SUPPLEMENTARY MATERIAL

Congmujingnosides B-G, Triterpene saponins from the stem of *Aralia chinensis* and Their Protective Effects against H_2O_2-Induced Myocardial Cell Injury

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Abstract: Phytochemical investigation of the stem of *Aralia chinensis* yielded six new oleanane-type triterpene saponins named as congmujingnosides B-G (**1**-**6**). The new ones were elucidated on the basis of the chemical and spectroscopic analysis. Protective effects of compounds **1**−**6** were tested against H_2O_2-induced H9c2 cardiomyocyte injury, and the data showed that compounds **1** and **5** had significant cell-protective effects. No significant DPPH radical scavenging activity was observed for compounds **1**−**6**.

Keywords: *Aralia chinensis*; triterpene saponins; cardiomyocyte oxidative injury; DPPH radical scavenging activity

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1. Experimental

1.1. General experimental procedures

Optical rotation data were obtained using a Perkin-Elmer 341 digital polarimeter (PerkinElmer, Norwalk, CT, USA). UV and IR spectra were recorded on Shimadzu UV2550 and FTIR-8400S spectrometer (Shimadzu, Kyoto, Japan), respectively. NMR spectra were obtained with a Bruker AV Ⅲ 600 NMR spectrometer (chemical shift values are presented as δ values with TMS as the internal standard) (Bruker, Billerica, German). HR-ESI-MS were performed on a LTQ-Orbitrap XL spectrometer (Thermo Fisher Scientific, Boston, MA, USA). C_{18} reversed-phase silica gel (40–63μm, Merck, Darmstadt, Germany), Sephadex LH-20 (Pharmacia, Uppsala, Sweden), MCI gel (CHP 20P, 75–150μm, Mitsubishi Chemical Corporation, Tokyo, Japan) and silica gel (100–200 and 300–400 mesh, Qingdao Marine Chemical plant, Qingdao, China) were used for column chromatography (CC). And precoated silica gel GF_{254} plates (Zhi Fu Huang Wu Pilot Plant of Silica Gel Development, Yantai, China) were used for TLC. All solvents used were of analytical grade (Beijing Chemical Works, Beijing, China).

1.2. Plant material

Stems of *A. chinensis* were collected in Yixian, Anhui Province, China in November 2015 and identified by Prof. Liu-Shou Jin of the College of Pharmacy，Anhui University of Chinese Medicine. A voucher specimen (NO. 13128) was deposited at the Chinese Academy of Medical Sciences, Peking Union Medical College, Institute of Medicinal Plant Development.

1.3. Extraction and isolation

The air-dried and powdered stems of *A. chinensis* (1.6 kg) were extracted three times with 75% ethanol (3 × 20 L, 2h each). Removal of ethanol under reduced pressure yielded an ethanol extract (356.0 g). The residue was suspended to H_2O (3 L), and partitioned with petroleum ether. (3 × 3 L), CH_2Cl_2. (3 × 3 L), EtOAc. (3 × 3 L), and n-BuOH. (3 × 3 L), successively. The n-BuOH. fraction (40.9 g) was subjected to

chromatography using ODS MPLC elution with MeOH-H_2O (30:70; 40:60; 50:50；60:40；70:30；80:20；90:10), yielding seven fractions A-G. Fr. E (5g) and F (7g)were all purified through semi-preparative HPLC elution using a MeOH-H_2O gradient solvent system. Finally, compounds **1** (8.3 mg), **2** (5.8 mg), and **3** (6.1 mg) were obtained at R_t 10.21 min, 14.65 min, and 26.53 min, respectively, using a MeOH-H_2O (85:15) system from Fr E, and compounds **4** (9.7 mg), **5** (4.7 mg), and **6** (6.2 mg) were obtained at R_t 10.93 min,15.95 min, and 25.44 min, respectivey, using a MeOH-H_2O (65:35) solvent system from Fr. F.

Congmujingnoside B (**1**): $C_{59}H_{96}O_{27}$, white amorphous powder; [α]20 D -20.6 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 203 (4.02) nm; IR (film) ν_{max} 3435 (OH), 1734 (C=O) and 1388 (CH_3) cm^{-1}; ^1H NMR and ^{13}C NMR see Table S1; HRESIMS *m/z* 1259.6067 (calcd for $C_{59}H_{96}O_{27}$ Na $[M + Na]^+$, 1259.6037).

Congmujingnoside C (**2**): $C_{59}H_{96}O_{27}$, white amorphous powder; [α]20 D +11.5 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 209 (3.88) nm; IR (film) ν_{max} 3370 (OH), 1693 (C=O) and 1460 (CH_3) cm^{-1}; ^1H NMR and ^{13}C NMR see Table S1; HRESIMS *m/z* 1259.6034 (calcd for $C_{59}H_{96}O_{27}$ Na $[M + Na]^+$, 1259.6037).

Congmujingnoside D (**3**): $C_{54}H_{88}O_{23}$, white amorphous powder; [α]20 D + 40.7 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 204 (3.67) nm; IR (film) ν_{max} 3370 (OH), 1693 (C=O) and 1460 (CH_3)cm^{-1}; ^1H NMR and ^{13}C NMR see Table S2; HRESIMS *m/z* 1127.5667 (calcd for $C_{54}H_{88}O_{23}$ Na $[M + Na]^+$, 1127.5614).

Congmujingnoside E (**4**): $C_{53}H_{86}O_{22}$, white amorphous powder; [α]20 D -17.0 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 210 (3.84) nm; IR (film) ν_{max} 3370 (OH), 1693 (C=O) and 1460 (CH_3) cm^{-1}; ^1H NMR and ^{13}C NMR see Table S2; HRESIMS *m/z* 1097.5500 (calcd for $C_{53}H_{86}O_{22}$ Na $[M + Na]^+$, 1097.5508).

Congmujingnoside F (**5**): $C_{59}H_{96}O_{26}$, white amorphous powder; [α]20 D -26.3 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 209 (4.52) nm; IR (film) ν_{max} 3370 (OH), 1693(C=O) and 1460 (CH_3) cm^{-1}; ^1H NMR and ^{13}C NMR see Table S3; HRESIMS *m/z* 1243.6085 (calcd for $C_{59}H_{96}O_{26}$ Na $[M + Na]^+$, 1243.6088).

Congmujingnoside G (**6**): $C_{53}H_{86}O_{21}$, white amorphous powder; [α]20 D -21.4 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 207 (4.15) nm; IR (film) ν_{max} 3370 (OH), 1693

(C=O) and 1460 (CH_3) cm^{-1}; ^1H NMR and ^{13}C NMR see Table S3; HRESIMS *m/z* 1081.5567 (calcd for $C_{53}H_{86}O_{21}Na$ $[M + Na]^+$, 1081.5559).

1.4. Acid hydrolysis and sugar identification

Hydrolysis of Saponins. Each of the saponins (2 mg) was heated in 4N TFA (trifluoroacetic acid, aqueous solution, 3 mL) at 95 °C for 4 h. The reaction mixture was extracted with $CHCl_3$ (3 × 3mL). Each remaining aqueous layer was concentrated to dryness to yield a residue that was subsequently dissolved in pyridine (2 mL), and L-cysteine methyl ester hydrochloride (2 mg) was added to the solution. The mixture was heated at 60 °C for 2 h, chlorotrimethylsilane (0.3 mL) was added, and the mixture was further heated at 60 °C for 2 h. After the reactions had been performed, the supernatant was analysed by GC under the following conditions: the column temperature was maintained at 80 °C for 5 min, then increased from 80 to 280 °C at a rate of 25 °C/min, and finally maintained at 280 °C for 5 min; the carrier gas was N2 (1.4 ml/min); the split ratio was 1/20; the injection temperature was 250 °C; and the injection volume was 1 μl. The absolute configurations of the monosaccharides were confirmed to be all D-glucose and D–xylose by comparison of the retention times of the monosaccharide derivatives with those of the standard samples D-glucose (13.489 min) and D–xylose (15.576 min).

1.5. Assay for Testing the Protective Effects against Myocardial Cell Injury Induced by H_2O_2

H9c2 cells (1×10^5/well; Cell Bank of the Chinese Academy of Sciences Shanghai, China) were seeded into 96-well plates. After incubation with different concentrations of compounds **1**−**6** (15−200 μM) for 12 h, the cells were treated with 200 μM H_2O_2 for 24 h. The cells in the control groups were treated with the same volume of phosphate-buffered saline (PBS). Cell viability was evaluated by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenylte-trazolium bromide (MTT) assay, which is based on the reduction of MTT by the mitochondrial dehydrogenase of intact cells to a purple formazan product. The quantity of formazan was determined by measuring the absorbance at 540 nm using an ELISA plate reader. The percentage cell viability was calculated as a ratio of the optical density (OD) value of the sample to the OD

value of the control. All experiments were done three times.

1.6. DPPH Radical Scavenging Capacity Assay

DPPH free radical scavenging activity of fractions and compounds was determined intriplicate according to the method proposed by Fujita. In brief, 100 μL of tested fraction or compound at final concentrations (5−200 μM) in methanol was added to 100 μL of a 0.5 mM DPPH radical solution in methanol. The mixture was shaken vigorously and allowed to stand for 30 min in the dark. Vitamin E was considered as a positive control. A freshly prepared DPPH solution exhibits a deep purple color with absorption maximum at 517 nm with a spectrophotometer. The radical scavenging rate of free radical DPPH in percent (I%) was calculated in the following way:

$$\text{I \%} = \frac{A_1 - A_0}{A_2 - A_0} \times 100$$

A_0: Blank wells OD A_1: Test wells OD A_2: control wells OD

(OD = optical density; Test wells = treated wells)

1.7. Statistical Analysis

Data were expressed as the mean ± SD and evaluated using one-way ANOVA. The post hoc test was done with Student's Dunnett test. $p < 0.05$ was considered statistically significant. Calculations were performed using the SPSS 16.0 statistical package.

2. List of Supplementary Material

Figure S16. HSQC spectrum of the new compound **3**.

Figure S17. HMBC spectrum of the new compound **3**.

Figure S18. ^{1}H-^{1}H COSY spectrum of the new compound **3**.

Figure S19. NOESY spectrum of the new compound **3**.

Figure S20. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **4**.

Figure S21. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **4**.

Figure S22. HSQC spectrum of the new compound **4**.

Figure S23. HMBC spectrum of the new compound **4**.

Figure S24. ^{1}H-^{1}H COSY spectrum of the new compound **4**.

Figure S25. NOESY spectrum of the new compound **4**.

Figure S26. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **5**.

Figure S27. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **5**.

Figure S28. HSQC spectrum of the new compound **5**.

Figure S29. HMBC spectrum of the new compound **5**.

Figure S30. ^{1}H-^{1}H COSY spectrum of the new compound **5**.

Figure S31. NOESY spectrum of the new compound **5**.

Figure S32. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **6**.

Figure S33. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **6**.

Figure S34. HSQC spectrum of the new compound **6**.

Figure S35. HMBC spectrum of the new compound **6**.

Figure S36. ^{1}H-^{1}H COSY spectrum of the new compound **6**.

Figure S37. NOESY spectrum of the new compound **6**.

Table S1. ^{1}H NMR and ^{13}C NMR spectroscopic data of compounds **1-2**

	1		**2**	
Position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	39.2, CH_2	1.37-1.40, m; 0.80-0.82, m	39.2, CH_2	1.38-1.41, m; 0.79-0.82, m
2	27.1, CH_2	2.13-2.16, m; 1.77-1,79, m	27.1, CH_2	2.12-2.15, m; 1.76-1.78, m
3	89.9, CH	3.23, dd, (4.2, 11.4)	79.1, CH	4.20 dd, (4.2, 10.8)
4	40.2, C		40.1, C	
5	56.4, CH	0.70-0.76, m	56.4, CH	0.71-0.73, m
6	19.0, CH_2	1.45-1.49, m; 1.27-1.30, m	19.0, CH_2	1.47-1.49, m; 1.30-1.34, m
7	33.6, CH_2	1.40-1.43, m; 1.26-1.29, m	33.6, CH_2	1.38-1.41, m; 1.24-1.26, m
8	40.3, C		40.4, C	
9	48.5, CH	1.56-1.59, m	48.5, CH	1.56-1.59, m
10	37.4, C		37.4, C	
11	24.2, CH_2	1.87-1.90, m; 1.83-1.85, m	24.2, CH_2	1.87-1.89, m; 1.83-1.86, m
12	122.3, CH	5.39, br.s	122.3, CH	5.40, br.s
13	144.6, C		144.7, C	
14	42.6, C		42.6, C	
15	28.7, CH_2	2.28-2.32, m; 1.13-1.16, m	28.8, CH_2	2.28-2.30, m; 1.14-1.16, m
16	23.8, CH_2	2.04-2.09, m; 1.92-1.96, m	23.9, CH_2	2.04-2.08, m; 1.93-1.95, m
17	47.5, C		47.5, C	
18	42.1, CH	3.17, dd, (3.6, 13.2)	42.2, CH	3.17, dd, (3.6, 13.2)
19	46.7, CH_2	1.70-1.73, m; 1.19-1.21, m	46.8, CH_2	1.71-1.74, m; 1.20-1.22, m
20	31.2, C		31.2, C	
21	34.4, CH_2	1.29-1.31, m; 1.08-1.10, m	34.5, CH_2	1.26-1.29, m; 1.06-1.08, m
22	33.0, CH_2	1.85-1.87, m; 1.72-1.75, m	33.0, CH_2	1.88-1.93, m; 1.74-1.77, m
23	28.3, CH_3	1.27, s	28.3, CH_3	1.25, s
24	16.9, CH_3	1.08, s	17.0, CH_3	1.06, s
25	16.1, CH_3	0.84, s	16.1, CH_3	0.83, s
26	17.9, CH_3	1.07, s	18.0, CH_3	1.08, s
27	26.6, CH_3	1.24, s	26.6, CH_3	1.24, s
28	177.0, C		177.0, C	
29	33.6, CH_3	0.87, s	33.6, CH_3	0.87, s
30	24.1, CH_3	0.86, s	24.1, CH_3	0.86, s
	3-glc'		28-glc'	
1'	105.3, CH	5.47, d, (7.8)	96.2, CH	6.24, d, (7.8)
2'	79.5, CH	4.22-4.25, m	79.8, CH	4.30-4.33, m
3'	85.3, CH	4.28-4.32, m	90.1, CH	3.23-3.26, m
4'	70.1, CH	3.98-4.02, m	70.6, CH	4.01-4.05, m
5'	78.9, CH	3.77-3.82, m	78.2, CH	3.81-3.83, m
6'	63.1, CH_2	4.56-4.58, m; 4.33-4.35, m	62.8, CH_2	4.43-4.44, m; 4.25-4.30, m
	glc"		glc"	
1"	105.9, CH	4.80, d, (7.8)	105.2, CH	4.81, d, (7.8)
2"	76.6, CH	3.82-3.85, m	74.4, CH	4.13-4.15, m
3"	79.2, CH	4.15-4.18, m	89.3, CH	4.25-4.27, m

4"	71.3, CH	4.08-4.12, m	71.4, CH	4.13-4.16, m
5"	78.4, CH	3.98-4.02, m	78.4, CH	4.09-4.11, m
6"	69.8, CH_2 glc‴	4.75-4.78, m; 4.33-4.36, m	69.8, CH_2 glc‴	4.69-4.71, m; 4.35-4.37, m
1‴	105.7, CH	5.36 , d, (7.8)	105.5, CH	5.36, d, (7.8)
2‴	75.8, CH	4.02-4.05, m	75.6, CH	3.95-4.00, m
3‴	78.8, CH	3.87-3.89, m	79.2, CH	3.86-3.88, m
4‴	71.8, CH	4.31-4.34, m	72.0, CH	4.33-4.35, m
5‴	77.7, CH	4.32-4.35, m	78.9, CH	4.30-4.35, m
6‴	62.8, CH_2 xyl⁗	4.44-4.47, m; 4.27-4.30, m	63.1, CH_2 xyl⁗	4.44-4.47, m; 4.33-4.35, m
1⁗	105.7, CH	5.02, d, (7.8)	105.1, CH	5.02, d, (7.8)
2⁗	75.6, CH	4.08-4.12, m	75.9, CH	4.09-4.13, m
3⁗	78.8, CH	3.96-4.00, m	79.4, CH	4.05-4.10, m
4⁗	72.0, CH	4.07-4.12, m	72.1, CH	4.09-4.13, m
5⁗	67.5, CH_2 28-glc⁗⁗	4.17-4.21, m; 3.64-3.67, m	67.7, CH_2 glc⁗⁗	4.27-4.30, m; 3.57-3.60, m
1⁗⁗	96.1, CH	6.25, d, (7.8)	105.7, CH	5.58, d, (7.8)
2⁗⁗	74.4, CH	4.09-4.13, m	76.7, CH	4.14-4.17, m
3⁗⁗	78.8, CH	4.20-4.25, m	79.4, CH	4.05-4.10, m
4⁗⁗	72.0, CH	4.09-4.11, m	71.9, CH	4.18-4.23, m
5⁗⁗	76.7, CH	4.07-4.11, m	75.6, CH	4.15-4.20, m
6⁗⁗	62.9, CH_2	4.35-4.40, m; 3.37-3.39, m	63.1, CH_2	4.44-4.47, m; 4.33-4.35, m

