Supporting Information

Title: Iridoids and Bis-iridoids from *Patrinia scabiosaefolia*

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Contents of Supporting Information

Figure 1.[1]H NMR spectrum of Patriscabioin A (**1**) in $CDCl_3$.

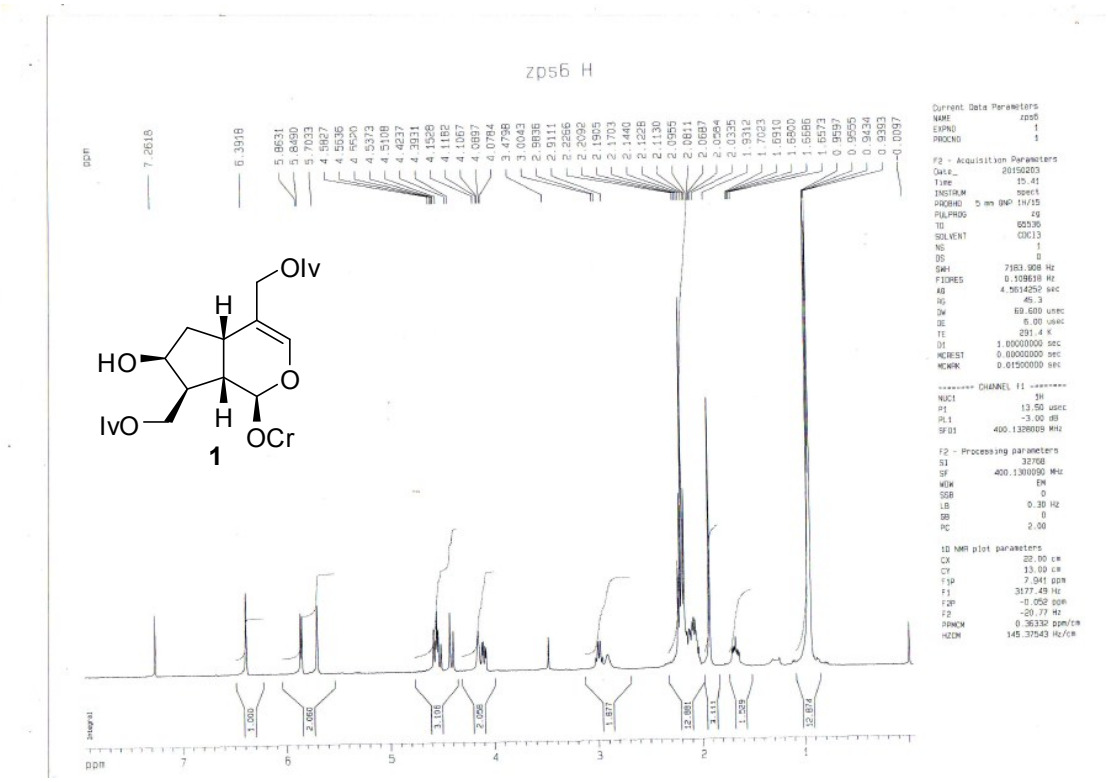
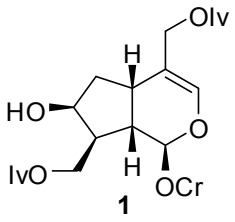


Figure 2.[13]C NMR spectrum of Patriscabioin A (**1**) in $CDCl_3$.



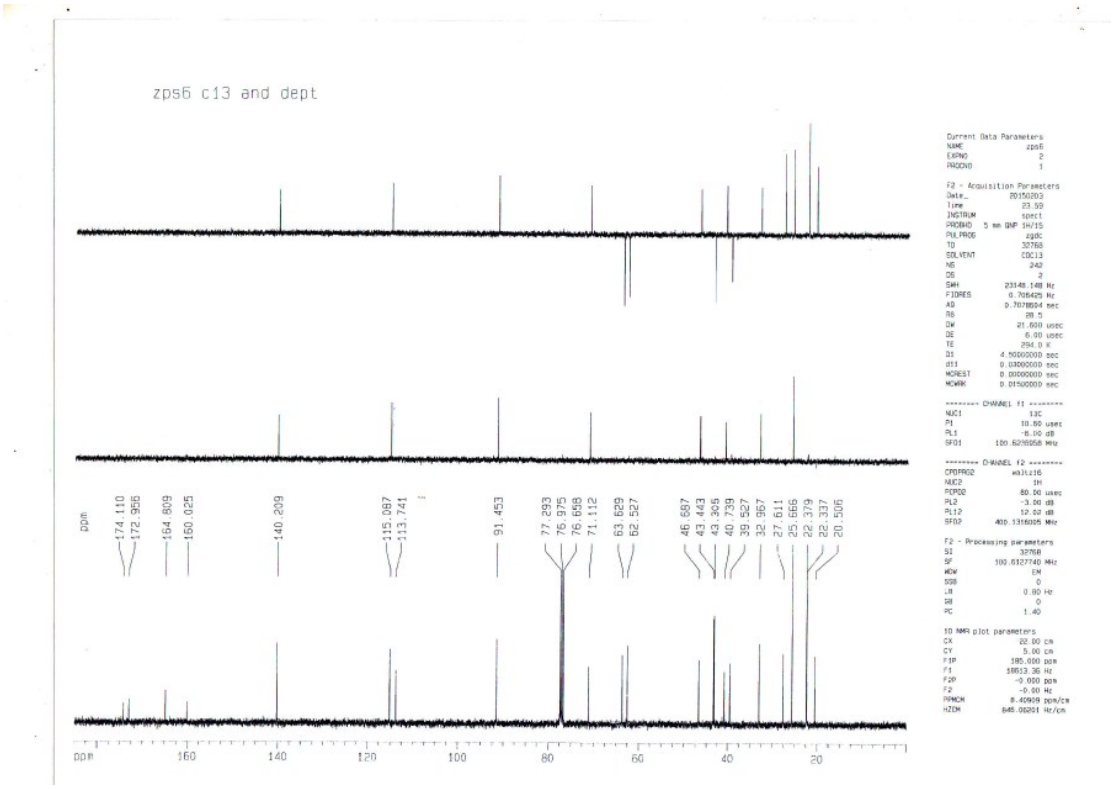


Figure 3. HSQC spectrum of Patriscabioin A (**1**) in $CDCl_3$.

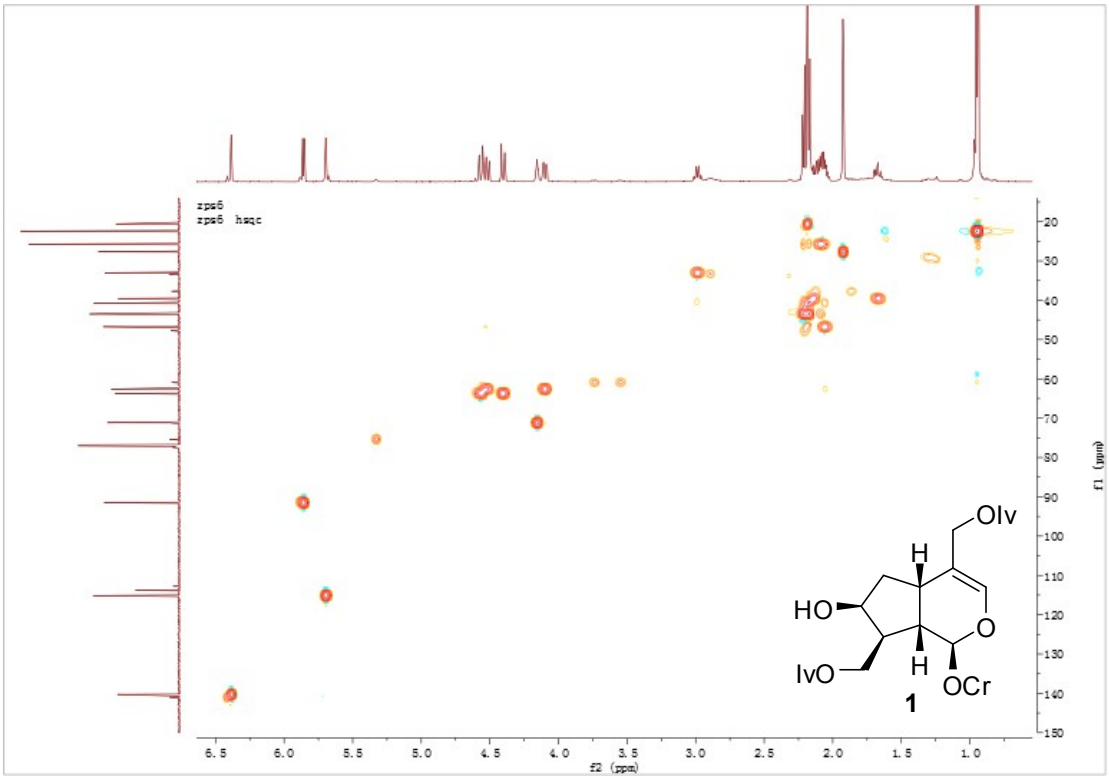


Figure 4. HMBC spectrum of Patriscabioin A (**1**) in $CDCl_3$.

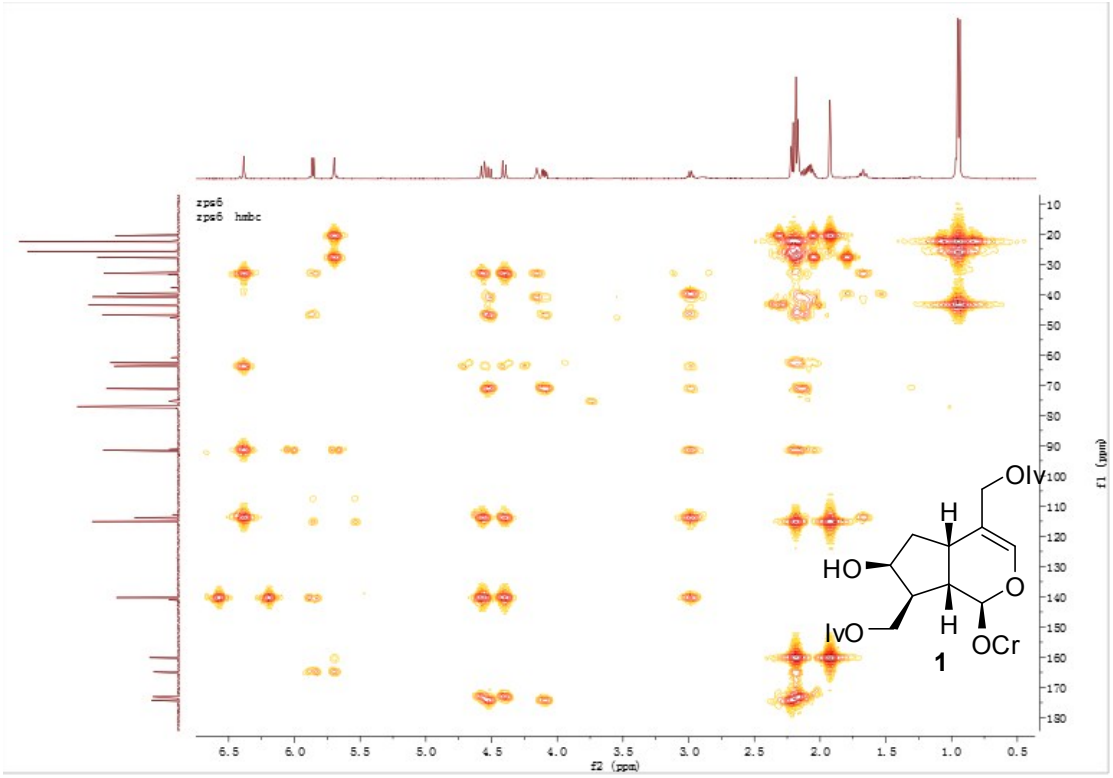


Figure 5. ^{1}H-^{1}H COSY spectrum of Patriscabioin A (**1**) in $CDCl_3$.

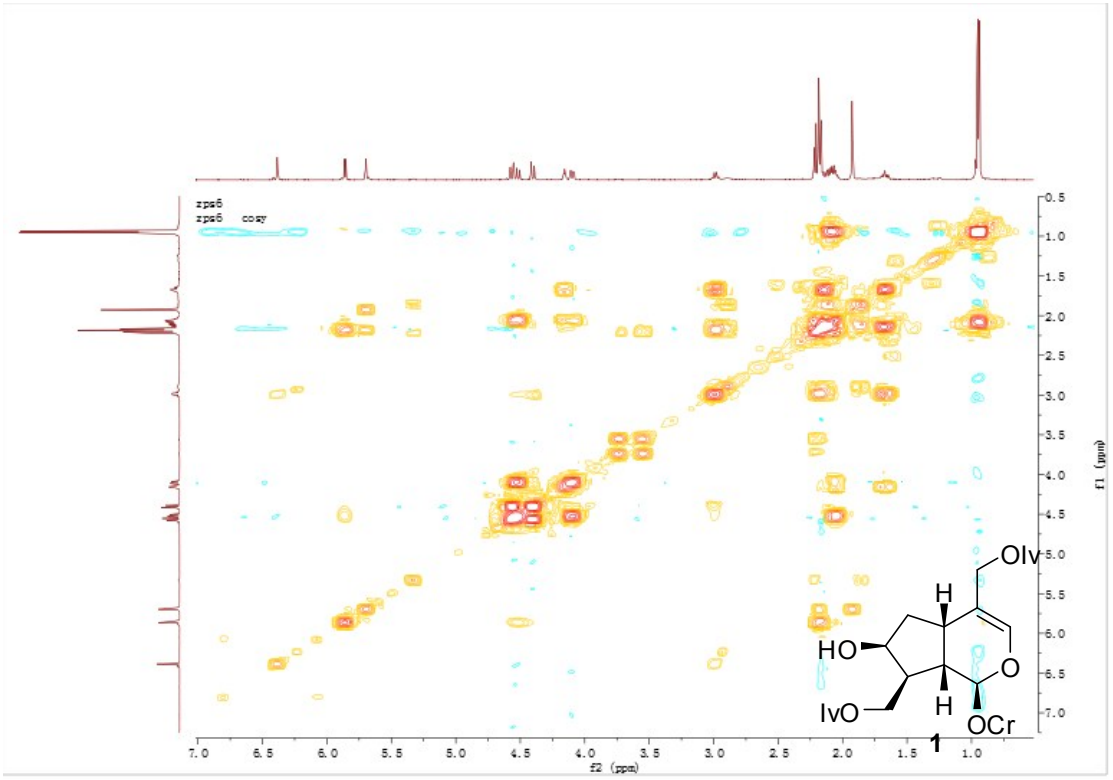


Figure 6. ROESY spectrum of Patriscabioin A (**1**) in $CDCl_3$.

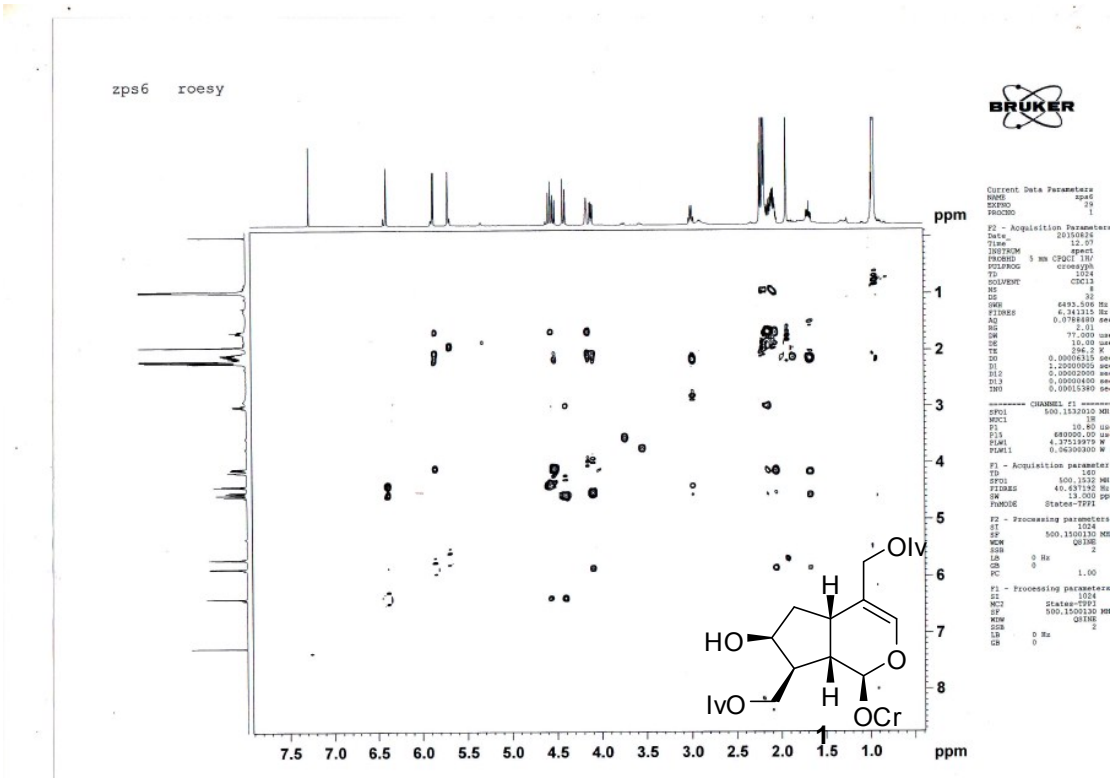


Figure 7. HREIMS spectrum of Patriscabioin A (**1**).

Formula Predictor Report - zps-6-3.lcd

Data File: E:\DATA\20151105\zps-6-3.lcd

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C	4	0	50	Br	1	0	0	
N	3	0	10					

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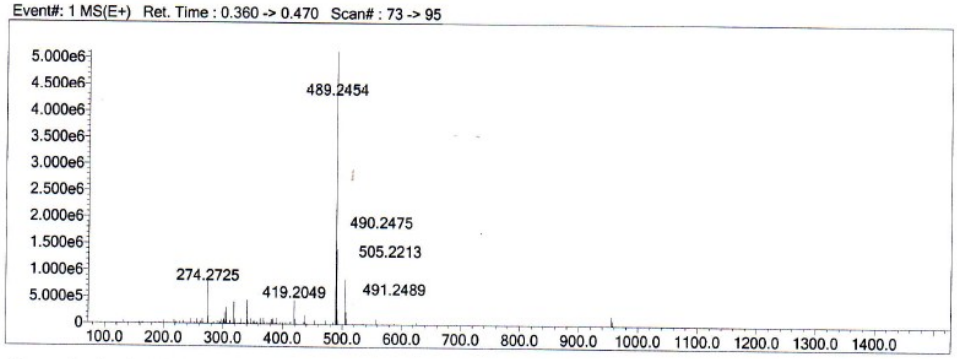
MSn Iso RI (%): 75.00

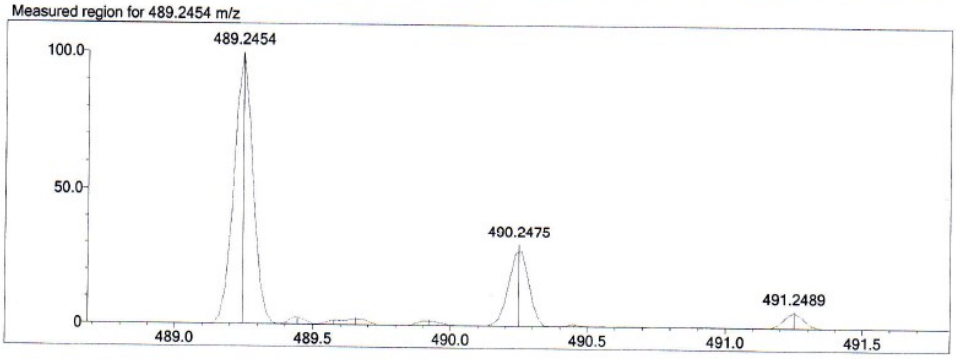
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 100

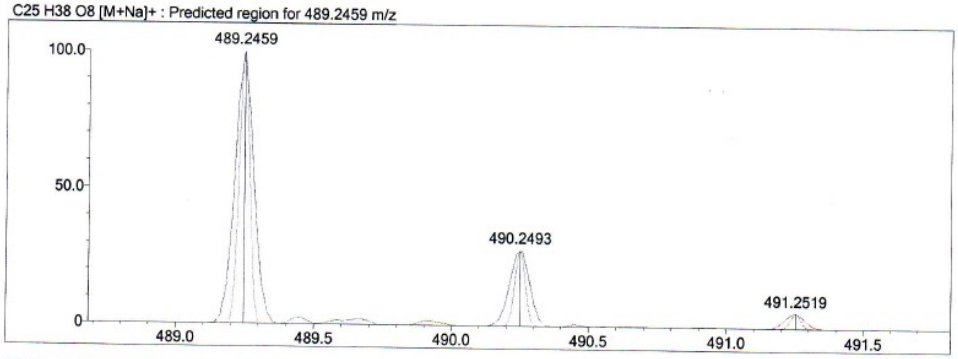
Event#: 1 MS(E+) Ret. Time : 0.360 -> 0.470 Scan# : 73 -> 95



Measured region for 489.2454 m/z

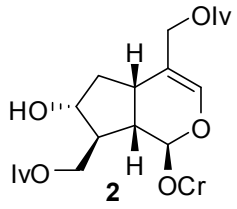


C25 H38 O8 [M+Na]+ : Predicted region for 489.2459 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	99.95	C25 H38 O8	[M+Na]+	489.2454	489.2459	-0.5	-1.02	100.00	7.0

Figure 8. ^{1}H NMR spectrum of Patriscabioin B (**2**) in $CDCl_3$.



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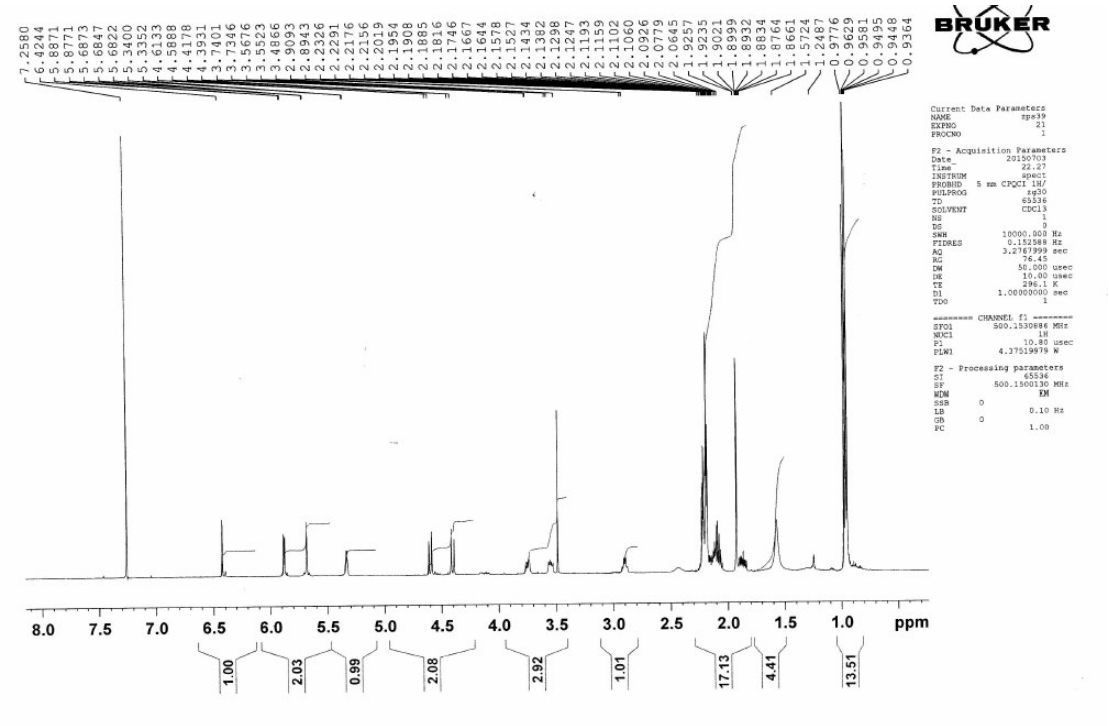

Figure 9.[13]C NMR spectrum of Patriscabioin B (**2**) in $CDCl_3$.

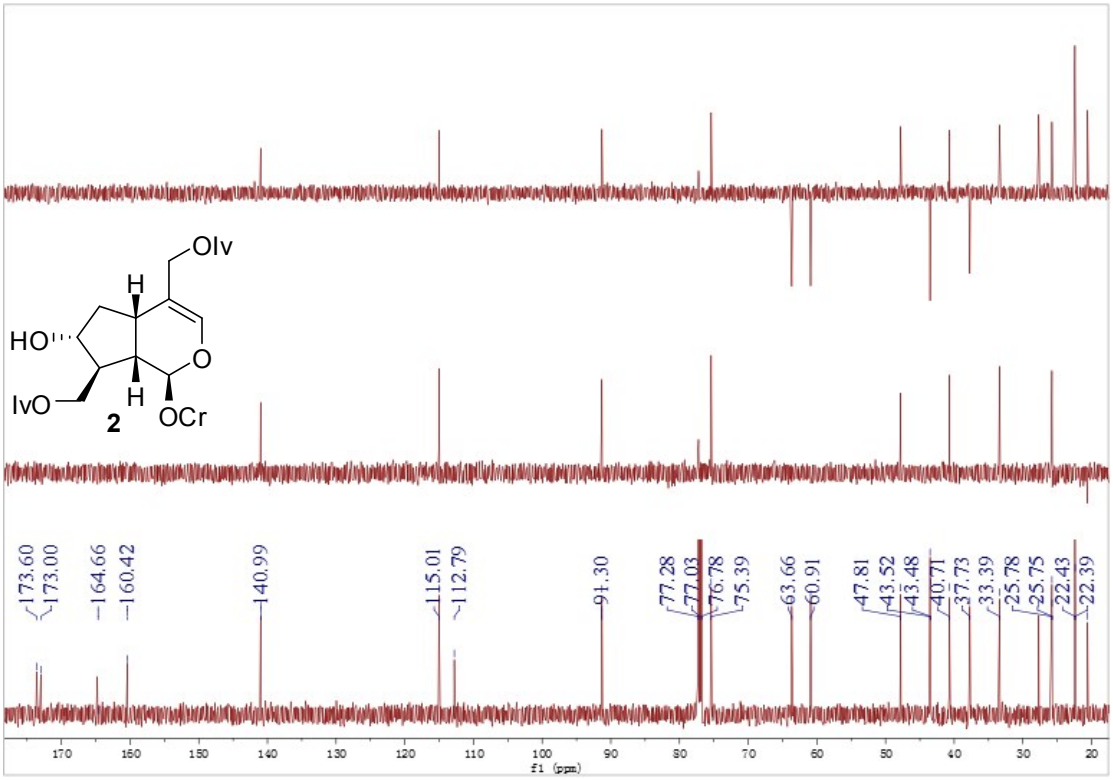

Figure 10. HSQC spectrum of Patriscabioin B (**2**) in $CDCl_3$.

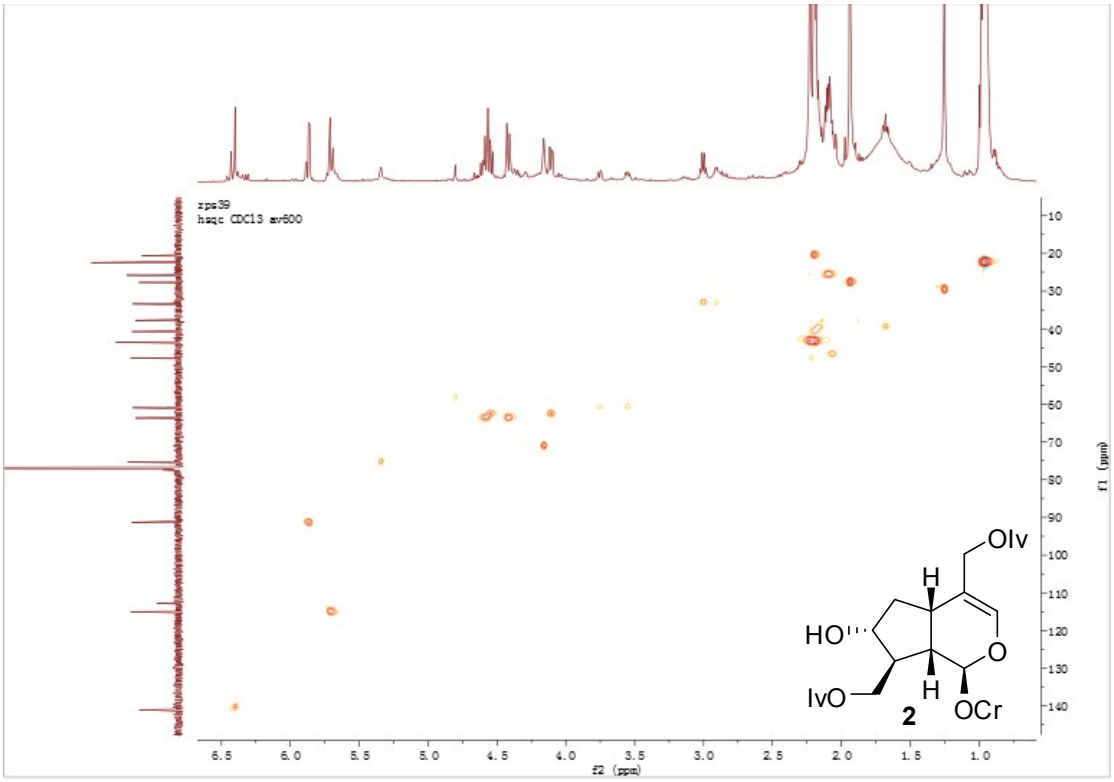

Figure 11. HMBC spectrum of Patriscabioin B (**2**) in $CDCl_3$.

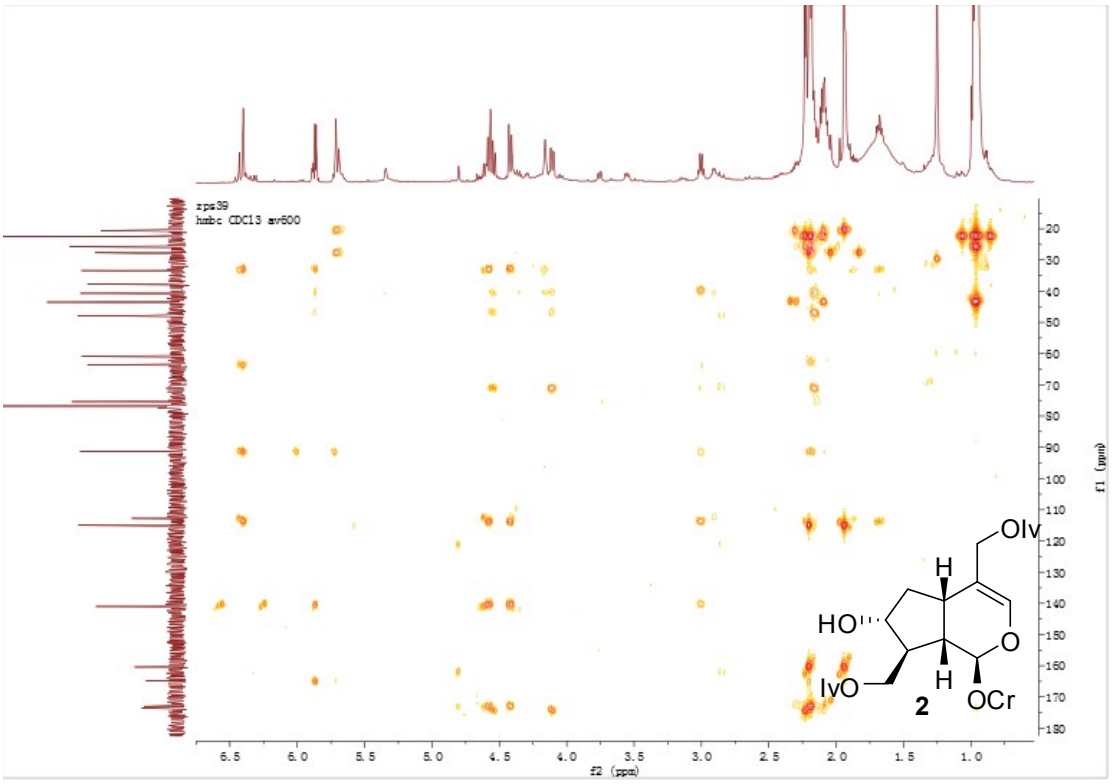

Figure 12. ^{1}H-^{1}H COSY spectrum of Patriscabioin B (**2**) in $CDCl_3$.

