Natural Product Research

Polycyclic polyprenylated acylphloroglucinols from *Hypericum choisianum*

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Contents

Table S1. ^{1}H and ^{13}C NMR data of **3**, **2** and **1a**.[a]

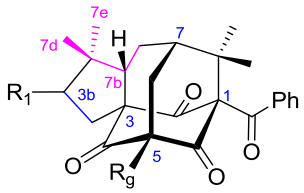
No.	**3**		**2**		**1a**[b]	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1	---	83.2	---	83.3	---	83.2
2	---	192.8	---	192.9	---	192.7
3	---	116.8	---	116.6	---	116.8
4	---	172.8	---	172.9	---	172.8
5	---	59.0	---	59.4	---	59.0
6	2.04 dd (13.0, 3.9)	38.0	2.01 dd (13.2, 4.3)	38.0	2.04 dd (13, 4)	38.0
	1.52 dd (13.0, 12.3)		1.51 dd (13.2, 12.6)		1.52 dd (13, 13)	
7	1.61 [c]	43.4	1.70 [c]	43.4	1.62 m	43.3
8	---	48.3	---	48.3	---	48.2
9	---	204.6	---	204.5	---	204.6
10	---	209.0	---	209.1	---	209.5
11	1.05 s	13.4	1.05 s	13.4	1.04 s	13.4
12	2.06 m	36.4	2.07 ddd (14.5, 13.4, 5.3)	36.6	2.07 m	36.3
	1.31 m		1.31 ddd (14.5, 11.9, 3.8)		1.31 m	
3a	3.15 dd (14.2, 7.3)	22.2	3.15 dd (14.3, 7.0)	22.2	3.13 br dd (15, 6.5)	22.2
	3.01 dd (14.2, 7.5)		3.01 dd (14.3, 7.7)		3.01 br dd (15, 6.5)	
3b	5.07 t (6.7)	121.0	5.07 t (7.3)	121.2	5.06 m	121.0
3c	---	132.4	---	132.4	---	132.5
3d	1.63 s	25.7	1.65 s	25.7	1.63 br s	25.7
3e	1.70 s	17.8	1.70 s	17.9	1.69 br s	17.8
5a	2.56 dd (13.2, 11.2)	31.2	2.66 dd (12.8, 11.2)	30.3	2.56 dd (13, 11)	31.1
	1.84 dd (13.2, 5.9)		1.77 dd (12.8, 5.6)		1.84 dd (13, 6)	
5b	4.89 dd (11.2, 5.9)	86.5	4.55 dd (10.8, 5.6)	90.1	4.89 dd (11, 6)	86.4
5c	---	83.1	---	70.9	---	83.0
5d	1.30 s	20.2	1.39 s	26.9	1.29 s	20.2
5e	1.28 s	19.8	1.22 s	24.1	1.28 s	19.8
7a	2.18 [c]; 1.76 [c]	27.1	2.17 [c]; 1.78 [c]	27.1	2.17 m; 1.77 m	27.1
7b	4.95 t (7.2)	122.3	4.95 t (6.5)	122.3	4.94 br dd (6.5, 6.5)	122.3
7c	---	133.5	---	133.5	---	133.5
7d	1.70 s	25.9	1.70 s	25.9	1.70 br s	25.9
7e	1.58 s	18.0	1.57 s	18.0	1.57 br s	18.0
12a	2.16 [c]; 1.94 [c]	25.3	2. 15 [c]; 1.93 [c]	25.3	2.15 m; 1.92 m	25.2
12b	5.04 t (7.5)	124.7	5.07 t (7.3)	124.7	5.05 m	124.7
12c	---	131.1	---	131.1	---	131.1
12d	1.64 s	25.7	1.65 s	25.7	1.65 br s	25.6
12e	1.60 s	17.7	1.60 s	17.7	1.59 br s	17.7
10a	1.74 m	48.7	1.74 m	48.7	1.98 m	41.9
10b	1.09 d (6.5)	16.5	1.09 d (6.4)	16.5	1.09 d (6.5)	20.4
10c	1.69 [c]; 1.30 [c]	27.4	1.70 [c]; 1.29 [c]	27.4	1.00 d (6.5)	21.3
10d	0.78 t (7.3)	11.5	0.77 t (7.4)	11.5		
OH	7.58 br s					