Recorded at 600 or 150 MHz for ^{1}H and ^{13}C, resp. In C_5D_5N

Table S2. ^{1}H NMR and ^{13}C NMR spectroscopic data of compounds **3-4**

	3		**4**	
Position	$\delta_{C,}$ type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	39.2, CH_2	1.34-1.37, m; 0.79-0.82, m	39.2, CH_2	1.30-1.33, m; 0.81-0.83, m
2	27.0, CH_2	2.12-2.14, m; 1.75-1.78, m	27.0, CH_2	2.13-2.15, m; 1.74-1,76, m
3	79.1, CH	4.20, dd, (4.2, 10.8)	79.8, CH	4.25, dd, (4.2, 10.8)
4	40.0, C		40.1, C	
5	56.3, CH	0.70-0.72, m	56.3, CH	0.72-0.74, m
6	19.0, CH_2	1.43-1.45, m; 1.23-1.26, m	19.0, CH_2	1.47-1.50, m; 1.27-1.30, m
7	33.6, CH_2	1.39-1.41, m; 1.28-1.31, m	33.6, CH_2	1.44-1.47, m; 1.35-1.37, m
8	40.3, C		40.4, C	
9	48.4, CH	1.52-1.56, m	48.5, CH	1.56-1.62, m
10	37.4, C		37.4, C	
11	24.2, CH_2	1.85-1.87, m; 1.82-1.84, m	24.2, CH_2	1.88-1.91, m; 1.84-1.86, m
12	123.3, CH	5.41, br.s	123.3, CH	5.41, br.s
13	144.6, C		144.6, C	
14	42.6, C		42.6, C	
15	28.7, CH_2	2.30-2.34, m; 1.12-1.14, m	28.7, CH_2	2.31-2.34, m; 1.13-1.16, m

16	23.9, CH_2	2.05-2.09, m; 1.94-1.96, m	23.9, CH_2	2.06-2.08, m; 1.95-1.97, m
17	47.5, C		47.5, C	
18	42.2, CH	3.17, dd, (3.6, 13.8)	42.2, CH	3.18, dd, (3.6, 13.8)
19	46.7, CH_2	1.71-1.74, m; 1.19-1.22, m	46.7, CH_2	1.72-1.75, m; 1.19-1.21, m
20	31.2, C		31.2, C	
21	34.5, CH_2	1.30-1.34, m; 0.98-1.01, m	34.5, CH_2	1.33-1.36, m; 1.07-1.09, m
22	33.0, CH_2	1.83-1.86, m; 1.74-1.77, m	33.0, CH_2	1.81-1.84, m; 1.73-1.76, m
23	28.6, CH_3	1.32, s	28.2, CH_3	1.25, s
24	17.2, CH_3	1.11, s	16.9, CH_3	1.06, s
25	16.0, CH_3	0.80, s	16.0, CH_3	0.79, s
26	17.9, CH_3	1.07, s	17.9, CH_3	1.08, s
27	26.6, CH_3	1.23, s	26.6, CH_3	1.25, s
28	176.9, C		176.9, C	
29	33.6, CH_3	0.89, s	33.6, CH_3	0.89, s
30	24.1, CH_3	0.87, s	24.1, CH_3	0.87, s
	28-glc'		28-glc'	
1'	96.2, CH	6.32, d, (8.4)	96.2, CH	6.32, d, (8.4)
2'	80.1, CH	4.37-4.39, m	78.3, CH	4.27-4.30, m
3'	89.8, CH	3.26-3.29, m	90.0, CH	3.23-3.26, m
4'	70.2, CH	4.60-4.62, m	70.6, CH	4.02-4.04, m
5'	78.2, CH	3.79-3.82, m	79.1, CH	3.80-3.84, m
6'	62.7, CH_2	4.44-4.47, m; 4.25-4.28, m	62.7, CH_2	4.42-4.44, m; 4.22-4.25, m
	glc"		glc"	
1"	105.5, CH	4.83, d, (7.8)	105.4, CH	4.81, d, (7.8)
2"	74.3, CH	4.10-4.13, m	75.8, CH	4.03-4.05, m
3"	89.1, CH	4.23-4.25, m	89.4, CH	4.29-4.32, m
4"	70.5, CH	4.02-4.05, m	71.6, CH	4.18-4.20, m
5"	79.1, CH	3.95-3.97, m	79.1, CH	4.04-4.05, m
6"	62.0, CH_2	4.49-4.52, m; 4.34-4.37, m	62.8, CH_2	4.45-4.47, m; 4.27-4.30, m
	glc"'		glc"'	
1"'	105.1, CH	5.57, d, (7.8)	105.2, CH	5.59, d, (7.8)
2"'	77.0, CH	4.15-4.17, m	76.7, CH	4.11-4.14, m
3"'	79.4, CH	4.05-4.10, m	79.4, CH	4.04-4.07, m
4"'	71.6, CH	4.17-4.20, m	72.0, CH	4.14-4.17, m
5"'	75.9, CH	4.11-4.14, m	75.4, CH	4.03-4.05, m
6"'	62.8, CH_2	4.43-4.45, m; 4.29-4.32, m	63.1, CH_2	4.45-4.48, m; 4.23-4.25, m
	glc""		xyl""	
1""	105.1, CH	5.33, d, (7.8)	105.1, CH	5.06, d, (7.8)
2""	75.8, CH	3.97-4.00, m	74.6, CH	4.01-4.03, m
3""	79.8, CH	3.89-3.92, m	79.8, CH	4.03-4.04, m
4""	72.0, CH	4.32-4.35, m	71.9, CH	4.15-4.18, m
5""	78.6, CH	4.30-4.33, m	67.7, CH_2	4.17-4.21, m; 3.68-3.70, m
6""	63.0, CH_2	4.46-4.49, m; 4.34-4.38, m		

Recorded at 600 or 150 MHz for ^{1}H and ^{13}C, resp. In C_5D_5N

Table S3. ^{1}H NMR and ^{13}C NMR spectroscopic data of compounds **5-6**

	5		**6**	
Position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	39.4, CH_2	1.45-1.47, m; 0.88-0.91, m	39.3, CH_2	1.45-1.47, m; 0.99-1.02, m
2	27.1, CH_2	2.04-2.06, m; 1.73-1,76, m	26.9, CH_2	2.01-2.03, m; 1.67-1,69, m
3	89.2, CH	3.27, dd, (4.2, 11.4)	79.2, CH	4.21, dd, (4.2, 10.8)
4	40.1, C		39.9, C	
5	56.5, CH	0.77-0.79, m	56.3, CH	0.74-0.76, m
6	19.0, CH_2	1.40-1.43, m; 1.24-1.27, m	18.9, CH_2	1.43-1.45, m; 1.24-1.27, m
7	33.5, CH_2	1.37-1.40, m; 1.18-1.21, m	33.6, CH_2	1.38-1.40, m; 1.18-1.21, m
8	40.3, C		40.3, C	
9	48.4, CH	1.59-1.62, m	48.5, CH	1.55-1.57, m
10	37.5, C		37.4, C	
11	24.3, CH_2	1.88-1.90, m; 1.83-1.85, m	24.2, CH_2	1.88-1.90, m; 1.85-1.87, m
12	123.3, CH	5.39, br.s	123.2, CH	5.40, br.s
13	144.6, C		144.5, C	
14	42.6, C		42.6, C	
15	28.7, CH_2	2.28-2.32, m; 1.17-1.20, m	28.7, CH_2	2.29-2.33, m; 1.20-1.23, m
16	23.8, CH_2	2.06-2.08, m; 1.94-1.96, m	23.8, CH_2	2.06-2.08, m; 1.96-1.99, m
17	47.5, C		47.5, C	
18	42.1, CH	3.17, dd, (3.2, 13.2)	42.1, CH	3.18, dd, (3.2, 13.2)
19	46.7, CH_2	1.70-1.73, m; 1.17-1.20, m	46.6, CH_2	1.70-1.73, m; 1.17-1.20, m
20	31.2, C		31.2, C	
21	34.4, CH_2	1.37-1.40, m; 1.01-1.05, m	34.4, CH_2	1.37-1.40, m; 0.98-1.02, m
22	33.0, CH_2	1.87-1.89, m; 1.77-1.80, m	33.0, CH_2	1.87-1.89, m; 1.77-1.80, m
23	28.7, CH_3	1.31, s	28.5, CH_3	1.25, s
24	17.6, CH_3	1.14, s	17.4, CH_3	1.17, s
25	16.1, CH_3	0.87, s	16.0, CH_3	0.88, s
26	17.9, CH_3	1.09, s	17.9, CH_3	1.11, s
27	26.5, CH_3	1.24, s	26.4, CH_3	1.24, s
28	177.0, C		176.9, C	
29	33.6, CH_3	0.90, s	33.5, CH_3	0.89, s
30	24.1, CH_3	0.86, s	24.1, CH_3	0.87, s
	3-glc'		28-glc'	
1'	107.3, CH	5.47, d, (7.8)	96.1, CH	6.26, d, (7.8)
2'	79.2, CH	4.15-4.20, m	78.4, CH	4.29-4.32, m
3'	83.7, CH	4.21-4.23, m	89.2, CH	3.22-3.26, m
4'	70.2, CH	3.91-3.93, m	69.0, CH	4.07-4.209, m
5'	78.8, CH	3.87-3.88, m	78.9, CH	3.87-3.89, m
6'	63.1, CH_2	4.35-4.38, m; 4.28-4.31, m	63.0, CH_2	4.47-4.49, m; 4.27-4.31, m
	glc"		glc"	
1"	105.9, CH	4.81, d, (7.8)	105.7, CH	4.90, d, (7.8)
2"	76.2, CH	3.97-3.99, m	75.6, CH	3.99-4.04, m
3"	79.1, CH	4.14-4.16, m	78.8, CH	4.27-4.29, m

4"	69.8 CH	4.07-4.11, m	72.8, CH	4.17-4.19, m
5"	74.4, CH	4.12-4.14, m	79.1, CH	4.07-4.09, m
6"	69.9, CH_2 qui'''	4.70-4.72, m; 4.37-4.39, m	62.8, CH_2 qui'''	4.45-4.48, m; 4.27-4.30, m
1'''	102.0, CH	6.20, br.s	102.2, CH	6.13, br.s
2'''	73.5, CH	4.13-4.16, m	73.0, CH	4.09-4.12, m
3'''	78.4, CH	3.95-3.98, m	78.9, CH	3.99-4.02, m
4'''	71.4, CH	4.25-4.28, m	71.9, CH	4.33-4.37, m
5'''	75.6, CH	4.29-4.31, m	76.4, CH	4.37-4.39, m
6'''	18.9, CH_3 xyl''''	1.52, d, (6.0)	19.0, CH_3 xyl''''	1.55, d, (6.0)
1''''	105.7, CH	5.02, d, (7.8)	105.2, CH	5.03, d, (7.8)
2''''	76.1, CH	4.11-4.13, m	74.5, CH	4.09-4.12, m
3''''	78.9, CH	4.02-4.05, m	78.8, CH	4.01-4.04, m
4''''	72.0, CH	4.09-4.13, m	71.9, CH	4.09-4.12, m
5''''	66.3, CH_2 28-glc'''''	4.25-4.28, m; 3.77-3.79, m	65.0, CH_2	4.27-4.31, m; 3.81-3.82, m
1'''''	96.1, CH	6.25, d, (8.4)		
2'''''	75.0, CH	4.09-4.13, m		
3'''''	79.0, CH	4.22-4.25, m		
4'''''	71.9, CH	4.07-4.12, m		
5'''''	76.4, CH	4.05-4.08, m		
6'''''	62.9, CH_2	4.36-4.39, m; 3.27-3.29, m		

Recorded at 600 or 150 MHz for ^{1}H and ^{13}C, resp. In C_5D_5N

Table S4. Protective Effects of Triterpenoidal Saponins from *Aralia chinensiss* on H_2O_2-Induced H9c2 Cell Injury

Compounds	concentration [a]					
	0 μM	15 μM	30 μM	60 μM	120 μM	200 μM
1	68.12 ± 2.56	65.24 ± 2.11	74.36 ± 2.36	78.10 ± 1.55*	82.35 ± 1.45**	84.22 ±3.51**
2	64.21 ± 1.33	64.12 ± 1.12	63.21 ± 1.78	64.32 ± 2.65	63.33 ±4.59	63.28 ± 4.36
3	64.32 ± 2.36	66.23 ± 2.15	68.21 ±3.22	67.12 ± 2.36	67.21 ± 2.65	62.58 ±2.09
4	63.89 ± 1.86	64.88 ± 1.29	62.58 ± 2.73	67.33 ± 5.12	75.34 ± 3.45	62.78 ± 2.12
5	64.25 ± 2.22	64.23 ± 4.71	75.21 ± 1.22**	81.32 ± 1.52**	87.13 ± 4.11**	90.58 ± 3.33**
6	68.98 ± 3.11	73.22 ± 4.12	73.10 ± 3.56	75.10 ± 1.36	76.33 ±2.08	77.45 ± 4.12
vitamin	63.42	65.11 ±	66.35 ±	68.12 ±	78.43 ±	82.36 ±

E [b]	±1.28	3.12	2.14	1.51	2.10*	1.39**

[a] *, $p < 0.05$, and **, $p < 0.01$, vs 0 μM group. [b] Positive control.

Table S5. Maximal Scavenging Rate of Compounds 1−6 against DPPH in Vitro

compound[a]	scavenging rate (100 μM)
1	11.26 ± 1.98
2	7.30 ± 2.34
3	6.49 ± 1.35
4	10.62 ± 2.19
5	8.34 ± 1.92
6	14.85 ± 3.12
vitamin E	50.44 ± 1.30

a For compounds 1−6, the test concentrations ranged from 5 to 100μM; for vitamin E, the test concentration was 100 μM.

