Supporting Information

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Protein Tyrosine Phosphatase 1B Inhibitors from the Root Bark of *Pseudolarix amabilis* (Nelson) Rehd. (Pinaceae)

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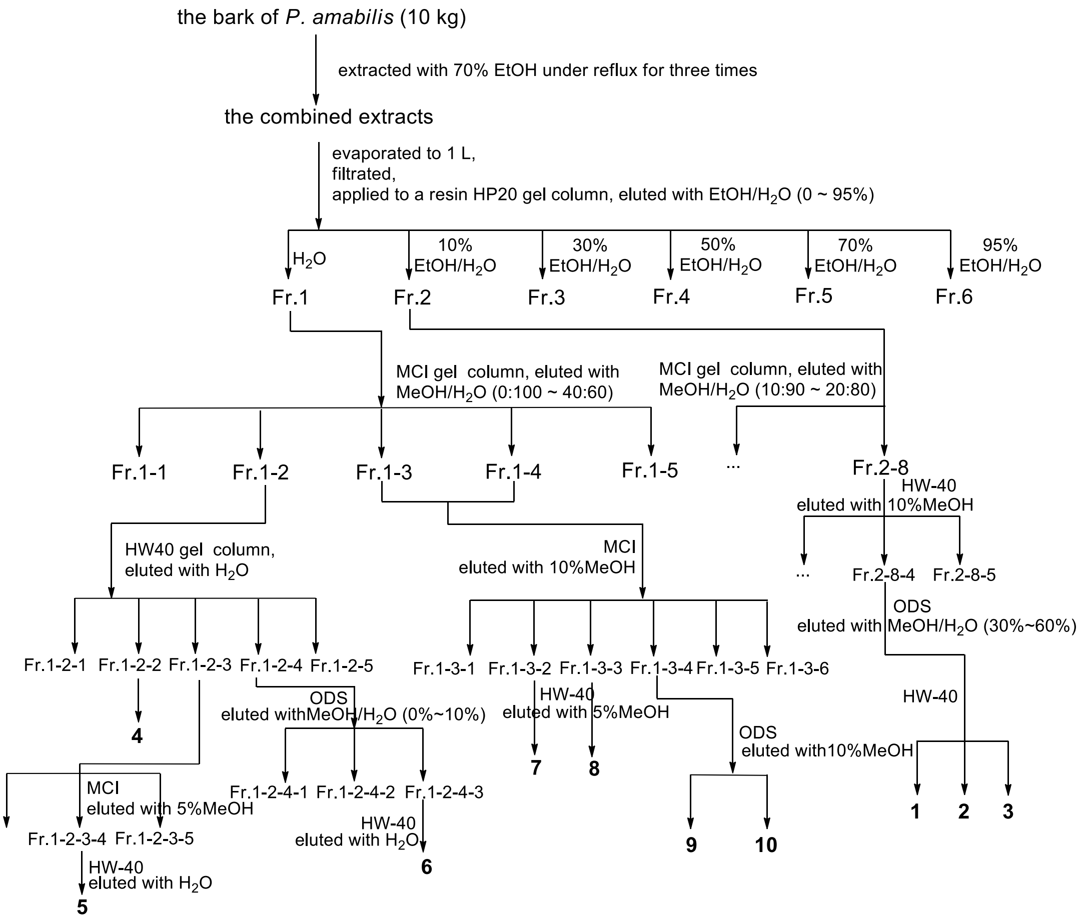
[†] These authors contributed equally to this work.

S1: The procedure of the extraction and isolation of the bark of *P. amabilis*

The bark of *P. amabilis* (10 kg) was extracted with 70% EtOH under reflux for three times. The combined extracts were evaporated to 1 L, filtrated and applied to a resin HP20 column, eluting with H_2O, 10% EtOH, 30% EtOH, 50% EtOH, 70% EtOH and 95% EtOH to give six fractions (Fr.1 – Fr.6). Fr.1 was subjected to column chromatography (CC) on MCI gel, eluting with gradient solvent system (MeOH-H_2O, 0:100 — 40:60) to yield five fractions (Fr.1-1 — Fr.1-5). Fr.1-2 was separated over HW-40 gel using H_2O as eluent to obtain eight fractions (Fr.1-2-1 — Fr.1-2-5). Fr.1-2-2 was purified by HW-40 gel repeatedly to afford **4** (8 mg). Fr.1-2-3 was subjected to MCI column eluting with 5%MeOH to yield five fractions (Fr.1-2-3-1 — Fr.1-2-3-5) and Fr.1-2-3-4 was purified by HW-40 gel repeatedly to afford **5** (12 mg). Fr.1-2-4 was subjected to ODS column eluting with 0 % — 10% MeOH to yield three fractions (Fr.1-2-4-1 — Fr.1-2-4-3). Fr.1-2-4-3 was purified by HW-40 gel to afford **6** (14 mg). Fr.1-3 and Fr.1-4 were combined and re-subjected to MCI column eluting with 10 % MeOH to yield six fractions (Fr.1-3-1 — Fr.1-3-6). Fr.1-3-2 and Fr.1-3-3 was purified by HW-40 gel eluting with 5%MeOH to afford **7** (8 mg) and **8** (36 mg), respectively. Fr.1-3-4 was purified by ODS gel eluting with 10%MeOH to afford **9** (40 mg) and **10** (6 mg). Fr.2 was subject to MCI column eluting with 10% — 20% MeOH to yield eight fractions (Fr.2-1 — Fr.2-8). Fr.2-8 was purified by HW-40 gel eluting with 10% MeOH to obtain five sub-fractions (Fr.2-8-1 — Fr.2-8-5). Fr.2-8-4 was purified by ODS gel eluting with 30% — 60% MeOH and HW-40 gel to afford **1** (14 mg), **2** (22 mg), and **3** (12 mg).



