Electronic Supporting Information

Isolation of new compounds related to xyloketals biosynthesis implies an alternative pathway for furan-fused-chromene formation

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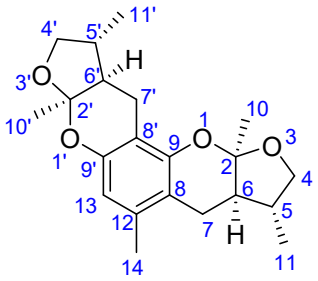
Supplementary Tables

Table S1. NMR data for compound 1 in $CDCl_3$.



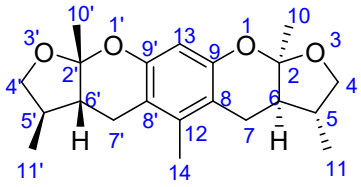
No.	δ_C[a], type	δ_H (J in Hz)[b, c]	^1H–^1H COSY[b]	HMBC[b]	NOESY[b]
2	107.3, C				
4	73.9, CH_2	a: 4.16, t (8.4)	4b, 5	2, 5, 6, 11	11
		b: 3.52, t (8.4)	4a, 5	2, 5, 11	6, 11
5	35.5, CH	2.11	4a, 4b, 6, 11	4, 6, 7, 11	
6	48.1, CH	1.93, ddd (10.8, 6.0, 1.8)	5, 7a, 7b	8	4b, 10, 11
7	21.9, CH_2	a: 2.71, dd (16.8, 6.0)	6, 7b	2, 5, 6, 8, 9, 12	11
		b: 2.67, dd (16.8, 1.8)	6, 7a	2, 5, 6, 8, 9, 12	10
8	109.1, C				
9	151.2, C				
10	23.2, CH_3	1.51, s		2, 6	6, 7b
11	16.1, CH_3	1.06, d (6.6)	5	4, 5, 6	4a, 4b, 6, 7a
2′	106.9, C				
4′	74.0, CH_2	a: 4.17, t (8.4)	4′b, 5′	2′, 5′, 6′, 11′	11′
		b: 3.51, t (8.4)	4′a, 5′	2′, 5′, 11′	6′, 11′
5′	35.5, CH	2.11	4′a, 4′b, 6′, 11′	4′, 6′, 7′, 11′	
6′	47.6, CH	1.88, br dd (10.8, 6.0)	5′, 7′a, 7′b	2′, 5′, 7′, 8′, 10′, 11′	4′b, 10′, 11′
7′	19.1, CH_2	a: 2.88, br d (18.0)	6′, 7′b	2′, 5′, 6′, 8′, 9′	11′
		b: 2.66, dd (18.0, 6.0)	6′, 7′a	2′, 5′, 6′, 8′, 9′	10′
8′	104.8, C				
9′	151.7, C				
10′	22.5, CH_3	1.48, s		2′, 6′	6′, 7′b
11′	15.9, CH_3	1.04, d (6.6)	5′	4′, 5′, 6′	4′a, 4′b, 6′, 7′a
12	135.4, C				
13	110.5, CH	6.31, s		8, 8′, 9′, 14	14
14	19.2, CH_3	2.16, s		8, 12, 13	13

[a] The data were measured at 150 MHz.

[b] The data were measured at 600 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S2. NMR data for compound 2 in $CDCl_3$.



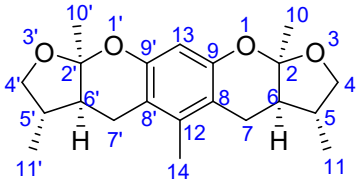
No.	δ_C[a], type	δ_H (*J* in Hz)[b, c]	^1H–^1H COSY[b]	HMBC[b]	NOESY[b]
2	106.7, C				
4	73.9, CH_2	a: 4.17, t (8.4)	4b, 5	2, 5, 6, 11	
		b: 3.50, t (8.4)	4a, 5	2, 5, 11	6, 11
5	35.4, CH	2.13	4a, 4b, 6, 11	4	
6	48.2, CH	1.91	5, 7a, 7b	8, 11	4b, 11
7	22.4, CH_2	a: 2.76	6, 7b	2, 5, 6, 8, 9, 12	
		b: 2.72	6, 7a	2, 5, 6, 8, 9, 12	
8	110.0, C				
9	152.3, C				
10	22.7, CH_3	1.49, s		2, 6	
11	16.0, CH_3	1.05, d (6.4)	5	4, 5, 6	4b, 6
2′	106.7, C				
4′	73.9, CH_2	a: 4.17, t (8.4)	4′b, 5′	2′, 5′, 6′, 11′	
		b: 3.50, t (8.4)	4′a, 5′	2′, 5′, 11′	6′, 11′
5′	35.4, CH	2.13	4′a, 4′b, 6′, 11′	4′	
6′	48.2, CH	1.91	5′, 7′a, 7′b	8′, 11′	4′b, 11′
7′	22.4, CH_2	a: 2.76	6′, 7′b	2′, 5′, 6′, 8′, 9′, 12	
		b: 2.72	6′, 7′a	2′, 5′, 6′, 8′, 9′, 12	
8′	110.0, C				
9′	152.3, C				
10′	22.7, CH_3	1.49, s		2′, 6′	
11′	16.0, CH_3	1.05, d (6.4)	5′	4′, 5′, 6′	4′b, 6′
12	135.1, C				
13	103.1, CH	6.25, s		8, 8′, 9, 9′	
14	14.8, CH_3	2.13, s		8, 8′, 12	

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S3. NMR data for compound 3 in $CDCl_3$.



No.	δ_C[a], type	δ_H (*J* in Hz)[b, d]	^1H–^1H COSY[b]	HMBC[c]	NOESY[c]
2	106.6, C				
4	73.9, CH_2	a: 4.17, t (8.4)	4b, 5	2, 5, 6, 11	
		b: 3.51, t (8.4)	4a, 5	2, 5, 11	6, 11
5	35.4, CH	2.14	4a, 4b, 6, 11	4, 6, 7	
6	48.3, CH	1.91, ddd (10.8, 6.0, 2.4)	5, 7a, 7b	2, 5, 8, 10, 11	4b, 10, 11
7	22.4, CH_2	a: 2.76, dd (16.0, 5.6)	6, 7b	2, 5, 6, 8, 9, 12	
		b: 2.71, dd (16.0, 2.4)	6, 7a	2, 5, 6, 8, 9, 12	
8	109.9, C				
9	152.3, C				
10	22.6, CH_3	1.49, s		2, 6	6
11	16.0, CH_3	1.05, d (6.8)	5	4, 5, 6	4b, 6
2′	106.6, C				
4′	73.9, CH_2	a: 4.17, t (8.4)	4′b, 5′	2′, 5′, 6′, 11′	
		b: 3.51, t (8.4)	4′a, 5′	2′, 5′, 11′	6′, 11′
5′	35.4, CH	2.14	4′a, 4′b, 6′, 11′	4′, 6′, 7′	
6′	48.3, CH	1.91, ddd (10.8, 6.0, 2.4)	5′, 7′a, 7′b	2′, 5′, 8′, 10′, 11′	4′b, 10′, 11′
7′	22.4, CH_2	a: 2.76, dd (16.0, 5.6)	6′, 7′b	2′, 5′, 6′, 8′, 9′, 12	
		b: 2.71, dd (16.0, 2.4)	6′, 7′a	2′, 5′, 6′, 8′, 9′, 12	
8′	109.9, C				
9′	152.3, C				
10′	22.6, CH_3	1.49, s		2′, 6′	6′
11′	16.0, CH_3	1.05, d (6.8)	5′	4′, 5′, 6′	4′b, 6′
12	135.1, C				
13	103.1, CH	6.25, s		8, 8′, 9, 9′	
14	14.8, CH_3	2.12, s		8, 8′, 12	

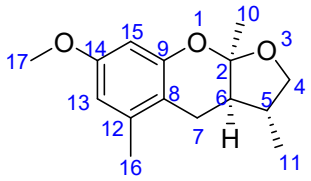
[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

[c] The data were measured at 600 MHz.

[d] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S4. NMR data for compound 4 in $CDCl_3$.



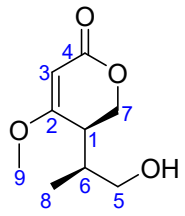
No.	δ_C[a], type	δ_H (*J* in Hz)[b, c]	^1H–^1H COSY[b]	HMBC[b]	ROESY[b]
2	107.1, C				
4	74.0, CH_2	a: 4.18, t (8.0)	4b, 5	2, 5, 6, 11	
		b: 3.52, t (8.0)	4a, 5	2, 5, 11	6, 11
5	35.4, CH	2.13	4a, 4b, 6, 11		
6	48.2, CH	1.93, ddd (10.8, 5.6, 2.0)	5, 7a, 7b	5, 8	4b, 10, 11
7	21.6, CH_2	a: 2.73, dd (16.8, 5.6)	6, 7b	2, 5, 6, 8, 9, 12	
		b: 2.68, dd (16.8, 2.0)	6, 7a	2, 5, 6, 8, 9, 12	10
8	109.4, C				
9	153.8, C				
10	22.8, CH_3	1.51, s		2, 6	6, 7b
11	15.9, CH_3	1.06, d (6.4)	5	4, 5, 6	4b, 6
12	137.9, C				
13	109.2, CH	6.36, d (2.4)	15	8, 14, 15, 16	17
14	158.8, C				
15	99.6, CH	6.28, d (2.4)	13	8, 9, 13, 14	17
16	19.5, CH_3	2.21, s		8, 12, 13	
17	55.1, CH_3	3.73, s		14	13, 15

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S5. NMR data for compound 5 in $CDCl_3$.



No.	δ_C[a], type	δ_H (*J* in Hz)[b]	^1H–^1H COSY[b]	HMBC[b]	NOESY[b]
1	39.0, CH	2.43, ddd (6.0, 4.2, 2.4)	6, 7a, 7b	2, 3, 5, 6, 7, 8	5a, 5b, 8
2	175.4, C				
3	90.5, CH	5.05, s		1, 2, 4	9
4	167.3, C				
5	65.1, CH_2	a: 3.49, dd (10.8, 6.0)	5b, 6	1, 6, 8	1, 7a, 7b, 8
		b: 3.45, dd (10.8, 6.0)	5a, 6	1, 6, 8	1, 7a, 7b, 8
6	36.6, CH	1.99, sept (6.0)	1, 5a, 5b, 8	1, 2, 5, 7, 8	7a, 7b
7	68.2, CH_2	a: 4.30, dd (11.4, 2.4)	1, 7b	1, 2, 4, 6	5a, 5b, 6, 8
		b: 4.27, dd (11.4, 4.2)	1, 7a	1, 2, 4, 6	5a, 5b, 6, 8
8	14.1, CH_3	0.88, d (7.2)	6	1, 5, 6	1, 5a, 5b, 7a, 7b
9	55.7, CH_3	3.66, s		2	3

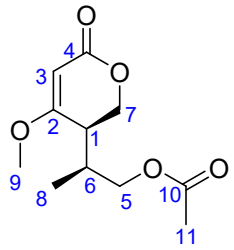
[a] The data were measured at 100 MHz.

[b] The data were measured at 600 MHz.

Table S6. Mean absolute error (MAE) values, R square (R^2) of the linear correlations, and DP4+ probability analysis of 5a and 5b.

No.	5	5a	AE	5b	AE
C-1	39.0	41.7	2.7	40.9	1.9
C-2	175.4	176.7	1.3	177.1	1.7
C-3	90.5	91.5	1.0	90.5	0.0
C-4	167.3	166.2	1.1	165.8	1.5
C-5	65.1	63.4	1.7	64.9	0.2
C-6	36.6	39.0	2.4	38.3	1.7
C-7	68.2	66.1	2.1	67.0	1.2
C-8	14.1	12.9	1.2	13.5	0.6
C-9	55.7	54.5	1.2	53.7	2.0
MAE			1.62		1.22
R^2			0.9988		0.9992
$DP4^+$			0.35%		99.65%

Table S7. NMR data for compound 6 in $CDCl_3$.



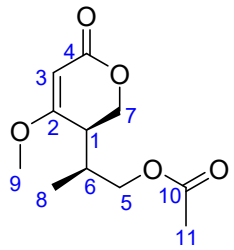
No.	δ_C[a], type	δ_H (*J* in Hz)[b, c]	^1H–^1H COSY[b]	HMBC[b]	NOESY[b]
1	39.4, CH	2.45	6, 7a, 7b	2, 6	5, 8
2	174.1, C				
3	91.4, CH	5.18, s		1, 2, 4	9
4	166.5, C				
5	66.9, CH_2	4.02, d (6.4)	6	1, 6, 8, 10	1, 8
6	33.9, CH	2.27, sept (6.4)	1, 5, 8		7b
7	67.9, CH_2	a: 4.38, dd (11.6, 4.4)	1, 7b	2, 4, 6	
		b: 4.32, dd (11.6, 2.4)	1, 7a	1, 2, 4, 6	6, 8
8	14.4, CH_3	1.01, d (7.2)	6	1, 5, 6	1, 5, 7b
9	55.8, CH_3	3.74, s		2	3
10	170.8, C				
11	20.8, CH_3	2.05, s		10	

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S8. ^{1}H and ^{13}C NMR data for Ac-5 in $CDCl_3$.



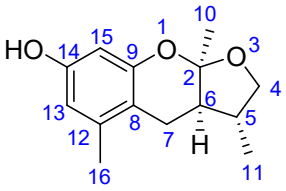
No.	δ_C[a], type	δ_H (J in Hz)[b, c]
1	39.5, CH	2.45
2	174.1, C	
3	91.4, CH	5.19, s
4	166.5, C	
5	66.9, CH_2	4.03, d (6.4)
6	33.9, CH	2.28, sept (6.4)
7	67.9, CH_2	a: 4.39, dd (11.6, 4.0)
		b: 4.33, dd (11.6, 2.4)
8	14.4, CH_3	1.02, d (7.2)
9	55.9, CH_3	3.74, s
10	170.8, C	
11	20.8, CH_3	2.06, s

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S9. ^{1}H and ^{13}C NMR data for 7 in $CDCl_3$.



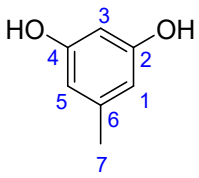
No.	δ_C[a], type	δ_H (J in Hz)[b, c]
2	107.1, C	
4	74.0, CH_2	a: 4.17, t (8.4)
		b: 3.51, t (8.4)
5	35.4, CH	2.13
6	48.1, CH	1.93, ddd (10.8, 5.4, 1.8)
7	21.5, CH_2	a: 2.71, dd (16.8, 5.4)
		b: 2.66, dd (16.8, 1.8)
8	109.6, C	
9	153.8, C	
10	22.8, CH_3	1.51, s
11	15.9, CH_3	1.05, d (6.6)
12	138.3, C	
13	109.6, C	6.29, br s
14	154.6, C	
15	101.6, CH	6.22, br s
16	19.4, CH_3	2.19, s

[a] The data were measured at 150 MHz.

[b] The data were measured at 600 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S10. ^{1}H and ^{13}C NMR data for 8 in CD_3OD.

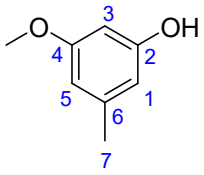


No.	δ_C[a], type	δ_H (*J* in Hz)[b]
1	108.5, CH	6.10, br s
2	159.3, C	
3	100.7, CH	6.05, br s
4	159.3, C	
5	108.5, CH	6.10, br s
6	141.1, C	
7	21.6, CH_3	2.16, s

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

Table S11. ^{1}H and ^{13}C NMR data for 9 in CD_3OD.

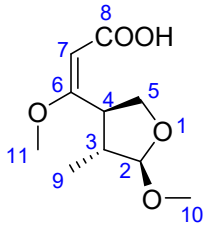


No.	δ_C[a], type	δ_H (J in Hz)[b]
1	109.6, CH	6.20, br s
2	159.4, C	
3	99.4, CH	6.14, br s
4	162.2, C	
5	107.0, CH	6.21, br s
6	141.2, C	
7	21.7, CH_3	2.20, s
4-OCH_3	55.5, CH_3	3.69, s

[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

Table S12. ^{1}H and ^{13}C NMR data for 10 in $CDCl_3$.



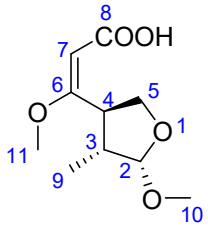
No.	δ_C[a], type	δ_H (J in Hz)[b, c]
2	112.1, CH	4.65, d (3.6)
3	44.3, CH	2.41
4	47.5, CH	4.21
5	69.0, CH_2	a: 4.02, t (7.8) b: 3.88, dd (10.2, 7.8)
6	173.7, C	
7	92.6, CH	5.11, s
8	172.6, C	
9	16.1, CH_3	1.10, d (7.2)
10	55.8, CH_3	3.39, s
11	56.0, CH_3	3.67, s

[a] The data were measured at 150 MHz.

[b] The data were measured at 600 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S13. ^{1}H and ^{13}C NMR data for 11 in $CDCl_3$.



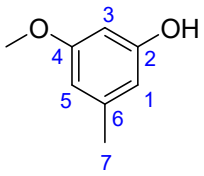
No.	δ_C[a], type	δ_H (J in Hz)[b, c]
2	106.5, CH	4.83, d (4.2)
3	42.6, CH	2.43
4	44.5, CH	4.38
5	69.5, CH_2	a: 4.14, t (8.4)
		b: 3.80, t (8.4)
6	175.1, C	
7	92.9, CH	5.12, s
8	172.6, C	
9	11.4, CH_3	0.99, d (6.6)
10	54.6, CH_3	3.35, s
11	56.0, CH_3	3.68, s

[a] The data were measured at 150 MHz.

[b] The data were measured at 600 MHz.

[c] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S14. ^{1}H and ^{13}C NMR data for authentic *O*-methylorcinol in CD_3OD.

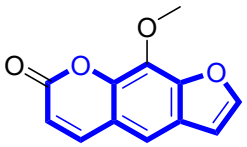


No.	δ_C[a], type	δ_H (*J* in Hz)[b]
1	109.6, CH	6.20, br s
2	159.3, C	
3	99.4, CH	6.14, br s
4	162.2, C	
5	107.0, CH	6.21, br s
6	141.2, C	
7	21.7, CH_3	2.20, s
4-OCH_3	55.4, CH_3	3.70, s

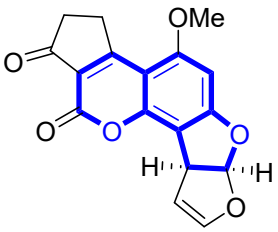
[a] The data were measured at 100 MHz.

[b] The data were measured at 400 MHz.

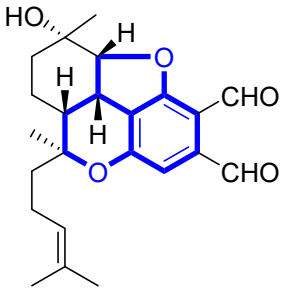
Supplementary Figures



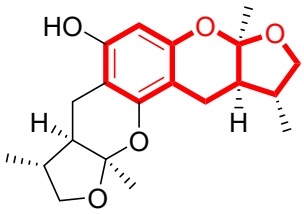
8-Methoxypsoralen



Aflatoxin B1



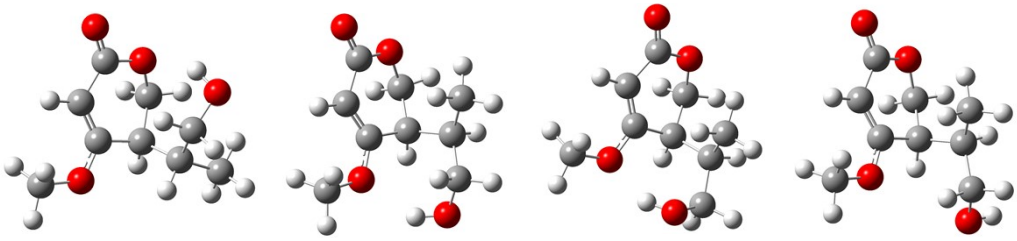
Bisabosqual A



Xyloketal B

Figure S1. Representative natural products containing furan-fused chromene units.

(1*R, 6*R**)-5a**



(1*S, 6*R**)-5b**

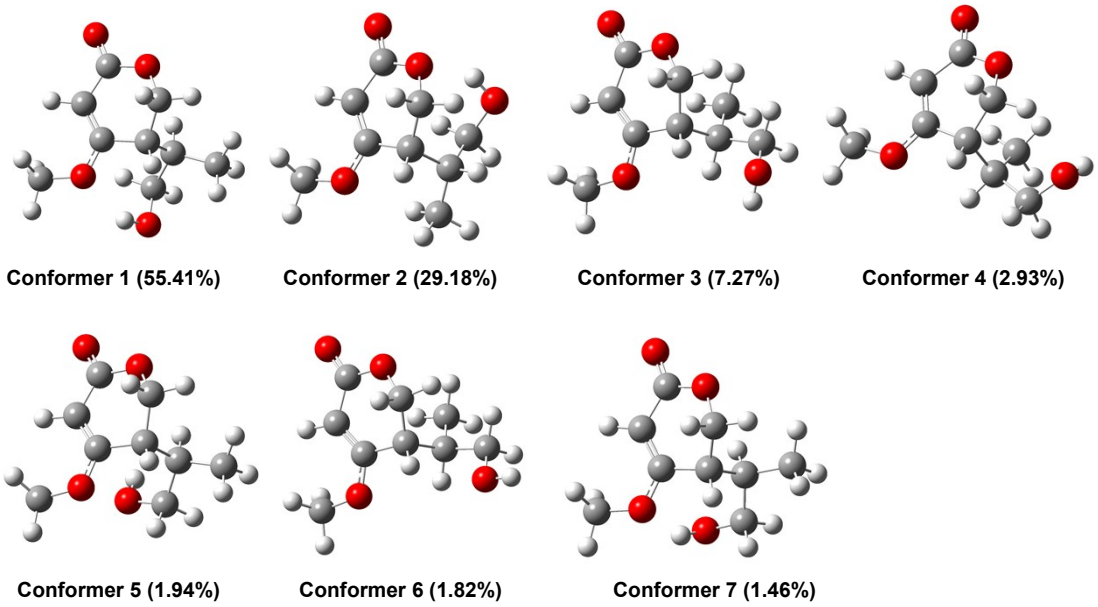


Figure S2. Most stable conformers of (1*R, 6*R**)-5a and (1*S**, 6*R**) -5b.**
The number in the parenthesis signifies the relative population.

