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Synthesis and cytotoxic screening of β–boswellic acid derivatives

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Abstract: Beta-boswellic acids are triterpenoids being generic to the plants of genus boswellia. Although they were shown to exhibit different biological activities, the cytotoxic potential of β-boswellic acid derivatives remained by and large unexploited. To expand the potential of these compounds we developed simple procedures for the interconversion of the most important β-boswellic acids **1**-**4** and prepared several other derivatives **5**-**48**. These compounds were screened for their cytotoxic activity in sulforhodamine B assays employing several human tumor cell lines and nonmalignant mouse fibroblasts. One of these compounds, a difluoromethylester of 3-*O*-acetyl-11-keto-β-boswellic acid **23**, was cytotoxic for human breast adenocarcinoma cells MCF-7 (EC_{50} = 6.5 μM) while being significantly less cytotoxic for the mouse fibroblasts.

Keywords: Frankincense, Boswellic acid, Cytostatic activity.

Introduction

During the last decade, the scientific interest in frankincense has risen considerably. A literature retrieval (SciFinder) searching for the index term „frankincense "showed 3905 hits (until May 2017): While during 1995-2004 only 76 articles dealt with this topic, the number of publications on frankincense increased during the period 2005-2011 to 1341 and grew even larger for the period 2012-2017 (May), and further 2409 papers have been noted for this time span.

Despite the increased interest in frankincense, the number of articles dealing with boswellic acids remained low [1-3], although boswellic acids account for 25-30% (by weight) of the resin acids, with ursane-derived β-boswellic acids dominating over oleanane-derived α-boswellic acids.

Analyses of commercial samples reported for β-boswellic acid (-derivatives) up to 10.1% of **BA** (**1**, β-boswellic acid), 6.8% of **ABA** (**2**, 3-*O*-acetyl-β-boswellic acid), 5.1% of β-KBA (**3**, 11-keto-β-boswellic acid) and 3.8% of **AKBA** (**4**, 3-*O*-acetyl-11-keto-β-boswellic acid) in frankincense [4]. These values vary highly in practice, and they strongly depend on the quality of the resin, its origin, the time of harvesting and from the species of boswellia (Fig. 1) [5].

The only source for these natural products (that are also generic to the plants of genus boswellia) is their extraction from the resin; there are no total or partial syntheses for boswellic acids. Because of these limitations, the number of publications dealing with synthetic transformations [2, 6-8] of boswellic acids remained low compared to the number of publications on frankincense; even less is known about the cytotoxicity of **BA** and derivatives [6, 8-13].

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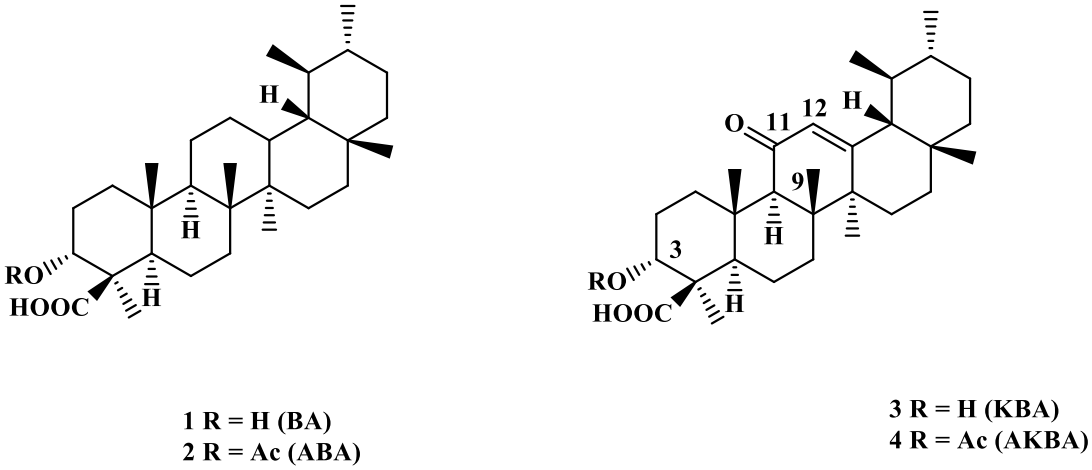
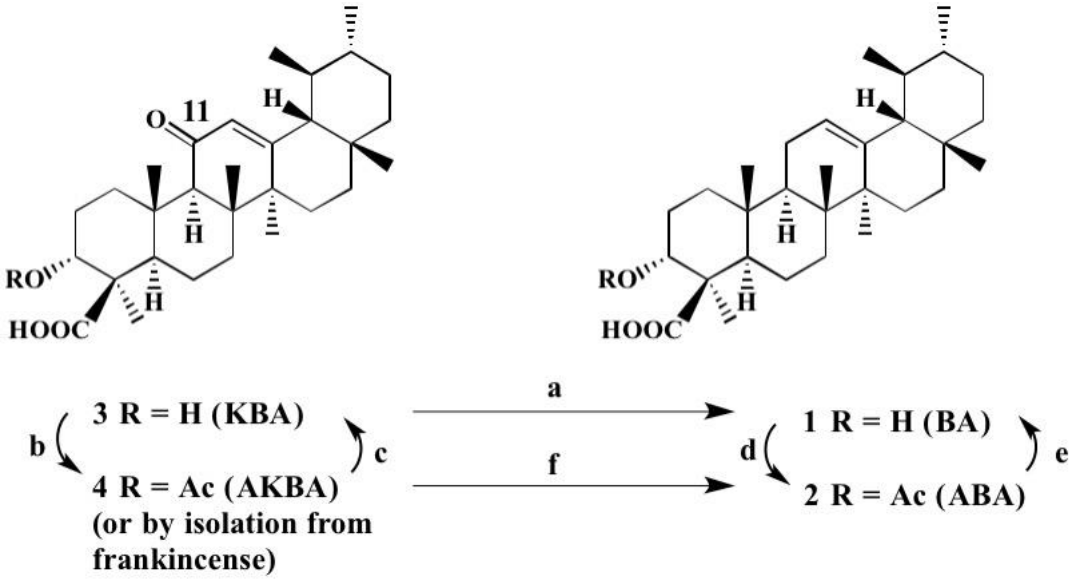


