SUPPORTING INFORMATION

Defensive Diterpene from the Aeolidoidean *Phyllodesmium longicirrum* (Gastropoda, Heterobranchia, Nudibranchia)

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Dedicated to Professors John Blunt and Murray Munro, of University of Canterbury, for their pioneering work on bioactive marine natural products.

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Figure S1: ^{1}H NMR spectrum of compound **1** in MeOH-d_4

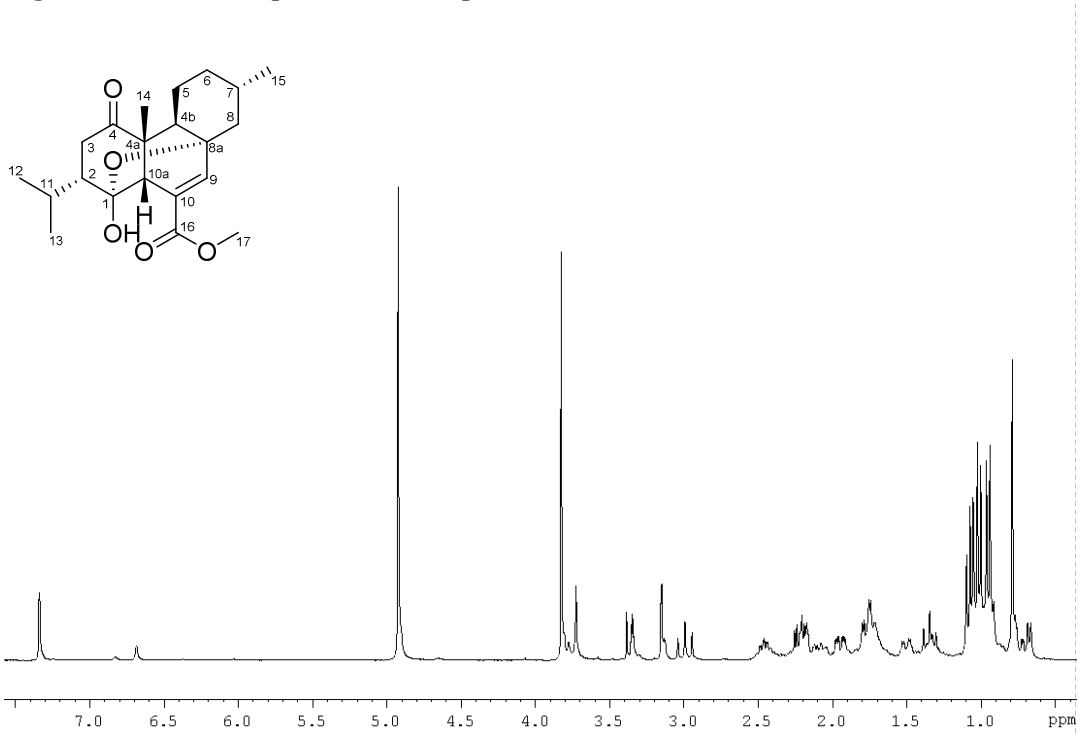


Figure S2: ^{13}C NMR spectrum of compound **1** in MeOH-d_4

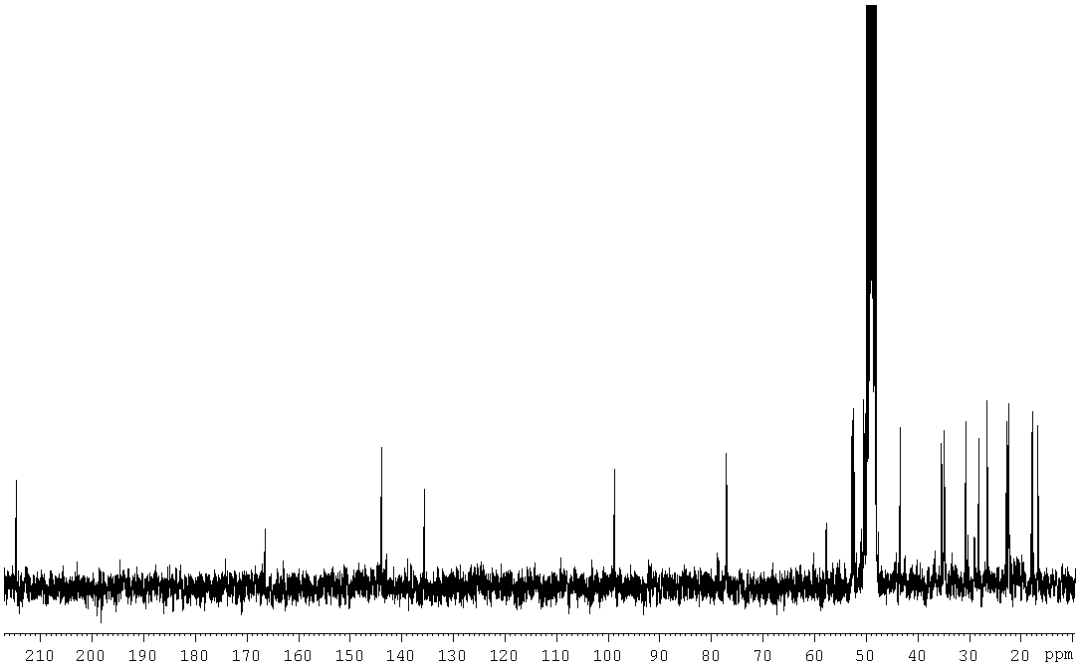


Figure S3. UV spectrum of compound **1** in acetonitrile

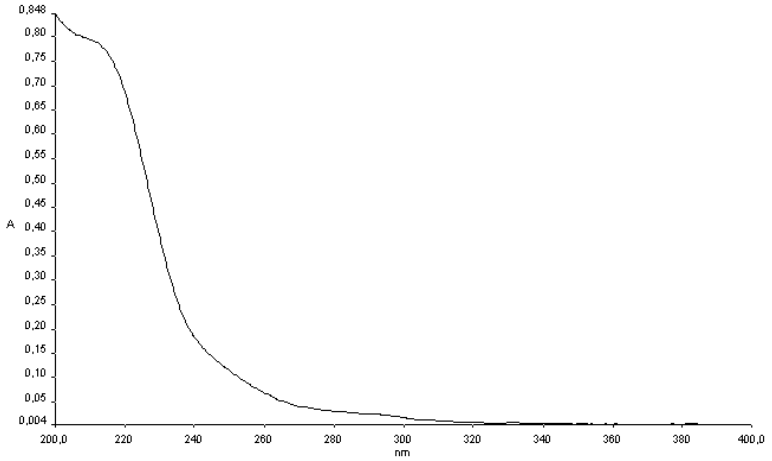


Figure S4. ECD spectrum of compound **1** in acetonitrile

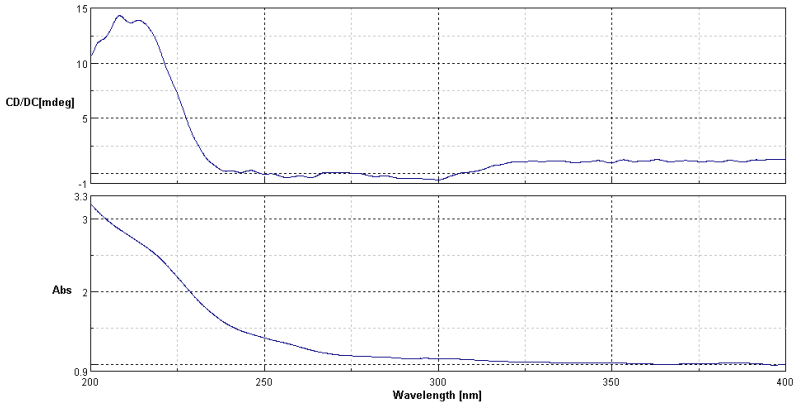


