Supporting Information

New glycosylated derivatives of versipelostatin, the GRP78/Bip molecular chaperone down-regulator, from *Streptomyces versipellis* 4083–SVS6

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Table S1 ^{1}H NMR (600 MHz) data for the aglycone moiety of versipelostatins B–E (**2**–**5**)

	2	**3**	**4**	**5**
#	δ (multi, *J* in Hz)[a]	δ (multi, *J* in Hz)[b]	δ (multi, *J* in Hz)[c]	δ (multi, *J* in Hz)[a]
5	2.43 (m)	2.83 (m)	2.39 (m)	2.43 (m)
6	2.45 (m)	2.72 (m)	2.48 (m)	2.45 (m)
8	2.48 (m)	2.85 (m)	2.40 (m)	2.41 (m)
	3.02 (dd, 15.0, 6.0)	3.31 (dd, 15.0, 6.0)	2.98 (dd, 15.0, 6.0)	3.02 (dd, 15.0, 6.0)
9	3.82 (m)	4.18 (m)	3.75 (m)	3.83 (m)
10	2.31 (m)	2.60 (m)	2.22 (m)	2.32 (m)
11	5.85 (br s)	6.37 (br d, 6.6)	5.88 (br s)	5.85 (br s)
13	3.10 (s)	4.48 (m)	3.06 (s)	3.09 (s)
15	5.12 (d, 10.3)	6.03 (d, 9.3)	5.15 (d, 9.8)	5.14 (d, 10.3)
16	2.31 (m)	2.66 (m)	2.36 (m)	2.30 (m)
17	0.62 (t, 11.0)	1.01 (m)	0.66 (t, 11.0)	0.61 (t, 12.0)
	1.58 (m)	1.56 (m)	1.59 (m)	1.59 (m)
18	1.97 (m)	2.11 (m)	1.96 (m)	1.96 (m)
19	3.21 (m)	3.22 (m)	3.22 (m)	3.22 (m)
20	1.63 (m)	1.43 (m)	1.63 (m)	1.62 (m)
21	1.11 (m)	1.29 (m)	1.16 (m)	1.13 (m)
	1.52 (m)	1.72 (m)	1.53 (m)	1.55 (m)
22	1.36 (m)	1.49 (m)	1.39 (m)	1.35 (m)
	1.60 (m)		1.62 (m)	1.62 (m)
23	1.27 (m)	1.79 (m)	1.28 (m)	1.28 (m)
	1.56 (m)		1.57 (m)	1.57 (m)
25	5.29 (br s)	5.67 (br s)	5.34 (br s)	5.28 (br s)
27	2.39 (m)	2.37 (m)	2.39 (m)	2.39 (m)
28	1.76 (dd, 13.7, 6.9)	1.86 (m)	1.77 (m)	1.77 (dd, 13.7, 6.8)
	2.25 (dd, 13.7, 6.9)	2.74 (m)	2.09 (br d, 12.7)	2.23 (dd, 13.7, 6.8)
31	2.12 (q, 7.6)	2.49 (m)	2.05 (q, 7.6)	2.15 (q, 7.6)
	2.54 (q, 7.6)	2.88 (m)	2.49 (m)	2.55 (q, 7.6)
32	0.95 (t, 6.2)	1.32 (t, 7.8)	0.92 (t, 5.8)	0.94 (t, 6.2)
33	0.95 (d, 6.2)	1.17 (d, 7.3)	1.00 (d, 7.2)	0.95 (d, 6.2)
34	1.66 (s)	1.74(s)	1.66 (s)	1.64 (s)
35	1.88 (q, 6.9)	2.06 (m)	1.93 (q, 7.8)	1.88 (q, 7.6)
	1.95 (q, 6.9)	2.13 (m)	1.95 (q, 7.8)	1.90 (q, 7.6)
36	0.91 (t, 6.9)	1.11 (t, 8.3)	0.94 (t, 7.8)	0.90 (t, 7.6)
37	3.42 (dd, 11.7, 3.5)	3.80 (dd, 12.0, 8.8)	3.39 (dd, 11.5, 4.9)	3.41 (dd, 11.3, 4.4)
	3.53 (dd, 10.3, 4.1)	4.01 (dd, 12.0, 3.9)	3.51 (dd, 11.5, 4.9)	3.56 (dd, 11.3, 4.5)
38	0.93 (d, 6.2)	1.13 (d, 7.3)	0.98 (d, 7.3)	0.93 (d, 6.2)
39	0.90 (d, 7.6)	0.55 (br s)	0.94 (d, 7.8)	0.91 (d, 7.6)
40	1.03 (s)	1.25 (s)	1.04 (s)	1.03 (s)
41	1.69 (s)	2.12 (s)	1.69 (s)	1.67 (s)
42	1.06 (d, 6.9)	1.21 (d, 7.3)	1.07 (d, 6.8)	1.06 (d, 6.9)

Data were recorded in [a]$CDCl_3$ for **2** and **5**, [b]C_5D_5N for **3**, and [c]$CDCl_3$/CD_3OD for **4**.

Table S2 ^{1}H NMR (600 MHz) data for VST (**1**)

no.	δ^a	δ^b	no.	δ^a	δ^b
5	2.40 (m)	2.88 (t, 10.8)	38	0.91	1.11 (d, 6.6)
6	2.45 (m)	2.73 (m)	39	0.88	0.66 (br d, 6.1)
8	2.41 (m)	2.93 (m)	40	1.01 (s)	1.26 (s)
	2.98 (dd, 14.0, 7.0)	3.30 (dd, 14.2, 5.9)			
9	3.77 (m)	4.11 (td, 9.8, 6.1)	41	1.66 (s)	1.94 (br s)
10	2.28 (m)	2.69 (br t, 11.7)	42	1.03 (d, 7)	1.21 (d, 7.3)
11	5.83 (br s)	6.39 (br s)	β-D-Dig		
13	3.06 (s)	4.21 (m)	1'	4.77 (d, 8.3)	5.22 (m)
15	5.09 (d, 9.6)	5.96 (d, 9.5)	2'	1.65 (m), 2.09 (dd, 10, 3)	1.95 (m), 2.41 (m)
16	2.28 (m)	2.73 (m)	3'	4.04 (br s)	4.55 (q, 2.7)
17	0.59 (t, 11.0), 1.59 (m)	0.90 (br t, 12.6), 1.74 (m)	4'	3.20 (dd, 10, 3)	3.48 (dd, 9.5, 2.4)
18	1.93 (m)	2.09 (m)	5'	3.77 (dq, 10, 6.5)	4.29 (m)
19	3.21 (m)	3.10 (br d, 4.2)	6'	1.17 (d, 6.5)	1.36 (d, 6.1)
20	1.61 (m)	1.43 (m)	α-L-Ole		
21	1.11 (m), 1.51 (m)	1.28 (m), 1.72 (m)	1"	4.92 (d, 2)	5.15 (m)
22	1.33 (m), 1.58 (m)	1.47 (m)	2"	1.53 (m), 2.11 (dd, 12, 4)	1.65 (td,), 2.38 (m)
23	1.26 (m), 1.53 (m)	1.80 (m)	3"	3.46 (dd, 12, 10)	3.71 (ddd, 10.9, 8.9, 4.5)
25	5.25 (br s)	5.52 (br s)	4"	3.27 (t, 10)	3.67 (t, 9.3)
27	2.37 (m)	2.40 (m)	5"	3.61 (dq, 10, 6.5)	4.31 (m)
28	1.74 (dd, 14.0, 7.0)	1.97 (m)	6"	1.24 (d, 6.5)	1.55 (d, 6.4)
	2.20 (dd, 14.0, 7.0)	2.57 (m)			
31	2.11 (q, 8.0)	2.49 (pentet, 7.5)	3"-OCH_3	3.36 (s)	3.18 (s)
	2.50 (q, 8.0)	2.94 (m)			
32	0.91	1.35 (t, 7.8)	β-D-Dig		
33	0.92	1.16 (d, 6.6)	1'"	5.01 (d, 8.3)	5.66 (dd, 9.5, 1.7)
34	1.63 (s)	1.73 (s)	2'"	1.61 (m), 2.09 (dd, 10, 3)	1.95 (m), 2.45(m)
35	1.87 (q, 7) , 1.92 (q, 7)	2.14 (m), 2.19 (m)	3'"	4.04 (br s)	4.45 (q, 2.9)
36	0.88	1.07 (t, 7.5)	4'"	3.21 (dd, 10, 3)	3.61 (dd, 9.5, 3.0)
37	3.41 (dd, 10, 4)	3.77 (dd, 10.5, 7.3)	5'"	3.63 (dq, 10, 6.5)	4.23 (m)
	3.50 (dd, 10, 4)	4.01 (dd, 10.5, 3.3)	6'"	1.22 (d, 6.5)	1.54 (d, 6.1)

[a] in $CDCl_3$, [b] in C_5D_5N. Dig: digitoxopyranosyl; Ole: oleandropyranosyl.

