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Synthesis and cytotoxicity of diastereomeric benzylamides derived from maslinic acid, augustic acid and bredemolic acid

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ABSTRACT

36 substituted benzylamides were prepared starting from maslinic acid, bredemolic acid, and augustic acid and evaluated for their cytotoxicity in SRB assays employing several human tumor cell lines as well as non-malignant fibroblasts. Thereby, the benzylamides of maslinic acid, however, were found to be more cytotoxic than those obtained from augustic acid or bredemolic acid. The best compound (**18**, derived from maslinic acid) showed an EC_{50} value of 1.3 μM against A375 melanoma cells. Additional staining experiments revealed that this compound acted rather by apoptosis than by necrosis.

1. Introduction

Recently, we observed that the benzylamide of 2,3-di-*O*-acetyl-maslinic acid (**EM2**, Fig. 1) held high cytotoxicity for a panel of different human tumor cell lines combined with a good selectivity for the tumor cells and lower cytotoxicity for non-malignant cell lines. [1,2] Since analogs derived from oleanolic acid or ursolic acid held significant lower cytotoxicity with the tumor cell lines, we deduced that the presence of a second acetoxy group in ring A of pentacyclic triterpene carboxylic acids exerts significant influence on their cytotoxic activity. A possible reason could be a higher bioavailability due to better solubility in physiological solutions. In order to obtain a statement whether this holds true for analogs of **EM2** and whether the higher cytotoxicity holds true for other triterpenoic acids with two vicinal acetoxy groups in ring A but with an altered absolute configuration of these acetoxy groups, we decided to prepare some substituted benzylamides derived from bredemolic acid (**1**) [3–6], maslinic acid (**2**) [7–12] and augustic acid (**3**) [13–15]. Furthermore, the scope of terpenoids has been enlarged recently due to their applications in nanoscience, green chemistry and especially by studies concerning their self-assembly [16].

While numerous studies exist for maslinic acid and its derivatives, dealing with a wide variety of biological properties, only a few studies are known for augustic acid and even less for bredemolic acid. The latter finding might also be since bredemolic acid can be obtained in only low yields from natural sources. However, partial syntheses from oleanolic acids have already been described for **1**–**3**, too. [4] Bredemolic acid and augustic acid differ from maslinic acid by the configuration of the two hydroxy groups in ring A. While maslinic acid is configured (2α, 3 β), bredemolic acid (2β, 3α) configurated and augustic acid holds a (2β, 3β) configuration.

2. Results and discussion

As mentioned above, bredemolic acid (**1**) is accessible by a partial synthesis from oleanolic acid. [4] Its acetylation (Scheme 1) gave the known diacetate **4**. [17] Reaction of **4** with oxalyl chloride followed by addition of substituted benzylamines gave products **5**–**16**. For comparison, analogous reactions were carried out starting from maslinic acid (**2**). This pentacyclic triterpenoic acid was either extracted from pitted olives or obtained by partial synthesis [4] starting from oleanolic acid. Acetylation of **2** gave known [2] diacetate **17** that was converted into amides **18**–**29**, respectively. In similar fashion augustic acid (**3**, also obtained by partial synthesis from oleanolic acid) [4] was acetylated, and di-acetate **30** [18] transformed into amides **31**–**42**.

The cytotoxicity of the compounds was determined in SRB assays; the results of these assays are summarized in Table 1.

Analysis of these data reveals a few structure–activity relationships. The assumption that derivatives with two acetoxy groups on ring A have a significantly higher cytotoxicity than the previously described analogs with an oleanolic acid backbone carrying only one acetoxy group in ring A is confirmed. There is no significant dependence of observed cytotoxicity on the substituent on the benzyl ring. However, it was found that, as a rule, those derivatives derived from maslinic acid are somewhat more cytotoxic than those derived from augustic acid. Bredemolic

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acid-derived derivatives are less cytotoxic. The lowest cytotoxicity was observed for HT29 and MCF-7 tumor cells while the highest cytotoxicity was established for A375 and A2780 cells. All derivatives are significantly more cytotoxic with malignant cell lines than for non-malignant fibroblasts NIH 3T3. This has previously [1,2] been demonstrated also for **EM2**.

Some extra staining experiments employing A375 cells and compound **35** are depicted in Fig. 2 (thereby, cells in R1 are necrotic, in R2 late apoptotic, viable cells are measured in R3 and apoptotic cells are detected in R4). The results indicate that A375 cells die rather by apoptosis than by necrosis.

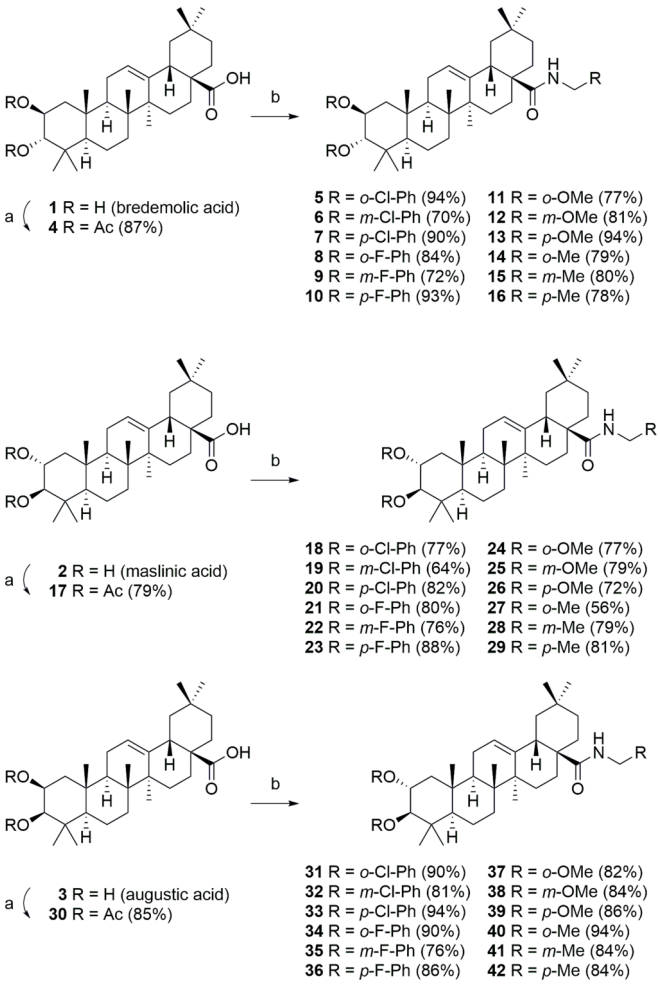
3. Conclusion

Based on our assumption that benzylamides of pentacyclic acetylated triterpenes are expected to exhibit particularly good cytotoxicity toward malignant cancer cell lines [based on a previous observation for a 2,3-di-*O*-acetyl-maslinic acid benzyl amide (**EM2**)], 36 new derivatives were prepared starting from maslinic acid, bredemolic acid, and augustic acid and evaluated for their cytotoxicity in SRB assays employing several human tumor cell lines as well as non-malignant fibroblasts. All compounds were found to be highly cytotoxic to cancer cells, while a significantly lower cytotoxicity was determined for the non-malignant fibroblasts. Benzylamides of maslinic acid, however, were found to be more cytotoxic than those obtained from augustic acid or bredemolic acid. The best compound (**35**) showed an EC_{50} value of 1.3 μM against A375 melanoma cells and 0.8 μM for ovarian carcinoma cells. Additional staining experiments revealed that this compound acted rather by apoptosis than by necrosis.

4. Experimental

4.1. General

NMR spectra were recorded using the Varian spectrometers (Darmstadt, Germany) DD2 and VNMRS (400 and 500 MHz, respectively). MS spectra were taken on a Advion expression^{L} CMS mass spectrometer (Ithaca, NY, USA; positive ion polarity mode, solvent: methanol, solvent flow: 0.2 mL/min, spray voltage: 5.17 kV, source voltage: 77 V, APCI corona discharge: 4.2 μA, capillary temperature: 250 °C, capillary voltage: 180 V, sheath gas: N_2). Thin-layer chromatography was performed on pre-coated silica gel plates supplied by Macherey-Nagel (Düren, Germany). IR spectra were recorded on a Spectrum 1000 FT-IR-spectrometer from Perkin Elmer (Rodgau, Germany). The UV/Vis-spectra were recorded on a Lambda 14 spectrometer from Perkin Elmer (Rodgau, Germany); optical rotations were measured at 20 °C using a JASCO-P2000 instrument (JASCO Germany GmbH, Pfungstadt, Germany). The melting points were determined using the Leica hot stage microscope Galen III (Leica Biosystems, Nussloch, Germany) and are uncorrected. The solvents were dried according to usual procedures. Microanalyses were performed with an Elementar Vario EL (CHNS) instrument (Elementar Analysensysteme GmbH, Elementar-Straβe 1, D-63505, Langenselbold, Germany). As checked by NMR and HPLC, the purity of all products was >95 %.



Scheme 1. Synthesis of amides **5**–**16** from bredemolic acid (**1**) and amides **18**–**29** from maslinic acid (**2**) and bredemolic acid derived benzyl amides 31–42; reactions and conditions: a) Ac_2O, DCM, NEt_3, DMAP (cat.), 21 °C, 12 h; b) $(COCl)_2$, DMF (cat.), then DCM, substituted benzylamine, 21 °C, 12 h, 21 °C.

All dry solvents were distilled over respective drying agents except for DMF which was distilled and stored under argon and molecular sieve. Reactions using air- or moisture-sensitive reagents were carried out under argon atmosphere in dried glassware. Triethylamine was stored over potassium hydroxide. Biological assays were performed as previously reported employing cell lines obtained from the Department of Oncology [Martin-Luther-University Halle Wittenberg; they were bought from ATCC: malignant: A 375, HT29, MCF7, A2780 and HeLa; non-malignant: NIH 3T3]. Oleanolic acid was obtained from Betulinines

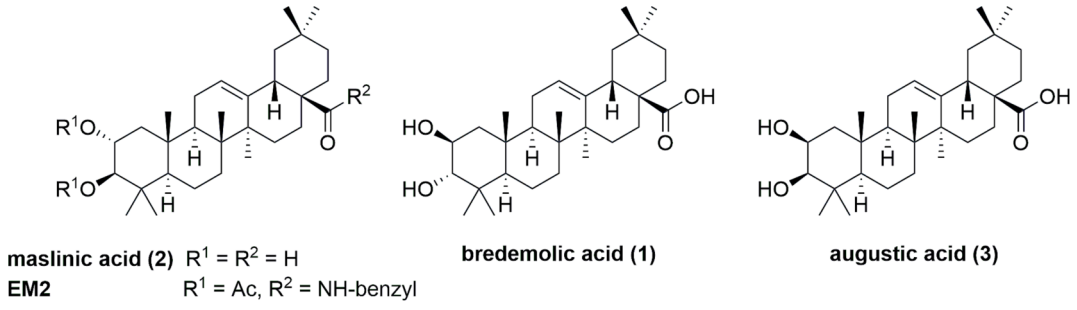


Fig. 1. Structure of bredemolic acid (**1**), maslinic acid (**2**), and augustic acid (**3**) and the benzyl amide of 2,3-di-*O*-acetyl-maslinic acid (**EM2**).

Table 1
Cytotoxicity of benzylamides **5**–**16**, **18**–**29** and **31**–**42** assessed from SRB-assays (EC_{50} values [μM] after 72 h of treatment). Human cancer cell lines: A375 (epithelial melanoma), HT29 (colorectal adenocarcinoma), MCF-7 (breast adenocarcinoma), A2780 (ovarian carcinoma), HeLa cervical carcinoma); non-malignant: NIH 3T3 (fibroblasts); n.d. not determined; n.s. not soluble under the conditions of the assay; positive control: doxorubicin (**DX**).

	A375	HT29	MCF-7	A2780	HeLa	NIH 3T3
5	3.3 ± 0.4	15.8 ± 3.6	> 20	5.4 ± 0.8	11.3 ± 2.7	>30
6	2.9 ± 0.1	10.7 ± 2.8	12.8 ± 2.7	2.9 ± 0.1	8.9 ± 2.7	>30
7	2.9 ± 0.2	11.5 ± 3.8	14.4 ± 3.5	4.2 ± 0.6	6.8 ± 1.8	>30
8	1.8 ± 0.2	6.0 ± 1.8	8.9 ± 1.5	3.2 ± 0.4	4.9 ± 1.0	>30
9	2.4 ± 0.1	10.5 ± 2.2	7.9 ± 1.5	3.2 ± 0.6	7.1 ± 1.1	>30
10	2.3 ± 0.9	6.1 ± 1.8	5.2 ± 2.2	1.6 ± 0.2	6.7 ± 0.9	>30
11	2.6 ± 0.7	7.0 ± 2.4	7.9 ± 2.4	2.5 ± 0.5	7.8 ± 1.0	>30
12	3.0 ± 0.1	8.4 ± 1.6	7.8 ± 1.1	3.1 ± 0.2	6.7 ± 0.8	>30
13	2.7 ± 0.6	10.1 ± 2.3	11.6 ± 1.4	3.3 ± 0.4	6.7 ± 2.0	>30
14	2.1 ± 0.3	4.4 ± 1.2	3.0 ± 0.6	1.7 ± 0.1	4.4 ± 0.5	>30
15	2.3 ± 0.6	6.0 ± 1.8	7.2 ± 1.0	2.7 ± 0.2	5.8 ± 1.1	>30
16	2.6 ± 0.5	7.4 ± 1.9	9.2 ± 1.5	2.4 ± 0.4	7.7 ± 1.9	>30
18	1.8 ± 0.3	6.8 ± 1.1	6.8 ± 0.9	1.9 ± 0.1	4.9 ± 0.5	>30
19	2.3 ± 0.3	13.5 ± 2.9	6.9 ± 1.3	1.6 ± 0.3	6.6 ± 0.4	>30
20	3.3 ± 0.3	>30	>30	2.9 ± 1.5	9.9 ± 0.8	>30
21	2.0 ± 0.1	4.5 ± 0.3	6.5 ± 1.0	2.4 ± 0.2	6.2 ± 0.5	>30
22	1.0 ± 0.1	4.5 ± 0.9	4.0 ± 0.4	0.8 ± 0.1	4.3 ± 0.4	>30
23	1.0 ± 0.1	4.4 ± 0.3	3.8 ± 0.5	0.8 ± 0.1	4.3 ± 0.8	18.3 ± 2.9
24	n.s.	n.s.	n.s.	n.s.	n.s.	>30
25	1.4 ± 0.1	5.1 ± 0.4	4.4 ± 0.7	1.3 ± 0.1	4.7 ± 0.4	>30
26	1.8 ± 0.1	7.2 ± 0.5	5.8 ± 0.8	1.6 ± 0.1	6.1 ± 07	>30
27	n.s.	n.s.	n.s.	n.s.	n.s.	>30
28	1.6 ± 0.2	6.2 ± 0.7	5.2 ± 0.5	1.4 ± 0.1	5.2 ± 0.3	>30
29	1.4 ± 0.2	9.9 ± 2.6	7.3 ± 0.9	1.6 ± 0.4	6.2 ± 0.6	> 30
31	2.5 ± 0.2	6.7 ± 1.1	7.9 ± 1.8	5.2 ± 0.6	7.8 ± 1.4	>30
32	2.2 ± 0.3	6.0 ± 1.9	7.1 ± 2.1	4.1 ± 0.3	13.2 ± 1.6	>30
33	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
34	2.3 ± 0.3	5.9 ± 1.6	6.3 ± 1.7	4.0 ± 0.7	7.4 ± 0.7	>30
35	1.0 ± 0.3	1.9 ± 0.4	2.9 ± 0.9	1.7 ± 0.5	2.9 ± 0.5	>30
36	n.s.	1.7 ± 0.7	3.0 ± 0.9	2.5 ± 0.2	2.8 ± 0.5	>30
37	1.7 ± 0.1	3.3 ± 0.6	4.7 ± 1.3	1.9 ± 0.4	2.9 ± 0.7	>30
38	1.8 ± 0.1	3.8 ± 0.3	3.8 ± 0.8	1.9 ± 0.3	5.8 ± 0.5	>30
39	1.3 ± 0.2	2.5 ± 0.7	4.3 ± 1.5	2.1 ± 0.3	4.1 ± 1.5	>30
40	1.3 ± 0.1	3.2 ± 0.3	3.9 ± 0.7	1.7 ± 0.2	4.8 ± 0.4	>30
41	1.5 ± 0.1	3.2 ± 0.5	4.0 ± 0.8	2.2 ± 0.3	4.8 ± 0.8	>30
42	1.3 ± 0.1	3.3 ± 0.6	4.4 ± 0.5	2.1 ± 0.1	4.4 ± 1.0	>30
DX	n.d.	0.25 ± 0.02	0.1 ± 0.01	0.1 ± 0.01	n.d.	0.01 ± 0.001

(Strbrna Skalice, Czech Republic) and used as received.

