Bioorganic & Medicinal Chemistry 18 (2010) 7458–7474

Contents lists available at ScienceDirect

Bioorganic & Medicinal Chemistry

journal homepage: www.elsevier.com/locate/bmc

Synthesis and antitumour activity of glycyrrhetinic acid derivatives

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ARTICLE INFO

Article history:
Received 30 June 2010
Revised 10 August 2010
Accepted 29 August 2010
Available online 18 September 2010

Keywords:
Glycyrrhetinic acid
SRB assay
Acridine orange/ethidium bromide assay
Apoptosis
Antitumour

ABSTRACT

Glycyrrhetinic acid (GA) is one of many interesting triterpenoic acids showing anticancerogenic potential. GA is known to trigger apoptosis in tumour cell lines, although GA has a low cytotoxicity. In our study we were able to prepare derivatives of GA that show lowered the IC_{50} values as determined by a sulforhodamine B (SRB) assay using 15 different human tumour cell lines. Thus, combining an ester group combined with the presence of an amino acid moiety led to a ca. 60-fold improved antitumor activity. Experiments on mouse embryonic fibroblasts (NiH3T3) revealed that these compounds showed a better selectivity for tumour cells compared to the parent compound GA. An apoptotic effect of some of these compounds was determined using an acridine orange/ethidium bromide (AO/EB) test and DNA laddering experiments.

1. Introduction

Glycyrrhetinic acid (GA) is not the most potent antitumour active triterpenoic acid; several other triterpenes, for example, betulinic acid,[1–3] are better known for their antitumour activity. GA, however, is still of special interest because of its apoptotic effect on to tumour cells. In addition, the extract of the licorice roots contains up to 24% GA—mainly as glycosidic glycyrrhizic acid.[4] Therefore, compared to other triterpenoic acids, GA can be obtained cheaper and in a higher amount than, for example, betulinic acid (2.44%,[5] 3.3%[6]) or oleanoic acid (3.1%[5]). Improving the antitumour activity of GA without forfeiting its apoptotic effect is one of the big challenges when dealing with the derivatization of GA. We thought that changing the polarity pattern of the molecule might be of some interest; introducing an extra amino group (for gain of polarity) and preparing esters of GA (for gain of lipophilicity) seemed appropriate.

Thus, we synthesized 25 derivatives of GA—esterified at C(30) and varied by coupling with an amino acid at C(3)—and compared their biological activity (IC_{50} values) using a sulforhodamine B assay (SRB assay) with up to 15 human tumour cell lines and mouse embryonic fibroblasts NiH3T3; extra acridine orange/ethidium bromide tests (AO/EB) were performed to test for an apoptotic behaviour.

2. Results

2.1. Influence of an ester moiety

Different esters of GA differing in the alcoholic part (Fig. 1) were prepared by reacting GA with alkyl halides in DMF in the presence of potassium carbonate.[7] We were able to synthesize the *tert*-butyl ester, too. However, this compound is unstable under the conditions of the SRB assay test and was excluded from this study.

In the SRB assay the esters showed an improved activity on to tumour cell lines (Fig. 2, left and Table 1). The most active substance was the benzyl ester showing IC_{50} values between 2.7–25.2 μM. The toxicity of these compounds for the mouse embryonic fibroblasts remained almost constant throughout this series (Fig. 2, right) except for the *i*-propyl ester that shows a lowered activity; the decrease in the IC_{50} values parallels the size and lipophilic character of the alkyl chain of the ester.

As far as GA is concerned, we found a more than four times higher toxicity on mouse embryonic fibroblasts than on tumour cell lines. A maximum of selectivity towards the tumour cells, however, was established for compound **4**; this derivative is approx. eight times more toxic for the SW1736 thyroid carcinoma (IC_{50} = 2.74 μM) than for the fibroblasts (IC_{50} = 21.02 μM).

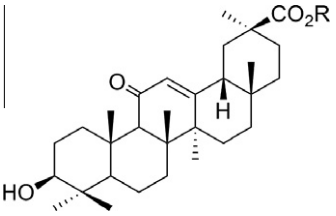

Figure 1. Esters of GA: **1**: R = Me; **2** R = Et; **3**: R = *i*-Pr; **4**: R = Bn.

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doi:10.1016/j.bmc.2010.08.054

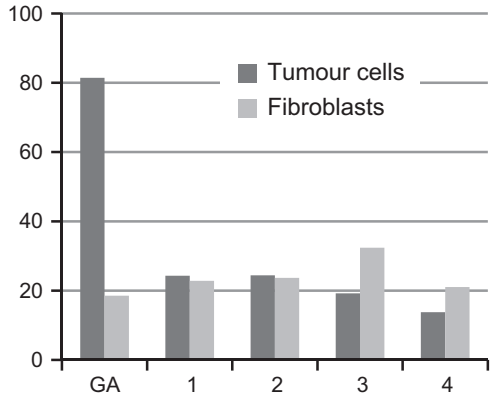

Figure 2. IC_{50} values (in μM) for GA and its esters **1**–**4** for tumour cells (averaged, 15 cell lines) and mouse fibroblastic cells (NiH3T3).

2.2. Amino acid derivatives of GA

In this series of compounds we introduced a polar proton acceptor group in position C(3). These compounds were synthesized by DCC mediated esterifications of *N*-Boc protected amino acids (glycine, D-alanine and β-alanine) followed by their deprotection using TFA in dry DCM[8] (for the amines) or by treating them with dry HCl gas in DCM (for the ammonium hydrochlorides).

For all esters (Tables 2 and 3 and Fig. 4), activity increases when C(3) is substituted with one of the three amino acids. In this series, the glycine substituted *i*-propyl ester was shown the most active compound; the ethyl ester, however, is the most active compound when a L-alaninyl or a β-alaninyl substituent was introduced. Interestingly enough, in this series of compounds the derivatives of β-alanine show the highest activity except for **14**. On average, the lowest IC_{50} values were obtained for **16** (substituted with *i*-propyl and β-alanine). All derivatives holding a free carboxylic group in position C(30) gave IC_{50} values >30 μM and were excluded from further investigations.

From the selected amino acids, the derivatives of β-alanine show the highest activity. The sole exception is derivative **14** (av 2.49 μM), substituted with glycine and esterified with *i*-propyl. The lowest average of the IC_{50} value we determined was for substance **16**, substituted with *i*-propyl and β-alanine. All derivatives having a free carboxyl group in position C(30) gave IC_{50} values higher than 30 μM; thus, they were excluded from further investigations.

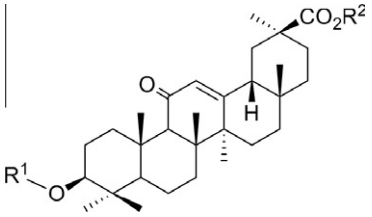

Figure 3. Amino acid derivatives of GA and of GA esters.

A priori, a dependency between biological activity and a counter-ion cannot be ruled out. Thus, to find out that the biological data obtained from amines and their respective ammonium hydrochlorides are comparable, we checked whether there is a difference in their cytotoxic activity. As a representative example, the methyl esters of the amino acid derivatives were investigated; the results from the SRB assay are compiled in Table 4.

These results suggest there is no significant difference in the biological activity between amines and their respective ammonium salts.

As far as the *N*-Boc protected derivatives are concerned, three derivatives (**23**–**25**) were tested in the SRB assay; all of them gave an IC_{50} >30 μmol.

2.3. Influence of a stereogenic centre

To work out if the stereogenic centre introduced in the amino acid derivatives of GA has any influence on the biological activity several derivatives containing a D-alaninyl residue were prepared and compared (SRB assay, 15 different tumour cell lines) with their respective L-alaninyl diastereomers. The data for this series are summarized in Table 5. In summary, the effect of the stereogenic centre is small and varies with the cell lines.

2.4. Apoptotic study using the AO/EB test and DNA laddering

As previously shown,[9–12] GA induces apoptosis. To prove whether this feature remains or is lost on derivatization, we tested four compounds for an induction of apoptosis in an AO/EB test. Figure 5 (left) depicts a section of A549 cells after being treated with GA. As expected, the cells showed apoptotic behaviour; this can easily be seen from the green fluorescence of the nucleus. The more active compounds **8**–**10** and **25** were investigated in the same way. In all of these samples, apoptotic cells were detected. Although this assay doesn't allow to quantify the ratio

Table 1
Results from the SRB assay for esters of glycyrrhetinic acid (results given in μM)

Derivative/cell line	GA	1	2	3	4
518A2	83.92 ± 4.20	27.54 ± 1.38	25.23 ± 1.26	18.15 ± 0.91	18.19 ± 0.91
8505C	86.50 ± 4.33	26.07 ± 1.30	24.58 ± 1.23	14.24 ± 0.71	8.10 ± 0.41
A253	80.78 ± 4.04	19.42 ± 0.97	25.04 ± 1.25	15.76 ± 0.79	10.67 ± 0.54
A2780	74.57 ± 3.73	25.54 ± 1.28	26.96 ± 1.35	24.95 ± 1.25	20.32 ± 1.02
A431	79.58 ± 3.99	25.28 ± 1.26	23.45 ± 1.17	32.01 ± 1.60	23.58 ± 1.18
A549	82.76 ± 4.14	23.50 ± 1.18	22.74 ± 1.14	14.41 ± 0.72	6.15 ± 0.31
DLD-1	81.21 ± 4.06	26.12 ± 1.31	28.14 ± 1.41	27.61 ± 1.38	22.69 ± 1.13
FaDu	84.55 ± 4.23	23.41 ± 1.17	23.76 ± 1.19	14.42 ± 0.72	5.48 ± 0.27
HCT-116	78.83 ± 3.94	22.10 ± 1.11	21.58 ± 1.08	26.44 ± 1.32	20.57 ± 1.03
HCT-8	78.85 ± 3.94	24.36 ± 1.22	43.42 ± 2.17	24.12 ± 1.21	25.23 ± 1.26
HT-29	80.09 ± 4.00	27.54 ± 1.38	22.14 ± 1.11	15.97 ± 0.80	11.48 ± 0.57
Lipo	81.44 ± 4.07	20.47 ± 1.02	27.66 ± 1.38	15.93 ± 0.80	11.54 ± 0.58
MCF-7	84.70 ± 4.24	22.14 ± 1.11	18.61 ± 0.93	16.04 ± 0.80	13.49 ± 0.67
SW1736	76.93 ± 3.85	34.87 ± 1.74	13.37 ± 0.67	12.77 ± 0.64	2.74 ± 0.14
SW480	86.80 ± 4.34	16.08 ± 0.80	19.10 ± 0.96	15.33 ± 0.77	6.17 ± 0.31
Average	81.43 ± 4.07	24.30 ± 1.22	24.39 ± 1.22	19.21 ± 0.96	13.76 ± 0.69
NiH3T3	18.52 ± 0.93	22.81 ± 1.14	23.66 ± 1.18	32.37 ± 1.62	21.02 ± 1.05

Table 2
Modifications of GA at positions C(3) and C(30)

Compd	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
R^1	Gly·HCl	L-Ala·HCl	β-Ala·HCl	Gly	L-Ala	β-Ala	Gly	L-Ala	β-Ala
R^2	H	H	H	Me	Me	Me	Et	Et	Et
	14	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
R^1	Gly	L-Ala	β-Ala	Gly	L-Ala	β-Ala	Gly·HCl	L-Ala·HCl	β-Ala·HCl
R^2	*i*-Pr	*i*-Pr	*i*-Pr	Bn	Bn	Bn	Me	Me	Me

Table 3
IC_{50} values (in μM) for GA derivatives substituted with amino acids in position C(3) and esterified in C(30) (Fig. 3)

Cell lines/derivatives	8505C	A253	A2780	A549	DLD-1	Lipo	Average
5	>30	>30	>30	>30	>30	>30	>30
6	>30	>30	>30	>30	>30	>30	>30
7	>30	>30	>30	>30	>30	>30	>30
8	7.45 ± 0.37	6.26 ± 0.31	5.99 ± 0.30	6.42 ± 0.32	8.59 ± 0.43	7.54 ± 0.38	7.04 ± 0.35
9	4.31 ± 0.22	3.61 ± 0.18	2.98 ± 0.15	2.77 ± 0.14	4.49 ± 0.22	4.30 ± 0.22	3.74 ± 0.19
10	2.55 ± 0.13	2.50 ± 0.13	1.72 ± 0.09	2.40 ± 0.12	2.51 ± 0.13	2.52 ± 0.13	2.37 ± 0.12
11	5.32 ± 0.27	3.59 ± 0.18	3.90 ± 0.20	5.39 ± 0.27	5.61 ± 0.28	4.32 ± 0.22	4.69 ± 0.23
12	3.87 ± 0.19	2.33 ± 0.12	2.59 ± 0.13	3.43 ± 0.17	3.72 ± 0.19	2.74 ± 0.14	3.11 ± 0.16
13	2.32 ± 0.12	2.23 ± 0.11	1.77 ± 0.09	2.18 ± 0.11	2.74 ± 0.14	2.38 ± 0.12	2.27 ± 0.11
14	2.76 ± 0.14	2.01 ± 0.10	2.24 ± 0.11	2.65 ± 0.13	2.54 ± 0.13	2.74 ± 0.14	2.49 ± 0.12
15	3.49 ± 0.17	3.51 ± 0.18	2.08 ± 0.10	3.43 ± 0.17	5.54 ± 0.28	3.53 ± 0.18	3.60 ± 0.18
16	1.96 ± 0.10	2.68 ± 0.13	1.31 ± 0.07	1.78 ± 0.09	3.52 ± 0.18	3.49 ± 0.17	2.46 ± 0.12
17	4.79 ± 0.24	5.03 ± 0.25	3.54 ± 0.18	5.07 ± 0.25	4.54 ± 0.23	4.81 ± 0.24	4.63 ± 0.23
18	3.10 ± 0.16	3.49 ± 0.17	2.85 ± 0.14	3.51 ± 0.18	5.02 ± 0.25	3.57 ± 0.18	3.59 ± 0.18
19	3.19 ± 0.16	3.05 ± 0.15	1.73 ± 0.09	2.76 ± 0.14	4.54 ± 0.23	3.25 ± 0.16	3.09 ± 0.15

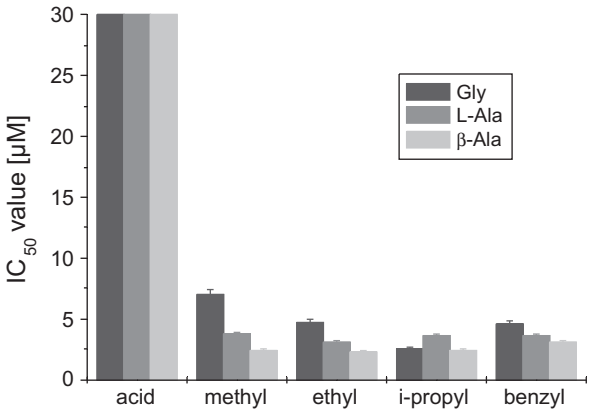

Figure 4. IC_{50} values (in μM) for the amino acid modified GA derivatives (averaged values, six tumour cell lines).

between apoptotic and necrotic cells, the ability of the compounds to trigger apoptosis is displayed unambiguously. Figure 5 (left to right) show sections from the samples showing the characteristic green fluorescent nucleus.

During apoptosis DNA is cleaved[13–15] into smaller fragments by endonucleases. These fragments are observable by gel electrophoresis as ladders. Thus, the floating cells (obtained after treatment with IC_{90}-concentrations for 24 h) were analyzed by DNA gel electrophoresis and the typical DNA ladders were observed. Some of these results are depicted in Figure 6.

3. Conclusion

In this study we were able to synthesize simple derivatives of GA; these compounds, however, showed an increased cytotoxicity for various human cancer cell lines. For several of these derivatives the selectivity index was increased, too. These results point out there is an increasing activity with increasing lipophilicity for GA esters. This tendency, however, is not found for derivatives substituted with an extra amino acid moiety. An unsubstituted carboxylic group in C(30) led to inactive (IC_{50} >30 μM) compounds; the same is true for *N*-Boc protected amino acid derivatives. The presence of an added stereogenic centre in the side chain seems not important for activity. Previously, numerous modifications[16] in the ring skeleton of GA have been reported. With respect to ring A modifications, most approaches have focused on the synthesis of C2 and/or C-3 modified derivatives. Some C-3 ester[17] and a

Table 4
SRB data for selected amines and their hydrochlorides (IC_{50} in μM)

Derivative/cell line	**9** amine	**21** hydrochloride	**8** amine	**20** hydrochloride	**10** amine	**22** hydrochloride
518A2	3.54 ± 0.18	3.56 ± 0.18	6.65 ± 0.33	5.82 ± 0.29	2.50 ± 0.13	2.51 ± 0.13
8505C	4.31 ± 0.22	3.58 ± 0.18	7.45 ± 0.37	5.71 ± 0.29	2.55 ± 0.13	2.51 ± 0.13
A253	3.61 ± 0.18	3.50 ± 0.18	6.26 ± 0.31	5.50 ± 0.28	2.50 ± 0.13	2.51 ± 0.13
A2780	2.98 ± 0.15	2.31 ± 0.12	5.99 ± 0.30	4.32 ± 0.22	1.72 ± 0.09	1.56 ± 0.08
A549	2.77 ± 0.14	3.52 ± 0.18	6.42 ± 0.32	5.54 ± 0.28	2.40 ± 0.12	1.61 ± 0.08
DLD-1	4.49 ± 0.22	3.61 ± 0.18	8.59 ± 0.43	6.42 ± 0.32	2.51 ± 0.13	3.52 ± 0.18
Lipo	4.30 ± 0.22	3.52 ± 0.18	7.54 ± 0.38	5.92 ± 0.30	2.52 ± 0.13	3.55 ± 0.18
MCF-7	3.54 ± 0.18	3.89 ± 0.19	7.10 ± 0.36	5.73 ± 0.29	2.50 ± 0.13	2.43 ± 0.12
SW1736	3.22 ± 0.16	3.98 ± 0.20	6.33 ± 0.32	5.62 ± 0.28	1.82 ± 0.09	2.48 ± 0.12
Average	3.64 ± 0.18	3.50 ± 0.18	6.93 ± 0.35	5.62 ± 0.28	2.34 ± 0.12	2.52 ± 0.13

Table 5
Comparison of L- and D-alanyl substituted derivatives (cytotoxicity, IC_{50} values in μM using 15 human tumour cell lines (error: 5%)

