Supporting Information

Banksialactones and Banksiamarins: Isochromanones and Isocoumarins from a new Australian Fungus, *Aspergillus banksianus*

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A. NMR tables

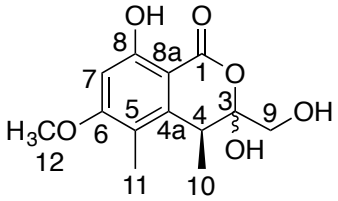

Table S1: NMR data for the major and minor isomers of banksialactone A (**1**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D Correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	168.9, C		169.1, C				
3	104.9, C		105.6, C				
4	35.0, CH	3.28, q (*7.0*)	33.6, C	3.39, q (*7.0*)	3, 5, 6, 8a, 9	10	10, 11, 9**
4a	143.7, C		143.0, C				
5	114.4, C		114.4, C				
6	163.9, C		163.8, C				
7	97.0, CH	6.45, s	97.3, CH	6.45, s	5, 6, 8, 8a, 1(w), 11(w)		12, 8-OH
8	161.9, C		161.8, C				
8a	99.7, C		98.8, C				
9	63.6, CH_2	3.64, d (*11.5*) 3.72, d (*11.5*)	64.5, CH_2	3.30, d (*11.5*) 3.44, d (*11.5*)	3, 4, 4a		10*, 4**
10	16.3, CH_3	1.06, d (*7.0*)	14.8, CH_3	1.08, d (*7.0*)	3, 4, 4a	4	4, 9*, 11
11	9.8, CH_3	2.00, s	9.7, CH_3	2.01, s	4a, 5, 6		4, 10
12	56.0, CH_3	3.84, s	55.9, CH_3	3.83, s	6, 7		7
3-OH		7.10, br s		7.45, br s			
8-OH		11.39, s		11.38, s	7, 8, 8a		7
9-OH		[a]		[a]			

[a] Not observed, *Observed only in the major isomer, ** Observed only in the minor isomer

Banksialactone A (1): Colorless oil; $[\alpha]^{24}_D$ +72 (*c* 0.34, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 224 (–15.52), 238 (+10.31), 249 (+1.19), 269 (+19.38), 309 (–6.96) nm; IR (ATR) ν_{max} 3209, 1662, 1617(sh), 1434, 1182, 1135, 1023, 839, 801, 723 cm^{-1}; NMR (600 MHz, DMSO-d_6) see Table S1; ESI-MS *m/z* 269.1 $[M + H]^+$.

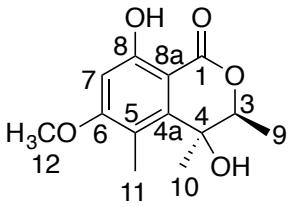

Table S2: NMR data for banksialactone B (**2**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	167.7, C				
3	68.8, CH	4.06, q (*6.3*)	1, 4, 4a, 9, 10	9, 10(w)	9, 10(w), 11
4	88.4, C				
4a	152.0, C				
5	110.2, C				
6	163.6, C				
7	98.9, CH	6.48, s	5, 6, 8, 8a, 1(w), 11 (w)	11(w)	12
8	156.3, C				
8a	103.8, C				
9	17.1, CH_3	0.73, d (*6.3*)	3, 4	9, 10 (w)	10 (w)
10	21.1, CH_3	1.60, s	3, 4, 9 (w), 4a	3(w), 11 (w)	9, 11
11	11.1, CH_3	2.05, s	4a, 5, 6, 4 (w), 10 (w)	7(w), 10 (w)	10
12	56.1, CH_3	3.81, s	6		7
4-OH		[a]			
8-OH		10.31, s			

[a] Not observed

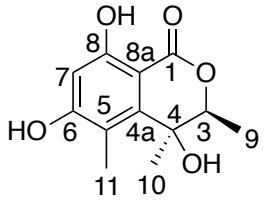

Table S3: NMR data for banksialactone C (**3**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	167.8, C				
3	68.7, CH	4.05, q (*6.3*)	1, 4, 4a, 9, 10	9, 10(w)	9, 10(w), 11
4	88.1, C				
4a	153.0, C				
5	108.9, C				
6	162.6, C				
7	102.2, CH	6.40, s	5, 6, 8, 8a, 1(w), 11(w)	11(w)	
8	155.8, C				
8a	103.1, C				
9	17.1, CH_3	0.71, d (*6.3*)	3, 4	10(w)	10(w)
10	21.1, CH_3	1.58, s	3, 4, 9(w), 4a	3(w), 9(w)	9, 11
11	11.0, CH_3	2.02, s	4a, 5, 6, 4(w), 10(w)	7(w), 10(w)	10
4-OH		[a]			
6-OH		10.39, s	5(w)		
8-OH		10.09, br s			

[a] Not observed

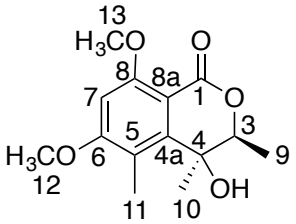

Table S4: NMR data for banksialactone D (**4**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	167.0, C				
3	68.7, CH	4.07, q (*6.3*)	1, 4, 4a, 9, 10	9, 10(w)	9, 10(w), 11
4	88.2, C				
4a	152.8, C				
5	111.0, C				
6	164.0, C				
7	95.6, CH	6.67, s	5, 6, 8, 8a, 1(w), 11(w)	11(w)	12, 13
8	157.7, C				
8a	104.8, C				
9	17.1, CH_3	0.71, d (*6.3*)	3, 4	10(w)	10
10	21.1, CH_3	1.60, s	3, 4, 9(w), 4a	3(w), 11(w)	9, 11
11	11.1, CH_3	2.08, s	4a, 5, 6, 4(w), 10(w)	7(w), 10(w)	10
12	56.4, CH_3	3.92, s	6		7
13	55.8, CH_3	3.89, s	8		7
4-OH		5.13, br s			

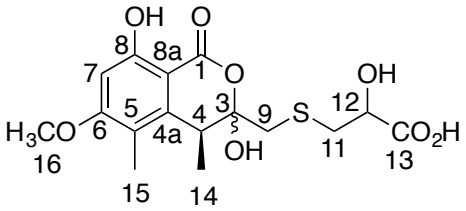

Table S5: NMR data for the major and minor isomers of banksialactone E (**5**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D Correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	168.7, C		168.7, C				
3	105.7, C		106.7, C				
4	35.8, CH	3.37, q (*7.1*)	34.8, CH	3.63, q (*7.1*)	3, 4a, 5, 9, 8a, 14	14	14, 15, 9**
4a	143.3, C		142.6, C				
5	114.5, C		114.6, C				
6	163.9, C		164.0, C				
7	97.0, CH	6.46, s	97.6, CH	6.47, s	5, 6, 8, 8a, 1(w), 15(w)		8, 16
8	161.9, C		162.1, C				
8a	99.4, C		98.6, C				
9	38.9 [b], CH_2	3.13, d (*13.8*) 3.19, d (*13.8*)	40.0 [b], CH_2	2.69 d, (*14.2*) 3.02 d, (*14.2*)	3, 4, 11		14*, 4**
11	36.6, CH_2	2.88, dd (*13.8, 6.9*) 2.98, dd (*13.8, 4.7*)	37.0, CH_2	2.72, dd (*13.8*, *5.1*) 2.73, dd (*13.8*, *6.6*)	9, 12, 13	12	12
12	70.4, CH	4.21, dd (*6.9, 4.7*)	70.5, CH	4.03, dd (*6.6, 5.1*)	11, 13	11	11
13	174.0, C		173.9, C				
14	16.4, CH_3	1.05, d (*7.1*)	14.6, CH_3	1.08, d (*7.1*)	3, 4, 4a	4	4, 9*
15	9.8, CH_3	2.00, s	9.8, CH_3	2.03, s	4a, 5, 6		
16	56.0 CH_3	3.84, s	56.1, CH_3	3.84, s	6		7
3-OH		7.40, br s		7.72, br s			
8-OH		11.32, s		11.30, s			7
12-OH		[a]		[a]			
13-OH		[a]		[a]			

[a]Not observed or not assignable, [b]masked under DMSO-d_6 peak * Observed only in the major isomer, **Observed only in the minor isomer

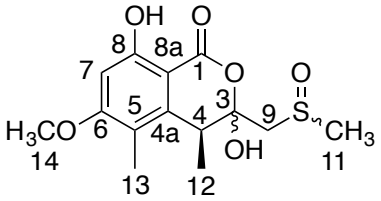

Table S6: NMR data for the isomers of banksialactone F (**6**) in DMSO-d_6

Position	I		II		III		IV		2D NMR correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (J, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	168.1, C		168.5, C		168.0, C		168.2, C				
3	104.2, C		104.2, C		104.0, C		104.8, C				
4	37.7, CH	3.43, q (*7.1*)	36.8, CH	3.65, q (*7.1*)	37.9, CH	3.37, q (*7.1*)	36.2, CH	3.62, q (*7.1*)	3, 4a, 5, 9, 8a, 14	12	$9^{II,IV}$, 12, 13
4a	143.3, C		142.7, C		42.8, C		142.3, C				
5	114.7, C		115.1, C		14.7, C		114.7, C				
6	164.2, C		164.0, C		64.0, C		164.2, C				
7	97.3, CH	6.47, s	97.6, CH	6.49, s	97.2, CH	6.47, s	97.2, CH	6.49, s	5, 6, 8, 8a, 1(w), 15(w)		8-OH, 14
8	162.0, C		162.0, C		161.9, C		162.0, C				
8a	99.3, C		98.4, C		99.2, C		99.4, C				
9	59.3, CH_2	3.27, d (*13.7*) 3.57, d (*13.7*)	60.5, CH_2	3.02, d (*13.4*) 3.12, d (*13.4*)	60.3, CH_2	3.25, d (*14.1*) 3.61, d (*14.1*)	61.2, CH_2	2.96, d (*14.3*) 3.26, d (*14.3*)	3, 4, 11		$4^{II,IV}$, $11^{I,II}12^{I,III}$
11	39.3 [b], CH_3	2.72, s	38.8 [b], CH_3	2.51 [b], s	40.0 [b], CH_3	2.75, s	39.5 [b], CH_3	2.55, s	9, 12, 13		$9^{I,III}$
12	17.3, CH_3	1.14, d (*7.1*)	14.1, CH_3	1.11, d (*7.1*)	16.9, CH_3	1.09, d (*7.1*)	16.9, CH_3	1.12, d (*7.1*)	3, 4, 4a,	4	4, $9^{I,II}$, 13
13	10.0, CH_3	1.98, s	9.5, CH_3	1.99, s	9.9, CH_3	2.00, s	10.0, CH_3	2.02, s	4a, 5, 6		4, 12
14	56.2, CH_3	3.85, s	56.0, CH_3	3.85, s	56.0, CH_3	3.85, s	56.1, CH_3	3.85, s	6		7
3-OH		7.87, s		8.22, s		[a]		[a]			
8-OH		11.21, s		11.23, s		11.24, s		11.26, s			7

[I, II, III, IV] Indicates ROESY observed for that isomer only, [a]Not observed or not assignable, [b] masked under DMSO-d_6 peak

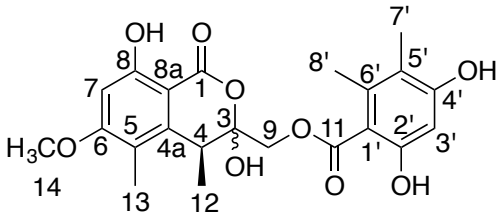

Table S7: NMR data for the major and minor isomers of banksialactone G (**7**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D Correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	168.0, C		168.0, C				
3	103.0, C		103.3, C				
4	35.4, CH	3.35 [b], q (*7.0*)	34.3, CH	3.35 [b], q (*7.0*)	3, 5, 6, 8a, 9	12	12, 13, 9**
4a	143.1, C		142.4, C				
5	114.6, C		114.5, C				
6	164.1, C		163.9, C				
7	97.2, CH	6.48, s	97.3, CH	6.42, s	1(w), 5, 6, 8, 8a, 13		8-OH, 14
8	162.0, C		161.9, C				
8a	99.3, C		98.3, C				
9	65.0, CH_2	4.35, d (*11.5*) 4.60, d (*11.5*)	65.9, CH_2	4.15, d (*11.5*) 4.25, d (*11.5*)	3, 4, 4a, 11		3-OH, 12*, 4**
11	168.3, C		168.4, C				
12	16.4, CH_3	1.11, d (*7.1*)	14.4, CH_3	1.10, d (*7.1*)	3, 4, 4a	4	4, 9*, 13
13	9.9, CH_3	2.00, s	9.9, CH_3	1.97, s	4a, 5, 6		4, 12
14	56.0, CH_3	3.85, s	56.0, CH_3	3.82, s	6		7
1'	111.7, C		111.7, C				
2'	154.5, C		154.5, C				
3'	100.0, CH	6.32, s	99.8, C	6.26, s	1', 2', 4', 5', 7', 11(w)		2'-OH, 4'-OH
4'	157.5, C		157.7, C				
5'	114.0, C		113.6, C				
6'	136.2, C		136.4, C				
7'	11.0, CH_3	1.97, br s	11.0, C	1.93, br s	4', 5', 6'	8'(w)	8', 4'-OH
8'	17.1, CH_3	2.16, br s	17.1, C	2.05, br s	1', 5', 6'	7'(w)	3-OH, 7', 2'-OH, 4'-OH
3-OH		7.64, br s		7.95, br s	3, 4		9, 8'
8-OH		11.24, s		11.21, s	6, 7, 8, 8a		7
2'-OH		9.74, s		9.74, s	1', 2', 3'		3', 8'
4'-OH		9.66, s		9.67, s	3', 4', 5'		3', 7', 8'

[*] Observed only in the major isomer, [**]Observed only in the minor isomer, [b] masked under water peak

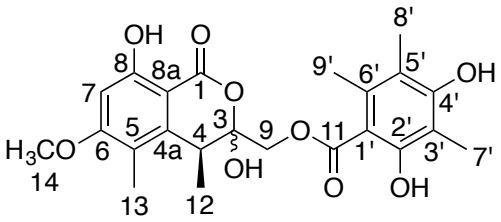

Table S8: NMR data for the major and minor isomers of banksialactone H (**8**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D Correlations		
	δ_C, type	δ_H, multi (*J*, Hz)	δ_C, type	δ_H, multi (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	167.9, C		168.4, C				
3	102.8, C		103.0, C				
4	35.6, CH	3.35 [b], q (*7.1*)	35.0, CH	3.35 [b], q (*7.1*)	3, 5, 4a, 8a, 9, 12	12	12, 13, 9**
4a	143.0, C		142.0, C				
5	114.7, C		114.5, C				
6	164.1, C		163.9, C				
7	97.2, CH	6.49, s	97.3, CH	6.29, s	5, 6, 8, 8a, 1(w), 13(w)		14, 8-OH
8	162.0, C		161.9, C				
8a	99.3, C		98.3, C				
9	65.4, CH_2	4.50, d (*11.5*)	65.9, CH_2	4.50, d (*11.5*)	3, 4, 4a(w), 11		3-OH, 4**, 12*,9'
11		4.58, d (*11.5*)		4.57, d (*11.5*)			
12	169.9, C		169.6, C		3, 4, 4a,	4	4, 9*, 13
13	16.4, C	1.12, d (*7.1*)	14.8, C	1.11, d (*7.1*)	4a, 5, 6		4, 12
14	9.9, CH_3	2.00, s	9.7, CH_3	1.95, s	6		7
1'	56.1, CH_3	3.85, s	55.9, CH_3	3.76, s			
2'	109.3, C		108.7, C				
3'	155.3, C		156.0, C				
4'	109.2, C		108.0, C				
5'	156.9, C		151.1, C				
6'	116.0, C		115.9, C				
7'	134.3, C		134.9, C		2', 3', 4'		2'-OH, 4'-OH
8'	9.3, CH_3	2.04, s	9.1, CH_3	1.99, s	4', 5', 6'		9', 4'-OH
9'	12.2, CH_3	2.07, s	12.1, CH_3	2.03, s	1', 5', 6'		8', 9, 3-OH,
	17.9, CH_3	2.31, s	18.0, CH_3	2.16, s			2'-OH, 4'-OH
3-OH		7.74, s		8.02, s	4, 3		9, 9'
8-OH		11.22, s		11.18, s	6, 7, 8, 8a		7
2'-OH		10.05, s		10.05, s	1', 2', 3'		7', 9'
4'-OH		8.86, s		8.85, s	3', 4', 5'		7', 8', 9'

[*] Observed only in the major isomer, [**]Observed only in the minor isomer, [b] masked under water peak

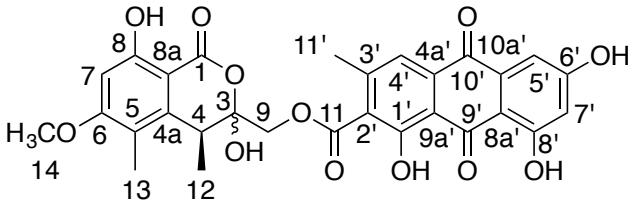

Table S9: NMR data for the major and minor isomers of banksialactone I (**9**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D Correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	167.9, C		168.2, C				
3	102.6, C		104.8, C				
4	35.5, CH	3.35 [c], q (*7.0*)	36.2, C	3.35 [b], q (*7.0*)	3, 5, 9, 12, 4a, 8a	12	12, 13, 9 [b]
4a	143.0, C		142.3, C				
5	114.7, C		114.7, C				
6	164.2, C		164.2, C				
7	97.3, CH	6.48, s	97.2, CH	6.47, s	1(w), 5, 6, 8, 8a, 13		8-OH, 14
8	162.0, C		162.0, C				
8a	99.2, C		99.4, C				
9	65.8, CH_2	4.55, d (*11.5*) 4.73, d (*11.5*)	66.7, CH_2	4.30, d (*11.5*) 4.38, d (*11.5*)	3, 4, 11		3-OH, 12 [a], 4 [b]
11	165.1, C		165.1, C				
12	16.4, CH_3	1.14, d (*7.1*)	16.9, CH_3	1.14, d (*7.1*)	3, 4, 4a	4	4, 9 [a] 13
13	9.9, CH_3	1.99, s	9.9, CH_3	1.99, s	4a, 5, 6		4, 12
14	56.1, CH_3	3.84, s	56.1, CH_3	3.80, s	6		7
1'	158.2, C		158.2, C				
2'	128.0, C		128.0, C				
3'	144.7, C		144.7, C				
4'	120.7, CH	7.63, br s	120.7, CH	7.59, br s	2', 9a', 10', 11'	11'	11'
5'	109.1, CH	7.17, d (*2.4*)	109.1, CH	7.17, d (*2.4*)	7', 10'	7'	7', 6'-OH
6'	165.9, C		165.9, C				
7'	108.2, CH	6.65, d (*2.4*)	108.2, CH	6.64, d (*2.4*)	5', 6', 8'	5'	5', 6'-OH, 8'-OH
8'	164.6, C		164.6, C				
9'	189.5, C		189.5, C				
10'	181.1, C		181.1, C				
11'	19.8, CH_3	2.46, br s	19.8, CH_3	2.34, br s	2', 3', 4'	4'	4'
4a'	135.2, C		135.2, C				
10a'	133.4, C		133.4, C				
8a'	109.2, C		109.1, C				
9a'	114.2, C		114.2, C				
3-OH		7.75, br s		7.57, br s	3, 4		9
8-OH		11.21, s		11.18, s	7, 8, 8a		7
1'-OH		11.50, s		11.50, s	1', 2', 9a'		
6'-OH		12.54, s		12.44, s	5', 6', 7'		5', 7'
8'-OH		11.93, s		11.92, s	7', 8', 8a', 6'(w)		7'

[a] Observed only in the major isomer, [b] Observed only in the minor isomer, [c] masked under water peak

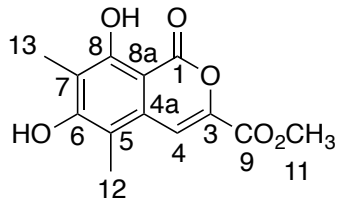

Table S10: NMR data of banksiamarin A (**10**) in DMSO-d_6

Position	δC, type	δ_H, mult (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	165.0, C				
3	140.9, C				
4	110.7, CH	7.63, s	3, 5, 8a, 9, 8(w)		12
4a	131.0, C				
5	113.4, C				
6	161.6, C				
7	113.7, C				
8	158.5, C				
8a	99.5, C				
9	160.2, C				
11	52.9, CH_3	3.88, s	9		
12	11.0, CH_3	2.27, s	4a, 5, 6		4
13	9.1, CH_3	2.14, s	6, 7, 8		8-OH
6-OH		10.05, br s			
8-OH		11.28, s	7, 8, 8a, 6(w)		13

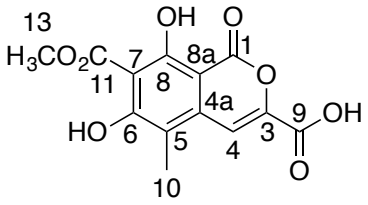

Table S11: NMR data of banksiamarin B (**11**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	164.9, C				
3	143.7, C				
4	109.3, CH	7.57, s	3, 5, 8a, 4a, 9, 8(w)		10
4a	136.1, C				
5	113.6, C				
6	161.8, C				
7	108.4, C				
8	159.5, C				
8a	99.9, C				
9	160.8, C				
10	10.4, CH_3	2.24, s	6, 7, 8		4
11	166.7, C				
13	52.7, CH_3	3.87, s	11		
6-OH		11.49, br s			
8-OH		11.75, s	7, 8, 8a, 6(w)		
9-OH		[a]			

[a] Not observed

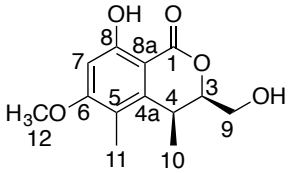

Table S12: NMR data for the major and minor isomers of clearanol I (**12**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	169.8, C				
3	81.2, CH	4.49, ddd (*2.7, 5.8, 7.0*)		4, 9	4, 9
4	29.8, CH	3.25, dq (*7.1, 2.7*)	3, 5, 6, 8a, 9	3, 10	3, 10, 11
4a	144.9, C				
5	113.6, C				
6	164.0, C				
7	97.5, CH	6.49, s	5, 6, 8, 8a, 1(w), 11(w)		12, 8
8	162.3, C				
8a	99.7, C				
9	60.6, CH_2	3.67, dd (*11.5, 5.8*) 3.74, dd (*11.5, 7.0*)	3, 4, 4a	3	10
10	12.6, CH_3	0.99, d (*7.1*)	3, 4, 4a	4	4, 9, 11
11	9.9, CH_3	2.01, s	4a, 5, 6		4, 10,
12	56.2, CH_3	3.84, s	6		7
8-OH		11.27, s	7, 8, 8a		7
9-OH		[a]			

[a] Not observed

Clearanol I (12): Colorless oil; $[\alpha]^{23}_D$ +17 (*c* 0.33, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 223 (–9.56), 238 (+11.75), 251 (0.99), 270 (+13.73), 313 (–4.60) nm; UV (MeOH) λ_{max} (log ε) 216 (4.22), 268 (4.05), 312 (3.74) nm; IR (ATR) ν_{max} 3361, 2974, 1750(w), 1652, 1616, 1589, 1441, 1384, 1332, 1292, 1244, 1193, 1161, 1138, 1081, 1044, 1021, 1000, 826, 800, 722, 705 cm^{-1}; NMR (600 MHz, DMSO-d_6) Table S12; HR-ESI(+)MS *m/z* 253.1067 $[M + H]^+$ (calcd for $C_{13}H_{17}O_5^+$, 253.1071).

Clearanol I (**12**) has a molecular formula of $C_{13}H_{16}O_5$ as confirmed by HRMS (Δmmu –0.3). A notable difference in the NMR spectra of **12** (Table S12), compared to **1**, was the presence of an additional resonance at δ_H 4.49 (ddd) and the presence of an oxymethine carbon resonance at δ_C 81.2 instead of the C-3 hemiketal carbon resonance at δ_C 104.9 in **1**. Notable differences in the chemical shifts of **12** (Table S12) and **1** (Table S1) were observed around C-4 and C-9, whereas the remaining ^1H and ^{13}C NMR resonances were quite similar. These observations suggested the presence of a proton instead of a C-2 hydroxy in **1**, which was further corroborated by a deficit in its mass of 16 amu compared to **1** and hence the structure of **12** was assigned. The absolute configuration at C-4 was assigned as *S* based on the ECD spectrum of **12** compared to those of **1** and **13**, which were virtually identical (Figures S29 and S33). The relative configuration at C-3 was assigned based on the observed ROESY correlations and coupling constant analysis. The observed coupling constant of 2.7 Hz between H-3 and H-4 suggested a dihedral angle of either +51° or –64°.[1] Molecular models generated for 3*S*,4*S* and 3*R*,4*S* configurations yielded dihedral angles between H-3 and H-4 of –71° and +58° respectively. Hence, the

observed coupling constant of 2.7 Hz was appropriate for either a 3*R*,4*S* or 3*S*,4*S* configuration. However, a strong ROESY correlation between H_2-9 and H_3-10 and a very weak ROESY between H_3-10 and H-3 are consistent with a 3*R*,4*S* configuration for **12** (Figure S12). These findings were further confirmed by comparison of the literature data.[2]

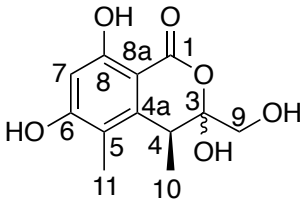

Table S13: NMR data for the major and minor isomers of dothideomynone A (**13**) in DMSO-d_6

Position	Major isomer		Minor isomer		2D NMR correlations		
	δ_C, type	δ_H, mult (*J*, Hz)	δ_C, type	δ_H, mult (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	168.8, C		169.0, C				
3	104.6, C		105.4, C				
4	34.9, CH	3.22, q (*7.2*)	33.7, CH	3.35, q (*7.2*)	3, 5, 6, 8a, 9	10	10, 11, 9[c]
4a	144.6, C		144.0, C				
5	113.4, C		113.5, C				
6	162.9, C		162.8, C				
7	99.8, CH	6.26, s	100.1, CH	6.26, s	5, 6, 8, 8a, 1(w), 11(w)		6-OH, 8-OH
8	161.2, C		161.1, C				
8a	98.9, C		98.1, C				
9	63.6, CH_2	3.61, d (*11.4*) 3.70, d (*11.4*)	64.4, CH_2	3.28, d (*11.4*) 3.42, d (*11.4*)	3, 4, 4a		10[b], 4[c]
10	16.2, CH_3	1.05, d (*7.2*)	14.4, CH_3	1.08, d (*7.2*)	3, 4, 4a	4	4, 9[b], 11
11	9.8, CH_3	1.98, s	9.7, CH_3	1.98, s	4a, 5, 6		4, 10
3-OH				[a]			
6-OH		10.57, s		10.60, s	5, 6, 7		7
8-OH		11.22, s		11.22, s	7, 8, 8a		7
9-OH		[a]		[a]			

[a]Not observed or not assignable, [b]Observed only in the major isomer, [c]Observed only in the minor isomer

Dothideomynone A (13): Colorless oil; $[\alpha]^{24}_D$ +28 (c 0.76, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 228 (–3.21), 240 (+1.58), 271 (+4.93), 237 (+7.00), 311 (–1.48) nm; NMR (600 MHz, DMSO-d_6) see Table S13; ESI-MS *m/z* 255.1 $[M + H]^+$.

