

Supporting Information

The formation of sesquiterpenoid presilphiperfolane and cameroonane metabolites in the *BcBot4* null mutant of *Botrytis cinerea*.

Gabriel Franco dos Santos,^{1,2#} Javier Moraga,^{1#} Jacqueline A. Takahashi,² Muriel Viaud,³ Rosario Hernández Galán,¹ James R. Hanson,⁴ Isidro G. Collado^{1*}

¹Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz. Spain.

²Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte-MG, Brazil, ³UMR BIOGER, INRA, AgroParisTech, Université Paris-Saclay, 78850 Thiverval-Grignon, France.

⁴Department of Organic Chemistry, University of Sussex, Brighton, Sussex, BN1 9QJ, United Kingdom.

Table of contents:

Spectroscopy constant Tables.....	S2-S7
¹ H and ¹³ C-NMR spectra	S8-S25

Table S1. NMR Spectroscopic data of presilphiperfolan-8 α ,10 β ,14-triol (16) (^1H at 500 MHz, ^{13}C at 125 MHz).

Position	Proton	δ_{H} (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	H-1 α	1.45 (1H, m)	44.9		C-2, C-9, C-10, C-11, C-15
2	H-2 α	1.94 (1H, m)	34.3	H-2 β , H-3 α	C-1, C-3, C-9
	H-2 β	2.36 (1H, m)		H-2 α , H-3 β , H-9 β	C-1, C-3, C-4, C-8, C-9
3	H-3 α	1.94 (1H, m)	34.1	H-2 α , H-3 β	C-1, C-3
	H-3 β	1.15 (1H, m)			C-4, C8, C-12
4	-		57.9	-	-
5	H-5 α	2.04 (1H, d, $J=12.1$ Hz)	43.5	H-5 β , H-14	C-3, C-4, C-6, C-12, C-13, C-14,
	H-5 β	1.03 (1H, d, $J=12.1$ Hz)		H-5 α , H-12, H-13	C-4, C-6, C-7, C-8, C-12, C-13
6	-	-	54.4	-	-
7	H-7 α	1.88 (1H, m)	45.9	H-11 α , H-14	C-4, C-6, C-8, C-10, C-11, C-13, C-14
8	-	-	95.3	-	-
9	H-9 β	1.43 (1H, m)	47.6		
10	H-10 α	3.25 (1H, ddd, $J=11, 9.4, 3.4$, Hz)	76.3	H-7 α , H-15	C-7, C-9, C-11, C-15
11	H-11 α	1.84 (1H, m)	36.9		C-7, C-8, C-10
	H-11 β	1.61 (1H, ddd, $J=12, 11$ Hz)		H-12, H-13	C-6, C-7, C-8, C-10
12	H-12	1.36 (3H, s)	29.0	H-13	C-3, C-4, C-5, C-8
13	H-13	1.18 (3H, s)	22.8	H-12	C-5, C-6, C-7, C-14
14	H-14	3.35 (2H, d superimposed, $J=10$ Hz)	72.5	H-5 α , H-7 α	C-5, C-6, C-7, C-13
15	H-15	0.99 (3H, d, $J=5.9$ Hz)	18.0	H-1 α , H-10 α , H-14	C-1, C-9, C-10,

Table S2. NMR Spectroscopic data of 8 α ,14-dihydroxypresilphiperfolan-10-one (17) (^1H at 600 MHz, ^{13}C at 150 MHz).

Position	Proton	δ_{H} (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	H-1 α	1.71 (1H, m)	48.09		C-4
2	H-2	2.05 (1H, m)	34.9		
	H-2'	2.50 (1H, m)			C-3, C-4, C-9
3	H-3	1.98 (1H, m)	32.7		C-1, C-2
	H-3'	1.26 (1H, m)			C-4
4	-		57.8		
5	H-5 α	2.17 (1H, d, J =12.1 Hz)	41.7		C-4, C-6, C-12, C-13, C-14
	H-5 β	1.14 (1H, d, J =12.1 Hz)		H-13	C-4, C-6, C-12, C-13, C-14
6	-	-	54.0		
7	H-7 α	2.20 (1H, m)	46.2		C-6, C-8, C-11
8	-	-	92.4		
9	H-9 β	2.43 (1H, dq, J = 12.4, 6.3 Hz)	48.13		C-2, C-15
10	H-10		213.7		
11	H-11 α	2.34 (1H, dd, J = 13.1, 8.7 Hz)	42.2		C-7, C-9, C-8, C-10
	H-11 β	2.52 (1H, dd (br), J = 13.1 Hz)		H-11, H-2 β	C-7, C-6, C-10
12	H-12	1.54 (3H, s)	28.14	H-9, H-11 β	C-3, C-4, C-5, C-8
13	H-13	1.14 (3H, s)	22.5		C-5, C-6, C-8, C-14
14	H-14	3.44 (2H, s(br))	71.5	H-13	C-5, C-6, C-7, C-13
15	H-15	0.98 (3H, d, J = 6.4 Hz)	13.5		C-9, C-10

Table S3. NMR Spectroscopic data of 8 α ,10 β ,14-trihydroxypresilphiperfol-1-ene (18) (^1H at 600 MHz, ^{13}C at 150 MHz).

Position	Proton	δ_{H} (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1			148.7		
2	H-2	4.94 (1H, dd, J = 2.5, 2.1 Hz)	116.2		C-3, C-4, C-8
3	H-3	2.40 (1H, dd, J = 17, 2.1 Hz)	50.25		C-1, C-2, C-4, C-8, C-12
	H-3'	2.25 (1H, dt, J = 17, 2.5, Hz)			C-1,C-2, C-4, C-5, C-12
4	-		47.1		
5	H-5	1.87 (1H, d, J = 13.3 Hz)	53.43		C-3, C-6, C-12, C-13, C-14
	H-5'	1.56 (1H, d, J = 13.3 Hz)			
6	-		46.4		
7	H-7 α	1.36 (1H, m)	53.4		C-6, C-8, C-11, C-13
8	-		93.5		
9	H-9 β	2.46 (1H, m)	39.7		
10	H-10	3.18 (1H, ddd, J = 10, 8.7, 5.3 Hz)	79.8		C-15
11	H-11	1.94 (1H, m)	30.5		C-7, C-8, C-10
	H-11'	1.86 (1H, m)			C-7, C-8, C-9, C-10
12	H-12	1.11 (3H, s)	29.7		C-3, C-4, C-5, C-8
13	H-13	1.07 (3H, s)	18.9		C-5, C-6, C-14
14	H-14	3.33 (2H, d(br), J = 4 Hz)	71.0		C-5, C-6, C-13
15	H-15	1.20 (3H, d, J = 6.5 Hz)	14.15		C-1, C-9, C-10

Table S4. NMR Spectroscopic Data of cameroonan-7 α , 10 β , 14-triol (19) (^1H at 500 MHz, ^{13}C at 125 MHz).

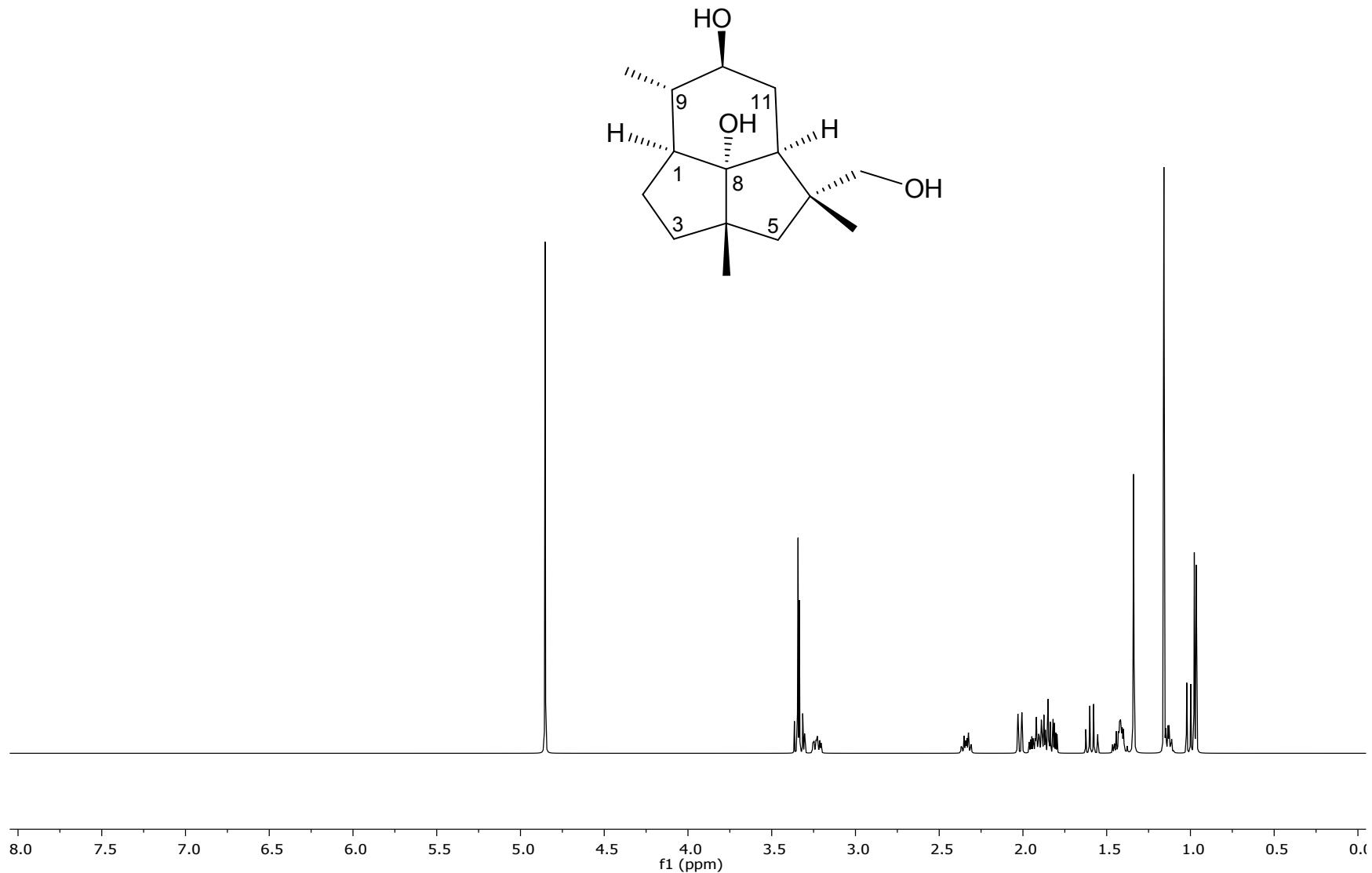
Position	Proton	δ_{H} (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	H-1 α	2.17 (1H, t, J = 9.0 Hz)	47.85	H-14, H-15	C-2, C-4, C-7, C-8, C-9, C-11, C-13, C-15
2	H-2	1.34 (1H, m)	28.62		C-4, C-8, C-9
	H-2'	1.80 (1H, m)			C-1, C-3, C-9
3	H-3	1.49 (2H, m)	38.93		C-2, C-4, C-12
	H-3'				
4	-	-	48.47		-
5	H-5	1.27 (1H, d superimposed)	47.42		C-3, C-4, C-6, C-7, C-8, C-12, C-13, C-14
	H-5'	1.39 (1H, d J = 14.5 Hz)			C-3, C-4, C-6, C-7, C-12, C-13, C-14
6	-	-	42.35		-
7	H-7 β	3.89 (1H, s)	91.52	H-9 β , H-11b, H-12	C-1, C-6, C-8, C-11, C-14, C-13
8	-	-	62.85		-
9	H-9 β	1.22 (1H, m)	49.96		
10	H-10 α	3.72 (1H, ddd, J = 11, 9.7, 6.0, Hz)	77.45	H-11a, H-11b, H-15	C-9, C-15
11	H-11	1.65 (1H, dd, 12.2, 11 Hz)	44.83	H-10 α	C-4, C-7, C-8, C-10
	H-11'	1.73 (1H, dd, J = 12.2, 6 Hz)		H-7 β , H-10 α	C-1, C-7, C-8, C-9
12	H-12	1.00 (3H, s)	25.03	H-9 β , H-11a, H-3	C-1, C-3, C-8
13	H-13	1.20 (3H, s)	27.39	H-7 β , H-14 α	C-5, C-6, C-7, C-14
14	H-14	3.21 (1H, d, J = 10.9 Hz)	69.61	H-9 β , H-5, H-14b	C-5, C-6, C-7, C-13
	H-14'	3.82 (1H, d, J = 10.9 Hz)		H-1, H-5, H-2, H-14a	C-5, C-6, C-7, C-13
15	H-15	1.05 (3H, d, J = 6.5 Hz)	16.36	H-1 α , H-10 α	C-1, C-9, C-10

