Supporting Information for

Biocatalytic and chemical derivatization of fungal meroditerpenoid chevalone E

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Supplementary Methods

Isolation and Purification of Each Metabolite

Purification conditions for chevalone F (**9**):

The extract from *A. oryzae* NSAR1 with *cle1, cle3, cle5, cle6, cle7*, and *olcF'* was subjected to silica-gel column chromatography and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **9** were further purified by reverse-phase preparative HPLC (70% aqueous acetonitrile, 3.0 mL/min, t_R = 20 min), to yield 7.0 mg of a white solid: $[\alpha]^{20}_D$ -89.3 (*c* 0.1, $CHCl_3$); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S5 and Figures S3 and S4; HRMS found *m/z* 413.2675 $[M + H]^+$ (calcd 413.2686 for $C_{26}H_{37}O_4$). The NMR data were in good agreement with the reported data.[1]

Purification conditions for chevalone N (**10**):

The extract from *A. oryzae* NSAR1 with *cle1, cle2, cle3, cle5, cle6, cle7*, and *olcF'* was subjected to silica-gel column dichloromethane and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **10** were further purified by reverse-phase preparative HPLC (65% aqueous acetonitrile, 3.0 mL/min, t_R = 8.6 min), to yield 3.6 mg of a white solid: $[\alpha]^{20}_D$ -87.3 (c 0.1, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S6 and Figures S5-S10; HRMS found *m/z* 429.2618 $[M + H]^+$ (calcd 429.2636 for $C_{26}H_{37}O_5$).

Purification conditions for chevalone O (**11**):

The extract from *A. oryzae* NSAR1 with *cle1, cle3, cle4, cle5, cle6, cle7*, and *olcF'* was purified by reverse-phase preparative HPLC with a solvent system of water (solvent A) and acetonitrile (solvent B) at a flow rate of 3.0 mL/min. Separation was performed with solvent B/solvent A using a linear gradient from 10:90 to 100:0 for 30 min (t_R = 23.5 min), which yielded 5.1 mg of a white solid: $[\alpha]^{20}_D$ -78.7 (*c* 0.1, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S7 and FiguresS11-S16; HRMS found *m/z* 429.2647 $[M + H]^+$ (calcd 429.2636 for $C_{26}H_{37}O_5$).

Purification conditions for chevalone P (**12**):

The extract from *A. oryzae* NSAR1 with *cle1, cle3, cle4, cle5, cle6, cle7*, and *olcF'* was purified by reverse-phase preparative HPLC with a solvent system of water (solvent A) and acetonitrile (solvent B) at a flow rate of 3.0 mL/min. Separation was performed with solvent B/solvent A using a linear gradient from 10:90 to 100:0 for 30 min (t_R = 15.1 min), which yielded 14.1 mg of a white solid: $[\alpha]^{20}_D$ -106.3 (*c* 0.2, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S8 and Figures S17-S22; HRMS found *m/z* 445.2605 $[M + H]^+$ (calcd 445.2585 for $C_{26}H_{37}O_6$).

Purification conditions for chevalone Q (**13**):

The extract from *A. oryzae* NSAR1 with *cle1, cle2, cle3, cle4, cle5, cle6, cle7*, and *olcF'* was subjected to silica-gel column dichloromethane and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **13** were further purified by reverse-phase preparative HPLC (40% aqueous acetonitrile, 3.0 mL/min, t_R = 13.2 min), to yield 8.0 mg of a white solid: $[\alpha]^{20}_D$ -14.0 (c 0.05, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S9 and Figures S23-S28; HRMS found *m/z* 445.2583 $[M + H]^+$ (calcd 445.2585 for $C_{26}H_{37}O_6$).

Purification conditions for chevalone R (**14**):

The extract from *A. oryzae* NSAR1 with *cle1, cle2, cle3, cle4, cle5, cle6, cle7*, and *olcF'* was subjected to silica-gel column dichloromethane and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **14** were further purified by reverse-phase preparative HPLC (30% aqueous acetonitrile, 3.0 mL/min, t_R = 16.0 min), to yield 1.6 mg of a white solid: $[\alpha]^{20}_D$ -26.7 (c 0.05, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S10 and Figures S29-S34; HRMS found *m/z* 461.2515 $[M + H]^+$ (calcd 461.2534 for $C_{26}H_{37}O_7$).

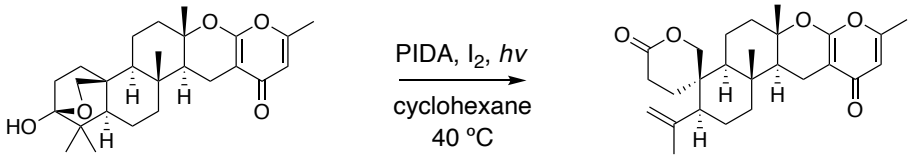
Purification conditions for chevalone S (**15**):

The *A. oryzae* NSAR1 transformant harboring *cle1+2+3+5+6+7* was cultivated in 200 ml of DPY medium at 30 °C and 200 rpm for 72 h, in the presence of 5 mg of **11**. After the incubation, the extract was subjected to silica-gel column dichloromethane and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **15** were further purified by reverse-phase preparative HPLC (60% aqueous acetonitrile, 3.0 mL/min, t_R = 7.2 min), to yield 1.5 mg of a white solid; for UV spectrum see Figure S1; HRMS found *m/z* 441.2275 $[M + H]^+$ (calcd 441.2277 for $C_{26}H_{33}O_6$); ^1H NMR (400 MHz, pyridine-d_5) δ_H 6.23 (brs, 1H), 5.01 (dd, J = 7.6, 3.5 Hz, 1H), 2.82 – 2.61 (m, 3H), 2.46 – 2.28 (m, 3H), 2.06 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H), 1.19 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 213.6 s, 180.2 s, 177.6 s, 163.3 s, 161.2 s, 112.9 d, 100.2 s, 83.3 s, 75.2 d, 56.9 d, 49.3 d, 48.6 d, 48.1 s, 47.5 s, 39.5 t, 34.7 t, 34.4 t, 34.0 s, 33.5 t, 27.3 q, 25.3 q, 21.7 q, 20.2 t, 19.3 q, 16.6 q, 16.5 t; for NMR data see Figures S35 and S36.

Purification conditions for chevalone T (**16**):

The extract from *A. oryzae* NSAR1 with *cle1, cle2, cle3, cle4, cle5, cle6, cle7*, and *olcF'* was subjected to silica-gel column dichloromethane and eluted stepwise using a dichloromethane: acetone gradient (100:0 to 50:50). Fractions that contained **16** were further purified by reverse-phase preparative HPLC (45% aqueous acetonitrile, 3.0 mL/min, t_R = 6.0 min), to yield 2.3 mg of a white solid: $[\alpha]^{20}_D$ -72.0 (c 0.05, CH_3OH); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S11 and Figures S37-S42; HRMS found *m/z* 457.2227 $[M + H]^+$ (calcd 457.2221 for $C_{26}H_{33}O_7$).

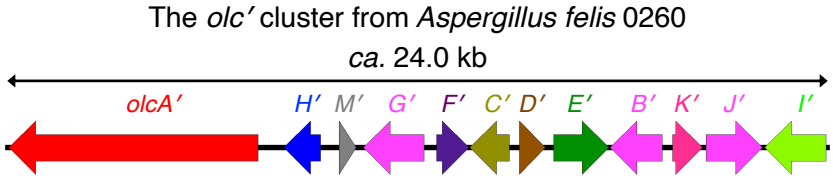
Chemical synthesis of 17 from 10:



10 **17**
42%, 66% brsm

According to the literature,[2] to a suspension of **10** (10 mg, 0.02 mmol), (diacetoxyiodo)benzene (PIDA) (12 mg, 0.03 mmol), and I_2 (6 mg, 0.02 mmol) in cyclohexane (5 mL) was irradiated with a tungsten-filament lamp (250 W) at 40 °C under an argon atmosphere for 8 h. The reaction was diluted with dichloromethane (15 mL) and quenched by saturated aqueous solution of $Na_2S_2O_3$ (0.8 mL). The organic layer was washed with brine (10 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by preparative HPLC (65% aqueous acetonitrile, 3.0 mL/min, t_R = 10.5 min), to give 4.2 mg of **17** (42% yields, 66% brsm.) with a white solid: $[\alpha]^{18}_D$ -132.3 (*c* 0.1, $CHCl_3$); for UV spectrum see Figure S1; for ^1H and ^{13}C NMR data see Table S12 and Figures S43-S48; HRMS found *m/z* 427.2464 $[M + H]^+$ (calcd 427.2479 for $C_{26}H_{35}O_5$).

Table S1. Annotation of each protein encoded by the *olc′* cluster.



Gene	Amino acids (base pairs)	Protein homologue, origin	Similarity/identity (%)	Proposed function
olcA′	2442 (7329)	OlcA, *Penicillium canescens*	57/42	polyketide synthase
olcB′	1534 (493)	OlcB, *Penicillium canescens*	75/57	cytochrome P450 monooxygenase
olcC′	1167 (335)	OlcC, *Penicillium canescens*	82/67	geranylgeranyl pyrophosphate synthase
olcD′	768 (236)	OlcD, *Penicillium canescens*	69/55	terpene cyclase
olcE′	1626 (501)	OlcE, *Penicillium canescens*	64/51	FAD-dependent monooxygenase
olcF′	948 (257)	OlcF, *Penicillium canescens*	79/65	short-chain dehydrogenase/reductase
olcG′	1781 (521)	OlcG, *Penicillium canescens*	71/55	cytochrome P450 monooxygenase
olcH′	1069 (321)	OlcH, *Penicillium canescens*	79/63	prenyltransferase
olcI′	1812 (572)	OlcI, *Penicillium canescens*	68/54	CoA ligase
olcJ′	1652 (511)	OlcJ, *Penicillium canescens*	79/63	cytochrome P450 monooxygenase
olcK′	876 (291)	OlcK, *Penicillium canescens*	75/59	Fe(II)/αKG-dependent dioxygenase
olcM′	504 (167)	LnaC, *Aspergillus flavus*	47/23	truncated cytochrome P450 monooxygenase

Table S2. Primers used in this study.

Primer	Sequence (5′ to 3′)
InF-adeA-SpeI-F	TTACCTAGAGGATCTACTAGCGACTCCAATCTTCAAGAGC
InF-adeA-SpeI-R	TCCCCAATCCATATGACTAGGTAAGATACATGAGCTTCGGTG
olcF′-F	CCCACAGCAAGCTCCGAATTATGGGCTGTCTCCAGAATCGCG
olcF′-R	CCGGGTACCGAGCTCGAATTTTATATAGTAGACCAGCCATCGT
olcB′-F	CCCACAGCAAGCTCCGAATTATGATGGCCCTTGTGCTCTG
olcB′-R	CCGGGTACCGAGCTCGAATTCTAATTACCTTTGCCCTTCCC
InF-PamyB-F	TGCCTGCAGGTCGACTCTAGACGACTCCAATCTTCAAGAGC
InF-TamyB-R	ATGACTAGTAGATCCTCTAGGTAAGATACATGAGCTTCGGTG
InF-linker-F1	TTGCTCGCGAGCGCGTTCCACTGCATCATCAGTCTAGA
InF-linker-R1	TGGAACGCGCTCGCGAGCAAGTACCATACAGTACCGCG
InF-pBARI-F	TGATTACGCCAAGCTTCGACTCCAATCTTCAAGAGC
InF-pBARI-R	GCAGGCATGCAAGCTTGTAAGATACATGAGCTTCG
pET28a-olcF′-NcoI-F	AGAAGGAGATATACCATGGGCTGTCTCCAGAATCGC
pET28a-olcF′-XhoI-R	GGTGGTGGTGCTCGTATATAGTAGACCAGCCATCGT

Table S3. Plasmids constructed in this study and PCR conditions for the amplification of the inserts for the plasmid constructions.

Plasmid	Vector	Insert	Primer 1	Primer 2	PCR Template
pTAex3-*olcF′*	pTAex3 digested with *Eco*RI	*olcF′*	olcF′-F	olcF′-R	*A. felis* gDNA
pTAex3-*olcB′*	pTAex3 digested with *Eco*RI	*olcB′*	olcB′-F	olcB′-R	*A. felis* gDNA
pET28a-*olcF′*	pET28a digested with *Nco*I and *Xho*I	*olcF′*	pET28a-*olcF′*-NcoI-F	pET28a-olcF′-XhoI-R	*A. felis* cDNA
pAdeA-*cle1+5+6*	pAdeA-*cle5+6* digested with *Spe*I	PamyB-*cle1*-TamyB	InF-adeA-SpeI-F	InF-adeA-SpeI-R	pTAex3-*cle1*
pBARI-*cle2+olcF′*	pBARI digested with *Hin*dIII	*PamyB-cle2-TamyB*	InF-pBARI-F	InF-linker-R1	pTAex3-*cle2*
		PamyB-olcF′-TamyB	InF-linker-F1	InF-pBARI-R	pTAex3-*olcF′*
pBARI-*cle4+olcF′*	pBARI digested with *Hin*dIII	*PamyB-cle4-TamyB*	InF-pBARI-F	InF-linker-R1	pTAex3-*cle4*
		PamyB-olcF′-TamyB	InF-linker-F1	InF-pBARI-R	pTAex3-*olcF′*

Table S4. *Aspergillus oryzae* NSAR1 transformants constructed in this study.

Strain	**Plasmids used for transformation**
A. oryzae / *cle1+3+5+6+7*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*
A. oryzae / *cle1+3+5+6+7+olcF′*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*; pTAex3-*olcF′*
A. oryzae / *cle1+2+3+5+6+7+olcF′*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*; pBARI-*cle2+olcF′*
A. oryzae / *cle1+3+4+5+6+7+olcF′*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*; pBARI-*cle4+olcF′*
A. oryzae / *cle1+2+3+4+5+6+7+olcF′*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*; pBARI-*cle2+olcF′*; pTAex3-*cle4*
A. oryzae / *cle1+2+3+5+6+7+olcB′+F′*	pAdeA-*cle1+5+6*; pUSA-*cle3+7*; pBARI-*cle2+olcF′;* pTAex3-*olcB′*

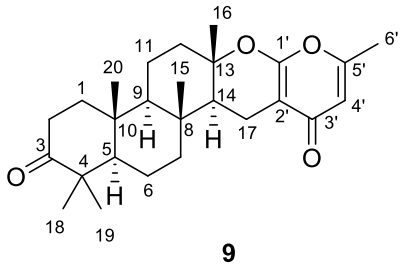


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Table S5. NMR data for chevalone F (**9**) (^{1}H NMR:400 MHz, ^{13}C NMR: 100 MHz, δ in ppm, recorded in $CDCl_3$).

	^{13}C	^{1}H		
position	δ (ppm)	δ (ppm)	Multiplicity	intensity
1	39.2 t	1.48	overlap	1H
		1.97	overlap	1H
2	34.0 t	2.50	m	2H
3	217.5 s			
4	47.4 s			
5	54.8 d	1.43α	overlap	1H
6	19.2 t	1.39	overlap	1H
		1.57	overlap	1H
7	40.3 t	1.08	overlap	1H
		1.95	overlap	1H
8	37.4 s			
9	59.7 d	0.95	overlap	1H
10	36.9 s			
11	19.3 t	1.42	overlap	1H
		1.73	overlap	1H
12	40.2 t	1.71	overlap	1H
		2.12	d (*J* = 6.3 Hz)	1H
13	84.2 s			
14	52.3 d	1.51α	overlap	1H
15	15.5 t	2.15	dd (*J* = 7.0, 3.4 Hz)	1H
		2.55	m	1H
16	20.7 q	1.30β	d (*J* = 0.8 Hz)	3H
17	15.8 q	0.92β	s	3H
18	16.3 q	0.93β	s	3H
19	26.8 q	1.01α	d (*J* = 2.2 Hz)	3H
20	21.0 q	1.04β	s	3H
1′	180.7 s			
2′	98.5 s			
3′	162.7 s			
4′	112.0 d	5.99	d (*J* = 1.0 Hz)	1H
5′	160.7 s			
6′	19.4 q	2.20	d (*J* = 0.9 Hz Hz)	3H

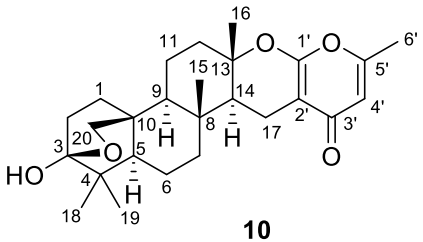

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Table S6. NMR data for chevalone N (**10**) (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in pyridine-d_5).

	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	35.7 t	1.09α	dd (*J* = 10.3, 7.6 Hz)	1H	2, 3, 5, 9, 10, 20	H-1β, H-2α	H-1β, H-2α, H-9α
		2.22β	dt (*J* = 12.5, 4.2 Hz)	1H	2, 3, 5, 10, 20	H-1α, H-2α, H-2β	H-1α, H-11β, H-20a, H-20b
2	30.9 t	2.11α	dd (*J* = 12.5, 3.3 Hz)	1H	1, 3, 4, 10	H-1α, H-1β	H-2β
		2.37β	td (*J* = 12.5, 5.5 Hz)	1H	1, 3, 4, 10	H-1α, H-1β	H-2α, H-19α
3	98.5 s						
4	41.3 s						
5	49.9 d	1.27α	dd (*J* = 8.9, 5.4 Hz)	1H	1, 3, 4, 6, 7, 9, 10, 18, 19, 20	H-6α, H-6β	H-6α, H-7α, H-9α, H$_3$-19α
6	20.1 t	1.12α	overlap	1H	4, 5, 7, 8, 10	H-5α, H-6β, H-7α, H-7β	H-5α, H-6β, H-7β
		1.03β	overlap	1H	4, 5, 7, 10	H-5α, H-6α, H-7α, H-7β	H-6α, H-7α, H$_3$-15β
7	38.6 t	1.69α	overlap	1H	6, 9, 14	H-6α, H-6β, H-7β	H-6α, H-7α
		0.92β	dd (*J* = 5.5, 3.5 Hz)	1H	5, 6, 8, 9, 15	H-6α, H-6β, H-7α	H-6α, H-7β, H$_3$-15β
8	36.9 s						
9	54.8 d	1.01α	overlap	1H	1, 5, 8, 10, 11, 12, 14, 15, 20	H-11β	H-1α, H-5α, H-7α, H-11α, H-12α, H-14α
10	36.1 s						
11	19.9 t	1.70α	overlap	1H	8, 9, 10, 12, 13	H-11β, H-12β	H-9α, H-11β, H-12α
		1.48β	m	1H	8, 9, 12, 13	H-9α, H-11α, H-12α, H-12β	H-11α, H$_3$-15β
12	40.9 t	2.02α	d (*J* = 3.8 Hz)	1H	9, 11, 13, 14, 16	H-11β, H-12β	H-9α, H-11α, H-14α
		1.67β	overlap	1H	9, 11, 13, 14, 16	H-11α, H-11β, H-12α	H-11β, H$_3$-16β
13	84.2 s						
14	52.2 d	1.45α	dd (*J* = 12.7, 4.9 Hz)	1H	7, 8, 9, 12, 13, 15, 16, 17, 2′	H-17α, H-17β	H-9α, H-12α, H-17α
15	14.9 q	0.69β	s	3H	7, 8, 9, 14		H-7β, H$_3$-16β, H-17β, H-20a, H-20b
16	21.0 q	1.18β	s	3H	12, 13, 14		H-11β, H-12β, H$_3$-15β, H-17β
17	16.6 t	2.79α	dd (*J* = 16.3, 4.9 Hz)	1H	8, 13, 14, 1′, 2′, 3′	H-14α, H-17β	H-14α, H-17β
		2.27β	dd (*J* = 16.3, 12.7 Hz)	1H	8, 13, 14, 1′, 2′, 3′	H-14α, H-17α	H$_3$-15β, H$_3$-16β, H-17α
18	19.9 q	1.32β	s	3H	3, 4, 5, 19		H-2β, H-6β, H$_3$-19α, H-20a, H-20b
19	27.9 q	1.25α	s	3H	3, 4, 5, 18		H-5α, H-6α, H$_3$-18β
20	67.9 t	4.26a	dd (*J* = 8.7, 2.8 Hz)	1H	1, 3, 5, 9, 10		H-1β, H-6β, H-11β, H$_3$-15β, H$_3$-18β
		3.83b	dd (*J* = 8.7, 2.0 Hz)	1H	1, 3, 5, 9, 10		H-1β, H-6β, H-11β, H$_3$-15β, H$_3$-18β
1′	163.1 s						
2′	99.1 s						
3′	180.3 s						
4′	112.7 d	6.20	s	1H	2′, 3′, 5′, 6′		H$_3$-6′
5′	161.1 s						
6′	19.3 q	2.04	s	3H	4′, 5′		H-4′

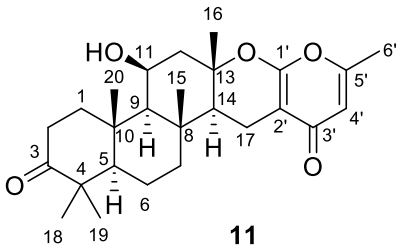

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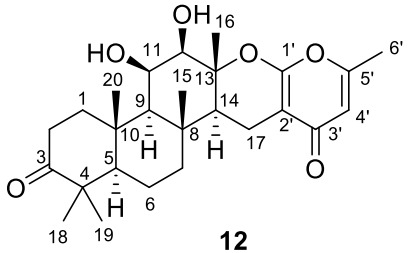
Table S7. NMR data for chevalone O (**11**) (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in $CDCl_3$).

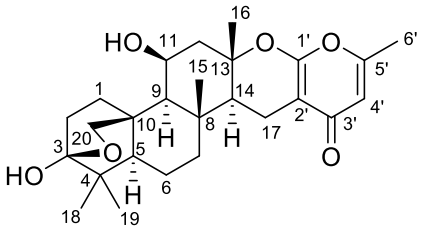
	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	39.1 t	1.49α	m	1H	2, 3, 5, 10, 20	H-1β, H-2α	H-1β, H-2α, H-9α
		2.13β	m	1H	2, 3, 5, 9, 10	H-1α, H-2β	H-1α, H-2β, H_3-20β
2	34.1 t	2.44α	ddd (J = 15.9, 7.0, 3.6 Hz)	1H	1, 3, 4, 10	H-1α	H-1β
		2.66β	m	1H	1, 3, 4, 10	H-1β	H-1α, H-2β
3	217.3 s						
4	47.5 s						
5	56.1 d	1.33α	dd (J = 12.4, 2.5 Hz)	1H	1, 4, 7, 8, 9, 10, 18, 19, 20	H-6β	H-6α, H-9α, H_3-19α
6	19.6 t	1.71α	m	1H	4, 5, 7, 8, 10	H-6β	H-5α, H-6β, H-7β
		1.57β	m	1H	4, 5, 7, 10	H-5α, H-6α, H-7α	H-6α
7	42.6 t	1.94α	dd (J = 5.4, 3.0 Hz)	1H	5, 6, 8, 14, 15	H-6β, H-7β	H-5α, H-6α, H-6β, H-7β
		1.05β	overlap	1H	5, 6, 8, 9, 15	H-6α, H-7α	H-6α, H-6β, H-7α, H_3-15β
8	37.7 s						
9	60.3 d	0.99α	s	1H	1, 5, 8, 10, 11, 12, 14, 15, 20	H-11α	H-1α, H-5α, H-14α
10	37.9 s						
11	67.6 d	4.66α	s	1H	8, 9, 12, 13	H-9α, H-11β	H-9α, H-12α, H-12β
12	48.5 t	2.26α	dd (J = 8.3, 5.6 Hz)	1H	9, 13, 16	H-12β	H-9α, H-11α, H-14α
		1.91β	overlap	1H	9, 13, 14, 16	H-11β	H-12α, H_3-16β
13	84.1 s						
14	53.0 d	1.53α	m	1H	7, 8, 9, 12, 15, 16, 17, 2′	H-17α, H-17β	H-9α, H-12α, H-17α
15	17.1 q	1.30β	s	3H	7, 8, 9, 14		H_3-16β, H-17β, H_3-20β
16	22.0 q	1.54β	s	3H	12, 13, 14		H-12β, H_3-15β, H-17β
17	15.5 t	2.61β	dd (J = 16.2, 4.6 Hz)	1H	8, 13, 14, 1′, 2′, 3′	H-14α, H-17α	H-7α, H-17β
		2.29α	overlap	1H	8, 13, 14, 1′, 2′	H-14α, H-17β	H-7β, H-14α, H-17α
18	21.3 q	1.08β	s	3H	3, 4, 5, 19		H-2β, H-6β, H_3-19α
19	26.6 q	1.07α	s	3H	3, 4, 5, 18		H-3α, H-5α, H_3-18β
20	17.3 q	1.37β	s	3H	1, 5, 9, 10		
1′	162.4 s						
2′	98.8 s						
3′	180.7 s						
4′	112.1 d	5.99	s	1H	2′, 3′, 5′, 6′		H_3-6′
5′	160.7 s						
6′	19.4 q	2.21	s	3H	4′, 5′		



12

Table S8. NMR data for chevalone P (**12**) (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in pyridine-d_5).

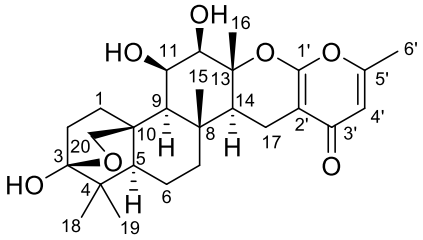
	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	39.3 t	1.36α	m	1H	2, 3, 5, 10, 20	H-1β, H-2α	H-1β, H-2α, H-9α
		2.07β	m	1H	2, 3, 5, 9, 10, 20	H-1α, H-1β, H-2β	H-1α, H-2α, H_3-20β
2	34.7 t	2.40α	ddd (J = 15.5, 7.0, 3.6 Hz)	1H	1, 3, 4, 10	H-1α, H-2β	H-1α, H-1β, H-2β
		2.65β	ddd (J = 15.5, 10.6, 7.5 Hz)	1H	1, 3, 10	H-1α, H-1β, H-2α,	H-1β, H-2α, H_3-18β
3	216.5 s						
4	47.8 s						
5	56.3 d	1.31α	dd (J = 12.4, 2.4 Hz),	1H	1, 4, 6, 7, 9, 10, 18, 19, 20	H_2-6	H-6α, H-6β, H-9α, H_3-19α
6	20.1 t	1.61α	dd (J = 12.4, 5.0 Hz)	1H			H-5α, H-6β, H-7α
		1.42β	overlap	1H	5, 8	H-5α, H-7α	H-5α, H-7β
7	42.9 t	1.71β	dt (J = 12.6, 3.3 Hz)	1H	5, 8, 9, 14	H_2-6, H-7α	H-6α, H-6β, H-7α, H_3-15β
		0.96α	td (J = 12.6, 3.7 Hz)	1H	5, 6, 8, 14, 15	H_2-6, H-7β	H-6α, H-6β, H-7β
8	38.3 s						
9	59.4 d	1.02α	s	1H	1, 5, 7, 8, 10, 11, 12, 14, 15, 20	H_2-11	H-1α, H-7α, H_2-11, H-14α
10	38.4 s						
11	71.8 d	4.73α	d (J = 1.2 Hz)	1H	8, 9, 12, 13	H-9α, H-12α	H-1α, H-9α, H-12α
12	78.4 d	4.06α	d (J = 3.4 Hz)	1H	13, 14, 16	H-11α	H-9α, H-11α, H-14α,
13	89.1 s						
14	51.9 d	1.64α	dd (J = 12.7, 4.8 Hz)	1H	7, 8, 9, 12, 13, 16, 2′	H-17α, H-17β	H-9α, H-12α, H-17α, H-17β
15	17.5 q	1.44β	s	3H	7, 8, 9, 14		H-7β, H_3-16β, H-17β, H_3-20β
16	16.4 q	1.80β	s	3H	12, 13, 14		H_3-15β, H-17β
17	16.3 t	2.90α	dd (J = 16.2, 4.8 Hz)	1H	13, 14, 1′, 2′, 3′	H-14α, H-17β	H-14α, H-17α
		2.58β	dd (J = 16.2, 12.7 Hz)	1H	8, 13, 14, 1′, 2′	H-14α, H-17β	H_3-15β, H_3-16β, H-17α
18	21.7 q	1.09β	s	3H	3, 4, 5, 19		H-2β, H_2-6, H_3-19α
19	27.0 q	1.15α	s	3H	3, 4, 5, 18		H-2α, H-5α, H_3-18β
20	18.0 t	1.59β	s	3H	1, 5, 9, 10		H-1β, H_3-15β, H_3-18β
1′	163.2 s						
2′	99.1 s						
3′	180.2 s						
4′	112.8 d	6.22	s	1H	2′, 3′, 5′, 6′		H_3-6′
5′	161.1 s						
6′	19.3 q	2.04	s	3H	4′, 5′		
11-OH		6.08		1H			
12-OH		5.02		1H			



13

Table S9. NMR data for chevalone Q (**13**) (^{1}H NMR:500 MHz, ^{13}C NMR: 125 MHz, δ in ppm, recorded in pyridine-d_5).