Dothideomynone A (**13**) was isolated as colorless oil with a molecular mass of 254 (ESI-MS). The ^1H NMR spectrum indicated a mixture of two inseparable stereoisomers in the ratio of 5.6:1 (Figure S13). The UV spectrum (Figure S26) and the $^1H/^{13}C$ NMR spectra (Table S13) were characteristic of an isochromanome and matched the reported spectroscopic data for dothideomynone A[3] and assignment of the 2D NMR data confirmed the structure as dothideomynone A. The ECD spectrum of **13** (Figure S39) was almost identical to **1**, confirming the same absolute configurations at C-3 and C-4, i.e., 3*R*,4*S* for the major and 3*S*,4*S* for the minor isomer. However, the observed specific optical rotation (+28 deg cm^2 g^{-1}) did not match the published specific rotation (+60 deg cm^2 g^{-1}) of dothideomynone A, despite being acquired under identical conditions (solvent and concentration), suggesting that our compound may be a diastereomer of the published structure.

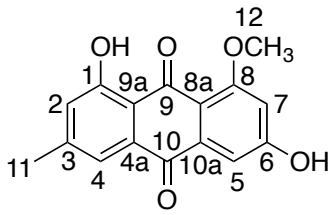

Table S14: NMR data for questin (**14**) in DMSO-d_6

Position	δ_C, type	δ_H, mult (*J*, Hz)	^{1}H-^{13}C HMBC	COSY	ROESY
1	161.8, C				
2	124.3, CH	7.14, m	1(w), 4, 11, 9a, 9(w)	4, 11	1-OH, 11
3	146.7, C				
4	119.2, CH	7.45, m	2, 9a, 10, 11	2, 11	11
5	107.3, CH	7.21, d (*2.3*)	7, 8a, 10, 6(w)	7	6-OH
6	164.9, C				
7	105.1, CH	6.84, d (*2.3*)	5, 8a, 6, 8	5	6-OH, 12
8	163.6, C				
9	186.4, C				
10	182.5, C				
4a	136.9, C				
10a	132.2, C				
8a	112.6, C				
9a	114.5, C				
11	21.5, CH_3	2.40, br s	2, 3, 4	2, 4	2, 4
12	56.4, CH_3	3.91, s	8		7, 6-OH
1-OH		13.29, s	1, 2, 8a		2
6-OH		11.26, br s	5, 6, 7		5, 7, 12

Questin (14): Yellow-orange solid; NMR (600 MHz, DMSO-d_6) see Table S14. ESI-MS *m/z* 281.1 $[M - H]^-$.

Questin (**14**) was isolated as a yellow-orange optically inactive solid. The UV-visible spectrum (Figure S27) with peak maxima at wavelengths 228, 246, 275, 430 nm and shoulder at 346 nm is characteristic of anthraquinones. The ESI-MS of **14** suggested a molecular mass of 284. The ^{1}H and the ^{13}C NMR spectra showed the presence of 12 hydrogens and 16 carbons respectively suggesting a molecular formula of $C_{12}H_{16}O_5$. A search for anthraquinones with this formula suggested **14** as a possible match, which was further confirmed by comparison of the observed chemical shifts of the ^{1}H and ^{13}C NMR spectra (Table S14) with those reported in the literature.[4]

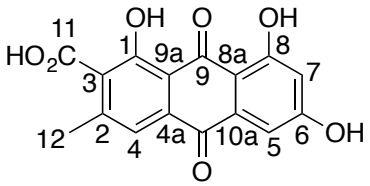

Table S15: NMR data for endocrocin (**15**) in DMSO-d_6

Position	δ_C, type	δ_H, multi (*J*, Hz)	^1H-^{13}C HMBC	COSY	ROESY
1	157.8 br, C				
2	130.5, C				
3	143.6, C				
4	120.5, CH	7.57, br s	2, 9a, 10, 12, 11(w), 9(w)	12	12
5	109.2, CH	7.15, d (*2.4*)	7, 10, 8a, 4a(w)	7	7, 6-OH
6	165.7, C				
7	108.0, CH	6.63, d (*2.4*)	5, 6, 8a, 9(w)	5	5, 6-OH, 7-OH
8	164.5, C				
9	189.4, C		s		
10	181.2, C				
11	167.1, C				
12	19.7, CH_3	2.41, br s	2, 3, 4	4	4
4a	135.1, C				
8a	108.9, C				
9a	114.0, C				
10a	132.6, C				
1-OH		12.42, br s			
6-OH		12.05, s	5, 7, 8, 6(w)		5, 7
8-OH		11.44, br s			

Endocrocin (**15**): Yellow-orange solid; NMR (600 MHz, DMSO-d_6) see Table S15. ESI-MS *m/z* 313.0 $[M - H]^-$.

Endocrocin (**15**) was isolated as a yellow to yellow-orange optically inactive solid. The UV-visible spectrum (Figure S28) was characteristic of anthraquinones, specifically 1,8-dihydroxyanthraquinones with peak maxima at wavelengths 224, 256, 266, 284, 448 nm with a shoulder at 368 nm. The ESI-MS of **15** revealed a molecular mass of 314. A search of the literature for anthraquinones with this mass suggested endocrocin as a possible match. Comparison of the observed ^1H and the ^{13}C NMR chemical shifts and assignment of the observed 2D NMR correlations (Table S15) confirmed the structure of **15** as endocrocin.

B. Figures

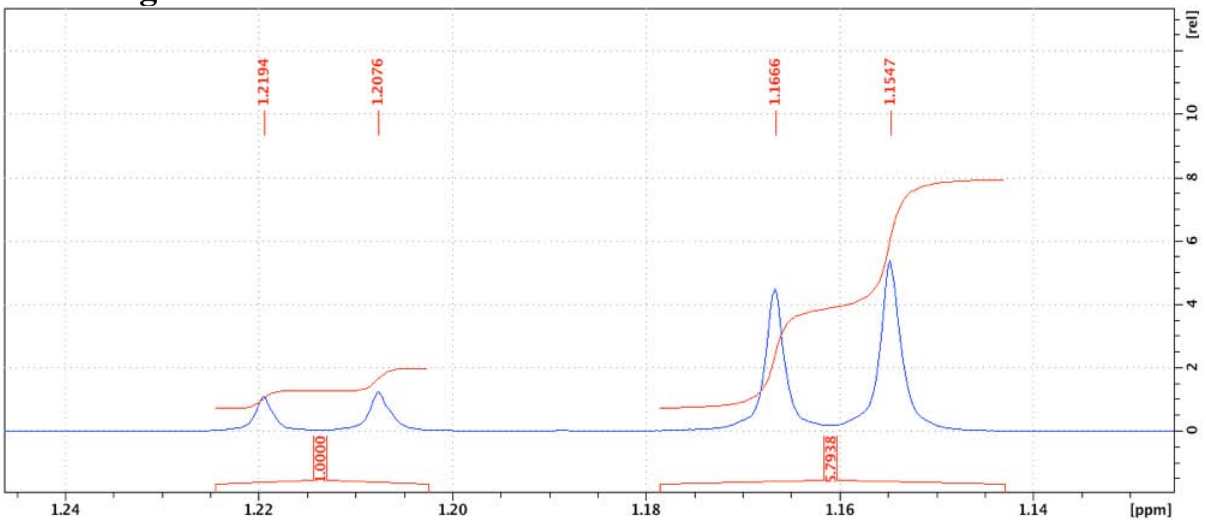

Figure S1: Expansion of the ^{1}H NMR spectrum of banksialactone A (**1**) in methanol-d_4 showing the ratio of the major to minor isomer as 5.8:1 at H_3–10.

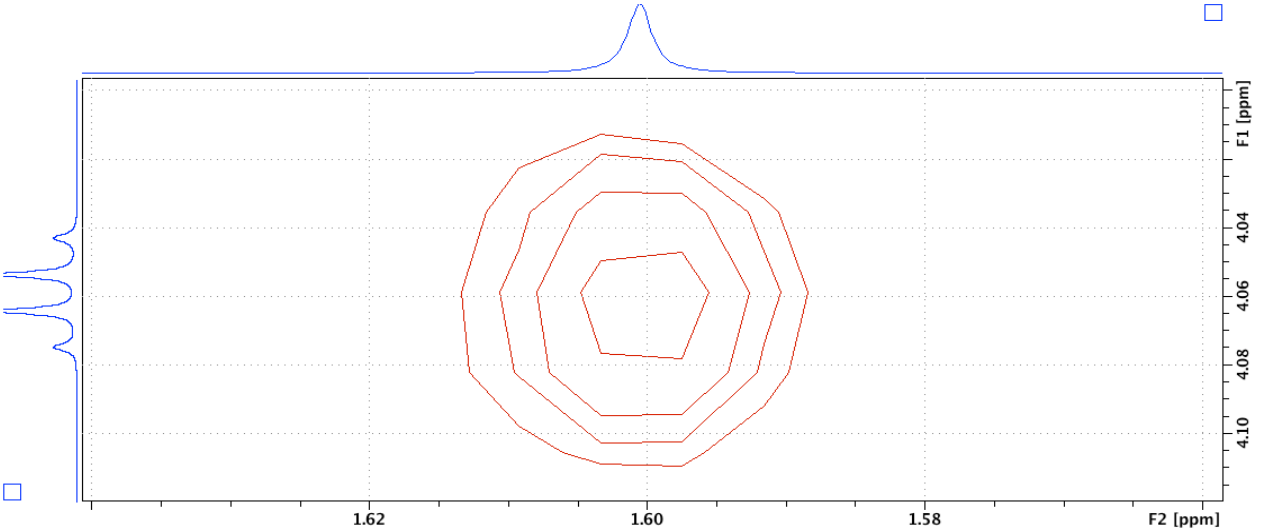

Figure S2: Expansion of the ROESY NMR spectrum of banksialactone B (**2**) showing strong correlation between H-3 and H_3-10 protons.

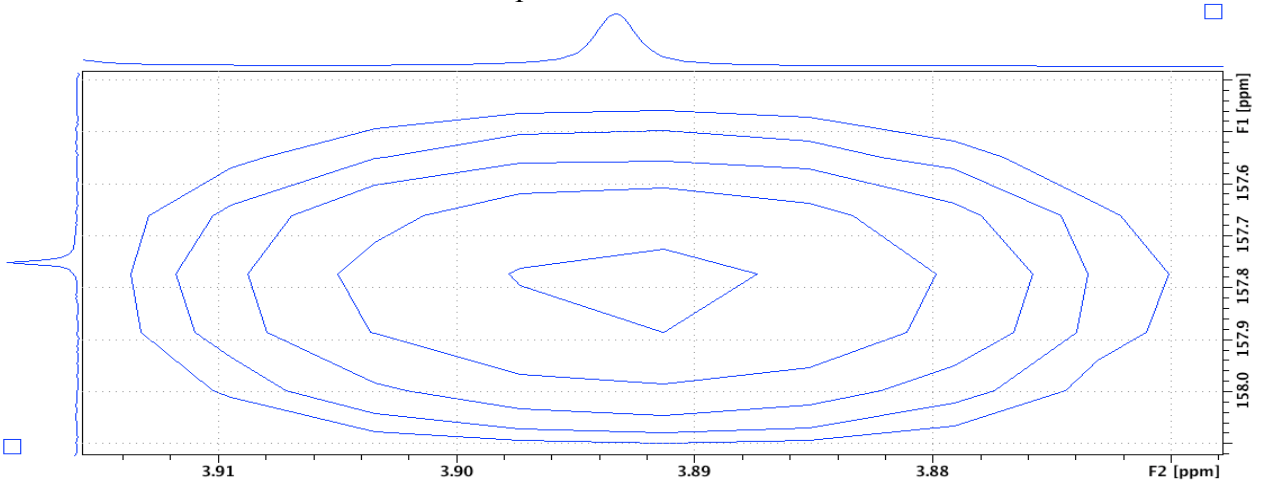

Figure S3: HMBC correlation from H_3-13 methoxy protons to C-8 in banksialactone D (**4**).

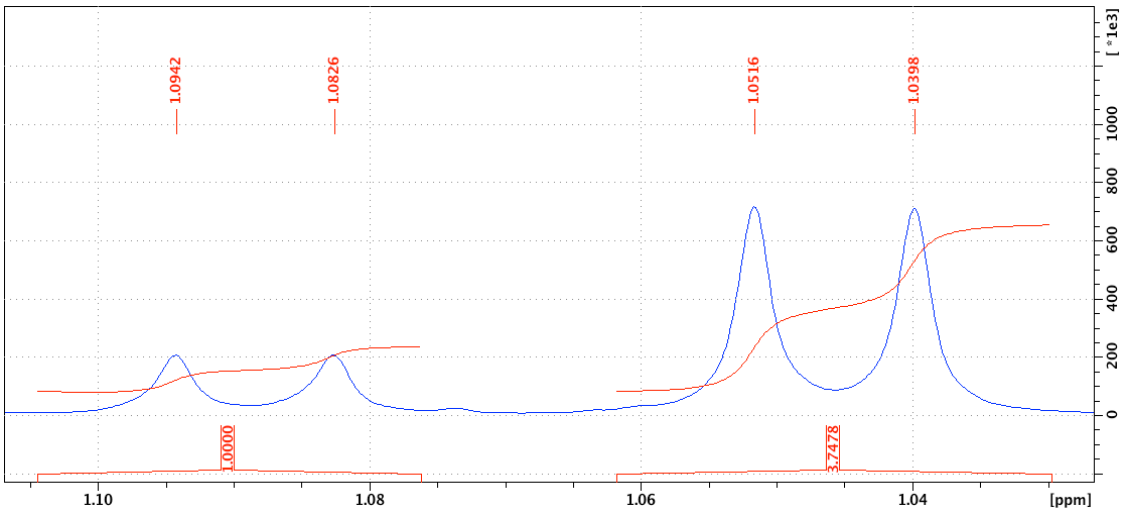

Figure S4: Section of the ^{1}H NMR spectrum of banksialactone E (**5**) showing the ratio of the minor to the major isomer as 1: 3.75 at H_3-14.

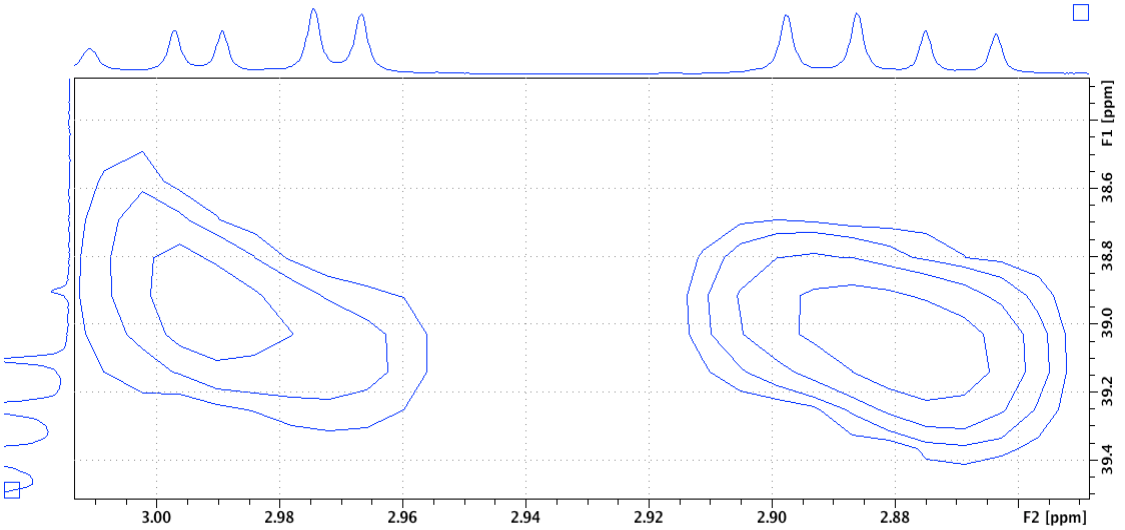

Figure S5: HMBC correlation from H_2-11 oxymethylene protons to C-9 showing connectivity between the isochromanyl and the 3-mercaptolactate moiety in banksialactone E (**5**)

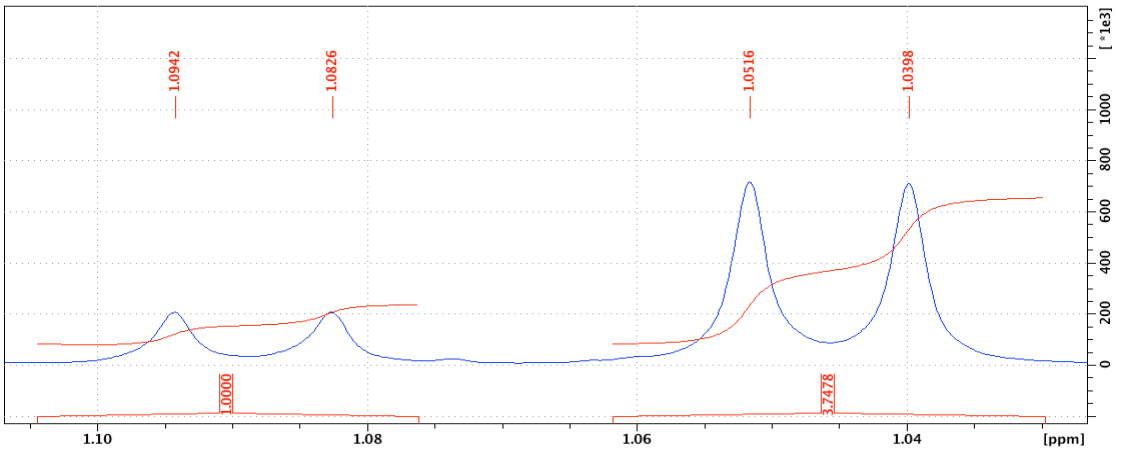

Figure S6: Expansion of the ^{1}H NMR spectrum showing the H_3-13 ratio of the four isomers of banksialactone F (**6**) as 1: 4.1: 6.7: 14.3

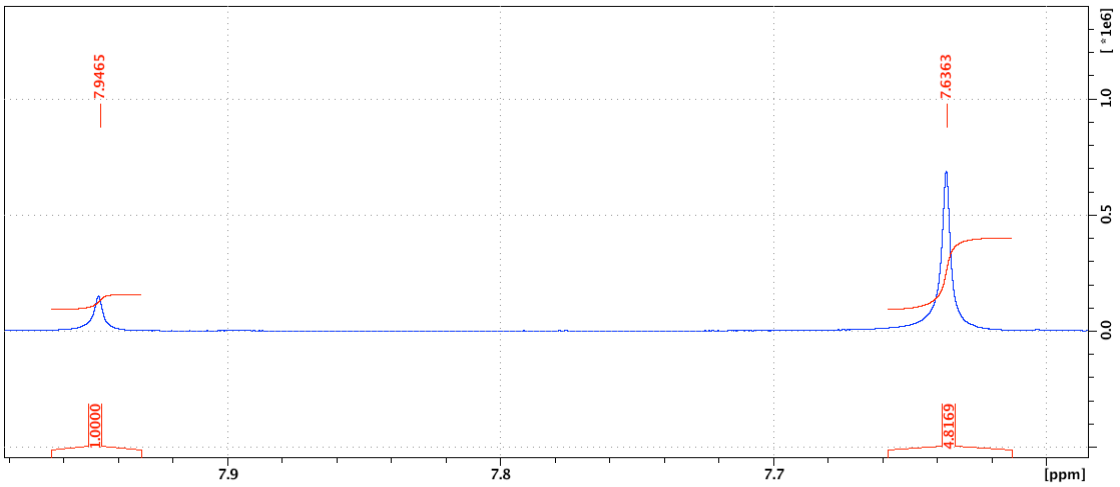

Figure S7: Expansion of the ^{1}H NMR spectrum showing the 3-OH ratio of the minor to the major isomer in banksialactone G (**7**) as 1: 4.8 in DMSO-d_6.

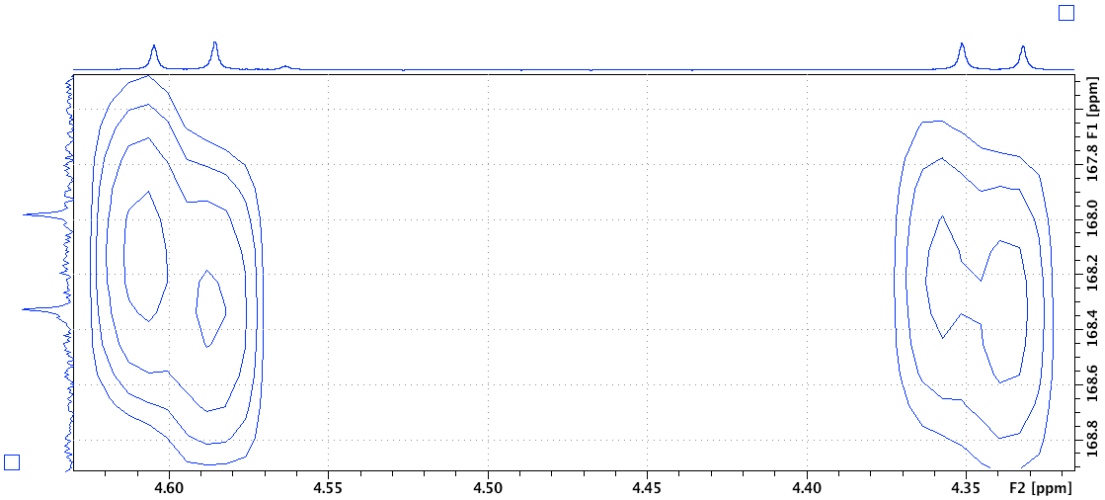

Figure S8: HMBC correlation from H_2-9 oxymethylene protons to C-11 showing connectivity between the isochromanyl and the orsellinate fragments in banksialactone G (**7**).

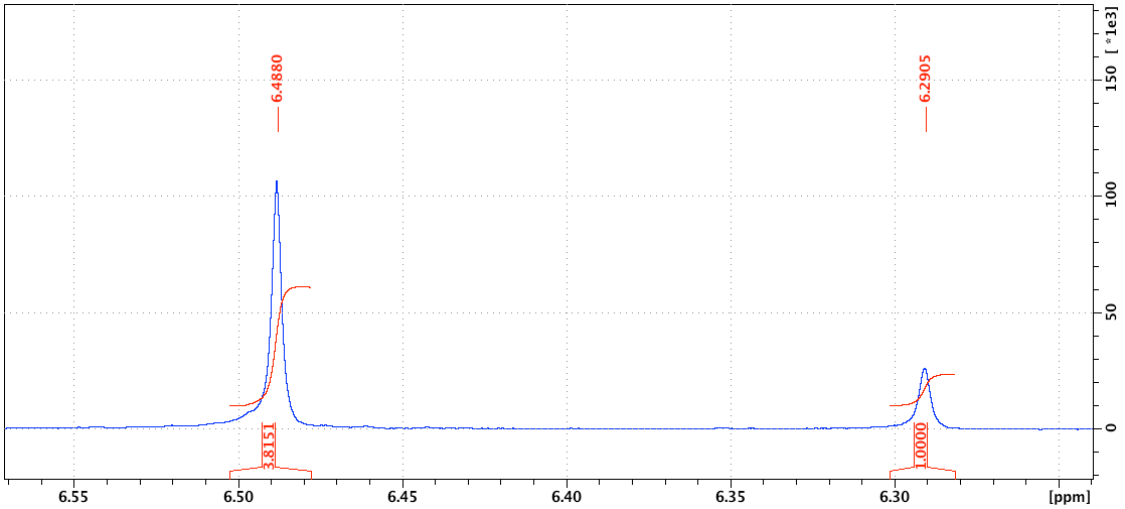

Figure S9: Expansion of ^{1}H NMR spectrum of banksialactone H (**8**) showing the H-7 ratio of the minor isomer to the major isomer as 1: 3.8 in DMSO-d_6.

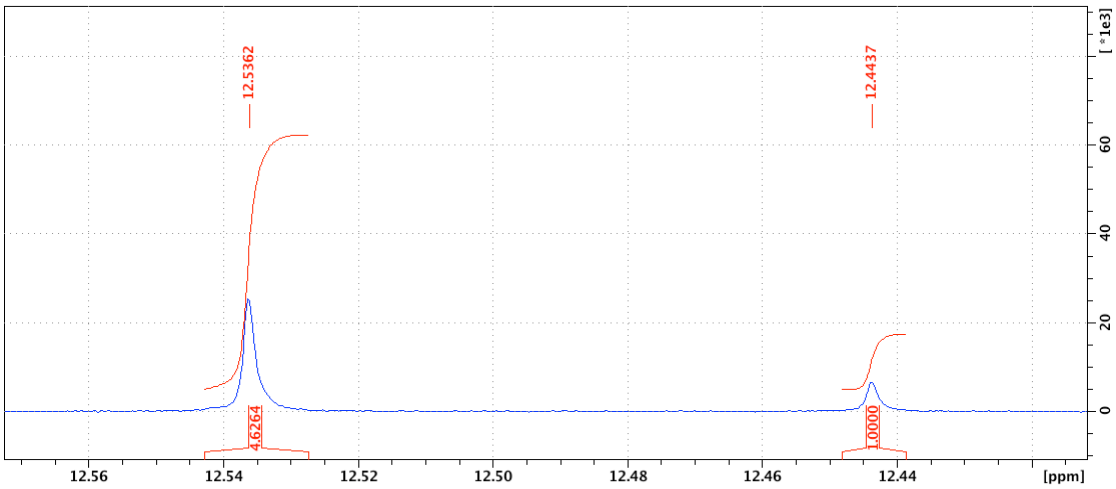

Figure S10: Expansion of the ^{1}H NMR spectrum of banksialactone I (**9**) showing the 1'-OH ratio of the two isomers as 1: 4.6 in DMSO-d_6.

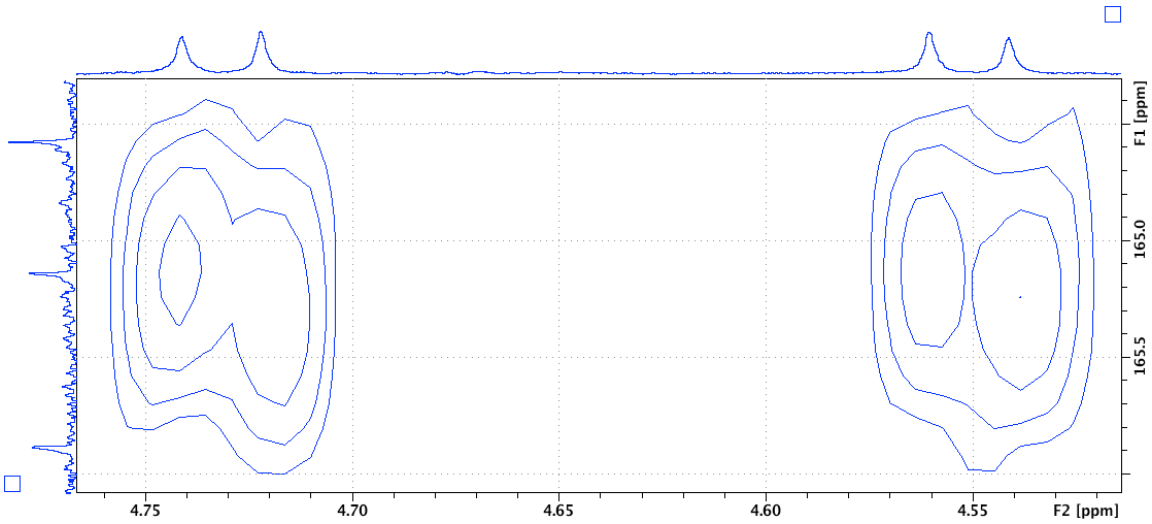

Figure S11: HMBC correlation from H_2-9 oxymethylene protons to C-11 showing connectivity between the isochromanyl and the endocrocin fragment of banksialactone I (**9**).