Derivative/cell line	**9** (L-form)	**23** (D-form)	**12** (L-form)	**24** (D-form)	**15** (L-form)	**25** (D-form)
518A2	3.54 ± 0.18	2.26 ± 0.11	2.72 ± 0.14	2.76 ± 0.14	5.09 ± 0.25	5.48 ± 0.27
8505C	4.31 ± 0.22	2.92 ± 0.15	3.87 ± 0.19	4.43 ± 0.22	3.49 ± 0.17	3.51 ± 0.18
A253	3.61 ± 0.18	2.26 ± 0.11	2.33 ± 0.12	2.55 ± 0.13	3.51 ± 0.18	3.50 ± 0.18
A2780	2.98 ± 0.15	2.24 ± 0.11	2.59 ± 0.13	3.26 ± 0.16	2.08 ± 0.10	1.70 ± 0.09
A431	3.48 ± 0.17	2.36 ± 0.12	2.27 ± 0.11	2.76 ± 0.14	3.49 ± 0.17	3.11 ± 0.16
A549	2.77 ± 0.14	2.26 ± 0.11	3.43 ± 0.17	4.35 ± 0.22	3.43 ± 0.17	3.17 ± 0.16
DLD-1	4.49 ± 0.22	3.35 ± 0.17	3.72 ± 0.19	4.49 ± 0.22	5.54 ± 0.28	5.67 ± 0.28
FaDu	4.52 ± 0.23	2.25 ± 0.11	4.25 ± 0.21	3.90 ± 0.20	5.39 ± 0.27	5.48 ± 0.27
HCT-116	2.74 ± 0.14	2.25 ± 0.11	2.82 ± 0.14	4.25 ± 0.21	5.03 ± 0.25	4.82 ± 0.24
HCT-8	2.80 ± 0.14	2.26 ± 0.11	2.21 ± 0.11	2.42 ± 0.12	5.13 ± 0.26	3.32 ± 0.17
HT-29	2.87 ± 0.14	2.80 ± 0.14	2.50 ± 0.13	4.38 ± 0.22	4.60 ± 0.23	3.47 ± 0.17
Lipo	4.30 ± 0.22	3.56 ± 0.18	2.74 ± 0.14	4.13 ± 0.21	3.53 ± 0.18	4.73 ± 0.24
MCF-7	3.54 ± 0.18	2.25 ± 0.11	3.55 ± 0.18	3.55 ± 0.18	3.52 ± 0.18	3.52 ± 0.18
SW1736	3.22 ± 0.16	2.25 ± 0.11	2.92 ± 0.15	4.11 ± 0.21	3.54 ± 0.18	3.46 ± 0.17
SW480	3.52 ± 0.18	3.52 ± 0.18	2.79 ± 0.14	3.32 ± 0.17	3.50 ± 0.18	3.47 ± 0.17
Average	3.51 ± 0.18	2.59 ± 0.13	2.98 ± 0.15	3.64 ± 0.18	4.06 ± 0.20	3.89 ± 0.19

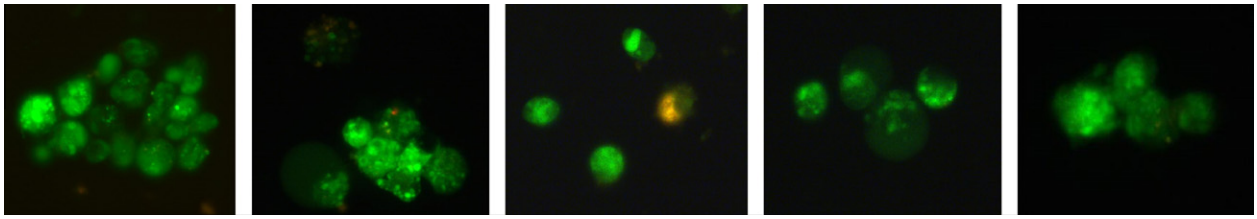

Figure 5. Results from the AO/EB test; treatment of A549 cells with (from left to right): GA (90 μM), **8** (8 μM), **9** (3.5 μM), **10** (3 μM) and **25** (3 μM).

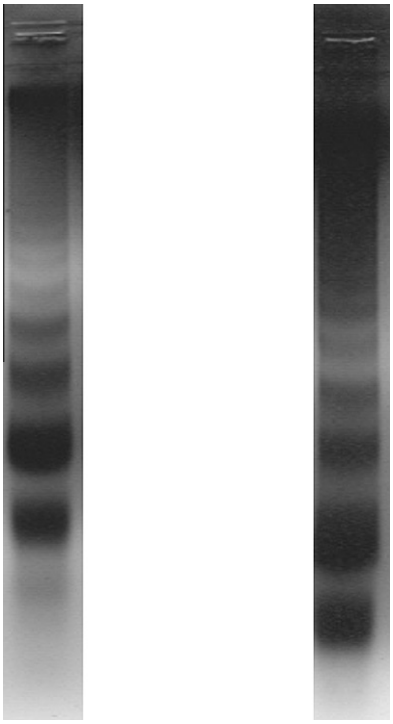

Figure 6. DNA laddering for the ovarian cancer cell line A2780 after treatment with IC_{90}-concentrations for 24 h; left trace: GA; right trace: compound **10**.

2-cyano-3,11-dioxo derivative [18–20] showed a cytotoxicity being comparable to the bioactivity observed for our compounds.

As demonstrated by fluorescence microscopy and DNA laddering experiments, the cytotoxicity of the compounds results from apoptotic processes. In summary, nearly of the GA derivatives showed a higher activity than GA and a better selectivity towards tumour cells.

4. Experimental

4.1. Biology

4.1.1. Cell lines and culture conditions

The cell lines 518A2, 8505C, A253, A2780, A431, A549, DLD-1, FaDu, HCT-116, HCT-8, HT-29, LIPO, MCF-7, NiH3T3, SW1736 and SW480 were included in this study. Cultures were maintained as monolayer in RPMI 1640 (PAA Laboratories, Pasching, Germany) supplemented with 10% heat inactivated foetal bovine serum (Biochrom AG, Berlin, Germany) and penicillin/streptomycin (PAA Laboratories) at 37 °C in a humidified atmosphere of 5% CO_2/95% air.

4.1.2. Cytotoxicity assay[21]

The cytotoxicity of the compounds was evaluated using the sulforhodamine B (SRB) (Sigma–Aldrich) microculture colorimetric assay. In short, exponentially growing cells were seeded into 96-well plates on day 0 at the appropriate cell densities to prevent confluence of the cells during the period of experiment. After 24 h, the cells were treated with serial dilutions of the compounds (0–100 μM) for 96 h. The final concentration of DMSO or DMF solvent never exceeded 0.5%, which was non-toxic to the cells. The percentages of surviving cells relative to untreated controls were determined 96 h after the beginning of drug exposure. After a 96 h treatment, the supernatant medium from the 96-well plates was thrown away and the cells were fixed with 10% TCA. For a thorough fixation, the plates were allowed to rest at 4 °C. After fixation, the cells were washed in a strip washer. The washing was done five times with water using alternate dispensing and aspiration procedures. Afterwards the plates were dyed with

100 μl of 0.4% SRB (sulforhodamine B) for about 20 min. The plates were washed with 1% acetic acid to remove the excess of the dye and allowed to air dry overnight. 100 μl of 10 mM Tris base solution were added to each well and absorbance was measured at 570 nm (using a 96-well plate reader, Tecan Spectra, Crailsheim, Germany). The IC_{50} was estimated by linear regression between the value before and after the 50% line is crossed in a dose–response curve.

4.1.3. Apoptosis test—acridine orange/ethidium bromide (AO/EB)[22]

Apoptotic cell death was analysed by acridine orange/ethidium bromide dye using fluorescence microscopy on A549 cells. Therefore approx. 500,000 cells were seeded in cell culture flasks and were allowed to grow for 24 h. The medium was removed and the substance loaded medium was added. After 24–48 h, the supernatant medium was collected and centrifuged; the pellet was suspended in phosphate-buffer saline (PBS) and centrifuged again. The liquid was removed, the pellet was suspended in PBS. After mixing the suspension with a solution of AO/EB, analysis was performed under a fluorescence microscope. While a green fluorescence shows apoptosis, a red coloured nucleus indicates necrotic cells.

4.1.4. Apoptosis test—DNA laddering

The DNA fragmentation assay was performed as described[23] previously.

4.2. Chemistry

4.2.1. General

Used reagents were bought from commercial suppliers without any further purification. NMR spectra were measured on VARIAN Gemini 200, Gemini 2000 or Unity 500 spectrometers at 27 °C with trimethylsilane as an internal standard, δ are given in ppm and J in Hertz. Mass spectra were taken on a FINNIGAN MAT TSQ 7000 (electronspray, voltage 4.5 kV, sheath gas nitrogen) instrument. IR spectra are recorded on a Perkin–Elmer FT-IR spectrometer Spectrum 1000, optical rotations on a Perkin–Elmer 341 polarimeter (1 cm micro cell) and UV–vis spectra on a Perkin–Elmer unit, Lambda 14. Melting points were measured with a LEICA hot stage microscope and are uncorrected. Elemental analysis was done on a Foss-Heraeus Vario EL unit. TLC was performed on silica gel (Merck 5554, detection by UV absorption). Solvents were dried before use according to usual procedures.

4.2.2. General procedure for the protection of the amino acids[24]

The amino acid (1 equiv) was dissolved in 1:1mixture of a potassium hydroxide solution (2 M in water) and 1,4-dioxane. Di *tert*-butyl dicarbonate (1.2 equiv) was added and the mixture allowed to stir at room temperature for 12 h. The solvent was removed under reduced pressure and ethyl acetate was added. After washing with aq sodium hydrogensulfate (10% in water), the mixture was extracted 3× with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and the solvent was evaporated. The crude protected amino acid was used without any further purification; for biological testing an analytic sample was obtained by chromatography.

4.2.3. General procedure for esterifications in position C(3) (method A)

The starting material (1 equiv) was dissolved in dry DCM, DMAP (20 mg, 0.16 mmol) and the protected amino acid (1.2 equiv) were added. After addition of DCC (1.2 equiv) the mixture was stirred at room temperature for 12 h, filtered and the filtrate was washed with water and brine, dried over sodium sulfate, filtered and the solvent was evaporated. Purification was performed by flash chromatography (SiO_2, hexane/ethyl acetate 8:2).

4.2.4. General procedure for deprotection (method B)

To a solution of the Boc-protected compound in dry DCM, trifluoroacetic acid (1 ml per 10 ml DCM) was added. The mixture was allowed to stir at room temperature for 12 h. After completion of the reaction (as monitored by TLC) the solution was washed with a satd aq sodium hydrogen carbonate. The aqueous layer was extracted with DCM, the combined organic extracts were washed with brine, dried over sodium sulfate, filtrated and evaporated to yield the amine.

4.2.5. General procedure for deprotection (method C)[25]

The solution of the benzyl ester (1 equiv) in a mixture of MeOH and THF (1:2) was purged with argon for 3 min, followed by the addition of ammonium formate (5 equiv). Palladium on activated coal (10%; 100 mg per mmol) was added and the mixture was stirred at room temperature for 12–14 h. The solvents were removed under reduced pressure and the residue was dissolved in DCM. Usual aqueous work-up followed by chromatography (SiO_2, hexane/ethyl acetate 1:1) yielded the product.

4.2.6. General procedure for deprotection (method D)

The Boc-protected compound was dissolved in dry DCM. After saturation with dry hydrogen chloride gas for 15 min stirring at room temperature was continued for 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed under reduced pressure. The residue was washed with ethyl acetate until no parent substance could be detected; analytical samples were obtained by re-crystallization.

4.2.6.1. Methyl 3β-hydroxy-11-oxo-olean-12-en-30-oate (1). To a solution of **GA** (31.00 g, 65.9 mmol) in dry DMF (150 ml) potassium carbonate (15.34 g, 111.0 mmol) was added. After 30 min of stirring at room temperatures, iodomethane (4.94 ml, 79.0 mmol) was added and the mixture was stirred for an additional 2 h. The solvents were evaporated and the crude residue was dissolved in a mixture of DCM (300 ml) and hydrochloric acid (50 ml, 1.0 M). The aqueous layer was extracted with DCM (3 × 50 ml), the combined organic layers were washed with brine (50 ml), dried (Na_2SO_4), filtered and the solvent was evaporated. Recrystallization from MeOH yielded **1** (29.09 g, 91.1%) as a colourless solid; mp 254–258 °C (lit. 254–258 °C,[26] 254 °C[27]); R_f = 0.48 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 141.18 (c 0.48, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 270 nm (4.15); MS (ESI): m/z (%) = 485.5 ($[M+H]^+$, 55), 507.5 ($[M+Na]^+$, 12), 539.1 ($[M+Na+MeOH]^+$, 100); IR (KBr): ν = 3614 (br), 2970 (s), 2955 (s), 2875 (m), 1726 (s), 1659 (s), 1466 (m), 1450 (m), 1364 (w), 1216 (m), 1189 (m), 1136 (w), 1085 (w), 1040 (w), 992 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.65 (s, 1H, H-12), 3.67 (s, 3H, $COOCH_3$), 3.21 (dd, 1H, H-3, J = 10.8, 5.7 Hz), 2.78 (ddd, 1H, H-1, J = 13.3, 3.3, 3.37 Hz), 2.32 (s, 1H, H-9), 2.06 (dd, 1H, H-18, J = 13.3, 3.87 Hz), 2.00 (m, 1H, H-15), 1.95 (m, 1H, H-21), 1.90 (dd, 1H, H-19, J = 13.8, 3.97 Hz), 1.83 (ddd, 1H, H-16, J = 14.3, 14.3, 5.27 Hz), 1.65 (m, 1H, H-2), 1.62 (m, 1H, H-7), 1.58 (m, 1H, H-2′), 1.57 (m, 1H, H-19′), 1.57 (m, 1H, H-6), 1.43 (m, 1H, H-6′), 1.38 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.30 (m, 1H, H-22′), 1.28 (m, 1H, H-21′), 1.17 (m, 1H, H-16′), 1.13 (s, 3H, H-28), 1.12 (s, 3H, H-25), 1.11 (s, 3H, H-26), 1.00 (m, 1H, H-15′), 0.99 (s, 3H, H-23), 0.96 (m, 1H, H-1′), 0.79 (s, 3H, H-24), 0.79 (s, 3H, H-29), 0.68 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.8 (C-30), 169.0 (C-13), 128.6 (C-12), 78.8 (C-3), 61.9 (C-9), 55.1 (C-5), 51.8 ($COOCH_3$), 48.5 (C-18), 45.5 (C-8), 44.1 (C-20), 43.3 (C-14), 41.2

(C-19), 39.2 (C-1), 39.2 (C-4), 37.8 (C-22), 37.2 (C-10), 32.9 (C-7), 31.9 (C-17), 31.2 (C-21), 28.6 (C-29), 28.4 (C-23), 28.2 (C-28), 27.4 (C-2), 26.6 (C-16), 26.6 (C-15), 23.5 (C-27), 18.8 (C-26), 17.6 (C-6), 16.4 (C-25), 15.6 (C-24).

4.2.6.2. Ethyl 3β-hydroxy-11-oxo-olean-12-en-30-oate (2). Following the procedure given for **1**, compound **2** was obtained from GA and iodoethane as a white solid (1.75 g, 82%); mp 220–224 °C (lit. 93–94 °C[7]); R_f = 0.40 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 144.35 (*c* 0.48, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 267 nm (3.90); MS (ESI): *m/z* (%) = 499.5 ($[M+H]^+$, 90), 521.4 ($[M+Na]^+$, 13), 552.9 ($[M+Na+MeOH]^+$, 100); IR (KBr): *ν* = 3543 (br), 2939 (s), 2869 (m), 1726 (s), 1651 (s), 1616 (m), 1455 (m), 1389 (m), 1364 (w), 1330 (m), 1312 (w), 1278 (w), 1257 (m), 1210 (m), 1172 (s), 1135 (w), 1086 (m), 1042 (m), 1028 (m), 994 (m), 920 (w), 880 (w), 767 (w), 704 (w), 671 (w), 604 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.61 (s, 1H, H-12), 4.16 (dq, 1H, methylene-*H*H′, *J* = 10.8, 7.17 Hz), 4.10 (dq, 1H, methylene-H*H*′, *J* = 10.8, 7.17 Hz), 3.19 (dd, 1H, H-3, *J* = 11.1, 5.17 Hz), 2.76 (ddd, 1H, H-1, *J* = 13.5, 3.6, 3.67 Hz), 2.31 (s, 1H, H-9), 2.07 (ddd, 1H, H-18, *J* = 12.5, 4.1, 1.17 Hz), 2.00 (ddd, 1H, H-15, *J* = 13.7, 13.7, 4.57 Hz), 1.96 (m, 1H, H-21), 1.88 (ddd, 1H, H-19, *J* = 13.5, 4.2, 2.87 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.37 Hz), 1.64 (m, 1H, H-2), 1.61 (m, 1H, H-7), 1.58 (m, 1H, H-2′), 1.57 (m, 1H, H-19′), 1.56 (m, 1H, H-6), 1.42 (ddd, 1H, H-6′, *J* = 12.4, 3.1, 3.17 Hz), 1.38 (m, 1H, H-7′), 1.35 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.28 (m, 1H, H-22′), 1.26 (m, 1H, H-21′), 1.23 (t, 3H, ethyl, *J* = 7.17 Hz), 1.15 (m, 1H, H-16′, *J* = 13.7, 4.5, 2.77 Hz), 1.11 (s, 3H, H-28), 1.11 (s, 3H, H-25), 1.10 (s, 3H, H-26), 0.99 (m, 1H, H-15′), 0.97 (s, 3H, H-23), 0.95 (ddd, 1H, H-1′, *J* = 10.4, 4.4, 4.47 Hz), 0.78 (s, 3H, H-24), 0.78 (s, 3H, H-29), 0.67 (dd, 1H, H-5, *J* = 11.5, 1.67 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.2 (C-11), 176.3 (C-30), 169.2 (C-13), 128.5 (C-12), 78.7 (C-3), 61.8 (C-9), 60.3 (ethylene), 54.9 (C-5), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.1 (C-19), 39.1 (C-1), 39.1 (C-4), 37.7 (C-22), 37.1 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 27.3 (C-2), 26.5 (C-16), 26.4 (C-15), 23.4 (C-27), 18.7 (C-26), 17.5 (C-6), 16.3 (C-25), 15.5 (C-24), 14.3 (methyl).