Table S5. NMR Spectroscopic Data of cameroonan-2 α , 3 β , 7 α -triol (20) (^1H at 500 MHz, ^{13}C at 125 MHz).

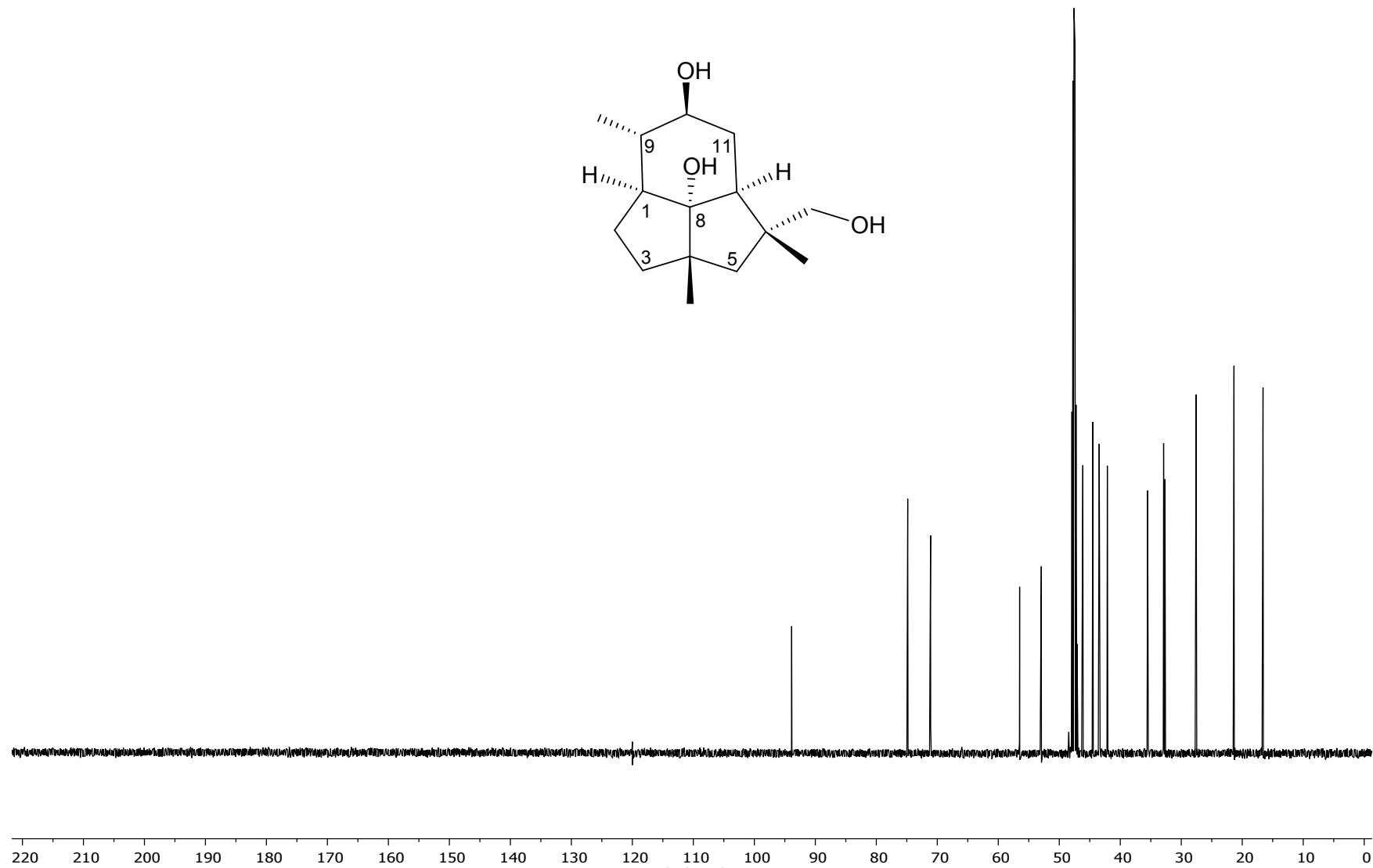
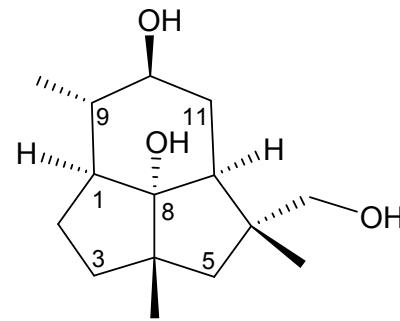
Position	Proton	δ_{H} (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	H-1 α	2.10 (1H, dd, J = 8.6, 3.7 Hz)	54.8		C-2, C-7, C-8, C-11, C-15
2	H-2 β	3.49 (1H, dd, J = 9.1, 8.6 Hz)	82.9	H-12, H-9	C-3, C-9
3	H-3 α	3.81 (1H, dbr, J = 9.1 Hz)	86.5	H-1, H-5 α , H-14	C-2, C-5, C-12
4	-		49.8		
5	H-5 α	1.83 (1H, d, J = 13.5 Hz)	52.85	H-5 β , H-3	C-7, C-3, C-8, C-4, C-6, C-13, C-14, C-12
	H-5 β	1.29 (1H, d, J = 13.5 Hz)			C-7, C-3, C-8, C-4, C-6, C-13, C-14, C-12
6	-		43.7		
7	H-7 β	3.33 (1H, s)	90.4	H-11 β , H-13	C-4, C-5, C-11, C-13, C-14
8	-		64.10		H-5, H-10, H-11, H-12
9	H-9 β	1.94 (1H, m)	38.61		C-2, C-8, C-11, C-15
10	H-10 α	1.34 (1H, m)	34.9		C-1, C-8, C-9, C-11, C-15
	H-10 β	1.73 (1H, m)			C-1, C-8, C-9, C-11, C-15
11	H-11 α	1.90 (1H, m)	35.7		C-10, C-9, C-7, C-4, C-1
	H-11 β	1.55 (1H, m)			C-10, C-9, C-7, C-4, C-1
12	H-12	0.95 (3H, s)	20.0		C-4, C-5, C-8, C-3
13	H-13	1.03 (3H, s)	29.4		C-5, C-6, C-7, C-14
14	H-14	1.03 (3H, s)	24.3		C-5, C-6, C-7, C-13
15	H-15	1.01 (1H, d, J = 6.9 Hz)	20.3	H-1, H-10 α	C-10, C-9, C-1

Table S6. NMR Spectroscopic Data of 7- α -hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (^1H at 500 MHz, ^{13}C at 125 MHz).