Figure S5. IR spectrum of compound **1**

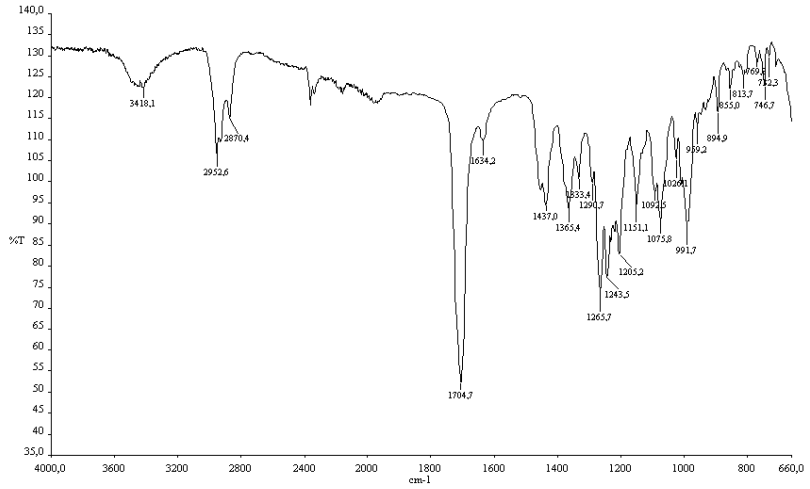


Figure S6: ^{1}H NMR spectrum of compound **2** in MeOH-d_4

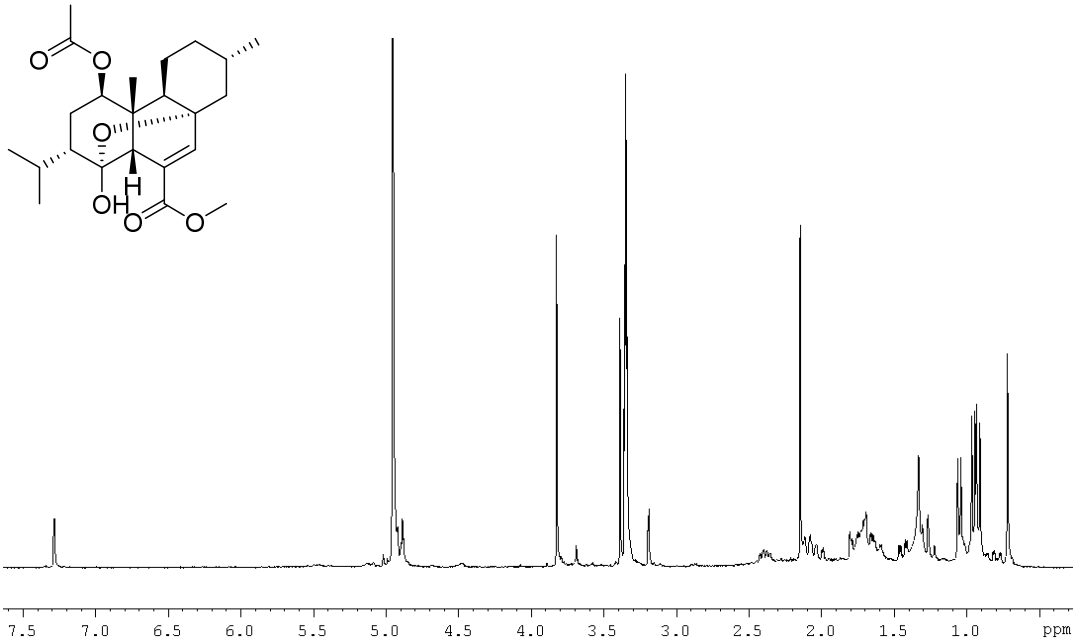


Figure S7: ^{13}C NMR spectrum of compound **2** in MeOH-d_4

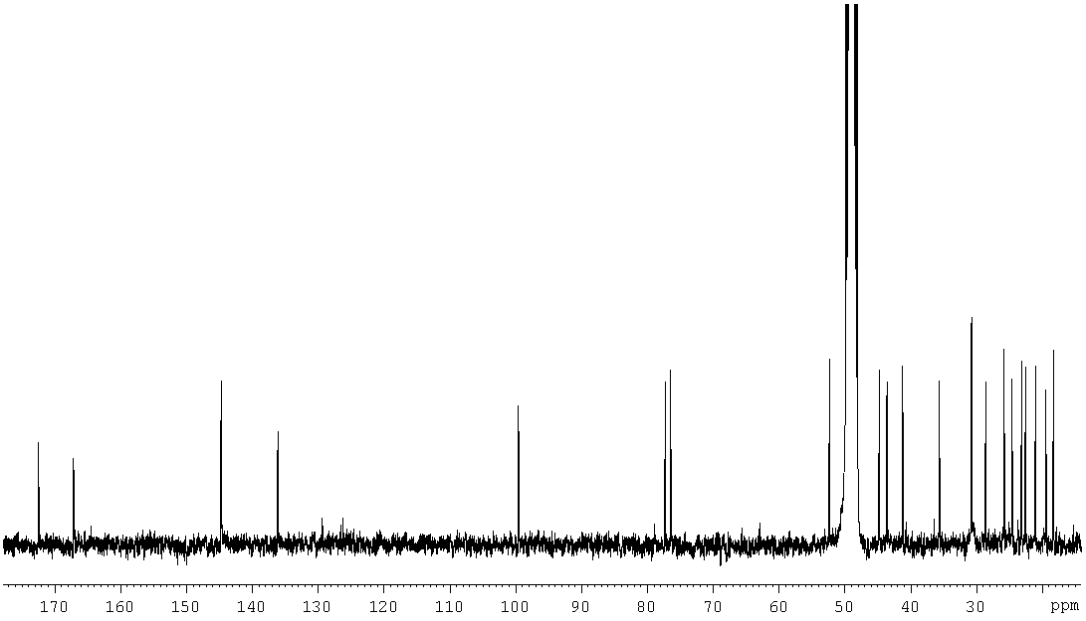


Figure S8. UV spectrum of compound **2** in acetonitrile

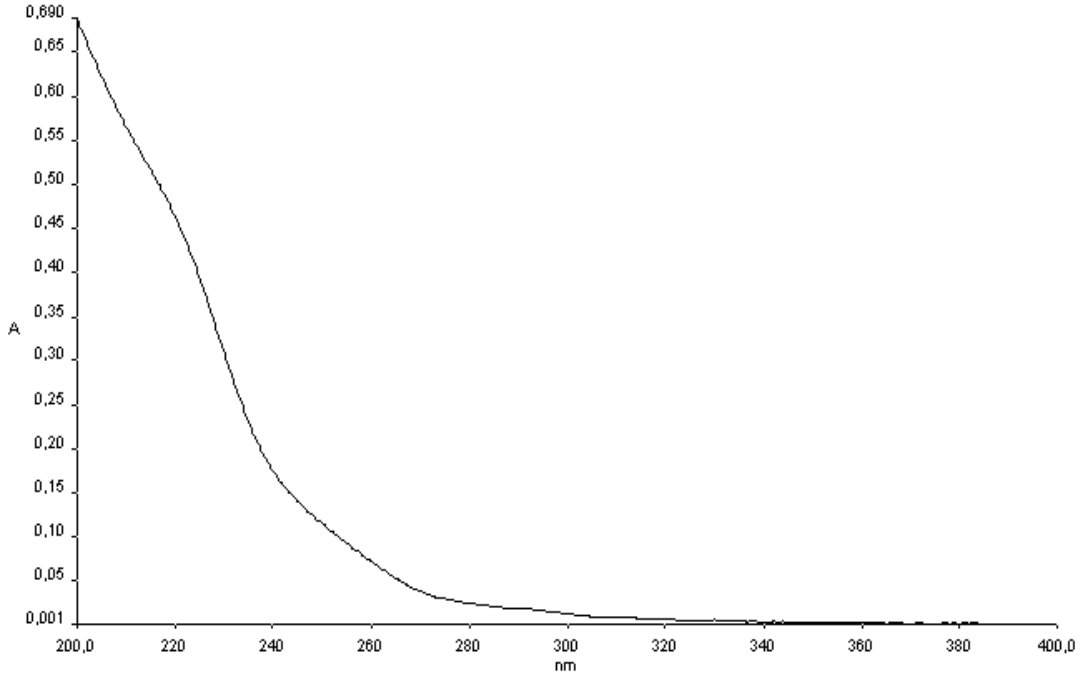


