Supporting Information

Marine Longilenes, Oxasqualenoids with PP2A Inhibition Activity

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Table S1. NMR data of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.

Carbon	δ ^{13}C	Multiplicity	δ ^{1}H	*J* in Hz
1	26.9	CH_3	1.19	s
2	80.1	C		
3	137.0	CH	5.43	d 15.6
4	125.8	CH	5.81	ddd 6.6, 8.5, 15.6
5	41.3	CH_2	1.78	dd 8.5, 13.3
			2.20	dd 6.6, 13.3
6	73.9	C		
7	85.1	CH	3.72	m
8	25.8	CH_2	1.89	m
			2.06	m
9	29.7	CH_2	1.49	m
			2.06	m
10	85.8	C		
11	85.8	CH	4.09	m
12	30.1	CH_2	1.50	m
			2.01	m
13	29.9	CH_2	1.50	m
			2.01	m
14	85.4	CH	4.09	m
15	85.4	C		
16	29.3	CH_2	1.46	m
			2.03	m
17	25.2	CH_2	1.89	m
			2.03	m
18	84.1	CH	3.72	m
19	73.8	C		
20	40.8	CH_2	1.88	dd 6.8, 13.4
			2.20	dd 7.0, 13.4
21	122.2	CH	5.75	ddd 6.8, 7.0, 15.6
22	141.2	CH	5.61	d 15.6
23	70.0	C		
24	29.4	CH_3	1.27	s
25	24.2	CH_3	1.37	s
26	24.3	CH_3	1.20	s
27	24.2	CH_3	1.09	s
28	23.6	CH_3	1.07	s
29	24.3	CH_3	1.27	s
30	29.6	CH_3	1.31	s
-OOH			10.57	s
-OH-6			5.24	s
-OH-19			5.03	s
-OH-23			3.29	s

Figure S1. ^{1}H-NMR spectrum of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.

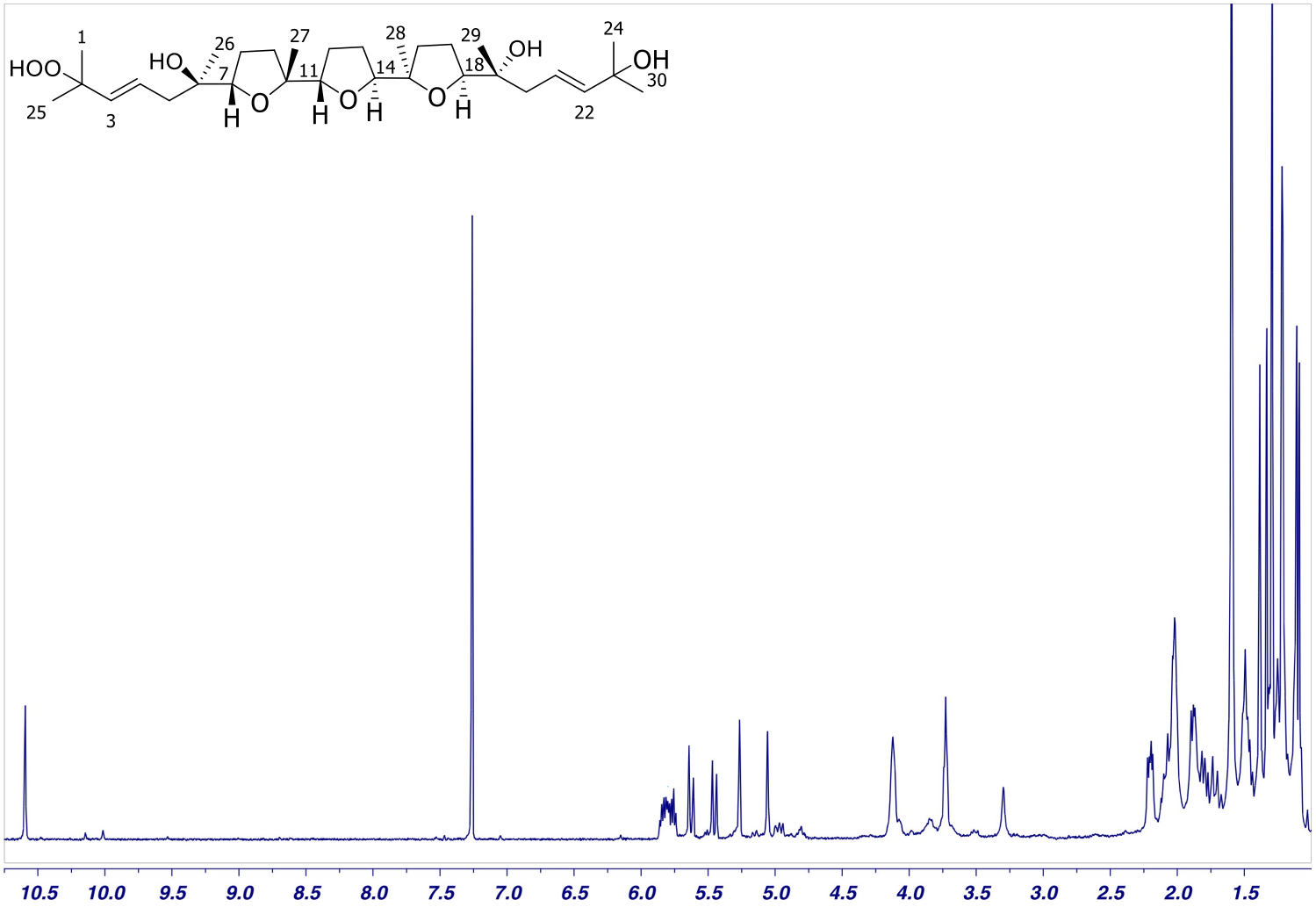
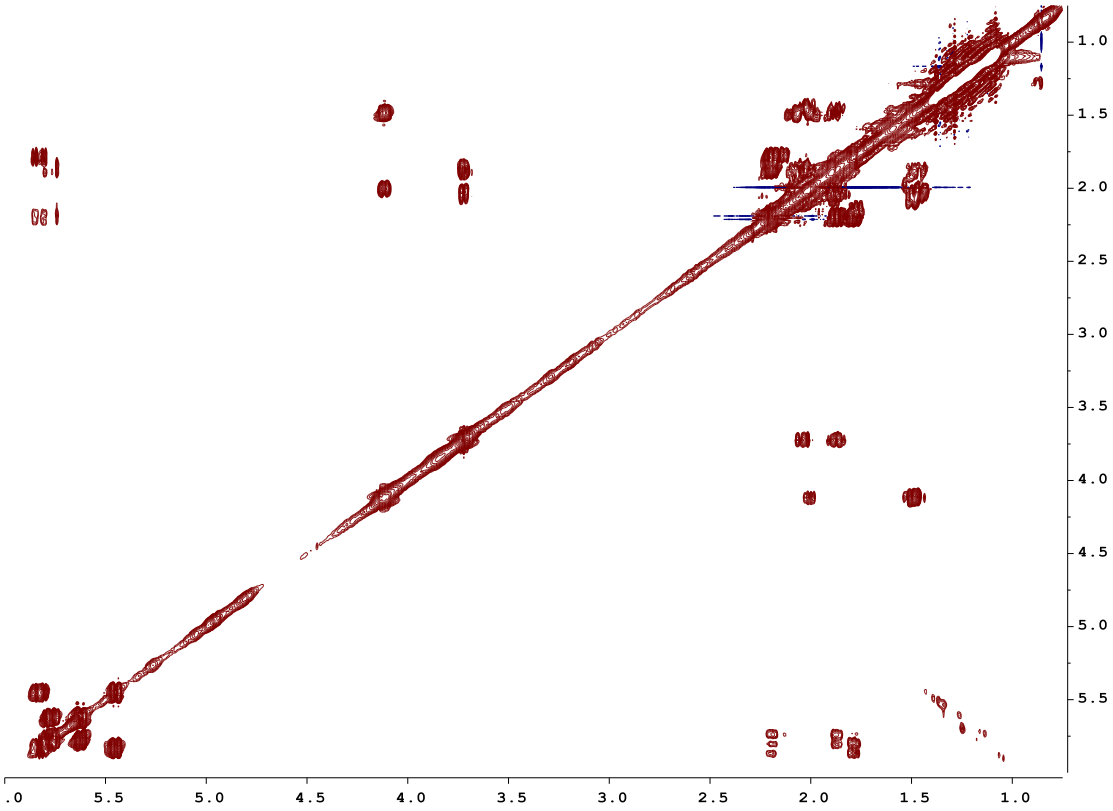


Figure S2. COSY spectrum of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.



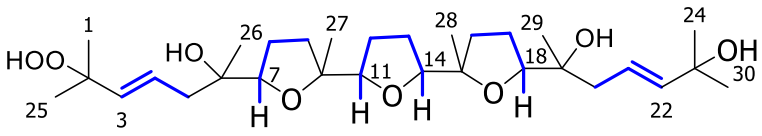
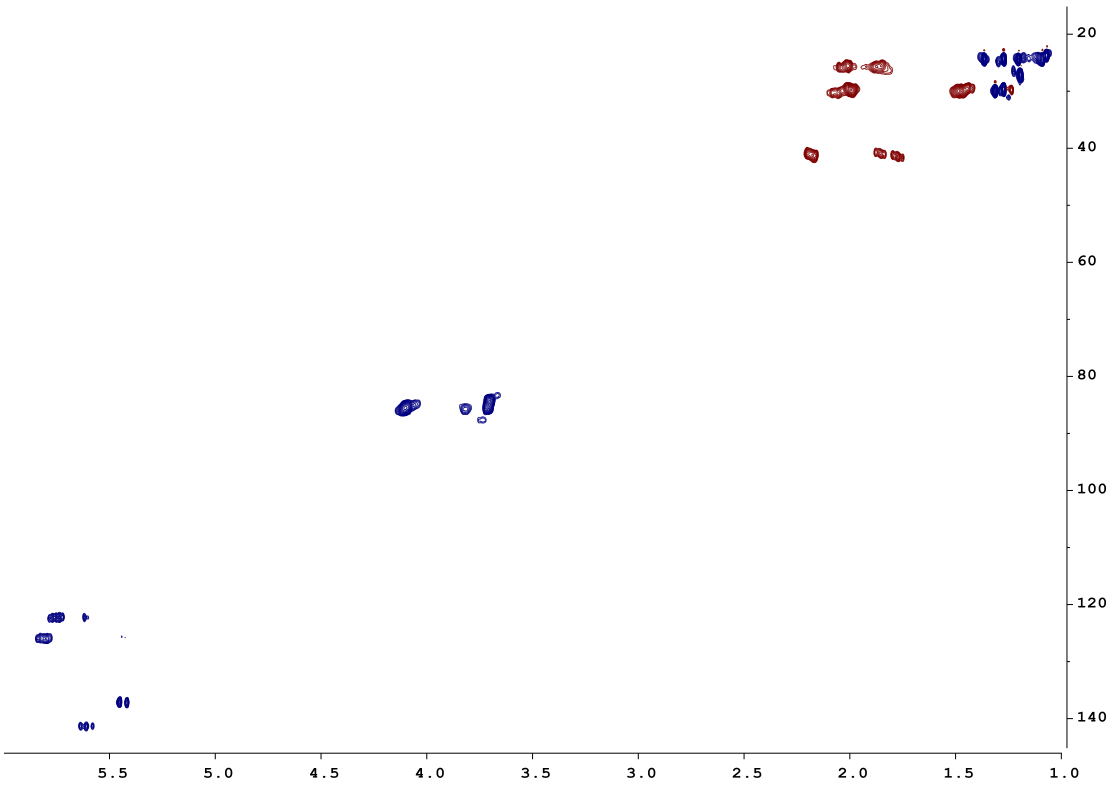


Figure S3. HSQCed spectrum of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.



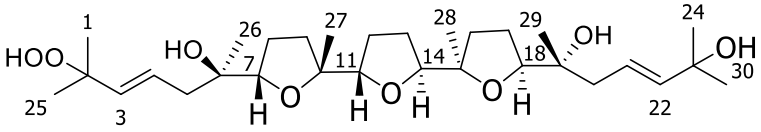
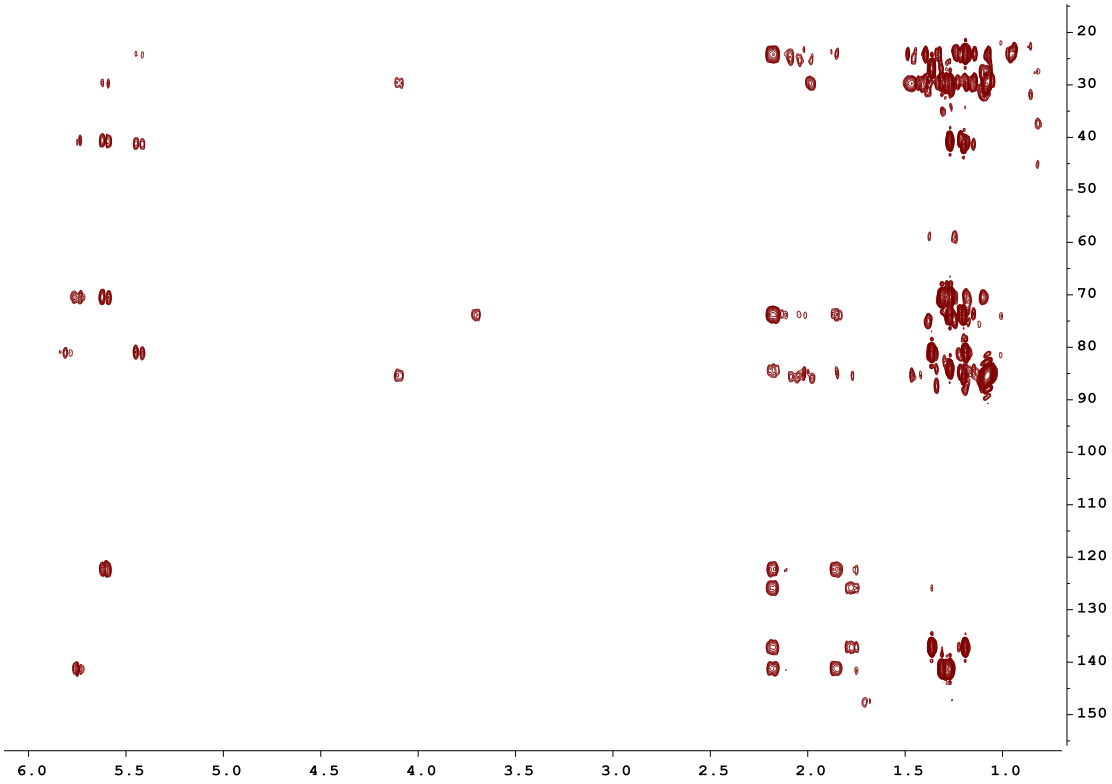


Figure S4. HMBC spectrum of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.