Fig. S1 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of versipelostatin B (2)

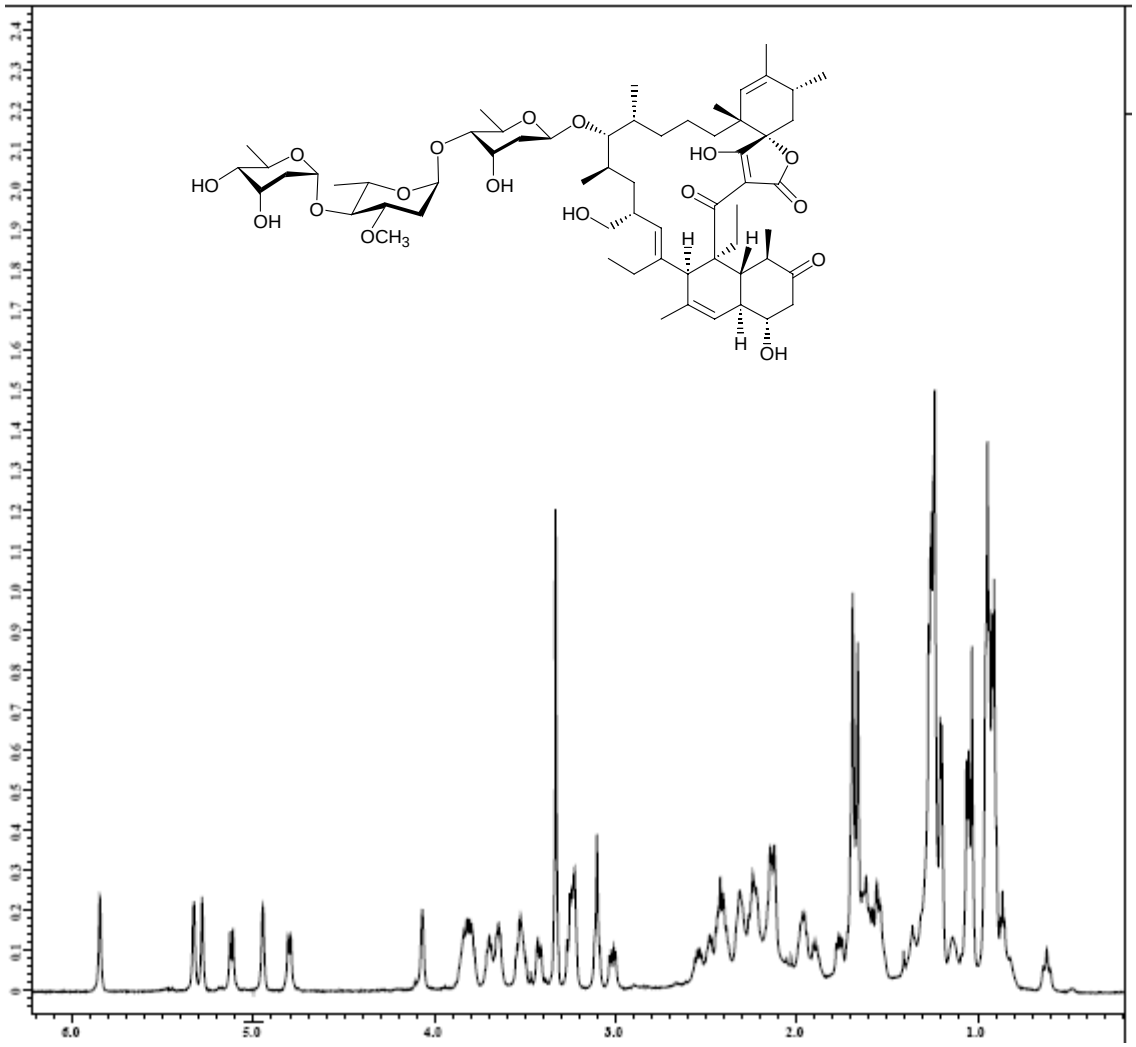

Fig. S2 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of versipelostatin B (2)

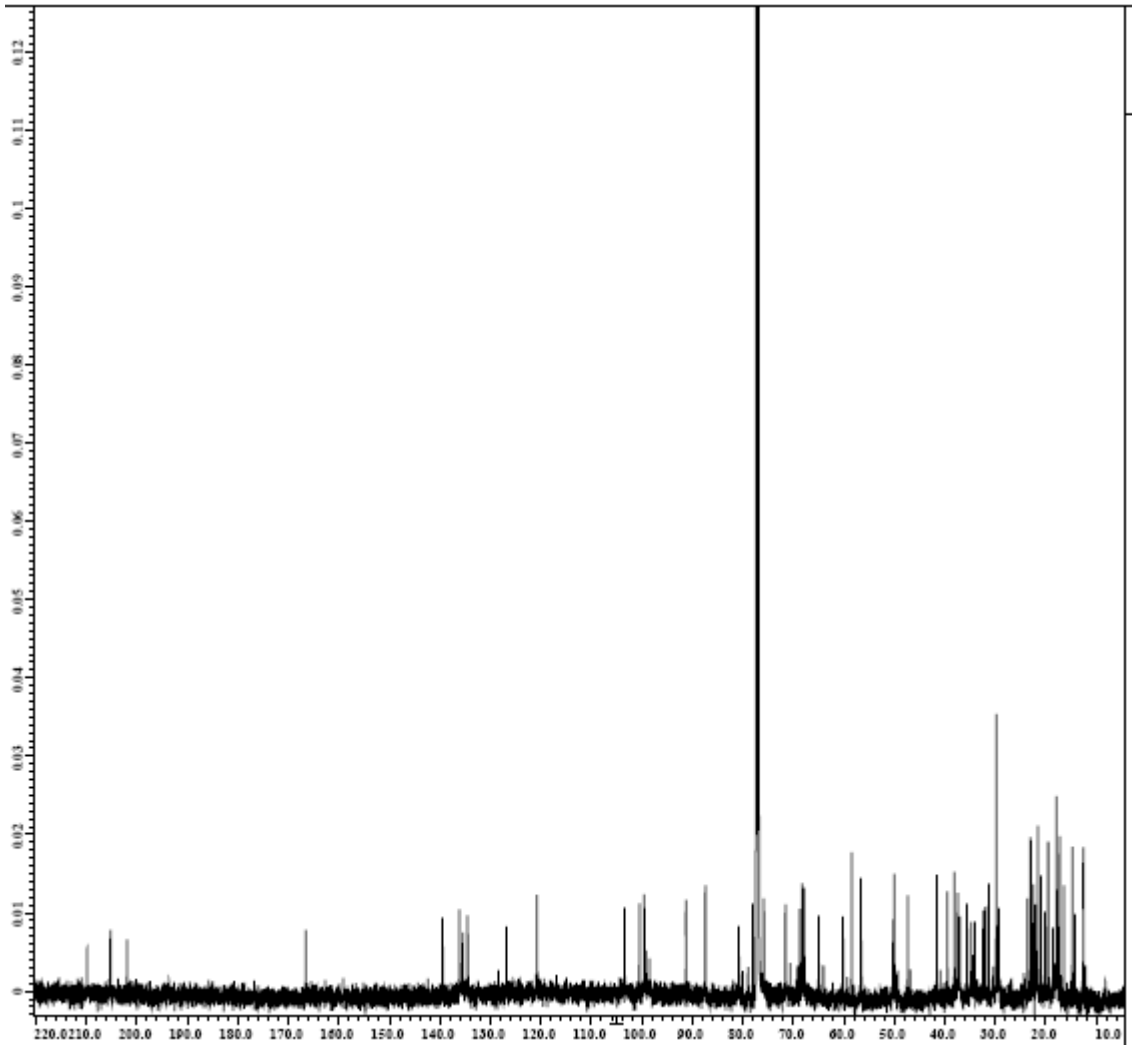

Fig. S3 HSQC (600 MHz, $CDCl_3$) spectrum of versipelostatin B (2)

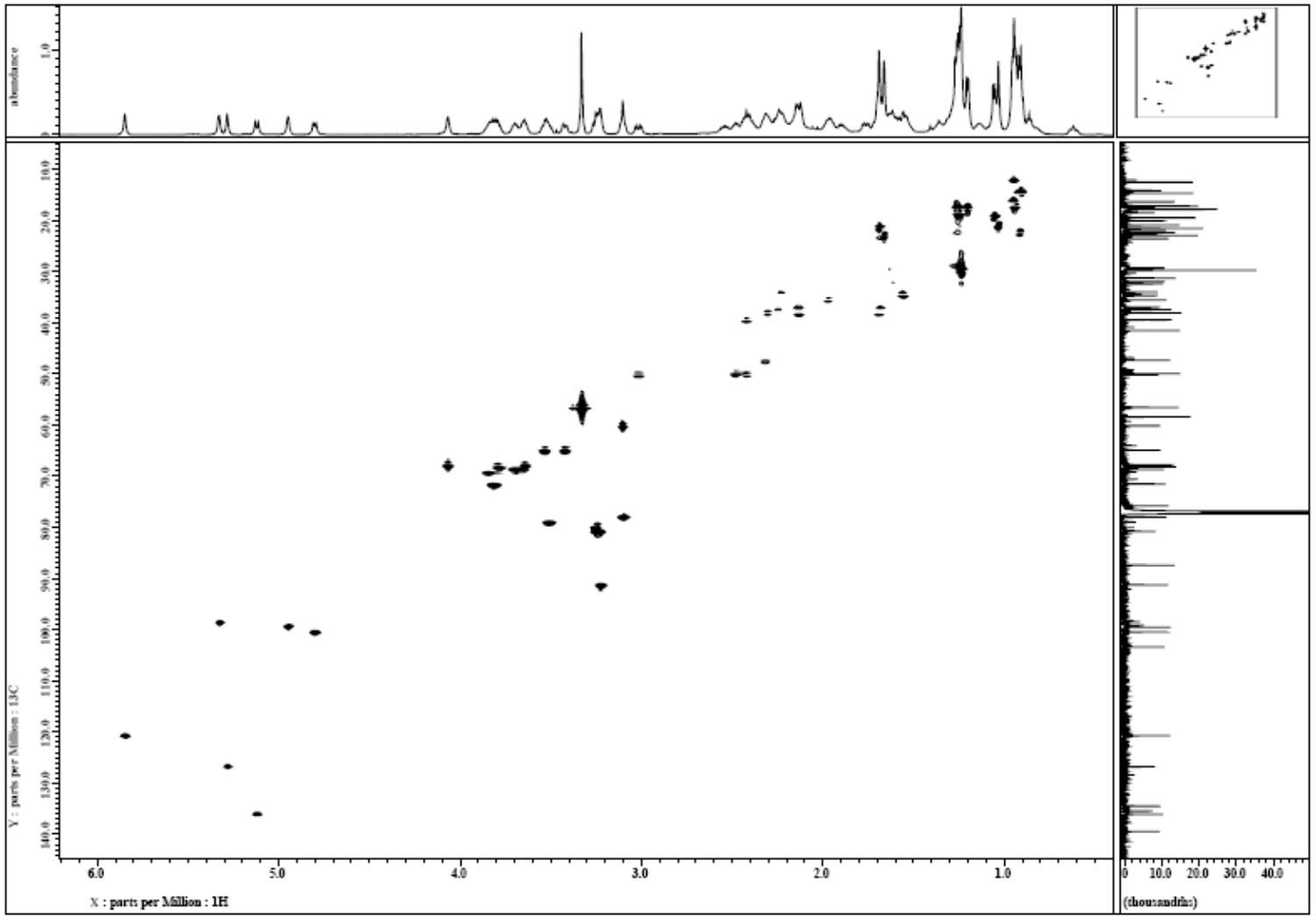

Fig. S4 DQF-COSY (600 MHz, $CDCl_3$) spectrum of versipelostatin B (2)