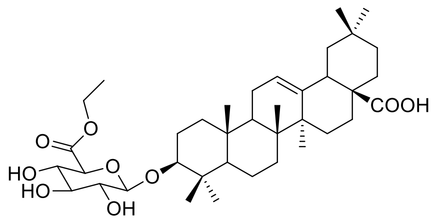


Figure S1: The Chemical Structure of **1**

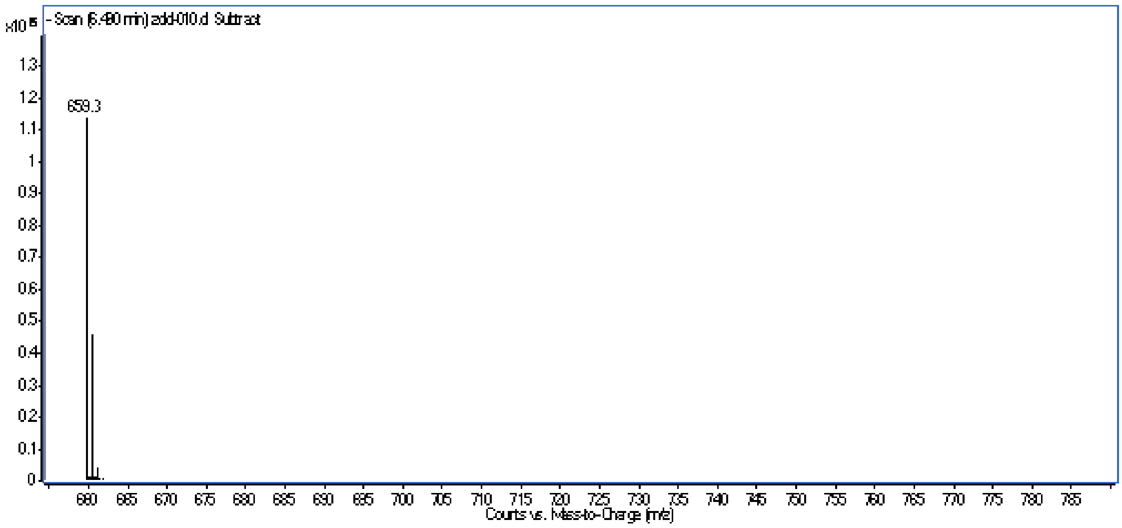


Figure S2: The ESIMS spectrum of compound **1**

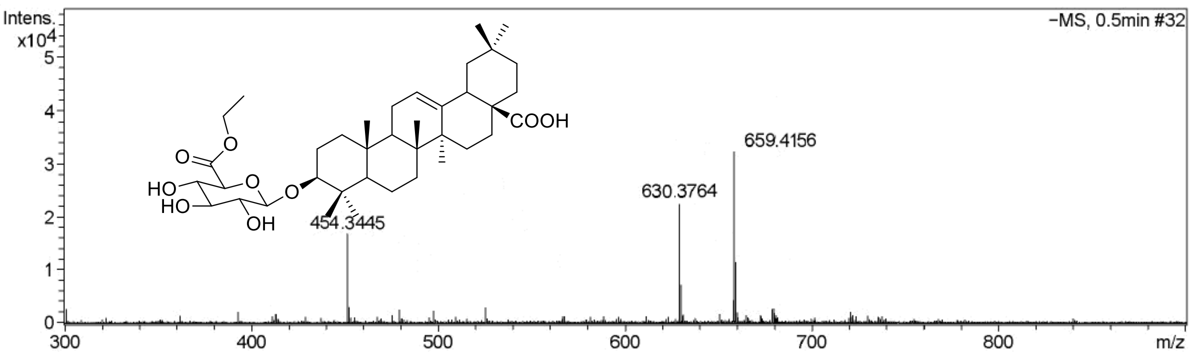


Figure S3: The HRESIMS spectrum of compound **1**

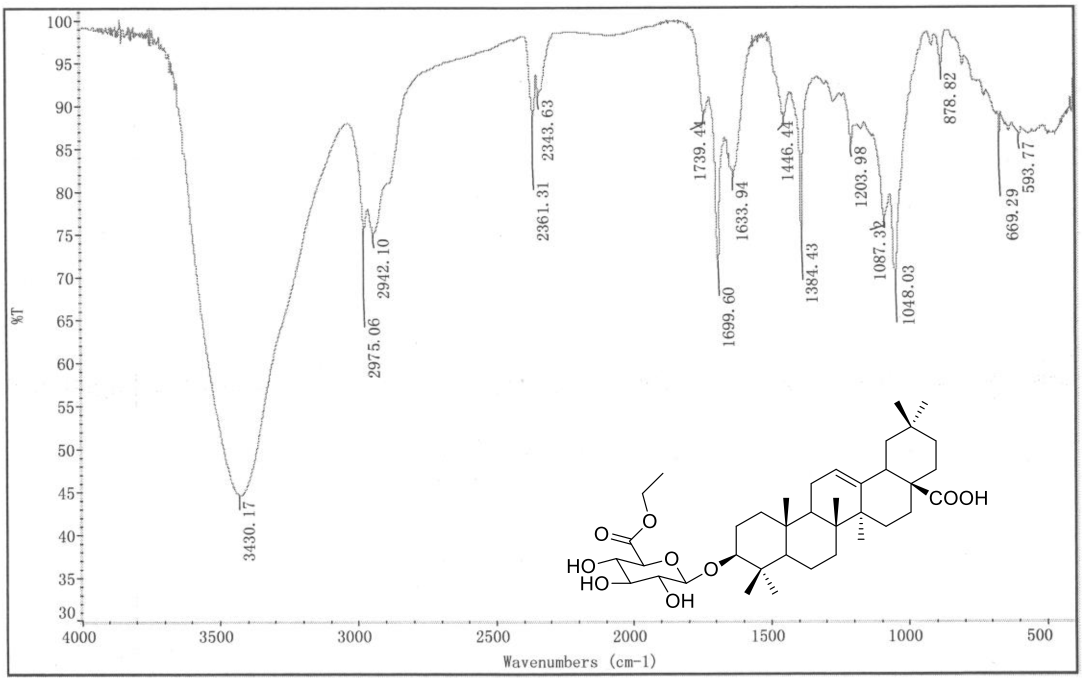


Figure S4: The IR spectrum of **1** (in KBr)

