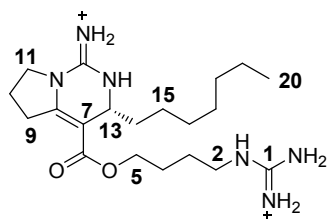


Eight-step Total Synthesis of (+)-Crambescin A

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(+)-Crambescin A (1)

Table S1. The NMR comparison of synthesized natural product

Atom	δ_{H}	δ_{C}	DEPT	^1H - ^1H COSY	HSQC	HMBC
1	/	158.5	C	/	/	H-2
2	3.23(t, $J = 7.2\text{Hz}$, 2H)	41.8	CH_2	H-3	+	H-3, H-4
3	1.70-1.66(m, 2H)	26.4	CH_2	H-2	+	H-2, H-3, H-4
4	1.79-1.74(m, 2H)	26.8	CH_2	H-5	+	
5	4.22 (td, $J = 14.4\text{Hz}$, 6.6Hz, 1H)	64.9	CH_2	H-4	+	H-3, H-4
6	/	165.9	C	/	/	H-5, H-13
7	/	103.0	C	/	/	H-9, H-13
8	/	152.6	C	/	/	H-9, H-10, H-11, H-13
9	3.35-3.31(m, 1H) 2.99(dt, $J = 18.0\text{Hz}$, 9.0Hz, 1H)	31.7	CH_2	H-10	+	H-10, H-11
10	2.26-2.18(m, 1H) 2.15-2.06(m, 1H)	22.7	CH_2	H-9, H-11	+	H-9, H-11
碳序号	δ_{H}	δ_{C}	DEPT	^1H - ^1H COSY	HSQC	HMBC
11	3.82 (td, $J = 8.4\text{Hz}$, 1.8Hz, 1H), 3.67(dd, J $= 16.2\text{Hz}$, 9.0Hz, 1H)	48.7	CH_2	H-10	+	H-9, H-10
12	/	152.9	C	/	/	H-13
13	4.40 (dd, $J = 6.6\text{Hz}$, 4.8Hz, 1H)	51.1	CH	H-14	+	H-14
14	1.62-1.54(m, 2H)	37.2	CH_2	H-13	+	H-13
15	1.44-1.30	25.0	CH_2		+	H-13
16	1.44-1.30	30.1	CH_2		+	H-14
17	1.44-1.30	30.0	CH_2		+	H-14
18	1.44-1.30	32.7	CH_2		+	H-20
19	1.44-1.30	23.5	CH_2		+	H-20
20	0.90(t, $J = 6.6\text{Hz}$, 3H)	14.2	CH_3	H-19	+	H-19, H-18

Table S2. The NMR comparison of synthesized natural product

Atom	synthesized natural product		literature data	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1	/	158.5		159.3
2	3.23(t, $J = 7.2\text{Hz}$, 2H)	41.8	3.30 (m, 2H)	41.2
3	1.70-1.66(m, 2H)	26.4	1.73 (m, 2H)	26.0
4	1.79-1.74(m, 2H)	26.8	1.79 (m, 2H)	26.0
5	4.22 (td, $J = 14.4\text{Hz}$, 6.6Hz, 1H)	64.9	4.21 (t, $J = 5.9$, 2H)	64.2
6	/	165.9		165.6
7	/	103.0		102.7
8	/	152.6		152.4
9			3.34 (ddd, $J = 18.2$, 8.3, 2.6Hz, 1H)	
	3.35-3.31(m, 1H)			
9	2.99(dt, $J = 18.0\text{Hz}$, 9.0Hz, 1H)	31.7	3.34 (ddd, $J = 18.2$, 8.3, 2.6Hz, 1H)	31.3
10	2.26-2.18(m, 1H)	22.7	2.30 (m, 1H)	22.3
	2.15-2.06(m, 1H)		2.16 (m, 1H)	
11	3.82 (td, $J = 8.4\text{Hz}$, 1.8Hz, 1H)	48.7	3.93 (dd, $J = 9.1$, 2.1 Hz, 1H)	48.1
	3.67(dd, $J = 16.2\text{Hz}$, 9.0Hz, 1H)		3.81 (dd, $J = 18.2$, 9.4 Hz, 1H)	
12	/	152.9		153.4
13	4.40 (dd, $J = 6.6\text{Hz}$, 4.8Hz, 1H)	51.1	4.37 (t, $J = 5.9\text{ Hz}$, 1H)	50.3
14	1.62-1.54(m, 2H)	37.2	1.5 (m, 2H)	37.0
15	1.44-1.30	25.0	1.29	29.8
16	1.44-1.30	30.1	1.29	29.8
17	1.44-1.30	30.0	1.29	29.8
18	1.44-1.30	32.7	1.29	29.8
19	1.44-1.30	23.5	1.29	29.8
20	0.90(t, $J=6.6\text{Hz}$, 3H)	14.2	0.87	14.0

