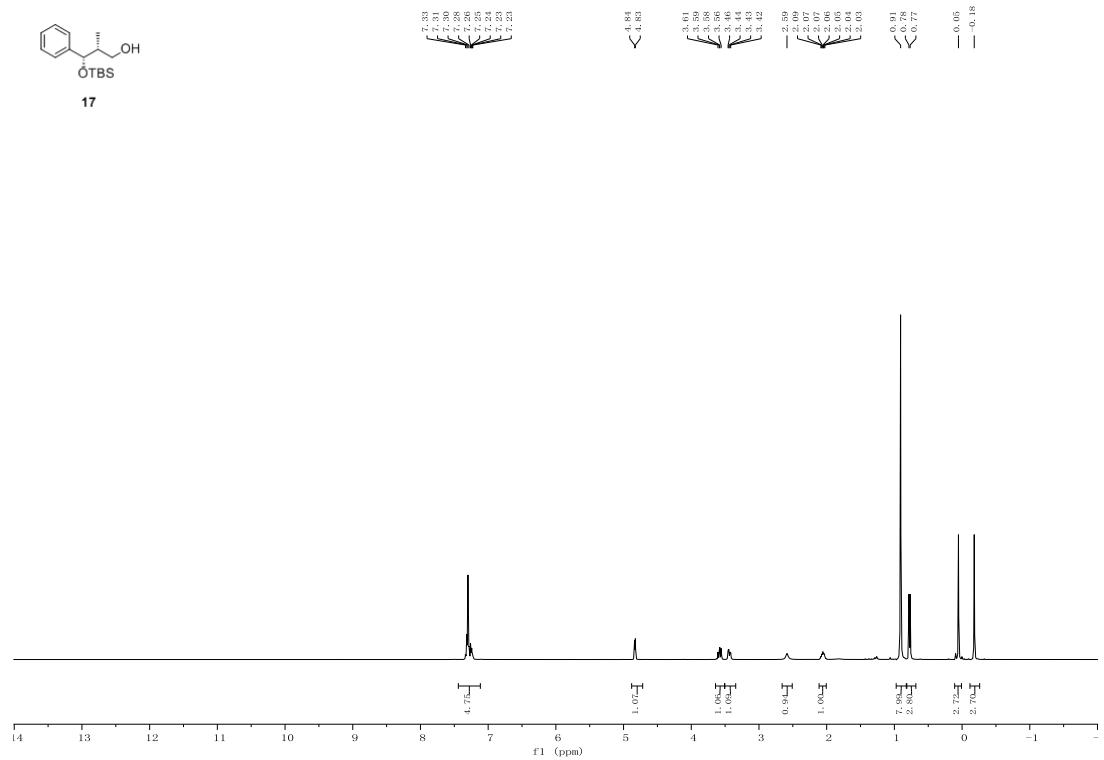


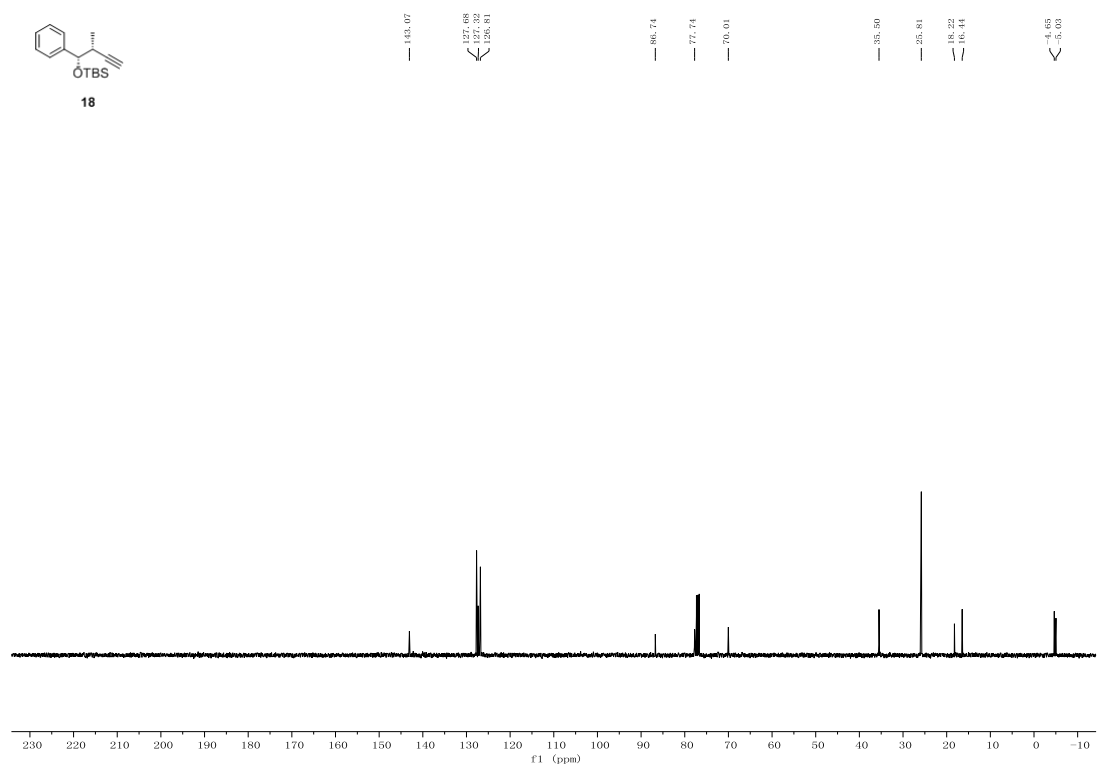
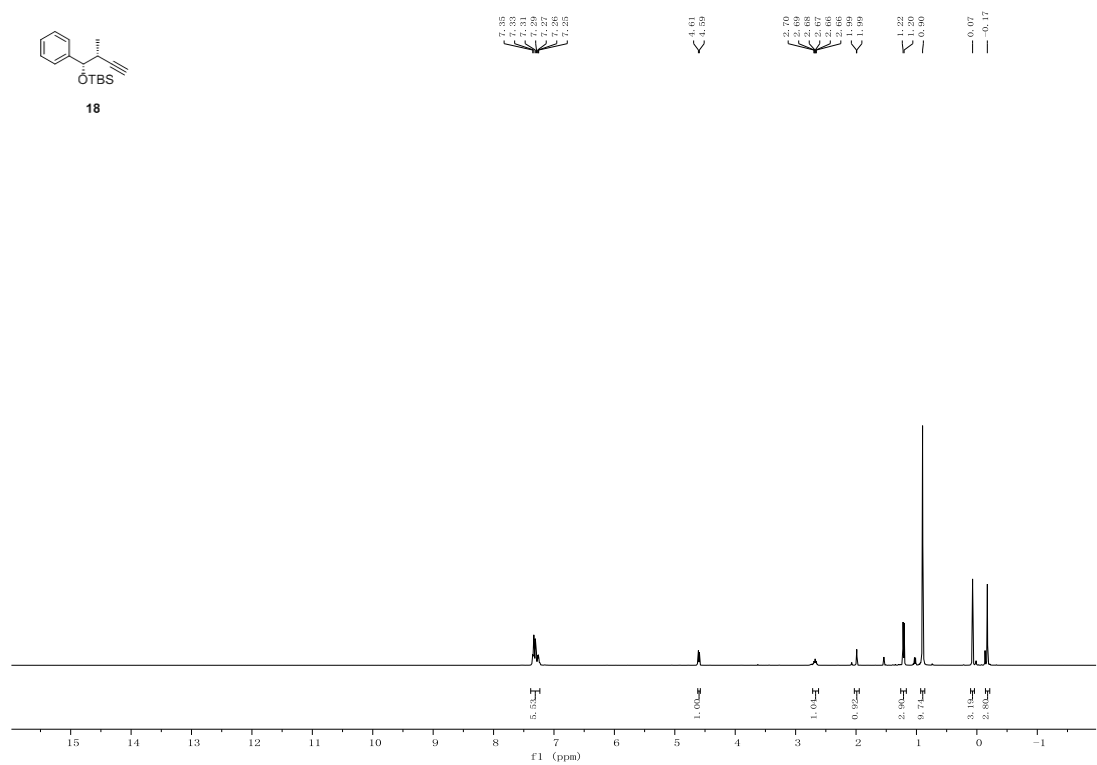


