Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information

Strong Acid-promoted Skeletal Remodeling of the Aphid Pigment: Red Uroleuconaphin to Green Viridaphin

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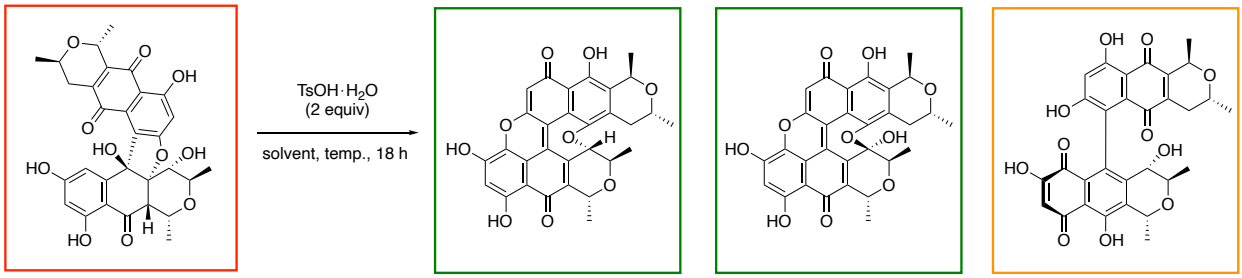
1. General

Infrared (IR) spectra were measured on a JASCO FT/IR-4200 spectrophotometer. Circular dichroism (CD) spectra were recorded on a JASCO J-725 spectropolarimeter. UV–vis spectra were measured on a JASCO V-650 spectrophotometer. Melting points (mp) were determined on a Büchi B-545 apparatus, and were uncorrected. Optical rotations were measured with a JASCO P-2300 polarimeter. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-S3000 Spiral TOF. For column chromatography, silica gel 60 N (Spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.) or C18 reversed-phase silica gel (Cosmosil 75C_{18} OPN, Nacalai Tesque Inc.) were used. For thin-layer chromatography (TLC) analysis, Merck precoated silica gel plates (60F_{254} or RP-18 WF_{254s}) were used. ^{1}H NMR spectra were recorded on a Varian Unity-600 (600 MHz), or a Bruker AVANCE-III (500 MHz) spectrometer with TMS as an internal standard. ^{13}C NMR spectra were recorded with a Varian Unity-600 (150 MHz), or a Bruker AVANCE-III (125 MHz) spectrometer; chemical shifts were referenced to the residual solvent signal (acetone-d_6: δ_C 29.8, DMSO-d_6: δ_C 39.5, $CDCl_3$: δ_C 77.0).

2. Optimization of transformation of uroleuconaphin A_1 (1)

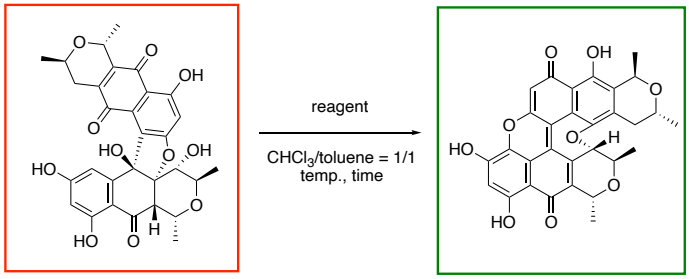
Table S1. Screening of solvent



uroleuconaphin A_1 (**1**) | viridaphin A_2 (**4**) | viridaphin A_1 (**3**) | **7**

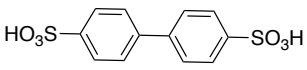
entry	solvent	temp. (°C)	yield (%)			recovery of **1** (%)
			4	**3**	**7**	
1	$CHCl_3$/toluene = 1/1	80	< 9	0	0	87
2	$CHCl_3$/toluene = 1/1	100	30	0	0	67
3	$CHCl_3$/toluene = 1/1	120	12	0	0	49
4	1,2-dichloroethane	100	trace	0	0	> 90
5	chlorobenzene	100	4	0	0	39
6	toluene	100	8	0	0	61
7	*t*-BuOH	100	7	12	12	67
8	*n*-BuOH	100	< 12	0	0	30
9	$HOCH_2CH_2OH$	100	12	0	0	0
10	DMF	100	0	0	0	< 9
11	DME	100	0	0	0	> 90
12	THF	80	0	0	0	> 90
13	1,2-dichloroethane/toluene = 1/1	100	< 10	0	0	80
14	*n*-BuOH/toluene = 1/1	100	10	0	0	64
15	THF/H_2O = 1/1	80	10	20	66	trace
16	dioxane/H_2O = 1/1	100	trace	trace	58	0
17	$HOCH_2CH_2OH$/H_2O = 1/1	80	trace	trace	43	0
18	MeCN/H_2O = 1/1	80	2	5	77	0
19	*t*-BuOH/H_2O = 1/1	80	2	6	68	0
20	1,4-butanediol/H_2O = 1/1	80	trace	trace	60	0
21	EtOH/H_2O = 1/1	80	trace	trace	77	0

Table S2. Screening of acid

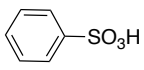


uroleuconaphin A_1 (**1**) viridaphin A_2 (**4**)

entry	reagent (equiv)	temp. (°C)	time (h)	yield of **4** (%)	recovery of **1** (%)
1	$TsOH \cdot H_2O$ (2)	100	18	30	67
2	$TsOH \cdot H_2O$ (5)	100	18	< 18	30
3	TFA (26)	100	54	5	95
4	CSA (16)	100	18	7	70
5	MsOH (5)	80	36	22	29
6	TfOH (2)	80	18	18	0
7	TsOH (2)	100	18	22	47
8	H_2SO_4 (4)	60→80	54	< 15	0
9	6 M HCl (20)	60→80	54	0	> 95
10	**A** (2)	100	18	trace	< 45
11	**B** (2)	100	18	20	50
12	**C** (2)	100	18	22	55
13	**D** (2)	100	18	trace	< 60
14	**E** (2)	100	18	17	12
15	**F** (2)	100	18	13	42



A



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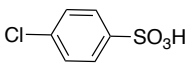

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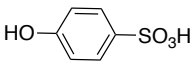
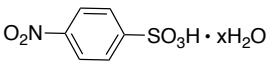


D



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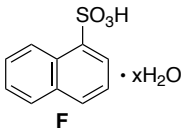
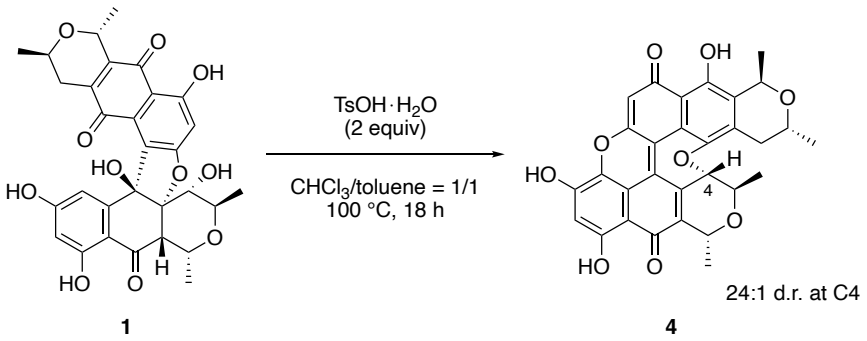


F

3. Procedure for transformation of uroleuconaphin A_1 (1) to viridaphin A_2 (4)

To a solution of **1** (22.1 mg, 39.2 μmol) in $CHCl_3$/toluene (10 mL/10 mL) was added $TsOH \cdot H_2O$ (17.5 mg, 92.0 μmol), and the mixture was heated at 100 °C. After stirring for 18 h, the reaction mixture was quenched by adding $NaHCO_3$ (7.7 mg, 92 μmol) in H_2O (10 mL) at room temperature. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl, and dried over $MgSO_4$. Concentration and purification by column chromatography (silica gel, hexane/EtOAc = 1/1→$CHCl_3$/MeOH = 20/1→15/1→10/1) afforded green pigment **4** (6.3 mg, 30%) as a green powder, and starting material **1** (14.9 mg, 67%) as a red powder.



1 4

Viridaphin A_2 (4)

R_f 0.36 ($CHCl_3$/MeOH = 7/1);

$[\alpha]_D^{24}$ +2898 (*c* 0.019, MeOH);

IR (ATR) 3383, 2977, 2926, 2849, 1617, 1433, 1303, 1260, 1229, 1192, 1120, 1046, 1023, 990, 825, 685, 631 cm^{-1};

^1H NMR ($CDCl_3$:CD_3OD = 35:1, 600 MHz) δ 1.40 (d, 3H, *J* = 6.2 Hz), 1.51 (d, 3H, *J* = 6.2 Hz), 1.69 (d, 3H, *J* = 6.7 Hz), 1.80 (d, 3H, *J* = 6.7 Hz), 2.44 (dd, 1H, *J* = 17.4 Hz, 10.4 Hz), 3.09 (dd, 1H, *J* = 17.4 Hz, 3.3 Hz), 4.21 (qdd, 1H, *J* = 6.2 Hz, 10.4 Hz, 3.3 Hz), 4.29 (d, 1H, *J* = 7.6 Hz), 4.43 (dq, 1H, *J* = 7.6 Hz, 6.2 Hz), 5.04 (q, 1H, *J* = 6.7 Hz), 5.21 (q, 1H, *J* = 6.7 Hz), 6.49 (s, 1H), 6.65 (s, 1H);

^{13}C NMR ($CDCl_3$:CD_3OD = 35:1, 150 MHz) δ 18.2, 18.9, 20.1, 21.5, 31.0, 62.4, 65.5, 67.7, 68.2, 79.5, 103.7, 105.4, 106.4, 112.1, 117.2, 119.1, 123.5, 130.2, 131.0, 132.7, 133.9, 138.9, 139.0, 149.3, 153.1, 155.1, 161.0, 163.0, 183.2, 186.3;

^{1}H NMR (DMSO-d_6, 600 MHz) δ 1.28 (d, 3H, J = 6.2 Hz), 1.37 (d, 3H, J = 5.9 Hz), 1.49 (d, 3H, J = 6.5 Hz), 1.63 (d, 3H, J = 6.8 Hz), 2.23 (dd, 1H, J = 16.5 Hz, 16.8 Hz), 2.93 (d, 1H, J = 16.5 Hz), 4.04–4.08 (m, 1H), 4.16–4.23 (m, 2H), 4.76 (brs, 1H), 4.86 (brs, 1H), 5.92 (s, 1H), 6.37 (s, 1H), 13.57 (s, 1H), 15.07 (s, 1H);

^{13}C NMR (DMSO-d_6, 150 MHz) δ 18.0, 18.7, 19.7, 21.6, 30.6, 61.7, 65.3, 66.6, 67.0, 78.1, 102.4, 104.3, 105.6, 110.9, 116.3, 118.2, 122.2, 129.9, 130.2, 132.2, 133.0, 138.0, 138.6, 148.5, 153.5, 154.8, 159.9, 162.7, 182.2, 184.7;

HRMS (MALDI) calcd for $C_{30}H_{25}O_9$ $[M+H]^+$ *m/z* 529.1493, found *m/z* 529.1508;

Mp 218 °C (dec).

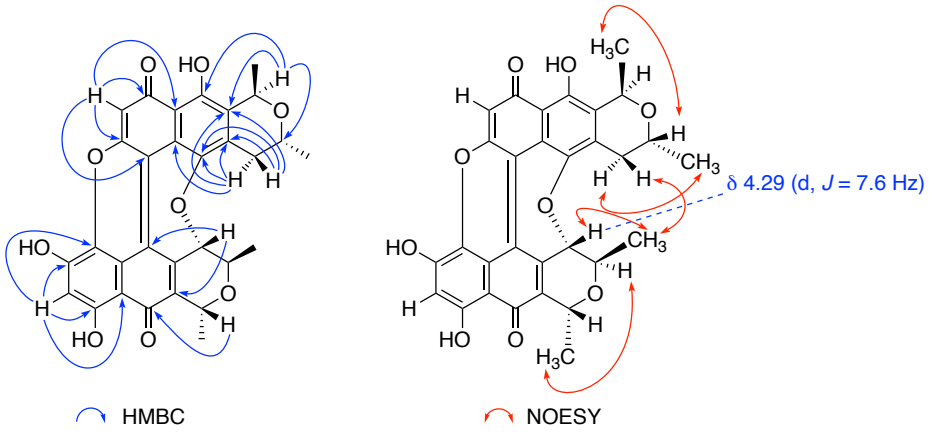
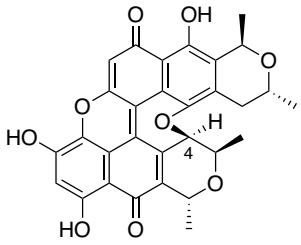


Figure S1. Key 2D NMR correlations of viridaphin A_2 (**4**) in $CDCl_3$ + CD_3OD



4

4-*epi* viridaphin A_2 (4'): green powders;

R_f 0.36 ($CHCl_3$/MeOH = 7/1);

$[\alpha]_D^{19}$ –1546 (*c* 0.013, MeOH);

IR (ATR) 3396, 2920, 2851, 1726, 1620, 1456, 1260, 1122, 800, 746, 502, 451, 419 cm^{-1};

^{1}H NMR ($CDCl_3$:CD_3OD = 35:1, 500 MHz) δ 1.42 (d, 3H, *J* = 6.1 Hz), 1.58 (d, 3H, *J* = 6.8 Hz), 1.60 (d, 3H, *J* = 6.8 Hz), 1.61 (d, 3H, *J* = 6.8 Hz), 2.65 (dd, 1H, *J* = 17.4 Hz, 11.0 Hz), 3.03 (dd, 1H, *J* = 17.4 Hz, 2.9 Hz), 4.05 (ddq, 1H, *J* = 11.0 Hz, 2.9 Hz, 6.8 Hz), 4.16 (d, 1H, *J* = 2.9 Hz), 4.29–4.33 (m, 1H), 5.29 (q, 1H, *J* = 6.8 Hz), 5.32 (q, 1H, *J* = 6.8 Hz), 6.55 (s, 1H), 6.73 (s, 1H);
^{13}C NMR ($CDCl_3$:CD_3OD = 35:1, 125 MHz) δ 17.1, 17.3, 18.7, 21.7, 32.2, 62.5, 65.3, 68.2, 68.5, 74.5, 103.9, 104.9, 106.4, 112.1, 117.2, 117.6, 123.0, 131.3, 131.4, 132.3, 134.0, 136.8, 138.0, 151.3, 155.0, 161.3, 162.7, 183.7, 186.9;
HRMS (MALDI) calcd for $C_{30}H_{24}O_9$ $[M]^-$ *m/z* 528.1415, found *m/z* 528.1397;
Mp 186 °C (dec).

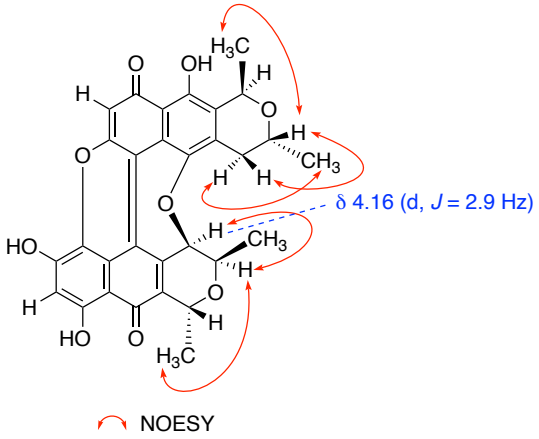


Figure S2. Key 2D NMR correlations of 4-*epi* viridaphin A_2 (**4'**) in $CDCl_3$ + CD_3OD

On large scale procedure

To a solution of **1** (85.2 mg, 151 μmol) in $CHCl_3$/toluene (38 mL/38 mL) was added TsOH·H_2O (66.6 mg, 350 μmol), and the mixture was heated at 100 °C. After stirring for 18 h, the reaction mixture was quenched by adding $NaHCO_3$ (30.8 mg, 350 μmol) in H_2O (40 mL) at room temperature. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl and dried over $MgSO_4$. Concentration and purification by column chromatography (silica gel, hexane/EtOAc = 1/1→$CHCl_3$/MeOH = 20/1→15/1→10/1) afforded green pigment **4** (21.5 mg, 27%) as a green powder, and starting material **1** (59.0 mg, 69%). The same reaction was repeated for other two cycles using the recovered **1**. A total of 16.9 mg and 9.5 mg of the green pigment **4** were collected in the second and third run, respectively. As a result, the green pigment **4** (total 47.9 mg, 60%) was obtained.

4. Plausible mechanism of acid-promoted conversion of uroleuconaphin A_1 (1)

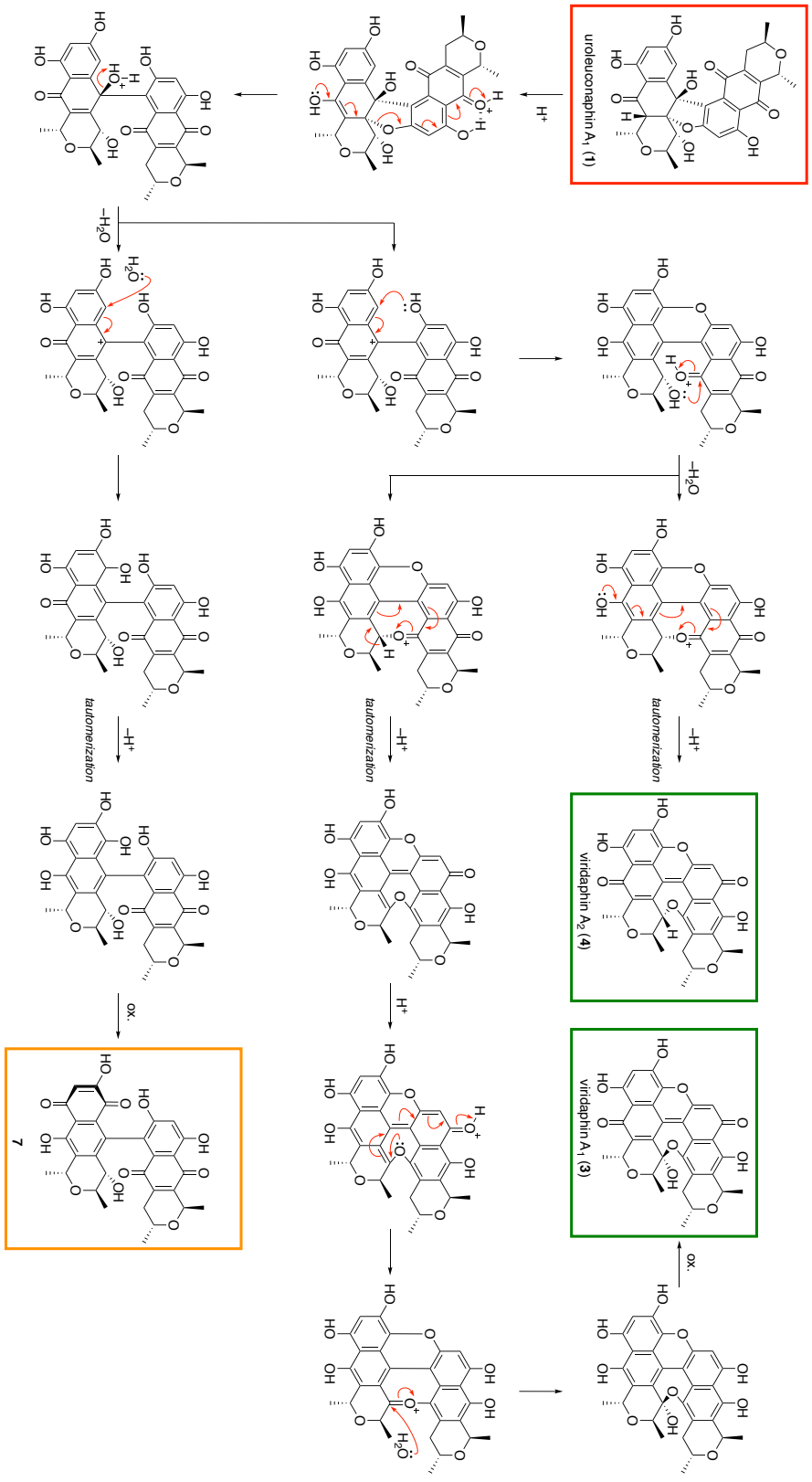
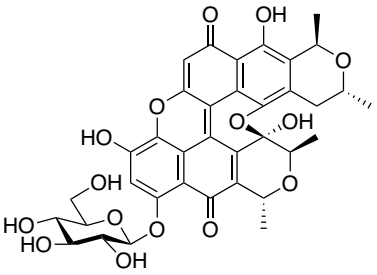


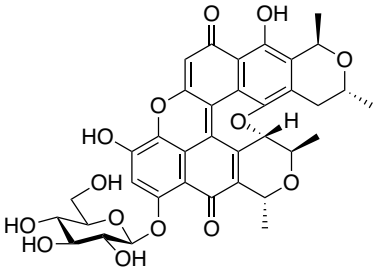
Figure S3. Plausible mechanism of acid-promoted conversion of **1**

5. Isolation of viridaphin A_2 glucoside (16) and viridaphin A_1 glucoside (15)

Based on our previous reported procedure,[1] the extraction and purification of **15** and **16** were performed as follows: the greenish aphid, *M. crassicauda* and *Acyrthosiphon pisum*, which were obtained from *Vicia sativa*. A mixture of these aphids (total 3.7 kg) was crushed with a pestle in *n*-hexane (total 9 L) and methanol (total 23 L) several times. The combined methanol solutions were evaporated to give crude extracts. The extracts were dissolved in water (total 2 L), and extracted with *n*-BuOH (×5, total 1L). The combined organic extracts were dried over $MgSO_4$, and concentrated in vacuo to give crude extracts (149 g). The residue was purified by silica gel chromatography (EtOAc/MeOH = 2/1) and further purified by reversed-phase silica gel chromatography (MeOH/H_2O =1/1) to afford the green pigment **15** (933 mg) and **16** (373 mg).