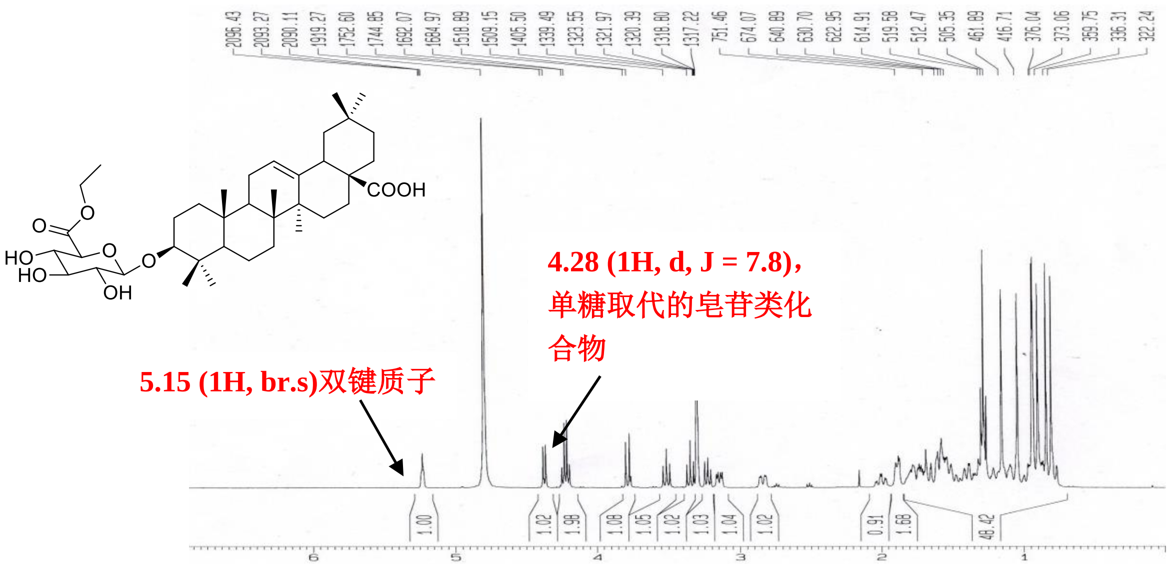


Figure S5: The ^{1}H-NMR spectrum of compound **1**

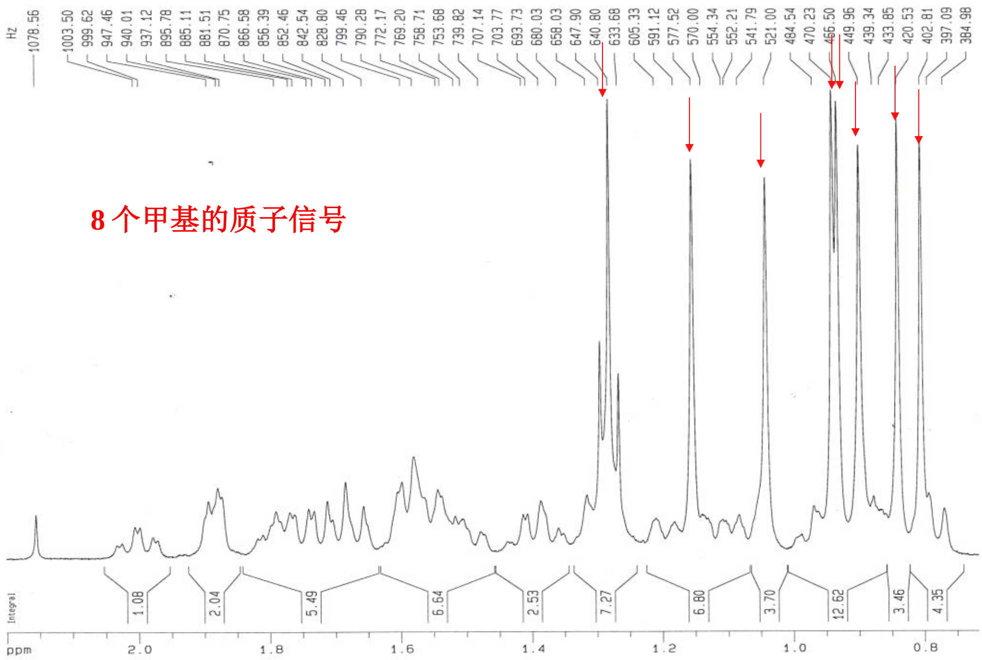


Figure S6: Expansion of the ^{1}H-NMR spectrum of compound **1**

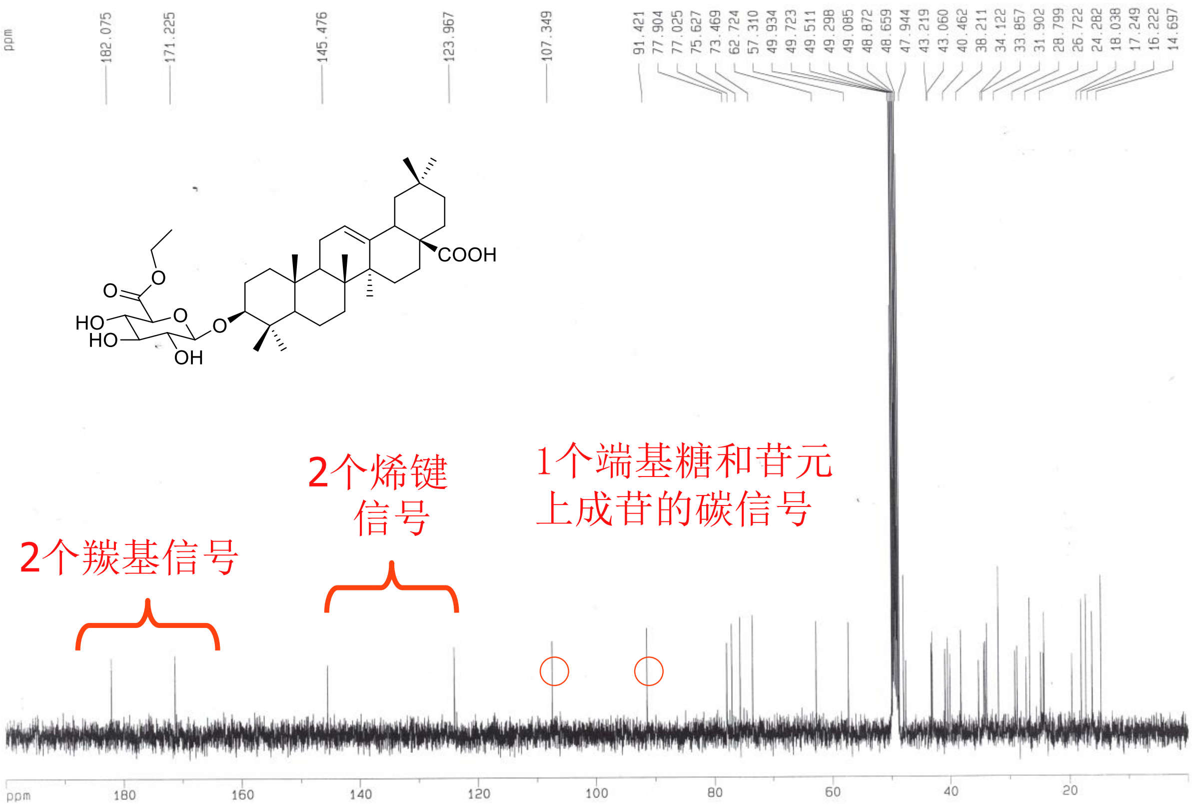


Figure S7: The ^{13}C-NMR spectrum of compound **1**

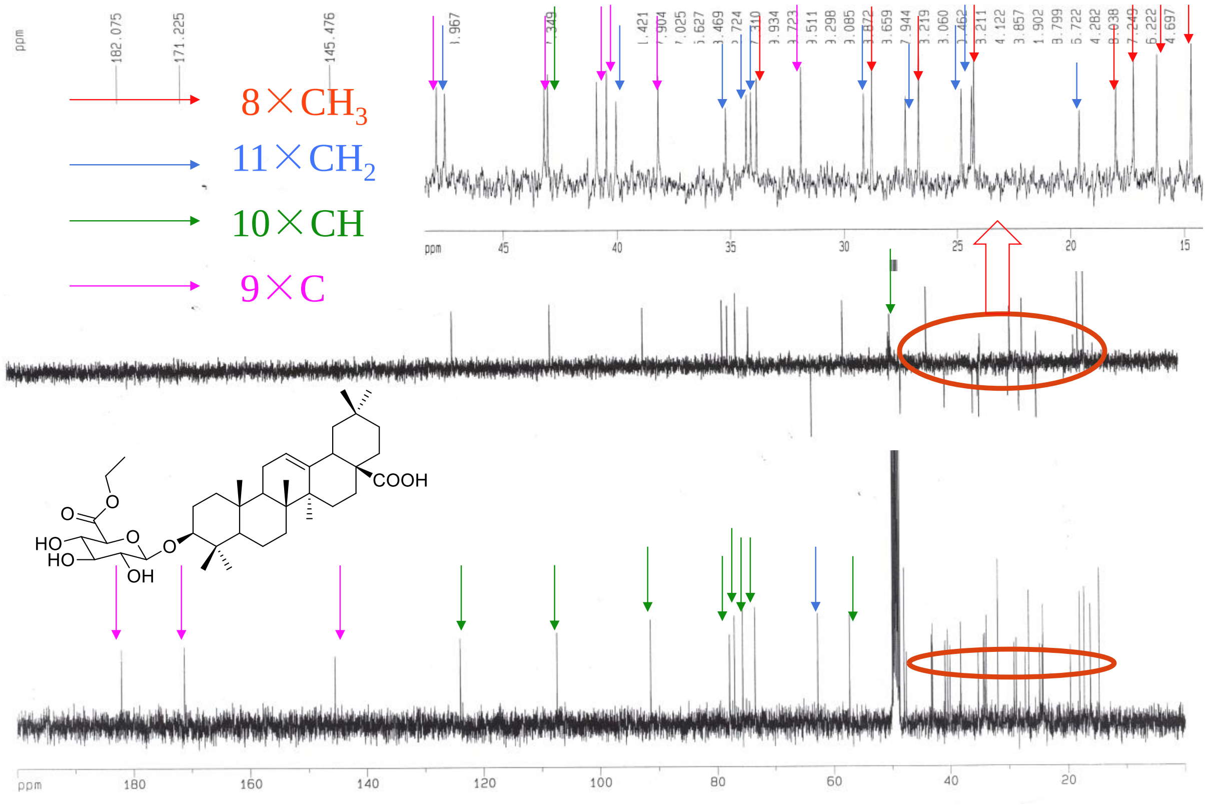


Figure S8: The DEPT spectrum of compound **1**

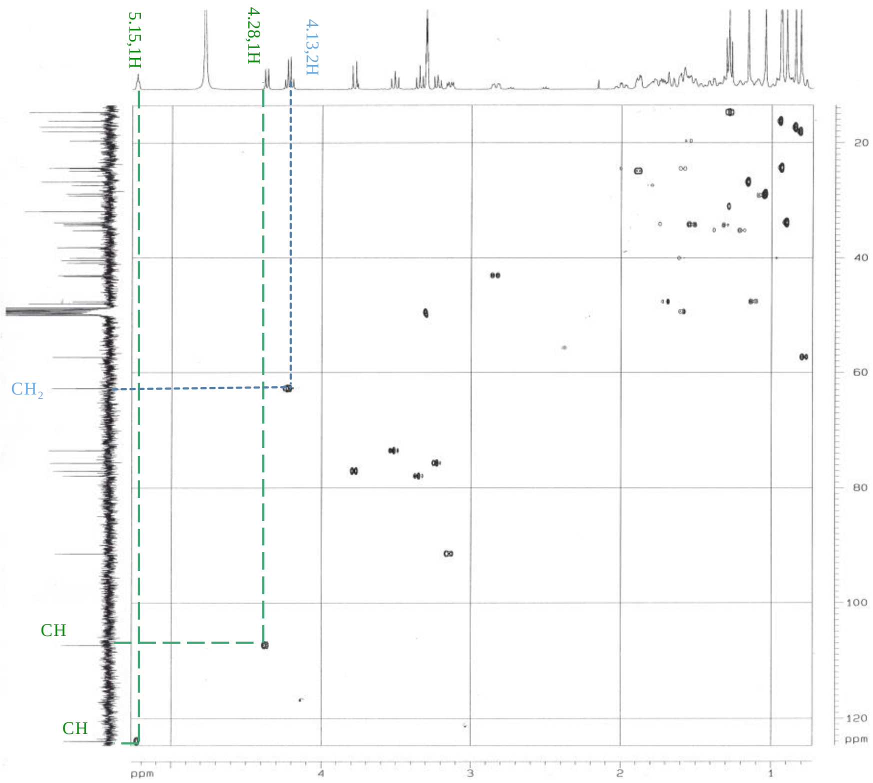


Figure S9: The HSQC spectrum of compound **1**

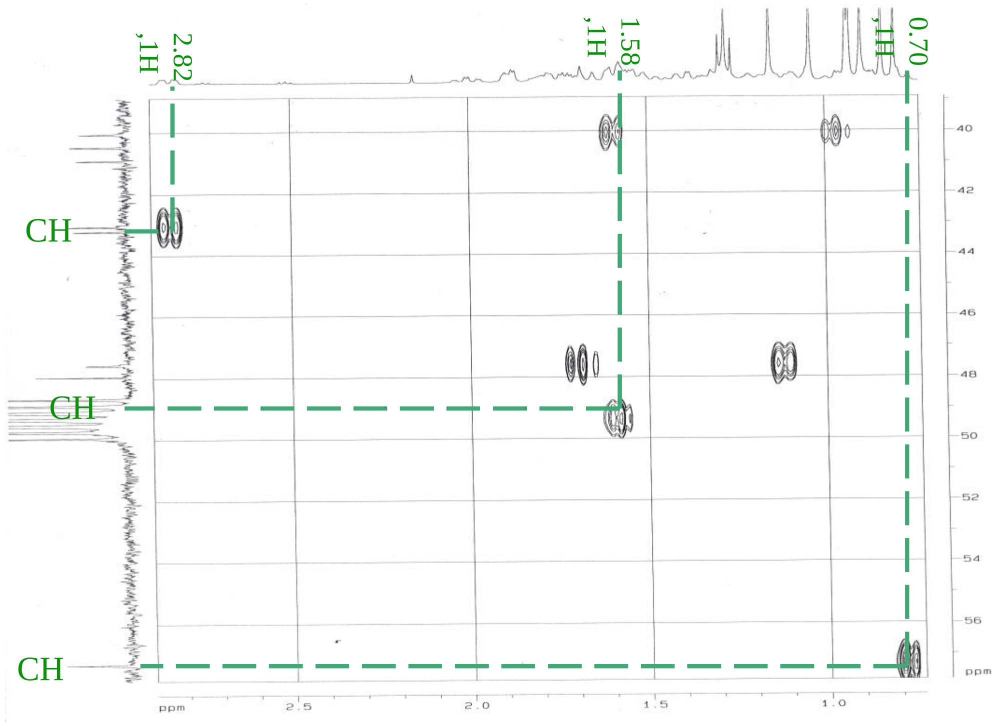


Figure S10: Expansion of the HSQC spectrum of of compound **1**

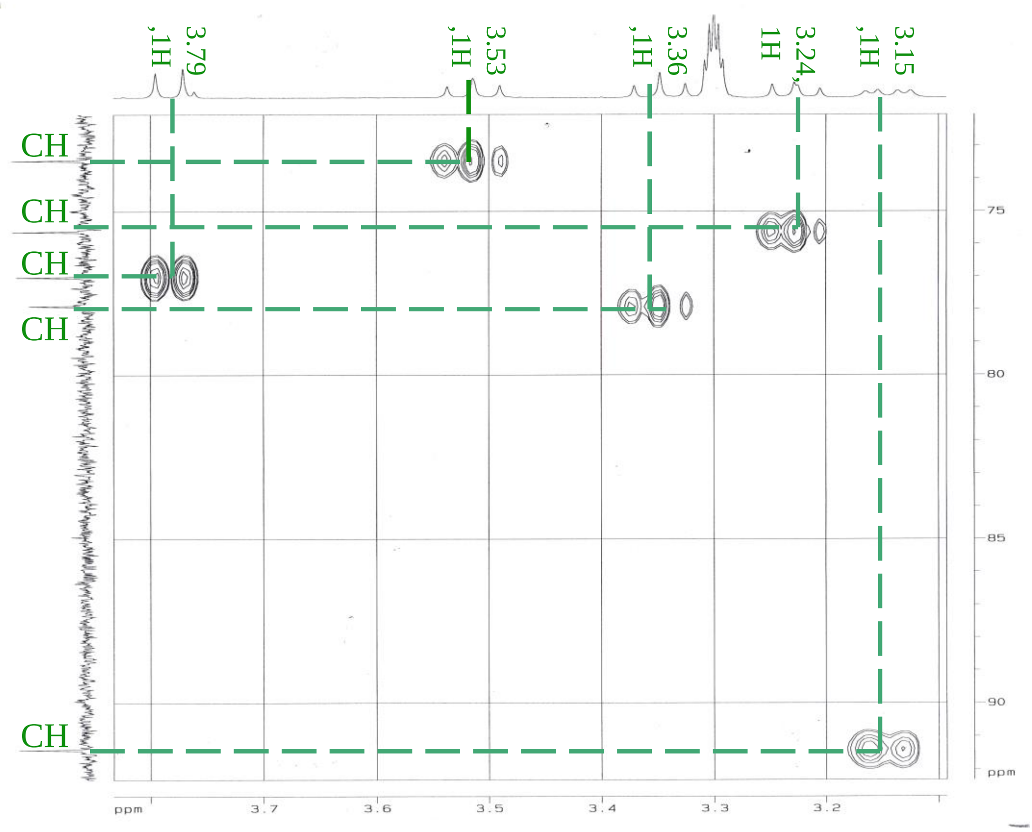


Figure S11: Expansion of the HSQC spectrum of of compound **1**