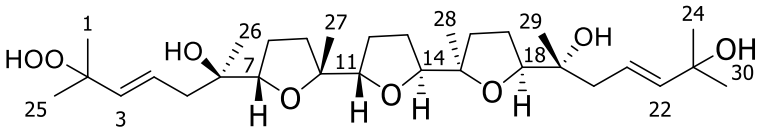
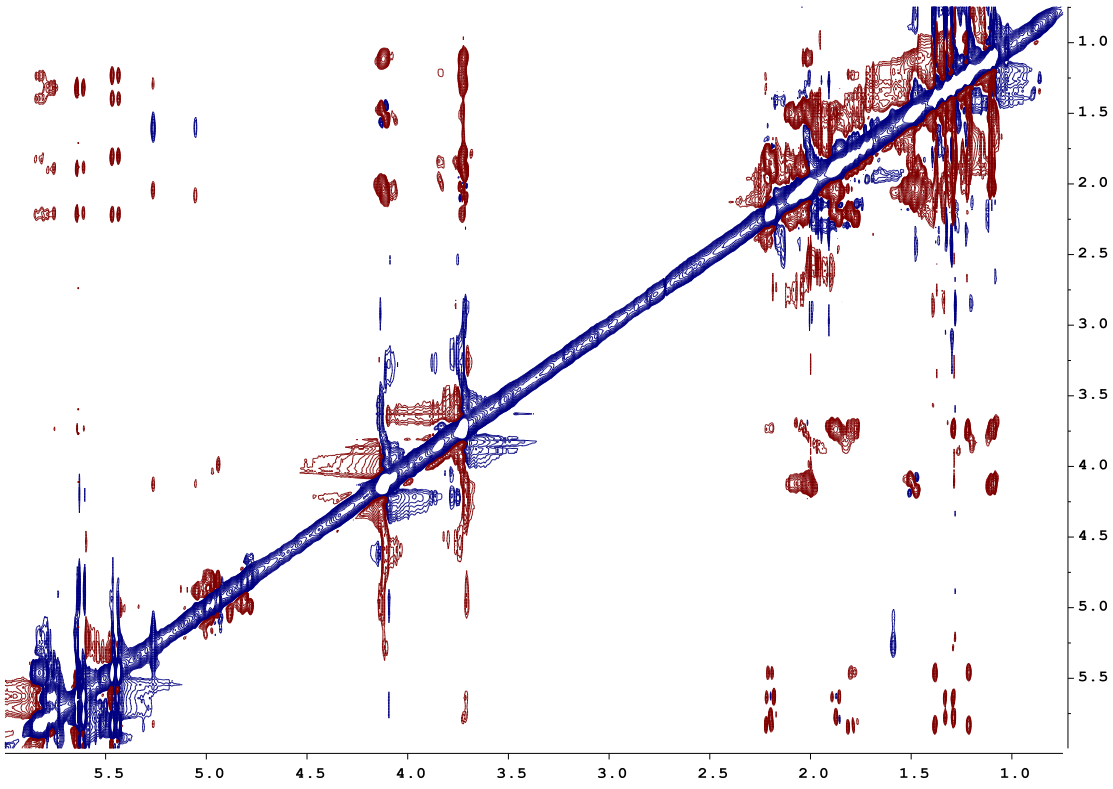


Figure S5. ROESY spectrum of (+)-longilene peroxide (**1**) in $CDCl_3$ at 300 K, 500 MHz.



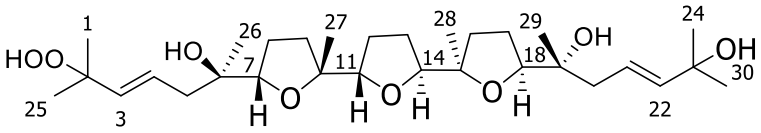
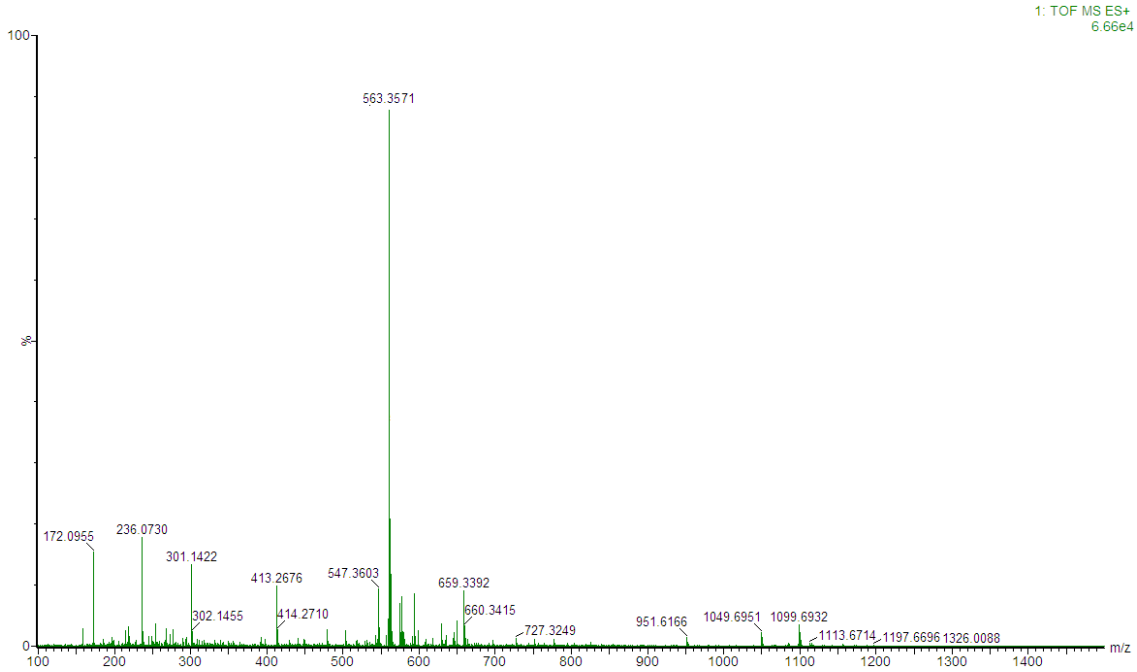


Figure S6. MS spectrum of (+)-longilene peroxide (**1**).



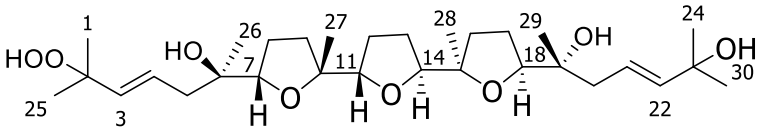


Table S2. NMR data of longilene (**2**) in $CDCl_3$ at 300 K, 500 MHz.

Carbon		δ ^{13}C	Multiplicity	δ ^{1}H	*J* in Hz
1	**24**	29.6	CH_3	1.29	s
2	**23**	70.4	C		
3	**22**	141.2	CH	5.62	d 15.6
4	**21**	122.0	CH	5.77	ddd 7.0, 7.4, 15.6
5	**20**	40.4	CH_2	1.78 2.15	dd 7.0, 13.4 dd 7.4, 13.4
6	**19**	74.0	C		
7	**18**	84.9	CH	3.70	dd 6.4, 6.6
8	**17**	25.6	CH_2	1.91 2.03	
9	**16**	30.0	CH_2	1.47 2.06	
10	**15**	85.7	C		
11	**14**	85.4	CH	4.11	dd 5.5, 5.6
12	**13**	30.0	CH_2	1.49 2.01	
25	**30**	29.8	CH_3	1.31	s
26	**29**	24.1	CH_3	1.24	s
27	**28**	23.7	CH_3	1.10	s

Figure S7. ^{1}H-NMR spectrum of longilene (**2**) in $CDCl_3$ at 300 K, 500 MHz.

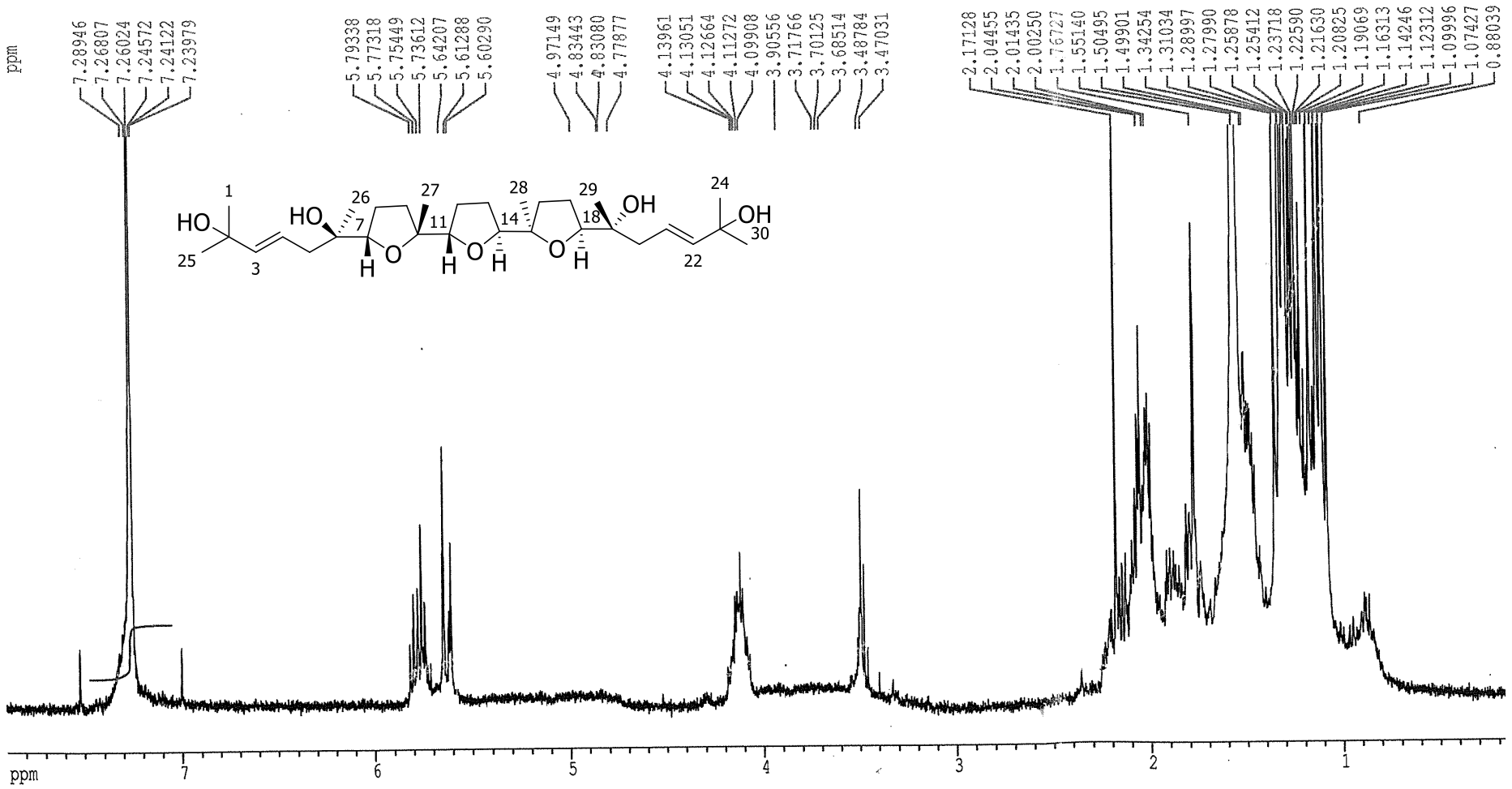
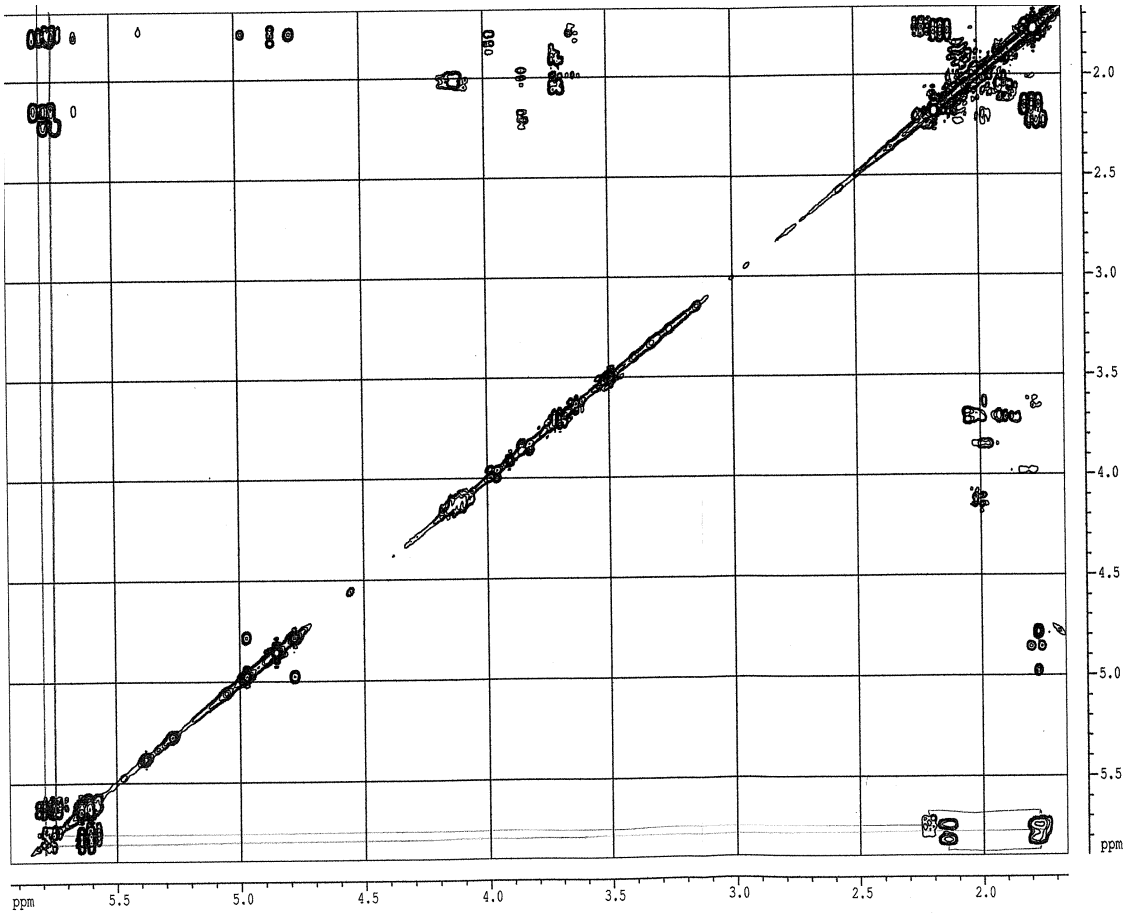


Figure S8. COSY spectrum of longilene (**2**) in $CDCl_3$ at 300 K, 500 MHz.