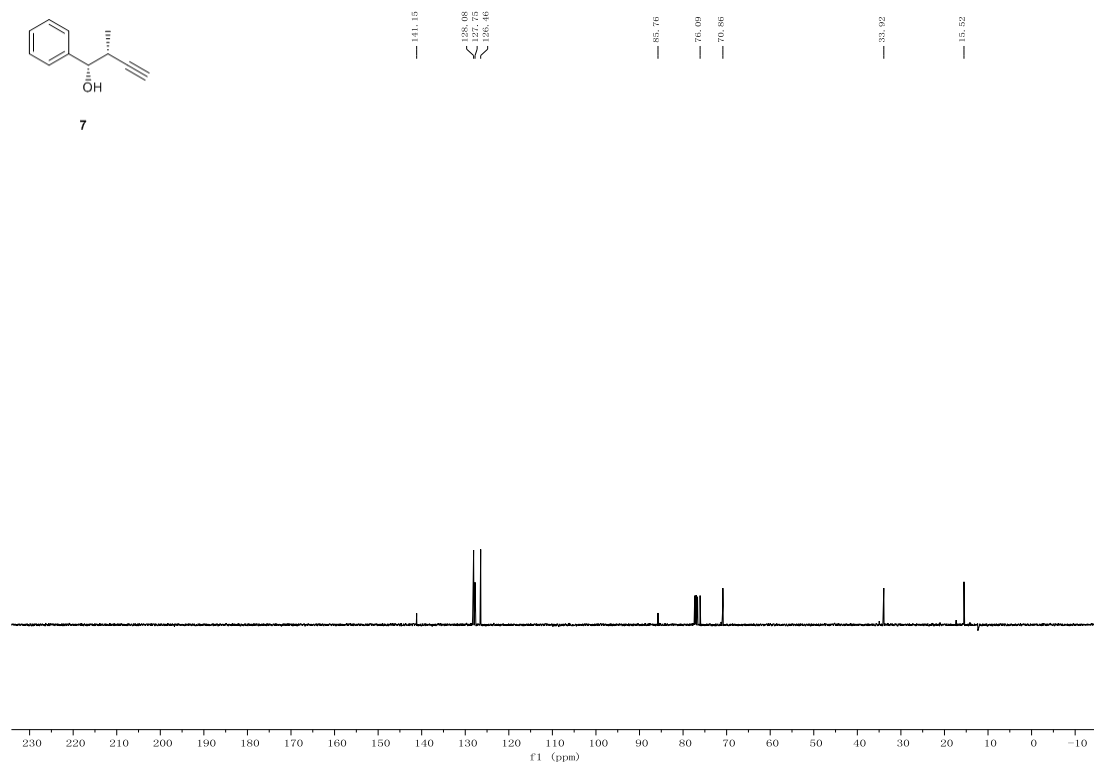
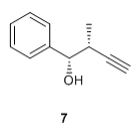
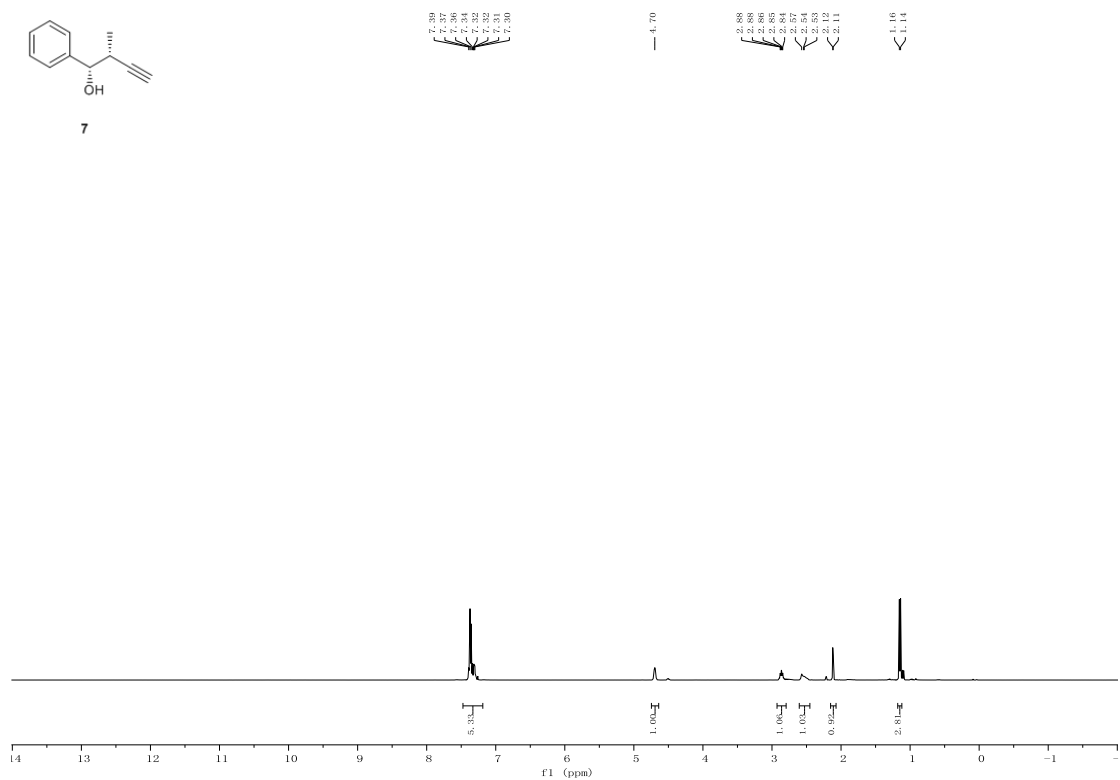
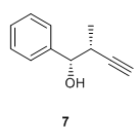


