Three new sesquiterpene glycosides from the roots of *Codonopsis pilosula*

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Supporting Information

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Detailed ECD Calculation of 1−3, their aglycones, the model compounds, and (−)-α-barbatenal-reduction product. Conformational analysis was performed by using the MMFF94 molecular mechanics force field calculation using the MOE (Molecular Operating Environment) software package.

Conformational analysis showed conformer(s) for **1−3**, their aglycones, the model compounds, and (−)-α-barbatenal-reduction product having relative energy within 2 kcal/mol, which were considered for further DFT calculations. Subsequently, using Gaussian 09 program package, the conformers were re-optimized using DFT at the B3LYP/6-31+G(d) level, and conductor-like polarizable continuum model (CPCM) was adopted to consider solvent effects using the dielectric constant of MeOH (ε = 32.6). The B3LYP/6-31G+(d) harmonic vibrational frequencies were calculated to confirm their stability. The energies, oscillator strengths, and rotational strengths of the first 30 electronic excitations of the conformers were calculated using the TDDFT methodology at the B3LYP/6-311++G (2d,2p) level in gas phase, and conformer(s) for **1−3**, the aglycones, the model compounds, and (−)-α-barbatenal-reduction product (Figures S1−S3, S5−S7, S9, S10, and S12) showed relative Gibbs free energies (ΔG) under 2 kcal/mol. The ECD spectra of the conformers were then simulated using the Gaussian function (σ = 0.28 eV), respectively. The final spectra of the compounds (Figures S4, S8, and S11) were obtained by averaging the simulated spectra of the lowest energy conformers according to the Boltzmann distribution theory, in which their Gibbs free energy (G) were adopted.

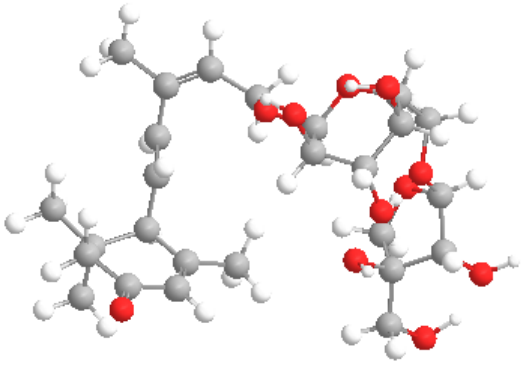
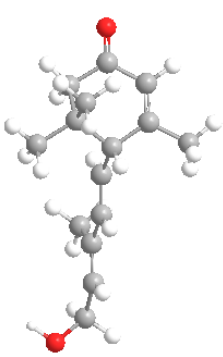
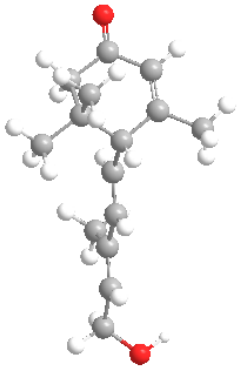


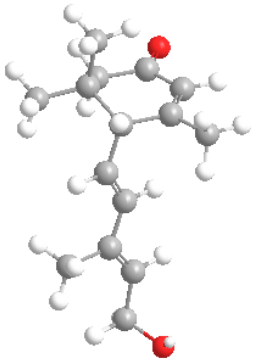
Figure S1.The re-optimized conformer of **1**.



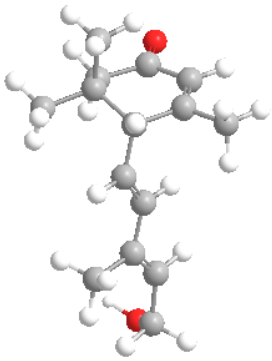
the aglycone of **1** C1 (31.2%)



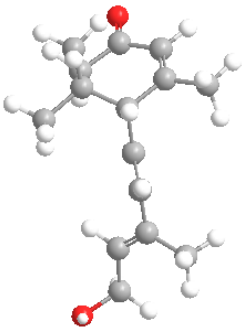
the aglycone of **1** C2 (32.2%)



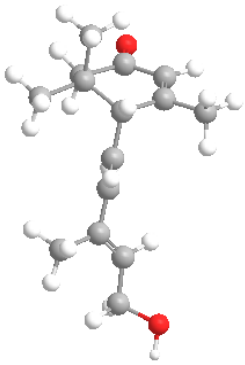
the aglycone of **1** C3 (2.3%)



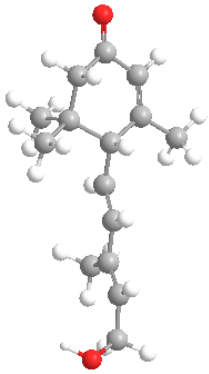
the aglycone of **1** C4 (1.0%)



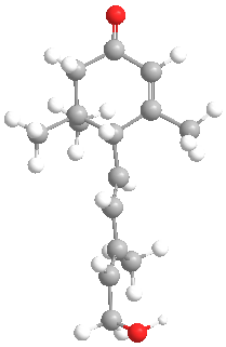
the aglycone of **1** C5 (0.6%)



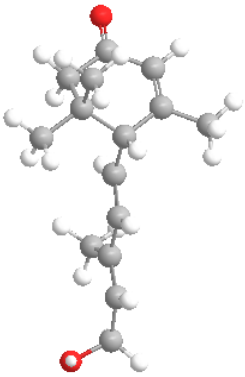
the aglycone of **1** C6 (0.3%)



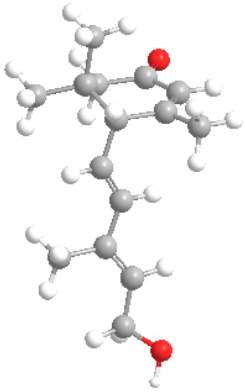
the aglycone of **1** C7 (7.0%)



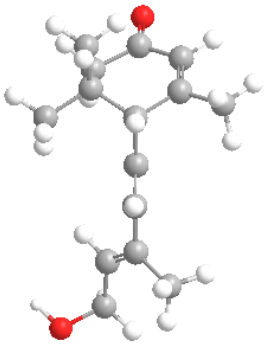
the aglycone of **1** C8 (4.8%)



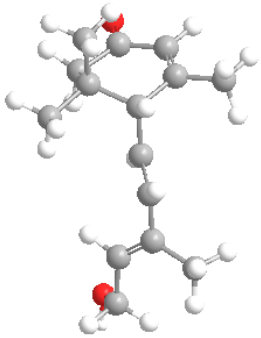
the aglycone of **1** C9 (18%)



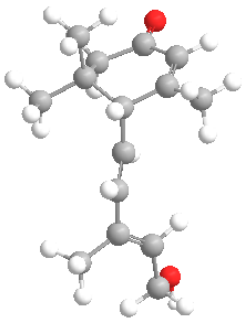
the aglycone of **1** C10 (1.0%)



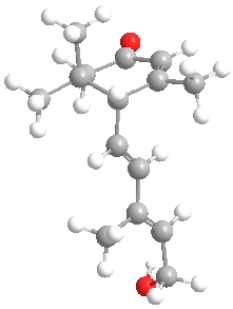
the aglycone of **1** C11 (0.6%)



the aglycone of **1** C12 (0.1%)

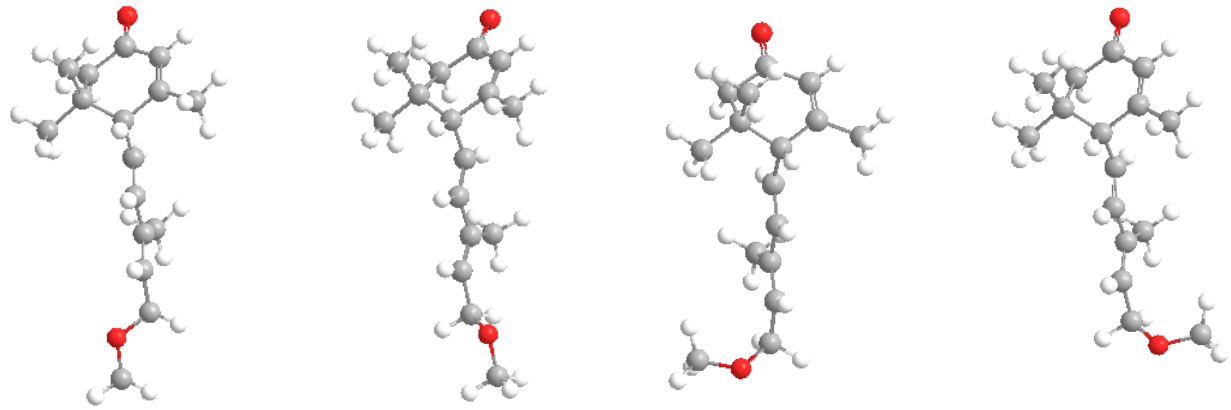


the aglycone of **1** C13 (0.2%)

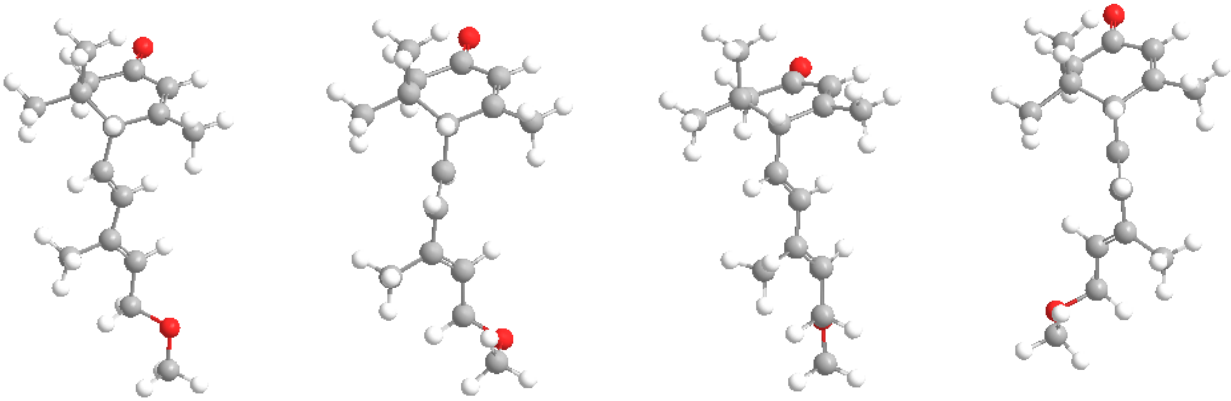


the aglycone of **1** C14 (0.6%)

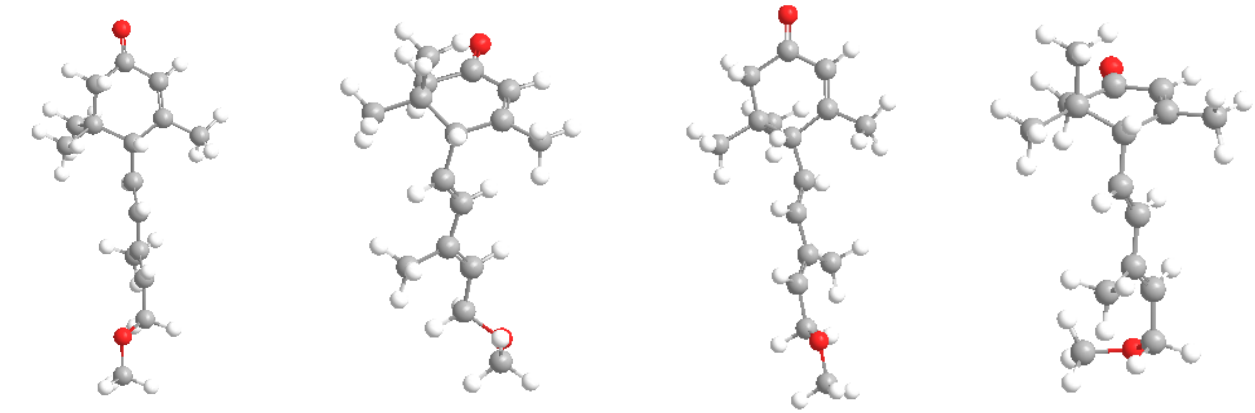
Figure S2. The re-optimized fourteen conformers of the aglycone of **1** and their equilibrium populations.



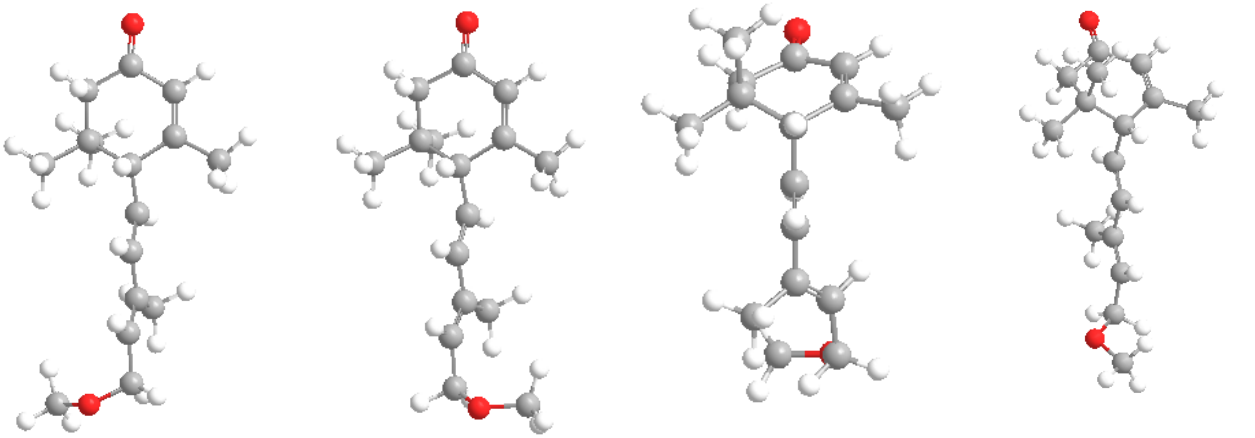
model C1 (34.8%) **model** C2 (31.6%) **model** C3 (6.4%) **model** C4 (7.2%)



model C5 (2.0%) **model** C6 (1.2%) **model** C7 (0.9%) **model** C8 (0.1%)



model C9 (3.5%) **model** C10 (0.3%) **model** C11 (4.6%) **model** C12 (0.7%)



model C13 (2.9%) **model** C14 (2.9%) **model** C15 (0.1%) **model** C16 (2.1%)

Figure S3. The re-optimized sixteen conformers of the **model** and their equilibrium populations.

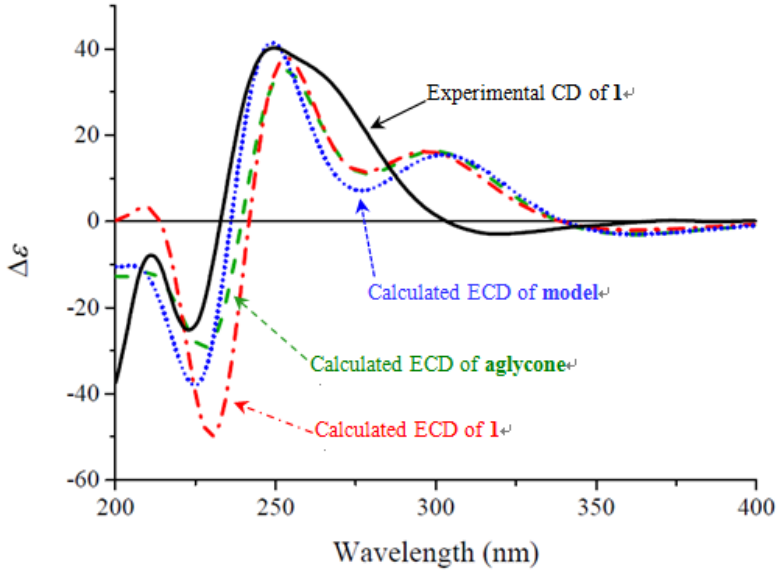


Figure 4. The experimental CD spectrum of **1** (black) and the calculated ECD spectra of **1** (dash dotted red), its aglycone (dashed green), and the **model** (dotted blue) in MeOH.

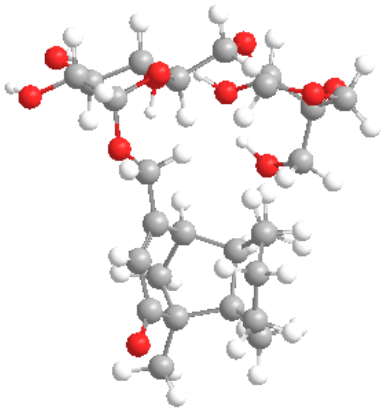
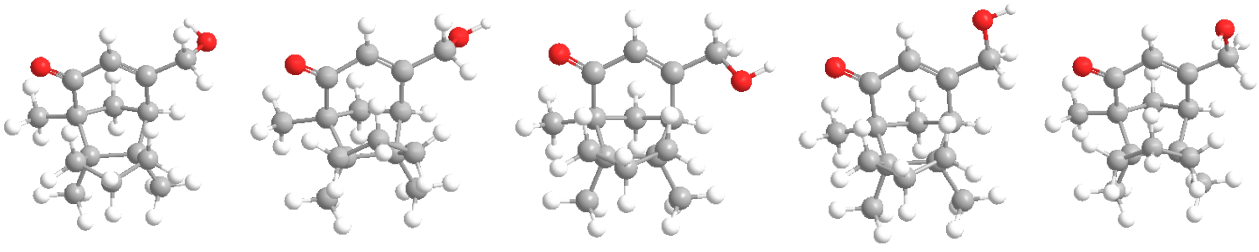
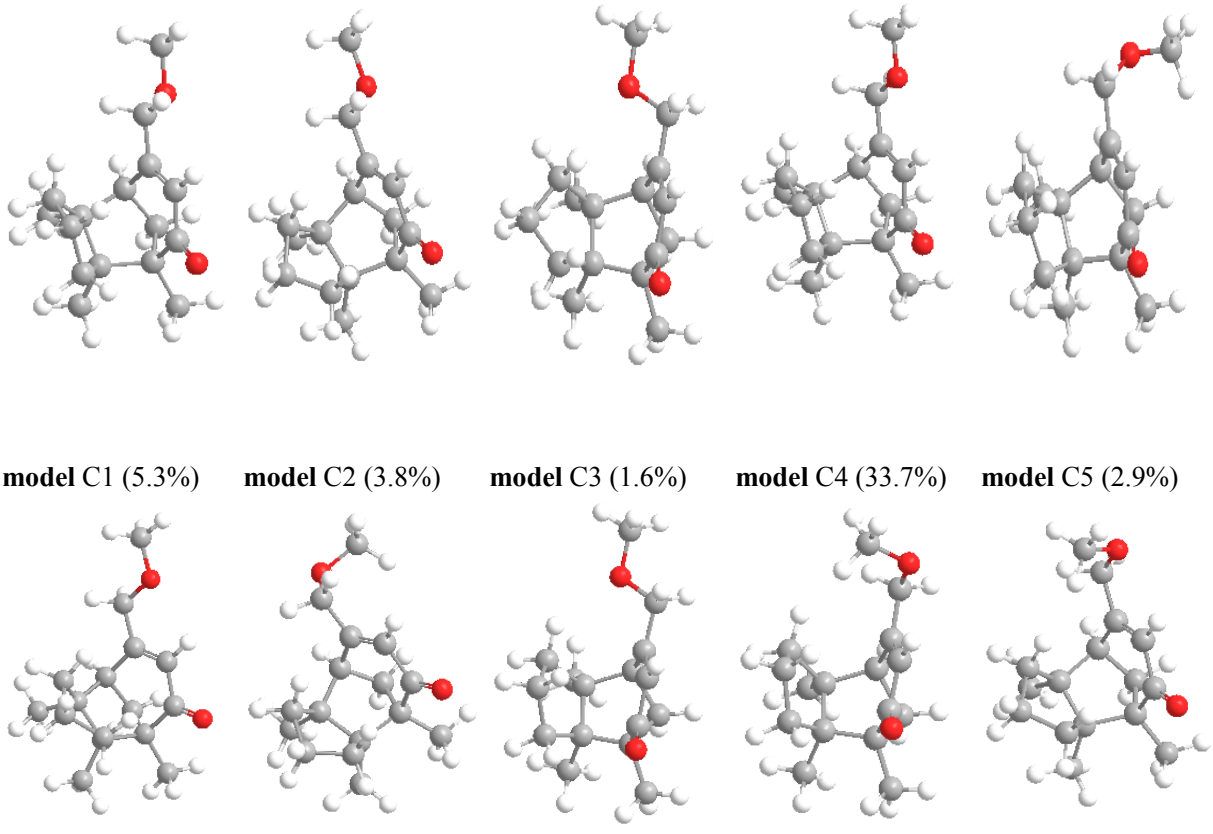


Figure S5.The re-optimized conformer of **2**.



the aglycone of **2** C1 (8.8%) | the aglycone of **2** C2 (4.5%) | the aglycone of **2** C3 (2.0%) | the aglycone of **2** C4 (30.6%) | the aglycone of **2** C5 (54.0%)

Figure S6. The re-optimized five conformers of the aglycone of **2** and their equilibrium populations.



model C1 (5.3%) **model** C2 (3.8%) **model** C3 (1.6%) **model** C4 (33.7%) **model** C5 (2.9%)

model C6 (44%) **model** C7 (1.9 %) **model** C8 (2.2%) **model** C9 (2.7%) **model** C10 (1.9%)

Figure S7.The re-optimized ten conformers of the **model** of **2** and their equilibrium populations.

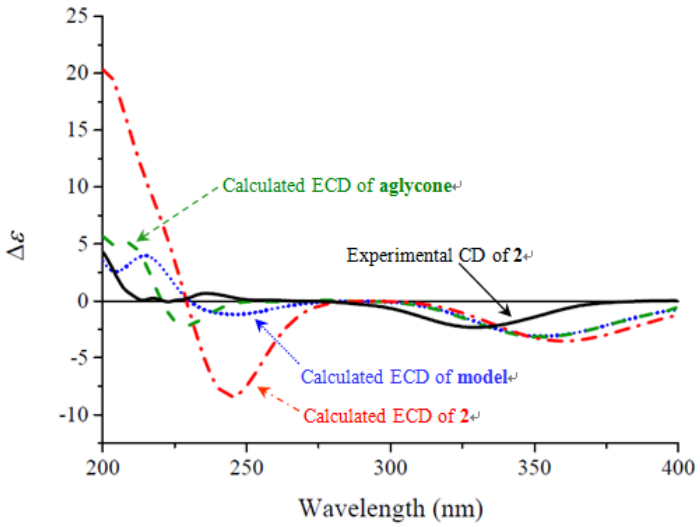


Figure 8. The experimental CD spectrum of **2** (black) and the calculated ECD spectra of **2** (dash dotted red), its aglycone (dashed green), and the **model** (dotted blue) in MeOH.

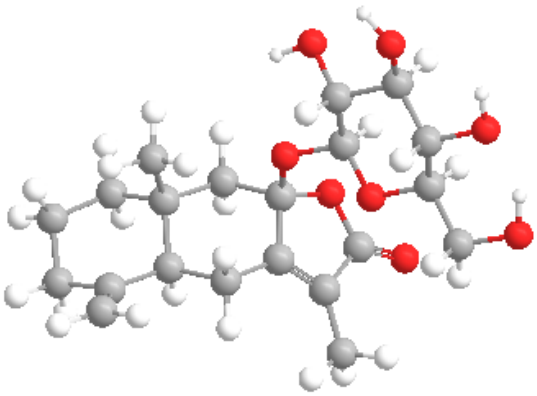


Figure S9.The re-optimized conformer of **3**.

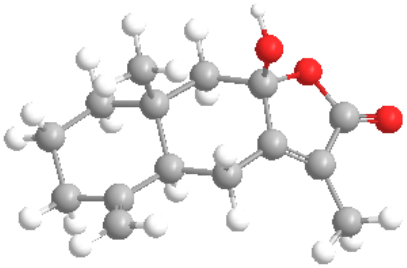


Figure S10.The re-optimized conformer of the aglycone of **3**.