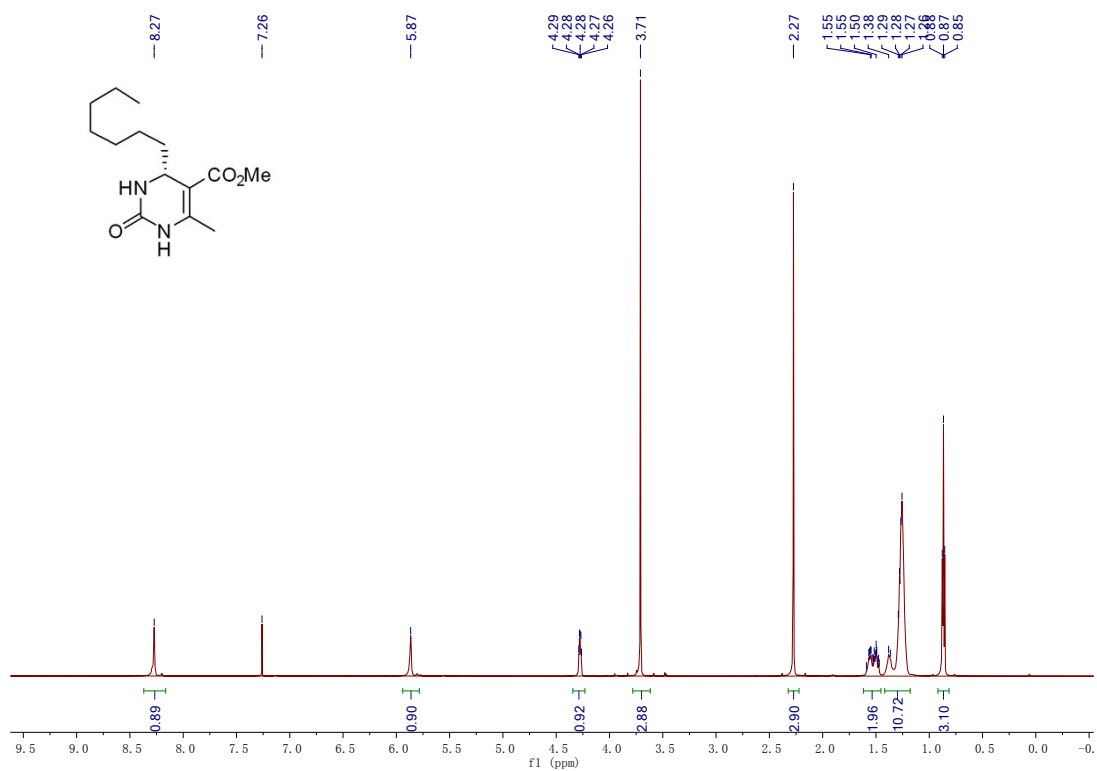


Fig.S 1 ¹H NMR of compound 11

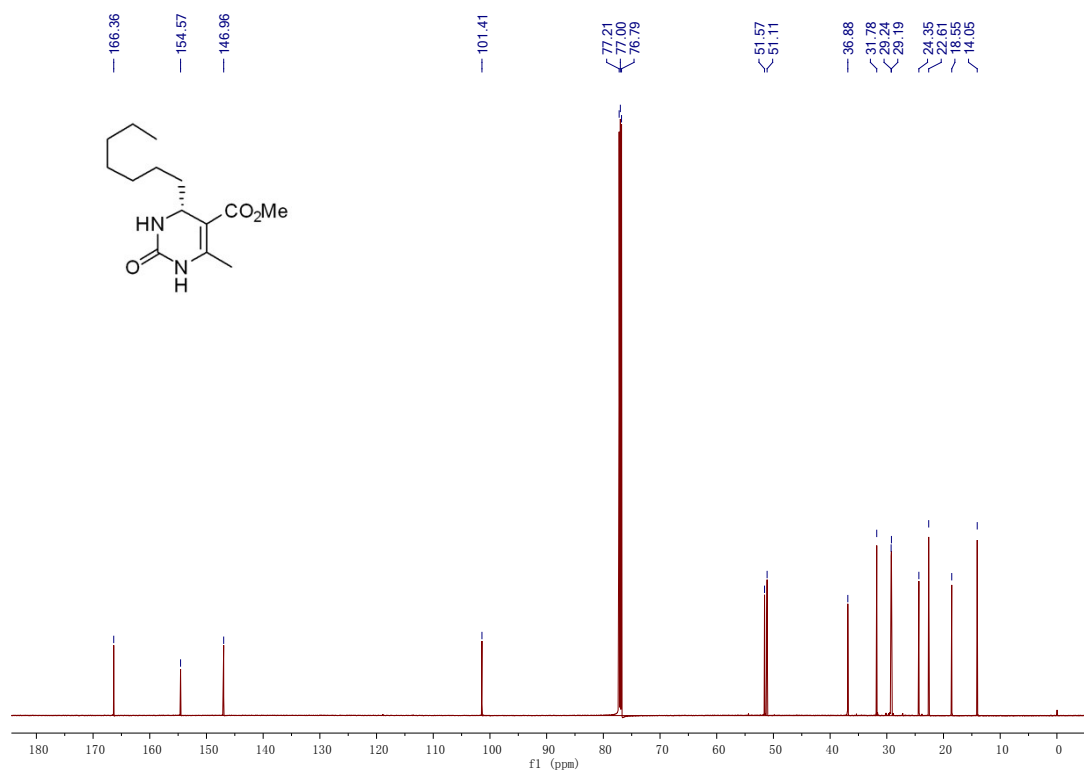


Fig.S 2 ¹³C NMR of compound 11

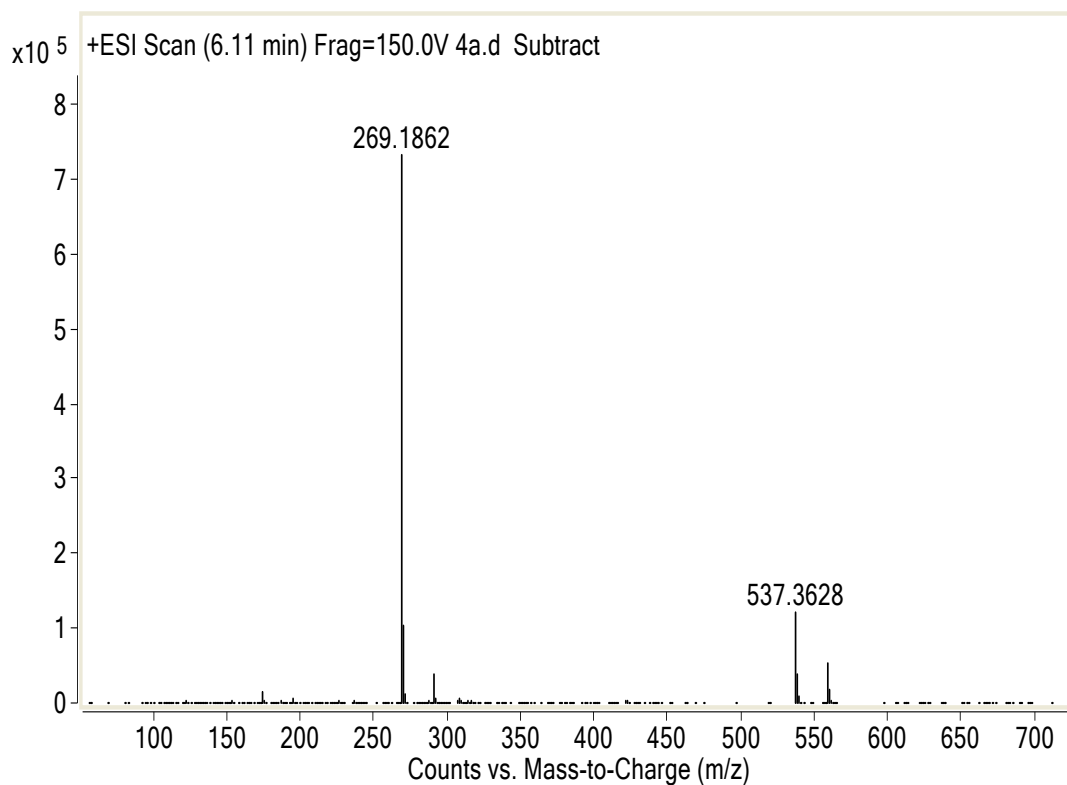
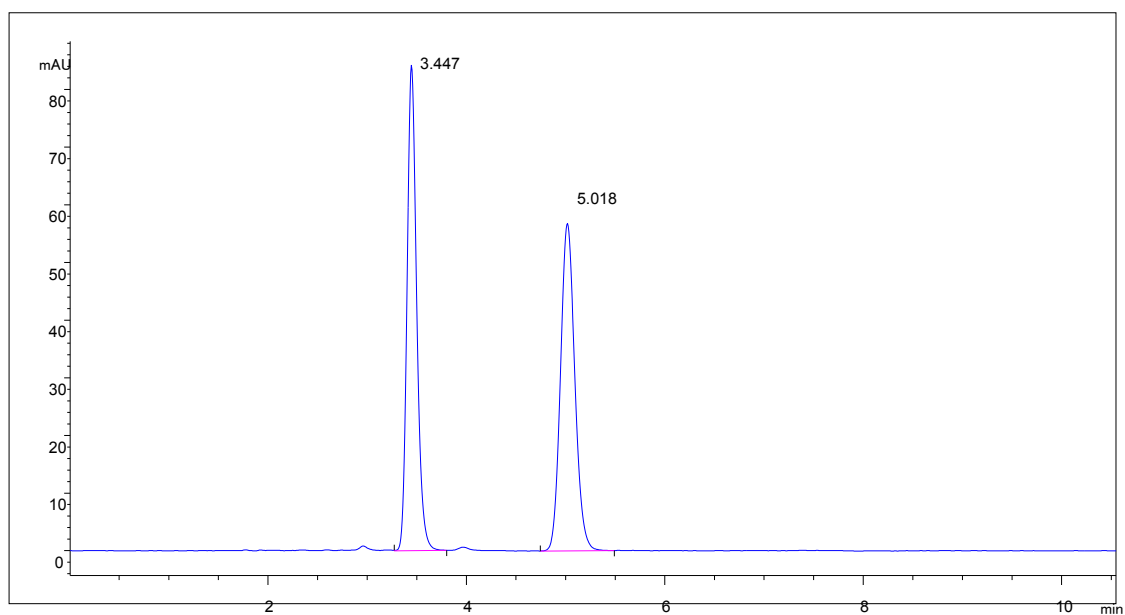
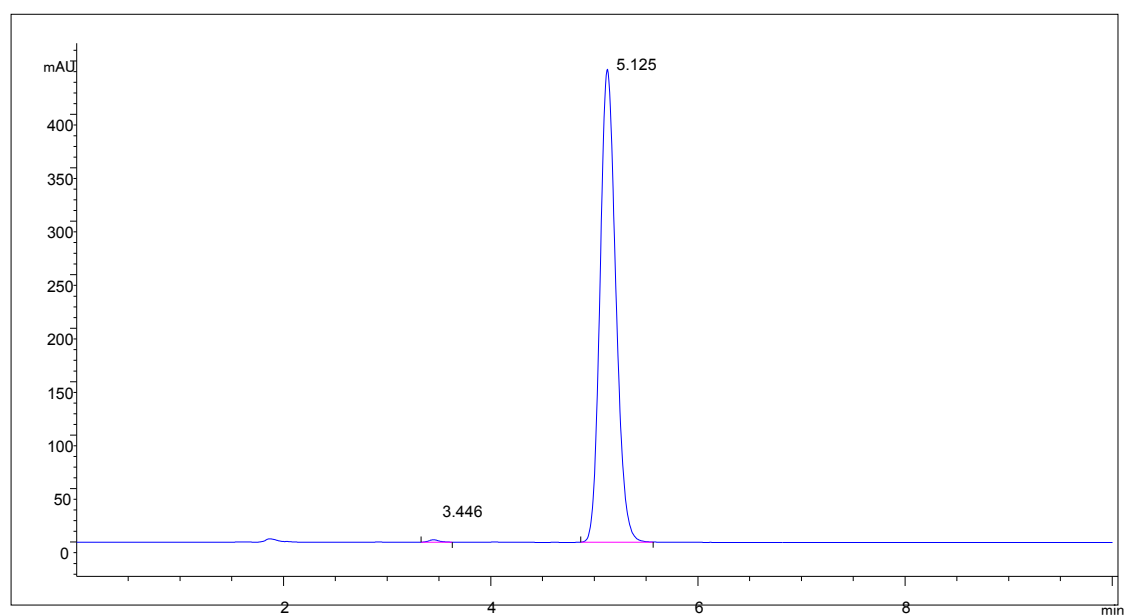