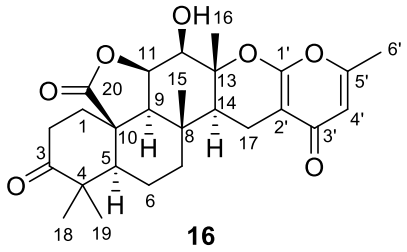
	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	35.6 t	1.22α	d (*J* = 7.4 Hz)	1H	3, 5, 9, 20	H-1β, H-2α	H-2α, H-5α
		2.48β	dd (*J* = 7.4, 5.2 Hz)	1H	2, 5, 10	H-1α, H-2β	H_2-20β
2	31.1 t	2.13α	m	1H	4, 10	H-1α, H-1β, H-2α	H-2β
		2.41β	m	1H	1	H-1β, H-2β	H-1β, H-2α
3	98.0 s						
4	41.3 s						
5	51.2 d	1.29α	d (*J* = 4.1 Hz)	1H	1, 3, 4, 7, 9, 10, 18, 19, 20	H-6β	H-1α, H-6α, H-9α, H_3-19α
6	20.6 t	1.56β	m	1H	5, 8, 10	H-5α	H-5α
		1.90α	overlap	1H	4, 5, 8, 10	H-7α	H-7β
7	41.5 t	1.02β	t (*J* = 12.8 Hz)	1H	8, 14, 15	H-7α, H-12β	H-7α, H_3-15β
		1.74α	d (*J* = 6.7 Hz)	1H	5, 6, 8, 9, 14, 15	H-6β, H-7β	H-14α, H-9α
8	37.4 s						
9	57.0 d	1.17α	s	1H	1, 5, 8, 10, 11, 12, 14, 15, 20	H-11α	H-12α, H-14α
10	37.4 s						
11	66.1 d	4.8α	br s	1H	13	H-9α, H-12α, H-12β	H-9α, H-12α, H-12β
12	48.5 t	2.02β	s	1H	13, 14, 16	H-7β, H-11α	H_3-16β
		2.45α	m	1H	9, 11, 13, 14, 16	H-11α	H-14α
13	84.8 s						
14	52.8 d	1.64α	dd (*J* = 12.6, 4.8 Hz)	1H	7, 8, 9, 12, 13, 15, 16	H-17α	H-7α, H-9α, H-12α, H-17α
15	16.7 q	1.32β	s	3H	7, 8, 9, 14		H_3-16β, H-20b
16	22.6 q	1.68β	s	3H	12, 13, 14		H_3-15β
17	16.7 t	2.52β	overlap	1H	8, 13, 14, 1′, 2′		H_3-15β, H_3-16β
		2.91α	dd (*J* = 16.4, 4.8 Hz)	1H	13, 14, 1′, 2′, 3′	H-14α, H-17β	H-14α
18	19.9 q	1.37β	s	3H	3, 4, 5, 19		H-20a
19	28.1 q	1.27α	s	3H	3, 4, 5, 18		H-5α
20	69.4 t	4.67a	dd (*J* = 9.4, 2.9 Hz)	1H	1, 5, 10	H-20a	H_3-17β
		5.01b	dd (*J* = 9.4, 1.8 Hz)	1H	1, 3, 5, 10	H-20b	H-20a
1′	163.0 s						
2′	99.4 s						
3′	180.3 s						
4′	112.7 d	6.22	s	1H	2′, 5′, 6′		H_3-6′
5′	161.1 s						
6′	19.3 q	2.05	s	3H	4′, 5′		H-4′



14

Table S10. NMR data for chevalone R (**14**) (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in pyridine-d_5).

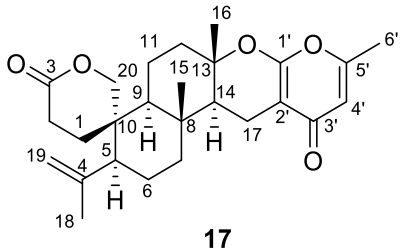
	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	35.5 t	2.45β	m	1H	2, 3, 5, 10, 20	H-1α	H-1α, H_2-20
		1.17α	m	1H	3, 10, 20	H-1β, H-2α	H-1β, H-2α
2	31.1 t	2.38β	td (J = 12.1, 5.4 Hz)	1H	3, 10	H-1β	H-1α
		2.09α	m	1H	1, 3, 10	H-1β	H-1α, H-1β
3	98.1 s						
4	41.5 s						
5	51.1 d	1.31α	dd (J = 13.0, 4.4 Hz)	1H	3, 4, 7, 10, 18, 19, 20	H_2-6	H-1α, H-7α, H-9α
6	20.7 t	1.90α	dd (J = 13.0, 3.3 Hz)	2H	4, 5, 7, 8	H-5α, H-7α	H-5α, H-6β
		1.57β	dd (J = 14.3, 4.4 Hz)				H-5α, H-6α, H-7α, H_3-15β
7	41.2 t	1.76α	d (J = 12.8 Hz)	1H	5, 8, 9, 14, 15	H_2-6, H-7β	H-5α, H-6α, H-7β, H-14α
		1.01β	td (J = 12.0, 4.5 Hz)	1H	5, 8, 9, 14, 15	H-7α	H-7α, H_3-15β, H-17β
8	37.5 s						
9	55.8 d	1.24α	s	1H	1, 5, 7, 8, 10, 11, 12, 14, 15, 20	H-11α	H-5α, H-11α, H-12α, H-14α
10	37.3 s						
11	71.1 d	4.80α	s	1H	8, 9, 12, 13	H-9α, H-12α	H-1α, H-12α
12	78.2 d	4.07α	t (J = 4.5 Hz)	1H	13, 16	H-11α	H-9α, H-11α, H-14α
13	89.0 s						
14	51.5 d	1.63α	dd (J = 12.5, 4.8 Hz)	1H	8, 9, 12, 13, 15, 16, 17, 2′	H-17α, H-17β	H-7α, H-9α, H-12α, H-17α
15	16.7 q	1.35β	s	3H	7, 8, 9, 14		H_3-16β, H-17β, H_2-20
16	16.6 q	1.79β	s	3H	12, 13, 14		H_3-15β, H-17β, H_2-20
17	16.5 t	2.95α	dd (J = 16.2, 4.8 Hz)	1H	8, 13, 14, 1′, 2′	H-14α, H-17β	H-7α, H-14α, H-17β
		2.55β	dd (J = 16.2, 12.5 Hz)	1H	13, 14, 1′, 2′, 3′	H-14α, H-17α	H_3-15β, H_3-16β, H-17α
18	20.0 q	1.38β	s	3H	3, 4, 5, 19		H-6β
19	28.1 q	1.26α	s	3H	3, 4, 5, 18		H-5α
20	69.7 t	5.05a	d (J = 9.4 Hz)	1H	1, 5, 9, 10	H-20b	H-20b
		4.73b	dd (J = 9.4, 2.8 Hz)	1H	1, 5, 9, 10	H-20a	H_3-18β, H-20a
1′	163.2 s						
2′	99.1 s						
3′	180.2 s						
4′	112.8 d	6.21	s	1H	2′, 3′, 5′, 6′		H_3-6′
5′	161.0 s						
6′	19.3 q	2.04	s	3H	4′, 5′		H-4′



16

Table S11. NMR data for chevalone T (**16**) (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in pyridine-d_5).

	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	33.2 t	2.37β	ddd (*J* = 13.5, 7.6, 3.2 Hz)	1H	2, 3, 5, 10, 20	H-1α	H-1β, H-2β
		1.85α	overlap	1H	2, 3, 9, 10, 20	H-1β, H-2α	H-1α, H-2α, H-9α
2	34.3 t	2.77β	ddd (*J* = 16.8, 10.7, 7.3 Hz)	1H	1, 3, 4	H-1α	H-1β
		2.62α	ddd (*J* = 16.8, 7.3, 3.2 Hz)	1H	1, 3, 4, 10	H-1α	H-1α, H-1β
3	213.5 s						
4	48.1 s						
5	49.2 d	2.09α	dd (*J* = 12.8, 6.2 Hz)	1H	1, 4, 6, 7, 10, 18, 19, 20	H_2-6	H-6α, H-9α, H_3-19α
6	20.3 t	1.76α	overlap	1H	4, 5, 7, 8	H-5α, H-6β, H-7α	H-5α, H-6β
		1.56β	overlap	1H	4, 5, 7, 8	H-5α, H-6α, H-7α	H-5α, H-6α, H-7β
7	35.1 t	1.58α	overlap	1H	5, 8, 9, 14	H_2-6, H-7β	H-5α, H-6α
		1.17β	overlap	1H	5, 8, 9, 14, 15	H-7α	H-7α
8	35.0 s						
9	56.4 d	1.90α	overlap	1H	1, 5, 7, 8, 10, 15, 20	H-11α	H-5α, H-11α, H-12α, H-19α
10	47.7 s						
11	78.8d	5.31α	dd (*J* = 5.3, 2.9 Hz)	1H	8, 9, 10, 12, 13	H-9α, H-12α	H-9α, H-12α
12	76.1 d	4.50α	t (*J* = 5.3 Hz)	1H	13, 16	H-11α	H-11α, H-14α
13	88.7 s						
14	47.3 d	1.77α	overlap	1H	8, 9, 12, 13, 15, 16, 17, 2′	H-17α, H-17β	H-9α, H-12α, H-17α
15	16.6 q	1.14β	s	3H	7, 8, 9, 14		H_3-16β, H-17β
16	19.9q	1.72β	s	3H	12, 13, 14		H_3-15β, H-17β
17	16.4 t	2.83α	dd (*J* = 16.2, 4.9 Hz)	1H	8, 13, 14, 1′, 2′	H-14α, H-17β	H-7α, H-14α, H-17β
		2.53β	dd (*J* = 16.2, 12.8 Hz)	1H	13, 14, 1′, 2′, 3′	H-14α, H-17α	H_3-15β, H_3-16β, H-17α
18	21.4q	1.61β	s	3H	3, 4, 5, 19		H-6β, H-7β
19	27.2 q	1.20α	s	3H	3, 4, 5, 18		H-5α, H-6α
20	177.8 s						
1′	163.1 s						
2′	99.3 s						
3′	180.1 s						
4′	112.8 d	6.23	s	1H	2′, 3′, 5′, 6′		H_3-6′
5′	161.4 s						
6′	19.3 q	2.07	s	3H	4′, 5′		H-4′



17

Table S12. NMR data for **17** (^{1}H NMR:600 MHz, ^{13}C NMR: 150 MHz, δ in ppm, recorded in $CDCl_3$).

	^{13}C	^{1}H					
position	δ (ppm)	δ (ppm)	Multiplicity	intensity	HMBC correlation	COSY correlation	NOESY correlation
1	30.0 t	1.67β	m	1H	2, 3, 5, 9, 10, 20	H-1α, H-2α	H-1α, H_3-15β
		2.32α	ddd (J = 14.3, 11.6, 6.1 Hz)	1H	2, 3, 5, 9, 10, 20	H-1β, H_2-2	H-6α
2	30.1 t	2.45	m	2H	1, 3, 10, 11	H_2-1	H-1β
3	173.6 s						
4	145.7 s						
5	55.5 d	1.96α	dd (J = 13.0, 2.8 Hz)	1H	1, 4, 6, 9, 10, 18, 19, 20	H-6α, H-6β	H-3α, H-6α, H-7α, H-9α, H_3-19α
6	23.6 t	1.88β	overlap	1H	4, 5	H-5α, H-6α, H-7α, H-7β	H-1α, H-6β, H-7β
		1.57α	overlap	1H	4, 5, 8, 9	H-5α, H-6β, H-7α, H-7β	H-5α, H-6α
7	39.2 t	1.14α	td (J = 13.0, 3.5 Hz)	1H	5, 6, 8, 9, 14, 15	H-6α, H-6β, H-7β	H-6α, H-7β, H_3-15β, H-17α
		1.92β	m	1H	5, 6, 8, 9, 11, 15	H-6α, H-6β, H-7α	H-6α, H-7α
8	37.8 s						
9	59.2 d	1.29α	dd (J = 12.3, 1.8 Hz)	1H	10, 11, 12, 14, 15, 20	H-11β	H-5α, H-7α, H-11α, H-12α, H-14α
10	40.6 s						
11	21.3 t	1.64β	overlap	1H	9, 12, 13, 14	H-9α, H-11α, H-12α, H-12β	H-11α, H_3-15β
		1.86α	m	1H	10, 13	H-11β, H-12β	H-1α, H-9α, H-11β, H-12α
12	40.4 t	2.20α	m	1H	9, 11, 13, 14, 16	H-11β, H-12β	H-9α, H-11α, H-14α
		1.74β	dd (J = 13.0, 3.7 Hz)	1H	9, 11, 13, 14, 16	H-11α, H-11β, H-12α	H-11β, H_3-16β
13	83.6 s						
14	52.1 d	1.54α	overlap	1H	8, 9, 13, 16, 17, 2′	H-17α, H-17β	H-9α, H-12α, H-17α
15	15.3 q	0.91β	s	3H	7, 8, 9, 14, 16, 20		H-1α, H-1β, H-7β, H_3-16β, H-17β
16	20.6 q	1.32β	s	3H	10, 13, 14		H-11β, H-12β, H_3-15β, H-17β
17	15.7 t	2.15β	dd (J = 16.3, 12.7 Hz)	1H	8, 13, 14, 1′, 2′, 3′	H-14α, H-17α	H-7β, H_3-15β, H_3-16β, H-17α
		2.59α	dd (J = 16.3, 4.9 Hz)	1H	8, 13, 14, 1′, 2′, 3′	H-14α, H-17β	H-14α, H-17β
18	21.0 q	1.78	s	3H	4, 5, 6, 10, 19		H-2β, H-5α
19	116.6 t	4.93a	s	1H	4, 5, 18		H_3-18β
		4.74b	s	1H	4, 5, 18		
20	67.9 t	4.44α	d (J = 12.4 Hz)	1H	1, 3, 5, 9, 10		H_3-15β
		4.15β	d (J = 12.4 Hz)	1H	1, 3, 5, 9, 10		H-11β, H_3-15β
1′	162.6 s						
2′	98.5 s						
3′	180.7 s						
4′	112.2 d	6.00	s	1H	2′, 3′, 5′, 6′		H_3-6′
5′	160.9 s						
6′	19.5 q	2.21	s	3H	4′, 5′		H-4′

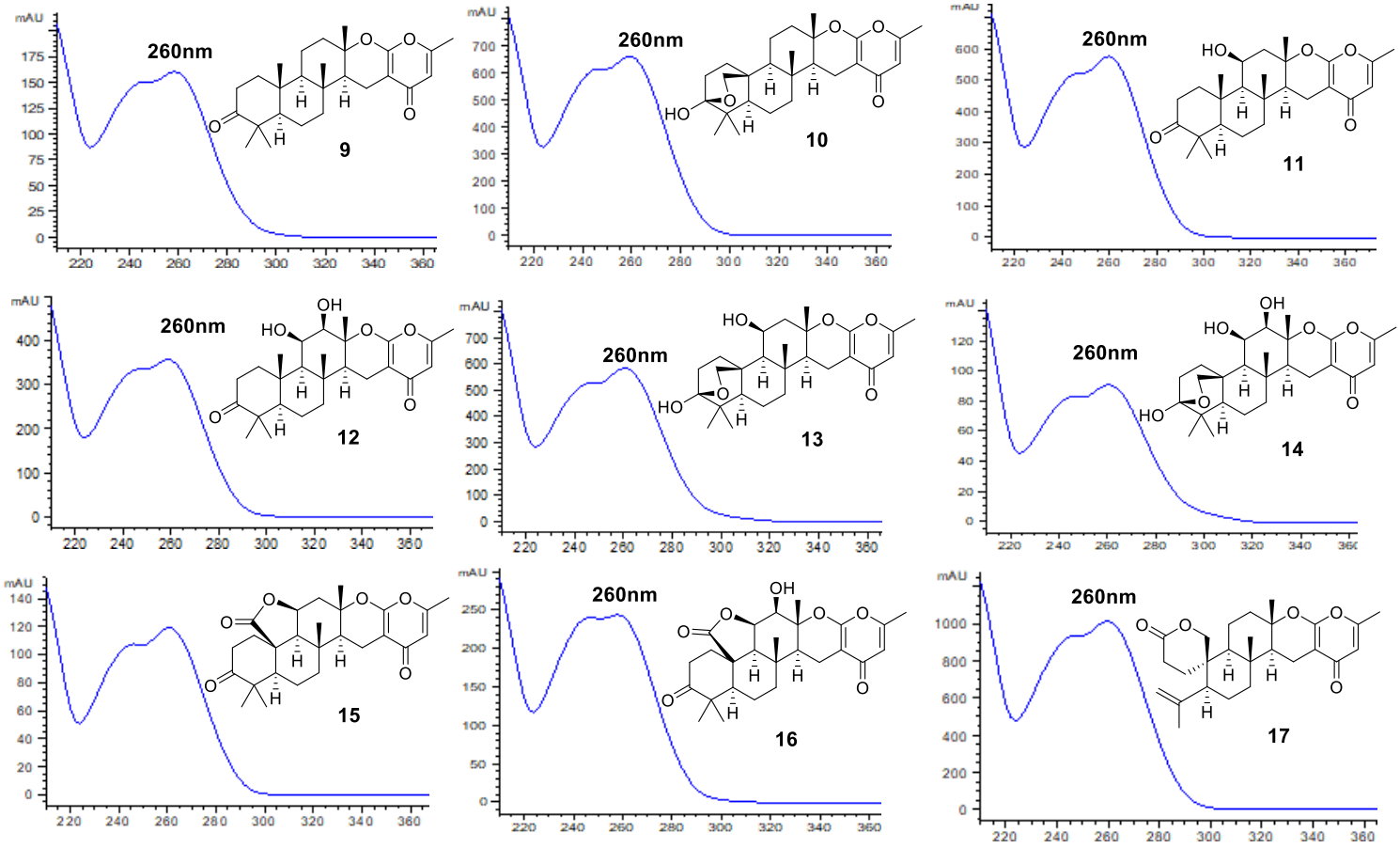


Figure S1. UV spectra of metabolites isolated in this study.

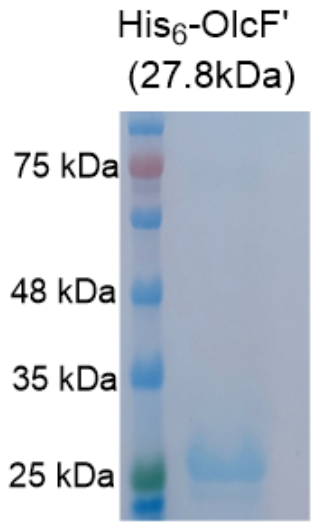


Figure S2. SDS-PAGE analysis of the purified protein OlcF′.

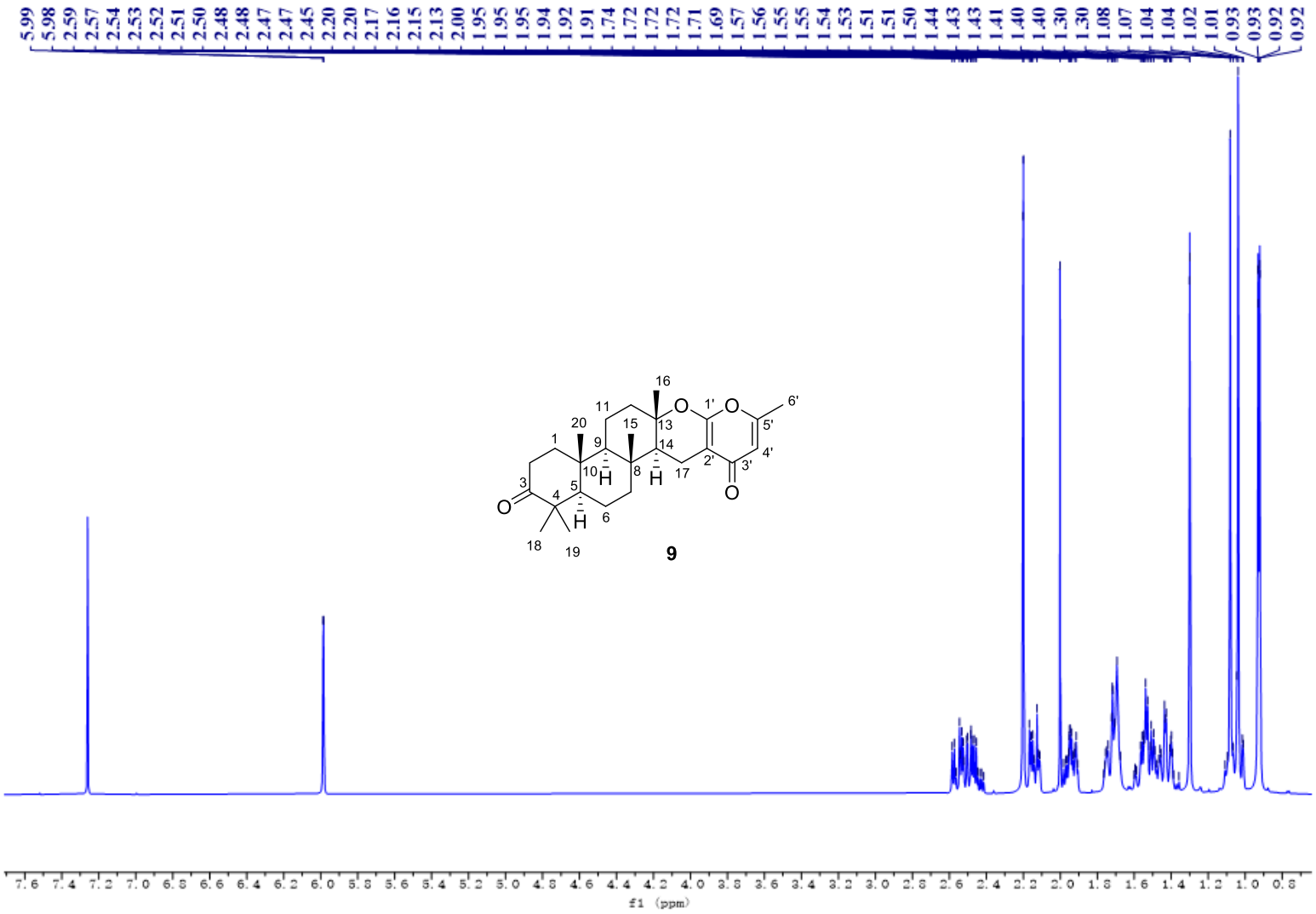


Figure S3. ^{1}H NMR spectrum of chevalone F (**9**).

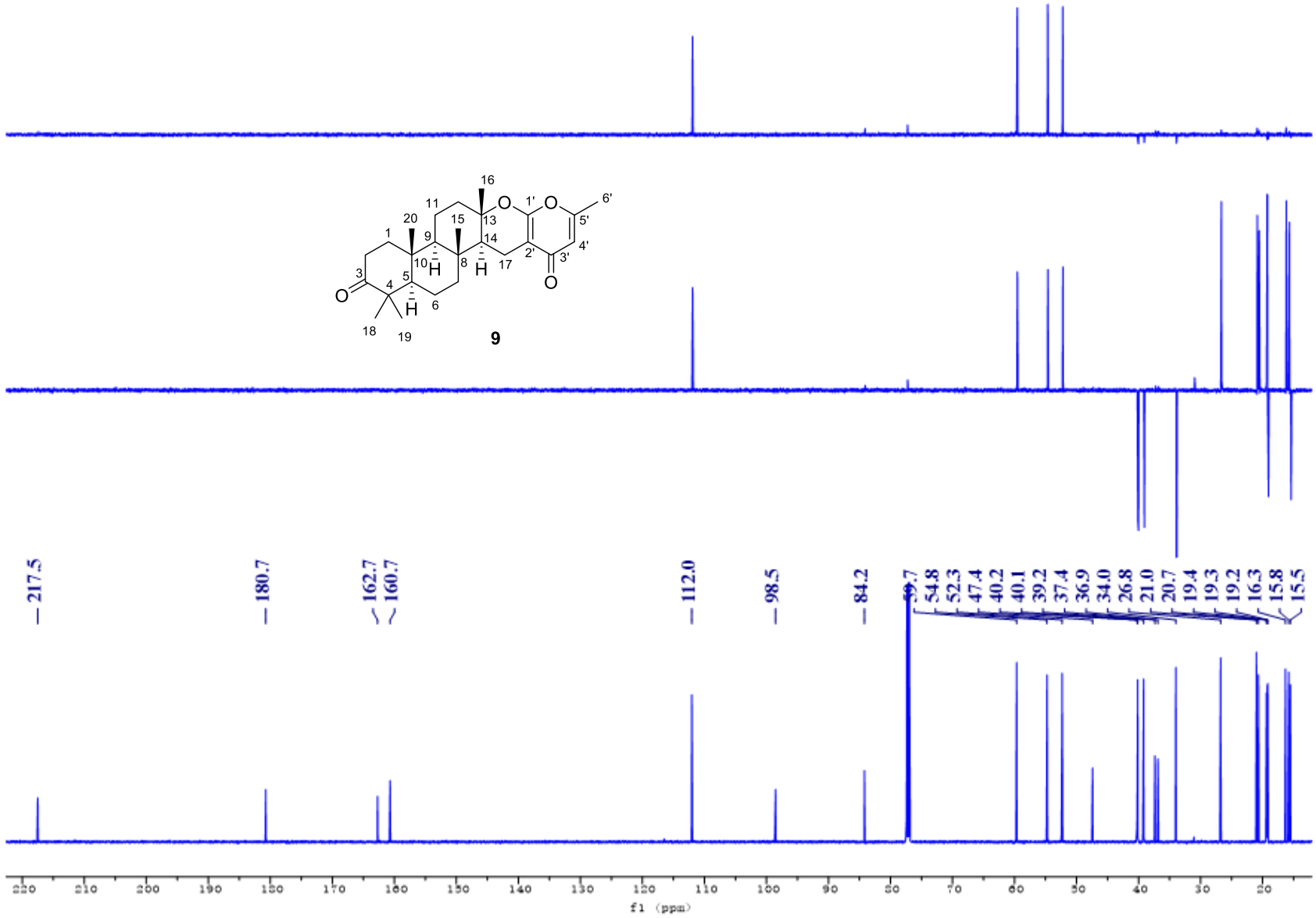


Figure S4. ^{13}C NMR spectrum of chevalone F (**9**).