Figure 1. Structure of the most important β-boswellic acids.

Results and Discussion

It was the merit of J. Jauch et al.[14] to provide an easy access to **AKBA** (**4**); thereby the resin is extracted, and the crude extract is oxidized and acetylated. This sequence transformed all boswellic acids finally into **AKBA** (**4**). While **4** is accessible by this approach in good yields, **BA** (**1**) and **ABA** (**2**) are converted during these operations, again limiting their availability. Hence, we became interested in the transformation of **AKBA** (**4**) to **ABA** (**2**) as well as of **KBA** (**3**) to **BA** (**1**).

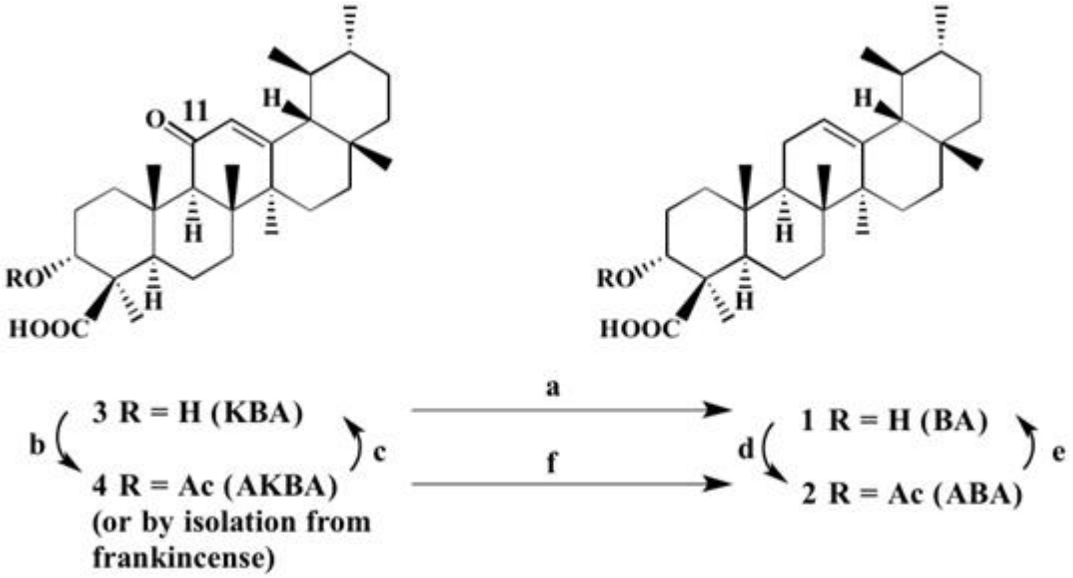
While the reduction of **4** with Pd/C failed to give **2**, the hydrogenation of **4** with Pt for 12 h at 85 bar [15,16] afforded **2** in 87% yield quite nicely (Scheme 1). Similarly, hydrogenolysis of **3** gave **BA** (**1**). This parallel previous findings for the reduction of the carbonyl group in the triterpene glycyrrhetinic acid [15,16]. The synthesis of **1** and **2** by hydrogenolysis of **3** or **4** seems more convenient than the previously reported reduction of **3** using powdered lithium in HMPA/*tert*-butanol [14,17]. Deacetylation of **2** or **4** afforded **1** or **3** in almost quantitative yield; acetylation of **1** or **3** furnished **2** and **4**, respectively.



Scheme 1. Interconversion of boswellic acids **1**-**4**. a) PtO_2, HOAc, H_2, 85 bar, 25 °C, 12 h, 87%; b) AcCl, pyridine, DMAP, 25 °C, 6 h, 91%; c) NaOH, EtOH, 25 °C, 12 h, 98%; d) AcCl, pyridine, DMAP, 25 °C, 6 h, 89%; e) NaOH (aq.), 25 °C, 12 h, 93%; f) PtO_2, HOAc, H_2, 85 bar, 25 °C, 12 h, 87%.

From the microwave-assisted reaction of **3** with lithium borohydride in diglyme for 1 hour allylic alcohols **5** and **6** (ratio **5**:**6** = 1.7:1) were obtained (Scheme 2). As by-products of this reaction triols **7** and **8** were formed. Products **7** and **8** were also obtained from the microwave-assisted reduction of **5** (or **6**) with $LiAlH_4$. The configuration of the hydroxyl group in **5** and **6** (as well as in **7** and **8**) was determined by NMR. Thus, NOESY spectra of **5** showed the close proximity between H-11 and H-9, while for **6** close

proximity between H-11 and H-25 was established. Triterpenoids carrying a hydroxyl group at C-11 seem to be of interest as enzyme inhibitors, for example [18-21] as inhibitors of the microsomal prostaglandin E2 synthase, of cathepsin or of acetylcholinesterase.