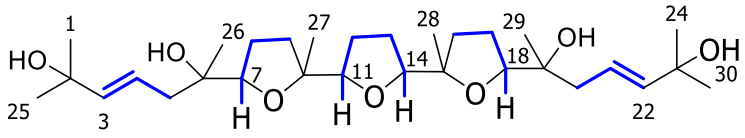
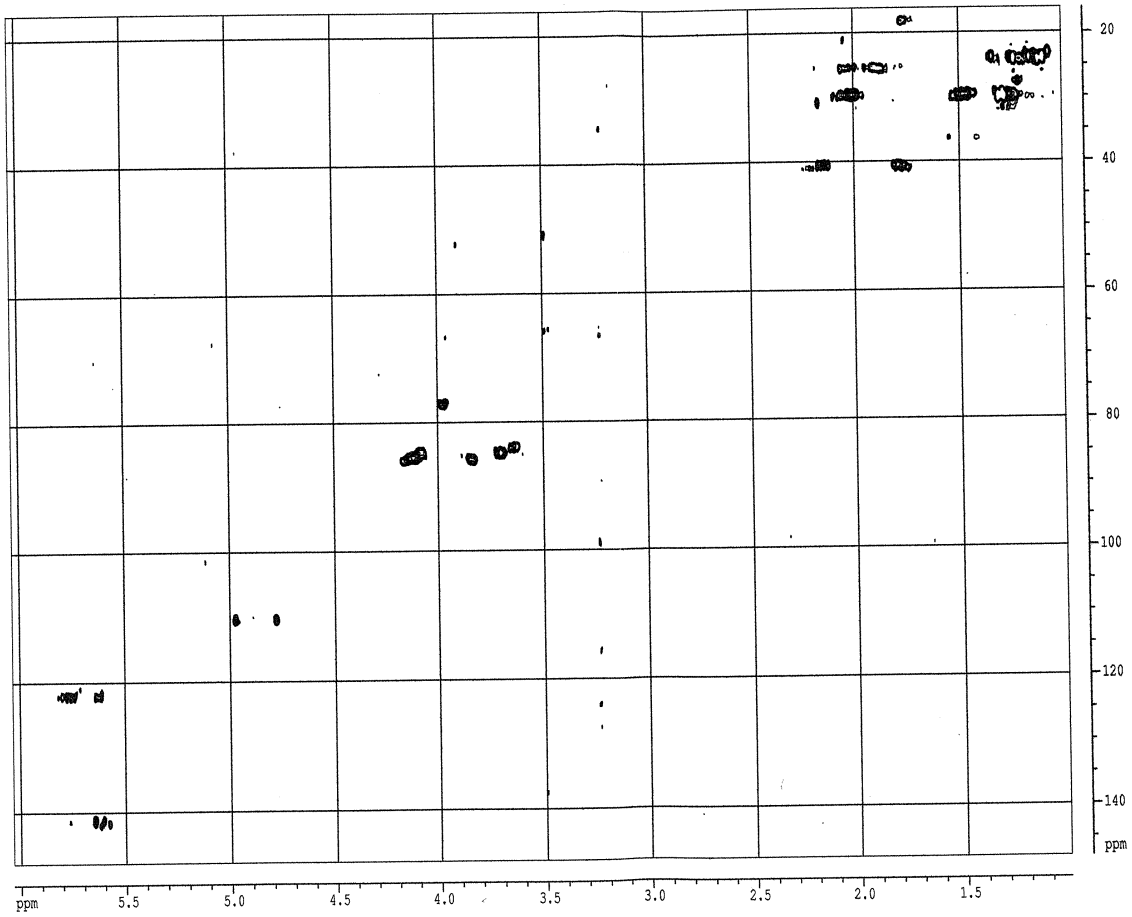


Figure S9. HSQC spectrum of longilene (**2**) in $CDCl_3$ at 300 K, 500 MHz.



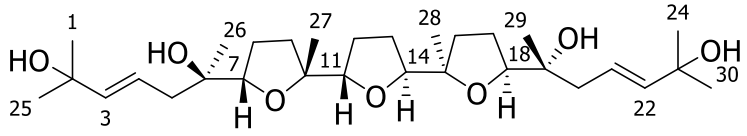
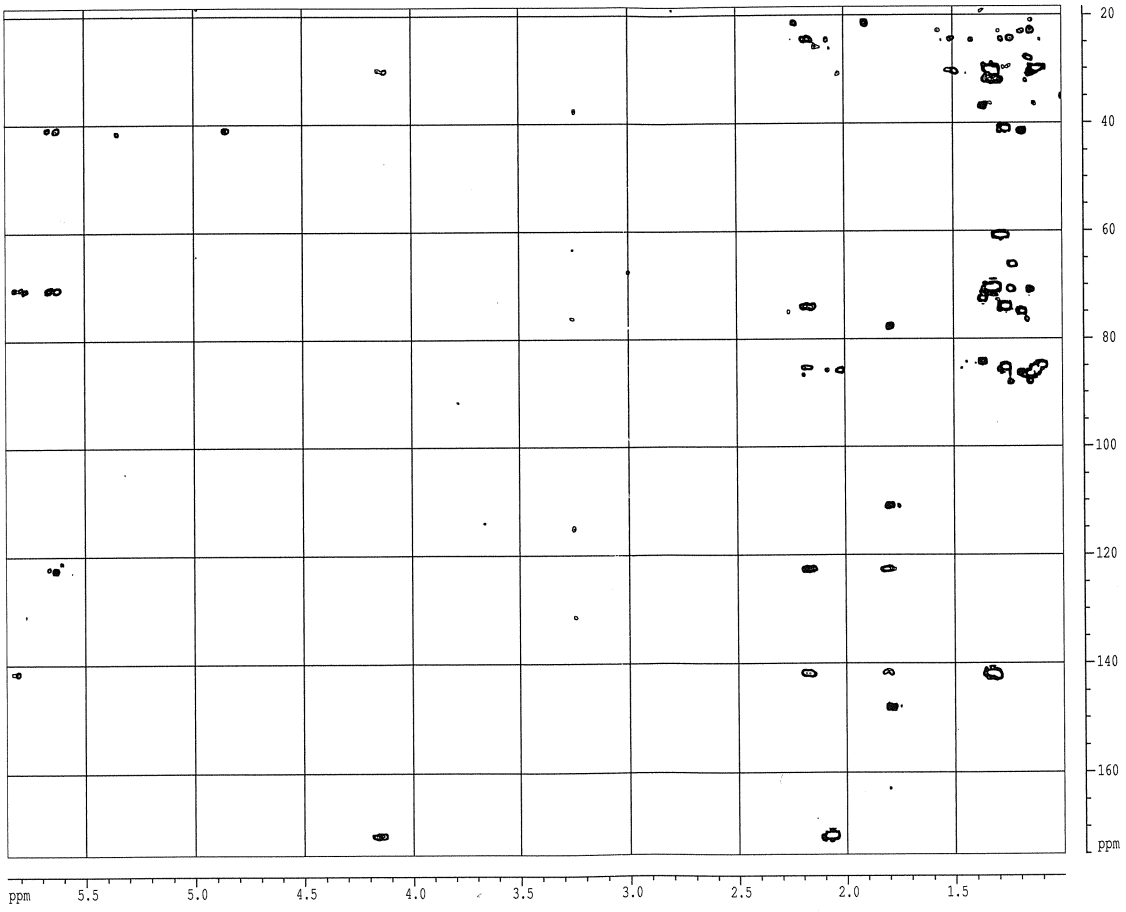


Figure S10. HMBC spectrum of longilene (**3**) in $CDCl_3$ at 298 K, 500 MHz.



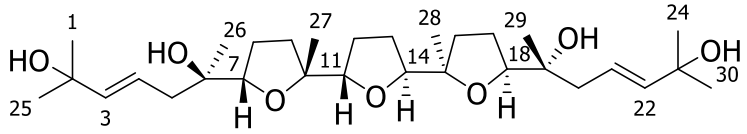


Figure S11. MS spectrum of longilene (**2**).

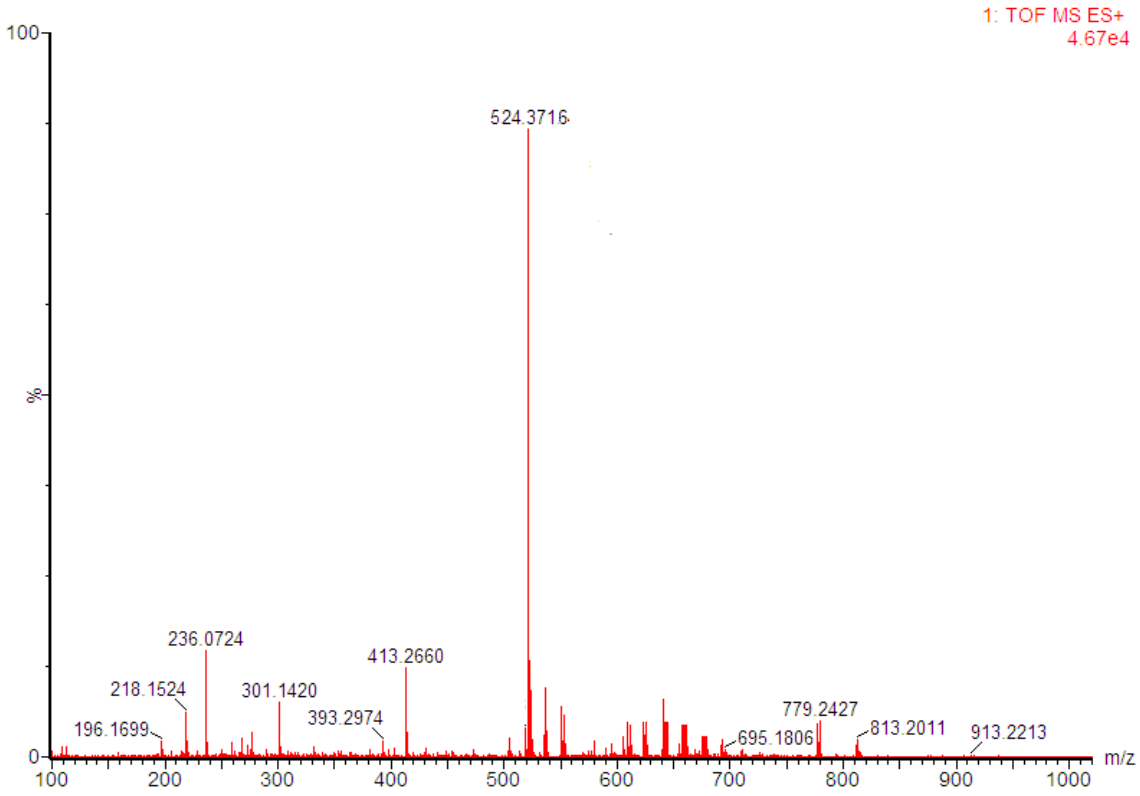


Table S3. NMR data of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.

Carbon	δ ^{13}C	Multiplicity	δ ^{1}H	*J* in Hz
1	17.7	CH_3	1.60	s
2	131.1	C		
3	124.8	CH	5.08	t 6.9
4	22.5	CH_2	1.97 2.04	
5	39.0	CH_2	1.29 1.43	
6	72.5	C		
7	83.4	CH	3.73	dd 6.9, 7.6
8	25.4	CH_2	1.80 1.91	
9	30.0	CH_2	1.46 2.04	
10	84.7	C		
11	85.0	CH	4.07	dd 5.4, 10.3
12	29.5	CH_2	1.50 1.99	
13	29.5	CH_2	1.50 1.99	
14	85.7	CH	4.13	dd 5.7, 10.3
15	85.8	C		
16	30.0	CH_2	1.46 2.06	
17	25.5	CH_2	1.93 2.14	
18	85.0	CH	3.81	dd 4.4, 8.1
19	74.1	C		
20	40.8	CH_2	1.83 2.17	
21	122.7	CH	5.74	ddd 6.2, 8.6, 15.2
22	141.0	CH	5.62	d 15.2
23	70.3	C		
24	29.8	CH_3	1.31	s
25	25.7	CH_3	1.66	s
26	24.9	CH_3	1.27	s
27	23.5	CH_3	1.08	s
28	24.0	CH_3	1.11	s
29	24.1	CH_3	1.20	s
30	30.1	CH_3	1.31	s
-OH-6			4.94	s
-OH-19			4.39	s
-OH-23			2.57	s

Figure S12. ^{1}H-NMR spectrum of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.