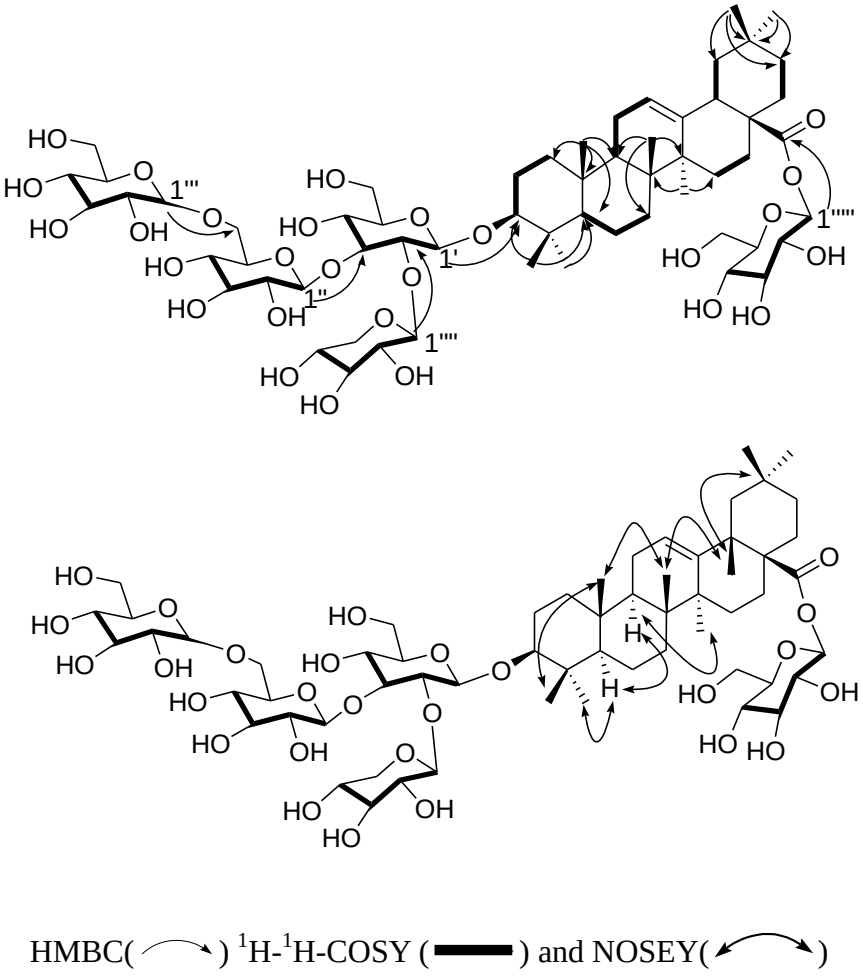

Figure S1. Key 2D NMR correlations of Compound **1**

Figure S2. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **1**

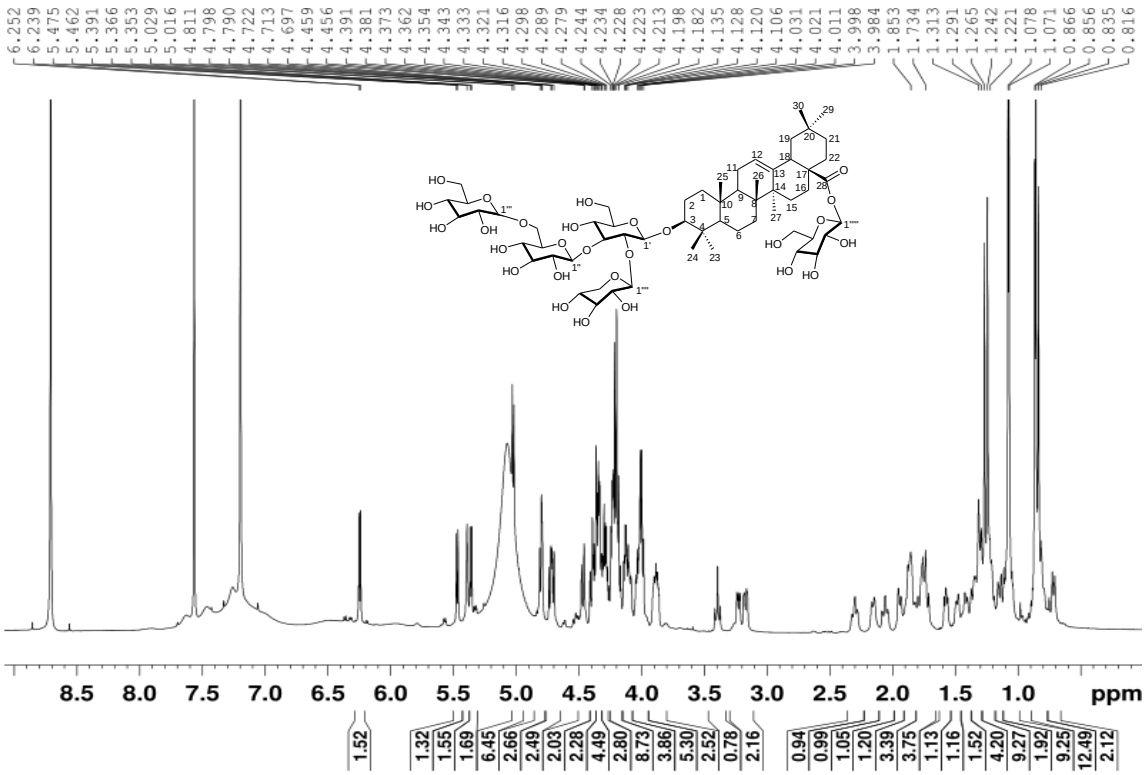

Figure S3. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **1**

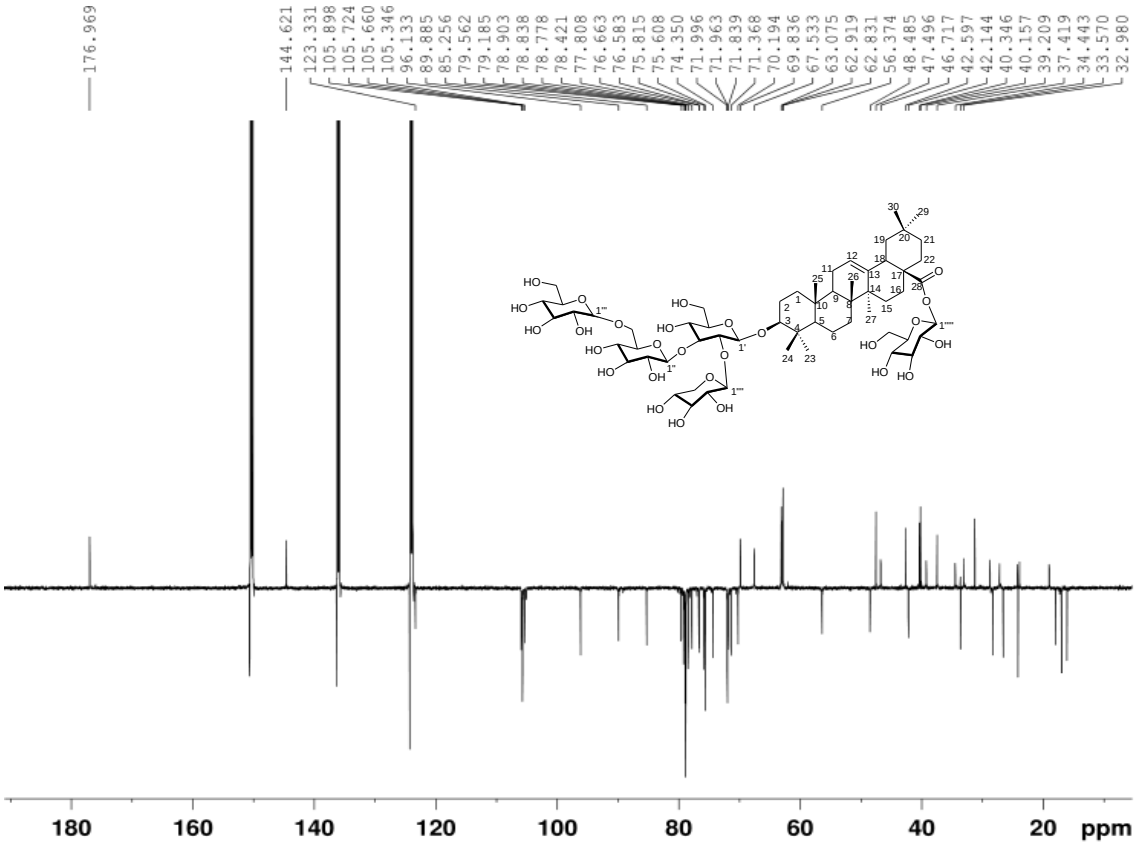

Figure S4. HSQC spectrum of the new compound **1**

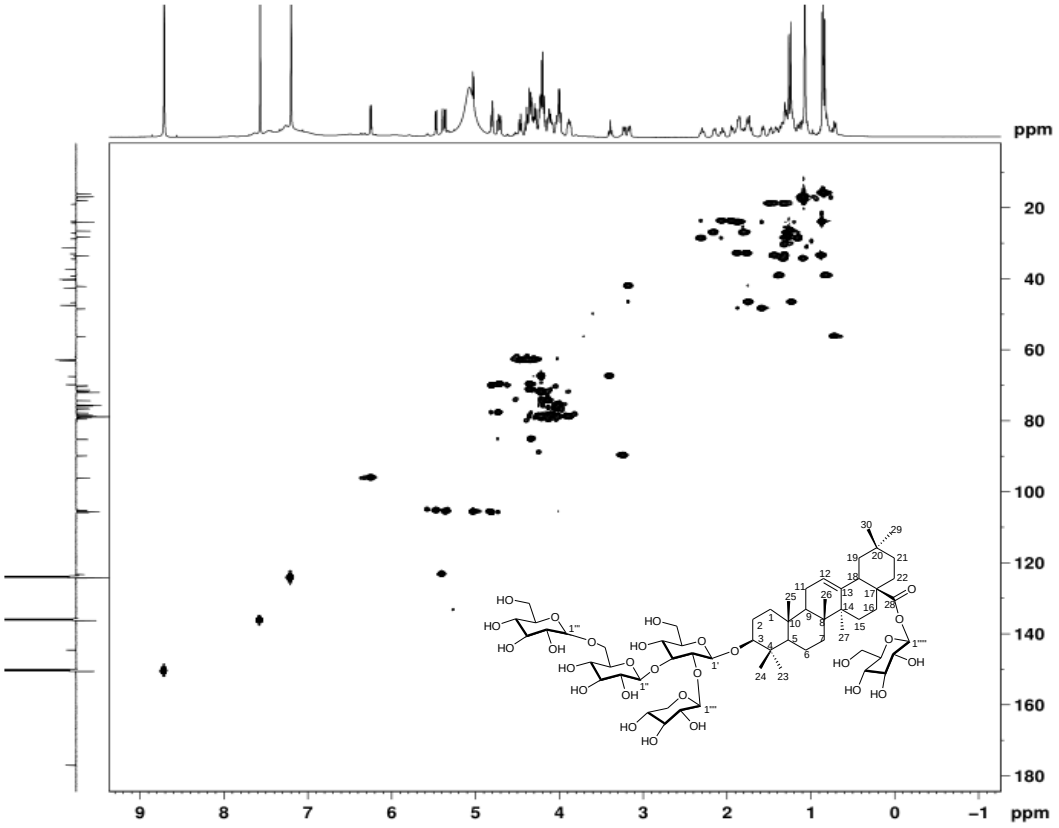

Figure S5. HMBC spectrum of the new compound **1**

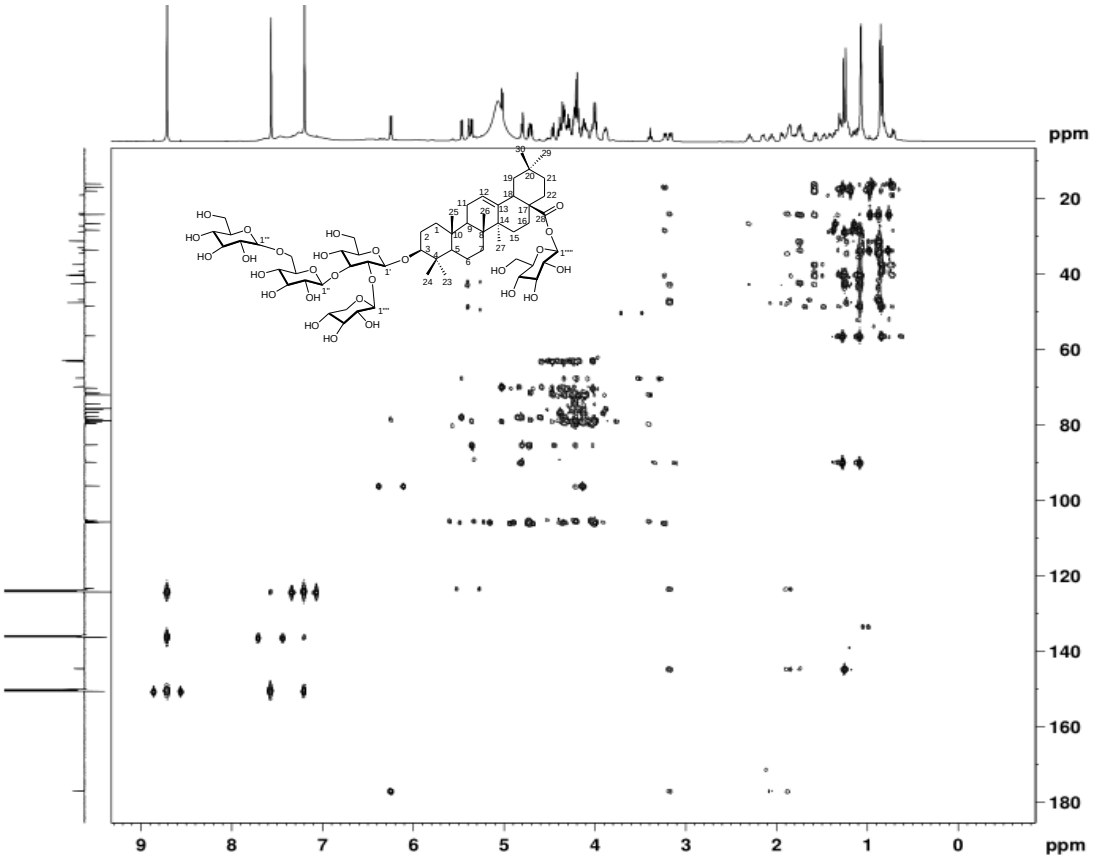

Figure S6. ^{1}H-^{1}H COSY spectrum of the new compound **1**

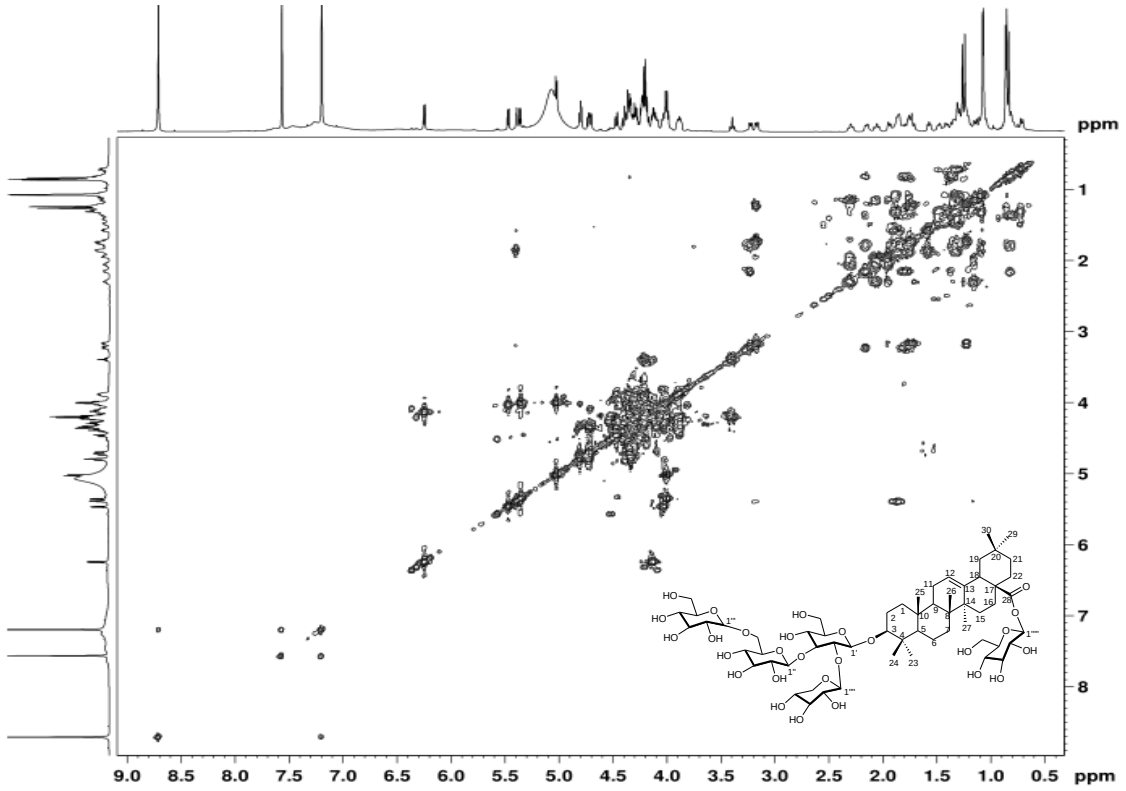