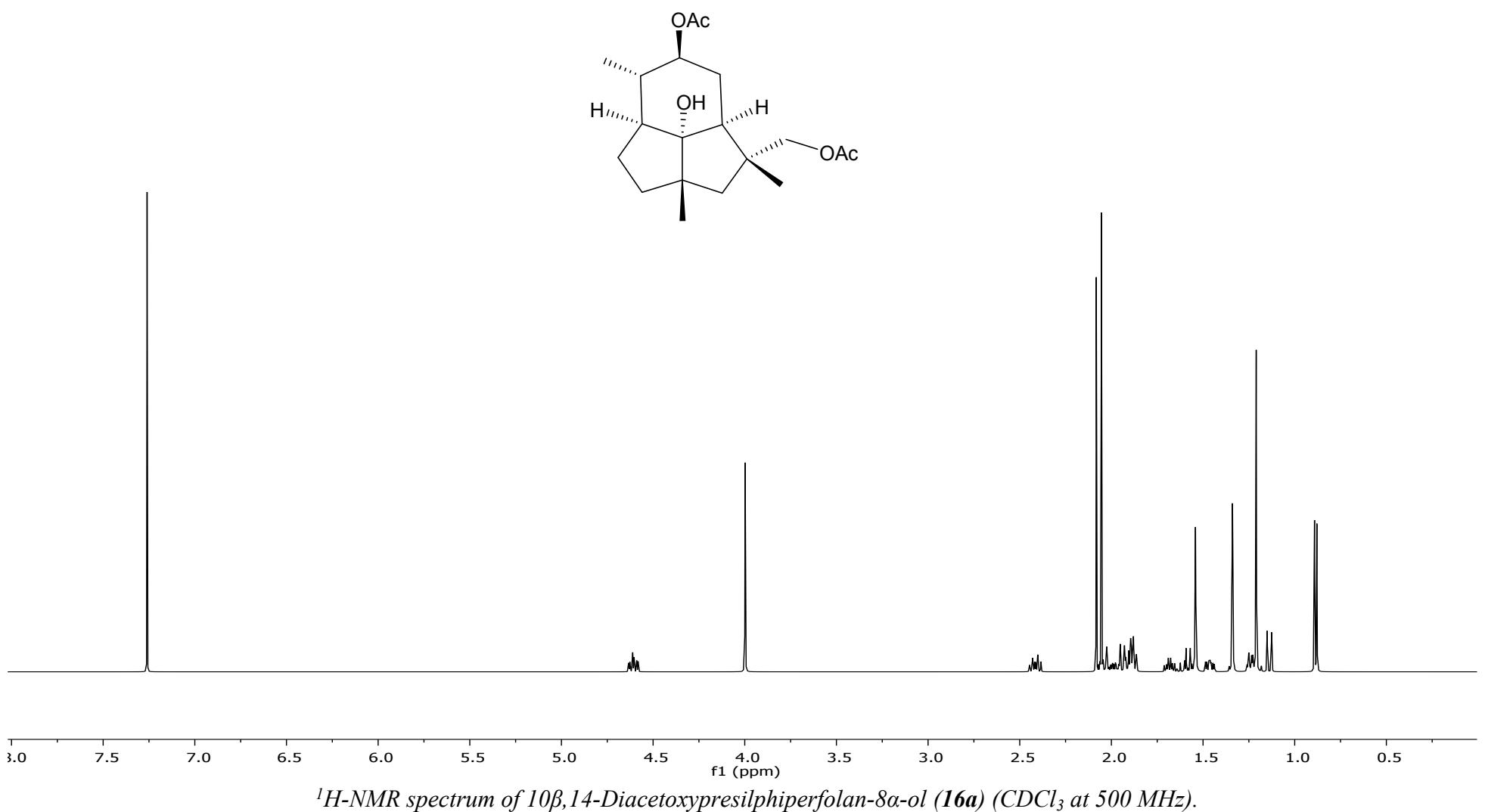
Position	Proton	δ_{H} (Hz)	δ_{C}	NOESY	HMBC
1	H-1 α	3.01 (1H, dt, J 6.7, 8.3 Hz)	50.71		C-2, C-4, C-7, C-8, C-9, C-11, C-15
2	H-2	1.52 (1H, m)	32.50		C-1, C-3, C-9
	H-2'	2.14 (overlap)			-
3	H-3 α	1.90 (1H, m)	42.63		C-2, C-4, C-5, C-12
	H-3 β	1.64 (1H, dd, J 12.7, 6.7 Hz)			C-1, C-2, C-4, C-8, C-12
4	-	-	54.83		-
5	H-5 α	2.28 (1H, d, J 14.4 Hz)	45.09		C-3, C-4, C-6, C-8, C-14
	H-5 β	1.37 (1H, d, J 14.4 Hz)		H-12, H-13	C-3, C-4, C-6, C-12, C-13, C-14
6	-	-	62.26		-
7	H-7 β	4.27 (1H, s)	93.64	H-13	C-4, C-5, C-8, C-11, C-13, C-14
8	-	-	65.33		-
9	H-9 β	2.52 (1H, dt, J 6.7, 8.3 Hz)	51.66	H-10 β	C-1, C-2, C-8, C-10, C-11, C-15
10	H-10 α	2.14 (overlap)	32.95		-
	H-10 β	2.04 (1H, m)			C-1, C-8, C-9, C-11, C-15
11	H-11 α	1.44 (1H, dd, J 13.2, 6.4 Hz)	31.12		C-1, C-4, C-7, C-8, C-9, C-10
	H-11 β	1.80 (1H, m)			C-4, C-7, C-8, C-9, C-10
12	H-12	1.07 (3H, s)	25.14	H-3 β , H-5 β , H-11 β	C-3, C-4, C-5, C-8
13	H-13	1.40 (3H, s)	18.00	H-5 β , H-7 β	C-5, C-6, C-7, C-14
14	-	-	175.74		-
15	-	-	180.62		-

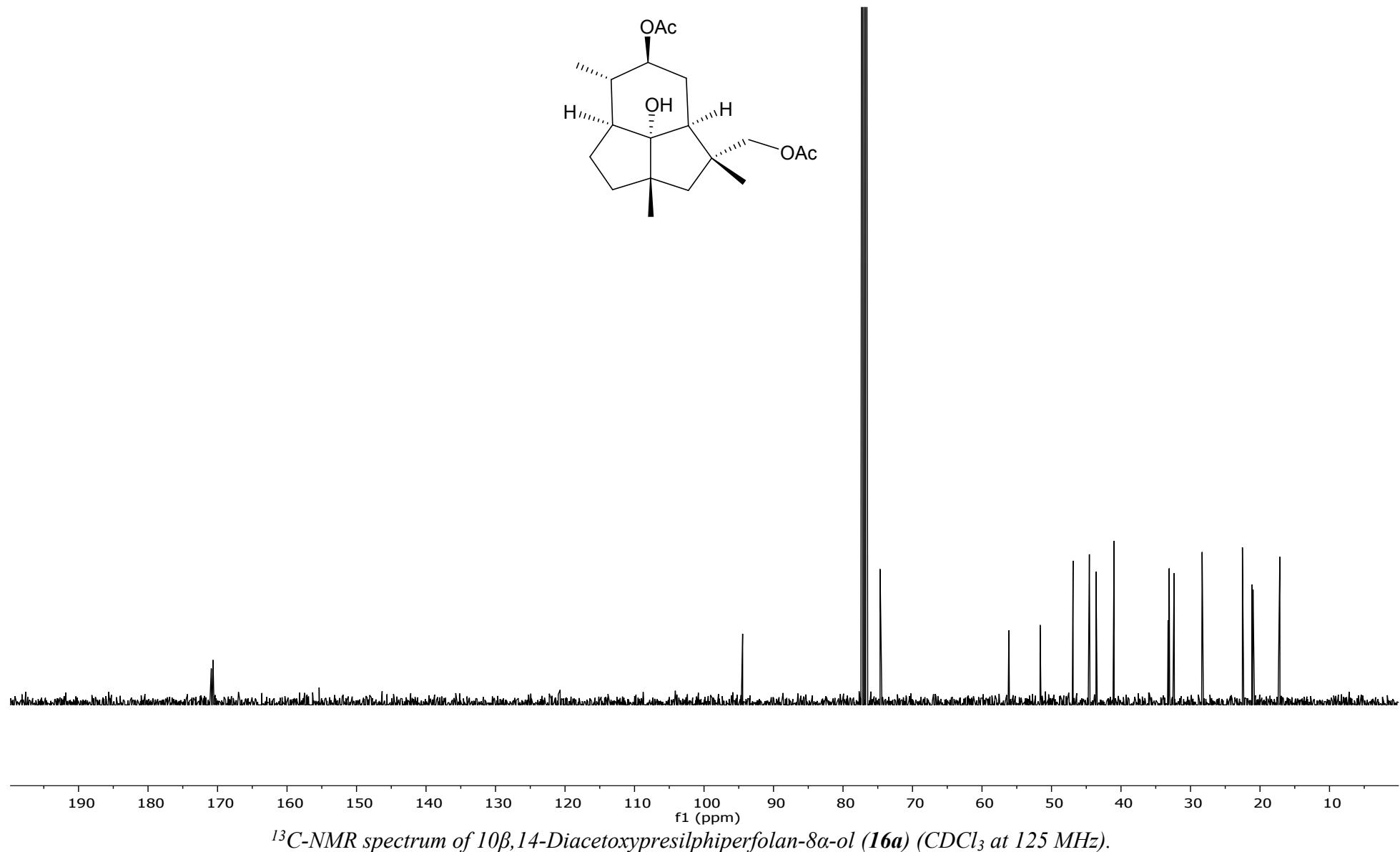


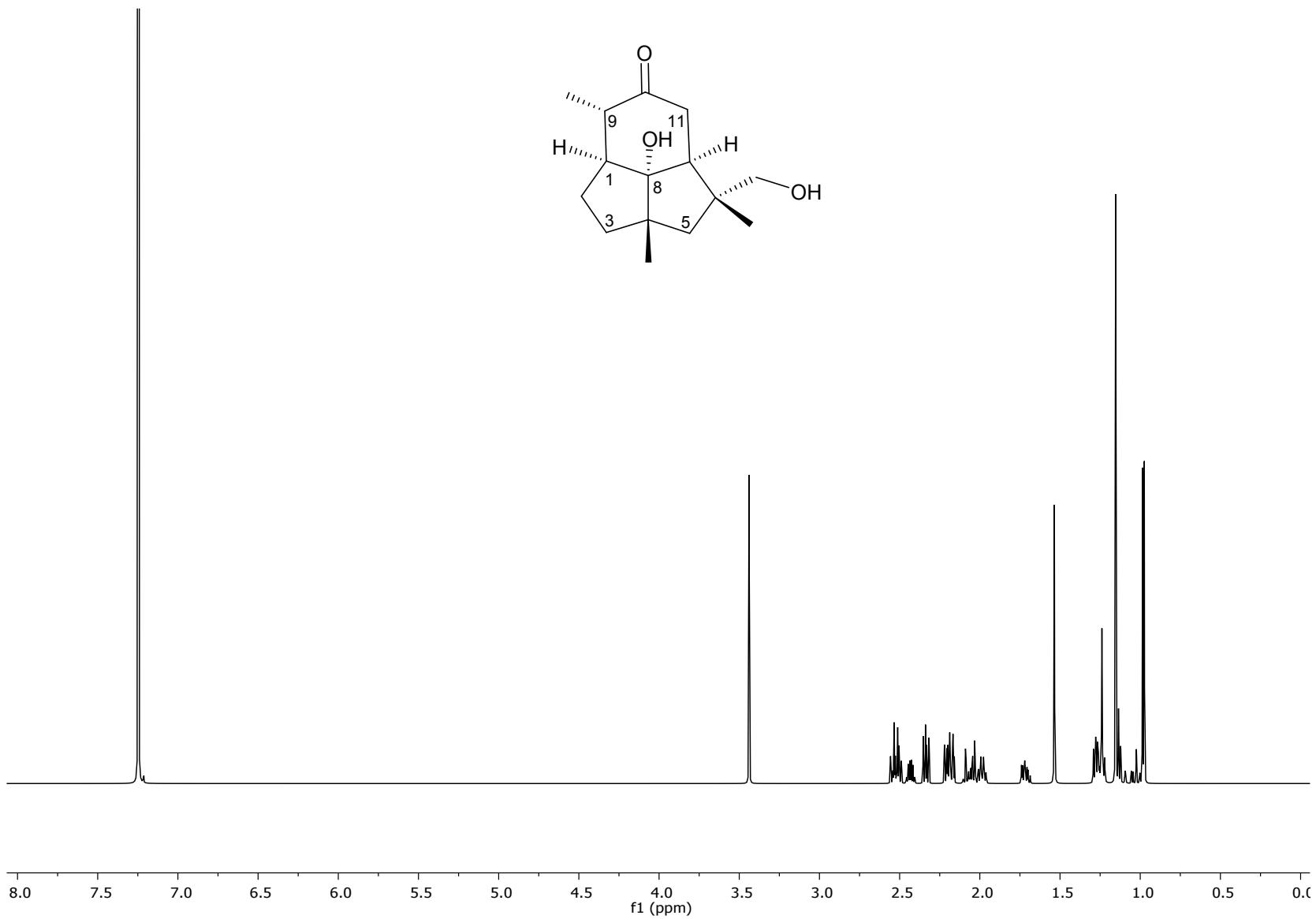
^1H -NMR spectrum of presilphiperfolan-8 α ,10 β ,14-triol (**I6**) (CD_3OD at 500 MHz).