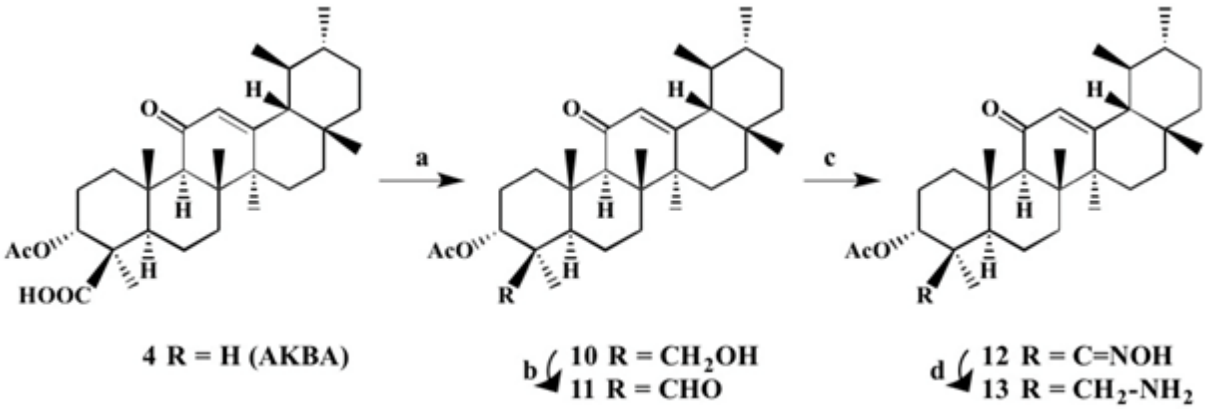
Scheme 2. Reductive transformations at positions 11 and 24 of **KBA**. a) $LiBH_4$, diglyme, microwaves, 140 °C, 1 h: 47% of **5**, 28% of **6**, 10% of **7**, 6 % of **8**; b) IR120 H^+, MeOH, 60 °C, 1 h, 91%.

The allylic alcohols **5** and **6,** however, were unstable towards traces of acids; and compound **9** [22, 23] was formed from **5** or **6** or from mixtures of **5** and **6** even upon prolonged standing in $CDCl_3$ solutions. Reaction of a methanolic solution of **5** or **6** with ion exchange resin IR120 H^+ for 1 hour at 60 °C gave pure product **9** in good yields. This compound has previously been isolated from the resin, too (but was most probably an artefact due to the acidic conditions during the isolation) [24]. The facile elimination reaction of **5** and **6** parallels previous findings of Rozen et al. for glycyrrhetinic acid derivatives [25].

Reaction of **4** with thionyl chloride (Scheme 3) followed by treating the intermediate acid chloride with sodium borohydride gave 72% of the alcohol **10**. Compound **10** is characterized in its ^1H NMR spectrum by the presence of signals for diastereomeric H-$24_{a,b}$ (each as a doublet) at δ = 3.75 and 3.52 ppm showing a geminal ^2J = 11.2 Hz. In the ^{13}C NMR spectrum of **10** C-24 was detected at δ = 65.5 ppm.

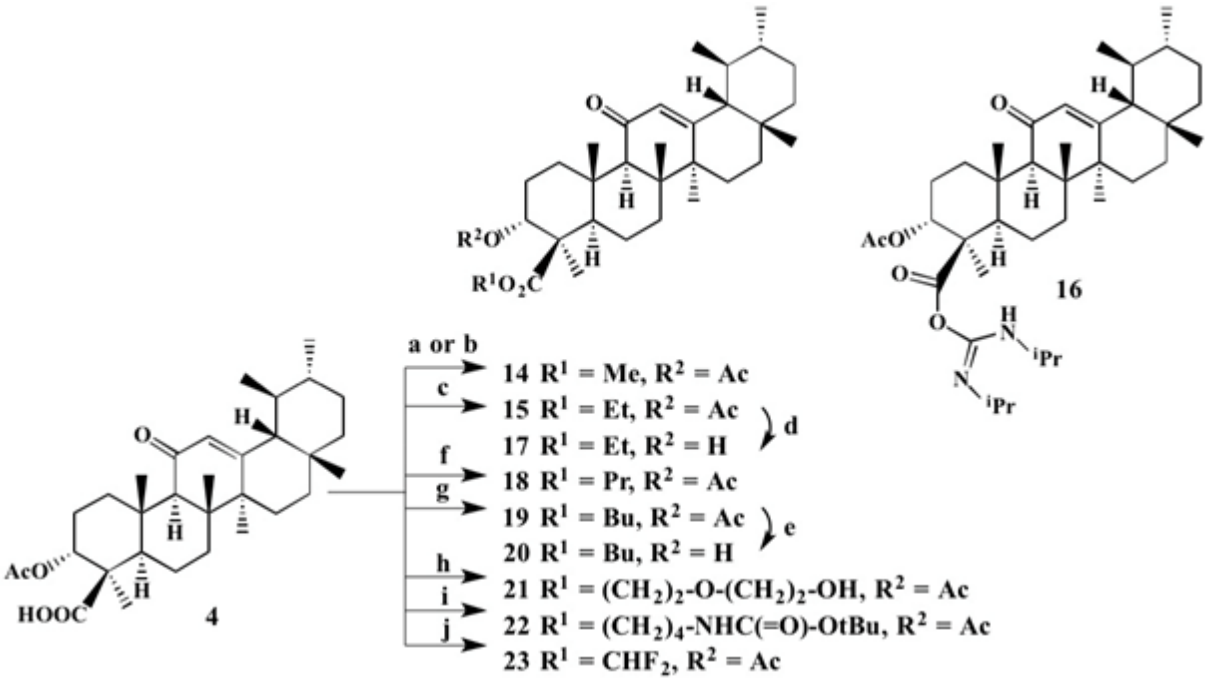
Oxidation of **10** with PCC in DCM for 5h at ambient temperature furnished aldehyde **11** albeit only in 31% isolated yield; this aldehyde is very unstable and deteriorates quickly. In its ^{13}C NMR spectrum the carbonyl carbon was detected at δ = 202.4 ppm. Reaction of **11** with hydroxylammonium chloride in dry pyridine [26] at 50 °C for 3 h gave 78% of the oxime **12**. This oxime showed in its IR spectrum the C=N valence vibrational band at ν = 1640 cm^{-1}, and in the ^{13}C NMR spectrum C-24 was detected at δ = 154.5 ppm. Furthermore, **12** was easily reduced [27] with sodium cyanoborohydride/$TiCl_3$ to afford amine **13**

