Supporting Information for

Antimalarial diterpenoid dimers of a new carbon skeleton from *Aphanamixis grandifolia*

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Figure S20. HRESI(+)MS spectrum for aphadilactone F (**2**).

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Figure S58. ^{1}H NMR spectrum for **5a** in CD_3OD.

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

Figure S64. ^{1}H NMR spectrum for **5b** in CD_3OD.
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Figure S66. NOESY spectrum for **5b** in CD_3OD.
Figure S67. ESI(+)MS spectrum for **5b**.
Figure S68. HRESI(+)MS spectrum for **5b**.

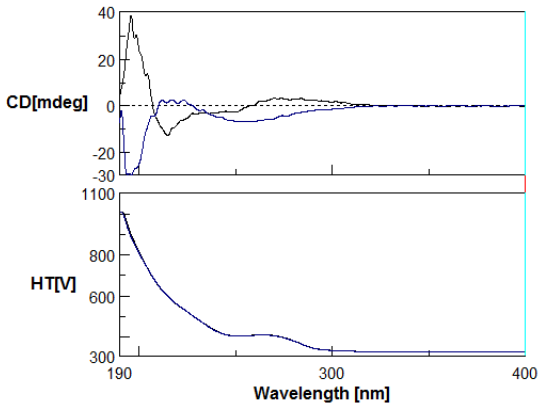
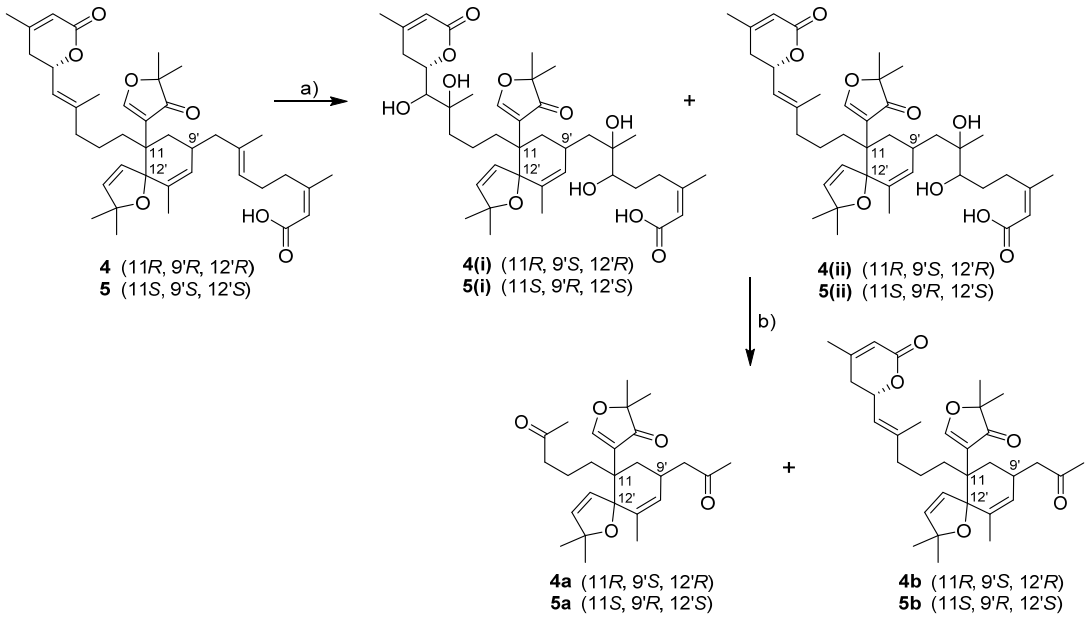
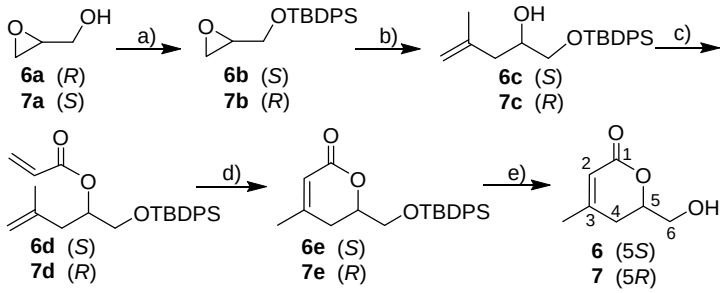


Figure S1. Experimental ECD spectra of **4** (black) and **5** (blue).



Scheme S1. Oxidative degradation of compounds **4**/**5** [Reaction conditions: a) 40 mol % $K_2OsO_4 \cdot 2H_2O$, 40 eq. $MeSO_2NH_2$, 120 eq. $K_3Fe(CN)_6$, 120 eq. K_2CO_3, ^tBuOH-H_2O (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, $CH_3CH(CH_2)MgBr$, THF, −30 to 0 °C; c) $CH_2CHCOCl$, Et_3N, DMAP, CH_2Cl_2, 0 °C; d) Grubbs' catalyst II, CH_2Cl_2, 50 °C; e) Bu_4NF, THF].

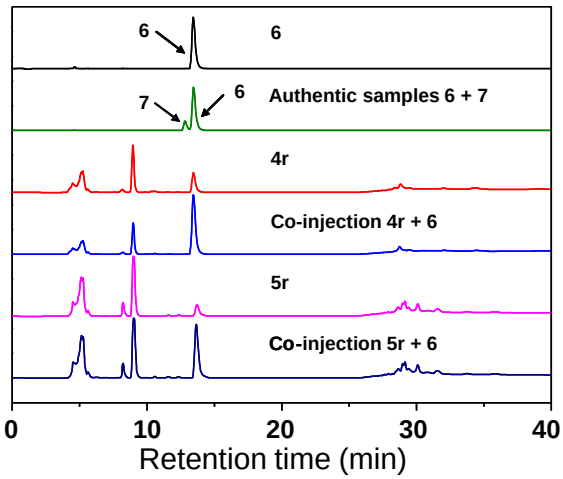


Figure S2. Chiral HPLC analysis of **4r**/**5r** from **4**/**5** and authentic synthetic samples (**6** & **7**)

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 (5*S*,11*S*,11′*S*,5′*S*) and (5*S*,11*R*,11′*R*,5′*S*), respectively.

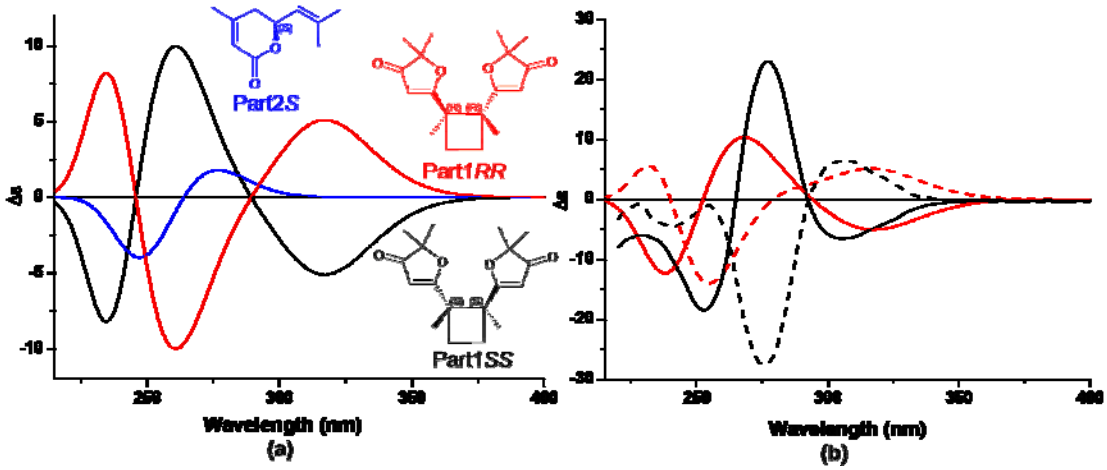


Figure S3. (a) B3LYP/6-311++G(2d,2p)//B3LYP/6-31+G(d) calculated ECD spectra for three structural fragments of **2** and **3**; (b) Experimental ECD spectra (220–400 nm) of **2** (black solid line) and **3** (black dashed line), and linear combination of (Part1*SS* + 2*Part2*S*) (red solid line) and (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.[1] The results showed three lowest energy conformers for Part1*SS* and only one for Part2*S* 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.[2] 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, $\sigma = 0.3$ eV),[3] and the first seven electronic excitations for Part1*SS* and the first two electronic excitations for Part2*S* 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 (ΔG). Theoretical ECD spectrum of Part1*RR* was obtained by directly inversing that of the

corresponding enantiomer Part1*SS*.

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 (σ = 0.3 eV),[3] 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 (ΔG). The theoretical ECD spectrum of **4a** was depicted by directly reversing that of **5a**. The results showed that the ECD spectrum of **4a** matched that of the enantiomer with (11*R*,9′*S*,12′*R*) configuration, and the ECD spectrum of **5a** matched that of the other enantiomer with (11*S*,9′*R*,12′*S*) configuration. Therefore, the absolute configurations of aphanamene H (**4**) and I (**5**) were identified to be (5*S*,11*R*,9′*R*,12′*R*) and (5*S*,11*S*,9′*S*,12′*S*), respectively.

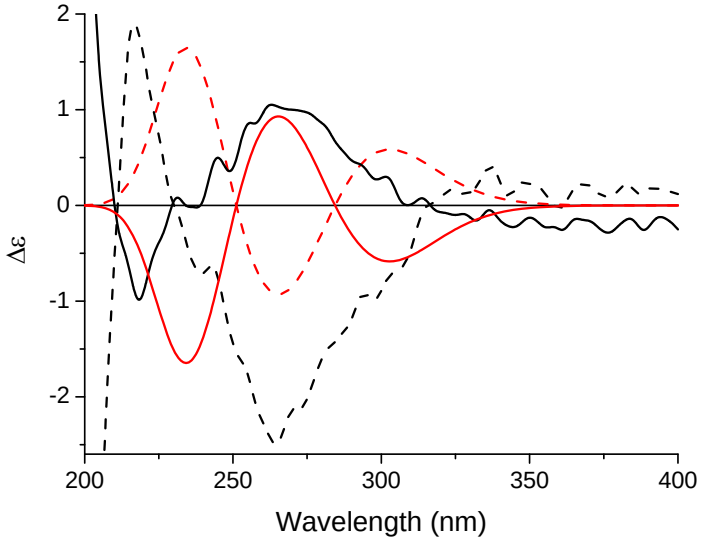


Figure S4. Calculated (red color) ECD spectra of **4a** (solid line) and **5a** (dashed line) versus their experimental (black color) ECD spectra.

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.;

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

Table S1. ^{1}H and ^{13}C NMR data of compounds **4** and **5** in CD_3OD.

Position	**4**		**5**	
	δ_H (mult, J_{HH})	δ_C	δ_H (mult, J_{HH})	δ_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)	
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		210.1
15		89.7		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)	23.2
18	1.79 (m)	31.3	1.79 (m)	31.3
	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)	16.0
20′	1.92 (d, 1.4, 3H)	25.4	1.92 (d, 1.3, 3H)	25.4

Table S2. ^{1}H and ^{13}C NMR data for compounds **4a**, **4b**, **5a**, and **5b** in CD_3OD.

Position	**4a**/**5a**		**4b**		**5b**	
	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)	δ_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

Figure S5. ^{1}H NMR spectrum for aphadilactone E (**1**) in CD_3OD.

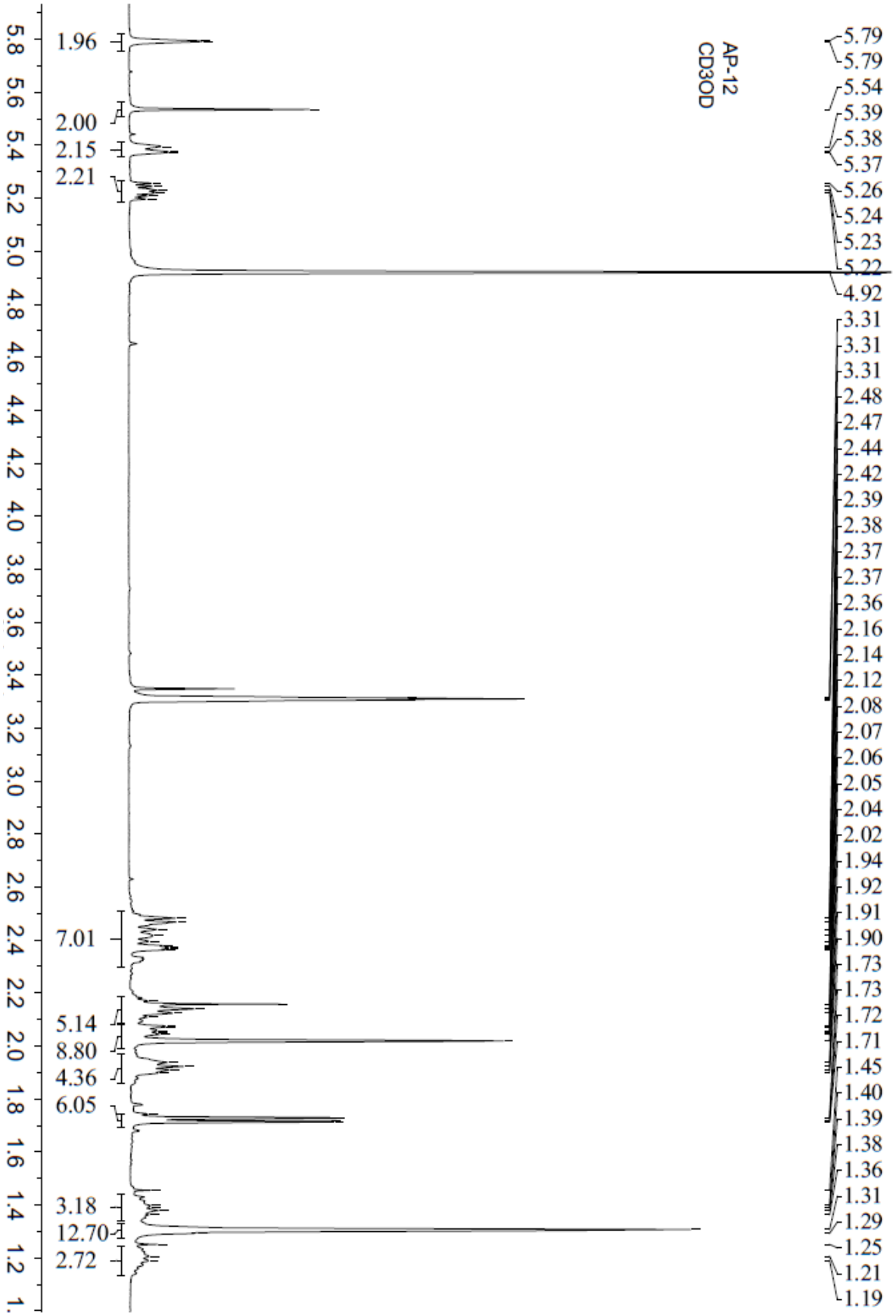


Figure S6. ^{13}C NMR spectrum for aphadilactone E (**1**) in CD_3OD.

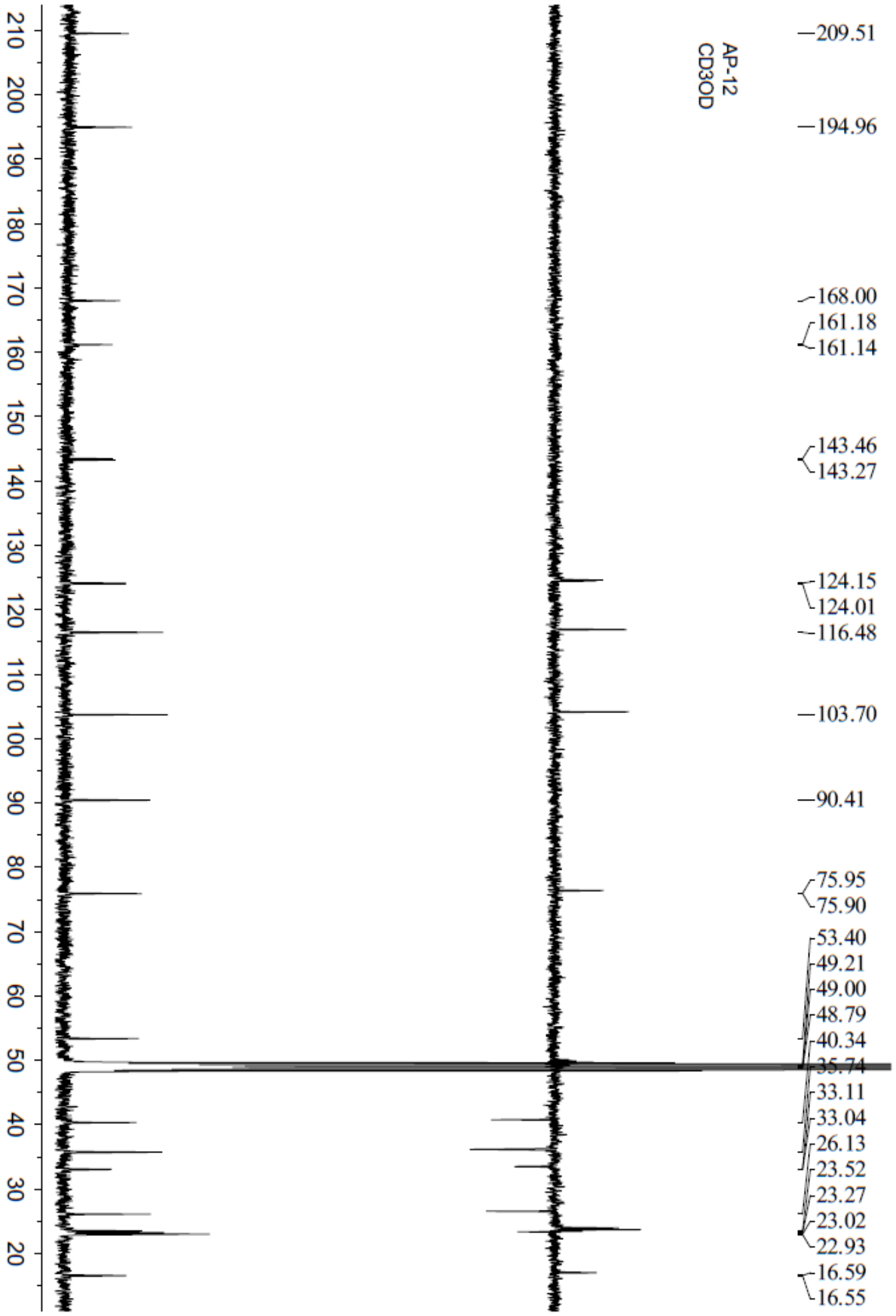


Figure S7. $^{1}H–^{1}H$ COSY spectrum for aphadilactone E (**1**) in CD_3OD.

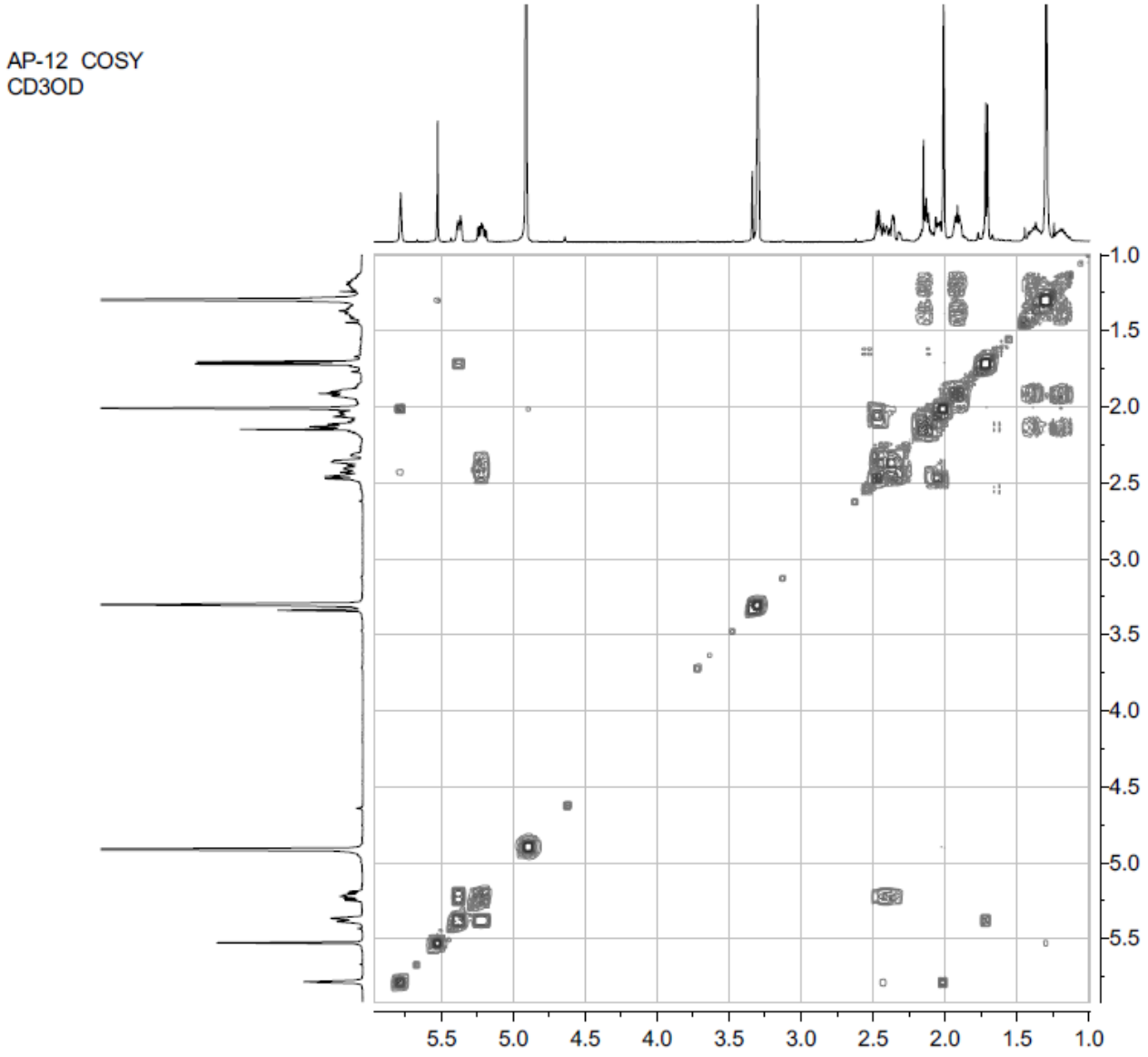


Figure S8. HSQC spectrum for aphadilactone E (**1**) in CD_3OD.

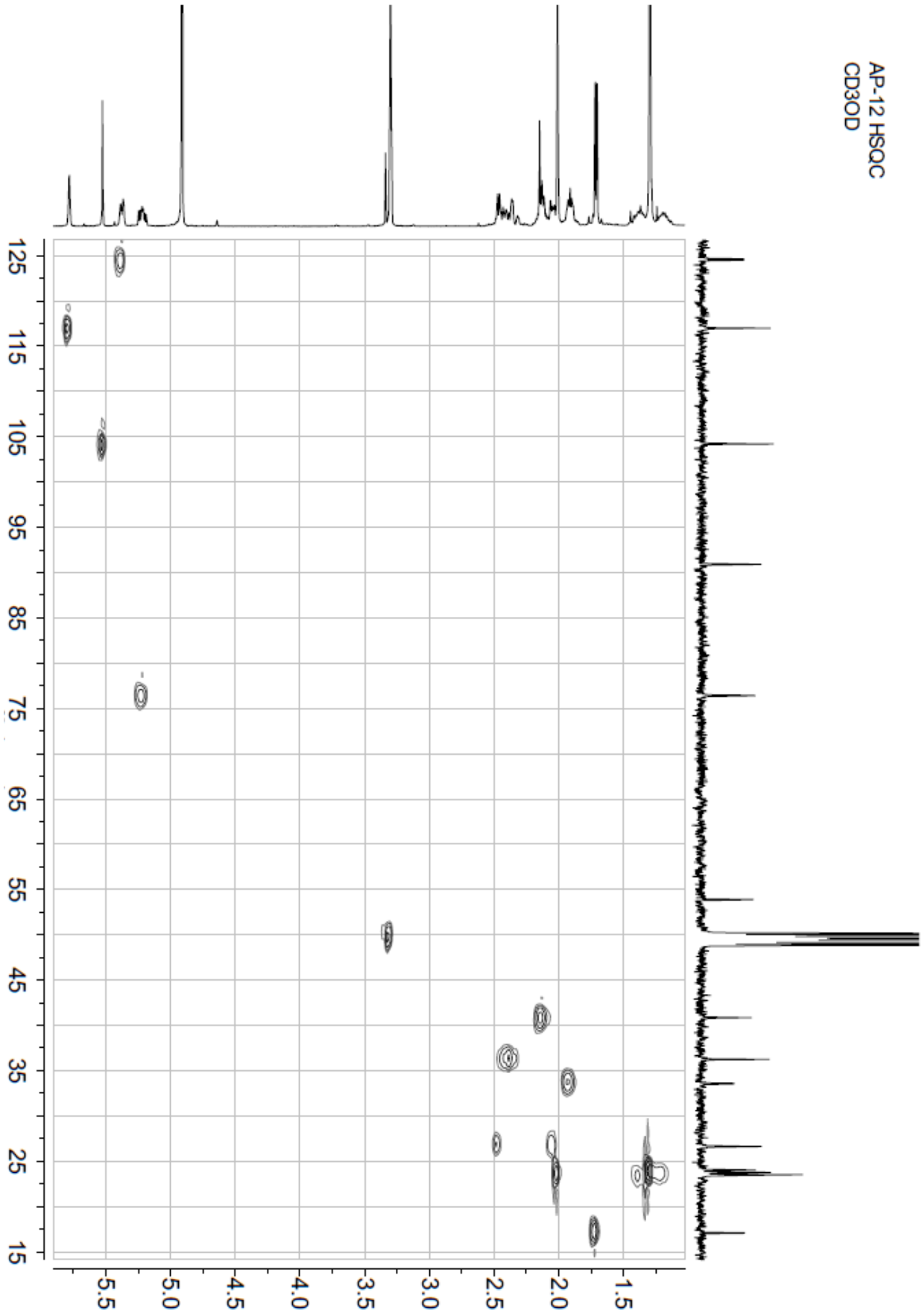


Figure S9. HMBC spectrum for aphadilactone E (**1**) in CD_3OD.

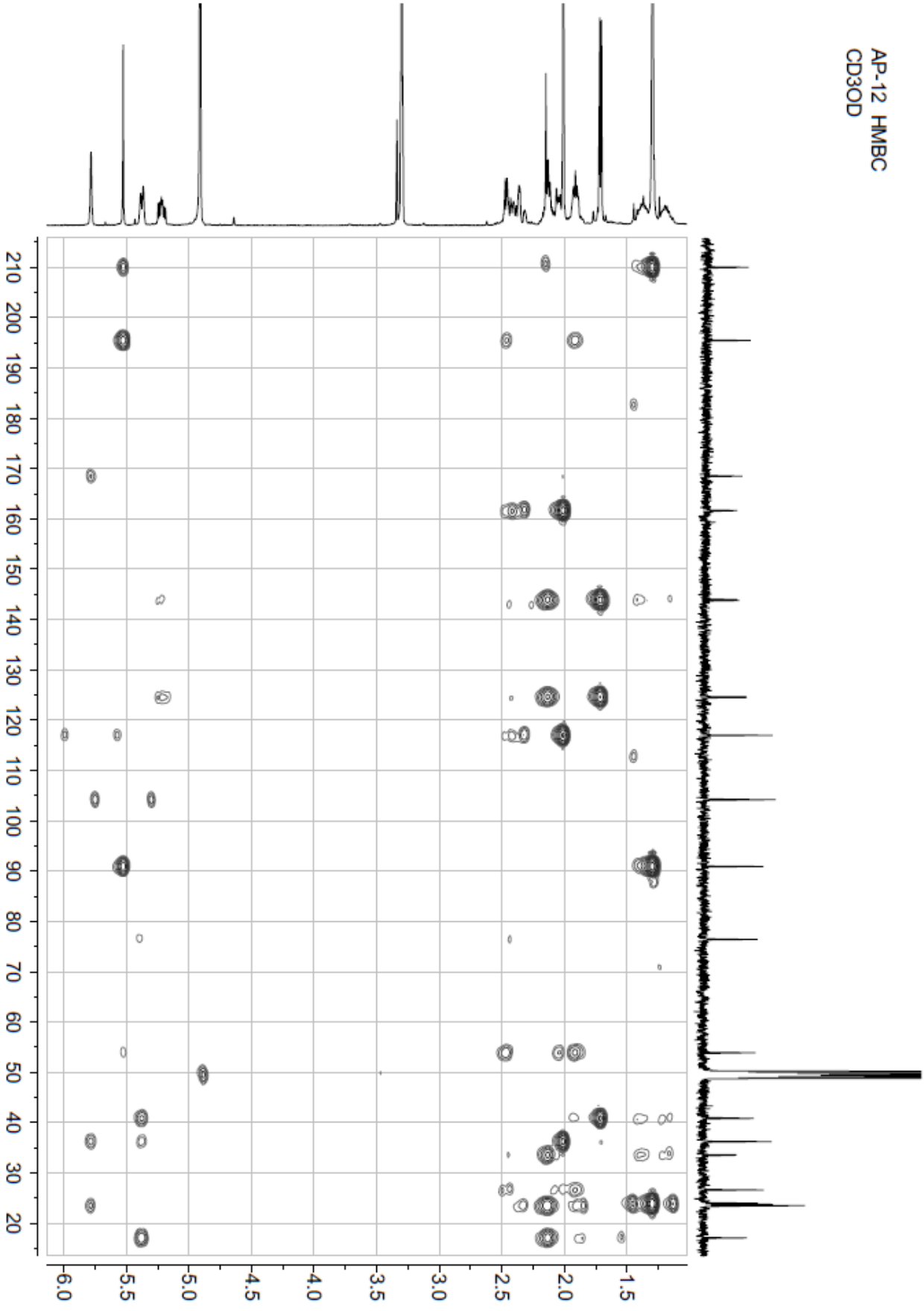


Figure S10. ROESY spectrum for aphadilactone E (**1**) in CD_3OD.