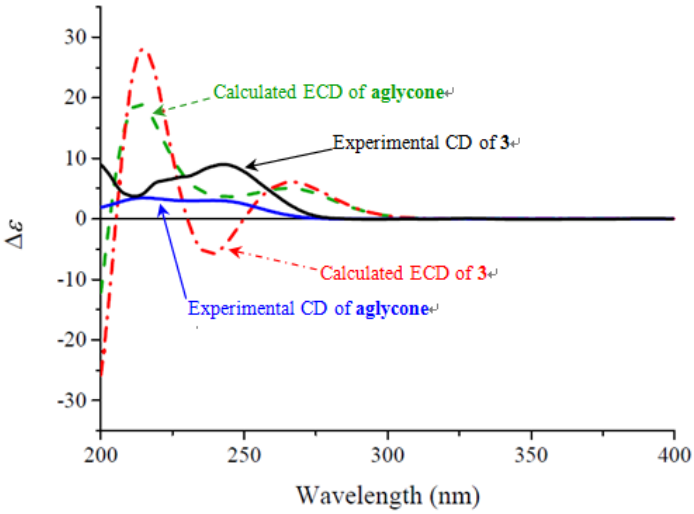
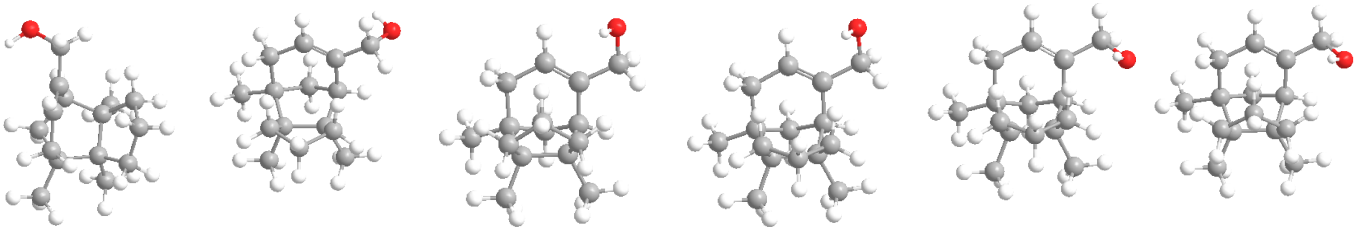


Figure S11. The experimental CD (black and blue) and calculated ECD (dashed and dotted red and green) spectra of **3** and its aglycone in MeOH.



C1 (47.3 %) C2 (11.9 %) C3 (11.8 %) C4 (12.0 %) C5 (6.9 %) C6 (10.1 %)

Figure S12. The reoptimized six conformers of (−)-α-barbatenal-reduction product.

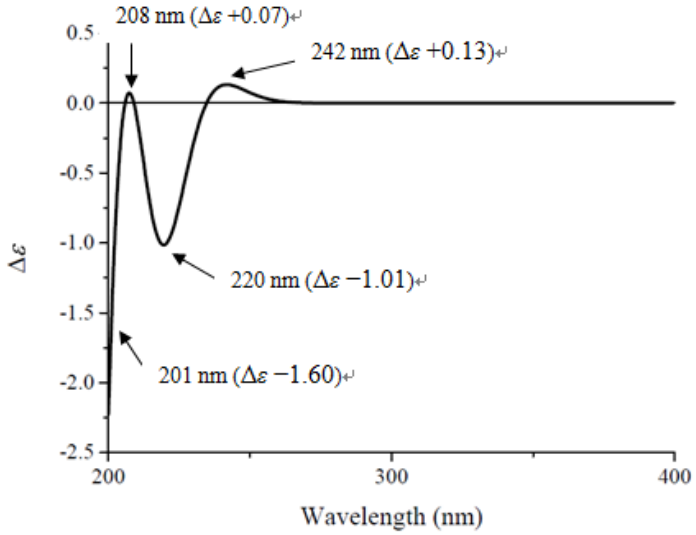


Figure S13. The calculated ECD spectrum of (−)-α-barbatenal-reduction product

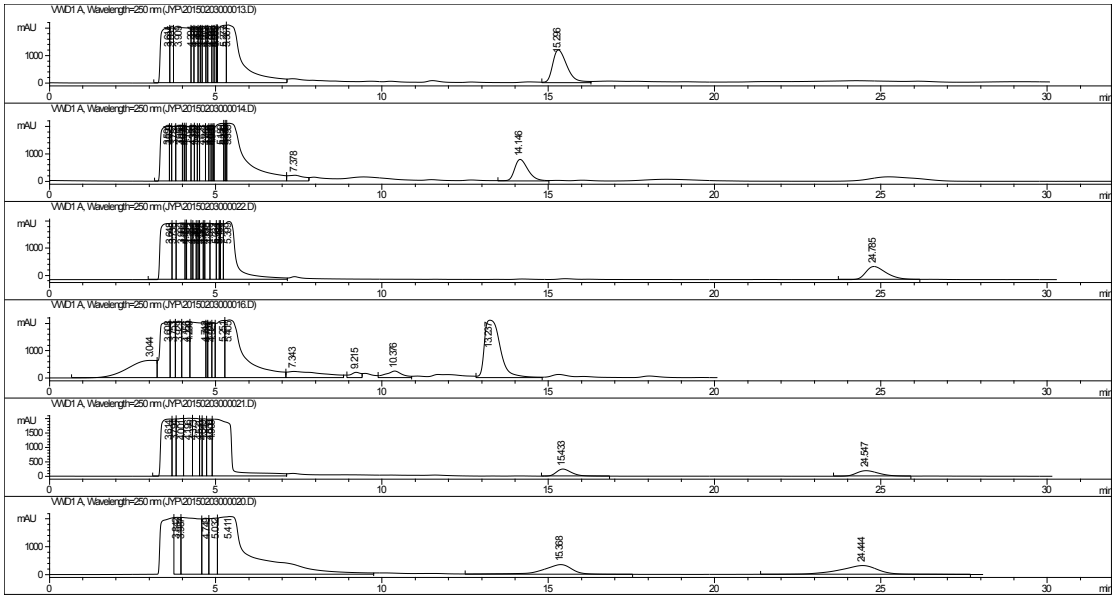
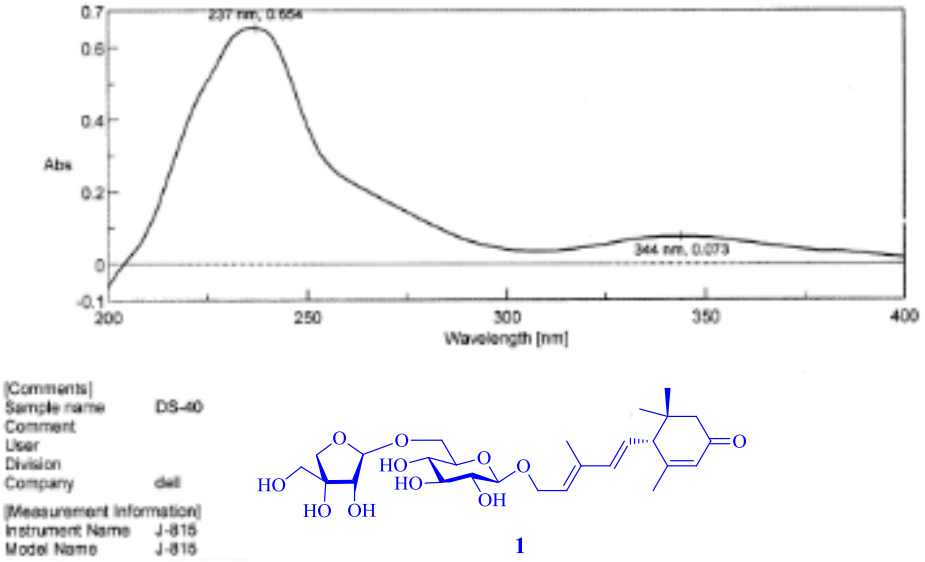


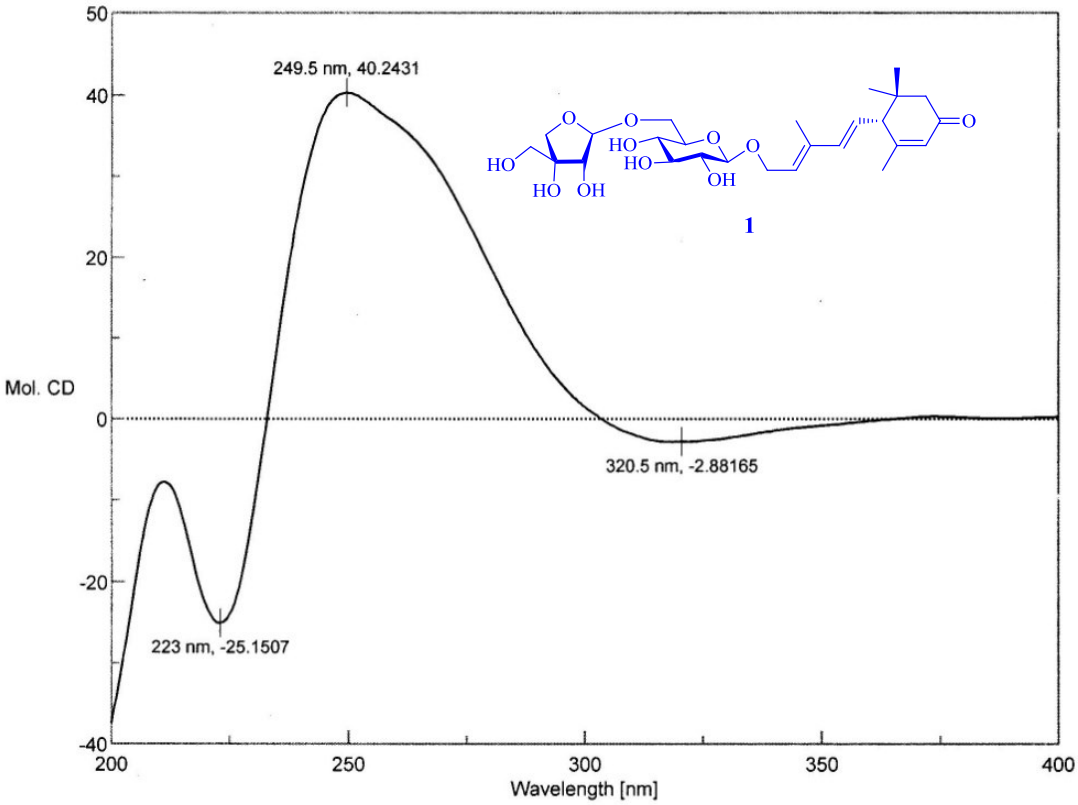
Figure S12.The HPLC chromatograms of the sugar derivatives, from top to bottom, for D-glucose, L-glucose, D-apiose, L-apiose, and sugars from hydrolysates of **1** and **2**.



[Comments]
Sample name DS-40
Comment
User
Division
Company dell
[Measurement Information]
Instrument Name J-815
Model Name J-815

1

Figure S13.The UV spectrum of compound **1** in MeOH.



[Comments]

Sample name	DS-40
Comment	
User	
Division	
Company	dell

[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	2 sec
Band width	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
PMT Voltage	Auto
Accumulations	3
Solvent	MEOH
Concentration	0.07 (w/v)%

[Detailed Information]

Creation date	2014-5-20 9:34
Data array type	Linear data array * 3
Horizontal axis	Wavelength [nm]
Vertical axis(1)	Mol. CD
Vertical axis(2)	HT [V]
Vertical axis(3)	Abs
Start	400 nm
End	200 nm
Data interval	0.5 nm
Data points	401

Figure S14.The CD spectrum of compound **1** in MeOH.

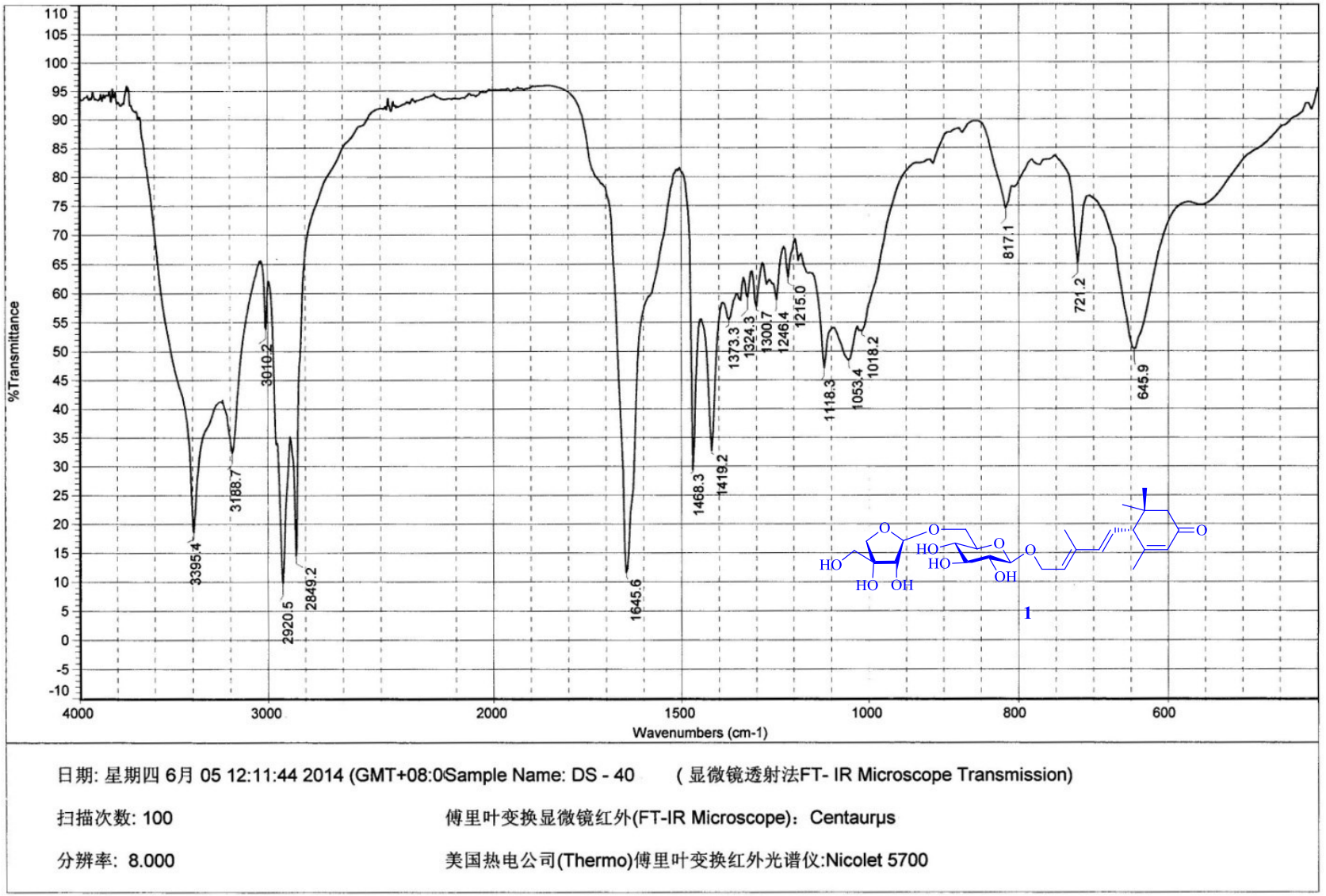


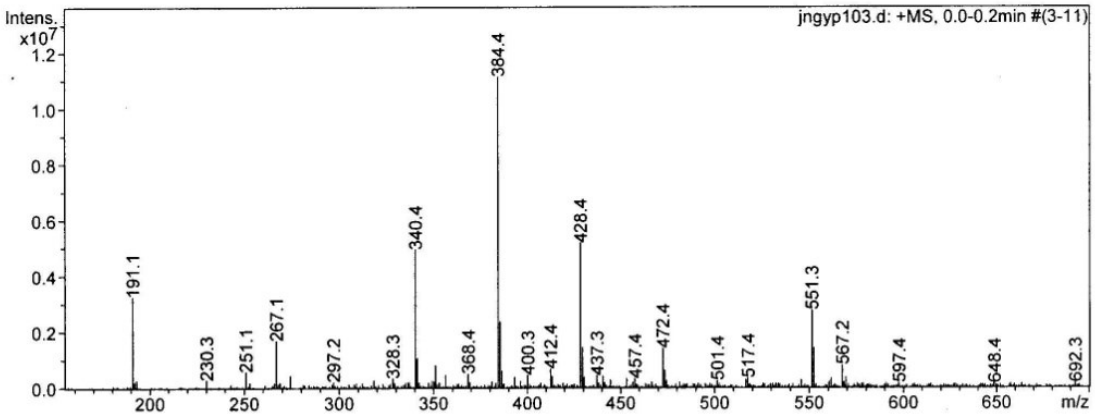
Figure S15. The IR spectrum of compound **1**.

Single Mass Spectrum Deconvolution Report

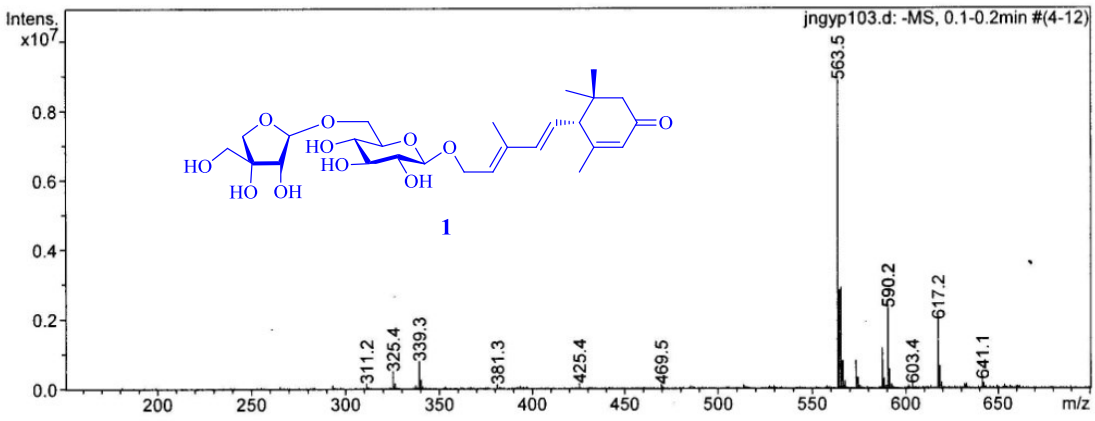
Analysis Name: jngyp103.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 12/23/2013 12:41:42 PM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 12/23/2013 11:42:49 AM
Sample Name: DS-40
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	36.3	Scan Begin	150 m/z
Ion Polarity	Positive	Octopole RF Amplitude	171.0 Vpp	Scan End	700 m/z
Ion Source Type	ESI	Capillary Exit	106.0 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	12.00 Volt	ICC Target	20000
Dry Gas (Set)	6.00 l/min	Oct 2 DC	1.70 Volt	Charge Control	on



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance



1

Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance

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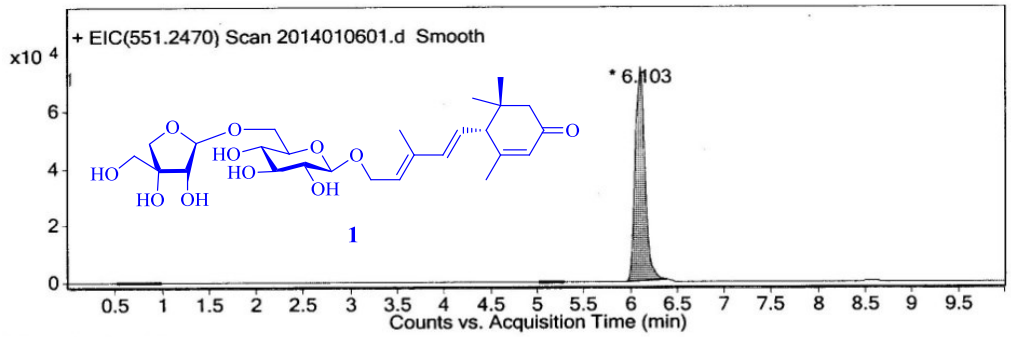
Figure S16. The ESI mass spectrum of compound **1**.

Qualitative Analysis Report

Data Filename	2014010601.d	**Sample Name**	DS-40
Sample Type	Sample	**Position**	P1-C3
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms

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



Integration Peak List

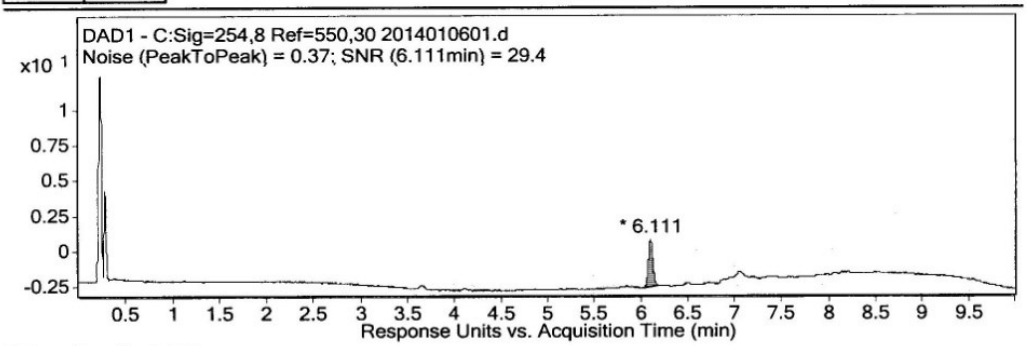
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.958	6.103	6.393	75115	534180	100	Infinity

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0

Noise Regions

Start	End
0.5	1
5	5.3
9.99	11



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.016	6.111	6.189	3.35	10.84	100	29.4

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.36907196

Noise Regions

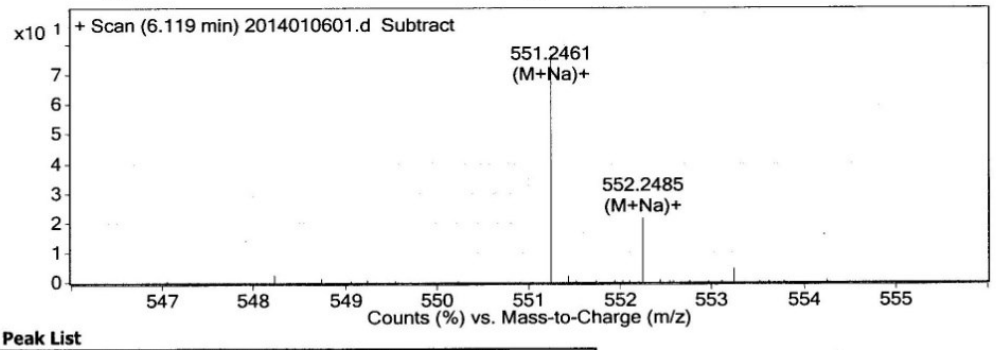
Start	End
0.5	1
5	5.3
9.99	11

User Spectra

Figure S17. The (+)-HR-ESI-MS report of compound **1**, page 1.

Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi

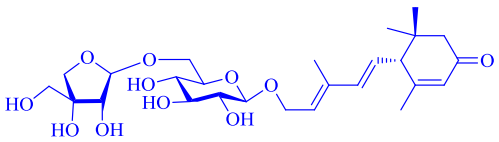


Peak List

m/z	z	Abund	Formula	Ion
101.0083		39257		
116.9859		43150		
133.0342	1	60415		
133.0966		39551		
277.128	1	90968		
284.1122	2	35480		
294.1545		45155		
299.1104	1	133236		
551.2461	1	102137	C26 H40 Na O11	(M+Na)+
597.2391	1	34096		

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	2
Cl	0	0
Br	0	0
Si	0	0
F	0	0
P	0	0



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Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C26 H40 O11	TRUE	528.2568	528.2571	0.43	C26 H40 Na O11	99.96
C27 H36 N4 O7		528.2568	528.2584	2.95	C27 H36 N4 Na O7	99.65
C30 H40 O6 S		528.2568	528.2546	-4.31	C30 H40 Na O6 S	98.51
C31 H36 N4 O2 S		528.2568	528.2559	-1.79	C31 H36 N4 Na O2 S	98.39
C27 H44 O6 S2		528.2568	528.2579	2.06	C27 H44 Na O6 S2	97.39
C28 H40 N4 O2 S2		528.2568	528.2593	4.58	C28 H40 N4 Na O2 S2	97.19
C22 H44 N2 O8 S2		528.2568	528.2539	-5.56	C22 H44 N2 Na O8 S2	96.83
C36 H36 N2 S		528.2568	528.2599	5.83	C36 H36 N2 Na S	96.57
C39 H32 N2		528.2568	528.2565	-0.55	C39 H32 N2 Na	96.3

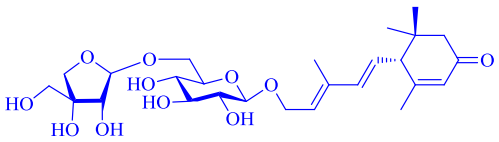
--- End Of Report ---

Figure S18. The (+)-HR-ESI-MS report of compound **1**, page 2.

MS Formula Results: + Scan (6.119 min) Sub (2014010601.d)

m/z	Ion	Formula	Abundance
551.2461	(M+Na)+	C26 H40 Na O11	102137

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☑	C26 H40 O11	C26 H40 Na O11	551.2463	99.96		528.2568	528.2571	0.43	0.43	99.93	99.91	99.99	551.2461	7
☐	C27 H36 N4 O7	C27 H36 N4 Na O7	551.2476	99.65		528.2568	528.2584	2.95	2.95	99.26	99.96	99.72	551.2461	12
☐	C30 H40 O6 S	C30 H40 Na O6 S	551.2438	98.51		528.2568	528.2546	-4.31	4.31	95.98	99.77	99.41	551.2461	11
☐	C31 H36 N4 O2 S	C31 H36 N4 Na O2 S	551.2451	98.39		528.2568	528.2559	-1.79	1.79	94.69	99.8	99.9	551.2461	16
☐	C27 H44 O6 S2	C27 H44 Na O6 S2	551.2472	97.39		528.2568	528.2579	2.06	2.06	91.51	99.52	99.86	551.2461	6
☐	C28 H40 N4 O2 S2	C28 H40 N4 Na O2 S2	551.2485	97.19		528.2568	528.2593	4.58	4.58	91.67	99.54	99.33	551.2461	11
☐	C22 H44 N2 O8 S2	C22 H44 N2 Na O8 S2	551.2431	96.83		528.2568	528.2539	-5.56	5.56	91.01	99.45	99.02	551.2461	2
☐	C36 H36 N2 S	C36 H36 N2 Na S	551.2491	96.57		528.2568	528.2599	5.83	5.83	89.94	99.84	98.92	551.2461	20
☐	C39 H32 N2	C39 H32 N2 Na	551.2458	96.3		528.2568	528.2565	-0.55	0.55	87.12	99.92	99.99	551.2461	25



1

page 1

Figure S19. The (+)-HR-ESI-MS report of compound **1**, page 3.

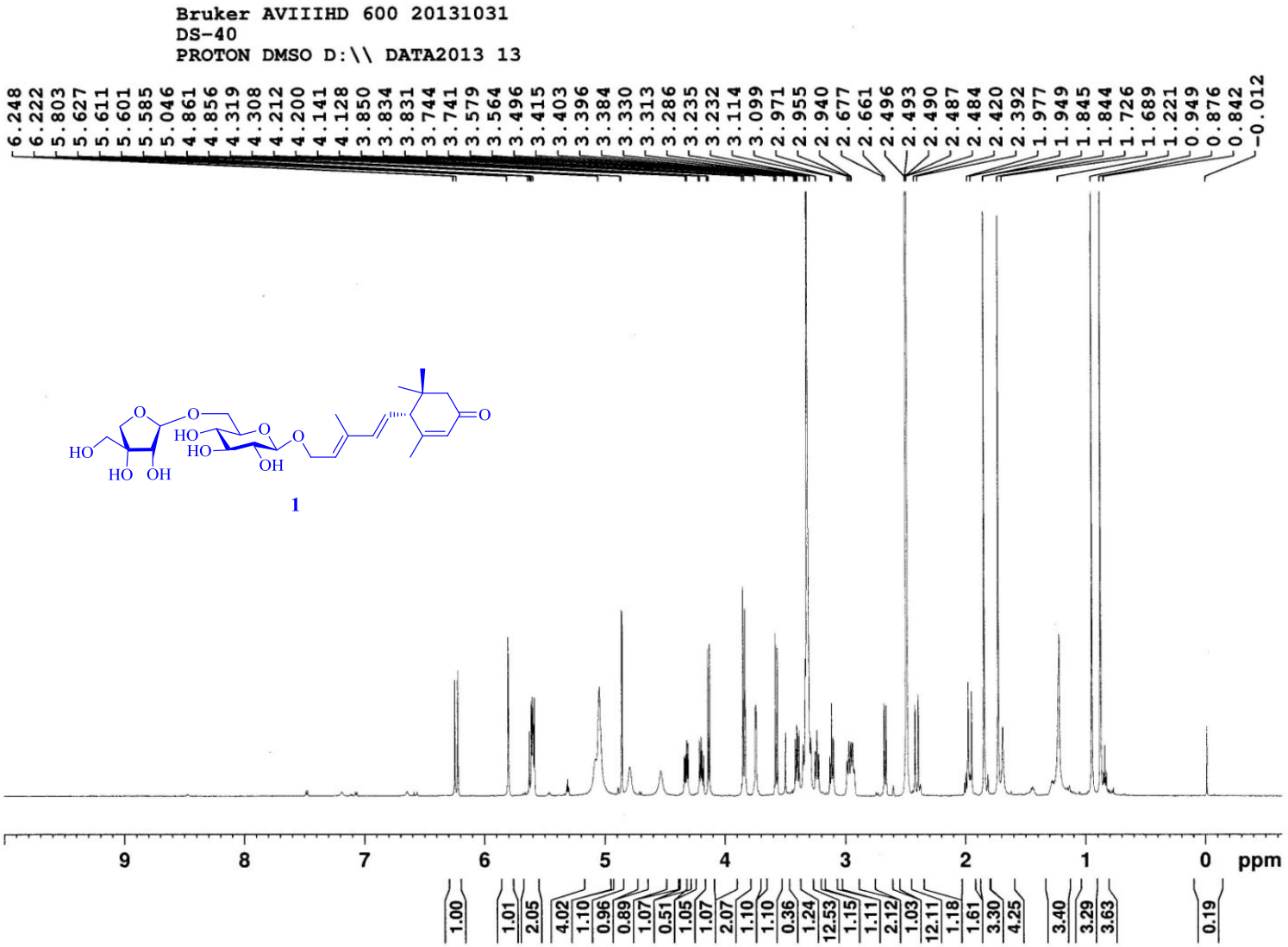


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Figure S20.The ^{1}H NMR spectrum of compound **1** in DMSO-d_6 (600 MHz).

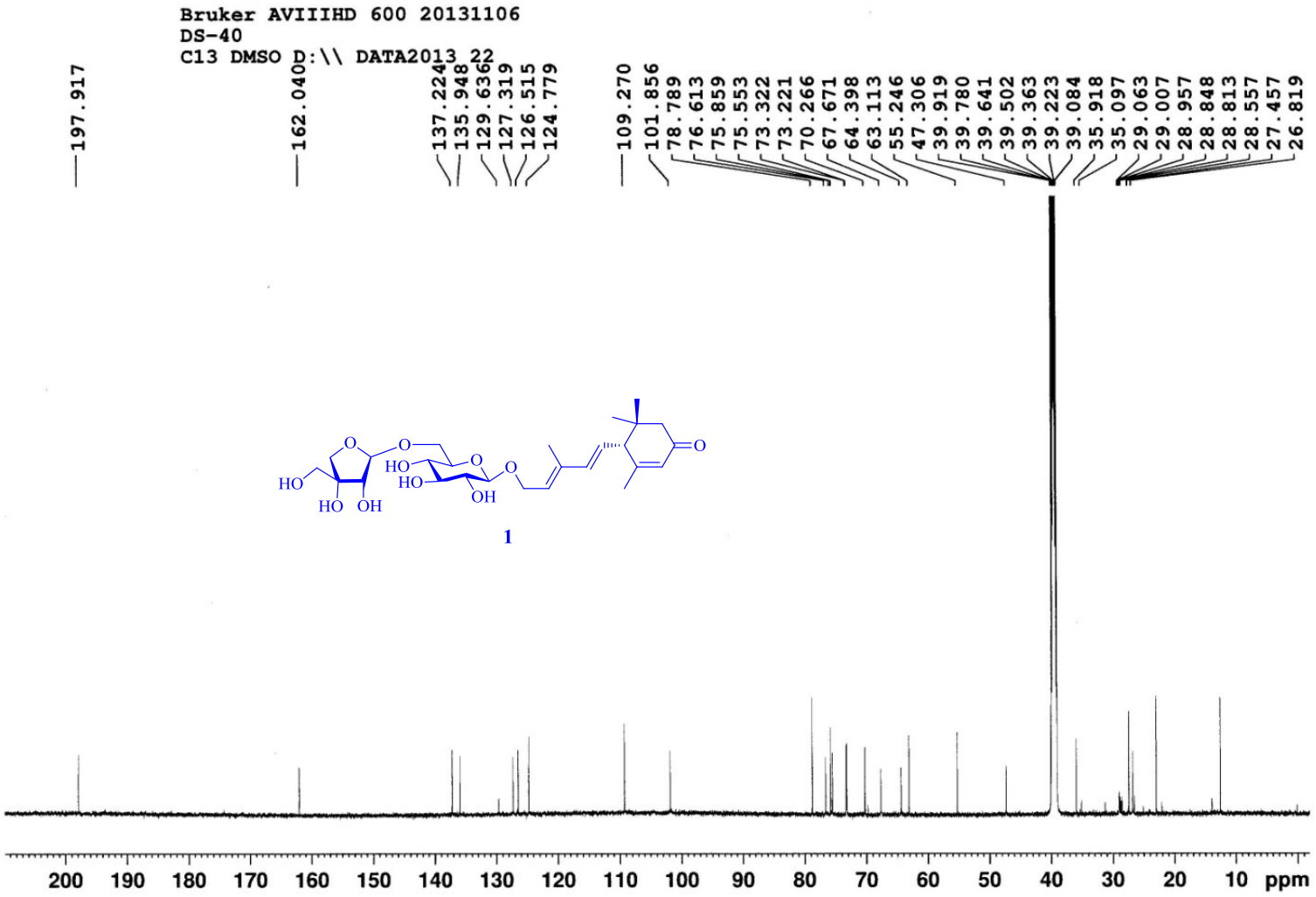


Figure S21.The ^{13}C NMR spectrum of compound **1** in DMSO-d_6 (150 MHz).

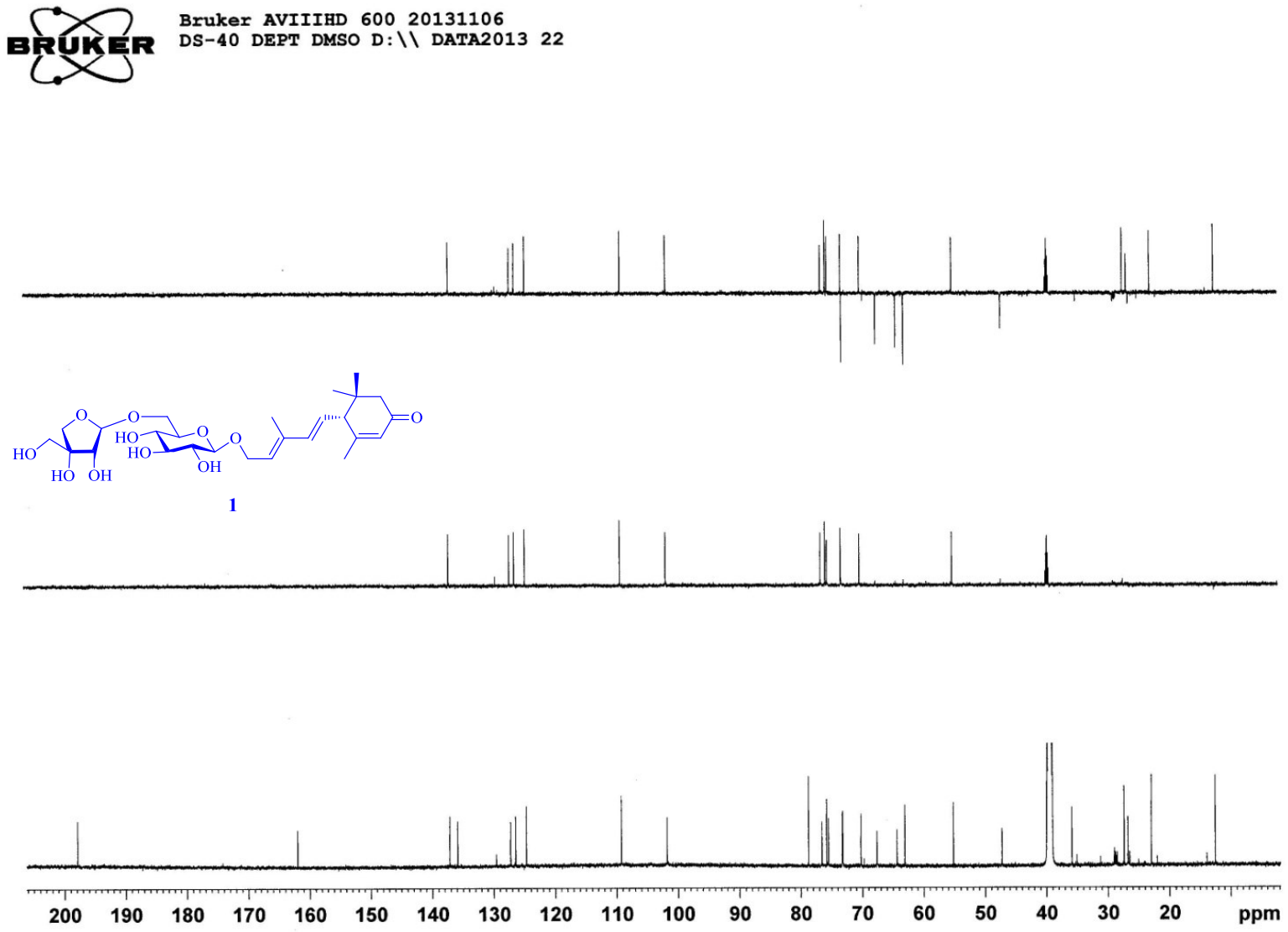


Figure S22.The DEPT spectrum of compound **1** in DMSO-d_6 (150 MHz).

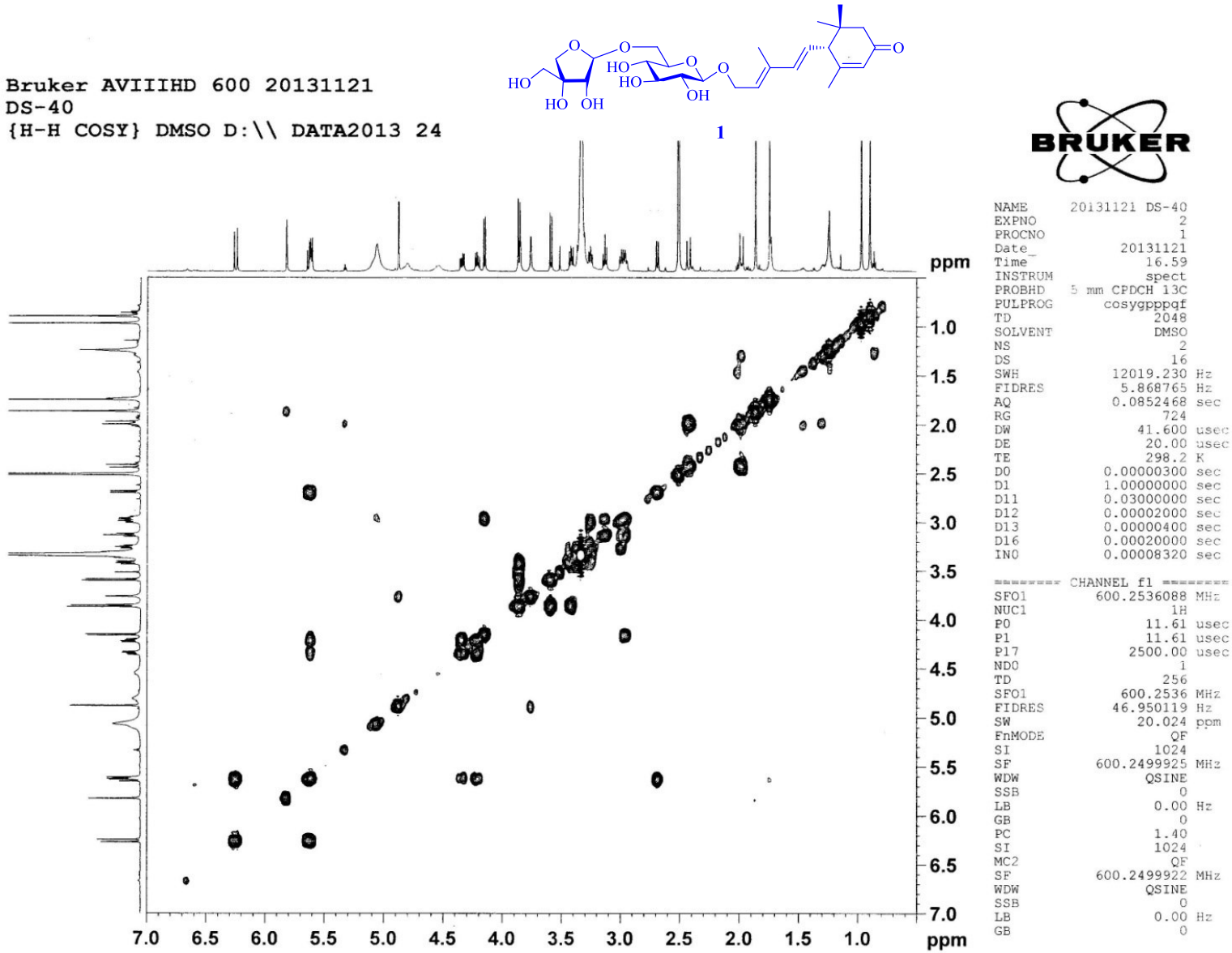


Figure S23.The ^{1}H-^{1}H COSY spectrum of compound **1** in DMSO-d_6 (600 MHz).

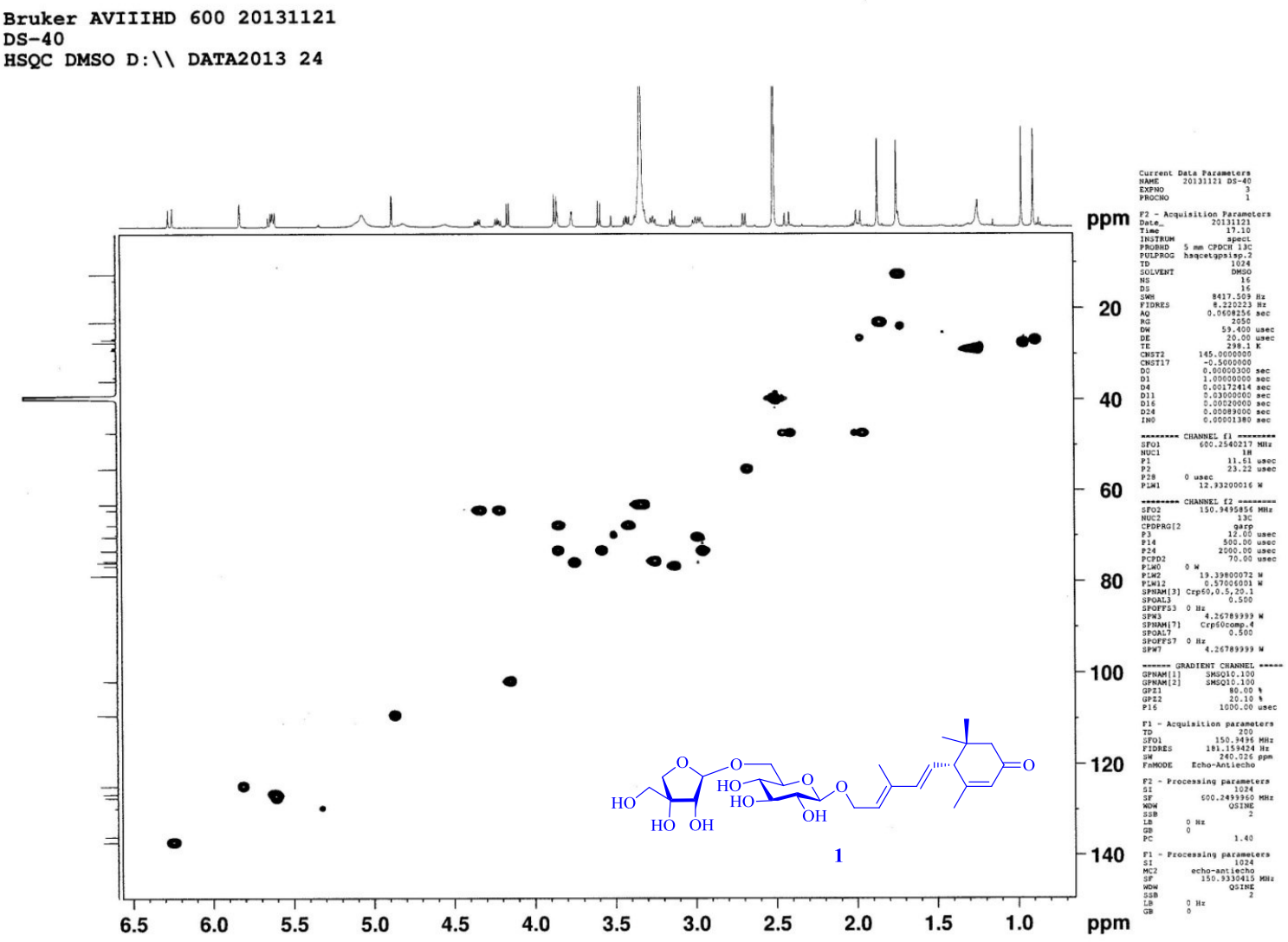


Figure S24.The HSQC spectrum of compound **1** in DMSO-d_6 (600 MHz for ^{1}H).