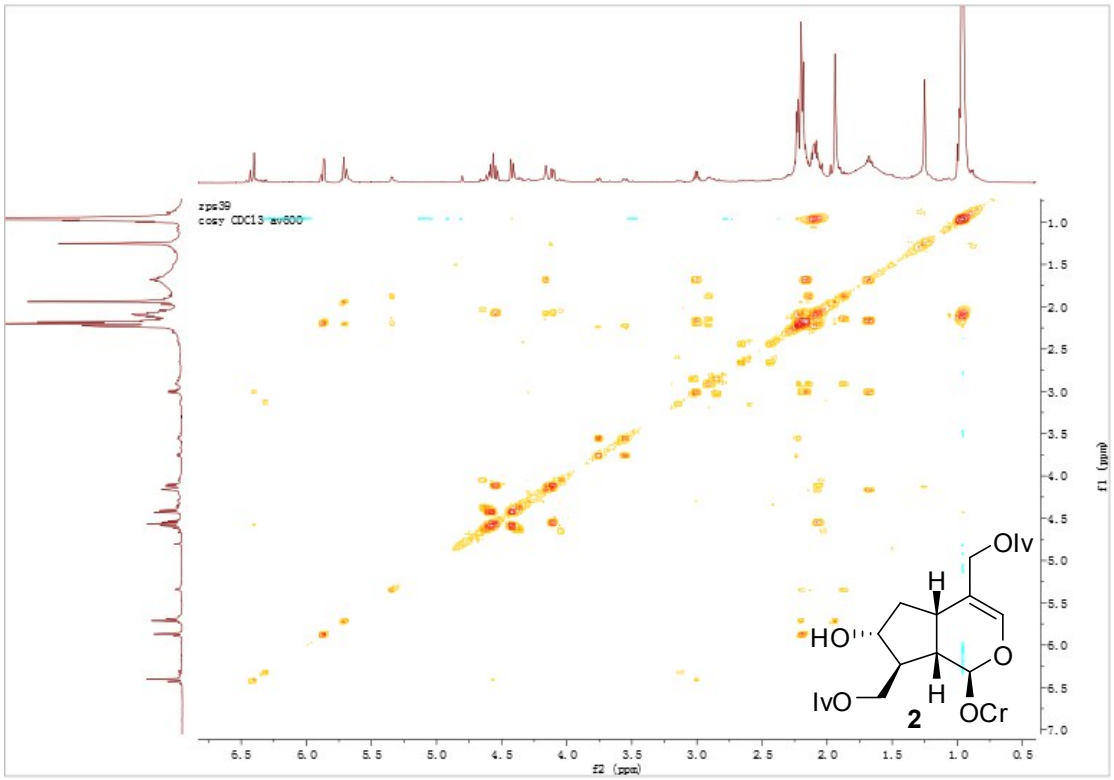

Figure 13. ROESY spectrum of Patriscabioin B (**2**) in $CDCl_3$.

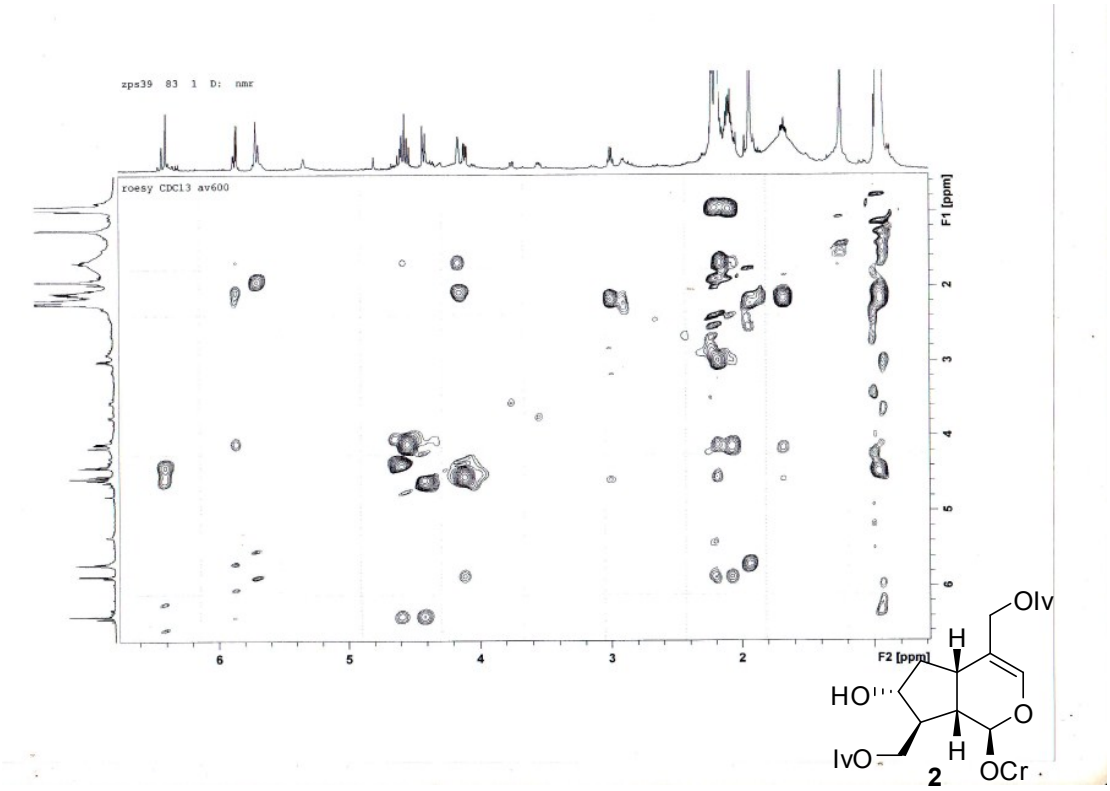

Figure 14. HREIMS spectrum of Patriscabioin B (**2**).

Qualitative Analysis Report

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Sample Type	Sample	**Position**	P1-C7
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Acq Method	SIBU.m	**Acquired Time**	4/19/2016 3:38:19 PM
IRM Calibration Status	Success	**DA Method**	ESI+.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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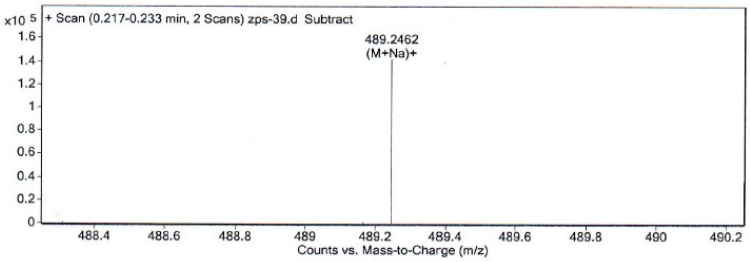

Peak List

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318.3008	1	195575.78		
319.3042	1	38183.13		
362.327	1	66658.2		
484.2908	1	70822.38		
489.2462	1	142474.86	C25 H38 O8	(M+Na)+
505.2202	1	137884		
955.5031	1	75508.64		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C25 H38 O8	466.2567	489.2459	489.2462	-0.7	-1.5	7.0000

--- End Of Report ---

Figure 15. ^{1}H NMR spectrum of Patriscabioin C (**3**) in $CDCl_3$.

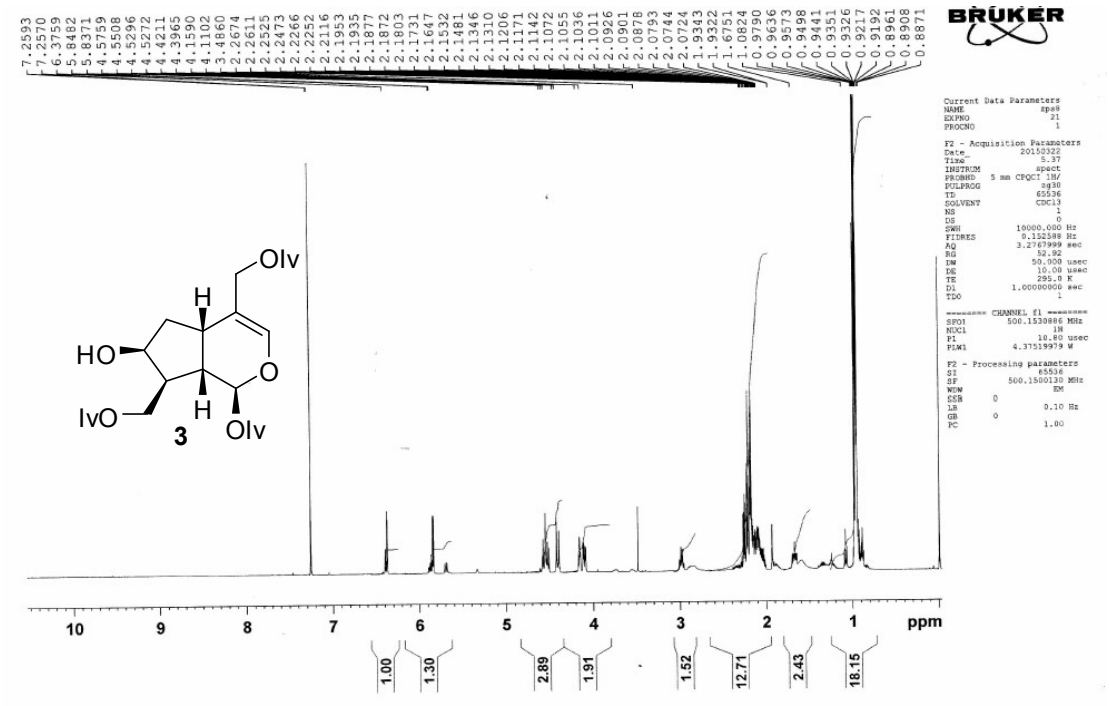

Figure 16. ^{13}C NMR spectrum of Patriscabioin C (**3**) in $CDCl_3$.

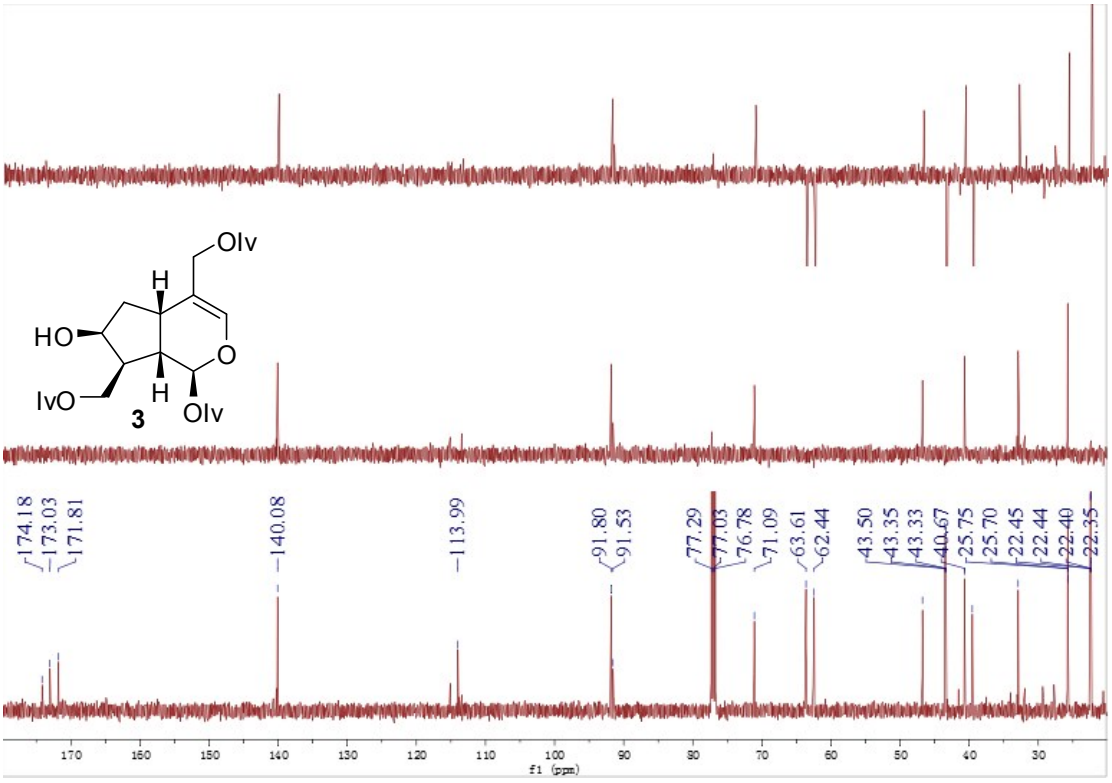

Figure 17. HSQC spectrum of Patriscabioin C (**3**) in $CDCl_3$.

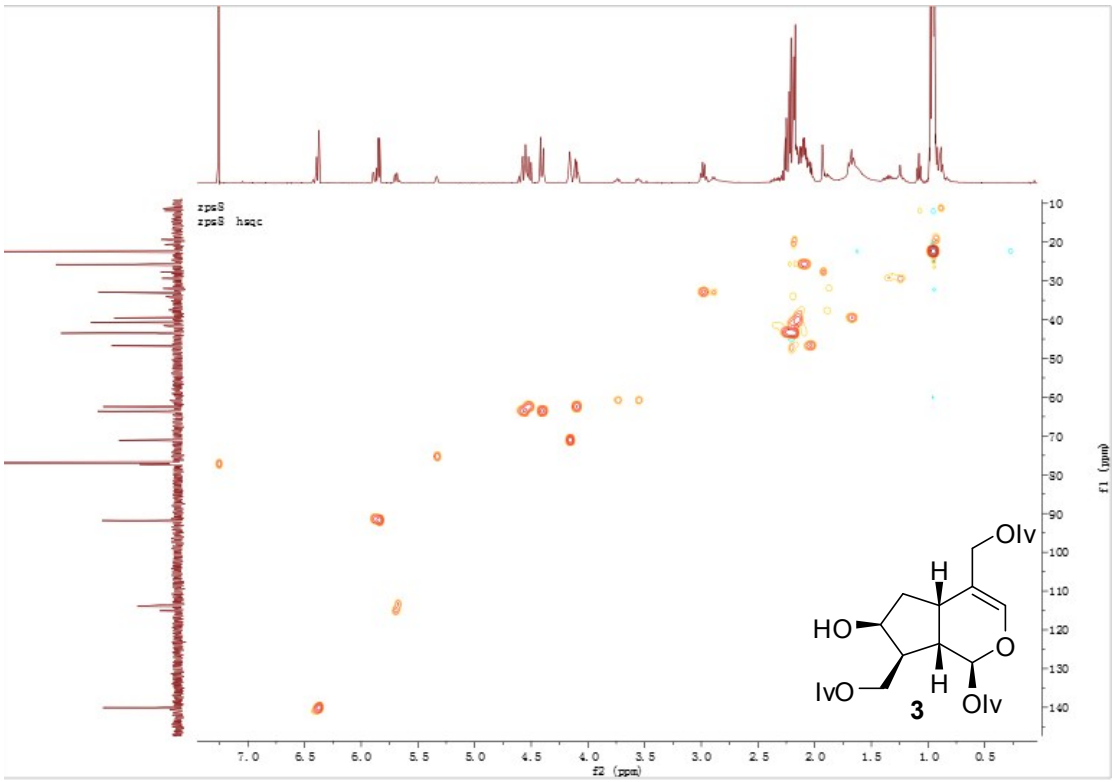

Figure 18. HMBC spectrum of Patriscabioin C (**3**) in $CDCl_3$

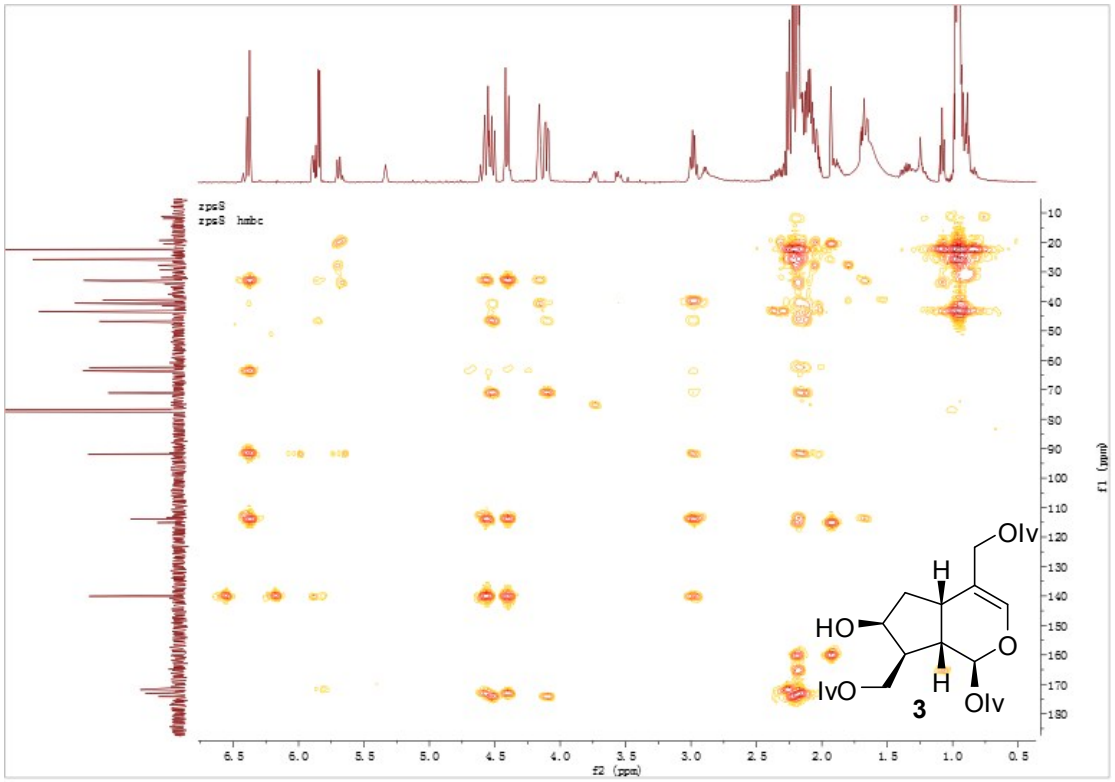

Figure 19. ^{1}H-^{1}H COSY spectrum of Patriscabioin C (**3**) in $CDCl_3$.

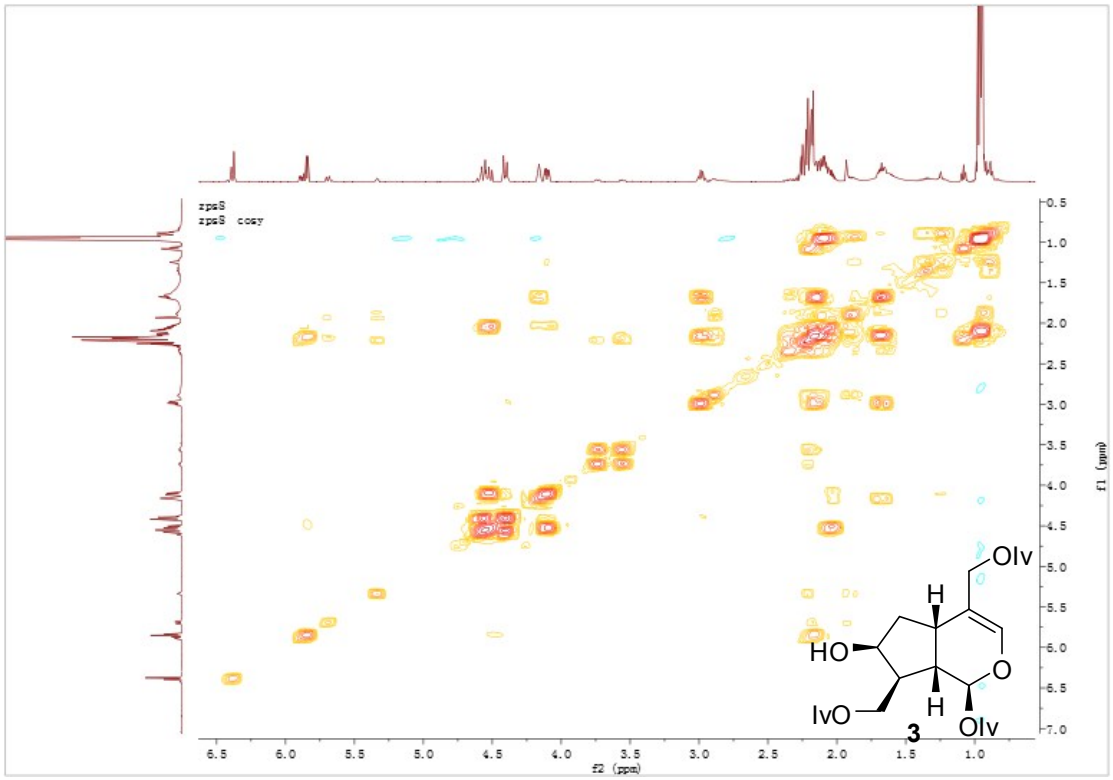

Figure 20. ROESY spectrum of Patriscabioin C (**3**) in $CDCl_3$.

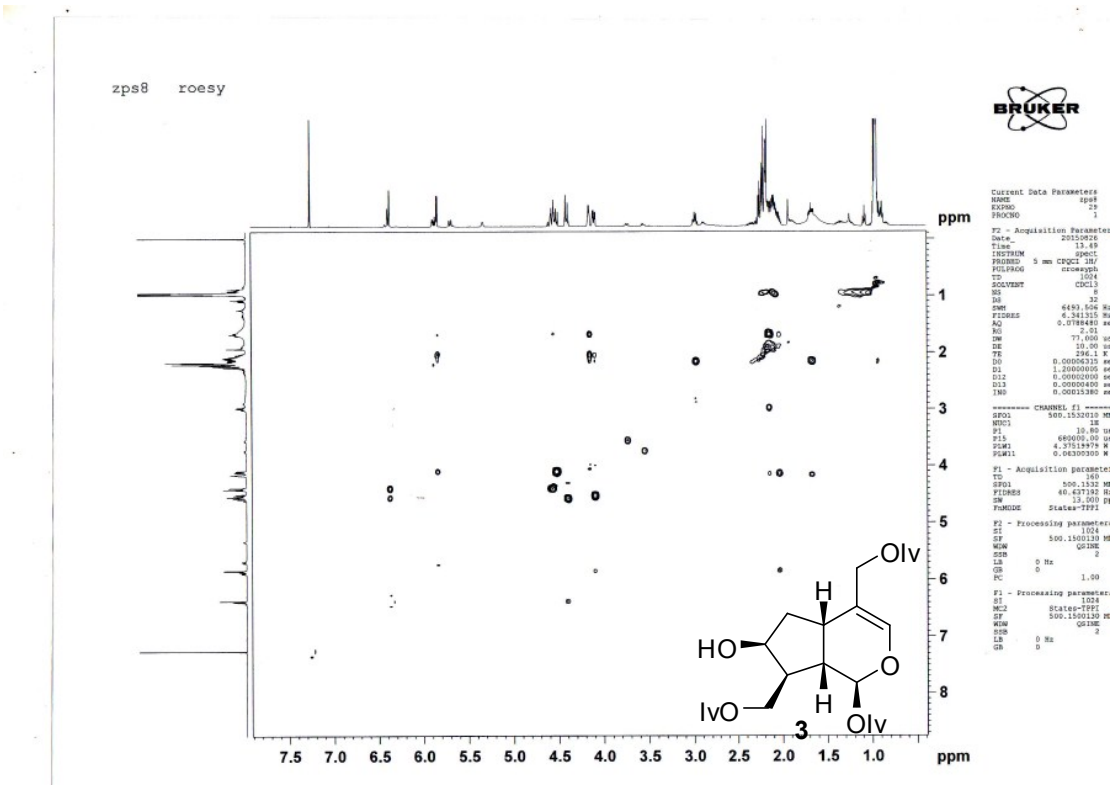

Figure 21. HREIMS spectrum of Patriscabioin C (**3**).

Formula Predictor Report - zps-8.lcd

Data File: E:\DATA\20151106\zps-8.lcd

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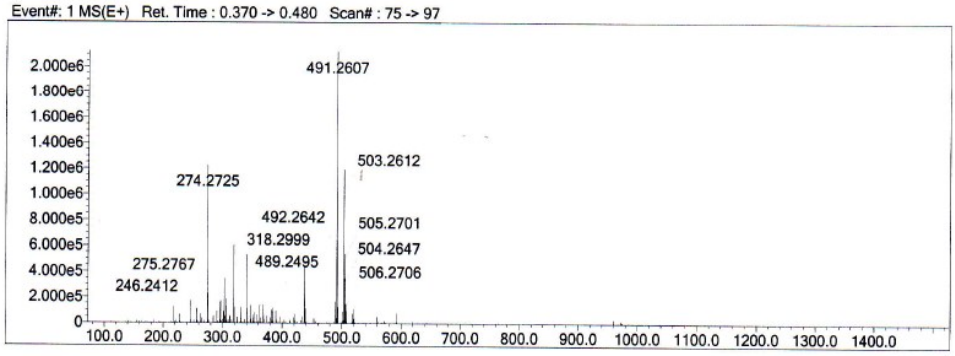
C	4	0	50	Br	1	0	0	
N	3	0	10					

Error Margin (ppm): 10
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

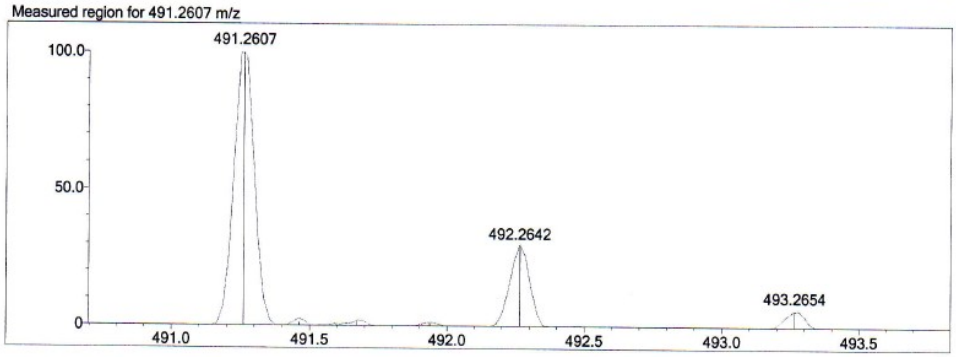
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 100

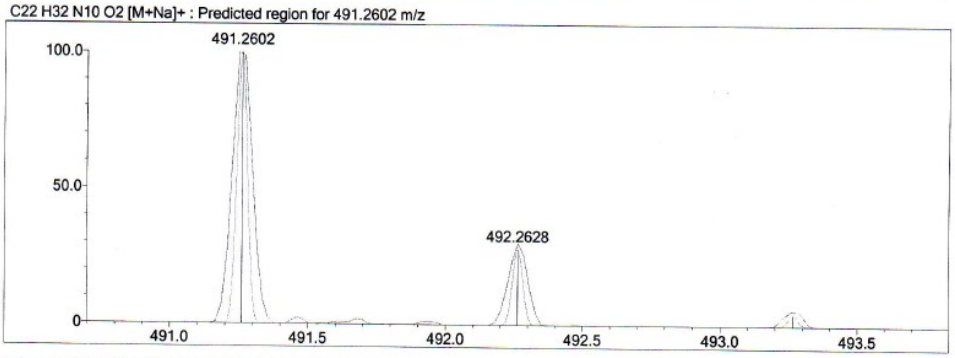
Event#: 1 MS(E+) Ret. Time : 0.370 -> 0.480 Scan# : 75 -> 97



Measured region for 491.2607 m/z



C22 H32 N10 O2 [M+Na]+ : Predicted region for 491.2602 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	99.95	C22 H32 N10 O2	[M+Na]+	491.2607	491.2602	0.5	1.02	100.00	12.0

Figure 22. ^{1}H NMR spectrum of Patriscabioin D (**4**) in $CDCl_3$.

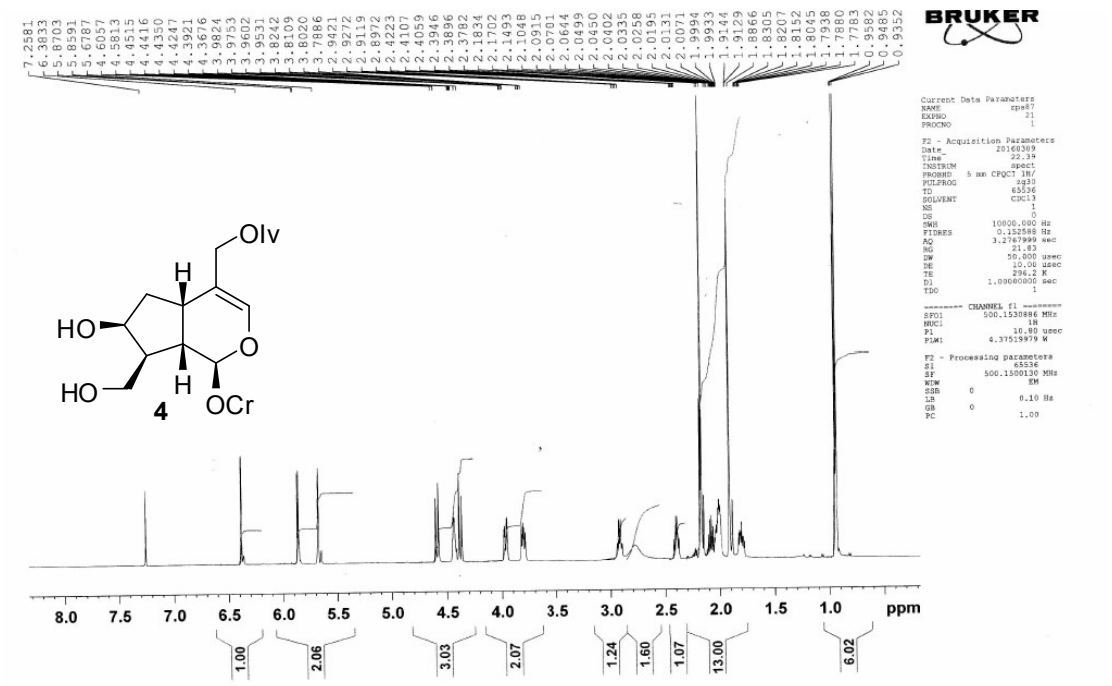


Figure 23. ^{13}C NMR spectrum of Patriscabioin D (**4**) in $CDCl_3$

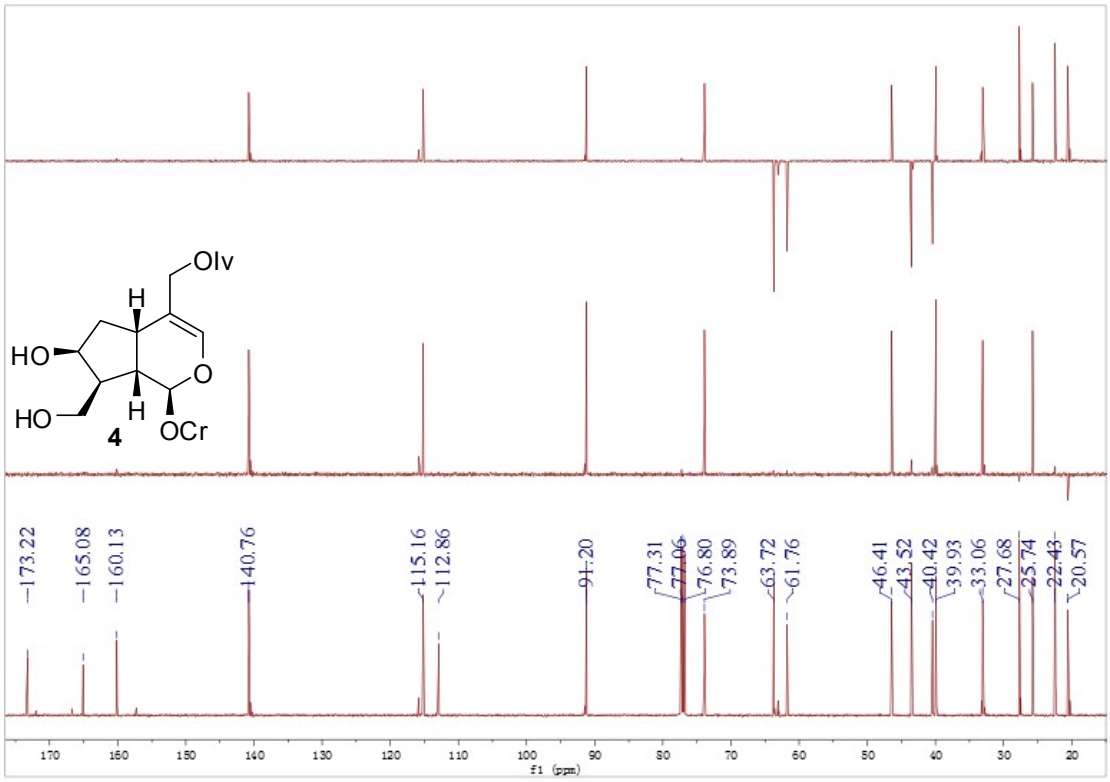


Figure 24. HSQC spectrum of Patriscabioin D (**4**) in $CDCl_3$.