15



16

Viridaphin A_2 glycoside (16)

R_f 0.40 (reversed phase, MeOH/H_2O = 3/1);

$[\alpha]_D^{22}$ +1777 (*c* 0.017, MeOH);

IR (ATR) 3351, 2927, 1585, 1422, 1362, 1231, 1020, 844, 506, 473, 431, 403 cm^{-1};

^1H NMR (DMSO-d_6, 600 MHz) δ 1.30 (d, 3H, *J* = 6.0 Hz), 1.37 (d, 3H, *J* = 6.2 Hz), 1.56 (d, 3H, *J* = 6.8 Hz), 1.64 (d, 3H, *J* = 6.6 Hz), 2.34 (dd, 1H, *J* = 17.2 Hz, 10.5 Hz), 3.05 (dd, 1H, *J* = 17.2 Hz, 2.7 Hz), 3.25 (dd, 1H, *J* = 9.2 Hz, 9.0 Hz), 3.23–3.51 (m, 3H), 3.57 (dd, 1H, *J* = 11.9 Hz, 5.5 Hz), 3.77 (brd, 1H, *J* = 11.9 Hz), 4.14–4.18 (m, 1H), 4.32 (qd, 1H, *J* = 6.2 Hz, 6.2 Hz), 4.46 (d, 1H, *J* = 6.2 Hz), 4.82 (q, 1H, *J* = 6.6 Hz), 4.89 (d, 1H, *J* = 7.3 Hz), 5.02 (q, 1H, *J* = 6.8 Hz), 5.08 (brs, 1H), 5.14 (brs, 1H), 6.27 (s, 1H), 7.04 (s, 1H), 15.46 (s, 1H);

^{13}C NMR (DMSO-d_6, 150 MHz) δ 18.5, 18.8, 19.7, 21.6, 30.8, 60.7, 61.8, 65.7, 67.1, 67.2, 69.5, 73.4, 75.9, 77.5, 78.5, 103.2, 103.4, 105.5, 108.9, 111.6, 118.4, 118.9, 121.7, 130.0, 132.0, 133.3, 134.7, 135.7, 140.3, 148.7, 154.6, 158.8, 160.7, 178.1, 185.3;

HRMS (MALDI) calcd for $C_{36}H_{34}O_{14}Na$ $[M+Na]^+$ *m/z* 713.1841, found *m/z* 713.1846;

Mp 258 °C (dec).

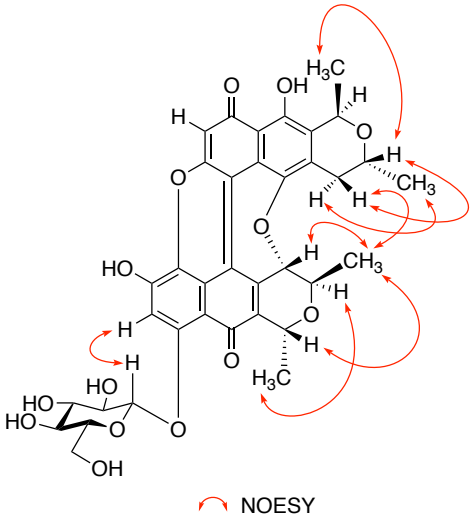


Figure S4. Key 2D NMR correlations of viridaphin A_2 glycoside (**16**) in DMSO-d_6

Fig. 1. Collecting aphids

Fig. 2. Crush aphids in hexane and methanol

Before crush aphids

After crush aphids

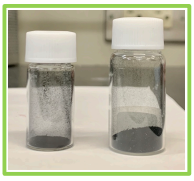
Fig. 3. Separate hexane solution and methanol solution

Fig. 4. Extract with *n*-BuOH

Right: water layer
Left: *n*-BuOH layer

Fig. 5. Purification by reversed-phase silica gel chromatography ($MeOH/H_2O$)

Fig. 6. reversed phase TLC
eluent: $MeOH/H_2O$ = 3/1
Right: **15**
Center: cospot of **15** and **16**
Left: **16**

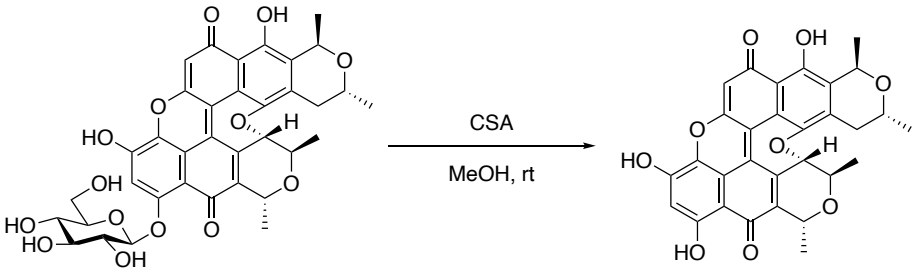


Right: viridaphin A_1 glucoside (**15**)
Left: viridaphin A_2 glucoside (**16**)

Figure S5. Isolation method

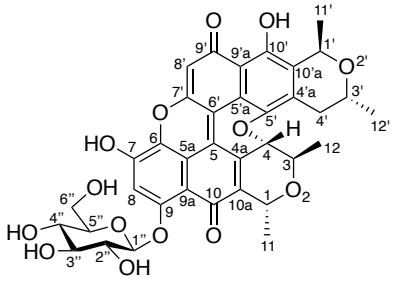
6. Hydrolysis of viridaphin A_2 glucoside (16)

To a solution of **16** (19.9 mg, 28.8 mmol) in MeOH (7.6 mL) was added 10-camphorsulfonic acid (18.0 mg, 77.5 mmol) at room temperature.[1] After stirring for 3 h, the reaction mixture was concentrated under reduced pressure to remove MeOH. The products were directly purified by column chromatography (silica gel, $CHCl_3$/MeOH = 40/1→30/1→20/1) to afford aglycon **4** (9.9 mg, 65%) as a green powder.

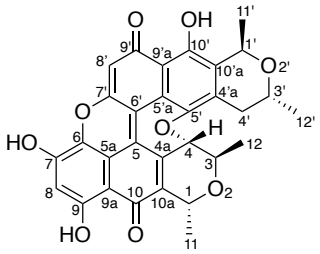


16 **4**

7. ^{1}H and ^{13}C NMR data of viridaphin A_2 glucoside (16) and viridaphin A_2 (4)



16



4

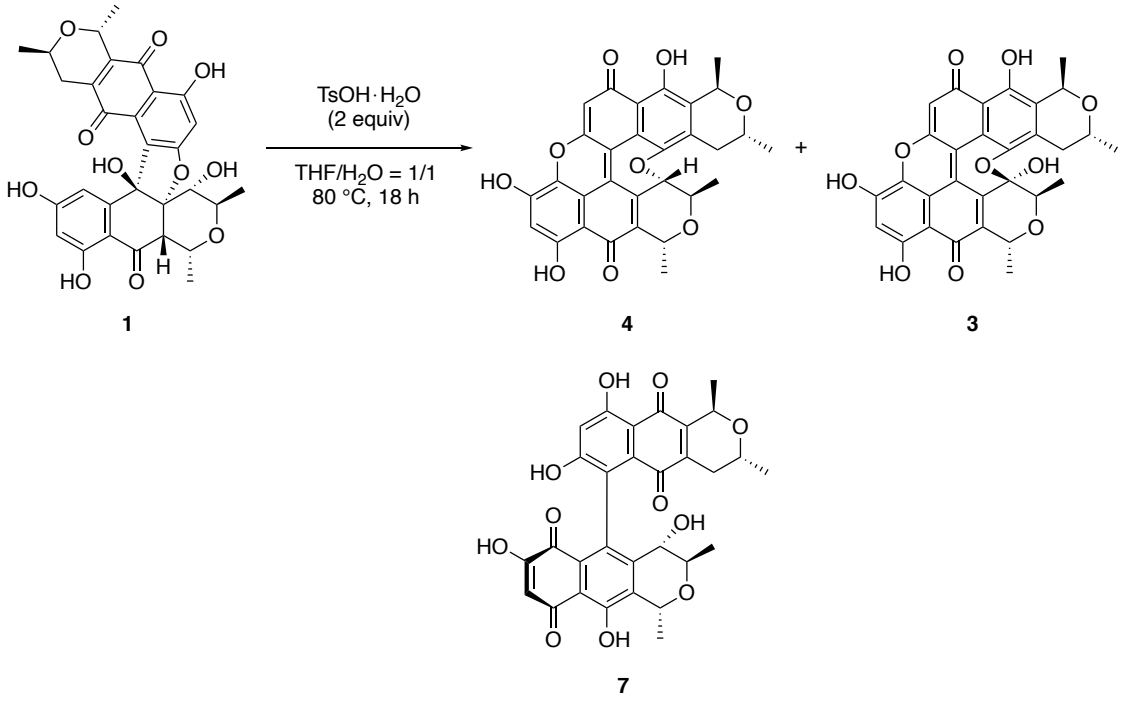
Table S3. ^{1}H (600 MHz) and ^{13}C (150 MHz) data of **16** and **4**

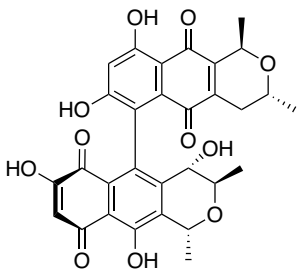
	16 in DMSO-d_6		**4** in $CDCl_3$ + CD_3OD		**4** in DMSO-d_6	
position	δ_c, type	δ_H, mult (*J* in Hz)	δ_c, type	δ_H, mult (*J* in Hz)	δ_c, type	δ_H, mult (*J* in Hz)
1	67.1, CH	4.82, q (6.6)	67.7, CH	5.04, q (6.7)	66.6, CH	4.76, br s
3	65.7, CH	4.32, qd (6.2, 6.2)	65.5, CH	4.43, dq (7.6, 6.2)	65.3, CH	4.20–4.22, m
4	78.5, CH	4.46, d (6.2)	79.5, CH	4.29, d (7.6)	78.1, CH	4.16-4.23, m
4a	140.3, C		138.9, C		138.6, C	
5	132.0, C		131.0, C		129.9, C	
5a	118.4, C		117.2, C		116.3, C	
6	133.3, C		132.7, C		132.2, C	
7	not observed[a]		163.0[b], C		162.7[c], C	
7-OH		not observed		not observed		not observed
8	108.9, C	7.04, s	106.4, C	6.65, s	105.6, C	6.37, s
9	158.8[a], C		153.1[b], C		153.5[c], C	
9-OH				not observed		13.57, s
9a	105.5, C		103.7, C		102.4, C	
10	178.1, C		183.2, C		182.2, C	
10a	135.7, C		139.0, C		138.0, C	
11	18.5, CH_3	1.64, d (6.6)	18.2, CH_3	1.80, d (6.7)	18.0, CH_3	1.63, d (6.8)
12	19.7, CH_3	1.37, d (6.2)	20.1, CH_3	1.51, d (6.2)	19.7, CH_3	1.37, d (5.9)
1’	67.2, CH	5.02, q (6.8)	68.2, CH	5.21, q (6.7)	67.0, CH	4.86, br s
3’	61.8, CH	4.14–4.18, m	62.4, CH	4.21, qdd (6.2, 10.4, 3.3)	61.7, CH	4.04–4.08, m
4’	30.8, CH_2	3.05, dd (2.7, 17.2) 2.34, dd (10.5, 17.2)	31.0, CH_2	3.09, dd (17.4, 3.3) 2.44, dd (17.4, 10.4)	30.6, CH_2	2.93, d (16.5) 2.23, dd (16.5, 16.8)
4’a	130.0, C		130.2, C		130.2, C	
5’	148.7, C		149.3, C		148.5, C	
5’a	118.9, C		119.1, C		118.2, C	
6’	121.7, C		123.5, C		122.2, C	
7’	160.7, C		161.0, C		159.9, C	
8’	103.4, CH	6.27, s	105.4, CH	6.49, s	104.3, CH	5.92, s
9’	185.3, C		186.3, C		184.7, C	
9’a	111.6, C		112.1, C		110.9, C	
10’	154.6, C		155.1, C		154.8, C	
10’-OH		15.46, s		not observed		15.07, s
10’a	134.7, C		133.9, C		133.0, C	
11’	18.8, CH_3	1.56, d (6.8)	18.9, CH_3	1.69, d (6.7)	18.7, CH_3	1.49, d (6.5)
12’	21.6, CH_3	1.30, d (6.0)	21.5, CH_3	1.40, d (6.2)	21.6, CH_3	1.28, d (6.2)
1”	103.2, CH	4.89, d (7.3)				
2”—5”	77.5, 75.9 73.4, 69.5, CH	3.23–3.51[d] (3H) 3.25, dd (9.2, 9.0)				
6”	60.7, CH_2	3.77, br d (11.9) 3.57, dd (5.5, 11.9)				
Other OH		5.08, br s 5.14, br s				

[a, b, c] These signals are not identified. [d] These signals overlapped with H_2O in DMSO-d_6.

8. Procedure for conversion of uroleuconaphin A_1 (1) in water-containing solvent

To a solution of **1** (30.6 mg, 54.3 μmol) in THF/H_2O (13 mL/13 mL) was added TsOH·H_2O (24.0 mg, 126 μmol), and the mixture was heated at 80 °C. After stirring for 18 h, the reaction mixture was quenched by adding $NaHCO_3$ (11.0 mg, 131 μmol) in H_2O (20 mL) at room temperature. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4. Concentration and purification by column chromatography (silica gel, EtOAc→$CHCl_3$/MeOH = 50/1→30/1→10/1→2/1) to afford green pigment **4** (2.9 mg, 10%) and **3** (6.0 mg, 20%) as a green powder, and biaryl compound **7** (20.2 mg, 66%) as an orange powder.





7

R_f 0.39 ($CHCl_3$/MeOH = 3/1);

$[\alpha]_D^{24}$ –320 (*c* 0.056, MeOH);

IR (ATR) 3358, 1645, 1603, 1355, 1255, 1193, 1149, 1099, 1066, 1034, 956, 824, 588, 524, 491, 476, 458, 449, 435, 413 cm^{-1};

^1H NMR (acetone-d_6, 600 MHz) δ 1.04 (d, 3H, *J* = 6.6 Hz), 1.19 (d, 3H, *J* = 6.0 Hz), 1.52 (d, 3H, *J* = 6.6 Hz), 1.63 (d, 3H, *J* = 6.6 Hz), 1.87 (ddd, 1H, *J* = 19.2 Hz, 10.2 Hz, 2.1 Hz), 2.40 (dd, 1H, *J* = 19.2 Hz, 3.6 Hz), 3.59–3.60 (m, 1H), 3.84 (brd, 1H, *J* = 7.8 Hz), 3.91–3.98 (m, 2H), 4.87 (dq, 1H, *J* = 2.1 Hz, 6.6 Hz), 5.10 (q, 1H, *J* = 6.6 Hz), 6.21 (s, 1H), 6.65 (s, 1H), 9.60 (s, 1H), 13.05 (s, 1H), 13.75 (s, 1H);

^{13}C NMR (acetone-d_6, 150 MHz) δ 17.6, 19.8, 20.0, 21.7, 30.6, 63.1, 66.8, 67.4, 68.4, 71.4, 107.8, 109.9, 110.0, 114.1, 125.7, 126.5, 129.8, 134.0, 138.8, 143.4, 144.0, 146.4, 158.6, 160.2, 165.4, 165.9, 181.3, 184.5, 188.0, 193.0;

HRMS (MALDI) calcd for $C_{30}H_{25}O_{11}$ $[M–H]^-$ *m/z* 561.1391, found *m/z* 561.1385;

Mp 196 °C (dec).

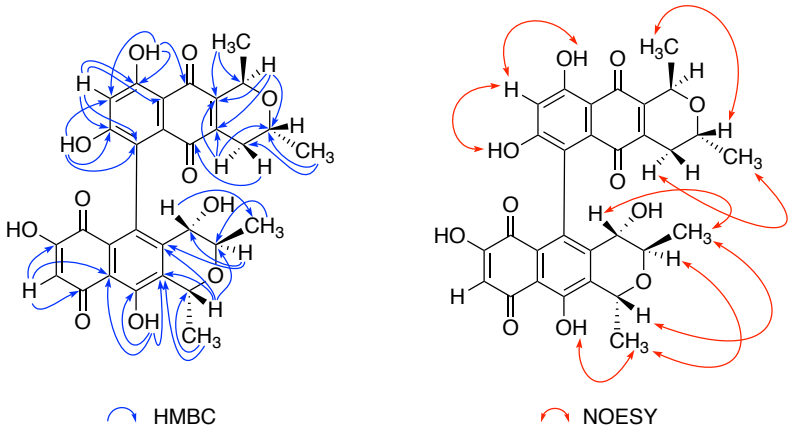
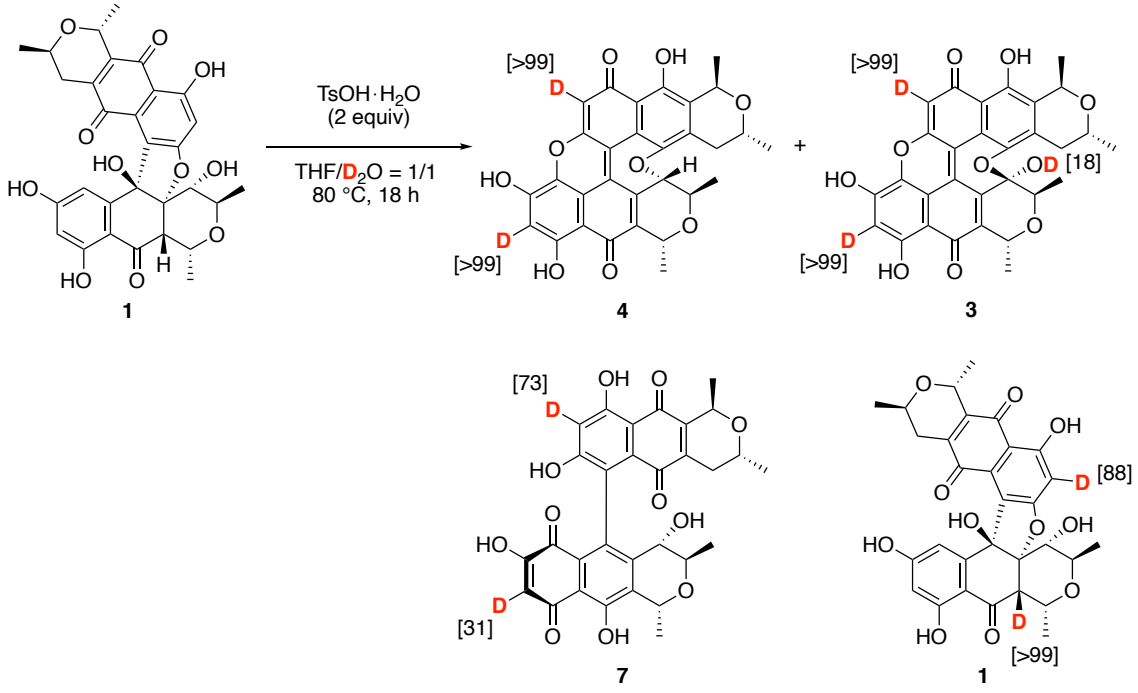


Figure S6. Key 2D NMR correlations of **7** in acetone-d_6

Procedure for conversion of uroleuconaphin A_1 (1) in deuterated water-containing solvent

To a solution of **1** (20.8 mg, 36.9 μmol) in THF/D_2O (9 mL/9 mL) was added TsOH·H_2O (16.2 mg, 85.2 μmol), and the mixture was heated at 80 °C. After stirring for 18 h, the reaction mixture was quenched by adding $NaHCO_3$ (7.1 mg, 85 μmol) in H_2O (10 mL) at room temperature. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4. Concentration and purification by column chromatography (silica gel, EtOAc→$CHCl_3$/MeOH = 40/1→20/1→10/1→2/1) to afford green pigment **4** (0.4 mg, 2%) and **3** (1.5 mg, 8%) as a green powder, biaryl compound **7** (11.2 mg, 54%) as an orange powder, and starting material **1** (5.1 mg, 25%) as a red powder.