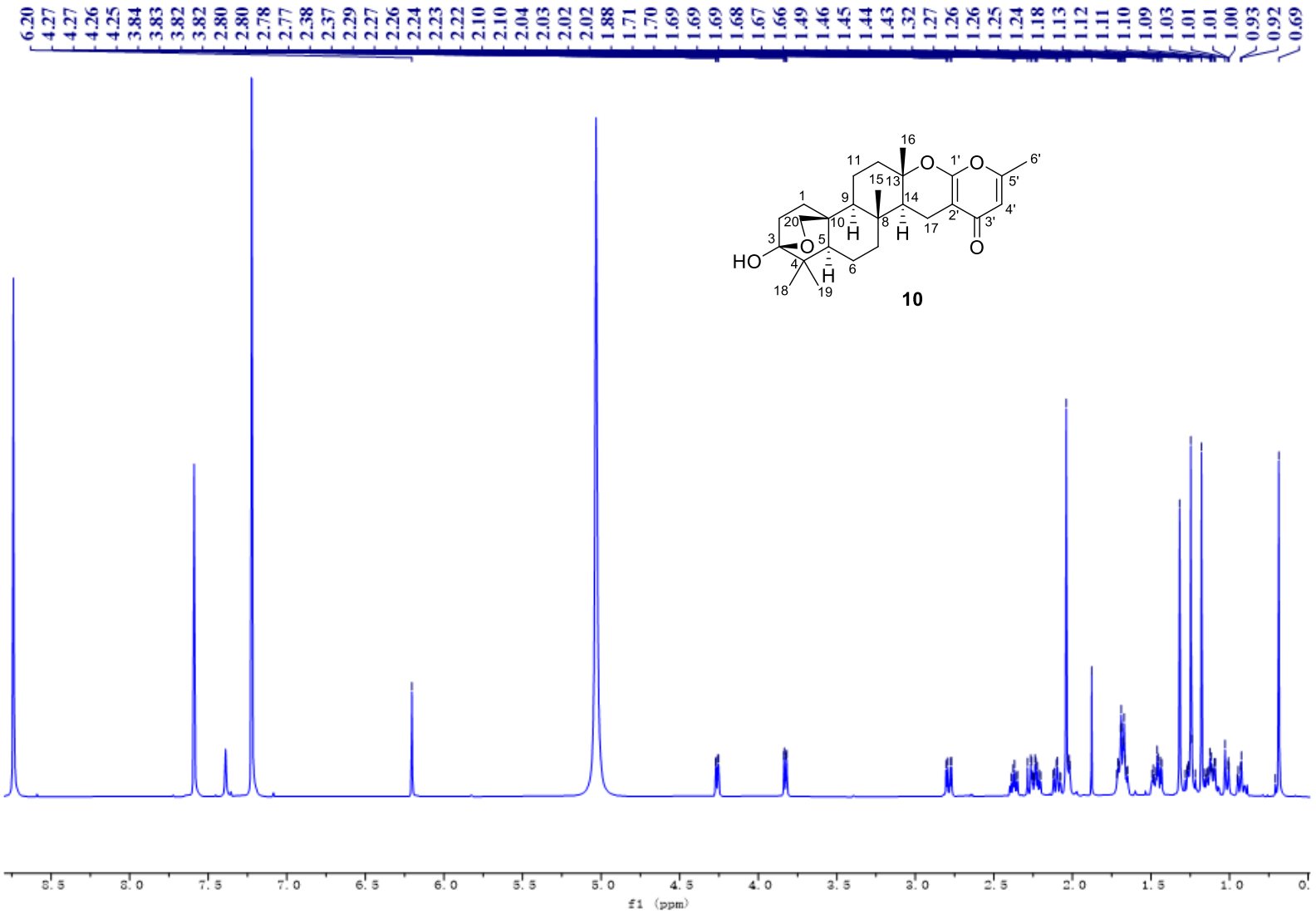


Figure S5. ^{1}H NMR spectrum of chevalone N (**10**).

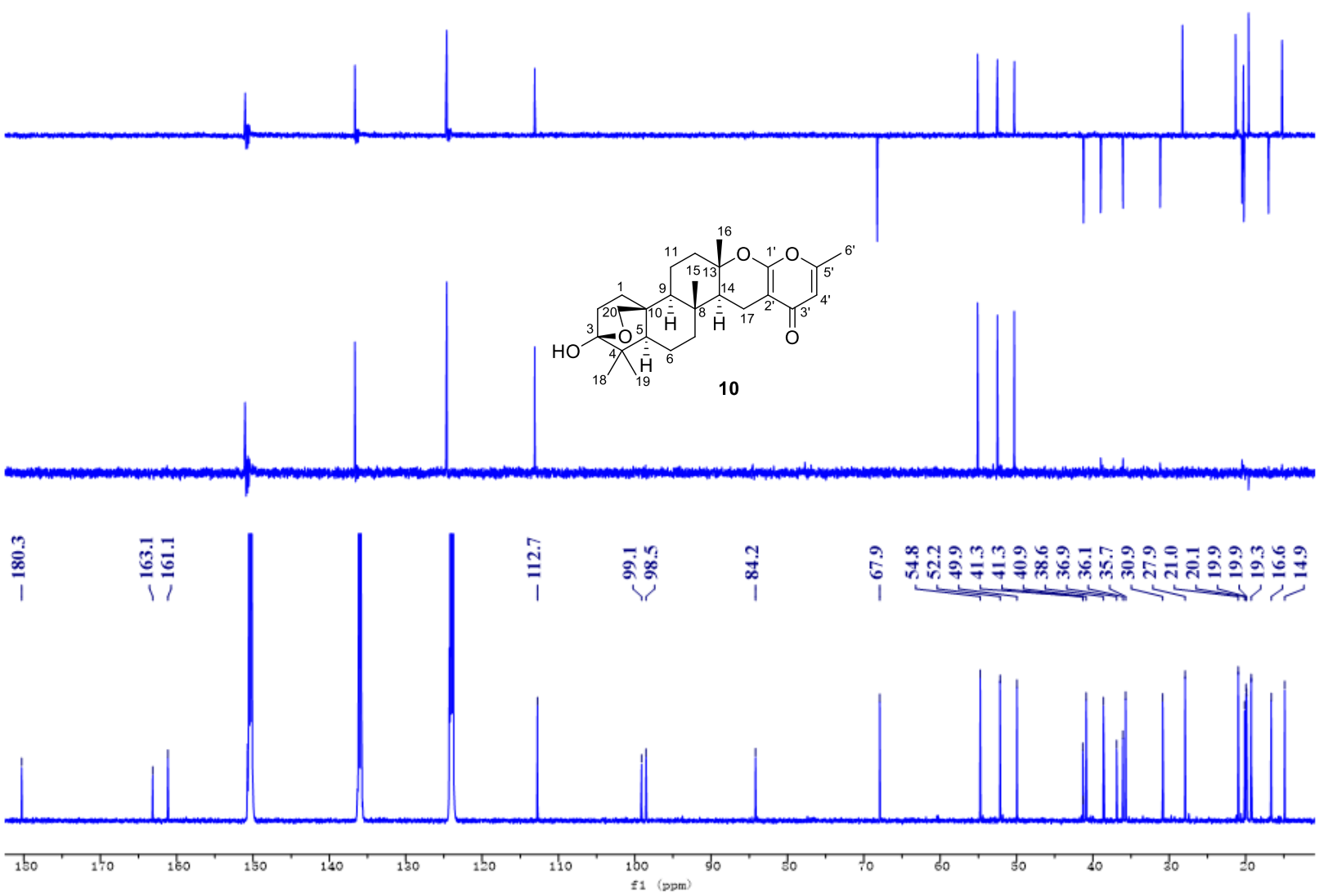


Figure S6. ^{13}C NMR spectrum of chevalone N (**10**).

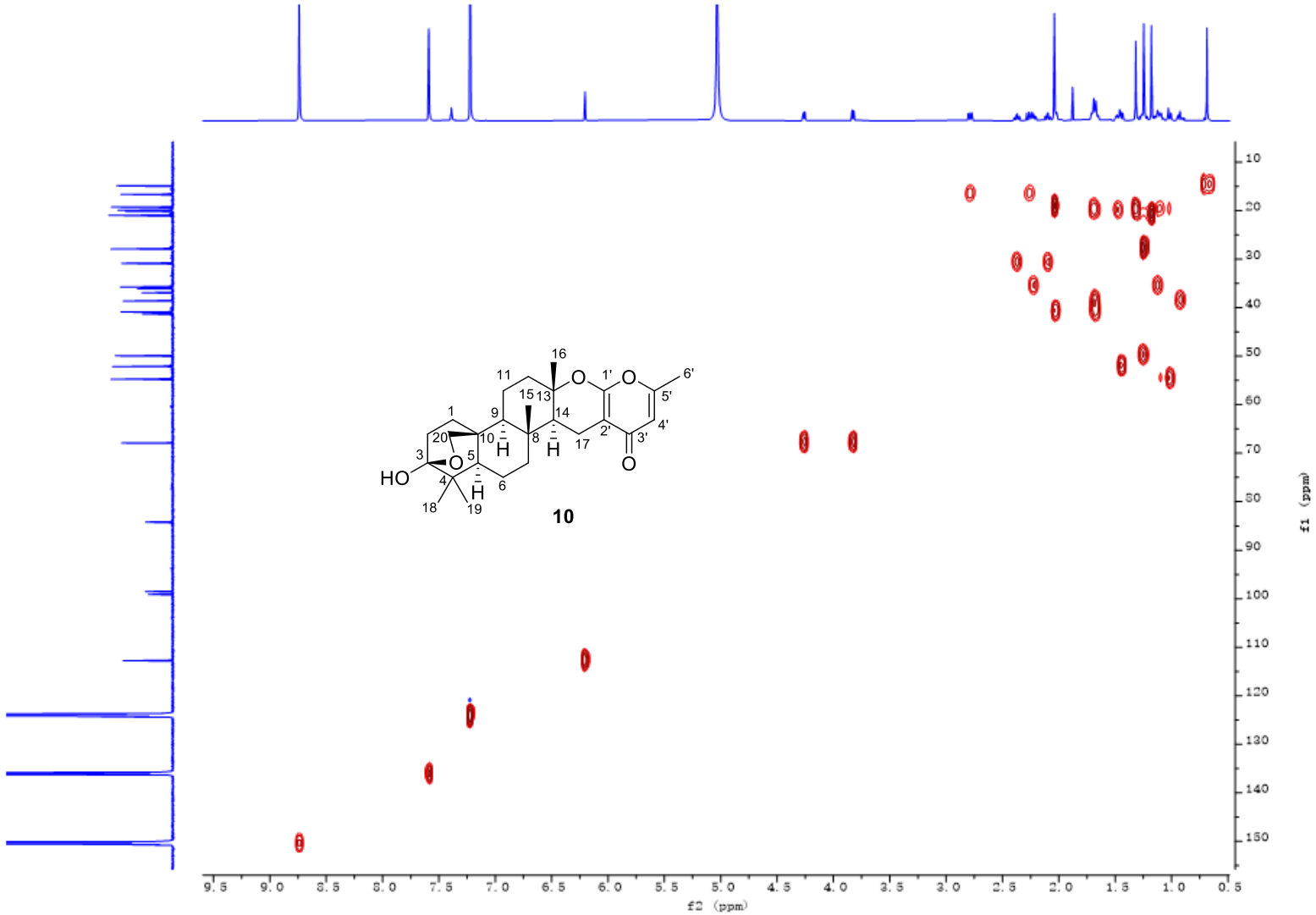


Figure S7. HSQC spectrum ofchevalone N (**10**).

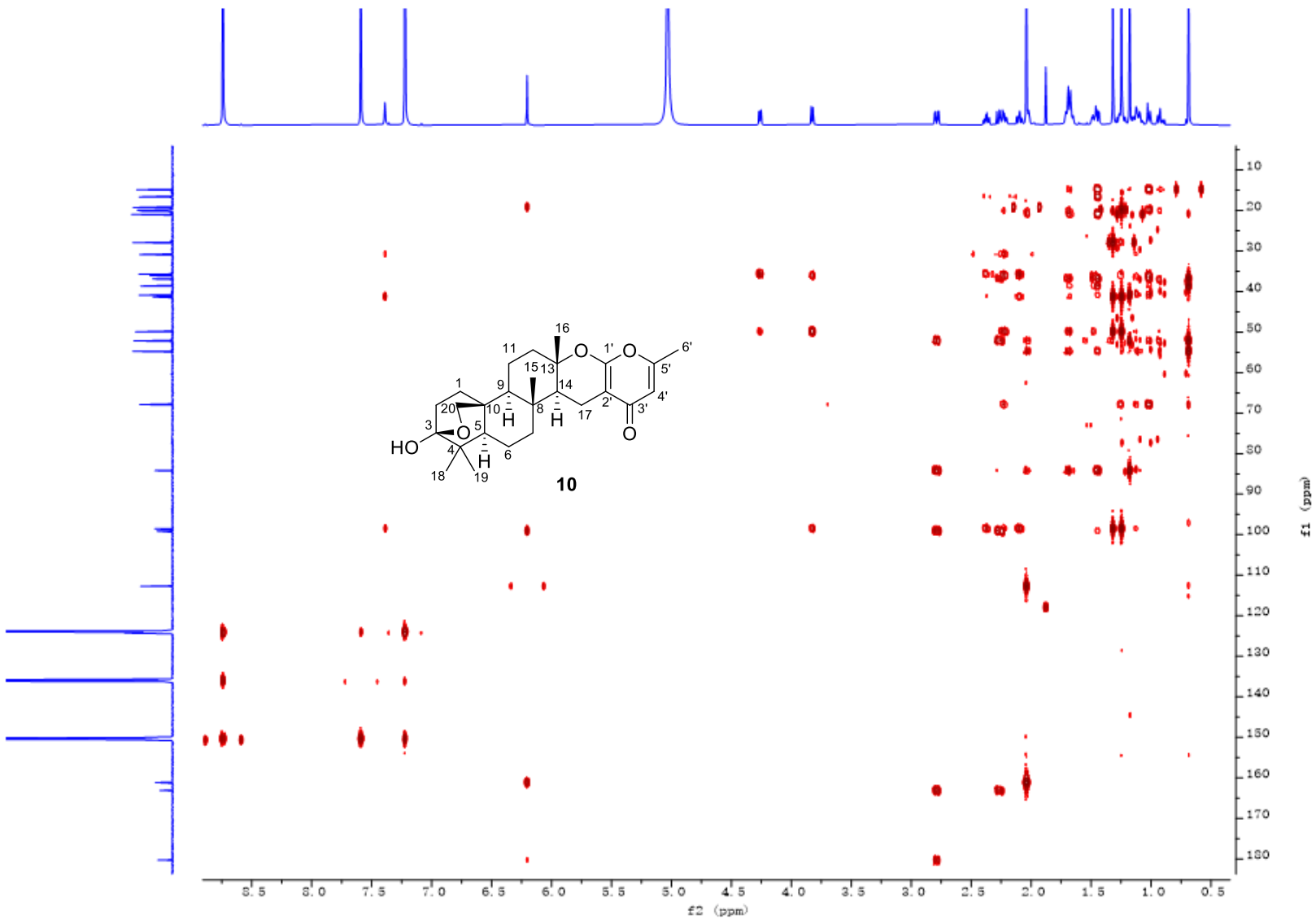


Figure S8. HMBC spectrum of chevalone N (**10**).

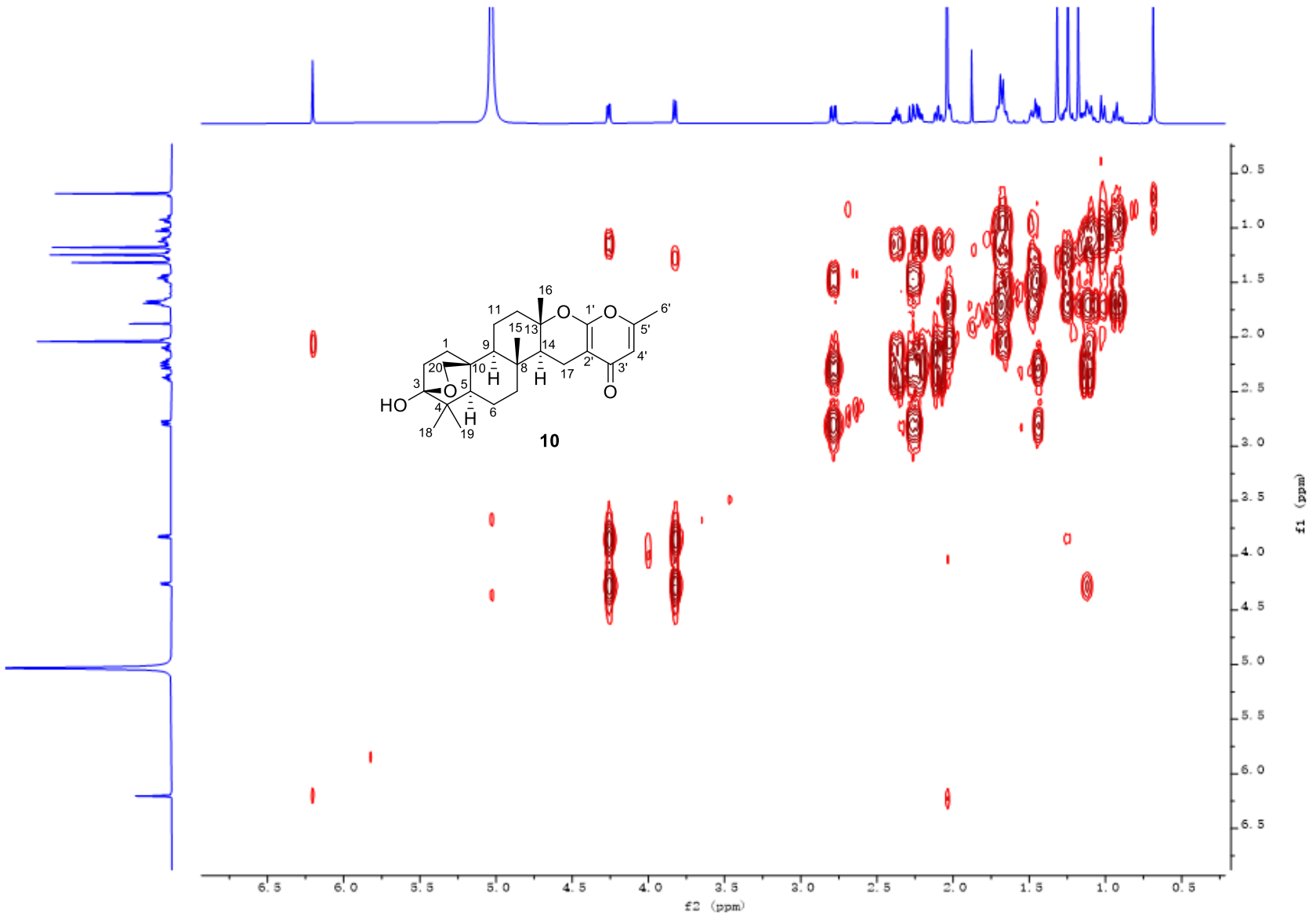


Figure S9. ^{1}H-^{1}H COSY spectrum of chevalone N (**10**).

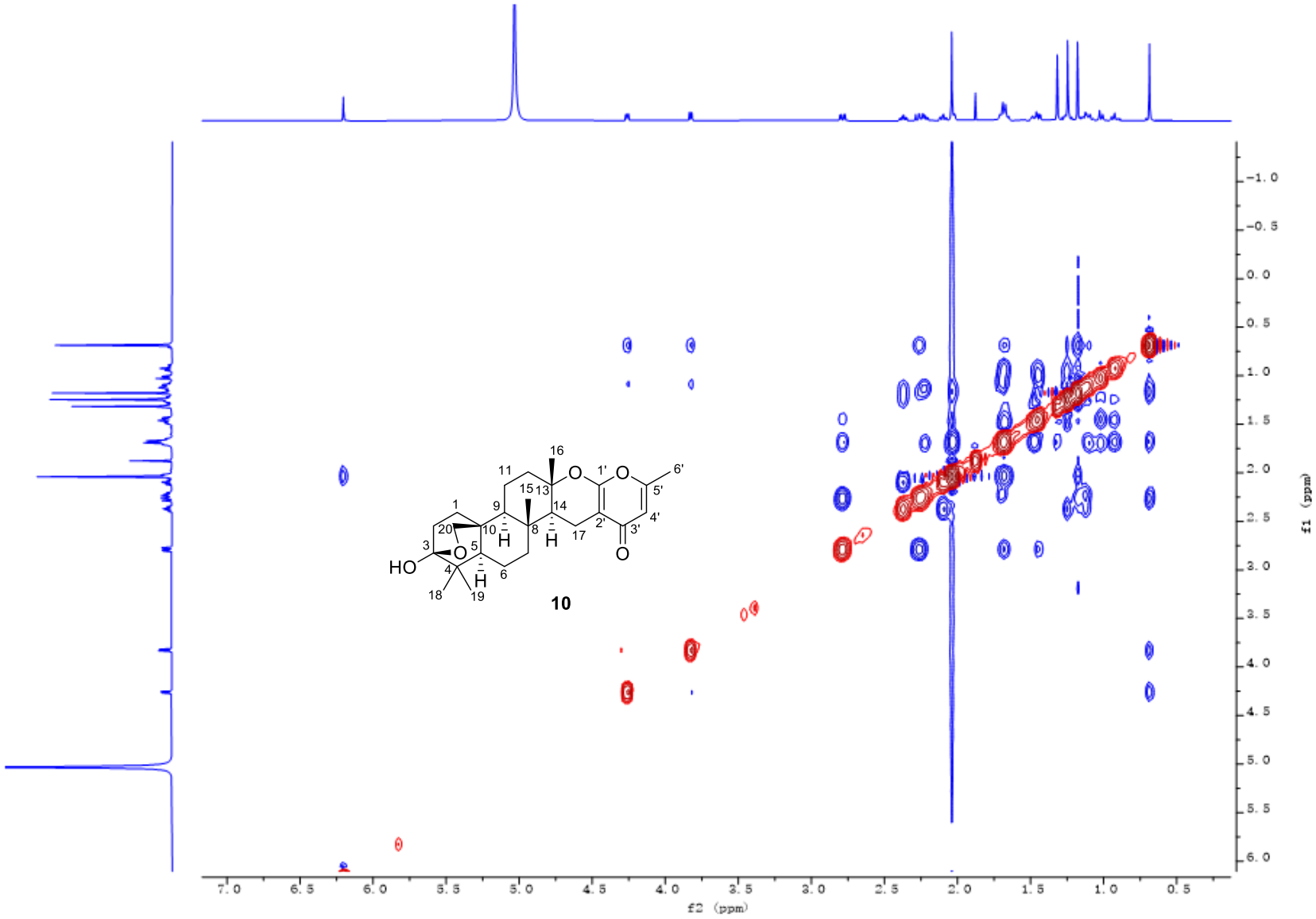


Figure S10. ROESY spectrum of chevalone N (**10**).

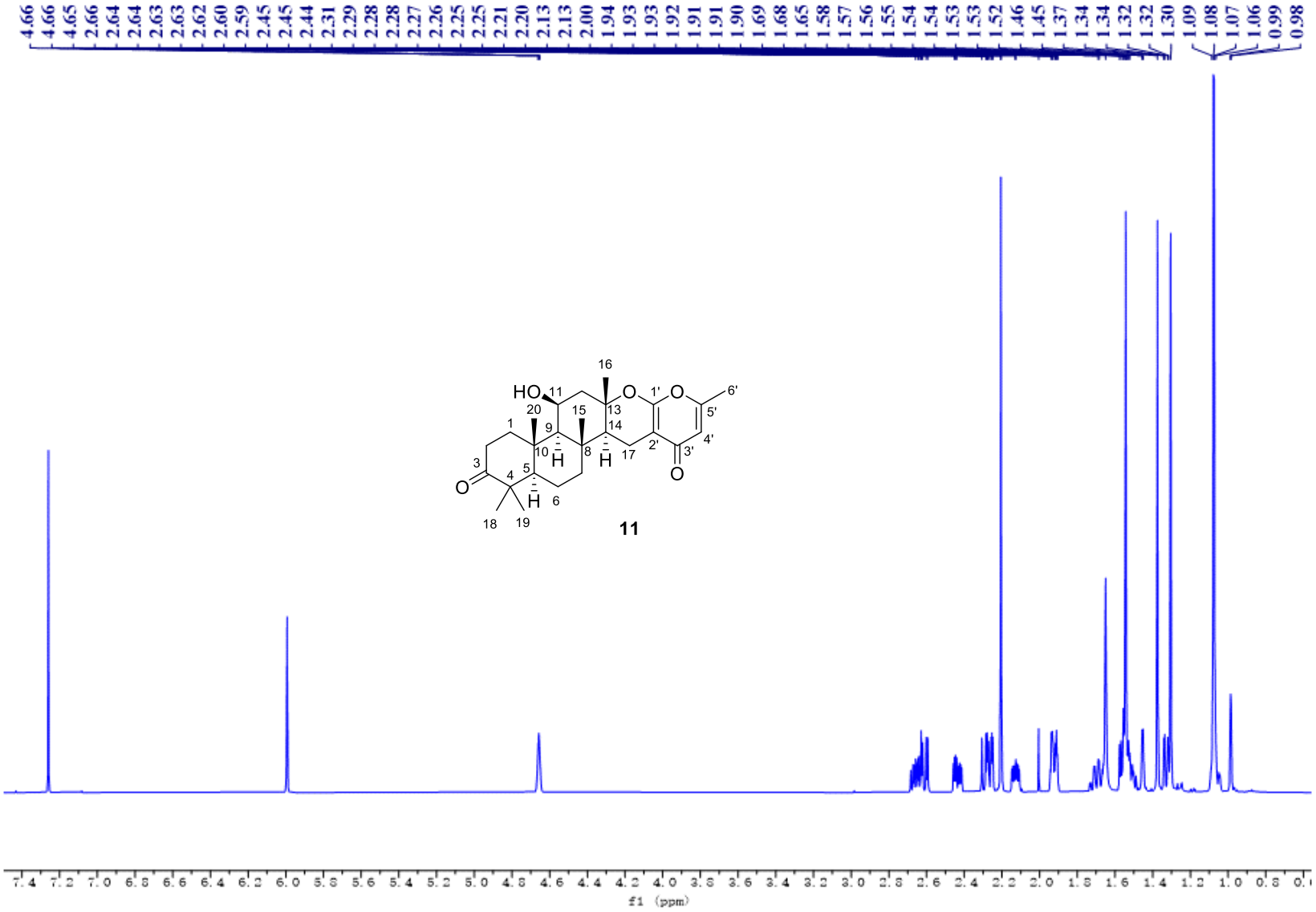


Figure S11. ^{1}H NMR spectrum of chevalone O (**11**).

