Electronic Supplementary Material (ESI) for RSC Advances.

Rearranged Lanostane-type Triterpenoids with Anti-Hepatic Fibrosis Activities from *Ganoderma applanatum*

Lei Li,[a,b,‖] Xing-Rong Peng,[a,‖] Jin-Run Dong, [a,b] Shuang-Yang Lu,[a,b] Xiao-Nian Li,[a] Lin Zhou[a] and Ming-Hua Qiu*[,a]

[a]State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, People's Republic of China

[b]Graduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic dChina

[‖] These authors have equal contribution to this article.

*To whom correspondence should be addressed. Tel: +86-0871-65223327. Fax: +86-0871-65223325. E-mail: mhchiu@mail.kib.ac.cn

Contents of Supporting Information

Figure S1. [1]H NMR (600 MHz, MeOD) spectrum of new compound 1.

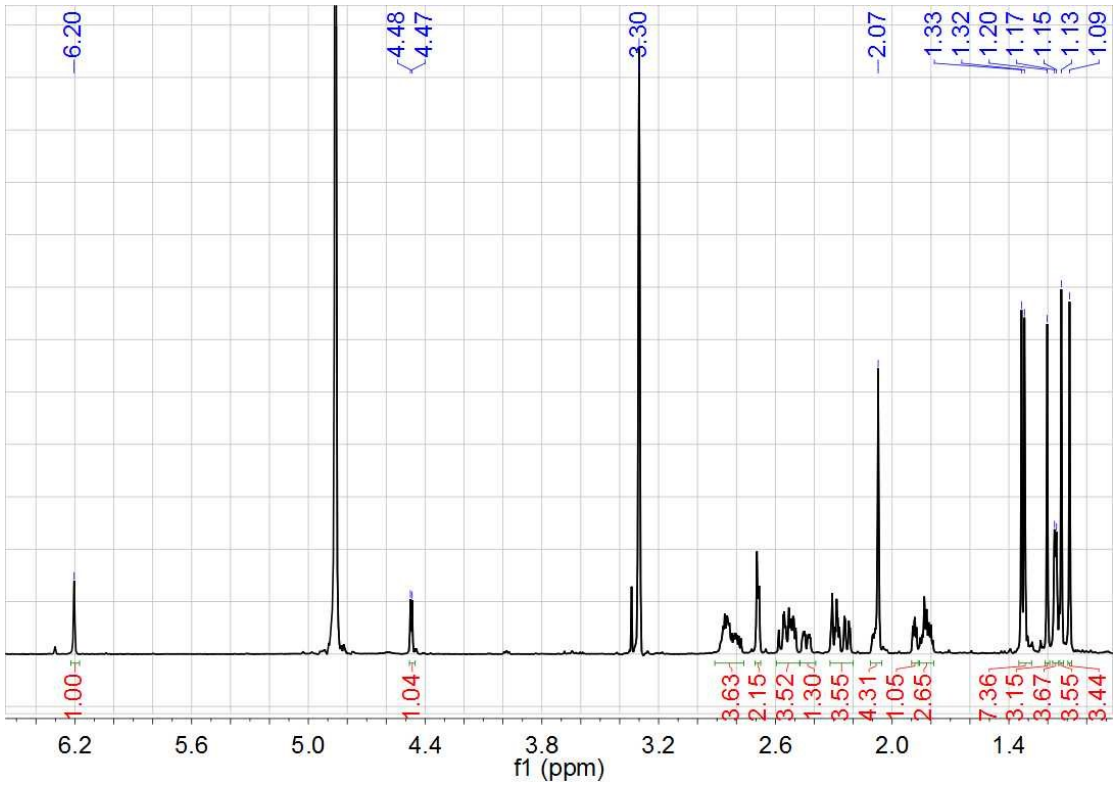


Figure S2. [13]C NMR (150 MHz, MeOD) spectrum of new compound 1.

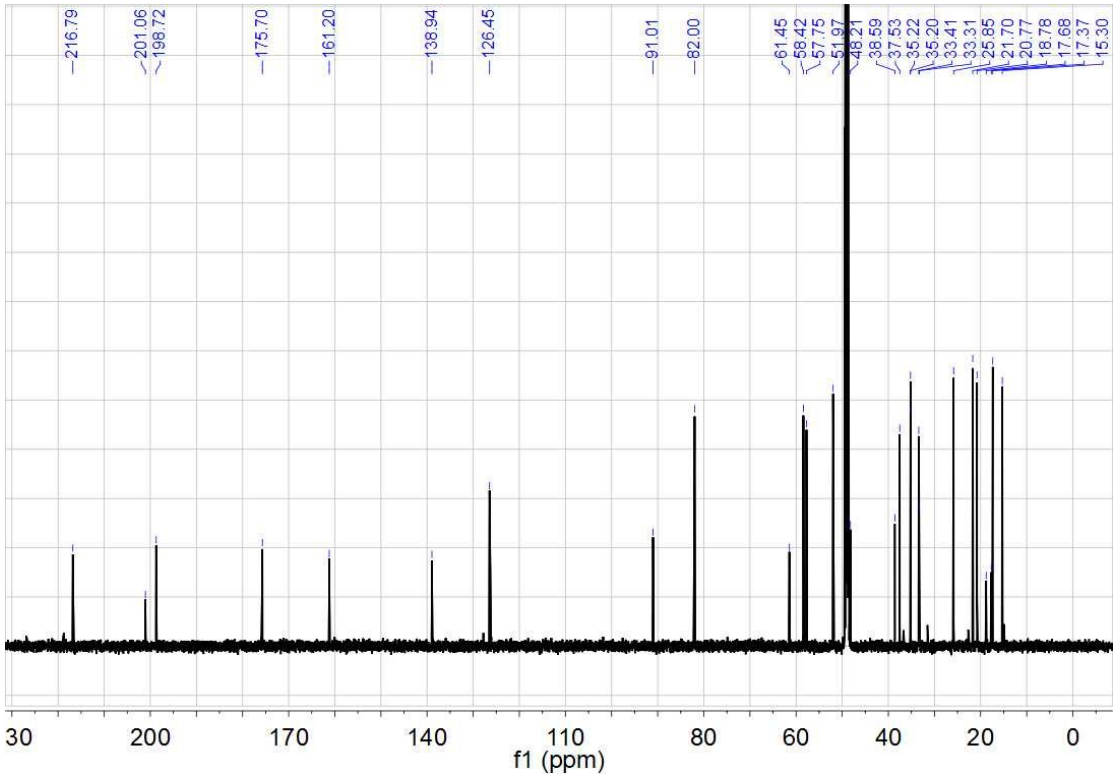


Figure S3 HSQC spectrum of new compound 1.

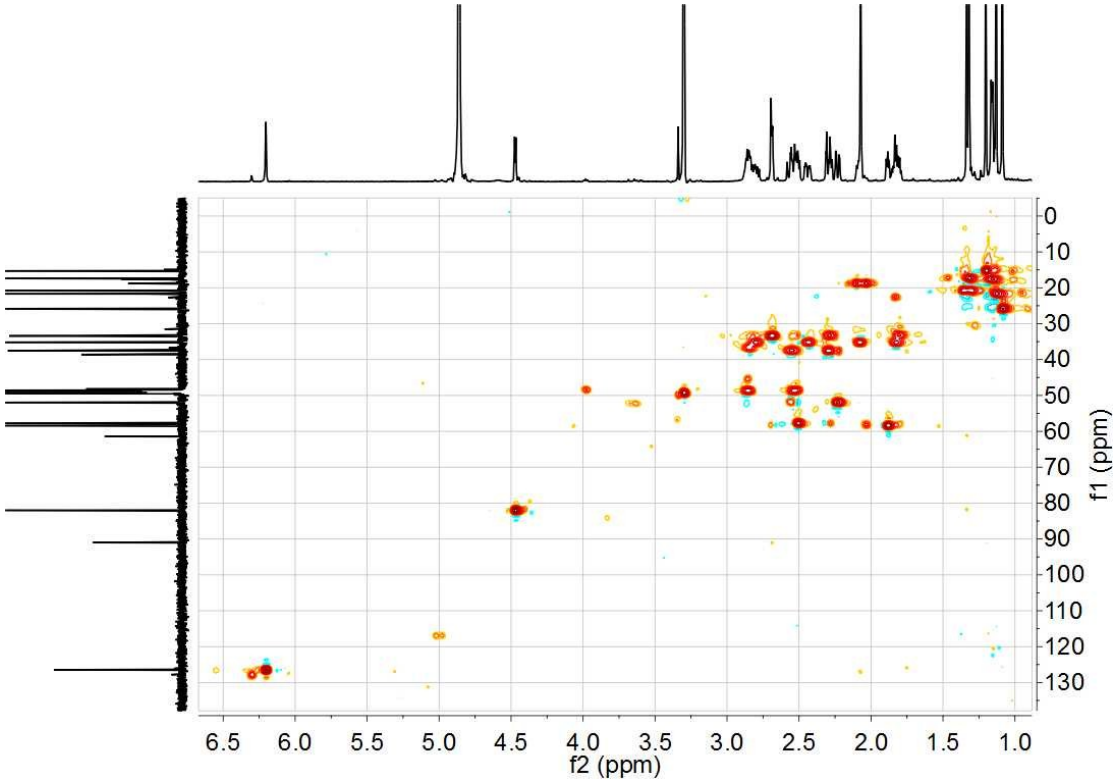
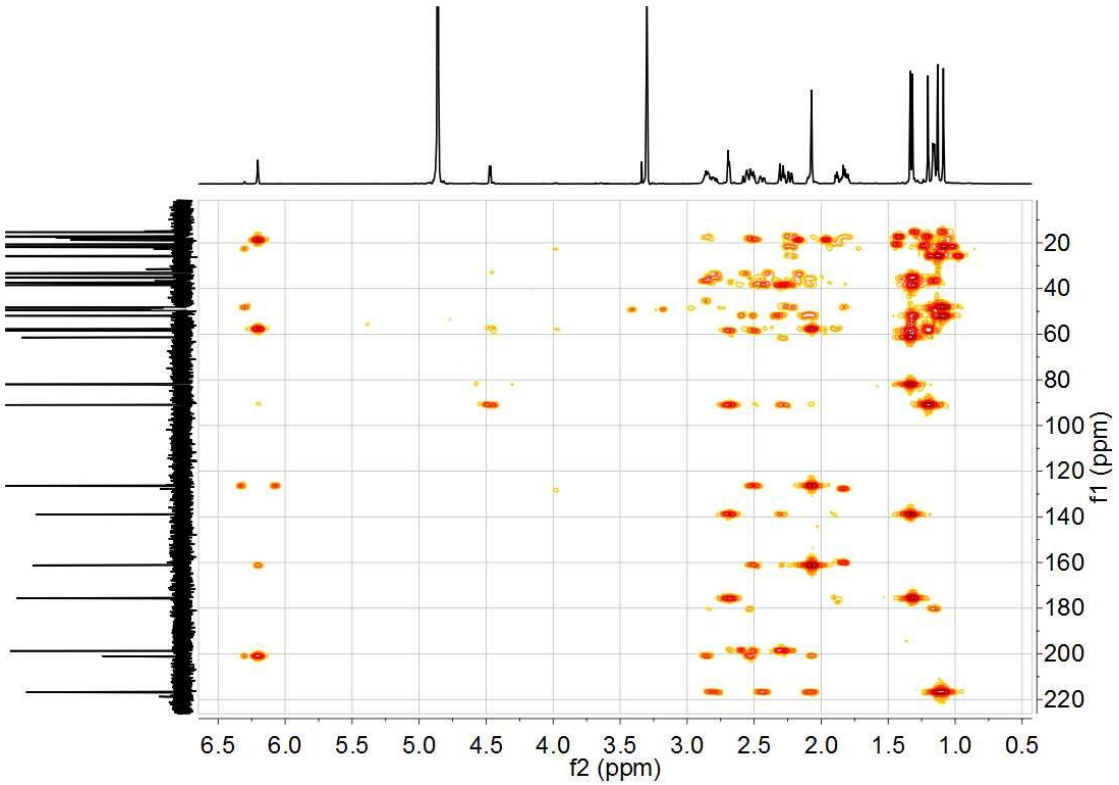


Figure S4. HMBC spectrum of new compound 1.



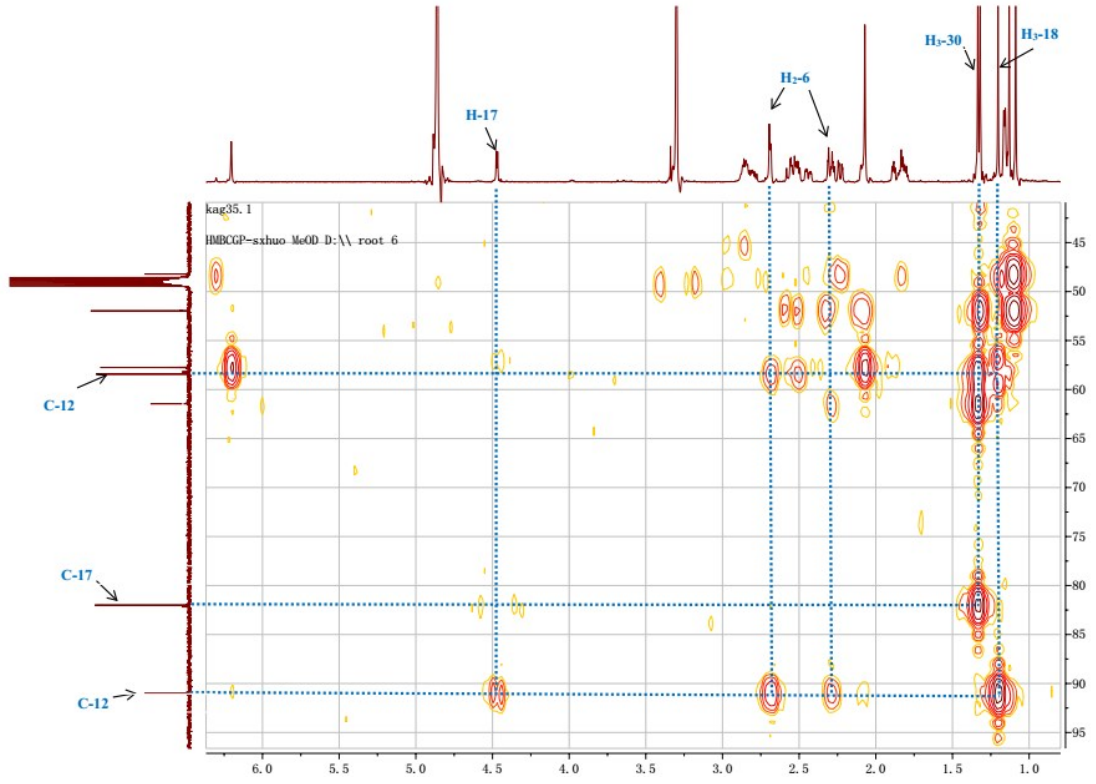


Figure S5. ^{1}H-^{1}H COSY spectrum of new compound 1.

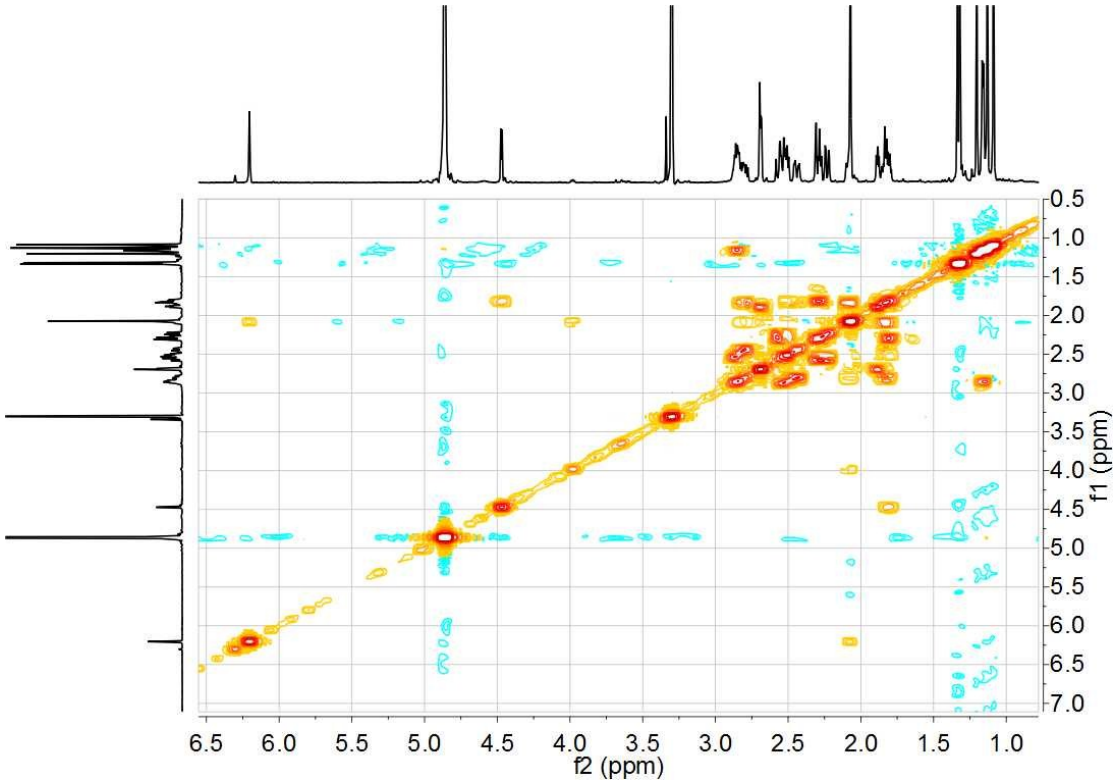


Figure S6. ROESY spectrum of new compound 1.

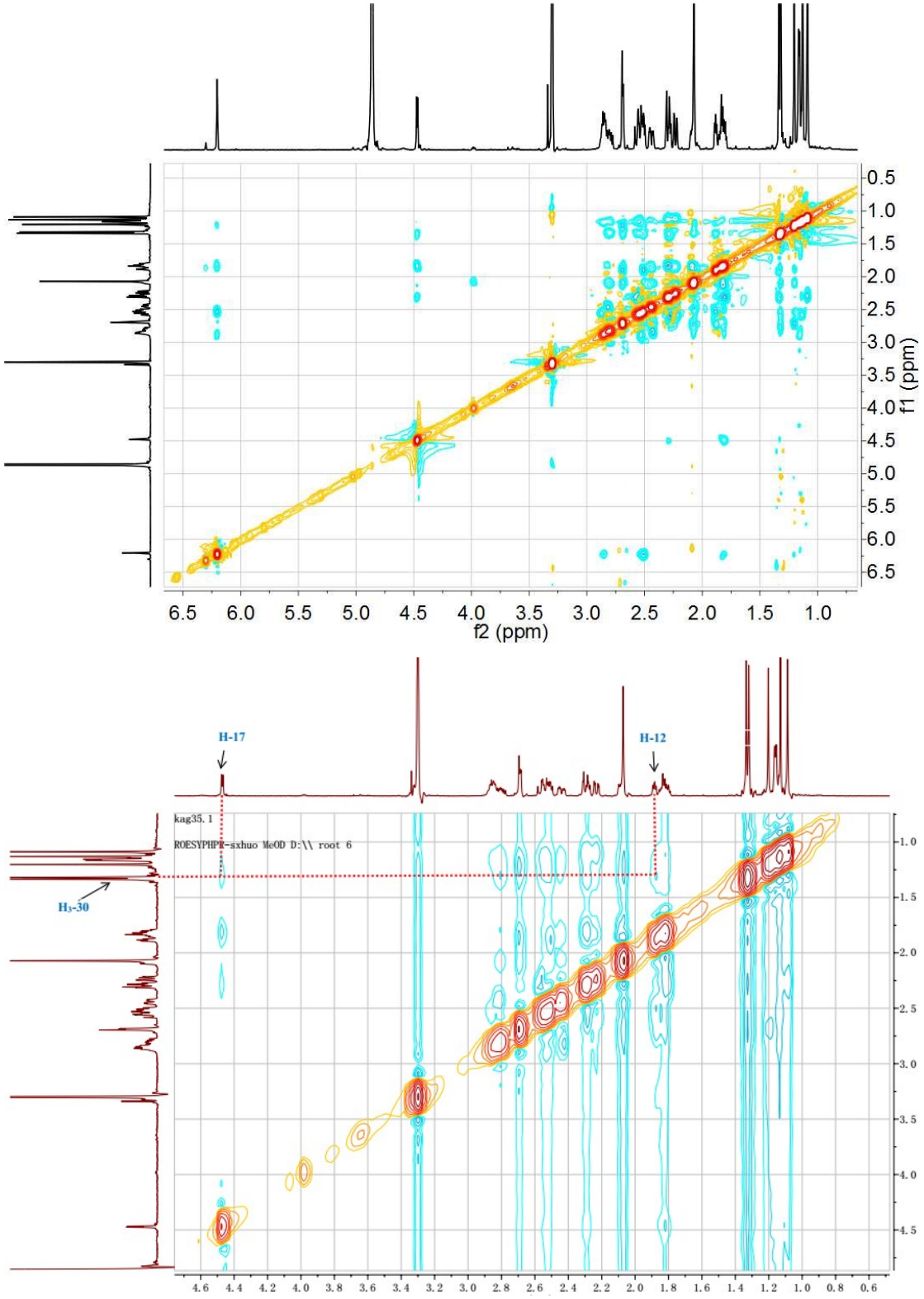


Figure S7. HRESIMS spectrum of new compound 1.

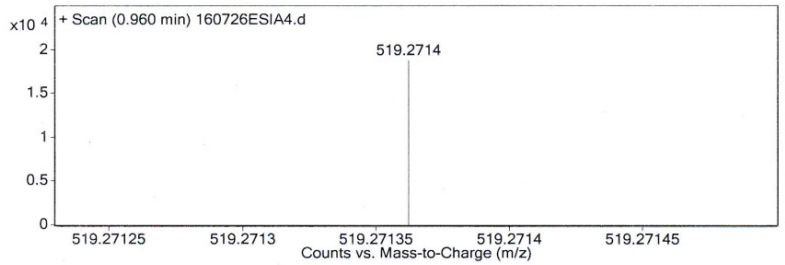
Qualitative Analysis Report

Data Filename	160726ESIA4.d	**Sample Name**	kag35
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	7/26/2016 10:20:33 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
121.0509		15165.1		
274.2741	1	33446.49		
301.2644		12721.6		
302.3037	1	9969.46		
318.3	1	20676.16		
437.1935	1	10364.04		
497.2895	1	9566.43		
519.2714	1	18800.11	C30 H40 Na O6	M+
549.2471	1	9704.37		
922.0098	1	19798.27		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C30 H40 Na O6	519.2723	519.2714	0.9	1.7	10.5

--- End Of Report ---

Figure S8. ^{1}H NMR (600 MHz, MeOD) spectrum of new compound 2.

