Supporting information

Synthesis of MeON-Glycoside derivatives of oleanolic acid by neoglycosylation and evaluation of cytotoxicity against selected cancer cell lines

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SUPPORTING INFORMATION CONTENTS

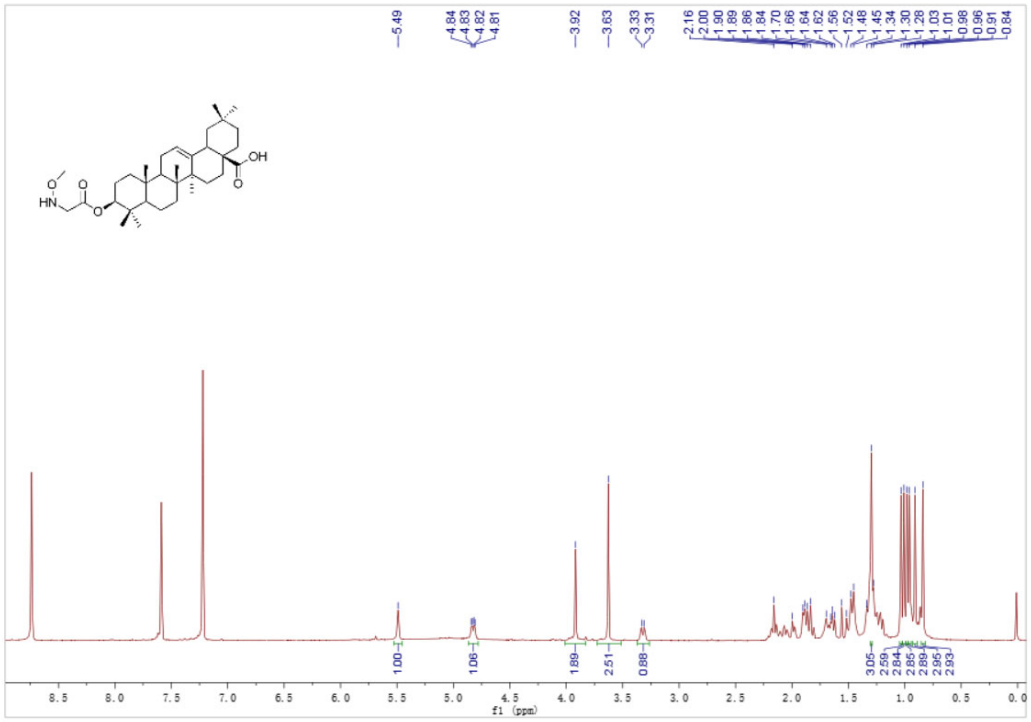
I. **Table S1.** ^{1}H NMR anomeric proton and HRMS characterization of C-3 or C-28 MeON-neoglycosides of oleanolic acid

Entry	neoglycoside	*α*-anomeric H1		*β*-anomeric H1		*α: β*	HRMS(ESI)MS m/z	
		δ (ppm)	J(Hz)	δ (ppm)	J(Hz)	ratio	measured	calculated
4a	D-glucose			4.83-4.81[d]		1 anomer	706.4525[a]	706.4525
4b	L-glucose	not observed		4.84	8.7	Only *β*	706.4533[a]	706.4525
4c	2-deoxy-D-glucose			4.81-4.79 [d]		1 anomer	690.4575[a]	690.4576
4d	3-O-methyl-D-glucose			4.82-4.76 [d]		1 anomer	720.4678[a]	720.4681
4e	D-galactose	5.34	5.7	4.87-4.81[c]	n/d[e]	n/d	706.4520[a]	706.4525
4f	2-deoxy-D-galactose	not observed		4.76	10.9	Only *β*	690.4581[a]	690.4576
4g	D-mannose	4.93	1.7	4.70-4.67[c]	n/d	n/d	706.4528[a]	706.4525
4h	D-arabinose	5.33	5.4	not observed		Only *α*	676.4413[a]	676.4419
4i	L-arabinose	5.32	5.4	4.64	9.0	1:1	676.4411[a]	676.4419
4j	D-fucose	5.29	5.3	4.70	9.1	2:1	690.4585[a]	690.4576
4k	L-fucose	5.31	5.3	4.72	9.0	2:1	688.4434[b]	688.4430
4l	D-xylose	not observed		4.70	8.4	Only *β*	676.4426[a]	676.4419
4m	L-xylose	not observed		4.72	8.2	Only *β*	676.4430[a]	676.4419
4n	L-lyxose	not observed		5.18	8.2	Only *β*	676.4417[a]	676.4419
4o	L-rhamnose	4.67	2.0	5.14-5.09[c]	n/d	n/d	690.4578[a]	690.4576
4p	D-ribose	5.41	2.9	5.08	8.2	1:2	676.4423[a]	676.4419
4q	L-ribose	5.42	3.7	5.10	8.6	1:2	676.4413[a]	676.4419
4r	2-deoxy-D-ribose	5.32	2.9	4.66-4.62[c]	n/d	n/d	658.4326[b]	658.4324
8a	D-glucose	not observed		4.61	7.9	Only *β*	634.4676[a]	634.4677