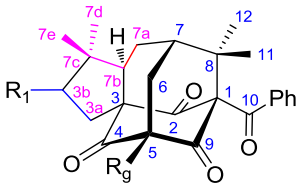
[a]) Measured in $CDCl_3$, 500/125 MHz for $^{1}H/^{13}C$ NMR);

[b]) **1a** = 33-Deoxy-33-hydroperoxyfurohyperforin (=Furohyperforin hydroperoxide). Data from Ref. (*J. Nat. Prod*. 2000, 63, 412);

[c]) Overlapped signals.

Table S2. [1]H NMR data of **14**, **15**, and **21**.[a]





14 R_1=β-$CHMe_2$
15 R_1=α-$CHMe_2$
17 R_1=β-C(Me)=CH_2
19 R_1=α-C(OH)Me_2
21 R_1=β-C(OH)Me_2

16 R_1=α-C(Me)=CH_2
18 R_1=α-C(OH)Me_2
20 R_1=β-C(OH)Me_2

No.	**14**	**15**	**21**
	δ_H mult. (*J* in Hz)	δ_H mult. (*J* in Hz)	δ_H mult. (*J* in Hz)
6	2.48 dd (14.8, 7.3)	2.48 dd (14.7, 6.7)	2.49 dd (14.7, 6.8)
	2.13 d (14.8)	2.20 br d (14.8)	2.17 dd (14.7, 7.3)
7	1.75 dd (9.6, 6.2)	2.07 br dd (9.6, 6.7)	2.02 [b]
11	1.40 s	1.41 s	1.41 s
12	1.38 s	1.39 s	1.39 s
3a	2.48 dd (12.8, 12.3)	2.55 dd (13.0, 7.2)	2.23 dd (13.9, 8.1)
	2.01 dd (12.6, 6.5)	2.13 t (13.0)	2.75 dd (13.9, 7.2)
3b	2.05 [b]	1.50 dt (13.0, 7.5)	2.18 dd (8.1, 7.2)
3c	1.63 [b]	1.66 m	---
3d	0.90, d (6.6)	0.96 d (6.6)	1.36 s
3e	0.95, d (6.6)	1.01 d (6.7)	1.36 s
7a	2.04 [b]	1.97 dd (14.0, 12.7)	2.04 [b]
	1.65 [b]	1.71 ddd (14.0, 9.6, 5.7)	1.74 [b]
7b	1.80 dd (13.3, 6.8)	1.90 dd (12.6, 5.6)	2.29 dd (12.5, 7.3)
7d	0.98 s	0.83 s	1.07 s
7e	0.99 s	1.02 s	1.21 s
10b(f)	7.10 dd (8.1, 1.1)	7.04 br d (7.3)	7.07 dd (8.2, 0.9)
10c(e)	7.29 dd (8.1, 7.5)	7.27 dd (8.0, 7.4)	7.29 dd (8.2, 7.3)
10d	7.40 t (7.5)	7.39 t (7.4)	7.40 t (7.3)
5a	2.63 dd (15.0, 7.8)	2.63 dd (15.0, 7.6)	2.62 dd (15.0, 7.7)
	2.58 dd (15.0, 7.3)	2.59 dd (15.0, 7.1)	2.58 dd (15.0, 7.4)
5b	5.27 t (7.5)	5.30 br t (7.4)	5.25 t (7.3)
5d	2.05 (2H) [b]	2.06 (2H) [b]	2.04 (2H) [b]
5e	1.66 s	1.66 s	1.66 s
5f	2.05 (2H) [b]	2.07 (2H) [b]	2.08 (2H) [b]
5g	5.06 t (6.3)	5.07 br t (6.6)	5.06 t (6.5)
5i	1.66 s	1.66 s	1.66 s
5j	1.58 s	1.59 s	1.58 s