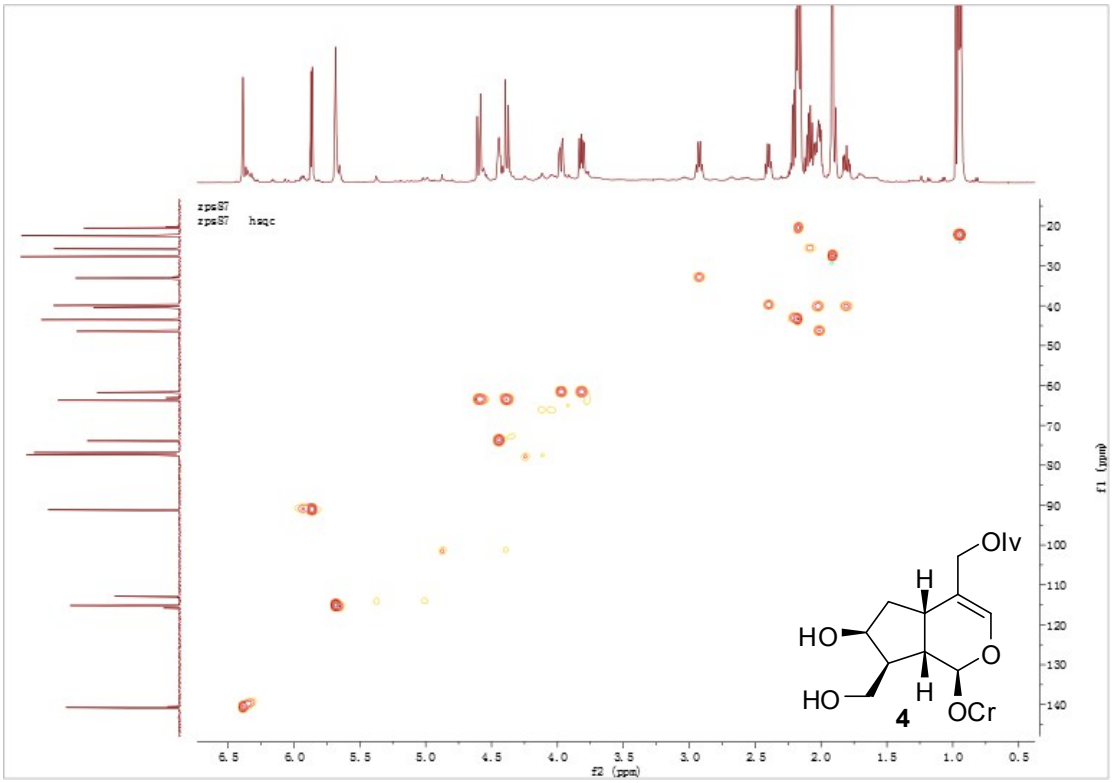


Figure 25. HMBC spectrum of Patriscabioin D (**4**) in $CDCl_3$.

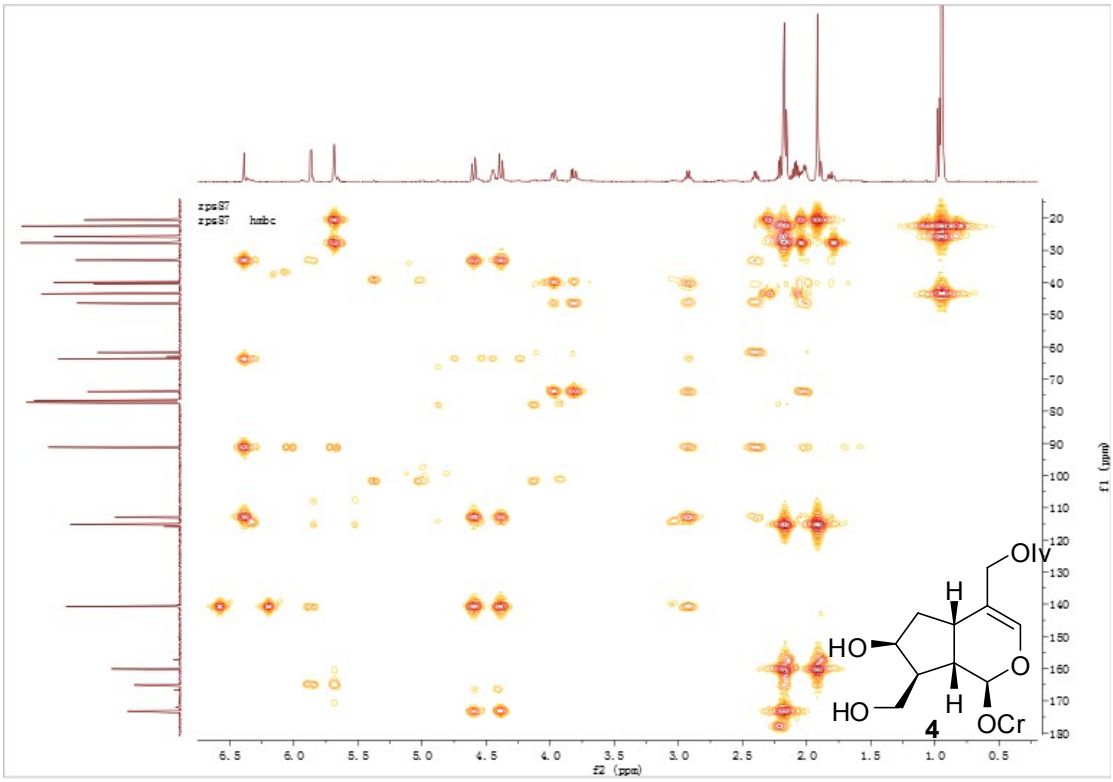


Figure 26. ^{1}H-^{1}H COSY spectrum of Patriscabioin D (**4**) in $CDCl_3$.

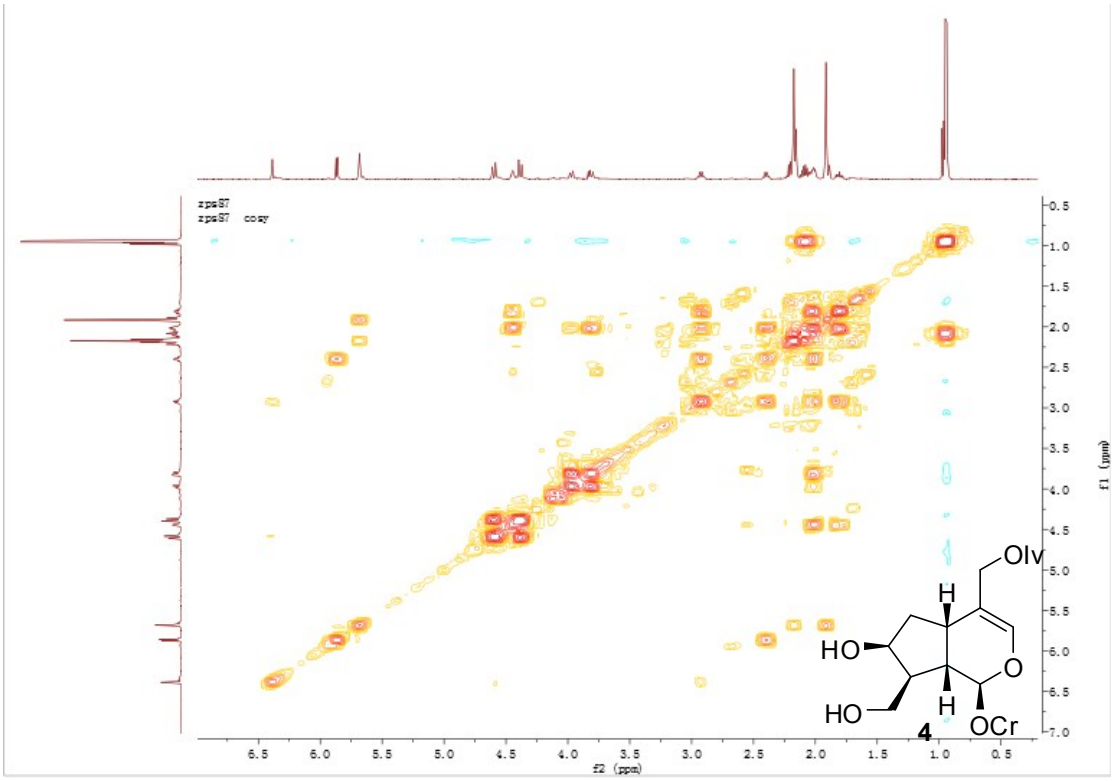


Figure 27. ROESY spectrum of Patriscabioin D (**4**) in $CDCl_3$.

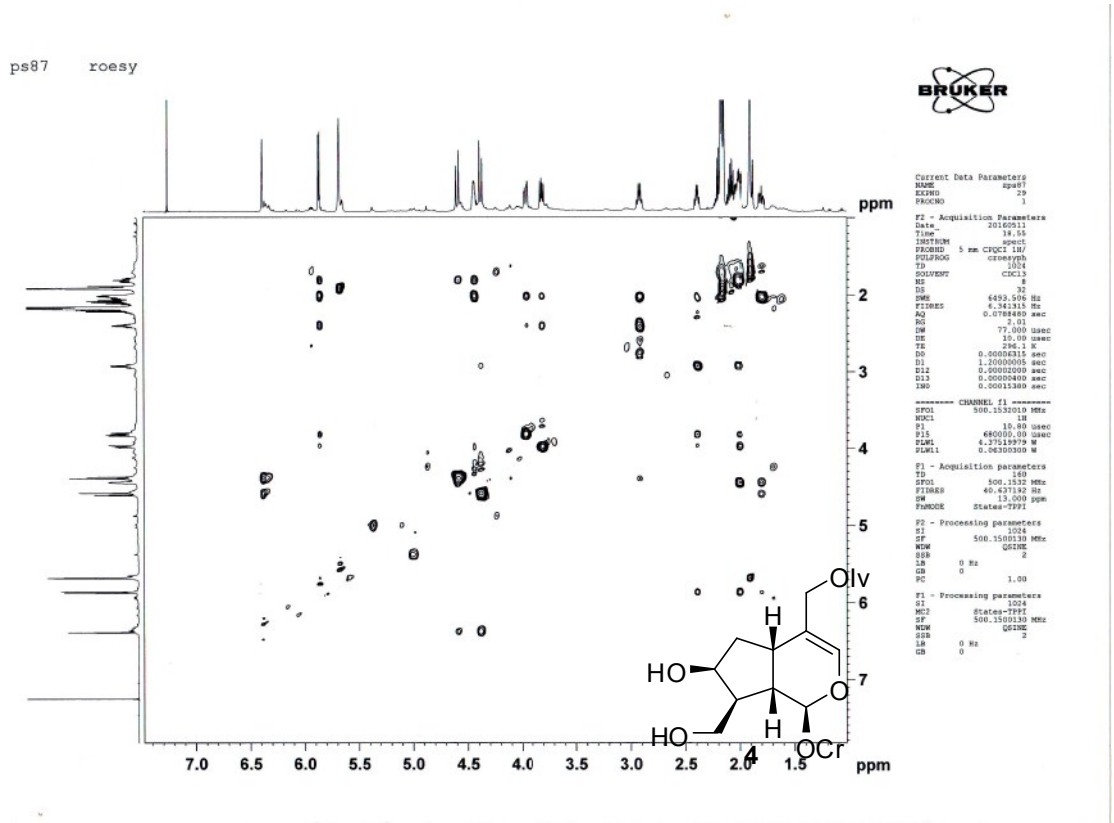


Figure 28. HREIMS spectrum of Patriscabioin D (**4**).

Qualitative Analysis Report

Data Filename	zps-87.d	**Sample Name**	zps-87
Sample Type	Sample	**Position**	P1-C8
Instrument Name	Instrument 1	**User Name**	
Acq Method	SIBU.m	**Acquired Time**	4/19/2016 3:39:44 PM
IRM Calibration Status	Success	**DA Method**	ESI+.m
Comment			

Sample Group **Info.**

Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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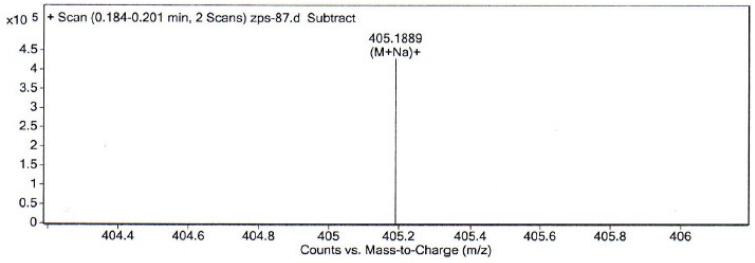

Peak List

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785.373	1	215689		
786.3758	1	86365.39		
787.3884		824728		
788.3919	1	338700.53		
789.3978	1	126465.7		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C20 H30 O7	382.1992	405.1884	405.1889	-0.8	-2.1	6.0000

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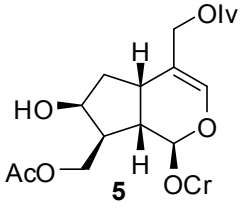
Figure 29. ^{1}H NMR spectrum of Patriscabioin E (**5**) in $CDCl_3$.



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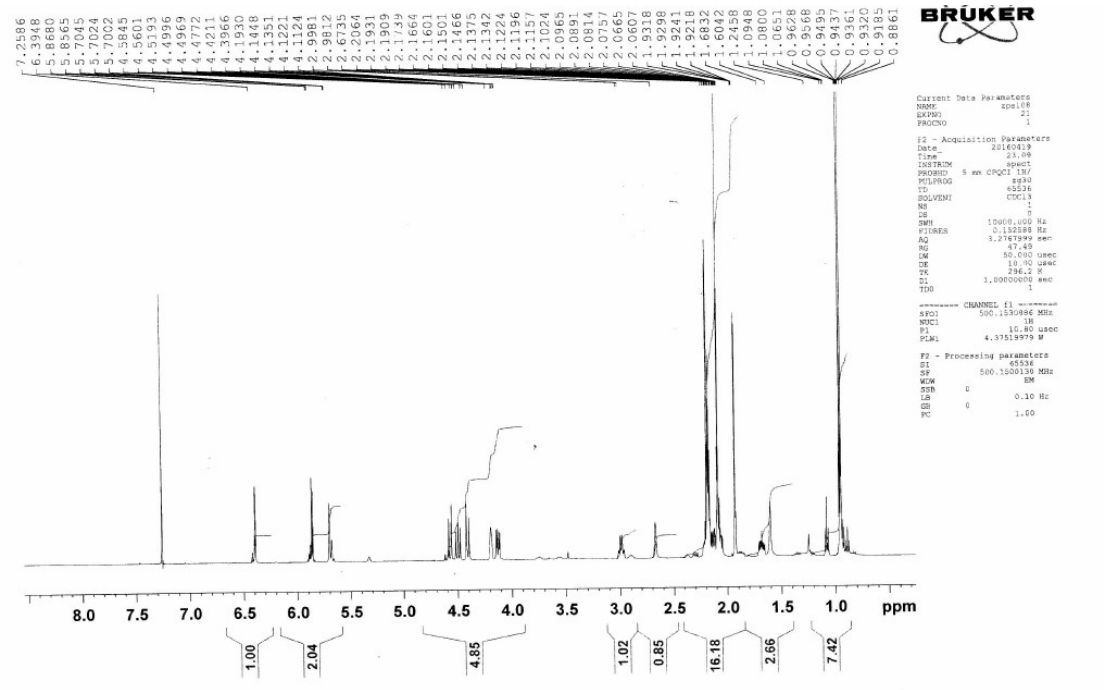


Figure 30. ^{13}C NMR spectrum of Patriscabioin E (**5**) in $CDCl_3$

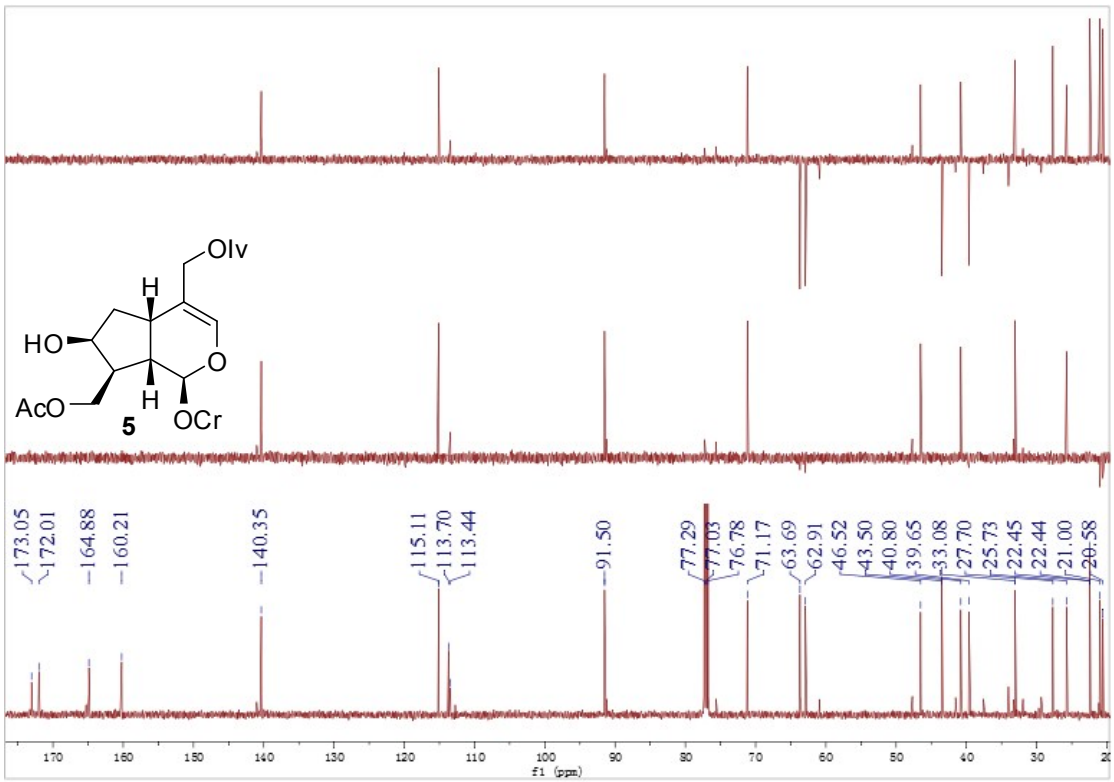


Figure 31. HSQC spectrum of Patriscabioin E (**5**) in $CDCl_3$.

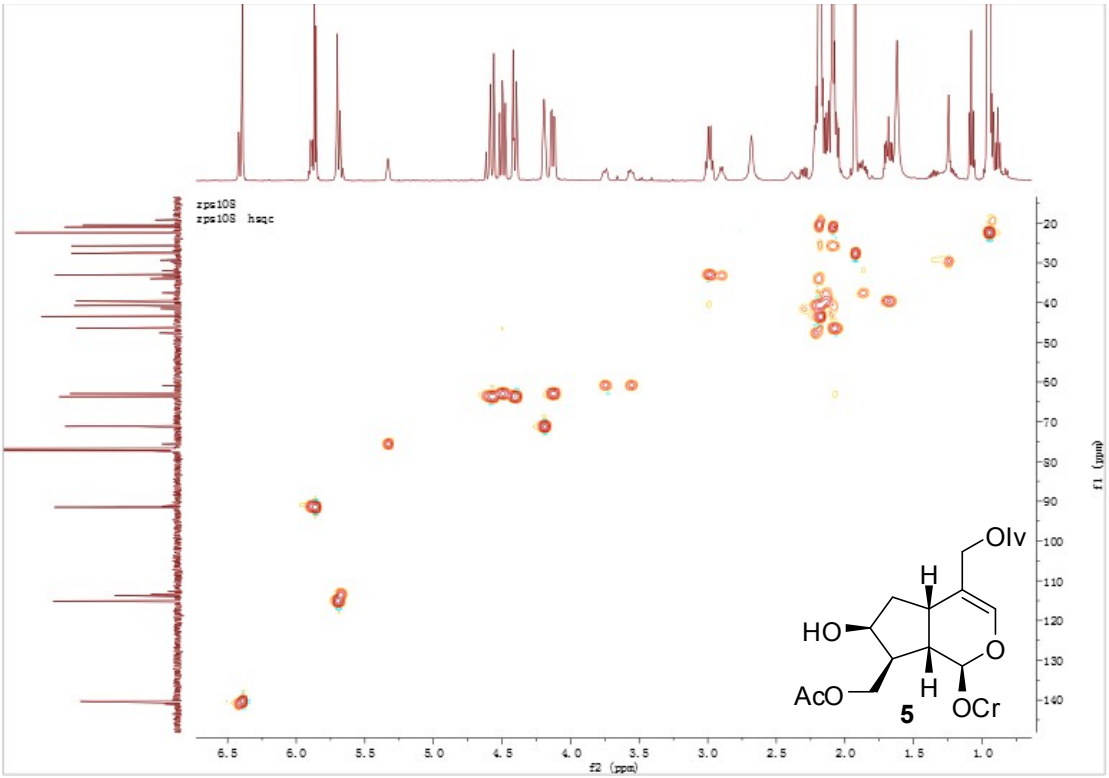


Figure 32. HMBC spectrum of Patriscabioin E (**5**) in $CDCl_3$.

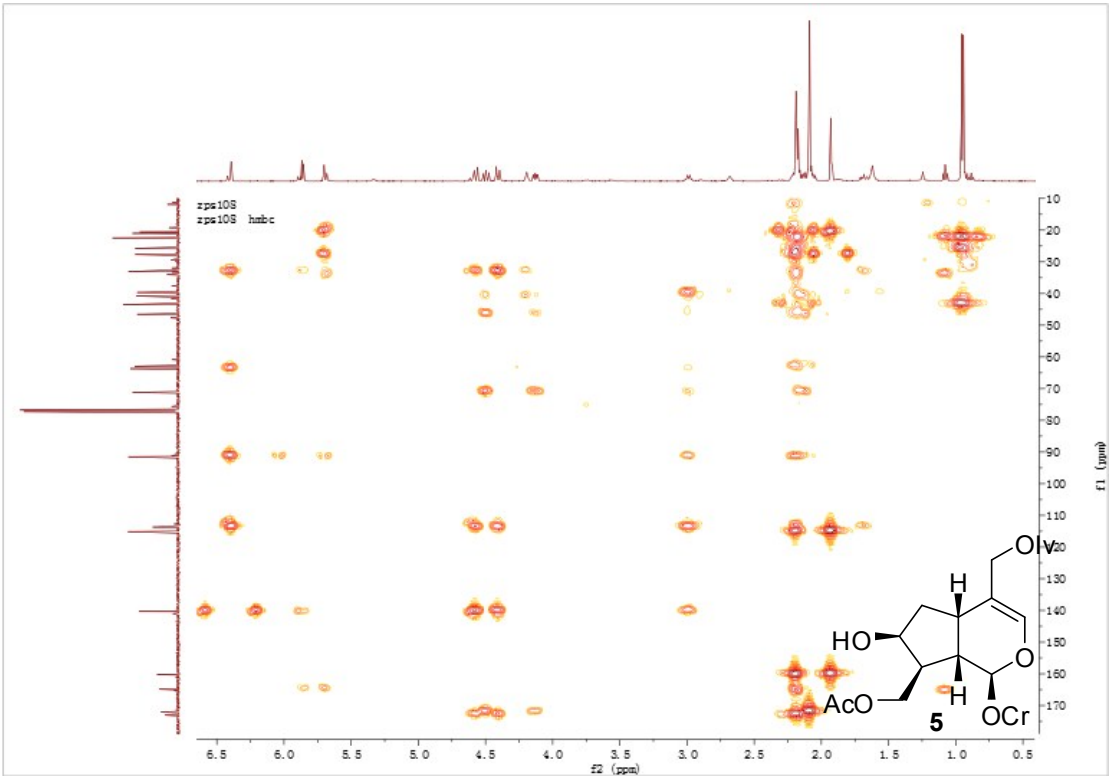


Figure 33. ^{1}H-^{1}H COSY spectrum of Patriscabioin E (**5**) in $CDCl_3$.

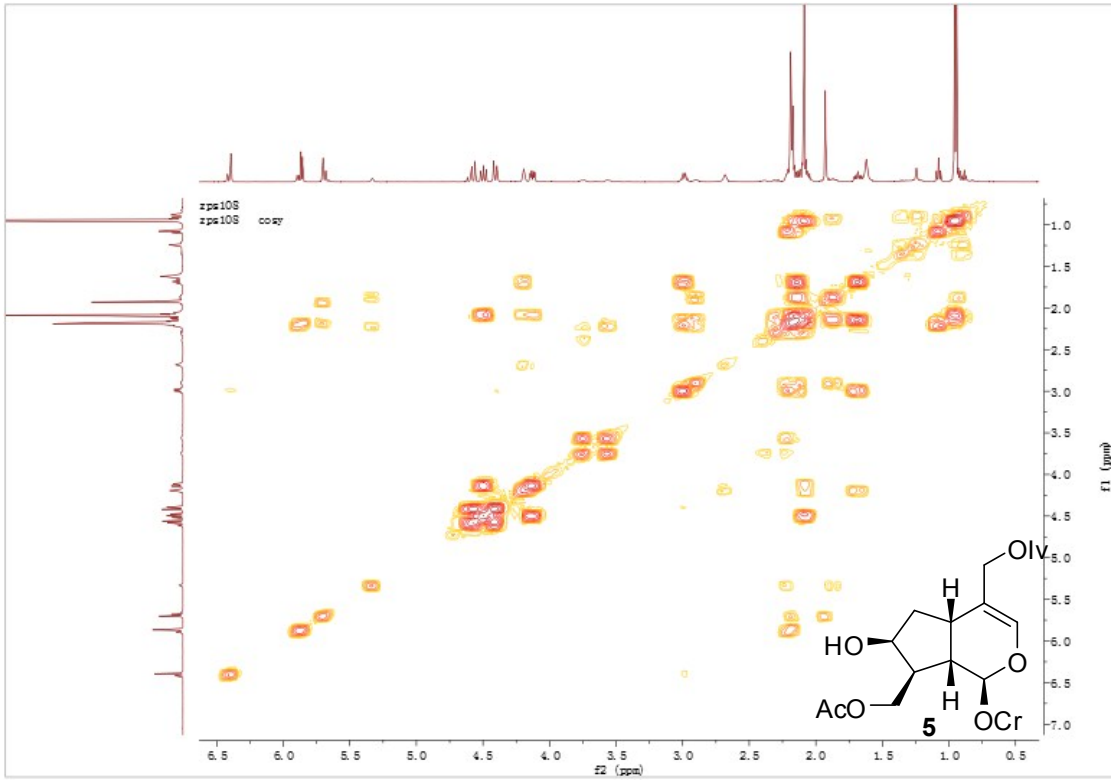


Figure 34. ROESY spectrum of Patriscabioin E (**5**) in $CDCl_3$.

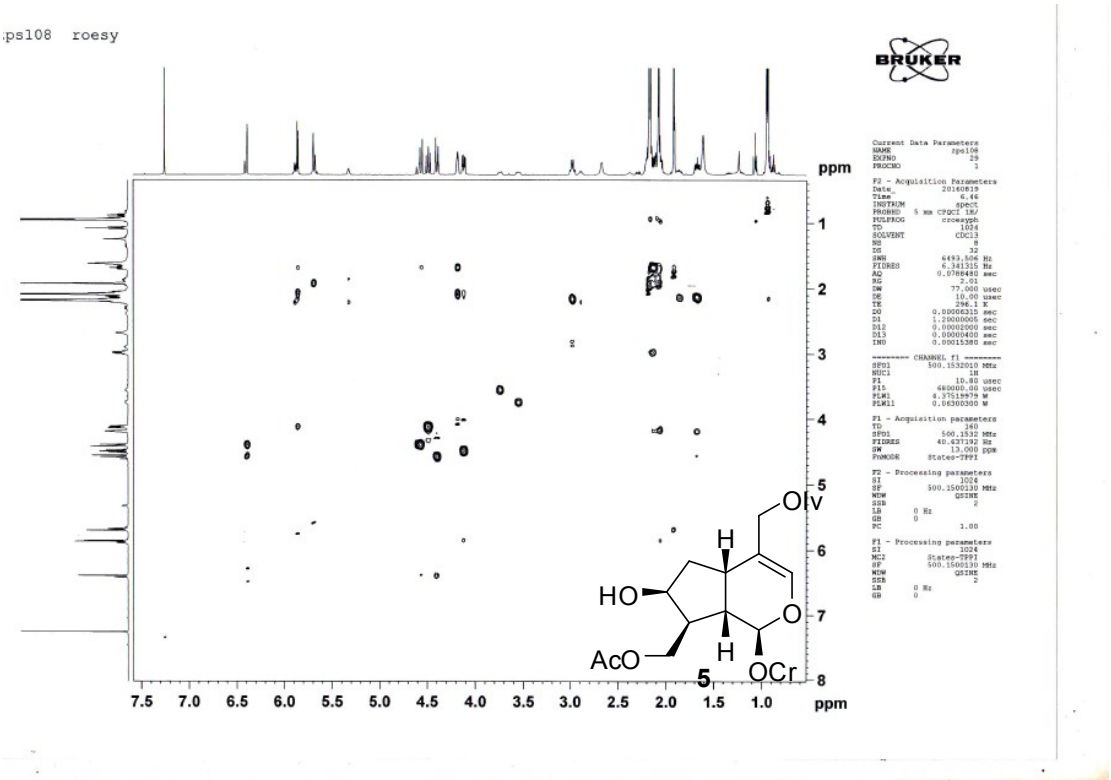


Figure 35. HREIMS spectrum of Patriscabioin E (**5**).

Formula Predictor Report - zps-108.lcd

Data File: E:\DATA\2016\0525\zps-108.lcd

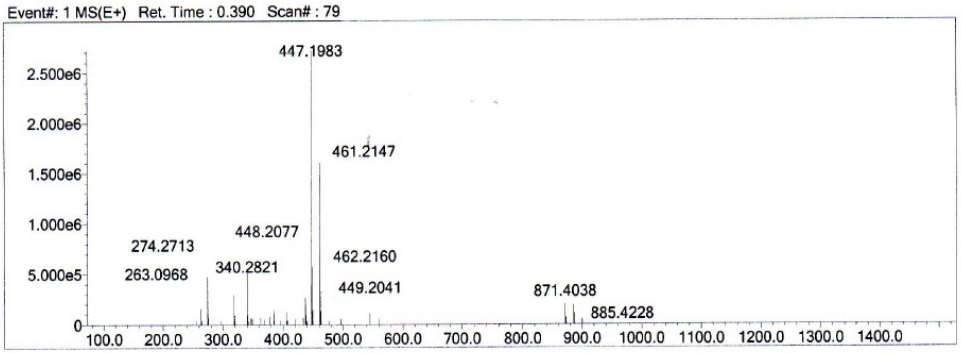
Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	20	Na	1	0	0	Cl	1	0	0	Na
B	3	0	0	O	2	0	40	Si	4	0	0	Br	1	0	0	
C	4	0	80	F	1	0	0	S	2	0	0	Pt	2	0	0	

Error Margin (ppm): 10
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

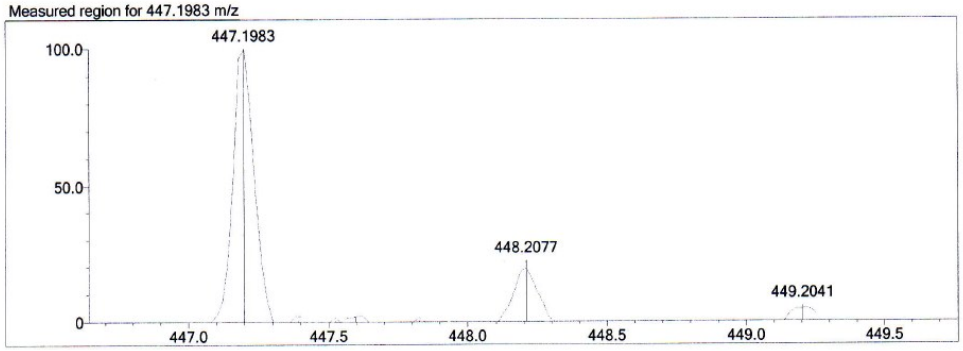
DBE Range: -2.0 - 100.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 10

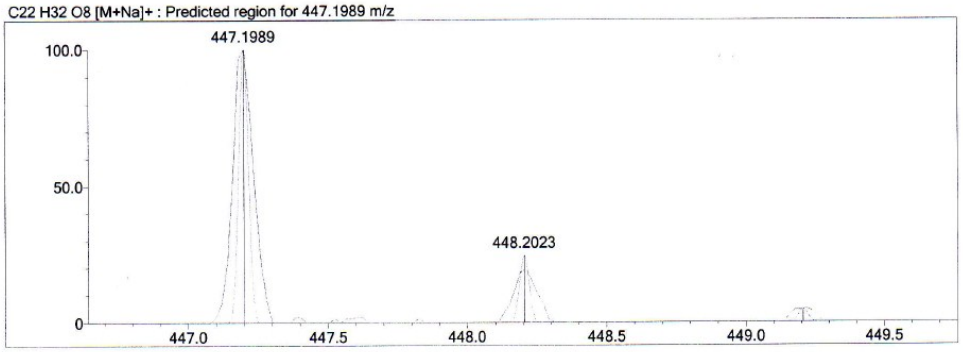
Event#: 1 MS(E+) Ret. Time : 0.390 Scan# : 79



Measured region for 447.1983 m/z



C22 H32 O8 [M+Na]+ : Predicted region for 447.1989 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	85.05	C22 H32 O8	[M+Na]+	447.1983	447.1989	-0.6	-1.34	85.78	7.0

Figure 36. ^{1}H NMR spectrum of Patriscabioin F (**6**) in $CDCl_3$.