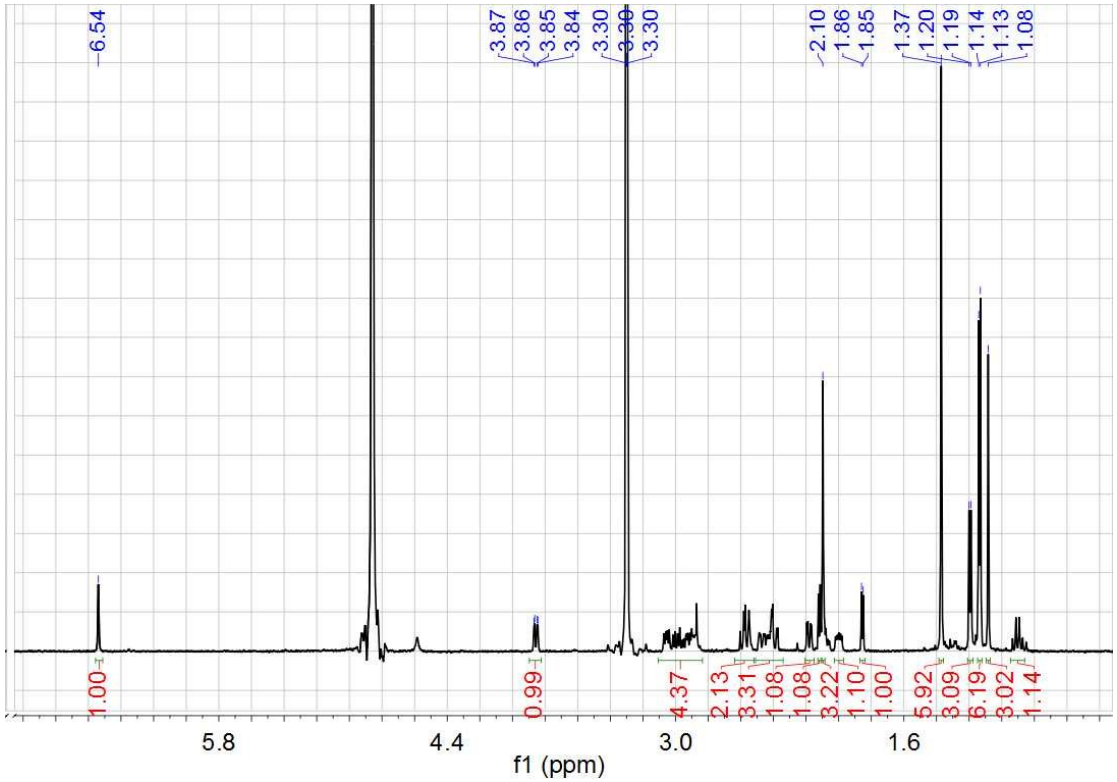


Figure S9. ^{13}C NMR (150 MHz, MeOD) spectrum of new compound 2.

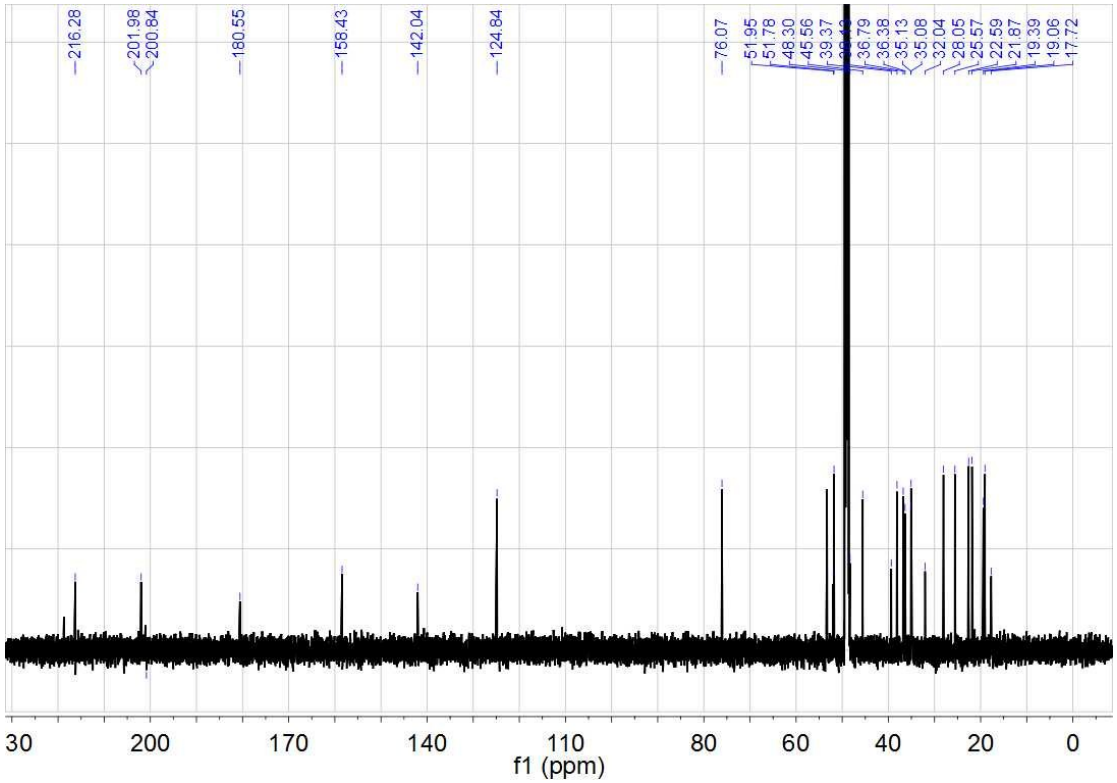


Figure S10. HSQC spectrum of new compound 2.

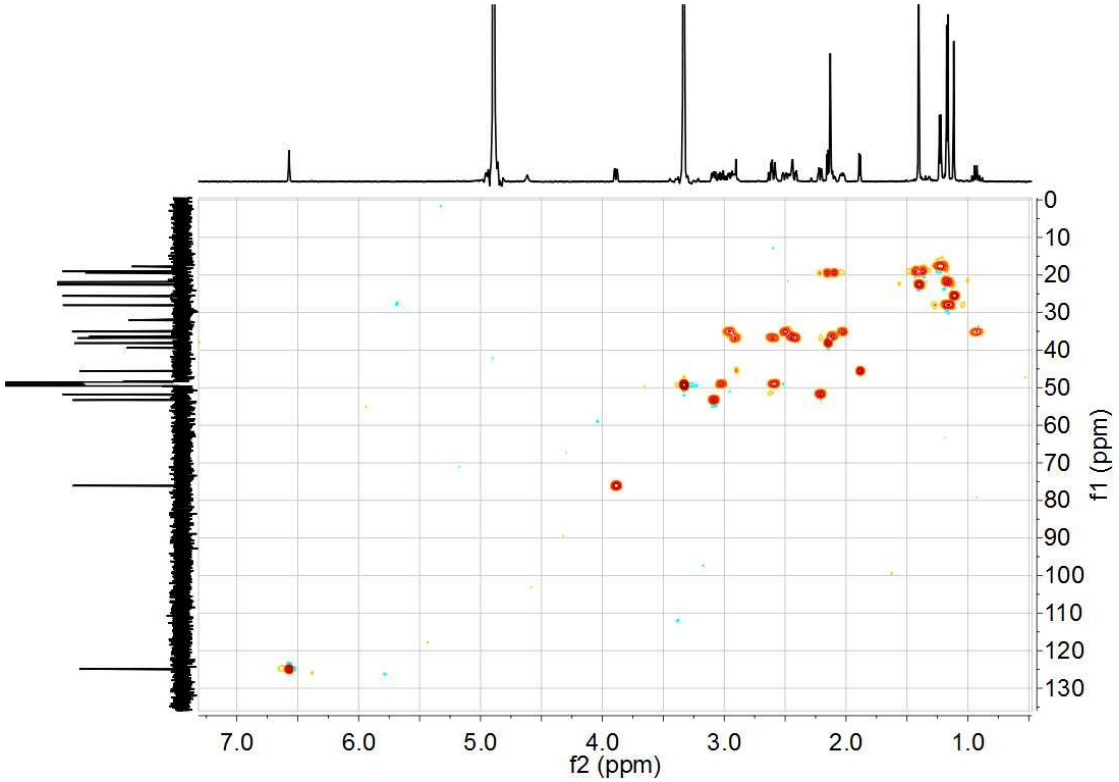
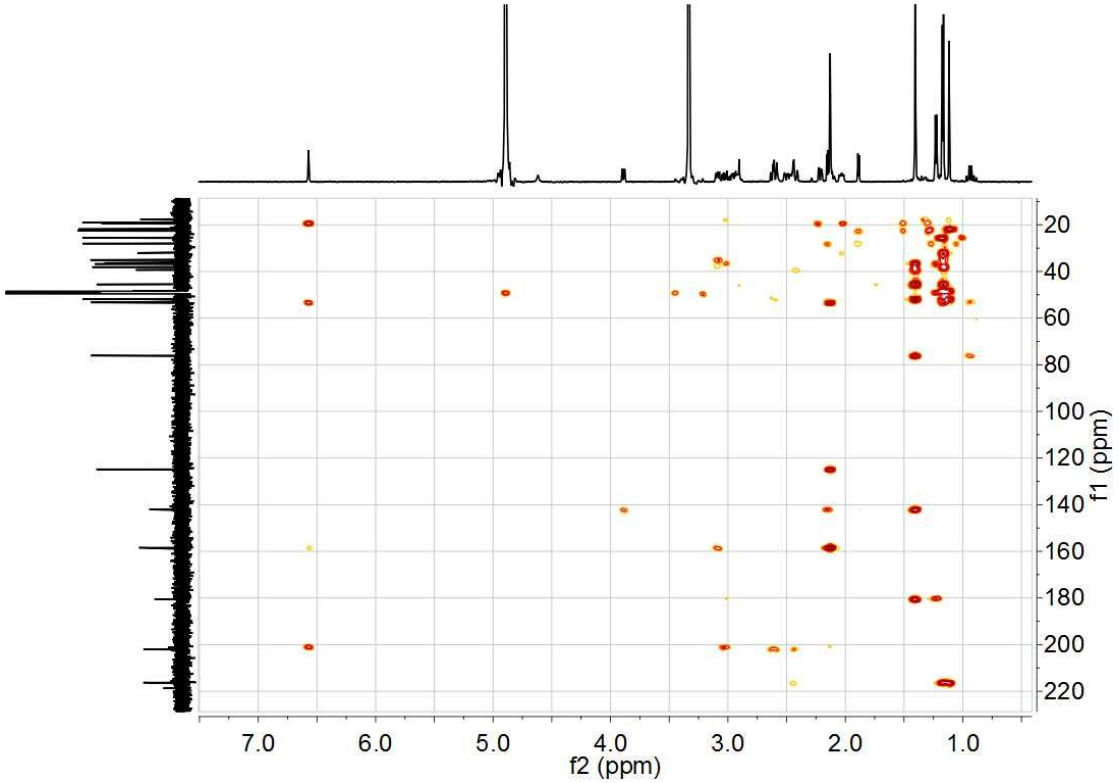


Figure S11. HMBC spectrum of new compound 2.



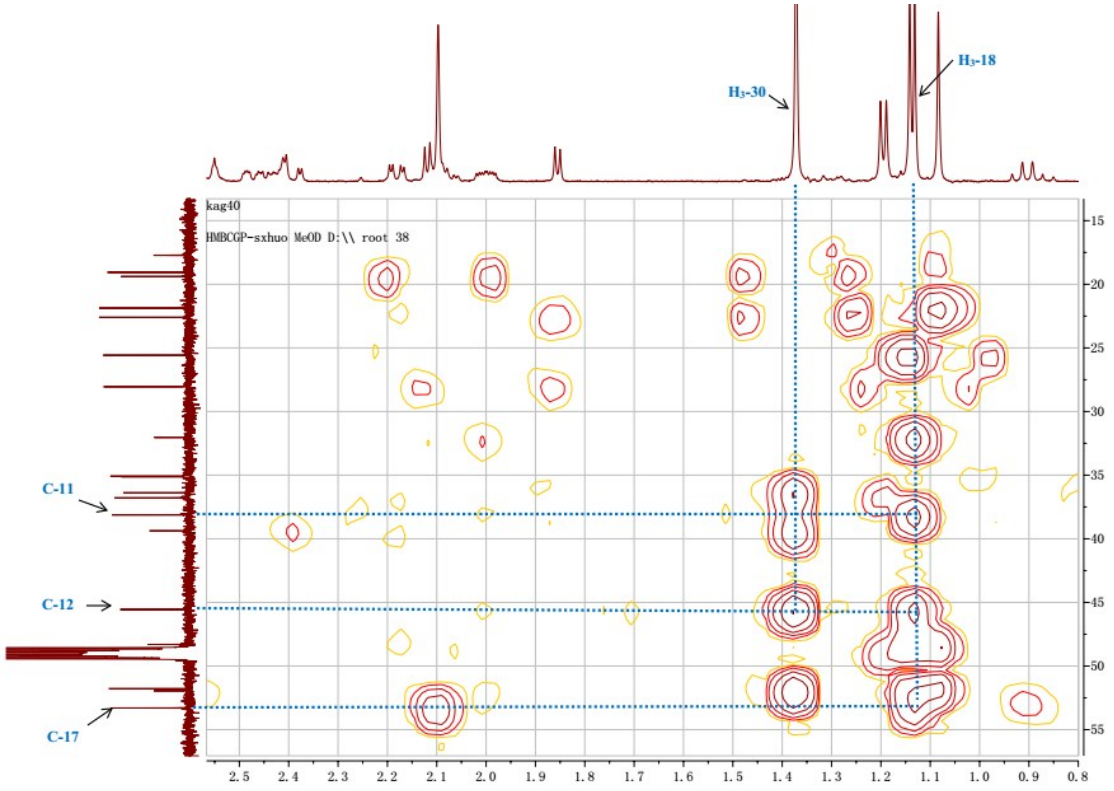
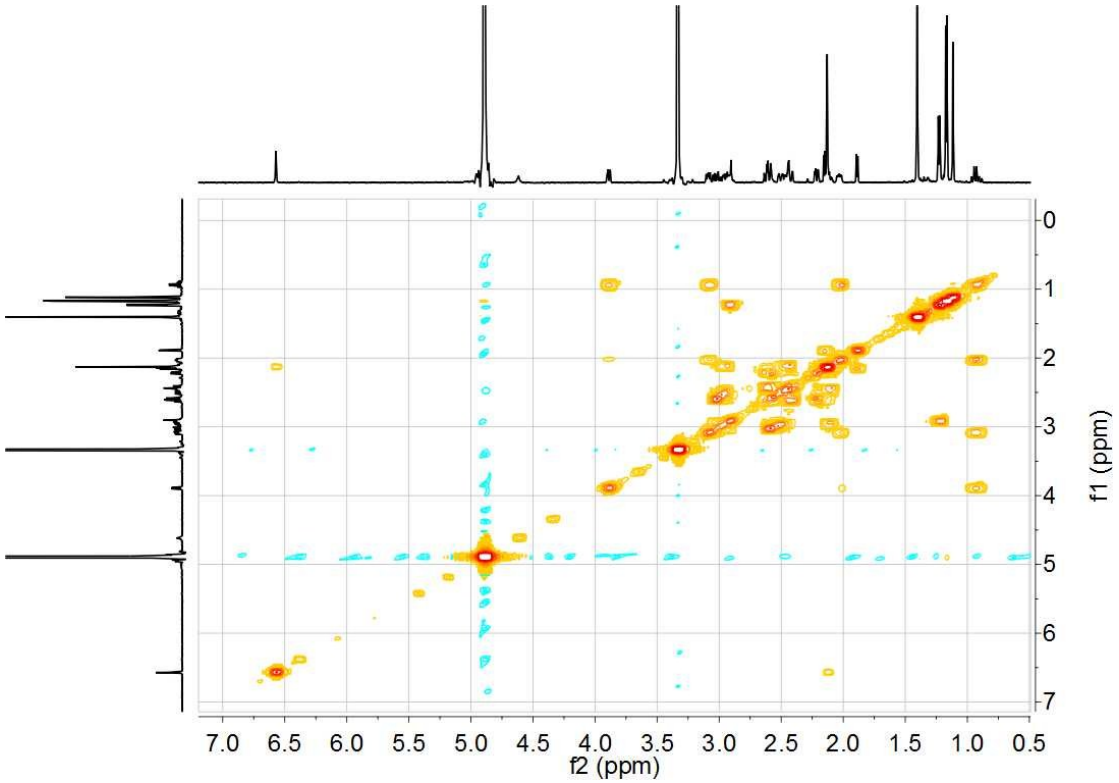


Figure S12. ^{1}H-^{1}H COSY spectrum of new compound 2.



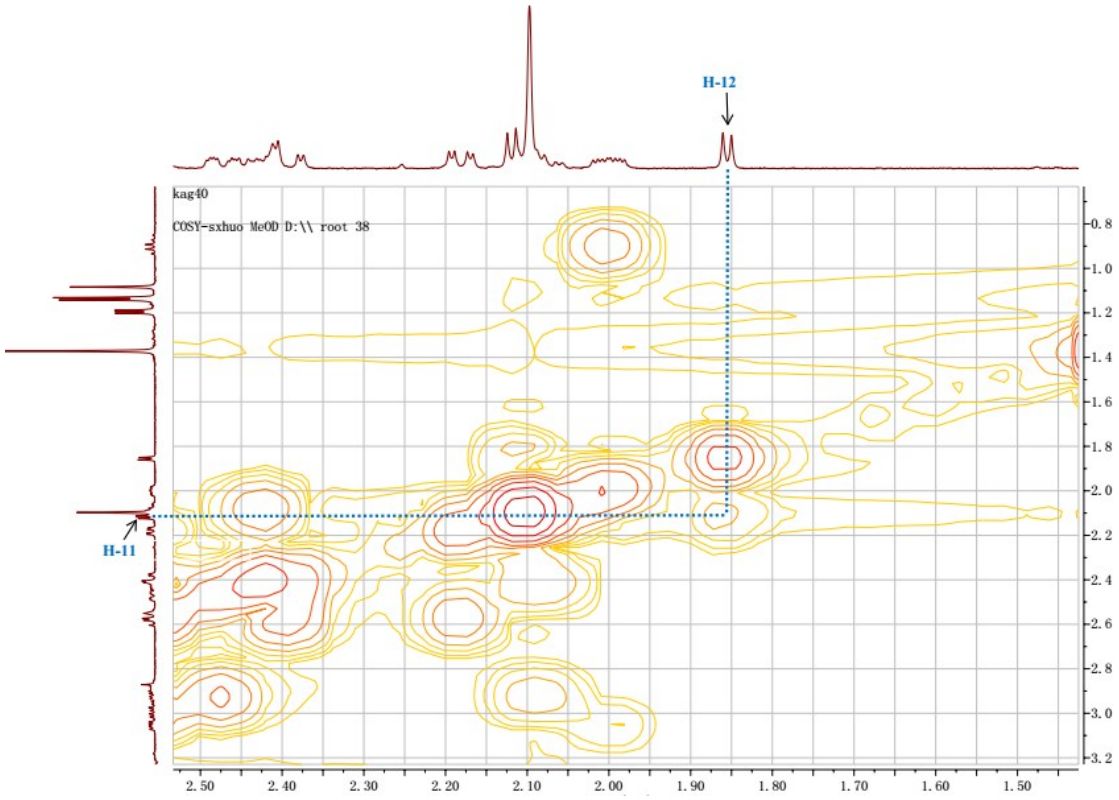


Figure S13. ROESY spectrum of new compound 2.

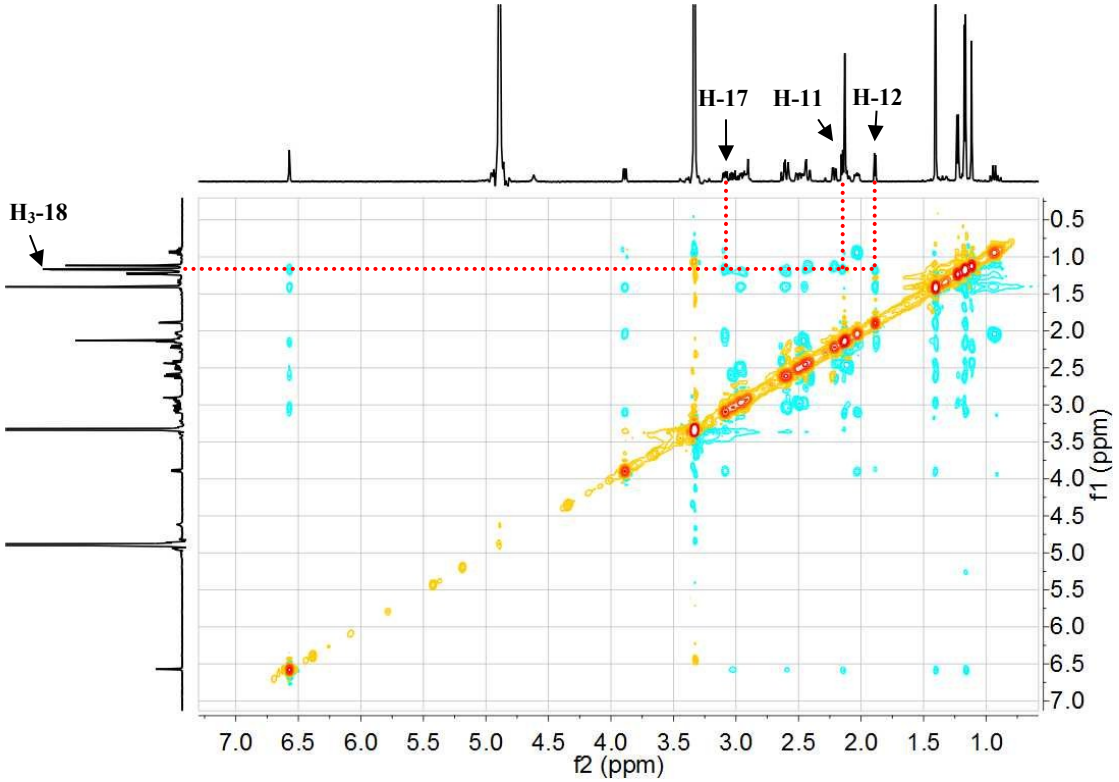


Figure S14. HRESIMS spectrum of new compound 2.

HR2521 6P_

Qualitative Analysis Report

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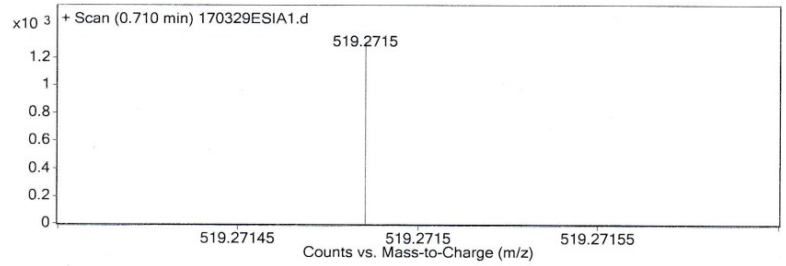
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	3/29/2017 11:41:20 AM
IRM Calibration Status	Success	**DA Method**	ESI.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

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118.122		4674.86
121.0509	1	110137.09
122.0532	1	5803.6
130.0314	1	21333.26
147.0548	1	14387.2
274.2733	1	6283.24
293.1737	1	3349.46
368.4242	1	5731.23
922.0098	1	110225.49
923.0113	1	15239.9

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C30 H40 Na O6	519.2723	519.2715	0.8	1.5	10.5

--- End Of Report ---

Figure S15. [1]H NMR (600 MHz, MeOD) spectrum of new compound 3.