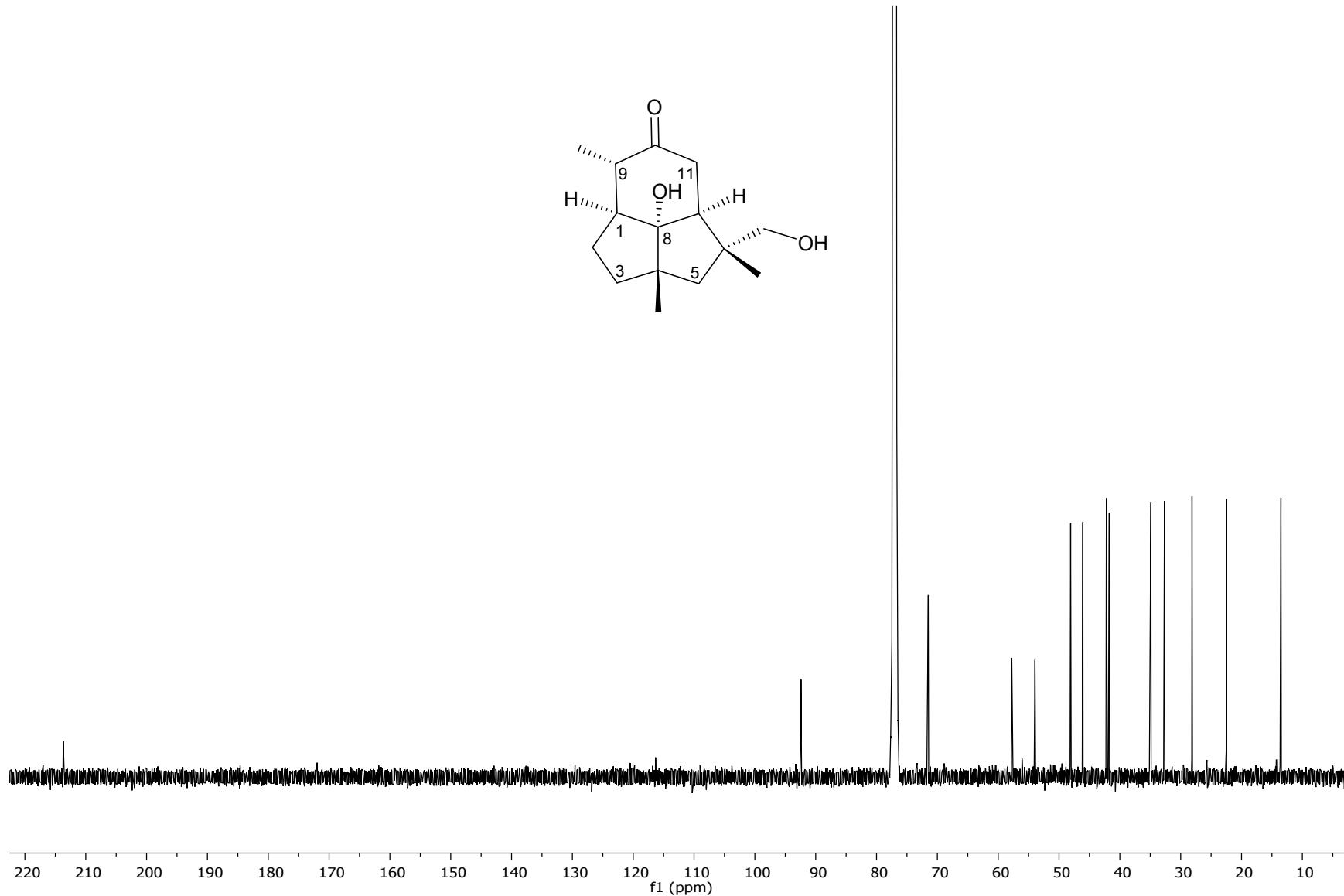
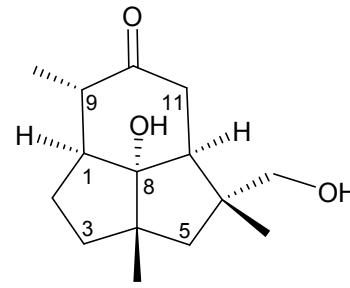
*¹³C-NMR spectrum of presilphiperfolan-8 α ,10 β ,14-triol (**16**) (CD_3OD , at 125 MHz).*



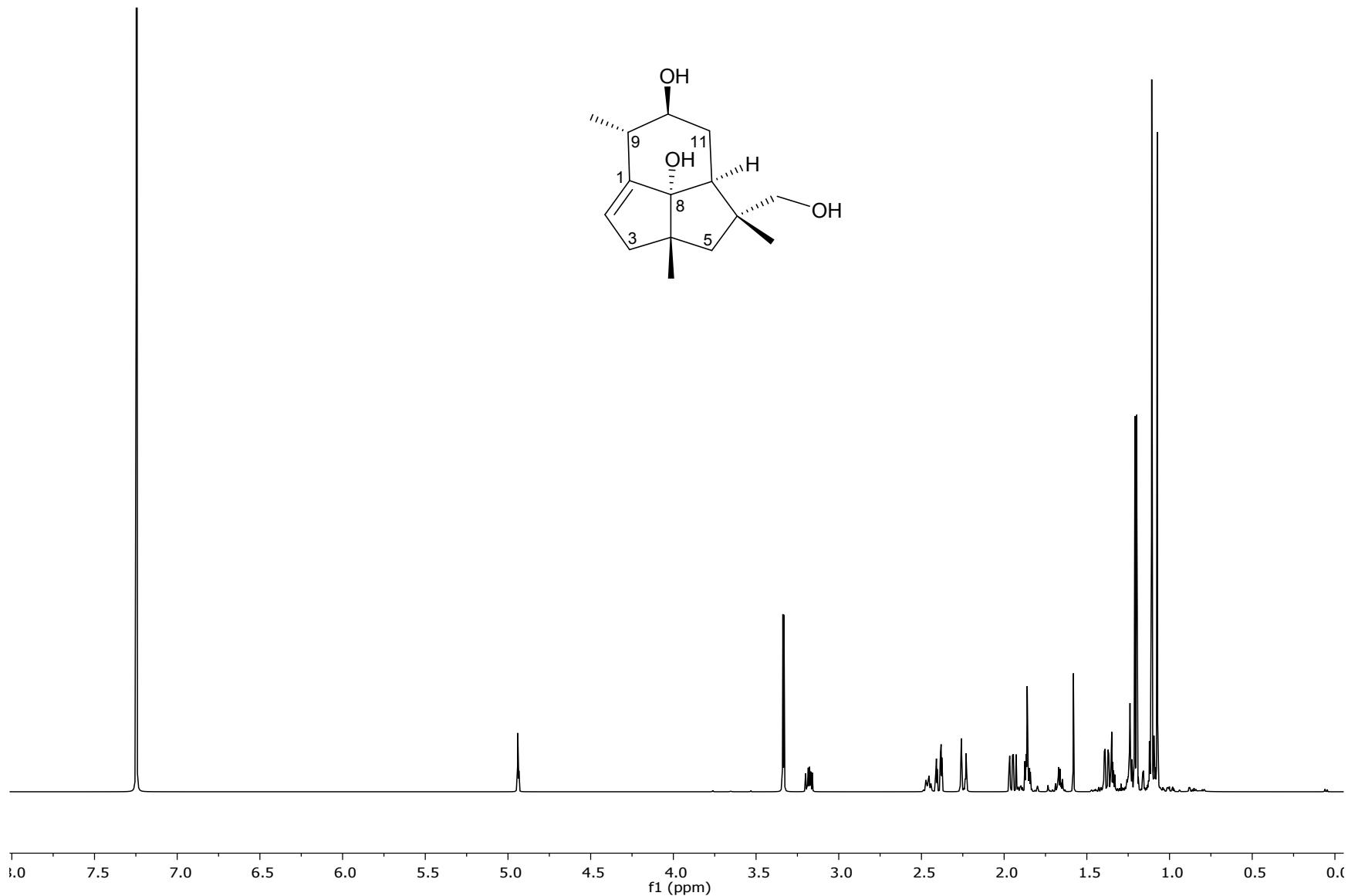




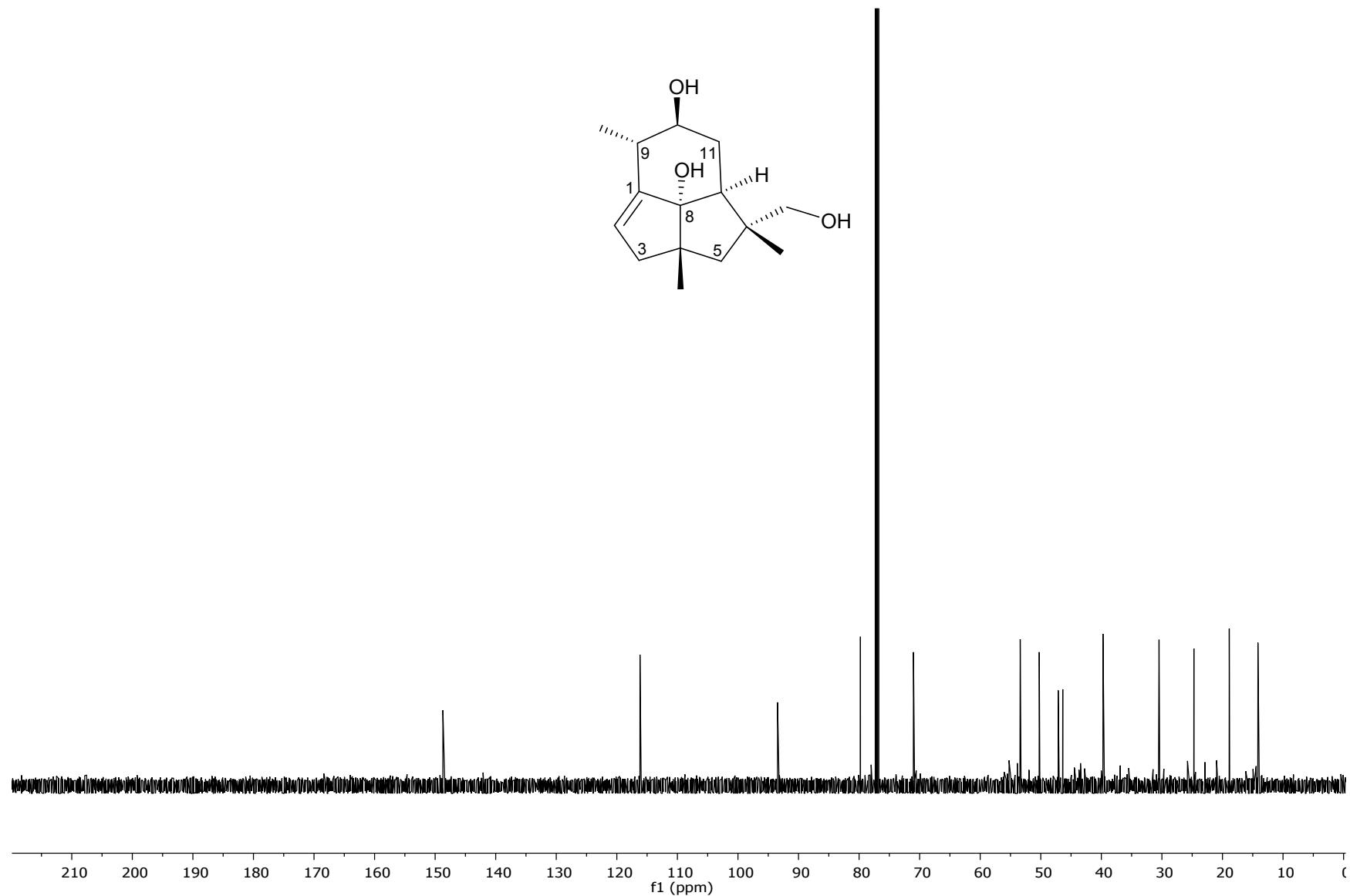
^1H -NMR spectrum of 8a,14-dihydroxypresilphiperfolan-10-one (17) (CDCl_3 at 600 MHz).



