

*Supporting Information Available*

**Chaetosemins A-E, New Chromones Isolated from an Ascomycete  
*Chaetomium seminudum* and Their Biological Activities**

He Li,<sup>a</sup> Jun-Mian Tian,<sup>a</sup> Hao-Yu Tang,<sup>a</sup> Shi-Yin Pan,<sup>b</sup> An-Ling Zhang,<sup>a\*</sup>  
and Jin-Ming Gao<sup>a\*</sup>

<sup>a</sup>Shaanxi Key Laboratory of Natural Products Chemical Biology, College of Science,  
Northwest A&F University, Yangling 712100, Shaanxi, China

<sup>b</sup> Xi'an No.1 Hospital, Shaanxi Institute of Ophthalmology, Xi'an 710002,  
Shaanxi, China

Corresponding author:

Prof. An-Ling Zhang and Prof. Dr. Jin-Ming Gao. Tel.: +86-29-87092515

E-mail: jinminggao@nwsuaf.edu.cn

Figure S1. $^1\text{H}$ spectra of chaetosemin A in $\text{CD}_3\text{OD}$ .....	3
Figure S2. $^{13}\text{C}$ spectra of chaetosemin A in $\text{CD}_3\text{OD}$ .....	3
Figure S3. HRESIMS spectra of chaetosemin A.....	4
Figure S4. HSQC spectra of chaetosemin A.....	5
Figure S5. COSY spectra of chaetosemin A.....	6
Figure S6. HMBC spectra of chaetosemin A.....	7
Figure S7. IR spectra of chaetosemin A.....	8
Figure S8. UV spectra of chaetosemin A.....	9
Table S1. Crystal data and structure refinement for chaetosemin A.....	10
Figure S9. $^1\text{H}$ spectra of chaetosemin B in $\text{CDCl}_3$ .....	11
Figure S10. $^{13}\text{C}$ spectra of chaetosemin B in $\text{CDCl}_3$ .....	12
Figure S11. HRESIMS spectra of chaetosemin B.....	113
Figure S12. HSQC spectra of chaetosemin B.....	14
Figure S13. COSY spectra of chaetosemin B.....	15
Figure S14. HMBC spectra of chaetosemin B.....	16
Figure S15. IR spectra of chaetosemin B.....	17
Figure S16. UV spectra of chaetosemin B.....	18
Figure S17. $^1\text{H}$ spectra of chaetosemin C in $\text{CD}_3\text{OD}$ .....	19
Figure S18. $^{13}\text{C}$ spectra of chaetosemin C in $\text{CD}_3\text{OD}$ .....	20
Figure S19. HRESIMS spectra of chaetosemin C.....	21
Figure S20. HSQC spectra of chaetosemin C.....	22
Figure S21. COSY spectra of chaetosemin C.....	223
Figure S22. HMBC spectra of chaetosemin C.....	24
Figure S23. IR spectra of chaetosemin C.....	25
Figure S24. UV spectra of chaetosemin C.....	26
Figure S25. $^1\text{H}$ spectra of chaetosemin D in $\text{CD}_3\text{OD}$ .....	27
Figure S26. $^{13}\text{C}$ spectra of chaetosemin D in $\text{CD}_3\text{OD}$ .....	28
Figure S27. HRESIMS spectra of chaetosemin D.....	29
Figure S28. HSQC spectra of chaetosemin D.....	30
Figure S29. HMBC spectra of chaetosemin D.....	31
Figure S30. IR spectra of chaetosemin D.....	322
Figure S31. UV spectra of chaetosemin D.....	333
Figure S32. $^1\text{H}$ spectra of chaetosemin E in $\text{DMSO-d}_6$ .....	344
Figure S33. $^{13}\text{C}$ spectra of chaetosemin E in $\text{DMSO-d}_6$ .....	355
Figure S34. HRESIMS spectra of chaetosemin E.....	366
Figure S35. HSQC spectra of chaetosemin E.....	377
Figure S36. COSY spectra of chaetosemin E.....	388
Figure S37. HMBC spectra of chaetosemin E.....	399
Figure S38. IR spectra of chaetosemin E.....	40
Figure S39. UV spectra of chaetosemin E.....	41

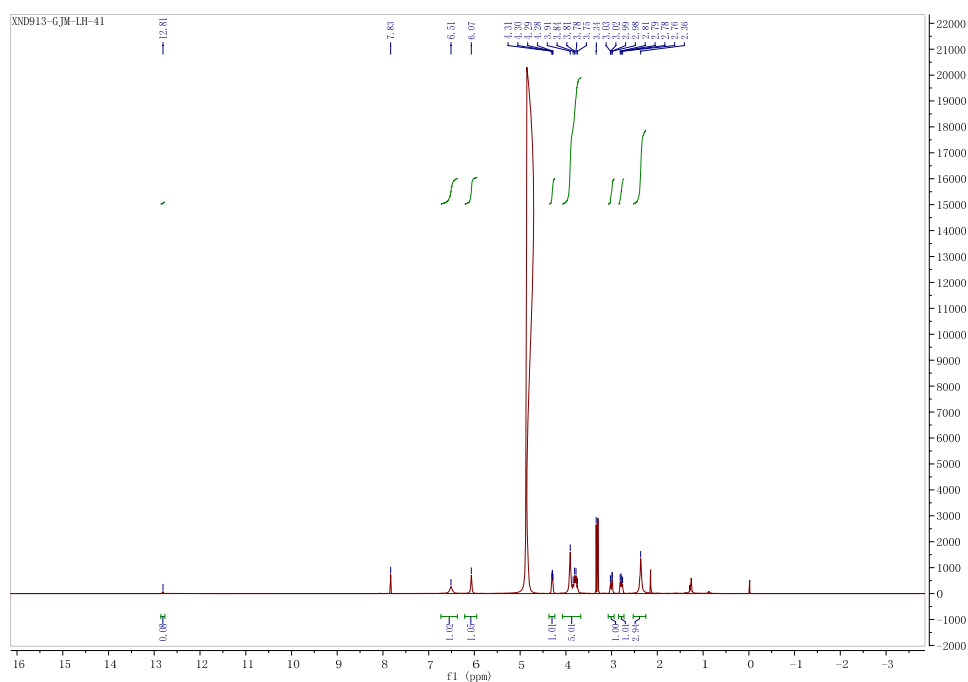


Figure S1.  $^1\text{H}$  spectra of chaetosemin A in  $\text{CD}_3\text{OD}$

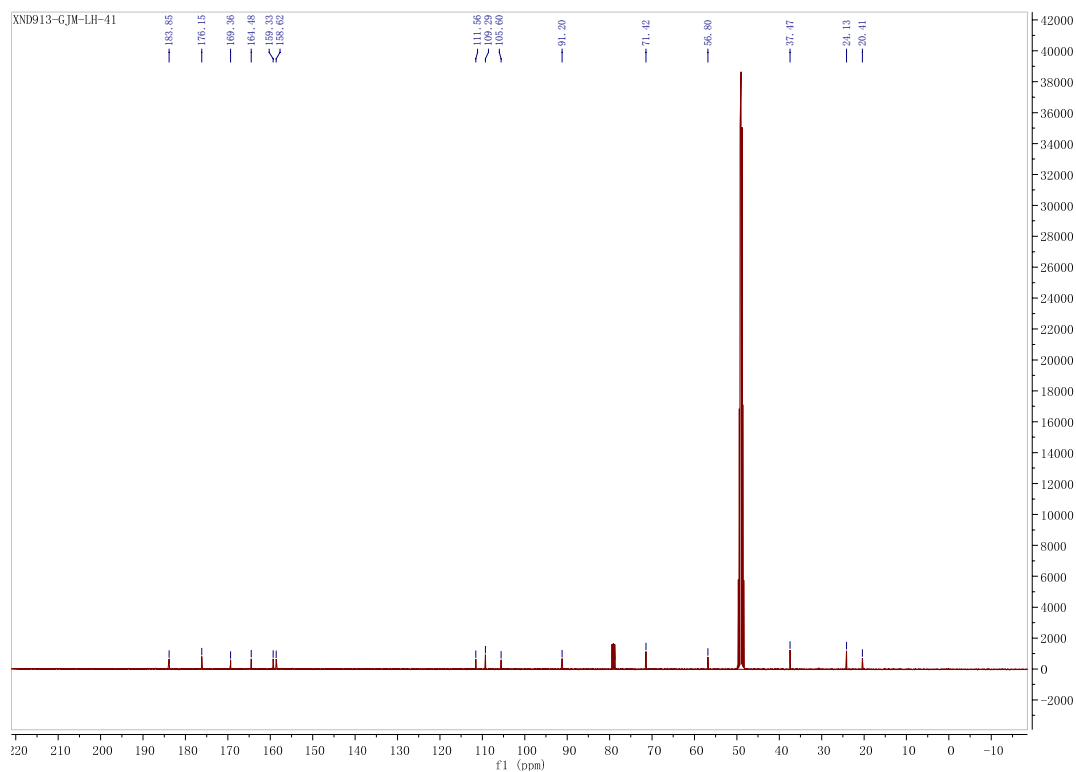


Figure S2.  $^{13}\text{C}$  spectra of chaetosemin A in  $\text{CD}_3\text{OD}$

Data File: D:\分子生物学\2013-07-29\cd-2\_LH-41\_20.kd

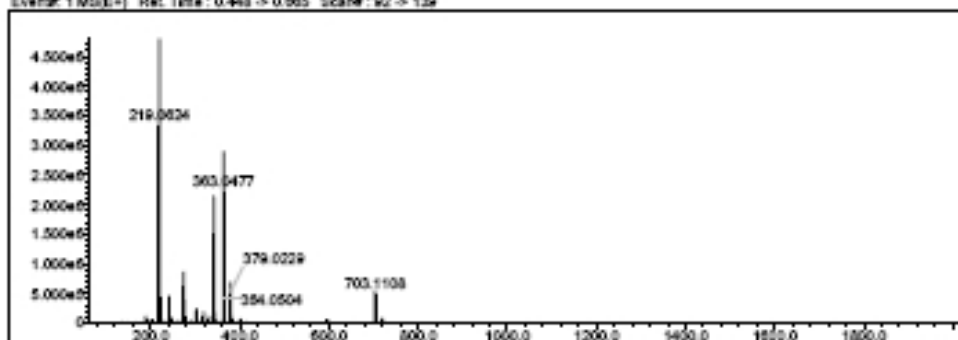
Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Use Adduct
H	1	0	200	N	3	0	0	P	3	0	0	Br	1	0	0	H
B	3	0	0	O	2	0	50	S	2	0	0	I	3	0	0	
C	4	0	100	F	1	0	0	Cl	1	0	0					

Error Margin (ppm): 20  
 HD Ratio: unlimited  
 Max Isotopes: all  
 MSn Iso RI (%): 75.00

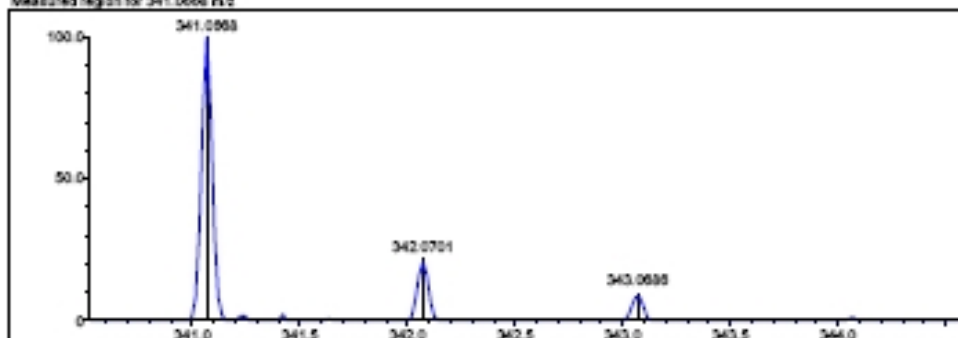
DBE Range: 0.0 - 30.0  
 Apply N Rule: no  
 Isotope RI (%): 1.00  
 MSn Logic Mode: OR

Electron Ion: both  
 Use MSn Info: yes  
 Isotope Res: 10000  
 Max Results: 500

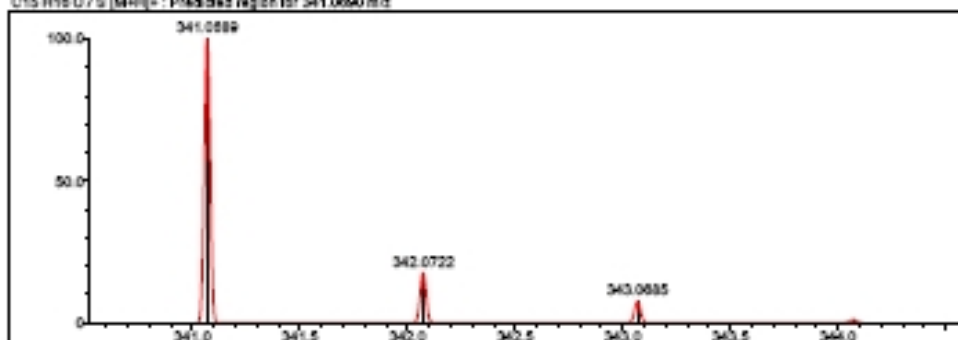
Event#: 1 (MS/E+). Ret. Time: 0.443 -> 0.965. Scan#: 92 -> 139