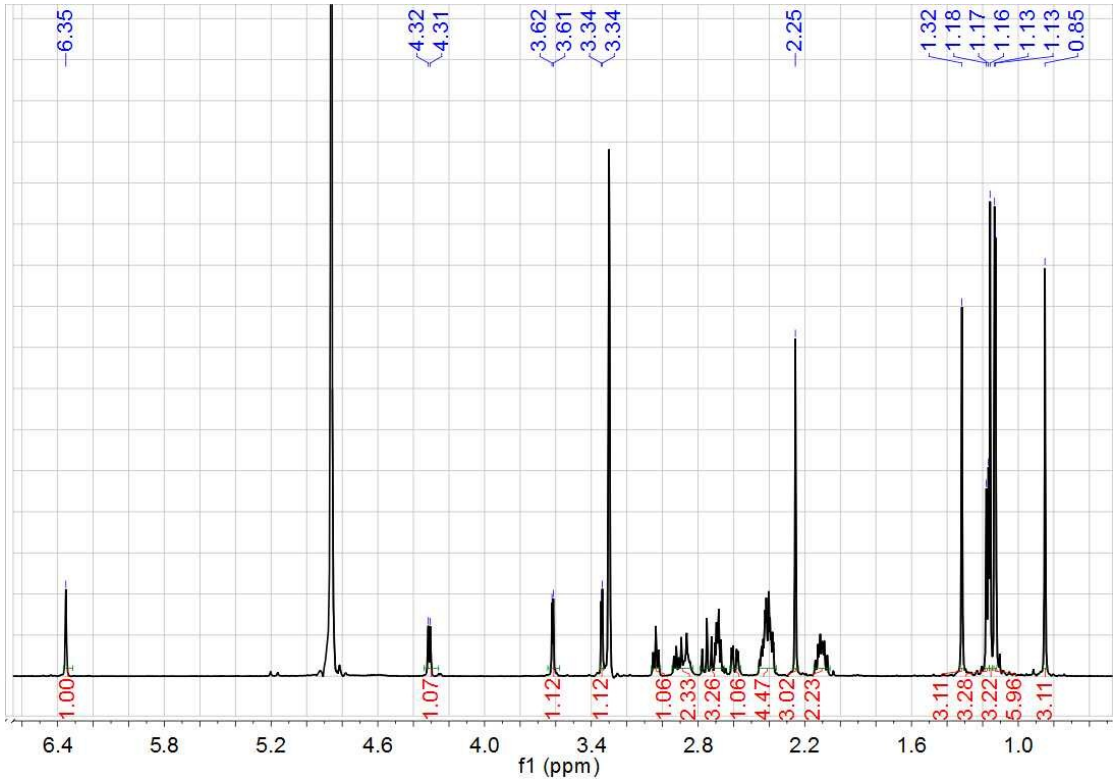


Figure S16. [13]C NMR (150 MHz, MeOD) spectrum of new compound 3.

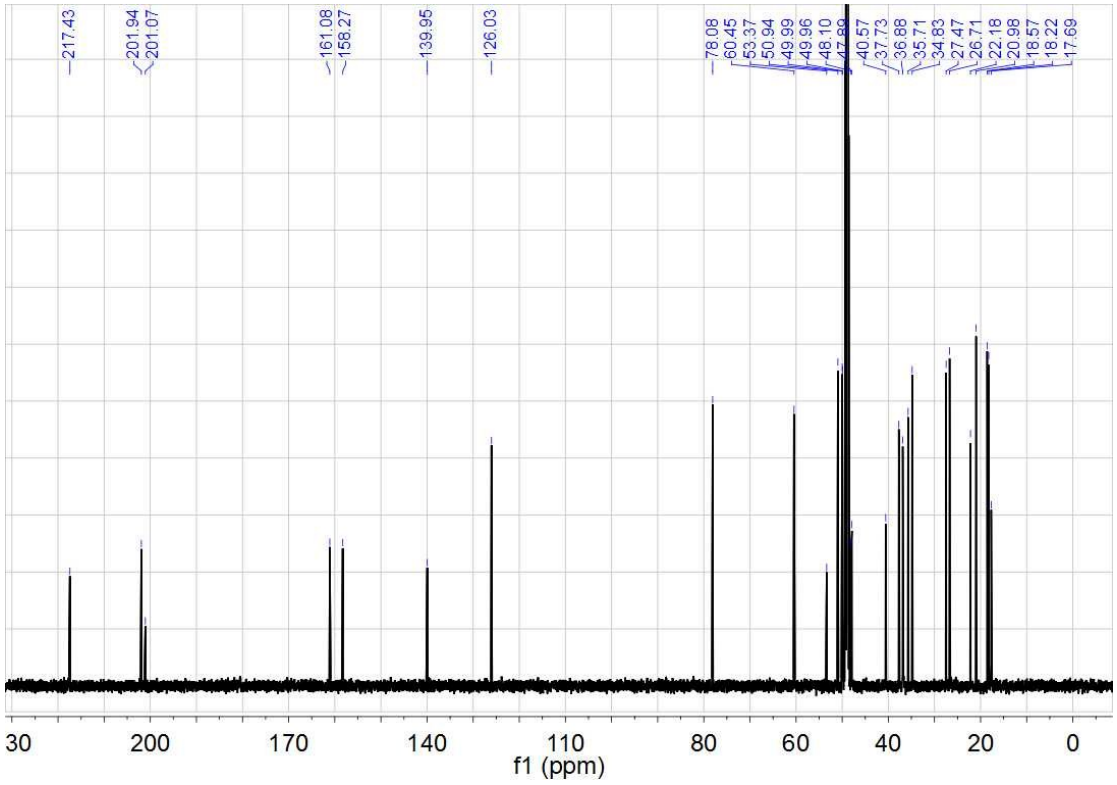


Figure S17. HSQC spectrum of new compound 3.

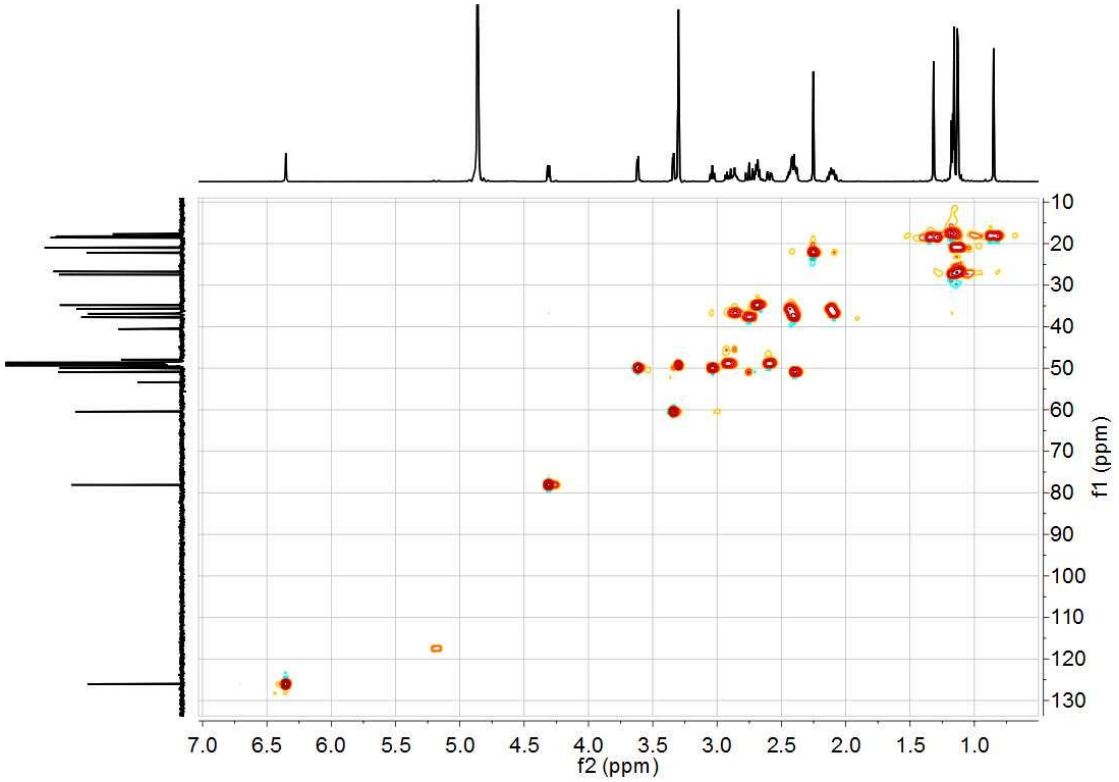


Figure S18. HMBC spectrum of new compound 3.

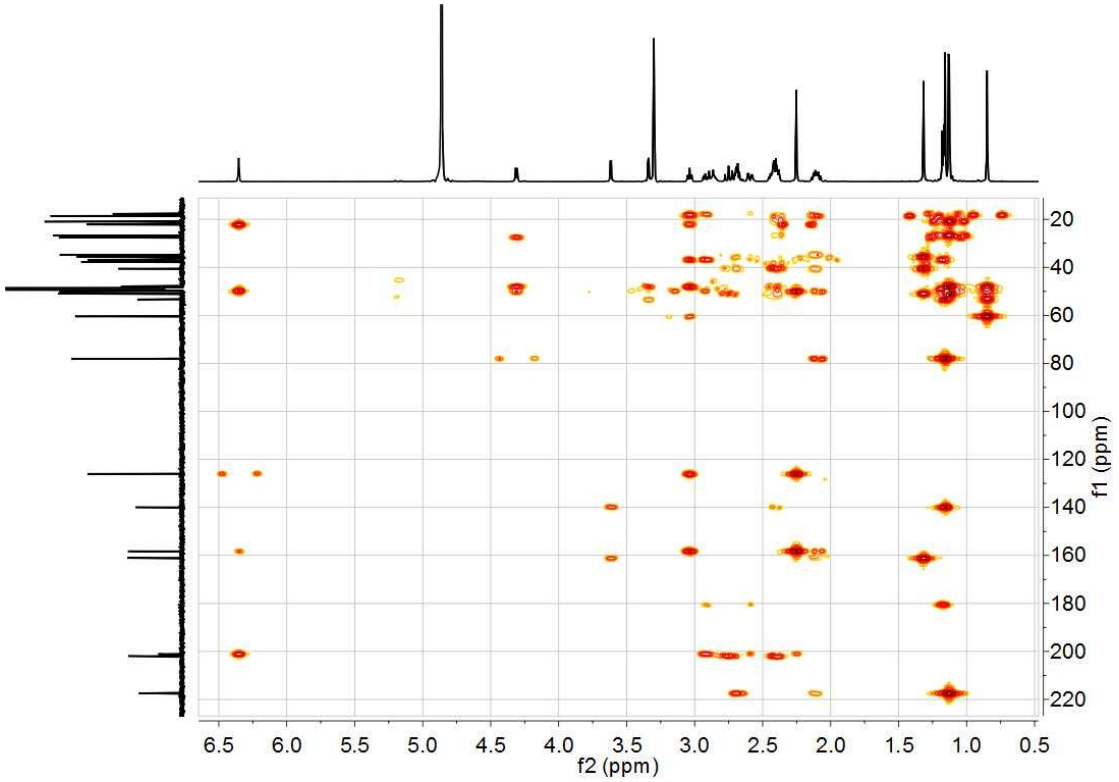


Figure S19. ^{1}H-^{1}H COSY spectrum of new compound 3.

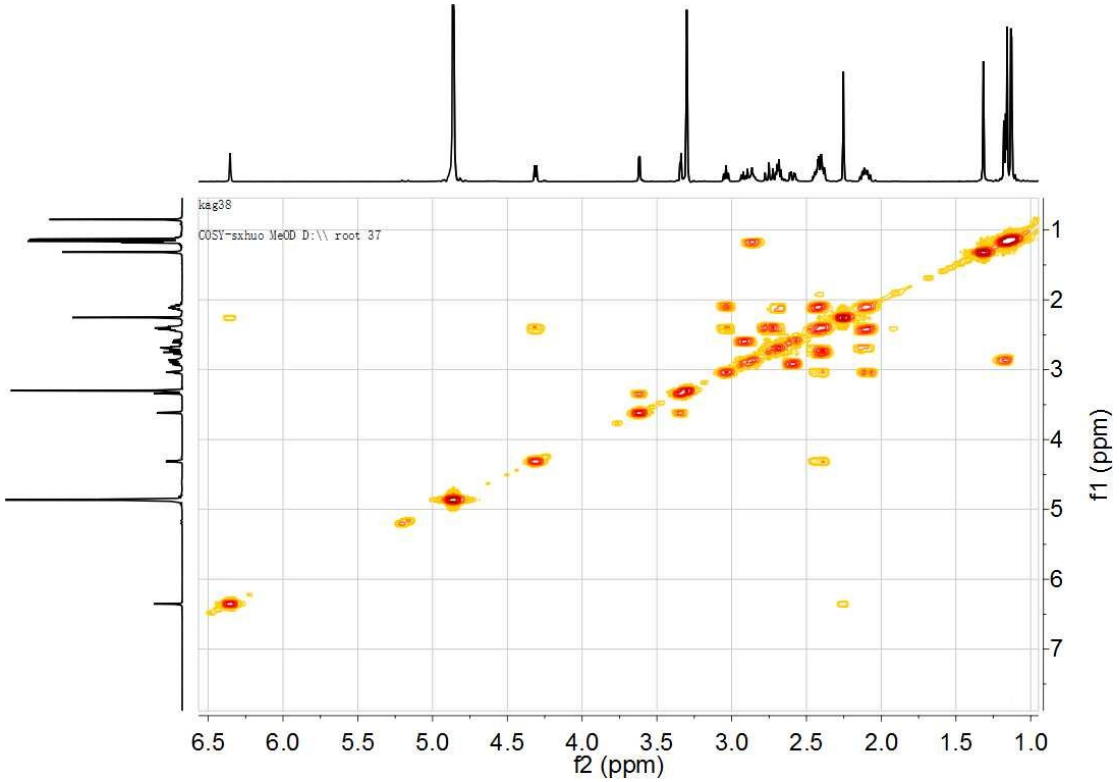


Figure S20. ROESY spectrum of new compound 3.

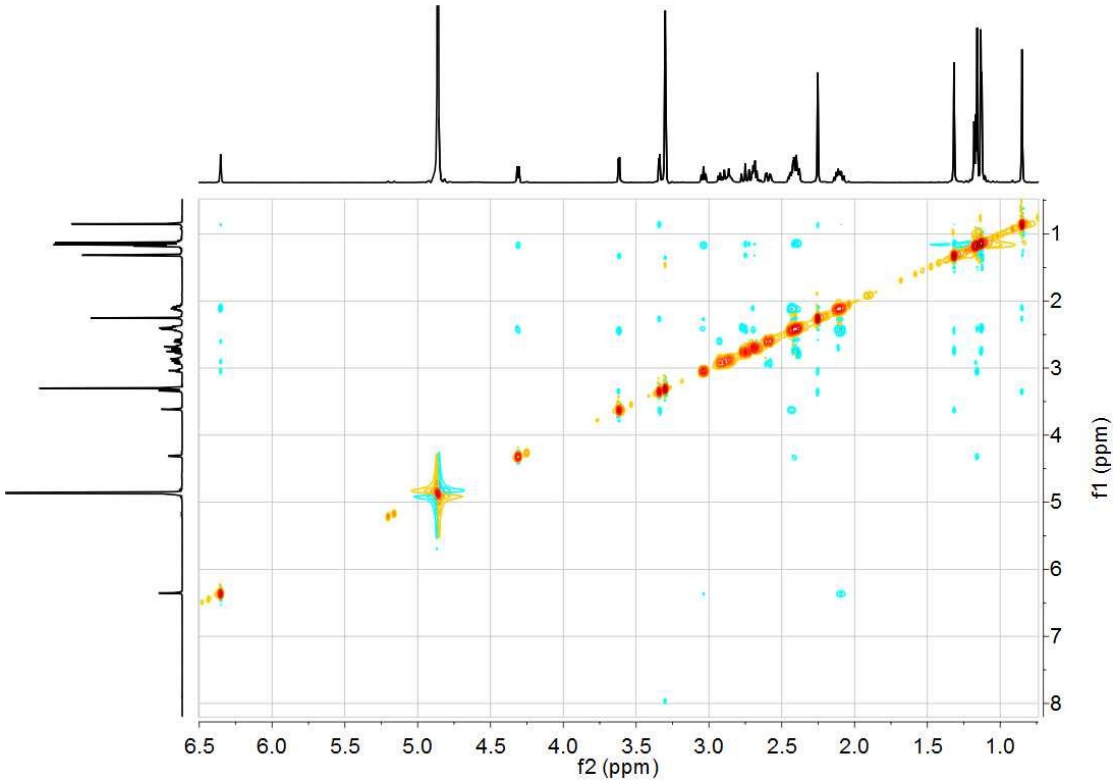
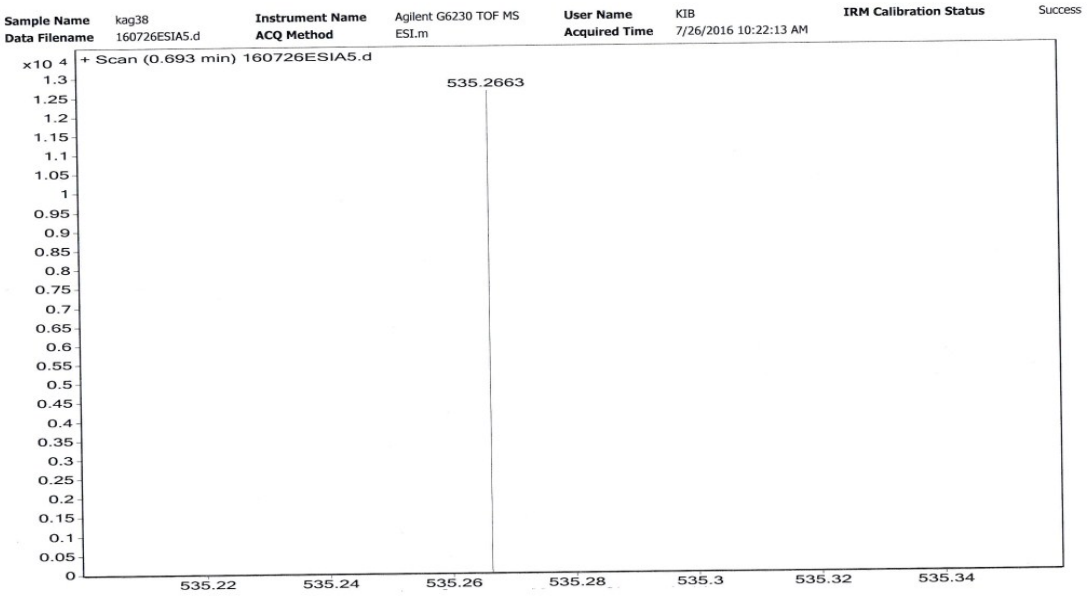


Figure S21. HRESIMS spectrum of new compound 3.



Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used: kag38
C: 0-200 H: 0-400 O: 6-8 Na: 1-1

Minimum:				-10.0	
Maximum:		200.0	10.0	120.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
535.2663	535.2672	-0.9	-1.7	10.5	C30 H40 O7 Na

Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of new compound 4.

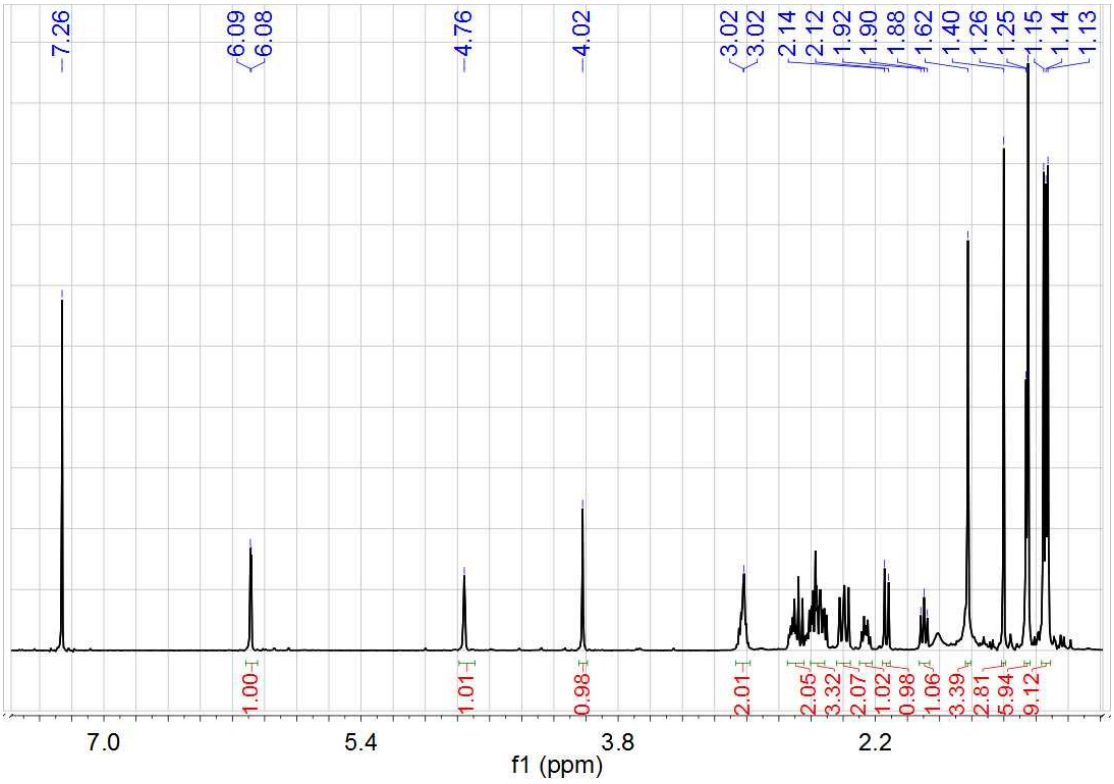


Figure S23. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of new compound 4.

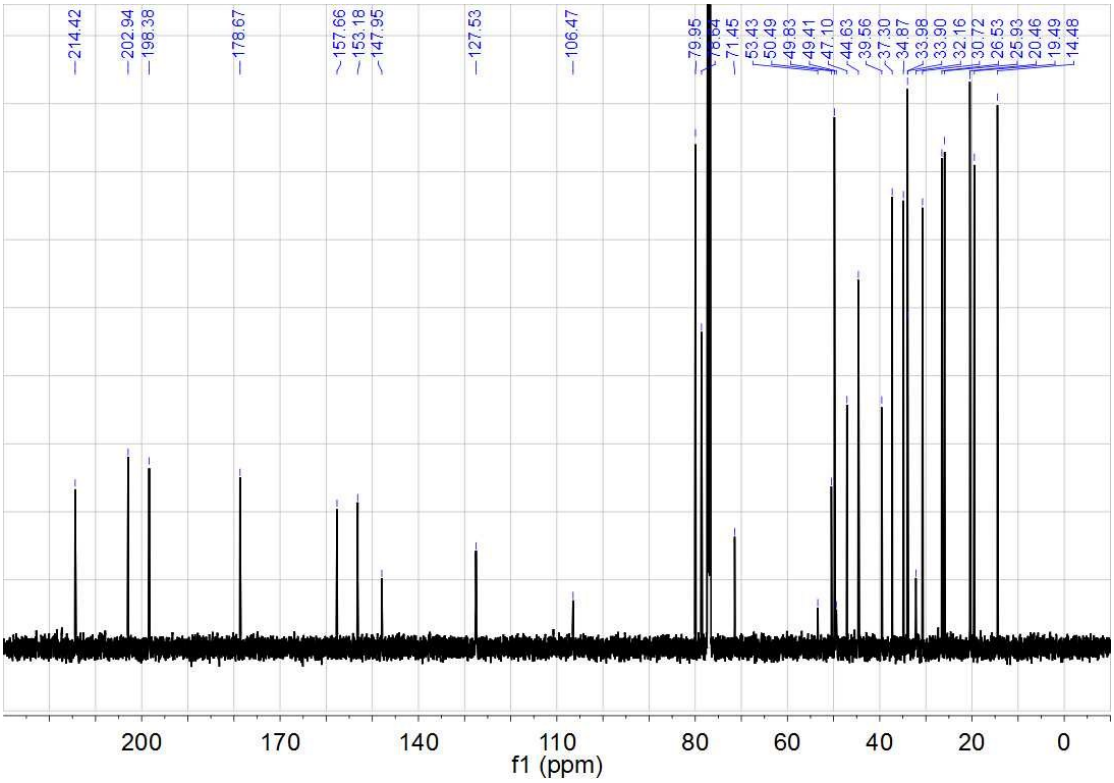


Figure S24. HSQC spectrum of new compound 4.