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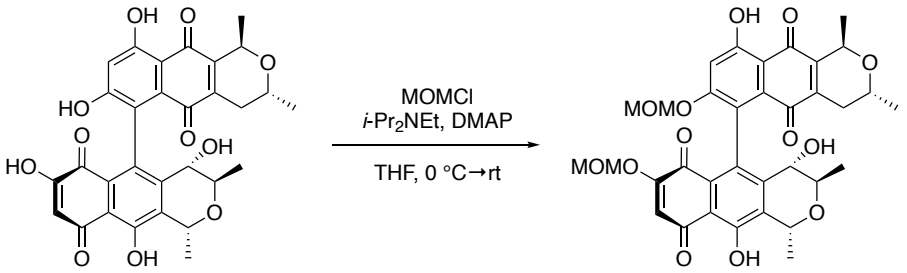
9. Preparation of compound 8



7 **8**

To a solution of **7** (6.8 mg, 12 μmol) in THF (1.0 mL) was successively added *N*,*N*-diisopropylethylamine (43 μL, 0.24 mmol) and DMAP (3.3 mg, 24 μmol) and MOMCl (9.2 μL, 0.12 mmol) at 0 °C, and allowed to warm to room temperature. After stirring for 2 h at this temperature, the reaction was quenched by adding saturated aqueous NH_4Cl. The products were extracted with EtOAc (×3) and combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afford bis-MOM ether **8** (4.4 mg, 56%) as an orange solid. Recrystallization from EtOAc gave **8** as orange needles.

R_f 0.52 (hexane/EtOAc = 1/2);

$[\alpha]_D^{18}$ –240 (*c* 0.018, $CHCl_3$);

IR (ATR) 3493, 2975, 2930, 1677, 1630, 1606, 1379, 1337, 1279, 1217, 1152, 1061, 958, 732, 439, 418 cm^{-1};

^1H NMR ($CDCl_3$, 500 MHz) δ 1.02 (d, 3H, *J* = 6.5 Hz), 1.25 (d, 3H, *J* = 6.0 Hz), 1.55 (d, 3H, *J* = 6.5 Hz), 1.70 (d, 3H, *J* = 6.5 Hz), 1.95 (dd, 1H, *J* = 19.0 Hz, 10.5 Hz), 2.11 (d, 1H, *J* = 8.0 Hz), 2.35 (dd, 1H, *J* = 19.0 Hz, 3.0 Hz), 3.30 (s, 3H), 3.44 (s, 3H), 3.78 (dd, 1H, *J* = 8.0 Hz, 2.5 Hz), 3.86–3.90 (m, 1H), 4.07 (qd, 1H, *J* = 6.5 Hz, 2.5 Hz), 4.98 (q, 1H, *J* = 6.5 Hz), 5.06 (d, 1H, *J* = 6.5 Hz), 5.12 (d, 1H, *J* = 6.5 Hz), 5.14 (d, 1H, *J* = 6.5 Hz), 5.19 (s, 2H), 6.36 (s, 1H), 7.03 (s, 1H), 12.93 (s, 1H), 13.39 (s, 1H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.7, 19.7, 20.7, 21.4, 30.0, 56.6, 57.3, 62.4, 65.2, 66.9, 67.0, 72.0, 95.1, 95.2, 108.1, 110.2, 112.1, 113.6, 124.5, 126.0, 128.7, 132.7, 136.8, 140.9, 142.3, 146.3, 158.0, 158.3, 162.7, 165.0, 179.5, 183.8, 186.9, 191.2;

HRMS (MALDI) calcd for $C_{34}H_{34}O_{13}Na$ $[M+Na]^+$ *m/z* 673.1892, found *m/z* 673.1895;

Mp 95–97 °C.

10. NMR spectra

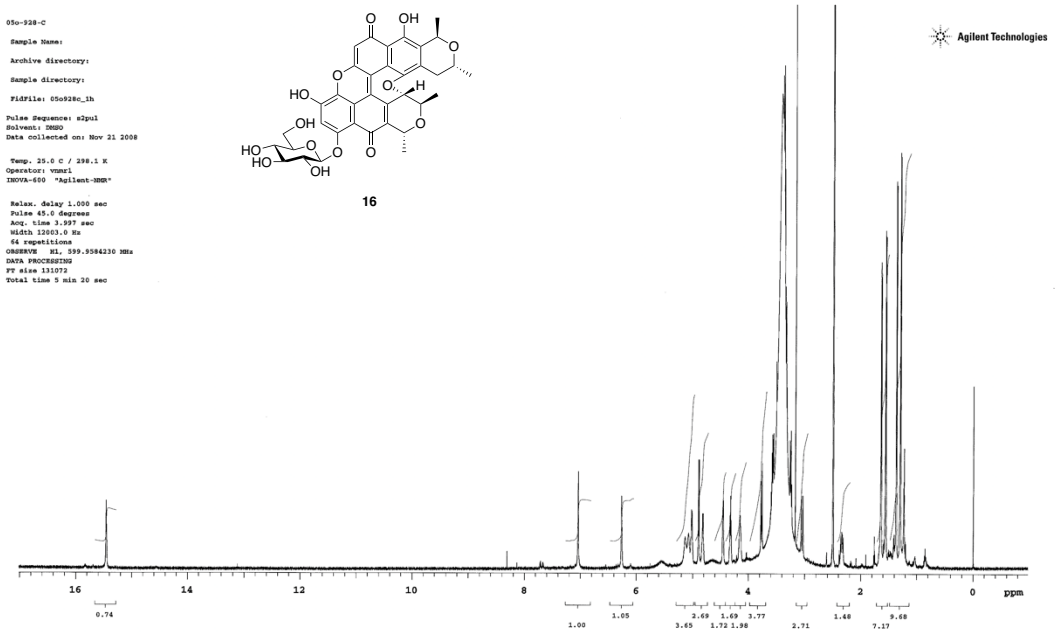


Figure S7. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of viridaphin A_2 glucoside (**16**)

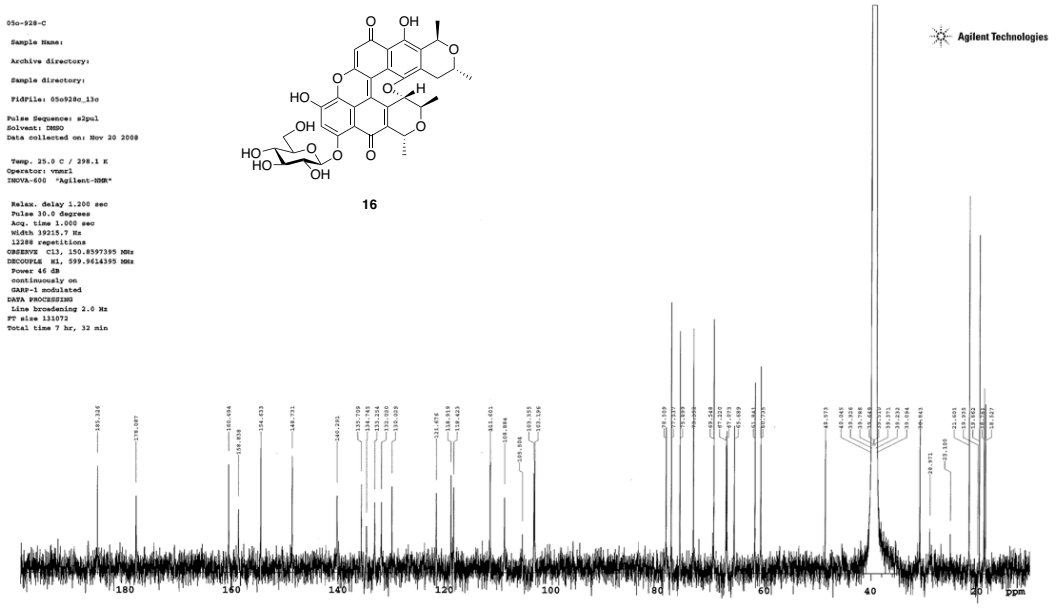


Figure S8. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of viridaphin A_2 glucoside (**16**)

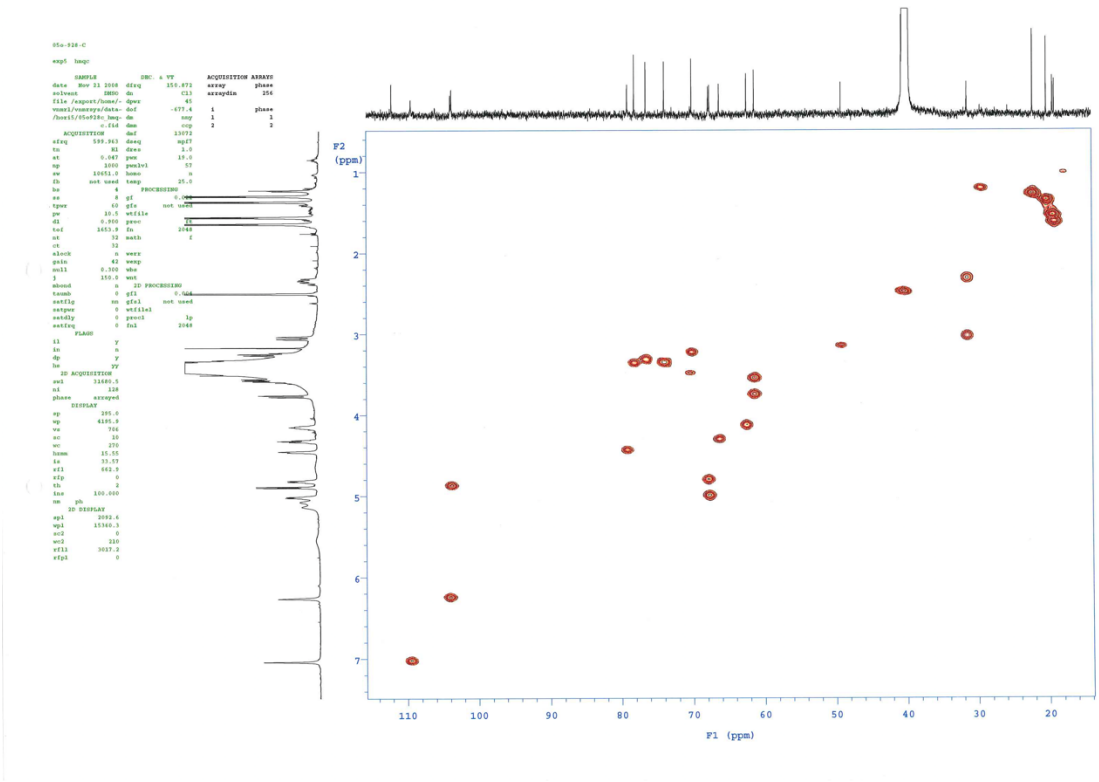


Figure S9. HSQC spectrum (DMSO-d_6) of viridaphin A_2 glucoside (**16**)

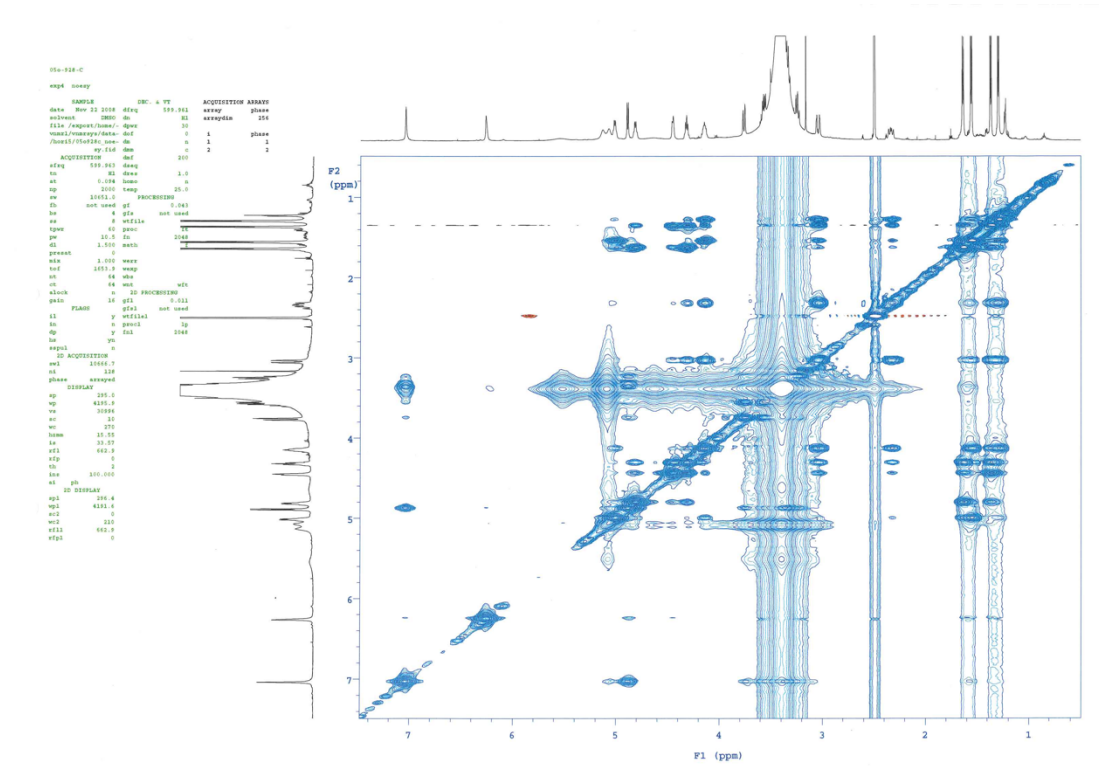


Figure S10. NOESY spectrum (DMSO-d_6) of viridaphin A_2 glucoside (**16**)

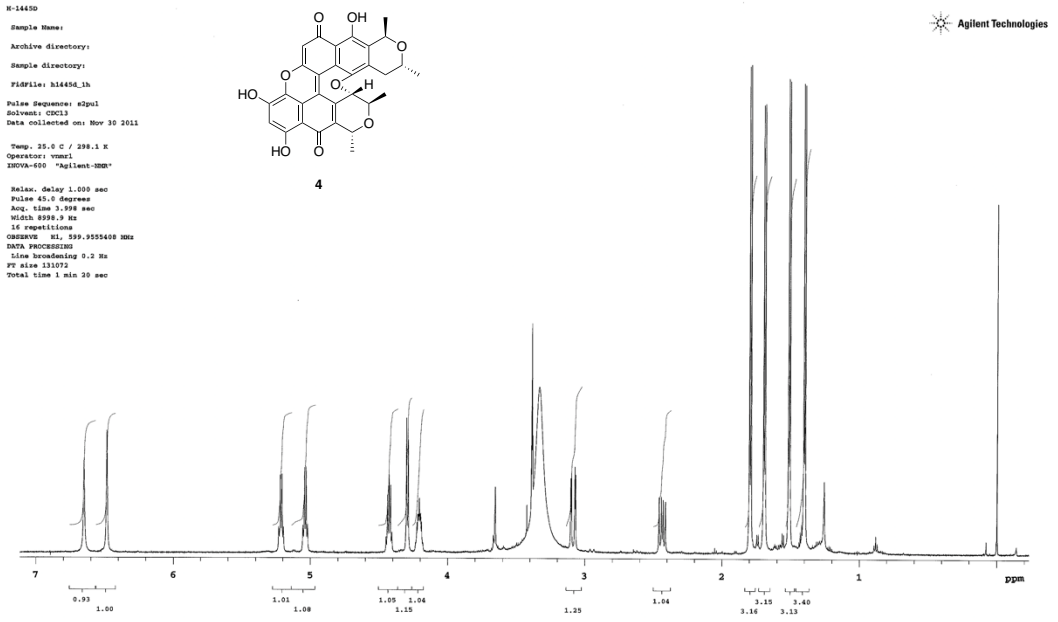


Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$+CD_3OD) of viridaphin A_2 (**4**)

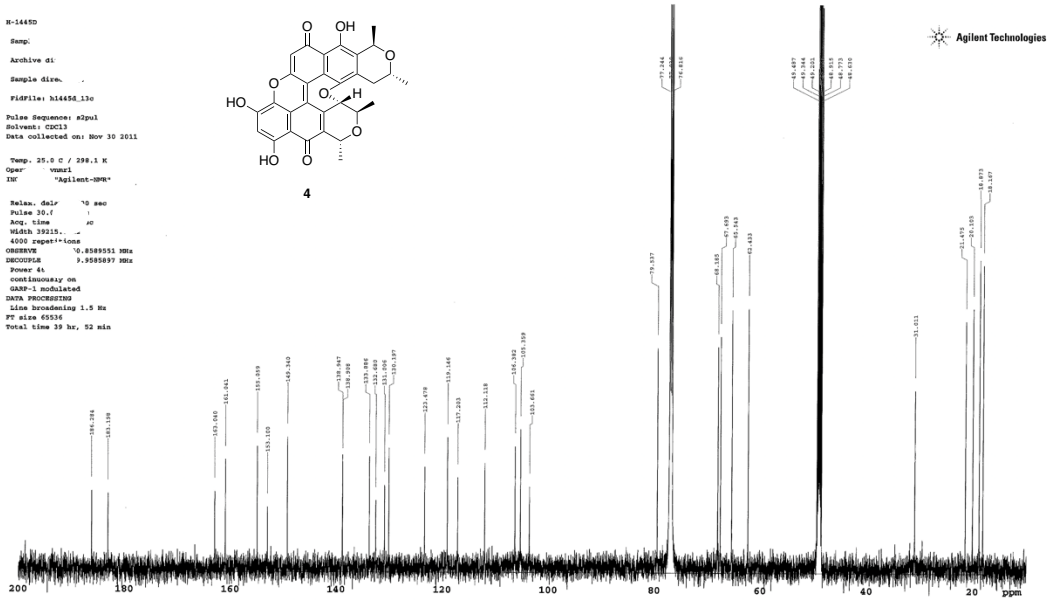


Figure S12. ^{13}C NMR spectrum (150 MHz, $CDCl_3$+CD_3OD) of viridaphin A_2 (**4**)

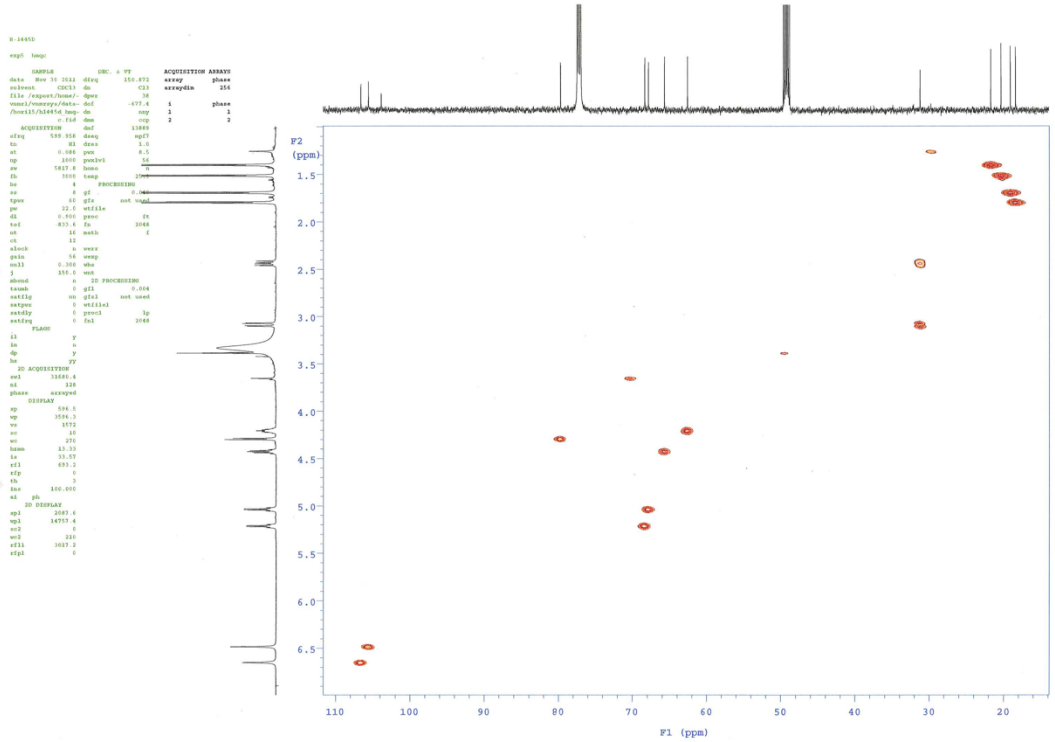


Figure S13. HSQC spectrum ($CDCl_3$+CD_3OD) of viridaphin A_2 (**4**)

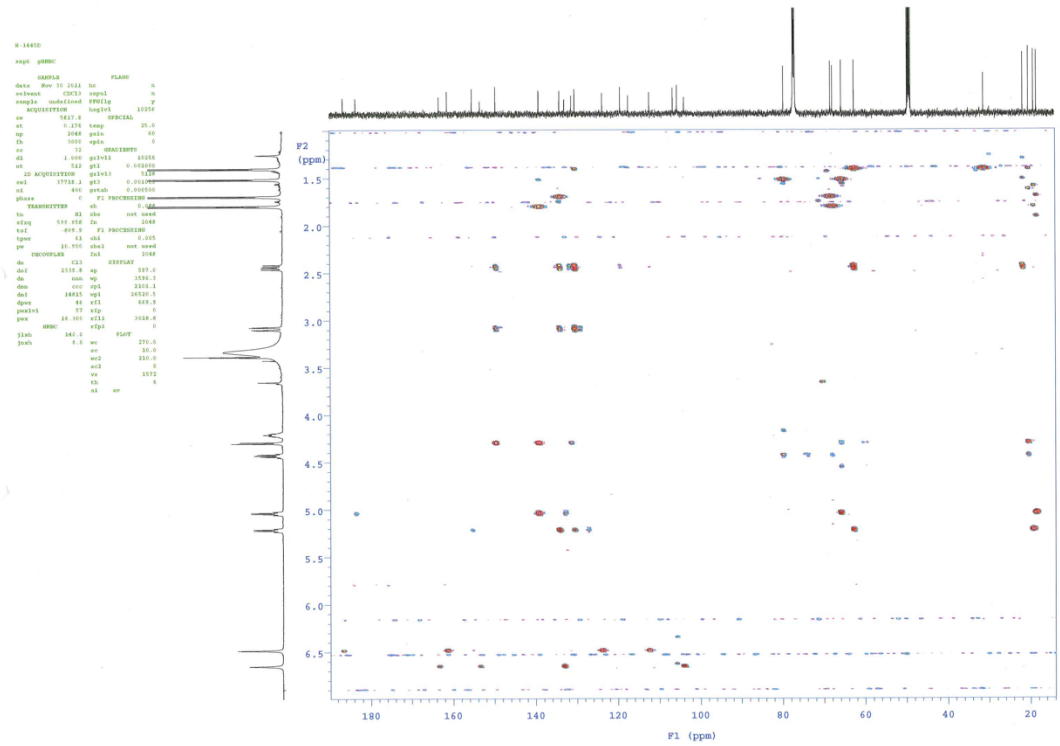


Figure S14. HMBC spectrum ($CDCl_3$+CD_3OD) of viridaphin A_2 (**4**)