4.2.6.3. *i*-Propyl 3β-hydroxy-11-oxo-olean-12-en-30-oate (3). Compound **3** was obtained from GA and *i*-propyl iodide as a white solid (3.48 g, 59%); mp 209–213 °C (lit. 238 °C (dec)[7]); R_f = 0.50 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 145.82 (*c* 0.37, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.09); MS (ESI): *m/z* (%) = 513.5 ($[M+H]^+$, 68), 567.0 ($[M+MeOH+Na]^+$, 92), 1025.3 ($[2M+H]^+$, 80), 1047.3 ($[2M+Na]^+$, 100); IR (KBr): *ν* = 3521 (br), 2980 (s), 2946 (s), 2856 (s), 1720 (s), 1642 (s), 1612 (m), 1457 (s), 1388 (s), 1327 (m), 1309 (m), 1278 (m), 1255 (m), 1210 (s), 1174 (s), 1135 (m), 1106 (s), 1084 (m), 1047 (m), 1028 (m), 996 (m), 981 (m), 948 (w), 917 (m), 878 (w), 848 (s), 769 (w), 715 (w), 702 (w), 688 (w), 673 (w), 636 (w), 591 (w), 541 (w), 475 (w), 424 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.00 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 3.20 (dd, 1H, H-3, *J* = 10.9, 5.57 Hz), 2.76 (ddd, 1H, H-1, *J* = 13.3, 3.6, 3.6), 2.32 (s, 1H, H-9), 2.07 (dd, 1H, H-18, *J* = 13.4, 3.47 Hz), 2.02 (ddd, 1H, H-15, *J* = 13.7, 13.7, 4.67 Hz), 1.97 (m, 1H, H-21), 1.87 (m, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.6, 13.6, 4.57 Hz), 1.67 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.1, 13.17 Hz), 1.57 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.34 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.28 (m, 1H, H-21′), 1.27 (m, 1H, H-22′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.16 (m, 1H, H-16′), 1.11 (s, 3H, H-28), 1.10 (s, 6H, H-25 and H-26), 0.99 (m, 1H, H-15′), 0.98 (s, 3H, H-23), 0.95 (m, 1H, H-1′), 0.78 (s, 3H, H-24), 0.77 (s, 3H, H-29), 0.67 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.2 (C-11), 175.8 (C-30), 169.4 (C-13), 128.5 (C-12), 78.8 (C-3), 67.4 (*i*-Pr-CH), 61.8 (C-9), 54.9 (C-5), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.1 (C-19), 39.1 (C-1), 39.1 (C-4), 37.7 (C-22), 37.1 (C-10), 32.8 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.2 (C-23), 28.1 (C-28), 27.3 (C-2), 26.5 (C-16), 26.4 (C-15), 23.4 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.7 (C-26), 17.5 (C-6), 16.3 (C-25), 15.6 (C-24).

4.2.6.4. Benzyl 3β-hydroxy-11-oxo-olean-12-en-30-oate (4). Compound **4** was obtained from GA and benzyl bromide as a white solid (8.61 g, 73%); mp 134–137 °C (lit. 125–126 °C,[7] 129–30 °C,[28] 131–133 °C[29]); R_f = 0.45 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 136.41 (*c* 0.25, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 207 nm (4.08), 249 nm (4.12); MS (ESI): *m/z* (%) = 561.5 ($[M+H]^+$, 56), 583.4 ($[M+Na]^+$, 26), 863.9 ($[3M+2Na]^{2+}$, 10), 1121.2 ($[2M+H]^+$, 54), 1143.3 ($[2M+Na]^+$, 100); IR (KBr): *ν* = 3432 (br), 2932 (s), 2870 (m), 1725 (s), 1654 (s), 1616 (w), 1467 (m), 1455 (m), 1387 (m), 1356 (w), 1323 (w), 1280 (w), 1257 (w), 1215 (m), 1188 (m), 1150 (s), 1084 (m), 1038 (m), 995 (m), 954 (w), 917 (w), 880 (w), 821 (w), 754 (w), 699 (m), 674 (w), 607 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 5H, H-Ar), 5.53 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.37 Hz), 5.07 (d, 1H, Bn-CH*H*′, *J* = 12.47 Hz), 3.20 (dd, 1H, H-3, *J* = 11.1, 5.47 Hz), 2.77 (ddd, 1H, H-1, *J* = 13.2, 3.7, 3.77 Hz), 2.30 (s, 1H, H-9), 2.02 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.95 (m, 1H, H-21), 1.91 (dd, 1H, H-19, *J* = 13.5, 3.9, 2.67 Hz), 1.79 (ddd, 1H, H-16, *J* = 13.4, 13.4, 4.57 Hz), 1.66 (m, 1H, H-2), 1.62 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.1, 13.17 Hz), 1.57 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.34 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.29 (m, 1H, H-21′), 1.28 (m, 1H, H-22′), 1.15 (m, 1H, H-16′), 1.14 (s, 3H, H-28), 1.12 (s, 3H, H-25), 1.09 (s, 3H, H-26), 0.99 (m, 1H, H-15′), 0.98 (s, 3H, H-23), 0.97 (m, 1H, H-1′), 0.78 (s, 3H, H-24), 0.71 (s, 3H, H-29), 0.67 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.1 (C-11), 176.2 (C-30), 168.9 (C-13), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.6 (C_{ar}), 128.4 (C-12), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 78.7 (C-3), 66.2 (Bn-CH_2), 61.8 (C-9), 54.9 (C-5), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.1 (C-14), 41.1 (C-19), 39.1 (C-1), 39.1 (C-4), 37.6 (C-22), 37.1 (C-10), 32.7 (C-7), 31.7 (C-17), 31.1 (C-21), 28.4 (C-29), 28.3 (C-23), 28.1 (C-28), 27.3 (C-2), 26.4 (C-16), 26.4 (C-15), 23.3 (C-27), 18.7 (C-26), 17.5 (C-6), 16.3 (C-25), 15.5 (C-24).

4.2.6.5. 3β-(Glycyl)-11-oxo-olean-12-en-30-oic acid hydrochloride (5). Obtained from **26** by method D as a colourless powder; yield: 210 mg, 63%; mp 300–302 °C (decomp.); R_f = 0.69 (MeOH); $[\alpha]_D^{20}$ = 82.99 (*c* 0.50, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (3.93); MS (ESI): *m/z* (%) = 528.2 ($[M+H]^+$, 100); IR (KBr): *ν* = 3420 (br), 2951 (s), 1746 (s), 1656 (s), 1466 (s), 1389 (s), 1324 (m), 1245 (s), 1086 (s), 987 (m), 909 (m), 819 (w), 749 (w), 670 (w), 589 (w), 542 (w), 462 (w) cm^{-1}; ^1H NMR (400 MHz, MeOH-d_4): δ = 5.59 (s, 1H, H-12), 4.68 (dd, 1H, H-3, *J* = 12.0, 4.67 Hz), 3.84 (dd, 2H, Gly-CH_2, *J* = 23.3, 17.17 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.6, 3.67 Hz), 2.50 (s, 1H, H-9), 2.20 (m, 1H, H-18), 2.15 (ddd, 1H, H-15, *J* = 13.3, 13.3, 4.67 Hz), 1.95 (m, 1H, H-21), 1.88 (m, 1H, H-16), 1.84 (m, 1H, H-19), 1.79 (m, 1H, H-2), 1.75 (m, 1H, H-7), 1.71 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.67 (m, 1H, H-2′), 1.64 (m, 1H, H-6), 1.53 (m, 1H, H-6′), 1.49 (m, 1H, H-7′), 1.47 (m, 1H, H-22), 1.43 (s, 3H, H-27), 1.39 (m, 1H, H-21′), 1.25 (m, 1H, H-22′), 1.23 (m, 1H, H-16′), 1.17 (s, 3H, H-25), 1.16 (s, 3H, H-28), 1.15 (s, 3H, H-28), 1.12 (m, 1H, H-1′), 1.04 (m, 1H, H-15′), 0.94 (s, 3H, H-23), 0.93 (s, 3H, H-24), 0.91 (m, 1H, H-5), 0.83 (s, 3H, H-29); ^{13}C NMR (125 MHz, MeOH-d_4): δ = 200.9 (C-11), 178.9 (C-30), 171.6 (Gly-COO), 167.0 (C-13), 127.4 (C-12), 83.2 (C-3), 61.4 (C-9), 54.6 (C-5), 48.5 (C-18), 45.3 (C-8), 43.2 (C-20), 41.0 (C-14), 39.7 (C-19), 38.2 (Gly-CH_2), 37.7 (C-1 and C-4), 37.6 (C-22), 36.8 (C-10), 32.2 (C-7), 31.5 (C-17), 30.6 (C-21), 27.8 (C-29), 27.3 (C-23), 27.0 (C-28), 26.2 (C-16), 25.9 (C-15), 23.0 (C-2), 22.4 (C-27), 17.8 (C-26), 17.0 (C-6), 15.6 (C-24), 15.5

(C-25). Anal. Calcd for $C_{32}H_{50}ClNO_5$ (564.20): C, 68.12; H, 8.93; Cl, 6.28; N, 2.48. Found: C, 68.01; H, 9.17; Cl, 6.13; N, 2.41.

4.2.6.6. 3β-(L-Alanyl)-11-oxo-olean-12-en-30-oic acid hydrochloride (6). Obtained from **27** by method D as a colourless powder; yield: 50 mg, 51%; mp 309–311 °C (decomp.); R_f = 0.75 (MeOH); $[\alpha]_D^{20}$ = 103.68 (*c* 0.58, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.01); MS (ESI): *m/z* (%) = 542.1 ($[M+H]^+$, 100); IR (KBr): ν = 3421 (br), 2962 (s), 2642 (m), 2585 (m), 2512 (w), 2012 (w), 1737 (s), 1707 (s), 1651 (s), 1604 (s), 1518 (m), 1456 (s), 1388 (s), 1364 (m), 1326 (m), 1290 (s), 1262 (s), 1213 (s), 1163 (s), 1111 (s), 1049 (m), 1021 (m), 984 (m), 958 (m), 913 (m), 885 (w), 869 (w), 804 (w), 771 (w), 748 (w), 700 (w), 683 (w), 672 (w), 589 (w), 542 (w) cm^{-1}; ^1H NMR (400 MHz, MeOH-d_4): δ = 5.59 (s, 1H, H-12), 4.67 (dd, 1H, H-3, *J* = 12.0, 4.57 Hz), 4.09 (q, 1H, Ala-CH, *J* = 7.27 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.6, 3.4, 3.47 Hz), 2.50 (s, 1H, H-9), 2.21 (m, 1H, H-18), 2.15 (ddd, 1H, H-15, *J* = 13.7, 13.7, 4.37 Hz), 1.94 (m, 1H, H-21), 1.89 (m, 1H, H-16), 1.84 (m, 1H, H-19), 1.78 (m, 1H, H-2), 1.75 (m, 1H, H-7), 1.71 (dd, 1H, H-19′, *J* = 13.2, 13.27 Hz), 1.67 (m, 1H, H-2′), 1.63 (m, 1H, H-6), 1.56 (d, 3H, Ala-CH_3, *J* = 7.37 Hz), 1.53 (m, 1H, H-6′), 1.49 (m, 1H, H-7′), 1.47 (m, 1H, H-22), 1.43 (s, 3H, H-27), 1.40 (m, 1H, H-21′), 1.25 (m, 1H, H-22′), 1.24 (m, 1H, H-16′), 1.18 (s, 3H, H-25), 1.17 (s, 3H, H-28), 1.15 (s, 3H, H-28), 1.13 (m, 1H, H-1′), 1.05 (m, 1H, H-15′), 0.95 (s, 3H, H-23), 0.93 (s, 3H, H-24), 0.92 (m, 1H, H-5), 0.83 (s, 3H, H-29); ^{13}C NMR (125 MHz, MeOH-d_4): δ = 200.9 (C-11), 178.9 (C-30), 171.6 (Ala-COO), 169.4 (C-13), 127.4 (C-12), 83.2 (C-3), 61.4 (C-9), 54.5 (C-5), 48.7 (Ala-CH), 48.5 (C-18), 45.3 (C-8), 43.2 (C-20), 41.0 (C-14), 38.2 (C-19), 37.9 (C-1), 37.6 (C-4), 37.6 (C-22), 36.8 (C-10), 32.2 (C-7), 31.5 (C-17), 30.6 (C-21), 27.8 (C-29), 27.3 (C-23), 27.1 (C-28), 26.2 (C-16), 25.9 (C-15), 23.0 (C-2), 22.4 (C-27), 17.8 (C-26), 16.9 (C-6), 15.7 (C-24), 15.5 (C-25), 15.0 (Ala-CH_3). Anal. Calcd for $C_{33}H_{52}ClNO_5$ (578.22): C, 68.55; H, 9.06; Cl, 6.13; N, 2.42. Found: C, 68.29; H, 9.21; Cl, 6.24; N, 2.34.

4.2.6.7. 3β-(β-Alanyl)-11-oxo-olean-12-en-30-oic acid hydrochloride (7). Obtained from **28** by method D as a colourless powder; yield: 100 mg, 39%; mp 305–309 °C (decomp.); R_f = 0.48 (MeOH); $[\alpha]_D^{20}$ = 117.25 (*c* 0.51, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.08); MS (ESI): *m/z* (%) = 542.3 ($[M+H]^+$, 100); IR (KBr): ν = 3355 (br), 3258 (m), 2957 (s), 2363 (w), 1724 (s), 1652 (s), 1582 (m), 1527 (m), 1466 (s), 1389 (s), 1365 (s), 1325 (m), 1306 (m), 1278 (m), 1233 (s), 1165 (s), 1105 (s), 1061 (w), 1022 (m), 983 (s), 918 (w), 883 (w), 850 (w), 750 (w), 700 (w), 683 (w), 669 (w), 589 (w), 541 (w) cm^{-1}; ^1H NMR (500 MHz, MeOH-d_4): δ = 5.57 (s, 1H, H-12), 4.57 (dd, 1H, H-3, *J* = 11.7, 5.07 Hz), 3.18 (t, 2H, Ala-CH_2NH_2, *J* = 6.77 Hz), 2.74 (m, 1H, H-1), 2.73 (m, 2H, Ala-CH_2COO), 2.47 (s, 1H, H-9), 2.19 (m, 1H, H-18), 2.13 (ddd, 1H, H-15, *J* = 13.6, 13.6, 4.27 Hz), 1.92 (m, 1H, H-21), 1.87 (m, 1H, H-16), 1.82 (m, 1H, H-19), 1.75 (m, 1H, H-7), 1.72 (m, 1H, H-2), 1.69 (dd, 1H, H-19′, *J* = 13.2, 13.27 Hz), 1.64 (m, 1H, H-2′), 1.60 (m, 1H, H-6), 1.51 (m, 1H, H-6′), 1.44 (m, 1H, H-7′), 1.41 (s, 3H, H-27), 1.40 (m, 3H, H-22 and H-21′ and H-22′), 1.23 (m, 1H, H-16′), 1.15 (s, 6H, H-25 and H-28), 1.13 (s, 3H, H-26), 1.09 (m, 1H, H-1′), 1.03 (m, 1H, H-15′), 0.90 (s, 6H, H-23 and H-24), 0.87 (m, 1H, H-5), 0.82 (s, 3H, H-29); ^{13}C NMR (125 MHz, MeOH-d_4): δ = 200.9 (C-11), 179.0 (C-30), 171.6 (Ala-COO), 170.6 (C-13), 127.4 (C-12), 81.7 (C-3), 61.5 (C-9), 54.7 (C-5), 48.5 (C-18), 45.3 (C-8), 43.5 (C-20), 43.2 (C-14), 41.0 (C-19), 38.3 (C-1), 37.7 (C-4), 37.6 (C-22), 36.8 (C-10), 35.0 (Ala-CH_2NH_2), 32.2 (C-7), 31.5 (C-17), 30.9 (Ala-CH_2COO), 30.6 (C-21), 27.8 (C-29), 27.3 (C-28), 27.1 (C-23), 26.2 (C-16), 25.9 (C-15), 23.0 (C-2), 22.4 (C-27), 17.8 (C-26), 17.0 (C-6), 15.7 (C-24), 15.5 (C-25). Anal. Calcd for $C_{33}H_{52}ClNO_5$ (578.22): C, 68.55; H, 9.06; Cl, 6.13; N, 2.42. Found: C, 68.43; H, 9.22; Cl, 6.24; N, 2.19.

4.2.6.8. Methyl 3β-(glycyl)-11-oxo-olean-12-en-30-oate (8). Obtained from **29** by method B as a colourless powder; yield: 200 mg, 79%; mp 280–282 °C; R_f = 0.57 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 123.02 (*c* 0.43, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.08); MS (ESI): *m/z* (%) = 542.2 ($[2M+2H]^{2+}$, 10); IR (KBr): ν = 3382 (br), 2966 (s), 2873 (m), 2856 (m), 2362 (w), 1743 (s), 1728 (s), 1651 (s), 1467 (m), 1454 (m), 1390 (m), 1361 (w), 1320 (w), 1278 (w), 1248 (w), 1217 (s), 1190 (m), 1155 (m), 1086 (m), 1049 (w), 1023 (w), 984 (w), 971 (m), 921 (m), 880 (w), 869 (s), 770 (w), 748 (w), 702 (w), 668 (w), 591 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.63 (s, 1H, H-12), 4.55 (dd, 1H, H-3, *J* = 11.6, 4.67 Hz), 3.66 (s, 3H, OMe), 3.41 (s, 2H, Gly-CH_2), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.6, 3.67 Hz), 2.33 (s, 1H, H-9), 2.05 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, *J* = 13.3, 3.7, 2.57 Hz), 1.79 (ddd, 1H, H-16, *J* = 14.2, 14.2, 4.67 Hz), 1.69 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.61 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.56 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.37 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.28 (m, 1H, H-21′), 1.15 (m, 1H, H-16′), 1.13 (s, 3H, H-25), 1.12 (s, 3H, H-26), 1.09 (s, 3H, H-28), 1.03 (ddd, 1H, H-1′, *J* = 13.3, 13.3, 3.87 Hz), 0.98 (m, 1H, H-15′), 0.85 (s, 6H, H-23 and H-24), 0.78 (m, 1H, H-5), 0.77 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 173.9 (Gly-COO), 169.2 (C-13), 128.5 (C-12), 81.4 (C-3), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 44.0 (Gly-CH_2), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{33}H_{51}NO_5$ (541.76): C, 73.16; H, 9.49; N, 2.59. Found: C, 73.02; H, 9.57; N, 2.41.

4.2.6.9. Methyl 3β-(L-alanyl)-11-oxo-olean-12-en-30-oate (9). Obtained from **30** by method B as a colourless powder; yield: 200 mg, 91%; mp 264–267 °C; R_f = 0.59 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 137.30 (*c* 0.35, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.07); MS (ESI): *m/z* (%) = 556.1 ($[M+H]^+$, 100); IR (KBr): ν = 3442 (br), 2958 (s), 2874 (m), 1731 (s), 1652 (s), 1616 (m), 1457 (m), 1389 (m), 1362 (w), 1318 (m), 1278 (w), 1248 (m), 1217 (s), 1191 (s), 1154 (s), 1087 (m), 1064 (w), 1050 (w), 1022 (w), 986 (m), 973 (w), 984 (w), 918 (w), 880 (w), 868 (w), 825 (w), 770 (w), 685 (w), 671 (w), 590 (w), 544 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.54 (dd, 1H, H-3, *J* = 11.9, 4.67 Hz), 3.66 (s, 3H, OMe), 3.55 (q, 1H, Ala-CH, *J* = 7.27 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.3, 3.6, 3.67 Hz), 2.34 (s, 1H, H-9), 2.06 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.90 (ddd, 1H, H-19, *J* = 13.8, 4.1, 2.67 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.9, 13.9, 4.77 Hz), 1.70 (m, 1H, H-2), 1.63 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.39 (m, 1H, H-7′), 1.35 (m, 1H, H-22), 1.35 (m, 3H, Ala-CH_3), 1.34 (s, 3H, H-27), 1.29 (m, 2H, H-22′ and H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.12 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.8, 13.8, 3.67 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.85 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 175.9 (Ala-COO), 169.2 (C-13), 128.5 (C-12), 81.2 (C-3), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 50.3 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 20.6 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{34}H_{53}NO_5$ (555.79): C, 73.47; H, 9.61; N, 2.52. Found: C, 73.28; H, 9.81; N, 2.34.

