

Supplementary Information

Phragmalin Limonoids from *Swietenia macrophylla* and Their Antifeedant Assay against Mahogany Predator

Sônia G. S. R. Pamplona,^a Mara S. P. Arruda,^a Kelly C. F. Castro,^b
Consuelo Y. Y. e Silva,^c Antonio G. Ferreira,^d Maria F. G. F. da Silva,^d
Orlando S. Ohashi^e and Milton N. da Silva^{*a}

^aLaboratório de Cromatografia Líquida, Instituto de Ciências Exatas e Naturais,
Universidade Federal do Pará, 66075-110 Belém-PA, Brazil

^bDepartamento de Biotecnologia, Universidade Federal do Oeste Paraense,
68035-110 Santarém-PA, Brazil

^cInstituto de Ciências da Saúde, Faculdade de Farmácia, Universidade Federal do Pará,
66074-110 Belém-PA, Brazil

^dDepartamento de Química, Universidade Federal de São Carlos,
13565-905 São Carlos-SP, Brazil

^eDepartamento de Entomologia, Universidade Federal Rural da Amazônia,
66077-830 Belém-PA, Brazil

12 α -Acetoxyl-20 β ,21 β -22 α ,23 α -diepoxyswietenphragmin C (**1**)

Amorphous white solid; $[\alpha]_D^{25} +53.3$ (*c* 0.012, CHCl₃); IR (film) ν_{\max} / cm⁻¹ 3389.4 (OH), 1733 (carboxyl group); ¹H NMR (400 MHz, CDCl₃), see Table S1; ¹³C NMR (75 MHz, CDCl₃), see Table S2; HR-ESI-ToF-MS at *m/z* 795.2846 [M + Na]⁺ (calculated for C₃₉H₄₈O₁₆Na, 795.2840).

12 α -Acetoxyswietenphragmin I (**2**)

Amorphous white solid; $[\alpha]_D^{25} +63.1$ (*c* 0.051, CHCl₃); IR (film) ν_{\max} / cm⁻¹ 3456.6 (OH), 1731 (carboxyl group); ¹H NMR (400 MHz, CDCl₃), see Table S1; ¹³C NMR (75 MHz, CDCl₃), see Table S2; HR-ESI-ToF-MS at *m/z* 763.2581 [M + Na]⁺ (calculated for C₃₈H₄₄O₁₅Na, 763.2578).

3 β -*O*-Detigloyl-3 β -*O*-benzoyl-12 α -acetoxyswietenphragmin I (**3**)

Amorphous white solid; $[\alpha]_D^{25} +21.1$ (*c* 0.1, CHCl₃); IR (film) ν_{\max} / cm⁻¹ 3398.5 (OH), 1730 (carboxyl group); ¹H NMR (400 MHz, CDCl₃), see Table S1; ¹³C NMR (75 MHz, CDCl₃), see Table S2; HR-ESI-ToF-MS at *m/z* 763.2581 [M + H]⁺ (calculated for C₄₀H₄₃O₁₅, 763.2602).

12 α -Acetoxyl-8,9,30-*ortho*-tigloylate-swietemacrophine (**4**)

Amorphous white solid; $[\alpha]_D^{25} +27.7$ (*c* 0.035, CHCl₃); IR (film) ν_{\max} / cm⁻¹ 3492.2 (OH), 1735 (carboxyl group); ¹H NMR (300 MHz, CDCl₃), see Table S1; ¹³C NMR (75 MHz, CDCl₃), see Table S2; HR-ESI-ToF-MS at *m/z* 739.2952 [M + H]⁺ (calculated for C₃₉H₄₇O₁₄, 739.2965).

*e-mail: yumilton@yahoo.com.br

2-Deacetyl-6-acetoxy-swietephragmin I (**5**)

Amorphous white solid; $[\alpha]_D^{25} +49.3$ (c 0.314, CHCl_3); IR (KBr) $\nu_{\text{max}} / \text{cm}^{-1}$ 3575 (OH), 1730 (carboxyl group); ^1H NMR (300 MHz, CDCl_3), see Table S1; ^{13}C NMR (75 MHz, CDCl_3), see Table S2; HR-ESI-ToF-MS at m/z 721.2488 $[\text{M} + \text{Na}]^+$ (calculated for $\text{C}_{36}\text{H}_{42}\text{O}_{14}\text{Na}$, 721.2472).

2-Deacetyl-12 α -acetoxy-swietephragmin I (**6**)

Amorphous white solid; $[\alpha]_D^{25} +67.6$ (c 0.278, CHCl_3); IR (KBr) $\nu_{\text{max}} / \text{cm}^{-1}$ 3550 (OH), 1735 (carboxyl group); ^1H NMR (300 MHz, CDCl_3), see Table S1; ^{13}C NMR (75 MHz, CDCl_3), see Table S2; HR-ESI-ToF-MS at m/z 721.2488 $[\text{M} + \text{Na}]^+$ (calculated for $\text{C}_{36}\text{H}_{42}\text{O}_{14}\text{Na}$, 721.2472).

3 β -*O*-Detigloyl-3 β -*O*-benzoyl-6-*O*-acetylswietephragmin D (**7**)

Amorphous white solid; $[\alpha]_D^{25} +41.3$ (c 0.023, CHCl_3); IR (film) $\nu_{\text{max}} / \text{cm}^{-1}$ 3467.9 (OH), 1730 (carboxyl group); ^1H NMR (300 MHz, CDCl_3), see Table S1; ^{13}C NMR (75 MHz, CDCl_3), see Table S2; HR-ESI-ToF-MS at m/z 749.2764 $[\text{M} + \text{H}]^+$ (calculated for $\text{C}_{40}\text{H}_{45}\text{O}_{14}$, 749.2809).

6-Acetoxy-12 α -deacetoxy-8,9,30-*ortho*-tigloylate-swietemacrophine (**8**)

Amorphous white solid; $[\alpha]_D^{25} +37.5$ (c 0.120, CHCl_3); IR (KBr) $\nu_{\text{max}} / \text{cm}^{-1}$ 3550 (OH), 1730 (carboxyl group); ^1H NMR (300 MHz, CDCl_3), see Table S1; ^{13}C NMR (75 MHz, CDCl_3), see Table S2; HR-ESI-ToF-MS at m/z 761.2819 $[\text{M} + \text{Na}]^+$ (calculated for $\text{C}_{39}\text{H}_{46}\text{O}_{14}\text{Na}$, 761.2785).

Table S1. ¹H NMR chemical shifts for compounds **1-8**

H	1	2	3	4	5	6	7	8
3	4.79 s	5.32 s	5.49 s	4.83 s	4.78 s	4.81 s	5.00 s	4.80 s
5	2.34 brs	2.34 d (11.5)	2.51 d (12.1)	2.42 d (15.6)	2.80 s	2.38 d (2.1)	2.97 brs	2.23 d (2.4)
6 α	3.26 d (14.4)	3.12 d (15.0)	3.20 d (16.4)	3.19 d (15.6)	5.48 s	3.17 d (15.0)	5.54 brs	5.49 s
6 β	2.42 d (14.4)	2.31 d (15.0)	2.39 d (16.4)	2.39 t (15.6)	–	2.40 dd (2.1, 15.0)	–	–
11 α	2.44 dd (13.8, 4.0)	2.28 dd (13.7, 4.0)	2.28 dd (16.8, 4.0)	2.24 dd (14.0, 4.0)	NO	2.20 dd (4.5, 13.8)	2.17 m	NO
11 β	2.20 m	1.99 t (13.7)	2.03 dd (16.8, 13.9)	2.00 t (14.0)	NO	1.97 t (13.8)	NO	NO
12	5.07 dd (13.2, 4.0)	4.83 dd (13.7, 4.0)	4.90 dd (13.9, 4.0)	4.80 dd (14.0, 4.0)	NO	4.76 dd (4.5, 13.8)	1.75 m	1.28 s
15	5.97 s	6.39 s	6.13 s	6.02 s	5.95 s	6.01 s	5.75 s	5.94 s
17	5.23 s	5.87 s	6.05 s	5.82 s	5.65 s	5.81 s	5.73 s	5.65 s
Me-18	1.35 s	1.31 s	1.35 s	1.32 s	1.27 s	1.28 s	1.24 s	1.32 s
Me-19	1.50 s	1.56 s	1.49 s	1.52 s	1.33 s	1.51 s	1.31 s	1.61 s
21	5.67 d (2.7)	7.47 brs	7.52 brs	7.39 brs	7.50 t (0.7)	7.39 t (1.5)	7.51 brs	7.51 brs
22	3.58 d (1.8)	6.57 brs	6.42 d (1.7)	6.54 brs	6.46 dd (1.8, 0.7)	6.55 d (1.5)	6.43 brs	6.46 d (1.5)
23	5.51 dd (2.7, 1.8)	7.42 t (1.7)	7.44 m	7.45 brs	7.43 t (1.8)	7.44 brs	7.44 brs	7.44 dd (3.6, 1.5)
Me-28	0.81 s	0.73 s	0.83 s	0.82 s	0.98 s	0.80 s	1.07 s	0.98 s
29 α	1.85 d (10.7)	1.98 d (11.5)	2.05 d (11.5)	1.97 d (13.8)	2.09 d (10.8)	1.99 d (13.8)	1.89 d (11.1)	2.10 d (11.1)
29 β	1.75 d (10.7)	1.74 d (11.5)	1.80 d (11.5)	1.81 d (13.8)	1.88 d (10.8)	1.95 d (13.8)	NO	NO
30	4.55 s	5.47 s	5.45 s	4.54 s	4.49 s	4.49 s	4.52 s	4.53 s
MeCO-2	–	2.20 s	2.22 s	–	–	–	–	–
MeCO-6	–	–	–	–	2.23 s	–	2.25 s	2.23 s
MeCO-12	2.21 s	1.52 s	1.53 s	1.52 s	–	1.52 s	–	–
2'	1.92 m	1.68 s	1.67 s	–	1.67 s	1.70 s	2.19 m	–
3'	1.22 m	–	–	6.14 dq (7.0, 1.4)	–	–	1.03 d (6.6)	6.14 dd (6.9, 1.5)
4'	0.93 t (7.3)	–	–	1.68 d (7.0)	–	–	1.03 d (6.6)	1.68 d (7.2)
5'	1.02 d (7.3)	–	–	1.71 brs	–	–	–	1.72 d (1.5)
2''	–	–	7.97 dd (8.3, 1.3)	–	–	–	8.08 d (7.5)	–
3''	6.79 dq (6.9, 1.4)	6.65 dq (6.9, 1.4)	7.43 m	6.94 dq (7.0, 1.4)	6.76 qq (6.9, 1.2)	6.94 qq (6.9, 1.2)	7.43 t (7.5)	6.78 dd (7.5, 1.5)
4''	1.79 dd (6.9, 1.2)	1.69 dd (6.9, 1.2)	7.58 m	1.71 d (7.0)	1.83 t (1.2)	1.82 brs	7.59 t (7.5)	1.75 s
5''	1.82 brs	1.86 t (1.2)	7.43 m	1.83 brs	1.73 dd (6.9, 0.9)	1.72 dd (6.9, 0.9)	7.43 t (7.5)	1.84 d (0.9)
6''	–	–	7.97 m	–	–	–	8.08 d (7.5)	–
1-OH	3.88 s	3.38 s	3.43 s	NO	3.53 s	3.40 s	3.62 s	NO
2-OH	3.56 s	NO	NO	NO	3.56 s	3.57 s	3.56 s	3.49 s
OCH ₃	3.64 s	3.71 s	3.74 s	3.74 s	3.75 s	3.73 s	3.82 s	3.76 s

¹H NMR spectrum was acquired in CDCl₃ at 400 MHz for **2**, **4** and **7**, and 300 MHz for **1** and **3** and. TMS was used as the internal standard. Chemical shifts are shown at the δ scale with *J* values (Hz) in parentheses.

Assignments are based on COSY, HSQC/HETCOR and HMBC experiments. NO = not observed.

Table S2. ^{13}C NMR chemical shifts for compounds **1-8** and models

Position	1	2	3	4	5	6	7	8	9	10	15	16
1-C	84.4	84.4	84.5	84.4	84.6	84.4	84.6	84.6	84.5	84.5	84.6	84.6
2-C	75.6	83.8	83.7	75.7	75.6	75.6	75.7	75.6	75.7	75.7	75.6	84.1
3-CH	86.7	84.7	85.6	86.5	87.4	86.8	86.9	86.9	86.4	86.6	86.9	84.7
4-C	43.8	44.7	44.8	43.7	43.5	43.7	43.7	43.5	43.9	43.8	43.7	44.8
5-CH	41.2	40.1	40.3	40.6	44.8	40.6	44.9	44.8	40.8	40.7	44.8	39.7
6-CH ₂	33.1	32.9	33.0	32.9	71.4(CH)	32.9	71.4(CH)	71.4(CH)	33.0	32.9	71.4(CH)	33.8
7-C	175.4	174.5	174.7	174.5	171.0	174.5	171.3	171.0	174.7	174.6	171.1	173.7
8-C	83.1	83.7	83.8	83.6	83.9	83.6	83.8	83.9	83.6	83.3	83.6	83.9
9-C	86.2	85.8	85.9	86.4	87.0	86.6	87.4	87.0	87.2	86.3	86.8	86.3
10-C	47.4	48.0	48.0	47.3	48.4	47.2	48.4	48.4	47.4	47.3	48.4	48.1
11-CH ₂	31.7	32.6	32.7	32.1	26.0	32.4	25.7	25.7	32.1	32.0	25.6	26.4
12-CH	69.1	68.9	68.8	68.6	29.4(CH ₂)	68.6	29.3(CH ₂)	29.3(CH ₂)	68.6	68.6	29.3(CH ₂)	29.5(CH ₂)
13-C	43.4	42.7	42.9	42.7	37.9	42.7	38.0	37.9	42.9	42.7	37.9	37.9
14-C	151.5	149.9	150.1	151.1	152.6	151.2	151.7	152.5	151.3	151.3	152.7	151.5
15-CH	123.5	124.9	124.5	123.9	122.5	123.9	122.2	122.5	123.7	123.9	122.4	123.4
16-C	160.9	162.7	161.8	162.3	162.7	162.2	161.8	162.8	161.3	162.4	162.8	163.2
17-CH	78.0	78.2	78.1	78.1	79.8	78.2	79.7	79.8	78.0	78.2	79.8	79.8
18-CH ₃	15.7	14.2	14.0	14.6	19.9	19.8	19.5	19.9	14.3	14.5	19.7	19.5
19-CH ₃	15.4	15.4	15.4	15.5	16.3	15.4	16.4	16.3	15.5	15.5	16.4	15.5
20-C	61.0	121.4	121.6	121.2	119.5	121.2	119.6	119.5	121.4	121.3	119.6	119.6
21-CH	91.2	141.8	141.7	141.8	141.8	141.8	141.8	141.8	141.8	141.9	141.8	141.8
22-CH	51.0	110.3	110.4	110.2	110.0	110.2	110.0	110.0	110.3	110.3	110.0	110.1
23-CH	92.5	143.1	143.1	143.1	143.1	143.0	143.1	143.1	143.0	143.0	143.1	143.1
28-CH ₃	14.5	13.8	13.8	14.4	15.5	14.6	15.5	15.5	14.4	14.4	15.5	14.0
29-CH ₂	38.8	39.5	39.5	38.9	39.9	38.9	39.8	39.9	39.8	38.9	39.8	39.2
30-CH	77.7	73.9	73.8	78.1	77.9	78.1	77.7	77.8	78.2	78.1	77.8	73.9
MeCO-2	–	21.8/169.9	21.8/169.9	–	–	–	–	–	–	–	–	21.9/169.9
MeCO-6	–	–	–	–	21.0/169.8	–	19.5/169.8	21.0/169.8	–	–	21.1/169.8	–
MeCO-12	21.4/171.8	19.8/170.4	19.8/170.5	19.8/170.4	–	19.8/170.4	–	–	19.8/170.4	19.8/170.4	–	–
1'-C	122.4	119.6	119.5	124.5	119.2	119.4	122.4	124.7	122.7	122.7	122.6	119.8
2'-CH ₃	35.5(CH)	16.4	16.4	129.1(C)	16.3	16.4	28.8(CH)	129.9(C)	29.0(CH)	35.5(CH)	28.9(CH)	16.6
3'-CH	23.7(CH ₂)	–	–	128.7	–	–	16.7(CH ₃)	128.5	16.6(CH ₃)	23.7(CH ₂)	16.7(CH ₃)	–
4'-CH ₃	11.6	–	–	13.4	–	–	16.8	13.3	16.7	11.6	16.8	–
5'-CH ₃	13.3	–	–	11.7	–	–	–	11.7	–	13.3	–	–
1''-C	167.7	167.5	131.2	167.8	167.6	167.8	129.4	167.6	129.7	167.8	167.6	167.6
2''-C	130.2	130.8	128.9	130.1	129.9	130.0	129.7	129.9	129.8	130.0	129.9	130.7
3''-CH	139.3	135.8	128.7	139.9	139.6	139.8	129.0	139.7	129.0	139.8	139.6	136.0
4''-CH ₃	14.3	13.6	133.2(CH)	14.3	12.4	12.4	134.2(CH)	12.4	134.1(CH)	14.6 ^a	14.4	13.7
5''-CH ₃	12.5	13.0	128.7(CH)	12.4	14.3	14.3	129.0(CH)	14.4	129.0(CH)	12.4 ^a	12.3 ^a	13.0
6''-CH	–	–	128.9	–	–	–	129.7	–	129.8	–	–	–
7''-C	–	–	166.5	–	–	–	166.5	–	166.7	–	–	–
CH ₃ O	52.2	52.1	52.3	52.2	53.3	52.1	53.4	53.3	52.2	52.1	53.2	52.2

^aData obtained in this study suggest that these resonances were previously assigned incorrectly. The spectra of **1-8** were run in CDCl₃ at 75 MHz. Assignments were based on HETCOR, HSQC and HMBC experiments.

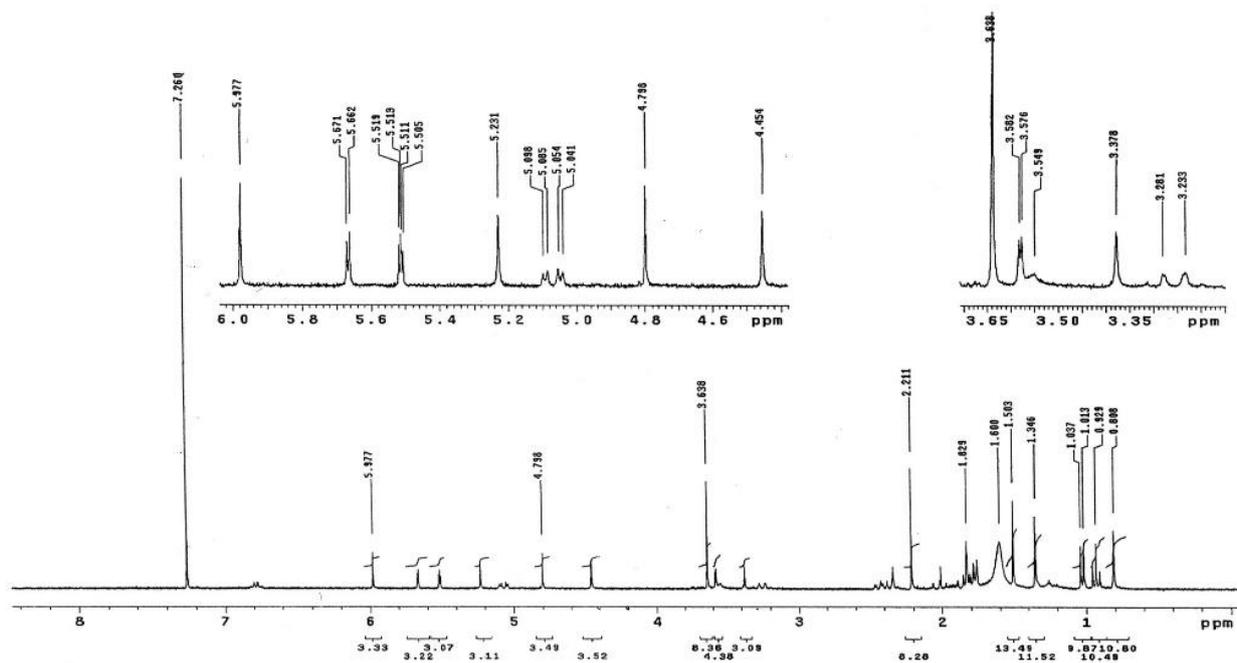
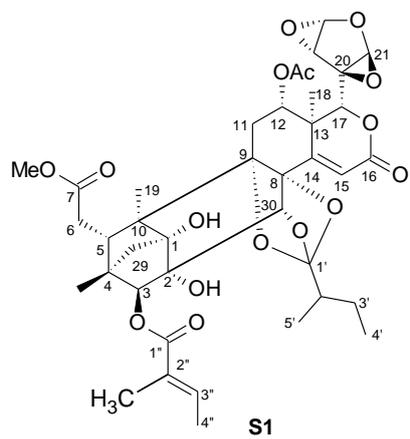


Figure S1. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **1**.

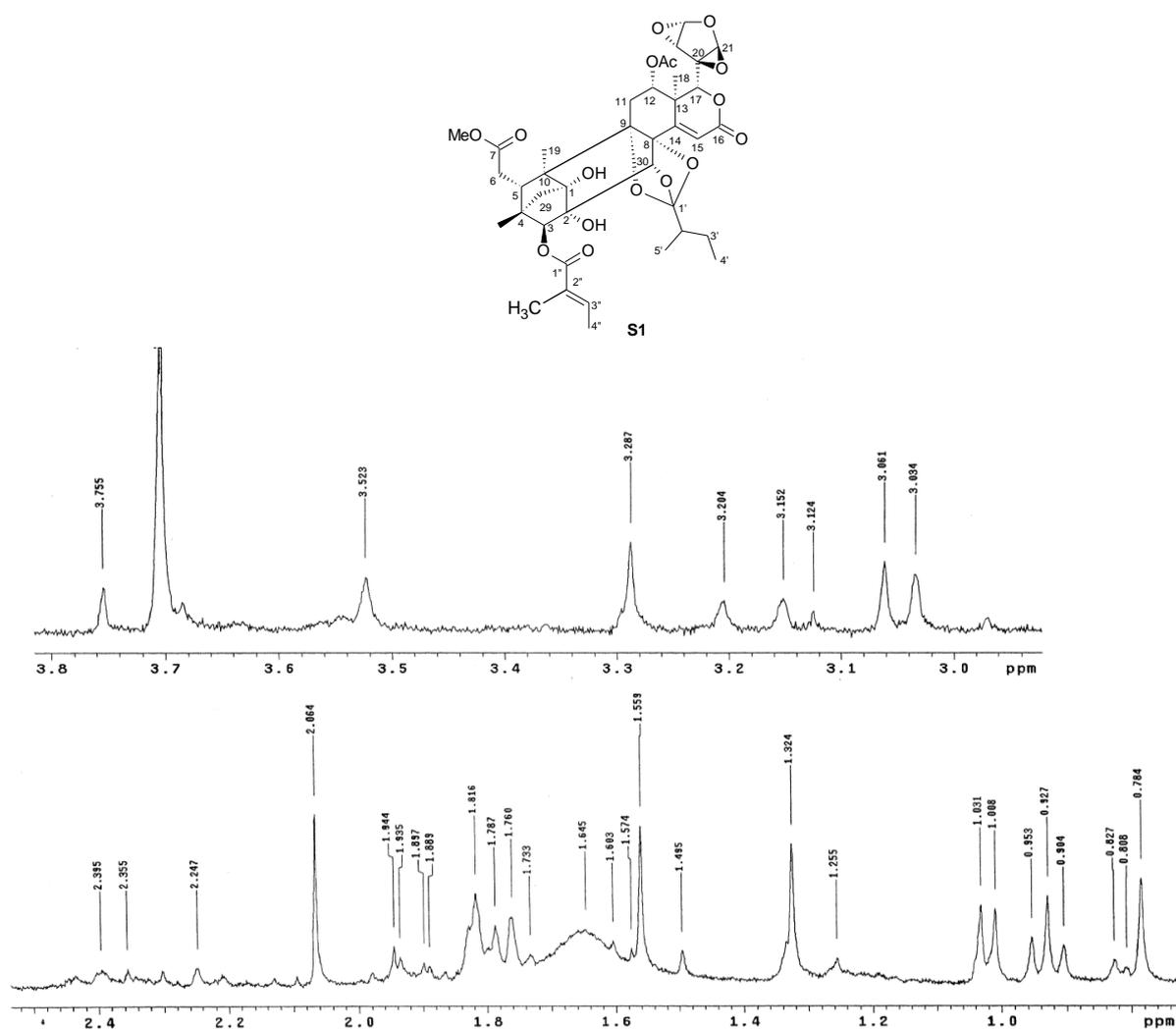


Figure S2. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **1**.

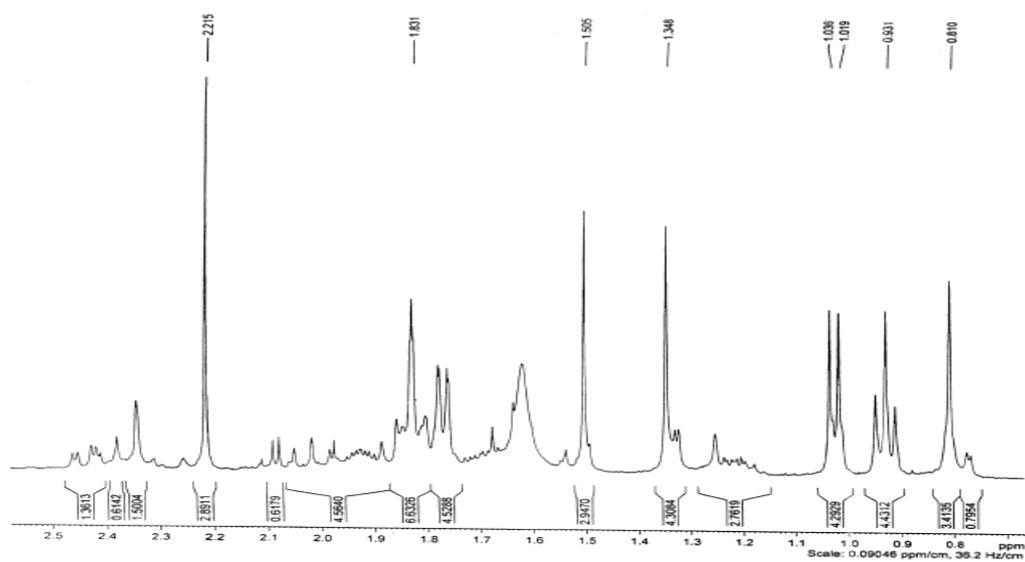


Figure S3. ^1H NMR (400 MHz, CDCl_3) spectrum of the new compound **1**.

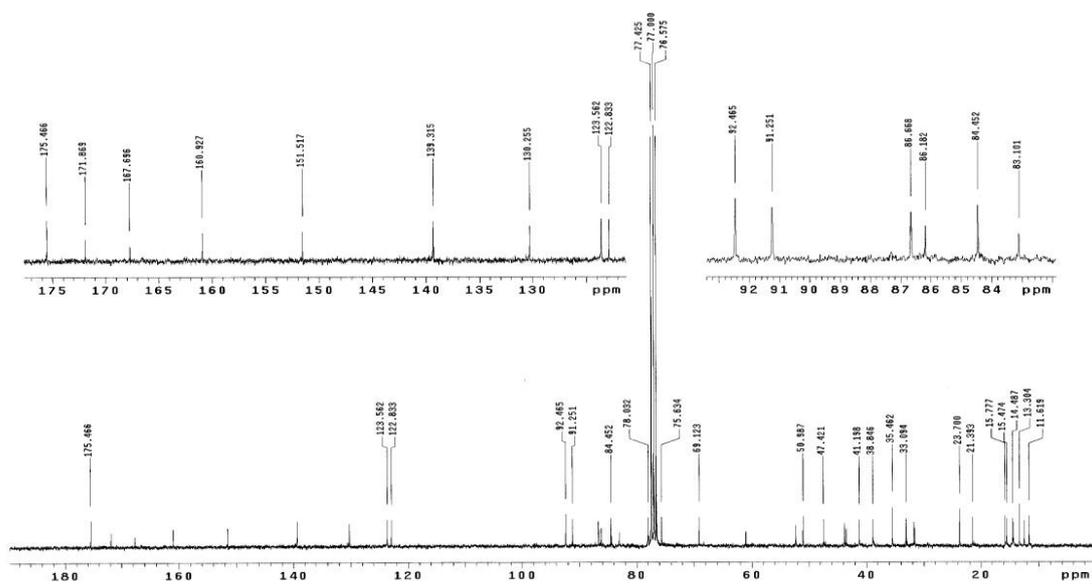
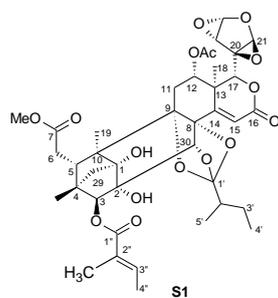


Figure S4. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound **1**.

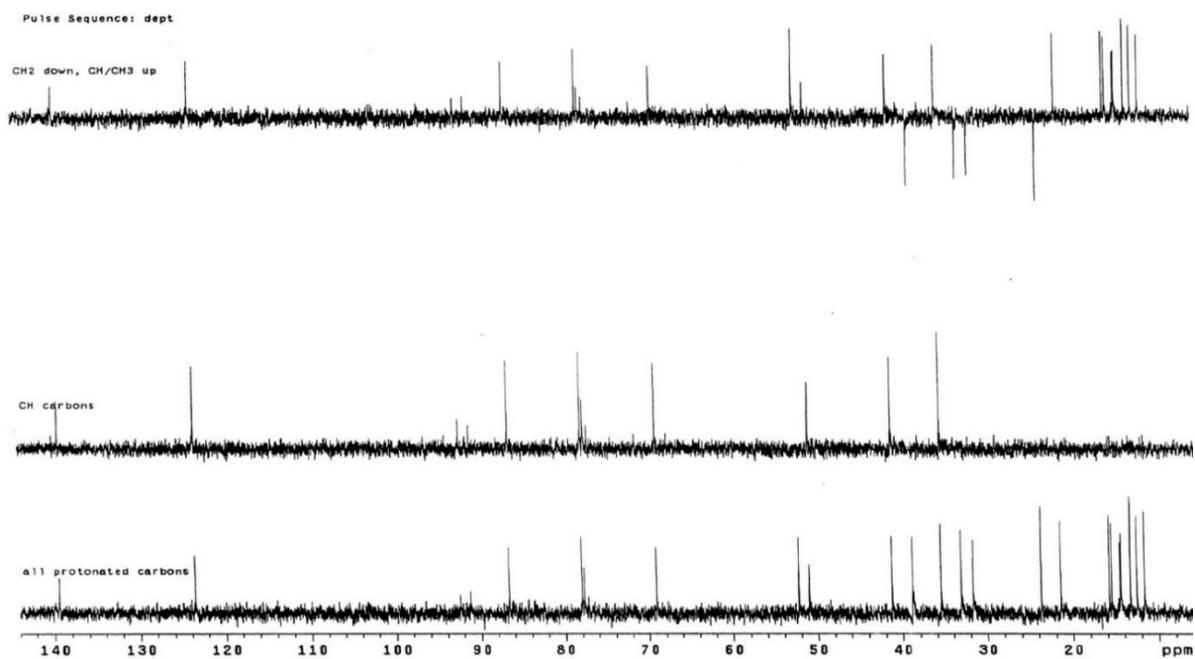


Figure S5. DEPT (75 MHz, CDCl_3) spectrum of the new compound **1**.

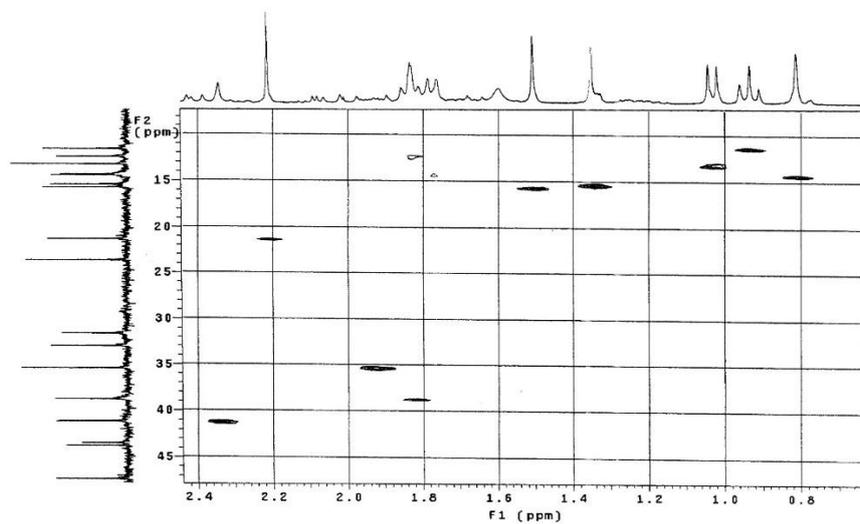
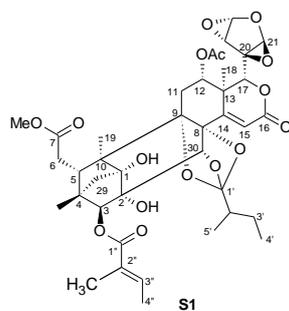


Figure S6. HETCOR (100 MHz, CDCl_3) spectrum of the new compound **1**.

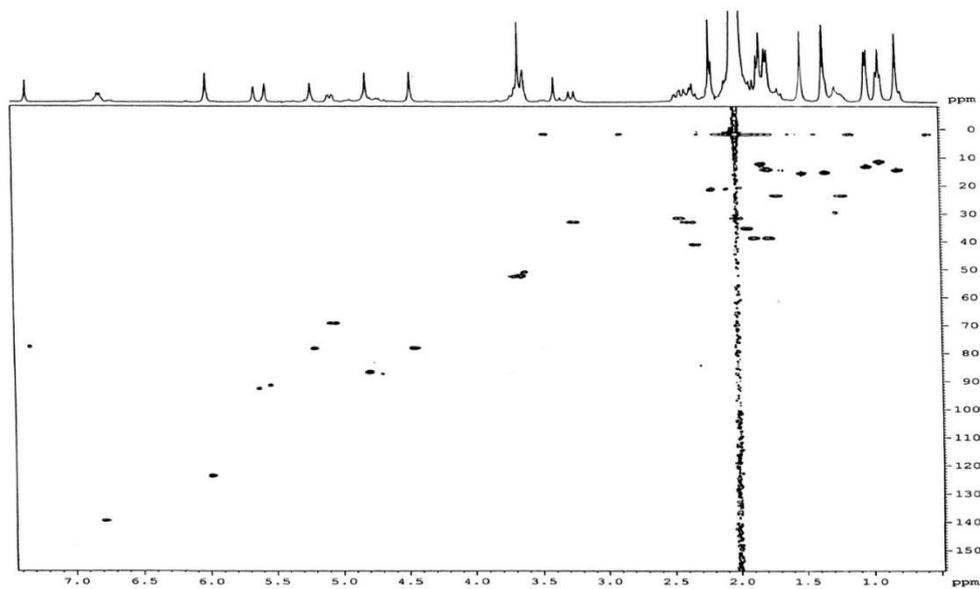


Figure S7. HETCOR (100 MHz, CDCl_3) spectrum of the new compound **1**.

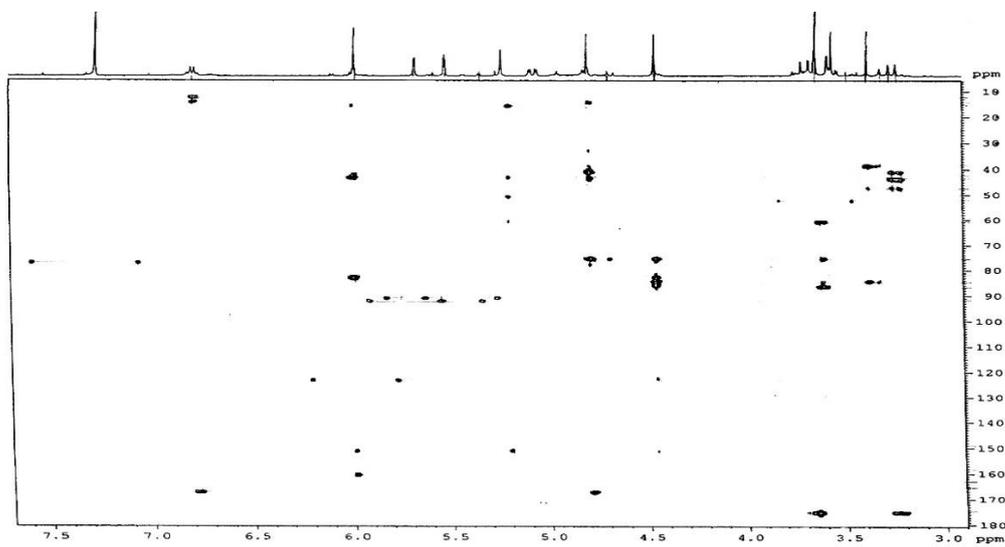
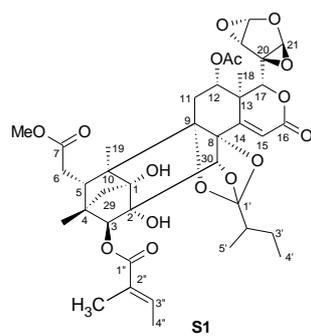


Figure S8. HMBC (400 MHz, CDCl₃) spectrum of the new compound **1**.

