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# **Supporting Information for**

## Antimalarial diterpenoid dimers of a new carbon skeleton from Aphanamixis

### grandifolia

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Figure S61. HMBC spectrum for 5a in CD<sub>3</sub>OD.
Figure S62. ESI(+)MS spectrum for 5a.
Figure S63. HRESI(+)MS spectrum for 5a.

**Figure S64.** <sup>1</sup>H NMR spectrum for **5b** in CD<sub>3</sub>OD.

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Figure S66. NOESY spectrum for 5b in CD<sub>3</sub>OD.

Figure S67. ESI(+)MS spectrum for 5b.

Figure S68. HRESI(+)MS spectrum for 5b.

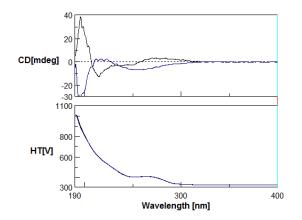
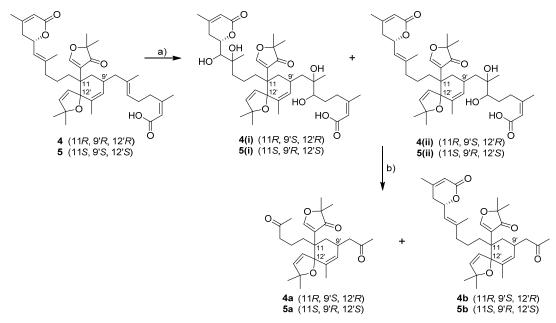
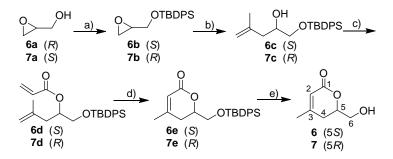


Figure S1. Experimental ECD spectra of 4 (black) and 5 (blue).



Scheme S1. Oxidative degradation of compounds 4/5 [Reaction conditions: a) 40 mol %  $K_2OsO_4 \cdot 2H_2O$ , 40 eq. MeSO<sub>2</sub>NH<sub>2</sub>, 120 eq.  $K_3Fe(CN)_6$ , 120 eq.  $K_2CO_3$ , <sup>t</sup>BuOH-H<sub>2</sub>O (1:1), r.t.; b) Pb(OAc)\_4, DCM, 0 °C].



Scheme S2. Synthesis of (*S*, 6) and (*R*, 7) forms of 6-(hydroxymethyl)-4-methyl-5,6-dihydro-2H-pyran-2-one [Reaction conditions: a) TBDPSiCl, imidazole, DMF; b) CuI, CH<sub>3</sub>CH(CH<sub>2</sub>)MgBr, THF, -30 to 0 °C; c) CH<sub>2</sub>CHCOCl, Et<sub>3</sub>N, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C; d) Grubbs' catalyst II, CH<sub>2</sub>Cl<sub>2</sub>, 50 °C; e) Bu<sub>4</sub>NF, THF].

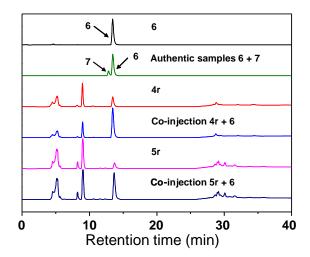
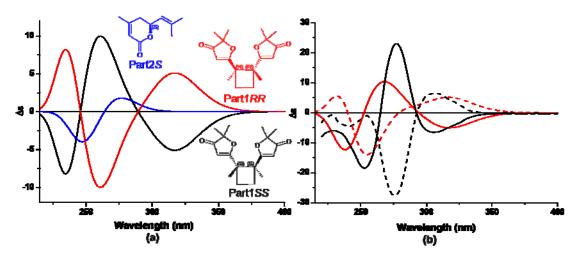


Figure S2. Chiral HPLC analysis of 4r/5r from 4/5 and authentic synthetic samples (6 & 7)

#### **1.1 ECD Calculations**

**1.1.1 Calculated ECD spectra for compounds 2 and 3.** In order to further determine the structures of compounds **2** and **3**, their theoretical ECD spectra were calculated by TDDFT computational chemistry method and compared with the corresponding experimental ones. Firstly, in order to avoid the inaccurate large amounts of lowest energy conformers caused by the flexible chains, ECD spectra of three structural fragments from **2** and **3** (Part1*SS*, Part1*RR*, and Part2*S*, Figure S3(a)) were calculated separately. Linear combination of ECD spectra of Part1*SS* and two Part2*S* gave an ECD curve matching the experimental one of **2**, with first negative, second positive, and third negative Cotton effects. Similarly, the calculated ECD curve of Part1*RR* plus two Part2*S* could simulate the experimental data of **3**. The above studies allowed us to differentiate the absolute configurations of **2** and **3** as (5S,11S,11'S,5'S) and (5S,11R,11'R,5'S), respectively.



**Figure S3.** (a) B3LYP/6-311++G(2d,2p)//B3LYP/6-31+G(d) calculated ECD spectra for three structural fragments of **2** and **3**; (b) Experimental ECD spectra (220–400 nm) of **2** (black solid line) and **3** (black dashed line), and linear combination of (Part1*SS* + 2\*Part2*S*) (red solid line) and (Part1*RR* + 2\*Part2*S*) (red dashed line).

In general, conformational analyses were carried out via Monte Carlo searching using molecular mechanism with MMFF94 force field in the SPARTAN 08 software package.<sup>1</sup> The results showed three lowest energy conformers for Part1SS and only one for Part2S with relative energy below 2.0 kcal/mol. Subsequently, the conformers were re-optimized using DFT at the B3LYP/6-31+G(d) level in gas phase by the GAUSSIAN 09 program.<sup>2</sup> The B3LYP/6-31+G(d) harmonic vibrational frequencies were also calculated to confirm their stability. The energies, oscillator strengths, and rotational strengths (velocity) of the first 60 electronic excitations were calculated using the TDDFT methodology at the B3LYP/6-311++G(2d,2p) level in vacuum. The ECD spectra were simulated by the overlapping Gaussian function (half the bandwidth at 1/e peak height,  $\sigma = 0.3 \text{ eV}$ ),<sup>3</sup> and the first seven electronic excitations for Part1SS and the first two electronic excitations for Part2S were adopted. To get the final spectra, the simulated spectra of the lowest energy conformers for each structure were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy ( $\Delta$ G). Theoretical ECD spectrum of Part1*RR* was obtained by directly inversing that of the

corresponding enantiomer Part1SS.

**1.1.2.** Calculated ECD spectra for compounds 4a and 5a. Theoretical ECD spectra of compounds 4a and 5a were also calculated using procedures same as those for 2 and 3. In brief, conformational analyses of 5a showed 10 lowest energy conformers with relative energy below 2.0 kcal/mol. The ECD spectra were simulated by the overlapping Gaussian function ( $\sigma = 0.3 \text{ eV}$ ),<sup>3</sup> and the velocity rotatory strengths of the first four electronic excitations were adopted. In order to get the final ECD spectrum of 2a, the simulated spectra of the 10 lowest energy conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy ( $\Delta G$ ). The theoretical ECD spectrum of 4a was depicted by directly reversing that of 5a. The results showed that the ECD spectrum of 5a matched that of the enantiomer with (11S,9'R,12'S) configuration. Therefore, the absolute configurations of aphanamene H (4) and I (5) were identified to be (5S,11R,9'R,12'R) and (5S,11S,9'S,12'S), respectively.

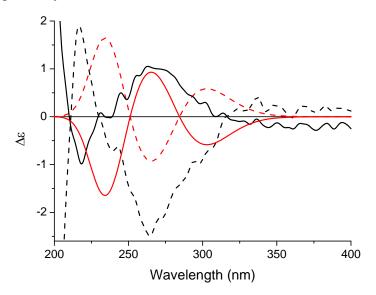


Figure S4. Calculated (red color) ECD spectra of 4a (solid line) and 5a (dashed line) versus their experimental (black color) ECD spectra.

#### Notes and references

[1]. Spartan 04; Wavefunction Inc.:Irvine, CA.

[2] Gaussian 09, Rev. C 01. 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.;

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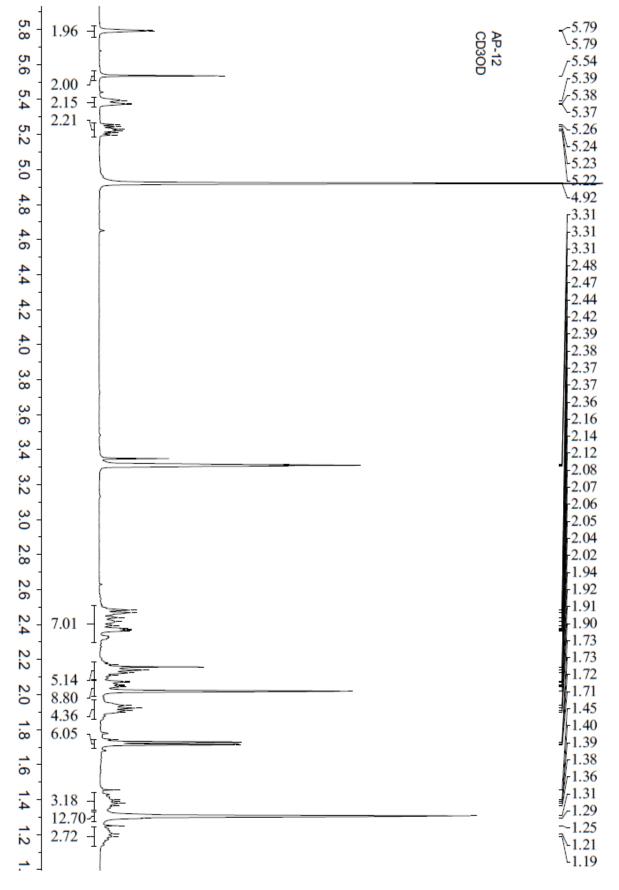
[3] Stephens, P. J.; Harada, N. ECD cotton effect approximated by the Gaussian curve and other methods. *Chirality* **2010**, *22*, 229–233.

Position	4		5			
rosition	$\delta_{ m H}({ m mult},J_{ m HH})$	$\delta_{ m C}$	$\delta_{ m H}({ m mult},J_{ m HH})$	$\delta_{ m C}$		
1		168.0		168.0		
2	5.79 (br s)	116.5	5.79 (br s)	116.5		
3		161.0		161.1		
4	2.32 (dd, 18.1, 4.5)	35.8	2.34 (dd, 18.1, 4.7)	35.8		
	2.40 (br dd, 18.1, 10.5)		2.40 (br dd, 18.1, 10.4)	$\begin{array}{c} & & & \\$		
5	5.21 (ddd, 10.5, 8.5, 4.5)	75.9	5.20 (ddd, 10.4, 8.5, 4.7)	75.9		
6	5.34 (br d, 8.5)	124.0	5.33 (br d, 8.5)	123.8		
7		143.3		143.5		
8	2.06 (br t, 7.2, 2H)	40.7	2.06 (br t, 7.3, 2H)	40.7		
9	1.24 (m)	24.4	1.22 (m)	24.6		
	1.38 (m)		1.41 (m)			
10	1.62 (ddd, 13.1, 13.1, 4.5)	32.4	1.65 (ddd, 13.3, 13.3, 4.7)	32.6		
	1.77 (m)					
11		51.7		51.8		
12		198.3		198.4		
13	5.52 (s)	105.9	5.52 (s)	105.9		
14		210.2				
15		89.7				
16	1.34 (s, 3H)	23.6	1.34 (s, 3H)	23.6		
17	1.34 (s, 3H)	23.2	1.34 (s, 3H)			
18	1.79 (m)	31.3	1.79 (m)			
	1.89 (dd, 13.4, 11.0)		1.89 (dd, 13.2, 10.8)			
19	1.71 (d, 1.4, 3H)	16.7	1.71 (d, 1.3, 3H)	16.8		
20	2.01 (br s, 3H)	23.0	2.01 (br s, 3H)	23.0		
1′		169.7		169.7		
2'	5.68 (br s)	117.6	5.68 (br s)	117.6		
3'		161.5		161.5		
4'	2.70 (m, 2H)	34.1	2.70 (m, 2H)	34.1		
5'	2.26 (br td, 7.5, 7.0, 2H)	27.7	2.25 (br td, 7.6, 6.9, 2H)	27.7		
6'	5.28 (br t, 7.0)	127.2	5.28 (br t, 6.9, 2H)	127.2		
7'		134.5		134.5		
8′	2.01 (m)	46.9	2.01 (dd, 13.2, 8.9)	46.9		
	2.16 (m)		2.17 (dd, 13.2, 5.9)			
9′	2.26 (m)	31.9	2.27 (m)	31.9		
10′	5.50 (br s)	131.1	5.51 (br s)	131.2		
11′		135.8		135.7		
12'		96.1		96.1		
13′	5.86 (d, 6.1)	128.1	5.84 (d, 6.1)	128.1		
14′	5.88 (d, 6.1)	137.7	5.88 (d, 6.1)	137.6		
15′		88.5		88.5		
16′	1.14 (s, 3H)	29.7	1.15 (s, 3H)	29.7		
17′	1.33 (s, 3H)	29.2	1.33 (s, 3H)	29.2		
18′	1.68 (dd, 2.4, 1.3, 3H)	21.6	1.68 (dd, 2.5, 1.4, 3H)	21.5		
19′	1.67 (br s, 3H)	16.1	1.67 (br s, 3H)			
20'	1.92 (d, 1.4, 3H)	25.4	1.92 (d, 1.3, 3H)			

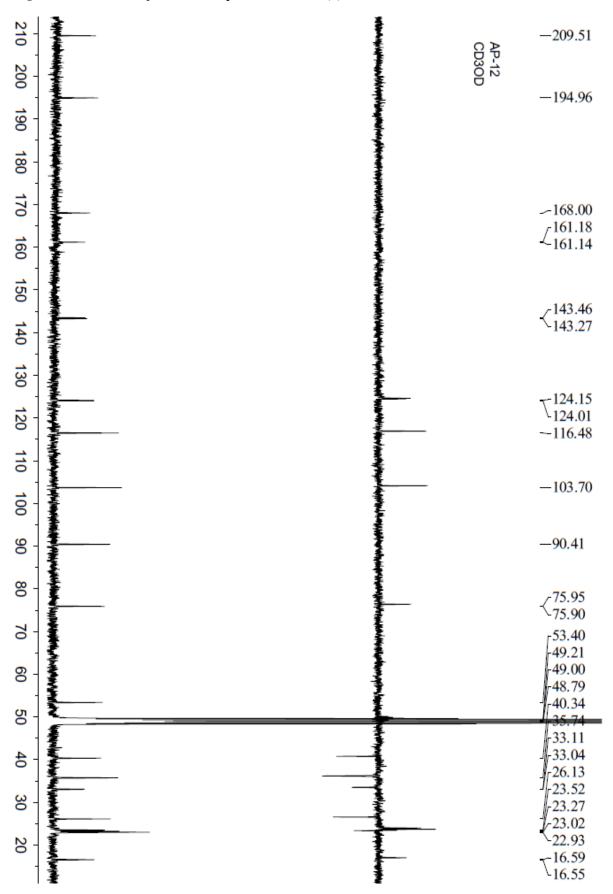
**Table S1.** <sup>1</sup>H and <sup>13</sup>C NMR data of compounds **4** and **5** in CD<sub>3</sub>OD.