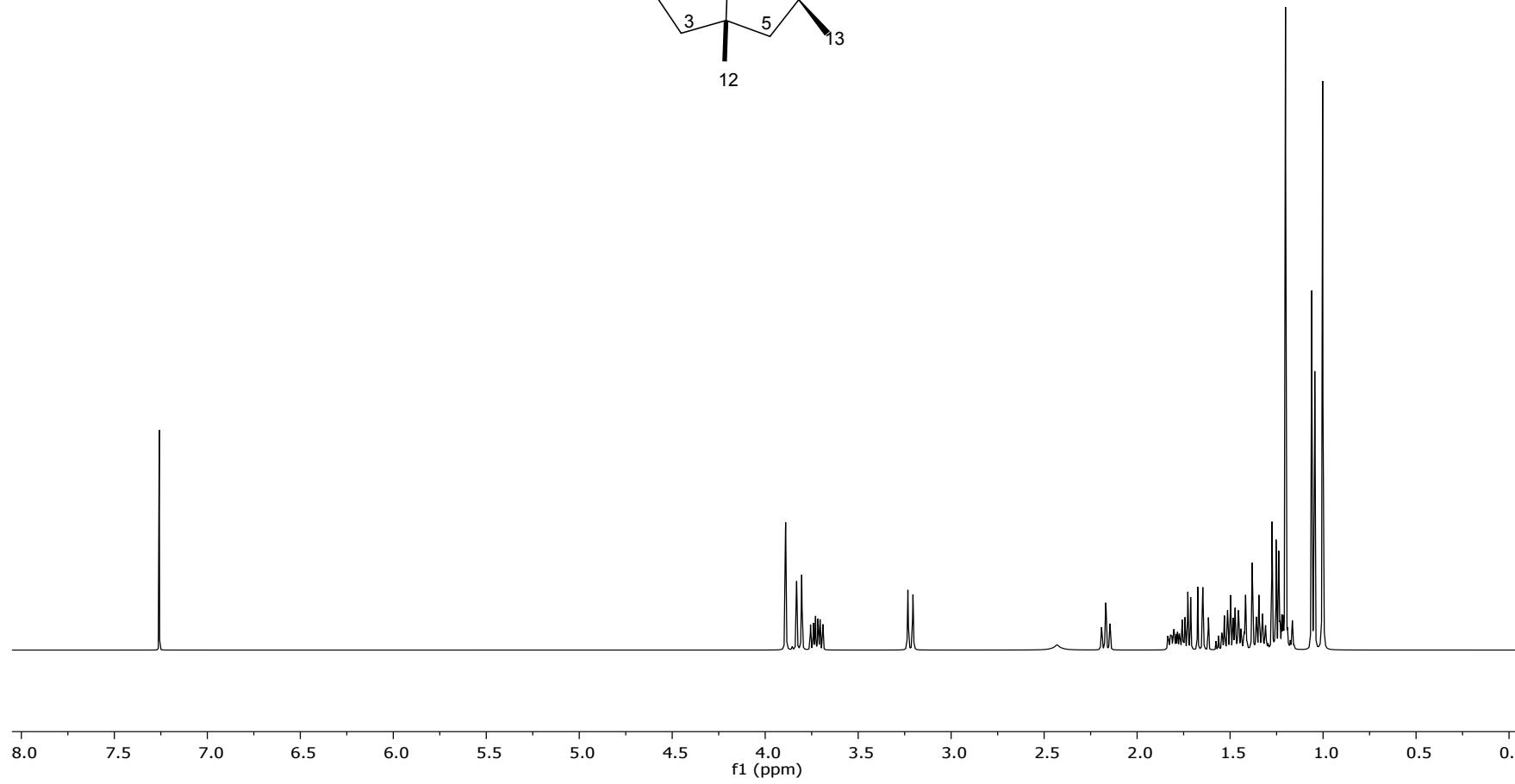
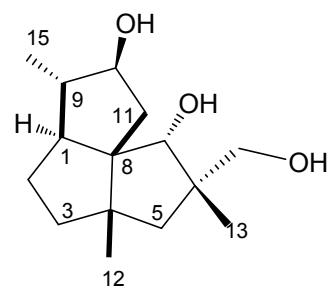
^{13}C -NMR spectrum of $8\alpha,14$ -dihydroxypresilphiperfolan-10-one (**17**) (CDCl_3 at 150 MHz).



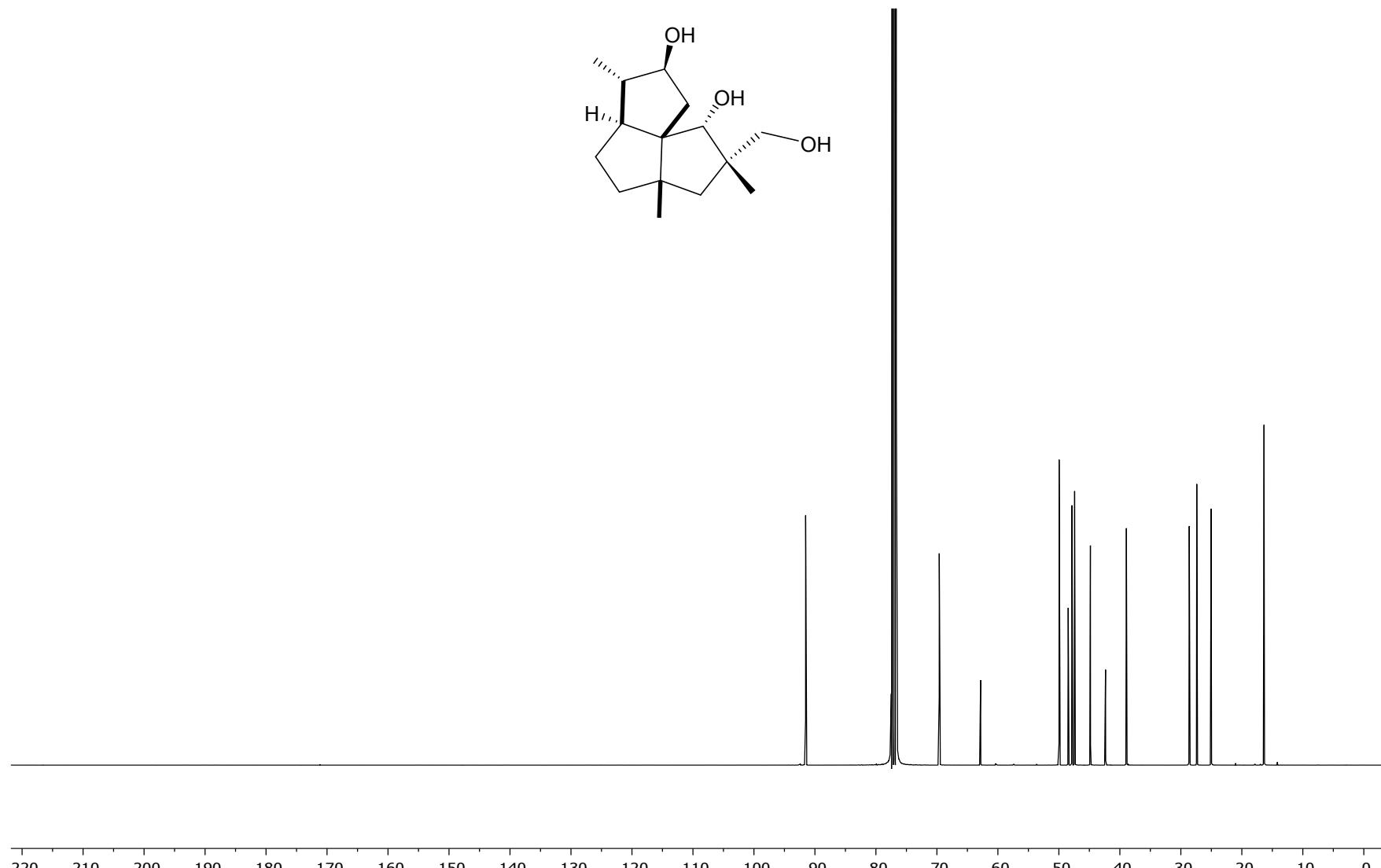
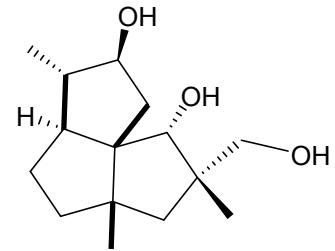
^1H -NMR spectrum of 8 α ,10 β ,14-trihydroxypresilphiperfol-1-ene (18) (CDCl_3 at 600 MHz).