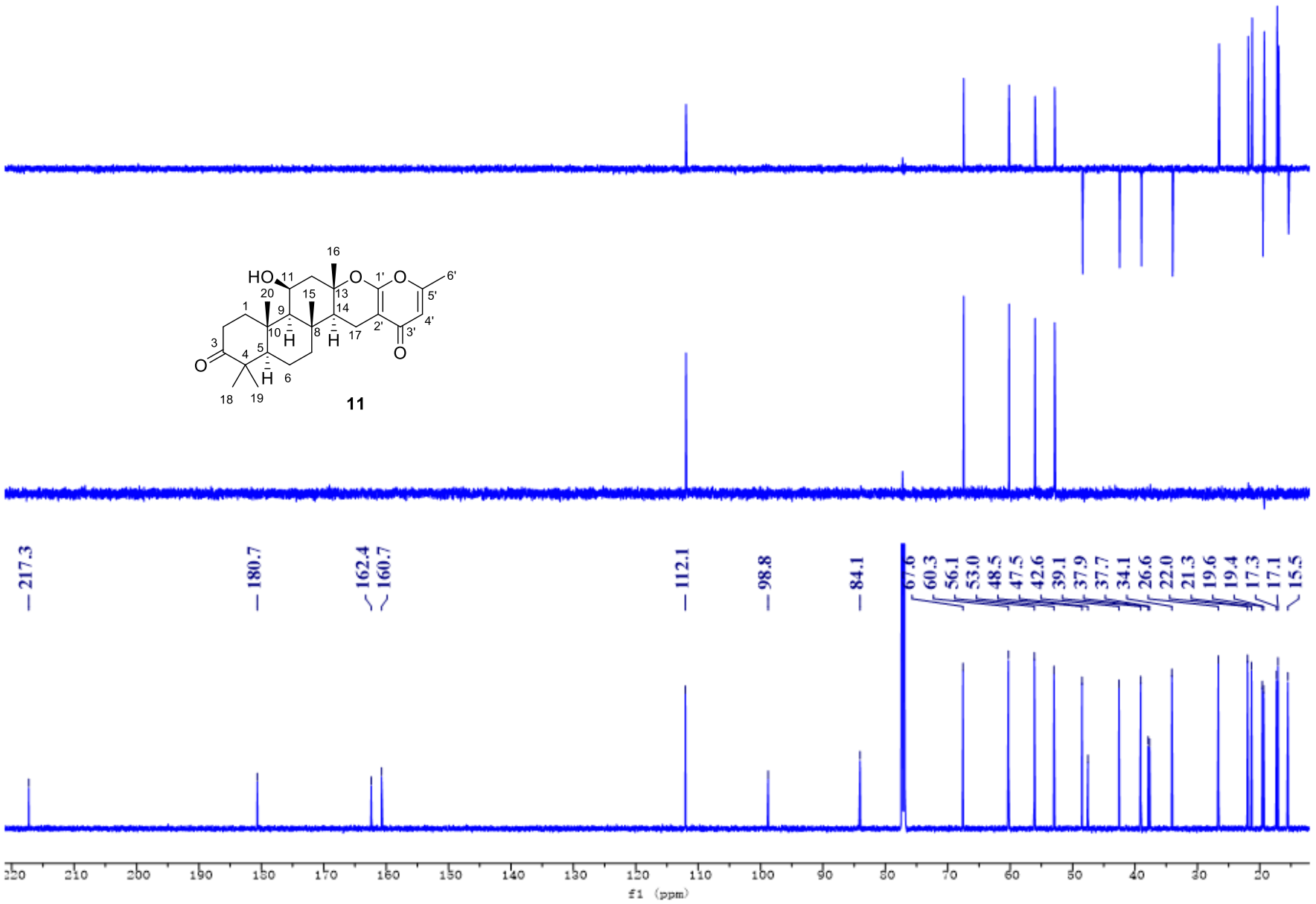


Figure S12. ^{13}C NMR spectrum of chevalone O (**11**).

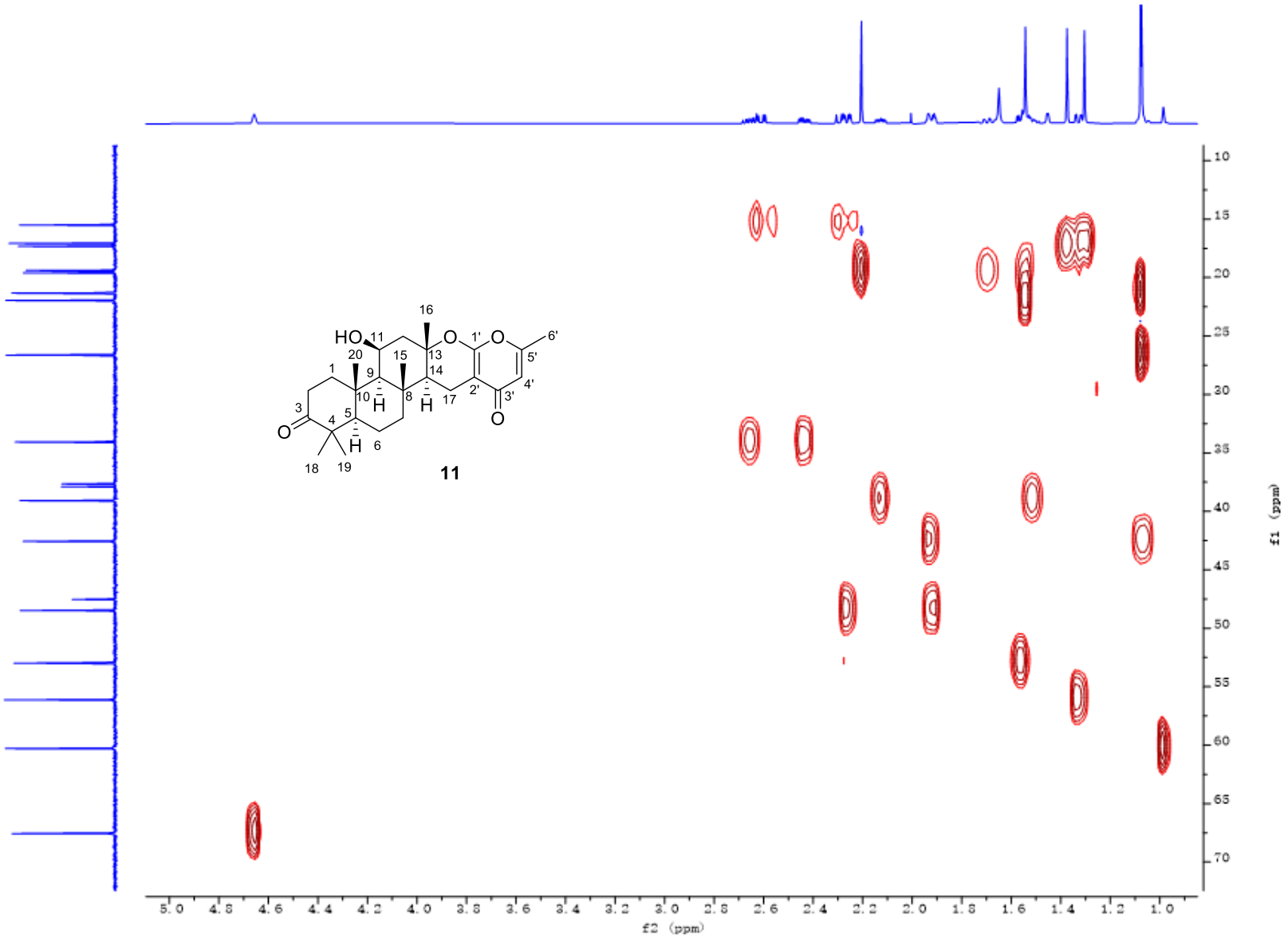


Figure S13. HSQC spectrum of chevalone O (**11**).

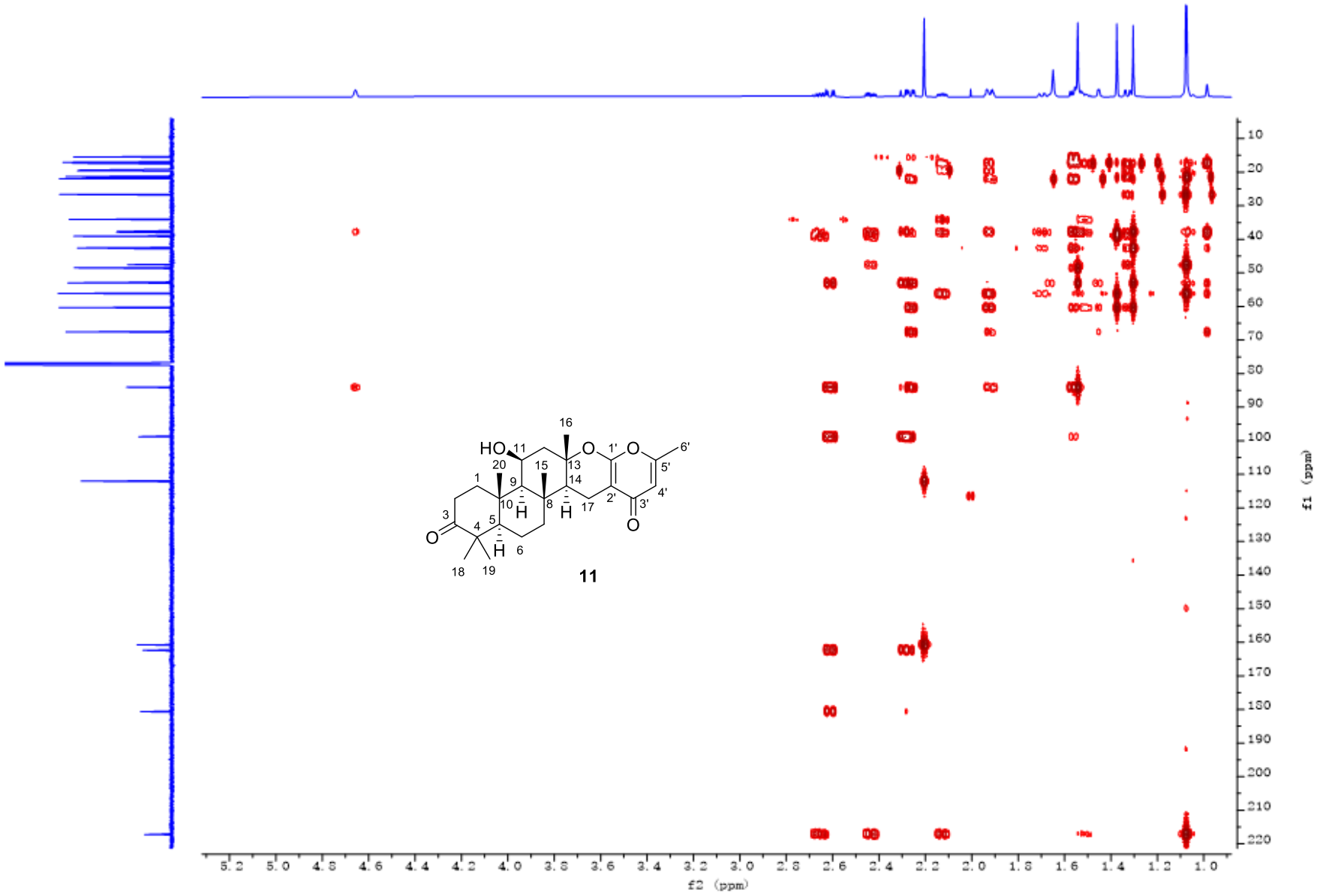


Figure S14. HMBC spectrum of chevalone O (**11**).

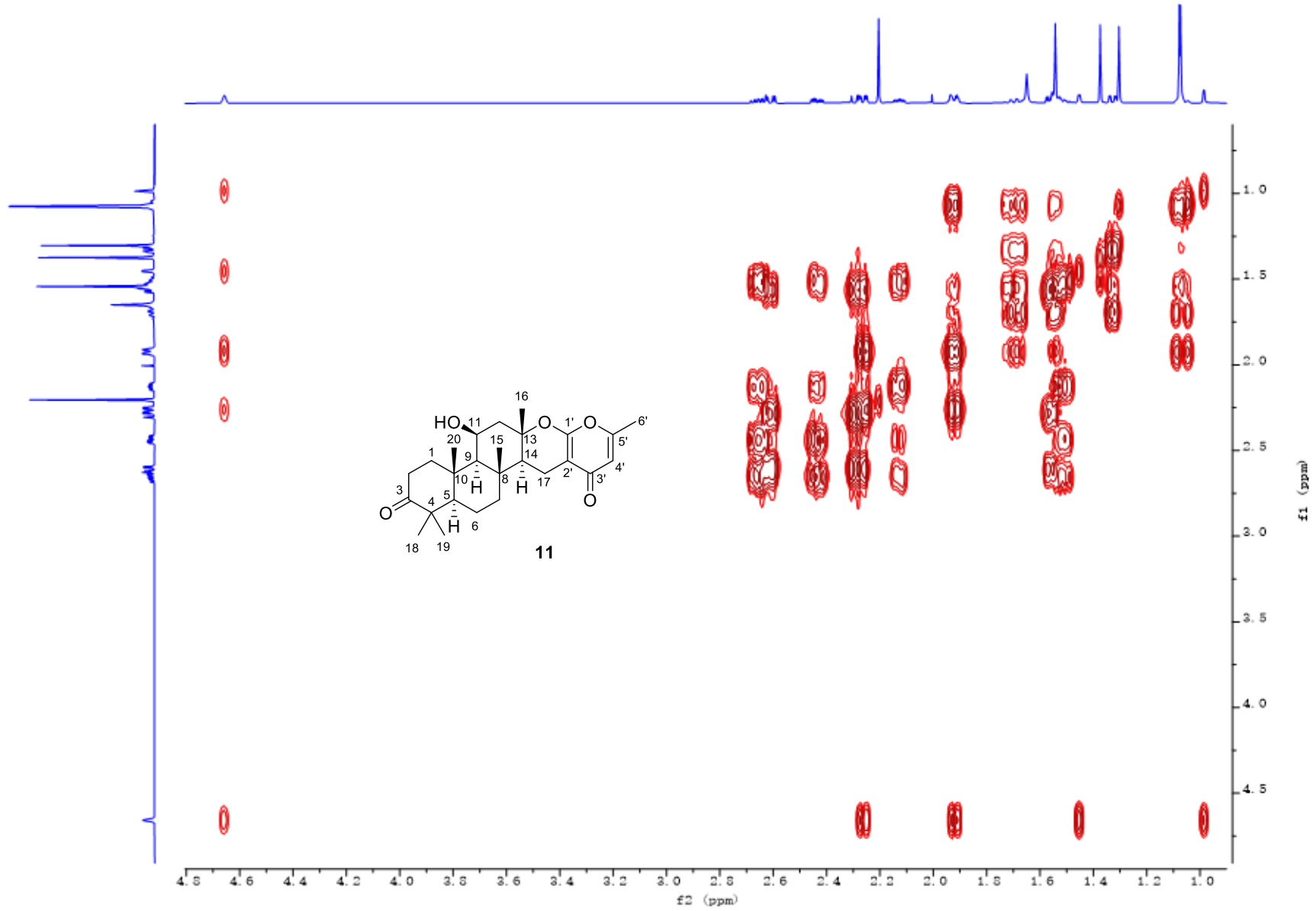


Figure S15. ^{1}H-^{1}H COSY spectrum of chevalone O (**11**).

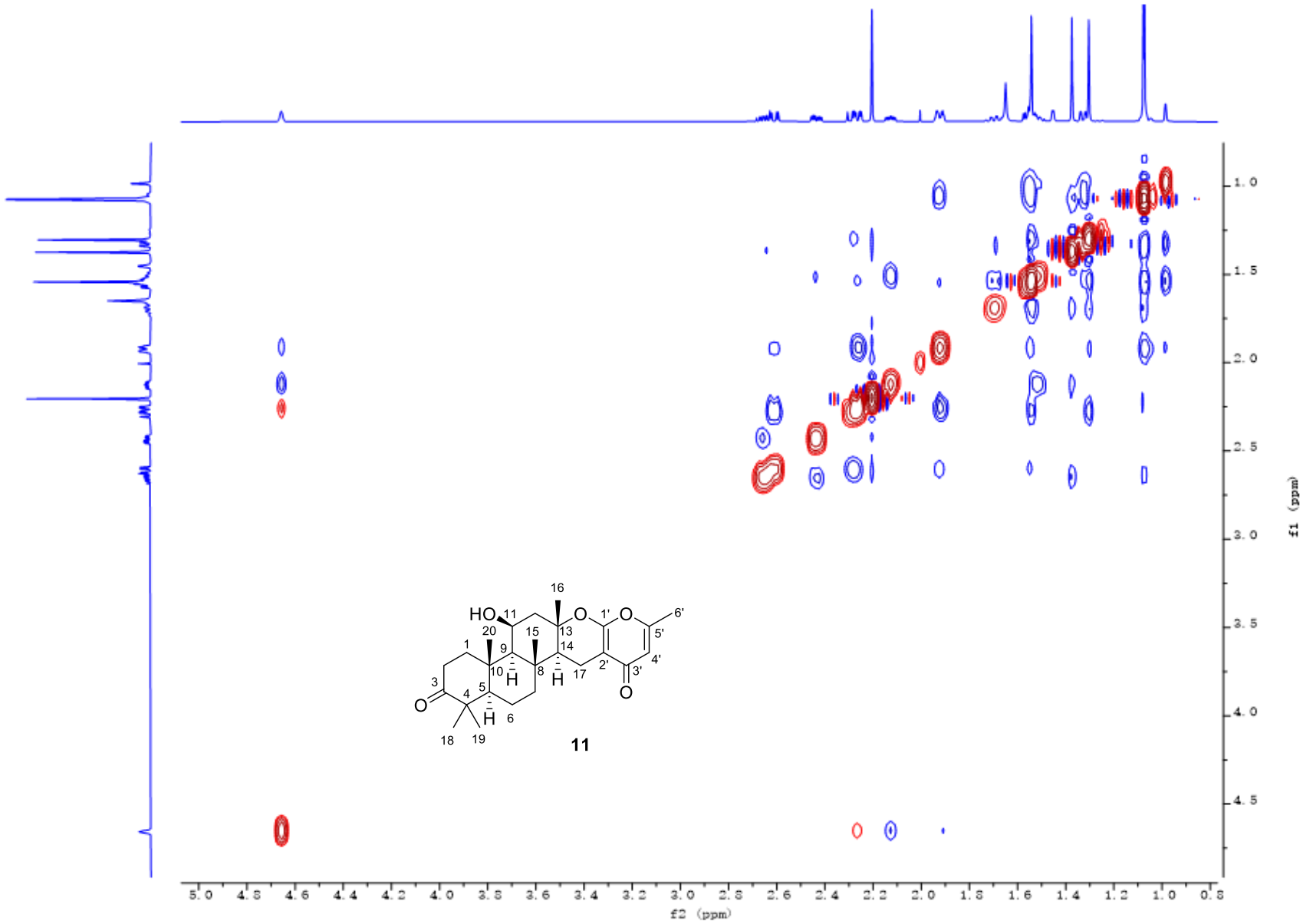


Figure S16. ROESY spectrum of chevalone O (**11**).

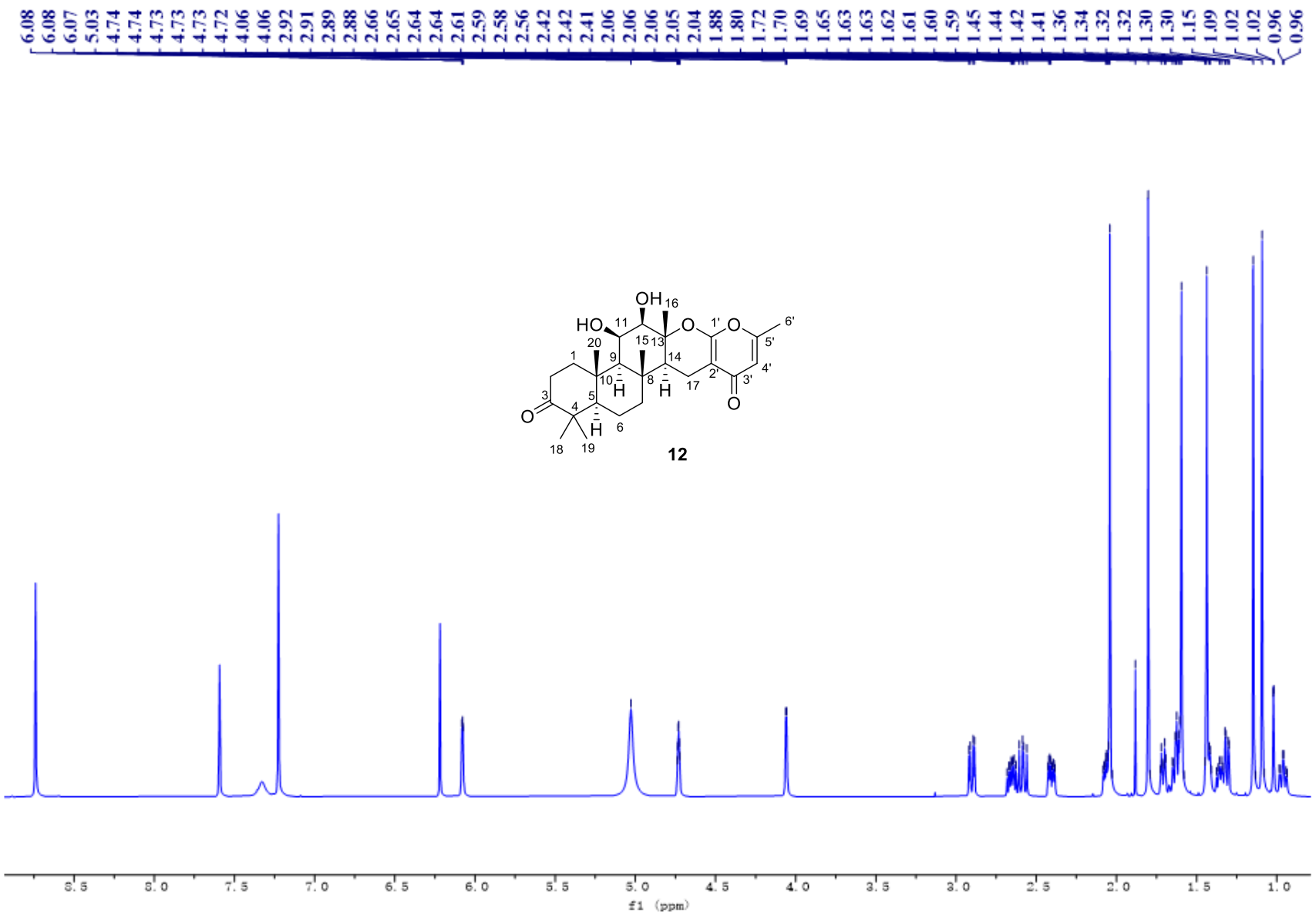


Figure S17. ^{1}H NMR spectrum of chevalone P (**12**).

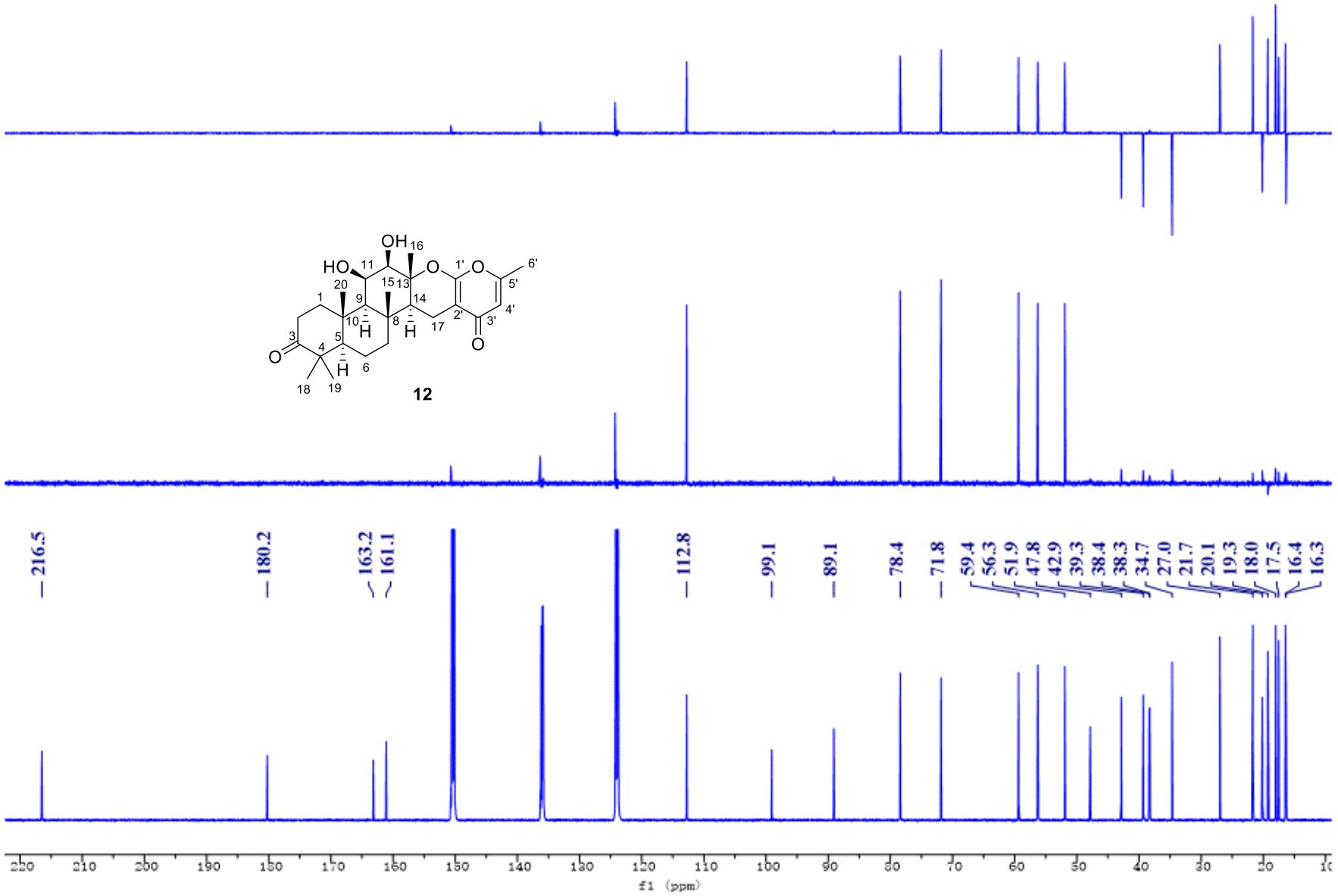


Figure S18. ^{13}C NMR spectrum of chevalone P (**12**).

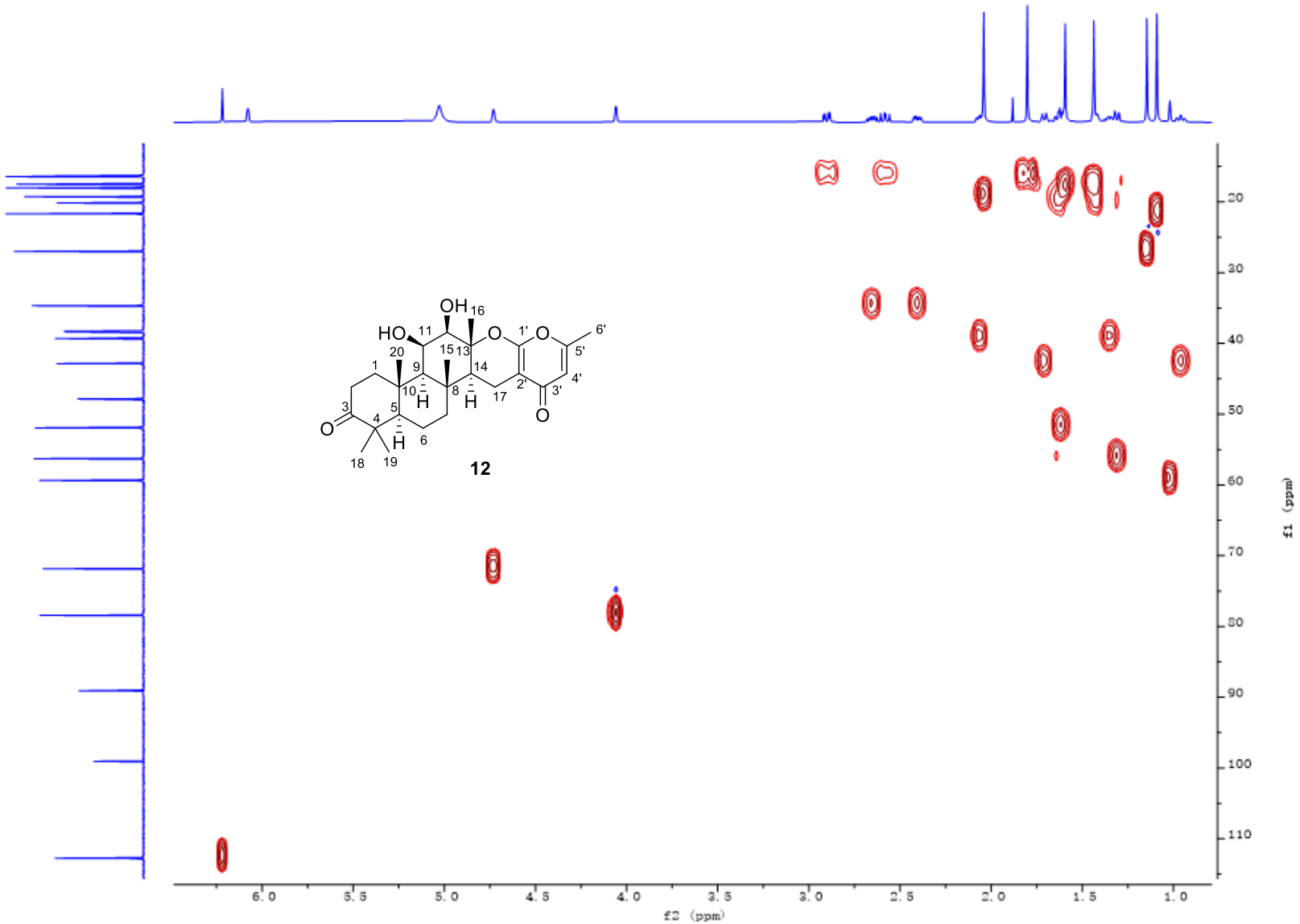


Figure S19. HSQC spectrum of chevalone P (**12**).