Position	4a/5a		4b		5b	5b		
Position	$\delta_{\rm H}$ (mult, J in Hz)	$\delta_{ m C}$	$\delta_{ m H}$ (mult, $J$ in Hz)	$\delta_{ m C}$	$\delta_{ m H}$ (mult, J in Hz)	${\delta_{\!\mathrm{C}}}^b$		
1				168.1		168.0		
2			5.79 (br s)	116.5	5.79 (br s)	116.5		
3				161.2		161.1		
4			2.37 (m)	35.8	2.34 (dd, 18.1, 4.5)	35.8		
			2.42 (m)		2.43 (br dd, 18.1, 10.6)			
5			5.22 (m)	76.0	5.20 (m)	75.9		
6			5.36 (br d, 8.6)	124.1	5.34 (br d, 8.5)	123.8		
7		211.2		143.2		143.7		
8	2.50 (m, 2H)	44.3	2.08 (br t, 7.2, 2H)	40.6	2.07 (br t, 7.2, 2H)	40.7		
9	1.67 (m, 2H)	20.6	1.24 (m)	24.1	1.22 (m)	24.3		
			1.53 (m)		1.57 (m)			
10	1.68 (m)	32.3	1.66 (m)	32.1	1.68 (m)	32.4		
	1.76 (ddd, 13.2, 13.2, 3.8)		1.78 (ddd, 13.1, 13.1, 4.0)		1.78 (13.0, 13.0, 3.9)			
11		51.8		51.7		51.7		
12		197.8		198.0		198.0		
13	5.53 (s)	106.0	5.52 (s)	105.9	5.52 (s)	105.9		
14		210.2		210.3		210.1		
15		89.8		89.7		89.7		
16	1.34 (s, 3H)	23.5	1.34 (s, 3H)	23.6	1.34 (s, 3H)	23.6		
17	1.34 (s, 3H)	23.2	1.34 (s, 3H)	23.2	1.33 (s, 3H)	23.2		
18	1.90 (dd, 13.4, 10.7)	30.9	1.88 (m)	30.9	1.88 (dd, 13.3, 9.9)	31.0		
	1.95 (br dd, 13.4, 6.0)		1.93 (m)		1.94 (br dd, 13.3, 5.4)			
19	2.12 (s, 3H)	29.8	1.72 (d, 1.4, 3H)	16.7	1.74 (d, 1.3, 3H)	16.8		
20			2.03 (br s, 3H)	23.0	2.02 (br s, 3H)	23.0		
7'		210.5		210.3		210.3		
8'	2.57 (dd, 17.3, 7.9)	49.8	2.58 (m)	49.3	2.57 (dd, 18.8, 9.8)	49.4		
	2.64 (dd, 17.3, 6.1)		2.65 (m)		2.66 (dd, 18.8, 5.3)			
9′	2.73 (m)	29.8	2.62 (m)	29.7	2.65 (m)	29.8		
10′	5.47 (m)	130.3	5.46 (br s)	130.3	5.47 (br s)	130.4		
11′		136.4		136.5		136.5		
12'		95.7		95.8		95.8		
13'	5.85 (d, 6.1)	128.0	5.87 (d, 6.1)	128.0	5.85 (d, 6.1)	128.0		
14'	5.88 (d, 6.1)	137.8	5.89 (d, 6.1)	137.8	5.89 (d, 6.1)	137.8		
15'		88.5		88.5		88.5		
16′	1.13 (s, 3H)	29.7	1.13 (s, 3H)	29.7	1.13 (s, 3H)	29.7		
17′	1.31 (s, 3H)	29.2	1.32 (s, 3H)	29.2	1.32 (s, 3H)	29.2		
18′	1.67 (dd, 2.4, 1.4)	21.6	1.68 (br s, 3H)	21.6	1.68 (br s, 3H)	21.6		
19′	2.18 (s, 3H)	30.3	2.17 (s, 3H)	30.5	2.17 (s, 3H)	30.4		

**Table S2.** <sup>1</sup>H and <sup>13</sup>C NMR data for compounds **4a**, **4b**, **5a**, and **5b** in CD<sub>3</sub>OD.

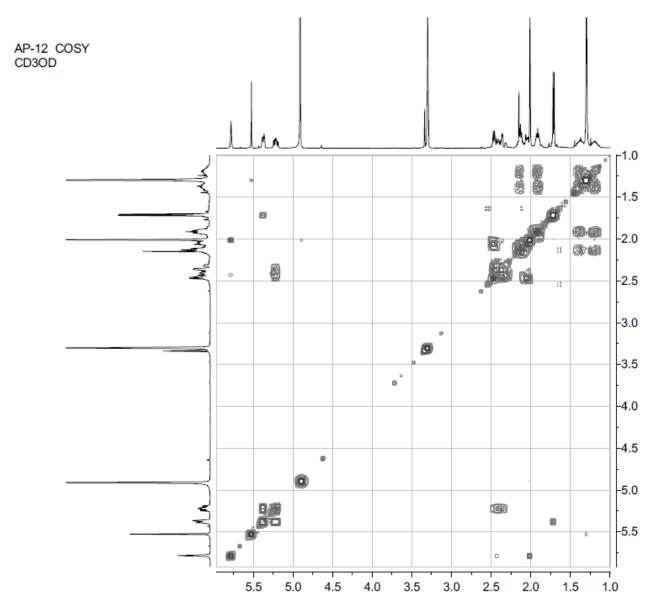


**Figure S5.** <sup>1</sup>H NMR spectrum for aphadilactone E (1) in  $CD_3OD$ .



**Figure S6.** <sup>13</sup>C NMR spectrum for aphadilactone E (1) in  $CD_3OD$ .

**Figure S7.**  ${}^{1}H-{}^{1}H$  COSY spectrum for aphadilactone E (1) in CD<sub>3</sub>OD.



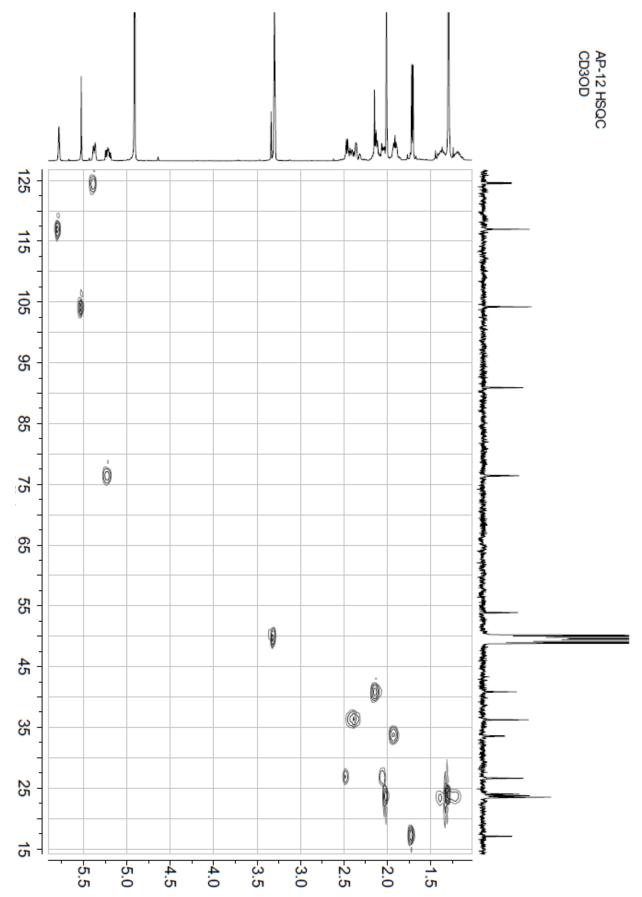


Figure S8. HSQC spectrum for aphadilactone E(1) in  $CD_3OD$ .

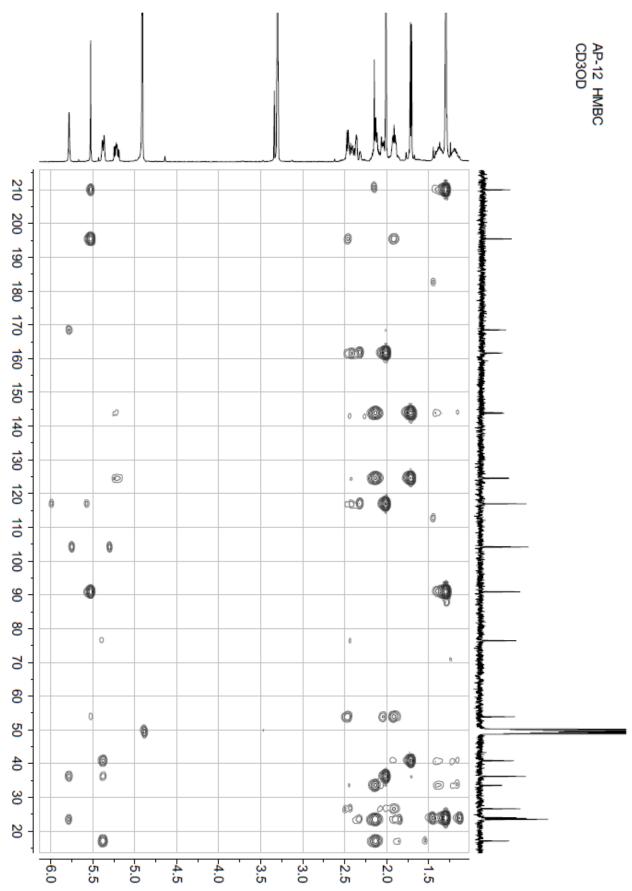
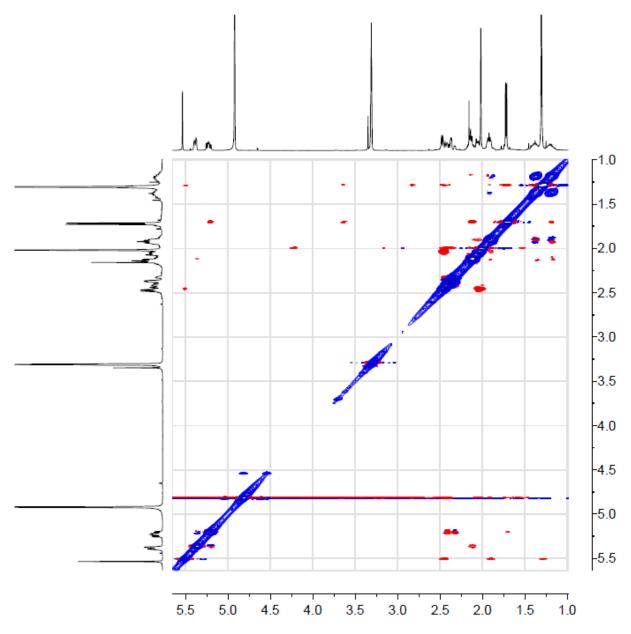
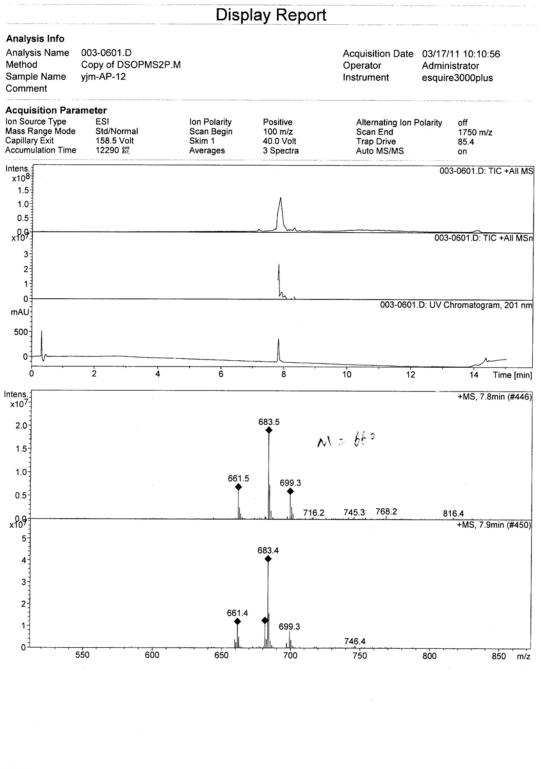


Figure S9. HMBC spectrum for aphadilactone E(1) in  $CD_3OD$ .

Figure S10. ROESY spectrum for aphadilactone E(1) in CD<sub>3</sub>OD.





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#### **Elemental Composition Report**

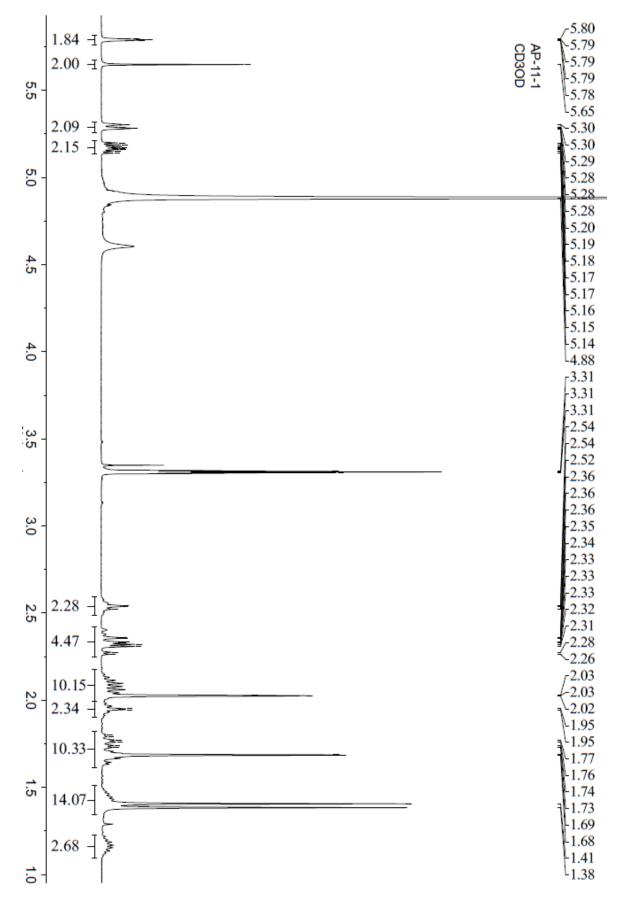
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Monoisotopic Mass, Even Electron Ions 285 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 O: 0-20 Na: 0-1 AP-12 LCT PXE KE324

AP-12	LCT PXE KE324								1	6-Oct-2014 09:44:15
AP-12_1016	41 (0.865) AM2 (Ar,	10000.0,0.00,1.0	0); ABS; Cm (39	9:50)						F MS ES+ 6.36e+004
100			683	3.3554						0.000 00 1
%	672.3558_673.3515	678.4043	680.3401	684.36	85.3640	3717.689.5140		94.5342	697 3365	698.3384 m/z
670.0	672.5 675.0	677.5 6	80.0 682.5	685.0	687.5	690.0	692.5	695.0	697.5	m/z
Minimum: Maximum:		5.0	3.0	-1.5 50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formu	la	
683.3554	683.3560	-0.6	-0.9	14.5	116.8	0.0		C40	H52 O8	Na