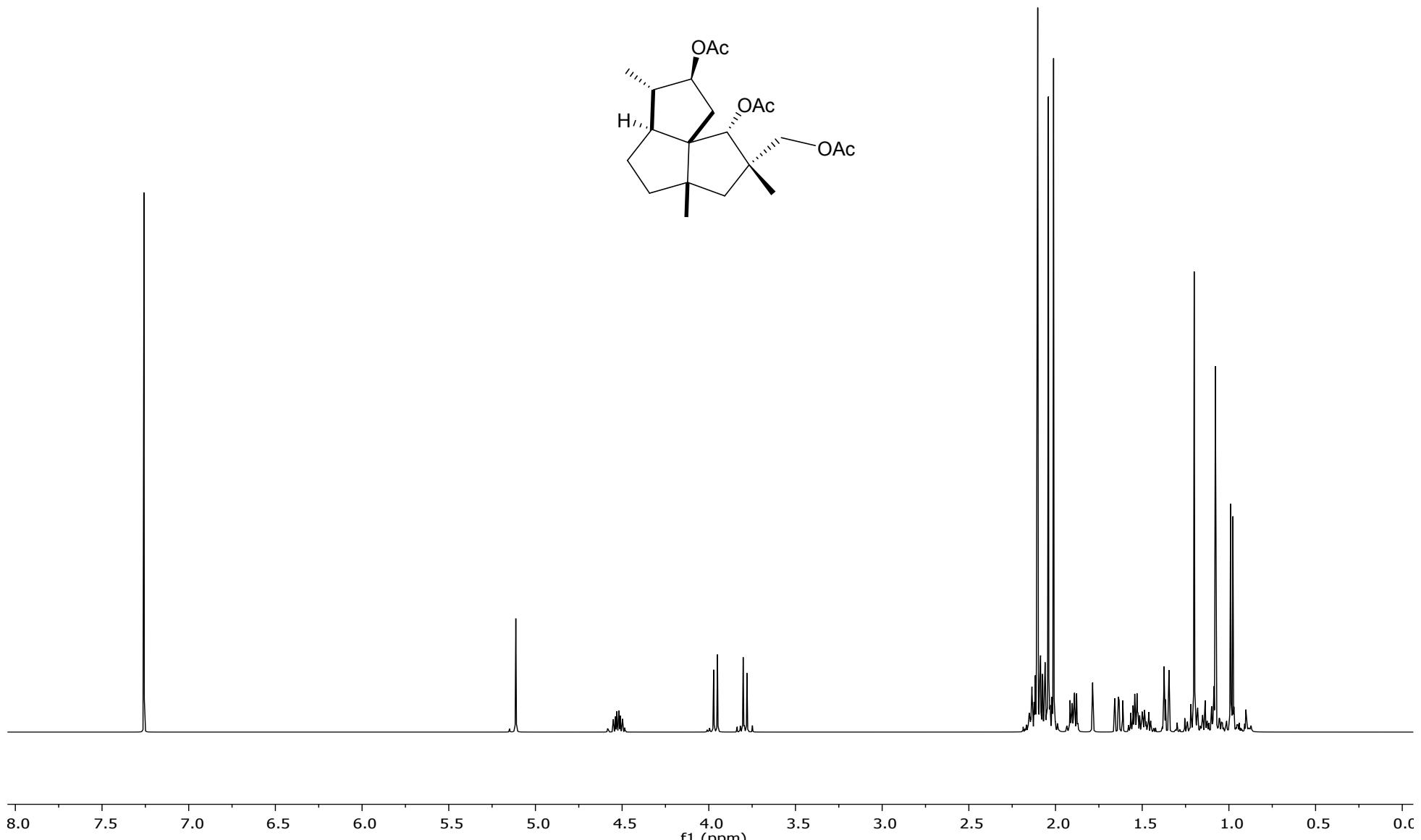
^{13}C -NMR spectrum of $8\alpha,10\beta,14$ -trihydroxypresilphiperfol-1-ene (**18**) (CDCl_3 at 150 MHz).



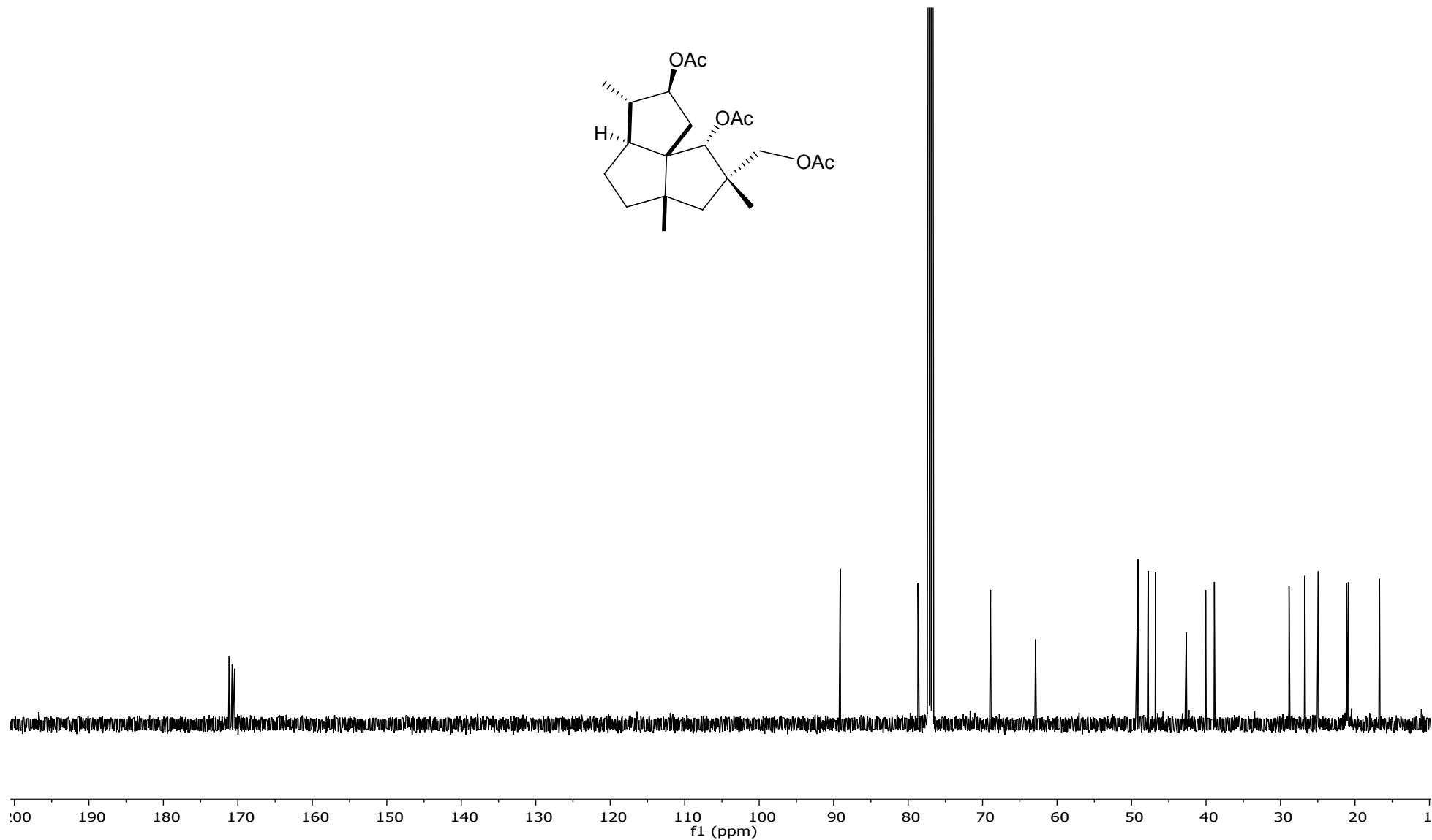
^1H -NMR spectrum of cameroonan-7 α ,10 β ,14-triol (**19**) (CDCl_3 at 500 MHz).



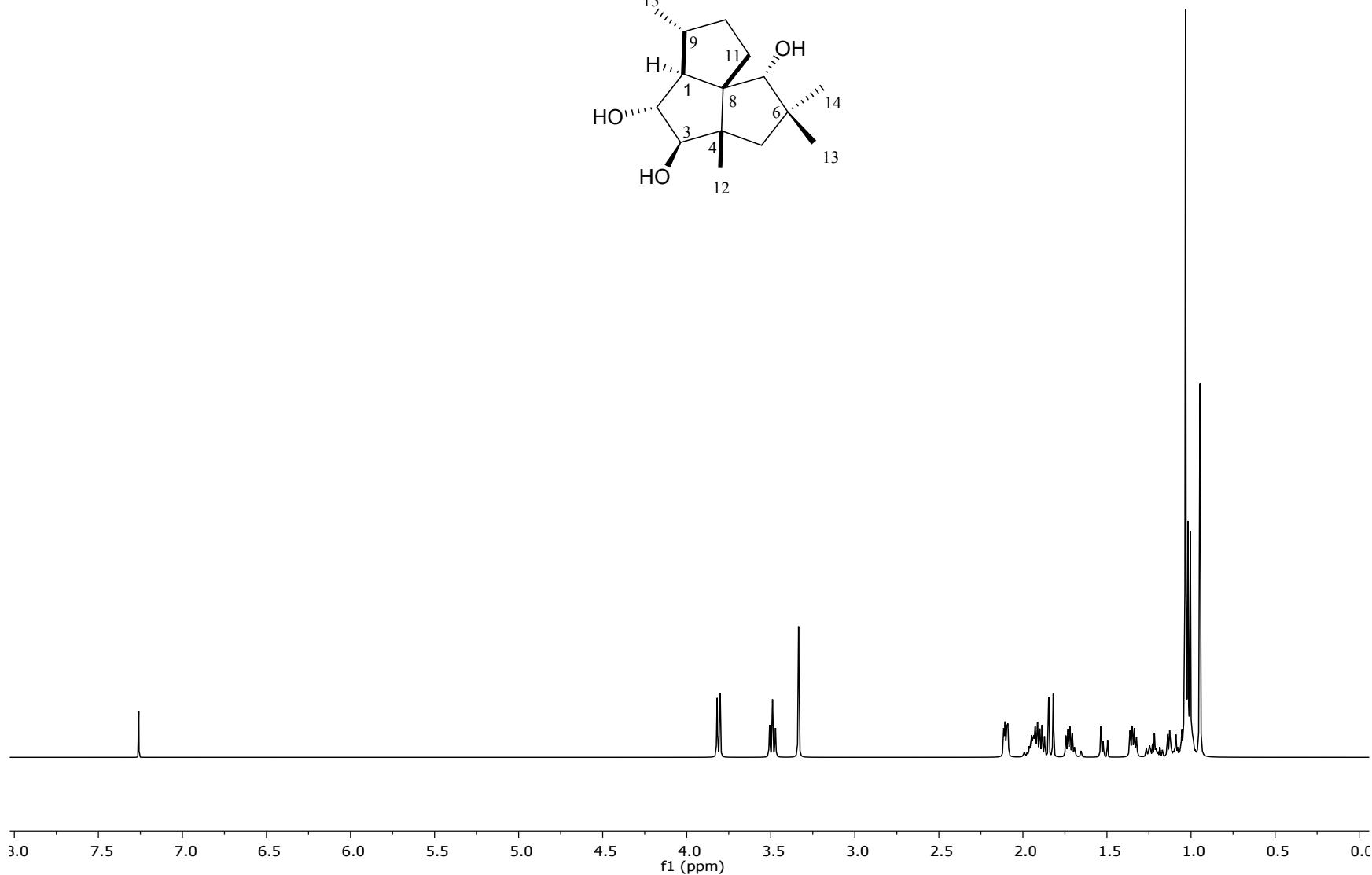
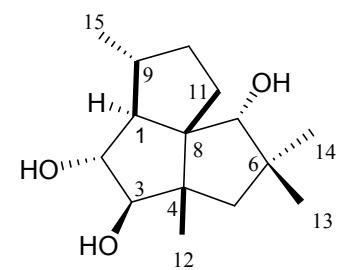
^{13}C -NMR spectrum of cameroonan-7 α ,10 β ,14-triol (19) (CDCl_3 at 125 MHz).