[a]) Measured in $CDCl_3$, 500 MHz;

[b]) overlapped signals

Table S3. ^{13}C NMR data of **14-21**.[a]

No.	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
1	82.0	81.4	81.0	82.1	81.1	81.4	81.5	81.8
2	204.1	203.6	204.1	203.8	204.2	203.3	205.9	204.5
3	72.5	72.0	74.2	72.4	73.5	71.0	73.3	73.3
4	204.8	205.0	205.0	204.6	204.9	204.9	205.2	204.6
5	67.9	67.7	69.1	67.9	69.2	67.7	68.6	67.9
6	35.2	35.3	**42.9**	35.1	**42.5**	35.3	**45.0**	35.3
7	42.7	42.5	44.1	42.7	44.0	42.4	43.5	42.5
8	**47.5**	**47.9**	**50.9**	**47.5**	**51.0**	**48.0**	**51.7**	**47.8**
9	204.9	203.8	206.5	204.9	206.6	203.8	205.9	205.7
10	193.2	193.1	192.7	193.2	192.7	193.0	192.9	193.0
11	25.3	25.4	25.4	25.3	25.4	25.4	26.0	25.3
12	22.7	22.8	23.0	22.6	23.0	22.6	22.9	22.7
3a	34.2	33.5	34.6	34.0	33.4	30.5	31.2	31.3
3b	56.0	57.5	55.2	56.0	57.8	59.6	59.7	59.2
3c	29.1	29.2	145.4	144.5	73.6	72.9	73.2	73.4
3d	22.3	22.6	112.0	113.1	30.3	31.2	30.4	30.5
3e	23.6	23.1	24.1	23.7	30.3	29.8	31.2	31.8
7a	26.1	23.2	29.1	26.4	28.8	22.8	28.5	25.0
7b	56.3	56.5	57.4	55.0	57.8	56.4	58.5	54.9
7c	44.8	46.5	44.5	44.7	45.1	46.6	47.4	46.9
7d	26.9	29.0	27.0	26.0	28.5	30.5	30.5	27.7
7e	27.3	**15.7**	27.3	28.3	27.3	**17.0**	**15.9**	27.1
10a	135.2	135.1	135.1	135.2	135.1	135.0	135.2	135.1
10b(f)	128.6	128.6	129.1	128.5	129.1	128.6	129.2	128.6
10c(e)	128.4	128.4	128.2	128.4	128.2	128.5	128.1	128.4
10d	132.4	132.3	132.2	132.4	132.2	132.4	132.1	132.4
5a	29.2	29.1	29.6	29.2	29.6	29.1	30.1	29.2
5b	119.1	119.2	119.2	119.1	119.2	119.1	119.2	119.0
5c	139.0	139.0	138.5	139.1	138.6	139.0	138.6	139.2
5d	40.2	40.2	40.1	40.2	40.1	40.2	40.1	40.2
5e	16.5	16.5	16.6	16.5	16.6	16.5	16.6	16.5
5f	26.7	26.7	26.8	26.7	26.8	26.7	26.8	26.7
5g	124.3	124.3	124.3	124.3	124.3	124.3	124.3	124.3
5h	131.6	131.6	131.5	131.6	131.5	131.6	131.5	131.6
5i	25.9	25.9	25.9	25.9	25.9	25.9	25.9	25.9
5j	17.8	17.8	17.8	17.9	17.9	17.8	17.9	17.8
$\Delta\delta_{7d\text{-}7e}$	-0.4	**13.3**	-0.3	-2.3	1.2	**13.5**	**14.6**	0.6

a) Measured in $CDCl_3$, 125 MHz;