Page 1

16-Oct-2014



**Figure S13.** <sup>1</sup>H NMR spectrum for aphadilactone F (2) in CD<sub>3</sub>OD.

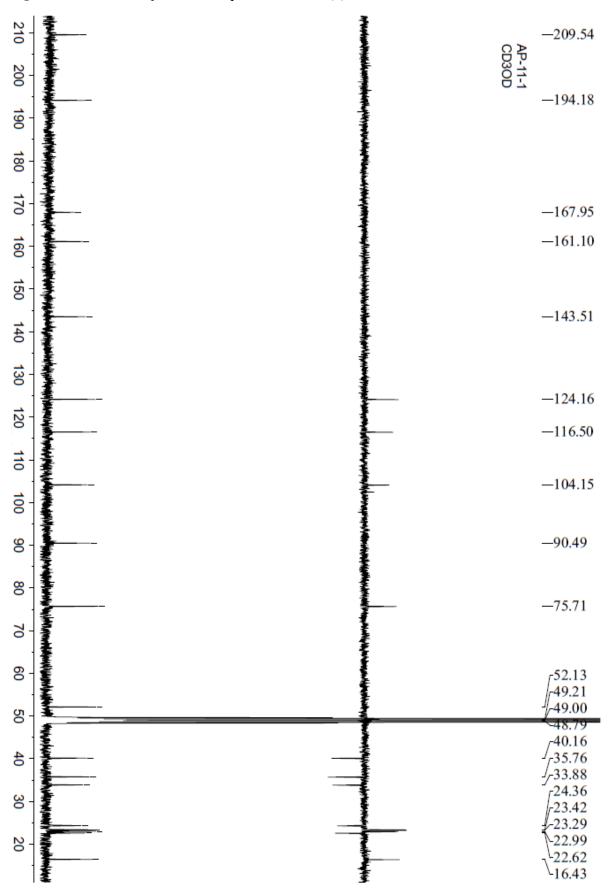
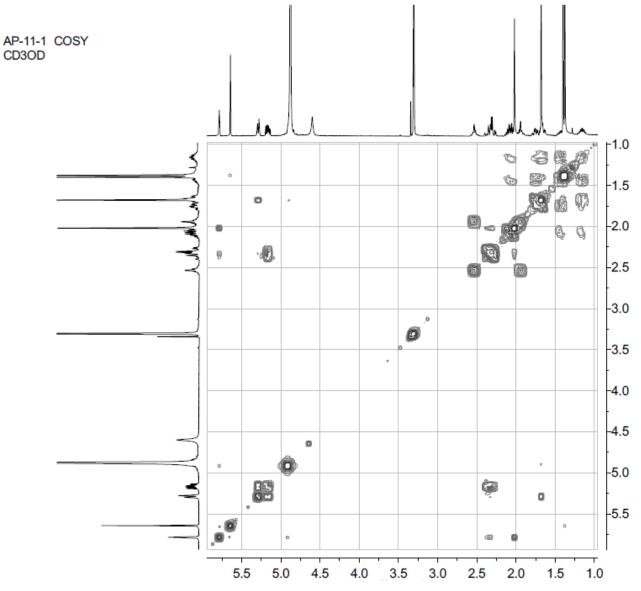


Figure S14. <sup>13</sup>C NMR spectrum for aphadilactone F (2) in  $CD_3OD$ .

Figure S15.  $^{1}H-^{1}H$  COSY spectrum for aphadilactone F (2) in CD<sub>3</sub>OD.



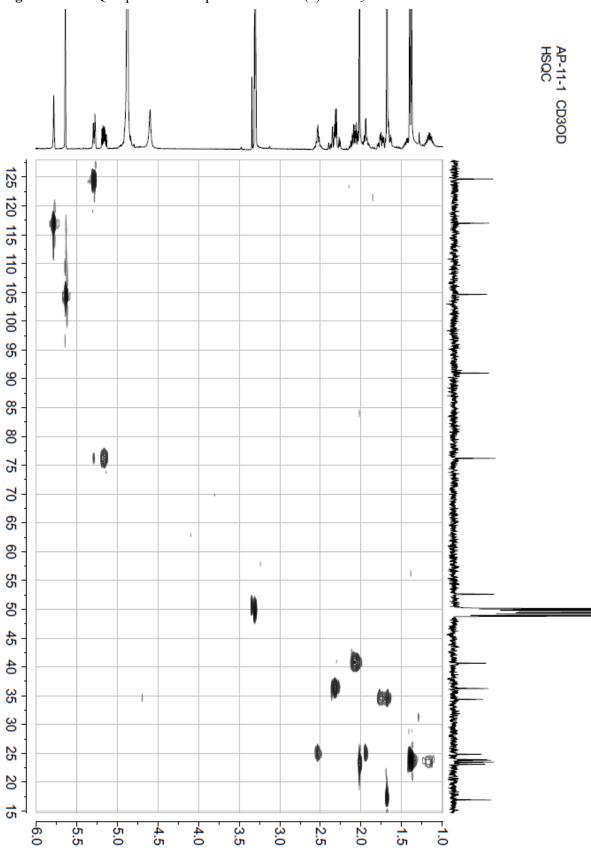


Figure S16. HSQC spectrum for aphadilactone F(2) in CD<sub>3</sub>OD.

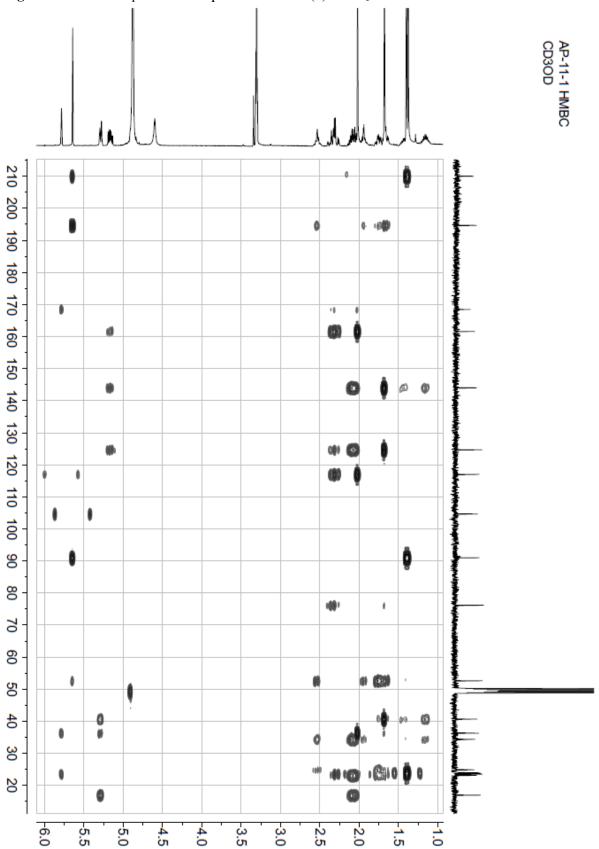
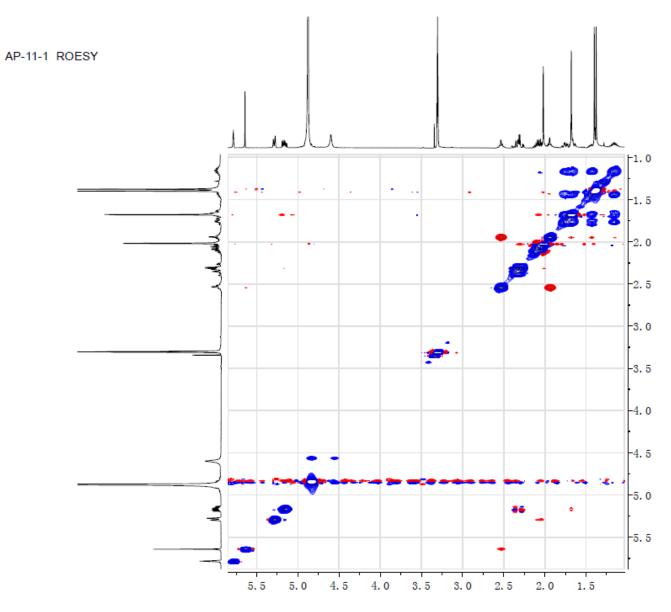
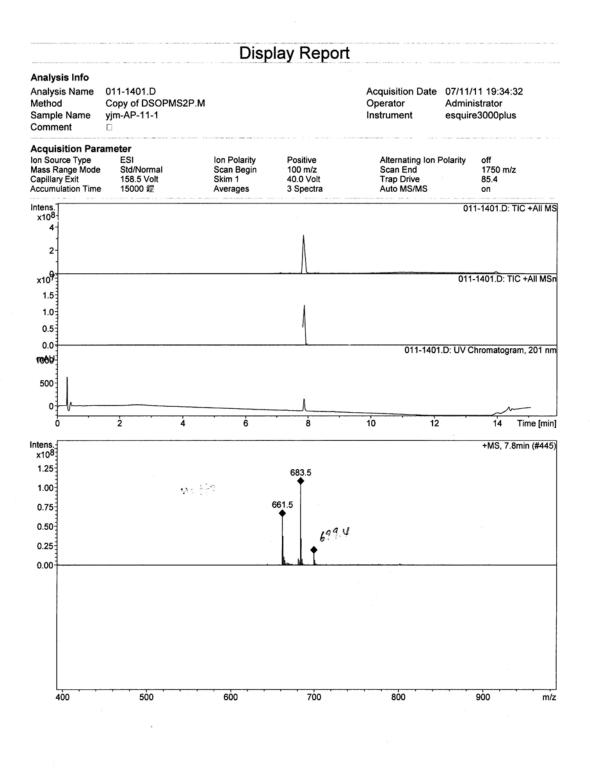


Figure S17. HMBC spectrum for aphadilactone F (2) in CD<sub>3</sub>OD.

Figure S18. ROESY spectrum for aphadilactone F (2) in CD<sub>3</sub>OD.





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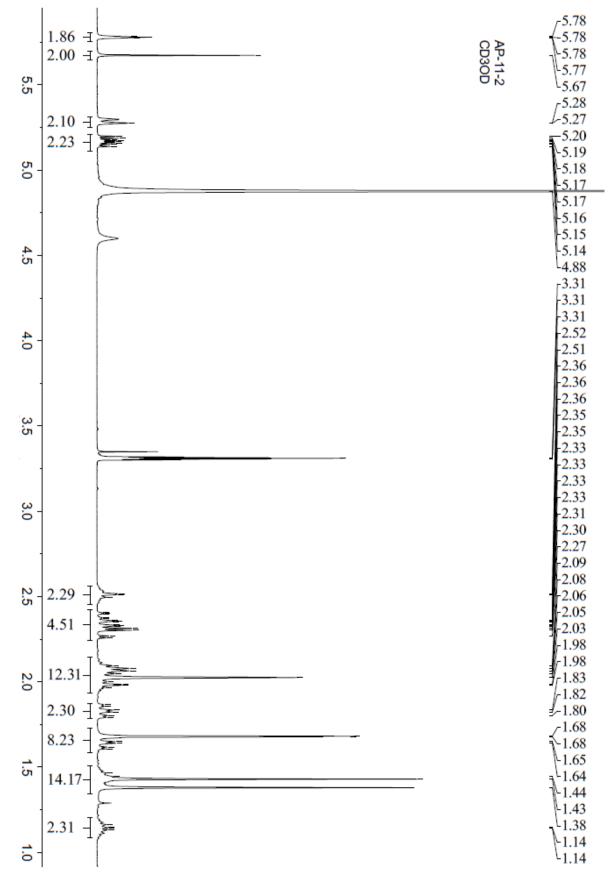
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Element	tal Compositi	on Report							Page 1	
Single Mass Analysis Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3										
Elements L	pic Mass, Even El a(e) evaluated wit Jsed: H: 2-120 O: 0-	th 1 results with	in limits (up t			r each mass)				
AP-11-1_1016 52 (1.128) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (41:54)										
	1. TOF MS E									
100		003.	3353							
-										
%-			684.3609							
672.:	3464 675.0	9.3848	685.36	687.8074	690.5256	695.3715 697.9	951 699.3575	705.1574	707.4369 m/z	
Minimum:		000.0	005.0	690.0		695.0	700.0	705.0		
Maximum:		5.0	3.0	-1.5 50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm) Fo	rmula		
683.3553	683.3560	-0.7	-1.0	14.5	23.9	0.0	C4	0 н52 о8	Na	



**Figure S21.** <sup>1</sup>H NMR spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.

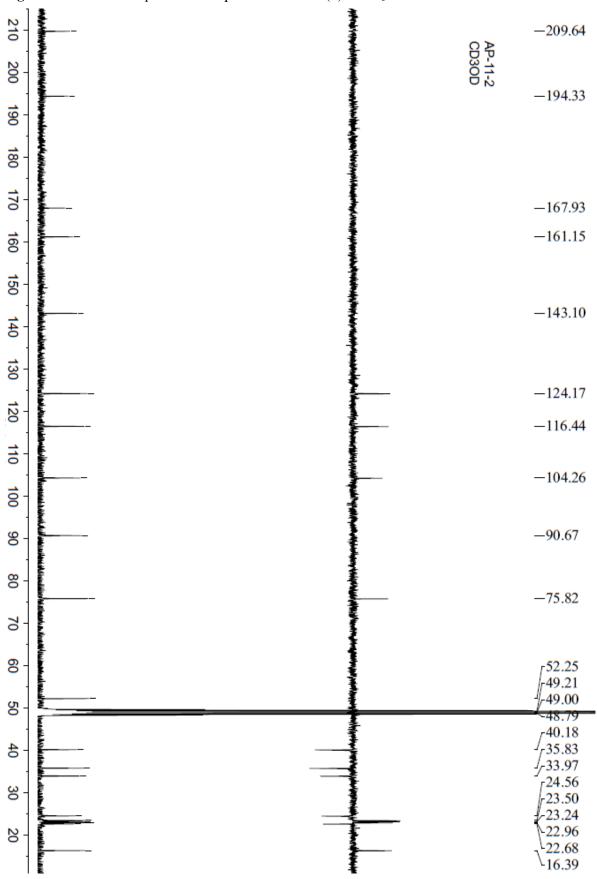
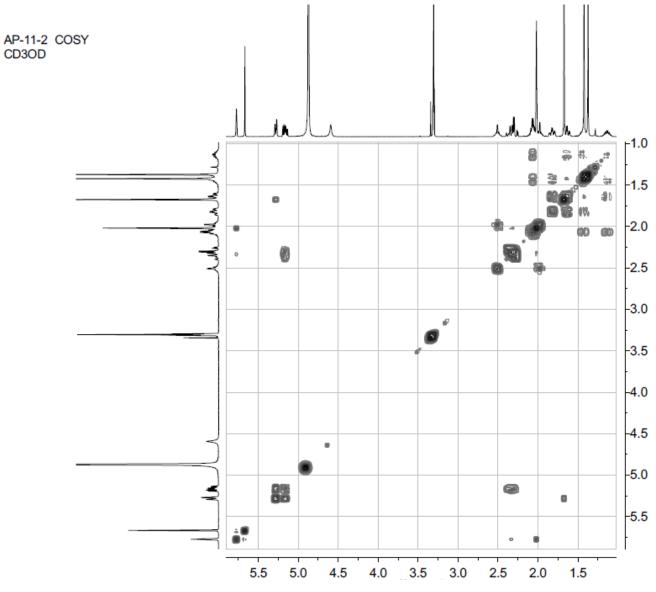


Figure S22. <sup>13</sup>C NMR spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.