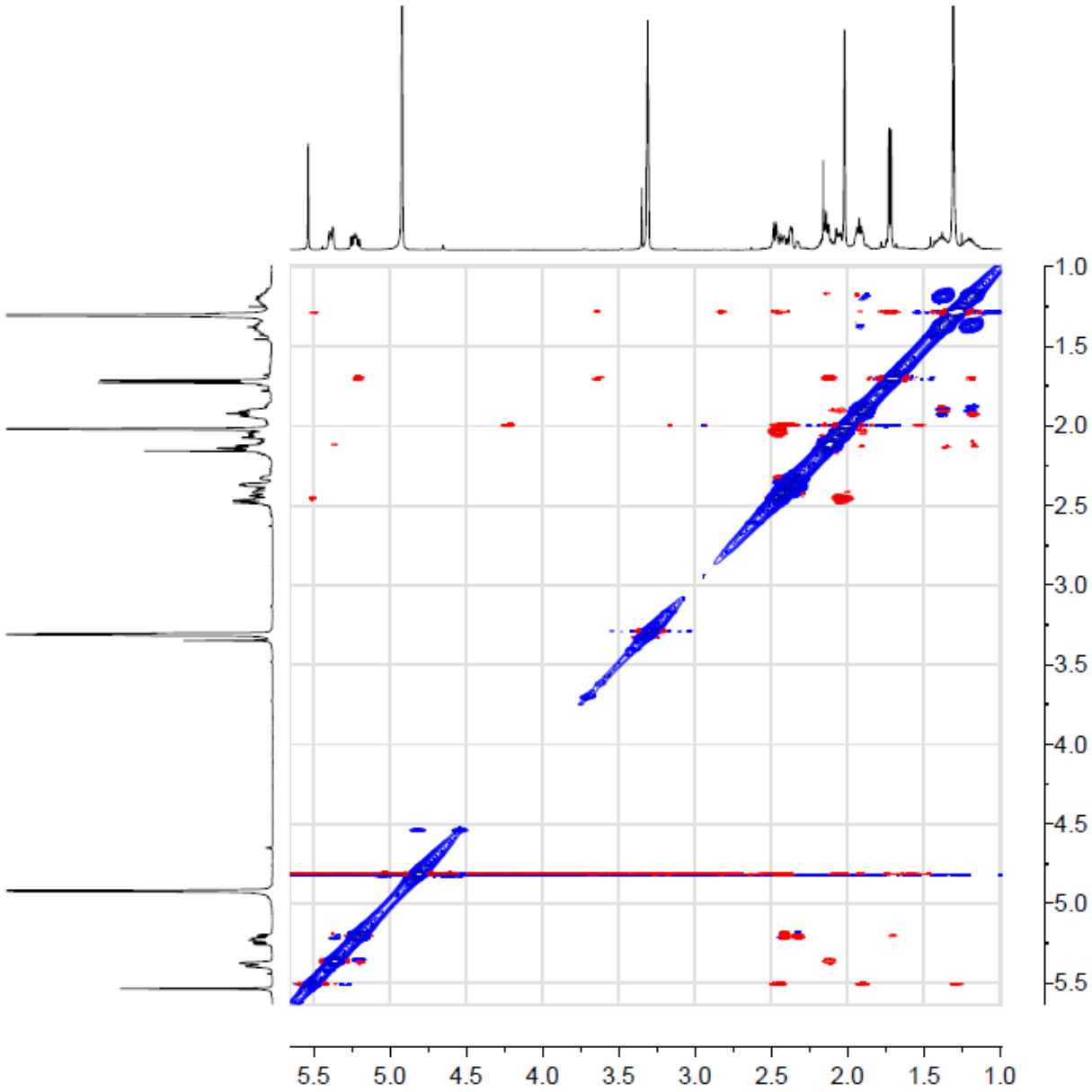


Figure S11. ESI(+)MS spectrum for aphadilactone E (**1**).

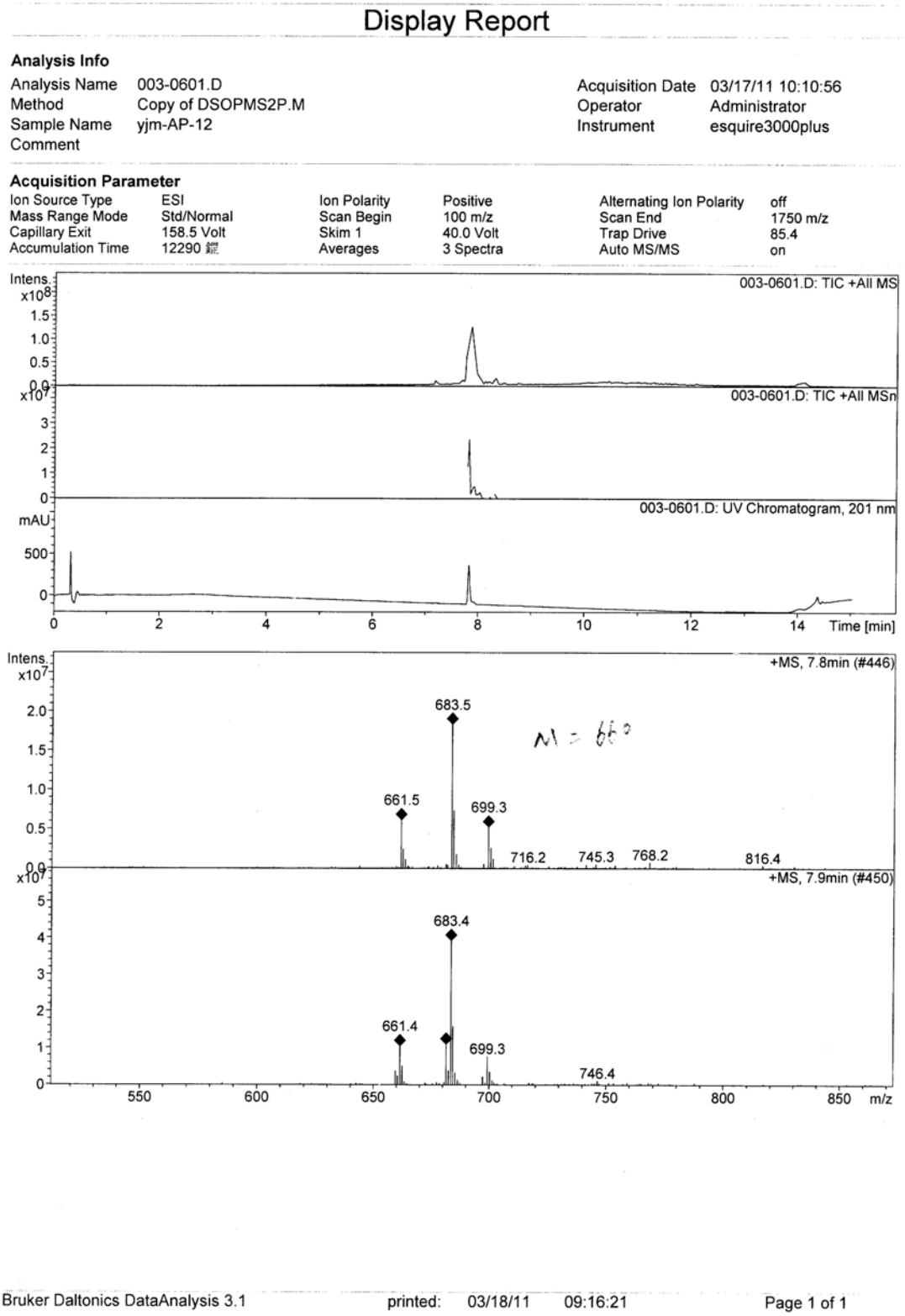


Figure S12. HRESI(+)MS spectrum for aphadilactone E (**1**).

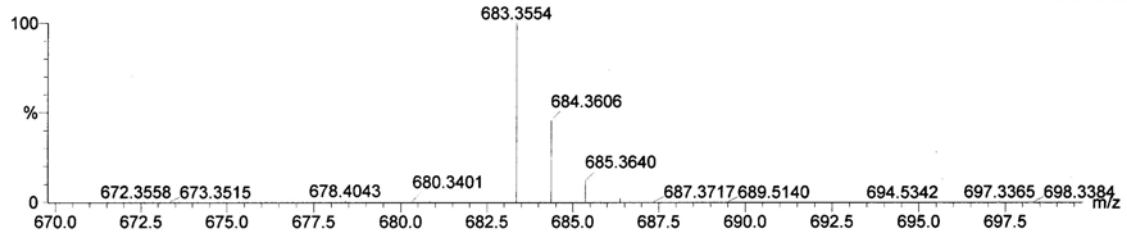
Elemental Composition Report **Page 1**

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

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 16-Oct-2014 09:44:15

AP-12_1016 41 (0.865) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (39:50) 1: TOF MS ES+ 6.36e+004



Minimum:				-1.5			
Maximum:		5.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
683.3554	683.3560	-0.6	-0.9	14.5	116.8	0.0	C40 H52 O8 Na

Figure S13. ^{1}H NMR spectrum for aphadilactone F (**2**) in CD_3OD.

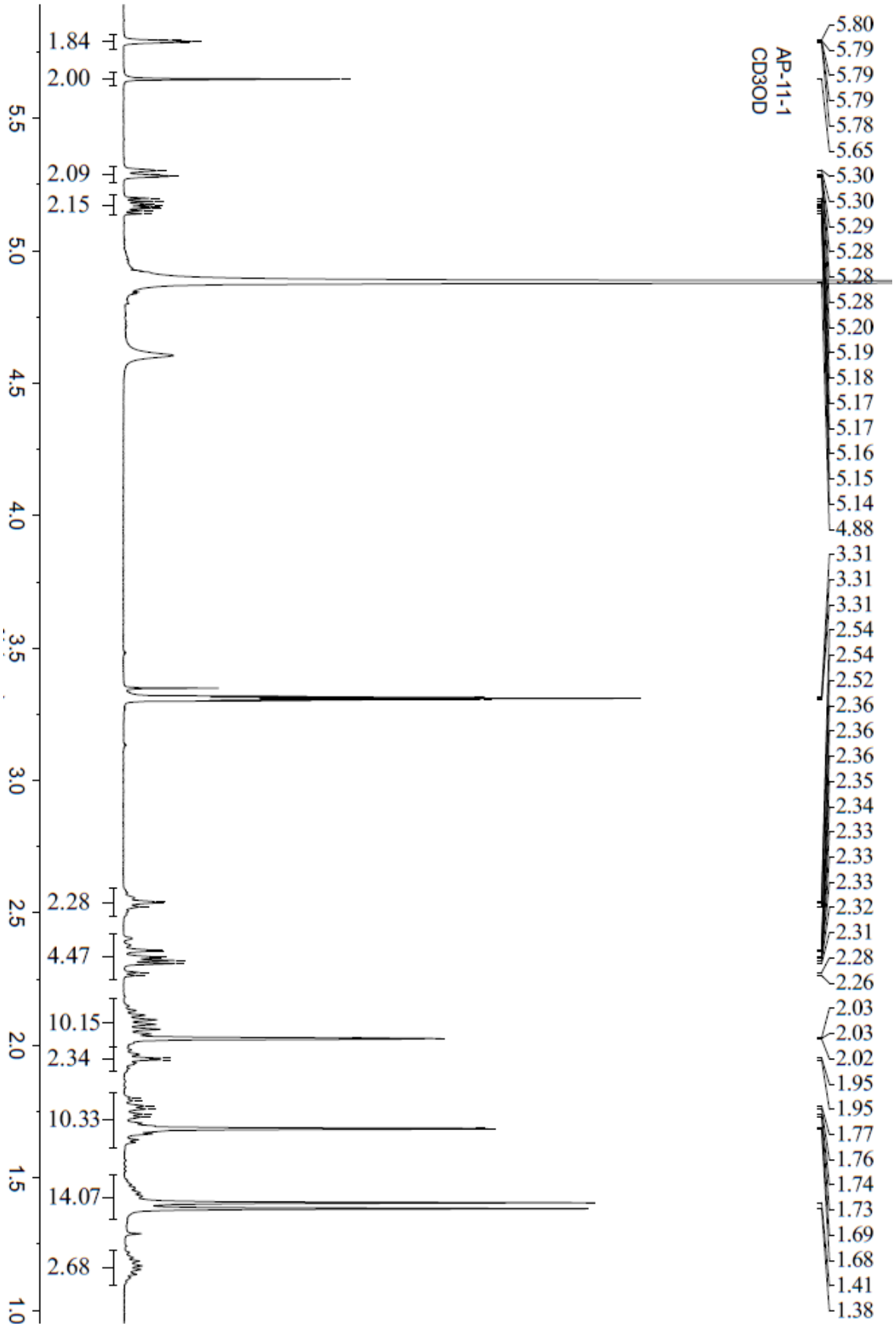


Figure S14. ^{13}C NMR spectrum for aphadilactone F (**2**) in CD_3OD.

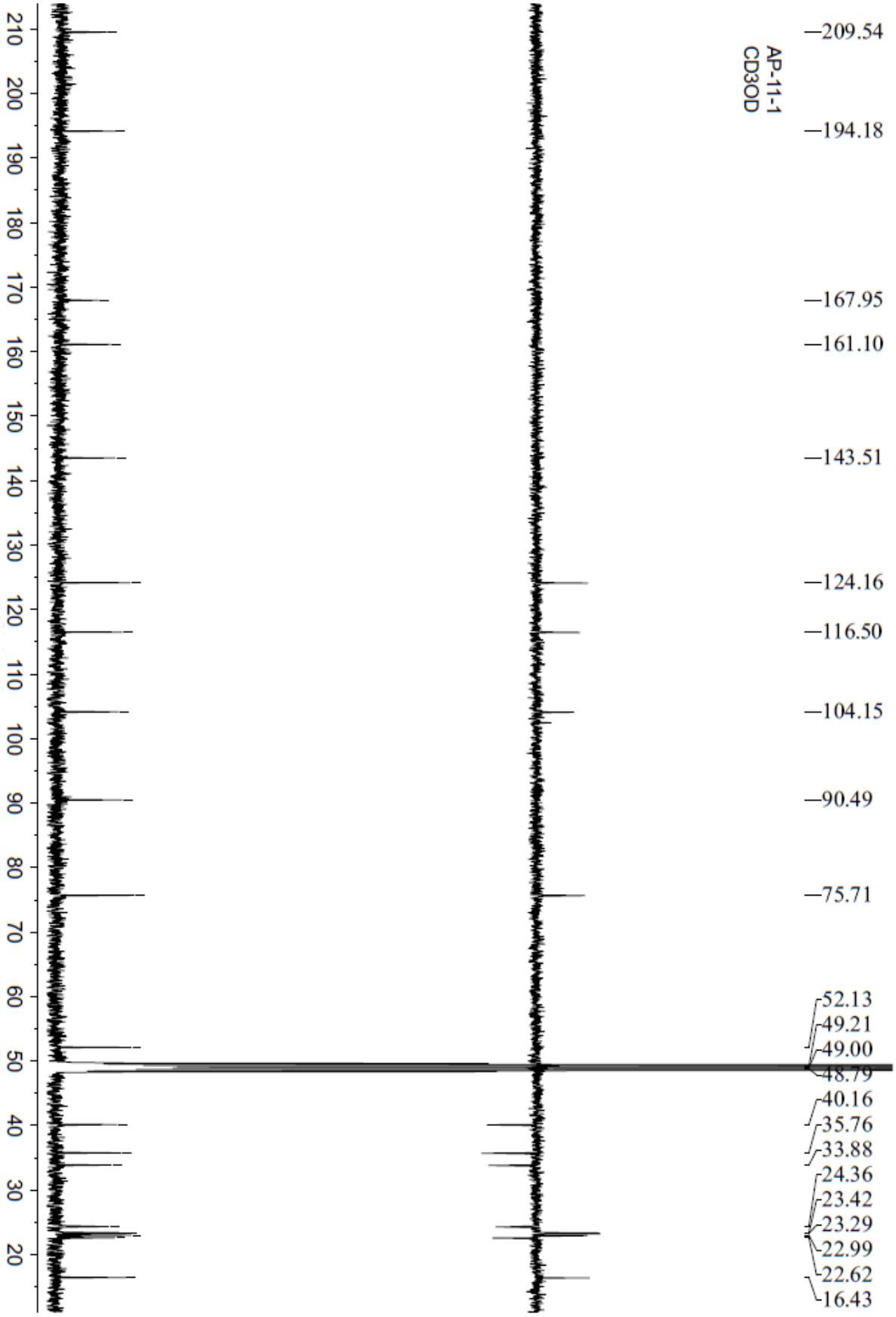


Figure S15. $^{1}H–^{1}H$ COSY spectrum for aphadilactone F (**2**) in CD_3OD.

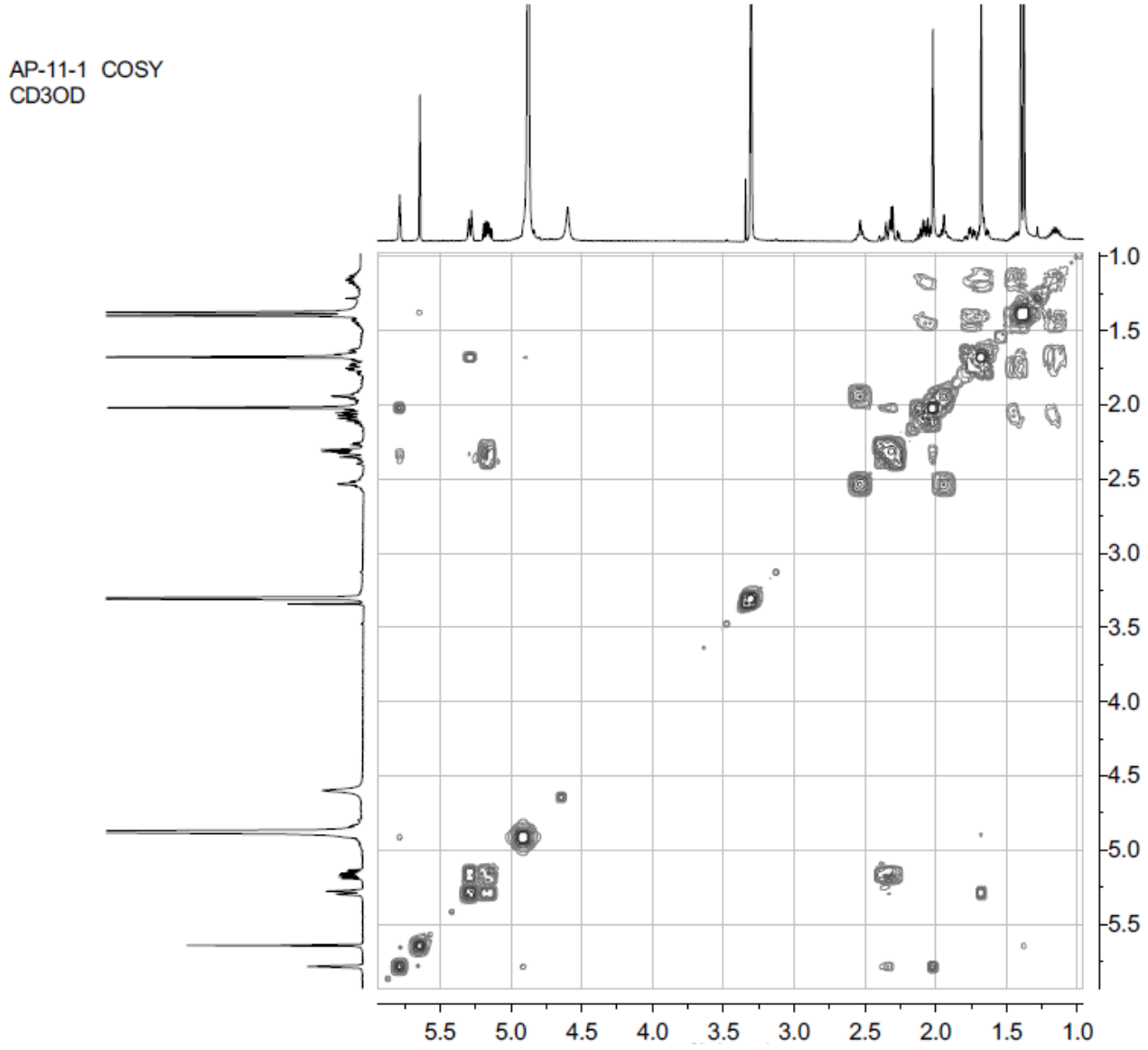


Figure S16. HSQC spectrum for aphadilactone F (**2**) in CD_3OD.

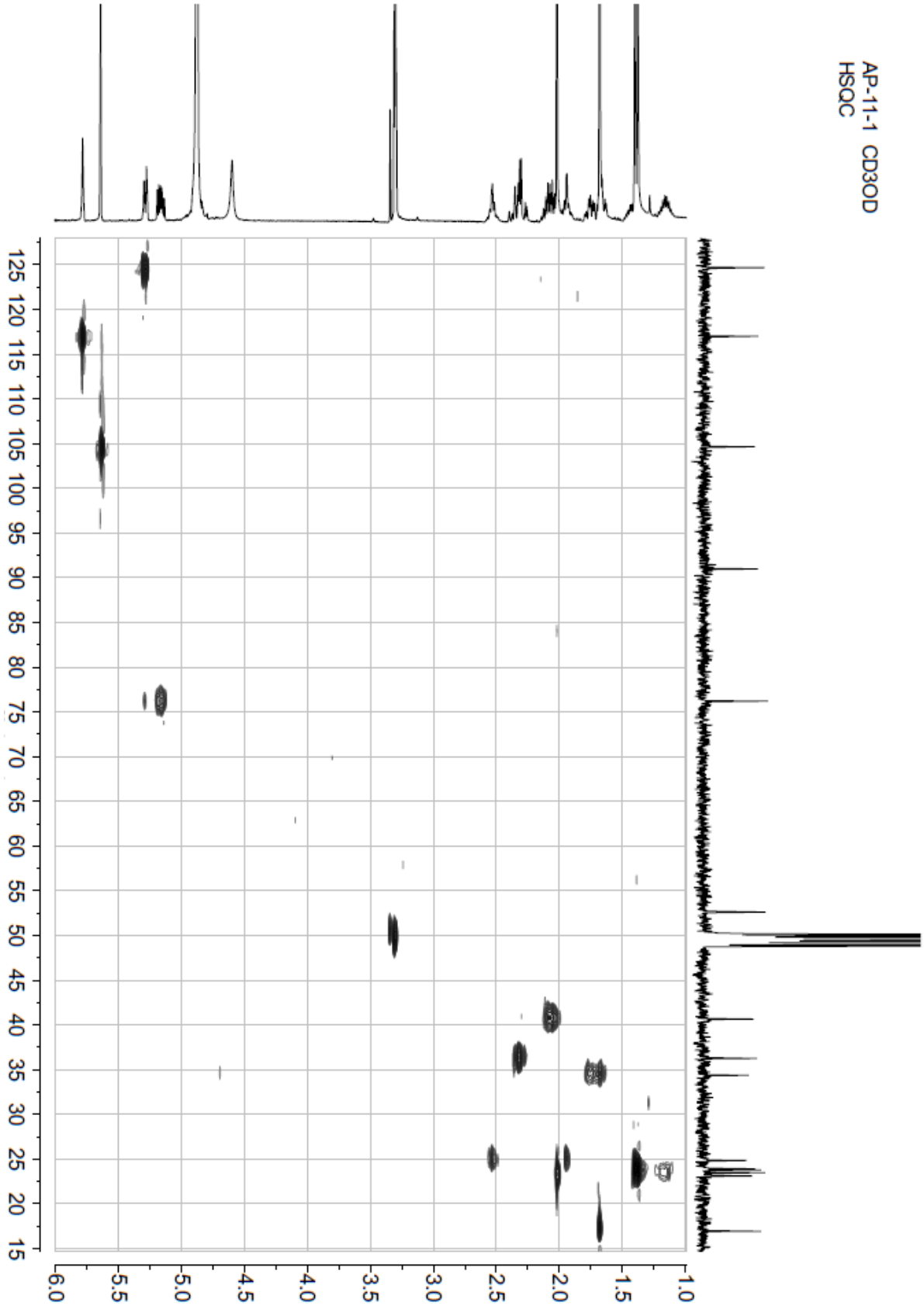


Figure S17. HMBC spectrum for aphadilactone F (**2**) in CD_3OD.

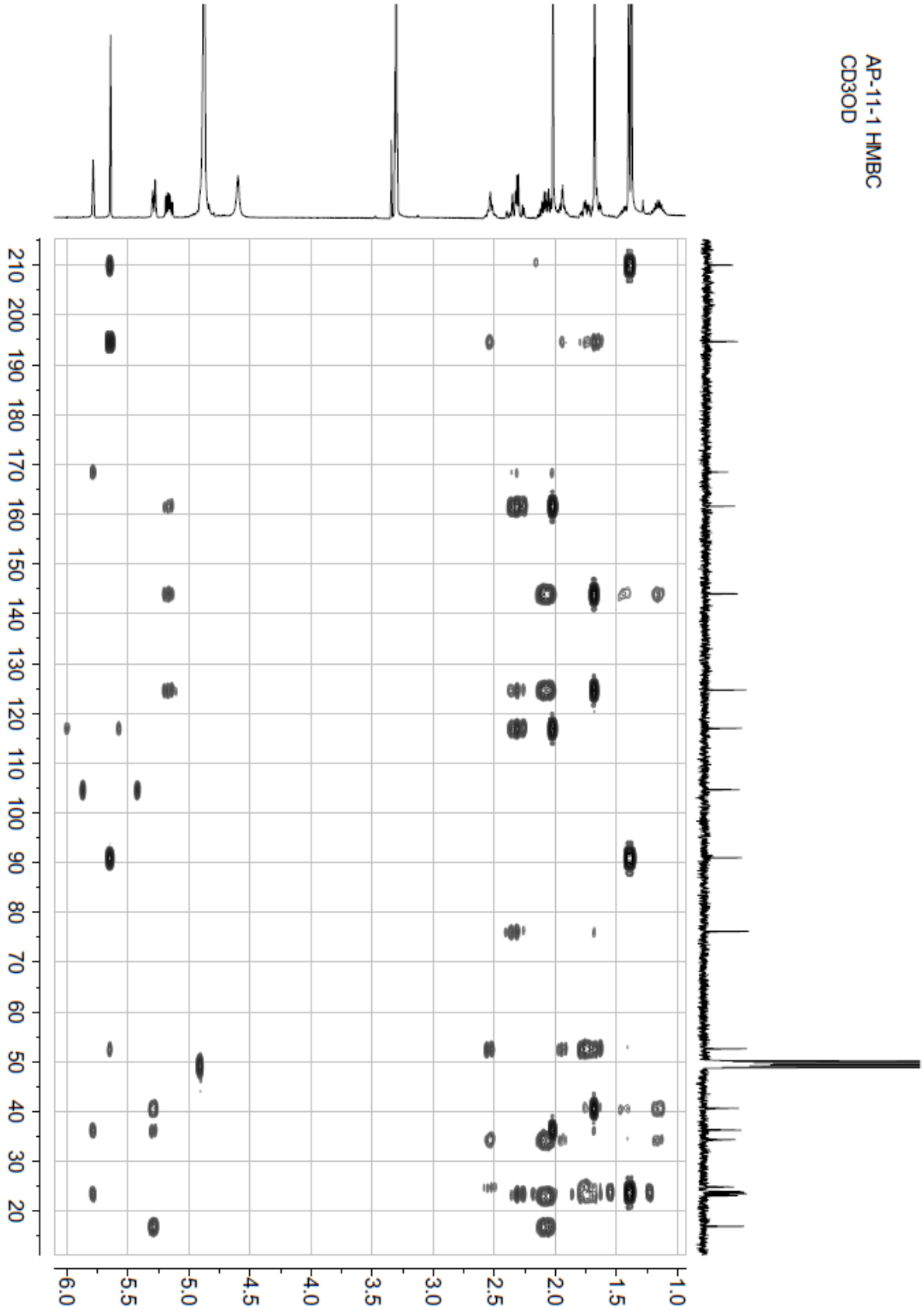


Figure S18. ROESY spectrum for aphadilactone F (**2**) in CD_3OD.