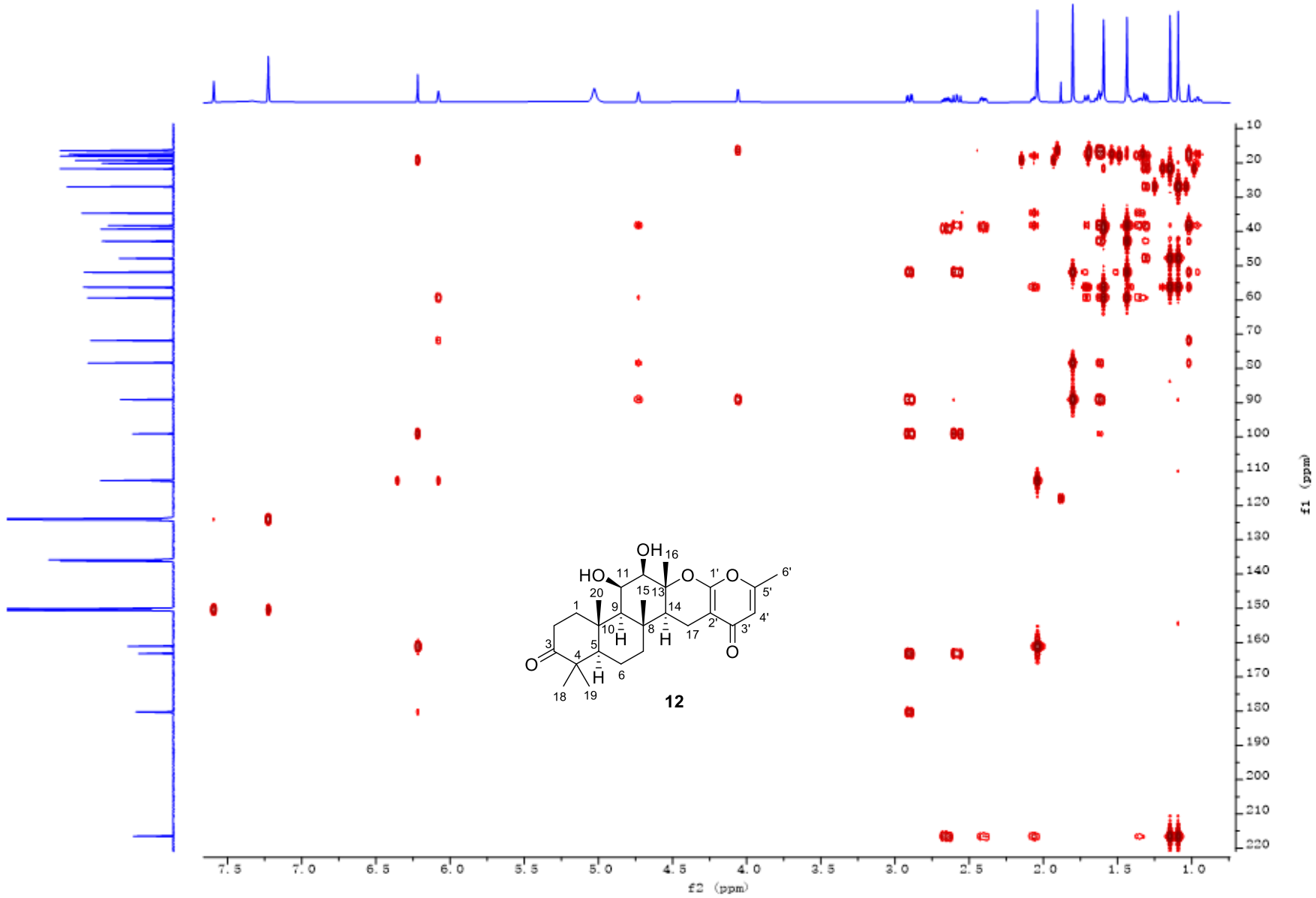


Figure S20. HMBC spectrum of chevalone P (**12**).

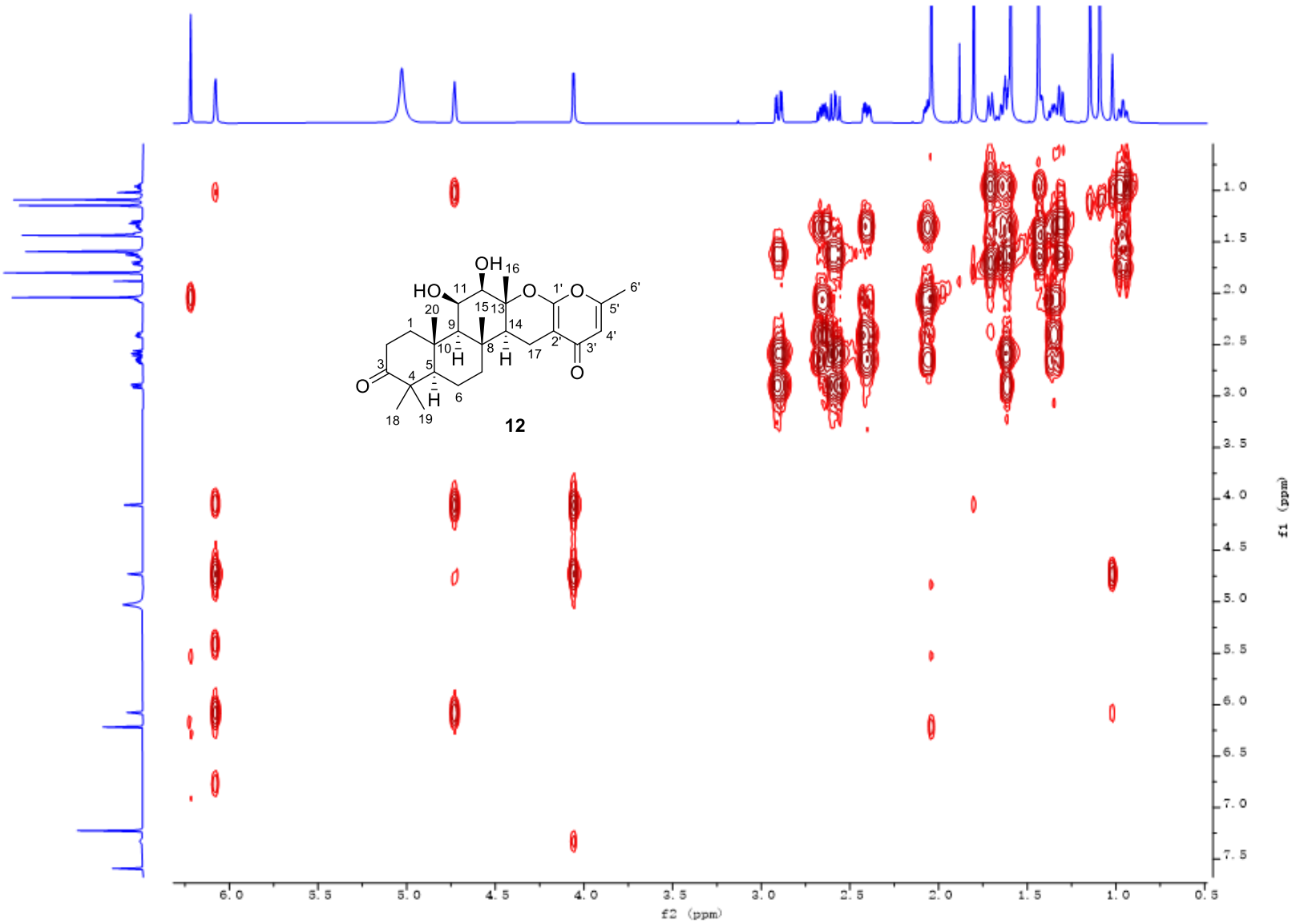


Figure S21. ^{1}H-^{1}H COSY spectrum of chevalone P (**12**).

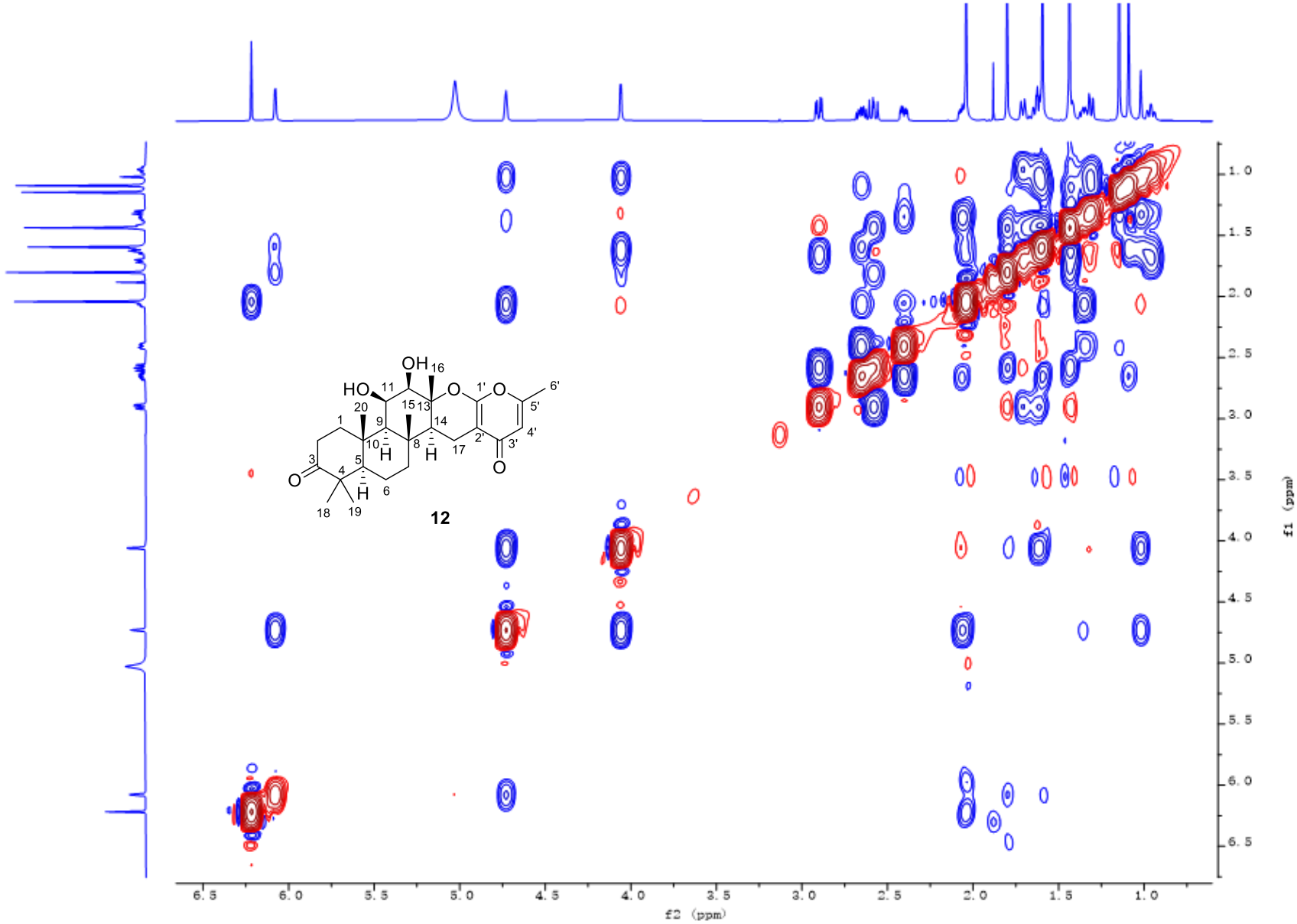


Figure S22. ROESY spectrum of chevalone P (**12**).

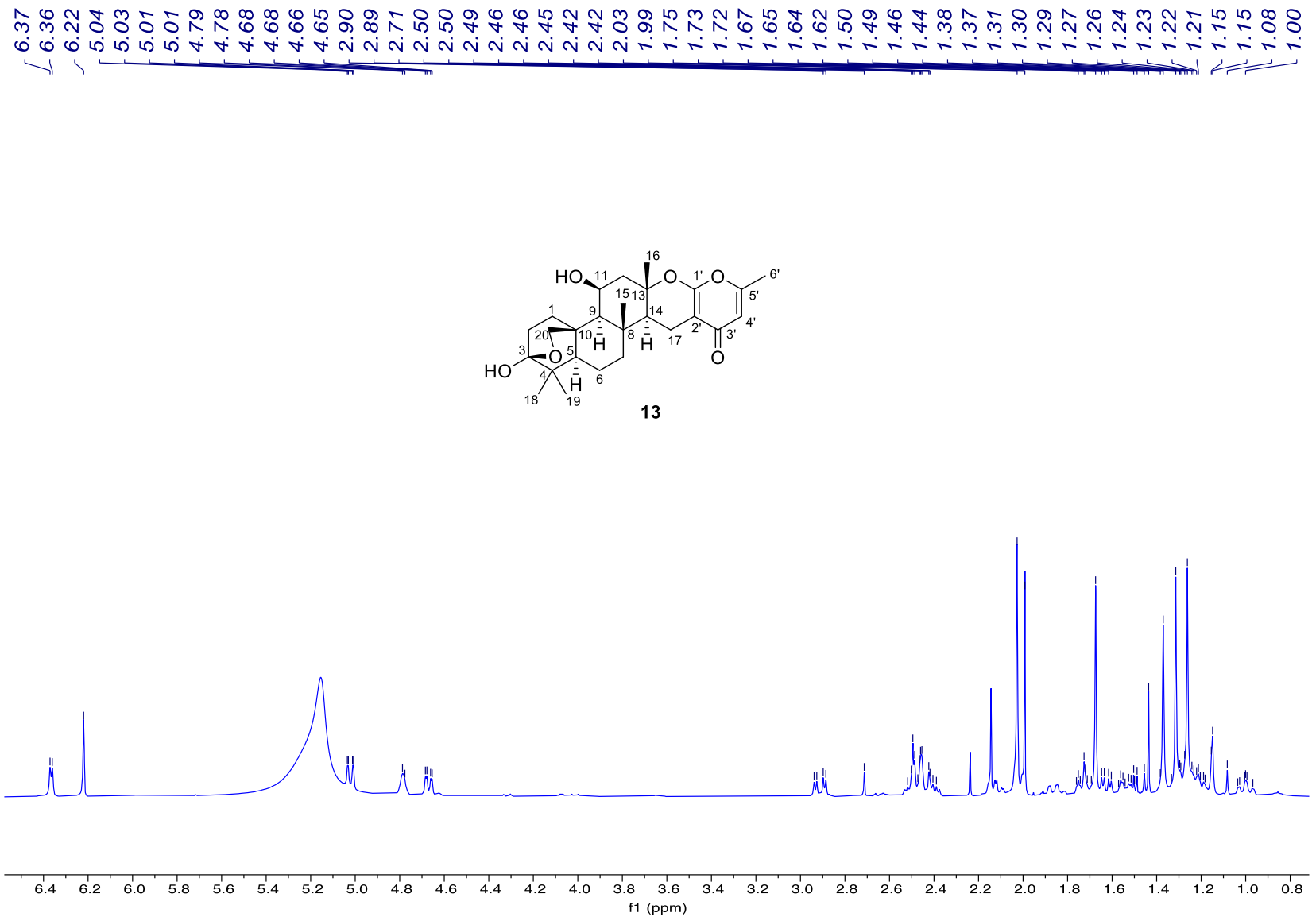


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Figure S23. ^{1}H NMR spectrum of chevalone Q (**13**).

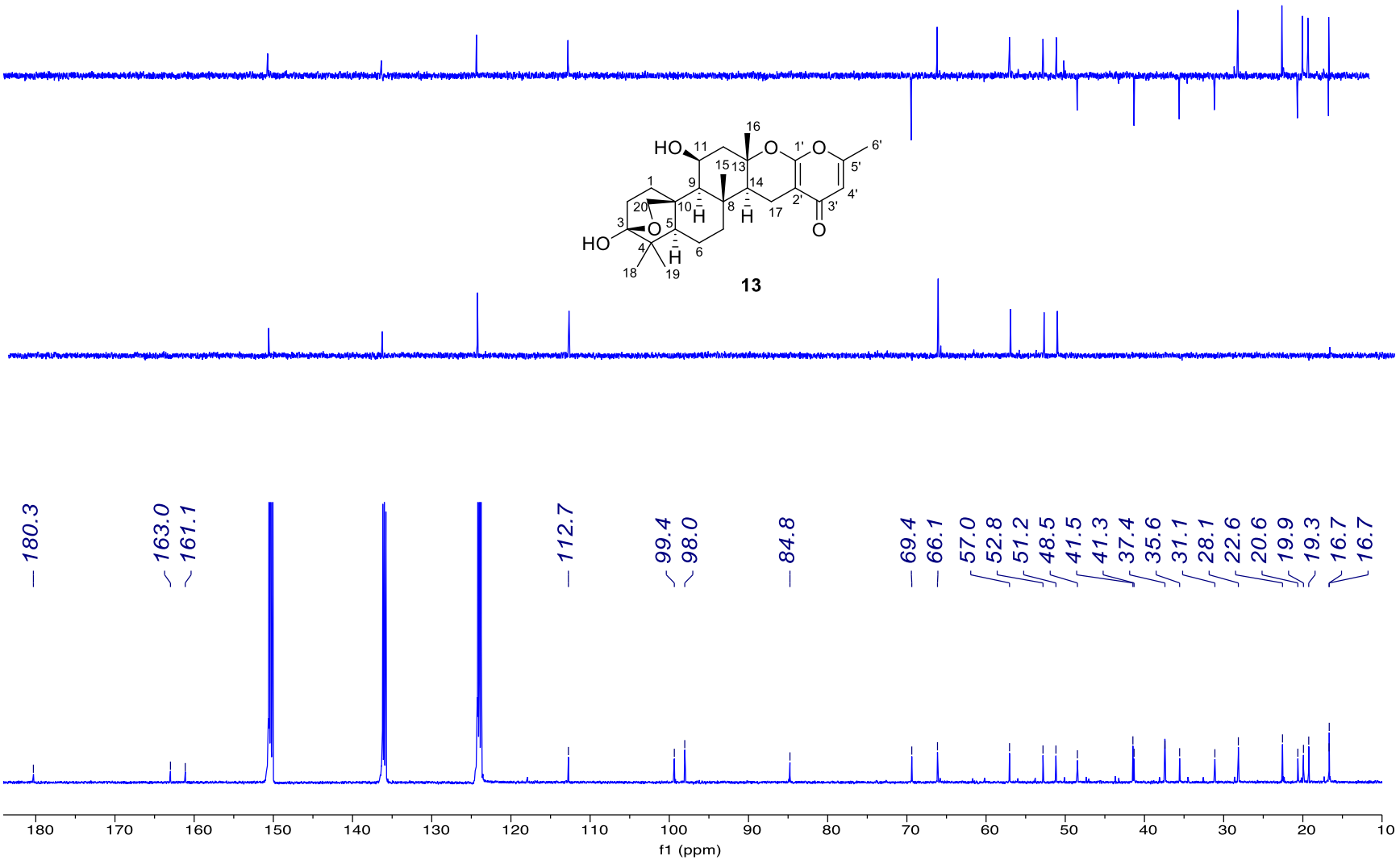

Figure S24. ^{13}C NMR spectrum of chevalone Q (**13**).

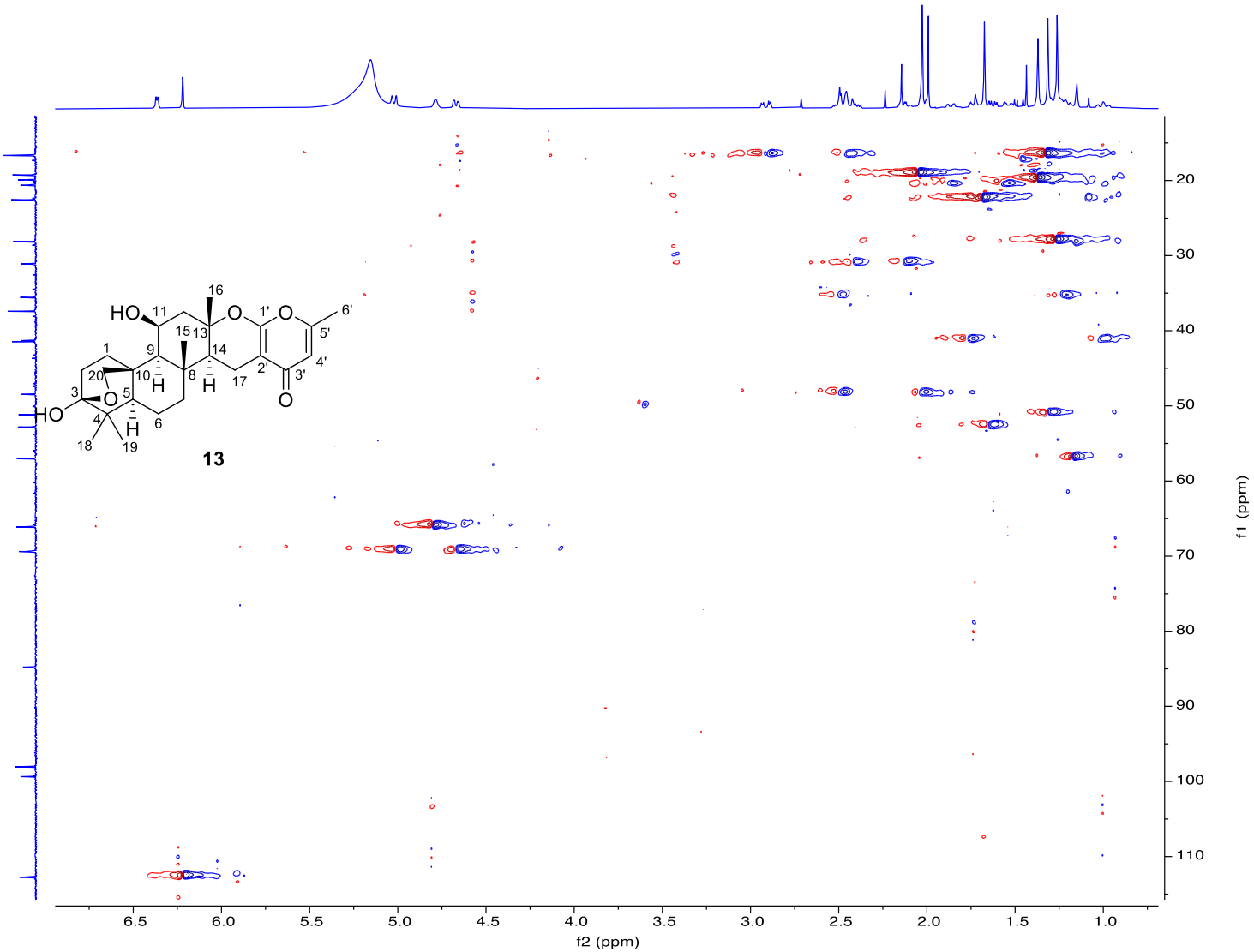

Figure S25. HSQC spectrum of chevalone Q (**13**).

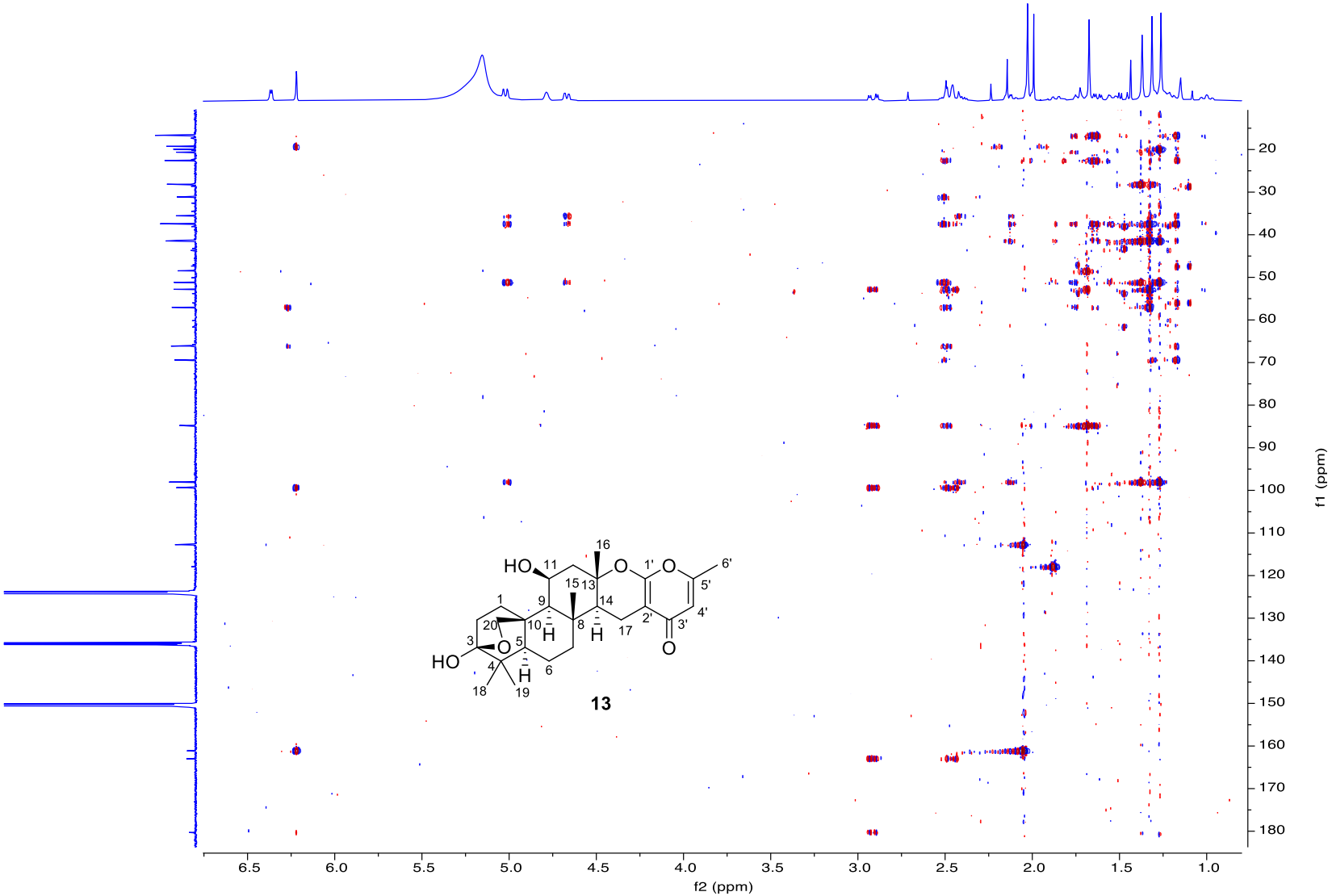

Figure S26. HMBC spectrum of chevalone Q (**13**).