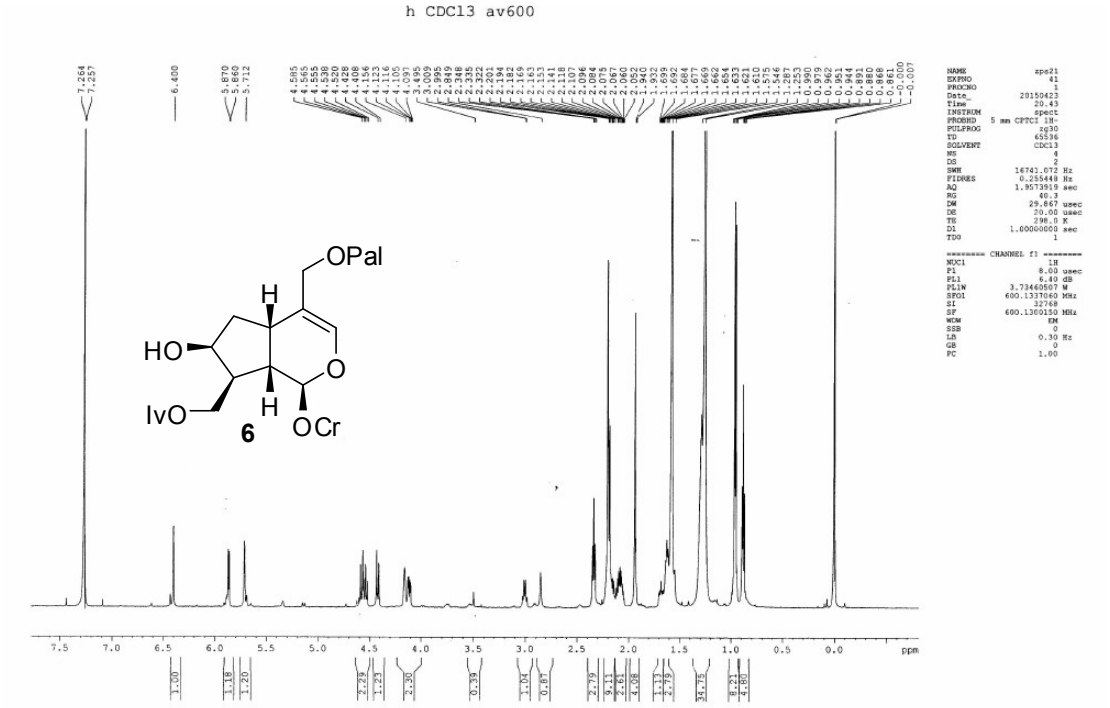


Figure 37. ^{13}C NMR spectrum of Patriscabioin F (**6**) in $CDCl_3$.

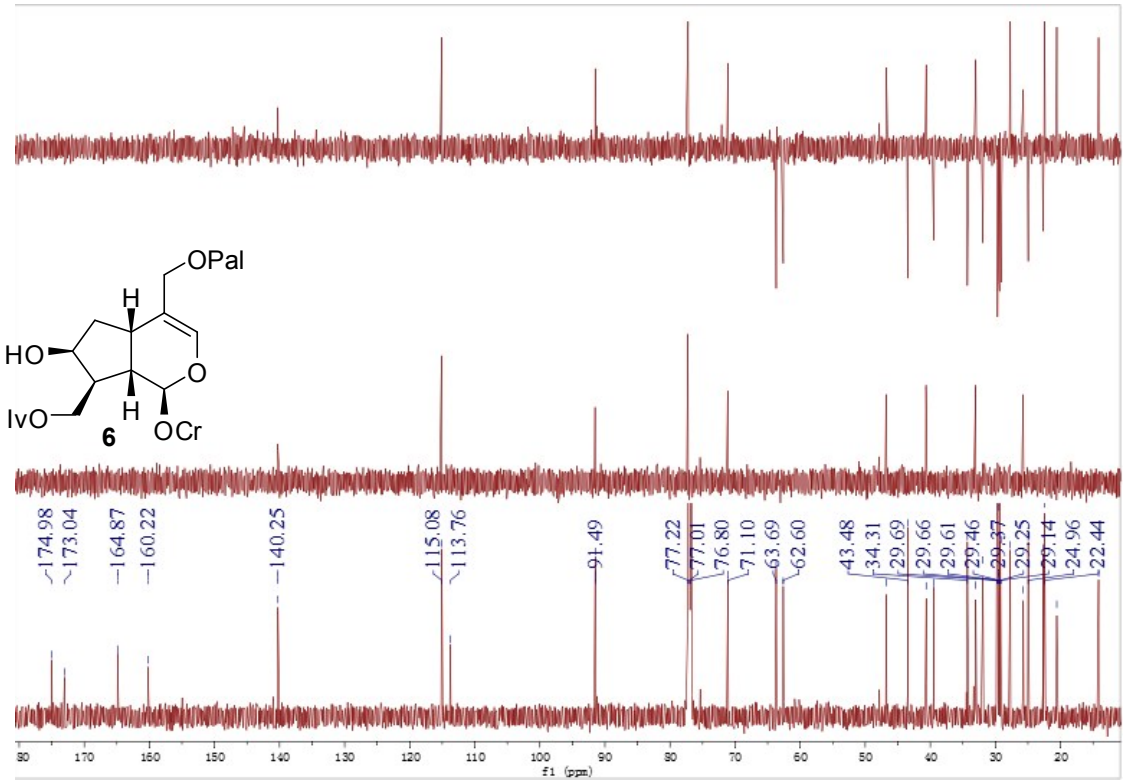


Figure 38. HSQC spectrum of Patriscabioin F (**6**) in $CDCl_3$.

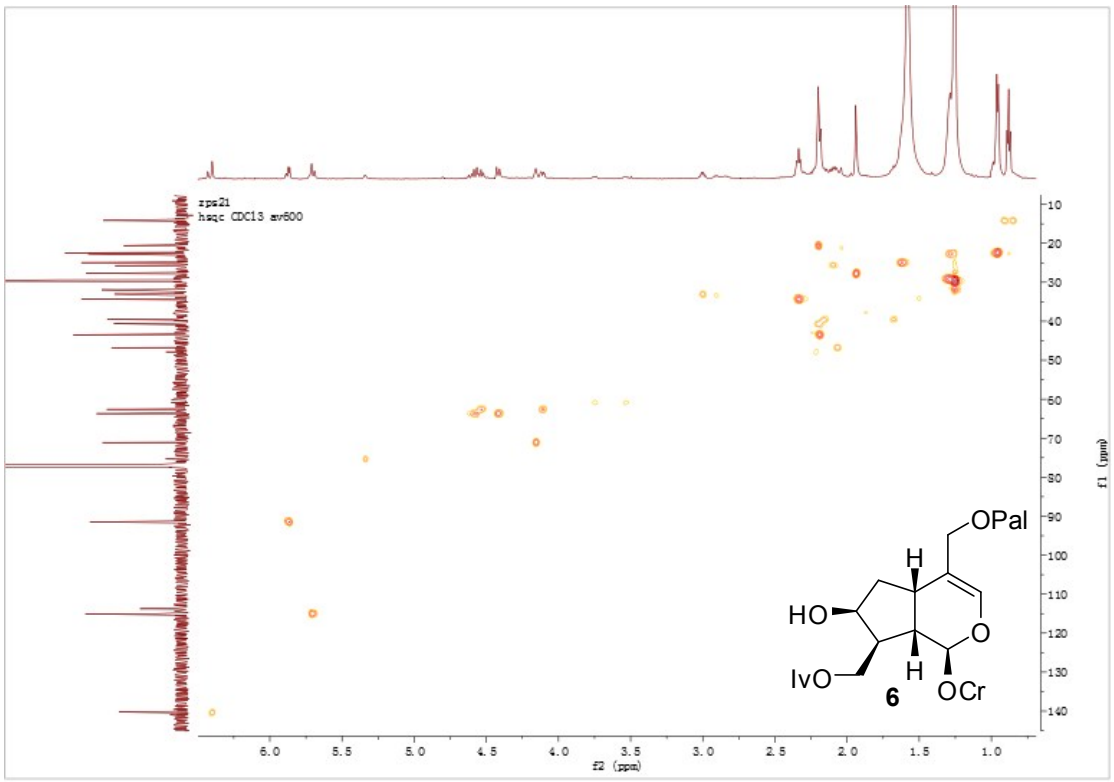


Figure 39. HMBC spectrum of Patriscabioin F (**6**) in $CDCl_3$.

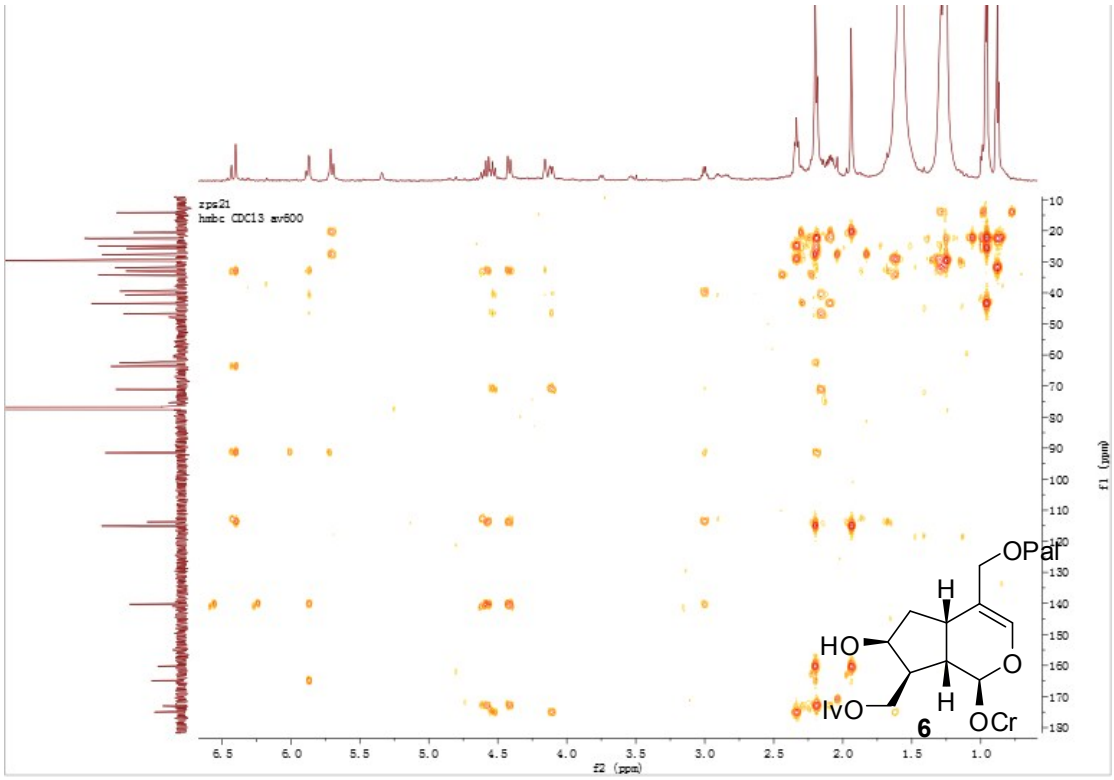


Figure 40. ^{1}H-^{1}H COSY spectrum of Patriscabioin F (**6**) in $CDCl_3$.

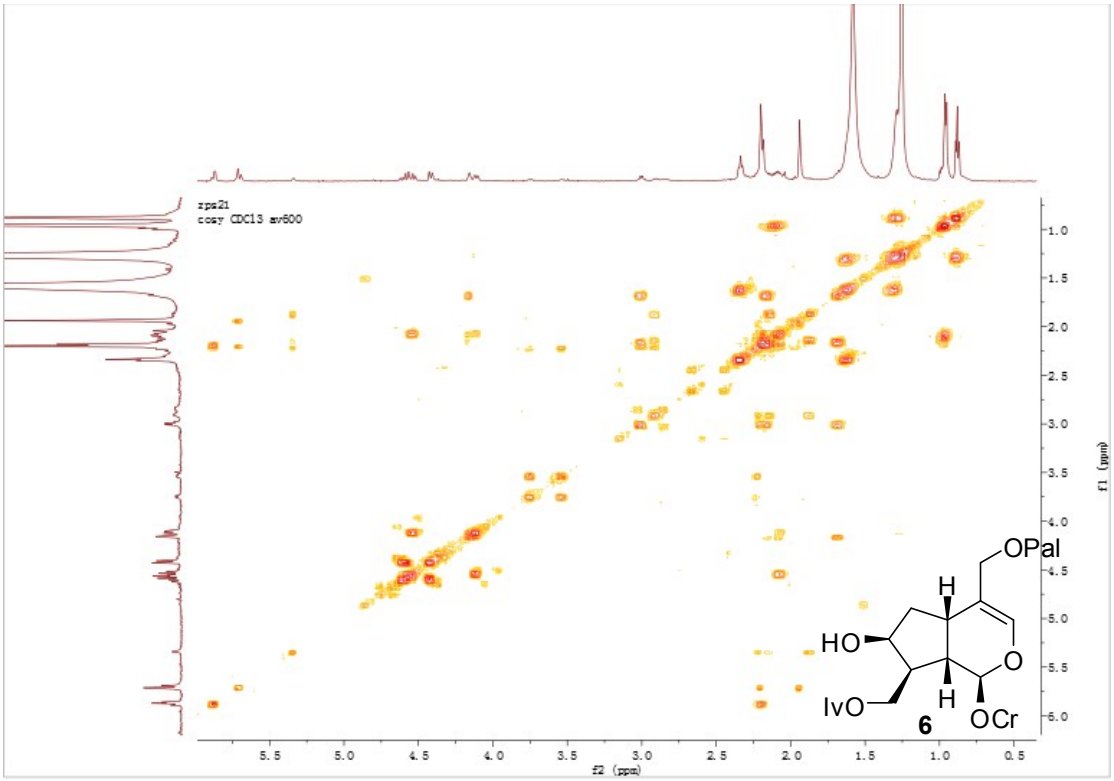


Figure 41. ROESY spectrum of Patriscabioin F (**6**) in $CDCl_3$.

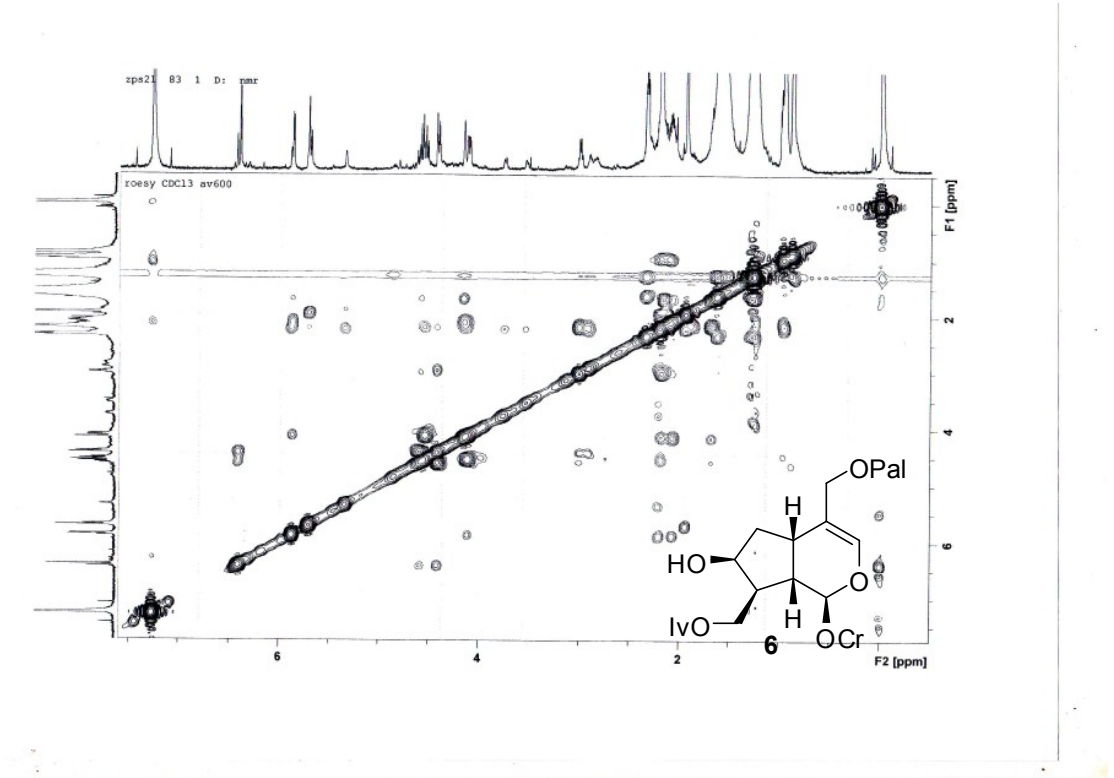


Figure 42. HREIMS spectrum of Patriscabioin F (**6**).

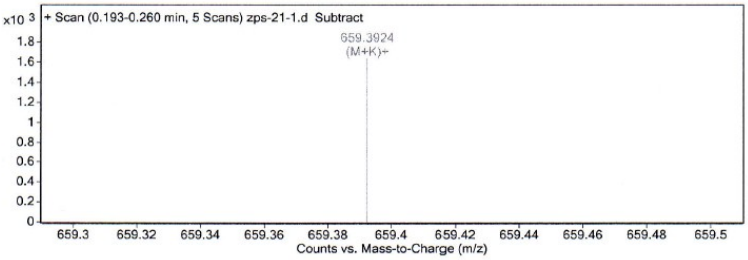
Qualitative Analysis Report

Data Filename	zps-21-1.d	**Sample Name**	zps-21
Sample Type	Sample	**Position**	P1-C6
Instrument Name	Instrument 1	**User Name**	
Acq Method	SIBU.m	**Acquired Time**	4/19/2016 3:54:34 PM
IRM Calibration Status	Success	**DA Method**	ESI+.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	**Collision Energy**	**Ionization Mode**
135	0	ESI



Peak List

m/z	z	Abund
274.2746	1	216462.16
275.2775	1	38565.11
318.3009	1	265295.72
319.304	1	49325.3
362.3269	1	86683.3
363.3301	1	18486.81
453.1676	1	20150.49
473.265	1	17250.22

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C36 H60 O8	620.4288	659.3920	659.3924	-0.3	-0.5	7.0000

--- End Of Report ---

Figure 43.[1]H NMR spectrum of Patriscabioin G (**7**) in $CDCl_3$.

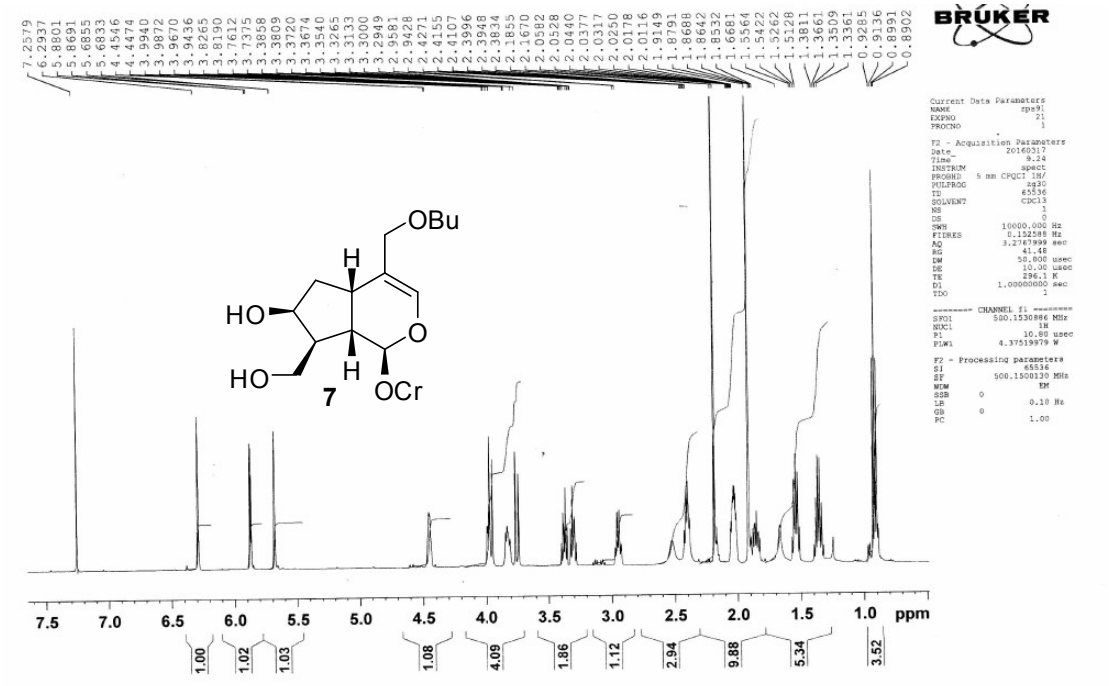


Figure 44.[13]C NMR spectrum of Patriscabioin G (**7**) in $CDCl_3$.

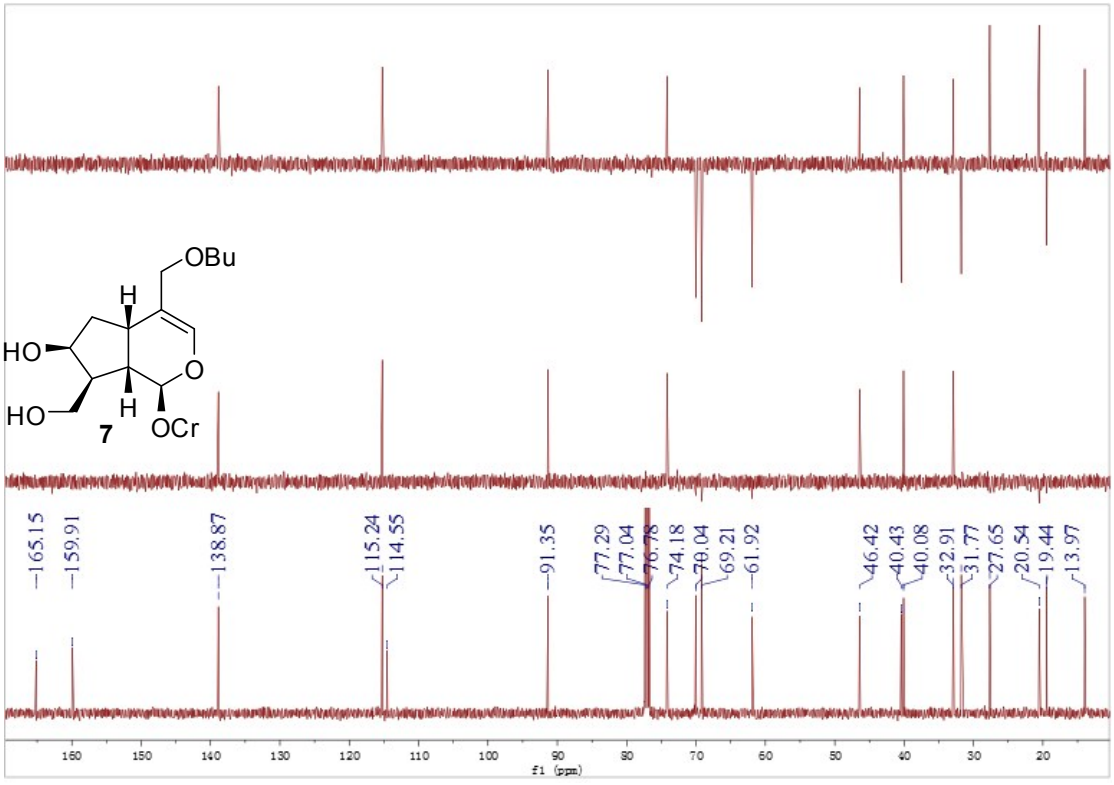


Figure 45. HSQC spectrum of Patriscabioin G (**7**) in $CDCl_3$.

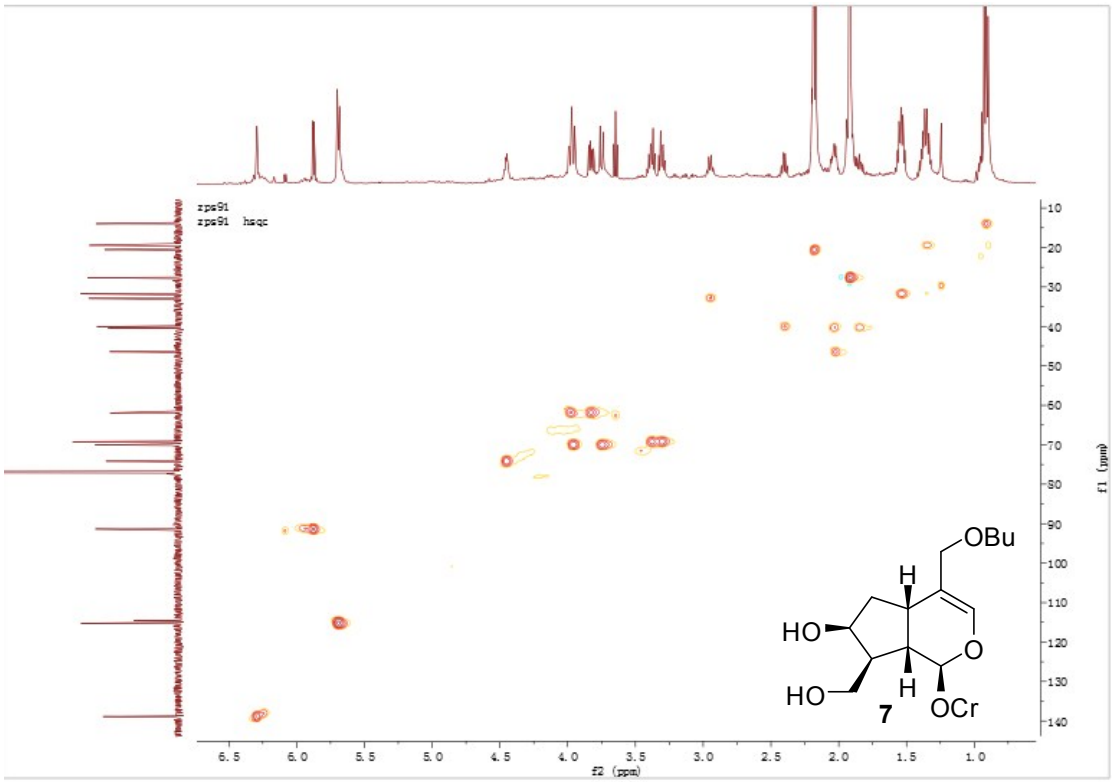


Figure 46. HMBC spectrum of Patriscabioin G (**7**) in $CDCl_3$.

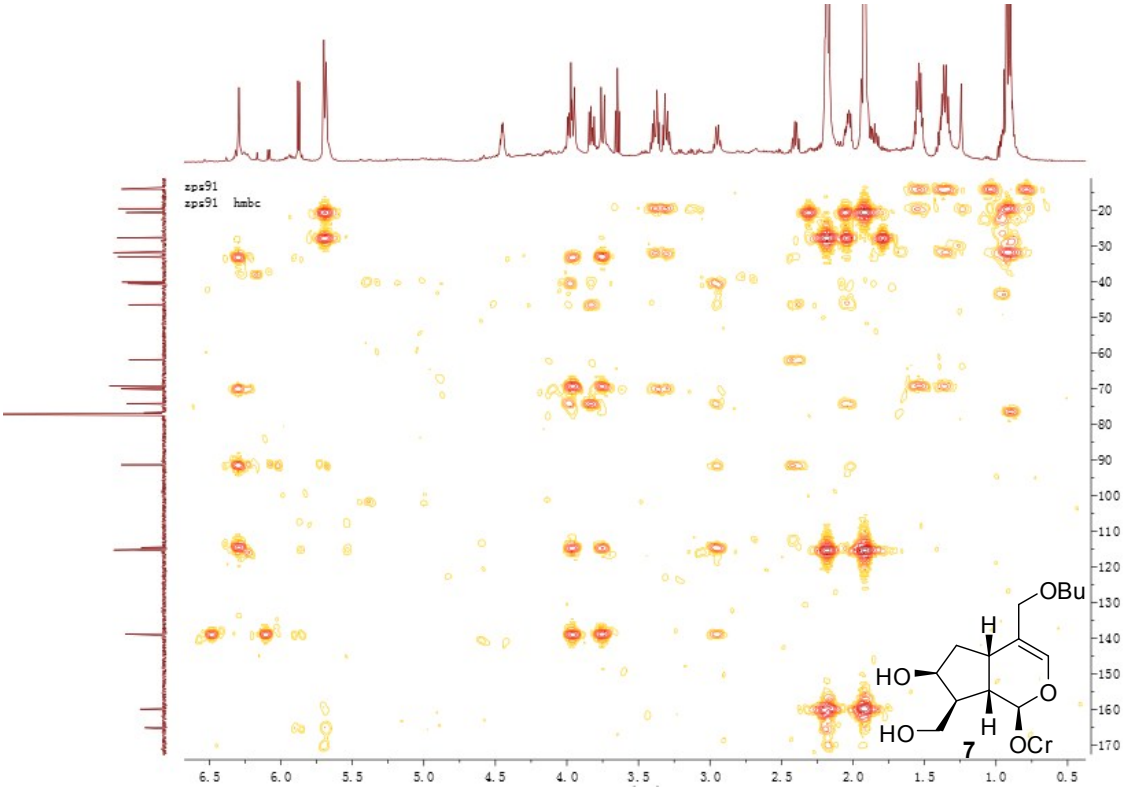


Figure 47. ^{1}H-^{1}H COSY spectrum of Patriscabioin G (**7**) in $CDCl_3$.

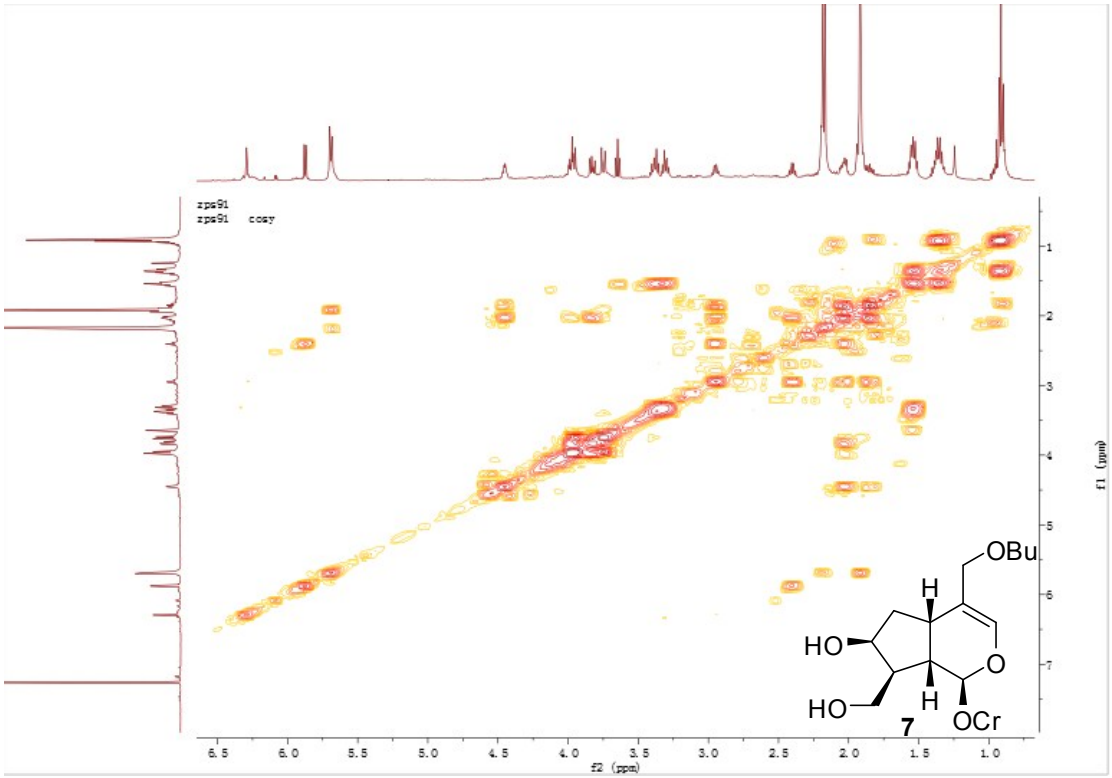


Figure 48. ROESY spectrum of Patriscabioin G (**7**) in $CDCl_3$.