Figure S9. IR spectrum of compound **2**

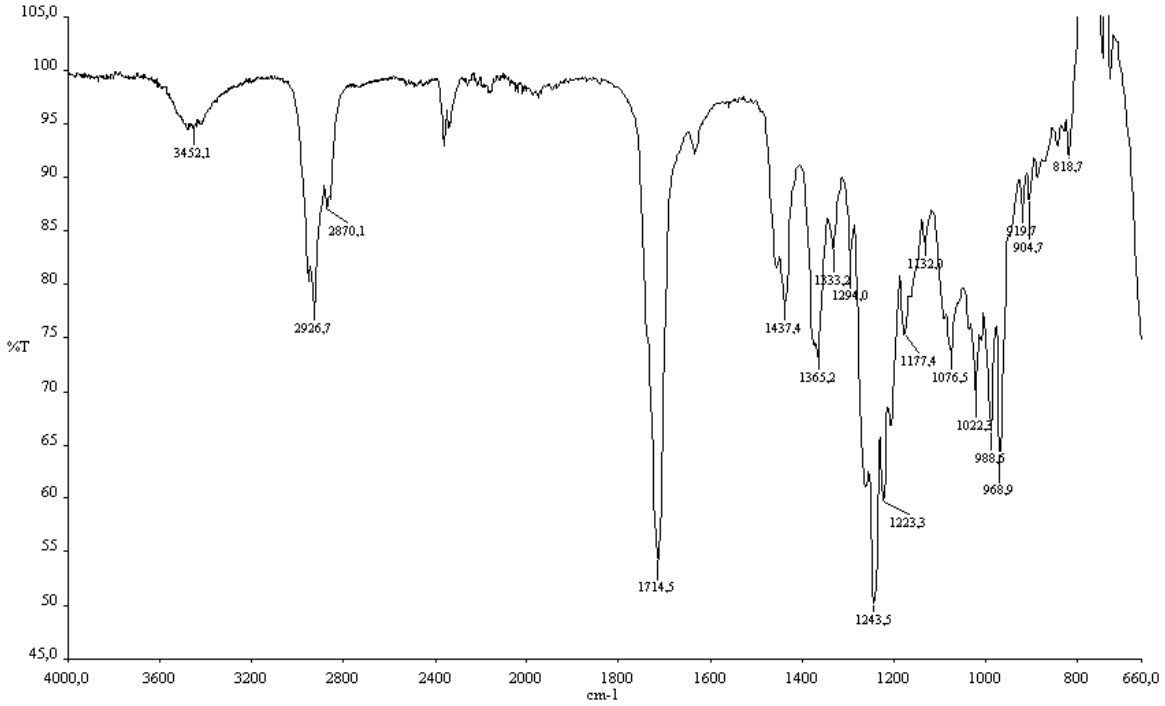


Figure S10: ^{1}H NMR spectrum of compound **3** in MeOH-d_4

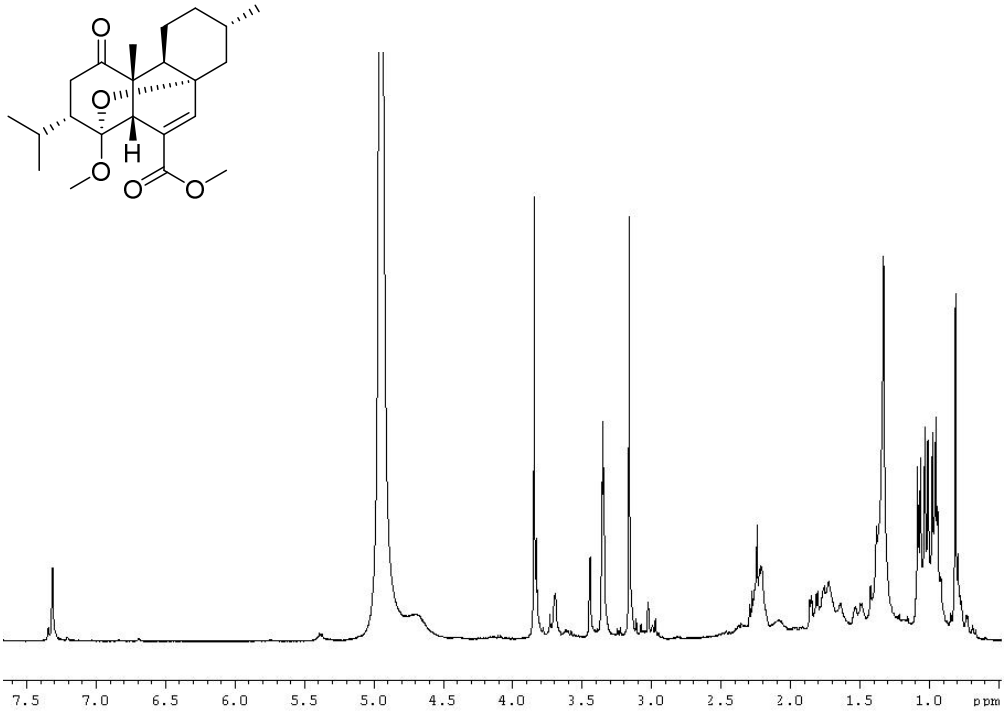


Figure S11: ^{13}C NMR spectrum of compound **3 i**n MeOH-d_4

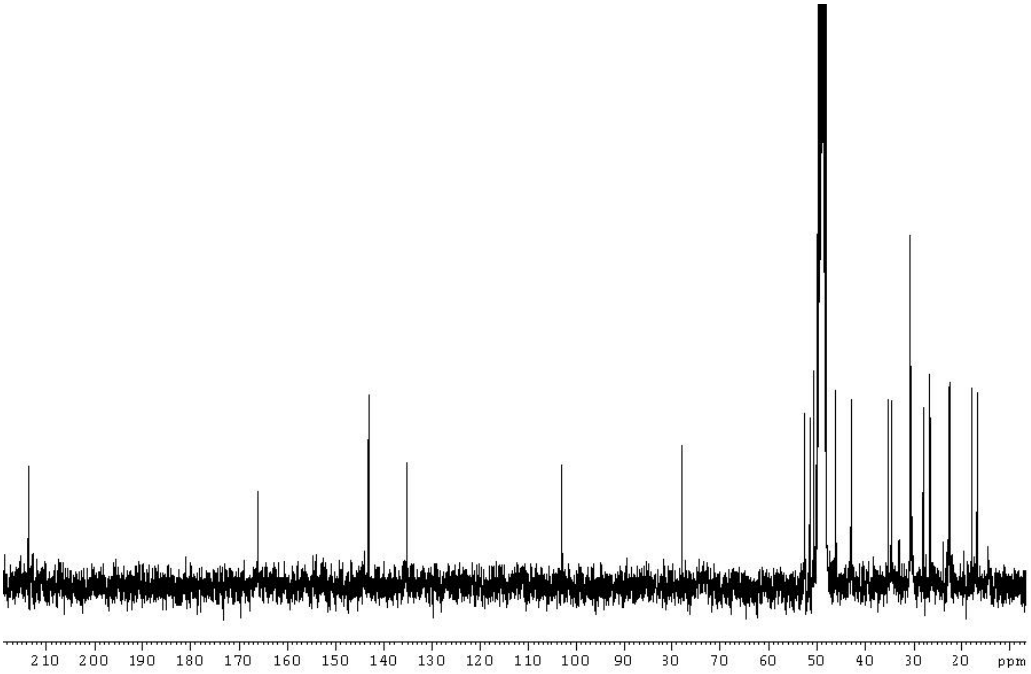


Figure S12. UV spectrum of compound **3** in acetonitrile

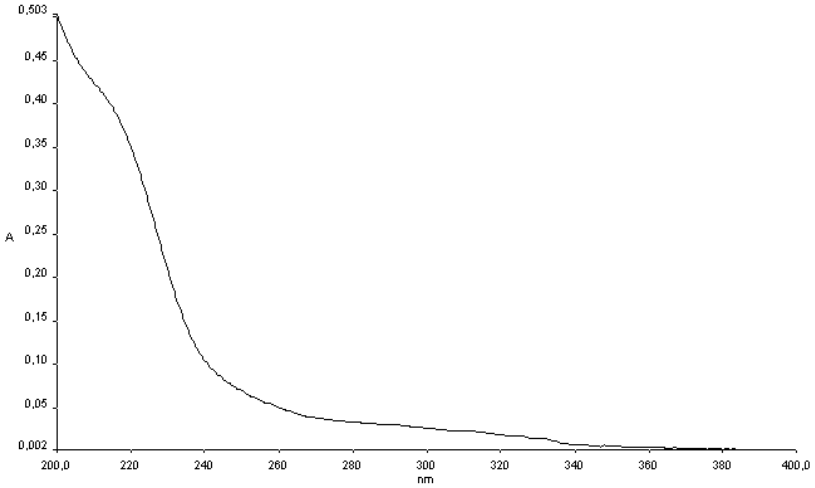