Fig.S 3 HRMS of compound **11**



#	Retention time (min)	Peak area (microvolt * sec)	Area/%
1	3.447	567.09	49.998
2	5.018	567.9	50.002

Fig.S 4 HPLC for racemic compound **2.5e**



#	Retention time (min)	Peak area (microvolt * sec)	Area/%
1	3.446	16.2	0.344
2	5.125	4700.1	99.656

Fig.S 5 HPLC for pure enantioenriched compound **11** after recrystallization

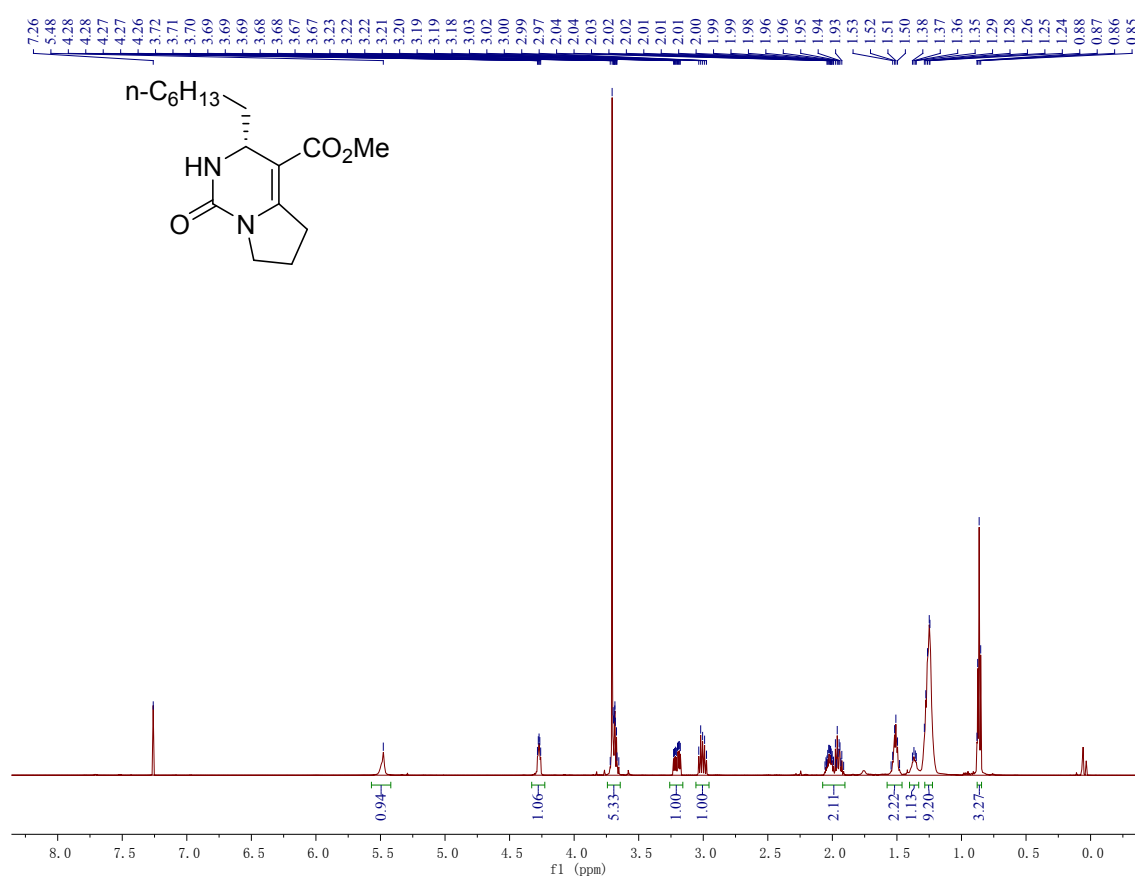


Fig.S 6 ¹H NMR of compound **10**

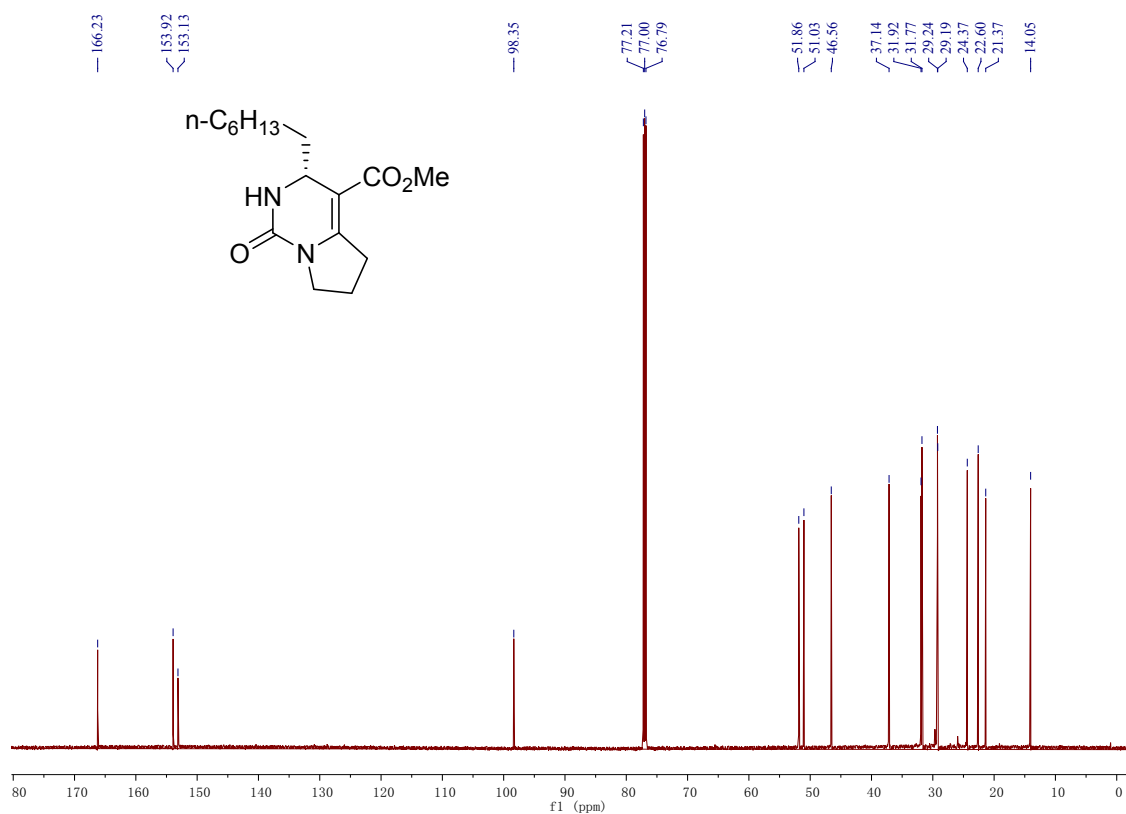


Fig.S 7 ¹³C NMR of compound **10**

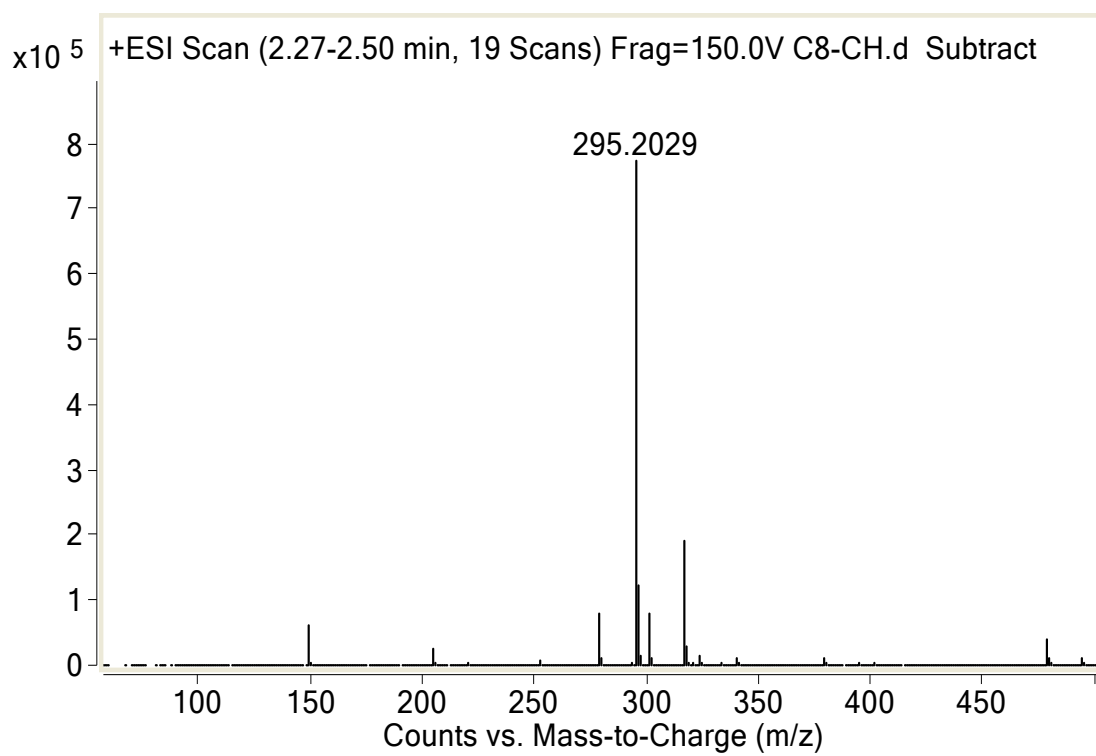
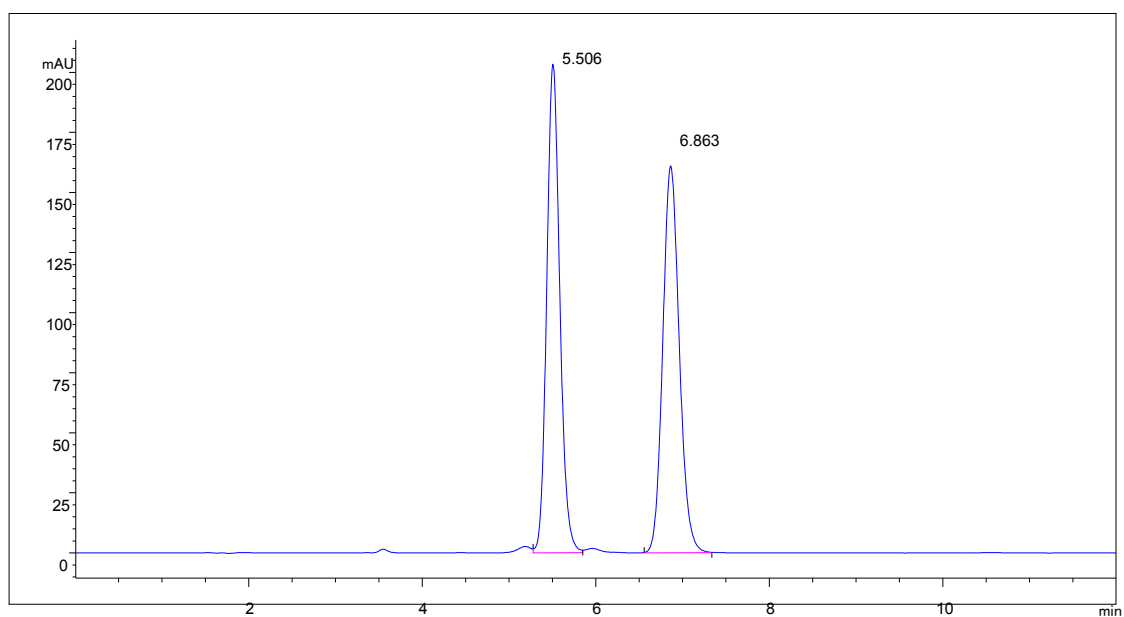
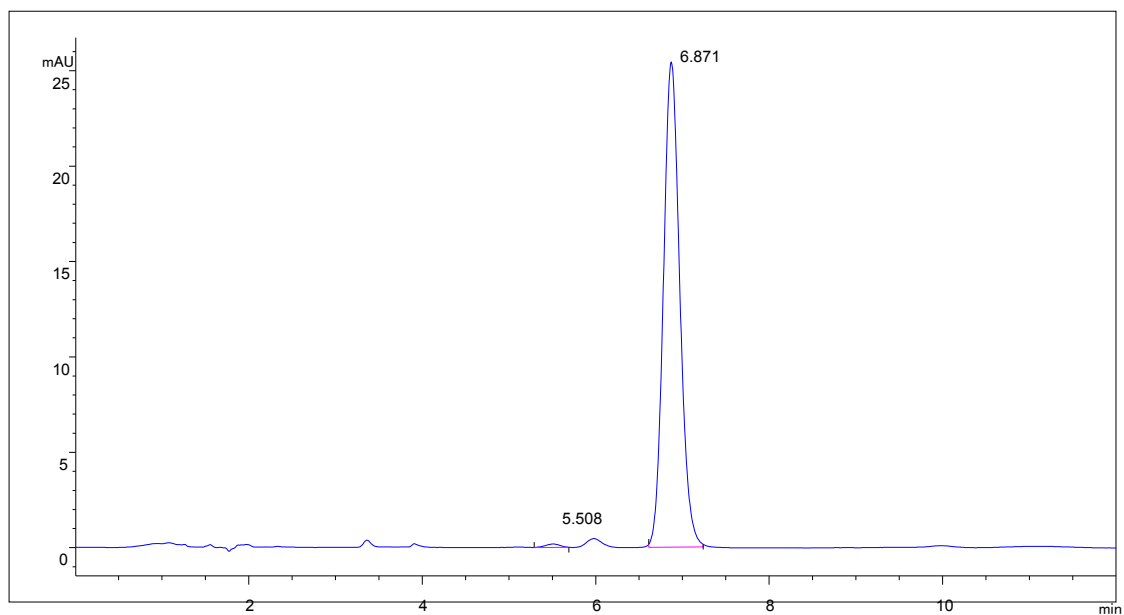