4.2.6.10. Methyl 3β-(β-alanyl)-11-oxo-olean-12-en-30-oate (10). Obtained from **31** by method B as a colourless powder;

yield: 370 mg, 95%; mp 267–270 °C; R_f = 0.21 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 121.76 (*c* 0.48, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.07); MS (ESI): *m/z* (%) = 556.2 ($[M+H]^+$, 100); IR (KBr): ν = 3380 (br), 2960 (s), 2874 (m), 1726 (s), 1652 (s), 1465 (m), 1388 (m), 1368 (m), 1318 (m), 1278 (w), 1250 (m), 1218 (s), 1188 (s), 1160 (s), 1087 (m), 1070 (w), 1023 (w), 986 (m), 948 (w), 918 (w), 880 (w), 853 (w), 824 (w), 770 (w), 721 (w), 685 (w), 669 (w), 590 (w), 543 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 4.49 (dd, 1H, H-3, *J* = 11.8, 4.77 Hz), 3.62 (s, 3H, OMe), 2.94 (m, 2H, Ala-CH_2NH_2), 2.74 (ddd, 1H, H-1, *J* = 13.8, 3.5, 3.57 Hz), 2.42 (t, 2H, Ala-CH_2COO, *J* = 6.37 Hz), 2.30 (s, 1H, H-9), 2.02 (dd, 1H, H-18, *J* = 13.8, 3.77 Hz), 1.96 (ddd, 1H, H-15, *J* = 13.7, 13.7, 4.57 Hz), 1.92 (m, 1H, H-21), 1.86 (ddd, 1H, H-19, *J* = 13.8, 4.2, 3.07 Hz), 1.76 (ddd, 1H, H-16, *J* = 13.8, 13.8, 4.57 Hz), 1.66 (ddd, 1H, H-2, *J* = 13.4, 13.4, 3.57 Hz), 1.60 (m, 1H, H-7), 1.56 (m, 1H, H-2′), 1.55 (dd, 1H, H-19′, *J* = 13.6, 13.67 Hz), 1.52 (m, 1H, H-6), 1.40 (ddd, 1H, H-6′, *J* = 12.8, 12.8, 3.27 Hz), 1.35 (m, 1H, H-7′), 1.31 (m, 1H, H-22), 1.30 (s, 3H, H-27), 1.25 (m, 2H, H-22′ and H-21′), 1.11 (m, 1H, H-16′), 1.10 (s, 3H, H-25), 1.08 (s, 3H, H-28), 1.06 (s, 3H, H-26), 0.99 (ddd, 1H, H-1′, *J* = 13.6, 13.6, 3.67 Hz), 0.95 (m, 1H, H-15′), 0.82 (s, 6H, H-23 and H-24), 0.75 (m, 1H, H-5), 0.74 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 172.4 (Ala-COO), 169.2 (C-13), 128.5 (C-12), 80.7 (C-3), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.0 (C-4 and Ala-CH_2COO), 37.9 (Ala-CH_2NH_2), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-28), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{34}H_{53}NO_5$ (555.79): C, 73.47; H, 9.61; N, 2.52. Found: C, 73.32; H, 9.83; N, 2.37.

4.2.6.11. Ethyl 3β-(glycyl)-11-oxo-olean-12-en-30-oate (11). Obtained from **32** by method B as a colourless powder; yield: 145 mg, 97%; mp 204–206 °C; R_f = 0.27 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 126.20 (*c* 0.57, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.05); MS (ESI): *m/z* (%) = 556.3 ($[2M+2H]^{2+}$, 100), 834.3 ($[3M+2H]^{2+}$, 10), 1111.8 ($[2M+H]^+$, 8); IR (KBr): ν = 3366 (br), 3216 (w), 2958 (s), 2874 (m), 1742 (s), 1713 (s), 1651 (s), 1616 (w), 1464 (m), 1390 (m), 1377 (w), 1363 (w), 1321 (m), 1278 (w), 1249 (w), 1217 (s), 1175 (s), 1114 (w), 1087 (w), 1032 (w), 986 (m), 970 (m), 948 (w), 919 (w), 901 (w), 879 (w), 770 (w), 751 (w), 669 (w), 589 (w), 544 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.57 (dd, 1H, H-3, *J* = 11.8, 4.87 Hz), 4.18 (dq, 1H, COOC*H*H′, *J* = 10.8, 7.17 Hz), 4.11 (dq, 1H, COOCH*H*′, *J* = 10.8, 7.17 Hz), 3.41 (s, 2H, Gly-CH_2), 2.81 (ddd, 1H, H-1, *J* = 13.7, 3.6, 3.67 Hz), 2.36 (s, 1H, H-9), 2.10 (ddd, 1H, H-18, *J* = 13.4, 4.0, 0.87 Hz), 2.02 (ddd, 1H, H-15, *J* = 13.6, 13.6, 4.47 Hz), 1.98 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, *J* = 13.6, 4.1, 2.87 Hz), 1.82 (ddd, 1H, H-16, *J* = 13.6, 13.6, 4.57 Hz), 1.71 (m, 1H, H-2), 1.68 (m, 1H, H-7), 1.66 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 13.7, 13.77 Hz), 1.57 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.36 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.31 (m, 1H, H-21′), 1.25 (t, 3H, $COOCH_2CH_3$, *J* = 7.17 Hz), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.12 (s, 3H, H-26), 1.06 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.67 Hz), 1.01 (m, 1H, H-15′), 0.87 (s, 6H, H-23 and H-24), 0.81 (m, 1H, H-5), 0.79 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 174.1 (Gly-COO), 169.4 (C-13), 128.4 (C-12), 81.3 (C-3), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 44.1 (Gly-CNH), 43.8 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{34}H_{53}NO_5$ (555.79): C, 73.47; H, 9.61; N, 2.52. Found: C, 73.51; H, 9.84; N, 2.28.

4.2.6.12. Ethyl 3β-(L-alanyl)-11-oxo-olean-12-en-30-oate (12). Obtained from **33** by method B as a colourless powder; yield: 297 mg, 92%; mp 201–205 °C; R_f = 0.27 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 131.56 (*c* 0.52, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.09); MS (ESI): *m/z* (%) = 570.4 ($[M+H]^+$, 100), 855.4 ($[[3M+2H]]^{2+}$, 10), 1139.9 ($[2M+H]^+$, 6); IR (KBr): ν = 3425 (br), 2960 (s), 2874 (m), 1728 (s), 1654 (s), 1617 (w), 1456 (m), 1389 (m), 1324 (w), 1279 (w), 1247 (w), 1217 (s), 1176 (s), 1086 (w), 1075 (w), 1031 (w), 985 (w), 972 (w), 948 (w), 917 (w), 866 (w), 768 (w), 685 (w), 589 (w), 544 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.62 (s, 1H, H-12), 4.54 (dd, 1H, H-3, *J* = 11.6, 4.67 Hz), 4.17 (dq, 1H, COOC*H*H′, *J* = 10.8, 7.17 Hz), 4.10 (dq, 1H, COOCH*H*′, *J* = 10.8, 7.17 Hz), 3.52 (q, 1H, Ala-C*H*NH_2, *J* = 7.17 Hz), 2.80 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.35 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.7, 3.77 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.3, 13.3, 4.27 Hz), 1.97 (m, 1H, H-21), 1.90 (ddd, 1H, H-19, *J* = 13.7, 4.2, 2.97 Hz), 1.81 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.67 Hz), 1.70 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.57 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.37 (m, 3H, H-27), 1.35 (s, 3H, H-27), 1.34 (d, 3H, Ala-CH_3, *J* = 7.17 Hz), 1.31 (m, 1H, H-22′), 1.29 (m, 1H, H-21′), 1.24 (t, 3H, $COOCH_2CH_3$, *J* = 7.17 Hz), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.12 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.77 Hz), 1.00 (m, 1H, H-15′), 0.88 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.80 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.4 (C-30 and Ala-COO), 169.4 (C-13), 128.4 (C-12), 81.1 (C-3), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0 (C-5), 50.3 (Ala-CNH), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 20.8 (Ala-CH_3), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{35}H_{55}NO_5$ (569.81): C, 73.77; H, 9.73; N, 2.46. Found: C, 73.51; H, 9.84; N, 2.22.

4.2.6.13. Ethyl 3β-(β-alanyl)-11-oxo-olean-12-en-30-oate (13). Obtained from **34** by method B as a colourless powder; yield: 127 mg, 93%; mp 181–184 °C; R_f = 0.12 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 125.66 (*c* 0.51, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.14); MS (ESI): *m/z* (%) = 570.3 ($[2M+2H]^{2+}$, 100); IR (KBr): ν = 3434 (br), 2958 (s), 2873 (m), 1727 (s), 1653 (s), 1465 (m), 1389 (m), 1362 (w), 1324 (m), 1278 (w), 1248 (m), 1218 (s), 1174 (s), 1087 (m), 1021 (w), 985 (m), 878 (w), 769 (w), 684 (w), 669 (w), 589 (w), 543 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.55 (dd, 1H, H-3, *J* = 11.8, 4.87 Hz), 4.18 (dq, 1H, COOC*H*H′, *J* = 10.8, 7.17 Hz), 4.11 (dq, 1H, COOCH*H*′, *J* = 10.8, 7.17 Hz), 2.98 (m, 2H, Ala-CH_2NH_2), 2.80 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.46 (t, 2H, Ala-CH_2COO, *J* = 6.67 Hz), 2.36 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 13.5, 3.67 Hz), 2.02 (ddd, 1H, H-15, *J* = 13.5, 13.5, 4.47 Hz), 1.98 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, *J* = 13.6, 3.8, 2.97 Hz), 1.82 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.77 Hz), 1.71 (m, 1H, H-2), 1.67 (m, 1H, H-7), 1.60 (dd, 1H, H-19′, *J* = 13.6, 13.67 Hz), 1.60 (m, 1H, H-2′), 1.58 (m, 1H, H-6), 1.46 (m, 1H, H-6′), 1.41 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.36 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.31 (m, 1H, H-21′), 1.25 (t, 3H, $COOCH_2CH_3$, *J* = 7.17 Hz), 1.17 (m, 1H, H-16′), 1.16 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.12 (s, 3H, H-26), 1.05 (ddd, 1H, H-1′, *J* = 13.5, 13.5, 3.57 Hz), 1.01 (m, 1H, H-15′), 0.88 (s, 6H, H-23 and H-24), 0.80 (m, 1H, H-5), 0.79 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.4 (C-30), 172.4 (Ala-COO), 169.3 (C-13), 128.4 (C-12), 80.7 (C-3), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0

(C-5), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.4 (Ala-CH_2COO), 38.0 (C-4 and Ala-CH_2NH_2), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-28), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{35}H_{55}NO_5$ (569.81): C, 73.77; H, 9.73; N, 2.46. Found: C, 73.62; H, 9.91; N, 2.32.

4.2.6.14. *i*-Propyl 3β-(glycyl)-11-oxo-olean-12-en-30-oate (14). Obtained from **35** by method B as a colourless powder; yield: 120 mg, 46%; mp 265–268 °C; R_f = 0.57 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 122.07 (*c* 0.34, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.09); MS (ESI): *m/z* (%) = 570.3 ($[M+H]^+$, 100), 855.3 ($[3M+2H]^{2+}$, 6); IR (KBr): *v* = 3404 (br), 2977 (s), 2858 (m), 1735 (s), 1655 (s), 1466 (m), 1389 (m), 1328 (w), 1311 (w), 1218 (s), 1179 (s), 1144 (m), 1108 (m), 1086 (m), 1020 (w), 974 (w), 917 (w), 849 (w), 669 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.01 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.56 (dd, 1H, H-3, *J* = 11.6, 4.97 Hz), 3.42 (s, 2H, Gly-CH_2), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.5, 3.57 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.5, 3.77 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.3, 4.4, 4.47 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, *J* = 13.2, 3.6, 2.97 Hz), 1.80 (ddd, 1H, H-16, *J* = 14.2, 14.2, 4.77 Hz), 1.70 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.56 (m, 1H, H-6), 1.46 (m, 1H, H-6′), 1.41 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.33 (m, 1H, H-22′), 1.27 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.10 (s, 6H, H-28 and H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.5, 13.5, 3.67 Hz), 0.99 (m, 1H, H-15′), 0.85 (s, 6H, H-23 and H-24), 0.79 (m, 1H, H-5), 0.77 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 173.9 (Gly-COO), 169.5 (C-13), 128.4 (C-12), 81.4 (C-3), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.7 (Gly-CH_2), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.2 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{35}H_{55}NO_5$ (569.81): C, 73.77; H, 9.73; N, 2.46. Found: C, 73.56; H, 9.93; N, 2.34.

4.2.6.15. *i*-Propyl 3β-(L-alanyl)-11-oxo-olean-12-en-30-oate (15). Obtained from **36** by method B as a colourless powder; yield: 160 mg, 96%; mp 249–252 °C; R_f = 0.56 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 114.82 (*c* 0.32, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.10); MS (ESI): *m/z* (%) = 584.3 ($[M+H]^+$, 100); IR (KBr): *v* = 3426 (br), 2976 (s), 2874 (s), 1725 (s), 1657 (s), 1619 (m), 1466 (m), 1387 (m), 1374 (m), 1325 (m), 1280 (m), 1258 (m), 1216 (s), 1174 (s), 1142 (m), 1109 (s), 1086 (m), 1048 (w), 1021 (w), 983 (m), 948 (w), 916 (w), 880 (w), 847 (w), 770 (w), 686 (w), 671 (w), 589 (w), 544 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.61 (s, 1H, H-12), 5.02 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.51 (dd, 1H, H-3, *J* = 11.8, 4.67 Hz), 3.57 (q, 1H, Ala-CH, *J* = 7.17 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.5, 3.5, 3.57 Hz), 2.35 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 13.5, 3.17 Hz), 2.01 (m, 1H, H-15), 1.96 (m, 1H, H-21), 1.89 (m, 1H, H-19), 1.80 (m, 1H, H-16), 1.71 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.5, 13.57 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.31 (d, 3H, Ala-CH_3, *J* = 7.07 Hz), 1.31 (m, 1H, H-22′), 1.30 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.18 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.11 (s, 6H, H-28 and H-26), 1.04 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.88 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.2 (C-30), 175.8 (Ala-COO), 169.5 (C-13), 128.4 (C-12), 81.3 (C-3), 67.4 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 50.3 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.2 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 20.5 (Ala-CH_3), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{36}H_{57}NO_7$ (583.84): C, 74.06; H, 9.84; N, 2.40. Found: C, 73.99; H, 10.01; N, 2.26.

4.2.6.16. *i*-Propyl 3β-(β-alanyl)-11-oxo-olean-12-en-30-oate (16). Obtained from **37** by method B as a colourless powder; yield: 200 mg, 76%; mp 266–269 °C (decomp.); R_f = 0.19 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 120.18 (*c* 0.36, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.08); MS (ESI): *m/z* (%) = 584.9 ($[2M+2H]^{2+}$, 100); IR (KBr): *v* = 3388 (br), 2956 (s), 1722 (s), 1655 (s), 1466 (m), 1387 (m), 1218 (s), 1173 (m), 1141 (m), 1111 (m), 1085 (m), 1022 (w), 987 (w), 917 (w), 878 (w), 830 (w), 670 (w), 545 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.01 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.53 (dd, 1H, H-3, *J* = 11.7, 4.57 Hz), 2.98 (m, 2H, Ala-CH_2NH_2), 2.78 (ddd, 1H, H-1, *J* = 13.2, 3.3, 3.37 Hz), 2.47 (t, 2H, Ala-CH_2COO, *J* = 5.47 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.7, 13.7, 4.77 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, *J* = 13.3, 3.7, 2.57 Hz), 1.80 (ddd, 1H, H-16, *J* = 14.1, 14.1, 4.77 Hz), 1.71 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.5, 13.57 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.38 (m, 1H, H-7′), 1.35 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.34 (m, 1H, H-22′), 1.32 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.10 (s, 6H, H-28 and H-26), 1.03 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.86 (s, 6H, H-23 and H-24), 0.79 (m, 1H, H-5), 0.77 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 172.3 (Ala-COO), 169.4 (C-13), 128.4 (C-12), 80.8 (C-3), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.5 (Ala-CH_2COO), 38.0 (C-4 and Ala-CH_2NH_2), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.2 (C-28), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.6 (C-26), 17.4 (C-6), 16.7 (C-24), 16.3 (C-25). Anal. Calcd for $C_{36}H_{57}NO_5$ (583.84): C, 74.33; H, 9.95; N, 2.34. Found: C, 74.21; H, 10.07; N, 2.28.

4.2.6.17. Benzyl 3β-(glycyl)-11-oxo-olean-12-en-30-oate (17). Obtained from **38** by method B as a colourless powder; yield: 200 mg, 89%; mp 186–190 °C; R_f = 0.58 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 123.22 (*c* 0.56, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.05); MS (ESI): *m/z* (%) = 618.3 ($[2M+2H]^{2+}$, 100), 927.3 ($[3M+3H]^{2+}$, 5); IR (KBr): *v* = 3393 (br), 2951 (s), 2874 (m), 1731 (s), 1655 (s), 1618 (w), 1498 (w), 1456 (m), 1388 (m), 1365 (m), 1324 (m), 1214 (s), 1147 (s), 1085 (m), 1049 (w), 1028 (w), 985 (m), 916 (w), 880 (w), 767 (w), 748 (w), 697 (w), 670 (w), 586 (w), 542 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H, H-Ar), 5.53 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.67 Hz), 5.07 (d, 1H, Bn-H*H*′, *J* = 12.17 Hz), 4.56 (dd, 1H, H-3, *J* = 11.5, 4.77 Hz), 3.41 (s, 2H, Gly-CH_2), 2.79 (ddd, 1H, H-1, *J* = 13.6, 3.6, 3.67 Hz), 2.32 (s, 1H, H-9), 2.02 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.92 (dd, 1H, H-19, *J* = 13.0, 3.8, 2.97 Hz), 1.79 (ddd, 1H, H-16, *J* = 14.0, 14.0, 4.57 Hz), 1.70 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 13.2, 13.27 Hz), 1.56 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.40 (m, 1H, H-7′), 1.35 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.30 (m, 1H, H-21′), 1.28 (m, 1H, H-22′), 1.15 (m, 1H, H-16′), 1.14 (s, 6H, H-28 and H-25), 1.09 (s, 3H, H-26), 1.04 (m, 1H, H-1′), 0.98 (m, 1H, H-15′), 0.86 (s, 6H, H-23 and H-24), 0.78 (m, 1H, H-5), 0.71 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11),

176.2 (C-30), 174.0 (Gly-COO), 169.1 (C-13), 136.1 (C_{ar}), 128.6 (C-12), 128.6 (C_{ar}), 128.4 (C_{ar}), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 81.3 (C-3), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 48.2 (C-18), 45.3 (C-8), 44.1 (Gly-CH_2), 44.0 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.1 (C-4), 37.6 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-29), 28.3 (C-23), 28.1 (C-28), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{39}H_{55}NO_5$ (617.86): C, 75.81; H, 8.97; N, 2.27. Found: C, 75.77; H, 9.12; N, 2.16.