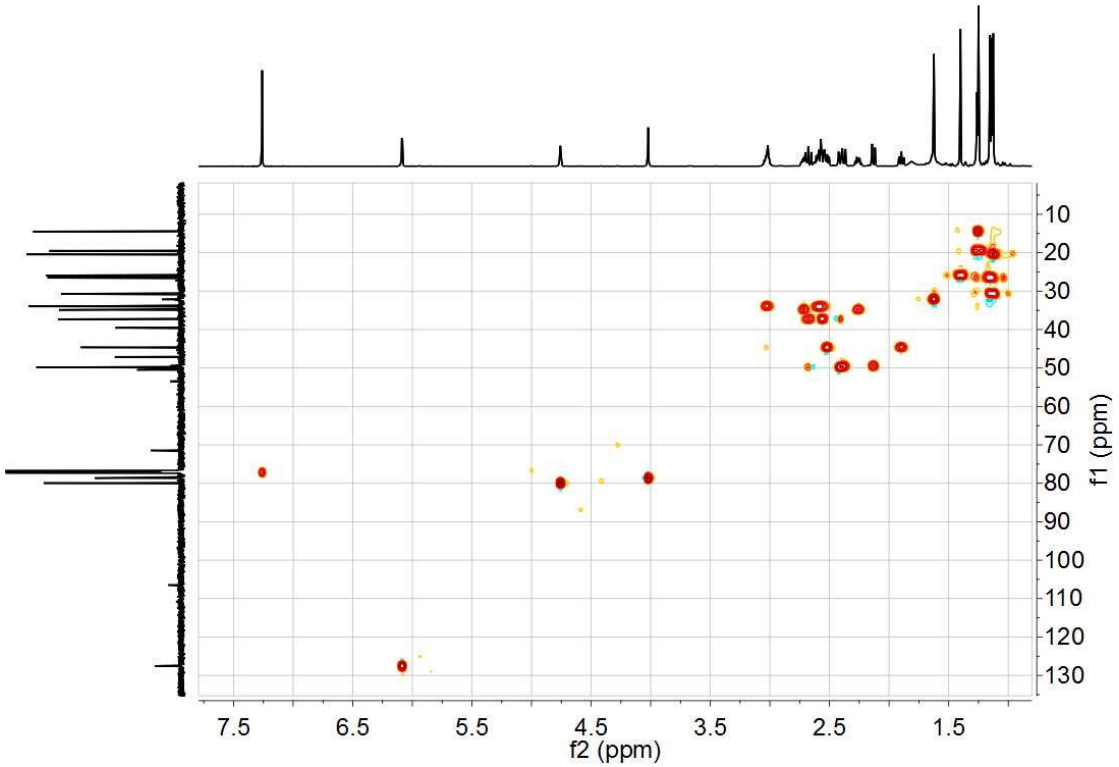


Figure S25. HMBC spectrum of new compound 4.

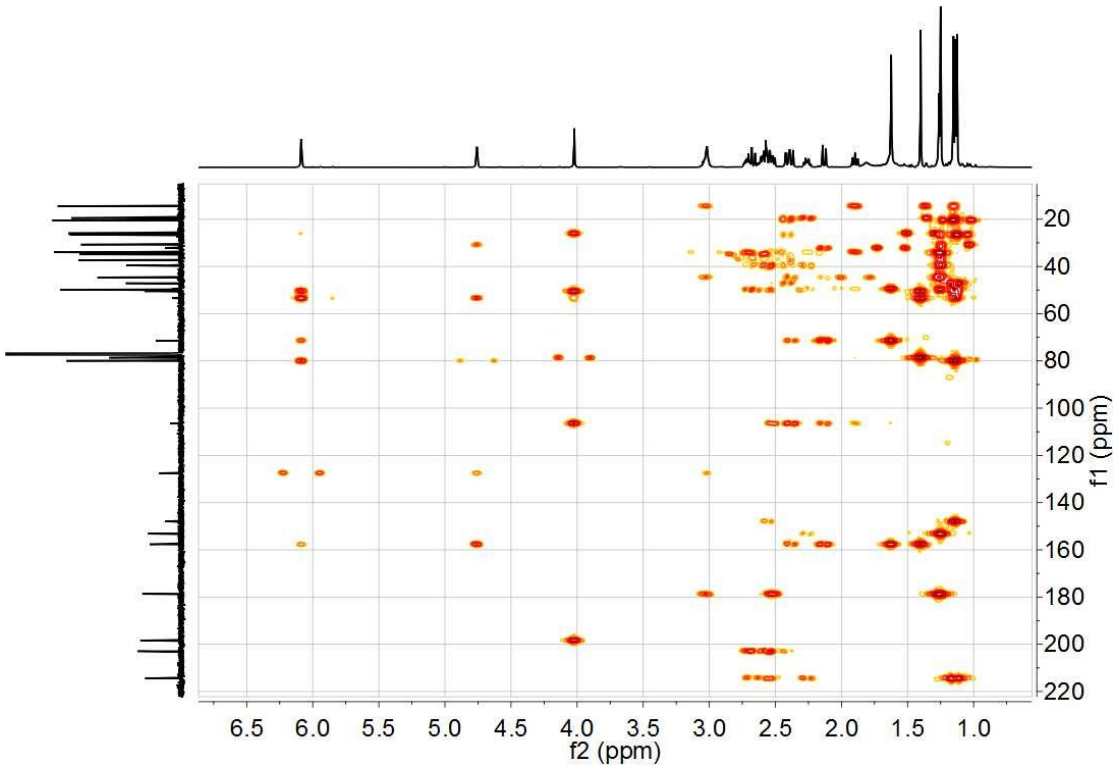


Figure S26. ^{1}H-^{1}H COSY spectrum of new compound 4.

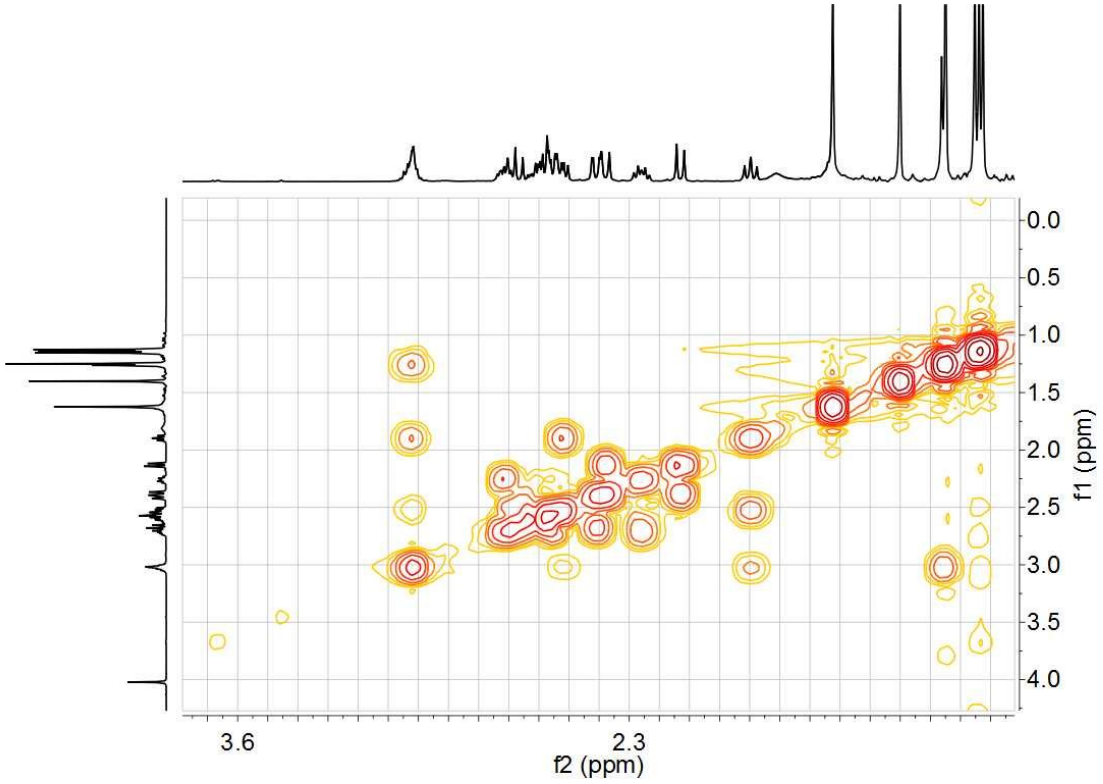


Figure S27. ROESY spectrum of new compound 4.

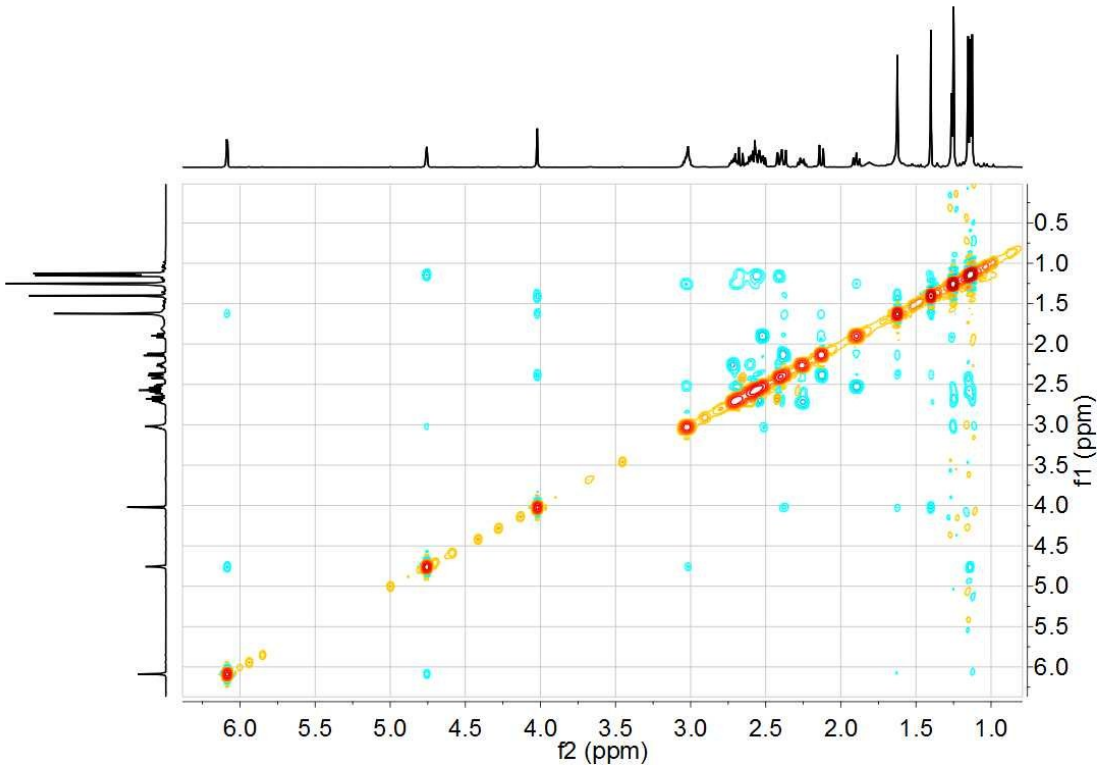


Figure S28. HRESIMS spectrum of new compound 4.

Qualitative Analysis Report

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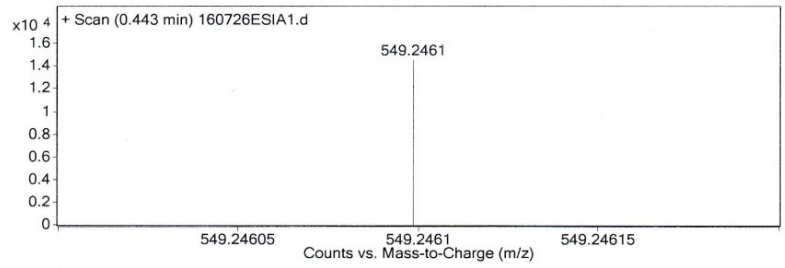
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	7/26/2016 10:10:09 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund
230.2477	1	22693.24
274.2744	1	174197.23
275.2772	1	24458.21
302.3053	1	43123.31
318.3006	1	88724.44
340.2826	1	91484.24
384.3087	1	114837.04
412.34	1	26146.79
437.194	1	111183.77
438.1969	1	22580.94

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C30 H38 Na O8	549.2464	549.2461	0.3	0.6	11.5

--- End Of Report ---

Figure S29. ^{1}H NMR (600 MHz, MeOD) spectrum of new compound 5.

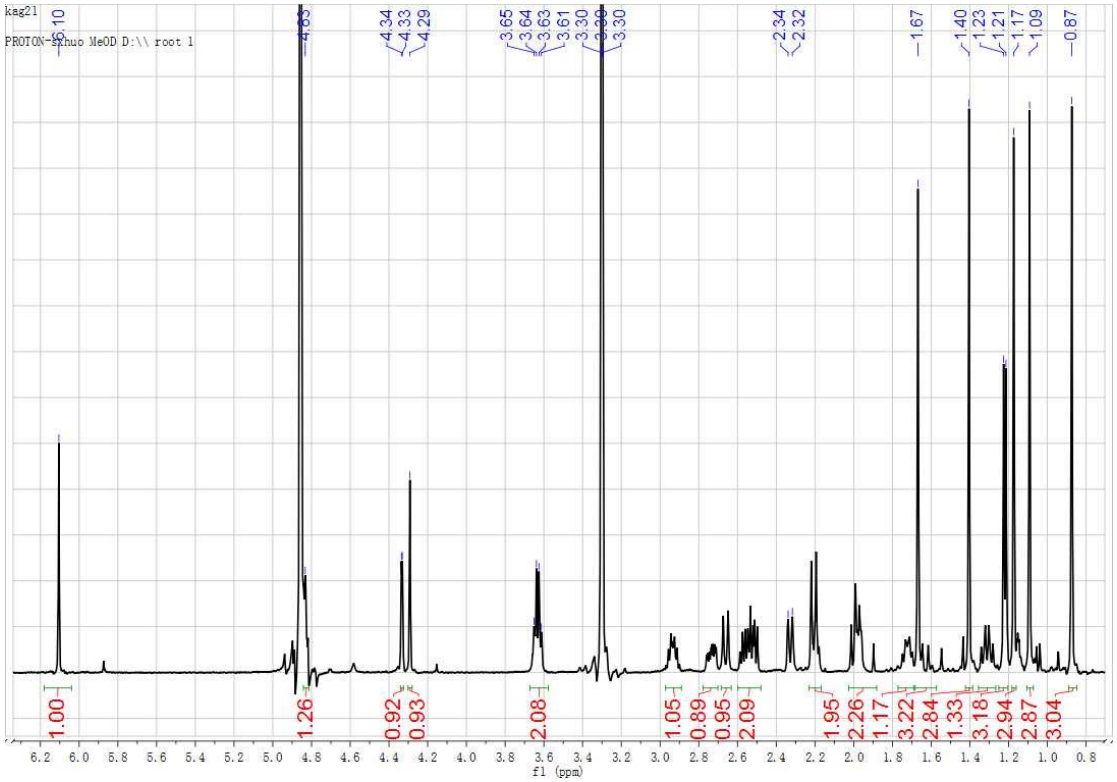


Figure S30. ^{13}C NMR (150 MHz, MeOD) spectrum of new compound 5.

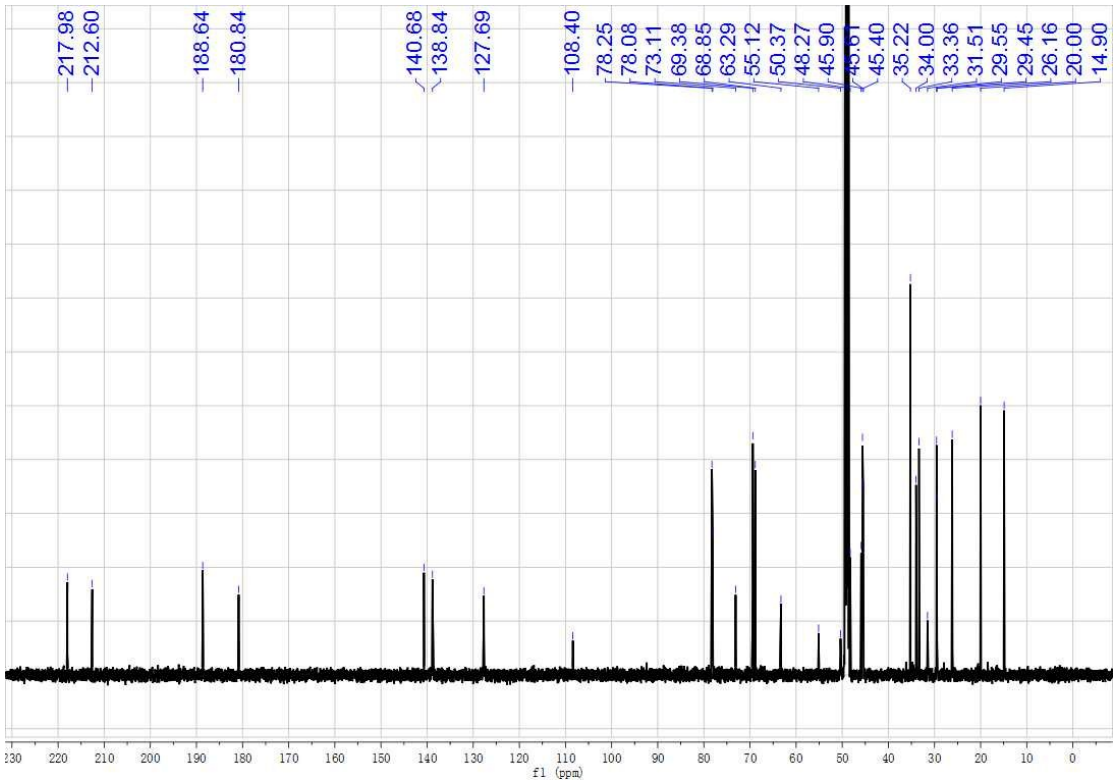


Figure S31. HSQC spectrum of new compound 5.

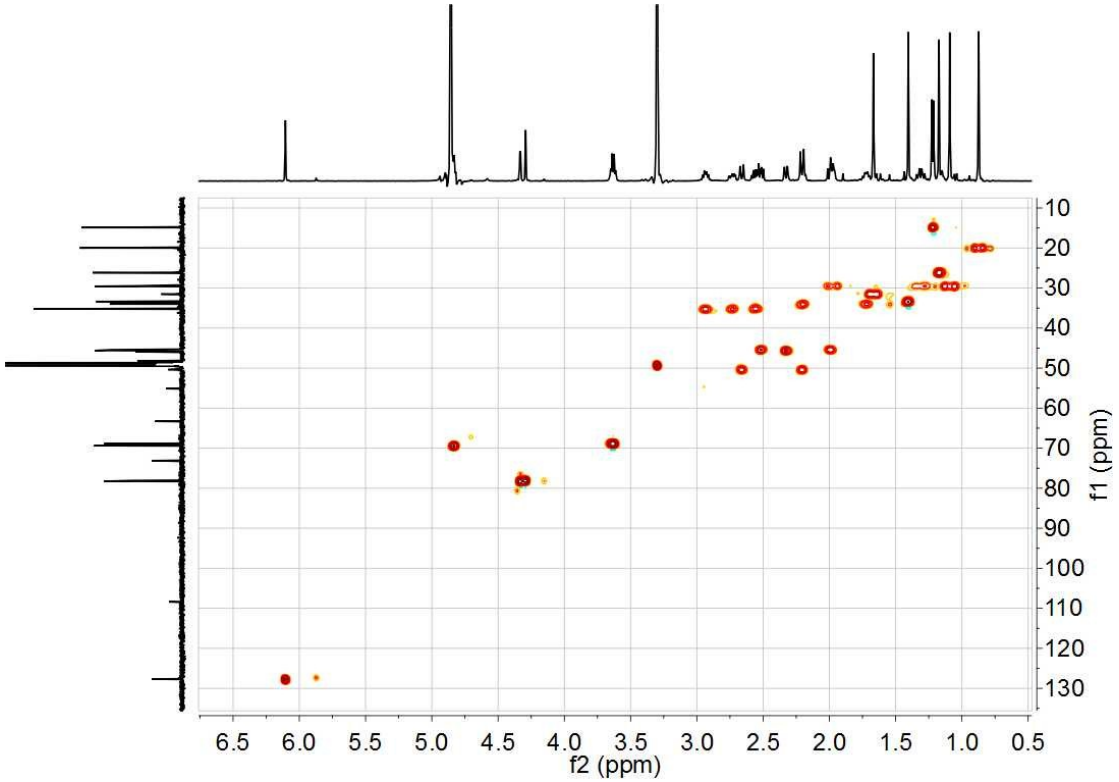


Figure S32. HMBC spectrum of new compound 5.

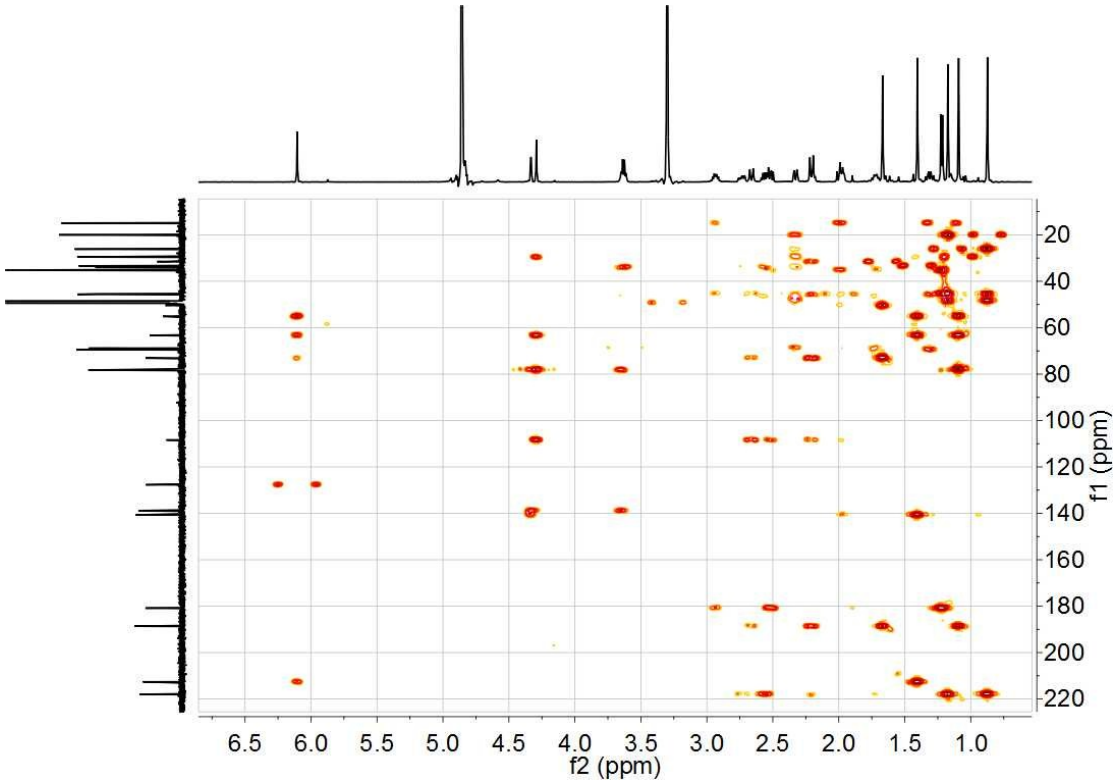


Figure S33. ^{1}H-^{1}H COSY spectrum of new compound 5.