Measured region for 341.0668 m/z

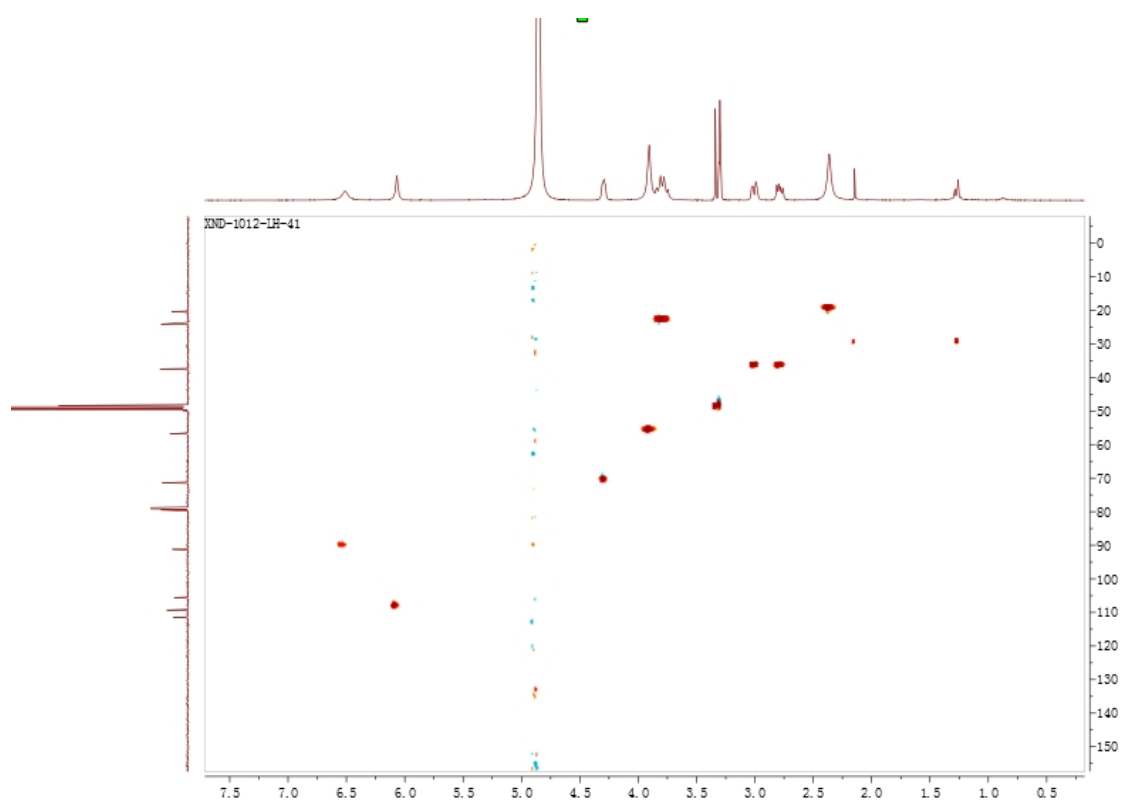


C15H16O7.2 (M+H)+ - Predicted region for 341.0690 m/z

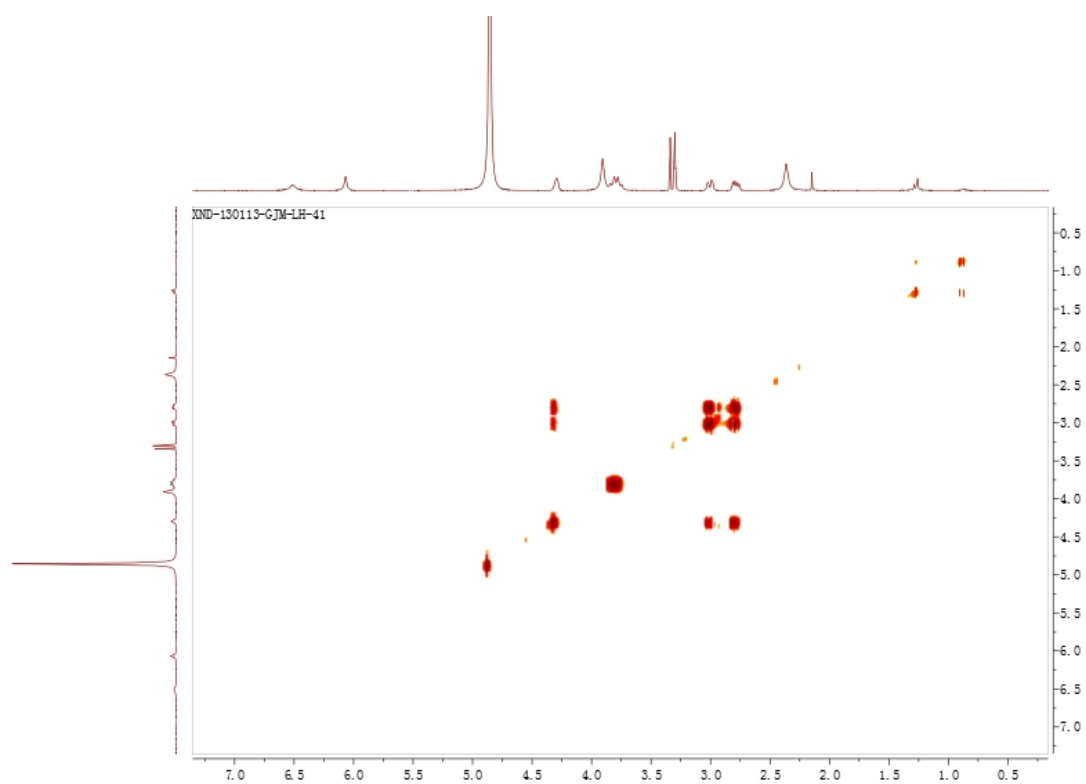


Rank	Score	Ion	Formula (M)	Pred. m/z	Mass. m/z	Df. (mDa)	Df. (ppm)	Isr	DBE
1	70.22	(M+H)+	C15H16O7.2	341.0690	341.0668	-2.2	-6.43	93.00	6.0

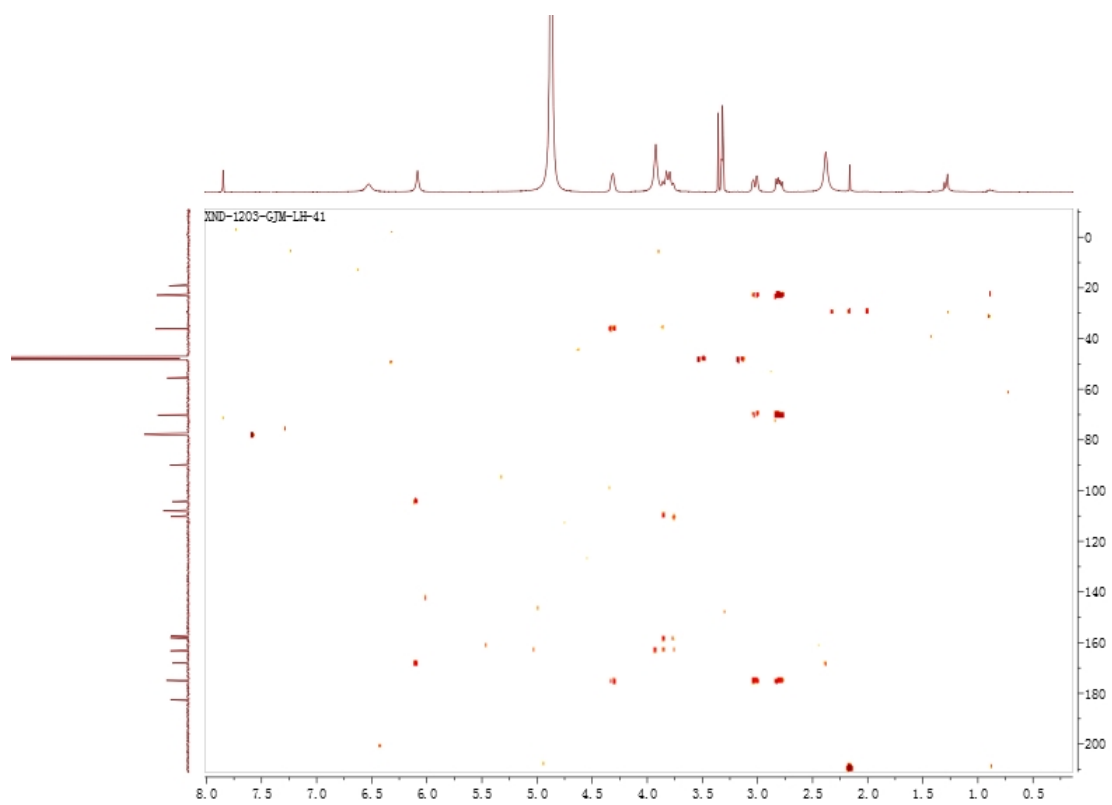
Figure S3. HRESIMS spectra of chaetosemin A



**Figure S4. HSQC spectra of chaetosemin A**



**Figure S5. COSY spectra of chaetosemin A**



**Figure S6. HMBC spectra of chaetosemin A**

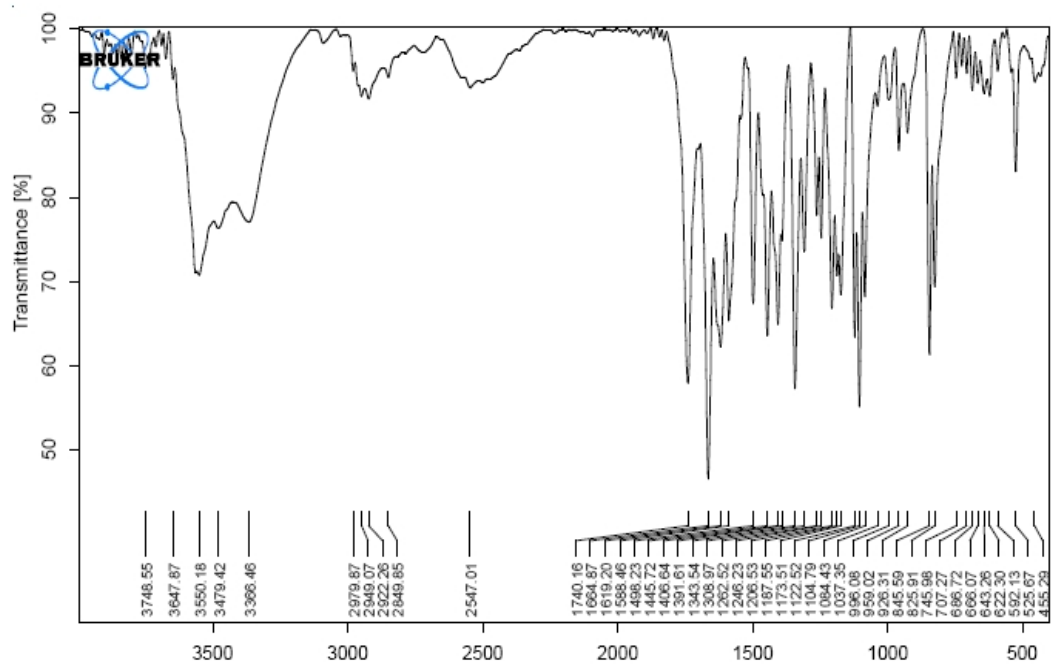


Figure S7. IR spectra of chaetosemin A



THERMO ELECTRON ~ VISIONpro SOFTWARE V4.10

Operator Name	(None Entered)	Date of Report	2013-7-27
Department	(None Entered)	Time of Report	19:15:28下午
Organization	(None Entered)		
Information	(None Entered)		

Scan Graph

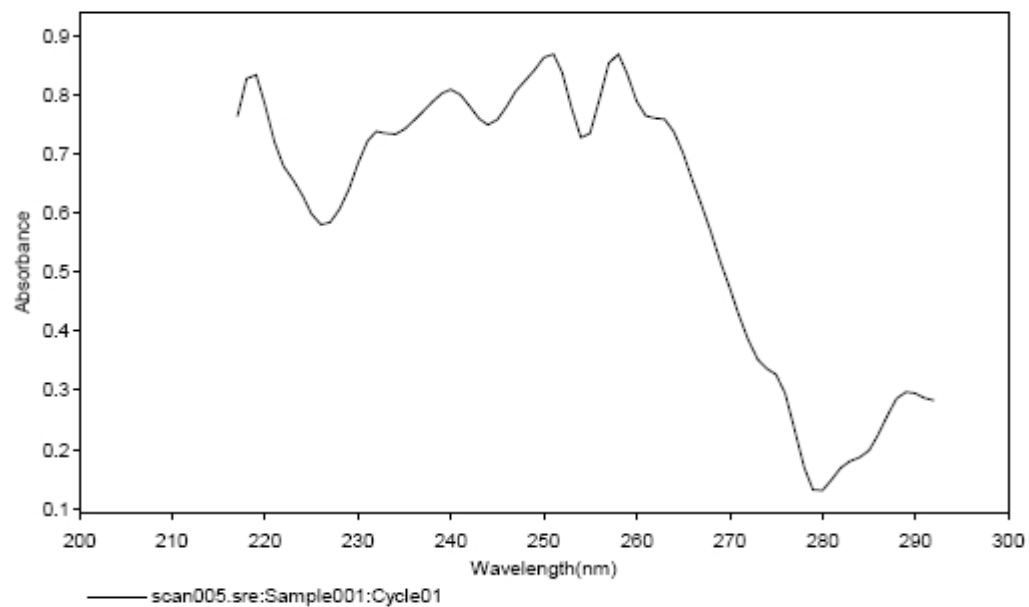
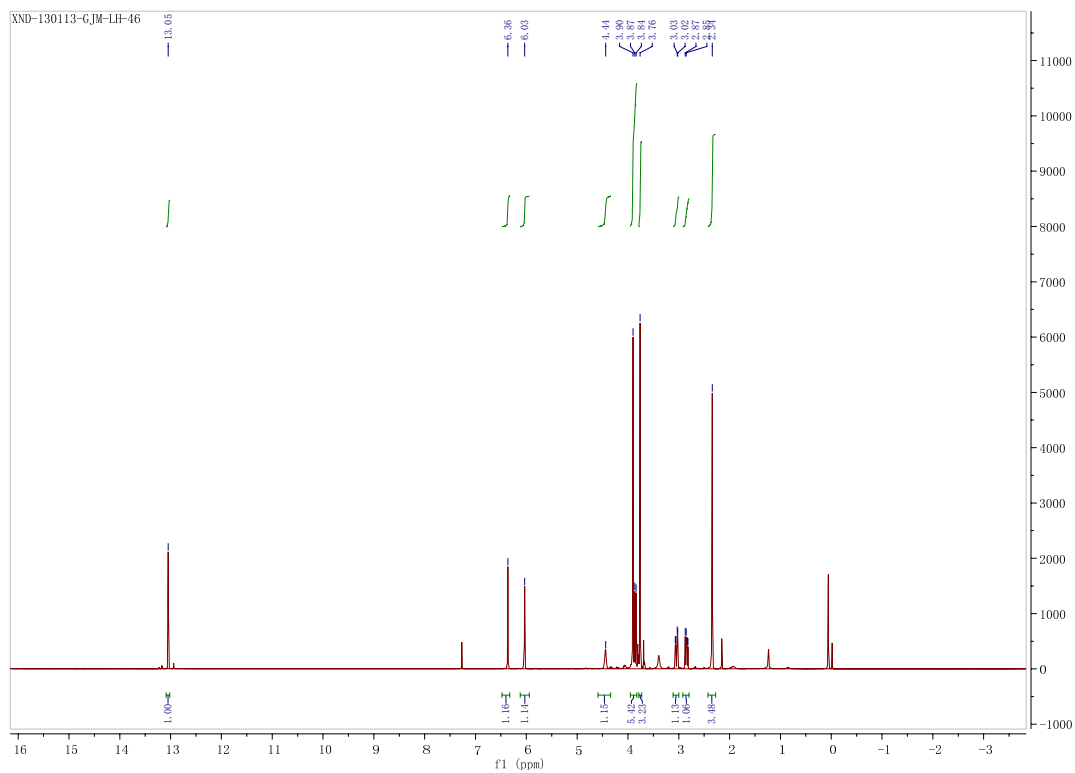