Figure S7. NOESY spectrum of the new compound **1**

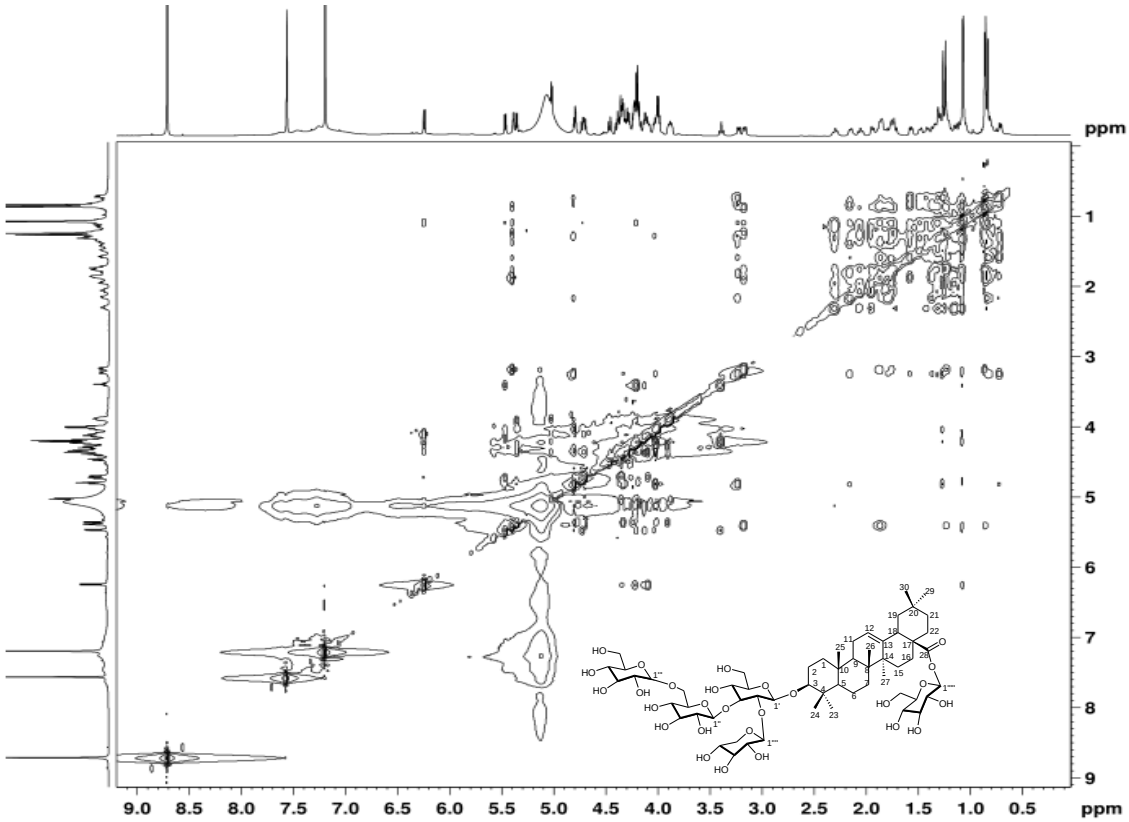

Figure S8. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **2**

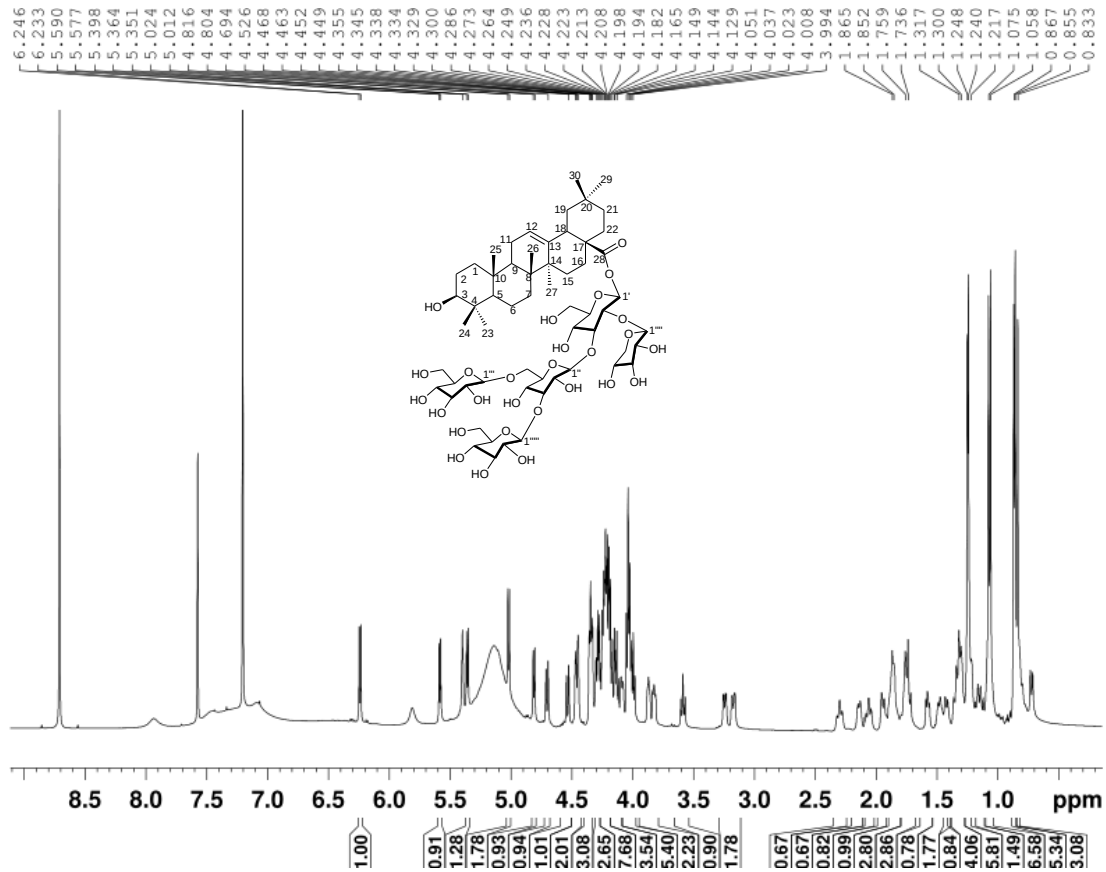

Figure S9. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **2**

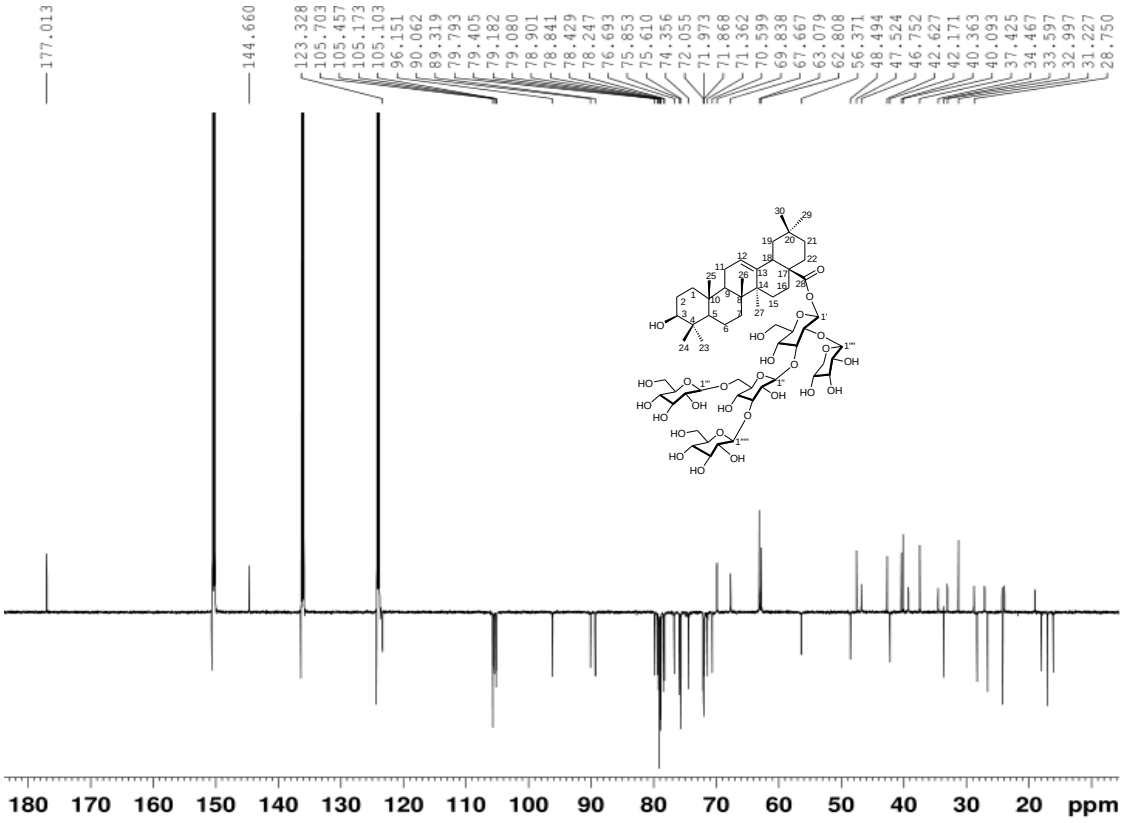

Figure S10. HSQC spectrum of the new compound **2**

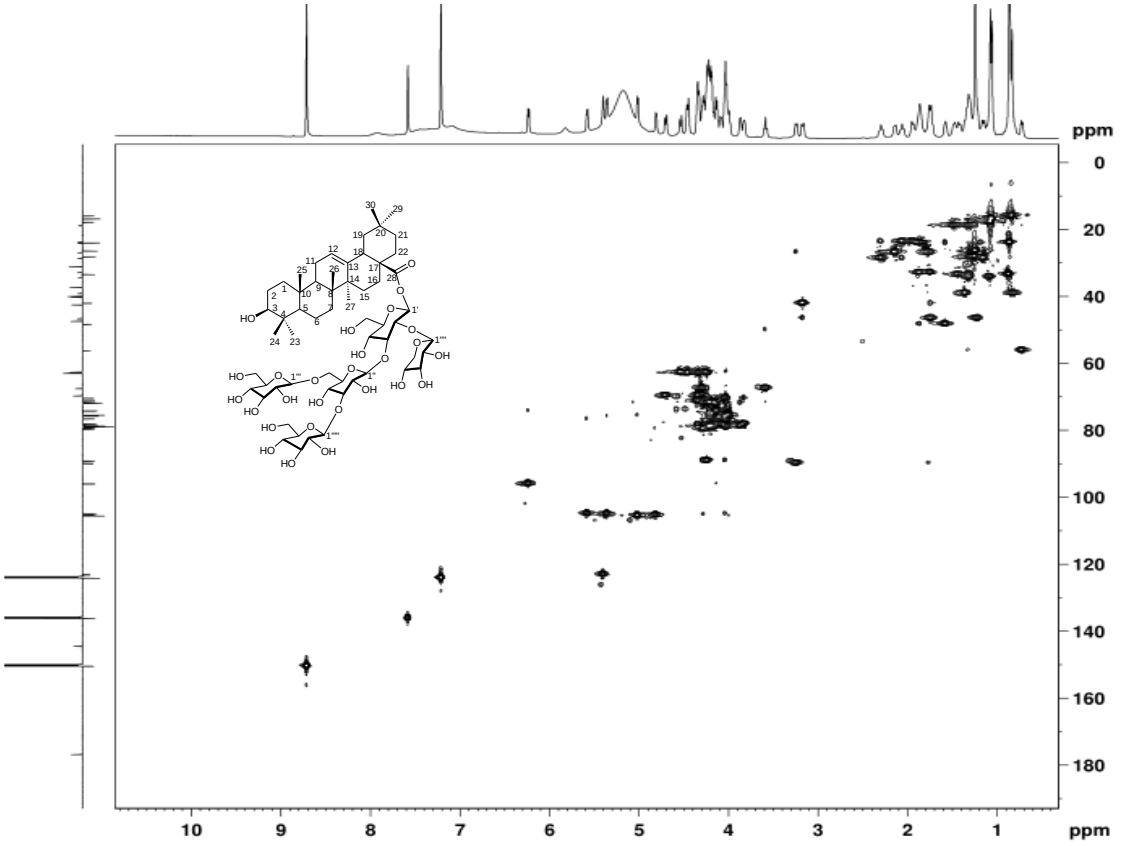

Figure S11. HMBC spectrum of the new compound **2**

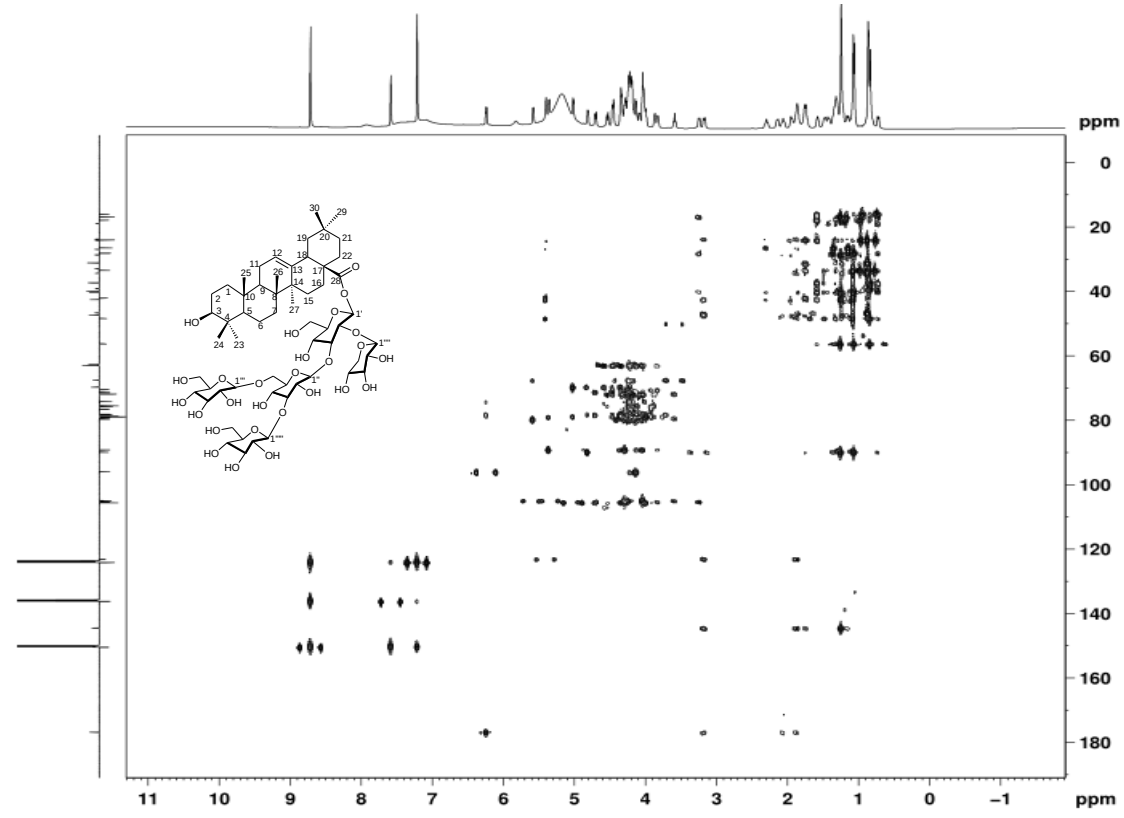

Figure S12. ^{1}H-^{1}H COSY spectrum of the new compound **2**

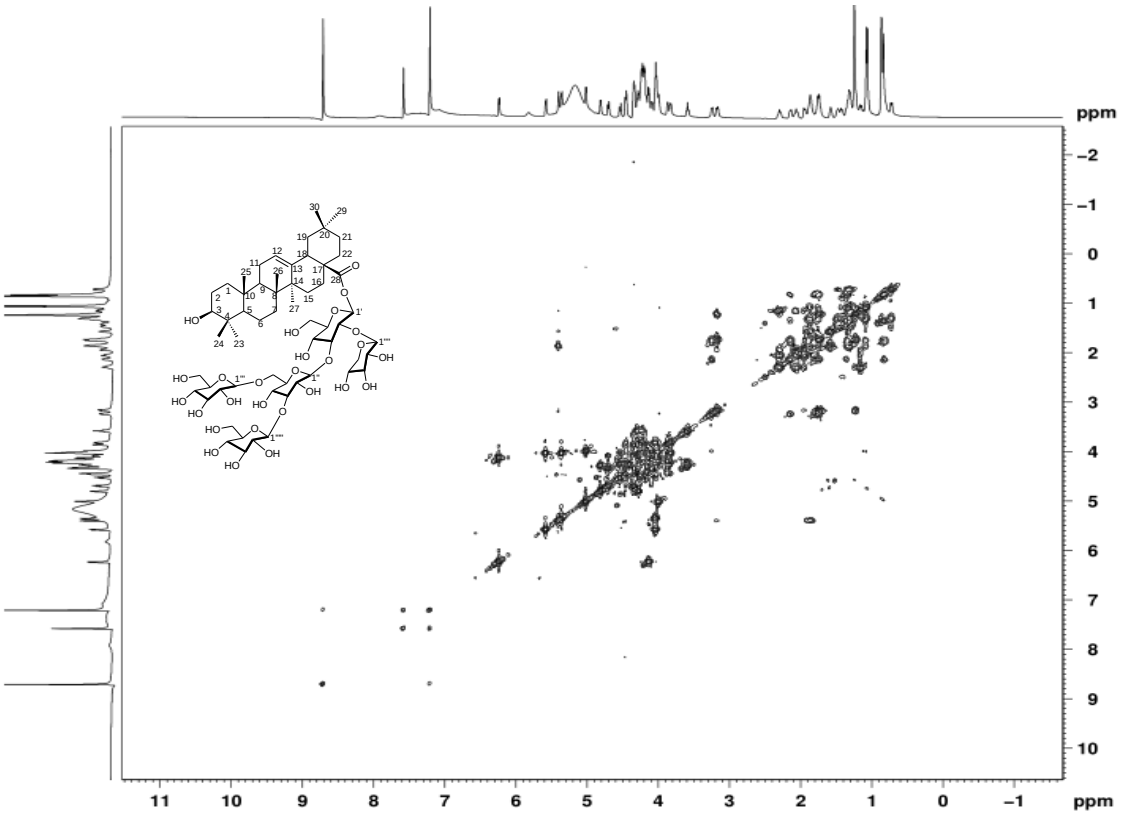

Figure S13. NOESY spectrum of the new compound **2**