Figure S23.  $^{1}H-^{1}H$  COSY spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.



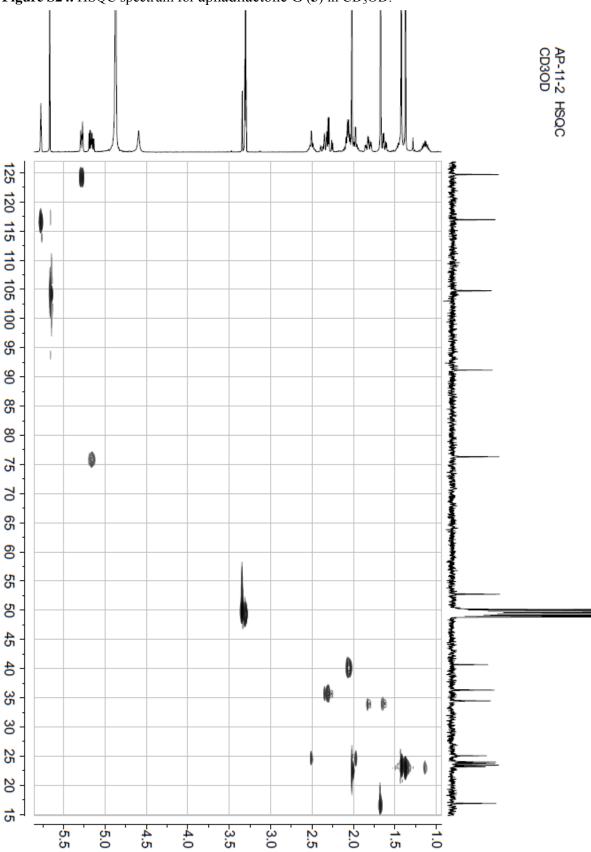


Figure S24. HSQC spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.

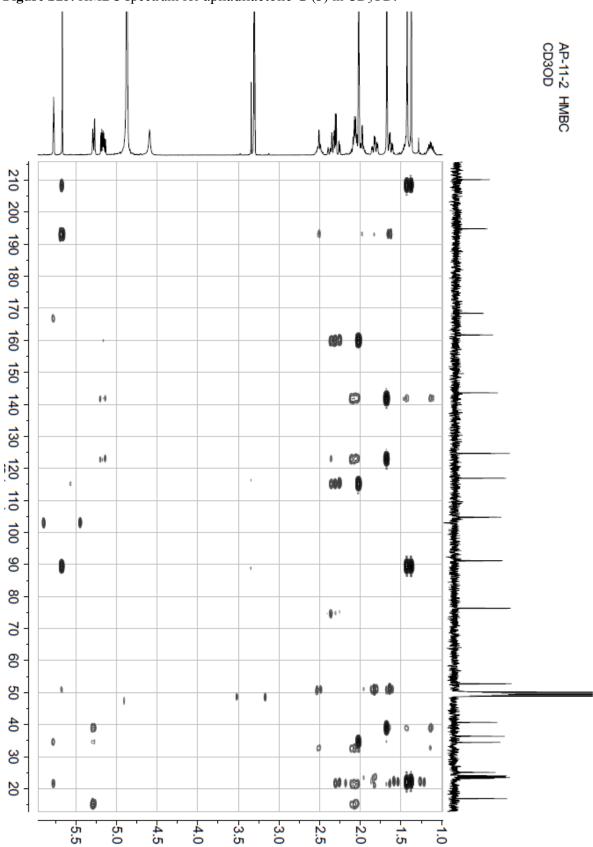
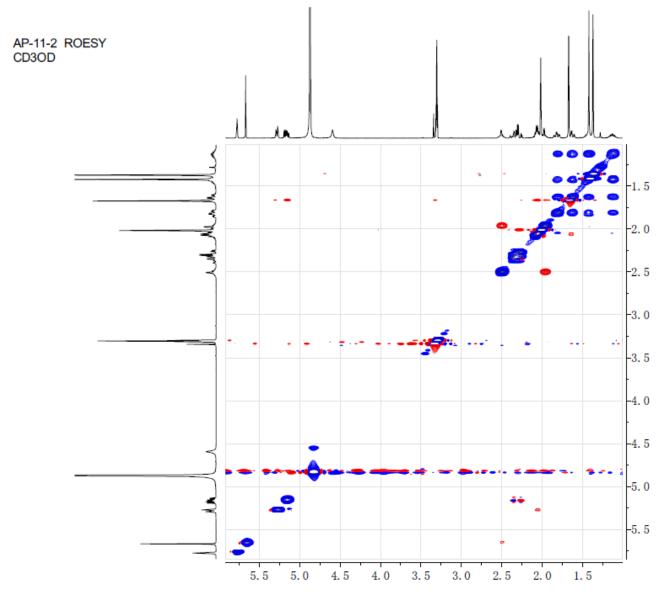
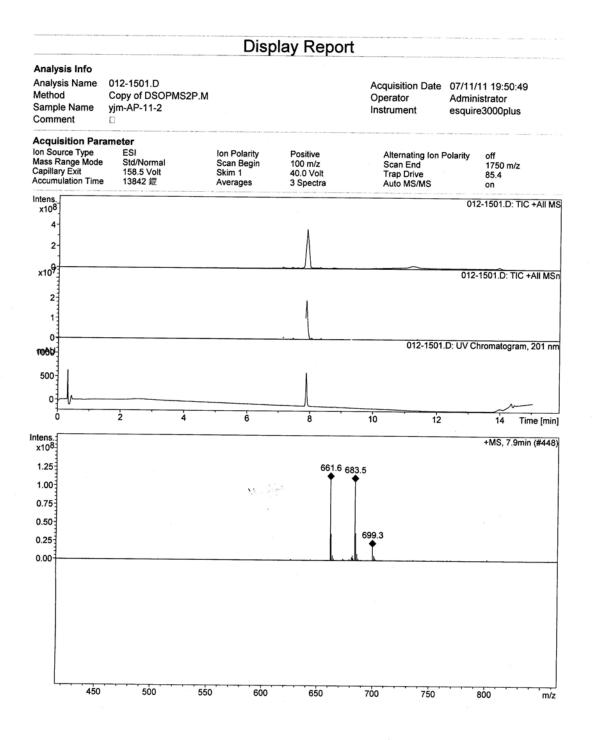


Figure S25. HMBC spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.

Figure S26. ROESY spectrum for aphadilactone G (3) in CD<sub>3</sub>OD.





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Figure S28. HRESI(+)MS spectrum for aphadilactone G (3).

#### Elemental Composition Report

#### Single Mass Analysis

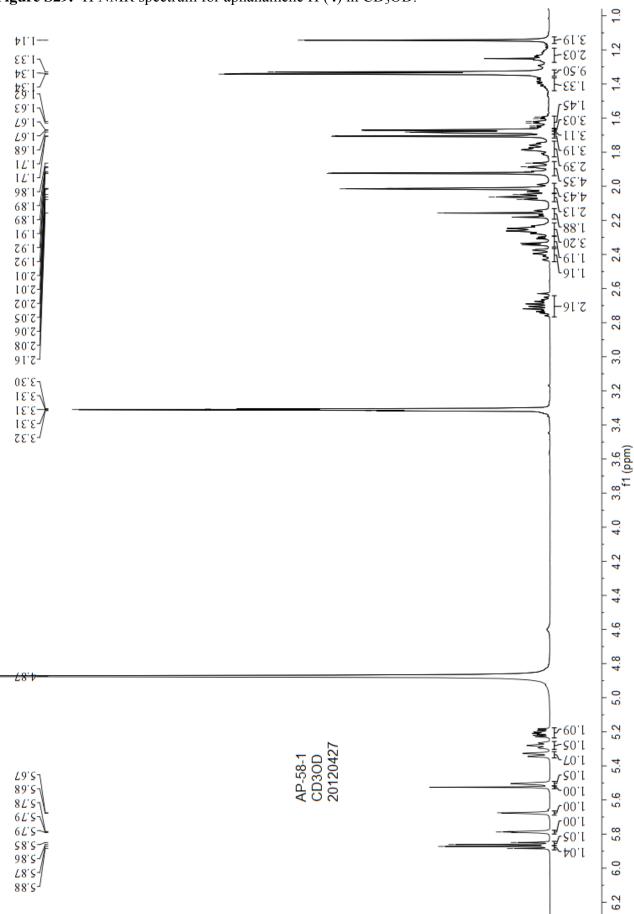
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 O: 0-20 Na: 0-1 AP-11-2 LCT PXE KE324

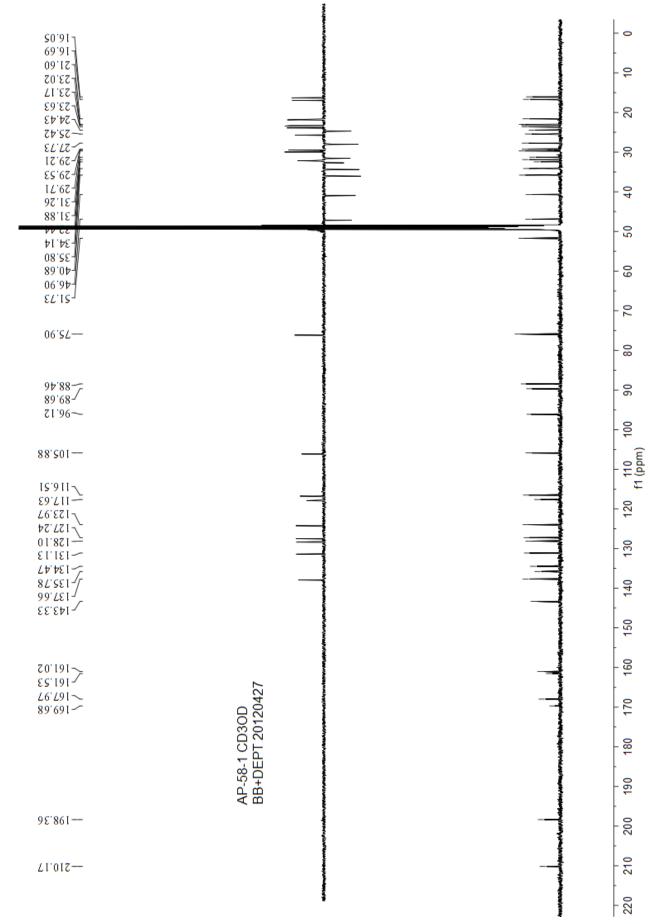
AP-11-2\_1016 44 (0.953) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (33:48)

1.88e+004 683.3566 100 684.3590 % 685.3644 647.0882 719.3922 661.3730663.3865 672.8691 678.4026 687.3737 699.3405 706.4271 715.3525 0 - m/z 720.0 650.0 660.0 670.0 680.0 690.0 700.0 710.0 -1.5 Minimum: Maximum: 5.0 3.0 50.0 PPM DBE i-FIT i-FIT (Norm) Formula Mass Calc. Mass mDa 0.0 C40 H52 O8 683.3566 683.3560 0.6 0.9 14.5 51.1 Na -2.6 683.3584 -1.8 17.5 56.2 5.2 C42 H51 08

16-Oct-2014 09:51:18 1: TOF MS ES+



**Figure S29.** <sup>1</sup>H NMR spectrum for aphanamene H (**4**) in CD<sub>3</sub>OD.



**Figure S30.** <sup>13</sup>C NMR spectrum for aphanamene H (**4**) in CD<sub>3</sub>OD.

**Figure S31.** <sup>1</sup>H–<sup>1</sup>H COSY spectrum for aphanamene H (**4**) in CD<sub>3</sub>OD.

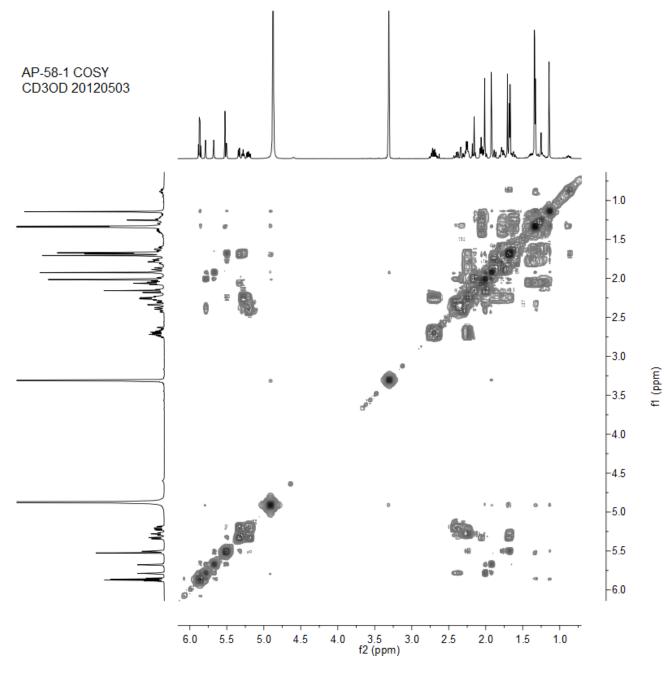
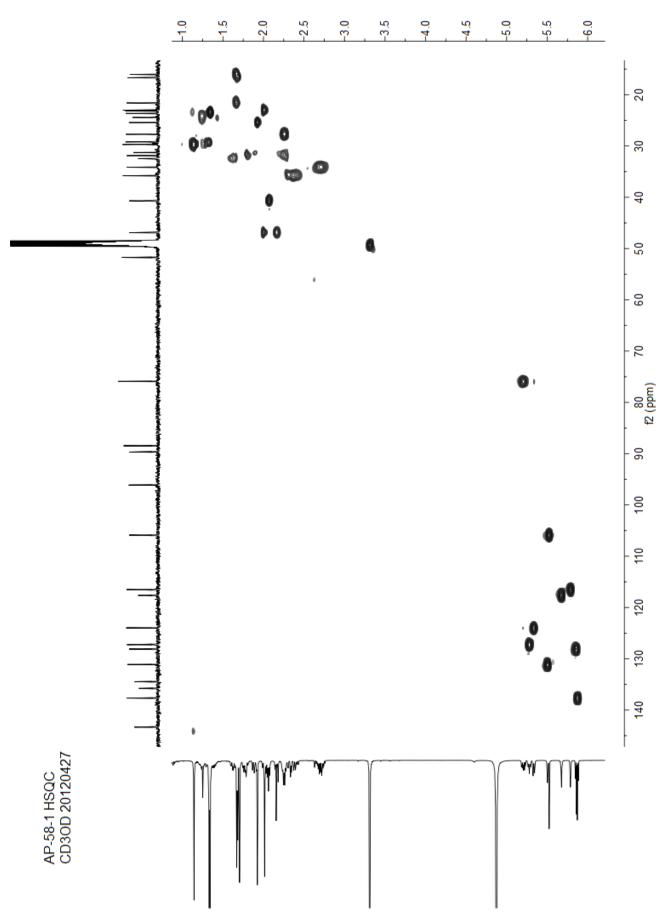


Figure S32. HSQC spectrum for aphanamene H (4) in CD<sub>3</sub>OD.