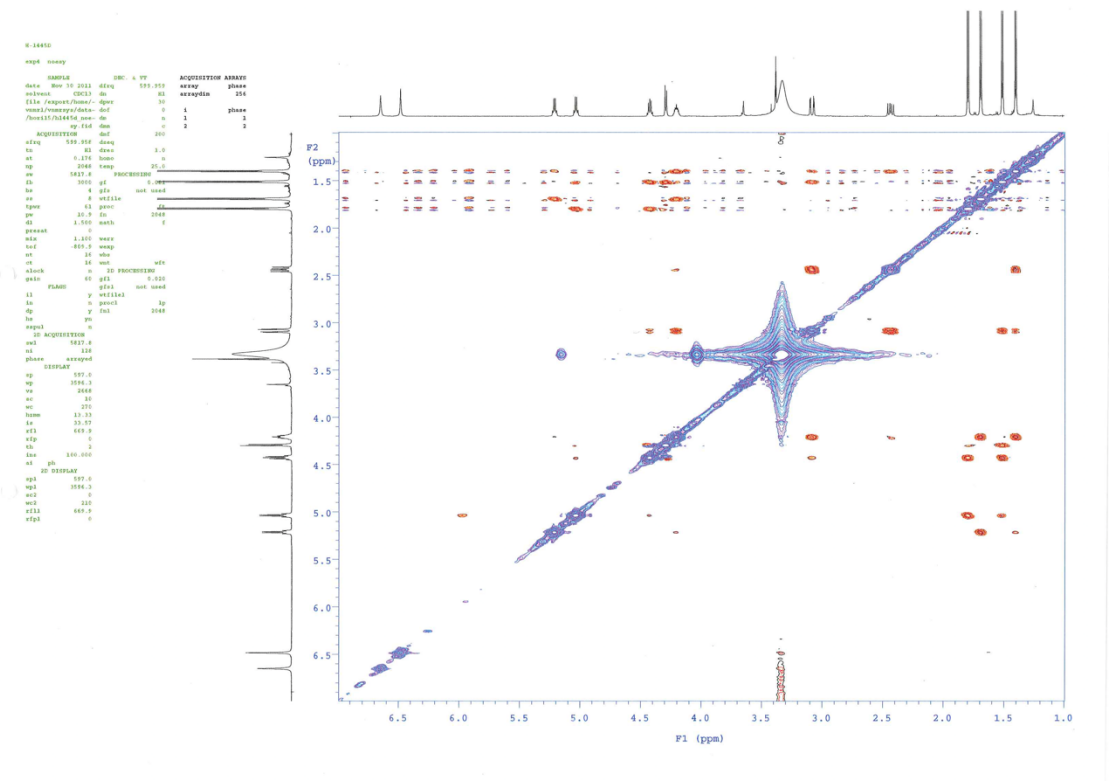


Figure S15. NOESY spectrum ($CDCl_3$+CD_3OD) of viridaphin A_2 (**4**)

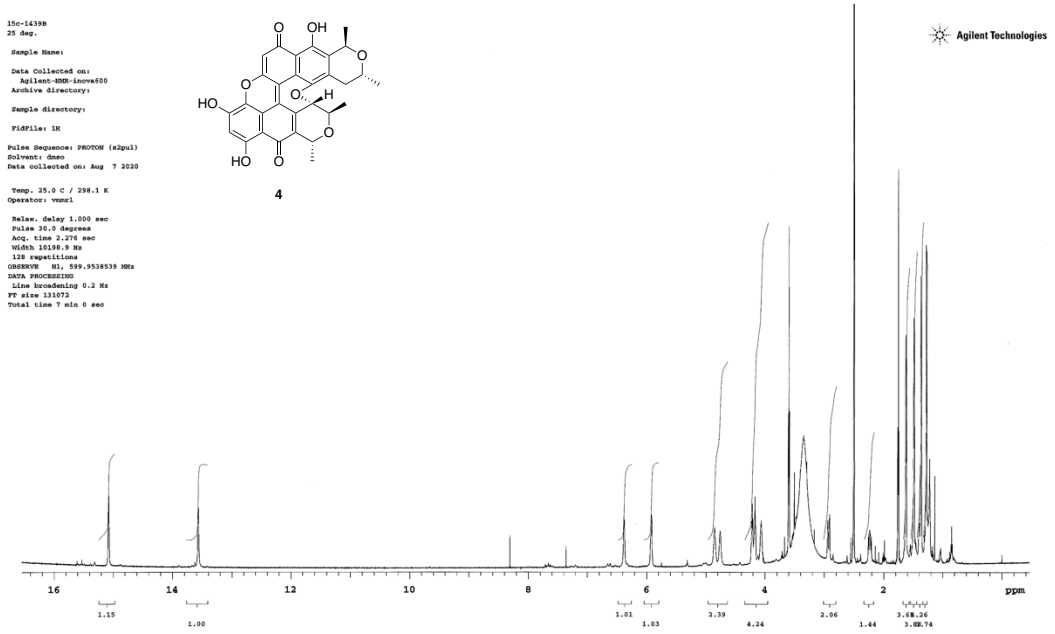


Figure S16. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of viridaphin A_2 (**4**)

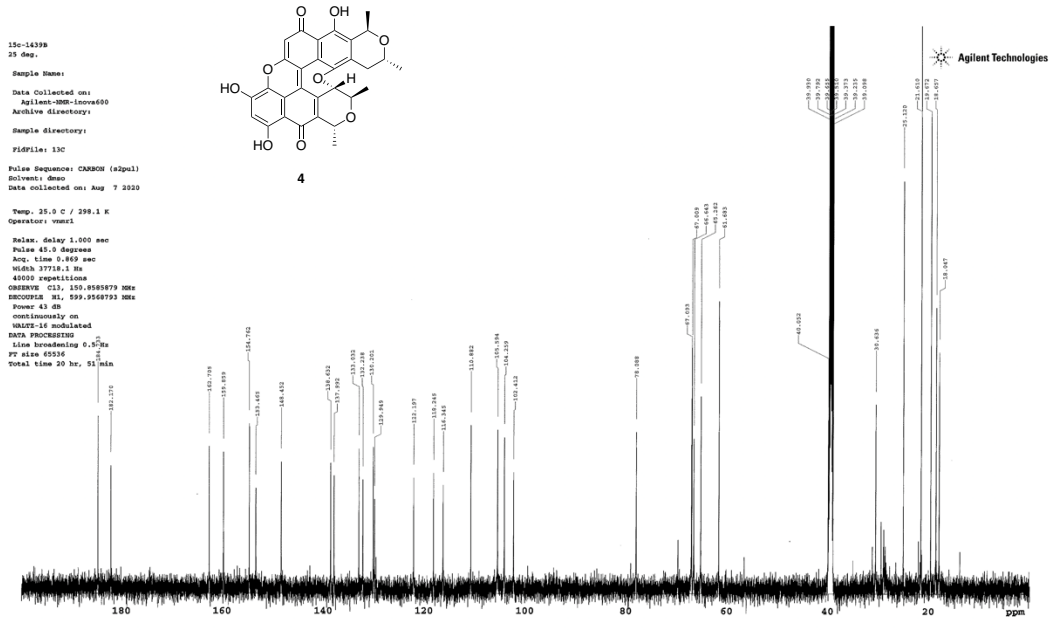


Figure S17. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of viridaphin A_2 (**4**)

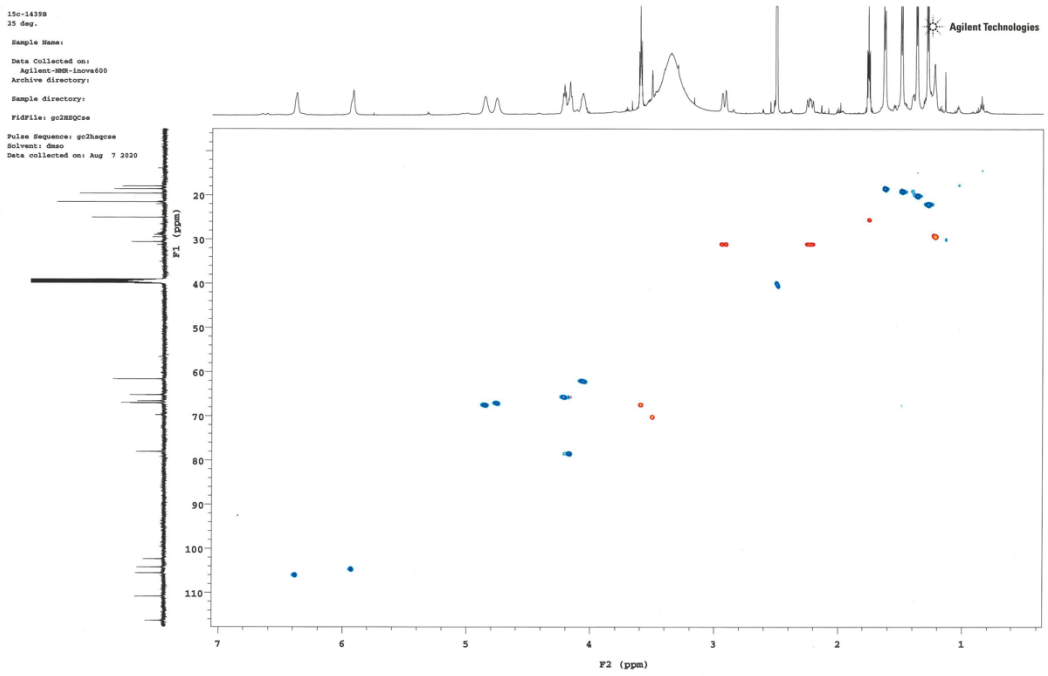


Figure S18. HSQC spectrum (DMSO-d_6) of viridaphin A_2 (**4**)

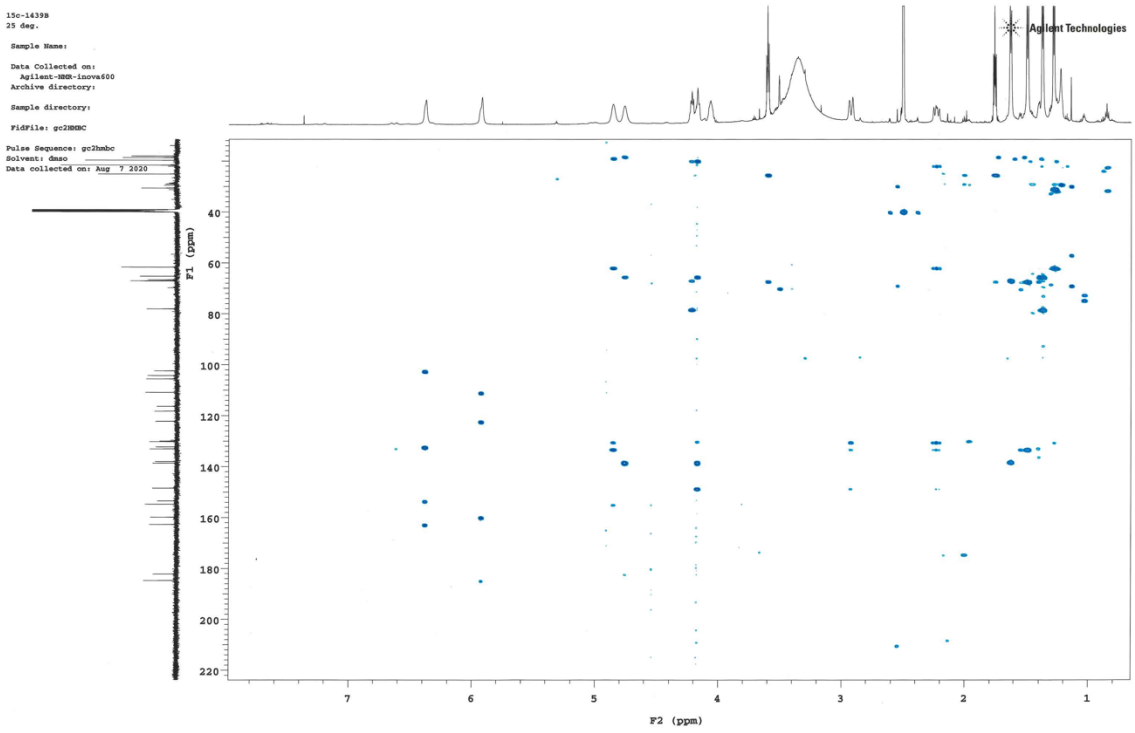


Figure S19. HMBC spectrum (DMSO-d_6) of viridaphin A_2 (**4**)

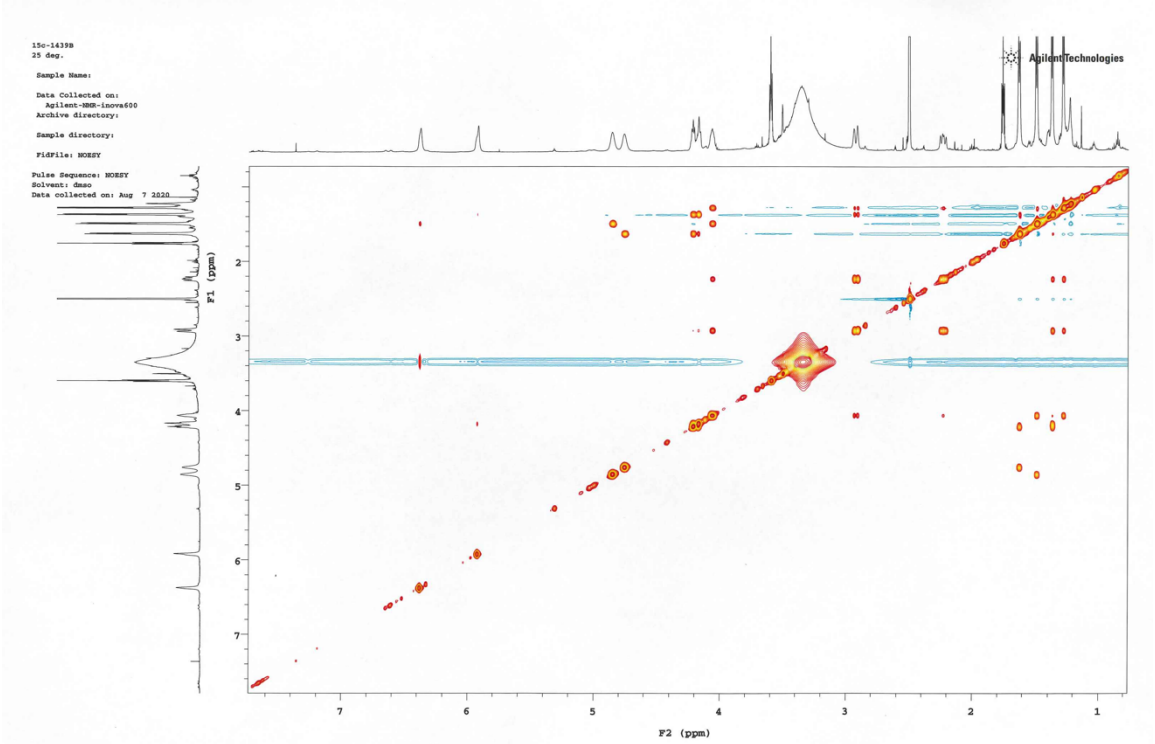


Figure S20. NOESY spectrum (DMSO-d_6) of viridaphin A_2 (**4**)

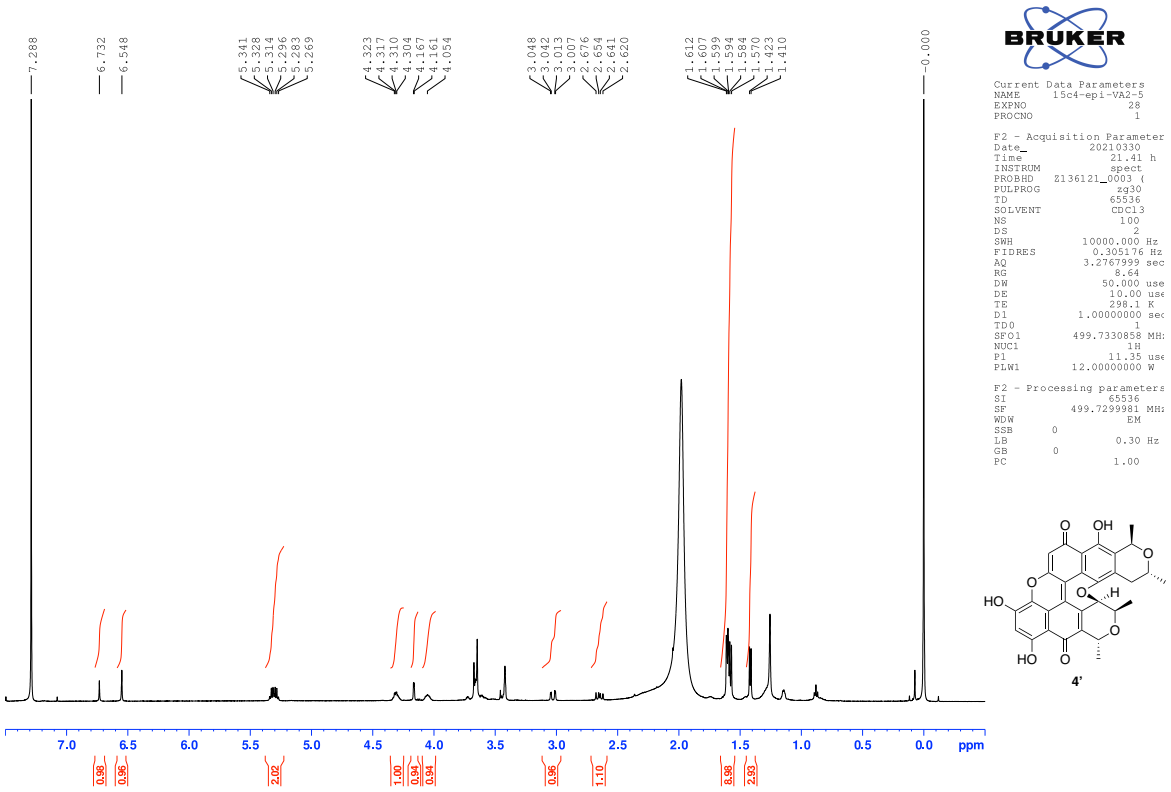


Figure S21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$+CD_3OD) of 4-*epi* viridaphin A_2 (**4'**)

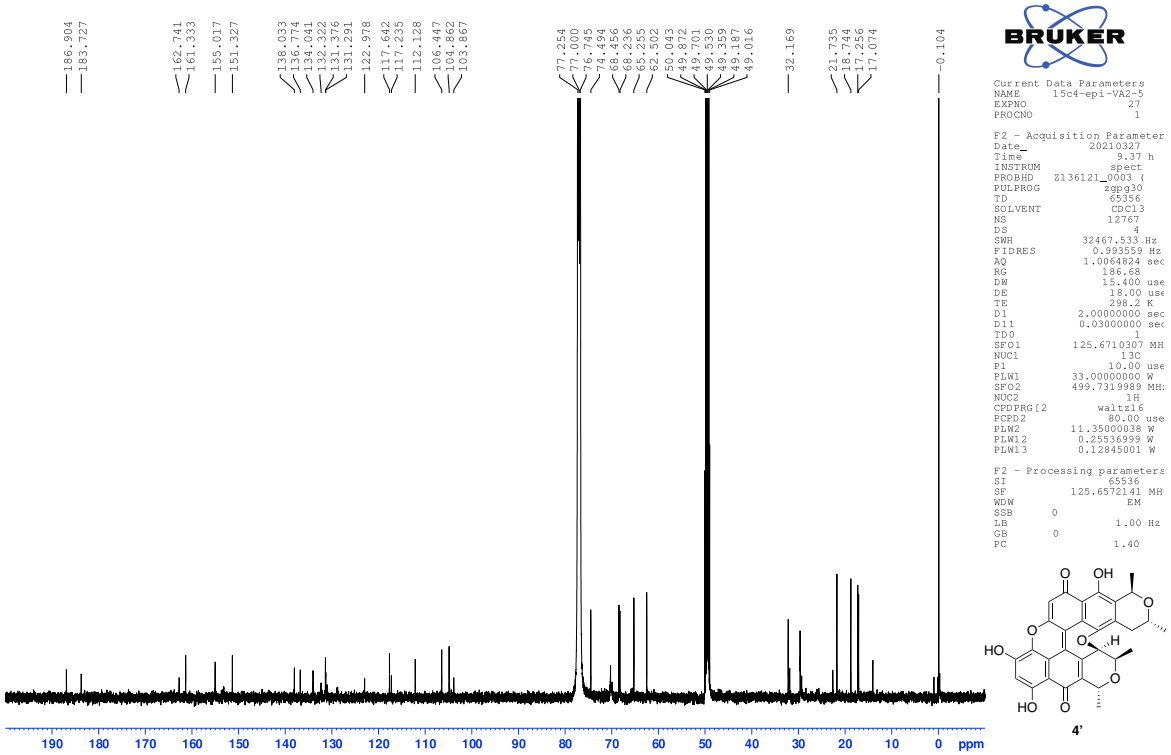


Figure S22. ^{13}C NMR spectrum (125 MHz, $CDCl_3$+CD_3OD) of 4-*epi* viridaphin A_2 (**4'**)