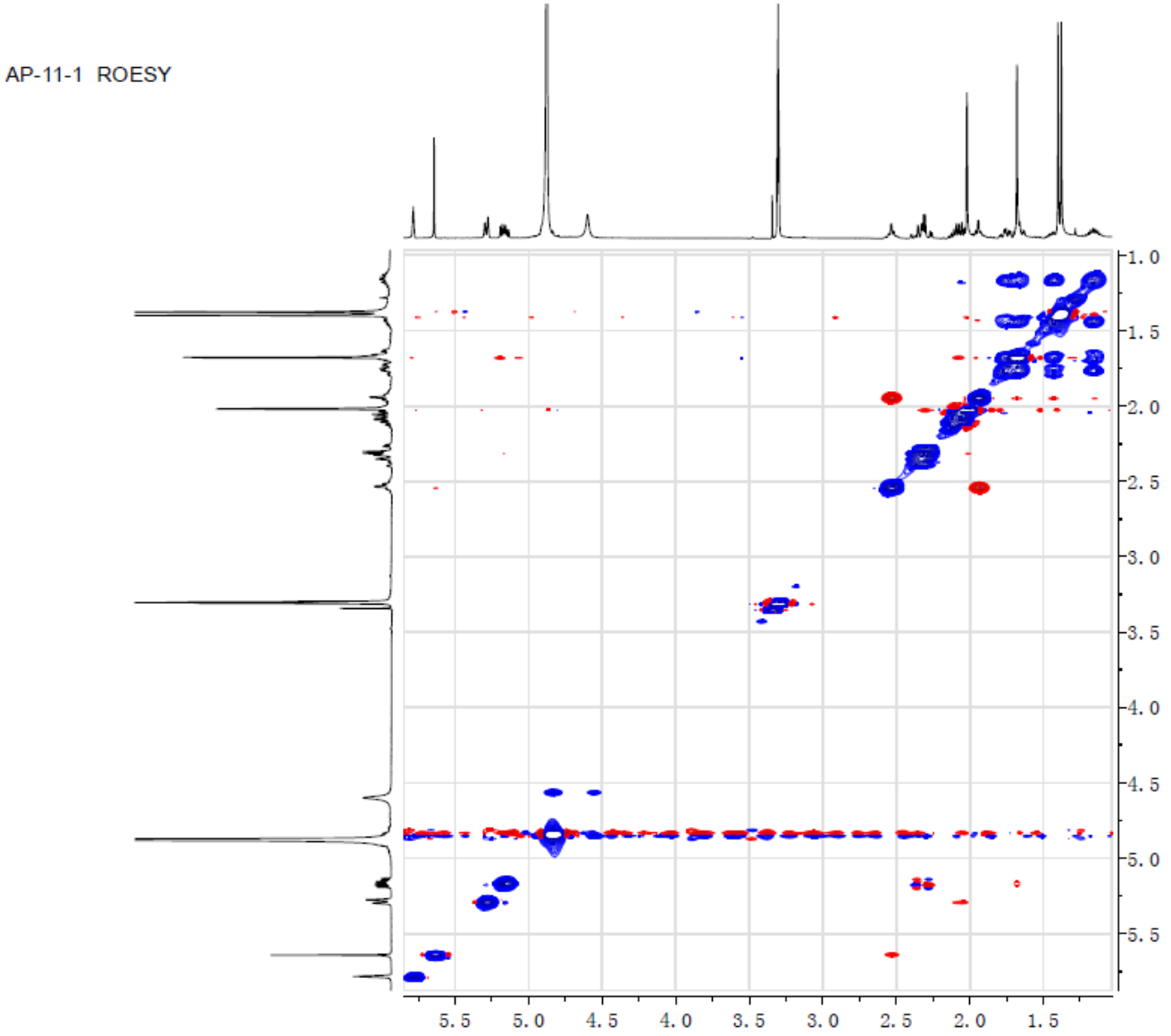


Figure S19. ESI(+)MS spectrum for aphadilactone F (**2**).

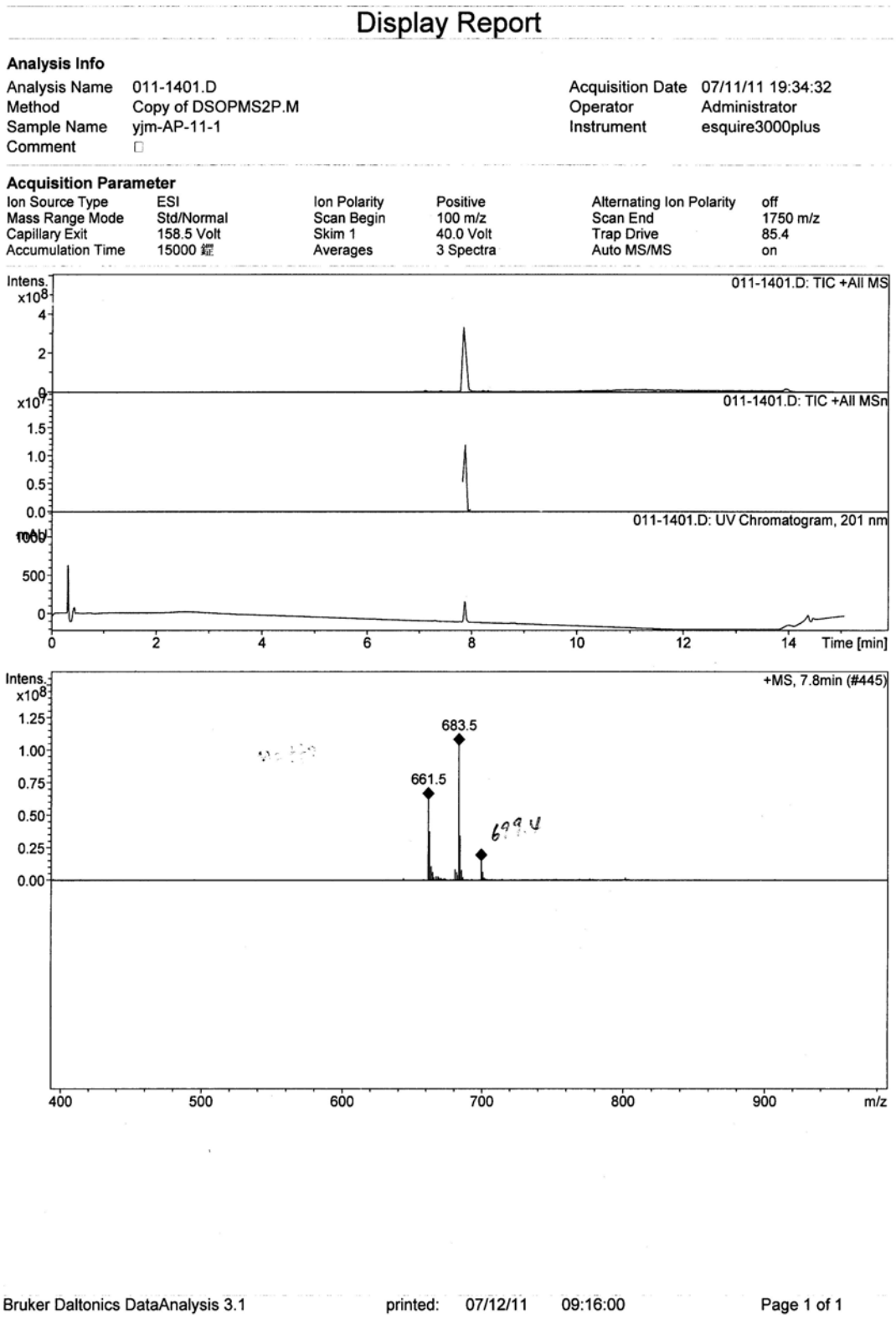


Figure S20. HRESI(+)MS spectrum for aphadilactone F (**2**).

Elemental Composition Report **Page 1**

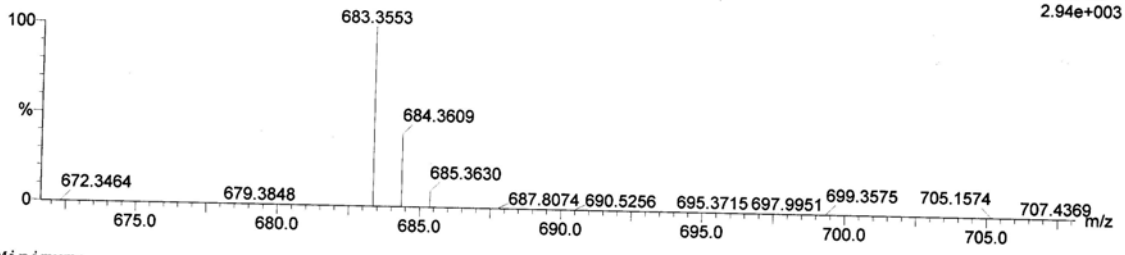
Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

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-11-1

LCT PXE KE324

16-Oct-2014
09:56:37
1: TOF MS ES+
2.94e+003

AP-11-1_1016 52 (1.128) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (41:54)



Minimum:				-1.5			
Maximum:		5.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
683.3553	683.3560	-0.7	-1.0	14.5	23.9	0.0	C40 H52 O8 Na

Figure S21. ^{1}H NMR spectrum for aphadilactone G (**3**) in CD_3OD.

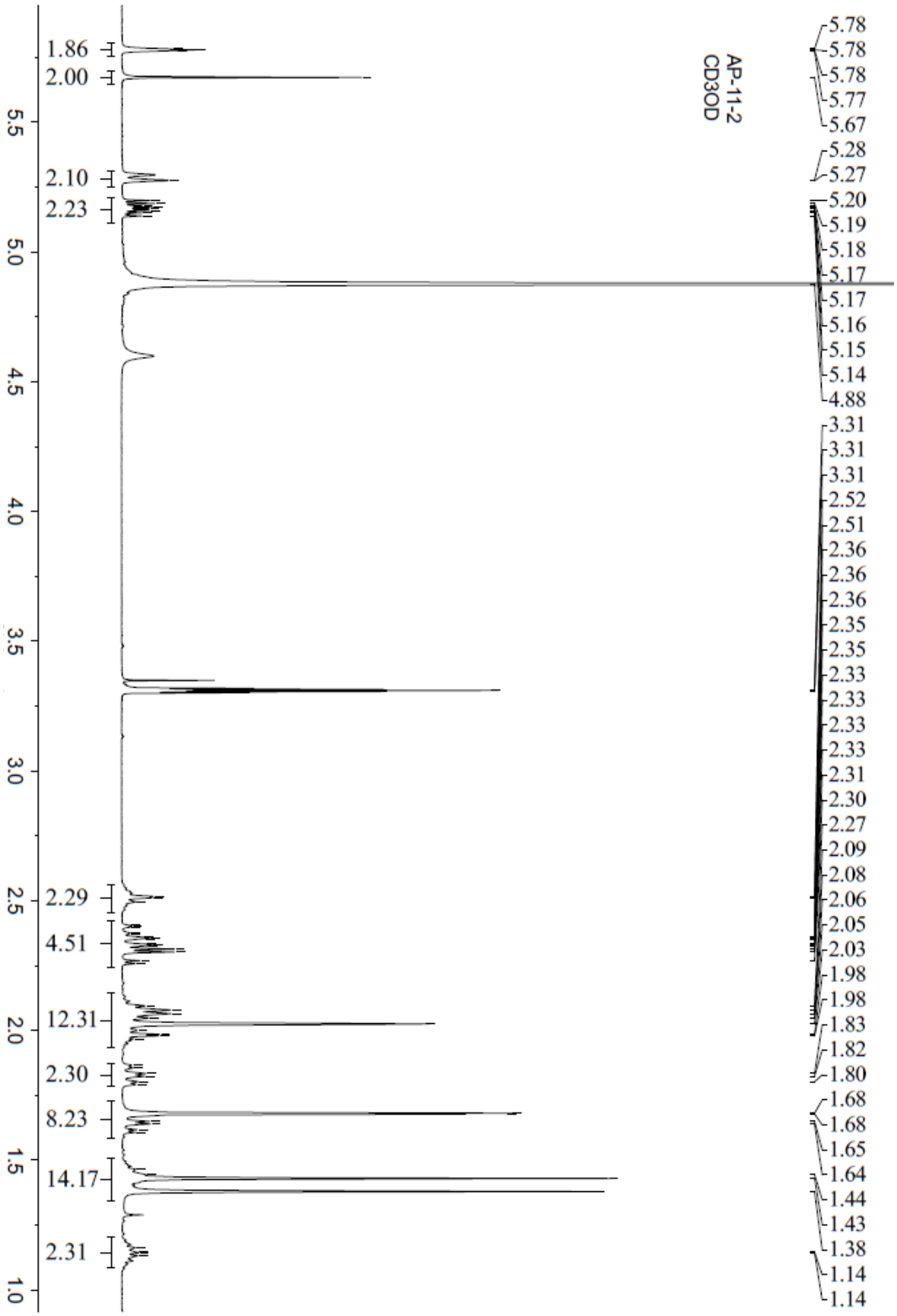


Figure S22. ^{13}C NMR spectrum for aphadilactone G (**3**) in CD_3OD.

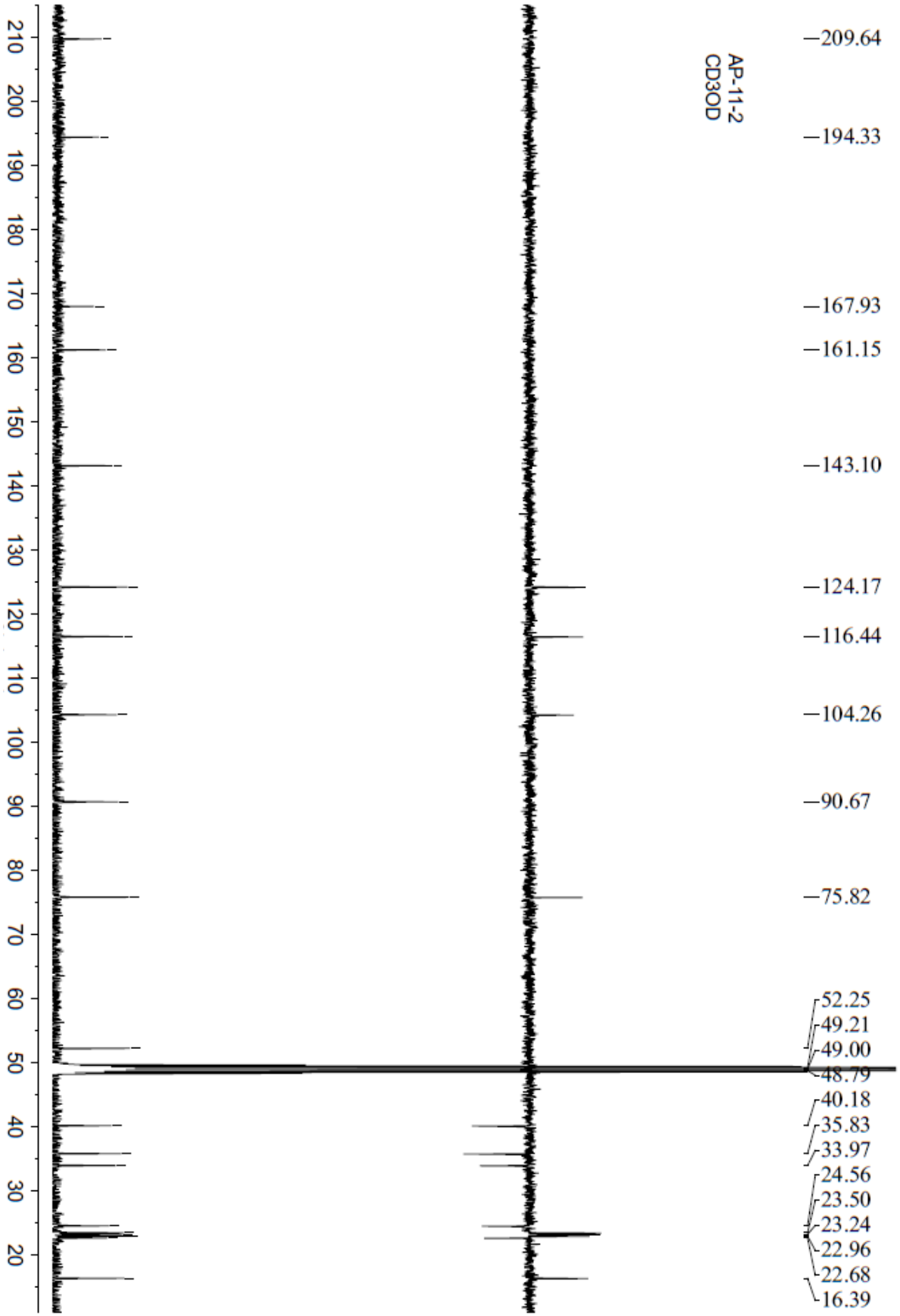


Figure S23. $^{1}H–^{1}H$ COSY spectrum for aphadilactone G (**3**) in CD_3OD.

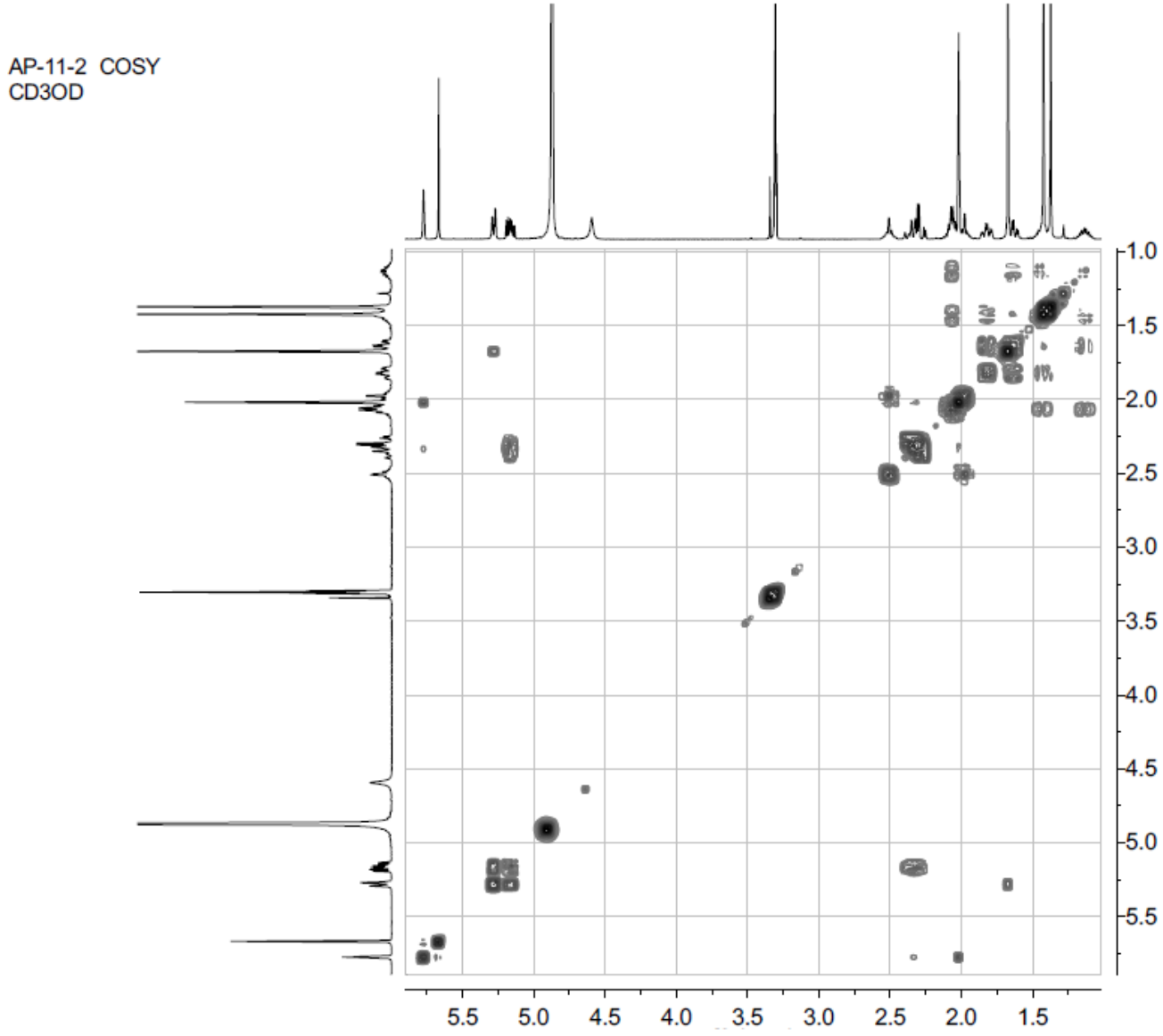


Figure S24. HSQC spectrum for aphadilactone G (**3**) in CD_3OD.

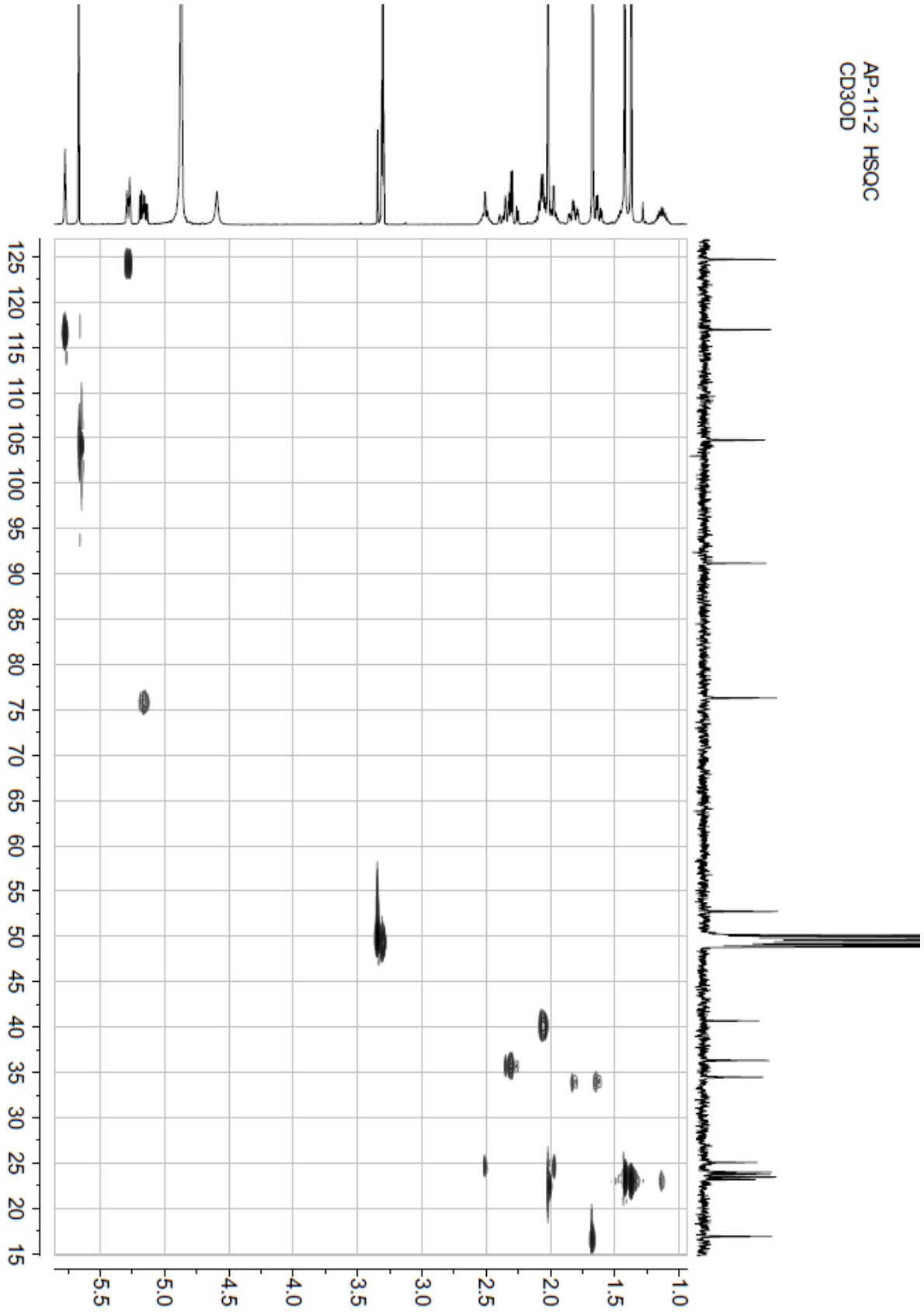


Figure S25. HMBC spectrum for aphadilactone G (**3**) in CD_3OD.

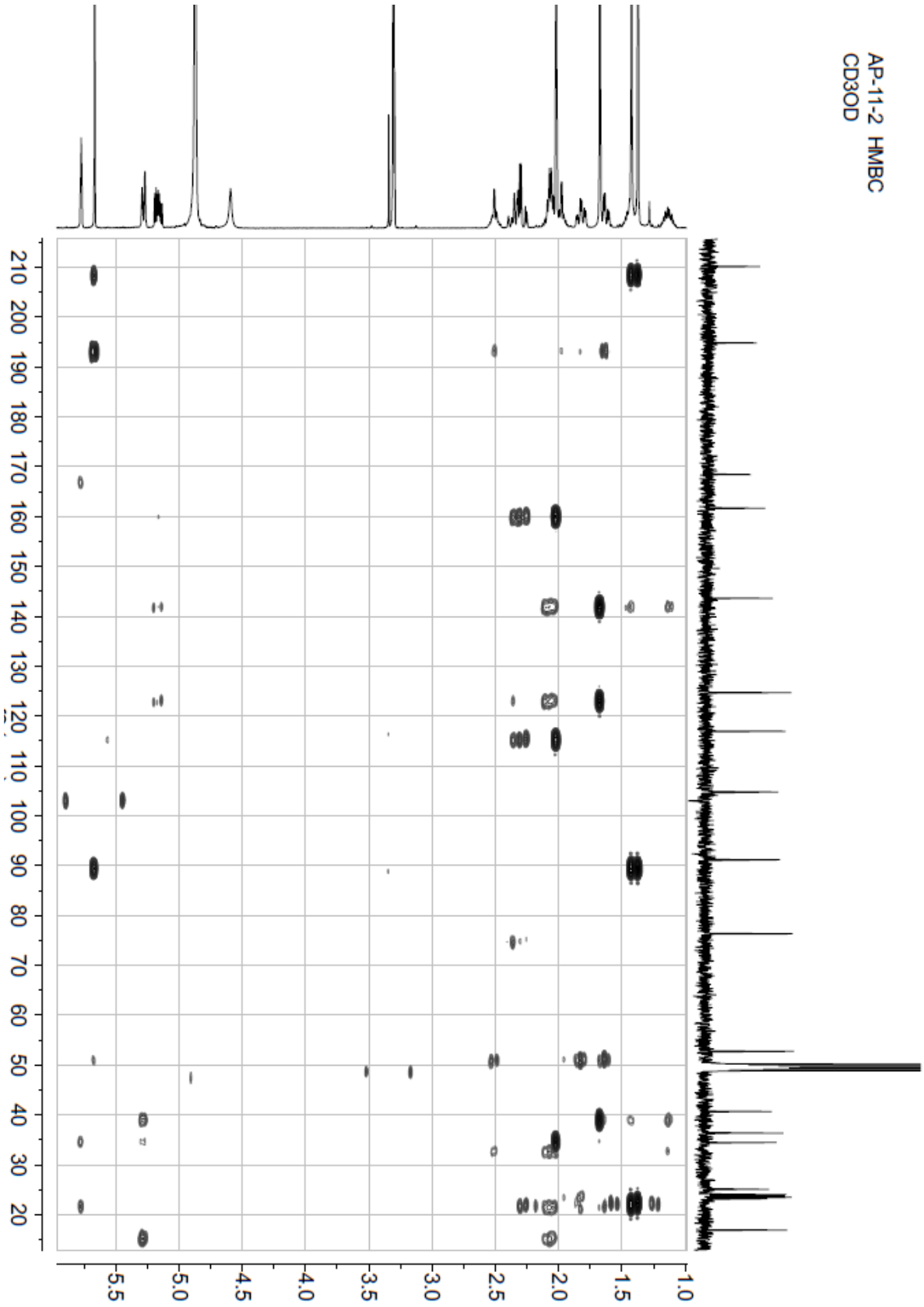


Figure S26. ROESY spectrum for aphadilactone G (**3**) in CD_3OD.