Figure S13. ECD spectrum of compound **3** in acetonitrile

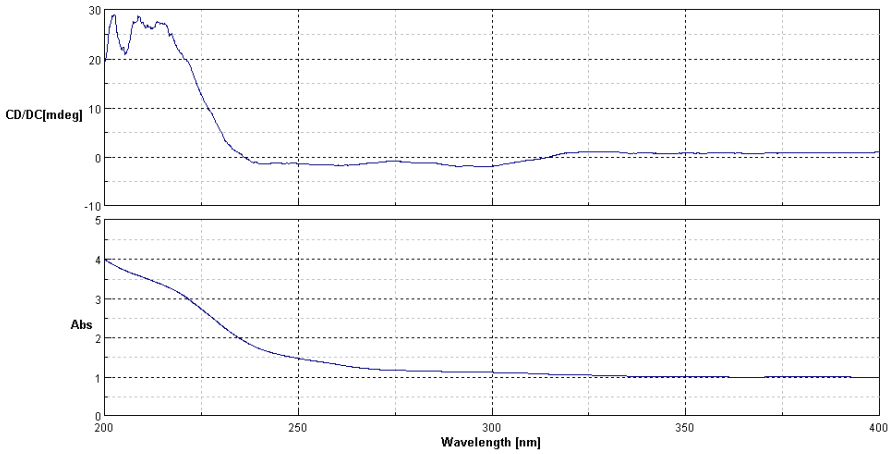


Figure S14. IR spectrum of compound **3**

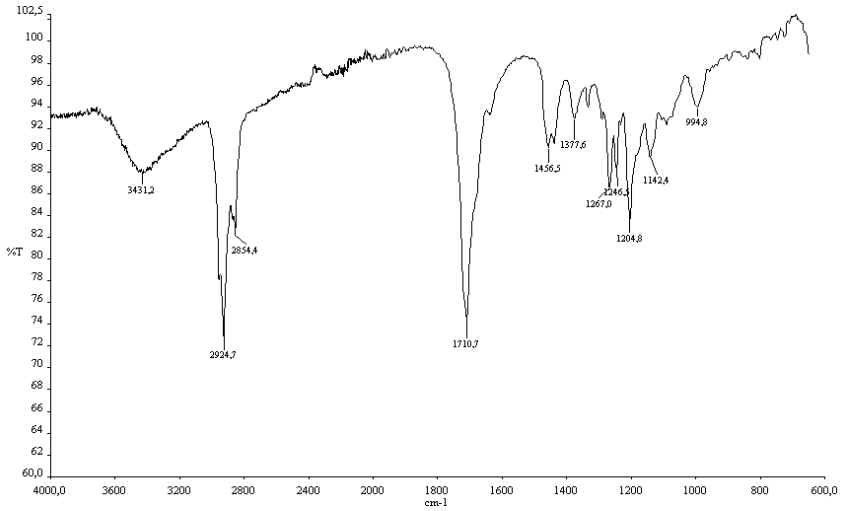


Figure S15: ^{1}H NMR spectrum of compound **4** in MeOH-d_4

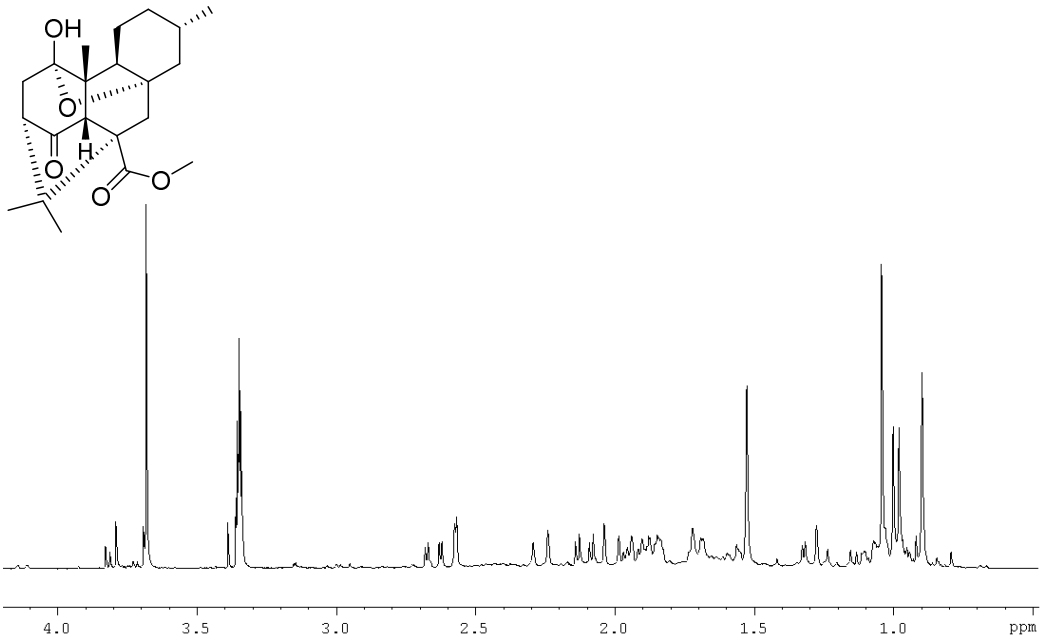


Figure S16: ^{13}C NMR spectrum of compound **4** in MeOH-d_4

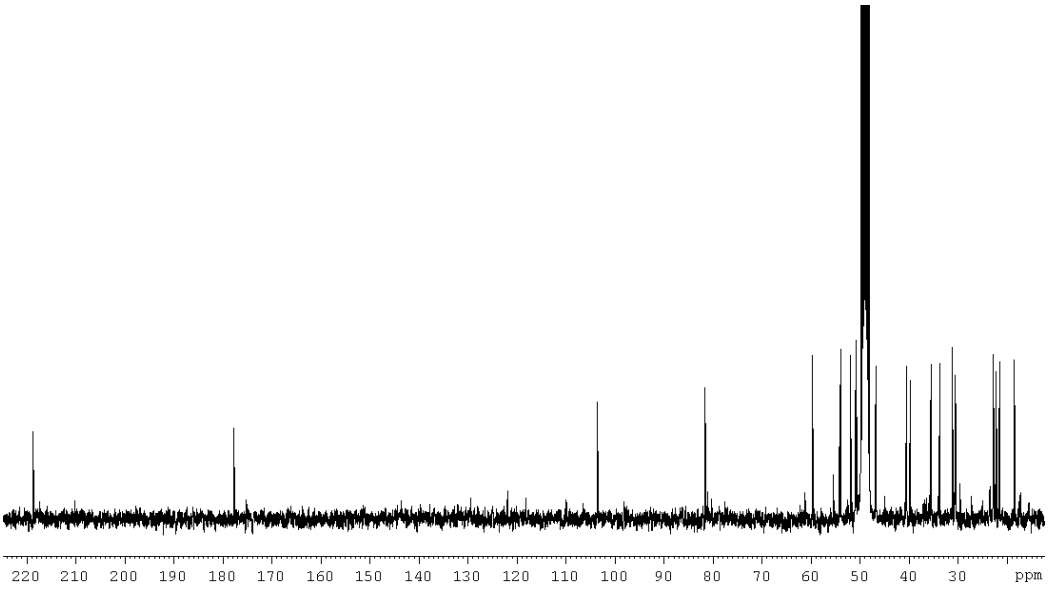