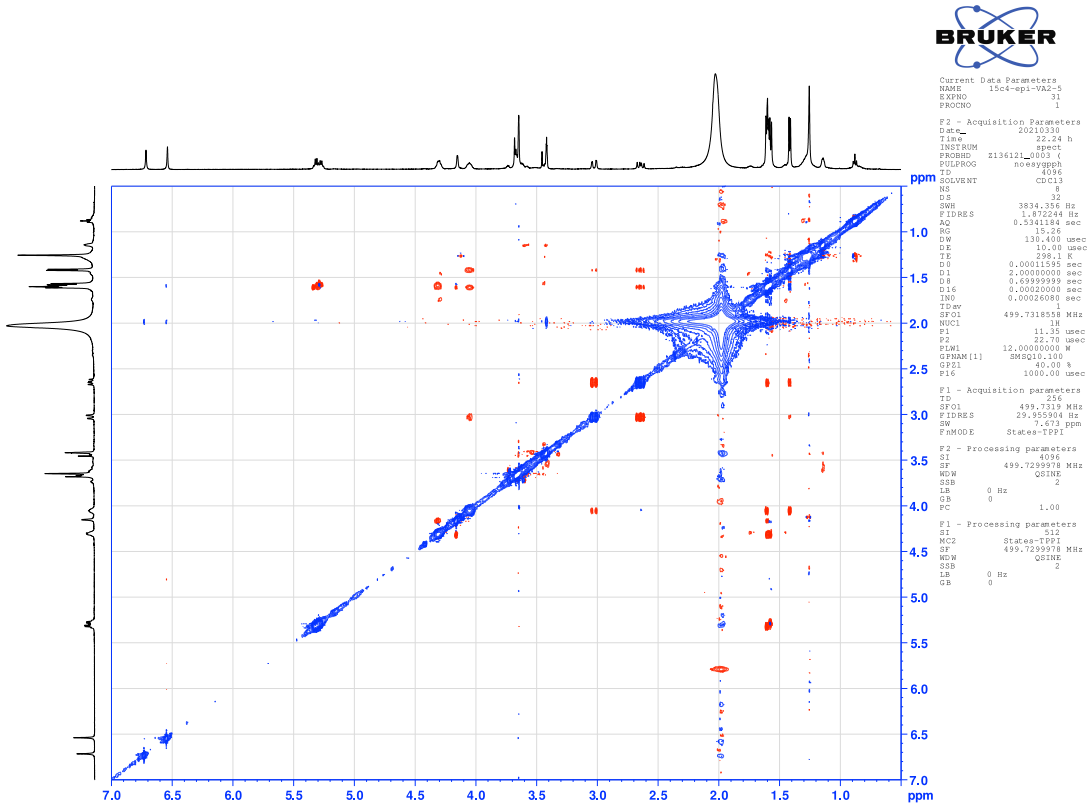


Figure S23. NOESY spectrum ($CDCl_3$+CD_3OD) of 4-*epi* viridaphin A_2 (**4'**)