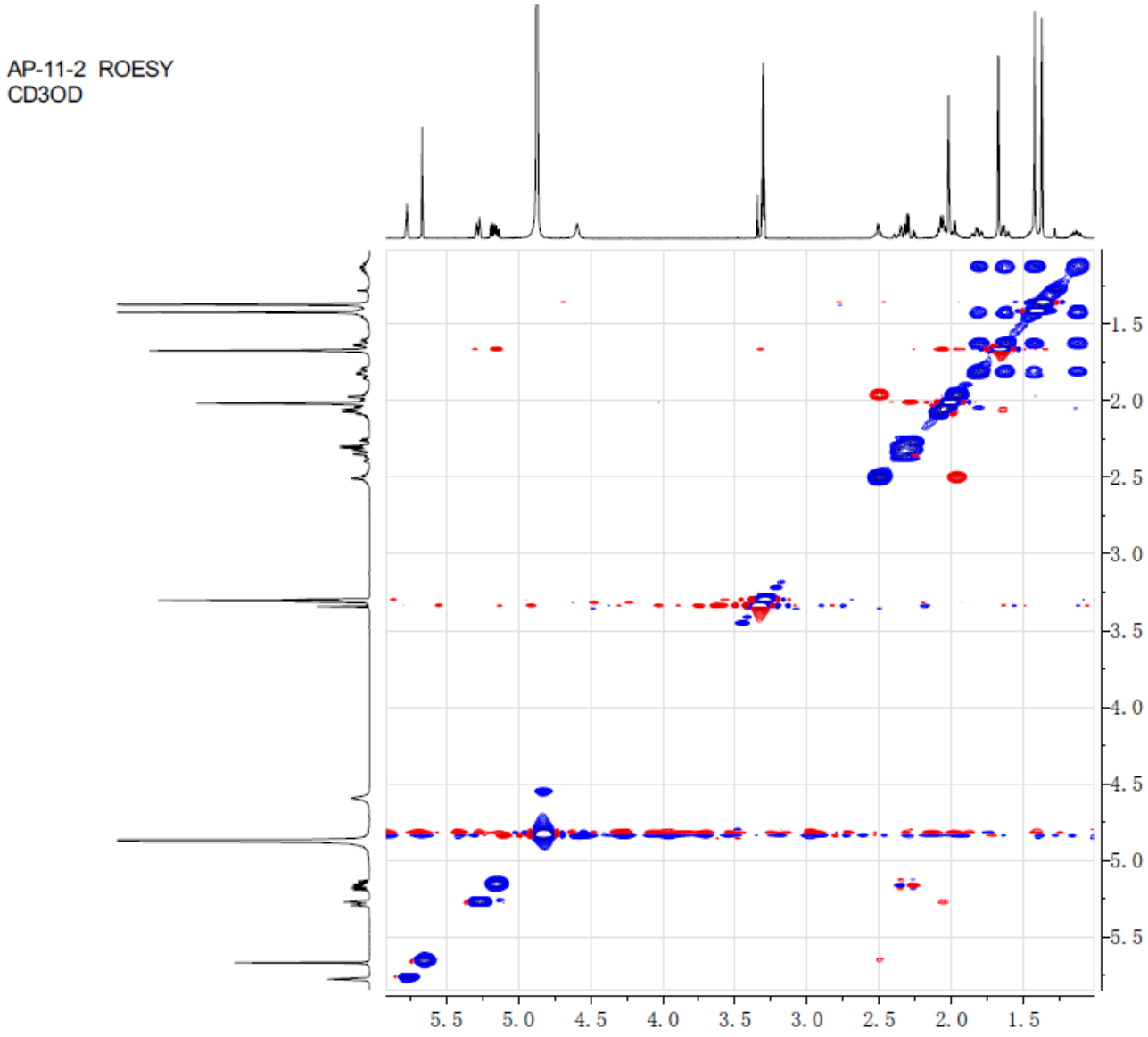


Figure S27. ESI(+)MS spectrum for aphadilactone G (**3**).

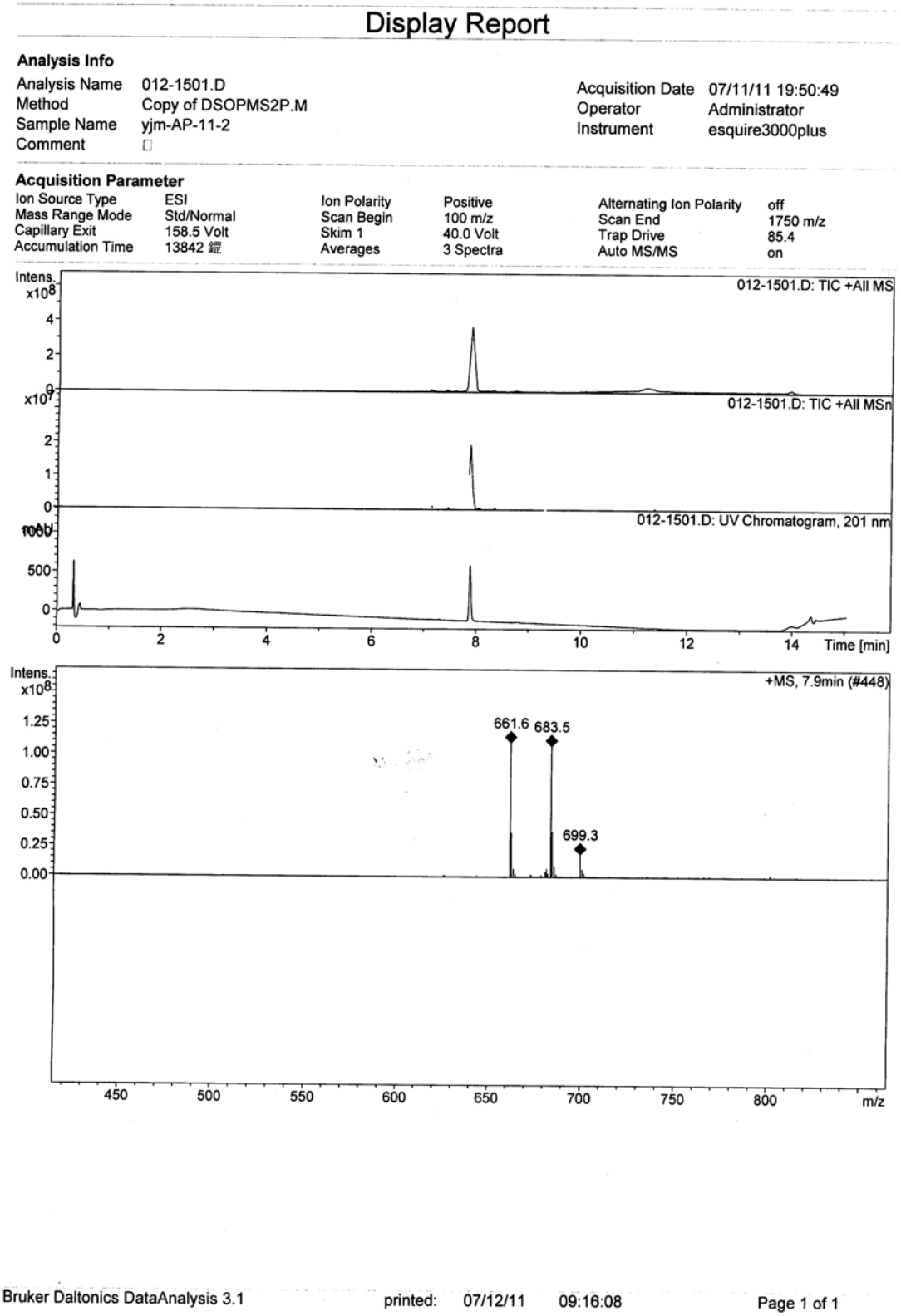


Figure S28. HRESI(+)MS spectrum for aphadilactone G (**3**).

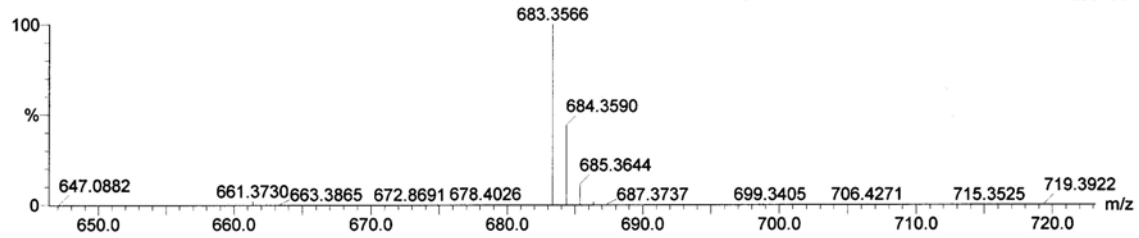
Elemental Composition Report **Page 1**

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

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 16-Oct-2014 09:51:18

AP-11-2_1016 44 (0.953) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (33:48) 1: TOF MS ES+ 1.88e+004



Minimum:				-1.5						
Maximum:		5.0	3.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
683.3566	683.3560	0.6	0.9	14.5	51.1	0.0	C40	H52	O8	Na
	683.3584	-1.8	-2.6	17.5	56.2	5.2	C42	H51	O8	

Figure S29. ^{1}H NMR spectrum for aphanamene H (**4**) in CD_3OD.

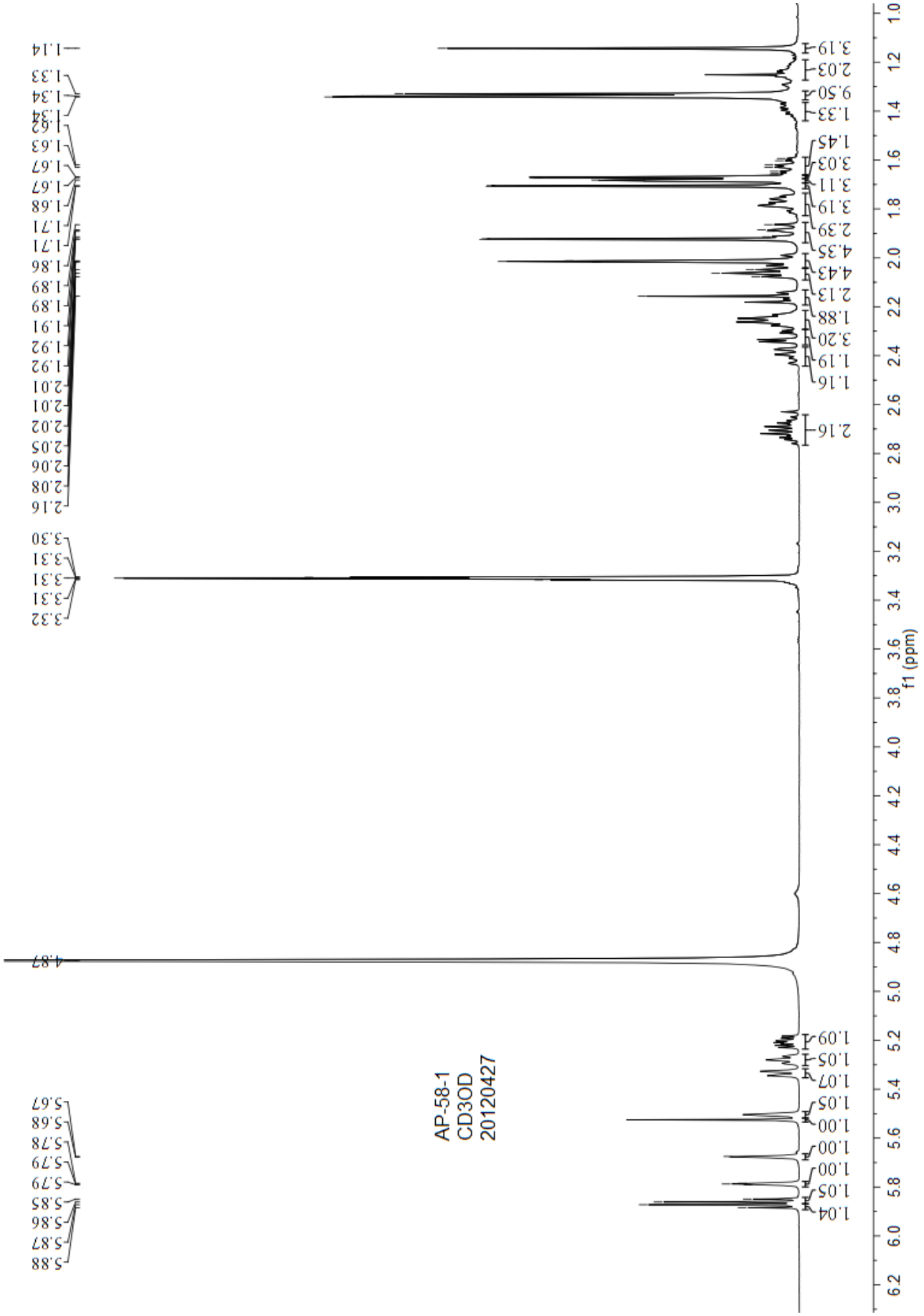


Figure S30. ^{13}C NMR spectrum for aphanamene H (**4**) in CD_3OD.

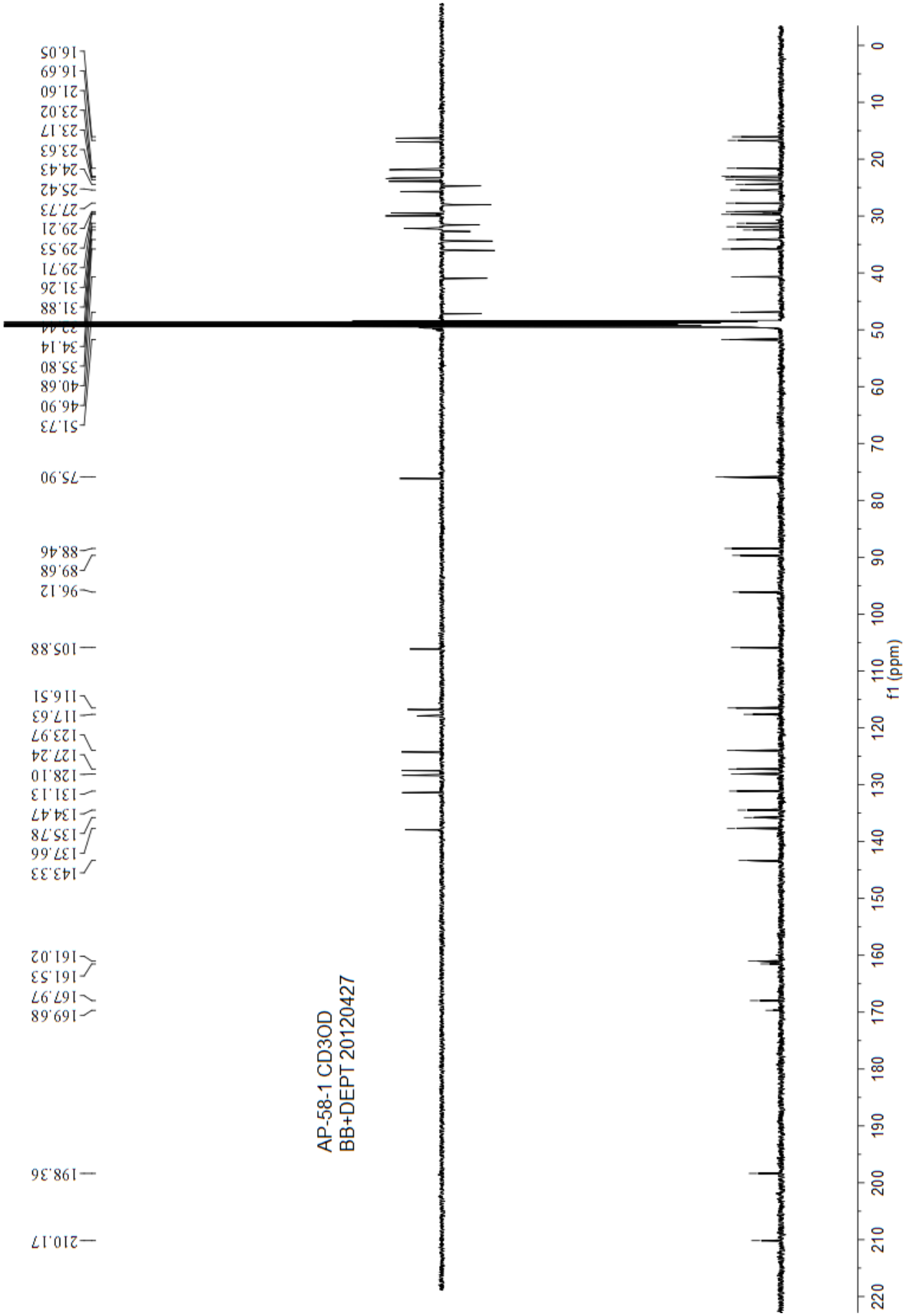


Figure S31. $^{1}H–^{1}H$ COSY spectrum for aphanamene H (**4**) in CD_3OD.

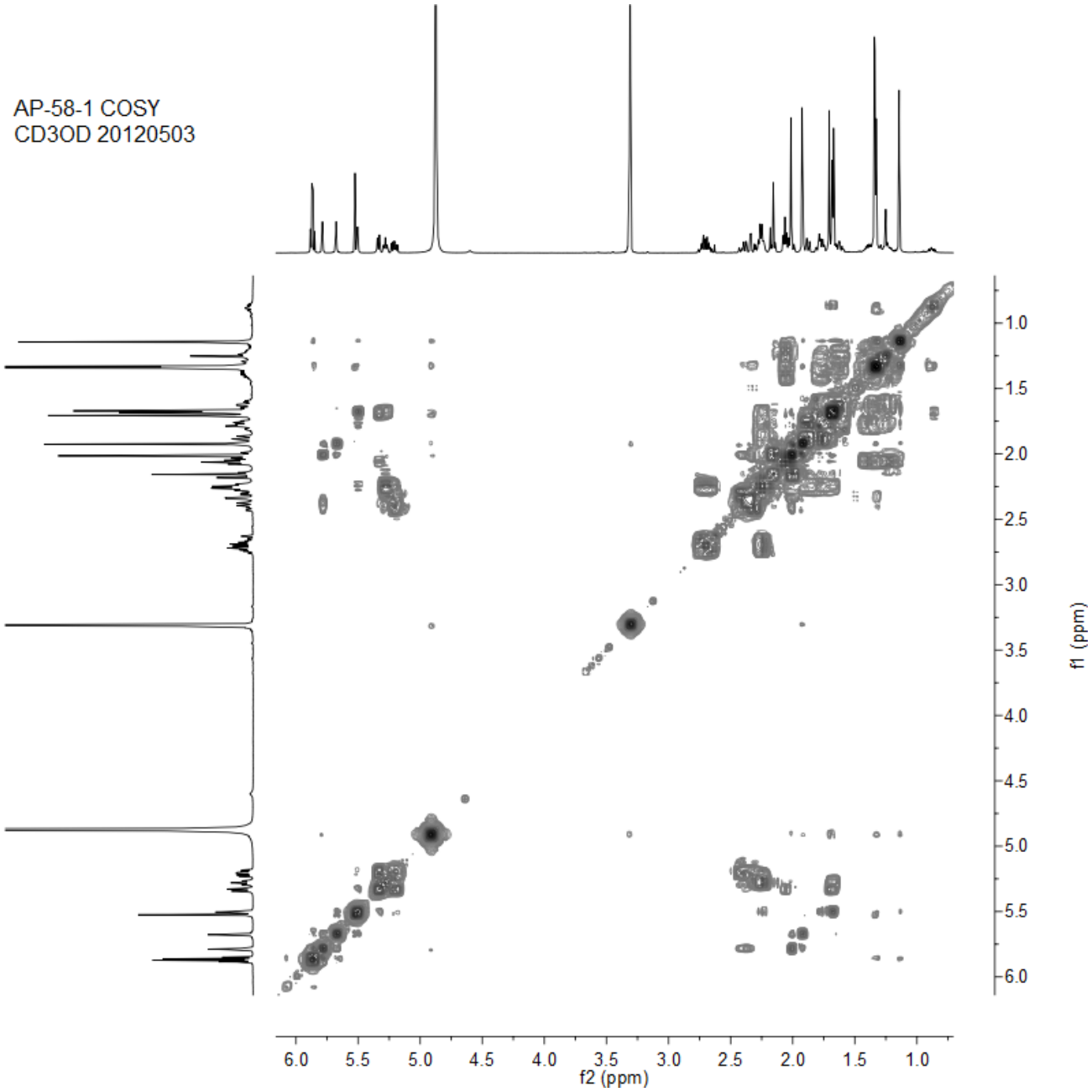


Figure S32. HSQC spectrum for aphanamene H (**4**) in CD_3OD.

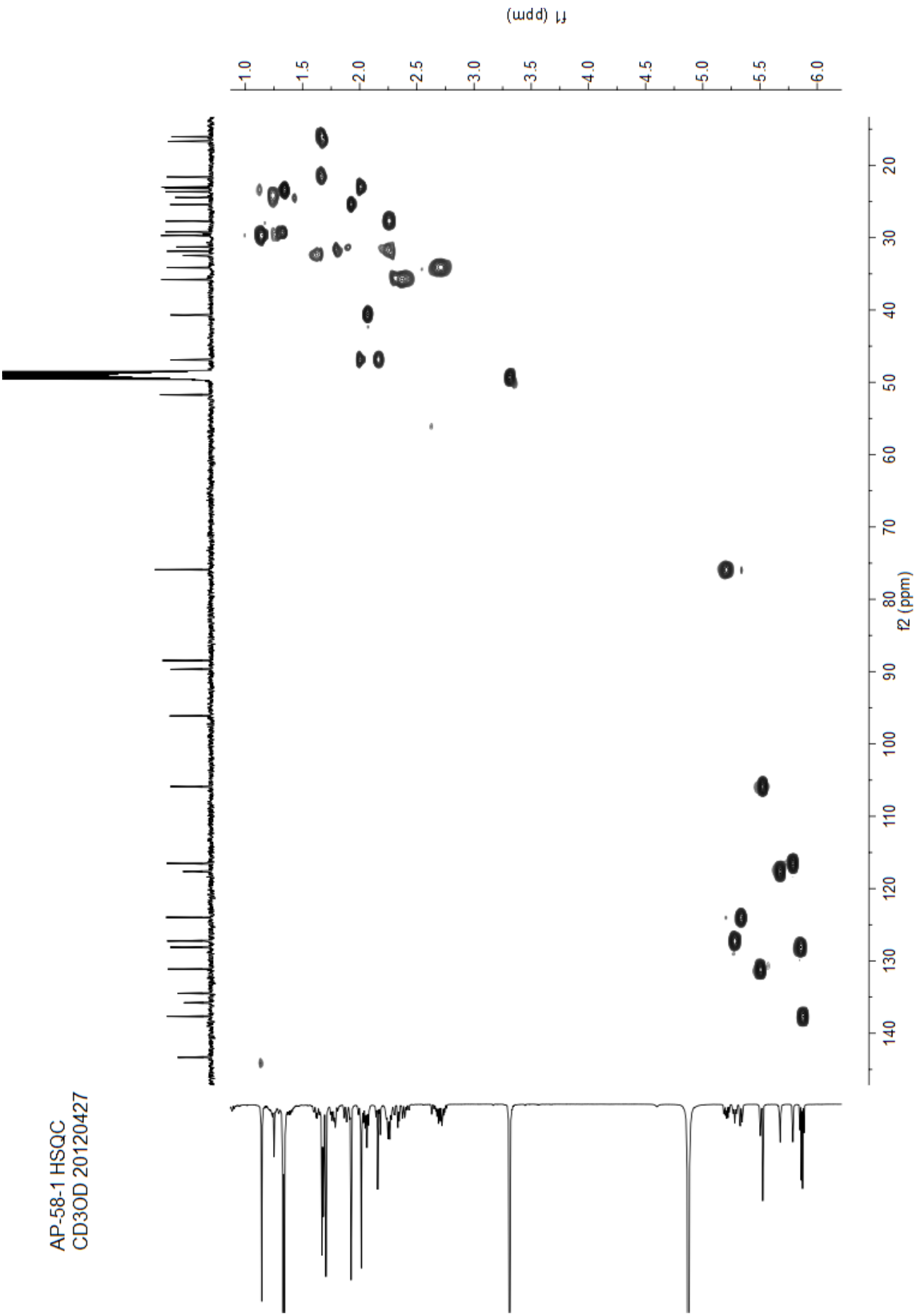


Figure S33. HMBC spectrum for aphanamene H (**4**) in CD_3OD.

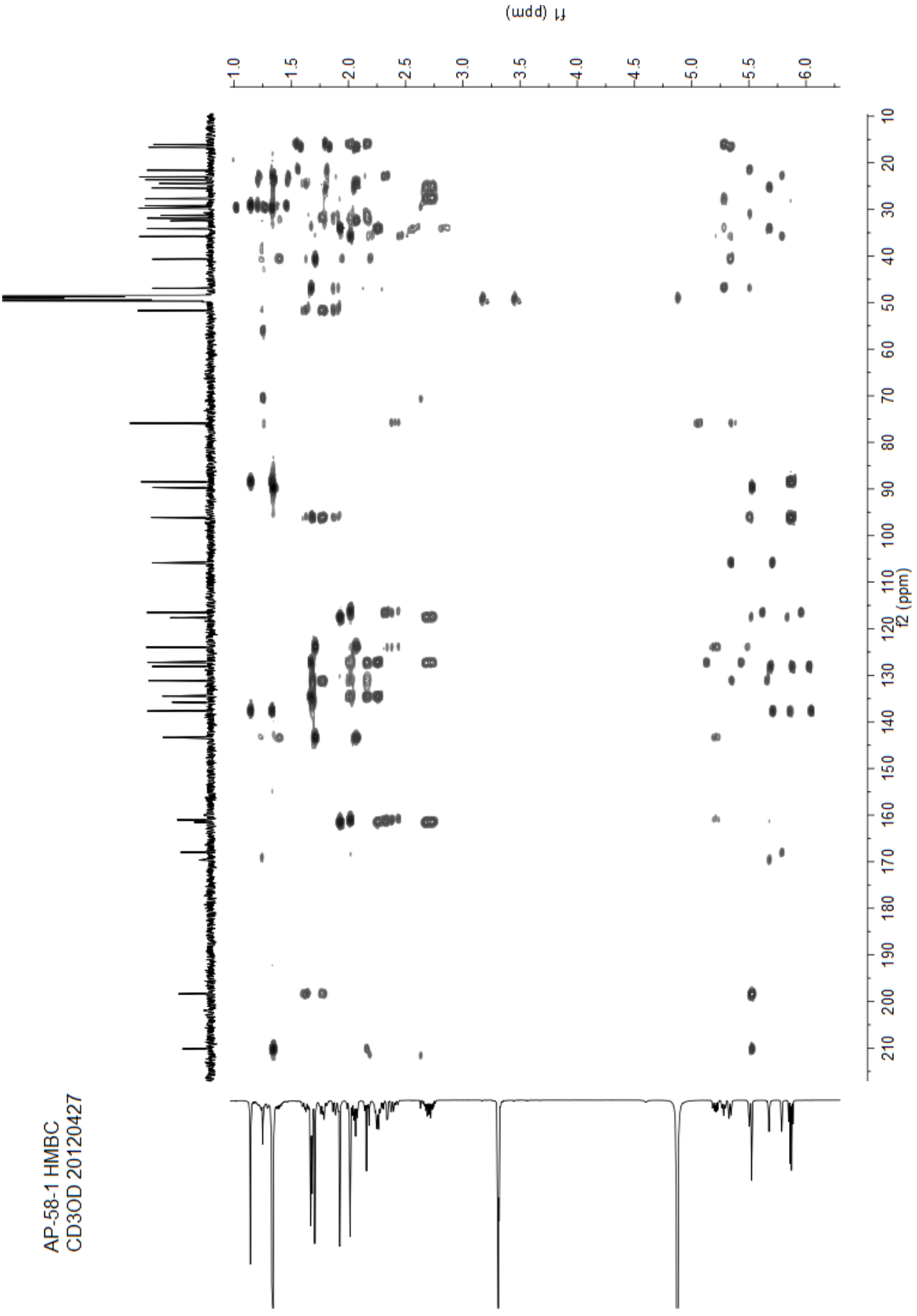


Figure S34. ROESY spectrum for aphanamene H (**4**) in CD_3OD.