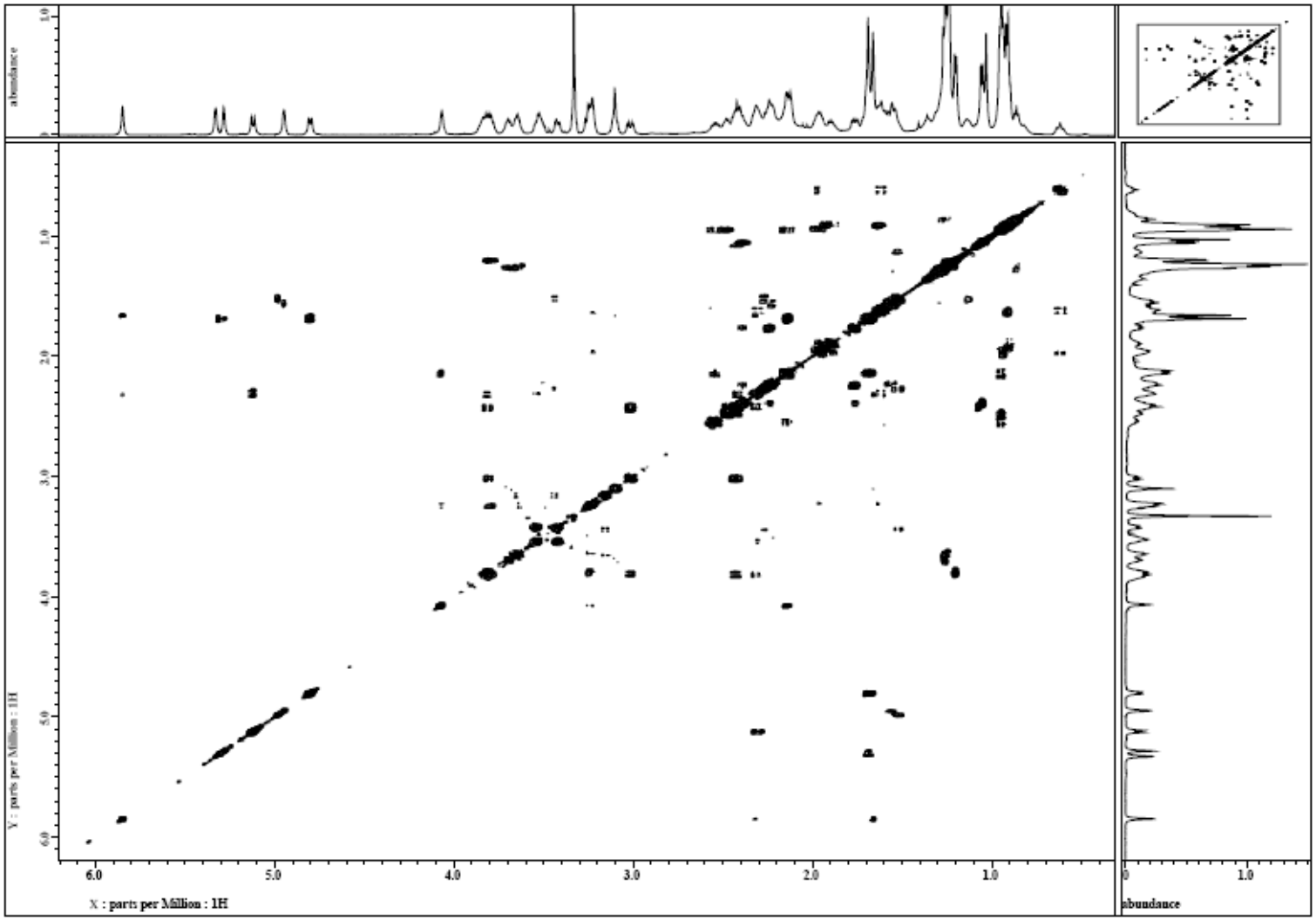

Fig. S5 HMBC (600 MHz, $CDCl_3$) spectrum of versipelostatin B (2)

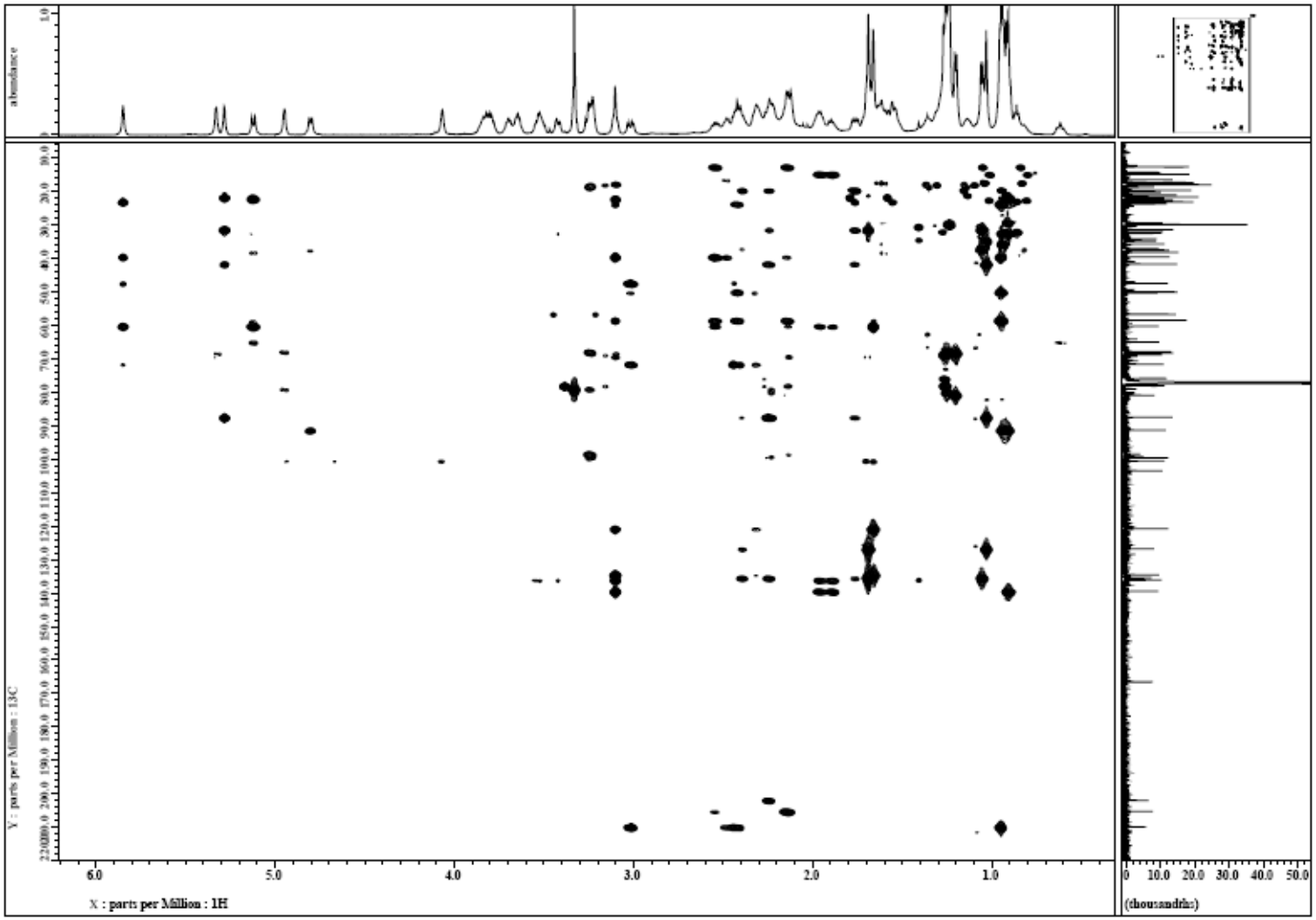

Fig. S6 ^{1}H NMR (600 MHz, C_5D_5N) spectrum of versipelostatin C (3)

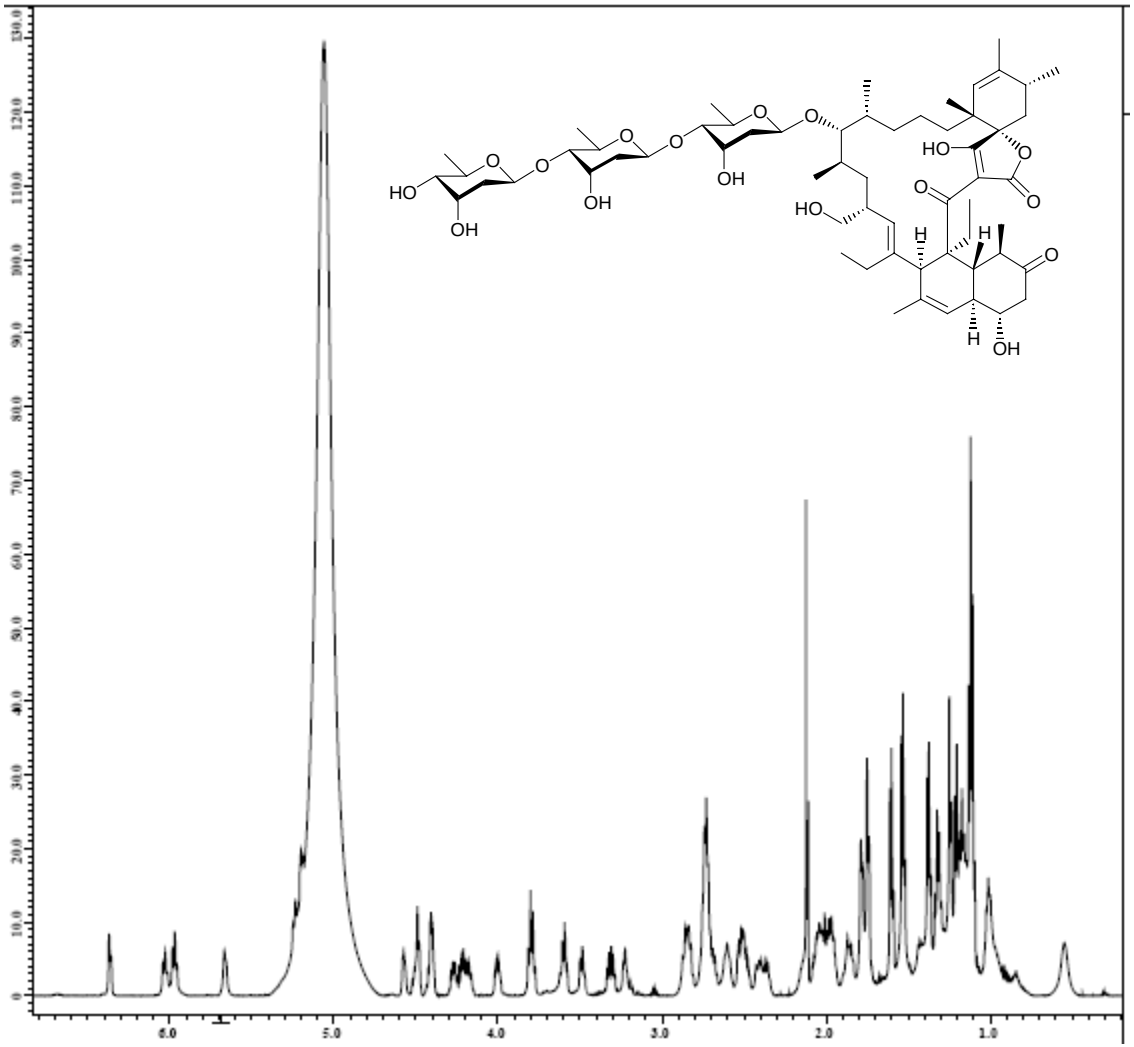

Fig. S7 ^{13}C NMR (150 MHz, C_5D_5N) spectrum of versipelostatin C (3)