For the SRB assay: cells were seeded into 96 well plates on day zero at appropriate cell densities to prevent confluence of the cells during the period of the experiment. After 24 h, the cells were treated with different concentrations (1, 3, 7, 12, 20 and 30 μM), but the final concentration of DMSO/DMF never exceeded 0.5 %, which was non-toxic to the cells. After 72 h treatment, the supernatant media from the 96 well plates were discarded, then the cells were fixed with 10 % trichloroacetic acid and allowed to rest at 4 °C. After 24 h of fixation, the cells were washed in a strip washer and then dyed with SRB solution (200 μL, 10 mM) for 20 min. Then the plates were washed four times with 1 % sacetic acid to remove the excess of the dye and allowed to air-dry overnight. Tris base solution (200 μL, 10 mM) was added to each well. The absorbance was measured with a 96 well plate reader from Tecan Spectra.

4.2. Syntheses

4.2.1. Bredemolic acid (1)

Starting from commercially available oleanolic acid, **1** was prepared as previously reported; m.p. 239–242 °C lit.: [4] 234–237 °C]; $[\alpha]_D$ = +92.8° (*c* 0.145, pyridine) [lit.: [4] + 91.13° (*c* 0,290, pyridine); MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 471.3 (100 %, $[M-H]^-$).

4.2.2. (2β,3α) Diacetyloxy-olean-12-en-28-oic acid (4)

Compound **4** was obtained from **1** following standard procedure for acetylation with acetic anhydride; yield 87 %; m.p. 165–167 °C [lit.: [19] 163–166 °C]; $[\alpha]_D$ = +78.2° (*c* 0.180, $CHCl_3$) [lit.: [19] + 75.98° (*c* 0.50, $CHCl_3$); MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 555.2 (100 %, $[M-H]^-$).

4.2.3. (2β,3α) N-(2-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (5)

Compound **5** (115 mg, 94 %) was obtained from **4** (100 mg, 0.18 mmol) according to GPA as a white solid; m.p. 118 °C; R_f = 0.37 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +47.9° (*c* 0.084, MeOH); IR (ATR): ν = 2944w, 1739 s, 1645w, 1515w, 1471w, 1463w, 1366 m, 1241 s, 1227 s, 1027 m, 749w, 606w, 534w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.41 – 7.30 (m, 2H, 39-H, 40-H), 7.23 – 7.16 (m, 2H, 37-H, 38-H), 6.44 (t, *J* = 6.0 Hz, 1H, NH), 5.35 (t, *J* = 3.7 Hz, 1H, 12-H), 4.97 (d, *J* = 6.4 Hz, 1H, 3-H), 4.94 – 4.89 (m, 1H, 2-H), 4.55 (dd, *J* = 14.5, 6.0 Hz, 1H, 35-H_a), 4.40 (dd, *J* = 14.5, 5.9 Hz, 1H, 35-H_a), 2.53 (dd, *J* = 12.7, 4.3 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 1.97 (dt, *J* = 13.7, 3.9 Hz, 1H, 16-H_a), 1.88 – 1.82 (m, 2H, 11-H), 1.80 – 1.73 (m, 1H, 19-H_a), 1.72 – 1.63 (m, 3H, 1-H_a, 16-H_a, 22-H_a), 1.61 – 1.51 (m, 3H, 1-H_a, 9-H, 22-H_a), 1.50 – 1.49 (m, 1H, 15-H_a), 1.48 – 1.40 (m, 2H, 6-H_a, 7-H_a), 1.38 – 1.30 (m, 2H, 6-H_a, 21-H_a), 1.25 – 1.17 (m, 4H, 5-H, 7-H_a, 21-H_a, 19-H_a), 1.16 (s, 3H, 27-H), 1.07 (s, 3H, 25-H), 1.04 – 1.02 (m, 1H, 15-H_a), 1.01 (s, 3H, 24-H), 0.91 – 0.87 (m, 9H, 23-H, 29-H, 20-H), 0.46 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.3 (C-31), 170.1 (C-33), 144.6 (C-13), 136.1 (C-36), 134.1 (C-41), 131.0 (C-40), 129.5 (C-39), 127.3 (C-38), 123.1 (C-12), 76.2 (C-3), 70.7 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-17), 46.7 (C-19), 42.7 (C-18), 42.4 (C-14), 41.6 (C-35), 41.3 (C-1), 39.5 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.2 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 25.9 (C-27), 23.9 (C-16), 23.7 (C-29), 23.6 (C-11), 22.3 (C-24), 21.5 (C-34), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.39, H 8.59, N 2.21; found: C 72.11, H 8.87 N 1.98.

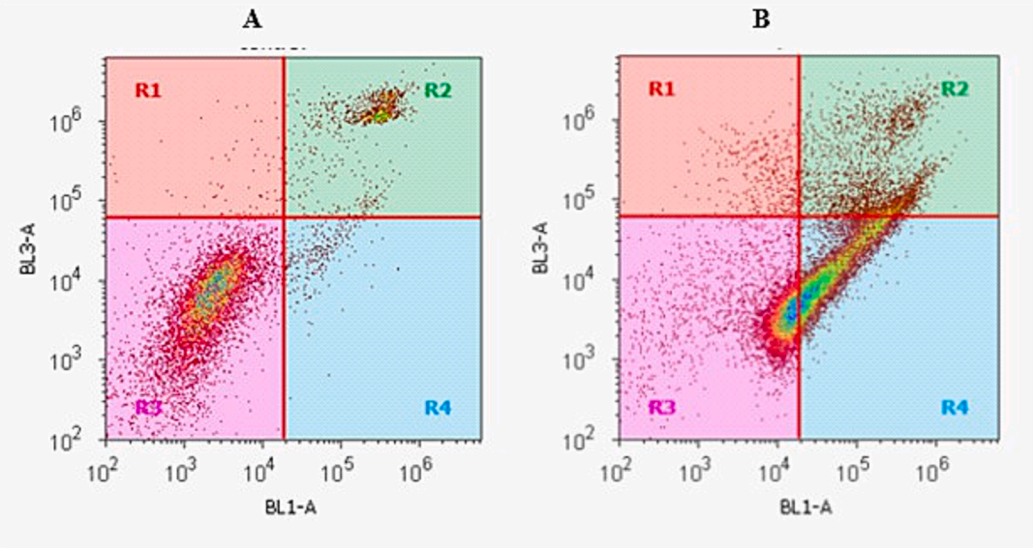


Fig. 2. FITC/Annexin V / Propidium iodide assay employing compound **35** and A375 cells (24 h, 2 × EC_{50} concentration); **A** control; **B** incubation with **35**.

4.2.4. (2β,3α) N-(3-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (6)

Compound **6** (85 mg, 70 %) was obtained from **4** (100 mg, 0.18 mmol) according to GPA as a white solid; m.p. 109 °C; $R_f = 0.29$ (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D = +51.2°$ (*c* 0.054, MeOH); IR (ATR): ν = 2945w, 1740 s, 1643w, 1517w, 1473w, 1433w, 1367 m, 1242 s, 1228 s, 1027 m, 681w, 605w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26 – 7.22 (m, 3H, 38-H, 39-H, 41-H), 7.17 – 7.12 (m, 1H, 37-H), 6.18 (t, *J* = 5.6 Hz, 1H, NH), 5.34 (t, *J* = 3.6 Hz, 1H, 12-H), 4.98 (d, *J* = 6.4 Hz, 1H, 3-H), 4.95 – 4.89 (m, 1H, 2-H), 4.54 (dd, *J* = 14.8, 6.1 Hz, 1H, 35-H_a), 4.16 (dd, *J* = 14.9, 5.0 Hz, 1H, 35-H_b), 2.57 – 2.51 (m, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.96 (m, 1H, 16-H_a), 1.90 – 1.84 (m, 2H, 11-H), 1.82 – 1.74 (m, 1H, 19-H_a), 1.73 – 1.64 (m, 3H, 1-H_a, 16-H_b, 22-H_a), 1.64 – 1.52 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.51 – 1.41 (m, 3H, 6-H, 7-H_a), 1.37 (dt, *J* = 13.7, 4.0 Hz, 1H, 21-H_a), 1.31 – 1.19 (m, 4H, 5-H, 7-H_b, 21-H_b, 19-H_b), 1.18 (s, 3H, 27-H), 1.11 (s, 3H, 25-H), 1.09 – 1.03 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.91 (s, 9H, 23-H, 29-H, 30-H), 0.66 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.3 (C-28), 170.3 (C-31), 170.1 (C-33), 145.0 (C-13), 140.7 (C-36), 134.6 (C-40), 130.1 (C-38), 128.1 (C-41), 127.7 (C-39), 126.1 (C-37), 123.0 (C-12), 76.2 (C-3), 70.6 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.6 (C-17), 43.2 (C-35), 42.6 (C-18), 42.5 (C-14), 41.3 (C-1), 39.7 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 24.0 (C-16), 23.7 (C-29), 23.5 (C-11), 22.3 (C-24), 21.4 (C-34), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.2 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.39, H 8.59, N 2.21; found: C 72.19, H 8.82 N 2.02.

4.2.5. (2β,3α) N-(4-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (6)

Compound **7** (110 mg, 90 %) was obtained from **4** (100 mg, 0.18 mmol) according to GPA as a white solid; m.p. 115 °C; $R_f = 0.71$ (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D = +46.6°$ (*c* 0.037, MeOH); IR (ATR): ν = 2945 m, 1739 s, 1643w, 1517w, 1492w, 1462w, 1367 m, 1242 s, 1227 s, 1091w, 1027 m, 1017 m, 801w, 754w, 605w, 556w, 475w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2H, 38-H, 40-H), 7.18 (d, *J* = 8.4 Hz, 2H, 37-H, 41-H), 6.17 (t, *J* = 5.6 Hz, 1H, NH), 5.32 (t, *J* = 3.6 Hz, 1H, 12-H), 4.98 (d, *J* = 6.4 Hz, 1H, 3-H), 4.95 – 4.86 (m, 1H, 2-H), 4.55 (dd, *J* = 14.8, 6.3 Hz, 1H, 35-H_a), 4.11 (dd, *J* = 14.7, 4.7 Hz, 1H, 35-H_b), 2.53 (dd, *J* = 13.2, 3.8 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.94 (m, 1H, 16-H_a), 1.85 (dd, *J* = 8.8, 3.6 Hz, 2H, 11-H), 1.81 – 1.63 (m, 4H, 1-H_a, 16-H_b, 22-H_a, 19-H_a), 1.63 – 1.53 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.53 – 1.41 (m, 3H, 6-H, 7-H_a), 1.36 (dt, *J* = 13.5, 4.3 Hz, 1H, 21-H_a), 1.30 – 1.19 (m, 4H, 5-H, 7-H_b, 21-H_b, 19-H_b), 1.18 (s, 3H, 27-H), 1.10 (s, 3H, 25-H), 1.08 – 1.03 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.92 – 0.89 (m, 9H, 23-H, 29-H, 30-H), 0.64 (s, 3H, 26-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.3 (C-28), 170.3 (C-31), 170.1 (C-33), 145.0 (C-13), 137.2 (C-36), 133.3 (C-39), 129.3 (C-37, 41), 128.9 (C-38, 40), 122.9 (C-12), 76.2 (C-3), 70.6 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-17), 46.6 (C-19), 43.0 (C-35), 42.5 (C-18), 42.4 (C-14), 41.2 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 24.0 (C-16), 23.7 (C-29), 23.6 (C-11), 22.2 (C-24), 21.4 (C-34), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.39, H 8.59, N 2.21; found: C 72.13, H 8.81, N 1.96.

4.2.6. (2β,3α) N-(2-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (8)

Compound **8** (150 mg, 84 %) was obtained from **4** (150 mg, 0.27 mmol) according to GPA as a white solid; m.p. 110 °C; $R_f = 0.28$ (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D = +48.1°$ (*c* 0.066, MeOH); IR (ATR): ν = 2944w, 1739 m, 1652w, 1517w, 1489w, 1457w, 1366 m, 1224 s, 1226 s, 1032 m, 832w, 754 m, 605w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (dt, *J* = 7.6, 1.8 Hz, 1H, 37-H), 7.25 – 7.21 (m, 1H, 39-H), 7.10 (dd, *J* = 7.5, 1.2 Hz, 1H, 38-H), 7.07 – 7.00 (m, 1H, 40-H), 6.29 (t, *J* = 5.9 Hz, 1H, NH), 5.34 (t, *J* = 3.7 Hz, 1H, 12-H), 4.98 (d, *J* = 6.4 Hz, 1H, 3-H), 4.95 – 4.87 (m, 1H, 2-H), 4.55 (dd, *J* = 14.7, 6.0 Hz, 1H, 35-H_a), 4.33 (dd, *J* = 14.7, 5.2 Hz, 1H, 35-H_b), 2.52 (dd, *J* = 13.1, 4.4 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.93 (m, 1H, 16-H_a), 1.88 – 1.82 (m, 2H, 11-H), 1.80 – 1.62 (m, 4H, 1-H_a, 16-H_b, 19-H_a, 22-H_a), 1.61 – 1.50 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.50 – 1.40 (m, 3H, 6-H, 7-H_a), 1.35 (dt, *J* = 13.6, 3.8 Hz, 1H, 21-H_a), 1.27 – 1.17 (m, 4H, 5-H, 7-H_b, 19-H_b, 21-H_b), 1.16 (s, 3H, 27-H), 1.07 (s, 3H, 25-H), 1.05 – 1.02 (m, 1H, 15-H_b), 1.01 (s, 3H, 24-H), 0.90 (s, 9H, 23-H, 29-H, 30-H), 0.54 (s, 3H, 26-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.1 (C-28), 170.3 (C-31), 170.1 (C-33), 161.44 (d, *J* = 245.8 Hz, C-41), 144.7 (C-13), 130.68 (d, *J* = 4.5 Hz, C-37), 129.31 (d, *J* = 7.7 Hz, C-39), 125.51 (d, *J* = 14.7 Hz, C-36), 124.46 (d, *J* = 3.6 Hz, C-38), 123.0 (C-12), 115.39 (d, *J* = 21.4 Hz, C-40), 76.2 (C-3), 70.7 (C-2), 50.5 (C-5), 48.0 (C-9), 46.7 (C-17), 46.6 (C-19), 44.96 (d, *J* = 49.9 Hz, C-35), 42.6 (C-18), 42.4 (C-14), 41.3 (C-1), 39.6 (C-8), 36.9 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 25.9 (C-27), 23.9 (C-16), 23.7 (C-29), 23.6 (C-11), 22.2 (C-24), 21.4 (C-34), 21.1

(C-32), 18.7 (C-6), 18.2 (C-25), 16.6 (C-26) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -119.04 ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 662.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.96, H 9.15 N 1.99.