Table S4. Inhibitory rate (%) of PPAPs on cell proliferation of A549 at 25 μM

Sample	Inhibitory rate ($\bar{x}$ ± SD)	**Sample**	Inhibitory rate ($\bar{x}$ ± SD)	**Sample**	Inhibitory rate ($\bar{x}$ ± SD)
1	44.3 ± 2.4	**8**	29.1 ± 1.3	**15**	1.3 ± 0.0
2	11.2 ± 2.8	**9**	10.1 ± 2.5	**16**	7.0 ± 5.4
3	3.9 ± 1.7	**10**	38.4 ± 5.2	**17**	5.2 ± 3.9
4	8.3 ± 4.5	**11**	4.6 ± 0.2	**18**	0.9 ± 2.3
5	-0.3 ± 1.4	**12**	5.2 ± 2.2	**19**	2.8 ± 1.9
6	54.4 ± 3.0	**13**	119.9 ± 3.0[a]	**20**	4.1 ± 0.5
7	16.0 ± 0.9	**14**	3.6 ± 2.2	**21**	6.6 ± 3.7

[a] IC_{50} of **13**: 1.731 ± 0.149 μM.

NMR spectra of hyperichoisin A (3)

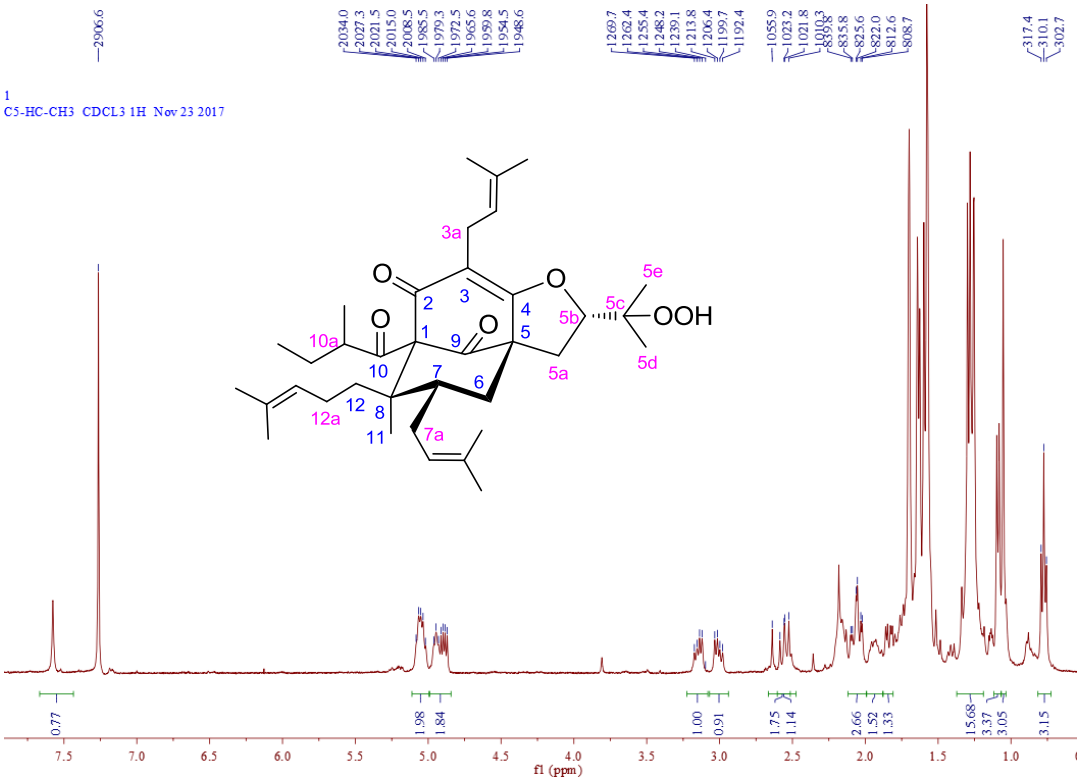


Figure S1 ^{1}H NMR spectrum of 3 in $CDCl_3$

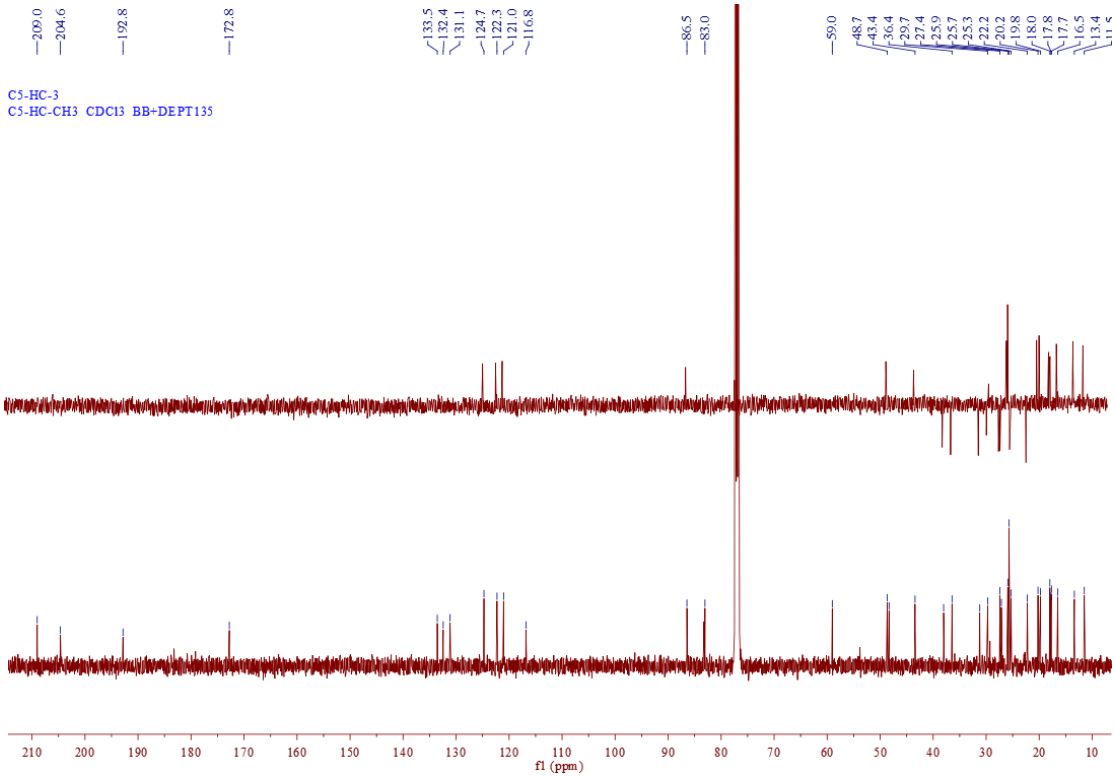


Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$

NMR spectra of hyperichoisin B (14)