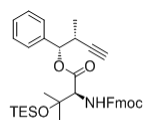




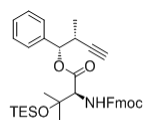
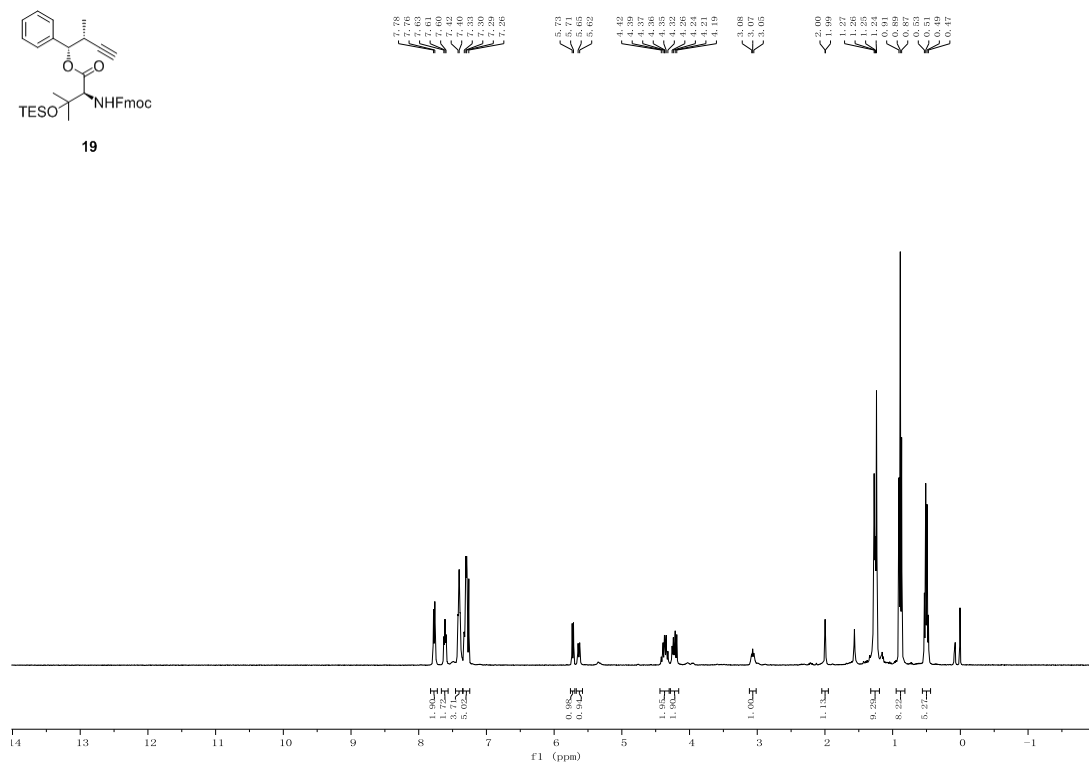