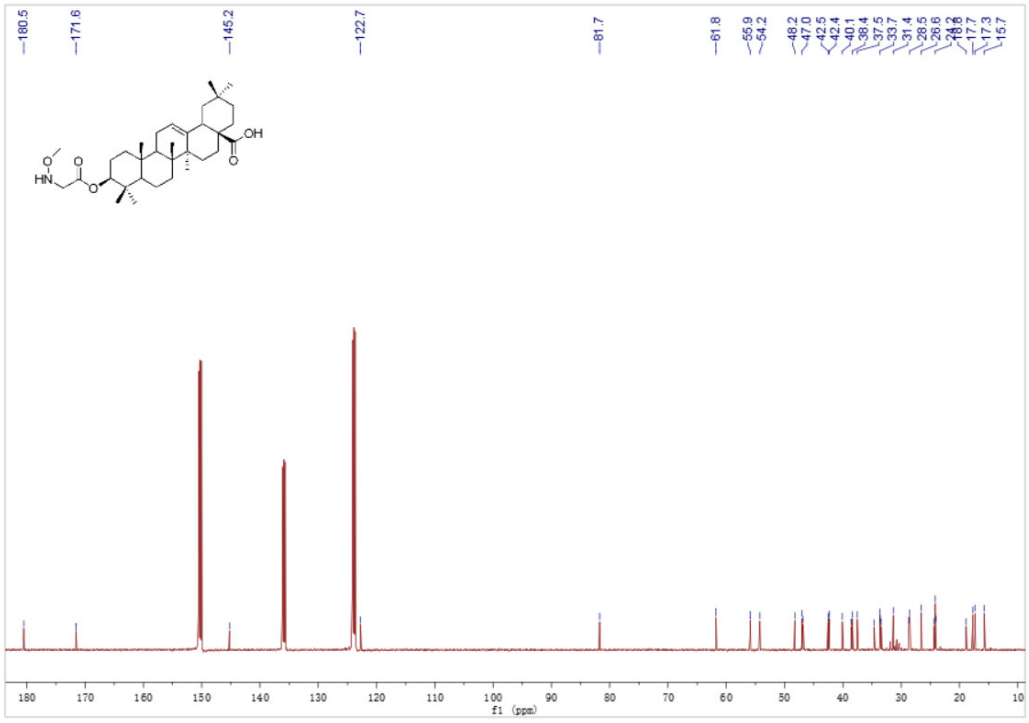
8b	L-glucose		not observed	4.60	8.0	Only β	634.4673[a]	634.4677
8c	2-deoxy-D-glucose		not observed	4.72	10.5	Only β	618.4730[a]	618.4728
8d	3-O-methyl-D-glucose		not observed	4.63	8.9	Only β	648.4825[a]	648.4834
8e	D-galactose	4.67	2.8	5.11	6.2	4:1	634.4676[a]	634.4677
8f	2-deoxy-D-galactose	5.36	6.5	4.68-4.63[c]	n/d	n/d	618.4739[a]	618.4728
8g	D-mannose	5.00	2.5	4.77-4.70[c]	n/d	n/d	634.4672[a]	634.4677
8h	D-arabinose	5.18	5.5	4.67-4.65[c]	n/d	n/d	604.4581[a]	604.4572
8i	L-arabinose	5.18	5.9	4.63-4.59[c]	n/d	n/d	604.4576[a]	604.4572
8j	D-fucose			4.55-4.51[d]		1 anomer	618.4733[a]	618.4728
8k	L-fucose		not observed	4.44	8.7	Only β	618.4732[a]	618.4728
8l	D-xylose		not observed	4.57	6.7	Only β	604.4572[a]	604.4572
8m	L-xylose		not observed	4.55	8.7	Only β	604.4587[a]	604.4572
8n	L-lyxose	5.88	3.5	4.77-4.75[c]	n/d	n/d	604.4575[a]	604.4572
8o	L-rhamnose	4.69	2.9	5.28	6.1	4:1	618.4733[a]	618.4728
8p	D-ribose	5.23	3.4	4.80-4.77[c]	n/d	n/d	604.4580[a]	604.4572
8q	L-ribose	5.20	3.1	4.81-4.78[c]	n/d	n/d	604.4575[a]	604.4572
8r	2-deoxy-D-ribose	5.30	3.3	4.70-4.65[c]	n/d	n/d	588.4616[a]	588.4623
1a	D-glucose		not observed	6.34	8.0	Only β	641.4029[f]	641.4024
1b	D-glucose		not observed	4.92	7.7	Only β	627.4231[f]	627.4231