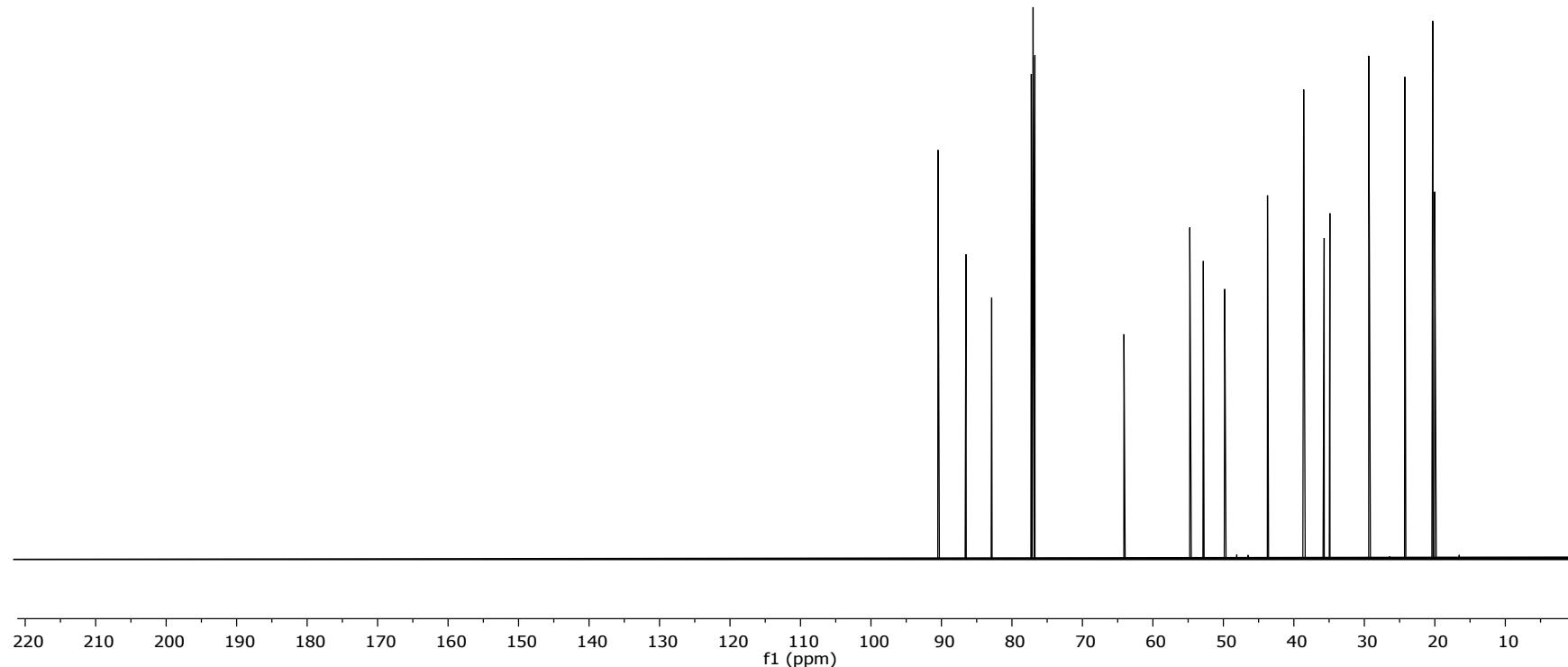
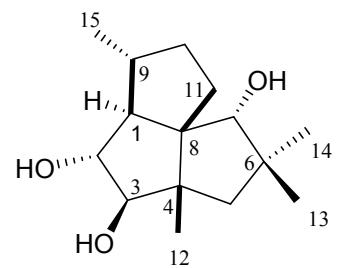
^1H -NMR spectrum of 7α , 10β , 14 -triacetoxycameroonane (**19a**) (CDCl_3 at 500 MHz).



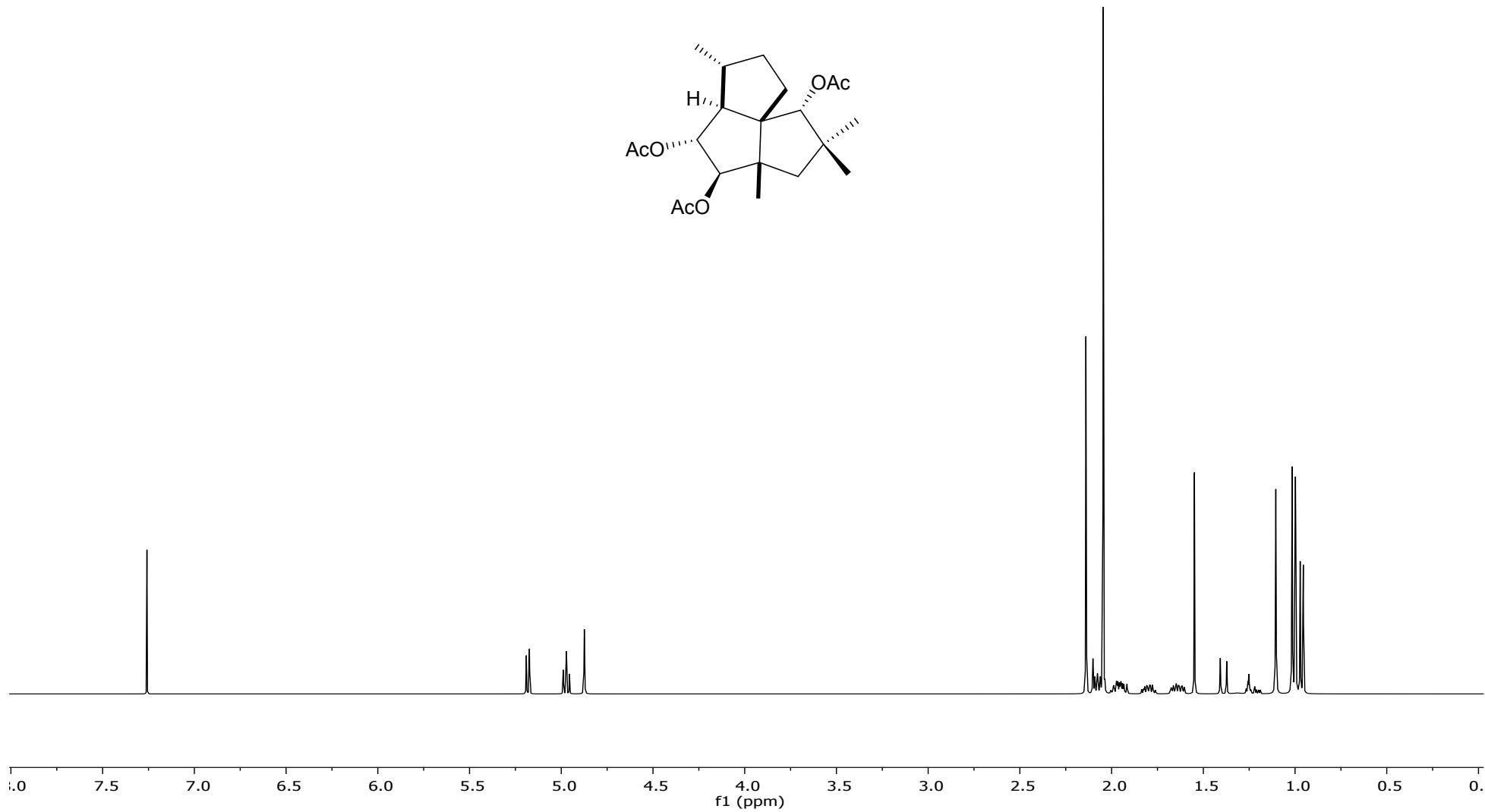
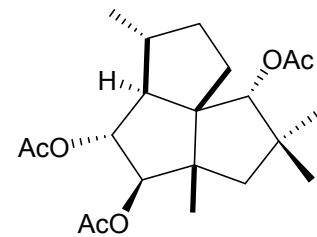
^{13}C -NMR spectrum of $7\alpha, 10\beta, 14$ -triacetoxycameroonane (**19a**) (CDCl_3 at 125 MHz).