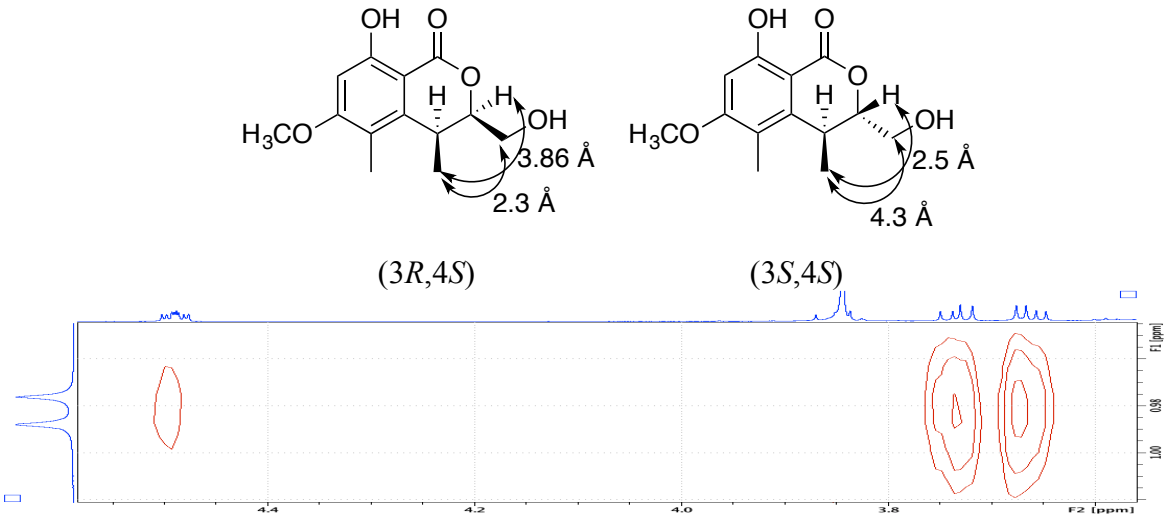

Figure S12: ROESY spectrum of clearanol I (**12**) showing ROE correlations between H_3-10 and H-3/ H_2-9.
The inset shows interproton distances from molecular modeling for (3*S*,4*S*)- and (3*R*,4*S*)-clearanol I. The observed ROEs fit for (3*R*,4*S*)-clearanol I, noting that the 4*S*-configuration is set from ECD/DFT results.

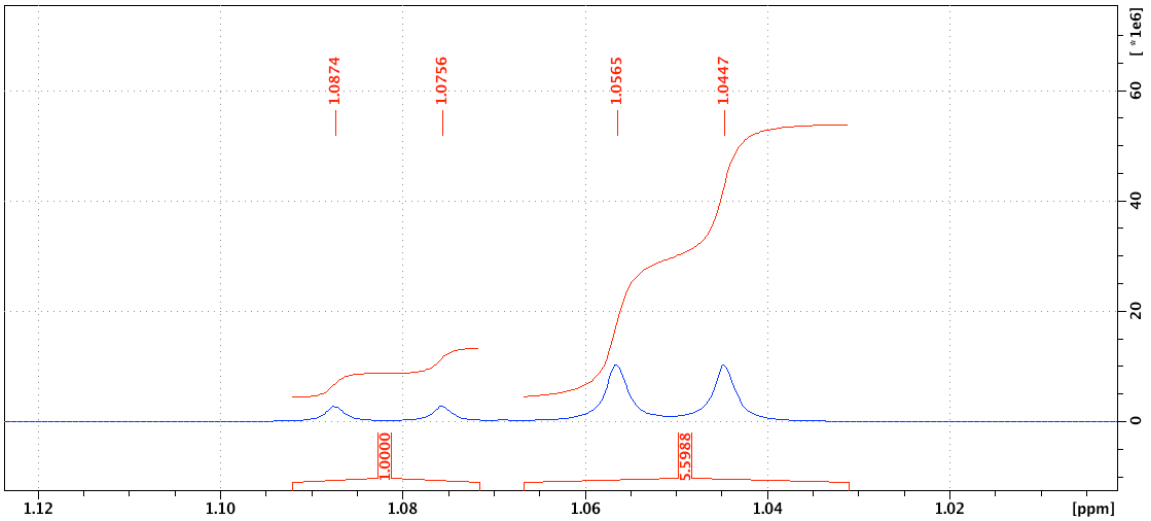

Figure S13: Expansion of the ^{1}H NMR spectrum of dothideomynone A (**13**) showing the ratio of the two isomers at H_3-10 as 1: 5.6 inDMSO-d_6.

C. UV-visible spectra

UV-visible spectra in CH_3CN/H_2O-water 0.05% HCOOH

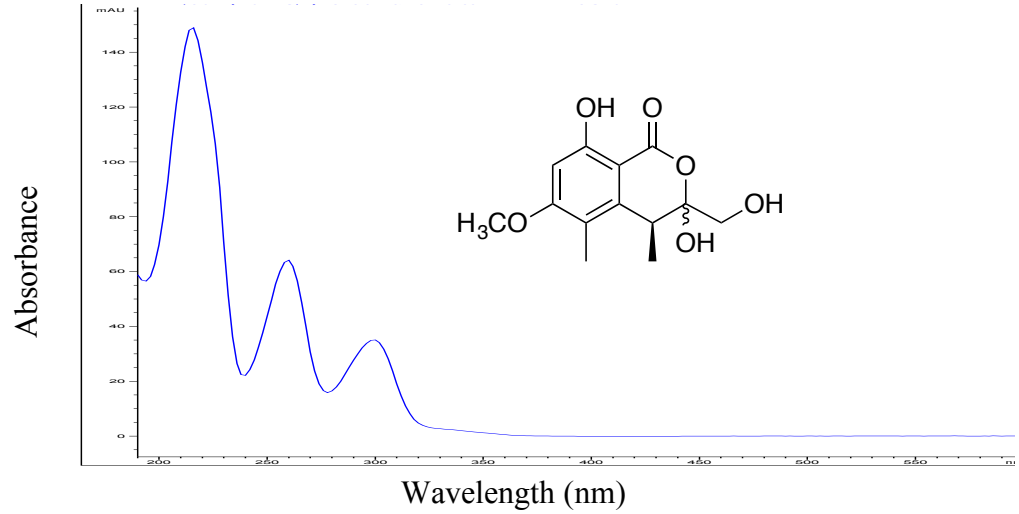

Figure S14: UV- visible spectrum of banksialactone A (**1**).

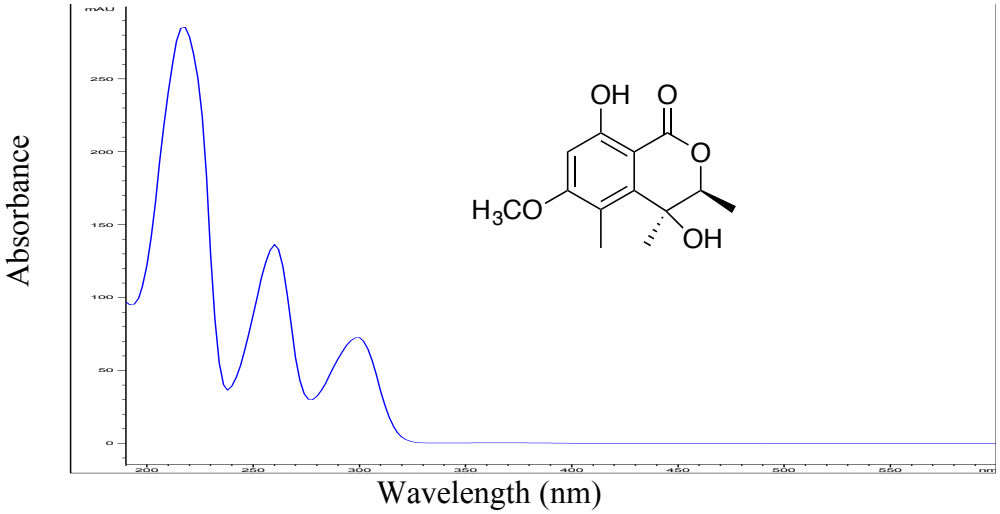

Figure S15: UV- visible spectrum of banksialactone B (**2**).

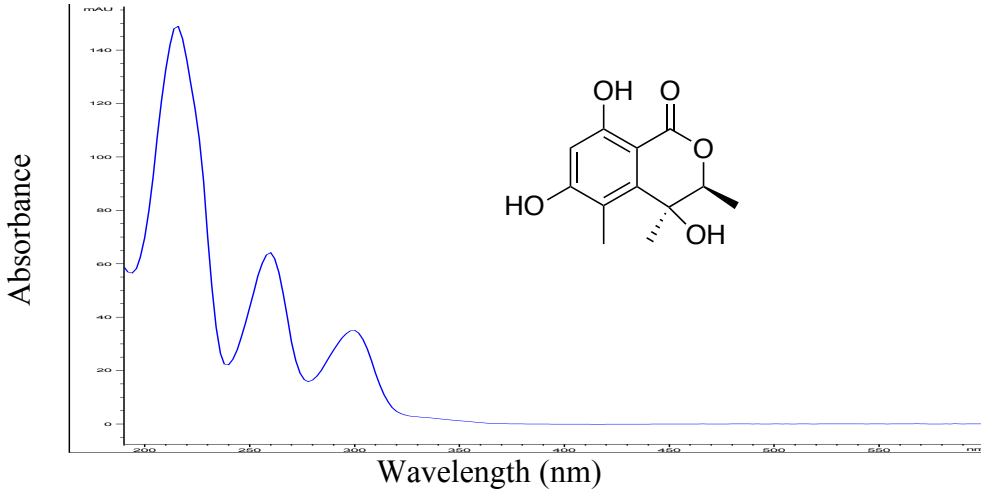

Figure S16: UV- visible spectrum of banksialactone C (**3**).

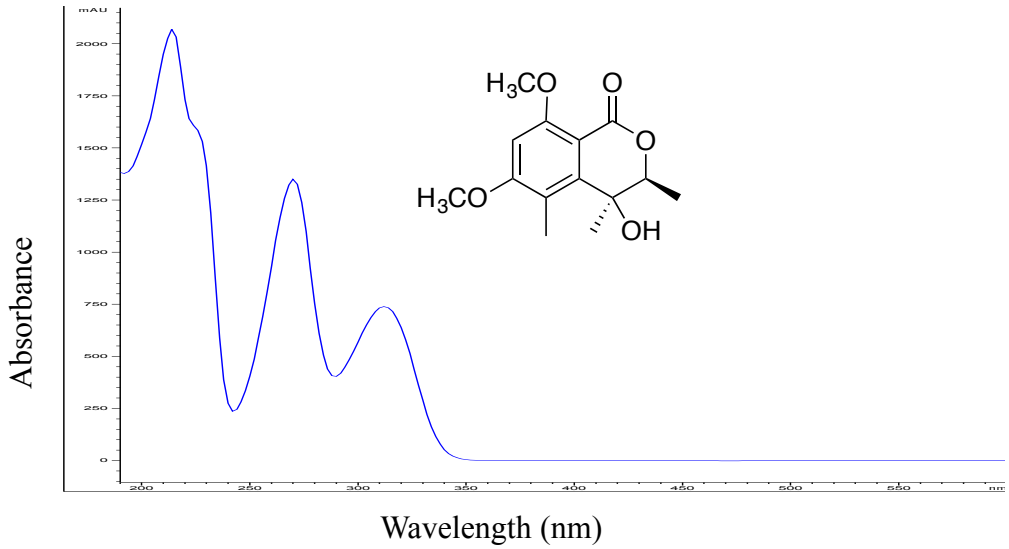

Figure S17: UV- visible spectrum of banksialactone D (**4**)

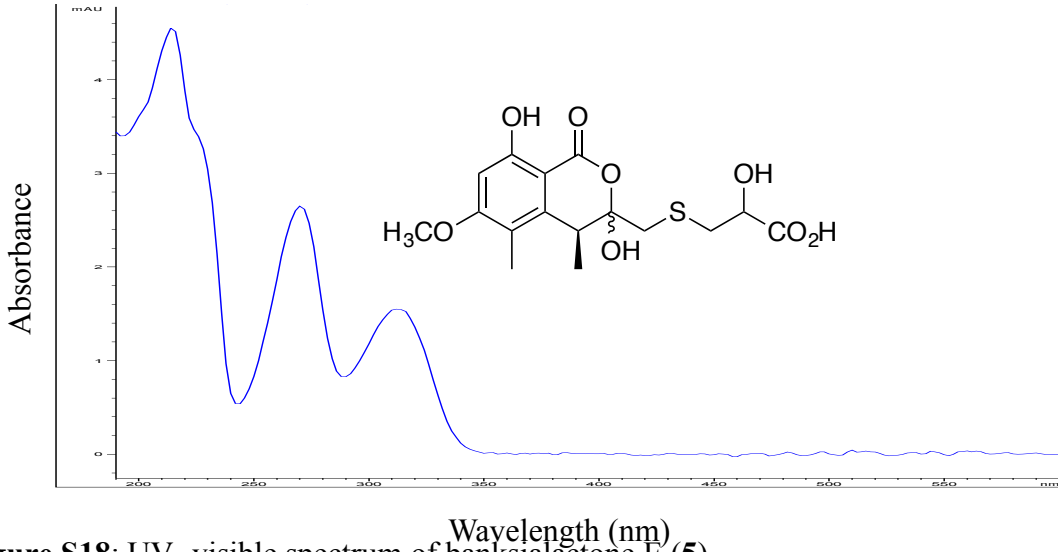

Figure S18: UV- visible spectrum of banksialactone E (**5**).

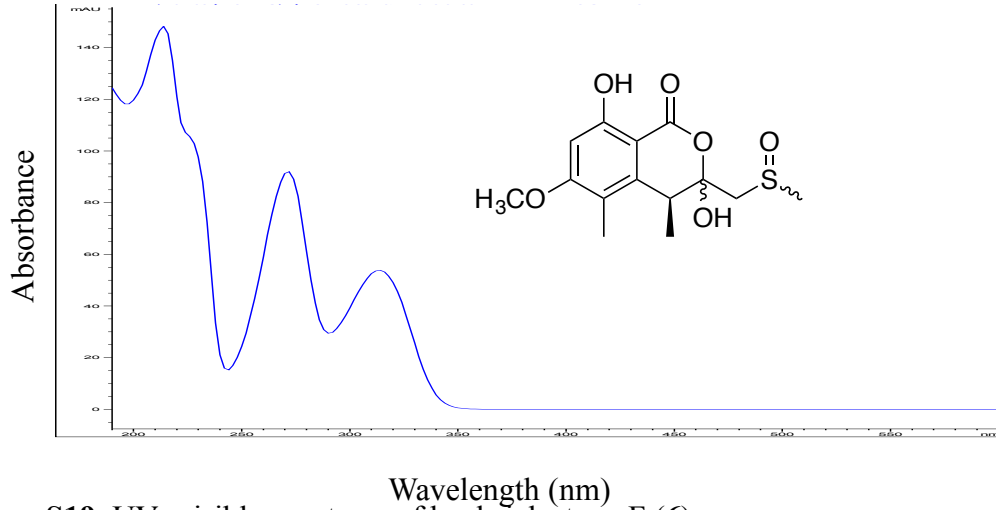

Figure S19: UV- visible spectrum of banksialactone F (**6**).

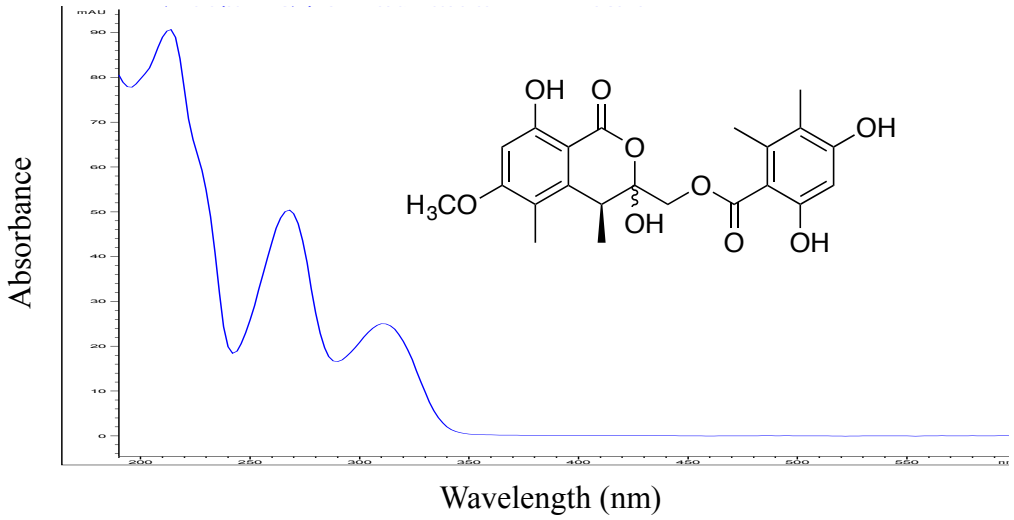

Figure S20: UV- visible spectrum of banksialactone G (**7**).

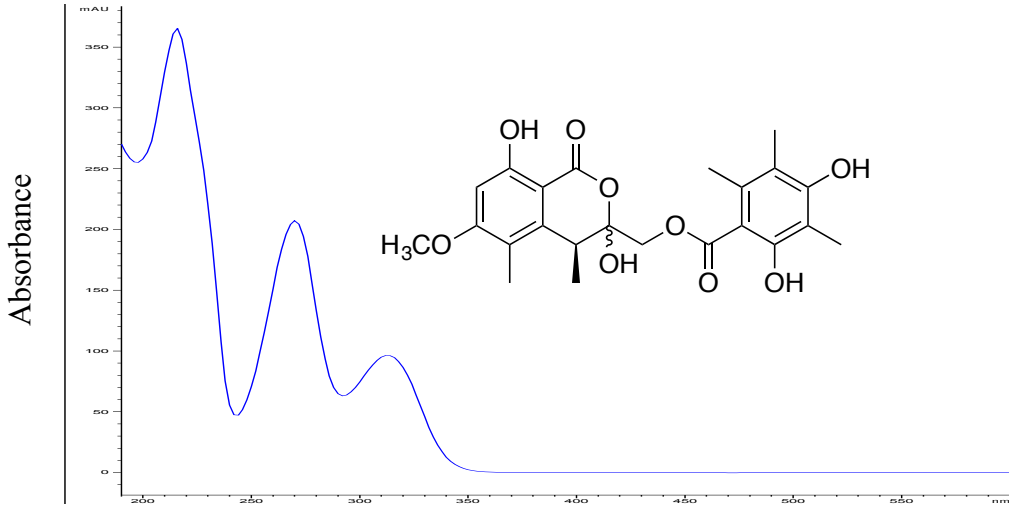

Figure S21: UV- visible spectrum of banksialactone H (**8**).

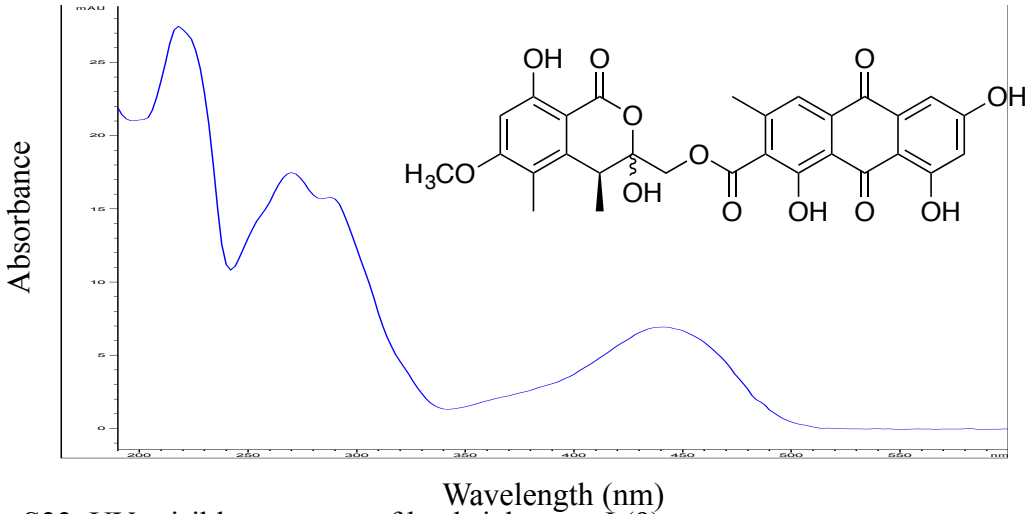

Figure S22: UV- visible spectrum of banksialactone I (**9**).

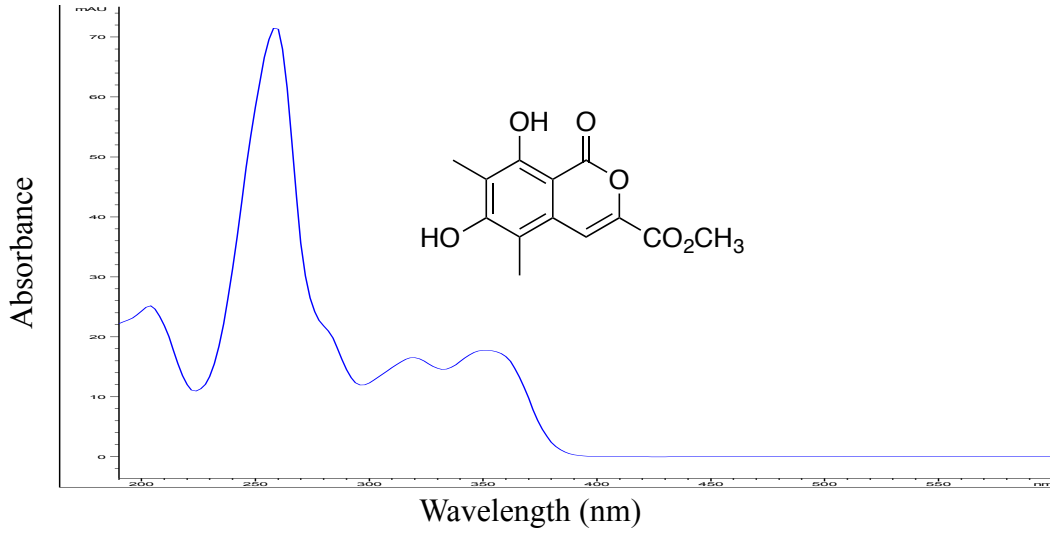

Figure S23: UV- visible spectrum of banksiamarin A (**10**).

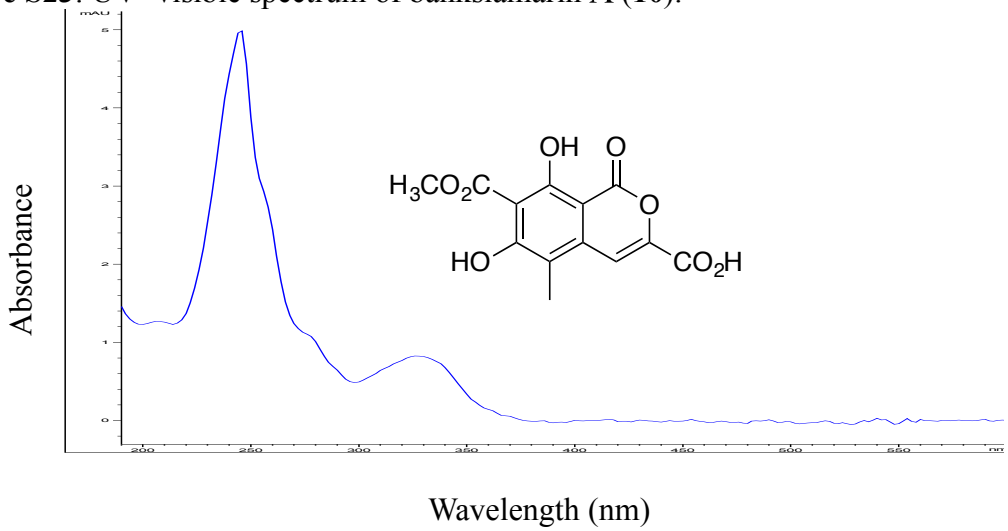

Figure S24: UV- visible spectrum of banksiamarin B (**11**).

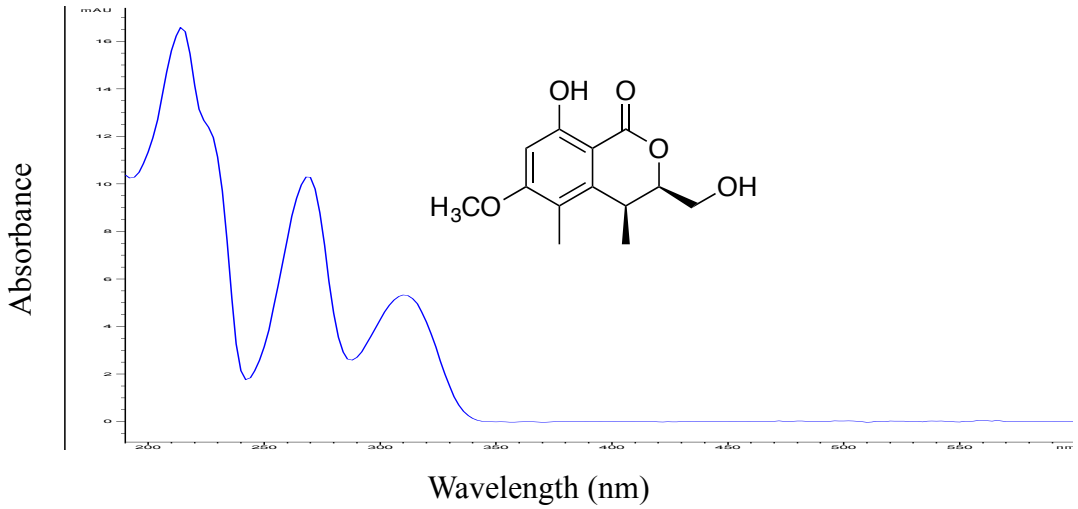

Figure S25: UV- visible spectrum of clearanol I (**12**).

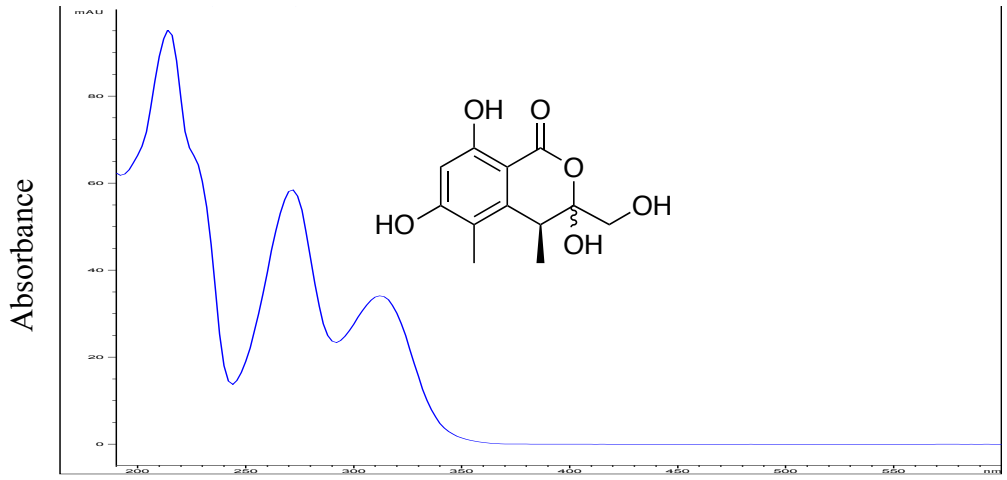

Figure S26: UV- visible spectrum of dothideomynone A (**13**).

