Supporting information

Flavans with cytotoxic activity from the stem and root bark of *Daphne giraldii*

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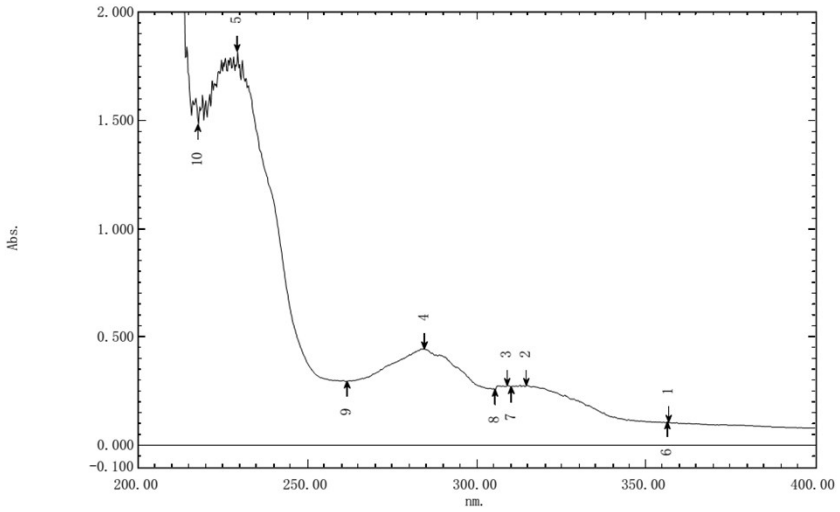
E-mail addresses: songsj99@163.com (S. J. Song).

List of supplementary content



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扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量: 0.3
体积 : 10
稀释:
光程长: 407
附加信息:

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7	↓	310.20	.271	
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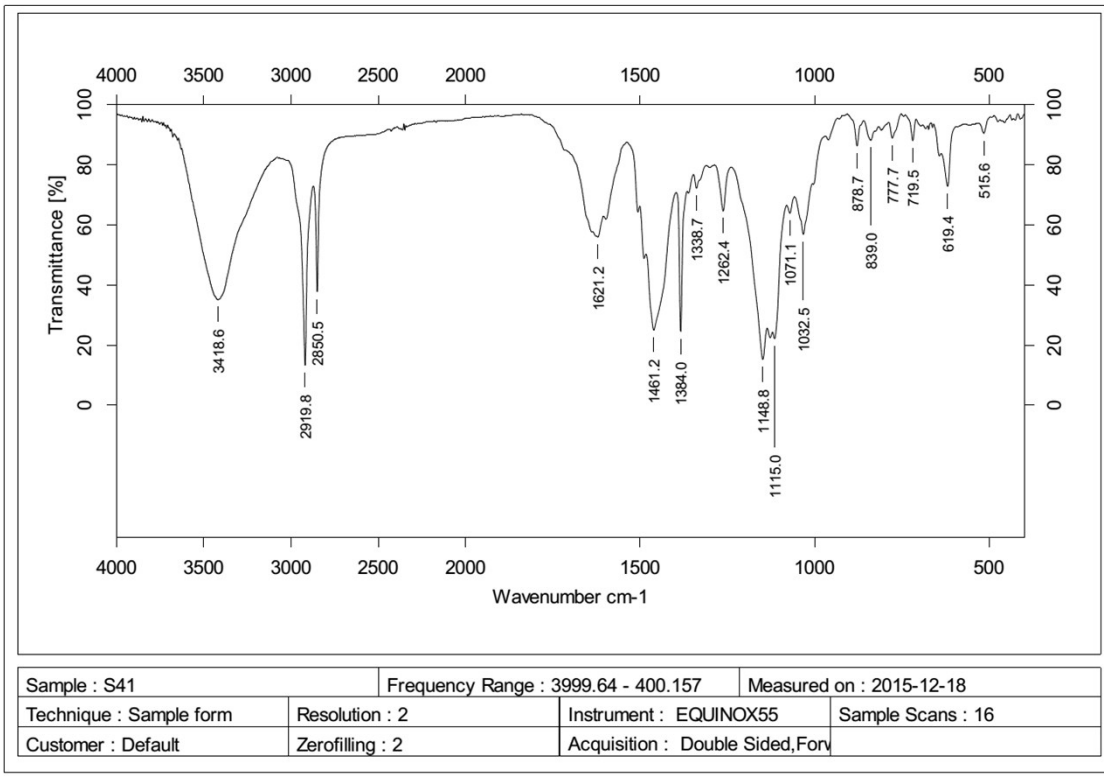
10	↓	217.80	1.483	

Figure S1.1 UV spectrum of compound **1**



Sample : S41	Frequency Range : 3999.64 - 400.157	Measured on : 2015-12-18	
Technique : Sample form	Resolution : 2	Instrument : EQUINOX55	Sample Scans : 16
Customer : Default	Zerofilling : 2	Acquisition : Double Sided,Forv	

Figure S1.2 IR spectrum of compound **1**

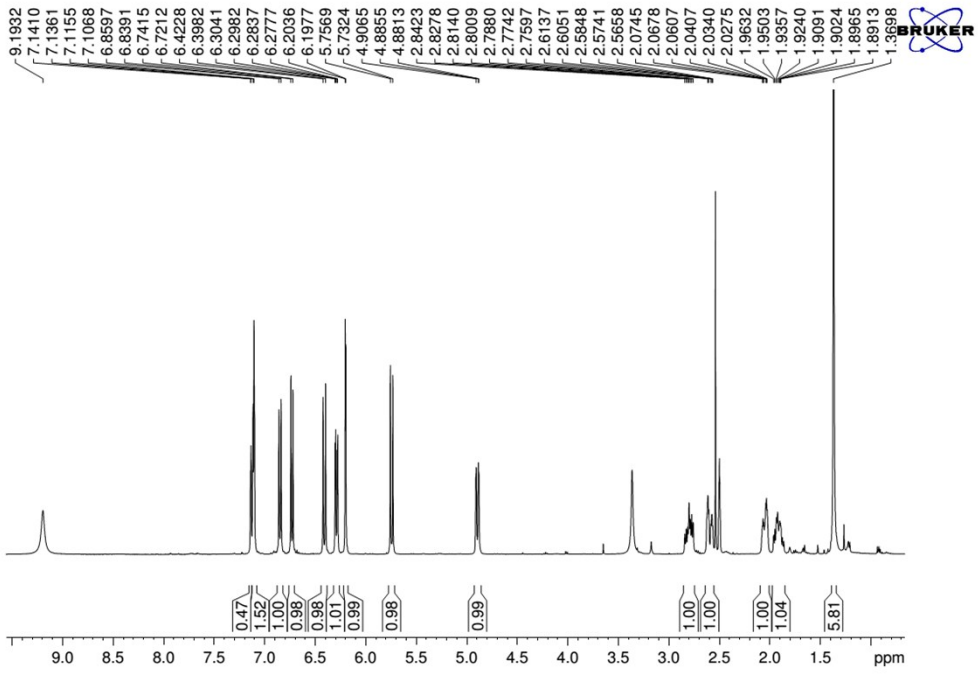


Figure S1.3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1**

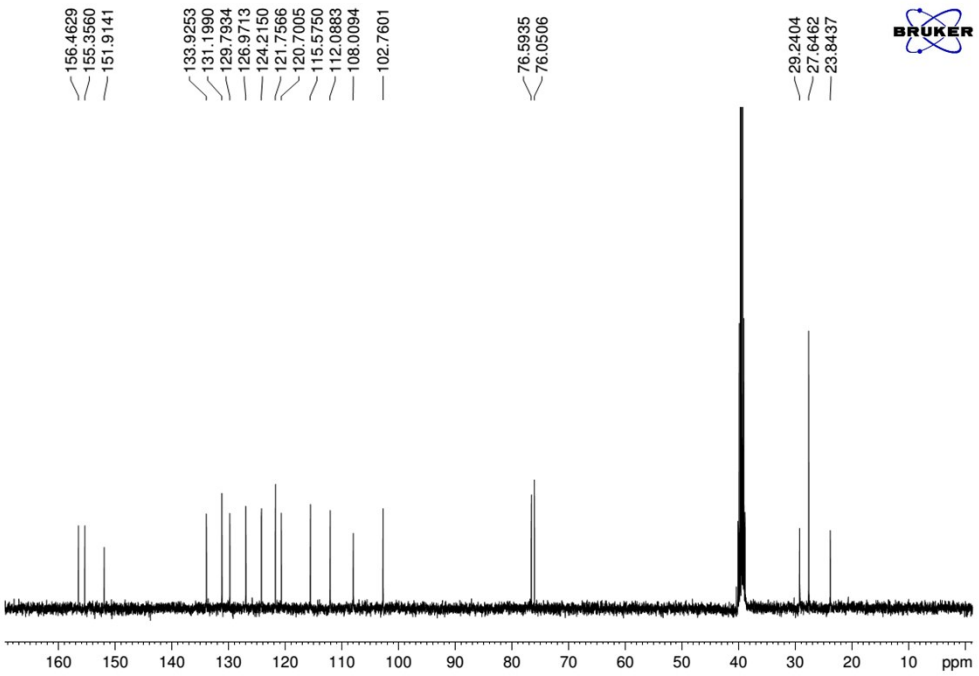


Figure S1.4 ^{13}C NMR spectrum (100 MHz,DMSO-d_6) of compound **1**

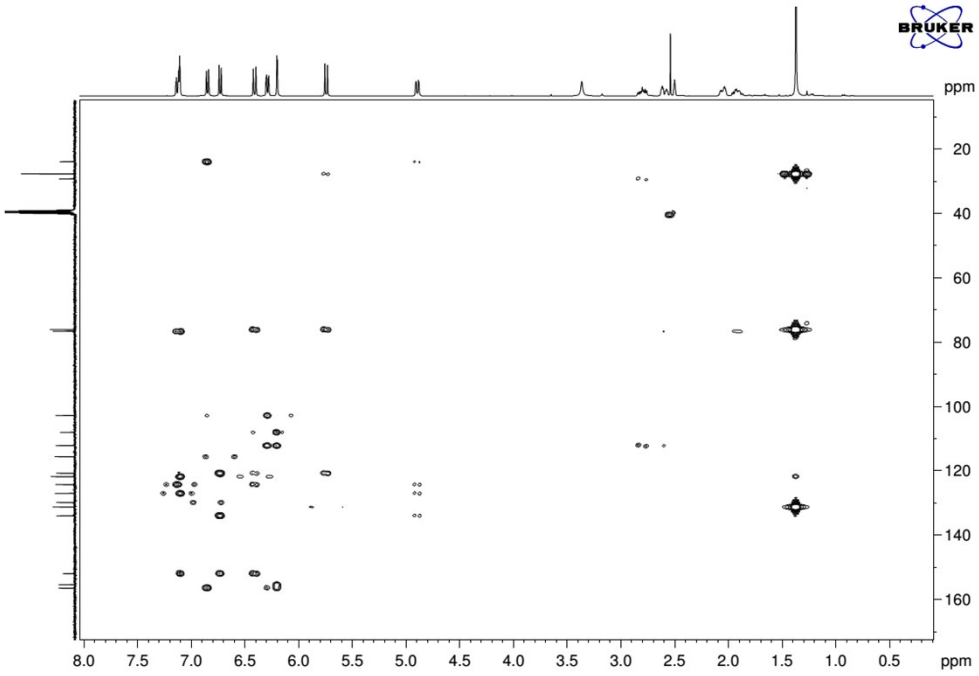


Figure S1.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **1**

Mass Spectrum Molecular Formula Report

Analysis Info

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Method	Liu_low_20131025.m	Operator	Bruker Customer
Sample Name	SQ-41	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C20H20O3H						
Formula, max.							
Measured m/z	309.148	Tolerance	5	ppm	Charge	1	
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Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						

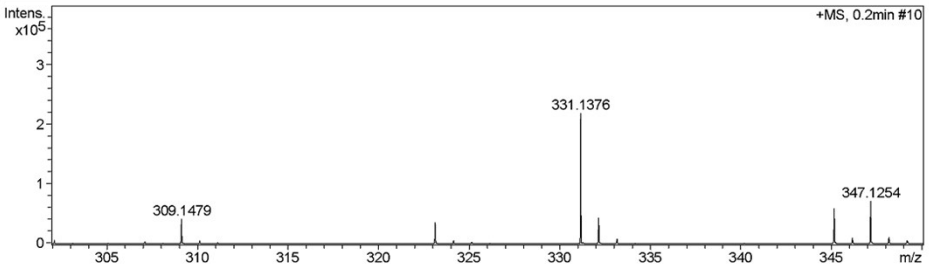

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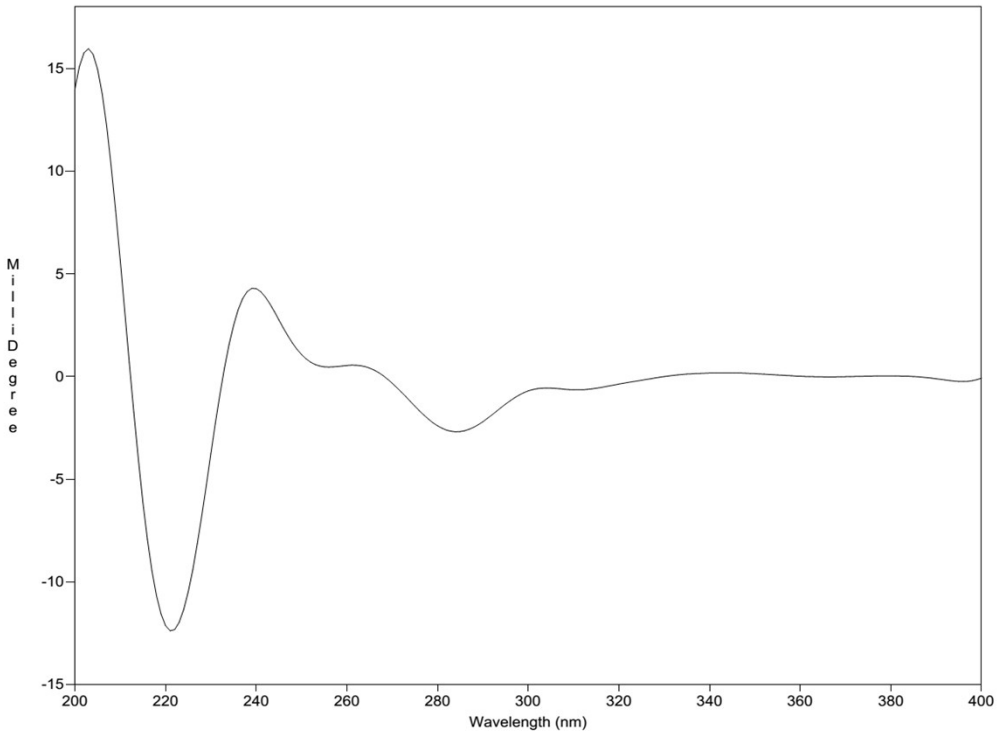
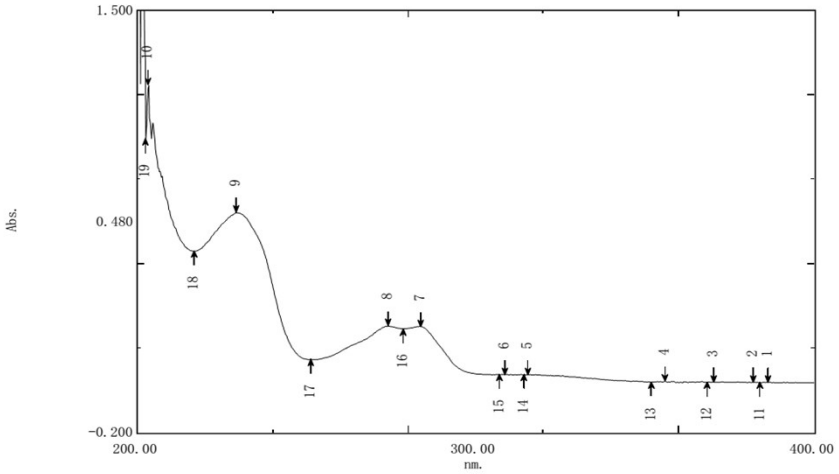
Figure S1.6 HRESIMS spectrum of compound **1**



Bio-Kine Software V4.74 Date : 2015-11-30 Time : 14:45:08

Figure S1.7 CD spectra of compound **1**



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扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 364.0 nm
S/R 转换: 标准

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1	↑	386.20	.004	
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4	↑	356.00	.007	
5	↑	315.40	.034	
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7	↑	283.60	.228	
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9	↑	229.20	.686	
10	↑	203.40	1.198	
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12	↓	368.40	.002	
13	↓	351.80	.003	
14	↓	314.40	.032	
15	↓	307.00	.033	
16	↓	278.60	.218	
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Figure S2.1 UV spectrum of compound **2**

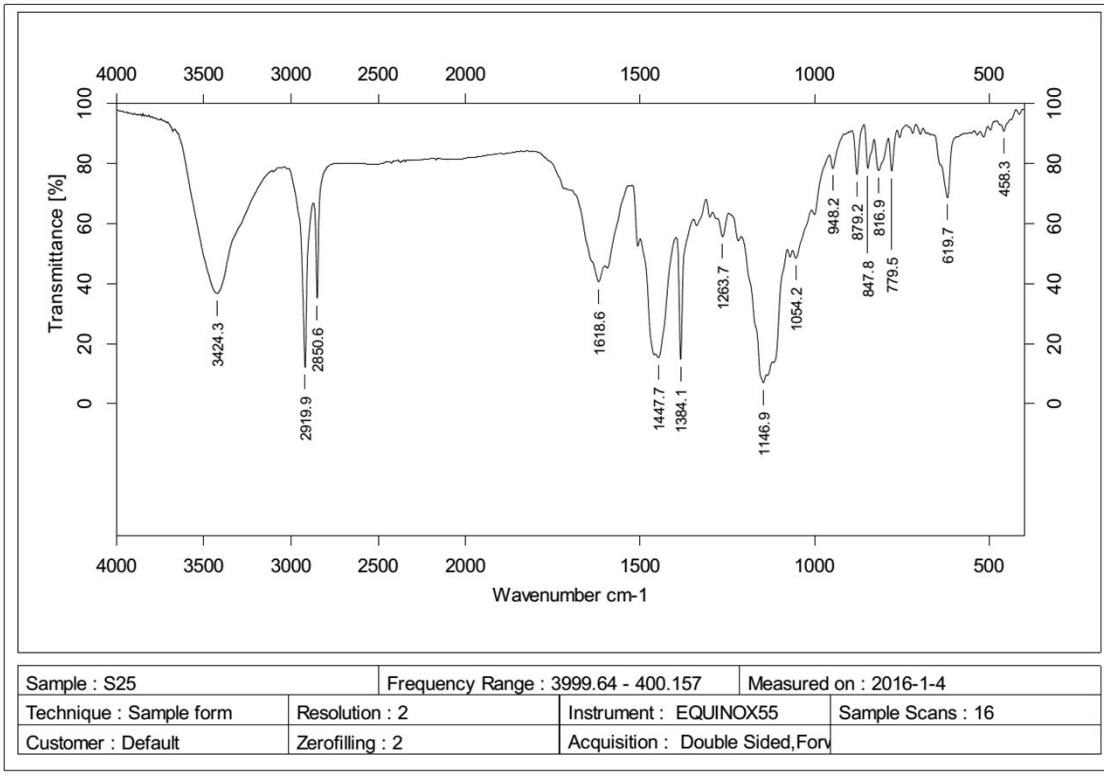


Figure S2.2 IR spectrum of compound **2**

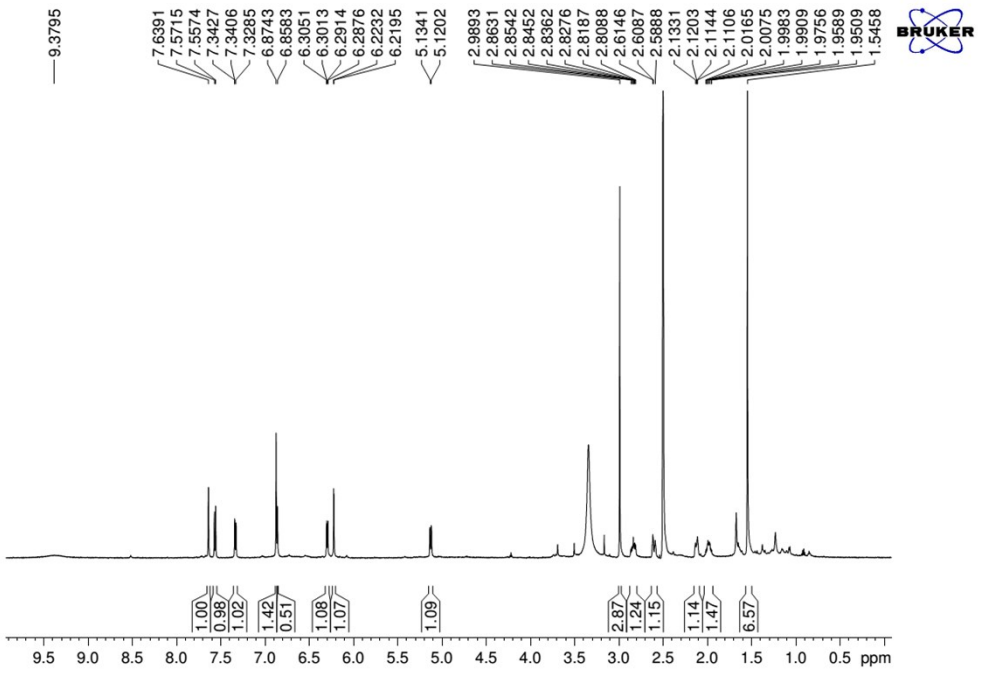


Figure S2.3 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **2**

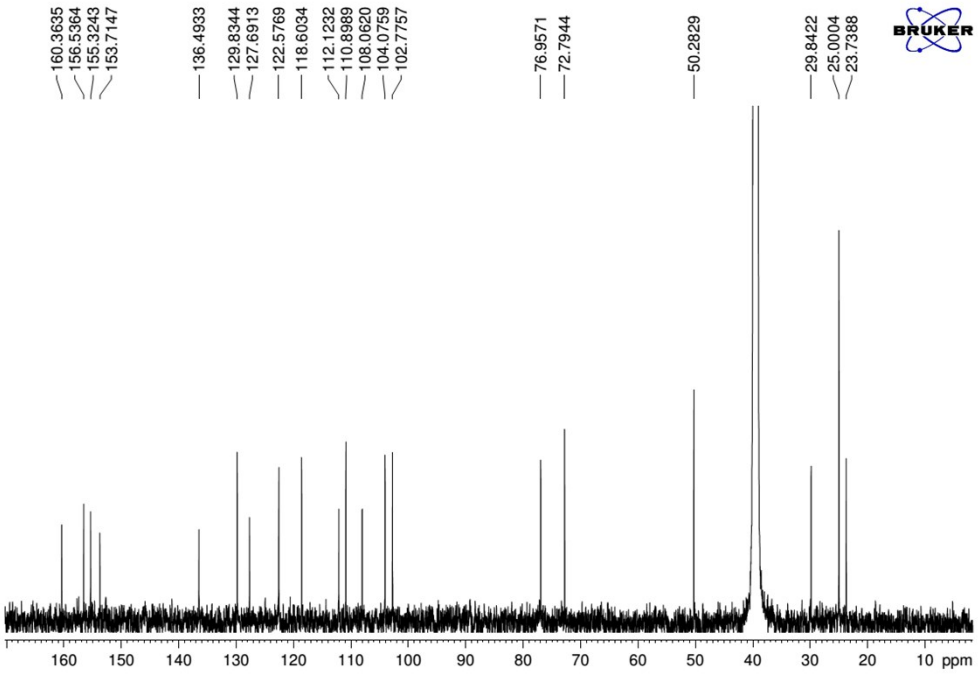


Figure S2.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **2**

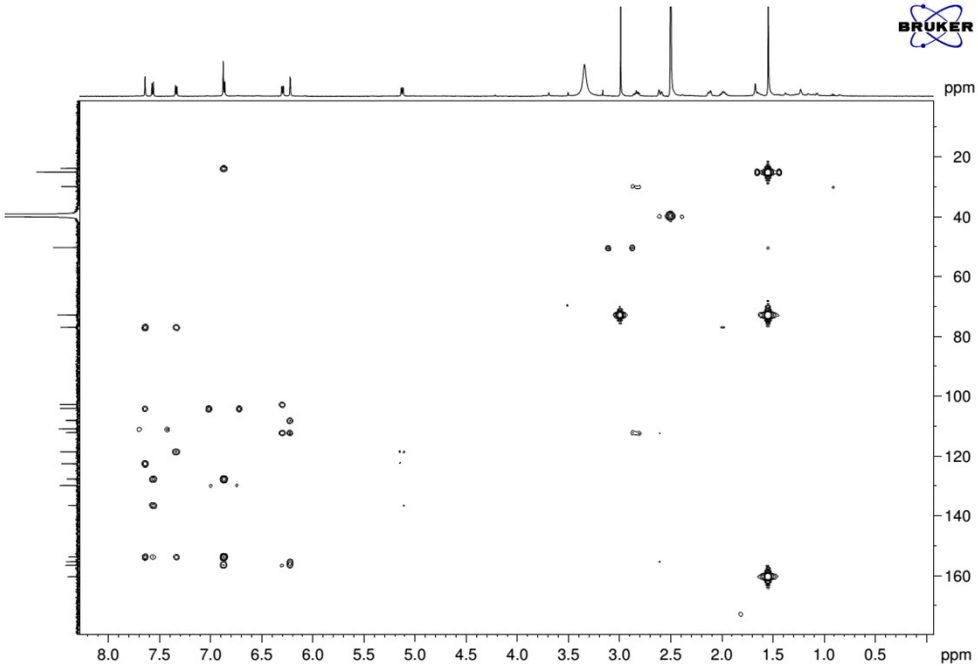
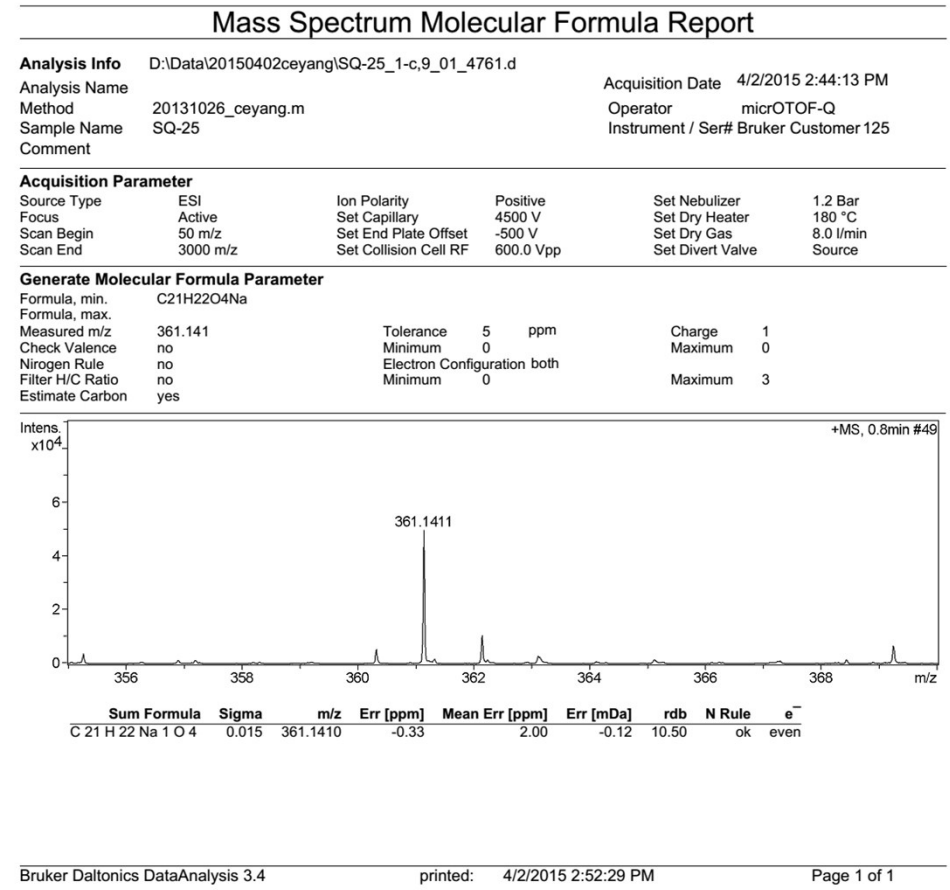


Figure S2.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **2**



Mass Spectrum Molecular Formula Report

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Method 20131026_ceyang.m
Sample Name SQ-25
Comment
Acquisition Date 4/2/2015 2:44:13 PM
Operator micrOTOF-Q
Instrument / Ser# Bruker Customer 125