Figure S8. UV spectra of chaetosemin A

**Table S1. Crystal data and structure refinement for chaetosemin A**

Empirical formula	C <sub>15</sub> H <sub>16</sub> O <sub>7</sub> S·H <sub>2</sub> O
Formula weight	358.35
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	
<i>a</i> (Å)	4.5675(5)
<i>b</i> (Å)	7.6532(8)
<i>c</i> (Å)	45.491(3)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	1590.18(26)
<i>Z</i>	4
Calculated density (mg/m <sup>3</sup> )	1.497
Absorption coefficient (mm <sup>-1</sup> )	0.245
F(0 0 0)	752
Crystal size (mm)	0.42 × 0.30 × 0.28
$\theta$ Range (°)	2.808-22.65
Limiting indices	
<i>h</i>	-5-5
<i>k</i>	-8-9
<i>l</i>	-53-39
Reflections collected	7980
Independent reflections	2790[R <sub>int</sub> = 0.0434, R <sub>sigma</sub> = 0.0530]
Data/restraints/parameters	2790/0/219
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0525, wR <sub>2</sub> = 0.1052
Final R indexes [all data]	R <sub>1</sub> = 0.0680, wR <sub>2</sub> = 0.1110
Largest diff. peak/hole / e Å <sup>-3</sup>	0.210/-0.213



**Figure S9.**  $^1\text{H}$  spectra of chaetoseminBin  $\text{CDCl}_3$

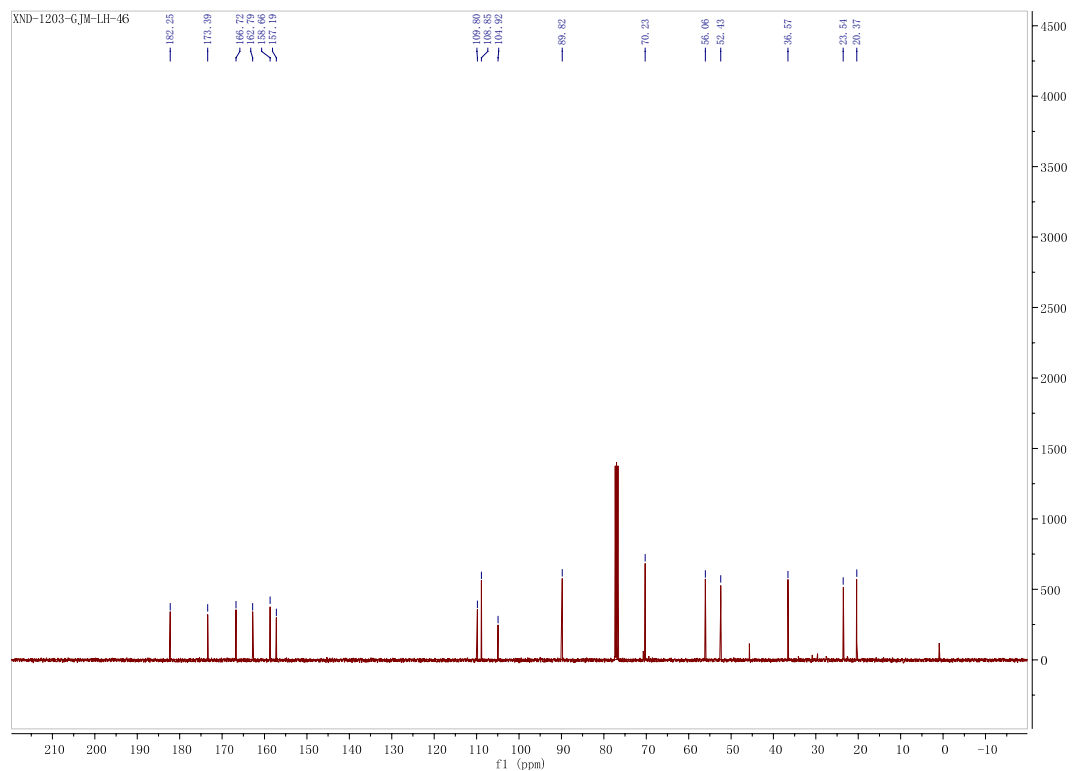


Figure S10.  $^{13}\text{C}$  spectra of chaetoseminBin  $\text{CDCl}_3$

Data File: D:\分子生物学\2013-07-26\cd\_2\_LH-46\_22.tol

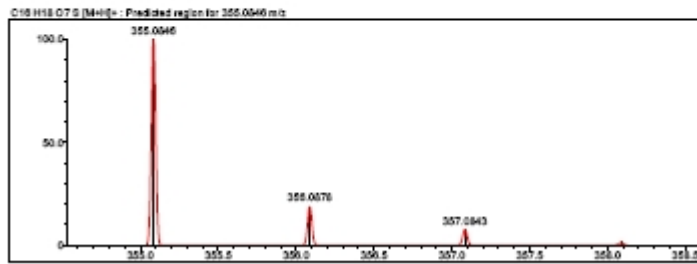
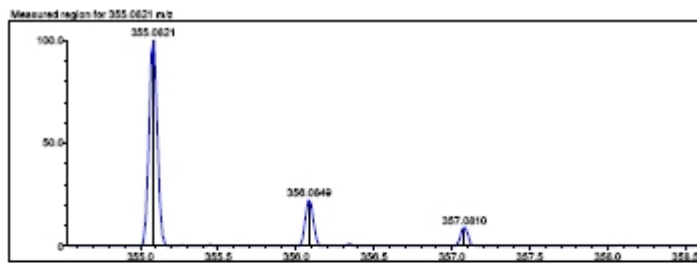
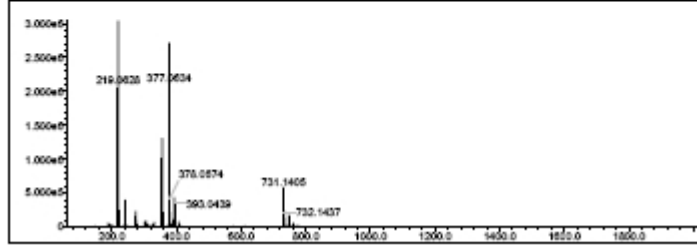
Elem.	Val.	Min.	Max.	Elem.	Val.	Min.	Max.	Elem.	Val.	Min.	Max.	Elem.	Val.	Min.	Max.	Elem.	Val.	Min.	Max.
H	1	0	200	N	3	0	0	P	3	0	0	Sr	1	0	0				
B	3	0	0	O	2	0	50	S	2	0	1	I	3	0	0				
C	4	0	100	F	1	0	0	Cl	1	0	0								

Error Margin (ppm): 20  
 HC Ratio: unlimited  
 Max Isotope: all  
 MSn Iso RI (%): 75.00

DBE Range: 0.0 - 30.0  
 Apply N Rule: no  
 Isotope RI (%): 1.00  
 MSn Logic Mode: OR

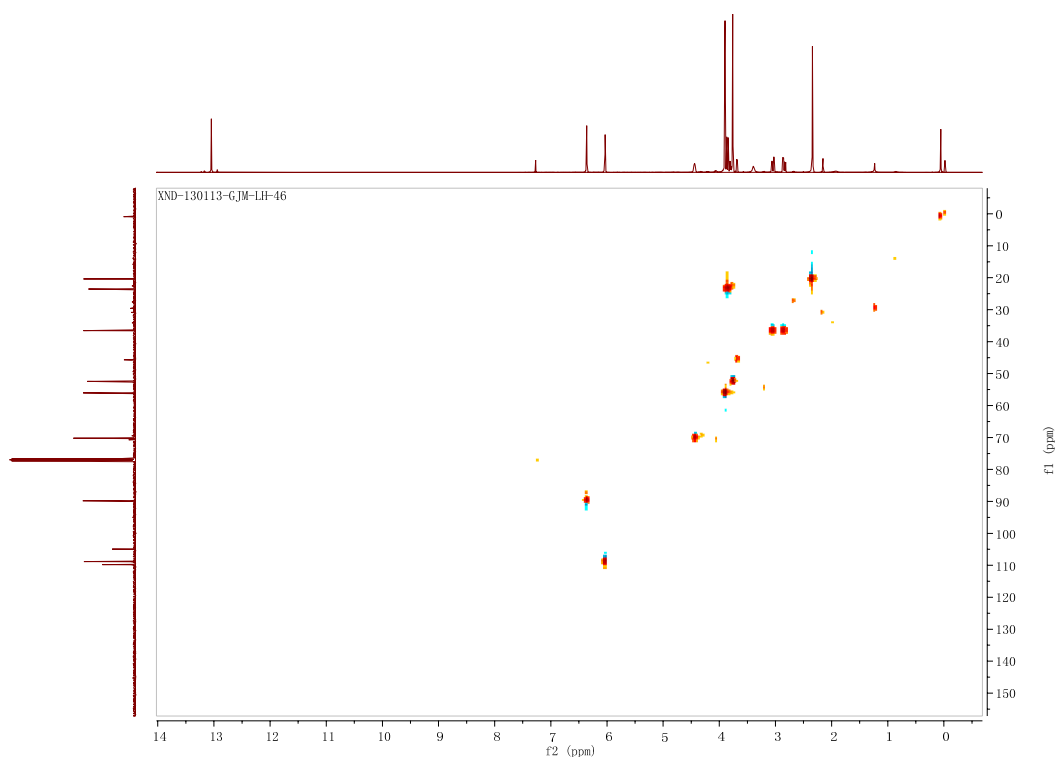
Electron Ion: both  
 Use MSn Info: yes  
 Isotope Res: 10000  
 Max Results: 500

Event#: 1 MS(E+) Rel. Time: 0.423 -> 0.650 Scan#: 66 -> 133

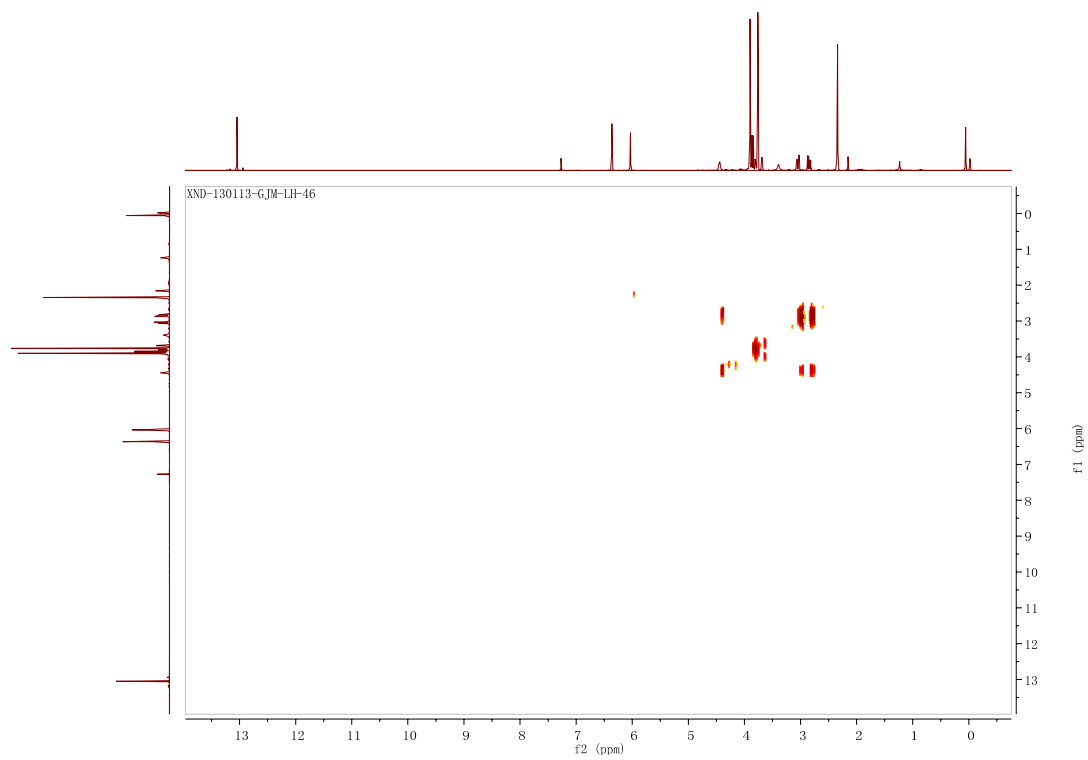


Rank	Score	Ion	Formula (M)	Pred. m/z	Mass. m/z	Df. (mDa)	CF. (ppm)	Isol	DBE
1	53.81	[M+H] <sup>+</sup>	C18H16O7S	355.0646	355.0621	-2.5	-7.04	77.31	0.0

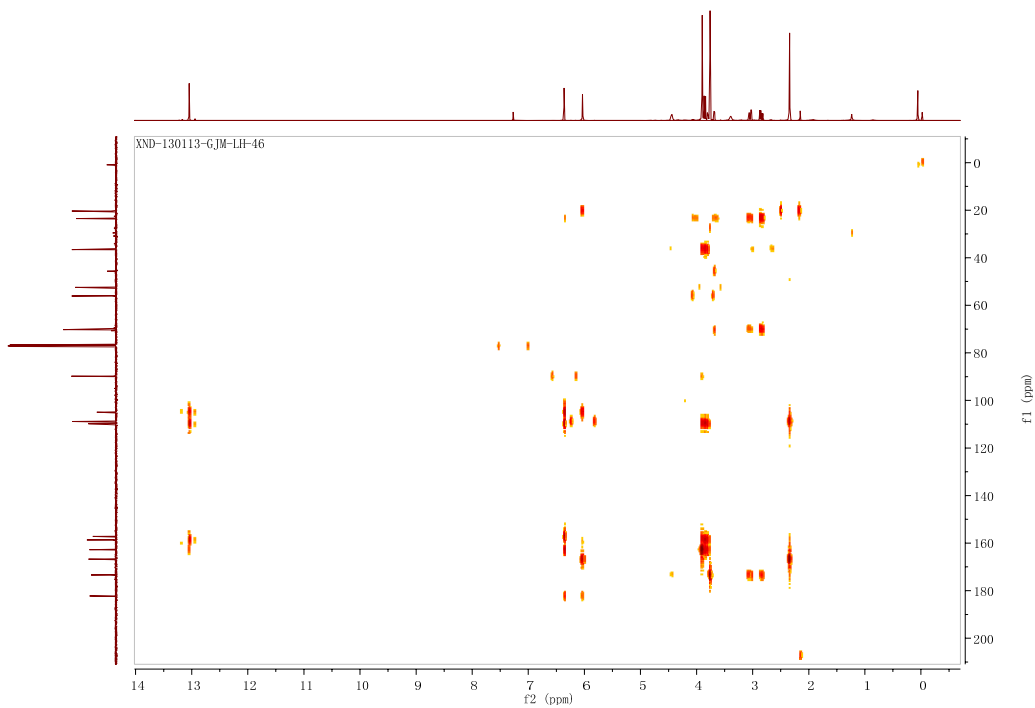
Figure S11.HRESIMS spectra of chaetoseminB