Fig.S 8 HRMS of compound **10**



#	Retention time (min)	Peak area (microvolt * sec)	Area/%
1	5.506	2129.8	49.996
2	6.863	2130.2	50.004

Fig.S 9 HPLC for racemic compound **10**



#	Retention time (min)	Peak area (microvolt * sec)	Area/%
1	5.508	2.2	0.647
2	6.871	333.4	99.353

Fig.S 10 HPLC for pure enantioenriched compound **10**

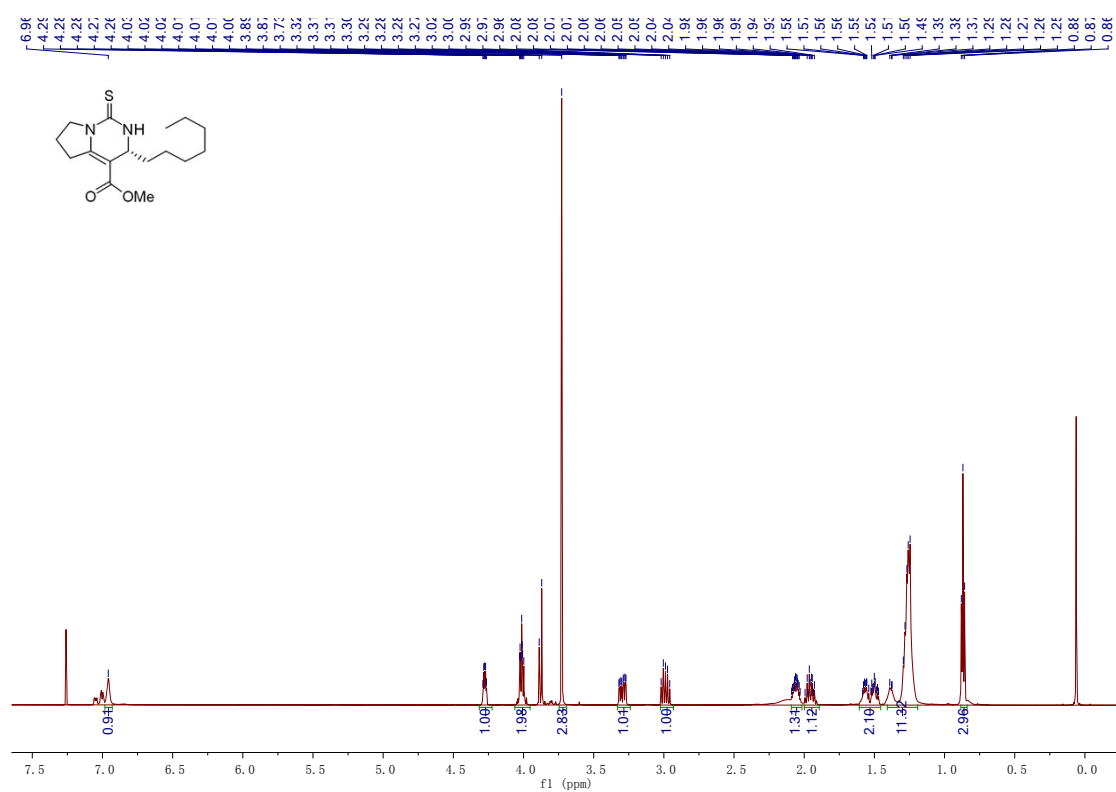


Fig.S 11 ¹H NMR of compound 17

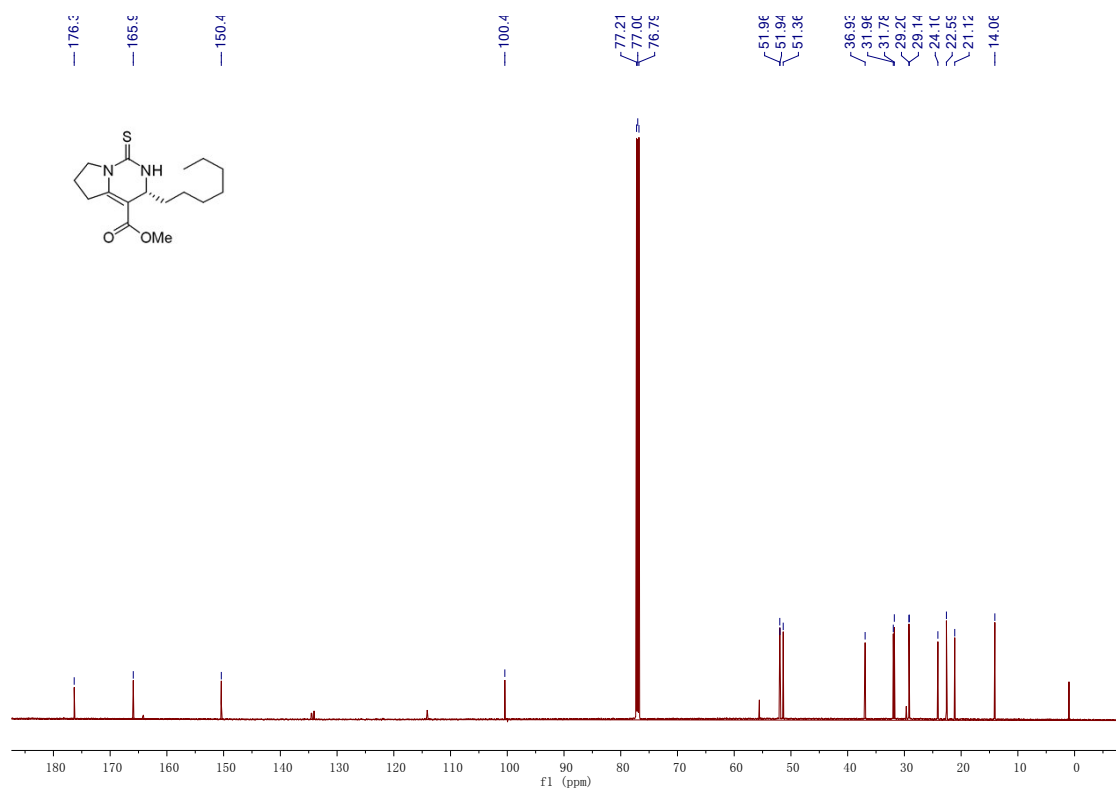


Fig.S 12 ¹³C NMR of compound 17

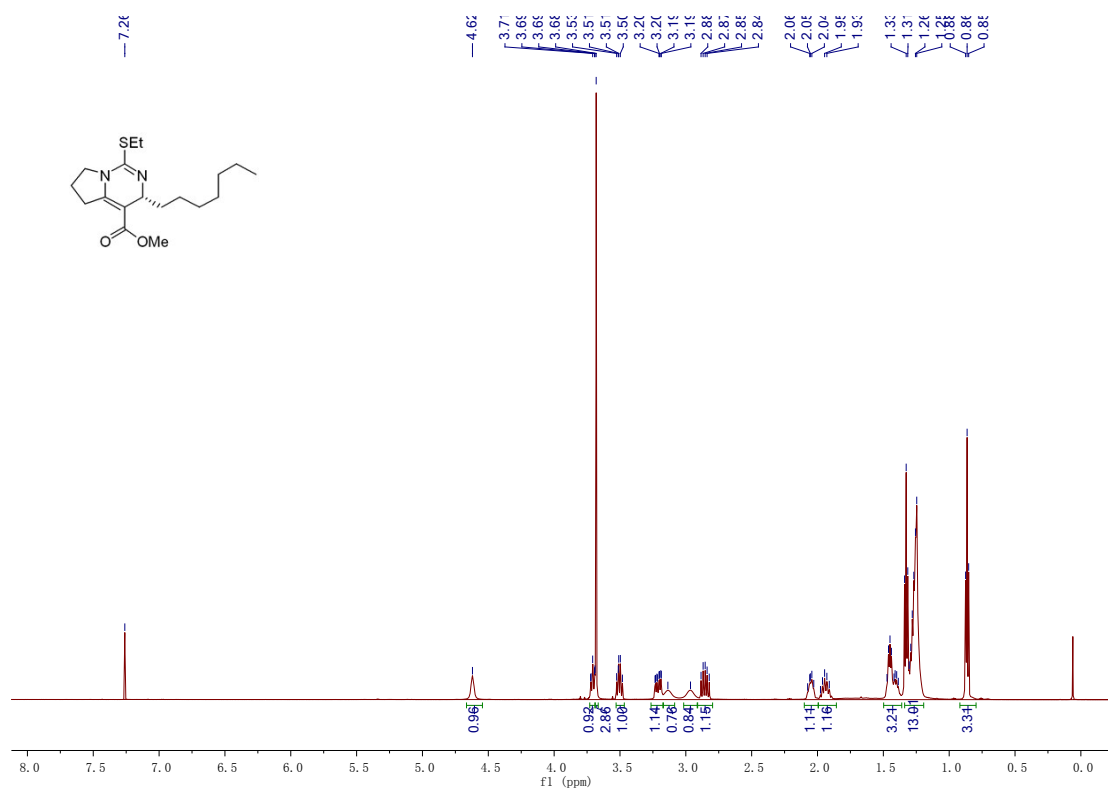


Fig.S 13 ¹H NMR of compound 18

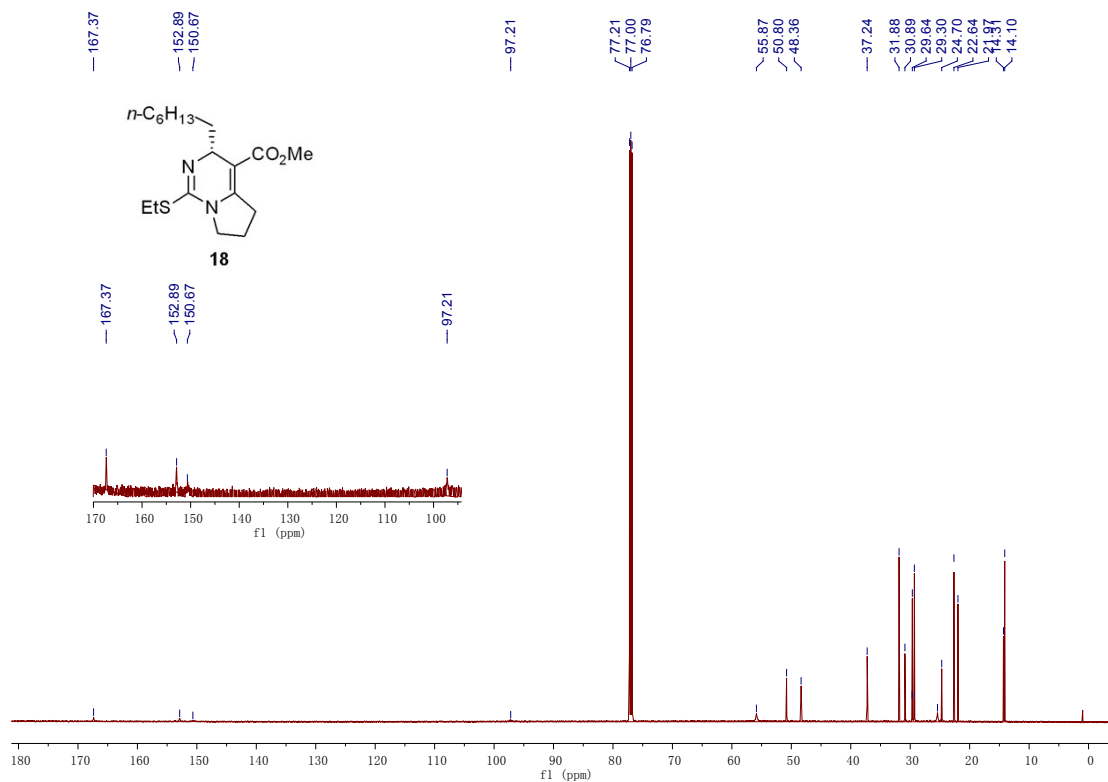