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C21H22O4Na						
Formula, max.							
Measured m/z	361.141	Tolerance	5	ppm	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
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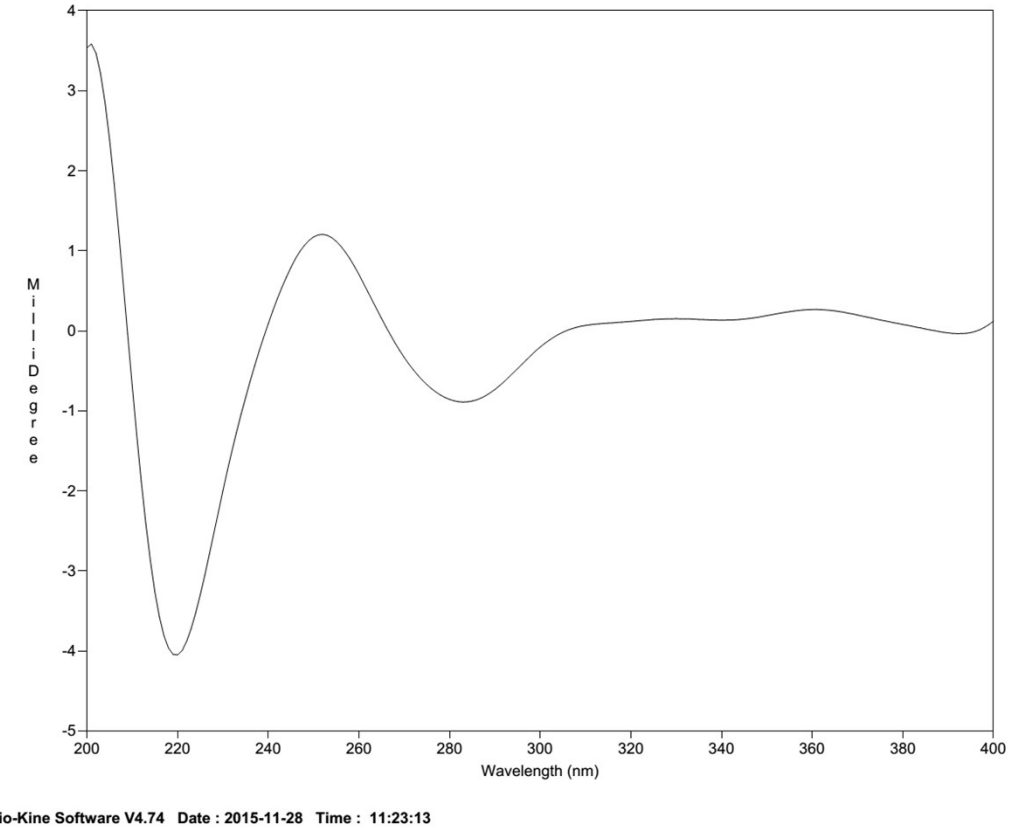
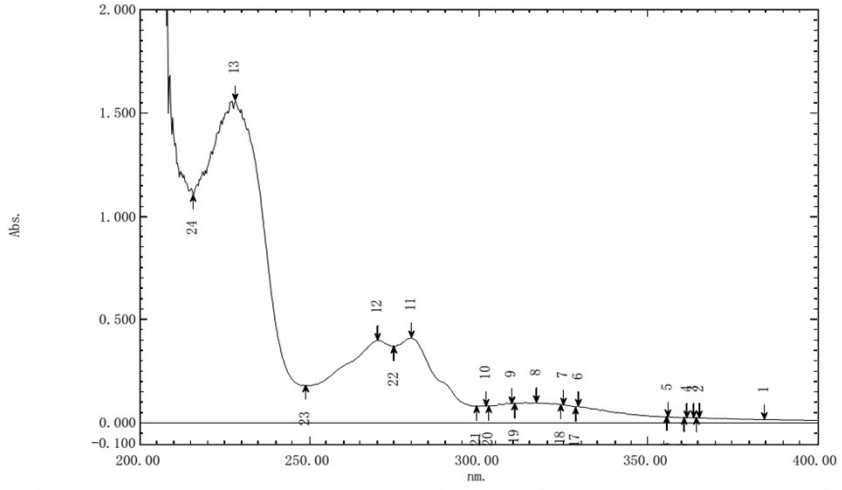
Figure S2.6 HRESIMS spectrum of compound **2**



Bio-Kine Software V4.74 Date : 2015-11-28 Time : 11:23:13

Figure S2.7 CD spectra of compound **2**



测定属性

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扫描速度:	高速
采样间隔:	0.2
自动采样间隔:	停用
扫描模式:	单一的

试样准备属性

重量:	0.3
体积 :	10
稀释:	
光程长:	407
附加信息:	

仪器属性

仪器类型:	UV-1700
测定方式:	吸收值
狭缝宽:	1.0 nm
光源改变波长:	340.8 nm
S/R 转换:	标准

附件属性

附件:	无

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5	↑	356.00	.030	
6	↑	329.40	.082	
7	↑	325.00	.089	
8	↑	317.00	.098	
9	↑	310.00	.096	
10	↑	302.40	.085	
11	↑	282.00	.412	
12	↑	270.00	.401	
13	↑	228.20	1.558	
14	↓	364.20	.024	
15	↓	360.80	.025	
16	↓	355.40	.029	
17	↓	328.60	.079	
18	↓	324.20	.088	
19	↓	310.80	.093	
20	↓	303.20	.082	
21	↓	299.20	.082	
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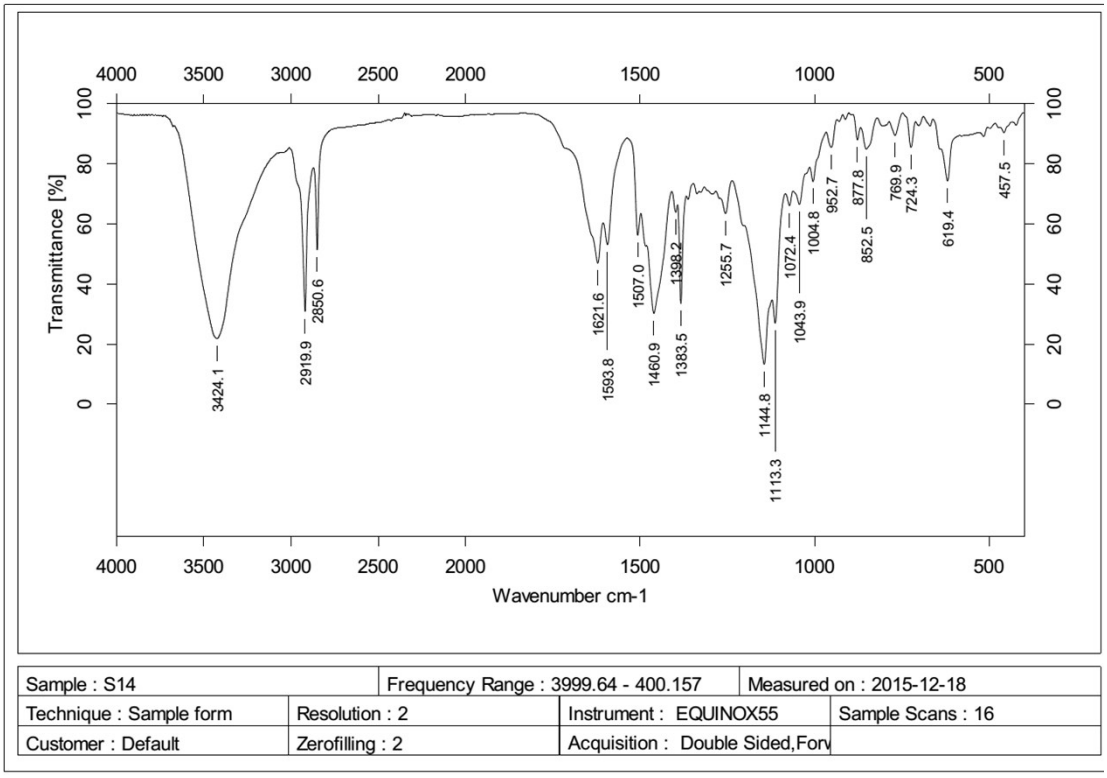
Figure S3.1 UV spectrum of compound **3**



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Customer : Default	Zerofilling : 2	Acquisition : Double Sided,Forv	

Figure S3.2 IR spectrum of compound **3**

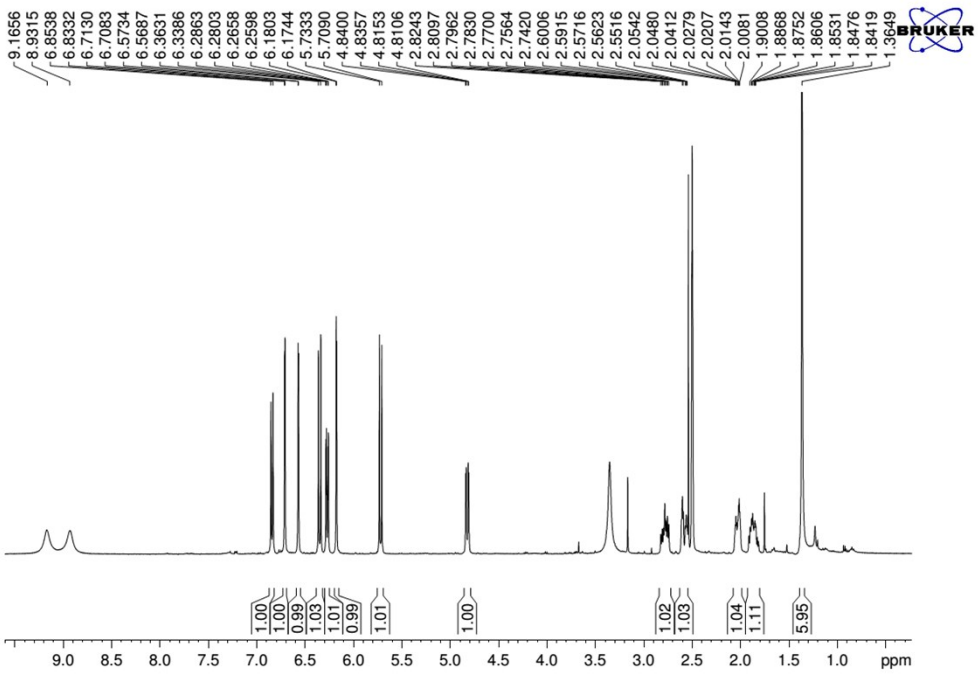


Figure S3.3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3**

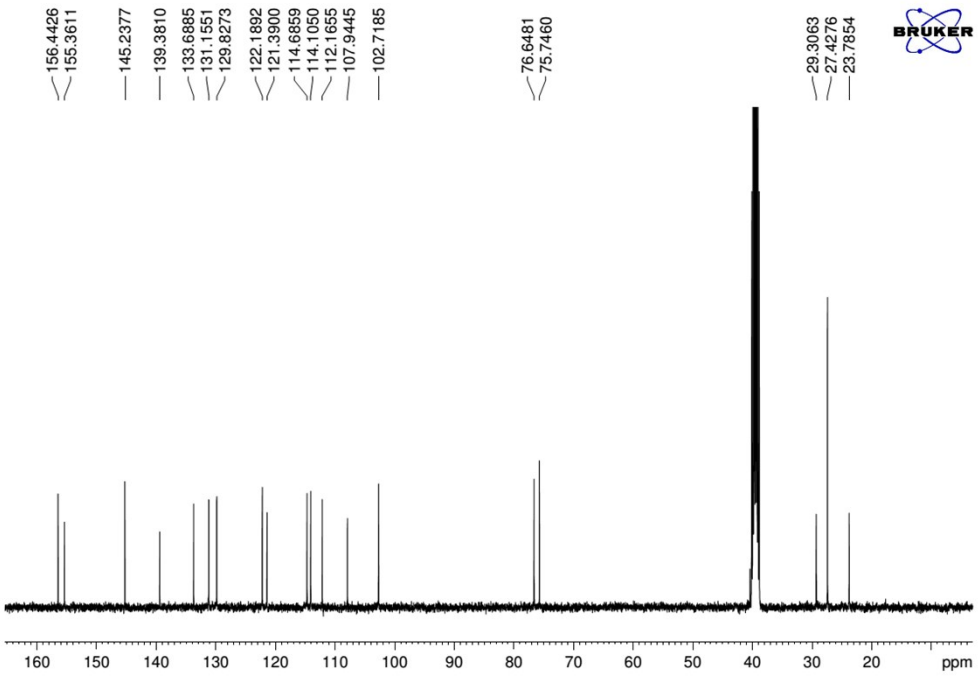


Figure S3.4 ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3**

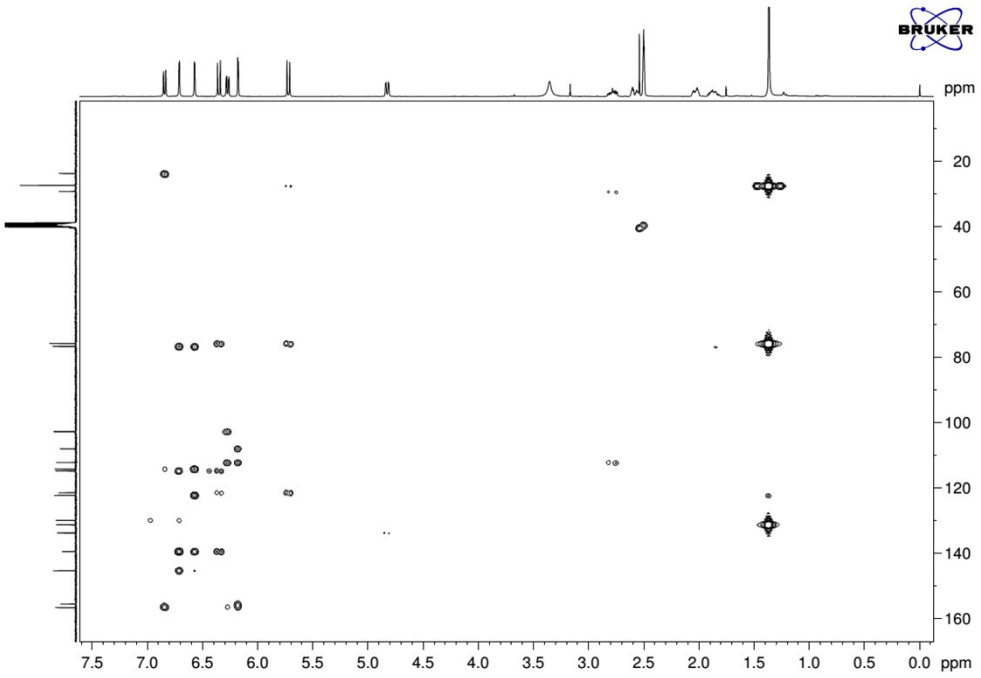


Figure S3.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **3**

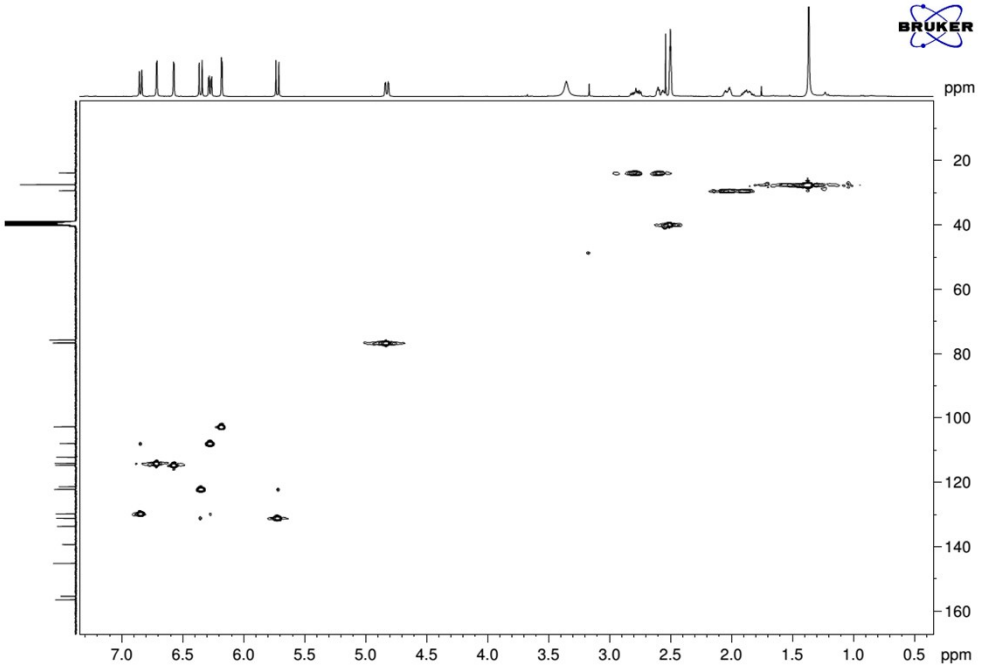
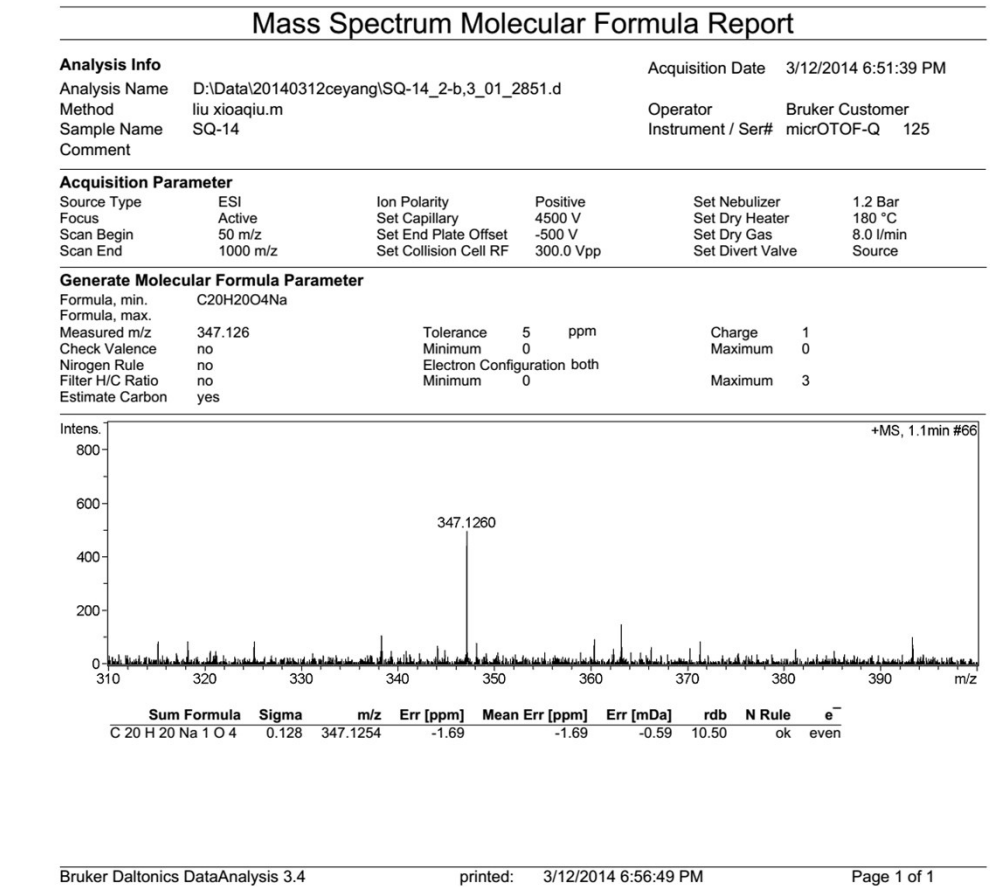


Figure S3.6 HSQC spectrum (600 MHz, DMSO-d_6) of compound **3**



Mass Spectrum Molecular Formula Report

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Sample Name	SQ-14	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source

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Formula, max.					
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Nirogen Rule	no	Electron Configuration	both		
Filter H/C Ratio	no	Minimum	0	Maximum	3
Estimate Carbon	yes				

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Bruker Daltonics DataAnalysis 3.4 printed: 3/12/2014 6:56:49 PM Page 1 of 1

Figure S3.7 HRESIMS spectrum of compound **3**

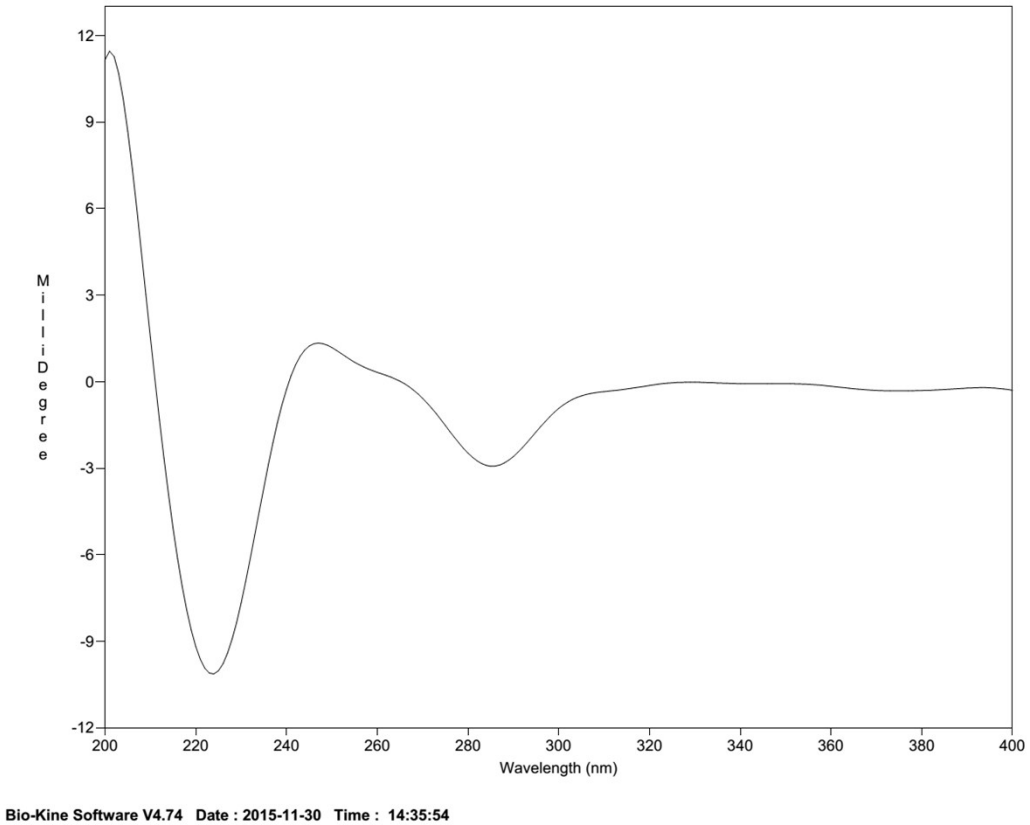
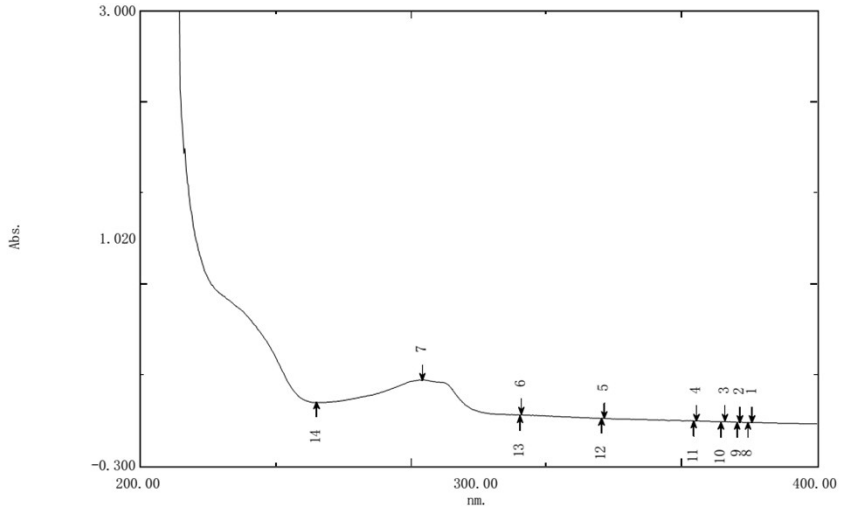


Figure S3.8 CD spectra of compound **3**



测定属性

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扫描速度:	高速
采样间隔:	0.2
自动采样间隔:	停用
扫描模式:	单一的

试样准备属性

重量:	
体积 :	
稀释:	
光程长:	
附加信息:	

仪器属性

仪器类型:	UV-1700

No.	P/V	Wavelength	Abs.	描述
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2	↑	377.20	.018	
3	↑	372.60	.021	
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5	↑	337.20	.046	
6	↑	312.80	.071	
7	↑	283.40	.324	
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9	↓	376.40	.017	
10	↓	371.60	.020	
11	↓	363.60	.025	
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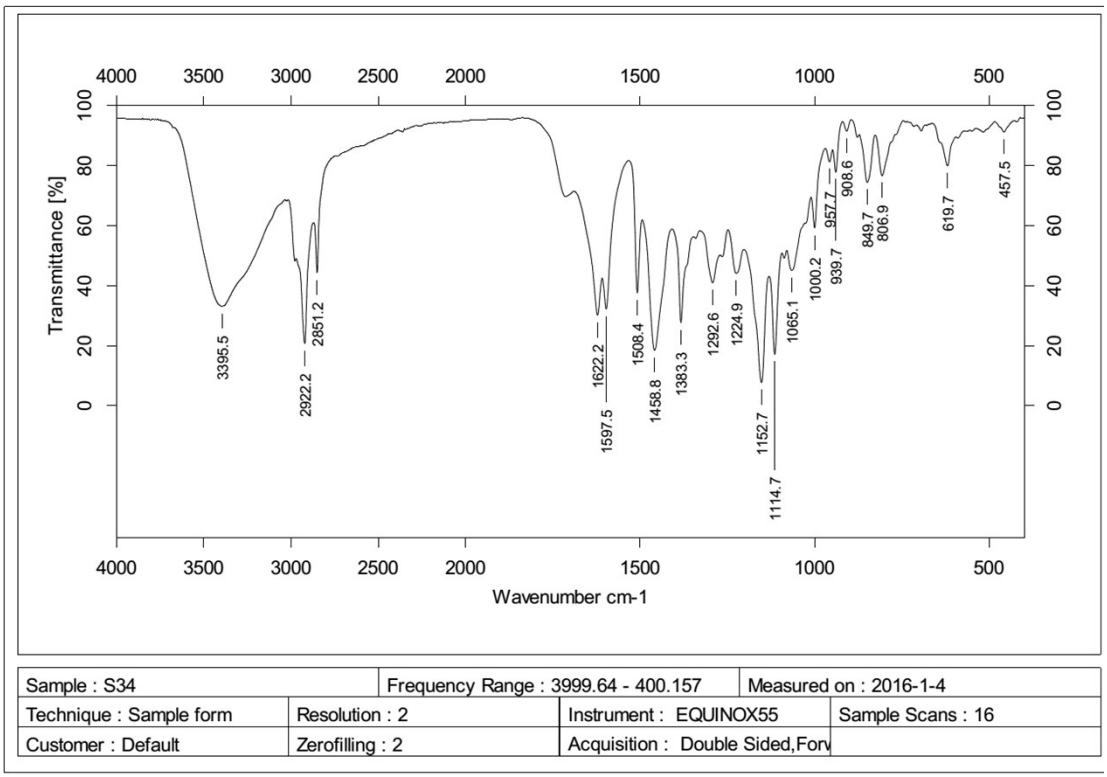
Figure S4.1 UV spectrum of compound **4**



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Technique : Sample form	Resolution : 2	Instrument : EQUINOX55	Sample Scans : 16
Customer : Default	Zerofilling : 2	Acquisition : Double Sided,Forv	

Figure S4.2 IR spectrum of compound **4**

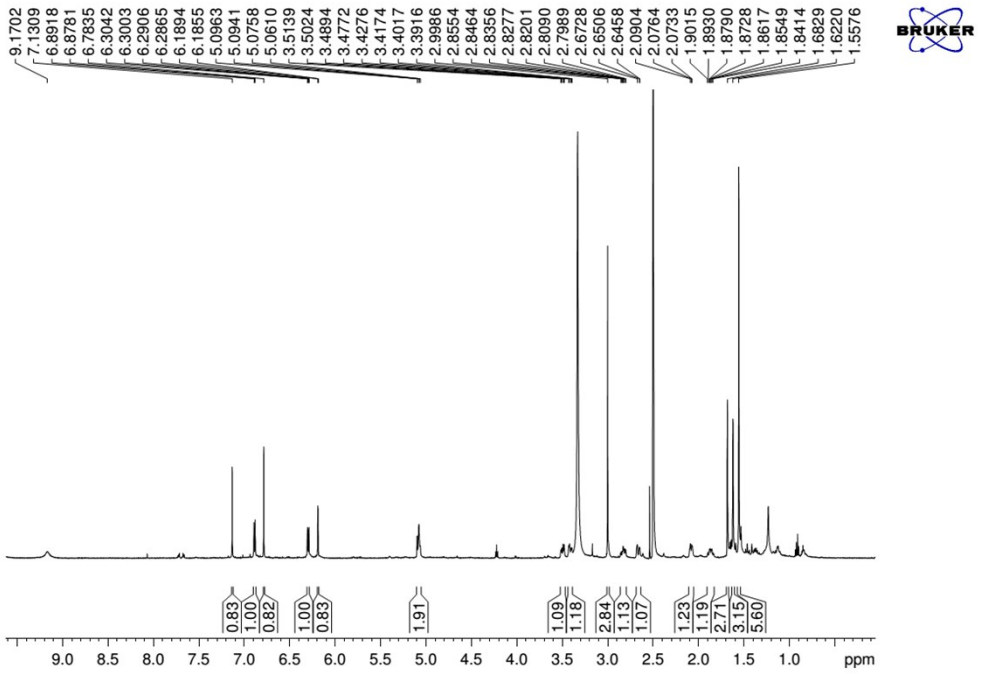

Figure S4.3 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **4**

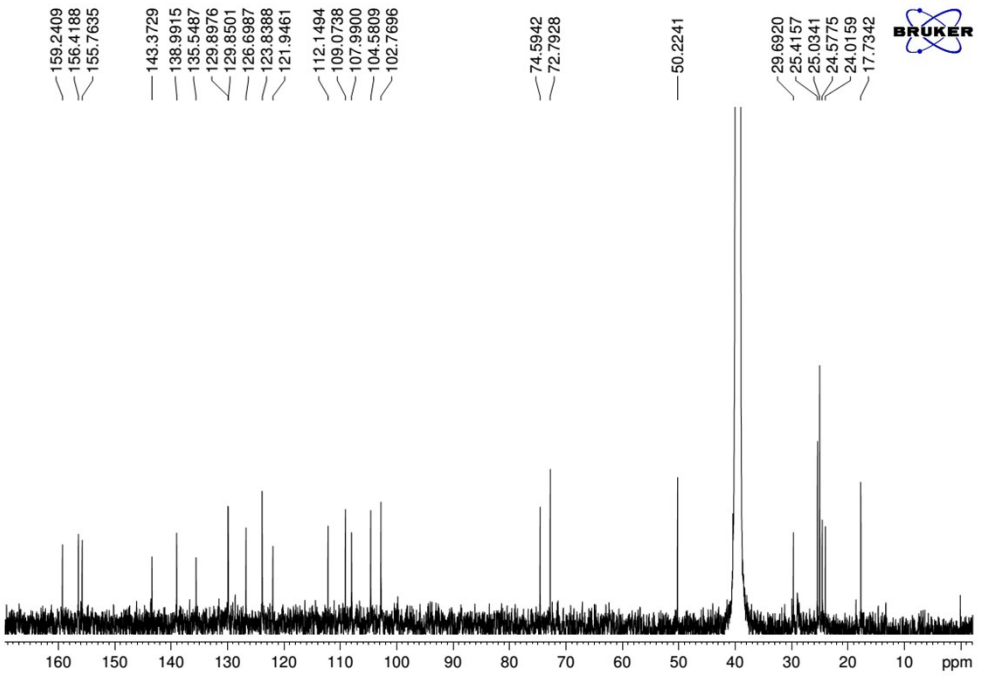

Figure S4.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **4**

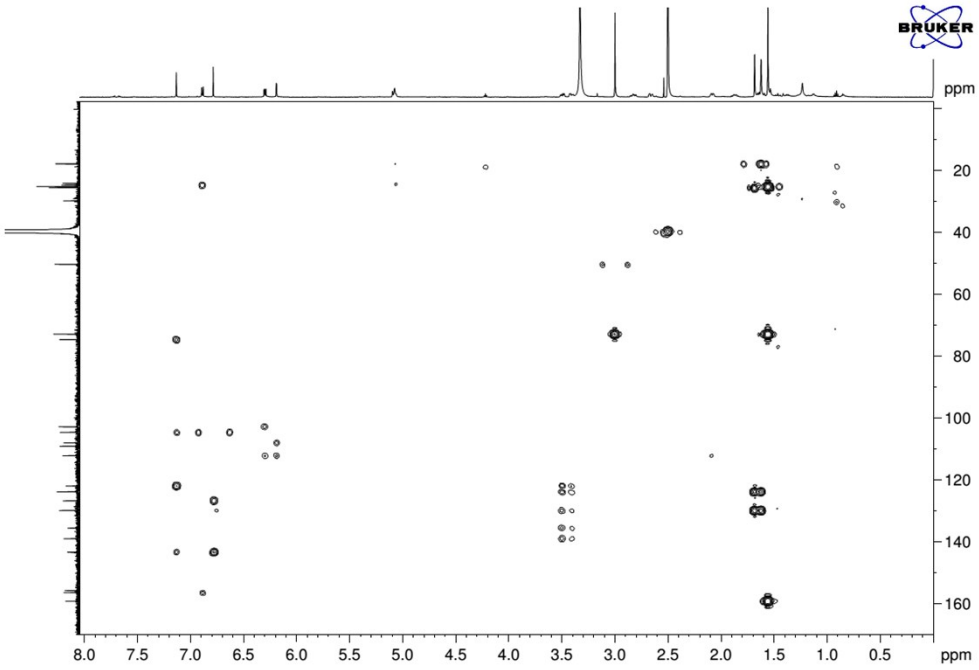

Figure S4.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **4**

Mass Spectrum Molecular Formula Report

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Comment
Acquisition Date 1/8/2015 11:31:46 AM
Operator micrOTOF-Q
Instrument / Ser# Bruker Customer 125

Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

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Formula, max.							
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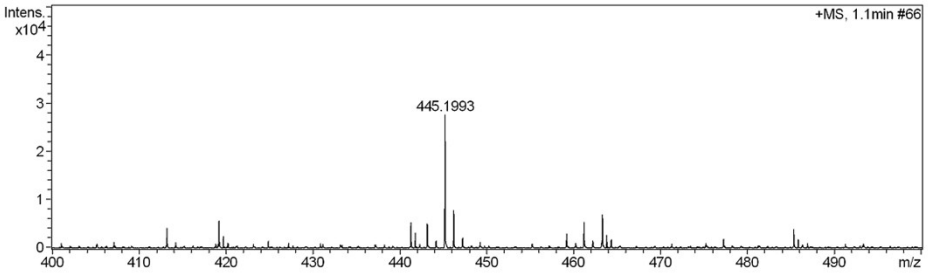
Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 26 H 30 Na 1 O 5	0.016	445.1985	-1.64	-2.11	-0.73	11.50	ok	even

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Figure S4.6 HRESIMS spectrum of compound **4**

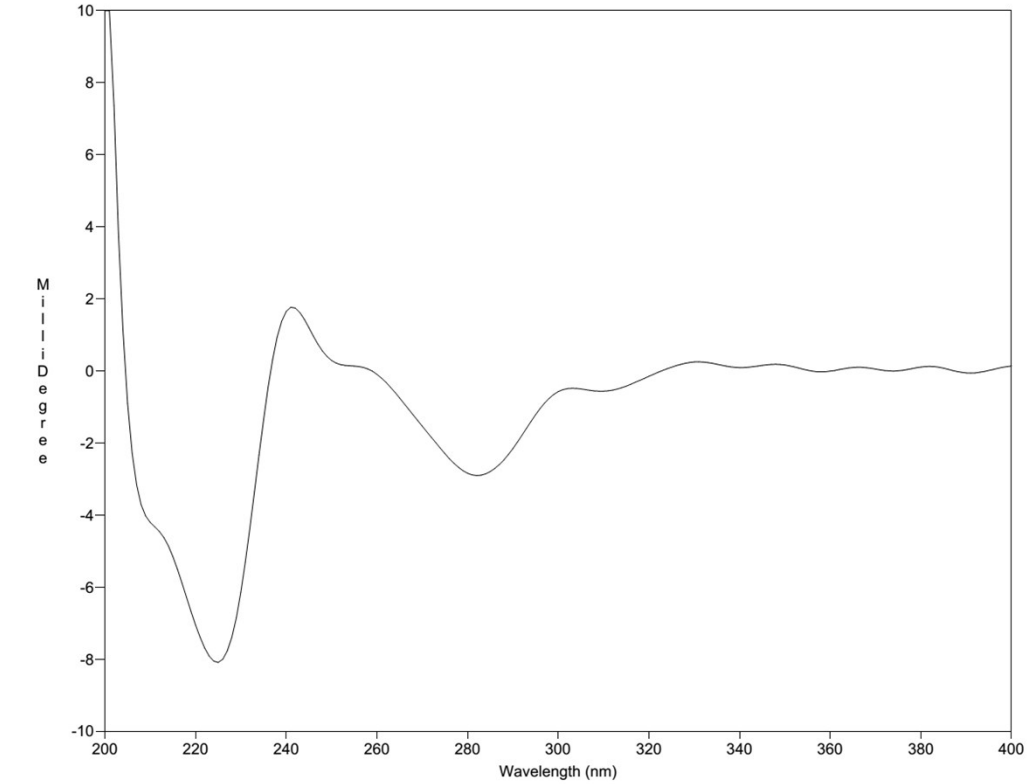
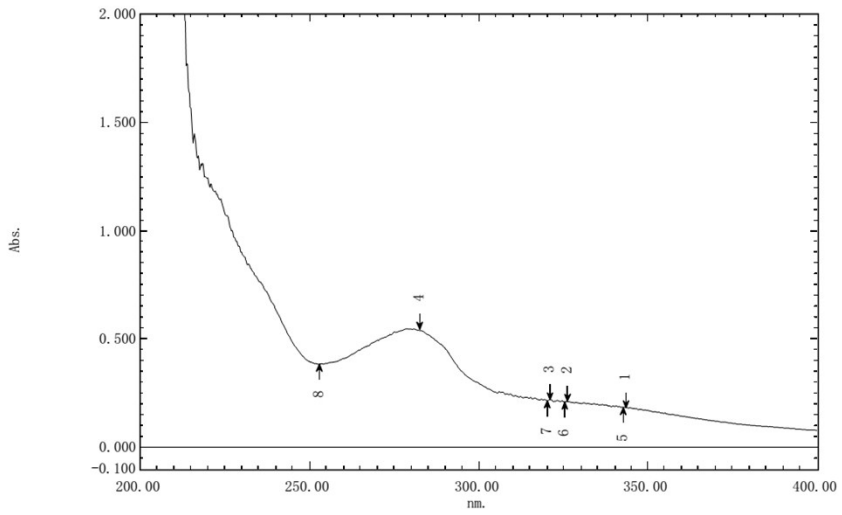


Figure S4.7 CD spectra of compound **4**



测定属性
波长范围（nm.）: 200.00到400.00
扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量: 0.3
体积 : 10
稀释:
光程长: 407
附加信息:

No.	P/V	Wavelength	Abs.	描述
1	↑	343.60	.185	
2	↑	326.40	.211	
3	↑	321.20	.221	
4	↑	282.80	.548	
5	↓	342.80	.184	
6	↓	325.40	.210	
7	↓	320.40	.215	
8	↓	252.80	.383	

Figure S5.1 UV spectrum of compound **5**

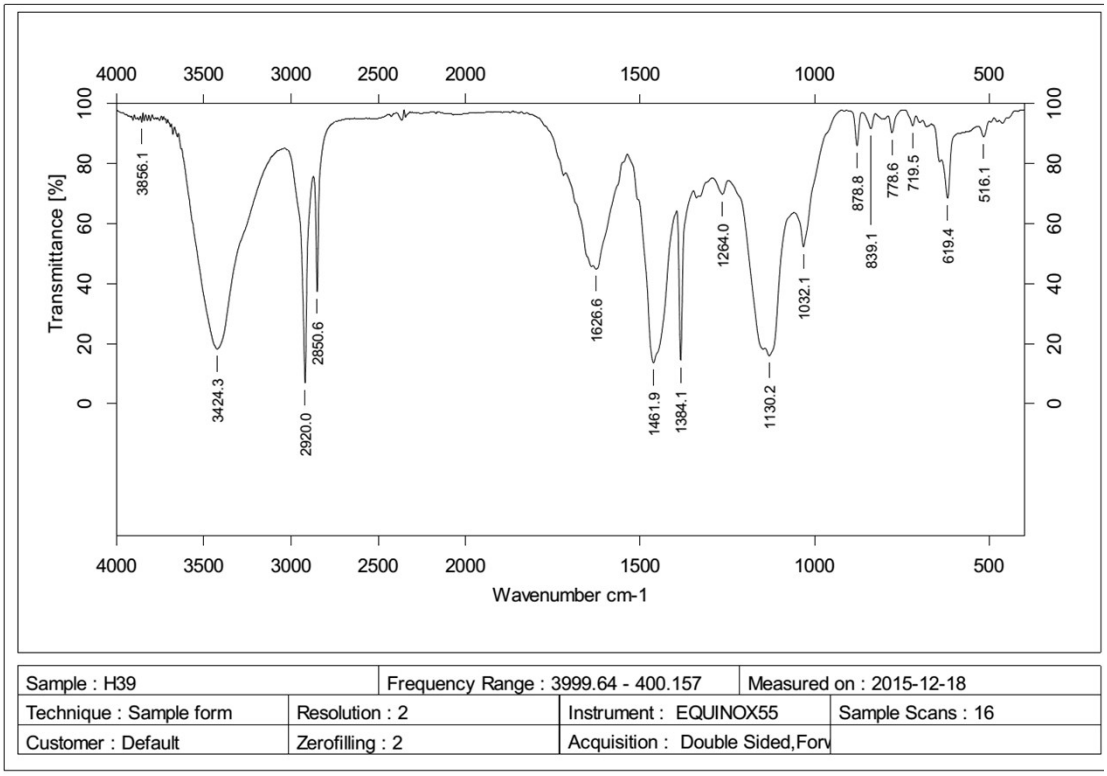


Figure S5.2 IR spectrum of compound **5**

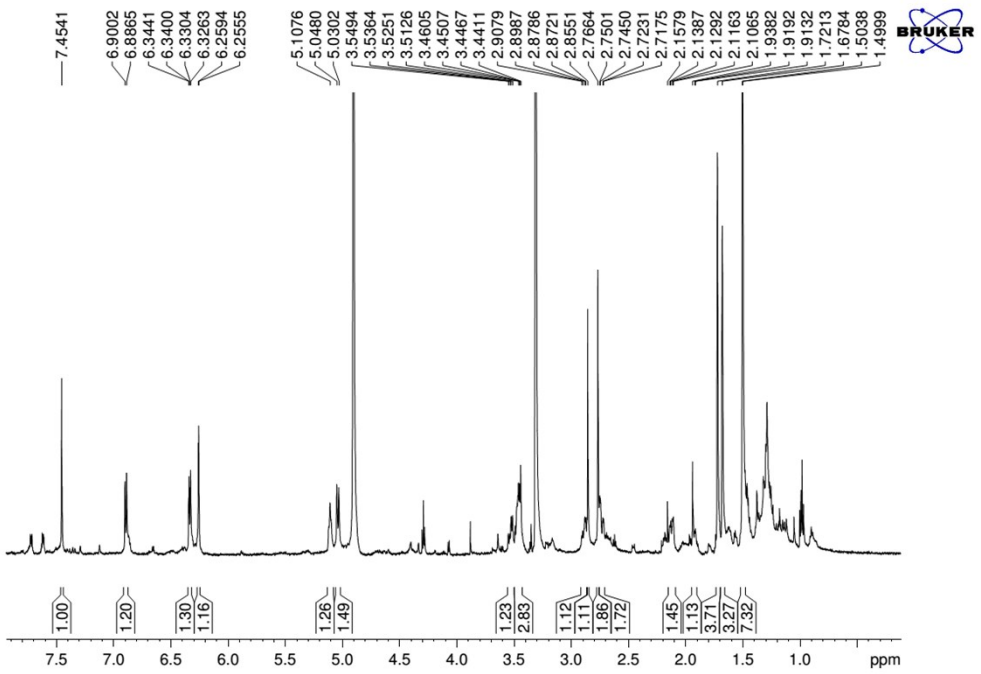


Figure S5.3 ^{1}H NMR spectrum (600 MHz, CD_3OD-d_4) of compound **5**

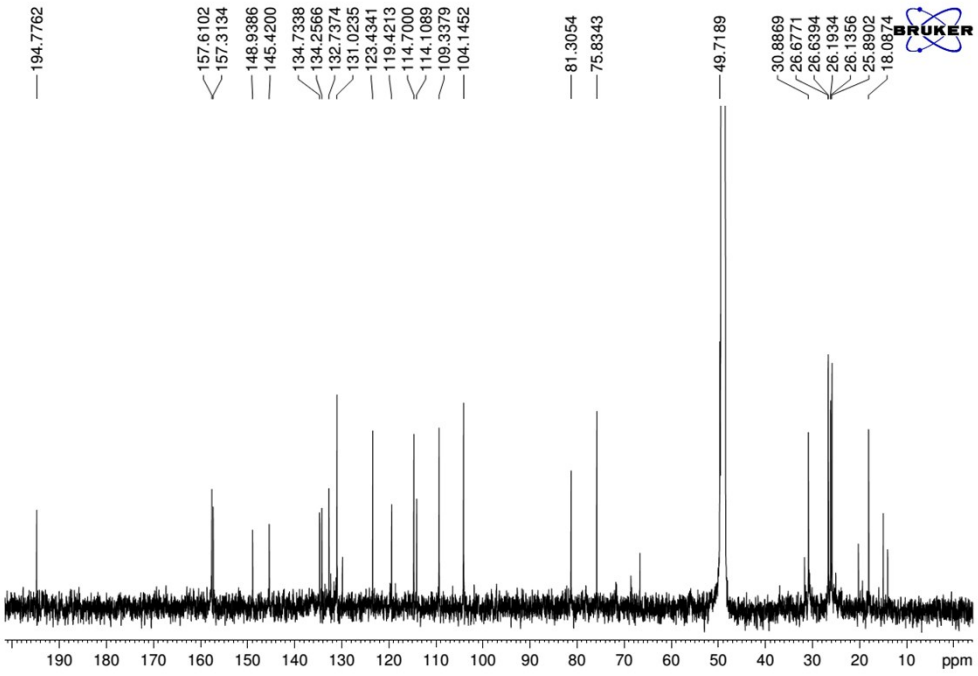


Figure S5.4 ^{13}C NMR spectrum (150 MHz, CD_3OD-d_4) of compound **5**

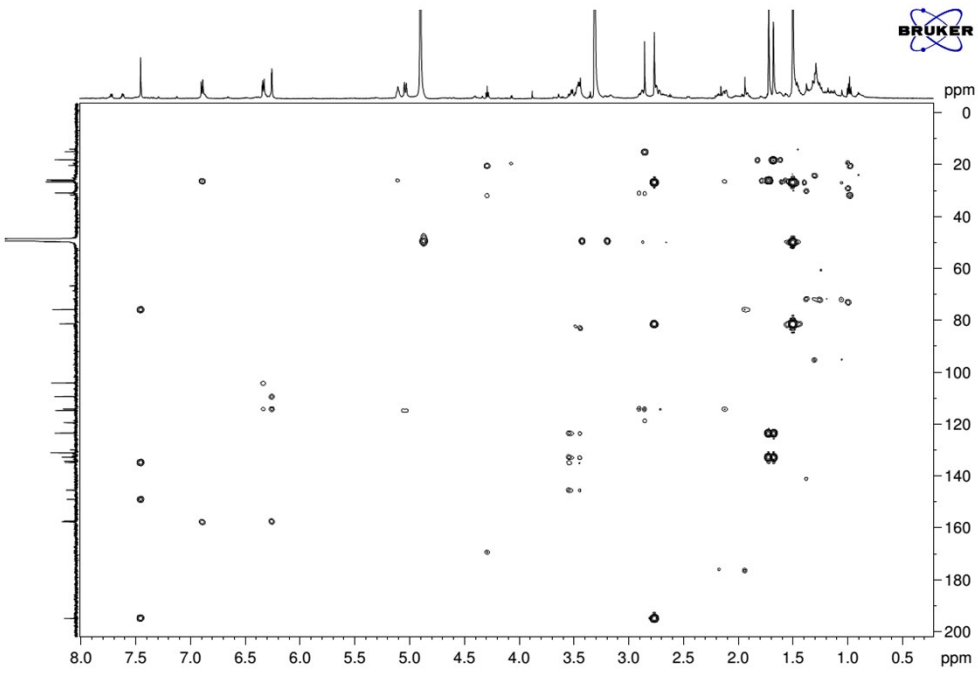


Figure S5.5 HMBC spectrum (600 MHz, CD_3OD-d_4) of compound **5**

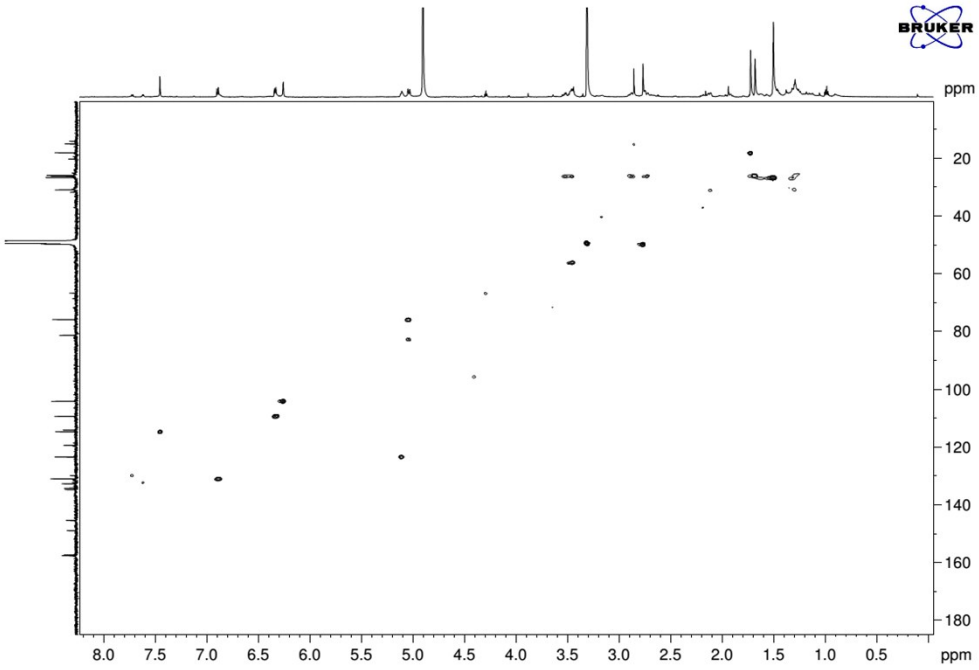


Figure S5.6 HSQC spectrum (600 MHz, CD_3OD-d_4) of compound **5**

Mass Spectrum Molecular Formula Report

Analysis Info

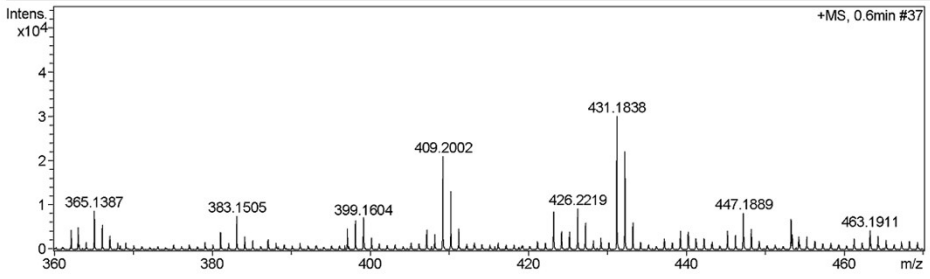
Analysis Name	D:\Data\20150710CEYANG\HRX-39_1-a,9_01_5472.d	Acquisition Date	7/10/2015 11:09:54 AM
Method	20131026_ceyang.m	Operator	micrOTOF-Q
Sample Name	HRX-39	Instrument / Ser#	Bruker Customer 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C25H28O5H				
Formula, max.					
Measured m/z	409.2	Tolerance	5 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	yes	Electron Configuration	both		
Filter H/C Ratio	yes	Minimum	0	Maximum	3
Estimate Carbon	yes				



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
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Figure S5.7 HRESIMS spectrum of compound **5**

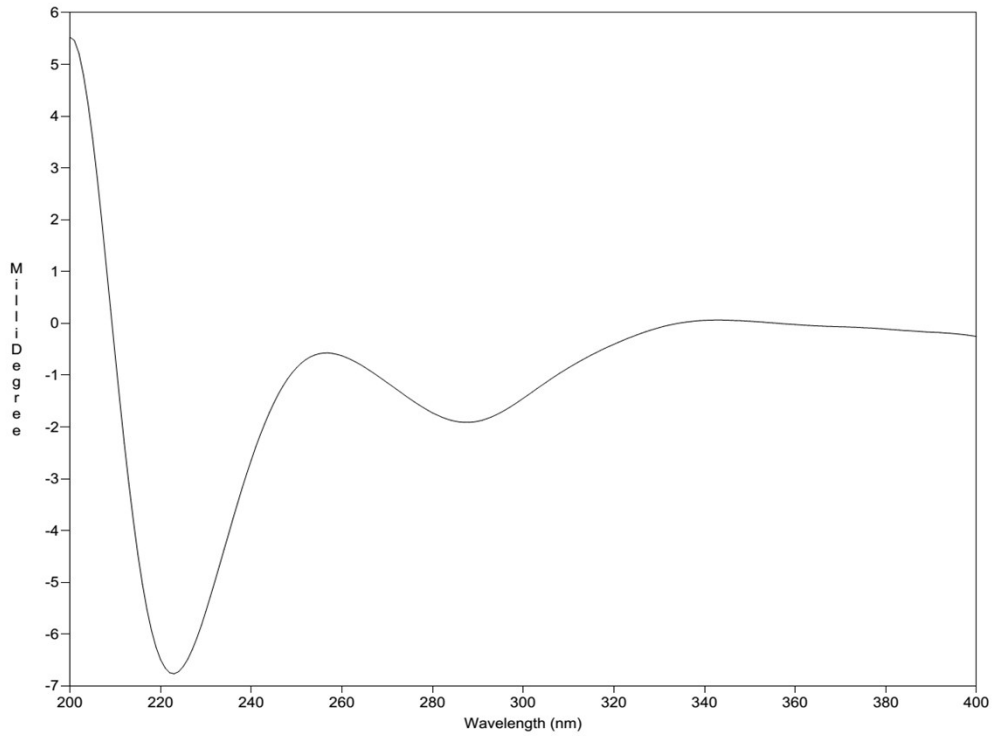
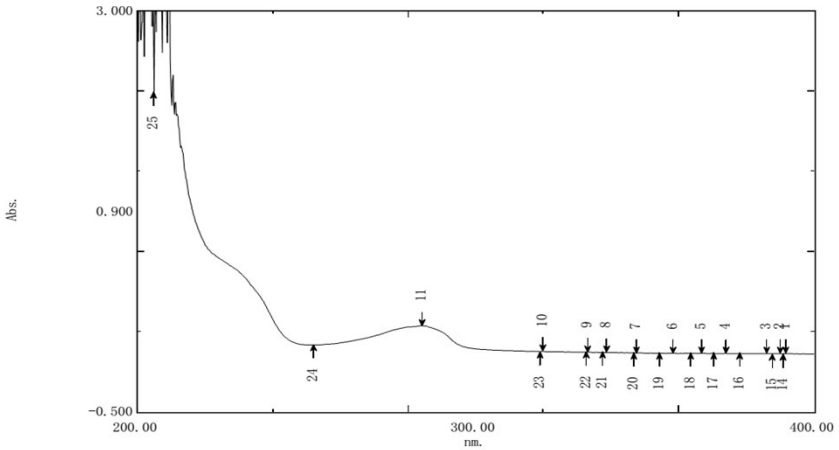


Figure S5.8 CD spectra of compound **5**



测定属性
波长范围 (nm.): 200.00到400.00
扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 364.0 nm
S/R 转换: 标准

附件属性
附件: 无

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2	↑	389.80	.007	
3	↑	386.00	.009	
4	↑	373.80	.010	
5	↑	366.60	.012	
6	↑	358.40	.013	
7	↑	347.40	.016	
8	↑	338.60	.019	
9	↑	333.20	.021	
10	↑	319.80	.028	
11	↑	284.20	.251	
12	↑	206.00	4.000	
13	↑	201.80	4.000	
14	↓	390.60	.006	
15	↓	387.40	.007	
16	↓	378.00	.007	
17	↓	370.20	.008	
18	↓	363.40	.008	
19	↓	354.40	.009	
20	↓	346.60	.014	
21	↓	337.60	.018	
22	↓	332.60	.020	
23	↓	319.00	.026	
24	↓	252.20	.084	
25	↓	205.00	2.290	