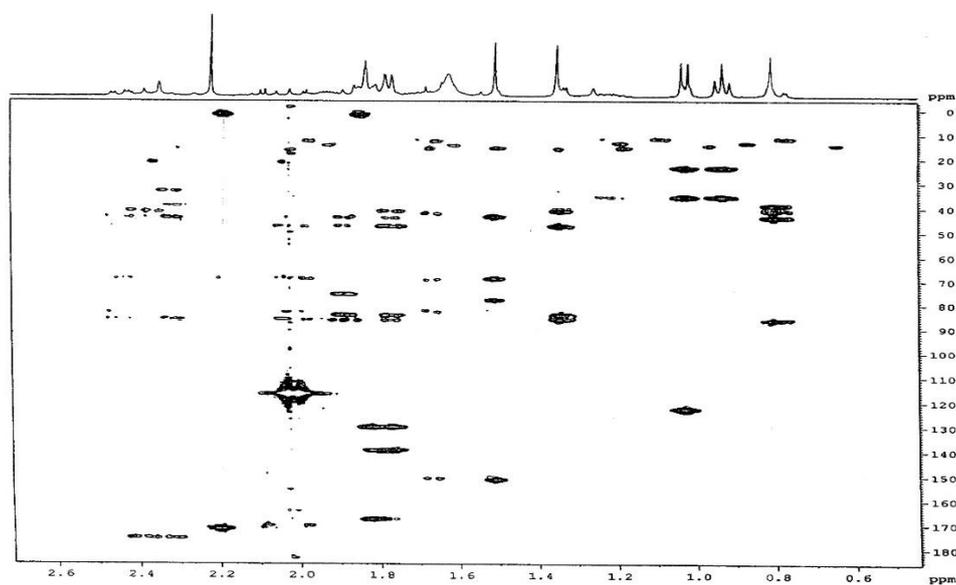


Figure S9. HMBC (400 MHz, CDCl₃) spectrum of the new compound **1**.

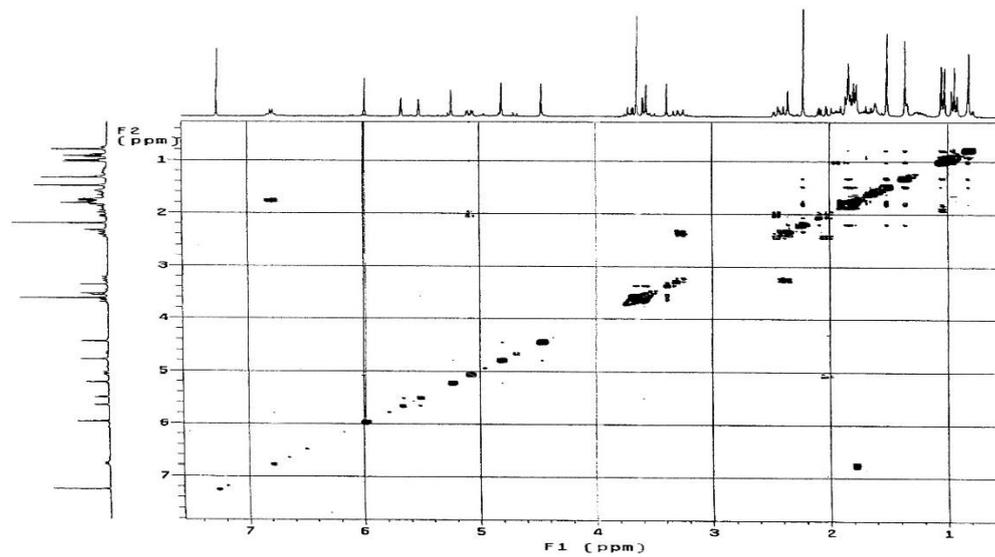
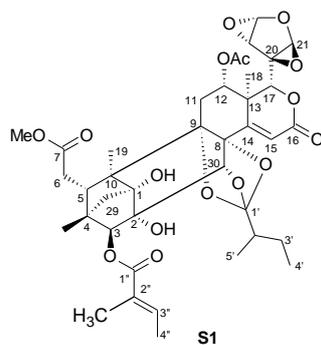


Figure S10. COSY (300 MHz, CDCl₃) spectrum of the new compound 1.

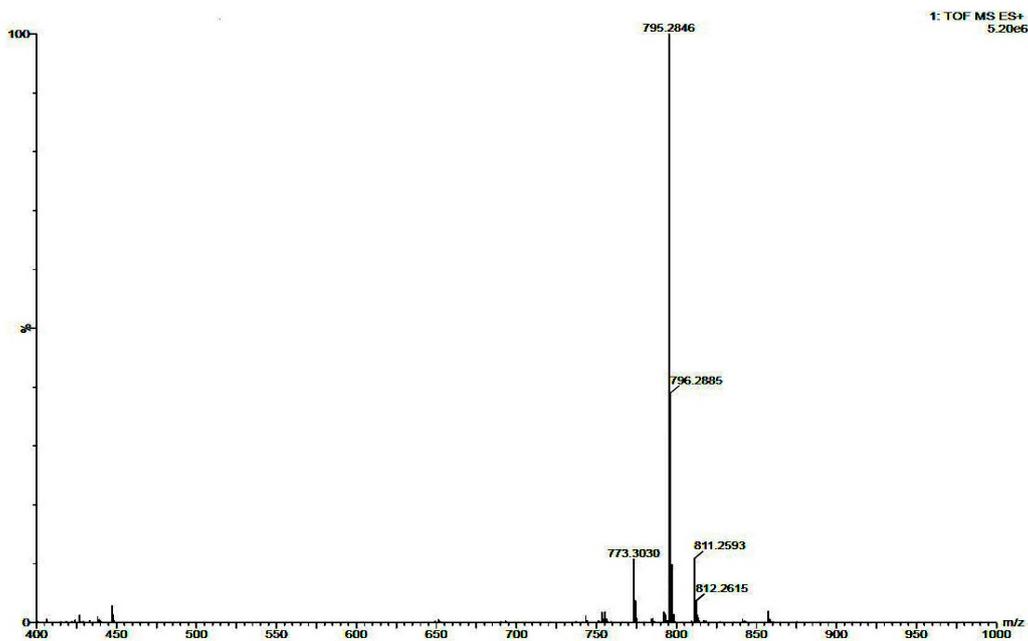
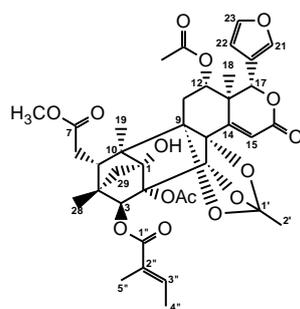


Figure S11. HR-ESI-ToF-MS of the new compound of 1.



S2

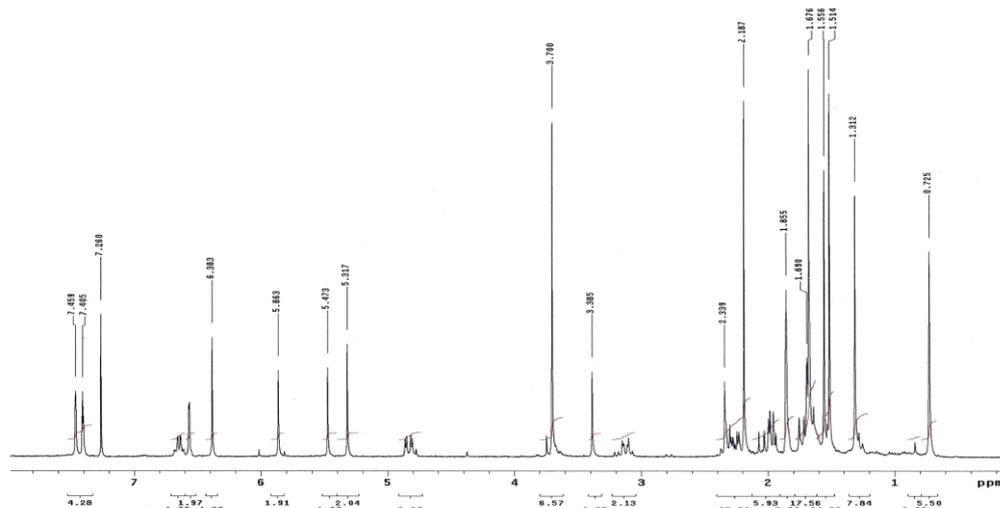


Figure S12. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound 2.

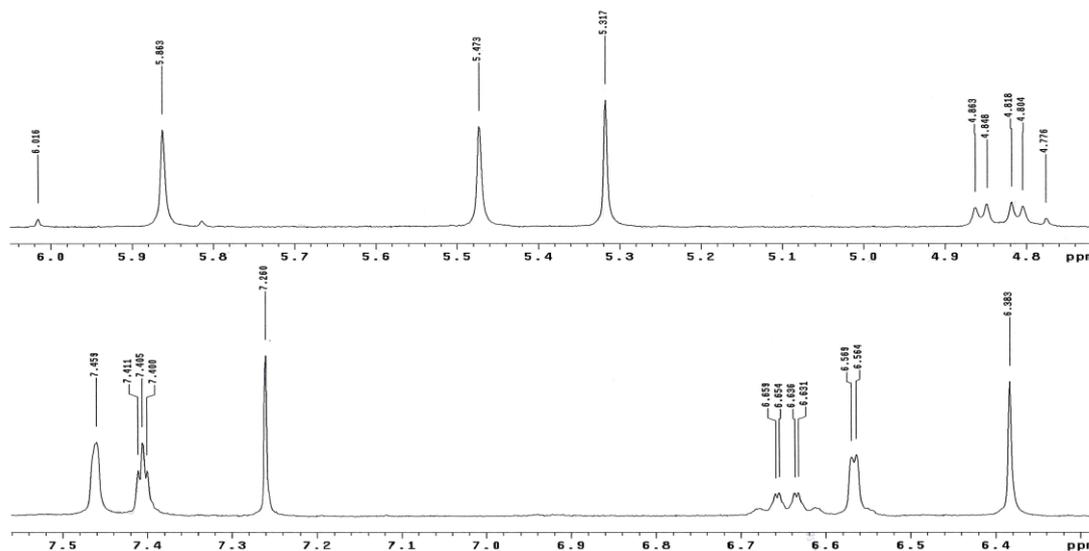
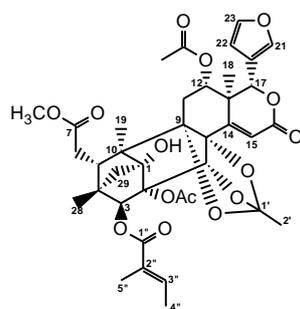


Figure S13. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound 2.



S2

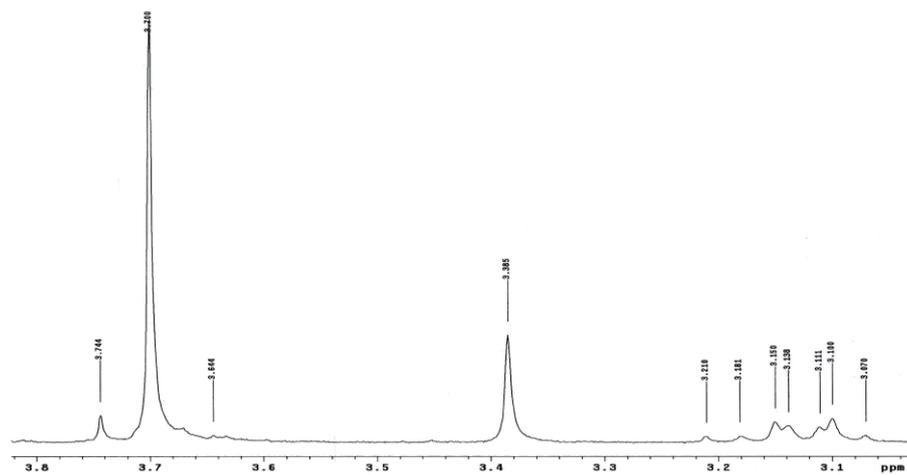


Figure S14. ¹H NMR (300 MHz, CDCl₃) spectrum of the new compound 2.

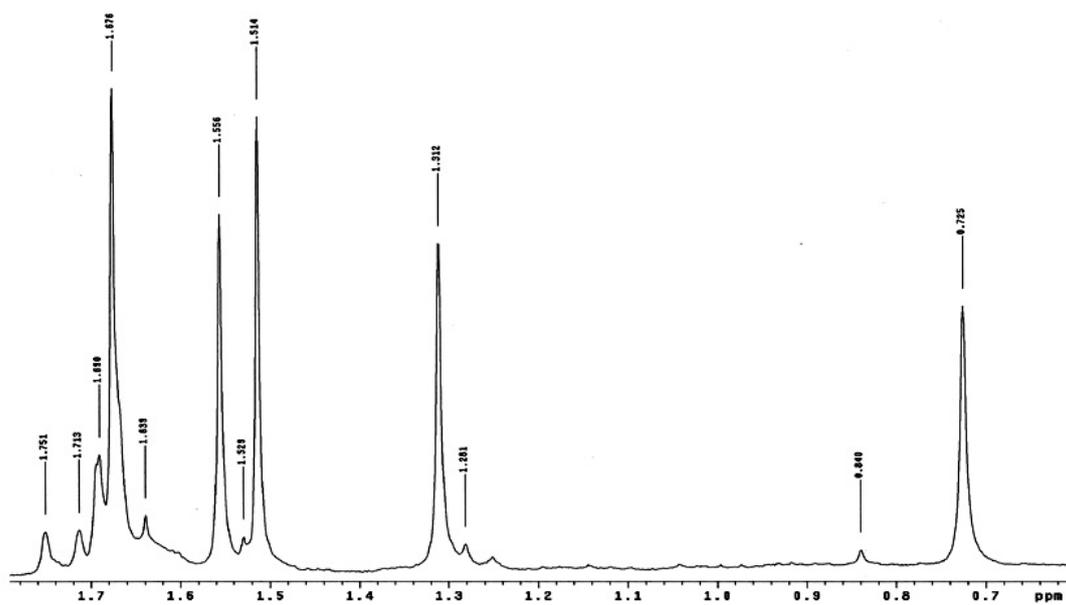


Figure S15. ¹H NMR (300 MHz, CDCl₃) spectrum of the new compound 2.

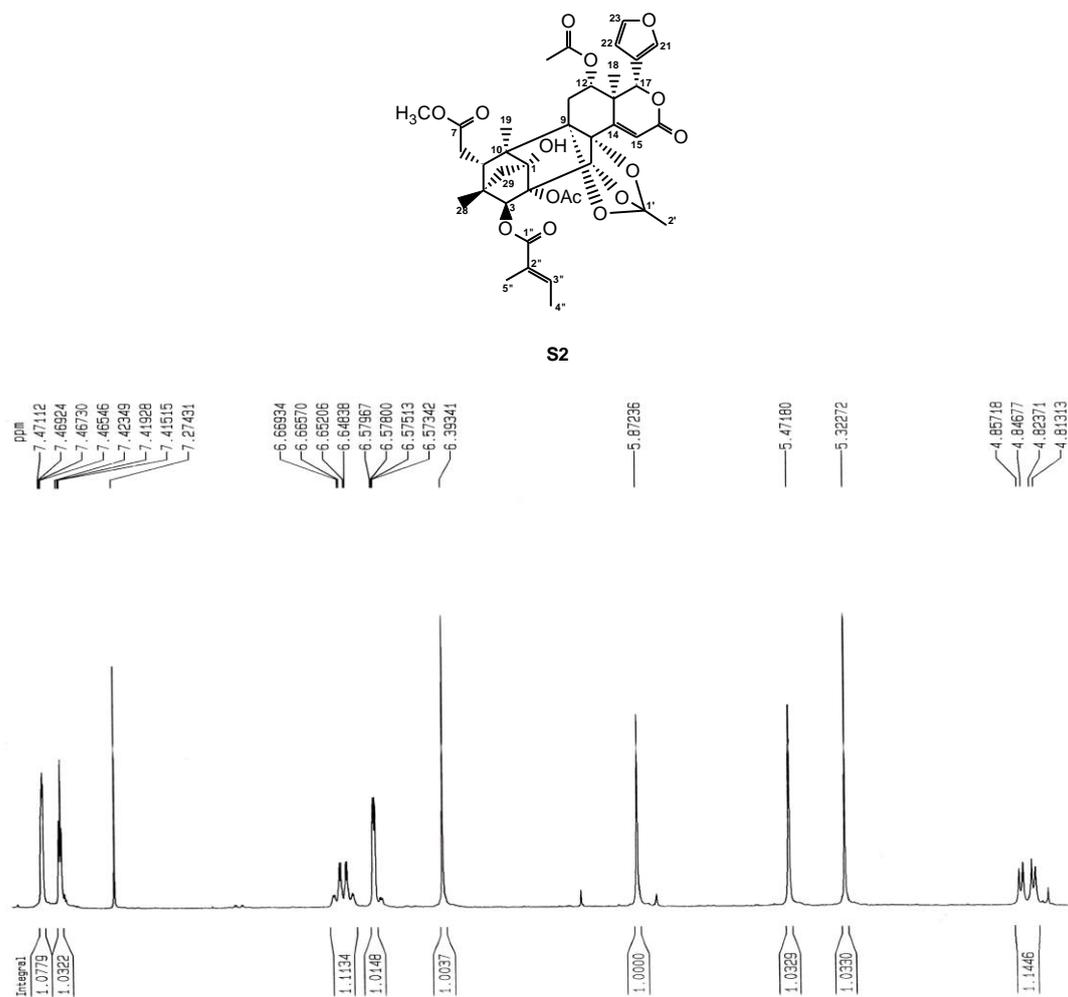


Figure S16. ¹H NMR (400 MHz, CDCl₃) spectrum of the new compound 2.

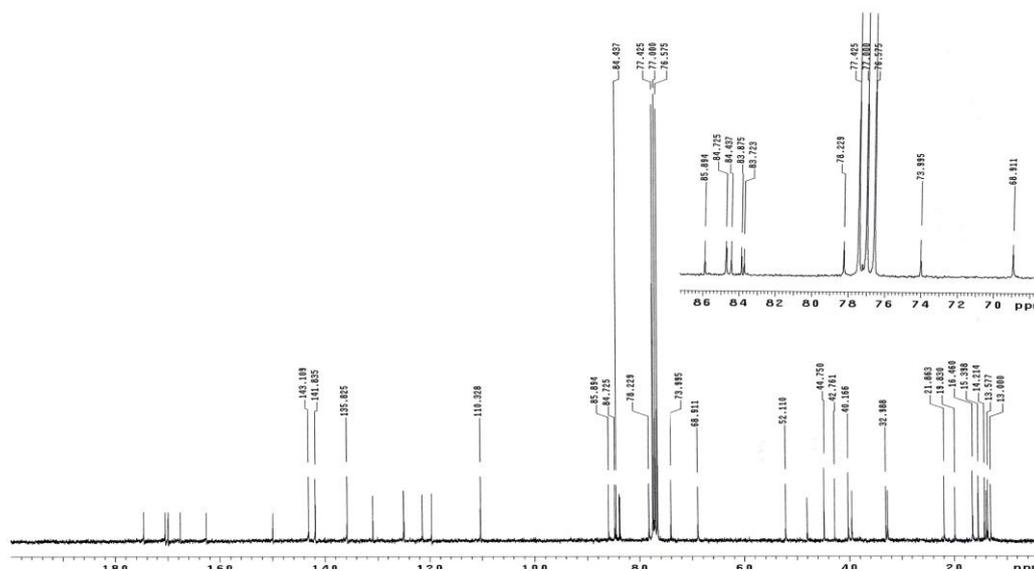
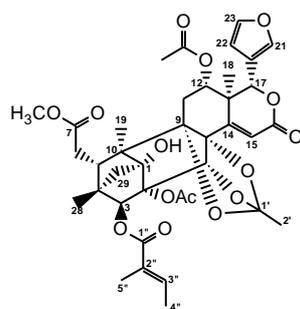


Figure S17. ¹³C NMR (75 MHz, CDCl₃) spectrum of the new compound 2.



S2

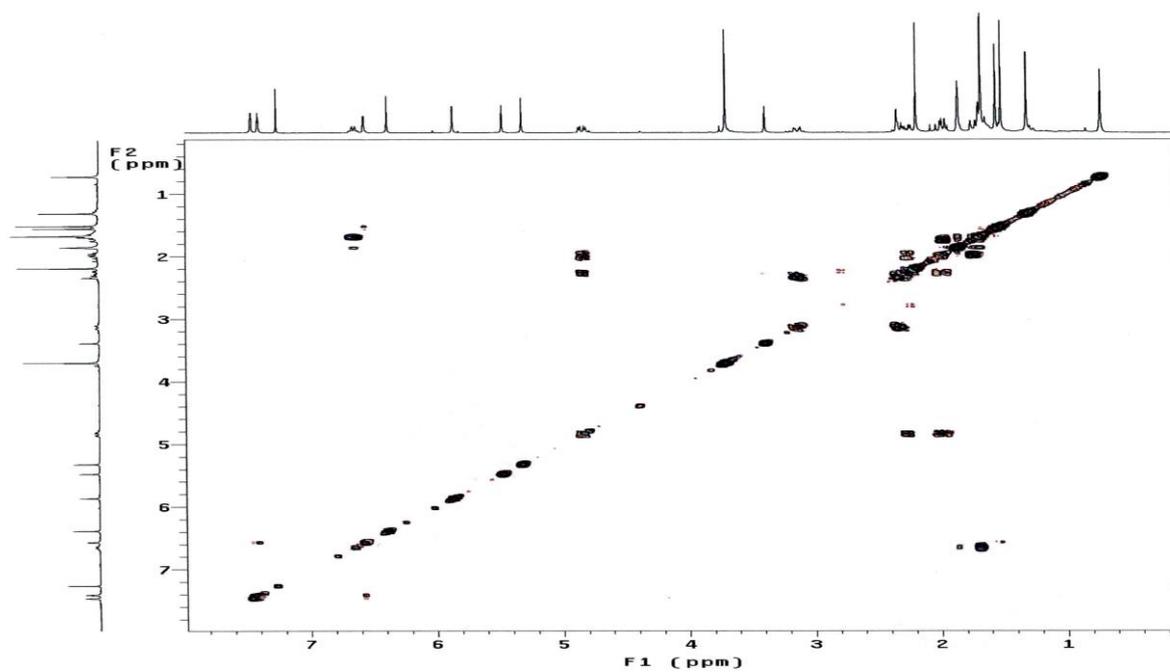


Figure S18. COSY (300 MHz, CDCl_3) spectrum of the new compound **2**.

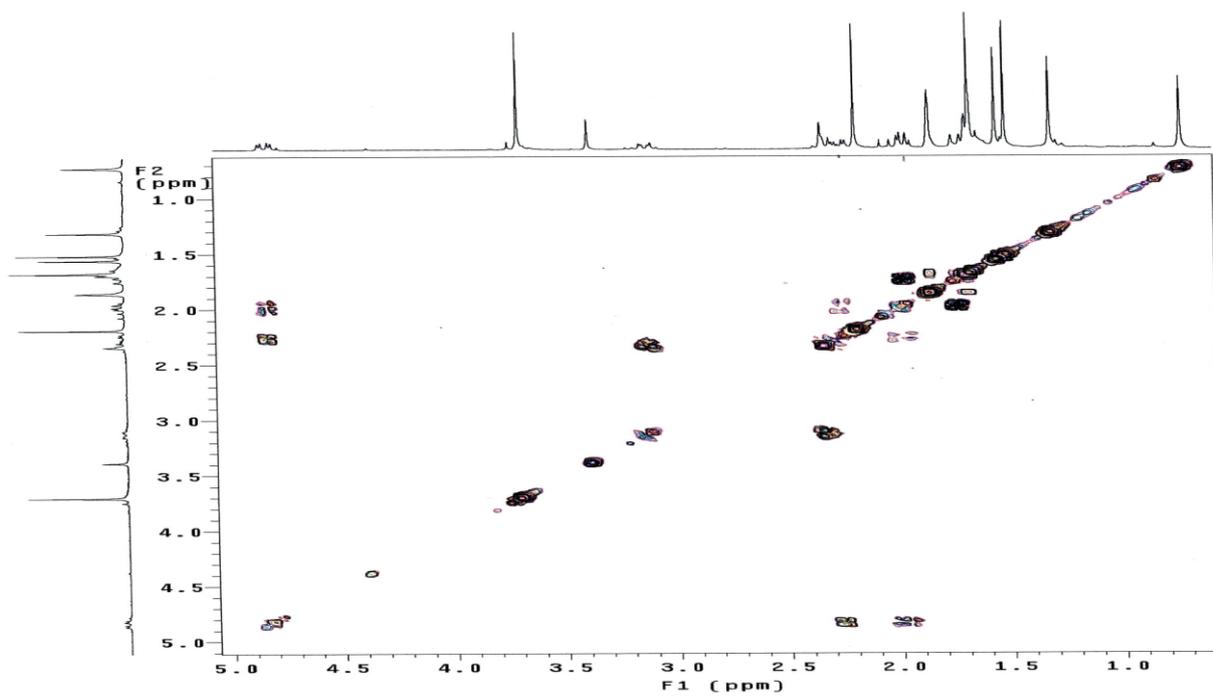
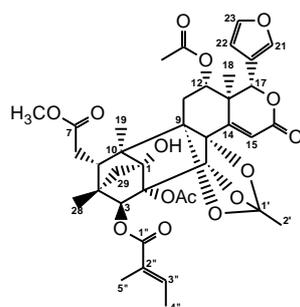


Figure S19. COSY (300 MHz, CDCl_3) spectrum of the new compound **2**.



S2

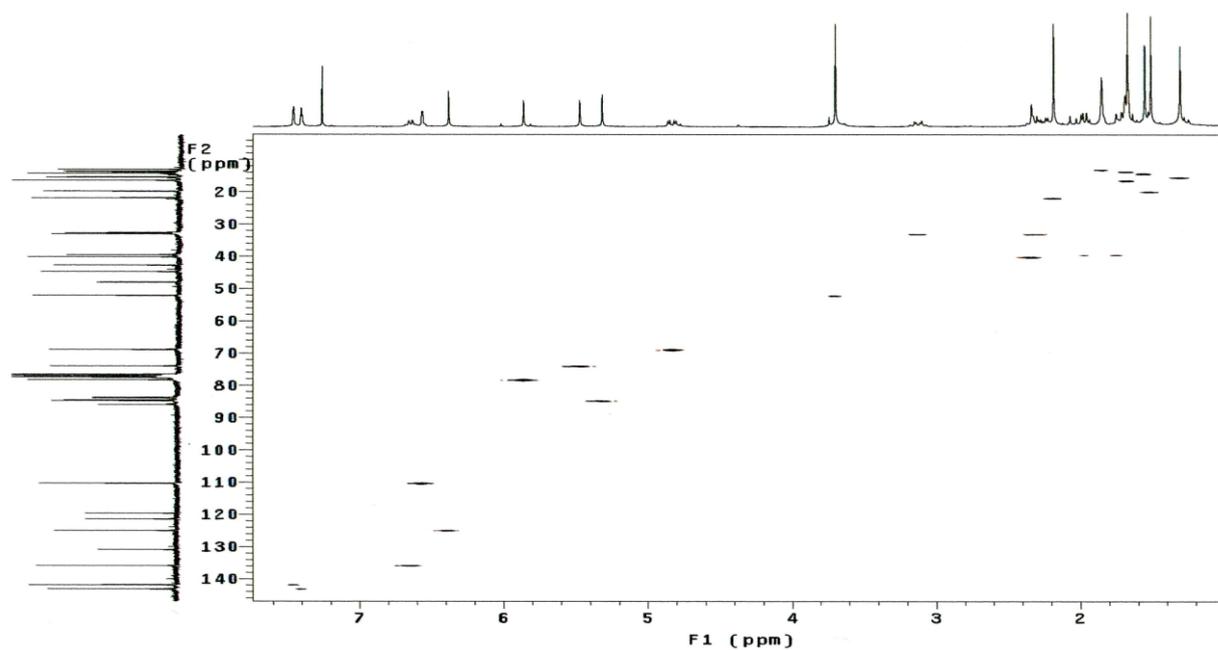


Figure S20. HETCOR (75 MHz, CDCl₃) spectrum of the new compound 2.

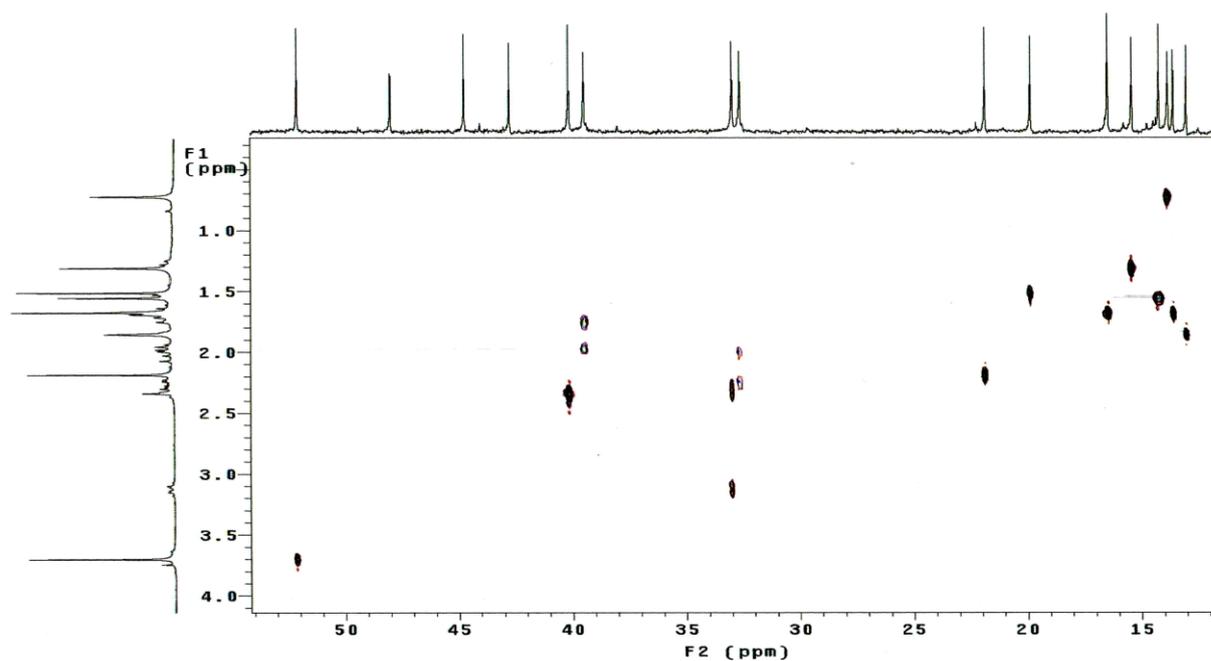
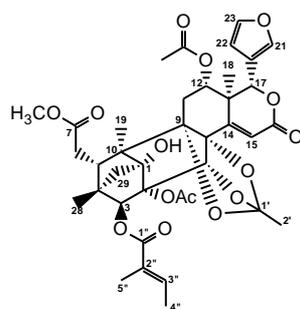


Figure S21. HETCOR (75 MHz, CDCl₃) spectrum of the new compound 2.



S2

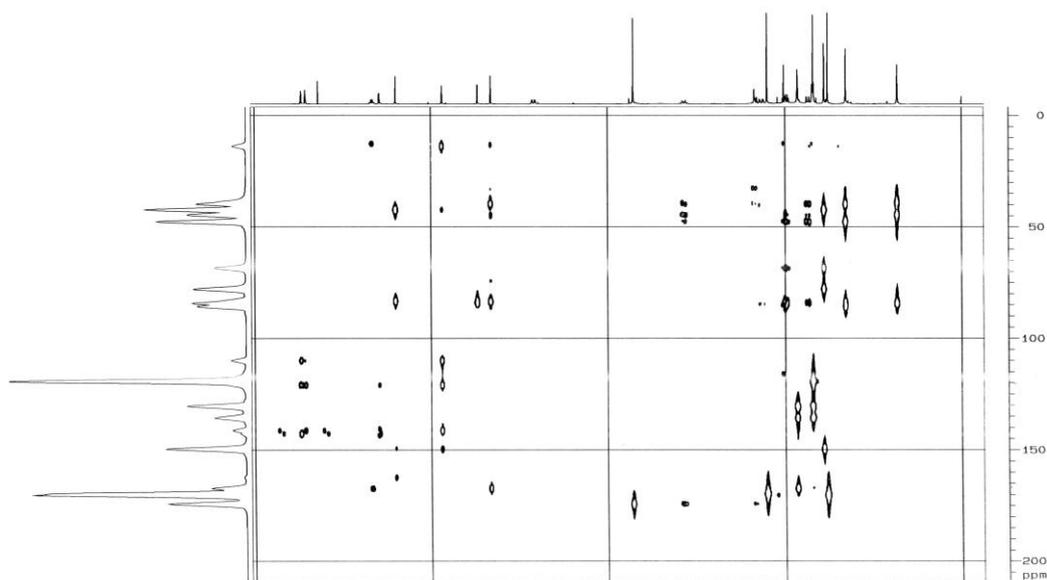


Figure S22. HMBC (400 MHz, CDCl₃) spectrum of the new compound 2.

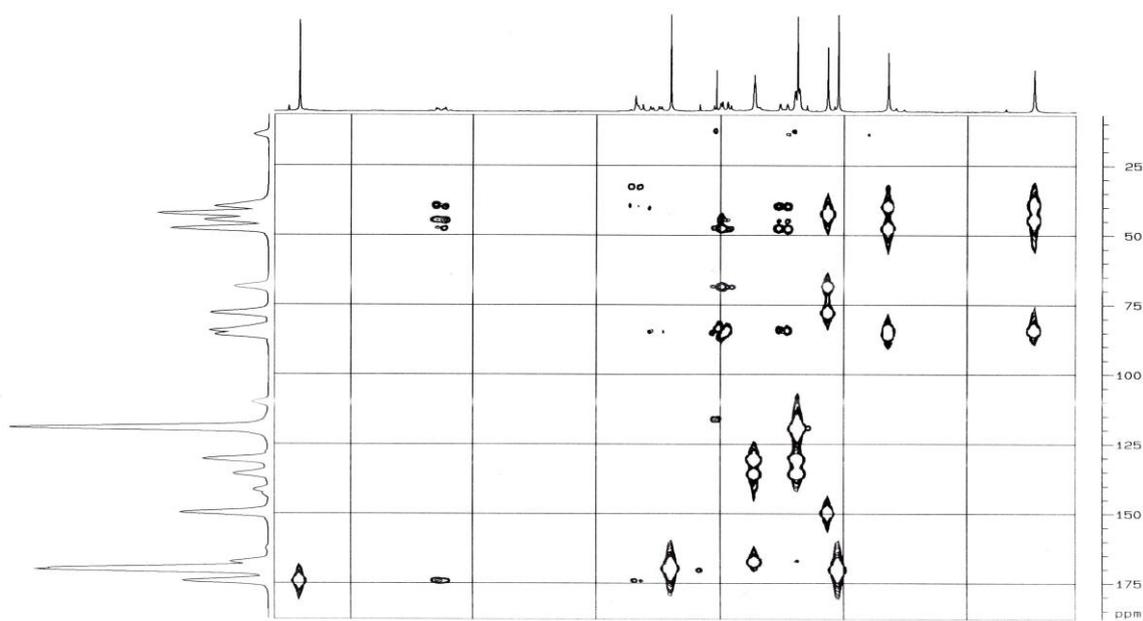
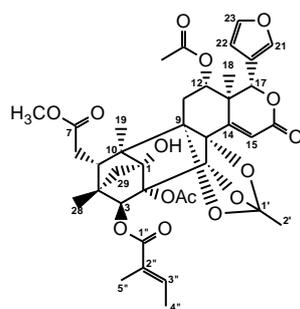


Figure S23. HMBC (400 MHz, CDCl₃) spectrum of the new compound 2.



S2

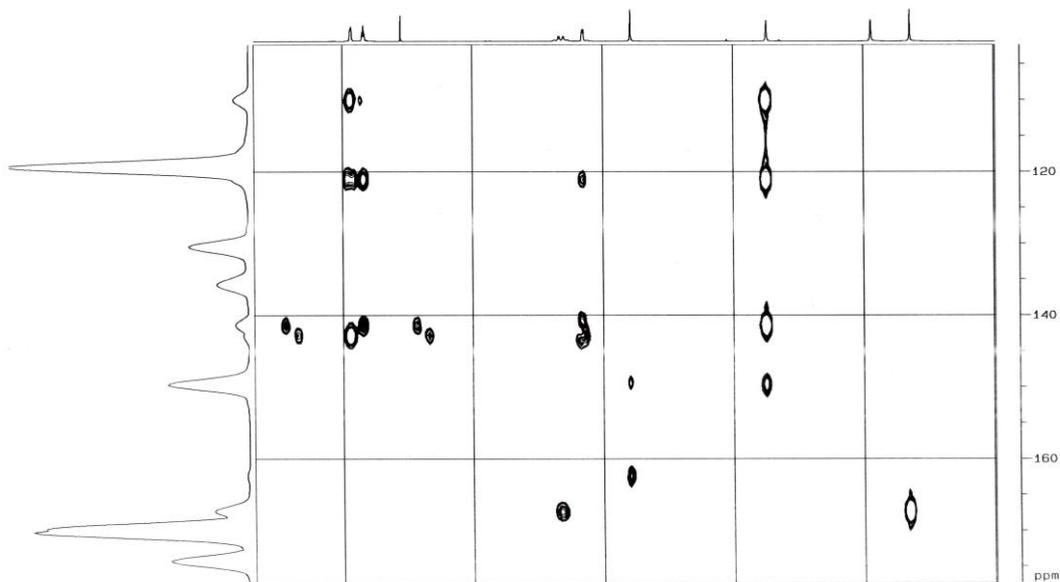


Figure S24. HMBC (400 MHz, CDCl₃) spectrum of the new compound 2.

