Supporting Information for

Unusual Pyridine-Containing, *Bisnor*- (C_{23}), *Tetranor*- (C_{21}) and *Pentanor*- (C_{20}) Sesterterpenoids from Tebitan *Leucosceptrum canum*

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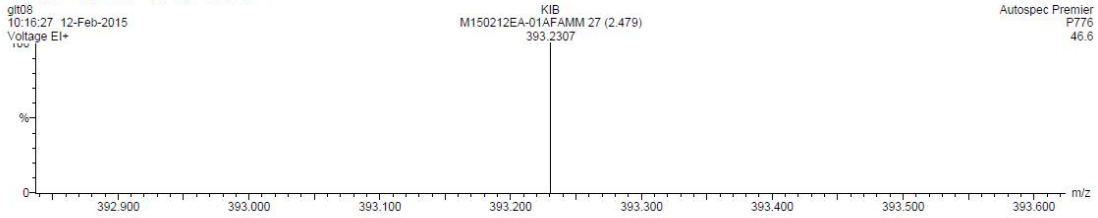
Figure S1. HREIMS of compound **1**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 18.0 mDa / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 1-1 O: 2-4



Minimum:				-10.0		
Maximum:		18.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
393.2307	393.2304	0.3	0.8	11.0	5546041.0	C25 H31 N O3

Figure S2. ^{1}H NMR spectrum of compound **1** in acetone-d_6 (400 MHz)

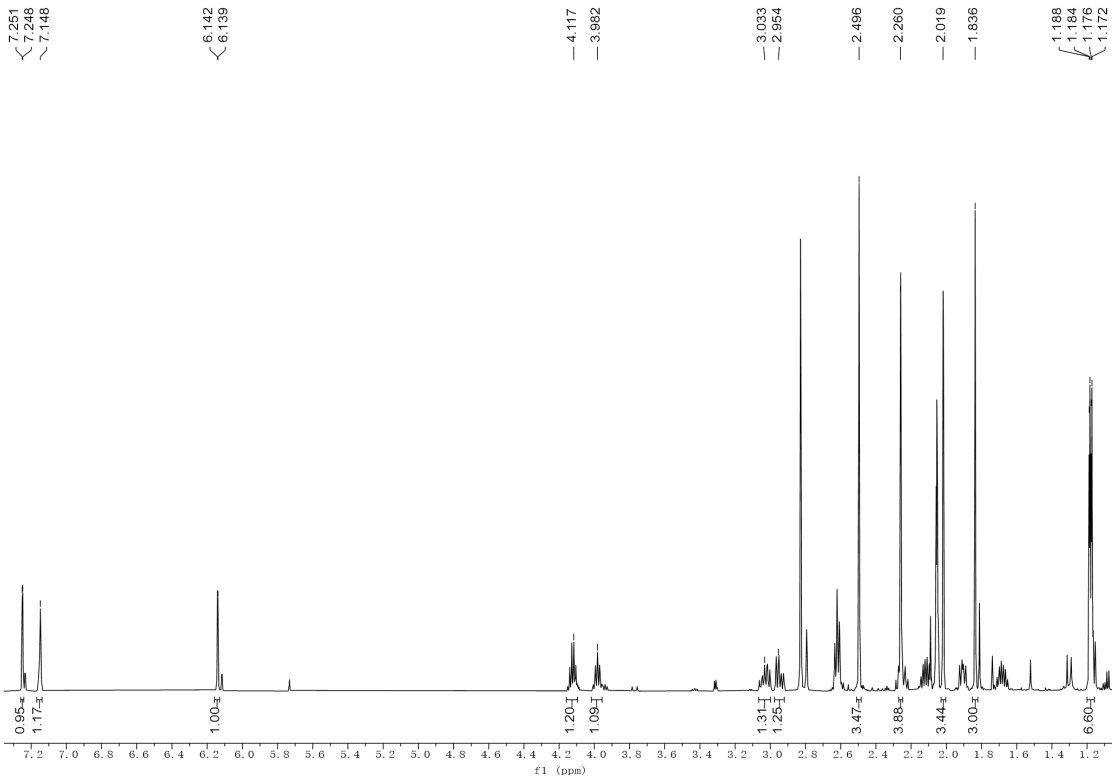


Figure S3. ^{13}C NMR (DEPT) spectrum of compound **1** in acetone-d_6 (100 MHz)