[a] HRMS (ESI) m/z for $[M+H]^+$, [b] HRMS (ESI) m/z for $[M-H]^-$, [c] Anomeric proton obscured by another peak, [d] Single anomeric proton signal detected but obscured by another peak, [e] Not determined, [f] HRMS (ESI) m/z for $[M+Na]^+$.

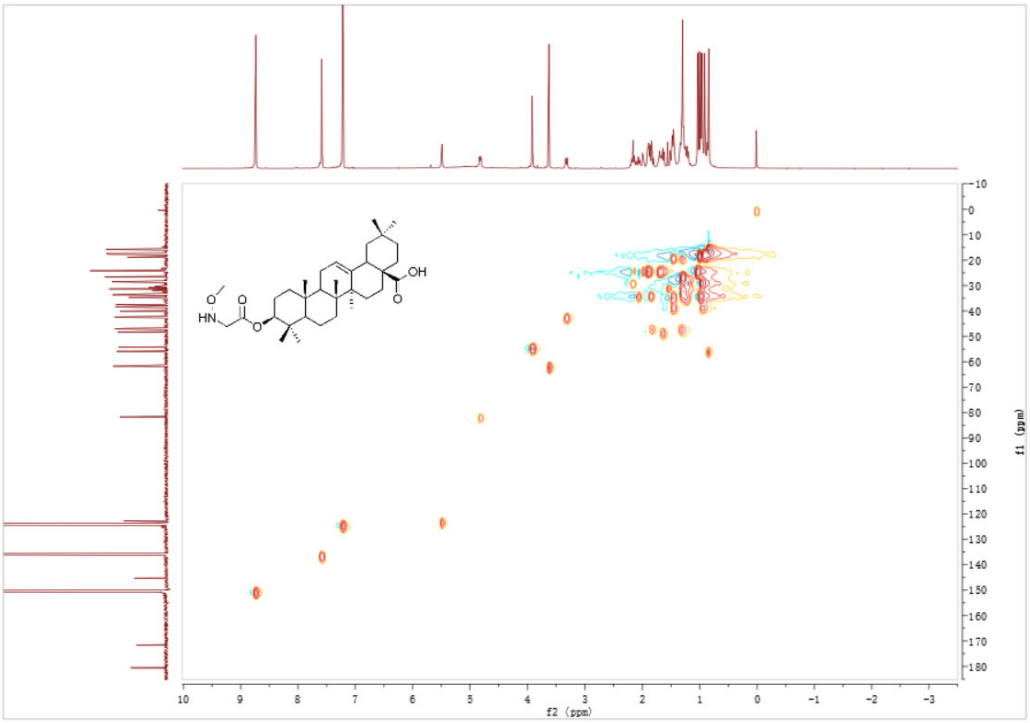
II. Figure S1 NMR spectra of neoaglycone and representative neoglycosides