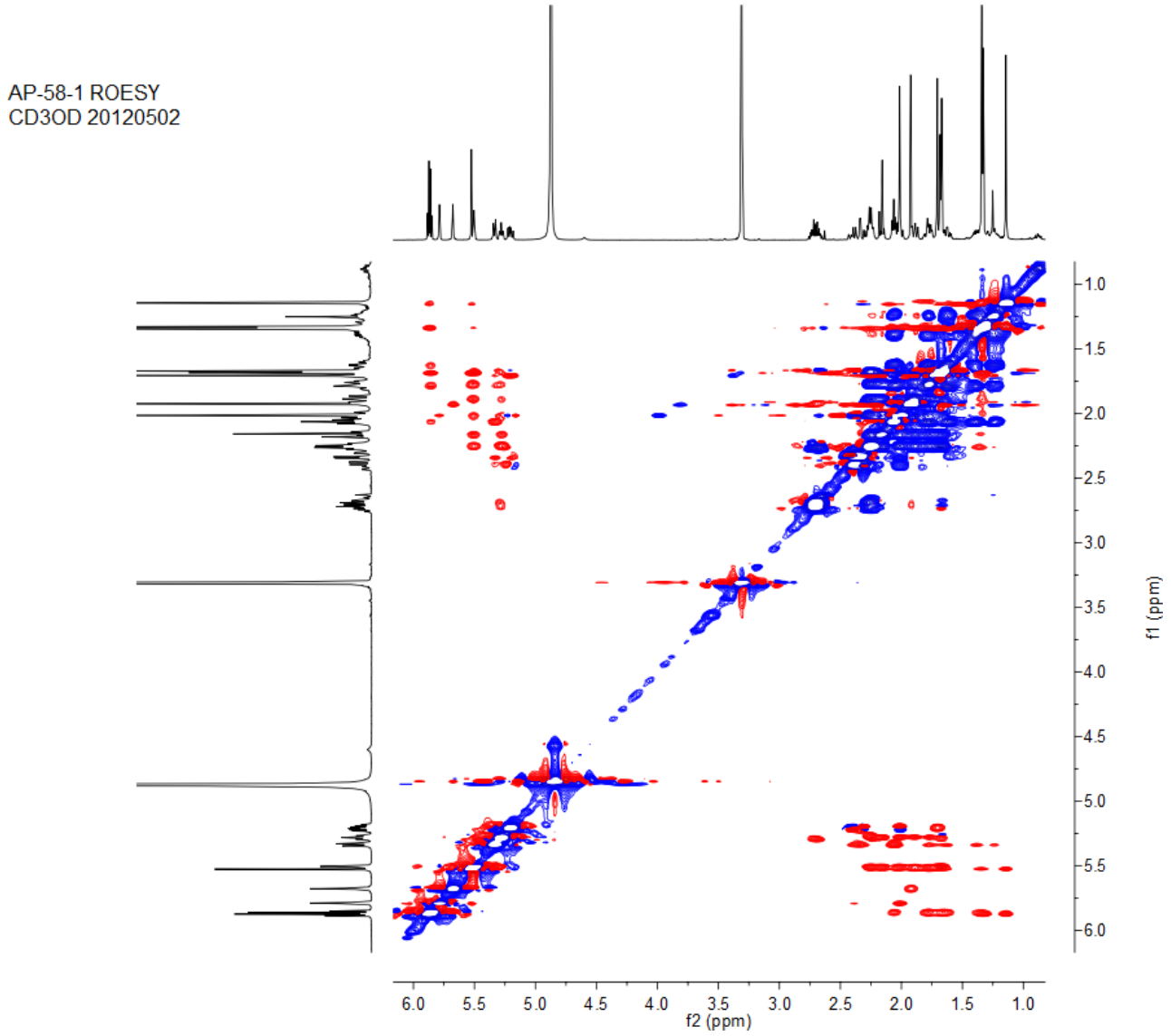


Figure S35. ESI(+)MS spectrum for aphanamene H (**4**).

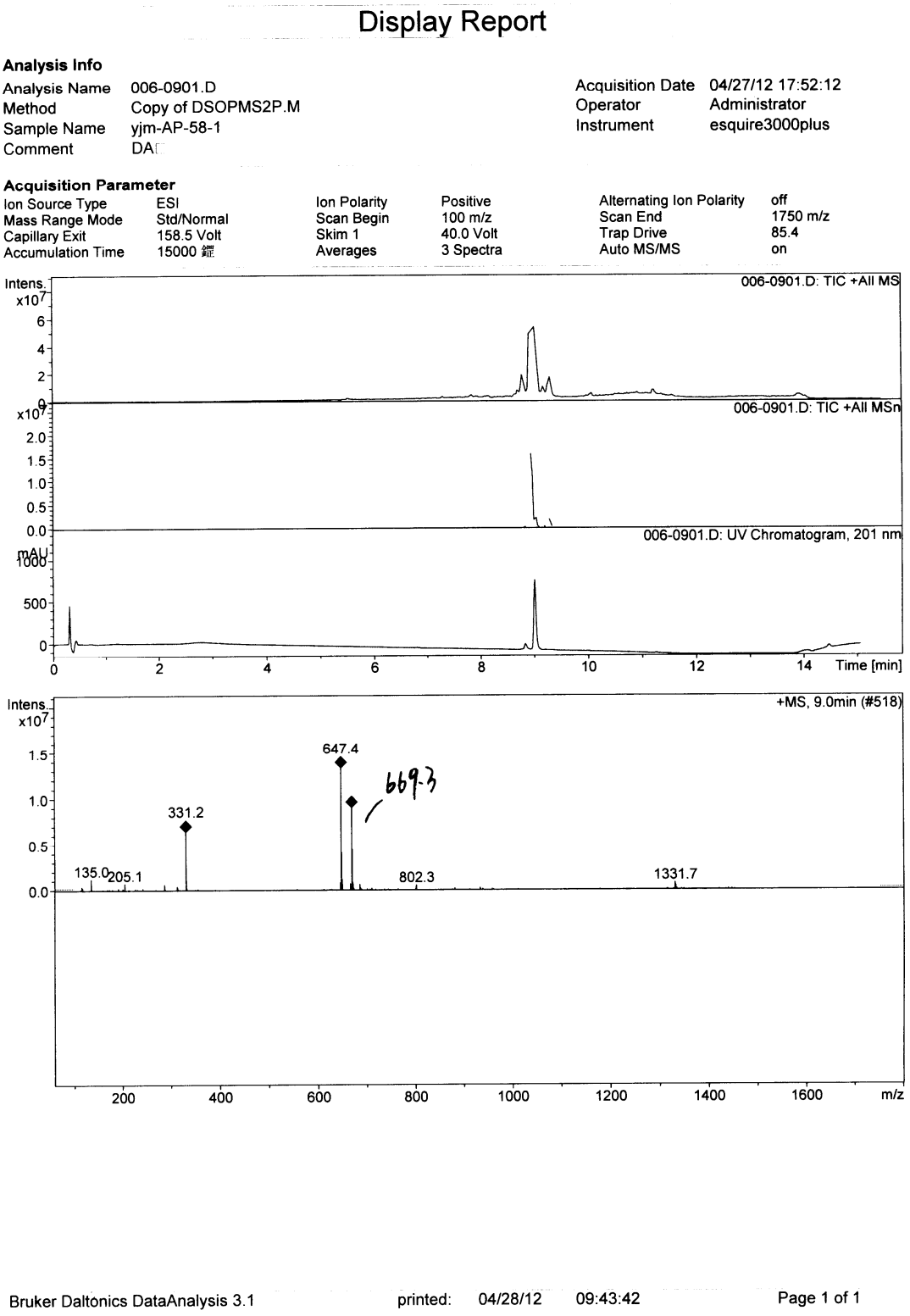


Figure S36. ESI(–)MS spectrum for aphanamene H (**4**).

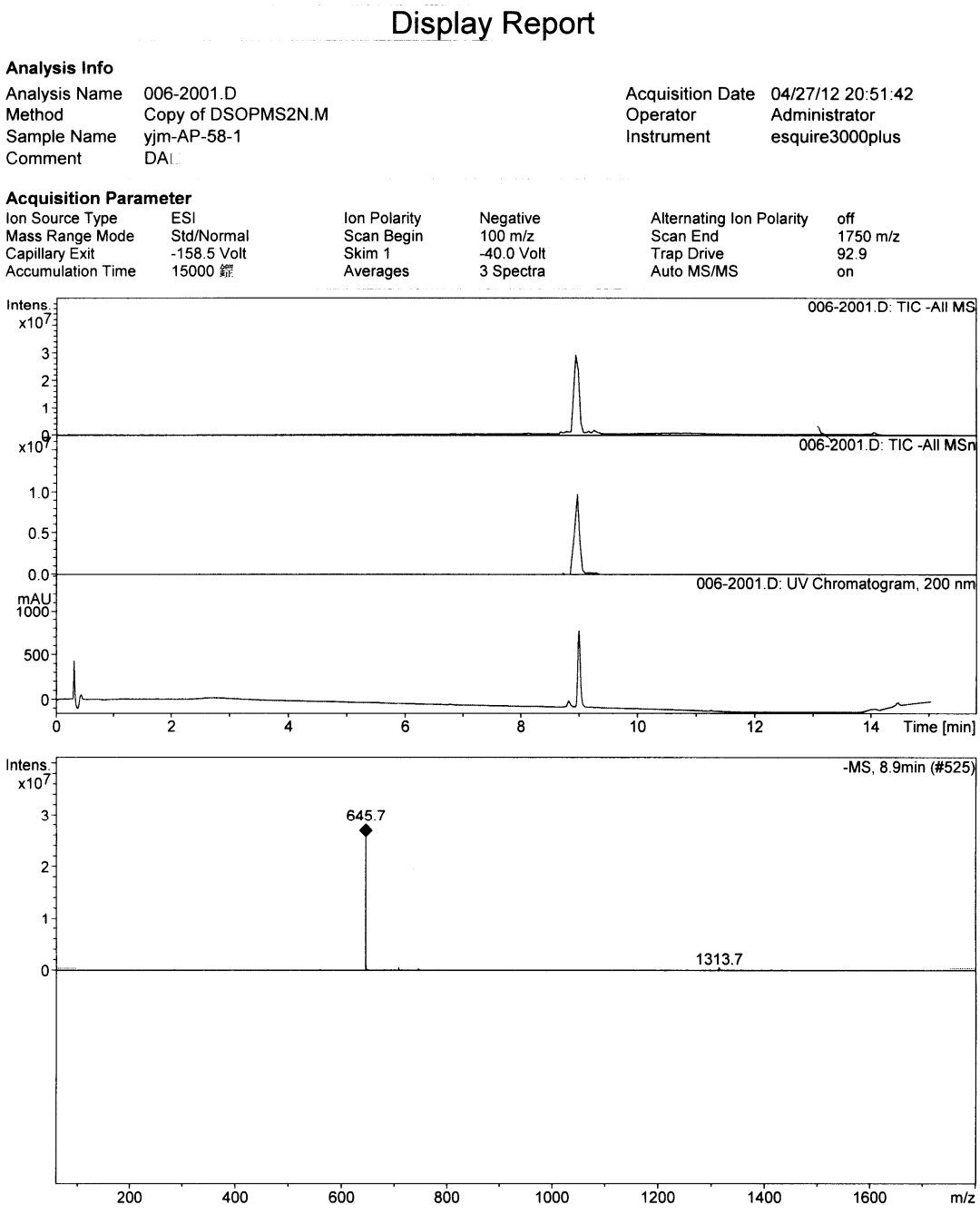


Figure S37. HRESI(+)MS spectrum for aphanamene H (**4**).

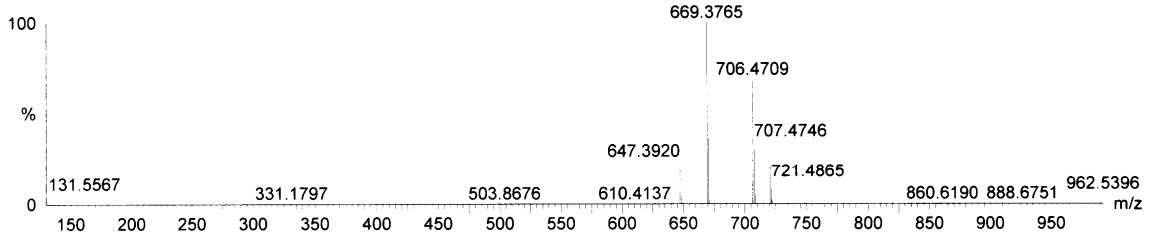
Elemental Composition Report **Page 1**

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

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

liujia LCT PXE KE324 04-May-2012 13:21:50

AP_58_1p 28 (0.600) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (25:39) 1: TOF MS ES+ 8.78e+002



Minimum:				-1.5			
Maximum:		5.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
669.3765	669.3767	-0.2	-0.3	13.5	13.8	0.0	C40 H54 O7 Na

Figure S38. ^{1}H NMR spectrum for aphanamene I (**5**) in CD_3OD.

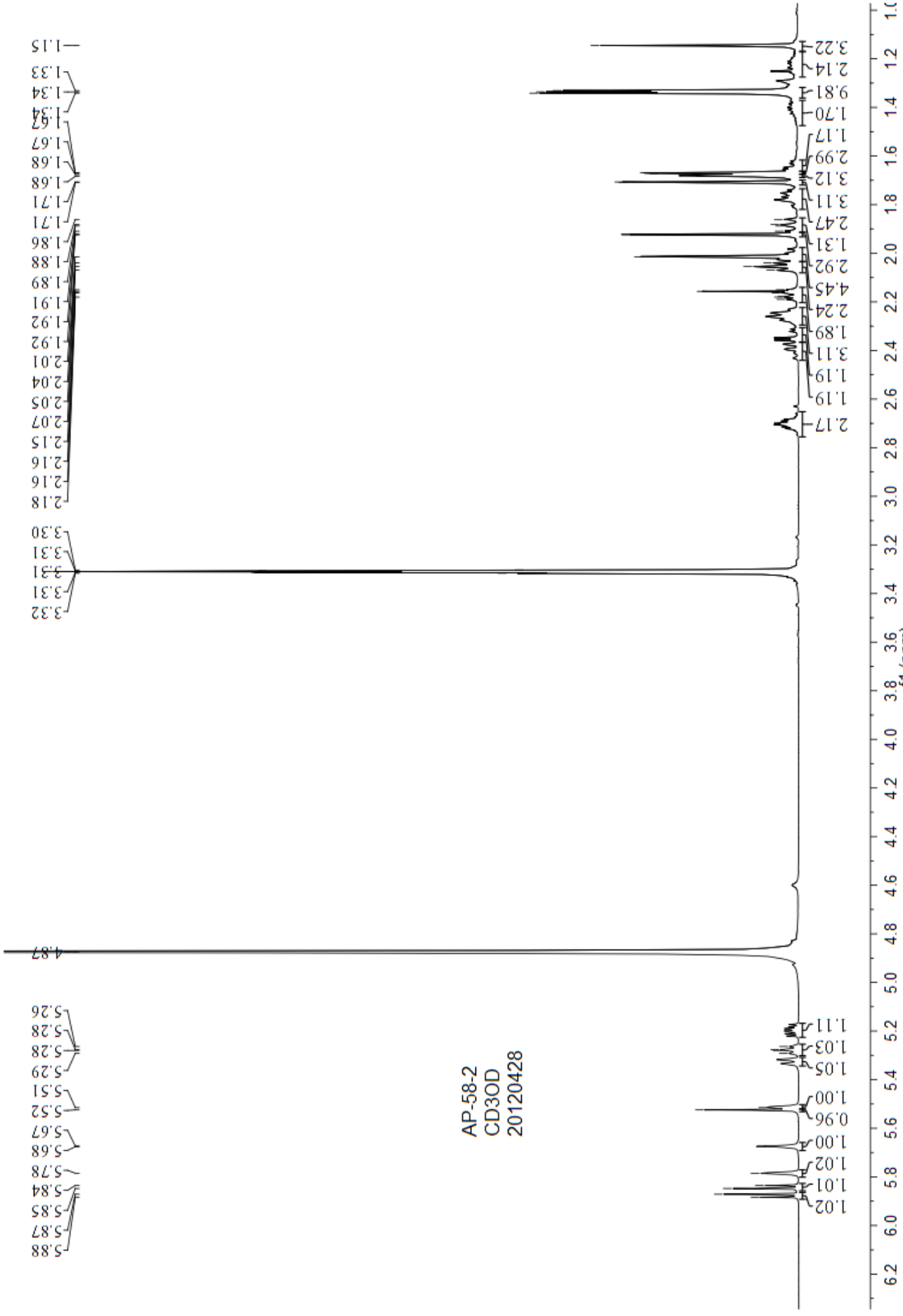


Figure S39. ^{13}C NMR spectrum for aphanamene I (**5**) in CD_3OD.

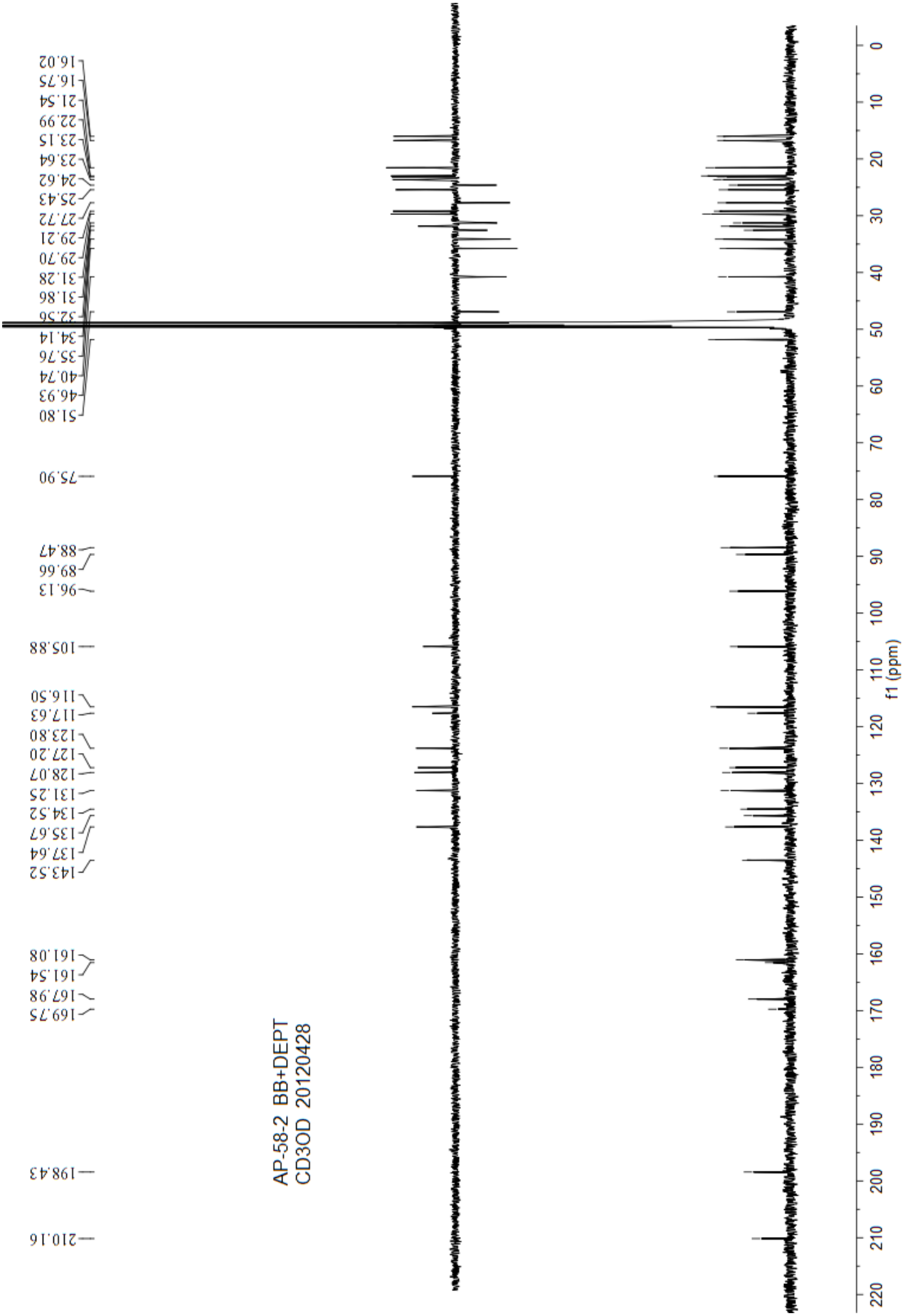


Figure S40. $^{1}H–^{1}H$ COSY spectrum for aphanamene I (**5**) in CD_3OD.

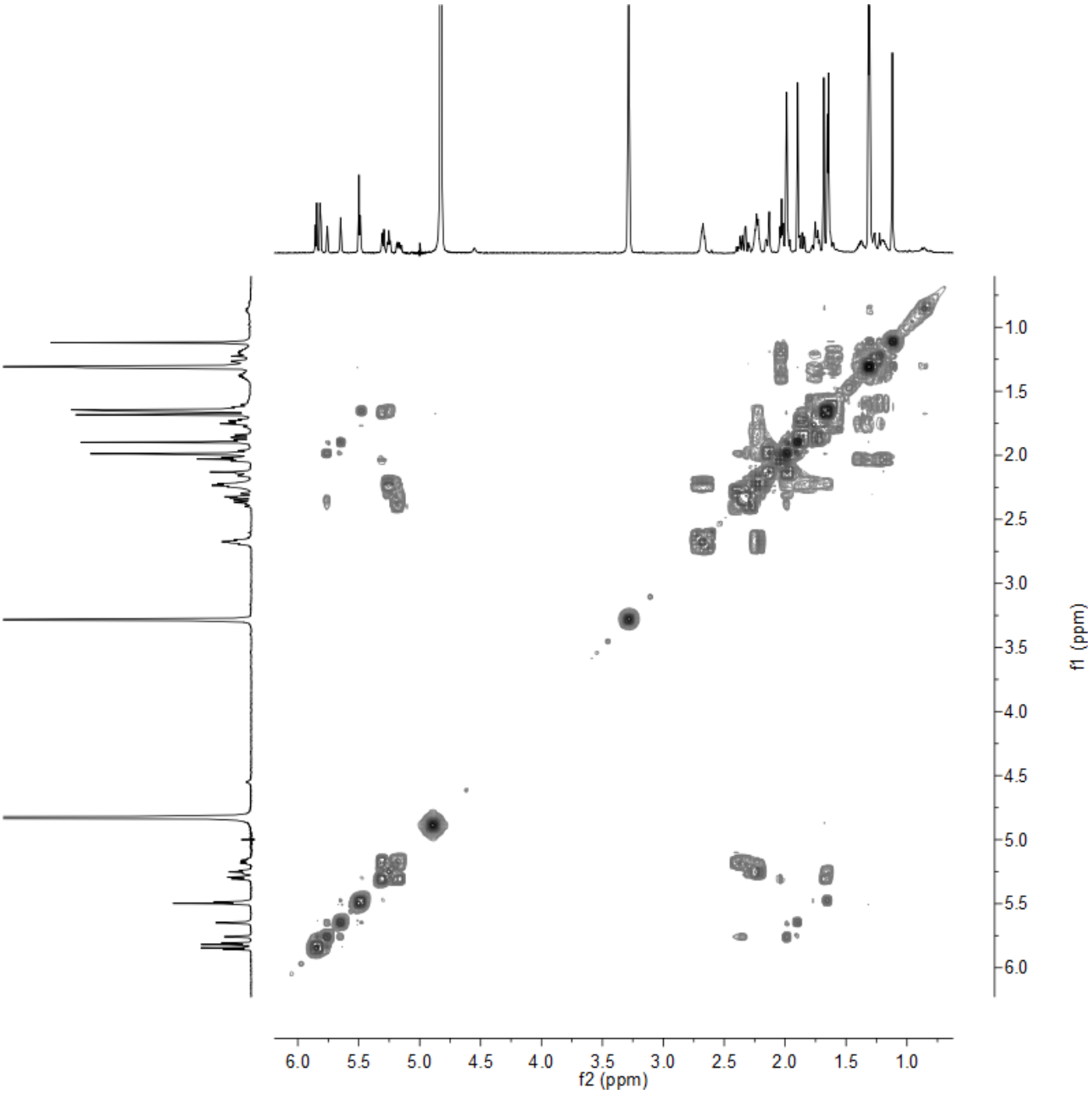


Figure S41. HSQC spectrum for aphanamene I (**5**) in CD_3OD.

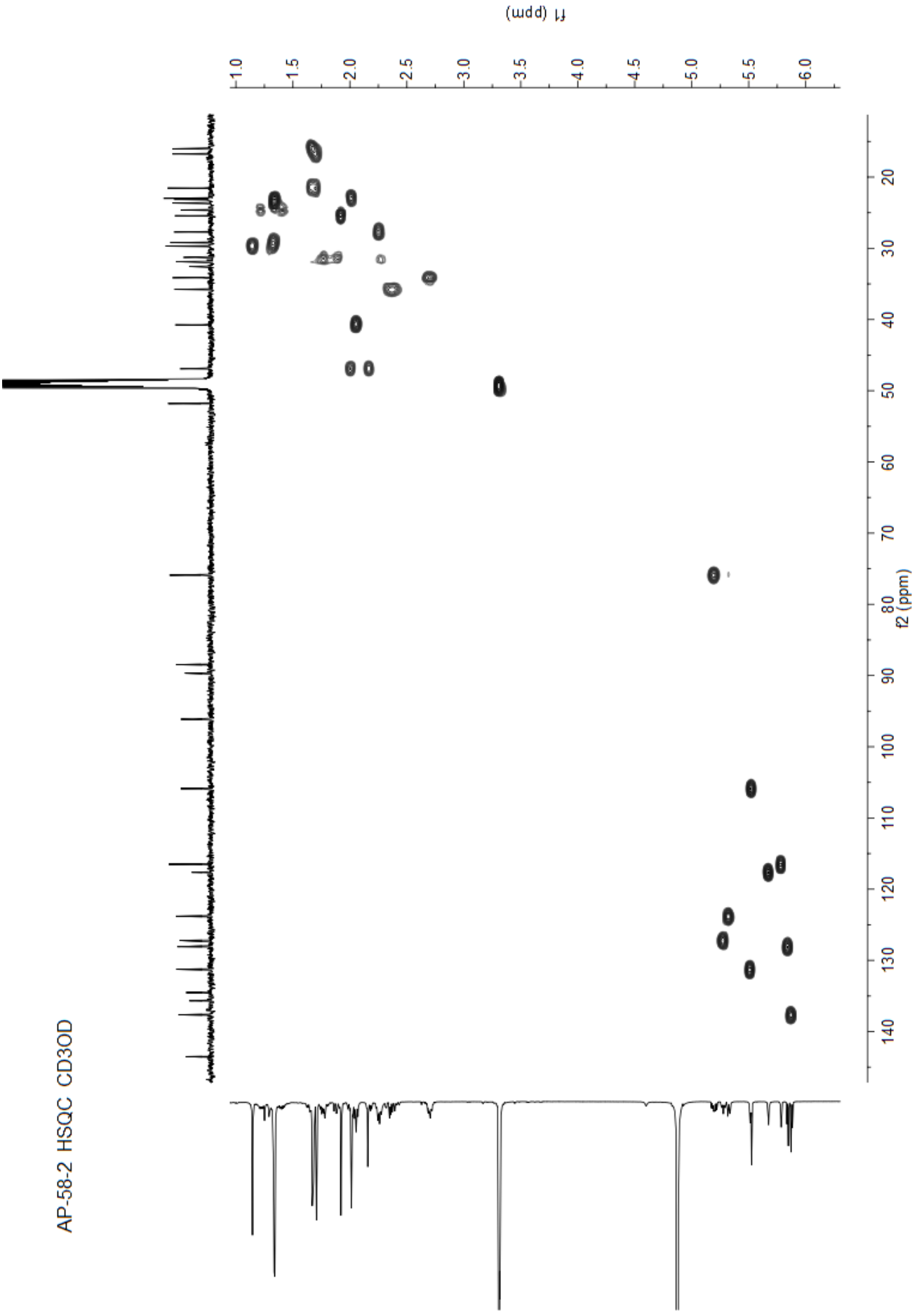


Figure S42. HMBC spectrum for aphanamene I (**5**) in CD_3OD.

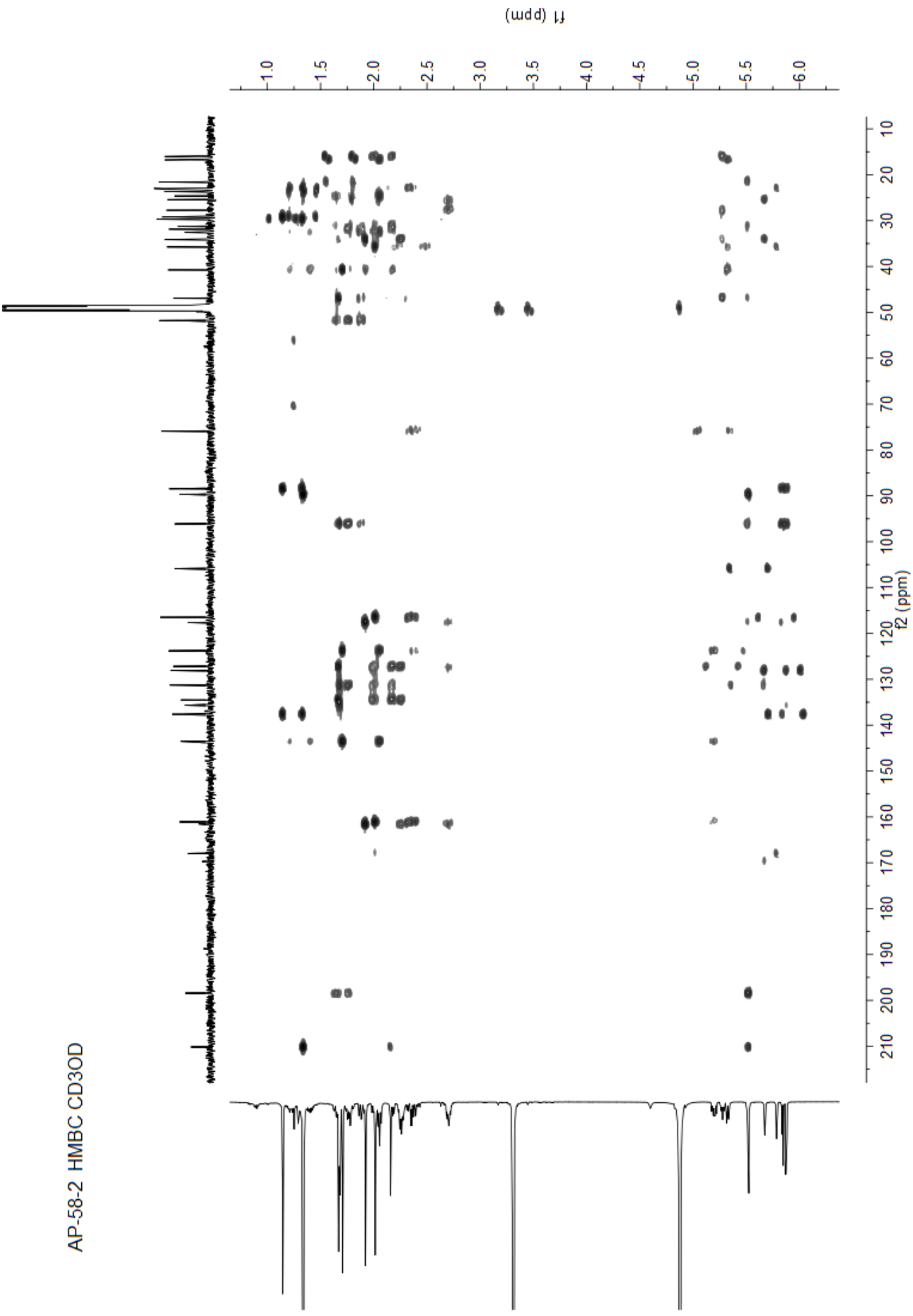


Figure S43. ROESY spectrum for aphanamene I (**5**) in CD_3OD.