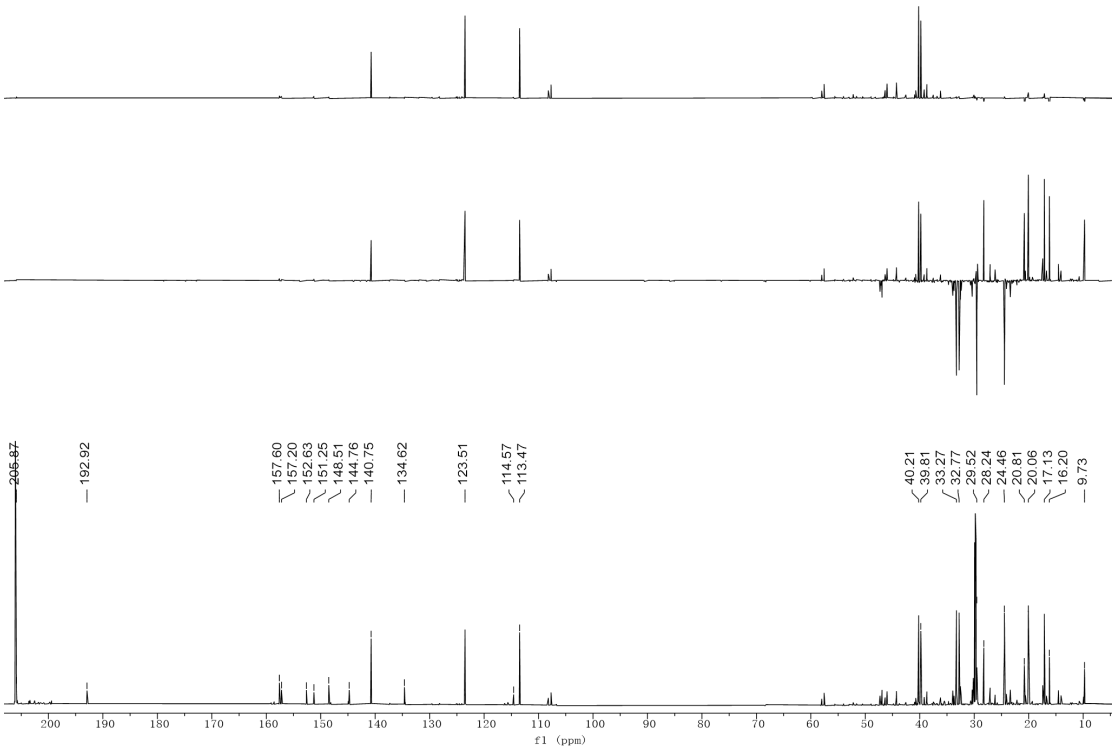


Figure S4. ^{1}H-^{1}H COSY spectrum of compound **1** in acetone-d_6

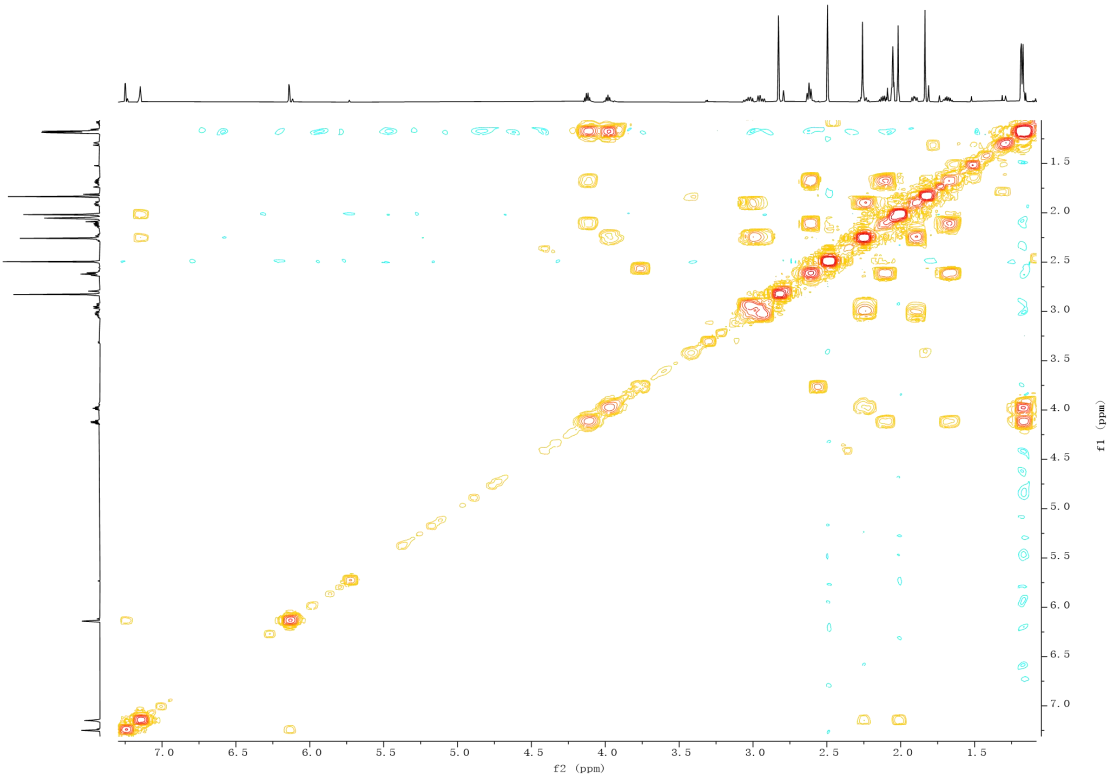


Figure S5. HSQC spectrum of compound **1** in acetone-d_6

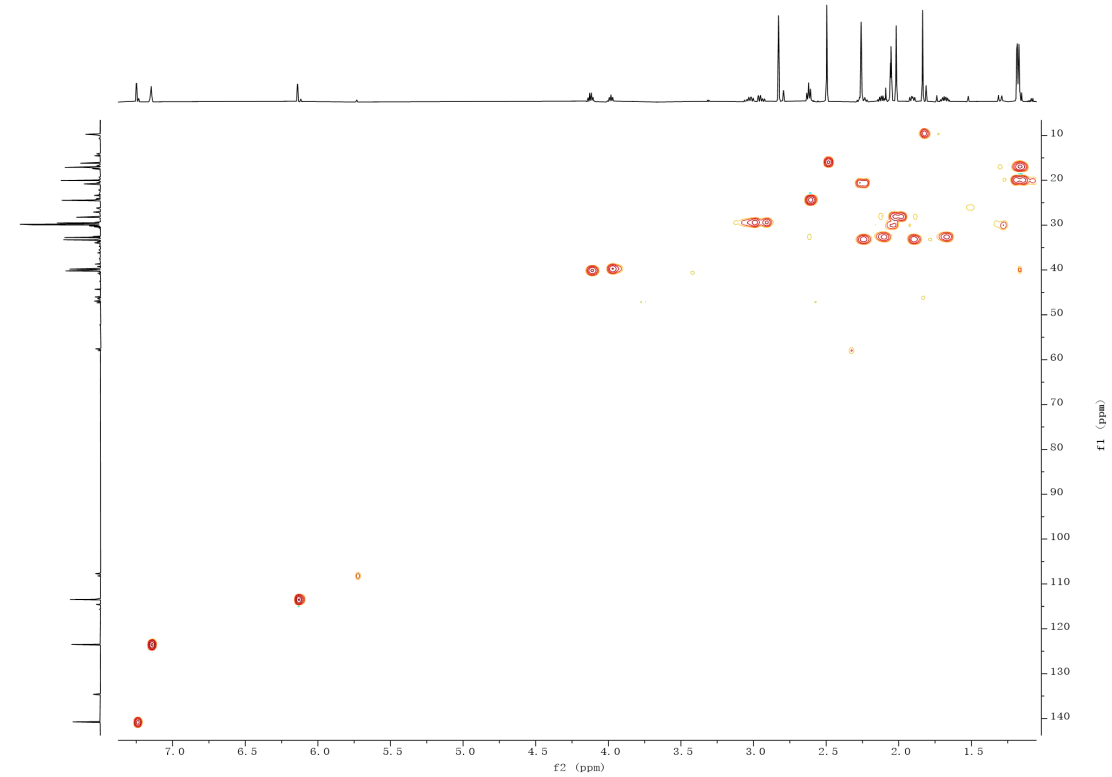


Figure S6. HMBC spectrum of compound **1** in acetone-d_6

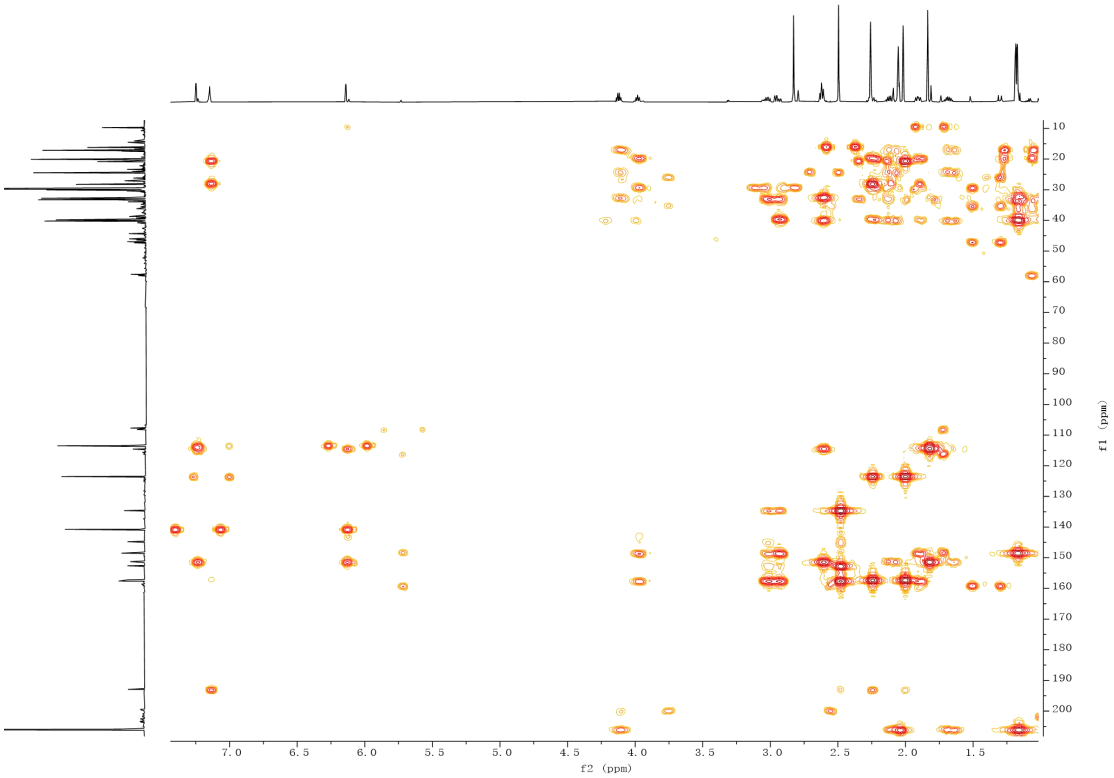


Figure S7. ROESY spectrum of compound **1** in acetone-d_6

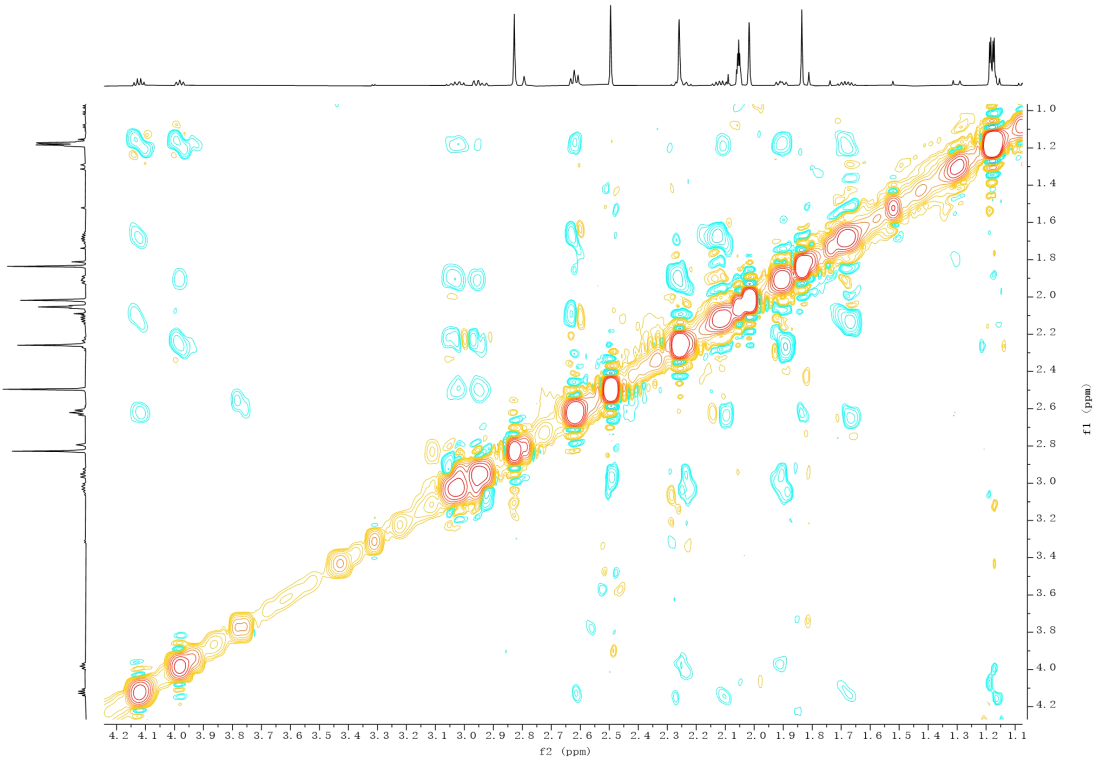


Figure S8. HRESIMS of compound **2**

Qualitative Analysis Report

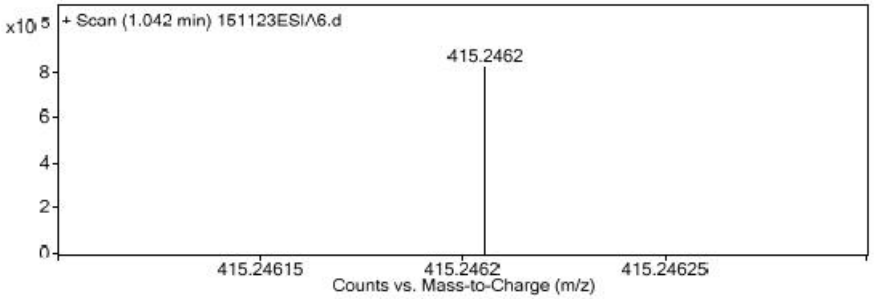
Data Filename	151123ESIA6.d	**Sample Name**	glt29c
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	11/23/2015 1:44:57 PM
IRM Calibration Status	Success	**DA Method**	ESI.m
Comment			

Sample Group **Info.**

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

User Spectra

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



Peak List

m/z	z	Abund	Formula	Ion
415.2462	1	823091.63	C23 H36 Na O5	M+
416.2492	1	183639.08	C23 H36 Na O5	M+
431.2205	1	37239.41		
515.261	1	31558		
807.5026	1	1291637.25		
808.5064	1	650595.88		
809.5086	1	176389.2		
810.5102	1	28470.76		
823.4776	1	28575.39		
845.4804	1	27896.14		

Formula Calculator Element Limits

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

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C23 H36 Na O5	415.2460	415.2455	415.2462	-0.6	-1.4	5.5000

Figure S9. ^{1}H NMR spectrum of compound **2** in acetone-d_6 (400 MHz)

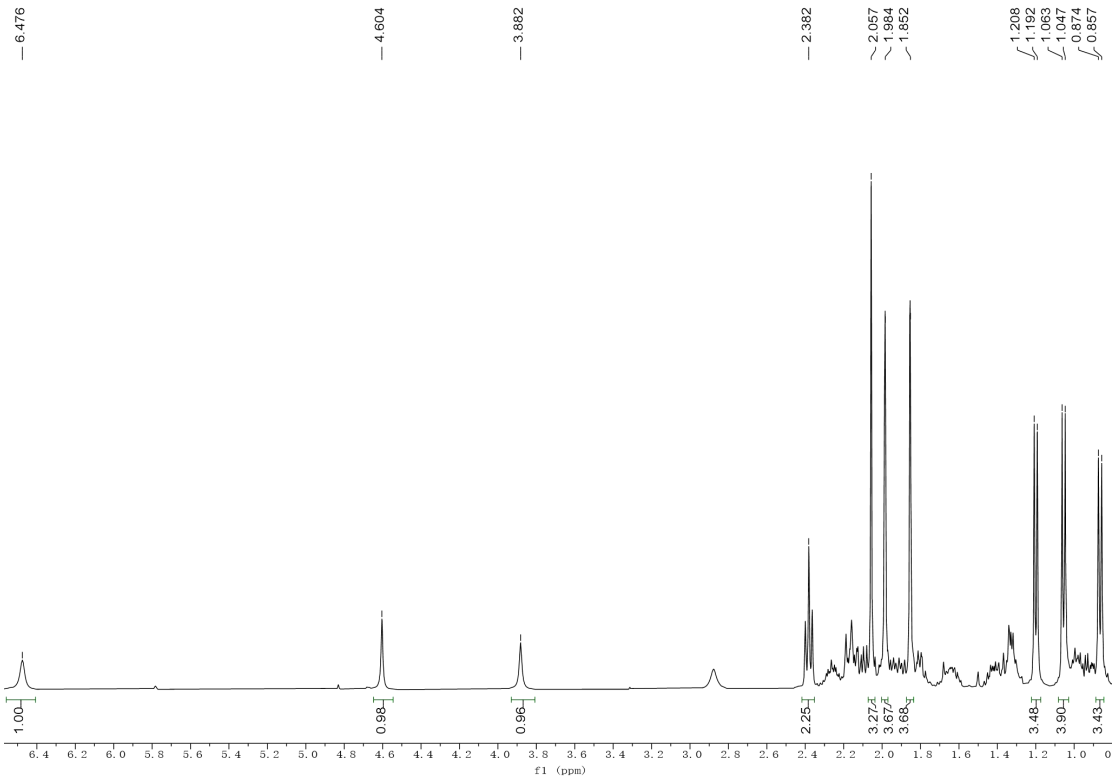


Figure S10. ^{13}C NMR (DEPT) spectrum of compound **2** in acetone-d_6 (100 MHz)