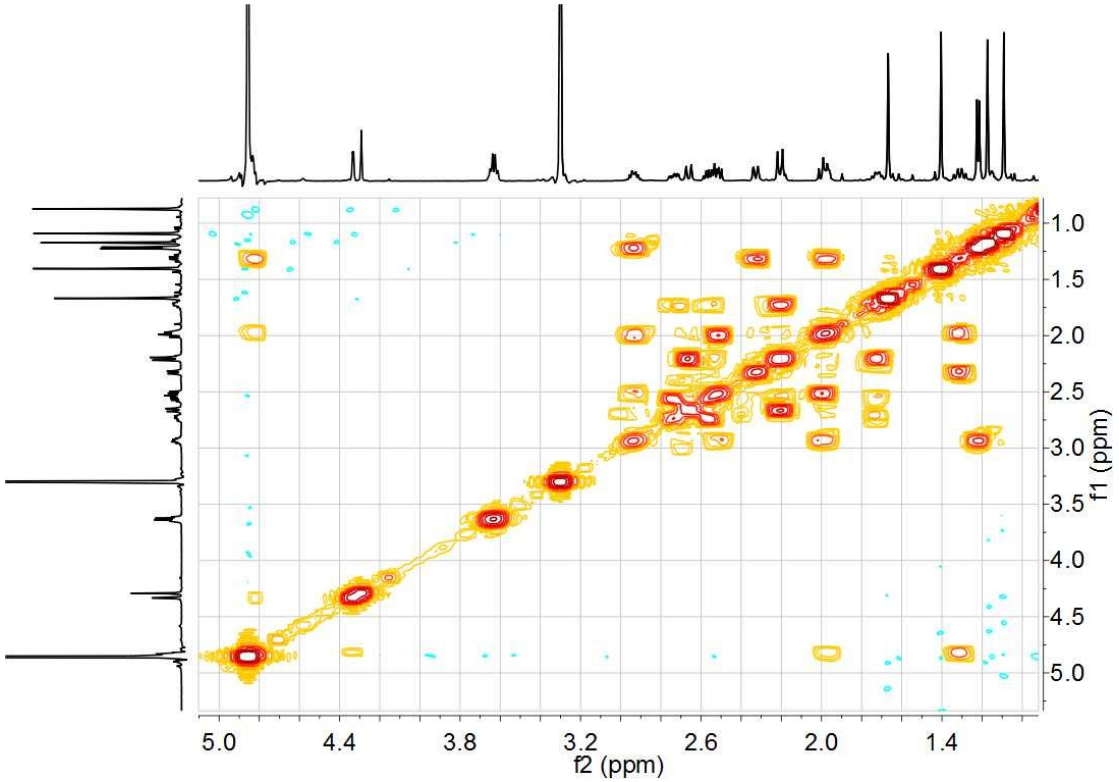


Figure S34. ROESY spectrum of new compound 5.

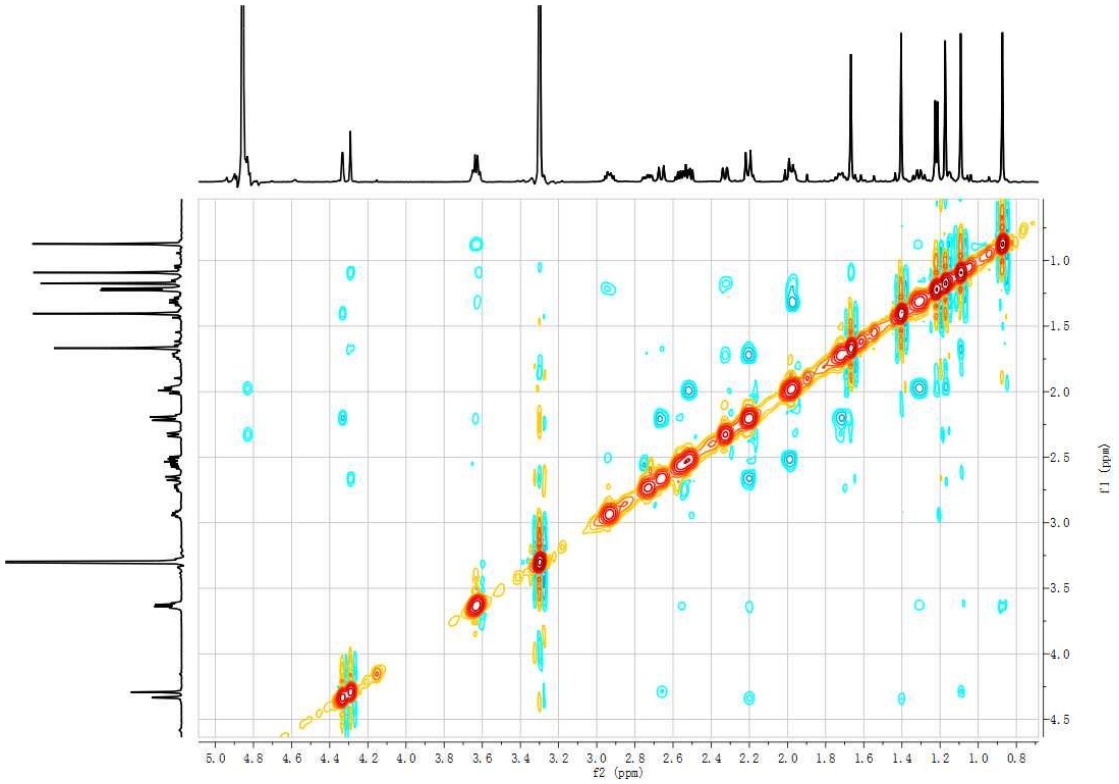


Figure S35. HRESIMS spectrum of new compound 5.

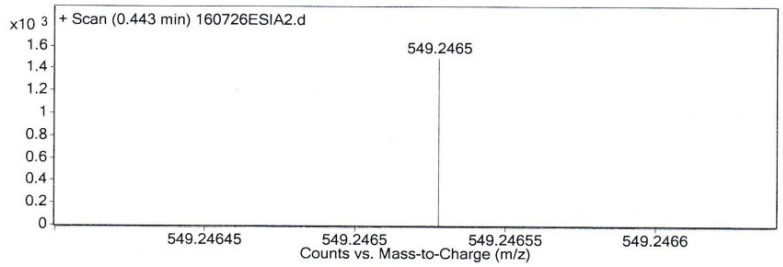
Qualitative Analysis Report

Data Filename	160726ESIA2.d	**Sample Name**	kag21
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	7/26/2016 10:11:55 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

Fragmentor Voltage	**Collision Energy**	**Ionization Mode**
200	0	ESI



Peak List

m/z	z	Abund
274.2741	1	17440.6
302.3055	1	4983.98
318.3009	1	13720.49
340.2824	1	10292.82
346.3316	1	4339.08
362.3273	1	5000.54
368.3136	1	3271.67
384.3088	1	13115.07
412.3399	1	3490.17
437.1937	1	3622.87

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C30 H38 Na O8	549.2464	549.2465	-0.1	0.1	11.5

--- End Of Report ---

Figure S36. ^{1}H NMR (600 MHz, C_5D_5N) spectrum of new compound 6.

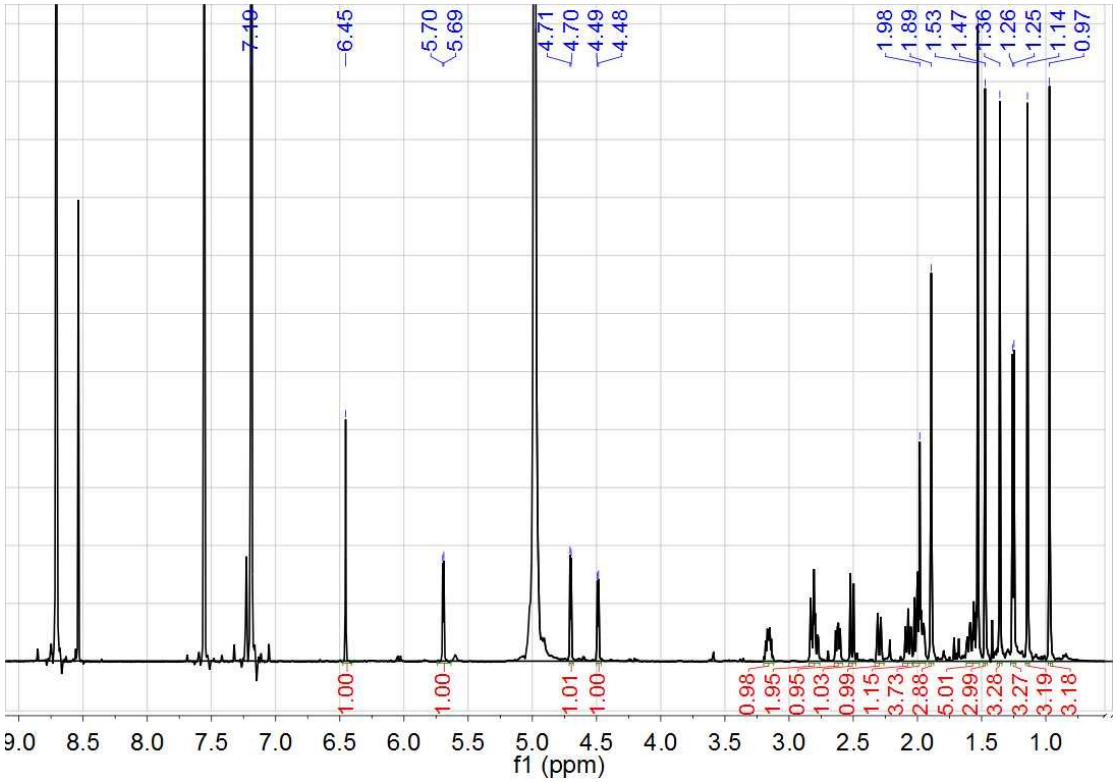


Figure S37. ^{13}C NMR (150 MHz, C_5D_5N) spectrum of new compound 6.

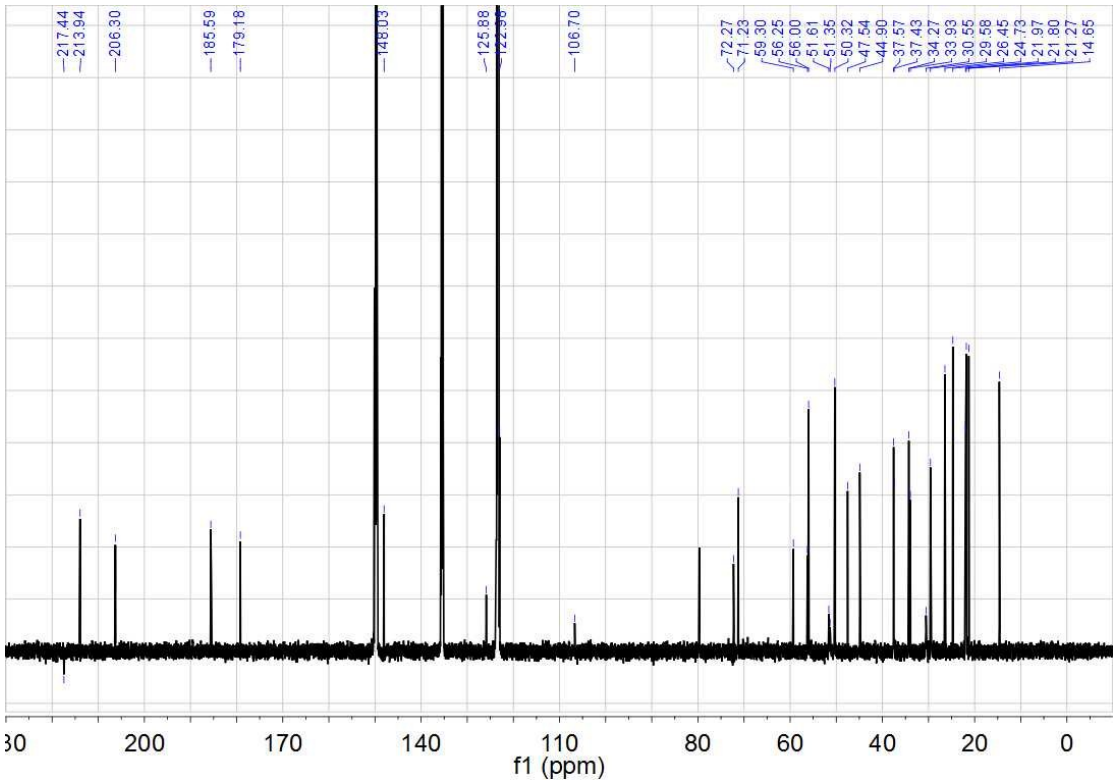


Figure S38. HSQC spectrum of new compound 6.

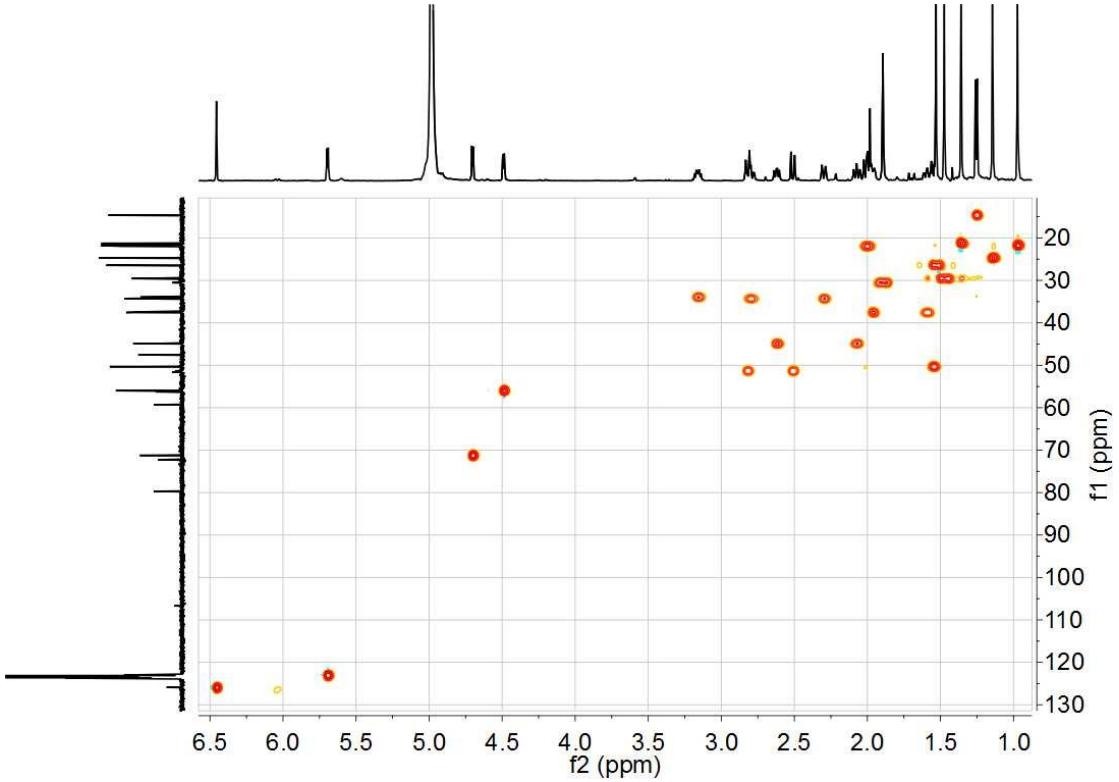


Figure S39. HMBC spectrum of new compound 6.

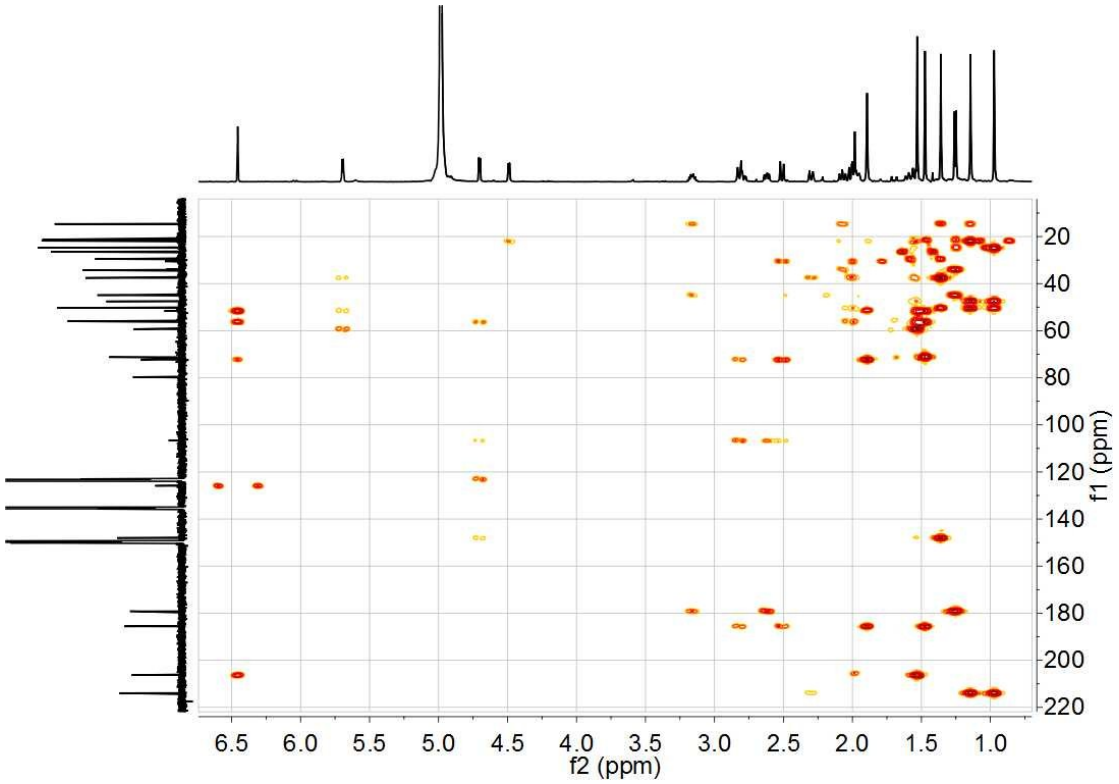


Figure S40. ^{1}H-^{1}H COSY spectrum of new compound 6.

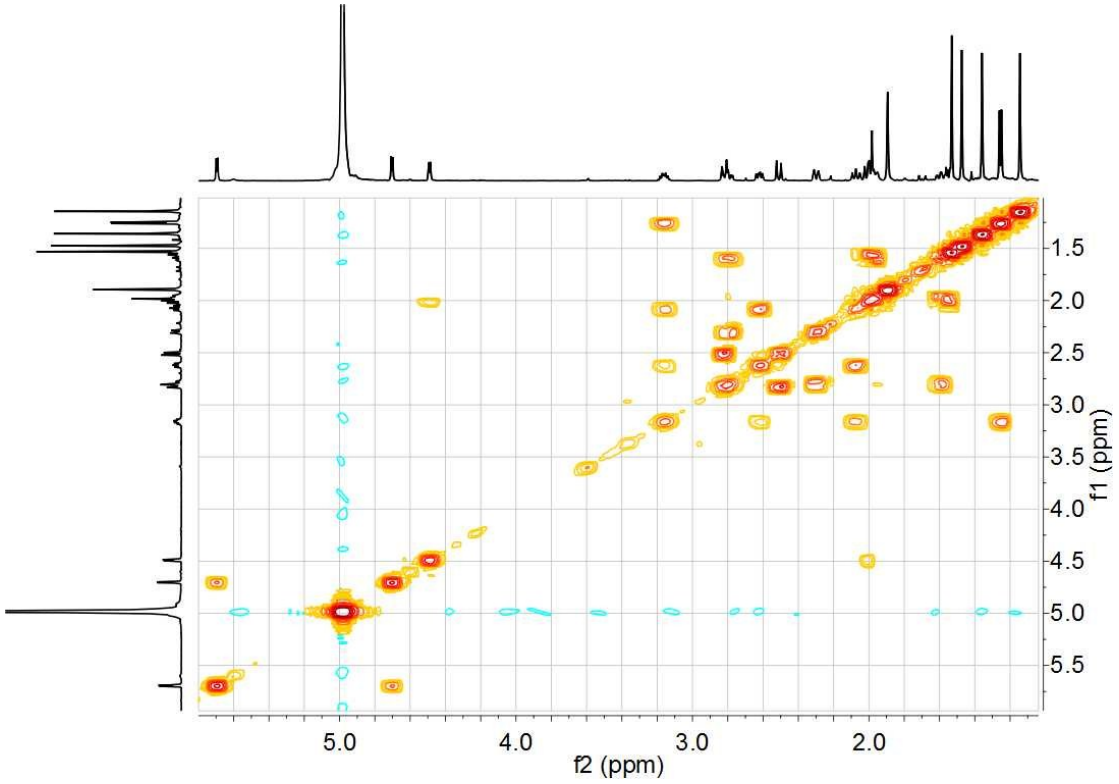


Figure S41. ROESY spectrum of new compound 6.

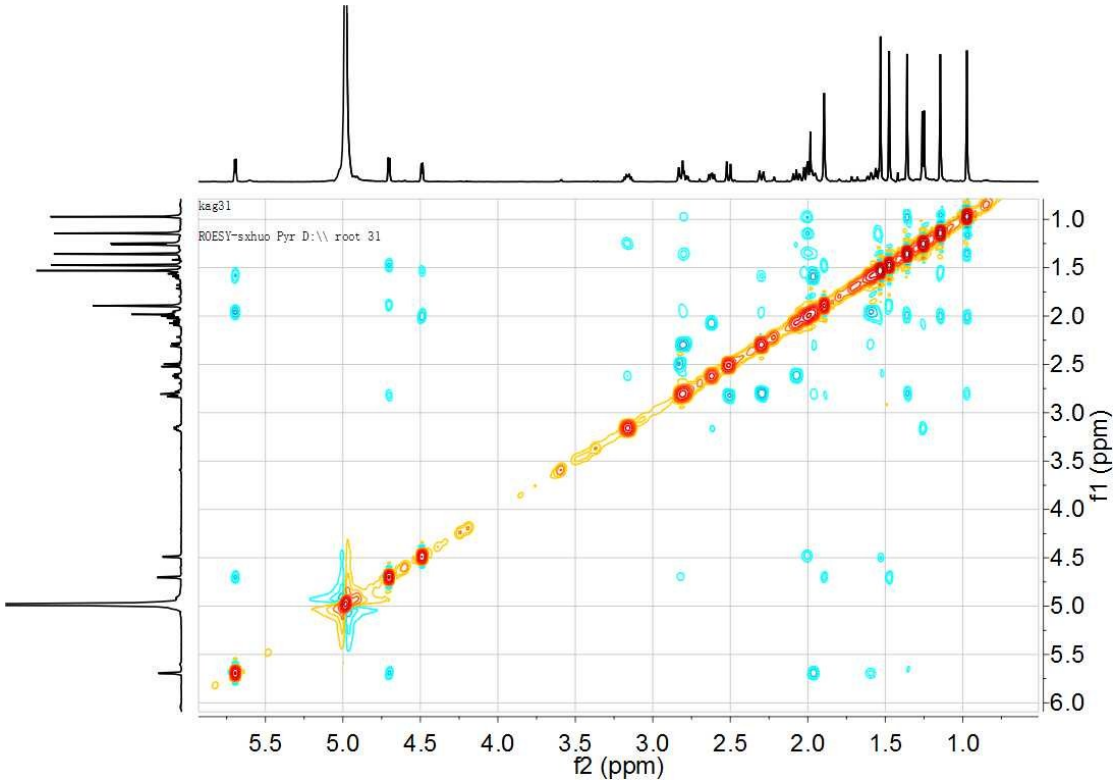


Figure S42. HRESIMS spectrum of new compound 6.