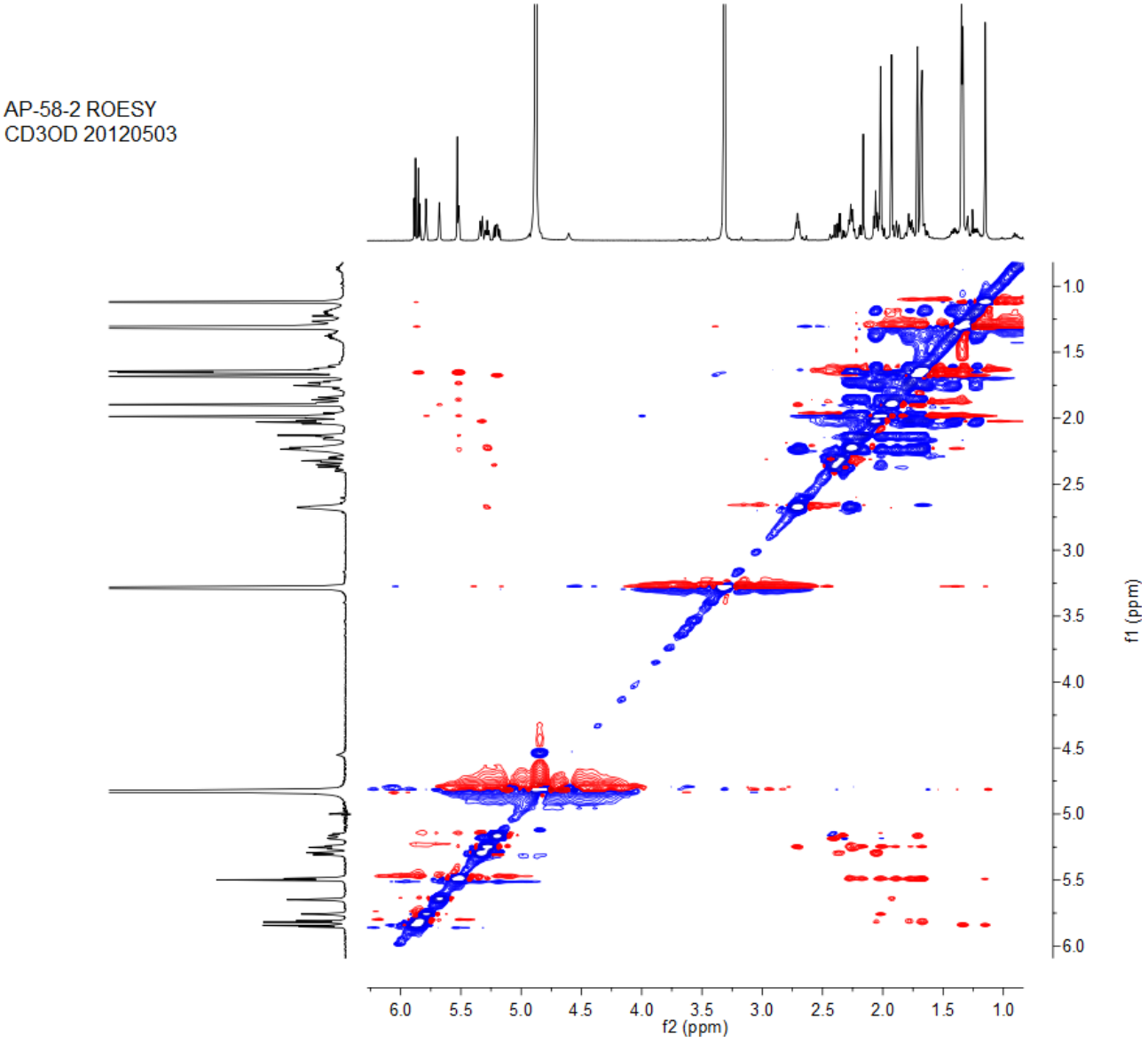


Figure S44. ESI(+)MS spectrum for aphanamene I (**5**).

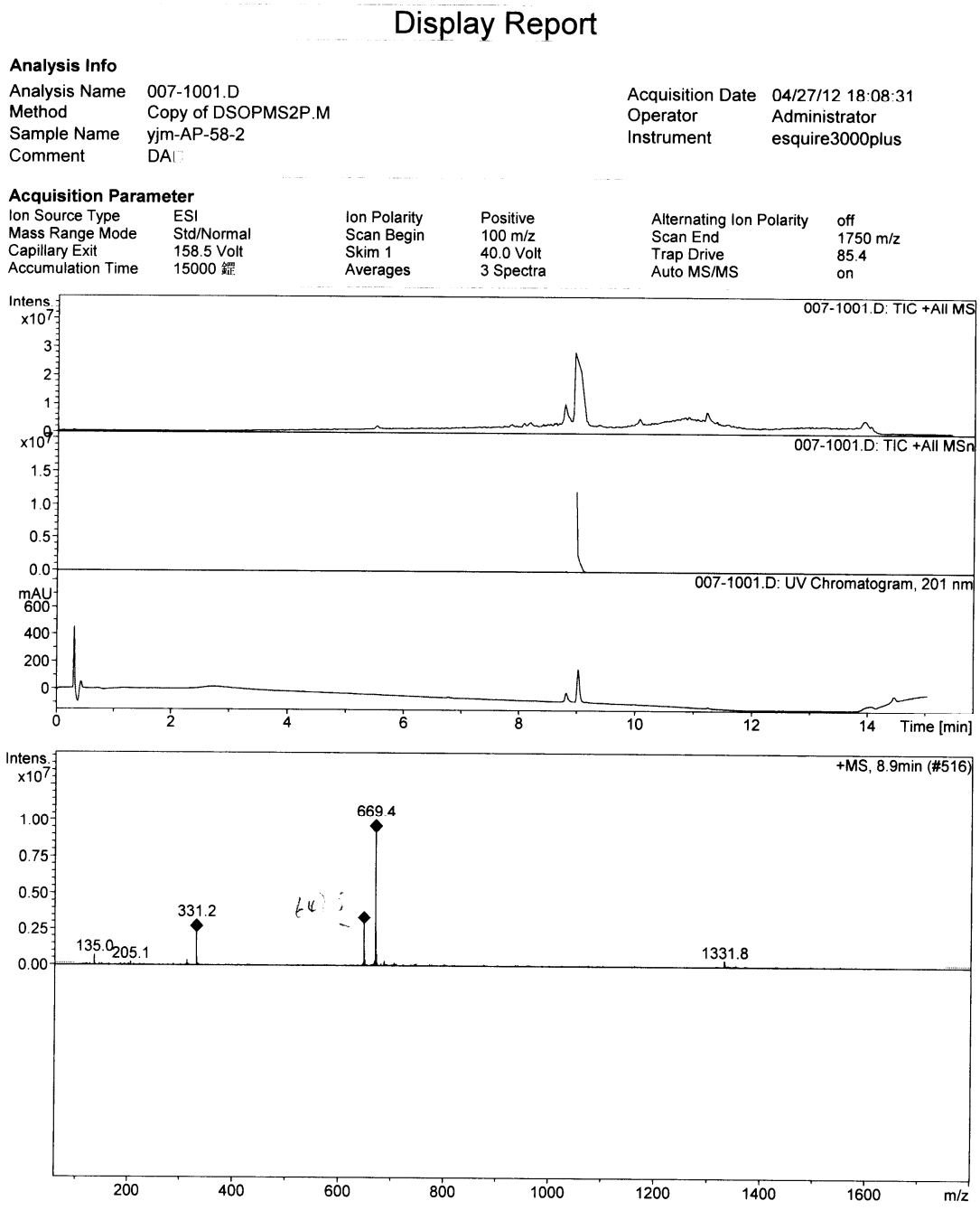
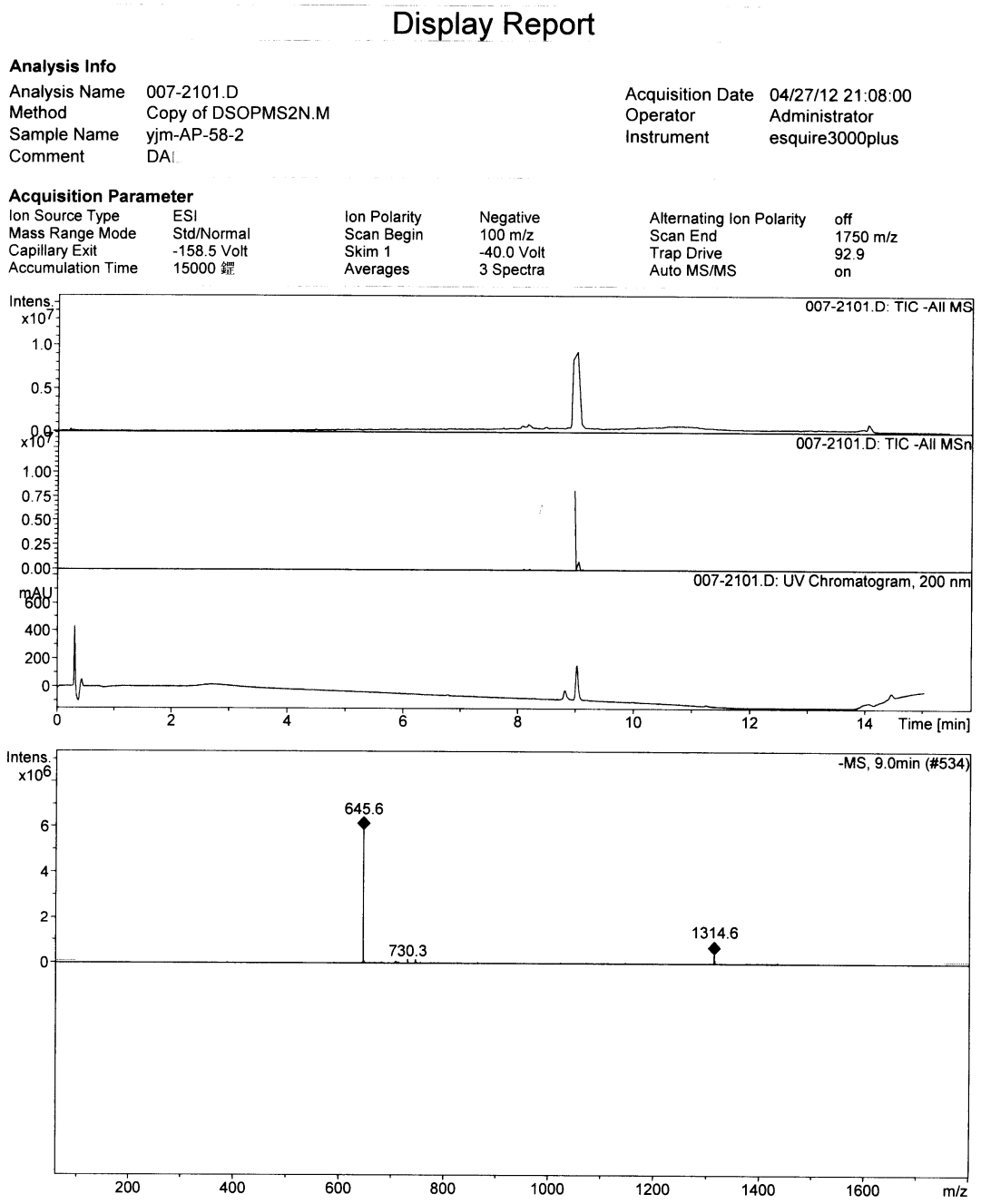


Figure S45. ESI(–)MS spectrum for aphanamene I (**5**).



Bruker Daltonics DataAnalysis 3.1 printed: 04/28/12 09:17:38 Page 1 of 1

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

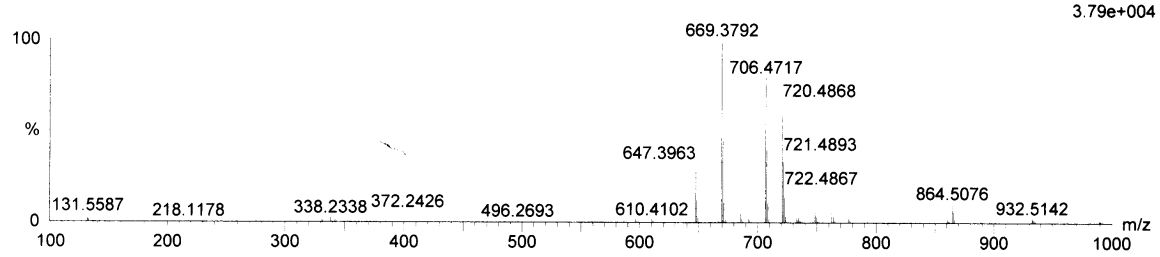
Elemental Composition Report **Page 1**

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 04-May-2012 13:42:14

AP-58-2_20120504 71 (1.555) AM2 (Ar,12000.0,0.00,0.70); ABS; Cm (53:84) 1: TOF MS ES+ 3.79e+004



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
669.3792	669.3767	2.5	3.7	13.5	98.2	0.0	C40 H54 O7 Na

Figure S47. ^{1}H NMR spectrum for **4a** in CD_3OD.

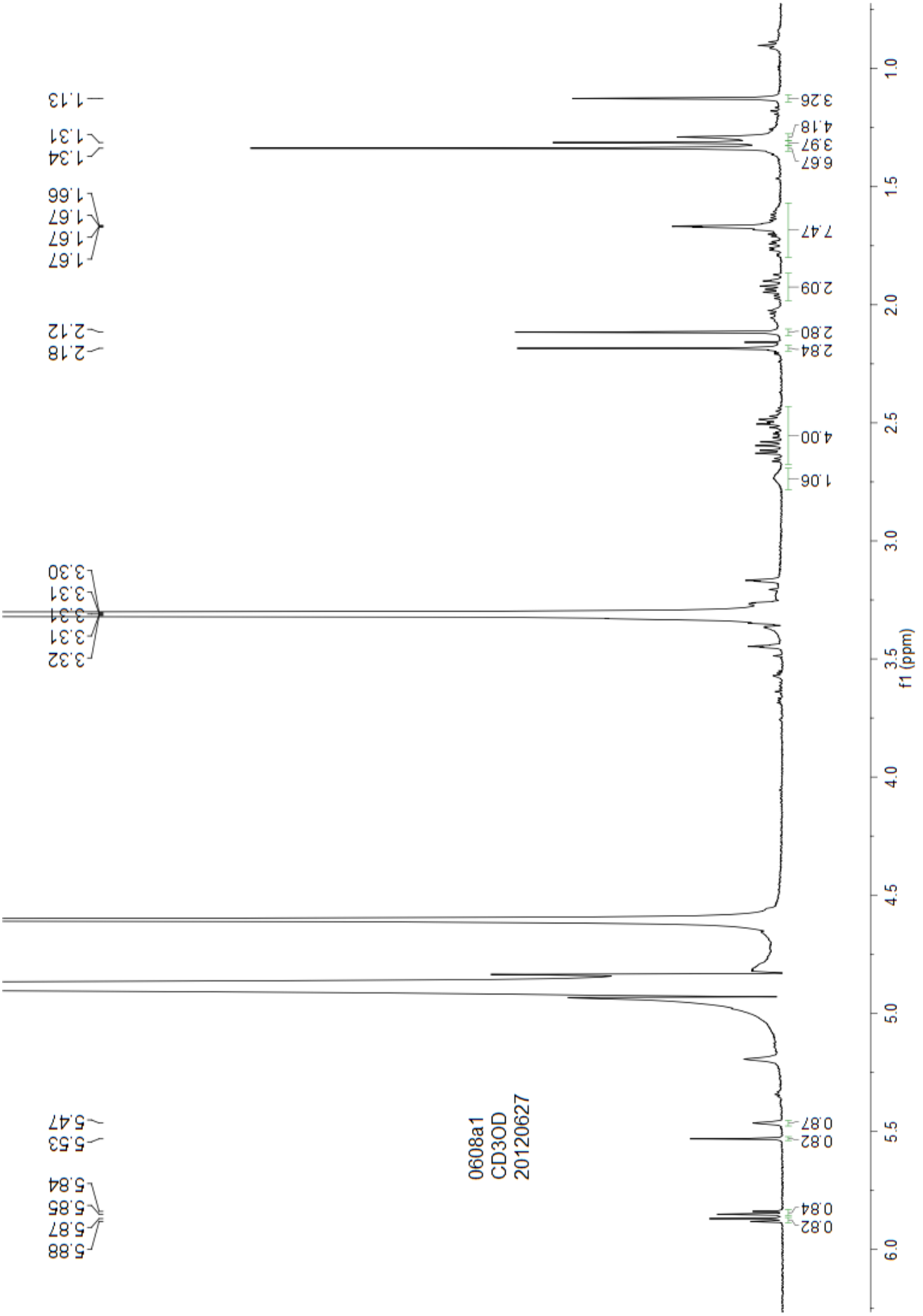


Figure S48. ^{13}C NMR spectrum for **4a** in CD_3OD.

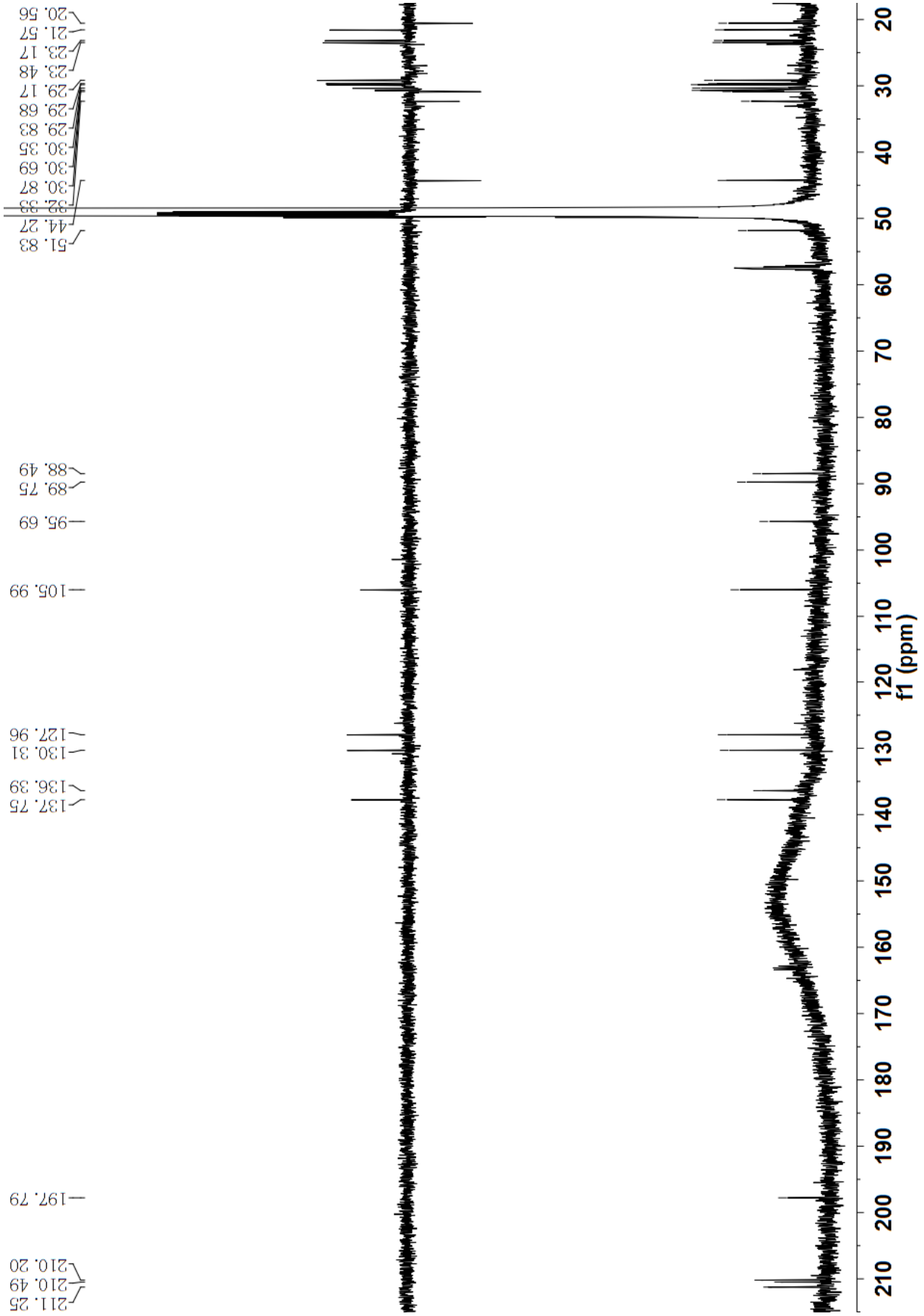


Figure S49. HSQC spectrum for **4a** in CD_3OD.

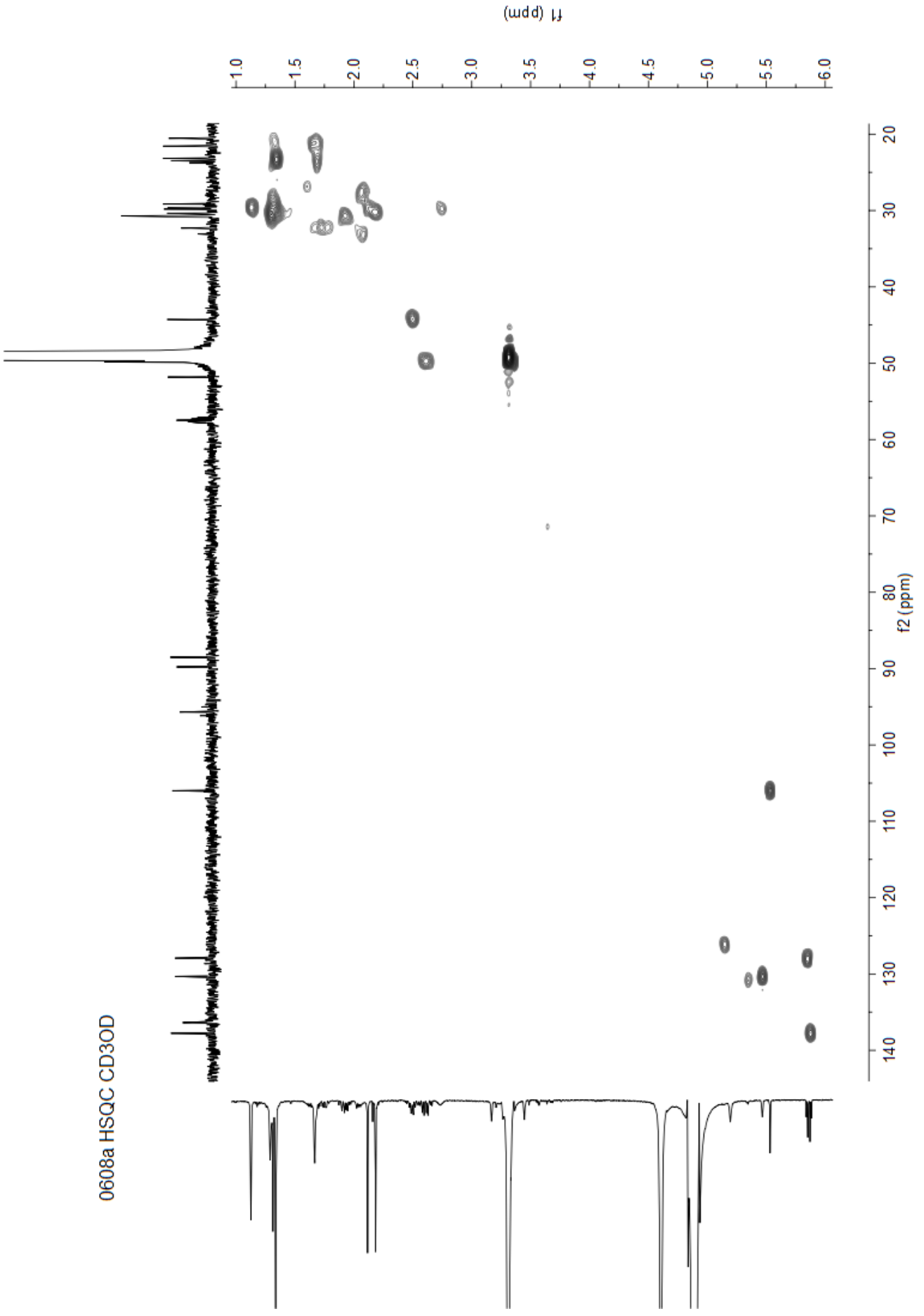


Figure S50. HMBC spectrum for **4a** in CD_3OD.

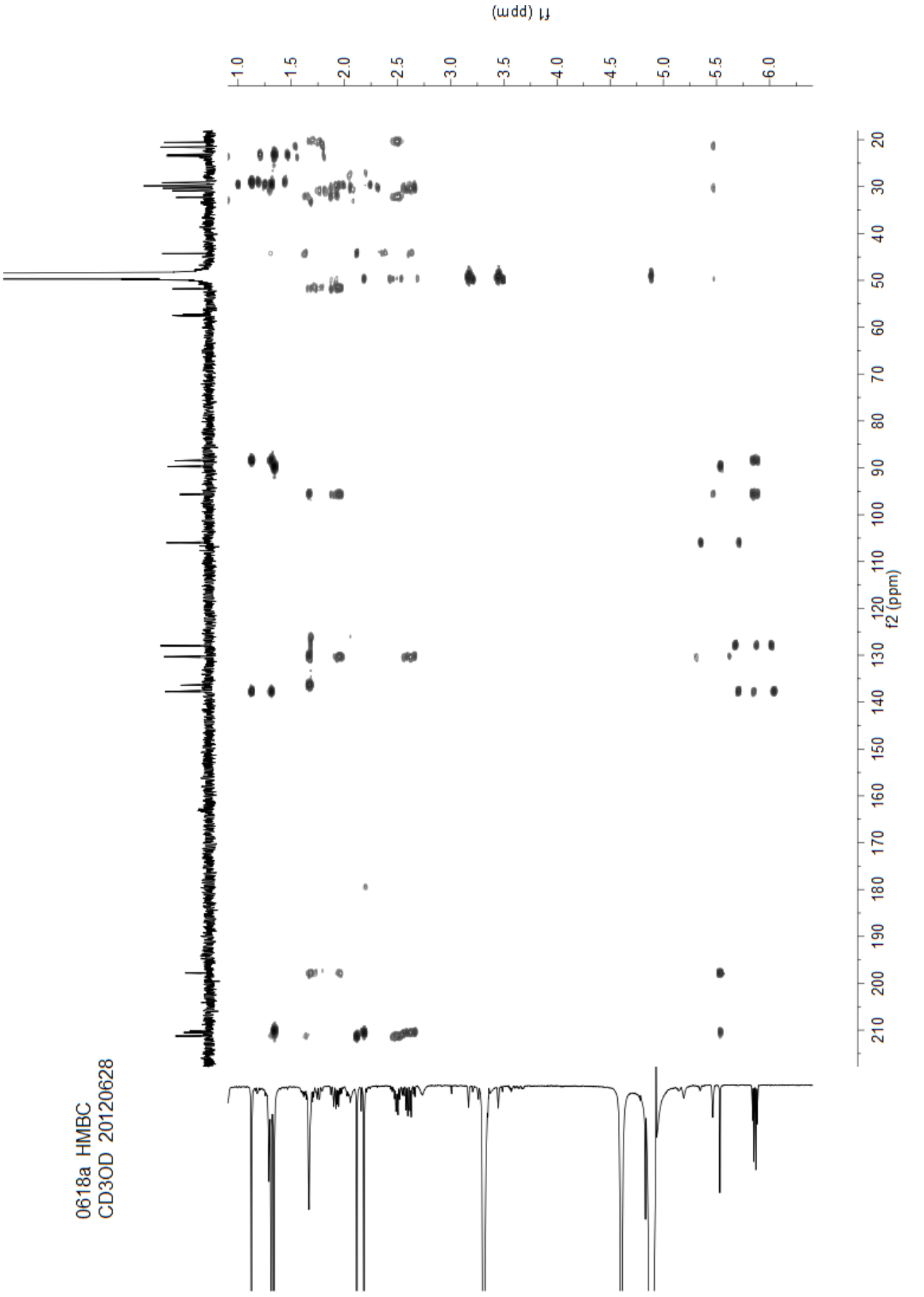


Figure S51. ESI(+)MS spectrum for **4a**.