Fig.S 14 ¹³C NMR of compound 18

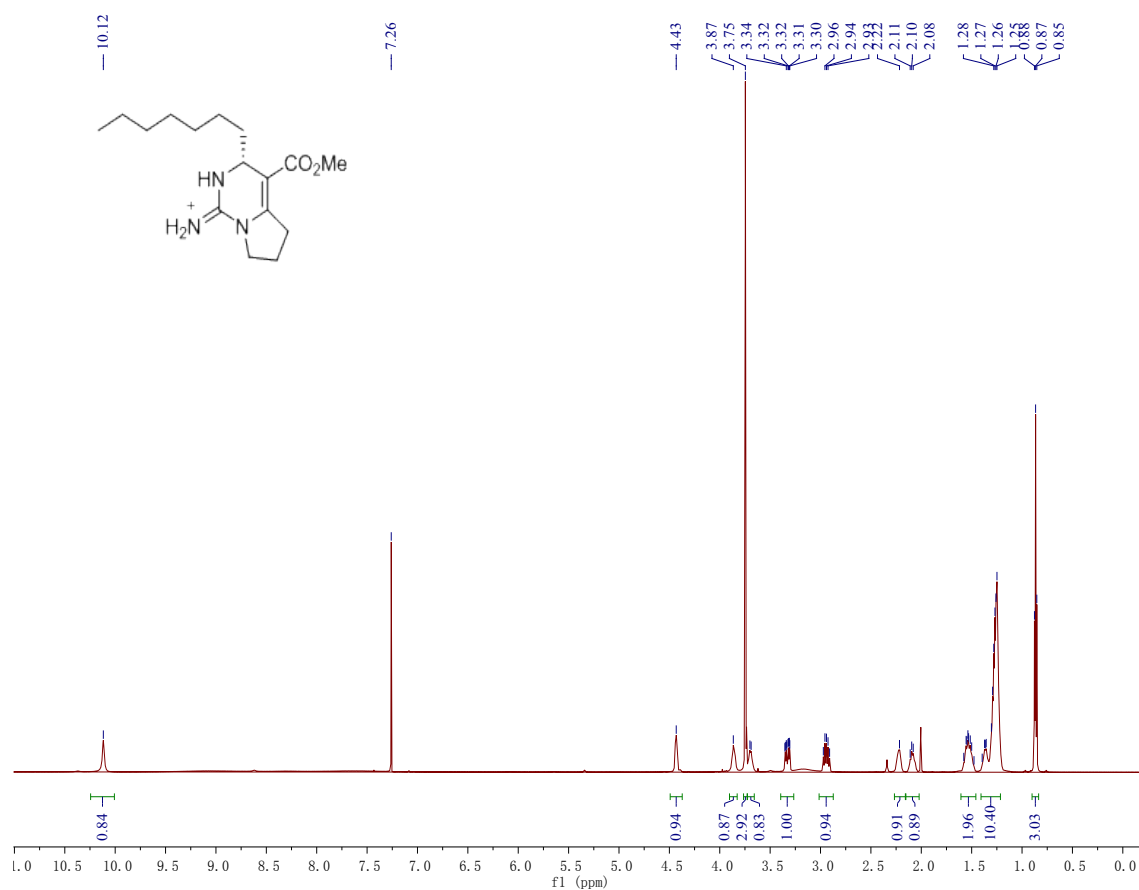


Fig.S 15 ¹H NMR of compound 16

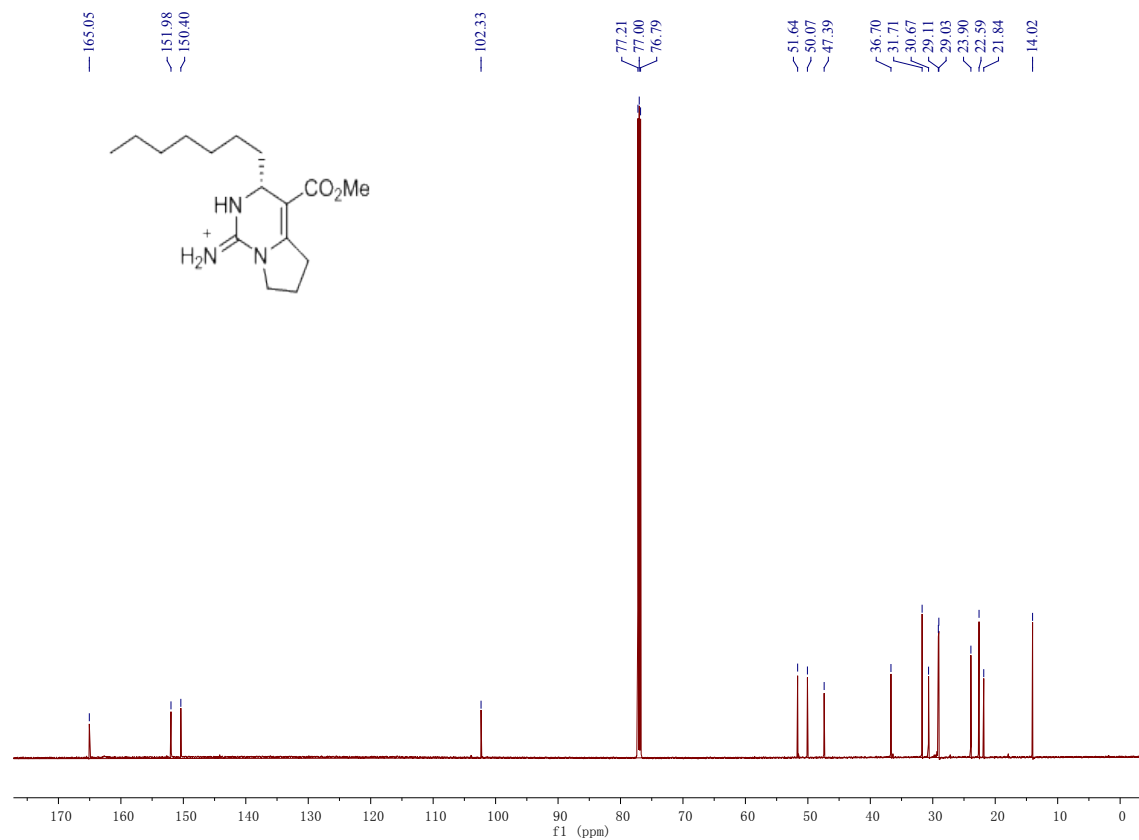


Fig.S 16 ¹³C NMR of compound 16

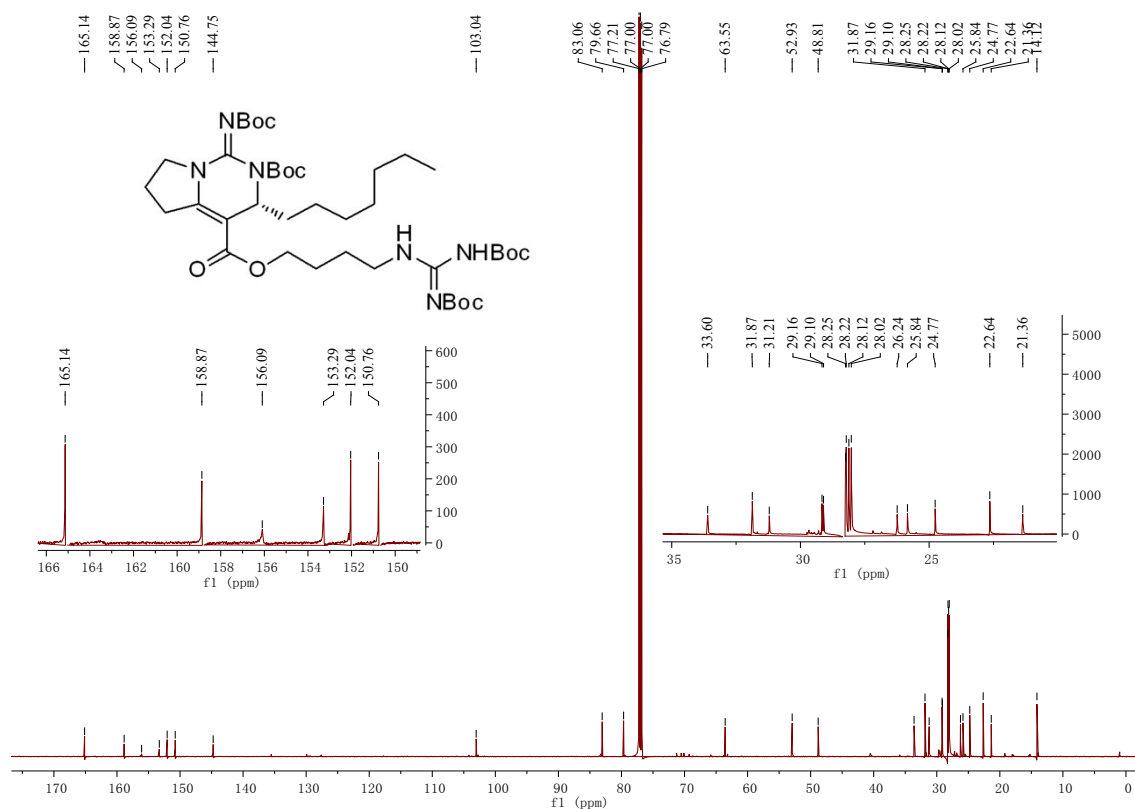


Fig.S 19 ^{13}C NMR of compound **20**

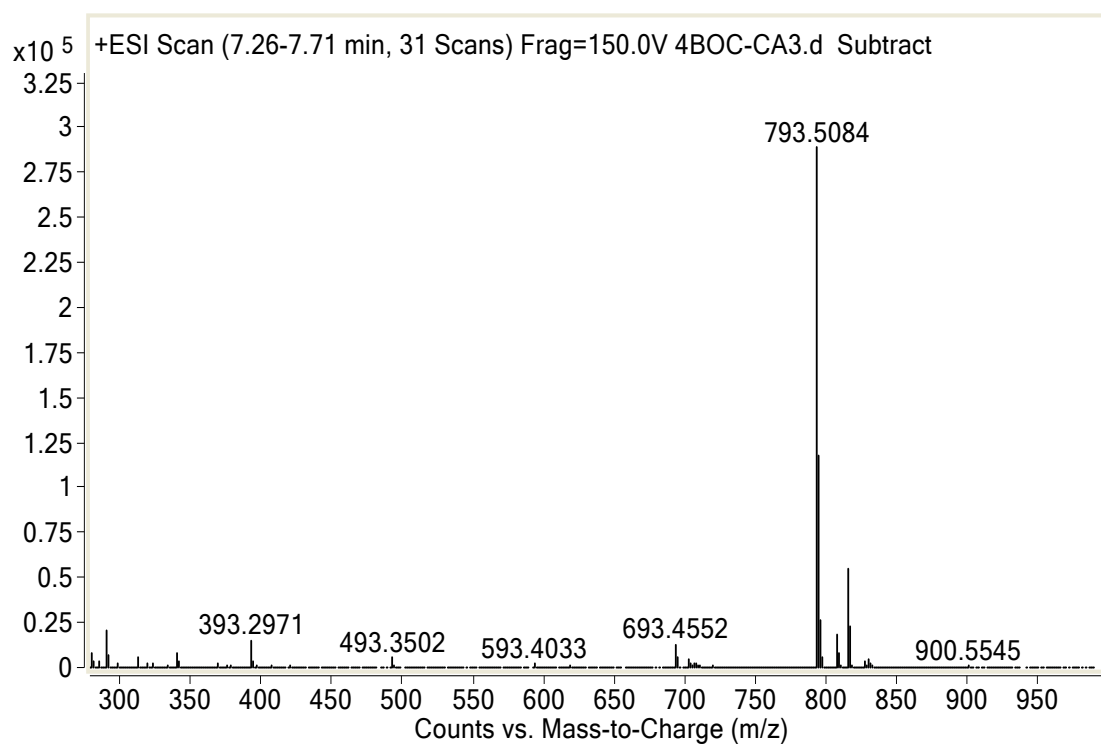