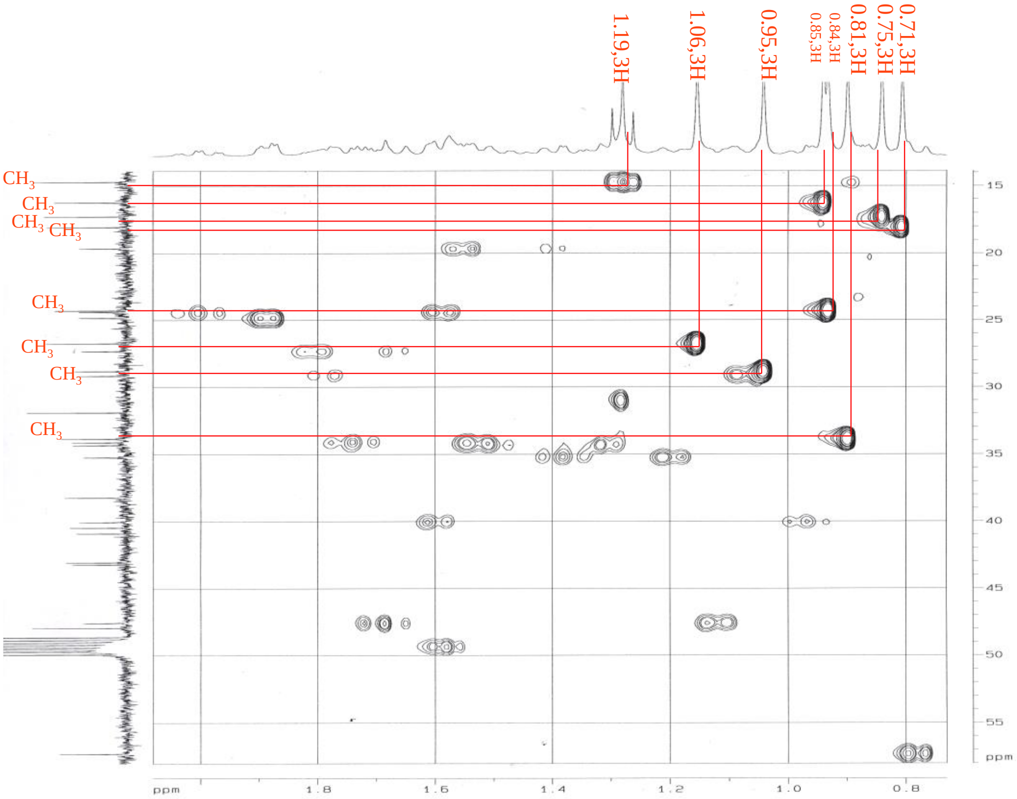


Figure S12: Expansion of the HSQC spectrum of of compound **1**

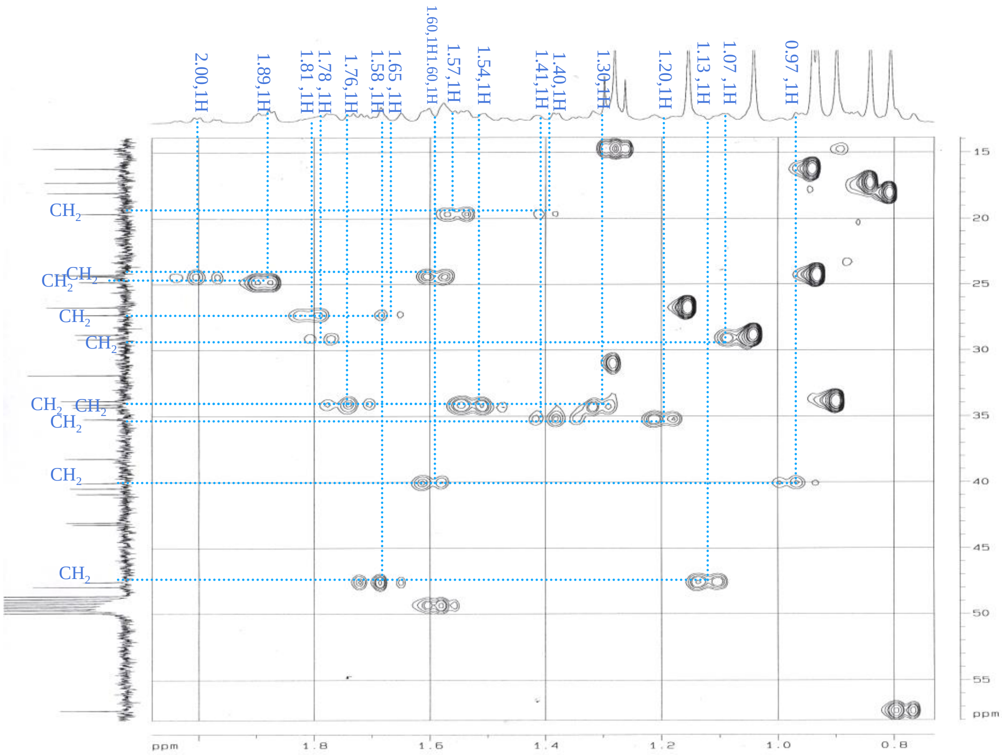


Figure S13: Expansion of the HSQC Spectrum of of compound **1**

Table S1. The HMBC assignments of **1**

No. [c]	δ_C [a]	δ_H [b]
1	40.0 (t)	0.97 (H-1a, *ca.*) 1.60 (H-1b, *ca.*)
2	27.3 (t)	1.65 (H-2a, *ca.*) 1.81 (H-2b, *ca.*)
3	91.4 (d)	3.15 (dd, 11.7, 4.4)
4	40.5 (s)	——
5	57.3 (d)	0.70 (d, 12.0)
6	19.6 (t)	1.57 (H-6a, *ca.*) 1.40 (H-6b, *ca.*)
7	34.3 (t)	1.30 (*ca.*)
8	40.9 (s)	——
9	49.0 (d)	1.58 (*ca.*)
10	38.2 (s)	——
11	24.8 (t)	1.89 (*ca.*)
12	124.0 (d)	5.15 (br.s)
13	145.5 (s)	——
14	43.2 (s)	——