(1*R*, 6*S*)-5

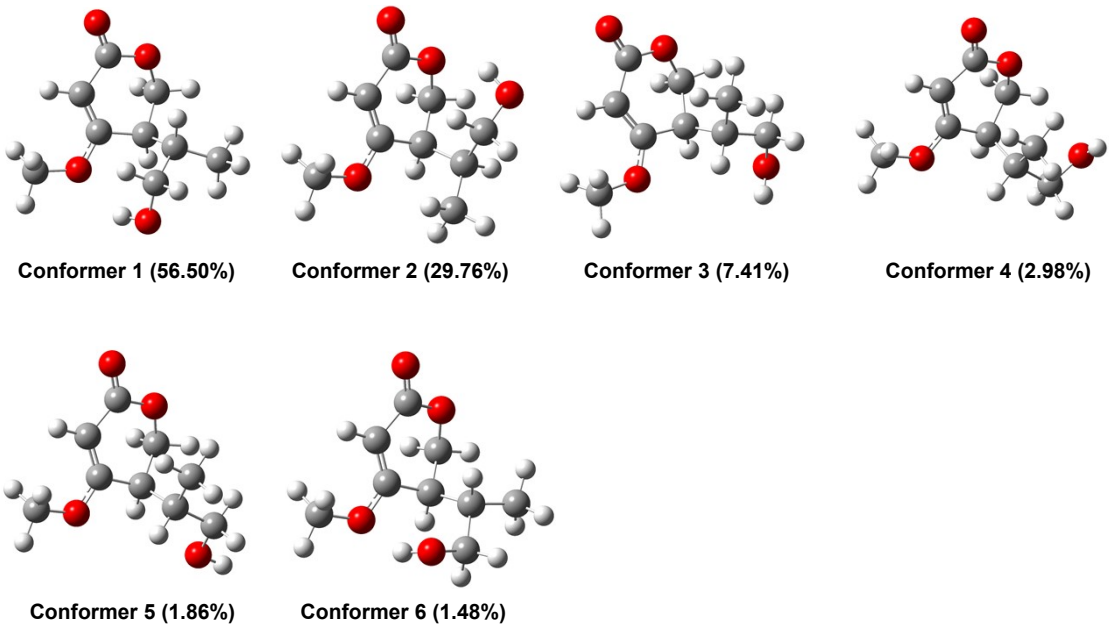


Figure S3. Most stable conformers of (1*R*, 6*S*)-5.
The number in the parenthesis signifies the relative population.

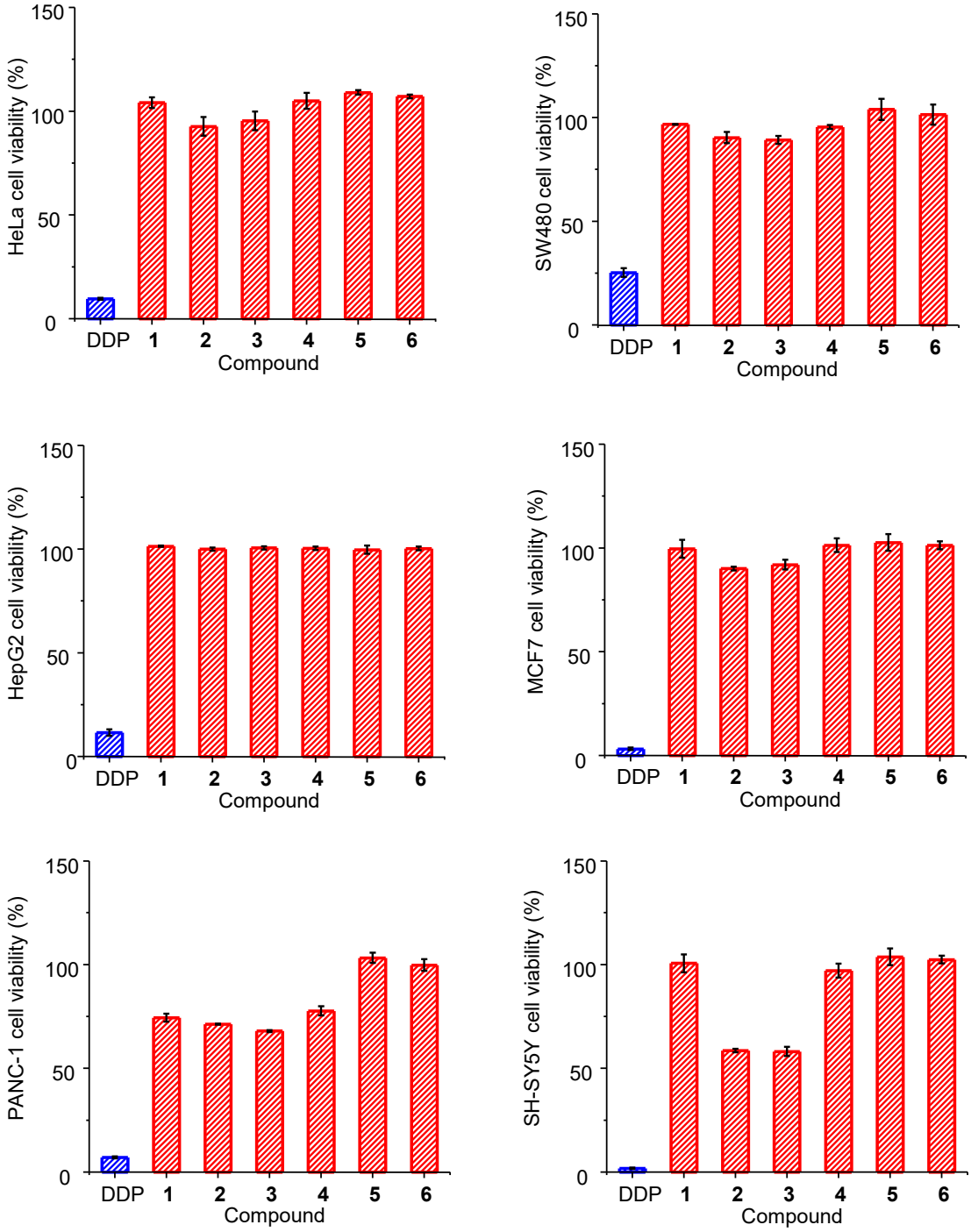


Figure S4. Cell viability of human cancer cells supplemented with the tested compound.

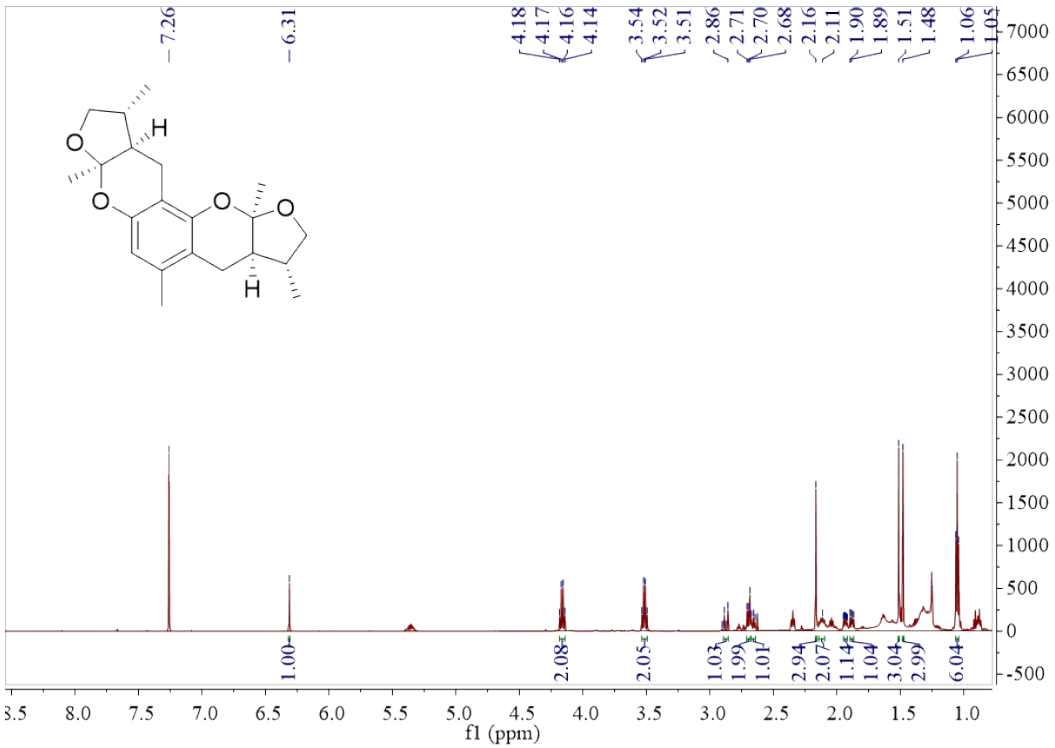


Figure S5. ^{1}H NMR spectrum of 1 in $CDCl_3$ at 600 MHz.

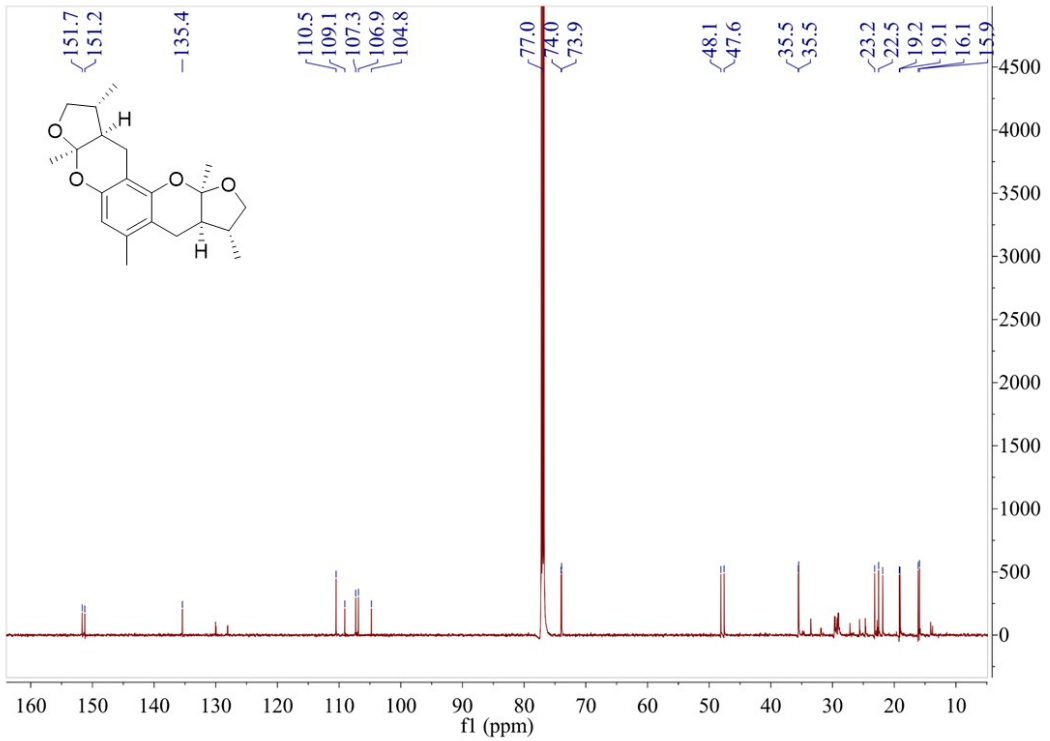


Figure S6. ^{13}C NMR spectrum of 1 in $CDCl_3$ at 150 MHz.

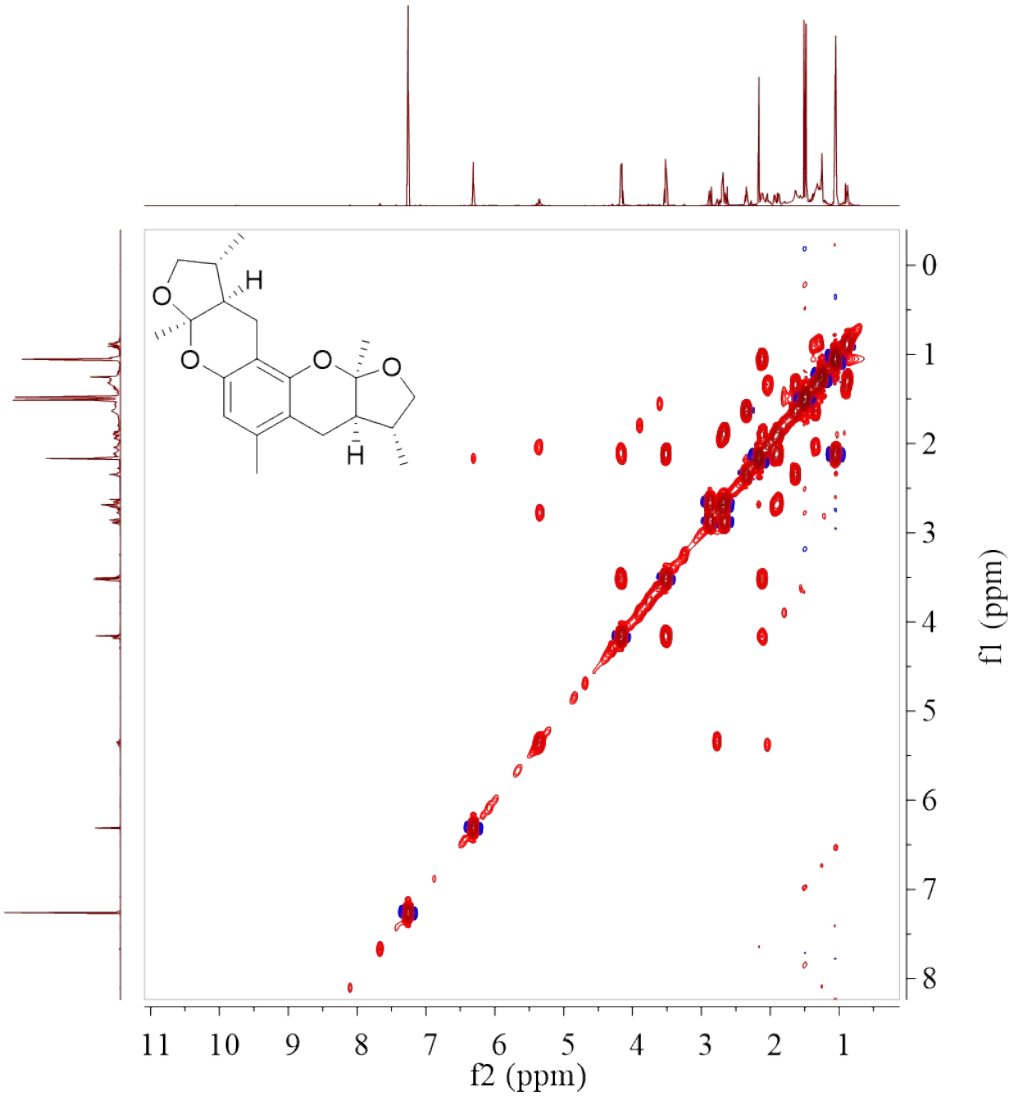


Figure S7. ^{1}H-^{1}H COSY spectrum of 1 in $CDCl_3$ at 600 MHz.

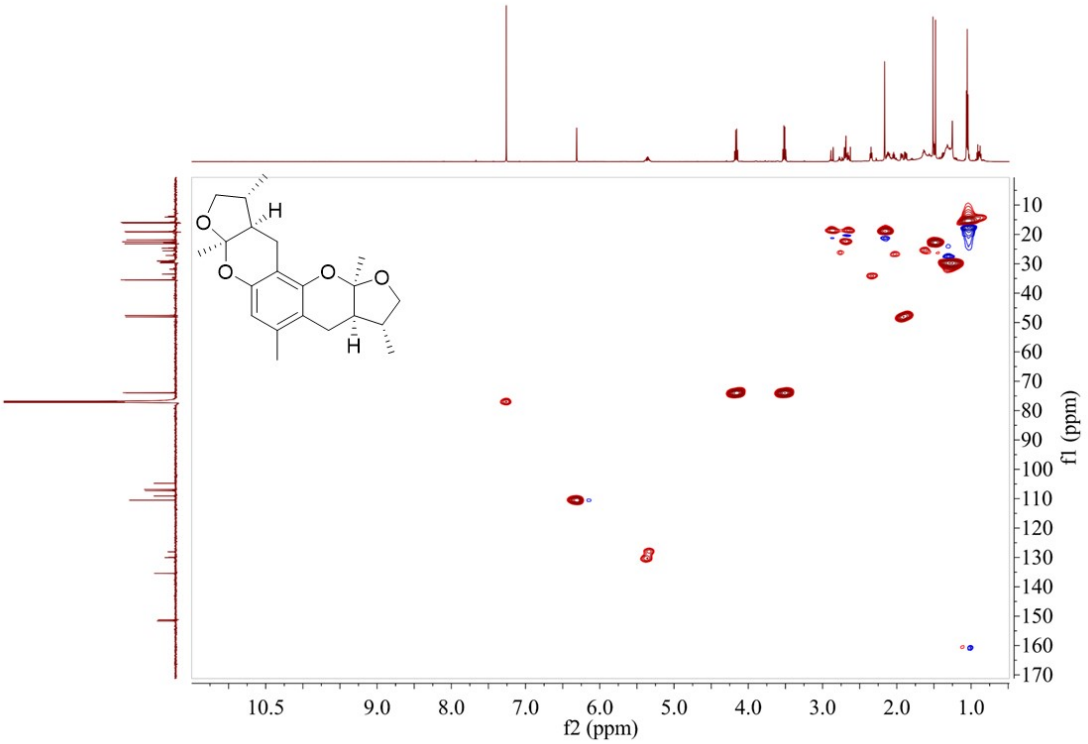


Figure S8. HSQC spectrum of 1 in $CDCl_3$ at 600 MHz.

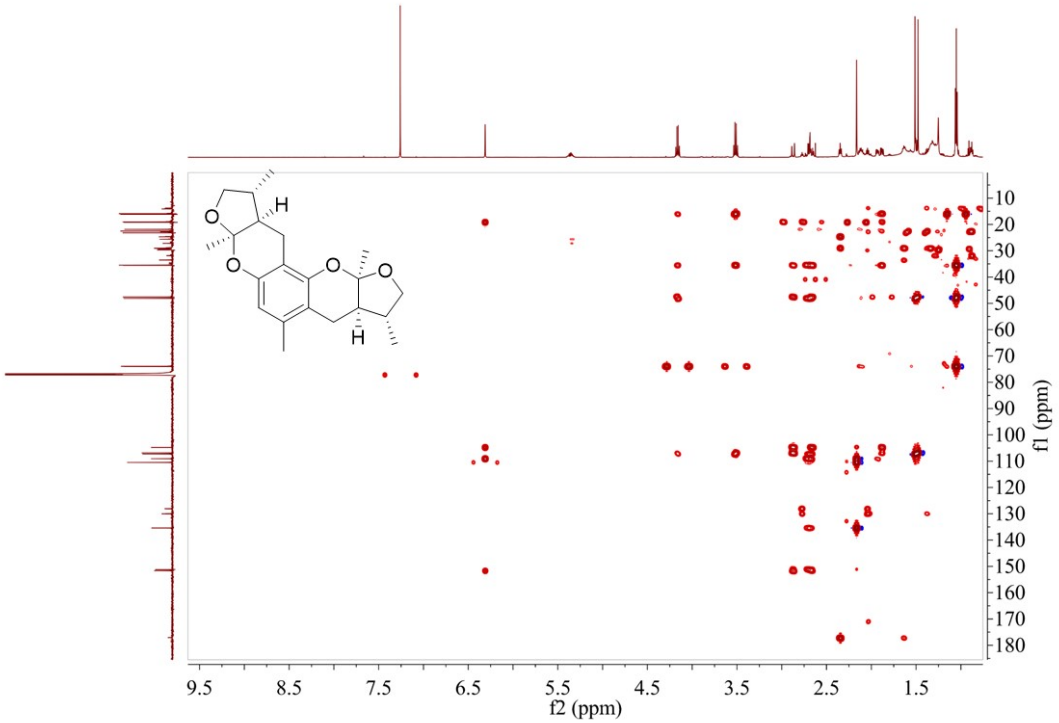


Figure S9. HMBC spectrum of 1 in $CDCl_3$ at 600 MHz.