**Figure S12. HSQC spectra of chaetoseminB**



**Figure S13. COSY spectra of chaetoseminB**



**Figure S14. HMBC spectra of chaetoseminB**



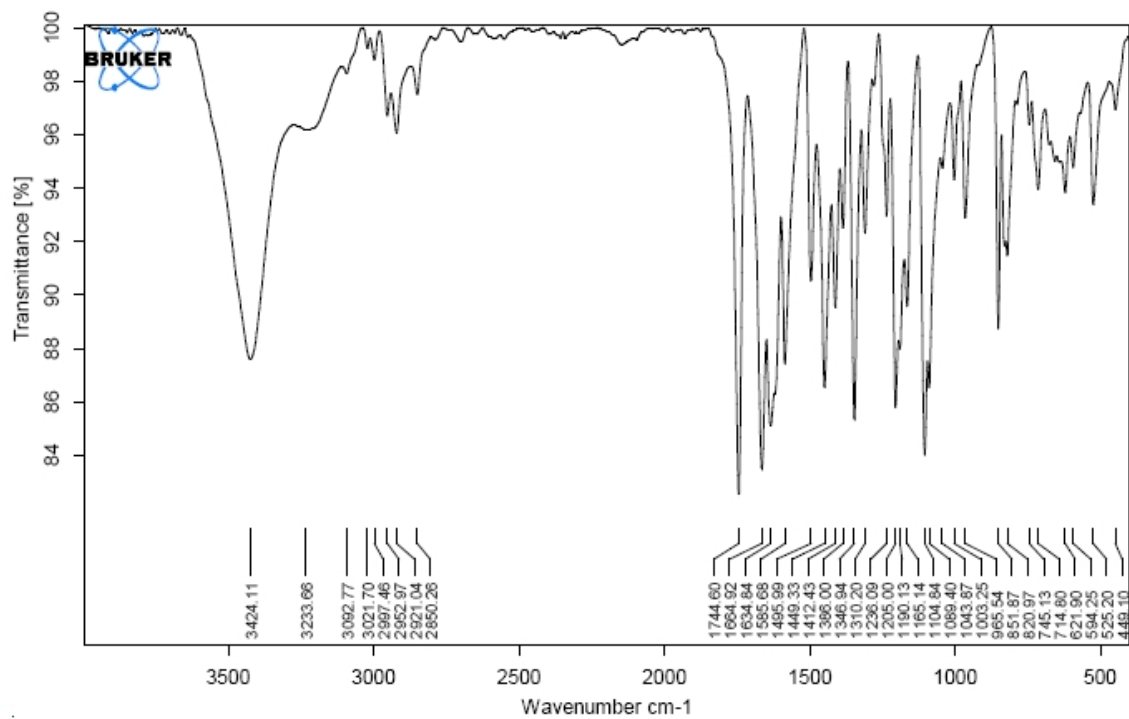


Figure S15. IR spectra of chaetoseminB

THERMO ELECTRON ~ VISIONpro SOFTWARE V4.10

Operator Name (None Entered)      Date of Report 2013-7-27  
Department (None Entered)      Time of Report 19:36:08下午  
Organization (None Entered)  
Information (None Entered)

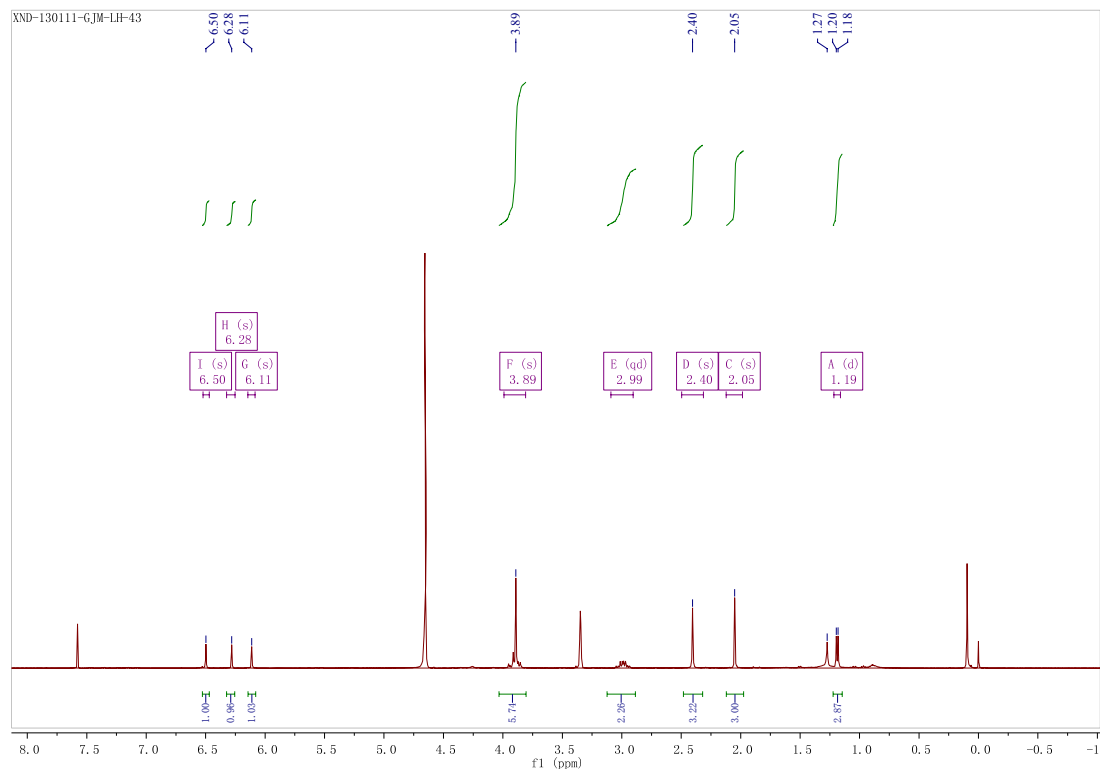
Scan Graph



Results Table - scan007,Sample001,Cycle01

nm	A	Peak Pick Method
232.00	.336	Find 8 Peaks Above -3.0000 A
238.00	.325	Start Wavelength 200.00 nm
251.00	.339	Stop Wavelength 300.00 nm
258.00	.394	Sort By Wavelength
Sensitivity	Auto	

Figure S16. UV spectra of chaetoseminB



**Figure S17.  $^1\text{H}$  spectra of chaetoseminCin MeOD**

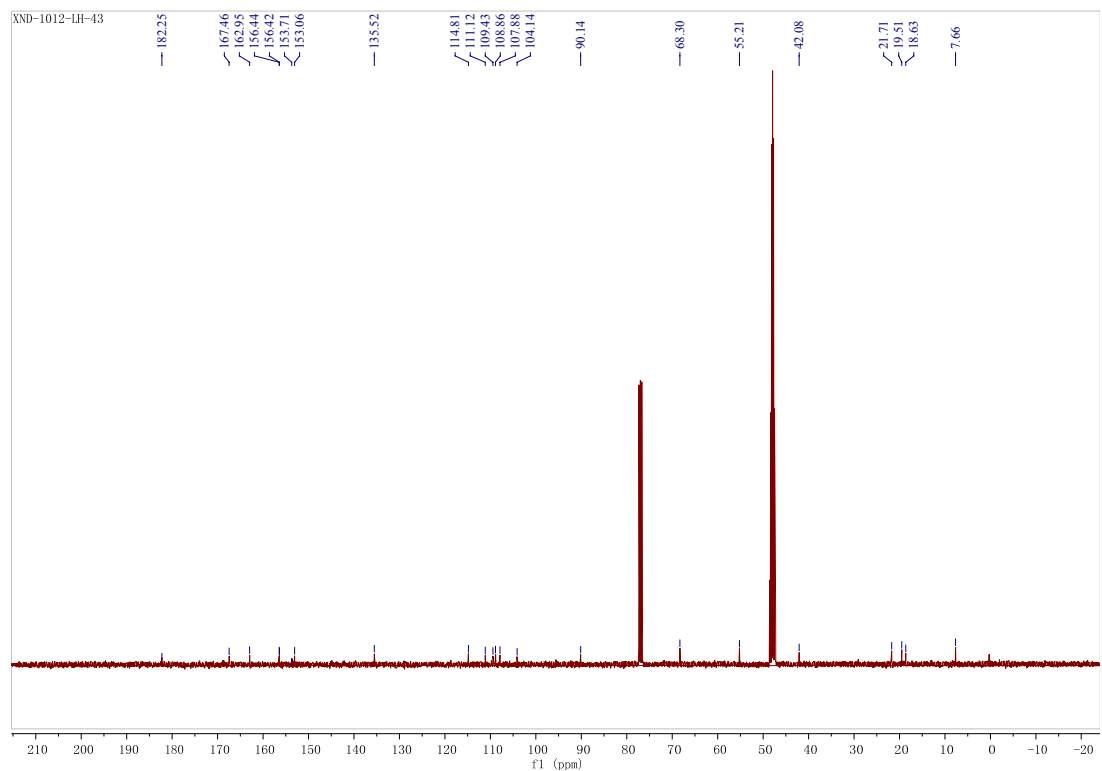


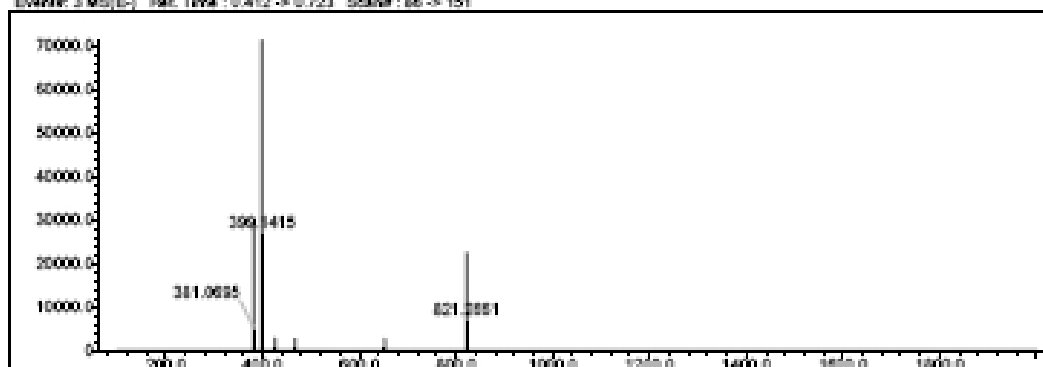
Figure S18.  $^{13}\text{C}$  spectra of chaetoseminCin MeOD

Data File: D:\分子毒理学\2013-07-29\ca2\_LH43\_21.tcd

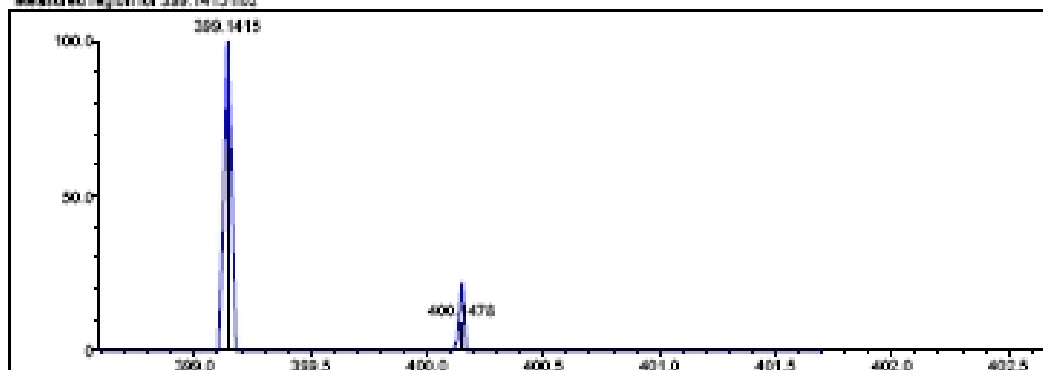
Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Use Adjust
H	1	0	300	H	3	0	0	P	3	0	0	Br	1	0	0	H
B	3	0	0	O	2	0	50	S	2	0	1	I	3	0	0	
C	4	0	100	F	1	0	0	Cl	1	0	0					

Error Margin (ppm): 20  
 NC Ratio: unlimited  
 Max Isotopes: all  
 MSn Iso RI (%): 75.00  
 OBE Range: 0.0 - 30.0  
 Apply H Rule: no  
 Isotope RI (%): 1.00  
 MSn Logic Mode: OR  
 Electron Ionv: both  
 Use MSn Info: yes  
 Isotope Rat: 10000  
 Max Results: 100

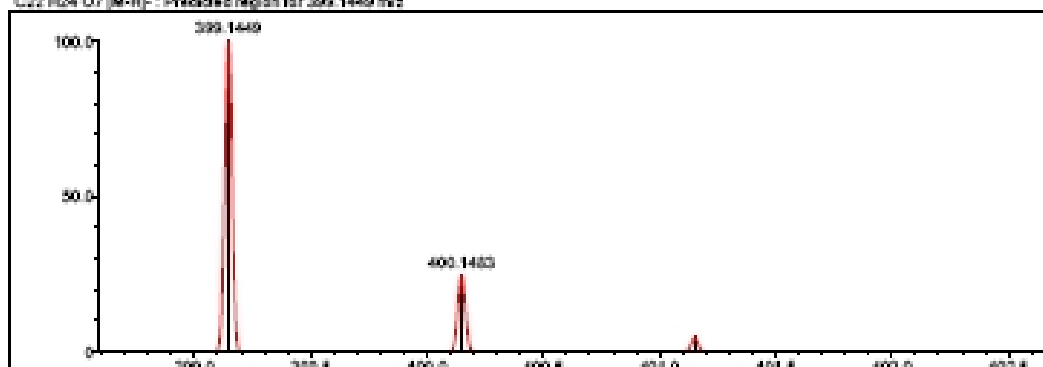
Event#: 3 MS(E-) Ret. Time: 0.412 -> 0.723 Scan#: 66 -> 151