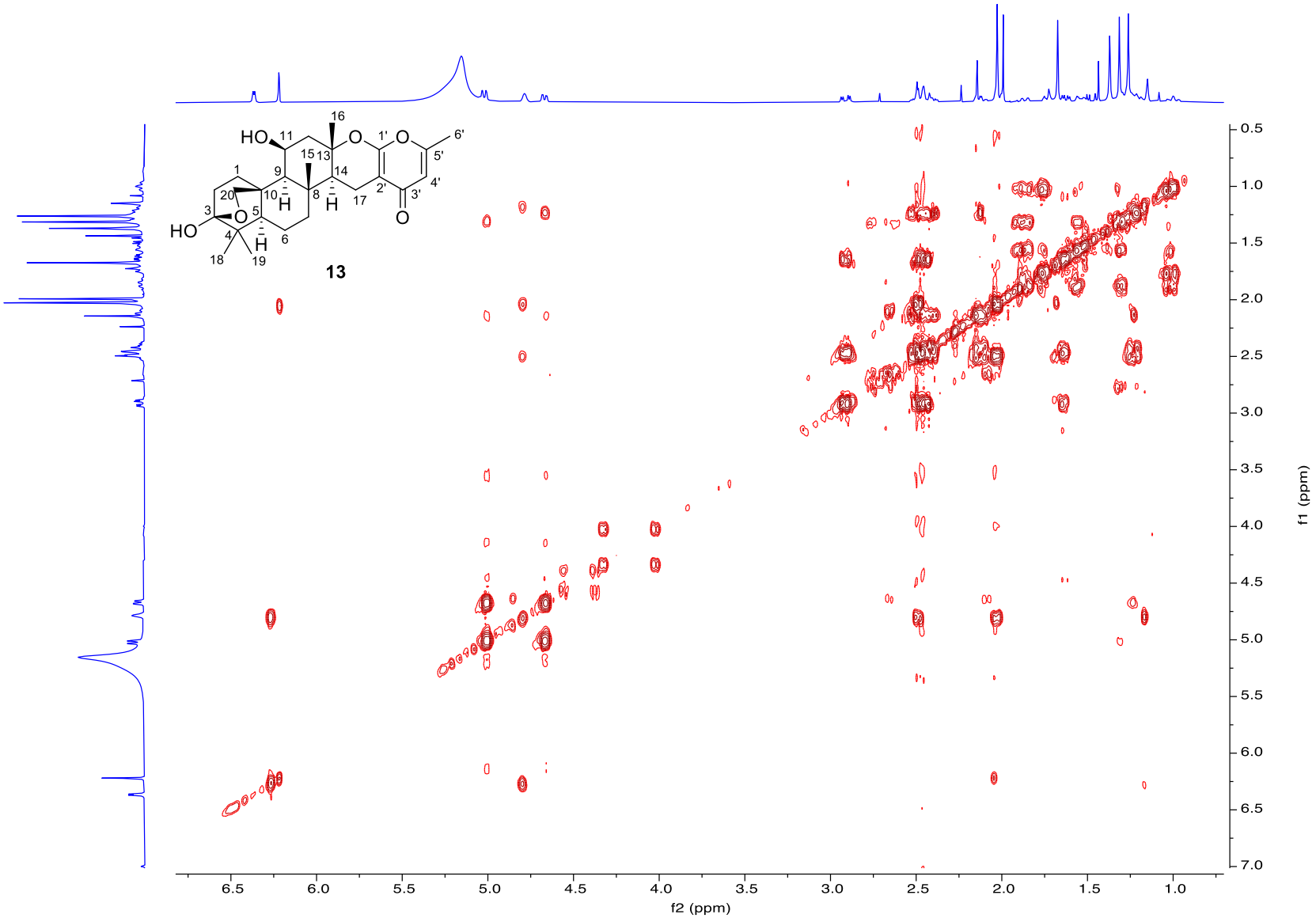

Figure S27. ^{1}H-^{1}H COSY spectrum of chevalone Q (**13**).

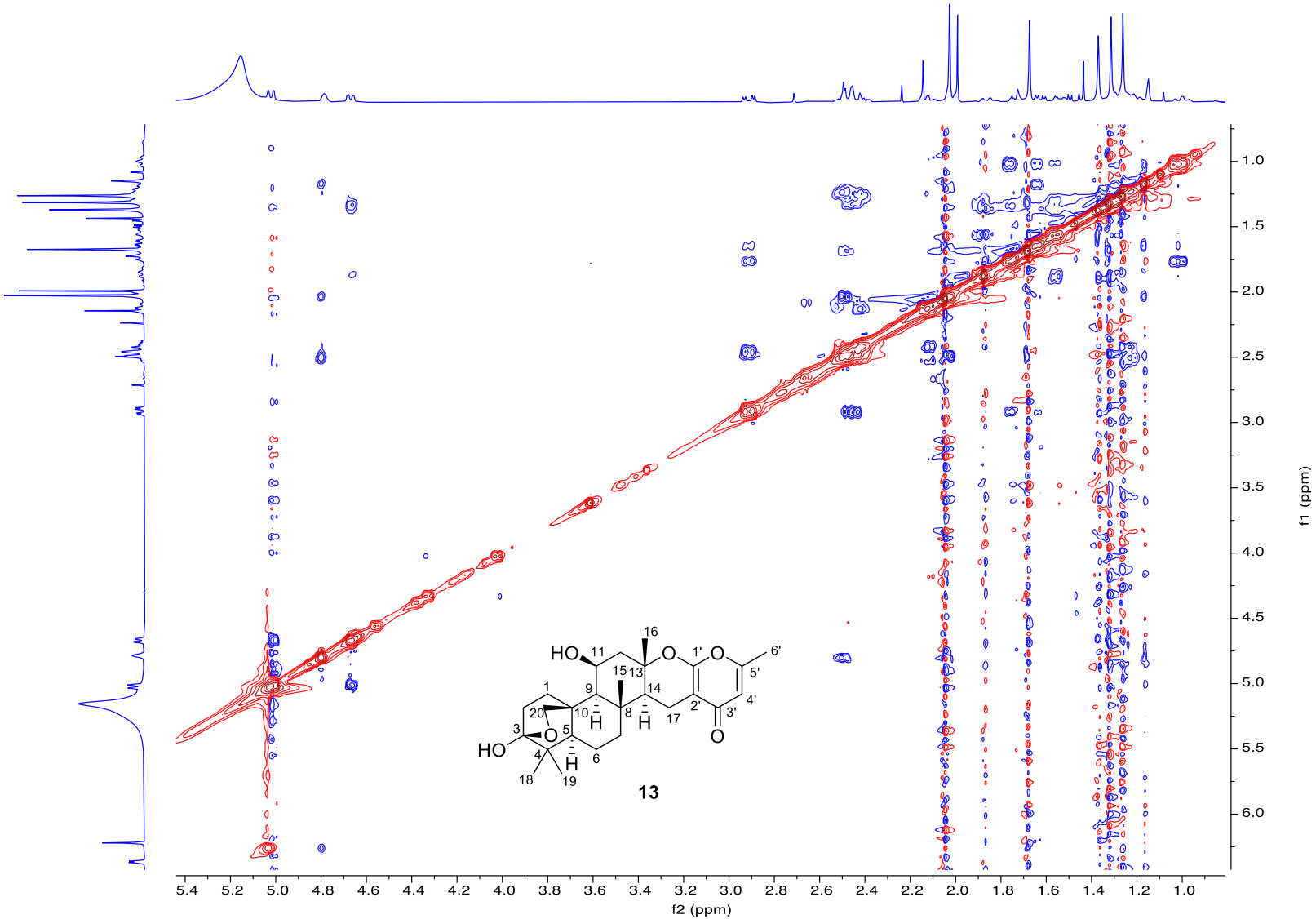

Figure S28. ROESY spectrum of chevalone Q (**13**).

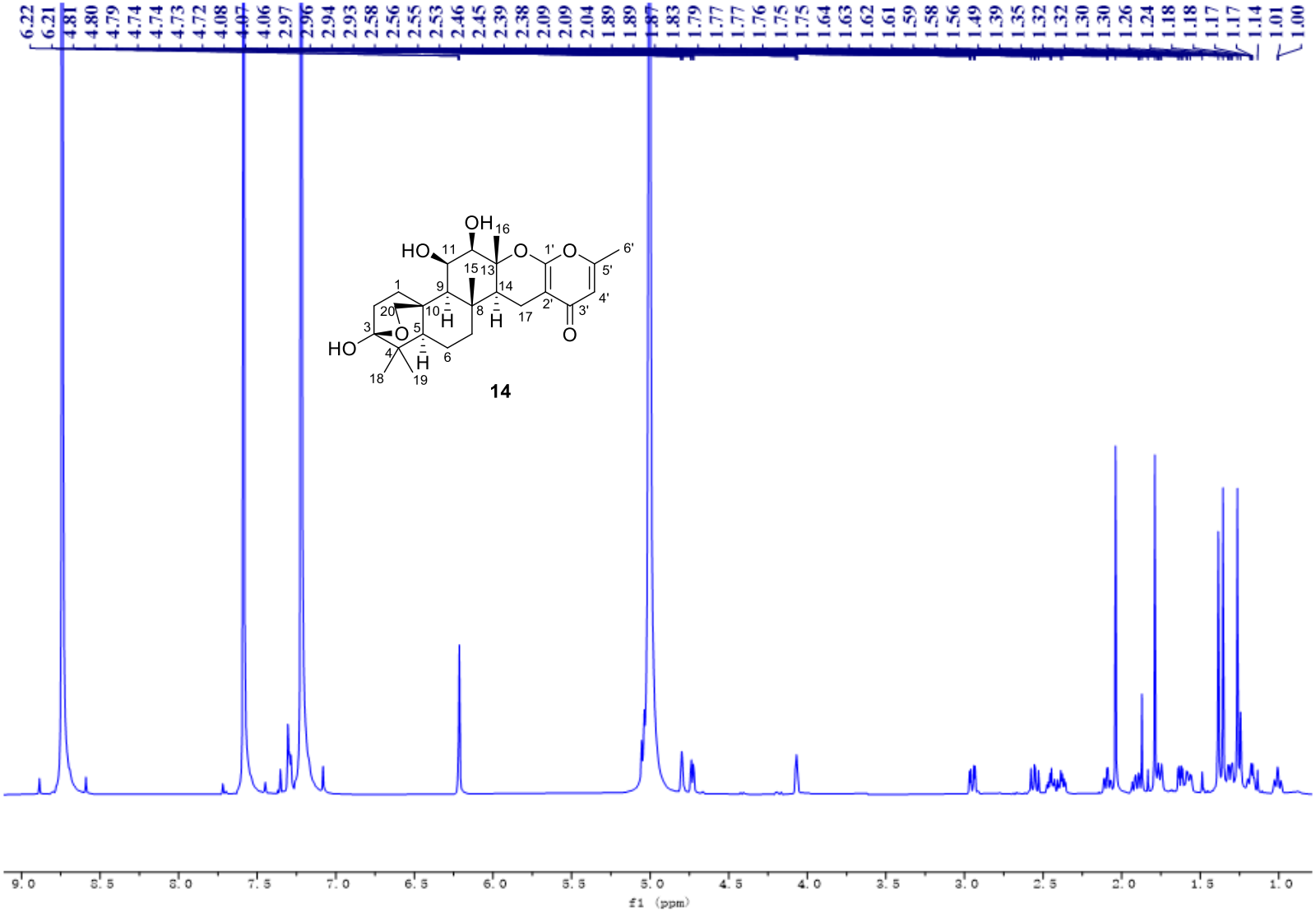

Figure S29. ^{1}H NMR spectrum of chevalone R (**14**).

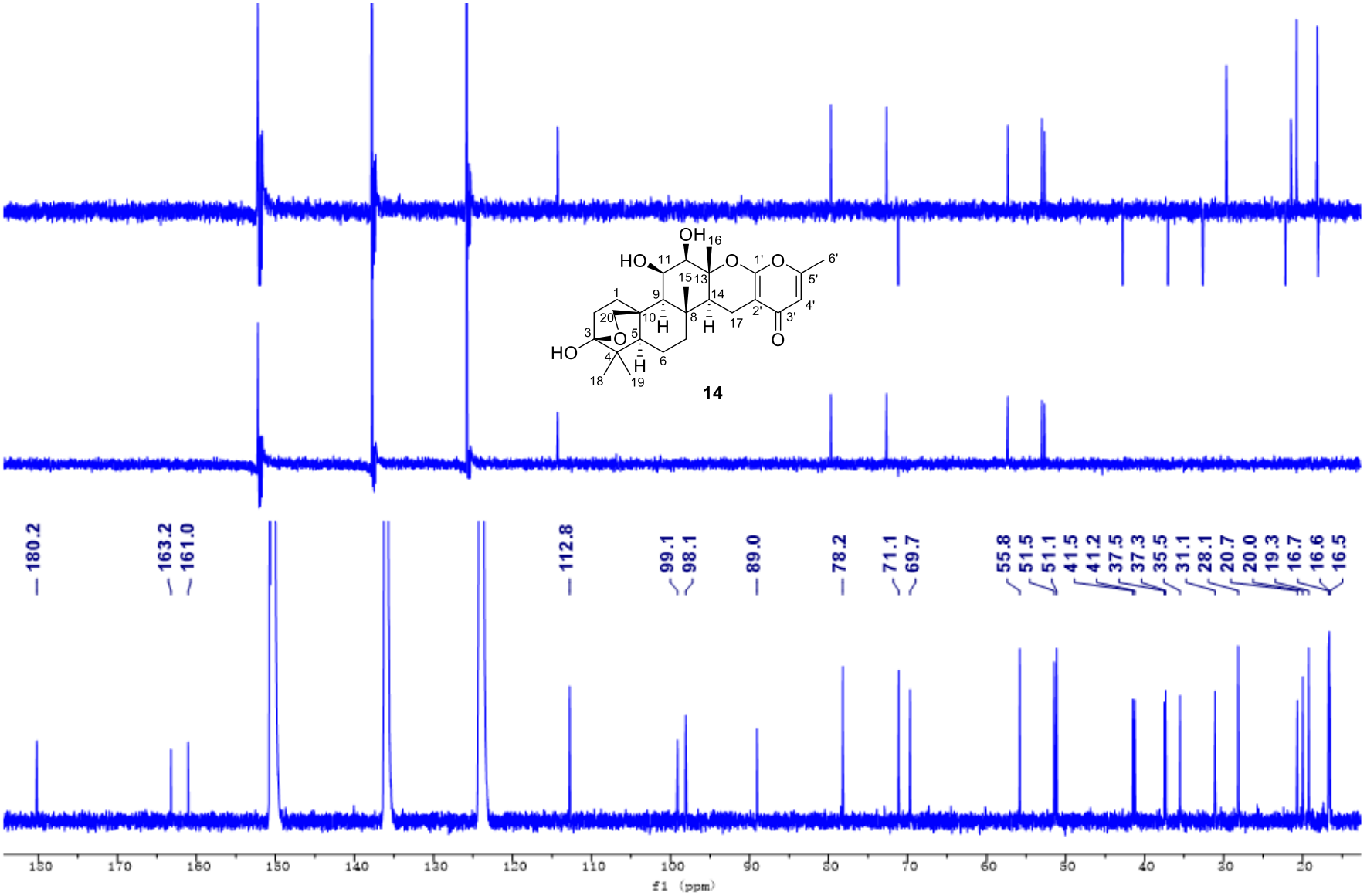

Figure S30. ^{13}C NMR spectrum of chevalone R (**14**).

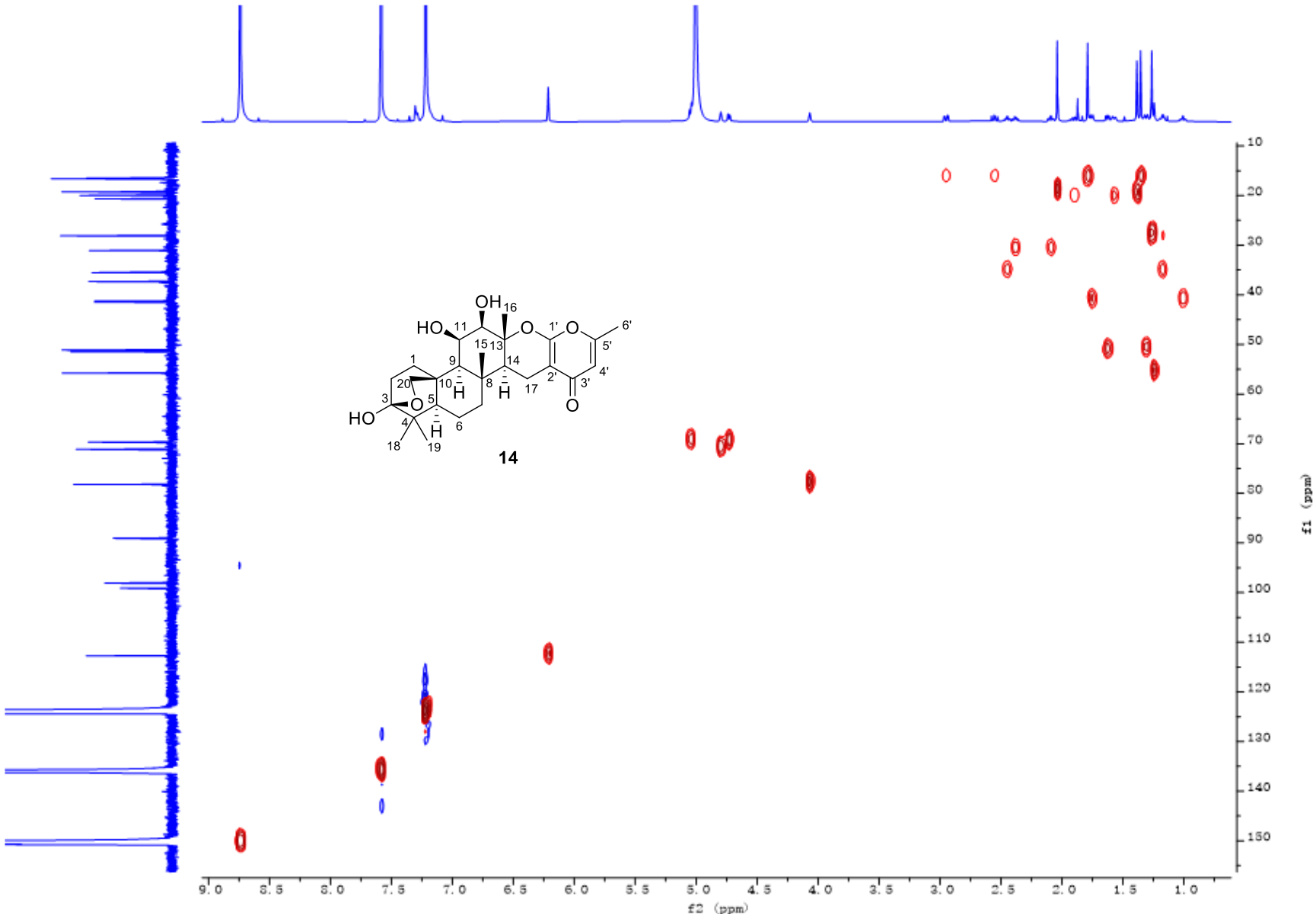

Figure S31. HSQC spectrum of chevalone R (**14**).

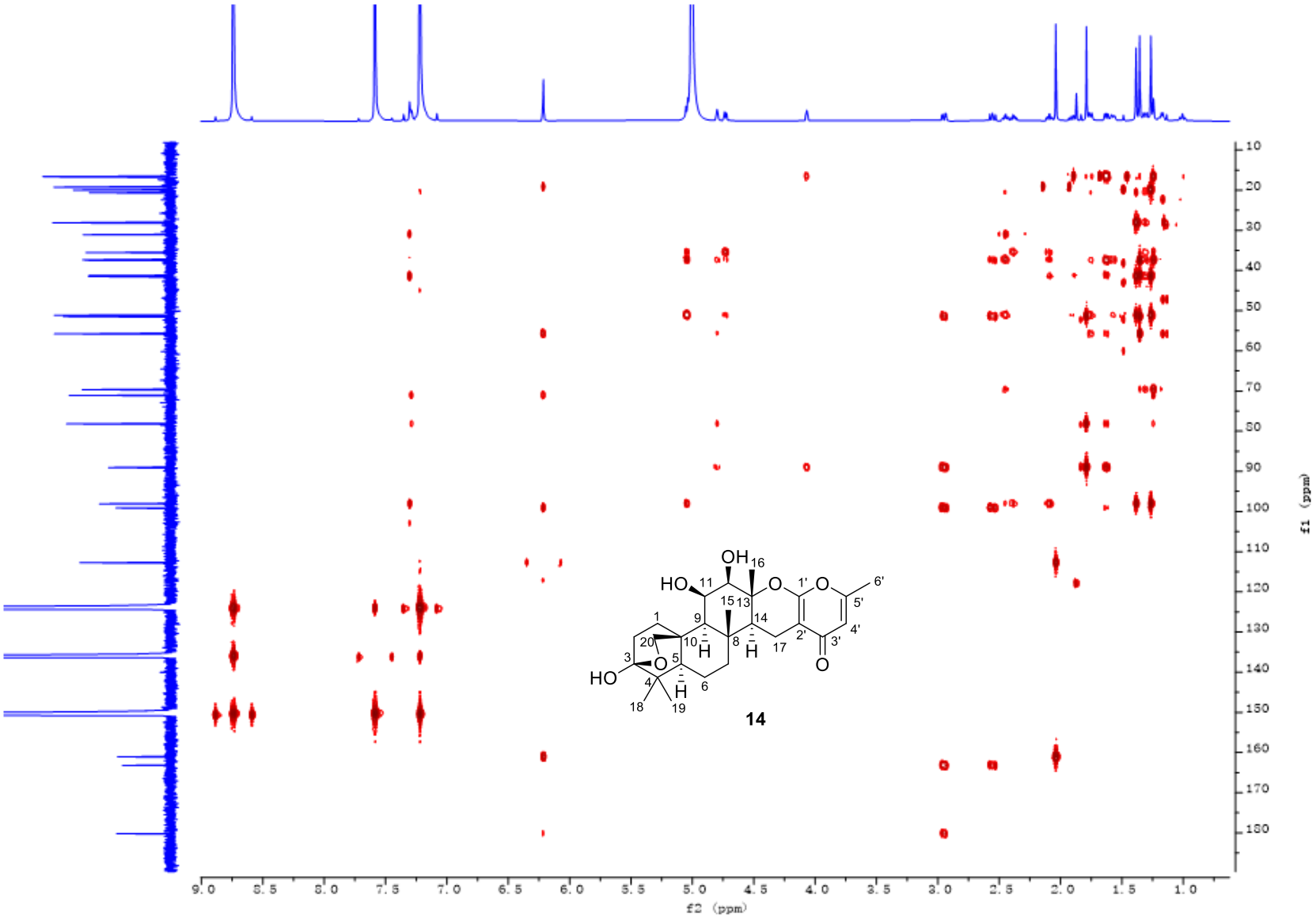

Figure S32. HMBC spectrum of chevalone R (**14**).

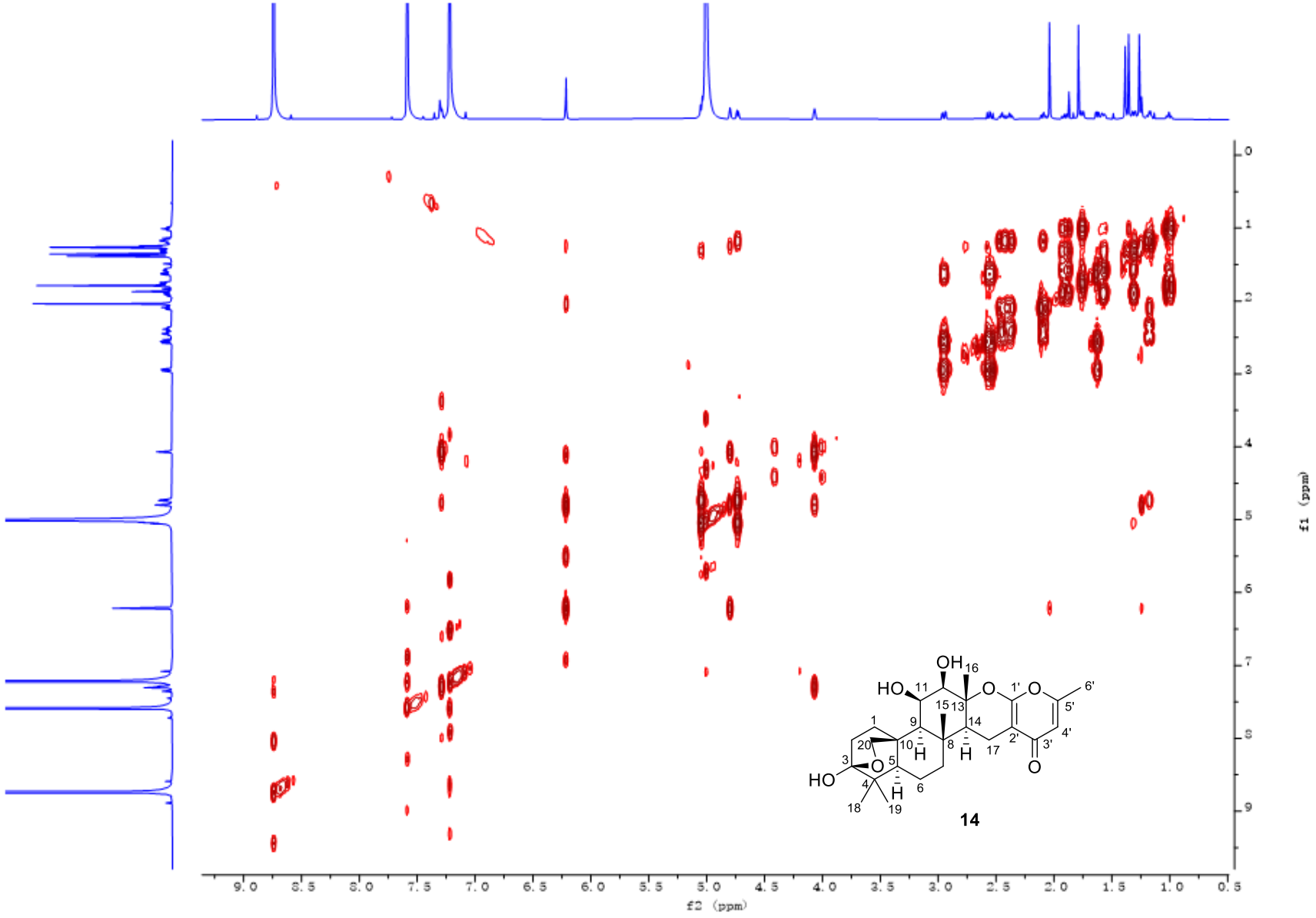

Figure S33. ^{1}H-^{1}H COSY spectrum of chevalone R (**14**).