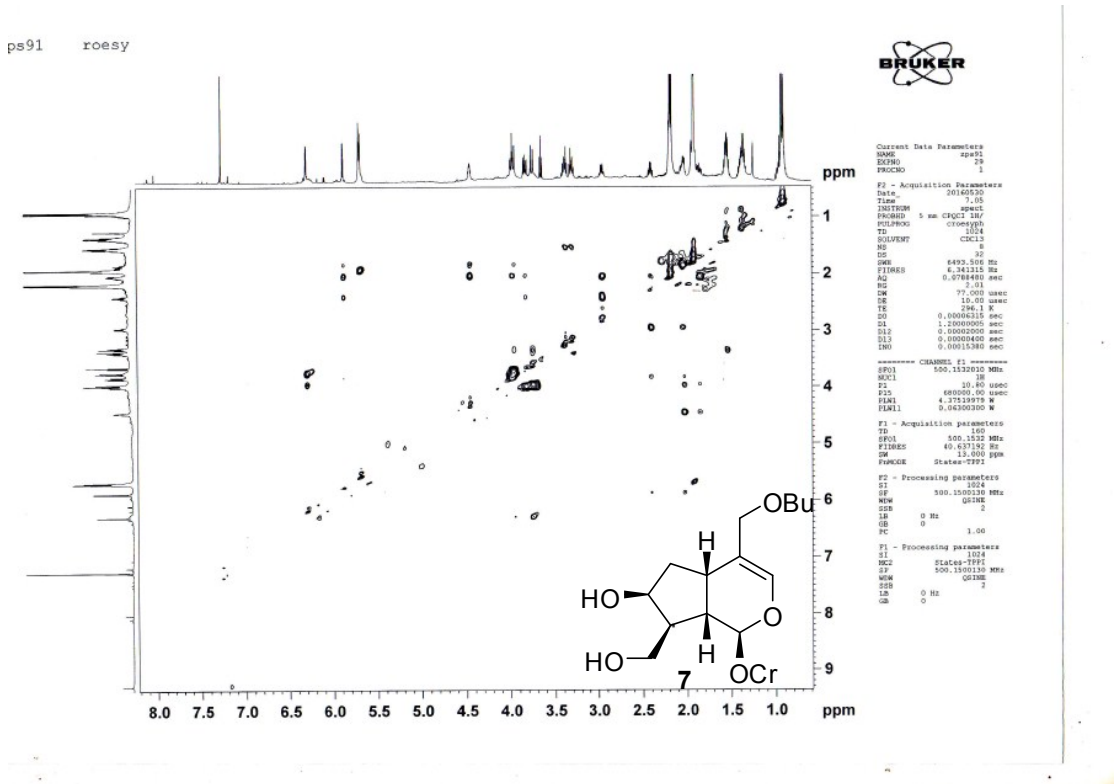


Figure 49. HREIMS spectrum of Patriscabioin G (**7**).

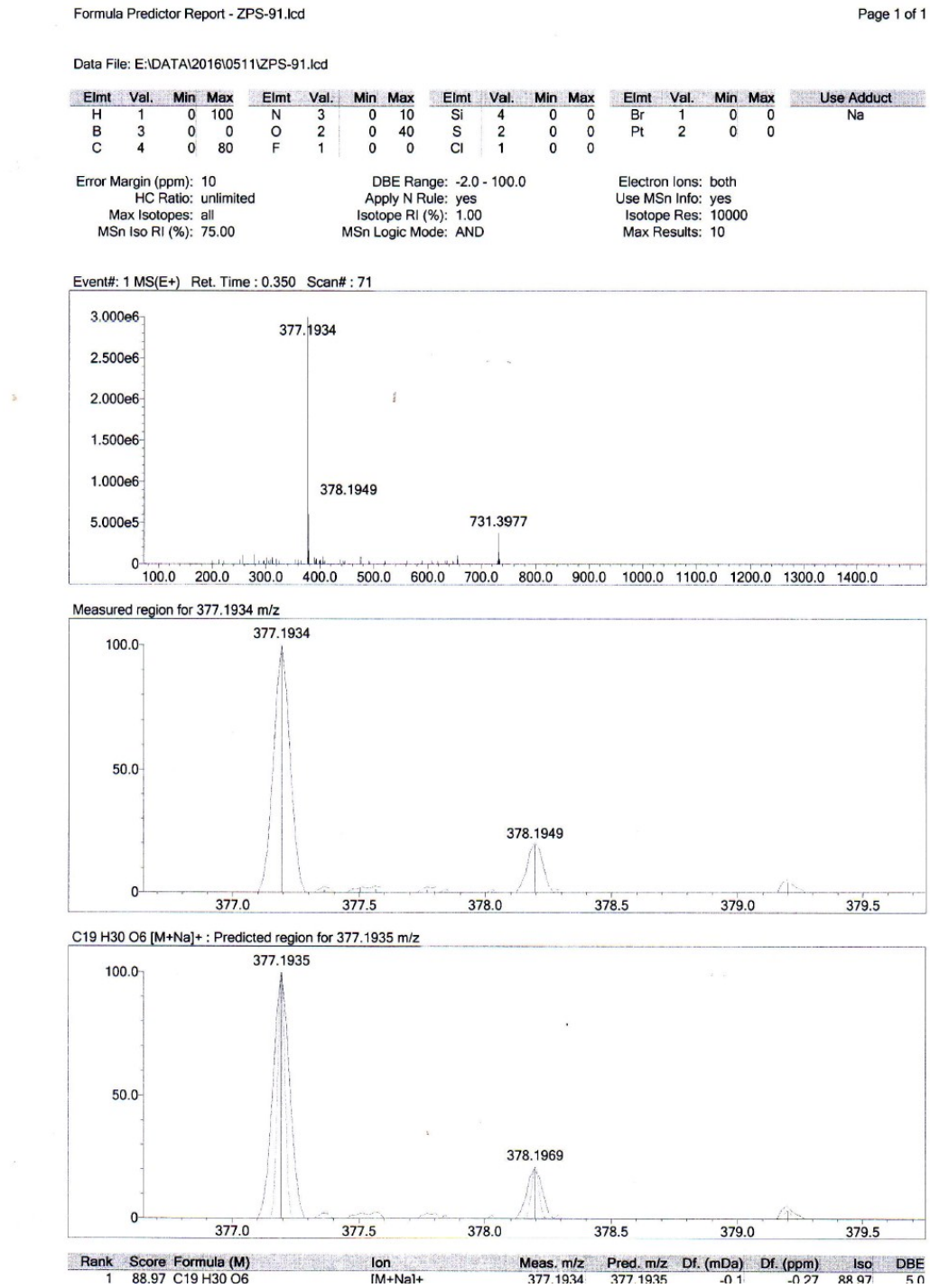


Figure 50. ^{1}H NMR spectrum of Patriscabioin H (**8**) in $CDCl_3$.

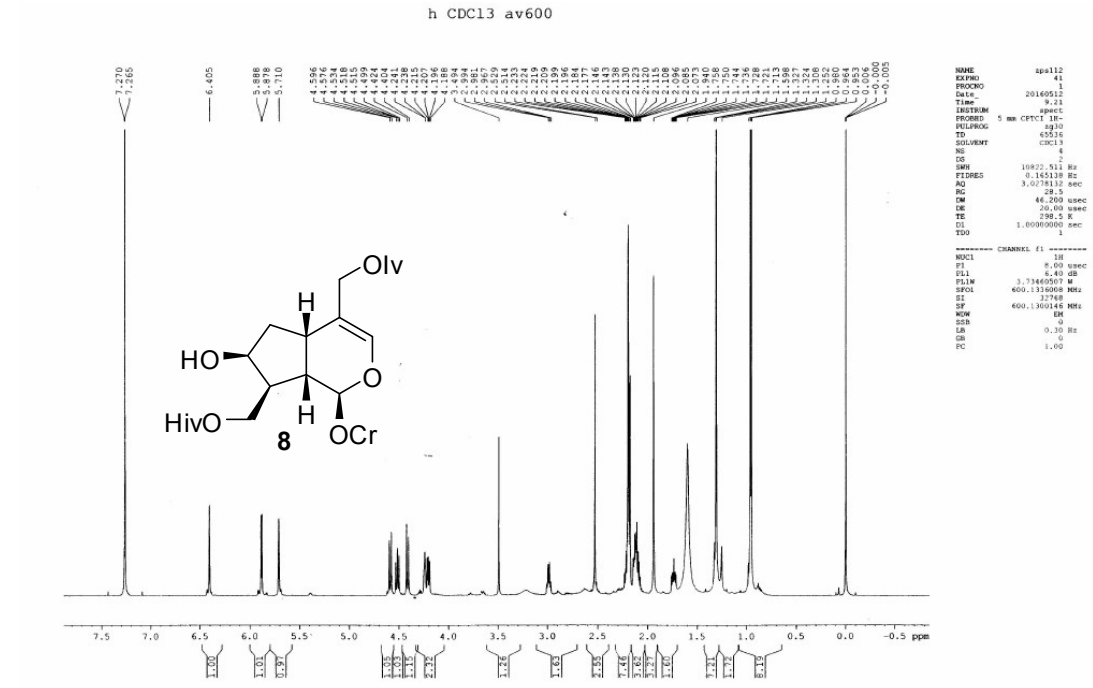


Figure 51. ^{13}C NMR spectrum of Patriscabioin H (**8**) in $CDCl_3$.

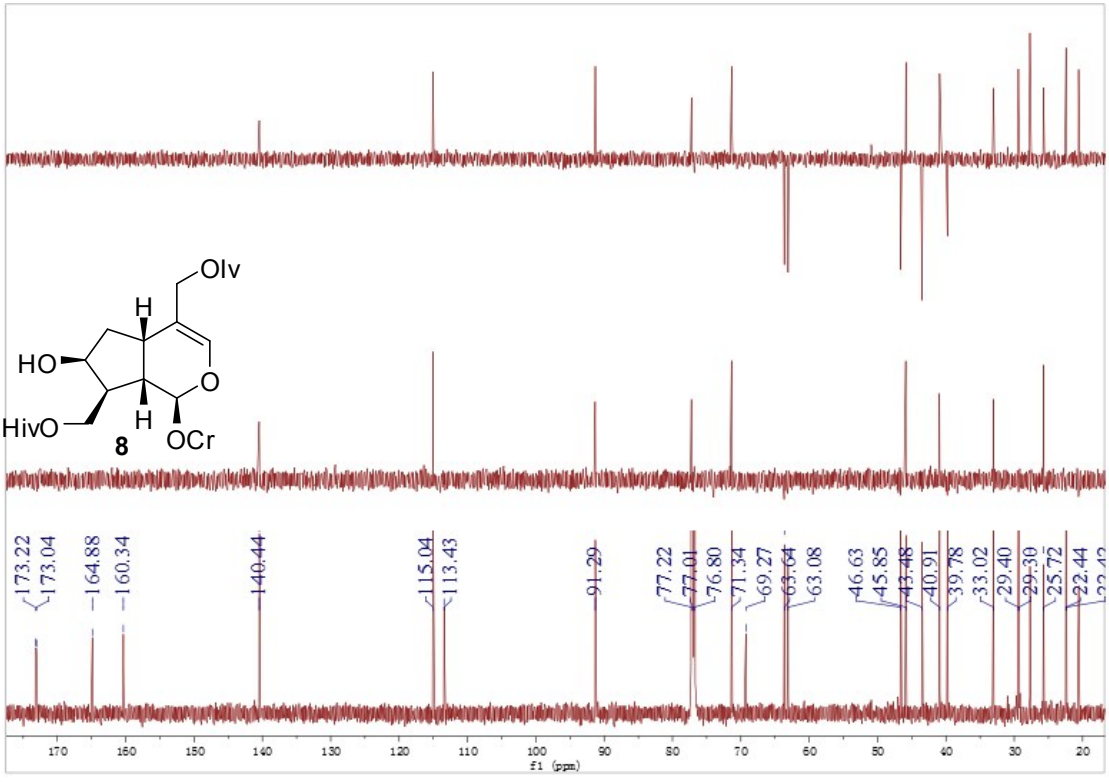


Figure 52. HSQC spectrum of Patriscabioin H (**8**) in $CDCl_3$.

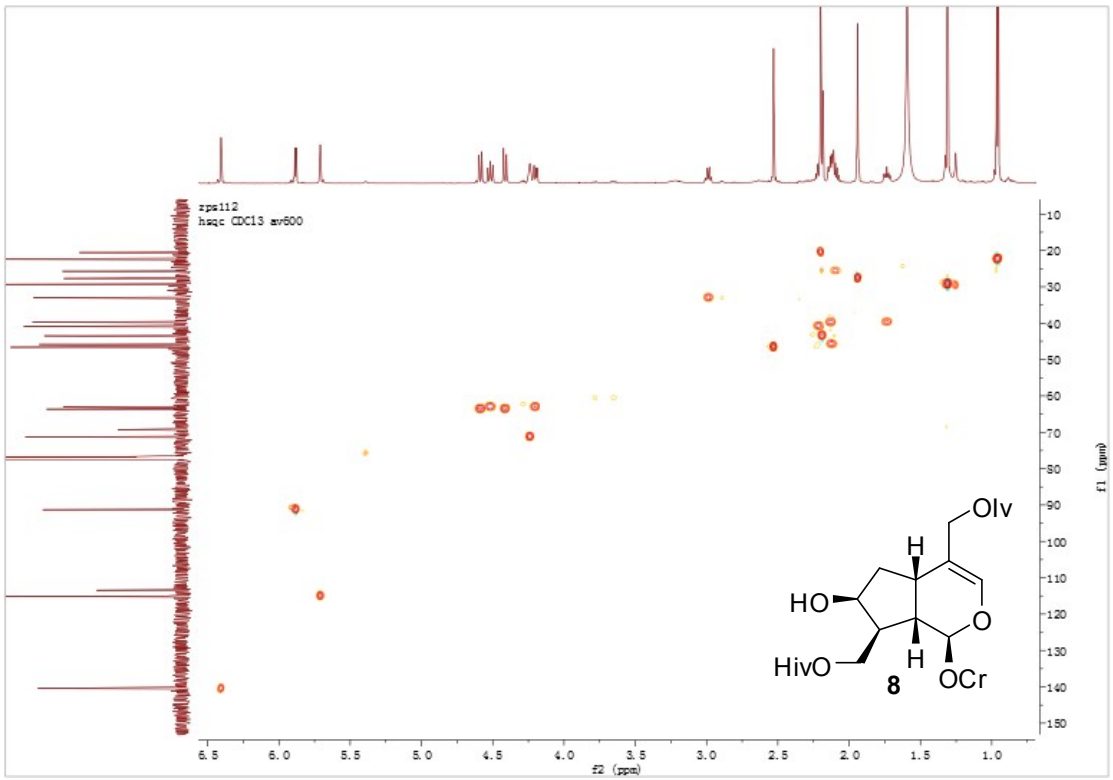


Figure 53. HMBC spectrum of Patriscabioin H (**8**) in $CDCl_3$.

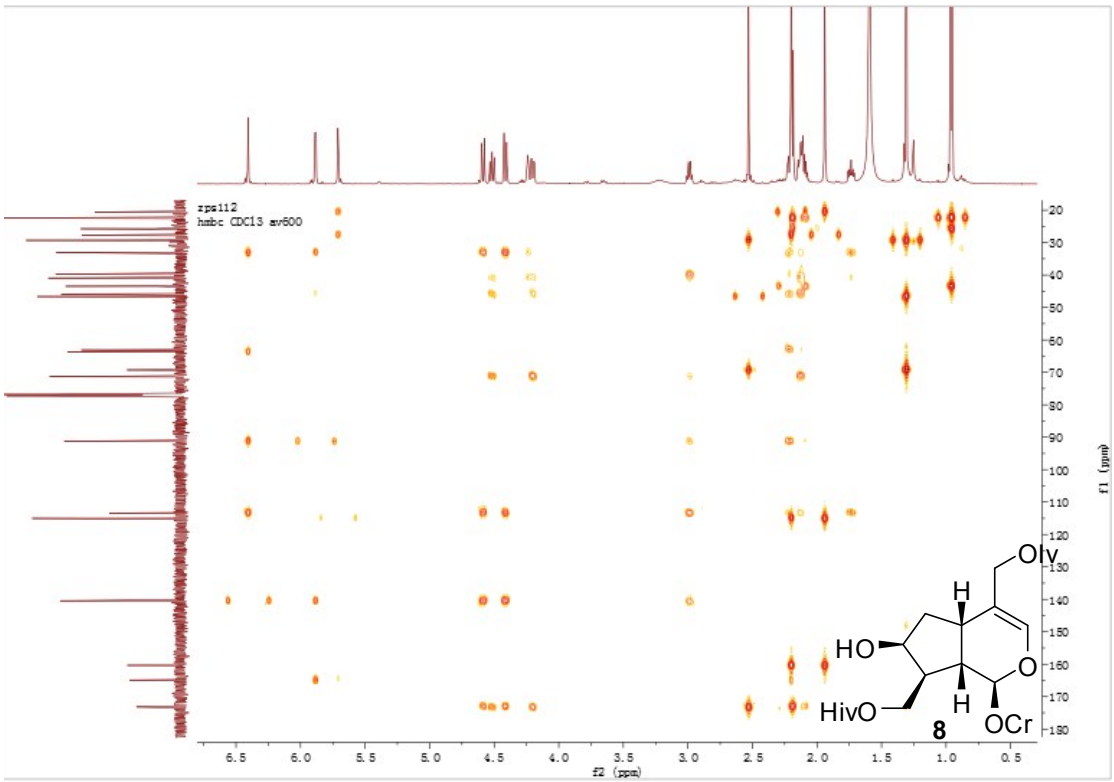


Figure 54. ^{1}H-^{1}H COSY spectrum of Patriscabioin H (**8**) in $CDCl_3$.

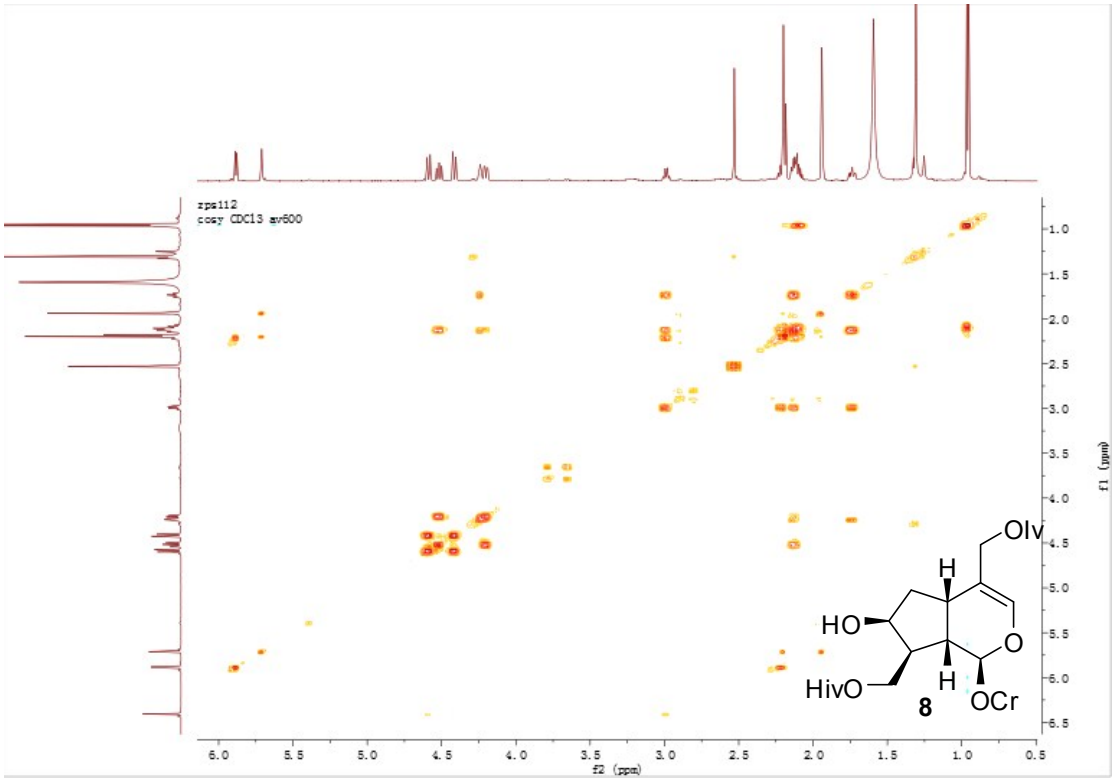


Figure 55. ROESY spectrum of Patriscabioin H (**8**) in $CDCl_3$.

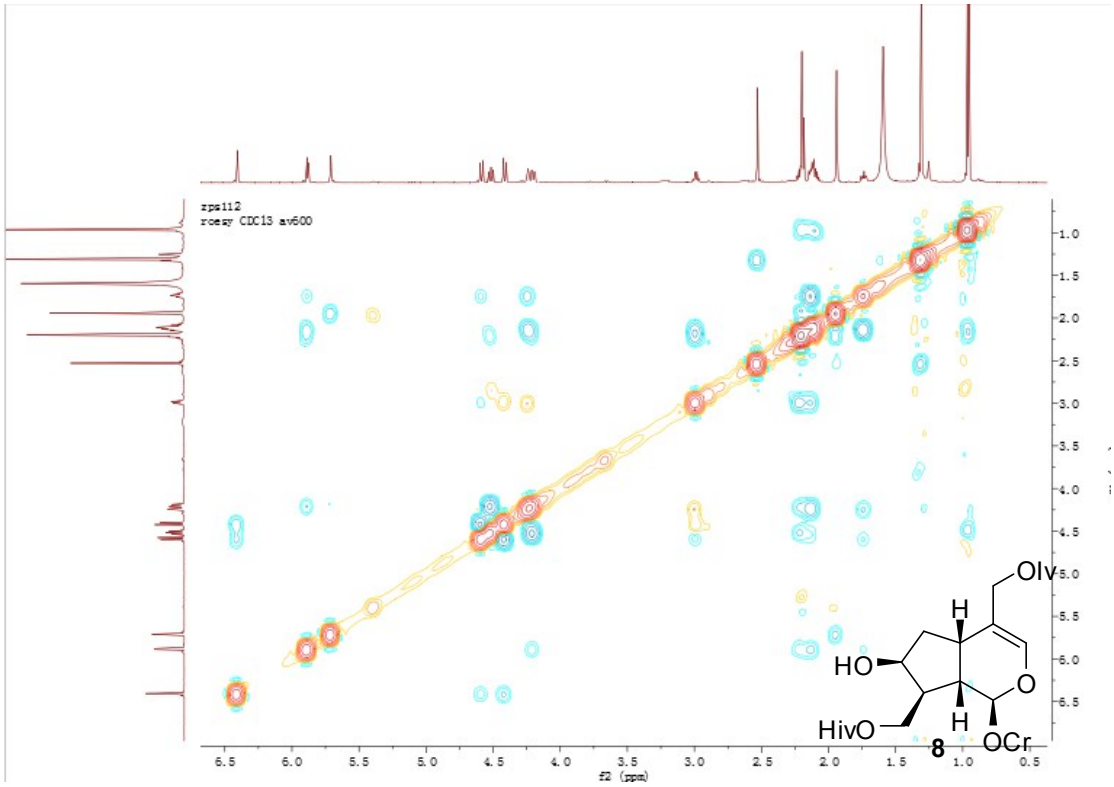


Figure 56. HREIMS spectrum of Patriscabioin H (**8**).

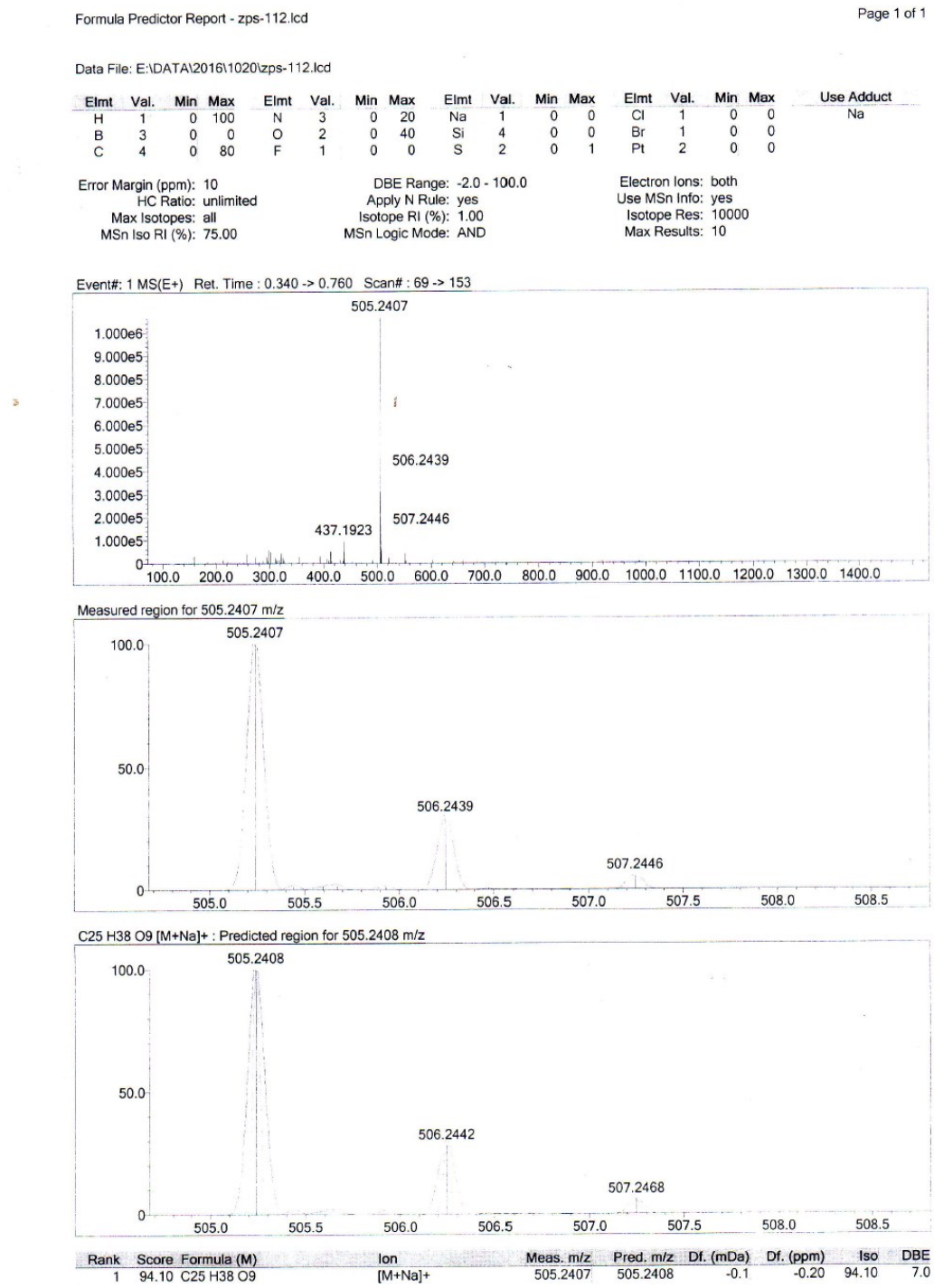


Figure 57.^{1}H NMR spectrum of Patriscabioin I (**9**) in $CDCl_3$.

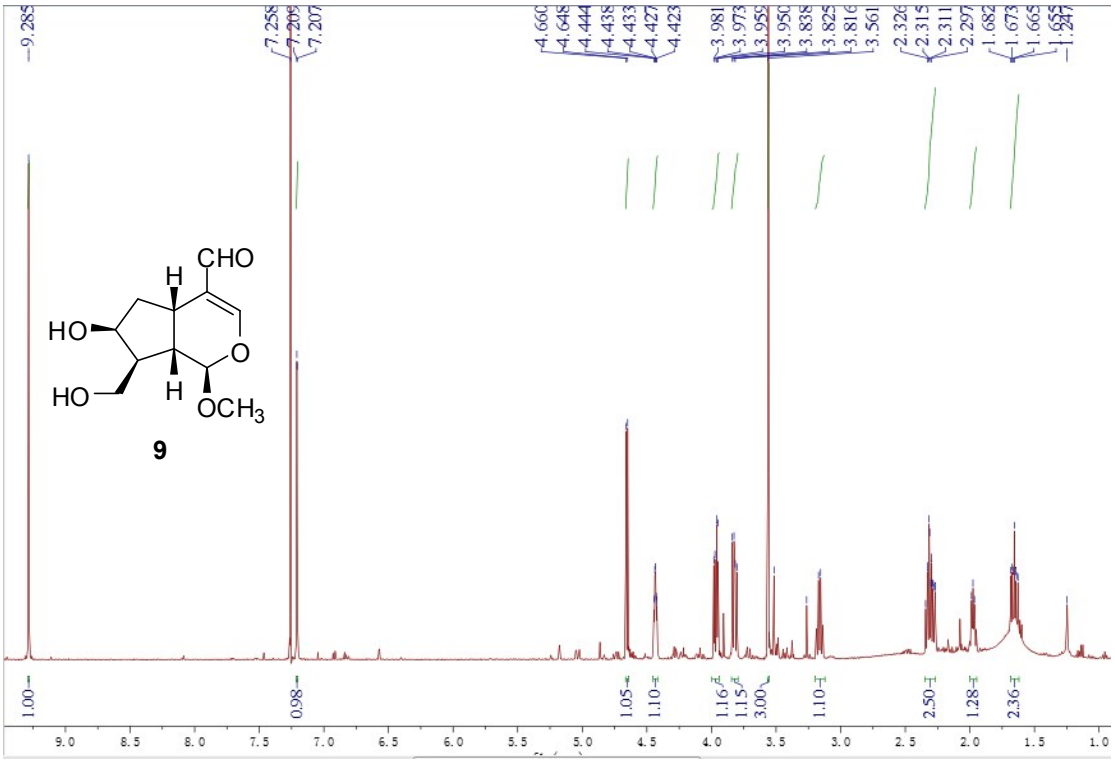


Figure 58.^{13}C NMR spectrum of Patriscabioin I (**9**) in $CDCl_3$.

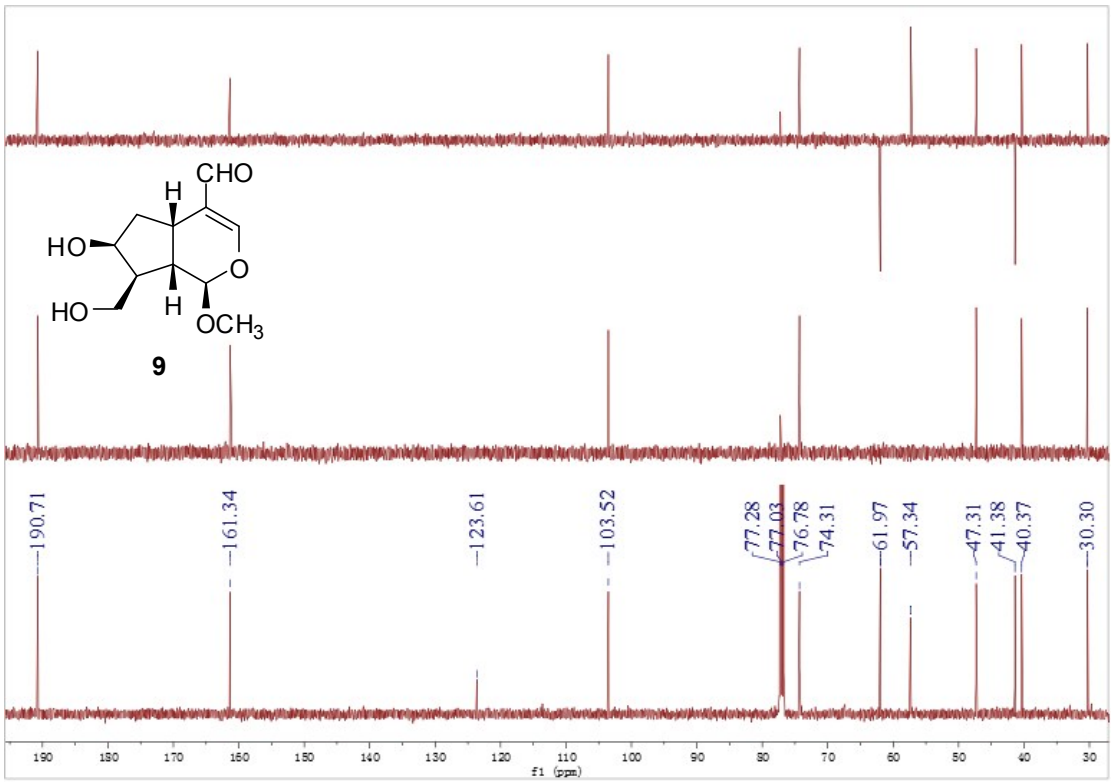


Figure 59. HSQC spectrum of Patriscabioin I (**9**) in $CDCl_3$.