(udd) µ



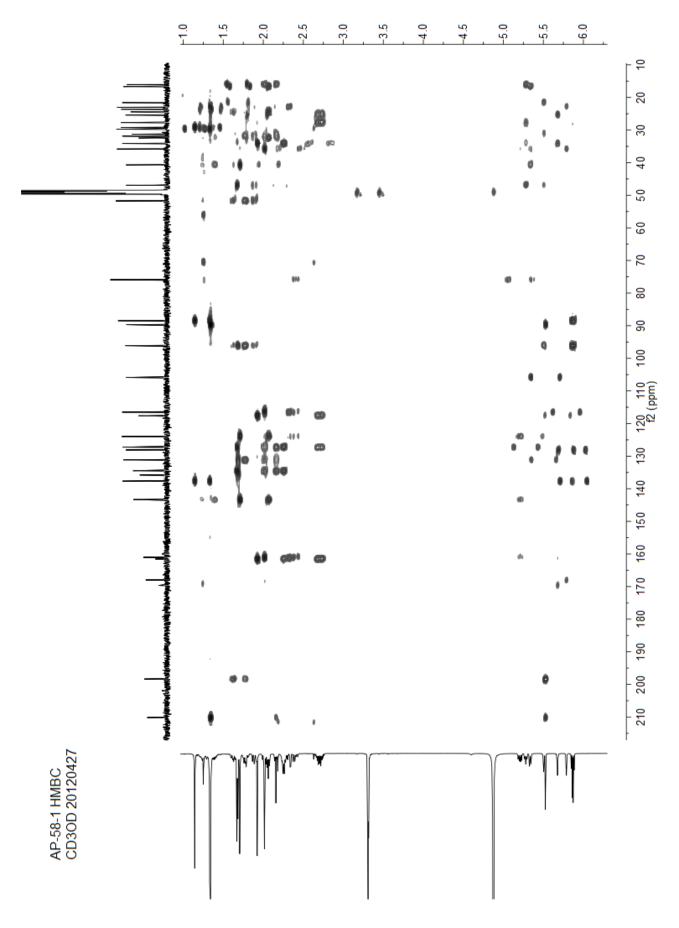
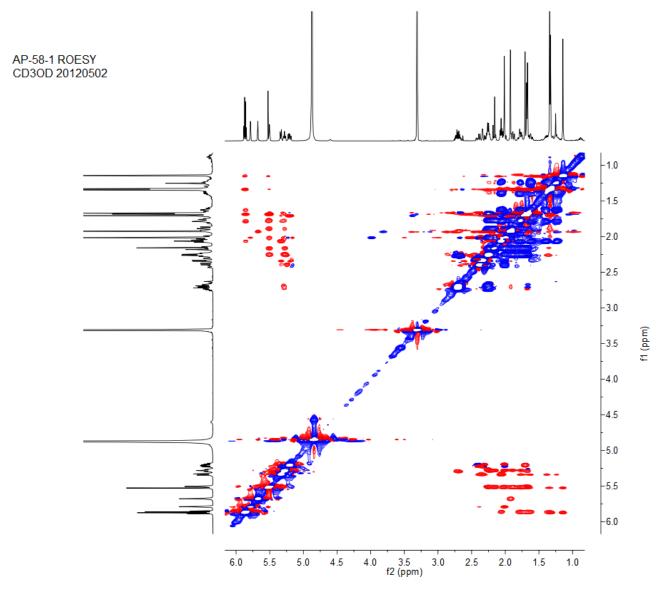
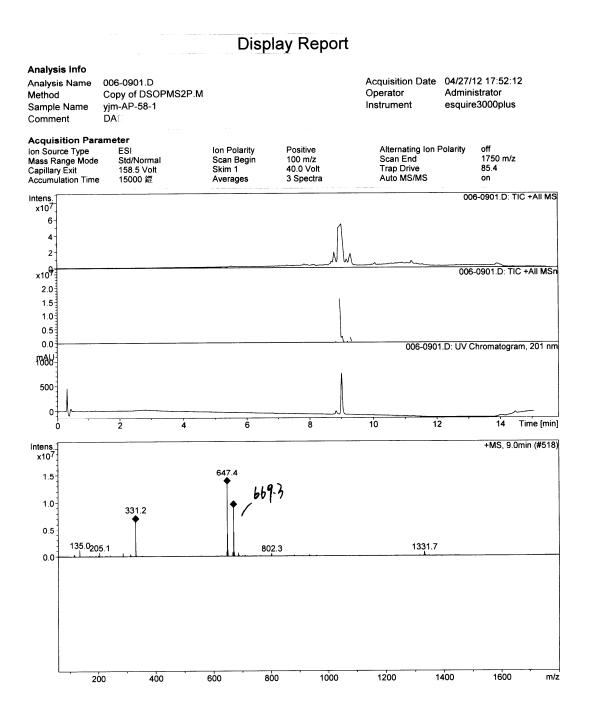


Figure S33. HMBC spectrum for aphanamene H (4) in  $CD_3OD$ . (udd) [J]

Figure S34. ROESY spectrum for aphanamene H (4) in CD<sub>3</sub>OD.

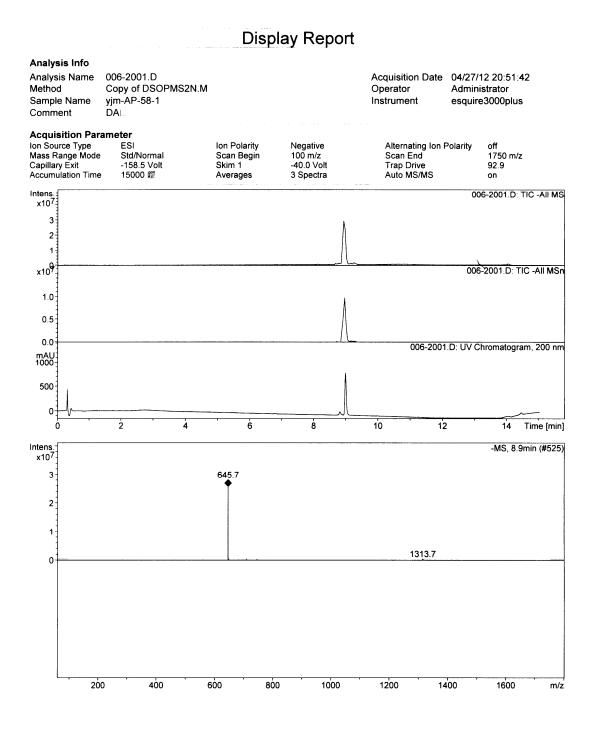


# Figure S35. ESI(+)MS spectrum for aphanamene H (4).



Bruker Daltonics DataAnalysis 3.1 printed: 04/28/12 09:43:42 Page 1 of 1

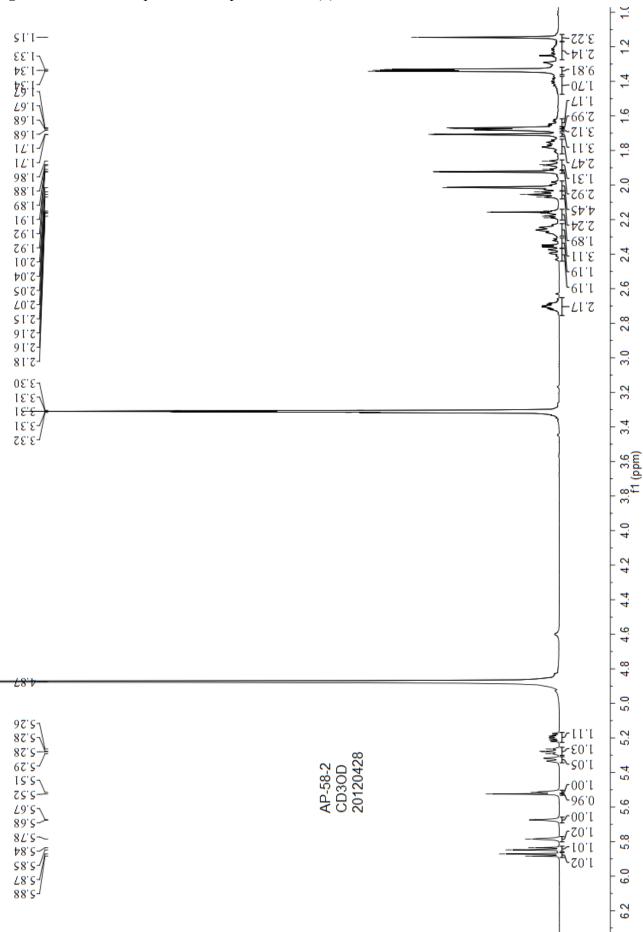
# Figure S36. ESI(-)MS spectrum for aphanamene H (4).



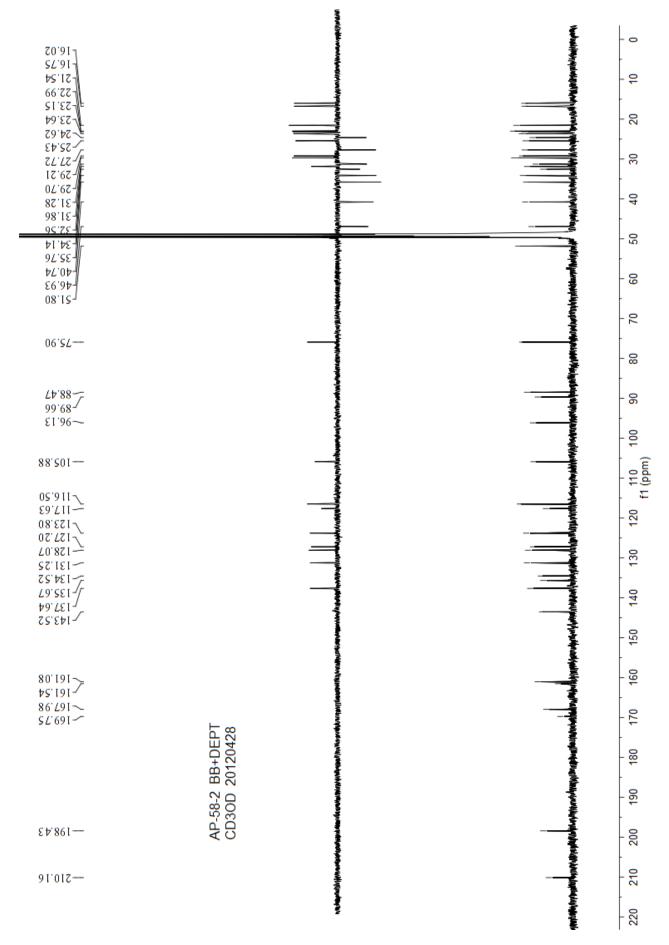
Bruker Daltonics DataAnalysis 3.1 printed: 04/28/12 09:17:32 Page 1 of 1

# Figure S37. HRESI(+)MS spectrum for aphanamene H (4).

Eler	nenta	al Coi	nposi	tion F	Report	:											Ра	ige 1
Tole Elerr	rance nent p	= 3.0 redicti	PPM on: Off pe peal	/ DBE	E: min = d for i-l		,	= 50.0										
173 f Elem		a(e) eva	aluated				limits (ı	up to 50 LC	best is T PXE	·	matche	es for e	each m	ass)				iy-2012 3:21:50
AP_5	8_1p 2	8 (0.600	)) <b>AM</b> 2 (	Ar,1000	0.0,0.00,	1.00); /	ABS; Cr	n (25:39)									1: TOF M	
100	1										669.3	3765					0.7	50.002
												706.47	709					
%	131.55	67								647.3		7	07.4746 721.480	55			96'	2.5396
0	150	200	250	331 300	.1797 350	400	450	503.867 500	6 550	610.41 600	37 650	700	750	800	860.61 850	90 888. 900	6751 007 950	— m/z
	.mum:	200	230	500	5.0	400	3.0	-	1.5 0.0	000	000	100	/ 50	000	000	500	500	
Mass	5	Ca	lc. Ma	SS	mDa		PPM	D	BE	i-:	FIT	i	-FIT	(Norm)	Form	ıla		
669.	3765	66	9.3767		-0.2	2	-0.3	1	3.5	13	.8	С	.0		C40	H54	07 Na	ì



**Figure S38.** <sup>1</sup>H NMR spectrum for aphanamene I (**5**) in CD<sub>3</sub>OD.



**Figure S39.** <sup>13</sup>C NMR spectrum for aphanamene I (**5**) in CD<sub>3</sub>OD.

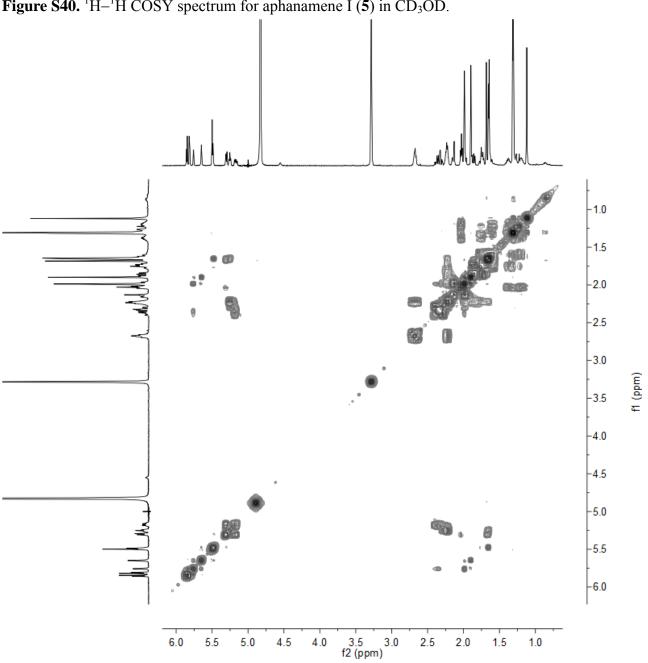


Figure S41. HSQC spectrum for aphanamene I (5) in CD<sub>3</sub>OD.