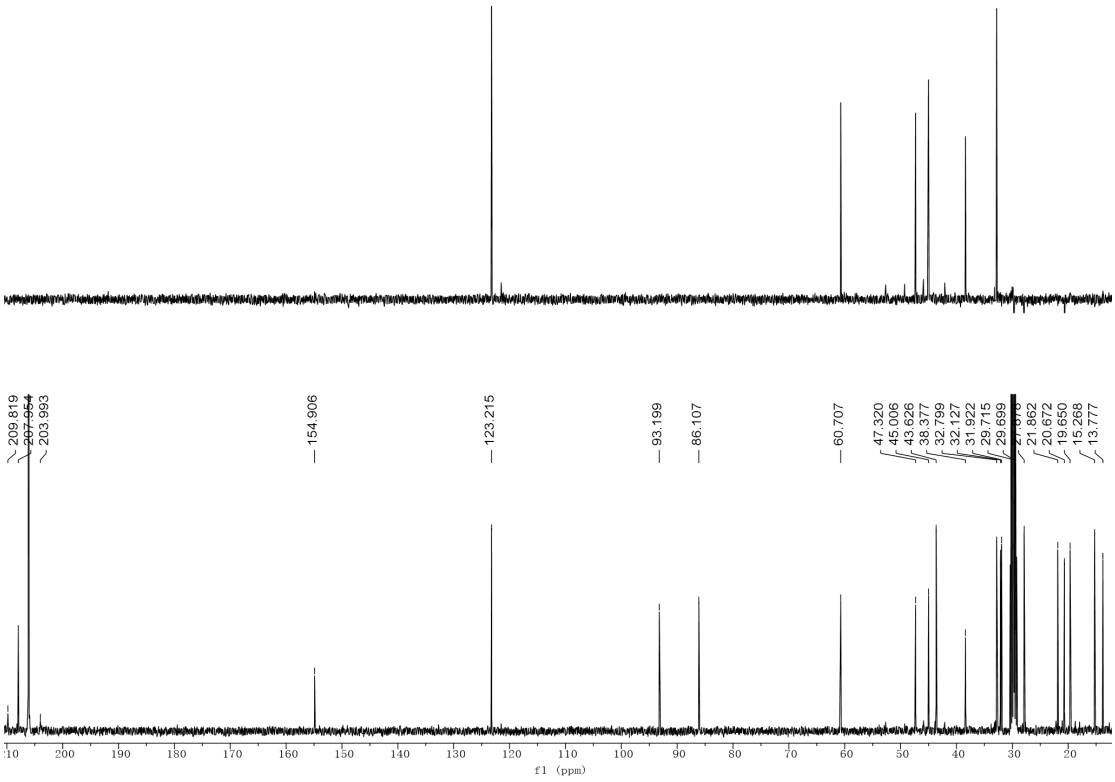


Figure S11. ^{1}H-^{1}H COSY spectrum of compound **2** in acetone-d_6

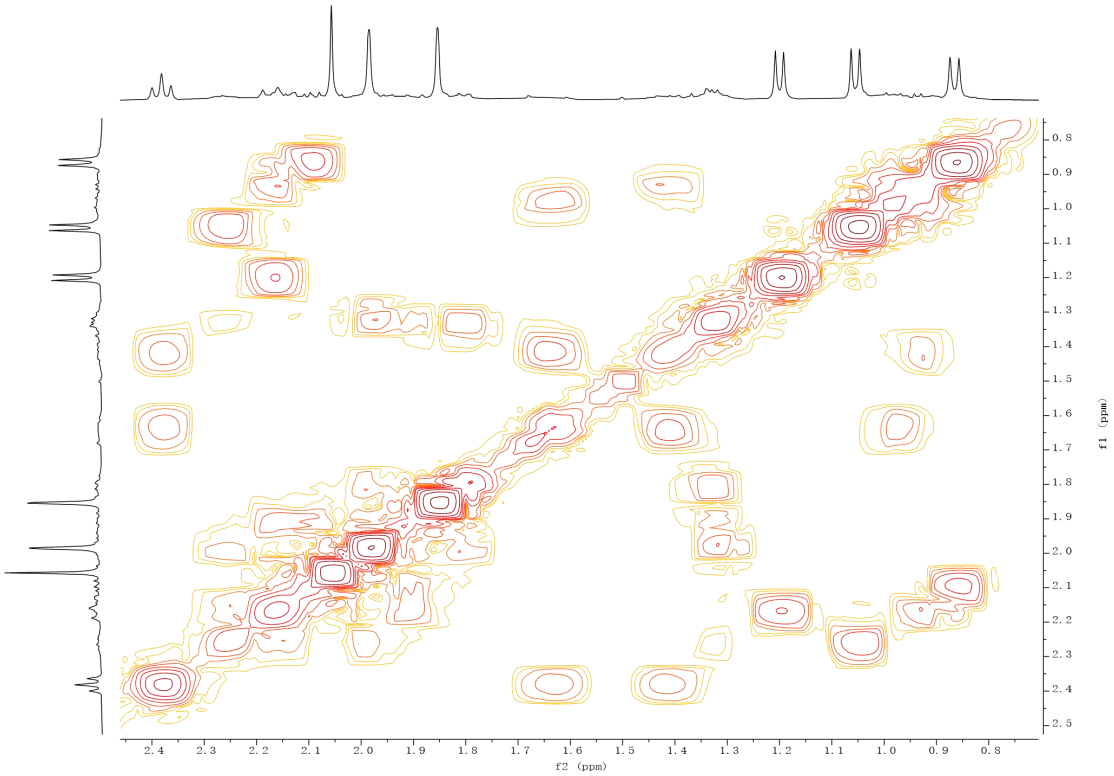


Figure S12. HSQC spectrum of compound **2** in acetone-d_6

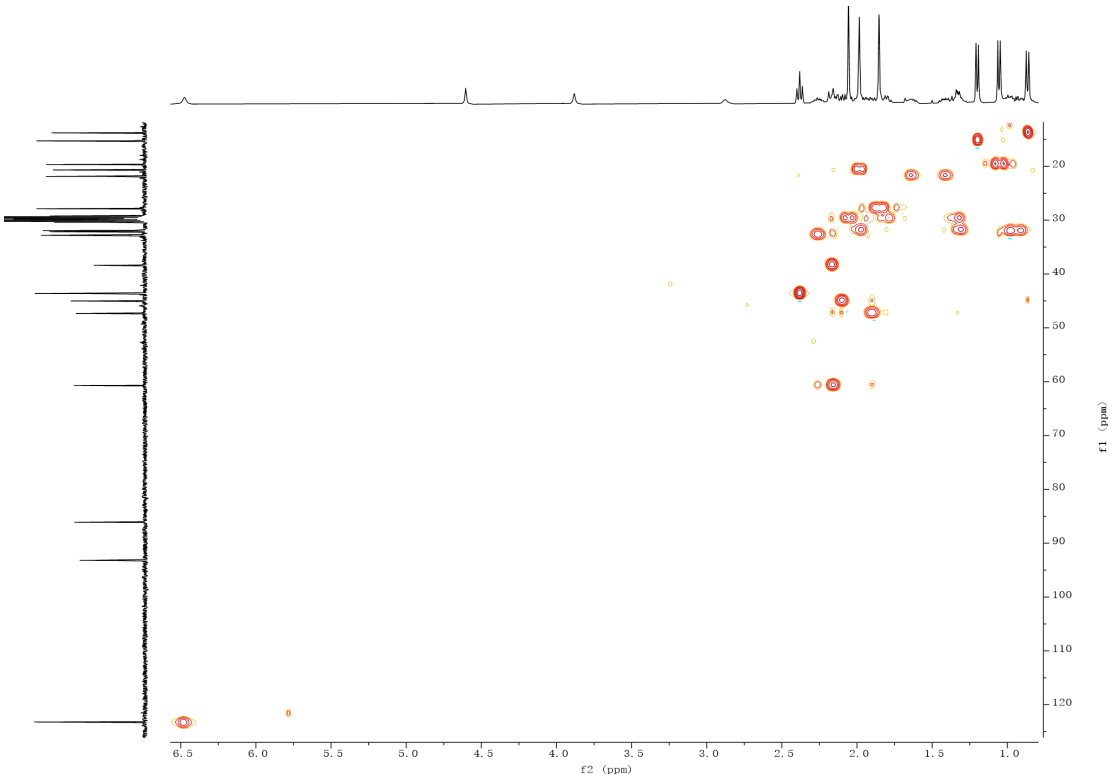


Figure S13. HMBC spectrum of compound **2** in acetone-d_6

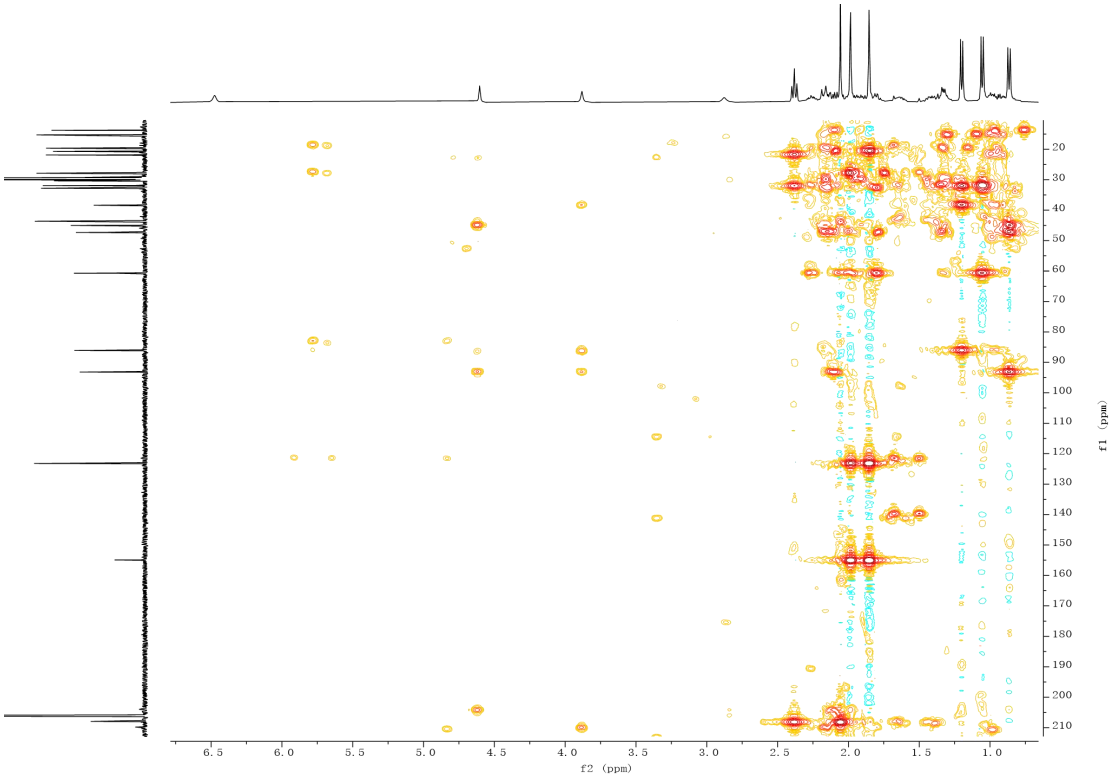


Figure S14. ROESY spectrum of compound **2** in acetone-d_6

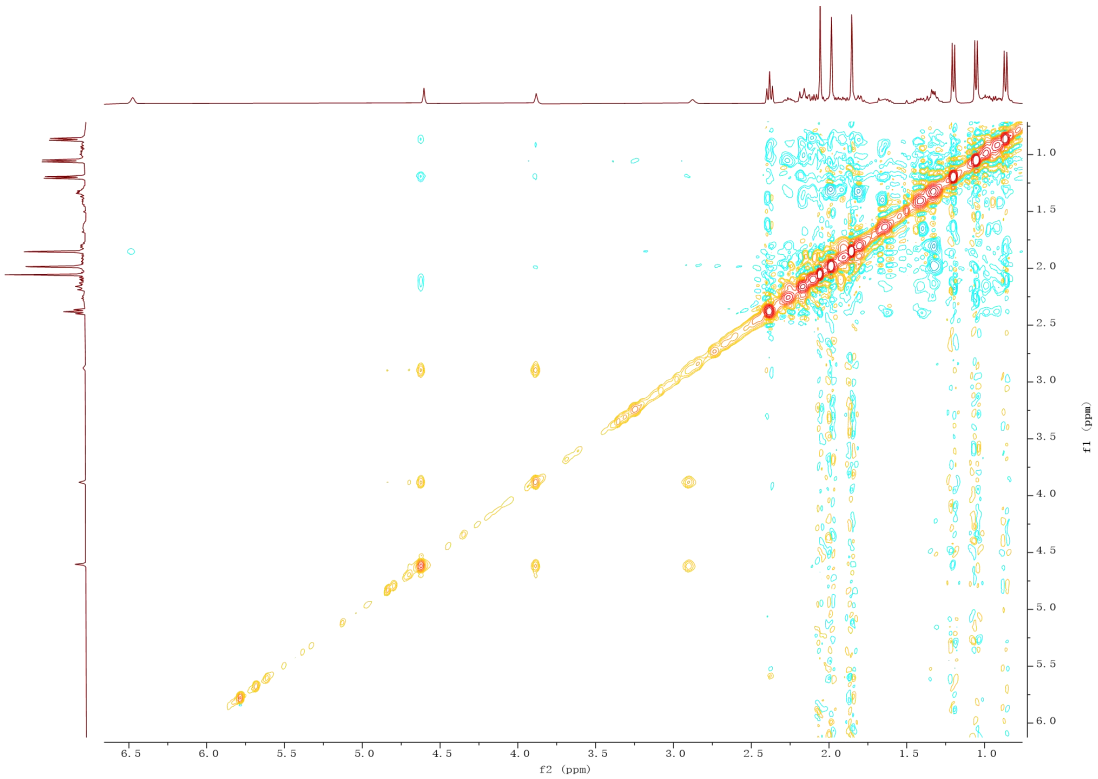
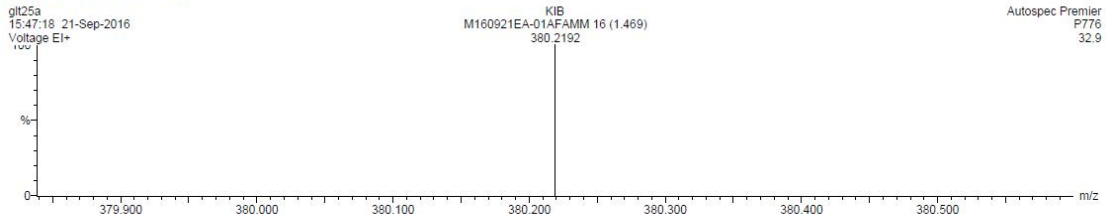


Figure S15. HREIMS of compound **3**

Elemental Composition Report **Page 1**

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

Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 5-7



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
380.2192	380.2199	-0.7	-1.8	6.0	5546033.5	C21 H32 O6

Figure S16. ^{1}H NMR spectrum of compound **3** in acetone-d_6 (400 MHz)

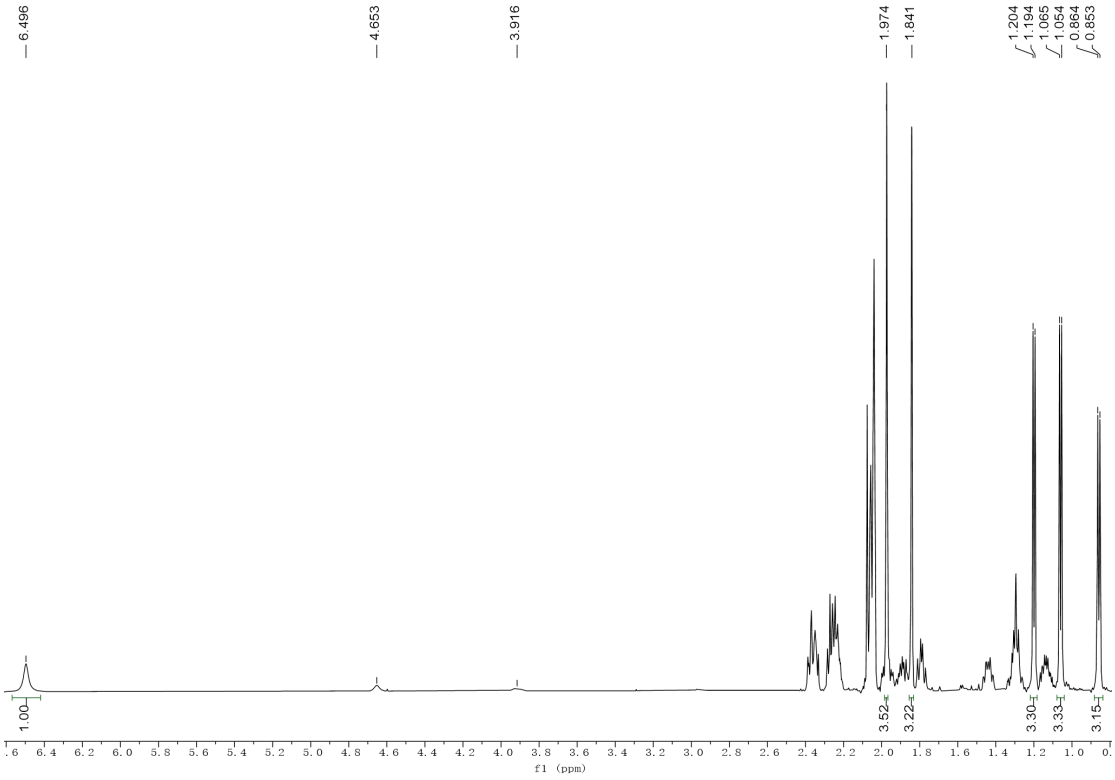


Figure S17. ^{13}C NMR (DEPT) spectrum of compound **3** in acetone-d_6 (100 MHz)