Figure S6.1 UV spectrum of compound **6**

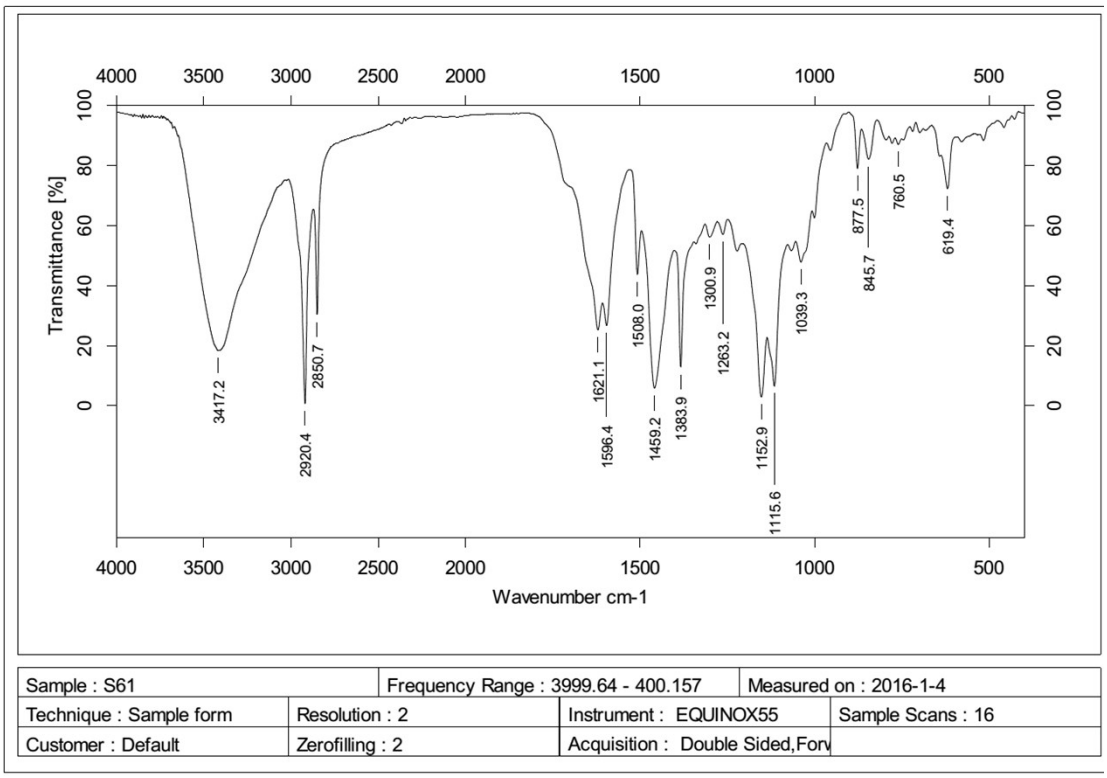


Figure S6.2 IR spectrum of compound **6**

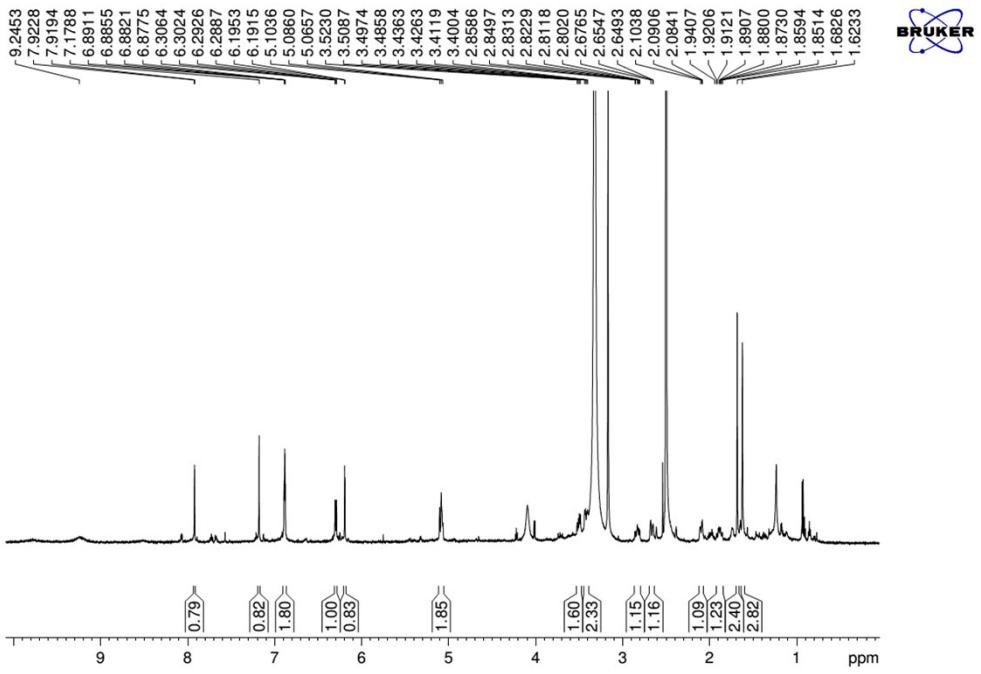


Figure S6.3 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **6**

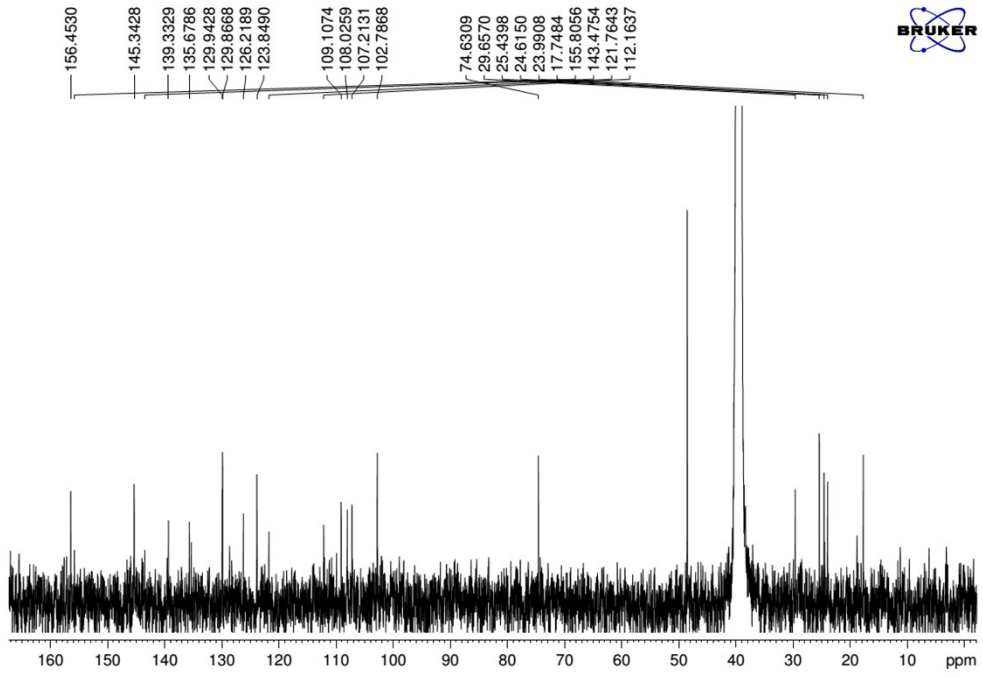


Figure S6.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **6**

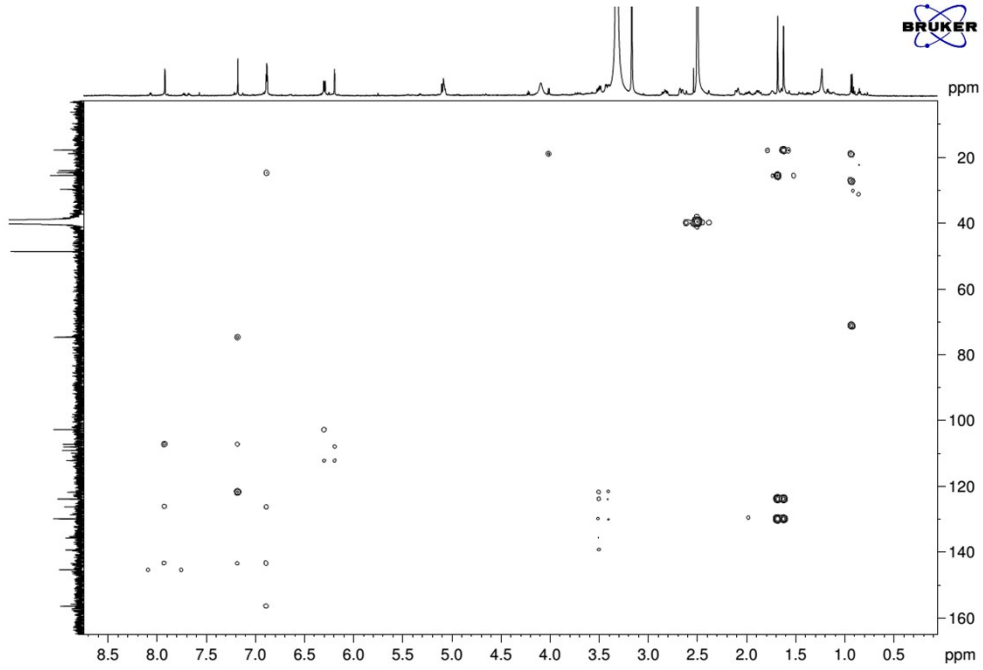


Figure S6.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **6**

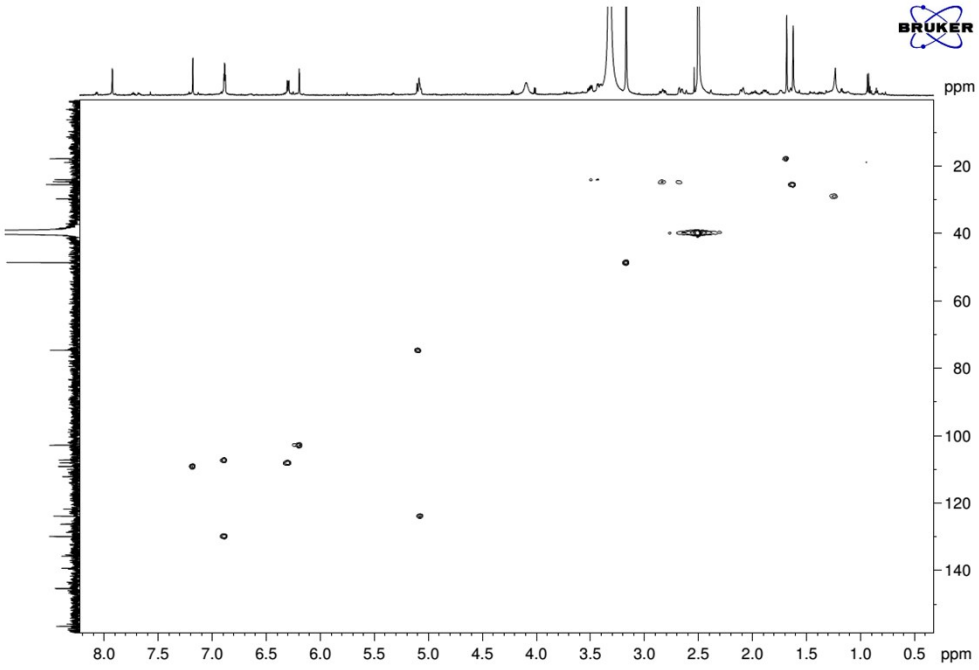


Figure S6.6 HSQC spectrum (600 MHz, DMSO-d_6) of compound **6**

Mass Spectrum Molecular Formula Report

Analysis Info

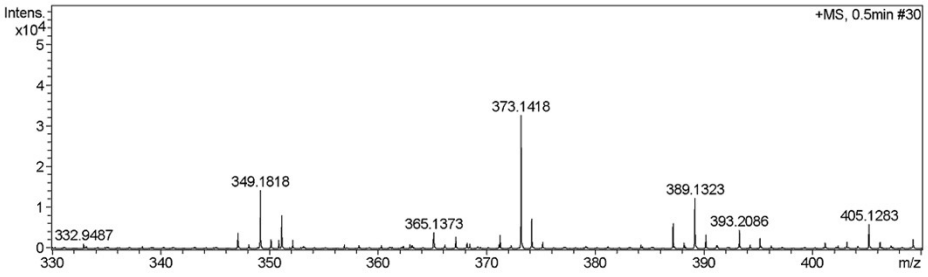
Analysis Name	D:\Data\20151113CEYANG\SQ-61_1-C,7_01_5936.d	Acquisition Date	11/13/2015 2:29:24 PM
Method	20131026_ceyang.m	Operator	micrOTOF-Q
Sample Name	SQ-61	Instrument / Ser#	Bruker Customer 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C22H22O4Na				
Formula, max.					
Measured m/z	373.142	Tolerance	5 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	yes	Electron Configuration	both		
Filter H/C Ratio	yes	Minimum	0	Maximum	3
Estimate Carbon	yes				



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
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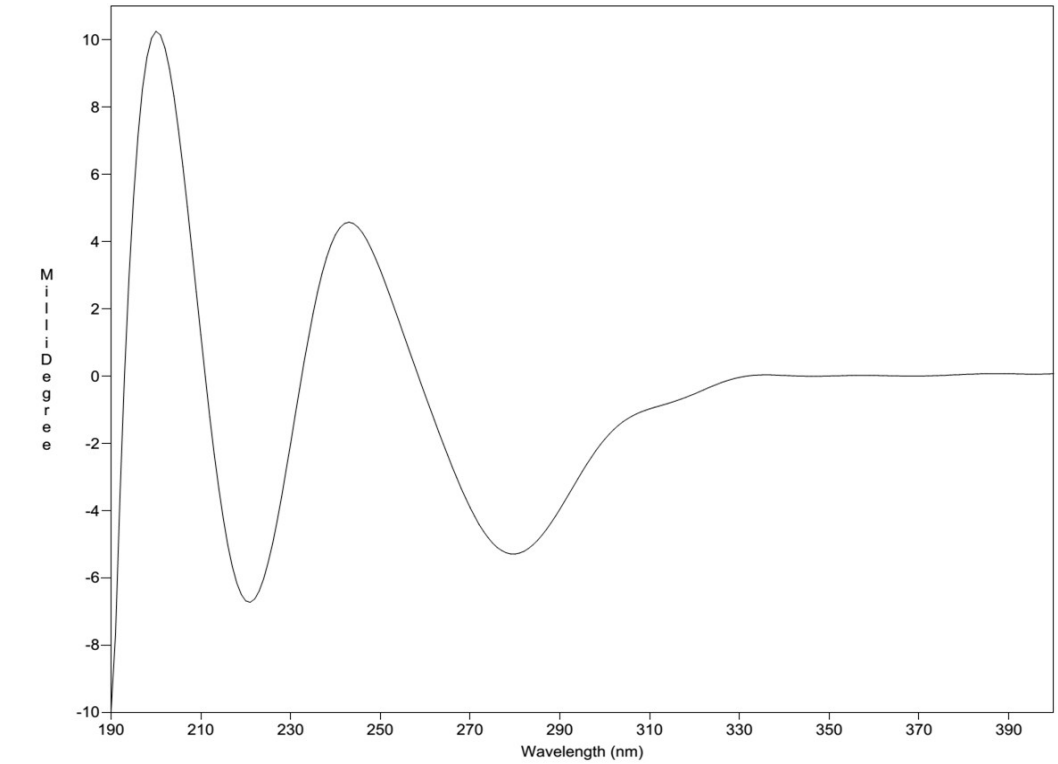
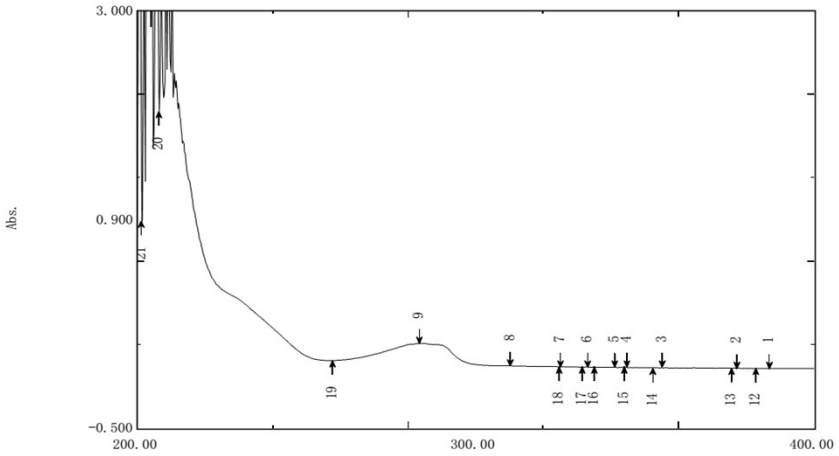
Figure S6.7 HRESIMS spectrum of compound **6**



Bio-Kine Software V4.74 Date : 2015-11-28 Time : 14:58:02

Figure S6.8 CD spectra of compound **6**



测定属性
波长范围 (nm.): 200.00到400.00
扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 364.0 nm
S/R 转换: 标准

附件属性
附件: 无

No.	P/V	Wavelength	Abs.	描述
1	↑	386.60	.003	
2	↑	377.00	.004	
3	↑	355.00	.009	
4	↑	344.60	.010	
5	↑	341.20	.012	
6	↑	333.20	.015	
7	↑	325.20	.017	
8	↑	310.20	.024	
9	↑	283.40	.212	
10	↑	209.20	4.000	
11	↑	202.80	4.000	
12	↓	382.60	.002	
13	↓	375.40	.002	
14	↓	352.20	.006	
15	↓	343.80	.009	
16	↓	335.00	.011	
17	↓	331.40	.013	
18	↓	324.60	.016	
19	↓	257.60	.068	
20	↓	206.60	2.157	
21	↓	201.40	1.230	

Figure S7.1 UV spectrum of compound **7**

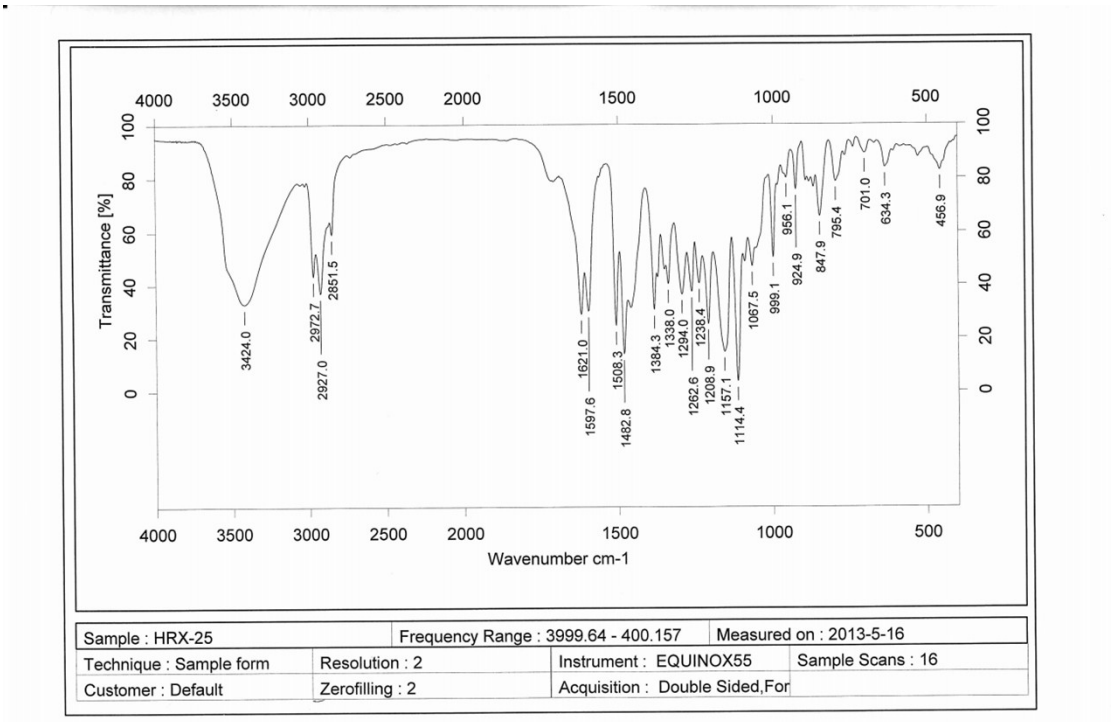


Figure S7.2 IR spectrum of compound **7**

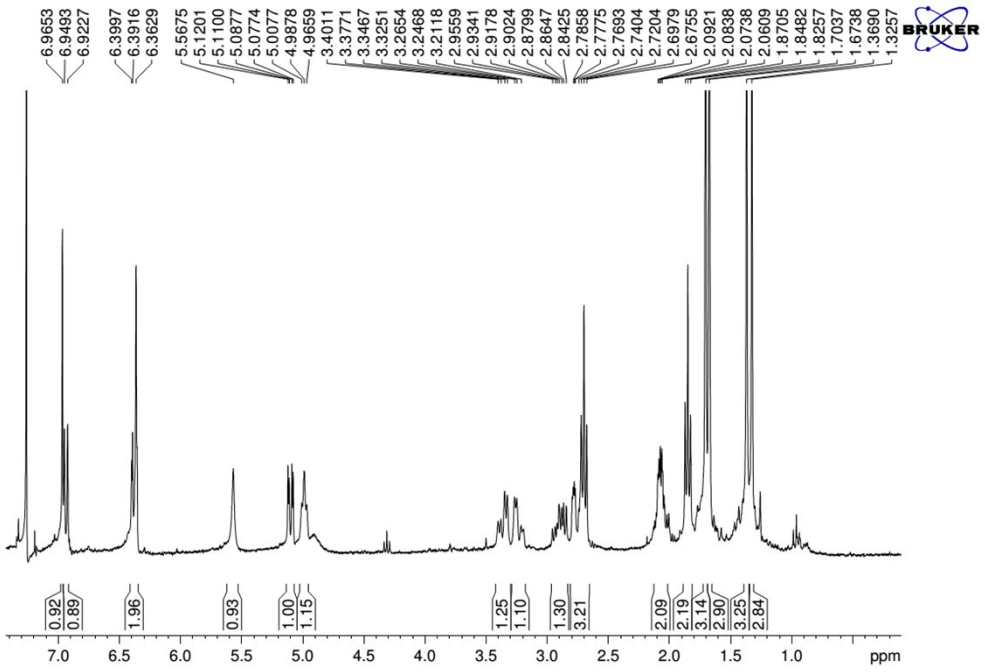


Figure S7.3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **7**

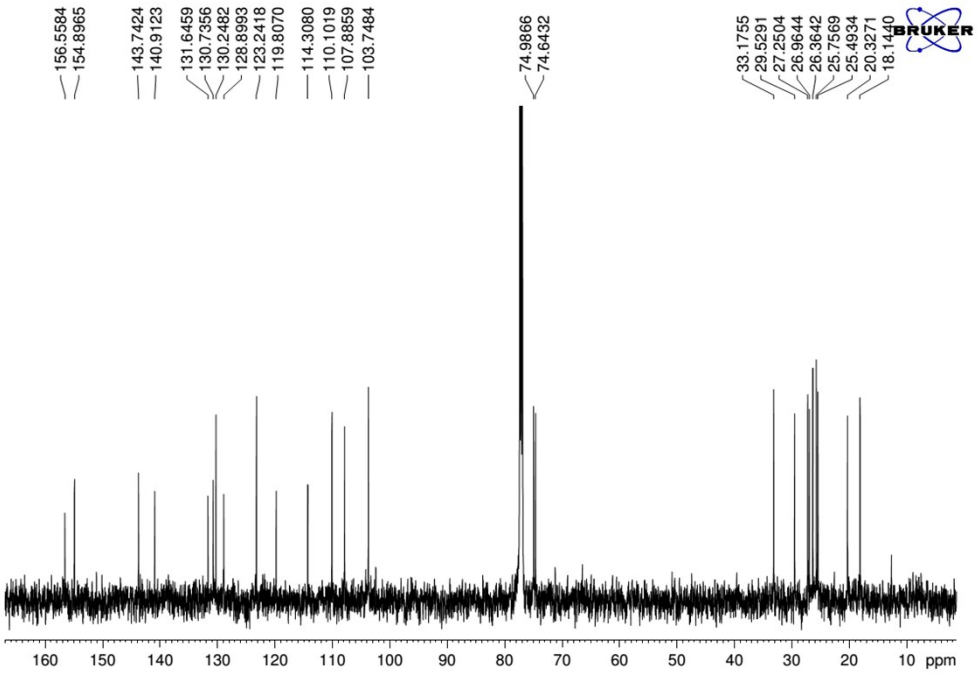


Figure S7.4 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **7**

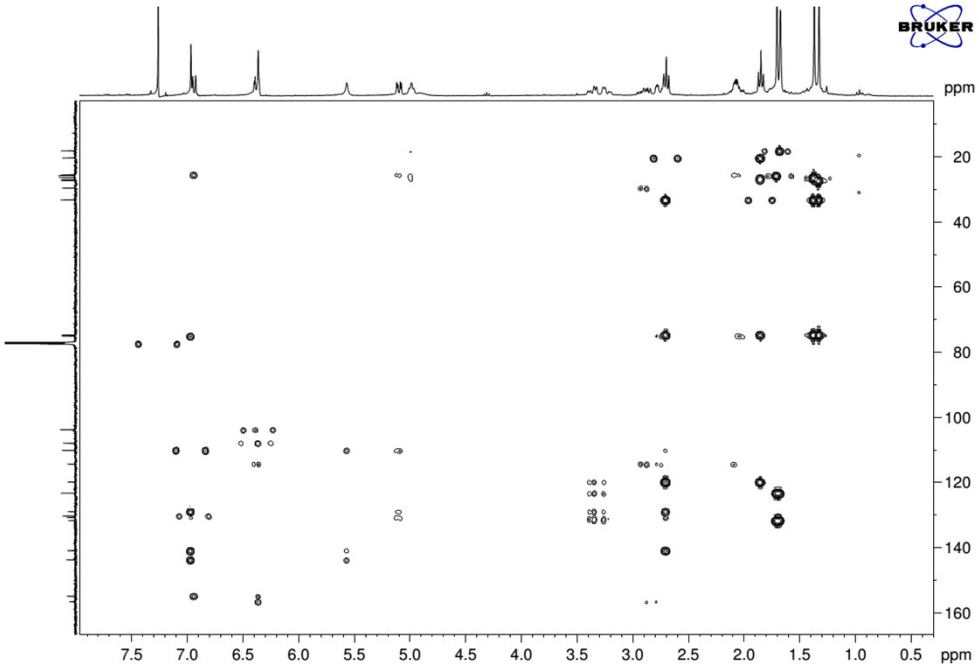


Figure S7.5 HMBC spectrum (600 MHz, $CDCl_3$) of compound **7**

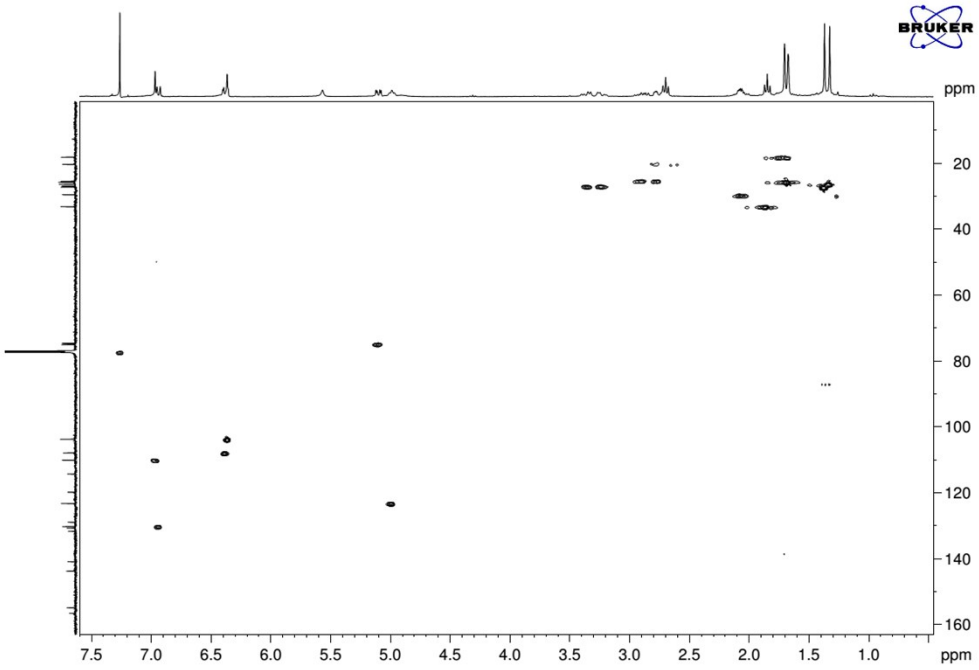


Figure S7.6 HSQC spectrum (600 MHz, $CDCl_3$) of compound **7**

Mass Spectrum Molecular Formula Report

Analysis Info

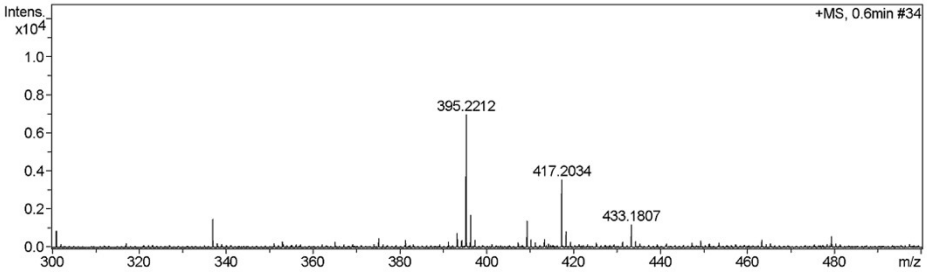
Analysis Name	D:\Data\20130620\HRX-25.d	Acquisition Date	6/20/2013 2:44:26 PM
Method	MA250-550POS.m	Operator	Bruker Customer
Sample Name	HRX-25	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

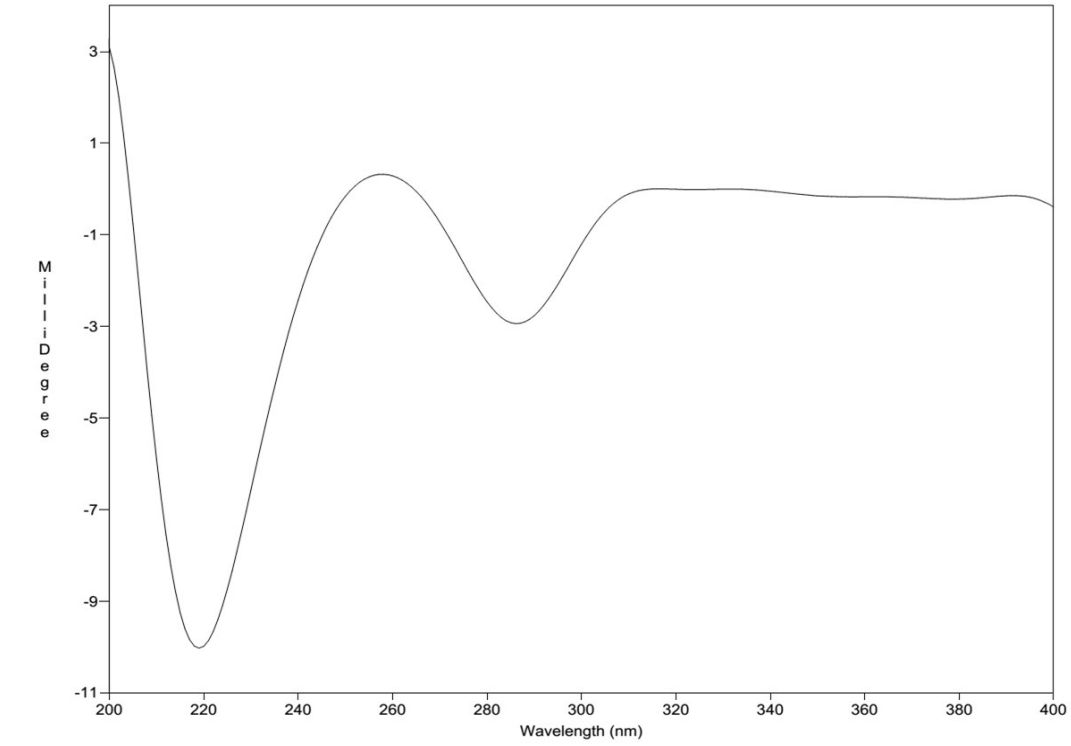
Formula, min.	C25H30O4Na						
Formula, max.							
Measured m/z	417.203	Tolerance	5	ppm	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 30 Na 1 O 4	0.161	417.2036	0.67	0.67	0.28	10.50	ok	even

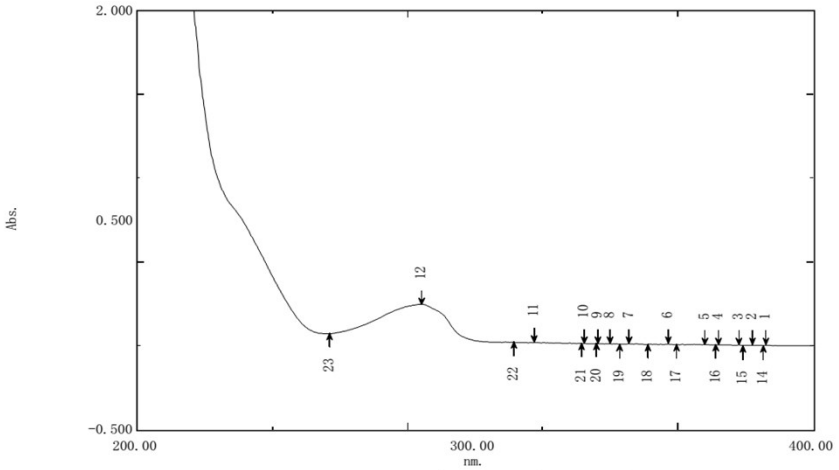
Bruker Daltonics DataAnalysis 3.4 printed: 6/27/2013 3:41:07 PM Page 1 of 1

Figure S7.7 HRESIMS spectrum of compound **7**



Bio-Kine Software V4.74 Date : 2015-11-30 Time : 14:49:04

Figure S7.8 CD spectra of compound **7**



测定属性
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扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 364.0 nm
S/R 转换: 标准

附件属性
附件: 无

No.	P/V	Wavelength	Abs.	描述
1	↑	386.00	.004	
2	↑	381.80	.005	
3	↑	378.00	.005	
4	↑	372.00	.007	
5	↑	368.00	.009	
6	↑	357.20	.012	
7	↑	345.40	.013	
8	↑	339.80	.013	
9	↑	336.40	.013	
10	↑	332.40	.016	
11	↑	317.60	.021	
12	↑	284.20	.249	
13	↑	213.20	4.000	
14	↓	385.20	.002	
15	↓	379.20	.003	
16	↓	371.20	.005	
17	↓	359.40	.007	
18	↓	351.00	.009	
19	↓	342.80	.011	
20	↓	335.80	.011	
21	↓	331.60	.013	
22	↓	311.40	.020	
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24	↓	212.80	3.806	