Fig.S 20 HRMS of compound **20**

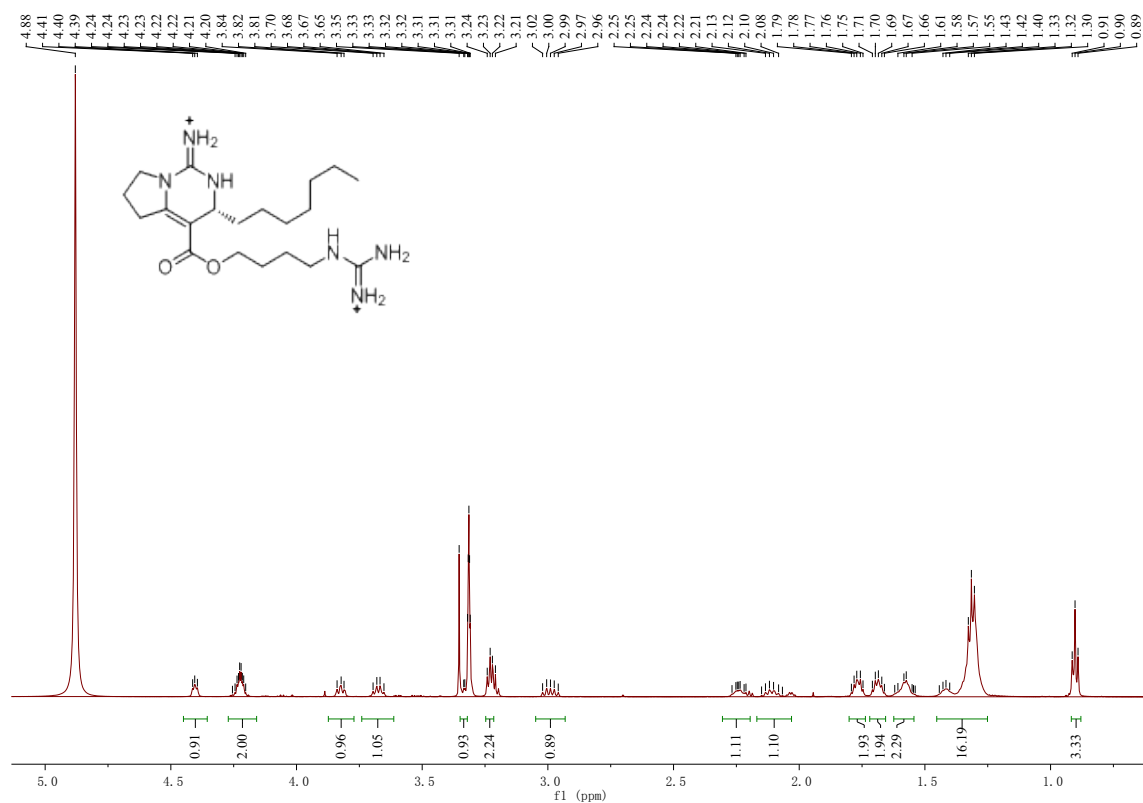


Fig.S 21 ¹H NMR of (+)-Crambescin A (1)

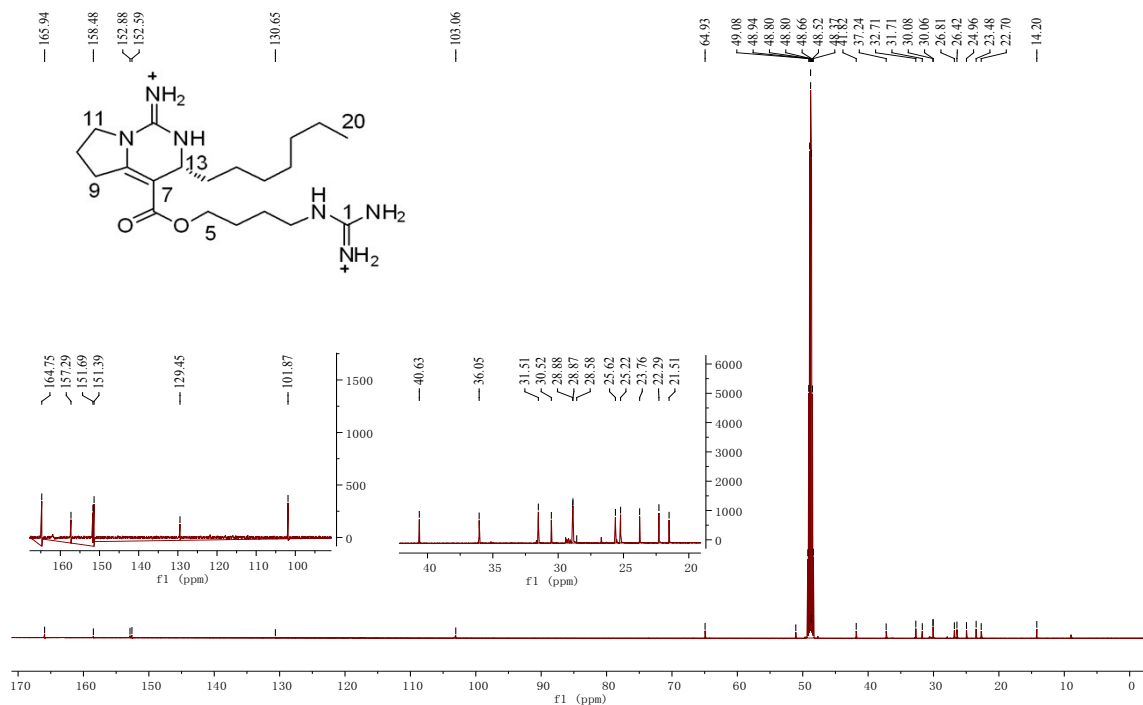


Fig.S 22 ¹³C NMR of (+)-Crambescin A (1)

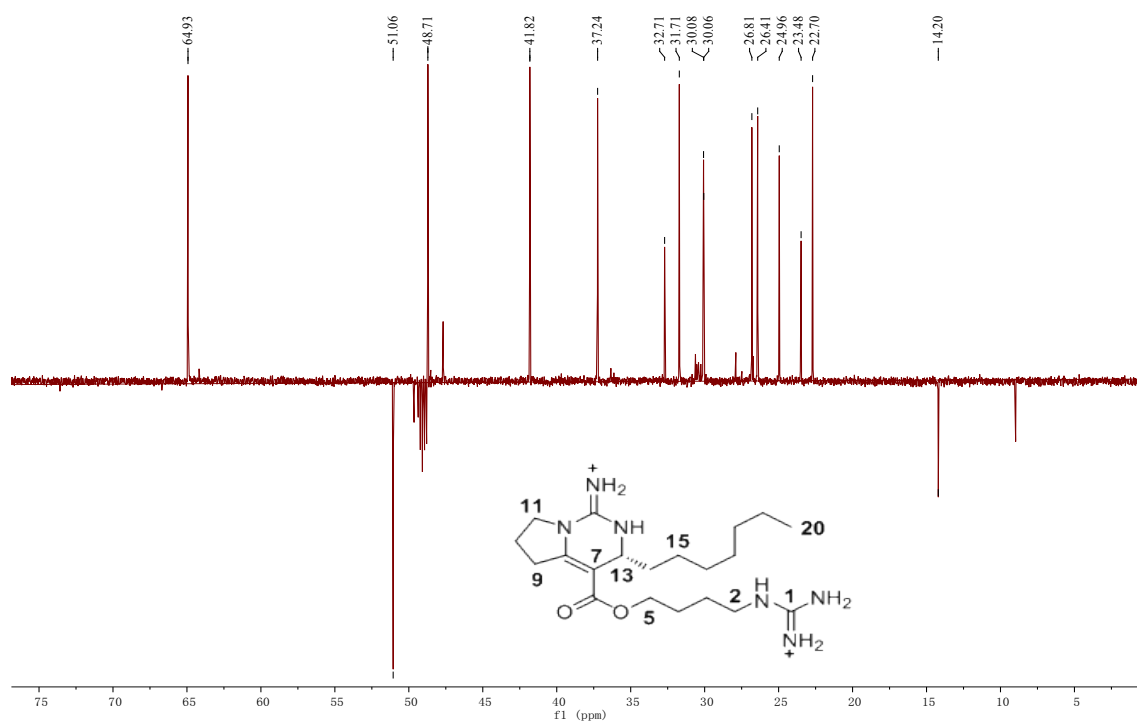


Fig.S 23 DEPT of (+)-Crambescin A (1)