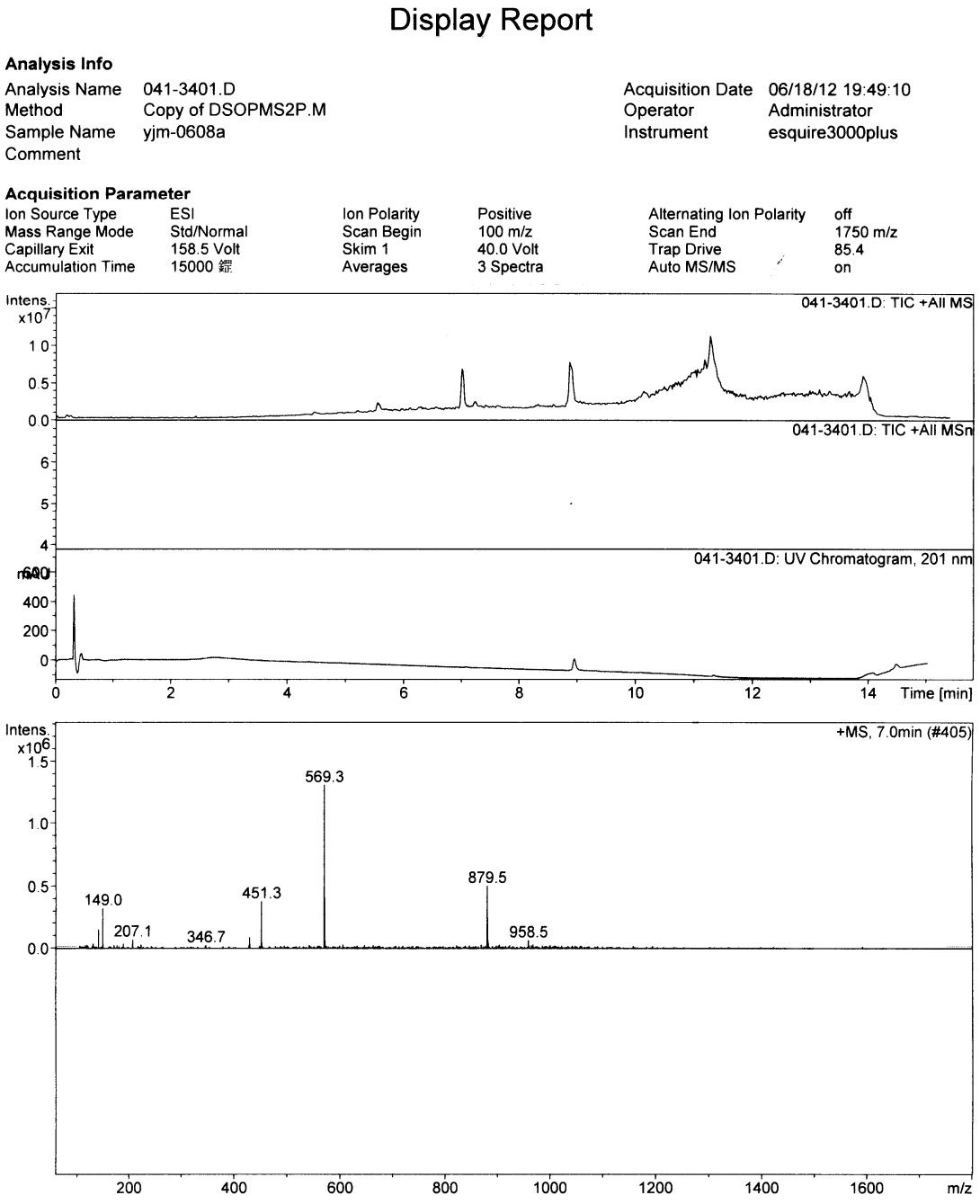


Figure S52. HRESI(+)MS spectrum for **4a**.

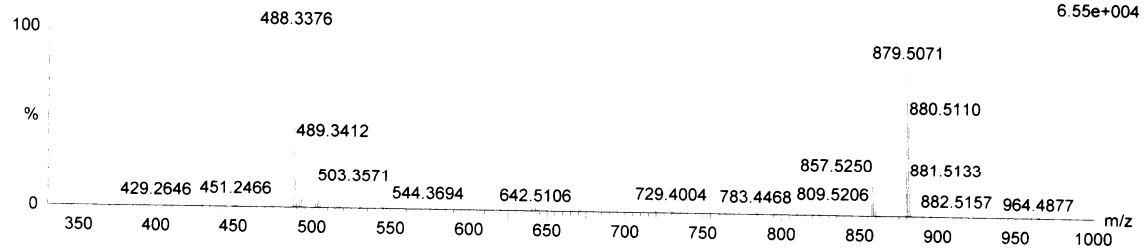
Elemental Composition Report **Page 1**

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

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
LJ

LCT PXE KE324
11-Jun-2012
09:09:34
1: TOF MS ES+
6.55e+004

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



Minimum:				-1.5			
Maximum:		3.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
451.2466	451.2460	0.6	1.3	8.5	27.9	0.0	C26 H36 O5 Na

Figure S53. ^{1}H NMR spectrum for **4b** in CD_3OD.

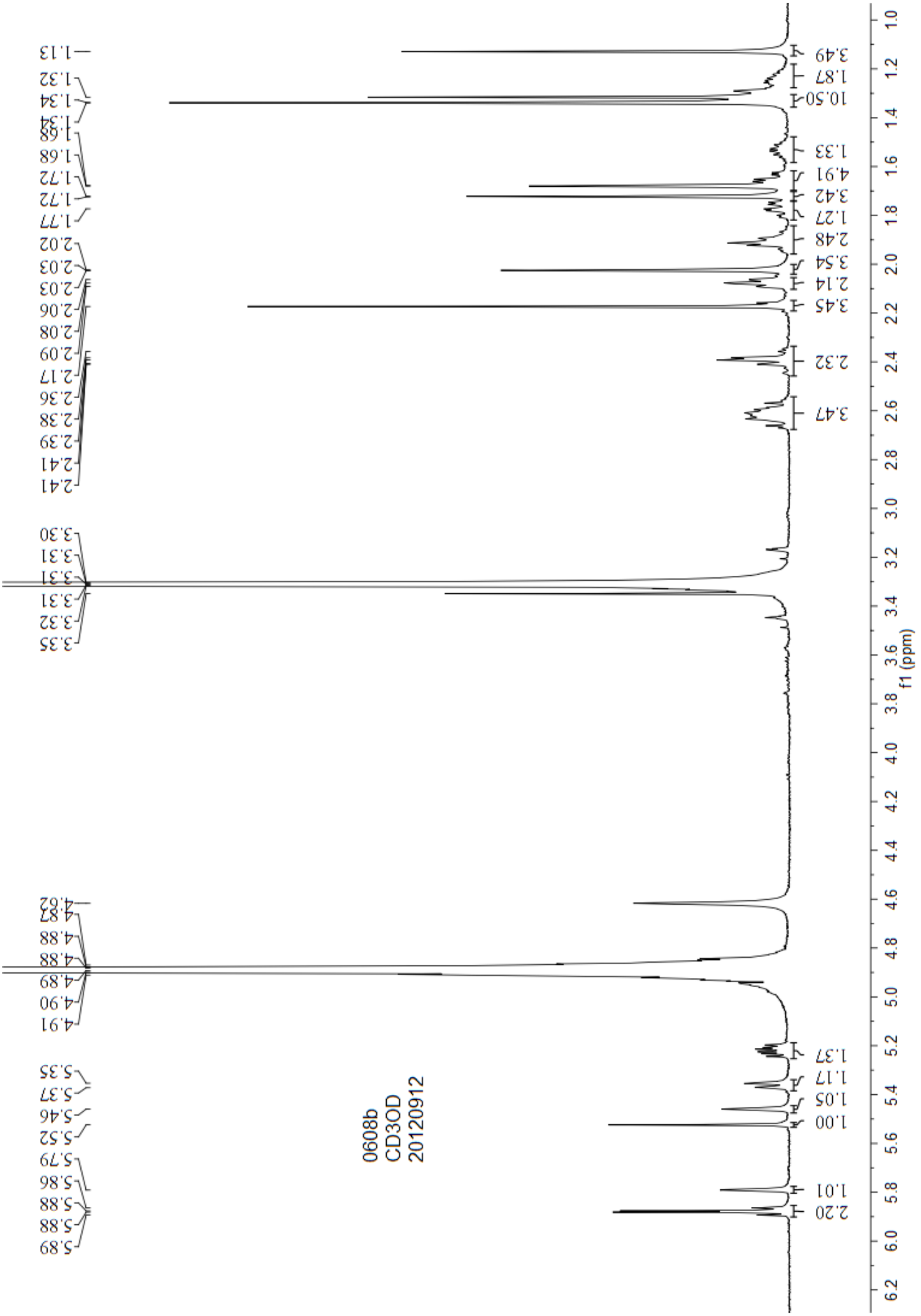


Figure S54. ^{13}C NMR spectrum for **4b** in CD_3OD.

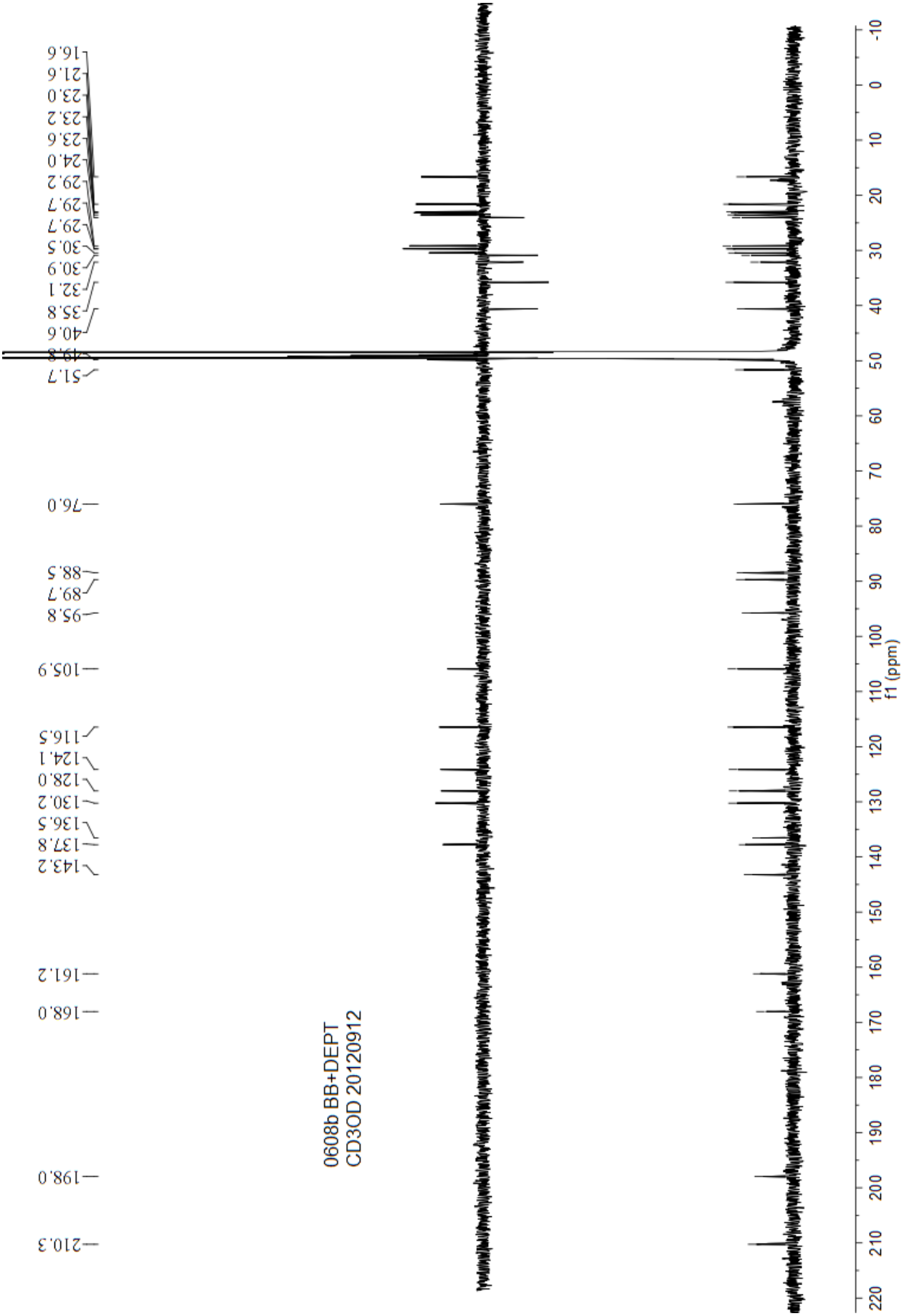


Figure S55. NOESY spectrum for **4b** in CD_3OD.

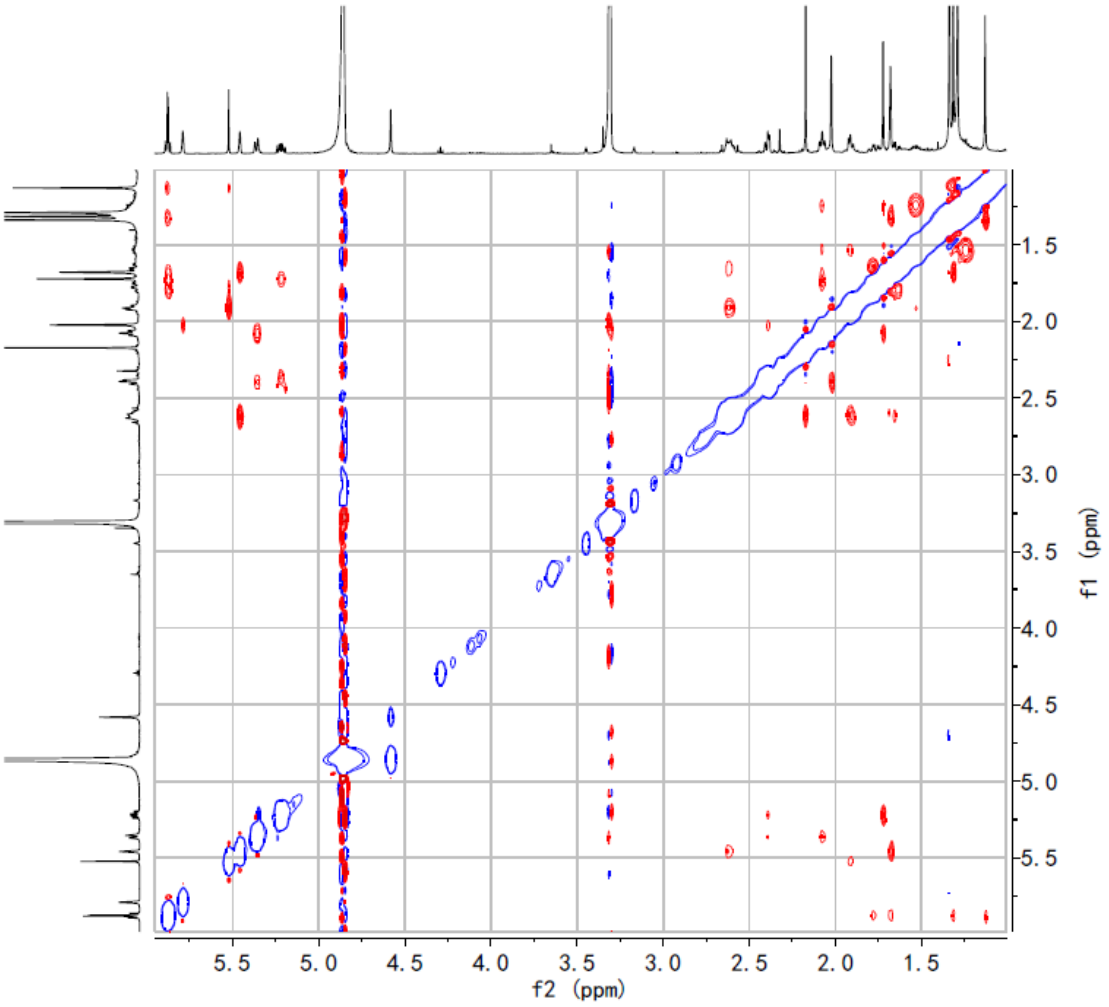


Figure S56. ESI(+)MS spectrum for **4b**.

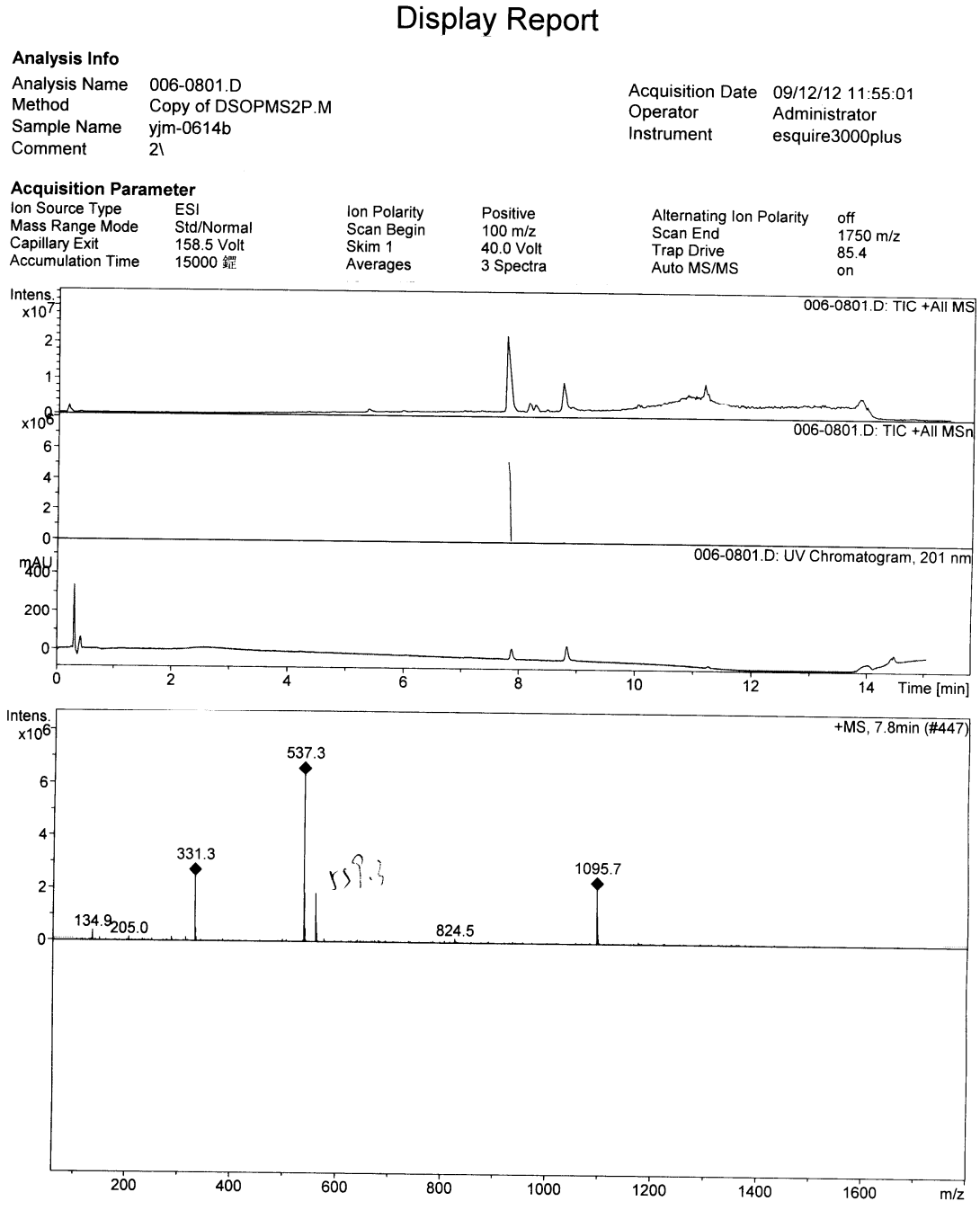


Figure S57. HRESI(+)MS spectrum for **4b**.

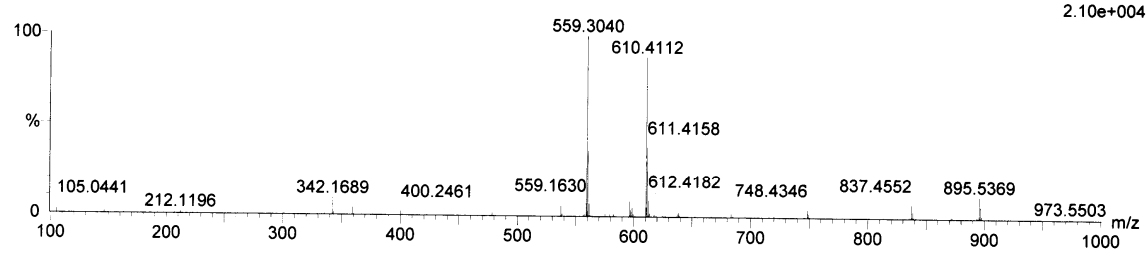
Elemental Composition Report **Page 1**

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 Ions
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 14-Sep-2012 10:51:02

0614b_20120914 14 (0.283) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (5:23) 1: TOF MS ES+ 2.10e+004



Minimum:				-1.5			
Maximum:		3.0	2.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
559.3040	559.3036	0.4	0.7	11.5	88.9	0.0	C33 H44 O6 Na

Figure S58. ^{1}H NMR spectrum for **5a** in CD_3OD.

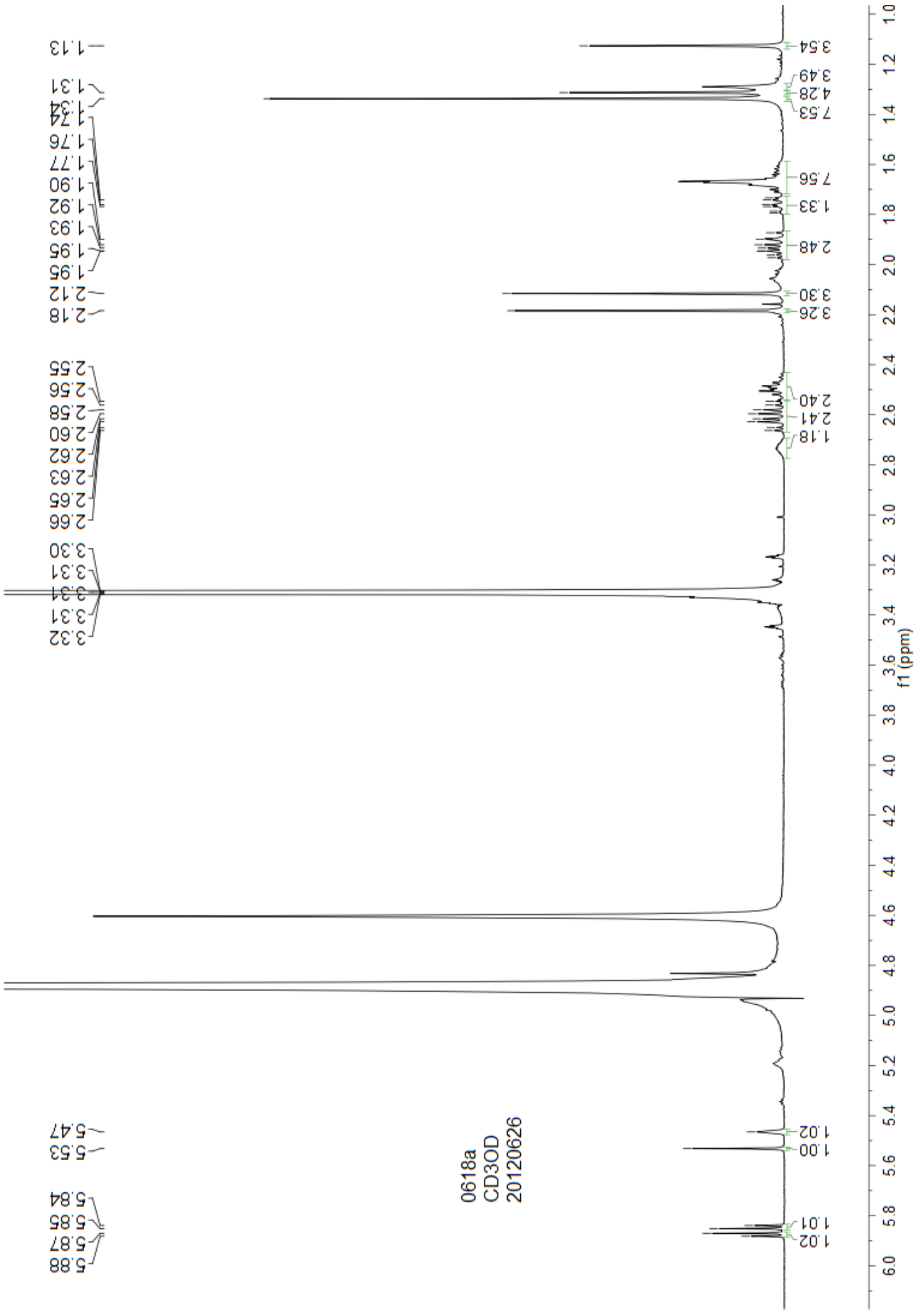


Figure S59. ^{13}C NMR spectrum for **5a** in CD_3OD.

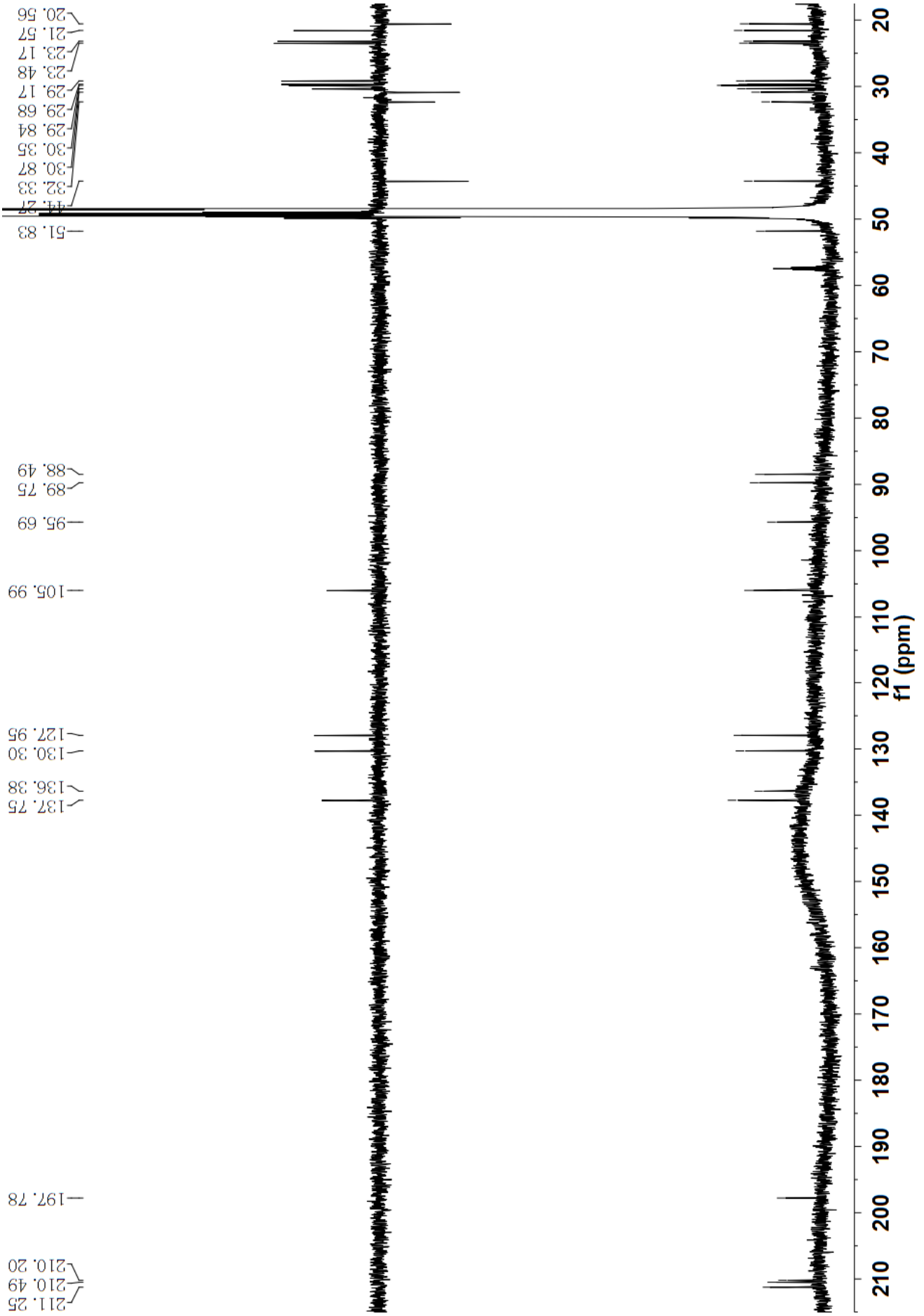


Figure S60. HSQC spectrum for **5a** in CD_3OD.