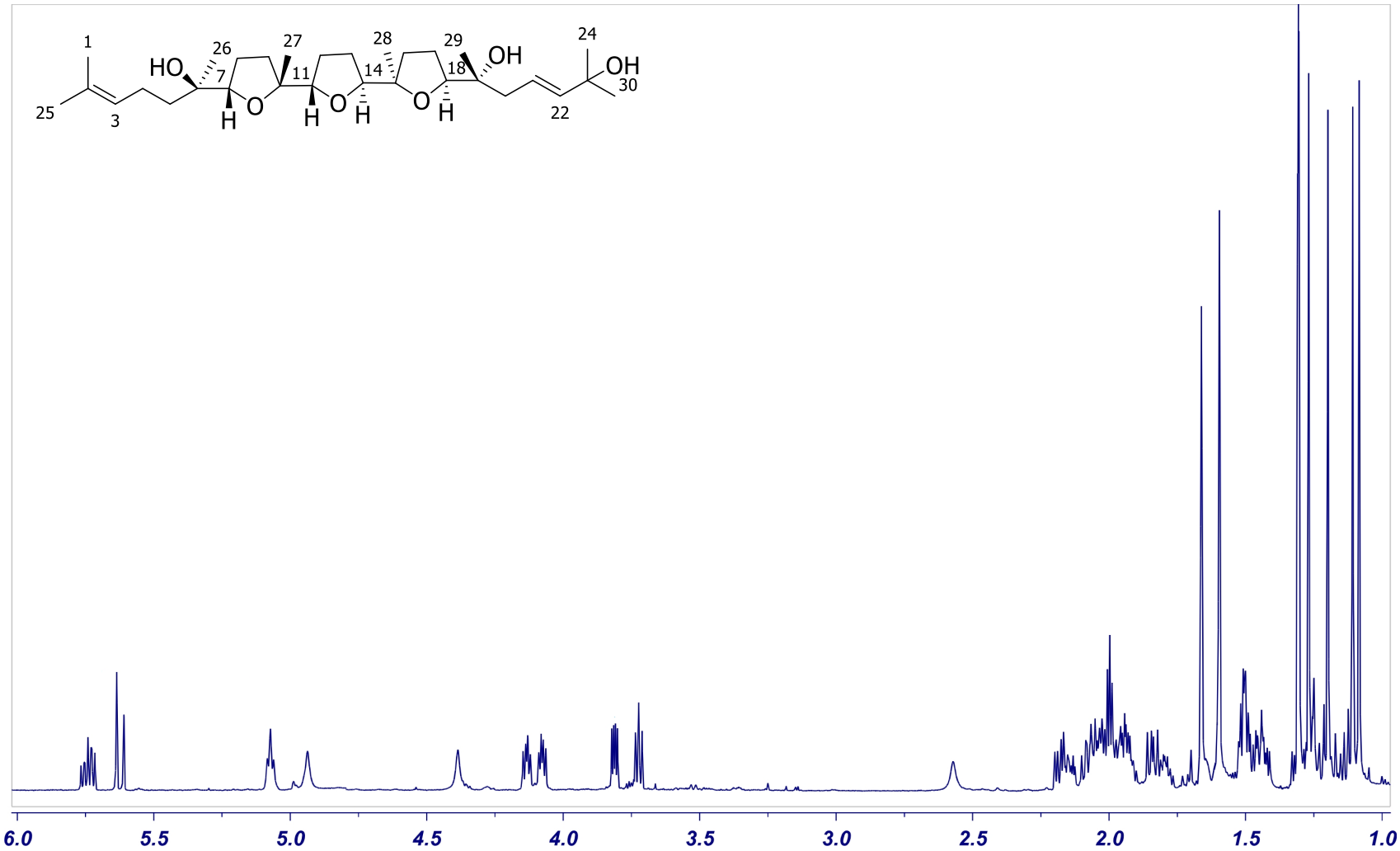
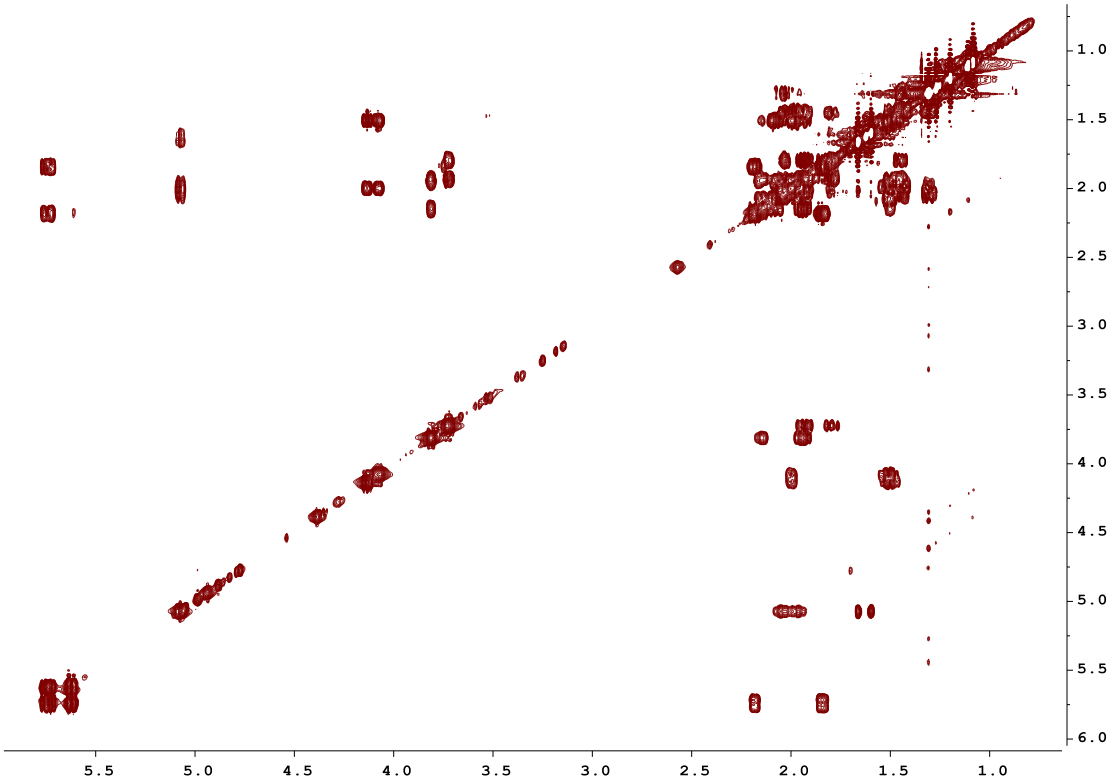


Figure S13. COSY spectrum of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.



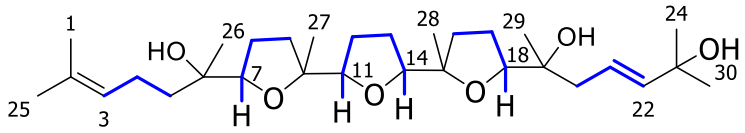
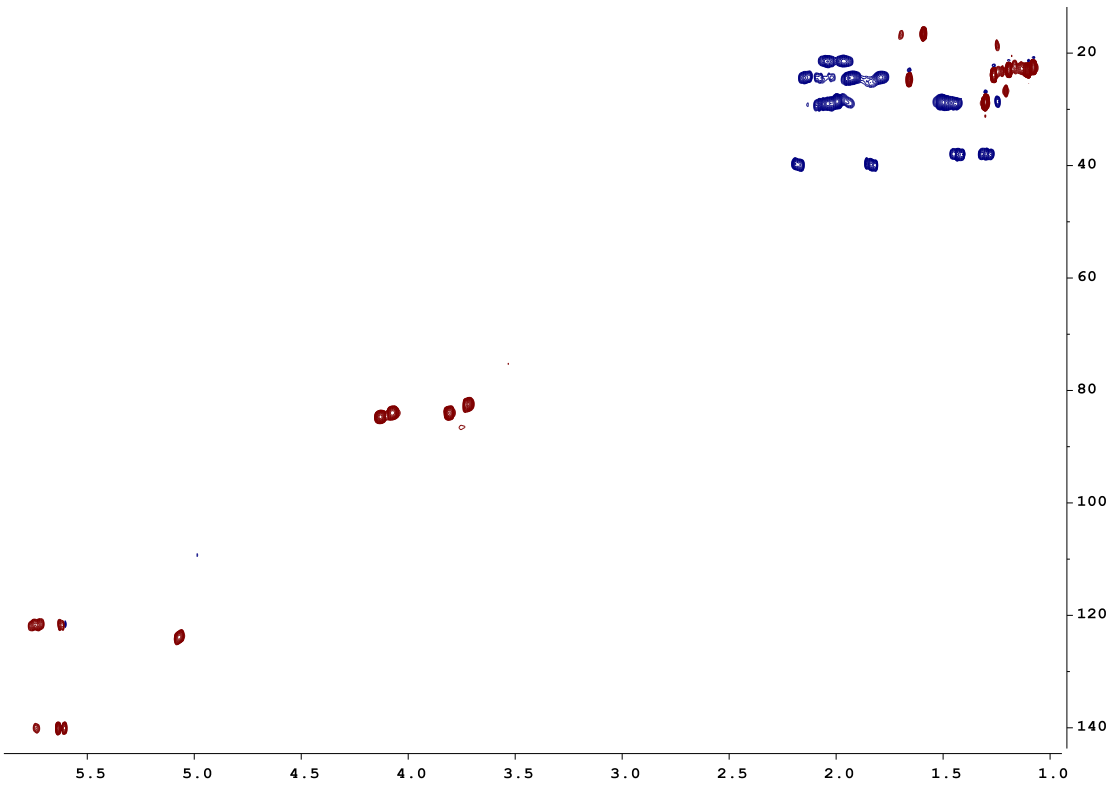


Figure S14. HSQCed spectrum of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.



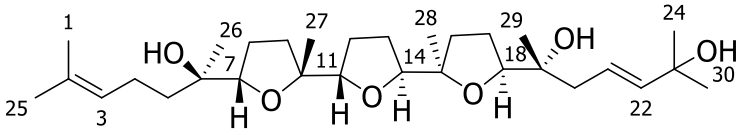
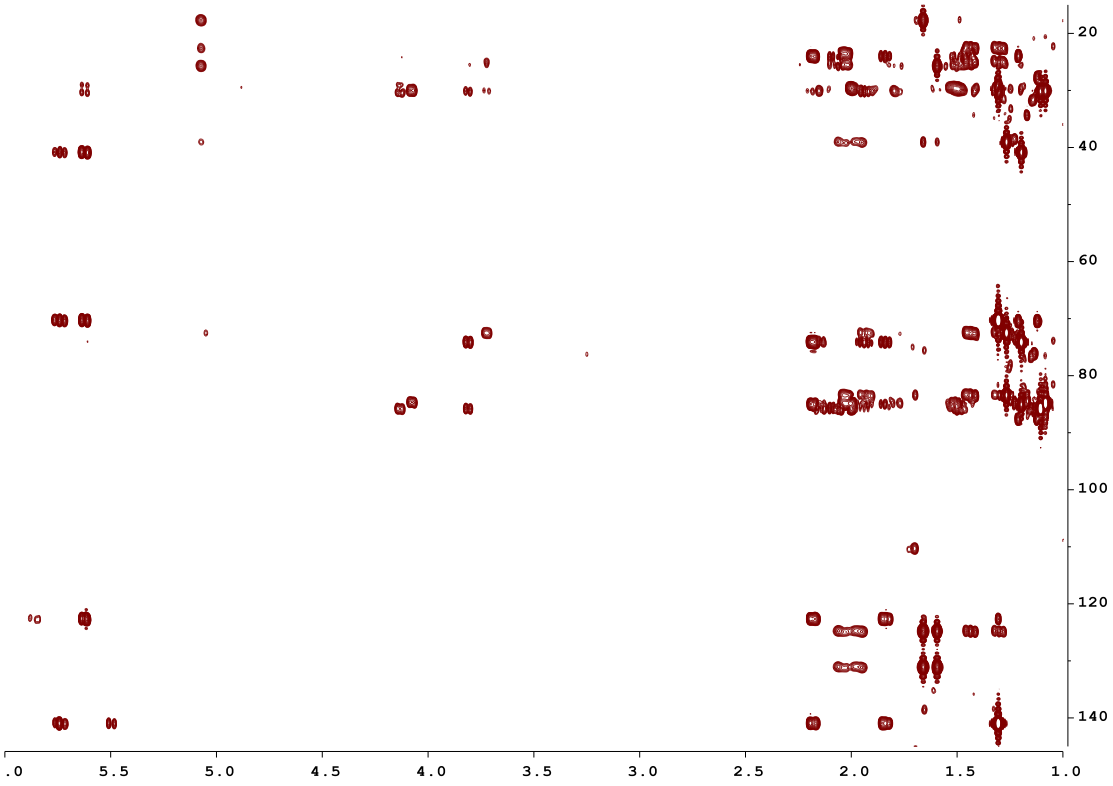


Figure S15. HMBC spectrum of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.