15	29.2 (t)	1.07 (H-15a, *ca.*) 1.78 (H-15b, *ca.*)
16	24.4 (t)	1.60 (H-16a, *ca.*) 2.00 (H-16b, *ca.*)
17	47.9 (s)	——
18	43.1 (d)	2.82 (dd, 13.5, 4.2)
19	47.6 (t)	1.13 (H-19a, *ca.*) 1.58 (H-19b, *ca.*)
20	32.0 (s)	——
21	35.2 (t)	1.20 (H-21a, *ca.*) 1.41 (H-21b, *ca.*)
22	34.1 (t)	1.54 (H-21a, *ca.*) 1.76 (H-21b, ca.)
23	28.8 (q)	0.95 (s)
24	17.2 (q)	0.75 (s)
25	16.2 (q)	0.85 (s)
26	18.0 (q)	0.71 (s)
27	26.7 (q)	1.06 (s)
28	182.1 (s)	——
29	33.9 (q)	0.81 (s)
30	24.3 (q)	0.84 (s)
GlcA-1′	107.4 (d)	4.28 (d, 7.8)
2′	75.6 (d)	3.24 (ca.)
3′	77.9 (d)	3.36 (ca.)
4′	73.5 (d)	3.53 (ca.)
5′	77.0 (d)	3.79 (ca.)
6′	171.2 (s)	——
$\underline{CH_2}CH_3$	62.7 (t)	4.13 (t, 7.1)
$CH_2\underline{CH_3}$	14.7 (q)	1.19 (q, 7.1)