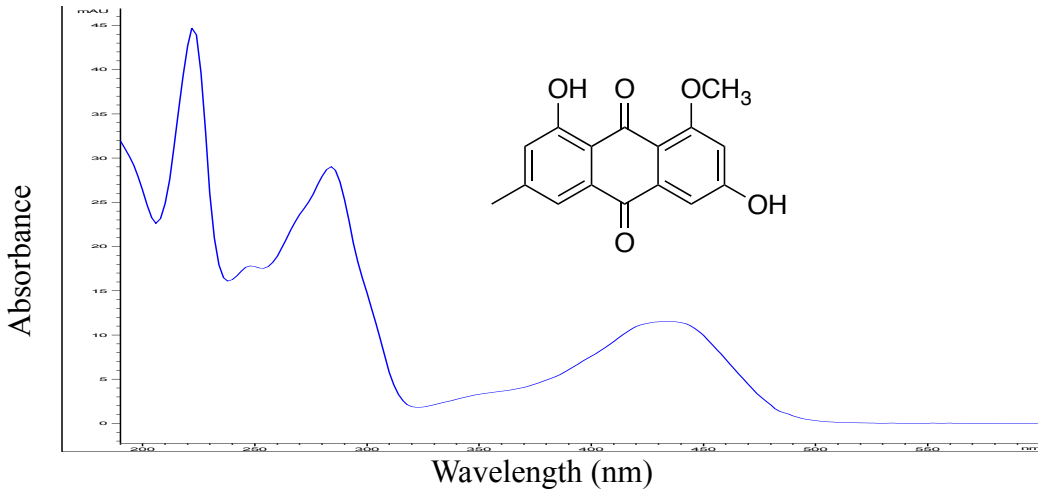

Figure S27: UV- visible spectrum of questin (**14**).

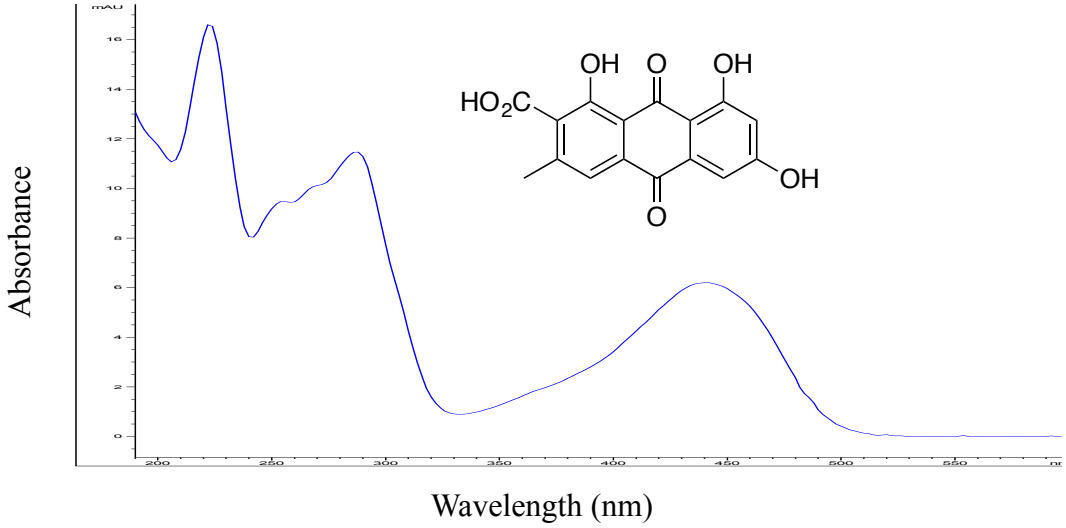

Figure S28: UV- visible spectrum of endocrocin (**15**).

D. ECD spectra

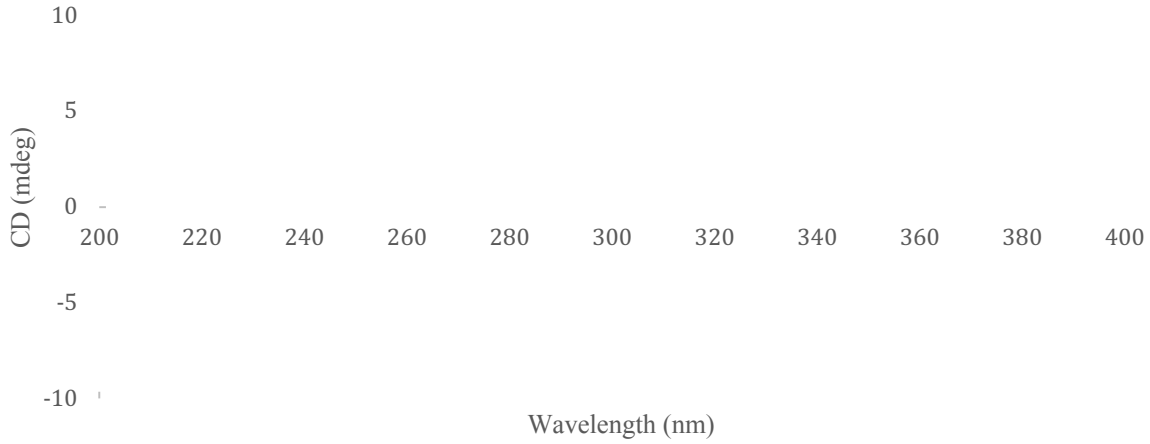

Figure S29: ECD spectrum of banksialactone A (**1**) in MeOH.

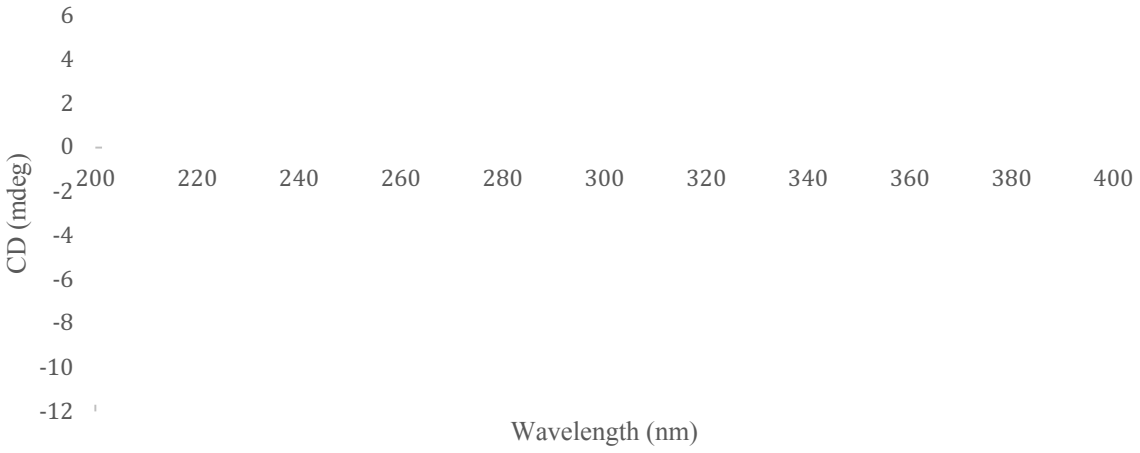

Figure S30: ECD spectrum of banksialactone B (**2**) in MeOH.

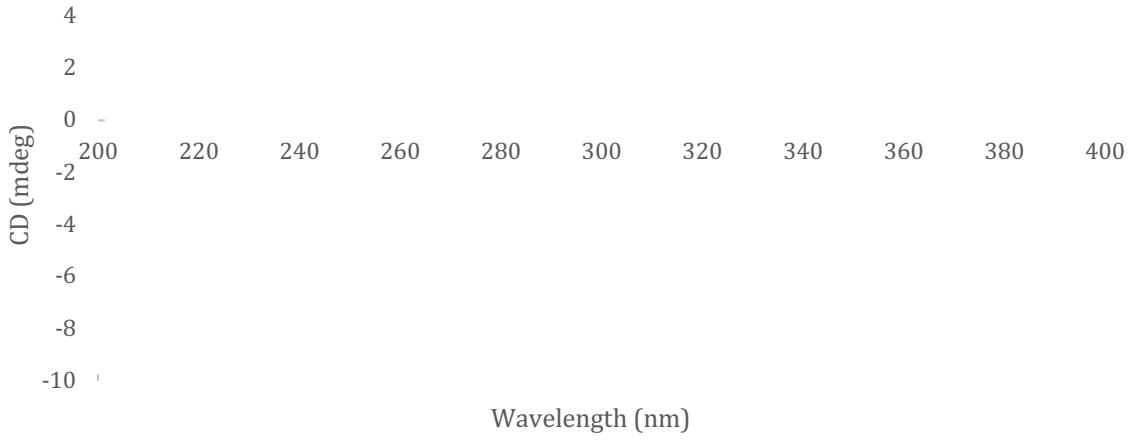

Figure S31: ECD spectrum of banksialactone C (**3**) in MeOH.

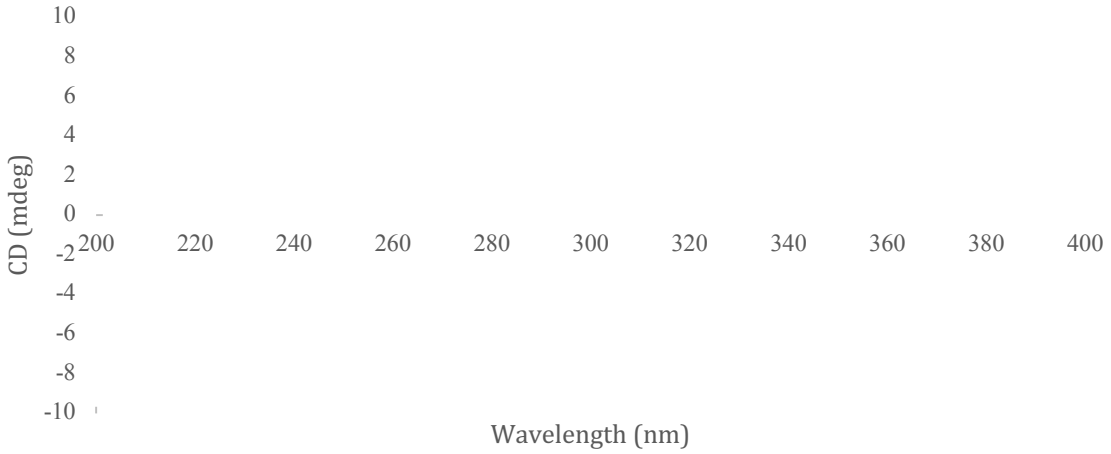

Figure S32: ECD spectrum of banksialactone D (**4**) in MeOH.

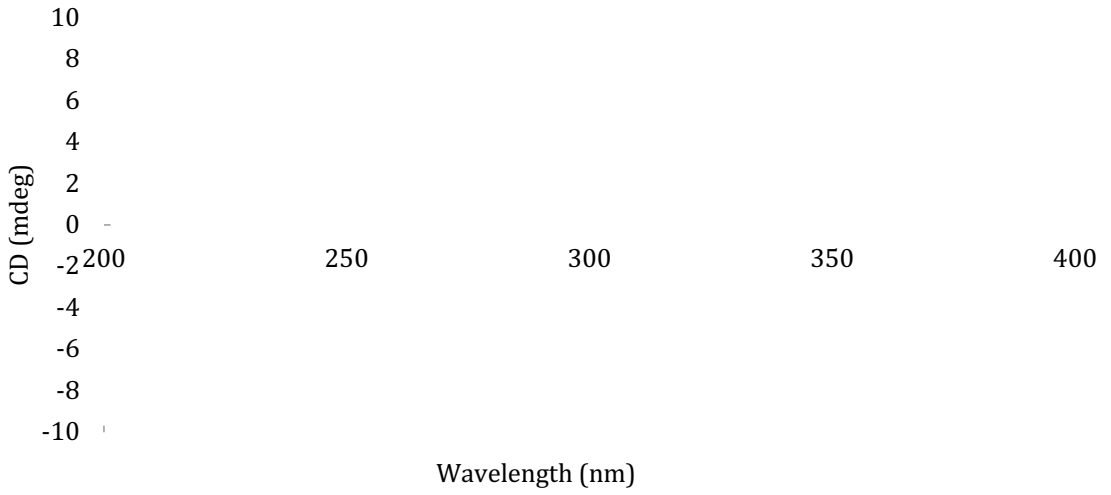

Figure S33: ECD spectrum of banksialactone E (**5**) in MeOH

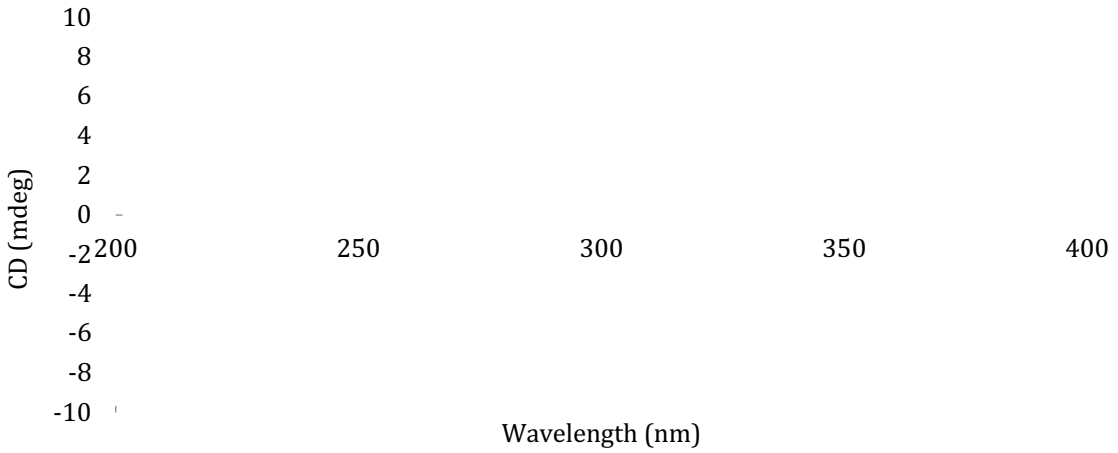

Figure S34: ECD spectrum of banksialactone F (**6**) in MeOH.

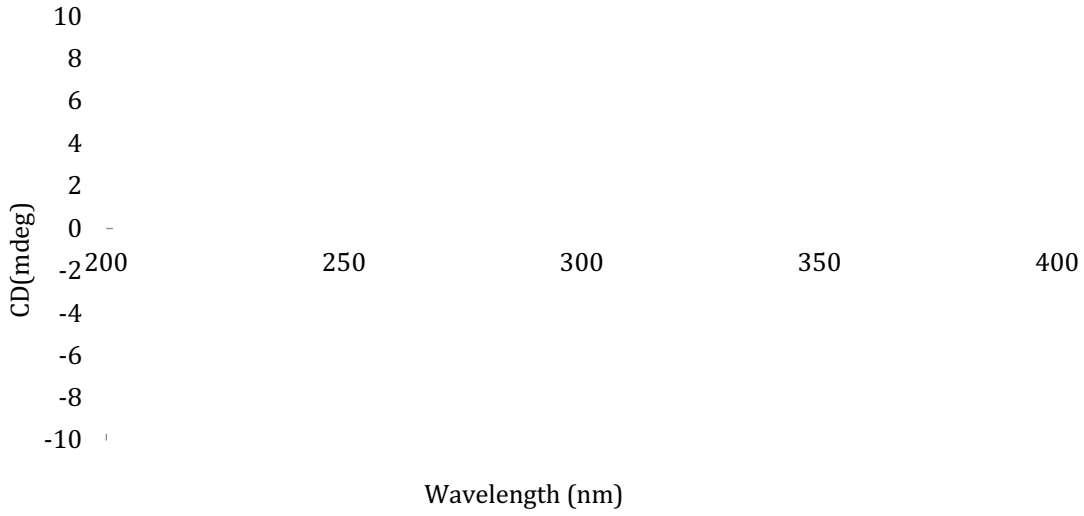

Figure S35: ECD spectrum of banksialactone G (**7**) in MeOH.

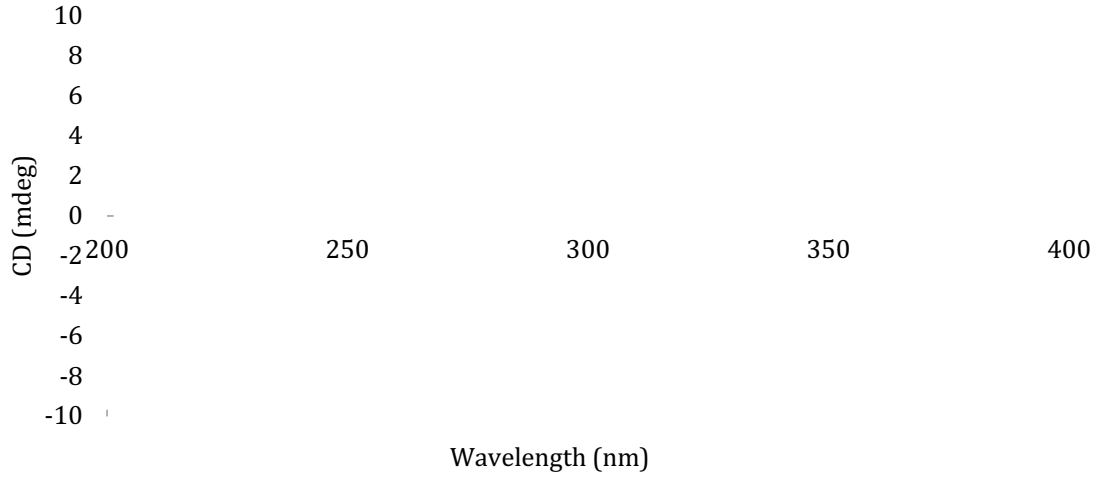

Figure S36: ECD spectrum of banksialactone H (**8**) in MeOH.

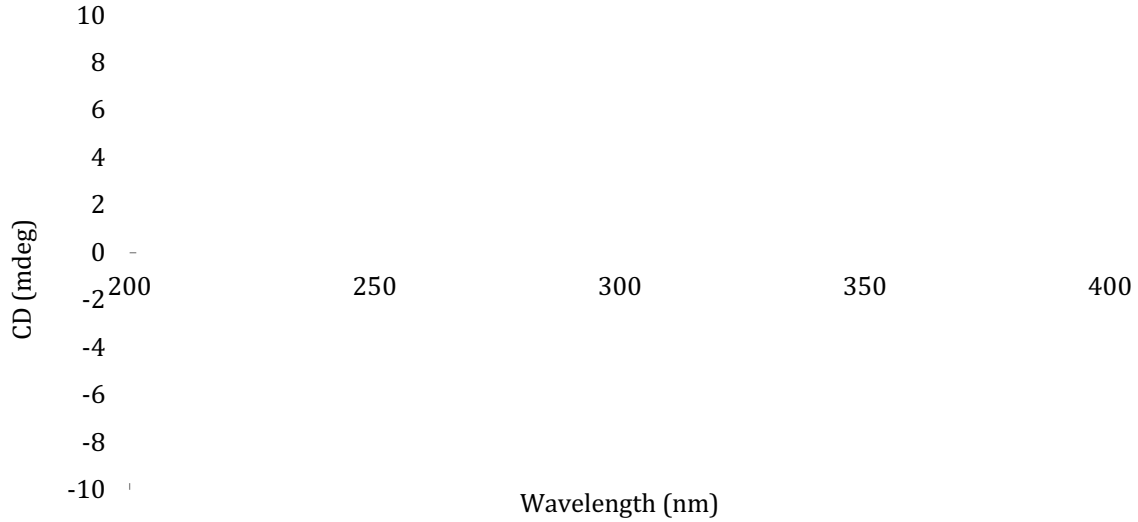

Figure S37: ECD spectrum of banksialactone I (**9**) in MeOH.

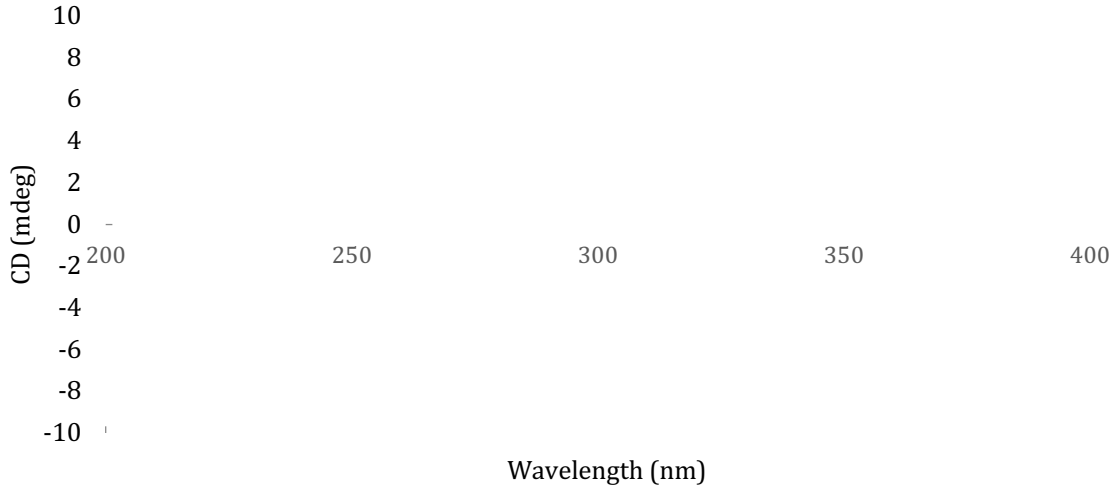

Figure S38: ECD spectrum of clearanol I (**12**) in MeOH.

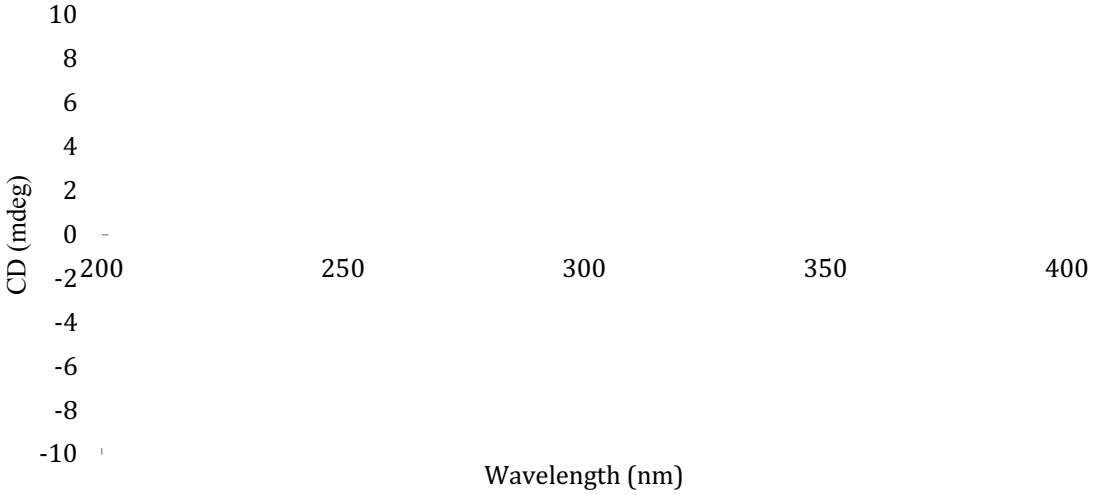

Figure S39: ECD spectrum of dothideomynone A (**13**) in MeOH.