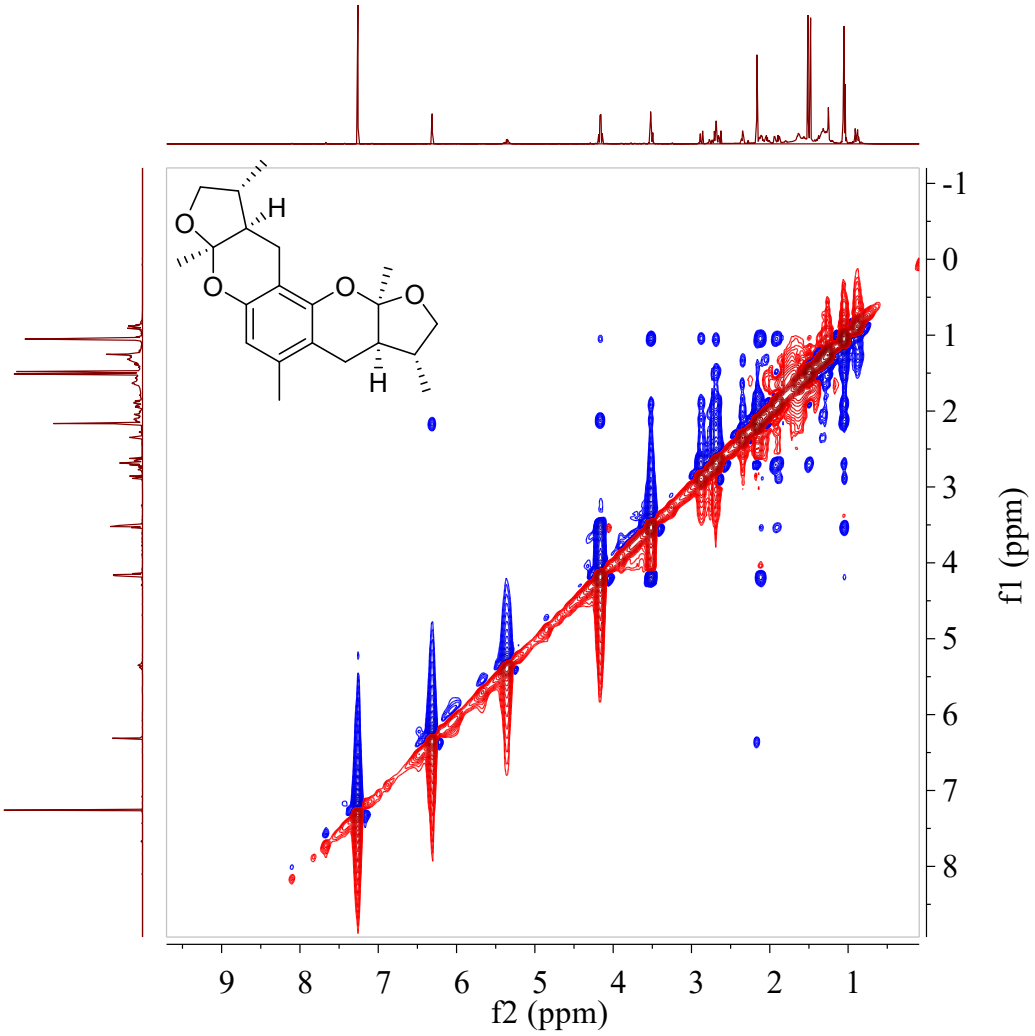


Figure S10. NOESY spectrum of 1 in $CDCl_3$ at 600 MHz.

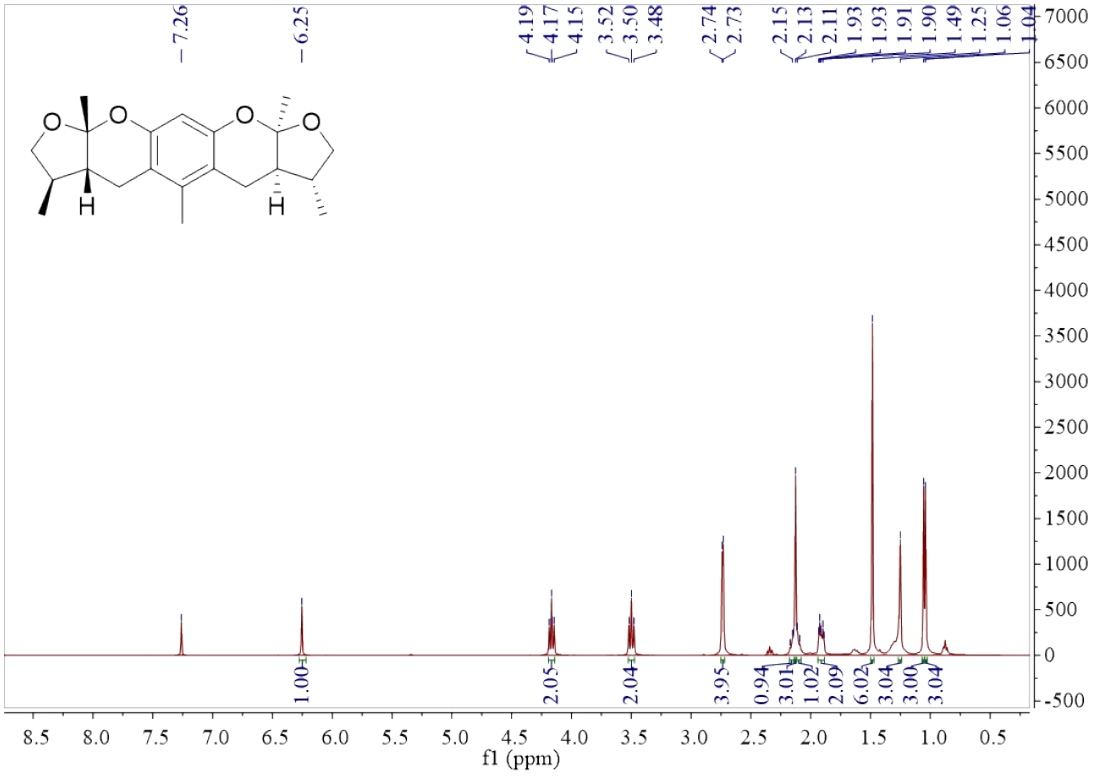


Figure S11. ^{1}H NMR spectrum of 2 in $CDCl_3$ at 400 MHz.

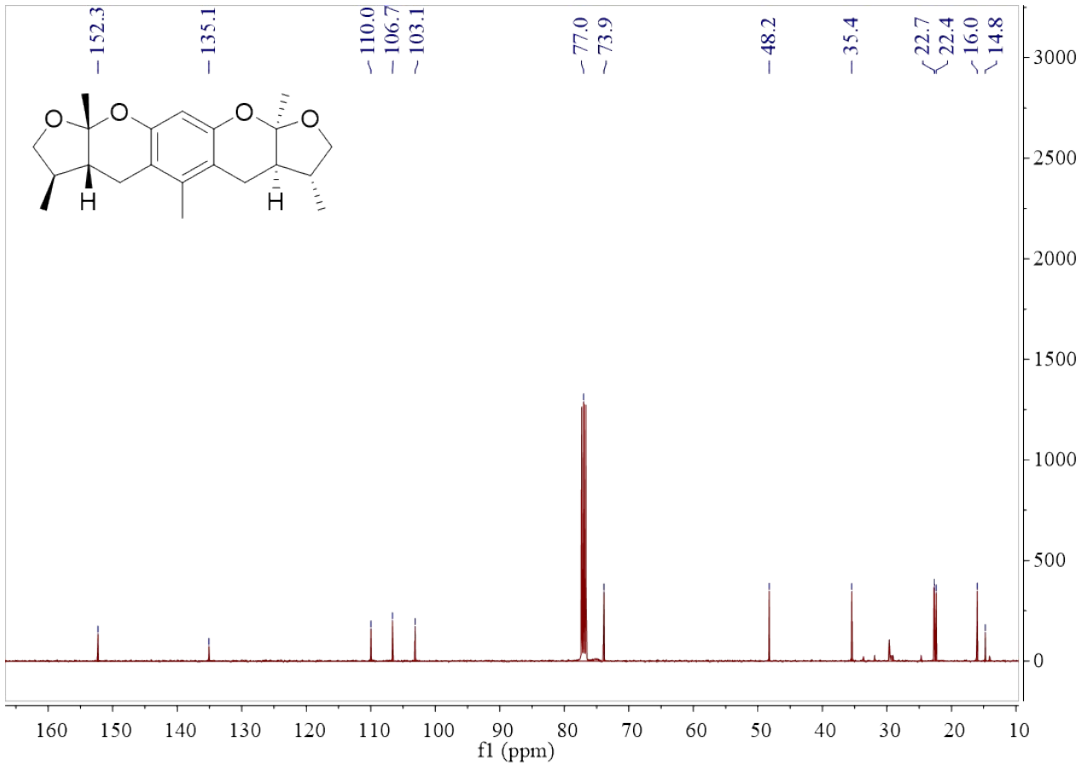


Figure S12. ^{13}C NMR spectrum of 2 in $CDCl_3$ at 100 MHz.

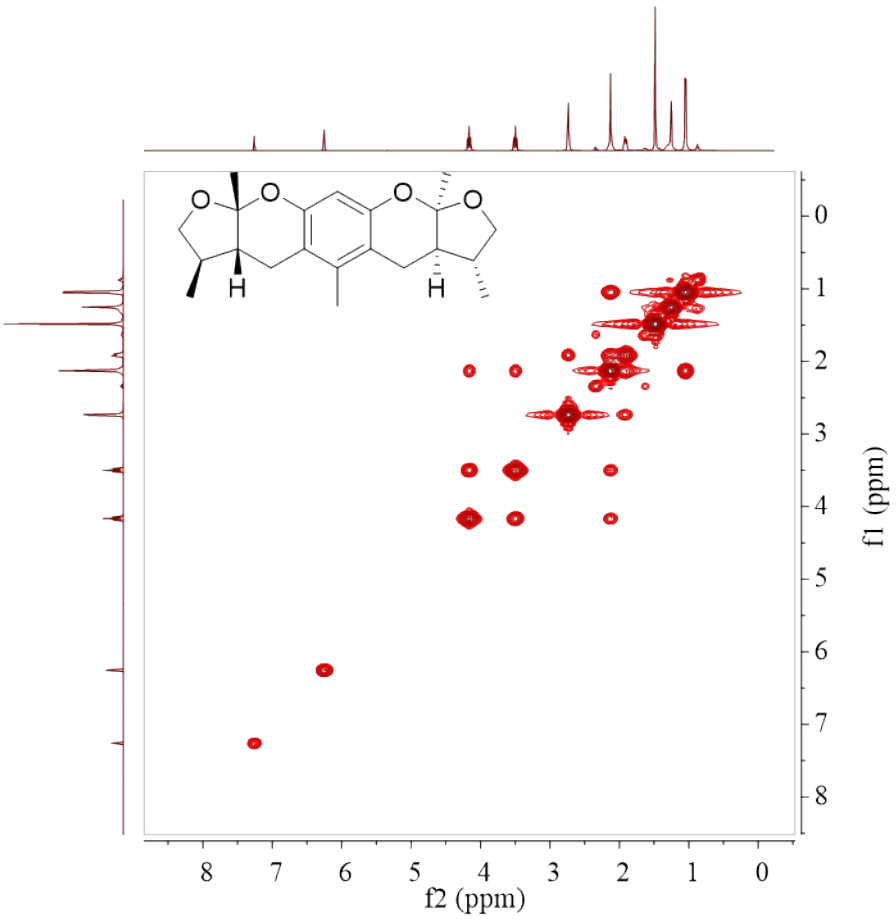


Figure S13. ^{1}H -^{1}H COSY spectrum of 2 in $CDCl_3$ at 400 MHz.

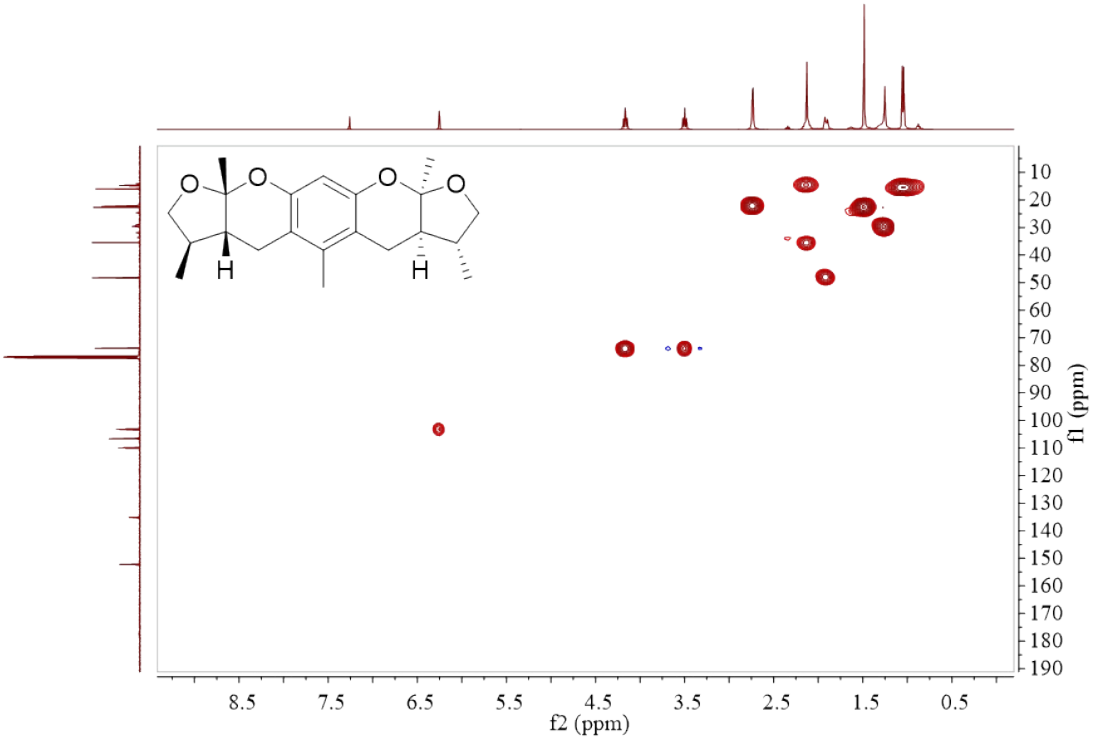


Figure S14. HSQC spectrum of 2 in $CDCl_3$ at 400 MHz.

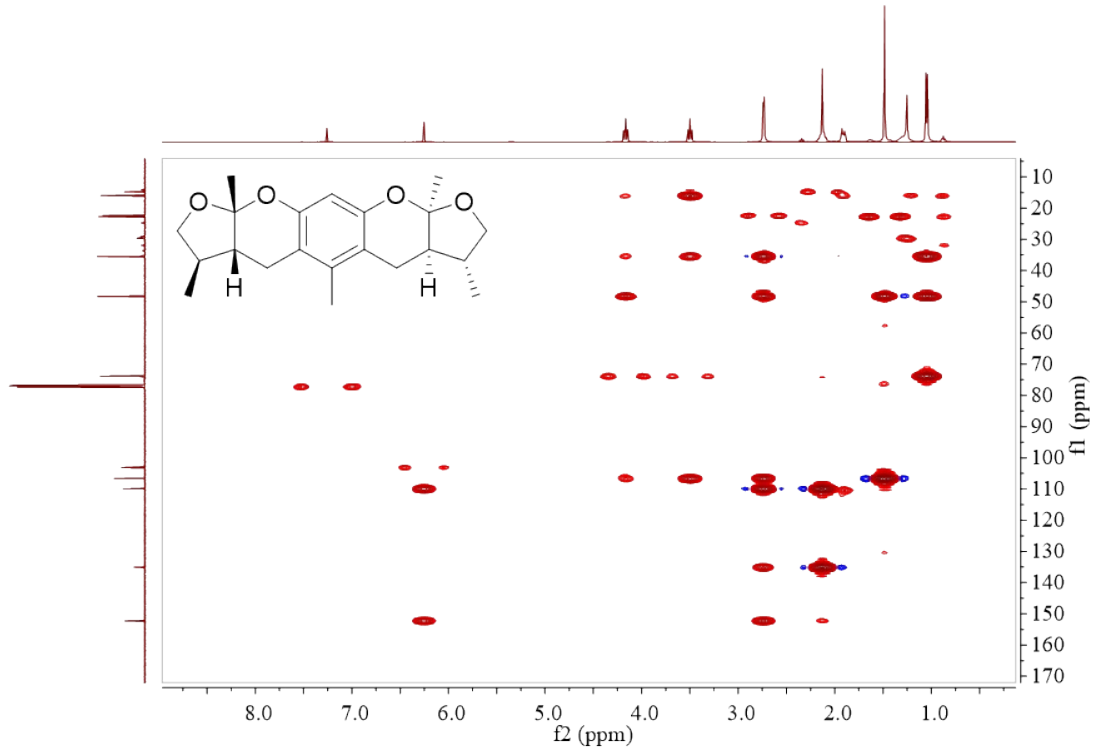


Figure S15. HMBC spectrum of 2 in $CDCl_3$ at 400 MHz.

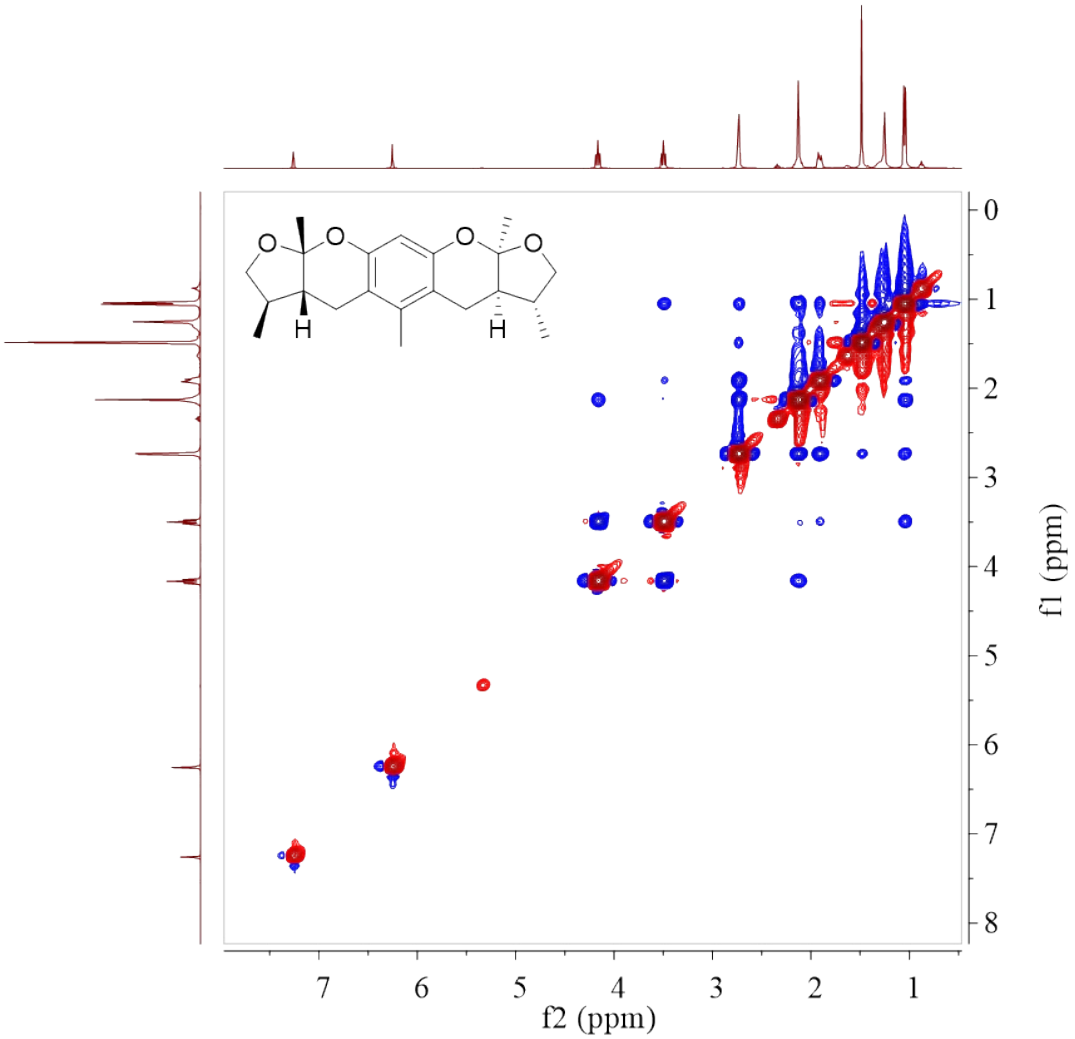


Figure S16. NOESY spectrum of 2 in $CDCl_3$ at 400 MHz.