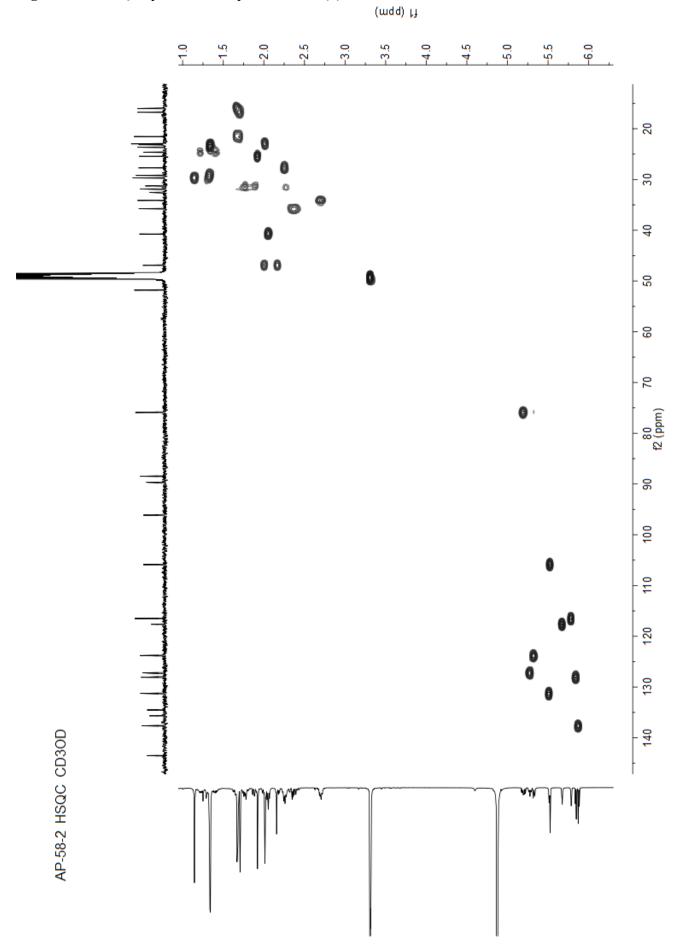
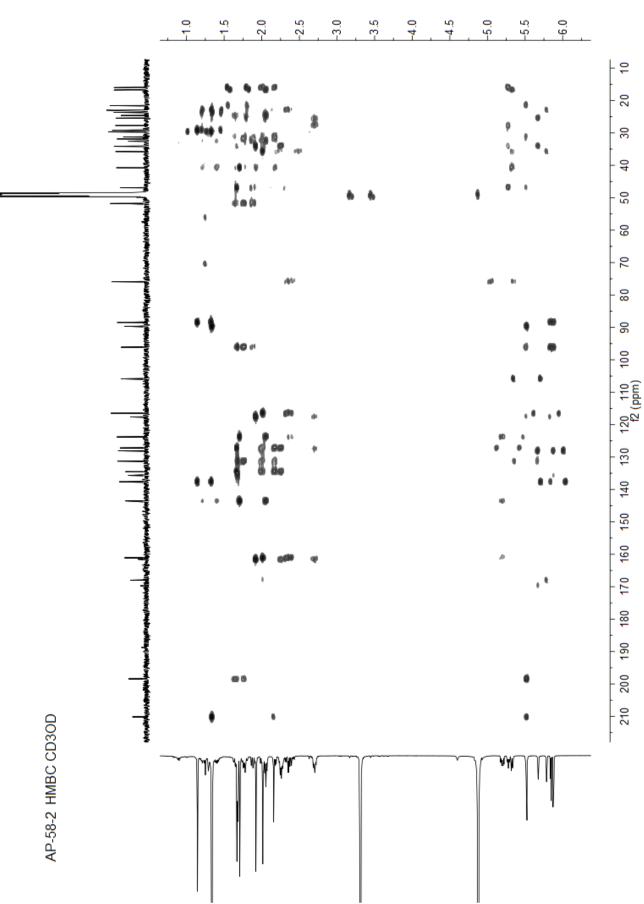
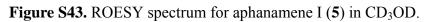
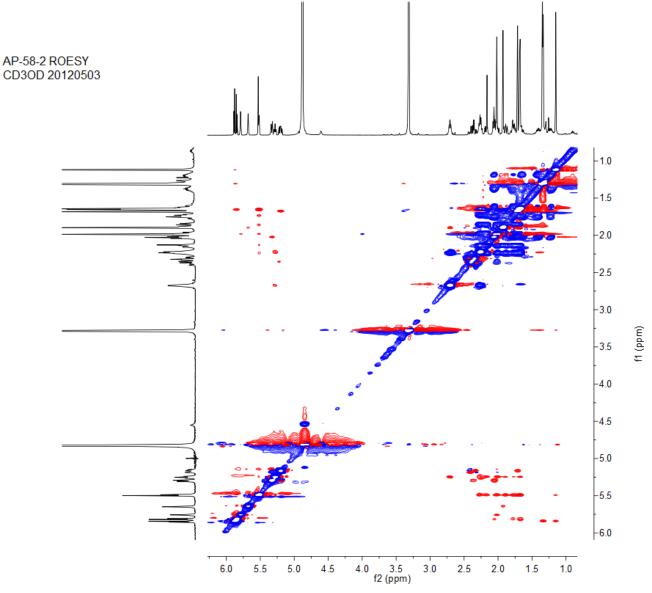


Figure S42. HMBC spectrum for aphanamene I (5) in CD<sub>3</sub>OD.

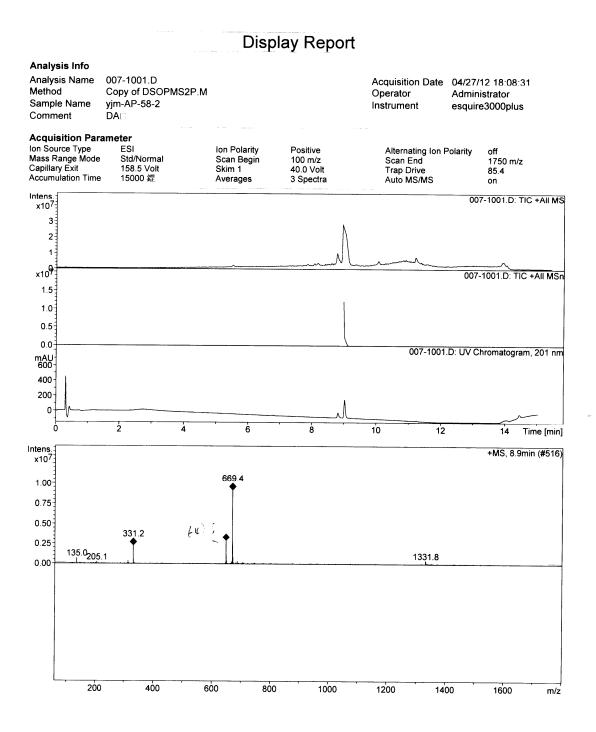


(udd) µ



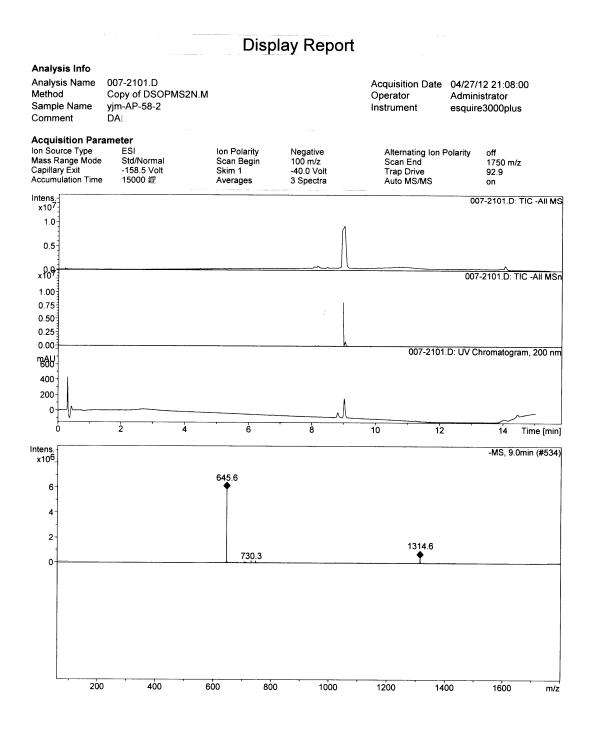


# Figure S44. ESI(+)MS spectrum for aphanamene I (5).



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# Figure S45. ESI(-)MS spectrum for aphanamene I (5).



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# Figure S46. HRESI(+)MS spectrum for aphanamene I (5).

#### **Elemental Composition Report**

Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 173 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-80 H: 1-110 O: 0-30 Na: 1-1

#### AP-58-2

#### LCT PXE KE324

AP-58-2\_20120504 71 (1.555) AM2 (Ar,12000.0,0.00,0.70); ABS; Cm (53:84)

# 04-May-2012 13:42:14 1: TOF MS ES+ 3.79e+004

100				0.3792								
						706.47	17 720.4868					
%			×.,		647.3963	1 1	721.4893 722.4867	004 5070				
131.5587	218.1178	338.2338	372.2426	496.2693	610.4102			864.5076 93	2.5142			
100	200	300	400	500	600	700	800	900		— m/z 1000		
Minimum: Maximum:		5.0	5.0	-1.5 50.0								
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-	FIT (Norm)	Formula				
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#### Page 1

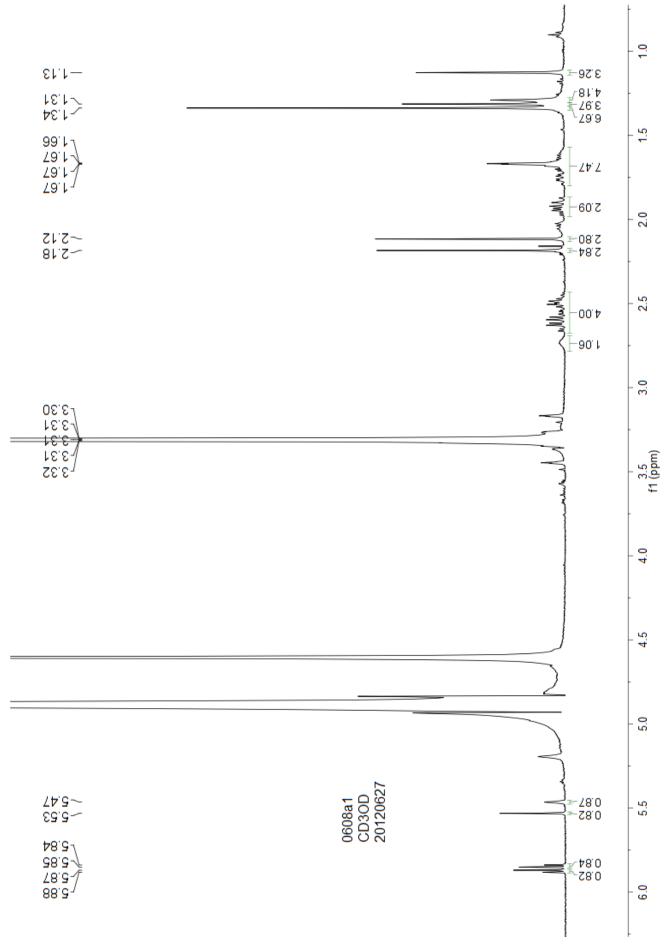


Figure S47. <sup>1</sup>H NMR spectrum for 4a in CD<sub>3</sub>OD.

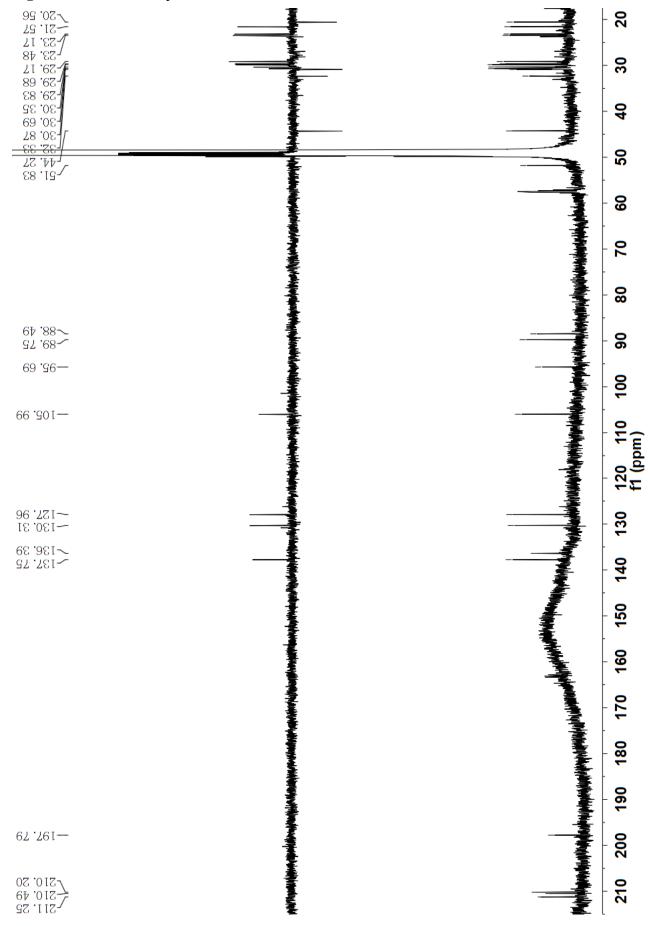
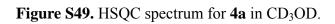


Figure S48. <sup>13</sup>C NMR spectrum for 4a in CD<sub>3</sub>OD.