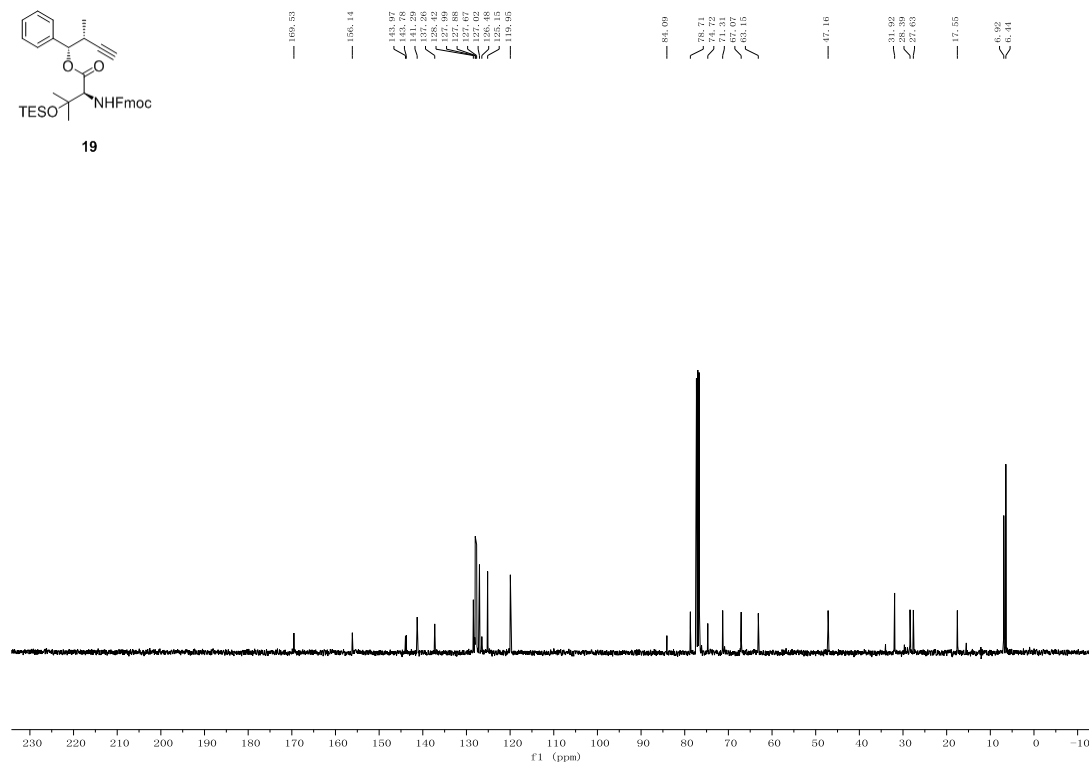


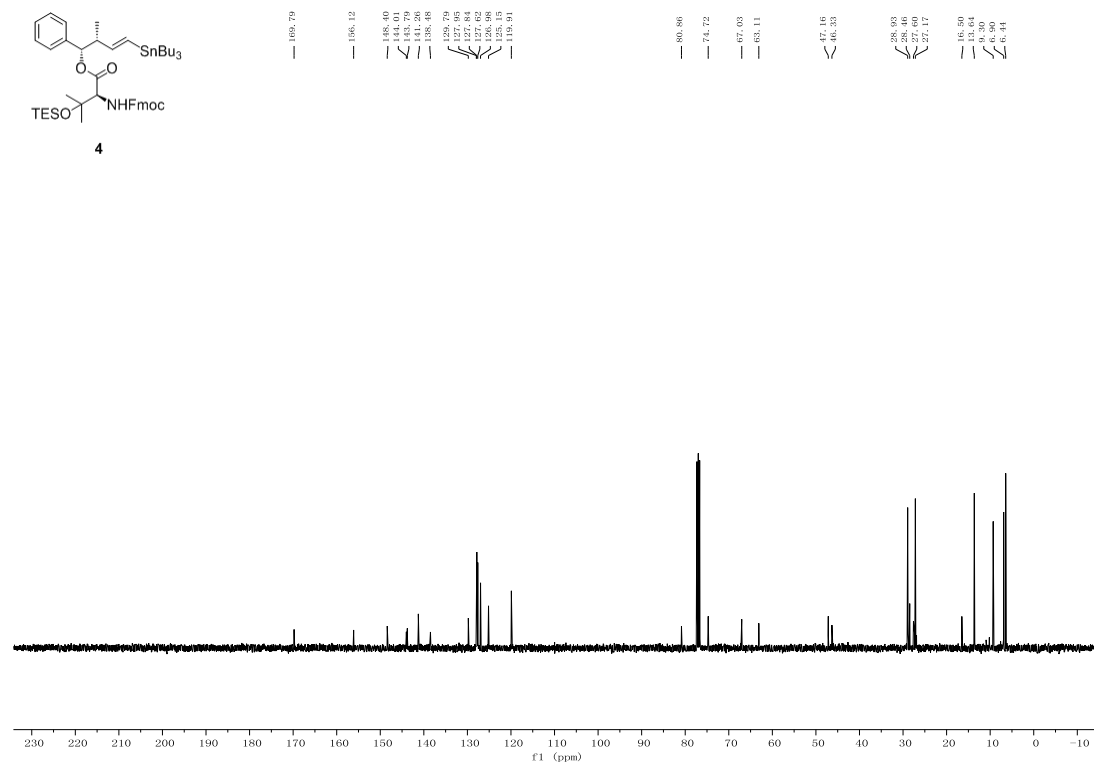
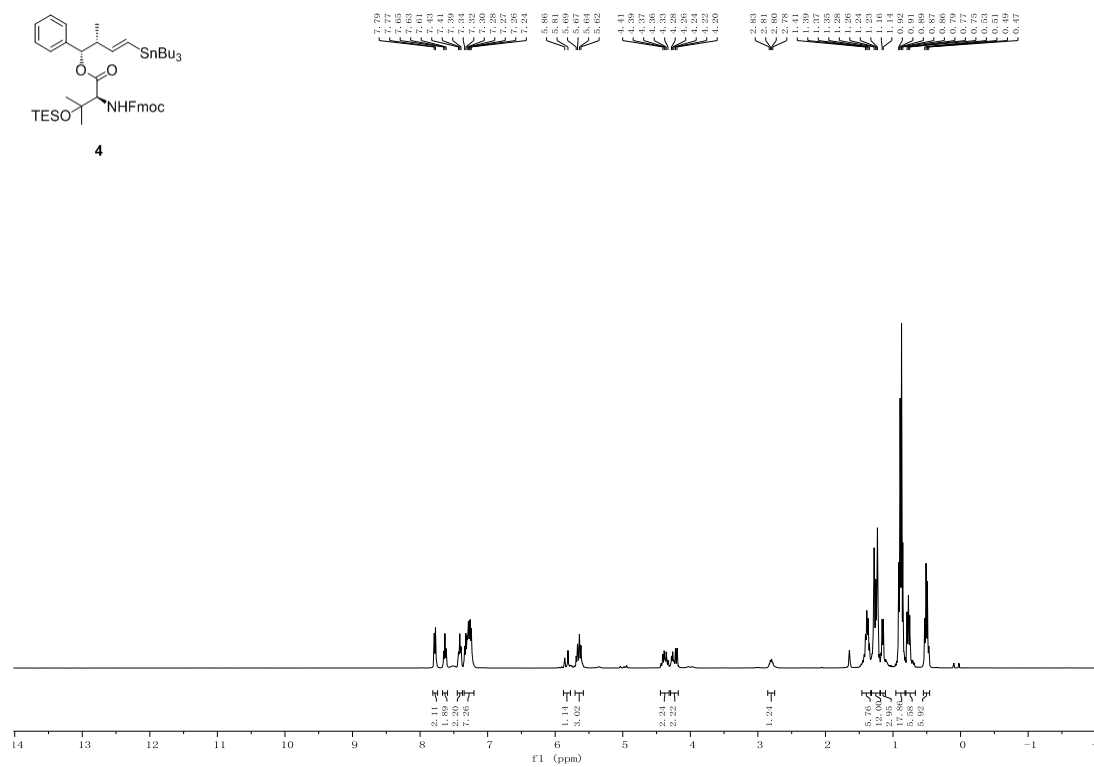


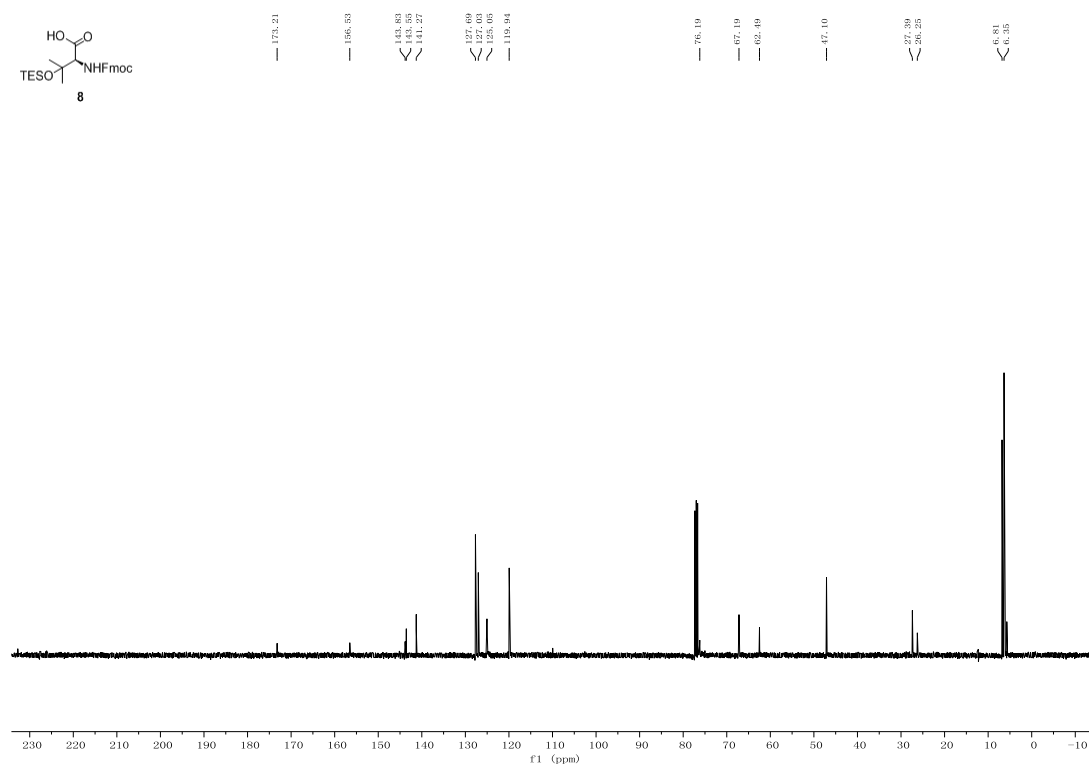
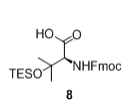
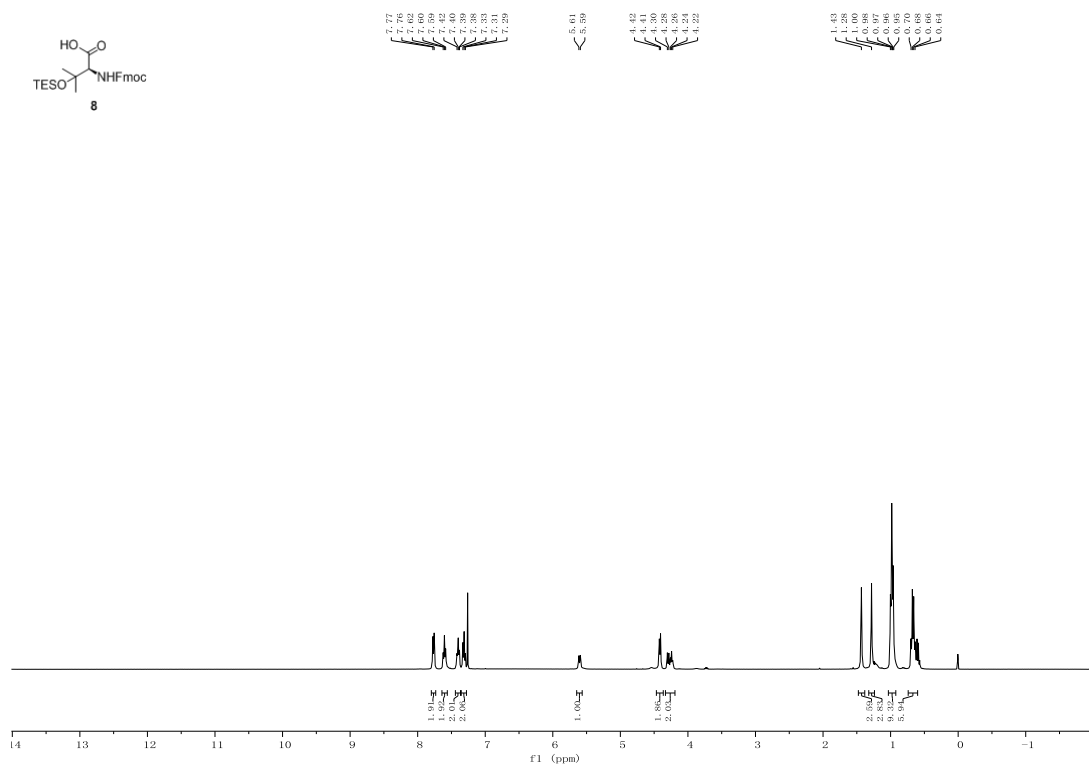
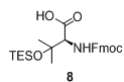
19