4.2.6.18. Benzyl 3β-(L-alanyl)-11-oxo-olean-12-en-30-oate (18). Obtained from **39** by method B as a colourless powder; yield: 330 mg, 98%; mp 200–203 °C; R_f = 0.58 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 128.39 (*c* 0.52, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 207 nm (4.08), 249 nm (4.10); MS (ESI): *m/z* (%) = 632.2 ($[2M+2H]^{2+}$, 100), 948.2 ($[3M+2H]^{2+}$, 10), 1263.7 ($[2M+H]^+$, 4); IR (KBr): *ν* = 3369 (br), 2958 (s), 2874 (m), 1728 (s), 1652 (s), 1616 (w), 1498 (w), 1455 (m), 1389 (m), 1368 (w), 1324 (m), 1278 (w), 1263 (w), 1214 (s), 1190 (s), 1146 (s), 1085 (m), 1063 (m), 1050 (w), 1029 (m), 972 (w), 916 (w), 890 (w), 868 (w), 850 (w), 768 (w), 742 (m), 696 (w), 613 (w), 587 (w), 544 (w), 471 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H, H-Ar), 5.52 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.57 Hz), 5.06 (d, 1H, Bn-CH*H*′, *J* = 12.37 Hz), 4.53 (dd, 1H, H-3, *J* = 11.7, 4.87 Hz), 3.52 (q, 1H, Ala-CH, *J* = 7.17 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.6, 3.4, 3.47 Hz), 2.32 (s, 1H, H-9), 2.01 (m, 1H, H-18), 1.99 (m, 1H, H-15), 1.96 (m, 1H, H-21), 1.92 (m, 1H, H-19), 1.78 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.67 Hz), 1.70 (m, 1H, H-2), 1.65 (m, 1H,H-7), 1.62 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.57 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.37 (m, 1H, H-7′), 1.34 (m, 1H, H-22), 1.34 (m, 3H, Ala-CH_3), 1.33 (s, 3H, H-27), 1.29 (m, 2H, H-22′ and H-21′), 1.15 (m, 1H, H-16′), 1.14 (s, 6H, H-25 and H-28), 1.09 (s, 3H, H-26), 1.03 (ddd, 1H, H-1′, *J* = 13.3, 13.3, 3.37 Hz), 0.97 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.85 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.71 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 176.2 (Ala-COO), 169.0 (C-13), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.6 (C_{ar}), 128.4 (C-12), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 81.1 (C-3), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 50.4 (Ala-CH), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.6 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-29), 28.3 (C-23), 28.1 (C-28), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 20.8 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{40}H_{57}NO_5$ (631.88): C, 76.03; H, 9.09; N, 2.22. Found: C, 75.87; H, 9.12; N, 2.17.

4.2.6.19. Benzyl 3β-(β-alanyl)-11-oxo-olean-12-en-30-oate (19). Obtained from **40** by method B as a colourless powder; yield: 150 mg, 91%; mp 233–236 °C (decomp.); R_f = 0.20 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 114.31 (*c* 0.59, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 207 nm (4.02), 250 nm (4.08); MS (ESI): *m/z* (%) = 632.3 ($[M+H]^+$, 100); IR (KBr): *ν* = 3424 (br), 2949 (s), 2872 (m), 1727 (s), 1657 (s), 1456 (m), 1387 (m), 1367 (m), 1324 (m), 1279 (m), 1248 (m), 1213 (s), 1148 (s), 1085 (m), 1048 (w), 1023 (w), 986 (m), 915 (w), 880 (w), 830 (w), 754 (w), 698 (m), 670 (w), 586 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H, H-Ar), 5.52 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.27 Hz), 5.06 (d, 1H, Bn-C*H*H′, *J* = 12.27 Hz), 4.54 (dd, 1H, H-3, *J* = 11.7, 5.17 Hz), 3.10 (m, 2H, Ala-CH_2NH_2), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.61 (m, 2H, Ala-CH_2COO), 2.32 (s, 1H, H-9), 2.01 (m 1H, H-18), 1.99 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, *J* = 13.3, 3.7, 2.97 Hz), 1.78 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.27 Hz), 1.70 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 13.5, 13.57 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.38 (m, 1H, H-7′), 1.34 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.30 (m, 1H, H-22′), 1.27 (m, 1H, H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 6H, H-25 and H-28), 1.09 (s, 3H, H-26), 1.02 (ddd, 1H, H-1′, *J* = 13.3, 13.3, 3.77 Hz), 0.97 (m, 1H, H-15′), 0.86 (s, 6H, H-23 and H-24), 0.78 (m, 1H, H-5), 0.71 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.2 (C-30), 172.0 (Ala-COO), 169.1 (C-13), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.5 (C-12), 128.6 (C_{ar}), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 81.4 (C-3), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.8 (C-1), 38.7 (Ala-CH_2COO), 38.1 (C-4), 38.1 (Ala-CH_2NH_2), 37.6 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-29), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{40}H_{57}NO_5$ (631.88): C, 76.03; H, 9.09; N, 2.22. Found: C, 75.79; H, 9.21; N, 2.11.

4.2.6.20. Methyl 3β-(glycyl)-11-oxo-olean-12-en-30-oate hydrochloride (20). Obtained from **29** by method D as a colourless powder; yield:130 mg, 48%; mp 288–292 °C (decomp.); R_f = 0.54 (MeOH); $[\alpha]_D^{20}$ = 130.16 (*c* 0.39, CH_2Cl_2); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.03); MS (ESI): *m/z* (%) = 542.3 ($[2M+2H]^{2+}$, 100), 812.9 ($[3M+2H]^{2+}$, 12), 1083.1 ($[2M+H]^+$, 6); IR (KBr): *ν* = 3439 (br), 2951 (s), 1731 (s), 1657 (s), 1618 (m), 1466 (s), 1432 (m), 1389 (m), 1323 (m), 1244 (s), 1155 (s), 1087 (m), 1049 (m), 987 (m), 911 (w), 880 (w), 825 (w), 770 (w), 686 (w), 670 (s), 590 (w), 544 (w), 501 (w) cm^{-1}; ^1H NMR (400 MHz, MeOH-d_4): δ = 5.57 (s, 1H, H-12), 4.68 (dd, 1H, H-3, *J* = 11.9, 4.77 Hz), 3.84 (dd, 2H, Gly-CH_2, *J* = 26.5, 7.07 Hz), 3.69 (s, 3H, OMe), 2.79 (ddd, 1H, H-1, *J* = 13.8, 3.7, 3.77 Hz), 2.49 (s, 1H, H-9), 2.14 (m, 1H, H-15), 2.12 (dd, 1H, H-18, *J* = 13.3, 4.17 Hz), 1.96 (m, 1H, H-21), 1.88 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.37 Hz), 1.86 (m, 1H, H-19), 1.81 (m, 1H, H-2), 1.77 (m, 1H, H-7), 1.73 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.67 (m, 1H, H-2′), 1.64 (m, 1H, H-6), 1.53 (m, 1H, H-6′), 1.47 (m, 1H, H-7′), 1.44 (m, 1H, H-22), 1.43 (s, 3H, H-27), 1.41 (m, 1H, H-21′), 1.28 (m, 1H, H-22′), 1.24 (m, 1H, H-16′), 1.17 (s, 3H, H-25), 1.14 (s, 6H, H-26 and H-28), 1.12 (m, 1H, H-1′), 1.04 (m, 1H, H-15′), 0.94 (s, 3H, H-23), 0.93 (s, 3H, H-24), 0.91 (m, 1H, H-5), 0.82 (s, 3H, H-29); ^{13}C NMR (125 MHz, MeOH-d_4): δ = 202.2 (C-11), 178.6 (C-30), 172.7 (Gly-COO), 168.4 (C-13), 128.9 (C-12), 84.6 (C-3), 62.9 (C-9), 56.0 (C-5), 52.3 (OMe), 49.9 (C-18), 46.7 (C-8), 44.7 (C-20), 44.6 (C-14), 42.4 (C-19), 41.1 (Gly-CH_2), 39.6 (C-1), 39.2 (C-4), 39.0 (C-22), 38.2 (C-10), 33.6 (C-7), 33.0 (C-17), 32.0 (C-21), 29.1 (C-29), 28.5 (C-23), 28.5 (C-28), 27.6 (C-16), 27.3 (C-15), 24.4 (C-2), 23.8 (C-27), 19.3 (C-26), 18.4 (C-6), 17.1 (C-24), 16.9 (C-25). Anal. Calcd for $C_{33}H_{52}ClNO_5$ (578.22): C, 68.55; H, 9.06; Cl, 6.13; N, 2.42. Found: C, 68.49; H, 9.27; Cl, 6.27; N, 2.13.

4.2.6.21. Methyl 3β-(L-alanyl)-11-oxo-olean-12-en-30-oate hydrochloride (21). Obtained from **30** by method D as a colourless powder; yield: 180 mg, 56%; mp 288–292 °C (decomp.); R_f = 0.61 (MeOH); $[\alpha]_D^{20}$ = 125.80 (*c* 0.36, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.02); MS (ESI): *m/z* (%) = 556.2 ($[M+H]^+$, 100), 833.8 ($[3M+2H]^{2+}$, 10); IR (KBr): *ν* = 3441 (br), 2951 (s), 2362 (w), 1743 (s), 1730 (s), 1661 (s), 1622 (w), 1517 (m), 1466 (m), 1387 (m), 1322 (w), 1257 (m), 1217 (m), 1191 (m), 1153 (m), 1122 (m), 1086 (w), 1049 (s), 985 (m), 914 (w), 867 (m), 823 (w), 769 (w), 670 (w), 546 (w) cm^{-1}; ^1H NMR (400 MHz, MeOH-d_4): δ = 5.58 (s, 1H, H-12), 4.67 (dd, 1H, H-3, *J* = 11.7, 5.07 Hz), 4.10 (q, 1H, Ala-CH, *J* = 7.47 Hz), 3.69 (s, 3H, OMe), 2.80 (ddd, 1H, H-1, *J* = 13.3, 3.3, 3.37 Hz), 2.50 (s, 1H, H-9), 2.16 (m, 1H, H-15), 2.13 (m, 1H, H-18), 1.97 (m, 1H, H-21), 1.90 (m, 1H, H-16), 1.84 (m, 1H, H-19), 1.81 (m, 1H, H-2), 1.77 (m, 1H, H-7), 1.72 (dd, 1H, H-19′, *J* = 13.2, 13.27 Hz), 1.68 (m, 1H, H-2′), 1.66 (m, 1H, H-6), 1.51 (m, 1H, H-6′), 1.47 (m, 1H, H-7′), 1.41 (m, 1H, H-22), 1.43 (s, 3H, H-27), 1.44 (m, 1H, H-21′), 1.56 (d, 3H, Ala-CH_3, *J* = 7.37 Hz), 1.29 (m, 1H, H-22′), 1.25 (m, 1H, H-16′),

1.18 (s, 3H, H-25), 1.15 (s, 6H, H-26 and H-28), 1.12 (m, 1H, H-1′), 1.04 (m, 1H, H-15′), 0.95 (s, 3H, H-24), 0.93 (s, 3H, H-23), 0.92 (m, 1H, H-5), 0.82 (s, 3H, H-29); ^{13}C NMR (125 MHz, MeOH-d_4): δ = 200.8 (C-11), 177.2 (C-30), 171.3 (Ala-COO), 169.4 (C-13), 127.5 (C-12), 83.2 (C-3), 61.4 (C-9), 54.5 (C-5), 50.9 (OMe), 48.5 (Ala-CH), 48.1 (C-18), 45.3 (C-8), 43.9 (C-20), 43.2 (C-14), 40.9 (C-19), 38.2 (C-1), 37.9 (C-4), 37.5 (C-22), 36.8 (C-10), 32.2 (C-7), 31.5 (C-17), 30.6 (C-21), 27.7 (C-29), 27.1 (C-23), 27.1 (C-28), 26.1 (C-16), 25.9 (C-15), 23.0 (C-2), 22.4 (C-27), 17.8 (C-26), 17.0 (C-6), 15.7 (C-24), 15.5 (C-25), 15.0 (Ala-CH_3). Anal. Calcd for $C_{34}H_{54}ClNO_5$ (592.25): C, 68.95; H, 9.19; Cl, 5.99; N, 2.37. Found: C, 68.68; H, 9.25; Cl, 6.09; N, 2.22.

4.2.6.22. Methyl 3β-(β-alanyl)-11-oxo-olean-12-en-30-oate hydrochloride (22). Obtained from **31** by method D as a colourless powder; yield: 160 mg, 76%; mp 282–285 °C (decomp.); R_f = 0.19 (MeOH); $[\alpha]_D^{20}$ = 128.78 (*c* 0.45, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 247 nm (4.17); MS (ESI): *m/z* (%) = 556.2 ([M+H]$^+$, 100), 834.3 ([3M+2H]$^{2+}$, 10), 1111.1 ([2M+H]$^+$, 4); IR (KBr): ν = 3437 (br), 2951 (s), 2034 (w), 1729 (s), 1660 (s), 1619 (m), 1465 (s), 1387 (m), 1323 (m), 1279 (m), 1218 (s), 1154 (s), 1108 (m), 1087 (m), 1049 (w), 1013 (w), 989 (s), 916 (w), 862 (w), 824 (w), 788 (w), 770 (w), 670 (w), 590 (w), 544 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.56 (s, 1H, H-12), 4.57 (dd, 1H, H-3, *J* = 11.8, 4.77 Hz), 3.67 (s, 3H, OMe), 3.18 (m, 2H, Ala-CH_2NH_2), 2.74 (m, 1H, H-1), 2.72 (m, 2H, Ala-*C*H$_2$COO), 2.47 (s, 1H, H-9), 2.13 (m, 1H, H-15), 2.11 (m, 1H, H-18), 1.95 (m, 1H, H-21), 1.86 (m, 1H, H-16), 1.84 (m, 1H, H-19), 1.73 (m, 1H, H-2), 1.71 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.66 (m, 1H, H-7), 1.63 (m, 1H, H-2′), 1.61 (m, 1H, H-6), 1.51 (m, 1H, H-6′), 1.45 (m, 1H, H-7′), 1.41 (s, 3H, H-27), 1.40 (m, 1H, H-22), 1.28 (m, 1H, H-21′), 1.25 (m, 1H, H-22′), 1.23 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.13 (s, 6H, H-28 and H-26), 1.09 (m, 1H, H-1′), 1.03 (m, 1H, H-15′), 0.90 (s, 6H, H-23 and H-24), 0.88 (m, 1H, H-5), 0.80 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.9 (C-11), 177.2 (C-30), 171.3 (Ala-COO), 170.6 (C-13), 127.5 (C-12), 81.8 (C-3), 61.5 (C-9), 54.7 (C-5), 50.9 (OMe), 48.5 (C-18), 45.3 (C-8), 43.9 (C-20), 43.2 (C-14), 40.9 (C-19), 38.3 (C-1), 37.7 (C-4), 37.5 (C-22), 36.8 (C-10), 35.0 (Ala-CH_2NH_2), 32.2 (C-7), 31.5 (C-17), 30.9 (Ala-*C*H$_2$COO), 30.6 (C-21), 27.7 (C-29), 27.1 (C-28), 27.1 (C-23), 26.1 (C-16), 25.9 (C-15), 23.0 (C-2), 22.4 (C-27), 17.8 (C-26), 17.0 (C-6), 15.7 (C-24), 15.5 (C-25). Anal. Calcd for $C_{34}H_{54}ClNO_5$ (592.25): C, 68.95; H, 9.19; Cl, 5.99; N, 2.37. Found: C, 68.87; H, 9.32; Cl, 6.12; N, 2.24.

4.2.6.23. Methyl 3β-(D-alanyl)-11-oxo-olean-12-en-30-oate (23). Obtained from **41** by method B as a colourless powder; yield: 220 mg, 76%; mp 243–247 °C; R_f = 0.58 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 123.94 (*c* 0.28, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.08); MS (ESI): *m/z* (%) = 556.7 ([2M+2H]$^{2+}$, 100); IR (KBr): ν = 3387 (br), 2958 (s), 2874 (m), 1731 (s), 1652 (s), 1455 (m), 1389 (m), 1323 (w), 1279 (w), 1248 (m), 1218 (m), 1190 (m), 1160 (m), 1087 (w), 1050 (w), 1022 (w), 985 (w), 973 (m), 917 (w), 867 (w), 825 (w), 770 (w), 669 (w), 590 (w), 544 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.51 (dd, 1H, H-3, *J* = 11.6, 4.87 Hz), 3.66 (s, 3H, OMe), 3.53 (q, 1H, Ala-CH, *J* = 7.07 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.8, 3.87 Hz), 2.34 (s, 1H, H-9), 2.06 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.90 (m, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.8, 13.8, 4.57 Hz), 1.70 (m, 1H, H-2), 1.63 (m, 1H, H-7), 1.59 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.6, 13.67 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.39 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.32 (d, 3H, Ala-CH3, *J* = 7.07 Hz), 1.29 (m, 2H, H-22′ and H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.12 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.5, 13.5, 4.17 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 176.1 (Ala-COO), 169.2 (C-13), 128.5 (C-12), 81.1 (C-3), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 50.2 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.4 (C-16), 26.4 (C-15), 23.4 (C-2), 23.3 (C-27), 20.6 (Ala-CH_3), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{34}H_{53}NO_5$ (555.79): C, 73.47; H, 9.61; N, 2.52. Found: C, 73.41; H, 9.77; N, 2.49.

4.2.6.24. Ethyl 3β-(D-alanyl)-11-oxo-olean-12-en-30-oate (24). Obtained from **42** by method B as a colourless powder; yield: 240 mg, 86%; mp 236–239 °C; R_f = 0.58 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 108.78 (*c* 0.33, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.06); MS (ESI): *m/z* (%) = 570.3 ([M+H]$^+$, 100), 854.8 ([3M+2Na]$^{2+}$, 10), 1139.2 ([2M+H]$^+$, 4); IR (KBr): ν = 3387 (br), 2958 (s), 2874 (m), 1725 (s), 1653 (s), 1626 (m), 1454 (m), 1389 (m), 1323 (w), 1279 (w), 1246 (m), 1216 (s), 1177 (s), 1087 (m), 1049 (w), 1022 (w), 984 (w), 972 (w), 916 (w), 878 (w), 841 (w), 755 (w), 670 (w), 544 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.62 (s, 1H, H-12), 4.51 (dd, 1H, H-3, *J* = 11.6, 4.77 Hz), 4.16 (dq, 1H, COOC*H*H′, *J* = 10.8, 7.17 Hz), 4.11 (dq, 1H, COOCH*H*′, *J* = 10.8, 7.17 Hz), 3.54 (q, 1H, Ala-CH, *J* = 7.17 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.8, 3.5, 3.57 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.8, 13.8, 4.57 Hz), 1.97 (m, 1H, H-21), 1.90 (m, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.6, 13.6, 4.67 Hz), 1.71 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.39 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.32 (d, 3H, Ala-CH_3, *J* = 7.17 Hz), 1.29 (m, 1H, H-22′), 1.27 (m, 1H, H-21′), 1.24 (t, 3H, Et-CH_3, *J* = 7.17 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.12 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.04 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-24), 0.86 (s, 3H, H-24), 0.80 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 176.1 (Ala-COO), 169.4 (C-13), 128.4 (C-12), 81.2 (C-3), 61.7 (C-9), 60.3 (Et-CH_2), 55.0 (C-5), 50.2 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.4 (C-2), 23.3 (C-27), 20.7 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25), 14.3 (Et-CH_3). Anal. Calcd for $C_{35}H_{55}NO_5$ (569.81): C, 73.77; H, 9.73; N, 2.46. Found: C, 73.56; H, 9.87; N, 2.42.