4.2.7. (2β,3α) N-(3-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (9)

Compound **9** (129 mg,72 %) was obtained from **4** (150 mg, 0.27 mmol) according to GPA as a white solid; m.p. 113 °C; R_f = 0.32 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +55.1° (*c* 0.054, MeOH); IR (ATR): ν = 2944w, 1739 s, 1643w, 1592w, 1517w, 1450w, 1367 m, 1243 s, 1227 s, 1027 m, 756w, 605w, 521w, 440w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 – 7.27 (m, 1H, H-38), 7.03 (dt, *J* = 7.7, 1.3 Hz, 1H, H-37), 6.98 – 6.93 (m, 2H, H-39, H-41), 6.20 (t, *J* = 5.7 Hz, 1H, NH), 5.34 (t, *J* = 3.6 Hz, 1H, 12-H), 4.98 (d, *J* = 6.4 Hz, 1H, 3-H), 4.94 – 4.87 (m, 1H, 2-H), 4.59 (dd, *J* = 14.9, 6.2 Hz, 1H, 35-H_a), 4.15 (dd, *J* = 14.9, 4.9 Hz, 1H, 35-H_b), 2.55 (dd, *J* = 12.9, 4.5 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.01 – 1.96 (m, 1H, 16-H_a), 1.88 – 1.84 (m, 2H, 11-H), 1.82 – 1.71 (m, 2H, 22-H_a, 19-H_a), 1.72 – 1.65 (m, 2H, 1-H_a, 16-H_b), 1.64 – 1.53 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.51 – 1.41 (m, 3H, 6-H, 7-H_a), 1.37 (dt, *J* = 13.4, 4.0 Hz, 1H, 21-H_a), 1.30 – 1.20 (m, 4H, 5-H, 7-H_b, 19-H_b, 21-H_b), 1.18 (s, 3H, 27-H), 1.10 (s, 3H, 25-H), 1.09 – 1.04 (m, 1H, 15-H_a), 1.02 (s, 3H, 24-H), 0.91 (m, 9H, 23-H, 29-H, 30-H), 0.67 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.3 (C-28), 170.3 (C-31), 170.1 (C-33), 163.13 (d, *J* = 246.6 Hz, C-40), 145.0 (C-13), 141.24 (d, *J* = 7.1 Hz, C-36), 130.30 (d, *J* = 8.2 Hz, C-38), 123.42 (d, *J* = 2.9 Hz, C-37), 122.9 (C-12), 114.77 (d, *J* = 21.9 Hz, C-39), 114.39 (d, *J* = 21.0 Hz, C-41), 76.2 (C-3), 70.6 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.6 (C-17), 43.19 (d, *J* = 1.9 Hz, C-35), 42.6 (C-18), 42.4 (C-14), 41.2 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 24.0 (C-16), 23.7 (C-29), 23.5 (C-11), 22.2 (C-24), 21.4 (C-34), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -112.84 ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 662.6 (38 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.87, H 9.14 N 1.97.

4.2.8. (2β,3α) N-(4-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (10)

Compound **10** (167 mg, 93 %) was obtained from **4** (150 mg, 0.27 mmol) according to GPA as a white solid; m.p. 117 °C; R_f = 0.25 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +52.2° (*c* 0.105, MeOH); IR (ATR): ν = 2943w, 1739 m, 1642w, 1509 m, 1462w, 1433w, 1367w, 1223 s, 1156w, 1027 m, 823w, 752w, 605w, 577w, 486w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.18 (m, 2H, 37-H, 41-H), 7.04 – 6.95 (m, 2H, 38-H, 40-H), 6.16 (t, *J* = 5.6 Hz, 1H, NH), 5.31 (t, *J* = 3.1 Hz, 1H, 12-H), 4.98 (d, *J* = 6.4 Hz, 1H, 3-H), 4.95 – 4.88 (m, 1H, 2-H), 4.54 (dd, *J* = 14.6, 6.2 Hz, 1H, 35-H_a), 4.13 (dd, *J* = 14.6, 4.5 Hz, 1H, 35-H_b), 2.53 (dd, *J* = 13.3, 4.4 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.93 (m, 1H, 16-H_a), 1.85 (dd, *J* = 8.9, 3.5 Hz, 2H, 11-H), 1.80 – 1.63 (m, 5H, 1-H_a, 16-H_b, 22-H, 19-H_a), 1.62 – 1.53 (m, 3H, 1-H_b, 9-H, 15-H_a), 1.52 – 1.41 (m, 3H, 6-H, 7-H_a), 1.36 (dt, *J* = 13.4, 4.2 Hz, 1H, 21-H_a), 1.28 – 1.20 (m, 4H, 5-H, 7-H_b, 21-H_b, 19-H_b), 1.18 (s, 3H, 27-H), 1.10 (s, 3H, 25-H), 1.07 – 1.04 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.94 – 0.88 (m, 9H, 23-H, 29-H, 30-H), 0.65 (s, 3H, 26-H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C-28), 170.3 (C-31), 170.1 (C-33), 162.27 (d, *J* = 245.9 Hz, C-39), 145.0 (C-13), 134.44 (d, *J* = 3.6 Hz, C-36), 129.65 (d, *J* = 8.3 Hz, C-37, C-41), 122.9 (C-12), 115.62 (d, *J* = 21.7 Hz, C-38, C-40), 76.2 (C-3), 70.6 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-17), 46.5 (C-19), 43.0 (C-35), 42.5 (C-18), 41.2 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 24.0 (C-16), 23.7 (C-29), 23.6 (C-11), 22.2 (C-24), 21.4 (C-34), 21.1, 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -115.26 ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 662.0 (86 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.85, H 9.15 N 1.85.

4.2.9. (2β,3α) N-(2-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (11)

Compound **11** (233 mg, 77 %) was obtained from **4** (250 mg, 0.45 mmol) according to GPA as a white solid; m.p. 114 °C; R_f = 0.73 (SiO_2, hexanes/ethyl acetate, 5:5); $[\alpha]_D$ = +38.5° (*c* 0.072, MeOH); IR (ATR): ν = 2943w, 1739 m, 1651w, 1514w, 1493w, 1367w, 1240 s, 1227 s, 1027 m, 751 m, 605w, 525w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 – 7.18 (m, 2H, 37-H, 39-H), 7.00 – 6.80 (m, 2H, 28-H, 40-H), 6.47 (t, *J* = 5.6 Hz, 1H, NH), 5.27 (t, *J* = 3.6 Hz, 1H, 12-H), 4.96 (d, *J* = 6.3 Hz, 1H, 3-H), 4.93 – 4.88 (m, 1H, 2-H), 4.45 (dd, *J* = 14.2, 5.7 Hz, 1H, 35-H_a), 4.36 (dd, *J* = 14.2, 5.6 Hz, 1H, 35-H_b), 3.87 (s, 3H, 42-H), 2.49 (dd, *J* = 12.6, 4.3 Hz, 1H, 18-H), 2.05 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 1.94 (dt, *J* = 14.7, 13.6, 4.8 Hz, 1H, 16-H_a), 1.83 – 1.78 (m, 2H, 11-H), 1.77 – 1.75 (m, 1H, 19-H_a), 1.74 – 1.63 (m, 3H, 1-H_a, 16-H_b, 22-H_a), 1.61 – 1.47 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.45 – 1.30 (m, 4H, 6-H, 7-H_a, 21-H_a), 1.28 – 1.16 (m, 4H, 5-H, 7-H_b, 19-H_b, 21-H_b), 1.15 (s, 3H, 27-H), 1.07 (m, 1H, 15-H_b), 1.04 (s, 3H, 25-H), 1.00 (s, 3H, 24-H), 0.91 – 0.87 (m, 9H, 23-H, 29-H, 30-H), 0.43 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.5 (C-28), 170.3 (C-31), 170.1 (C-33), 157.8 (C-41), 145.0 (C-13), 130.2 (C-39), 128.8 (C-37), 126.6 (C-36), 122.4 (C-12), 120.9 (C-38), 110.2 (C-40), 76.2 (C-3), 70.7 (C-2), 55.4 (C-42), 50.5 (C-5), 48.0 (C-9), 46.6 (C-17), 42.6 (C-18), 42.4 (C-14), 39.6 (C-35), 39.5 (C-8), 36.9 (C-4), 36.7 (C-10), 34.3 (C-21), 33.2 (C-30), 32.8 (C-22), 30.9 (C-20), 25.9 (C-27), 23.7 (C-29), 22.2 (C-24), 21.5 (C-34), 21.1 (C-32), 18.1 (C-25), 16.4 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 674.1 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 73.63, H 9.10, N 2.07; found: C 73.40, H 9.41, N 1.86.

4.2.10. (2β,3α) N-(3-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (12)

Compound **12** (245 mg, 81 %) was obtained from **4** (250 mg, 0.45 mmol) according to GPA as a white solid; m.p. 110 °C; R_f = 0.85 (SiO_2, hexanes/ethyl acetate, 5:5); $[\alpha]_D$ = +49.1° (*c* 0.023, MeOH); IR (ATR): ν = 2942w, 1738 m, 1641w, 1518w, 1489w, 1460w, 1367 m, 1241 s, 1227 s, 1027 m, 756w, 693w, 605w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 7.9 Hz, 1H, 38-H), 6.87 – 6.75 (m, 3H, 37-H, 39-H, 41-H), 6.16 (t, *J* = 5.4 Hz, 1H, NH), 5.32 (t, *J* = 3.6 Hz, 1H, 12-H), 4.99 (d, *J* = 6.5 Hz, 1H, 3-H), 4.96 – 4.89 (m, 1H, 2-H), 4.59 (dd, *J* = 14.7, 6.3 Hz, 1H, 35-H_a), 4.12 (dd, *J* = 14.7, 4.5 Hz, 1H, 35-H_b), 3.80 (s, 3H, 42-H), 2.54 (dd, *J* = 13.3, 4.4 Hz, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.95 (m, 1H, 16-H_a), 1.89 – 1.84 (m, 2H, 11-H), 1.80 – 1.72 (m, 2H, 19-H_a, 22-H_a), 1.72 – 1.52 (m, 6H, 1-H, 9-H, 15-H_a, 16-H_b, 22-H_b), 1.50 – 1.32 (m, 4H, 6-H, 7-H_a, 21-H_a), 1.30 – 1.20 (m, 4H, 5-H, 7-H_b, 21-H_b, 19-H_b), 1.18 (s, 3H, 27-H), 1.10 (s, 3H, 25-H), 1.08 – 1.04 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.93 – 0.88 (m, 9H, 23-H, 29-H, 30-H), 0.69 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.1 (C-28), 170.3 (C-31), 170.1 (C-33), 160.0 (C-40), 145.0 (C-13), 140.1 (C-36), 129.9 (C-38), 122.9 (C-12), 120.1 (C-37), 113.5 (C-39), 113.0 (C-41), 76.2 (C-3), 70.7 (C-2), 55.4 (C-42), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.6 (C-17), 43.7 (C-35), 42.6 (C-18), 42.4 (C-14), 41.3 (C-1), 39.7 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 24.0 (C-16), 23.7 (C-29), 23.5 (C-11), 22.3 (C-24), 21.4 (C-34), 21.1 (C-32), 18.8 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 676.3 (100 %, $[M + H]^+$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 73.63, H 9.10, N 2.07; found: C 73.47, H 9.33, N 1.96.

4.2.11. (2β,3α) N-(4-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (13)

Compound **13** (286 mg, 94 %) was obtained from **4** (250 mg, 0.45 mmol) according to GPA as a white solid; m.p. 112 °C; R_f = 0.79 (SiO_2, hexanes/ethyl acetate, 5:5); $[\alpha]_D$ = +44.9° (*c* 0.078, MeOH); IR (ATR): ν = 2943w, 1739 m, 1642w, 1512 m, 1463w, 1367w, 1242 s, 1227 s, 1174w, 1031 m, 821w, 605w, 523w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ

= 7.17 (d, J = 8.6 Hz, 2H, 37-H, 41-H), 6.86 (d, J = 8.6 Hz, 2H, 38-H, 40-H), 6.10 – 6.08 (m, 1H, NH), 5.29 (t, J = 3.7 Hz, 1H, 12-H), 4.98 (d, J = 6.4 Hz, 1H, 3-H), 4.95 – 4.91 (m, 1H, 2-H), 4.52 (dd, J = 14.5, 6.1 Hz, 1H, 35-H_a), 4.09 (dd, J = 14.4, 4.4 Hz, 1H, 35-H_b), 3.80 (s, 3H, 42-H), 2.58 – 2.44 (m, 1H, 18-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 1.99 – 1.94 (m, 1H, 16-H_a), 1.84 (dd, J = 8.9, 3.5 Hz, 2H, 11-H), 1.79 – 1.71 (m, 2H, 19-H_a, 22-H_a), 1.70 – 1.63 (m, 2H, 1-H_a, 16-H_b), 1.63 – 1.52 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.51 – 1.32 (m, 4H, 6-H, 7-H_a, 21-H_a), 1.30 – 1.20 (m, 3H, 5-H, 7-H_b, 21-H_b), 1.17 (s, 3H, 27-H), 1.15 – 1.12 (m, 1H, 19-H_b), 1.10 (s, 3H, 25-H), 1.08 – 1.03 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.93 – 0.87 (m, 9H, 23-H, 29-H, 30-H), 0.68 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.3 (C-31), 170.1 (C-33), 159.1 (C-39), 145.0 (C-13), 130.6 (C-36), 129.3, 129.3 (C-37, 41), 122.8 (C-12), 114.2 (C-38, 40), 76.2 (C-3), 70.7 (C-2), 55.4 (C-42), 50.5 (C-5), 48.0 (C-9), 46.8, 46.5 (C-17), 43.3 (C-35), 42.6 (C-18), 42.4 (C-14), 41.3 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 23.9 (C-16), 23.7 (C-29), 23.5 (C-11), 22.3 (C-24), 21.4 (C-34), 21.1 (C-32), 18.8 (C-6), 18.2 (C-25), 17.0 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 674.0 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 73.63, H 9.10, N 2.07; found: C 73.49, H 9.25, N 1.82.

4.2.12. (2β,3α) N-(2-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (14)

Compound **14** (235 mg, 79 %) was obtained from **4** (250 mg, 0.45 mmol l) according to GPA as a white solid; m.p. 111 °C; R_f = 0.78 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +46.7° (c 0.101, MeOH); IR (ATR): ν = 2943w, 1739 s, 1644w, 1514w, 1462w, 1466 m, 1242 s, 1226 s, 1027 m, 739 m, 605w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 – 7.11 (m, 4H, 37-H, 38-H, 39-H, 40-H), 6.05 (dd, J = 6.4, 4.2 Hz, 1H, NH), 5.28 (t, J = 3.7 Hz, 1H, 12-H), 4.98 (d, J = 6.4 Hz, 1H, 3-H), 4.95 – 4.91 (m, 1H, 2-H), 4.61 (dd, J = 14.7, 6.4 Hz, 1H, 35-H_a), 4.15 (dd, J = 14.7, 4.1 Hz, 1H, 35-H_b), 2.52 (dd, J = 13.6, 4.7 Hz, 1H, 18-H), 2.31 (s, 3H, 42-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.00 – 1.95 (m, 1H, 16-H_a), 1.84 – 1.79 (m, 2H, 11-H), 1.78 – 1.75 (m, 1H, 19-H_a), 1.75 – 1.71 (m, 1H, 22-H_a), 1.71 – 1.64 (m, 2H, 1-H_a, 16-H_b), 1.58 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.47 (dd, J = 13.9, 8.6 Hz, 3H, 6-H, 7-H_a), 1.41 – 1.31 (m, 1H, 21-H_a), 1.30 – 1.19 (m, 3H, 5-H, 7-H_b, 21-H_b), 1.17 (s, 3H, 27-H), 1.15 – 1.12 (m, 1H, 19-H_b), 1.09 (s, 3H, 25-H), 1.07 – 1.03 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.92 – 0.87 (m, 9H, 23-H, 29-H, 30-H), 0.67 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.3 (C-31), 170.1 (C-33), 145.1 (C-13), 136.5 (C-36), 136.2 (C-41), 130.6 (C-40), 128.5 (C-37), 127.7 (C-39), 126.3 (C-38), 122.9 (C-12), 76.2 (C-3), 70.7 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.6 (C-17), 42.6 (C-18), 42.4 (C-14), 41.7 (C-35), 41.2 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 25.9 (C-27), 24.0 (C-16), 23.7 (C-29), 23.5 (C-11), 22.2 (C-24), 21.4 (C-34), 21.1 (C-32), 19.2 (C-42), 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.7 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.95): C 76.44, H 9.32, N 2.12; found: C 76.20, H 9.53, N 1.97.