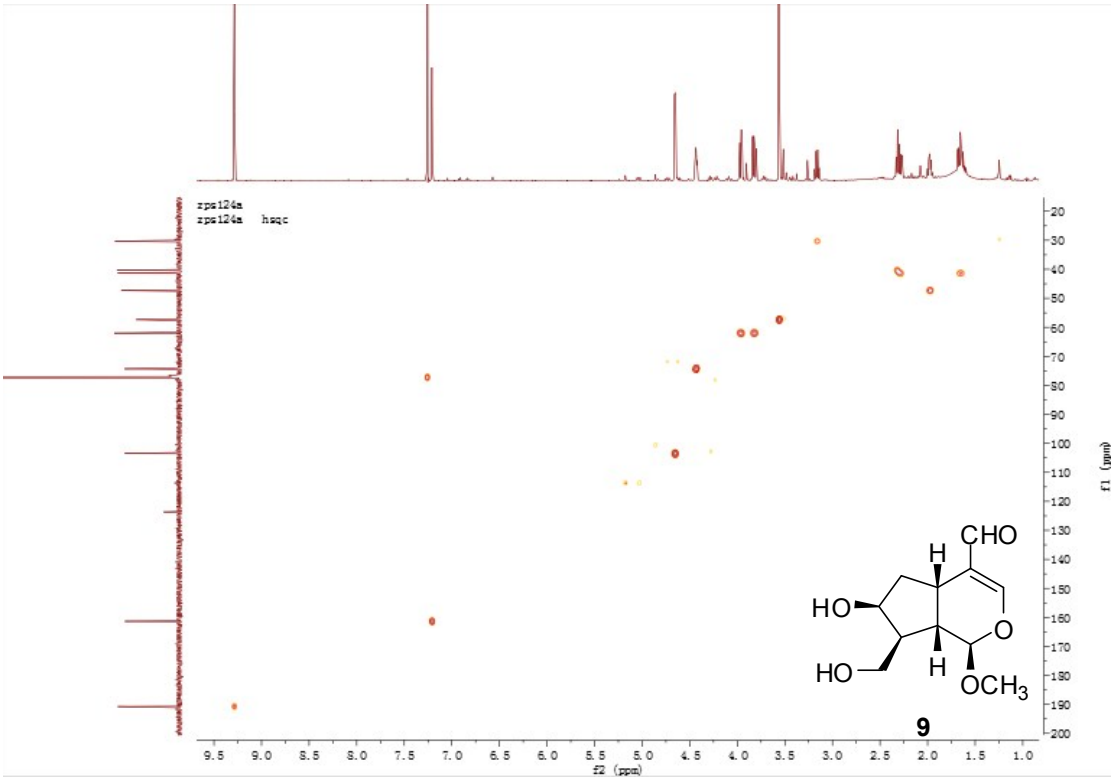


Figure 60. HMBC spectrum of Patriscabioin I (**9**) in $CDCl_3$.

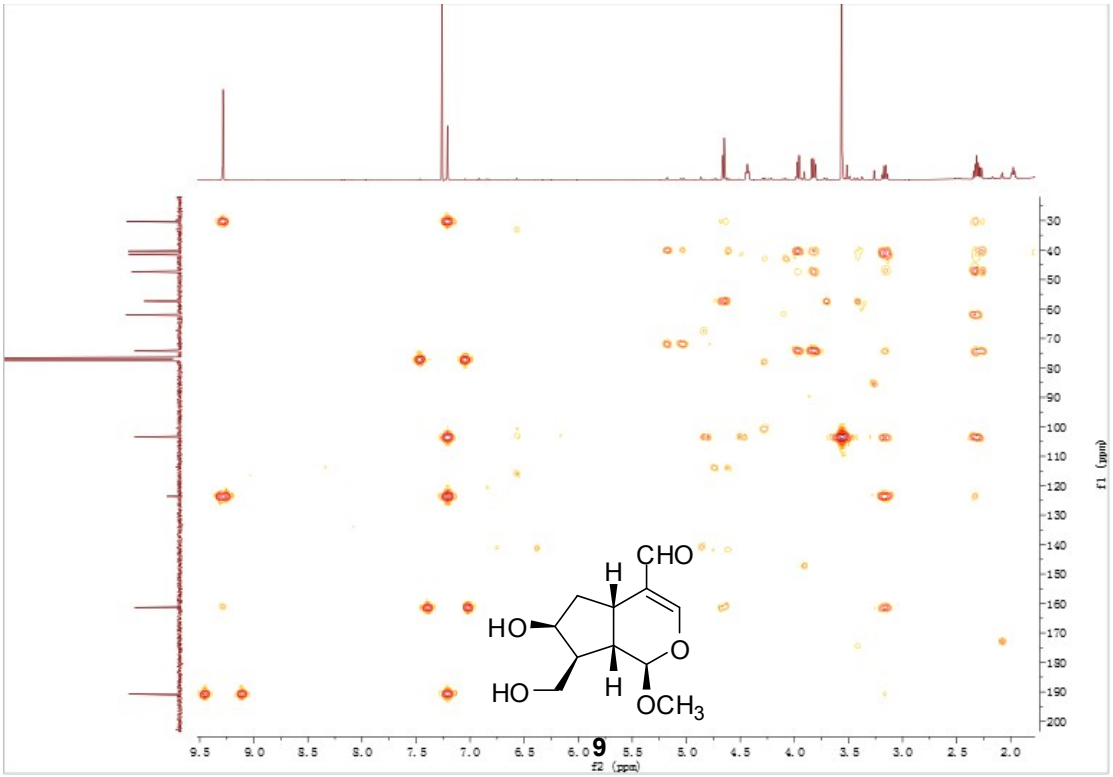


Figure 61. ^{1}H-^{1}H COSY spectrum of Patriscabioin I (**9**) in $CDCl_3$.

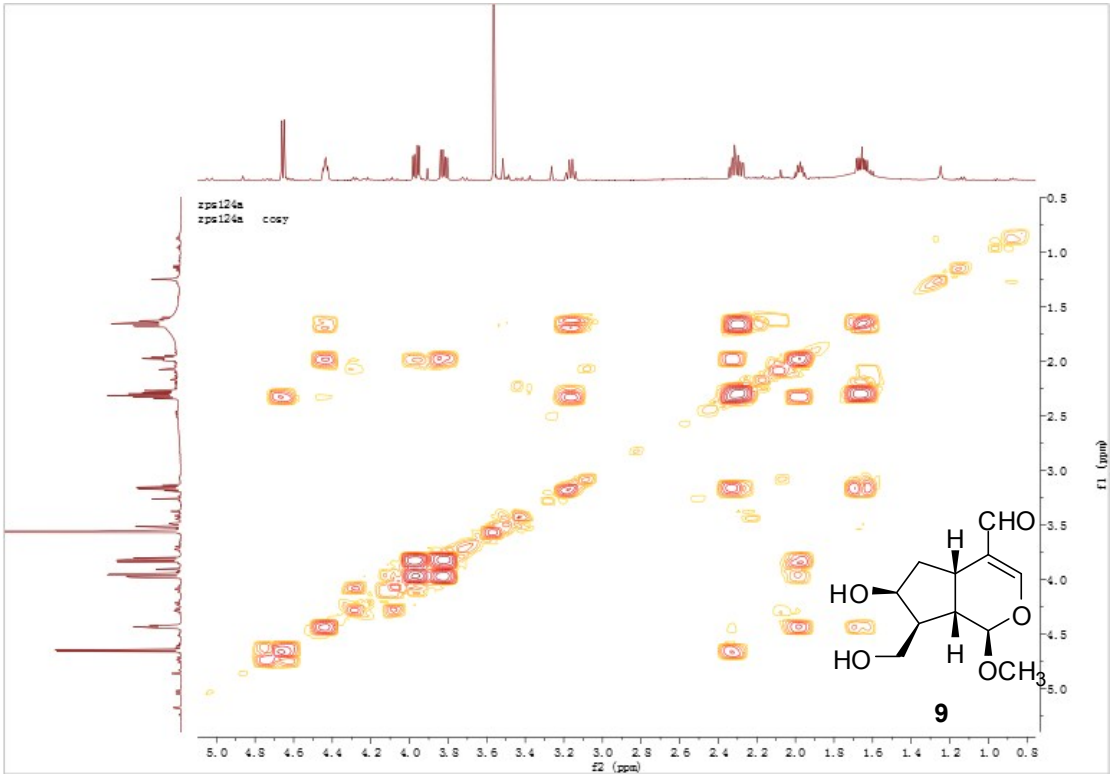


Figure 62. ROESY spectrum of Patriscabioin I (**9**) in $CDCl_3$.

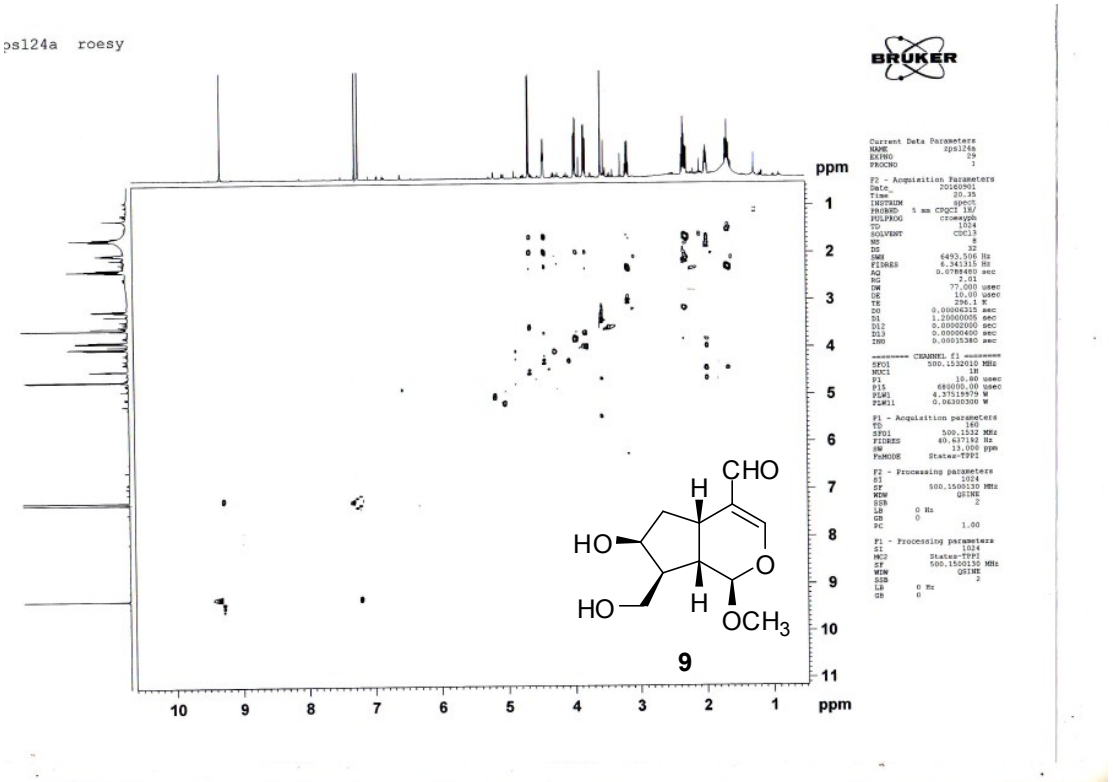


Figure 63. HREIMS spectrum of Patriscabioin I (**9**).

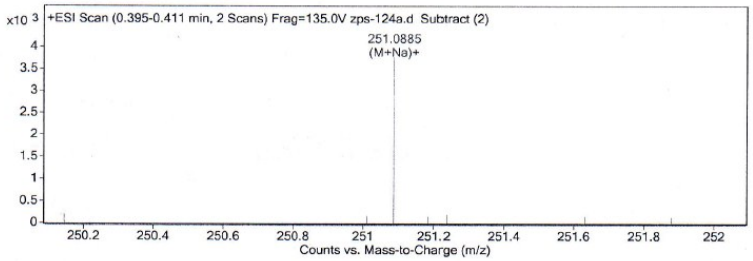
Qualitative Analysis Report

Data Filename	zps-124a.d	**Sample Name**	zps-124a
Sample Type	Sample	**Position**	P1-A4
Instrument Name	Instrument 1	**User Name**	
Acq Method	SIBU.m	**Acquired Time**	8/10/2016 4:00:09 PM
IRM Calibration Status	Success	**DA Method**	ESI+.m
Comment			

Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
251.0885		3771.13	C11 H16 O5	(M+Na)+
264.2331	1	1664.45		
267.0644		4069.74		
274.2738	1	1906.64		
437.1925	1	1903.3		
447.1409	1	1564.14		
453.1656	1	3295.84		
479.1877	1	1607.98		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C11 H16 O5	228.0998	251.0890	251.0885	0.5	2.1	4.0000

--- End Of Report ---

Figure 64. ^{1}H NMR spectrum of Patriscabioin J (**10**) in $CDCl_3$.

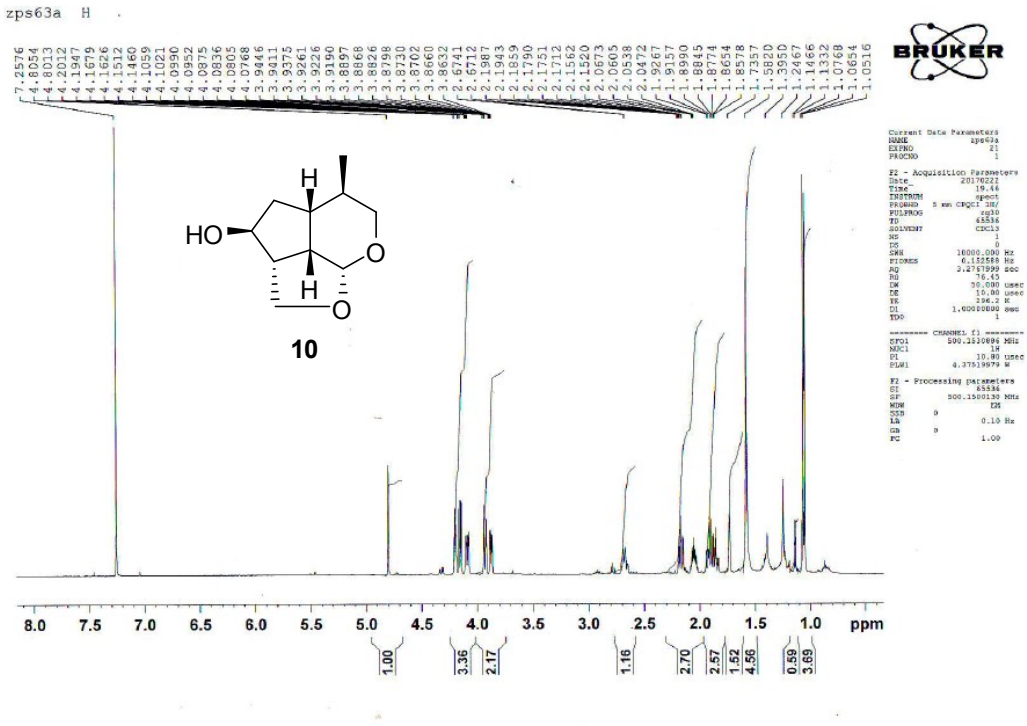


Figure 65. ^{13}C NMR spectrum of Patriscabioin J (**10**) in $CDCl_3$.

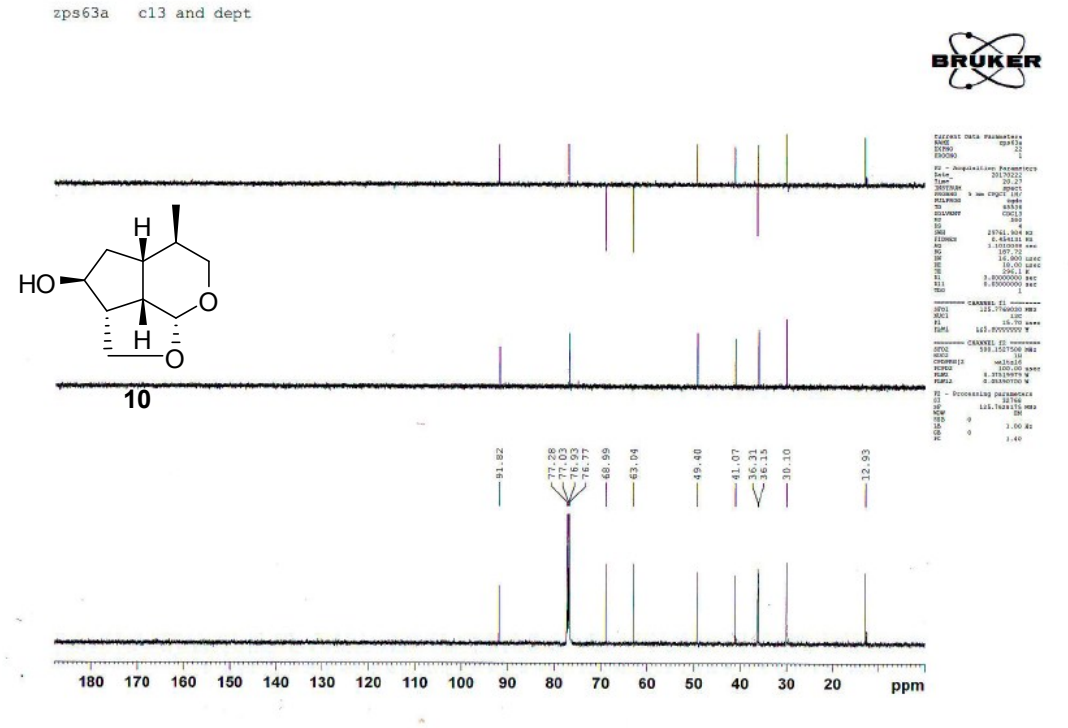


Figure 66. HSQC spectrum of Patriscabioin J (**10**) in $CDCl_3$.

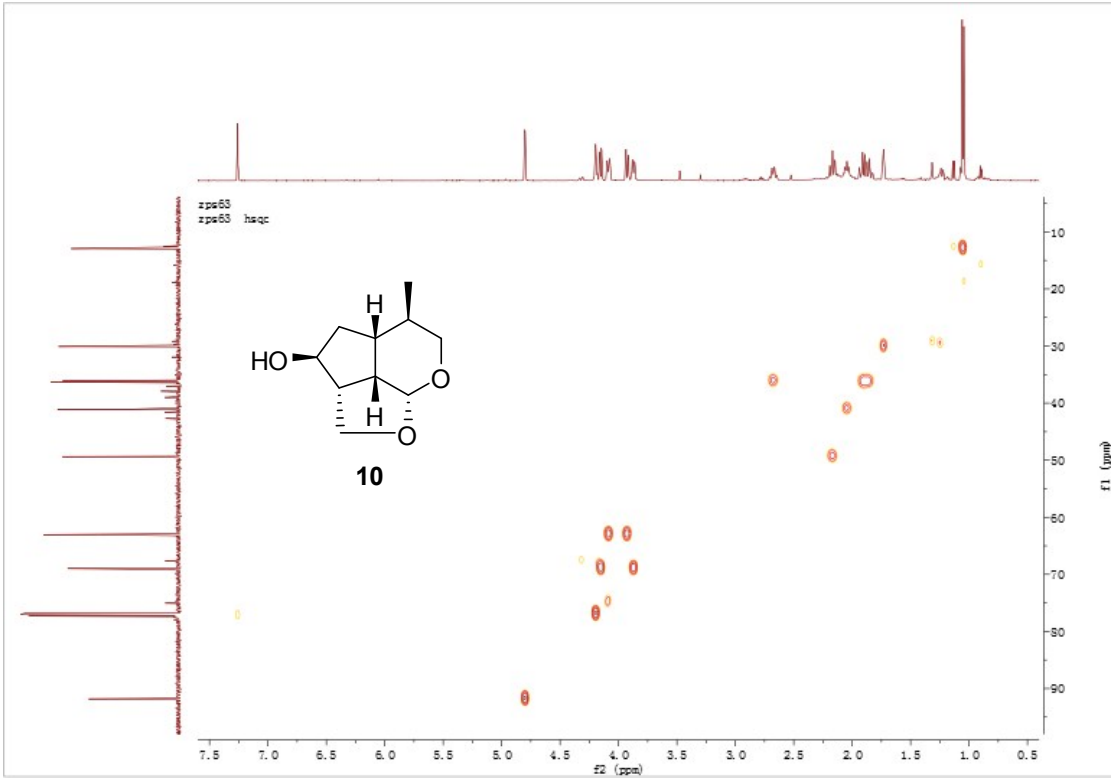


Figure 67. HMBC spectrum of Patriscabioin J (**10**) in $CDCl_3$.

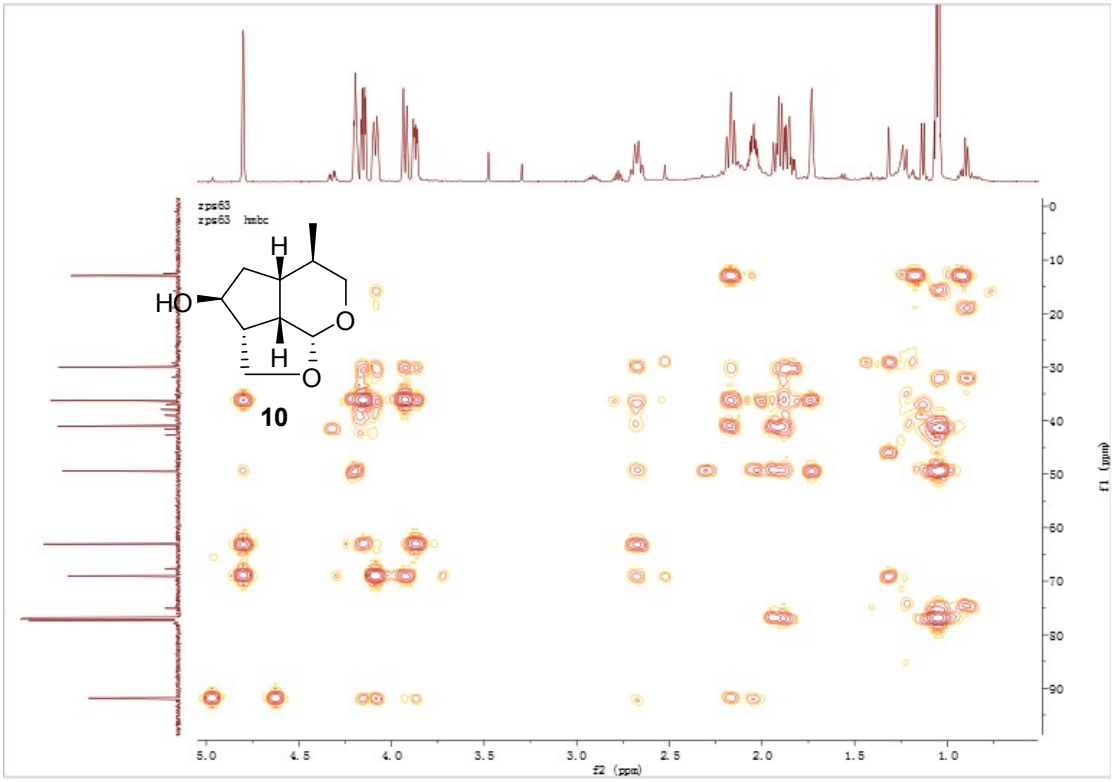


Figure 68. ^{1}H-^{1}H COSY spectrum of Patriscabioin J (**10**) in $CDCl_3$.

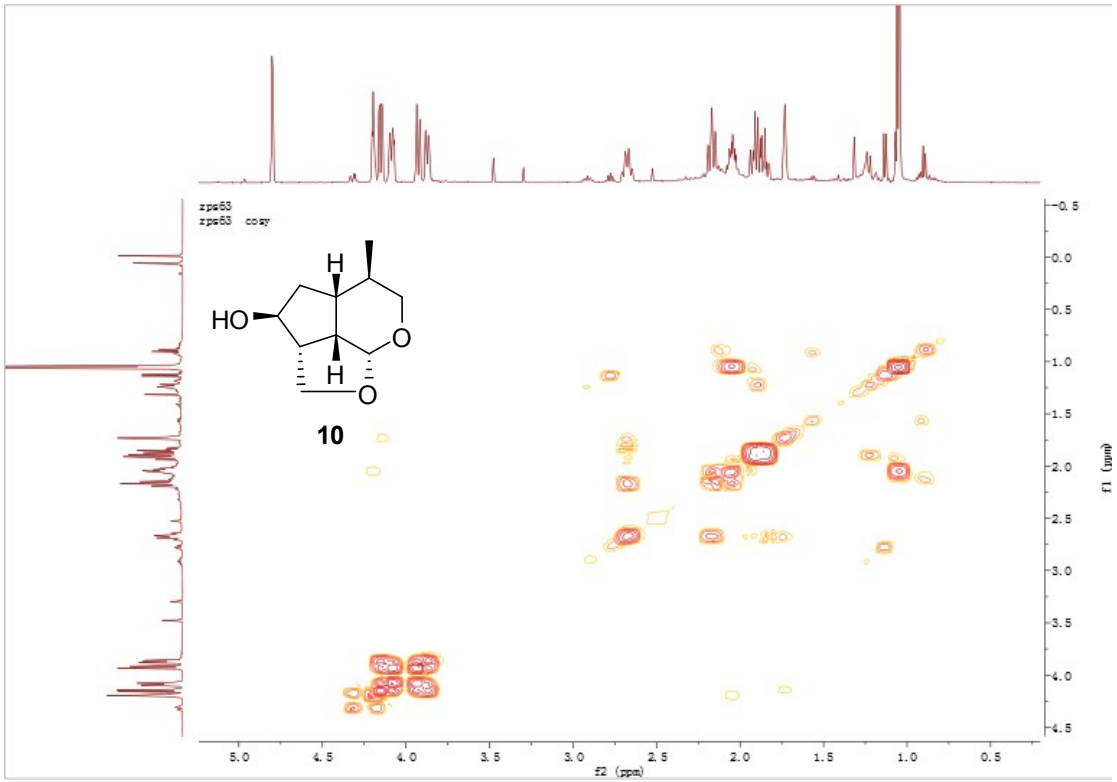


Figure 69. ROESY spectrum of Patriscabioin J (**10**) in $CDCl_3$.

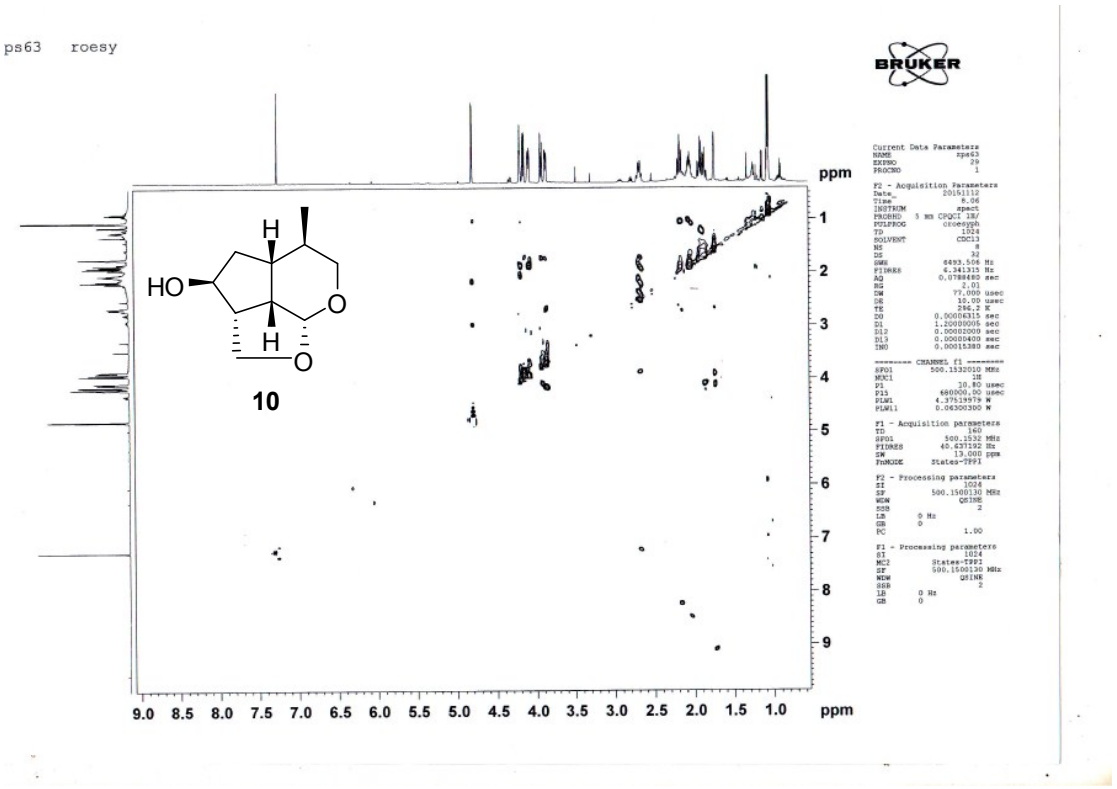


Figure 70. HREIMS spectrum of Patriscabioin J (**10**).