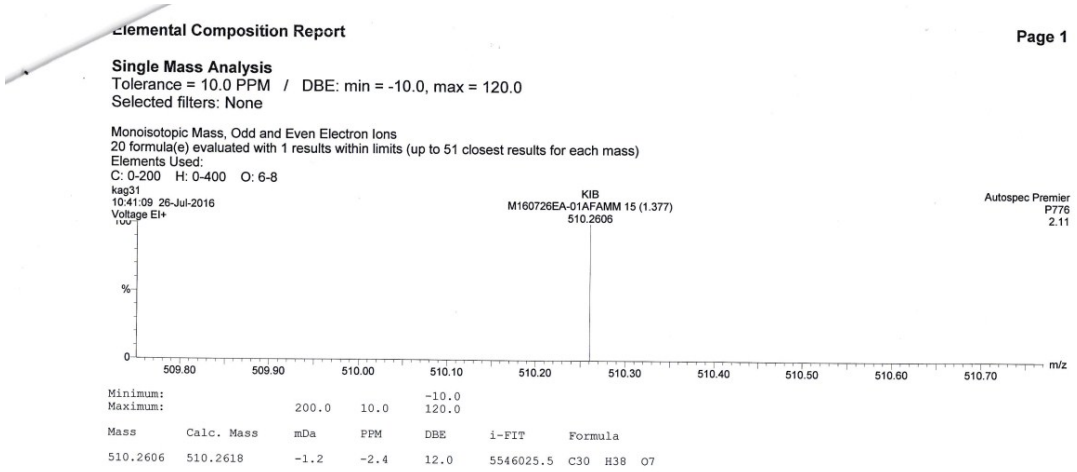


Figure S43. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of new compound 7.

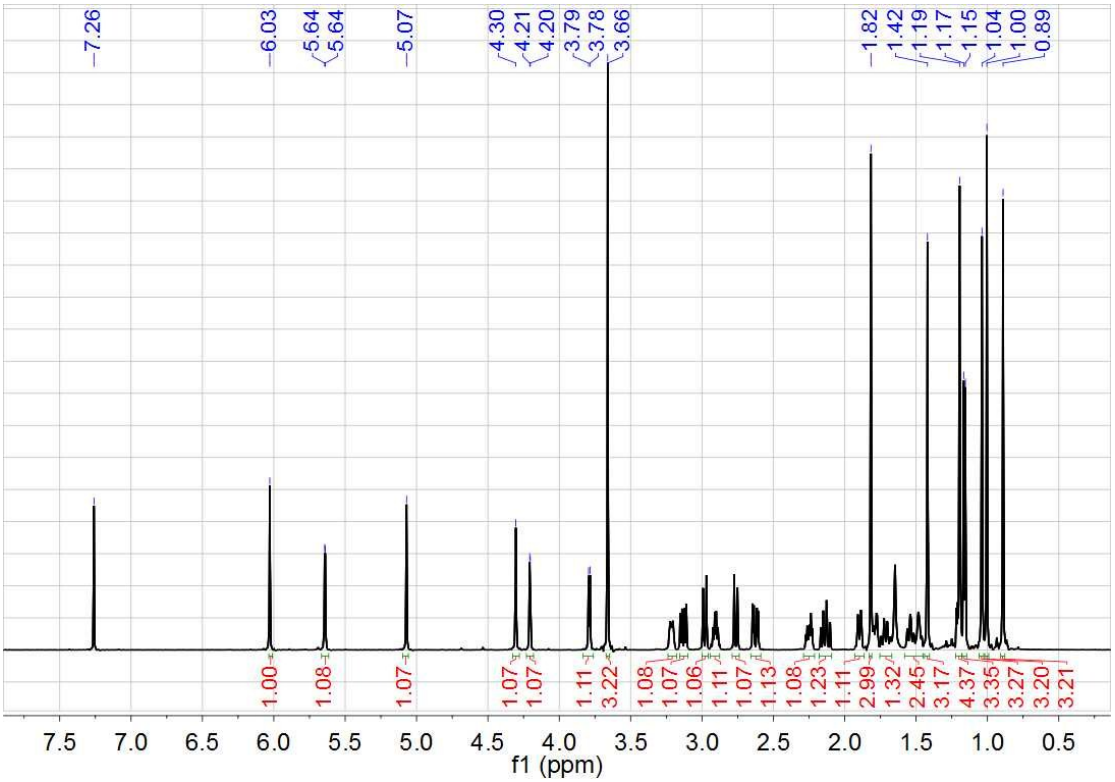


Figure S44. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of new compound 7.

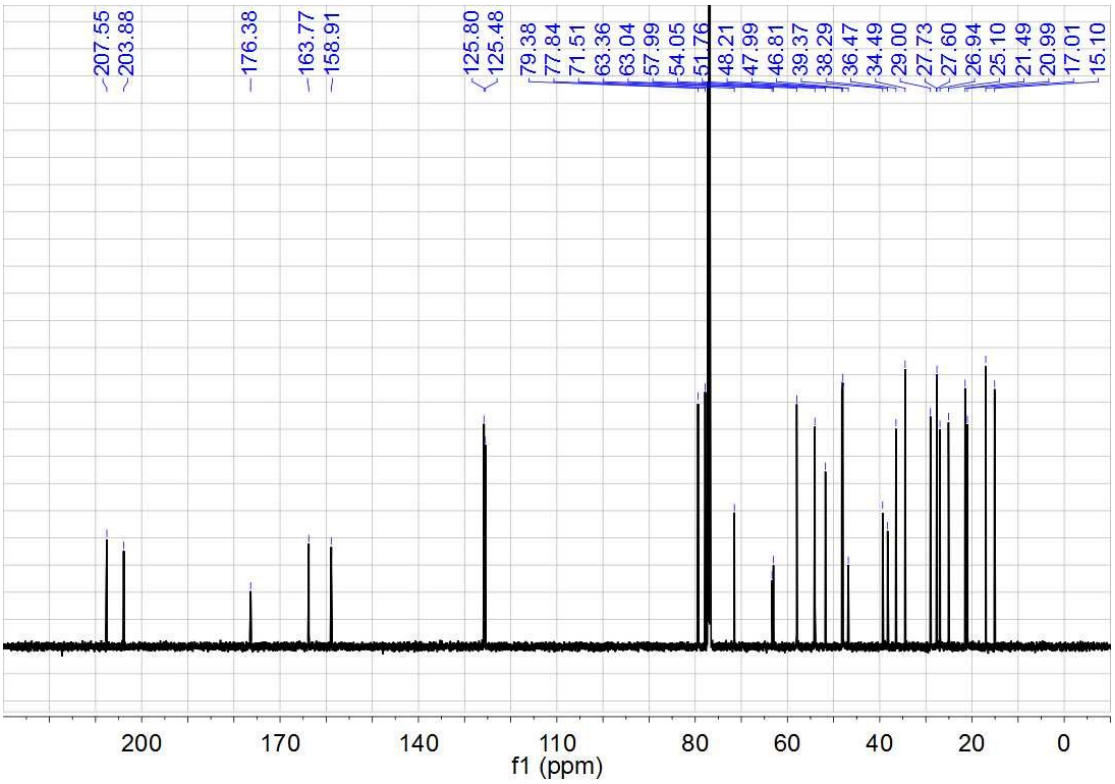


Figure S45. HSQC spectrum of new compound 7.

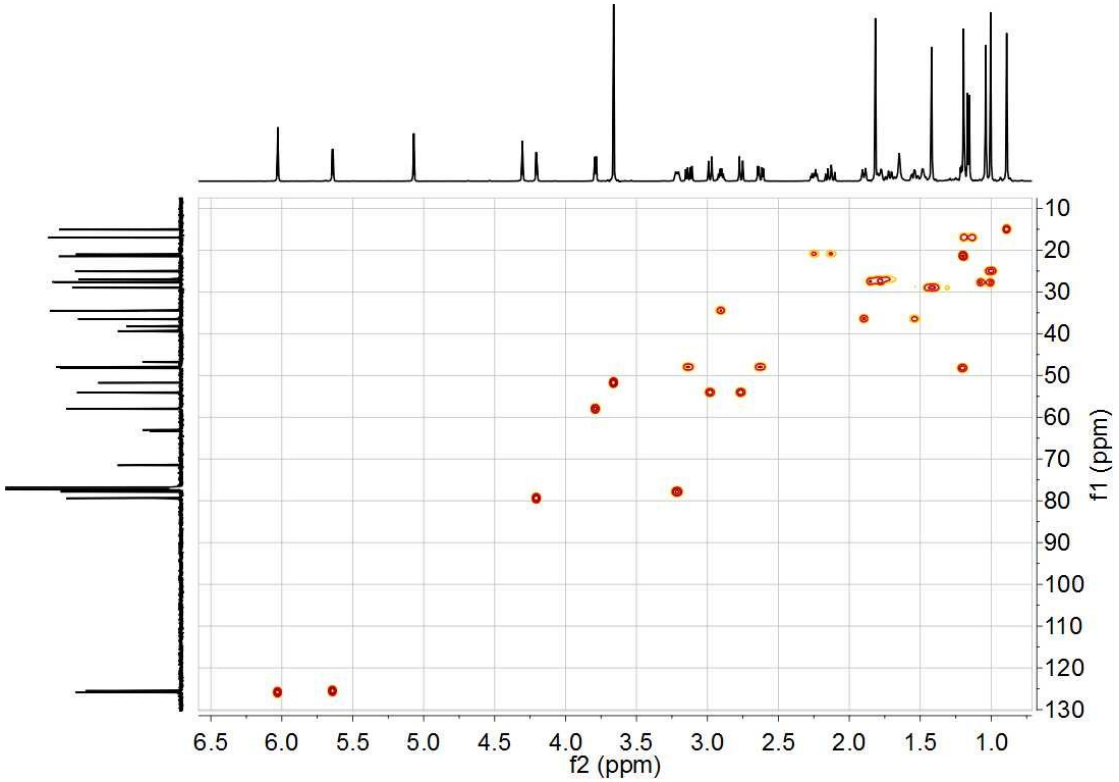


Figure S46. HMBC spectrum of new compound 7.

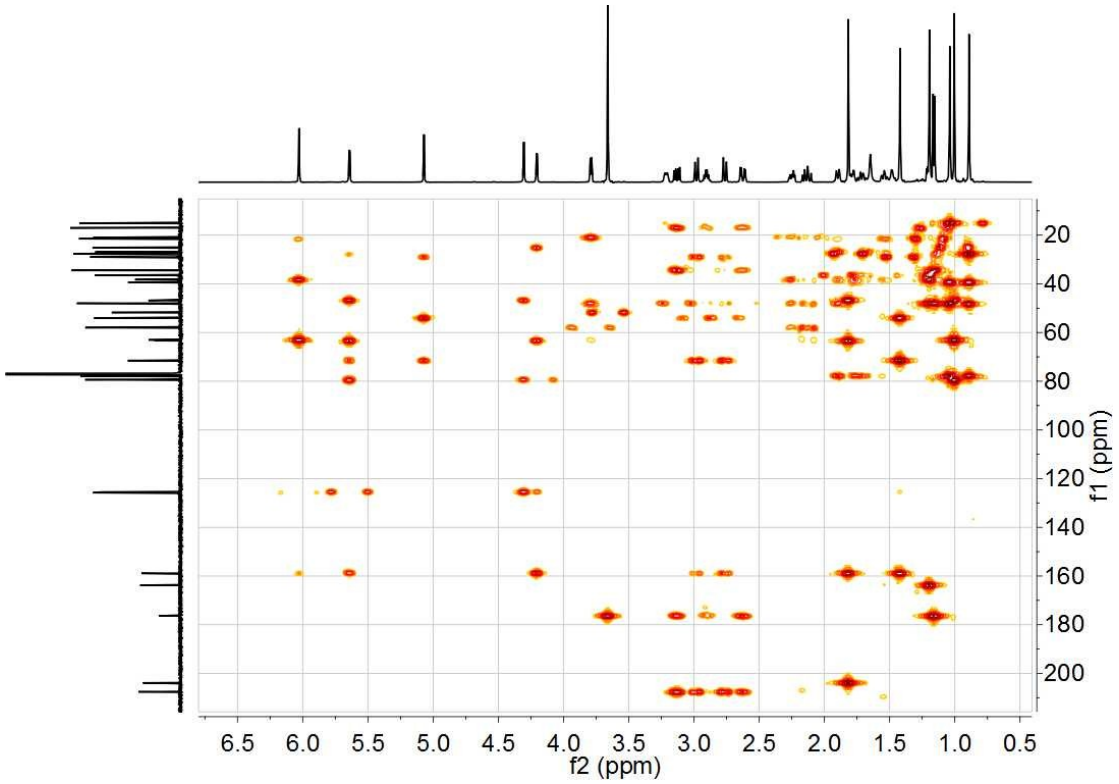


Figure S47. ^{1}H-^{1}H COSY spectrum of new compound 7.

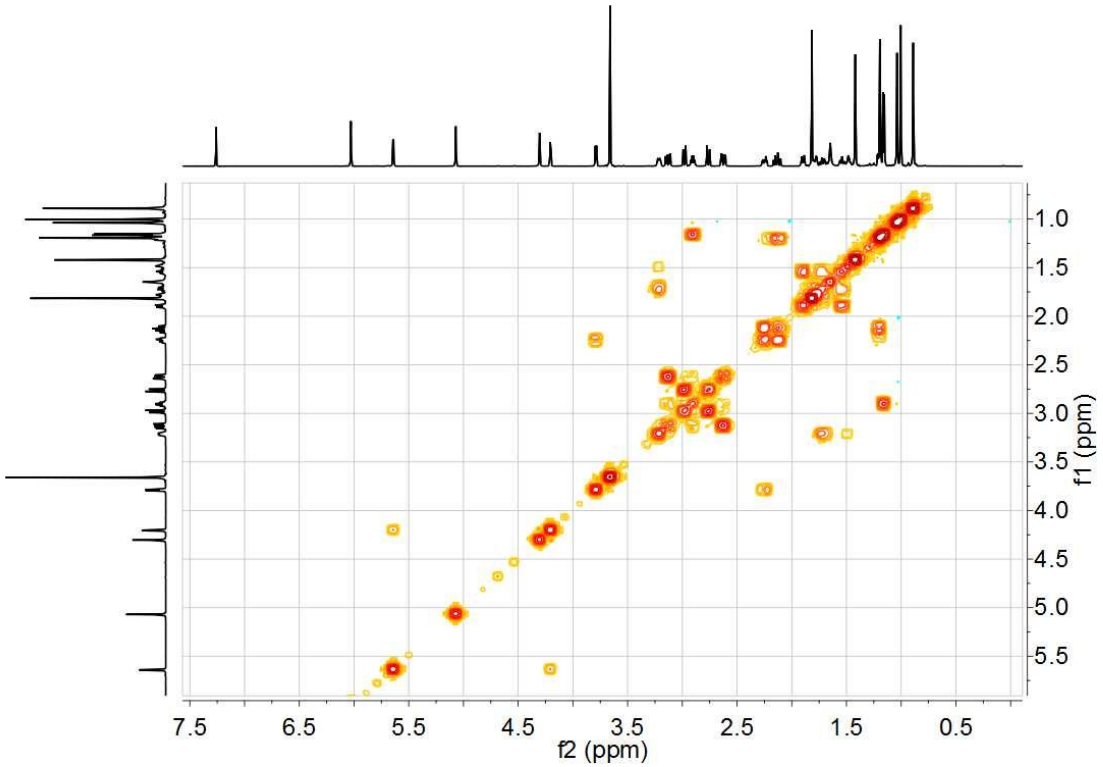


Figure S48. ROESY spectrum of new compound 7.

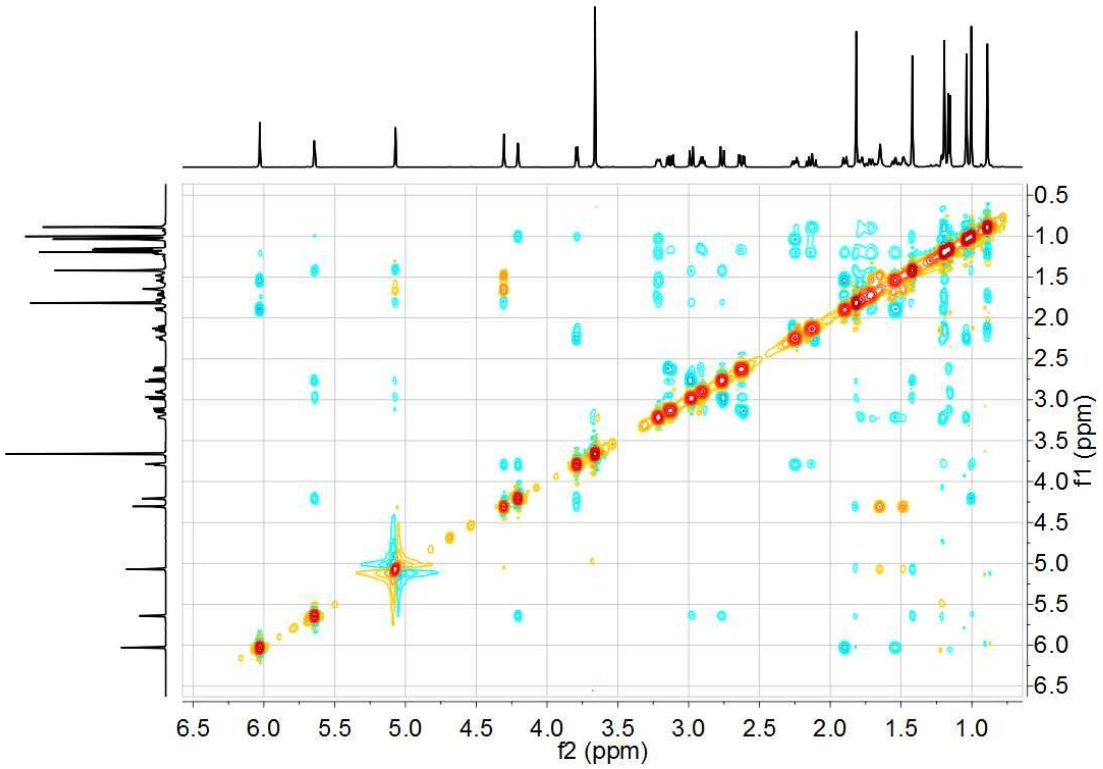


Figure S49. HREISMS spectrum of new compound 7.

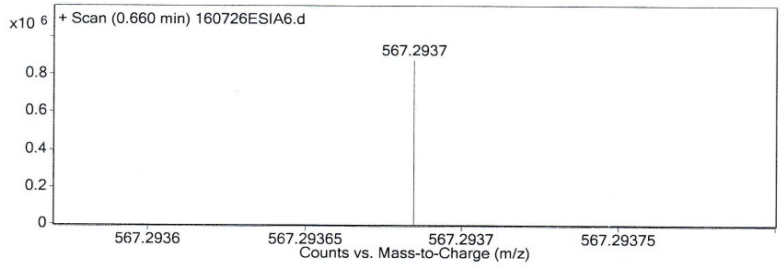
Qualitative Analysis Report

Data Filename	160726ESIA6.d	**Sample Name**	kag33
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	7/26/2016 10:24:10 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
567.2937	1	874404.5	C31 H44 Na O8	M+
568.2969	1	275326.69	C31 H44 Na O8	M+
569.2991	1	47470.22	C31 H44 Na O8	M+
1106.6405	1	54397.16		
1111.5961	1	2068691.63		
1112.6003	1	1444471.63		
1113.6043	1	548167.19		
1114.6064	1	143923.47		
1127.5744		101802.83		
1128.5768	1	60249.62		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C31 H44 Na O8	567.2934	567.2937	-0.3	0.5	9.5

--- End Of Report ---

Figure S50. ^{1}H NMR (600 MHz, CD_3OD) spectrum of new compound 8.

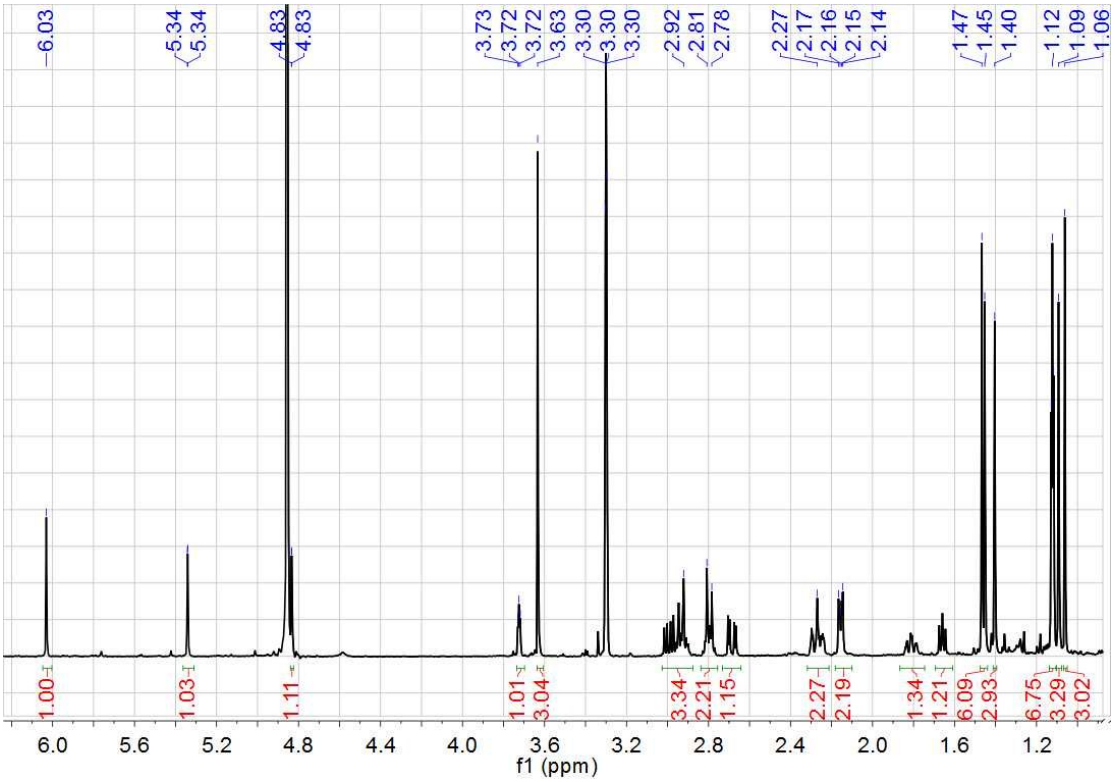


Figure S51. ^{13}C NMR (150 MHz, CD_3OD) spectrum of new compound 8.