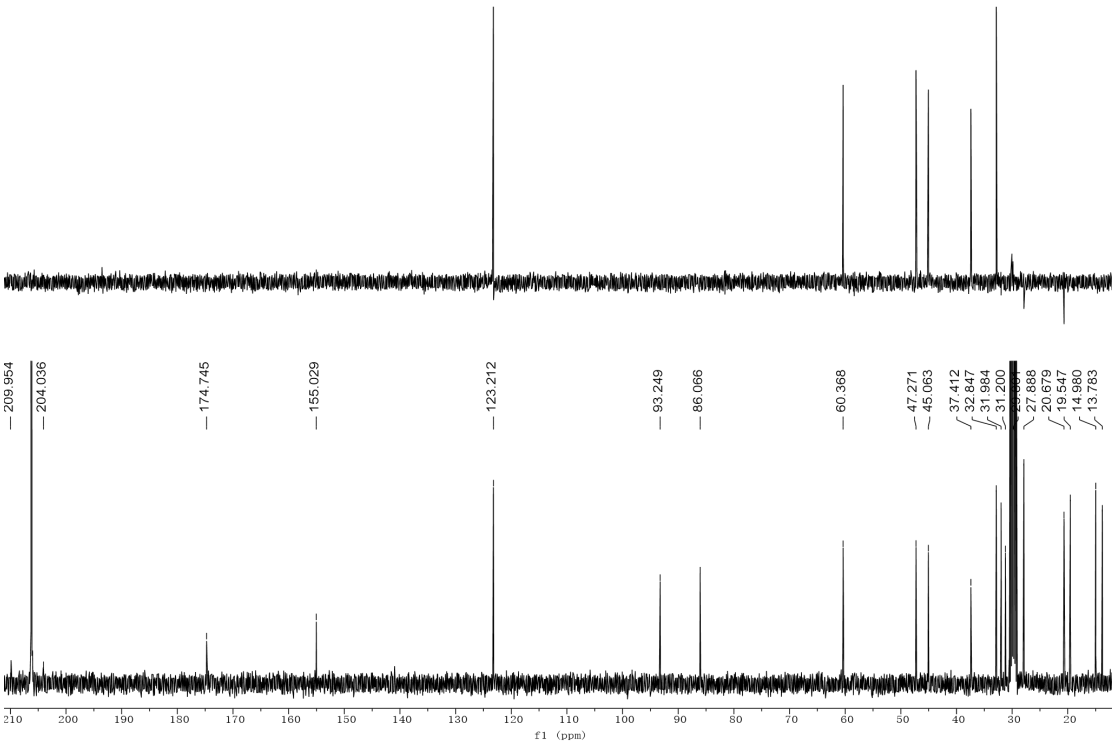


Figure S18. ^{1}H-^{1}H COSY spectrum of compound **3** in acetone-d_6

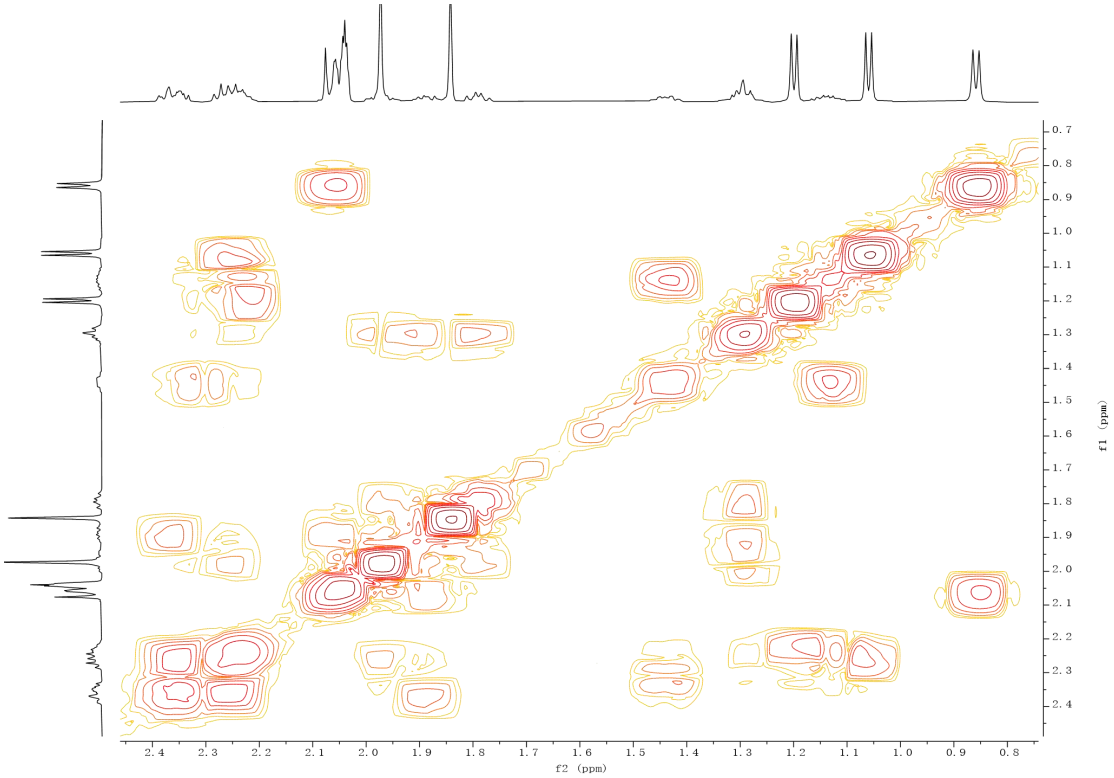


Figure S19. HSQC spectrum of compound **3** in acetone-d_6

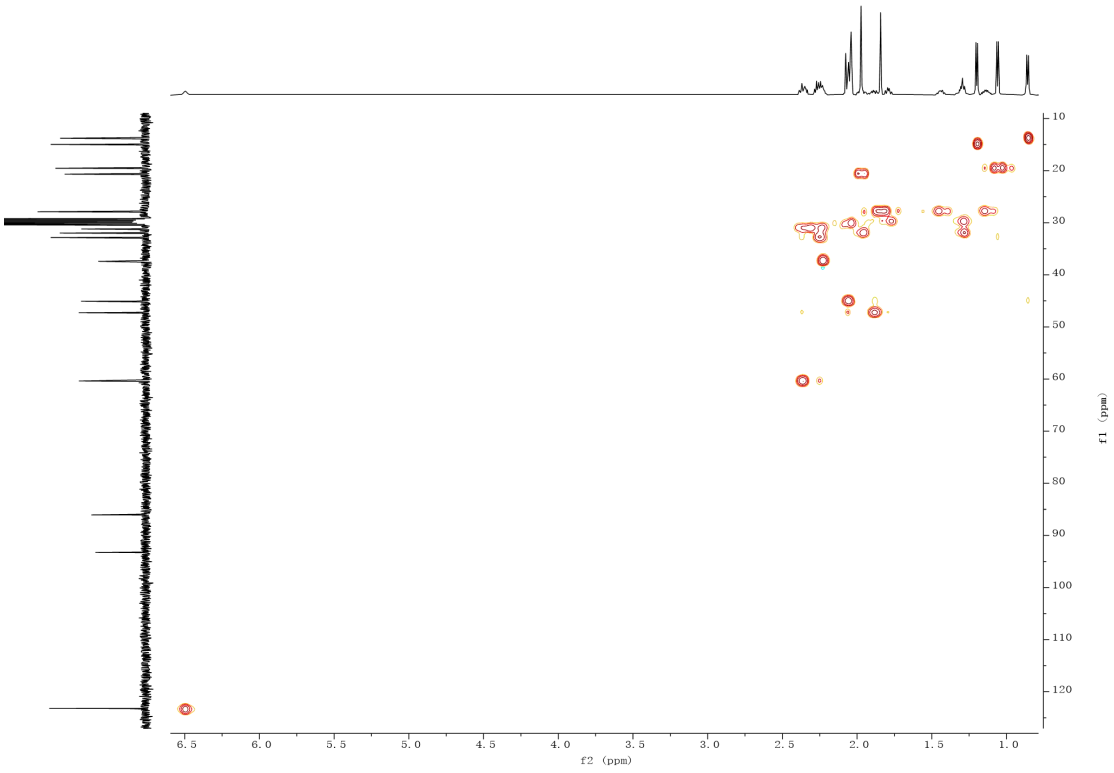


Figure S20. HMBC spectrum of compound **3** in acetone-d_6

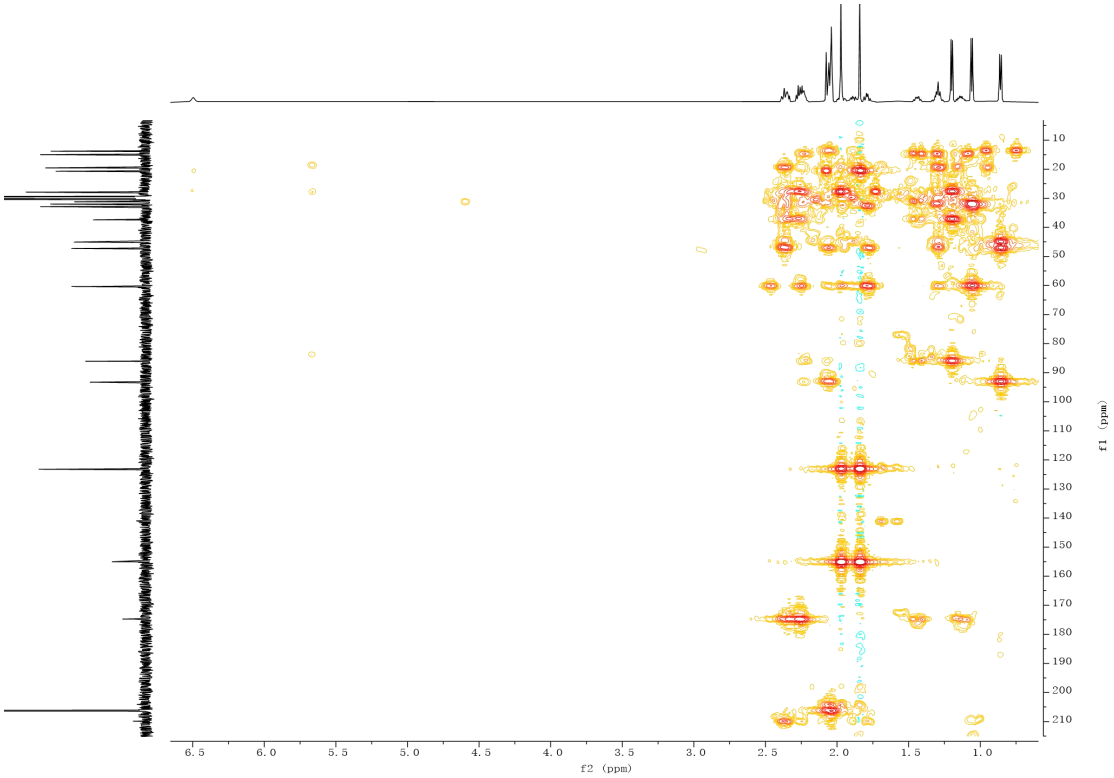


Figure S21. ROESY spectrum of compound **3** in acetone-d_6

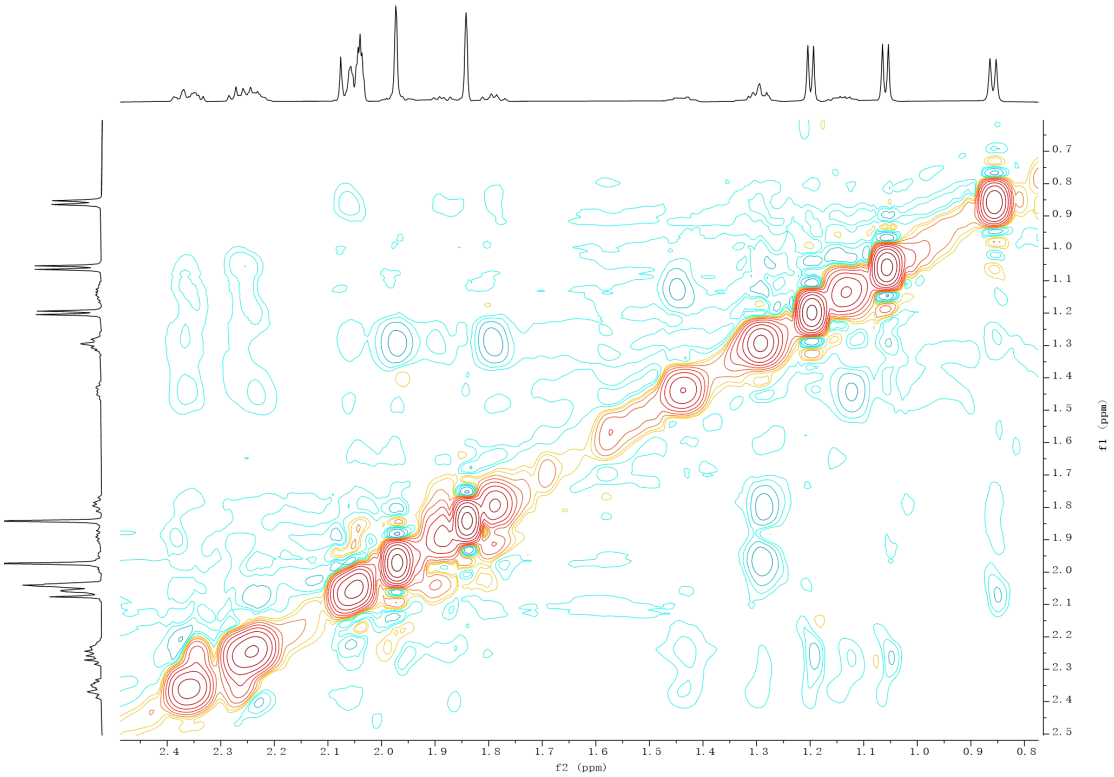


Figure S22. HREIMS of compound **4**

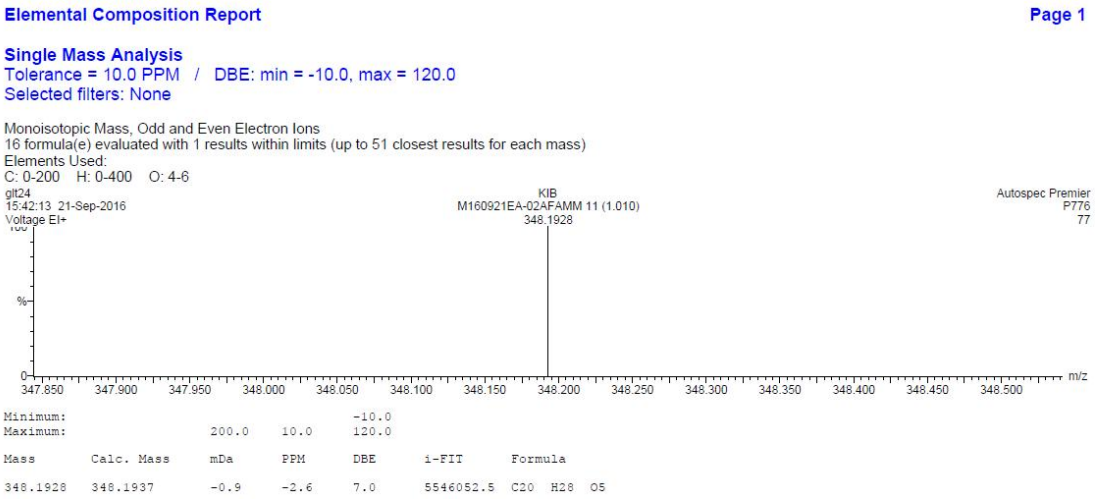


Figure S23. ^{1}H NMR spectrum of compound **4** in acetone-d_6 (400 MHz)