Measured region for 399.1415 m/z

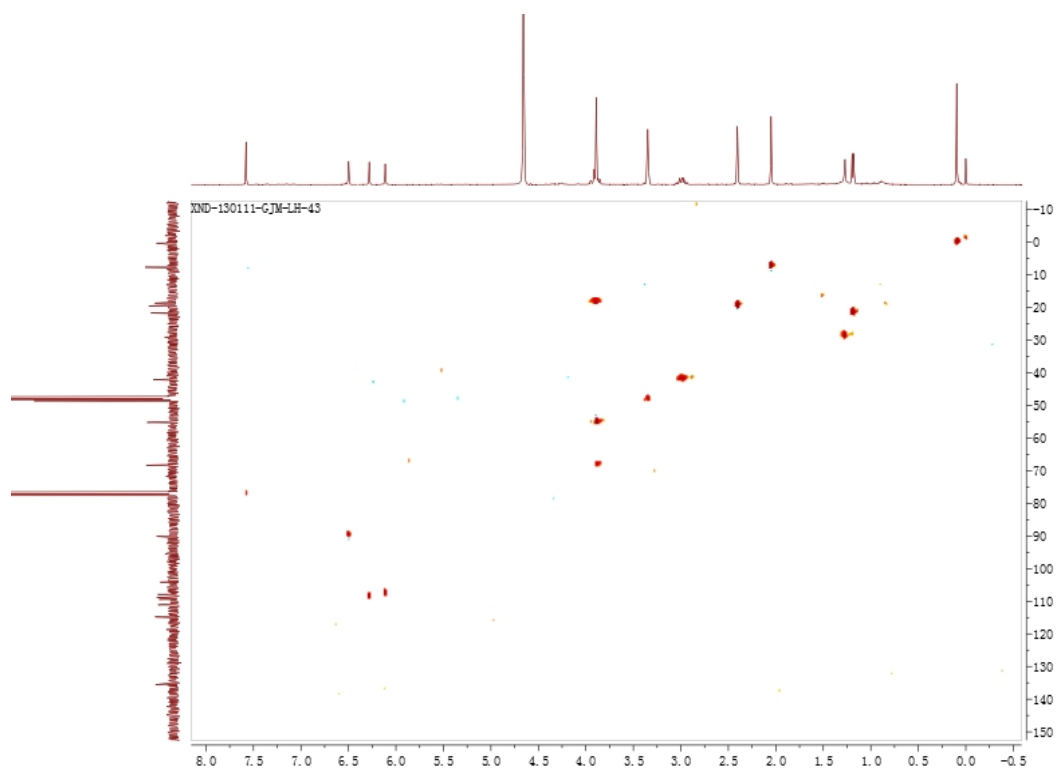


C22 H24 O7 (M-H)- : Predicted region for 399.1449 m/z

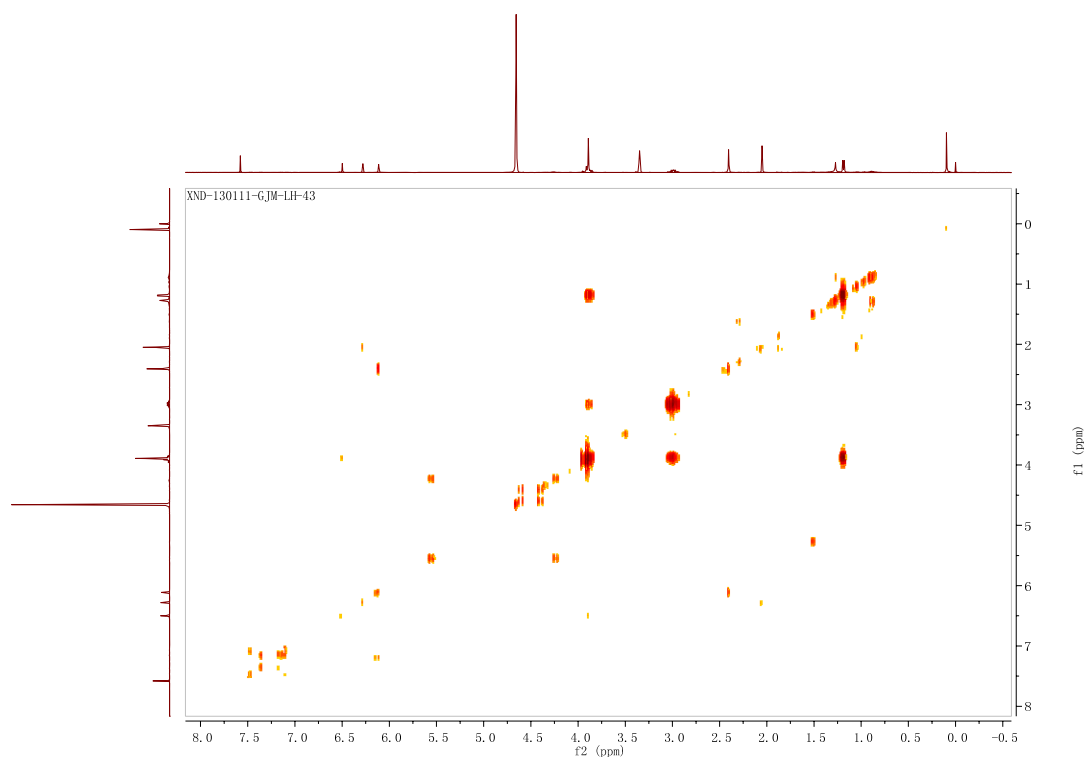


Rank	Score	Ion	Formula (M)	Pred. m/z	Mass. m/z	CF (mDa)	CF (ppm)	Isr	OBE
1	28.75	(M-H)-	C22 H24 O7	399.1449	399.1415	-3.4	-8.52	52.48	11.0

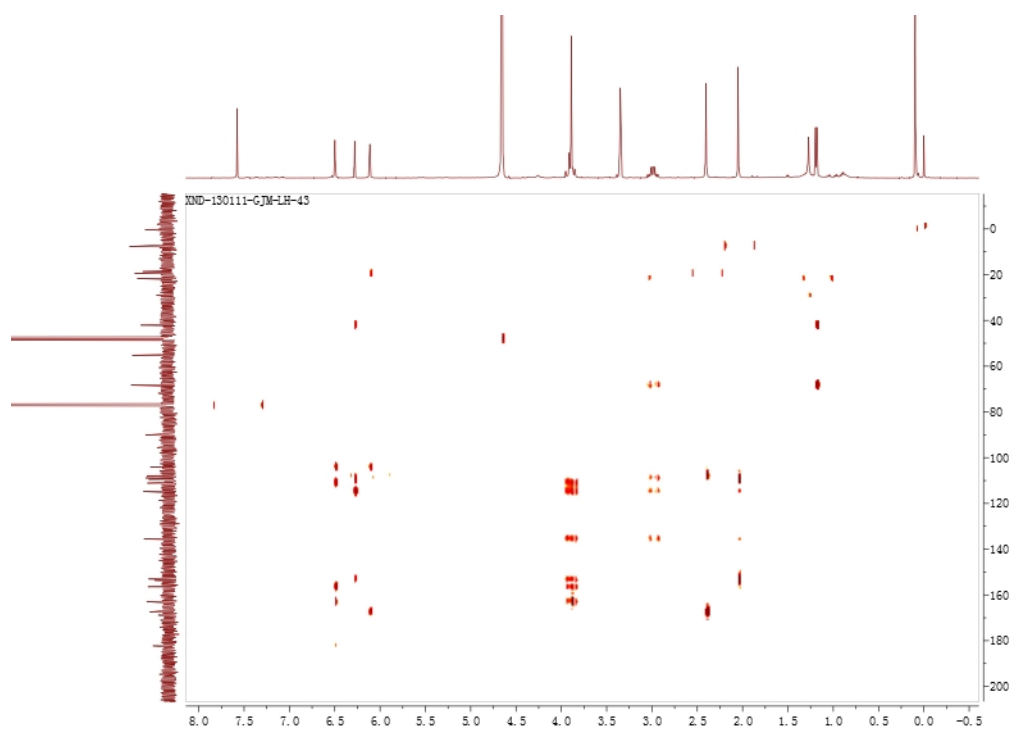
Figure S19.HRESIMS spectra of chaetoseminC



**Figure S20. HSQC spectra of chaetoseminC**

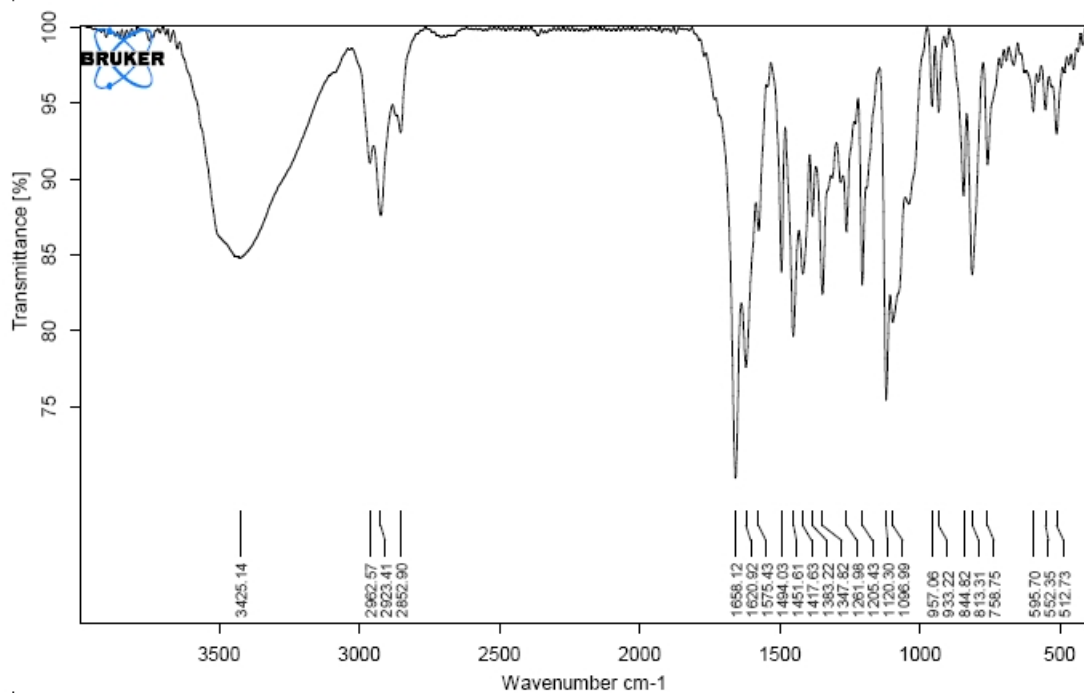


**Figure S21. COSY spectra of chaetoseminC**



**Figure S22. HMBC spectra of chaetoseminC**



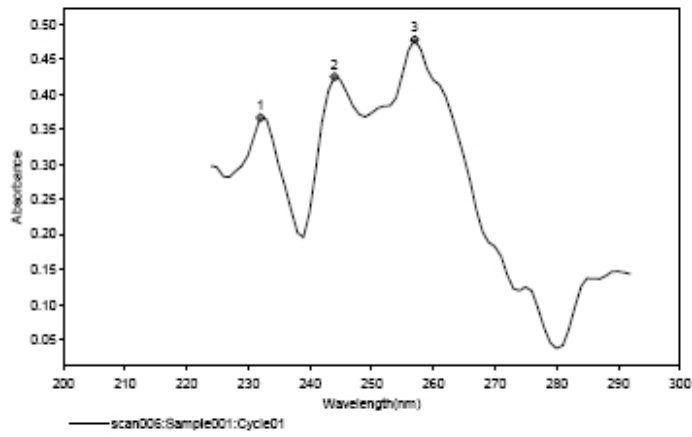


**Figure S23. IR spectra of chaetoseminC**

THERMO ELECTRON ~ VISIONpro SOFTWARE V4.10

Operator Name (None Entered)      Date of Report    2013-7-27  
Department (None Entered)        Time of Report    19:26:04下午  
Organization (None Entered)  
Information (None Entered)

Scan Graph



Results Table - c:\can008.srs, Sample001, Cycle01

nm	A	Peak Pick Method
232.00	.367	Find 8 Peaks Above -3.0000 A
244.00	.426	Start Wavelength 200.00 nm
257.00	.479	Stop Wavelength 300.00 nm
		Sort By Wavelength

Sensitivity    Auto

Figure S24. UV spectra of chaetoseminC

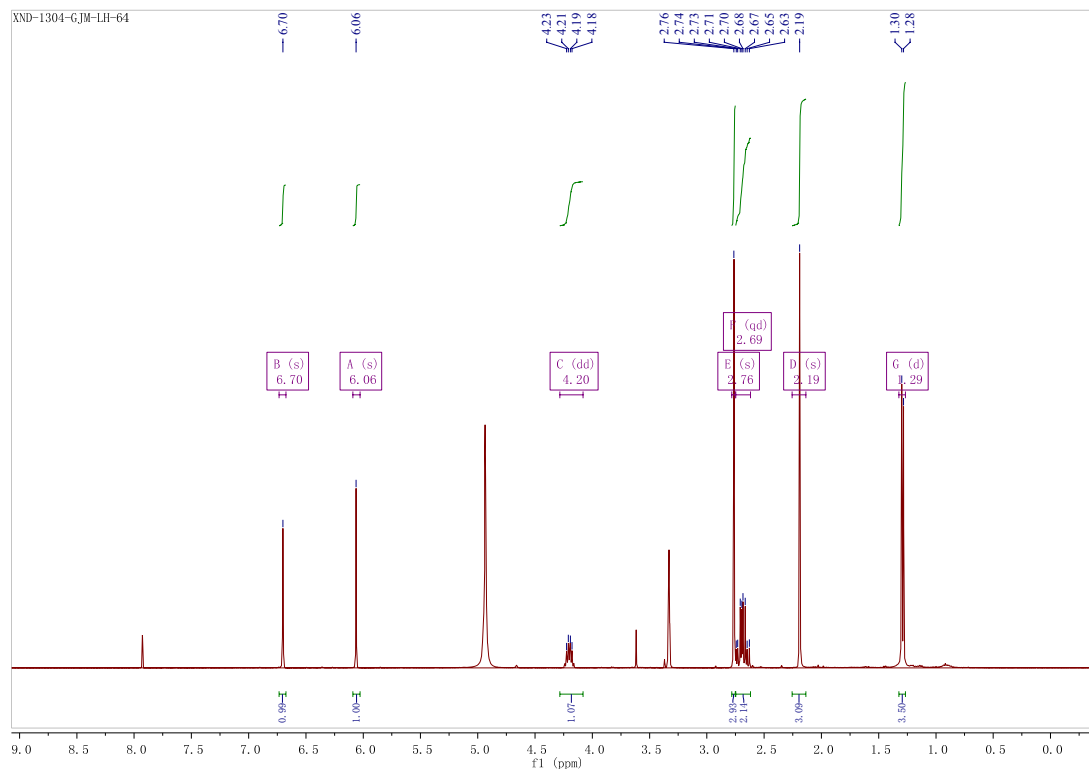
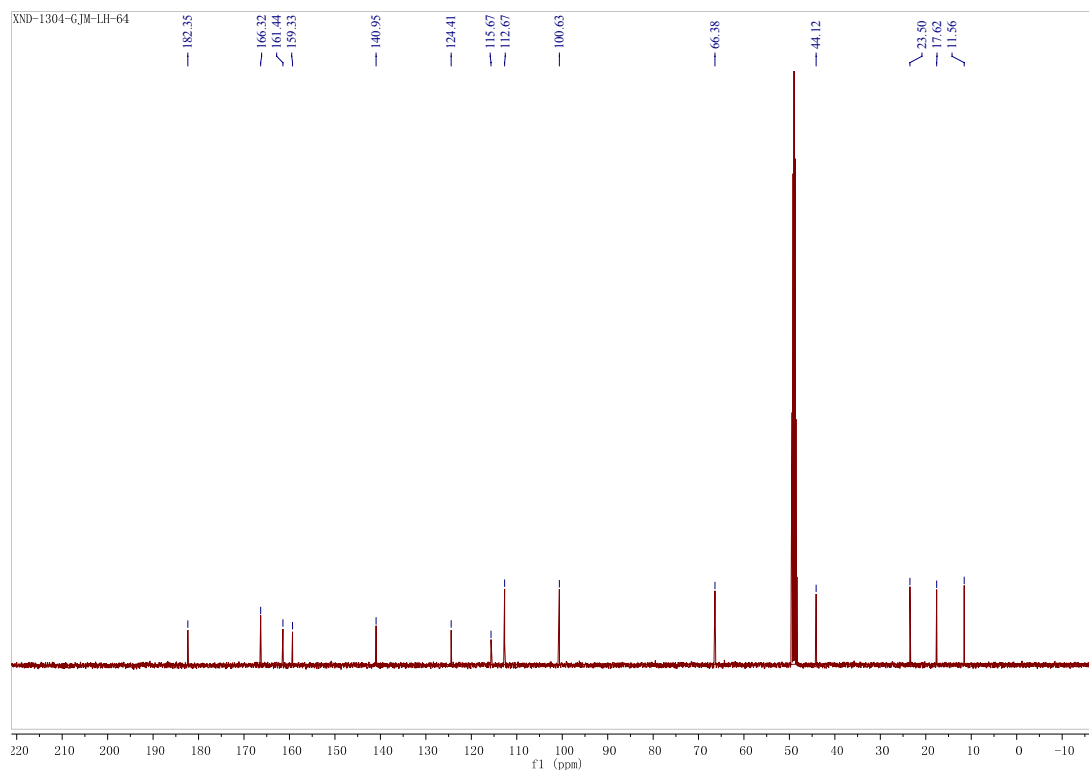