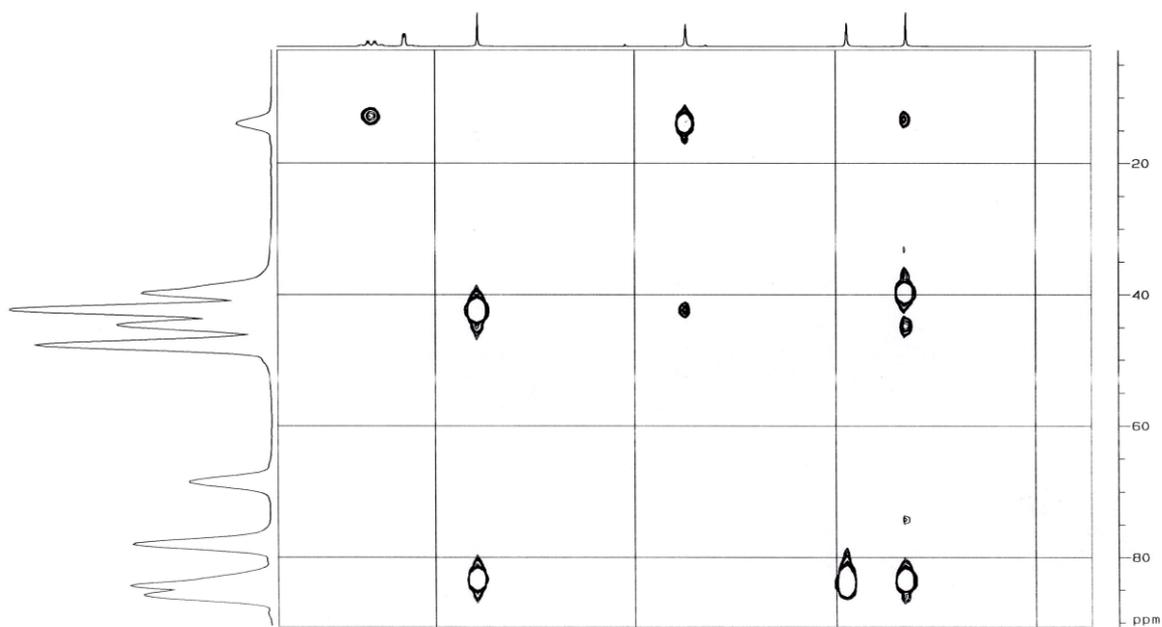
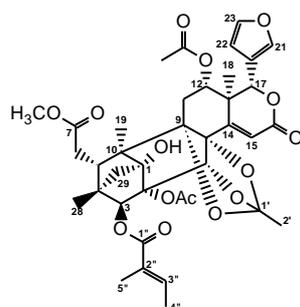


Figure S25. HMBC (400 MHz, CDCl₃) spectrum of the new compound 2.



S2

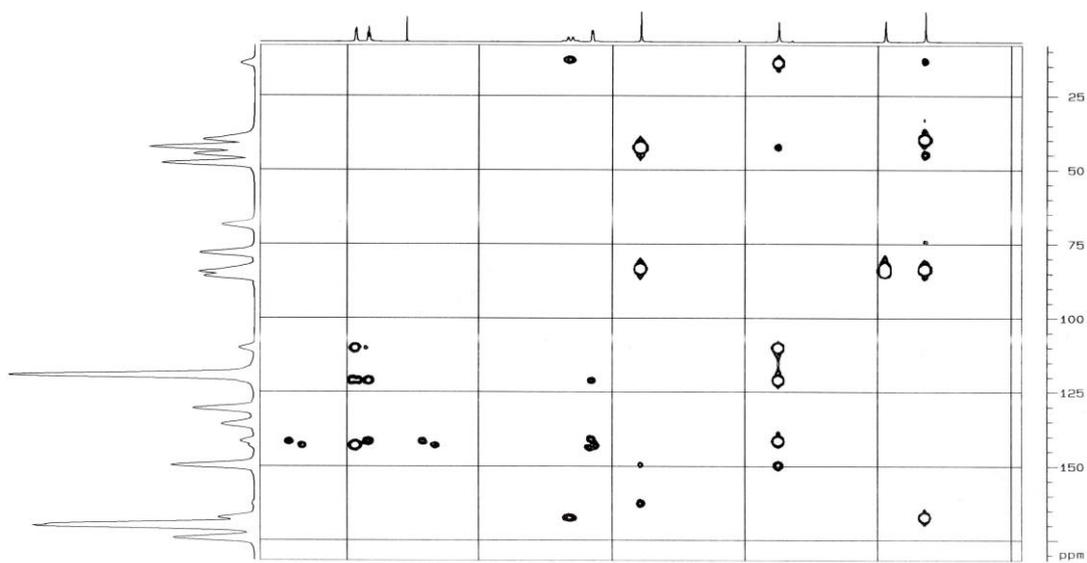


Figure S26. HMBC (400 MHz, CDCl_3) spectrum of the new compound **2**.

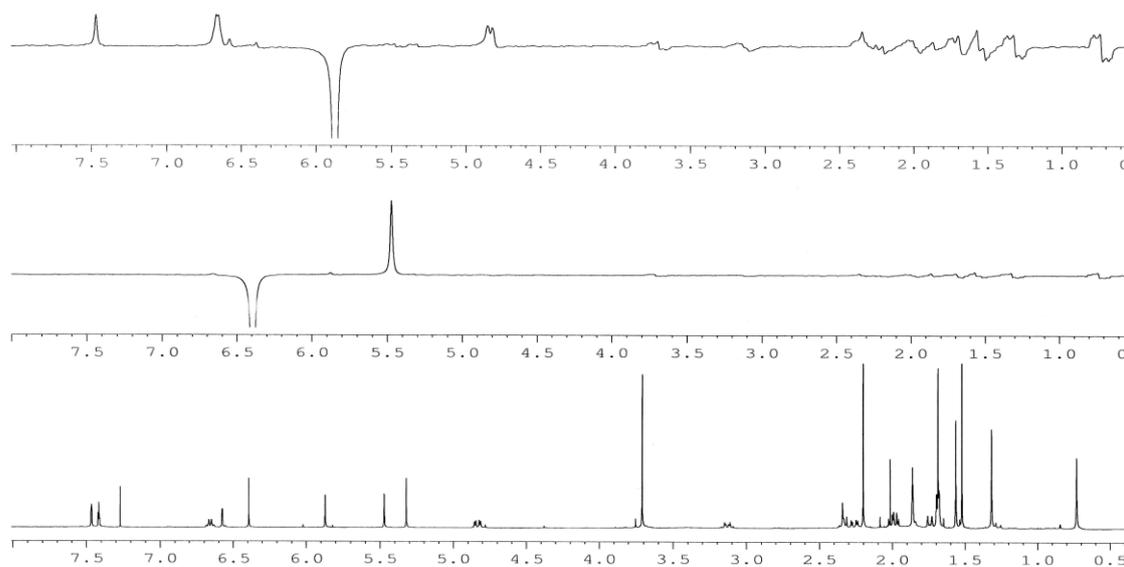
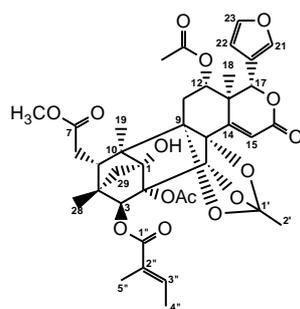


Figure S27. g-NOESY (400 MHz, CDCl_3) spectrum of the new compound **2**.



S2

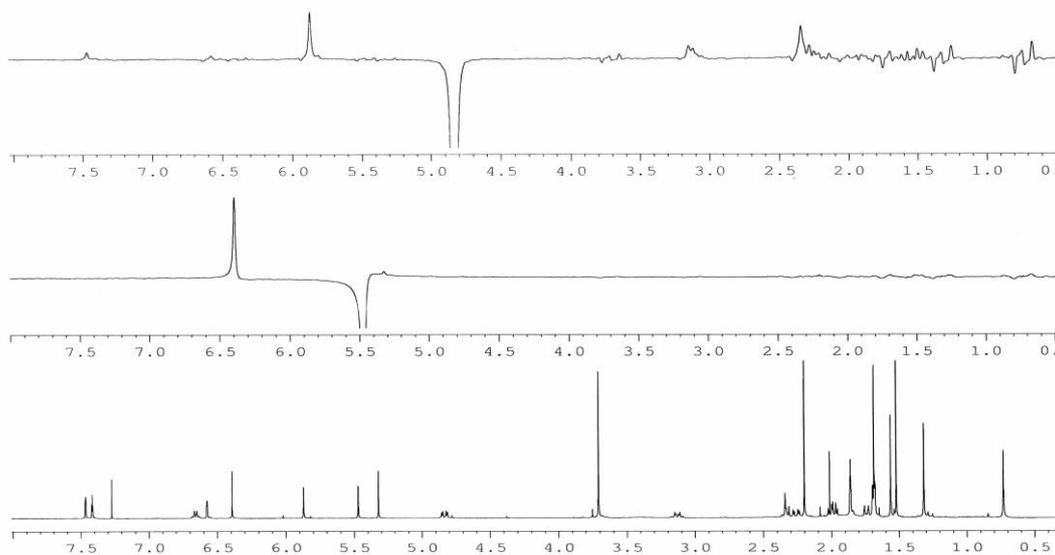


Figure S28. g-NOESY (400 MHz, CDCl₃) spectrum of the new compound **2**.

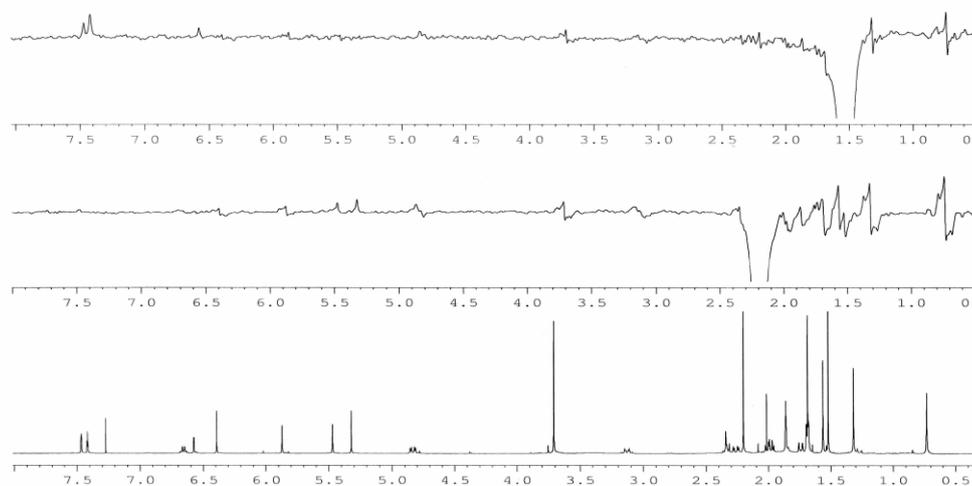
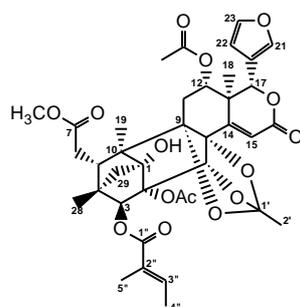


Figure S29. g-NOESY (400 MHz, CDCl₃) spectrum of the new compound **2**.



S2

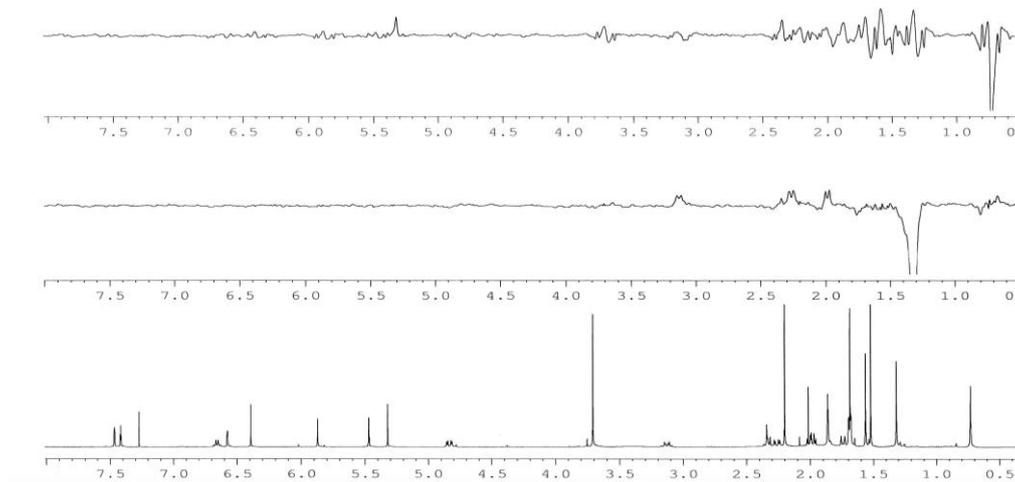


Figure S30. g-NOESY (400 MHz, CDCl₃) spectrum of the new compound 2.

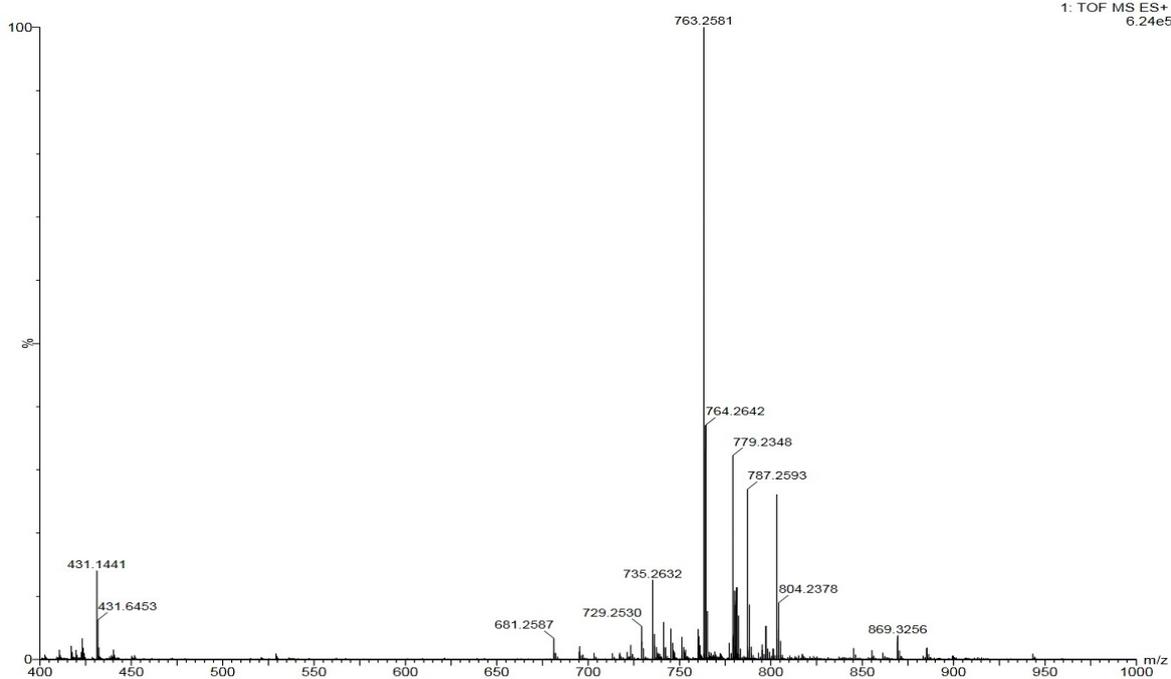


Figure S31. HR-ESI-ToF-MS spectrum of the new compound 2.

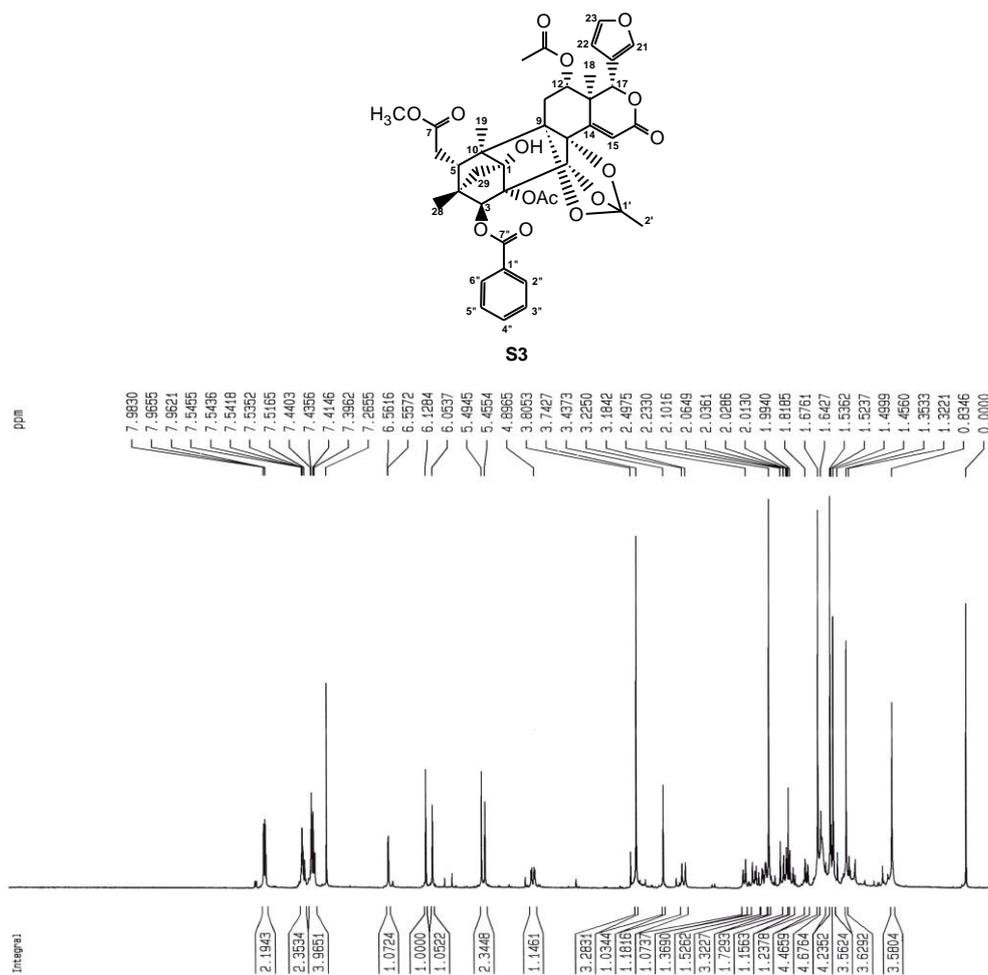


Figure S32. ^1H NMR (400 MHz, CDCl_3) spectrum of the new compound **3**.

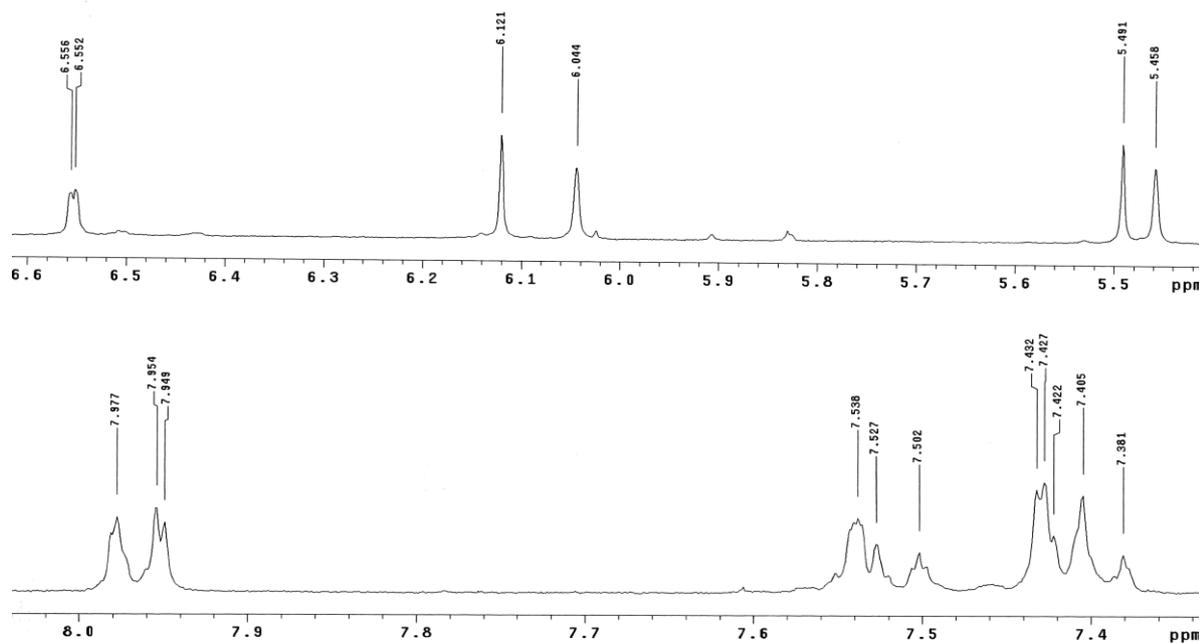


Figure S33. ^1H NMR (400 MHz, CDCl_3) spectrum of the new compound **3**.

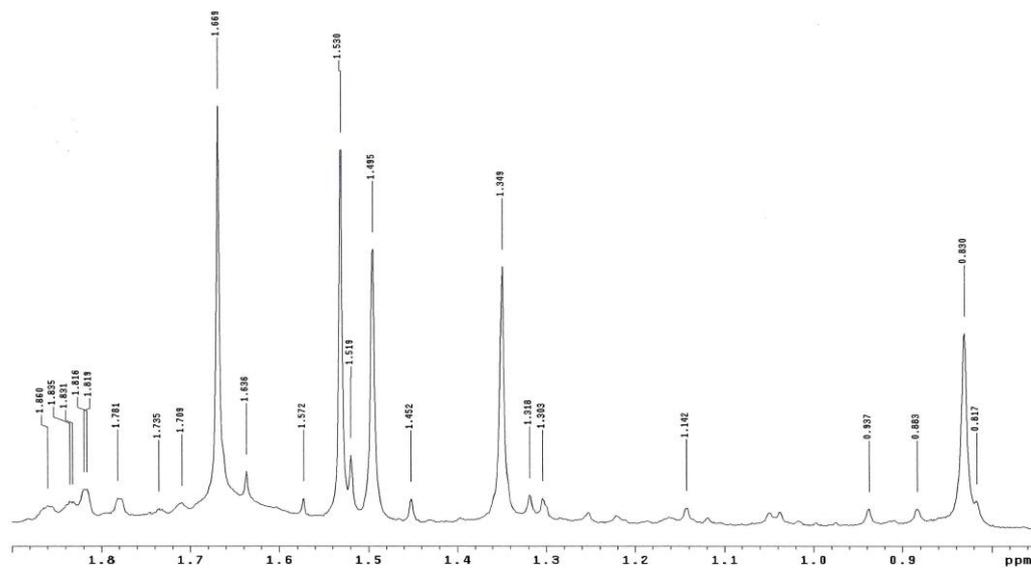
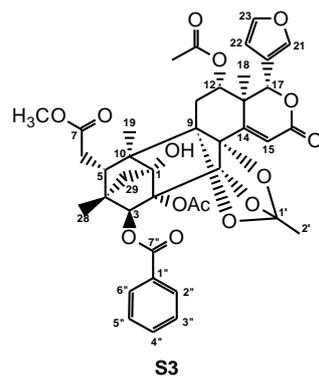


Figure S34. ¹H NMR (400 MHz, CDCl₃) spectrum of the new compound **3**.

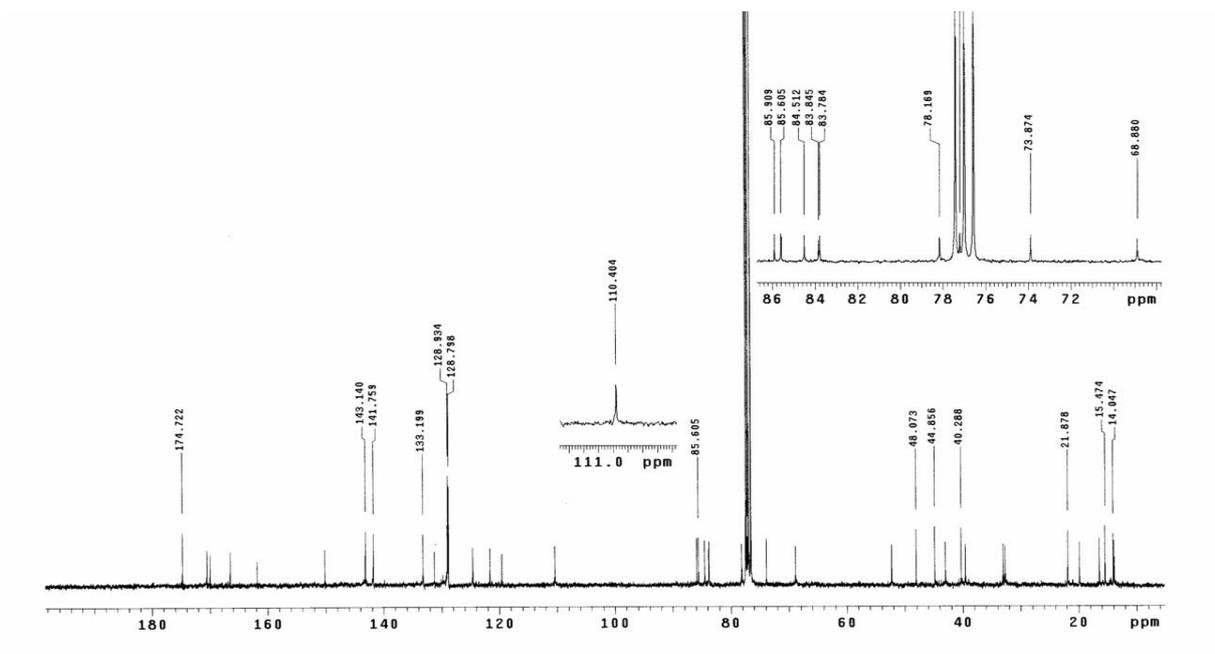
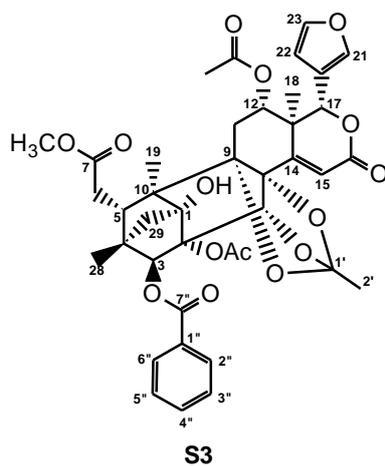


Figure S35. ¹³C NMR (75 MHz, CDCl₃) spectrum of the new compound **3**.

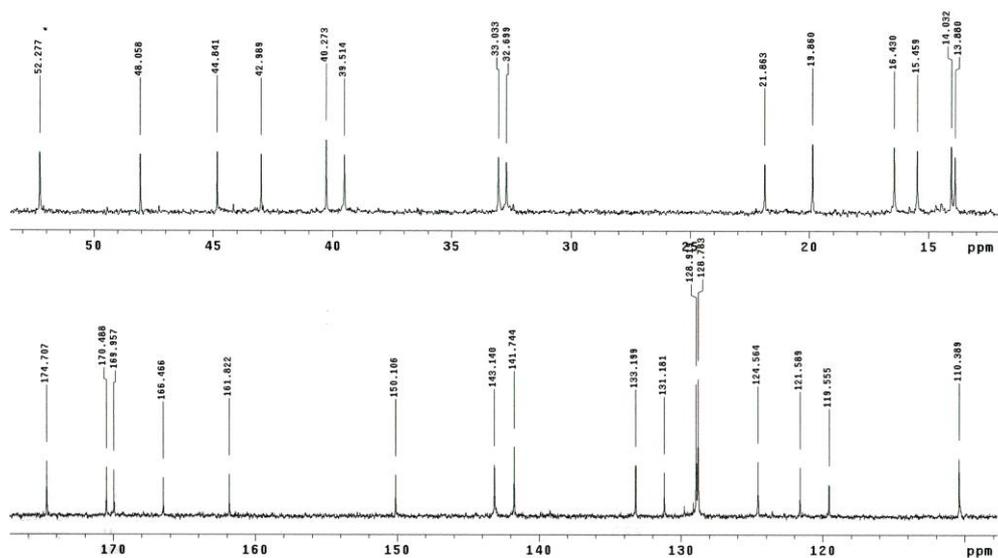
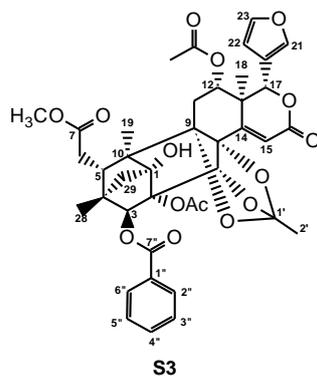


Figure S36. ¹³C NMR (75 MHz, CDCl₃) spectrum of the new compound **3**.

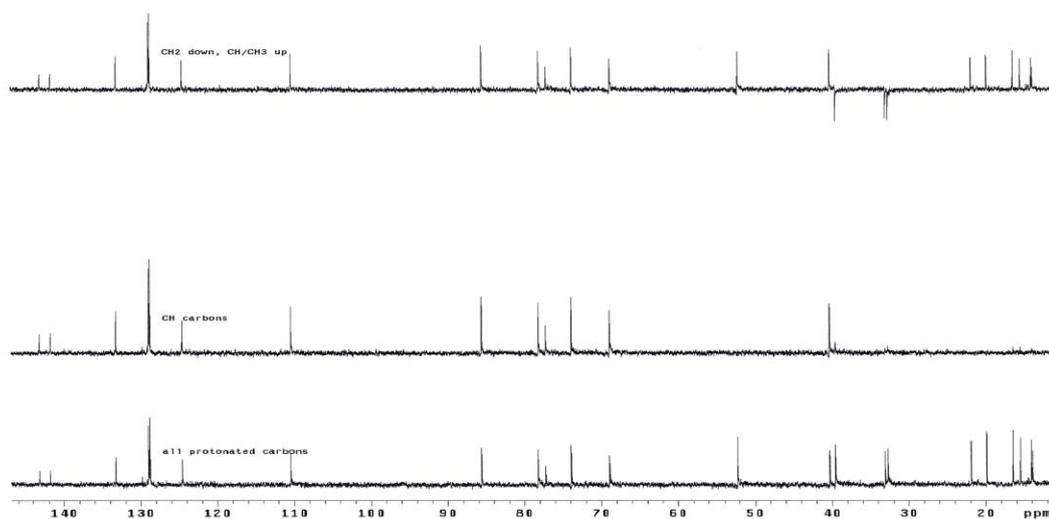


Figure S37. ¹³C-DEPT (75 MHz, CDCl₃) spectrum of the new compound **3**.

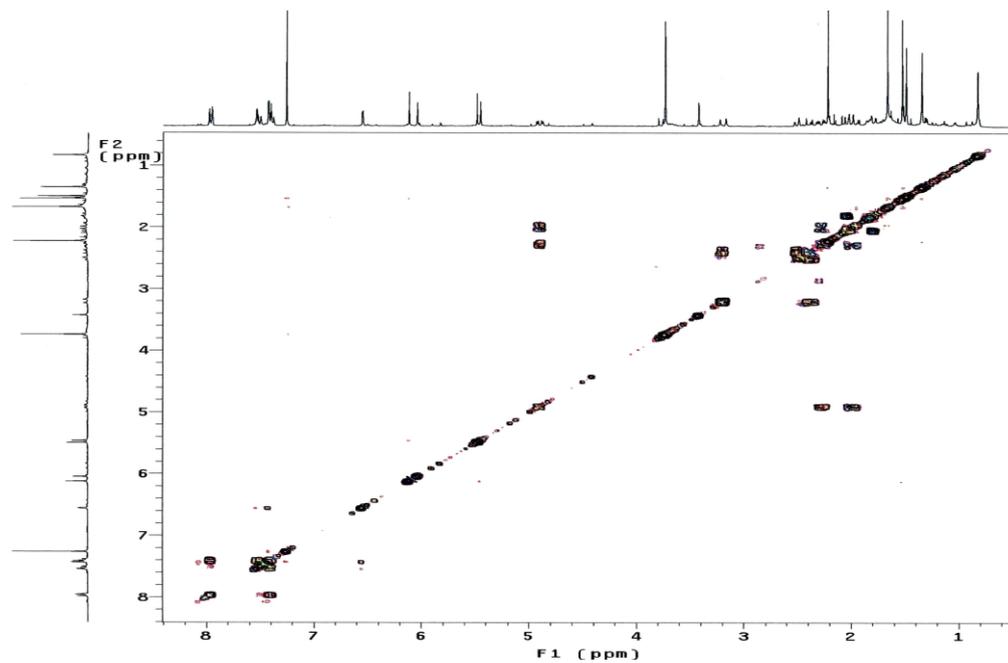
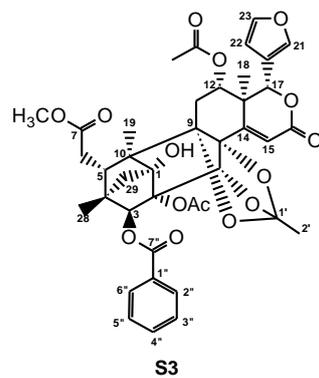


Figure S38. COSY (300 MHz, CDCl_3) spectrum of the new compound **3**.

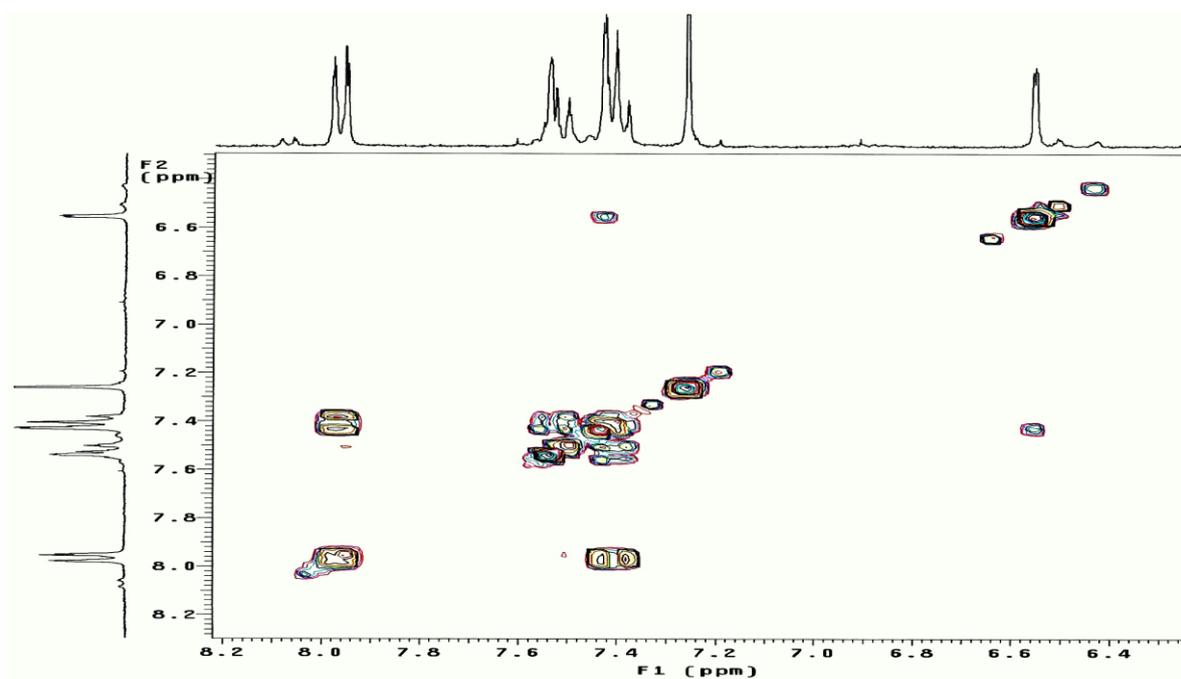


Figure S39. COSY (300 MHz, CDCl_3) spectrum of the new compound **3**.

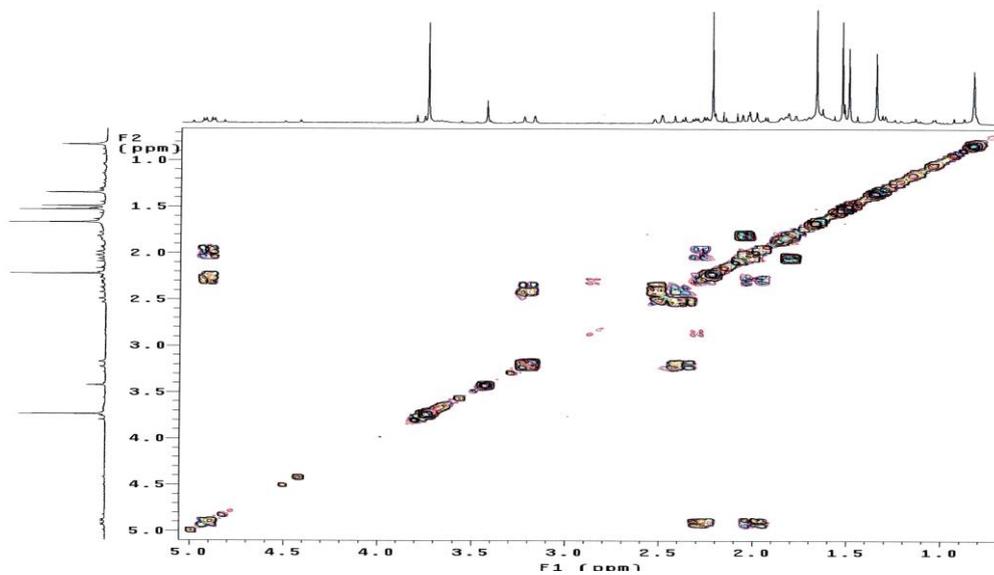
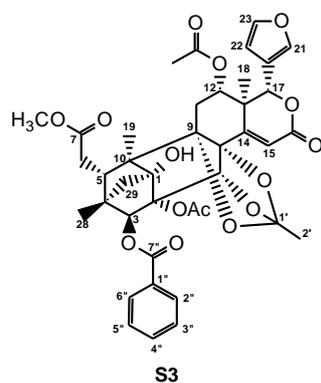


Figure S40. COSY (300 MHz, CDCl_3) spectrum of the new compound **3**.