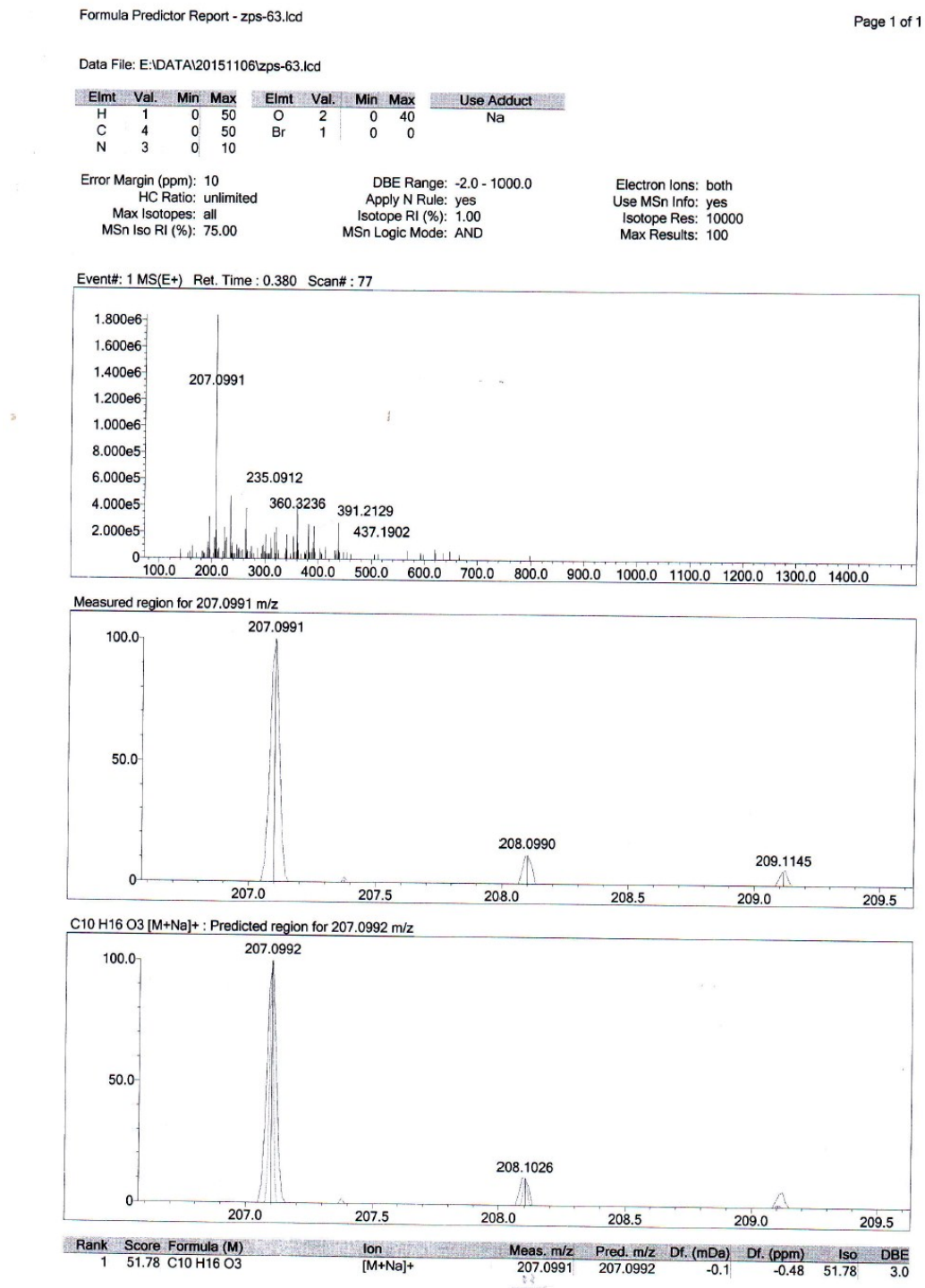


Figure 71.[1]H NMR spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

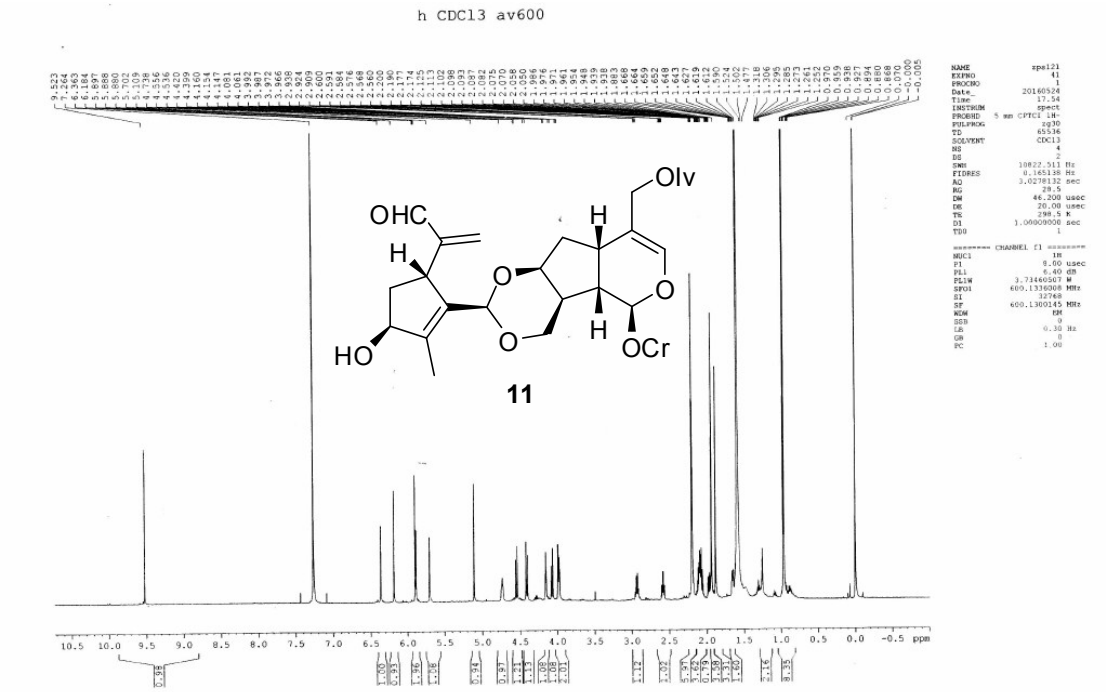


Figure 72.[13]C NMR spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

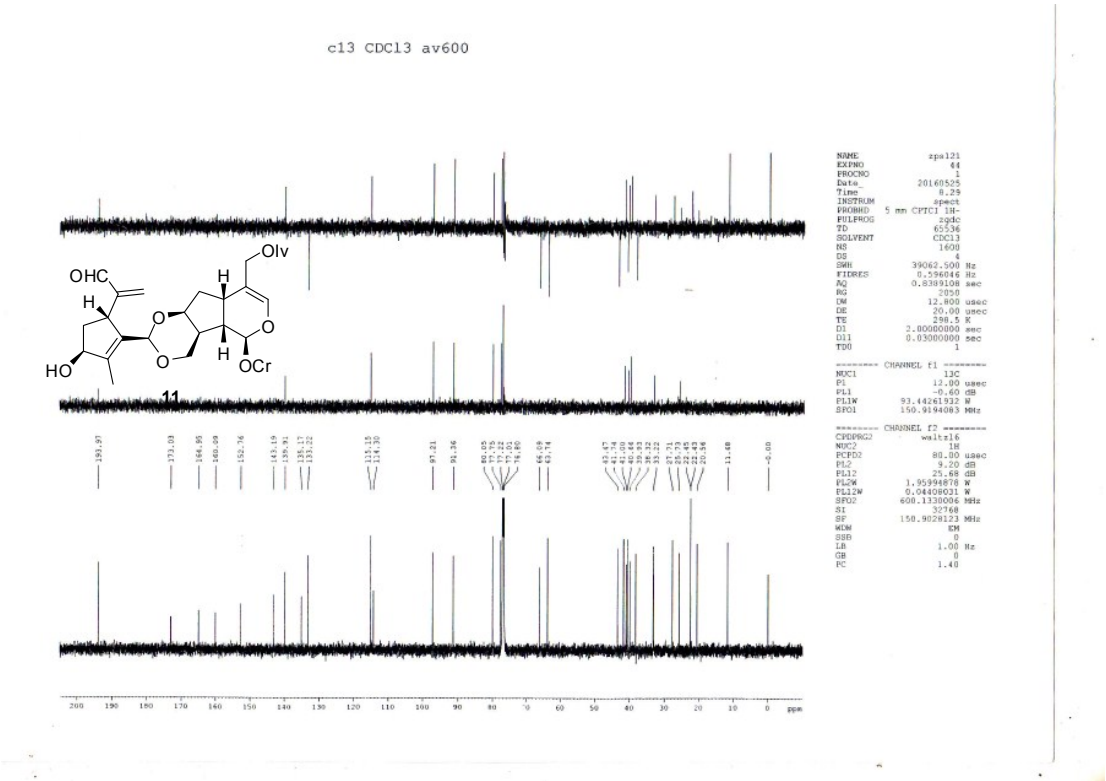


Figure 73. HSQC spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

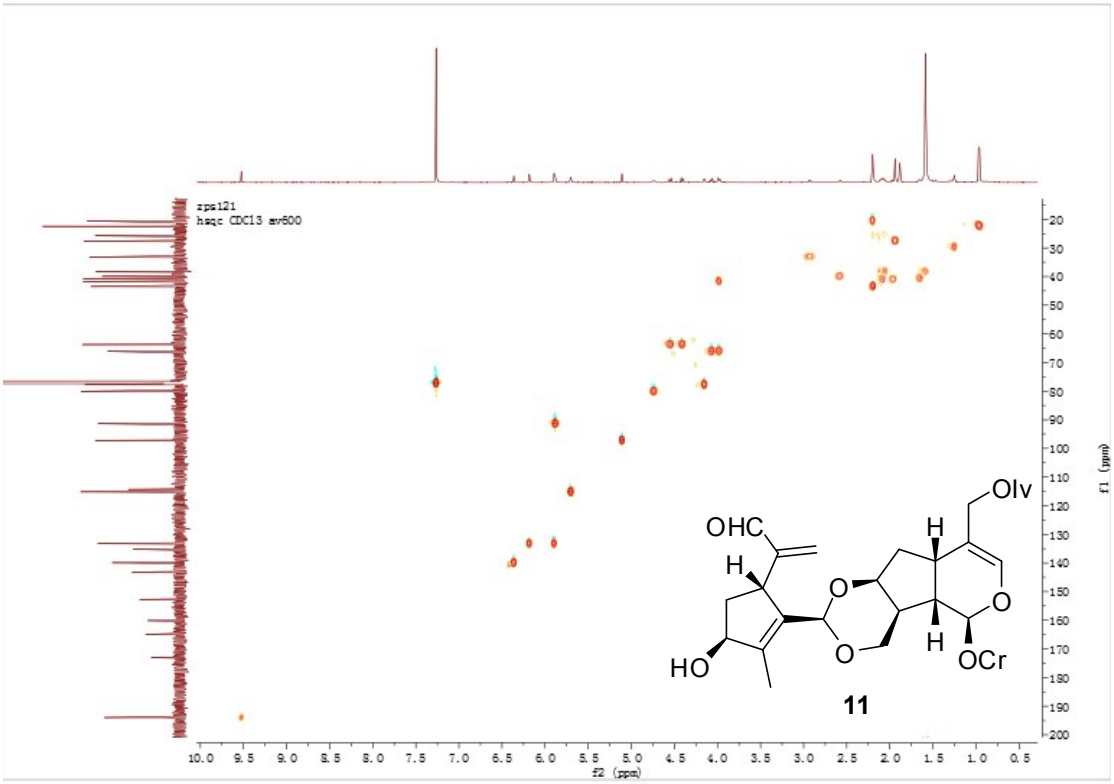


Figure 74. HMBC spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

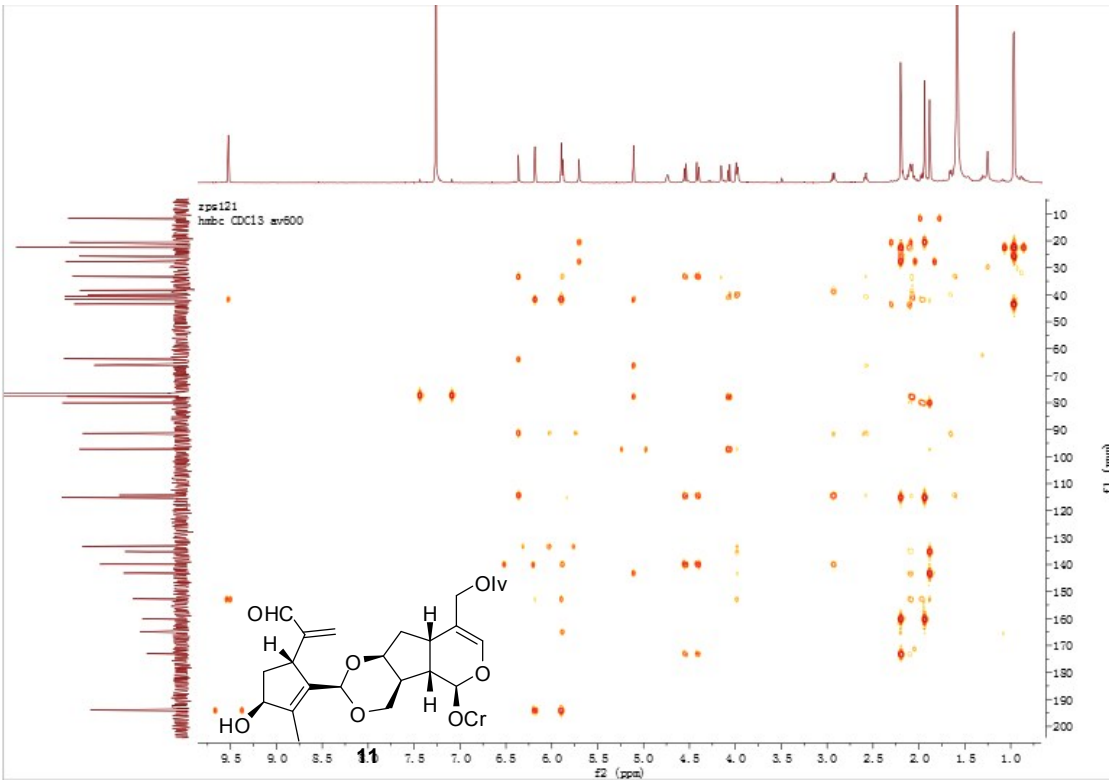


Figure 75. ^{1}H-^{1}H COSY spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

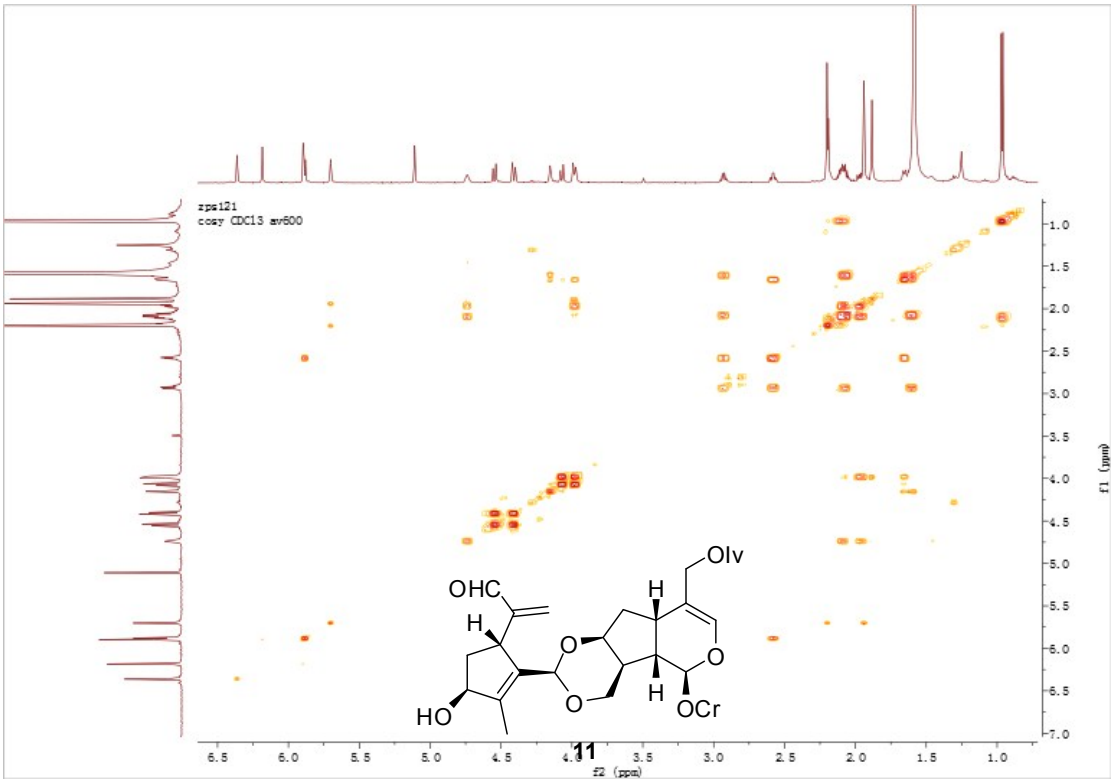


Figure 76. ROESY spectrum of Patriscabiobisin A (**11**) in $CDCl_3$.

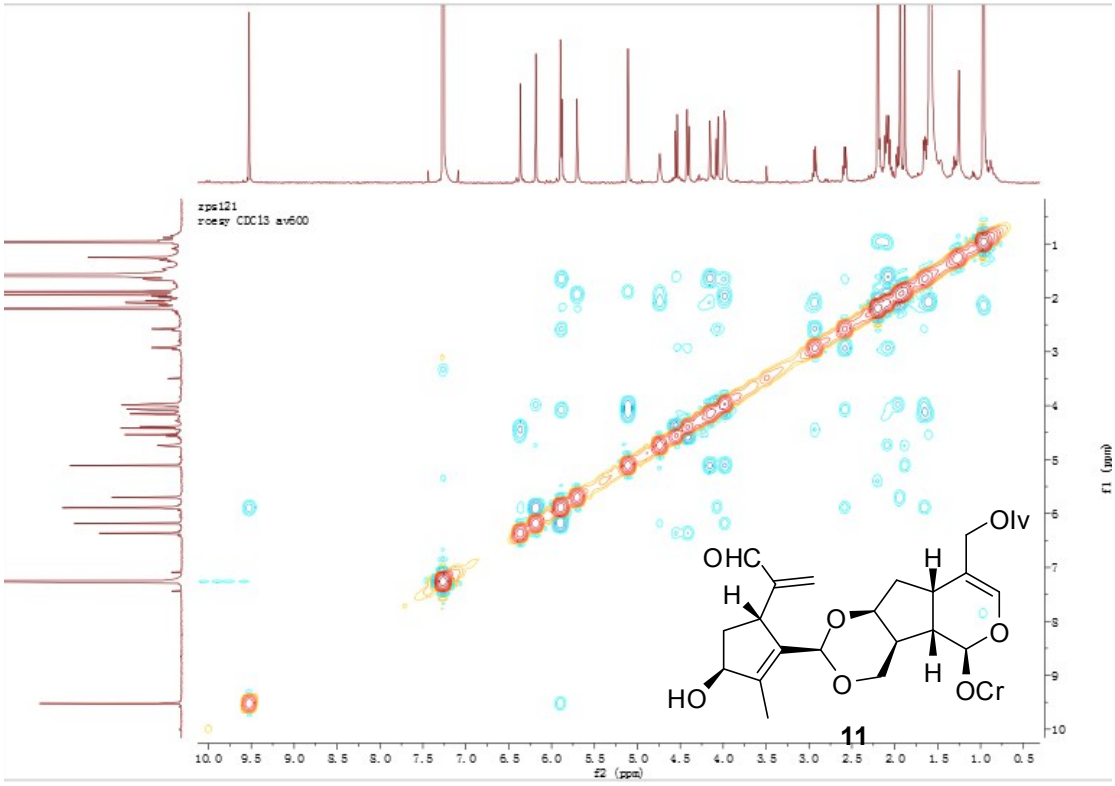


Figure 77. HREIMS spectrum of Patriscabiobisin A (**11**).

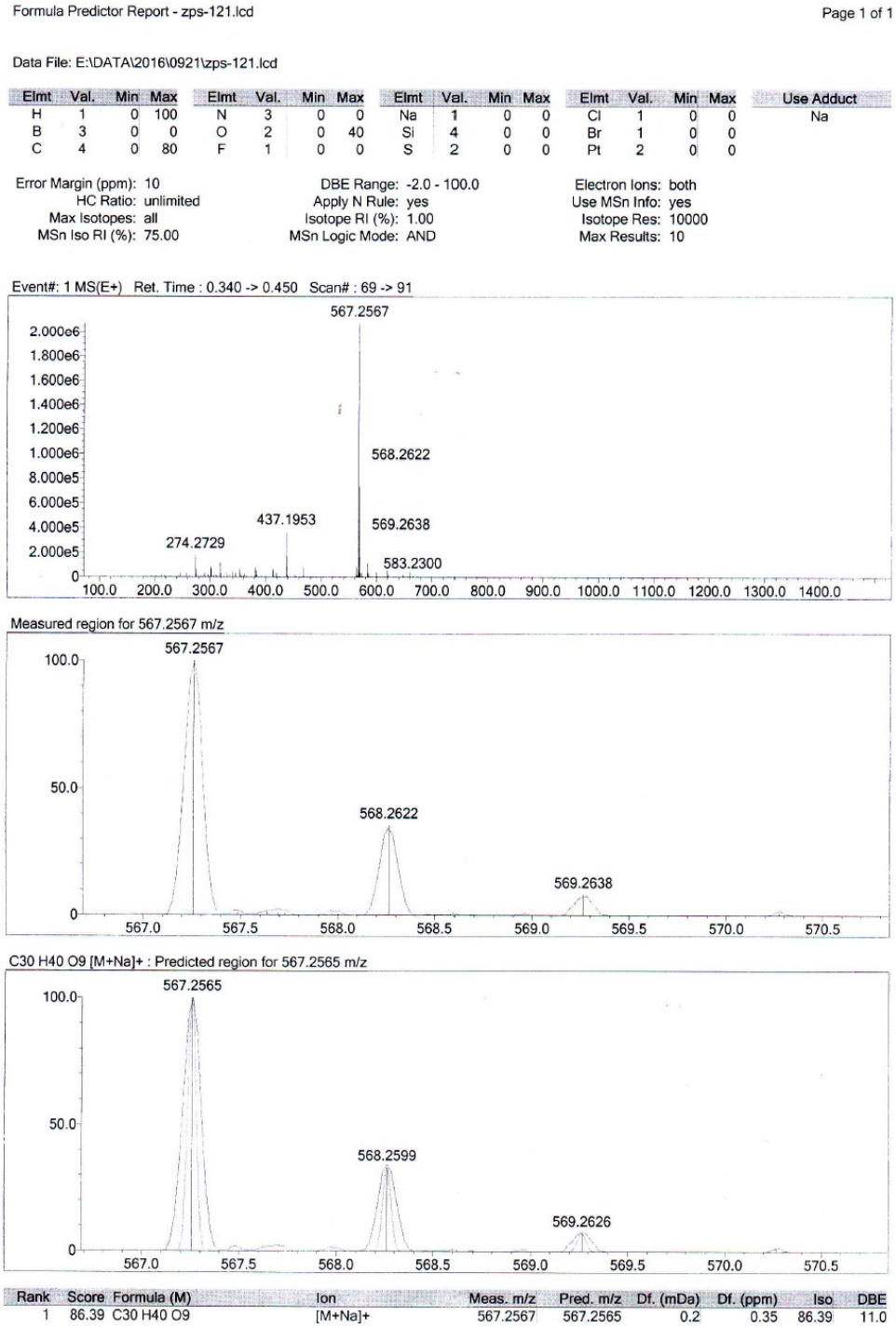


Figure 78. ECD spectrum of Patriscabiobisin A (**11**).

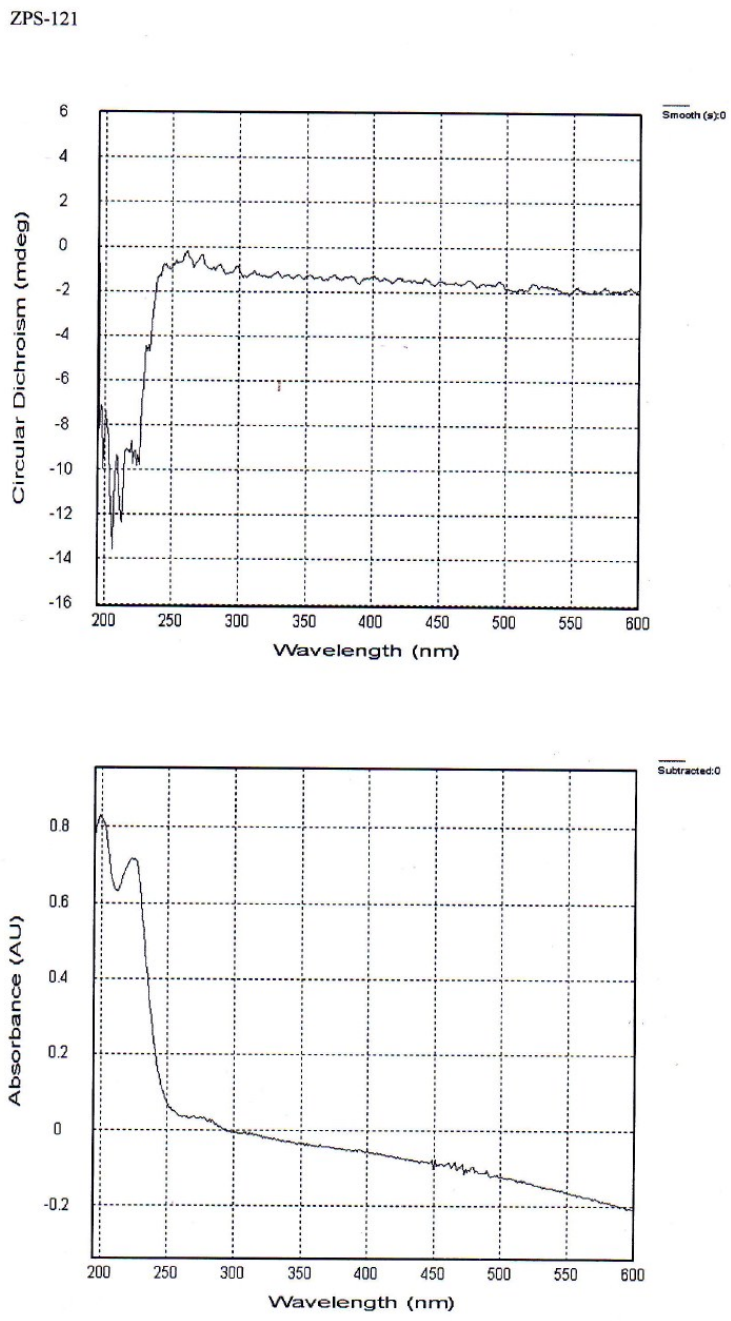


Figure 79.[1]H NMR spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

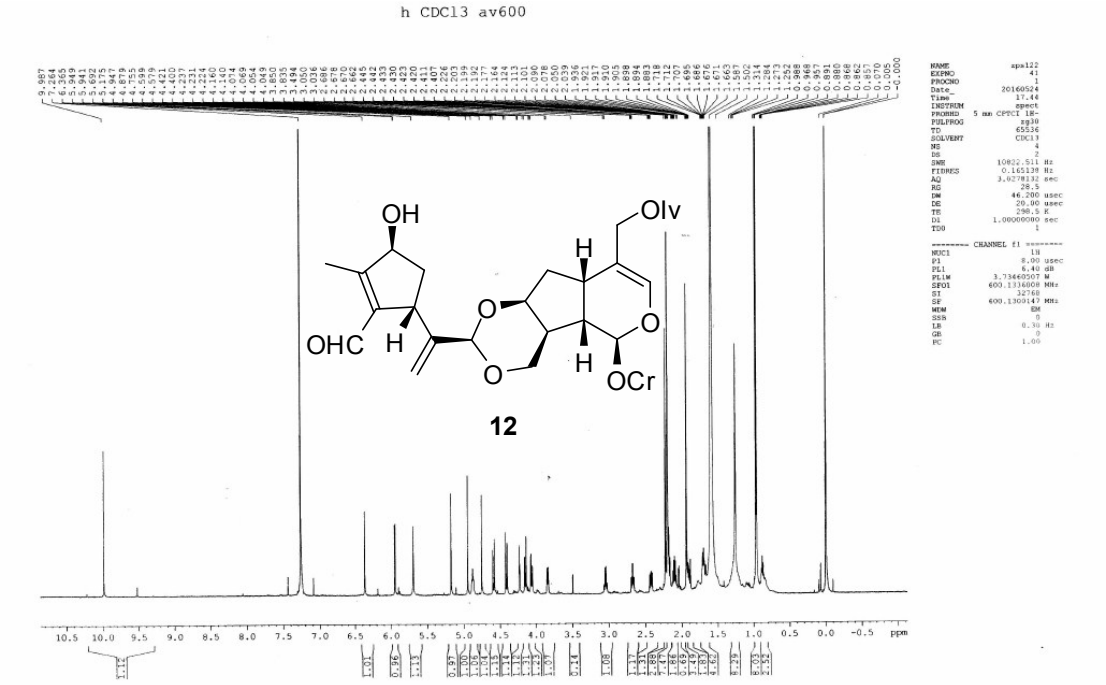


Figure 80.[13]C NMR spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

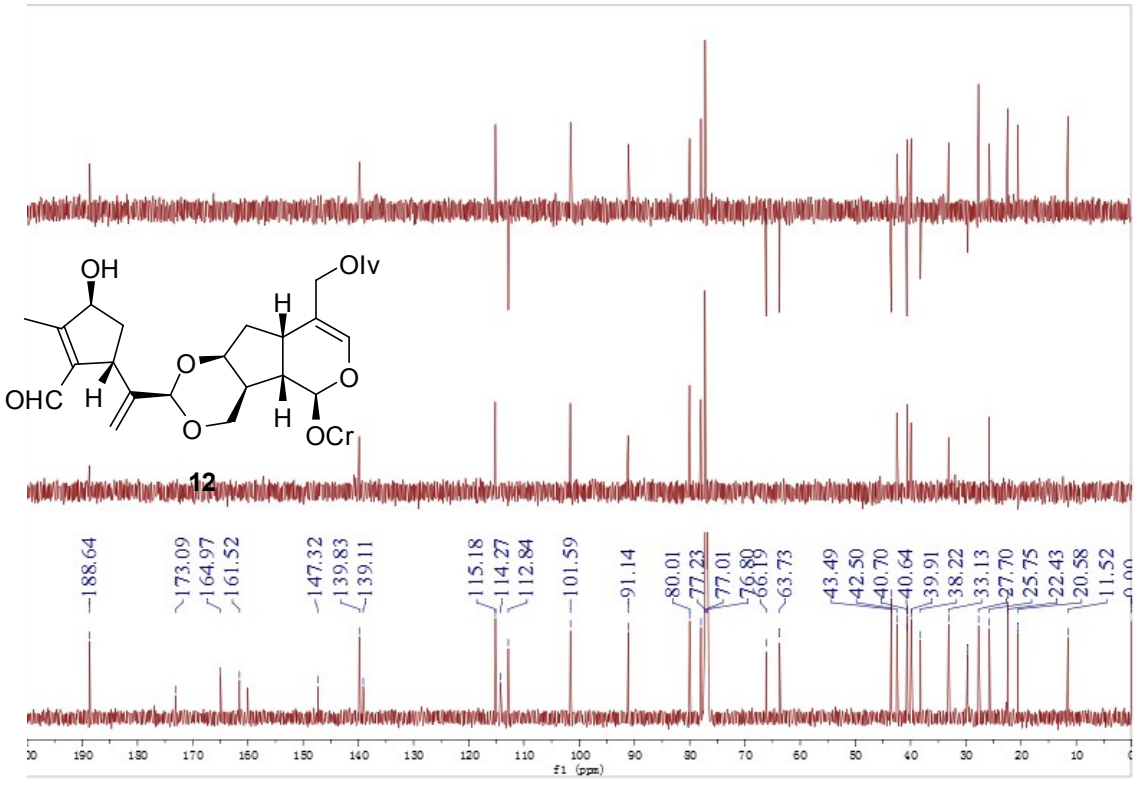


Figure 81. HSQC spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

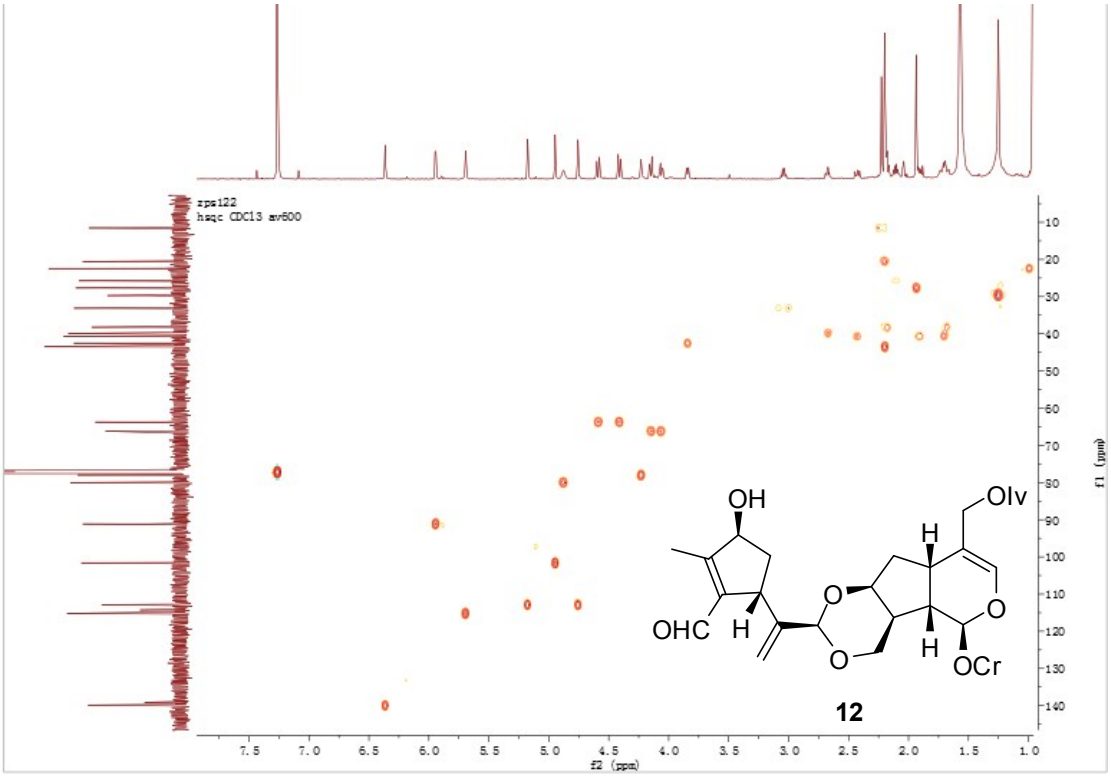


Figure 82. HMBC spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

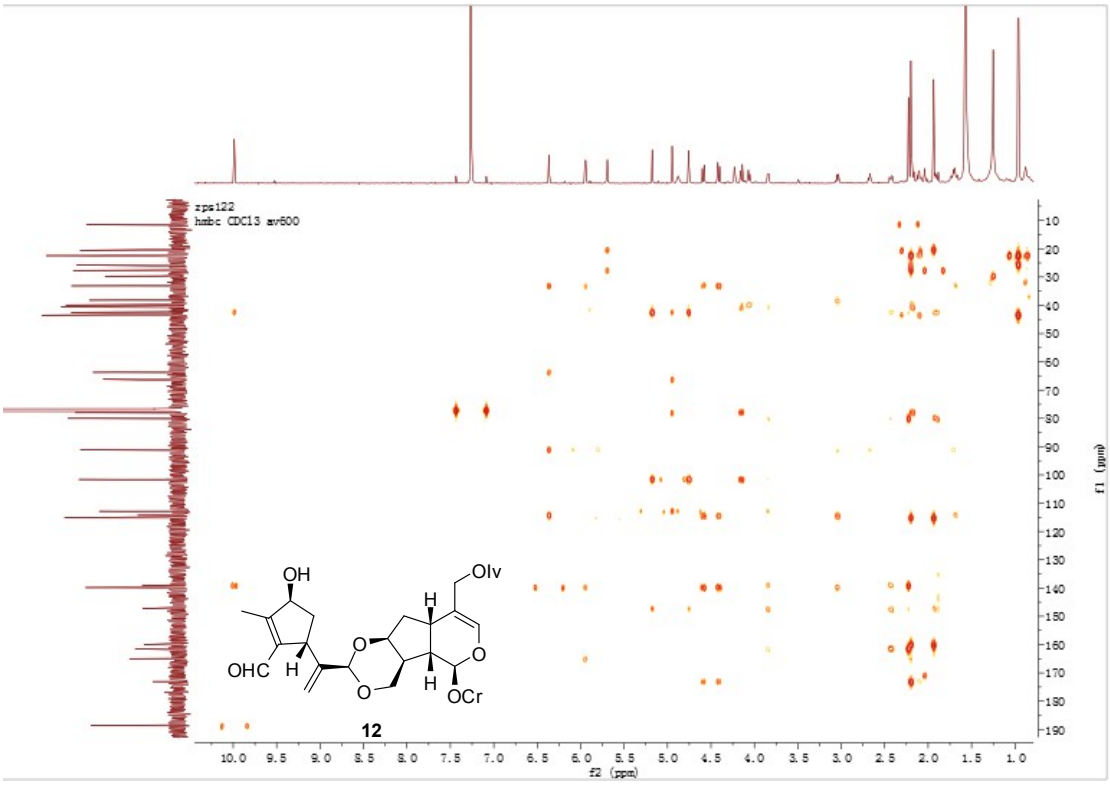


Figure 83. ^{1}H-^{1}H COSY spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