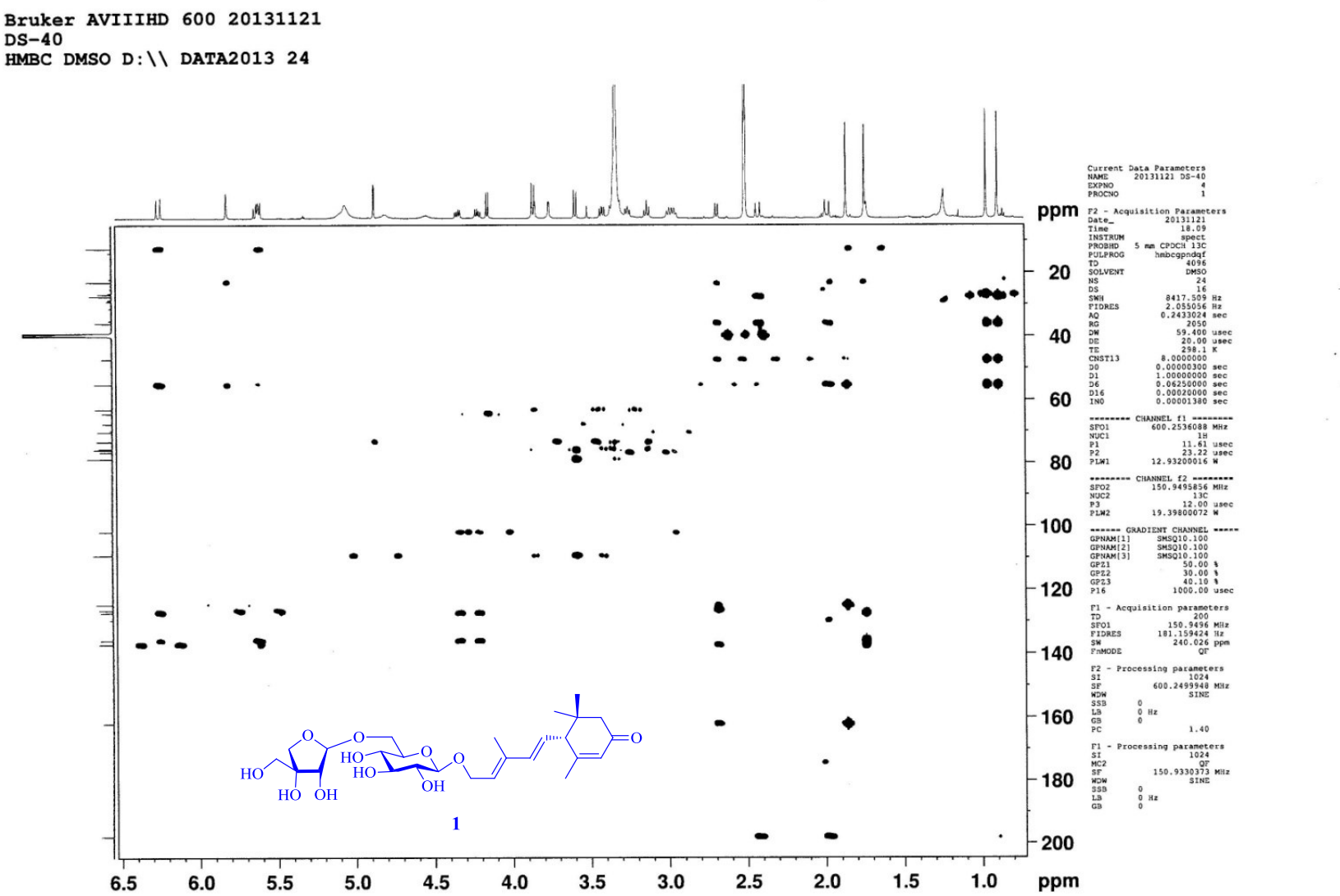


Figure S25.The HMBC spectrum of compound **1** in DMSO-d_6 (600 MHz for ^{1}H).

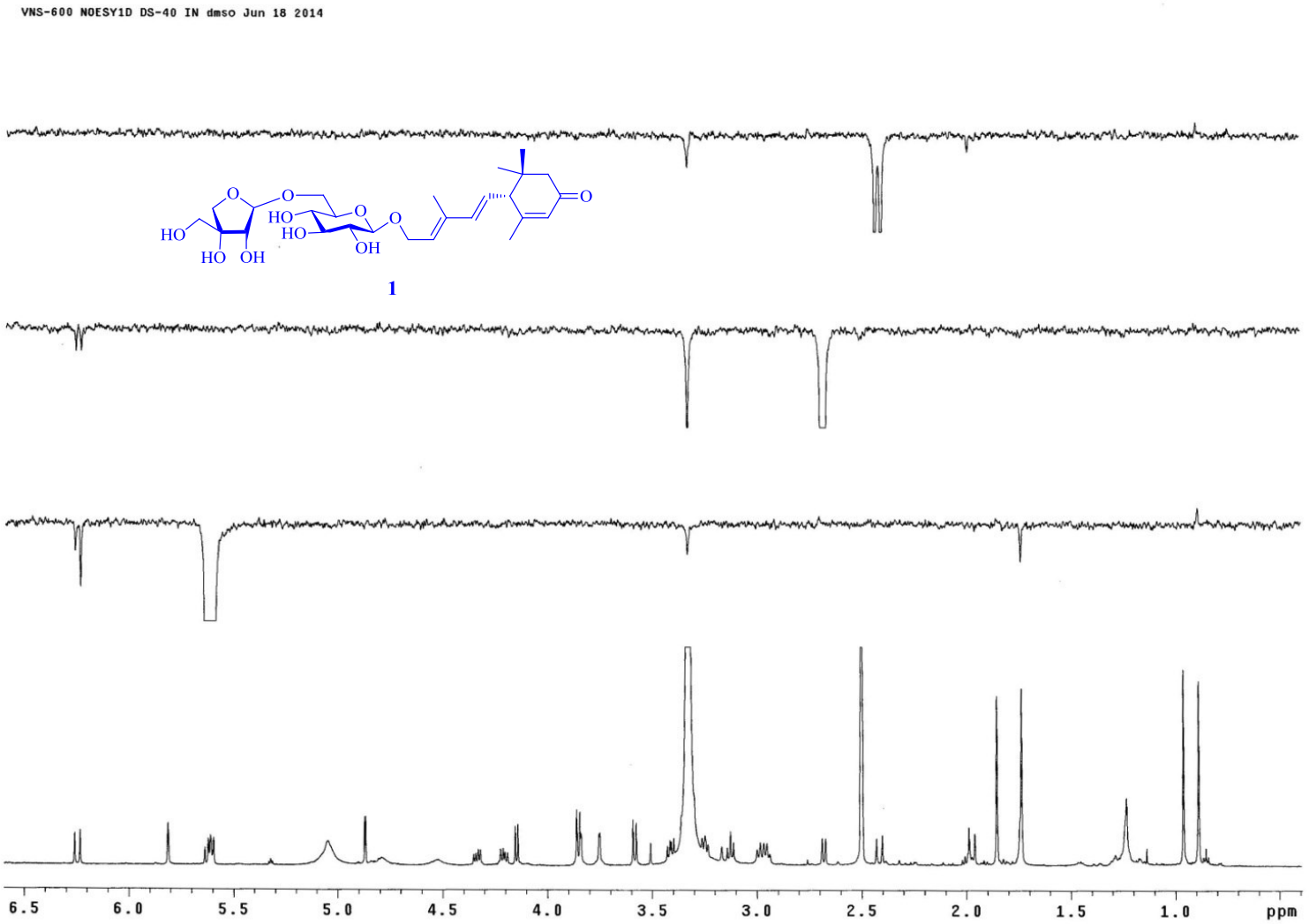
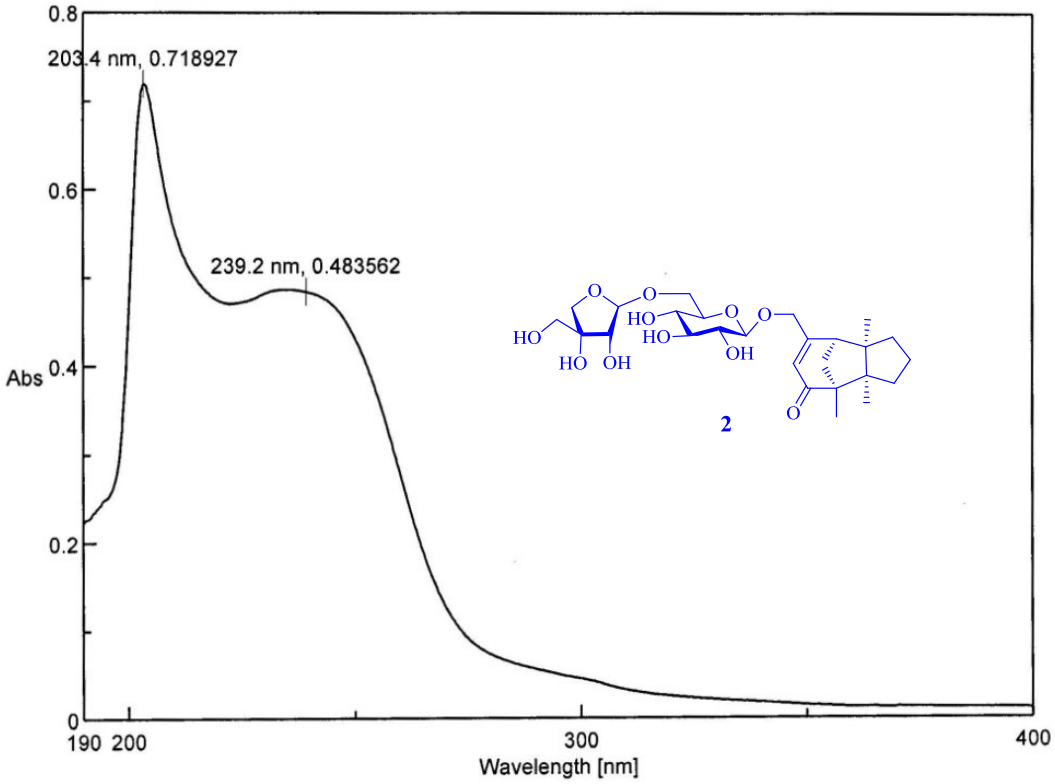


Figure S26. The NOE difference spectrum of **1** in DMSO-d_6 (600 MHz).



ds-77b

[Comment]
Sample Name ds-77b
Comment 0.02
User
Division UV
Company 324
[Measurement Information]
Instrument Name V-650
Model Name V-650
Serial No. A034461150

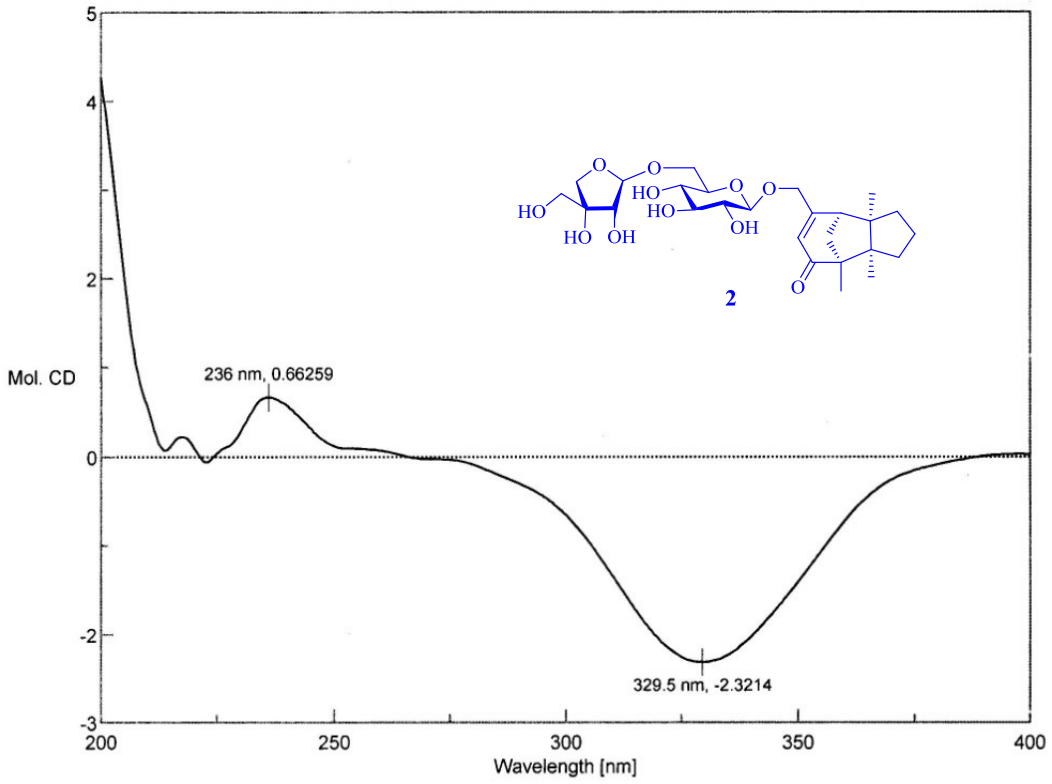
Accessory PSC-718
Accessory S/N A001761114
Position 1
Cell Length 10 mm
Temperature 19.97 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

[Data Information]
Creation Date 2015-3-10 19:39

Data array type Linear data array
Horizontal Wavelength [nm]
Vertical Abs
Start 400 nm
End 190 nm
Data pitch 0.2 nm
Data points 1051

Figure S27.The UV spectrum of compound **2** in MeOH.



[Comments]

Sample name	DS-77B
Comment	
User	
Division	
Company	dell

[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	2 sec
Band width	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
PMT Voltage	Auto
Accumulations	3
Solvent	MEOH
Concentration	0.48 (w/v)%

[Detailed Information]

Creation date	2014-5-20 10:25
Data array type	Linear data array * 3
Horizontal axis	Wavelength [nm]
Vertical axis(1)	Mol. CD
Vertical axis(2)	HT [V]
Vertical axis(3)	Abs
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End	200 nm
Data interval	0.5 nm
Data points	401

Figure S28.The CD spectrum of compound **2** in MeOH.

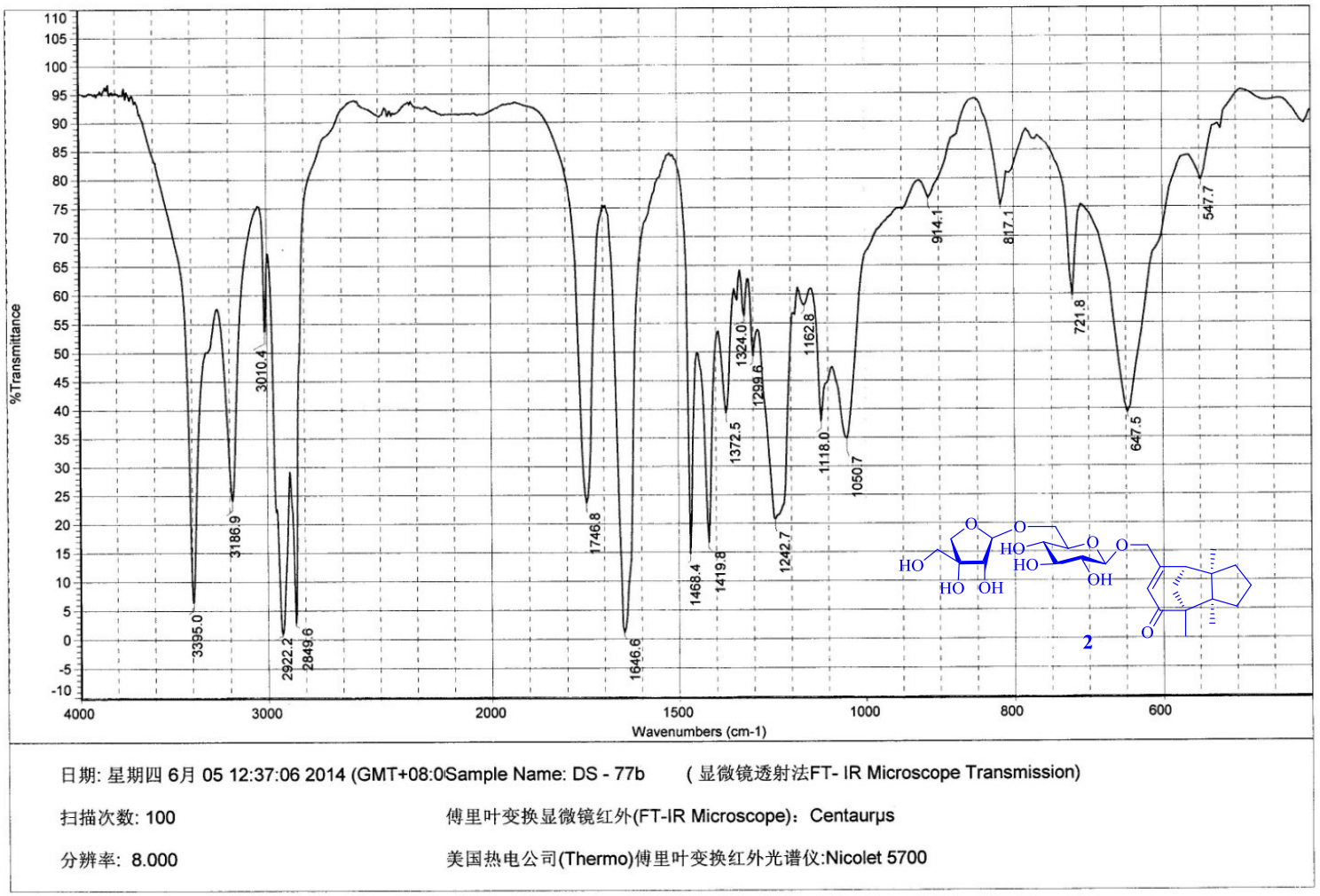


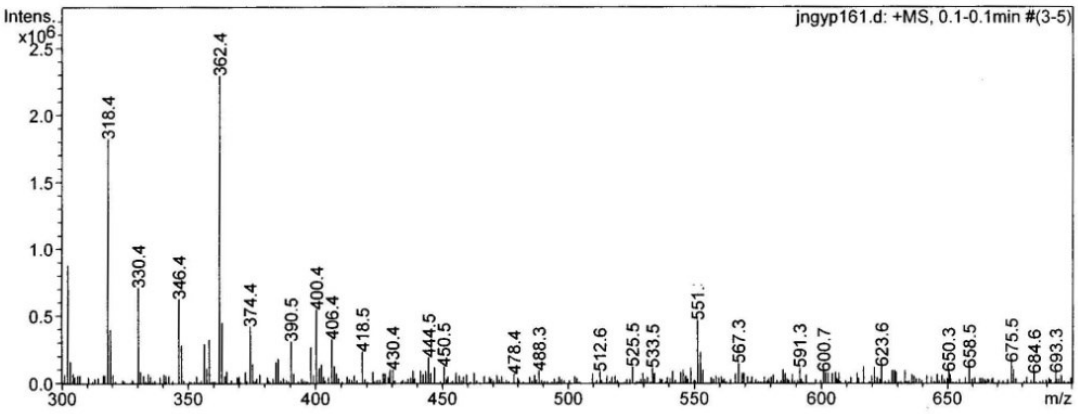
Figure S29. The IR spectrum of compound **2**.

Single Mass Spectrum Deconvolution Report

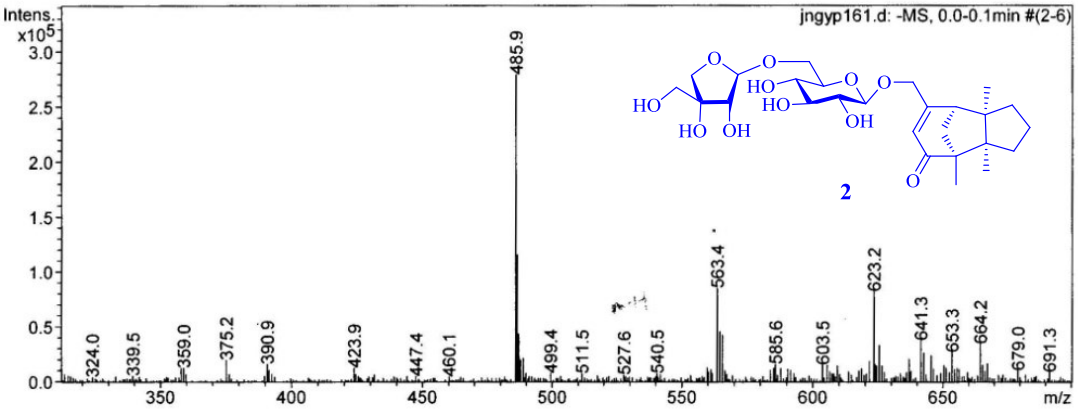
Analysis Name: jngyp161.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 6/27/2014 3:10:18 PM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 6/27/2014 1:56:20 PM
Sample Name: DS-77b
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	47.2	Scan Begin	300 m/z
Ion Polarity	Positive	Octopole RF Amplitude	194.5 Vpp	Scan End	700 m/z
Ion Source Type	ESI	Capillary Exit	132.3 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	12.00 Volt	ICC Target	20000
Dry Gas (Set)	6.00 l/min	Oct 2 DC	1.70 Volt	Charge Control	on



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance

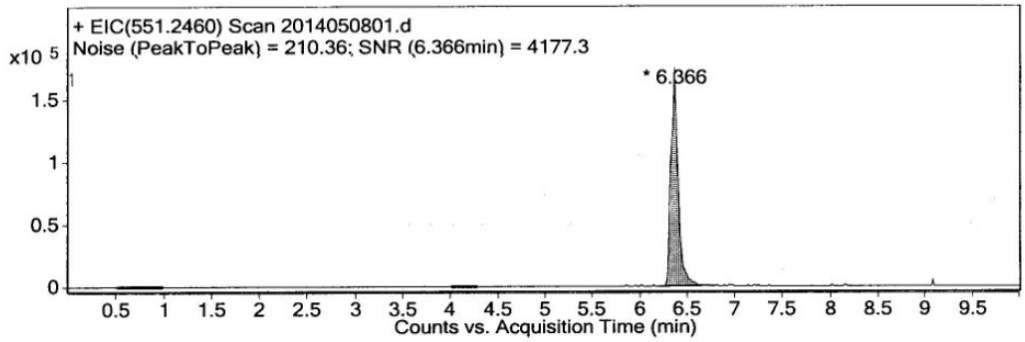
Figure S30. The ESI mass spectrum of compound **2**.

Qualitative Analysis Report

Data Filename	2014050801.d	**Sample Name**	DS-77b
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST LCMS.m	**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms

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



Integration Peak List

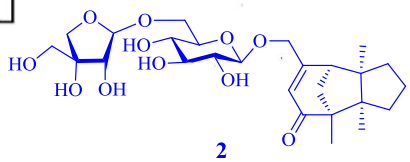
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.221	6.366	6.736	175229	878751	100	4177.3

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	210.3635864

Noise Regions

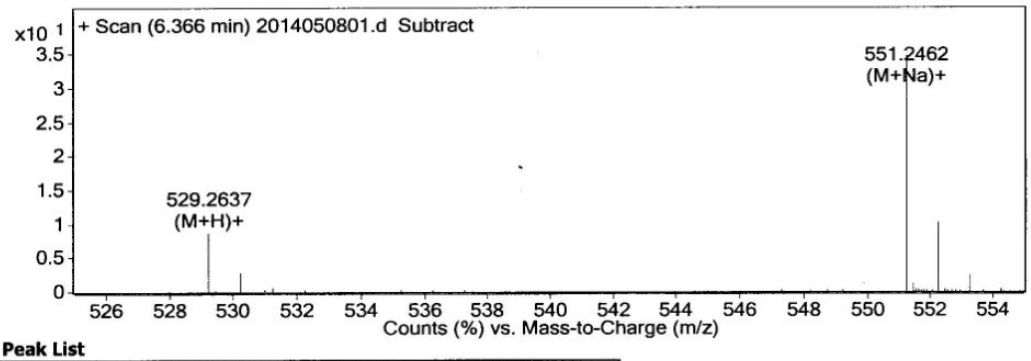
Start	End
0.5	1
4	4.3
9.99	11



2

User Spectra

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



Peak List

m/z	z	Abund	Formula	Ion
199.1804	1	506216		
200.1827	1	71124		
214.0896	1	213460		
221.1609		56675		
231.1157		63052		
236.072		53527		
257.1678	1	254513		
397.2219	1	139477		

Figure S31.The (+)-HR-ESI-MS report of compound **2**, page 1.