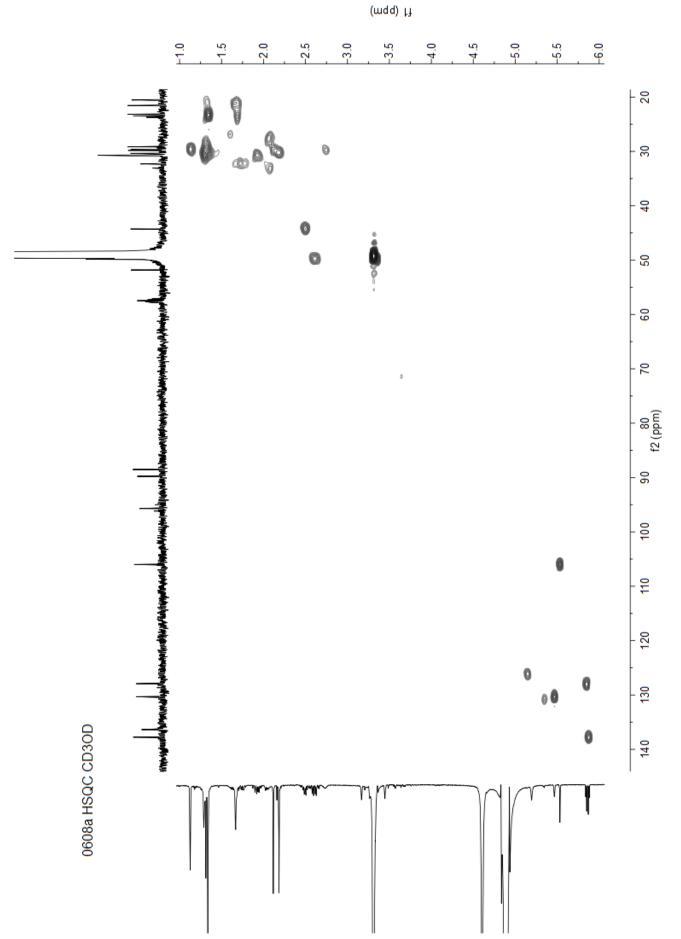
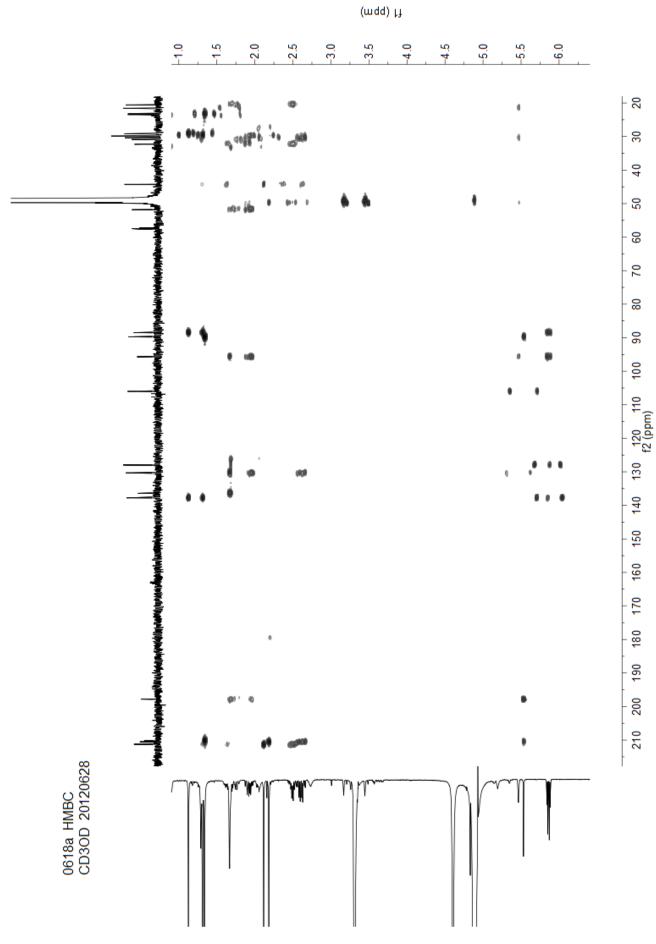
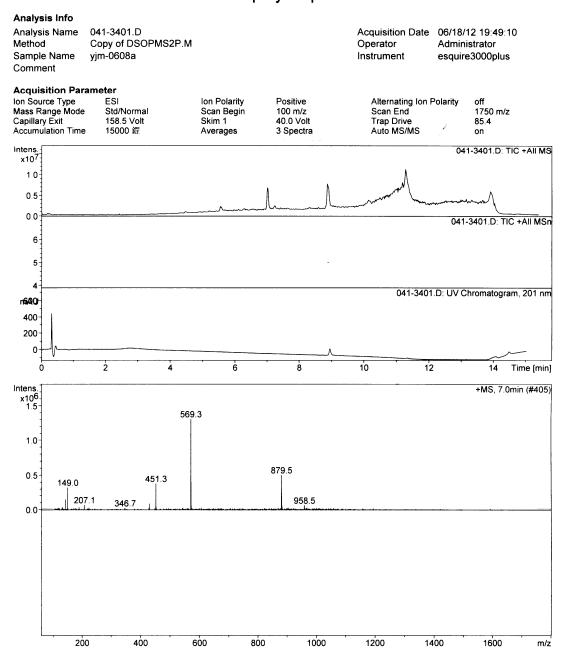


Figure S50. HMBC spectrum for 4a in CD<sub>3</sub>OD.



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# Figure S51. ESI(+)MS spectrum for 4a.



# **Display Report**

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Elemental	Composition	Report
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Single Mass Analysis Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 179 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 10-60 H: 1-110 O: 0-30 Na: 0-1 LCT PXE KE324

100

0608a 69 (1.481) AM2 (Ar,12000.0,0.00,0.70); ABS; Cm (50:86)

488.3376

11-Jun-2012 09:09:34 1: TOF MS ES+ 6.55e+004

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Page 1

879.5071

%			489.341	12							880.	5110		
0	429.2646	451.2466	503.3	3571 544.36	94	642.5106	729	9.4004 7	8 83.4468 80	57.5250 09.5206	881. 882	5133 2.5157	964.4	877
350	400	450	500	550	600	650	700	750	800	850	90		950	m/z 1000
Minimum: Maximum:			3.0	3.0		-1.5 50.0								
Mass	Calc.	Mass	mDa	PPM		DBE	i-F]	ΓT	i-FIT	(Norm)	Form	ula		
451.2466	451.24	160	0.6	1.3		8.5	27.9	)	0.0		C26	Н36	05	Na

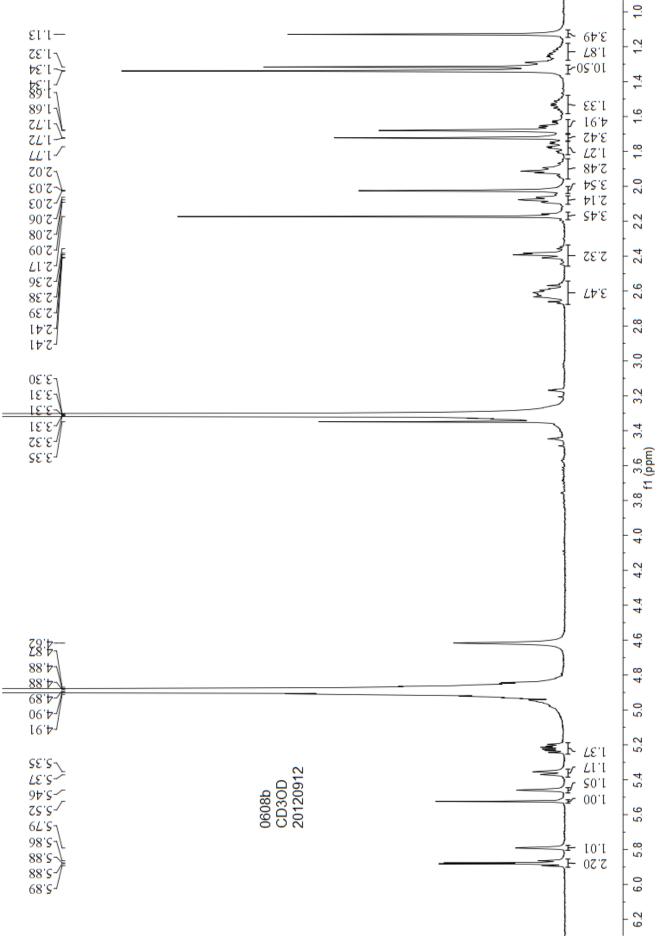


Figure S53. <sup>1</sup>H NMR spectrum for 4b in CD<sub>3</sub>OD.

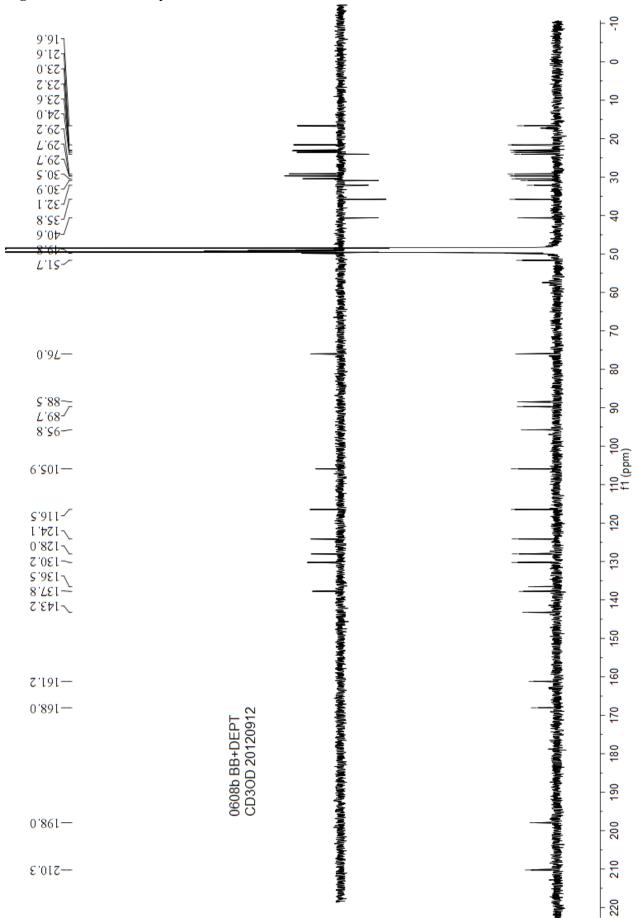
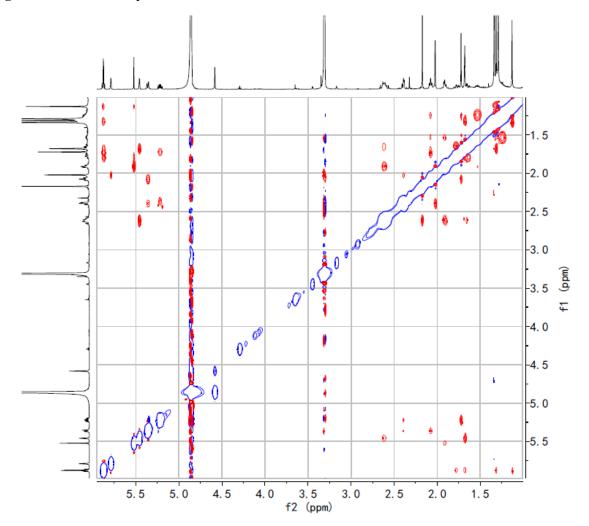
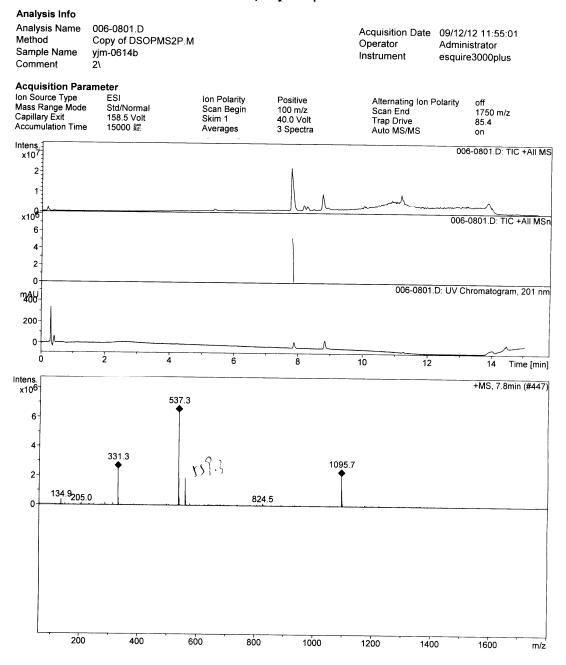


Figure S54. <sup>13</sup>C NMR spectrum for 4b in CD<sub>3</sub>OD.

Figure S55. NOESY spectrum for 4b in CD<sub>3</sub>OD.



# Figure S56. ESI(+)MS spectrum for 4b.



# **Display Report**

Bruker Daltonics DataAnalysis 3.1

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# Figure S57. HRESI(+)MS spectrum for 4b.

#### **Elemental Composition Report** Page 1

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Single Mass Analysis Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron lons 268 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 6-60 H: 2-110 O: 0-30 Na: 0-1 0614b LCT PXE KE324

0614b				LCT PXE H	<b>(E324</b>					14	4-Sep-2012
0614b_2012	0914 14 (0.283) AM	2 (Ar,10000.0,0	.00,1.00); ABS	S; Cm (5:23)							10:51:02 F MS ES+
100-				559.3	040 610.4112						2.10e+004
%					611.4158						
105.04	<sup>141</sup> 212.1196	342.1689	400.2461	559.1630	612.4182	748.4346	837.45	52 8	95.5369		5503
0 105.04 100	<sup>141</sup> 212.1196 200	342.1689 300	400.2461 400	559.1630 500	612.4182 600	748.4346	837.45 800	52 8	95.5369		.5503 m/z 1000
0	212.1196	· · · · · · · · · · · · · · · · · · ·		<u></u>		·····		52 8			m/z
0 100 Minimum:	212.1196	300	400	<b>500</b> -1.5		·····		-	900		m/z

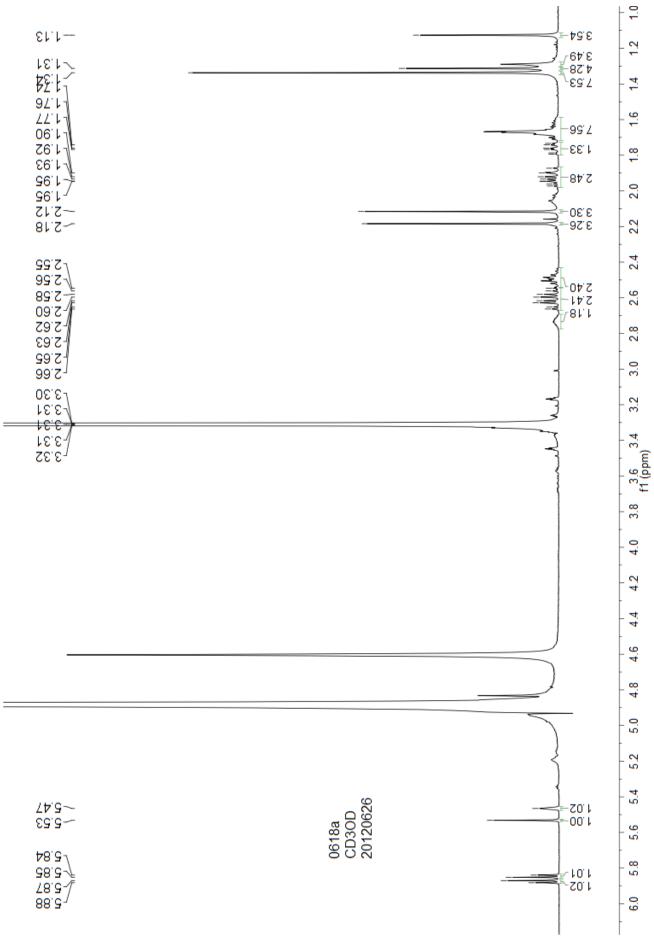


Figure S58. <sup>1</sup>H NMR spectrum for 5a in CD<sub>3</sub>OD.

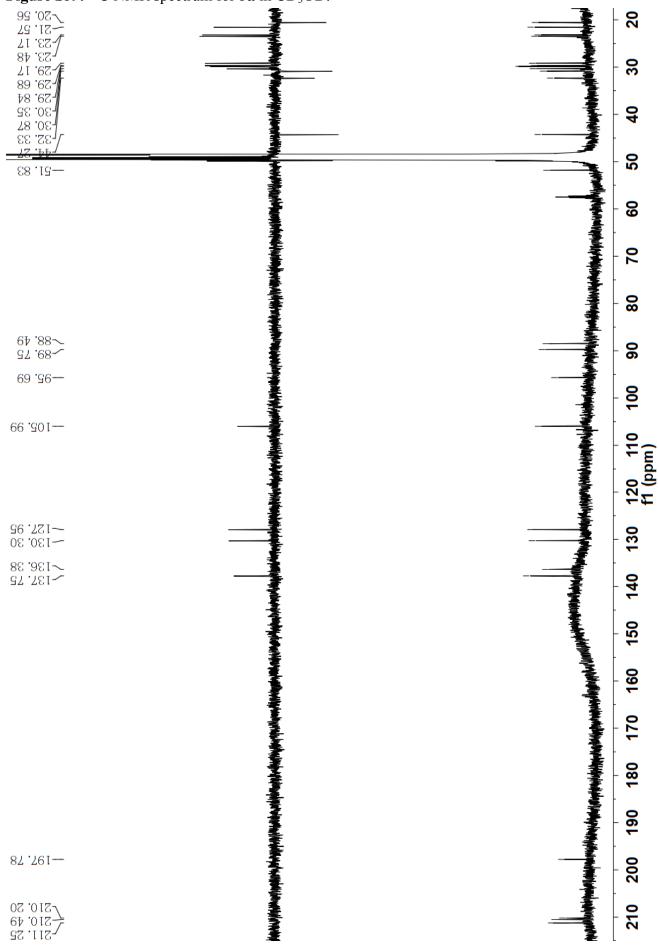
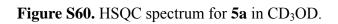


Figure S59. <sup>13</sup>C NMR spectrum for 5a in CD<sub>3</sub>OD.