Figure S8.1 UV spectrum of compound **8**

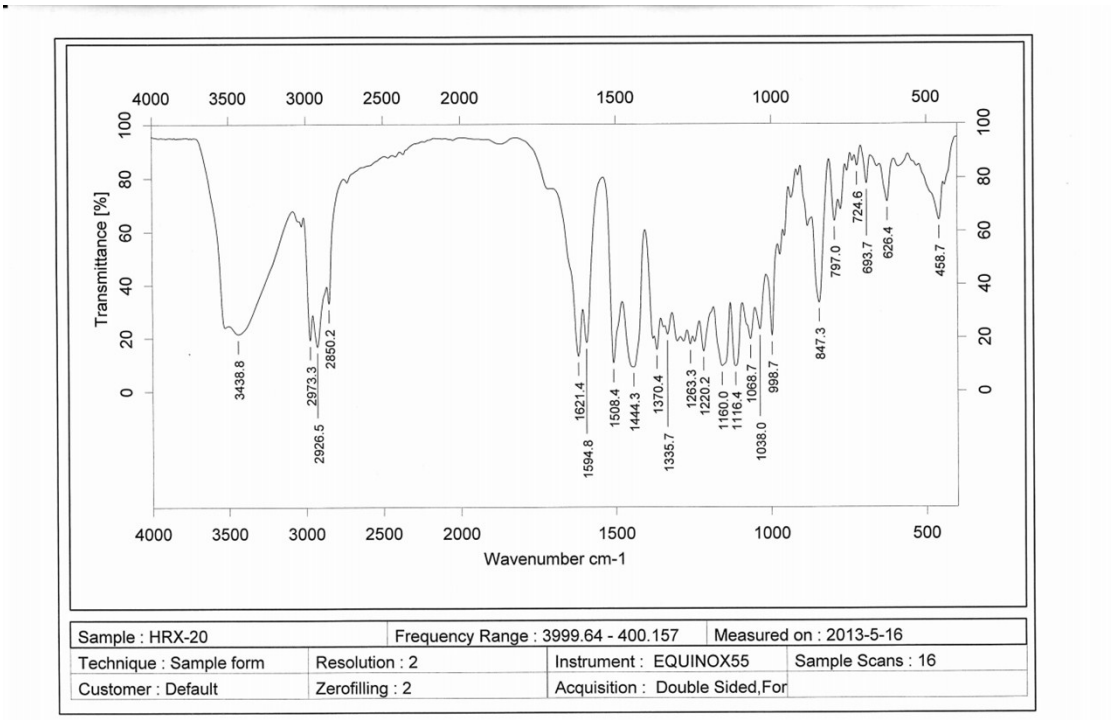


Figure S8.2 IR spectrum of compound **8**

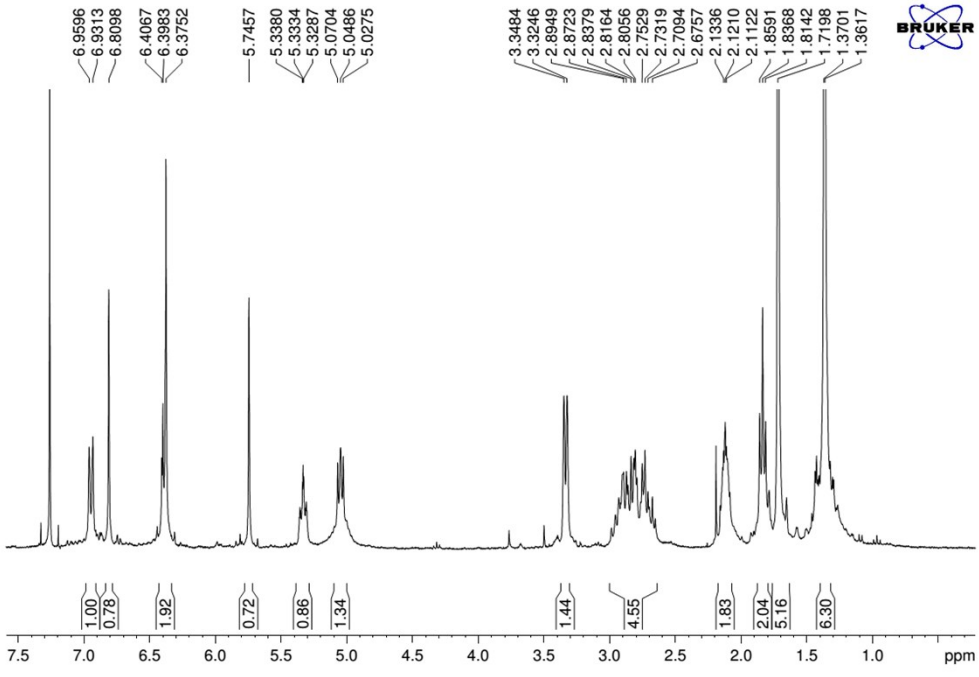


Figure S8.3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **8**

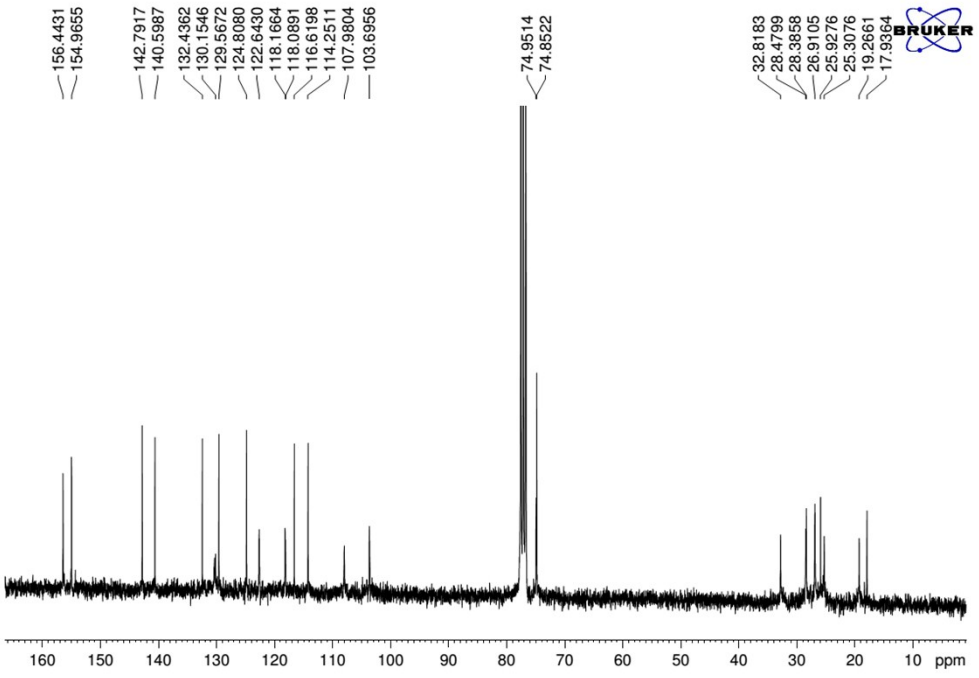


Figure S8.4 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **8**

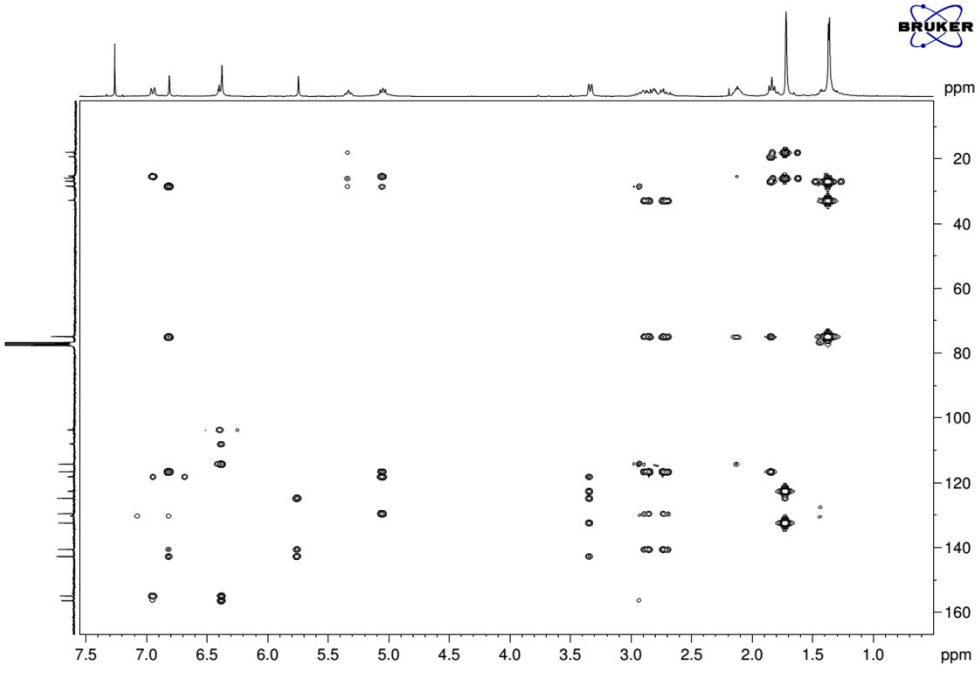


Figure S8.5 HMBC spectrum (600 MHz, $CDCl_3$) of compound **8**

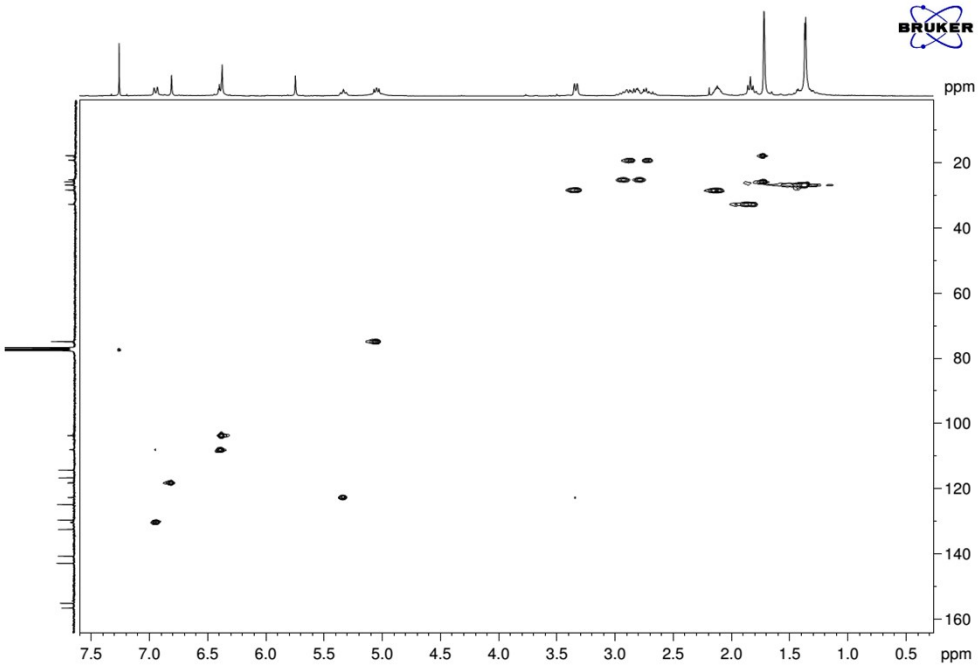


Figure S8.6 HSQC spectrum (600 MHz, $CDCl_3$) of compound **8**

Mass Spectrum Molecular Formula Report

Analysis Info

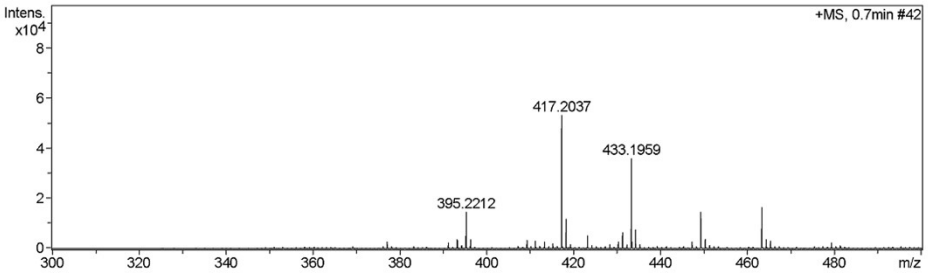
Analysis Name	D:\Data\20130516\HRX-20.d	Acquisition Date	5/16/2013 3:05:59 PM
Method	MA250-550POS.m	Operator	Bruker Customer
Sample Name	HRX-20	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

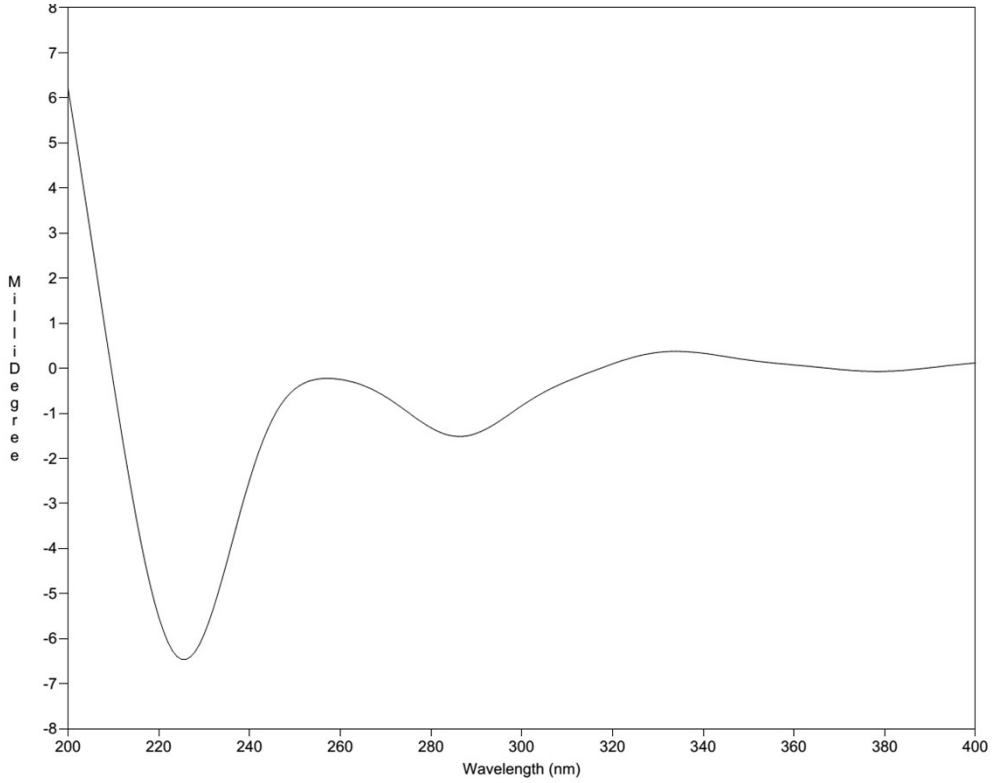
Generate Molecular Formula Parameter

Formula, min.	C25H30Na1O4				
Formula, max.					
Measured m/z	417.204	Tolerance	10 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	yes	Electron Configuration	both		
Filter H/C Ratio	no	Minimum	0	Maximum	3
Estimate Carbon	yes				



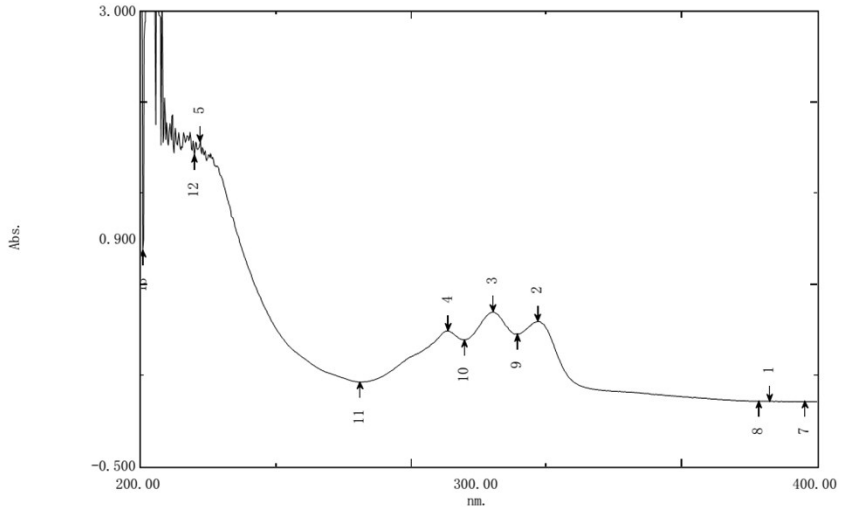
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 30 Na 1 O 4	0.161	417.2036	-0.23	-0.23	-0.09	10.50	ok	even

Figure S8.7 HRESIMS spectrum of compound **8**



Bio-Kine Software V4.74 Date : 2015-11-28 Time : 11:18:10

Figure S8.8 CD spectra of compound **8**



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扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性

No.	P/V	Wavelength	Abs.	描述
1	↑	386.00	.002	
2	↑	317.60	.615	
3	↑	304.40	.687	
4	↑	290.80	.542	
5	↑	217.80	1.997	
6	↑	201.80	4.000	
7	↓	396.20	-.002	
8	↓	382.60	.000	
9	↓	311.40	.516	
10	↓	295.80	.474	
11	↓	264.80	.149	
12	↓	216.00	1.890	
13	↓	200.80	1.160	

Figure S9.1 UV spectrum of compound **9**

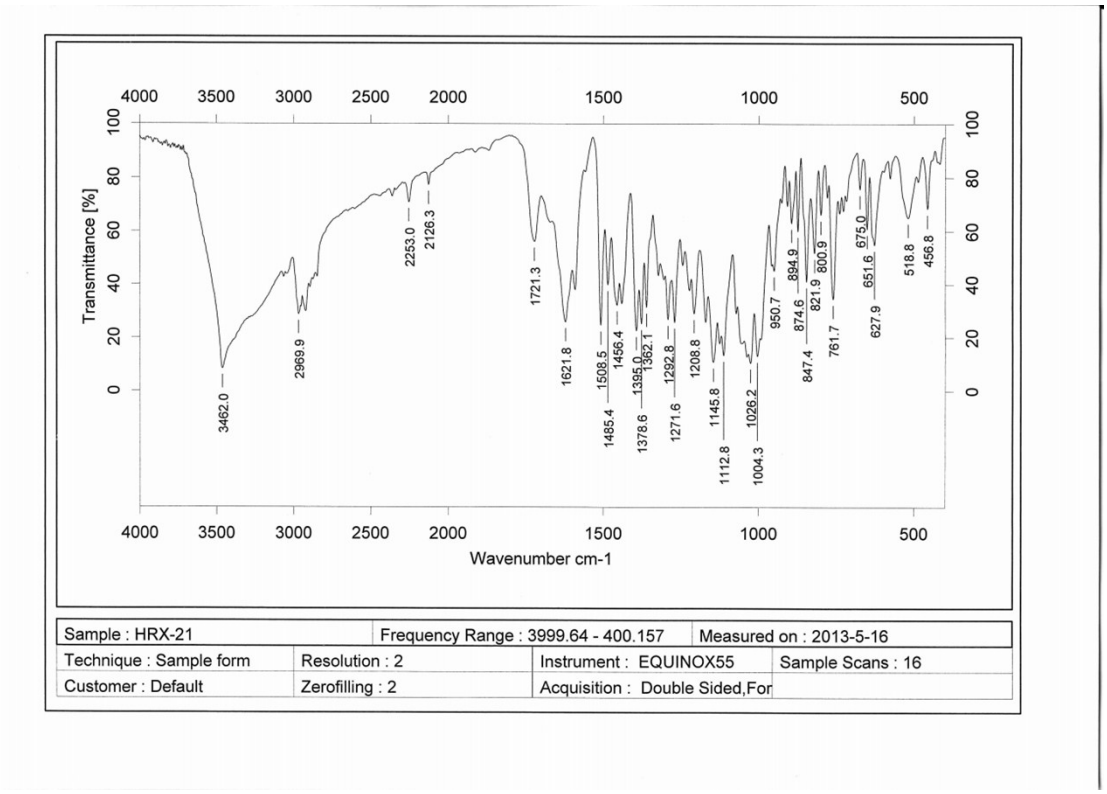


Figure S9.2 IR spectrum of compound **9**

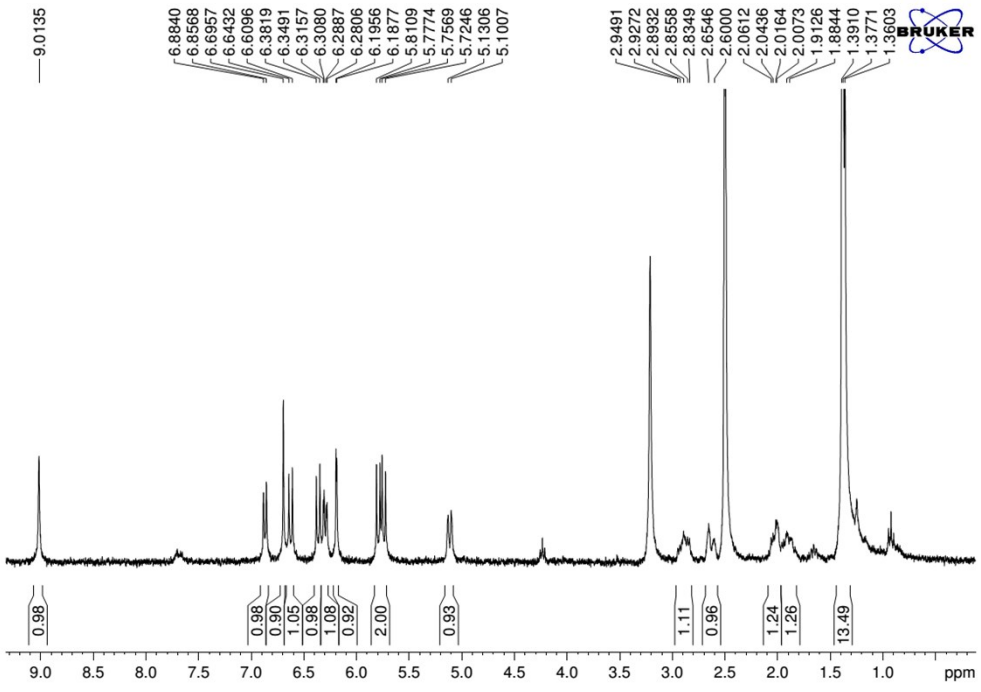


Figure S9.3 ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **9**

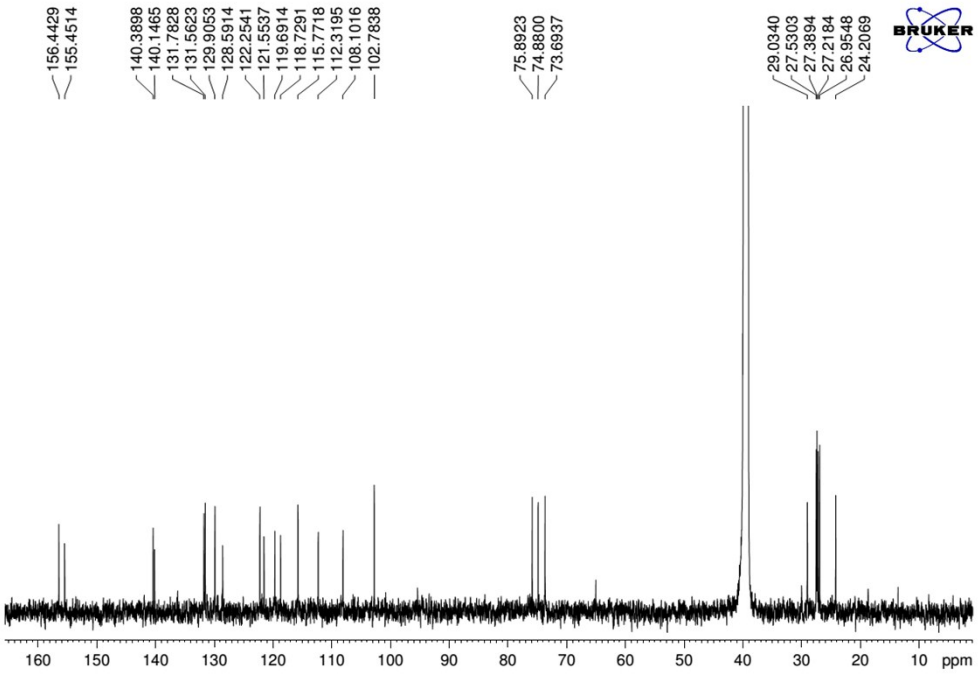


Figure S9.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **9**

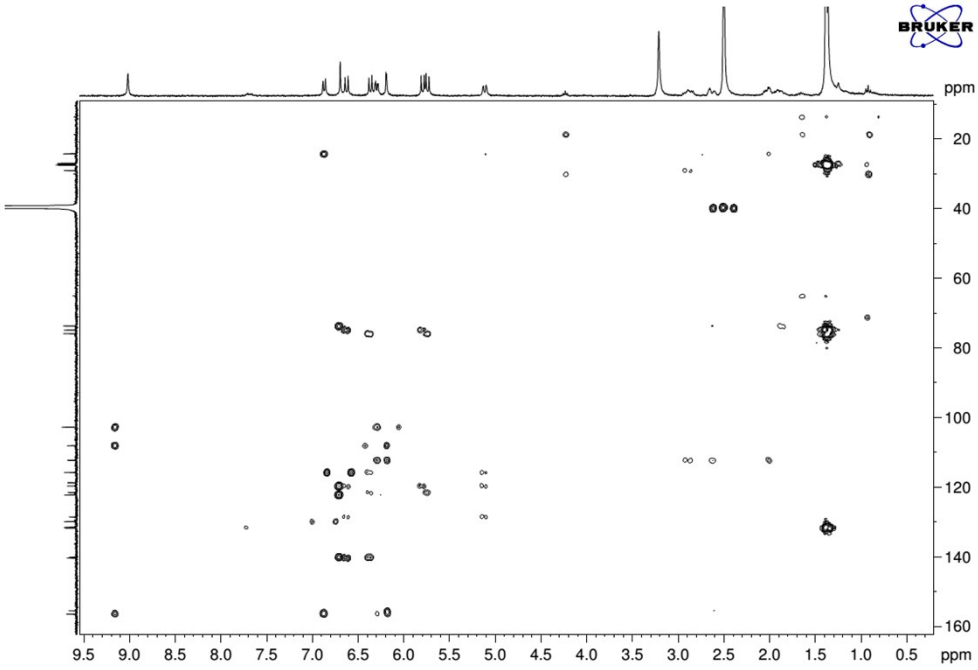


Figure S9.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **9**

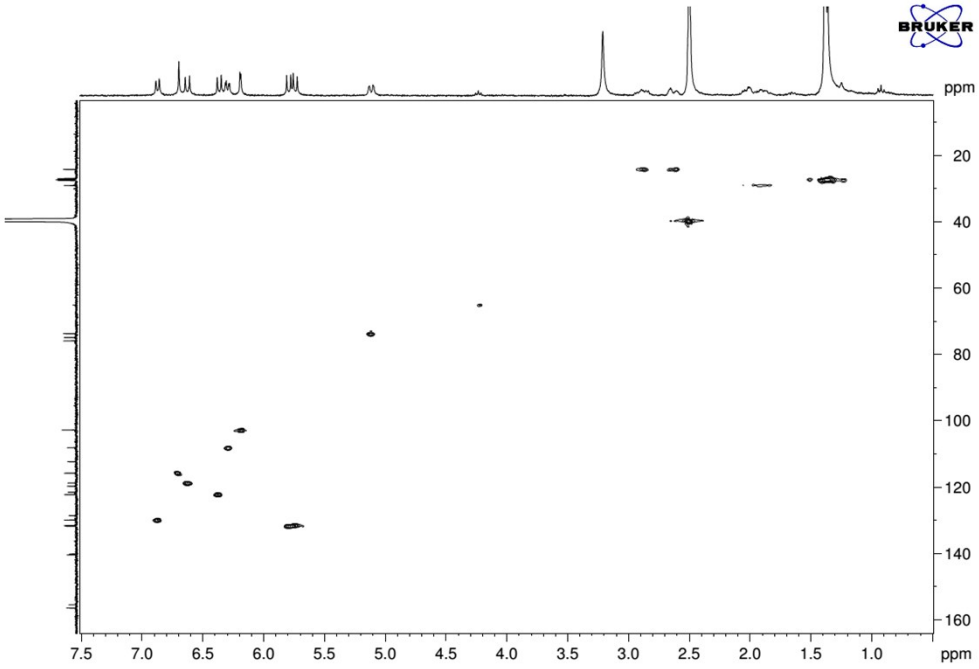


Figure S9.6 HSQC spectrum (600 MHz, DMSO-d_6) of compound **9**

Mass Spectrum Molecular Formula Report

Analysis Info

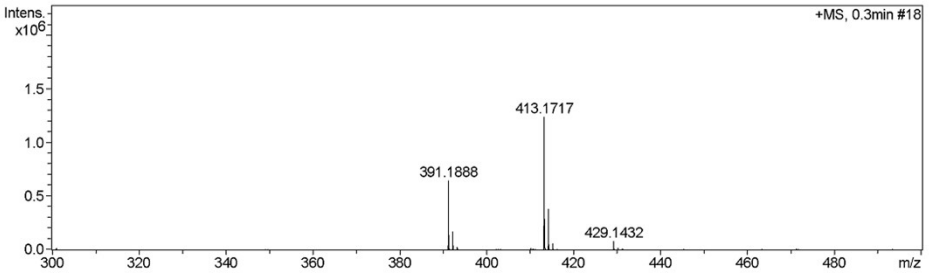
Analysis Name	D:\Data\20130516\HRX-21.d	Acquisition Date	5/16/2013 3:08:47 PM
Method	MA250-550POS.m	Operator	Bruker Customer
Sample Name	HRX-21	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C25H26Na1O4				
Formula, max.					
Measured m/z	413.172	Tolerance	10 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	yes	Electron Configuration	both		
Filter H/C Ratio	no	Minimum	0	Maximum	3
Estimate Carbon	yes				



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 26 Na 1 O 4	0.161	413.1723	1.54	1.54	0.64	12.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/9/2013 3:35:06 PM Page 1 of 1

Figure S9.7 HRESIMS spectrum of compound **9**

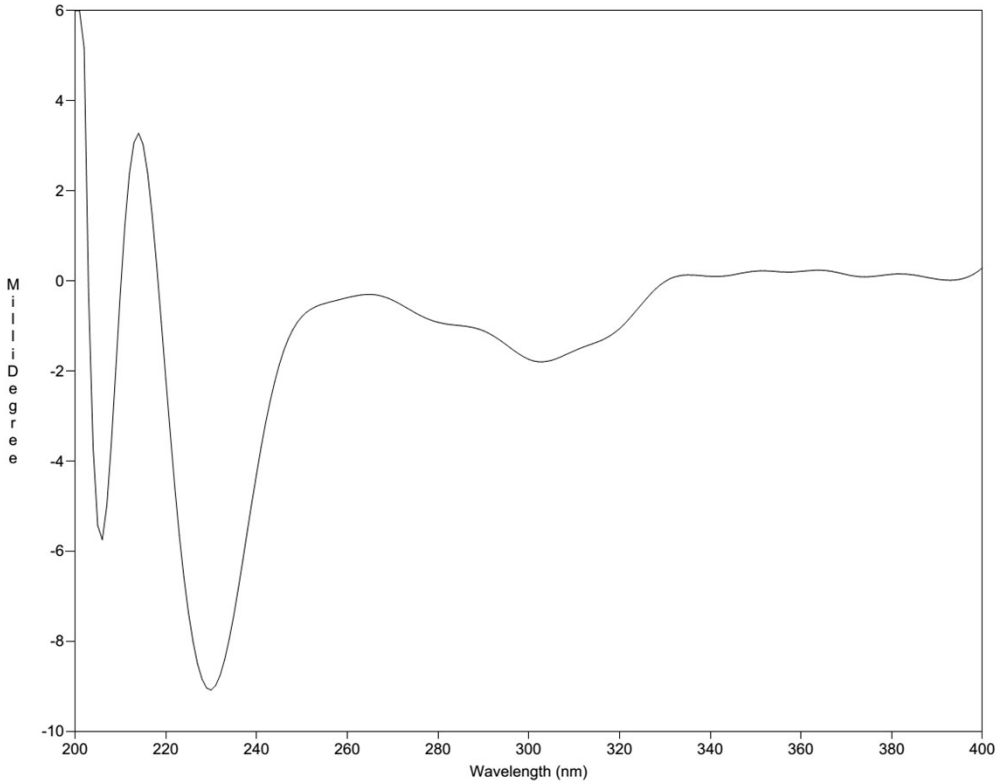
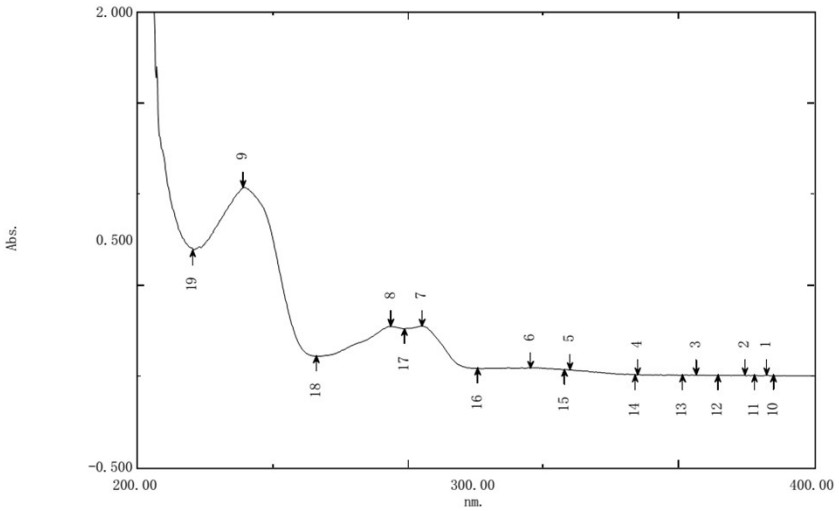