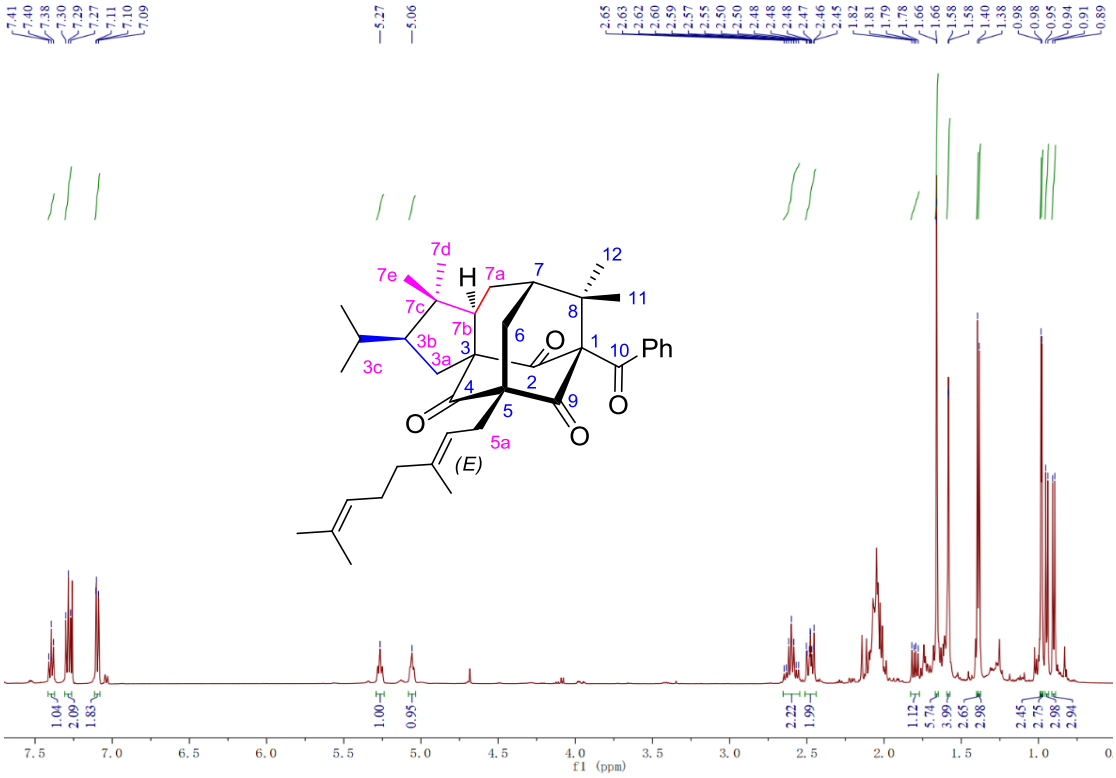


Figure S3. ^{1}H NMR spectrum of **14** in $CDCl_3$

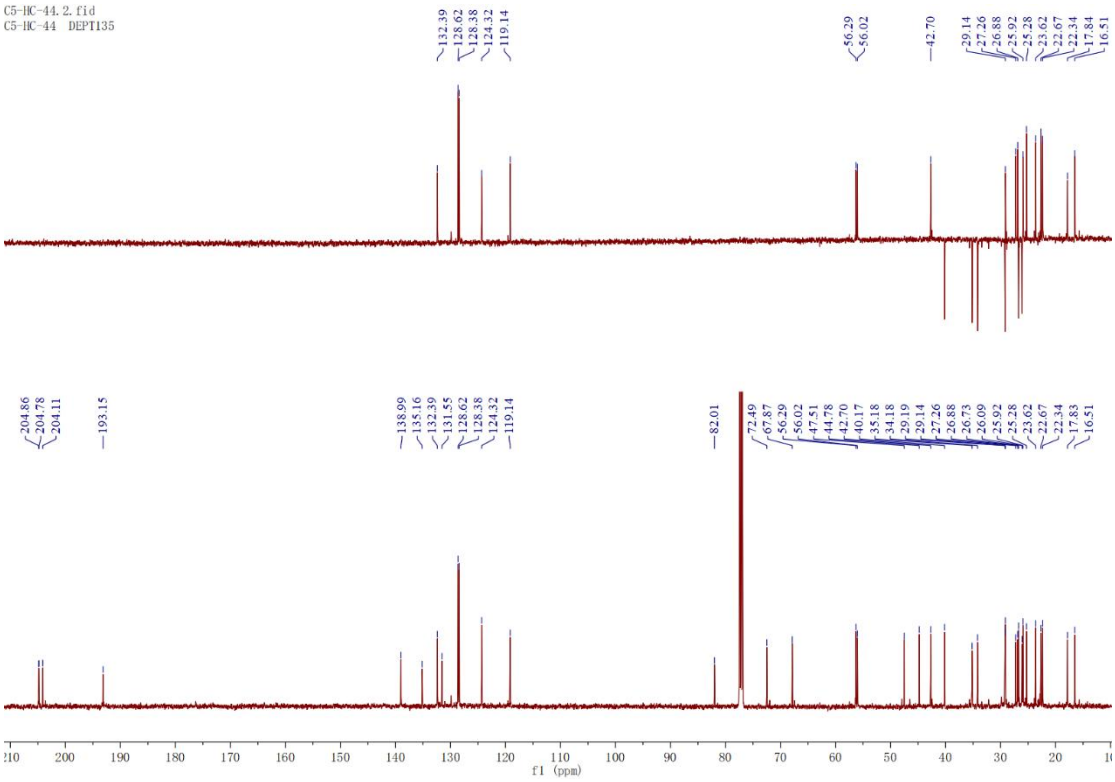


Figure S4. ^{13}C NMR spectrum of **14** in $CDCl_3$

Spectra of hyperichoisin C (21)