4.2.13. (2β,3α) N-(3-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (15)

Compound **15** (238 mg, 80 %) was obtained from **4** (250 mg, 0.45 mmol) according to GPA as a white solid; m.p. 127 °C; R_f = 0.76 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +47.9° (c 0.124, MeOH); IR (ATR): ν = 2944w, 1740 m, 1653 m, 1510 m, 1455w, 1367 m, 1241 s, 1227 s, 1032 m, 755 m, 694w, 605w, 535w, 446w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 – 7.19 (m, 1H, 38-H), 7.13 – 7.02 (m, 3H, 27-H, 39-H, 41-H), 6.13 (d, J = 5.4 Hz, 1H, NH), 5.30 (t, J = 3.6 Hz, 1H, 12-H), 4.98 (d, J = 6.5 Hz, 1H, 3-H), 4.95 – 4.91 (m, 1H, 2-H), 4.55 (dd, J = 14.6, 6.1 Hz, 1H, 35-H_a), 4.15 – 4.10 (m, 1H, 35-H_b), 2.53 (dd, J = 13.2, 4.5 Hz, 1H, 18-H), 2.34 (s, 3H, 42-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 2.01 – 1.94 (m, 1H, 16-H_a), 1.84 (dd, J = 8.8, 3.6 Hz, 2H, 11-H), 1.78 – 1.75 (m, 1H, 19-H_a), 1.75 – 1.72 (m, 1H, 22-H_a), 1.72 – 1.64 (m, 3H, 1-H_a, 16-H_b, 22-H_b), 1.64 – 1.55 (m, 3H, 1-H_b, 9-H, 15-H_a), 1.52 – 1.33 (m, 4H, 6-H, 7-H_a, 21-H_a), 1.30 – 1.19 (m, 3H, 5-H, 7-H_b, 21-H_b), 1.18 (s, 3H, 27-H), 1.15 – 1.11 (m, 1H, 19-H_b), 1.10 (s, 3H, 25-H), 1.08 – 1.04 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.91 – 0.90 (m, 9H, 23-H, 29-H, 30-H), 0.69 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.3 (C-31), 170.1 (C-33), 145.1 (C-13), 138.4 (C-36), 138.4 (C-40), 128.7 (C-38, 41), 128.2 (C-39), 125.0 (C-37), 122.8 (C-12), 76.2 (C-3), 70.6 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.5 (C-17), 43.8 (C-35), 42.6 (C-18), 42.4 (C-14), 41.3 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.0 (C-23), 26.0 (C-27), 23.9 (C-16), 23.7 (C-29), 23.5 (C-11), 22.3 (C-24), 21.5 (C-42), 21.4 (C-34), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 17.0 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.5 (100 %, $[M-H]^-$); $]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.95): C 76.44, H 9.32, N 2.12; found: C 76.17, H 9.55, N 1.83.

4.2.14. (2β,3α) N-(4-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (16)

Compound **16** (232 mg, 78 %) was obtained from **4** (250 mg, 0.45 mmol) according to GPA as a white solid; m.p. 127 °C; R_f = 0.76 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +49.4° (c 0.166, MeOH); IR (ATR): ν = 2943w, 1740 m, 1651w, 1516w, 1460w, 1432w, 1366 m, 1241 s, 1226 s, 1032 m, 806w, 754w, 605w, 579w, 474w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 – 7.06 (m, 4H, 37-H, 38-H, 40-H, 41-H), 6.12 (t, J = 5.5 Hz, 1H, NH), 5.29 (t, J = 3.6 Hz, 1H, 12-H), 4.98 (d, J = 6.5 Hz, 1H, 3-H), 4.95 – 4.87 (m, 1H, 2-H), 4.56 (dd, J = 14.5, 6.1 Hz, 1H, 35-H_a), 4.10 (dd, J = 14.5, 4.6 Hz, 1H, 35-H_b), 2.56 – 2.48 (m, 1H, 18-H), 2.33 (s, 3H, 42-H), 2.06 (s, 3H, 32-H), 2.02 (s, 3H, 34-H), 1.99 – 1.94 (m, 1H, 16-H_a), 1.84 (dd, J = 8.9, 3.5 Hz, 2H, 11-H), 1.78 – 1.71 (m, 2H, 19-H_a, 22-H_a), 1.71 – 1.64 (m, 2H, 1-H_a, 16-H_b), 1.63 – 1.53 (m, 4H, 1-H_b, 9-H, 15-H_a, 22-H_b), 1.52 – 1.41 (m, 3H, 6-H, 7-H_a), 1.39 – 1.32 (m, 1H, 21-H_a), 1.30 – 1.19 (m, 3H, 5-H, 7-H_b, 21-H_b), 1.17 (s, 3H, 27-H), 1.15 – 1.11 (m, 1H, 19-H_b), 1.09 (s, 3H, 25-H), 1.07 – 1.04 (m, 1H, 15-H_b), 1.02 (s, 3H, 24-H), 0.92 – 0.88 (m, 9H, 23-H, 29-H, 30-H), 0.67 (s, 3H, 26-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.3 (C-31), 170.1 (C-33), 145.0 (C-13), 137.2 (C-36), 135.5 (C-39), 129.5 (C-38, 40), 127.9 (C-37, 41), 122.8 (C-12), 76.2 (C-3), 70.7 (C-2), 50.5 (C-5), 48.0 (C-9), 46.8 (C-19), 46.5 (C-17), 43.5 (C-35), 42.6 (C-18), 42.4 (C-14), 41.2 (C-1), 39.6 (C-8), 37.0 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-22), 32.1 (C-7), 30.9 (C-20), 27.4 (C-15), 27.0 (C-23), 26.0 (C-27), 23.9 (C-16), 23.7 (C-29), 23.5 (C-11), 22.3 (C-24), 21.4 (C-34), 21.2 (C-42), 21.1 (C-32), 18.7 (C-6), 18.2 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.3 (100 %, $[M-H]^-$); $]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.95): C 76.44, H 9.32, N 2.12; found: C 76.21, H 9.49, N 1.90.

4.2.15. (2α,3β) Dihydroxyolean-12-en-28-acid (maslinic acid) (2) [4373–41–5]

Preserved, pitted green olives (2 kg) were crushed and dried at 110 °C for 24 h. The dried olives (399 g) were extracted with methanol (700 mL) for 4 days. The solid residue was filtered off and extracted two times with methanol (700 mL, each) each for another 4 days. The methanol was evaporated, the residue was washed with hexanes and mixed 1:1 with silica gel and the mixture was grounded. The powder was extracted for 24 h in a Soxhlet extraction with diethyl ether, the extract concentrated and the solid was purified by column chromatography (SiO_2, hexanes/ethyl acetate/chloroform, 6:4:10). The product was recrystallized from ethyl acetate and **2** (1.2 g, 0.3 % on dry weight basis) was obtained as a colorless solid; m.p. 263 – 267 °C, (lit.: [16] 269 – 271 °C); R_f = 0.22 (SiO_2, hexanes/ethyl acetate, 6:4); $[\alpha]_D$ = + 55.0° (c 0.42, $CHCl_3$) (lit: [20] + 60.0° (c 0.1, $CHCl_3$); MS (ESI, MeOH): m/z = 471.5 (43 %, $[M-H]^-$), 517.0 (100 %, $[M + HCO_2]^-$), 943.1 (62 %, $[2M-H]^-$).

4.2.16. (2α,3β) Diacetyloxy-olean-12-en-28-acid (17)

Acetylation of **2** as previously described followed by

chromatography (SiO_2, hexanes/ethyl acetate, 5:1) furnished **15** (2.6 g, 79 %) as a colorless solid; m.p. 179–181 °C (lit.: [2] 170–173 °C); R_f = 0.32 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +28.37° (*c* 0.43, $CHCl_3$) (lit.: [2] + 30°, (*c* 0.83, $CHCl_3$); MS (ESI, MeOH): *m/z* = 557.4 (49 %, $[M + H]^+$), 574.5 (100 %, $[M + NH_4]^+$), 579.5 (51 %, $[M + Na]^+$).

4.2.17. (2α,3β) N-(2-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (18)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **18** (187 mg, 77 %) was obtained as a colorless solid; m.p. 129 °C; R_f = 0.44 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -11.3° (*c* 0.174, $CHCl_3$); IR (KBr): ν = 3422vw, 2944 m,: 2864w, 1740 s, 1659 m, 1512 m, 1471 m, 1445 m, 1367 m, 1248vs, 1230vs, 1155w, 1039 s, 990w, 965w, 918w, 824w, 750 s, 667w, 641w, 598w, 527w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.31 (m, 2H, 38-H + 39-H), 7.23 – 7.17 (m, 2H, 40-H + 41-H), 6.43 (dd, *J* = 5.9, 5.9 Hz, 1H, NH), 5.33 (t, *J* = 3.6 Hz, 1H, 12-H), 5.07 (ddd, *J* = 11.4, 10.2, 4.6 Hz, 1H, 2-H), 4.73 (d, *J* = 10.4 Hz, 1H, 3-H), 4.54 (dd, *J* = 14.5, 5.8 Hz, 1H, 35-H_a), 4.40 (dd, *J* = 14.5, 5.9 Hz, 1H, 35-H_b), 2.57 – 2.49 (m, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 – 1.97 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.83 (dd, *J* = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.80 – 1.59 (m, 4H, 7-H_a + 7-H_b + 22-H_b + 19-H_a), 1.59 – 1.29 (m, 6H, 6-H_a + 6-H_b + 9-H + 15-H_a + 16-H_a + 21-H_a), 1.28 – 1.13 (m, 3H, 15-H_b + 21-H_b + 19-H_b), 1.11 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.07 – 0.99 (m, 2H, 1-H_b + 16-H_b), 0.98 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.94 (d, *J* = 2.0 Hz, 1H, 5-H), 0.91 – 0.85 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.43 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.9 (C-33), 170.7 (C-31), 144.6 (C-13), 136.0 (C-36), 134.1 (C-37), 131.0 (C-38), 129.5 (C-39), 129.0 (C-41), 127.3 (C-40), 122.8 (C-12), 80.7 (C-3), 70.1 (C-2), 54.9 (C-5), 47.6 (C-9), 46.7 (C-17), 46.7 (C-19), 44.0 (C-1), 42.6 (C-35), 42.2 (C-14), 41.7, 39.5 (C-4), 39.4 (C-8), 38.2 (C-10), 34.2 (C-21), 33.1 (C-30), 32.8 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5, 27.4 (C-16), 25.8, 23.8 (C-22), 23.7 (C-29), 23.7 (C-11), 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7, 16.6 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.6 (100 %, $([M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.09, H 8.76, N 2.04.

4.2.18. (2α,3β) N-(3-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (19)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **19** (156 mg, 64 %) was obtained as a colorless solid; m.p. 135 °C; R_f = 0.39 (SiO_2, hexanes/ethyl acetate, 9:1); $[\alpha]_D$ = -1.17° (*c* 0.172, $CHCl_3$); IR (KBr): ν = 3422vw, 2944 m, 1739 s, 1654 m, 1647 m, 1598w, 1576w, 1514 m, 1472 m, 1432 m, 1367 m, 1247vs, 1230vs, 1154w, 1097w, 1079w, 1042 s, 1031 s, 989 m, 958w, 918w, 823w, 771 m, 755 m, 703w, 681 m, 597 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.22 (m, 3H, 37-H + 39-H + 40-H), 7.17 – 7.09 (m, 1H, 41-H), 6.17 (dd, *J* = 5.6, 5.6 Hz, 1H, NH), 5.32 (t, *J* = 3.6 Hz, 1H, 12-H), 5.08 (ddd, *J* = 11.5, 10.3, 4.6 Hz, 1H, 2-H), 4.73 (d, *J* = 10.3 Hz, 1H, 3-H), 4.53 (dd, *J* = 14.8, 6.1 Hz, 1H, 35-H_a), 4.21 – 4.06 (m, 1H, 35-H_b), 2.58 – 2.50 (m, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.04 – 1.98 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.91 – 1.81 (m, 2H, 11-H_a + 11-H_b), 1.81 – 1.64 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.63 – 1.49 (m, 4H, 6-H_a + 7-H_b + 9-H + 16-H_b), 1.48–1.31 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.22–1.31 (m, 1H, 15-H_b), 1.22 – 1.17 (m, 2H, 19-H_b + 21-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.10 – 1.03 (m, 2H, 1-H_b + 16-H_b), 1.02 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.95 (dd, *J* = 11.2, 2.0 Hz, 2H, 5-H), 0.92 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.64 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.8 (C-33), 170.5 (C-31), 144.9 (C-13), 140.5 (C-36), 134.5 (C-38), 129.9 (C-40), 127.9 (C-37), 127.5 (C-39), 125.9 (C-41), 122.5 (C-12), 80.5 (C-3), 69.9 (C-2), 54.8 (C-5), 47.4 (C-9), 46.6 (C-19), 46.4 (C-17), 43.9 (C-1), 43.0 (C-35), 42.3 (C-18), 42.1 (C-14), 39.4 (C-4), 39.3 (C-8), 38.0 (C-10), 34.1 (C-21), 33.0 (C-30), 32.7 (C- 7), 32.2 (C-15), 30.7 (C-20), 28.4 (C-24), 27.2 (C-16), 25.7 (C-27), 23.7 (C-22), 23.6 (C-29), 23.5 (C-11), 21.1 (C-32), 20.9 (C-34), 18.1 (C-6), 17.6 (C-23), 16.9 (C-25), 16.4 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.6 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.11, H 8.82, N 1.95.

4.2.19. (2α,3β) N-(4-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (20)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **20** (201 mg, 82 %) was obtained as a colorless solid; m.p. 130 °C; R_f = 0.38 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -4.77° (*c* 0.186, $CHCl_3$); IR (KBr): ν = 3423vw, 2944 m, 2864w, 1739 s, 1646 m, 1514 m, 1492 m, 1463w, 1432w, 1367 m, 1248vs, 1230vs, 1091 m, 1042 m, 1031 s, 1016 m, 989 m, 958w, 918w, 819w, 800 m, 771 m, 754 m, 654w, 641w, 597w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H, 38-H + 40-H), 7.21 – 7.14 (m, 2H, 37-H + 41-H), 6.16 (dd, *J* = 5.6, 5.6 Hz, 1H, NH), 5.31 (t, *J* = 3.6 Hz, 1H, 12-H), 5.08 (ddd, *J* = 11.5, 10.3, 4.6 Hz, 1H, 2-H), 4.73 (d, J = 10.3, 1H, 3-H), 4.59 – 4.49 (m, 1H, 35-H_a), 4.10 (dd, *J* = 14.8, 4.8 Hz, 1H, 35-H_b), 2.53 (dd, *J* = 13.1, 4.4 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.01 (dd, *J* = 5.0, 1.2 Hz, 2H, 1a + 22a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.85 (dd, *J* = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.79 – 1.51 (m, 7H, 6-H_a + 7-H_a + 7-H_b + 9-H + 16-H_a + 19-H_a + 22-H_b), 1.51 – 1.30 (m, 3H, 6-H_b + 15-H_a + 21-H_b), 1.30 – 1.15 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.10 – 1.03 (m, 2H, 1-H_b + 16-H_b), 1.02 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.97 – 0.91 (m, 1H, 5-H), 0.92 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.63 (s, 3H, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C-28), 171.0 (C-33), 170.7 (C-31), 145.1 (C-13), 137.2 (C-36), 133.3 (C-39), 129.3 (C-37, C-41), 128.9 (C-38, C-40), 122.6 (C-12), 80.6 (C-3), 70.1 (C-2), 54.9 (C-5), 47.6 (C-9), 46.7 (C-19), 46.5 (C-17), 44.0 (C-1), 43.0 (C-35), 42.4 (C-18), 42.2 (*c* 14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.2 (C-21), 33.1 (C-30), 32.8 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.9 (C-22), 23.7 (C-29), 23.7 (C-11), 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 17.0 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 678.7 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.13, H 8.73, N 1.98.