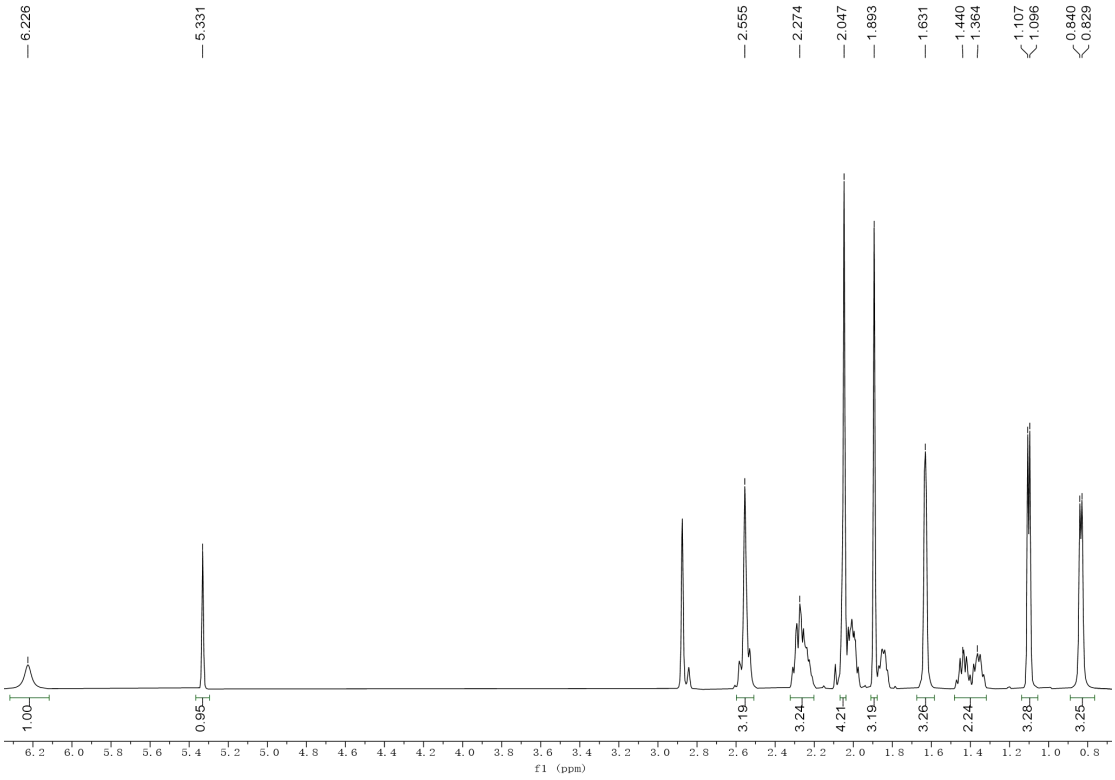


Figure S24. ^{13}C NMR (DEPT) spectrum of compound **4** in acetone-d_6 (100 MHz)