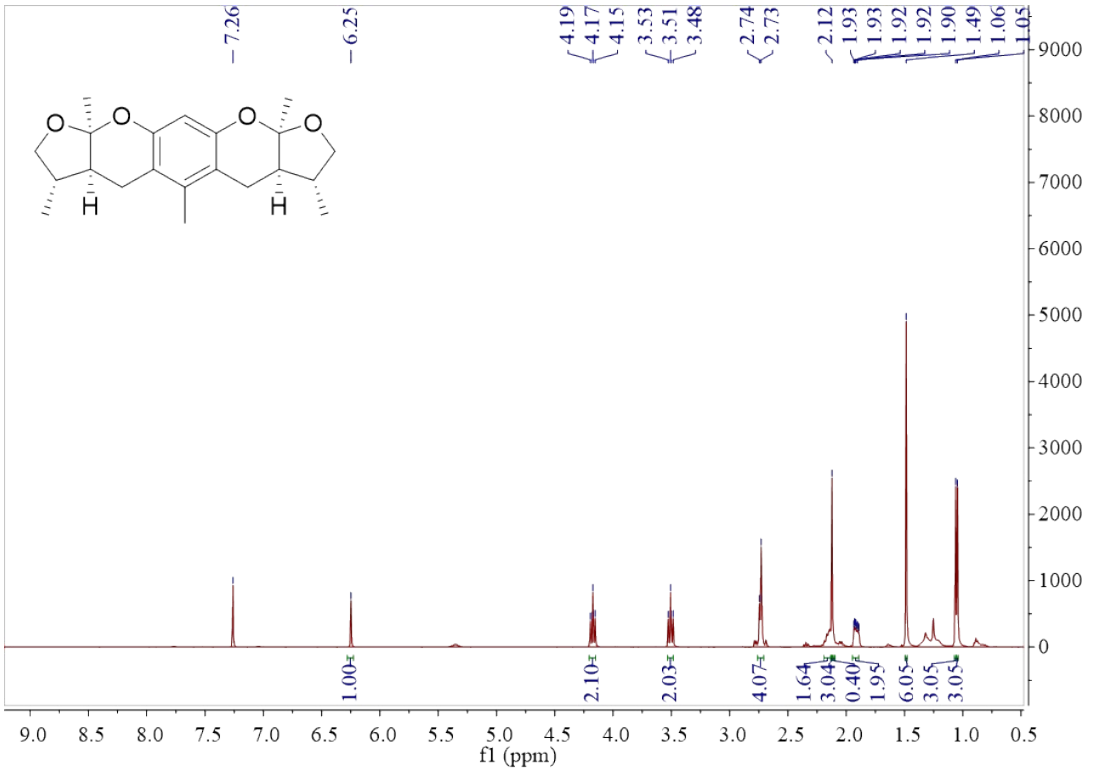


Figure S17. ^{1}H NMR spectrum of 3 in $CDCl_3$ at 400 MHz.

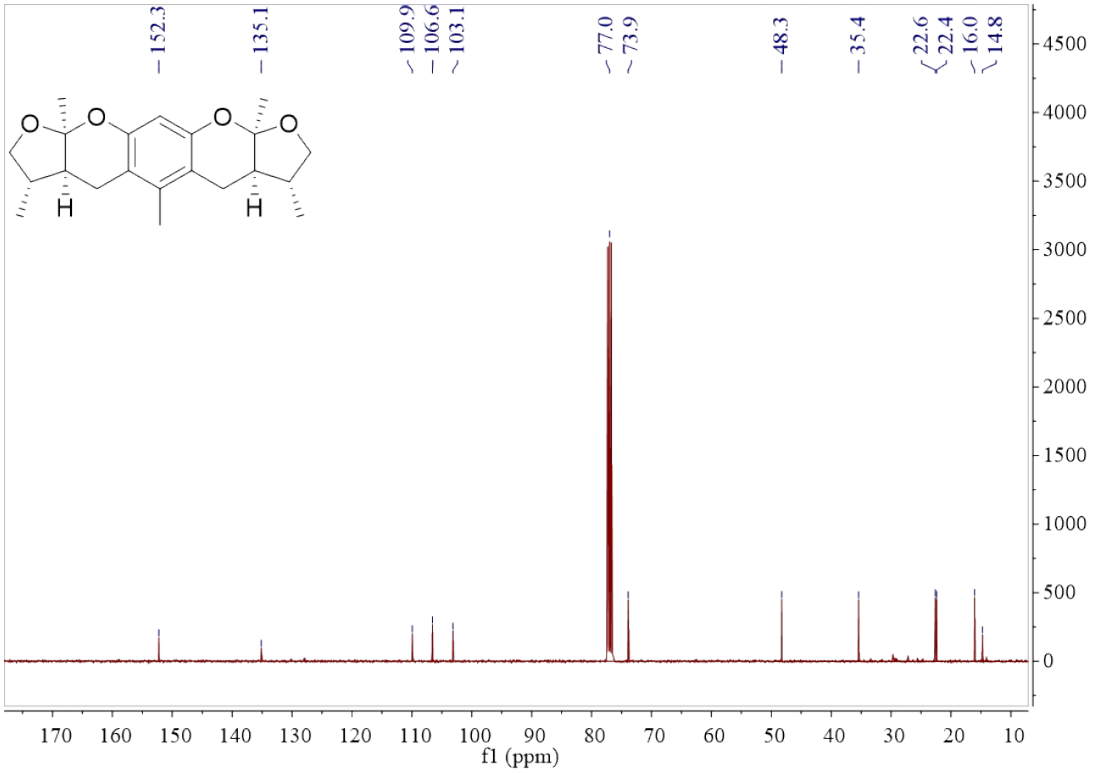


Figure S18. ^{13}C NMR spectrum of 3 in $CDCl_3$ at 100 MHz.

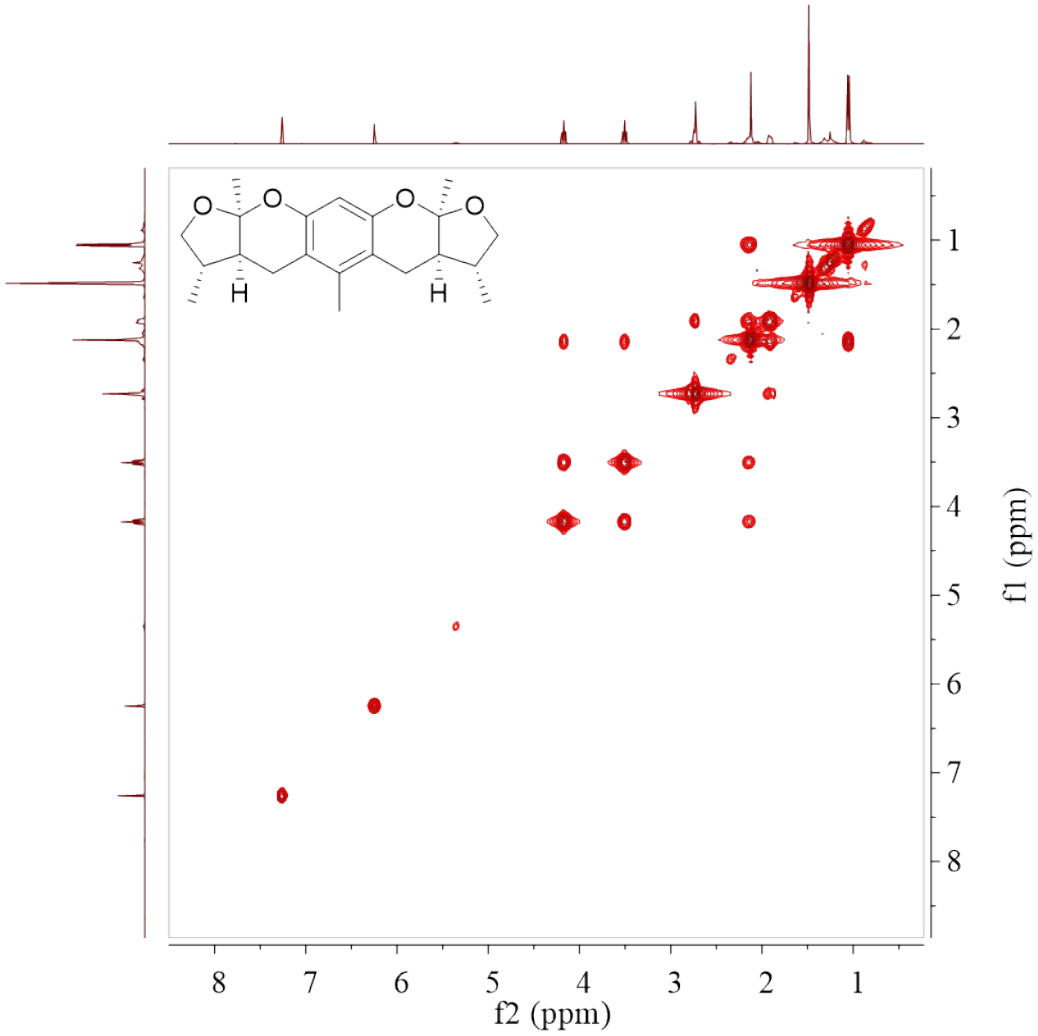


Figure S19. ^{1}H -^{1}H COSY spectrum of 3 in $CDCl_3$ at 400 MHz.

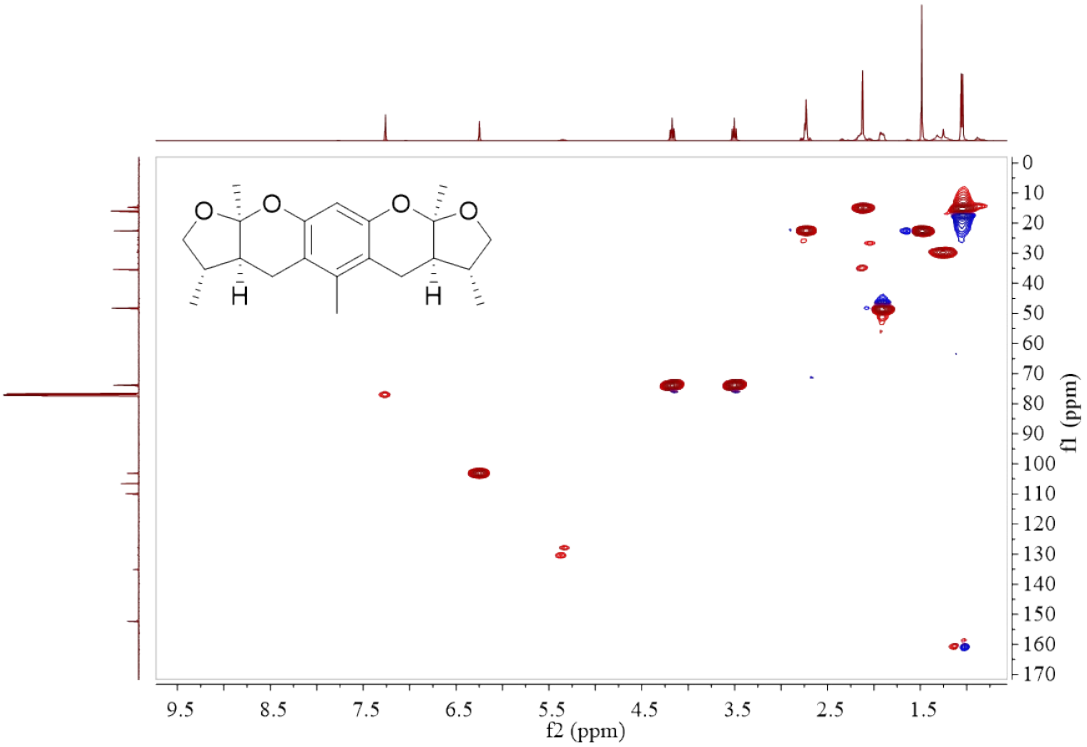


Figure S20. HSQC spectrum of 3 in $CDCl_3$ at 600 MHz.

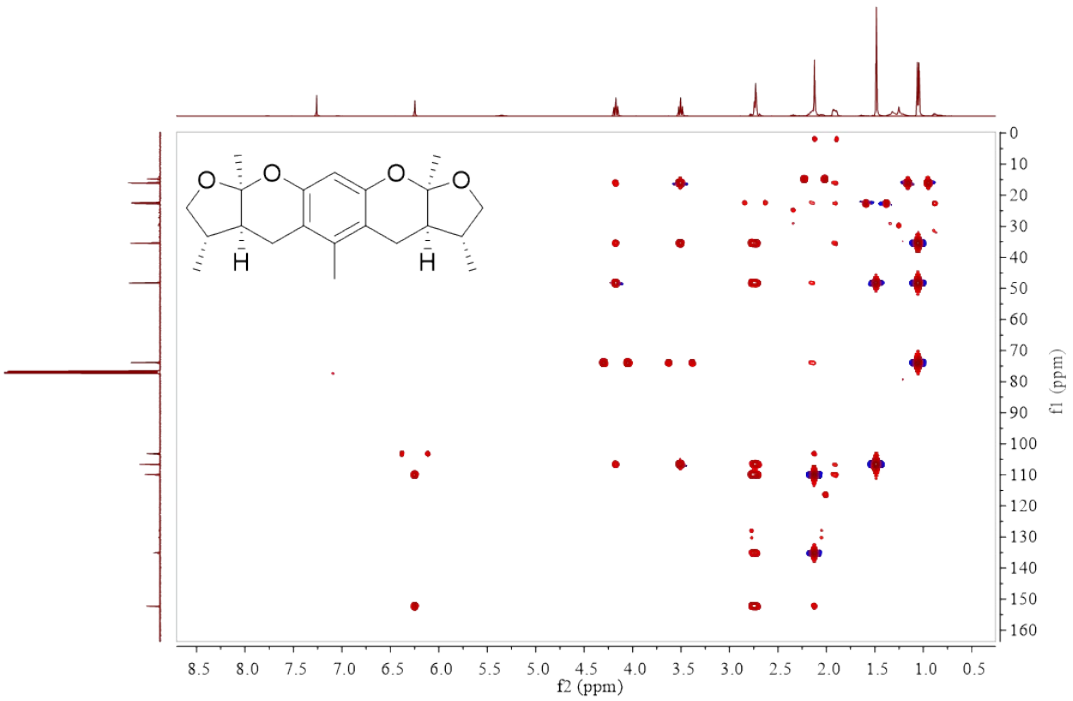


Figure S21. HMBC spectrum of 3 in $CDCl_3$ at 600 MHz.

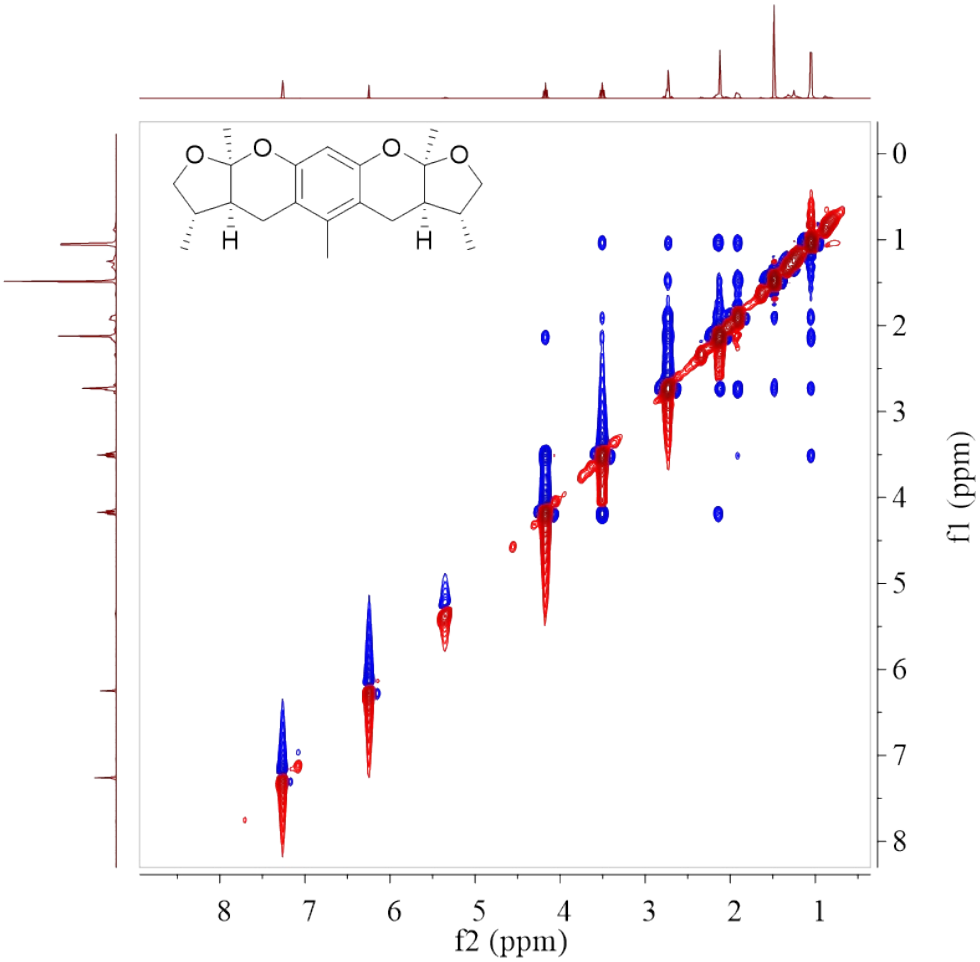


Figure S22. NOESY spectrum of 3 in $CDCl_3$ at 600 MHz.

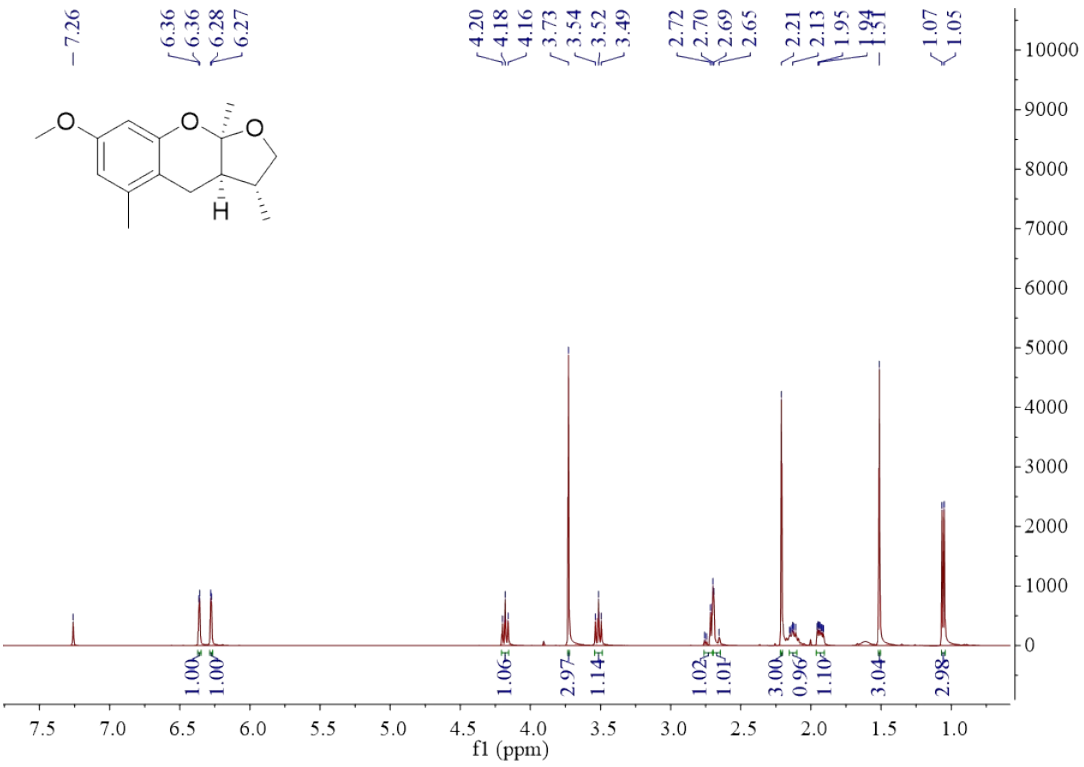


Figure S23. ^{1}H NMR spectrum of 4 in $CDCl_3$ at 400 MHz.

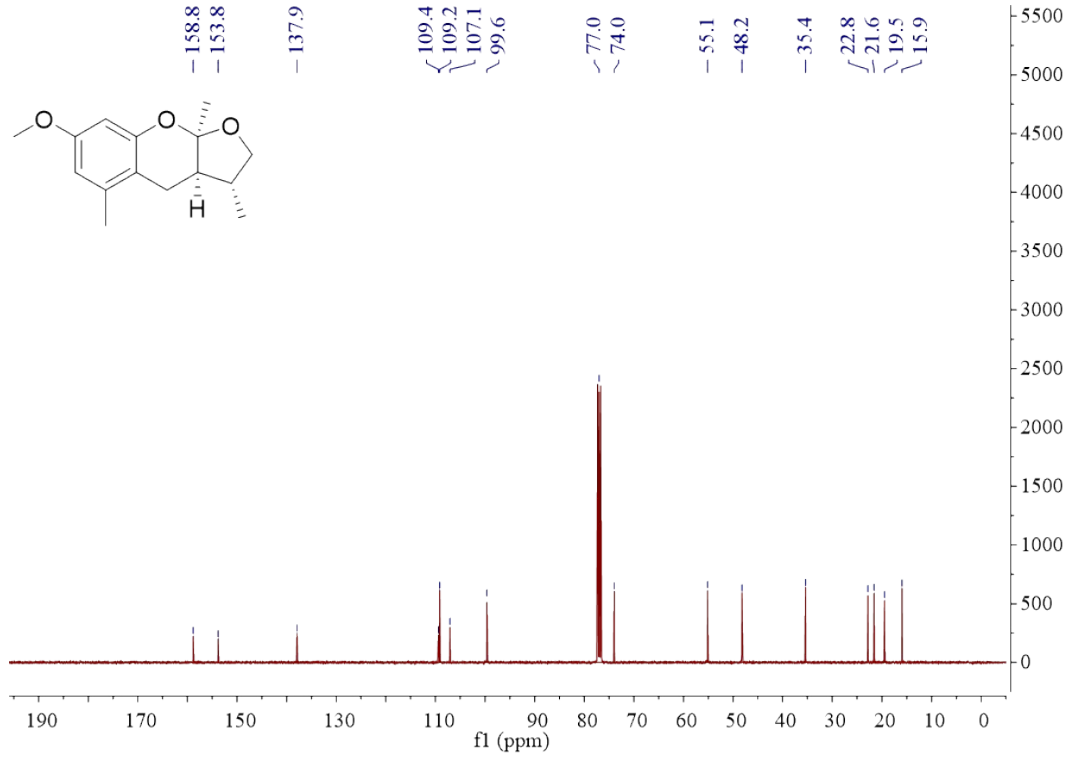


Figure S24. ^{13}C NMR spectrum of 4 in $CDCl_3$ at 100 MHz.