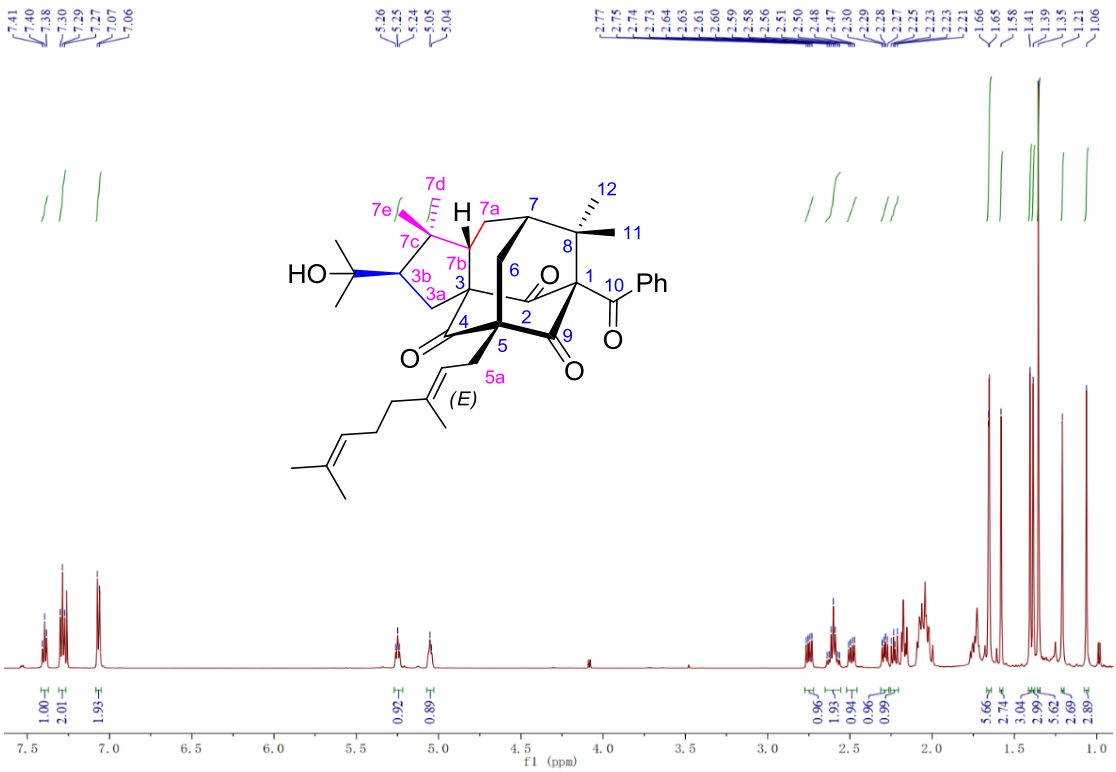


Figure S5. ^{1}H NMR spectrum of **21** in $CDCl_3$

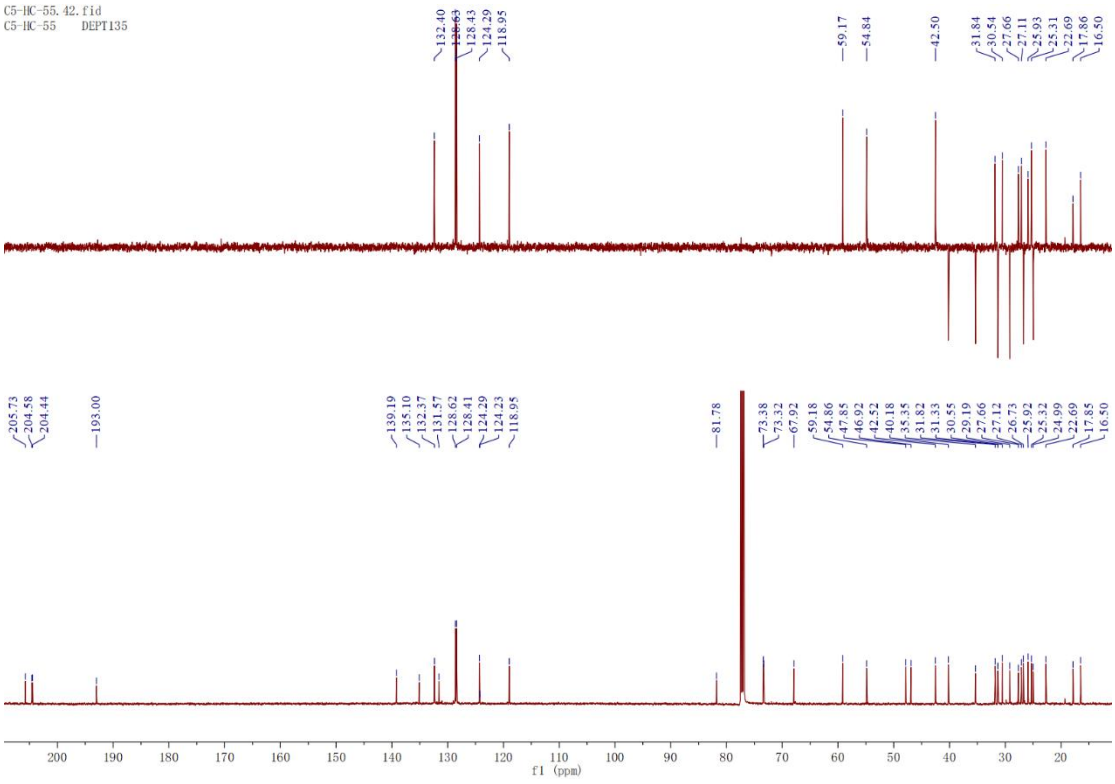