4.2.20. (2α,3β) N-(2-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (21)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **21** (190 mg, 80 %) was obtained as a colorless solid; m.p. 125 °C; R_f = 0.37 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -5.04° (*c* 0.174, $CHCl_3$); IR (KBr): ν = 3423vw, 2944w, 2865w, 1739 s, 1645 m, 1587w, 1516 m, 1489 m, 1456 m, 1433w, 1367 m, 1301w, 1248 s, 1228vs, 1191 m, 1153w, 1106w, 1041 m, 1032 m, 989w, 959w, 918w, 832w, 806w, 755 s, 641w, 598w, 524w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.21 (m, 1H, 41-H), 7.13 – 6.97 (m, 3H, 38-H + 39-H + 40-H), 6.28 (dd, *J* = 5.7, 5.7 Hz, 1H, NH), 5.35 – 5.29 (m, 1H, 12-H), 5.07 (dt, *J* = 11.0, 4.6 Hz, 1H, 2-H), 4.73 (d, *J* = 10.3 Hz, 1H, 3-H), 4.53 (dd, *J* = 14.7, 5.8 Hz, 1H, 35-H_a), 4.33 (dd, *J* = 14.7, 5.2 Hz, 1H, 35-H_b), 2.52 (dd, *J* = 13.0, 4.3 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 – 1.97 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.83 (dd, *J* = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.80 – 1.65 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.65 – 1.45 (m, 4H, 6-H_a + 7-H_b + 15-H_a + 16-H_a), 1.46 – 1.27 (m, 2H, 6-H_b + 21-H_a), 1.27 – 1.13 (m, 3H, 15′-H_b + 19-H_b + 21-H_b), 1.12 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.08 – 0.99 (m, 2H, 1-H_b + 16-H_b), 0.98 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.93 (dd, *J* = 11.4, 1.9 Hz, 1H, 5-H), 0.91 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.51 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.9 (C-33), 170.7 (C-31),

161.4 (d, J = 245.5 Hz, C-37), 144.8 (C-13), 130.7 (d, J = 4.5 Hz, C-41), 129.3 (d, J = 8.2 Hz, C-39), 125.5 (d, J = 15.1 Hz, C-36), 124.5 (d, J = 3.5 Hz, C-40), 122.7 (C-12), 115.4 (d, J = 21.4 Hz, C-38), 80.7 (C-3), 70.1 (C-2), 54.9 (C-5), 47.6 (C-9), 46.7 (C-17), 46.6 (C-19), 44.0 (C-1), 42.5 (C-18), 42.2 (C-14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 37.7 (d, J = 3.3, C-35), 34.2 (C-21), 33.1 (C-30), 32.7 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.8 (C-22), 23.7 (C-29), 23.7, 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 16.7 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 662.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.81, H 9.03, N 1.92.

4.2.21. (2α,3β) N-(3-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (22)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **22** (182 mg, 76 %) was obtained as a colorless solid; m.p. 131 °C; R_f = 0.34 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -0.85° (*c* 0.164, $CHCl_3$); IR (KBr): ν = 3422vw, 2944 m, 1740 s, 1649 m, 1617w, 1592w, 1514 m, 1487 m, 1451 m, 1367 m, 1248vs, 1230vs, 1140w, 1042 s, 1031 s, 990 m, 962w, 918w, 788w, 689w, 598w, 520 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 1H, 40-H), 7.02 (d, J = 7.6 Hz, 1H, 41-H), 6.99 – 6.92 (m, 2H, 37-H + 39-H), 6.23 – 6.16 (m, 1H, NH), 5.34 – 5.30 (m, 1H, 12-H), 5.08 (ddd, J = 11.5, 10.2, 4.6 Hz, 1H, 2-H), 4.73 (d, J = 10.3 Hz, 1H, 3-H), 4.58 (dd, J = 14.9, 6.2 Hz, 1H, 35-H_a), 4.14 (dd, J = 14.9, 4.8 Hz, 1H, 35-H_b), 2.55 (dd, J = 13.0, 4.4 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.00 (dd, J = 7.2, 4.8 Hz, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.85 (dd, J = 8.8, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.81 – 1.63 (m, 4H, 7-H_a + 7-H_b + 19-H_a + 22-H_b), 1.64 – 1.49 (m, 3H, 6-H_a + 9-H + 16-H_a), 1.48 – 1.31 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.30 – 1.17 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.09 – 1.02 (m, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.95 (dd, J = 11.4, 2.0 Hz, 1H, 5-H), 0.93 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.65 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C-28), 170.9 (C-33), 170.7 (C-31), 163.1 (d, J = 246.4 Hz, C-38), 145.1 (C-13), 141.2 (d, J = 7.1 Hz, C-36), 130.3 (d, J = 8.3 Hz, C-40), 123.4 (d, J = 2.9 Hz, C-41), 122.7 (C-12), 123.4 (d, J = 2.9 Hz, C-37), 114.5 (d, J = 36.5 Hz, C-39), 80.6 (C-3), 70.1 (C-2), 54.9 (C-5), 47.5 (C-9), 46.7 (C-19), 46.5 (C-17), 44.0 (C-1), 43.2 (d, J = 1.9 Hz, C-35), 42.5 (C-18), 42.2 (C-14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.2 (C-21), 33.1 (C-30), 32.8 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.9 (C-22), 23.7 (C-29), 23.7 (C-11), 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 17.0 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 662.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.85, H 9.16, N 1.85.

4.2.22. (2α,3β) N-(4-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (23)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **23** (211 mg, 88 %) was obtained as a colorless solid; m.p. 106 °C; R_f = 0.31 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -0.24° (*c* 0.194, $CHCl_3$); IR (KBr): ν = 3419vw, 2944 m, 1739 s, 1645 m, 1604w, 1509 m, 1463 m, 1432w, 1367 m, 1248vs, 1229vs, 1193 m, 1156 m, 1097w, 1042 s, 1031 s, 990 m, 962w, 918w, 851w, 823 m, 751 m, 667w, 640w, 597w, 577 m, 487 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.17 (m, 2H, 37-H + 41-H), 7.05 – 6.94 (m, 2H, 38-H + 40-H), 6.15 (dd, J = 5.5, 5.5 Hz, 1H, NH), 5.34 – 5.25 (m, 1H, 12-H), 5.15 – 5.01 (m, 1H, 2-H), 4.73 (d, J = 10.3 Hz, 1H, 3-H), 4.61 – 4.49 (m, 1H, 35-H_a), 4.12 (dd, J = 14.7, 4.5 Hz, 1H, 35-H_b), 2.58 – 2.47 (m, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.04 – 1.97 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.84 (dd, J = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.80 – 1.66 (m, 2H, 7-H_a + 19-H_a), 1.66 – 1.48 (m, 5H, 6-H_a + 7-H_b + 9-H + 16-H_a + 22-H_b), 1.48 – 1.30 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.30 – 1.15 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.13 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.10 – 1.03 (m, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.98 – 0.92 (m, 1H, 5-H), 0.92 – 0.84 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.63 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.4 (C-28), 171.3 (C-33), 171.0 (C-31), 162.6 (d, J = 245.6 Hz, C-39), 145.4 (C-13), 134.8 (d, J = 3.2 Hz, C-36), 129.9 (d, J = 8.0 Hz, C-37, C-41), 122.9 (C-12), 115.9 (d, J = 21.4 Hz, C-38, C-40), 81.0 (C-3), 70.4 (C-2), 55.2 (C-5), 47.9 (C-9), 47.1 (C-19), 46.8 (C-17), 44.3 (C-1), 43.3 (C-35), 42.7 (C-18), 42.5 (C-14), 39.8 (C-4), 39.8 (C-8), 38.5 (C-10), 34.6 (C-21), 33.4 (C-30), 33.1 (C-7), 32.6 (C-15), 31.2 (C-20), 28.8 (C-24), 27.7 (C-16), 24.2 (C-22), 24.1 (C-29), 24.0 (C-11), 21.6 (C-32), 21.3 (C-34), 18.6 (C-6), 18.1 (C-23), 17.3 (C-25), 16.9 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 662.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 74.92, H 9.03, N 1.92.

4.2.23. (2α,3β) N-(2-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (24)

Following GPA from **15** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **22** (188 mg, 77 %) was obtained as a colorless solid; m.p. 204 °C; R_f = 0.31 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -18.42° (*c* 0.162, $CHCl_3$); IR (KBr): ν = 3427vw, 2945w, 2916w, 2862w, 1743 s, 1657 m, 1512 m, 1494 m, 1461 m, 1434w, 1369 m, 1250vs, 1224 s, 1119w, 1042 m, 1026 m, 965w, 939w, 919w, 803w, 774 s, 753 m, 639w, 597w, 510 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 – 7.19 (m, 2H, 39-H, 41-H), 6.92 – 6.81 (m, 2H, 38-H + 40-H), 6.49 (dd, J = 5.7, 5.7 Hz, 1H, NH), 5.25 (t, J = 3.6 Hz, 1H, 12-H), 5.06 (dt, J = 10.9, 4.6 Hz, 1H, 2-H), 4.73 (d, J = 10.3 Hz, 1H, 3-H), 4.49 – 4.32 (m, 2H, 35-H_a + 35-H_b), 3.86 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.47 (dd, J = 12.9, 4.3 Hz, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 – 1.98 (m, 1H, 1-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.92 (dd, J = 13.7, 3.9 Hz, 1H, 11-H_a), 1.83 – 1.64 (m, 5H, 22-H_a + 22-H_b + 19-H_a + 11-H_b + 7-H_a), 1.62 – 1.44 (m, 4H, 7-H_b + 9-H + 16-H_a + 6-H_a), 1.43–1.24 (m, 3H, 6-H_b + 21-H_a + 15-H_a), 1.23 – 1.13 (m, 3H, 21-H_b + 15-H_b + 19-H_b), 1.10 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.06 – 0.97 (m, 2H, 1-H_b, 16-H_b), 0.95 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.93 (d, J = 2.1, 1H, 5-H), 0.91–0.85 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.39 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.5 (C-28), 170.9 (C-33), 170.7 (C-31), 157.8 (C-37), 144.9 (C-13), 130.2 (C-39), 128.9 (C-41), 126.5 (C-36), 122.2 (C-12), 120.9 (C-40), 110.1 (C-38), 80.6 (C-3), 70.2 (C-2), 55.3 (C-42), 54.9 (C-5), 47.6 (C-9), 46.8 (C-19), 46.6 (C-17), 44.0 (C-1), 42.6 (C-18), 42.1 (C-14), 39.7 (C-35), 39.5 (C-4), 39.4 (C-8), 38.1 (C-10), 34.3 (C-21), 33.1 (C-30), 32.7 (C-7), 32.3 (C-15), 30.8 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.7 (C-29), 23.7 (C-22), 23.7 (C-11), 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 16.5 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 674.7 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.45, H 9.38, N 1.85.

4.2.24. (2α,3β) N-(3-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (25)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **25** (192 mg, 79 %) was obtained as a colorless solid; m.p. 118 °C; R_f = 0.28 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -3.54° (*c* 0.175, $CHCl_3$); IR (KBr): ν = 3422vw, 2943 m, 2865w, 1739 s, 1655 m, 1602w, 1587w, 1514 m, 1490 m, 1464 m, 1434 m, 1367 m, 1248vs, 1230vs, 1191w, 1153 m, 1042 s, 965w, 918w, 872w, 823w, 772w, 735w, 694w, 641w, 597w, 554w, 523w, 464w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 7.8, 7.8 Hz, 1H, 40-H), 6.85 – 6.76 (m, 3H, 37-H + 39-H + 41-H), 6.15 (dd, J = 6.3, 4.4 Hz, 1H, NH), 5.33 – 5.27 (m, 1H, 12-H), 5.13 – 5.02 (m, 1H, 2-H), 4.73 (d, J = 10.4 Hz, 1H, 3-H), 4.57 (dd, J = 14.7, 6.2 Hz, 1H, 35-H_a), 4.12 (dd, J = 14.7, 4.3 Hz, 1H, 35-H_b), 3.79 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.58 – 2.50 (m, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 – 1.98 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c),

1.84 (dd, J = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.81 – 1.64 (m, 3H, 7-H_a + 22-H_b + 19-H_a), 1.64 – 1.48 (m, 4H, 6-H_a + 7-H_b + 9-H + 16-H_a), 1.40 (ddt, J = 28.6, 13.3, 4.1 Hz, 3H, 6-H_b + 15-H_a + 21-H_a), 1.30 – 1.16 (m, 3H, 15-H_b + 21-H_b + 19-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.05 (dt, J = 10.2, 4.8 Hz, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.98 – 0.93 (m, 1H, 5-H), 0.92 – 0.81 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.66 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.8 (C-33), 170.5 (C-31), 159.9 (C-38), 144.9 (C-13), 139.9 (C-36), 129.7 (C-40), 122.5 (C-12), 119.9 (C-41), 113.4 (C-39), 112.8 (C-37), 80.5 (C-3), 70.0 (C-2), 55.2 (C-42), 54.8 (C-5), 47.4 (C-9), 46.6 (C-19), 46.3 (C-17), 43.9 (C-1), 43.5 (C-35), 42.3 (C-18), 42.1 (C-14), 39.4 (C-4), 39.3 (C-8), 38.0 (C-10), 34.1 (C-21), 33.0 (C-30), 32.6 (C-7), 32.2 (C-20), 30.7 (C-15), 28.4 (C-24), 27.3 (C-16), 25.7 (C-27), 23.7 (C-22), 23.6 (C-29), 23.5 (C-11), 21.1 (C-32), 20.9 (C-34), 18.1 (C-6), 17.6 (C-23), 16.9 (C-25), 16.4 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, (4:1)): m/z = 674.6 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.49, H 9.40, N 1.79.