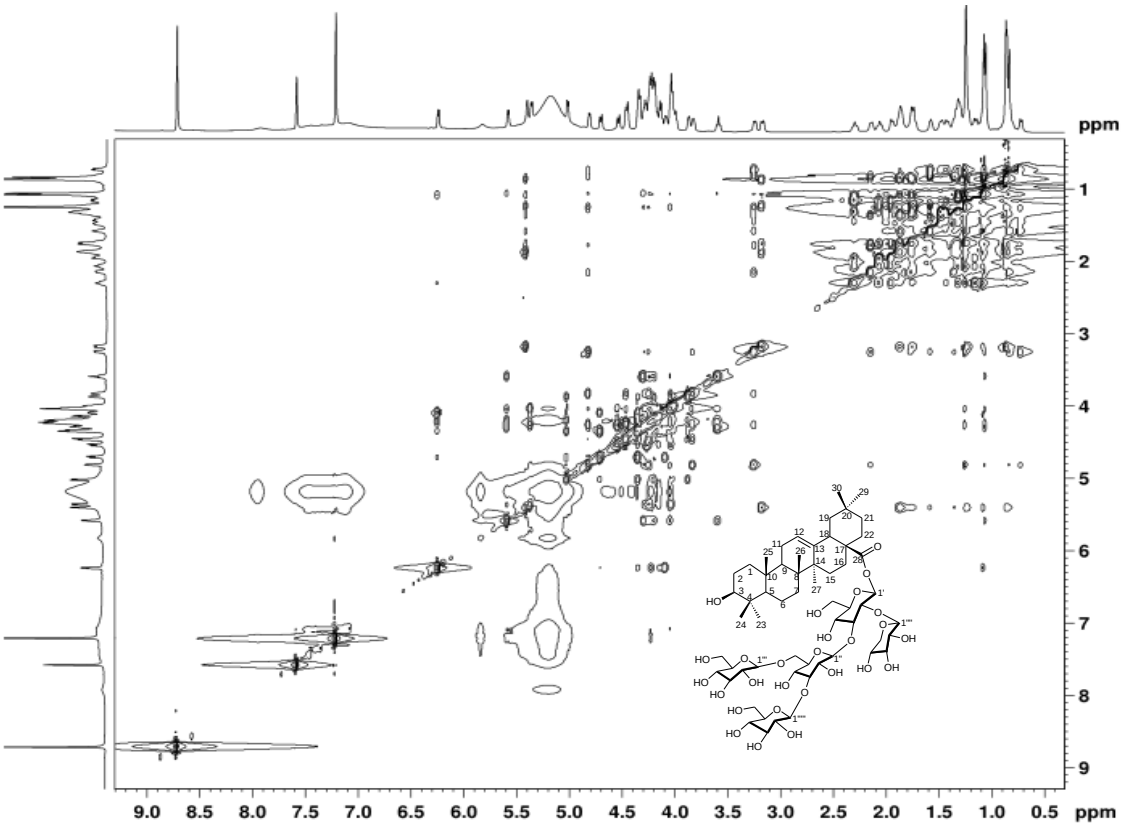

Figure S14. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **3**

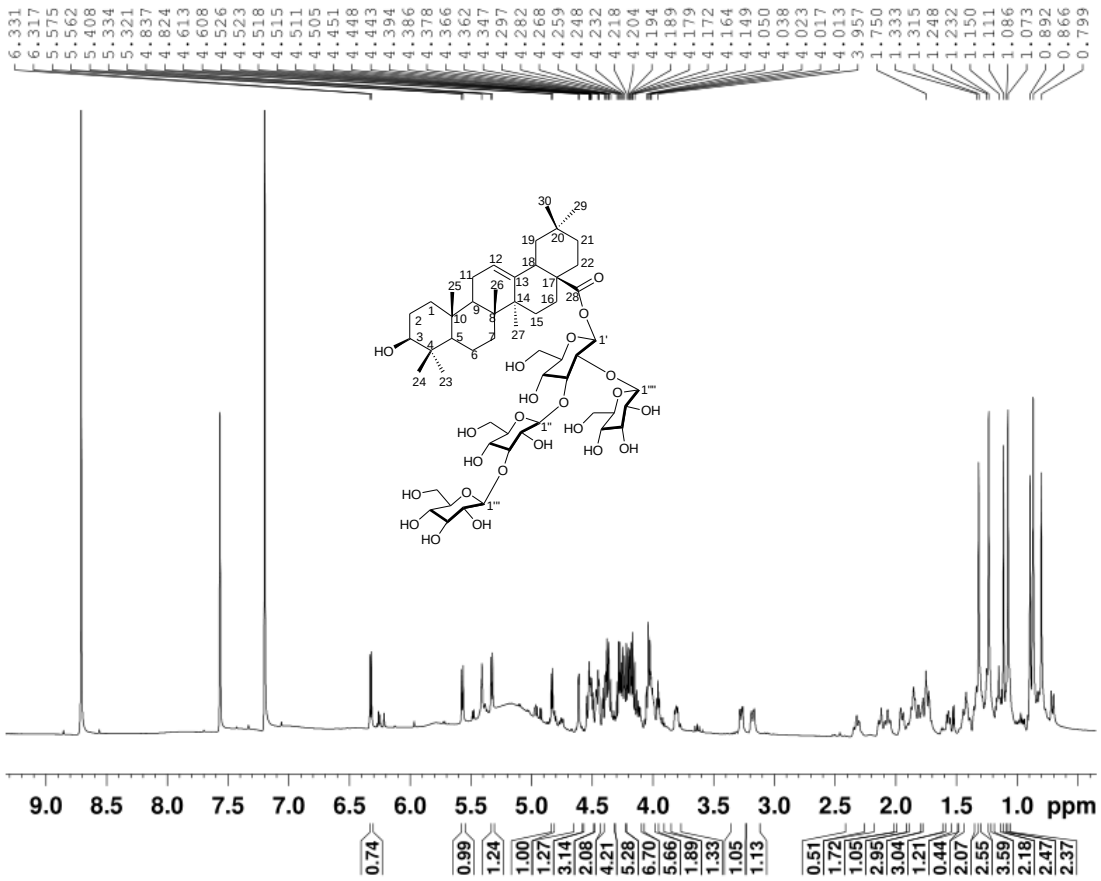

Figure S15. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **3**

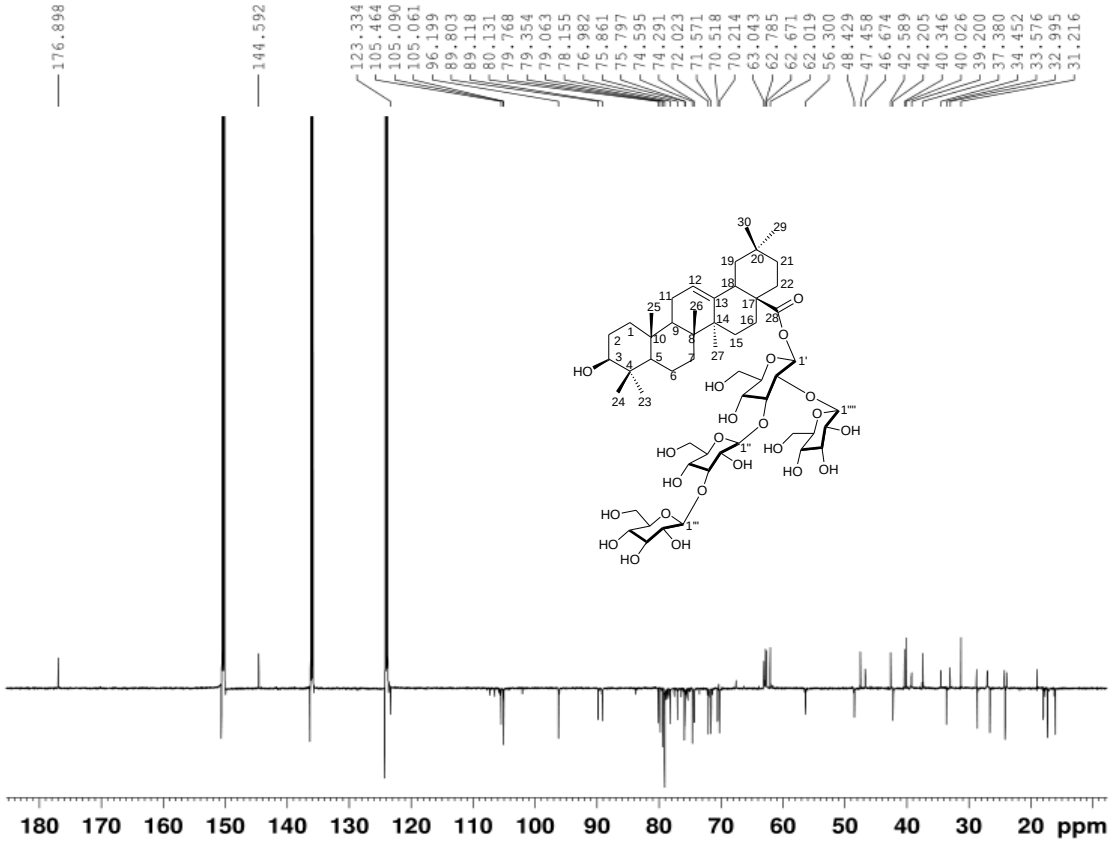

Figure S16. HSQC spectrum of the new compound **3**

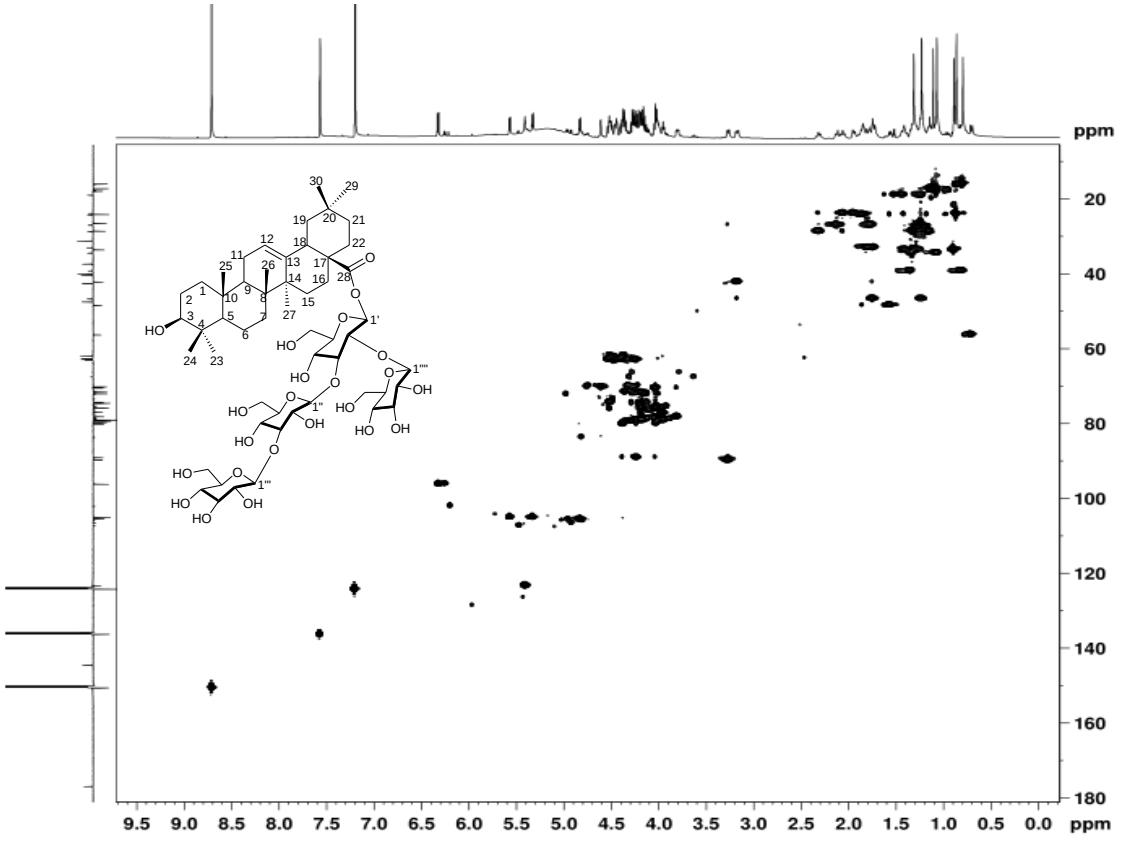

Figure S17. HMBC spectrum of the new compound **3**

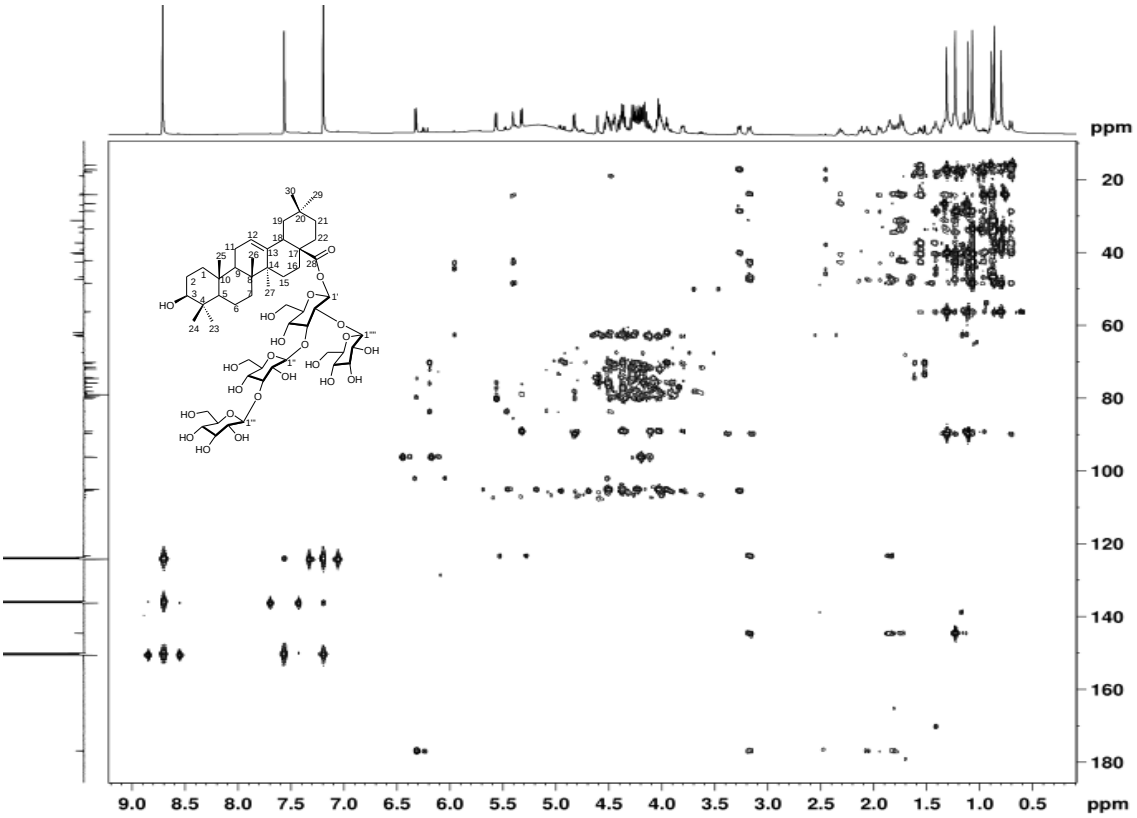

Figure S18. ^{1}H-^{1}H COSY spectrum of the new compound **3**

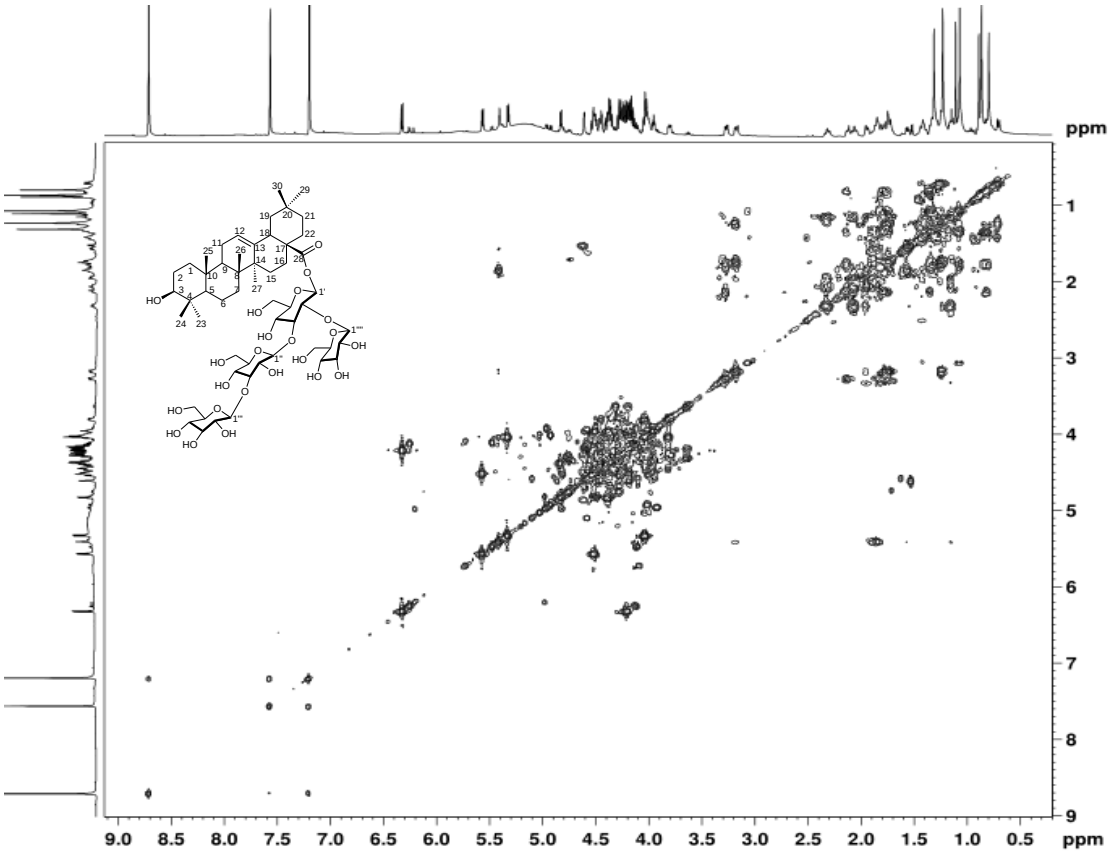

Figure S19. NOESY spectrum of the new compound **3**