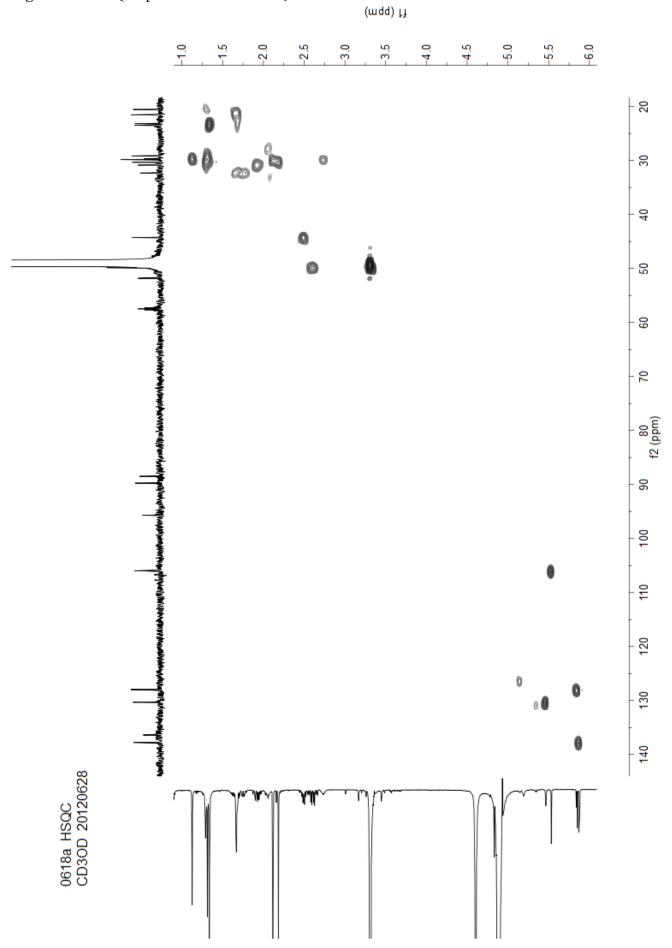
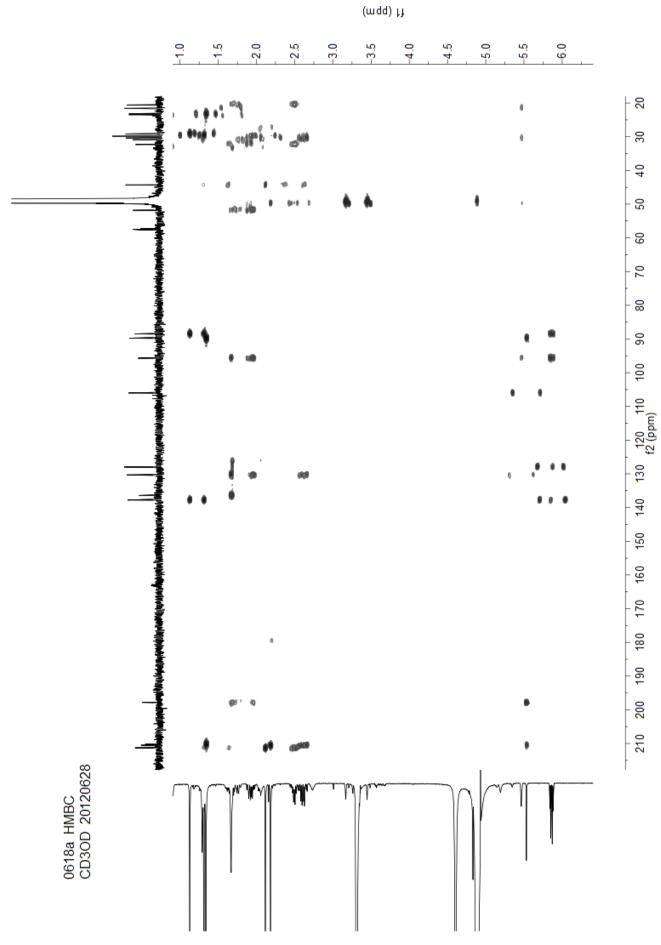
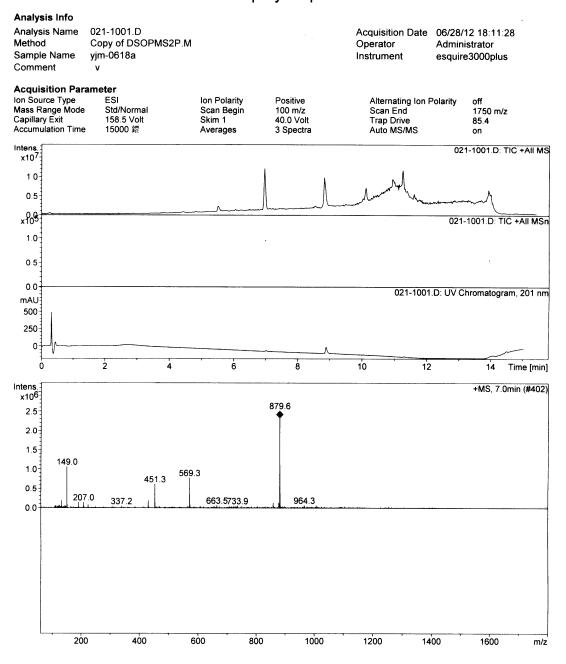


Figure S61. HMBC spectrum for 5a in CD<sub>3</sub>OD.



# Figure S62. ESI(+)MS spectrum for 5a.



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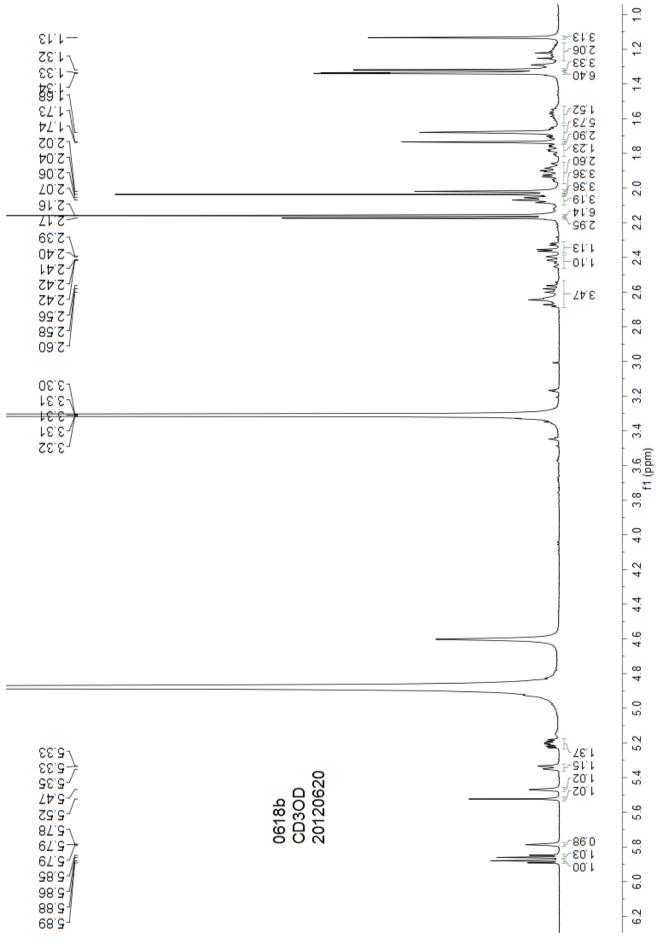
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# Figure S63. HRESI(+)MS spectrum for 5a.

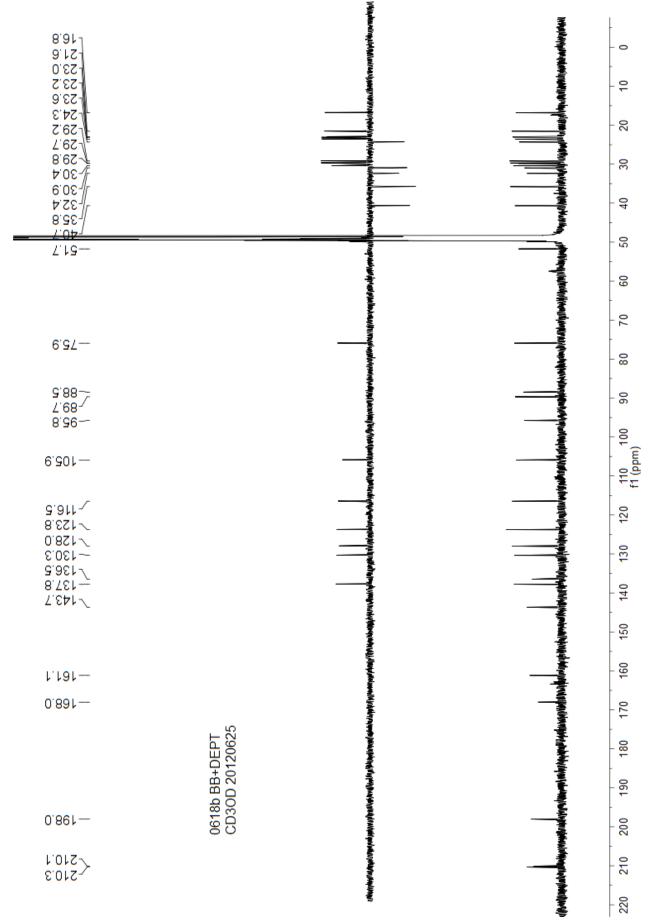
451.2455 451.2460 -0.5 -1.1

Elemental Composition	Report			Page 1
Single Mass Analysis Tolerance = 3.0 PPM / DB Element prediction: Off Number of isotope peaks use	Ξ: min = -1.5, max = 50.0 ed for i-FIT = 3	:		
Monoisotopic Mass, Even Electr 185 formula(e) evaluated with 1 Elements Used: C: 6-60 H: 2-110 O: 0-30	on lons results within limits (up to 50 closest Na: 0-1	results for each mass)		
LJ	LCT PXE KE	324		19-Jul-2012
0618a_20120719 28 (0.600) AM2 (A	r,12500.0,0.00,0.70); ABS; Cm (21:44)		1: <b>T</b>	13:59:20 OF MS ES+
100			8	2.77e+004 79.5030
			-	880.5068
				000.0000
%				
492 2716				
451.2455	3.2778 581.3658 669.410	3 683 3605 727.3672	799 4420 857.51	99
40		3 683.3605 727.3672 675 700 725 750	799.4420 857.519 775 800 825 850	99 m/z 875
451.2455 493	581.3658 669.410	3 683.3605	700.1420	m/z
451.2455         493           0         400         425         450         475         500	581.3658         669.410           525         550         575         600         625         650	3 683.3605	700.1420	m/z

8.5 16.1 0.0 C26 H36 O5 Na



# Figure S64. <sup>1</sup>H NMR spectrum for 5b in CD<sub>3</sub>OD.



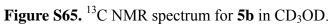
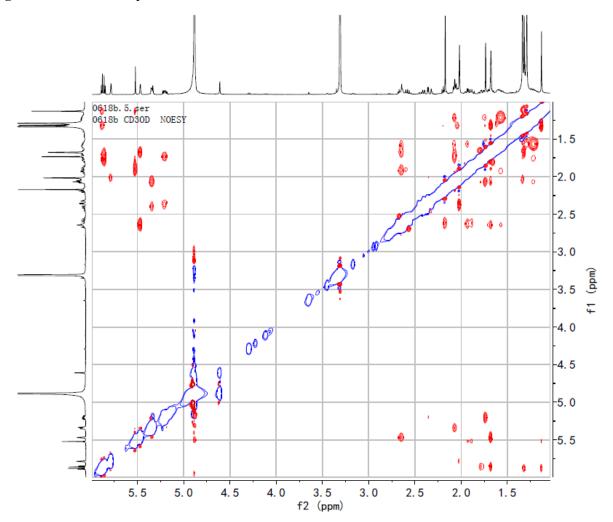
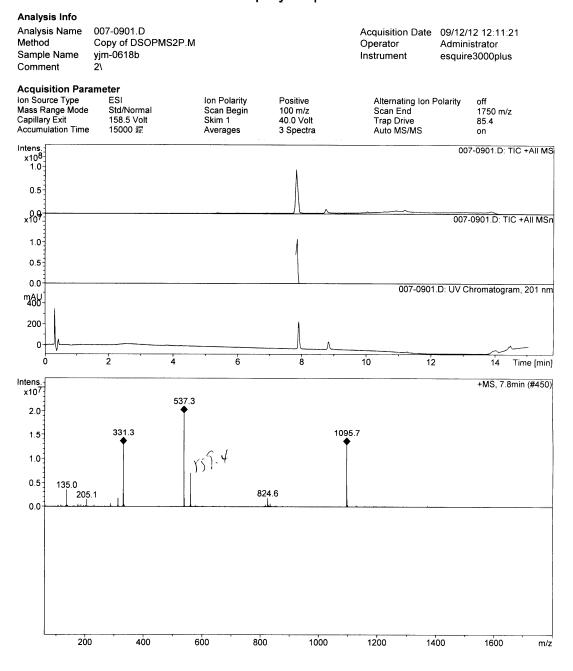


Figure S66. NOESY spectrum for 5b in CD<sub>3</sub>OD.



# Figure S67. ESI(+)MS spectrum for 5b.



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# Figure S68. HRESI(+)MS spectrum for 5b.

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Elemental	Compositio	n Report							Page 1
Tolerance = Element pre		)BE: min = - ised for i-FI1		50.0					
268 formula( Elements Us	c Mass, Even Ele e) evaluated with ed: : 2-110 O: 0-3	1 results with	hin limits (up	to 50 close		ch mass)			14-Sep-2012 10:56:07
0618b_20120	914 28 (0.583) AM	2 (Ar,10000.0,0	0.00,1.00); AB	S; Cm (6:29)				1:	TOF MS ES+ 2.27e+004
100				559.	3035				
%				537.3210	610.4113 611.4153 612.4171		007.4504		
0 105.043	· · · · · · · · · · · · · · · · · · ·	331.1099.3	59.2324	.2958	$[ ] \\ [ \\ [$	748.43	<del>,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</del>	895.54	<sup>07</sup> 949.5905 m/z
	200	300	400	500	600	700	800	900	1000
Minimum: Maximum:		3.0	2.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm) Form	nula	
559.3035	559.3036	-0.1	-0.2	11.5	75.6	0.0	C33	Н44 С	06 Na