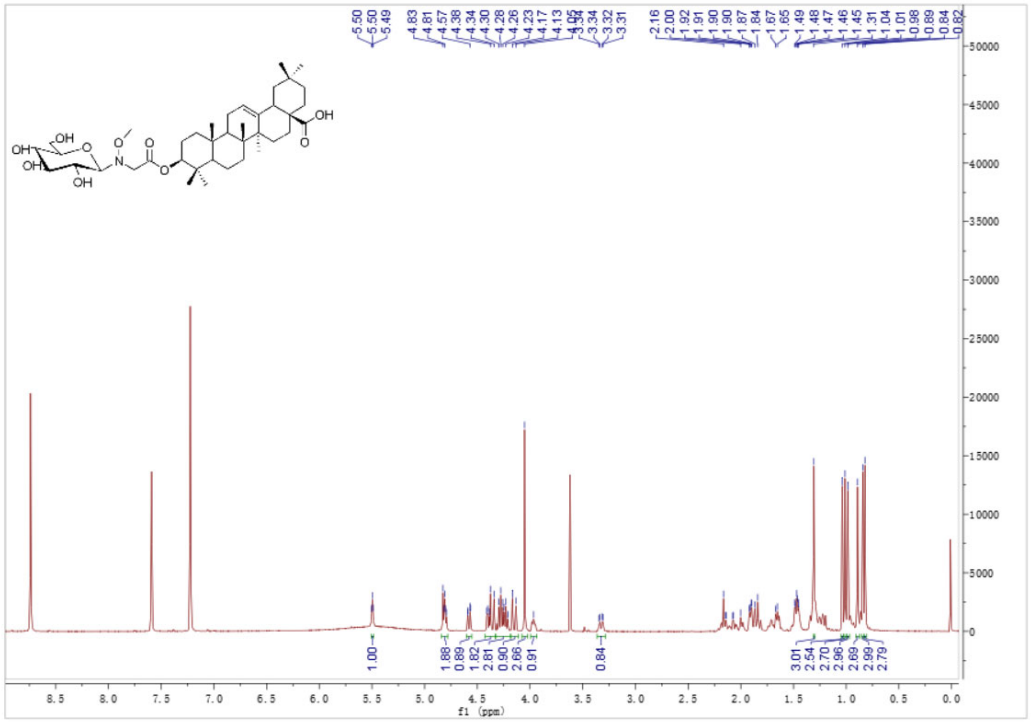
The ^{1}H NMR spectrum of compound **3** (500 MHz, in C_5D_5N)



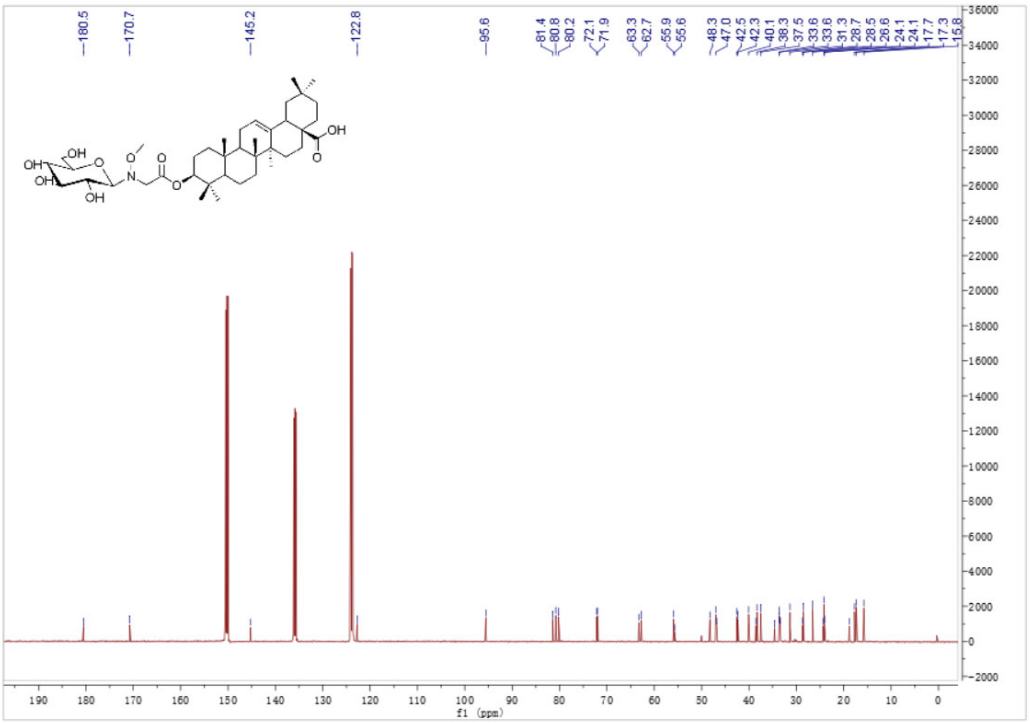
The ^{13}C NMR spectrum of compound **3** (125 MHz, in C_5D_5N)