Figure S17. UV spectrum of compound **4** in acetonitrile

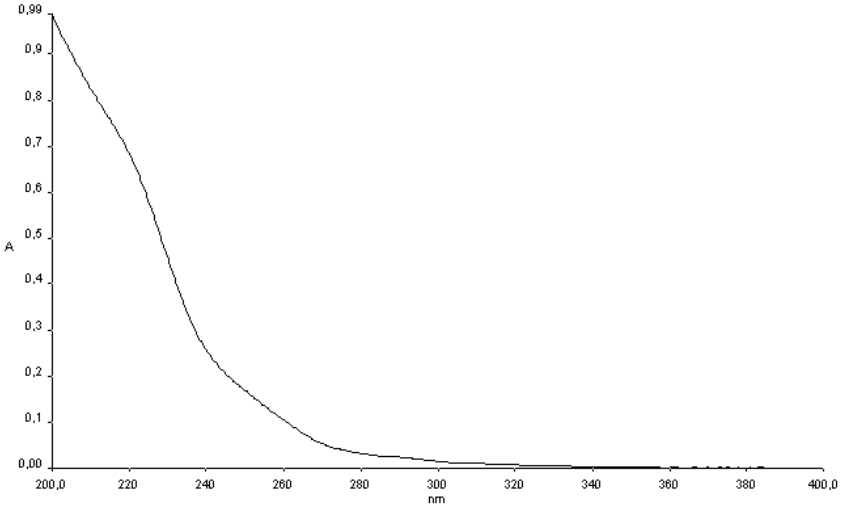


Figure S18. ECD spectrum of compound **4** in acetonitrile

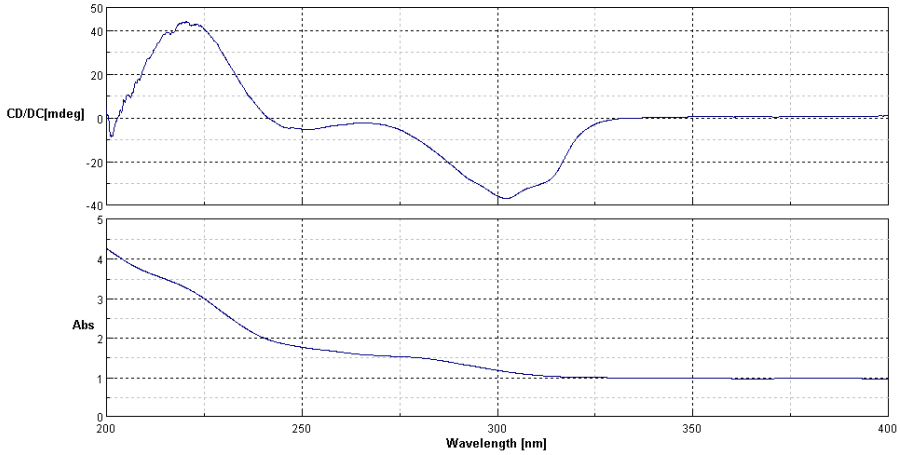


Figure S19. IR spectrum of compound **4**

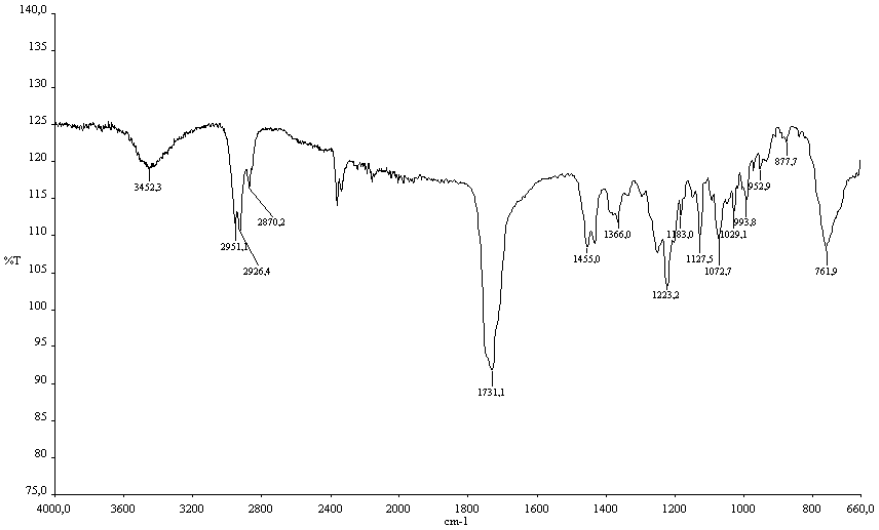


Figure S20. Minimum energy conformation with key NOESY correlations of compound **1**