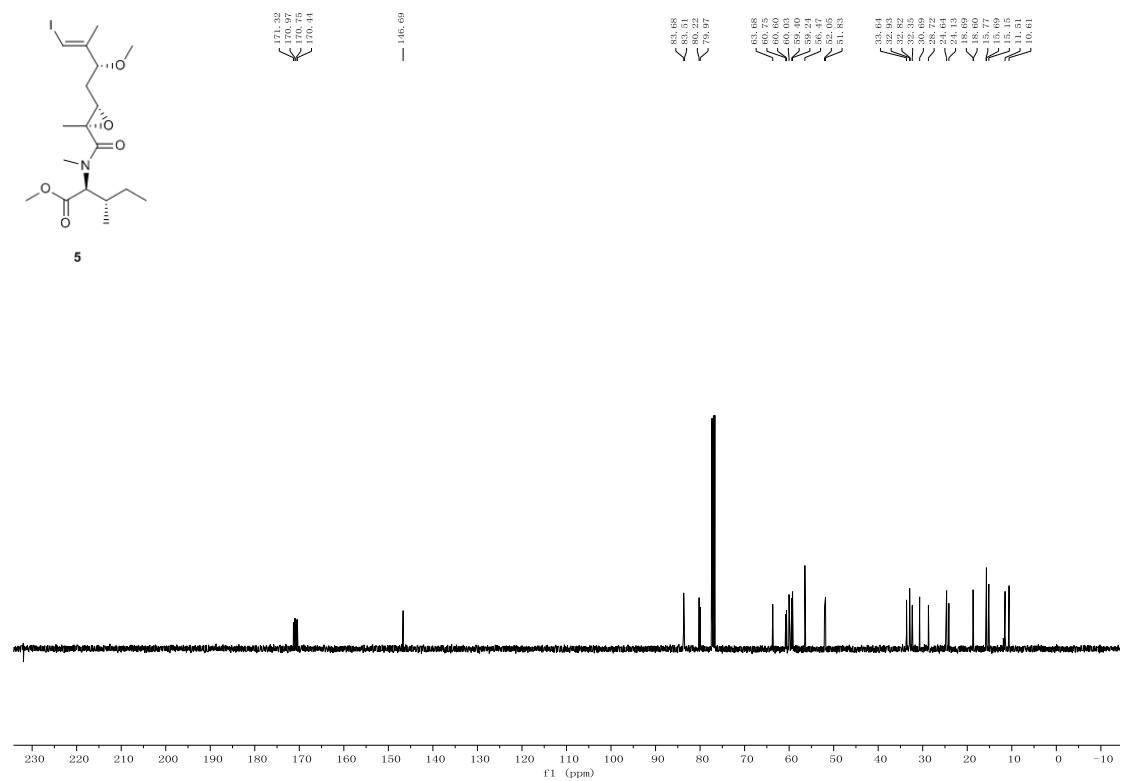
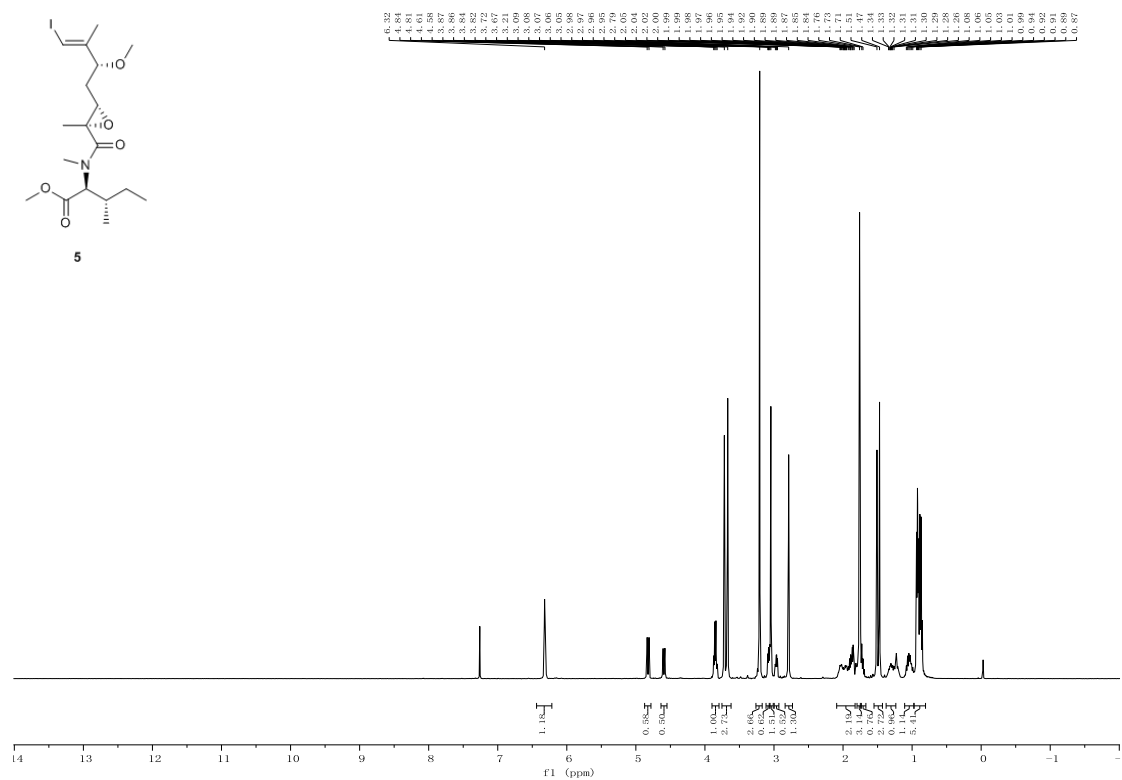