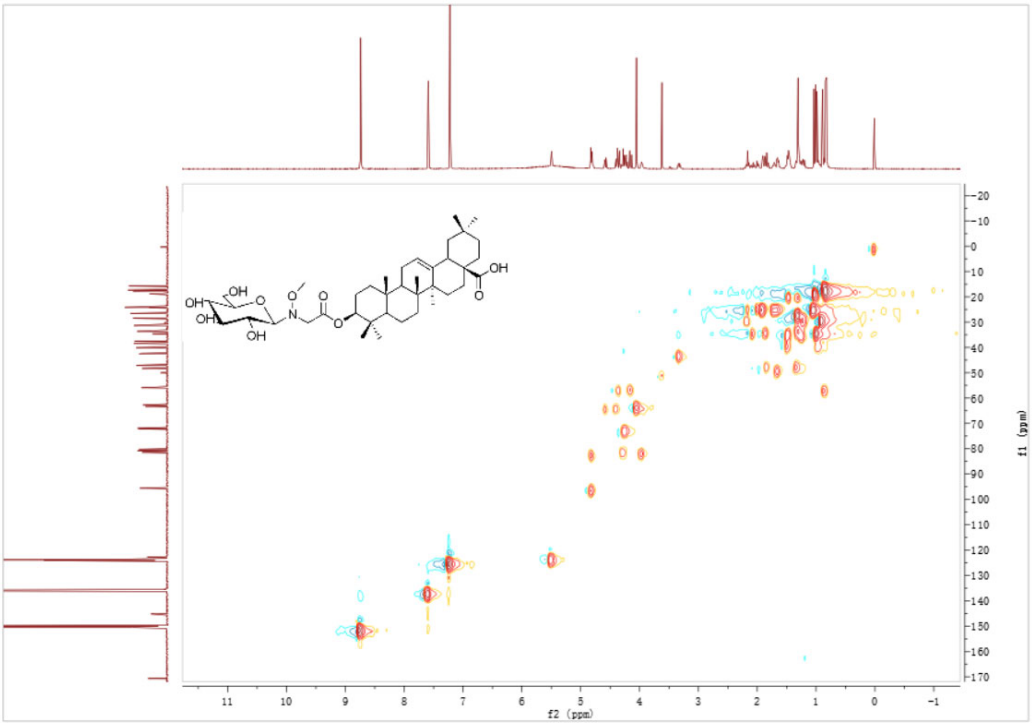
The HSQC spectrum of compound **3** (500 MHz, in C_5D_5N)



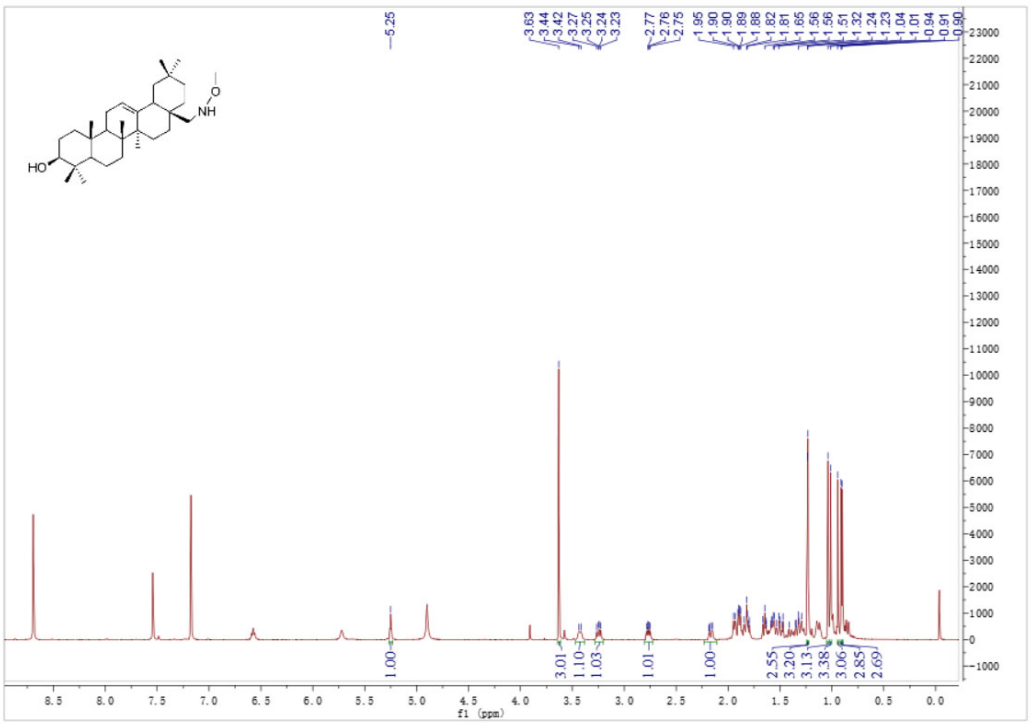
The ^{1}H NMR spectrum of compound **4a** (500 MHz, in C_5D_5N)