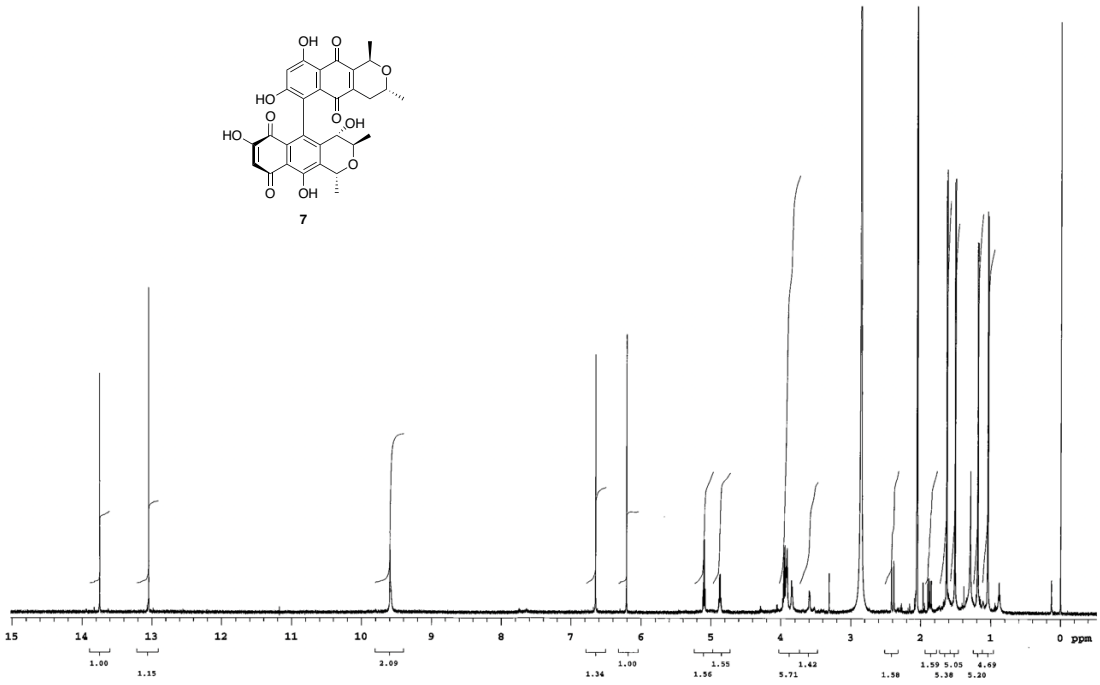


Figure S24. [1]H NMR spectrum (600 MHz, acetone-d_6) of **7**

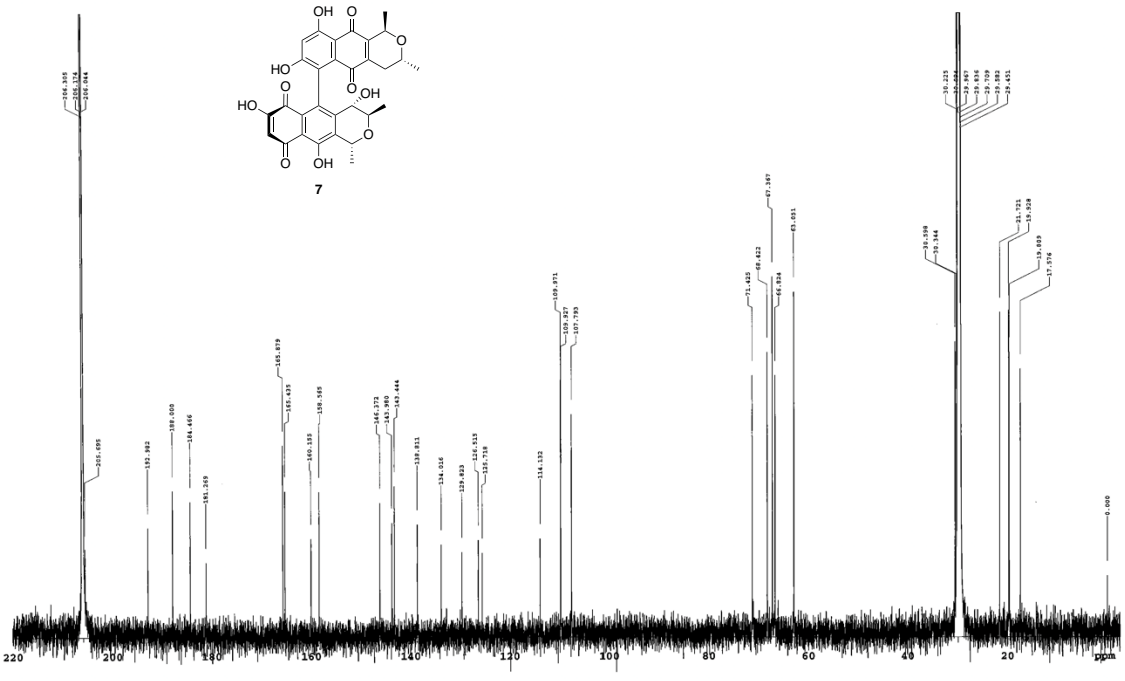


Figure S25. [13]C NMR spectrum (150 MHz, acetone-d_6) of **7**

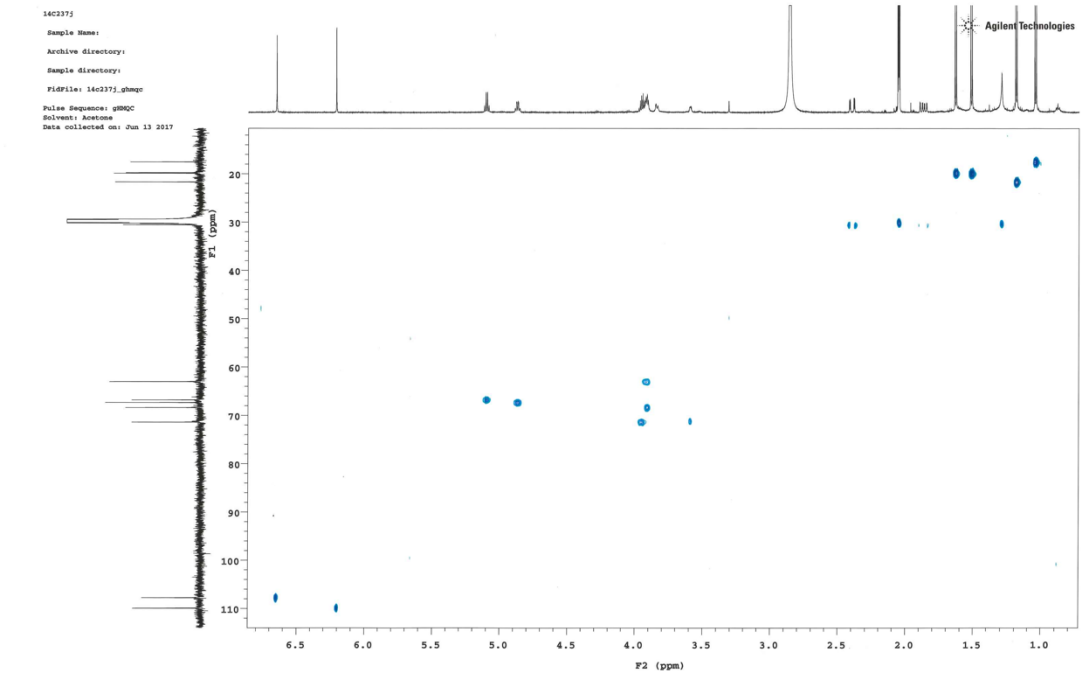


Figure S26. HSQC spectrum (acetone-d_6) of **7**

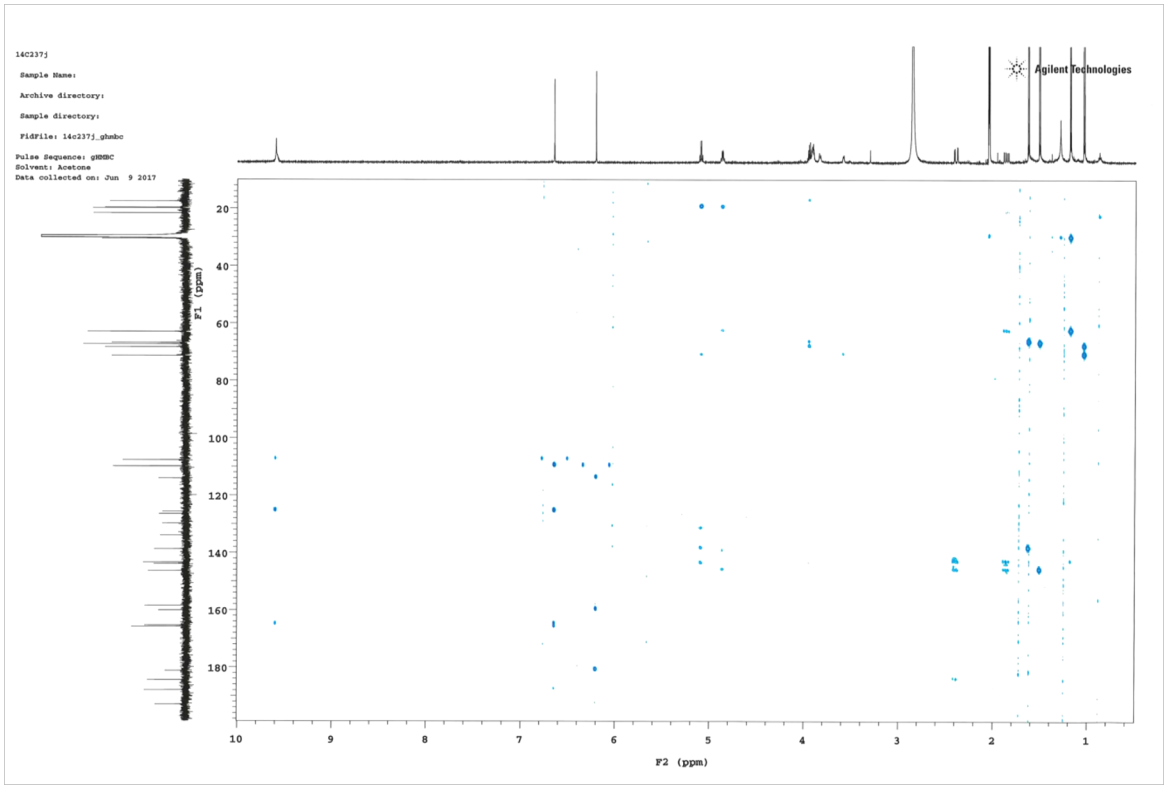


Figure S27. HMBC spectrum (acetone-d_6) of **7**

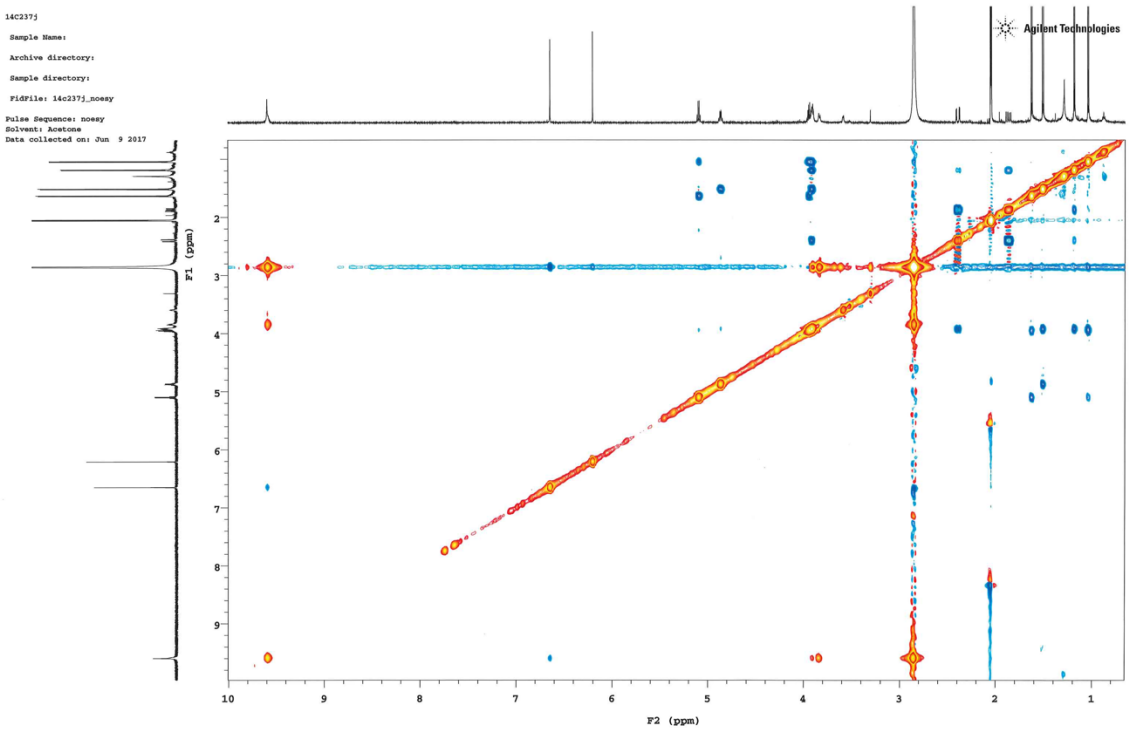


Figure S28. NOESY spectrum (acetone-d_6) of **7**

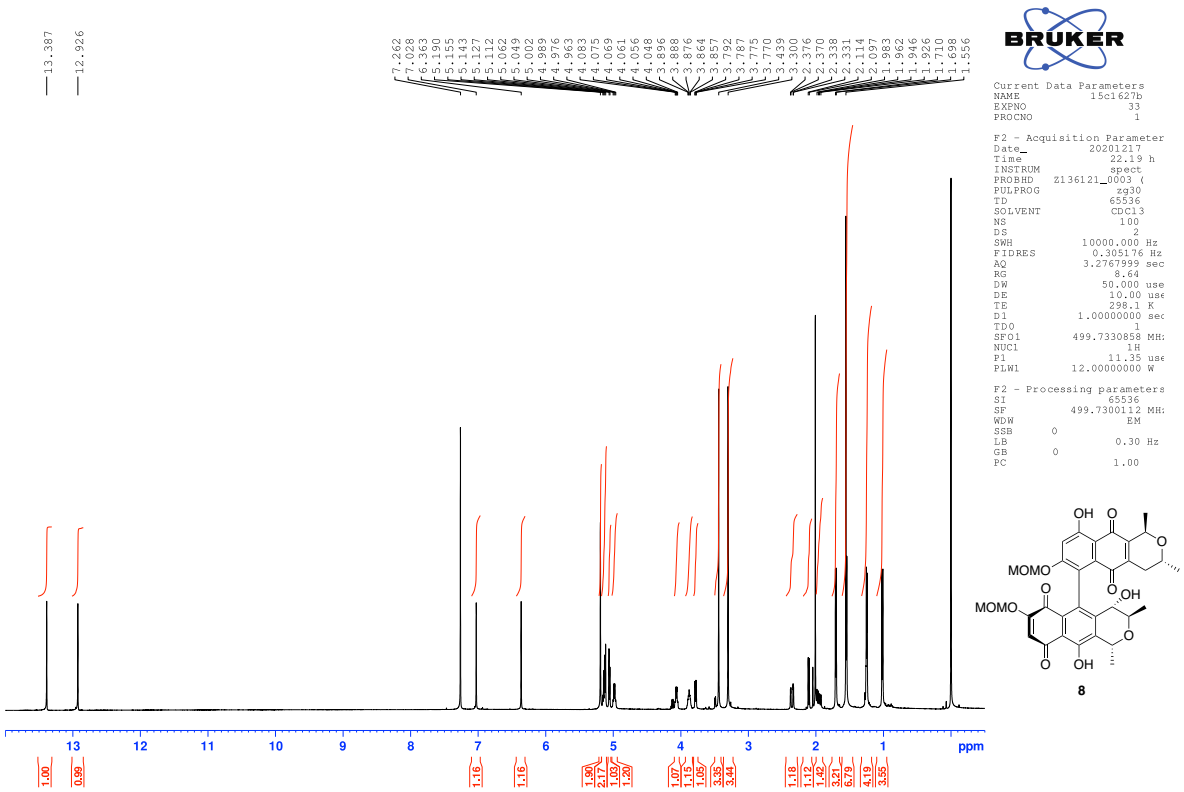


Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **8**

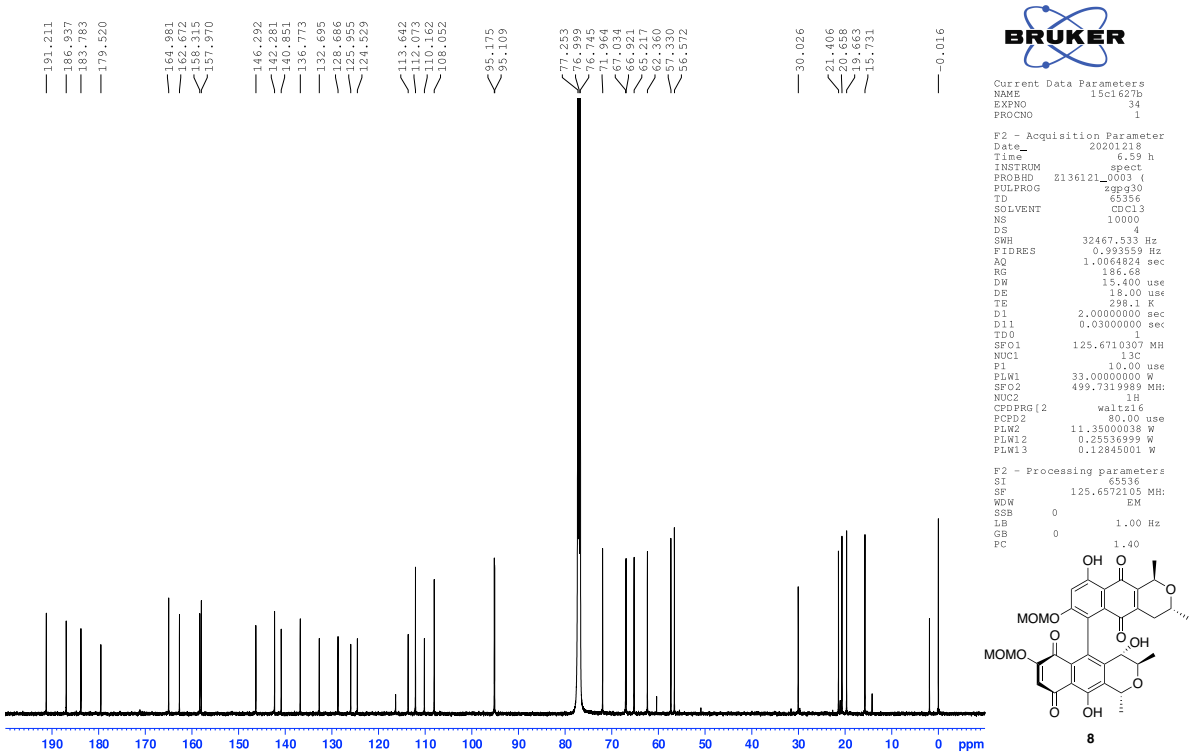


Figure S30. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **8**

11. IR spectra

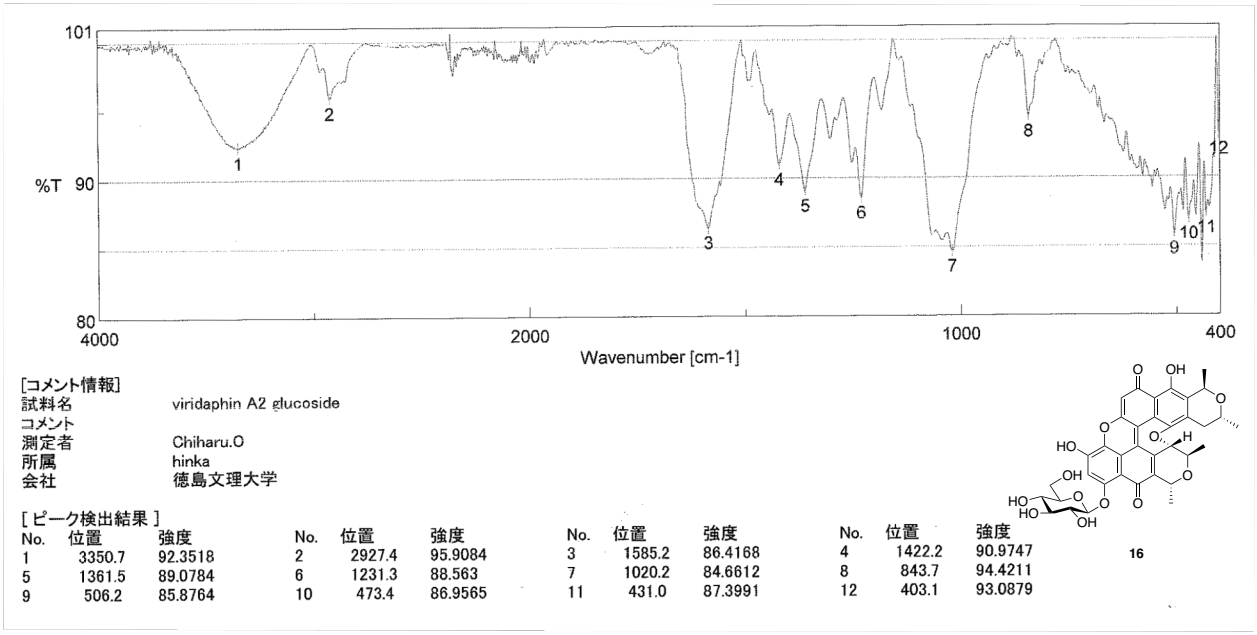


Figure S31. IR spectrum of viridaphin A_2 glucoside (**16**)

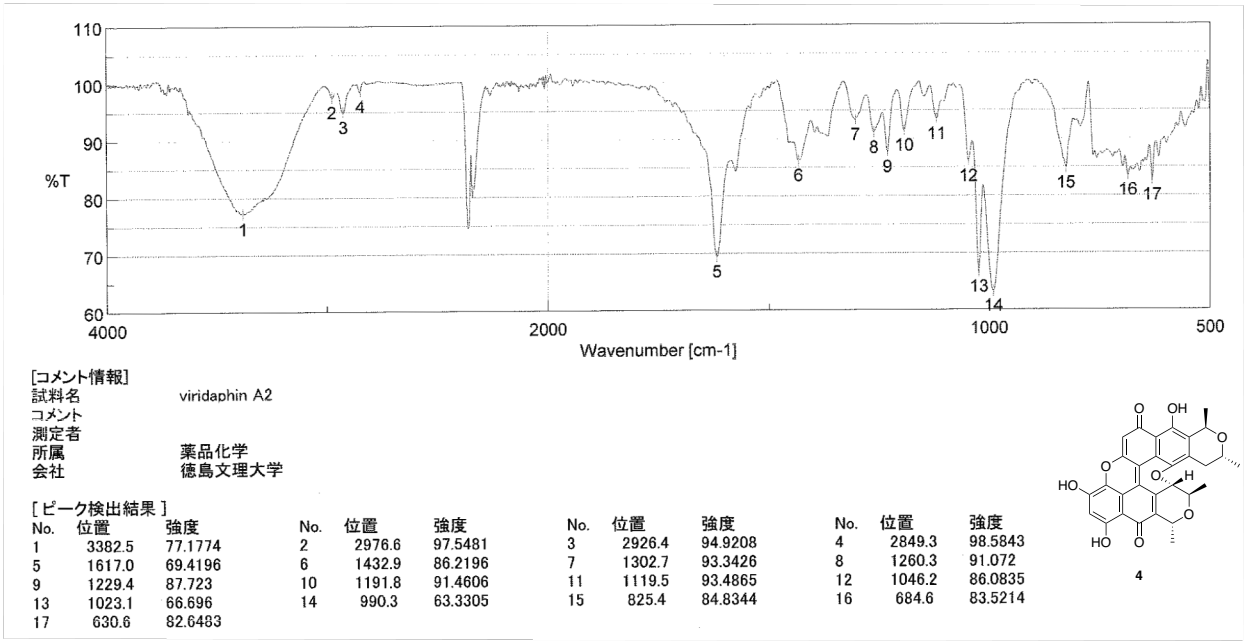
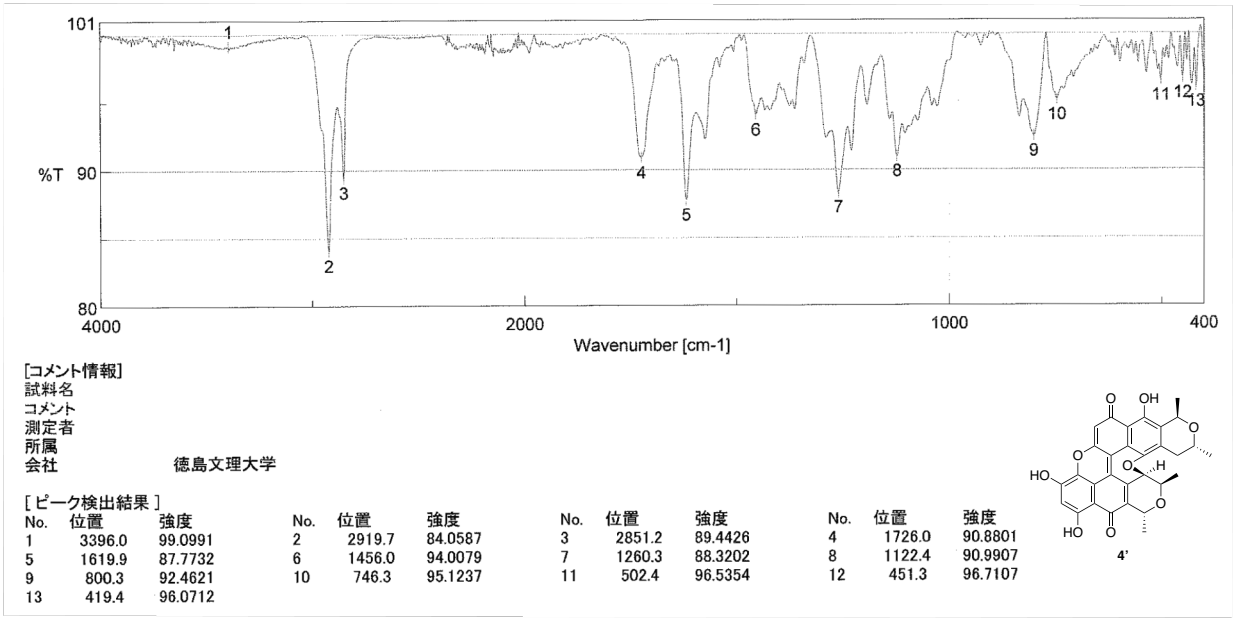


Figure S32. IR spectrum of viridaphin A_2 (**4**)

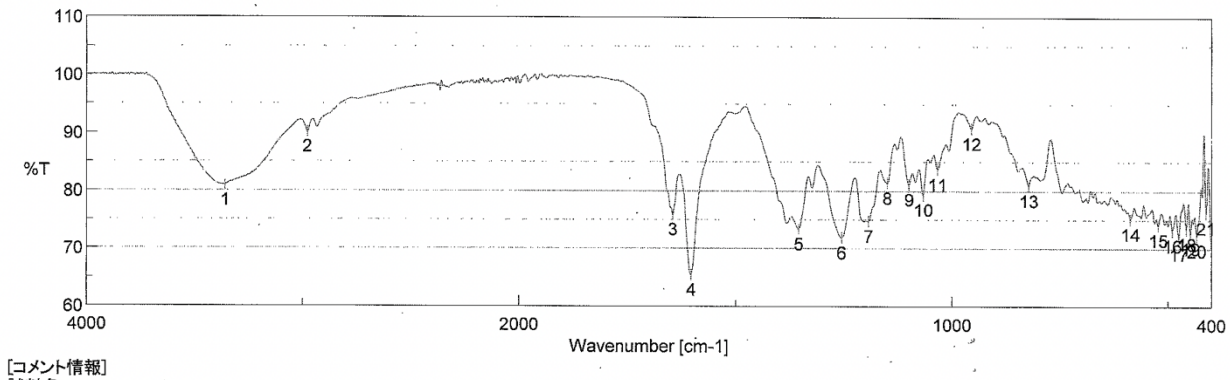


[コメント情報]
試料名
コメント
測定者
所属
会社 徳島文理大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3396.0	99.0991	2	2919.7	84.0587	3	2851.2	89.4426	4	1726.0	90.8801
5	1619.9	87.7732	6	1456.0	94.0079	7	1260.3	88.3202	8	1122.4	90.9907
9	800.3	92.4621	10	746.3	95.1237	11	502.4	96.5354	12	451.3	96.7107
13	419.4	96.0712									

Figure S33. IR spectrum of 4-*epi* viridaphin A_2 (**4'**)



[コメント情報]
試料名 14c321e
コメント
測定者 TT
所属 hinka
会社 徳島文理大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3358.4	80.9456	2	2978.5	90.1894	3	1645.0	75.8571	4	1602.6	65.5138
5	1354.7	73.3285	6	1255.4	71.8343	7	1192.8	74.6906	8	1149.4	81.3728
9	1099.2	81.1221	10	1066.4	79.3154	11	1033.7	83.7244	12	955.6	90.7146
13	823.5	80.9227	14	588.2	75.0582	15	523.6	74.021	16	490.8	73.0787
17	476.3	71.6943	18	458.0	73.3474	19	449.3	72.6051	20	434.9	72.2363
21	412.7	76.1438									

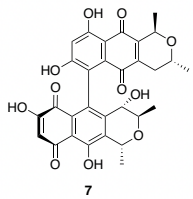


Figure S34. IR spectrum of **7**

12. HRMS spectra

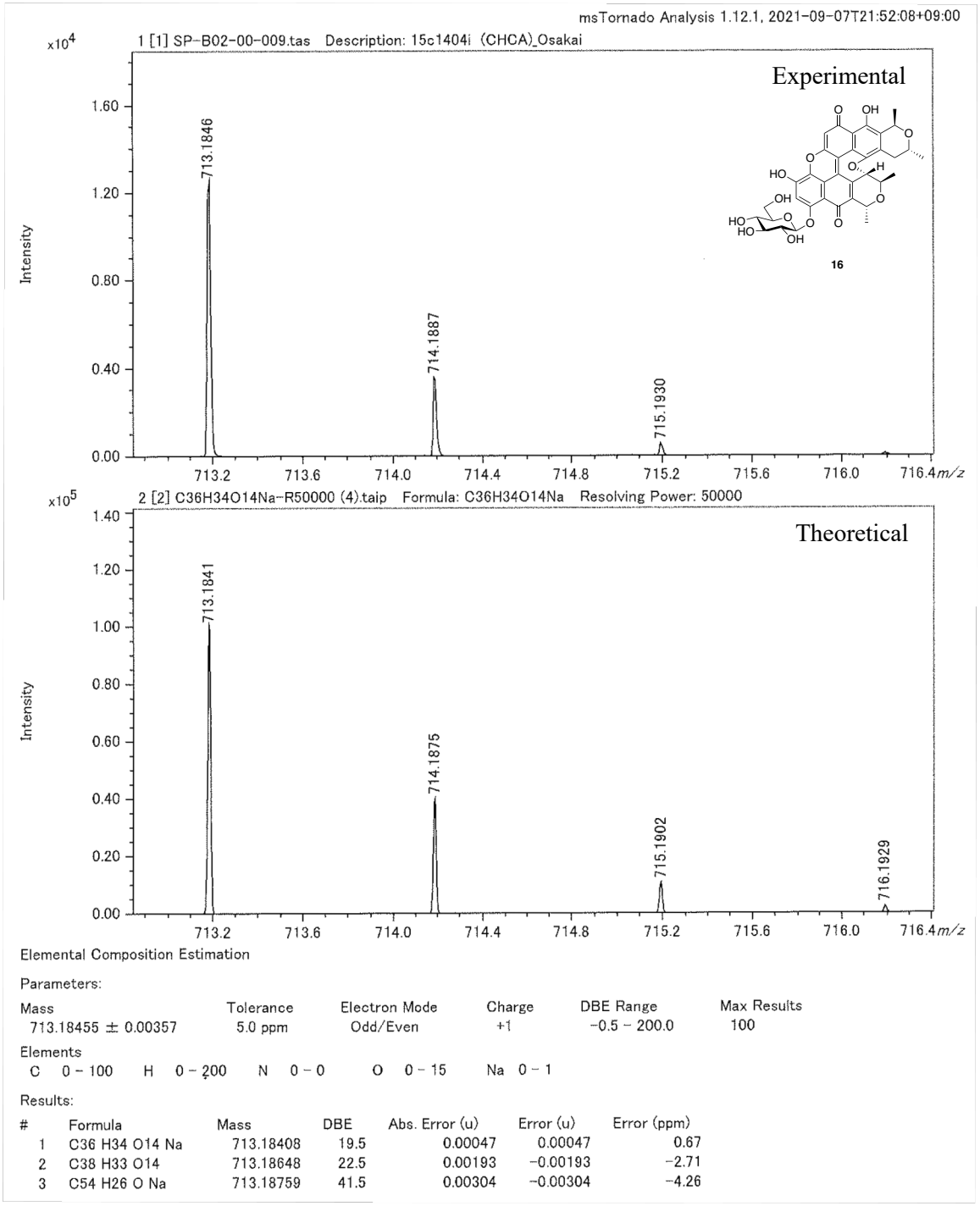


Figure S35. HRMS (MALDI) spectrum of viridaphin A_2 glucoside (**16**)

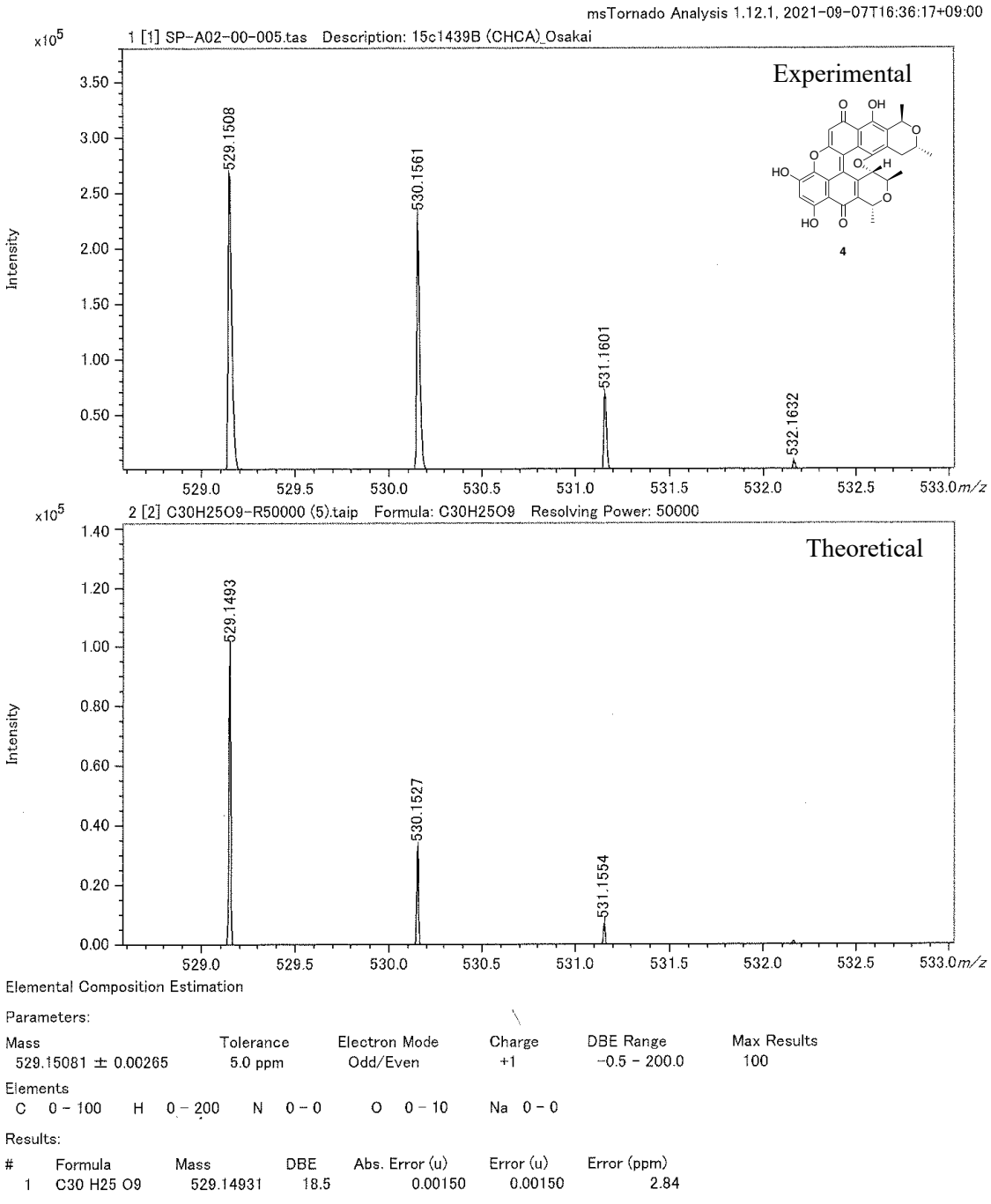


Figure S36. HRMS (MALDI) spectrum of viridaphin A_2 (**4**)