4.2.25. (2α,3β) N-(4-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (26)

Following GPA from **15** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **24** (176 mg, 72 %) was obtained as a colorless solid; m.p. 130 °C; R_f = 0.25 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -6.39° (*c* 0.178, $CHCl_3$); IR (KBr): ν = 3419vw, 2943w, 1740 s, 1654w, 1613w, 1512 m, 1463w, 1433w, 1367 m, 1301w, 1246vs, 1231vs, 1175 m, 1109w, 1032 s, 965w, 918w, 822w, 773w, 640w, 596w, 582w, 523w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.13 (m, 2H, 37-H + 41-H), 6.88 – 6.82 (m, 2H, 38-H + 40-H), 6.11 – 6.05 (m, 1H, NH), 5.30 – 5.25 (m, 1H, 12-H), 5.08 (ddd, J = 11.5, 10.3, 4.6 Hz, 1H, 2-H), 4.73 (d, J = 10.2 Hz, 1H, 3-H), 4.51 (dd, J = 14.4, 6.1 Hz, 1H, 35-H_a), 4.09 (dd, J = 14.5, 4.3 Hz, 1H, 35-H_b), 3.80 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.51 (dd, J = 13.2, 4.4 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.04 – 1.98 (m, 2H, 1-H_a + 22-H_b), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.83 (dd, J = 8.8, 3.7 Hz, 2H, 11-H_a + 11Hb), 1.79 – 1.62 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.45 (m, 5H, 6-H_a + 7-H_b + 9-H + 16-H_a + 15-H_a), 1.45 – 1.24 (m, 3H, 6-H_b + 21-H_b + 15-H_b), 1.24 – 1.15 (m, 2H, 21-H_b + 19-H_b), 1.13 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.09 – 1.03 (m, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 1.00 – 0.92 (m, 1H, 5-H), 0.92 – 0.86 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.66 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.9 (C-33), 170.7 (C-31), 159.1 (C-39), 145.1 (C-13), 130.5 (C-36), 129.3 (C-37, C-41), 122.5 (C-12), 114.2 (C-38, C-40), 80.7 (C-3), 70.1 (C-2), 55.4 (C-42), 54.9 (C-5), 47.6 (C-9), 46.7 (C-19), 46.4 (C-17), 44.0 (C-1), 43.3 (C-35), 42.5 (C-18), 42.2 (C-14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.3 (C-21), 33.1 (C-30), 32.7 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.8 (C-22), 23.8 (C-29), 23.7 (C-11), 21.3 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 17.1 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 674.6 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.45, H 9.36, N 1.75.

4.2.26. (2α,3β) N-(2-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (27)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **27** (132 mg, 56 %) was obtained as a colorless solid; m.p. 261 °C (decomp.); R_f = 040 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -8.99° (*c* 0.184, $CHCl_3$); IR (KBr): ν = 3429w, 2971w, 2945 m, 2916w, 2870w, 1744 s, 1656 s, 1504 m, 1464w, 1433w, 1369 m, 1252Vs, 1223 s, 1190w, 1043 m, 1031 m, 821w, 803w, 771 s, 639w, 599w, 515w, 493w, 452w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.10 (m, 4H, 38-H + 39-H + 40-H + 41-H), 6.04 (dd, J = 5.2, 5.2 Hz, 1H, NH), 5.27 (t, J = 3.6 Hz, 1H, 12-H), 5.12 – 5.02 (m, 1H, 2-H), 4.73 (d, J = 10.3 Hz, 1H, 3-H), 4.60 (dd, J = 14.7, 6.3 Hz, 1H, 35-H_a), 4.15 (dd, J = 14.6, 4.0 Hz, 1H, 35-H_b), 2.52 (dd, J = 12.9, 4.4 Hz, 1H, 18-H), 2.31 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 – 1.97 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.86 – 1.78 (m, 2H, 11-H_a + 11-H_b), 1.78 – 1.63 (m, 3H, 7-H_a + 19-H_a + 22-H_a), 1.63 – 1.51 (m, 4H, 6-H_a + 7-H_b + 9-H + 16-H_a), 1.49 – 1.31 (m, 3H, 6-H_b + 15-H_a + 21-H_b), 1.30 – 1.15 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.13 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.04 (dd, J = 13.2, 4.1 Hz, 2H, 1-H_b + 16-H_b), 1.00 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.97 – 0.91 (m, 1H, 5-H), 0.92 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.64 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.9 (C-33), 170.7 (C-31), 145.1 (C-13), 136.5 (C-36), 136.2 (C-37), 130.6 (C-38), 128.5 (C-41), 127.7 (C-39), 126.3 (C-40), 122.6 (C-12), 80.6 (C-3), 70.1 (C-2), 54.9 (C-5), 46.7 (C-19), 46.6 (C-17), 44.0 (C-1), 42.5 (C-18), 42.2 (C-14), 41.7 (C-35), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.3 (C-21), 33.1 (C-30), 32.7 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.9 (C-22), 23.7 (C-29), 23.6 (C-11), 21.3 (C-32), 21.0 (C-34), 19.2 (C-42), 18.3 (C-6), 17.7 (C-23), 17.0 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.5 100 %, ($[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.19, H 9.62, N 1.96.

4.2.27. (2α,3β) N-(3-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (28)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **28** (187 mg, 79 %) was obtained as a colorless solid; m.p. 121 °C; R_f = 0.36 (SiO_2, hexanes/ethyl acetate, 3;1); $[\alpha]_D$ = -2.85° (*c* 0.164, $CHCl_3$); IR (KBr): ν = 3425vw, 2944 m, 2864w, 1740 s, 1645 m, 1610w, 1514 m, 1462 m, 1433w, 1367 m, 1247vs, 1229vs, 1192w, 1154w, 1096w, 1042 s, 1031 s, 989 m, 965w, 918w, 822w, 773w, 757w, 699w, 640w, 597w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.18 (m, 1H, 40-H), 7.11 – 7.01 (m, 3H, 37-H + 39-H + 41-H), 6.12 (dd, J = 5.3, 5.3 Hz, 1H, NH), 5.28 (t, J = 3.6 Hz, 1H, 12-H), 5.08 (dt, J = 11.0, 4.6 Hz, 1H, 2-H), 4.74 (d, J = 10.3 Hz, 1H, 3-H), 4.59 – 4.49 (m, 1H, 35-H_a), 4.13 (dd, J = 14.6, 4.3 Hz, 1H, 35-H_b), 2.53 (dd, J = 13.2, 4.4 Hz, 1H, 18-H), 2.34 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 – 1.98 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.83 (dd, J = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.80 – 1.68 (m, 2H, 7-H_a + 19-H_a), 1.69 – 1.51 (m, 5H, 6-H_a + 7-H_b + 9-H + 16-H_a + 22-H_b), 1.51 – 1.31 (m, 3H, 6-H_b + 15-H_a + 21-H_b), 1.31 – 1.16 (m, 3H, 15-H_b + 19 + Hb + 21-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.11 – 1.03 (m, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.98 – 0.91 (m, 1H, 5-H), 0.93 – 0.87 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.67 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.9 (C-33), 170.7 (C-31), 145.1 (C-13), 138.4 (C-36), 138.3 (C-38), 128.7 (C-37, C-40), 128.3 (C-39), 125.0 (C-41), 122.6 (C-12), 80.6 (C-3), 70.1 (C-2), 54.9 (C-5), 47.6 (C-9), 46.7 (C-19), 46.5 (C-17), 44.0 (C-1), 43.8 (C-35), 42.5 (C-18), 42.2 (C-14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.8 (C-22), 23.7 (C-29), 23.6 (C-11), 21.5 (C-42), 21.3 (C-32), 21.0 (C-42), 18.3 (C-6), 17.7 (C-23), 17.1 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.5 (100 %, $[M-H]^-$), analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.21, H 9.65, N 2.00.

4.2.28. (2α,3β) N-(4-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (29)

Following GPA from **17** (0.2 g, 0.36 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **29** (191 mg, 81 %) was obtained as a colorless solid; m.p. 136 °C; R_f = 0.34 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = -7.56° (*c* 0.173, $CHCl_3$); IR (KBr): ν = 3427vw, 2944 m, 2864w, 1740 s, 1647 m, 1515 m, 1462w, 1432w, 1367 m,

1248vs, 1230vs, 1185w, 1154w, 1042 m, 1031 m, 959w, 918w, 807w, 755w, 640w, 598w, 578w, 475 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 – 7.07 (m, 4H, 37-H + 38-H + 40-H + 41-H), 6.16 – 6.06 (dd, J = 5.3, 5.3 Hz, 1H, NH), 5.32 – 5.25 (m, 1H, 12-H), 5.12 – 5.02 (m, 1H, 2-H), 4.74 (d, J = 10.3 Hz, 1H, 3-H), 4.55 (dd, J = 14.5, 6.1 Hz, 1H, 35-H_a), 4.11 (dd, J = 14.6, 4.3 Hz, 1H, 35-H_b), 2.56 – 2.47 (m, 1H, 18-H), 2.33 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 – 1.97 (m, 2H, 1-H_a + 22-H_a), 1.97 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.82 (dd, J = 8.9, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.79 – 1.68 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.68 – 1.49 (m, 4H, 6-H_b + 7-H_b + 9-H + 16-H_b), 1.49 – 1.30 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.31 – 1.15 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.13 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.09 – 1.02 (m, 2H, 1-H_b + 16-H_b), 1.01 (s, 3H, 26-H_a + 26-H_b + 26-H_c), 0.99 – 0.91 (m, 1H, 5-H), 0.92 – 0.86 (m, 12H, 23-H_a + 23-H_b + 23-H_c + 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.65 (s, 3H, 25-H_a + 25-H_b + 25-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.9 (C-33), 170.7 (C-31), 145.1 (C-13), 137.2 (C-36), 135.4 (C-39), 129.5 (C-38, 40), 127.9 (C-37, C-41), 122.6 (C-12), 80.6 (C-3), 70.1 (C-2), 54.9 (C-5), 47.6 (C-9), 46.7 (C-19), 46.4 (C-17), 44.0 (C-1), 43.5 (C-35), 42.5 (C-18), 42.2 (C-14), 39.5 (C-4), 39.5 (C-8), 38.2 (C-10), 34.2 (C-21), 33.1 (C-30), 32.7 (C-7), 32.3 (C-15), 30.9 (C-20), 28.5 (C-24), 27.4 (C-16), 25.8 (C-27), 23.8 (C-22), 23.8 (C-29), 23.6 (C11), 21.3 (C-42), 21.2 (C-32), 21.0 (C-34), 18.3 (C-6), 17.7 (C-23), 17.0 (C-25), 16.5 (C-26) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.5 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.21, H 9.51, N 1.86.

4.2.29. Augustic acid 26707-60-8 (3)

Augustic acid was prepared as previously reported; m.p. 310–314 °C (lit.: [4] 40 308–310 °C); R_f = 0.49 (SiO_2, hexanes/ethyl acetate, 1:1); $[\alpha]_D$ = +88.05° (c 0.31, THF) (lit.: [4] 43 + 93.5° (c 0.17, pyridine); MS (ESI, MeOH): m/z = 471.3 (100 %, $[M-H]^-$), 943.3 (30 %, [2 M−H]$^-$).

4.2.30. (2β,3β) Diacetyloxy-olean-12-en-28-acid (30)

Acetylation as previously reported provided **30** (5.1 g, 55 %) as a colorless solid; m.p. 322 °C (decomp.); R_f = 0.24 (SiO_2, hexanes/ethyl acetate, 8:2); $[\alpha]_D$ = +83.81° (c 0.32 $CHCl_3$); MS (ESI, MeOH): m/z = 557.2 (13 %, $[M + H]^+$), 574.3 (100 %, $([M + NH_4]^+$).

4.2.31. (2β,3β) N-(2-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (31)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **31** (196 mg, 90 %) was obtained as a colorless solid; m.p. 101–104 °C; R_f = 0.47 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +28.99° (c 0.15, $CHCl_3$); IR (KBr): ν = 3359vw, 2928 m, 2869w, 1742 s, 1647 m, 1515 m, 1469 m, 1444 m, 1363 m, 1247vs, 1232vs, 1192 m, 1158w, 1054 m, 1030 s, 1009 m, 991 m, 945 m, 822w, 748 m, 605 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.30 (m, 2H, 38-H + 39-H), 7.24 – 7.17 (m, 2H, 40-H + 41-H), 6.45 (dd, J = 6.0, 6.0 Hz, 1H, NH), 5.34 (t, J = 3.6 Hz, 1H, 12-H), 5.30 (dd, J = 3.7, 3.7 Hz, 1H, 2-H), 4.60 (d, J = 3.9 Hz, 1H, 3-H), 4.55 (dd, J = 14.6, 5.9 Hz, 1H, 35-H_a), 4.40 (dd, J = 14.6, 5.8 Hz, 1H, 35-H_b), 2.53 (dd, J = 13.1, 4.3 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.99 – 1.90 (m, 2H, 1-H_a + 22-H_a), 1.90 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.81 – 1.63 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.45 (m, 4H, 6-H_a + 7-H_b + 9-H + 16-H_a), 1.45 – 1.36 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.36 – 1.14 (m, 4H, 1-H_b + 15-H_b + 19-H_b + 21-H_b), 1.12 (s, 6H, 23-H_a + 23-H_b + 23-H_c + 27-H_a + 27-H_b + 27-H_c), 1.04 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.02 – 0.92 (m, 2H, 5-H + 16-H_b), 0.90 (s, 6H, 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.88 (s, 3H, 24-H_a + 24-H_b + 24-H_c), 0.48 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.7 (C-33), 170.2 (C-31), 144.6 (C-13), 135.9 (C-36), 133.9 (C-37), 130.9 (C-38), 129.3 (C-39), 128.8 (C-41), 127.1 (C-40), 122.8 (C-12), 77.9 (C-3), 69.6 (C-2), 55.1 (C-5), 48.0 (C-9), 46.6 (C-17), 46.5 (C-19), 42.4 (C-18), 42.1 (C-14), 41.9 (C-1), 41.5 (C-35), 39.4 (C-8), 37.3 (C-4), 36.6 (C-10), 34.1 (C-21), 33.0 (C-30), 32.7 (C-7), 32.3 (C-15), 30.7 (C-20), 29.0 (C-24), 27.2 (C-16), 25.7 (C-27), 23.6 (C-22), 23.6 (C- 29), 23.5 (C-11), 21.3 (C-34), 20.8 (C-32), 17.9 (C-6), 17.6 (C-25), 16.6 (C-26), 15.9 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 678.5 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.07, H 8.83, N 1.92.

4.2.32. (2β,3β) N-(3-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (32)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **35** (178 mg, 81 %) was obtained as a colorless solid; m.p. 118.8 °C; R_f = 0.41 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +34.98° (c 0.158, $CHCl_3$); IR (KBr): ν = 3382vw, 2945 m, 2867w, 1741 s, 1647 m, 1599w, 1574w, 1517 m, 1472 m, 1432 m, 1397w, 1364 m, 1248vs, 1232vs, 1196 m, 1161w, 1078w, 1056 m, 1030 m, 991 m, 945w, 822w, 787w, 755 m, 703w, 681 m, 625w, 605 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.21 (m, 3H, 37-H + 39-H + 40-H), 7.17 – 7.10 (m, 1H, 41-H), 6.19 (dd, J = 5.5, 5.5 Hz, 1H, NH), 5.36 – 5.27 (m, 2H, 2-H, 12-H), 4.61 (d, J = 3.8 Hz, 1H, 3-H), 4.58 – 4.48 (m, 1H, 35-H_a), 4.17 (dd, J = 14.9, 4.8 Hz, 1H, 35-H_b), 2.54 (dd, J = 13.1, 4.3 Hz, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.97 (ddd, J = 14.8, 8.9, 3.4 Hz, 2H, 1-H_a + 22-H_a), 1.91 – 1.83 (m, 2H, 11-H_a + 11-H_b), 1.80 – 1.63 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.63 – 1.44 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.41 – 1.25 (m, 3H, 1-H_b + 15-H_b + 21-H_a), 1.25–1.15 (m, 2H, 19-H_b + 21-H_b), 1.15 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.01 (q, J = 5.3, 4.5 Hz, 1H, 16-H_b), 0.99 – 0.92 (m, 1H, 5-H), 0.91 (s, 6H, 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 3H, 24-H_a + 24-H_b + 24-H_c), 0.67 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.3 (C-28), 170.9 (C-33), 170.4 (C-31), 145.1 (C-13), 140.6 (C-36), 134.6 (C-38), 130.1 (C-40), 128.1 (C-37), 127.6 (C-39), 126.1 (C-41), 122.9 (C-12), 78.0 (C-3), 69.7 (C-2), 55.3 (C-5), 48.1 (C-9), 46.7 (C-17), 46.6 (C-19), 43.2 (C-35), 42.5 (C-18), 42.4 (C-14), 42.0 (C-1), 39.6 (C-8), 37.5 (C-4), 36.8 (C-10), 34.2 (C-21), 33.1 (C-30), 32.8, 32.5 (C-15), 30.9 (C-20), 29.2 (C-24), 27.3 (C-16), 25.9 (C-27), 23.9 (C-22), 23.7 (C-29), 23.6 (C-11), 21.4 (C-34), 21.0 (C-32), 18.1 (C-6), 17.8 (C-25), 17.2 (C-26), 16.0 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 678.6 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.11, H 8.86, N 2.00.