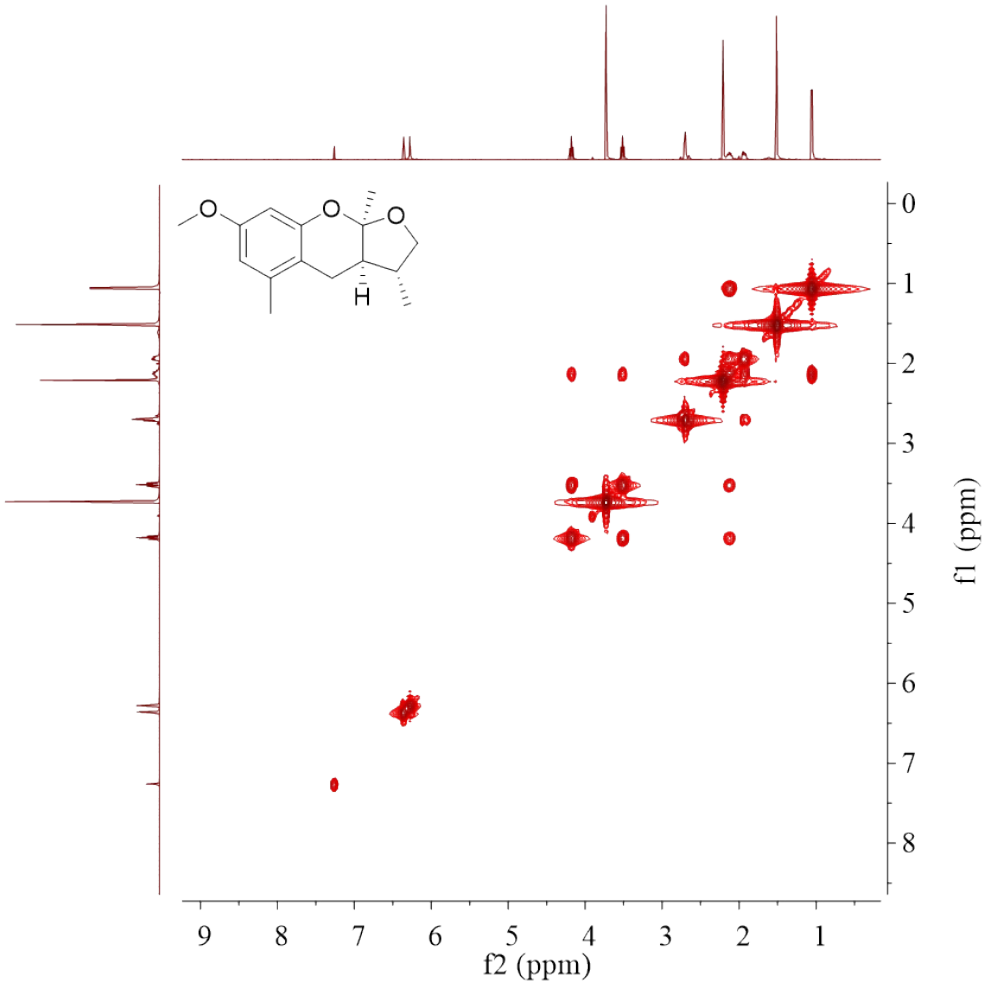


Figure S25. ^{1}H-^{1}H COSY spectrum of 4 in $CDCl_3$ at 400 MHz.

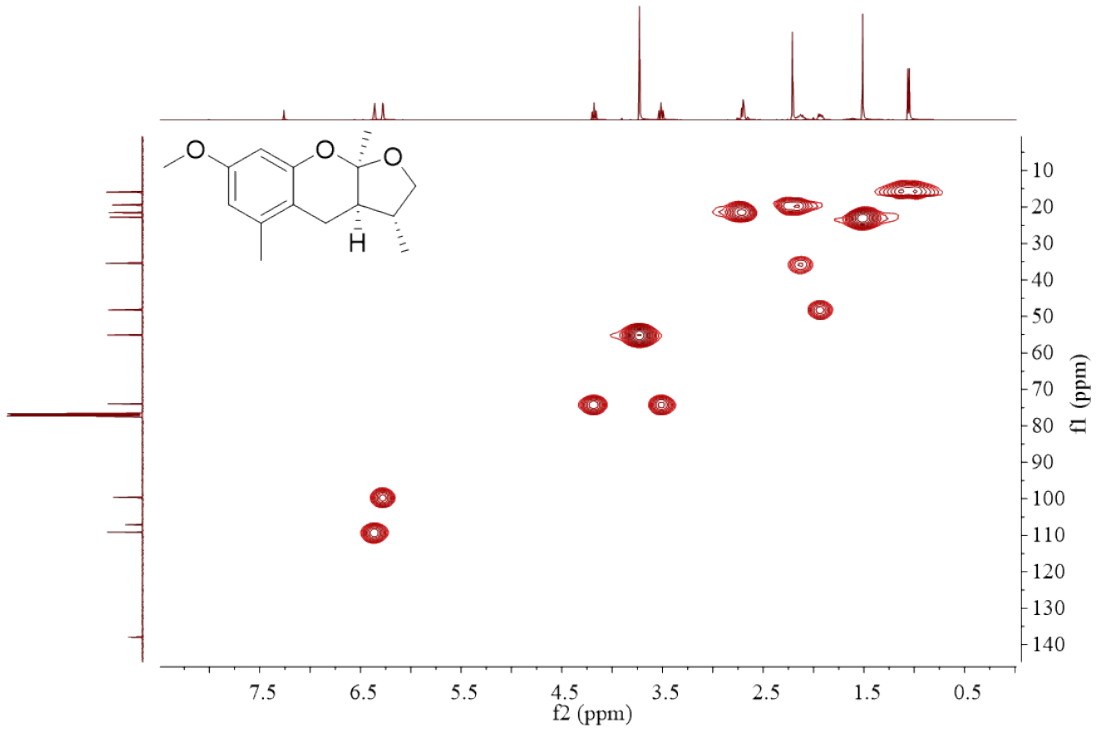


Figure S26. HSQC NMR spectrum of 4 in $CDCl_3$ at 400 MHz.

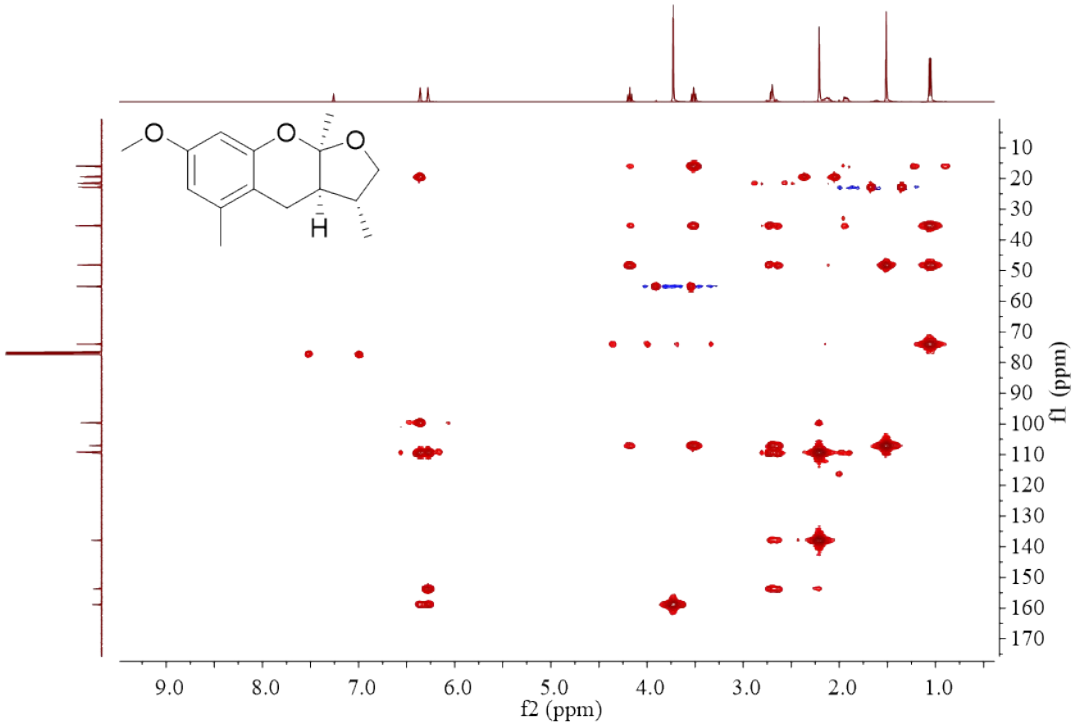


Figure S27. HMBC spectrum of 4 in $CDCl_3$ at 400 MHz.

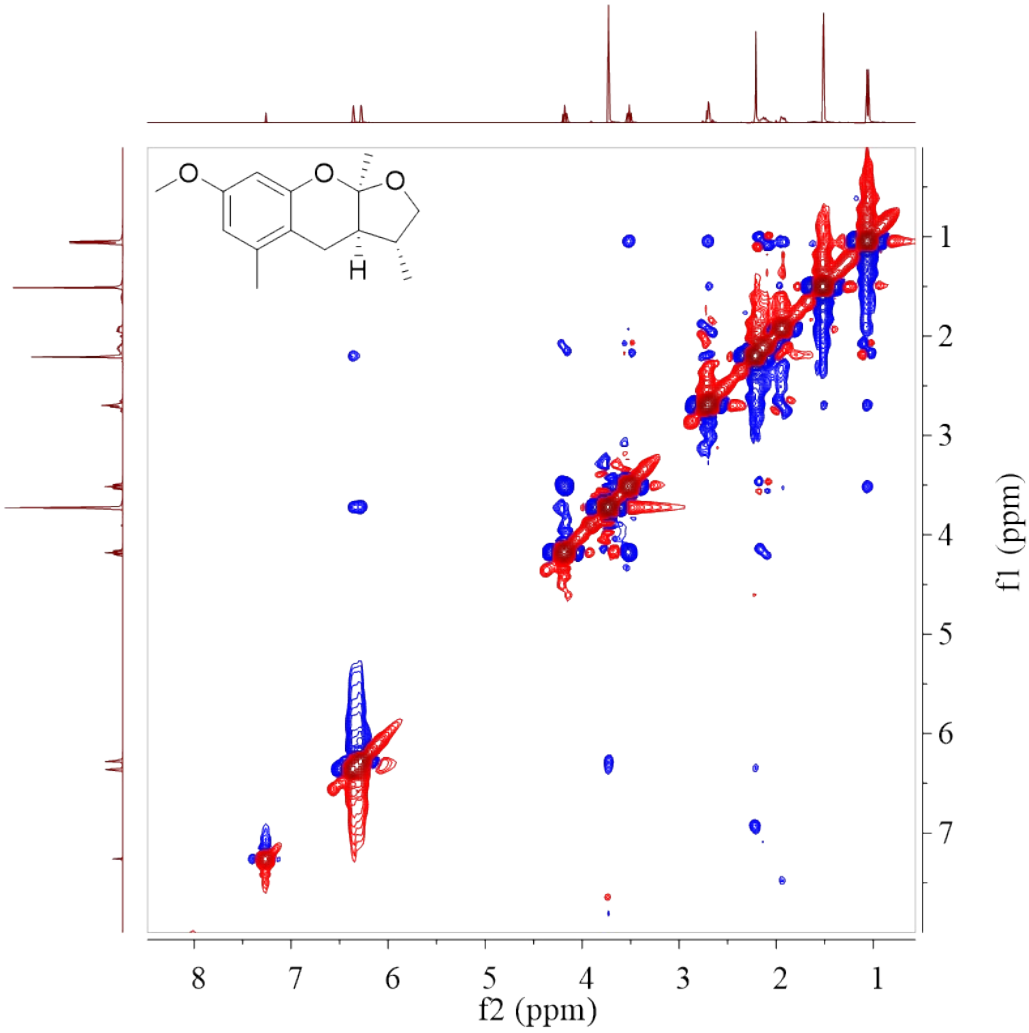


Figure S28. ROESY spectrum of 4 in $CDCl_3$ at 400 MHz.

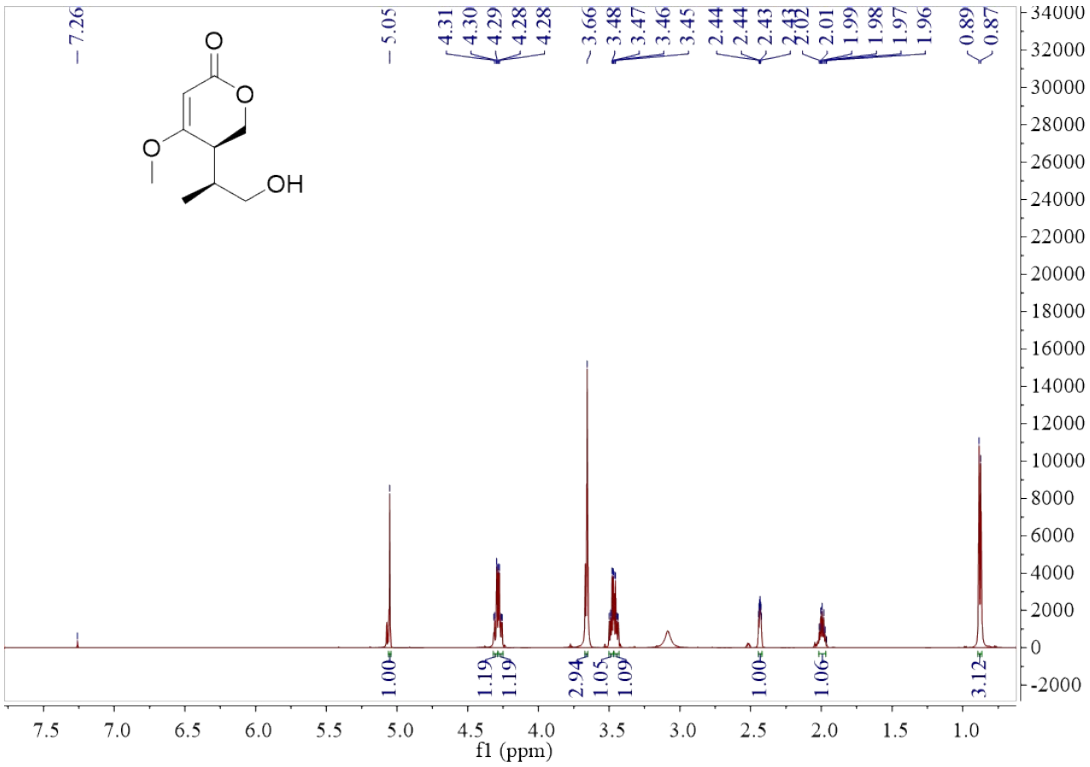


Figure S29. ^{1}H NMR spectrum of 5 in $CDCl_3$ at 600 MHz.

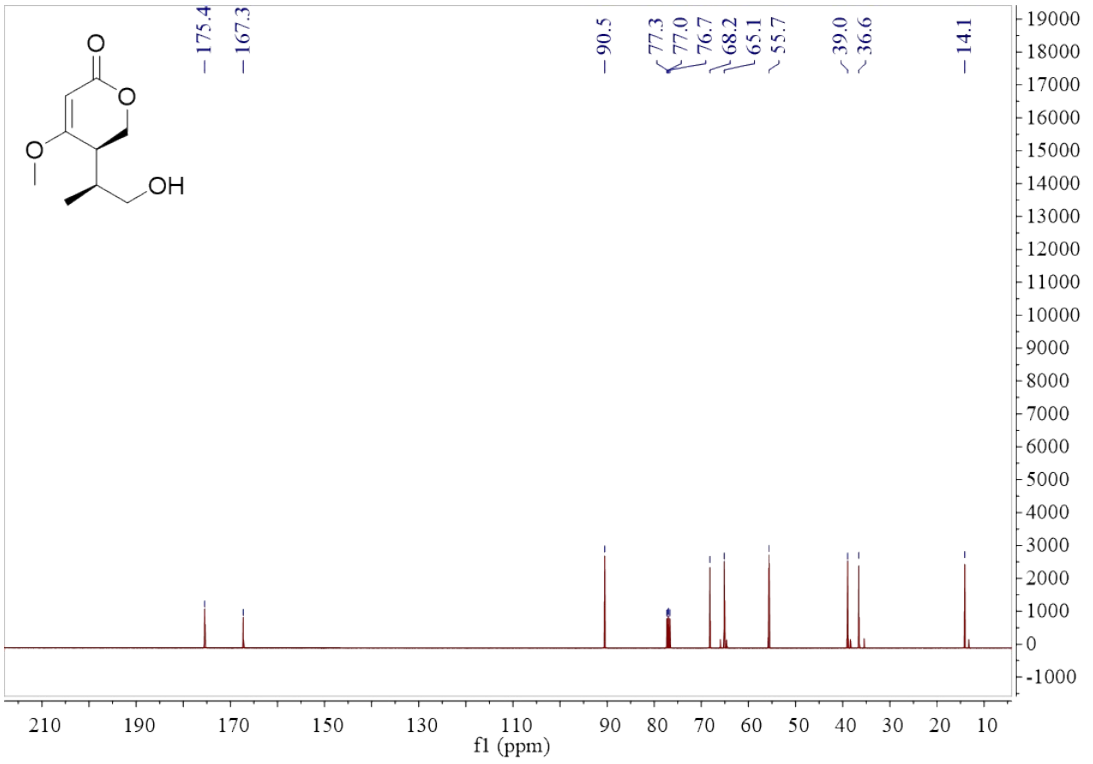


Figure S30. ^{13}C NMR spectrum of 5 in $CDCl_3$ at 100 MHz.

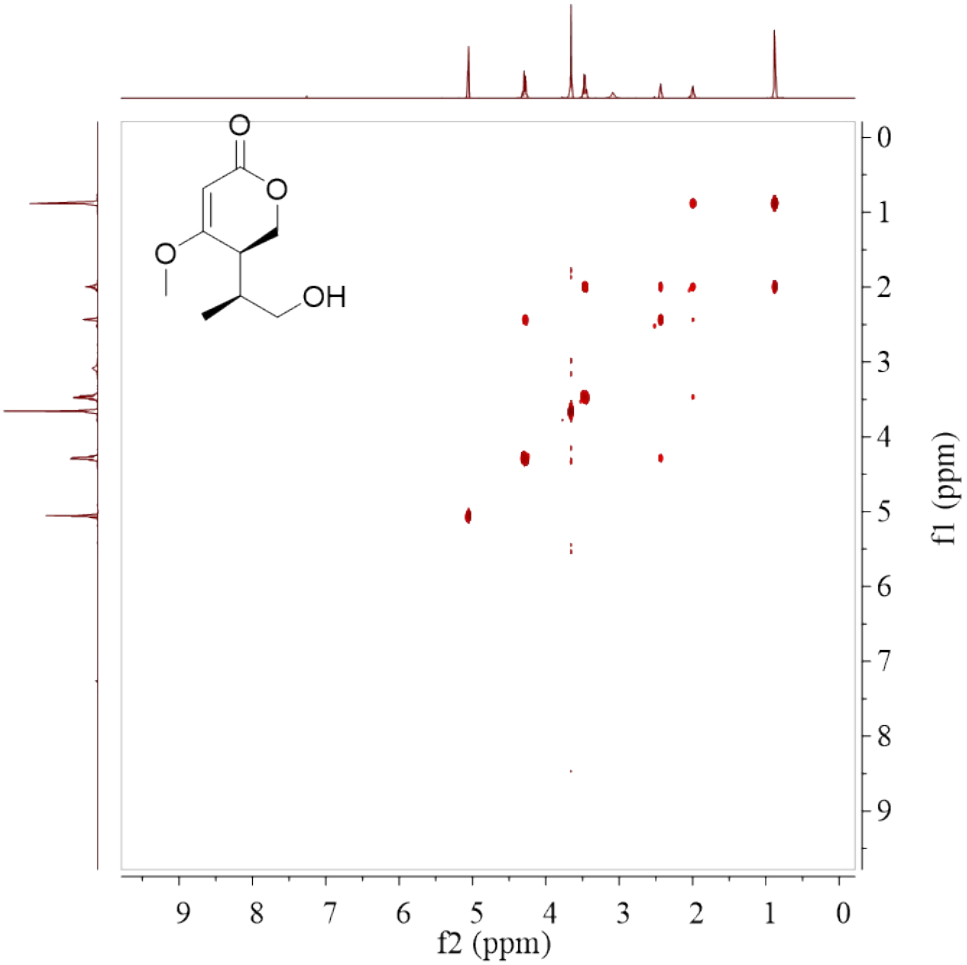


Figure S31. ^{1}H-^{1}H COSY spectrum of 5 in $CDCl_3$ at 600 MHz.