Figure S9.8 CD spectra of compound **9**



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波长范围 (nm.):	200.00到400.00
扫描速度:	高速
采样间隔:	0.2
自动采样间隔:	停用
扫描模式:	单一的
试样准备属性	
重量:	
体积 :	
稀释:	
光程长:	
附加信息:	
仪器属性	
仪器类型:	UV-1700
测定方式:	吸收值
狭缝宽:	1.0 nm
光源改变波长:	364.0 nm
S/R 转换:	标准

No.	P/V	Wavelength	Abs.	描述
1	↑	385.80	.006	
2	↑	379.40	.006	
3	↑	365.20	.008	
4	↑	348.00	.011	
5	↑	327.80	.037	
6	↑	316.40	.048	
7	↑	284.00	.277	
8	↑	274.80	.274	
9	↑	231.40	1.038	
10	↓	387.80	.004	
11	↓	382.40	.004	
12	↓	371.60	.005	
13	↓	361.00	.005	
14	↓	347.20	.009	
15	↓	326.20	.036	
16	↓	300.60	.043	
17	↓	279.00	.261	
18	↓	253.00	.111	
19	↓	216.60	.696	

Figure S10.1 UV spectrum of compound **10**

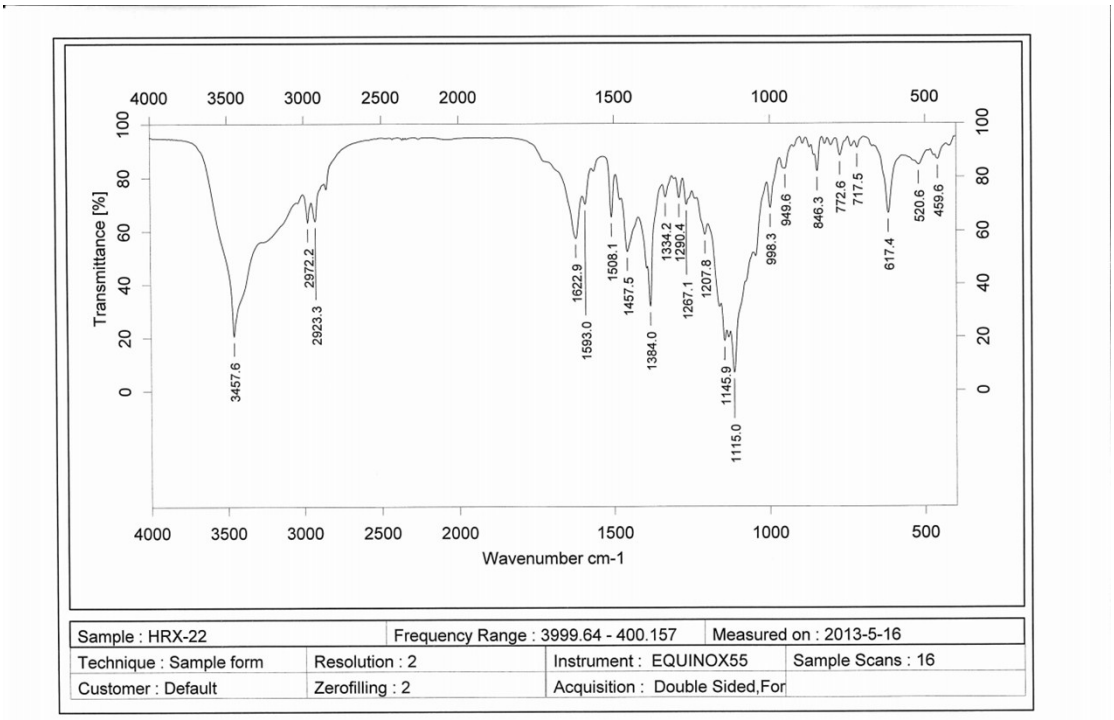


Figure S10.2 IR spectrum of compound **10**

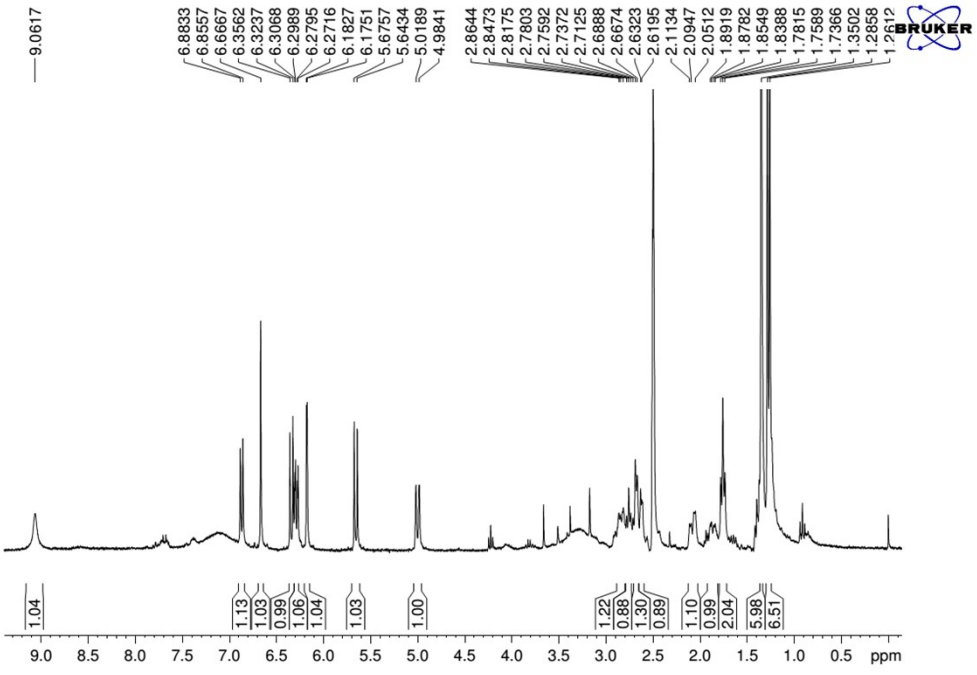


Figure S10.3 ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **10**

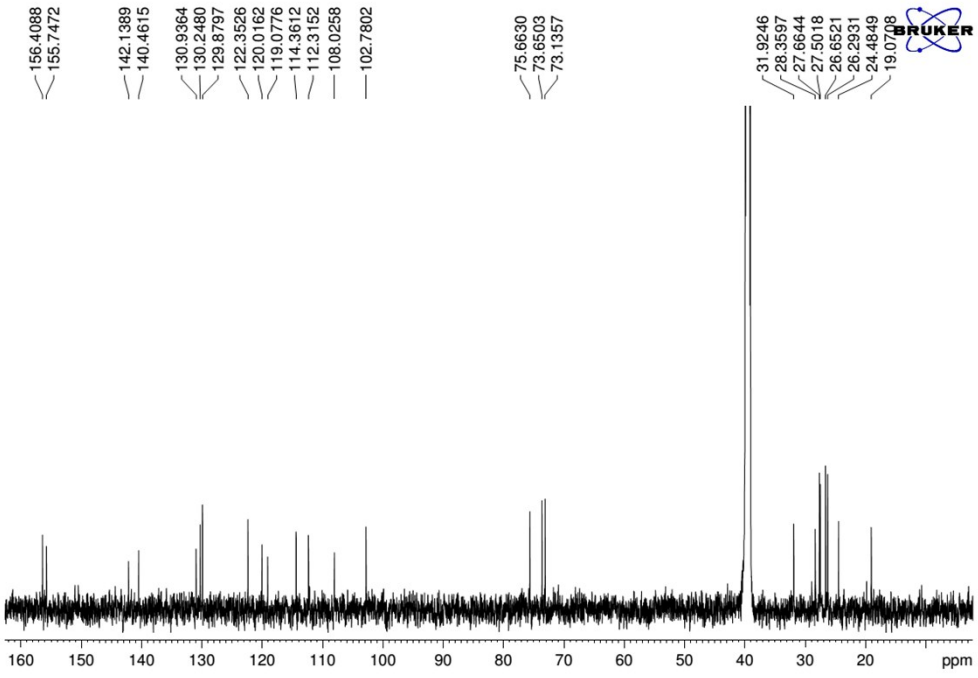


Figure S10.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **10**

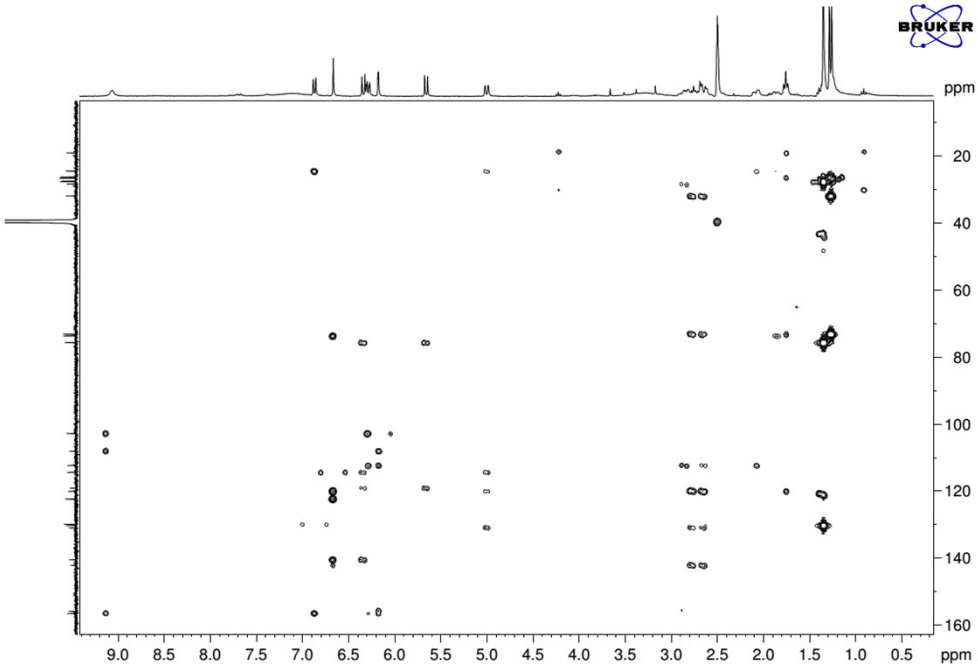


Figure S10.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **10**

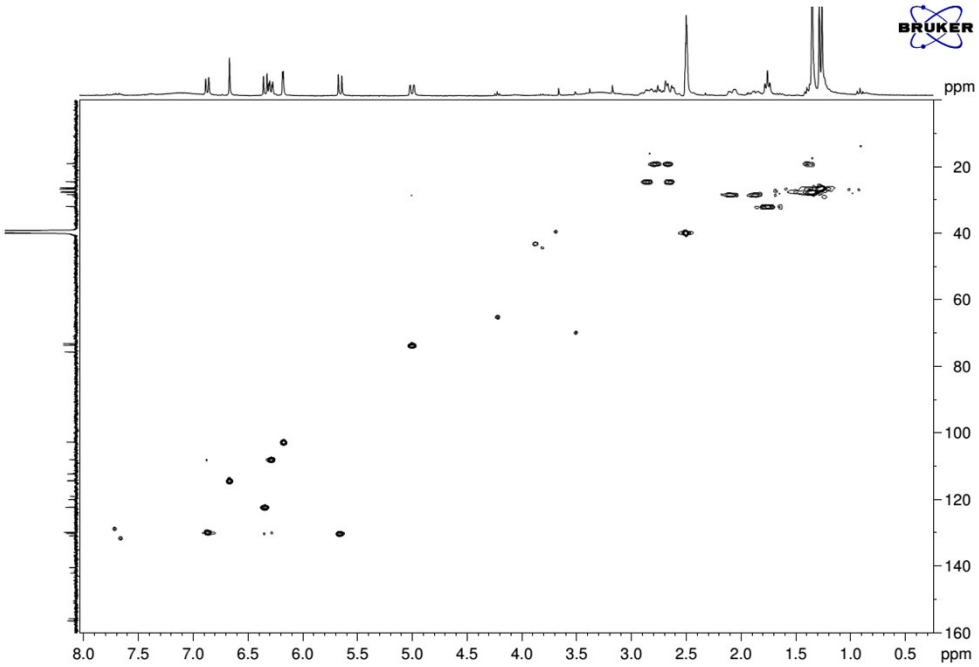


Figure S10.6 HSQC spectrum (600 MHz, DMSO-d_6) of compound **10**

Mass Spectrum Molecular Formula Report

Analysis Info

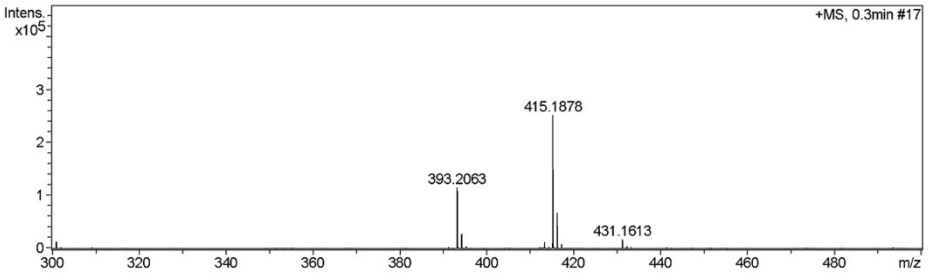
Analysis Name	D:\Data\20130516\HRX-22.d	Acquisition Date	5/16/2013 3:13:19 PM
Method	MA250-550POS.m	Operator	Bruker Customer
Sample Name	HRX-22	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C25H28Na1O4				
Formula, max.					
Measured m/z	415.188	Tolerance	10 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	yes	Electron Configuration	both		
Filter H/C Ratio	no	Minimum	0	Maximum	3
Estimate Carbon	yes				



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 28 Na 1 O 4	0.161	415.1880	0.46	0.46	0.19	11.50	ok	even

Figure S10.7 HRESIMS spectrum of compound **10**

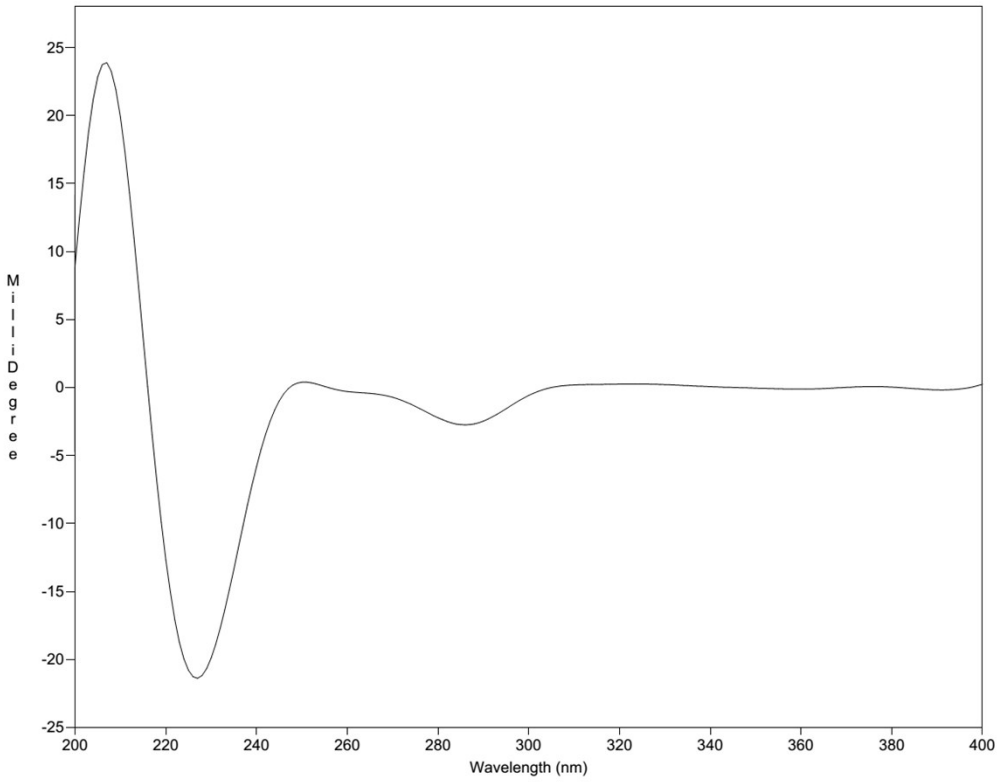
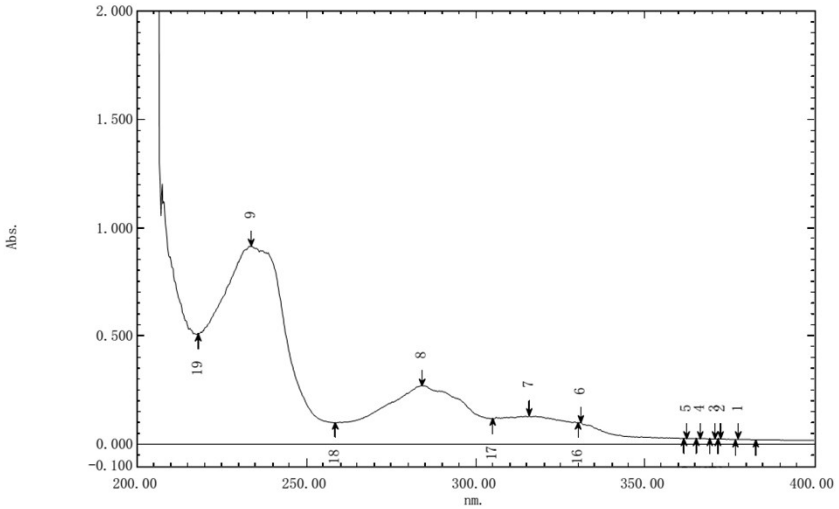


Figure S10.8 CD spectra of compound **10**



测定属性

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扫描速度:	高速
采样间隔:	0.2
自动采样间隔:	停用
扫描模式:	单一的

试样准备属性

重量:	0.3
体积 :	10
稀释:	
光程长:	407
附加信息:	

仪器属性

仪器类型:	UV-1700
测定方式:	吸收值
狭缝宽:	1.0 nm
光源改变波长:	340.8 nm
S/R 转换:	标准

No.	P/V	Wavelength	Abs.	描述
1	↑	377.60	.023	
2	↑	372.40	.025	
3	↑	370.80	.025	
4	↑	366.20	.027	
5	↑	362.40	.028	
6	↑	331.20	.100	
7	↑	315.80	.130	
8	↑	284.20	.271	
9	↑	233.60	.915	
10	↓	382.60	.020	
11	↓	376.80	.022	
12	↓	371.60	.023	
13	↓	369.00	.024	
14	↓	365.20	.025	
15	↓	361.40	.026	
16	↓	330.40	.099	
17	↓	305.20	.116	
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19	↓	218.00	.507	

Figure S11.1 UV spectrum of compound **11**

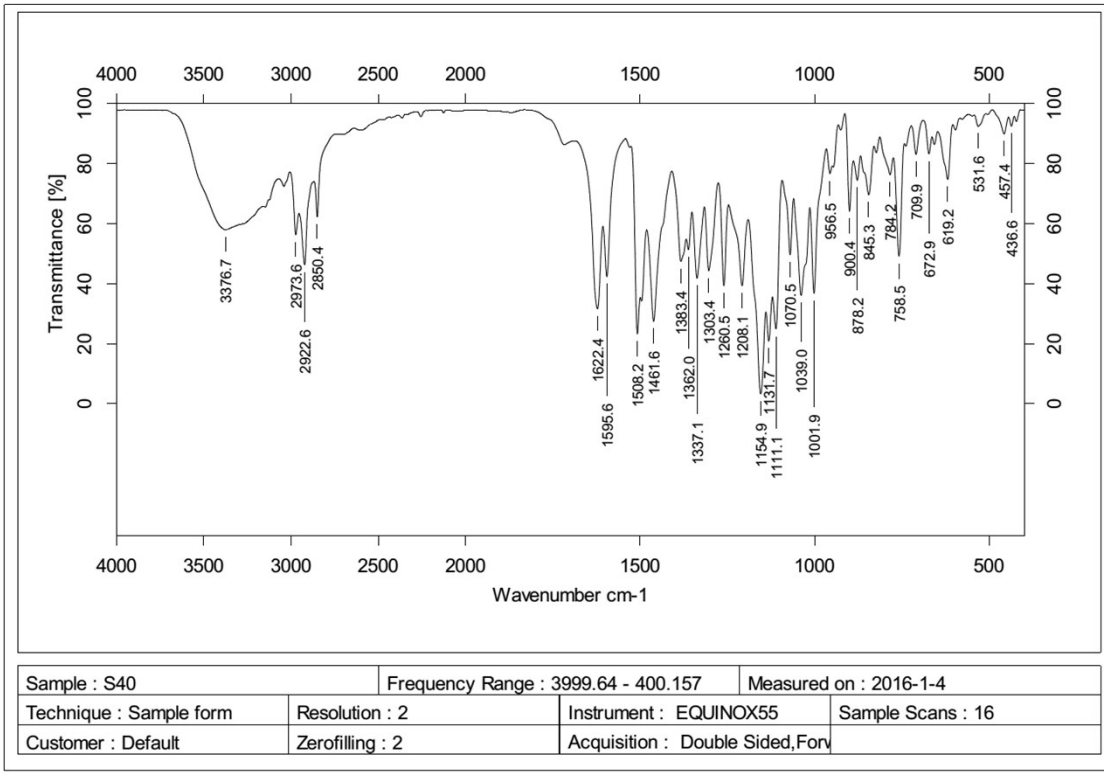


Figure S11.2 IR spectrum of compound **11**

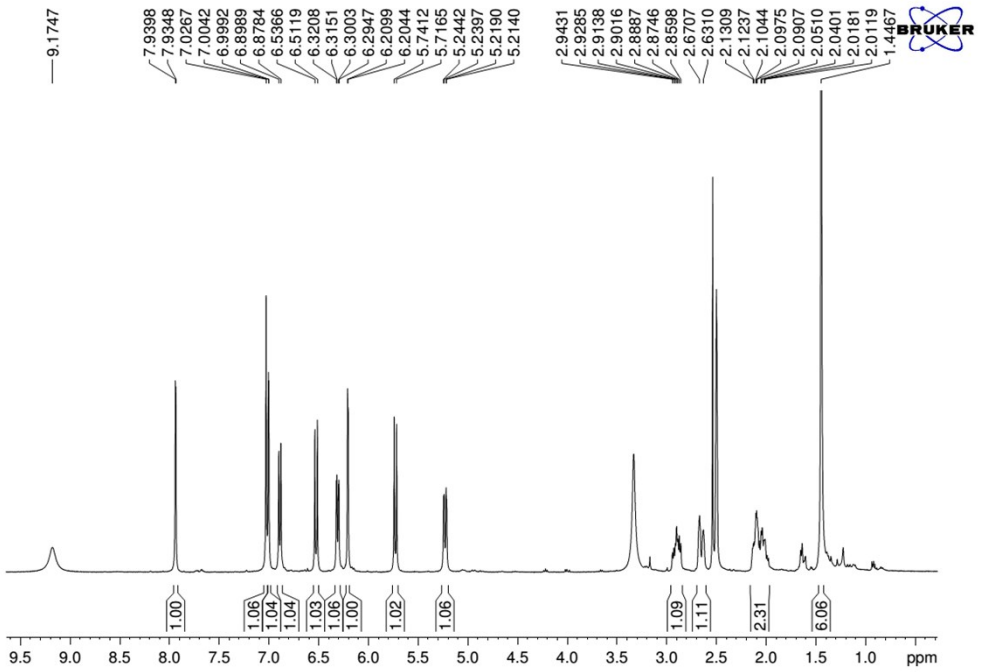


Figure S11.3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **11**

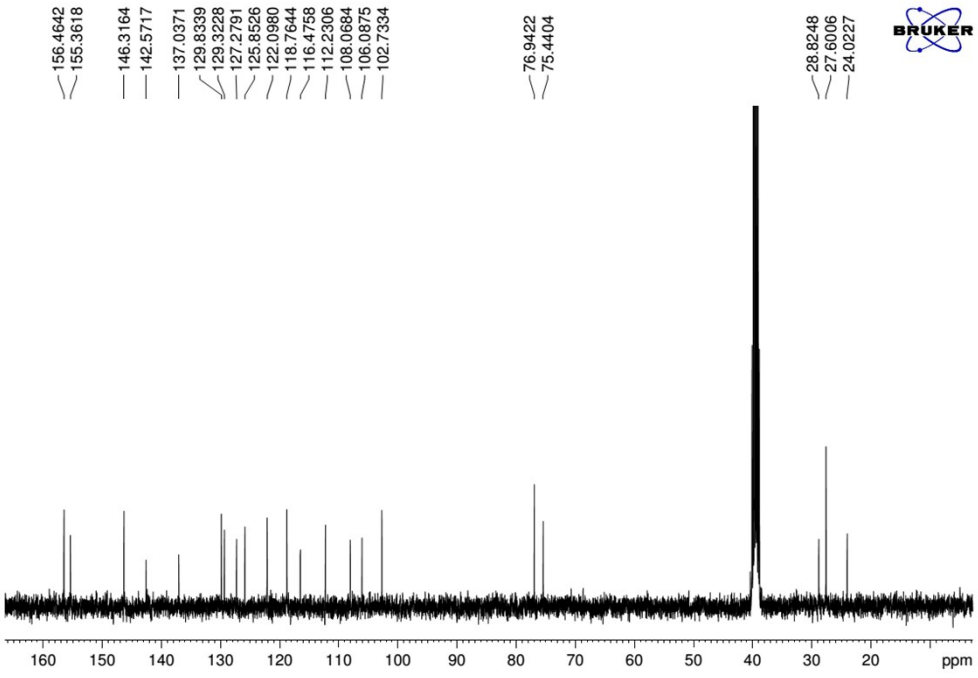


Figure S11.4 ^{13}C NMR spectrum (100 MHz,DMSO-d_6) of compound **11**

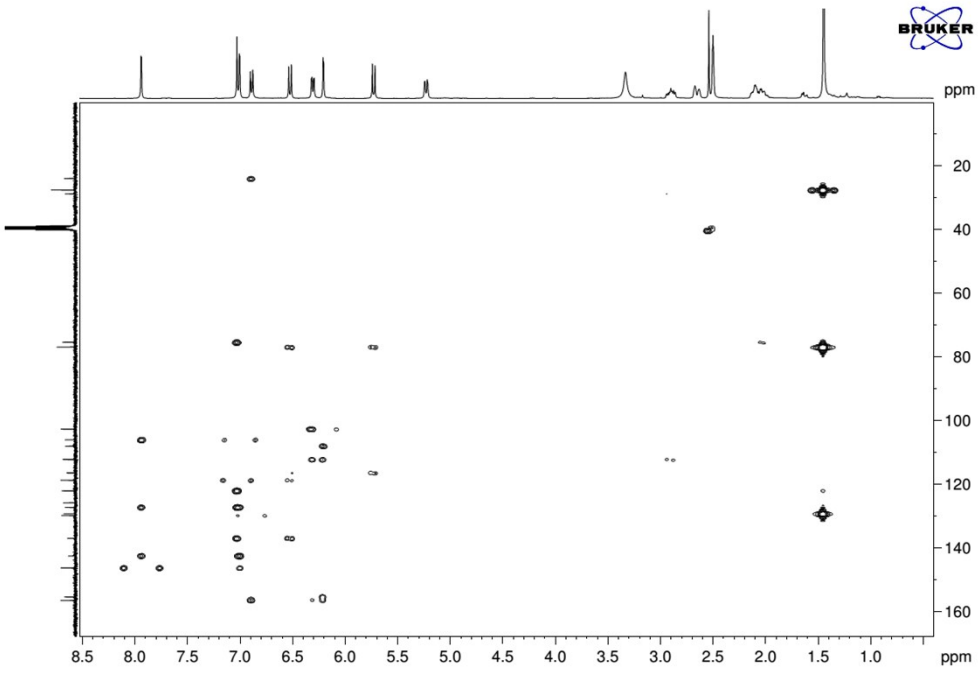
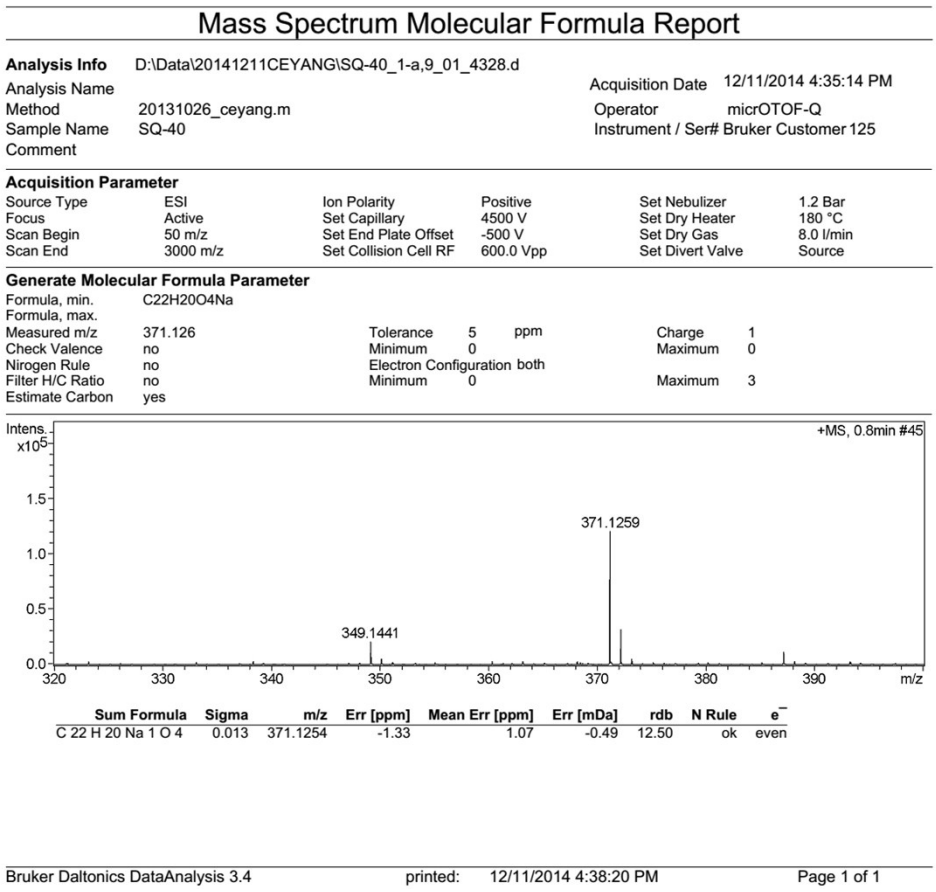