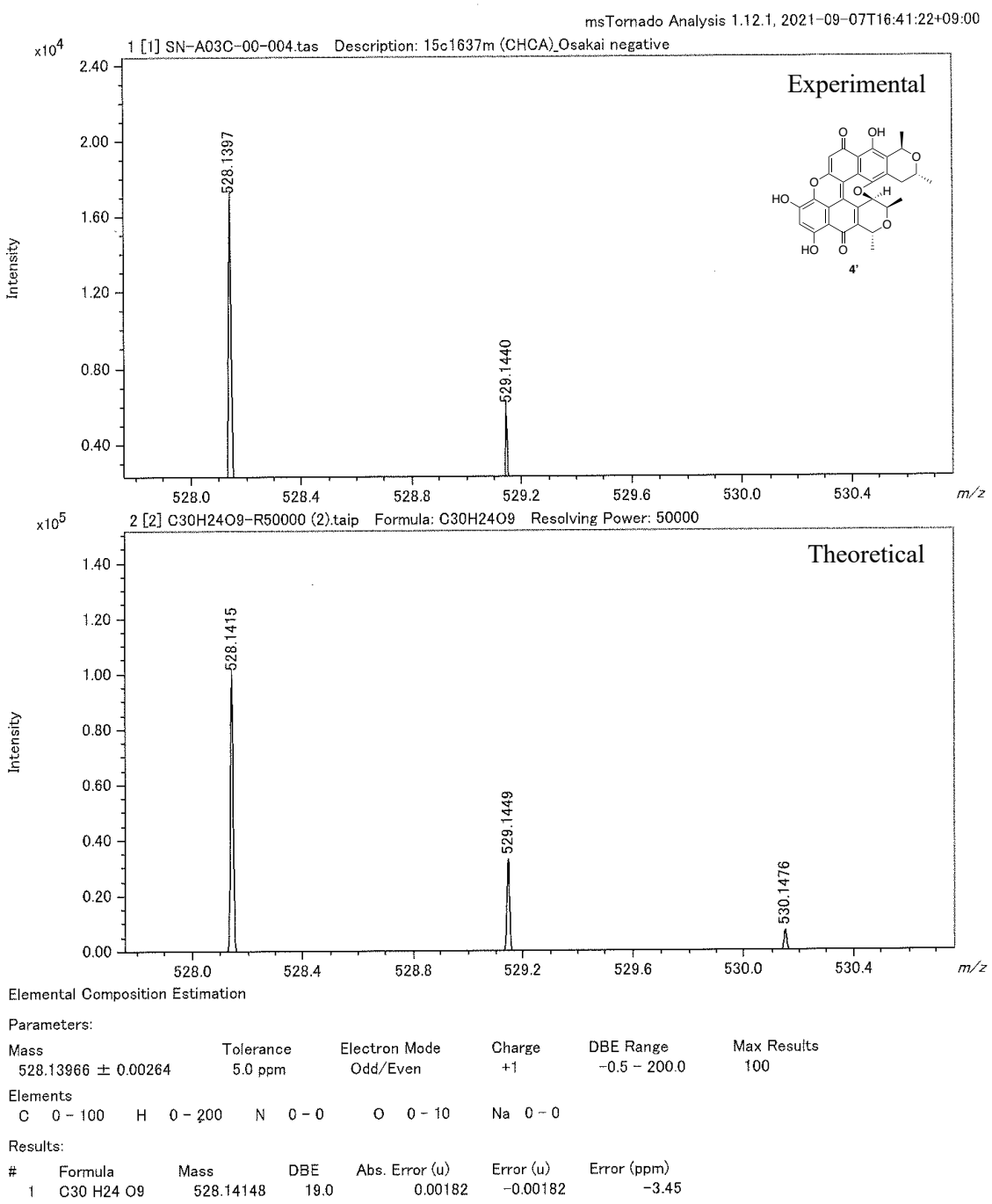
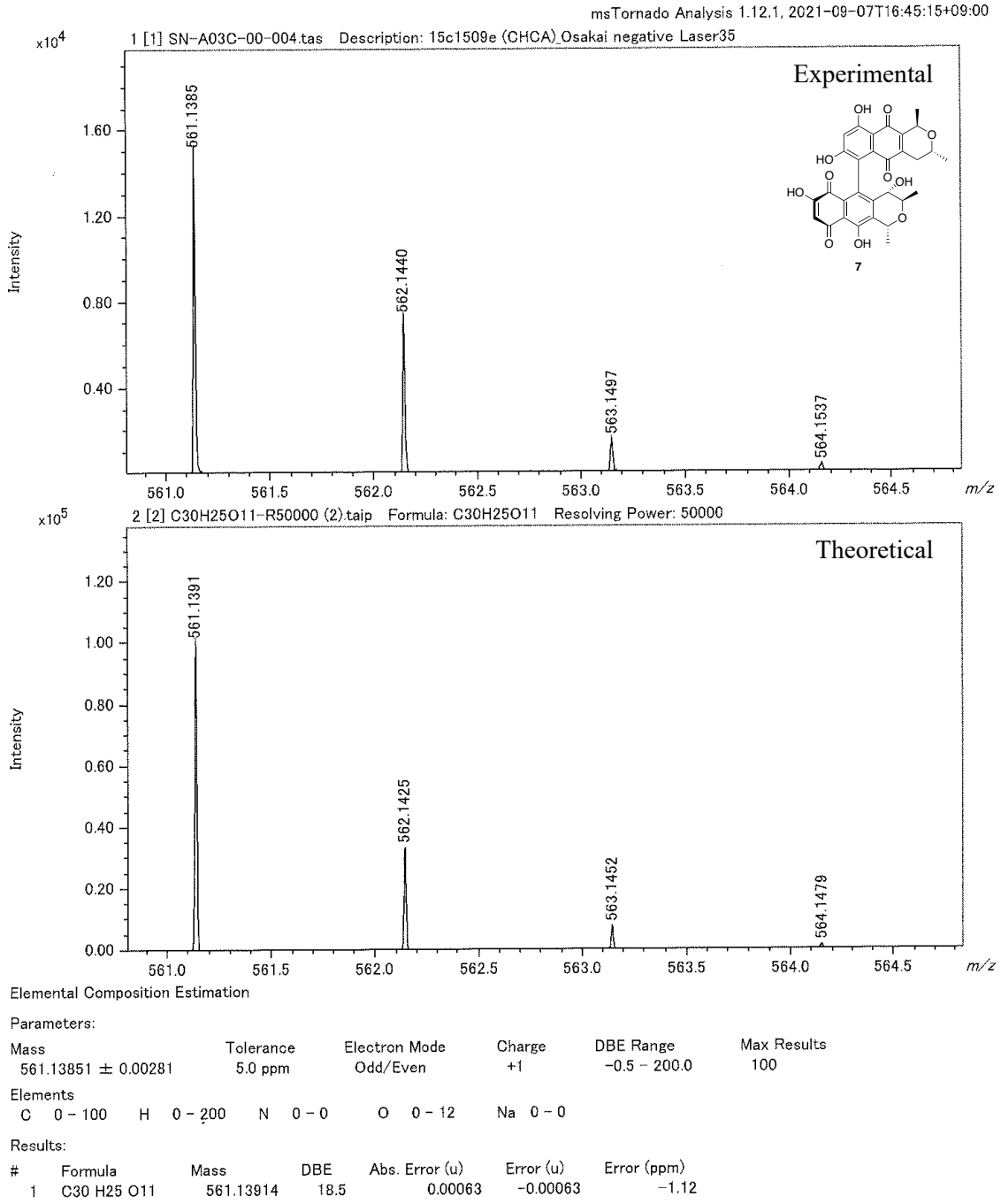


Figure S37. HRMS (MALDI) spectrum of 4-*epi* viridaphin A_2 (**4'**)



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
561.13851 ± 0.00281	5.0 ppm	Odd/Even	+1	-0.5 – 200.0	100

Elements

C 0 – 100 H 0 – 200 N 0 – 0 O 0 – 12 Na 0 – 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C30 H25 O11	561.13914	18.5	0.00063	-0.00063	-1.12

Figure S38. HRMS (MALDI) spectrum of **7**

13. CD spectra

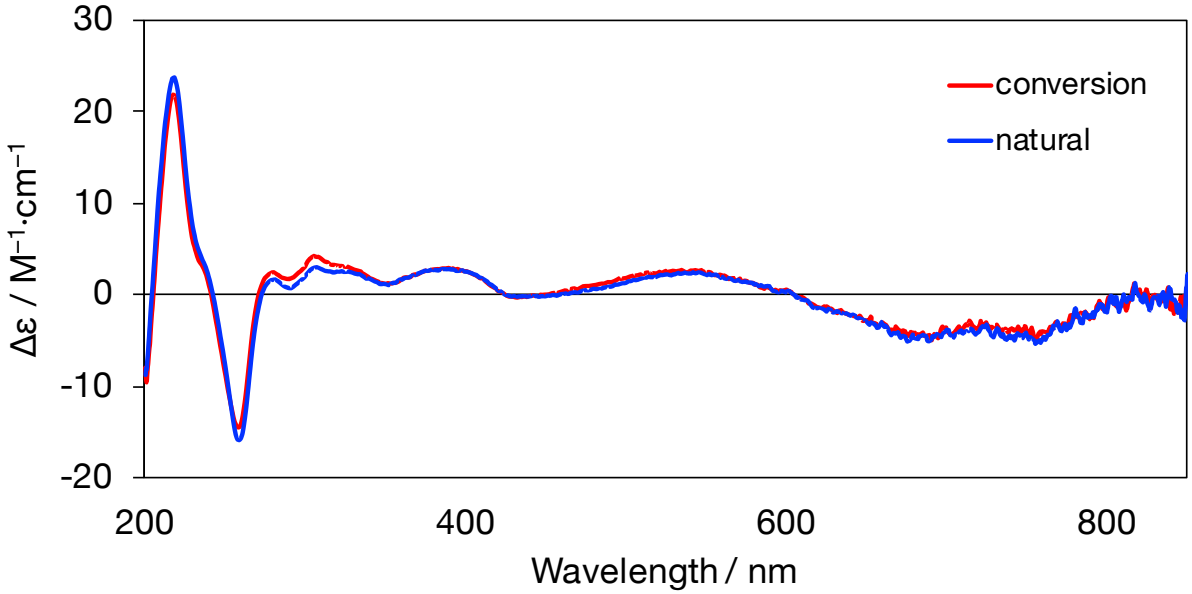


Figure S39. CD spectra of viridaphin A_2 (**4**) (2×10^{-5} M, MeOH)

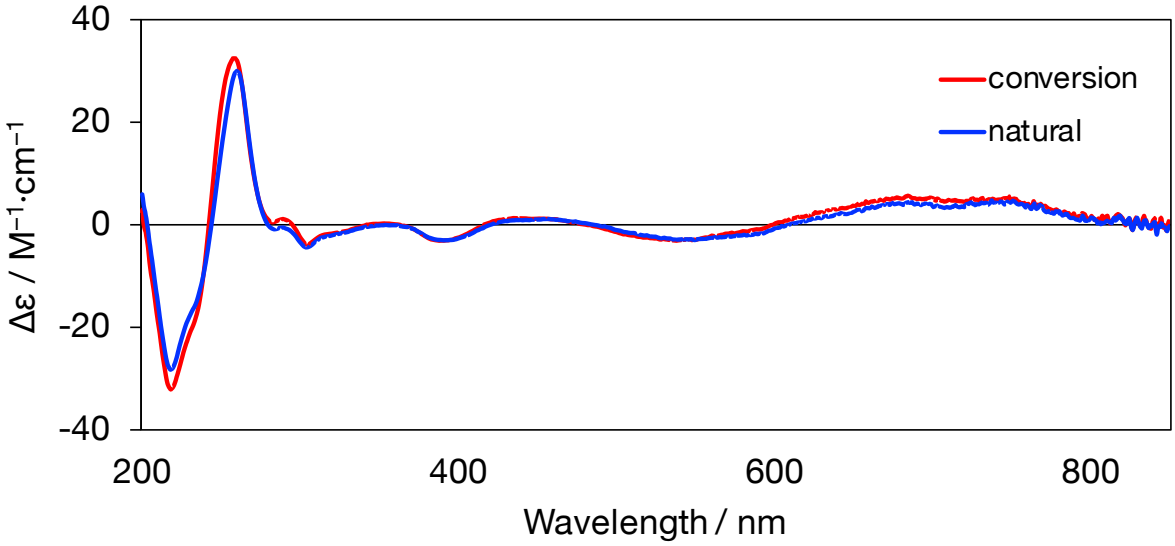


Figure S40. CD spectra of viridaphin A_1 (**3**) (2×10^{-5} M, MeOH)

14. HPLC spectra

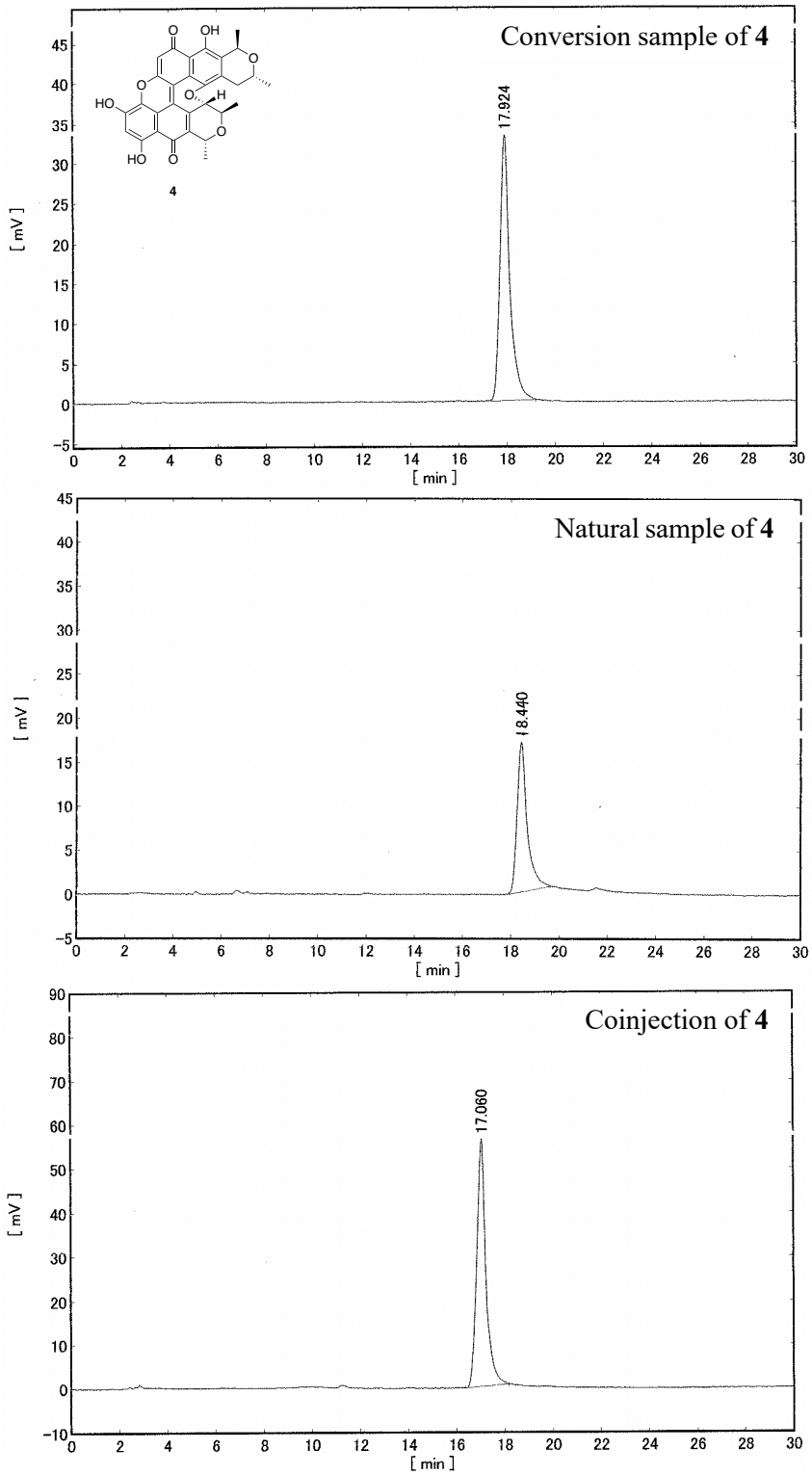


Figure S41. HPLC chromatogram of viridaphin A_2 (**4**)

(ODS, MeCN/H_2O/TFA = 75/25/0.1, flow rate: 1.0 mL/min, detector UV: 680 nm)

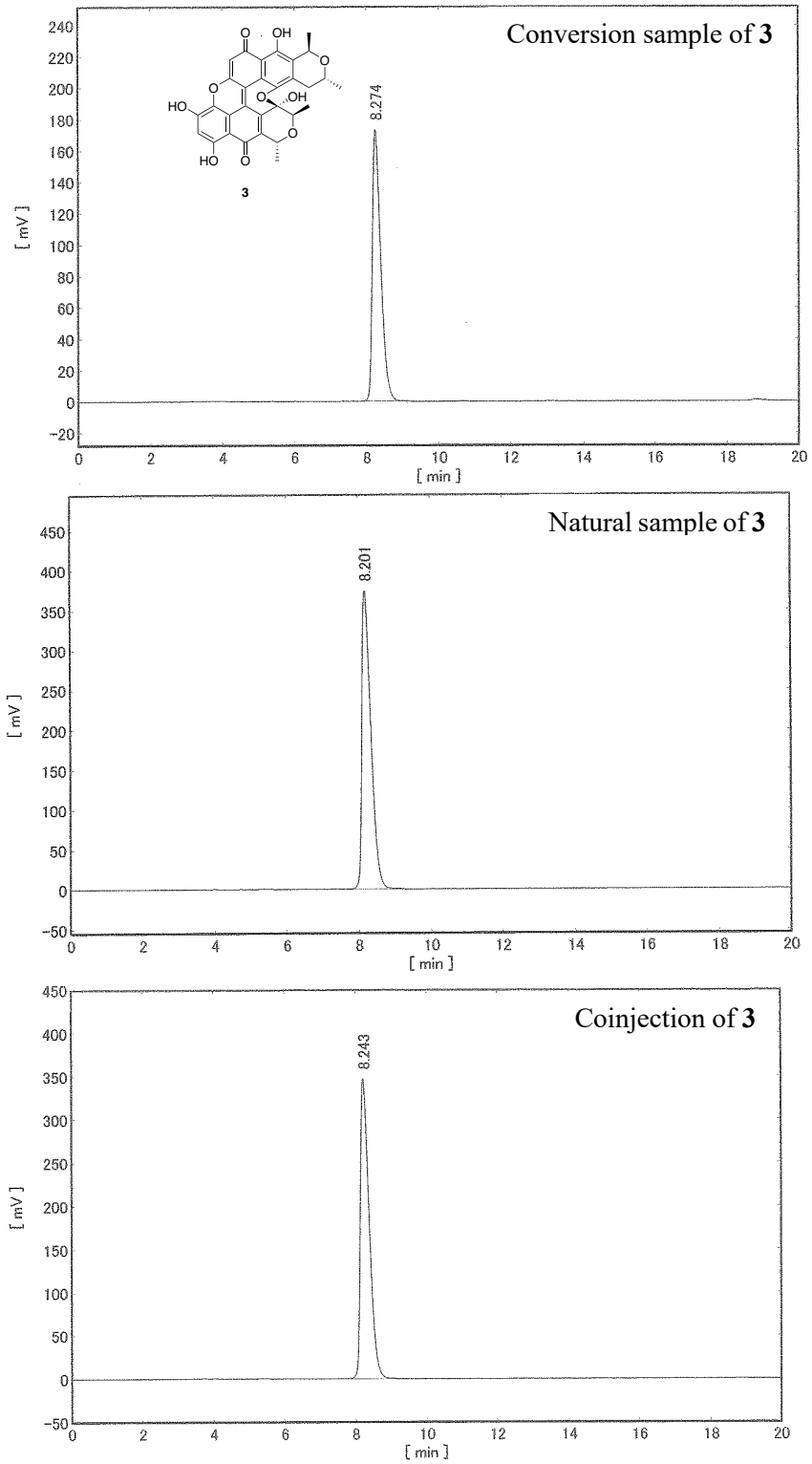


Figure S42. HPLC chromatogram of viridaphin A_1 (**3**)

(ODS, MeCN/H_2O/TFA = 80/20/0.1, flow rate: 1.0 mL/min, detector UV: 680 nm)

15. UV–Vis spectra

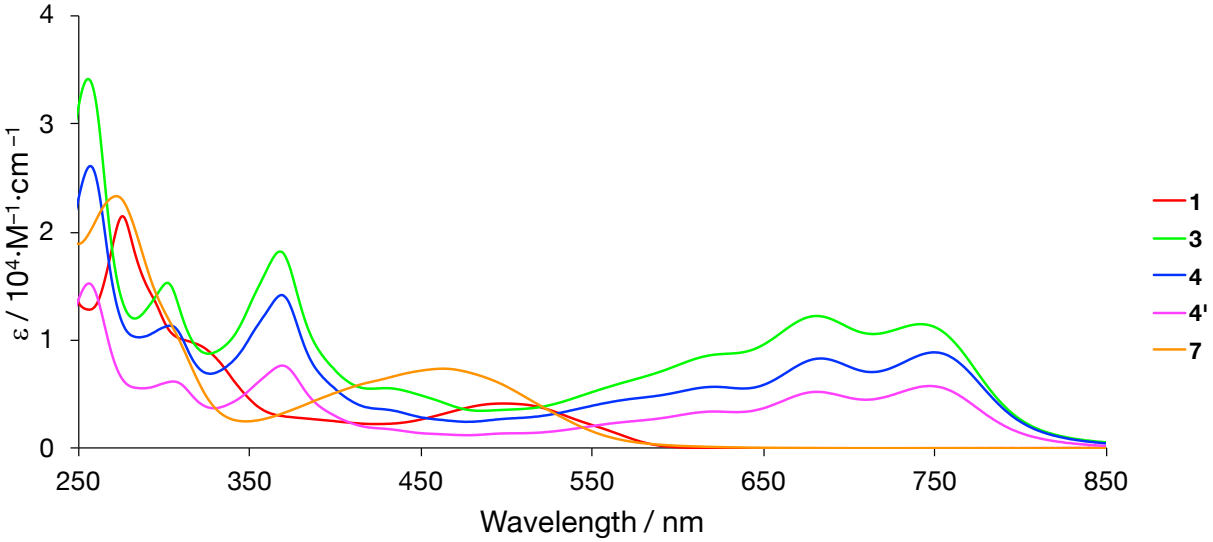
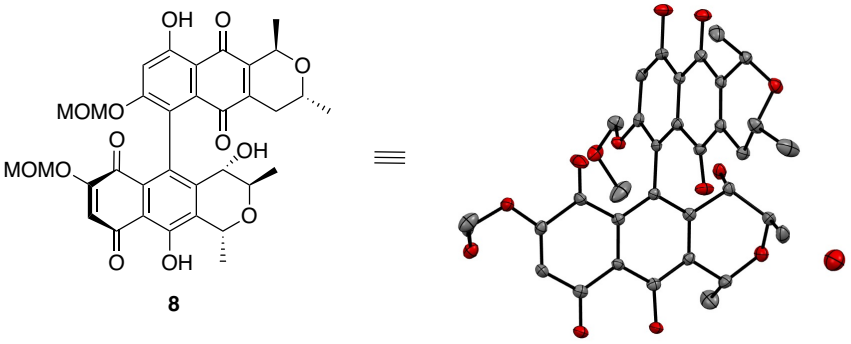