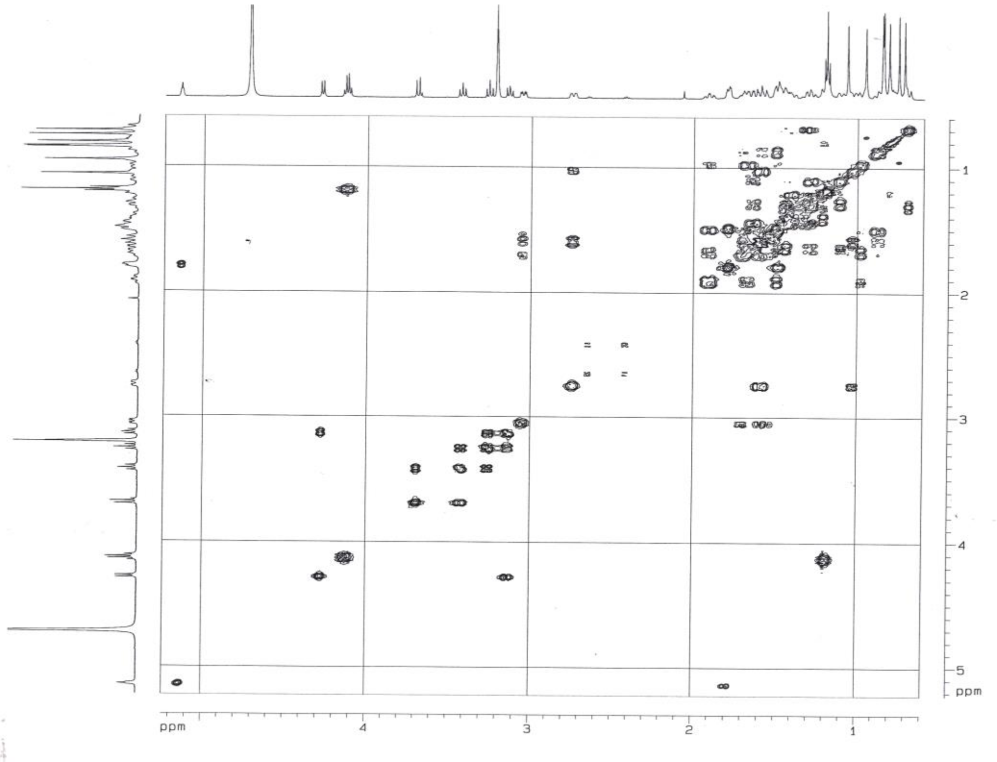


Figure S14: The ^{1}H-^{1}H COSY spectrum of compound **1**

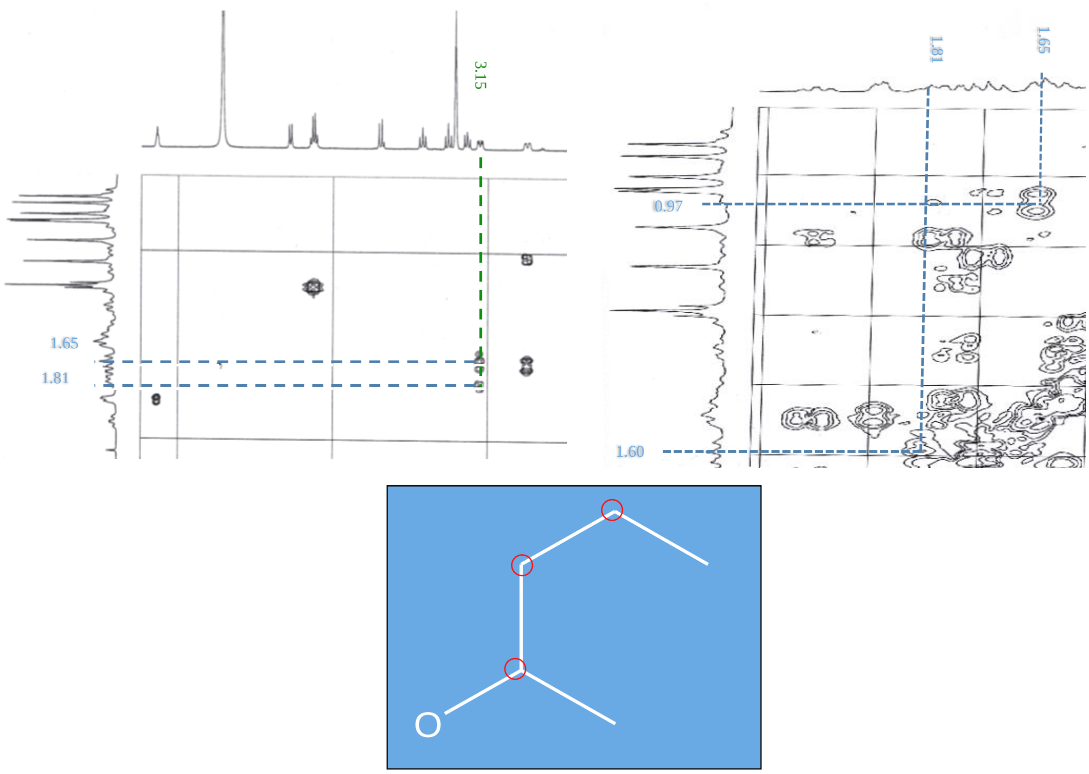


Figure S15: Expansion of the ^{1}H-^{1}H COSY spectrum of compound **1**

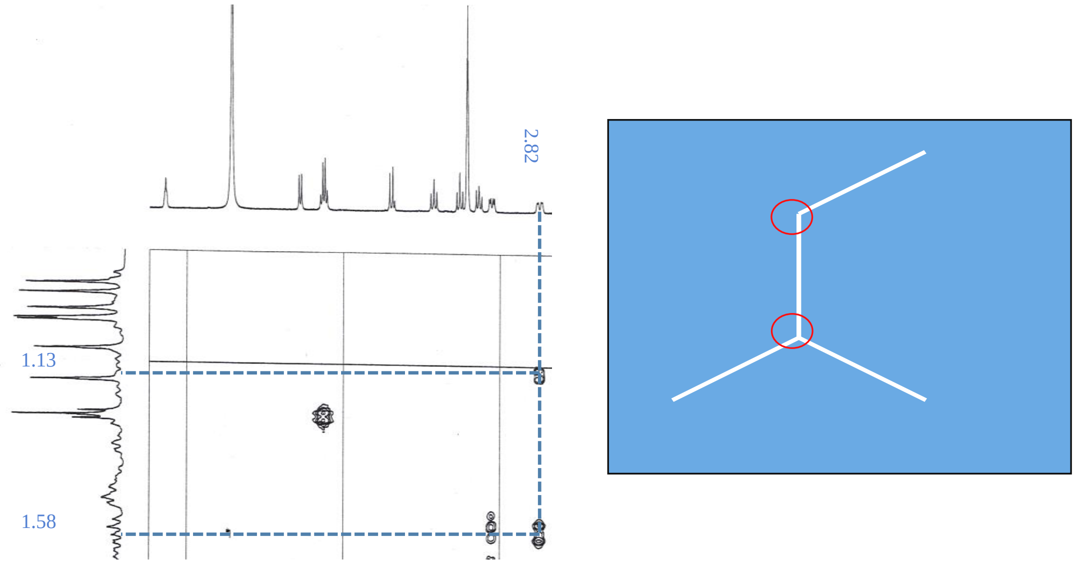


Figure S16: Expansion of the ^{1}H-^{1}H COSY spectrum of compound **1**

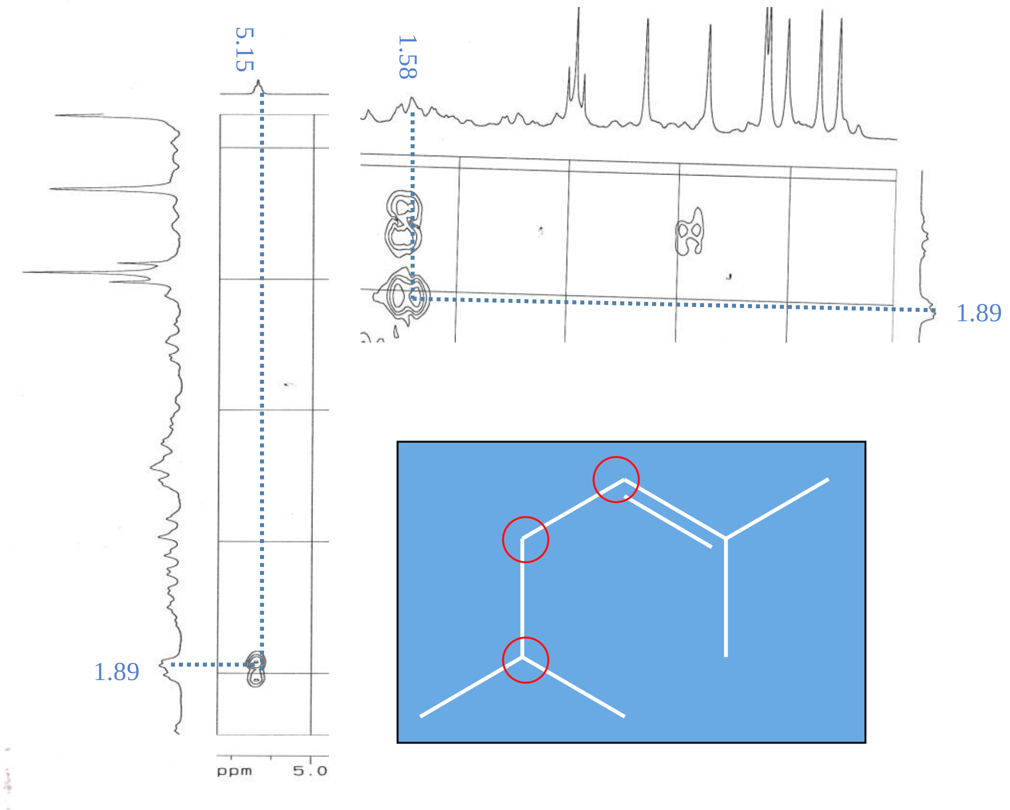


Figure S17: Expansion of the ^{1}H-^{1}H COSY spectrum of compound **1**

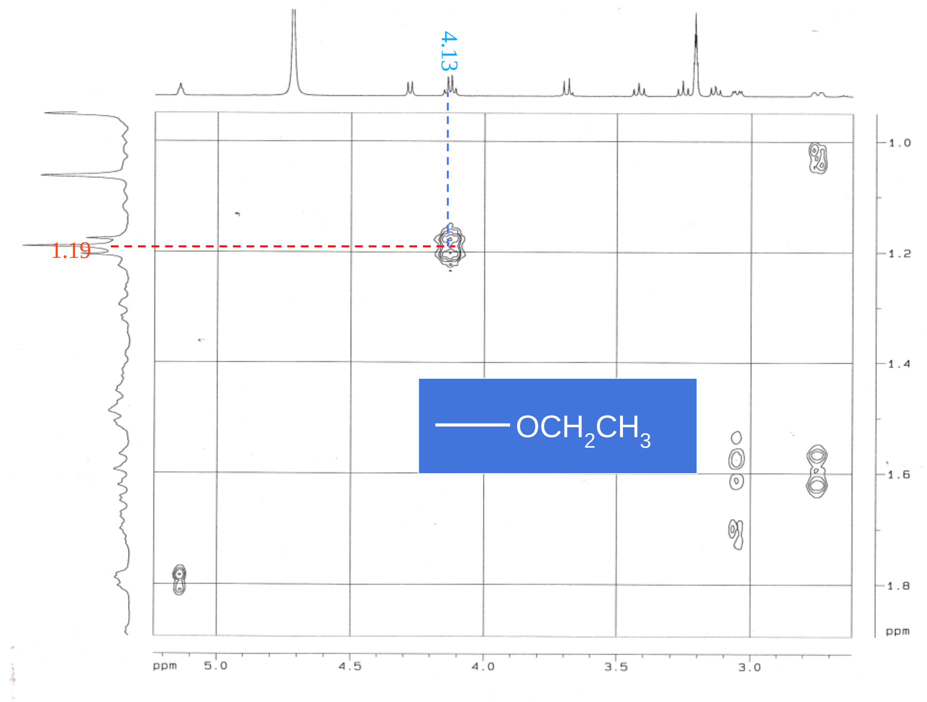


Figure S18: Expansion of the ^{1}H-^{1}H COSY spectrum of compound **1**

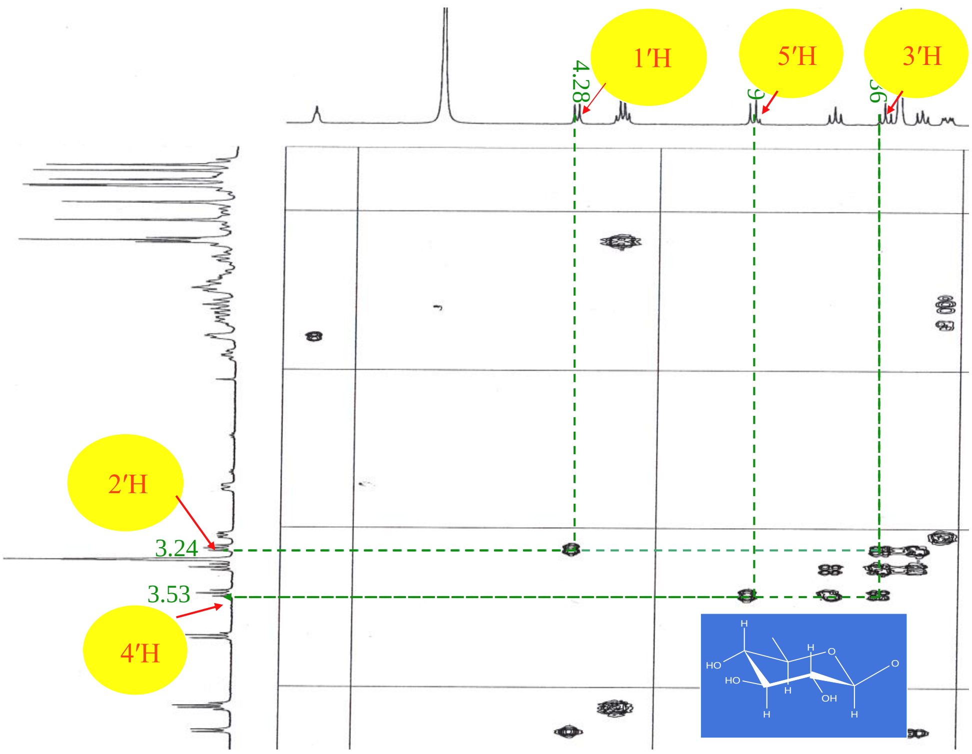


Figure S19: Expansion of the ^{1}H-^{1}H COSY spectrum of compound **1**

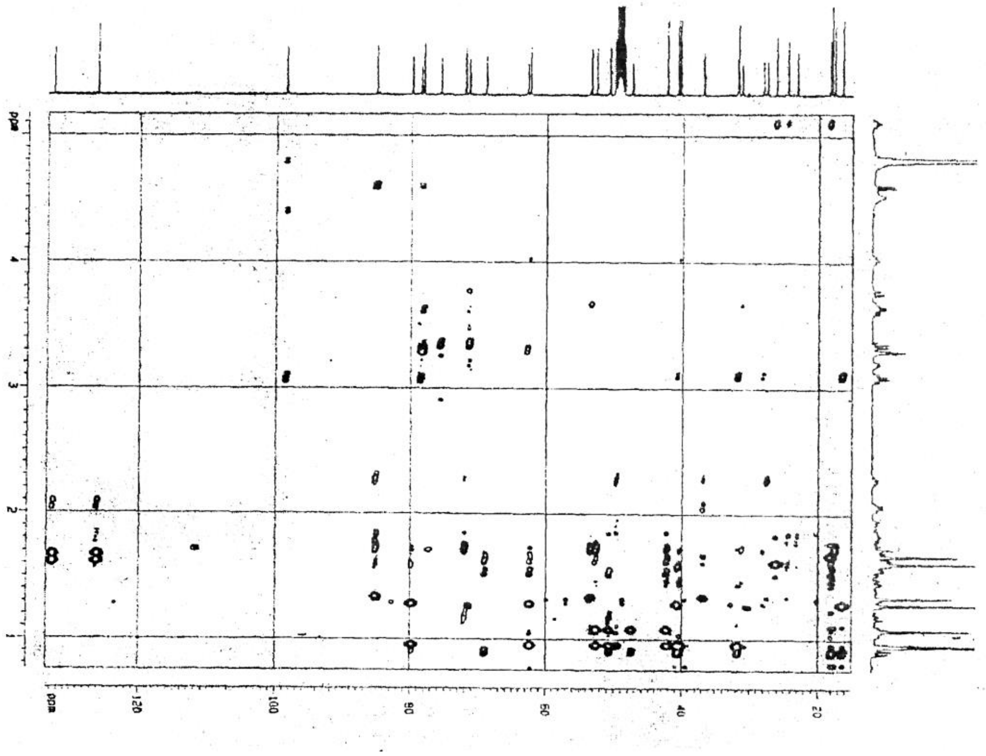


Figure S20: The HMBC spectrum of compound **1**

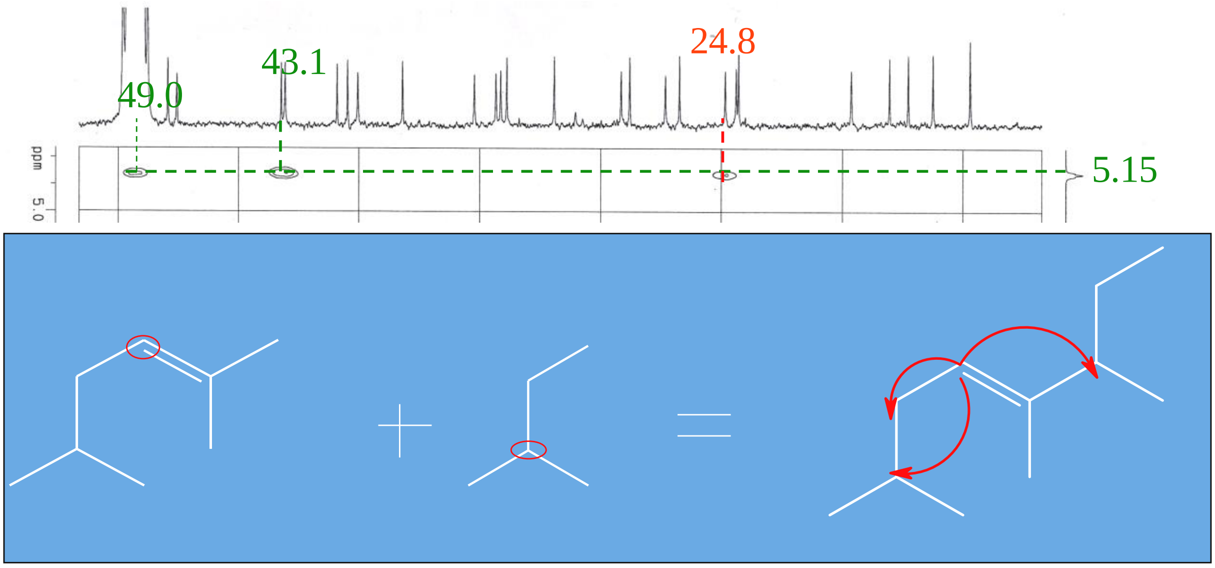


Figure S21: Expansion of the HMBC spectrum of compound **1**

Figure S22: Expansion of the HMBC spectrum of compound **1**

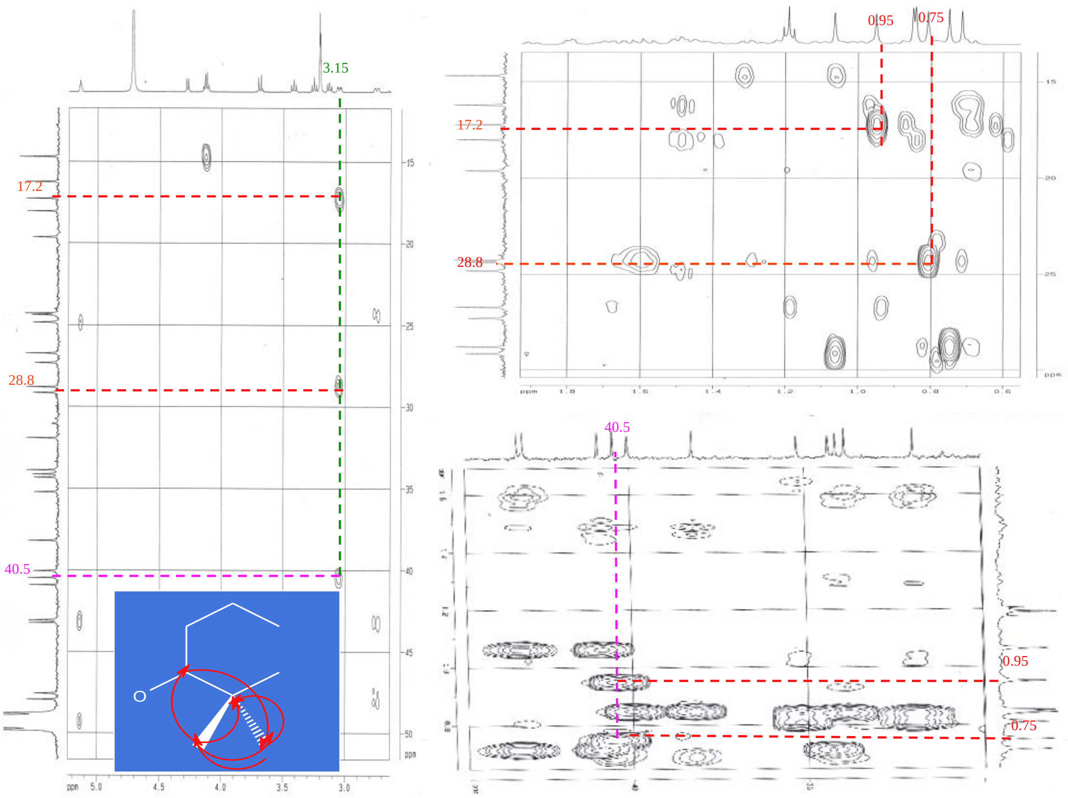


Figure S23: Expansion of the HMBC spectrum of compound **1**

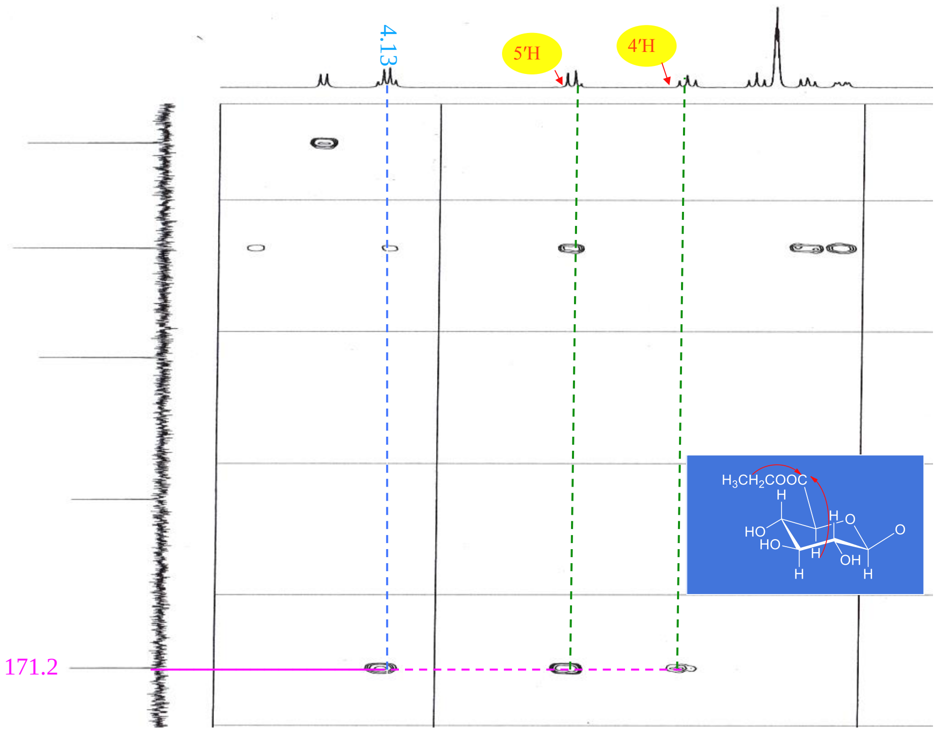


Figure S24: Expansion of the HMBC spectrum of compound **1**

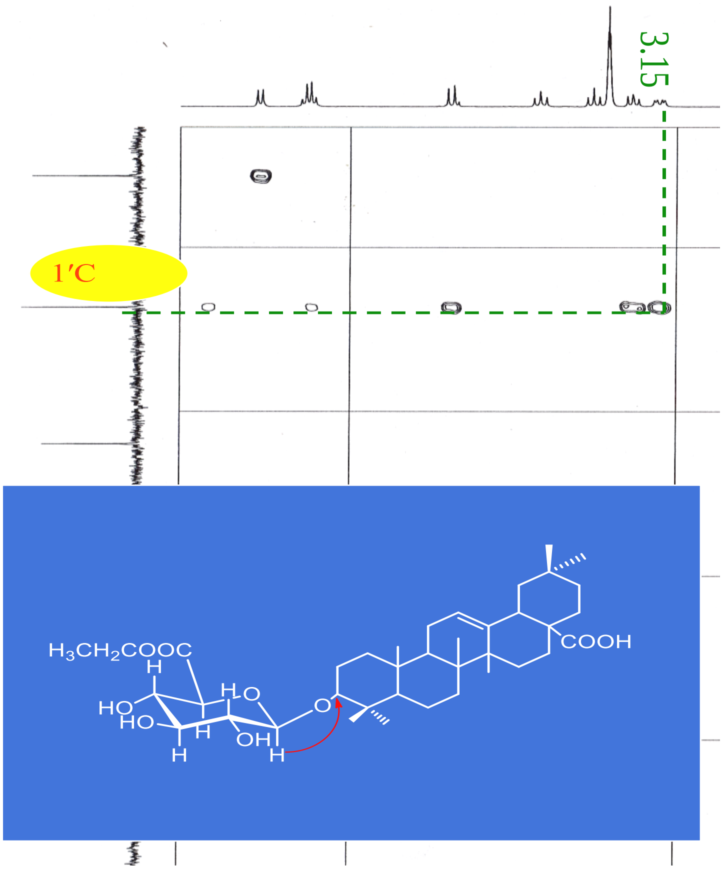