4.2.33. (2β,3β) N-(4-chlorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (33)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **33** (206 mg, 94 %) was obtained as a colorless solid; m.p. 128.2 °C; R_f = 0.40 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +34.95° (c 0.157, $CHCl_3$); IR (KBr): ν = 3408vw, 2945 m, 1742 s, 1645 m, 1514 m, 1492 m, 1463 m, 1432w, 1364 m, 1247vs, 1232vs, 1192 m, 1161w, 1091 m, 1056 m, 1030 s, 1015 m, 991 m, 945w, 820 m, 800w, 606w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.26 (m, 2H, 38-H + 40-H), 7.22 – 7.15 (m, 2H, 37-H + 41-H), 6.17 (dd, J = 5.5, 5.5 Hz, 1H, NH), 5.35 – 5.27 (m, 2H, 2-H + 12-H), 4.61 (d, J = 3.9 Hz, 1H, 3-H), 4.55 (dd, J = 14.8, 6.2 Hz, 1H, 35-H_a), 4.12 (dd, J = 14.8, 4.7 Hz, 1H, 35-H_b), 2.57 – 2.49 (m, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.97 (ddd, J = 14.9, 8.2, 3.5 Hz, 2H, 1-H_a + 22-H_a), 1.90 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.78 – 1.62 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.43 (m, 5H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.39 – 1.15 (m, 5H, 1-H_b + 15-H_b + 19-H_b + 21-H_a + 21-H_b), 1.15 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.99 (m, 1H, 16-H_b), 0.98 – 0.93 (m, 1H, 5-H), 0.91 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c), 0.66 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.3 (C-28), 170.9 (C-33), 170.4 (C-31), 145.1 (C-13), 137.2 (C-36), 133.3 (C-39), 129.3 (C-37, C-41), 128.9

(C-38, C-40), 122.8 (C-12), 78.0 (C-3), 69.7 (C-2), 55.3 (C-5), 48.1 (C-9), 46.7 (C-17), 46.5 (C-19), 43.0 (C-35), 42.5 (C-18), 42.3 (C-14), 42.0 (C-1), 39.6 (C-8), 37.5 (C-4), 36.8 (C-10), 34.2 (C-21), 33.1 (C-30), 32.8 (C-7), 32.4 (C-15), 30.9 (C-20), 29.2 (C-24), 27.3 (C-16), 25.9 (C-27), 23.9 (C-22), 23.7 (C-29), 23.6 (C-11), 21.4 (C-34), 21.0 (C-32), 18.1 (C-6), 17.8 (C-25), 17.2 (C-26), 16.1 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 678.7 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5Cl$ (680.37): C 72.38, H 8.59, N 2.21; found: C 72.17, H 8.77, N 1.93.

4.2.34. (2β,3β) N-(2-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (34)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **34** (192 mg, 90 %) was obtained as a colorless solid; m.p. 106.6 °C; R_f = 0.44 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +37.02° (*c* 0.174, $CHCl_3$); IR (KBr): ν = 3418vw, 2945 m, 2864w, 1742 s, 1658 m, 1587w, 1514 m, 1489 m, 1457 m, 1433w, 1364 m, 1247vs, 1229vs, 1191 m, 1161w, 1107w, 1056 m, 1030 m, 1011 m, 990 m, 945w, 822w, 754 s, 685w, 667w, 606 m, 510w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.34 – 7.28 (m, 1H, 41-H), 7.28 – 7.22 (m, 1H, 39-H), 7.09 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H, 40-H), 7.06 – 7.00 (m, 1H, 38-H), 6.29 (dd, *J* = 5.8, 5.8 Hz, 1H, NH), 5.33 (t, *J* = 3.6 Hz, 1H, 12-H), 5.32 – 5.29 (m, 1H, 2-H), 4.60 (d, *J* = 3.9 Hz, 1H, 3-H), 4.55 (dd, *J* = 14.7, 5.9 Hz, 1H, 35-H_a), 4.33 (dd, *J* = 14.7, 5.3 Hz, 1H, 35-H_b), 2.52 (dd, *J* = 13.0, 4.0 Hz, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.96 (dt, *J* = 14.9, 3.6 Hz, 2H, 1-H_a + 22-H_a), 1.88 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.78 – 1.62 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.41 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.40 – 1.14 (m, 5H, 1-H_b + 15-H_b + 19-H_b + 21-H_a + 21-H_b), 1.13 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.12 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.04 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.97 (m, 1H, 16-H_b), 0.97 – 0.91 (m, 1H, 5-H), 0.90 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.89 (s, 3H, 29-H_a + 29-H_b + 29-H_c), 0.89 (s, 3H, 24-H_a + 24-H_b + 24-H_c), 0.56 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.1 (C-28), 170.8 (C-33), 170.4 (C-31), 161.4 (d, *J* = 245.6 Hz, C-37), 144.8 (C-13), 130.7 (d, *J* = 4.4 Hz, C-41), 129.3 (d, J = 8.2 HZ, C-39), 125.5 (d, *J* = 15.0 Hz, C-36), 124.5 (d, *J* = 3.5 Hz, C-40), 122.9 (C-12), 115.4 (d, *J* = 21.4 Hz, C-38), 78.0 (C-3), 69.7 (C-2), 55.3 (C-5), 48.1 (C-9), 46.6 (C-19), 42.5 (C-18), 42.3 (C-17), 42.0 (C-1), 39.5 (C-14), 37.9 (C-35), 37.8 (C-8), 37.4 (C-4), 36.8 (C-10), 34.2 (C-21), 33.1 (C-30), 32.7 (C-7), 32.5 (C-15), 30.8 (C-20), 29.2 (C-24), 27.3 (C-16), 25.9 (C-27), 23.8 (C-22), 23.7 (C-29), 23.7 (C-11), 21.4 (C-34), 21.0 (C-32), 18.1 (C-6), 17.8 (C-25), 16.8 (C-26), 16.0 (C-23) ppm; MS (ESI): m/z = 662.6 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.75, H 9.03, N 1.95.

4.2.35. (2β,3β) N-(3-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (35)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **35** (164 mg, 76 %) was obtained as a colorless solid; m.p. 120–122 °C; R_f = 0.40 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +38.62° (*c* 0.172, $CHCl_3$); IR (KBr): ν = 3401vw, 2945 m, 2866w, 1742 s, 1646 m, 1616w, 1592w, 1513 m, 1487w, 1450 m, 1364 m, 1248vs, 1232vs, 1191 m, 1159w, 1139w, 1056 m, 1030 m, 1009 m, 991 m, 944 m, 915w, 887w, 822w, 772 m, 741w, 684 m, 605w, 578w, 520w, 494w, 439w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.24 (m, 1H, 40-H), 7.03 (d, *J* = 7.8 Hz, 1H, 41-H), 6.99 – 6.92 (m, 2H, 37-H + 39-H), 6.24 – 6.17 (m, 1H, NH), 5.35 – 5.28 (m, 2H, 2-H + 12-H), 4.62 – 4.60 (m, 1H, 3-H), 4.60 – 4.54 (m, 1H, 35-H_a), 4.20 – 4.10 (m, 1H, 35-H_b), 2.55 (dd, *J* = 13.1, 4.4 Hz, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.01 – 1.91 (m, 2H, 1-H_a + 22-H_a), 1.90 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.81 – 1.64 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.64 – 1.44 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.44 – 1.33 (m, 1H, 21-H_a), 1.33 – 1.18 (m, 4H, 1-H_b + 15-H_b + 19-H_b + 21-H_b), 1.15 (s, 6H, 23-H_a + 23-H_b + 23-H_c + 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.93 (m, 2H, 5-H + 16-H_b), 0.91 (s, 6H, 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 3H, 24-H_a + 24-H_b + 24-H_c), 0.68 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.6 (C-28), 171.2 (C-33), 170.7 (C-31), 163.4 (d, *J* = 246.4 Hz, C-38), 145.4 (C-13), 141.5 (d, *J* = 7.0 Hz, C-36), 130.6 (d, *J* = 8.2 Hz, C-40), 123.73 (d, *J* = 2.8 Hz, C-41), 123.1 (C-12), 115.0 (d, *J* = 40.9 Hz, C-37), 114.8 (d, *J* = 40.3 Hz, C-39), 78.3 (C-3), 70.0 (C-2), 55.6 (C-5), 48.4 (C-9), 47.0 (C-19), 46.9 (C-17), 43.5 (d, *J* = 1.9 Hz, C-35), 42.8 (C-18), 42.7 (C-14), 42.3 (C-1), 39.9 (C-8), 37.8 (C-4), 37.1 (C-10), 34.5 (C-21), 33.4 (C-30), 33.1 (C-7), 32.8 (C-15), 31.2 (C-20), 29.5 (C-24), 27.6 (C-16), 26.2 (C-27), 24.2 (C-22), 24.1 (C-29), 23.9, 21.7 (C-34), 21.3 (C-32), 18.4 (C-6), 18.1 (C-25), 17.5 (C-26), 16.4 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 662. (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.84, H 9.13, N 1.86.

4.2.36. (2β,3β) N-(4-fluorobenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (36)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **39** (186 mg, 86 %) was obtained as a colorless solid; m.p. 123–126 °C; R_f = 0.38 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +40.72° (*c* 0.153, $CHCl_3$); IR (KBr): ν = 3411vw, 2945 m, 1742 s, 1645 m, 1605w, 1509 s, 1463w, 1433w, 1364 m, 1247vs, 1231vs, 1193 m, 1156 m, 1096w, 1056 m, 1030 m, 1015 m, 991 m, 946w, 822 m, 686w, 667w, 605w, 577 m, 487 m, 429w cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.19 (m, 2H, 37-H + 41-H), 7.03 – 6.97 (m, 2H, 38-H + 40-H), 6.16 (dd, *J* = 5.4, 5.4 Hz, 1H, NH), 5.33 – 5.27 (m, 2H, 2-H + 12-H), 4.60 (d, *J* = 3.9 Hz, 1H, 3-H), 4.53 (dd, *J* = 14.6, 6.1 Hz, 1H, 35-H_a), 4.17 – 4.08 (m, 1H, 35-H_b), 2.56 – 2.49 (m, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.00 – 1.92 (m, 2H, 1-H_a + 22-H_a), 1.87 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.80 – 1.62 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.43 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.37 – 1.17 (m, 5H, 1-H_a + 15-H_b + 19-H_b + 21-H_a + 21-H_b), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.14 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.93 (m, 2H, 5-H + 16-H_b), 0.90 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.89 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c), 0.66 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0 (C-28), 170.7 (C-33), 170.2 (C-31), 162.1 (d, *J* = 245.6 Hz, C-39), 145.0 (C-13), 134.3 (d, *J* = 3.0 Hz, C-36), 129.5 (d, *J* = 8.1 Hz, C-37, C-41), 122.6 (C-12), 115.4 (d, *J* = 21.5 Hz, C-38, C-40), 77.9 (C-3), 69.5 (C-2), 55.1 (C-5), 47.9 (C-9), 46.5 (C-19), 46.3 (C-17), 42.9 (C-35), 42.3 (C-18), 42.2 (C-14), 41.9 (C-1), 39.5 (C-8), 37.3 (C-4), 36.6 (C-10), 34.1 (C-21), 32.9 (C-30), 32.6 (C-7), 32.3 (C-15), 30.7 (C-20), 29.0 (C-24), 27.2 (C-16), 25.7 (C-27), 23.8 (C-22), 23.6 (C-29), 23.5 (C-11), 21.3, 20.8 (C-32), 17.9 (C-6), 17.6 (C-25), 17.0 (C-26), 15.9 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 662.7 (100 %, $[M-H]^-$); analysis calcd for $C_{41}H_{58}NO_5F$ (663.92): C 74.17, H 8.81, N 2.11; found: C 73.73, H 9.05, N 1.84.

4.2.37. (2β,3β) N-(2-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (37)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **37** (180 mg, 82 %) was obtained as a colorless solid; m.p. 122–126 °C; R_f = 0.35 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +27.41° (*c* 0.162, $CHCl_3$); IR (KBr): ν = 3430vw, 2944 m, 2866w, 1741 s, 1654 m, 1604w, 1493 m, 1463 m, 1437w, 1364 m, 1242vs, 1193 m, 1161w, 1120w, 1054 m, 1029 s, 990w, 945w, 822w, 751 s, 685w, 666w, 606w, 574w, 513w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.19 (m, 2H, 39-H + 41-H), 6.92 – 6.82 (m, 2H, 38-H + 40-H), 6.49 (dd, *J* = 5.7, 5.7 Hz, 1H, NH), 5.29 (dd, *J* = 3.8, 3.6 Hz, 1H, 2-H), 5.27 (t, *J* = 3.6 Hz, 1H, 12-H), 4.59 (d, *J* = 3.9 Hz, 1H, 3-H), 4.46 (dd, *J* = 14.2, 5.5 Hz, 1H, 35-H_a), 4.36 (dd, *J* = 14.2, 5.6 Hz, 1H, 35-H_b), 3.87 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.48 (dd, *J* = 13.3, 4.0 Hz, 1H, 18-H), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.00 – 1.87 (m, 2H, 1-H_a + 22-H_a), 1.85 – 1.78 (m, 2H, 11-H_a + 11-H_b), 1.77 – 1.63 (m, 3H, 7-H_a + 19-H_a + 22-

H_b), 1.62 – 1.45 (m, 4H, 6-H_a + 7-H_b + 9-H + 16-H_a), 1.44 – 1.36 (m, 3H, 6-H_b + 15-H_a + 21-H_a), 1.37 – 1.24 (m, 1H, 1-H_b), 1.24 – 1.13 (m, 3H, 15-H_b + 19-H_b + 21-H_b), 1.11 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.09 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.04 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 0.97 – 0.91 (m, 2H, 5-H + 16-H_b), 0.89 (s, 6H, 29-H_a + 29-H_b + 29-H_c + 30-H_a + 30-H_b + 30-H_c), 0.88 (s, 3H, 24-H_a + 24-H_b + 24-H_c), 0.45 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.6 (C-28), 170.8 (C-33), 170.4 (C-31), 157.8 (C-37), 145.0 (C-13), 130.2 (C-39), 128.8 (C-41), 126.5 (C-36), 122.4 (C-12), 120.9 (C-40), 110.1 (C-38), 78.0 (C-3), 69.8 (C-2), 55.4 (C-5), 55.3 (C-42), 48.1 (C-9), 46.7 (C-19), 46.6 (C-17), 42.5 (C-18), 42.3 (C-14), 42.0 (C-1), 39.7 (C-35), 39.5 (C-8), 37.4 (C-4), 36.7 (C-10), 34.3 (C-21), 33.1 (C-30), 32.7 (C-7), 32.5 (C-15), 30.8 (C-20), 27.3 (C-16), 25.9 (C-27), 23.7 (C-29), 23.7 (C- 22), 23.7 (C-11), 21.4 (C-34), 21.0 (C-32), 18.0 (C-6), 17.8 (C-25), 16.6 (C-26), 16.0 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 674.7 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.50, H 8.88, N 1.83.