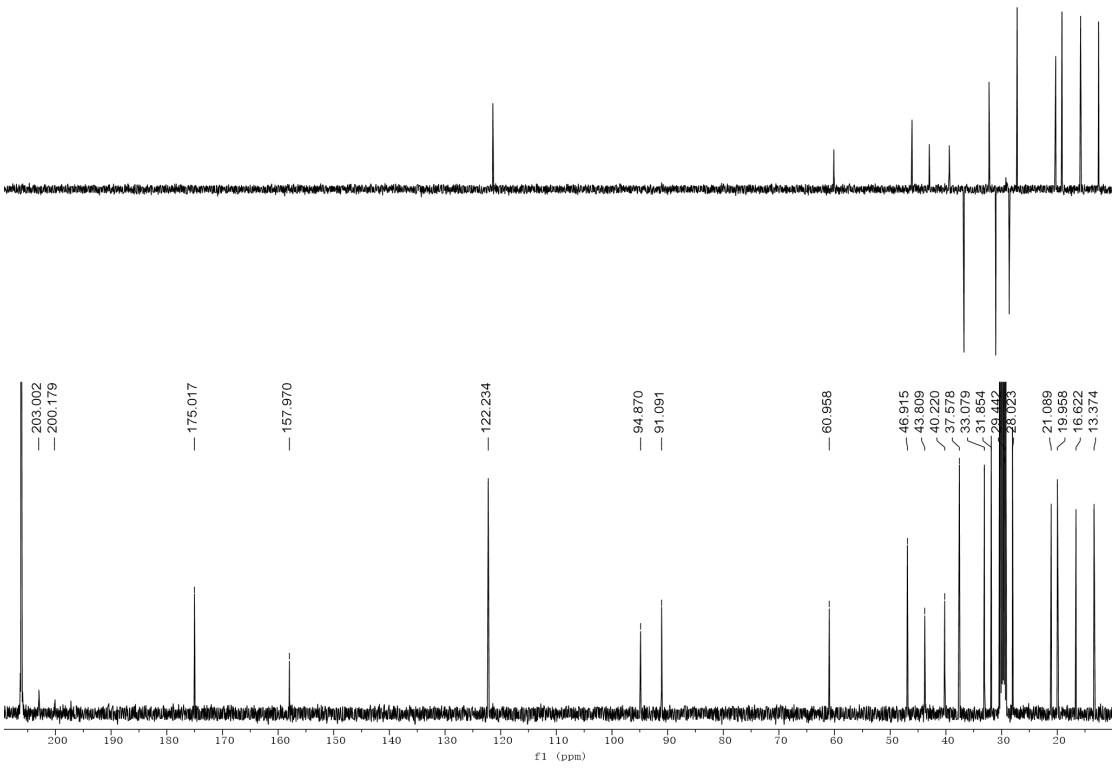


Figure S25. ^{1}H-^{1}H COSY spectrum of compound **4** in acetone-d_6

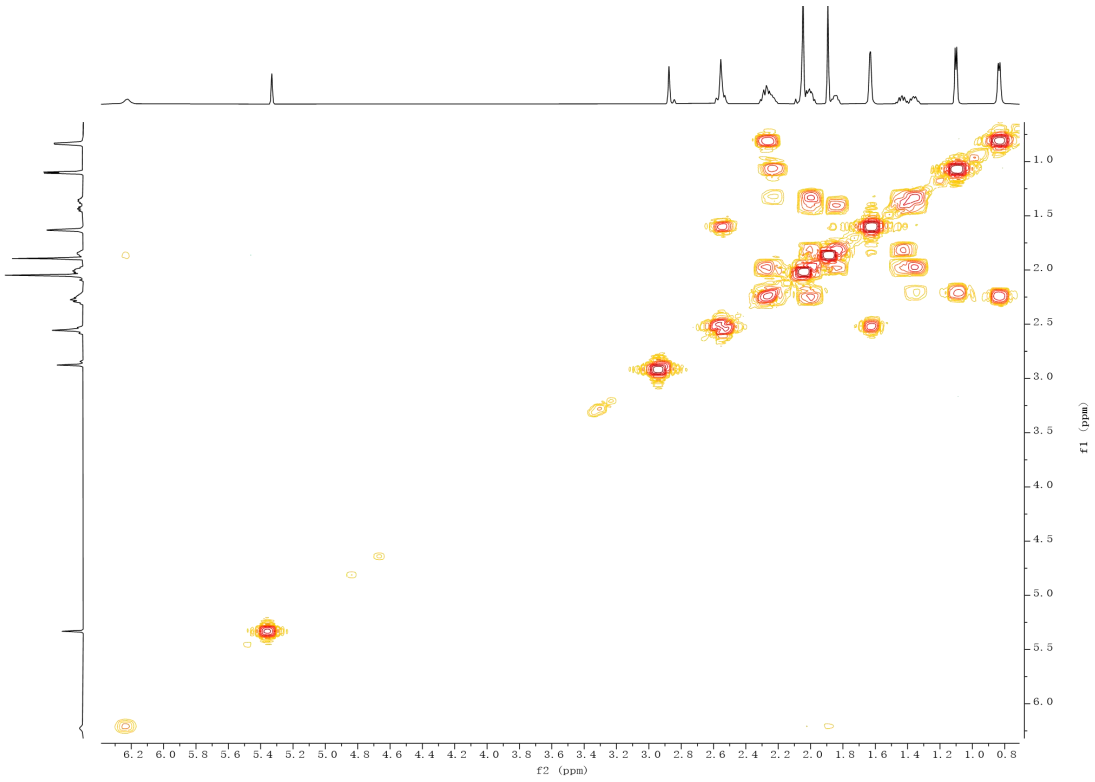


Figure S26. HSQC spectrum of compound **4** in acetone-d_6

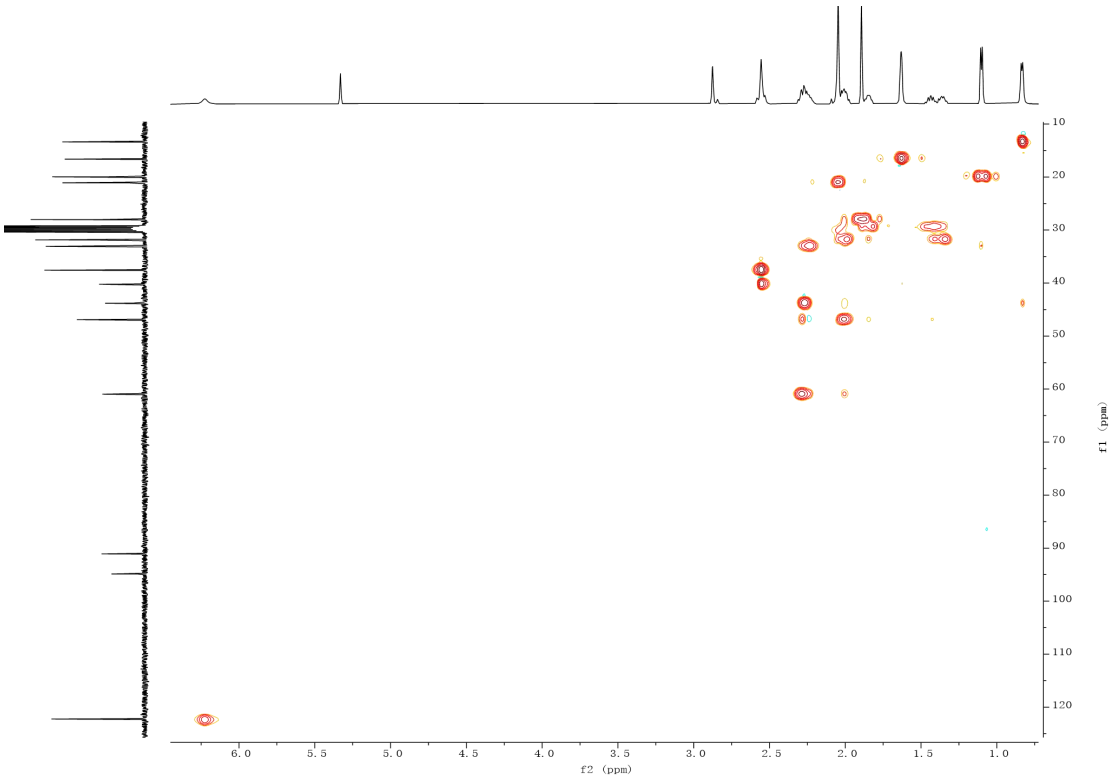


Figure S27. HMBC spectrum of compound **4** in acetone-d_6

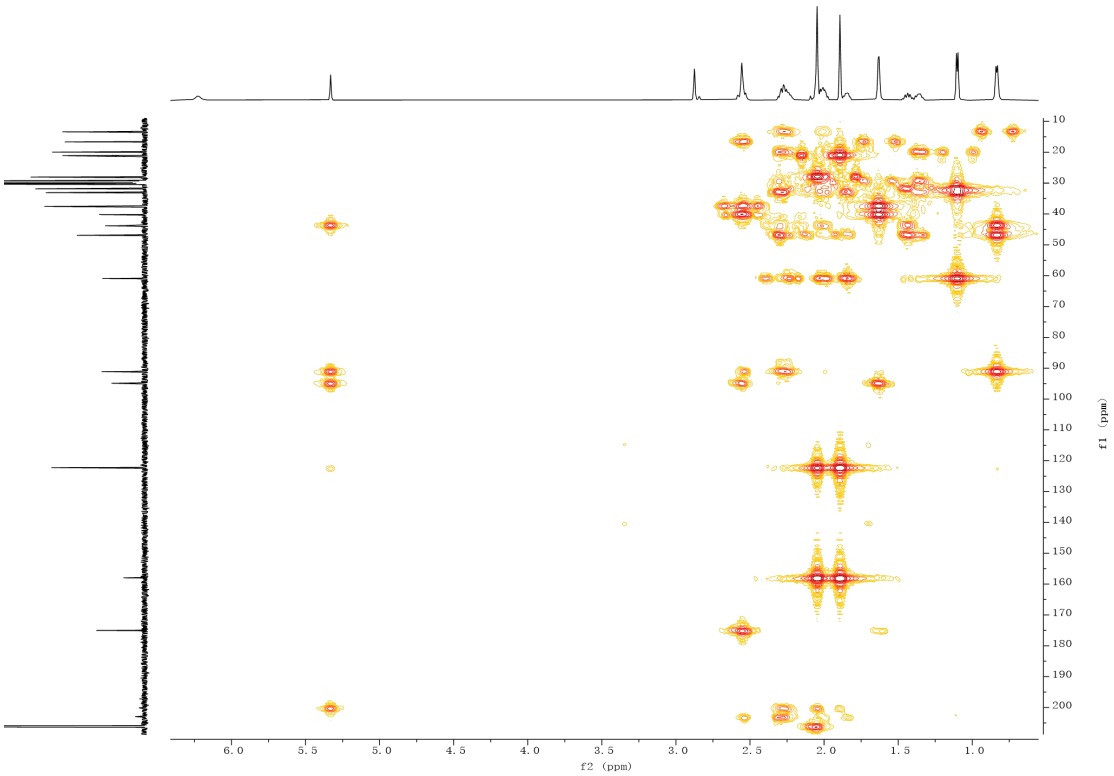


Figure S28. ROESY spectrum of compound **4** in acetone-d_6

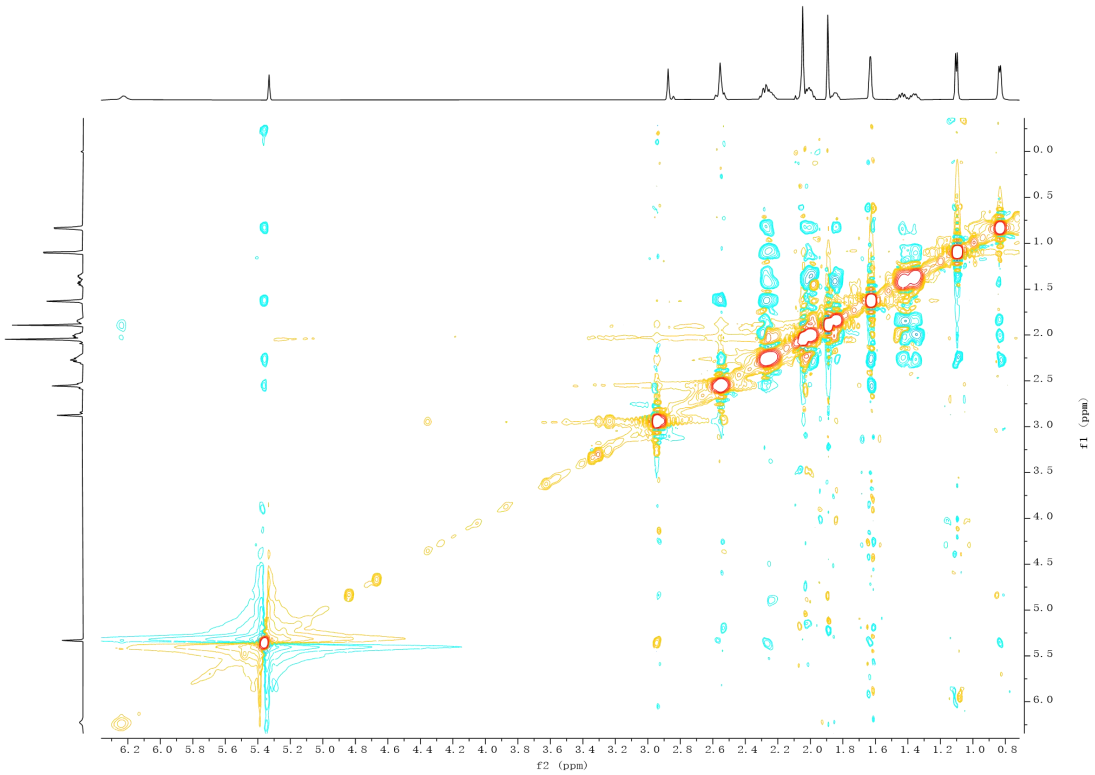


Figure S29. HRESIMS of compound **5/6**

Qualitative Analysis Report

Data Filename	160923ESIA2.d	**Sample Name**	glt27
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESI.m	**Acquired Time**	9/23/2016 9:29:52 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
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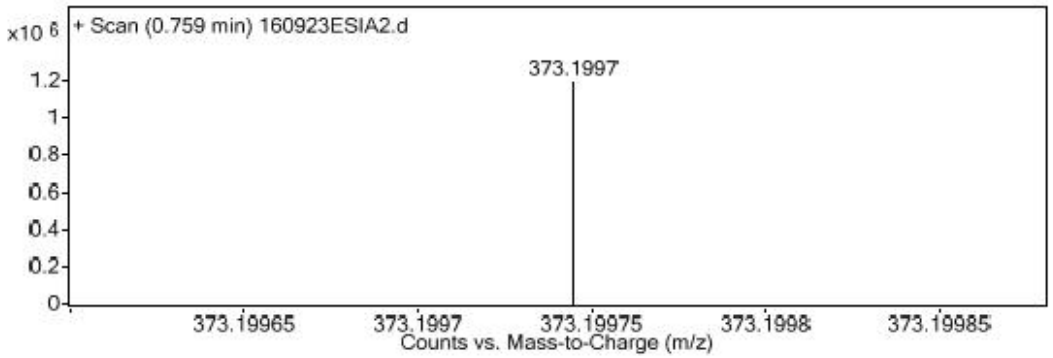

Peak List

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373.1997	1	1194207.75	C20 H30 Na O5	M+
374.2039	1	320892.66	C20 H30 Na O5	M+
718.4536	1	165897.5		
723.4085	1	2584483.75		
724.413	1	1541276.5		
725.4176	1	493923.09		
726.4205	1	102351.91		
1209.5924	1	143698.88		
1210.5968	1	129251.21		

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
C20 H30 Na O5	373.1991	373.1997	-0.6	1.6	5.5

Figure S30. ^{1}H NMR spectrum of compound **5**/**6** in acetone-d_6 (400 MHz)

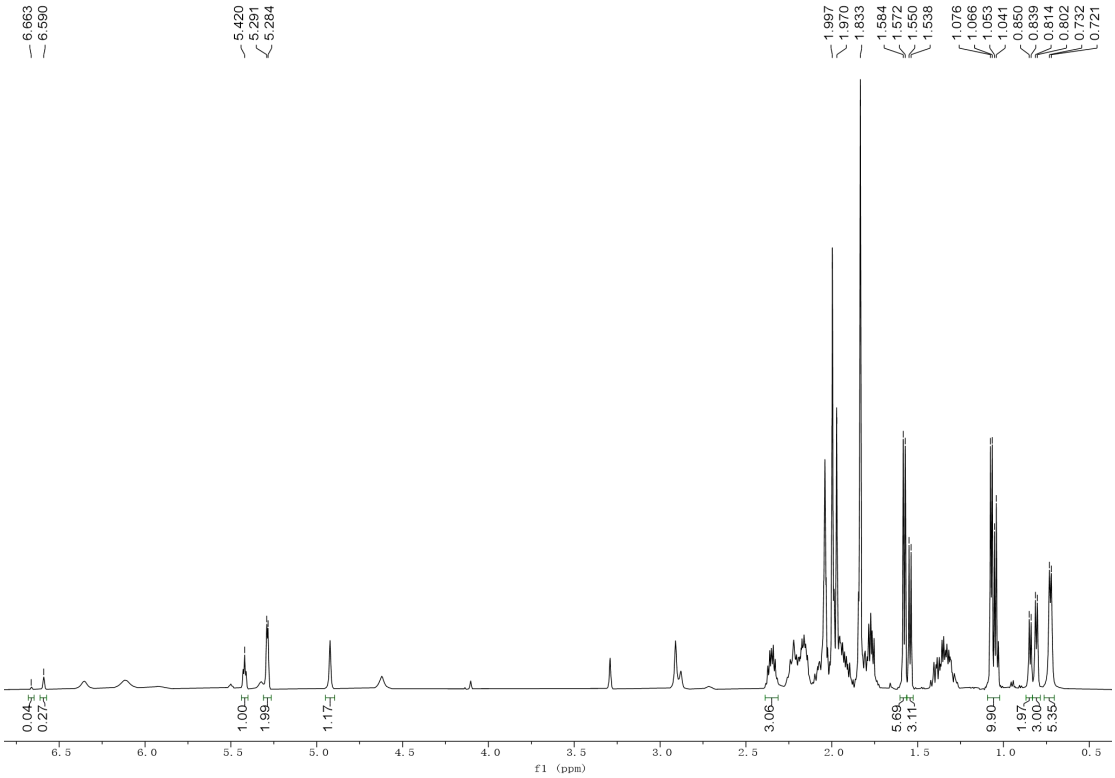


Figure S31. ^{13}C NMR (DEPT) spectrum of compound **5**/**6** in acetone-d_6 (100 MHz)