To obtain derivatives of higher lipophilicity, **4** was esterified with several alcohols (Scheme 4). Thus, the reaction of **4** with Cs_2CO_3/MeI gave 95% of methyl ester **14**; esterification of **4** with thionyl chloride/sodium methanolate gave **14** in 78% isolated yield.



Scheme 3. Synthesis of compounds **10**-**13.** a) $SOCl_2$, reflux, 3 h then $NaBH_4$, THF, 25 °C, 12 h, 72%; b) PCC, DCM, 25 °C, 5 h, 31%; c) $NH_2OH.HCl$, pyridine, 50 °C, 3 h, 78%; d) $NaBH_3CN$, $TiCl_3$, MeOH, 25 °C, 12 h, 96%.

Esters were also accessible from the DMAP/diisopropyl carbodiimide (DIC) catalysed reaction of the triterpenoids with alcohols. Thus, reaction of **4** with DIC /EtOH/DMAP gave 69% of the ethyl ester **15** together with *O*-acylurea **16** (7%) as a by-product. Deacetylation of **15** (or **19**, *vide infra*) under Zemplén conditions gave **17** (or **20** from **19**) in good yields; lower yields were observed when these deacetylations were carried out with KOH in methanol.



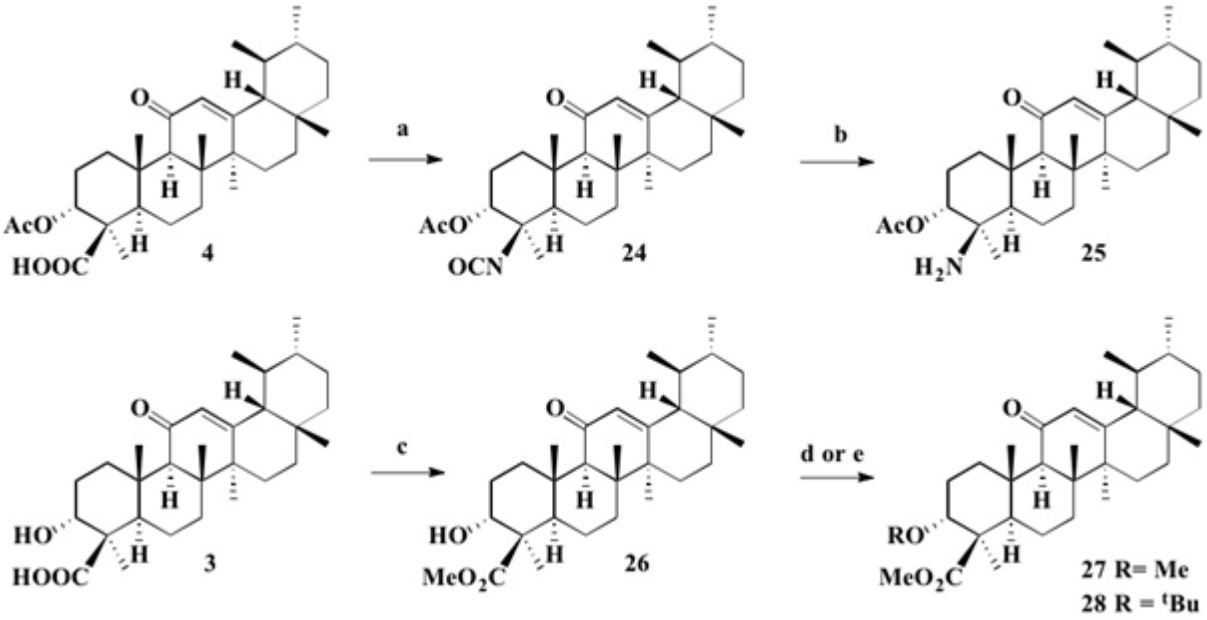
Scheme 4. Synthesis of different esters derived from **AKBA**. a) Cs_2CO_3, MeI, 25 °C, 12 h, 95%; b) $SOCl_2$, NaOMe, 25 °C, 12 h, 78%; c) DIC, DMAP, DCM, EtOH, 25 °C, 12 h, 69% (isolated byproduct **16**: 7%); d) EtOH, NaOEt (cat.), 25 °C, 12 h, 90%; e) *n*-BuOH, NaOBu (cat.), 25 °C, 12 h, 86%; f) DIC, DMAP, DCM, *n*-Pr-OH, 25 °C, 12 h, 69%; g) DIC, DMAP, DCM, *n*-BuOH, 25 °C, 12 h, 87%; h) $SOCl_2$, DCM, then glycol, 25 °C, 12 h, 60%; i) $SOCl_2$, DCM, then BocNH-$(CH_2)_4$-OH, 25 °C, 12 h, 58%; j) ClF_2CCO_2Na, glyme, 190 °C, 3 h, 71%.