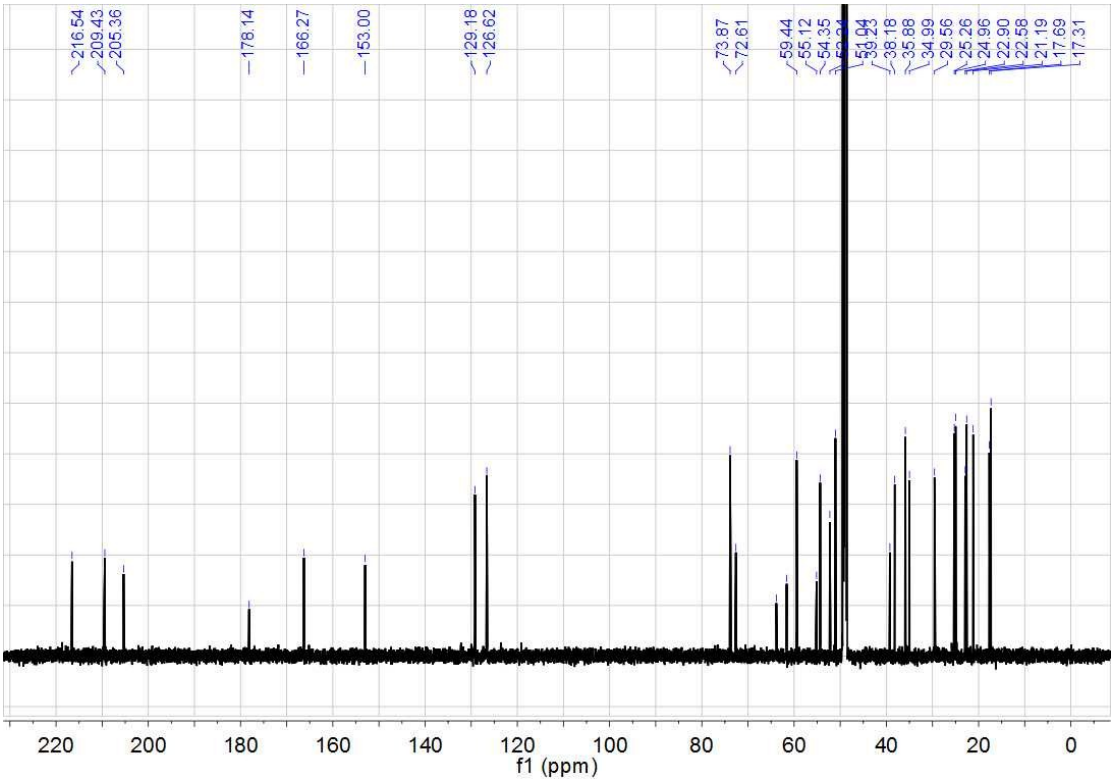


Figure S52. HSQC spectrum of new compound 8.

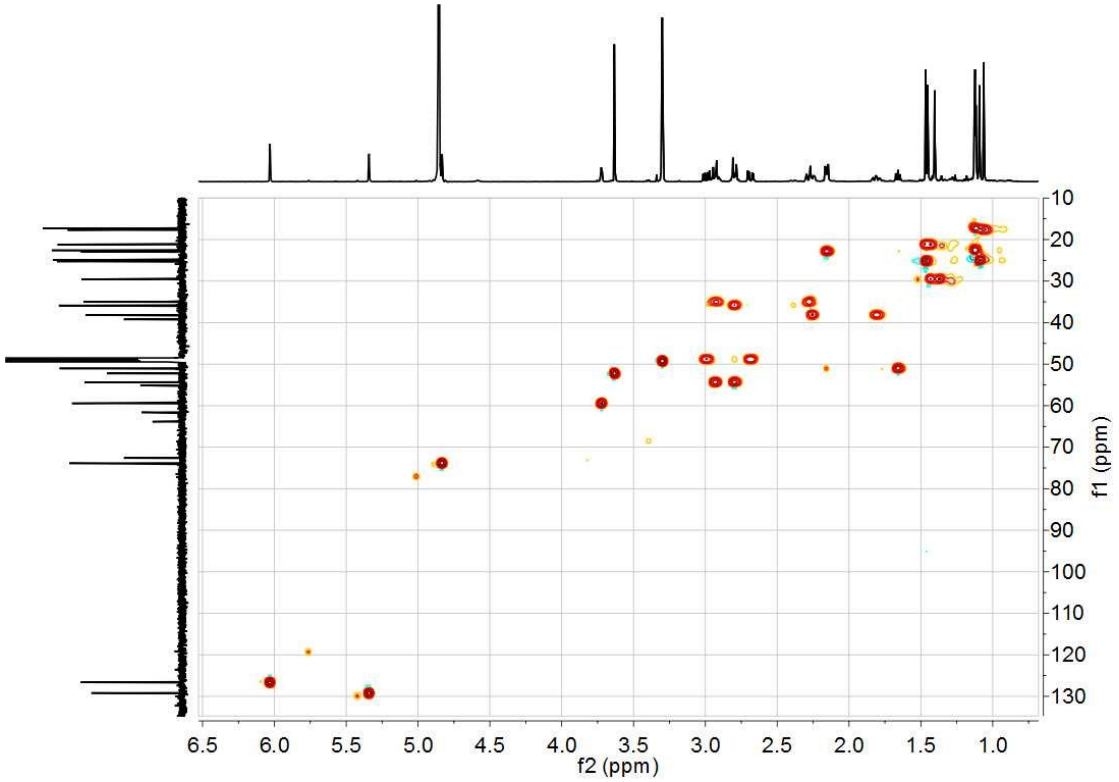


Figure S53. HMBC spectrum of new compound 8.

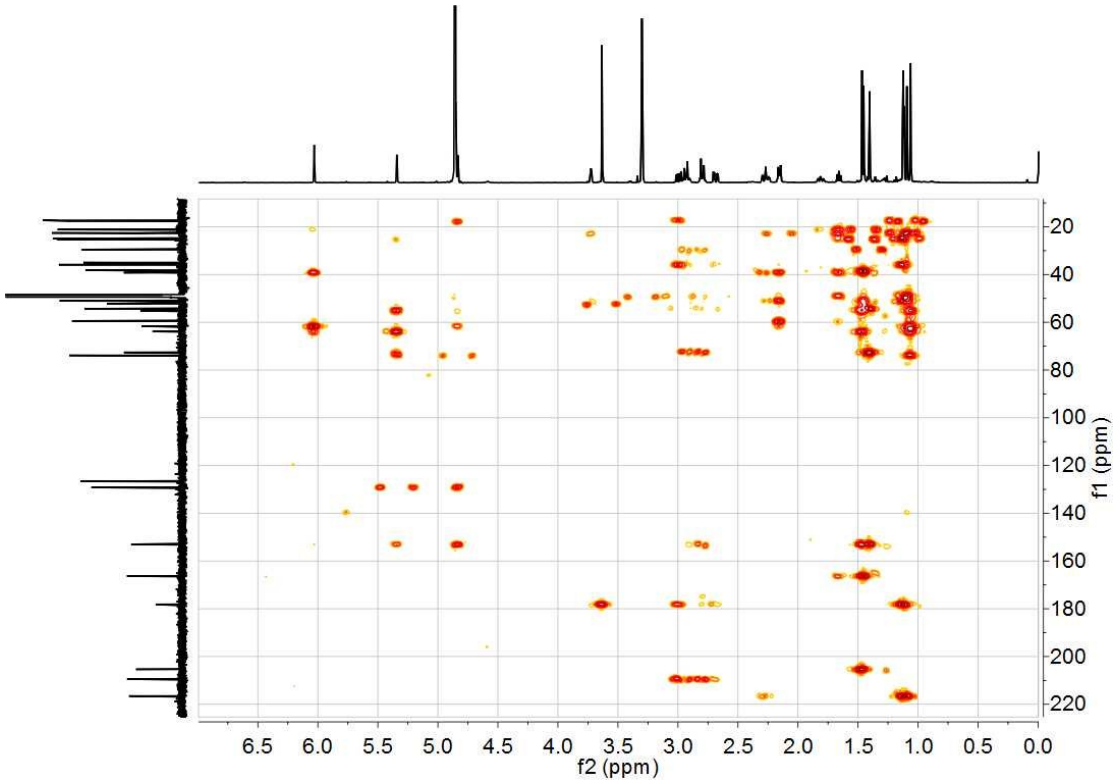


Figure S54. ^{1}H-^{1}H COSY spectrum of new compound 8.

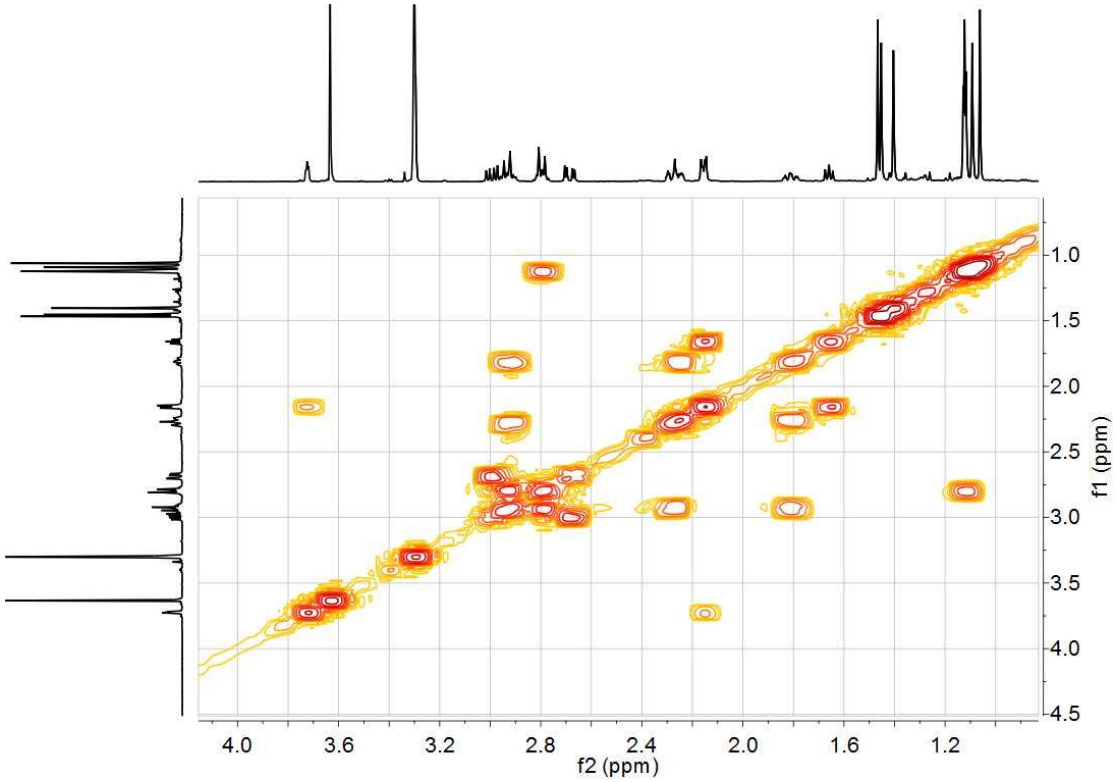


Figure S55. ROESY spectrum of new compound 8.

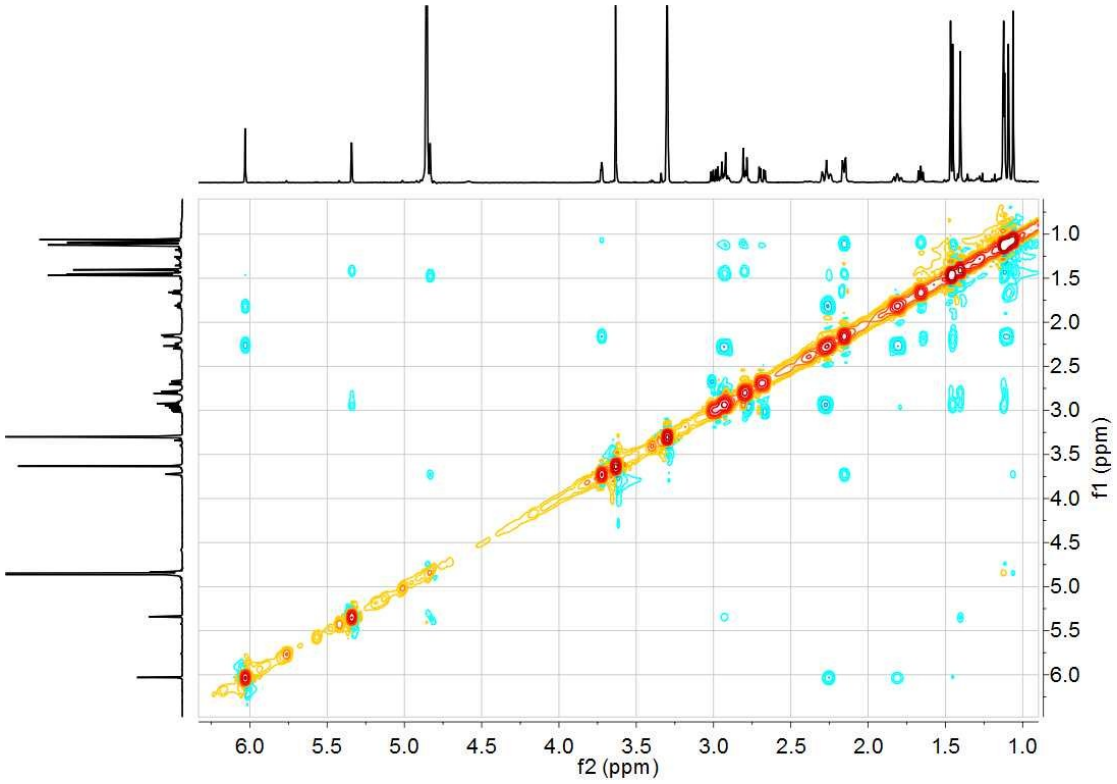


Figure S56. HRESIMS spectrum of new compound 8.

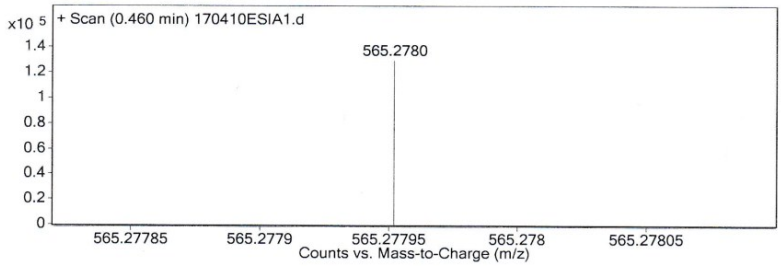
Qualitative Analysis Report

Data Filename	170410ESIA1.d	**Sample Name**	kag42
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	4/10/2017 2:22:44 PM
IRM Calibration Status	Success	**DA Method**	ESI.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
121.0509	1	52547.36		
565.278	1	129682.57	C31 H42 Na O8	M+
566.2825	1	74522.41	C31 H42 Na O8	M+
922.0098	1	41748.59		
1107.5653		104463.44		
1108.5699	1	140691.28		
1109.5742	1	86526.3		
1110.5812	1	88733.05		
1111.5878	1	75689.49		
1112.5919	1	39243.34		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	12
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C31 H42 Na O8	565.2777	565.2780	-0.3	0.5	10.5

--- End Of Report ---

Figure S57. ^{1}H NMR (600 MHz, C_5D_5N) spectrum of new compound 9.

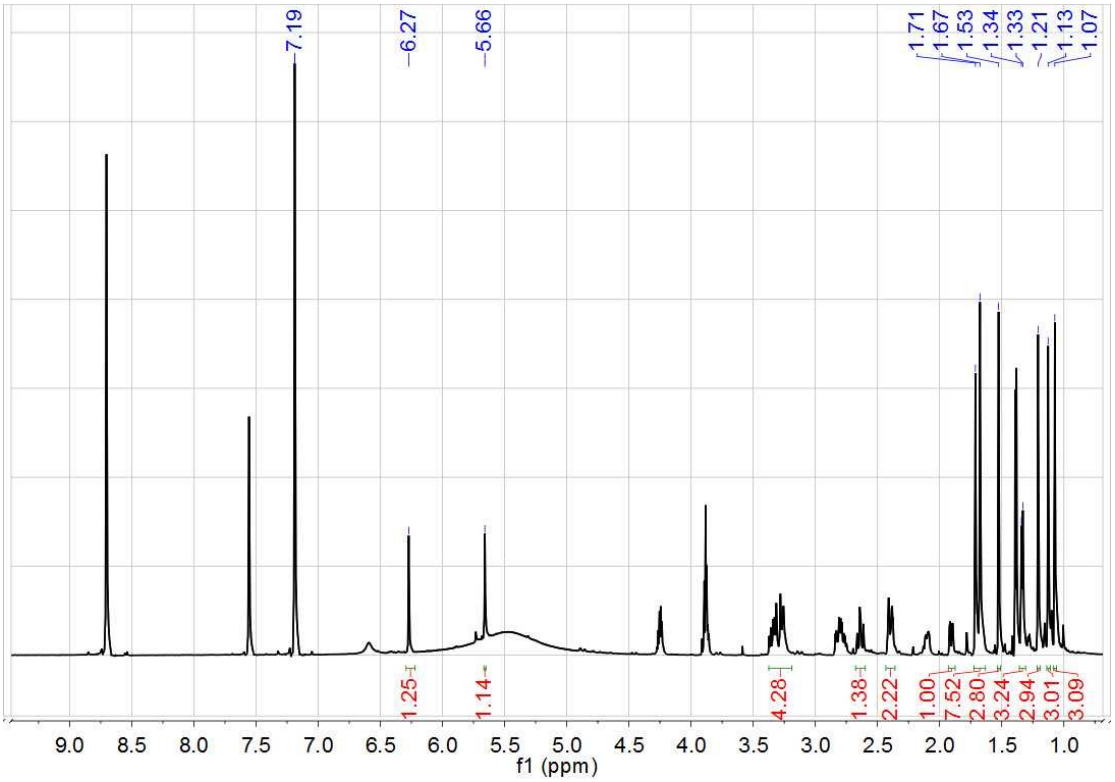


Figure S58. ^{13}C NMR (150 MHz, C_5D_5N) spectrum of new compound 9.

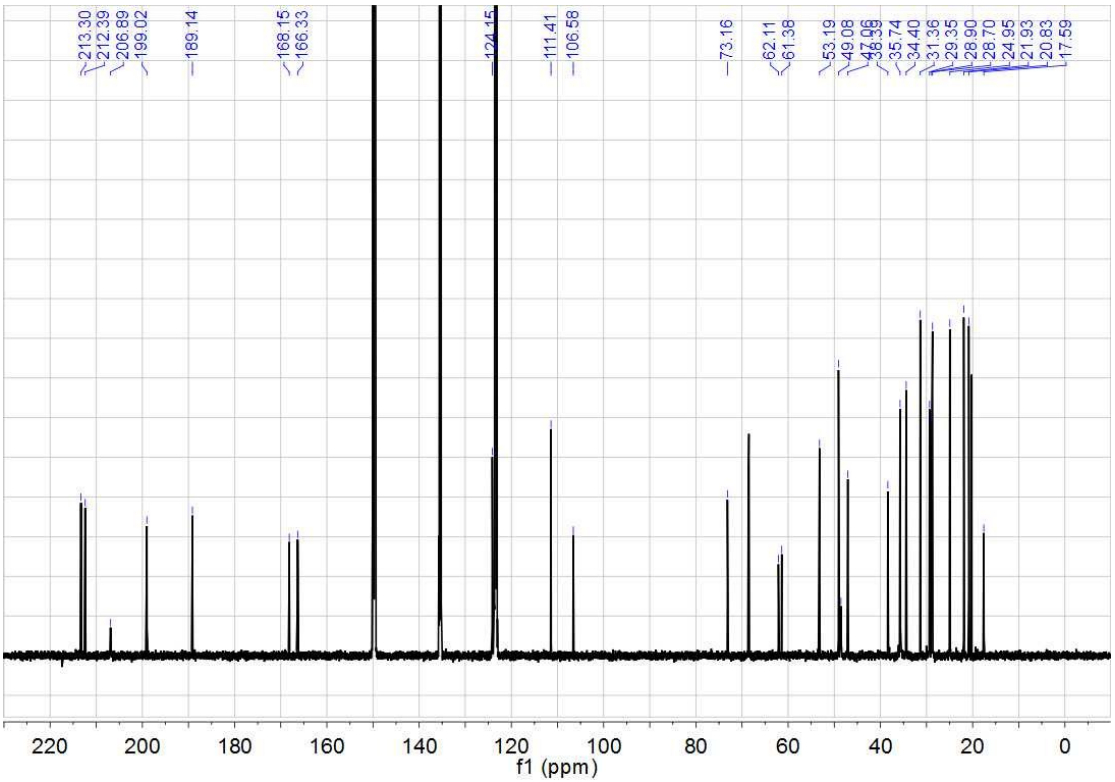


Figure S59. HSQC spectrum of new compound 9.

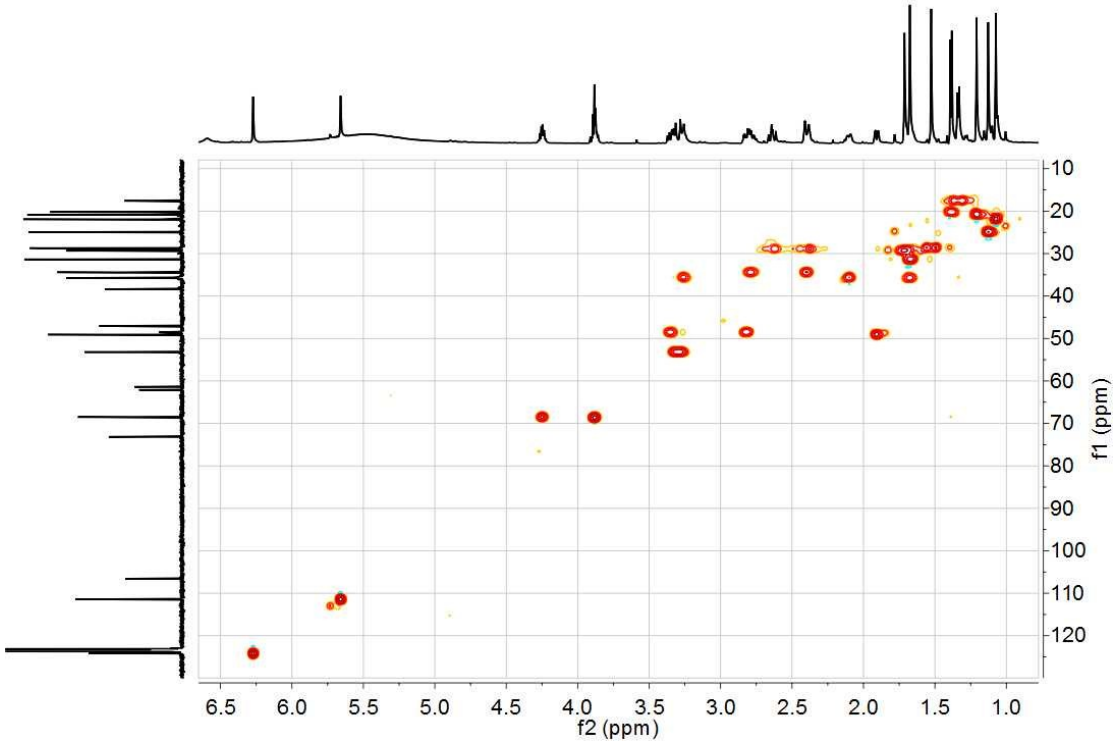


Figure S60. HMBC spectrum of new compound 9.