Qualitative Analysis Report

m/z	z	Abund	Formula	Ion
551.2462	1	175385	C26 H40 Na O11	(M+Na)+
552.2494	1	51318	C26 H40 Na O11	(M+Na)+

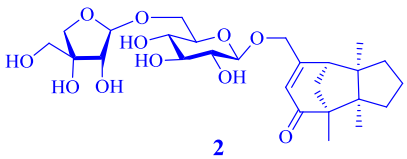
Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	0
Cl	0	0
Br	0	0
Si	0	0
F	0	0
P	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C26 H40 O11	TRUE	528.257	528.2571	0.11	C26 H40 Na O11	99.98
C27 H36 N4 O7		528.257	528.2584	2.63	C27 H36 N4 Na O7	99.74
C27 H36 N4 O7		528.2565	528.2584	3.68	C27 H37 N4 O7	99.72
C26 H40 O11	TRUE	528.2564	528.2571	1.17	C26 H41 O11	99.67
C39 H32 N2		528.2565	528.2565	0.19	C39 H33 N2	98.2

--- End Of Report ---



2

Figure S32.The (+)-HR-ESI-MS report of compound **2**, page 2

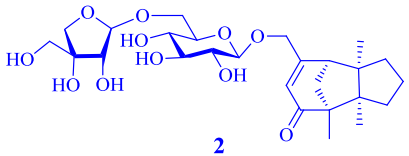
MS Formula Results: + Scan (6.366 min) Sub (2014050801.d)

m/z	Ion	Formula	Abundance
529.2637	(M+H)+	C26 H41 O11	43614.1

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C27 H36 N4 O7	C27 H37 N4 O7	529.2657	99.72		528.2565	528.2584	3.68	3.68	99.83	99.96	99.53	529.2637	12
☑	C26 H40 O11	C26 H41 O11	529.2643	99.67		528.2564	528.2571	1.17	1.17	98.94	99.99	99.95	529.2637	7
☐	C39 H32 N2	C39 H33 N2	529.2638	98.2		528.2565	528.2565	0.19	0.19	93.72	99.98	100	529.2637	25

m/z	Ion	Formula	Abundance
551.2462	(M+Na)+	C26 H40 Na O11	175384.6

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☑	C26 H40 O11	C26 H40 Na O11	551.2463	99.98		528.257	528.2571	0.11	0.11	99.95	99.99	100	551.2462	7
☐	C27 H36 N4 O7	C27 H36 N4 Na O7	551.2476	99.74		528.257	528.2584	2.63	2.63	99.47	100	99.78	551.2462	12



2

page 1

Figure S33.The (+)-HR-ESI-MS report of compound **2**, page 3.

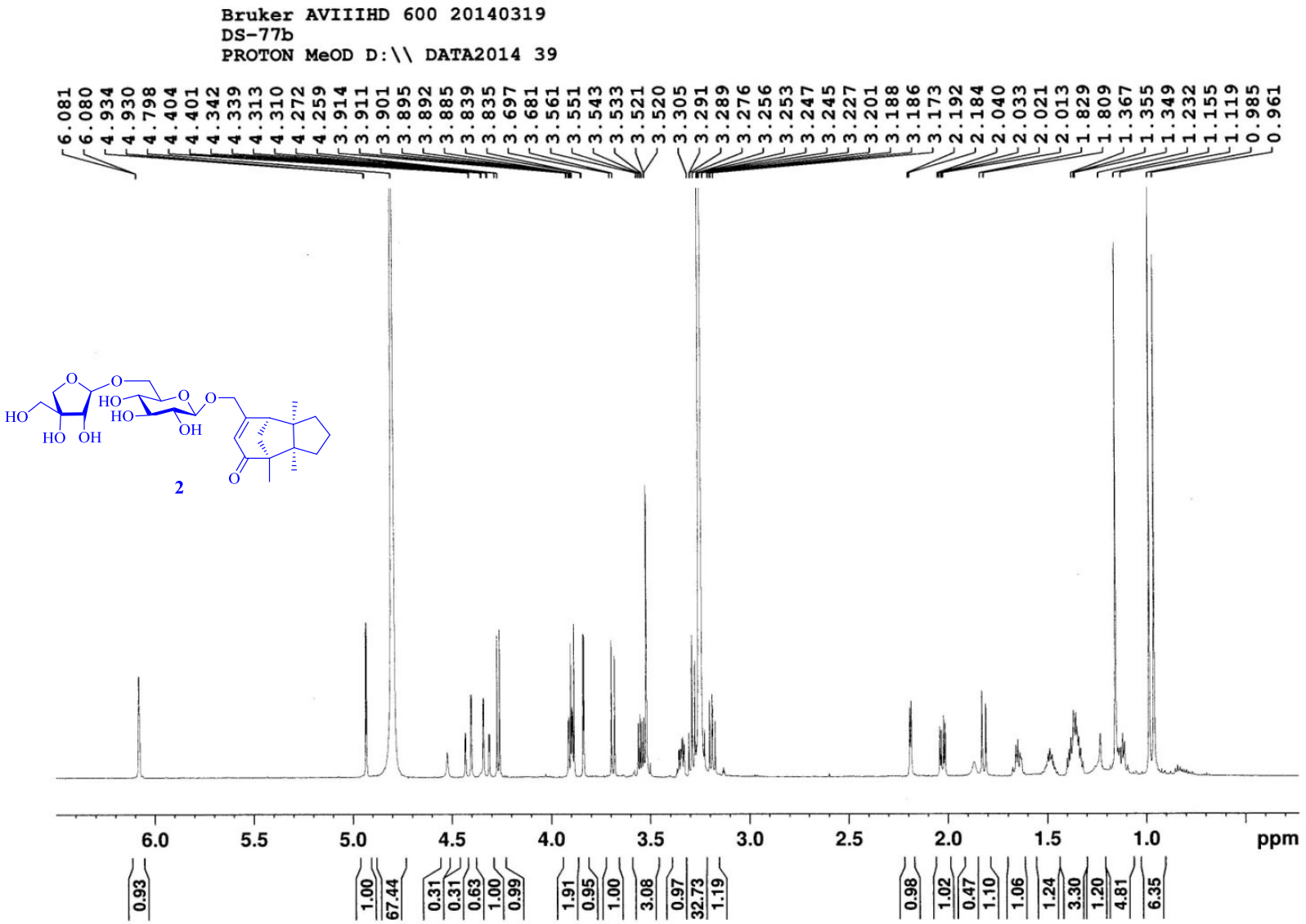


Figure S34.The ^{1}H NMR spectrum of compound **2** in MeOH-d_4 (600 MHz).

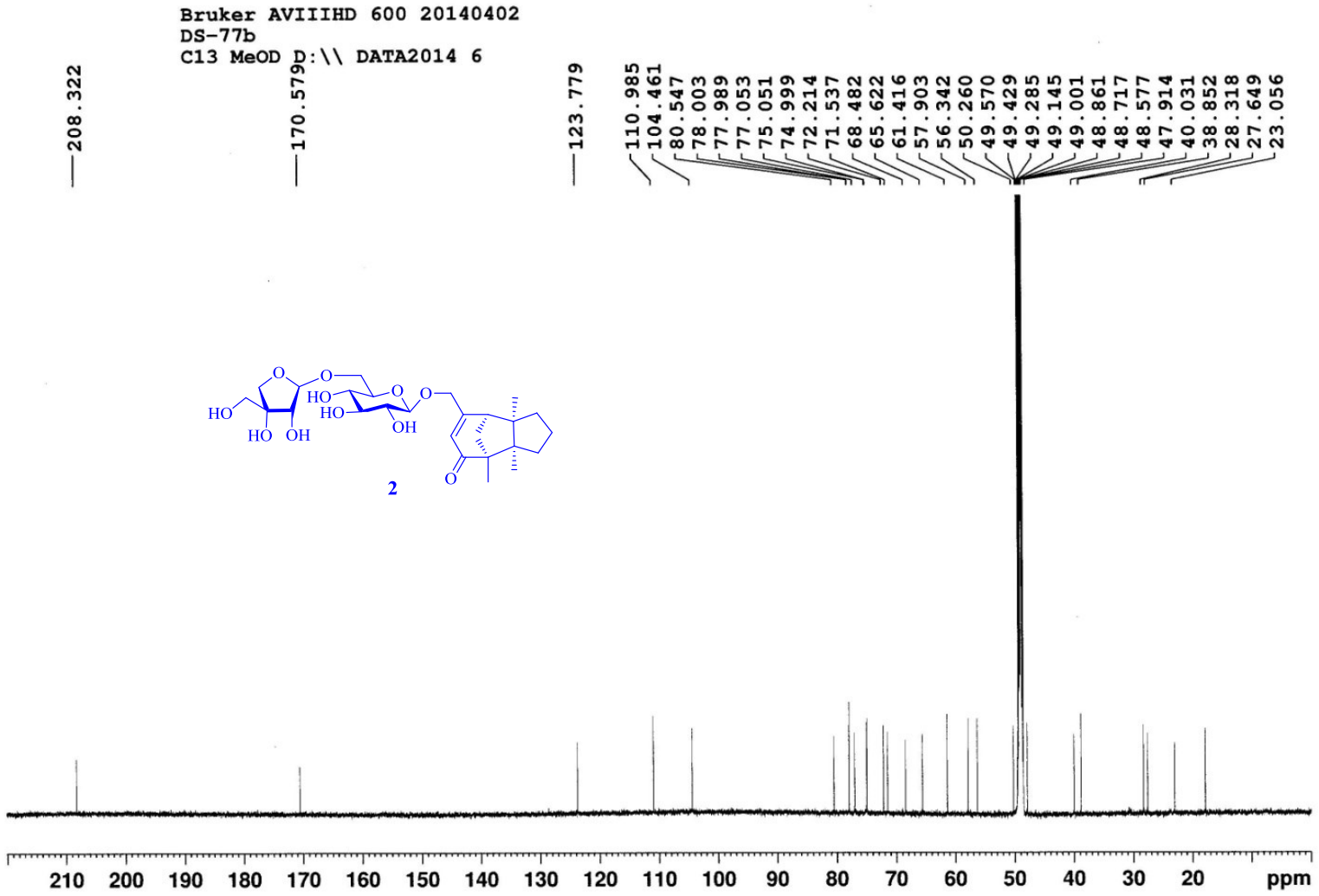


Figure S35. The ^{13}C NMR spectrum of compound **2** in MeOH-d_4 (150MHz).

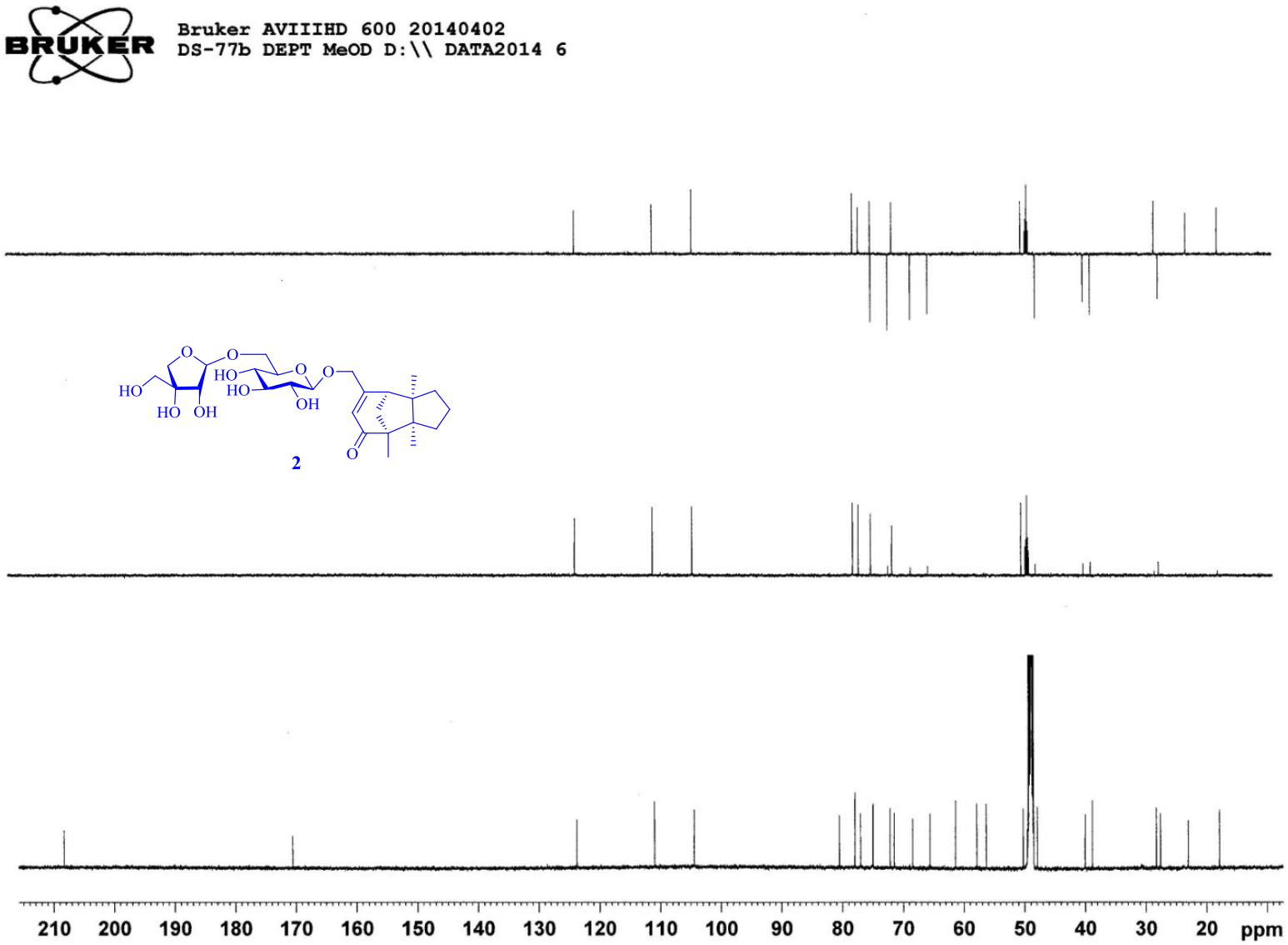


Figure S36. The DEPT spectrum of compound **2** in MeOH-d_4 (150 MHz).

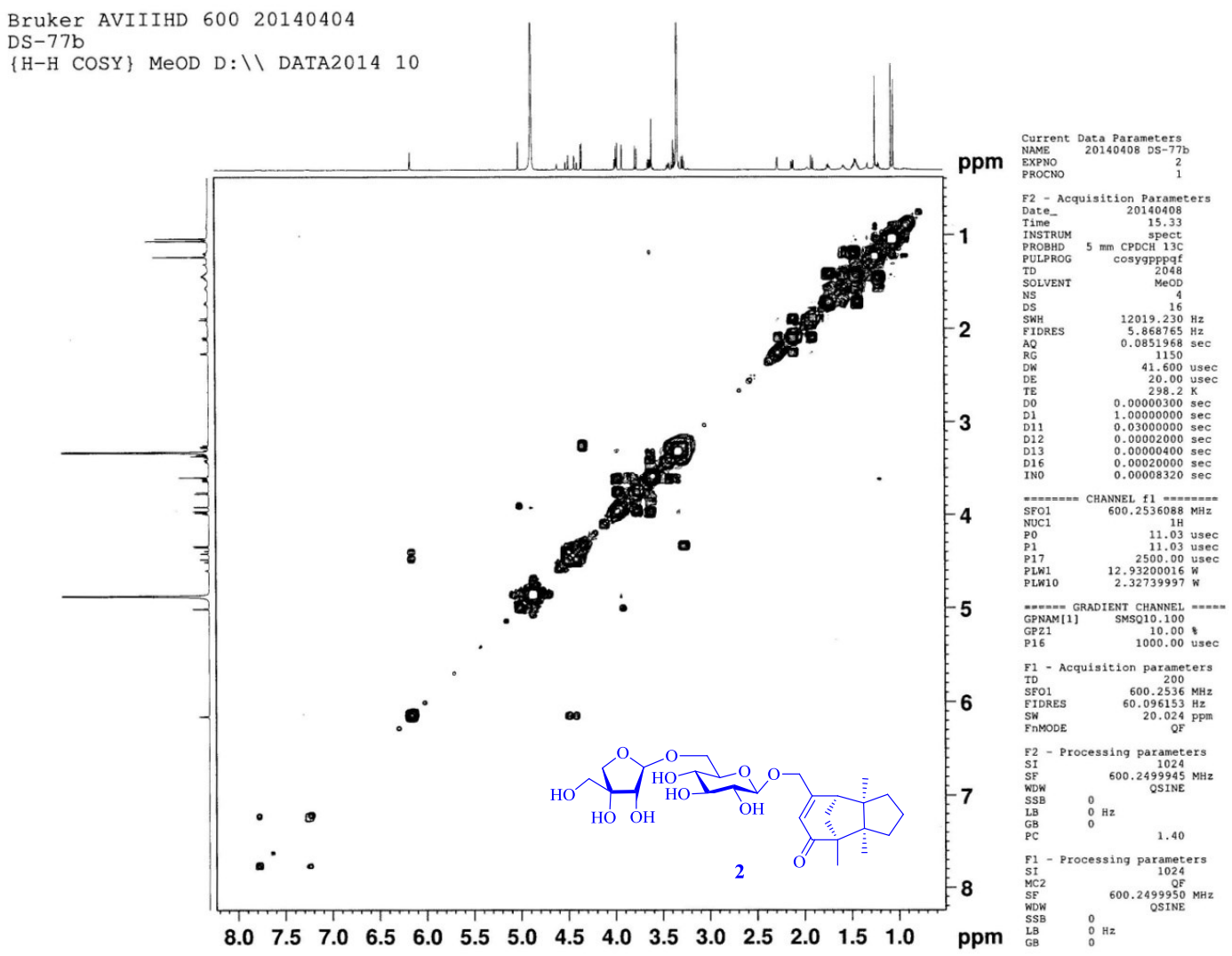


Figure S37. The ^{1}H-^{1}H COSY spectrum of compound **2** in MeOH-d_4 (600 MHz).

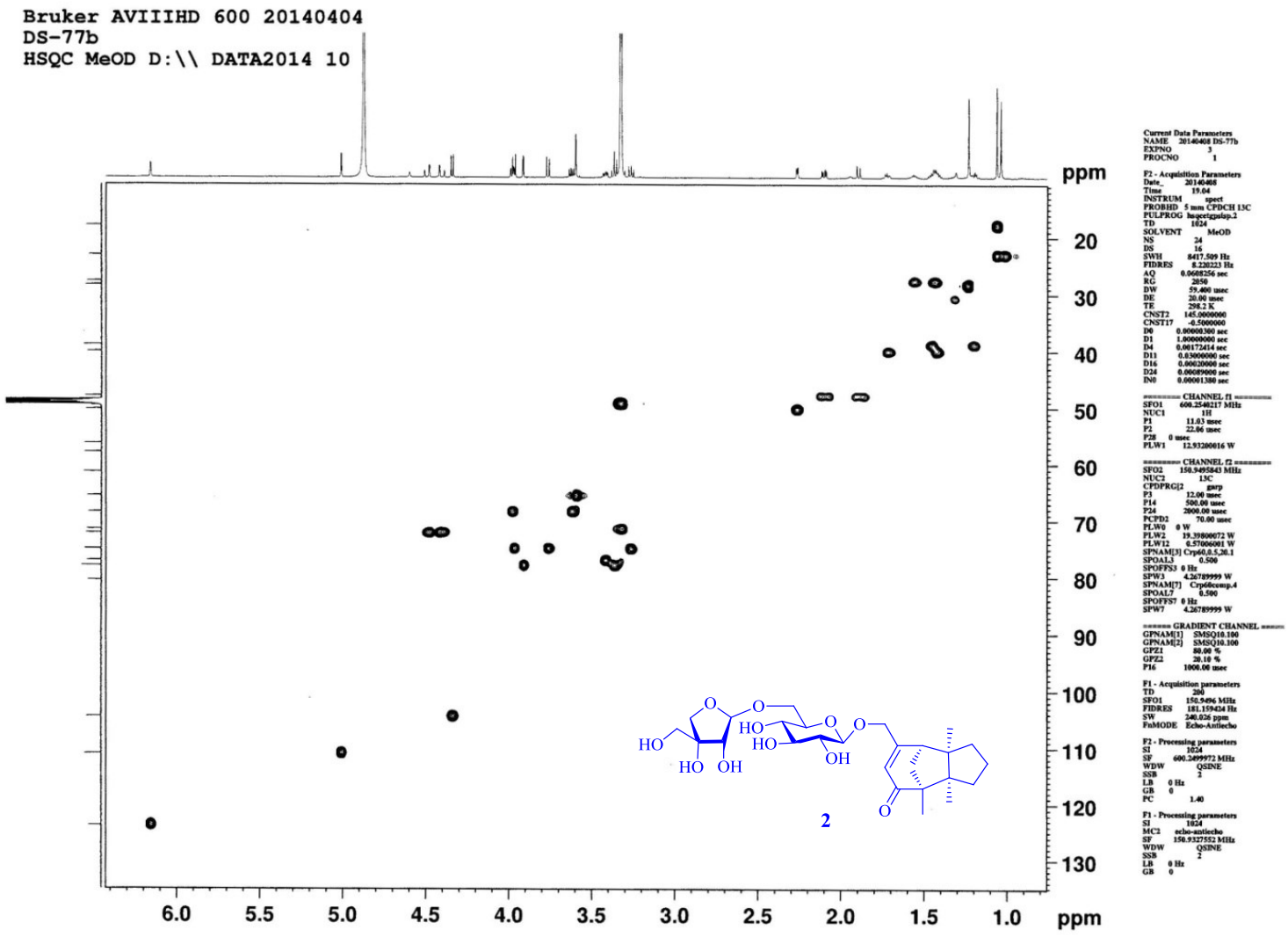


Figure S38.The HSQC spectrum of compound **2** in MeOH-d_4 (600 MHz for ^{1}H).

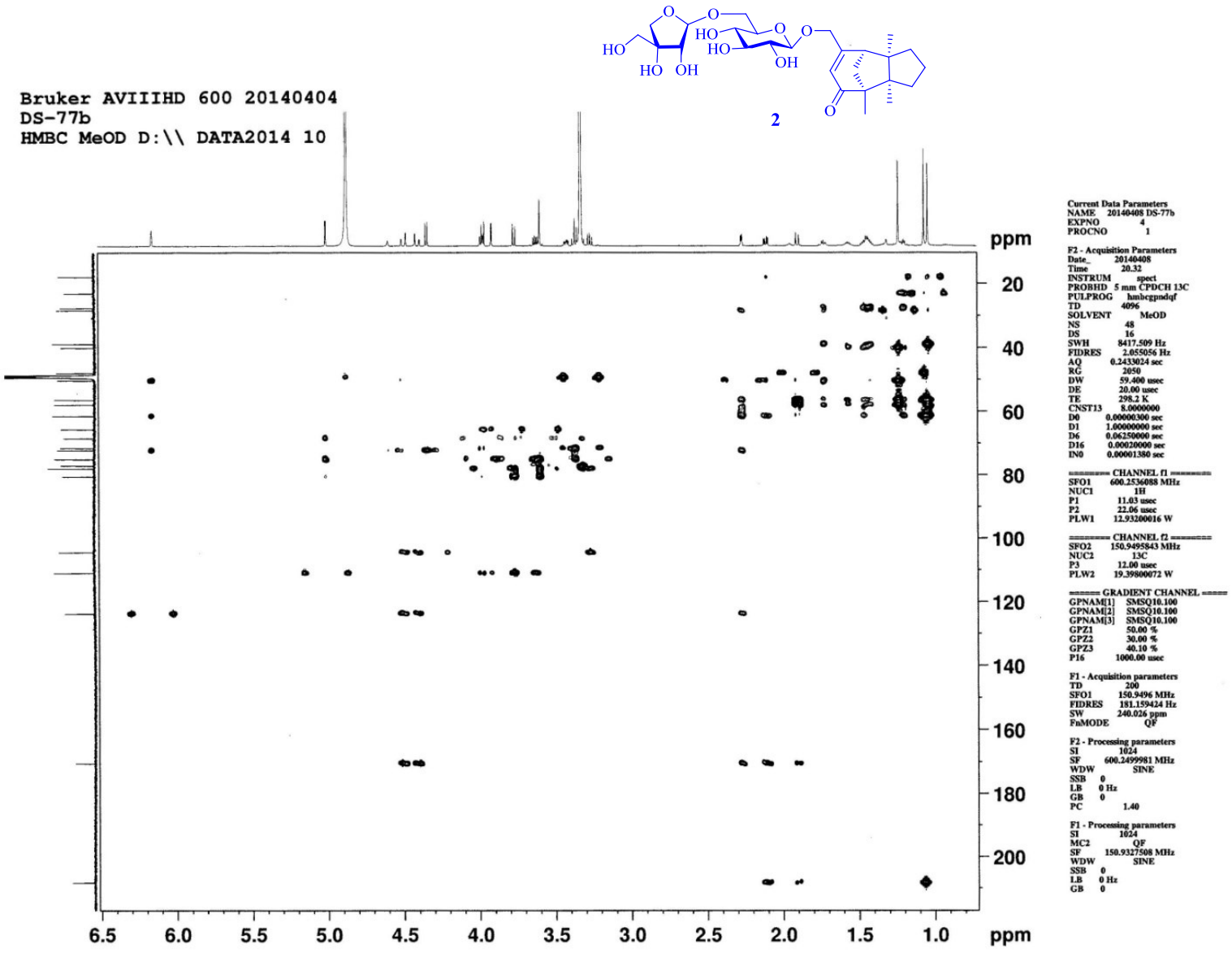


Figure S39.The HMBC spectrum of compound **2** in MeOH-d_4 (600 MHz for ^{1}H).