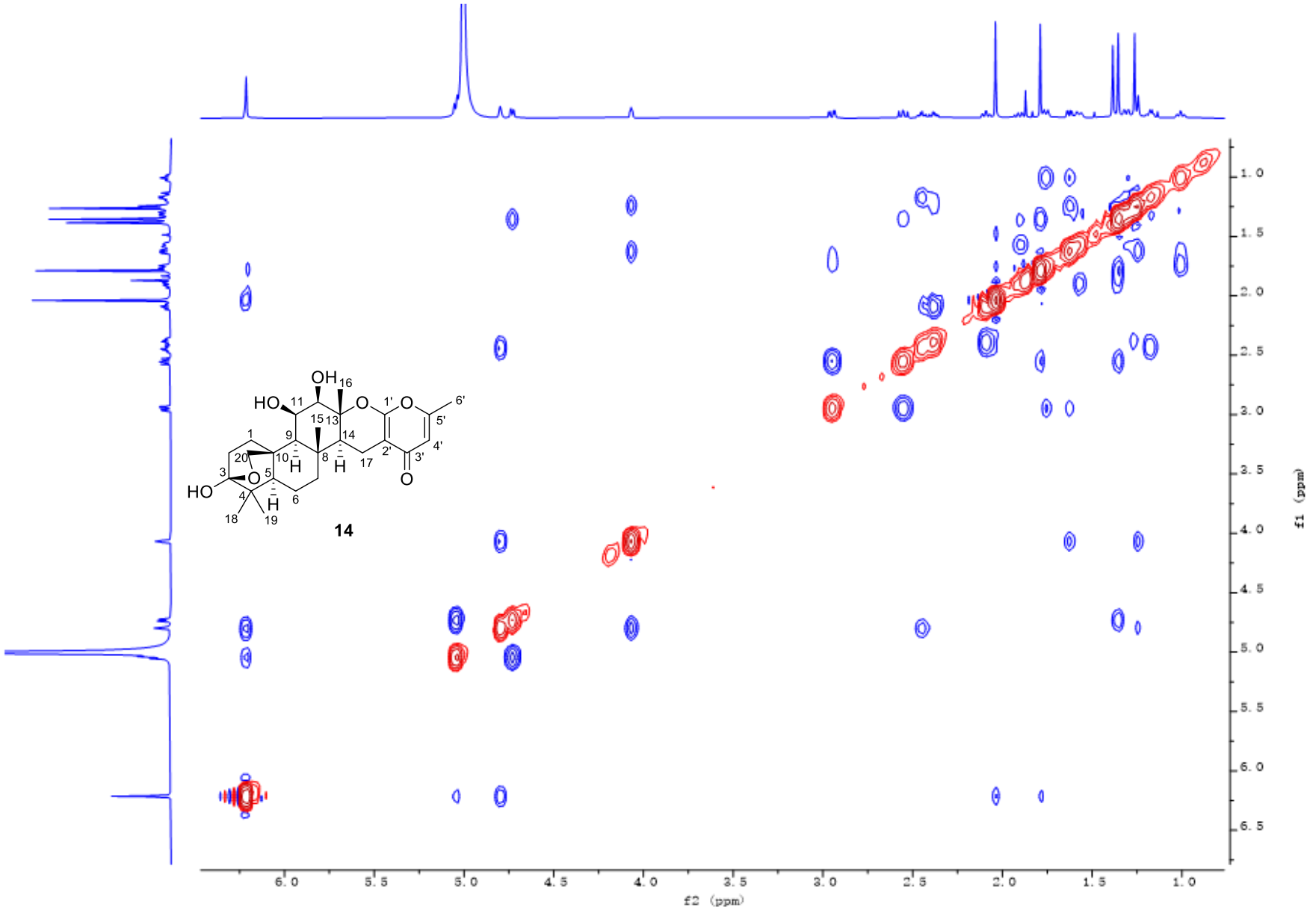

Figure S34. ROESY spectrum of chevalone R (**14**).

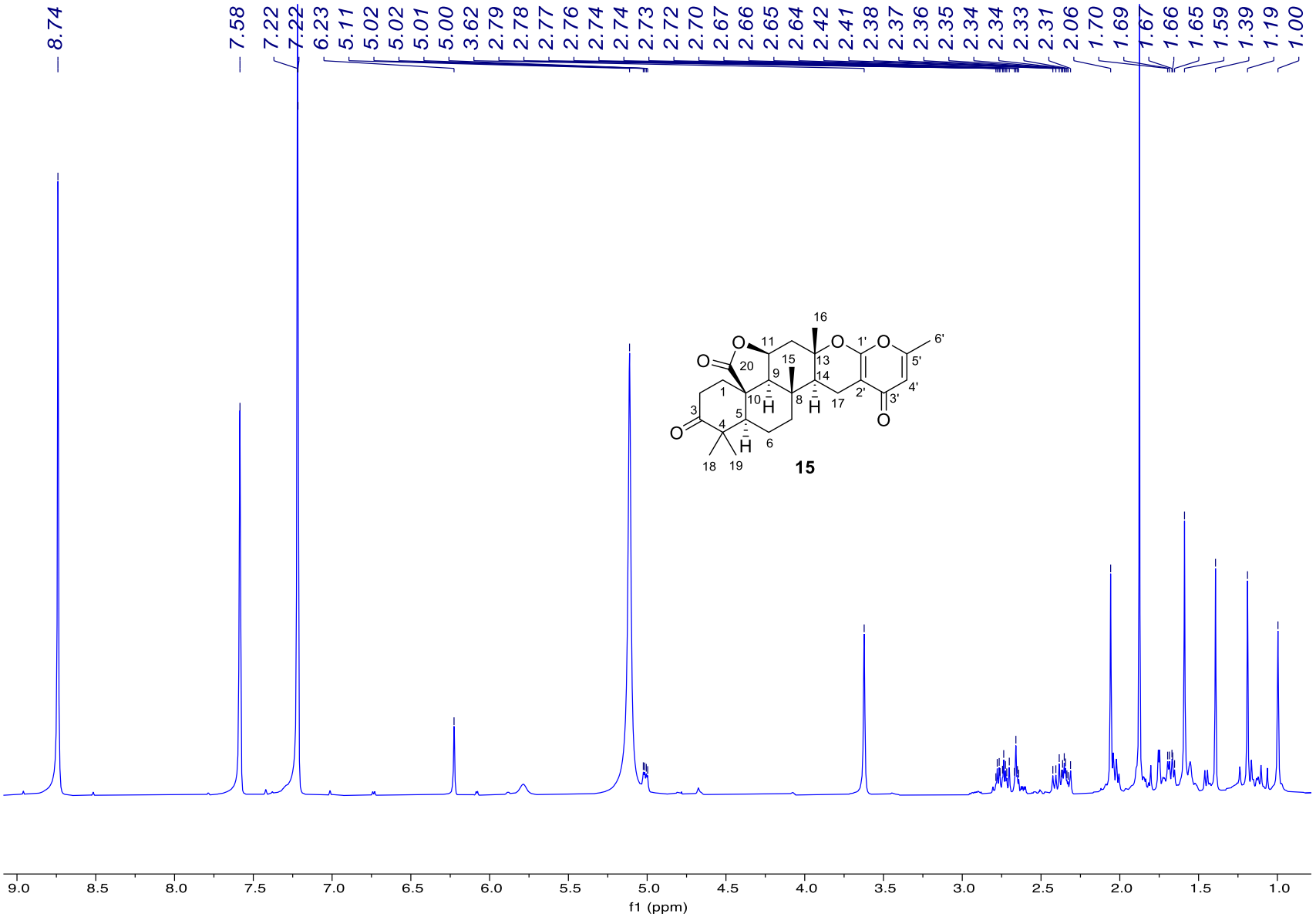

Figure S35. ^{1}H NMR spectrum of chevalone S (**15**).

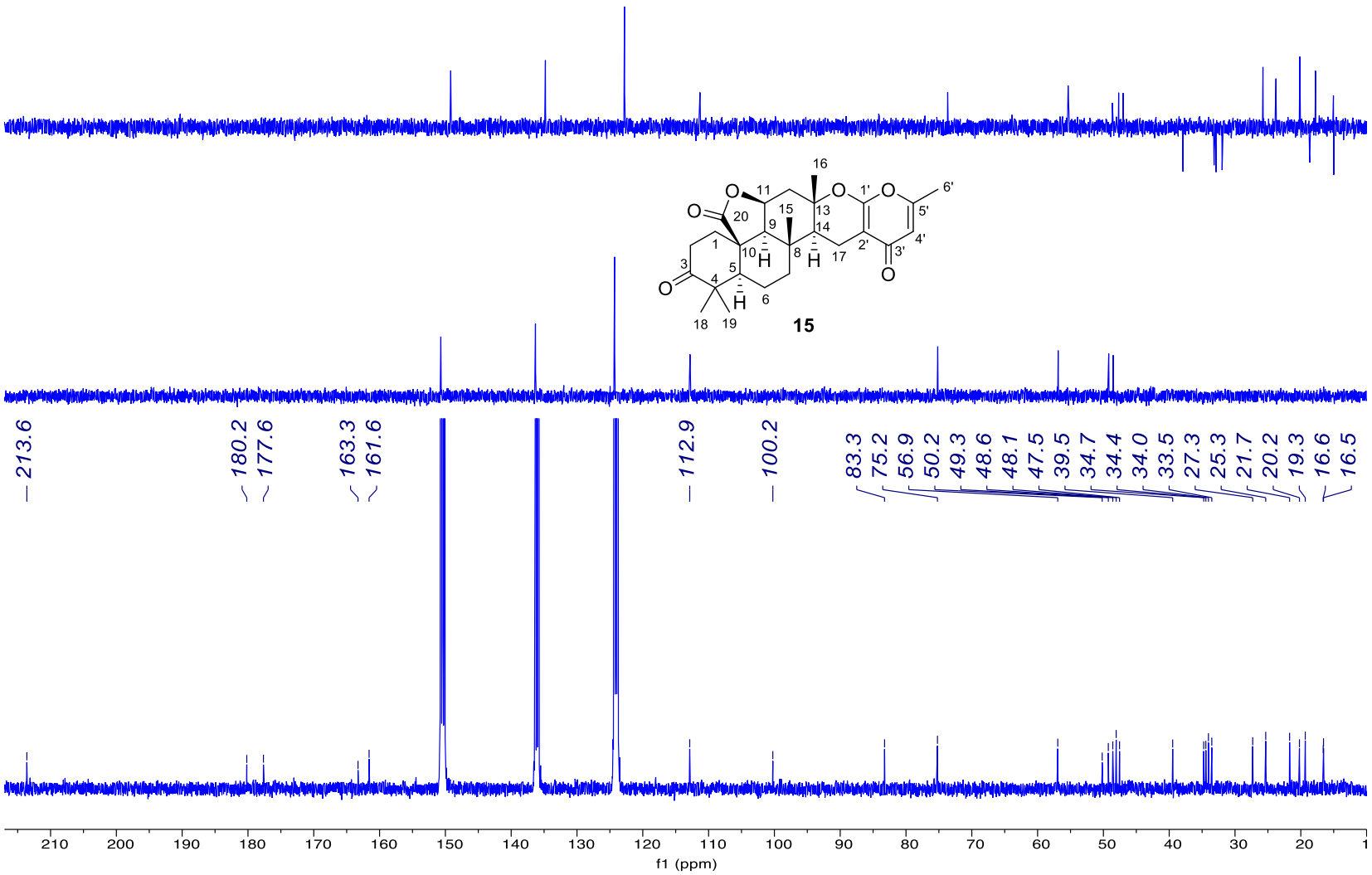

Figure S36. ^{13}C NMR spectrum of chevalone S (**15**).

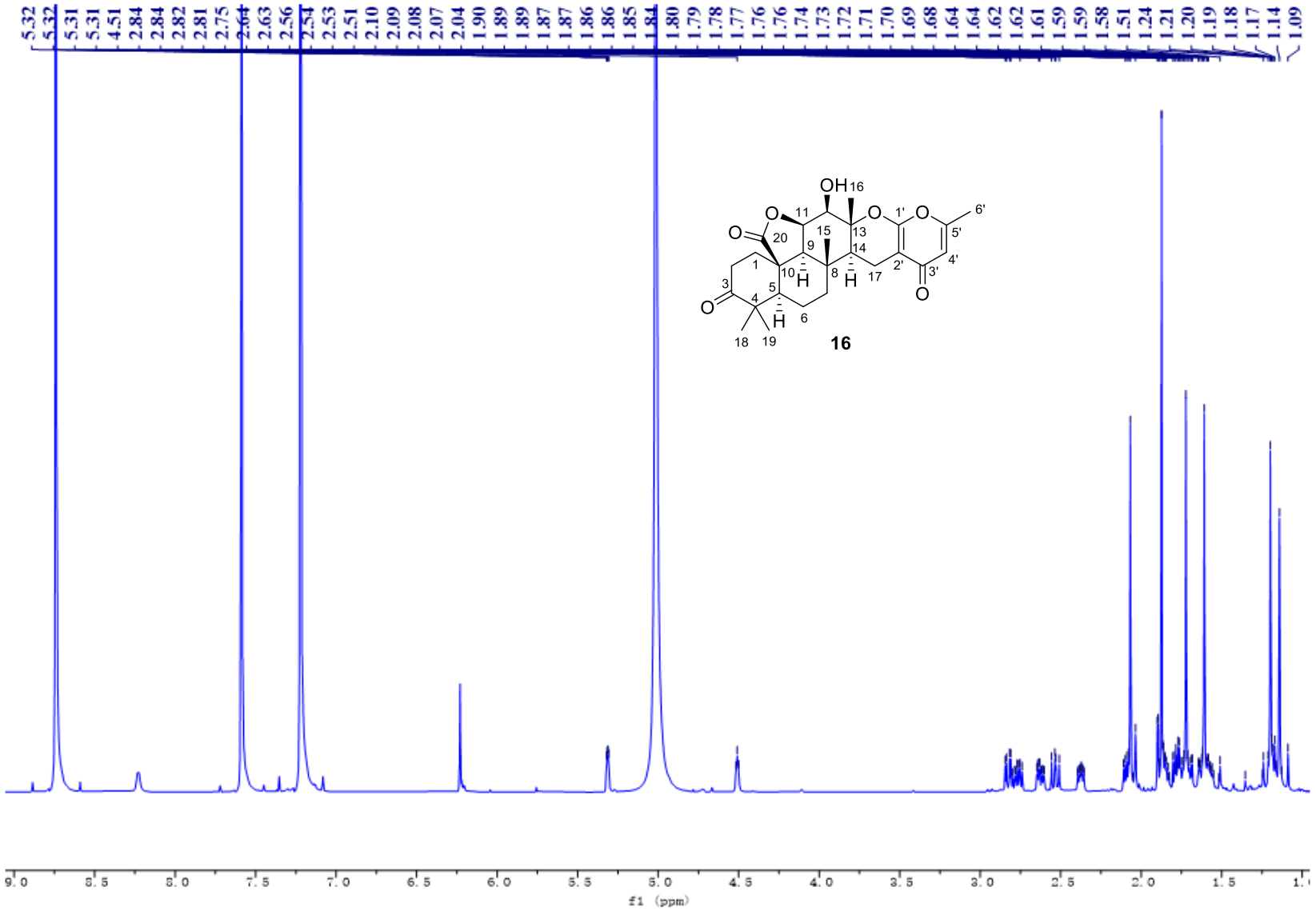

Figure S37. ^{1}H NMR spectrum of chevalone T (**16**).

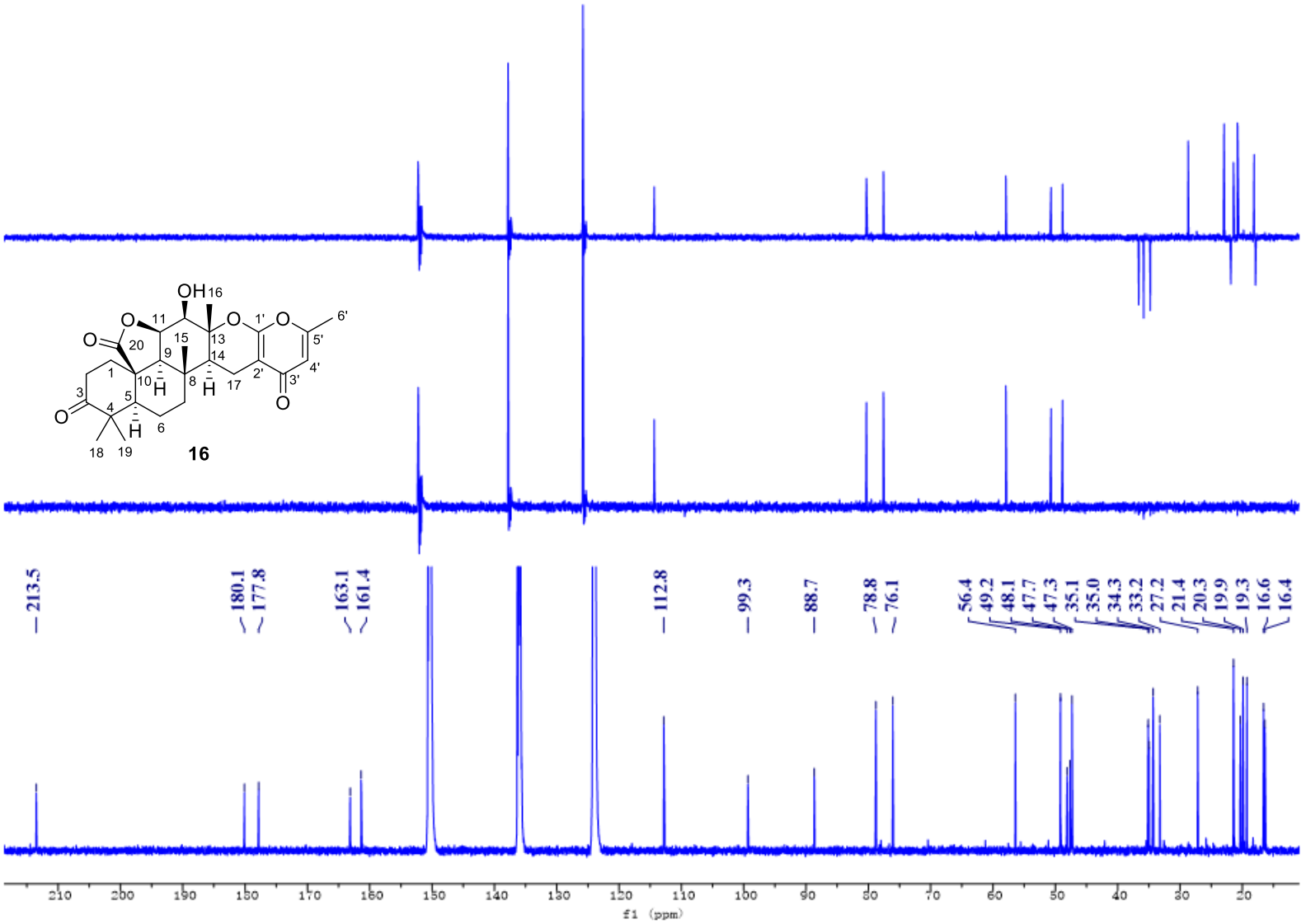

Figure S38. ^{13}C NMR spectrum of chevalone T (**16**).

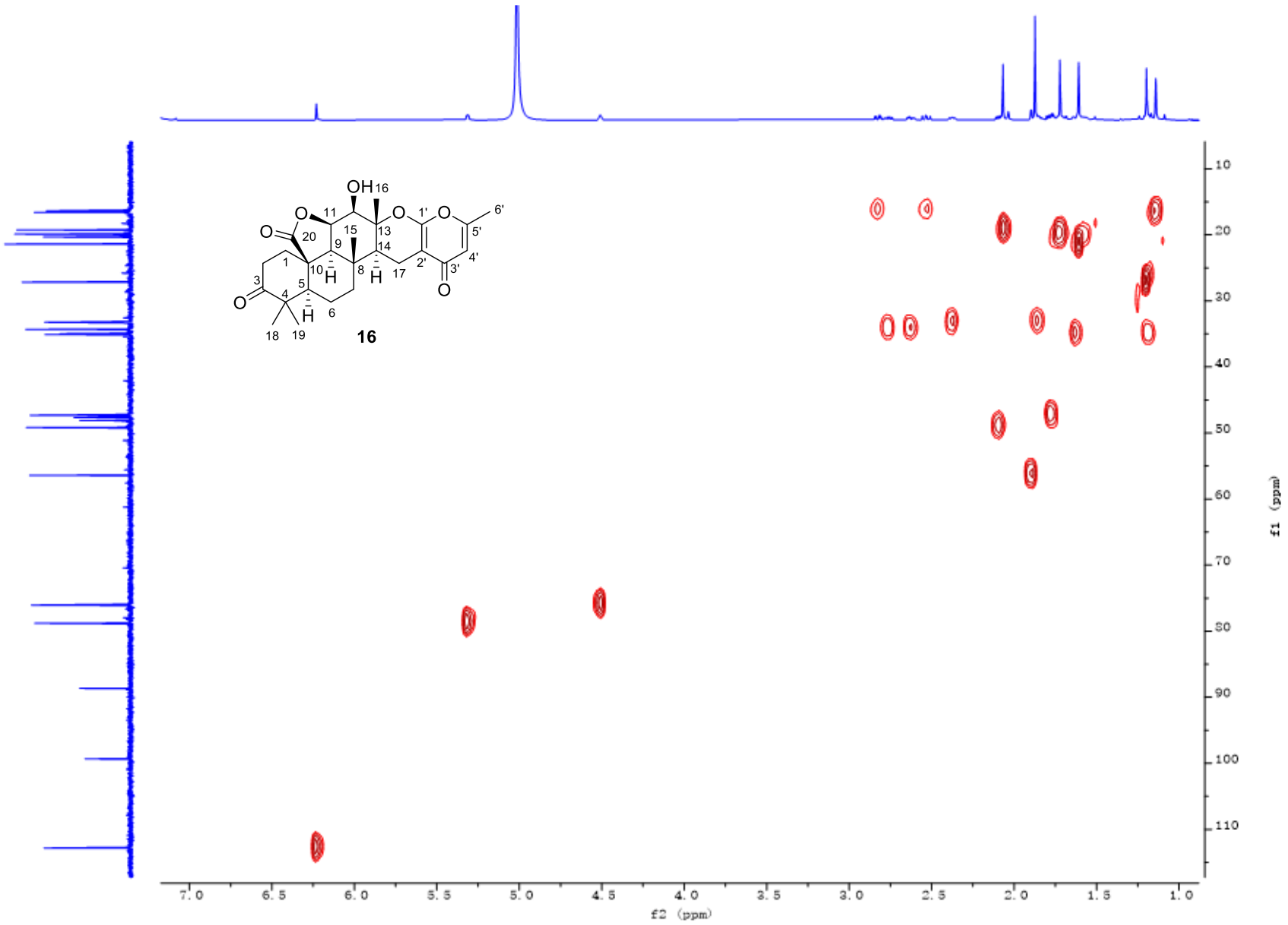

Figure S39. HSQC spectrum of chevalone T (**16**).

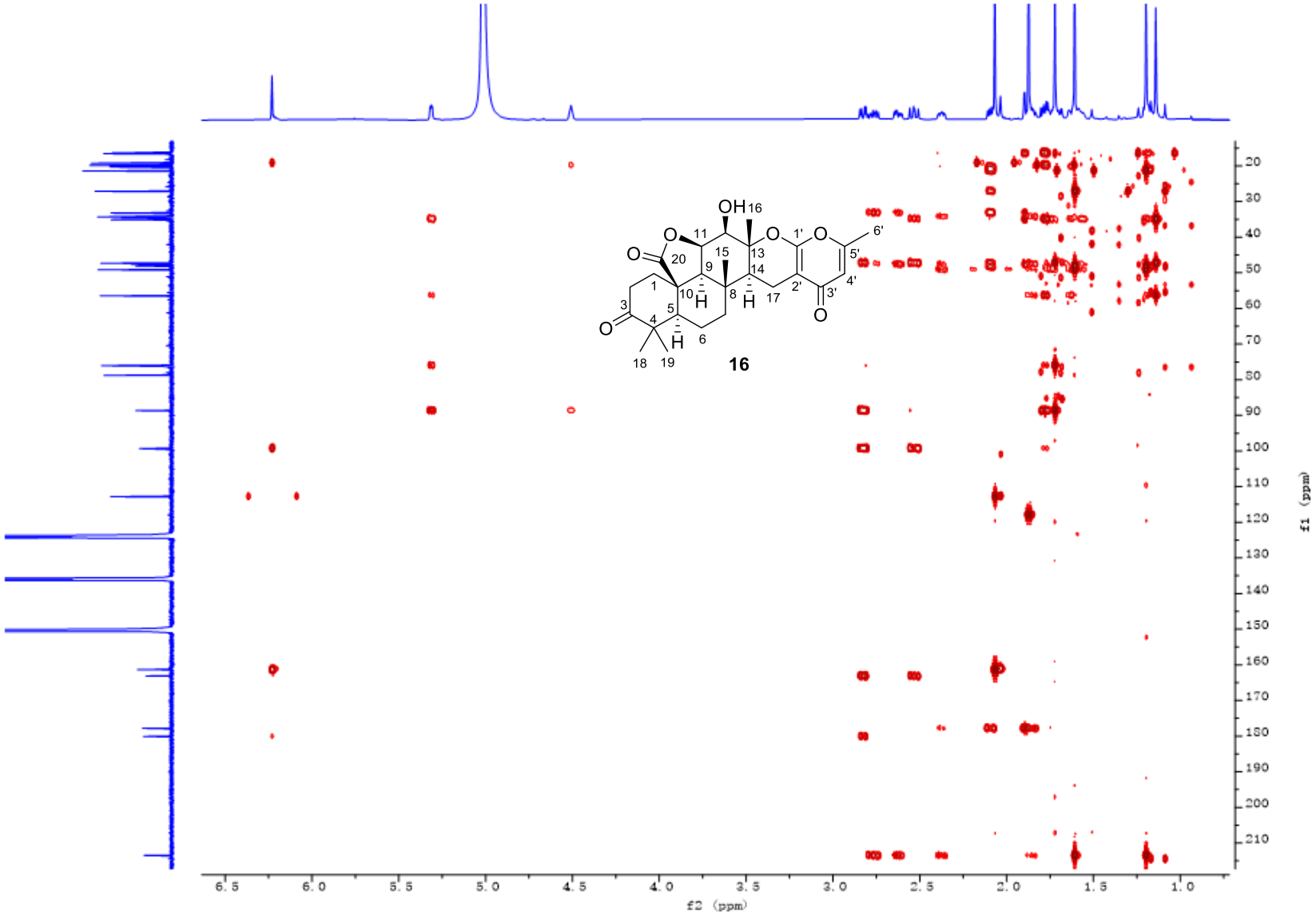

Figure S40. HMBC spectrum of chevalone T (**16**).

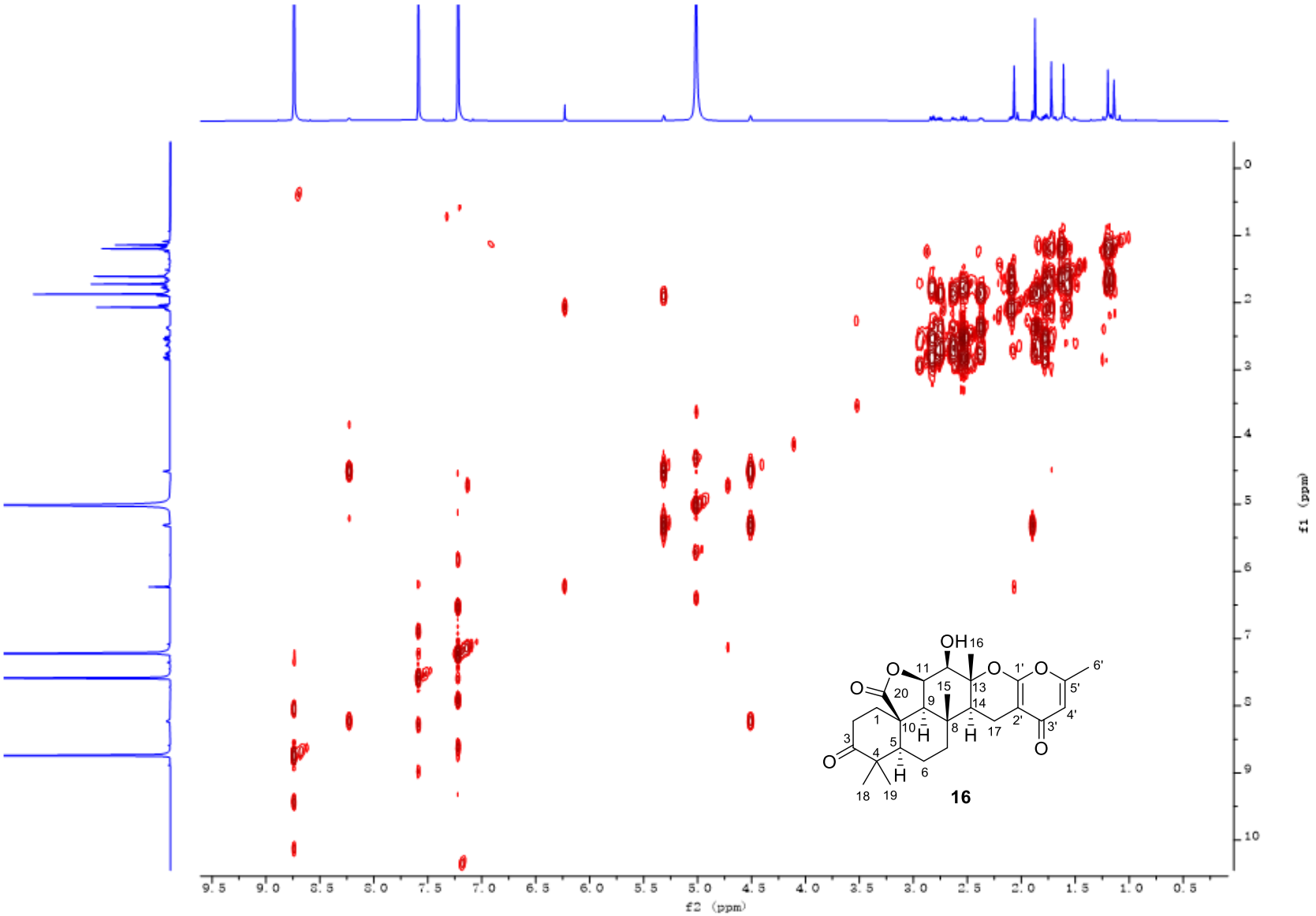

Figure S41. ^{1}H-^{1}H COSY spectrum of chevalone T (**16**).