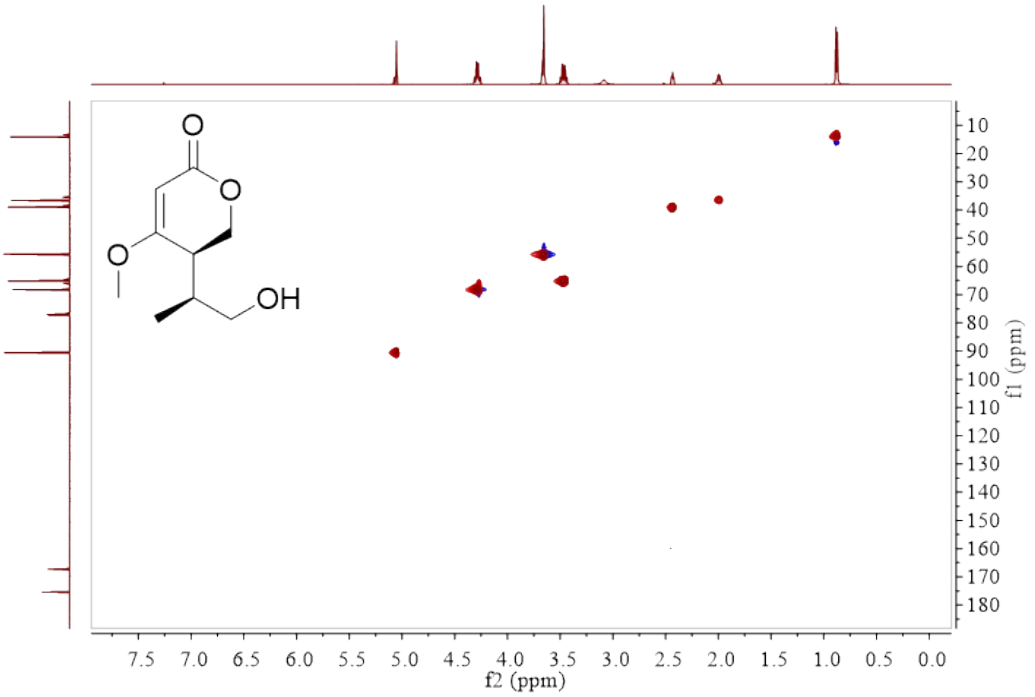


Figure S32. HSQC spectrum of 5 in $CDCl_3$ at 600 MHz.

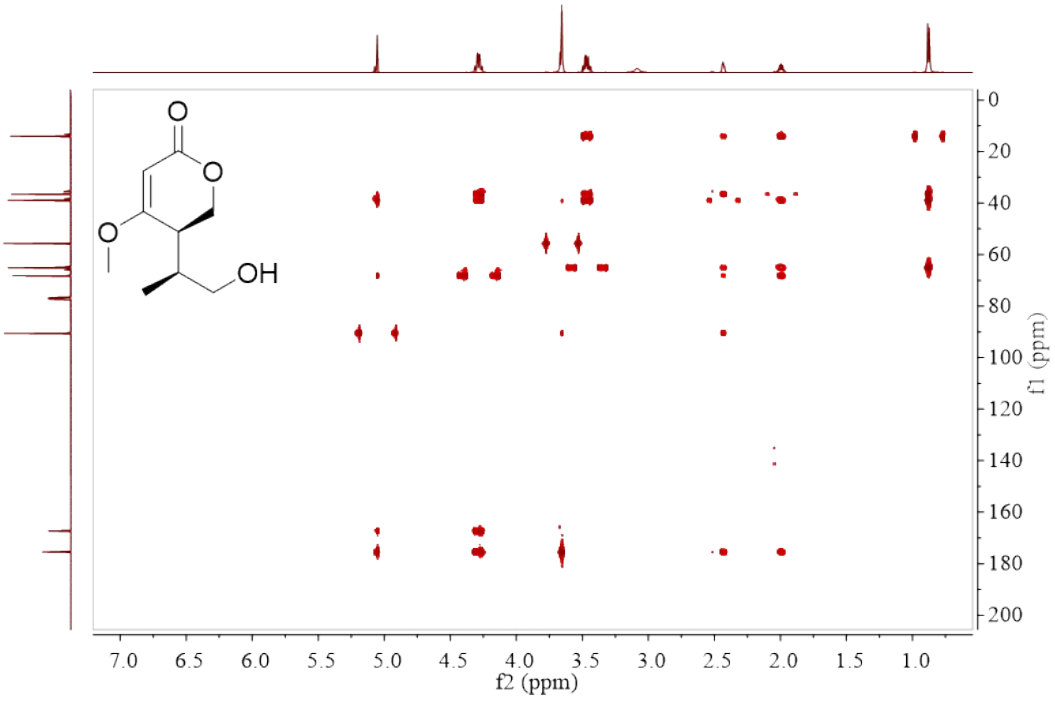


Figure S33. HMBC spectrum of 5 in $CDCl_3$ at 600 MHz.

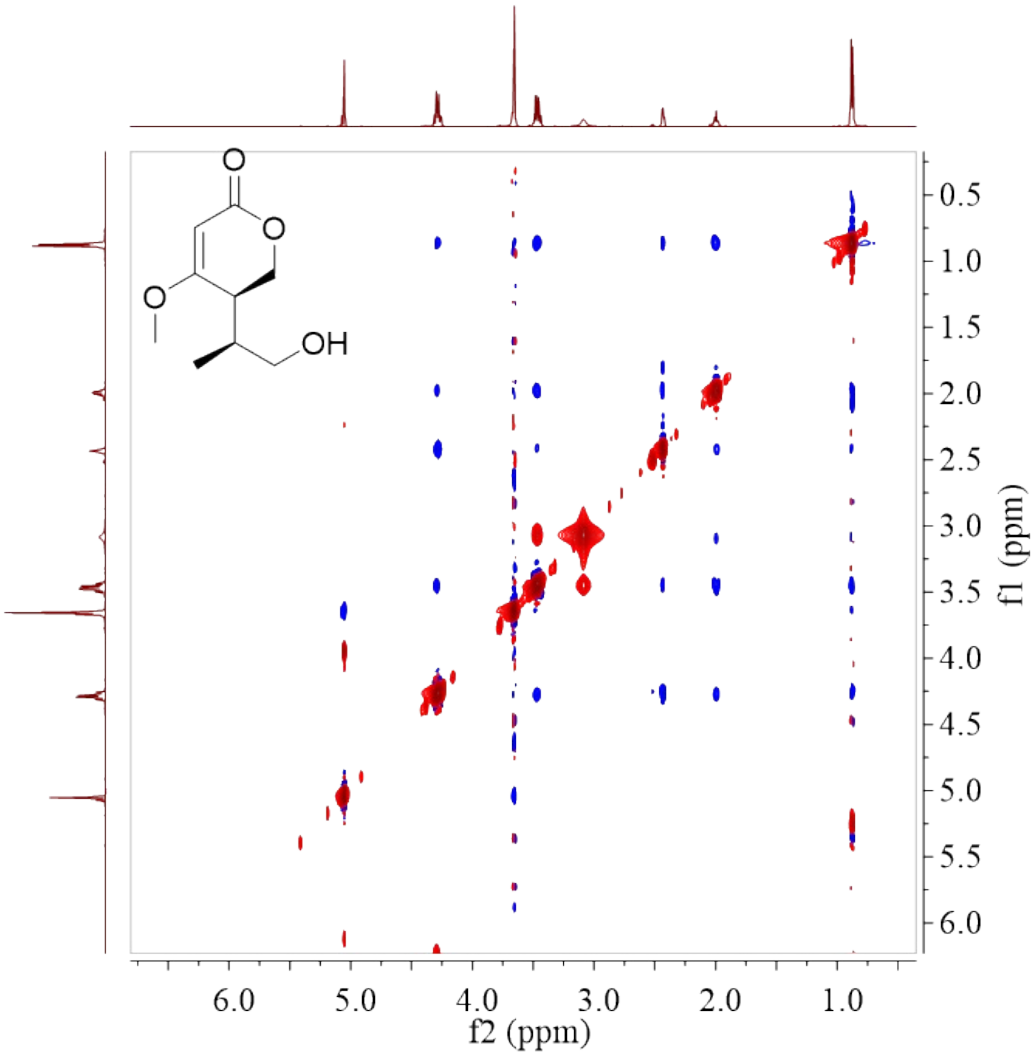


Figure S34. NOESY spectrum of 5 in $CDCl_3$ at 600 MHz.

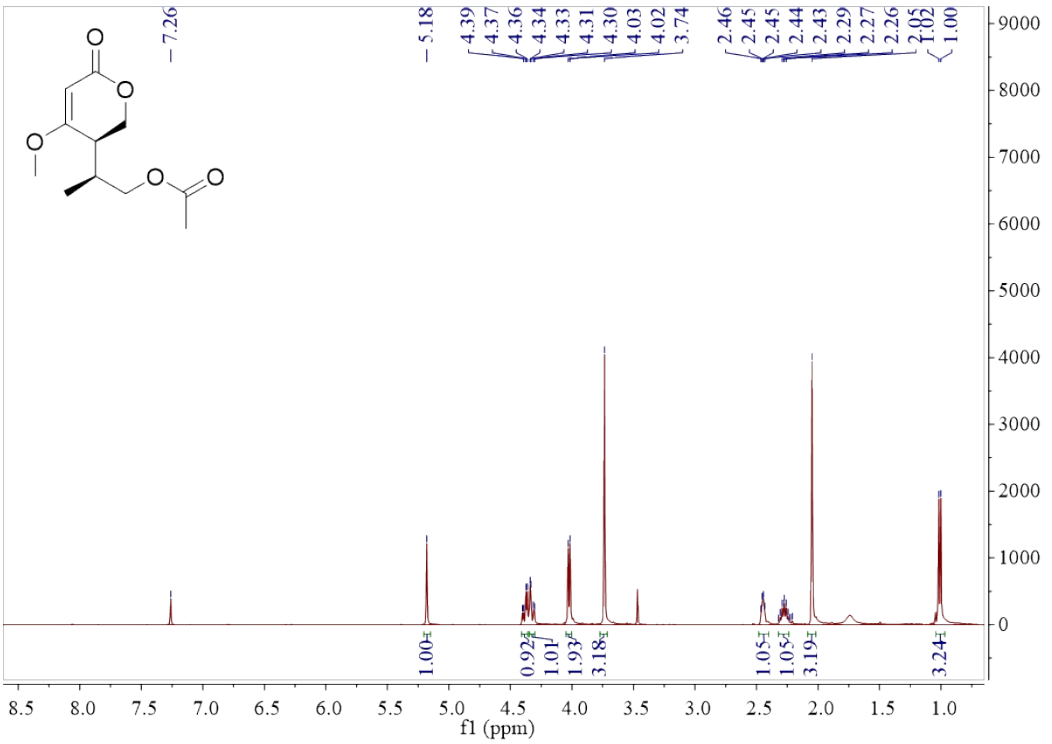


Figure S35. ^{1}H NMR spectrum of 6 in $CDCl_3$ at 400 MHz.

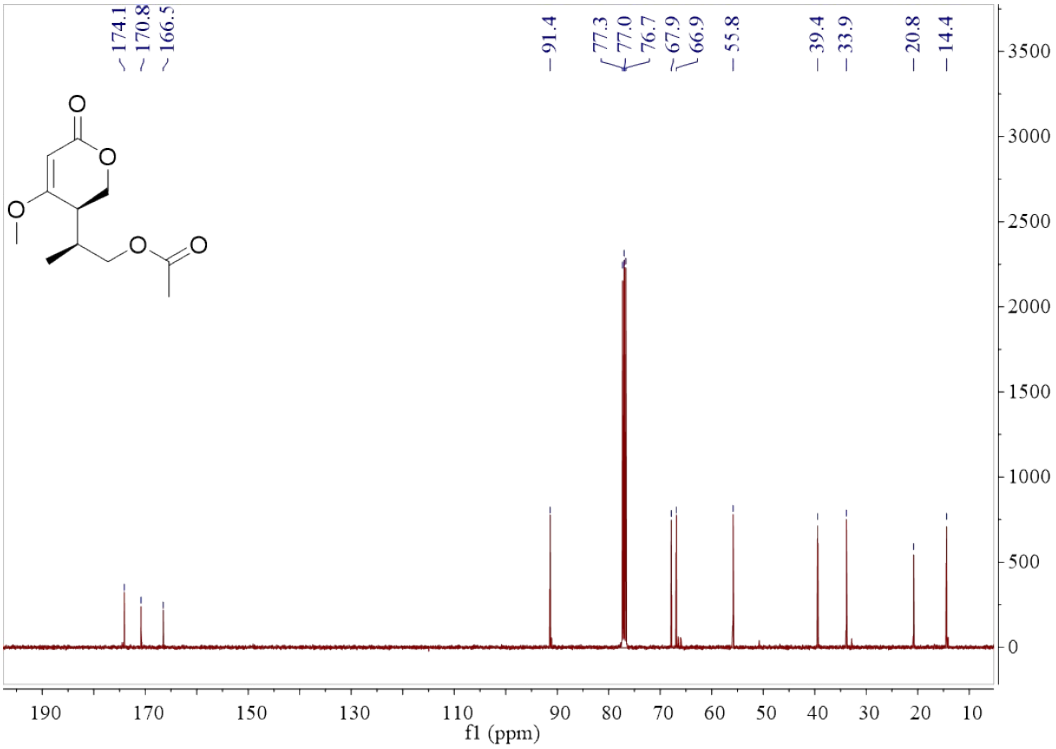


Figure S36. ^{13}C NMR spectrum of 6 in $CDCl_3$ at 100 MHz.

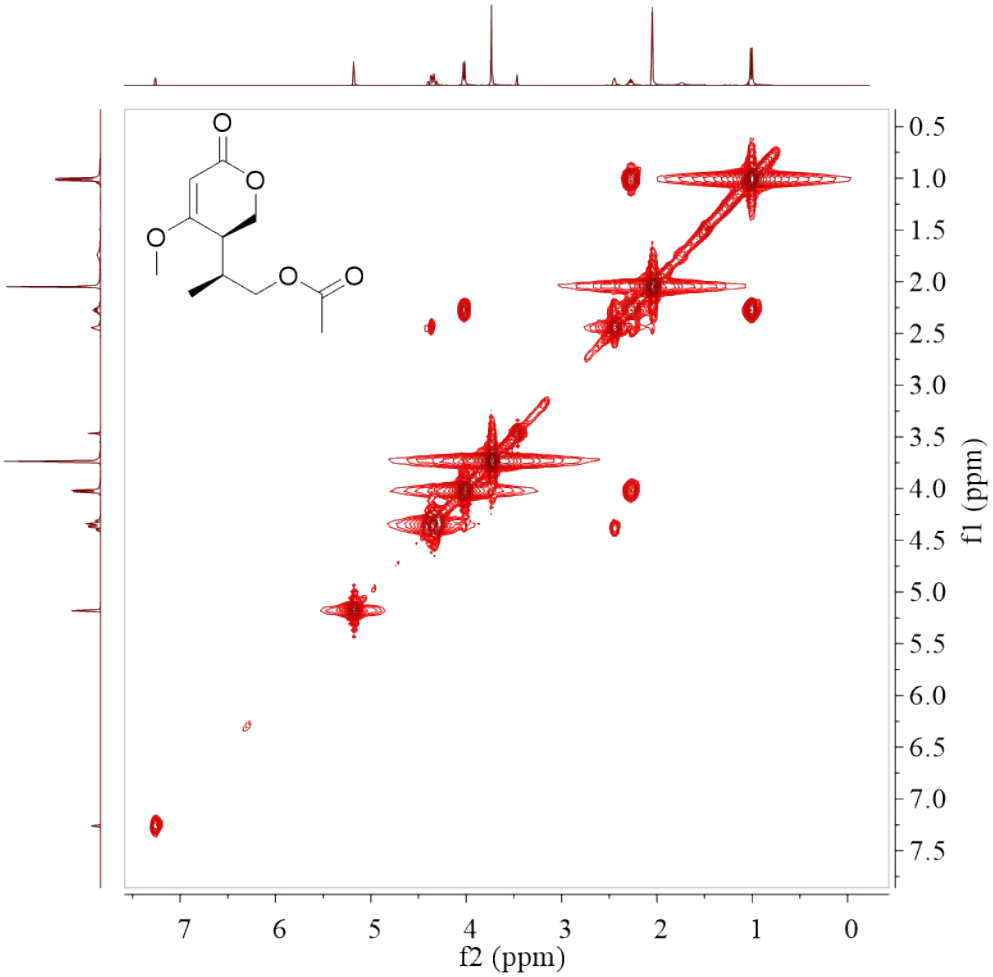


Figure S37. ^{1}H -^{1}H COSY spectrum of 6 in $CDCl_3$ at 400 MHz.

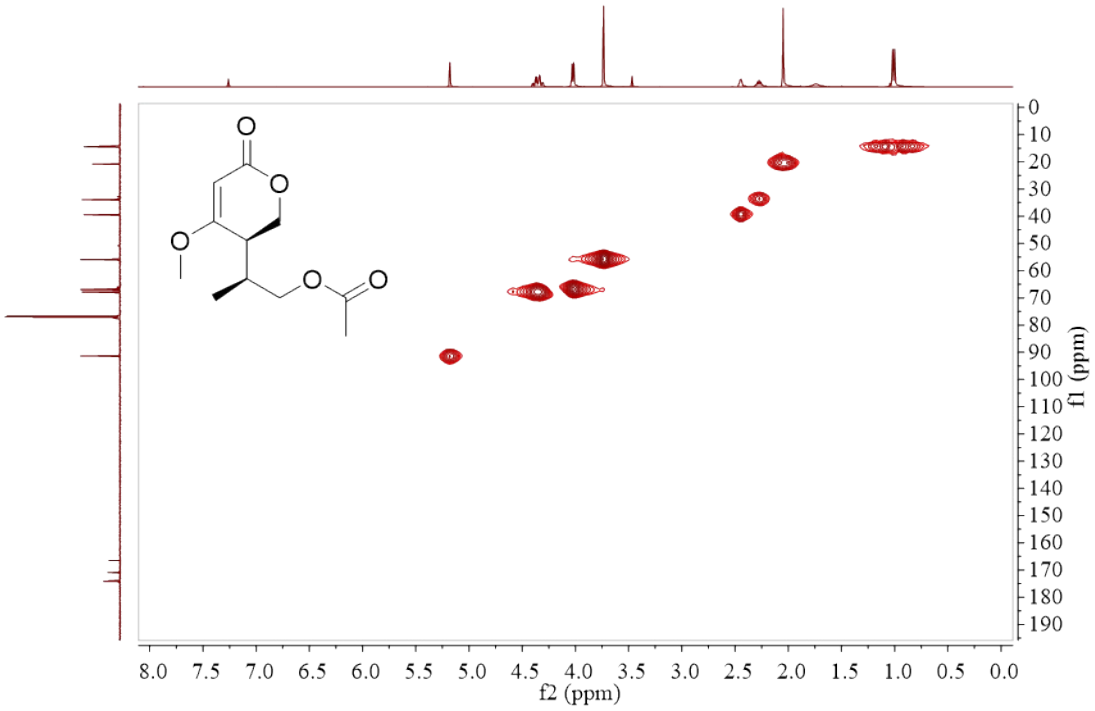


Figure S38. HSQC spectrum of 6 in $CDCl_3$ at 400 MHz.

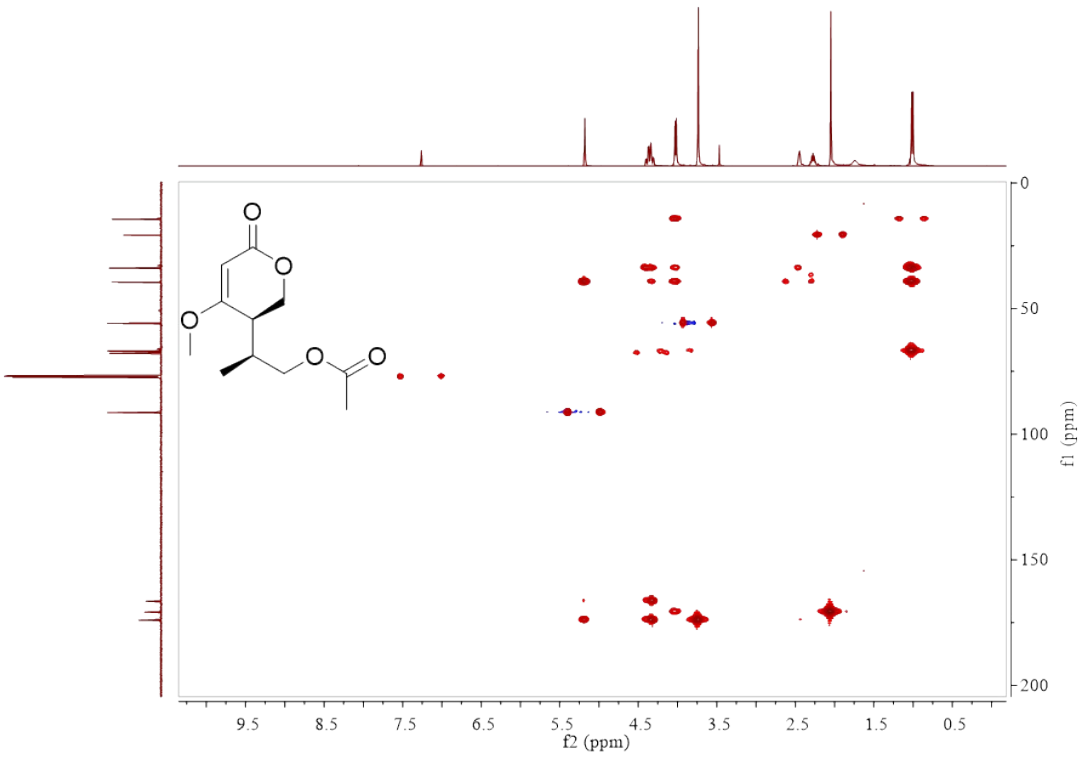


Figure S39. HMBC spectrum of 6 in $CDCl_3$ at 400 MHz.