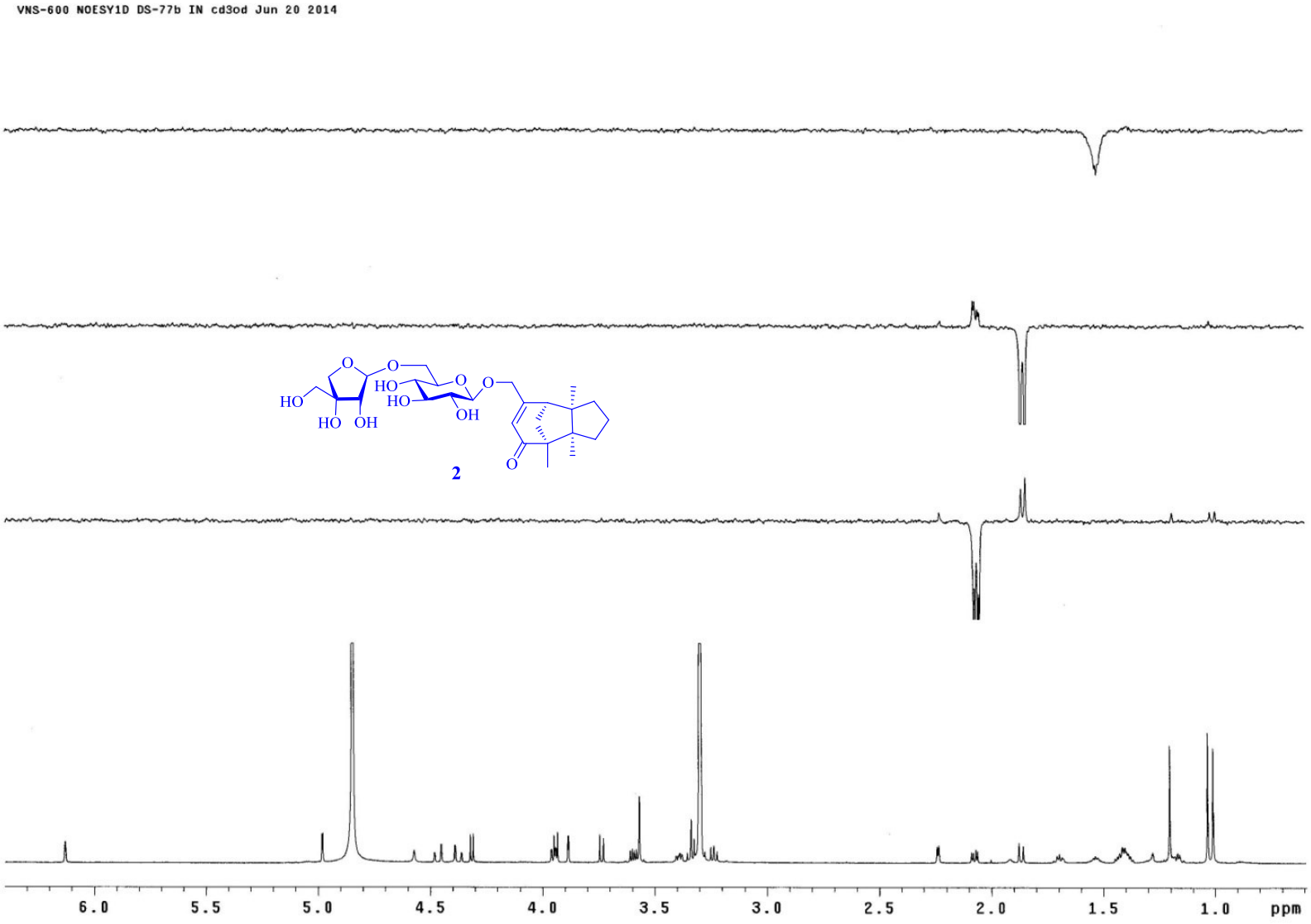


Figure S40.The NOE difference spectrum of **2** in MeOH-d_4 (600 MHz).

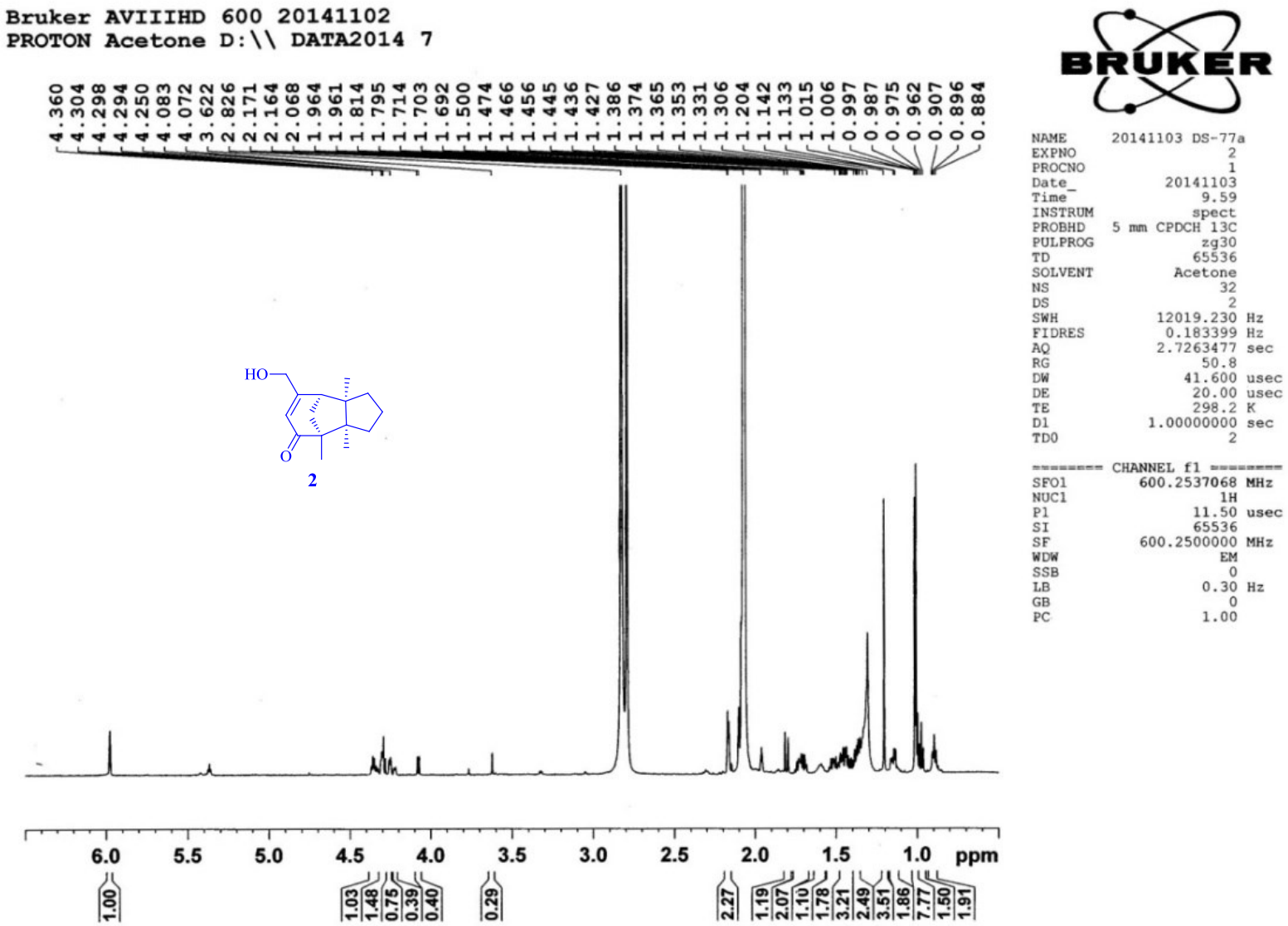
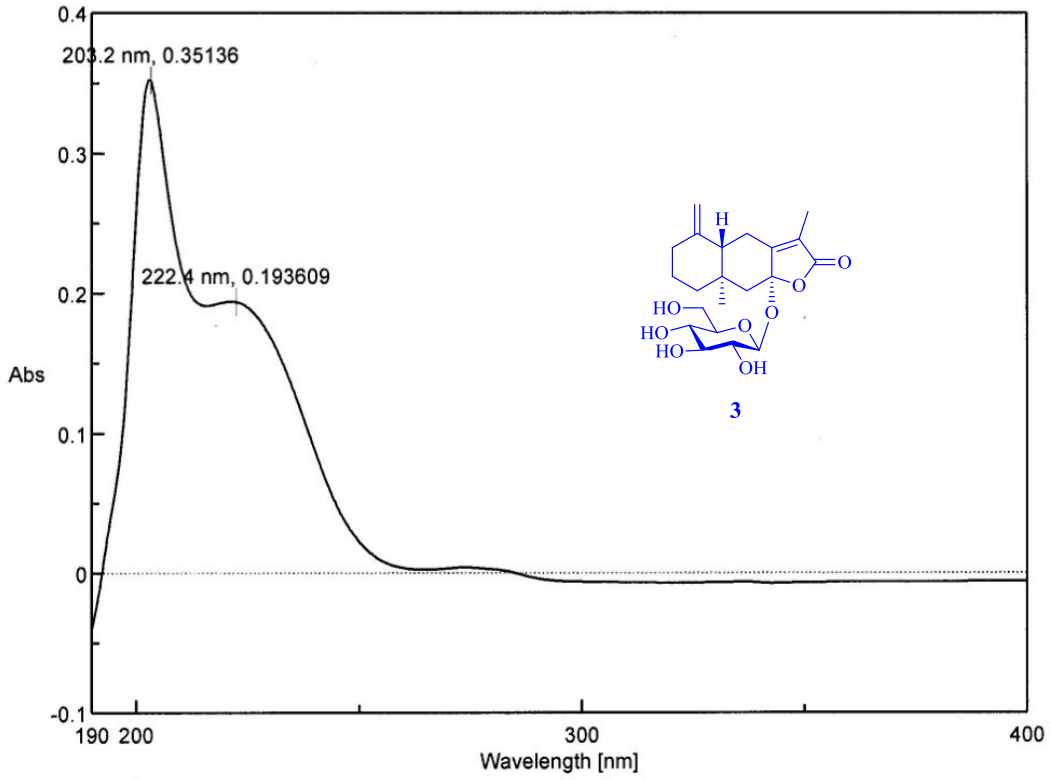


Figure S41.The ^{1}H NMR spectrum of the aglycone of **2** in MeOH-d_4 (600 MHz).



DS-135

[Comment]
Sample Name DBT
Comment 0.02
User
Division UV
Company 324
[Measurement Information]
Instrument Name V-650
Model Name V-650
Serial No. A034461150

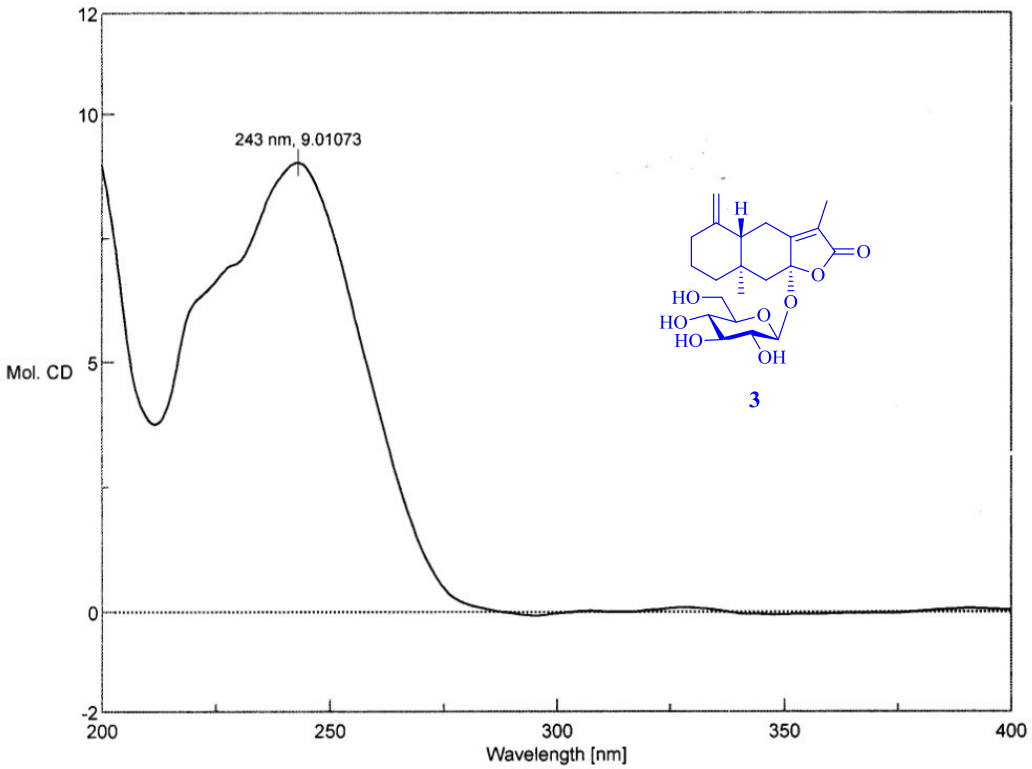
Accessory PSC-718
Accessory S/N A001761114
Position 1
Cell Length 10 mm
Temperature 19.94 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

[Data Information]
Creation Date 2014-6-10 19:21

Data array type Linear data array
Horizontal Wavelength [nm]
Vertical Abs
Start 400 nm
End 190 nm
Data pitch 0.2 nm
Data points 1051

Figure S42.The UV spectrum of compound **3** in MeOH.



[Comments]

Sample name	DS-135
Comment	
User	
Division	
Company	dell

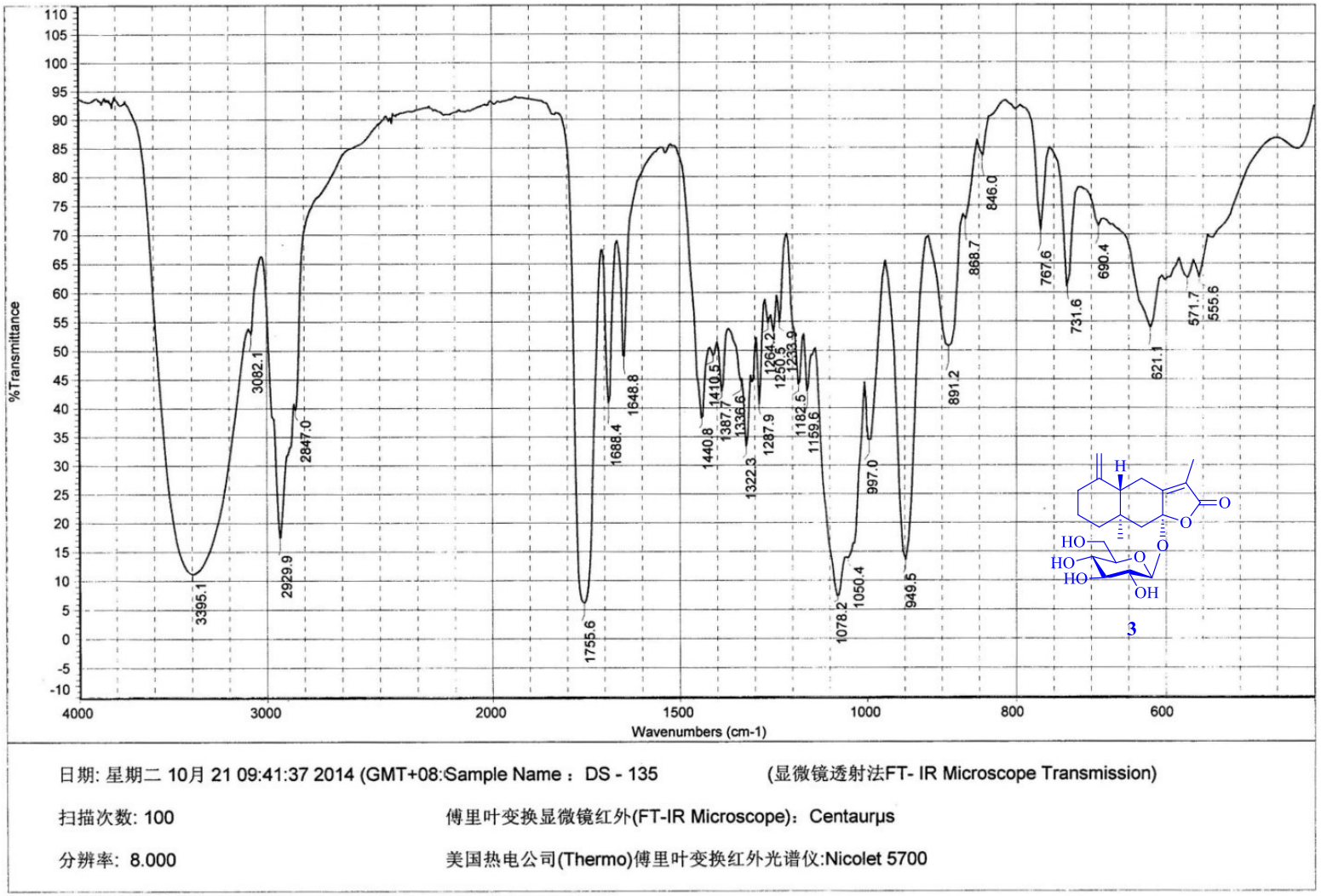
[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	2 sec
Band width	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
PMT Voltage	Auto
Accumulations	3
Solvent	MEOH
Concentration	0.2462 (w/v)%

[Detailed Information]

Creation date	2014-6-20 11:11
Data array type	Linear data array * 3
Horizontal axis	Wavelength [nm]
Vertical axis(1)	Mol. CD
Vertical axis(2)	HT [V]
Vertical axis(3)	Abs
Start	400 nm
End	200 nm
Data interval	0.5 nm
Data points	401

Figure S43.The CD spectrum of compound **3** in MeOH.



日期: 星期二 10月 21 09:41:37 2014 (GMT+08:Sample Name ： DS - 135 (显微镜透射法FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换显微镜红外(FT-IR Microscope)： Centaurμs

分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

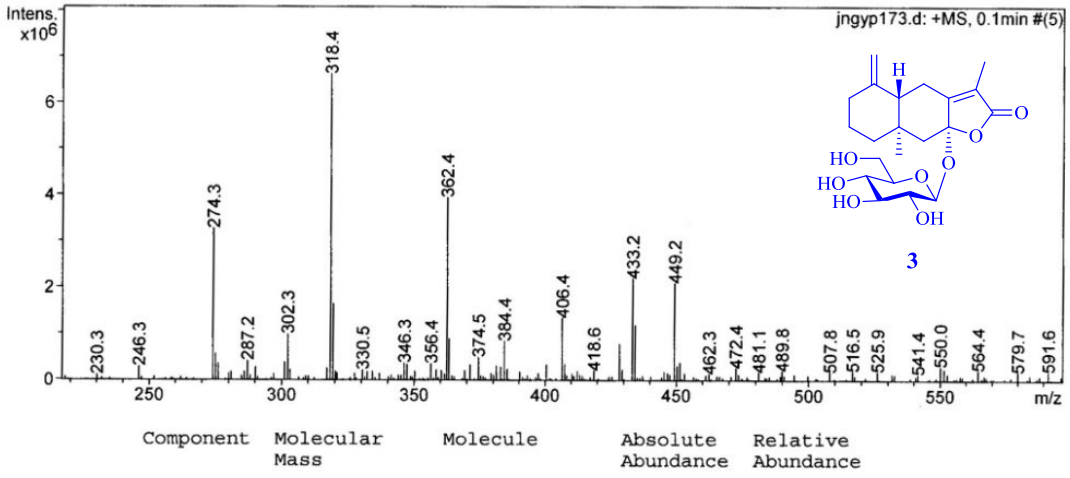
Figure S44. The IR spectrum of compound **3**.

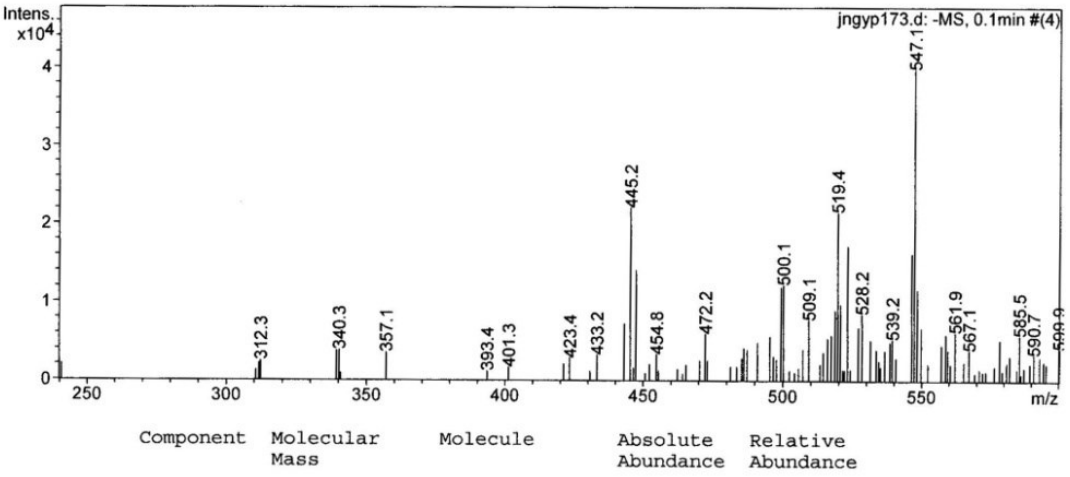
Single Mass Spectrum Deconvolution Report

Analysis Name: jngyp173.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 6/27/2014 3:31:53 PM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 6/27/2014 2:26:26 PM
Sample Name: DS-135
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	36.3	Scan Begin	200 m/z
Ion Polarity	Positive	Octopole RF Amplitude	171.0 Vpp	Scan End	600 m/z
Ion Source Type	ESI	Capillary Exit	121.0 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	12.00 Volt	ICC Target	20000
Dry Gas (Set)	6.00 l/min	Oct 2 DC	1.70 Volt	Charge Control	on





3

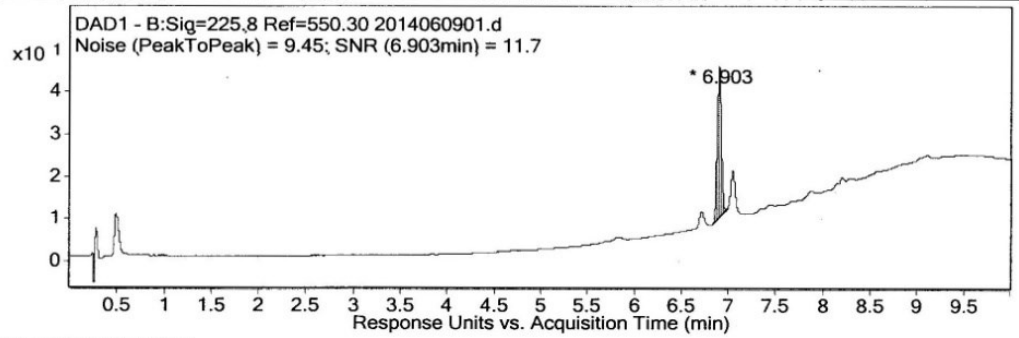
MSD Trap Report v 4 (A4-Opt2) Page 1 of 1 Agilent Technologies

Figure S45. The ESI mass spectra of Compound **3**.