Figure S25: Expansion of the HMBC spectrum of compound **1**

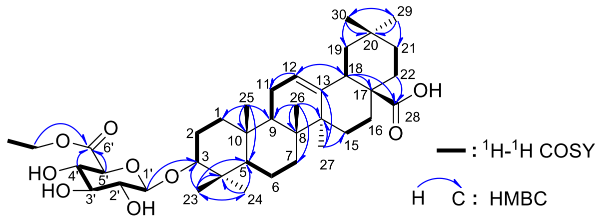


Figure S26: ^{1}H-^{1}H COSY and key HMBC correlations of **1**

Table S2. The ^{1}H-^{1}H COSY, HMBC assignments of **1**

No.[c]	δ_C[a]	δ_H[b]	^{1}H-^{1}H COSY	HMBC
1	40.0 (t)	0.97 (H-1a, *ca.*) 1.60 (H-1b, *ca.*)	H-2	C-2, C-3, C-10, C-25
2	27.3 (t)	1.65 (H-2a, *ca.*) 1.81 (H-2b, *ca.*)	H-1, H-3	C-1, C-3, C-10
3	91.4 (d)	3.15 (dd, 11.7, 4.4)	H-2	C-1′, C-4, C-23, C-24
4	40.5 (s)	——	——	——
5	57.3 (d)	0.70 (d, 12.0)	H-6	C-4, C-6, C-10, C-23, C-24, C-25
6	19.6 (t)	1.57 (H-6a, *ca.*) 1.40 (H-6b, *ca.*)	H-5, H-7	C-5, C-7
7	34.3 (t)	1.30 (*ca.*)	H-6	C-6, C-8, C-26
8	40.9 (s)	——	——	——
9	49.0 (d)	1.58 (*ca.*)	H-11	C-8, C-10, C-11, C-12, C-25, C-26
10	38.2 (s)	——	——	——
11	24.8 (t)	1.89 (*ca.*)	H-9, H-12	C-9, C-12, C-13
12	124.0 (d)	5.15 (br.s)	H-11	C-11, C-13, C-14, C-18
13	145.5 (s)	——	——	——
14	43.2 (s)	——	——	——
15	29.2 (t)	1.07 (H-15a, *ca.*) 1.78 (H-15b, *ca.*)	H-16	C-8, C-13, C-14, C-16, C-27
16	24.4 (t)	1.60 (H-16a, *ca.*) 2.00 (H-16b, *ca.*)	H-15	C-15, C-17, C-28
17	47.9 (s)	——	——	——
18	43.1 (d)	2.82 (dd, 13.5, 4.2)	H-19	C-12, C-13, C-16, C-17, C-19, C-28