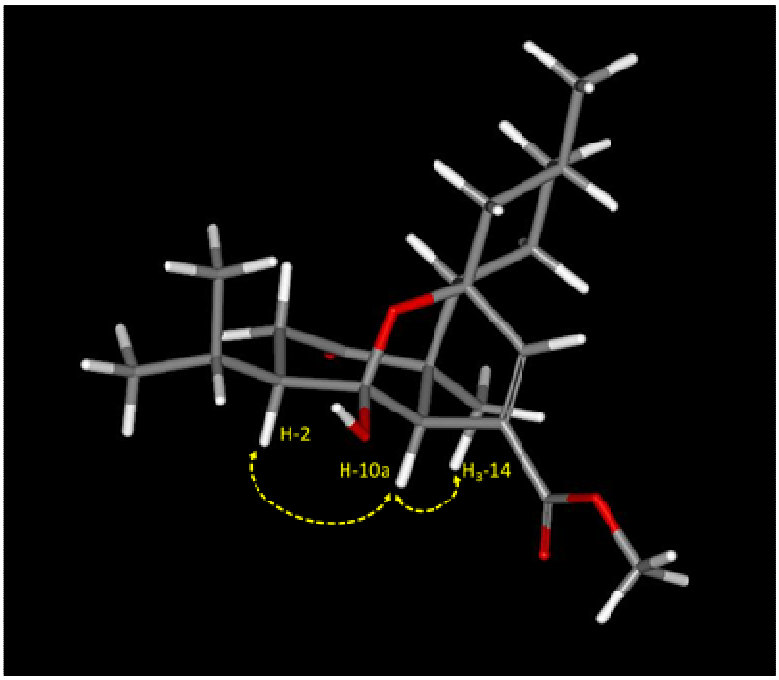
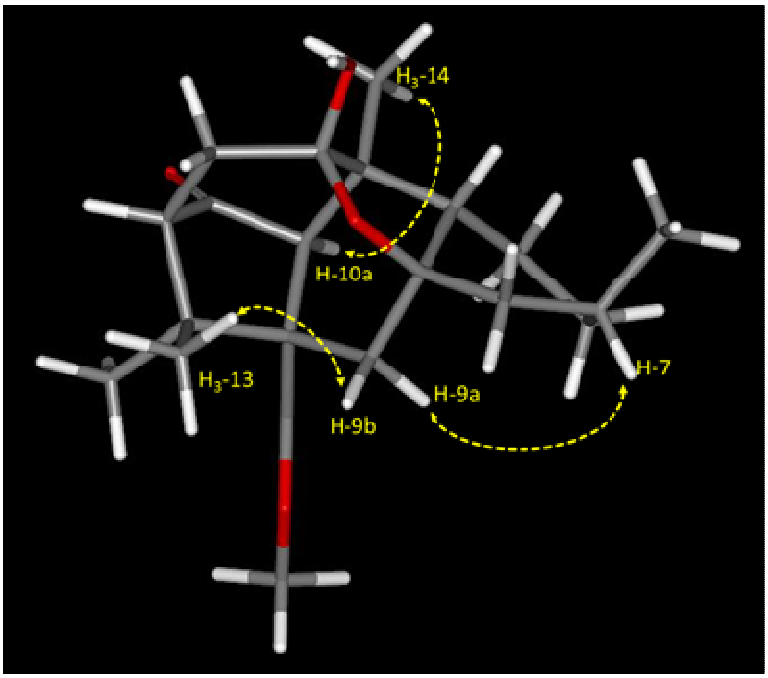


Figure 21. Minimum energy conformation with key NOESY correlations of compound **4**



Minimum energy conformations were calculated employing conformation search (Boltzman jump) with a cff1.01 standard force field as implemented in the Cerius2 4.0 (MSI) molecular modeling software package. Models were further refined with 1500 iterations of minimization. Calculations were performed using a Silicon Graphics O2 workstation (Irix 6.5.6).

Table S1. NMR Spectroscopic Data of Compound **1** in MeOH-d_4

C	δ_H, mult (*J* in Hz)	δ_C, mult	COSY	HMBC	NOESY
1		98.8, C			
2	1.95, ddd (2.6, 5.1, 13.9)	49.9, CH	H_2-3, H-11	C-1, C-3, C-4, C-11, C-12, C-13	H-10a
3	a 3.00, t (13.9)	35.0, CH_2	H-2, H-3b	C-1, C-2, C-4, C-11	H-3b
	b 2.23, dd (5.1, 13.9)		H-2, H-3a	C-1, C-2, C-4, C-11	H-3a, H-4b
4		214.6, C			
4a		50.3, C			
4b	1.78, dd (4.0, 13.2)	50.5, CH	H_2-5	C-4, C-4a, C-5, C-6, C-8, C-8a,C-10a	H-3b
5	a 1.51, dq (13.2, 3.7)	28.2, CH_2	H-4b, H-5b, H_2-6	C-4a, C-4b, C-6, C-7, C-8a	H-5b
	b 0.75, m		H-4b, H-5a, H_2-6	C-4a, C-4b, C-6, C-7, C-8a	H-5a
6	a 1.74, m	35.5, CH_2	H-5b, H-6b, H-7	C-5, C-7	H-6b
	b 1.00, m		H-5a, H-6a, H-7	C-5, C-7	H-6a
7	1.76, m	30.8, CH	H_2-6, H_2-8, H_3-15		H-9, H_3-15
8	a 2.20, m	43.5, CH_2	H-7, H-8b	C-4b, C-6, C-7, C-8a, C-9, C-10	H-8b, H-9
	b 1.35, t (12.4)		H-7, H-8a	C-4b, C-6, C-7, C-8a, C-9, C-10	H-8a
8a		77.1, C			
9	7.34, d (1.8)	144.0, CH	H-10a	C-8, C-8a, C-10, C-10a, C-16	H-7, H-8a, H_3-17
10		135.7, C			
10a	3.15, d (1.5)	52.8, CH	H-9	C-1, C-4a, C-4b, C-8a, C-9, C-10, C-14, C-16	H-2, H_3-14,
11	2.47, m	26.6, CH	H-2, H_3-12, H_3-13	C-1, C-2, C-3, C-12, C-13	H_3-12, H_3-13
12	0.96, d (7.0)	22.8, CH_3	H-11	C-2, C-11, C-13	H-11, H_3-13
13	1.02, d (7.0)	17.9, CH_3	H-11	C-2, C-11, C-12	H-11, H_3-12
14	0.79, s	16.8, CH_3		C-1, C-4, C-4a, C-4b, C-10a	H-10a
15	1.07, d (6.2)	22.5, CH_3	H-7	C-6, C-7, C-8, C-8a	H-7
16		166.5, C			
17	3.83, s	52.5, CH_3		C-16	H-9

Table S2. NMR Spectroscopic Data of Compound **2** in MeOH-d_4

C	δ_H, mult (*J* in Hz)	δ_C, mult	COSY	HMBC	NOESY
1		99.6, C			
2	1.78, m	44.8, CH	H_2-3, H-11		H-10a
3	a 2.04, m b 1.69, m	24.7, CH_2	H-2, H-3b, H-4 H-2, H-3a, H-4		H-3b H-3a, H-4b
4	4.88, t (2.9)	76.5, C	H_2-3	C-2, C-3, C-4a, C-4b, C-15, C-19	H-4b
4a		41.3, C			
4b	1.44, dd (4.0, 13.2)	49.4, CH	H_2-5		H-3b, H-4
5	a 1.61, dq (13.2, 3.7) b 0.80, m	28.7, CH_2	H-4b, H-5b, H-6b H-4b, H-5a		H-5b H-5a
6	a 1.74, m b 1.00, m	35.7, CH_2	H-6b, H-7 H-6a, H-7		H-6b H-6a
7	1.70, m	30.8, CH	H_2-6, H_2-8, H_3-19		H-12, H_3-19
8	a 2.10, m b 1.25, t (13.2)	43.6, CH_2	H-8b, H-9 H-8a		H-8b H-8a, H-9
8a		77.3, C			
9	7.28, d (1.8)	144.8, CH	H-10a	C-4b, C-8, C-8a, C-10, C-10a, C-16	H-7, H-8b, H_3-17
10		136.2, C			
10a	3.19, d (1.5)	49.3, CH	H-9	C-1, C-4a, C-4b, C-8a, C-9, C-10, C-14, C-17	H-2, H_3-14,
11	2.38, m	25.8, CH	H-2, H_3-12, H_3-13	C-1, C-2, C-12, C-13	H_3-12, H_3-13
12	0.92, d (7.0)	23.2, CH_3	H-11	C-2, C-11, C-13	H-11, H_3-13
13	0.96, d (7.0)	18.3, CH_3	H-15	C-2, C-11, C-12	H-11, H_3-12
14	0.72, s	19.5, CH_3		C-4, C-4a, C-4b	H-10a
15	1.05, d (6.2)	22.6, CH_3	H-7	C-6, C-7, C-8, C-8a	H-7
16		167.1, C			
17	3.82, s	52.4, CH_3		C-16	H-9
18		172.4, C			
19	2.15, s	21.1, CH_3		C-18	