Figure S11.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **11**



Mass Spectrum Molecular Formula Report

Analysis Info D:\Data\20141211CEYANG\SQ-40_1-a,9_01_4328.d
Analysis Name
Method 20131026_ceyang.m
Sample Name SQ-40
Comment
Acquisition Date 12/11/2014 4:35:14 PM
Operator micrOTOF-Q
Instrument / Ser# Bruker Customer 125

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C22H20O4Na				
Formula, max.					
Measured m/z	371.126	Tolerance	5 ppm	Charge	1
Check Valence	no	Minimum	0	Maximum	0
Nirogen Rule	no	Electron Configuration	both		
Filter H/C Ratio	no	Minimum	0	Maximum	3
Estimate Carbon	yes				

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 22 H 20 Na 1 O 4	0.013	371.1254	-1.33	1.07	-0.49	12.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 12/11/2014 4:38:20 PM Page 1 of 1

Figure S11.6 HRESIMS spectrum of compound **11**

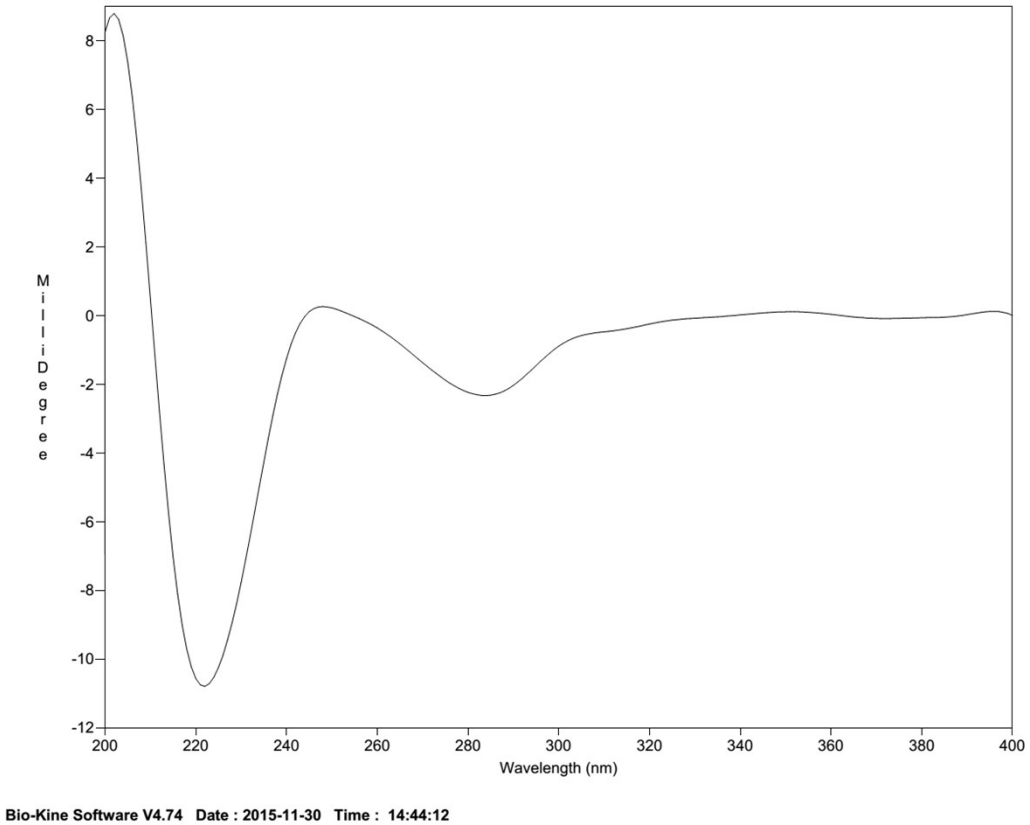
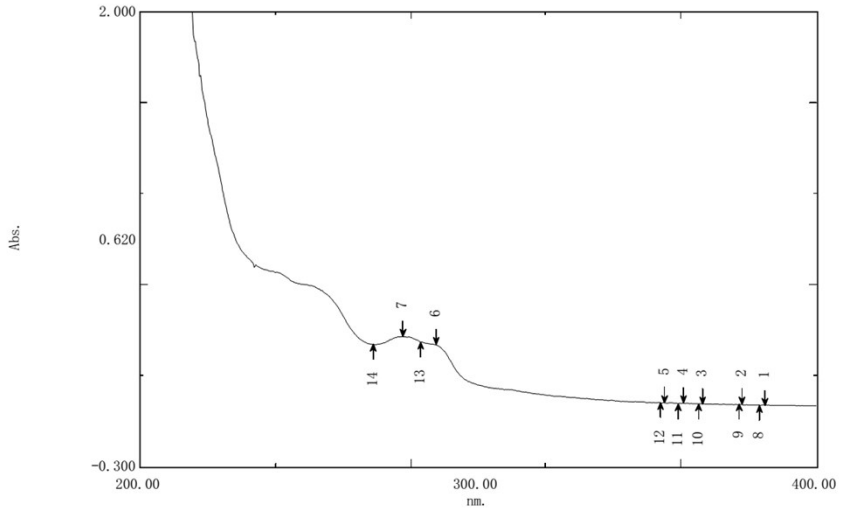


Figure S11.7 CD spectra of compound **11**



测定属性
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扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700

No.	P/V	Wavelength	Abs.	描述
1	↑	384.60	.012	
2	↑	377.80	.013	
3	↑	366.20	.019	
4	↑	360.80	.021	
5	↑	355.00	.025	
6	↑	284.60	.316	
7	↑	277.60	.358	
8	↓	383.20	.010	
9	↓	377.00	.012	
10	↓	365.20	.017	
11	↓	359.00	.018	
12	↓	354.00	.021	
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Figure S12.1 UV spectrum of compound **12**

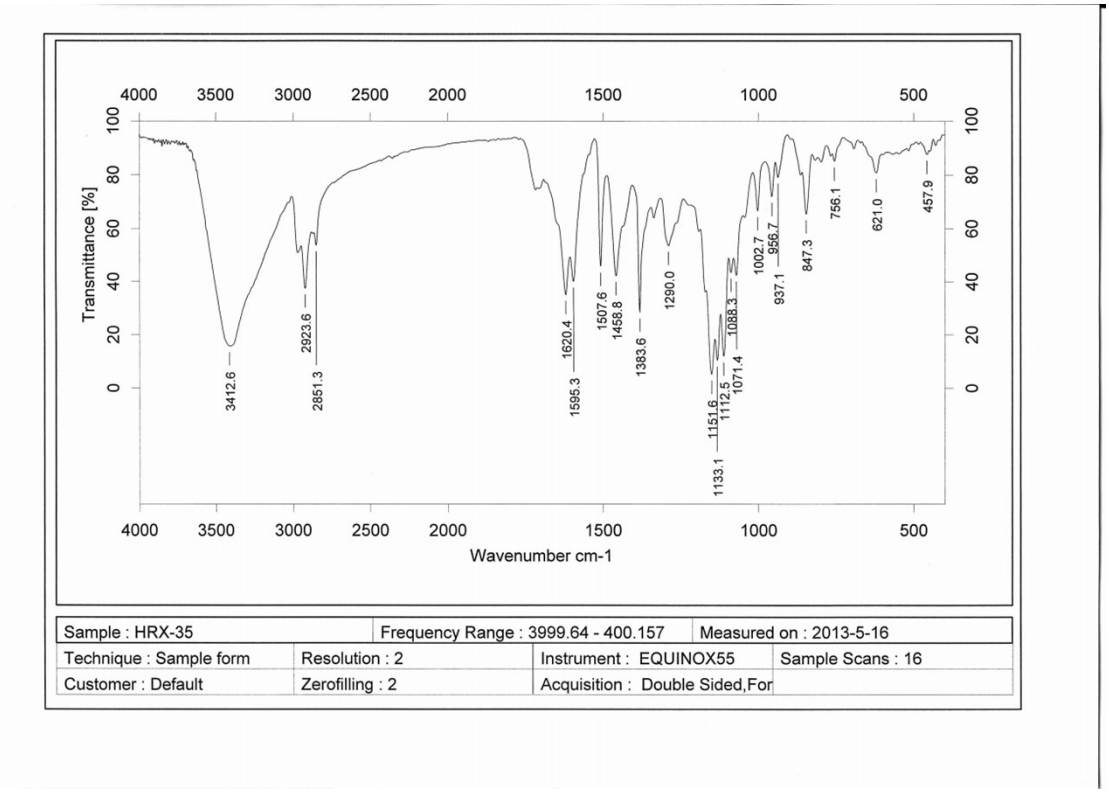


Figure S12.2 IR spectrum of compound **12**

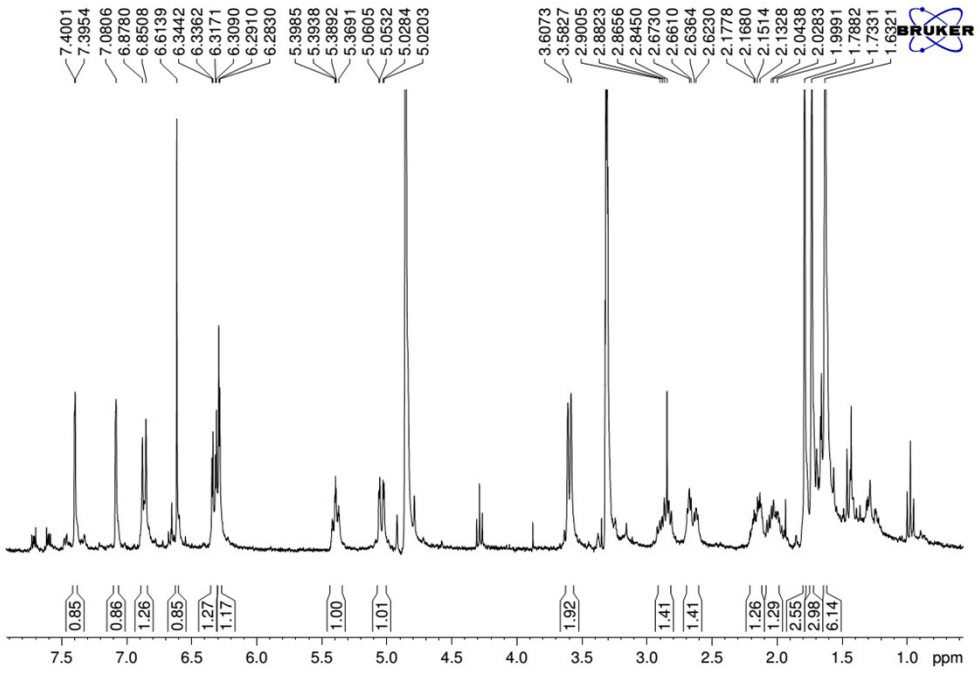


Figure S12.3 ^{1}H NMR spectrum (300 MHz, CD_3OD-d_4) of compound **12**

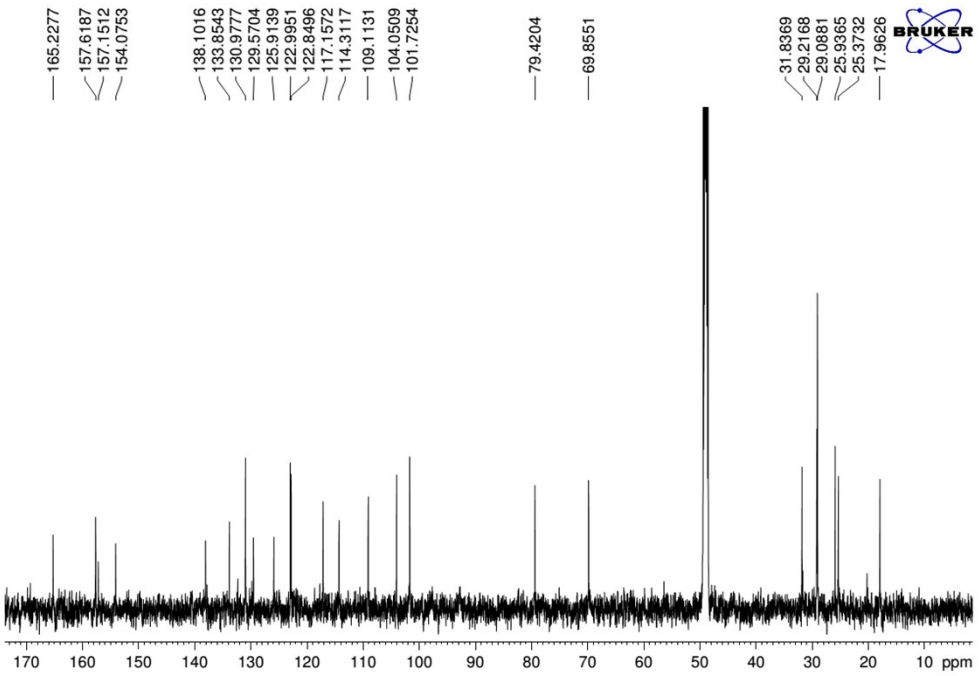


Figure S12.4 ^{13}C NMR spectrum (150 MHz, CD_3OD-d_4) of compound **12**

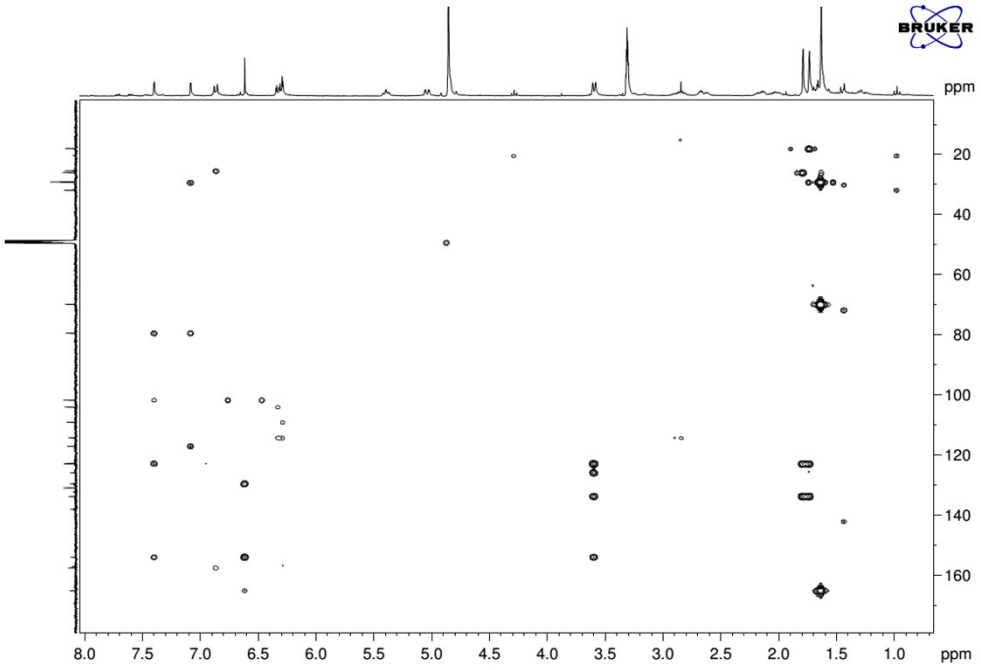


Figure S12.5 HMBC spectrum (600 MHz, CD_3OD-d_4) of compound **12**

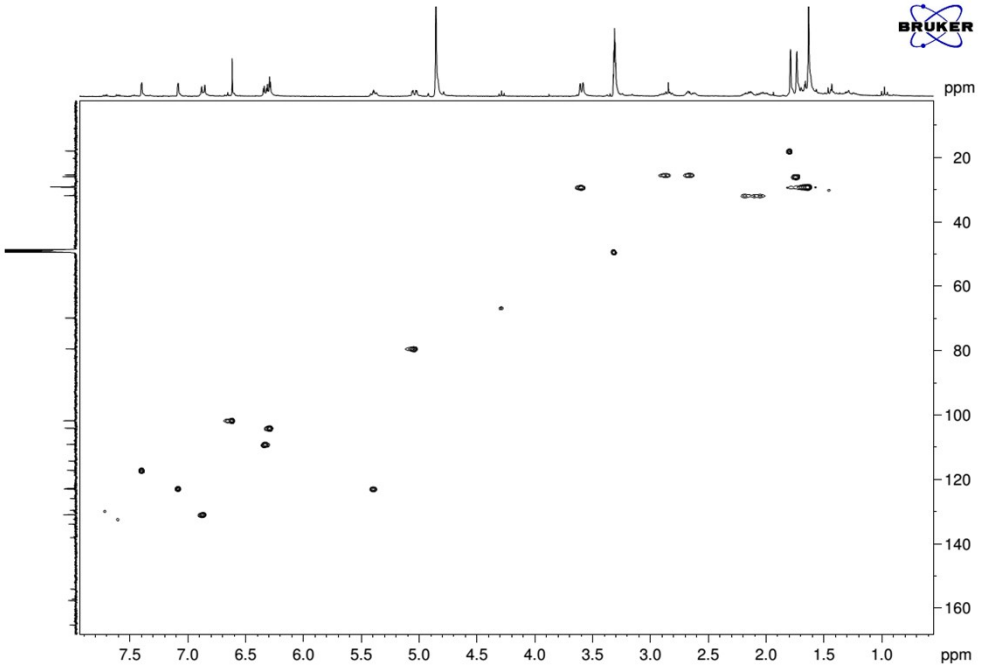
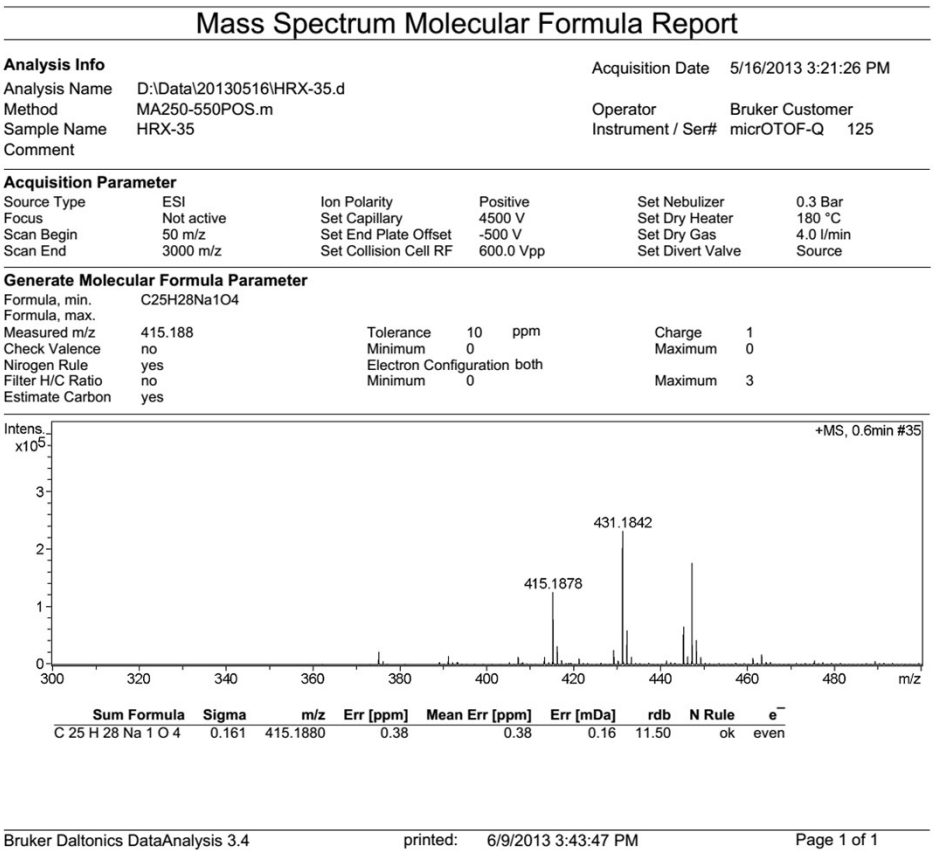


Figure S12.6 HSQC spectrum (600 MHz, CD_3OD-d_4) of compound **12**



Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\20130516\HRX-35.d	Acquisition Date	5/16/2013 3:21:26 PM
Method	MA250-550POS.m	Operator	Bruker Customer
Sample Name	HRX-35	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

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Formula, max.							
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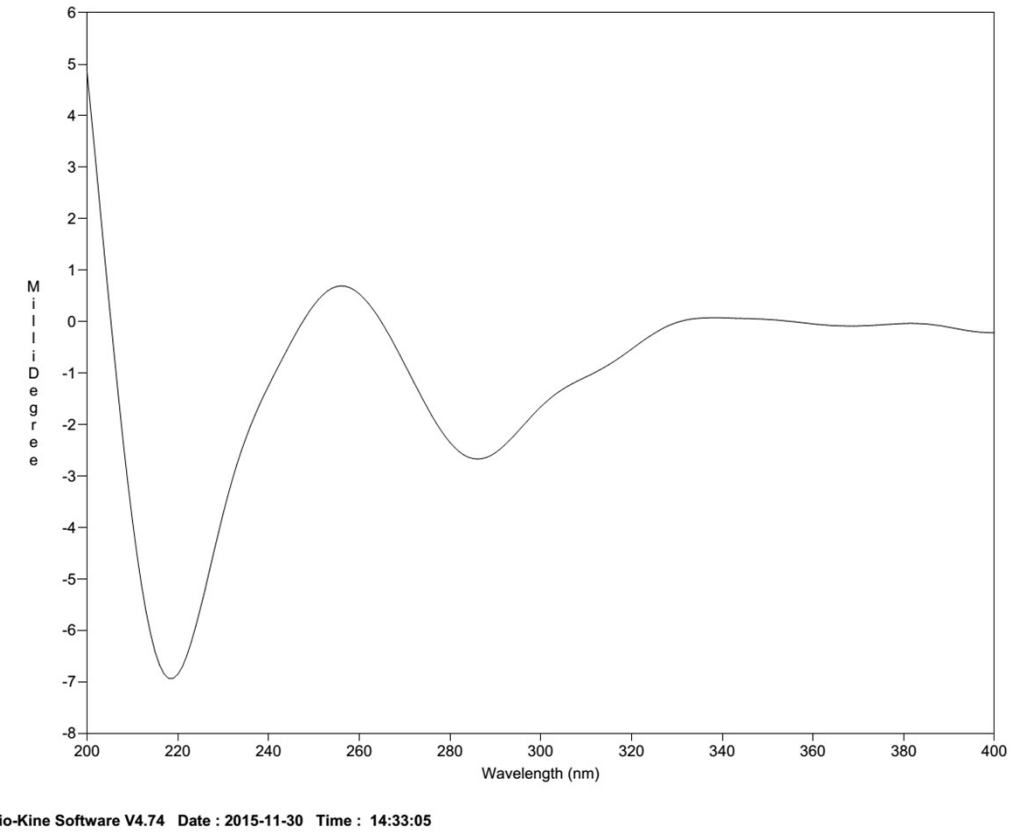
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 28 Na 1 O 4	0.161	415.1880	0.38	0.38	0.16	11.50	ok	even

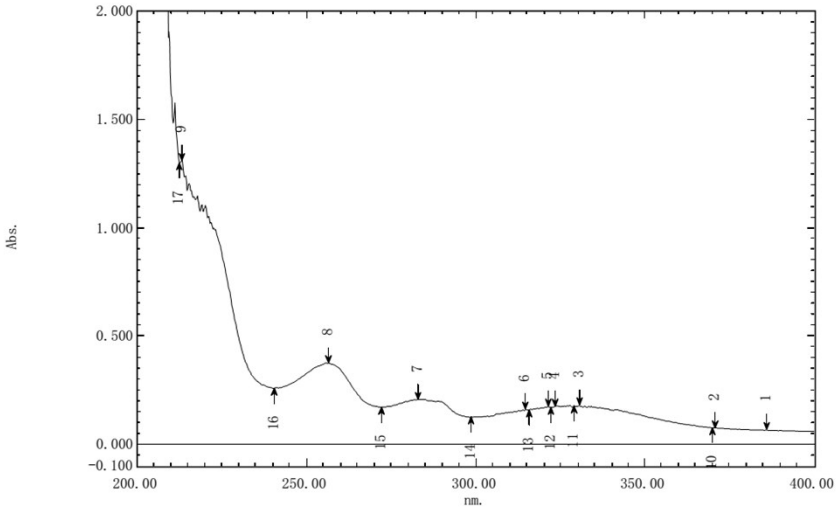
Bruker Daltonics DataAnalysis 3.4 printed: 6/9/2013 3:43:47 PM Page 1 of 1

Figure S12.7 HRESIMS spectrum of compound **12**



Bio-Kine Software V4.74 Date : 2015-11-30 Time : 14:33:05

Figure S12.8 CD spectra of compound **12**



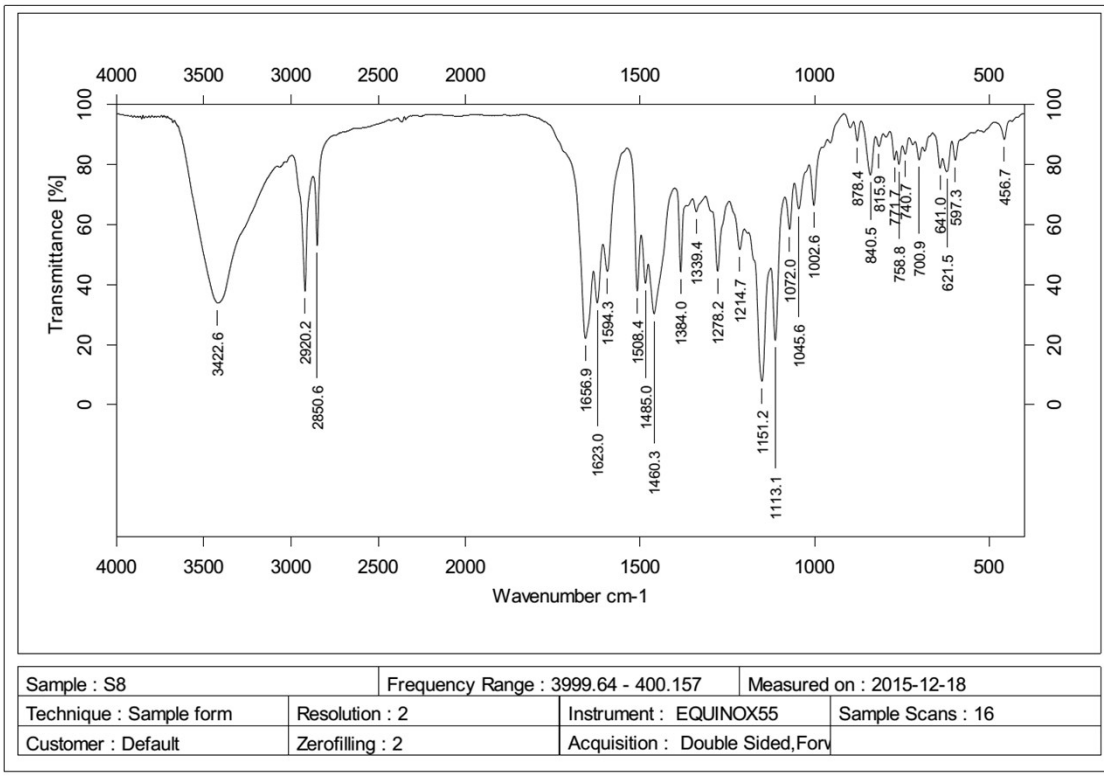
测定属性
波长范围 (nm.): 200.00到400.00
扫描速度: 高速
采样间隔: 0.2
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量: 0.3
体积 : 10
稀释:
光程长: 407
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 340.8 nm
S/R 转换: 标准

No.	P/V	Wavelength	Abs.	描述
1	↑	386.00	.066	
2	↑	370.80	.077	
3	↑	330.60	.180	
4	↑	323.60	.177	
5	↑	321.40	.175	
6	↑	314.80	.162	
7	↑	283.00	.208	
8	↑	256.60	.375	
9	↑	213.20	1.312	
10	↓	370.00	.076	
11	↓	329.00	.173	
12	↓	322.20	.171	
13	↓	315.80	.158	
14	↓	298.40	.125	
15	↓	272.00	.171	
16	↓	240.40	.259	
17	↓	212.60	1.295	

Figure S13.1 UV spectrum of compound **13**



Sample : S8	Frequency Range : 3999.64 - 400.157	Measured on : 2015-12-18	
Technique : Sample form	Resolution : 2	Instrument : EQUINOX55	Sample Scans : 16
Customer : Default	Zerofilling : 2	Acquisition : Double Sided,For	