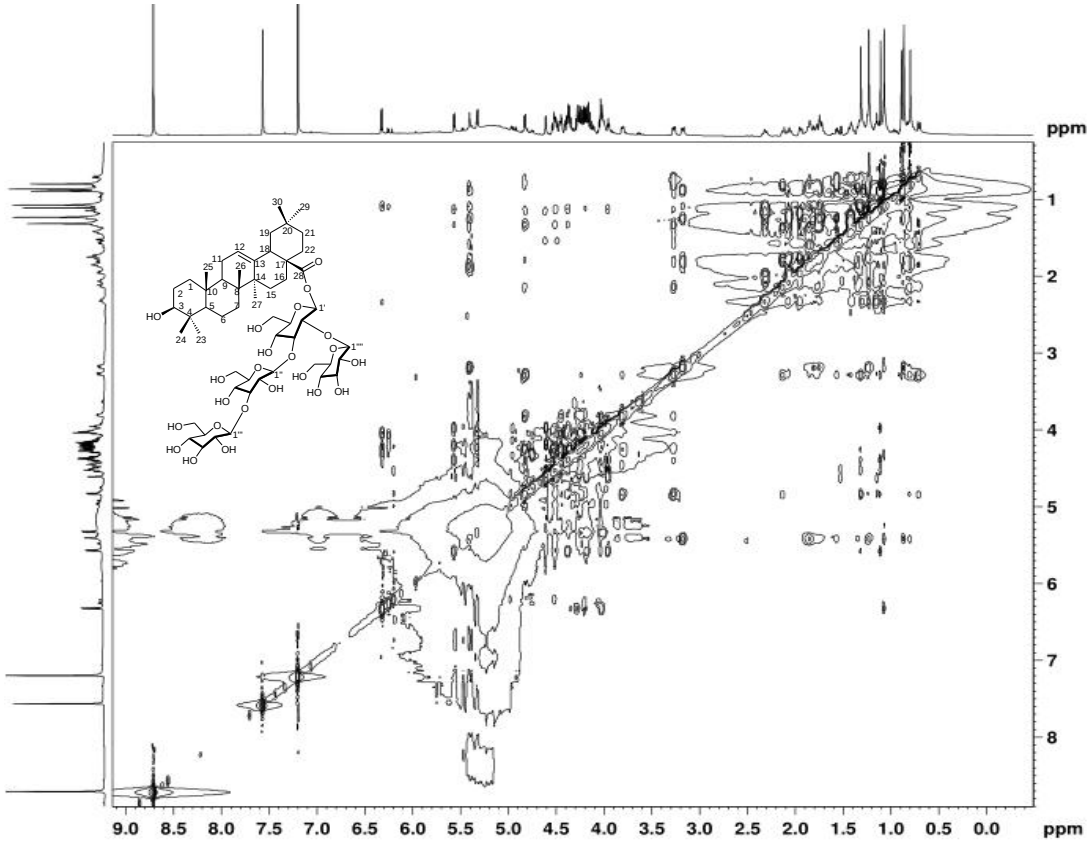

Figure S20. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **4**

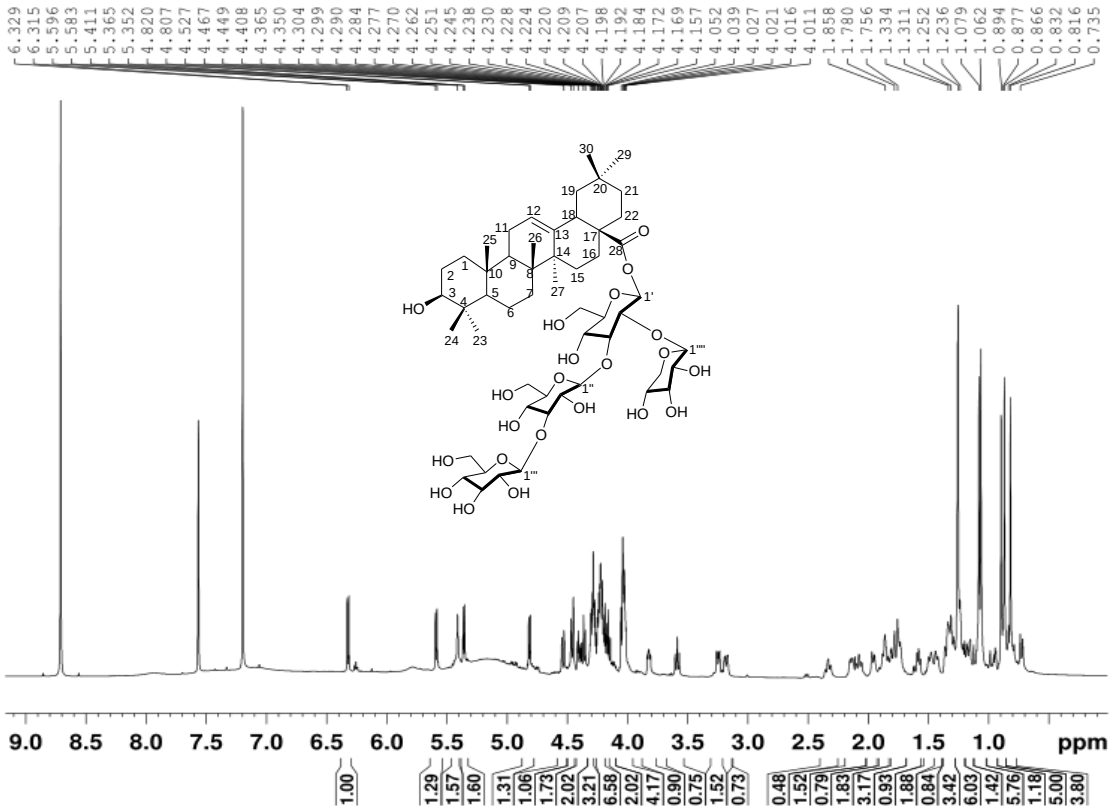

Figure S21. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **4**

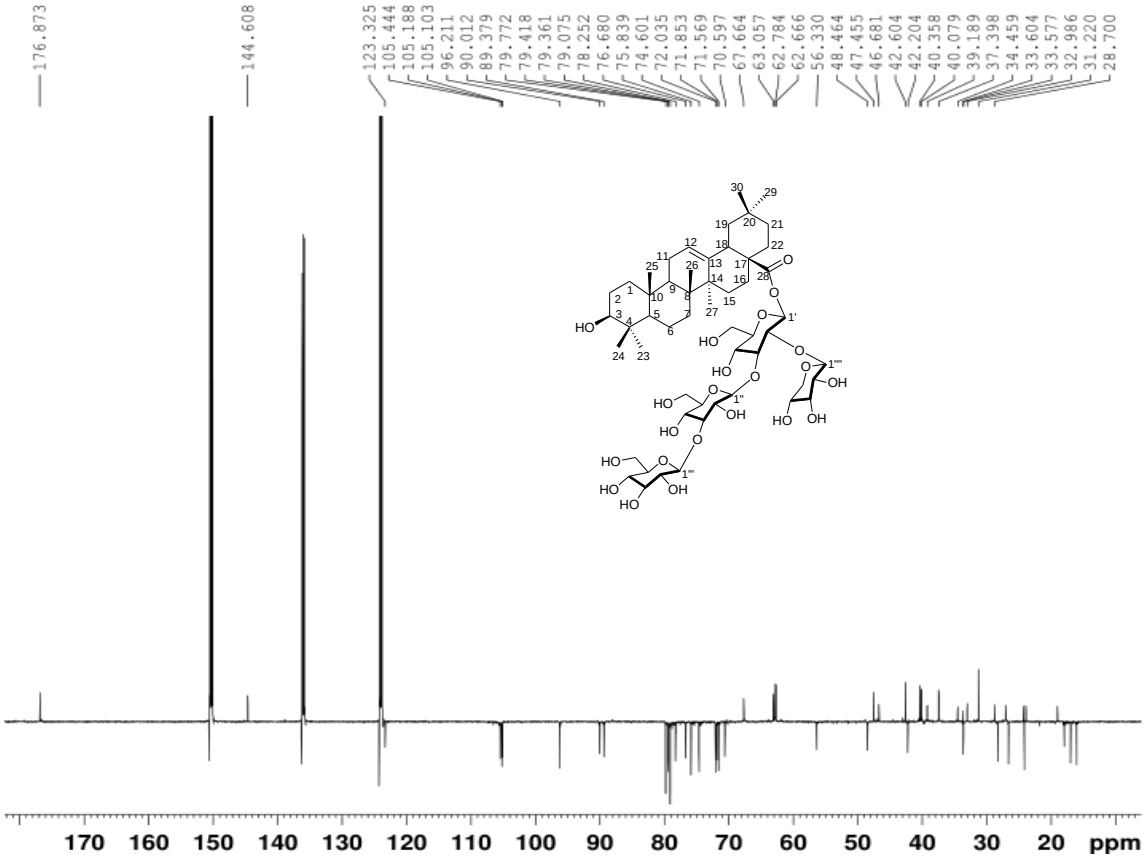

Figure S22. HSQC spectrum of the new compound **4**

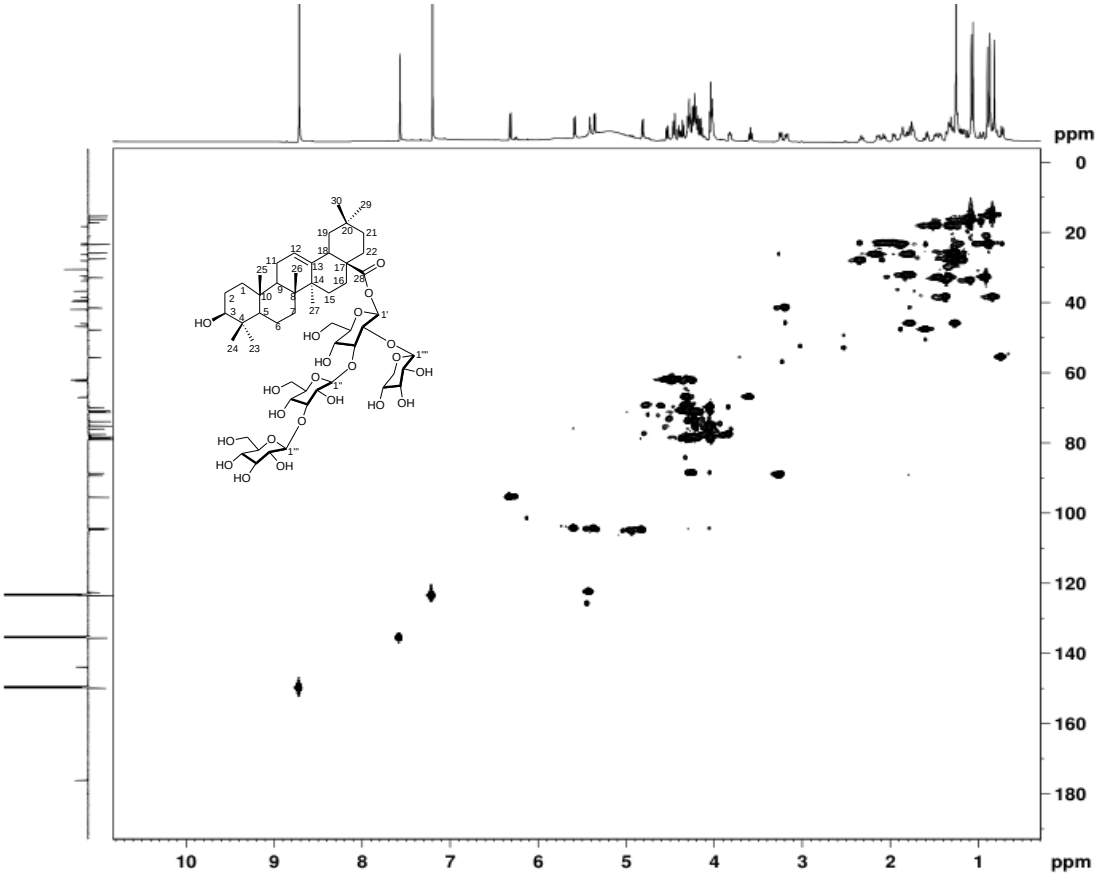

Figure S23. HMBC spectrum of the new compound **4**

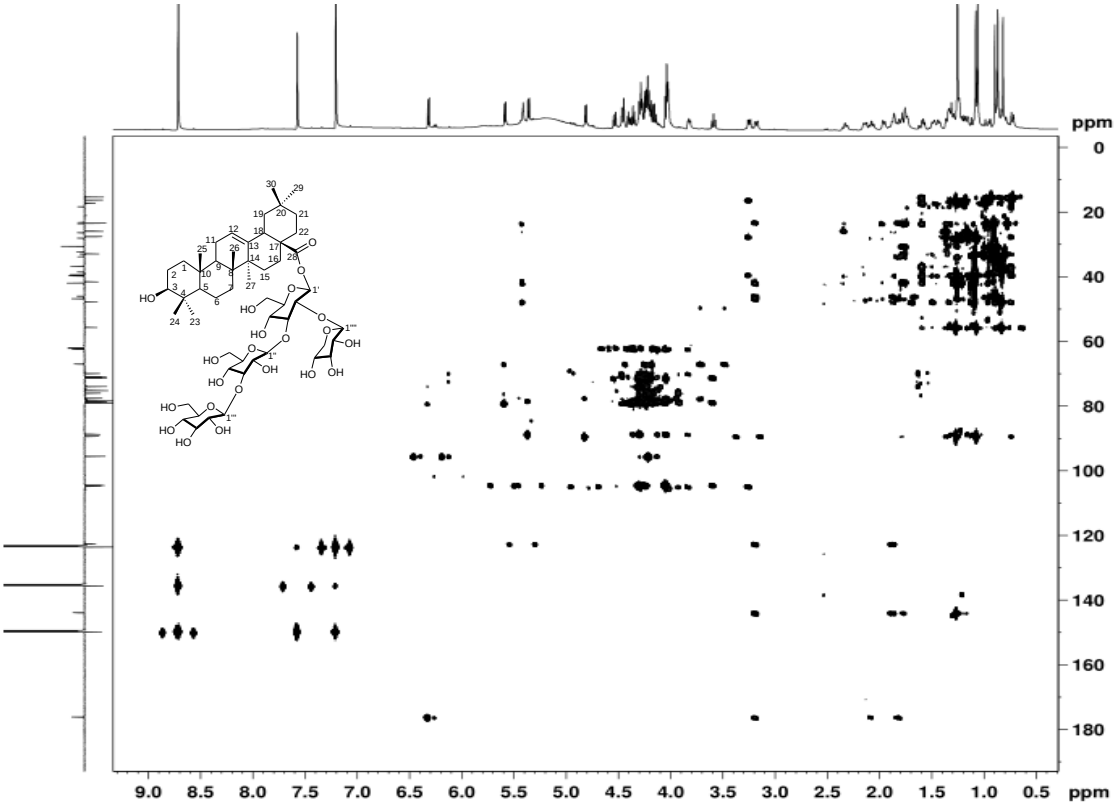

Figure S24. ^{1}H-^{1}H COSY spectrum of the new compound **4**

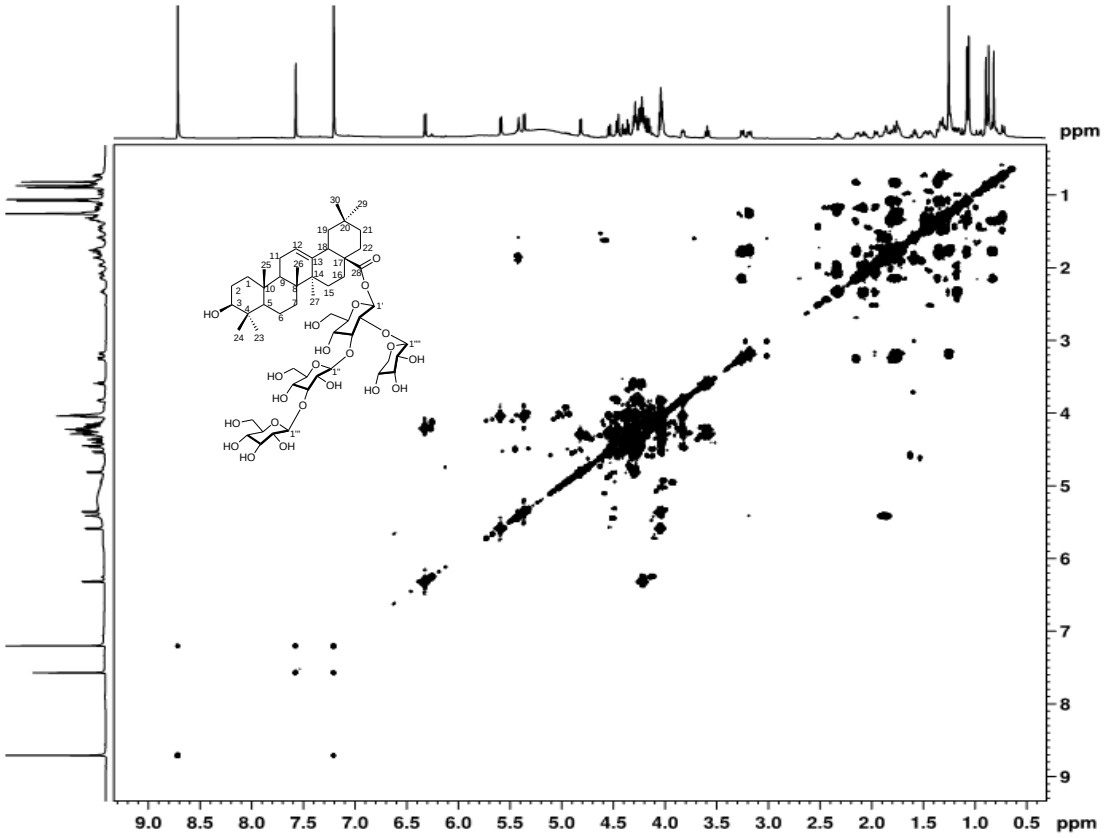

Figure S25. NOESY spectrum of the new compound **4**