Table S3. NMR Spectroscopic Data of Compound **3** in MeOH-d_4

C	δ_H, mult (*J* in Hz)	δ_C, mult	COSY	HMBC	NOESY
1		102.9, C			
2	2.22, m	46.1, CH	H_2-3, H-11	C-1, C-3, C-4, C-11, C-12, C-13	H-10a
3	a 3.03, m	34.7, CH_2	H-2, H-3b	C-1, C-2, C-4, C-11	H-3b
	b 2.26, m		H-2, H-3a		H-3a, H-4b
4		213.7, C			
4a		50.1, C			
4b	1.84, dd (4.0, 13.2)	50.7, CH	H_2-5	C-4, C-4a, C-5, C-6, C-8, C-8a, C-10a	H-3b
5	a 1.52, dq (13.2, 3.7)	28.1, CH_2	H-4b, H-5b	C-4a, C-4b, C-6, C-7, C-8a	H-5b
	b 0.76, m		H-4b, H-5a	C-4a, C-4b, C-6, C-7, C-8a	H-5a
6	a 1.75, m	35.4, CH_2	H-5b, H-6b, H-7	C-5, C-7	H-6b
	b 1.02, m		H-5a, H-6a, H-7	C-5, C-7	H-6a
7	1.78, m	30.8, CH	H_2-6, H_2-8, H_3-15		H-9, H_3-15
8	a 2.25, m	43.0, CH_2	H-8b	C-4b, C-6, C-7, C-8a, C-9, C-10	H-8b, H-9
	b 1.39, m		H-7, H-8a	C-4b, C-6, C-7, C-8a, C-9, C-10	H-8a
8a		77.9, C			
9	7.32, d (1.8)	143.3, CH	H-10a	C-8, C-8a, C-10, C-10a, C-16	H-7, H-8a, H_3-17
10		135.1, C			
10a	3.44, d (1.8)	48.9, CH	H-9	C-1, C-4a, C-4b, C-8a, C-9, C-10, C-14, C-16	H-2, H_3-14
11	2.25, m	26.5, CH	H-2, H_3-12, H_3-13	C-1, C-2, C-3, C-12, C-13	H_3-12, H_3-13
12	0.97, d (7.0)	22.6, CH_3	H-11	C-2, C-11, C-13	H-11, H_3-13
13	1.03, d (7.0)	17.8, CH_3	H-11	C-2, C-11, C-12	H-11, H_3-12
14	0.82, s	16.8, CH_3		C-1, C-4, C-4a, C-4b, C-10a	H-10a
15	1.08, d (6.2)	22.5, CH_3	H-7	C-6, C-7, C-8, C-8a	H-7
16		166.1, C			
17	3.85, s	52.6, CH_3		C-16	H-9
18	3.16, s	51.5, CH_3		C-4a	

Table S4. NMR Spectroscopic Data of Compound **4** in MeOH-d_4

C	δ_H, mult (*J* in Hz)	δ_C, mult	COSY	HMBC	NOESY
1		218.9, C			
2	1.84, m	59.7, CH	H_2-3, H-10a	C-1, C-3, C-4	
3	a 2.65, dd (3.3, 15.0)	40.6, CH_2	H-2, H-3b	C-1, C-2, C-4, C-4a, C-11	H-3b
	b 2.11, dd (4.3, 15.0)		H-2, H-3a	C-1, C-2, C-4, C-4a, C-11	H-3a
4		103.6, C			
4a		54.2, C			
4b	1.71, m	50.8, CH	H_2-5	C-4, C-4a, C-5, C-6, C-8, C-8a, C-10a, C-14	H-6a
5	a 1.58, m	21.6, CH_2	H-4b, H-5b, H-6b	C-6, C-7, C-8a	H-5b
	b 1.07, m		H-4b, H-5a, H-6a	C-6, C-7, C-8a	H-5a
6	a 1.88, m	35.6, CH_2	H-5b, H-6b, H-7	C-7, C-15	H-4b, H-6b
	b 1.04, m		H-5a, H-6a, H-7	C-7, C-15	H-6a
7	1.65, m	31.2, CH	H_2-6, H_2-8, H_3-15		H-9a, H_3-15
8	a 1.93, m	46.9, CH_2	H-7, H-8b	C-4b, C-6, C-7, C-8a, C-19, C-10	H-8b
	b 1.28, t (12.1)		H-7, H-8a	C-4b, C-6, C-7, C-8a, C-19, C-10	H-8a
8a		81.7, C			
9	a 2.27, d (15.7)	33.8, CH_2	H-9b	C-8, C-8a, C-10, C-10a, C-11, C-16	H-7, H-9b
	b 2.01, d (15.7)		H-9a	C-8, C-8a, C-10, C-10a, C-11, C-16	H-9a, H_3-13
10		51.0, C			
10a	2.57, d (1.8)	54.0, CH	H-2	C-1, C-2, C-4, C-4a, C-8a, C-9, C-10, C-14, C-16	H_3-14
11		39.8, C			
12	0.90, s	30.6, CH_3	H_3-13	C-2, C-10, C-11, C-13	
13	1.53, s	22.2, CH_3	H_3-12	C-2, C-10, C-11, C-12	H-3b, H-9b
14	1.04, s	18.5, CH_3		C-4, C-4a, C-4b, C-10a	H-10a
15	0.99, d (6.2)	22.9, CH_3	H-7	C-6, C-7, C-8, C-8a	H-7
16		177.8, C			
17	3.68, s	52.0, CH_3		C-16	