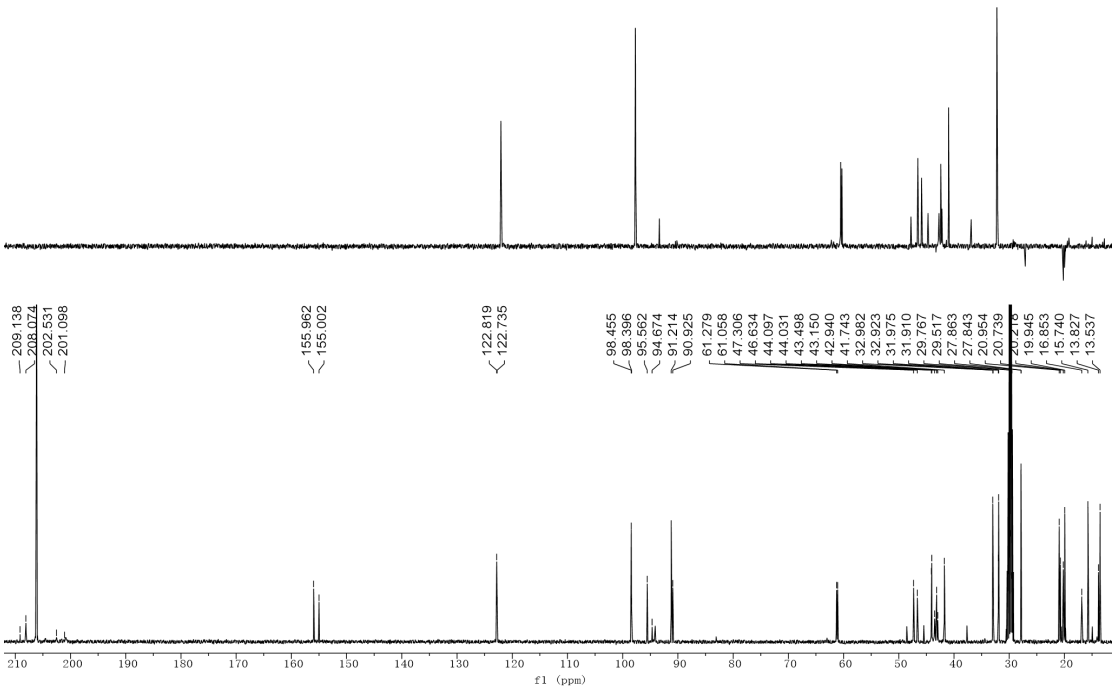


Figure S32. ^{1}H-^{1}H COSY spectrum of compound **5**/**6** in acetone-d_6

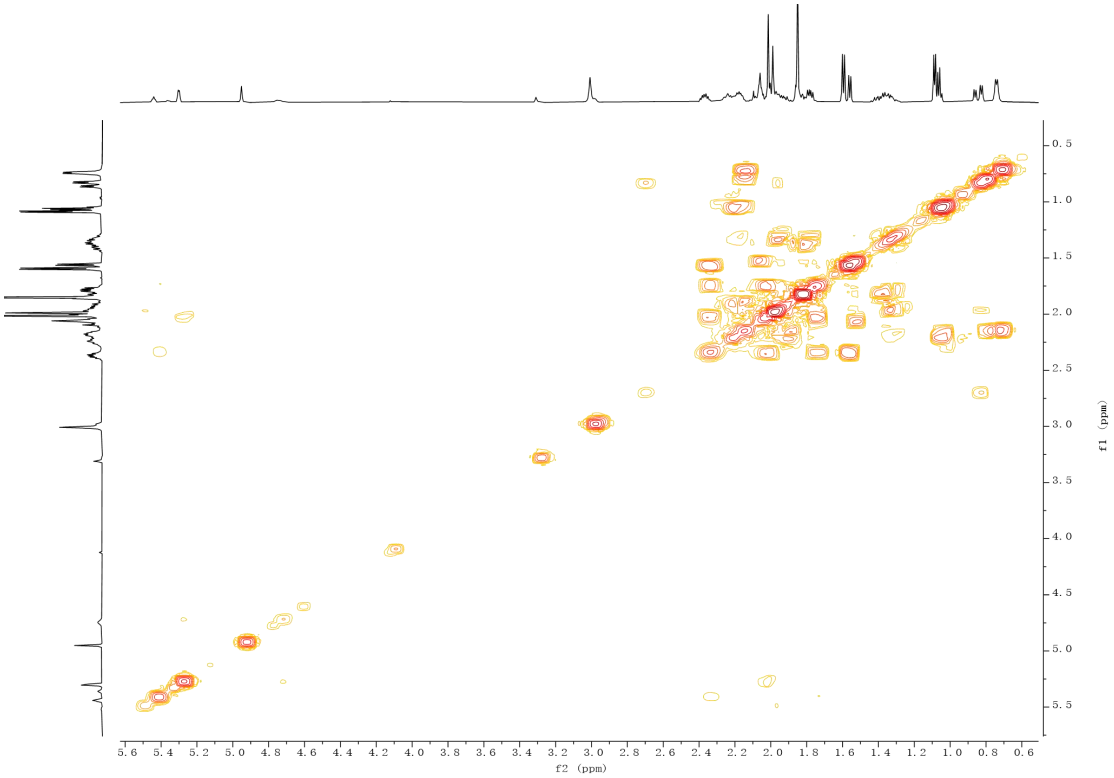


Figure S33. HSQC spectrum of compound **5**/**6** in acetone-d_6

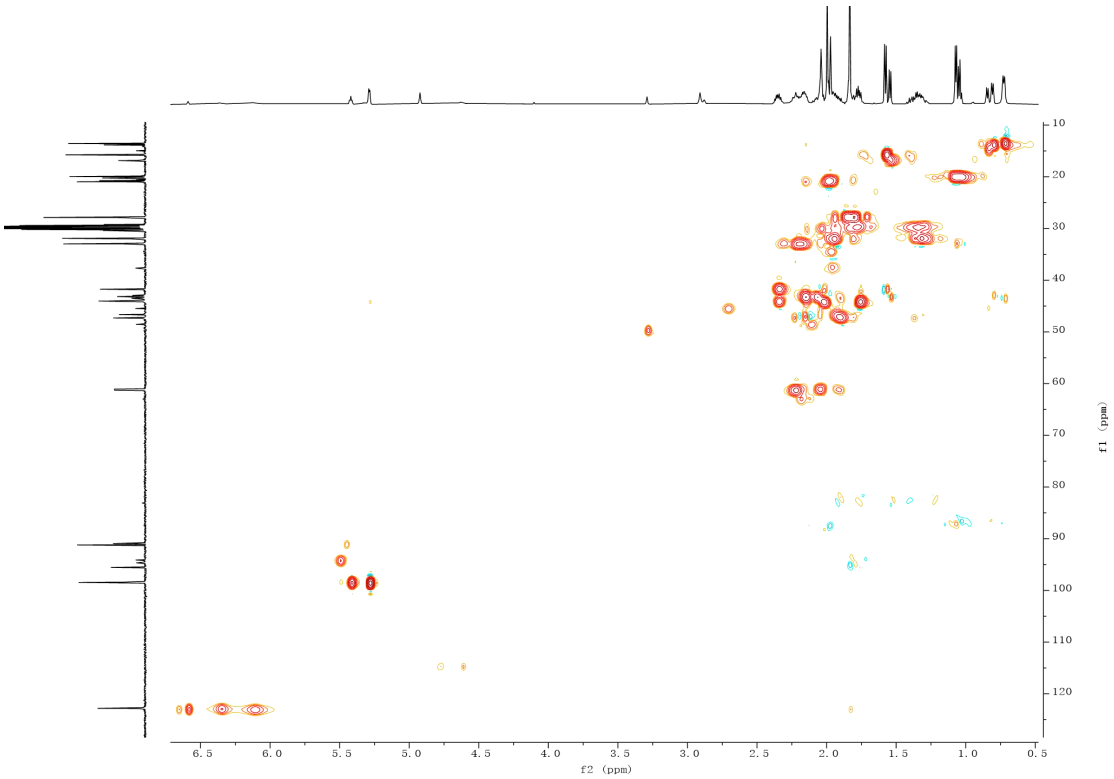


Figure S34. HMBC spectrum of compound **5**/**6** in acetone-d_6

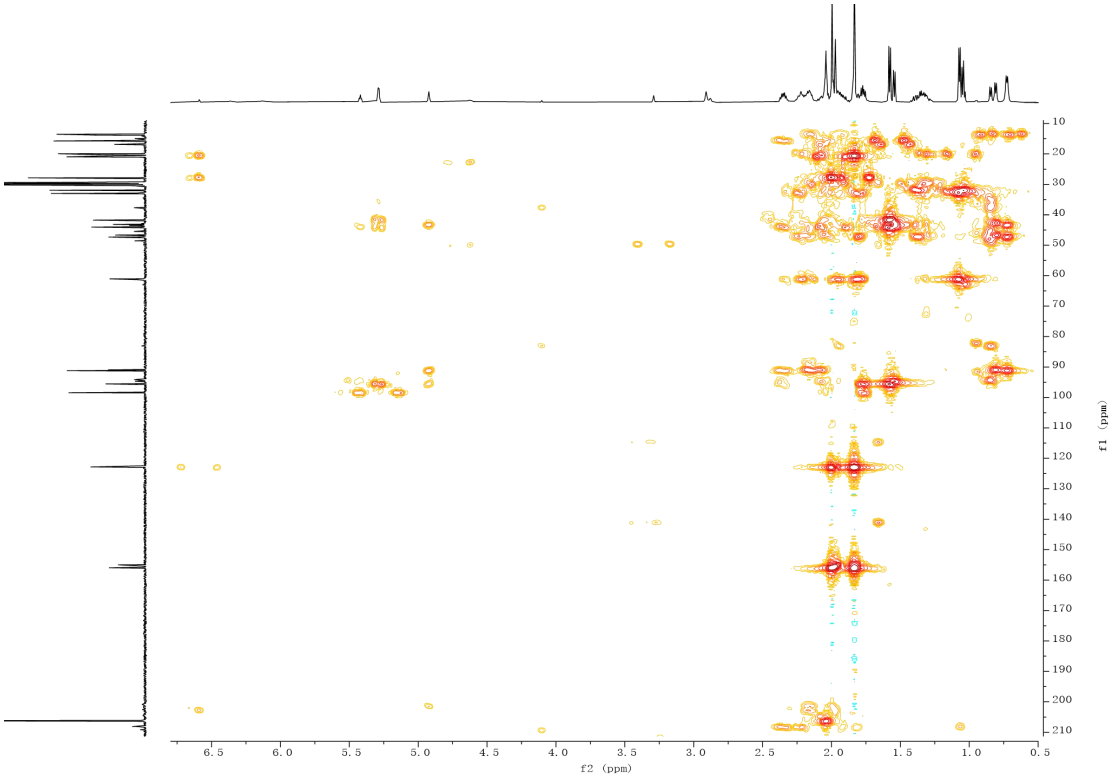
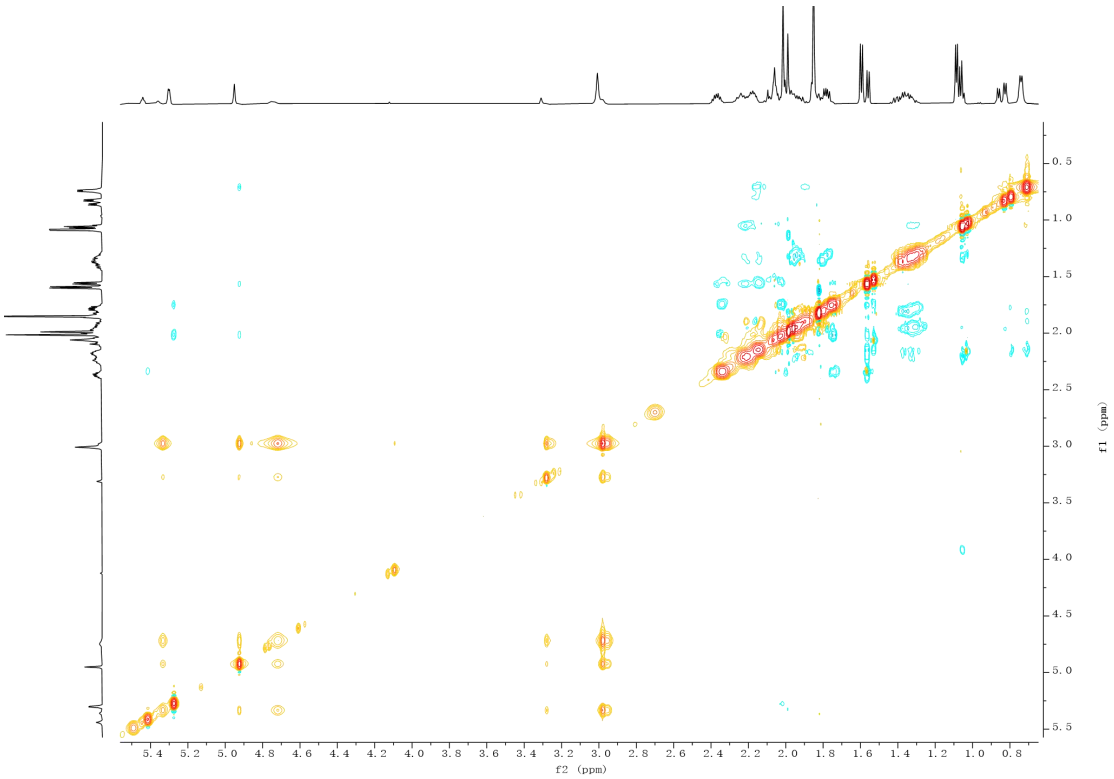
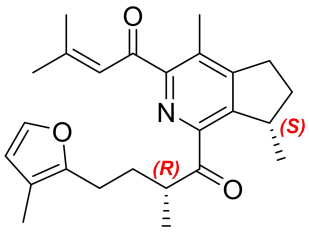


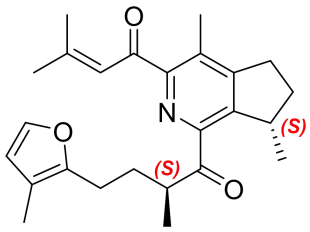
Figure S35. ROESY spectrum of compound **5**/**6** in acetone-d_6



NMR calculation by DP4+ analysis



1a (Isomer 1)



1b (Isomer 2)

Conformational analyses of the structures (**1a** and **1b**) were carried out via Monte Carlo searching using molecular mechanism with MMFF force field in the Spartan 18 program.[1] The force field minimum energy conformers thus obtained were subsequently optimized by applying the density functional theory (DFT) with the B3LYP/6-31+G(d,p) level in vacuum, implemented in the Gaussian 09 software package.[2] Harmonic vibrational frequencies were also performed to confirm no imaginary frequencies of the finally optimized conformers. Gauge independent atomic orbital (GIAO) calculations of NMR chemical shifts were accomplished by DFT at the mPW1PW91/6-311+G(d,p) level in acetone with the polarizable continuum model (PCM) in Gaussian 09 software.[2,3] NMR chemical shifts of TMS were calculated in the same level and used as the references. The experimental and calculated data were analyzed by the improved probability DP4+ method for isomeric compounds. Regression analysis of calculated versus experimental NMR chemical shifts of **1a** and **1b** were carried out.

References

1. Spartan 18; Wavefunction Inc.:Irvine, CA.

2. Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

3. Grimblat, N.; Zanardi, M. M.; Sarotti, A. M. *J. Org. Chem.* 2015, *80*, 12526-12534.

Table S1. Optimized lowest energy 3D conformers and energy analysis for **1a**

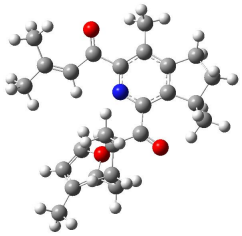
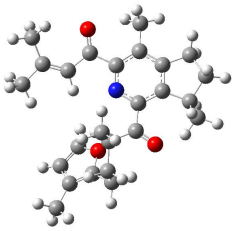
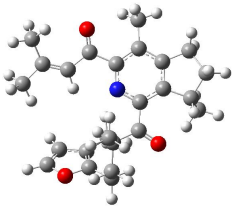
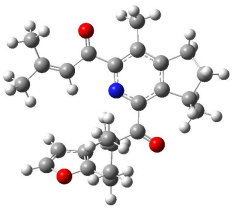
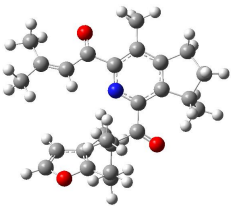
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
1a-1		-1251.393688	0.001805	7.69%
1a-2		-1251.393752	0.001741	8.23%
1a-3		-1251.394251	0.001242	13.95%
1a-4		-1251.394501	0.000992	18.18%
1a-5		-1251.395493	0.000000	51.96%

Table S2. Optimized lowest energy 3D conformers and energy analysis for **1b**

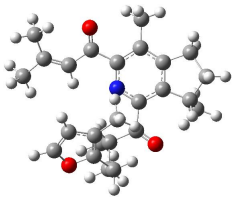
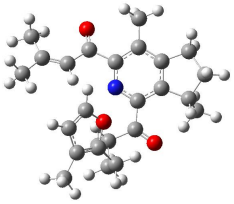
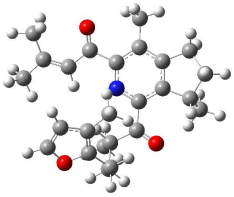
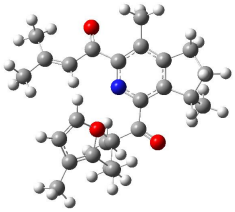
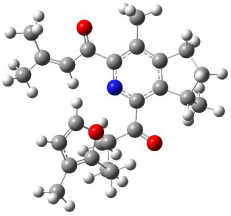
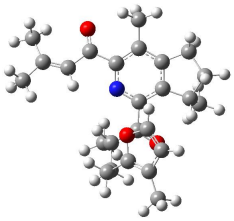
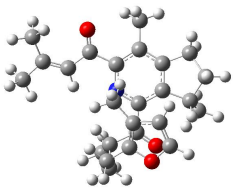
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
1b-1		-1251.394683	0.000000	30.50%
1b-2		-1251.393866	0.000817	12.84%
1b-3		-1251.394645	0.000038	29.30%
1b-4		-1251.393863	0.000820	12.80%
1b-5		-1251.393809	0.000874	12.09%
1b-6		-1251.391689	0.002994	1.28%
1b-7		-1251.391619	0.003064	1.19%

Table S3. Calculated ^{13}C NMR results of **1a** and **1b**

No.	Experimental NMR data	**1a**		**1b**	
		Unscaled shifts	Scaled shifts	Unscaled shifts	Scaled shifts
C-1	20.8	24.8	21.5	25.5	21.7
C-2	157.2	176.9	167.4	176.9	167.4
C-3	123.6	127.3	119.9	127.3	119.7
C-4	192.9	200.1	189.7	200.2	189.8
C-5	152.7	156.7	148.1	156.8	148.1
C-6	134.6	146.5	138.2	146.6	138.3
C-7	157.6	165.8	156.8	165.9	156.8
C-8	29.5	34.1	30.4	34.5	30.4
C-9	33.3	36.7	32.9	36.9	32.7
C-10	39.8	46.6	42.4	46.7	42.2
C-11	148.5	159.2	150.4	159.1	150.3
C-12	144.8	149.2	140.8	149.1	140.7
C-13	205.9	218.2	207.0	218.1	207.1
C-14	40.2	43.1	39.0	43.6	39.1
C-15	32.8	34.3	30.6	35.6	31.4
C-16	24.5	26.9	23.6	27.3	23.5
C-17	151.3	159.4	150.7	159.7	150.9
C-18	114.6	124.4	117.1	124.2	116.7
C-19	113.5	119.5	112.4	119.6	112.3
C-20	140.8	148.0	139.6	147.9	139.5
C-21	28.2	31.9	28.4	32.4	28.3
C-22	16.2	21.0	17.9	21.6	18.0
C-23	20.1	20.6	17.5	20.8	17.2
C-24	17.1	22.3	19.1	23.1	19.4
C-25	9.8	11.7	8.9	12.1	8.8