Qualitative Analysis Report

Data Filename	2014060901.d	**Sample Name**	DS-135
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	Success
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms



Integration Peak List

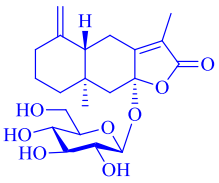
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.833	6.903	6.992	35.38	110.59	100	11.7

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	9.44852829

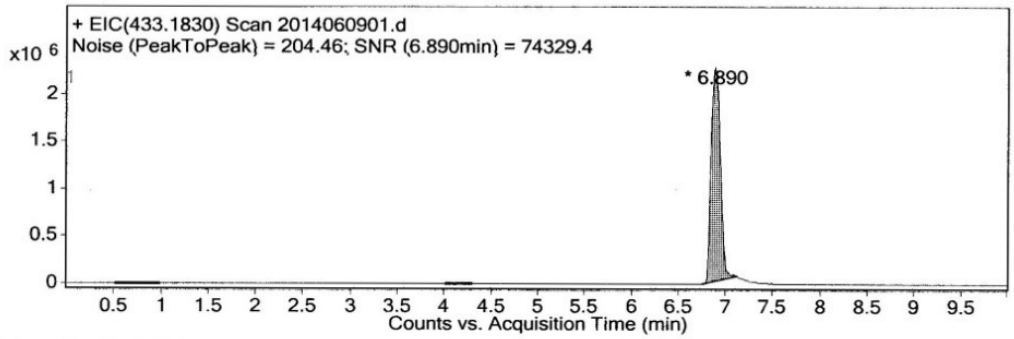
Noise Regions

Start	End
0.5	1
4	4.3
9.99	11



3

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



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.745	6.89	7.132	2258026	15197083	100	74329.4

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	204.4558563

Noise Regions

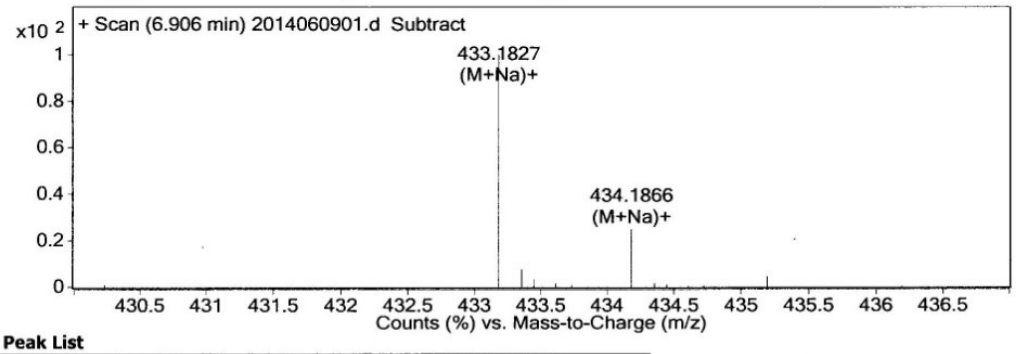
Start	End
0.5	1
4	4.3
9.99	11

User Spectra

Figure S46. The (+)-HR-ESI-MS report of compound **3**, page 1.

Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi

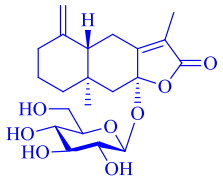


Peak List

m/z	z	Abund	Formula	Ion
249.1479		119082		
428.2276		405647		
433.1827	1	2145478	C21 H30 Na O8	(M+Na)+
433.3571		157937		
434.1866	1	532157	C21 H30 Na O8	(M+Na)+
843.3769	1	387325		
844.3787	1	175409		

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	2
Cl	0	0
Br	0	0
Si	0	0
F	0	0
P	0	0



3

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H30 O8	TRUE	410.1935	410.1941	1.39	C21 H30 Na O8	99.91
C22 H26 N4 O4		410.1935	410.1954	4.64	C22 H26 N4 Na O4	99.62
C25 H30 O3 S		410.1935	410.1916	-4.72	C25 H30 Na O3 S	98.83
C22 H34 O3 S2		410.1935	410.1949	3.5	C22 H34 Na O3 S2	97.38

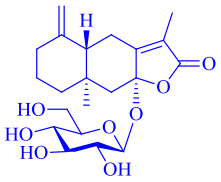
--- End Of Report ---

Figure S47. The (+)-HR-ESI-MS report of compound **3**, page 2.

MS Formula Results: + Scan (6.906 min) Sub (2014060901.d)

m/z	Ion	Formula	Abundance
433.1827	(M+Na)+	C21 H30 Na O8	2145477.5

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☑	C21 H30 O8	C21 H30 Na O8	433.1833	99.91		410.1935	410.1941	1.39	1.39	99.8	99.96	99.94	433.1827	7
☐	C22 H26 N4 O4	C22 H26 N4 Na O4	433.1846	99.62		410.1935	410.1954	4.64	4.64	99.82	99.89	99.36	433.1827	12
☐	C25 H30 O3 S	C25 H30 Na O3 S	433.1808	98.83		410.1935	410.1916	-4.72	4.72	97.42	99.54	99.33	433.1827	11
☐	C22 H34 O3 S2	C22 H34 Na O3 S2	433.1842	97.38		410.1935	410.1949	3.5	3.5	92.17	99.13	99.63	433.1827	6



3

page 1

Figure S48. The (+)-HR-ESI-MS report of compound **3**, page 3.

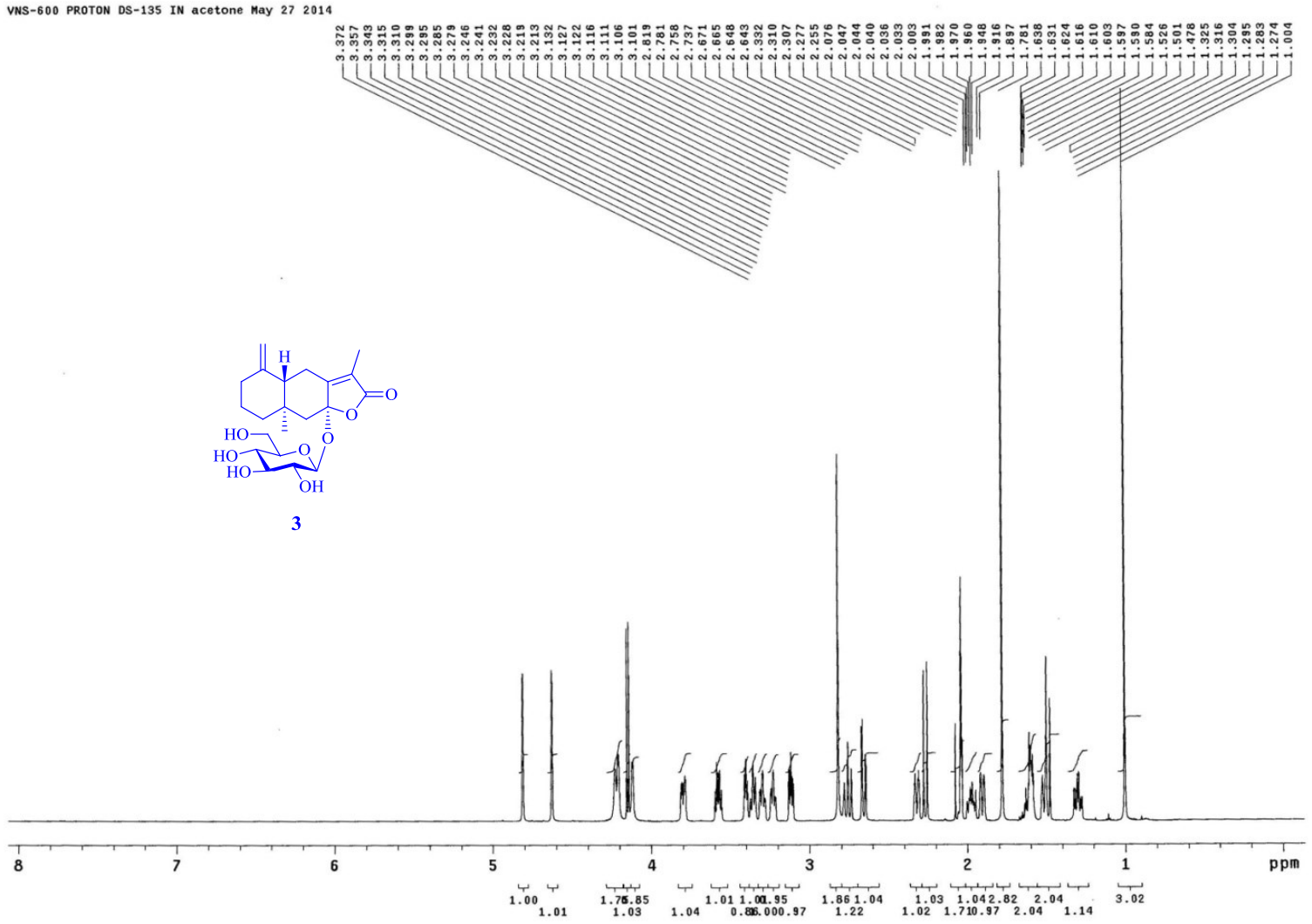
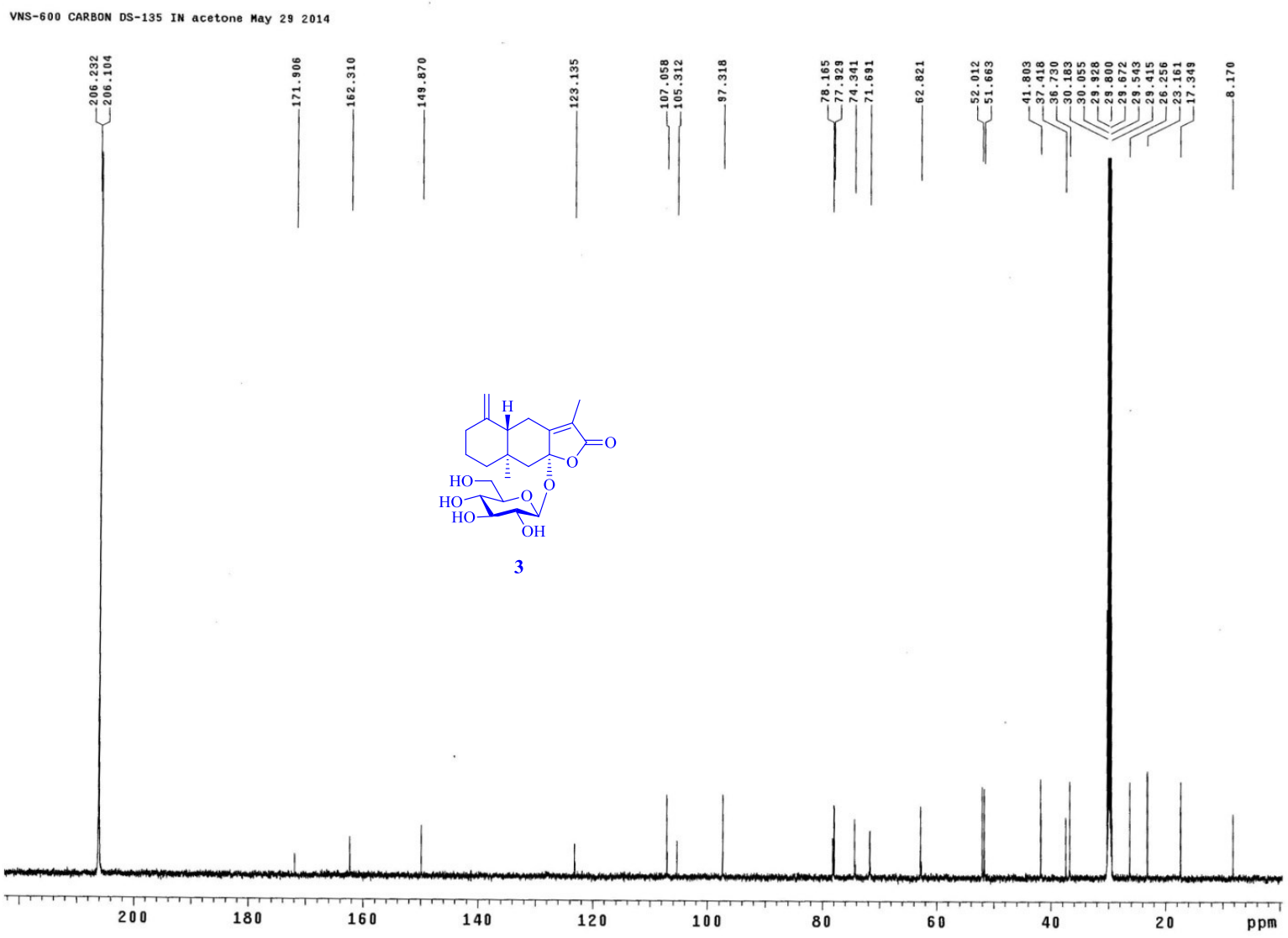


Figure S49. The ^{1}H NMR spectra of compound **3** in acetone-d_6 (600 M).



3

Figure S50. The ^{13}C NMR spectrum of compound **3** in acetone-d_6 (150 M).

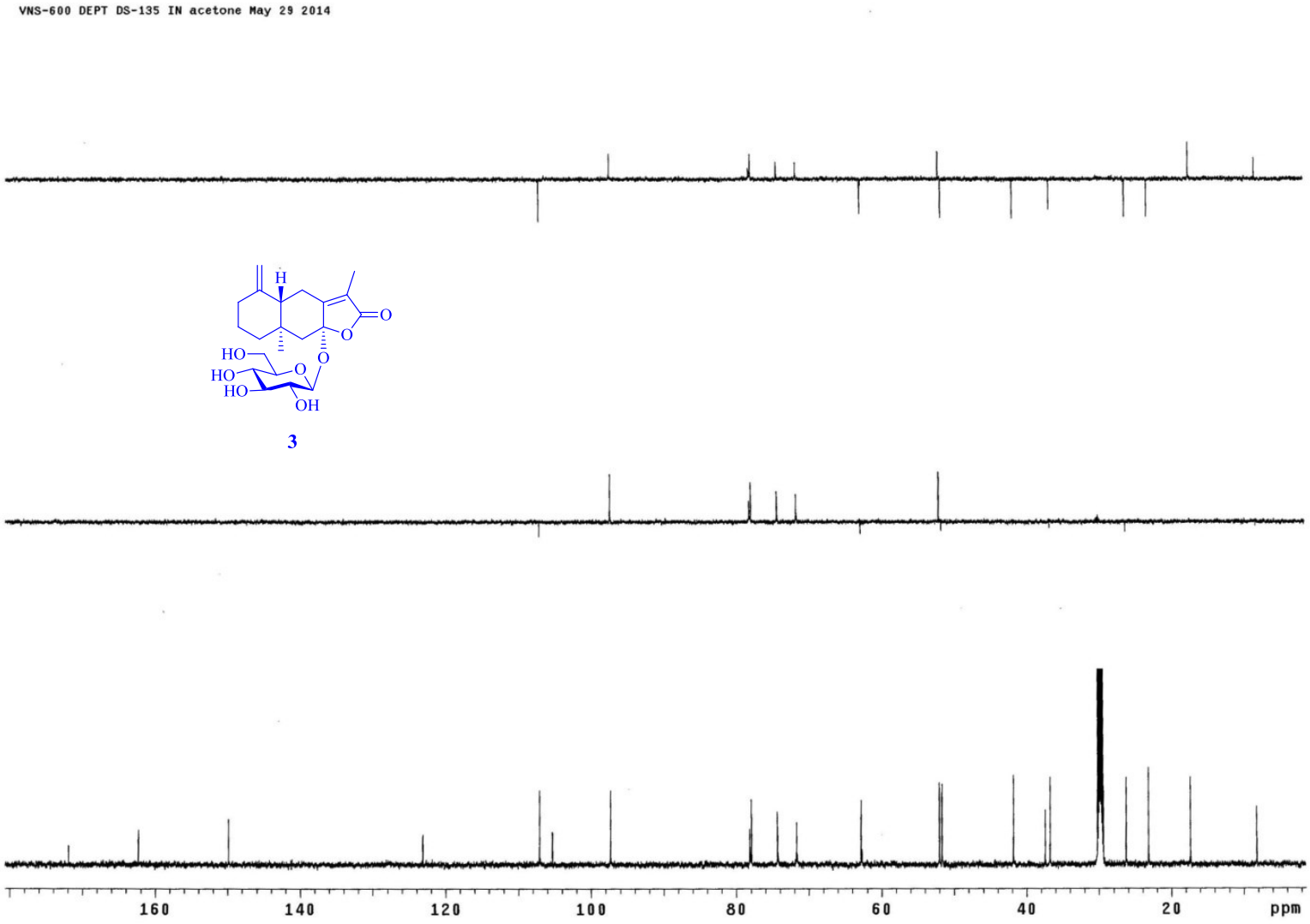
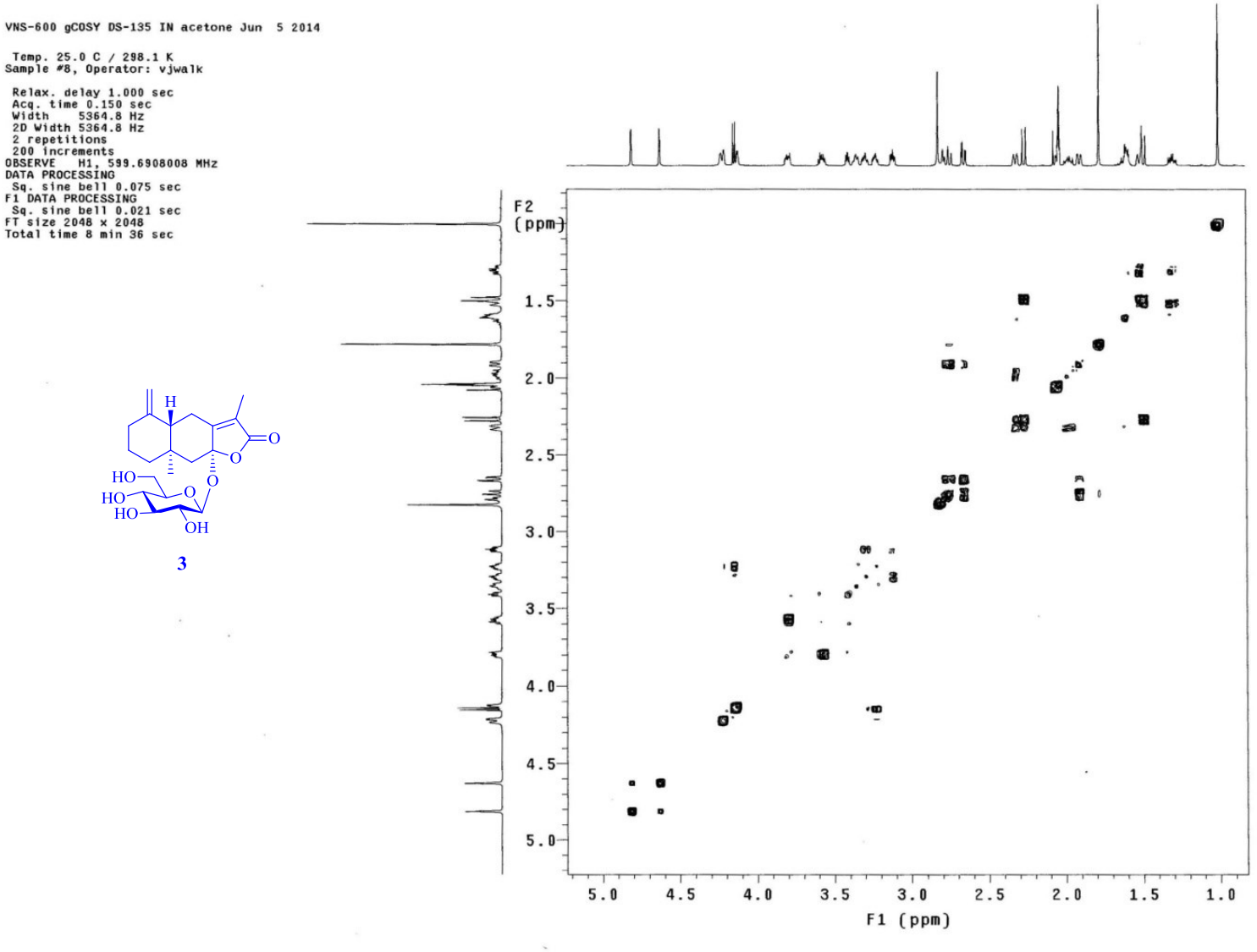


Figure S51. The DEPT spectra of compound **3** in acetone-d_6 (150 M).



3

Figure S52.The ^{1}H-^{1}H gCOSY spectrum of compound **3** in acetone-d_6 (600 MHz).

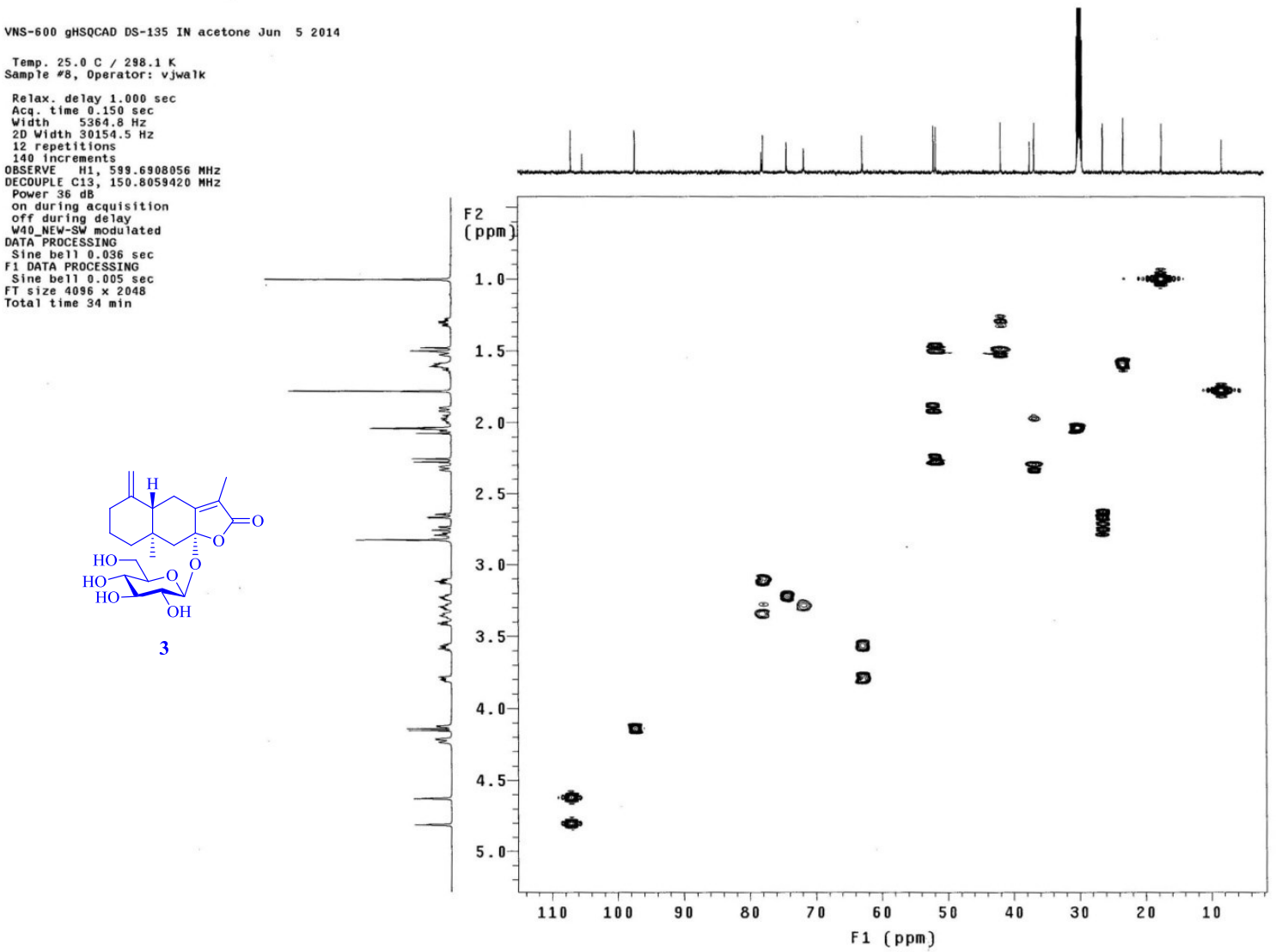


Figure S53.The gHSQC spectrum of compound **3** in acetone-d_6 (600 MHz for ^{1}H).