4.2.38. (2β,3β) N-(3-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (38)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **38** (182 mg, 84 %) was obtained as a colorless solid; m.p. 113.7 °C; R_f = 0.33 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +35.40° (*c* 0.132, $CHCl_3$); IR (KBr): ν = 3406vw, 2945 m, 1741 s, 1649 m, 1602w, 1587w, 1514 m, 1489 m, 1464 m, 1455 m, 1434 m, 1365 m, 1248vs, 1232vs, 1192 m, 1154 m, 1031 s, 991 m, 945 m, 913w, 873w, 822w, 771 m, 757 m, 691 m, 667w, 605 m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 – 7.21 (m, 1H, 40-H), 6.87 – 6.76 (m, 3H, 37-H + 39-H + 41-H), 6.16 (dd, *J* = 6.7, 5.91 Hz, 1H, NH), 5.34 – 5.28 (m, 2H, 2-H + 12-H), 4.61 (d, *J* = 4.0 Hz, 1H, 3-H), 4.58 (d, *J* = 6.3 Hz, 1H, 35-H_a), 4.15 – 4.08 (m, 1H, 35-H_b), 3.79 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.54 (dd, *J* = 12.9, 4.5 Hz, 1H, 18-H), 2.06 – 2.03 (m, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.00 – 1.93 (m, 2H, 1-H_a + 22-H_a), 1.90 – 1.80 (m, 2H, 11-H_b + 11-H_b), 1.79 – 1.68 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.68 – 1.42 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.42 – 1.25 (m, 3H, 1-H_b + 15-H_b + 21-H_a), 1.25 – 1.15 (m, 2H, 19-H_b + 21-H_b), 1.14 (s, 6H, 23-H_a + 23-H_b + 23-H_c + 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.04 – 0.93 (m, 2H, 5-H + 16-H_b), 0.91 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c), 0.71 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.7 (C-33), 170.2 (C-31), 159.9 (C-38), 145.0 (C-13), 140.0 (C-36), 129.7 (C-40), 122.6 (C-12), 119.9 (C-41), 113.2 (C-39), 112.9 (C-37), 77.9 (C-3), 69.5 (C-2), 55.2 (C-42), 55.2, 48.0 (C-9), 46.5 (C-19), 46.4 (C-17), 43.5 (C-35), 42.3 (C-18), 42.2 (C-14), 39.5 (C-8), 37.3 (C-4), 36.6 (C-10), 34.1 (C-21), 33.0 (C-30), 32.6 (C-7), 32.3 (C-15), 30.7 (C-20), 29.0 (C-24), 27.2 (C-16), 25.8 (C-27), 23.8 (C-22), 23.6 (C-29), 23.5 (C-11), 21.3 (C-34), 20.8 (C-32), 17.9 (C-6), 17.6 (C-25), 17.0 (C-26), 15.9 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 674.6 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.41, H 9.37, N 1.86.

4.2.39. (2β,3β) N-(4-methoxybenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (39)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **39** (210 mg, 96 %) was obtained as a colorless solid; m.p. 118 °C; R_f = 0.29 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +32.02° (*c* 0.169, $CHCl_3$); IR (KBr): ν = 3419vw, 2944w, 2882w, 1742 s, 1649w, 1613w, 1512 m, 1463 m, 1433w, 1364 m, 1301w, 1246vs, 1192 m, 1175 m, 1111w, 1055 m, 1031 s, 990w, 946w, 821 m, 753w, 686w, 667w, 604w, 582w, 524w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 – 7.13 (m, 2H, 37-H + 41-H), 6.90 – 6.81 (m, 2H, 38-H + 40-H), 6.13 – 6.05 (m, 1H, NH), 5.33 – 5.25 (m, 2H, 2-H + 12-H), 4.61 (d, *J* = 3.9 Hz, 1H, 3- H), 4.55 – 4.48 (m, 1H, 35-H_a), 4.09 (dd, *J* = 14.4, 4.2 Hz, 1H, 35-H_b), 3.80 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.56 – 2.48 (m, 1H, 18-H), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 1.96 (ddd, *J* = 14.9, 7.9, 3.5 Hz, 2H, 1-H_a + 22-H_a), 1.88 – 1.81 (m, 2H, 11-H_a + 11-H_b), 1.79 – 1.63 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.62 – 1.42 (m, 6H, 6-H_a + 6-H_b + 7-H_b + 9-H + 15-H_a + 16-H_a), 1.41 – 1.25 (m, 3H, 1-H_b + 15-H_b + 21-H_a), 1.25 – 1.16 (m, 2H, 19-H_b + 21-H_b), 1.15 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.93 (m, 2H, 5-H + 16-H_b), 0.92 – 0.89 (m, 6H, 24-H_a + 24-H_b + 24-H_c + 30-H_a + 30-H_b + 30-H_c), 0.89 (s, 3H, 29-H_a + 29-H_b + 29-H_c), 0.71 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.3 (28), 171.1 (C-33), 170.6 (C-31), 159.3 (C-39), 145.4 (C-13), 130.9 (C-36), 129.5 (C-37, C-41), 123.0 (C-12), 114.4 (C-38, C-40), 78.3 (C-3), 70.0 (C-2), 55.7 (C-5), 55.5 (C-42), 48.4 (C-9), 46.9 (C-17), 46.7 (C-19), 43.5 (C-35), 42.7 (C-18), 42.6 (C-14), 42.3 (C-1), 39.9 (C-8), 37.7 (C-4), 37.0 (C-10), 34.5 (C-21), 33.4 (C-30), 33.0 (C-7), 32.7 (C-15), 31.1 (C-20), 29.5 (C-24), 27.6 (C-16), 26.2 (C-27), 24.1 (C-22), 24.0 (C-29), 23.9 (C-11), 21.7 (C-34), 21.3 (C-32), 18.3 (C-6), 18.0 (C-25), 17.5 (C-26), 16.3 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 674.5 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_6$ (675.95): C 74.63, H 9.10, N 2.07; found: C 74.41, H 9.37, N 1.85.

4.2.40. (2β,3β) N-(2-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (40)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **40** (200 mg, 94 %) was obtained as a colorless solid; m.p. 114–117 °C; R_f = 0.42 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +34.59° (*c* 0.159, $CHCl_3$); IR (KBr): ν = 3410vw, 2945 m, 2866w, 1742 s, 1658 m, 1513 m, 1462 m, 1433w, 1364 m, 1247vs, 1231vs, 1191 m, 1158w, 1055 m, 1029 m, 1012 m, 990 m, 945w, 911w, 822w, 739 m, 685w, 667w, 605w, 514w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.12 (m, 4H, 38-H + 39-H + 40-H + 41-H), 6.06 (dd, *J* = 6.4, 4.2 Hz, 1H, NH), 5.33 – 5.24 (m, 2H, 2-H + 12-H), 4.67 – 4.55 (m, 2H, 3-H + 35-H_a), 4.15 (dd, *J* = 14.7, 4.1 Hz, 1H, 35-H_b), 2.57 – 2.48 (m, 1H, 18-H), 2.31 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.04 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.01 – 1.83 (m, 2H, 1-H_a + 22-H_a), 1.82 (dd, *J* = 8.8, 3.6 Hz, 2H, 11-H_a + 11-H_b), 1.80 – 1.68 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.68 – 1.56 (m, 3H, 6-H_a + 7-H_b + 16-H_a), 1.56 – 1.44 (m, 3H, 6-H_b + 9-H + 15-H_a), 1.43 – 1.17 (m, 5H, 1-H_b + 15-H_b + 19-H_b + 21-H_a + 21-H_b), 1.14 (s, 6H, 23-H_a + 23-H_b + 23-H_c + 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.93 (m, 2H, 5-H + 16-H_b), 0.90 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c), 0.68 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.9 (C-28), 170.7 (C-33), 170.2 (C-31), 145.0 (C-13), 136.4 (C-36), 136.0 (C-37), 130.5 (C-38), 128.3 (C-41), 127.6 (C-39), 126.2 (C-40), 122.7 (C-12), 69.5 (C-2), 55.1 (C-5), 47.9 (C-9), 46.5 (C-19), 46.4 (C-17), 42.4 (C-18), 42.2 (C-14), 41.9 (C-1), 41.6 (C-35), 39.4 (C-8), 37.3 (C-4), 36.6 (C-10), 34.1 (C-21), 32.9 (C-30), 32.6 (C-7), 32.3 (C-15), 30.7 (C-20), 29.0 (C-24), 27.2 (C-16), 25.7 (C-27), 23.8 (C-22), 23.6 (C-29), 23.5 (C-11), 21.3 (C-34), 20.8 (C-32), 19.1 (C-42), 17.9 (C-6), 17.6 (C-25), 17.0 (C-26), 15.9 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): *m/z* = 658.6 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.19, H 9.64, N 1.92.

4.2.41. (2β,3β) N-(3-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (41)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **41** (178 mg, 84 %) was obtained as a colorless solid; m.p. 116–119 °C; R_f = 0.40 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +40.98° (*c* 0.166, $CHCl_3$); IR (KBr): ν = 3405vw, 2943 m, 2877w, 1742 s, 1646 m, 1514 m, 1462 m, 1433 m, 1364 m, 1246vs, 1231vs, 1192 m, 1158 m, 1056 m, 1030 s, 1010 m, 991 m, 973 m, 945 m, 912w, 822w, 772 m, 737w, 691 m, 667w, 625w, 604 m, 578w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 7.4, 7.4 Hz, 1H, 40-H), 7.12 – 7.01 (m, 3H, 37-H + 39-H + 41-H), 6.18 – 6.10 (m, 1H, NH), 5.33 – 5.27 (m, 2H, 2-H + 12-H), 4.61 (d, *J* = 3.9 Hz, 1H, 3-H), 4.59 – 4.50 (m, 1H, 35-H_a), 4.13 (dd, *J* = 14.6, 4.3 Hz, 1H, 35-H_b), 2.58 – 2.49

(m, 1H, 18-H), 2.34 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.02 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.00–1.91 (m, 2H, 1-H_a + 22-H_a), 1.89 – 1.81 (m, 2H, 11-H_a + 11-H_b), 1.81 – 1.56 (m, 6H, 6-H_a + 7-H_a + 7-H_b + 16-H_a + 19-H_a + 22-H_b), 1.56 – 1.43 (m, 3H, 6-H_b + 9-H + 15-H_a), 1.43 – 1.16 (m, 5H, 1-H_b + 15-H_b + 19-H_b + 21-H_b + 21-H_b), 1.14 (s, 6H, 23-H_a + 23-H_b + 23-H_c + 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.03 – 0.94 (m, 2H, 5-H + 16-H_b), 0.90 (s, 3H, 30-H_a + 30-H_b + 30-H_c), 0.90 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 29-H_a + 29-H_b + 29-H_c), 0.71 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.1 (C-28), 170.8 (C-33), 170.4 (C-31), 145.1 (C-13), 138.4 (C-36), 138.3 (C-38), 128.7 (C-37, C-40), 128.2 (C-39), 124.9 (C-41), 122.7 (C-12), 78.0 (C-3), 77.5, 77.2, 76.8, 69.7 (C-2), 55.3 (C-5), 48.1 (C-9), 46.7 (C-19), 46.5 (C-17), 43.8 (C-35), 42.5 (C-18), 42.3 (C-14), 42.0 (C-1), 39.6 (C-8), 37.5 (C-4), 36.8 (C-10), 34.3 (C-21), 33.1 (C-30), 32.8 (C-7), 32.5 (C-15), 30.9 (C-20), 29.2 (C-24), 27.3 (C-16), 25.9 (C-27), 23.9 (C-22), 23.7 (C-29), 23.6 (C-11), 21.5 (C-34), 21.4 (C-42), 21.0 (C-32), 18.1 (C-6), 17.8 (C-25), 17.2, 16.0 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.8 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.22, H 9.54, N 1.87.

4.2.42. (2β,3β) N-(4-methylbenzyl) 2,3-bis(acetyloxy)-olean-12-en-28-amide (42)

Following GPA from **30** (180 mg, 0.32 mmol) followed by chromatography (SiO_2, hexanes/ethyl acetate, 9:1) **42** (185 mg, 84 %) was obtained as a colorless solid; m.p. 124.6 °C; R_f = 0.40 (SiO_2, hexanes/ethyl acetate, 3:1); $[\alpha]_D$ = +35.56° (*c* 0.181, $CHCl_3$); IR (KBr): ν = 3409vw, 2945 m, 2877w, 1743 s, 1645 m, 1515 m, 1462 m, 1432w, 1364 m, 1247vs, 1232vs, 1192 m, 1159w, 1056 m, 1030 m, 991 m, 972w, 945w, 912w, 807 m, 754 m, 686w, 666w, 603w, 579w, 475 m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13 (s, 4H, 37-H + 38-H + 40-H + 41-H), 6.12 (dd, *J* = 6.3, 4.3 Hz, 1H, NH), 5.33 – 5.27 (m, 2H, 2-H + 12-H), 4.61 (d, *J* = 3.9 Hz, 1H, 3-H), 4.57 (dd, *J* = 14.6, 6.2 Hz, 1H, 35-H_a), 4.10 (dd, *J* = 14.6, 4.3 Hz, 1H, 35-H_b), 2.56 – 2.49 (m, 1H, 18-H), 2.34 (s, 3H, 42-H_a + 42-H_b + 42-H_c), 2.05 (s, 3H, 34-H_a + 34-H_b + 34-H_c), 2.03 (s, 3H, 32-H_a + 32-H_b + 32-H_c), 2.00–1.93 (m, 2H, 1-H_a + 22-H_a), 1.88 – 1.82 (m, 2H, 11-H_a + 11-H_b), 1.80 – 1.67 (m, 3H, 7-H_a + 19-H_a + 22-H_b), 1.66 – 1.56 (m, 3H, 6-H_a + 7-H_b + 16-H_a), 1.56 – 1.42 (m, 3H, 6-H_b + 9-H + 15-H_a), 1.42 – 1.24 (m, 3H, 1-H_b + 15-H_b + 21-H_a), 1.24 – 1.16 (m, 2H, 19-H_b + 21-H_b), 1.15 (s, 3H, 23-H_a + 23-H_b + 23-H_c), 1.14 (s, 3H, 27-H_a + 27-H_b + 27-H_c), 1.05 (s, 3H, 25-H_a + 25-H_b + 25-H_c), 1.04 – 0.91 (m, 2H, 5-H + 16-H_b), 0.90 (s, 6H, 24-H_a + 24-H_b + 24-H_c + 30-H_a + 30-H_b + 30-H_c), 0.89 (s, 3H, 29-H_a + 29-H_b + 29-H_c), 0.70 (s, 3H, 26-H_a + 26-H_b + 26-H_c) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.3 (C-28), 171.1 (C-33), 170.6 (C-31), 145.4 (C-13), 137.4 (C-36), 135.7 (C-39), 129.7 (C-38, C-40), 128.1 (C-37, C-41), 123.0 (C-12), 78.3 (C-3), 70.0 (C-2), 55.5 (C-5), 48.4 (C-9), 46.9 (C-19), 46.7 (C-17), 43.8 (C-35), 42.7 (C-18), 42.6 (C-14), 42.3 (C-1), 39.9 (C-8), 37.7 (C-4), 37.0 (C-10), 34.5 (C-21), 33.4 (C-30), 33.0 (C-7), 32.7 (C-15), 31.1 (C-20), 29.5 (C-24), 27.6 (C-16), 26.2 (C-27), 24.1 (C-22), 24.0 (C-29), 23.9 (C-11), 21.7 (C-34), 21.5 (C-42), 21.2 (C-32), 18.3, 18.0 (C-25), 17.4 (C-26), 16.3 (C-23) ppm; MS (ESI, MeOH/$CHCl_3$, 4:1): m/z = 658.6 (100 %, $[M-H]^-$); analysis calcd for $C_{42}H_{61}NO_5$ (659.45): C 76.44, H 9.32, N 2.12; found: C 76.25, H 9.56, N 1.89.

CRediT authorship contribution statement

Niels V. Heise: Investigation. **Julia Heisig:** Investigation. **Linda Höhlich:** Investigation. **Sophie Hoenke:** Investigation. **René Csuk:** Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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