E. ^{1}H (600 MHz) and ^{13}C NMR (150 MHz) NMR spectra

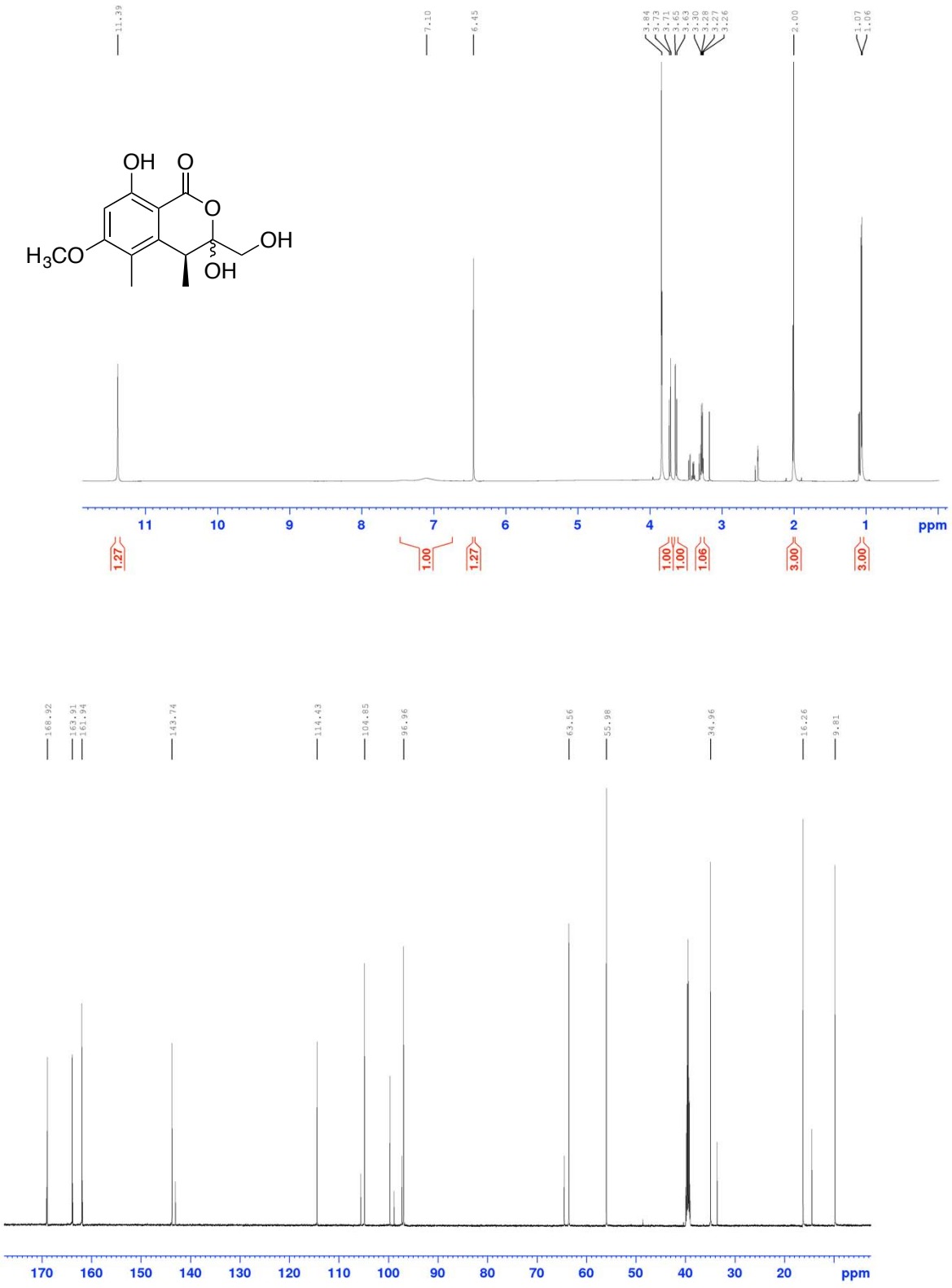

Figure S40: ^{1}H and ^{13}C NMR spectra of banksialactone A (**1**) in DMSO-d_6

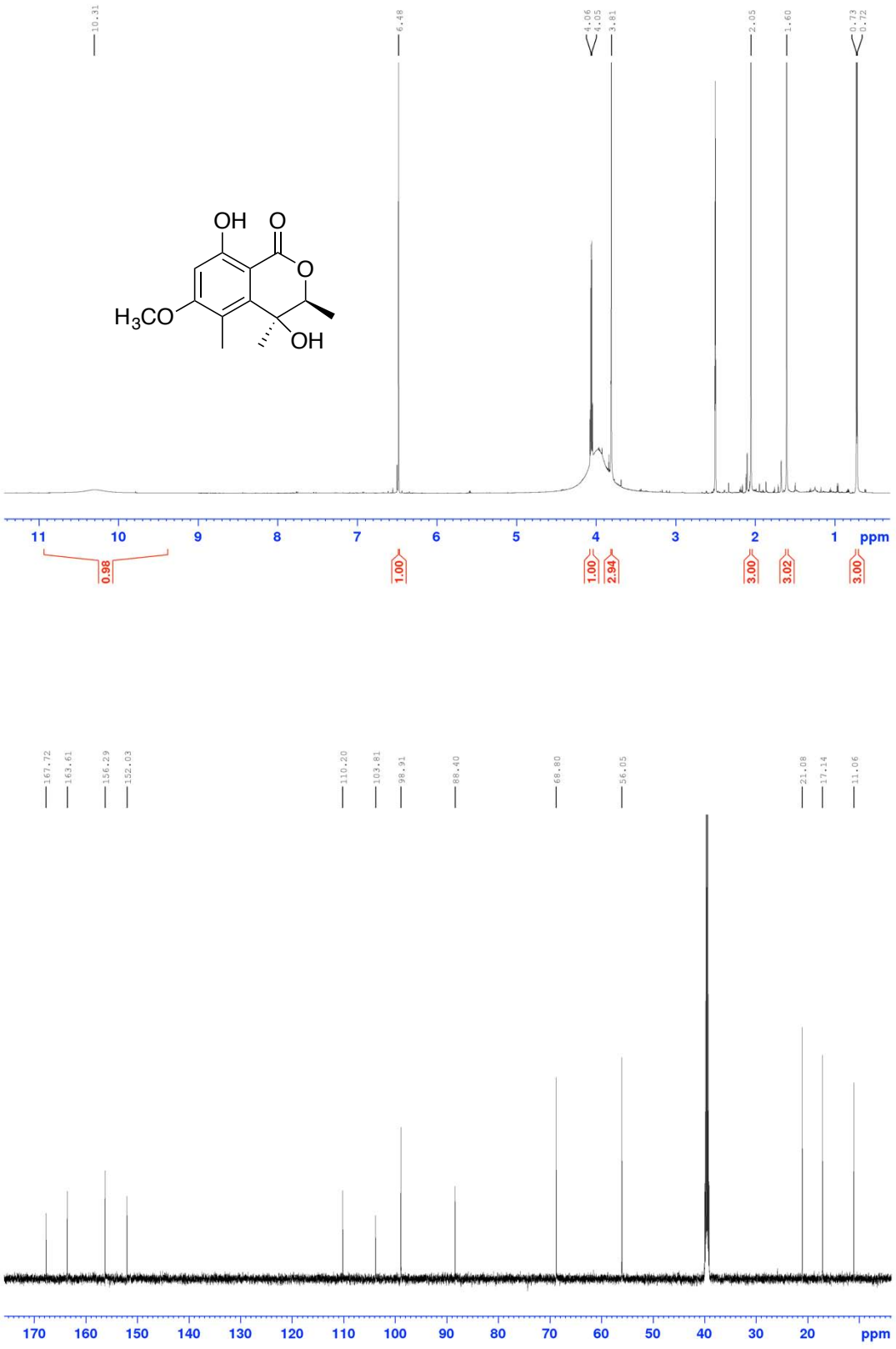

Figure S41: ^{1}H and ^{13}C NMR spectra of banksialactone B (**2**) in DMSO-d_6

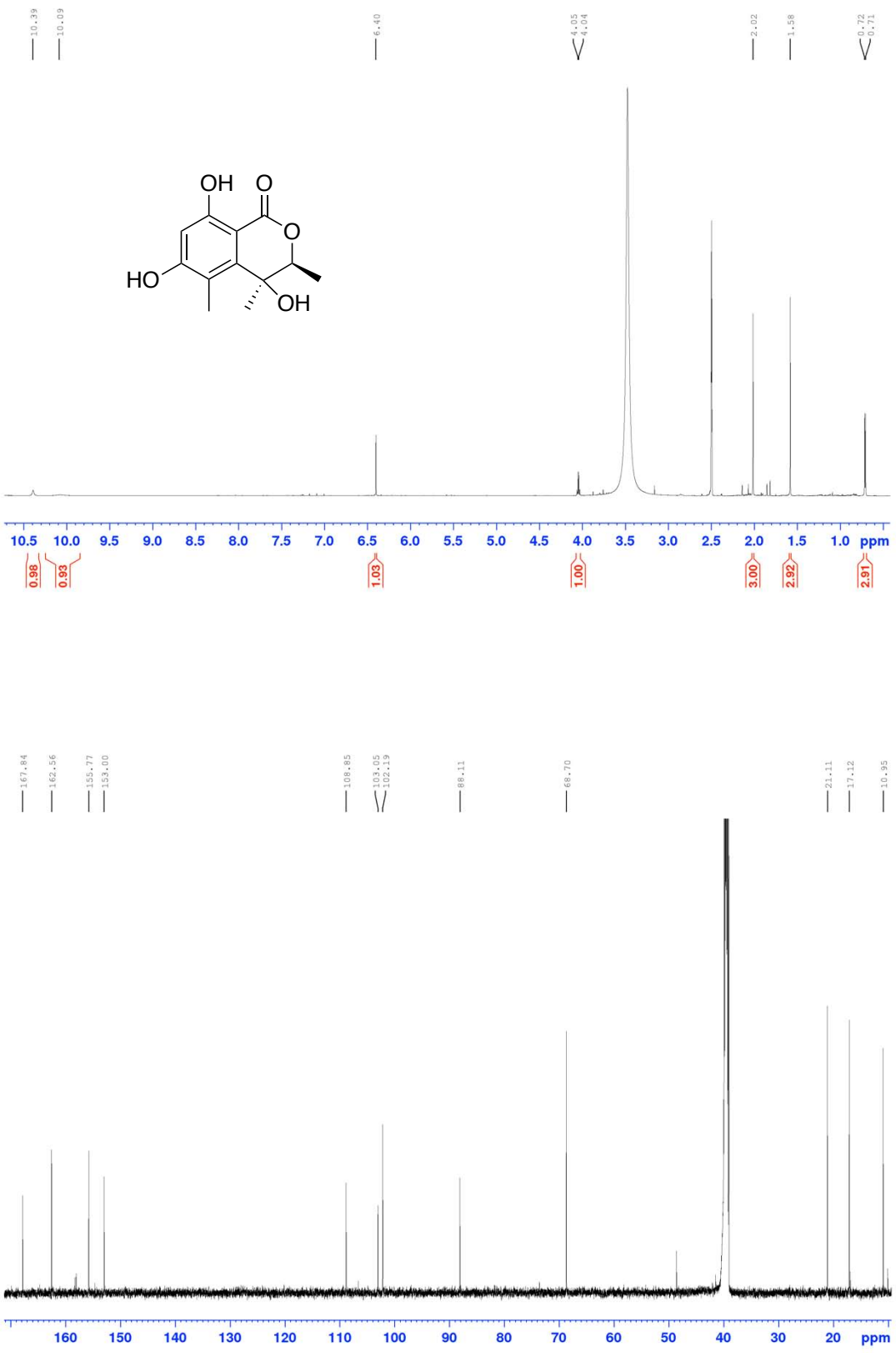

Figure S42: ^{1}H and ^{13}C NMR spectra of banksialactone C (**3**) in DMSO-d_6

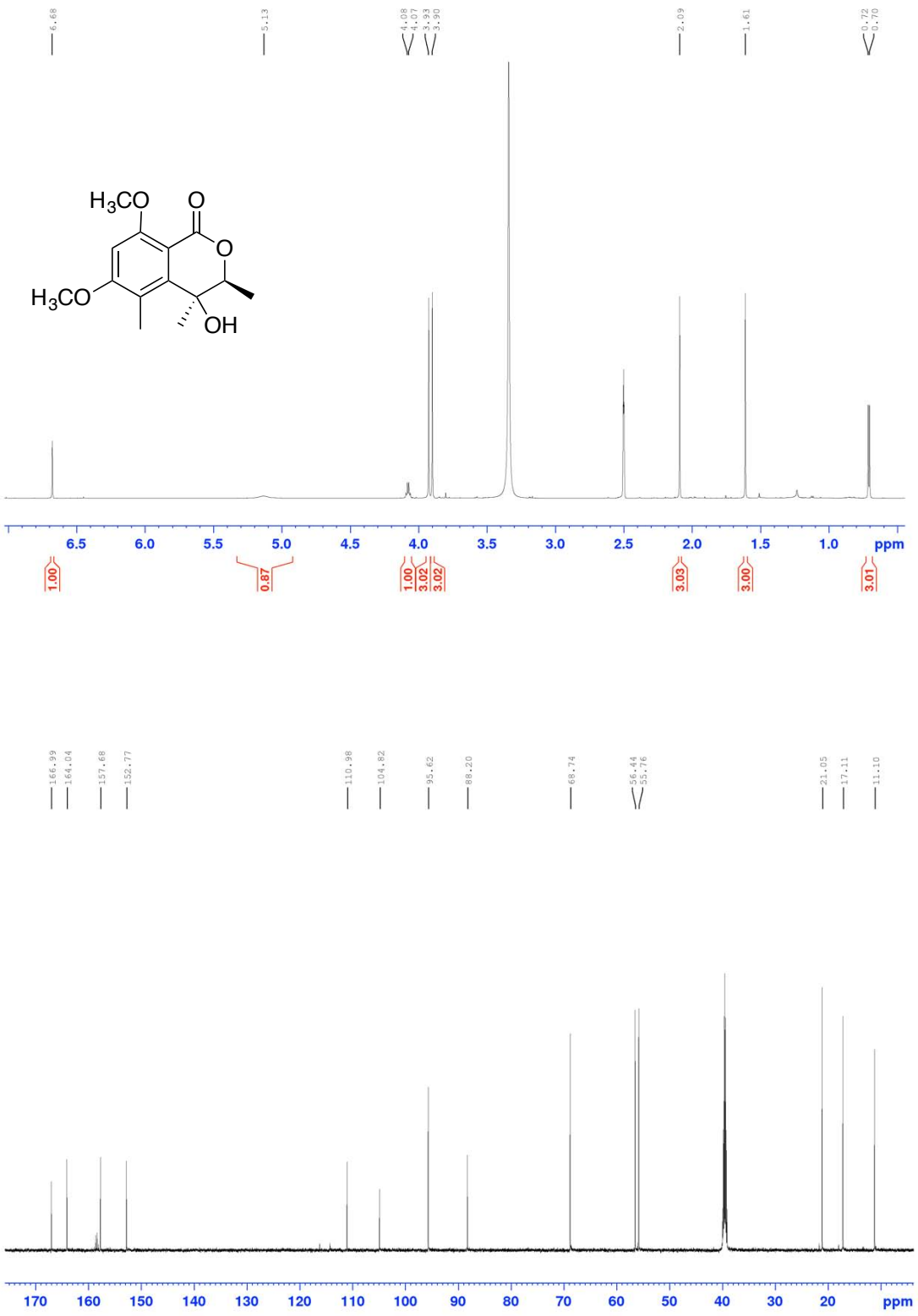

Figure S43: ^{1}H and ^{13}C NMR spectra of banksialactone D (**4**) in DMSO-d_6

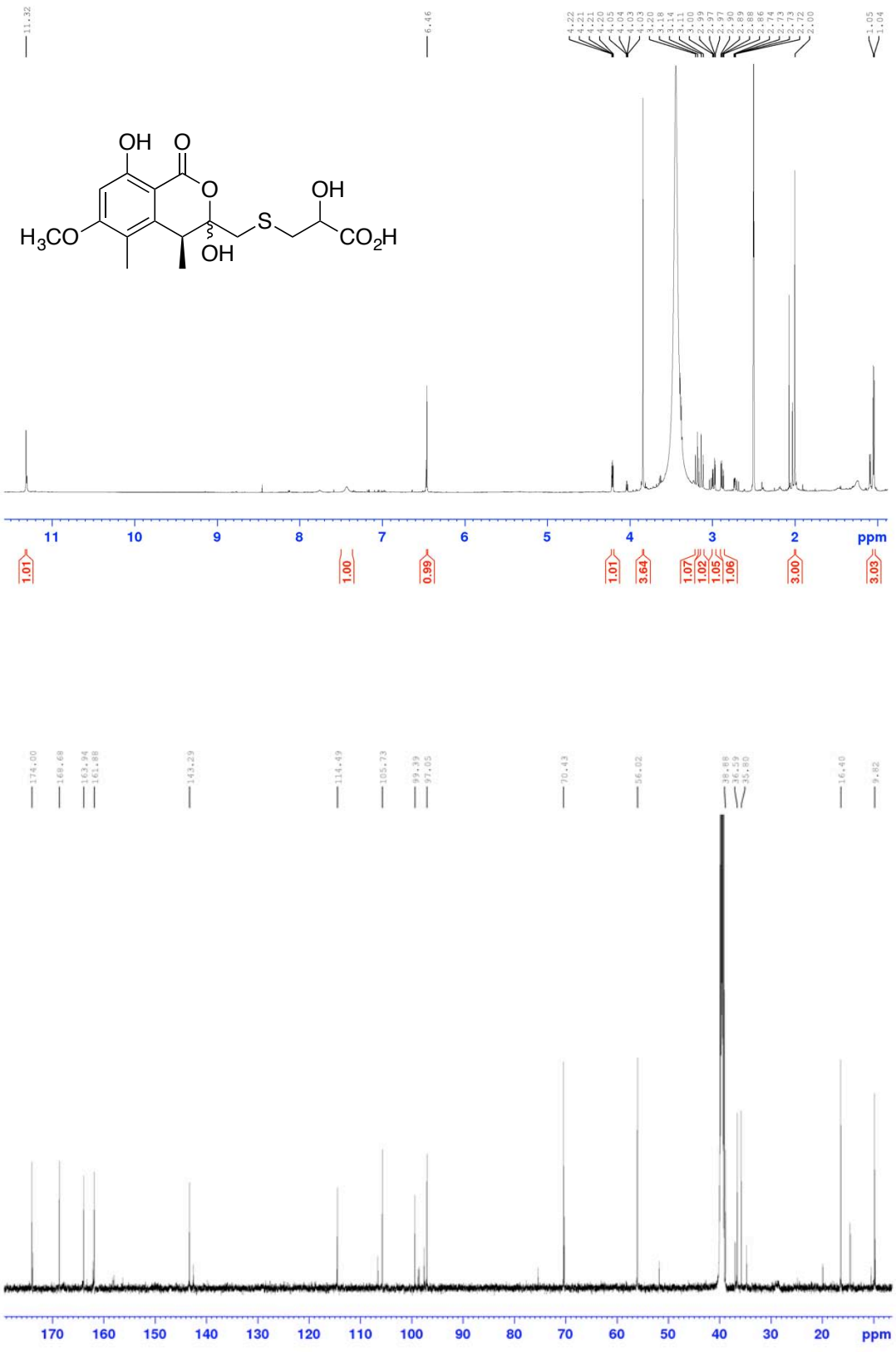

Figure S44: ^{1}H and ^{13}C NMR spectra of banksialactone E (**5**) in DMSO-d_6

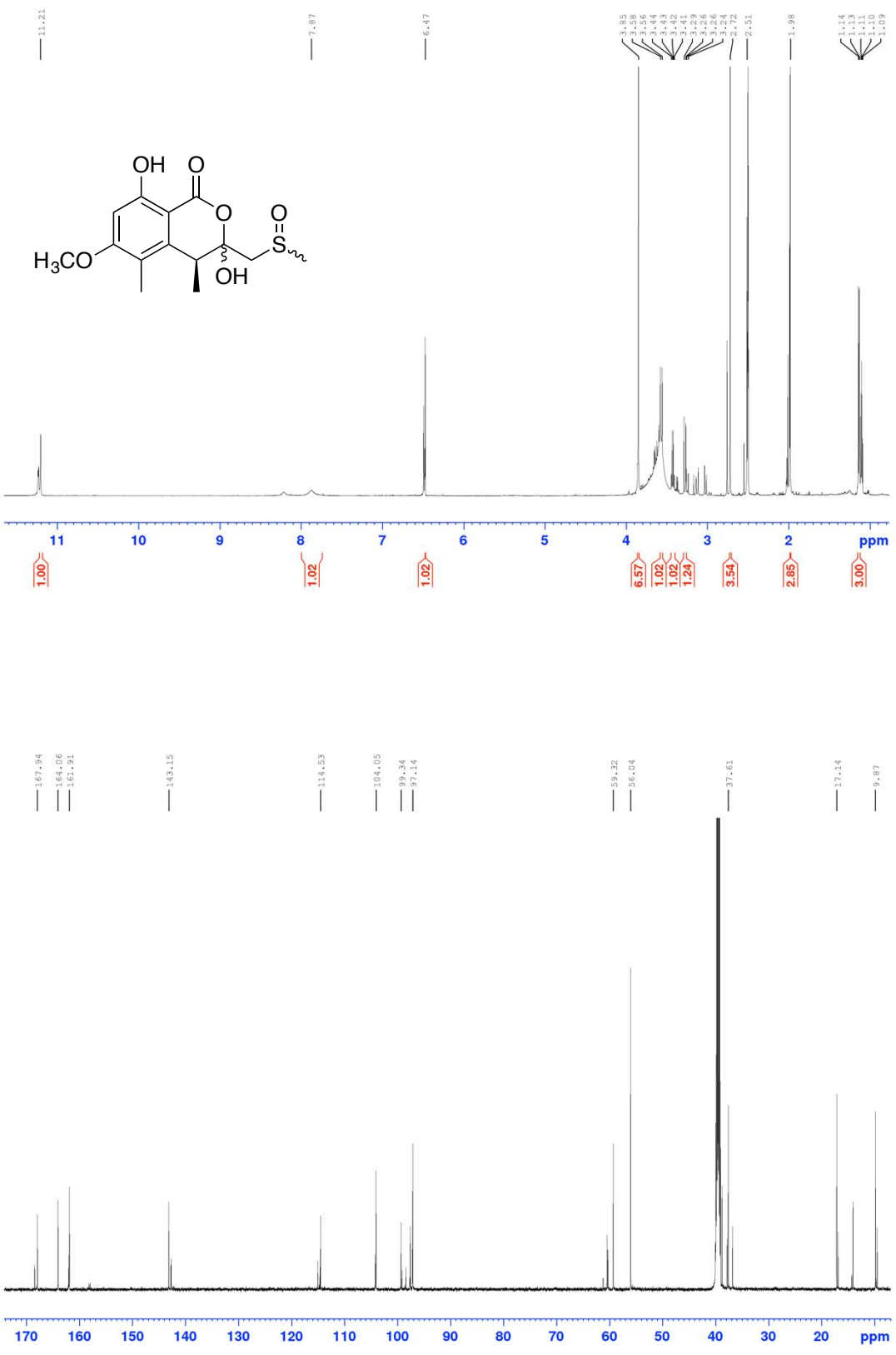

Figure S45: ^{1}H and ^{13}C NMR spectra of banksialactone F (**6**) in DMSO-d_6

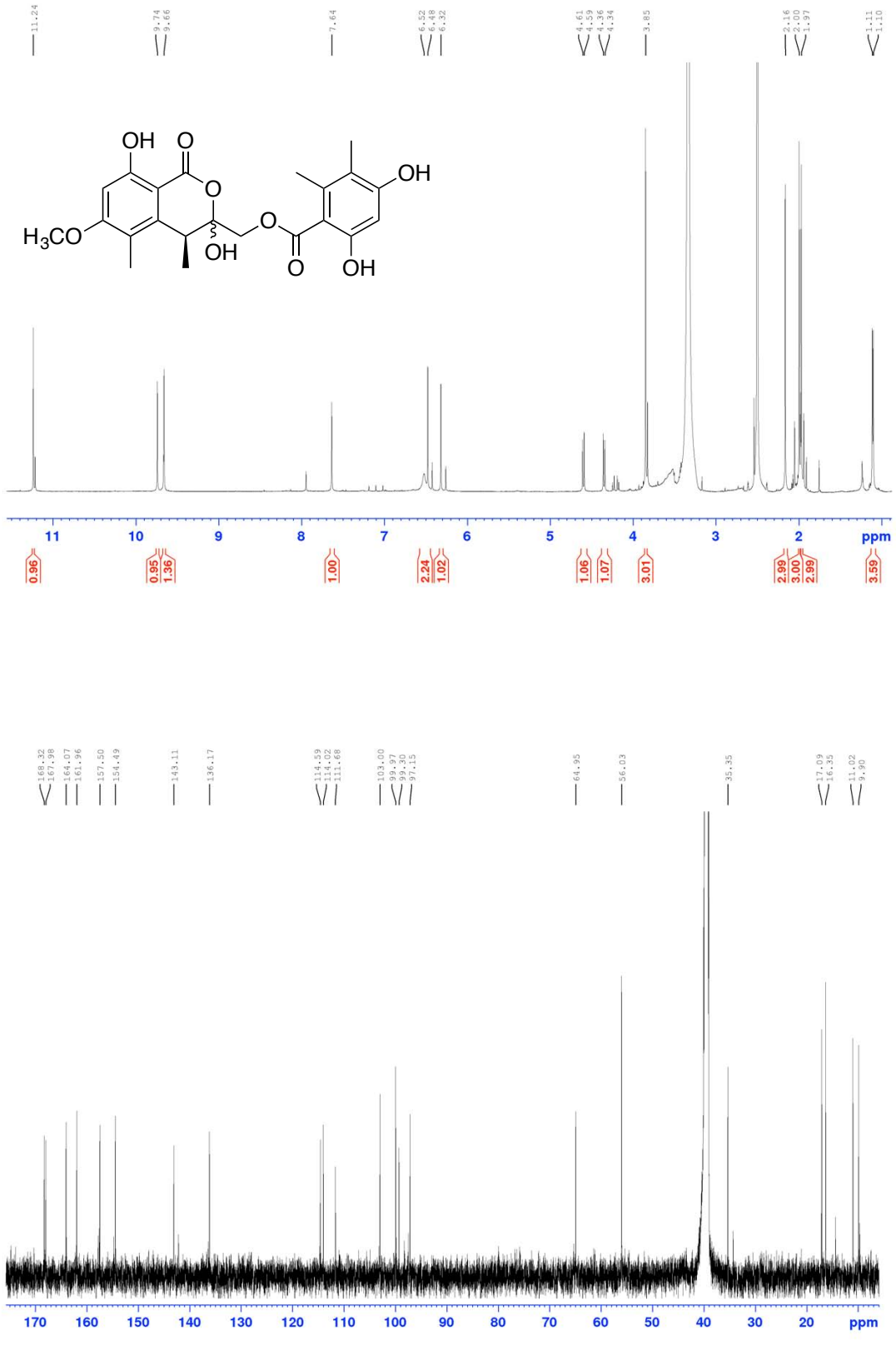

Figure S46: ^{1}H and ^{13}C NMR spectra of banksialactone G (**7**) in DMSO-d_6

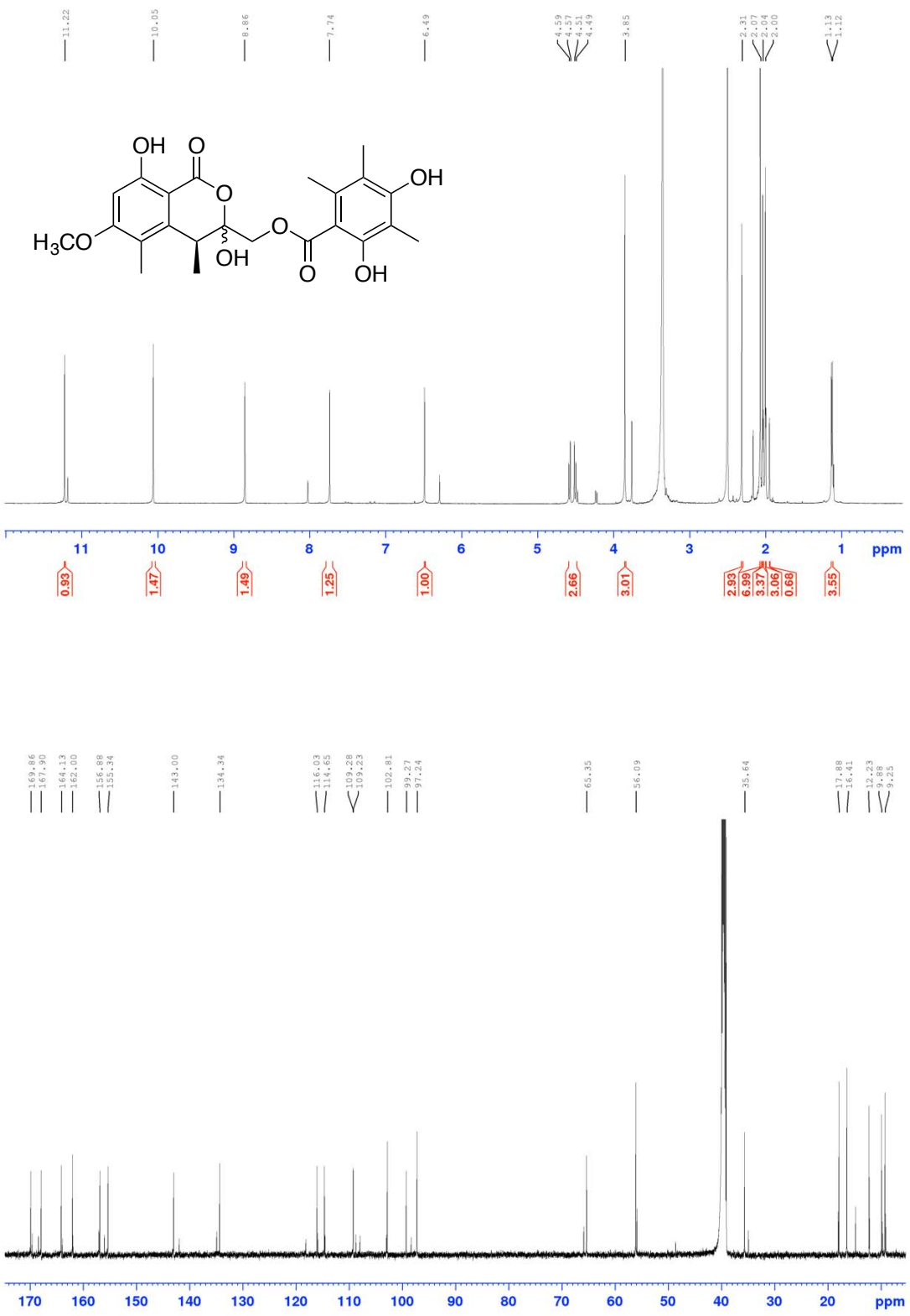

Figure S47: ^{1}H and ^{13}C NMR spectra of banksialactone H (**8**) in DMSO-d_6