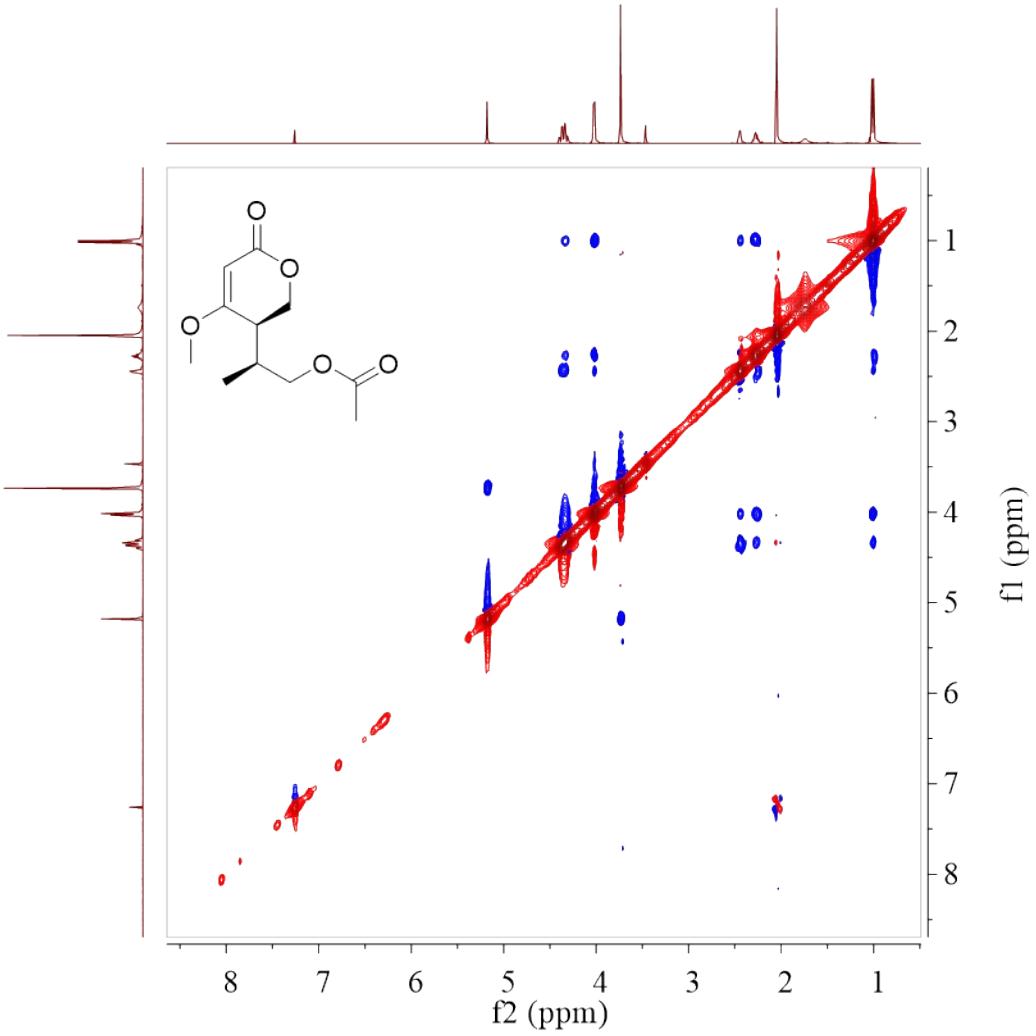


Figure S40. NOESY spectrum of 6 in $CDCl_3$ at 600 MHz.

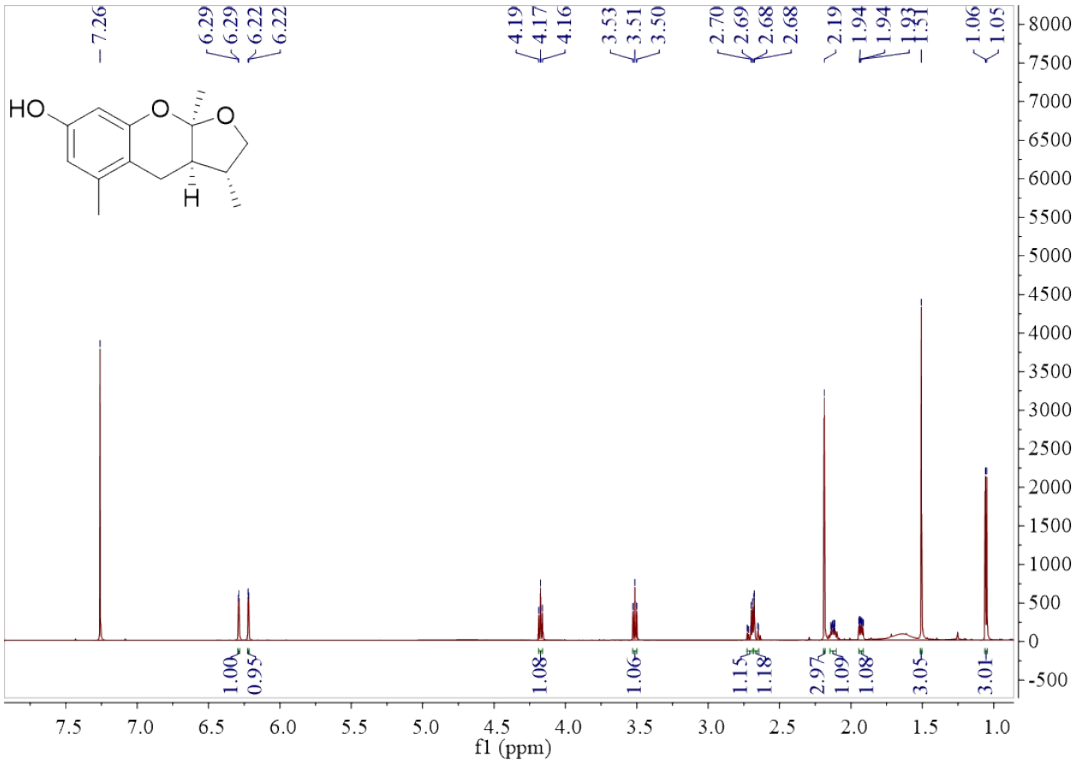


Figure S41. ^{1}H NMR spectrum of 7 in $CDCl_3$ at 600 MHz.

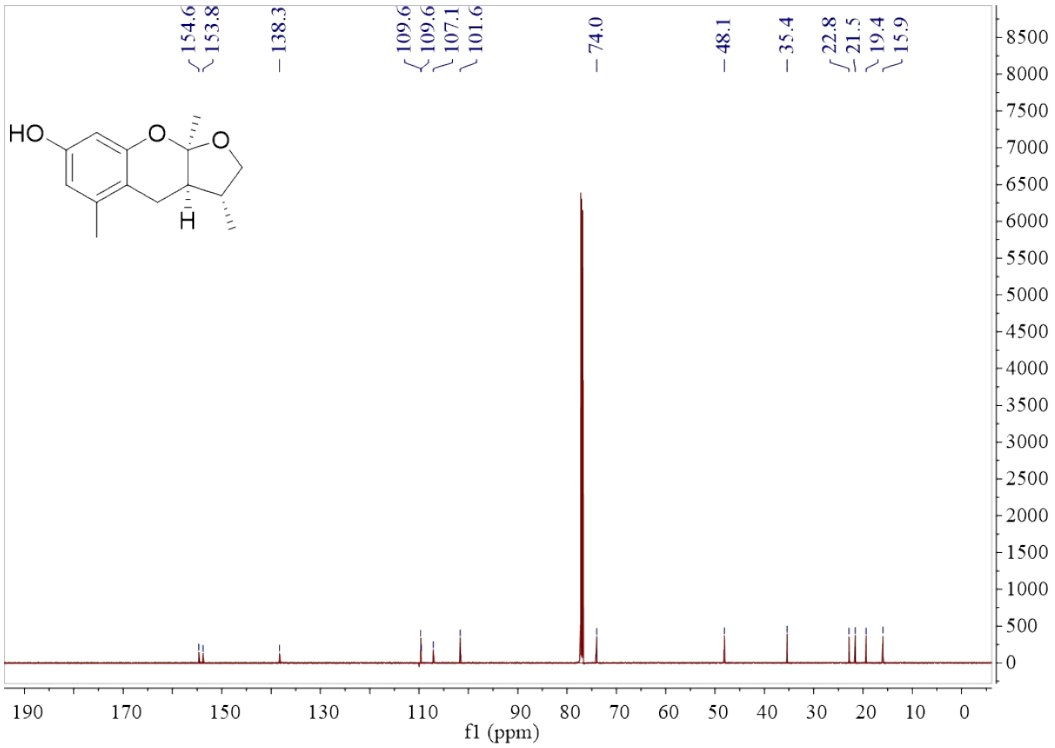


Figure S42. ^{13}C NMR spectrum of 7 in $CDCl_3$ at 150 MHz.

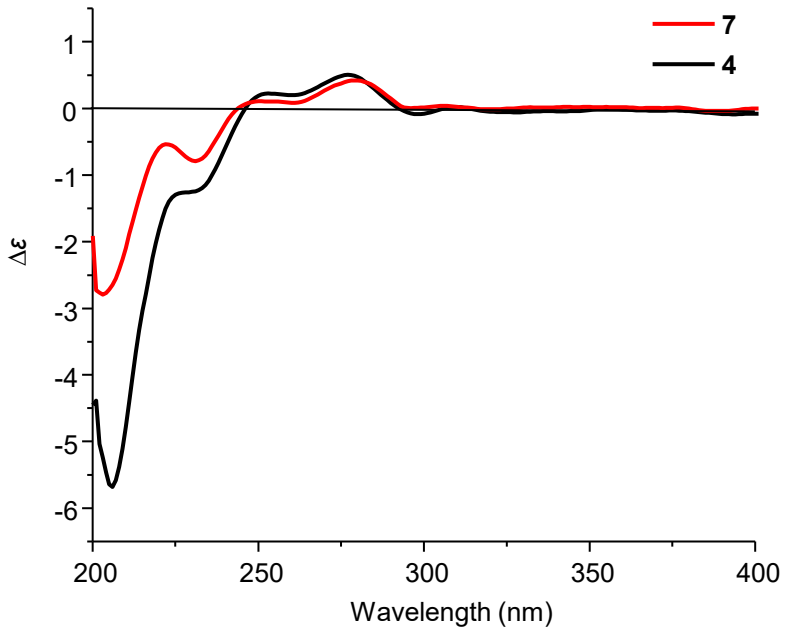


Figure S43. ECD spectra of 4 and 7.

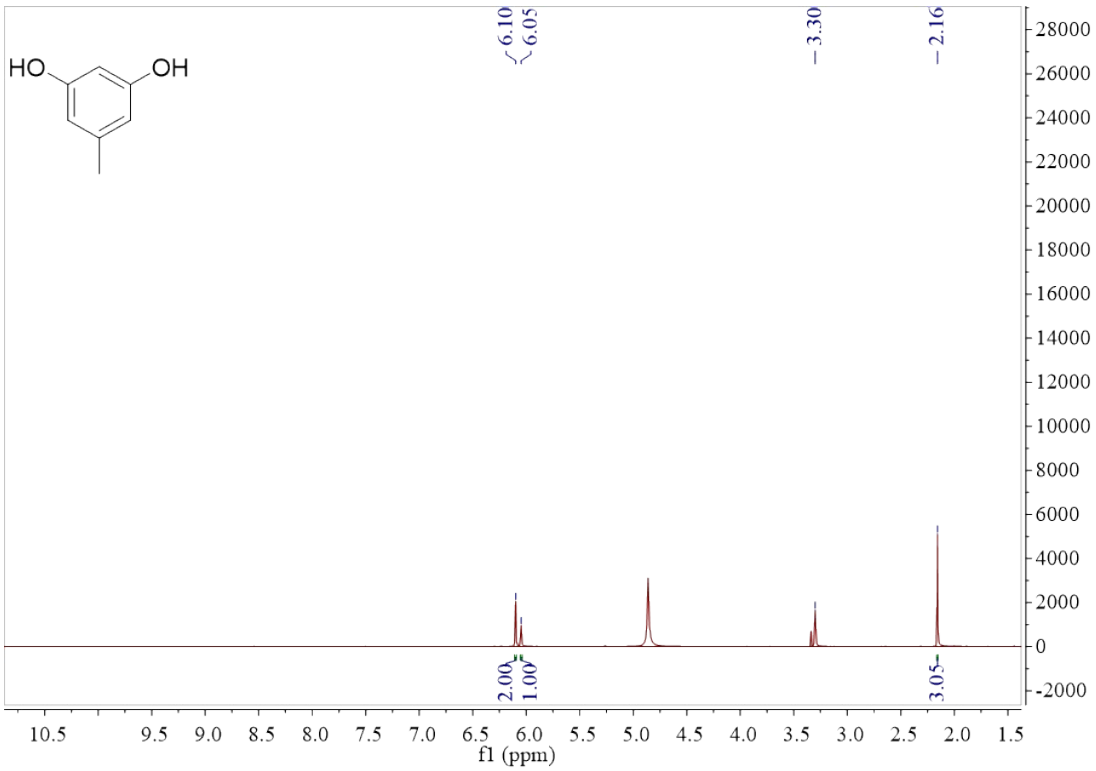


Figure S44. ^{1}H NMR spectrum of 8 in CD_3OD at 400 MHz.

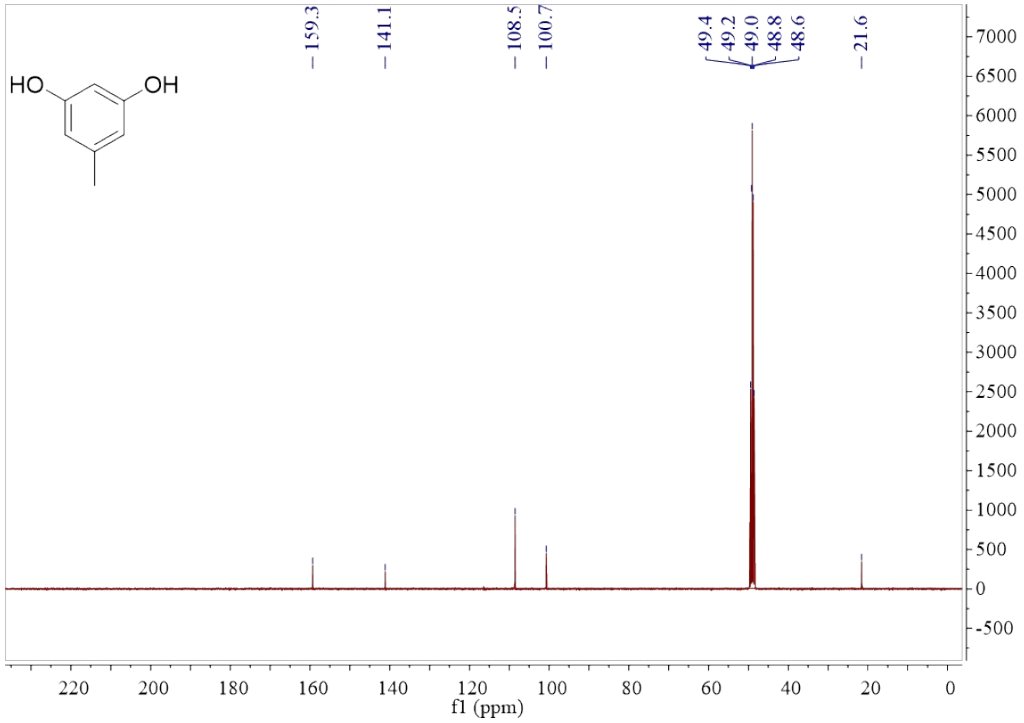


Figure S45. ^{13}C NMR spectrum of 8 in CD_3OD at 100 MHz.

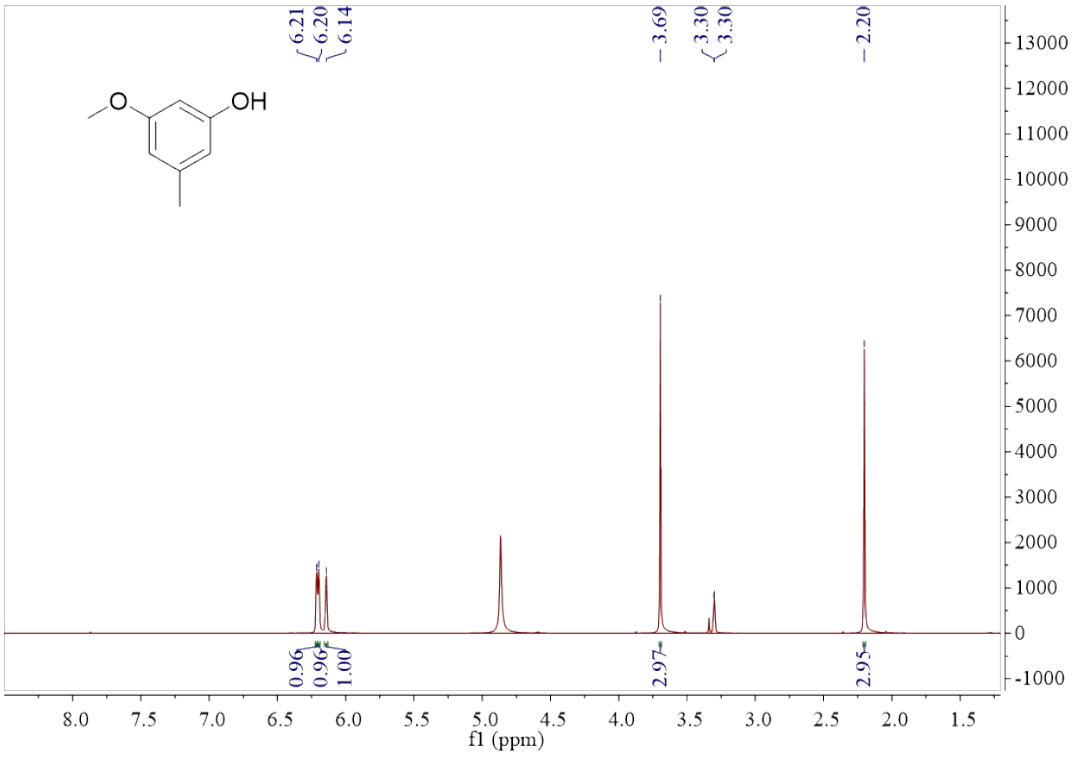


Figure S46. ^{1}H NMR spectrum of 9 in CD_3OD at 400 MHz.

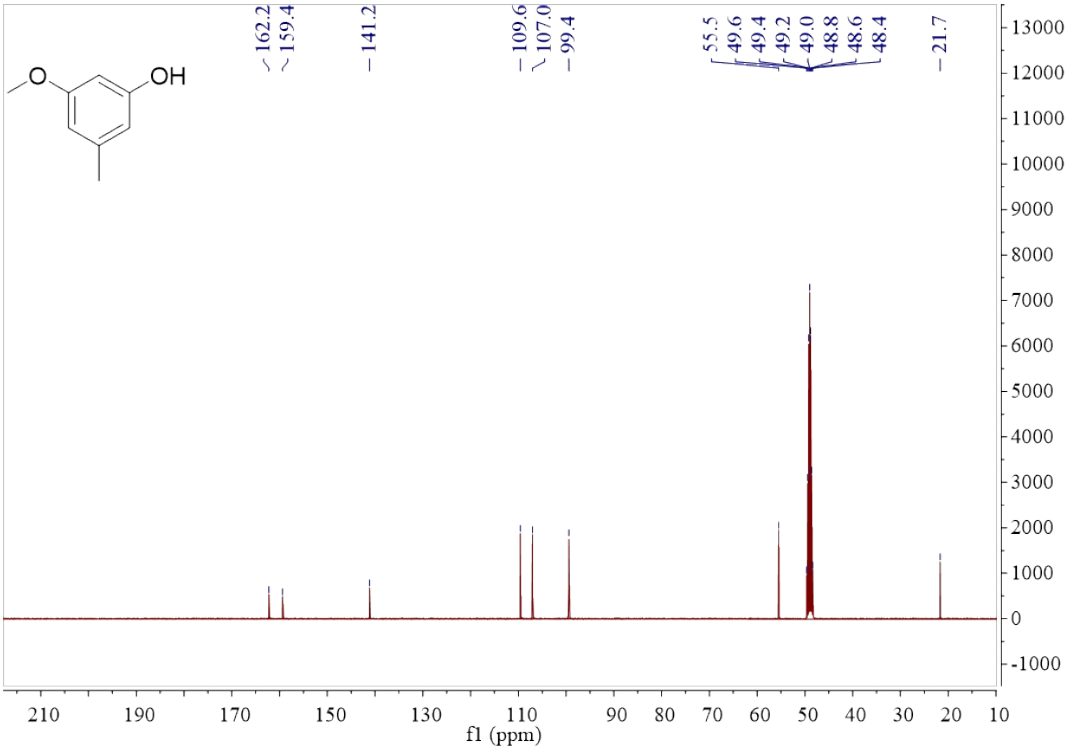


Figure S47. ^{13}C NMR spectrum of 9 in CD_3OD at 100 MHz.