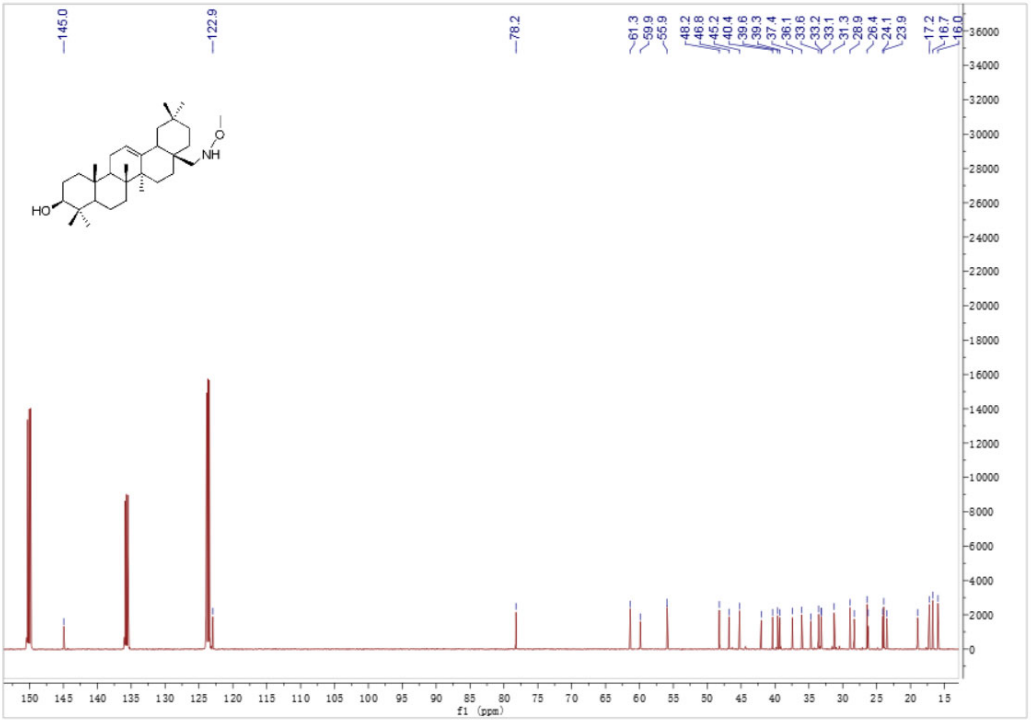
The ^{13}C NMR spectrum of compound **4a** (125 MHz, in C_5D_5N)



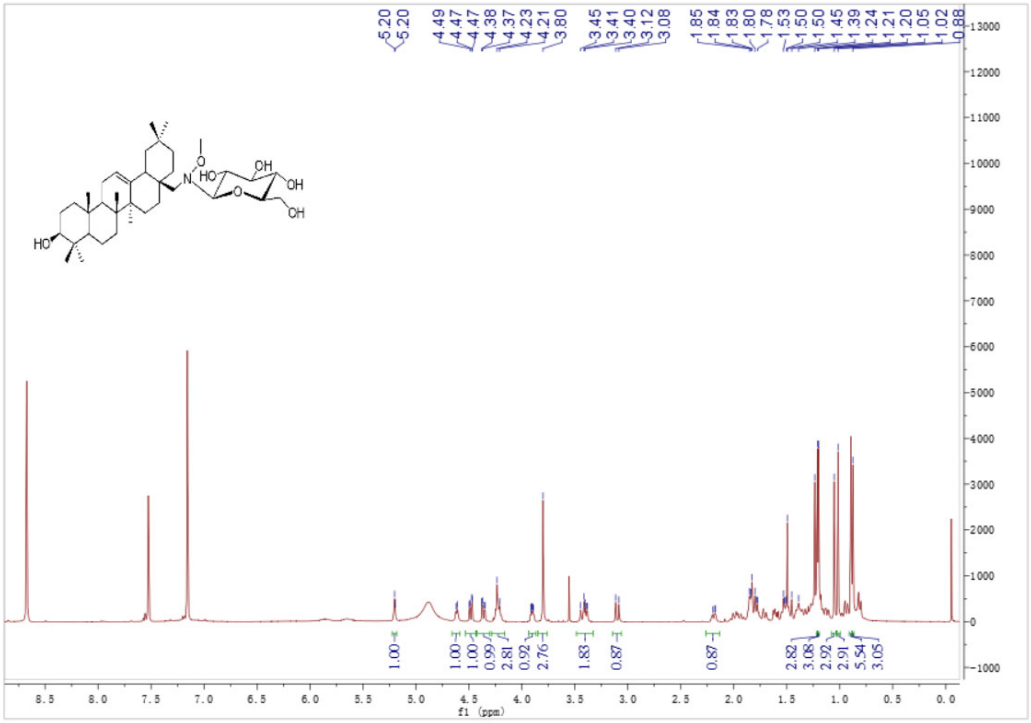
The HSQC spectrum of compound **4a** (500 MHz, in C_5D_5N)