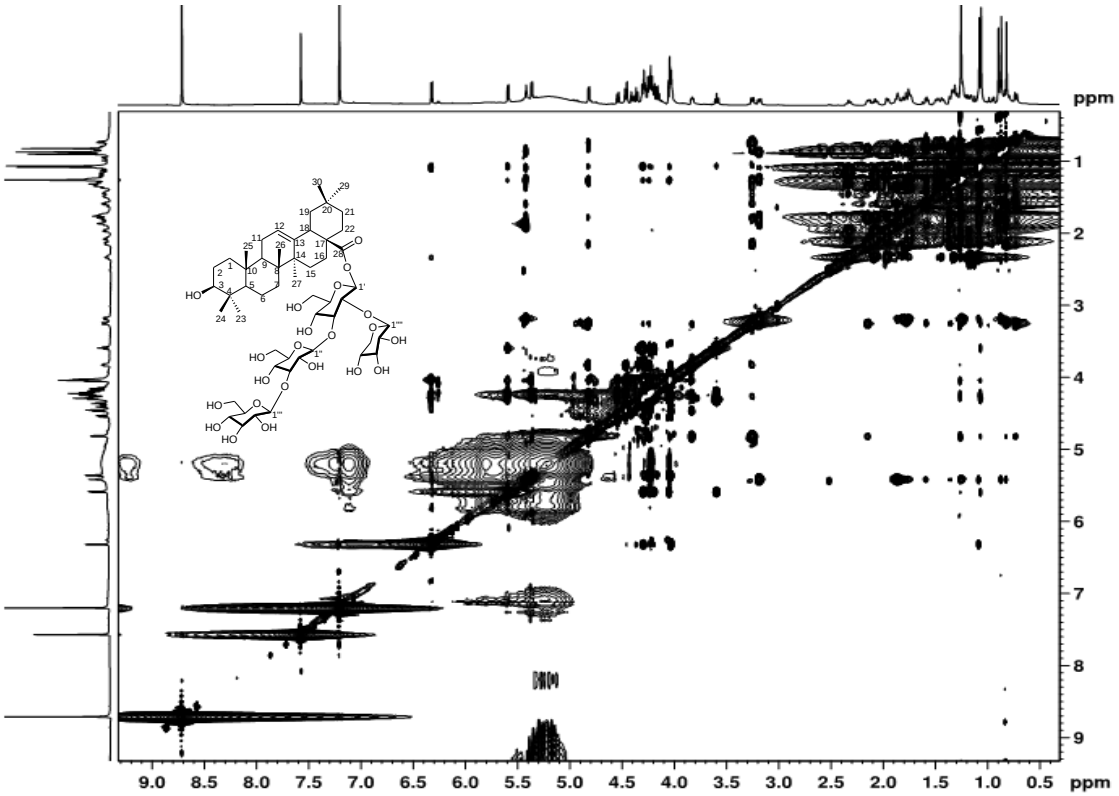

Figure S26. [1]H-NMR (600 MHz, C5D5N) spectrum of the new compound **5**

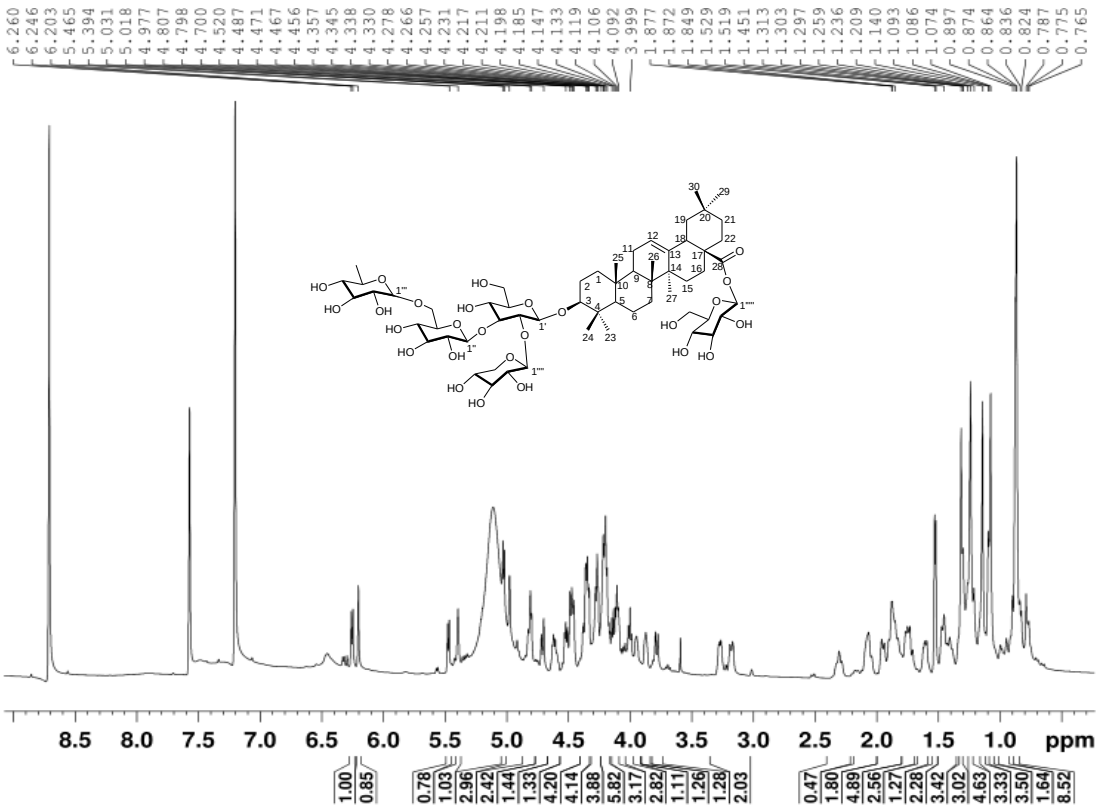

Figure S27. [13]C-APT (150 MHz, C5D5N) spectrum of the new compound **5**

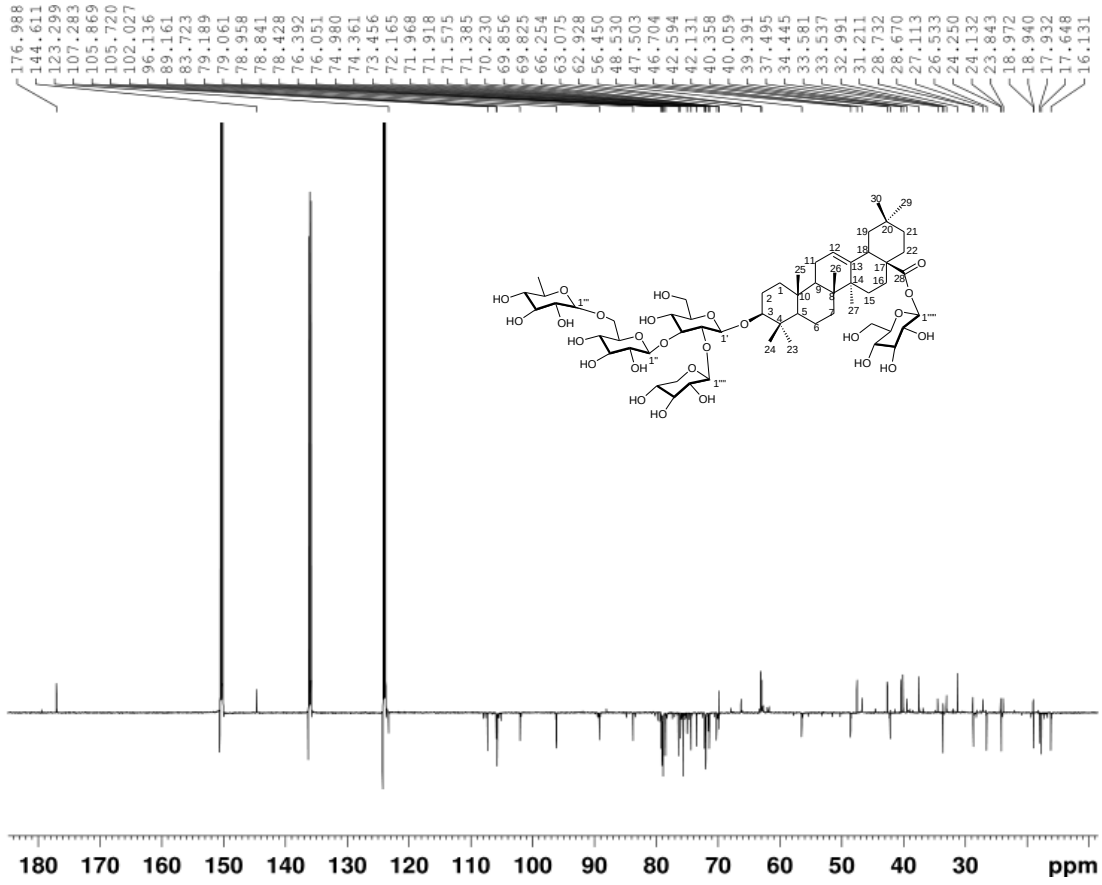

Figure S28. HSQC spectrum of the new compound **5**

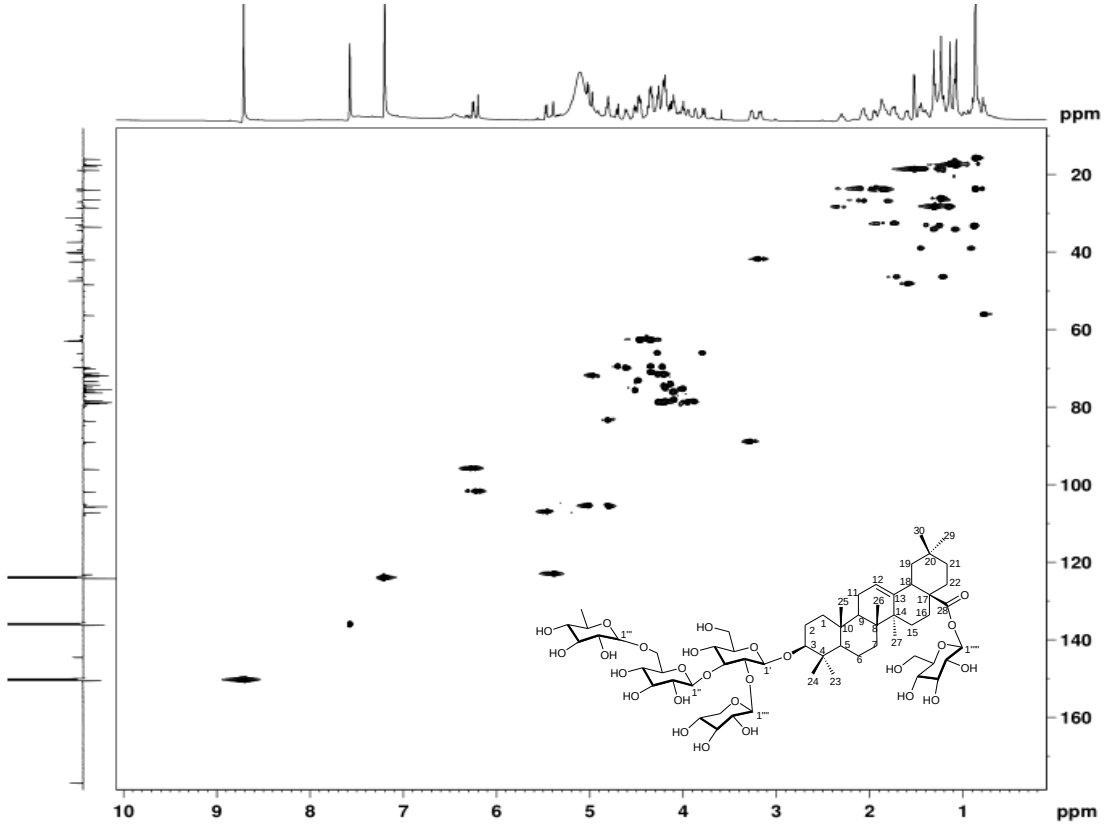

Figure S29. HMBC spectrum of the new compound **5**

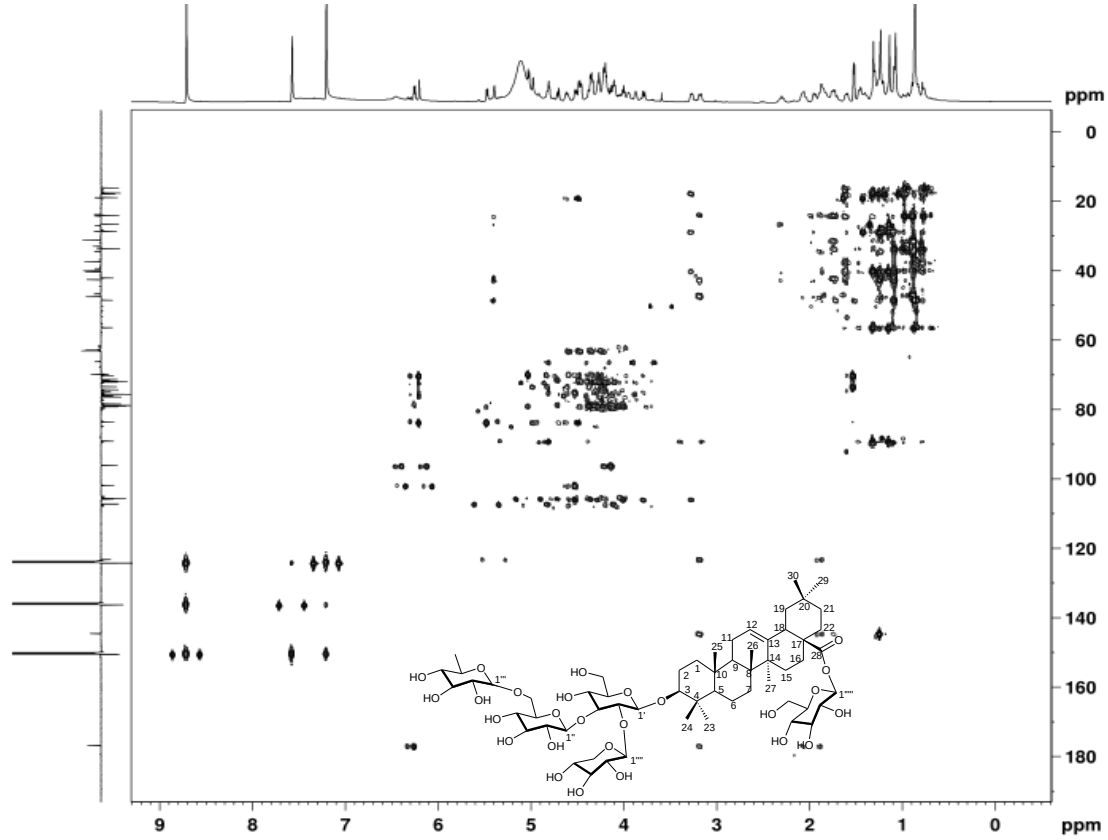

Figure S30. ^{1}H-^{1}H COSY spectrum of the new compound **5**

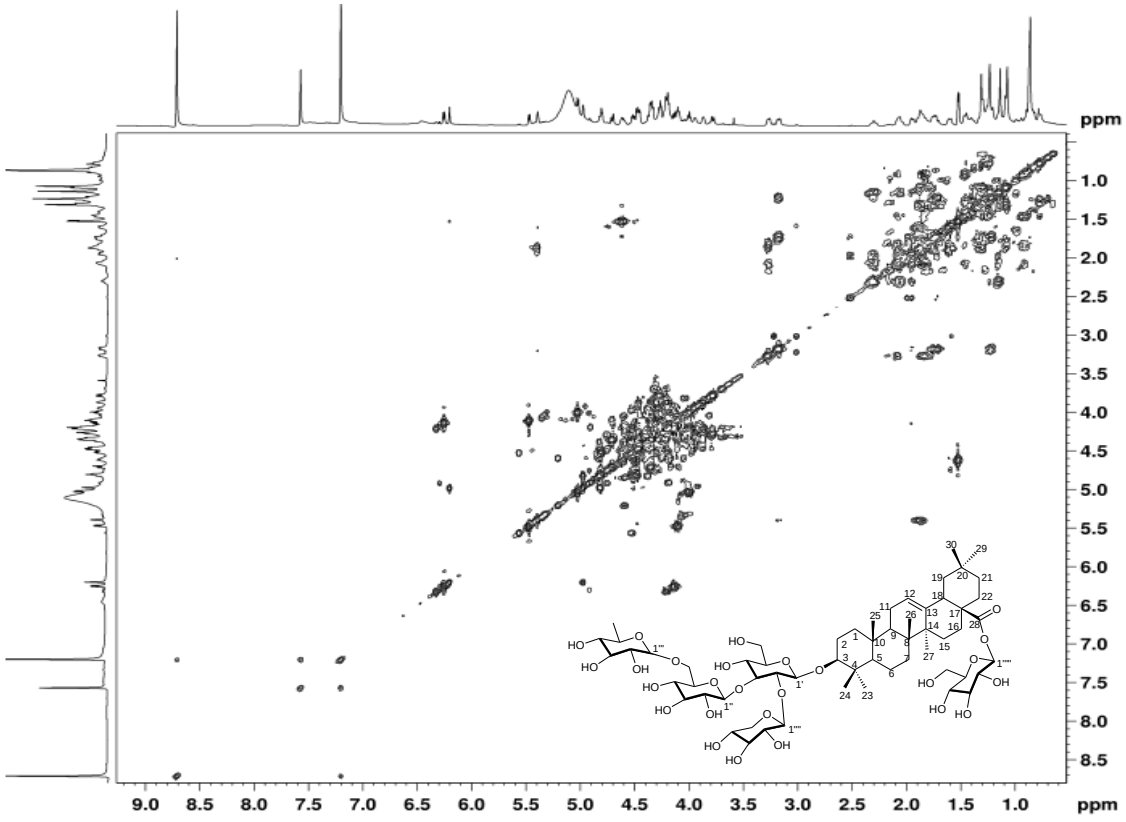

Figure S31. NOESY spectrum of the new compound **5**