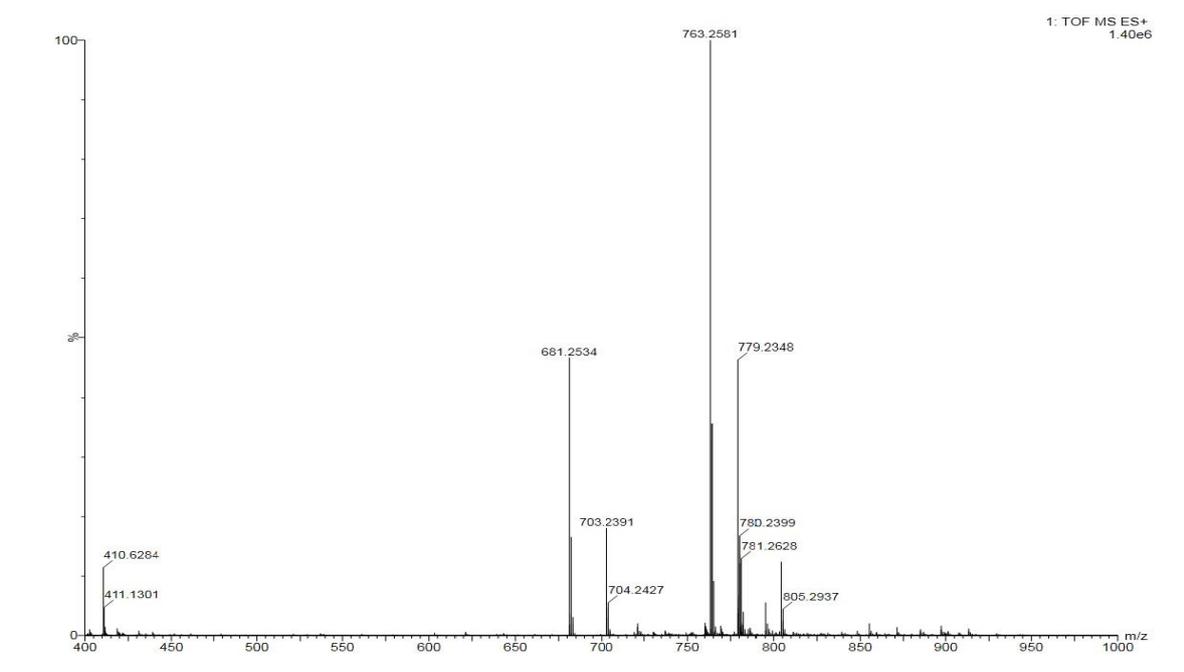


Figure S41. HR-ESI-ToF-MS spectrum of the new compound **3**.

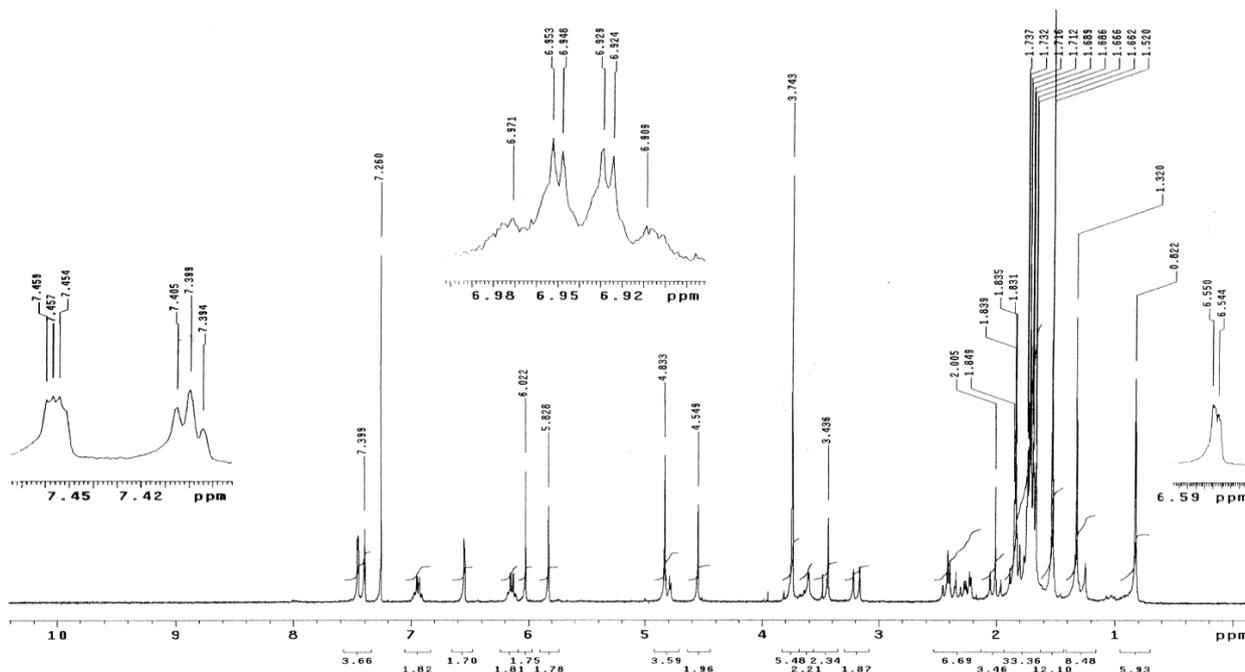
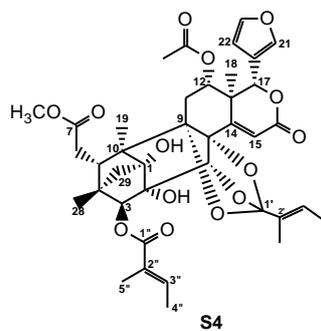


Figure S42. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **4**.

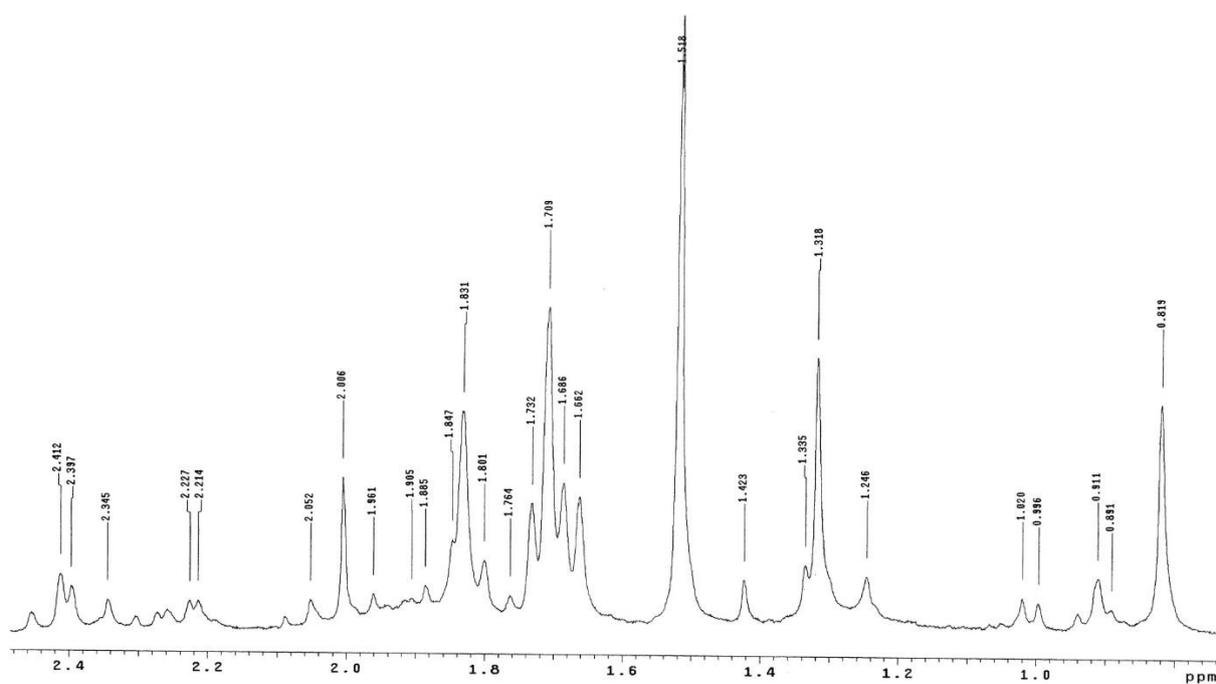


Figure S43. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **4**.

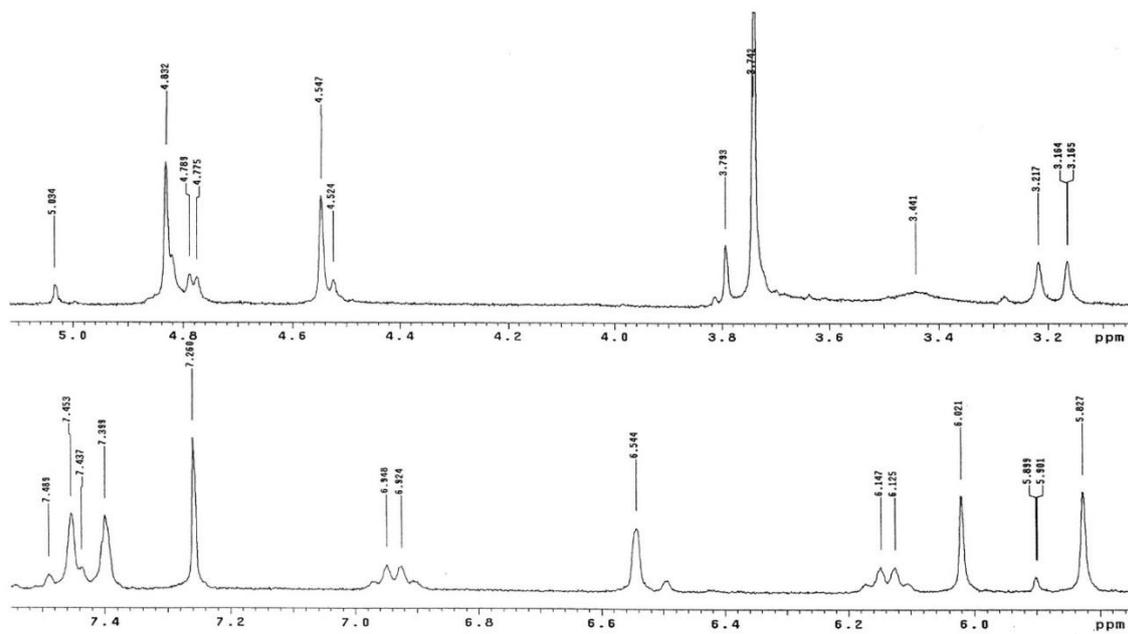
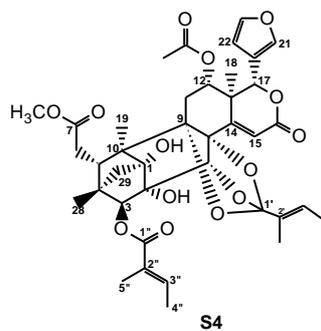


Figure S44. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **4**.

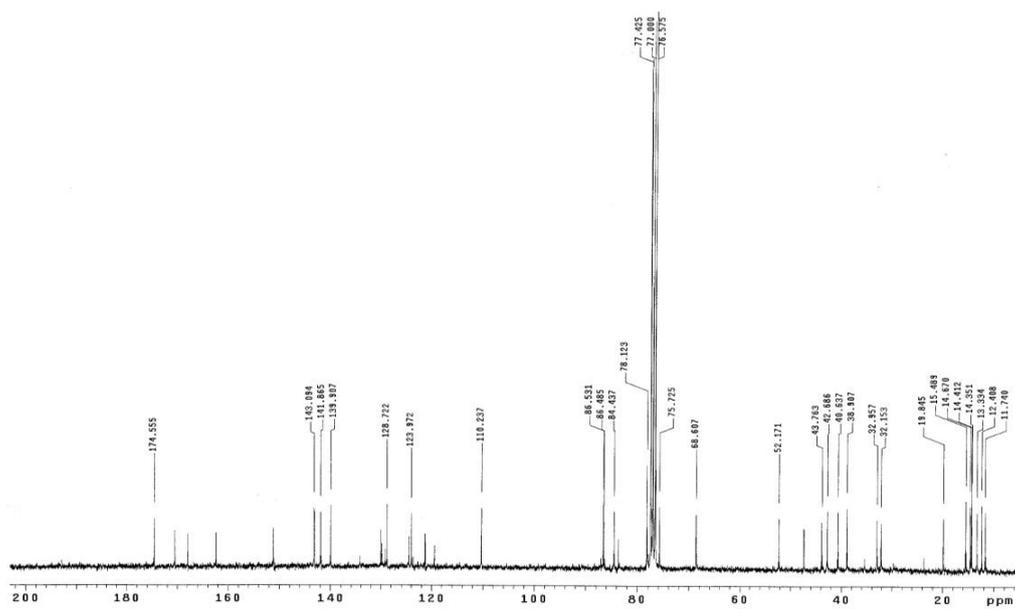


Figure S45. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound **4**.

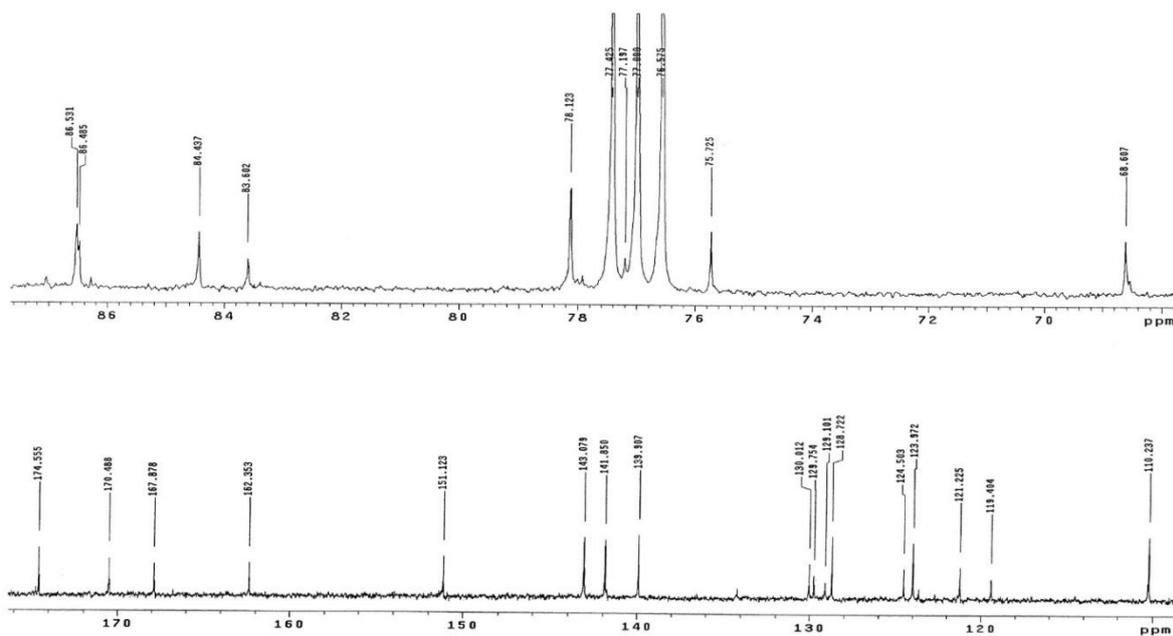
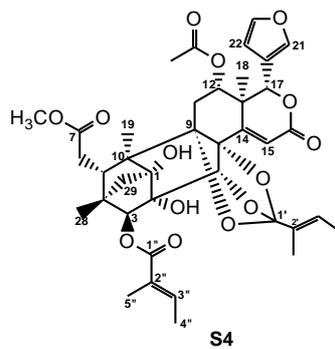


Figure S46. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound **4**.

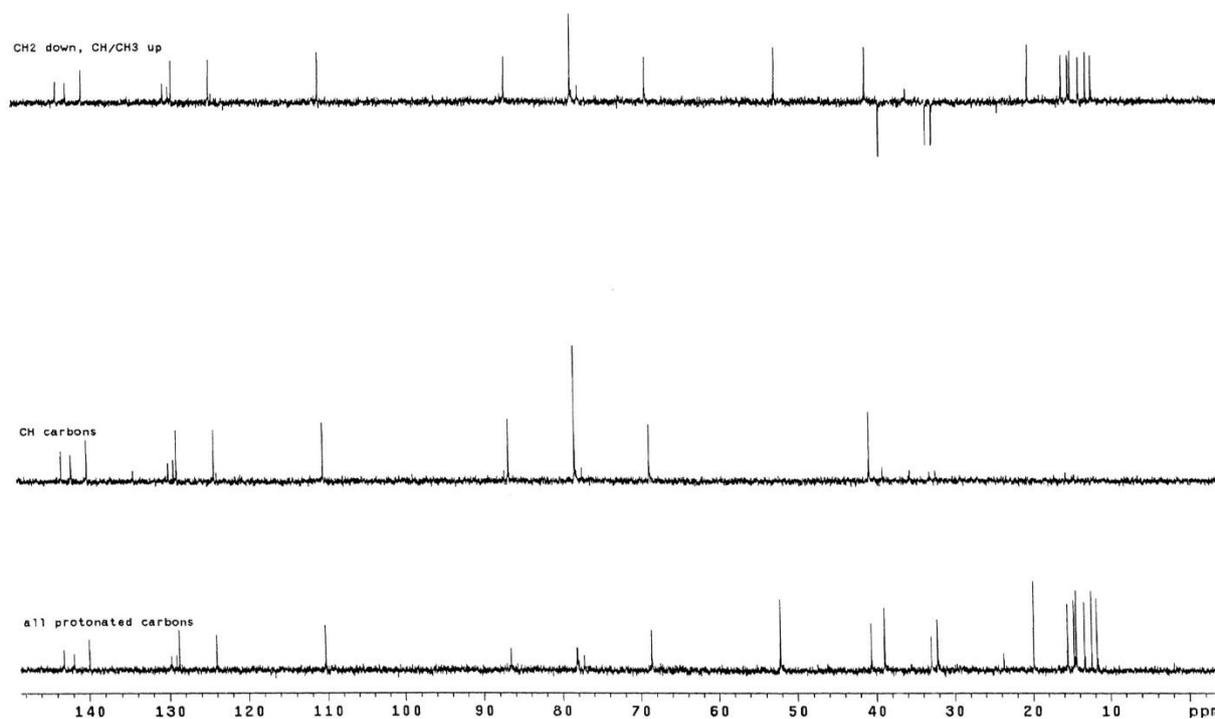


Figure S47. DEPT (75 MHz, CDCl_3) spectrum of the new compound **4**.

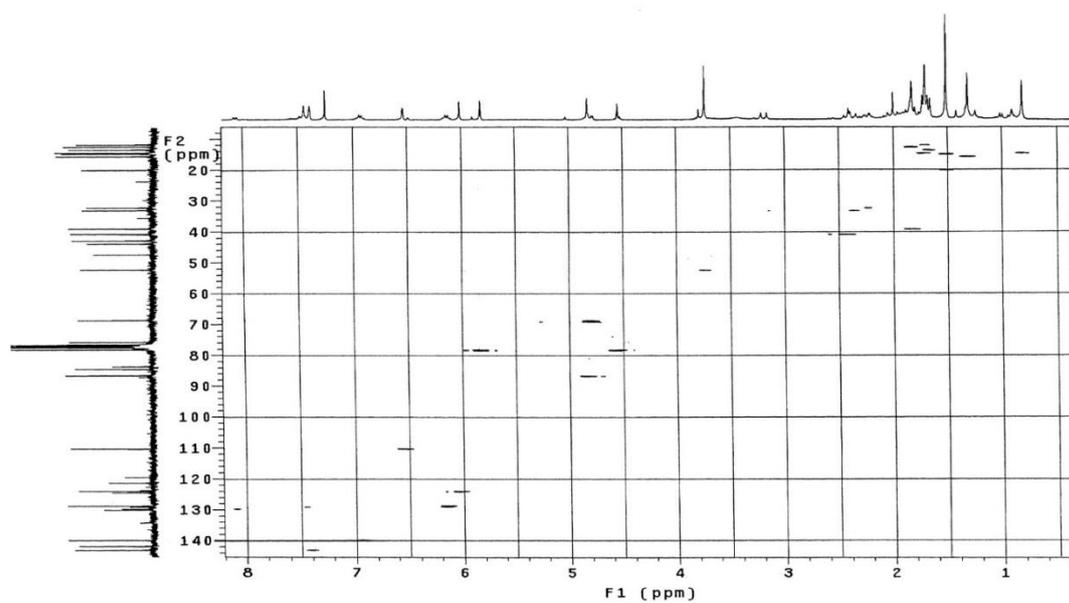
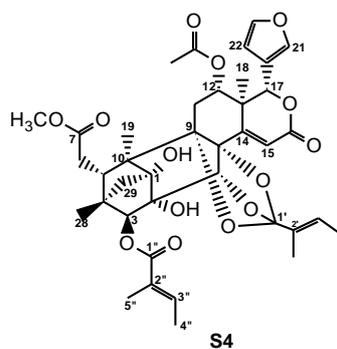


Figure S48. HETCOR (75 MHz, CDCl₃) spectrum of the new compound **4**.

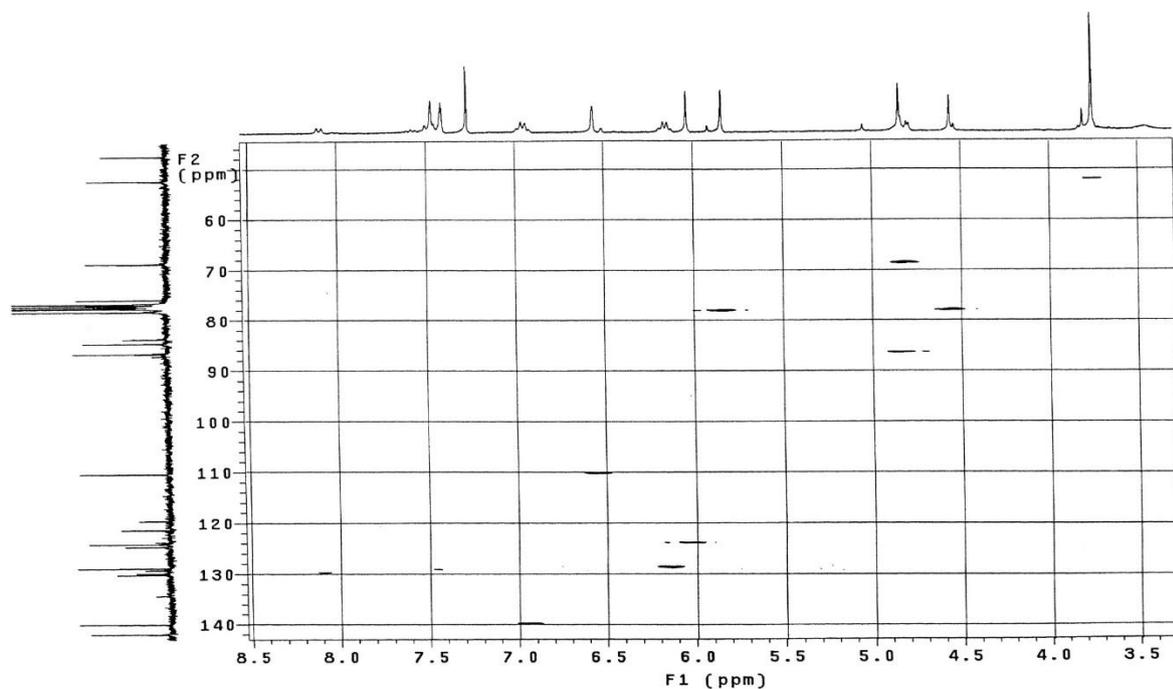


Figure S49. HETCOR (75 MHz, CDCl₃) spectrum of the new compound **4**.

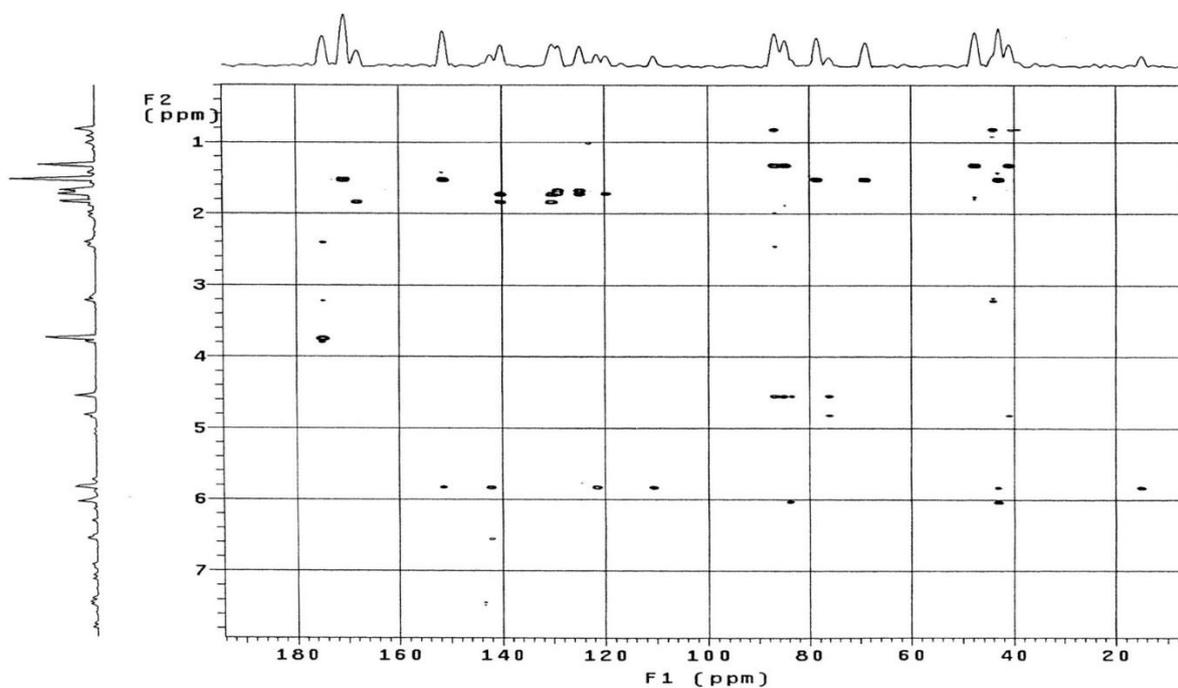
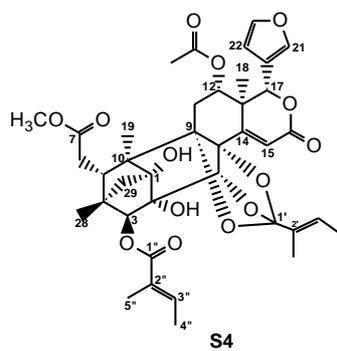


Figure S50. HMBC (300 MHz, CDCl_3) spectrum of the new compound **4**.

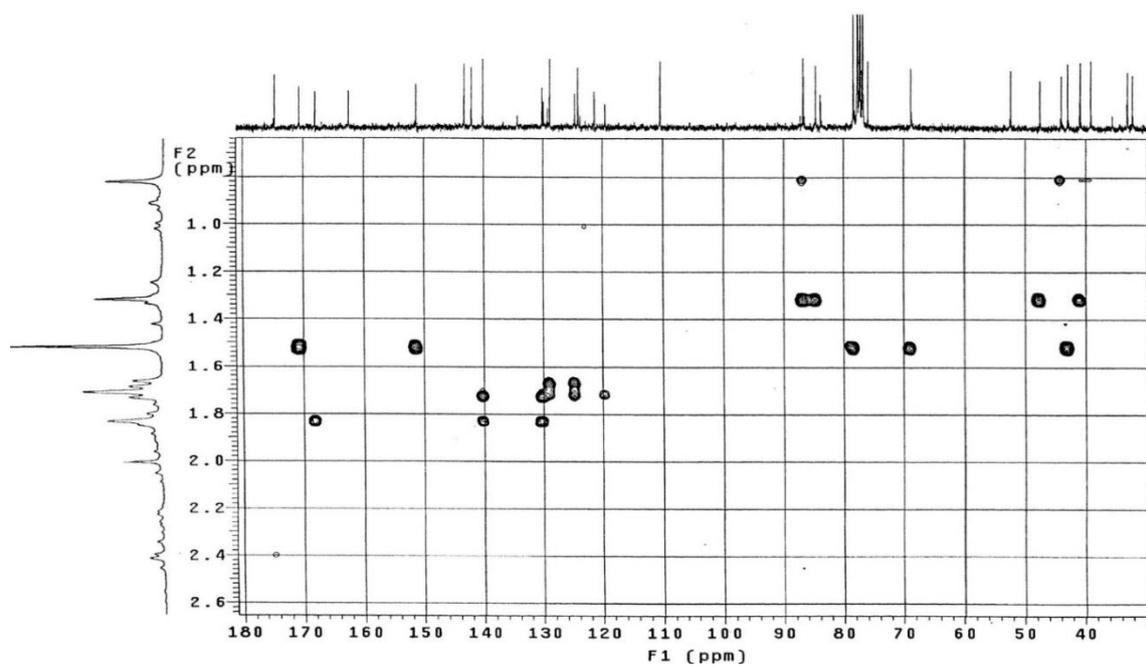


Figure S51. HMBC (300 MHz, CDCl_3) spectrum of the new compound **4**.

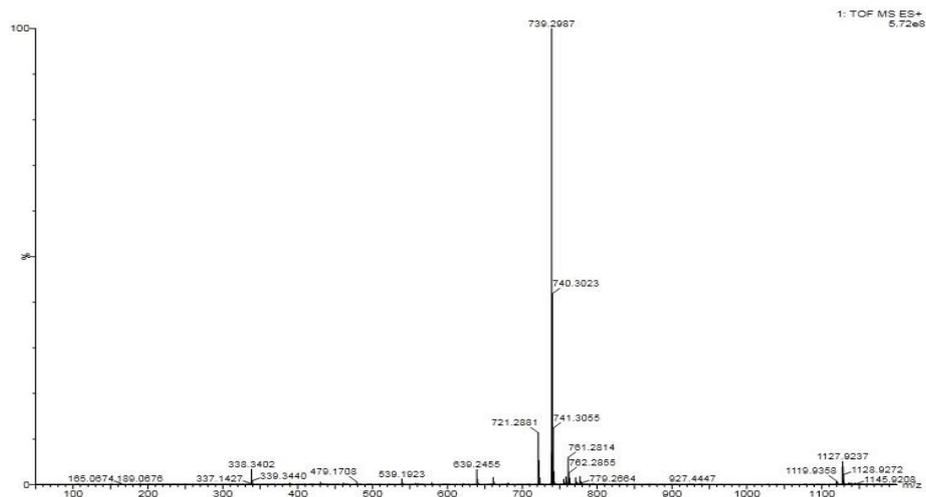
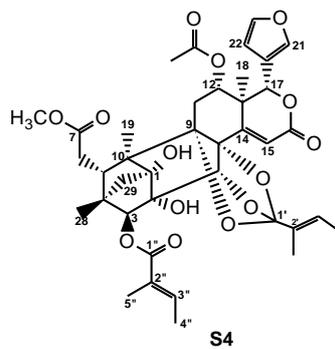
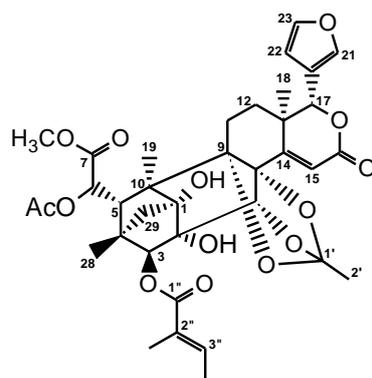
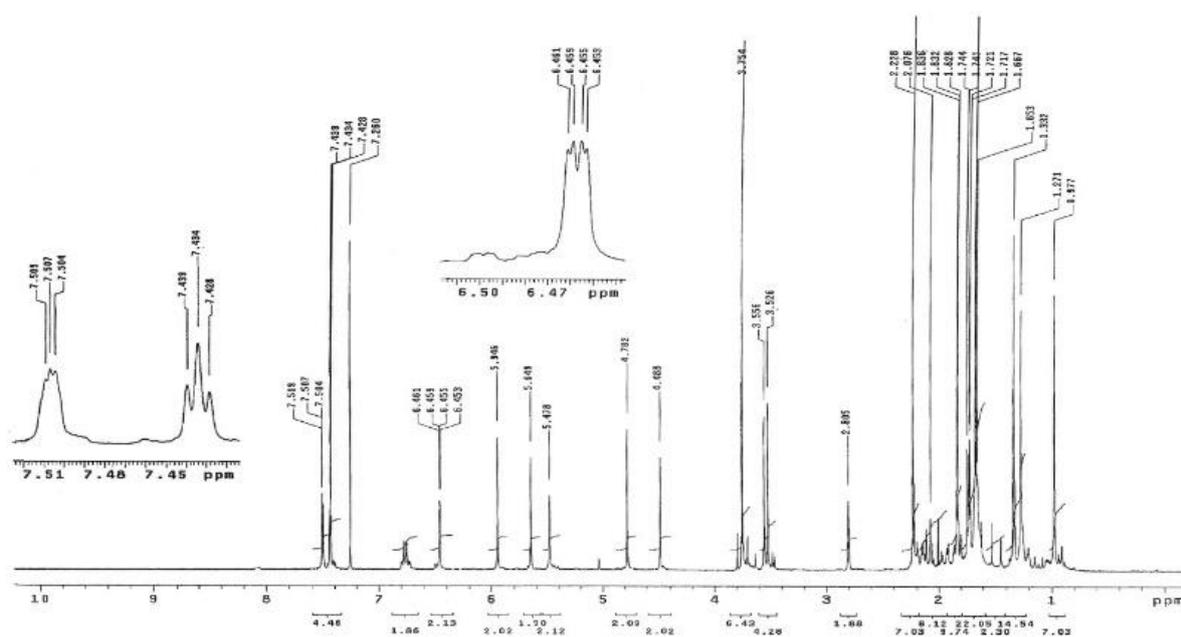
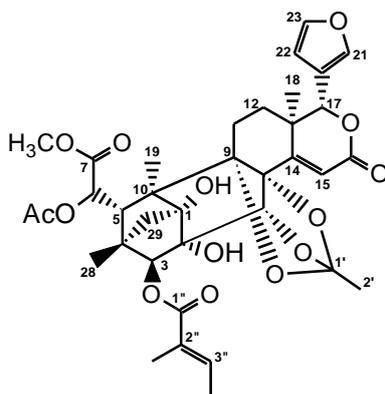


Figure S54. HR-ESI-ToF-MS of the new compound **4**.



S5





S5

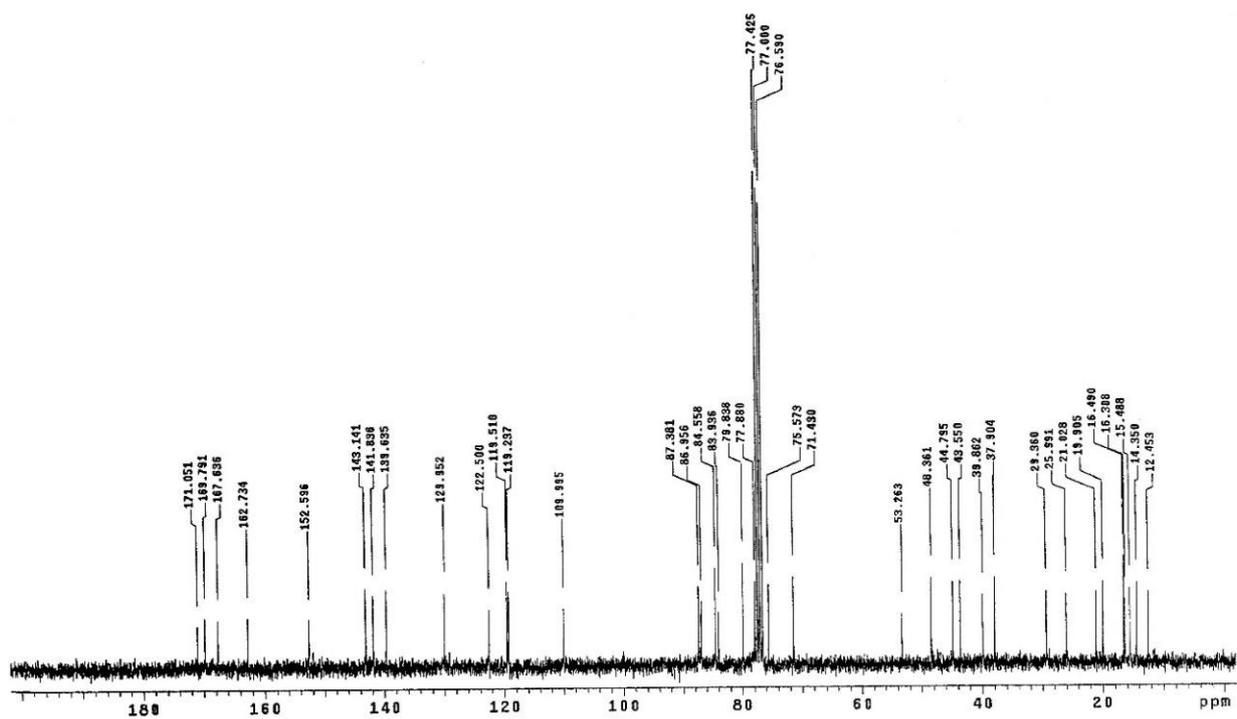
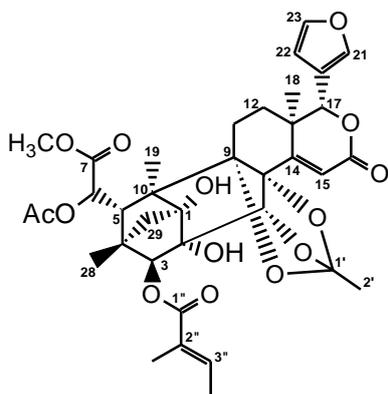


Figure S56. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound 5.