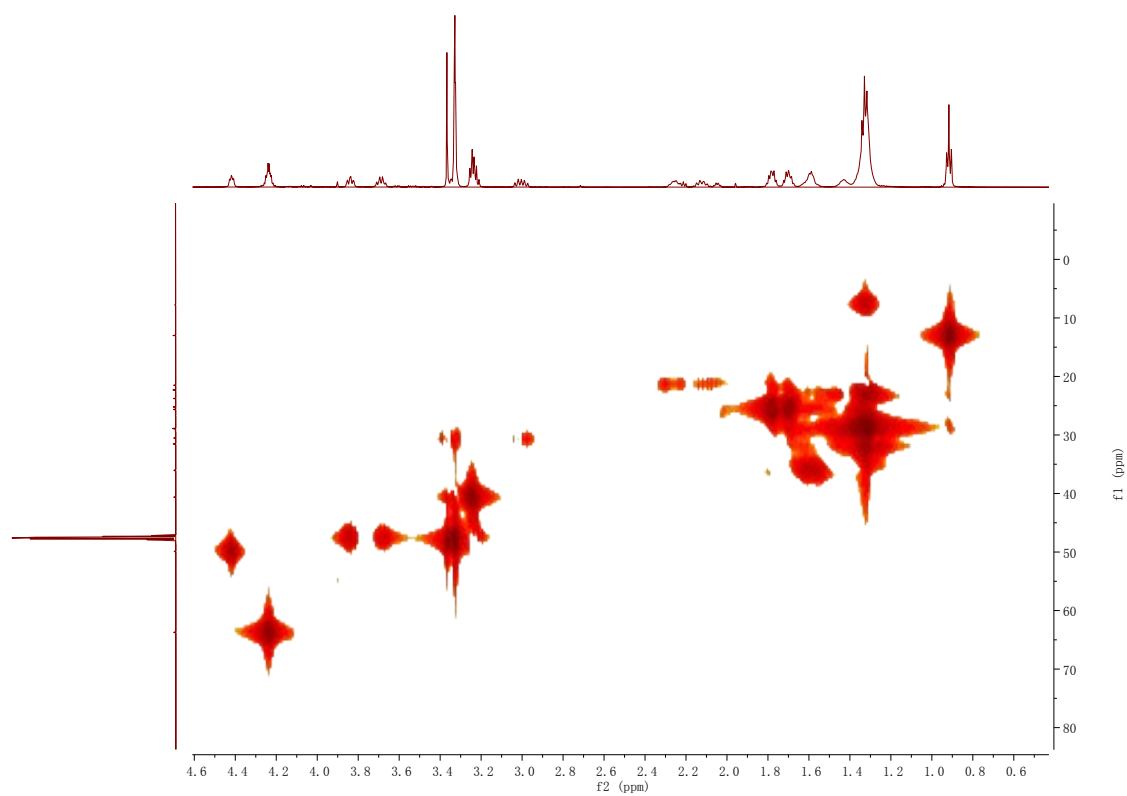


Fig.S 24 HMBC of (+)-Crambescin A (1)

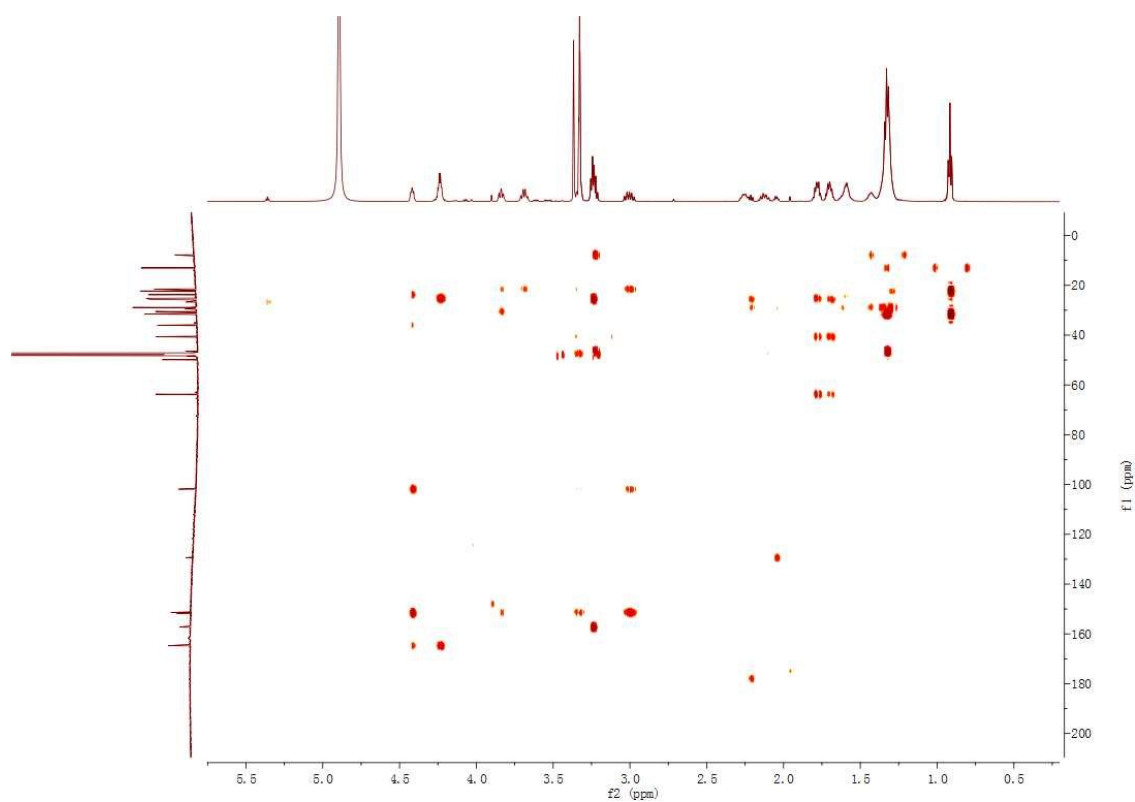


Fig.S 25 HMBC of (+)-Crambescin A (1)

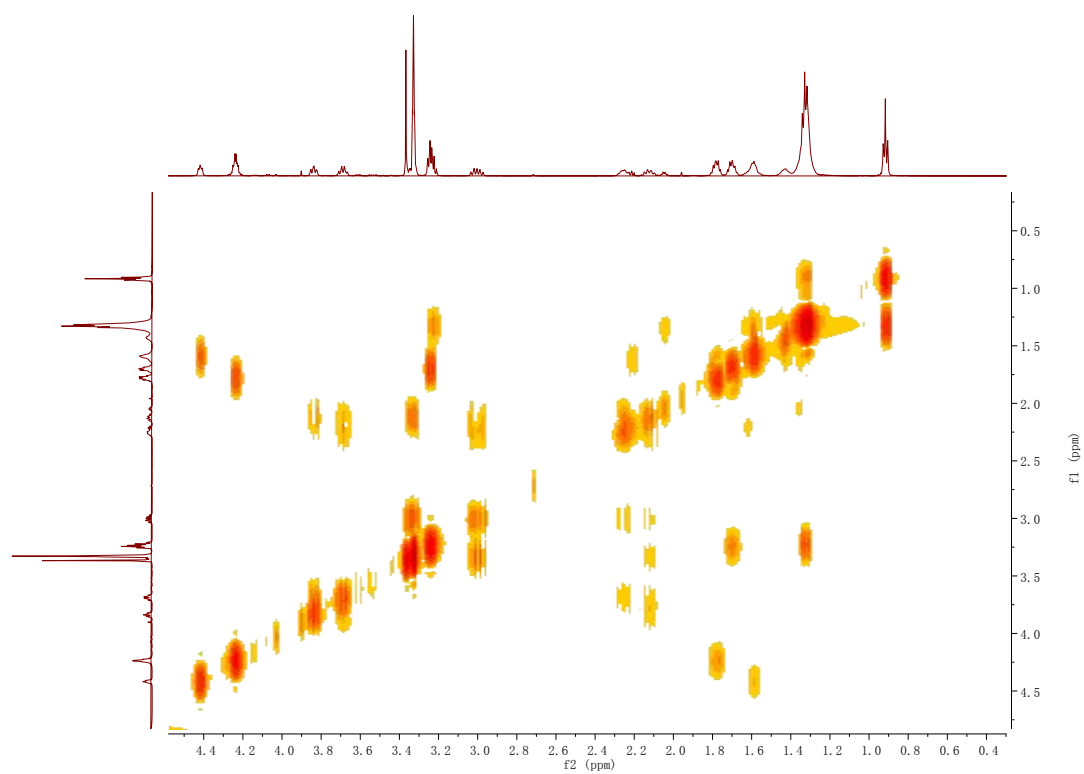


Fig.S 26 ^1H - ^1H COSY of (+)-Crambescin A (1)