Figure S25.  $^1\text{H}$  spectra of chaetoseminDin MeOD

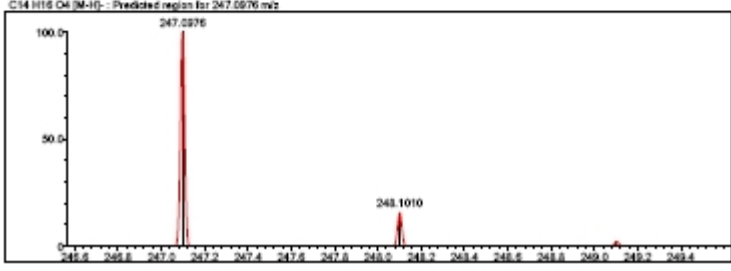
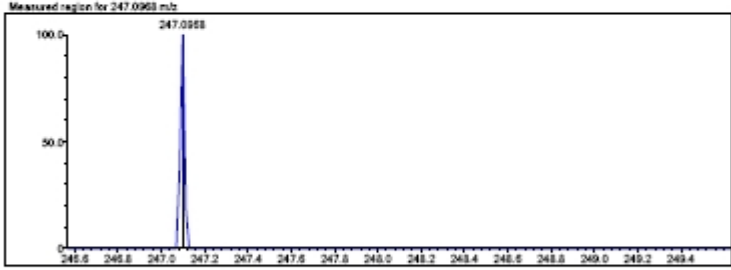
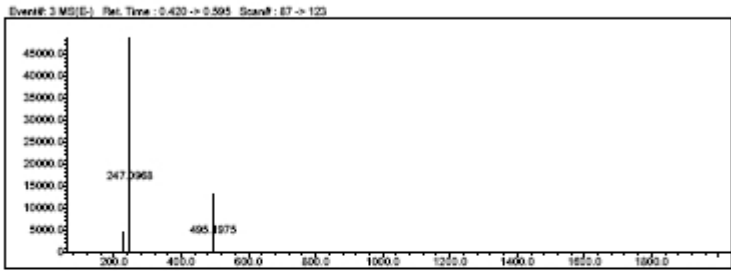


**Figure S26.**  $^{13}\text{C}$  spectra of chaetoseminDin MeOD

Data File: D:\分子量测定\2013-07-29\col-2\_LH-64\_25.fcd

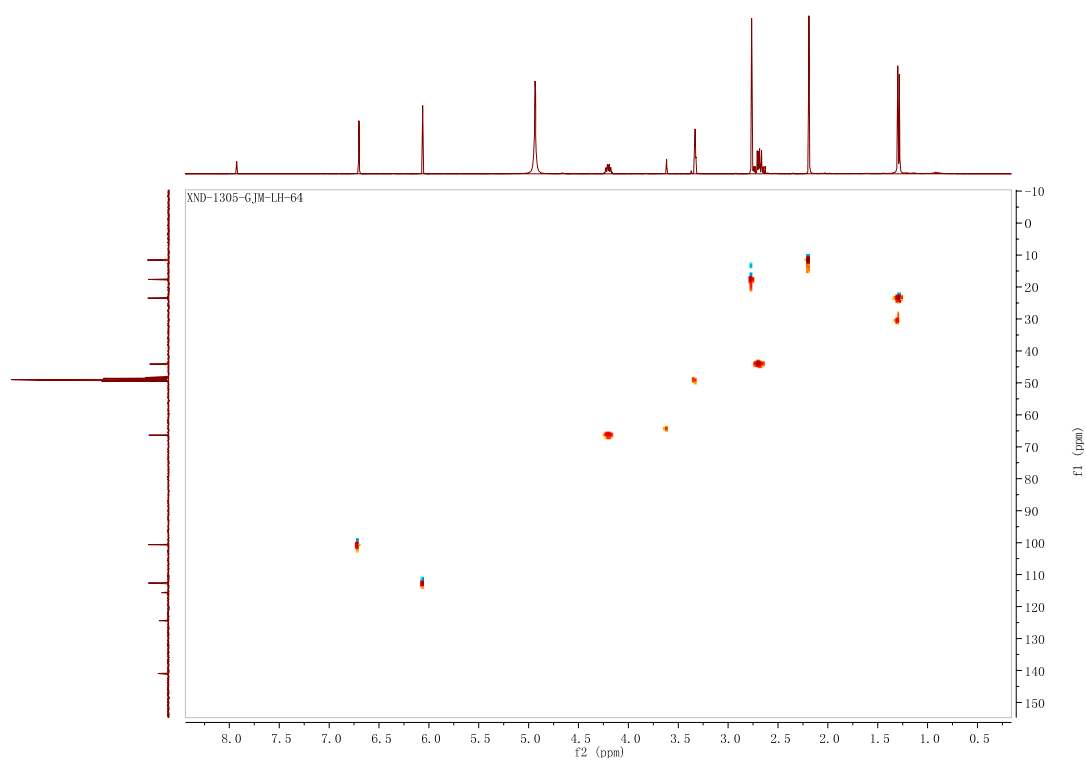
Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Use Adduct
H	1	0	200	N	3	0	0	P	3	0	0	Br	1	0	0	H
S	3	0	0	O	2	0	50	S	2	0	1	I	3	0	0	
C	4	100	100	F	1	0	0	Cl	1	0	0	Q	0	0	0	

Error Margin (ppm): 20  
 IIC Ratio: unlimited  
 Max Isotopes: all  
 MSn Ino RI (%): 75.00  
 DBE Range: 0.0 - 30.0  
 Apply N Rule: no  
 Isotope RI (%): 1.00  
 MSn Logic Mode: OR  
 Electron Ion: both  
 Use MSn Info: yes  
 Isotope Rat: 10000  
 Max Results: 100

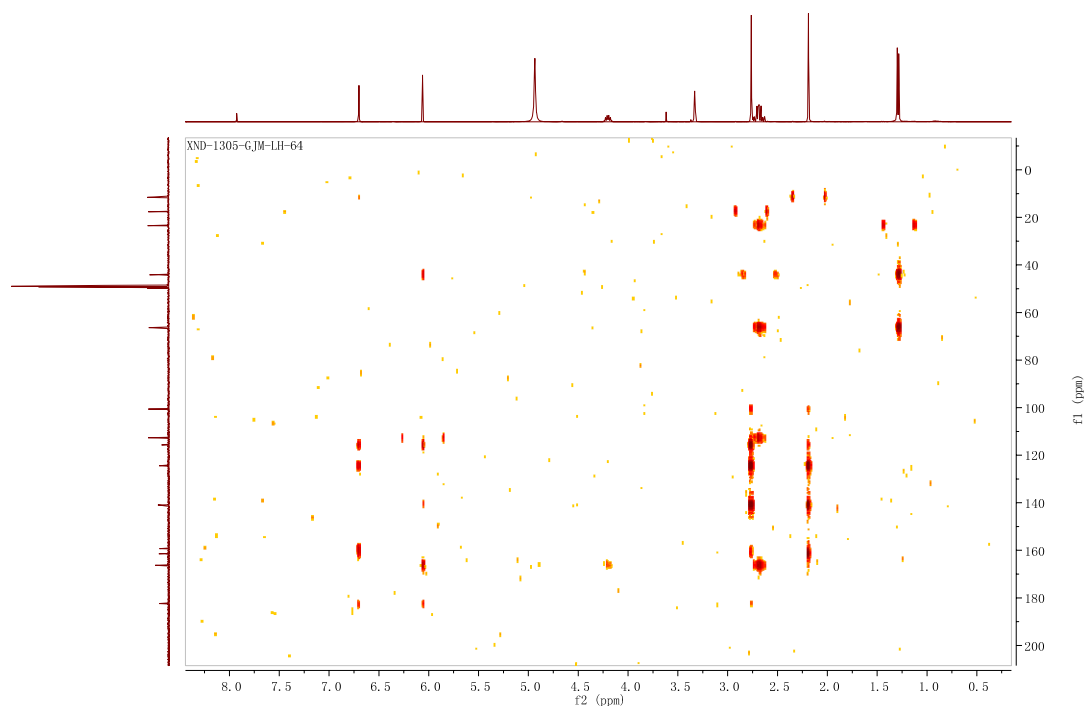


Scan	Score	In	Formula (M)	Pred. m/z	Mass. m/z	CV (mDa)	CV (ppm)	Is	DBE
1	0.00	[M-H]	C14 H16 O4	247.0976	247.0968	-0.3	-3.24	0.00	7.0

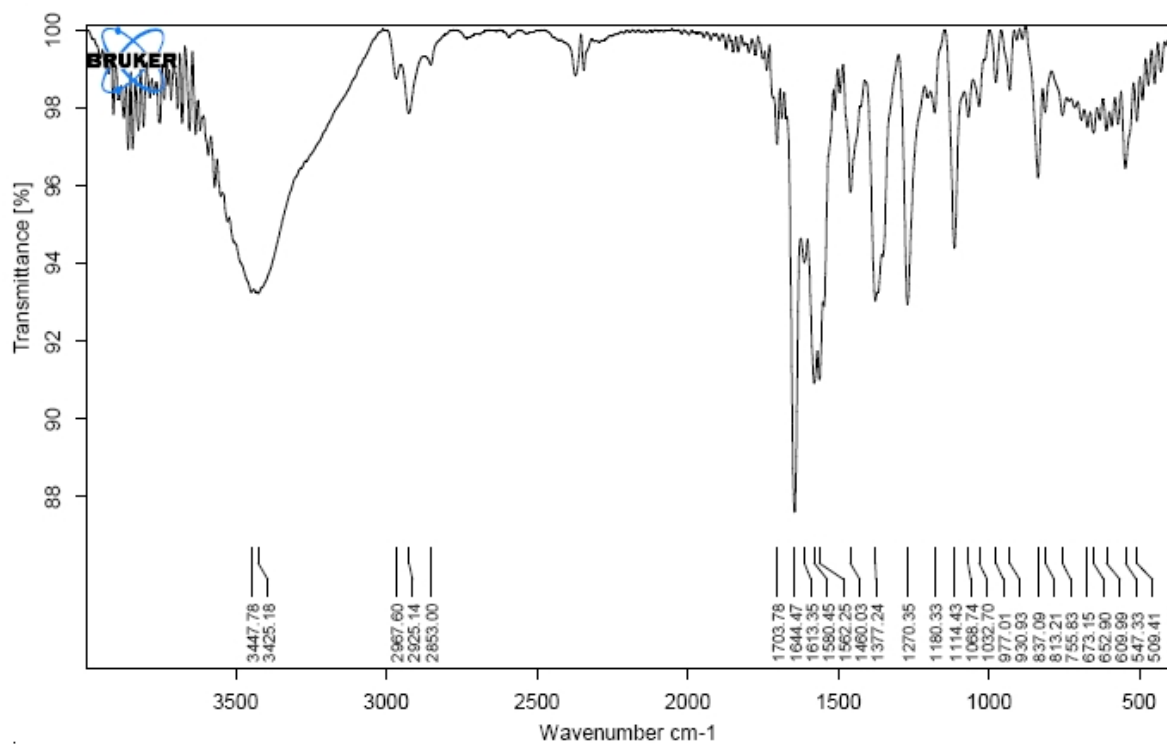
Figure S27.HRESIMS spectra of chaetoseminD



**Figure S28. HSQC spectra of chaetoseminD**



**Figure S29. HMBC spectra of chaetoseminD**



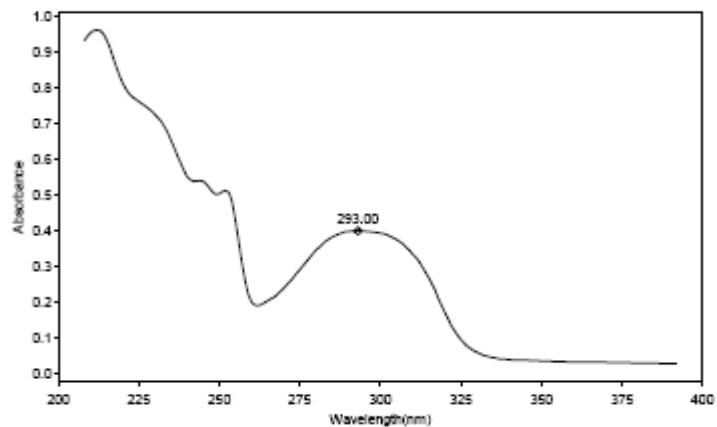
**Figure S30. IR spectra of chaetoseminD**