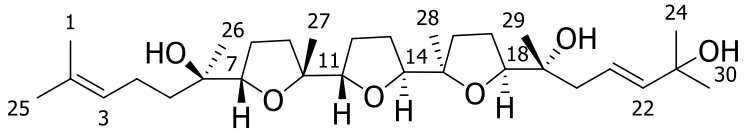
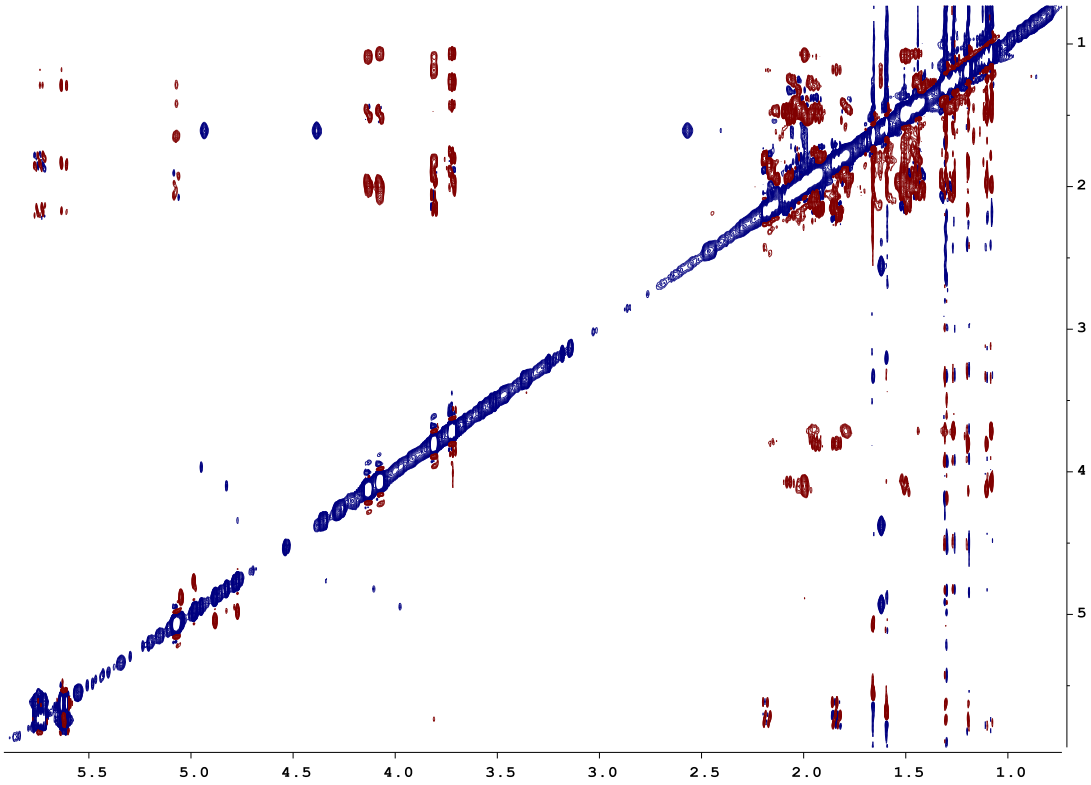


Figure S16. ROESY spectrum of (+)-prelongilene (**3**) in $CDCl_3$ at 300 K, 500 MHz.



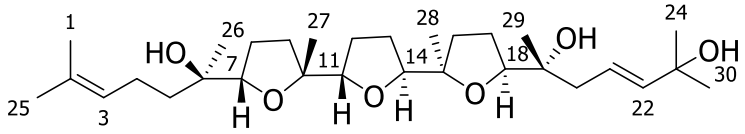
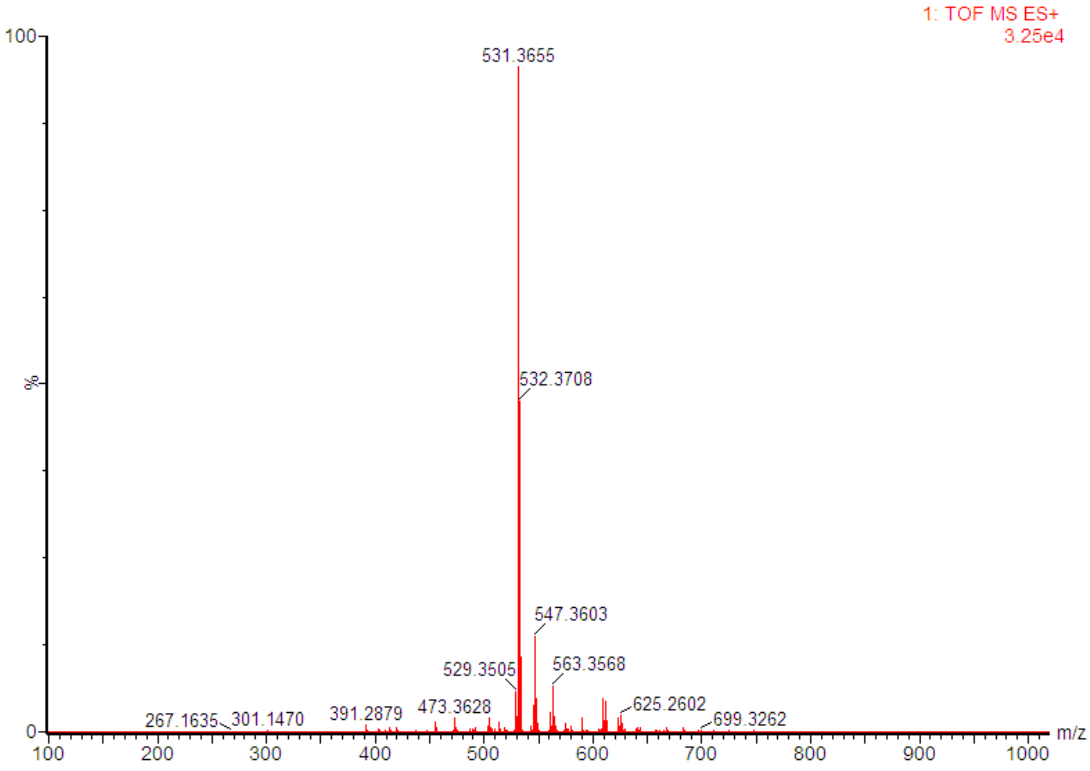


Figure S17. MS spectrum of (+)-prelongilene (**3**).



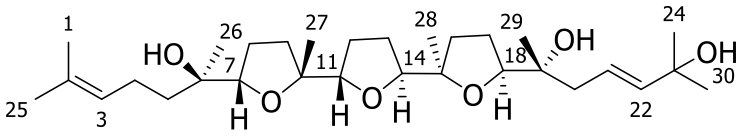


Figure S18. Conversion of (+)-prelongilene (**3**) to compound **5** for ^{1}H NMR; 0 h.

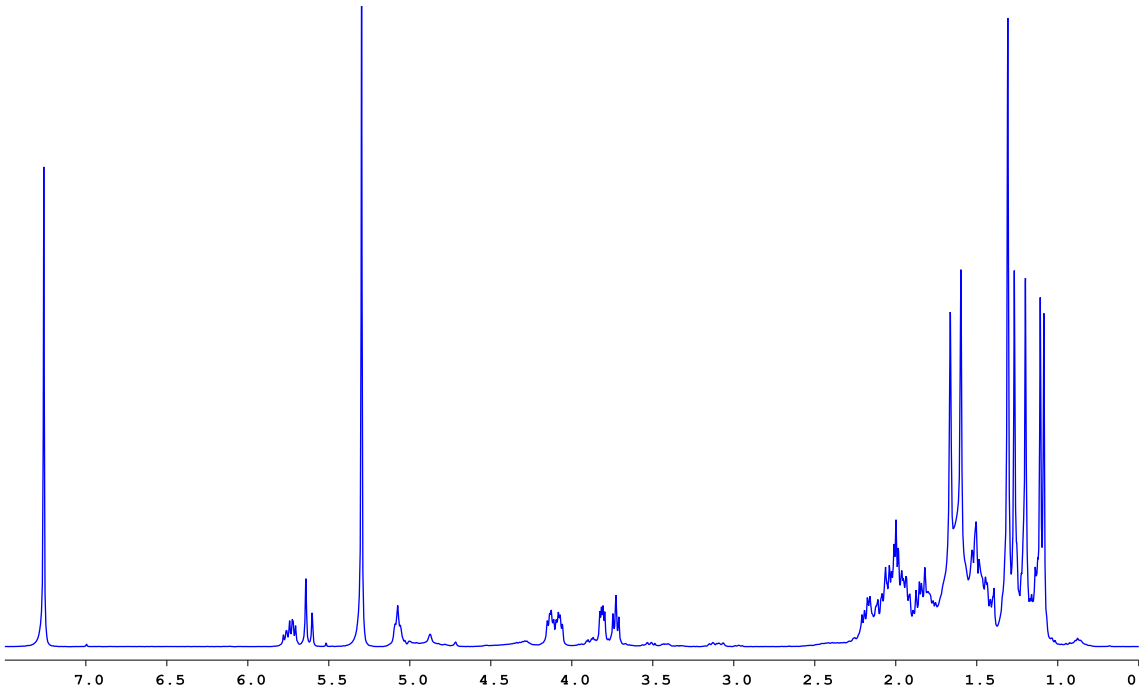


Figure S19. Conversion of (+)-prelongilene (**3**) to compound **5** for ^{1}H NMR; 24 h.

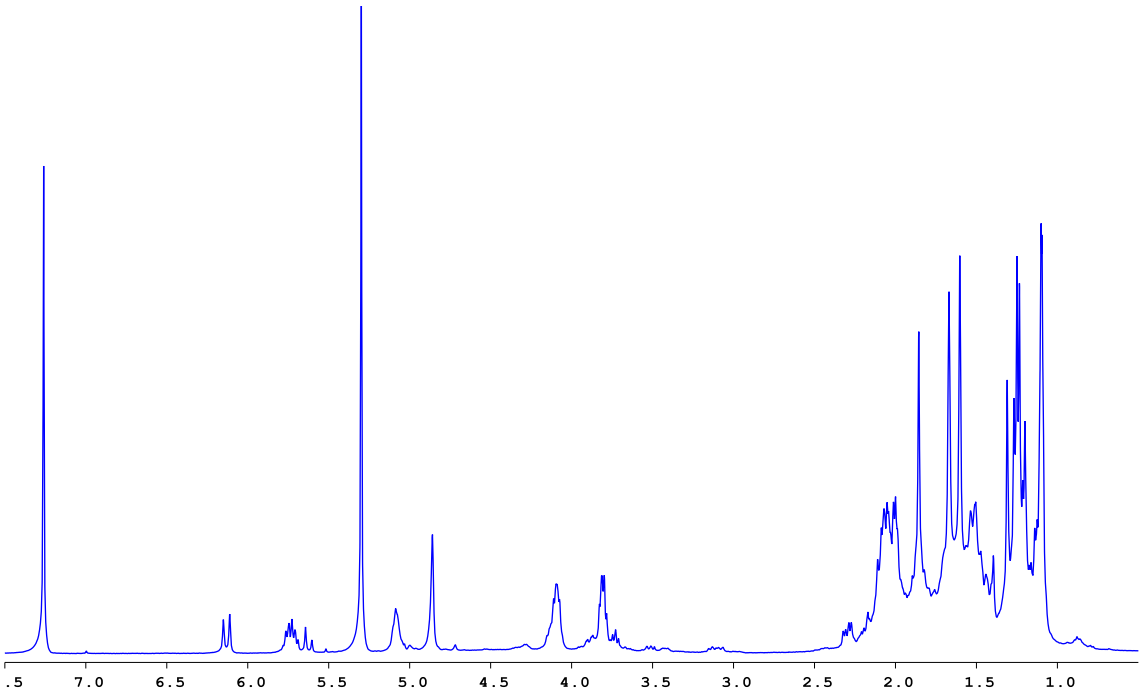


Figure S20. Conversion of (+)-prelongilene (**3**) to compound **5** for ^{1}H NMR; 48 h.

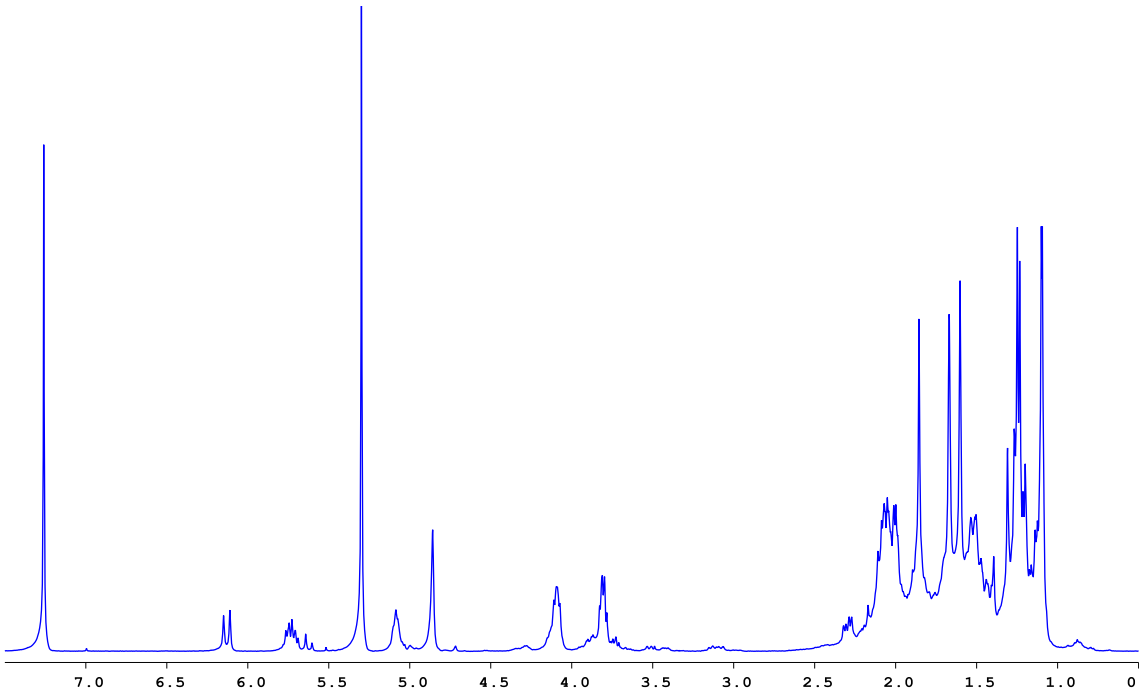


Figure S21. Conversion of (+)-prelongilene (**3**) to compound **5** for ^{1}H NMR; 72 h.