S5

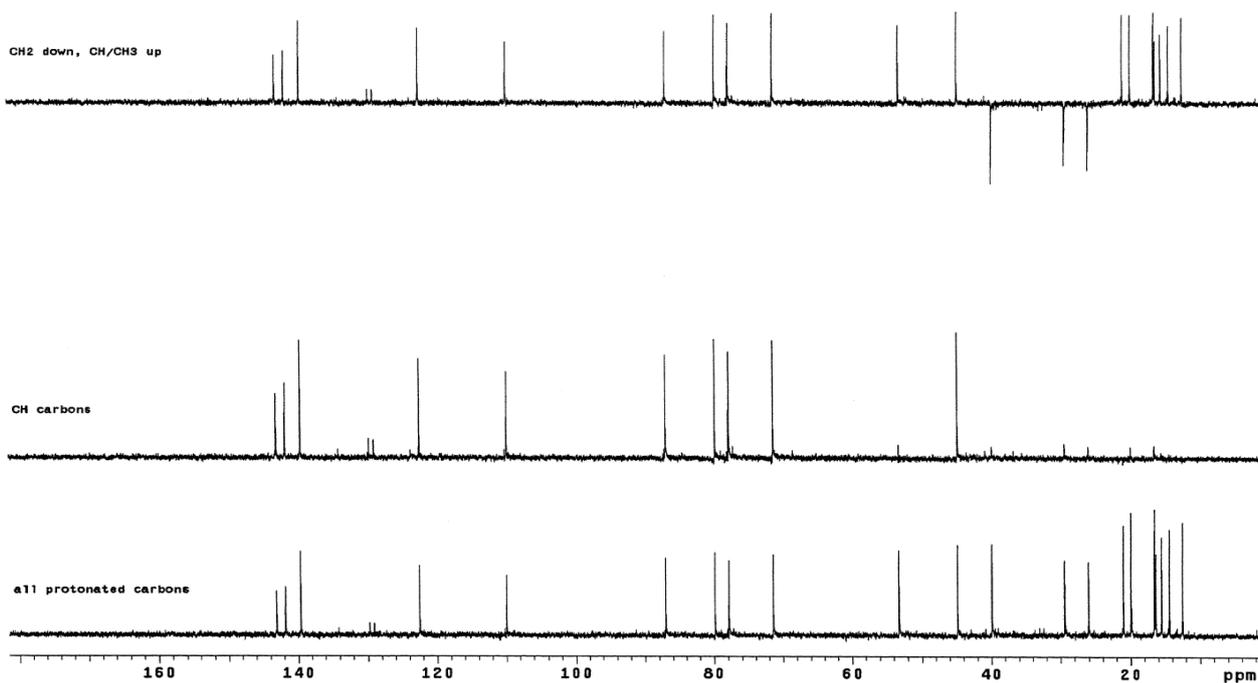
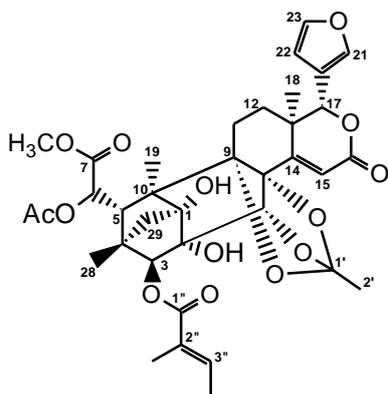


Figure S57. ¹³C-DEPT (75 MHz, CDCl₃) spectrum of the new compound 5.



S5

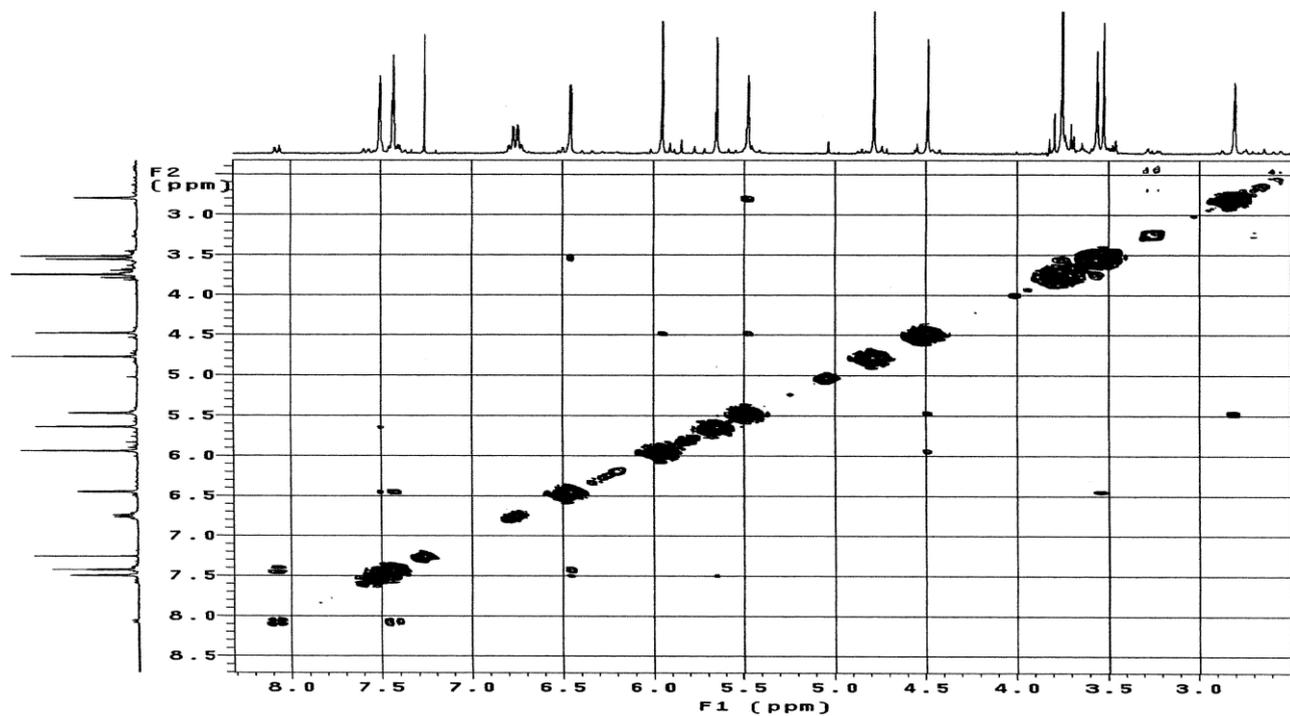
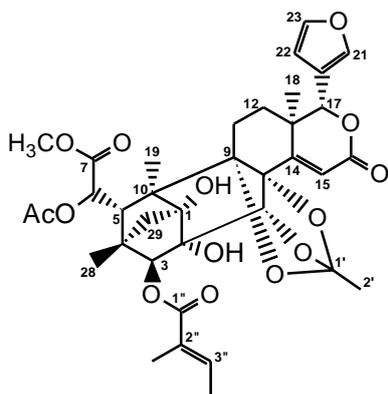


Figure S58. COSY (300 MHz, CDCl₃) spectrum of the new compound 5.



S5

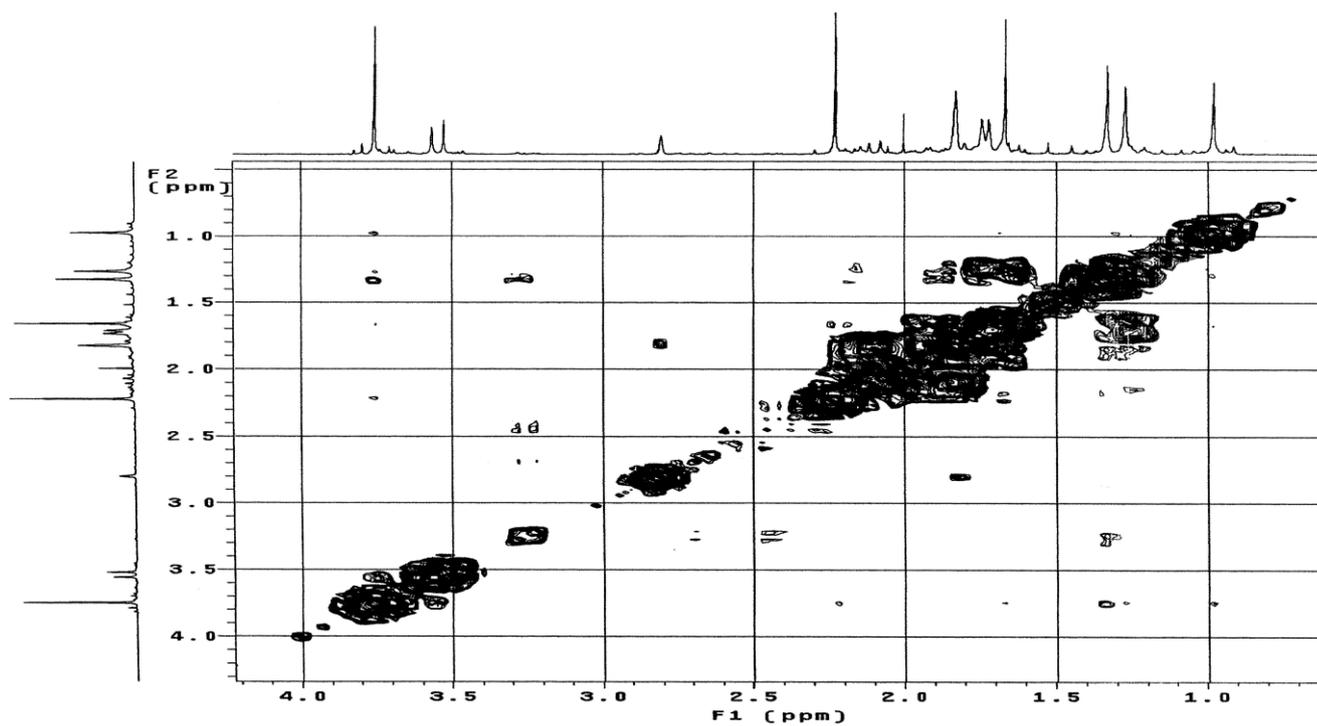
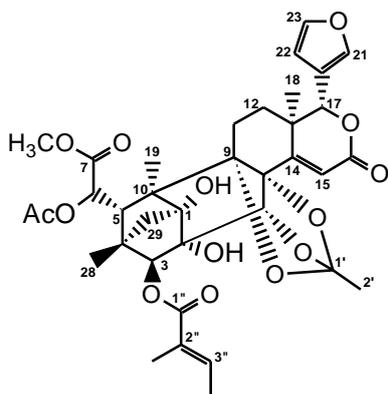


Figure S59. COSY (300 MHz, CDCl₃) spectrum of the new compound 5.



S5

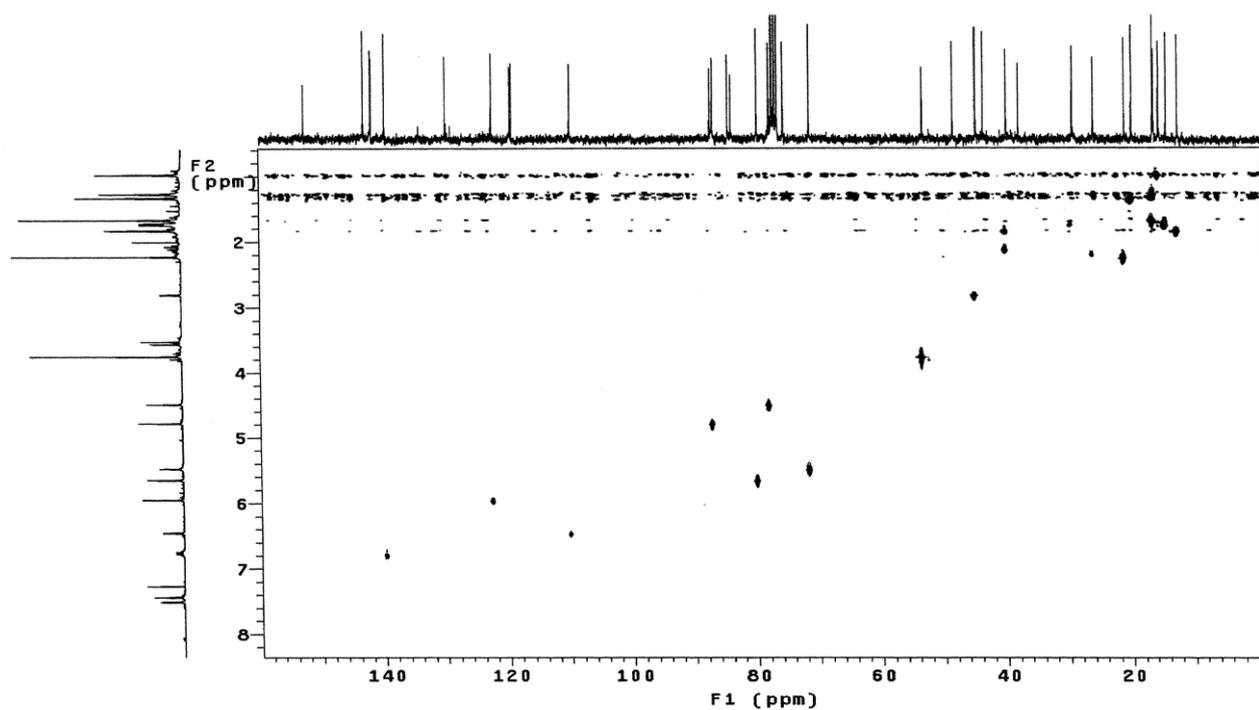
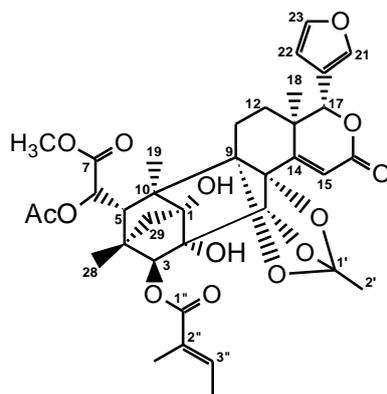


Figure S60. HSQC (75 MHz, CDCl₃) spectrum of the new compound 5.



S5

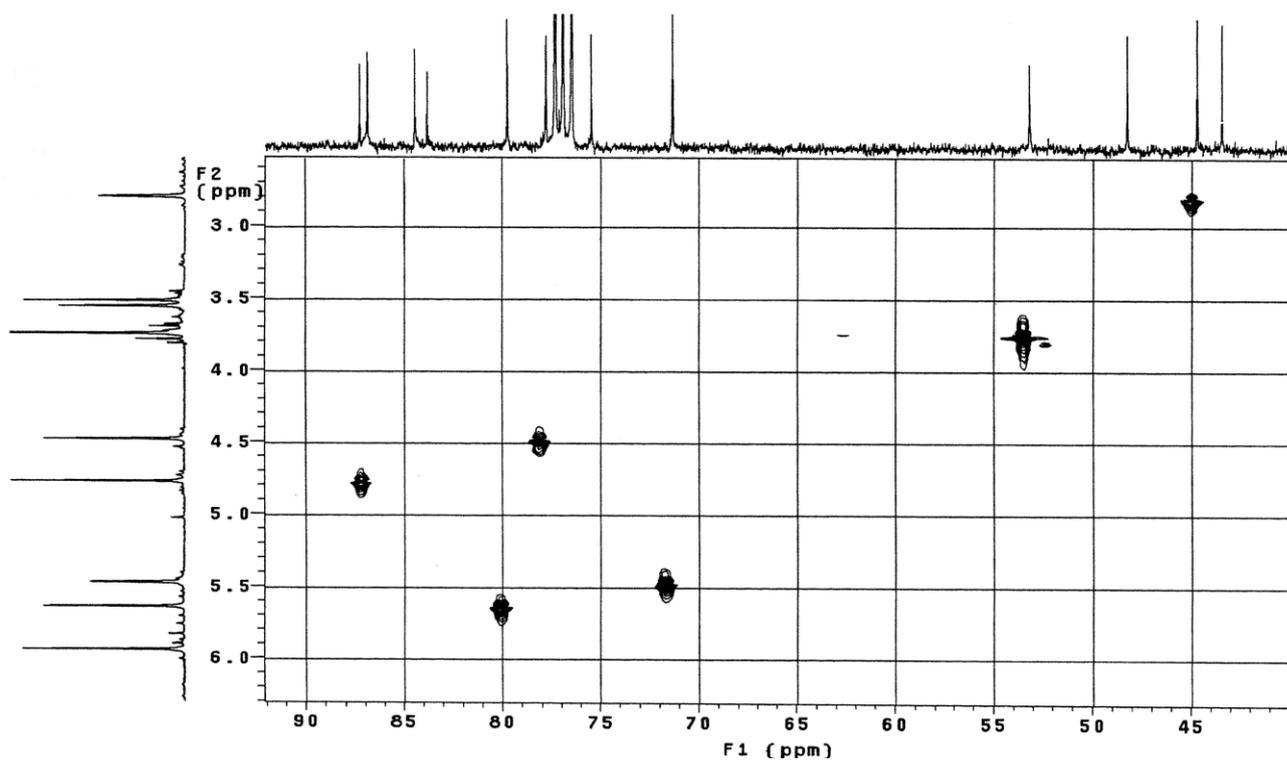
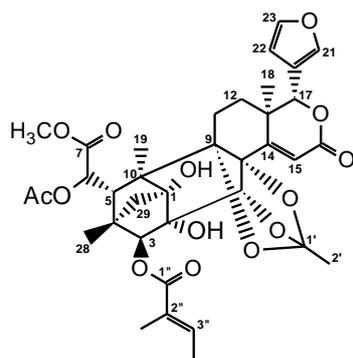


Figure S61. HSQC (75 MHz, CDCl₃) spectrum of the new compound 5.



S5

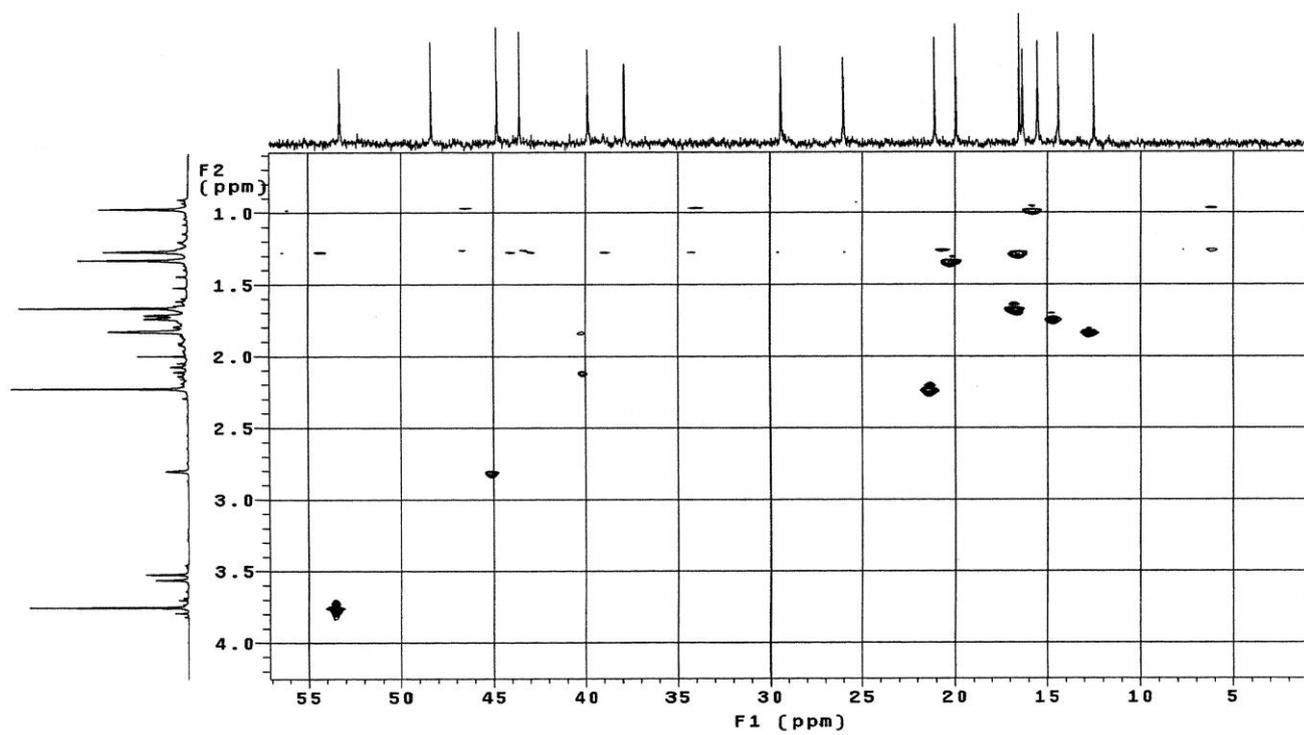
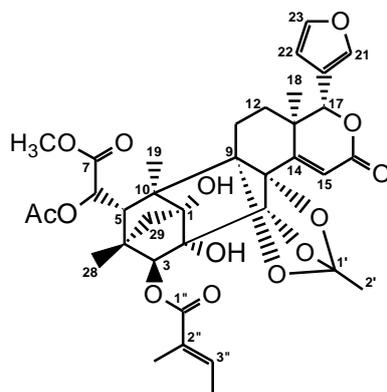


Figure S62. HSQC (75 MHz, CDCl₃) spectrum of the new compound 5.



S5

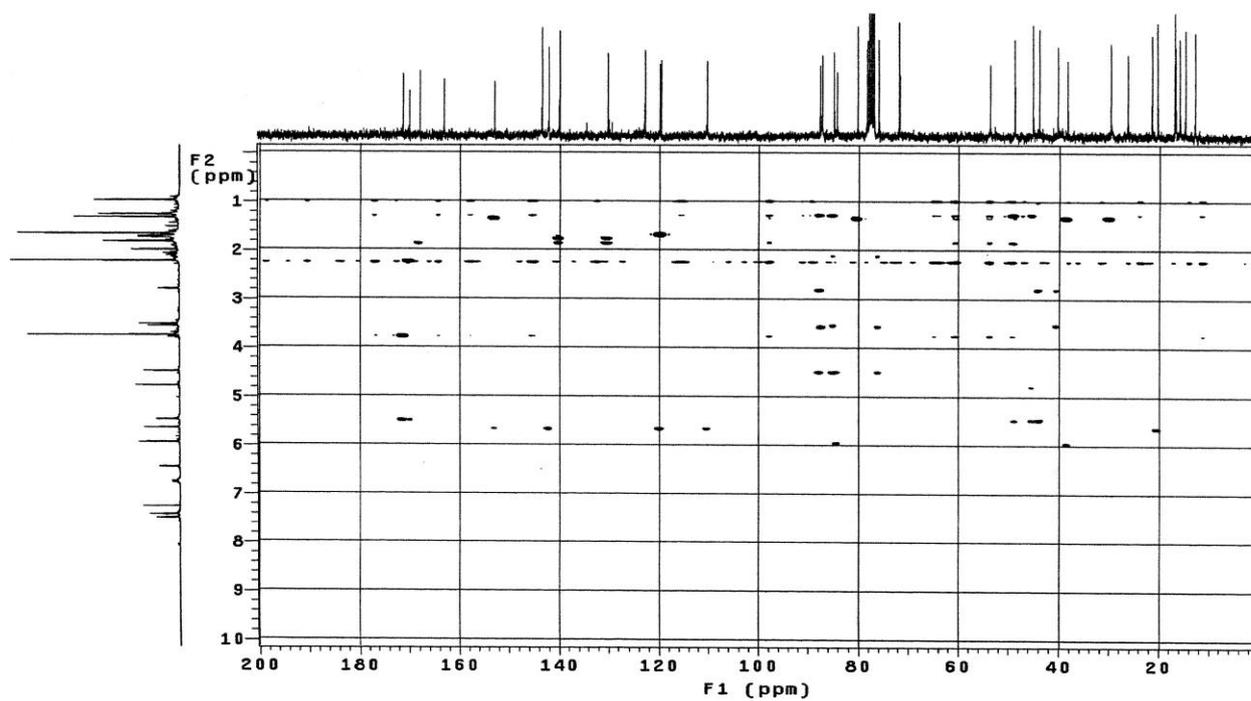
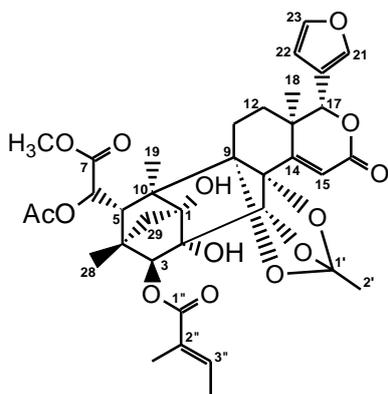


Figure S63. HMBC (300 MHz, CDCl_3) spectrum of the new compound 5.



S5

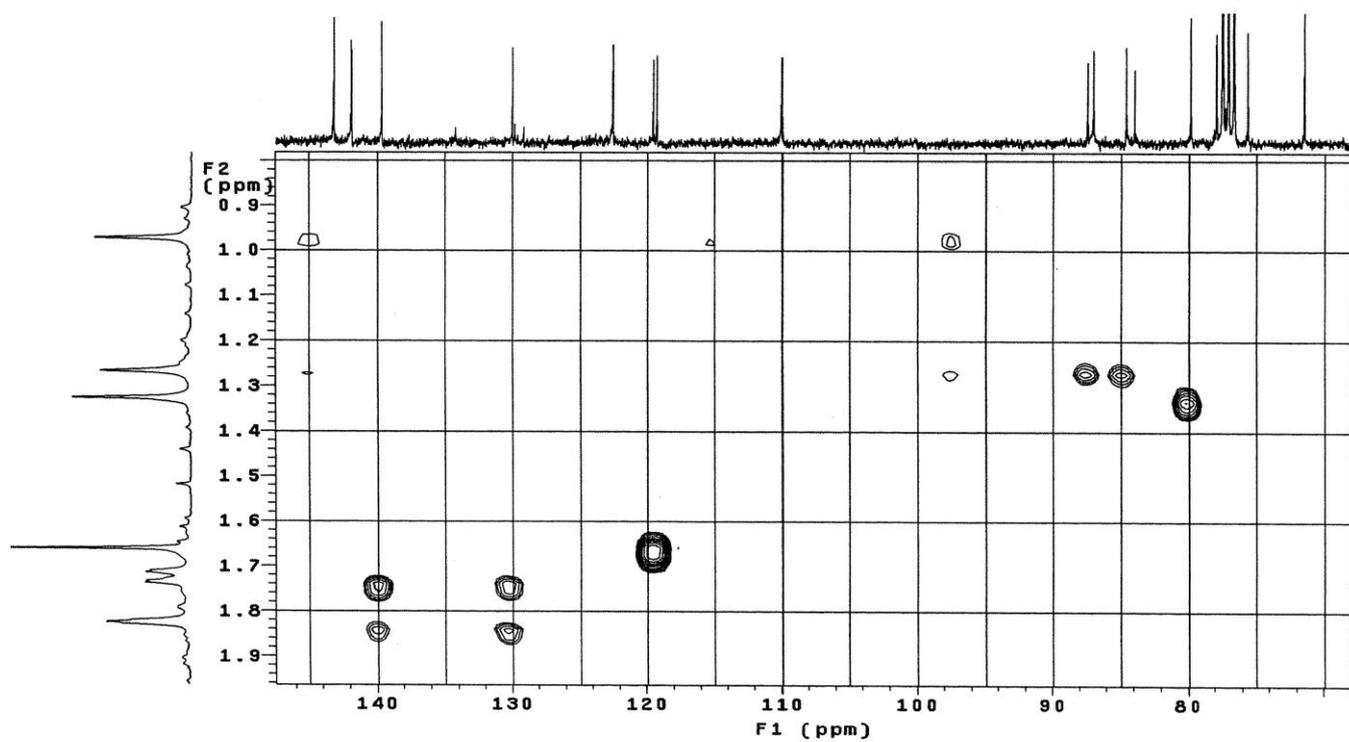
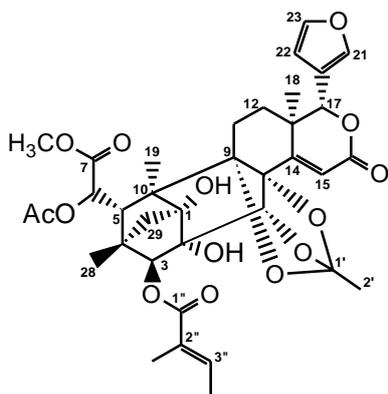


Figure S64. HMBC (300 MHz, CDCl_3) spectrum of the new compound 5.



S5

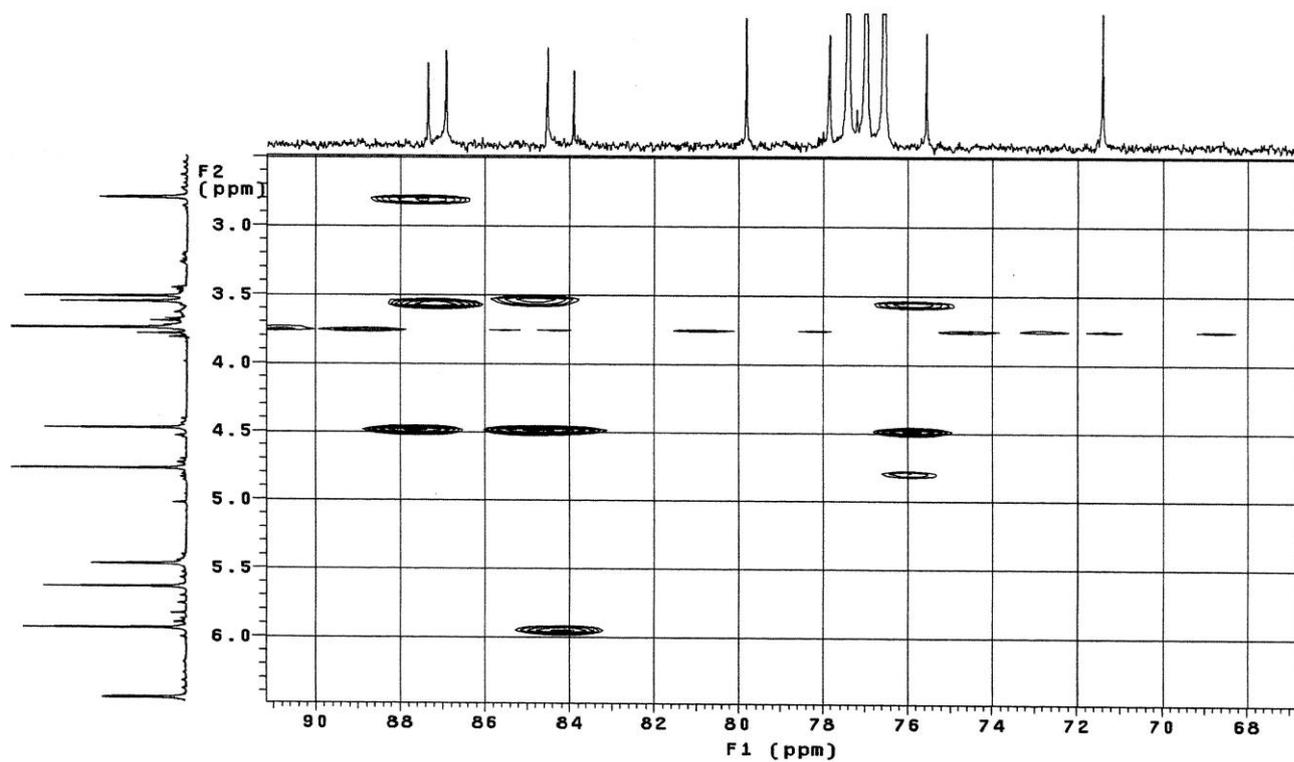
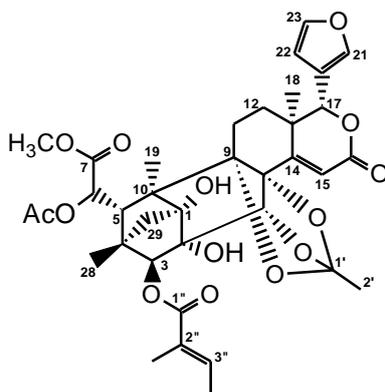


Figure S65. HMBC (300 MHz, CDCl₃) spectrum of the new compound 5.



S5

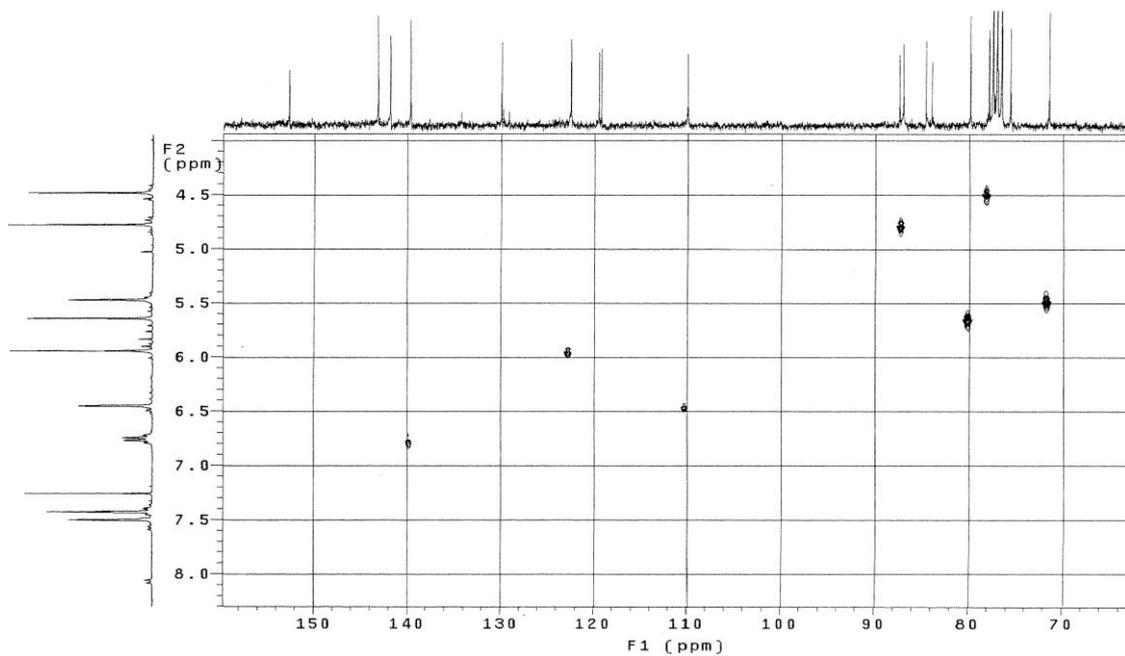


Figure S66. HMBC (300 MHz, CDCl₃) spectrum of the new compound 5.

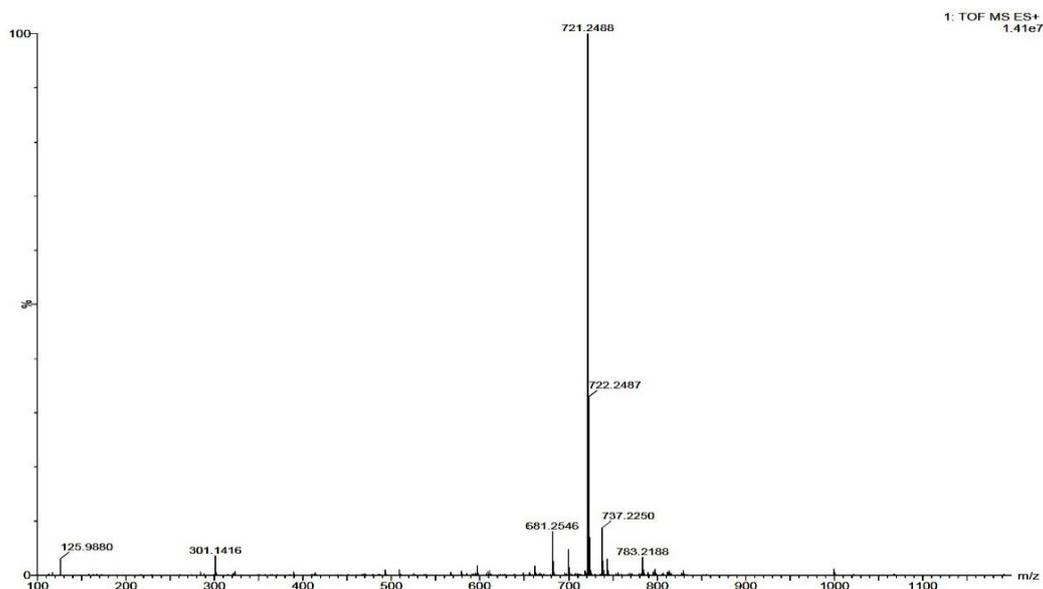


Figure S67. HR-ESI-ToF-MS spectrum of the new compound 5.