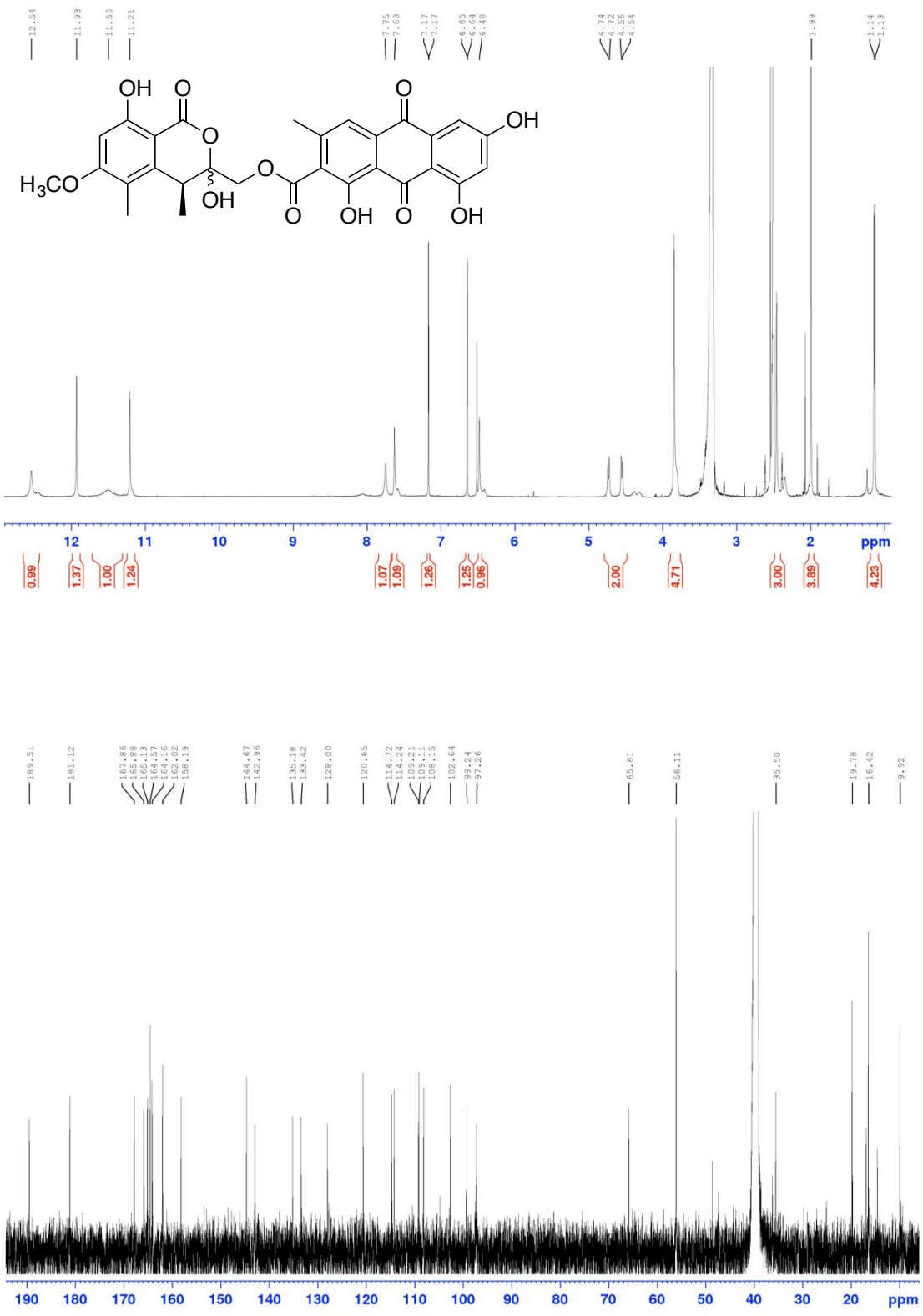

Figure S48: ^{1}H and ^{13}C NMR spectra of banksialactone I (**9**) in DMSO-d_6

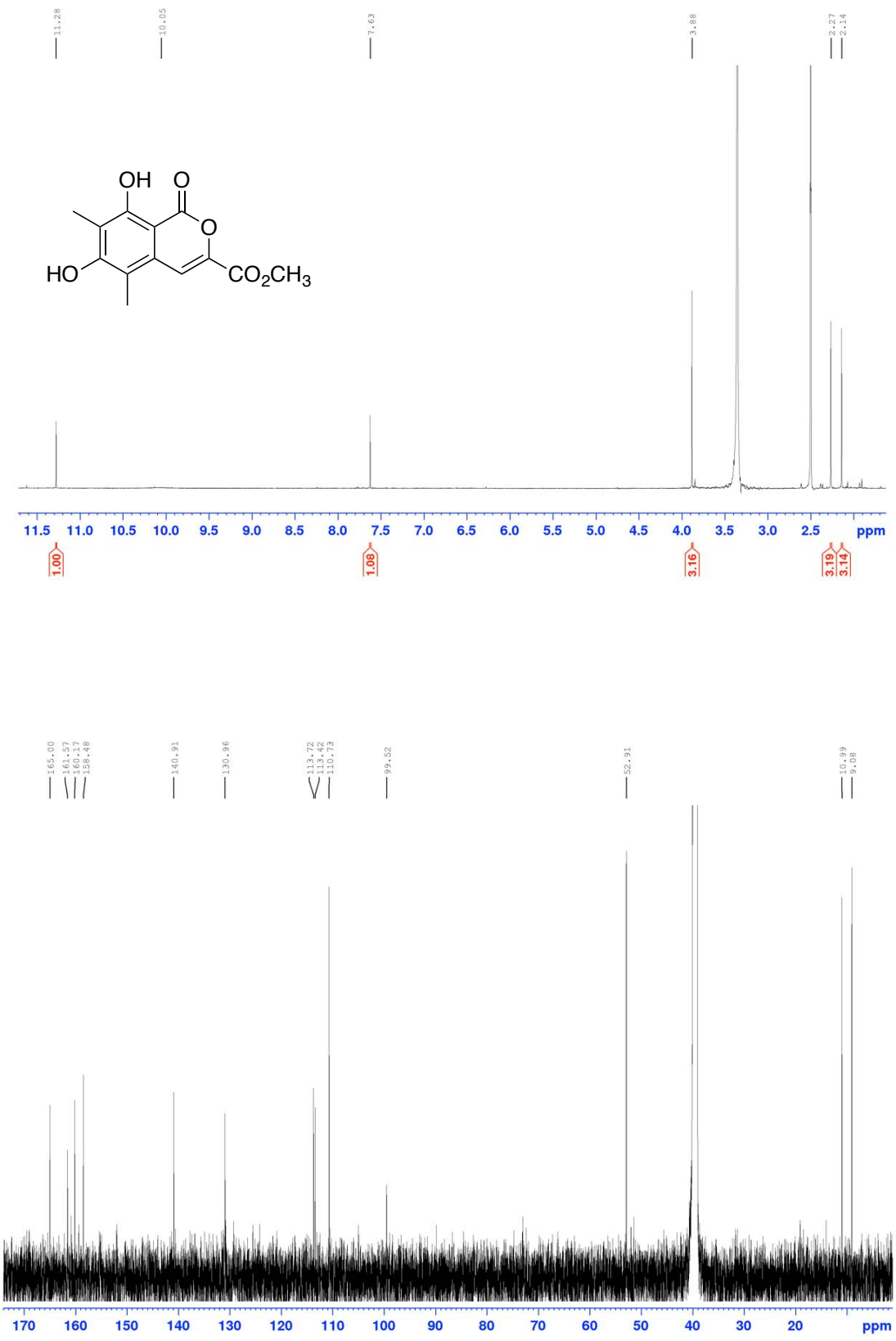

Figure S49: ^{1}H and ^{13}C NMR spectra of banksiamarin A (**10**) in DMSO-d_6

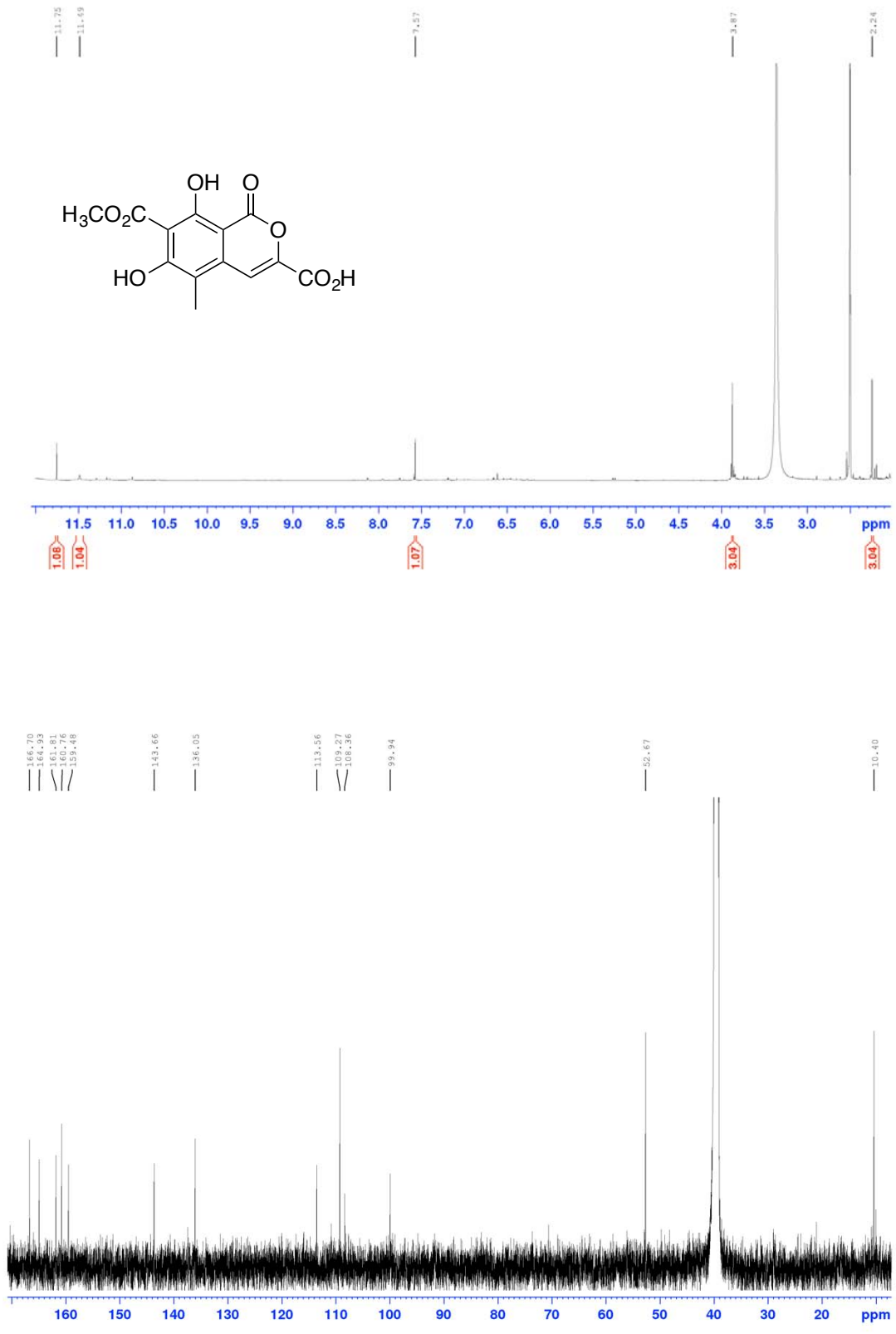

Figure S50: ^{1}H and ^{13}C NMR spectra of banksiamarin B (**11**) in DMSO-d_6

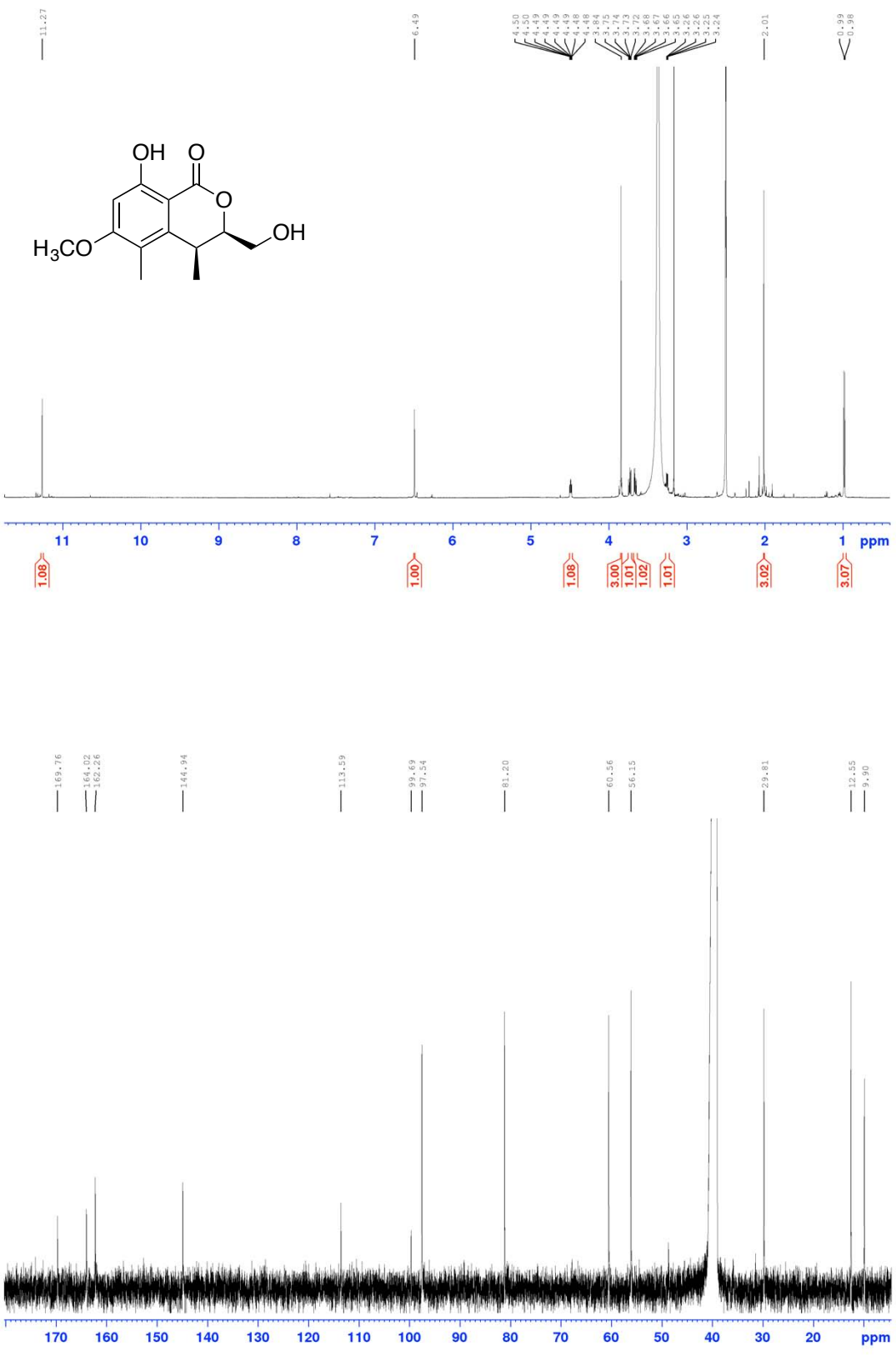

Figure S51: ^{1}H and ^{13}C NMR spectra of clearanol I (**12**) in DMSO-d_6

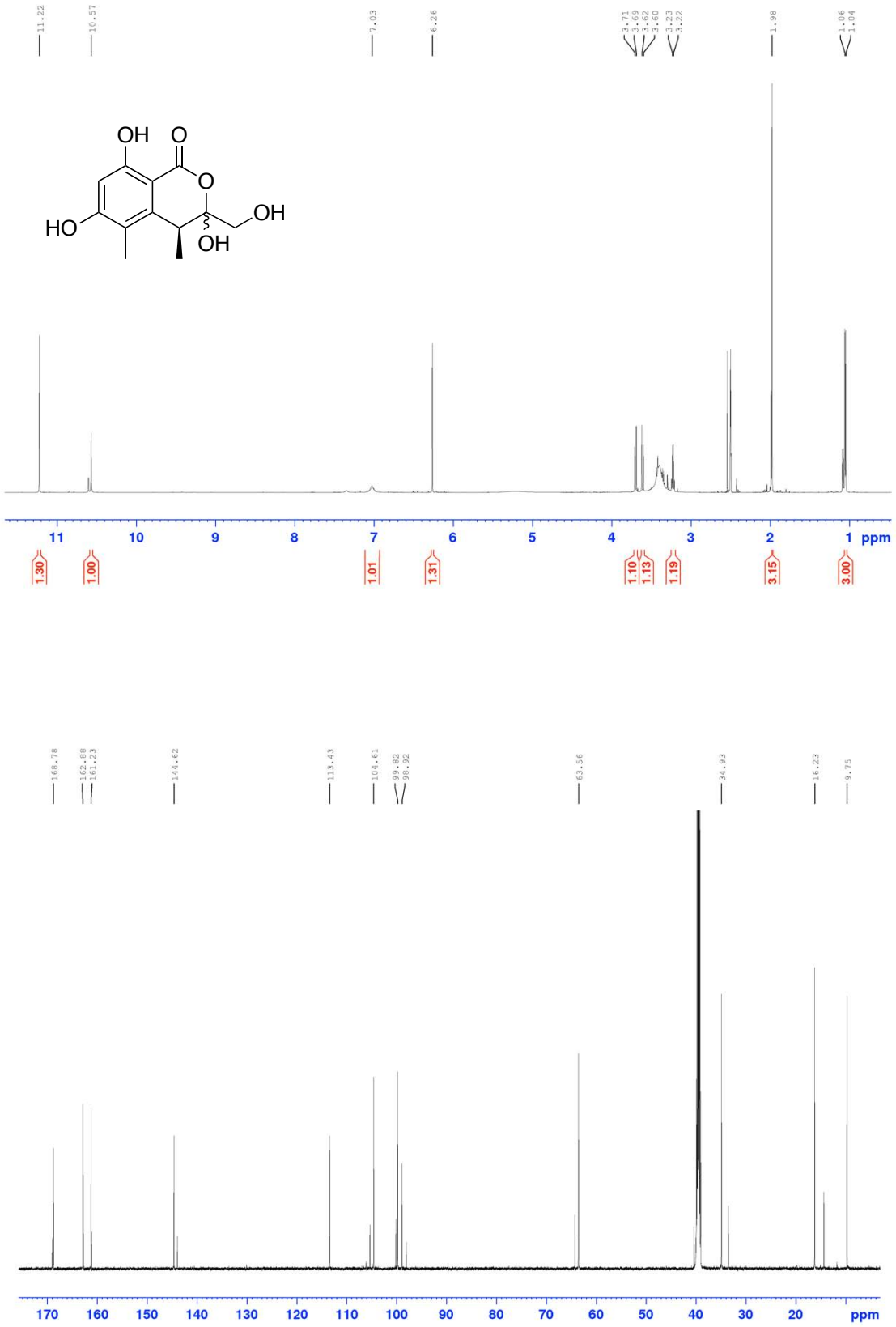

Figure S52: ^{1}H and ^{13}C NMR spectra of dothideomynone A (**13**) in DMSO-d_6

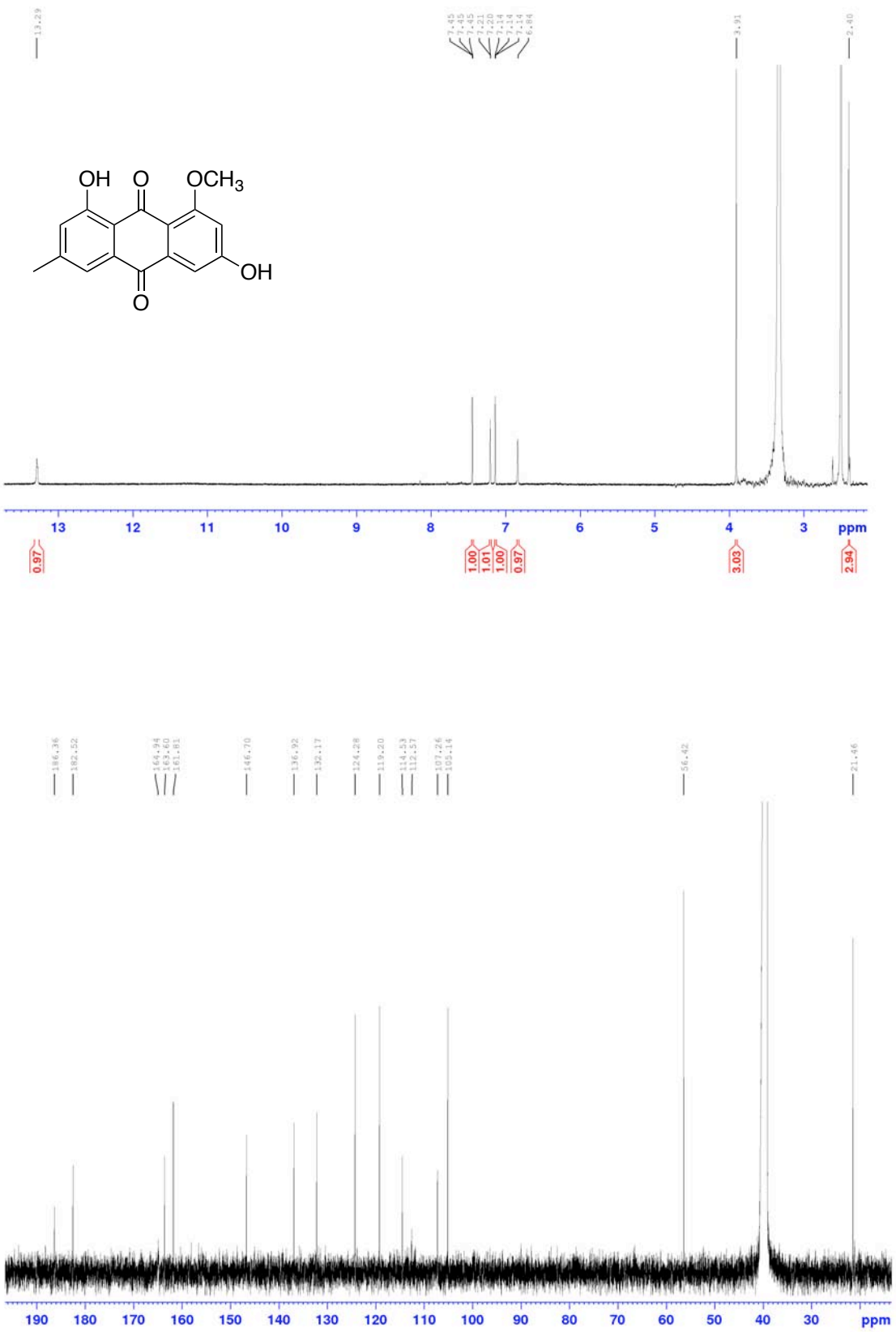

Figure S53: ^{1}H and ^{13}C NMR spectra of questin (**14**) in DMSO-d_6

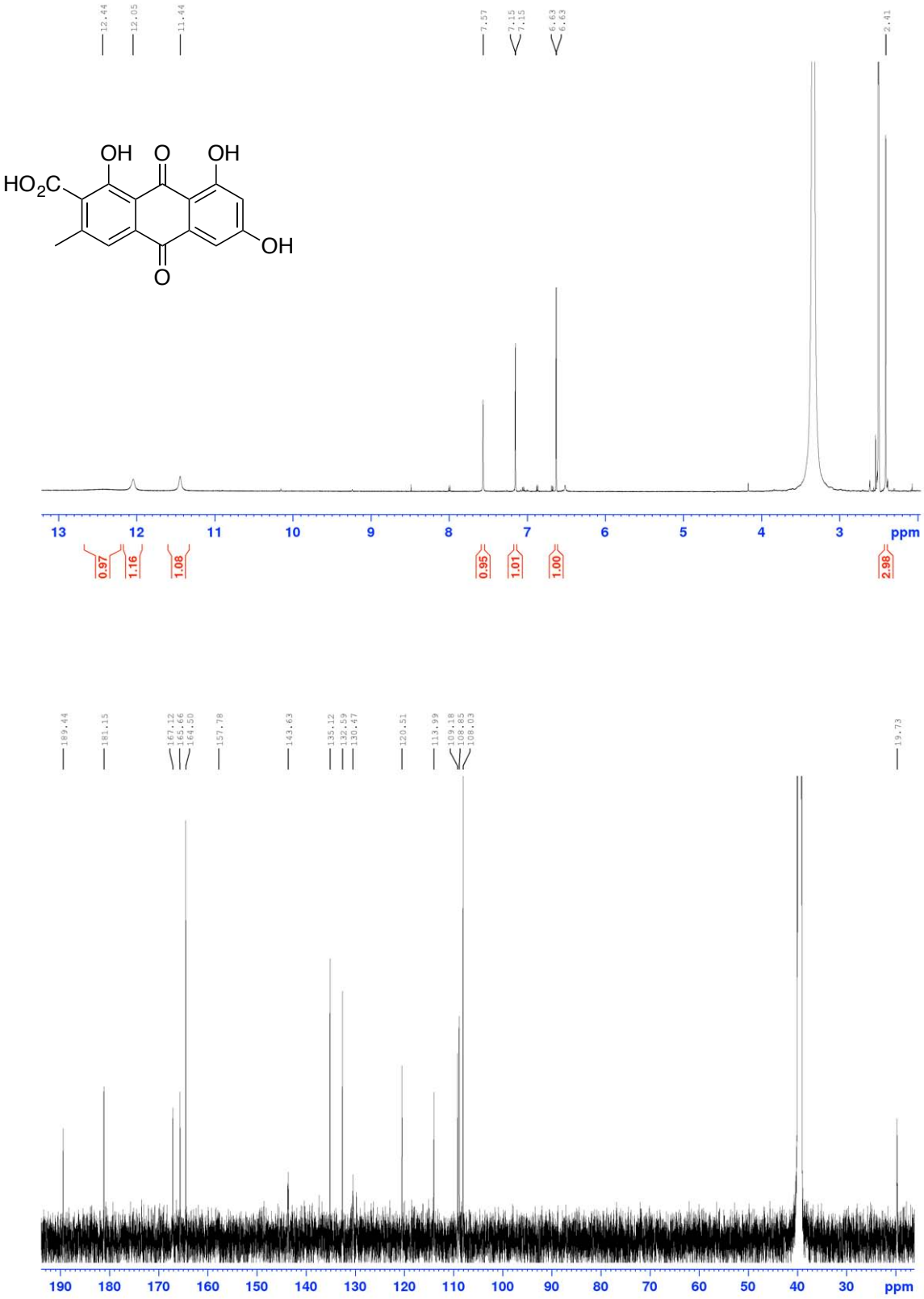

Figure S54: ^{1}H and ^{13}C NMR spectra of endocrocin (**15**) in DMSO-d_6

F. IR spectra

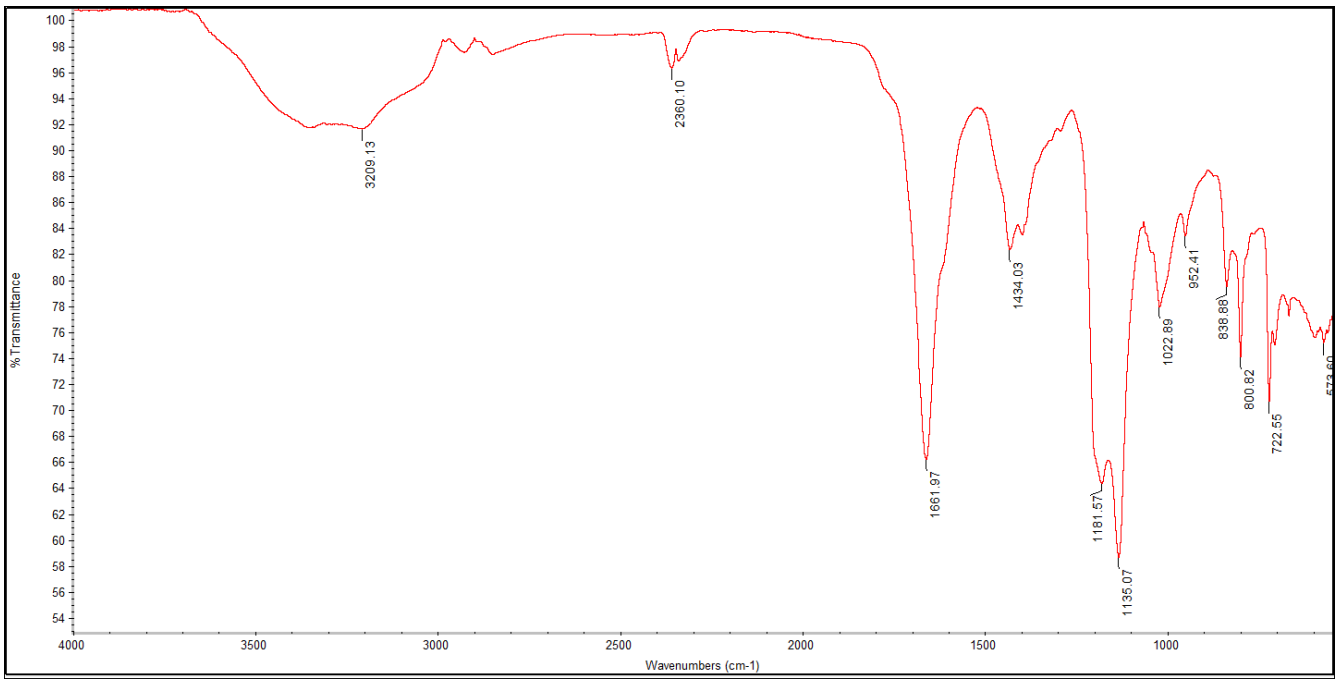

Figure S55: IR spectrum of banksialactone A (**1**). Peak at 2360 cm^{-1} is residual CO_2.