4.2.6.25. *i*-Propyl 3β-(D-alanyl)-11-oxo-olean-12-en-30-oate (25). Obtained from **43** by method B as a colourless powder; yield: 200 mg, 90%; mp 263–266 °C; R_f = 0.59 (DCM/MeOH 9:1); $[\alpha]_D^{20}$ = 113.51 (*c* 0.24, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.07); MS (ESI): *m/z* (%) = 584.1 ([M+H]$^+$, 100), 876.3 ([3M+3Na]$^{2+}$, 8), 1167.3 ([2M+H]$^+$, 4); IR (KBr): ν = 3420 (br), 2971 (s), 2875 (s), 1721 (s), 1652 (s), 1455 (m), 1388 (m), 1313 (m), 1279 (m), 1217 (s), 1180 (s), 1142 (m), 1108 (s), 1086 (m), 1021 (w), 986 (m), 972 (m), 917 (m), 879 (w), 848 (w), 770 (w), 686 (w), 545 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.01 (qq, 1H, *i*-Pr-CH, *J* = 6.4, 6.47 Hz), 4.51 (dd, 1H, H-3, *J* = 11.7, 4.57 Hz), 3.53 (q, 1H, Ala-CH, *J* = 7.17 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.6, 3.5, 3.57 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.2, 3.37 Hz), 2.01 (dd, 1H, H-15, *J* = 13.7, 4.67 Hz), 1.96 (m, 1H, H-21), 1.89 (m, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.6, 13.6, 4.57 Hz), 1.71 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.2, 13.27 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.32 (d, 3H, Ala-CH_3, *J* = 7.07 Hz), 1.31 (m, 1H, H-22′), 1.30 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H,

i-Pr-CH_3, J = 6.27 Hz), 1.18 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.10 (s, 6H, H-28 and H-26), 1.04 (ddd, 1H, H-1′, J = 13.1, 13.1, 3.27 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.77 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.2 (C-30), 175.8 (Ala-COO), 169.5 (C-13), 128.4 (C-12), 81.1 (C-3), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 50.2 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.2 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.4 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 20.7 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{36}H_{57}NO_5$ (583.84): C, 74.06; H, 9.84; N, 2.40. Found: C, 73.99; H, 9.95; N, 2.35.

4.2.6.26. 3β-(Boc-glycyl)-11-oxo-olean-12-en-30-oic acid (26). Obtained from **38** by method C as a colourless powder; yield: 320 mg, 58%; mp 288–290 °C (decomp.); R_f = 0.14 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 115.49 (c 0.43, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.06); MS (ESI): m/z (%) = 650.4 ([M+Na]$^+$, 100), 964.2 ([3M+2Na]$^{2+}$, 14), 1278.1 ([2M+Na]$^+$, 18); IR (KBr): ν = 3295 (br), 2973 (s), 2874 (m), 1752 (s), 1719 (s), 1651 (s), 1514 (m), 1456 (m), 1390 (s), 1368 (s), 1281 (m), 1258 (m), 1217 (s), 1164 (s), 1088 (w), 1051 (m), 1028 (m), 984 (m), 948 (w), 916 (w), 883 (w), 867 (w), 777 (w), 754 (w), 700 (w), 671 (w), 590 (w), 558 (w), 442 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (s, 1H, H-12), 4.98 (m, 1H, Gly-NH), 4.57 (dd, 1H, H-3, J = 11.6, 4.87 Hz), 3.88 (m, 2H, Gly-CH_2), 2.79 (ddd, 1H, H-1, J = 13.7, 3.3, 3.37 Hz), 2.34 (s, 1H, H-9), 2.17 (dd, 1H, H-18, J = 12.9, 4.27 Hz), 2.01 (ddd, 1H, H-15, J = 13.3, 13.3, 4.27 Hz), 1.98 (m, 1H, H-21), 1.91 (m, 1H, H-19), 1.81 (ddd, 1H, H-16, J = 13.3, 13.3, 3.77 Hz), 1.72 (m, 1H, H-2), 1.68 (m, 1H, H-7), 1.63 (m, 1H, H-2′), 1.61 (dd, 1H, H-19′, J = 13.7, 13.77 Hz), 1.57 (m, 1H, H-6), 1.43 (s, 9H, Boc-CH_3), 1.42 (m, 1H, H-6′), 1.39 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.37 (s, 3H, H-27), 1.36 (m, 1H, H-22′), 1.32 (m, 1H, H-21′), 1.20 (s, 3H, H-28), 1.19 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.11 (s, 3H, H-26), 1.03 (m, 1H, H-1′), 1.01 (m, 1H, H-15′), 0.86 (s, 6H, H-23 and H-24), 0.81 (s, 3H, H-29), 0.78 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.1 (C-11), 180.6 (C-30), 170.1 (Gly-COO), 169.4 (C-13), 155.6 (Boc-COO), 128.5 (C-12), 82.0 (C-3), 77.3 (Boc-*quart*.-C), 61.7 (C-9), 55.0 (C-5), 48.2 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 42.7 (Gly-CH_2), 40.9 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.9 (C-17), 31.0 (C-21), 28.5 (C-29), 28.4 (C-23), 28.3 (Boc-CH_3), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.4 (C-27), 18.7 (C-26), 17.4 (C-6), 16.6 (C-24), 16.4 (C-25). Anal. Calcd for $C_{37}H_{57}NO_7$ (627.85): C, 70.78; H, 9.15; N, 2.23. Found: C, 70.75; H, 9.25; N, 2.12.

4.2.6.27. 3β-(Boc-L-alanyl)-11-oxo-olean-12-en-30-oic acid (27). Obtained from **39** by method C as a colourless powder; yield: 220 mg, 66%; mp 231–234 °C (decomp.); R_f = 0.71 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 95.89 (c 0.45, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.81); MS (ESI): m/z (%) = 642.2 ([M+H]$^+$, 4), 664.4 ([M+Na]$^+$, 100), 985.3 ([3M+2Na]$^+$, 22); IR (KBr): ν = 3383 (br), 2976 (s), 2876 (m), 1719 (s), 1661 (s), 1499 (m), 1455 (s), 1390 (s), 1368 (s), 1306 (m), 1259 (m), 1214 (s), 1167 (s), 1087 (m), 1066 (m), 1023 (m), 973 (m), 916 (w), 881 (w), 865 (w), 754 (w), 699 (s), 668 (w), 588 (w), 541 (w), 464 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 (s, 1H, H-12), 5.06 (m, 1H, Ala-NH), 4.55 (dd, 1H, H-3, J = 11.6, 4.67 Hz), 4.28 (m, 1H, Ala-CH), 2.80 (ddd, 1H, H-1, J = 13.7, 3.4, 3.47 Hz), 2.35 (s, 1H, H-9), 2.17 (dd, 1H, H-18, J = 13.3, 3.37 Hz), 2.02 (m, 1H, H-15), 1.98 (m, 1H, H-21), 1.92 (m, 1H, H-19), 1.82 (m, 1H, H-16), 1.71 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.61 (dd, 1H, H-19′, J = 13.4, 13.47 Hz), 1.57 (m, 1H, H-6), 1.43 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.40 (m, 1H, H-7′), 1.38 (d, 3H, Ala-CH_3, J = 7.17 Hz), 1.36 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.33 (m, 2H, H-22′ and H-21′), 1.21 (s, 3H, H-28), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.11 (s, 3H, H-26), 1.03 (m, 1H, H-1′), 1.01 (m, 1H, H-15′), 0.87 (s, 3H, H-24), 0.85 (s, 3H, H-23), 0.82 (s, 3H, H-29), 0.79 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.2 (C-11), 181.0 (C-30), 173.0 (Ala-COO), 169.4 (C-13), 155.0 (Boc-COO), 128.4 (C-12), 81.7 (C-3), 77.9 (Boc-*quart*.-C), 61.6 (C-9), 55.0 (C-5), 49.5 (Ala-CH), 48.2 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 40.9 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 30.9 (C-21), 28.5 (C-29), 28.4 (C-23), 28.3 (Boc-CH_3), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.9 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{38}H_{59}NO_7$ (641.88): C, 71.10; H, 9.26; N, 2.18. Found: C, 71.00; H, 9.31; N, 2.12.

4.2.6.28. 3β-(Boc-β-alanyl)-11-oxo-olean-12-en-30-oic acid (28). Obtained from **40** by method C as a colourless powder; yield: 190 mg, 52%; mp 227–231 °C (decomp.); R_f = 0.09 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 113.35 (c 0.21, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.08); MS (ESI): m/z (%) = 664.4 ([M+Na]$^+$, 100), 985.3 ([3M+2Na]$^{2+}$, 8), 1305.1 ([2M+Na]$^+$, 20); IR (KBr): ν = 3356 (br), 2968 (s), 1739 (s), 1703 (s), 1653 (s), 1528 (m), 1452 (m), 1390 (m), 1368 (m), 1326 (m), 1302 (m), 1257 (m), 1210 (m), 1179 (s), 1072 (w), 1022 (w), 984 (w), 915 (m), 880 (w), 860 (w), 754 (w), 542 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 (s, 1H, H-12), 4.96 (m, 1H, Ala-NH), 4.52 (dd, 1H, H-3, J = 11.7, 4.67 Hz), 3.37 (dt, 2H, Ala-CH_2NH_2, J = 5.8, 5.87 Hz), 2.79 (ddd, 1H, H-1, J = 13.8, 3.3, 3.37 Hz), 2.51 (m, 2H, Ala-CH_2COO), 2.35 (s, 1H, H-9), 2.17 (dd, 1H, H-18, J = 12.8, 3.77 Hz), 2.01 (m, 1H, H-15), 1.98 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, J = 13.8, 4.1, 2.47 Hz), 1.82 (m, 1H, H-16), 1.71 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.63 (m, 1H, H-2′), 1.61 (dd, 1H, H-19′, J = 13.2, 13.27 Hz), 1.57 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.39 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.33 (m, 1H, H-22′), 1.31 (m, 1H, H-21′), 1.21 (s, 3H, H-28), 1.20 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.11 (s, 3H, H-26), 1.03 (m, 1H, H-1′), 1.01 (m, 1H, H-15′), 0.86 (s, 3H, H-24), 0.85 (s, 3H, H-23), 0.82 (s, 3H, H-29), 0.78 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.2 (C-11), 180.6 (C-30), 172.1 (Ala-COO), 169.3 (C-13), 155.6 (Boc-COO), 128.5 (C-12), 81.1 (C-3), 77.3 (Boc-*quart*.-C), 61.7 (C-9), 55.0 (C-5), 48.2 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 40.9 (C-19), 38.8 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 36.4 (Ala-CH_2NH_2), 34.7 (Ala-CH_2COO), 32.7 (C-7), 31.9 (C-17), 31.0 (C-21), 28.5 (C-29), 28.4 (C-23 and Boc-CH_3), 28.1 (C-28), 26.5 (C-16), 26.5 (C-15), 23.6 (C-2), 23.4 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{38}H_{59}NO_7$ (641.88): C, 71.10; H, 9.26; N, 2.18. Found: C, 71.02; H, 9.33; N, 2.05.

4.2.6.29. Methyl 3β-(Boc-glycyl)-11-oxo-olean-12-en-30-oate (29). Obtained from **1** and Boc-Gly by method A as a colourless powder; yield: 450 mg, 96%; mp 251–254 °C (decomp.); R_f = 0.58 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 92.72 (c 0.29, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.03); MS (ESI): m/z (%) = 641.9 ([M+H]$^+$, 12), 659.0 ([M+NH$_4$]$^+$, 12), 664.3 ([M+Na]$^+$, 100); IR (KBr): ν = 3397 (br), 2969 (s), 2874 (m), 1754 (s), 1724 (s), 1651 (s), 1522 (s), 1464 (m), 1390 (s), 1366 (s), 1348 (m), 1319 (m), 1248 (m), 1215 (s), 1164 (s), 1106 (m), 1087 (m), 1053 (m), 1024 (m), 985 (m), 948 (w), 916 (w), 881 (w), 868 (w), 825 (w), 756 (s), 686 (w), 667 (w), 590 (w), 551 (w), 537 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.63 (s, 1H, H-12), 4.98 (m, 1H, Gly-NH), 4.56 (dd, 1H, H-3, J = 11.6, 5.07 Hz), 3.87 (d, 2H, Gly-CH_2, J = 5.07 Hz), 3.66 (s, 3H, OMe), 2.79 (ddd, 1H, H-1, J = 13.7, 3.6, 3.67 Hz), 2.33 (s, 1H, H-9), 2.05 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.96 (m, 1H, H-21), 1.90 (ddd, 1H, H-19, J = 13.7, 3.7,

2.57 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.77 Hz), 1.72 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.63 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.7, 13.77 Hz), 1.56 (m, 1H, H-6), 1.43 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.39 (m, 1H, H-7′), 1.37 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.28 (m, 1H, H-21′), 1.16 (m, 1H, H-16′), 1.13 (s, 3H, H-25), 1.12 (s, 3H, H-26), 1.10 (s, 3H, H-28), 1.02 (ddd, 1H, H-1′, *J* = 13.3, 13.3, 3.77 Hz), 0.99 (m, 1H, H-15′), 0.85 (s, 6H, H-23 and H-24), 0.78 (s, 3H, H-29), 0.77 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 170.1 (Gly-COO), 169.2 (C-13), 155.6 (Boc-COO), 128.5 (C-12), 81.9 (C-3), 77.8 (Boc-*quart*.-C), 61.6 (C-9), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 42.6 (Gly-CH_2), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.6 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23 and Boc-CH_3), 28.0 (C-28), 26.4 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.6 (C-26), 17.3 (C-6), 16.6 (C-24), 16.4 (C-25). Anal. Calcd for $C_{38}H_{59}NO_7$ (641.88): C, 71.10; H, 9.26; N, 2.18. Found: C, 71.08; H, 9.35; N, 2.11.

4.2.6.30. Methyl 3β-(Boc-L-alanyl)-11-oxo-olean-12-en-30-oate (30). Obtained from **1** and Boc-L-Ala by method A as a colourless powder; yield: 400 mg, 72%; mp 249–252 °C (decomp.); R_f = 0.68 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 98.76 (*c* 0.43, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.08); MS (ESI): *m/z* (%) = 655.9 ($[M+H]^+$, 14), 673.1 ($M+NH_4$, 16), 678.3 ($[M+Na]^+$, 100); IR (KBr): ν = 3393 (br), 2972 (s), 2931 (s), 2874 (m), 1746 (s), 1722 (s), 1706 (s), 1652 (s), 1514 (s), 1455 (s), 1390 (m), 1365 (m), 1336 (s), 1280 (w), 1248 (m), 1216 (s), 1165 (s), 1094 (m), 1052 (s), 1029 (m), 985 (m), 970 (m), 917 (w), 882 (w), 866 (w), 850 (w), 827 (w), 780 (w), 772 (w), 686 (w), 670 (w), 590 (w), 538 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 5.04 (m, 1H, Ala-NH), 4.54 (dd, 1H, H-3, *J* = 11.6, 4.67 Hz), 4.28 (m, 1H, Ala-CH), 3.66 (s, 3H, OMe), 2.80 (ddd, 1H, H-1, *J* = 13.5, 3.4, 3.47 Hz), 2.34 (s, 1H, H-9), 2.06 (dd, 1H, H-18, *J* = 13.7, 3.77 Hz), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.90 (ddd, 1H, H-19, *J* = 13.7, 3.7, 2.47 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.8, 13.8, 4.77 Hz), 1.72 (m, 1H, H-2), 1.63 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.38 (d, 3H, Ala-CH_3, *J* = 7.27 Hz), 1.37 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.29 (m, 2H, H-22′ and H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.03 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.87 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.85 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 173.0 (Ala-COO), 169.2 (C-13), 155.0 (Boc-COO), 128.5 (C-12), 81.7 (C-3), 79.6 (Boc-*quart*.-C), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 49.5 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (Boc-CH_3), 28.3 (C-23), 28.0 (C-28), 26.4 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.9 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{39}H_{61}NO_7$ (655.90): C, 71.42; H, 9.37; N, 2.14. Found: C, 71.18; H, 9.42; N, 2.08.

4.2.6.31. Methyl 3β-(Boc-β-alanyl)-11-oxo-olean-12-en-30-oate (31). Obtained from **1** and Boc-β-Ala by method A as a colourless powder; yield: 460 mg, 88%; mp 188–191 °C (decomp.); R_f = 0.58 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 105.52 (*c* 0.28, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.08); MS (ESI): *m/z* (%) = 656.2 ($[M+H]^+$, 15), 678.3 ($[M+Na]^+$, 100); IR (KBr): ν = 3406 (br), 2973 (s), 1731 (s), 1660 (m), 1508 (m), 1456 (m), 1390 (m), 1366 (m), 1249 (m), 1216 (m), 1170 (s), 1086 (w), 986 (w), 880 (w), 755 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.65 (s, 1H, H-12), 4.94 (m, 1H, Ala-NH), 4.52 (dd, 1H, H-3, *J* = 11.7, 4.77 Hz), 3.67 (s, 3H, OMe), 3.37 (dt, 2H, Ala-CH_2NH_2, *J* = 5.8, 5.87 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.51 (m, 2H, Ala-CH_2COO), 2.34 (s, 1H, H-9), 2.06 (m, 1H, H-18), 2.01 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.91 (m, 1H, H-19), 1.81 (ddd, 1H, H-16, *J* = 13.2, 13.2, 4.27 Hz), 1.71 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, *J* = 13.3, 13.37 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (s, 9H, Boc-CH_3), 1.40 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.31 (m, 1H, H-22′), 1.28 (m, 1H, H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.13 (s, 3H, H-26), 1.11 (s, 3H, H-28), 1.03 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.86 (s, 3H, H-24), 0.85 (s, 3H, H-23), 0.79 (s, 3H, H-29), 0.78 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 172.3 (Ala-COO), 169.2 (C-13), 156.3 (Boc-COO), 128.5 (C-12), 81.1 (C-3), 79.6 (Boc-*quart*.-C), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.8 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 36.4 (Ala-CH_2NH_2), 34.7 (Ala-CH_2COO), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.4 (Boc-CH_3), 28.3 (C-28), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{39}H_{61}NO_7$ (655.90): C, 71.42; H, 9.37; N, 2.14. Found: C, 71.19; H, 9.52; N, 1.99.