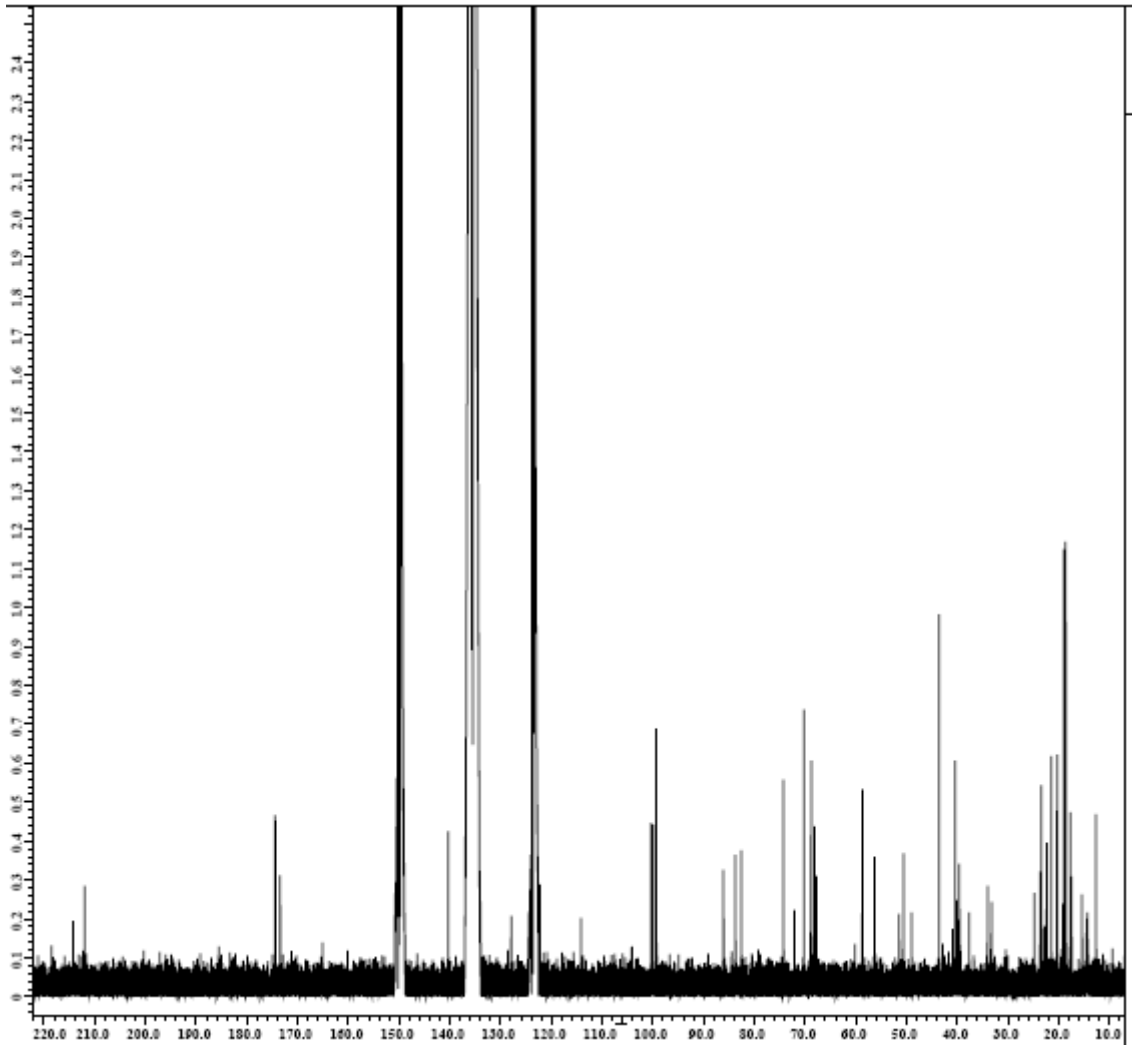

Fig. S8 HSQC (600 MHz, C_5D_5N) spectrum of versipelostatin C (3)

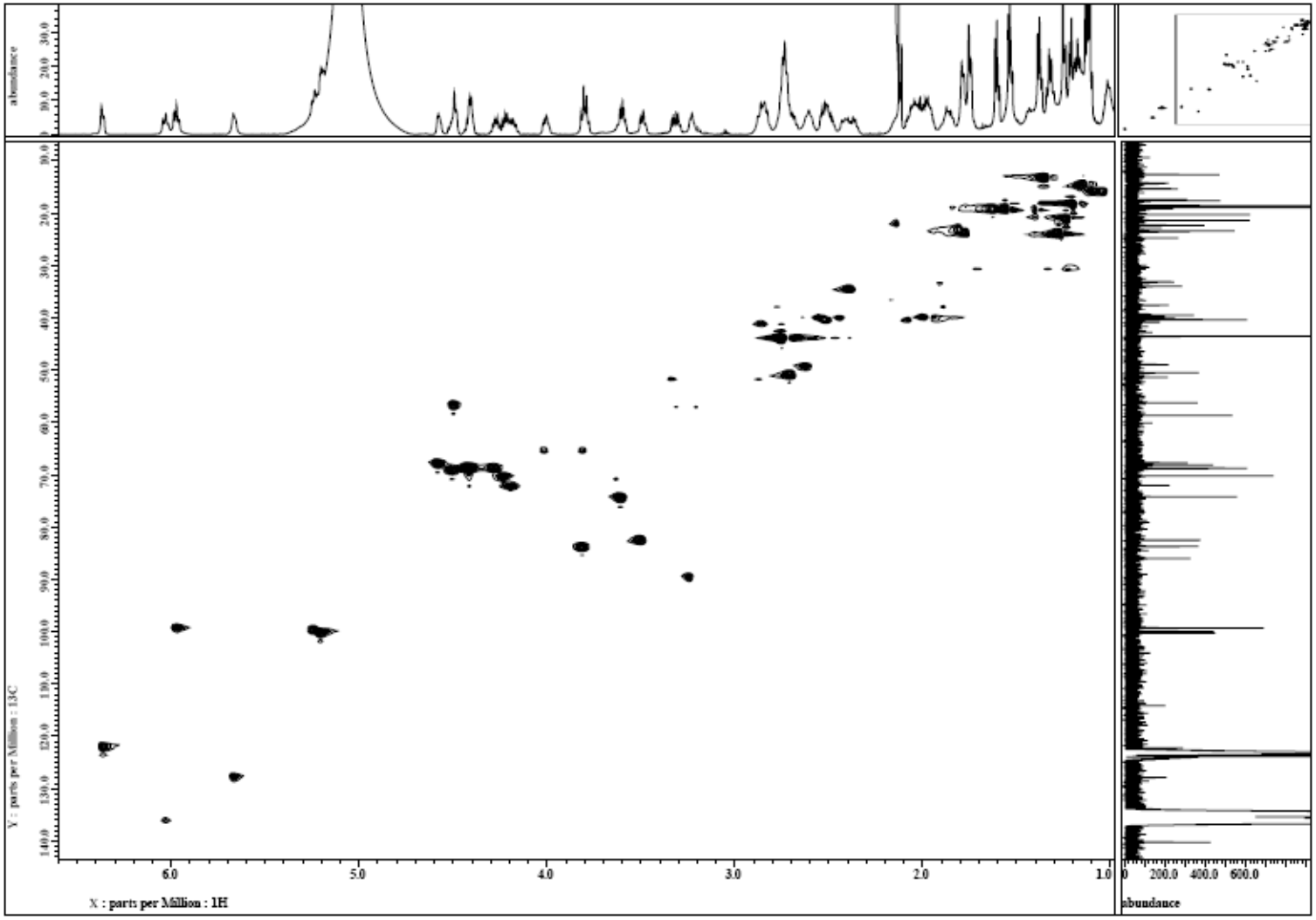

Fig. S9 DQF-COSY (600 MHz, C_5D_5N) spectrum of versipelostatin C (3)