Figure S43. UV–Vis spectra (MeOH, 2.0×10^{-5} M)

	λ_{max} nm (log ε)
1	276 (4.33), 498 (3.42)
3	256 (4.53), 302 (4.19), 368 (4.26), 621 (3.94), 682 (4.09), 742 (4.06)
4	257 (4.42), 303 (4.06), 369 (4.15), 622 (3.76), 684 (3.92), 749 (3.95)
4'	257 (4.18), 306 (3.79), 369 (3.89), 622 (3.54), 681 (3.72), 747 (3.76)
7	273 (4.47), 466 (3.97)

16. Single crystal X-ray diffraction data of compound 8



8

CCDC 2104603

Identification code	CCDC 2104603
Moiety formula	$C_{34}H_{34}O_{13}$, H_2O
Formula weight	668.65
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Until cell dimensions	a = 10.2753 (13) Å α = 90°
	b = 15.0618 (19) Å β = 90°
	c = 19.8940 (3) Å γ = 90°
Volume	3078.9 (7) Å^3
Z	4
Density (calculated)	1.404 g/cm^3
Absorption coefficient	0.108 mm^{-1}
F (000)	1368.0
Crystal size	0.030 × 0.150 × 0.500 mm^3
Theta range for data collection	1.70 to 27.60°
Index ranges	–13<=h<=12, –13<=k<=19, –19<=l<=25
Reflections collected	18486
Independent reflections	5678 [R(int) = 0.0459]
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	7121 / 3 / 448
Goodness-of-fit on F^2	1.009
Final R indices [I>2σ (I)]	R_1= 0.0459, wR_2 = 0.0945
R indices (all data)	R_1 = 0.0639, wR_2 = 0.1030
Absolute structure parameter	–0.3 (6)
Largest diff. peak and hole	0.229 and –0.355 e.Å^{-3}

17. Antibacterial activity assay

Bacillus subtilis NBRC13719, *Staphylococcus aureus* NBRC100910, *Mycobacterium smegmatis* NBRC13167, *Escherichia coli* NBRC102203, *Pseudomonas aeruginosa* NBRC106052 and *Klebsiella pneumoniae* NBRC3512 were purchased from National institute of Technology and Evaluation, Biological Resource Center (Chiba, Japan). Methicillin-resistant *Staphylococcus aureus* subsp. *aureus* derived from ATCC 33592 (MRSA) was purchased from Microbiologics (Minnesota, USA). Each strain was maintained in YP medium plate (0.5% peptone (Becton, Dickinson and Co., NJ, USA), 0.3% yeast extract (Becton, Dickinson and Co.), 0.1% $MgSO_4 \cdot 7H_2O$ (Nacalai Tesque, Kyoto, Japan) and 2% agar (Nacalai Tesque) at 37 °C (*B. subtilis, S. aureus* and *E. coli*) or 30 °C (*M. smegmatis*, *P. aeruginosa* and *K. pneumonia*). Each strain was inoculated to YP medium and incubated for 12 h and adjusted the bacterial density of a 0.5 to 1 MacFarland standard. Adjusted microbial culture was further diluted 500 times and added to 96-well plate (100 μL/well). Stock solutions of samples were prepared at 10 mg/mL in DMSO and were added to dilute into each concentration in 96-well plates which contains microbial culture. After 24 h incubation, activity of compounds was determined by the turbidity of medium. For the culture and test of MRSA strain, Cation-Adjusted Mueller Hinton Broth (Becton, Dickinson and Co.) was applied instead of YP medium. All tests were carried out in triplicate. As positive controls, ampicillin (Nacalai Tesque) and oxacillin (Tokyo Chemical Industry Co. LTd, Tokyo, Japan) were applied.

18. Calculations

DFT calculations were performed with the Gaussian 16 program.[2] Geometry optimizations were carried out at the RB3LYP level of density functional theory with the 6-311G(d) basis set for compounds **4**, **4'**, **7**, and **7'**.

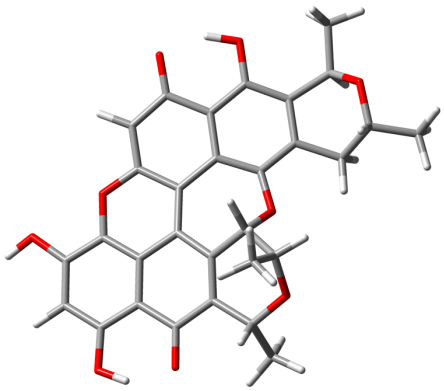


Table S4. Cartesian coordinates of the optimized structure for viridaphin A_2 (**4**)

Atom	X	Y	Z
C	2.9911972	-0.401161	-0.4916501
C	3.8622197	0.674506	-0.3816569
C	3.3420024	1.9197816	0.0297854
C	1.6276174	-0.2786005	-0.1741217
C	-0.80977	2.6256384	0.2337065
O	-2.1104919	3.0088877	0.1240392
C	-3.0964461	2.1084598	-0.0862088
C	-4.396363	2.6159932	-0.2952692
C	-5.2208485	0.3482473	-0.4652476
C	0.052429	3.6509191	0.4455098
H	-0.3240003	4.6608904	0.5446249
C	-5.4440202	1.7314947	-0.4864086
H	-6.4564089	2.0867411	-0.6501729
C	1.461252	3.4421369	0.5065069
C	1.9490314	2.0805583	0.2354124
C	1.0373128	0.9735852	0.1216519
C	-0.423796	1.2148851	0.1789151
C	-1.4785021	0.2852468	0.1475934

C	-1.3319294	-1.146965	0.3266874
C	-2.3175414	-2.0464684	0.0522942
C	-3.6855653	-1.5887817	-0.2246601
C	-3.9153973	-0.1583122	-0.2547937
C	-2.840914	0.7498034	-0.0633064
C	-2.0734225	-3.5440964	0.0895006
H	-2.7099746	-3.9825033	0.8717268
C	-0.044646	-3.0785199	1.3119618
C	4.8817251	-2.0106317	-0.1530369
H	4.6034733	-2.3092137	0.8662225
C	5.3170395	0.3485862	-0.7056659
H	5.3603522	0.1490942	-1.7890241
O	-4.6179298	-2.4076897	-0.3661543
O	2.2352604	4.4012229	0.7263878
O	-4.5353825	3.9596648	-0.2891483
H	-5.4597083	4.1949178	-0.4334947
O	-6.2731767	-0.4509285	-0.6510982
H	-5.9482188	-1.3838536	-0.5951898
O	4.1881267	2.9428829	0.1784329
H	3.6495349	3.7350337	0.4586635
O	5.7056706	-0.8477901	-0.0063555
O	-0.7062089	-3.8713719	0.3395114
C	6.3993712	1.3650838	-0.3777294
H	6.2664294	2.2874471	-0.9396527
H	6.4026397	1.6078657	0.6842895
H	7.3626639	0.9202463	-0.636202
C	5.7001602	-3.1269144	-0.7919178
H	5.1317277	-4.0616221	-0.8298276
H	5.9920432	-2.8591791	-1.8115624
H	6.610963	-3.302051	-0.2158217
C	3.589214	-1.7110121	-0.9288543
H	2.8830433	-2.5305514	-0.8117162

H	3.8230484	-1.6508678	-2.0003047
C	-0.6176572	-3.2445548	2.7228147
H	-0.6833163	-4.3070169	2.9651284
H	0.0321561	-2.7689952	3.4623741
H	-1.6148395	-2.8099628	2.8264693
H	0.9852706	-3.4433385	1.3018653
C	-0.0182175	-1.6204027	0.8595026
H	0.2894083	-0.9903646	1.7017658
O	0.9392956	-1.4549251	-0.19461
C	-2.3975729	-4.2253367	-1.2428568
H	-2.1120628	-5.2765482	-1.1702104
H	-3.4579786	-4.1550774	-1.4718397
H	-1.8153274	-3.7697241	-2.0469016

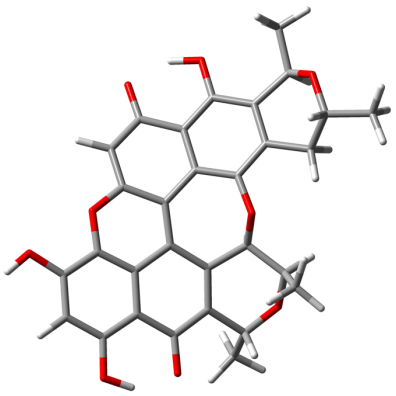


Table S5. Cartesian coordinates of the optimized structure for epi-viridaphin A_2 (**4'**)

Atom	X	Y	Z
C	-3.0432243	-0.550641	-0.1367884
C	-3.9278018	0.4493389	0.2630252
C	-3.3990035	1.6887587	0.6774398
C	-1.659464	-0.3377629	-0.1351357
C	0.6666408	2.5991281	0.0511728
O	1.8865243	3.0273729	-0.3648115
C	2.915408	2.158838	-0.4833939
C	4.1634967	2.7122136	-0.84646

C	5.1629441	0.5264218	-0.6318191
C	-0.1804048	3.5844945	0.443294
H	0.161193	4.6113904	0.4670892
C	5.2734188	1.8912296	-0.9262777
H	6.248371	2.2851242	-1.1947681
C	-1.5272689	3.3035304	0.8325469
C	-2.0038485	1.9303178	0.6034363
C	-1.096505	0.8983136	0.2140105
C	0.3451151	1.1732107	0.0820073
C	1.4212651	0.2696772	0.0307613
C	1.3639438	-1.1615901	0.3341871
C	2.4907737	-1.9165162	0.4913706
C	3.8103116	-1.4169816	0.0910501
C	3.9083179	-0.0242358	-0.2764788
C	2.7576987	0.8065951	-0.2291835
C	2.4545859	-3.3427952	1.0009392
H	2.9353376	-3.9827718	0.2496789
C	0.1519129	-3.3751302	0.3190394
C	-4.83572	-1.6160621	-1.5068014
H	-4.4320469	-1.2608482	-2.4641587
C	-5.3993274	0.049193	0.2277136
H	-5.5453985	-0.6923989	1.0307872
O	4.7952179	-2.1849556	0.059549
O	-2.2707041	4.2037548	1.2786467
O	4.189607	4.0405456	-1.0892713
H	5.0847073	4.314146	-1.3227776
O	6.2718732	-0.212497	-0.6951363
H	6.0244304	-1.1388	-0.4498047
O	-4.2364984	2.6340204	1.11618
H	-3.6918681	3.4421729	1.321212
O	-5.7042809	-0.5812326	-1.0296794
O	1.12996	-3.8139384	1.2471806

C	-6.4614709	1.1260234	0.3899027
H	-6.417926	1.5879003	1.3739927
H	-6.347727	1.9066647	-0.3620015
H	-7.4367072	0.6537063	0.254927
C	-5.6613471	-2.8735179	-1.7506513
H	-5.0586159	-3.657734	-2.2196228
H	-6.0652605	-3.2610654	-0.810869
H	-6.5016365	-2.6475644	-2.4100877
C	-3.6512646	-1.8594947	-0.5607936
H	-2.9146387	-2.4960942	-1.0483921
H	-4.00761	-2.403372	0.3250193
C	0.4079305	-3.8443537	-1.11284
H	0.5384086	-4.9289792	-1.1136521
H	-0.4406534	-3.5974921	-1.7515929
H	1.2969792	-3.3919823	-1.556344
H	-0.7806132	-3.8222583	0.6715963
C	3.2006322	-3.5062489	2.3264597
H	3.0725727	-4.5336412	2.6734849
H	4.2628067	-3.3036892	2.203118
H	2.7846963	-2.8367404	3.0829465
C	0.0300023	-1.8501037	0.4850794
H	-0.4018137	-1.648033	1.471851
O	-0.865883	-1.3816628	-0.525471

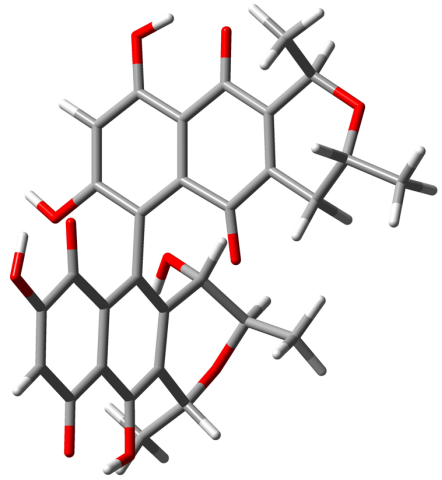


Table S6. Cartesian coordinates of the optimized structure for **7**

Atom	X	Y	Z
O	-4.6323246	-0.3616443	2.0502475
O	1.1779677	4.9971226	0.2077611
O	4.6138199	2.6568303	-1.9693353
O	-3.0400556	-0.1889658	4.0743862
C	-2.8706557	-0.2229723	-1.0518016
C	-3.9022361	-0.2525272	-0.184272
C	-3.6616227	-0.2655983	1.2785222
C	-2.0616455	-0.1108926	3.1699991
C	-2.2951925	-0.1647256	1.7750914
C	-0.7557881	0.0380018	3.6445667
C	-1.1912961	-0.0961856	0.8851542
C	0.1095861	0.0598336	1.3560581
O	4.8048013	0.1183063	-1.7900661
C	3.7091688	0.1692241	-1.0208249
C	1.336293	0.1291104	0.499596
C	1.8339649	3.893486	-0.1439116
C	2.9389576	3.8924317	-0.9150169
C	3.5999997	2.6448207	-1.2504226
C	3.0514762	1.3731431	-0.7252604
C	1.8726948	1.34533	0.0676392
H	0.4290364	4.6998873	0.762698

H	-3.890615	-0.2875289	3.5859891
H	-0.6032937	0.0852932	4.7184104
H	5.0128095	1.0452487	-2.0693507
H	3.36664	4.8079942	-1.305492
C	-1.4575769	-0.1974369	-0.5814585
O	-0.5552168	-0.2748028	-1.4030039
C	1.2302354	2.6277185	0.3985378
O	0.2279651	2.7727922	1.090927
O	-5.4149891	-0.7033197	-2.036179
C	-5.3384059	-0.342542	-0.6596372
H	-5.8093197	-1.1750365	-0.1302878
C	-4.5416124	0.0318525	-2.8990072
H	-4.7192693	1.1083637	-2.7635756
C	-3.0882652	-0.2714849	-2.5386439
H	-2.4061229	0.4254709	-3.0341056
H	-2.8100028	-1.2678663	-2.9044435
C	-6.1504523	0.9277426	-0.3605162
H	-7.1605604	0.8017764	-0.755666
H	-6.2133717	1.0952163	0.7145403
H	-5.7070725	1.813266	-0.8222532
C	-4.8989366	-0.3568943	-4.3228239
H	-5.9368662	-0.0970845	-4.5396717
H	-4.2546422	0.1573197	-5.0409274
H	-4.7825854	-1.4348886	-4.4610639
C	0.302242	0.1357691	2.7606902
C	2.02044	-1.0735377	0.1937356
C	3.2203159	-1.0565277	-0.5051853
O	3.3652809	-3.4985481	-0.2576607
C	1.4363632	-2.4165189	0.6068385
H	0.34798	-2.3681893	0.5861012
C	1.9328776	-3.5172766	-0.3310932
H	1.664709	-4.474532	0.1228946

C	4.0015468	-2.330943	-0.7851964
H	4.0994079	-2.4338085	-1.8749226
C	5.4017326	-2.3284953	-0.1676471
H	5.8596826	-3.3049501	-0.3375357
H	6.0281617	-1.55871	-0.6125824
H	5.3418506	-2.1623041	0.9110456
C	1.3844865	-3.4629302	-1.7541445
H	1.8704765	-4.2258036	-2.36692
H	0.3109851	-3.6700129	-1.7479194
H	1.5246871	-2.49084	-2.2300747
O	1.7690558	-2.7426052	1.9574277
H	2.7048252	-2.9872532	1.9531668
O	1.5723294	0.3260636	3.182851
H	1.6112279	0.283288	4.1457076

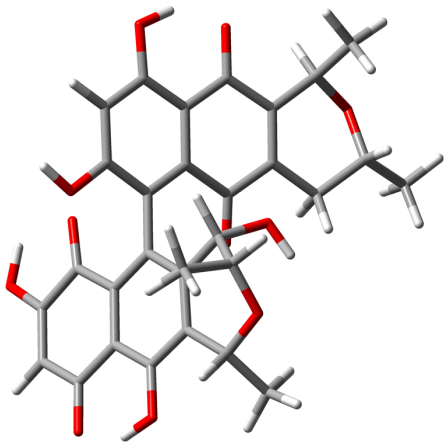


Table S7. Cartesian coordinates of the optimized structure for **7'**.

Atom	X	Y	Z
O	-4.6122515	-1.6997892	1.2313369
O	2.586888	-4.1780736	-2.4433297
O	5.3640296	-0.3978435	-2.3103492
O	-3.0342794	-2.9767649	2.8243767
C	-2.8208742	0.4166082	-1.0146599
C	-3.8607981	-0.1379597	-0.3609315
C	-3.6345016	-1.1415029	0.7036598

C	-2.0456621	-2.3447381	2.187347
C	-2.2671715	-1.4480364	1.115495
C	-0.7391885	-2.5868887	2.6220408
C	-1.1567905	-0.8343479	0.484023
C	0.1446317	-1.0692337	0.9179631
O	4.7436623	1.6523959	-0.9224142
C	3.6461767	0.9751285	-0.5574943
C	1.3520077	-0.3829047	0.3600189
C	2.9230413	-2.9578068	-2.0327608
C	4.0352318	-2.3116441	-2.4349397
C	4.330448	-0.9801769	-1.940472
C	3.3847499	-0.3316475	-1.0005111
C	2.2220599	-1.0024169	-0.5413355
H	1.7454983	-4.3923149	-1.9922969
H	-3.8826115	-2.6977687	2.4059683
H	-0.5930743	-3.2725095	3.4513423
H	5.2662738	1.065206	-1.5243656
H	4.7373786	-2.7562783	-3.129836
C	-1.4136445	0.037544	-0.7054654
O	-0.5178654	0.4164785	-1.4402308
C	1.9511309	-2.3540921	-1.0570291
O	0.9907047	-3.055942	-0.7606173
O	-5.3789214	0.8449736	-1.9890058
C	-5.2955069	0.1831528	-0.7293548
H	-5.8176202	-0.7650071	-0.8821603
C	-4.4560514	1.9247815	-2.1625197
H	-4.574439	2.6396448	-1.3356424
C	-3.0255928	1.3884856	-2.1418775
H	-2.3016553	2.2044139	-2.0575505
H	-2.7955009	0.8848029	-3.0889134
C	-6.0371462	0.9603893	0.3695544
H	-7.048816	1.1830662	0.0238988

H	-6.1020237	0.3641742	1.2797796
H	-5.5382746	1.9022655	0.609963
C	-4.8198677	2.6085543	-3.4688333
H	-5.8393836	2.9966653	-3.4249874
H	-4.1402908	3.4393984	-3.676731
H	-4.7623052	1.8971435	-4.2966537
C	0.3269733	-1.9590203	2.0053793
C	1.6475677	0.9261552	0.8114017
C	2.7442307	1.6244544	0.3190098
O	2.0871356	3.5651506	1.6827848
C	0.7761023	1.5931432	1.8659215
H	0.3739167	0.8412739	2.5459741
C	1.5921084	2.6256832	2.6449265
H	0.88847	3.2122183	3.2409453
C	3.036254	3.0565025	0.7384236
H	4.038522	3.0805236	1.1882195
C	3.0025177	4.0431797	-0.4308252
H	3.1266502	5.0544775	-0.038362
H	3.7984261	3.836673	-1.1427908
H	2.0403765	3.9902715	-0.9465188
C	2.6688724	2.0510771	3.5615073
H	3.2415127	2.8627052	4.0159847
H	2.2053682	1.4744678	4.3669961
H	3.3633591	1.3895367	3.0397696
O	-0.3705746	2.2222686	1.2888474
H	-0.0464388	3.0146762	0.8384544
O	1.6067803	-2.153758	2.4170724
H	1.626367	-2.7970294	3.1357724

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