THERMO ELECTRON ~ VISIONpro SOFTWARE V4.10

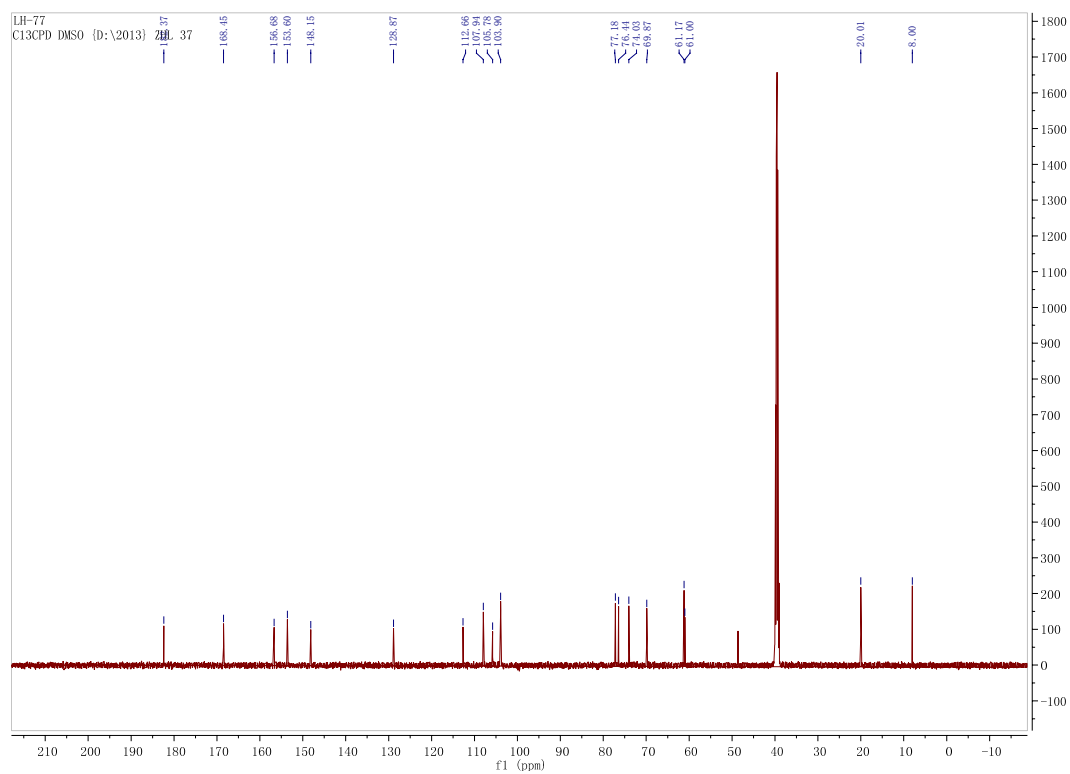
Operator Name (None Entered)      Date of Report    2013-10-24  
Department (None Entered)        Time of Report    21:22:24下午  
Organization (None Entered)  
Information (None Entered)

Scan Graph



**Figure S31. UV spectra of chaetoseminD**





**Figure S33.** <sup>13</sup>C spectra of chaetoseminEin DMSO

Data File: C:\分子生物学\2014-01-12\2014-01-12 2 MS\_LH-77\_11.txt

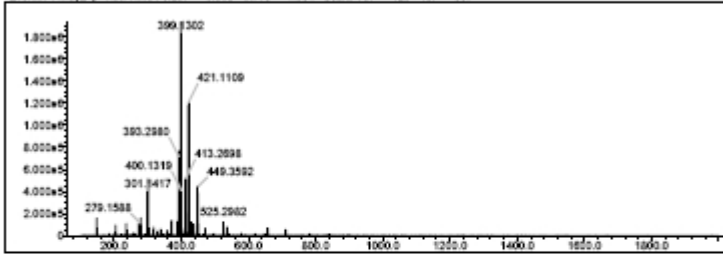
Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Elem	Val	Min	Max	Use Adduct
H	1	0.0	200	N	3	0	3	P	3	0	0	Br	1	0	0	H
S	3	0.0	0	O	2	0	100	S	2	0	0	I	3	0	0	
C	4	0.0	100	F	1	0	0	Cl	1	0	1					

Error Margin (ppm): 20  
 HC Ratio: 0.0 - 3.0  
 Max Isotopes: all  
 MSn Iso RI (%): 75.00

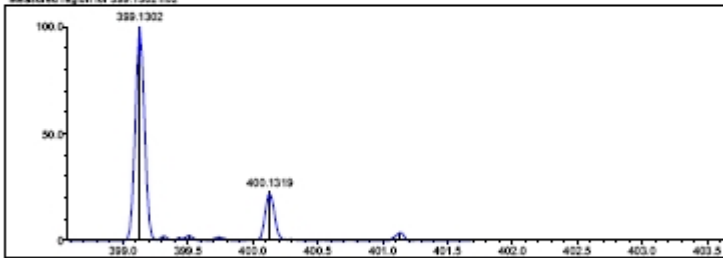
DBE Range: 0.0 - 30.0  
 Apply N Rule: yes  
 Isotope RI (%): 1.00  
 MSn Logic Mode: OR

Electron Ion: both  
 Use MSn Info: yes  
 Isotope Res: 10000  
 Max Results: 500

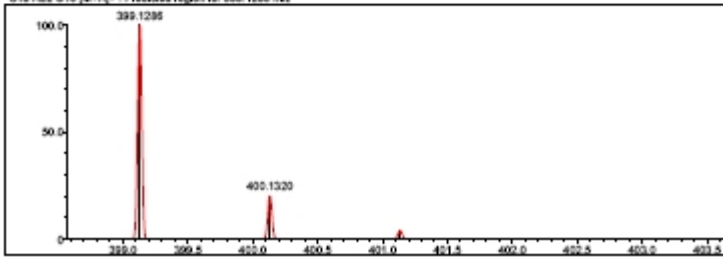
Event# 1 MS(E+) Rel. Time - 0.257 -> 0.588 - 0.715 -> 1.534 Scan# : 57 -> 125 - 157 -> 337



Measured region for 399.1302 m/z

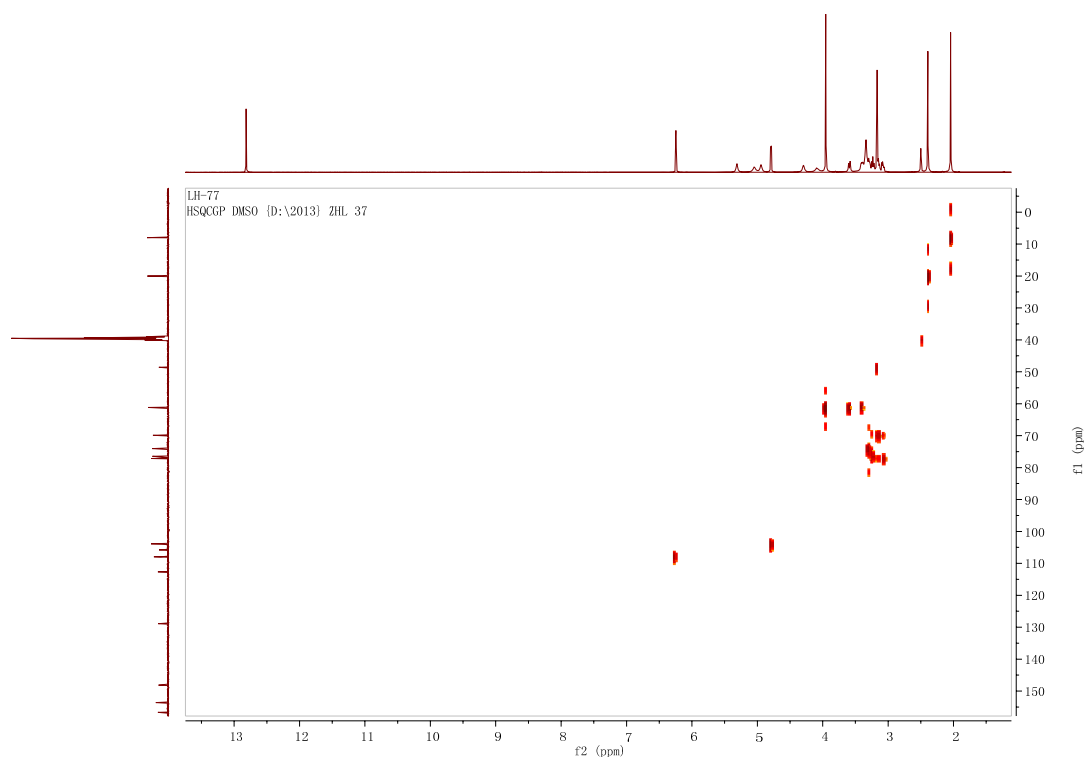


C18 H22 O10 (M+H)+ Predicted region for 399.1286 m/z

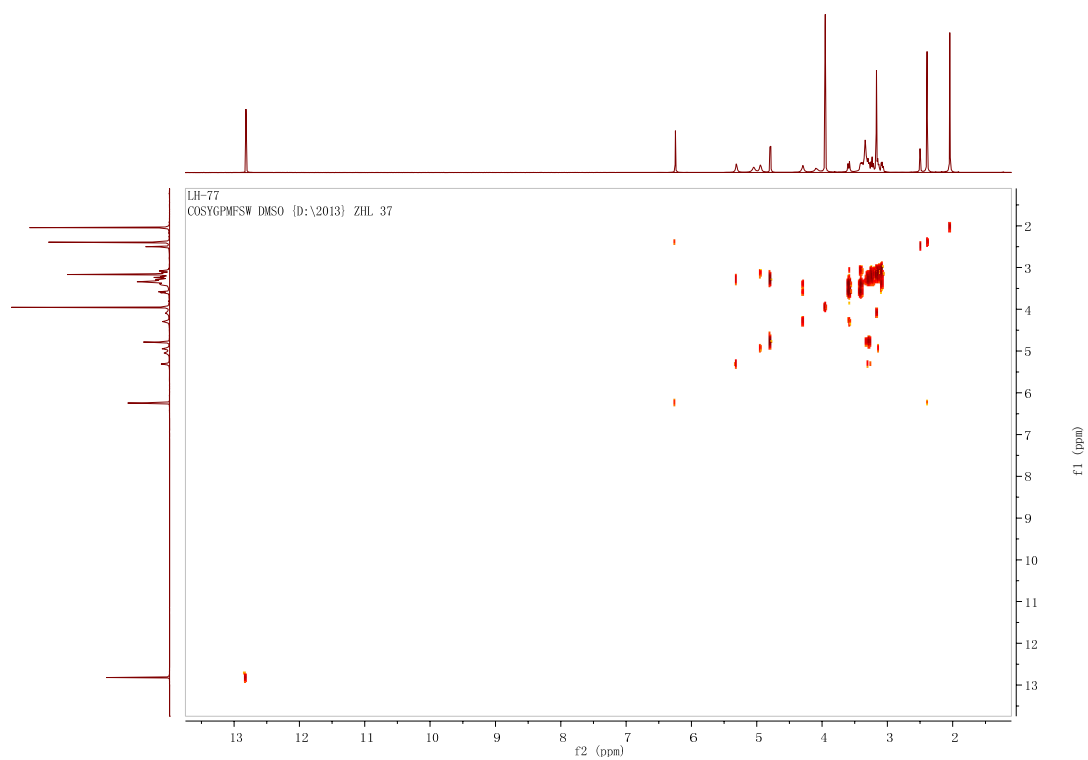


Rank	Score	Ion	Formula (M)	Prod. m/z	Mass. m/z	CV (m/z)	DF (ppm)	Tag	DBE
1	74.01	[M+H] <sup>+</sup>	C18H22O10	399.1286	399.1302	1.6	4.01	60.00	8.0

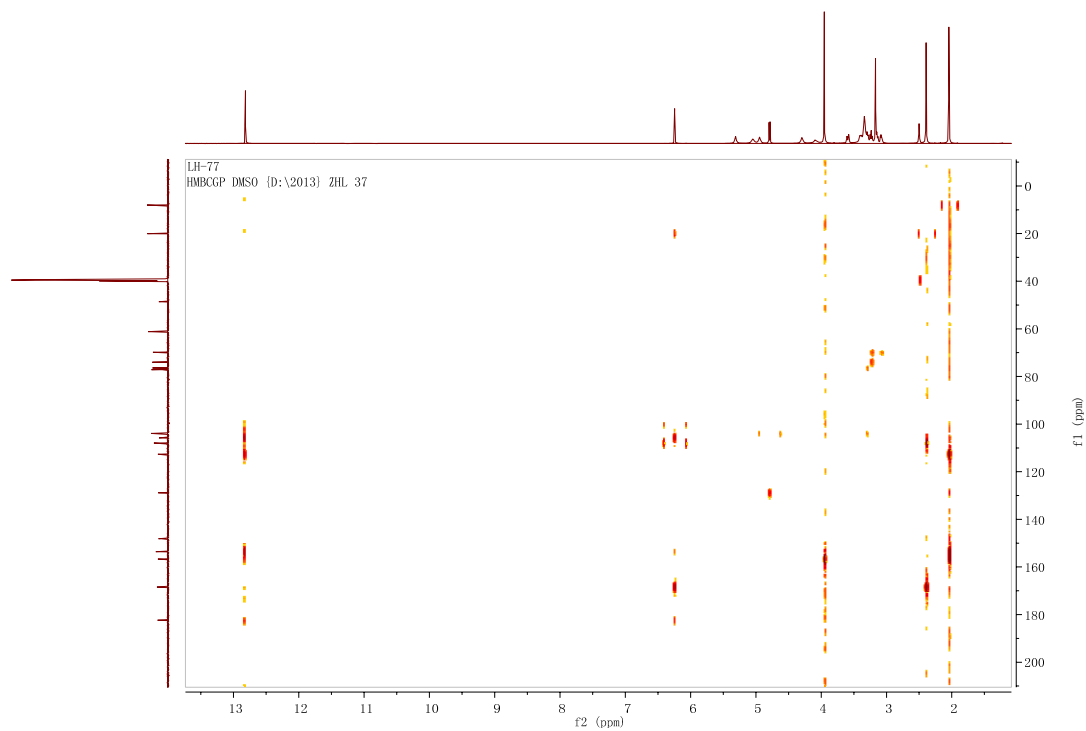
Figure S34.HRESIMS spectra of chaetoseminE