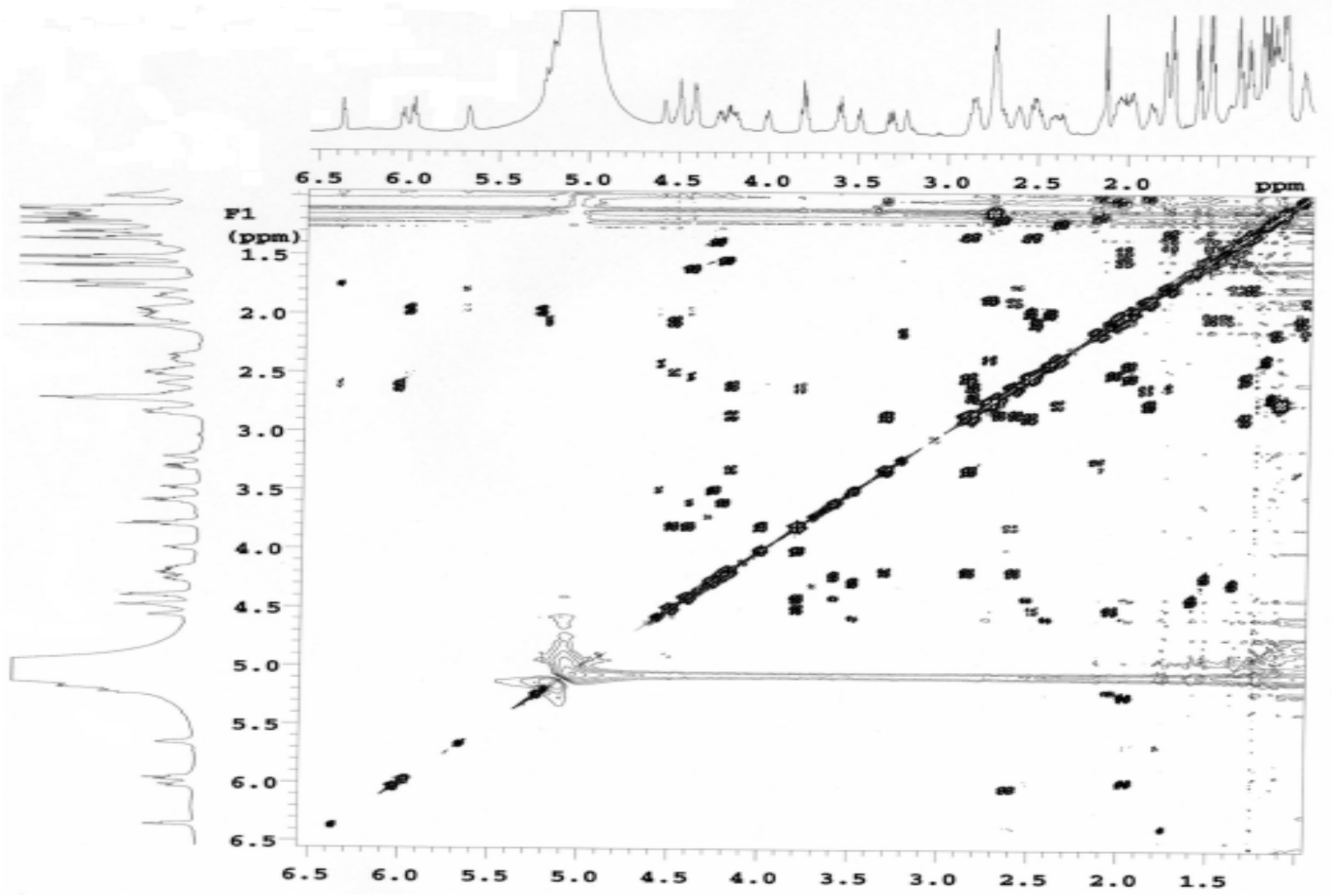

Fig. S10 HMBC (600 MHz, C_5D_5N) spectrum of versipelostatin C (3)

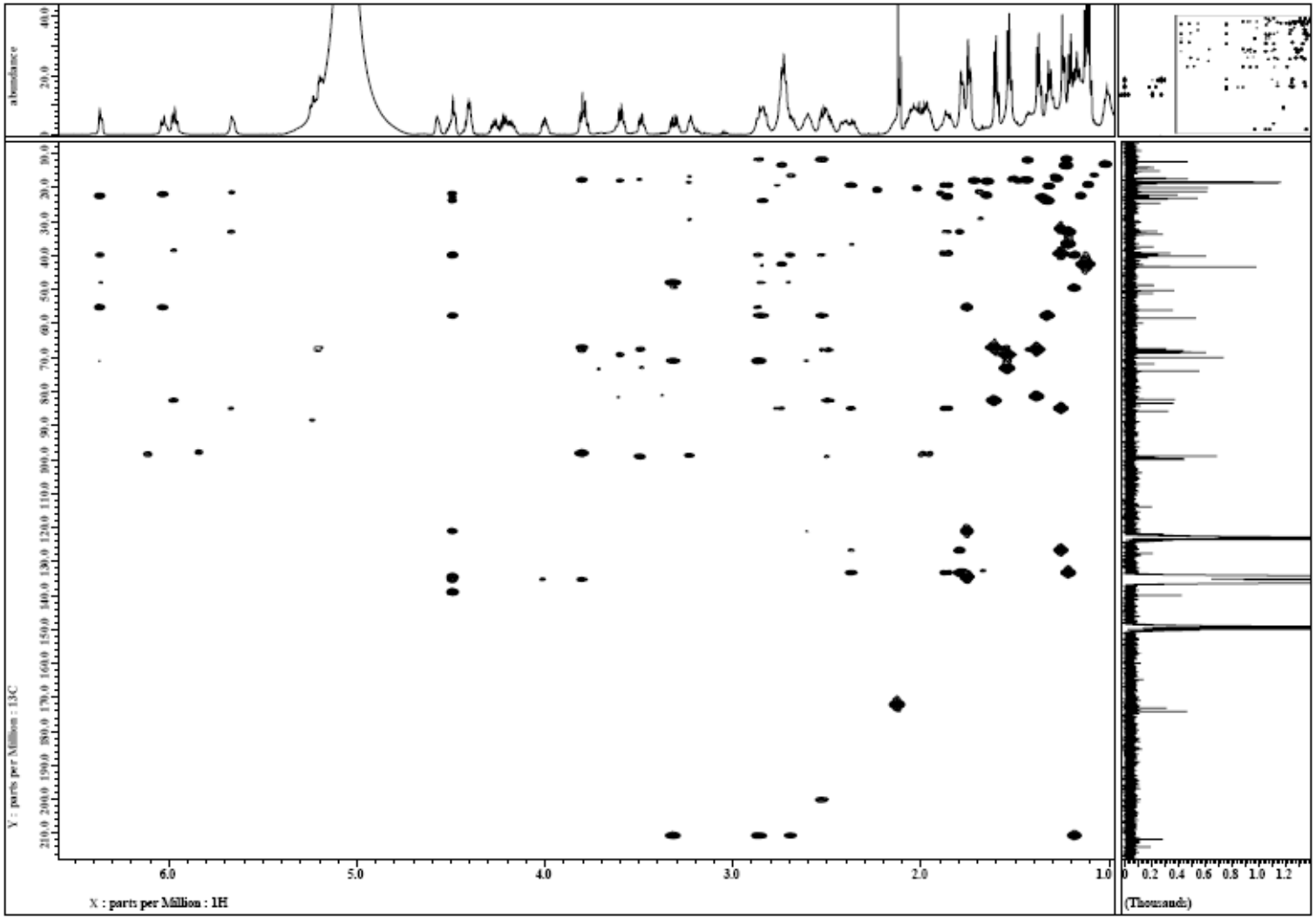

Fig. S11 ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$) spectrum of versipelostatin D (4)

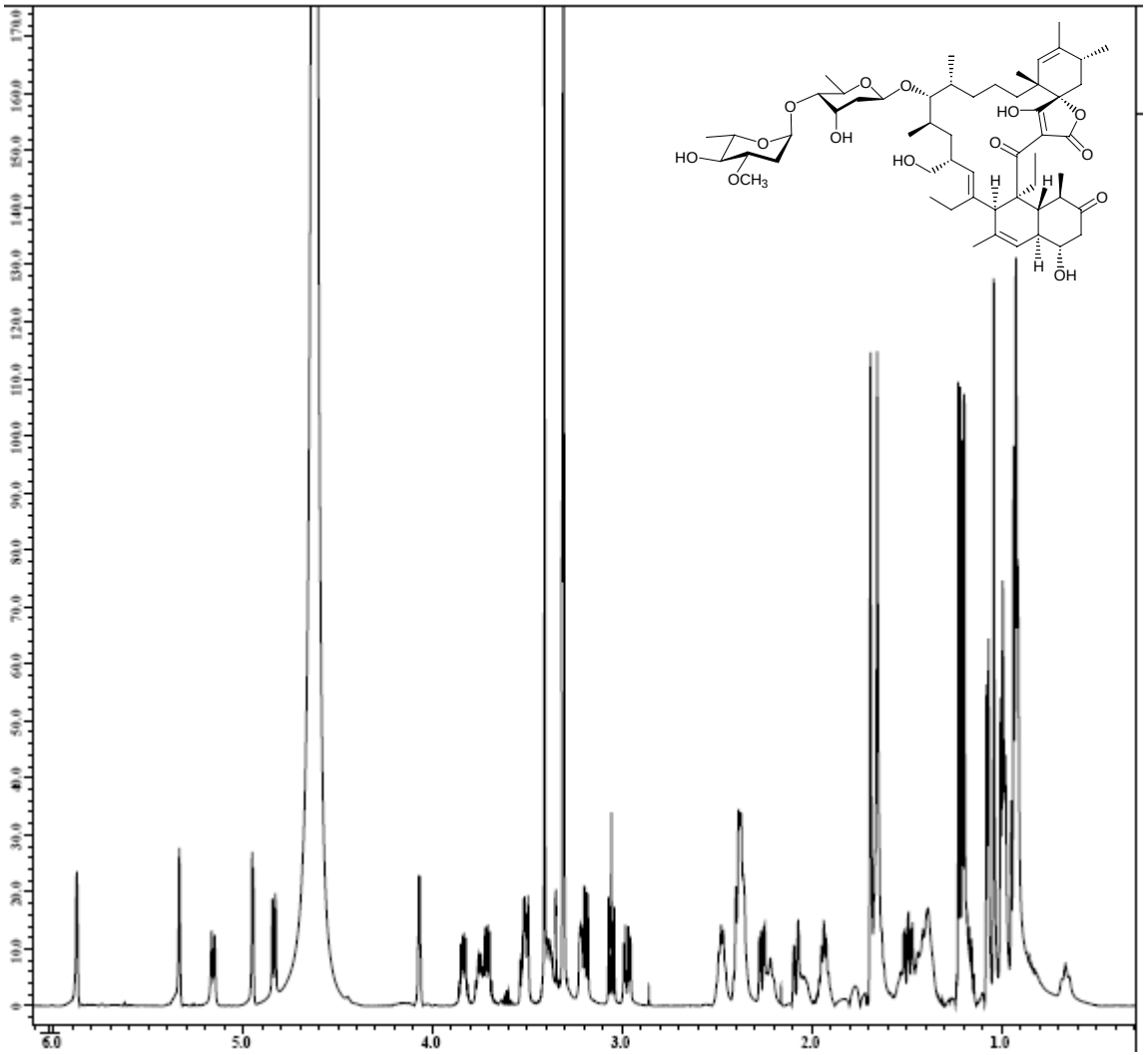

Fig. S12 ^{13}C NMR (150 MHz, $CDCl_3/CD_3OD$) spectrum of versipelostatin D (4)