4.2.6.32. Ethyl 3β-(Boc-L-glycyl)-11-oxo-olean-12-en-30-oate (32). Obtained from **2** and Boc-Gly by method A as a colourless powder; yield: 372 mg, 71%; mp 227–229 °C (decomp.); R_f = 0.56 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 108.70 (*c* 0.40, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.10); MS (ESI): *m/z* (%) = 656.3 ($[M+H]^+$, 7), 667.3 ($[2M+H+Na]^{2+}$, 19), 678.4 ($[M+Na]^+$, 100), 1006.5 ($[3M+2Na]^{2+}$, 34), 1333.8 ($[2M+Na]^+$, 60); IR (KBr): ν = 3407 (br), 2978 (s), 1724 (s), 1659 (s), 1508 (w), 1456 (m), 1390 (m), 1366 (m), 1249 (m), 1215 (s), 1172 (s), 1086 (w), 1053 (w), 1022 (w), 985 (w), 867 (w), 769 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.99 (t, 1H, Gly-NH, *J* = 4.97 Hz), 4.58 (dd, 1H, H-3, *J* = 11.7, 4.8 7 Hz), 4.18 (dq, 1H, COOC*H*H′, *J* = 10.7, 7.27 Hz), 4.12 (dq, 1H, COOCH*H*′, *J* = 10.7, 7.27 Hz), 3.89 (d, 2H, Gly-CH_2NH, *J* = 4.97 Hz), 2.81 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.35 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.02 (ddd, 1H, H-16, *J* = 13.6, 13.6, 4.57 Hz), 1.98 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, *J* = 13.7, 4.0, 2.67 Hz), 1.82 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.57 Hz), 1.72 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.63 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 1.34, 13.47 Hz), 1.58 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.44 (s, 9H, Boc-CH_3), 1.42 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.30 (m, 1H, H-21′), 1.25 (t, 3H, $COOCH_2CH_3$, *J* = 7.27 Hz), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.12 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.6, 13.6, 3.47 Hz), 1.01 (m, 1H, H-15′), 0.87 (s, 6H, H-23 and H-24), 0.79 (s, 3H, H-29), 0.79 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 170.1 (Gly-COO), 169.4 (C-13), 156.2 (Boc-COO), 128.4 (C-12), 82.0 (C-3), 79.7 (Boc-*quart*.-C), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 42.6 (Gly-CNH), 41.0 (C-19), 38.7 (C-1), 38.1 (C-10), 37.7 (C-22), 36.9 (C-4), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (3× Boc-CH_3 and C-23), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.6 (C-26), 17.3 (C-6), 16.6 (C-24), 16.4 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{39}H_{61}NO_7$ (655.90): C, 71.42; H, 9.37; N, 2.14. Found: C, 71.27; H, 9.52; N, 2.05.

4.2.6.33. Ethyl 3β-(Boc-L-alanyl)-11-oxo-olean-12-en-30-oate (33). Obtained from **2** and Boc-L-Ala by method A as a colourless powder; yield: 589 mg, 95%; mp 202–205 °C (decomp.); R_f = 0.66 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 99.75 (*c* 0.61, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.09); MS (ESI): *m/z* (%) = 670.3 ($[M+H]^+$, 23), 629.4 ($[M+Na]^+$, 100), 1027.3 ($[3M+2Na]^{2+}$, 28), 1339.2 ($[2M+H]^+$, 22), 1362.2 ($[2M+Na]^+$, 26); IR (KBr): ν = 3397 (br), 2972 (s), 2874 (m), 1746 (s), 1720 (s), 1652 (s), 1512 (m),

1456 (m), 1390 (m), 1367 (m), 1336 (m), 1280 (w), 1248 (w), 1216 (s), 1169 (s), 1087 (w), 1051 (m), 1029 (m), 984 (w), 970 (w), 917 (w), 881 (w), 865 (w), 770 (w), 670 (w), 589 (w), 538 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.63 (s, 1H, H-12), 5.06 (d, 1H, Ala-N*H*), 4.55 (dd, 1H, H-3, *J* = 11.9, 4.77 Hz), 4.29 (m, 1H, Ala-C*H*NH), 4.17 (dq, 1H, COOC*H*H′, *J* = 10.8, 7.27 Hz), 4.11 (dq, 1H, COOCH*H*′, *J* = 10.8, 7.27 Hz), 2.81 (ddd, 1H, H-1, *J* = 13.7, 3.5, 3.57 Hz), 2.35 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 13.1, 3.77 Hz), 2.02 (ddd, 1H, H-15, *J* = 13.4, 13.4, 4.67 Hz), 1.98 (m, 1H, H-21), 1.91 (ddd, 1H, H-19, *J* = 13.6, 4.1, 2.77 Hz), 1.81 (ddd, 1H, H-16, *J* = 13.4, 13.4, 4.77 Hz), 1.72 (m, 1H, H-2), 1.61 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 13.6, 13.67 Hz), 1.45 (m, 1H, H-7), 1.43 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.40 (m, 1H, H-22), 1.39 (d, 3H, Ala-CH_3, *J* = 7.27 Hz), 1.38 (m, 1H, H-6), 1.37 (m, 1H, H-6′), 1.35 (s, 3H, H-27), 1.34 (m, 1H, H-22′), 1.30 (m, 1H, H-21′), 1.25 (t, 3H, $COOCH_2CH_3$, *J* = 7.27 Hz), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.11 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.47 Hz), 1.00 (m, 1H, H-15′), 0.88 (s, 3H, H-24), 0.86 (s, 3H, H-23), 0.80 (m, 1H, H-5), 0.79 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.3 (C-30), 173.0 (Ala-COO), 169.3 (C-13), 155.0 (Boc-COO), 128.4 (C-12), 81.7 (C-3), 79.6 (Boc-*quart*.-C), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0 (C-5), 49.5 (Ala-CNH), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (3× Boc-CH_3), 28.2 (C-28), 28.0 (C-23), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.9 (Ala-CH_3), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{40}H_{63}NO_7$ (669.93): C, 71.71; H, 9.48; N, 2.09. Found: C, 71.51; H, 9.53; N, 1.87.

4.2.6.34. Ethyl 3β-(Boc-β-alanyl)-11-oxo-olean-12-en-30-oate (34). Obtained from **2** and Boc-β-Ala by method A as a colourless powder; yield: 225 mg, 55%; mp 79–82 °C; R_f = 0.59 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 108.65 (*c* 0.55, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.07); MS (ESI): *m/z* (%) = 670.3 ($[M+H]^+$, 42), 692.5 ($[M+Na]^+$, 100), 1024.9 ($[3M+K+H]^{2+}$, 30), 1027.5 ($[3M+2Na]^{2+}$, 34), 1362.3 ($[2M+Na]^+$, 50); IR (KBr): ν = 3421 (br), 2975 (s), 1727 (s), 1660 (m), 1508 (w), 1457 (w), 1389 (m), 1366 (m), 1325 (w), 1249 (m), 1215 (m), 1174 (s), 1086 (w), 1020 (w), 985 (w), 862 (w), 770 (w), 543 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 4.96 (br, 1H, Ala-NH), 4.54 (dd, 1H, H-3, *J* = 11.7, 4.87 Hz), 4.18 (dq, 1H, COOC*H*H′, *J* = 10.7, 7.27 Hz), 4.12 (dq, 1H, COOCH*H*′, *J* = 10.7, 7.27 Hz), 3.39 (dt, 2H, Ala-NHCH_2, *J* = 5.9, 5.97 Hz), 2.81 (ddd, 1H, H-1, *J* = 13.7, 3.7, 3.77 Hz), 2.52 (m, 2H, CH_2COO), 2.36 (s, 1H, H-9), 2.10 (dd, 1H, H-18, *J* = 13.7, 3.87 Hz), 2.03 (ddd, 1H, H-15, *J* = 13.6, 13.6, 4.57 Hz), 1.99 (m, 1H, H-21), 1.92 (ddd, 1H, H-19, *J* = 13.7, 4.0, 2.77 Hz), 1.82 (ddd, 1H, H-16, *J* = 13.4, 13.4, 4.97 Hz), 1.71 (m, 1H, H-2), 1.68 (m, 1H, H-7), 1.60 (dd, 1H, H-19′, *J* = 13.7, 13.77 Hz), 1.58 (m, 1H, H-2′), 1.57 (m, 1H, H-6), 1.46 (m, 1H, H-6′), 1.43 (s, 9H, Boc-CH_3), 1.40 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.36 (s, 3H, H-27), 1.33 (m, 1H, H-22′), 1.31 (m, 1H, H-21′), 1.26 (t, 3H, $COOCH_2CH_3$, *J* = 7.17 Hz), 1.17 (m, 1H, H-16′), 1.15 (s, 3H, H-25), 1.14 (s, 3H, H-28), 1.12 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.77 Hz), 1.01 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.80 (s, 3H, H-29), 0.79 (m, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 172.7 (Ala-COO), 169.3 (C-13), 156.9 (Boc-COO), 128.4 (C-12), 81.1 (C-3), 79.7 (Boc-*quart*.-C), 61.7 (C-9), 60.3 ($COOCH_2$), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1 and CH_2COO), 38.0 (C-4 and CH_2NH), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.4 (Boc-CH_3), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25), 14.3 ($COOCH_2CH_3$). Anal. Calcd for $C_{40}H_{63}NO_7$ (669.93): C, 71.71; H, 9.48; N, 2.09. Found: C, 71.52; H, 9.56; N, 2.01.

4.2.6.35. *i*-Propyl 3β-(Boc-β-glycyl)-11-oxo-olean-12-en-30-oate (35). Obtained from **3** and Boc-Gly by method A as a colourless powder; yield: 410 mg, 96%; mp 220–222 °C (decomp.); R_f = 0.69 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 90.23 (*c* 0.50, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.07); MS (ESI): *m/z* (%) = 692.3 ($[M+Na]^+$, 100), 1027.3 ($[3M+2Na]^{2+}$, 14), 1361.2 ($[2M+Na]^+$, 12); IR (KBr): ν = 3405 (br), 2978 (s), 2875 (m), 1723 (s), 1661 (s), 1509 (m), 1456 (m), 1388 (m), 1367 (m), 1281 (m), 1250 (m), 1216 (s), 1172 (s), 1108 (m), 1086 (w), 1054 (w), 1028 (w), 985 (m), 948 (w), 916 (w), 866 (w), 770 (w), 588 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.61 (s, 1H, H-12), 5.02 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.98 (m, 1H, Gly-NH), 4.56 (dd, 1H, H-3, *J* = 11.5, 4.47 Hz), 3.88 (d, 2H, Gly-CH_2, *J* = 4.97 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.6, 3.67 Hz), 2.34 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.3, 5.0, 5.07 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.27 Hz), 1.73 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.5, 13.57 Hz), 1.57 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.43 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.32 (m, 1H, H-22′), 1.26 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.11 (s, 6H, H-28 and H-26), 1.03 (ddd, 1H, H-1′, *J* = 13.7, 13.7, 3.77 Hz), 0.99 (m, 1H, H-15′), 0.86 (s, 6H, H-23 and H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 170.1 (Gly-COO), 169.5 (C-13), 155.7 (Boc-COO), 128.4 (C-12), 82.0 (C-3), 79.9 (Boc-*quart*.-C), 67.4 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 42.7 (Gly-CH_2), 41.0 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.3 (Boc-CH_3), 28.2 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.7 (C-26), 17.4 (C-6), 16.6 (C-24), 16.4 (C-25). Anal. Calcd for $C_{40}H_{63}NO_7$ (669.93): C, 71.71; H, 9.48; N, 2.09. Found: C, 71.56; H, 9.64; N, 1.94.

4.2.6.36. *i*-Propyl 3β-(Boc-L-alanyl)-11-oxo-olean-12-en-30-oate (36). Obtained from **3** and Boc-L-Ala by method A as a colourless powder; yield: 280 mg, 75%; mp 224–228 °C (decomp.); R_f = 0.59 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 93.61 (*c* 0.29, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (4.10); MS (ESI): *m/z* (%) = 684.0 ($[M+H]^+$, 7), 706.4 ($[M+Na]^+$, 100), 1048.3 ($[3M+2Na]^{2+}$, 6), 1389.2 ($[2M+Na]^+$, 18); IR (KBr): ν = 3443 (br), 3388 (m), 2978 (s), 2876 (m), 1724 (s), 1656 (s), 1618 (w), 1496 (m), 1454 (s), 1368 (s), 1354 (m), 1311 (m), 1280 (m), 1248 (m), 1216 (s), 1170 (s), 1110 (m), 1087 (m), 1053 (m), 1022 (m), 972 (w), 916 (w), 879 (w), 863 (w), 770 (w), 671 (w), 466 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.04 (m, 1H, Ala-NH), 5.01 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.54 (dd, 1H, H-3, *J* = 11.7, 4.87 Hz), 4.28 (m, 1H, Ala-CH), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.4, 3.47 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, *J* = 13.3, 3.37 Hz), 2.01 (dd, 1H, H-15, *J* = 13.7, 4.67 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, *J* = 13.6, 4.2, 2.37 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.37 Hz), 1.72 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.6, 13.67 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.40 (m, 1H, H-7′), 1.38 (d, 3H, Ala-CH_3, *J* = 7.27 Hz), 1.35 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.31 (m, 2H, H-22′ and H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.10 (s, 6H, H-28 and H-26), 1.03 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.85 (s, 3H, H-24), 0.79 (m, 1H, H-5), 0.77 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 173.0 (Ala-COO), 169.4 (C-13), 155.0 (Boc-COO), 128.4 (C-12), 81.7 (C-3), 79.6 (Boc-*quart*.-C), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 49.5 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9

(C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.3 (Boc-CH_3), 28.2 (C-23), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.8 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25). Anal. Calcd for $C_{41}H_{65}NO_7$ (683.96): C, 72.00; H, 9.58; N, 2.05. Found: C, 71.88; H, 9.71; N, 1.96.

4.2.6.37. *i*-Propyl 3β-(Boc-β-alanyl)-11-oxo-olean-12-en-30-oate (37). Obtained from **3** and Boc-β-Ala by method A as a colourless powder; yield: 400 mg, 97%; mp 114–116 °C (decomp.); R_f = 0.44 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 98.00 (*c* 0.50, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.05); MS (ESI): *m/z* (%) = 684.2 ($[M+H]^+$, 22), 706.3 ($[M+Na]^+$, 100), 1048 ($[3M+2Na]^{2+}$, 28), 1390.2 ($[2M+Na]^+$, 30); IR (KBr): ν = 3405 (br), 2977 (s), 1724 (s), 1660 (s), 1509 (m), 1456 (m), 1389 (m), 1366 (m), 1326 (w), 1280 (m), 1250 (m), 1217 (m), 1174 (s), 1109 (m), 1086 (w), 1020 (w), 985 (w), 879 (w), 770 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.02 (qq, 1H, *i*-Pr-CH, *J* = 6.2, 6.27 Hz), 4.95 (m, 1H, Ala-NH), 4.52 (dd, 1H, H-3, *J* = 11.7, 5.07 Hz), 3.37 (dt, 2H, Ala-CH_2NH_2, *J* = 5.8, 5.87 Hz), 2.79 (ddd, 1H, H-1, *J* = 13.7, 3.4, 3.47 Hz), 2.47 (t, 2H, Ala-CH_2COO, *J* = 6.27 Hz), 2.34 (s, 1H, H-9), 2.09 (dd, 1H, H-18, *J* = 12.9, 3.77 Hz), 2.01 (ddd, 1H, H-15, *J* = 13.6, 13.6, 4.57 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, *J* = 13.3, 3.3, 2.57 Hz), 1.80 (ddd, 1H, H-16, *J* = 13.8, 13.8, 4.77 Hz), 1.71 (ddd, 1H, H-2, *J* = 13.3, 13.3, 3.37 Hz), 1.66 (m, 1H, H-7), 1.59 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, *J* = 13.5, 13.57 Hz), 1.55 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (s, 9H, Boc-CH_3), 1.38 (m, 1H, H-7′), 1.37 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.33 (m, 1H, H-22′), 1.27 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.20 (d, 3H, *i*-Pr-CH_3, *J* = 6.27 Hz), 1.19 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.10 (s, 6H, H-28 and H-26), 1.03 (ddd, 1H, H-1′, *J* = 13.5, 13.5, 3.57 Hz), 0.99 (m, 1H, H-15′), 0.86 (s, 3H, H-24), 0.85 (s, 3H, H-23), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 172.1 (Ala-COO), 169.5 (C-13), 156.6 (Boc-COO), 128.4 (C-12), 81.1 (C-3), 79.5 (Boc-*quart.*-C), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.0 (C-19), 38.7 (C-1), 38.0 (C-4), 37.7 (C-22), 36.9 (C-10), 36.3 (Ala-CH_2NH_2), 34.9 (Ala-CH_2COO), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.4 (Boc-CH_3), 28.2 (C-28), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{41}H_{65}NO_7$ (683.96): C, 72.00; H, 9.58; N, 2.05. Found: C, 71.86; H, 9.63; N, 1.85.

4.2.6.38. Benzyl 3β-(Boc-glycyl)-11-oxo-olean-12-en-30-oate (38). Obtained from **4** and Boc-Gly by method A as a colourless powder; yield: 120 mg, 47%; mp 186–189 °C (decomp.); R_f = 0.55 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 107.04 (*c* 0.51, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 205 (4.03), 250 nm (4.05); MS (ESI): *m/z* (%) = 740.4 ($[M+Na]^+$, 100), 1099.3 ($[3M+2Na]^{2+}$, 17.3), 1458.2 ($[2M+Na]^+$, 20.2); IR (KBr): ν = 3398 (br), 2973 (s), 2873 (m), 1727 (s), 1660 (s), 1619 (w), 1499 (m), 1456 (m), 1388 (m), 1366 (s), 1280 (m), 1249 (m), 1213 (s), 1165 (s), 1085 (m), 1052 (w), 1028 (w), 984 (m), 915 (w), 881 (w), 866 (w), 768 (w), 752 (w), 698 (w), 670 (w), 586 (w), 464 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 5H, H-Ar), 5.54 (s, 1H, H-12), 5.20 (d, 1H, Bn-C*H*H′, *J* = 12.57 Hz), 5.08 (d, 1H, Bn-C*H*H′, *J* = 12.57 Hz), 4.98 (m, 1H, Gly-NH), 4.58 (dd, 1H, H-3, *J* = 11.7, 4.77 Hz), 3.90 (d, 2H, Gly-CH_2, *J* = 5.17 Hz), 2.81 (ddd, 1H, H-1, *J* = 13.6, 3.3, 3.37 Hz), 2.33 (s, 1H, H-9), 2.03 (m 1H, H-18), 2.02 (m, 1H, H-15), 2.01 (m, 1H, H-21), 1.93 (m, 1H, H-19), 1.80 (ddd, 1H, H-16, *J* = 13.9, 13.9, 4.87 Hz), 1.73 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.62 (m, 1H, H-2′), 1.61 (dd, 1H, H-19′, *J* = 13.6, 13.6), 1.57 (m, 1H, H-6), 1.45 (s, 9H, Boc-CH_3), 1.43 (m, 1H, H-6′), 1.41 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.34 (s, 3H, H-27), 1.32 (m, 1H, H-21′), 1.29 (m, 1H, H-22′), 1.16 (s, 3H, H-25), 1.16 (s, 3H, H-28), 1.14 (m, 1H, H-16′), 1.10 (s, 3H, H-26), 1.04 (ddd, 1H, H-1′, *J* = 13.3, 13.3, 3.67 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 6H, H-24 and H-23), 0.79 (m, 1H, H-5), 0.73 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.2 (C-30), 170.0 (Gly-COO), 169.1 (C-13), 155.7 (Boc-COO), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.6 (C_{ar}), 128.4 (C-12), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 82.0 (C-3), 77.2 (Boc-*quart.*-C), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 42.8 (Gly-CH_2), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.6 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-29), 28.3 (Boc-CH_3), 28.3 (C-23), 28.1 (C-28), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.6 (C-24), 16.4 (C-25). Anal. Calcd for $C_{44}H_{63}NO_7$ (717.97): C, 73.61; H, 8.84; N, 1.95. Found: C, 73.52; H, 8.69; N, 1.85.