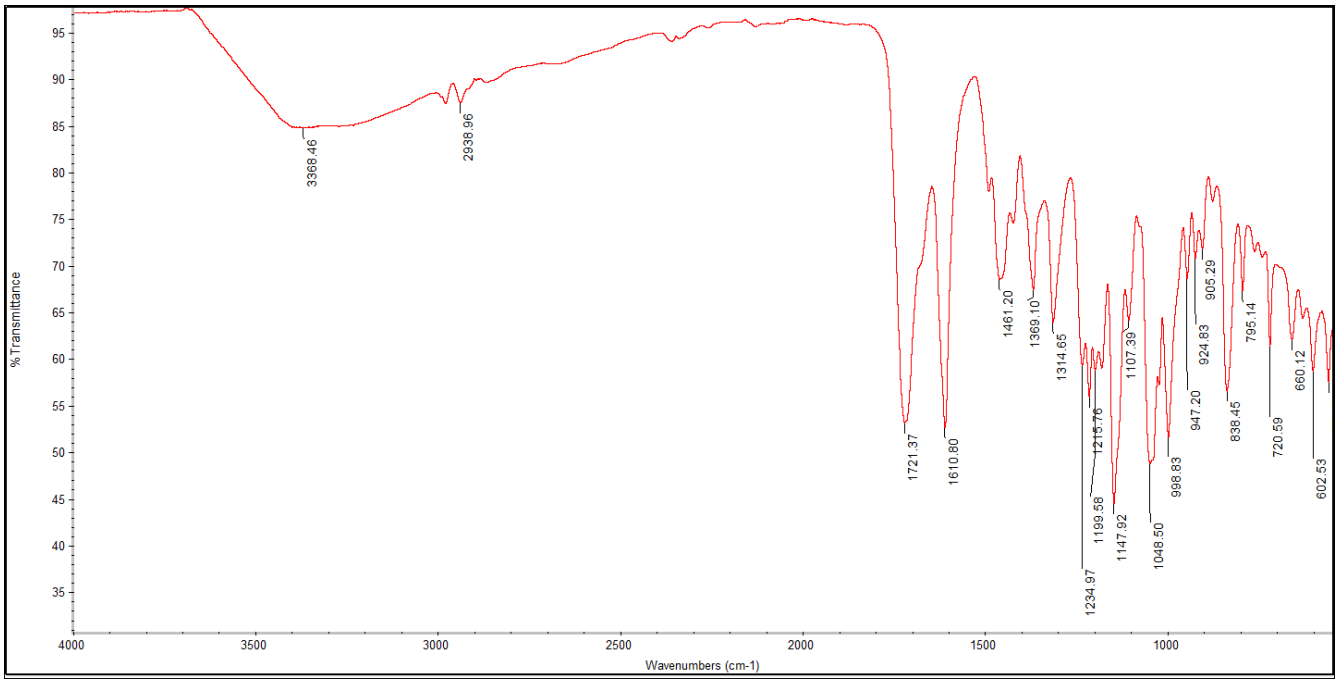

Figure S56: IR spectrum of banksialactone B (**2**)

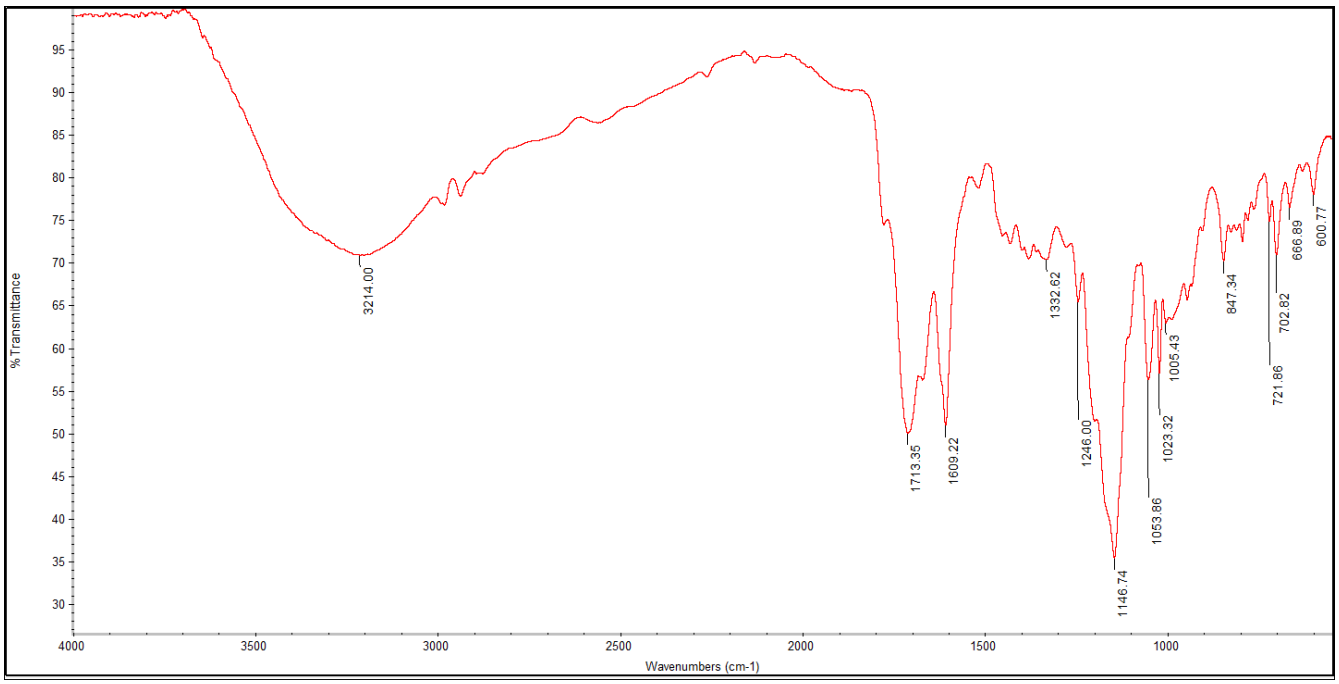

Figure S57: IR spectrum of banksialactone C (**3**)

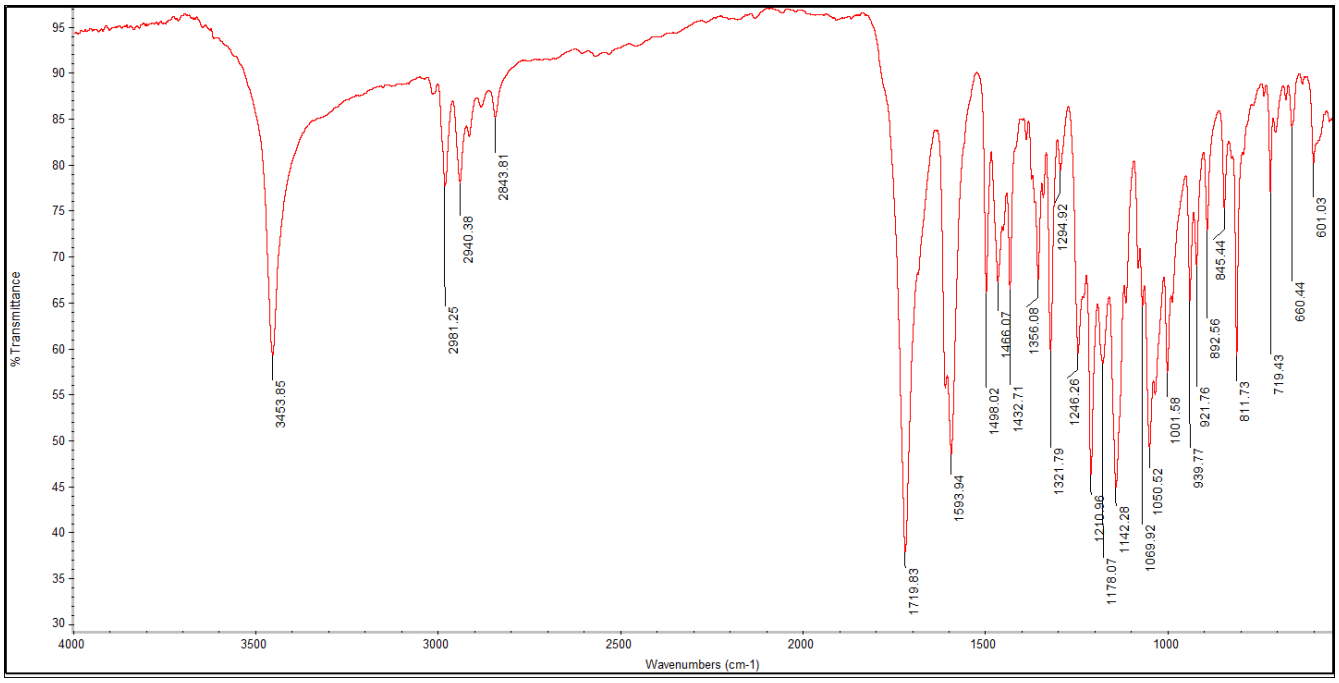

Figure S58: IR spectrum of banksialactone D (**4**)

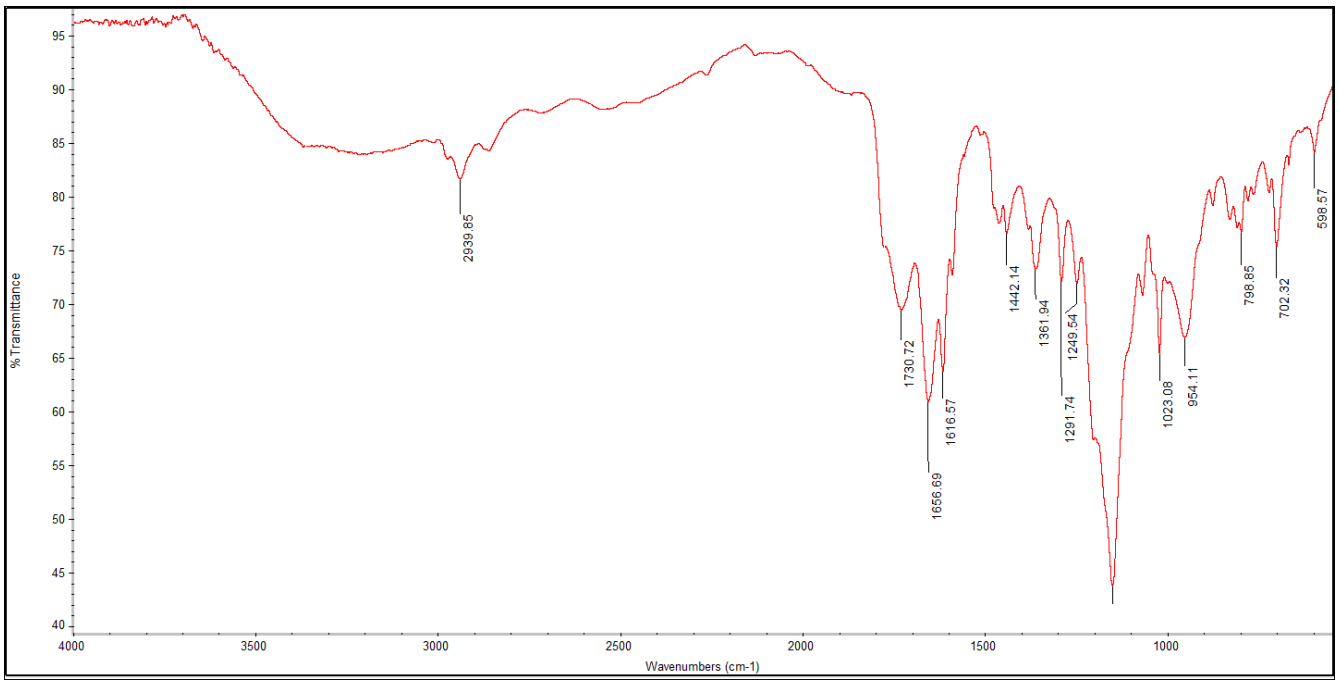

Figure S59: IR spectrum of banksialactone E (**5**)

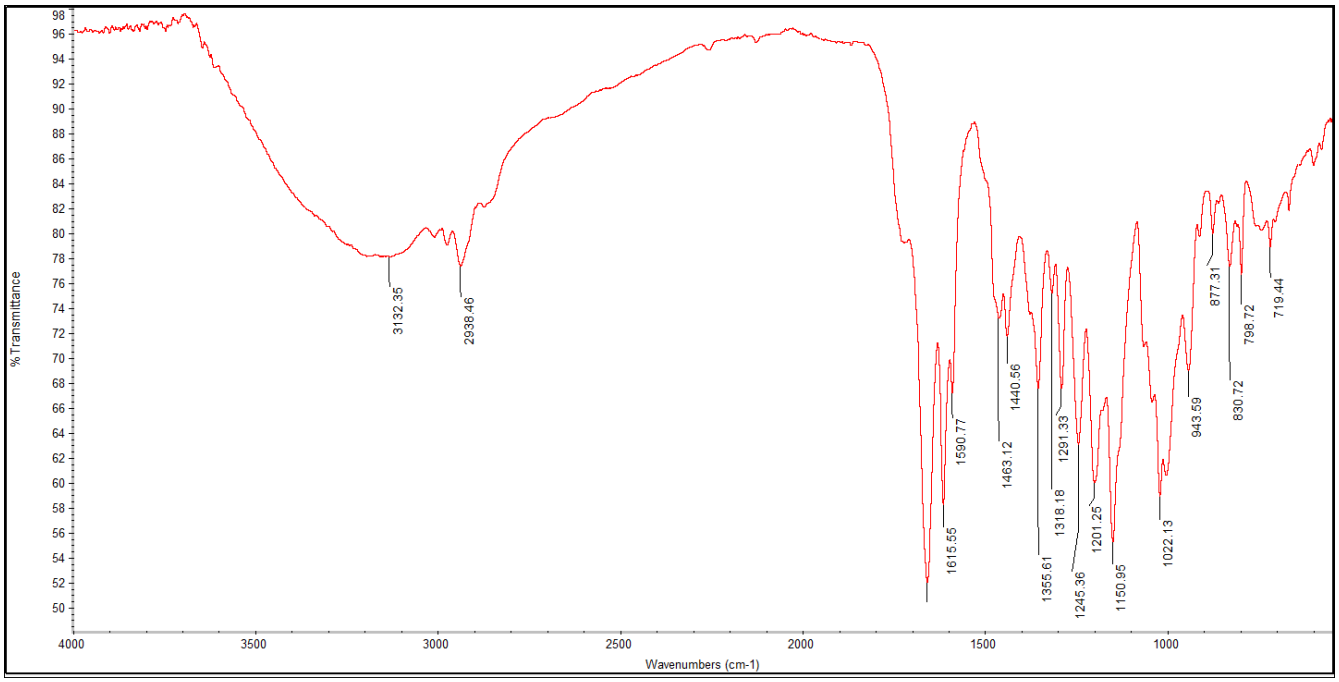

Figure S60: IR spectrum of banksialactone F (**6**)

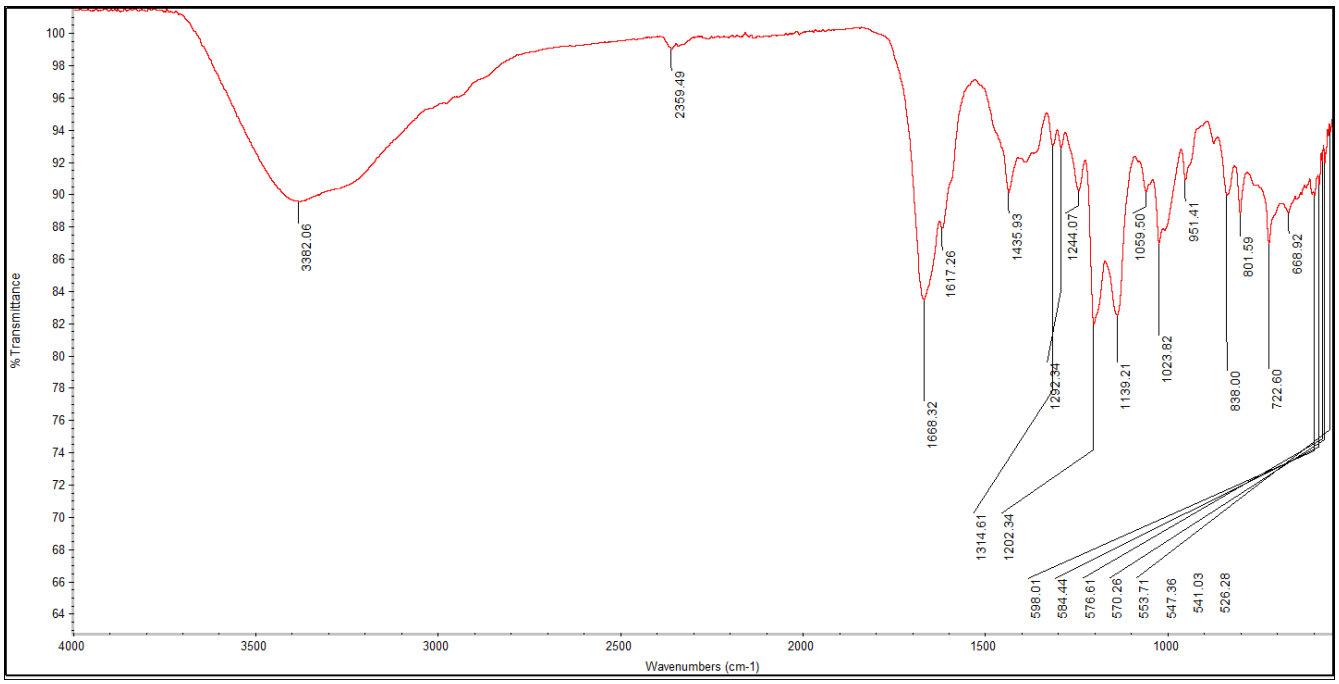

Figure S61: IR spectrum of banksialactone G (**7**). Peak at 2360 cm^{-1} is residual CO_2.

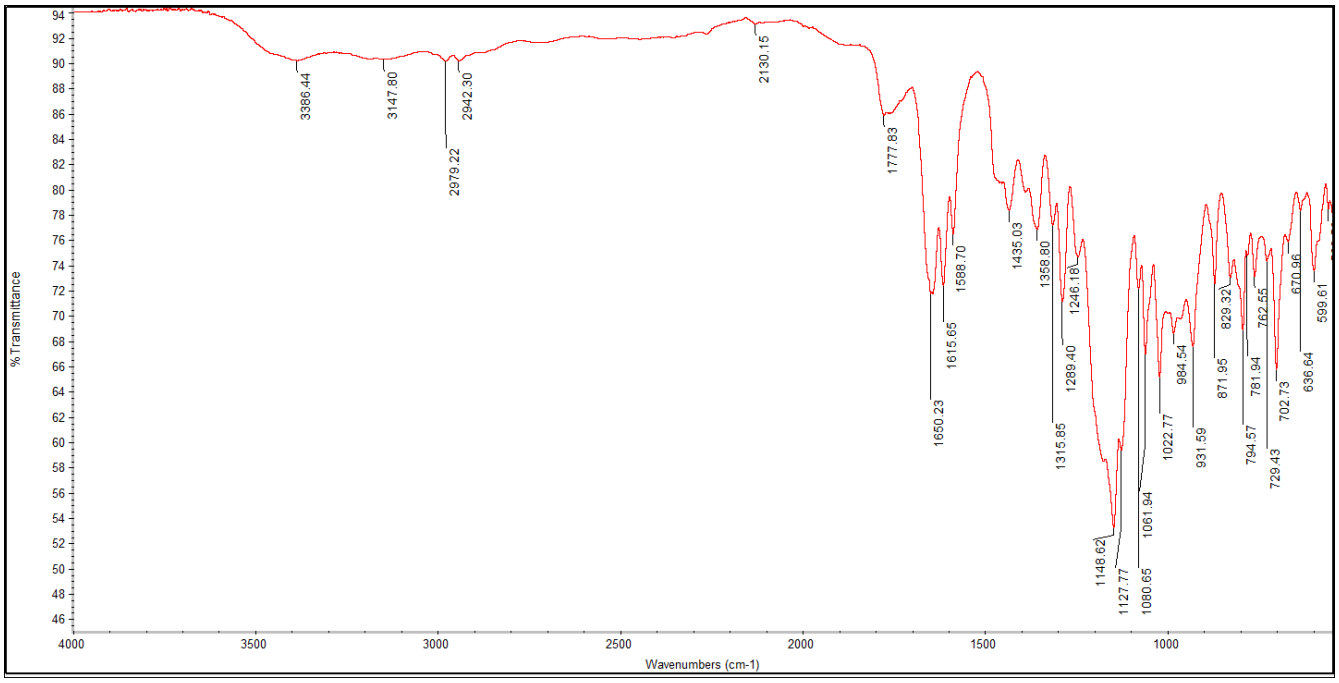

Figure S62: IR spectrum of banksialactone H (**8**)

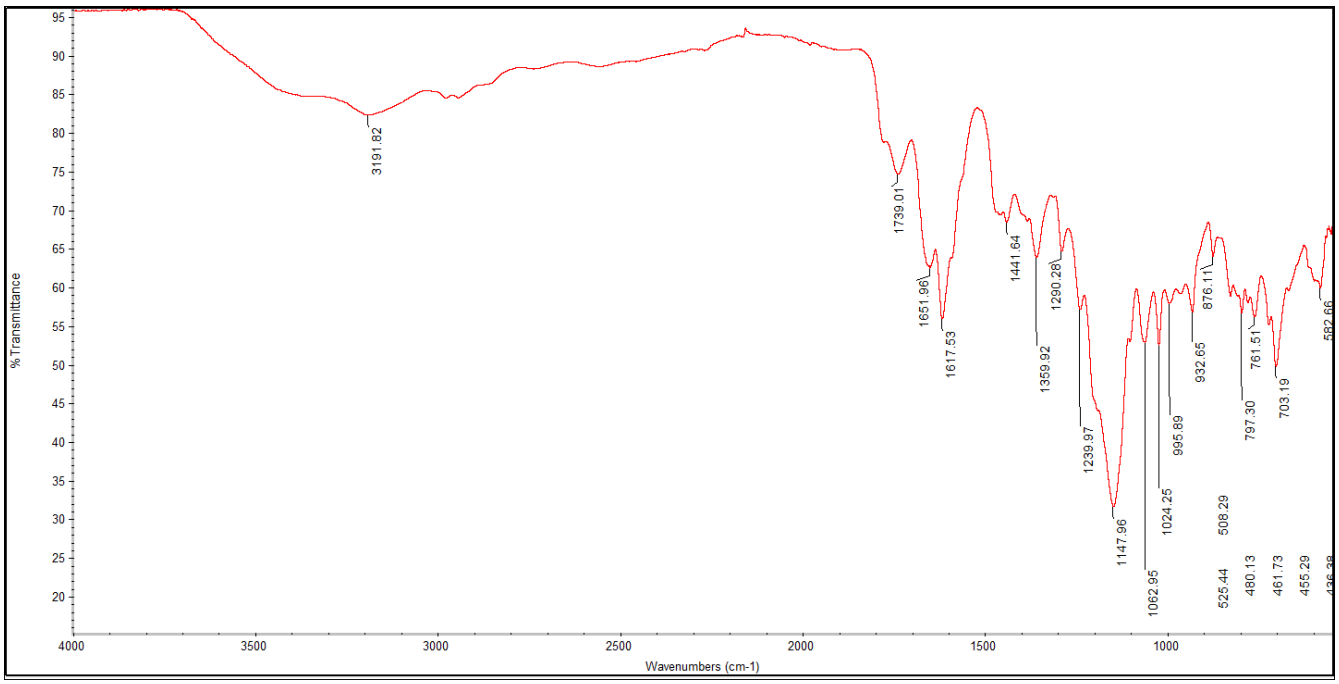

Figure S63: IR spectrum of banksialactone I (**9**)

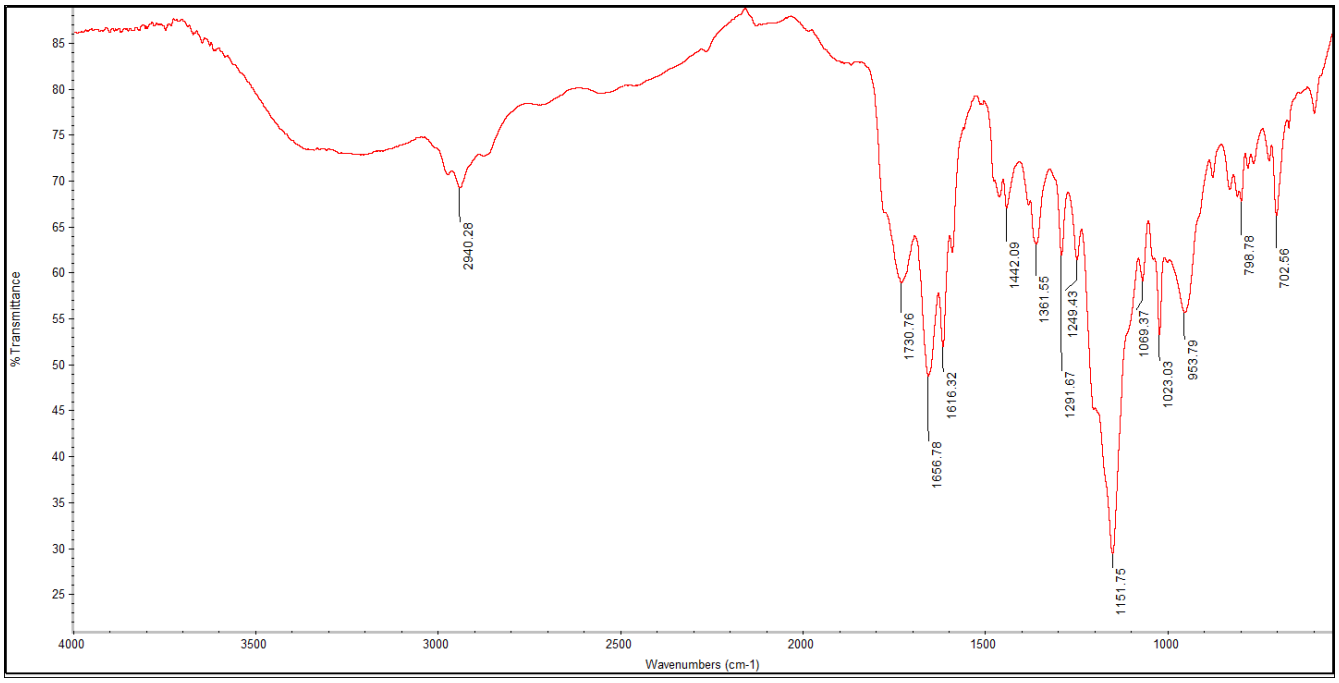

Figure S64: IR spectrum of banksiamarin A (**10**)

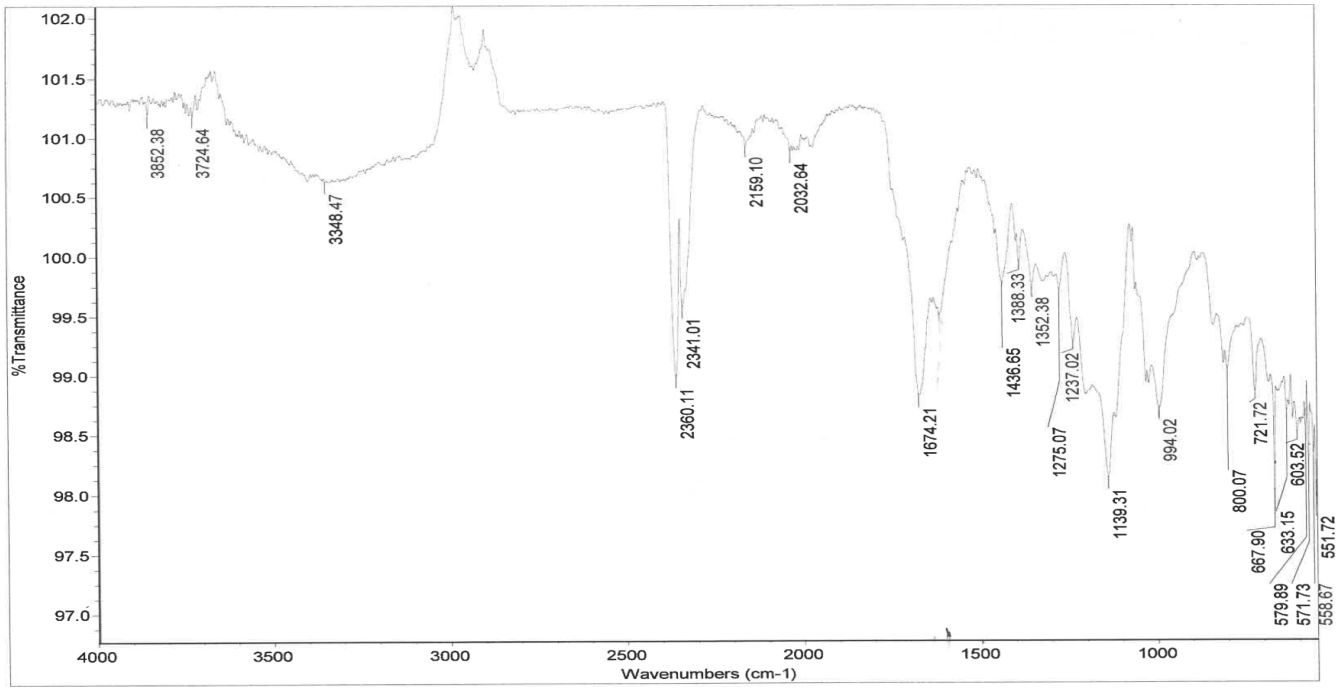

Figure S65: IR spectrum of banksiamarin B (**11**). Peak at 2360/2341 cm^{-1} is residual CO_2.