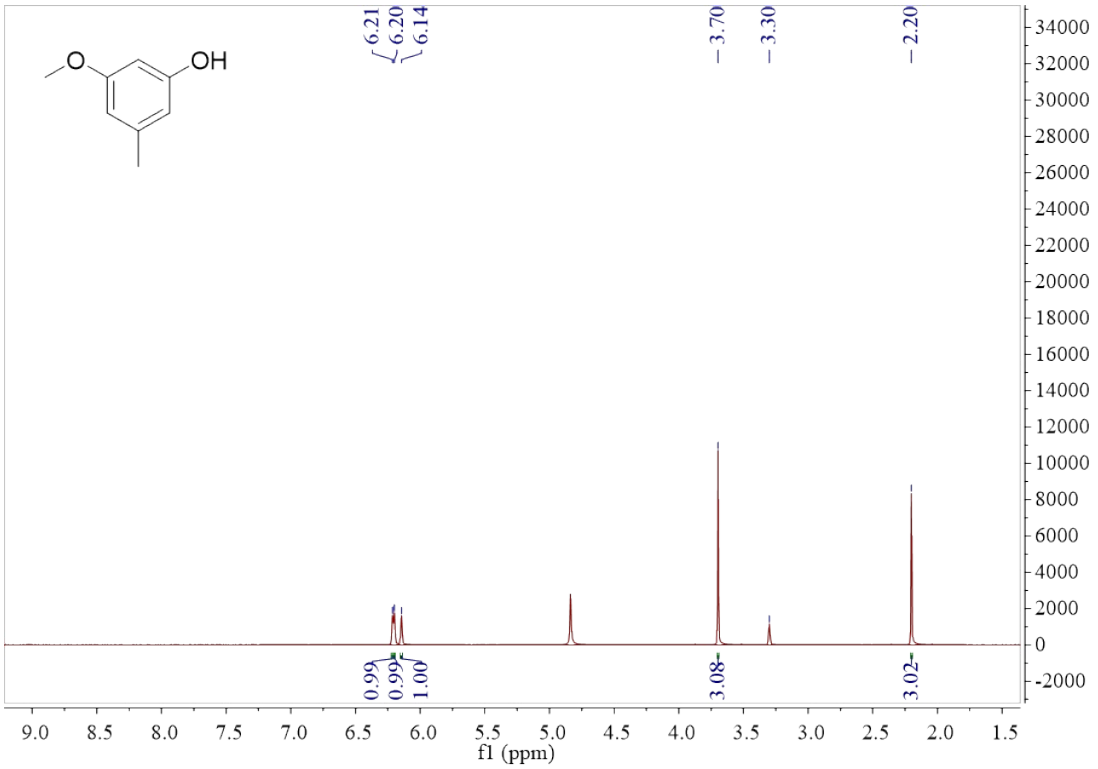


Figure S48. ^{1}H NMR spectrum of authentic *O*-methylorcinol in CD_3OD at 400 MHz.

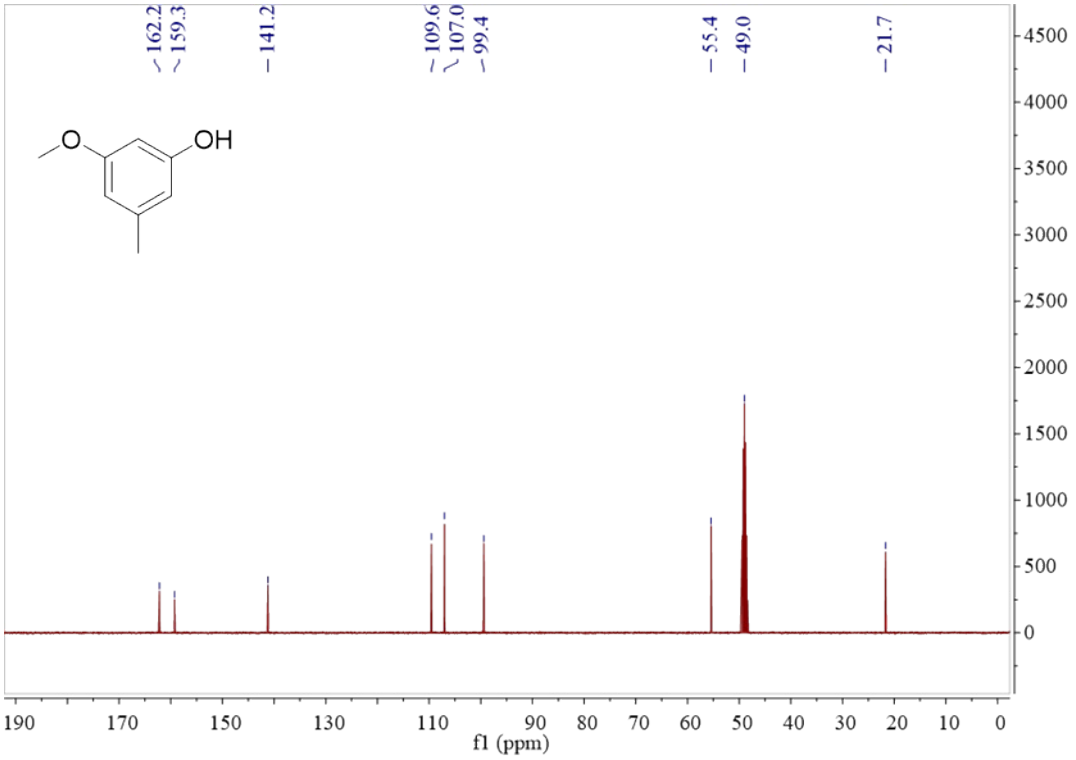


Figure S49. ^{13}C NMR spectrum of authentic *O*-methylorcinol in CD_3OD at 400 MHz.

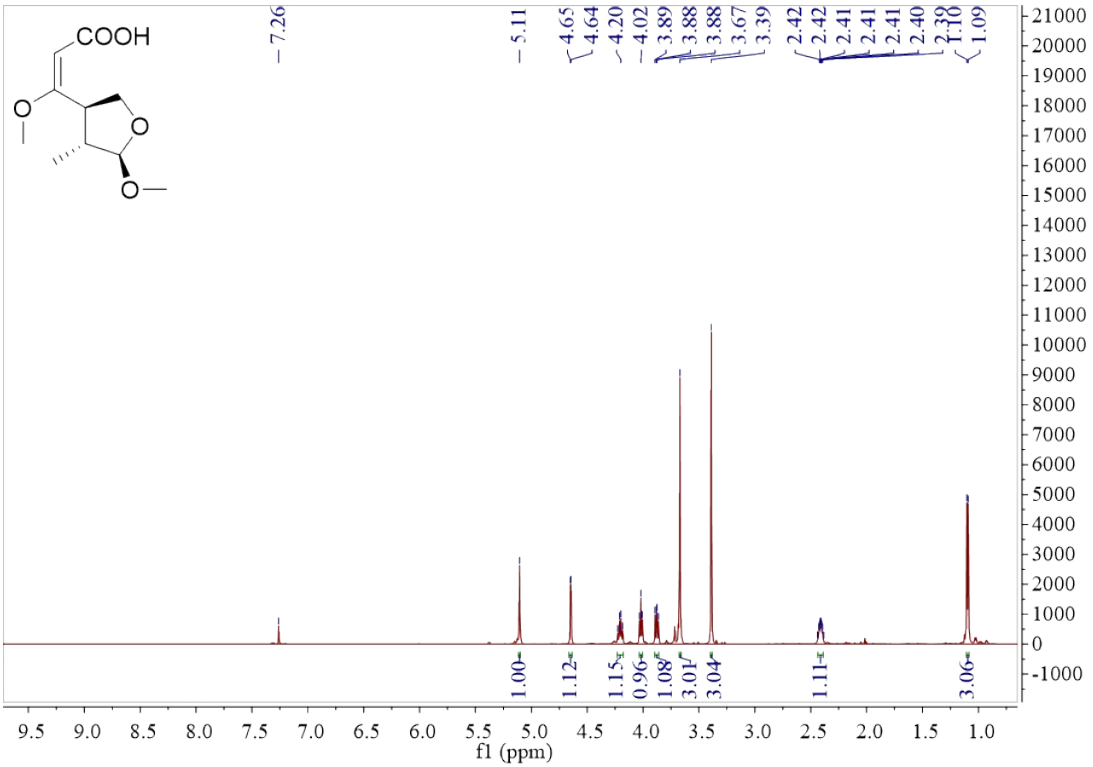


Figure S50. ^{1}H NMR spectrum of 10 in $CDCl_3$ at 400 MHz.

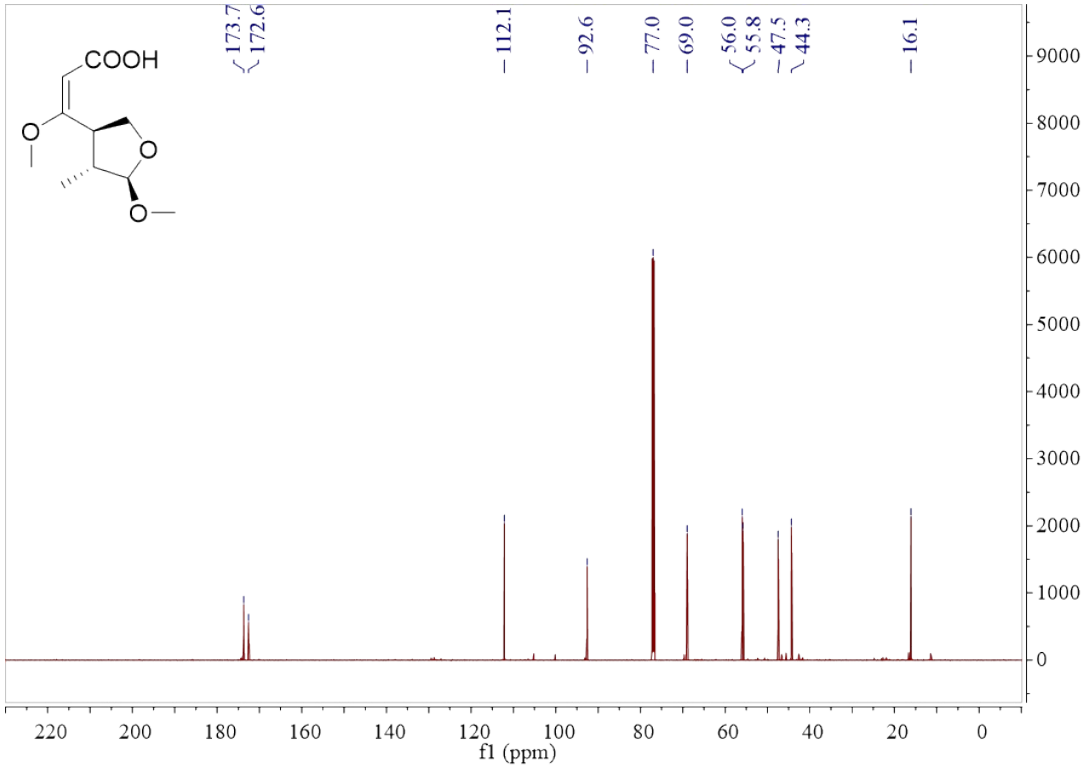


Figure S51. ^{13}C NMR spectrum of 10 in $CDCl_3$ at 100 MHz.

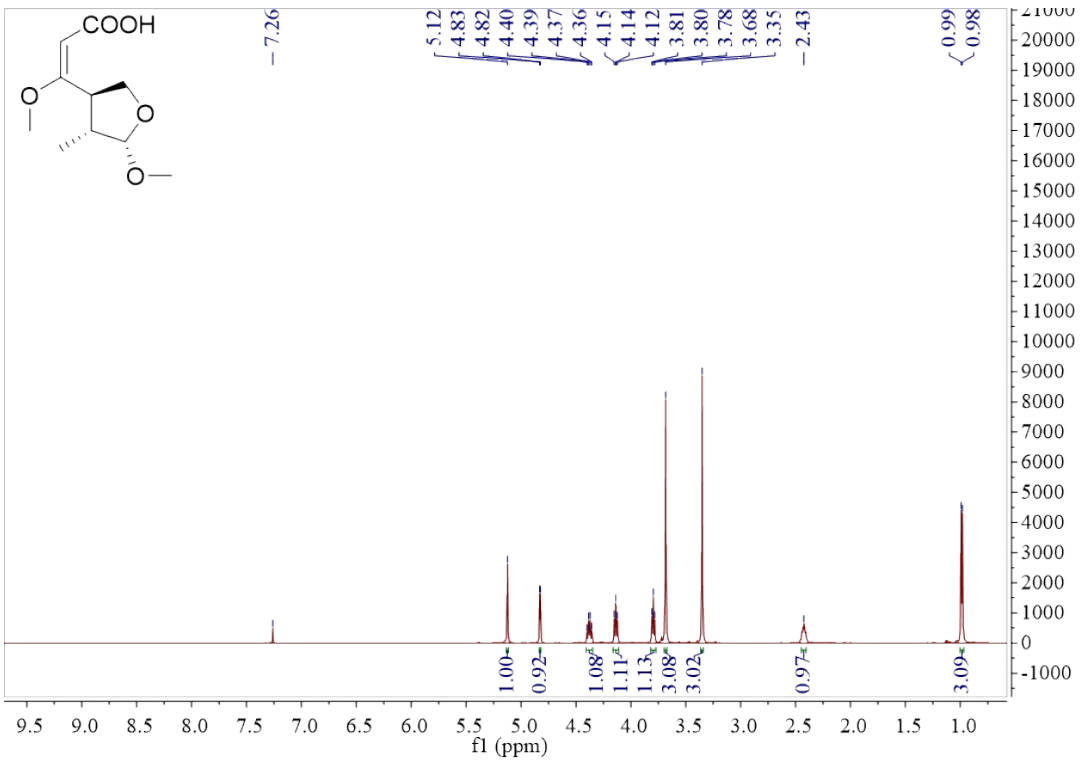


Figure S52. ^{1}H NMR spectrum of 11 in $CDCl_3$ at 600 MHz.

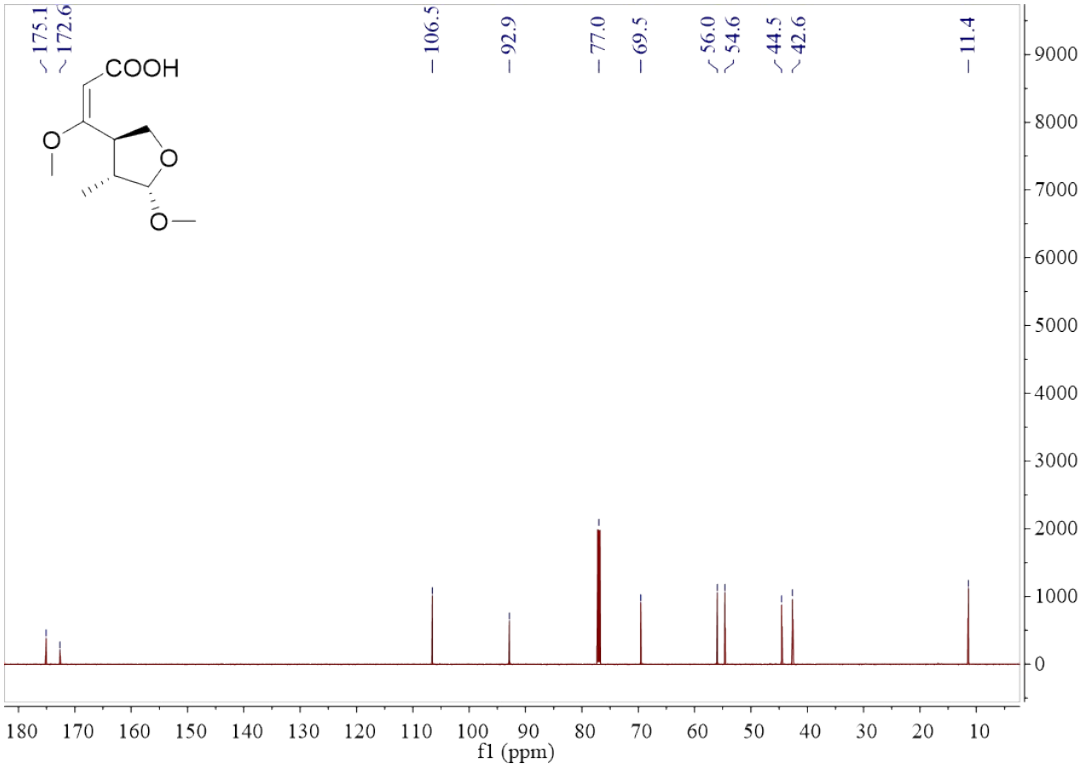


Figure S53. ^{13}C NMR spectrum of 11 in $CDCl_3$ at 150 MHz.

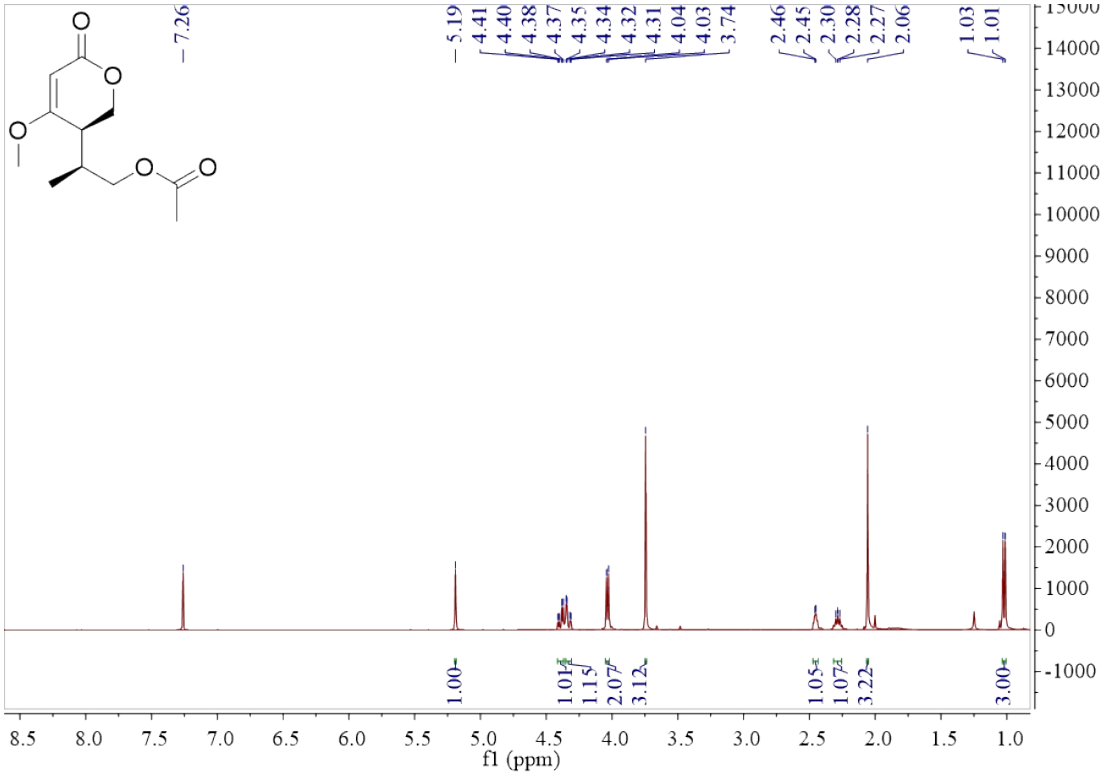


Figure S54. ^{1}H NMR spectrum of Ac-5 in $CDCl_3$ at 400 MHz.

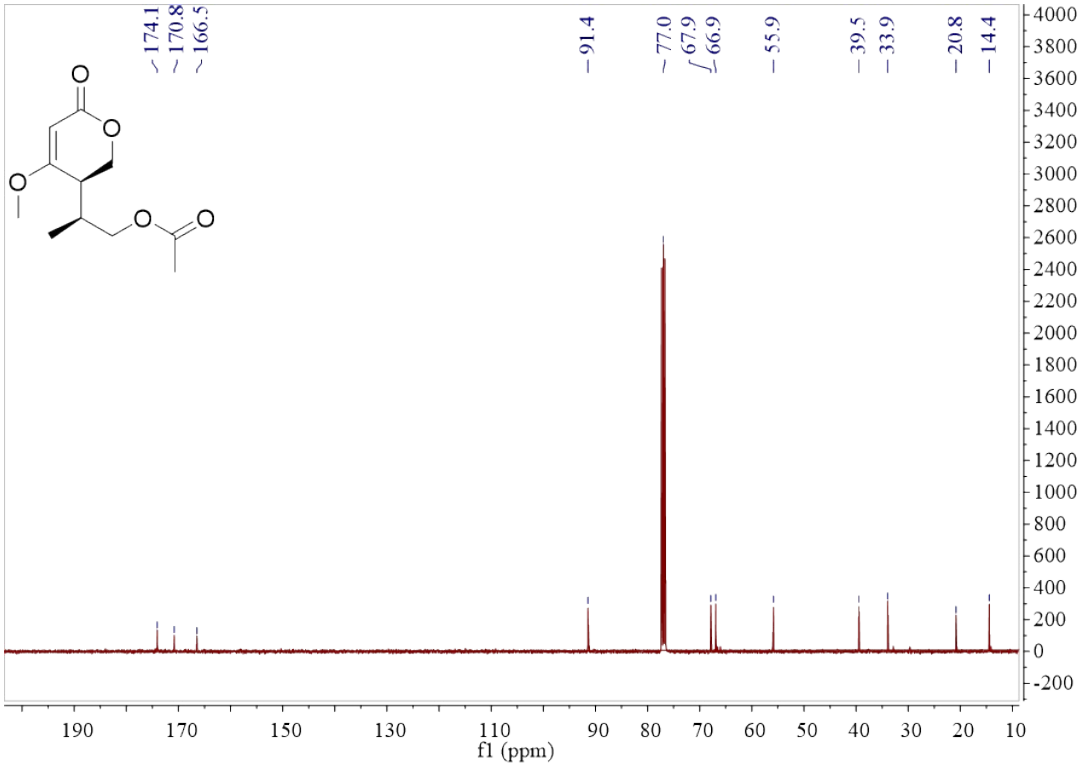


Figure S55. ^{13}C NMR spectrum of Ac-5 in $CDCl_3$ at 100 MHz.