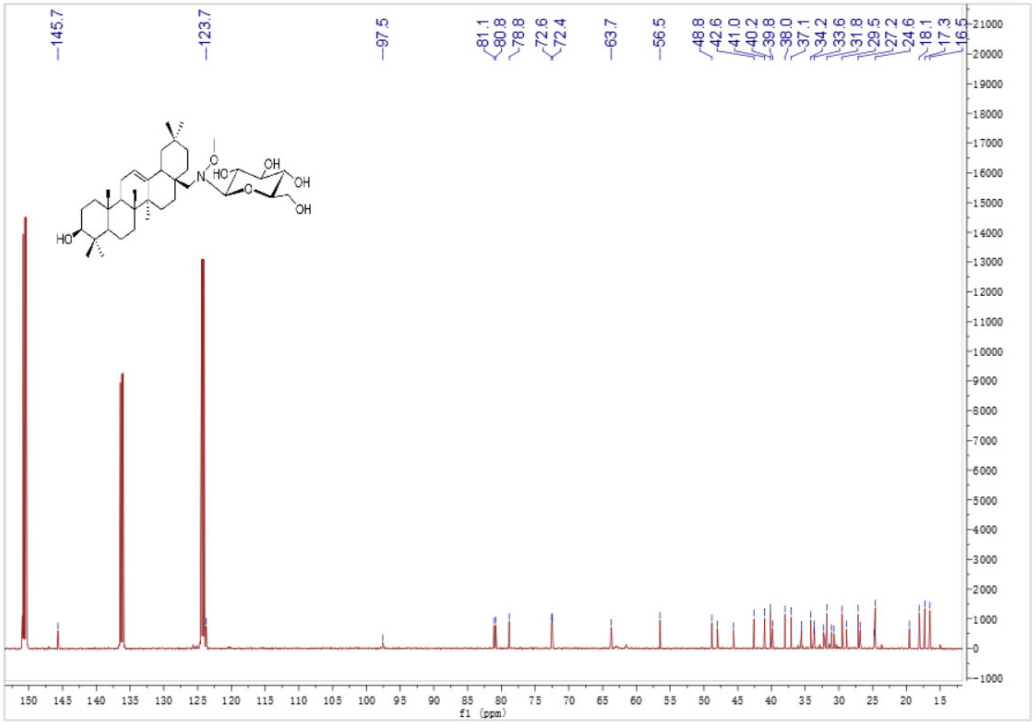
The ^{1}H NMR spectrum of compound **7** (500 MHz, in C_5D_5N)