AKBA derived esters carrying medium chain alkyl moieties (such as propyl **18** or butyl ester **19 9]**) were easily prepared from **4** in good yields. In addition, several esters (holding additional functional groups, such as 2-(2-hydroxyethoxy)-ethyl ester **21,** N-*tert*-butyloxycarbonylamino-butyl ester **22** or the difluoromethyl ester **23**) were synthesized, too. The latter compound was obtained from the reaction of **4** with sodium chlorodifluoro acetate in glyme at 190 °C for 3 h. Compound **23** is characterized in its ^{19}F NMR spectrum by the presence of two diastereomeric fluorine substituents showing signals

at δ = -92.7 and -92.3 ppm with a geminal $^2J_{F,F}$ = 92 Hz. The moderate yields observed for some of these reactions can be explained by the formation of side-products (not isolated) and subsequent loss of product during column chromatography.

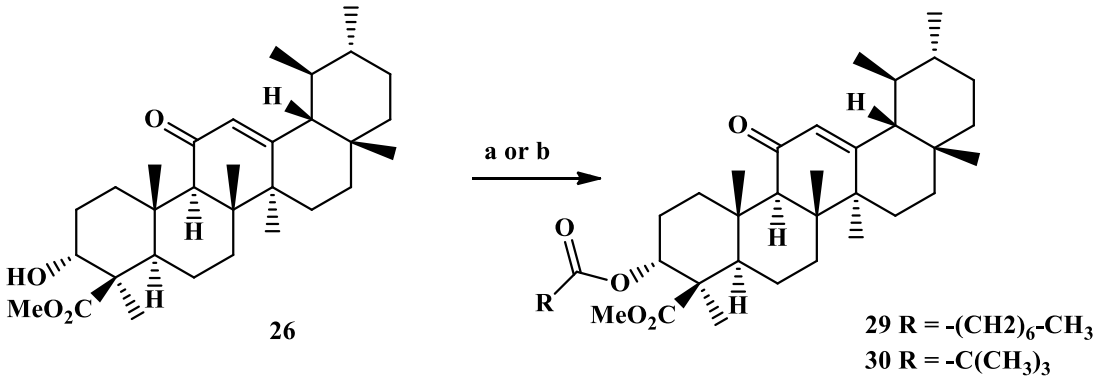
From the reaction of **4** with diphenylphosphoryl azide (DPPA)/NEt_3 in *tert*-butanol at 70 °C for 3 h the isocyanate **24** [28] was obtained (Scheme 5). Reaction of **24** with aq. HCl (conc.) gave access to amine **25** [28].

Etherification at position OH-C(3) proceeded smoothly, when **26** (from the esterification of **3** with cesium carbonate /methyl iodide in THF) [29] was used as a starting material. Thus, reaction of **26** with NaH/MeI gave 91% of **27**, and from the reaction of **26** with di-*tert*. butyldicarbonate in the presence of magnesium perchlorate [30] 86% of **28** were obtained.



Scheme 5. Synthesis of derivatives **24**-**28**. a) ^{t}BuOH, NEt_3, DPPA, 70 °C, 3 h, 59%; b) aq. HCl, 60 °C, 5 h, 72%; c) Cs_2CO_3, THF, MeI, 25 °C, 12 h, 95%; d) NaH, THF, MeI, 25 °C, 12 h, 91% (of **27**); e) $Mg(ClO_4)_2$, Boc_2O, 25 °C, 3 d, 86% (of **28**).

Acylation of OH-C(3) in **26** was easily performed, and (Scheme 6) highly lipophilic 3-octanoyl **29** or 3-pivaloyl **30** derivatives (both from **26**) were obtained in good yields.