19	47.6 (t)	1.13 (H-19a, *ca.*) 1.58 (H-19b, *ca.*)	H-18	C-17, C-18, C-20, C-21, C-29, C-30
20	32.0 (s)	——	——	——
21	35.2 (t)	1.20 (H-21a, *ca.*) 1.41 (H-21b, *ca.*)	H-22	C-20, C-22, C-29, C-30
22	34.1 (t)	1.54 (H-21a, *ca.*) 1.76 (H-21b, ca.)	H-21	C-17, C-21, C-28
23	28.8 (q)	0.95 (s)	——	C-3, C-4, C-5, C-24
24	17.2 (q)	0.75 (s)	——	C-3, C-4, C-5, C-23
25	16.2 (q)	0.85 (s)	——	C-1, C-5, C-9, C-10
26	18.0 (q)	0.71 (s)	——	C-7, C-8, C-9, C-14
27	26.7 (q)	1.06 (s)	——	C-8, C-13, C-14, C-15
28	182.1 (s)	——	——	——
29	33.9 (q)	0.81 (s)	——	C-19, C-20, C-21, C-30
30	24.3 (q)	0.84 (s)	——	C-19, C-20, C-21, C-29
GlcA-1′	107.4 (d)	4.28 (d, 7.8)	H-2′	C-3, C-2′
2′	75.6 (d)	3.24 (ca.)	H-1′, H-3′	C-1′, C-3′
3′	77.9 (d)	3.36 (ca.)	H-2′, H-4′	C-2′, C-4′
4′	73.5 (d)	3.53 (ca.)	H-3′, H-5′	C-5′, C-6′
5′	77.0 (d)	3.79 (ca.)	H-4′	C-1′, C-3′, C-4′, C-6′
6′	171.2 (s)	——	——	——
$\underline{CH_2}CH_3$	62.7 (t)	4.13 (t, 7.1)	$CH_2\underline{CH_3}$	C-6′, $CH_2\underline{CH_3}$
$CH_2\underline{CH_3}$	14.7 (q)	1.19 (q, 7.1)	$\underline{CH_2}CH_3$	$\underline{CH_2}CH_3$

a. ^{1}H-NMR at 500 MHz, δ in MeOH-d_4, in ppm from TMS, coupling constants (J) in Hz are given in parentheses.
b. ^{13}C-NMR at 125 MHz, δ in MeOH-d_4, in ppm from TMS.
c. GlcA, glucuronyl.