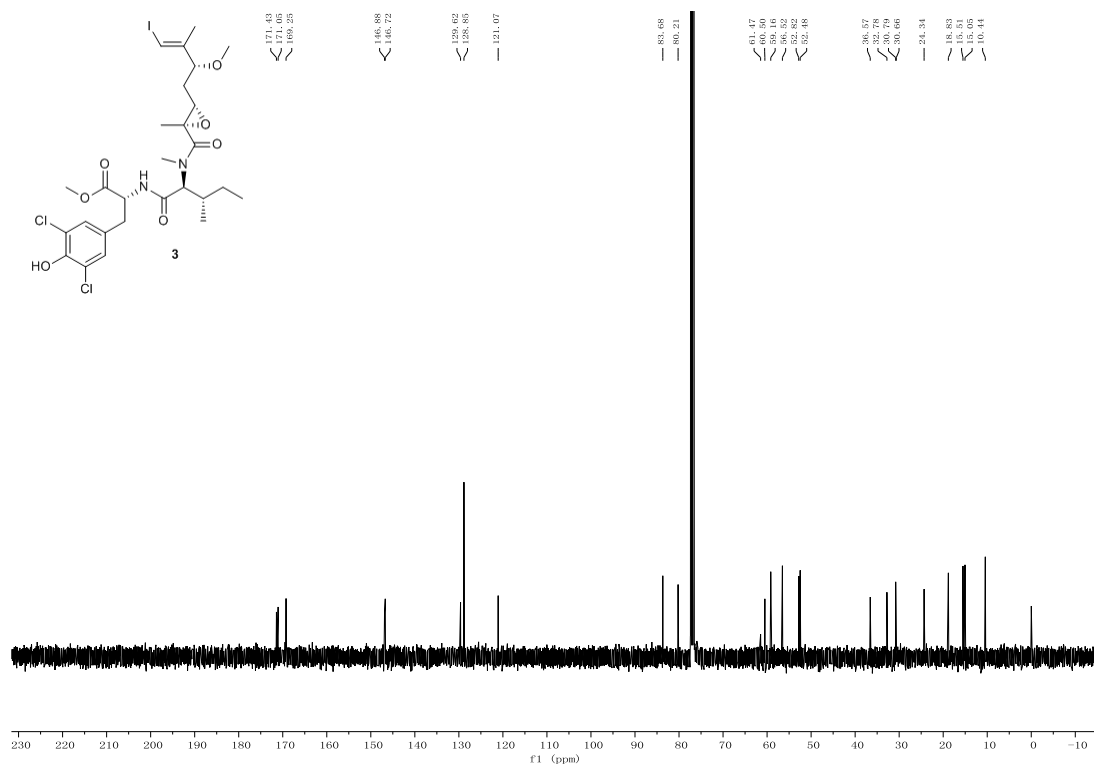
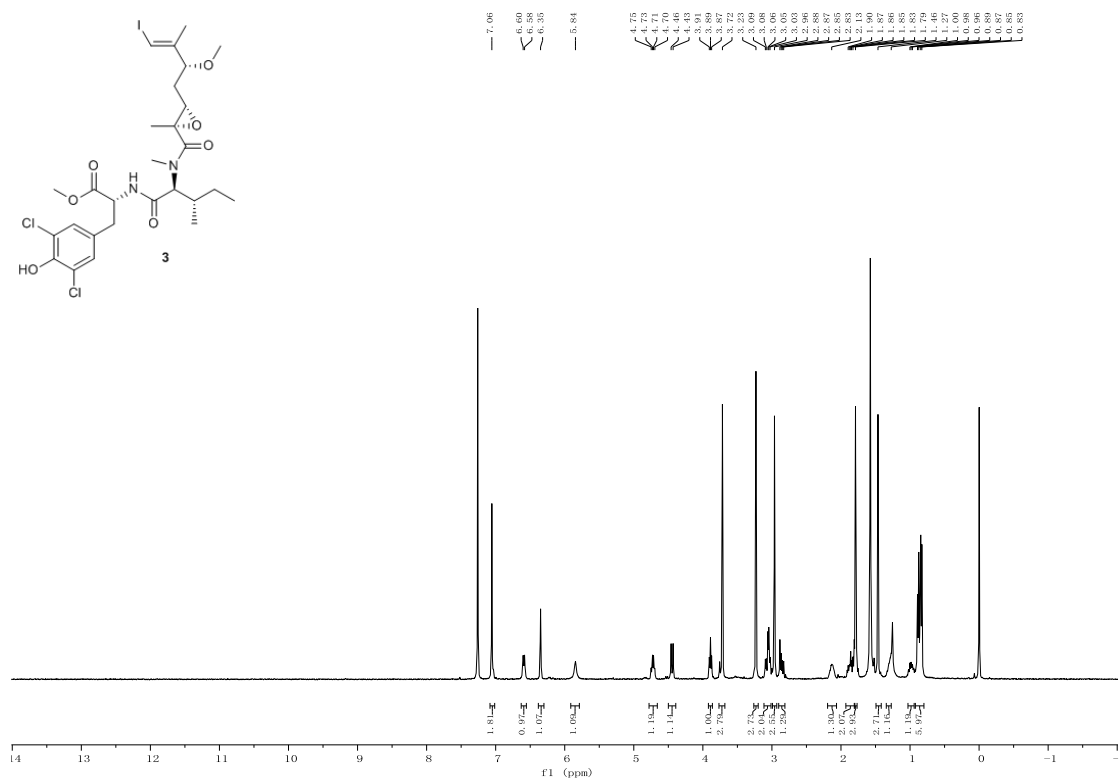
19