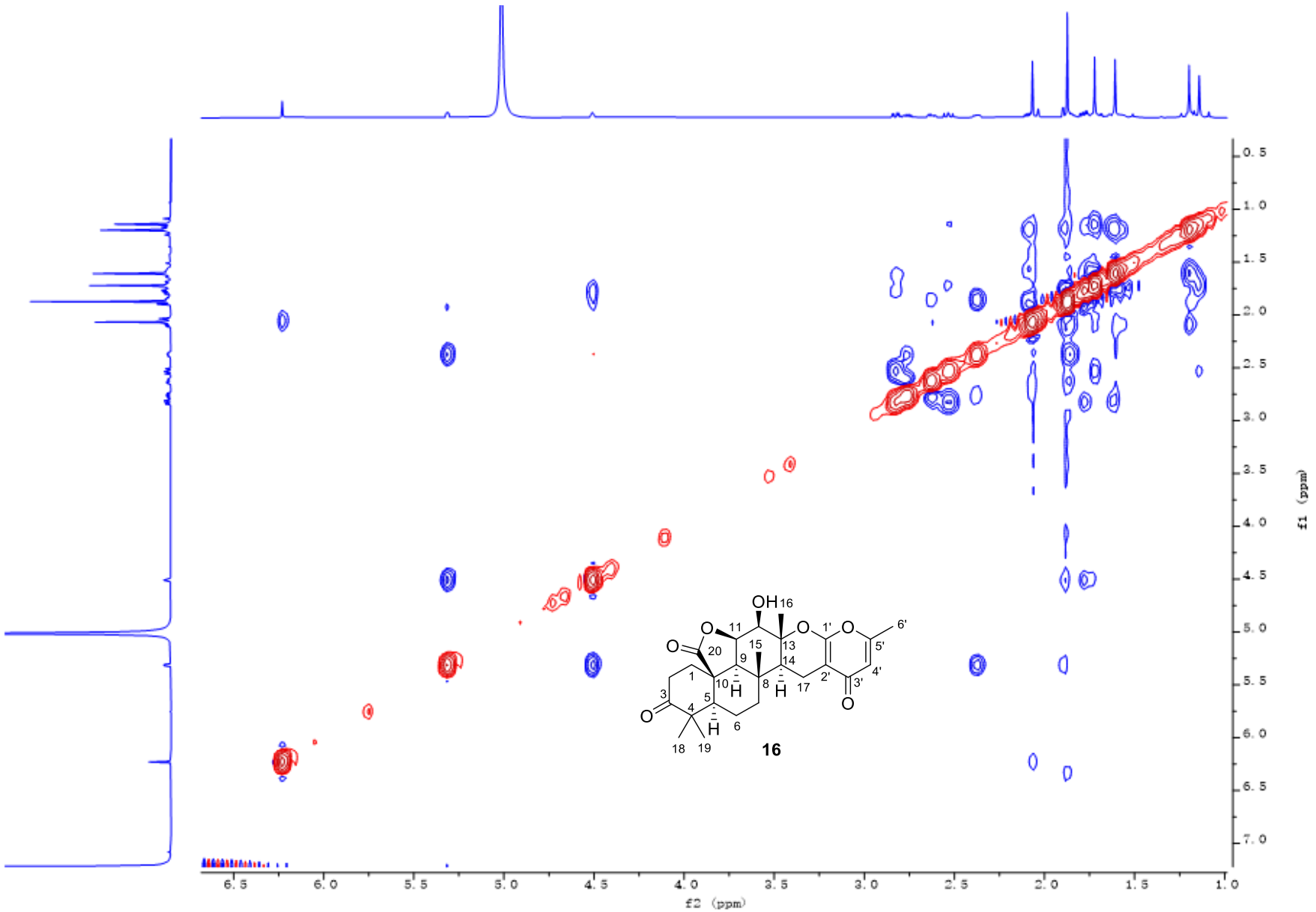

Figure S42. ROESY spectrum of chevalone T (**16**).

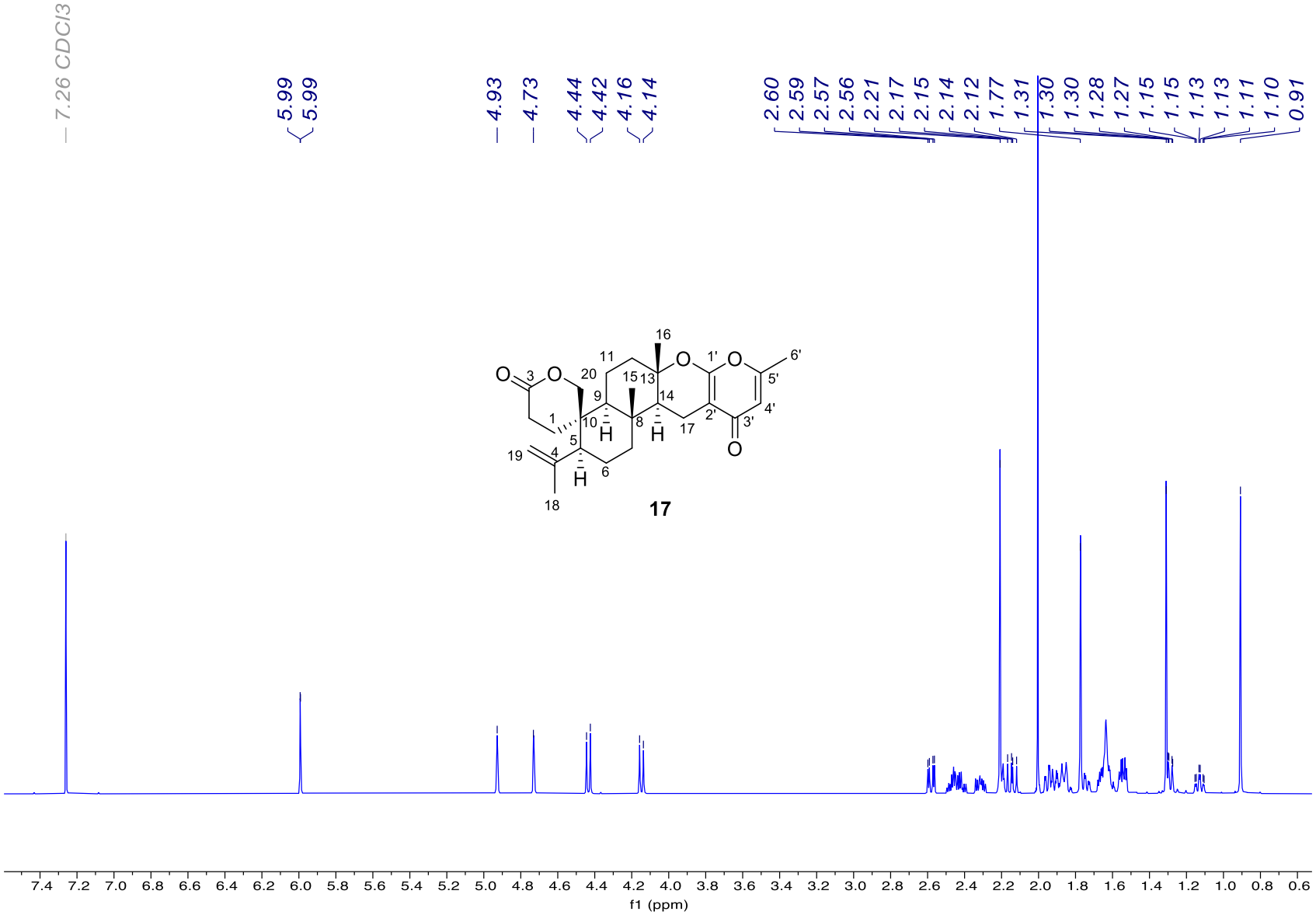

Figure S43. ^{1}H NMR spectrum of **17**.

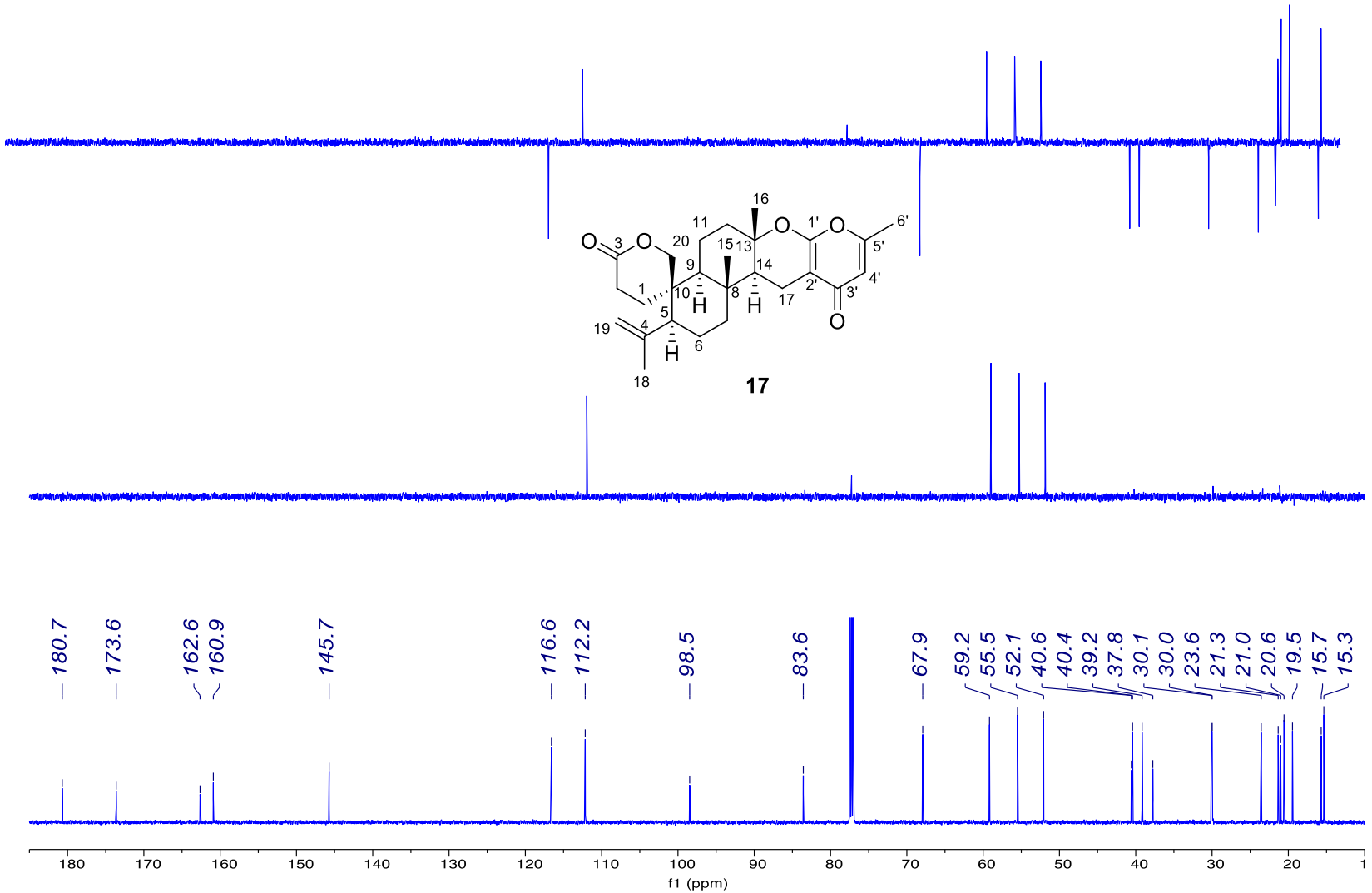

Figure S44. ^{13}C NMR spectrum of **17**.

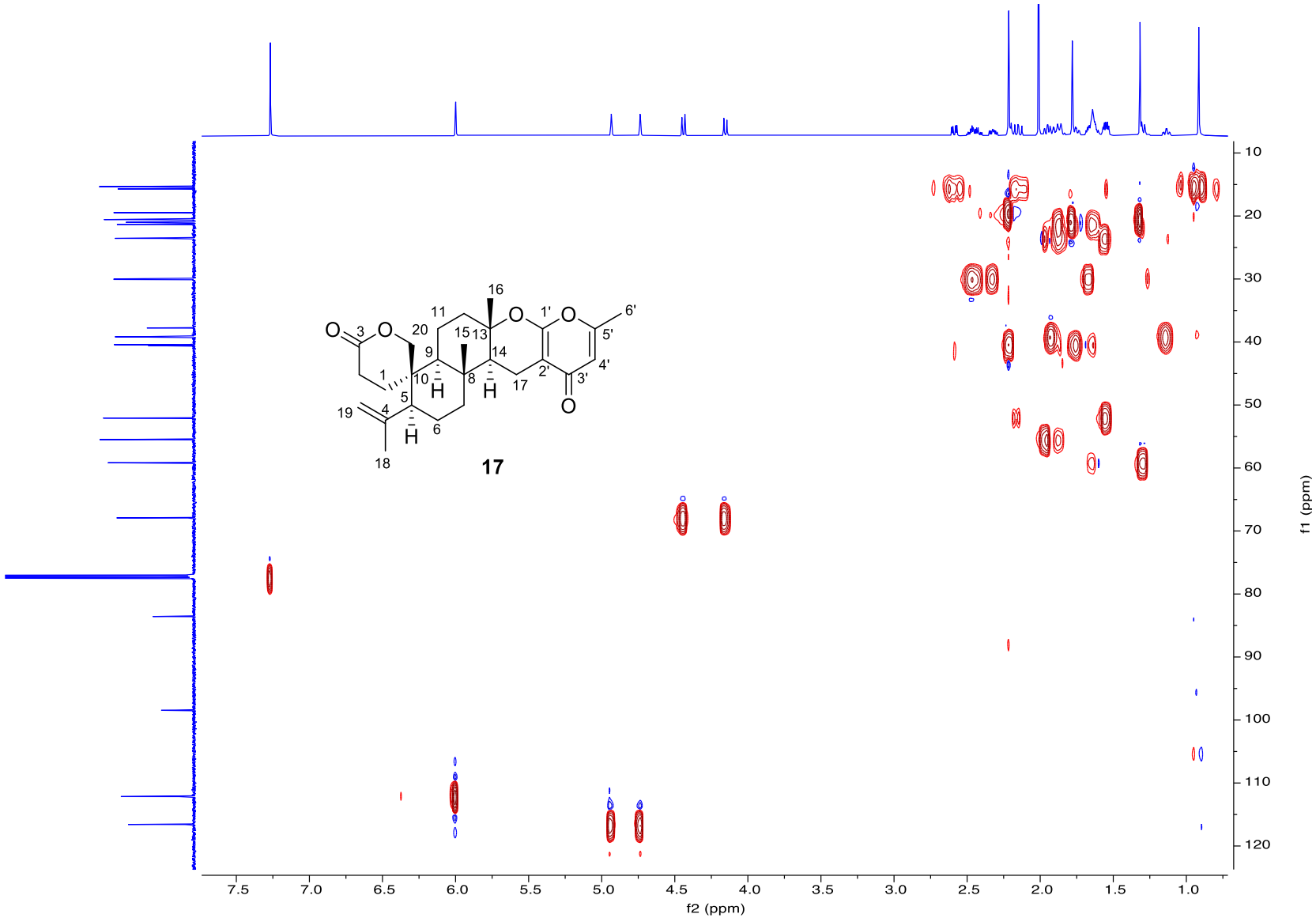

Figure S45. HSQC spectrum of **17**.

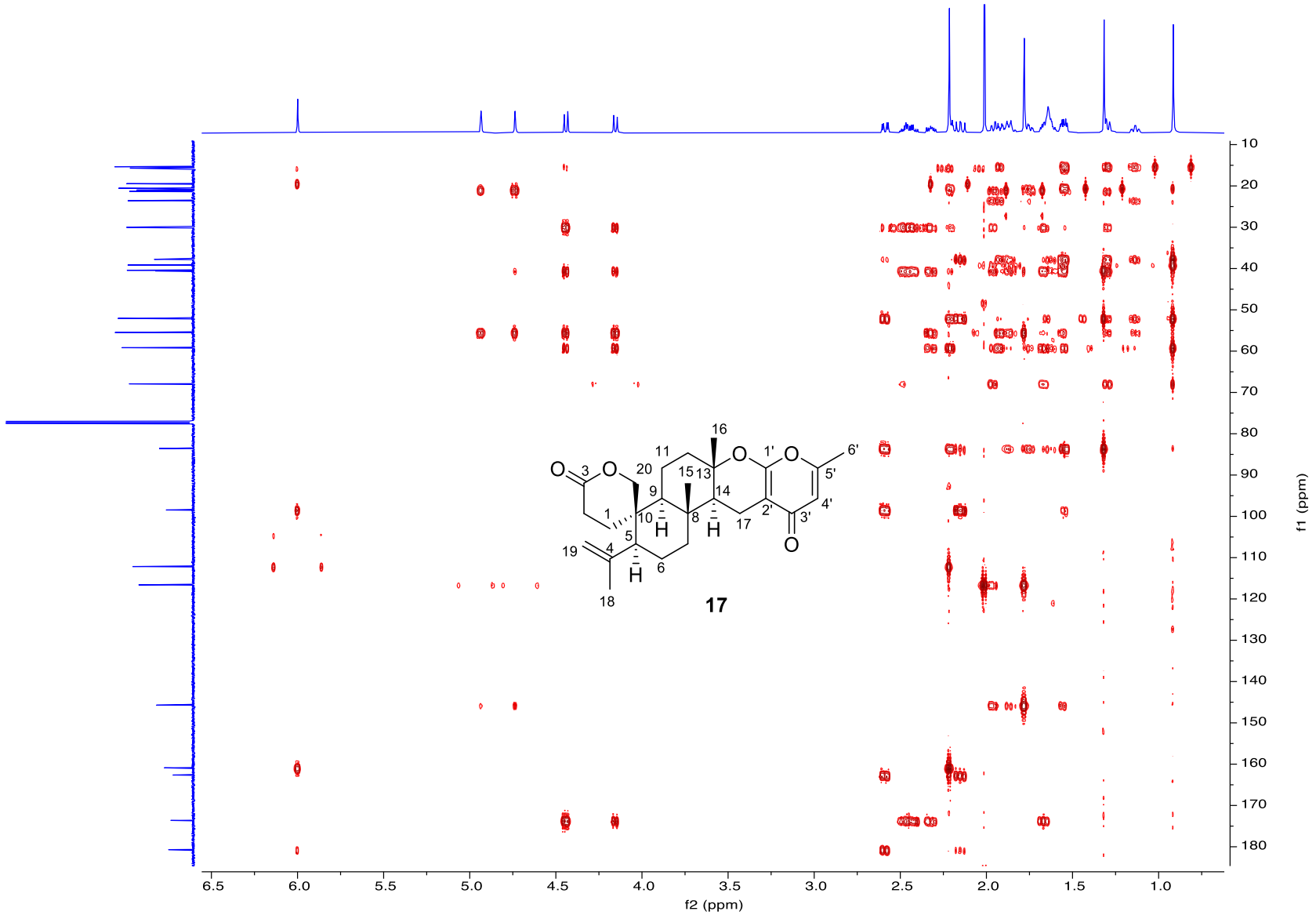

Figure S46. HMBC spectrum of **17**.

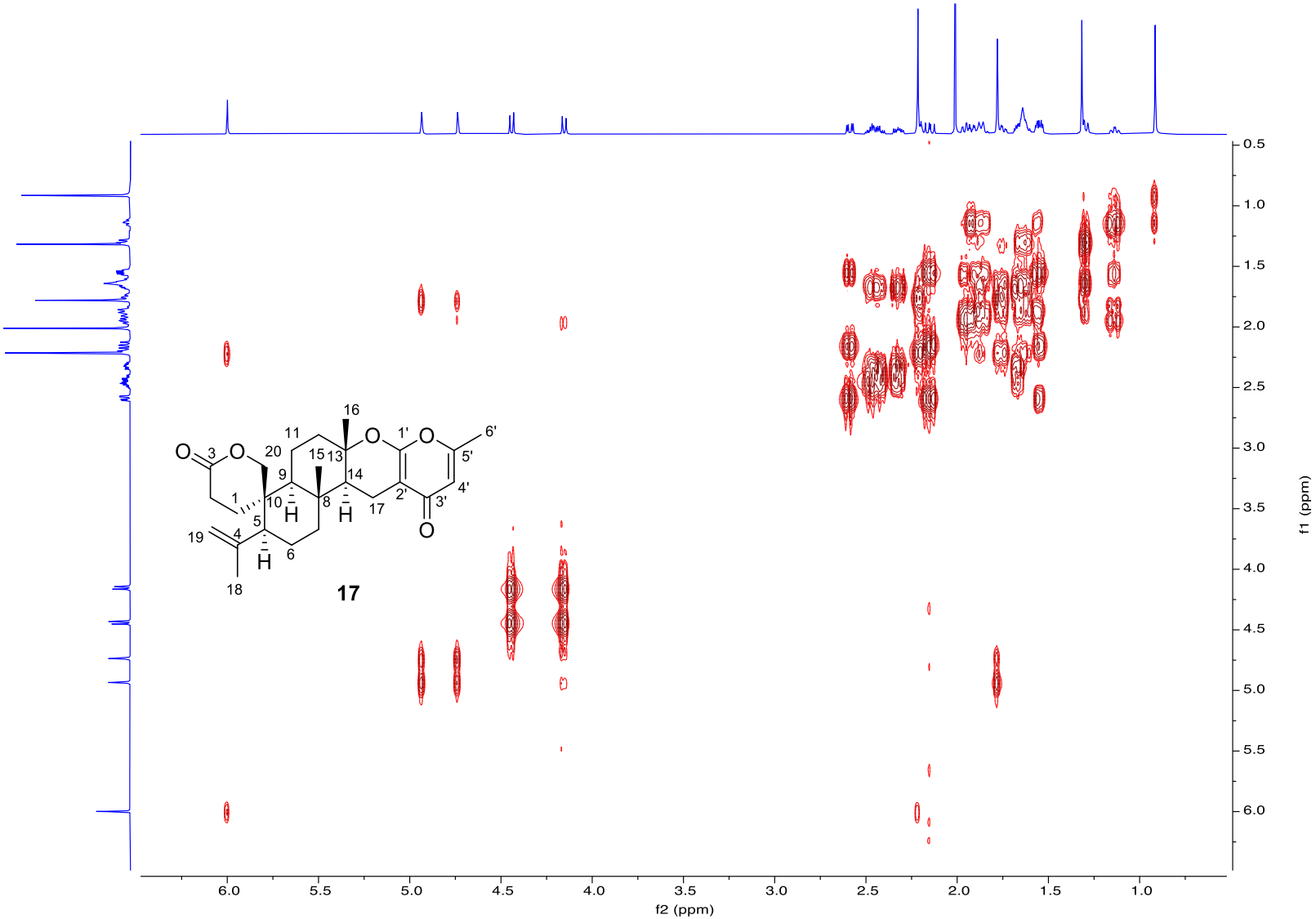

Figure S47. ^{1}H-^{1}H COSY spectrum of **17**.

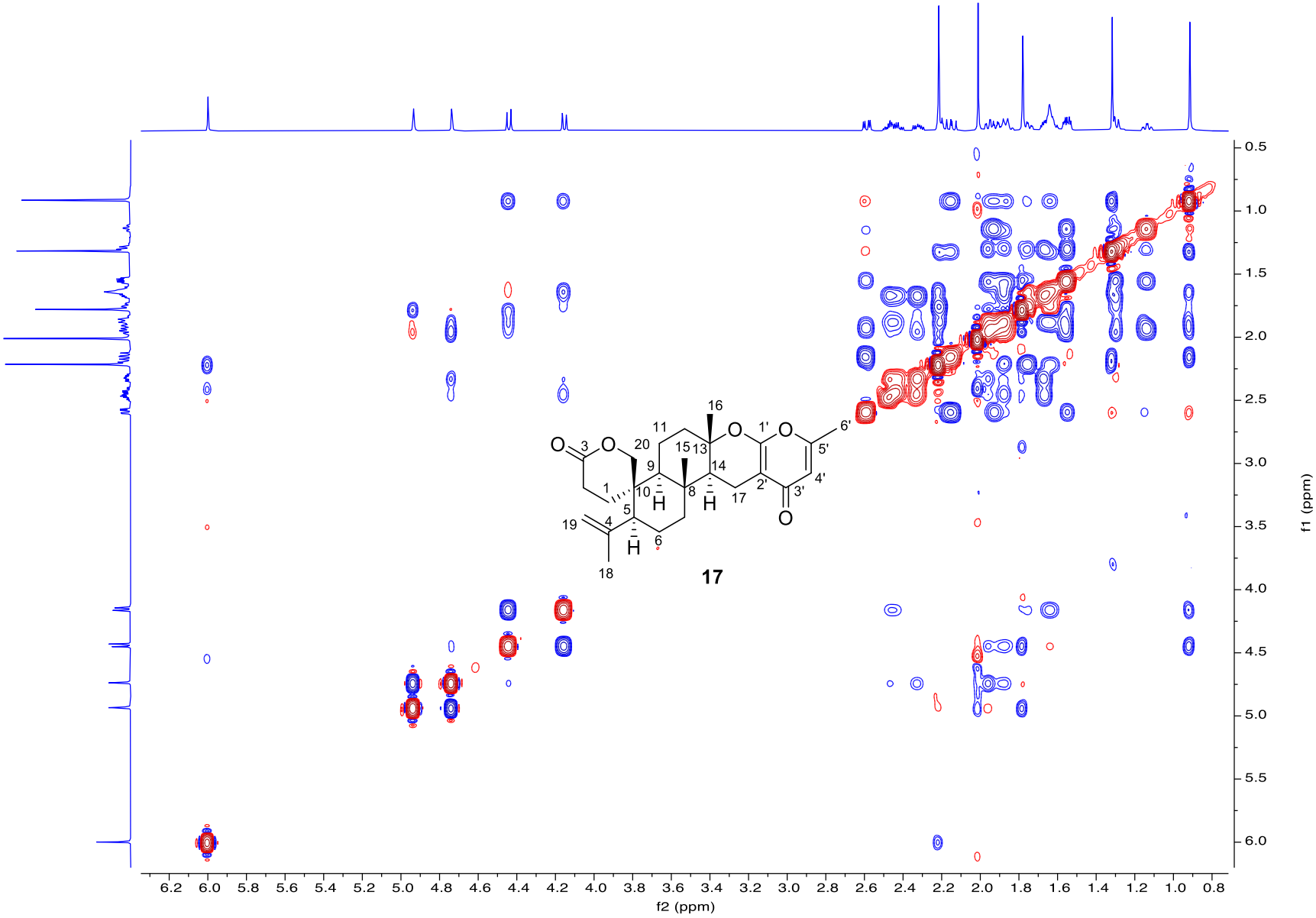

Figure S48. ROESY spectrum of **17**.

Supplementary References

1. J. Paluka, K. Kanokmedhakul, M. Soytong, K. Soytong and S. Kanokmedhakul, *Fitoterapia*, 2019, **137**, 104257.
2. A. Boto, R. Freire, R. Hernández, E. Suárez and M. S. Rodríguez, *J. Org. Chem.*, 1997, **62**, 2975-2981.