4.2.6.39. Benzyl 3β-(Boc-L-alanyl)-11-oxo-olean-12-en-30-oate (39). Obtained from **4** and Boc-L-Ala by method A as a colourless powder; yield: 430 mg, 46%; mp 199–203 °C (decomp.); R_f = 0.59 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 101.74 (*c* 0.24, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 206 nm (4.16), 250 nm (4.16); MS (ESI): *m/z* (%) = 754.4 ($[M+Na]^+$, 100), 1120.3 ($[3M+2Na]^{2+}$, 8), 1485.2 ($[2M+Na]^+$, 14); IR (KBr): ν = 3440 (br), 2969 (s), 2876 (m), 1731 (s), 1715 (s), 1654 (s), 1496 (m), 1455 (m), 1398 (m), 1366 (m), 1215 (s), 1162 (s), 1086 (m), 1050 (m), 1026 (m), 986 (w), 970 (w), 914 (w), 879 (s), 861 (w), 768 (w), 745 (w), 733 (w), 697 (w), 670 (w), 586 (w), 475 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H, H-Ar), 5.53 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.47 Hz), 5.07 (d, 1H, Bn-CH*H*′, *J* = 12.47 Hz), 5.04 (m, 1H, Ala-NH), 4.54 (dd, 1H, H-3, *J* = 11.8, 4.77 Hz), 4.28 (m, 1H, Ala-CH), 2.80 (ddd, 1H, H-1, *J* = 13.7, 3.3, 3.37 Hz), 2.32 (s, 1H, H-9), 2.02 (m, 1H, H-18), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.92 (m, 1H, H-19), 1.79 (ddd, 1H, H-16, *J* = 13.7, 13.7, 4.27 Hz), 1.72 (m, 1H, H-2), 1.65 (m, 1H, H-7), 1.61 (m, 1H, H-2′), 1.60 (dd, 1H, H-19′, *J* = 13.4, 13.47 Hz), 1.57 (m, 1H, H-6), 1.45 (m, 1H, H-6′), 1.43 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.38 (m, 1H, H-22), 1.38 (d, 3H, Ala-CH_3, *J* = 7.0), 1.33 (s, 3H, H-27), 1.29 (m, 2H, H-22′ and H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 6H, H-25 and H-28), 1.09 (s, 3H, H-26), 1.03 (m, 1H, H-1′), 0.98 (m, 1H, H-15′), 0.87 (s, 3H, H-23), 0.85 (s, 3H, H-24), 0.78 (m, 1H, H-5), 0.72 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.2 (C-30), 173.0 (Ala-COO), 169.0 (C-13), 155.0 (Boc-COO), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.6 (C_{ar}), 128.4 (C-12), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 81.7 (C-3), 78.3 (Boc-*quart.*-C), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 49.6 (Ala-CH), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.1 (C-14), 41.0 (C-19), 38.7 (C-1), 38.2 (C-4), 37.6 (C-22), 36.9 (C-10), 32.7 (C-7), 31.7 (C-17), 31.1 (C-21), 28.4 (C-29), 28.3 (Boc-CH_3), 28.2 (C-23), 28.0 (C-28), 26.4 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.9 (Ala-CH_3), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{45}H_{65}NO_7$ (732.00): C, 73.84; H, 8.95; N, 1.91. Found: C, 73.77; H, 9.01; N, 1.78.

4.2.6.40. Benzyl 3β-(Boc-β-alanyl)-11-oxo-olean-12-en-30-oate (40). Obtained from **4** and Boc-β-Ala by method A as a colourless powder; yield: 600 mg, 66%; mp 176–179 °C (decomp.); R_f = 0.36 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 132.62 (*c* 0.34, MeOH); UV–vis (MeOH): λ_{max} (log ε) = 207 nm (4.06), 250 nm (4.10); MS (ESI): *m/z* (%) = 732.3 ($[M+H]^+$, 14), 754.4 ($[M+Na]^+$, 100), 763.3 ($[M+MeOH]^+$, 6), 770.3 ($[M+K]^+$, 20); IR (KBr): ν = 3436 (br), 2964 (s), 2873 (m), 1725 (s), 1654 (s), 1498 (m), 1456 (m), 1390 (m), 1365 (m), 1331 (m), 1256 (m), 1213 (m), 1170 (s), 1146 (s), 1076 (w), 1063 (w), 1022 (w), 984 (w), 915 (w), 878 (s), 756 (w), 699 (w), 545 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H, H-Ar), 5.52 (s, 1H, H-12), 5.18 (d, 1H, Bn-C*H*H′, *J* = 12.57 Hz), 5.06 (d, 1H, Bn-C*H*H′, *J* = 12.57 Hz), 4.94 (m, 1H, Ala-NH), 4.52 (dd, 1H, H-3, *J* = 11.7, 5.27 Hz), 3.37 (dt, 2H,

Ala-CH_2NH_2, J = 5.8, 5.87 Hz), 2.78 (ddd, 1H, H-1, J = 13.8, 3.8, 3.87 Hz), 2.50 (m, 2H, Ala-CH_2COO), 2.32 (s, 1H, H-9), 2.02 (m 1H, H-18), 1.97 (m, 1H, H-15), 1.96 (m, 1H, H-21), 1.92 (m, 1H, H-19), 1.78 (ddd, 1H, H-16, J = 13.9, 13.9, 4.17 Hz), 1.71 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, J = 13.6, 13.67 Hz), 1.55 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (s, 9H, Boc-CH_3), 1.38 (m, 1H, H-7′), 1.33 (m, 1H, H-22), 1.33 (s, 3H, H-27), 1.31 (m, 1H, H-21′), 1.28 (m, 1H, H-22′), 1.15 (m, 1H, H-16′), 1.14 (s, 6H, H-25 and H-28), 1.09 (s, 3H, H-26), 1.02 (m 1H, H-1′), 0.97 (m, 1H, H-15′), 0.86 (s, 3H, H-24), (s, 3H, H-23), 0.77 (m, 1H, H-5), 0.71 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.1 (C-30), 172.1 (Ala-COO), 169.0 (C-13), 155.7 (Boc-COO), 136.1 (C_{ar}), 128.6 (C_{ar}), 128.6 (C_{ar}), 128.4 (C-12), 128.3 (C_{ar}), 128.2 (C_{ar}), 128.2 (C_{ar}), 81.1 (C-3), 77.3 (Boc-*quart*.-C), 66.2 (Bn-CH_2), 61.6 (C-9), 55.0 (C-5), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 41.0 (C-19), 38.8 (C-1), 38.0 (C-4), 37.6 (C-22), 36.9 (C-10), 36.5 (Ala-CH_2COO), 34.9 (Ala-COO), 32.7 (C-7), 31.7 (C-17), 31.1 (C-21), 28.4 (C-29), 28.4 (Boc-CH_3), 28.2 (C-23), 28.1 (C-28), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). Anal. Calcd for $C_{45}H_{65}NO_7$ (732.00): C, 73.84; H, 8.95; N, 1.91. Found: C, 73.74; H, 9.11; N, 1.69.

4.2.6.41. Methyl 3β-(Boc-D-alanyl)-11-oxo-olean-12-en-30-oate (41). Obtained from **1** and Boc-D-Ala by method A as a colourless powder; yield: 450 mg, 97%; mp 205–208 °C (decomp.); R_f = 0.74 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 82.74 (c 0.41, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 249 nm (3.97); MS (ESI): m/z (%) = 656.0 ($[M+H]^+$, 8), 678.3 ($[M+Na]^+$, 100), 1006.3 ($[3M+2Na]^{2+}$, 12), 1334.1 ($[2M+Na]^+$, 14); IR (KBr): ν = 3371 (br), 2950 (s), 2874 (m), 1734 (s), 1718 (s), 1650 (s), 1509 (m), 1455 (m), 1388 (m), 1366 (m), 1306 (m), 1248 (m), 1216 (s), 1168 (s), 1088 (w), 1074 (m), 1049 (w), 1023 (w), 986 (w), 916 (w), 882 (w), 866 (w), 851 (w), 834 (w), 754 (s), 666 (w), 601 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H, H-12), 5.03 (m, 1H, Ala-NH), 4.53 (dd, 1H, H-3, J = 11.6, 4.47 Hz), 4.27 (m, 1H, Ala-CH), 3.67 (s, 3H, OMe), 2.80 (ddd, 1H, H-1, J = 13.7, 3.8, 3.87 Hz), 2.34 (s, 1H, H-9), 2.06 (dd, 1H, H-18, J = 13.7, 3.77 Hz), 2.00 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.90 (ddd, 1H, H-19, J = 13.7, 3.3, 2.97 Hz), 1.80 (ddd, 1H, H-16, J = 13.7, 13.7, 4.67 Hz), 1.70 (m, 1H, H-2), 1.64 (m, 1H, H-7), 1.61 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, J = 13.7, 13.77 Hz), 1.57 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.41 (m, 1H, H-7′), 1.37 (m, 1H, H-22), 1.35 (d, 3H, Ala-CH_3, J = 7.17 Hz), 1.34 (s, 3H, H-27), 1.29 (m, 2H, H-22′ and H-21′), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.13 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.03 (ddd, 1H, H-1′, J = 13.7, 13.7, 3.77 Hz), 1.00 (m, 1H, H-15′), 0.87 (s, 6H, H-23 and H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 172.0 (Ala-COO), 169.3 (C-13), 155.0 (Boc-COO), 128.5 (C-12), 81.7 (C-3), 78.4 (Boc-*quart*.-C), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 50.6 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23 and Boc-CH_3), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.4 (C-2), 23.3 (C-27), 18.8 (Ala-CH_3), 18.7 (C-26), 17.3 (C-6), 16.6 (C-24), 16.4 (C-25). Anal. Calcd for $C_{39}H_{61}NO_7$ (655.90): C, 71.42; H, 9.37; N, 2.14. Found: C, 71.28; H, 9.54; N, 1.95.

4.2.6.42. Ethyl 3β-(Boc-D-alanyl)-11-oxo-olean-12-en-30-oate (42). Obtained from **2** and Boc-D-Ala by method A as a colourless powder; yield: 440 mg, 98%; mp 175–178 °C (decomp.); R_f = 0.54 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 90.56 (c 0.29, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.03); MS (ESI): m/z (%) = 670.2 ($[M+H]^+$, 6), 692.4 ($[M+Na]^+$, 100), 1027.3 ($[3M+2Na]^{2+}$, 14) 1339.3 ($[2M+H]^+$, 8), 1361.3 ($[2M+Na]^+$, 24); IR (KBr): ν = 3366 (br), 2979 (s), 2873 (m), 1715 (s), 1698 (s), 1649 (s), 1625 (m), 1575 (w), 1514 (m), 1454 (m), 1389 (m), 1366 (m), 1313 (m), 1246 (m), 1215 (s), 1168 (s), 1088 (m), 1074 (m), 1049 (m), 1024 (m), 966 (w), 916 (w), 880 (w), 865 (w), 753 (s), 666 (w), 602 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (s, 1H, H-12), 5.03 (m, 1H, Ala-NH), 4.52 (dd, 1H, H-3, J = 11.6, 4.67 Hz), 4.30 (m, 1H, Ala-CH), 4.16 (dq, 1H, COOC*H*H′, J = 10.8, 7.17 Hz), 4.11 (dq, 1H, COOCH*H*′, J = 10.8, 7.17 Hz), 2.80 (ddd, 1H, H-1, J = 13.7, 3.8, 3.87 Hz), 2.34 (s, 1H, H-9), 2.08 (dd, 1H, H-18, J = 13.6, 3.77 Hz), 2.01 (m, 1H, H-15), 1.97 (m, 1H, H-21), 1.90 (m, 1H, H-19), 1.81 (m, 1H, H-16), 1.71 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.59 (dd, 1H, H-19′, J = 13.3, 13.37 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.41 (s, 9H, Boc-CH3), 1.39 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.35 (s, 3H, H-27), 1.35 (d, 3H, Ala-CH_3, J = 7.17 Hz), 1.29 (m, 1H, H-22′), 1.27 (m, 1H, H-21′), 1.24 (t, 3H, Et-CH_3, J = 7.17 Hz), 1.16 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.12 (s, 3H, H-28), 1.10 (s, 3H, H-26), 1.04 (m, 1H, H-1′), 0.99 (m, 1H, H-15′), 0.86 (s, 3H, H-23), 0.86 (s, 3H, H-24), 0.80 (m, 1H, H-5), 0.79 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.3 (C-30), 171.8 (Ala-COO), 169.4 (C-13), 155.0 (Boc-COO), 128.4 (C-12), 81.6 (C-3), 78.1 (Boc-*quart*.-C), 61.7 (C-9), 60.3 (Et-CH_2), 55.0 (C-5), 50.8 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.8 (C-20), 43.2 (C-14), 41.0 (C-19), 38.6 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-23), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.3 (C-2), 23.3 (C-27), 18.8 (Ala-CH_3), 18.6 (C-26), 17.3 (C-6), 16.6 (C-24), 16.4 (C-25), 14.3 (Et-CH_3). Anal. Calcd for $C_{40}H_{63}NO_7$ (669.93): C, 71.71; H, 9.48; N, 2.09. Found: C, 71.52; H, 9.63; N, 1.86.

4.2.6.43. *i*-Propyl 3β-(Boc-D-alanyl)-11-oxo-olean-12-en-30-oate (43). Obtained from **3** and Boc-D-Ala by method A as a colourless powder; yield: 380 mg, 84%; mp 178–181 °C (decomp.); R_f = 0.55 (hexane/ethyl acetate 7:3); $[\alpha]_D^{20}$ = 101.37 (c 0.39, $CHCl_3$); UV–vis (MeOH): λ_{max} (log ε) = 250 nm (4.04); MS (ESI): m/z (%) = 684.1 ($[M+H]^+$, 10), 706.3 ($[M+Na]^+$, 100), 1048.3 ($[3M+2Na]^{2+}$, 8), 1390.1 ($[2M+Na]^+$, 13); IR (KBr): ν = 3382 (br), 2978 (s), 2876 (m), 1723 (s), 1661 (s), 1621 (w), 1499 (m), 1455 (s), 1389 (s), 1367 (s), 1312 (m), 1249 (m), 1216 (s), 1171 (s), 1109 (s), 1087 (m), 1086 (m), 1022 (m), 973 (m), 916 (w), 880 (w), 864 (w), 770 (w), 669 (w), 539 (w), 464 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 1H, H-12), 5.04 (m, 1H, Ala-NH), 5.01 (qq, 1H, *i*-Pr-CH, J = 6.5, 6.57 Hz), 4.53 (dd, 1H, H-3, J = 11.7, 4.67 Hz), 4.27 (m, 1H, Ala-CH), 2.79 (ddd, 1H, H-1, J = 13.7, 3.5, 3.57 Hz), 2.34 (s, 1H, H-9), 2.09 (dd, 1H, H-18, J = 13.3, 3.77 Hz), 2.01 (dd, 1H, H-15, J = 13.3, 5.07 Hz), 1.96 (m, 1H, H-21), 1.89 (ddd, 1H, H-19, J = 13.7, 4.2, 2.57 Hz), 1.80 (ddd, 1H, H-16, J = 13.8, 13.8, 4.57 Hz), 1.70 (m, 1H, H-2), 1.66 (m, 1H, H-7), 1.60 (m, 1H, H-2′), 1.58 (dd, 1H, H-19′, J = 13.2, 13.27 Hz), 1.56 (m, 1H, H-6), 1.44 (m, 1H, H-6′), 1.42 (s, 9H, Boc-CH_3), 1.38 (m, 1H, H-7′), 1.36 (m, 1H, H-22), 1.35 (m, 3H, Ala-CH_3), 1.34 (s, 3H, H-27), 1.33 (m, 1H, H-22′), 1.31 (m, 1H, H-21′), 1.23 (d, 3H, *i*-Pr-CH_3, J = 6.3), 1.20 (d, 3H, *i*-Pr-CH_3, J = 6.37 Hz), 1.19 (m, 1H, H-16′), 1.14 (s, 3H, H-25), 1.11 (s, 6H, H-28 and H-26), 1.03 (ddd, 1H, H-1′, J = 13.3, 13.3, 3.37 Hz), 0.99 (m, 1H, H-15′), 0.87 (s, 6H, H-23 and H-24), 0.79 (m, 1H, H-5), 0.78 (s, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 175.8 (C-30), 171.2 (Ala-COO), 169.5 (C-13), 156.7 (Boc-COO), 128.4 (C-12), 81.6 (C-3), 79.2 (Boc-*quart*.-C), 67.3 (*i*-Pr-CH), 61.7 (C-9), 55.0 (C-5), 49.3 (Ala-CH), 48.4 (C-18), 45.4 (C-8), 43.7 (C-20), 43.2 (C-14), 41.0 (C-19), 38.6 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.6 (C-29), 28.3 (Boc-CH_3), 28.2 (C-23), 28.0 (C-28), 26.5 (C-16), 26.4 (C-15), 23.3 (C-2), 23.3 (C-27), 21.9 (*i*-Pr-CH_3), 21.7 (*i*-Pr-CH_3), 18.8 (Ala-CH_3), 18.6 (C-26), 17.3 (C-6), 16.6 (C-24), 16.3 (C-25). Anal. Calcd for $C_{41}H_{65}NO_7$ (683.96): C, 72.00; H, 9.58; N, 2.05. Found: C, 71.89; H, 9.71; N, 1.94.

Acknowledgements

We like to thank Dr. Harish Kommera and PD Dr. Reinhard Paschke from Biosolutions Halle GmbH for support. Furthermore we thank the Stiftung der Deutschen Wirtschaft e.V. (SDW) for a personal scholarship (to S.S.). Many thanks are due to Dr. Ralph Kluge (for ESI-MS), Dr. Dieter Ströhl (for the NMR measurements) and to Dr. Thomas Müller from the Dept. of Haematology/Oncology for providing the cell lines.

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