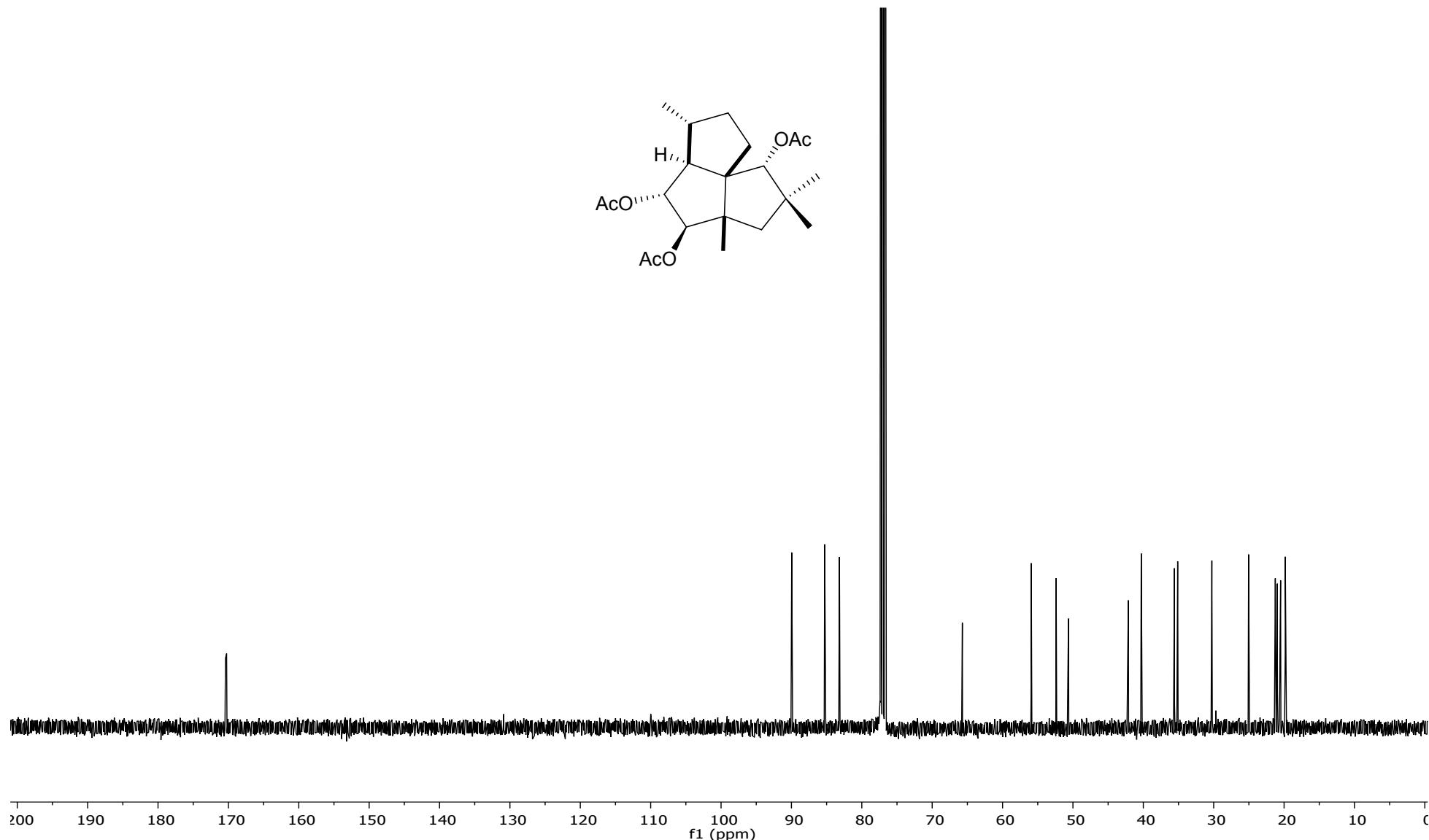
^1H -NMR spectrum of cameroonan-2 α , 3 β , 7 α -triol (20) (CDCl_3 at 500 MHz).



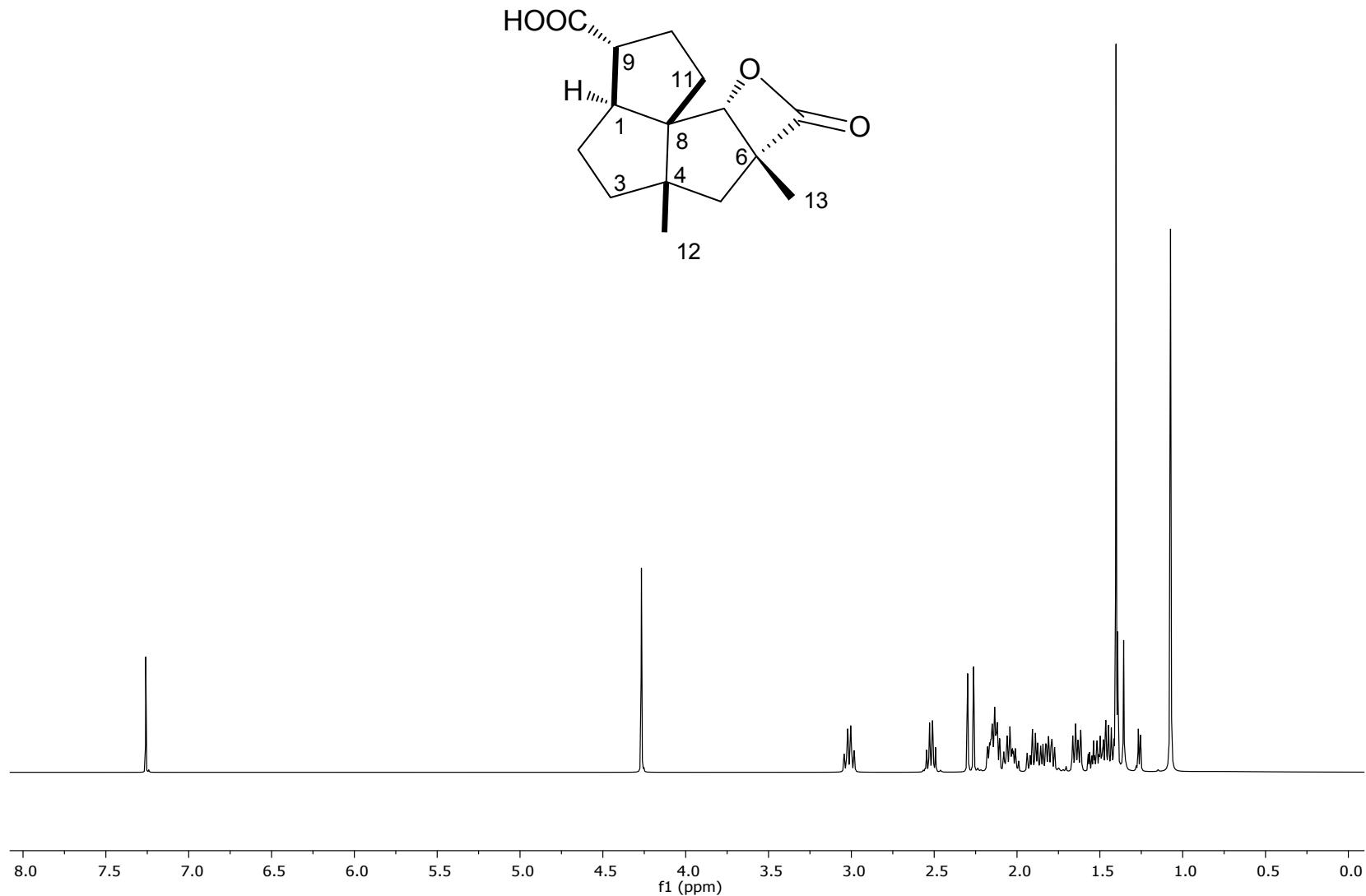
^{13}C -NMR spectrum of cameroonan-2 α , 3 β , 7 α -triol (**20**) (CDCl_3 at 125 MHz).



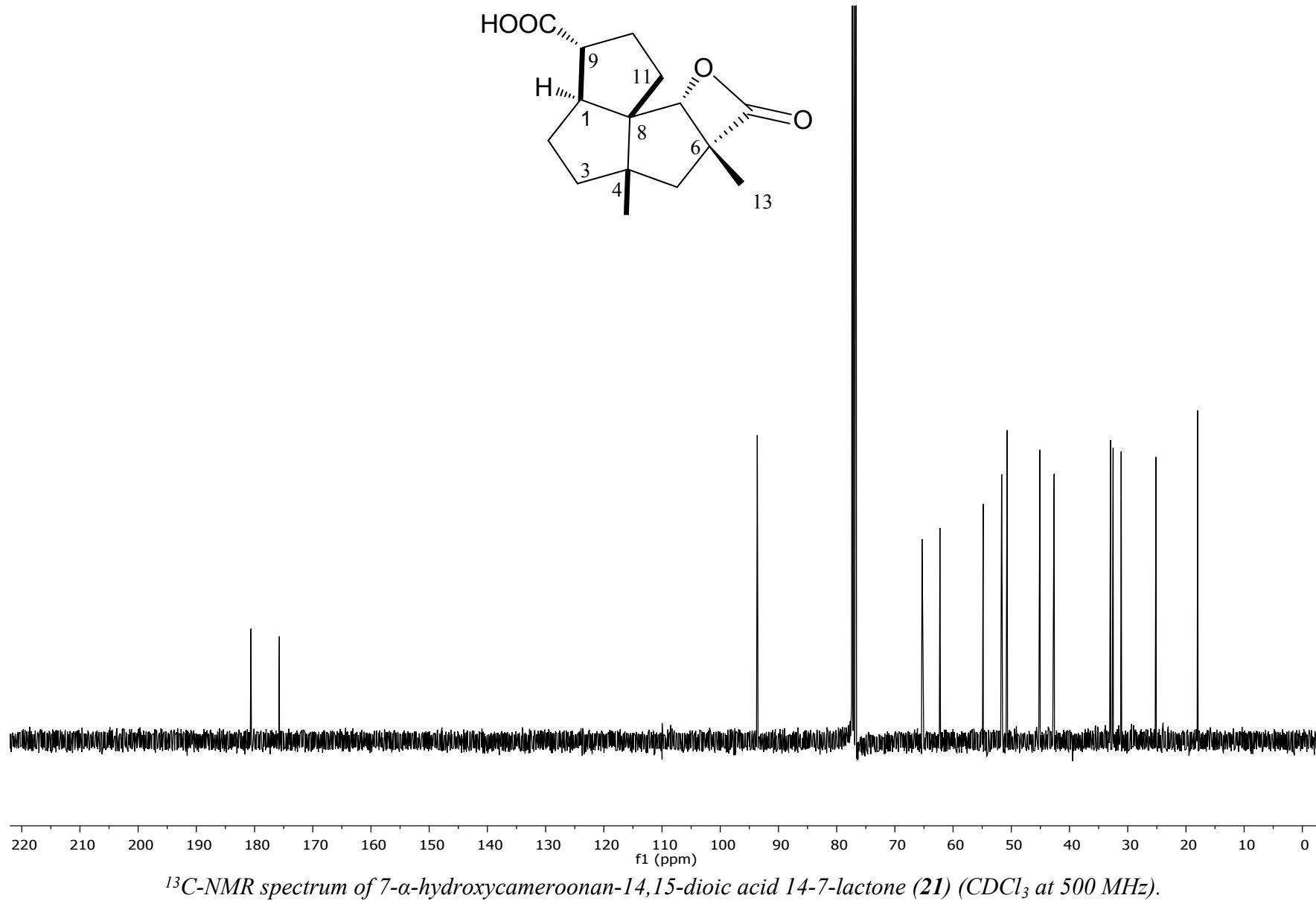
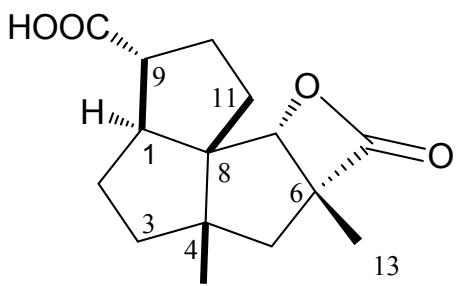
^1H -NMR spectrum of 2α , 3β , 7α -triacetoxycameroonane (**20a**) (CDCl_3 at 400 MHz).



^{13}C -NMR spectrum of $2\alpha, 3\beta, 7\alpha$ -triacetoxyacameroonane (**20a**) (CDCl_3 at 100 MHz).



^1H -NMR spectrum of 7- α -hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (CDCl_3 at 500 MHz).



^{13}C -NMR spectrum of 7- α -hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (CDCl_3 at 500 MHz).