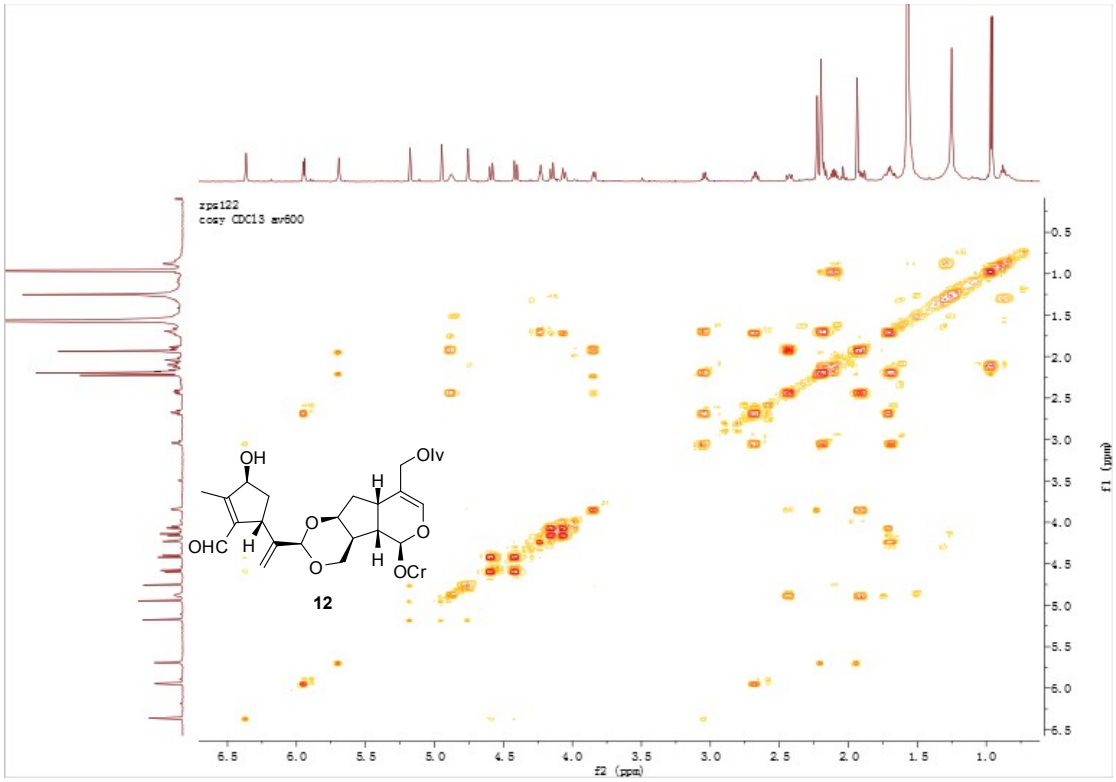


Figure 84. ROESY spectrum of Patriscabiobisin B (**12**) in $CDCl_3$.

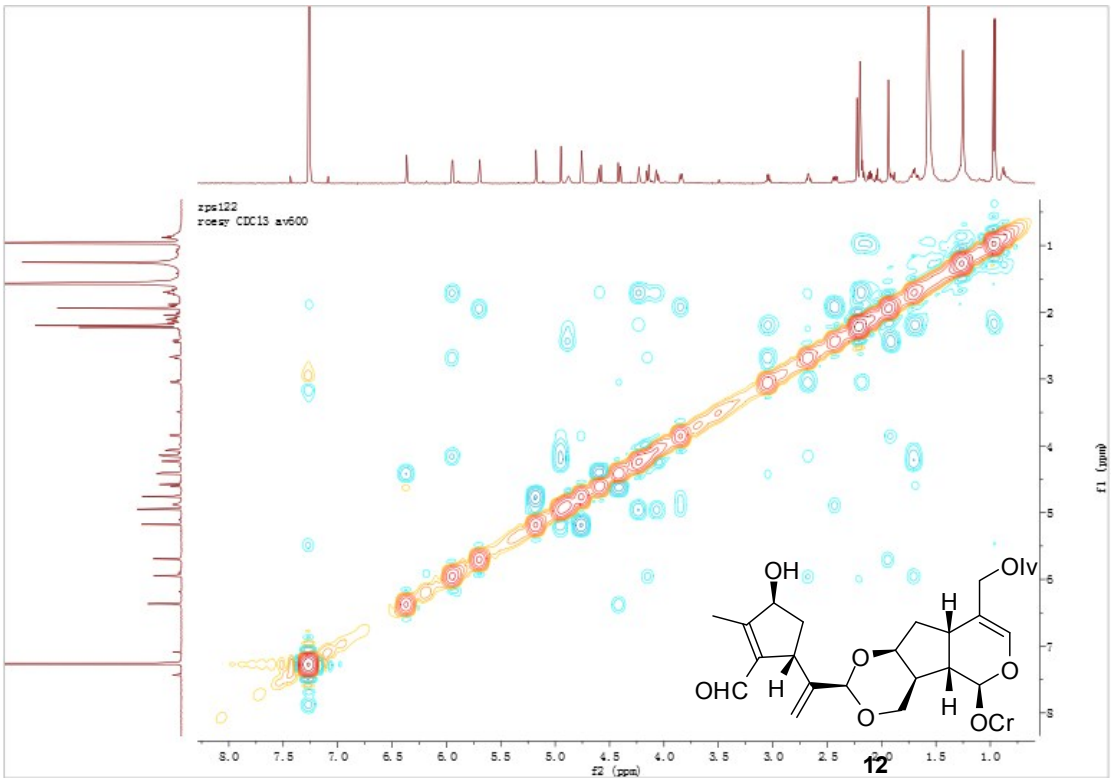


Figure 85. HREIMS spectrum of Patriscabiobisin B (**12**).

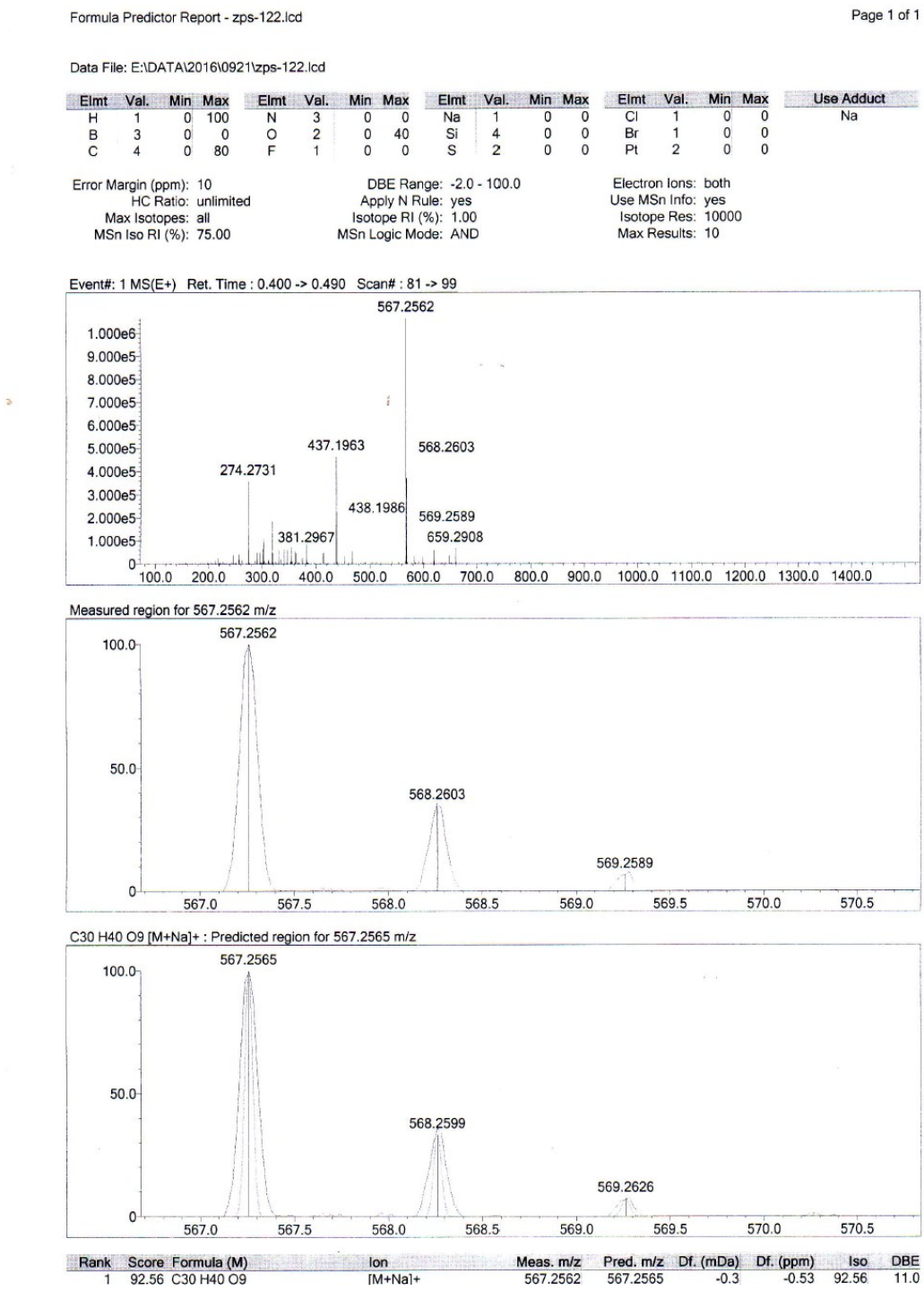


Figure 86. ECD spectrum of Patriscabiobisin B (**12**).

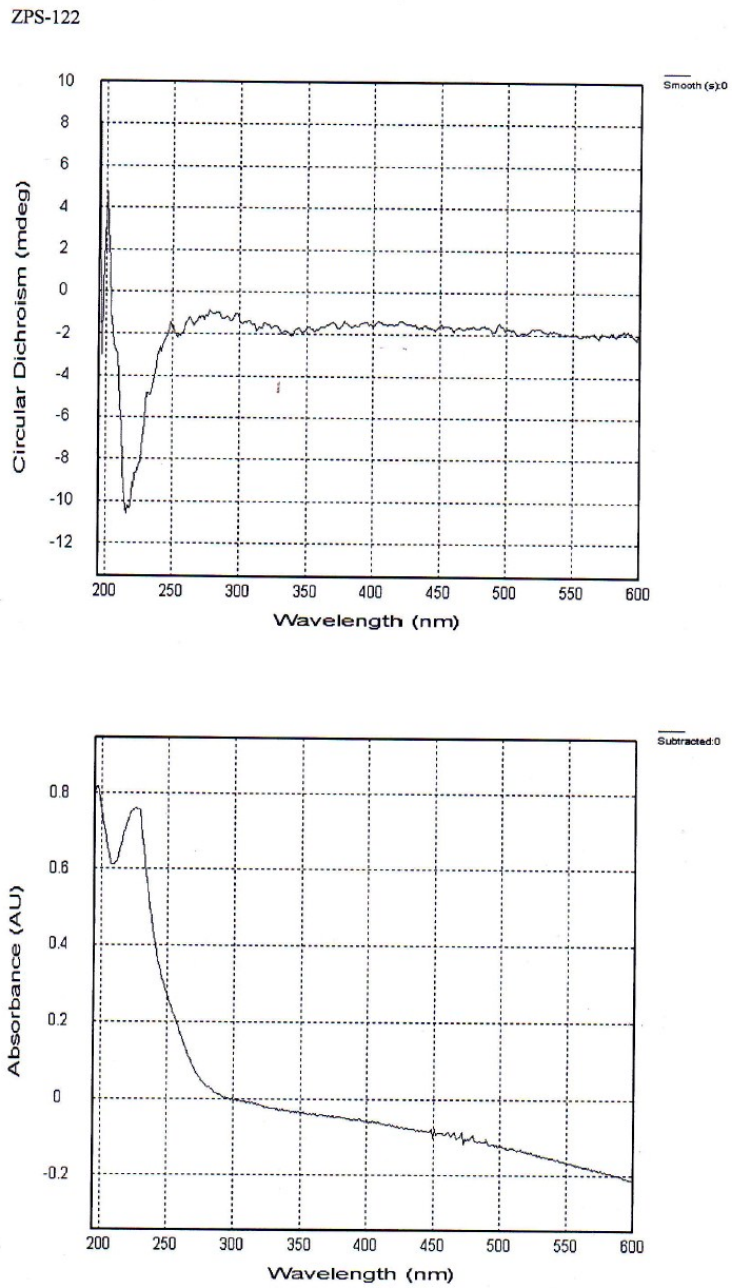


Figure 87.[1]H NMR spectrum of Patriscabiobisin C (**13**) in MeOH.

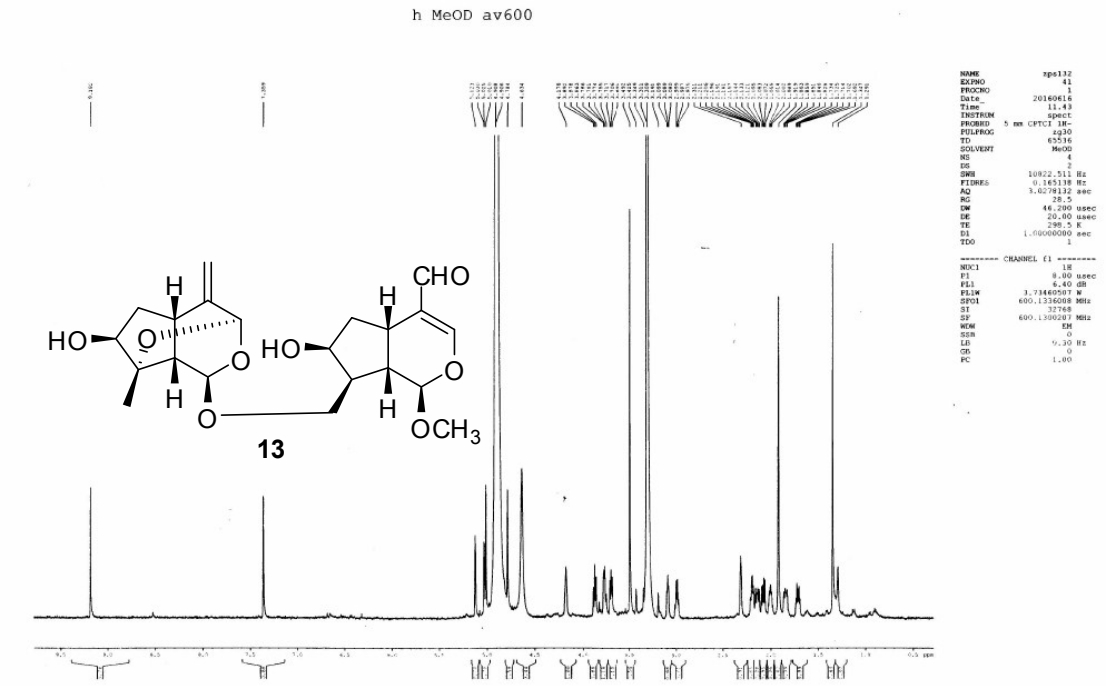


Figure 88.[13]C NMR spectrum of Patriscabiobisin C (**13**) in MeOH.

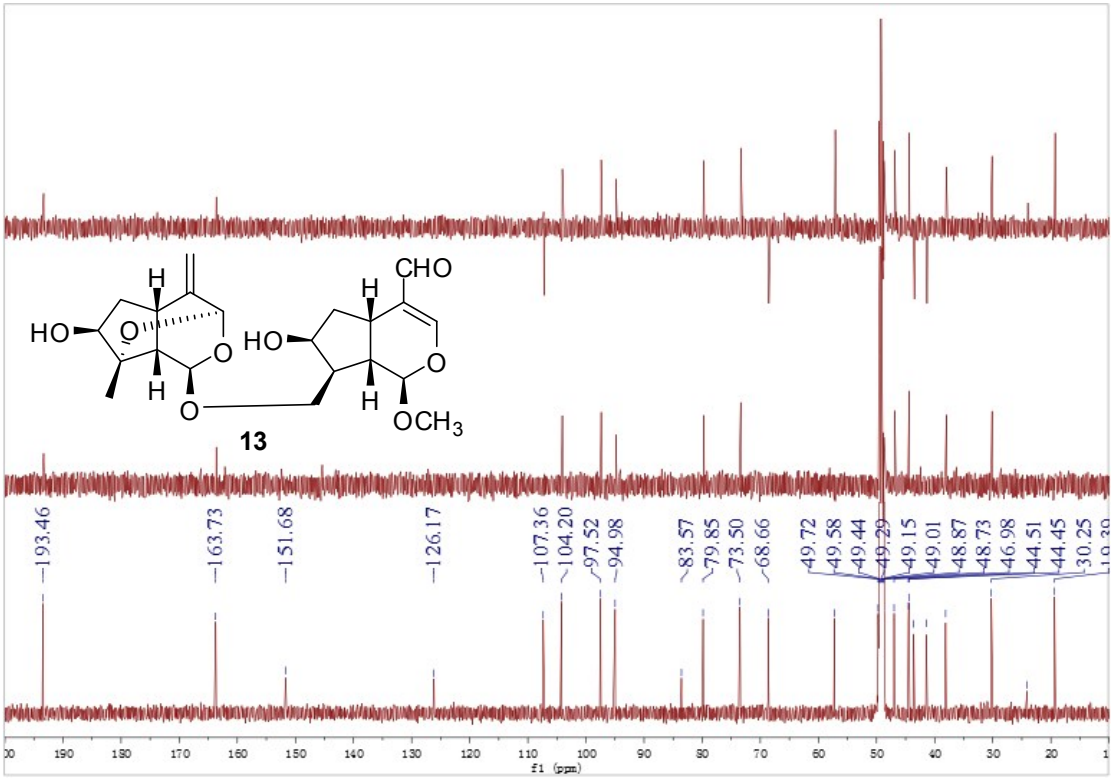


Figure 89. HSQC spectrum of Patriscabiobisin C (**13**) in MeOH.

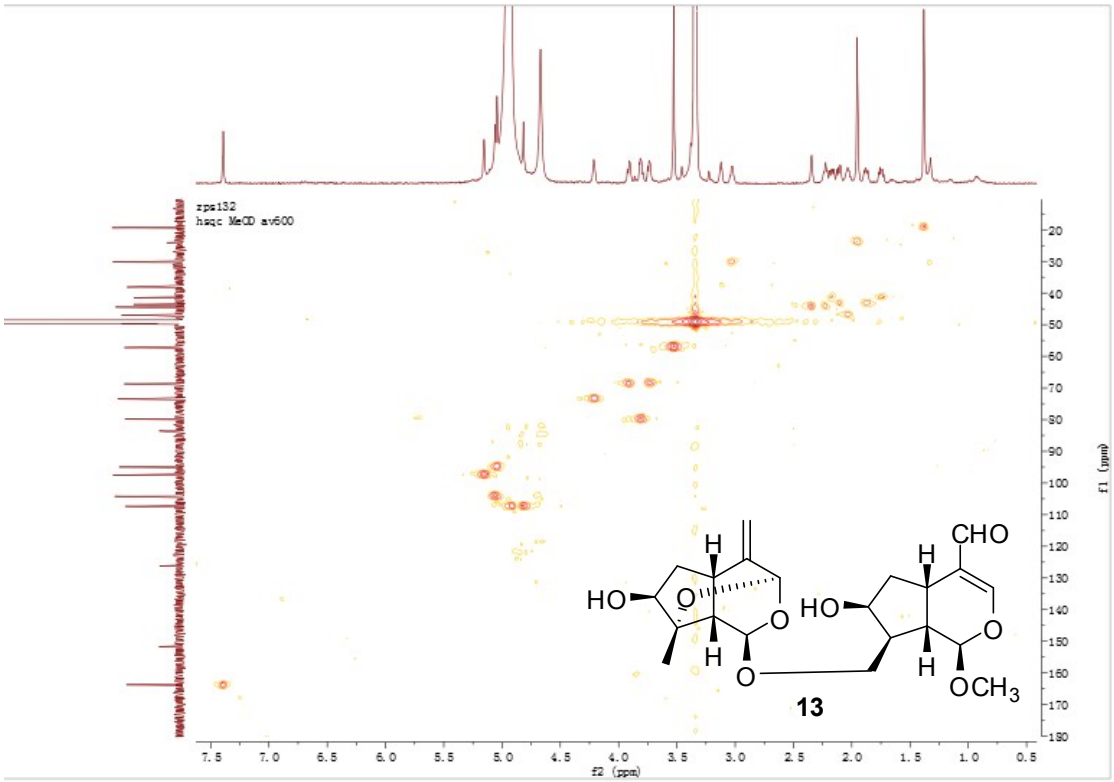


Figure 90. HMBC spectrum of Patriscabiobisin C (**13**) in MeOH.

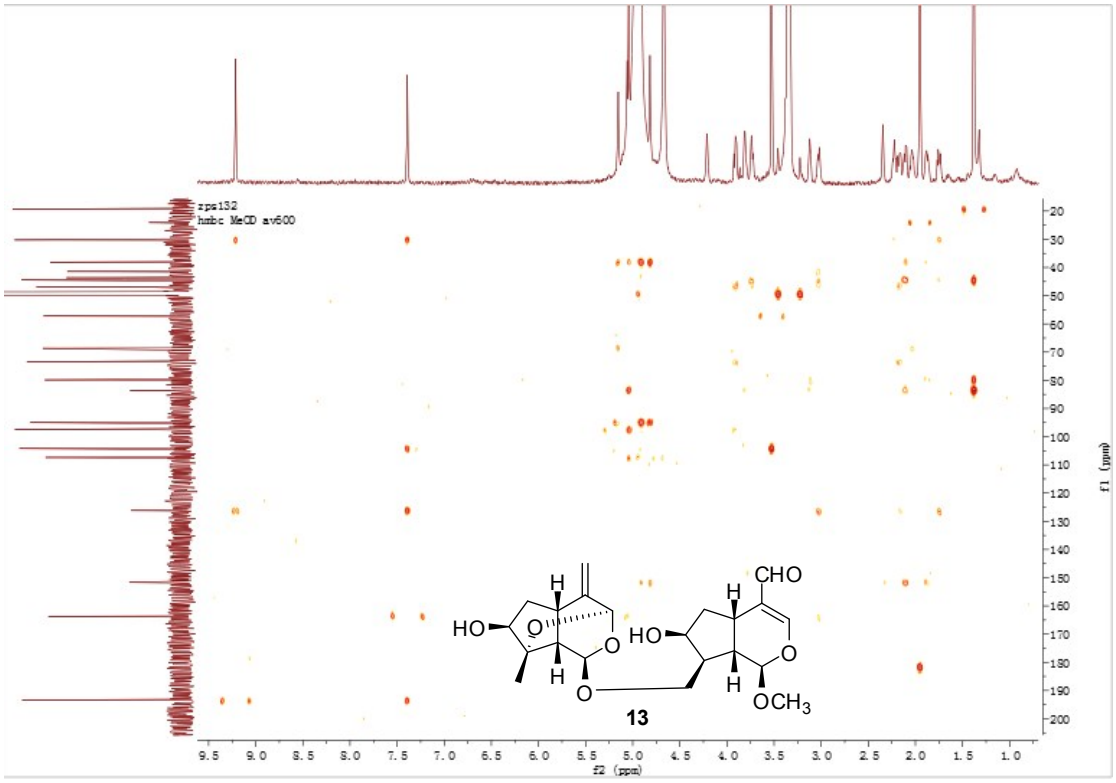


Figure 91. ^{1}H-^{1}H COSY spectrum of Patriscabiobisin C (**13**) in MeOH.

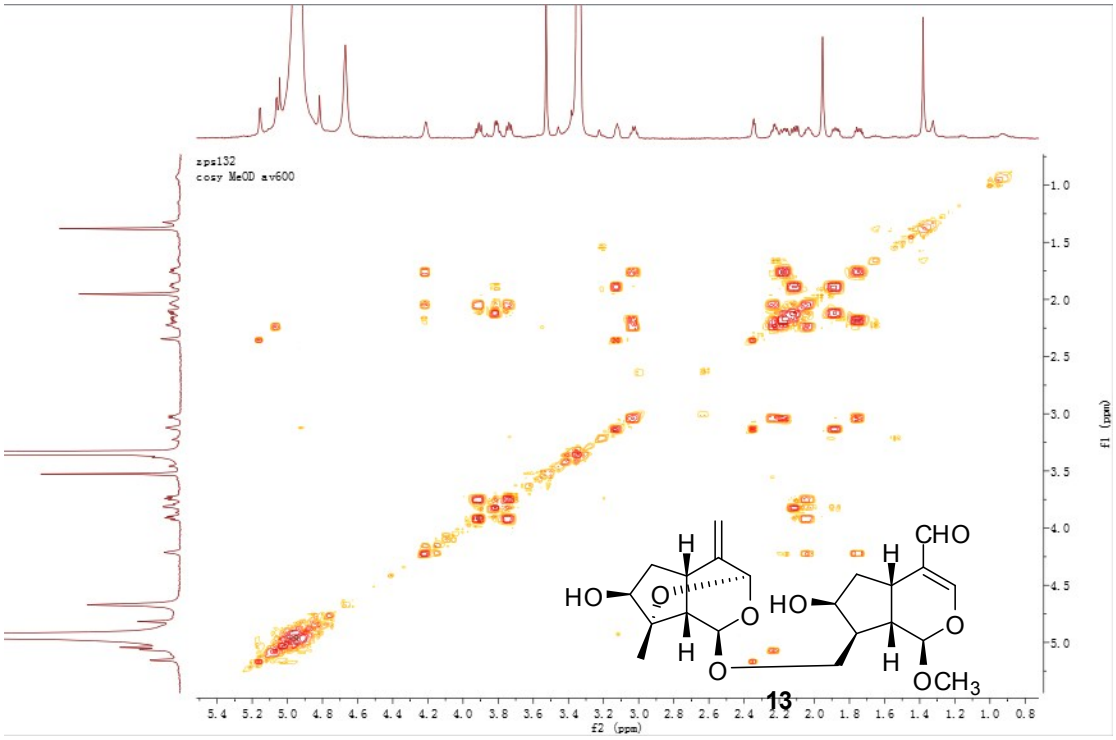


Figure 92. ROESY spectrum of Patriscabiobisin C (**13**) in MeOH

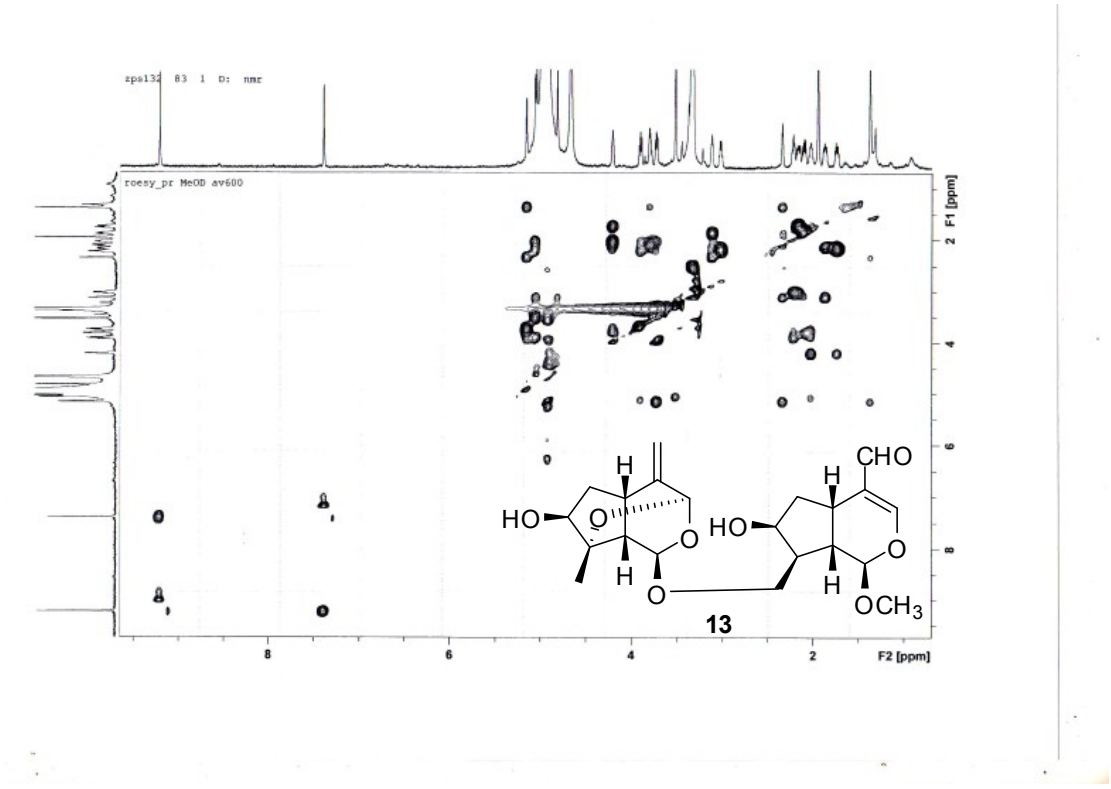


Figure 93. HREIMS spectrum of Patriscabiobisin C (**13**).

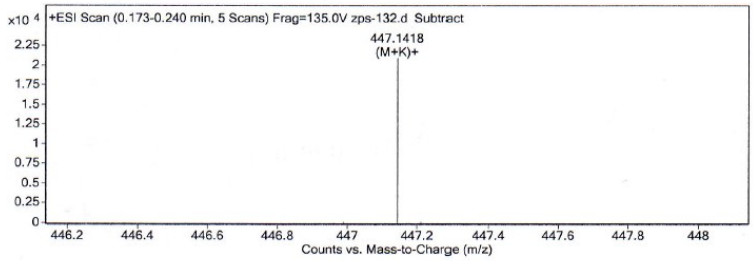
Qualitative Analysis Report

Data Filename	zps-132.d	**Sample Name**	zps-132
Sample Type	Sample	**Position**	P1-E4
Instrument Name	Instrument 1	**User Name**	
Acq Method	SIBU.m	**Acquired Time**	8/9/2016 3:36:47 PM
IRM Calibration Status	Success	**DA Method**	ESI+.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
431.1677	1	15275.19		
432.1704	1	3197.25		
447.1418	1	20988.99	C21 H28 O8	(M+K)+
448.1455	1	4808.09	C21 H28 O8	(M+K)+
449.1431	1	2544.16	C21 H28 O8	(M+K)+
453.167	1	3390.04		
839.3455	1	7524.07		
840.3491	1	3542.7		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C21 H28 O8	408.1784	447.1416	447.1418	-0.3	-0.7	8.0000

--- End Of Report ---

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