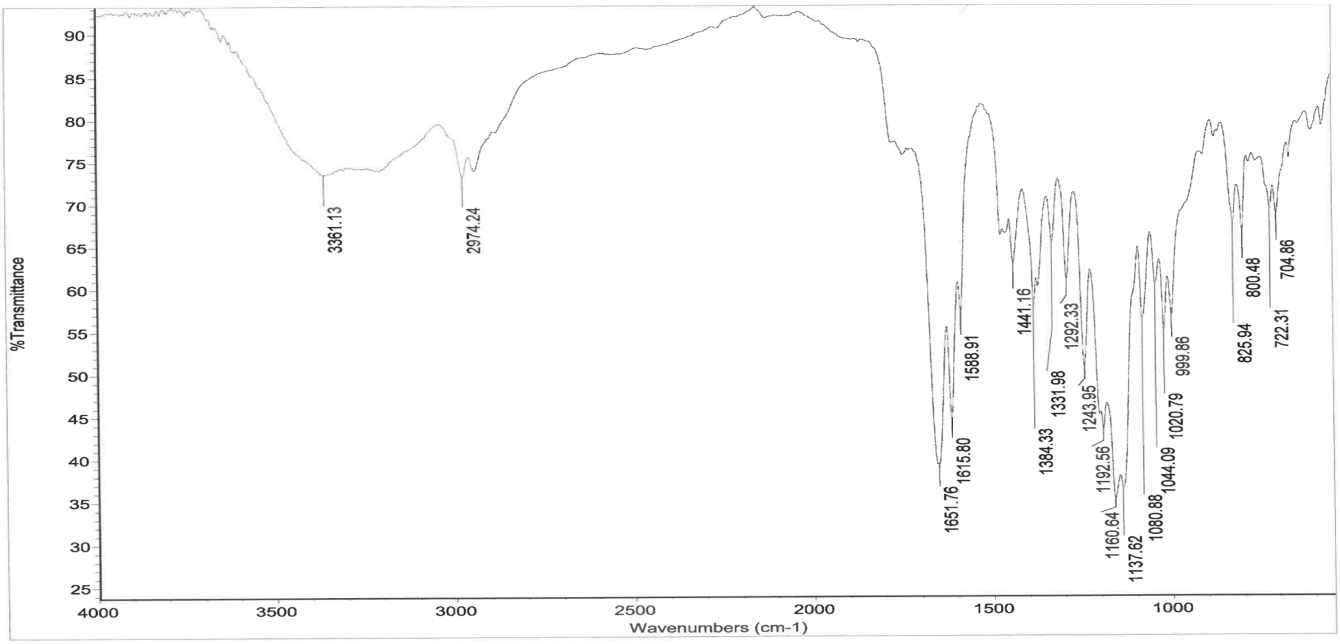

Figure S66: IR spectrum of clearanol I (**12**)

G. DFT calculations

Molecular Modelling was performed in MOE (Molecular Operating Environment).[5] Low mode molecular dynamics with a RMSD of 0.25 Å and a 7 kcal/mol energy window was used to generate a database of conformations of all possible stereoisomers of banksialactone A (**1**) and banksialactone B (**2**). Structures were minimized to an RMS gradient of <0.001 kcal/mol using the MMFF94x forcefield and ranked by energy. The ten lowest structures that were within 2.0 kcal/mol of each other were further geometry optimized using density functional theory (DFT).

DFT calculations were carried out using Turbomole 7.1.1 (Cosmologic GmbH).[6] Structures were energy minimized (DFT//bp86/SV(P) then DFT-D3//bp86/def2-TZVPP) in methanol (COSMO; n = 1.3284, ε = 32.7). UV and ECD spectra were calculated at the same level of theory (TD-DFT//bp86/def2-TZVPP) in vacuo and the calculated electronic transitions Gaussian broadened with a standard deviation of 13 nm to simulate the rho vibrational broadening of the experimental UV-Vis spectrum. The 15 lowest energy transitions were calculated and the rotary strengths and oscillator strengths were used to plot the theoretical UV and ECD spectra respectively. The calculated spectra were all blue shifted by 24 nm to account for the error in the HOMO-LUMO gap at this level of theory.

(3*R*,4*R*)-banksialactone A.xyz

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35

C 2.01558 -0.94063 -0.74704
C 3.05820 -1.89552 -0.61652
O 3.07455 -3.02924 -1.34879
H 2.27105 -2.96041 -1.95674
C 4.09696 -1.67150 0.29142
H 4.88089 -2.41919 0.38264
C 4.10778 -0.49373 1.04017
O 5.08288 -0.20102 1.93775
C 6.14282 -1.15446 2.13641
H 6.71024 -1.30828 1.20784
H 5.74501 -2.11373 2.49555
H 6.79264 -0.71447 2.89816
C 3.09734 0.50692 0.90838
C 3.23407 1.76195 1.73190
H 2.38912 2.44286 1.59569
H 4.15156 2.30872 1.46825
H 3.31026 1.52347 2.80236
C 2.05876 0.26183 0.01259
C 0.92928 -1.21644 -1.67183
O 0.92852 -2.18386 -2.46277
C 0.97955 1.28950 -0.28004
H 0.78666 1.89191 0.61805
C 1.42451 2.23910 -1.41100
H 1.59925 1.69006 -2.34572
H 2.36214 2.73425 -1.12889
H 0.66593 3.00855 -1.59429
C -0.34495 0.59058 -0.59332
O -1.27351 1.49360 -1.07953
H -2.14967 1.08078 -0.90455
C -0.94144 -0.17411 0.60407
O -2.28941 -0.52959 0.26119
H -2.85438 -0.36660 1.03298
H -0.92254 0.48781 1.48078
H -0.35020 -1.07441 0.82599
O -0.14444 -0.40270 -1.70216
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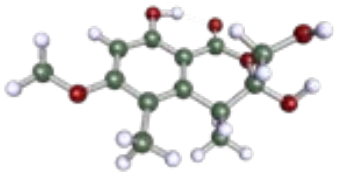

(3*S*,4*S*)-banksialactone A.xyz

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C 1.09009 -1.14609 -0.15961
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O 0.33396 -3.27361 -1.02475
H -0.45924 -2.89965 -0.52400
```

```
C 2.57377 -2.62732 -1.40397
H 2.72123 -3.55777 -1.94675
C 3.60518 -1.70465 -1.22349
O 4.85538 -1.89190 -1.71685
C 5.12565 -3.08941 -2.46857
H 6.17587 -3.01752 -2.76504
H 4.48939 -3.14262 -3.36290
H 4.97494 -3.98350 -1.84771
C 3.42869 -0.49292 -0.48896
C 4.62488 0.40632 -0.31113
H 4.37988 1.32384 0.23230
H 5.05172 0.69116 -1.28337
H 5.42439 -0.10752 0.24263
C 2.16259 -0.23061 0.02961
C -0.23941 -0.87597 0.36049
O -1.16601 -1.71431 0.34744
C 1.87660 0.97998 0.89979
H 2.52116 1.81588 0.59591
C 2.16234 0.66457 2.38232
H 1.51994 -0.14779 2.74743
H 1.99695 1.54922 3.00797
H 3.20632 0.34731 2.49662
C 0.44398 1.46602 0.67322
O 0.09512 2.42183 1.61068
H -0.64206 2.92810 1.19970
C 0.19295 2.01374 -0.74518
O -1.07675 2.68384 -0.73274
H -0.98820 3.51555 -1.22460
H 0.19042 1.19864 -1.48350
H 1.00228 2.71404 -0.99207
O -0.51604 0.33161 0.89147
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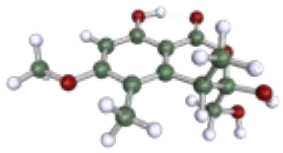

(3*R*,4*S*)-banksialactone A.xyz

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C 0.93569 -1.08729 0.09707
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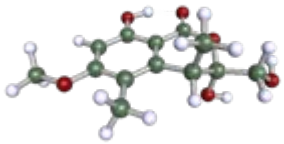
O -0.66009 -2.79686 -0.52077
H -0.91794 -2.52866 0.41722
C 1.05092 -2.23838 -2.04948
H 0.63996 -2.97540 -2.73510
C 2.18710 -1.49033 -2.36160
O 2.85231 -1.61759 -3.53793
C 2.34921 -2.54668 -4.51529
H 2.36109 -3.57316 -4.12305
H 3.02845 -2.46908 -5.36893
H 1.33013 -2.27600 -4.82464
C 2.74780 -0.53800 -1.45797
C 4.00006 0.18709 -1.87944
H 3.86475 0.66862 -2.85820
H 4.84373 -0.51063 -1.98913
H 4.29584 0.95761 -1.16112
C 2.10501 -0.34930 -0.23669
C 0.24362 -0.88753 1.35639
O -0.70264 -1.60273 1.74573
C 2.65066 0.57997 0.83131
H 3.15096 1.43290 0.35480
C 3.67172 -0.15456 1.72308
H 4.14279 0.52639 2.44380
H 4.46646 -0.58172 1.09936
H 3.19905 -0.97655 2.27648
C 1.49245 1.19041 1.62196
O 0.72061 1.98209 0.76950
H 0.23608 2.60329 1.35752
C 1.90669 2.00785 2.85710
O 0.81817 2.83358 3.28996
H 0.20320 2.28082 3.80254
H 2.71971 2.68677 2.57050
H 2.25299 1.34806 3.66264
O 0.62846 0.11223 2.18120
```



(3*S*,4*R*)-banksialactone A.xyz

```
35

C 1.80847 -0.85548 -0.99109
C 2.98156 -1.54381 -1.40009
O 2.93567 -2.54322 -2.30716
H 1.96840 -2.60064 -2.58607
C 4.21812 -1.19364 -0.85205
H 5.10154 -1.74254 -1.16864
C 4.28867 -0.15566 0.08108
O 5.45421 0.22272 0.66700
C 6.66241 -0.47203 0.30849
H 6.59142 -1.53877 0.56230
H 7.45465 -0.00293 0.89878
H 6.87863 -0.35585 -0.76263
C 3.13739 0.58664 0.48077
C 3.28982 1.71279 1.47415
H 2.55498 2.50840 1.30783
H 4.28840 2.15895 1.40945
H 3.16303 1.35590 2.50865
C 1.91027 0.21475 -0.06303
C 0.52832 -1.26954 -1.53440
O 0.40618 -2.11352 -2.44580
C 0.63478 0.97442 0.24962
H 0.68610 1.36708 1.27385
C 0.44980 2.15411 -0.72699
H 0.31272 1.79988 -1.75712
H 1.34000 2.79481 -0.70930
H -0.41354 2.77379 -0.45244
```

```
C -0.55031 0.00740 0.24568
O -0.38779 -0.92483 1.27143
H -1.28800 -1.27717 1.44972
C -1.93292 0.67078 0.35974
O -2.91992 -0.30400 0.71935
H -3.16111 -0.80027 -0.08195
H -2.19795 1.18281 -0.57412
H -1.90294 1.40280 1.17721
O -0.61107 -0.72213 -1.05423
```

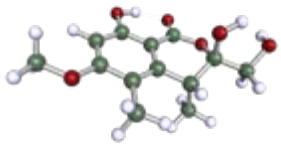


Figure S67. Coordinates (XYZ format) of optimized (DFT-D3//bp86/TZVPP-COSMO) ground state structures of the four stereoisomers of banksilactone A (**1**).

TD-DFT calculations were performed at the same level of theory to calculate the theoretical UV and ECD spectra (Figure S6). The 15 lowest energy transitions were calculated and the rotary strengths and oscillator strengths were used to plot the theoretical UV and ECD spectra respectively. Gaussian broadening with a 12 nm standard deviation and a 24 nm offset was applied to simulate experimental UV and ECD spectra (Figures 1, 2).

(3*R*,4*R*)-banksialactone A

Wavelength	Oscillator Strength	Rotary Strength
248.55557912889	0.10670026679617	6.3137455946898
266.17594055521	0.0065008193580907	-10.217791646514
272.02388877685	6.3836934561797E-4	3.0820876951222
295.54827312551	0.22062727173991	-0.5407719669969
333.54277263207	0.10900421661005	2.7079518225854

(3*S*,4*S*)-banksialactone A

Wavelength	Oscillator Strength	Rotary Strength
248.41865442066	0.10652818829843	-6.3575011250704
266.38318580491	0.0070893754936129	10.452723275186
271.96764439094	7.5112887713731E-4	-3.225023028662
295.63508253929	0.22056077581353	0.25053696793619
333.38622610665	0.10917890363138	-3.0773303073764

(3*R*,4*S*)-banksialactone A

Wavelength	Oscillator Strength	Rotary Strength
247.08262850164	0.11690852201455	-13.340016369069
255.29872839474	0.00175784665765	2.949557716996328
278.21645075288	0.00176260083804	-7.618293881961576
292.55434112476	0.23727168848895	10.942556900338
335.33439414409	0.11483968965088	-0.28701572125964

(3*S*,4*R*)-banksialactone A

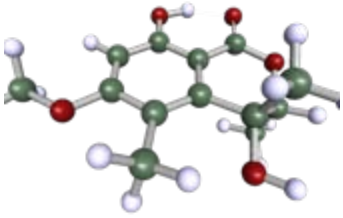
Wavelength	Oscillator Strength	Rotary Strength
247.21624920229	0.11685379278877	12.572314065178
255.49190256394	0.001764261033436	-3.1600833624572
278.26479902234	0.001787974008351	7.7313416090135
292.6444330333	0.23682730377315	-10.396048250309
335.49232941804	0.11464097125771	0.81444189671222

Figure S68. TD-DFT//bp86/TZVPP-COSMO calculated oscillator and rotary strengths for the five lowest energy electronic transitions for banksialactone A (**1**) at the ground state conformation (Figure S67).

(3*R*,4*R*)-banksialactone B.xyz

```
34

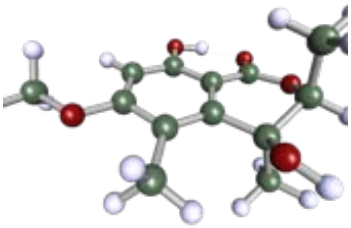
C -0.916285 -0.976495 0.245092
C -0.915594 -1.855771 -0.870302
O -1.765752 -2.899194 -0.954013
H -2.264323 -2.900810 -0.074082
C -0.022472 -1.645810 -1.921918
H -0.057901 -2.314939 -2.777365
C 0.906534 -0.612911 -1.827324
O 1.817355 -0.360065 -2.799654
C 1.812722 -1.193436 -3.971771
H 2.613484 -0.806930 -4.607954
H 0.850693 -1.122472 -4.497722
H 2.018481 -2.240123 -3.707682
C 0.991091 0.248247 -0.689208
C 2.134798 1.231639 -0.665769
H 3.046763 0.745500 -1.035023
H 2.313397 1.624090 0.334977
H 1.941715 2.088074 -1.329210
C 0.039441 0.082031 0.313553
C -1.870691 -1.235031 1.309476
O -2.582902 -2.259671 1.364564
C -0.009970 0.919943 1.587991
O 0.386443 2.272303 1.306407
H 0.552560 2.707060 2.160918
C 0.907968 0.302511 2.652161
H 0.880533 0.909573 3.569179
H 1.938937 0.262116 2.281359
H 0.590890 -0.716296 2.906601
C -1.468006 0.992841 2.097946
H -1.452411 1.426605 3.106307
C -2.422577 1.771488 1.206839
H -2.456408 1.351964 0.192709
H -3.431319 1.741644 1.636288
H -2.100928 2.815807 1.137906
O -2.006279 -0.353481 2.318722
```



(3*S*,4*S*)-banksialactone B.xyz

```
34

C -0.370584 -1.134634 -0.654555
C 0.570278 -1.354878 -1.695778
O 0.511344 -2.443656 -2.489308
H -0.329530 -2.928397 -2.205897
C 1.596336 -0.434234 -1.913896
H 2.319597 -0.637276 -2.698956
C 1.640246 0.727431 -1.146715
O 2.596255 1.674755 -1.312895
C 3.603249 1.457287 -2.316370
H 3.150872 1.389431 -3.315247
H 4.176595 0.544577 -2.102810
H 4.260316 2.329556 -2.264437
C 0.669551 1.026297 -0.140016
C 0.764707 2.384386 0.511145
H 0.988965 3.142678 -0.249784
H 1.583805 2.420712 1.245322
H -0.155169 2.652623 1.030042
C -0.298288 0.060226 0.124223
C -1.415068 -2.126441 -0.464154
O -1.617355 -3.075761 -1.250803
C -1.399169 0.221139 1.168471
O -0.901248 0.953628 2.300373
H -1.668999 1.195580 2.847476
C -2.602971 0.944211 0.548602
H -2.299181 1.932348 0.183737
H -3.394608 1.068699 1.302091
H -3.017119 0.375984 -0.293493
C -1.809923 -1.172176 1.698594
H -2.723094 -1.051104 2.296007
C -0.744000 -1.891164 2.509885
H -1.118621 -2.875309 2.815952
H 0.177898 -2.026954 1.929393
H -0.504110 -1.312199 3.407874
O -2.240987 -2.037363 0.595928
```



(3*R*,4*S*)-banksialactone B.xyz

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34
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C -0.374841 -1.316542 -0.374305
C 0.329601 -1.857505 -1.484149
O 0.009723 -3.055848 -2.013527
H -0.815112 -3.352474 -1.510433
C 1.384277 -1.143873 -2.053467
H 1.924977 -1.588182 -2.884515
C 1.685847 0.126754 -1.567284
O 2.684267 0.885969 -2.083029
C 3.453628 0.349751 -3.172975
H 3.965191 -0.575244 -2.872418
H 4.190851 1.119276 -3.416855
H 2.813317 0.156357 -4.044745
C 0.955571 0.739193 -0.503045
C 1.313002 2.165994 -0.167752
H 2.249246 2.218896 0.407427
H 0.538913 2.656548 0.421423
H 1.476077 2.732391 -1.093589
C -0.039643 -0.017874 0.112738
C -1.482803 -2.084872 0.163542
O -1.929060 -3.123527 -0.367527
C -0.881555 0.506436 1.276463
O -0.025354 1.249710 2.164931
H -0.588454 1.851334 2.680412
C -2.029869 1.370472 0.744780
H -1.640765 2.164731 0.097627
H -2.586616 1.831848 1.571939
H -2.729651 0.761469 0.158456
C -1.376043 -0.698494 2.110758
H -0.476586 -1.210744 2.485404
C -2.302281 -0.358270 3.259496
H -2.536819 -1.267683 3.825725
H -1.817518 0.347315 3.945129
H -3.240879 0.080857 2.900372
O -2.100636 -1.664171 1.282998
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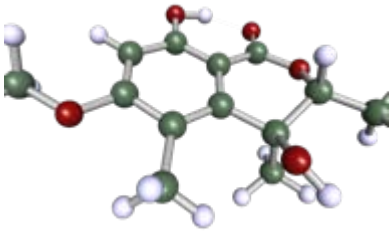

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34

C -1.020399 -0.986410 -0.018334
C -1.005612 -1.855867 -1.142697
O -1.851435 -2.901603 -1.242808
H -2.351558 -2.919064 -0.364464
C -0.100264 -1.636193 -2.180745
H -0.124214 -2.297736 -3.042441
C 0.828352 -0.604010 -2.064952
O 1.749786 -0.342133 -3.024943
C 1.761287 -1.167078 -4.203036
H 2.568532 -0.773750 -4.826752
H 0.805530 -1.094959 -4.740043
H 1.966934 -2.215025 -3.943948
C 0.897587 0.246406 -0.919044
C 2.032209 1.239661 -0.877032
H 2.948717 0.769811 -1.255656
H 2.211859 1.616306 0.129708
H 1.829277 2.107496 -1.522207
C -0.066303 0.070665 0.072137
C -1.963649 -1.274906 1.046775
O -2.666873 -2.305518 1.091099
C -0.121079 0.925614 1.338643
O 0.164543 2.292879 0.985125
H 0.479566 2.743853 1.786580
C 0.872863 0.390706 2.374620
H 0.914666 1.049585 3.252819
H 1.876034 0.322390 1.939174
H 0.575160 -0.610304 2.712195
C -1.577145 0.943655 1.859174
H -2.189787 1.394744 1.063351
C -1.790752 1.678056 3.166030
H -1.249043 1.196980 3.989955
H -1.455470 2.718079 3.077196
H -2.859270 1.689034 3.412569
O -2.090050 -0.411361 2.071954
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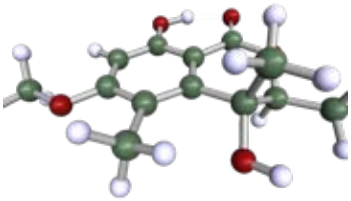

(3*S*,4*R*)-banksialactone B.xyz

Figure S69. Coordinates (XYZ format) of optimized (DFT-D3//bp86/TZVPP-COSMO; methanol) ground state structures of the four stereoisomers of banksilactone B (**2**).

(3*R*,4*R*)-banksialactone B

Wavelength	Oscillator Strength	Rotary Strength
249.68298772672	0.1137137423171	5.0142213161928
269.1752661952	0.0011629943693955	5.6194386712473
288.63706831638	0.12924661977421	11.184952346264
305.4503343246	0.10094518681289	-13.106175548252
336.98761041349	0.10026911601185	1.2732460044568

(3*S*,4*S*)-banksialactone B

Wavelength	Oscillator Strength	Rotary Strength
249.75611633579	0.1136482555199	0.10078906149582
269.26762204785	0.00114476986615	-4.1674752224513
288.4840427125	0.12564026400728	-5.7166217761128
305.16545458498	0.10394448155459	-9.9017521202184
336.93094751488	0.10078906149582	12.668667788872

(3*R*,4*S*)-banksialactone B

Wavelength	Oscillator Strength	Rotary Strength
250.36186213246	0.12300806409559	0.40739814014117
267.73313981529	7.1149909370072E-4	-3.9613312195483
286.88894475859	0.12469321419044	-14.214284987886
303.43164840421	0.10195138186668	20.825355088939
336.12581729368	0.10478762619091	-2.185353365327

(3*S*,4*R*)-banksialactone B

Wavelength	Oscillator Strength	Rotary Strength
250.47007594805	0.12319726288887	-0.0798379825668
267.63529602833	7.2768006511054E-4	3.9122712063005
286.65305282209	0.12170245625467	15.201978634618
302.98367428838	0.10364109569861	-20.42016414398
336.0266740457	0.10531530810323	2.4570466650996

Figure S69. TD-DFT//bp86/TZVPP-COSMO calculated oscillator and rotary strengths for the five lowest energy electronic transitions for banksialactone B (**2**) at the ground state conformation (Figure S68).

Simulated ECD spectra of banksialactone A (**1**) (Figure 1B) were calculated by mixing the predicted ECD spectrum of (3*R*,4*R*) and (3*S*,4*R*) in a ratio of 1:5.8 according to the observed diastereomeric ratio at C-4 in the NMR spectrum of **1** (methanol-d_4) (Figure S1). Similarly, a ratio of 1:5.8 of the predicted ECD spectra for (3*S*,4*S*) and (3*R*,4*S*) was used to calculate the observed spectrum shown in Figure 1C, which was a good match for the experimental spectrum.

H. References

(1) Haasnoot, C.; de Leeuw, F. A.; Altona, C. *Tetrahedron* **1980,** *36* (19), 2783-2792.
(2) Luo, X.; Lin, X.; Salendra, L.; Pang, X.; Dai, Y.; Yang, B.; Liu, J.; Wang, J.; Zhou, X.; Liu, Y. *Mar. drugs* **2017,** *15* (7), 204.
(3) Hewage, R. T.; Aree, T.; Mahidol, C.; Ruchirawat, S.; Kittakoop, P. *Phytochemistry* **2014,** *108*, 87-94.
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