Figure S6. ^{13}C NMR spectrum of **21** in $CDCl_3$

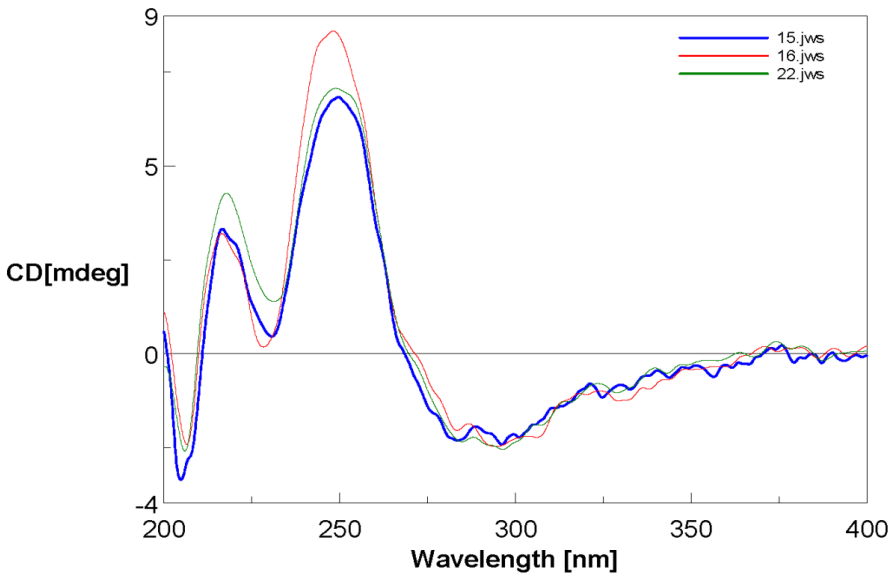


Figure S7. CD spectra of **14, 15** and **21.**