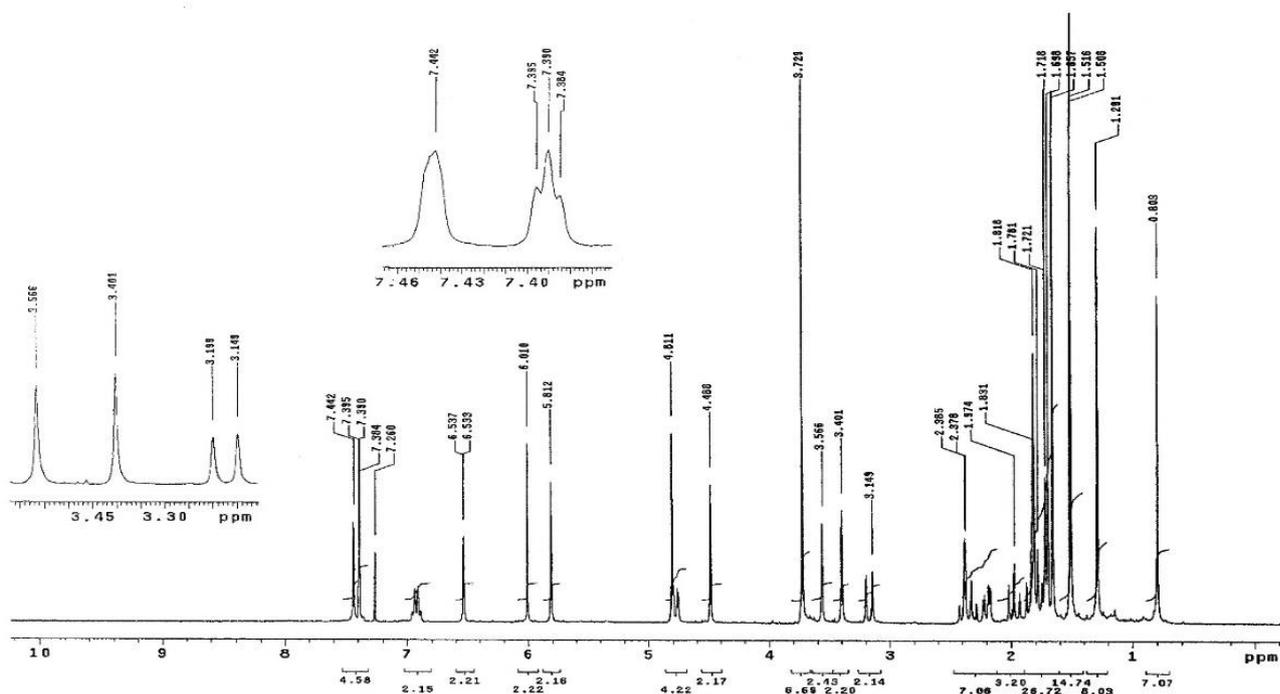
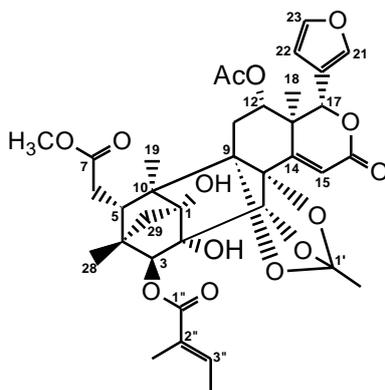


Figure S68. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **6**.

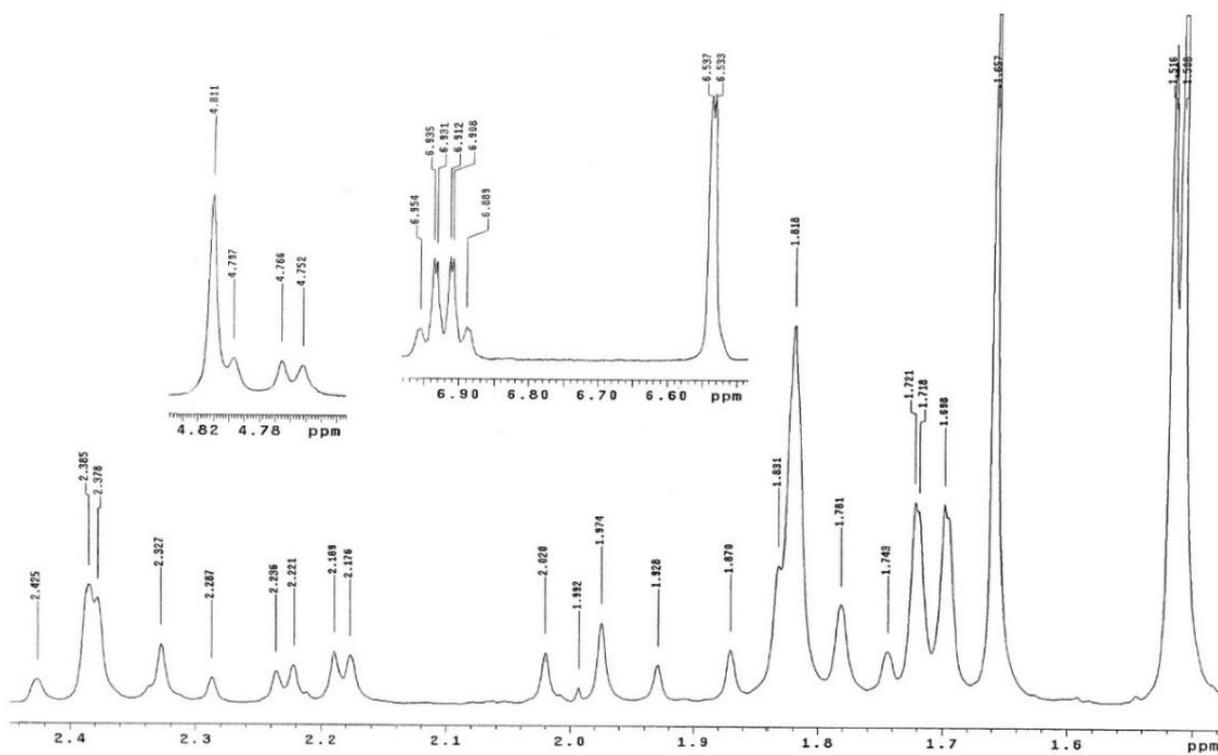
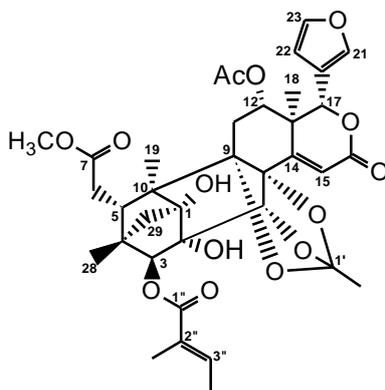


Figure S69. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **6**.



S6

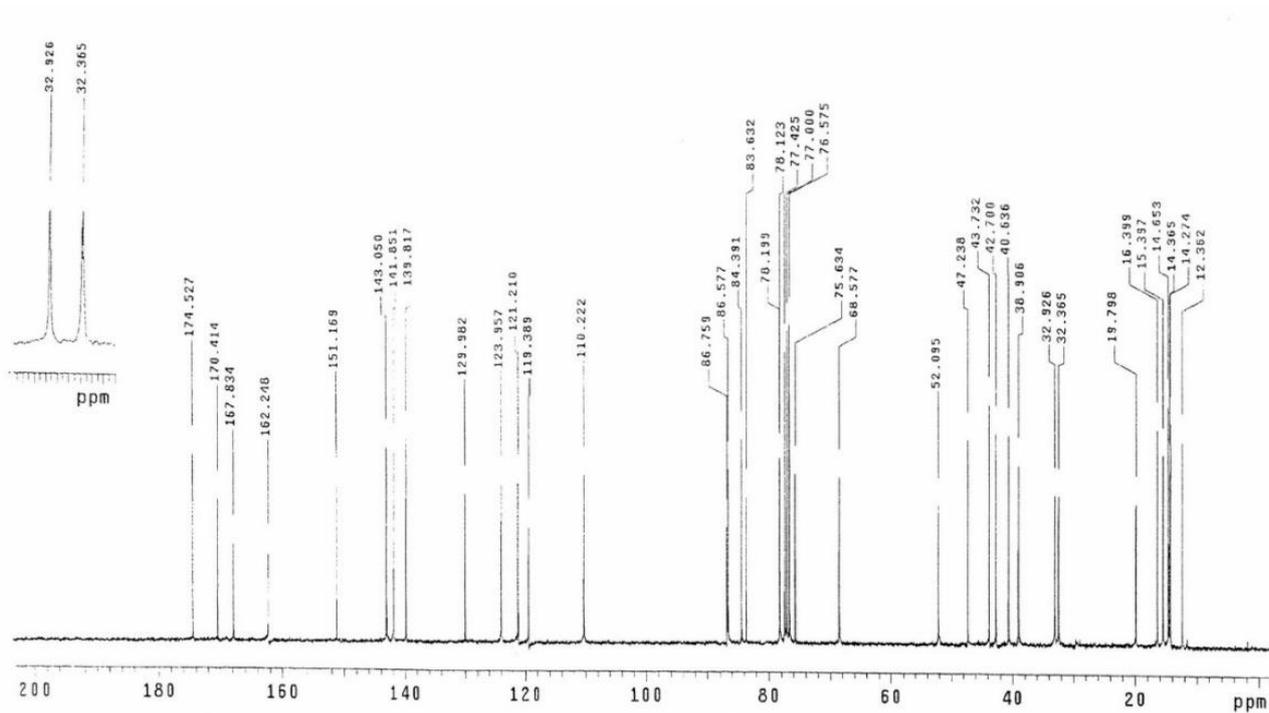
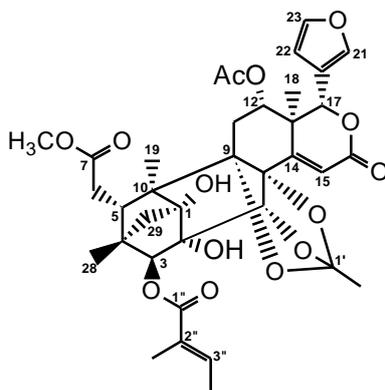


Figure S70. ¹³C NMR (75 MHz, CDCl₃) spectrum of the new compound 6.



S6

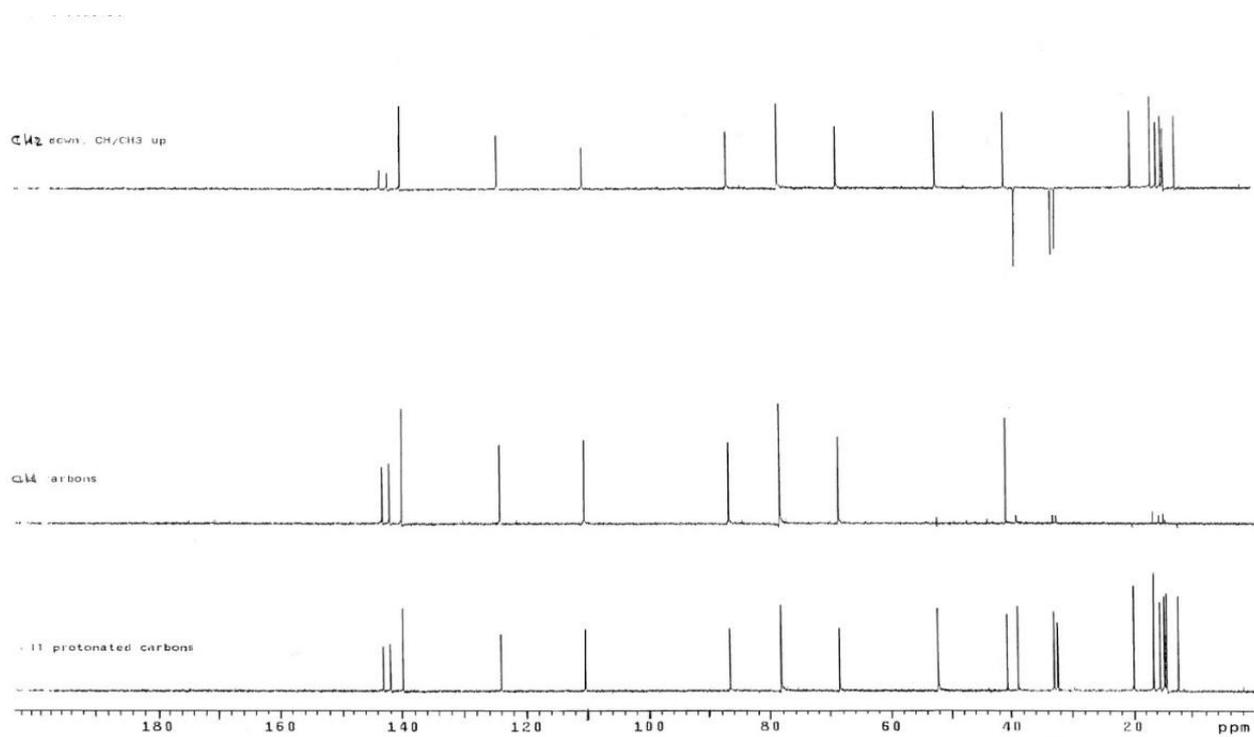
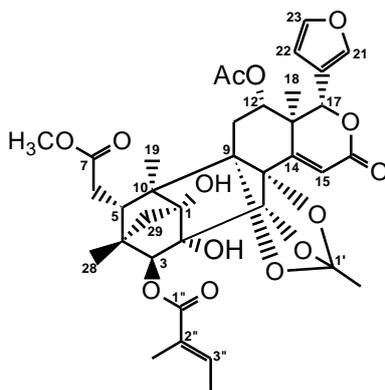


Figure S71. ¹³C-DEPT (75 MHz, CDCl₃) spectrum of the new compound 6.



S6

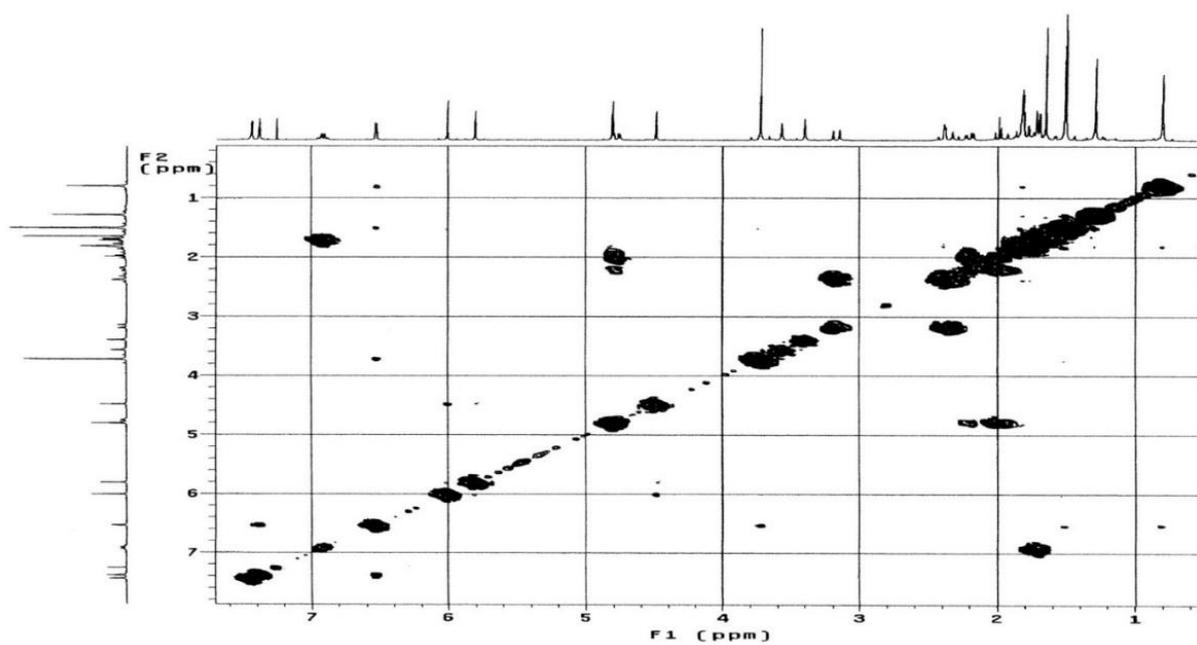


Figure S72. COSY (300 MHz, CDCl₃) spectrum of the new compound 6.

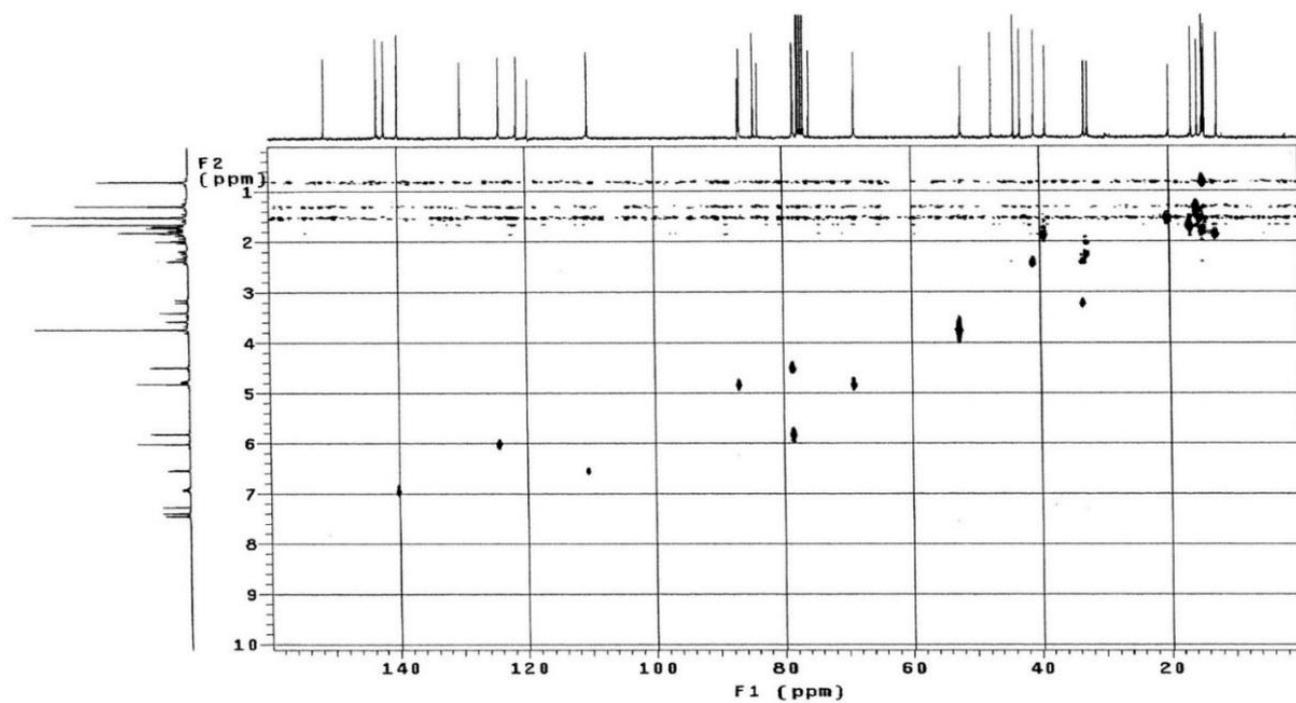
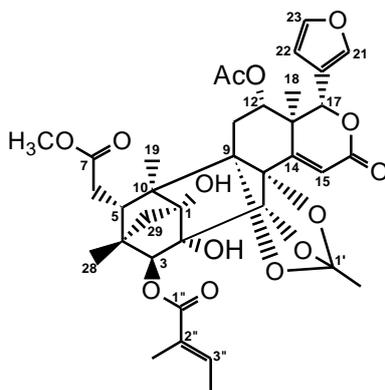


Figure S73. HSQC (75 MHz, CDCl₃) spectrum of the new compound **6**.



S6

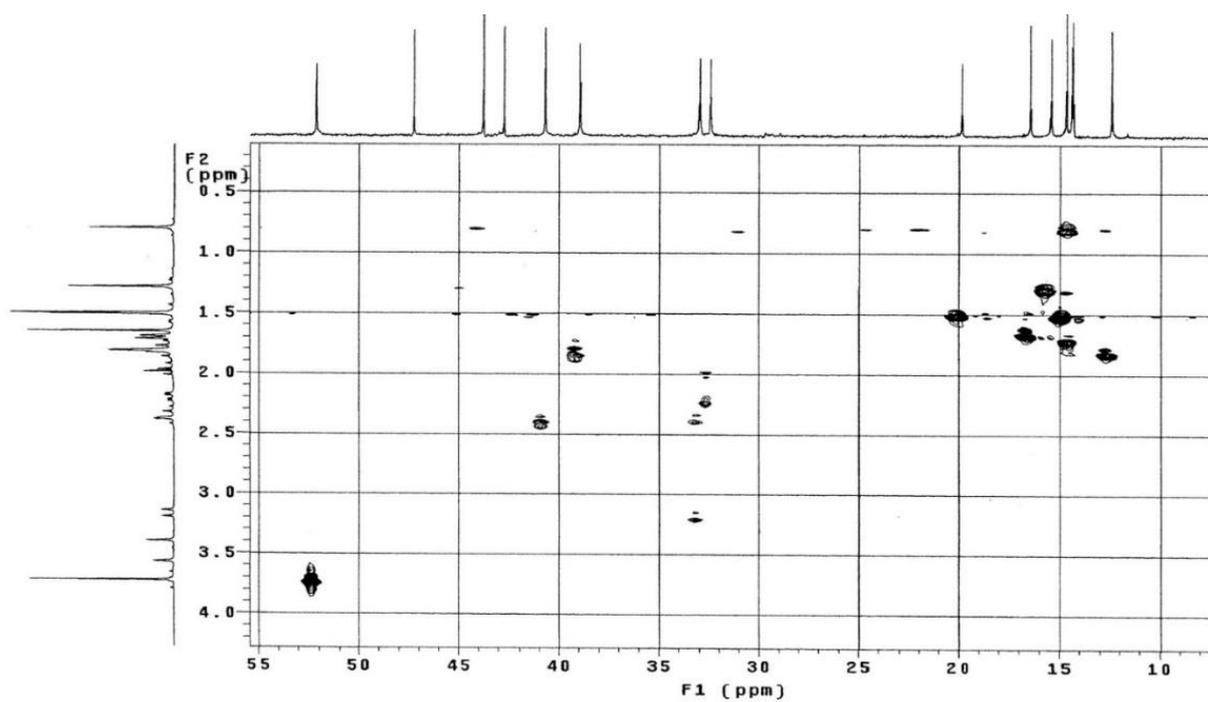
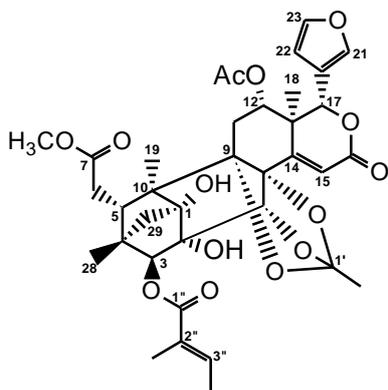


Figure S74. HSQC (75 MHz, CDCl₃) spectrum of the new compound 6.



S6

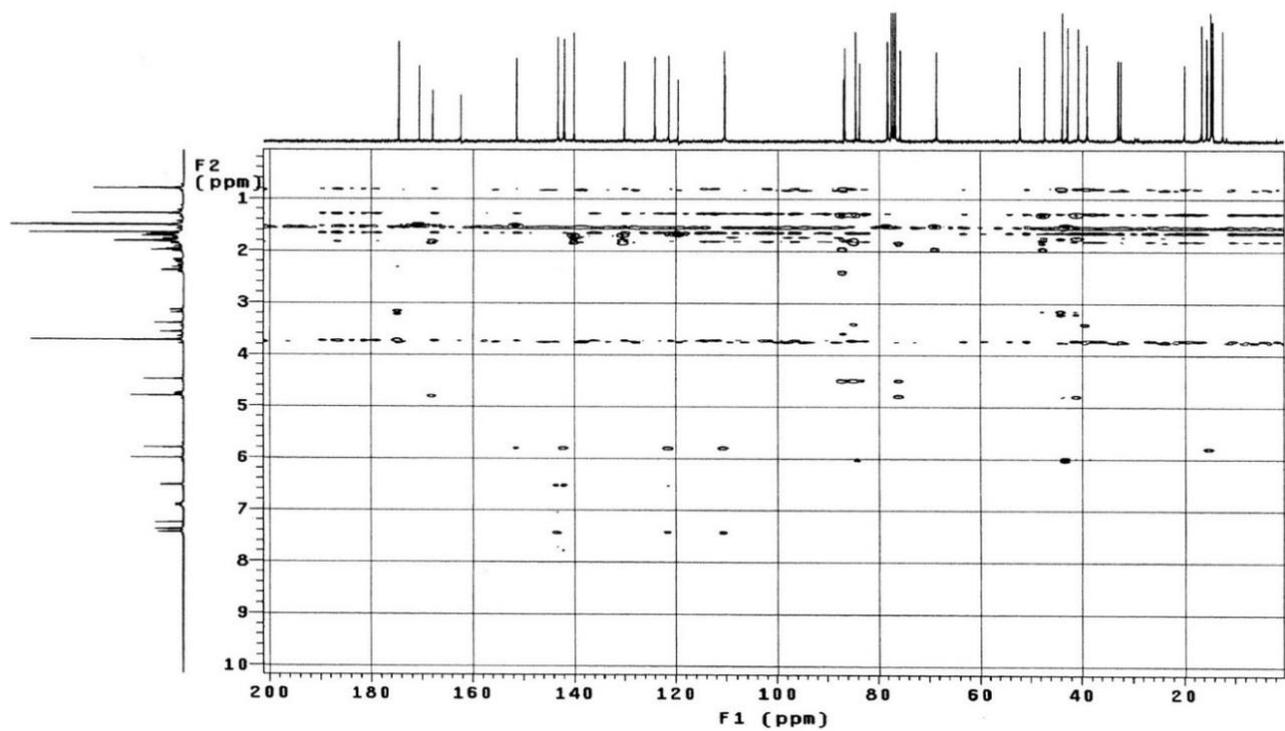
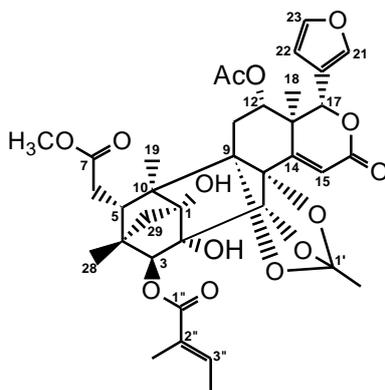


Figure S75. HMBC (300 MHz, CDCl_3) spectrum of the new compound 6.



S6

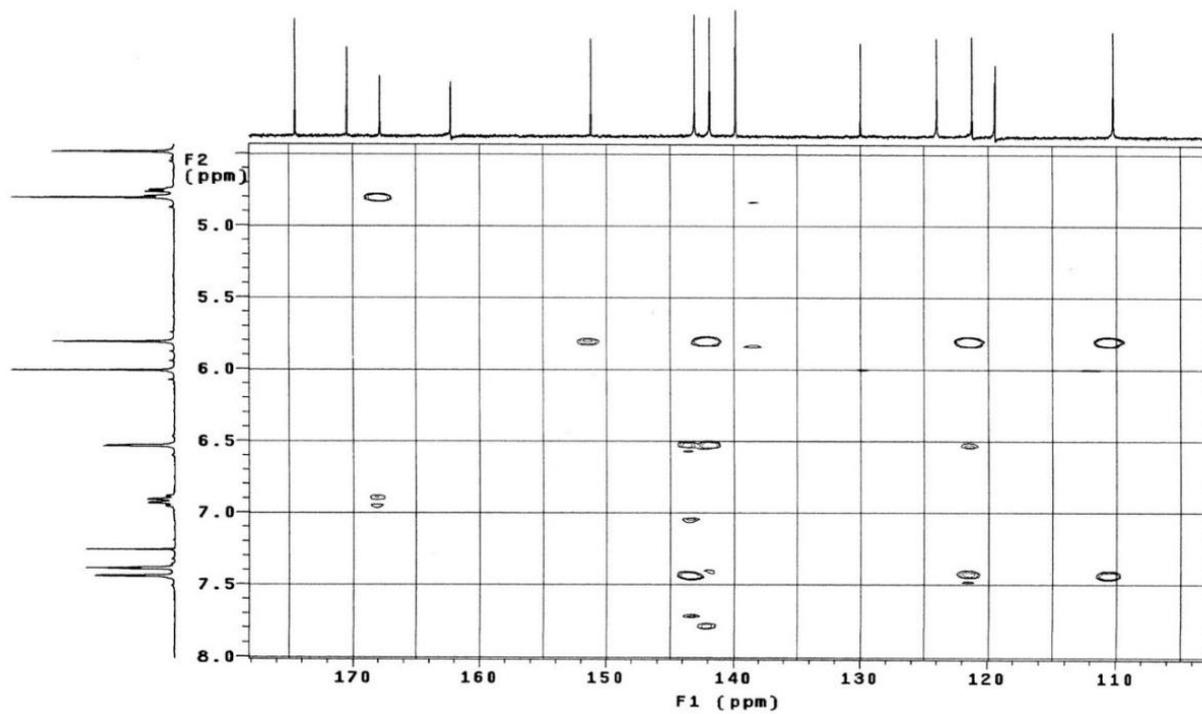


Figure S76. HMBC (300 MHz, CDCl₃) spectrum of the new compound 6.

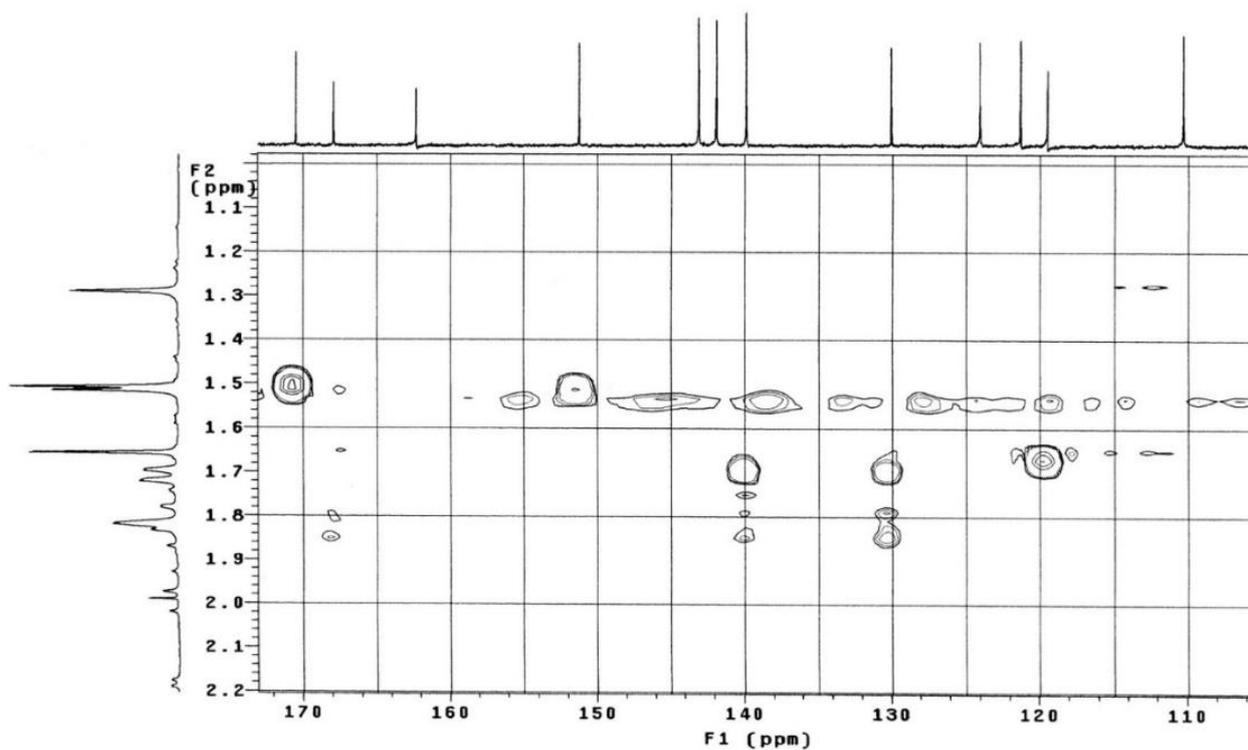
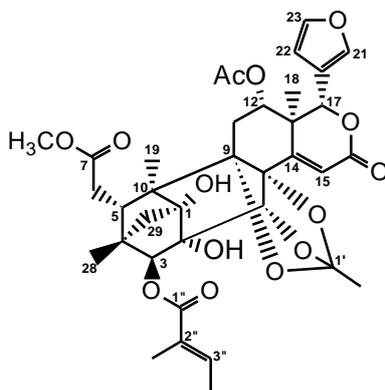


Figure S77. HMBC (300 MHz, CDCl₃) spectrum of the new compound **6**.



S6

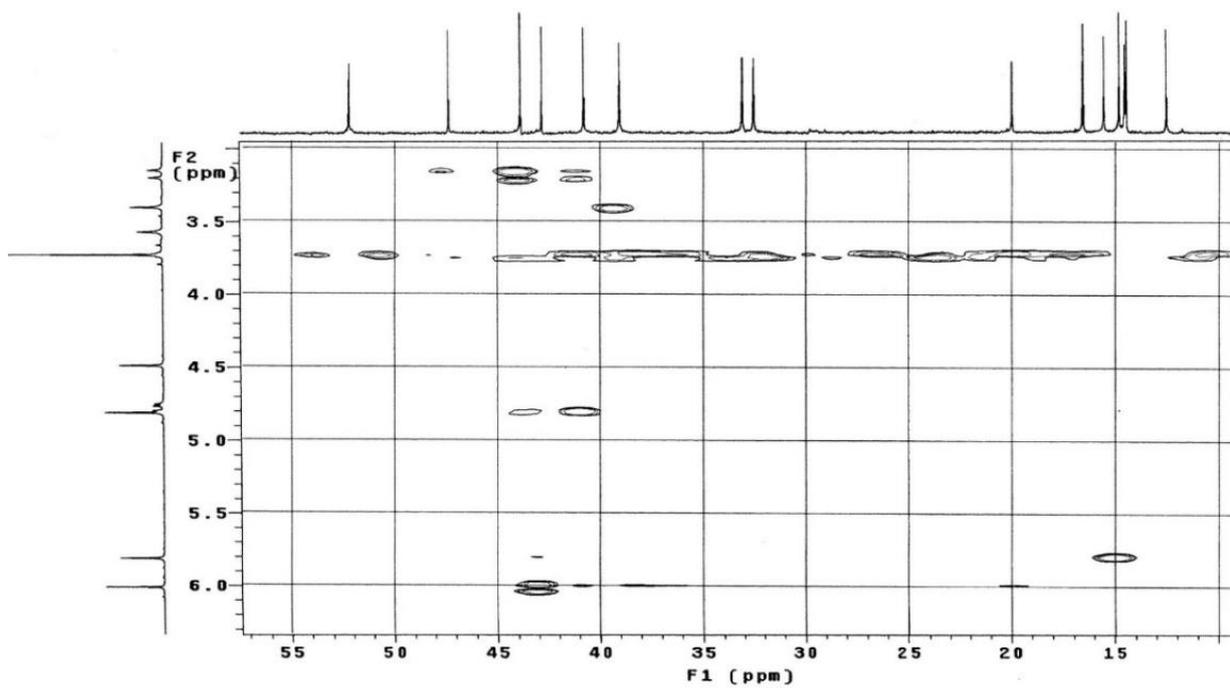


Figure S78. HMBC (300 MHz, CDCl₃) spectrum of the new compound 6.

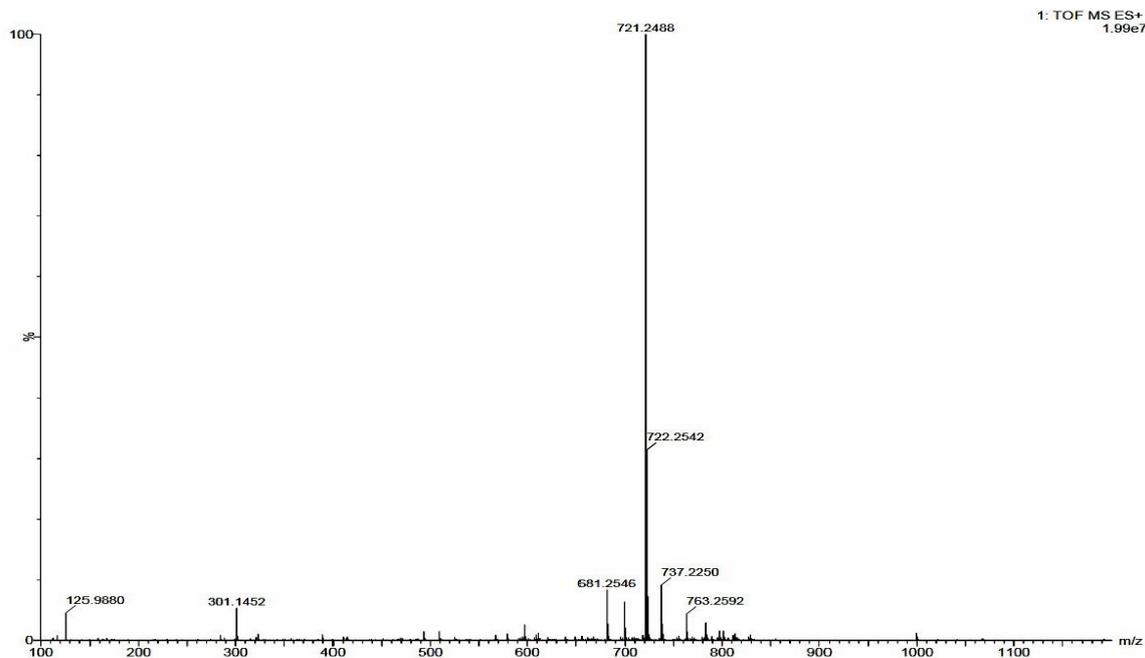


Figure S79. HR-ESI-ToF-MS spectrum of the new compound **6**.