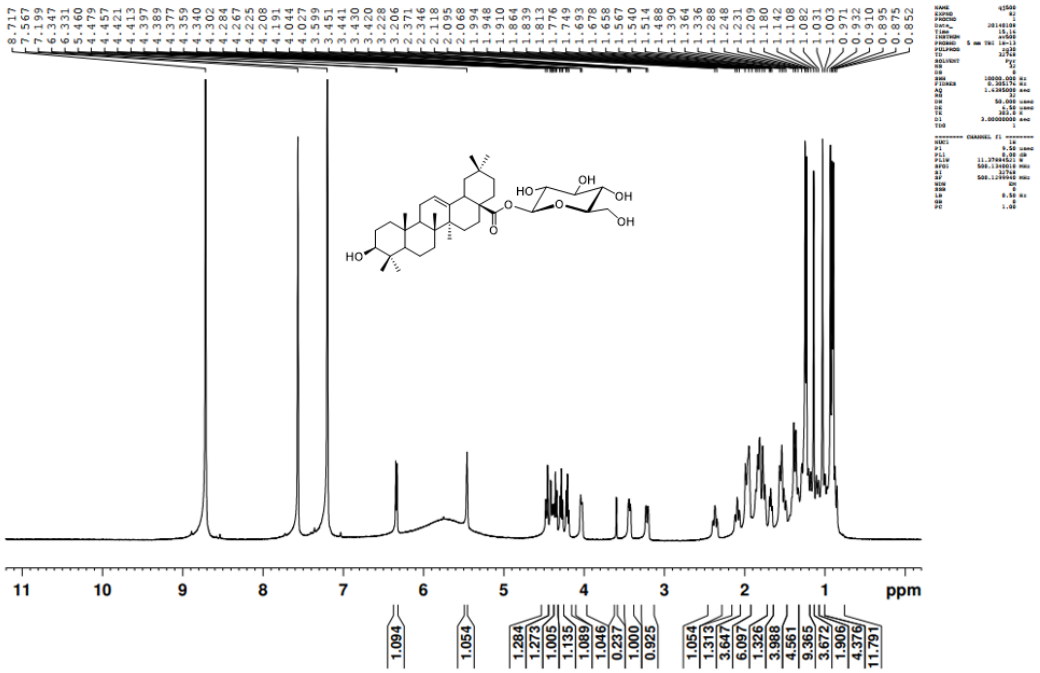
The ^{13}C NMR spectrum of compound **7** (125 MHz, in C_5D_5N)



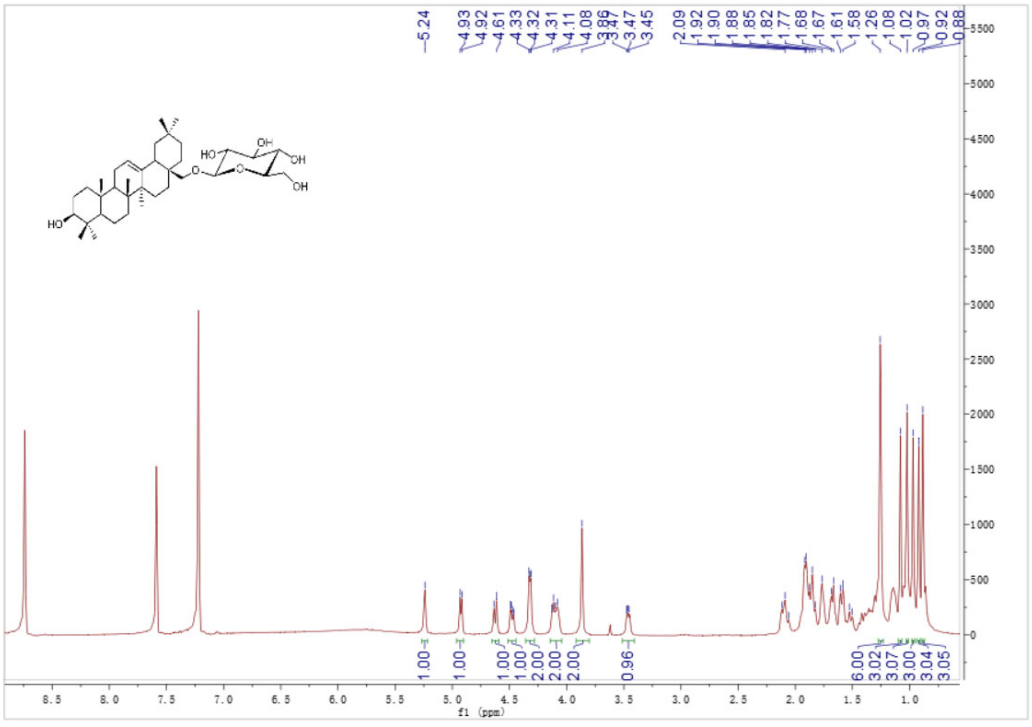
The ^{1}H NMR spectrum of compound **8a** (500 MHz, in C_5D_5N)



The ^{13}C NMR spectrum of compound **8a** (125 MHz, in C_5D_5N)



The ^{1}H NMR spectrum of compound **1a** (500 MHz, in C_5D_5N)



The ^{1}H NMR spectrum of compound **1b** (500 MHz, in C_5D_5N)