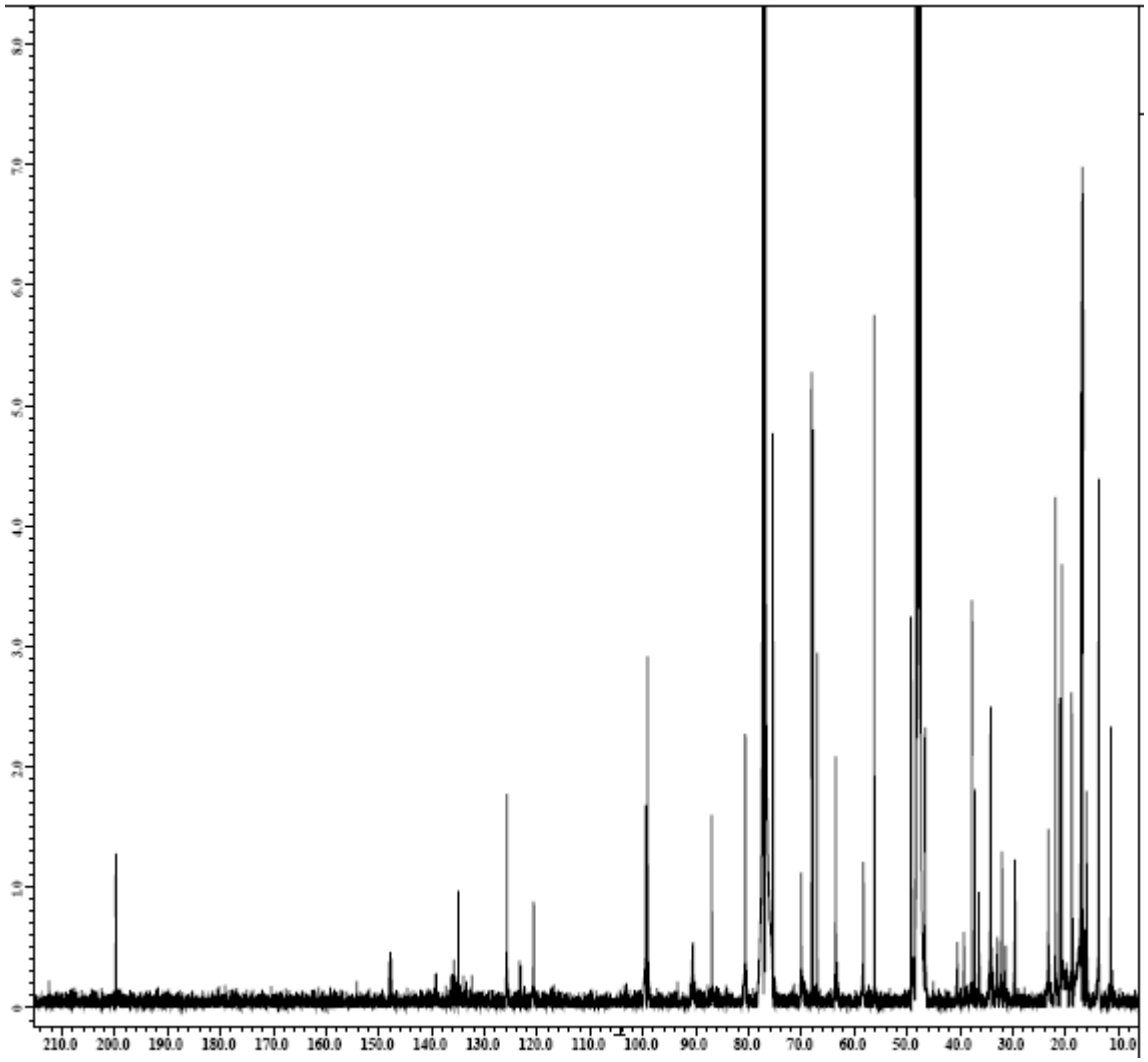

Fig. S13 HSQC (600 MHz, $CDCl_3/CD_3OD$) spectrum of versipelostatin D (4)

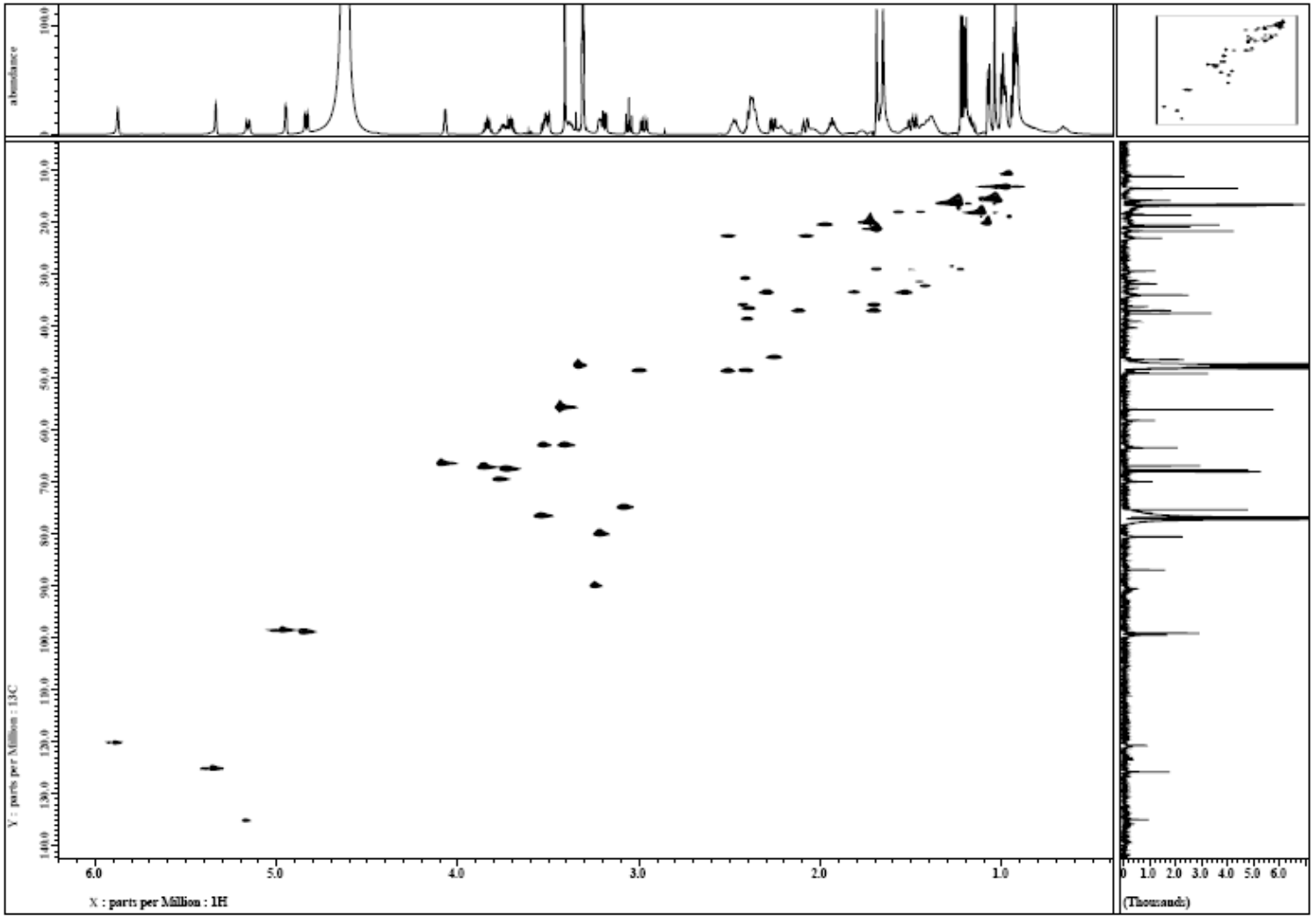

Fig. S14 DQF-COSY (600 MHz, $CDCl_3/CD_3OD$) spectrum of versipelostatin D (4)

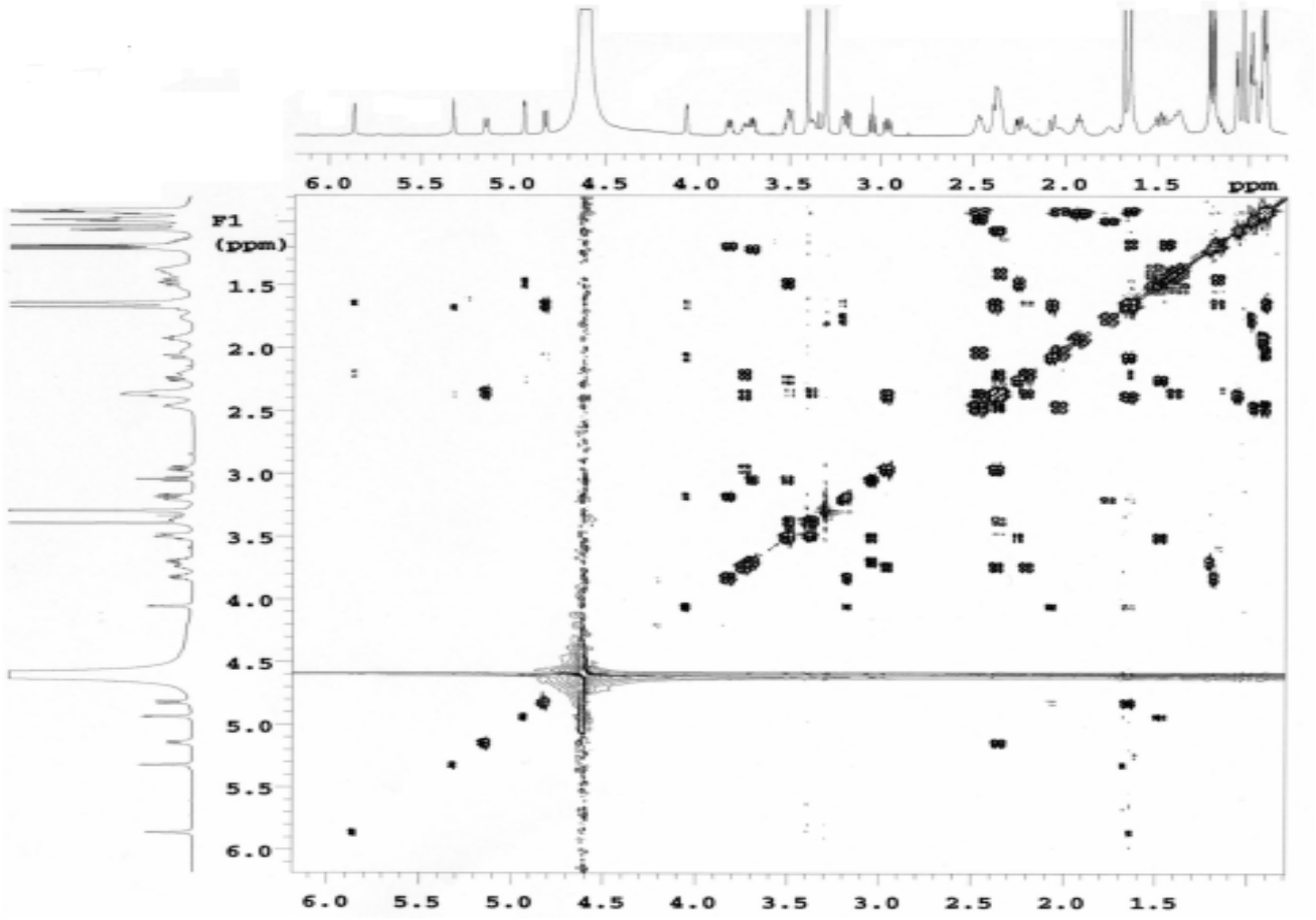

Fig. S15 HMBC (600 MHz, $CDCl_3/CD_3OD$) spectrum of versipelostatin D (4)