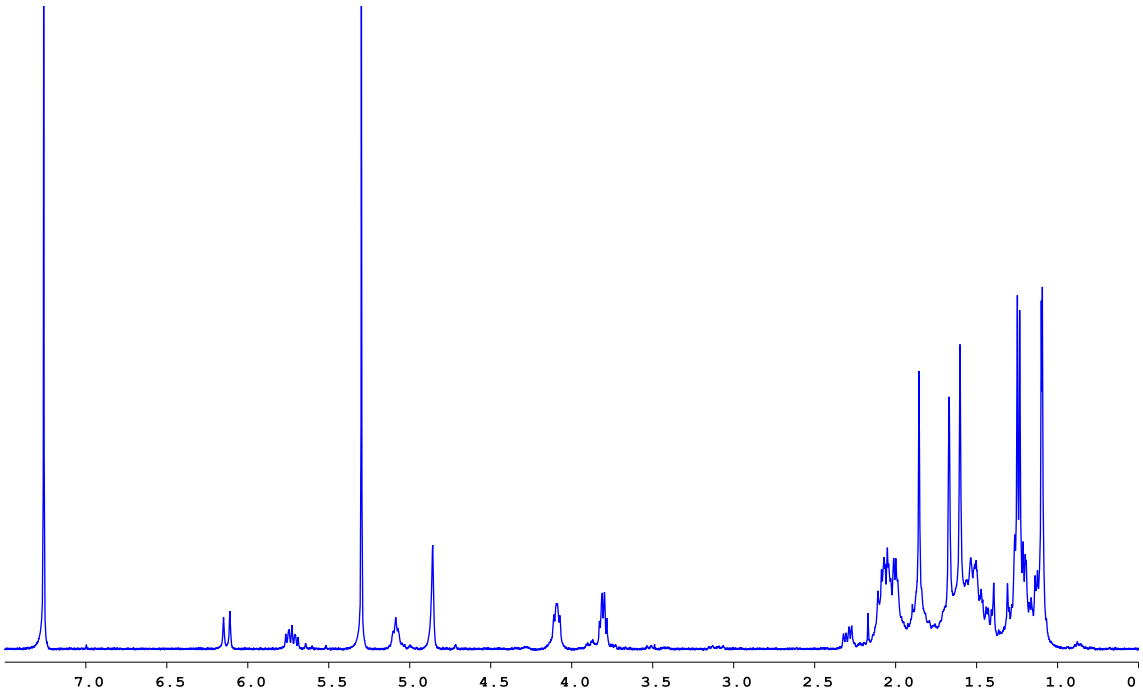


Table S4. NMR data of compound **5** in $CDCl_3$ at 300 K, 500 MHz.

Carbon	δ ^{13}C	Multiplicity	δ ^{1}H	*J* in Hz
1	17.7	CH_3	1.60	s
2	131.2	C		
3	124.9	CH	5.08	t 6.8
4	22.2	CH_2	1.99 2.09	
5	38.6	CH_2	1.27 1.43	
6	73.0	C		
7	84.1	CH	3.81	dd 6.5, 11.7
8	25.3	CH_2	1.87 2.06	
9	30.4	CH_2	1.50 2.04	
10	85.3	C		
11	85.2	CH	4.09	dd 5.2, 9.3
12	29.5	CH_2	1.53 2.03	
13	29.5	CH_2	1.53 2.03	
14	85.2	CH	4.09	dd 5.2, 9.3
15	85.4	C		
16	30.4	CH_2	1.50 2.04	
17	25.3	CH_2	1.85 2.06	
18	84.1	CH	3.81	dd 6.5, 11.7
19	73.4	C		
20	42.5	CH_2	2.09 2.29	
21	126.4	CH	5.72	ddd 6.3, 8.7, 15.3
22	135.1	CH	6.13	d 15.6
23	142.3	C		
24	114.4	CH	4.86	s
25	25.7	CH_3	1.67	s
26	24.3	CH_3	1.23	s
27	23.5	CH_3	1.09	s
28	23.6	CH_3	1.10	s
29	24.3	CH_3	1.25	s
30	18.8	CH_3	1.86	s

Figure S22. ^{1}H-NMR spectrum of compound **5** in $CDCl_3$ at 300 K, 500 MHz.

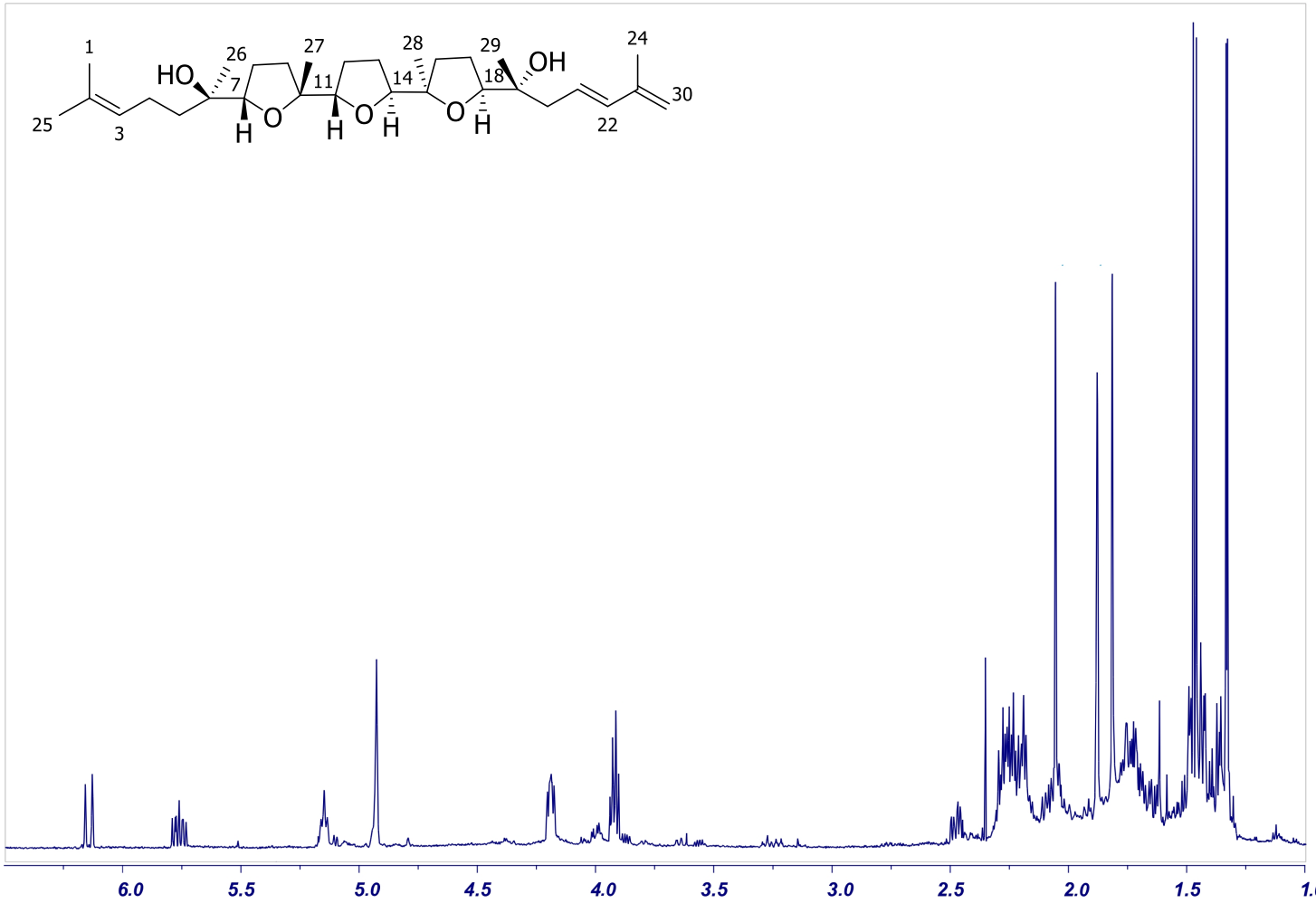
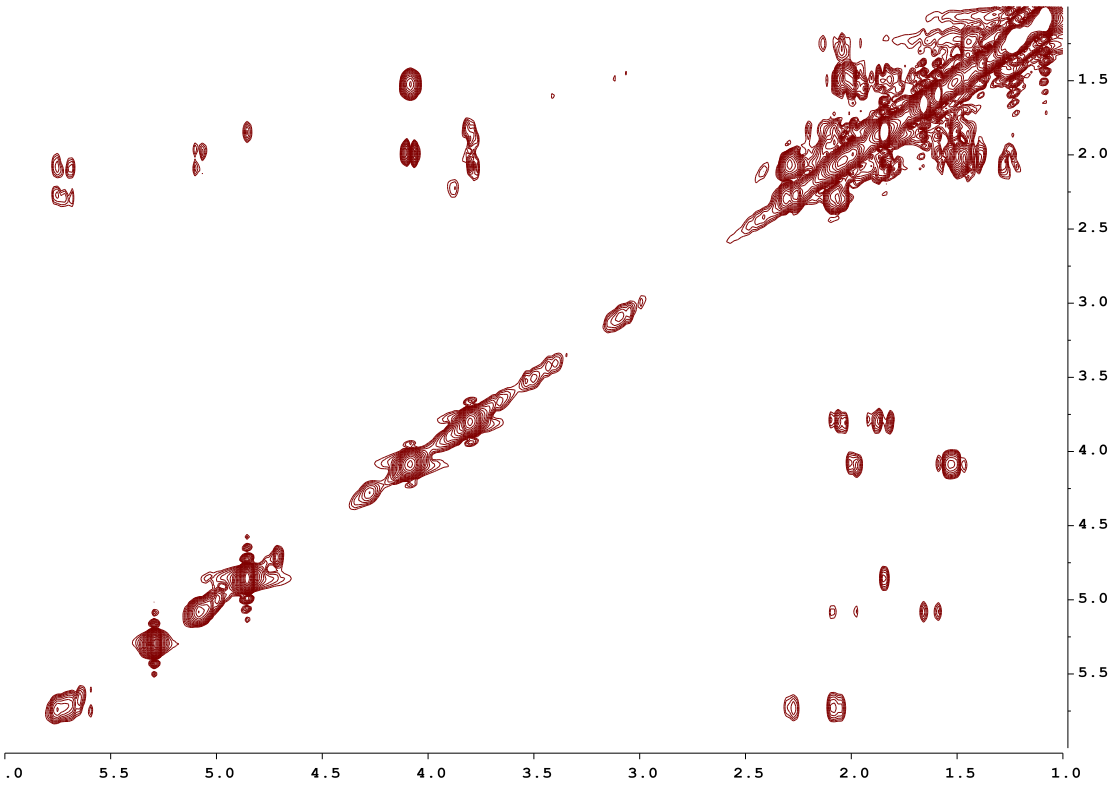


Figure S23. COSY spectrum of compound **5** in $CDCl_3$ at 300 K, 500 MHz.



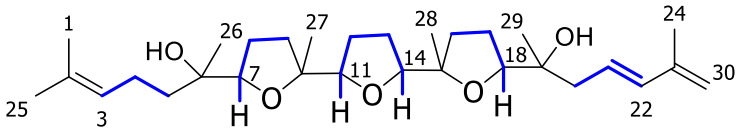
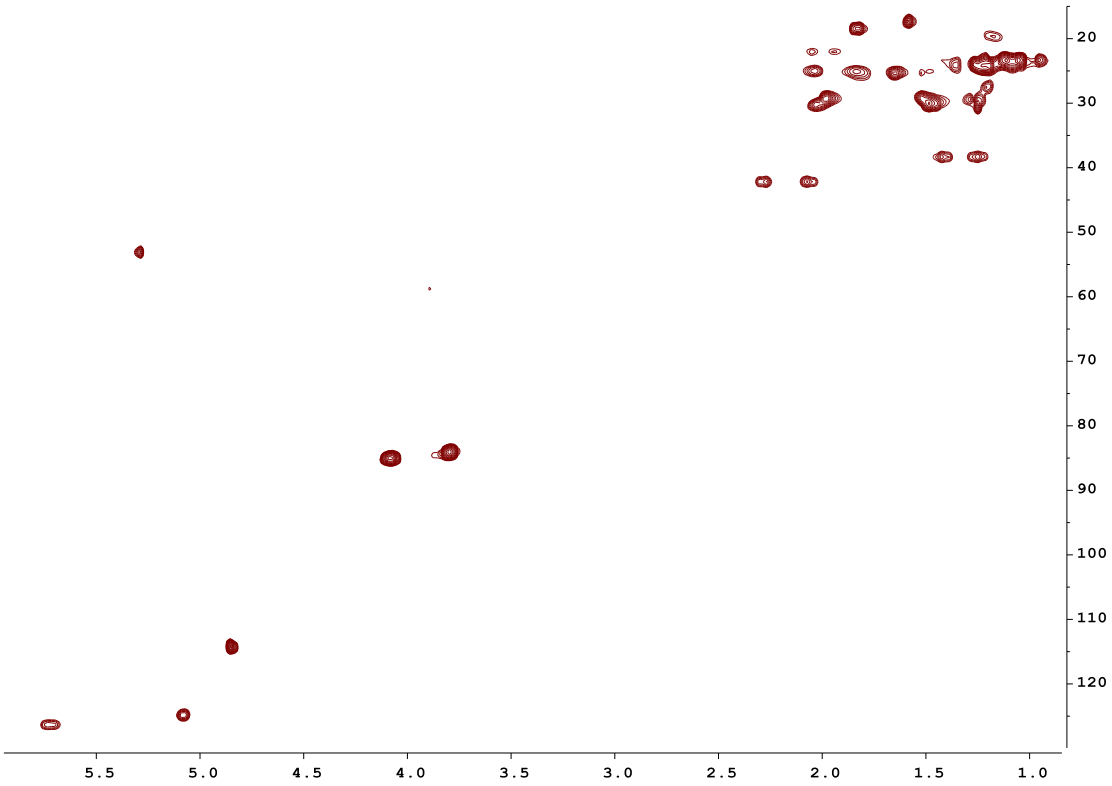


Figure S24. HSQC spectrum of compound **5** in $CDCl_3$ at 300 K, 500 MHz.