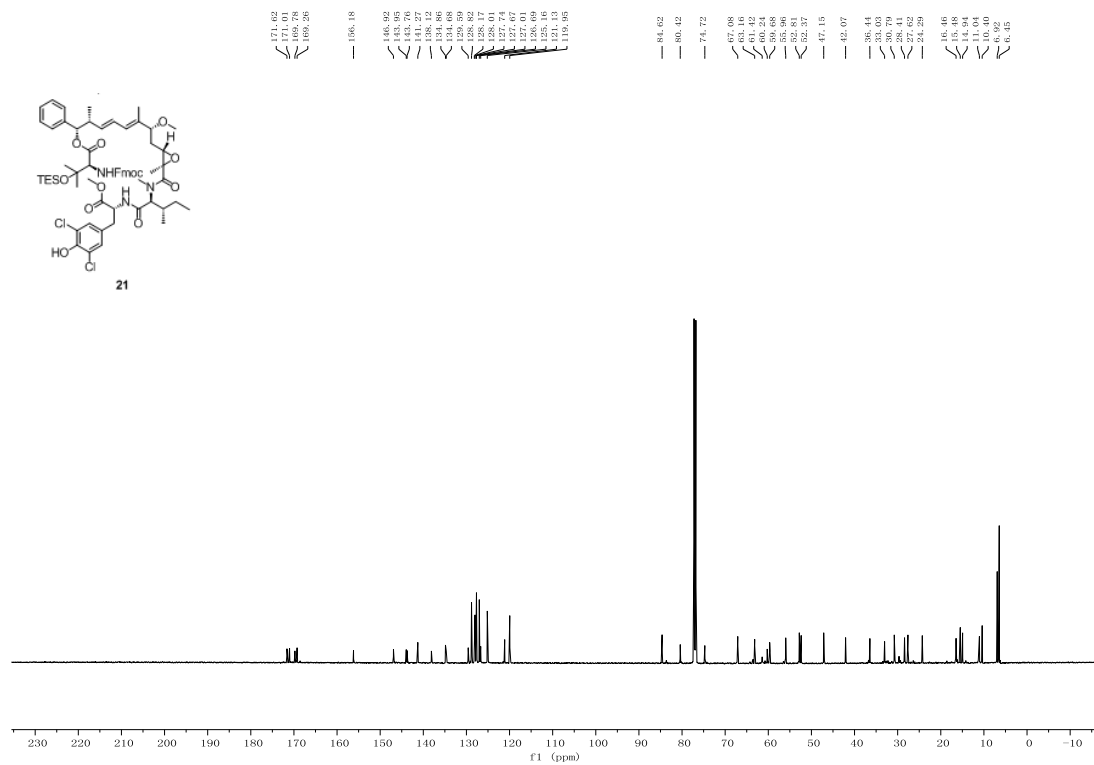
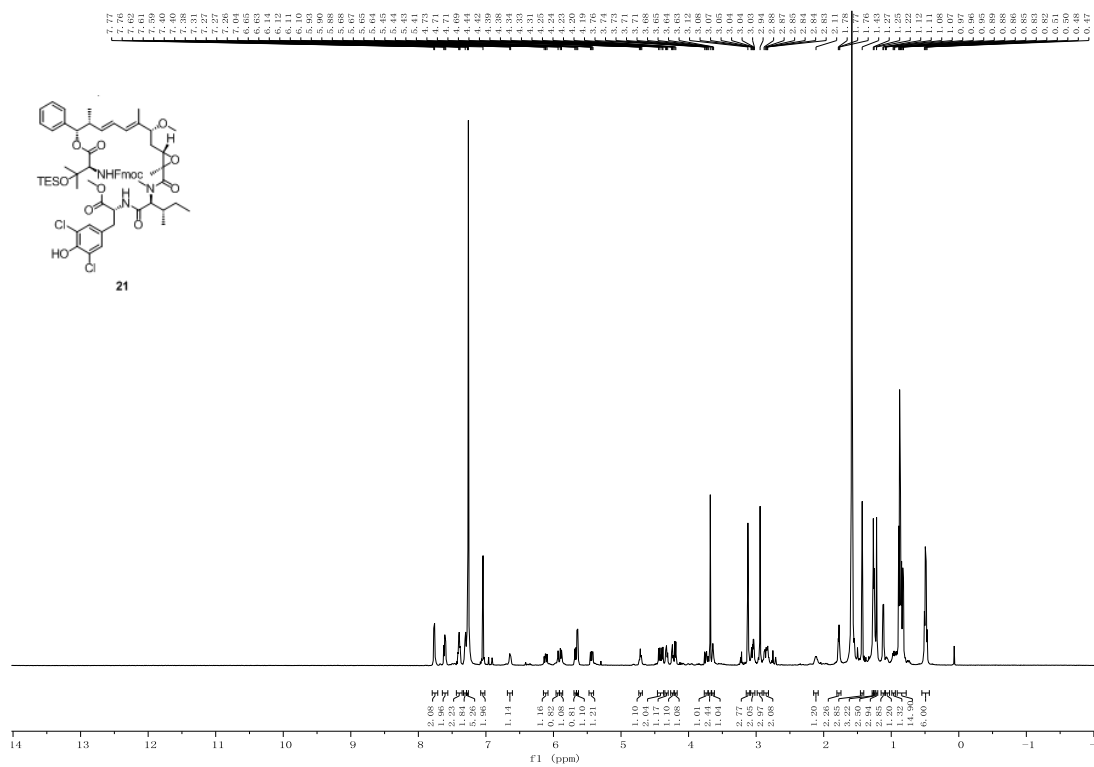


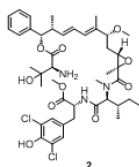
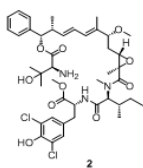


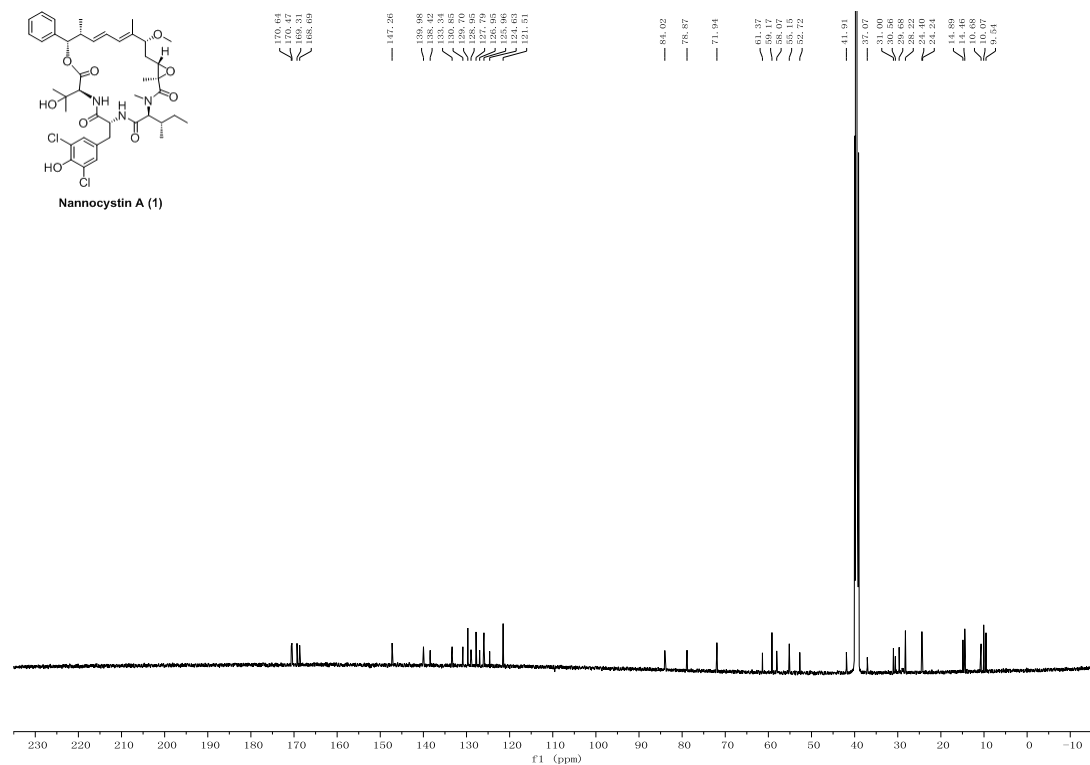
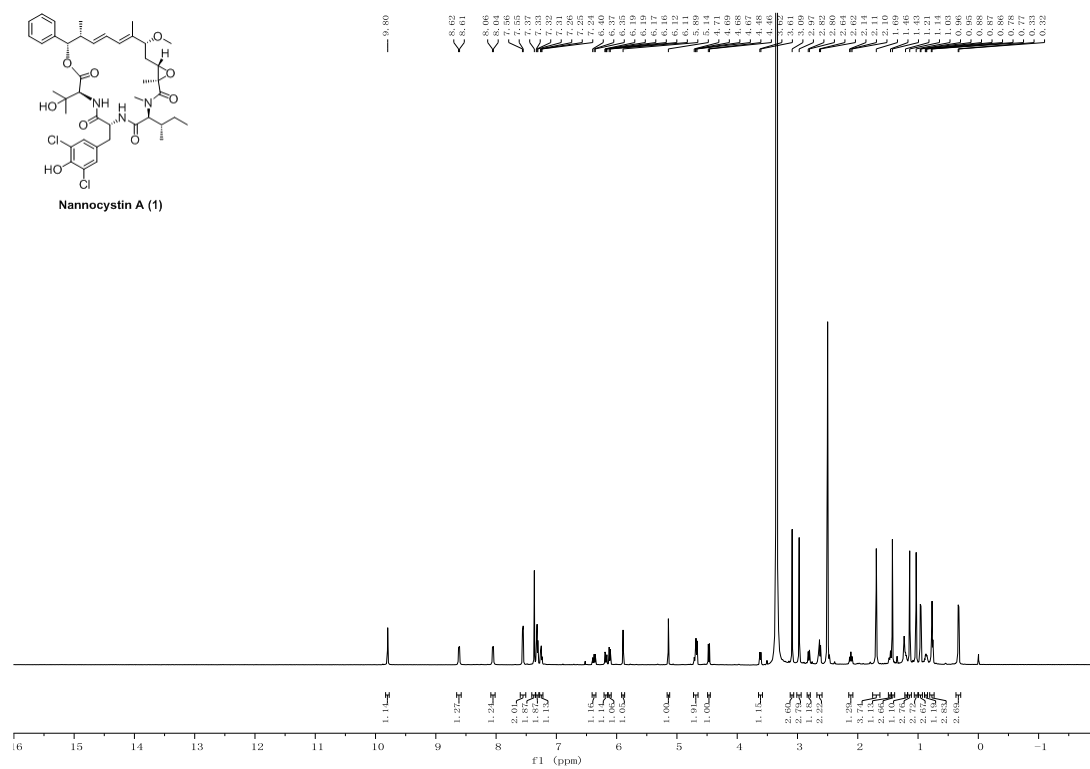