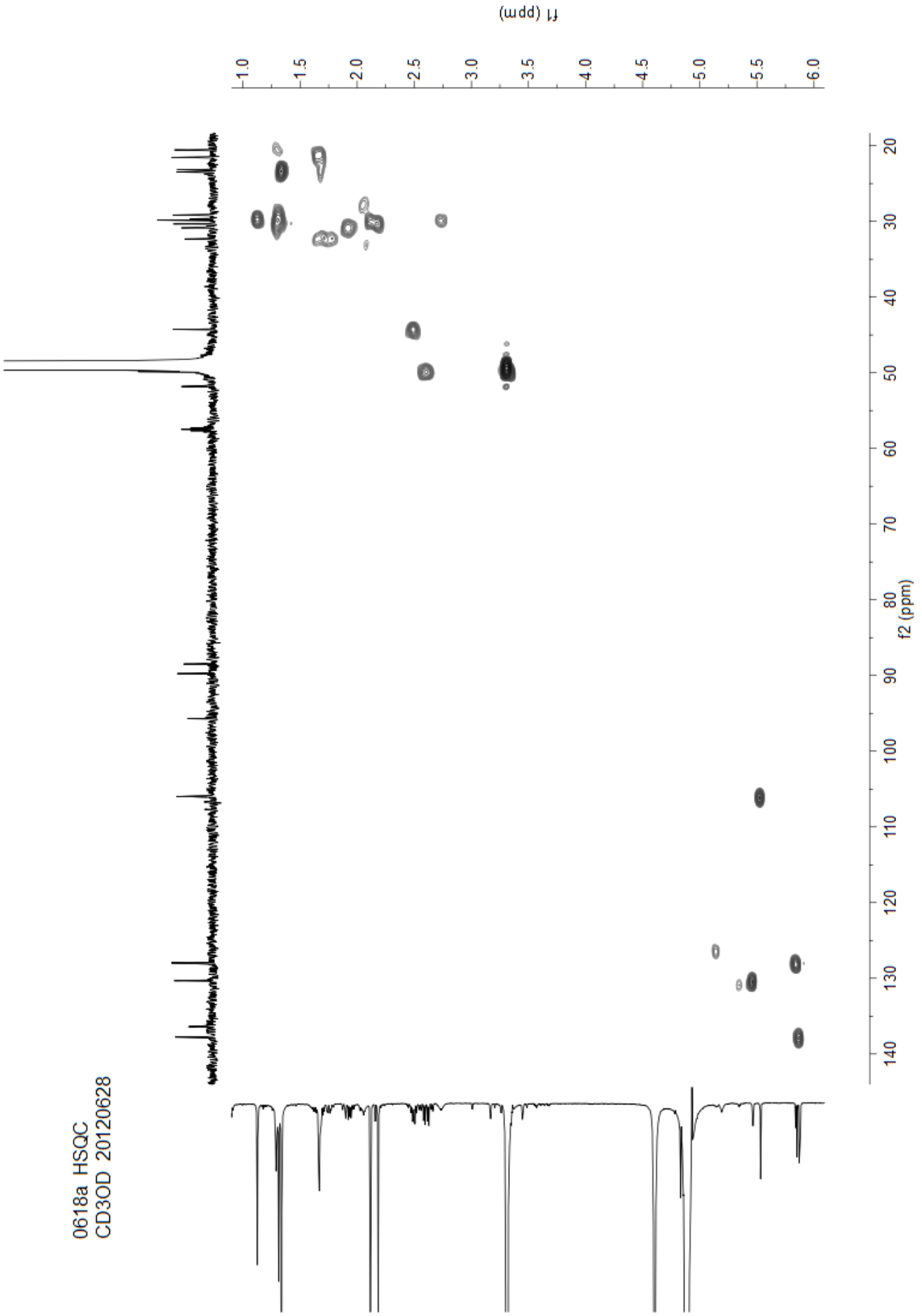


Figure S61. HMBC spectrum for **5a** in CD_3OD.

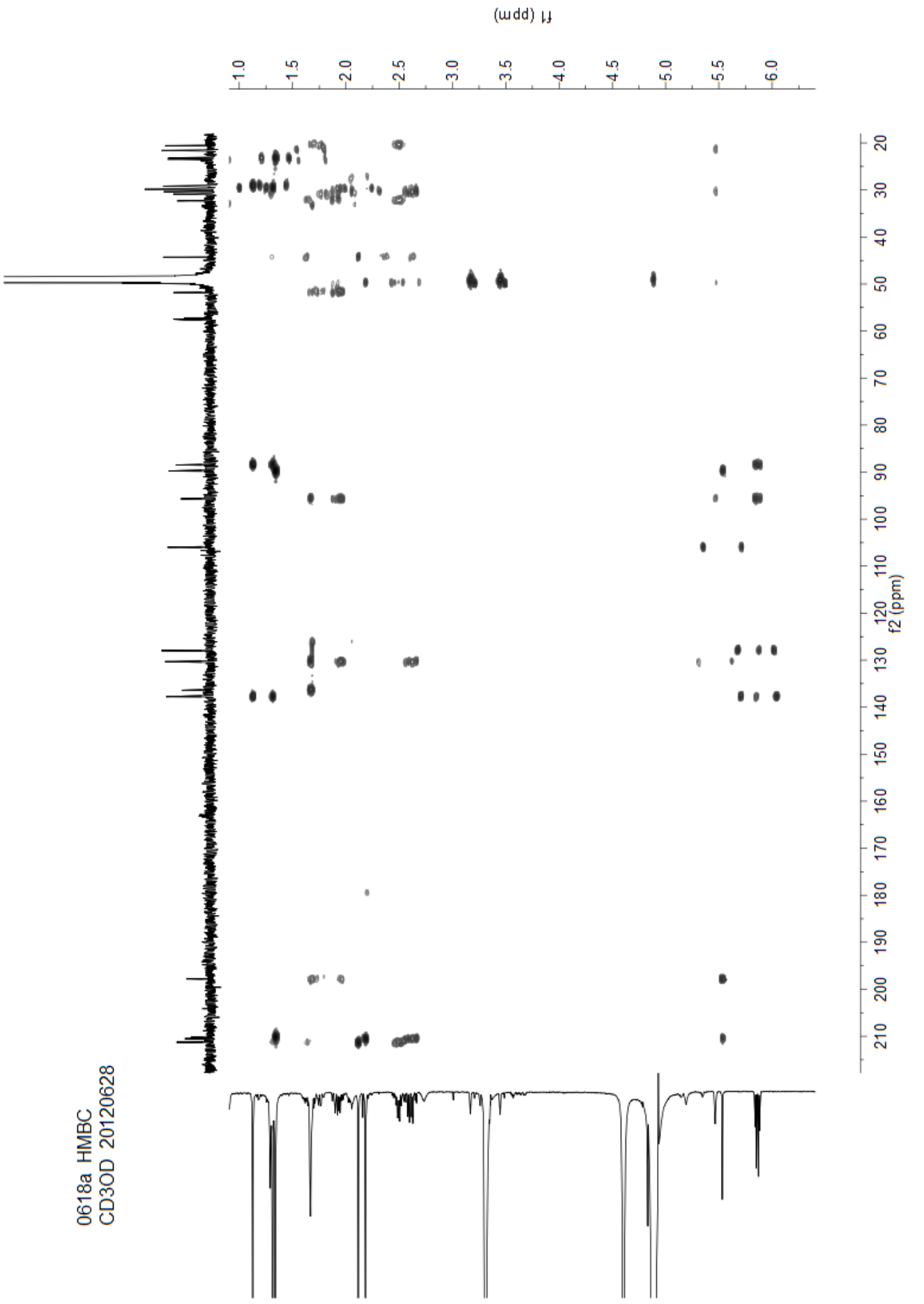


Figure S62. ESI(+)MS spectrum for **5a**.

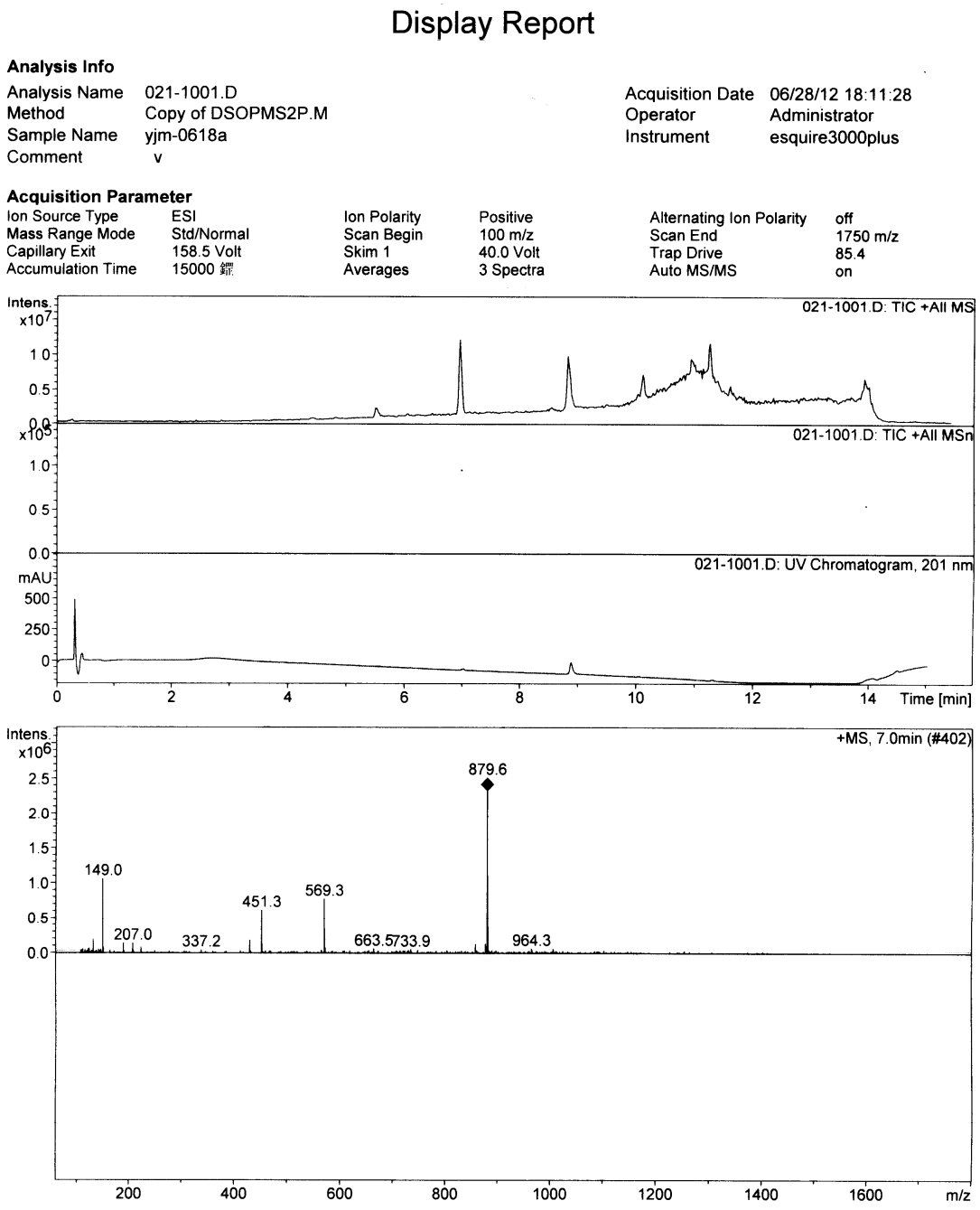


Figure S63. HRESI(+)MS spectrum for **5a**.

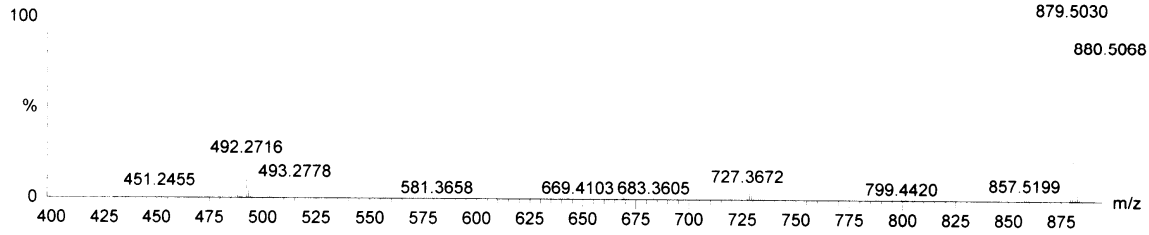
Elemental Composition Report **Page 1**

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

Monoisotopic Mass, Even Electron Ions
185 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

LJ LCT PXE KE324 19-Jul-2012 13:59:20

0618a_20120719 28 (0.600) AM2 (Ar,12500.0,0.00,0.70); ABS; Cm (21:44) 1: TOF MS ES+ 2.77e+004



Minimum:				-1.5			
Maximum:		3.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
451.2455	451.2460	-0.5	-1.1	8.5	16.1	0.0	C26 H36 O5 Na

Figure S64. ^{1}H NMR spectrum for **5b** in CD_3OD.

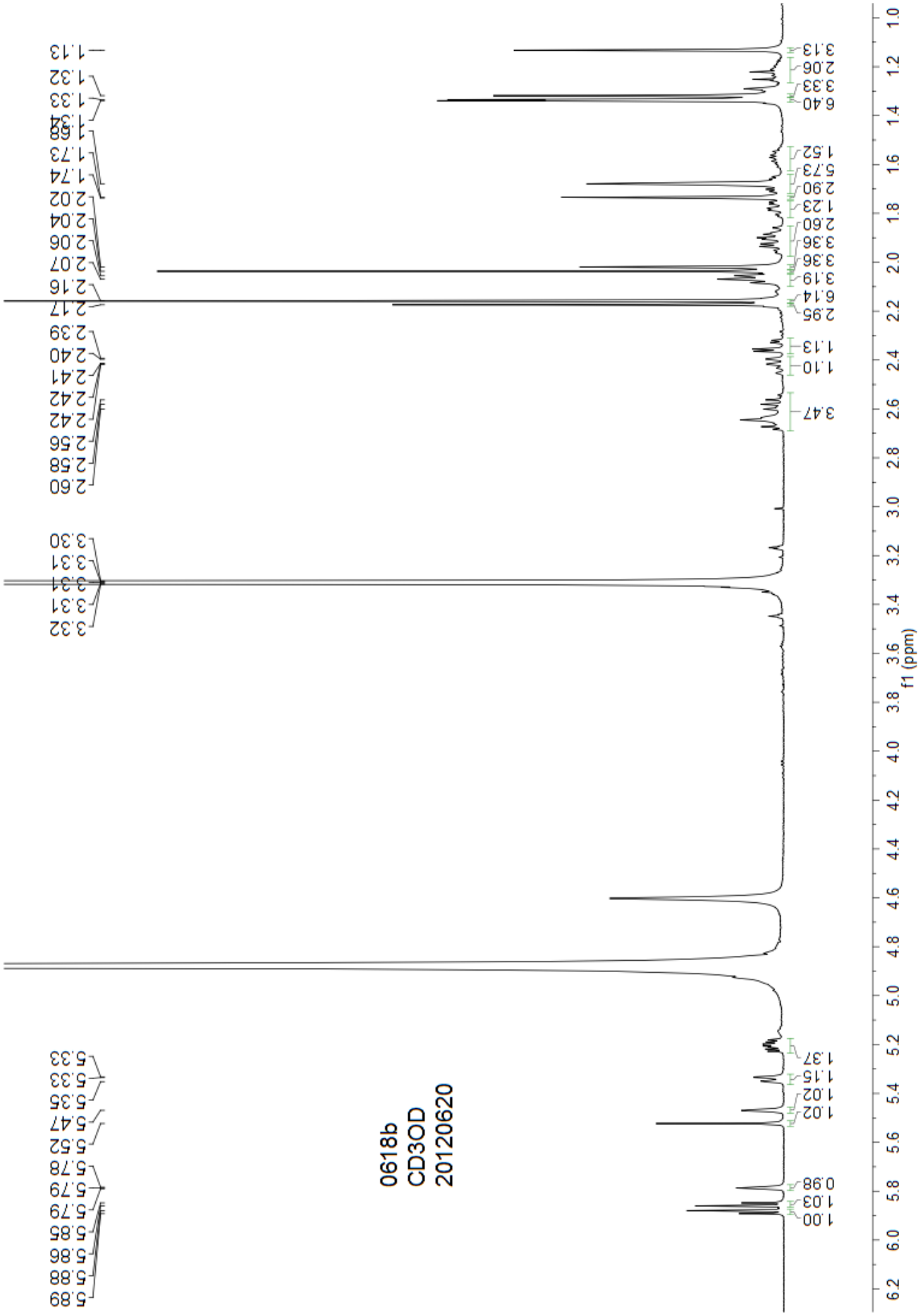


Figure S65. ^{13}C NMR spectrum for **5b** in CD_3OD.

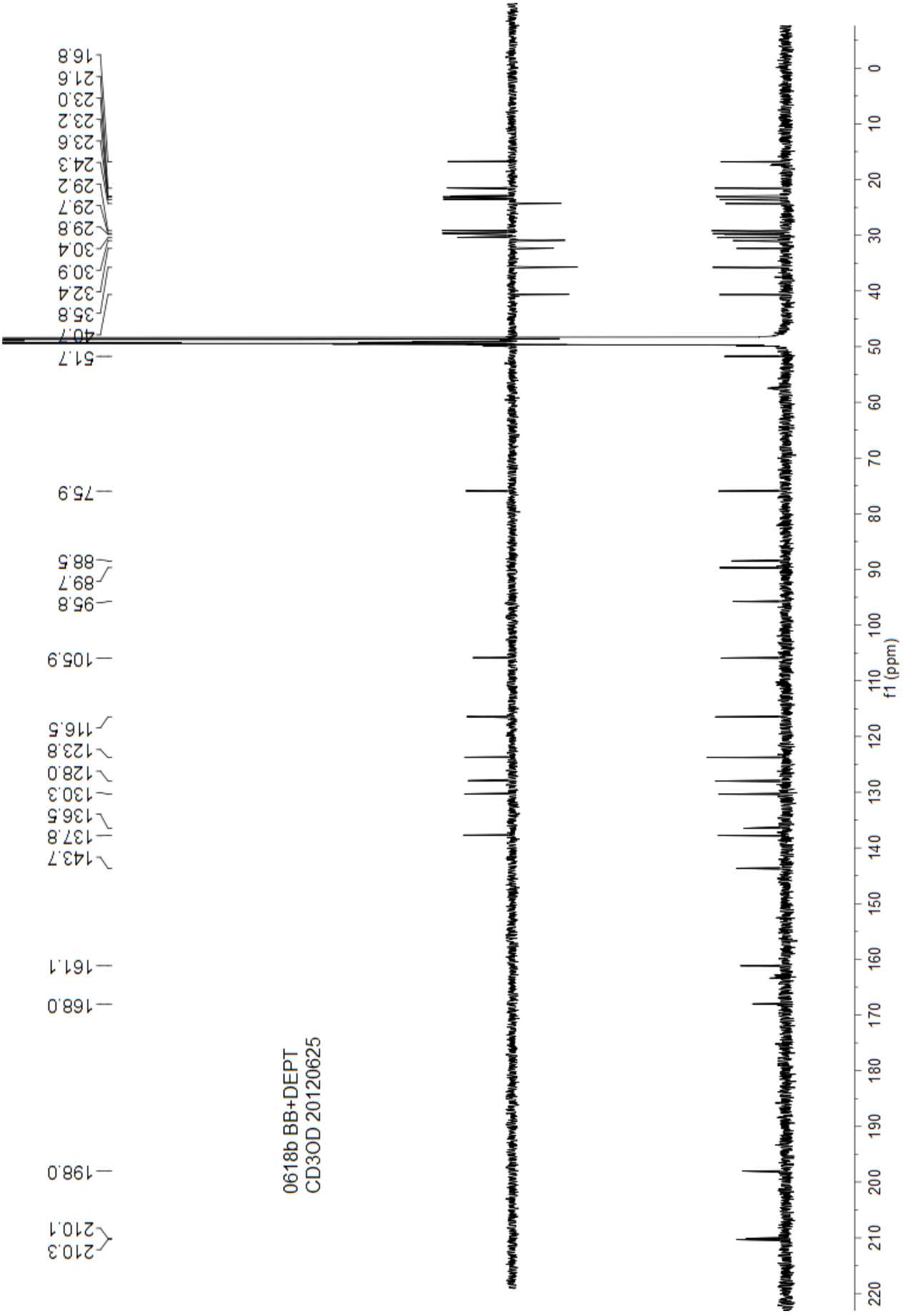


Figure S66. NOESY spectrum for **5b** in CD_3OD.

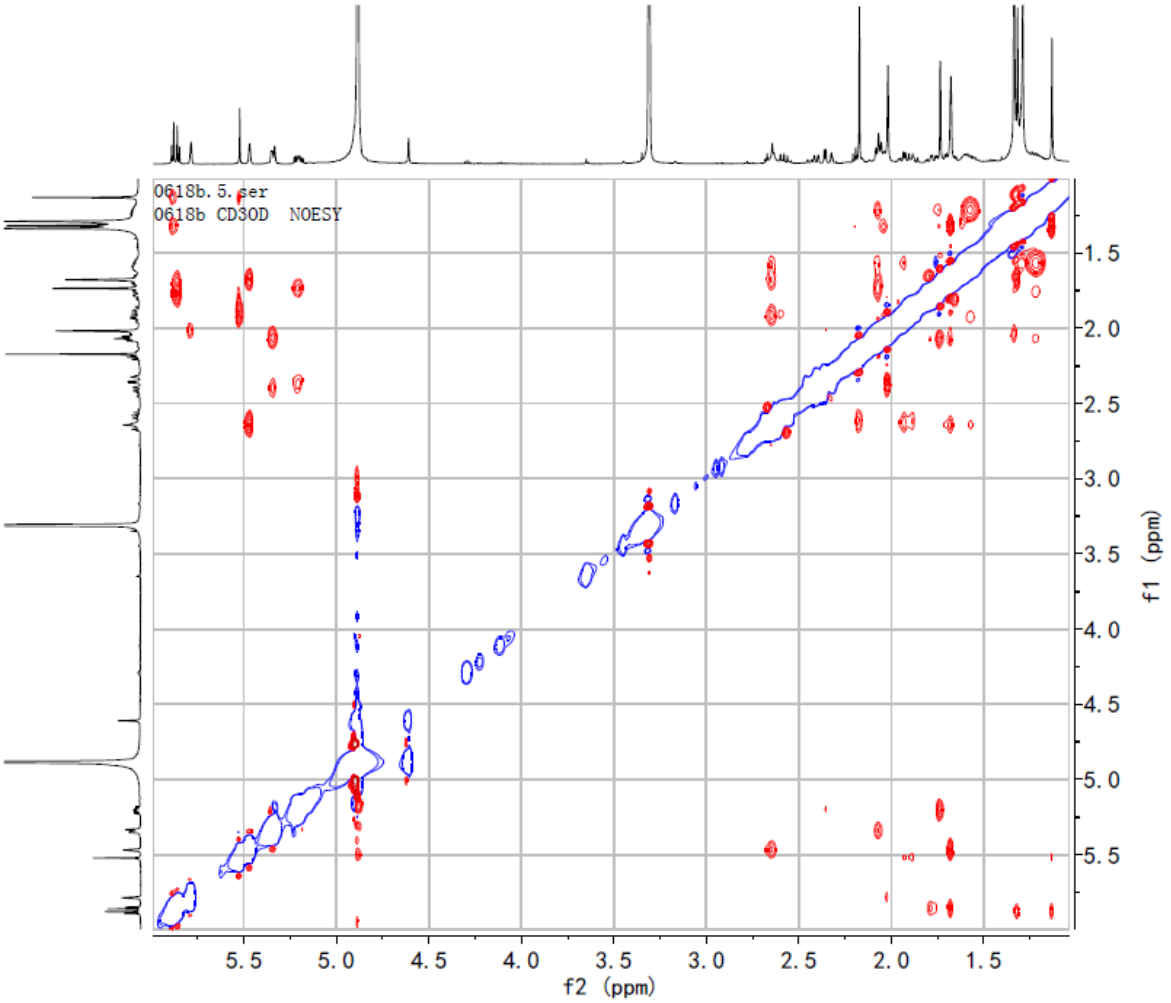


Figure S67. ESI(+)MS spectrum for **5b**.

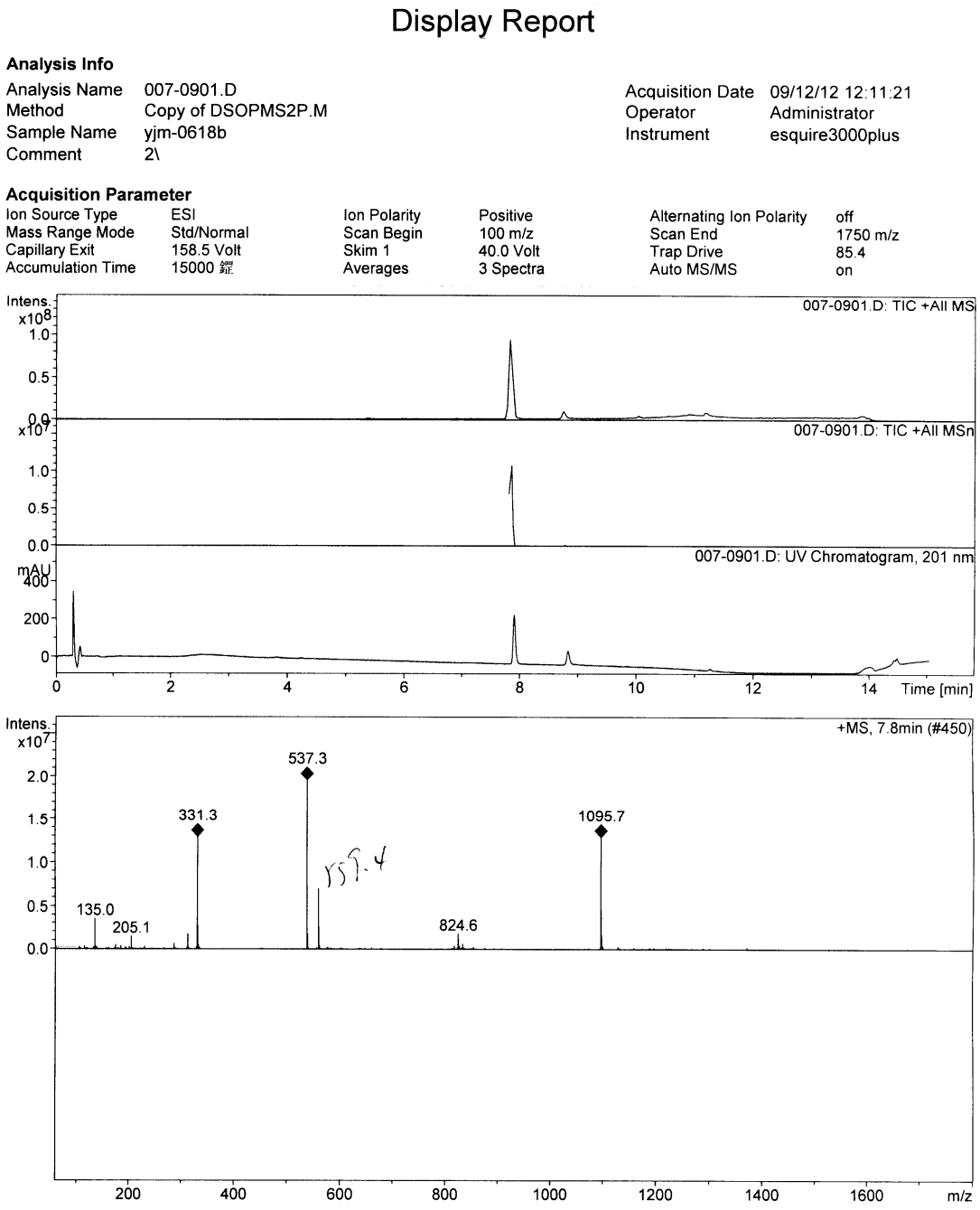


Figure S68. HRESI(+)MS spectrum for **5b**.

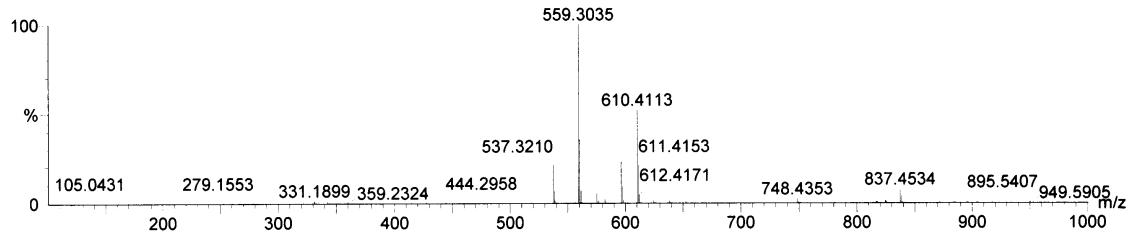
Elemental Composition Report **Page 1**

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 Ions
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

0618b LCT PXE KE324 14-Sep-2012 10:56:07

0618b_20120914 28 (0.583) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (6:29) 1: TOF MS ES+ 2.27e+004



Minimum:				-1.5			
Maximum:		3.0	2.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
559.3035	559.3036	-0.1	-0.2	11.5	75.6	0.0	C33 H44 O6 Na