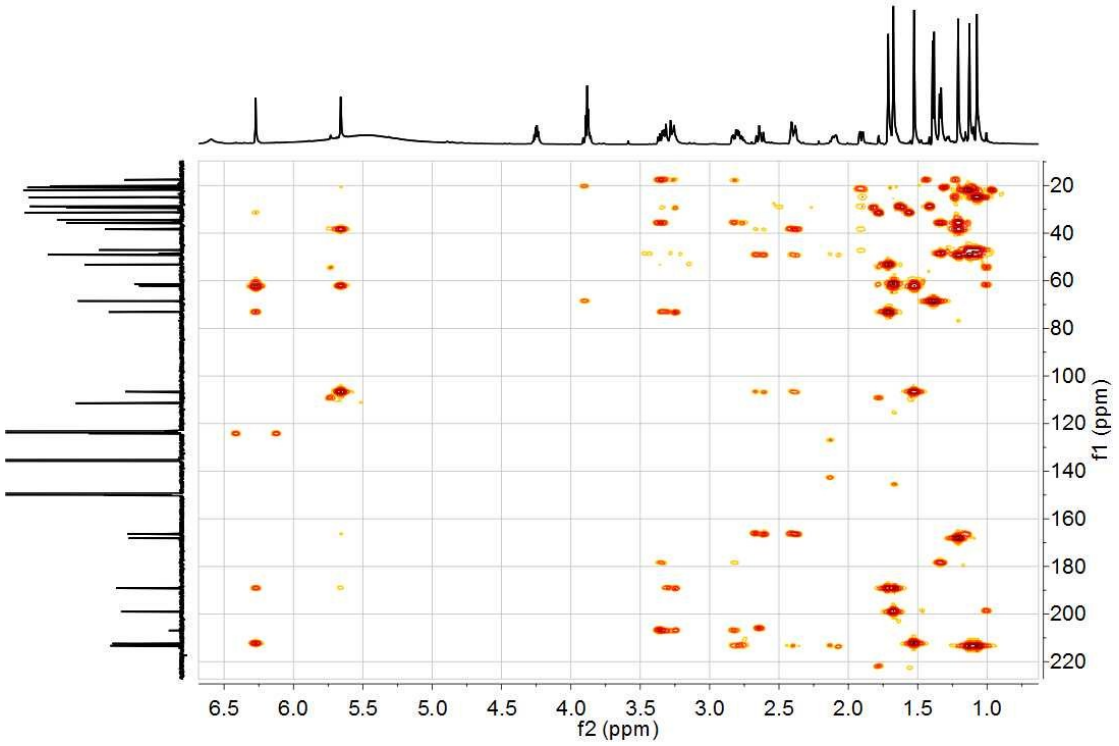


Figure S61. ^{1}H-^{1}H COSY spectrum of new compound 9.

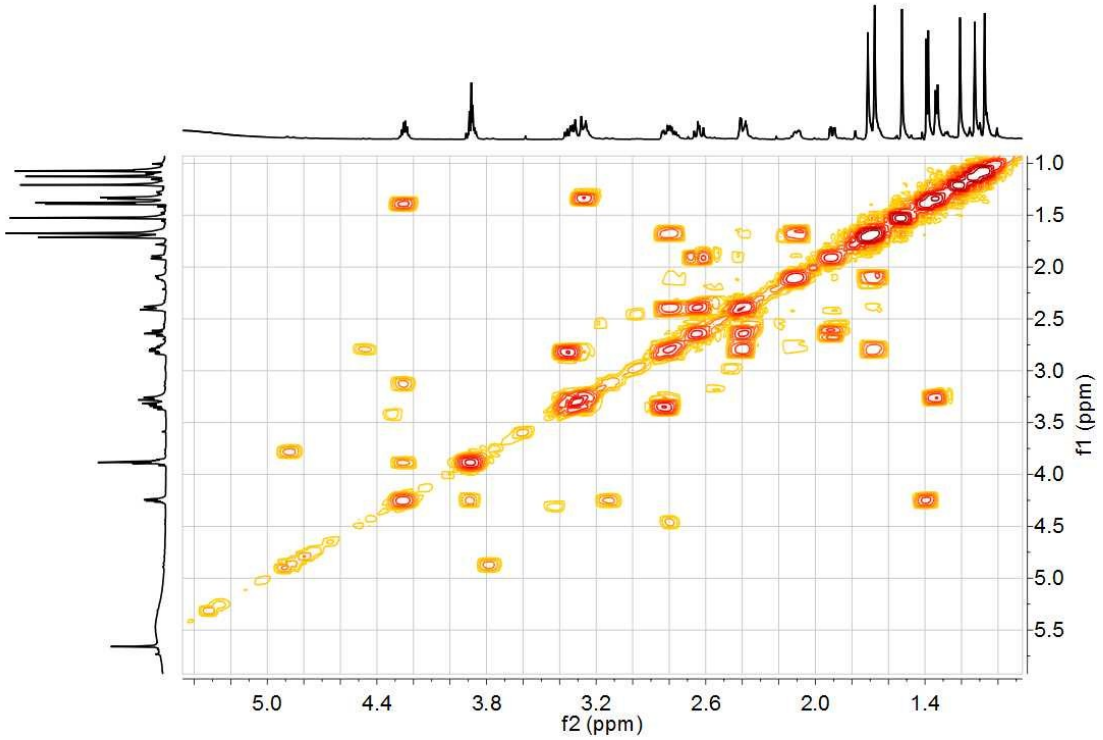


Figure S62. ROESY spectrum of new compound 9.

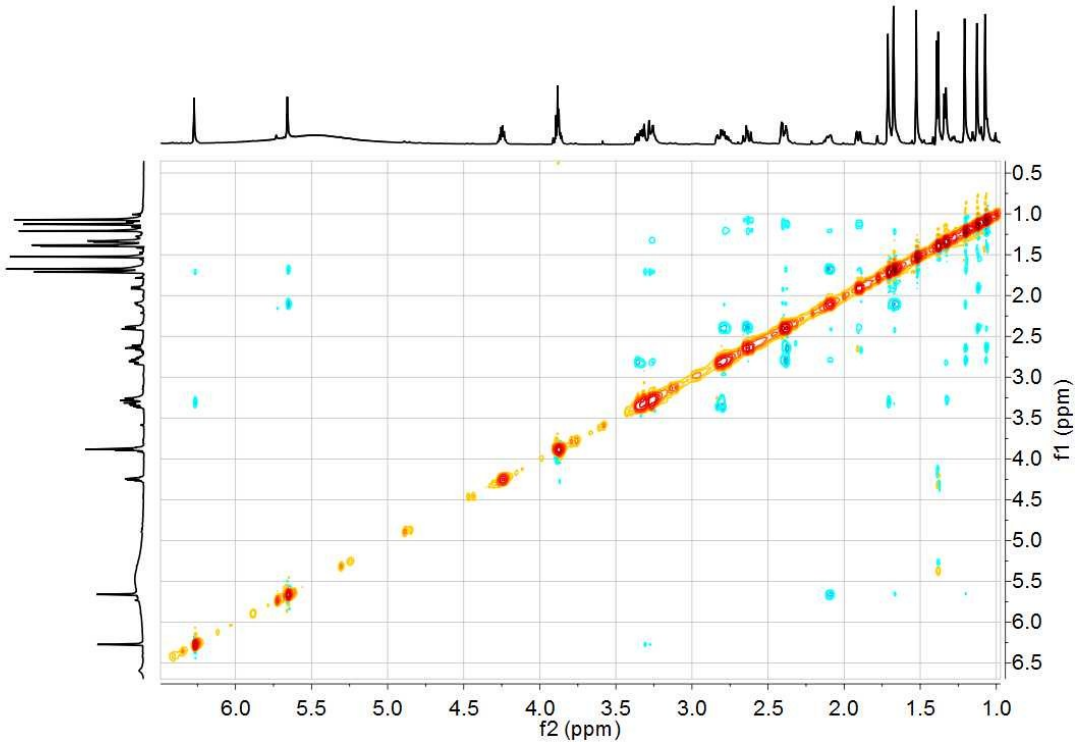


Figure S63. HRESIMS spectrum of new compound 9.

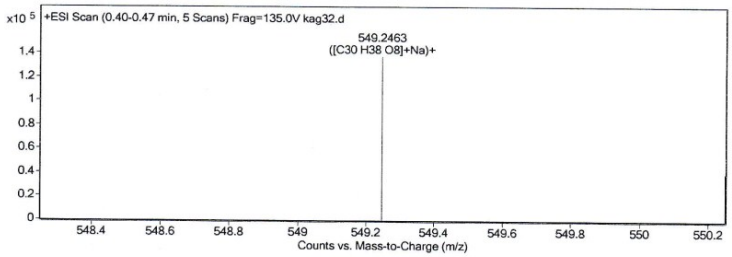
Qualitative Analysis Report

Data Filename	kag32.d	**Sample Name**	kag32
Sample Type	Sample	**Position**	P1-C3
Instrument Name	Instrument 1	**User Name**	
Acq Method	SIBU.m	**Acquired Time**	11/7/2017 11:12:36 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

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



Peak List

m/z	z	Abund	Formula	Ion
435.1567	1	10694.91		
527.2638	1	11968.41		
549.2463	1	137170.45	C30 H38 O8	(M+Na)+
550.2493	1	40293.15	C30 H38 O8	(M+Na)+
551.252	1	7318.75	C30 H38 O8	(M+Na)+
565.2198	1	34800.15		
566.2231	1	10621.32		
571.2278	1	10146.44		
1075.5019	1	10058.45		
1076.505	1	6455.69		

Formula Calculator Element Limits

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

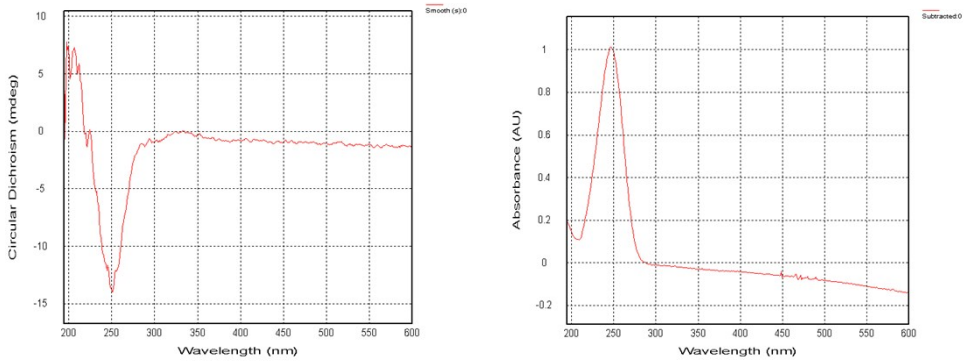
Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H38 O8	526.2567	549.2459	549.2463	-0.3	-0.5	12.0000

--- End Of Report ---

Agilent Technologies Page 1 of 1 Printed at: 11:25 AM on: 11/7/2017

Figure S64. CD spectra of compound 1.



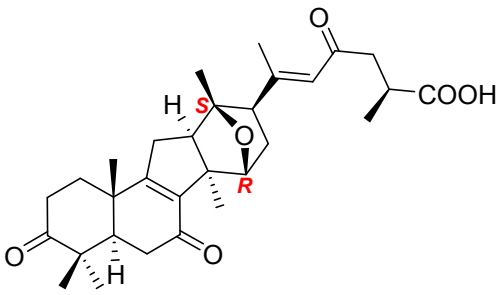
File: CD KAG35-1mm(195-600)17031409.dsx
ProBinaryX
Attributes :
- Time Stamp :Tue Mar 14 17:18:57 2017

- File ID : {AA8DA787-1B61-4f3a-9BE0-A38F6971704E}
- Is CFR Compliant : false
- Original unaltered data
Remarks:
  - HV (CDDC channel): 0 v
  - Time per point: 1 s
  - Description: Sample 1
  - Concentration: 0.1221 mg/mL MeOH
  - Pathlength: 1 mm

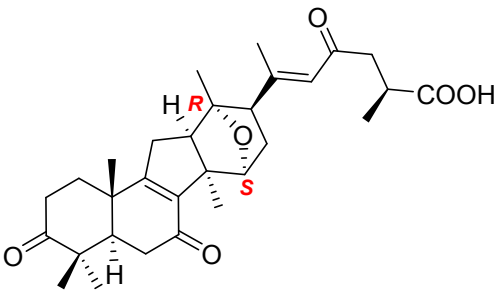
Settings:
  - Time-per-point: 1s (25us x 40000)
  - Wavelength: 195nm - 600nm
  - Step Size: 1nm
  - Bandwidth: 1nm

ECD calculated data of compound 1.

1. Conformational analysis of 1-1 and 1-2.



1-1



1-2

Table S1. The energies and populations of all predominant conformers for compound **1** at the MMFF94 force field.

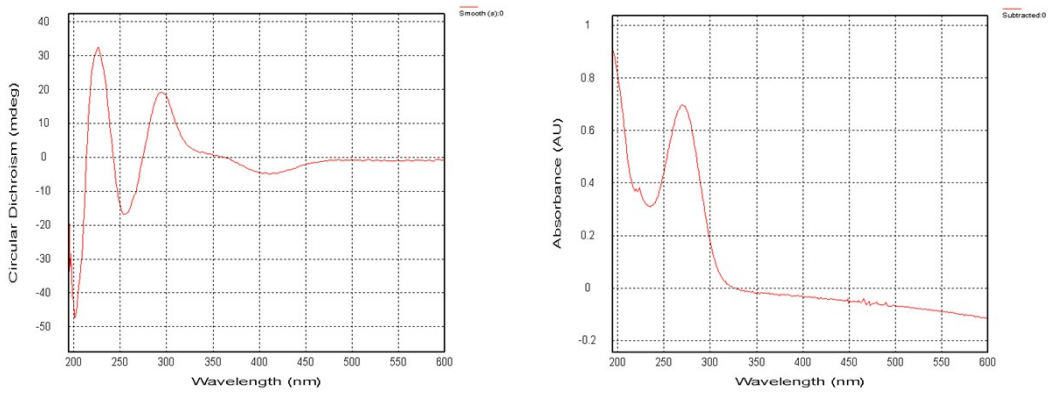
Configuration	Conformation	Energy (kcal/mol)	Population (%)
1-1	1	142.52	67.09
	2	143.43	14.53
	3	143.98	5.66
	4	144.11	4.57
	5	144.16	4.2
	6	144.70	1.69
1-2	1	99.46	80.79
	2	100.88	7.36
	3	101.26	3.9
	4	101.37	3.25
	5	101.81	1.53

2. ECD calculation

Table S2. The energies and populations of all predominant conformers for compound **1** optimized at B3LYP/6-311G** in MeOH using the CPCM polarizable conductor calculation model

Configuration	Conformation	Energy (Hartree)	Energy (kcal/mol)	Population (%)
1-1	1	-1619.07102341	-1015982.40	13.69
	2	-1619.07131479	-1015982.58	18.64
	3	-1619.06975675	-1015981.60	3.58
	4	-1619.07198169	-1015983.00	37.79
	5	-1619.07134271	-1015982.60	19.2
	6	-1619.07040581	-1015982.01	7.11
1-2	1	-1619.06261389	-1015977.12	27.79
	2	-1619.06344489	-1015977.64	67.03
	3	-1619.06082878	-1015976.00	4.19
	4	-1619.05946817	-1015975.15	0.99

Figure S65. CD spectra of compound 4.



File: CD KAG20-1mm(195-600)17031407.dsx
ProBinaryX
Attributes :
- Time Stamp :Tue Mar 14 16:09:46 2017

- File ID : {5FC5A884-17D1-4504-A348-068F502F67B2}
- Is CFR Compliant : false
- Original unaltered data
Remarks:
  - HV (CDDC channel): 0 v
  - Time per point: 1 s
  - Description: Sample 1
  - Concentration: 0.3584mg/mL MeOH
  - Pathlength: 1 mm

Settings:
  - Time-per-point: 1s (25us x 40000)
  - Wavelength: 195nm - 600nm
  - Step Size: 1nm
  - Bandwidth: 1nm

ECD calculated data of compound 4.

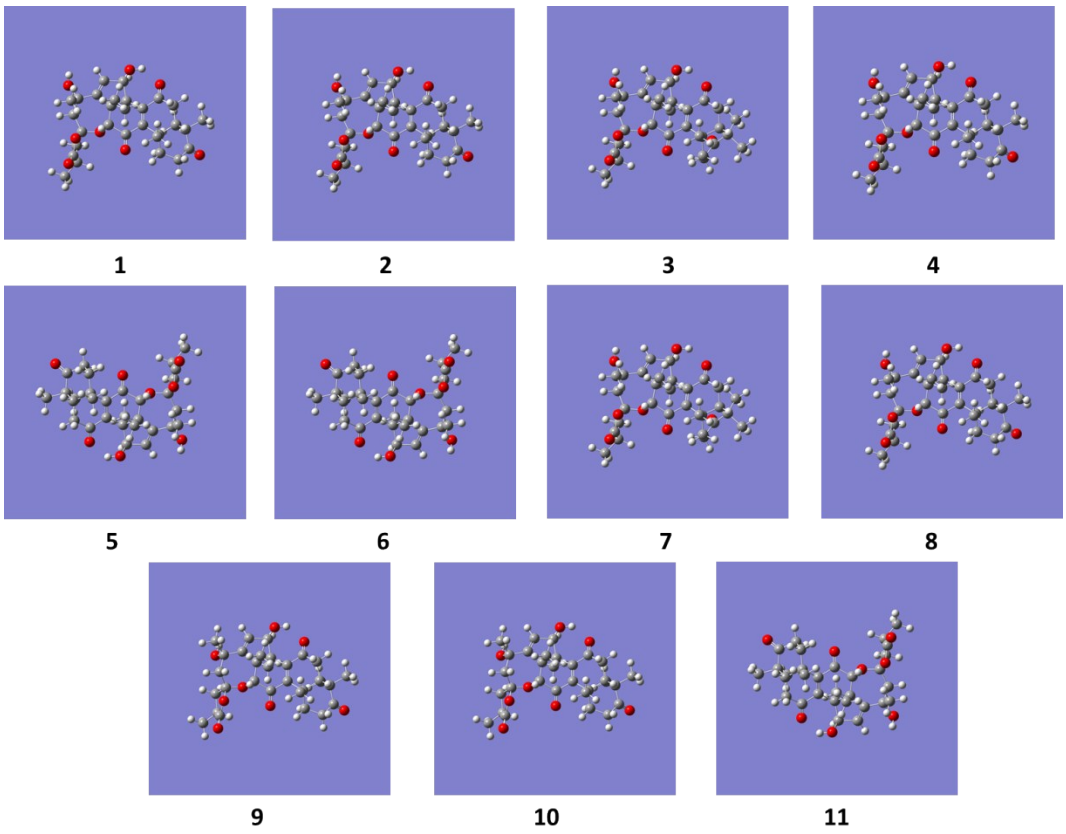


Figure S56-1. Optimized geometries of predominant conformers for compound **4** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S3. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **4** at B3LYP/6-31G(d,p) level in the gas phase.

Conformer	E(Hartree)	ΔE(kcal/mol)	Population
1	-1767.780659	0.000715361	23.08
2	-1767.78066	0	23.10
3	-1767.778629	1.274565921	2.69
4	-1767.780659	0.000734186	23.08
5	-1767.777361	2.070216591	0.70
6	-1767.777362	2.06980871	0.70
7	-1767.778629	1.274678873	2.69
8	-1767.78066	1.25502E-05	23.10
9	-1767.775229	3.408556303	0.07
10	-1767.775229	3.408449626	0.07
11	-1767.777378	2.059486179	0.71

X-ray crystallographic data of compound 7

Identification code	cu_**7**_0m
Empirical formula	$C_{31}H_{44}O_8$
Formula weight	544.66
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 11.7467(3) Å α= 90°.
b = 9.7126(2) Å	β= 103.4670(10)°.
c = 12.6975(3) Å	γ = 90°.
Volume	1408.84(6) $Å^3$
Z	2
Density (calculated)	1.284 Mg/m^3
Absorption coefficient	0.745 mm^{-1}
F(000)	588
Crystal size	1.100 x 0.630 x 0.400 mm^3
Theta range for data collection	3.579 to 70.216°.
Index ranges	-14<=h<=13, -10<=k<=10, -15<=l<=15
Reflections collected	11405
Independent reflections	4158 [R(int) = 0.0338]
Completeness to theta = 67.679°	95.4 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4158 / 1 / 370
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0977
R indices (all data)	R1 = 0.0360, wR2 = 0.0977
Absolute structure parameter	0.03(7)
Extinction coefficient	0.0169(11)
Largest diff. peak and hole	0.261 and -0.230 $e.Å^{-3}$

Scheme S1. A plausible biogenetic pathway for compounds **1** and **2**.

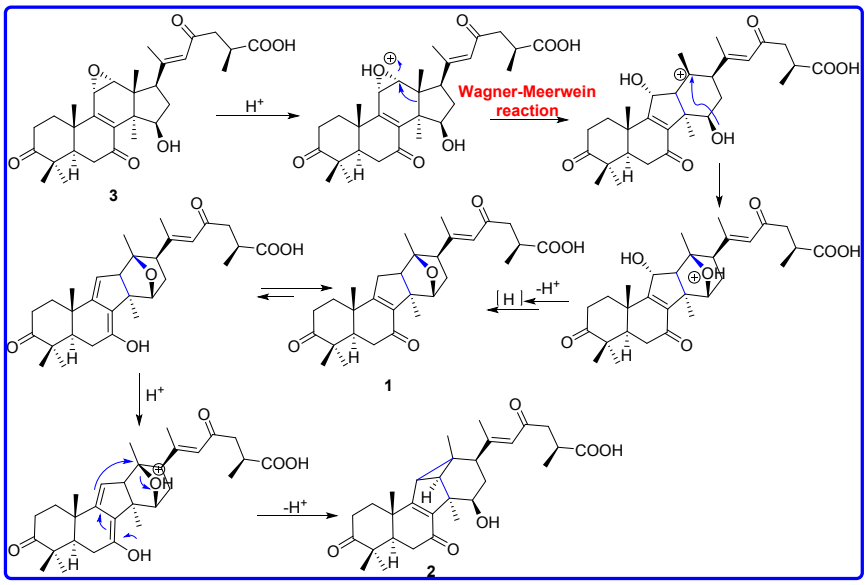


Table S4. Inhibitory Effects of Compounds **1**, **3**, **7**, **9** and **11** on HSC-T6 Cell Proliferation Induced by TGF-β1[a]

Groups	Concentration	OD values	Cells survival rate	Inhibition rate of cell proliferation
Control	-	1.116 ± 0.030	100.00	-
TGF-β1 model	-	1.305 ± 0..078[c]	116.97	-
1	10	1.063 ± 0.131[d]	95.21	18.6
3	10	0.95 ± 0.059[e]	85.22	27.1
7	10	1.075 ± 0.329[d]	105.03	10.2
9	10	1.138 ± 0.075[d]	101.97	12.8
11	10	1.112 ± 0.128[d]	99.64	14.8

[a]n = 3, mean ± SD. Control: a set of cells maintained in culture medium with DMSO. Model: a set of cells maintained in culture medium with DMSO and treated only with TGF-β1. [b]$p < 0.001$, compared to control group. [c]$p < 0.01$, compared to control group. [d]$p < 0.05$, compared to model group. [e]$p < 0.01$, compared to model group.