Table S4. Calculated ^{1}H NMR results of **1a** and **1b**

No.	Experimental NMR data	**1a**		**1b**	
		Unscaled shifts	Scaled shifts	Unscaled shifts	Scaled shifts
H-1	2.26	2.48	2.36	2.56	2.35
H-3	7.15	7.73	7.30	7.92	7.40
H-8a	2.99	3.24	3.06	3.27	3.02
H-8b	2.91	3.08	2.92	3.14	2.90
H-9a	2.25	2.32	2.21	2.43	2.23
H-9b	1.90	2.03	1.93	2.09	1.91
H-10	3.98	4.09	3.87	4.44	4.12
H-14	4.12	4.25	4.02	4.34	4.02
H-15a	2.10	2.38	2.26	2.49	2.28
H-15b	1.67	1.87	1.78	1.85	1.68
H-16	2.61	2.67	2.54	2.71	2.49
H-19	6.13	6.46	6.10	6.49	6.05
H-20	7.24	7.61	7.18	7.52	7.03
H-21	2.01	2.13	2.02	2.23	2.03
H-22	2.49	2.71	2.57	2.79	2.56
H-23	1.18	1.36	1.30	1.31	1.17
H-24	1.17	1.08	1.04	1.29	1.15
H-25	1.83	1.63	1.55	1.75	1.59

Table S5. DP4+ evaluation of theoretical and experimental NMR data of **1**

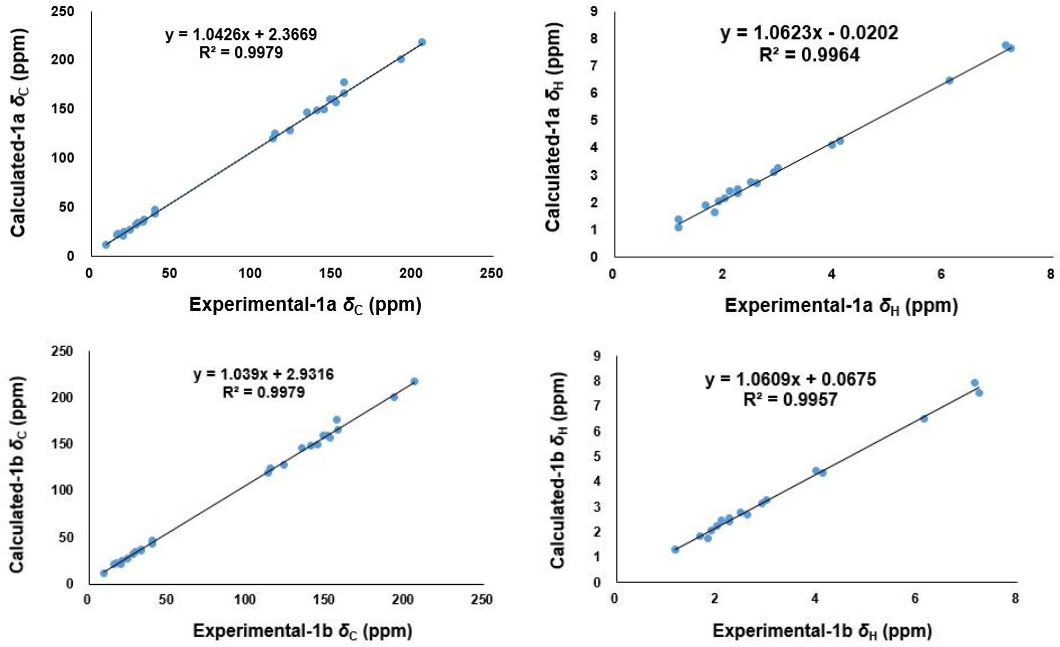
Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Unscaled Shifts

		DP4+	99.88%	0.12%	-	-	-
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C		20.8	24.8	25.5			
C	x	157.2	176.9	176.9			
C	x	123.6	127.3	127.3			
C	x	192.9	200.1	200.2			
C	x	152.7	156.7	156.8			
C	x	134.6	146.5	146.6			
C	x	157.6	165.8	165.9			
C		29.5	34.1	34.5			
C		33.3	36.7	36.9			
C		39.8	46.6	46.7			
C	x	148.5	159.2	159.1			
C	x	144.8	149.18	149.12			
C	x	205.9	218.16	218.09			
C		40.2	43.07	43.57			
C		32.8	34.26	35.56			
C		24.5	26.93	27.32			
C	x	151.3	159.44	159.70			
C	x	114.6	124.42	124.16			
C	x	113.5	119.53	119.64			
C	x	140.8	147.96	147.86			
C		28.2	31.93	32.35			
C		16.2	21.04	21.59			
C		20.1	20.60	20.76			
C		17.1	22.27	23.06			
C		9.8	11.69	12.11			
H		2.26	2.48	2.56			
H	x	7.15	7.73	7.92			
H		2.99	3.24	3.27			
H		2.91	3.08	3.14			
H		2.25	2.32	2.43			
H		1.9	2.03	2.09			
H		3.98	4.09	4.44			
H		4.12	4.25	4.34			
H		2.1	2.38	2.49			
H		1.67	1.87	1.85			
H		2.61	2.67	2.71			
H	x	6.13	6.46	6.49			
H	x	7.24	7.61	7.52			
H		2.01	2.13	2.23			
H		2.49	2.71	2.79			
H		1.18	1.36	1.31			
H		1.17	1.08	1.29			
H		1.83	1.63	1.75			

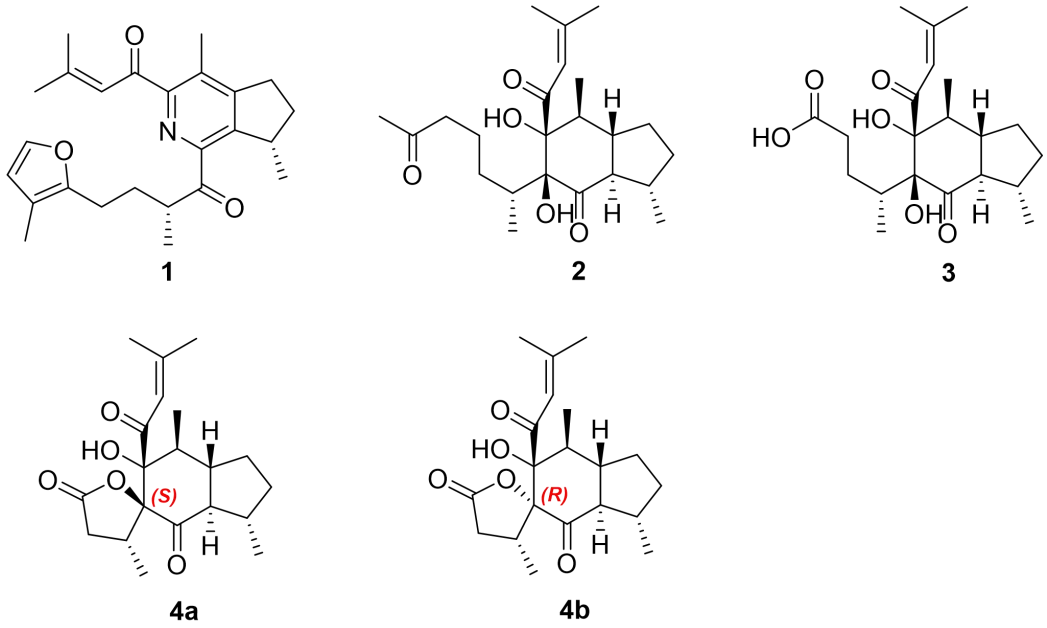
Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Unscaled Shifts

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	36.29%	63.71%	-	-	-	-
sDP4+ (C data)	45.39%	54.61%	-	-	-	-
sDP4+ (all data)	32.14%	67.86%	-	-	-	-
uDP4+ (H data)	99.97%	0.03%	-	-	-	-
uDP4+ (C data)	33.56%	66.44%	-	-	-	-
uDP4+ (all data)	99.94%	0.06%	-	-	-	-
DP4+ (H data)	99.95%	0.05%	-	-	-	-
DP4+ (C data)	29.57%	70.43%	-	-	-	-
DP4+ (all data)	99.88%	0.12%	-	-	-	-

Figure S36. Regression analysis of experimental *vs* calculated NMR data of **1a** and **1b**



ECD calculations



Conformational analyses of candidate structures were carried out via Monte Carlo searching using molecular mechanism with MMFF force field in the Spartan 18 program. The force field minimum energy conformers thus obtained were subsequently optimized by applying the density functional theory (DFT) with the B3LYP/6-31+G(d,p) level in vacuum, implemented in the Gaussian 09 software package. Harmonic vibrational frequencies were also performed to confirm no imaginary frequencies of the finally optimized conformers (Grimme et al., 2010). The optimized conformations with Boltzmann distributions of Gibbs free energies more than 1% were further applied to the ECD calculations using the TD-DFT method with the basis set cam-B3LYP/6-31+G(2d,p) with the polarizable continuum model (PCM) in methanol. The overall calculated ECD curves were generated by Boltzmann weighting of their selected low-energy conformers using SpecDis 1.62 with σ = ~0.3 eV.

Table S6. Optimized lowest energy 3D conformers and energy analysis for **1**

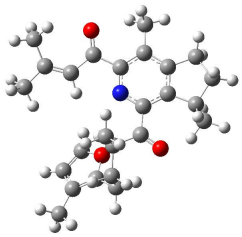
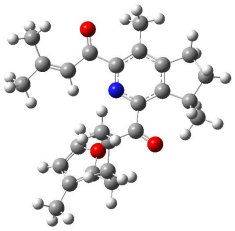
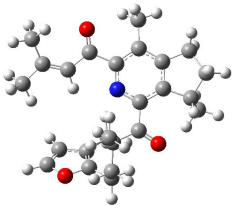
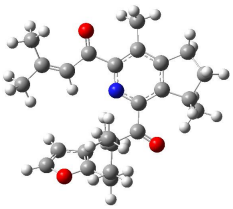
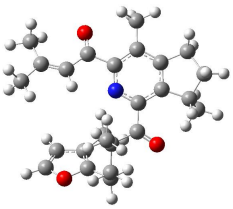
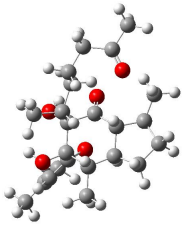
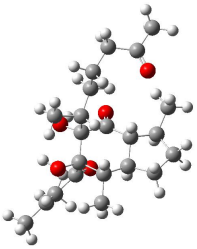
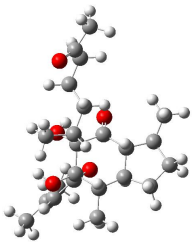
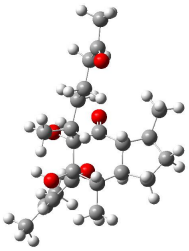
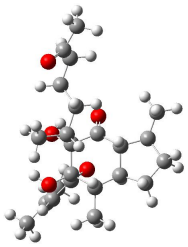
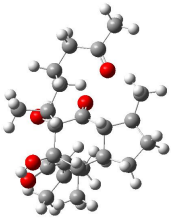
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
1-1		-1251.393688	0.001805	7.69%
1-2		-1251.393752	0.001741	8.23%
1-3		-1251.394251	0.001242	13.95%
1-4		-1251.394501	0.000992	18.18%
1-5		-1251.395493	0.000000	51.96%

Table S7. Optimized lowest energy 3D conformers and energy analysis for **2**

Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
2-1		-1273.839486	0.001793	6.89%
2-2		-1273.839490	0.001789	6.92%
2-3		-1273.837951	0.003328	1.36%
2-4		-1273.841279	0.000000	45.98%
2-5		-1273.837950	0.003329	1.36%
2-6		-1273.840633	0.000646	23.20%

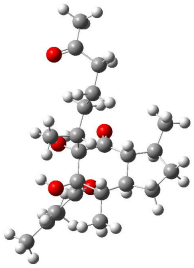
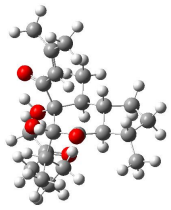
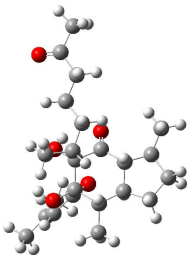
2-7		-1273.839551	0.001728	7.38%
2-8		-1273.839197	0.002082	5.07%
2-9		-1273.838240	0.003039	1.84%

Table S8. Optimized lowest energy 3D conformers and energy analysis for **3**

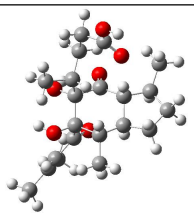
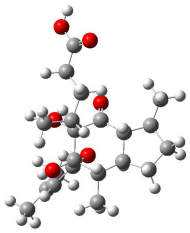
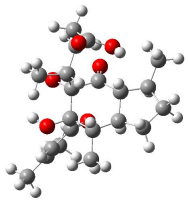
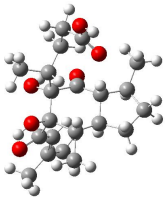
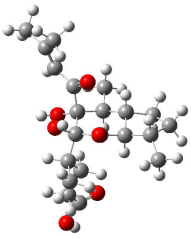
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
3-1		-1270.501893	0.001352	17.34%
3-2		-1270.501029	0.002216	6.95%
3-3		-1270.499646	0.003599	1.61%
3-4		-1270.503245	0.000000	72.55%
3-5		-1270.499621	0.003624	1.56%

Table S9. Optimized lowest energy 3D conformers and energy analysis for **4a**

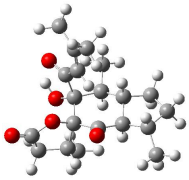
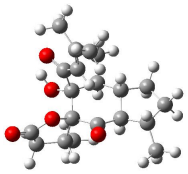
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
4a-1		-1154.790986	0.000000	50.03%
4a-2		-1154.790985	0.000001	49.93%

Table S10. Optimized lowest energy 3D conformers and energy analysis for **4b**

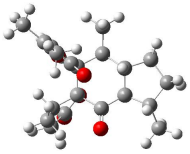
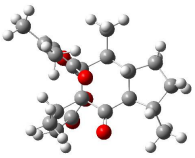
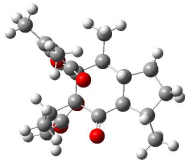
Conformers		Free energies		
No.	3D conformers	E (Hartree)	ΔE (Hartree)	Distribution
4b-1		-1154.794721	0.000002	33.31%
4b-2		-1154.794723	0.000002	33.38%
4b-3		-1154.794721	0.000000	33.31%

Figure S37. Key ROESY correlations of compounds **2**−**6**