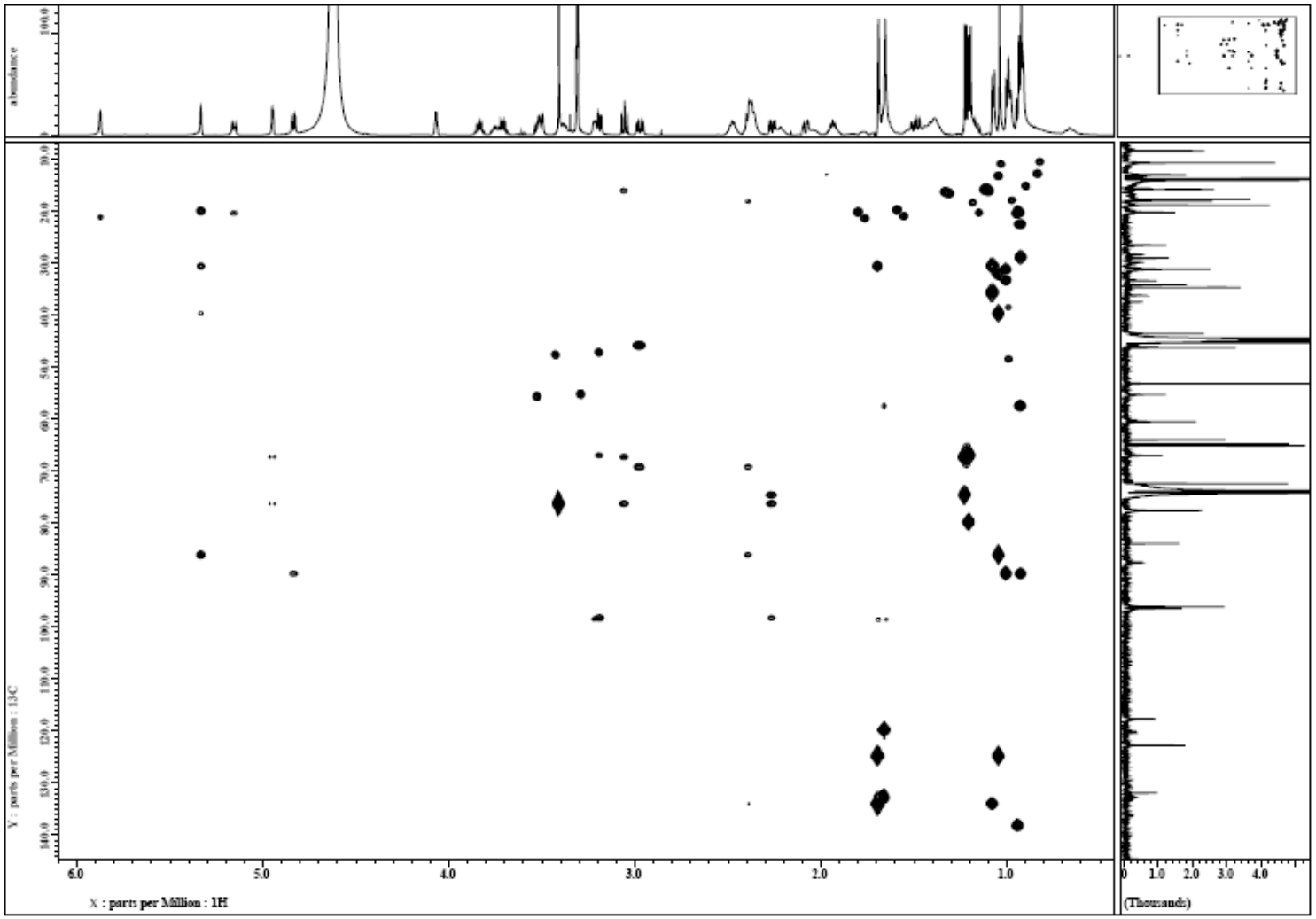

Fig. S16 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of versipelostatin E (5)

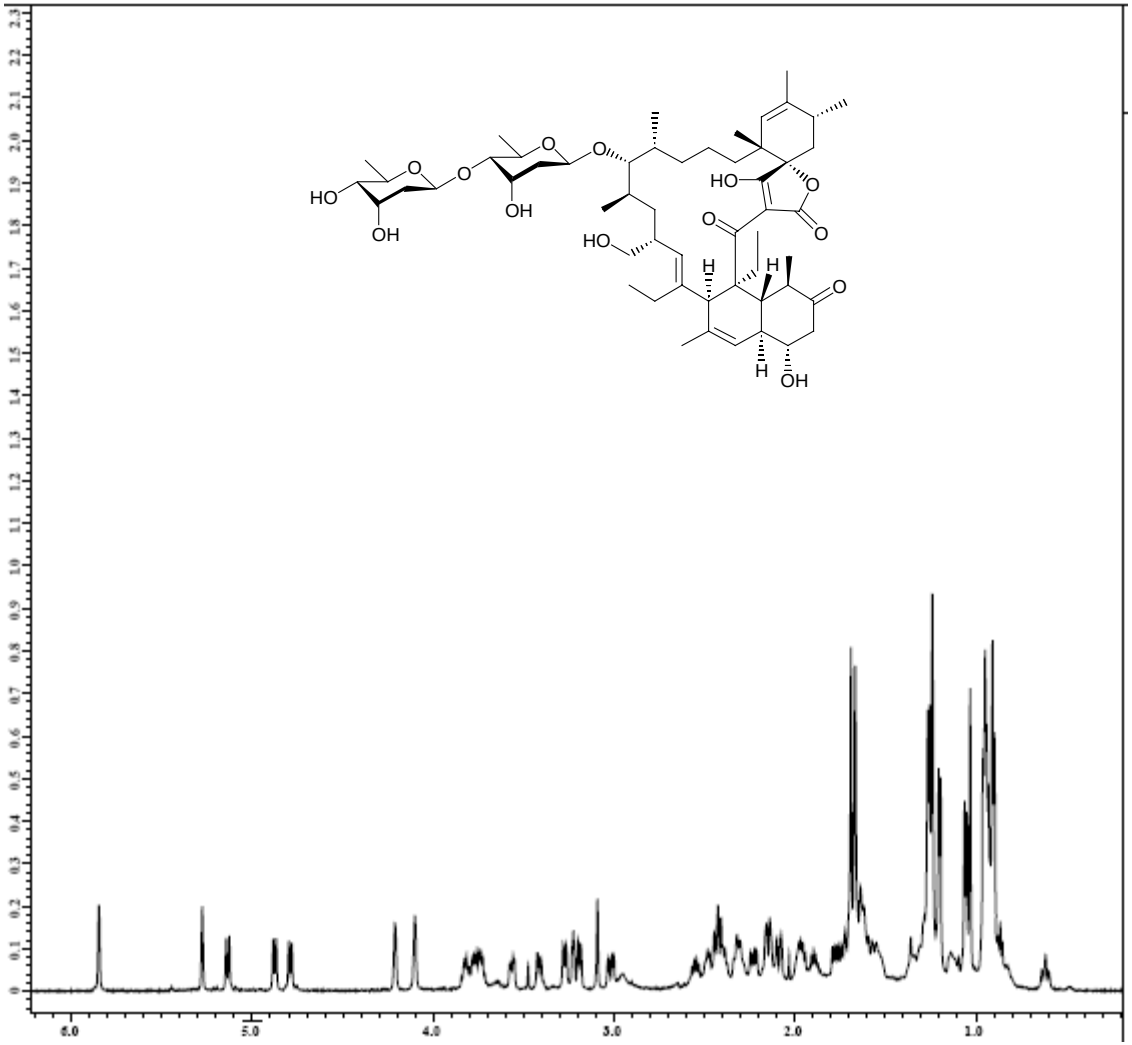

Fig. S17 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of versipelostatin E (5)