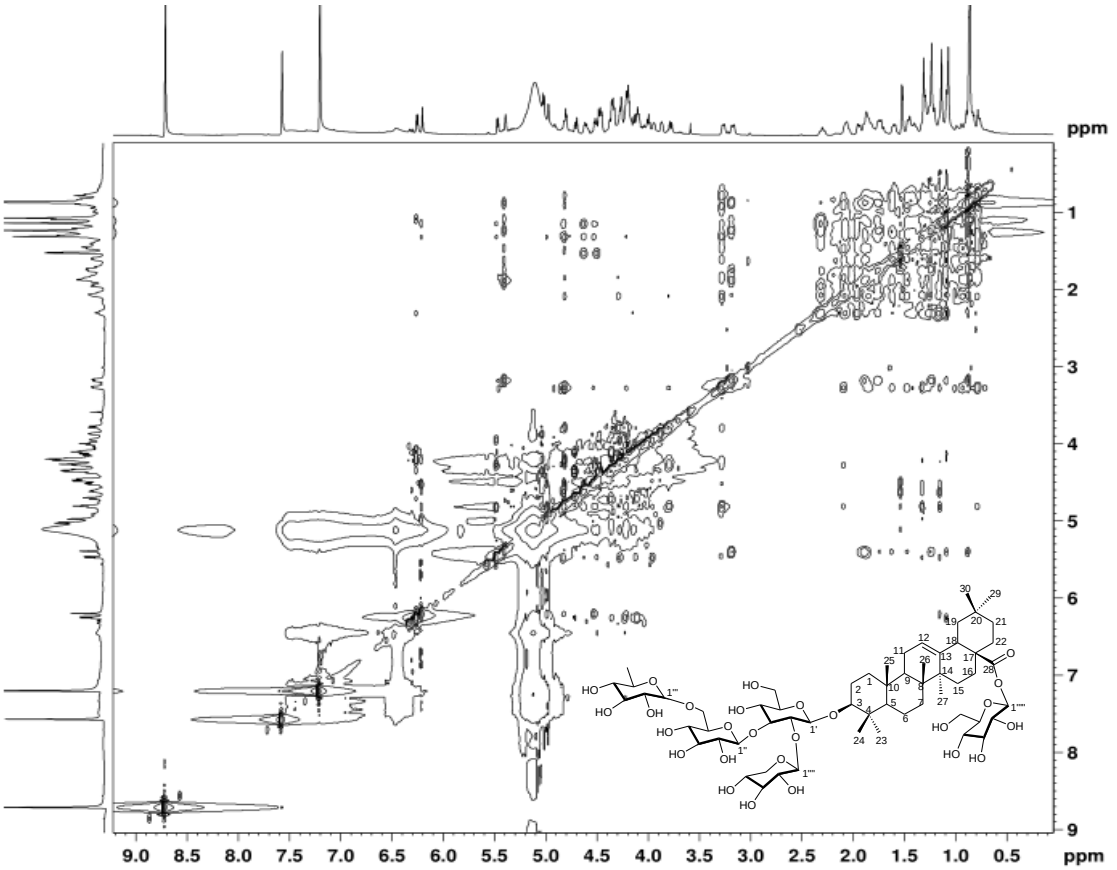

Figure S32. ^{1}H-NMR (600 MHz, C5D5N) spectrum of the new compound **6**

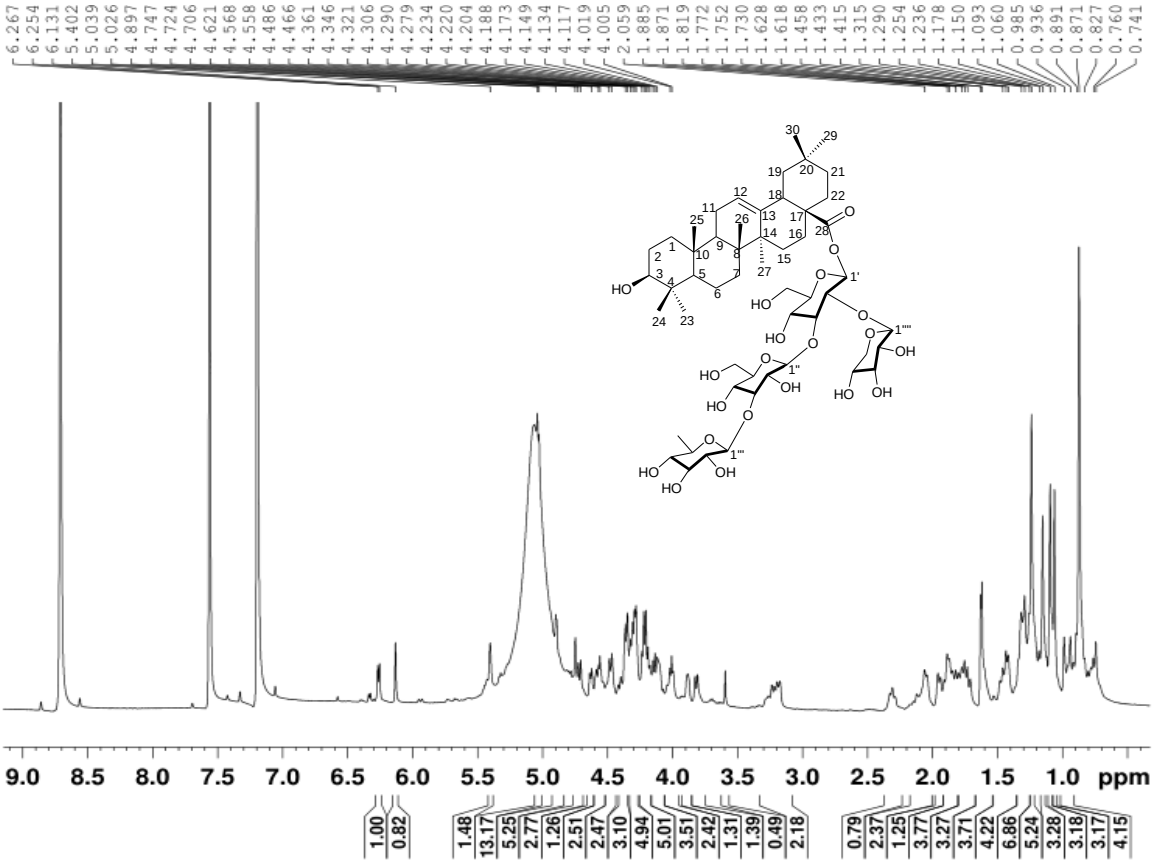

Figure S33. ^{13}C-APT (150 MHz, C5D5N) spectrum of the new compound **6**

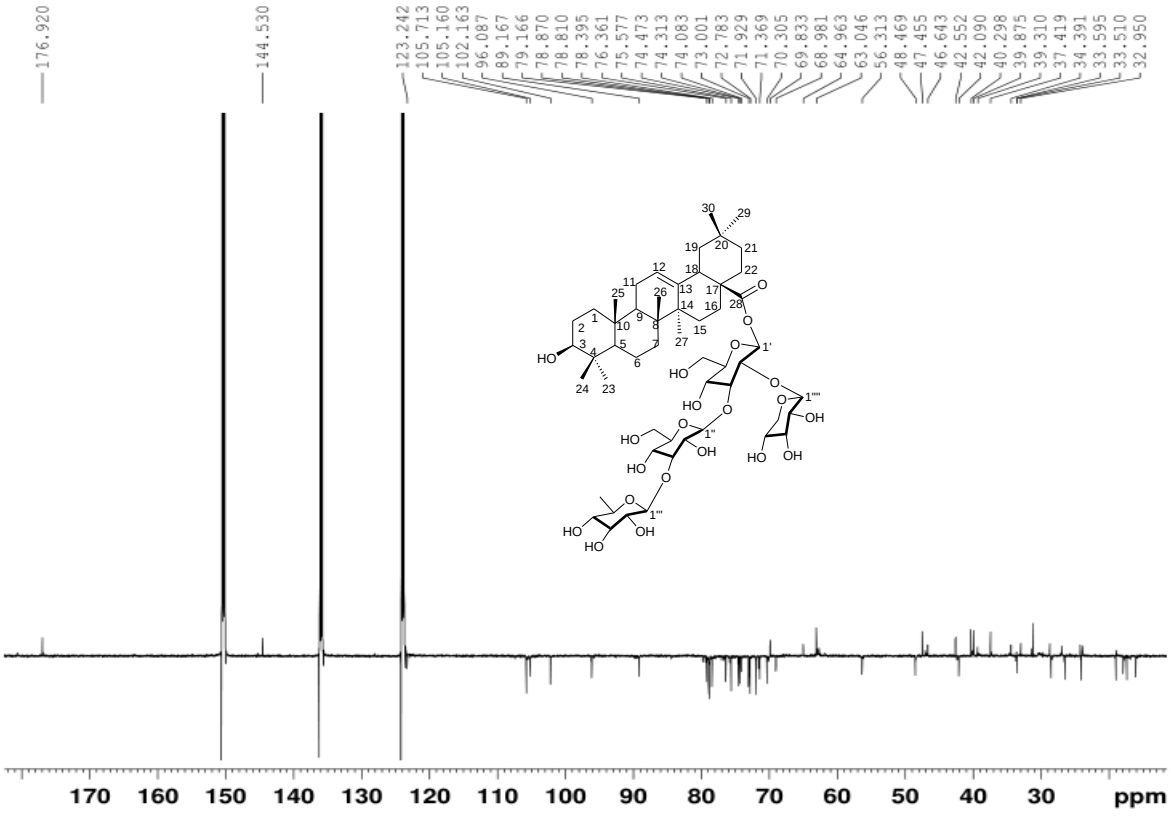

Figure S34. HSQC spectrum of the new compound **6**

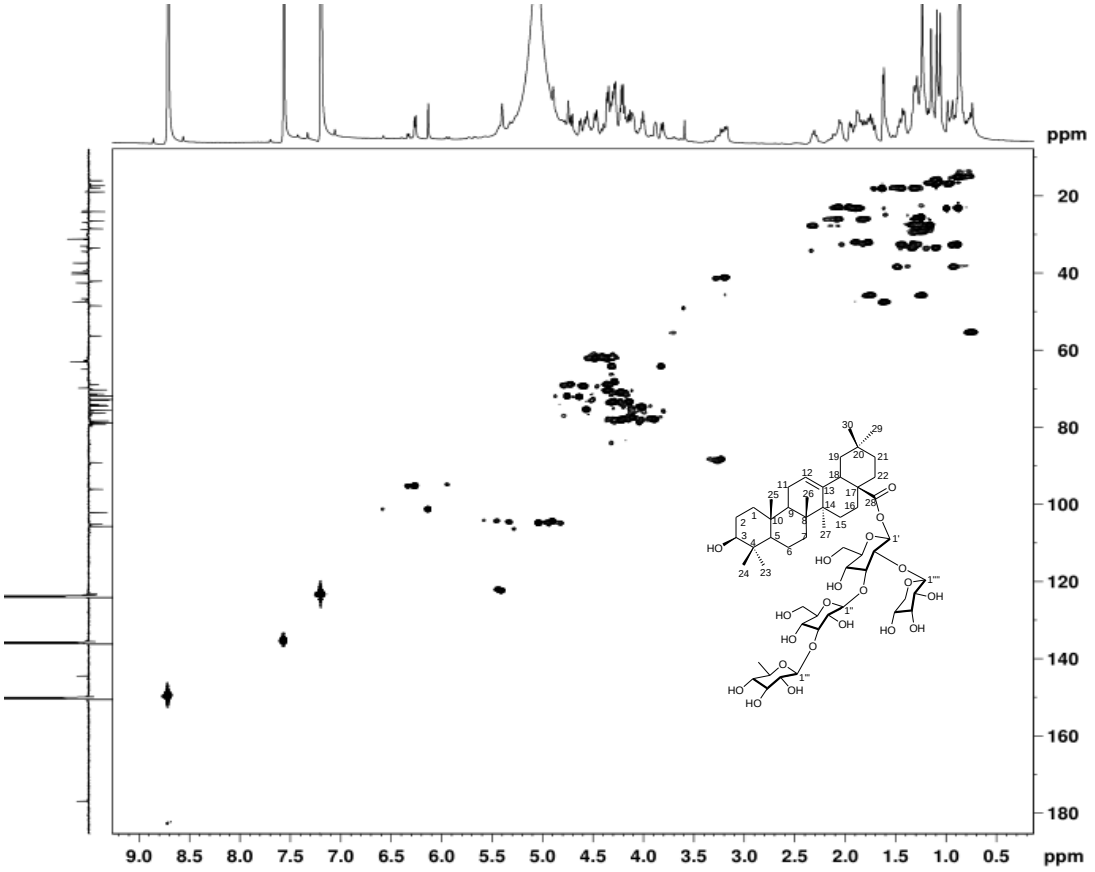

Figure S35. HMBC spectrum of the new compound **6**

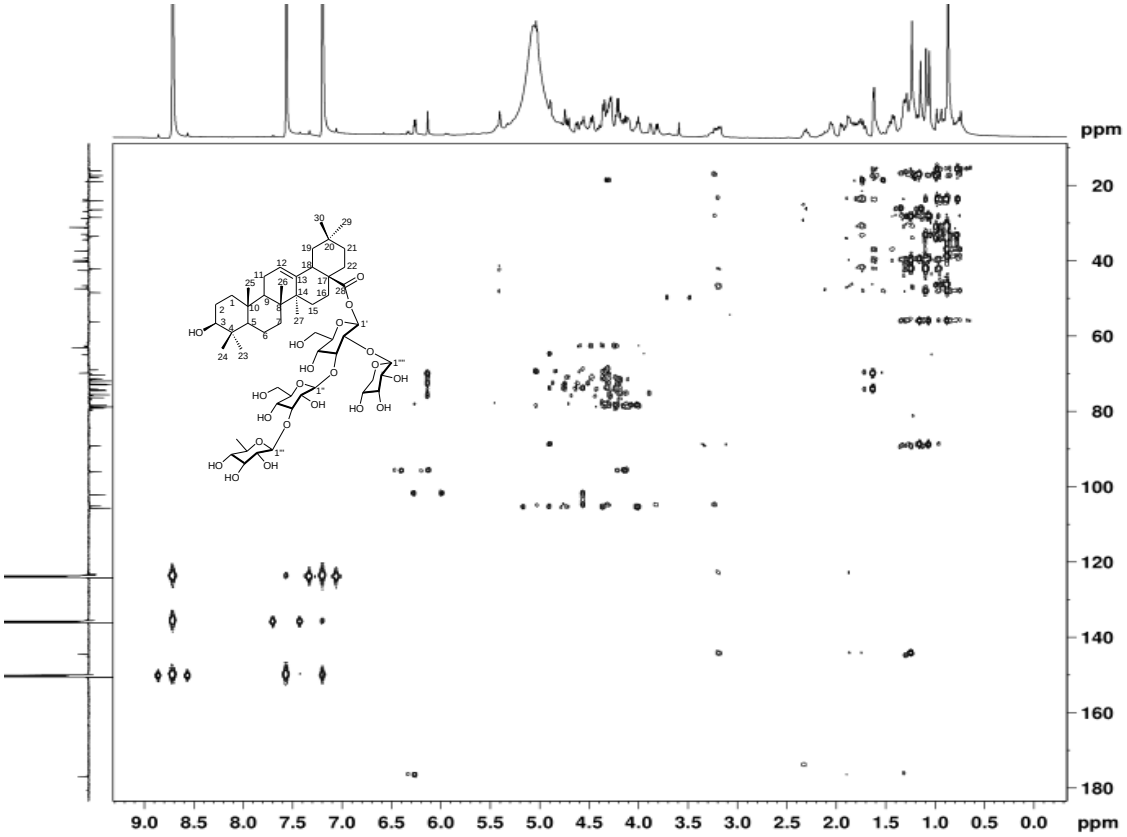

Figure S36. ^{1}H-^{1}H COSY spectrum of the new compound **6**

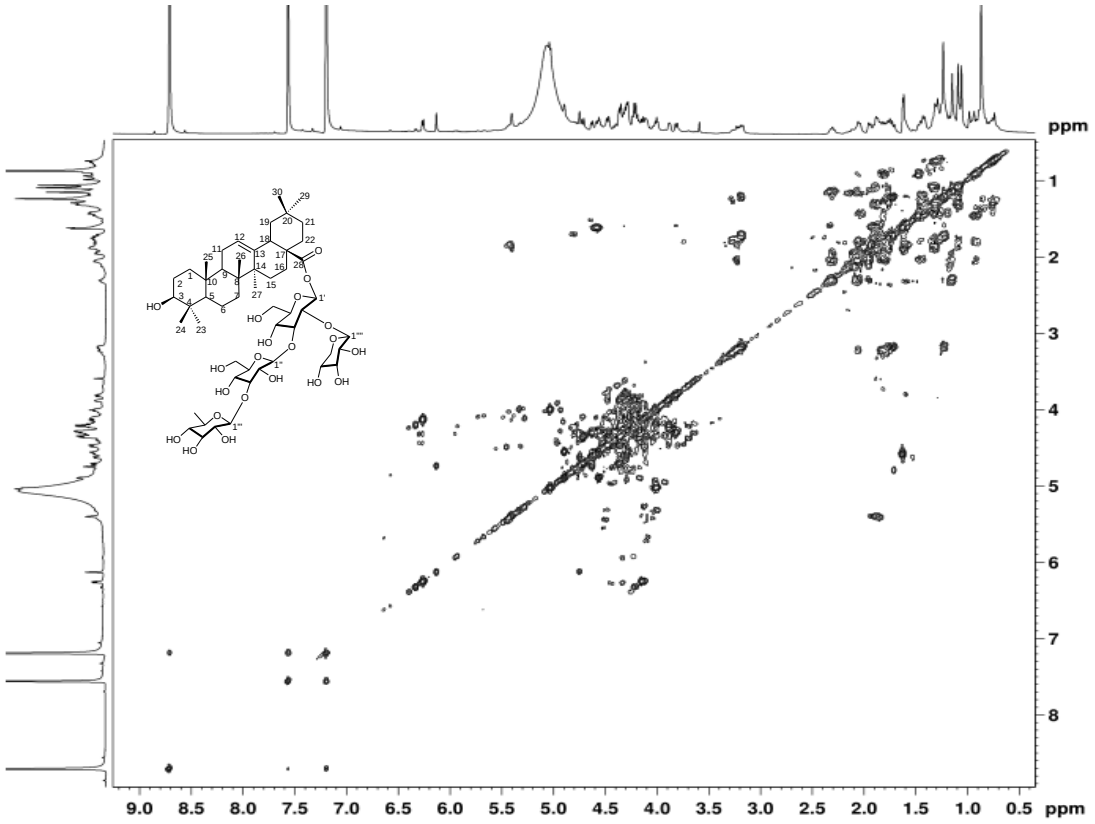

Figure S37. NOESY spectrum of the new compound **6**