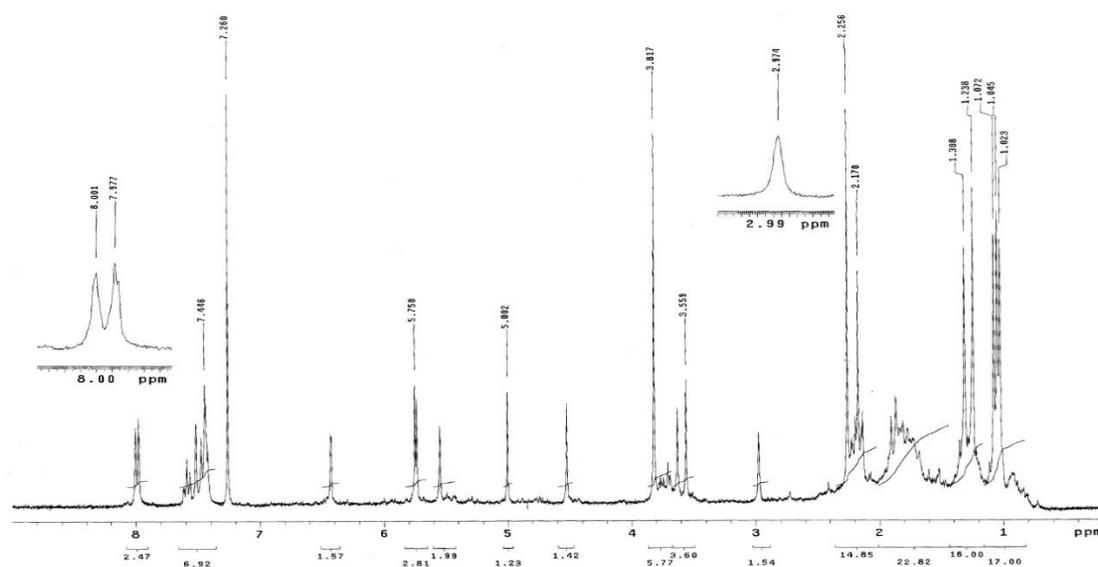
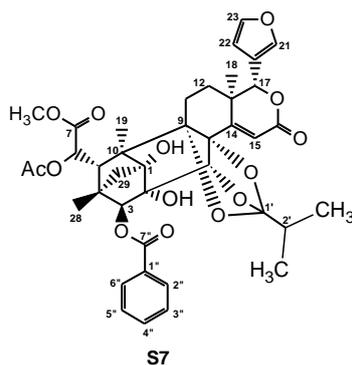


Figure S80. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **7**.

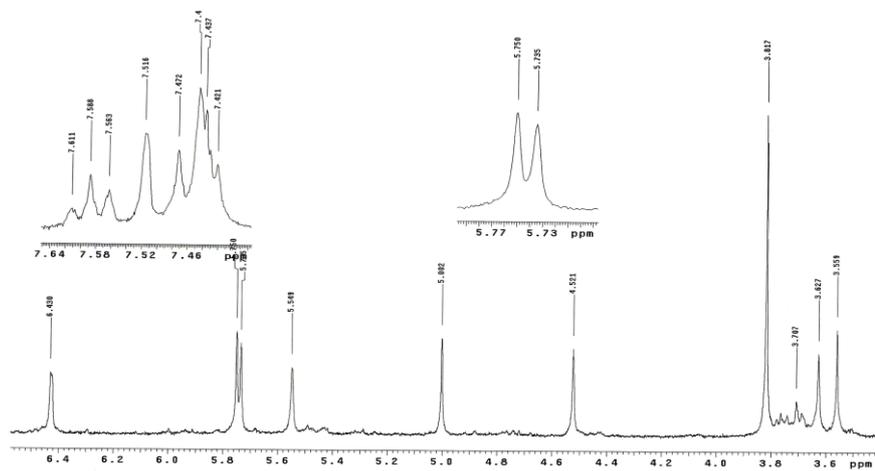
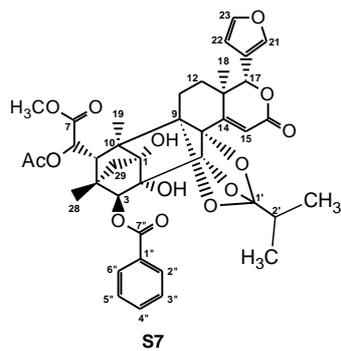


Figure S81. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **7**.

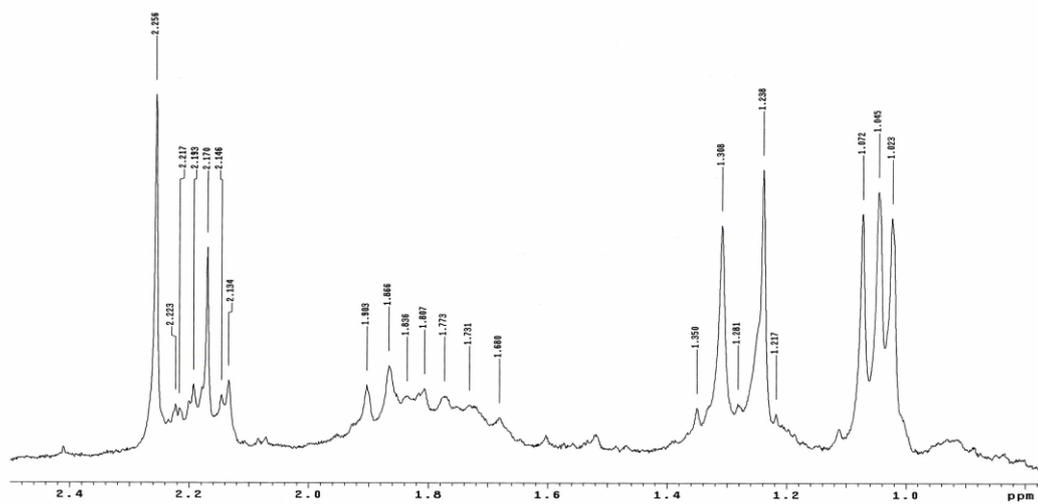


Figure S82. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **7**.

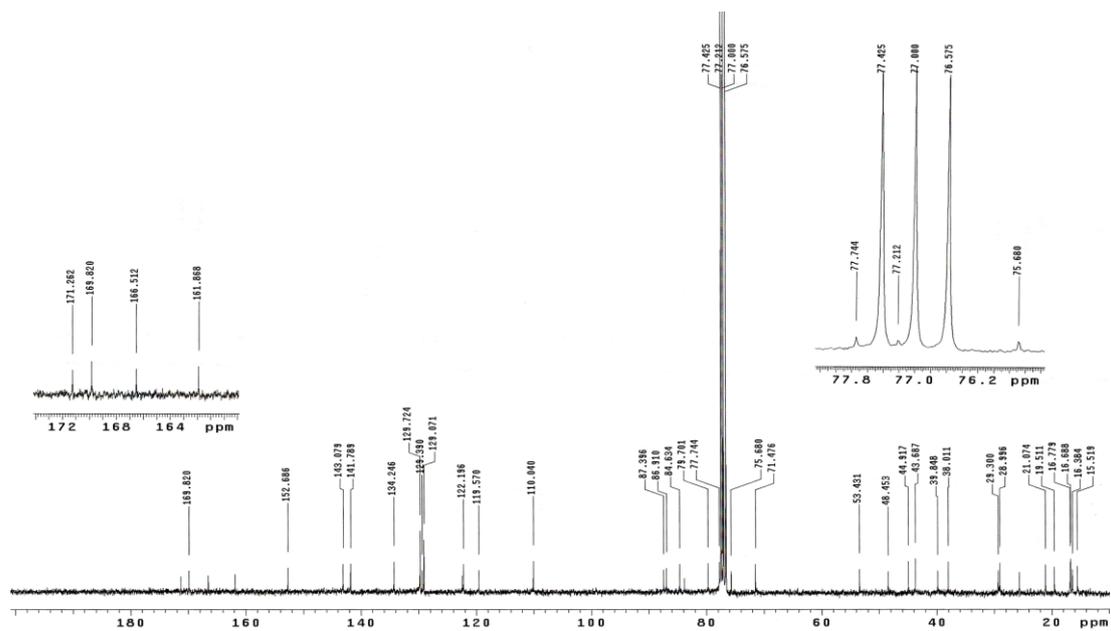
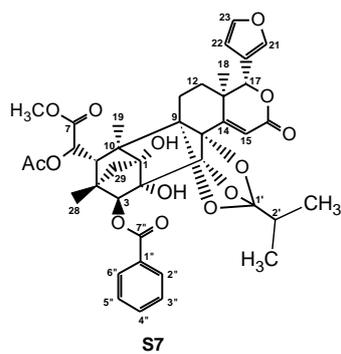


Figure S83. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound **7**.

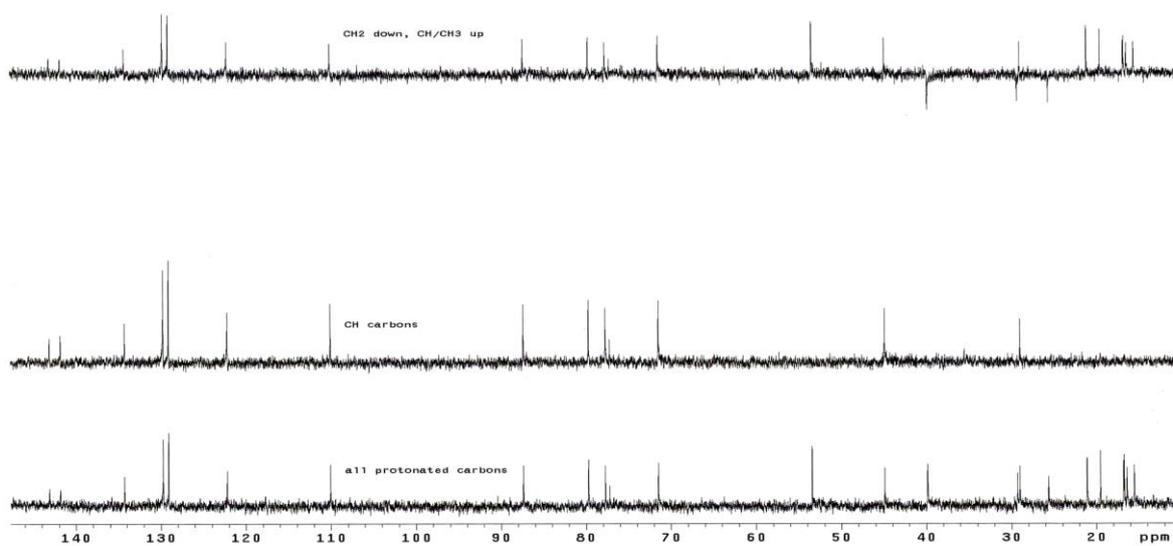


Figure S84. ^{13}C DEPT (75 MHz, CDCl_3) spectrum of the new compound **7**.

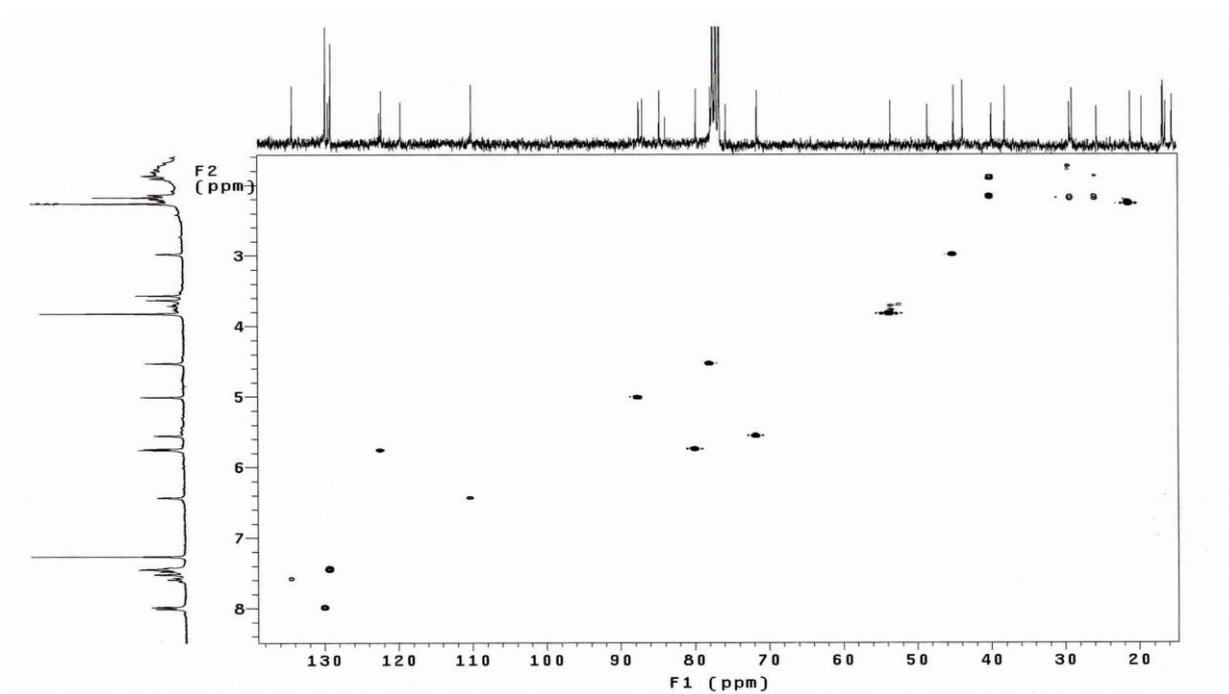
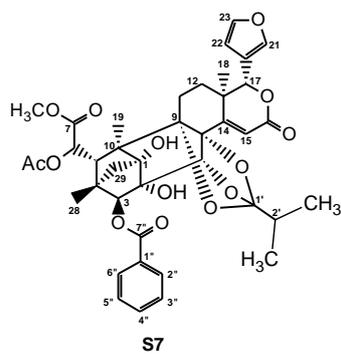


Figure S85. HSQC (75 MHz, CDCl₃) spectrum of the new compound 7.

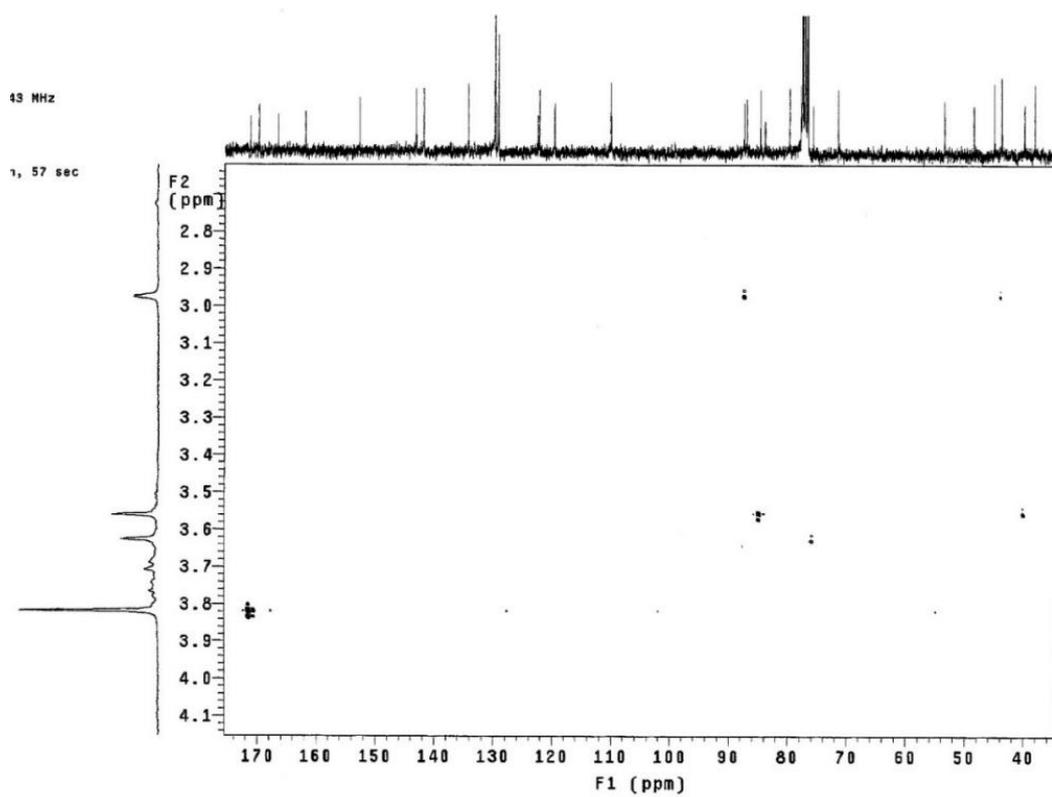


Figure S86. HSQC (75 MHz, CDCl_3) spectrum of the new compound **7**.

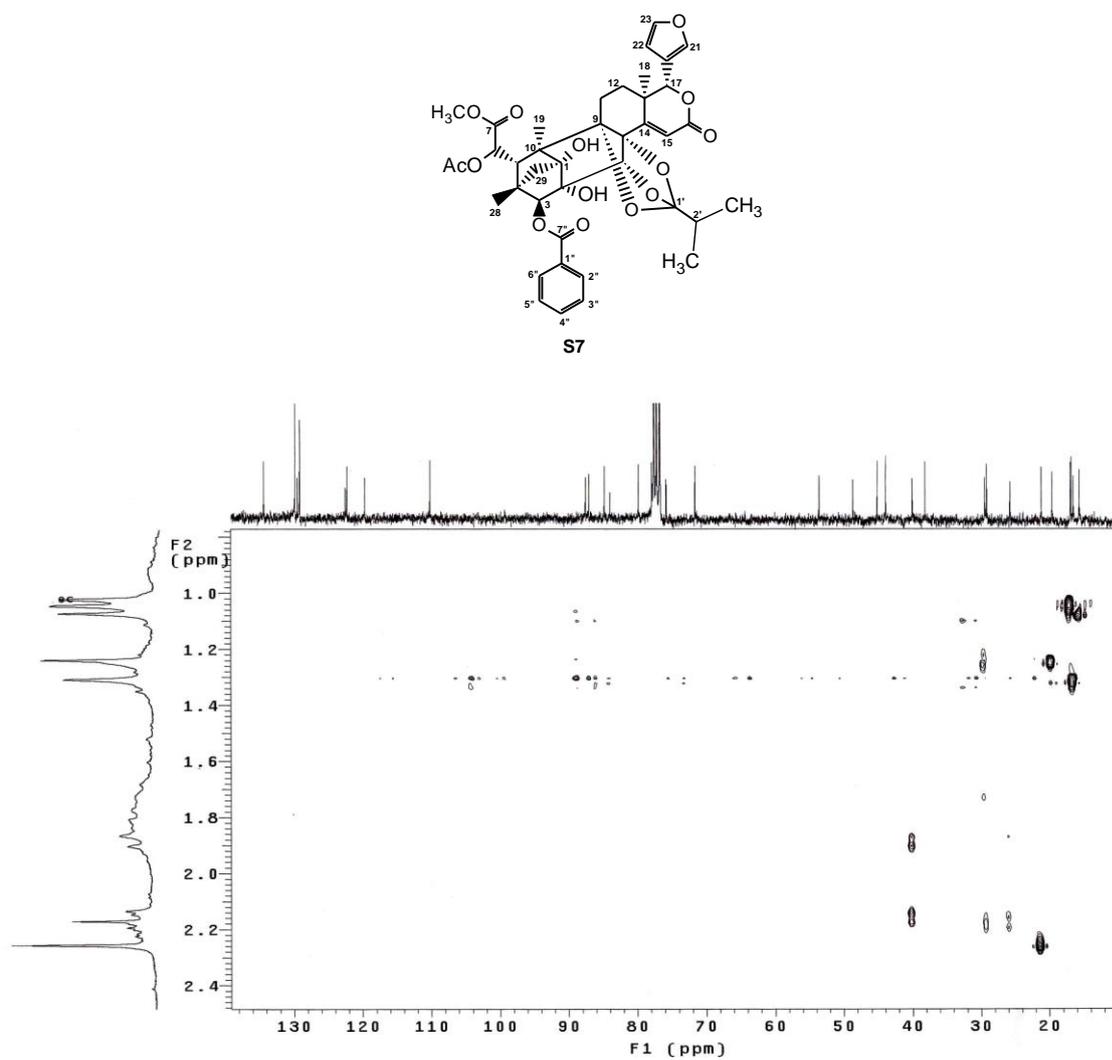


Figure S87. HMBC (75 MHz, CDCl₃) spectrum of the new compound 7.

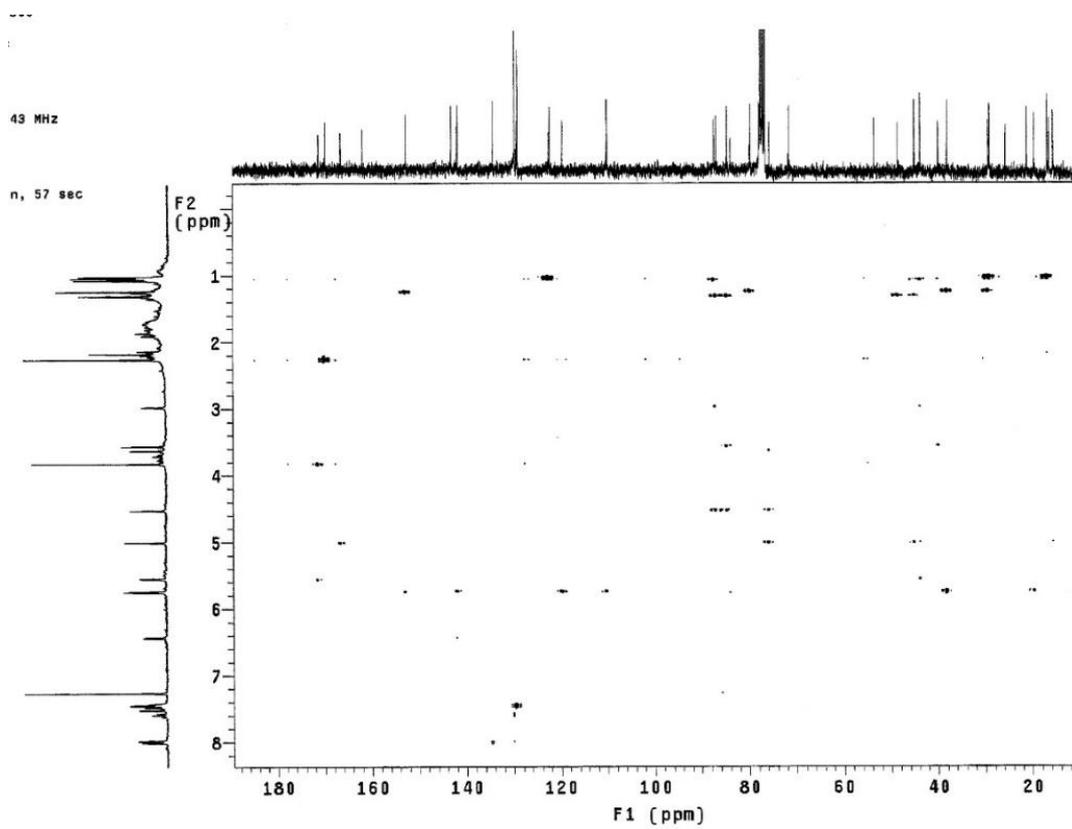


Figure S88. HMBC (75 MHz, CDCl₃) spectrum of the new compound **7**.

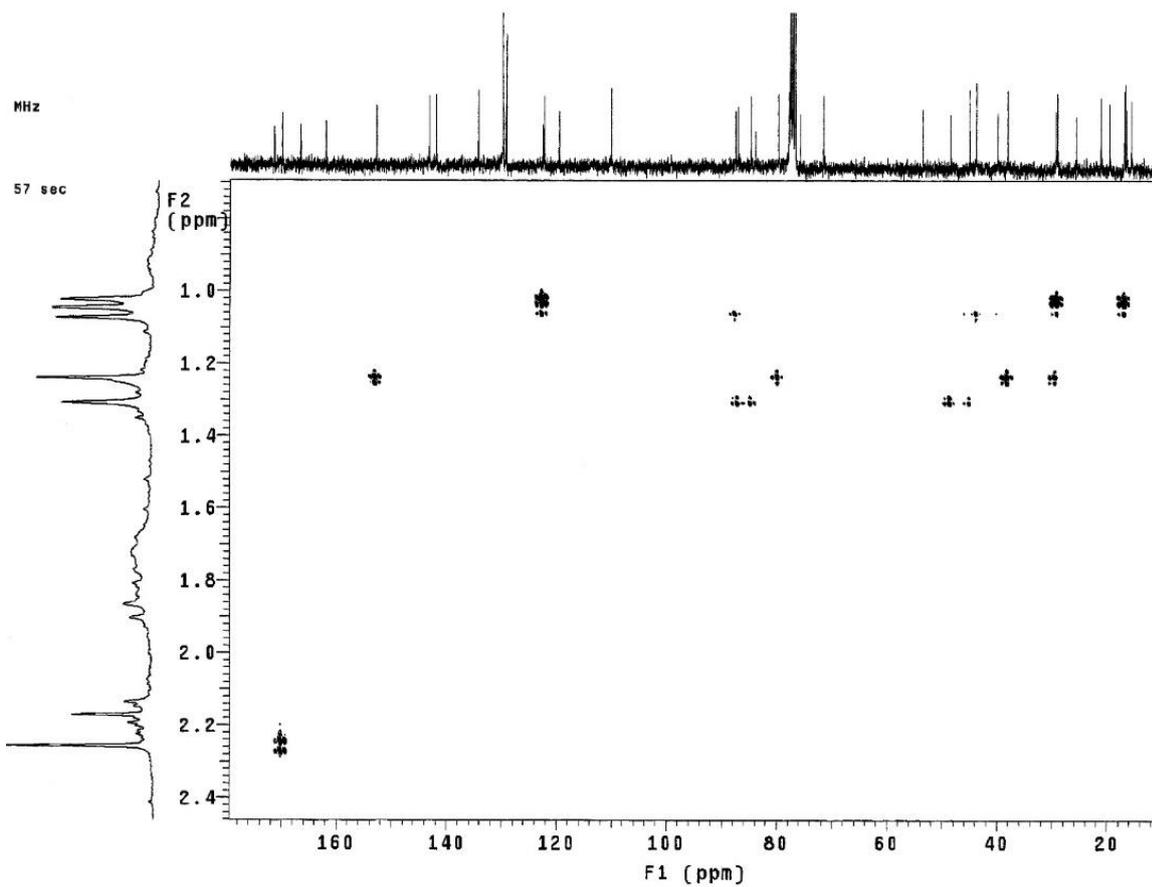
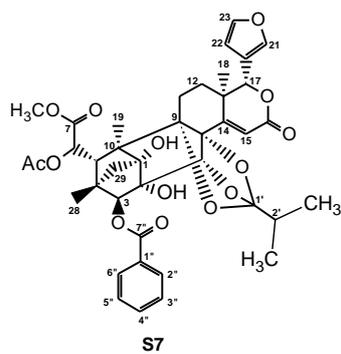


Figure S89. HMBC (75 MHz, CDCl₃) spectrum of the new compound 7.

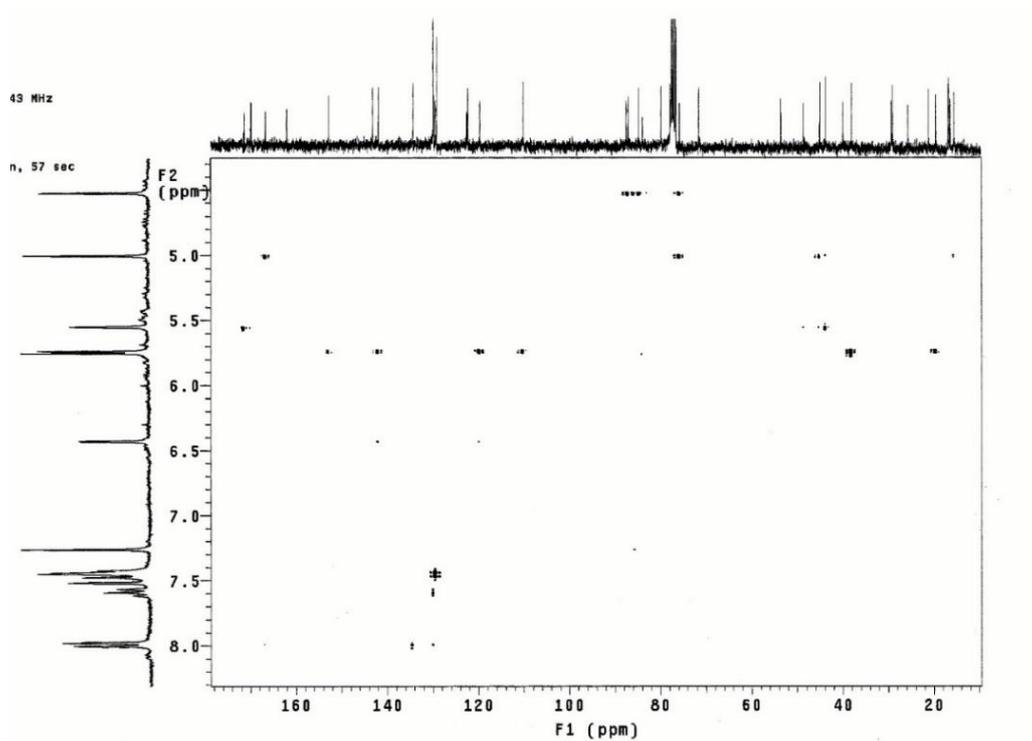


Figure S90. HMBC (75 MHz, CDCl_3) spectrum of the new compound **7**.

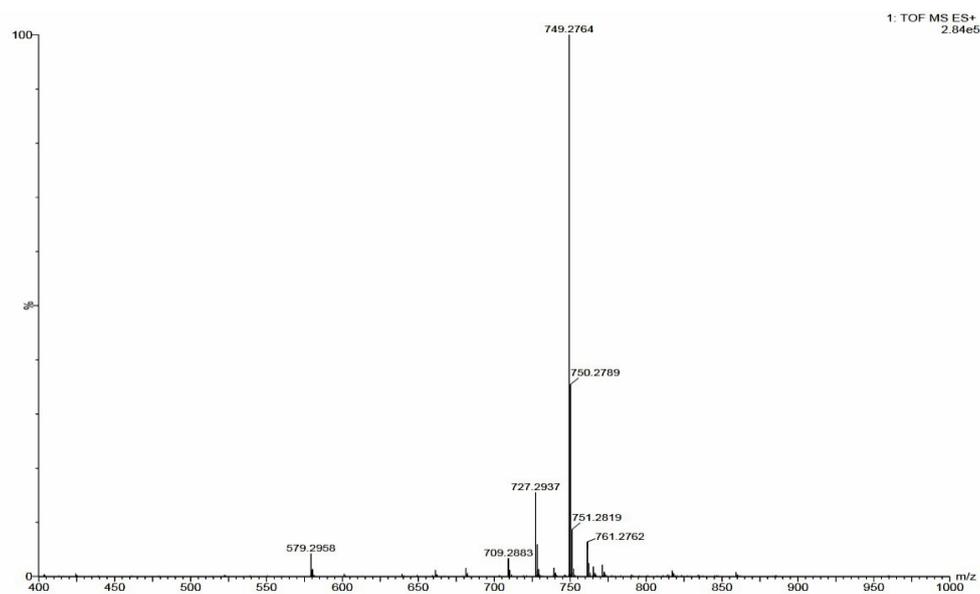
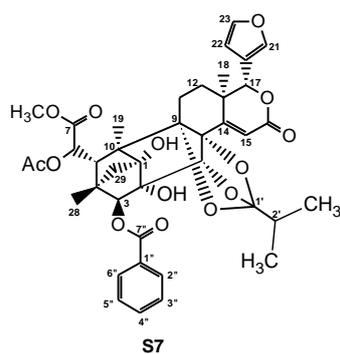


Figure S91. HR-ESI-ToF-MS spectrum of the new compound **7**.

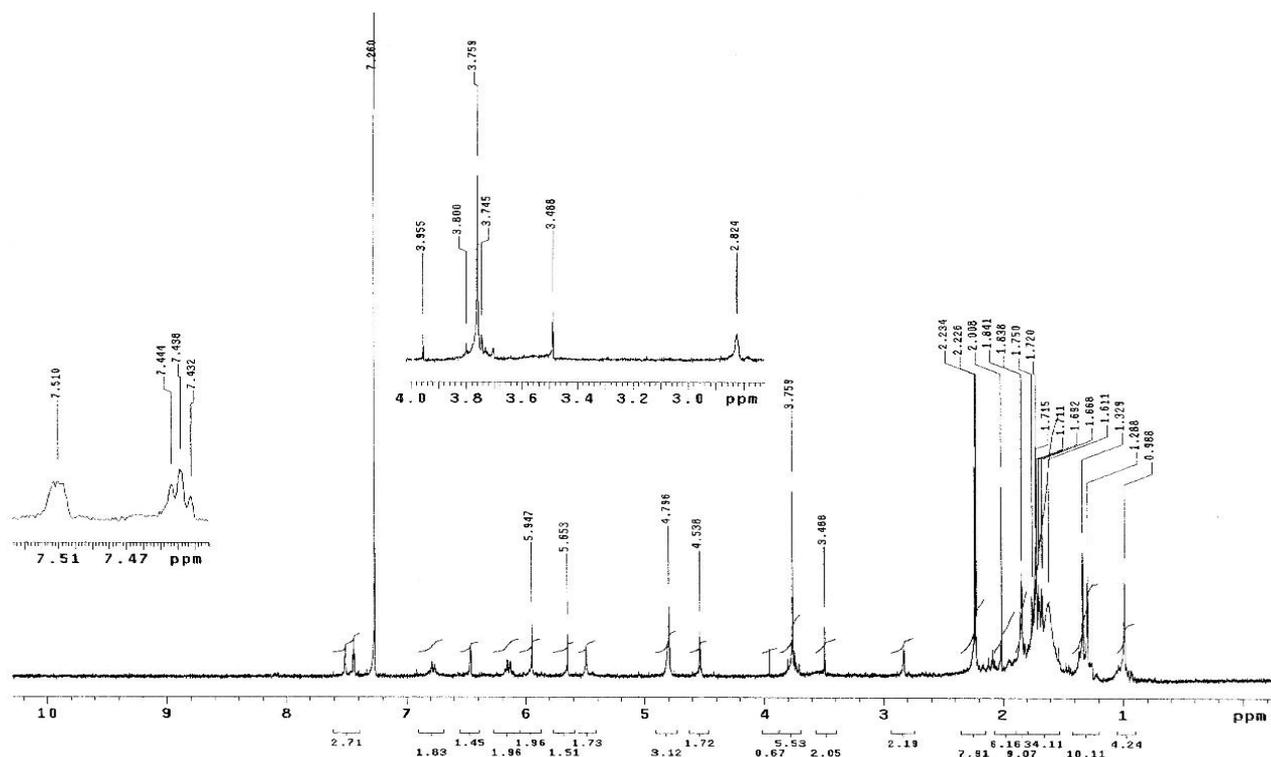
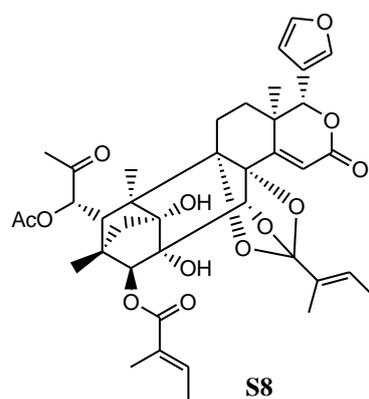


Figure S92. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **8**.

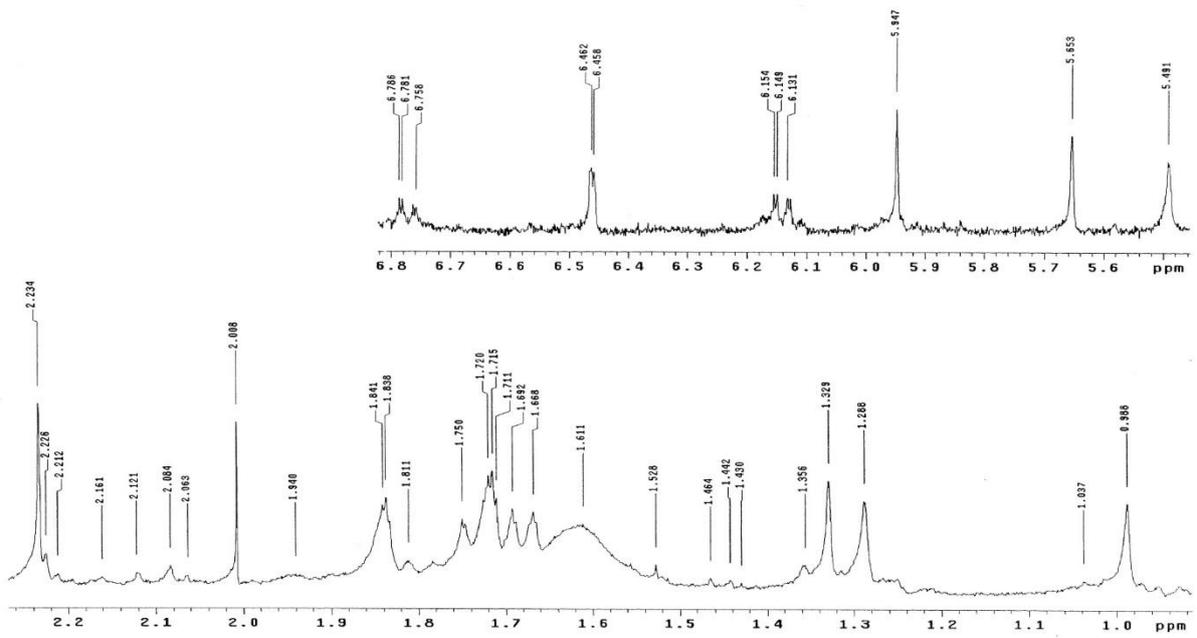


Figure S93. ¹H NMR (300 MHz, CDCl₃) spectrum of the new compound 8.