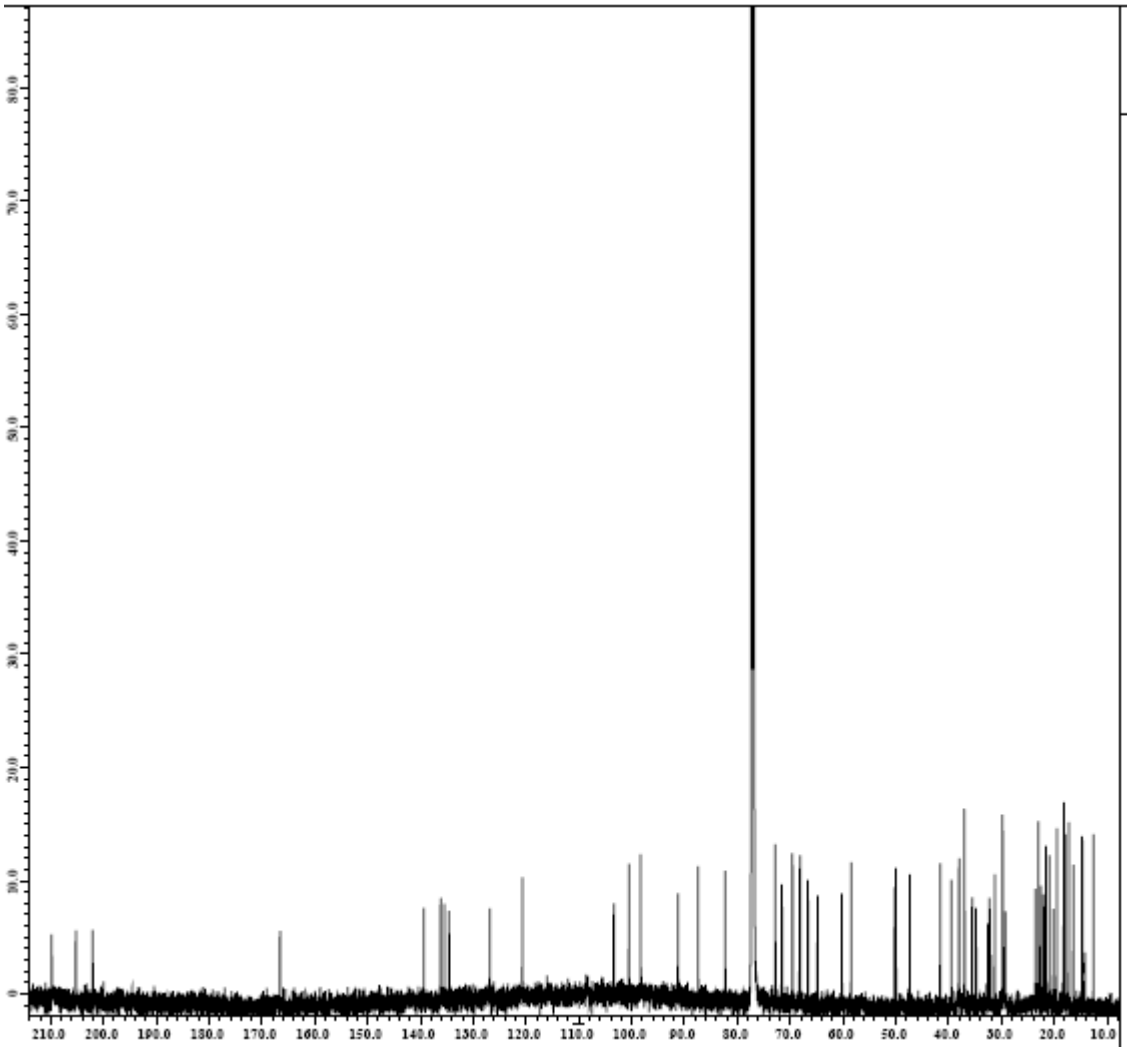

Fig. S18 HSQC (600 MHz, $CDCl_3$) spectrum of versipelostatin E (5)

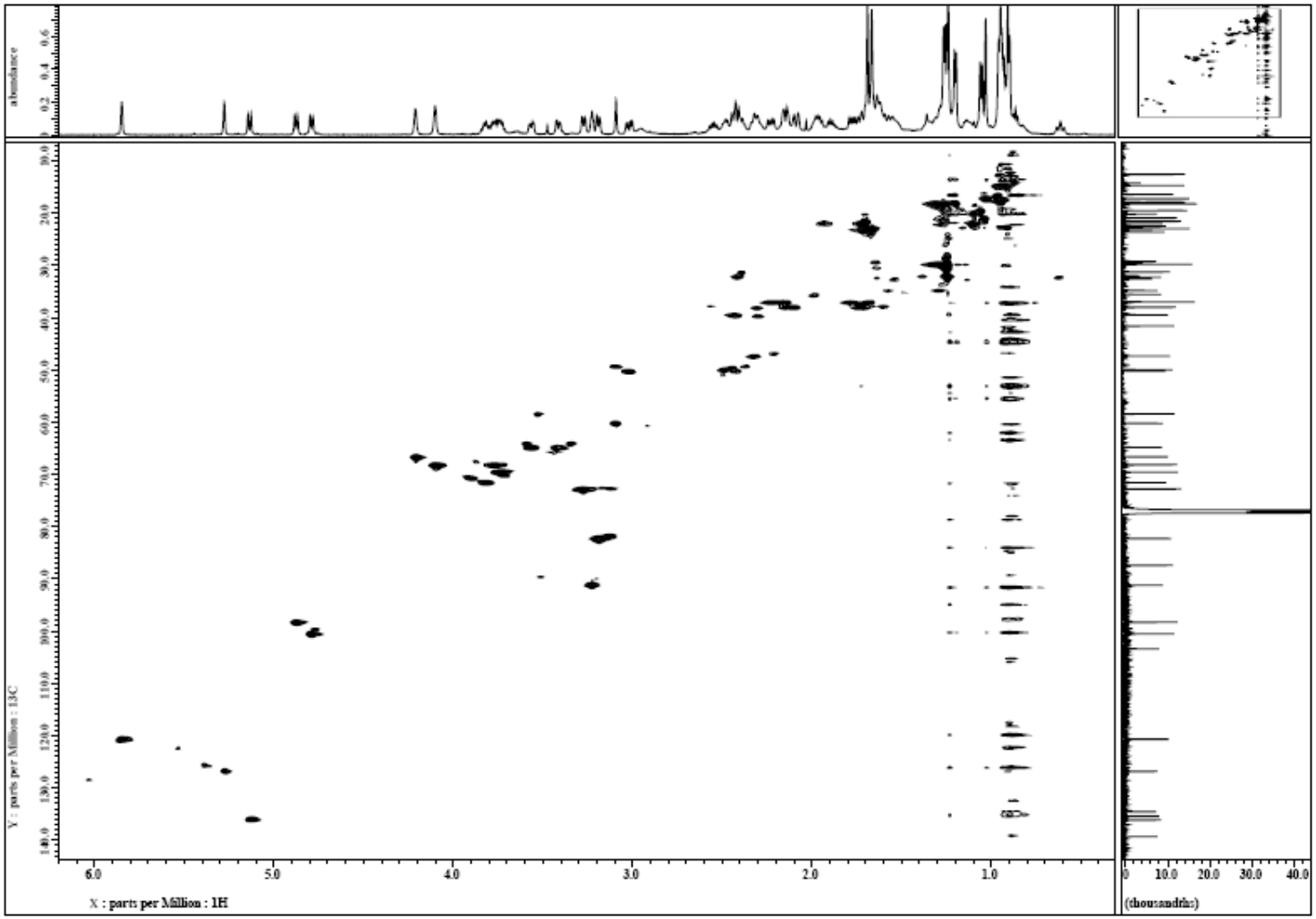

Fig. S19 DQF-COSY (600 MHz, $CDCl_3$) spectrum of versipelostatin E (5)

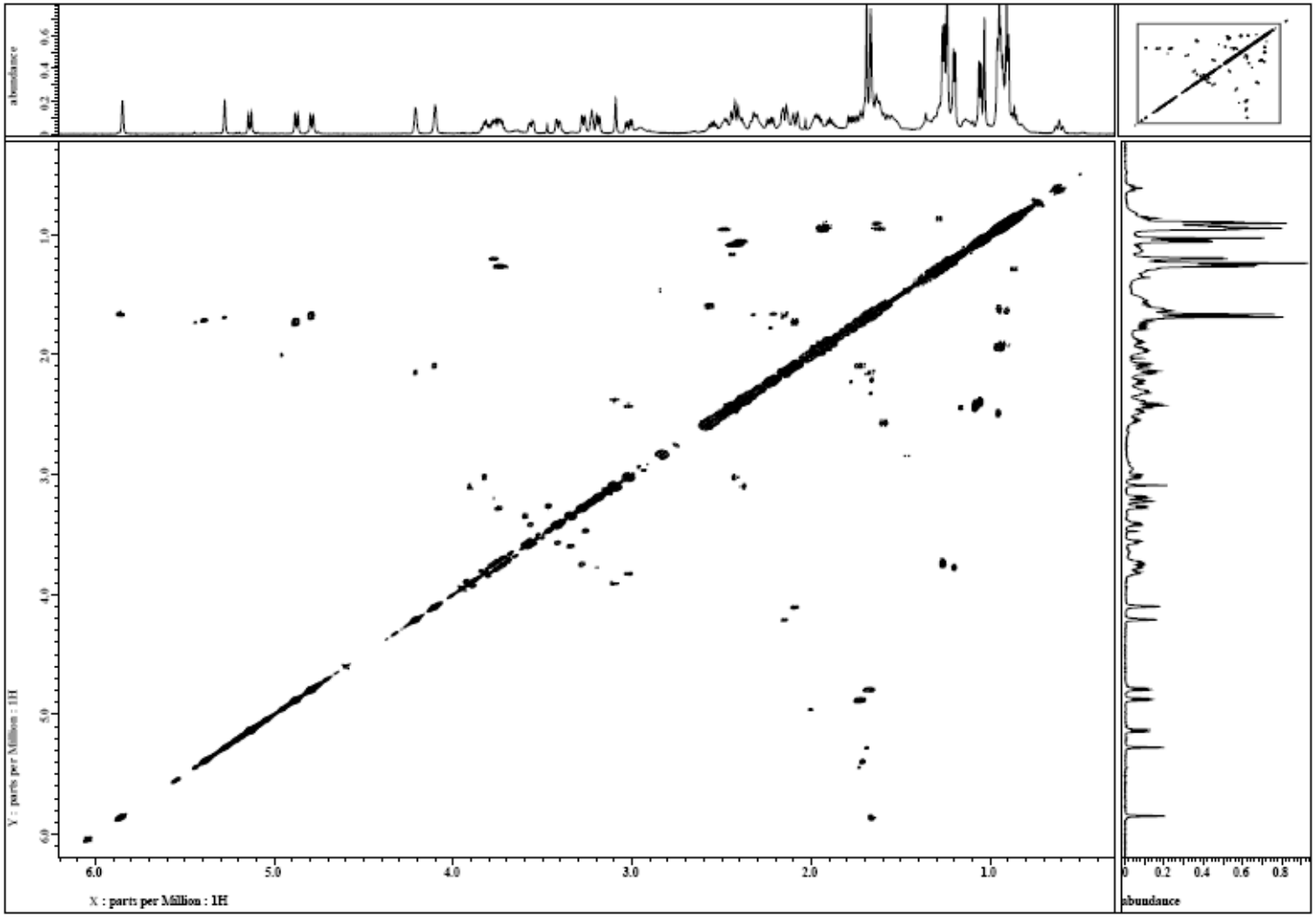

Fig. S20 HMBC (600 MHz, $CDCl_3$) spectrum of versipelostatin E (5)