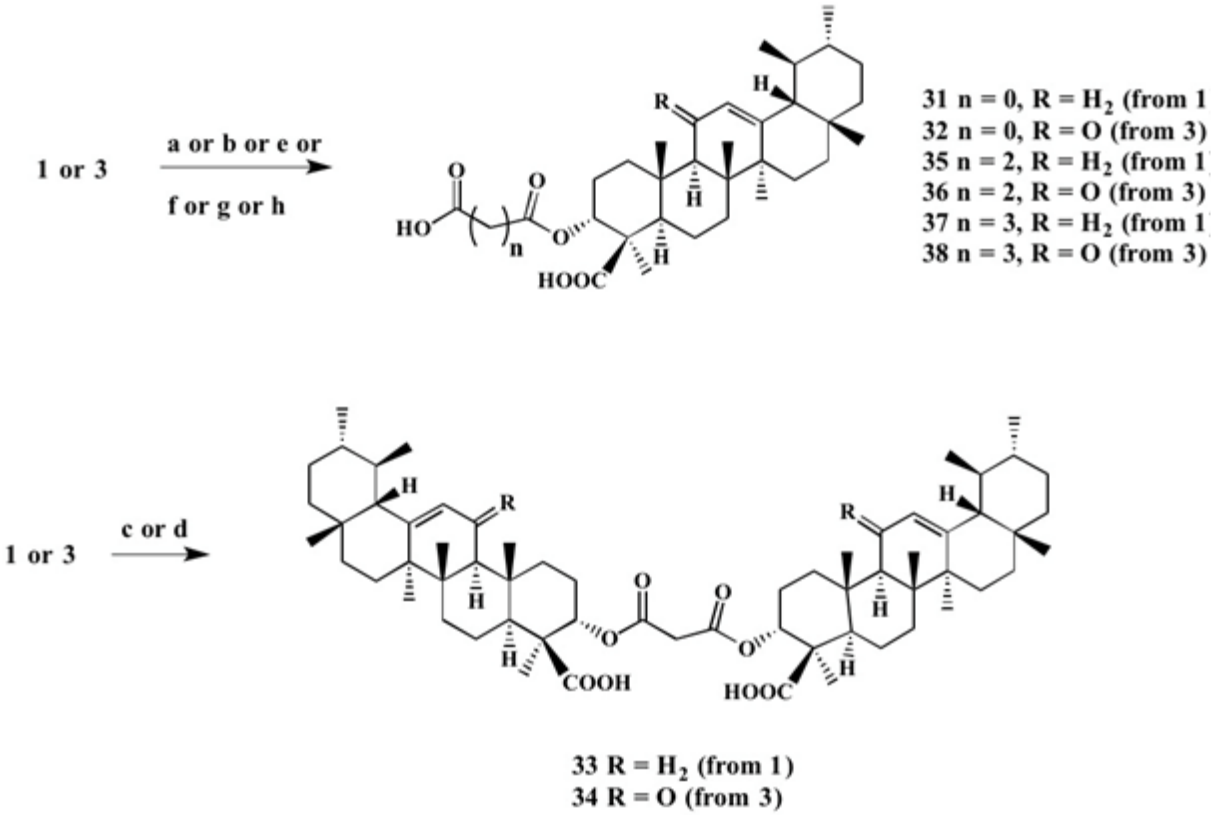


Scheme 6. Synthesis of derivatives **29** and **30**. a) H_3C-$(CH_2)_6$-COCl, pyridine, DMAP, DCM, 25 °C, 12 h, 98%; b) pivaloyl chloride, DCM, DMAP, pyridine, 25 °C, 12 h, 93%.

Somewhat unexpected products were obtained, however, from some of the reactions of **1** or **3** with di-acid di-chlorides (Scheme 7). The reaction of **1** with oxalyl chloride furnished 85% of the 3-oxalyl derivative **31**, and from **3** 84% of **32** were obtained. As previously shown, oxalyl derivatives may serve as valuable starting materials for the synthesis of cytotoxic triterpene derivatives [31]. The reactions of **1**

and **3** with malonyl chloride proceeded sluggish, and only 47% of dimeric **33** and 57% of dimeric **34** were isolated, respectively.

Higher yields but no dimers were obtained for the reaction of **1** with succinic anhydride [19], and 86% of **35** were obtained. In a similar manner, **3** gave under the same conditions 71% of **36**. Yields were similar for the reaction of **1** with an excess of glutaric anhydride, and 83% of **37** were obtained. Under the same conditions **3** gave 75% of 3-*O*-glutaroylated **38**.