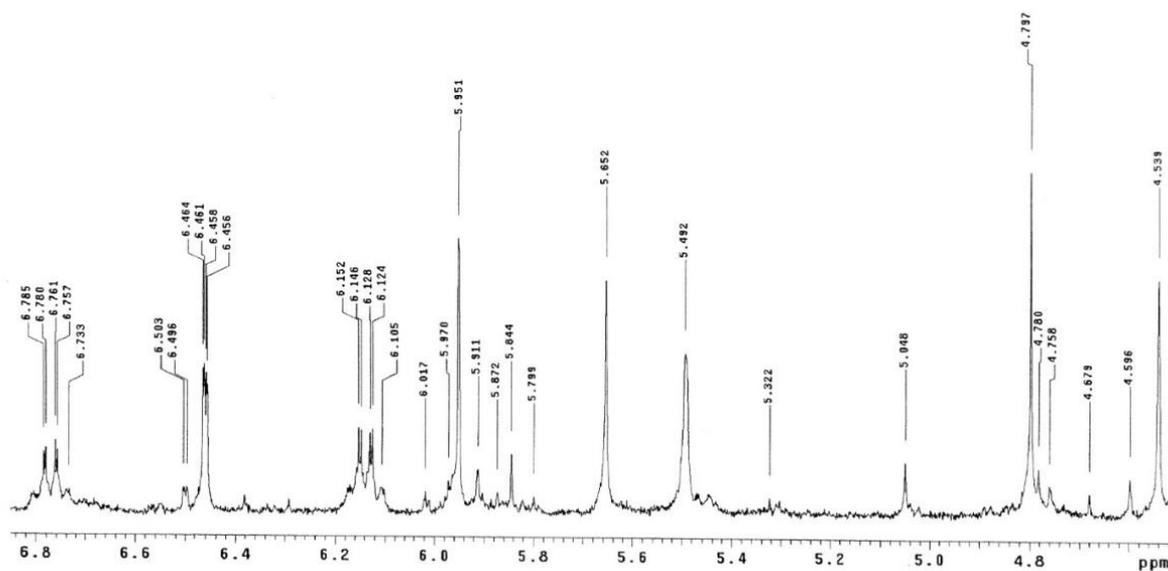
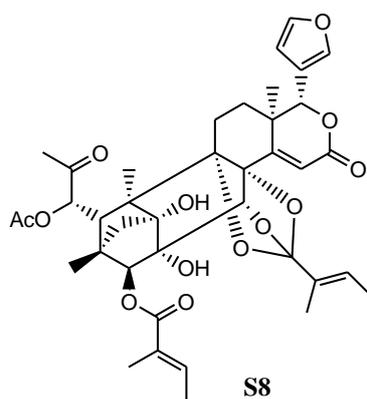


Figure S94. ^1H NMR (300 MHz, CDCl_3) spectrum of the new compound **8**.

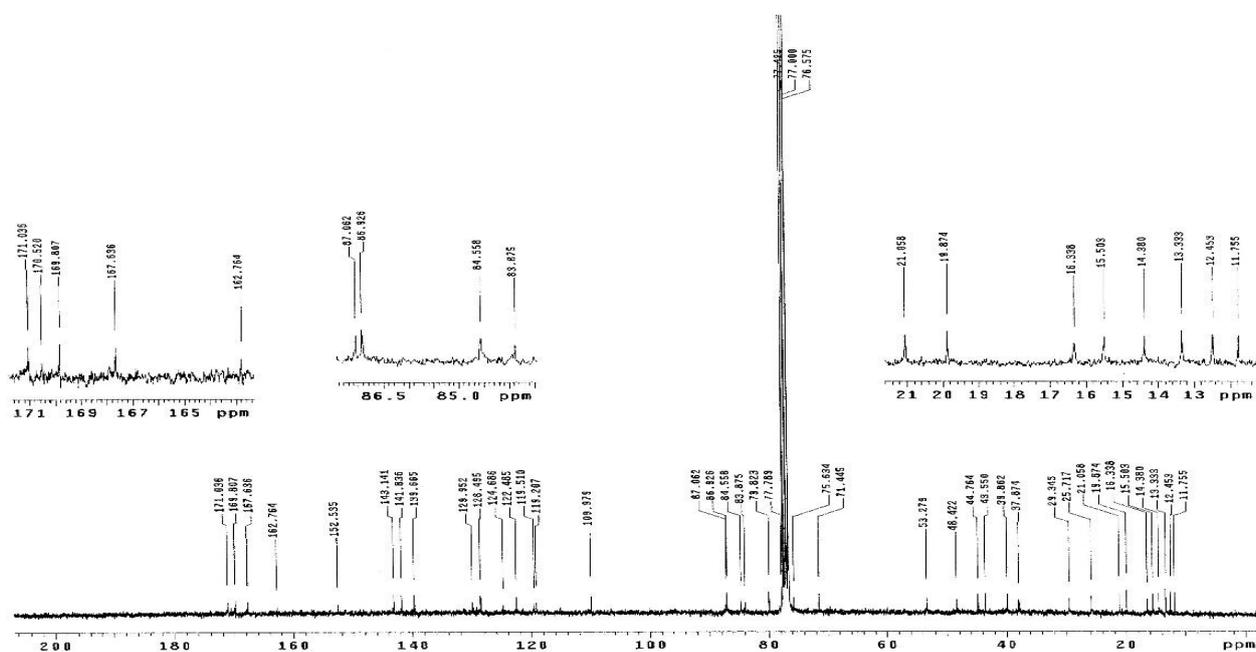


Figure S95. ^{13}C NMR (75 MHz, CDCl_3) spectrum of the new compound **8**.

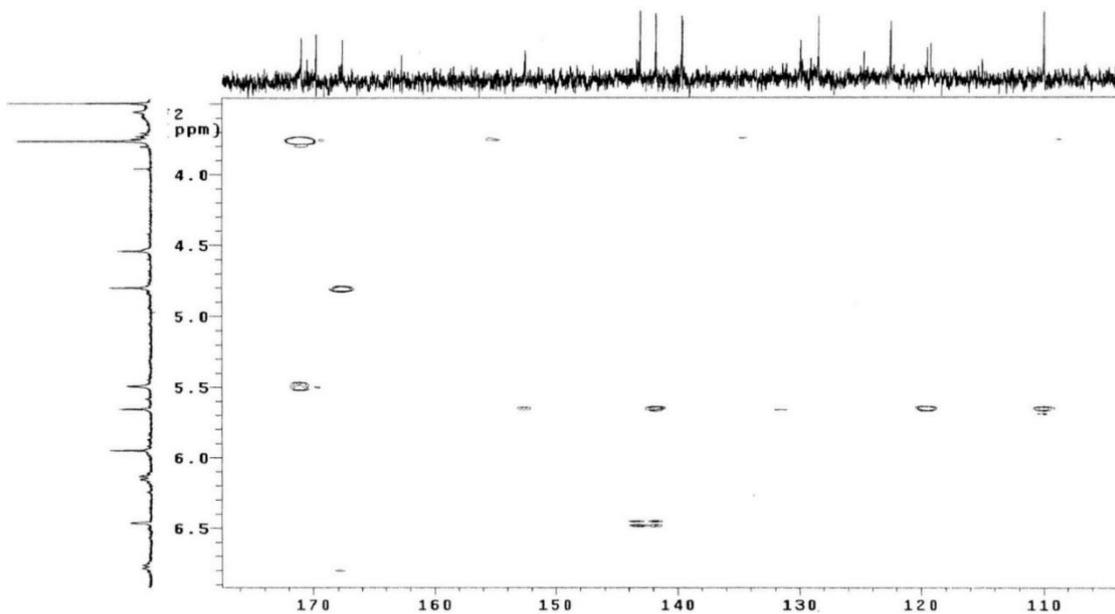
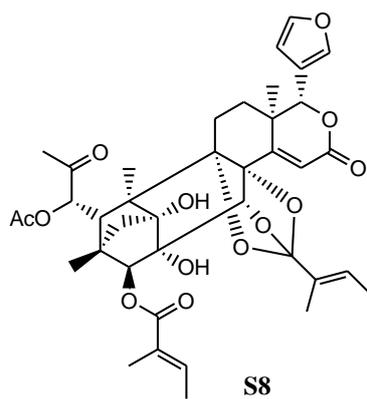


Figure S100. HETCOR (75 MHz, CDCl_3) spectrum of the new compound **8**.

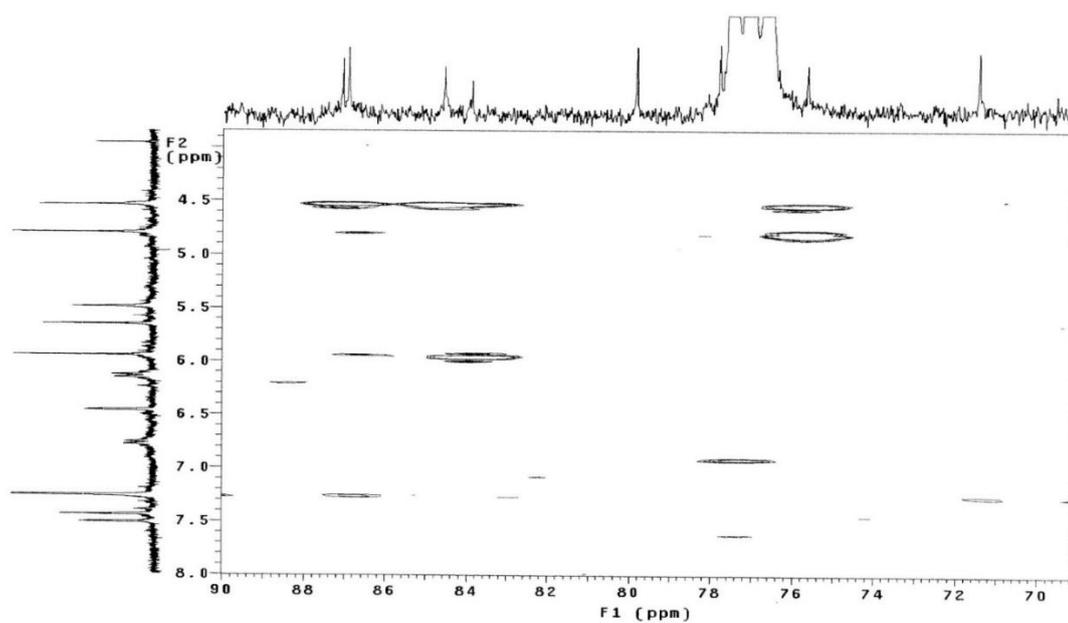


Figure S101. HETCOR (75 MHz, CDCl_3) spectrum of the new compound **8**.

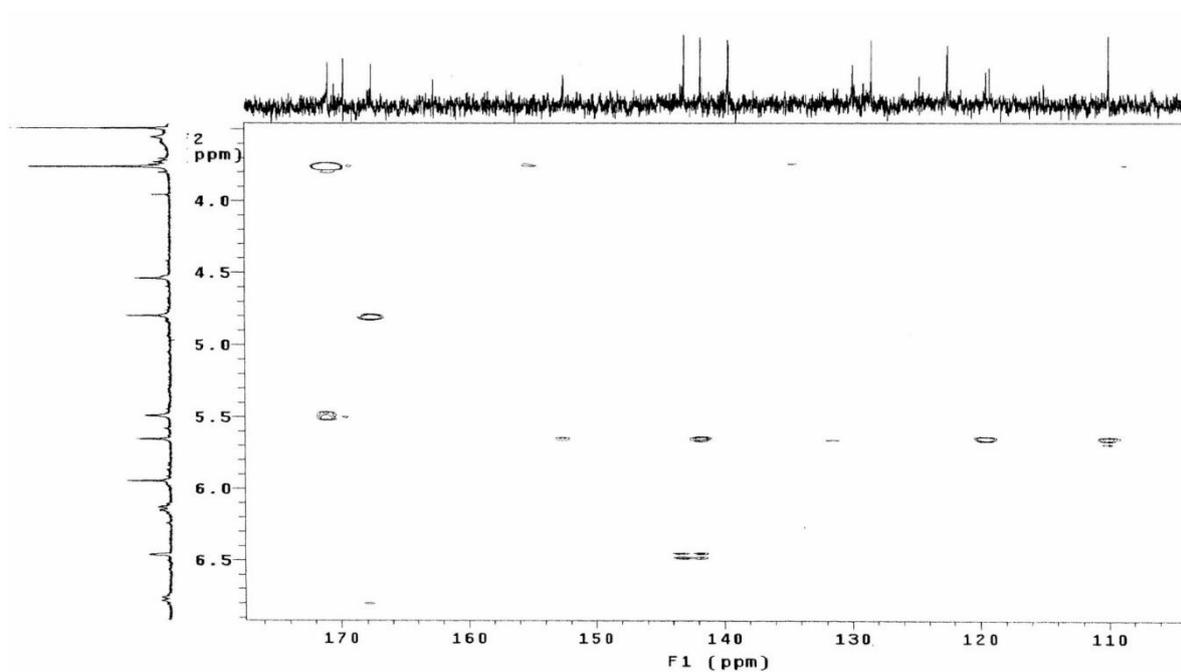
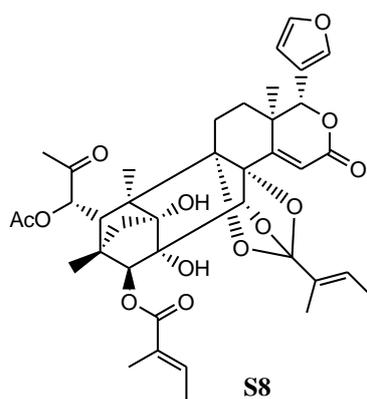


Figure S104. HMBC (300 MHz, CDCl₃) spectrum of the new compound 8.

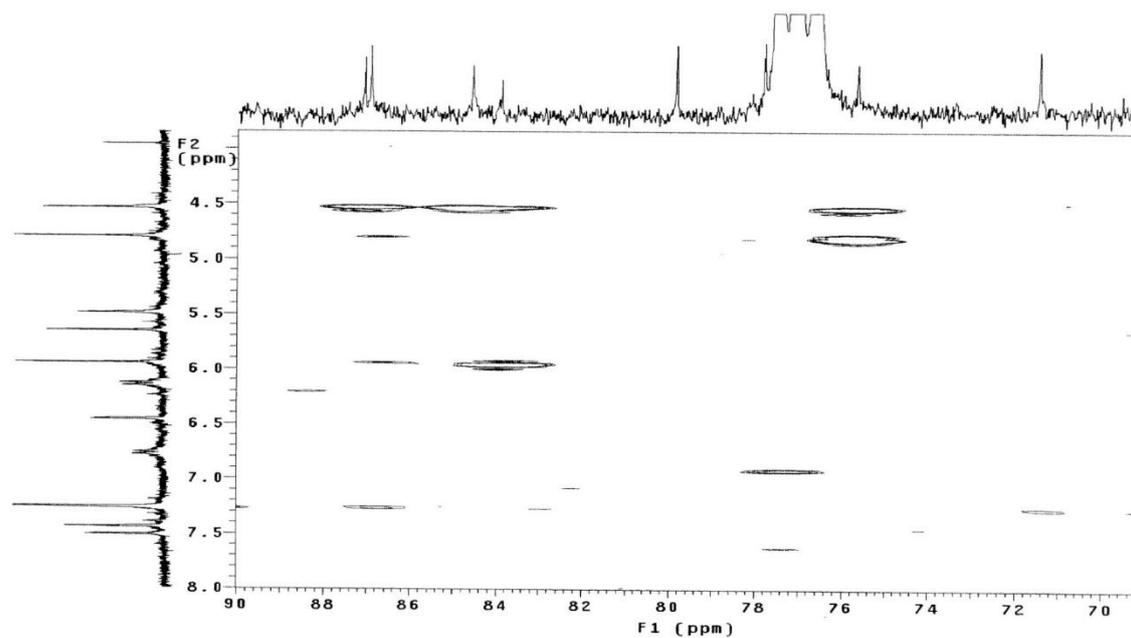


Figure S105. HMBC (300 MHz, CDCl₃) spectrum of the new compound 8.

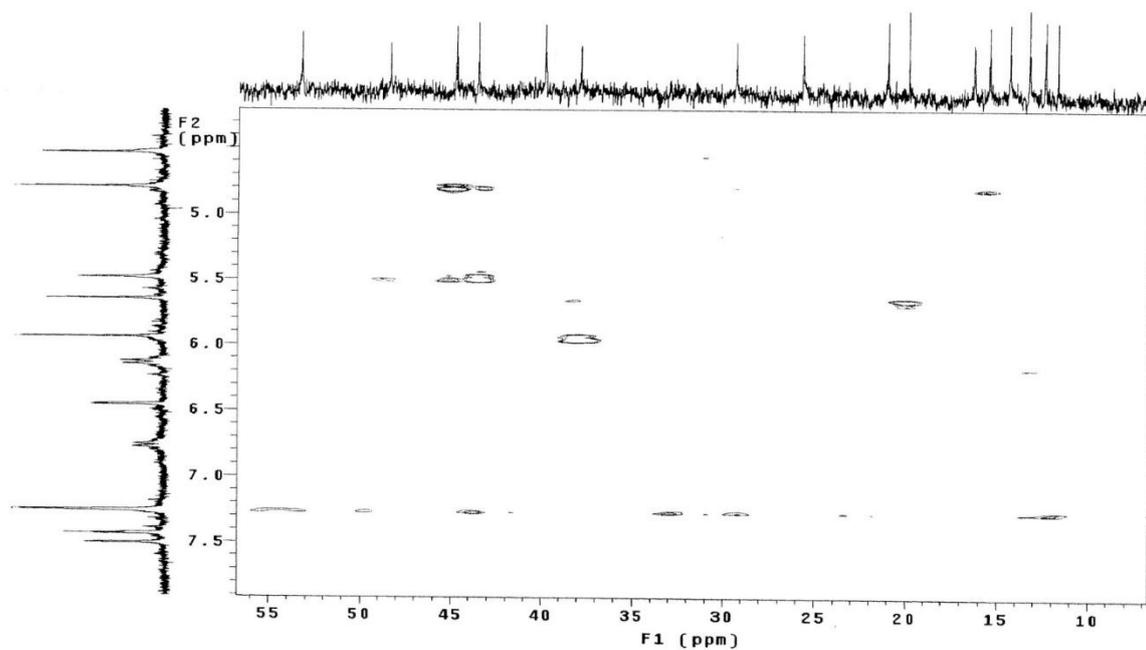
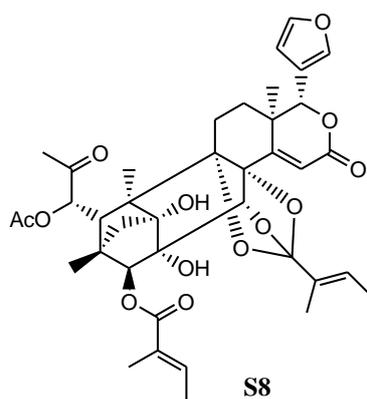


Figure S106. HMBC (300 MHz, CDCl_3) spectrum of the new compound **8**.

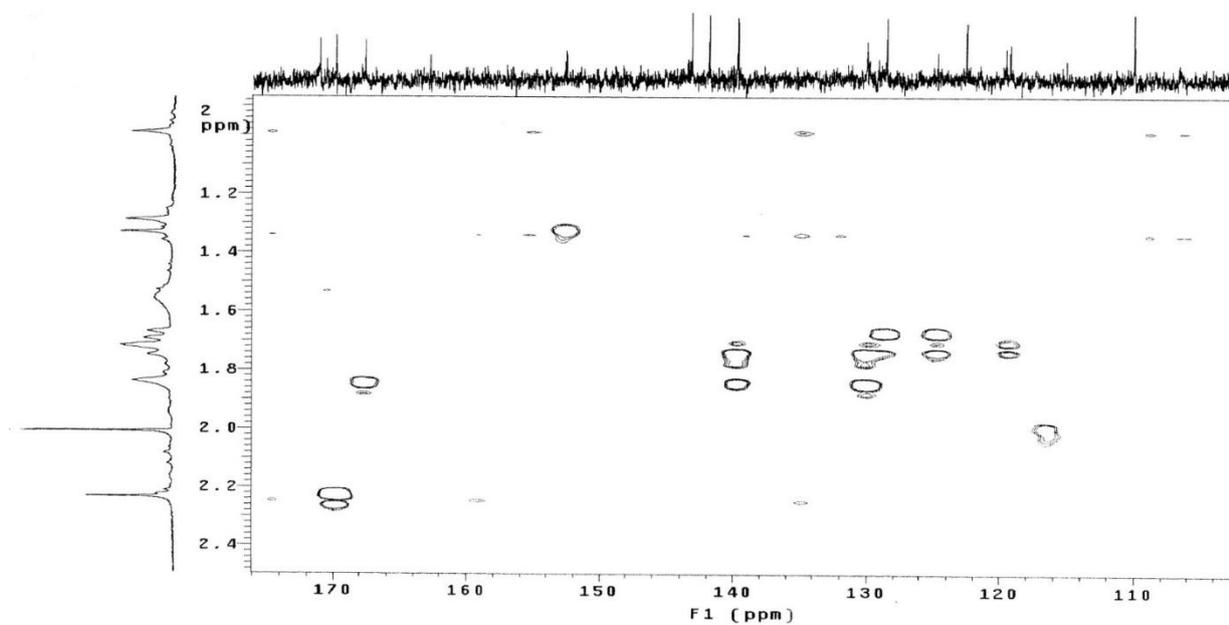


Figure S107. HMBC (300 MHz, CDCl_3) spectrum of the new compound **8**.

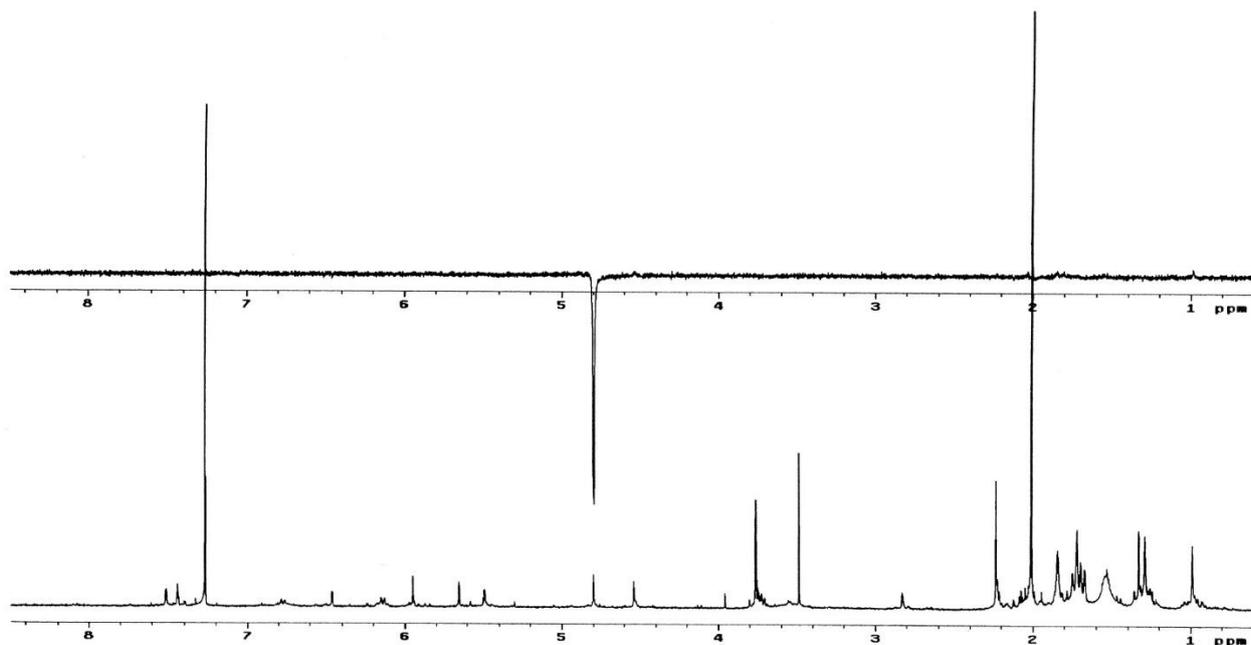
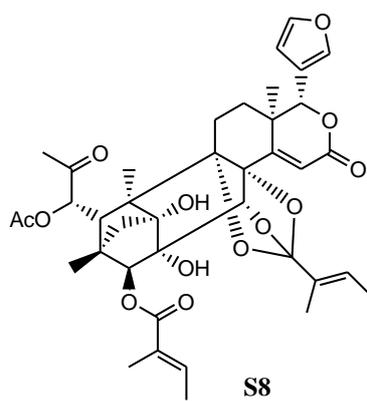


Figure S110. NOE-diff (300 MHz, CDCl_3) spectrum of the new compound **8**.

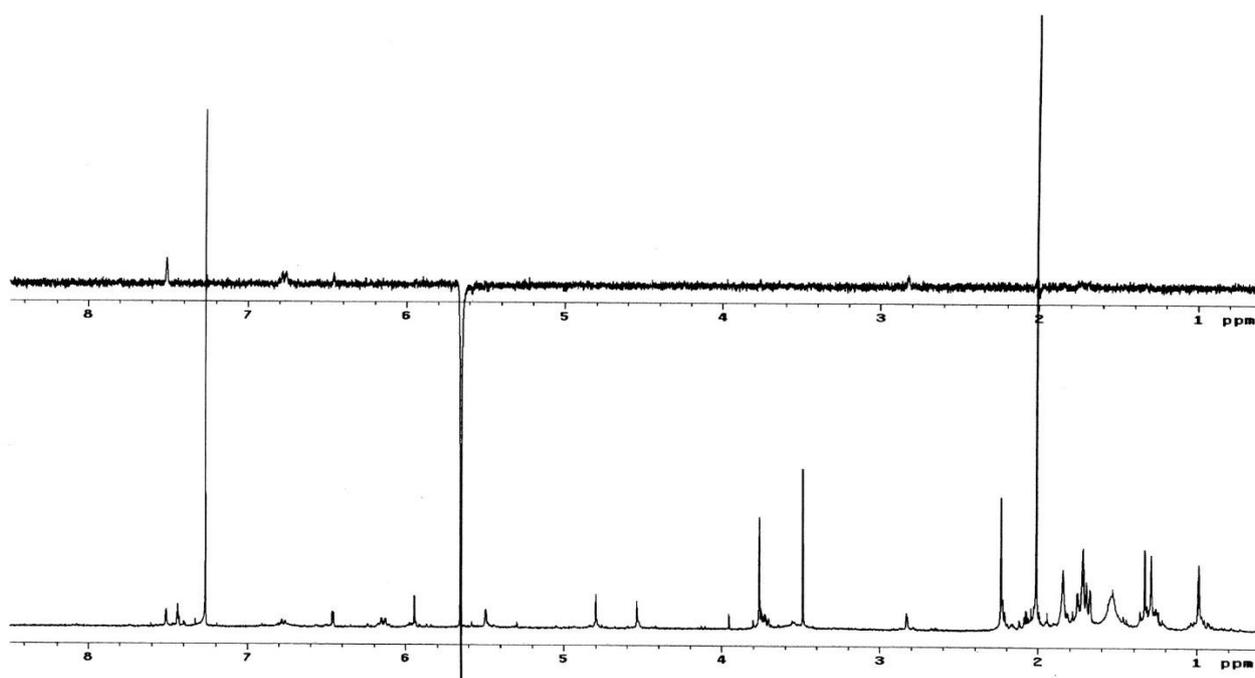


Figure S111. NOE-diff (300 MHz, CDCl_3) spectrum of the new compound **8**.

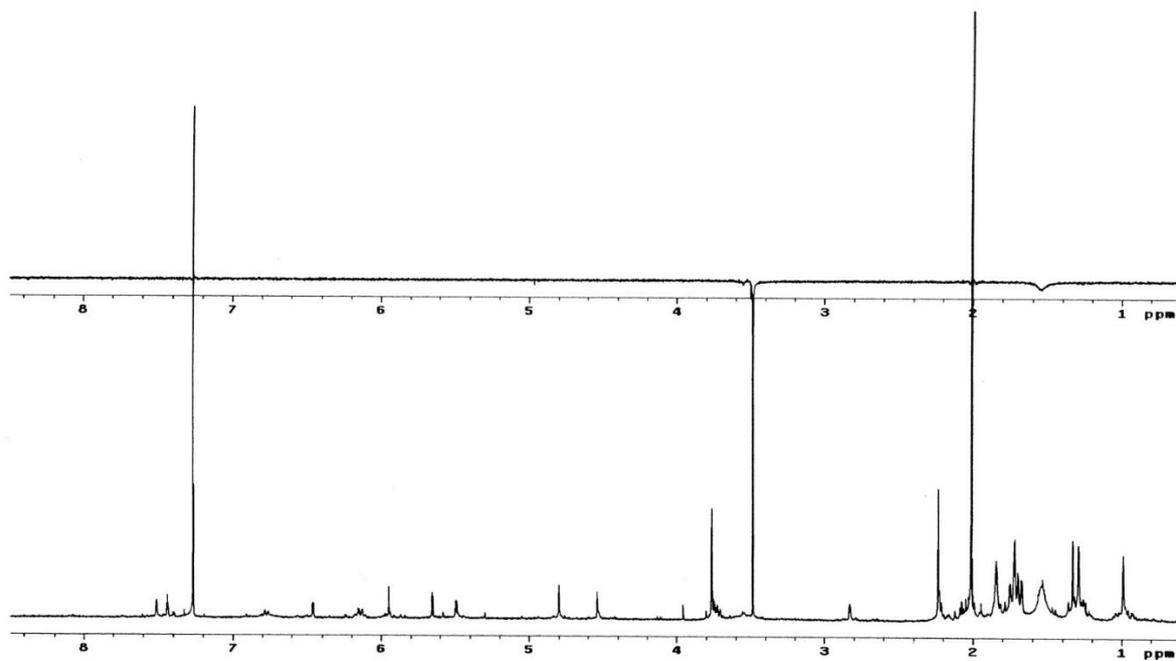
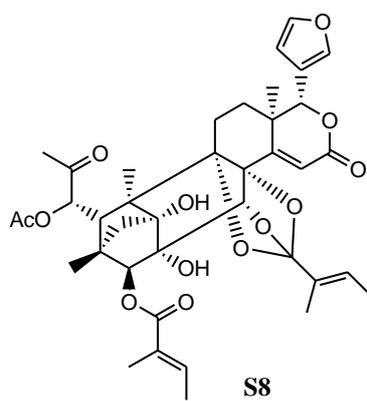


Figure S112. NOE-diff (300 MHz, CDCl_3) spectrum of the new compound 8.

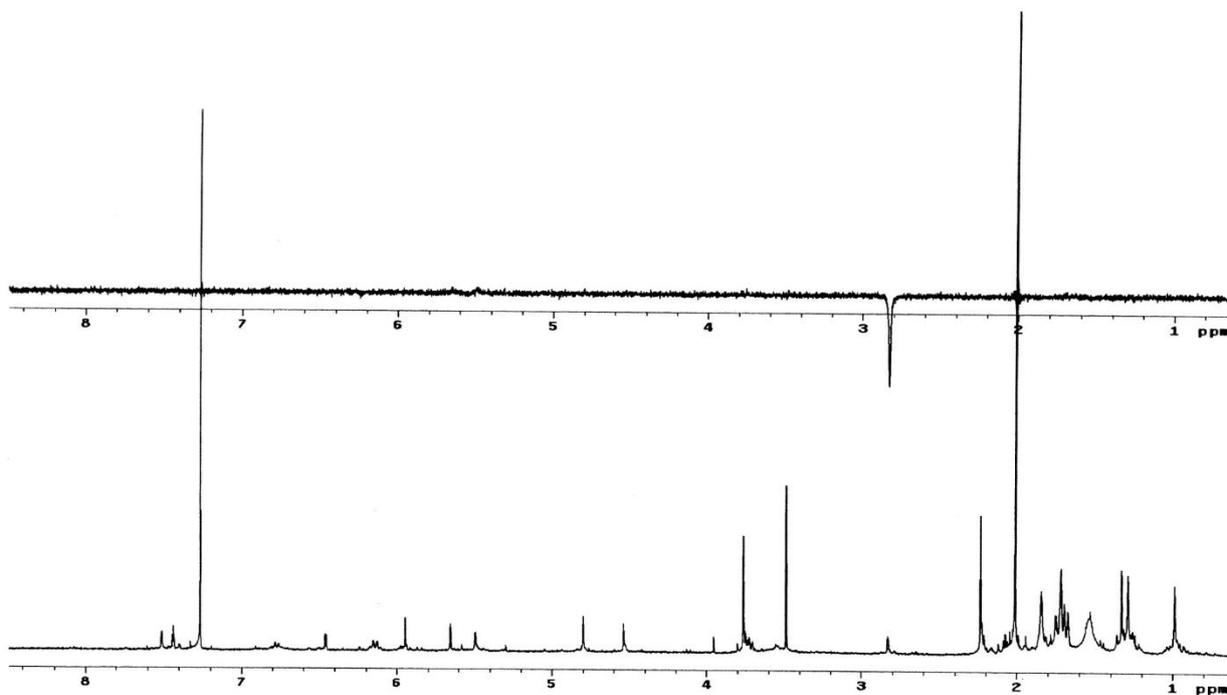


Figure S113. NOE-diff (300 MHz, CDCl_3) spectrum of the new compound 8.

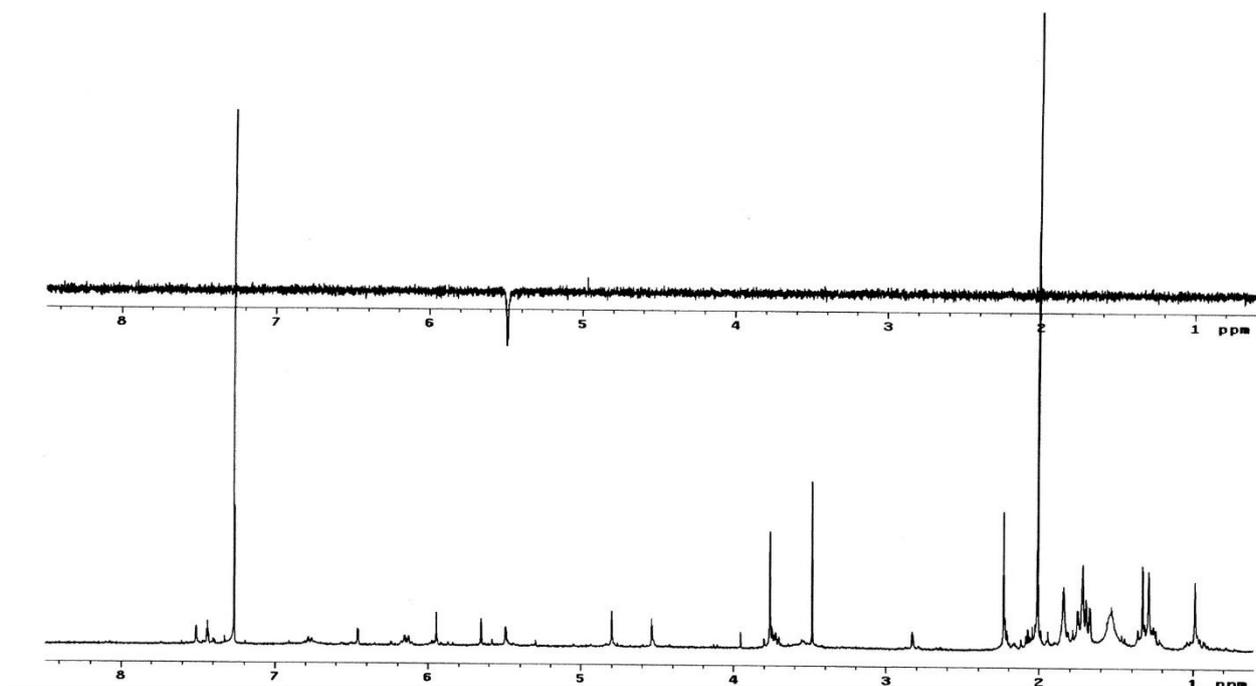
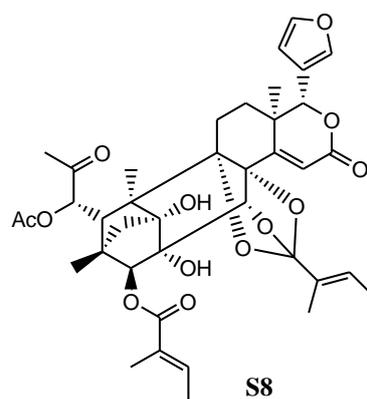


Figure S114. NOE-diff (300 MHz, CDCl_3) spectrum of the new compound **8**.

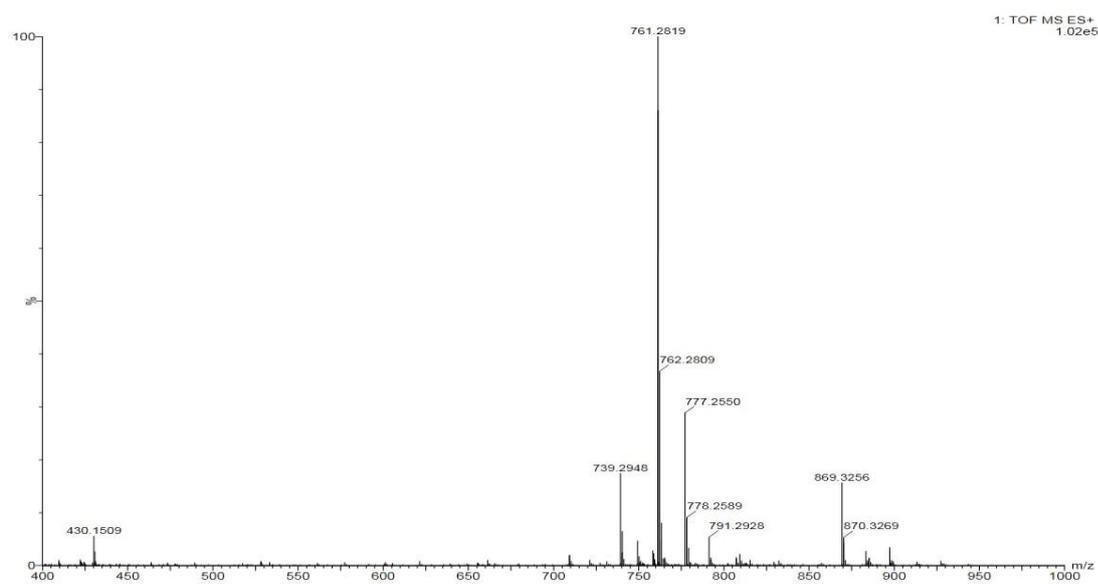


Figure S115. HR-ESI-ToF-MS spectrum of the new compound **8**.