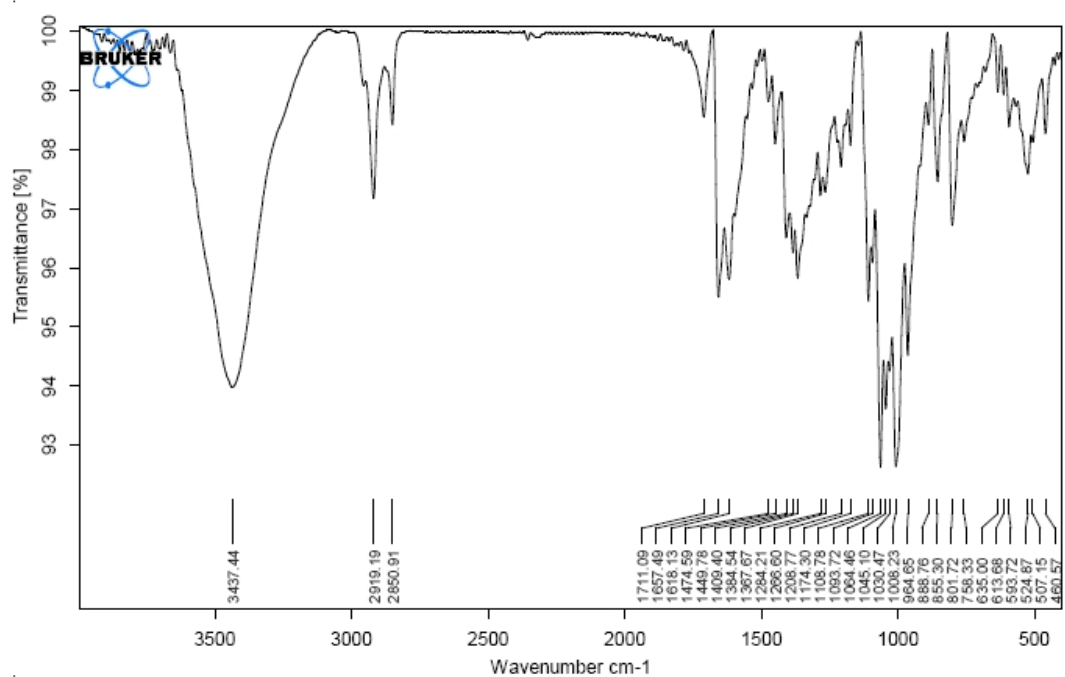
**Figure S35. HSQC spectra of chaetoseminE**



**Figure S36. COSY spectra of chaetoseminE**



**Figure S37. HMBC spectra of chaetoseminE**



**Figure S38. IR spectra of chaetoseminE**



THERMO ELECTRON ~ VISIONpro SOFTWARE V4.10

Operator Name	(None Entered)	Date of Report	2013-10-24
Department	(None Entered)	Time of Report	21:47:24下午
Organization	(None Entered)		
Information	(None Entered)		

Scan Graph

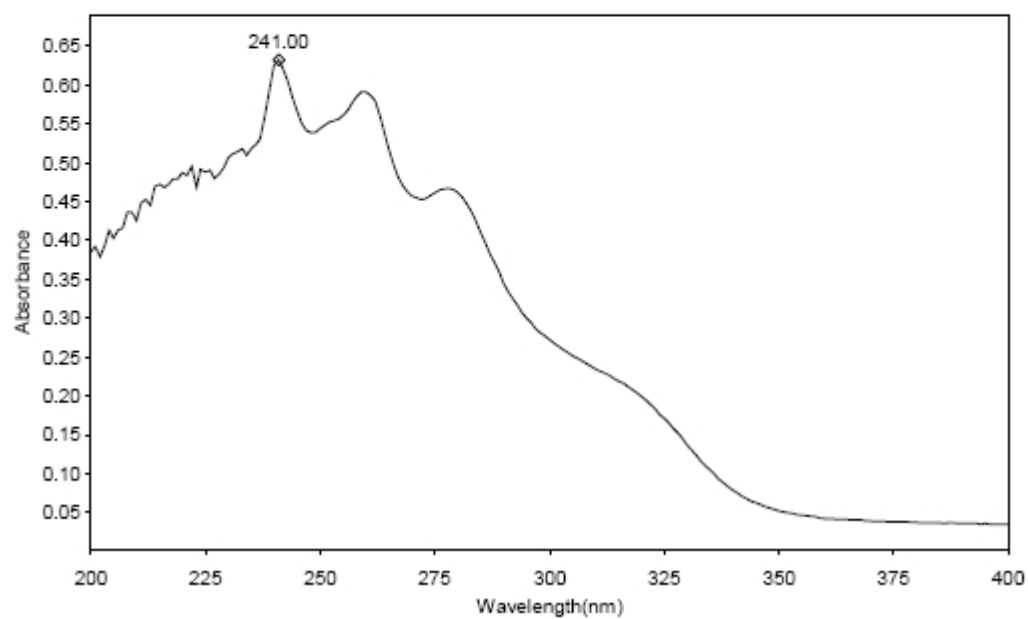


Figure S39. UV spectra of chaetoseminE

Compound **6**, white powder,ESI-MS (negative)  $m/z$  219.33[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ 12.78(1H, s, 5-OH), 6.34(1H, s, H-8), 6.02(1H, s, H-3), 3.88(s, 3H, 7-OCH<sub>3</sub>), 2.34(s, 3H, 2-CH<sub>3</sub>), 2.08(s, 3H, 6-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)  $\delta$ 182.38(C-4), 166.29(C-2), 163.21(C-7), 158.36(C-5), 156.27(C-8a), 108.80(C-6), 108.77(C-3), 104.89(C-4a), 89.11(C-8), 55.79(7-OCH<sub>3</sub>), 20.39(2-CH<sub>3</sub>), 7.18(6-CH<sub>3</sub>);

Compound **7**, white powder,ESI-MS (negative)  $m/z$  249.33[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ 13.03 (1H, s, 5-OH), 6.37(1H, s, H-8), 6.05(1H, s, H-3), 4.55(2H, s, CH<sub>2</sub>OCH<sub>3</sub>), 3.91(s, 3H, 7-OCH<sub>3</sub>), 3.41(3H, s, CH<sub>2</sub>OCH<sub>3</sub>), 2.36(s, 3H, 2-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)  $\delta$ 182.39(C-4), 166.59(C-2), 164.14(C-7), 160.5(C-5), 158.13(C-8a), 109.04(C-3), 108.88(C-6), 104.98(C-4a), 89.55(C-8), 61.54(CH<sub>2</sub>OCH<sub>3</sub>), 58.16(CH<sub>2</sub>OCH<sub>3</sub>), 56.12(7-OCH<sub>3</sub>), 20.39(2-CH<sub>3</sub>);

Compound **8**, white powder,ESI-MS (positive)  $m/z$  236.92 [M+H]<sup>+</sup>, <sup>1</sup>H-NMR (400MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ 13.78 (1H, s, 5-OH), 6.48(1H, s, H-8), 6.15(1H, s, H-3), 5.20(2H, s, CH<sub>2</sub>), 3.76(3H, s, 7-OCH<sub>3</sub>), 2.15(s, 3H, 2-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  183.24(C-4), 167.73(C-2), 164.66(C-7), 160.51(C-5), 158.29(C-8a), 113.96(C-6), 109.35(C-3), 105.74(C-4a), 90.66(C-8), 56.42(7-OCH<sub>3</sub>), 52.47(CH<sub>2</sub>), 20.28(2-CH<sub>3</sub>);

Compound **9**, pale yellow powder,ESI-MS (negative)  $m/z$  205.42[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ 13.04 (1H, s, 5-OH), 6.38(1H, s, H-8), 6.13(1H, s, H-3), 2.33(s, 3H, 2-CH<sub>3</sub>), 1.95(s, 3H, 6-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)  $\delta$ 181.73(C-4), 167.29(C-2), 162.00(C-7), 158.53(C-5), 155.38(C-8a), 107.84(C-3), 106.66(C-6), 103.06(C-4a), 92.77(C-8), 19.91(2-CH<sub>3</sub>), 7.32(6-CH<sub>3</sub>);

Compound **10**, white powder, ESI-MS (positive)  $m/z$  221.00[M+H]<sup>+</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  12.77 (1H, s, 5-OH), 6.37(1H, s, H-6), 6.01(1H, s, H-3), 3.89(3H, s, 7-OCH<sub>3</sub>), 2.38(s, 3H, 2-CH<sub>3</sub>), 2.15(s, 3H, 8-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  183.02(C-4), 166.79(C-2), 162.91(C-7), 160.15(C-5), 154.86(C-8a), 108.16(C-3), 104.54(C-4a), 103.63(C-8), 94.71(C-6), 55.94(7-OCH<sub>3</sub>), 20.55(2-CH<sub>3</sub>), 7.42(8-CH<sub>3</sub>);

Compound **11**, white powder, ESI-MS (negative)  $m/z$  368.25[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>:CD<sub>3</sub>OD = 1:1)  $\delta$  6.37 (1H, s, H-8), 5.99 (1H, s, H-3), 4.33 (2H, s, H-1'), 3.99 (3H, s, 7-OCH<sub>3</sub>), 3.82 (2H, s, H-4'), 3.58 (2H, s, H-3'), 2.27 (3H, s, 2-CH<sub>3</sub>), 1.82 (3H, s, H-7'); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  182.16(C-4), 171.36(C-6'), 167.64(C-2), 163.42(C-7), 159.35(C-5), 158.39(C-8a), 108.68(C-3), 104.64(C-4a), 99.78(C-6), 90.39(C-8), 56.18(7-OCH<sub>3</sub>), 52.07(C-3'), 32.57(C-4'), 22.21(C-7'), 20.06 (2-CH<sub>3</sub>);

Compound **12**, white powder, ESI-MS (negative)  $m/z$  357.42[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  12.82 (1H, s, 5-OH), 6.32(1H, s, H-8), 6.01(1H, s, H-3), 5.20(1H, s, H-4'), 4.40(1H, s, H-7'), 3.84(3H, s, 7-OCH<sub>3</sub>), 2.74(1H, m, H-2'), 2.64(1H, m, H-1'a), 2.90(1H, m, H-1'b), 2.35(3H, s, 2-CH<sub>3</sub>), 2.30 (2H, m, H-6'), 1.40(3H, d, 7'-CH<sub>3</sub>), 1.09(3H, d, 2'-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  193.54(C-5'), 182.37 (C-4), 181.49(C-3'), 166.46 (C-2), 163.18(C-7), 158.97(C-5), 156.73(C-8a), 110.48 (C-6), 108.80 (C-3), 104.86 (C-4a), 102.40(C-4'), 89.29 (C-8), 75.35 (C-7'), 55.78(7-OCH<sub>3</sub>), 42.64(C-6'), 38.38(C-2'), 27.06 (C-1'), 20.34 (2-CH<sub>3</sub>), 20.27(C-8'), 17.14(2'-CH<sub>3</sub>);

Compound **13**, white powder, ESI-MS (negative)  $m/z$  357.42[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) δ 12.82 (1H, s, 5-OH), 6.32(1H, s, H-8), 6.01(1H, s, H-3), 5.09(1H, s, H-4'), 4.35(1H, s, H-7'), 3.84(3H, s, 7-OCH<sub>3</sub>), 2.74(1H, m, H-2'), 2.70, 2.95(2H, m, H-1'), 2.35(s, 3H, 2-CH<sub>3</sub>), 2.30 (2H, m, H-6') 1.95(s, 3H, H-14), 1.15(3H, d, 2'-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>) δ 193.64(C-5'), 182.40 (C-4), 181.19(C-3'), 166.47 (C-2), 163.13(C-7), 158.83(C-5), 156.73(C-8a), 110.48 (C-6), 108.80 (C-3), 104.82 (C-4a), 102.99(C-4'), 89.23(C-8), 75.56 (C-7'), 55.75 (7-OCH<sub>3</sub>), 42.53(C-6'), 38.81 (C-2'), 27.00(C-1'), 20.34 (2-CH<sub>3</sub>), 20.25 (C-8'), 17.38(2'-CH<sub>3</sub>);

Compound **14**, white powder,  $[\alpha]_D^{25} = +33.86$  ( $c = 0.1$ , CHCl<sub>3</sub>), ESI-MS (negative)  $m/z$  425.42[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, C<sub>5</sub>D<sub>5</sub>N) δ 6.46(1H, s, H-8), 6.08(1H, s, H-3), 4.56(1H, m, H-3'), 3.97(2H, s, H-9), 3.79(3H, s, 7-OCH<sub>3</sub>), 3.45(1H, dd,  $J = 16.4$ , 3.0 Hz, H-4'a), 2.67 (1H, dd,  $J = 16.4$ , 11.8 Hz, H-4'b), 2.21(1H, s, 2-CH<sub>3</sub>), 2.20(3H, s, 7'-CH<sub>3</sub>), 1.39(3H, d,  $J = 6.3$  Hz, 3'-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, C<sub>5</sub>D<sub>5</sub>N) δ 182.92(C-4), 171.62(C-1'), 168.10(C-2), 163.69(C-7), 161.49(C-8'), 161.02(C-6'), 158.24(C-5), 157.19(C-8a), 137.62(C-4a'), 116.07(C-5'), 111.09(C-7'), 110.12(C-6), 108.80(C-3), 105.08(C-4a), 101.01(C-8a'), 90.90(C-8), 75.59(C-3'), 56.18(7-OCH<sub>3</sub>), 32.36(C-4'), 20.77(3'-CH<sub>3</sub>), 19.82(2-CH<sub>3</sub>), 19.39 (C-9), 8.49(7'-CH<sub>3</sub>).

Compound **15**, white powder, ESI-MS (negative)  $m/z$  333.33[M-H]<sup>-</sup>, <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) δ 12.85 (1H, s, 5-OH), 6.35(1H, s, H-8), 6.03(1H, s, H-3), 3.85(3H, s, 7-OCH<sub>3</sub>), 3.37(1H, m, H-13), 2.51-2.93(5H, m, H-9, H-10, H-12), 2.34(s, 3H, 2-CH<sub>3</sub>), 1.16(3H, d,  $J = 6.0$  Hz, H-14), 1.04(3H, d,  $J = 6.6$  Hz, 10-CH<sub>3</sub>); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>) δ 216.14(C-12), 182.40(C-4), 165.54(C-2), 163.13(C-7,

158.95(C-5), 156.80(C-8a), 110.23(C-7), 108.86(C-3), 104.93(C-4a), 89.40(C-8),  
63.94(C-13), 55.81(7-OCH<sub>3</sub>), 48.65(C-12), 46.10(C-10), 25.39(C-9), 22.23(C-14),  
20.39(2-CH<sub>3</sub>), 15.51(10-CH<sub>3</sub>).