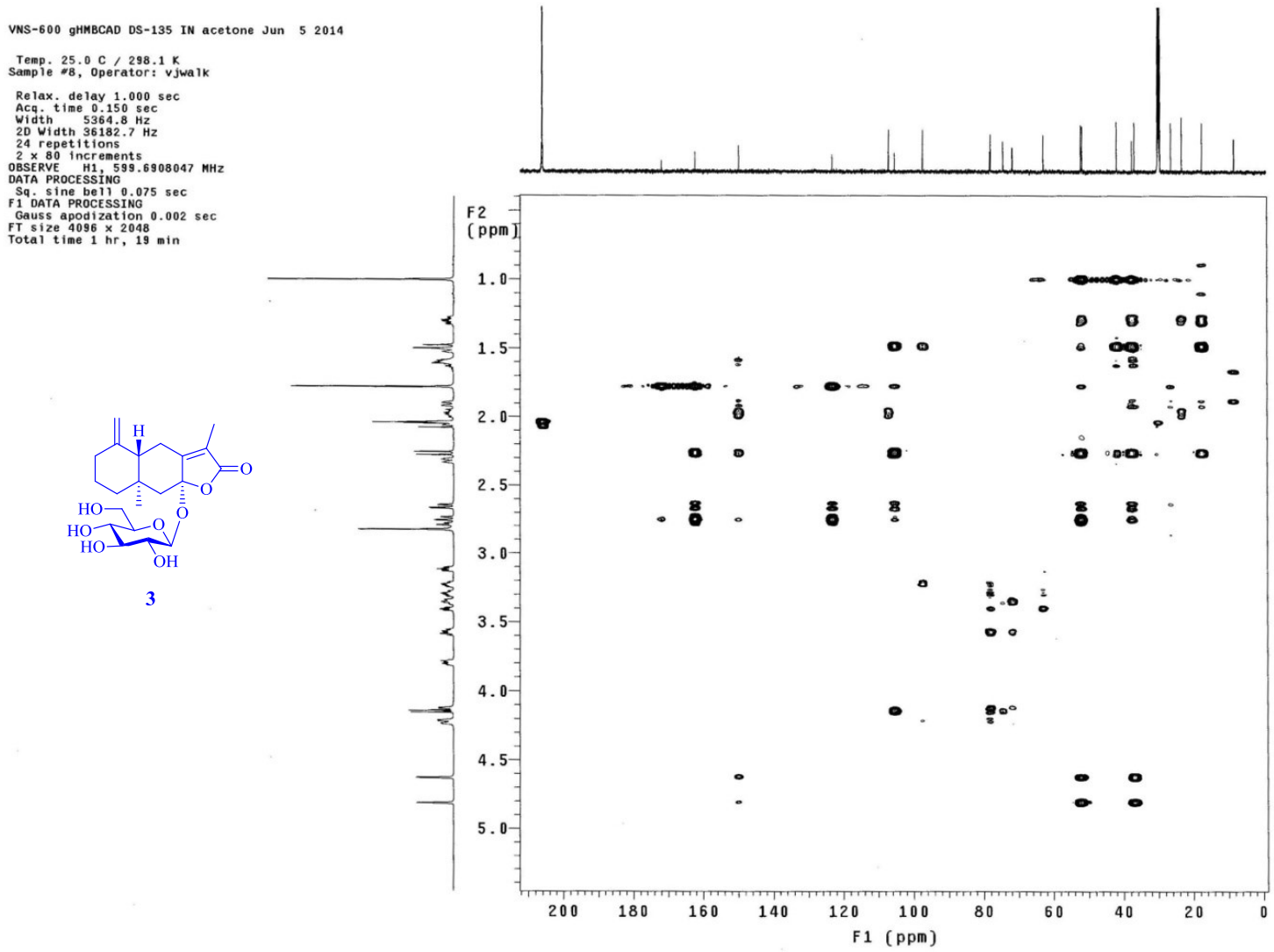


Figure S54.The gHMBC spectrum of compound **3** in acetone-d_6 (600 MHz for ^{1}H).

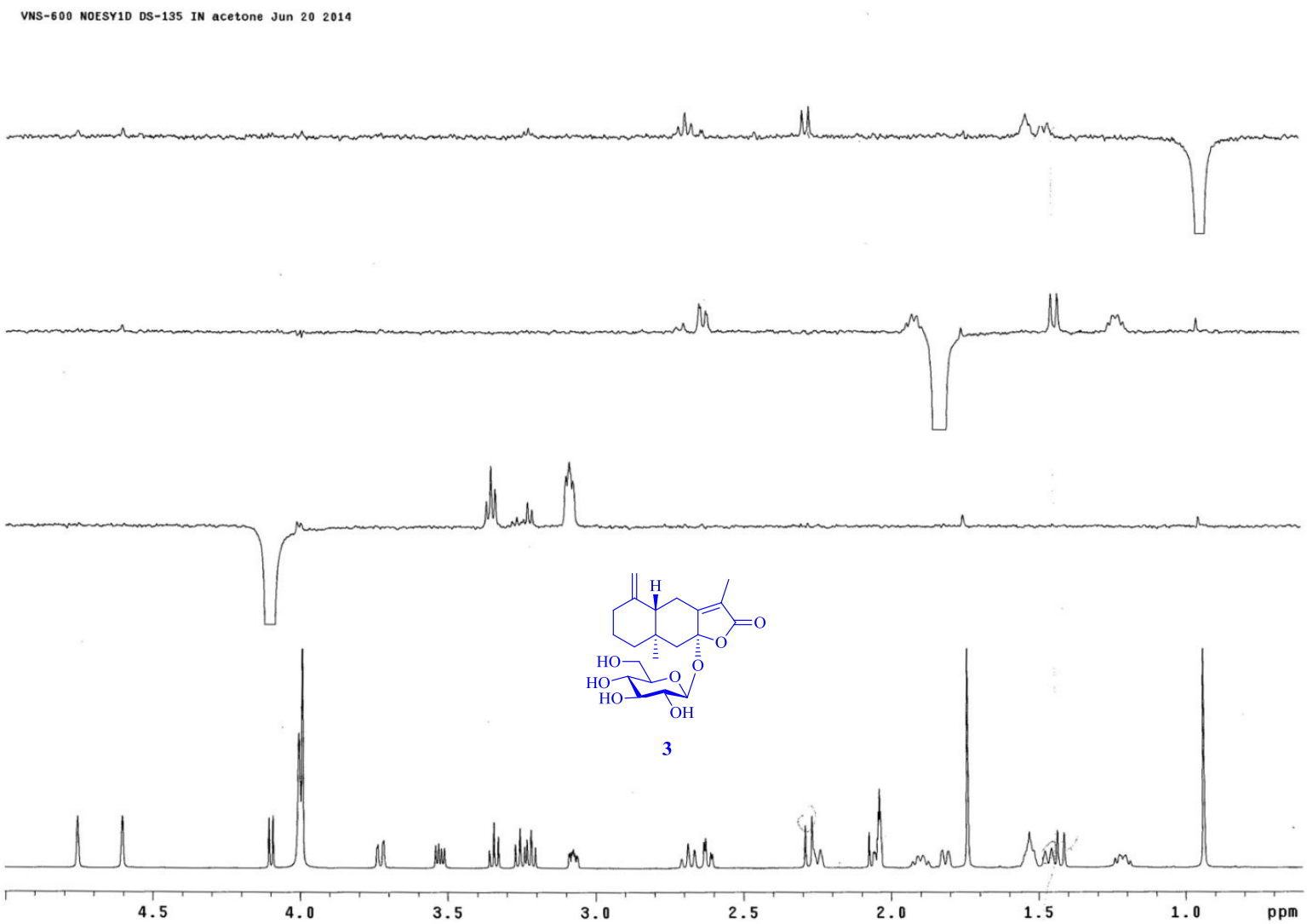


Figure S55. The NOE difference spectrum of **3** in acetone-d_6 (600 MHz).

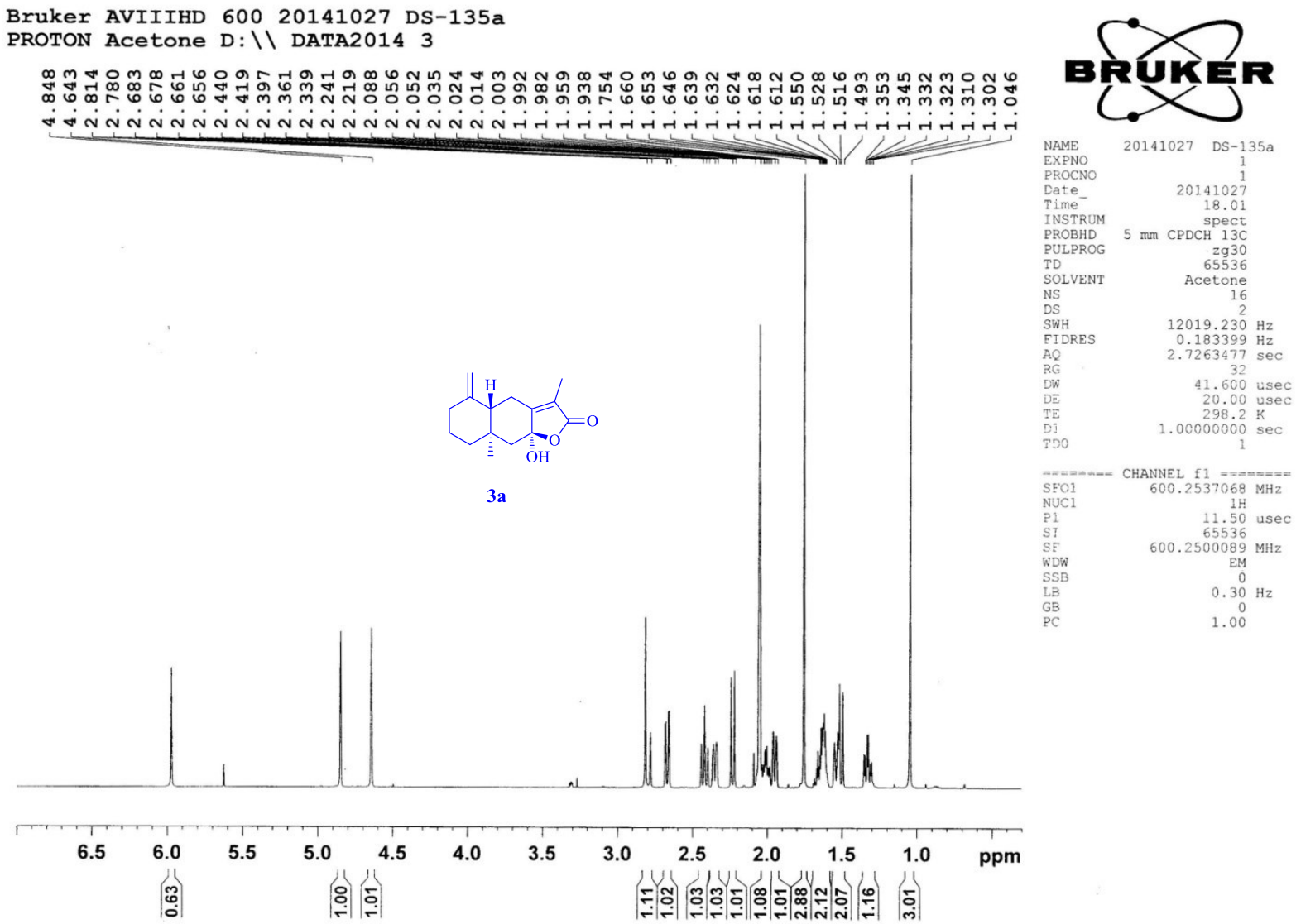
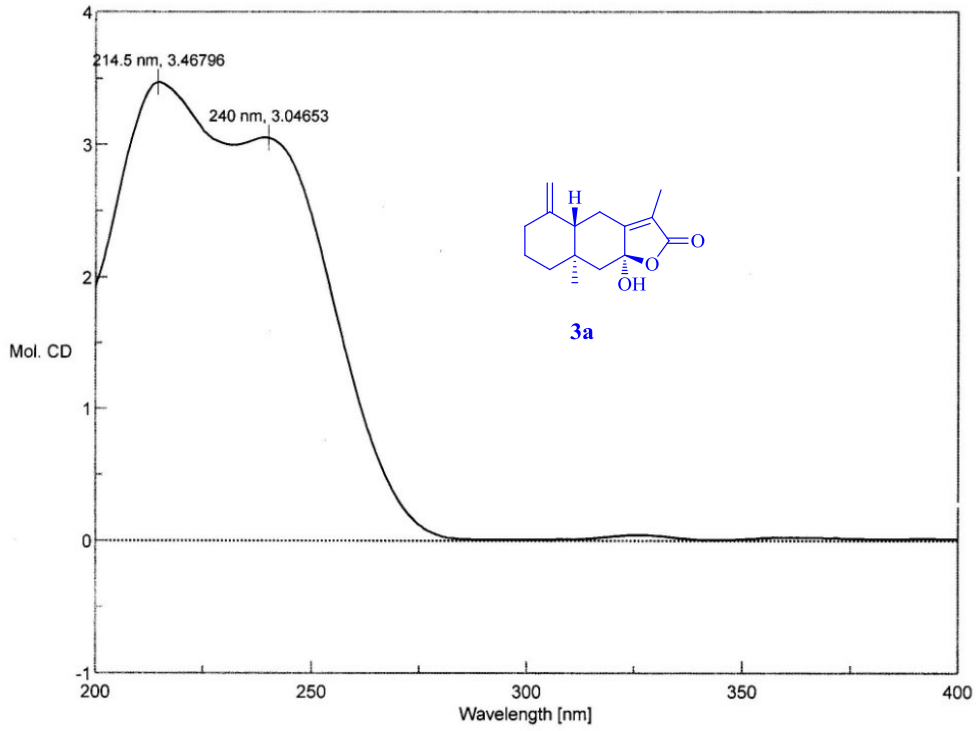


Figure S56. The ^{1}H NMR spectrum of the aglycone of **3** in acetone-d_6 (600 M).



3a

[Comments]
Sample name DS-F1
Comment
User
Division
Company dell

[Measurement Information]
Instrument Name J-815
Model Name J-815
Serial No. A024461168

Accessory Standard
Accessory S/N A024461168
Cell Length 1 mm

Photometric Mode CD, HT, Abs
Measure Range 400 - 200 nm
Data pitch 0.5 nm
Sensitivity Standard
D.I.T. 2 sec
Band width 2.00 nm
Start Mode Immediately
Scanning Speed 100 nm/min
Baseline Correction Baseline
Shutter Control Auto
PMT Voltage Auto
Accumulations 3
Solvent MEOH
Concentration 0.41 (w/v)%

[Detailed Information]
Creation date 2014-5-19 16:07

Data array type Linear data array * 3
Horizontal axis Wavelength [nm]
Vertical axis(1) Mol. CD
Vertical axis(2) HT [V]
Vertical axis(3) Abs
Start 400 nm
End 200 nm
Data interval 0.5 nm
Data points 401

Figure S57. The CD spectrum of the aglycone of **3** in MeOH.

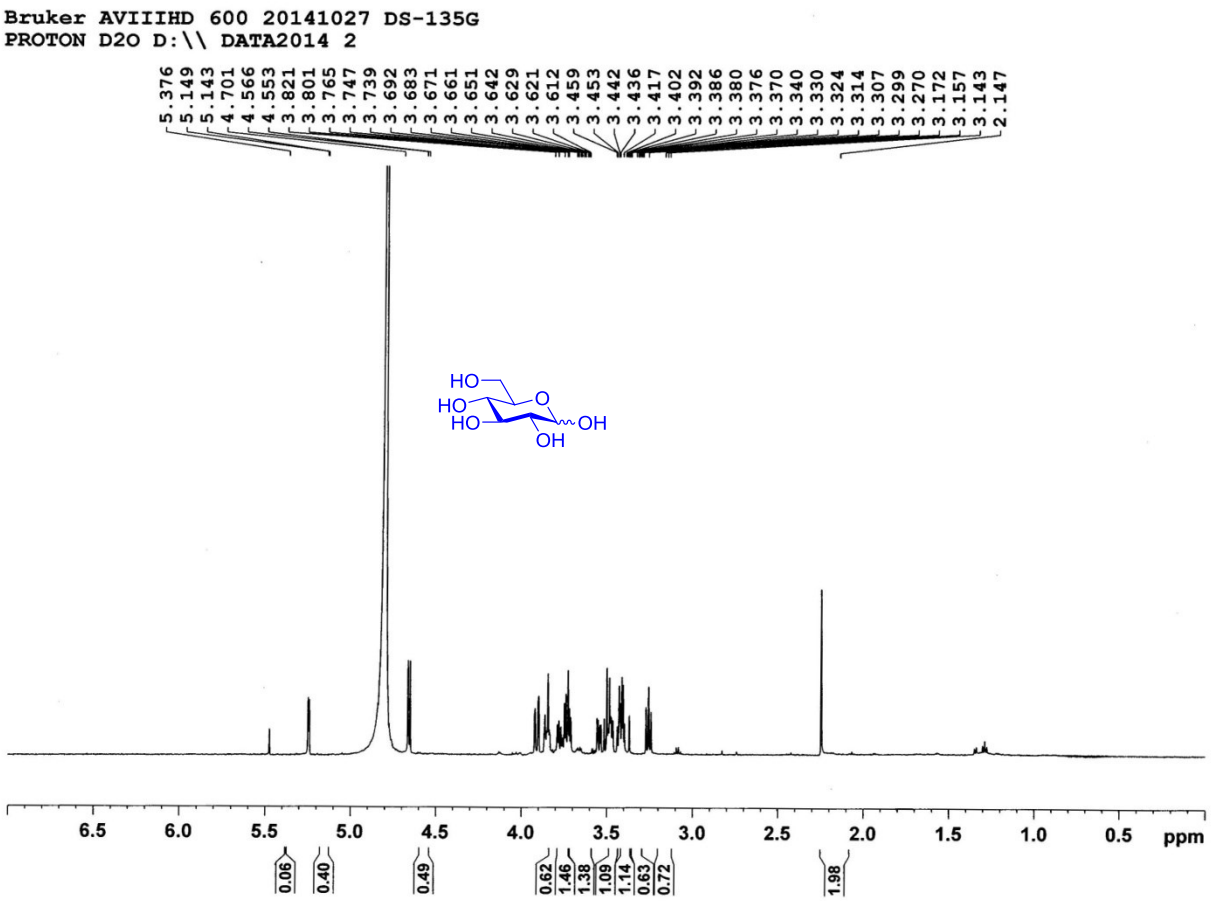


Figure S58. The ^{1}H NMR spectrum of D-glucose isolated from the hydrolysate of **3** in D_2O (600 M).

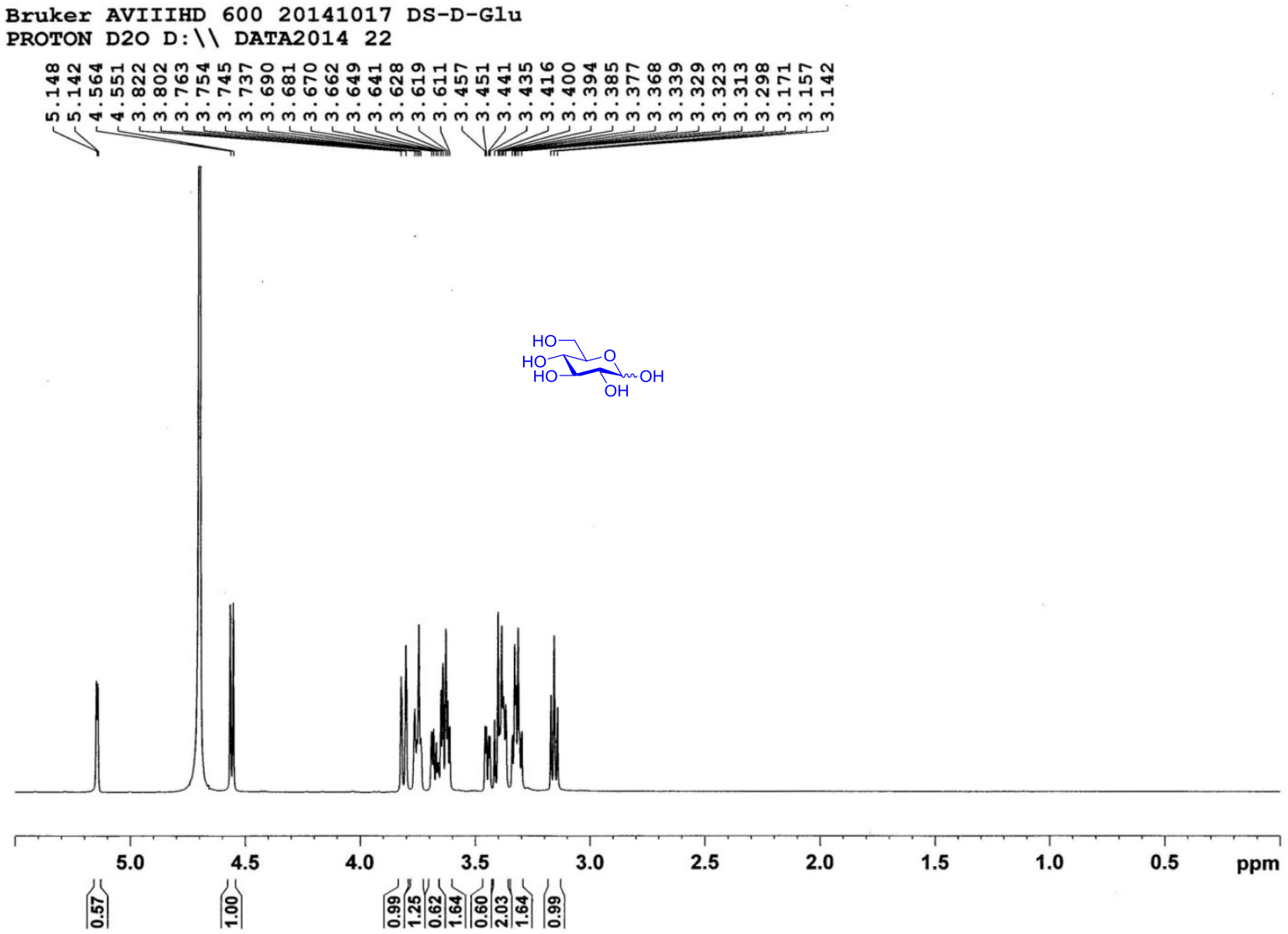


Figure S59. The ^{1}H NMR spectrum of the authentic D-glucose in D_2O (600 M).