2. Tabulated comparison of ^1H NMR data of the synthetic nannocystin A with that reported by Dr. Dominic Hoepfner and coworkers (*Angew. Chem. Int. Ed.* 2015, 54, 10149)

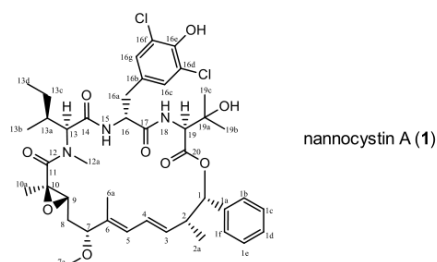


Table S1. Comparison of ^1H NMR data of the synthetic with nature nannocystin A.

Position	Nature δ_1 (J in Hz)	Synthetic δ_2 (J in Hz)	$\Delta\delta^1 = \delta_1 - \delta_2$
18	8.66 d (10.0 Hz)	8.61 d (10.2 Hz)	0.05
15	8.12 d (9.8 Hz)	8.05 d (9.6 Hz)	0.07
1f	7.57 d (7.6 Hz)	7.56 d (7.8 Hz)	0.01
16c, 16g	7.37 s	7.37 s	0
1c, 1e	7.34 t (7.6 Hz)	7.32 t (7.8 Hz)	0.02
1d	7.26 t (7.6 Hz)	7.25 t (7.2 Hz)	0.01
4	6.38 m	6.38 m	0
3	6.21 dd (15.4, 4.3 Hz)	6.18 dd (15.6, 4.8 Hz)	0.03
5	6.13 d (10.9 Hz)	6.11 d (10.8 Hz)	0.02
1	5.90 br	5.89 br	0.01
19a-OH	5.19 s	5.14 s	0.05
16, 19	4.68 m	4.68 m	0
13	4.48 d (11.2 Hz)	4.47 d (11.4 Hz)	0.01
7	3.63 m	3.62 m	0.01
7a	3.09 s	3.09 s	0
12a	2.99 s	2.97 s	0.02
16a	2.81 d (11.6 Hz)	2.81 d (12.0 Hz)	0
2	2.65 m	2.64 m	0.01
9	2.62 m	2.62 m	0
16a	2.50 m	In DMSO	
8	2.13 t (11.8 Hz)	2.12 t (12.0 Hz)	0.01
6a	1.70 s	1.70 s	0
13a	1.70 m	1.70 m	0
8	1.46 m	1.45 m	0.01
10a	1.44 s	1.43 s	0.01
13c	1.24 m	1.20 m	0.04
19b	1.14 s	1.14 s	0

19c	1.04 s	1.03 s	0.01
2a	0.97 d (6.8 Hz)	0.96 d (6.6 Hz)	0.01
13c	0.85 m	0.85 m	0
13d	0.78 t (7.2 Hz)	0.77 t (7.2 Hz)	0.01
13b	0.33 d (6.5 Hz)	0.33 d (6.6 Hz)	0

3. Tabulated comparison of ^{13}C NMR data of the synthetic nannocystin A with that reported by Dr. Dominic Hoepfner and coworkers (*Angew. Chem. Int. Ed.* 2015, 54, 10149)

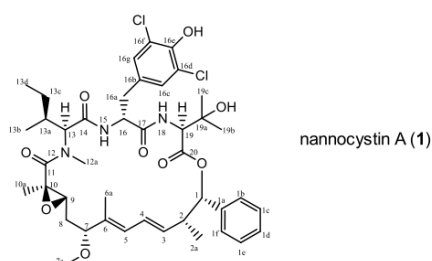


Table S2. Comparison of ^{13}C NMR data of the synthetic with nature nannocystin A.

Carbon No.	Nature (& ₁)	Synthetic(& ₂)	$\Delta \&^1 = \&_1 - \&_2$
2a	9.6	9.5	0.1
13d	10.1	10.1	0
6a	10.7	10.7	0
13b	14.5	14.5	0
10a	14.9	14.9	0
13c	24.3	24.2	0.1
19b	24.4	24.4	0
19c	28.2	28.2	0
12a	29.7	29.7	0
8	30.5	30.6	-0.1
13a	31.0	31.0	0
16a	37.1	37.1	0
2	41.9	41.9	0
16	52.7	52.7	0
7a	55.2	55.2	0
9	58.1	58.1	0
13	59.2	59.2	0
19	59.2	59.2	0
10	61.4	61.4	0
19a	72.0	71.9	0.1
1	78.8	78.9	-0.1

7	84.0	84.0	0
16d	121.5	121.5	0
16f	121.5	121.5	0
4	124.7	124.6	0.1
1b	126.0	126.0	0
1f	126.0	126.0	0
1d	127.0	127.0	0
1c	127.8	127.8	0
1e	127.8	127.8	0
5	129.0	129.0	0
16c	129.7	129.7	0
16g	129.7	129.7	0
16b	130.8	130.9	-0.1
6	133.3	133.3	0
3	138.4	138.4	0
1a	140.0	140.0	0
16e	147.3	147.3	0
14	168.7	168.7	0
11	169.3	169.3	0
17	170.5	170.5	0
20	170.7	170.6	0.1