Figure S13.2 IR spectrum of compound **13**

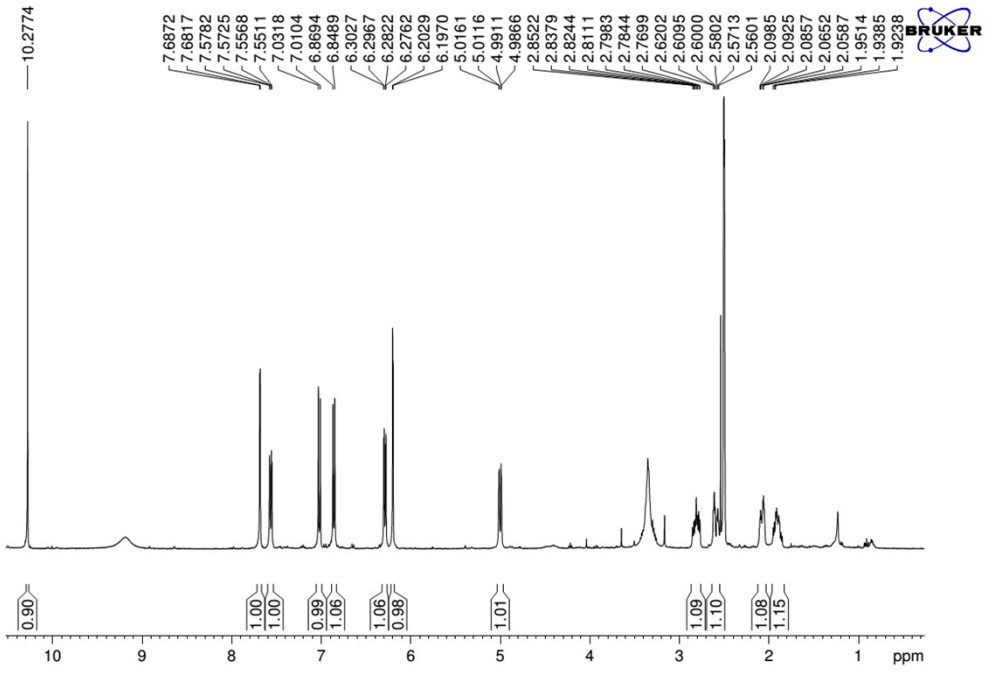


Figure S13.3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **13**

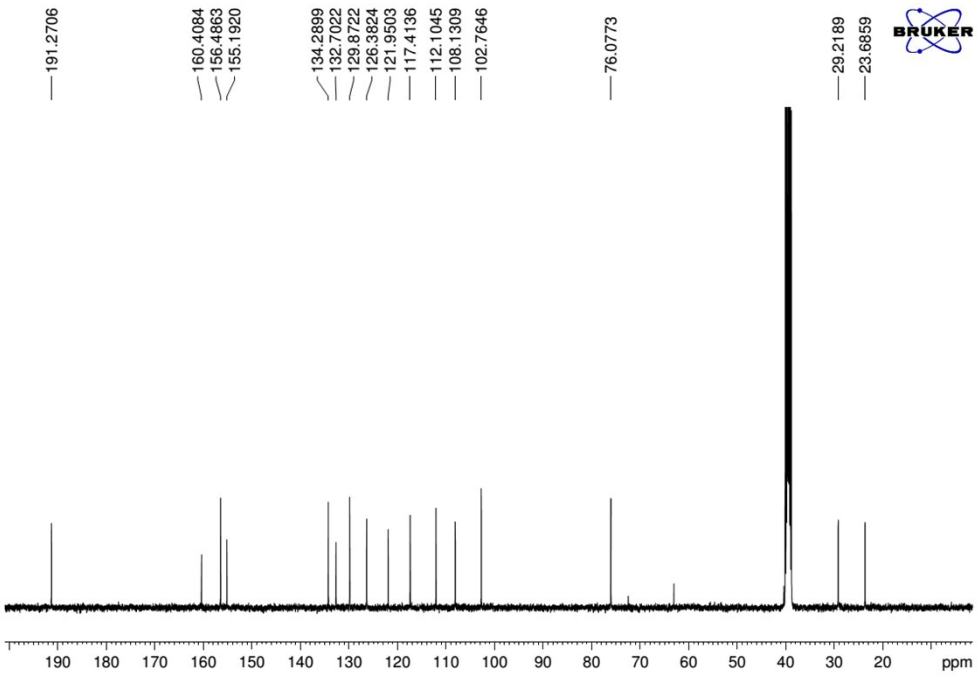


Figure S13.4 ^{13}C NMR spectrum (100 MHz,DMSO-d_6) of compound **13**

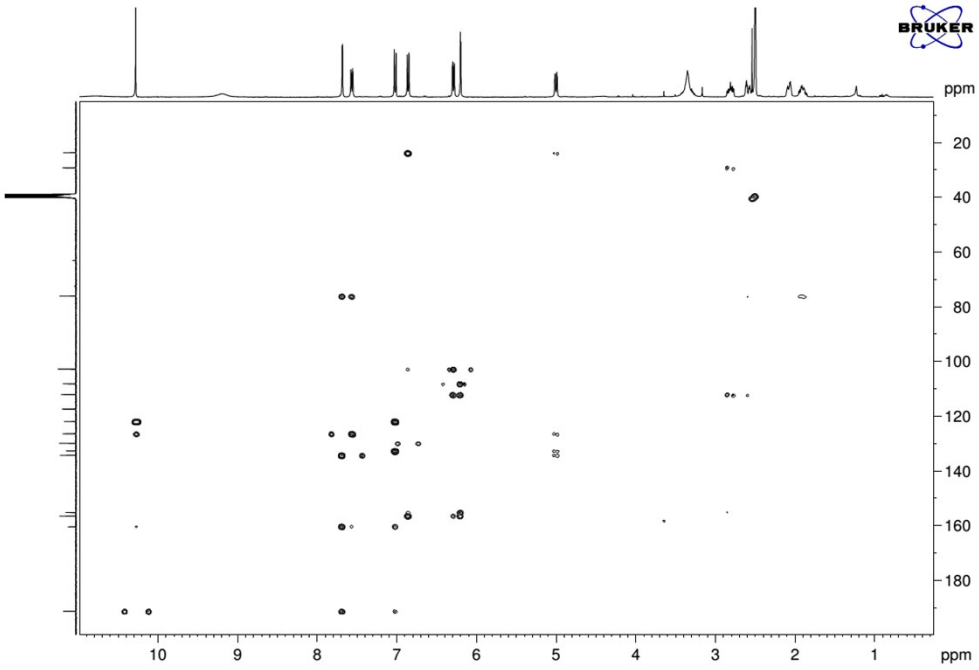


Figure S13.5 HMBC spectrum (600 MHz, DMSO-d_6) of compound **13**

Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\20160106CEYANG\S8.d	Acquisition Date	1/6/2016 6:51:03 PM
Method	20131026_ceyang.m	Operator	Bruker Customer
Sample Name	S8	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C16H14O4Na						
Formula, max.							
Measured m/z	293.077	Tolerance	5	ppm	Charge	1	
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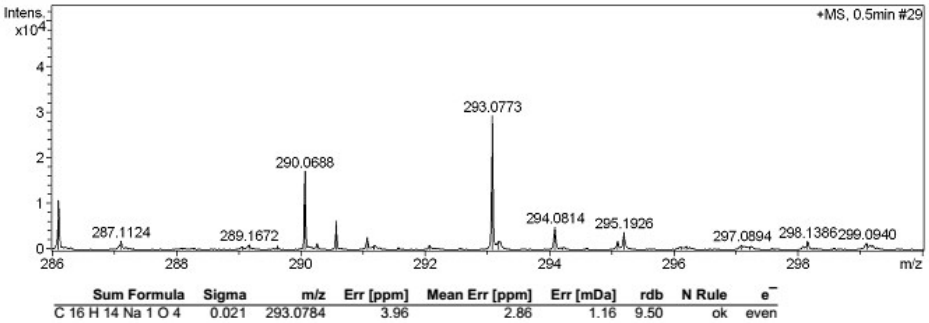
Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
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Figure S13.6 HRESIMS spectrum of compound **13**

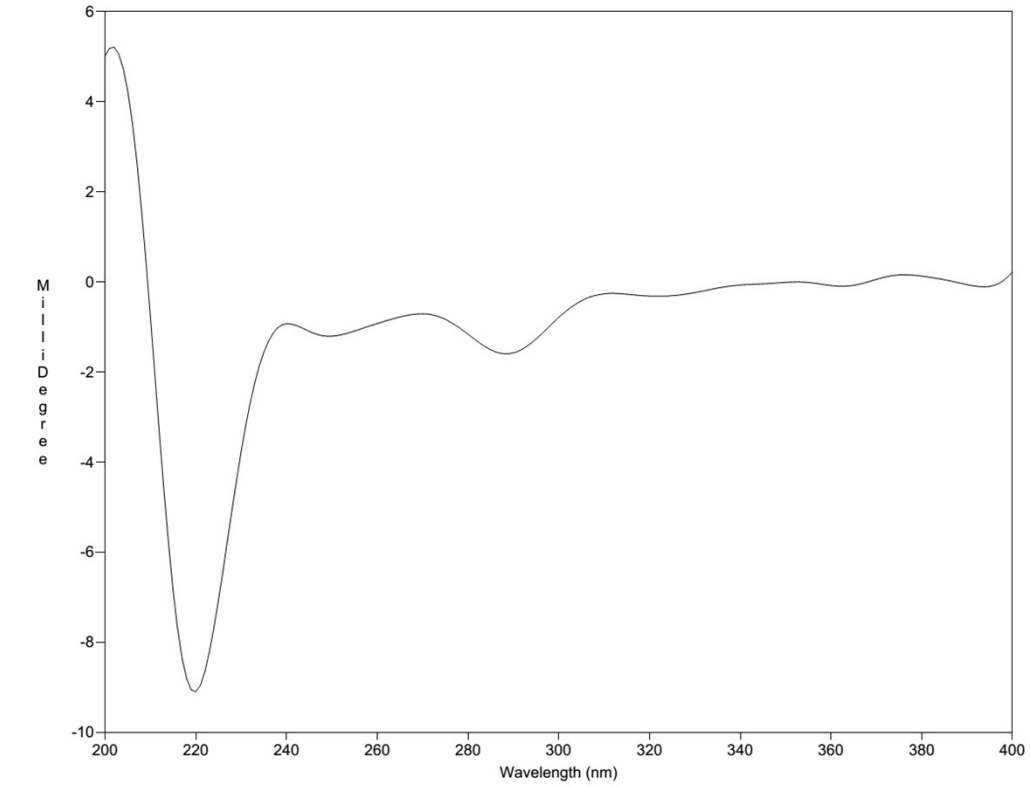

Figure S13.7 CD spectra of compound **13**

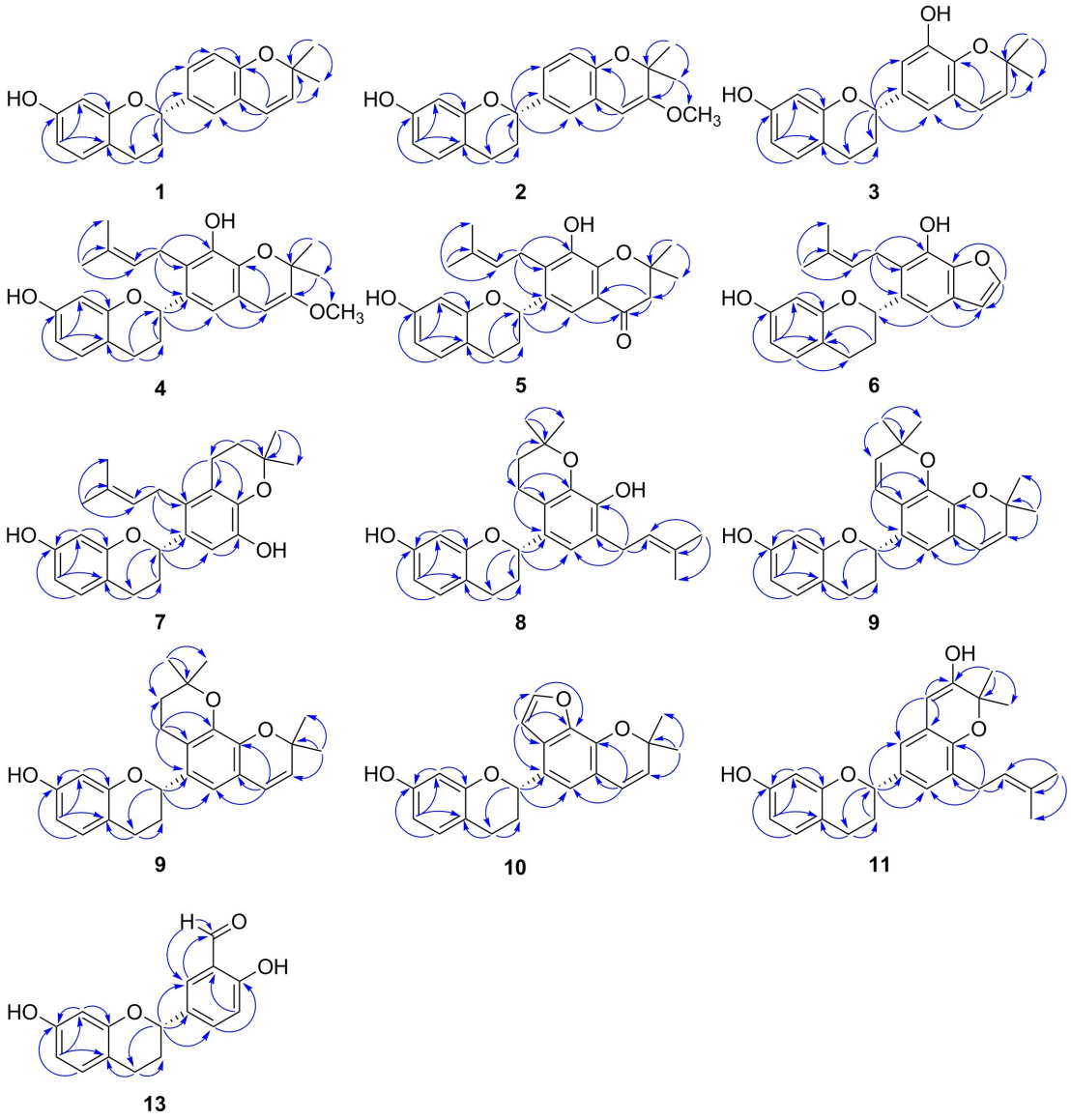

Figure S14 Key HMBC correlations of new compounds daphnegiravans A–M (**1**–**13**)

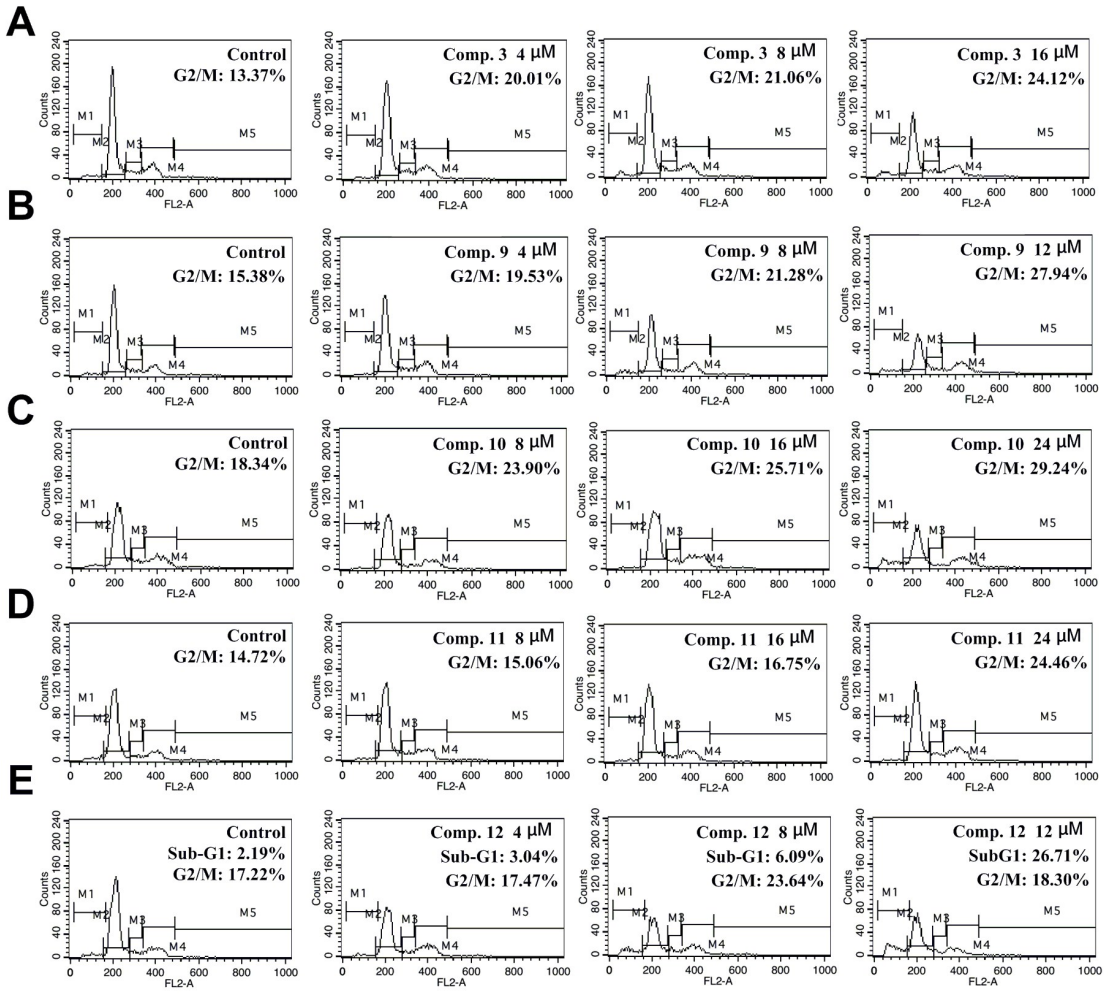

Figure S15 The flow cytometry histograms in Hep3B cells after treatment with compounds **3**, **9-12** at the indicated concentrations for 48 h. The experiments were performed three times and the results of representative experiments are shown.

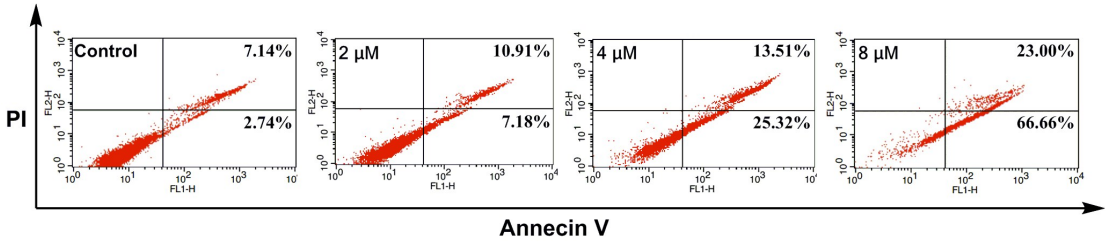

Figure S16 The AV−FITC binding and PI staining flow cytometry histograms in Hep3B cells after treatment with compound **12** at the indicated concentrations for 48 h. The experiments were performed three times and the results of representative experiments are shown.

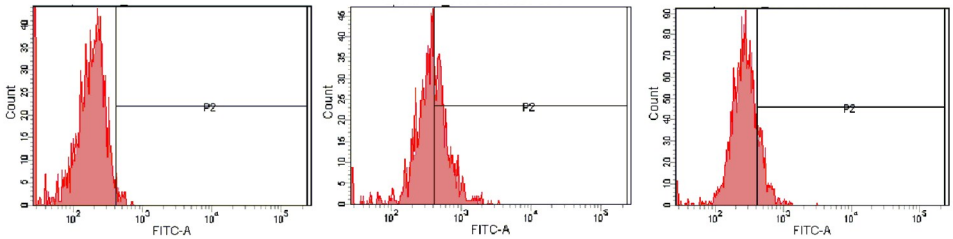

Figure S17 The ROS level flow cytometry histograms in Hep3B cells after treatment with compounds **9** and **12** for 48 h. The experiments were performed three times.

NMR data of known compounds

(2*S*)-7, 4'-dihydroxy-3'-prenylflavan (**14**). Brown powder; CD (MeOH) nm ($\Delta\varepsilon$) 221 (-3.19), 284 (-0.96); HRESIMS *m/z* 333.1465 $[M+Na]^+$ (calcd for $C_{20}H_{22}O_3Na$, 333.1461); ^{1}H NMR (400 MHz, CD_3OD): δ 4.83 (1H, dd, J = 9.6, 2.2 Hz, H-2), 2.03, 1.94 (each 1H, m, H-3), 2.80, 2.61 (each 1H, m, H-4), 6.83 (1H, d, J = 8.2 Hz, H-5), 6.31 (1H, dd, J= 8.2, 1.6 Hz, H-6), 6.25 (1H, d, J = 1.6 Hz, H-8), 7.06 (1H, d, J = 1.8 Hz, H-2'), 6.74 (1H, d, J = 8.0 Hz, H-5'), 7.02 (1H, dd, J = 8.0, 1.8 Hz, H-6'), 3.28 (2H, d, J = 7.2 Hz, H-1''), 5.30 (1H, m, H-2''), 1.68 (3H, s, Me-4''), 1.71 (3H, s, Me-5''); ^{13}C NMR (100 MHz, CD_3OD): δ 79.1 (C-2), 31.2 (C-3), 25.4 (C-4), 130.9 (C-5), 109.0 (C-6), 157.5 (C-7), 104.0 (C-8), 157.2 (C-9), 114.3 (C-10), 134.0 (C-1'), 128.5 (C-2'), 129.1 (C-3'), 155.7 (C-4'), 115.6 (C-5'), 125.6 (C-6'), 29.3 (C-1''), 123.9 (C-2''), 133.0 (C-3''), 17.8 (C-4''), 25.9 (C-5'').

(2*S*)-kazinol I (**15**). Brown oil; CD (MeOH) nm ($\Delta\varepsilon$) 220 (-3.02), 285 (-0.88); HRESIMS *m/z* 417.2043 $[M+Na]^+$ (calcd for $C_{25}H_{30}O_4Na$, 417.2036; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.93 (1H, d, J = 10.1 Hz, H-2), 1.98, 1.78 (each 1H, m, H-3), 2.78, 2.63 (each 1H, m, H-4), 6.86 (1H, d, J = 8.1 Hz, H-5), 6.27 (1H, d, J = 8.1 Hz, H-6), 6.15 (1H, brs, H-8), 6.73 (1H, s, H-2'), 3.24 (2H, m, H-1''), 5.01 (1H, t, J = 6.6 Hz, H-2''), 1.63 (3H, s, H-4''), 1.69 (3H, s, H-5''), 3.17 (2H, m, H-1'''), 4.94 (1H, o, H-2'''), 1.63 (6H, s, H-4''', H-5'''); ^{13} C NMR (100MHz, DMSO-d_6): δ 74.3 (C-2), 29.5 (C-3), 24.6 (C-4), 129.8 (C-5), 107.9 (C-6), 156.4 (C-7), 102.7 (C-8), 155.9 (C-9), 112.1 (C-10), 129.9 (C-1'), 110.8 (C-2'), 142.8 (C-3'), 142.7 (C-4'), 126.7 (C-5'),

127.8 (C-6'), 26.6 (C-1''), 124.4 (C-2''), 129.7 (C-3''), 17.7 (C-4''), 25.4 (C-5''), 25.1 (C-1'''), 123.8 (C-2'''), 129.8 (C-3'''), 17.7 (C-4'''), 25.4 (C-5''').

(2*S*)-7, 4'-dihydroxyflavane (**16**). Yellowish crystal; CD (MeOH) nm ($\Delta\varepsilon$) 222 (-2.71), 285 (-0.73); HRESIMS *m/z* 265.0847 $[M+Na]^+$ (calcd for $C_{15}H_{14}O_3Na$, 265.0841); ^1H NMR (300 MHz, CD_3OD): δ 4.90 (1H, dd, J = 10.5, 2.7 Hz, H-2), 2.10, 2.01 (each 1H, m, H-3), 2.88, 2.67 (each 1H, m, H-4), 6.86 (1H, d, J=8.1 Hz, H-5), 6.31 (1H, dd, J = 8.1, 2.4 Hz, H-6), 6.25 (1H, d, J = 2.4 Hz, H-8), 7.23 (2H, d, J = 8.4 Hz, H-2', 6'), 6.78 (2H, d, J = 8.4 Hz, H-3', 5').

(2*S*)-7, 4'-dihydroxy-3'-methoxyflavan (**17**) Yellowish powder; CD (MeOH) nm ($\Delta\varepsilon$) 220 (-3.29), 288 (-0.95); HRESIMS *m/z* 295.0946 $[M+Na]^+$ (calcd for $C_{16}H_{16}O_4Na$, 295.0941); ^1H NMR (300 MHz, CD_3OD): δ 4.88 (1H, dd, J = 9.9, 2.4 Hz, H-2), 2.09, 2.00 (each 1H, m, H-3), 2.84, 2.63 (each 1H, m, H-4), 6.85 (1H, d, J = 8.1 Hz, H-5), 6.31 (1H, dd, J = 8.1, 2.4 Hz, H-6), 6.26 (1H, d, J = 2.4 Hz, H-8), 6.97 (1H, d, J = 1.8 Hz, H-2'), 6.78 (1H, d, J = 8.1 Hz, H-5'), 6.84 (1H, dd, J = 8.1, 1.8 Hz, H-6'), 3.84 (3H, s, OMe-3'); ^{13}C NMR (75 MHz, CD_3OD): δ 79.2 (C-2), 31.4 (C-3), 25.5 (C-4), 131.0 (C-5), 109.1 (C-6), 157.5 (C-7), 104.0 (C-8), 157.1 (C-9), 114.3 (C-10), 134.9 (C-1'), 110.9 (C-2'), 148.9 (C-3'), 147.2 (C-4'), 116.0 (C-5'), 119.9 (C-6'), 56.4 (OMe-3').

(2*S*)-7, 3'-dihydroxy-4'-methoxyflavan (**18**) Yellowish powder; CD (MeOH) nm ($\Delta\varepsilon$) 220 (-2.67), 288 (-0.87); HRESIMS *m/z* 295.0945 $[M+Na]^+$ (calcd for $C_{16}H_{16}O_4Na$, 295.0941); ^1H NMR (300 MHz, CD_3OD): δ 4.86 (1H, dd, J = 9.9, 2.4 Hz, H-2), 2.09, 1.95 (each 1H, m, H-3), 2.83, 2.61 (each 1H, m, H-4), 6.84 (1H, d, J = 8.1 Hz, H-5), 6.31 (1H, dd, J = 8.1, 2.4 Hz, H-6), 6.26 (1H, d, J = 2.4 Hz, H-8), 6.85 (1H, d, J = 1.8 Hz, H-2'), 6.87 (1H, d, J = 8.1 Hz, H-5'), 6.81 (1H, dd, J = 8.1, 1.8 Hz, H-6'), 3.83 (3H, s, OMe-4'); ^{13}C NMR (75 MHz, CD_3OD): δ 78.8 (C-2), 31.4 (C-3), 25.3 (C-4), 130.9 (C-5), 109.0 (C-6), 157.5 (C-7), 104.0 (C-8), 157.0 (C-9), 114.3 (C-10), 136.3 (C-1'), 112.5 (C-2'), 147.4 (C-3'), 148.5 (C-4'), 114.2 (C-5'), 118.5 (C-6'), 56.3 (OMe-4').

(2*S*)-3', 4'-dimethoxy-7-hydroxyflavan (**19**). Brown oil; CD (MeOH) nm ($\Delta\varepsilon$) 220 (-2.89), 286 (-0.85); HRESI-MS *m/z* 309.1097 $[M+Na]^+$ (calcd for $C_{17}H_{18}O_4Na$, 309.1097). ^1H NMR (400 MHz, DMSO-d_6): δ 4.94 (1H, dd, J = 9.9, 2.1 Hz, H-2), 2.06, 1.95 (each 1H, m, H-3), 2.80, 2.60 (each 1H, m, H-4), 6.85 (1H, d, J = 8.2 Hz, H-5), 6.29 (1H, dd, J = 8.2, 2.4 Hz, H-6), 6.20 (1H, d, J = 2.4 Hz, H-8), 6.93 (2H, o, H-2', 5'), 6.99 (1H, brs, H-6'), 3.75 (3H, s, OMe-3'), 3.74 (3H, s, OMe-4'); ^{13}C NMR (100 MHz, DMSO-d_6): δ 76.8 (C-2), 29.4 (C-3), 23.8 (C-4), 129.8 (C-5), 108.0 (C-6), 156.5 (C-7), 102.8 (C-8), 155.5 (C-9), 112.1 (C-10), 134.1 (C-1'), 111.6 (C-2'), 148.3 (C-3'), 148.6 (C-4'), 118.3 (C-5'), 111.0 (C-6'), 55.5 (OMe-3'), 55.4 (OMe-4').

(2*S*)-4'-hydroxy-7-methoxyflavan (**20**). Brown oil; CD (MeOH) nm ($\Delta\varepsilon$) 220 (-2.74), 286 (-0.79); HRESI-MS *m/z* 257.1168 $[M+H]^+$ (calcd for $C_{16}H_{17}O_3$, 257.1172); ^1H NMR (400MHz, DMSO-d_6): δ 4.93 (1H, dd, J = 10.1, 2.0 Hz, H-2), 2.06, 1.94 (each 1H, m, H-3), 2.84, 2.64 (each 1H, m, H-4), 6.97 (1H, d, J = 8.4 Hz, H-5), 6.43 (1H, dd, J = 8.4, 2.4 Hz, H-6), 6.36 (1H, J = 2.4 Hz, H-8), 7.21 (2H, d, J = 8.5 Hz, H-2', 6'), 6.76 (2H, d, J = 8.5 Hz, H-3', 5'); ^{13} C NMR (100MHz, DMSO-d_6): δ 77.0 (C-2), 29.1 (C-3), 23.9 (C-4), 129.9 (C-5), 106.9 (C-6), 158.5 (C-7), 101.2 (C-8), 155.7 (C-9), 113.8 (C-10), 131.6 (C-1'), 127.5 (C-2', 6'), 115.0 (C-3', 5'), 157.1 (C-4').

(2*S*)-7, 3'-dimethoxy-4'-hydroxyflavan (**21**). Brown oil; CD (MeOH) nm ($\Delta\varepsilon$) 221 (-2.37), 286 (-0.80); HRESI-MS *m/z* 309.1095 $[M+Na]^+$ (calcd for $C_{17}H_{18}O_4Na$, 309.1097); ^1H NMR (400MHz, DMSO-d_6): δ 4.93 (1H, dd, J = 9.0, 2.0 Hz, H-2), 2.06, 1.90 (each 1H, m, H-3), 2.83, 2.62 (each 1H, m, H-4), 6.97 (1H, d, J = 8.3 Hz, H-5), 6.43 (1H, dd, J = 8.3, 2.5 Hz, H-6), 6.36 (1H, J = 2.5 Hz, H-8), 6.83 (1H, d, J = 2.0 Hz, H-2'), 6.90 (1H, d, J = 8.2 Hz, H-5'), 6.78 (1H, dd, J = 8.2, 2.0 Hz, H-6'); ^{13} C NMR (100MHz, DMSO-d_6): δ 76.8 (C-2), 29.3 (C-3), 23.7 (C-4), 129.9 (C-5), 106.8 (C-6), 158.6 (C-7), 101.2 (C-8), 155.5 (C-9), 113.8 (C-10), 134.1 (C-1'), 111.9 (C-2'), 147.2 (C-3'), 146.4 (C-4'), 113.4 (C-5'), 116.9 (C-6').