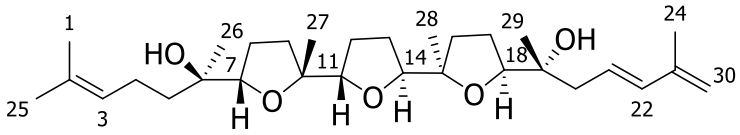
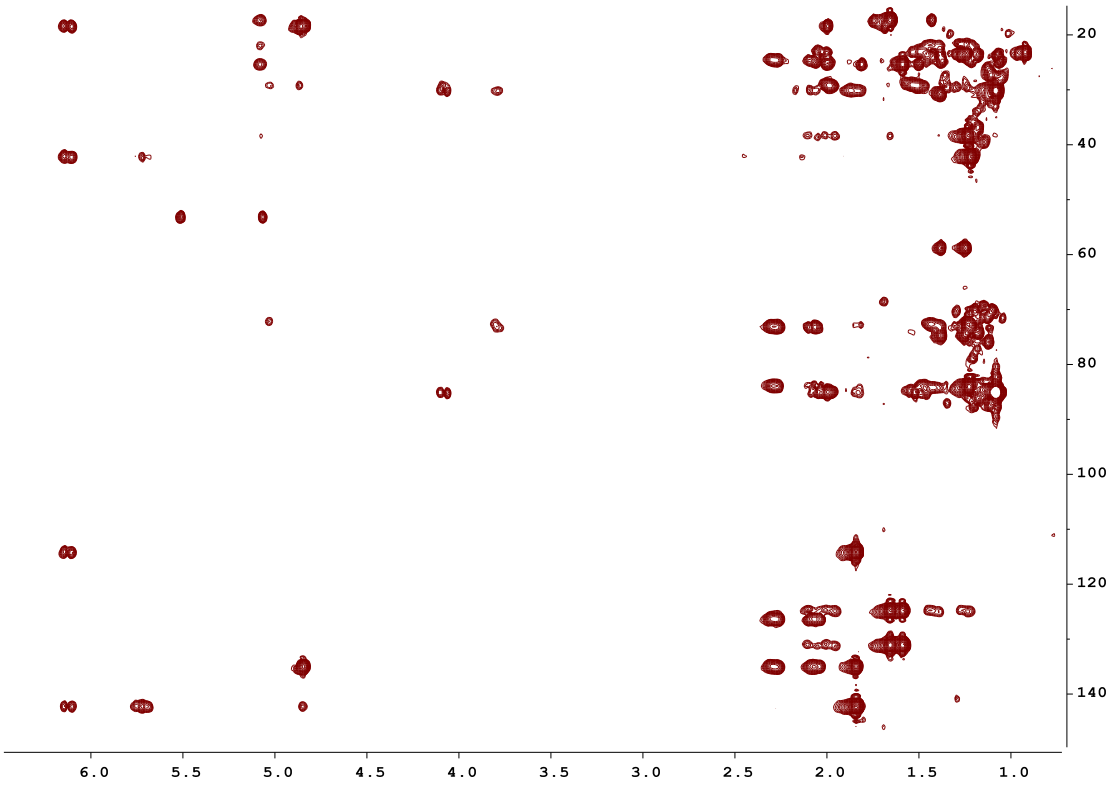


Figure S25. HMBC spectrum of compound **5** in $CDCl_3$ at 300 K, 500 MHz.



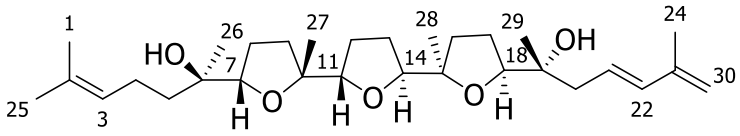
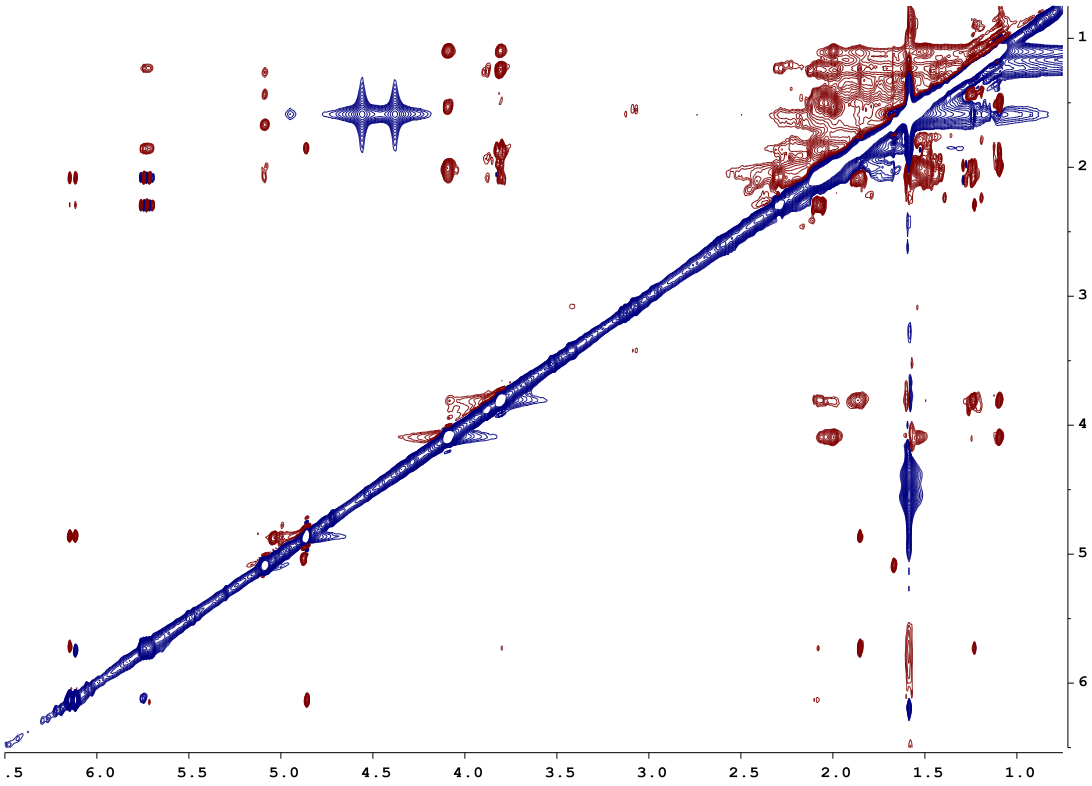


Figure S26. NOESY spectrum of compound **5** in $CDCl_3$ at 300 K, 500 MHz.



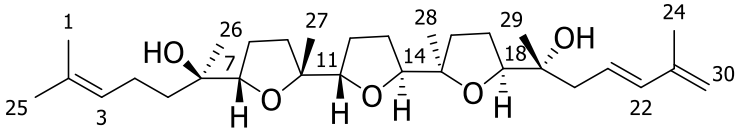
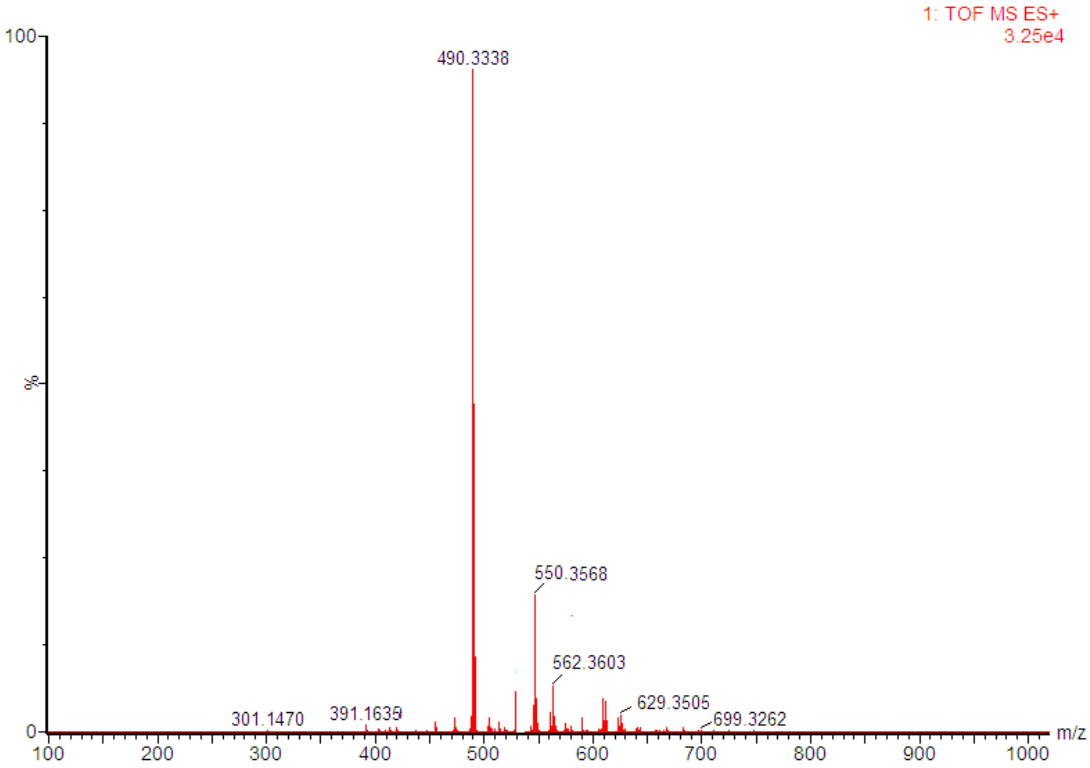


Figure S27. MS spectrum of compound **5**.



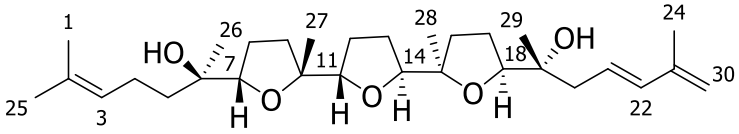


Table S5. NMR data of compound **4** in $CDCl_3$ at 300 K, 500 MHz.

Carbon		δ ^{13}C	Multiplicity	δ ^{1}H	*J* in Hz
1	**24**	18.4	CH_3	1.85	s
2	**23**	142.3	C		
3	**22**	135.2	CH	6.13	d 15.6
4	**21**	126.2	CH	5.72	ddd 7.2, 7.7, 15.6
5	**20**	42.3	CH_2	2.07 2.29	dd 7.2, 13.1 dd 7.7, 13.1
6	**19**	73.5	C		
7	**18**	84.0	CH	3.82	dd 5.9, 6.5
8	**17**	25.2	CH_2	1.88 2.09	
9	**16**	30.4	CH_2	1.52 2.04	
10	**15**	85.7	C		
11	**14**	85.4	CH	4.10	dd 5.4, 8.7
12	**13**	29.2	CH_2	1.49 2.01	
25	**30**	114.5	CH_3	4.86	bs
26	**29**	24.4	CH_3	1.24	s
27	**28**	23.3	CH_3	1.10	s

Figure S28. ^{1}H-NMR spectrum of compound **4** in $CDCl_3$ at 300 K, 500 MHz.