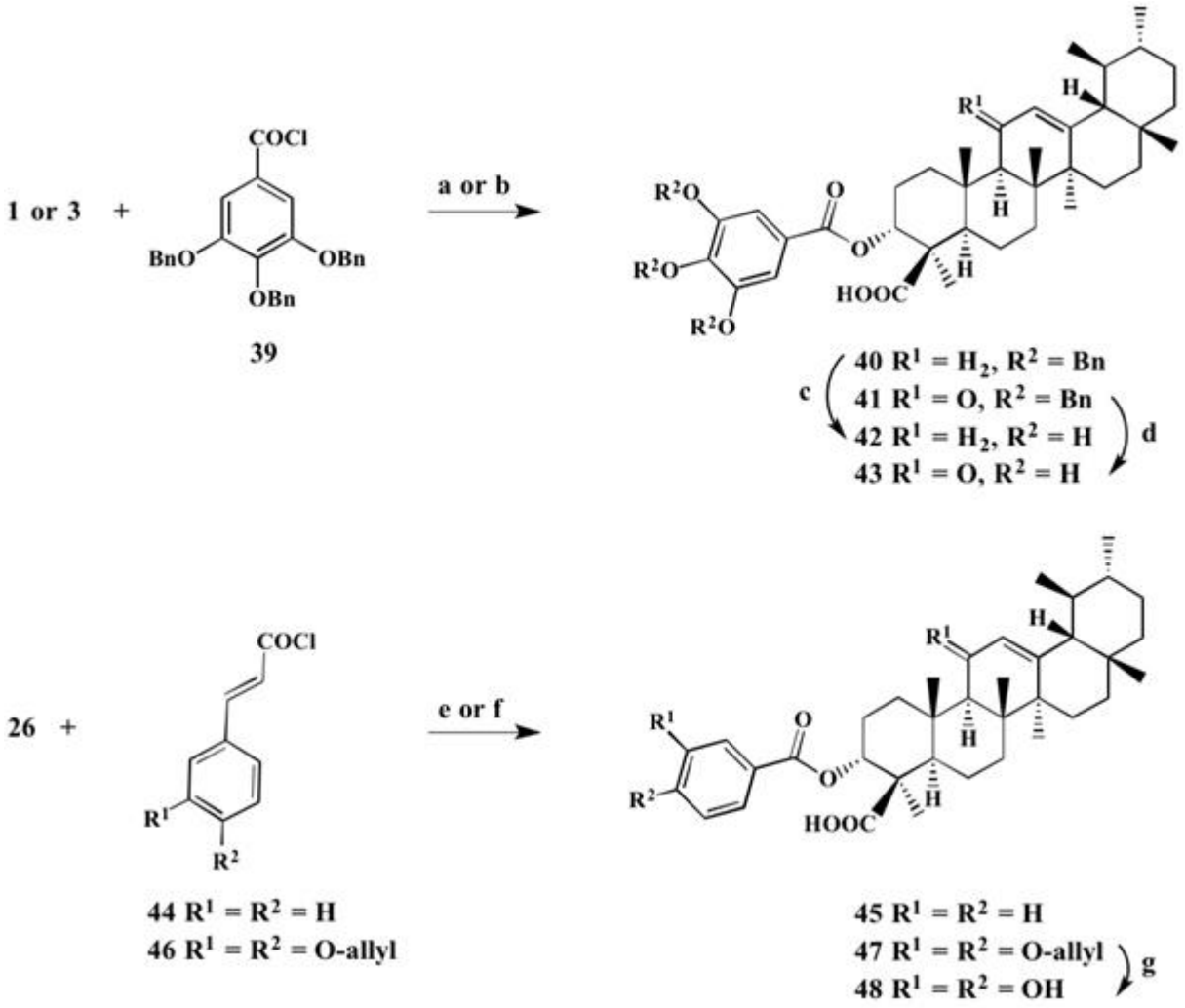


Scheme 7. Synthesis of acylated compounds **31**, **32**, **35**-**38** and formation of dimeric **33** and **34**. a) oxalyl chloride, THF, 25 °C, 12 h, 85% (of **31**); b) oxalyl chloride, THF, 25 °C, 12 h, 84% (of **32**); c) malonyl chloride, THF, 25 °C, 10 min, 47% (of **33**); d) malonyl chloride, THF, 25 °C, 10 min, 57% (of **34**); e) succinic anhydride, NEt_3, DMAP, 25 °C, 1 d, 86% (of **35**); f) succinic anhydride, NEt_3, DMAP, 25 °C, 1d, 71% (of **36**); g) glutaric anhydride, NEt_3, DMAP, 25 °C, 1 d, 83% (of **37**); h) glutaric anhydride, NEt_3, DMAP, 25 °C, 1 d, 75% (of **38**).

Reaction of 3,4,5-*O*-tri-benzyl-galloyl chloride **39**, obtained from the benzylation of gallic acid followed by its conversion to the corresponding benzoyl chloride by treatment with oxalyl chloride/DMF (cat.) in DCM) [32] with **1** and **3** (Scheme 8) gave derivatives **40** and **41**, respectively. Hydrogenation of **40** and **41** in the presence of Pd/C (10%) for several hours furnished products **42** and **43**, respectively.

Similarly, *trans*-cinnamic acid was converted into its chloride **44** whose reaction with **26** gave 73% of **45**. From the reaction of **46** with **26** 69% of **47** were obtained. Deprotection of **47** with tetrakistriphenyl palladium and morpholine [33] yielded 78% of **48**.

Compounds **5**-**48** were screened for their cytotoxic activity in sulforhodamine B assays [34] using a panel of different human tumor cell lines as well non-malignant mouse fibroblasts (NIH 3T3) using betulinic acid as a standard. Betulinic acid is generally regarded as an ideal standard when comparing triterpenoids and their cytotoxic activity. The results from these assays are compiled in Table 1. Except for **23**, none of the compounds gave EC_{50} values smaller than 10 μM. The reason for the high activity of **23** for MCF7 breast adenocarcinoma cells remains unclear and will be subject to subsequent investigations. The differences in the EC_{50} values of the other compounds are too small (and their cytotoxic activity is too low) to deduce reliable structure-activity relationships.



Scheme 8. Synthesis of derivatives **40**-**48**. a) **39**, pyridine, 25 °C, 2 d, 63% (of **40**); b) **39**, pyridine, DCM, DMAP, 25 °C, 2 d, 69% (of **41**); c) Pd/C (10%), 1 atm H_2, THF, 25 °C, 6 h, 87% (of **42**); d) Pd/C (10%), 1 atm H_2, THF, 25 °C, 6 h, 81% (of **43**); e) **44**, DCM, DMAP, pyridine, 25 °C, 12 h, 73% (of **45**); f) **46**, DCM, DMAP, pyridine. 25 °C, 12 h, 69% (of **47**); g) $Pd(PPh_3)_4$, morpholine, DCM, 25 °C, 12 h, 78% (of **48**).