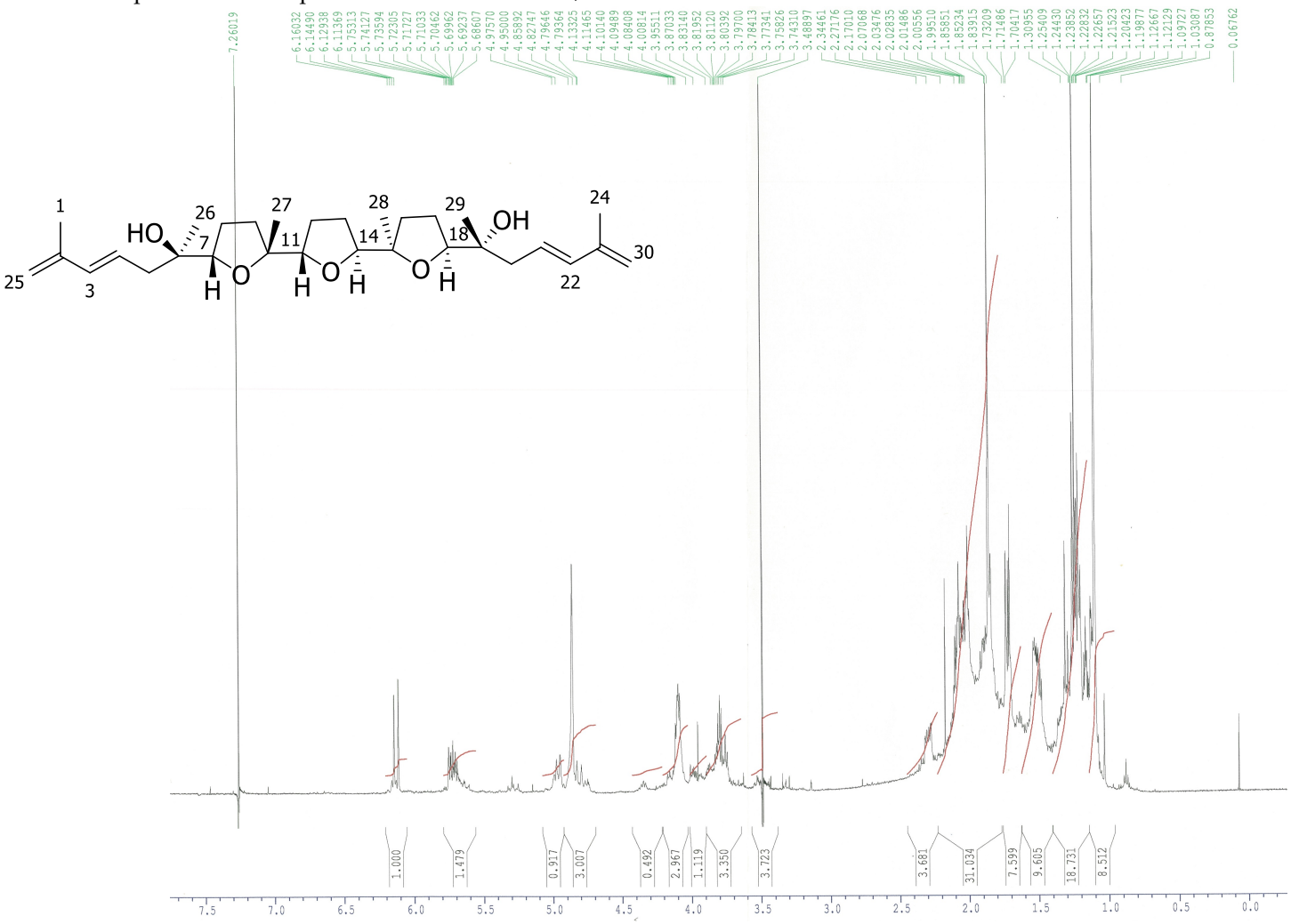
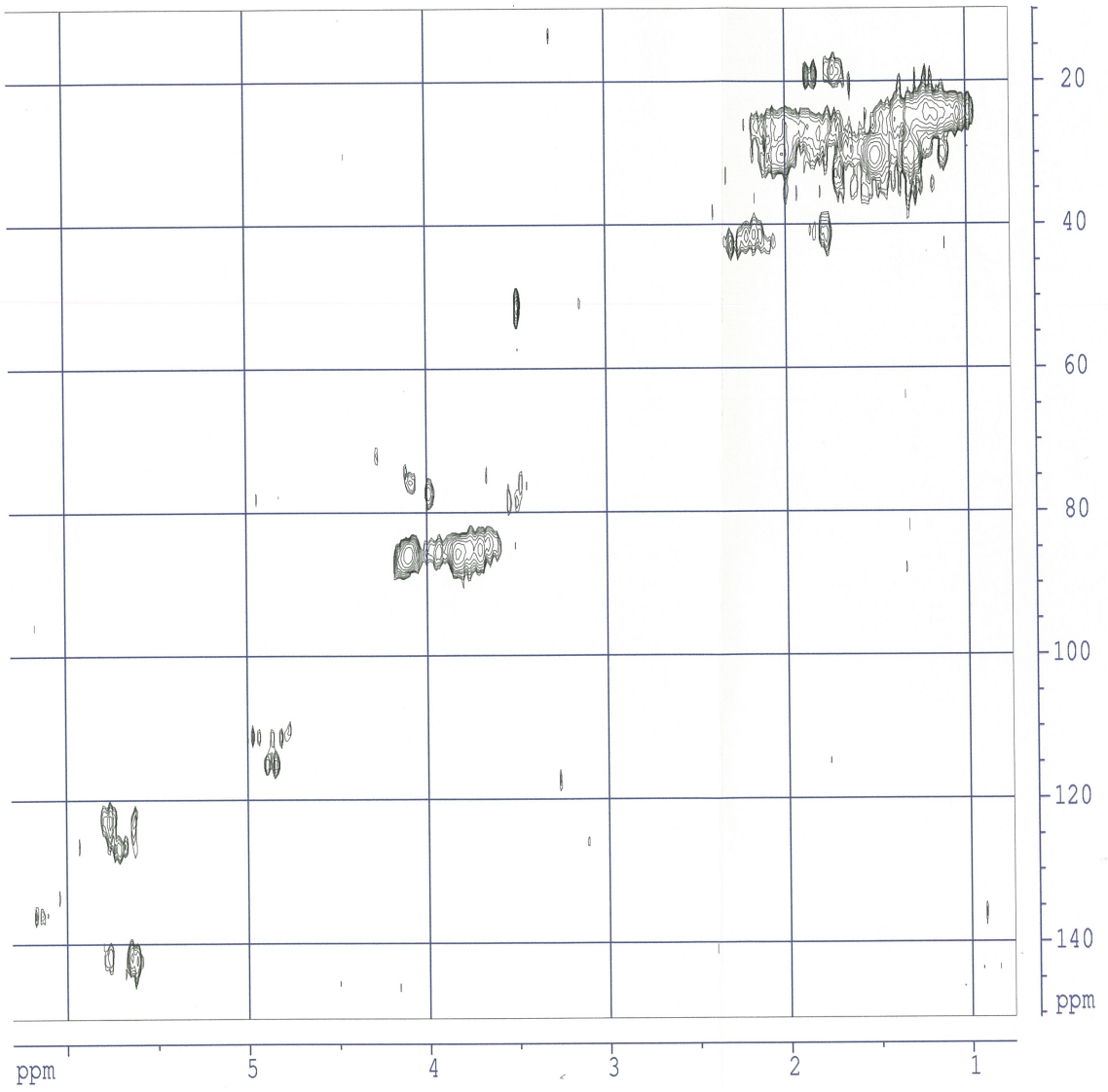


Figure S29. HSQC spectrum of compound **4** in $CDCl_3$ at 300 K, 500 MHz.



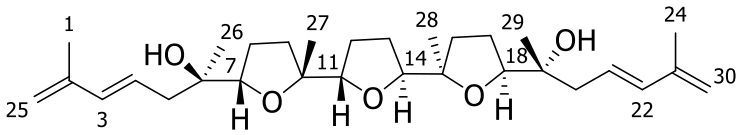
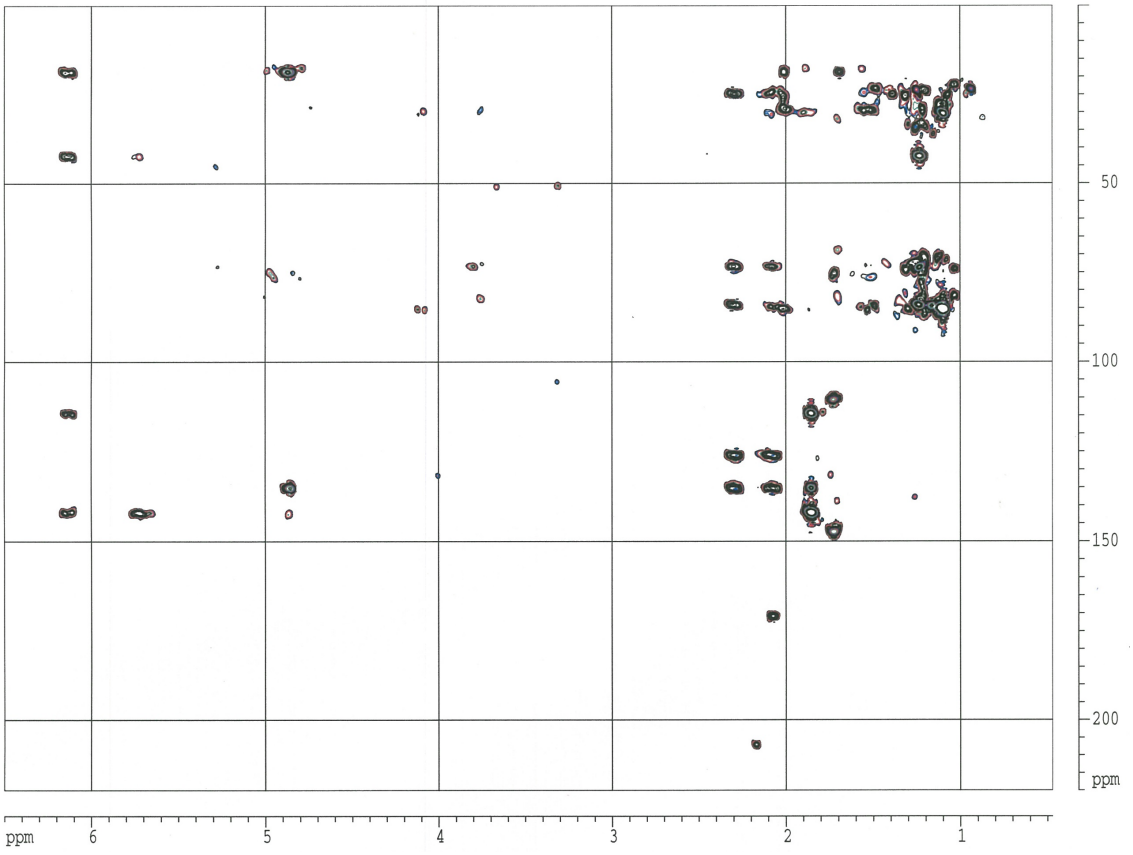


Figure S30. HMBC spectrum of compound **4** in $CDCl_3$ at 300 K, 500 MHz.



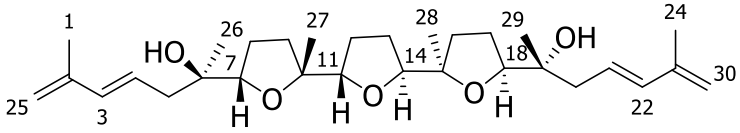
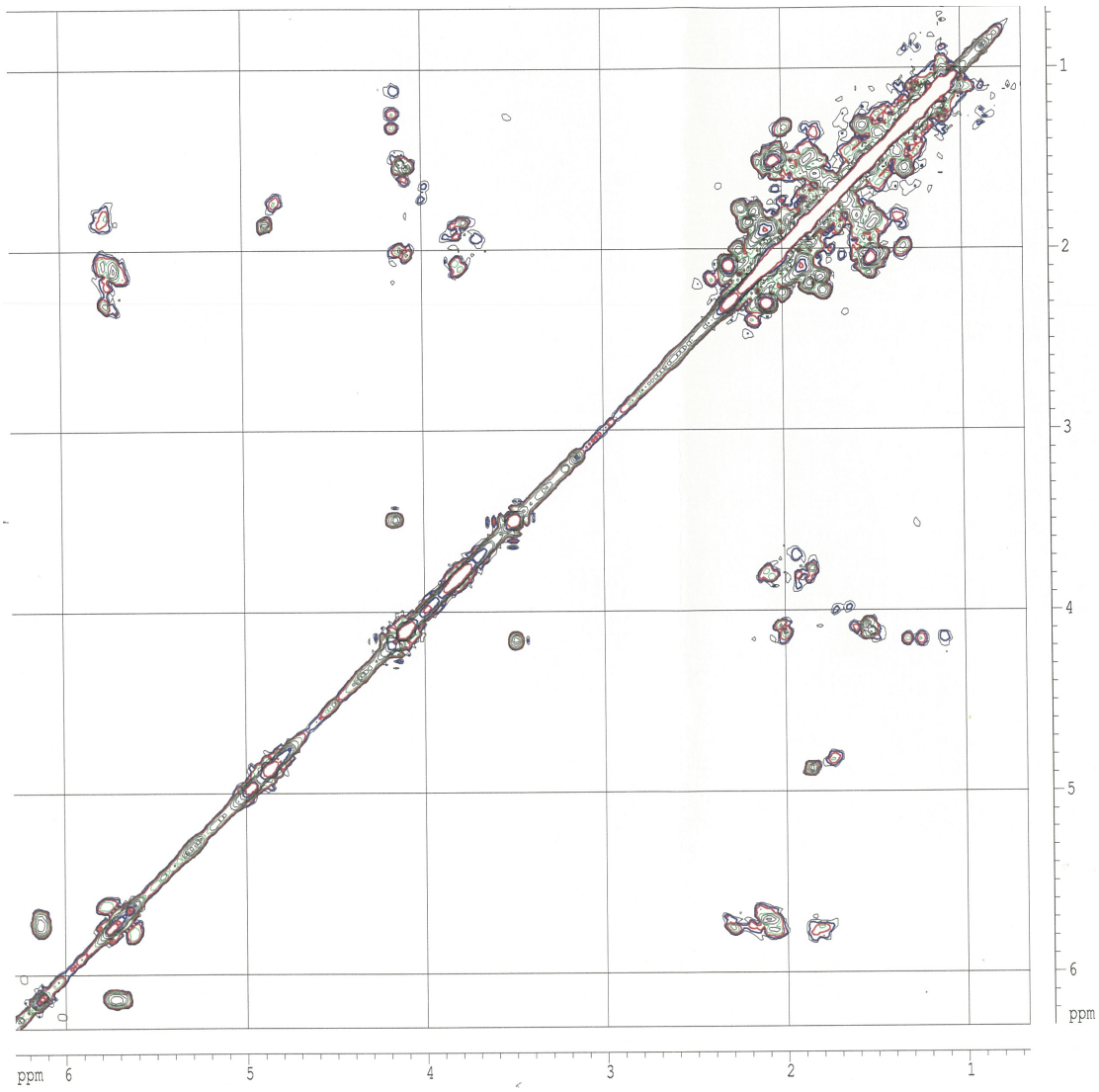


Figure S31. NOESY spectrum of compound **4** in $CDCl_3$ at 300 K, 500 MHz.



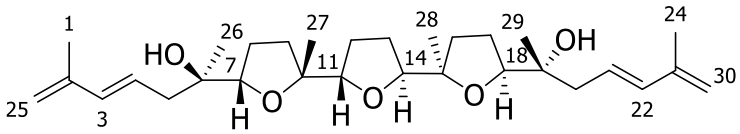


Figure S32. *In vitro* inhibitory effect of (+)-longilene peroxide (**1**) on PP2A