Conclusion

Although β-boswellic acids exhibit different biological activities, the cytotoxic potential of β-boswellic acid derivatives remained unexploited. While **AKBA** (**4**) can easily be accessed from the resin, β-boswellic acid **1**-**3** could be obtained from the resin up to now by exhaustive chromatography purification only. We herein expanded the potential of these compounds by developing simple procedures for the interconversion of the most important β-boswellic acids **1**-**4**. Several derivatives **5**-**48** were prepared and screened for their cytotoxic activity in sulforhodamine B assays employing several human tumor cell lines and non-malignant mouse fibroblasts. As a result, 25 of these compounds showed EC50 values < 30 μM. However, one of these compounds, a difluoromethylester of 3-*O*-acetyl-11-keto-β-boswellic acid **23** was cytotoxic for human breast adenocarcinoma cells MCF-7 (EC_{50} = 6.5 μM) while being significantly less cytotoxic for the mouse fibroblasts.

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Table 1: Cytotoxicity of selected compounds (EC_{50} values in μM from SRB assays after 96 hours of treatment; the values are averaged from three independent experiments performed each in triplicate; confidence interval CI = 95 %, cut-off of the assay 30 μM); standard: betulinic acid). Human cancer cell lines: HT29 (colorectal adenocarcinoma), MCF7 (breast adenocarcinoma), and nonmalignant mouse fibroblast NIH 3T3.

Compound	HT-29	MCF7	NIH 3T3
3	> 30	> 30	> 30
4	19.3 ± 2.4	17.4 ± 1.1	26.4 ± 3.0
5	14.2 ± 2.0	13.9 ± 2.3	19.2 ± 2.5
6	16.1 ± 1.7	17.4 ± 2.0	18.7 ± 1.4
7	> 30	> 30	> 30
8	> 30	> 30	> 30
9	> 30	> 30	> 30
10	24.4 ± 0.9	19.3 ± 2.1	21.1 ± 1.7
14	18.1 ± 0.7	18.9 ± 1.4	16.2 ± 2.2
15	17.3 ± 2.4	19.2 ± 0.8	15.1 ± 2.6
17	17.4 ± 2.0	19.7 ± 1.2	21.2 ± 1.5
18	15.2 ± 1.3	18.4 ± 2.7	29.0 ± 1.7
19	22.1± 0.5	14.5 ± 2.3	18.7 ± 1.3
20	22.0 ± 1.5	14.8 ± 1.7	19.3 ± 1.1
21	16.1 ± 1.9	19.3 ± 1.6	22.2 ± 1.2
22	15.1 ± 1.1	13.7 ± 2.2	12.0 ± 2.9
23	28.2 ± 2.9	6.5 ± 0.9	17.4 ± 2.0
26	18.4 ± 2.0	29.2 ± 3.0	> 30
27	21.2 ± 3.1	19.5 ± 2.6	27.2 ± 2.4
28	17.4 ± 1.8	24.9 ± 2.0	21.9 ± 2.1
29	19.1 ± 2.5	27.6 ± 1.5	26.2 ± 3.1
30	16.2 ± 2.6	19.9 ± 3.1	17.3 ± 1.6
31	> 30	> 30	> 30
32	29.4 ± 1.7	28.3 ± 1.2	27.9 ± 1.5
33	> 30	> 30	> 30
34	> 30	> 30	> 30
35	> 30	> 30	> 30
36	25.2 ± 3.0	17.3 ± 1.5	26.4 ± 2.2
37	> 30	> 30	> 30
38	24.8 ± 2.8	19.3 ± 1.4	19.1 ± 2.5
42	24.1 ± 2.4	21.3 ± 1.7	27.4 ± 1.6
43	19.7 ± 1.1	18.7 ± 1.7	25.5 ± 2.0
45	21.9 ± 1.5	24.1 ± 2.6	28.1 ± 1.7
48	19.2 ± 1.9	16.2 ± 1.1	17.0 ± 1.9
betulinic acid	14.4 ± 0.7	10.2 ± 1.8	16.1 ± 1.1

Experimental

Melting points are uncorrected (*Leica* hot stage microscope), NMR spectra were recorded using the Varian spectrometers Gemini 2000 or Unity 500 (δ given in ppm, *J* in Hz), MS spectra were taken on a Finnigan MAT LCQ 7000 (electrospray, voltage 4.5 kV, sheath gas nitrogen) instrument. The optical rotation was measured on a Perkin-Elmer polarimeter at 20 °C. Analytical TLC was performed on silica gel (Merck 5554), and purification of the compounds was done by preparative column chromatography (silica gel, Merck 230-400 mesh). Elemental analyses were performed on a Vario EL (CHNS). The solvents were dried according to usual procedures. The purity of the compounds was determined by HPLC and found to be

> 97%. Frankincense was bought from different commercial suppliers in bulk quantities. The SRB assays were performed as previously reported [6,8,34]. NMR assignments were in full agreement with data previously published.[6-8, 14,35] Figure 2 shows the most important C,H-couplings obtained from HMBC experiments for compound **4**.

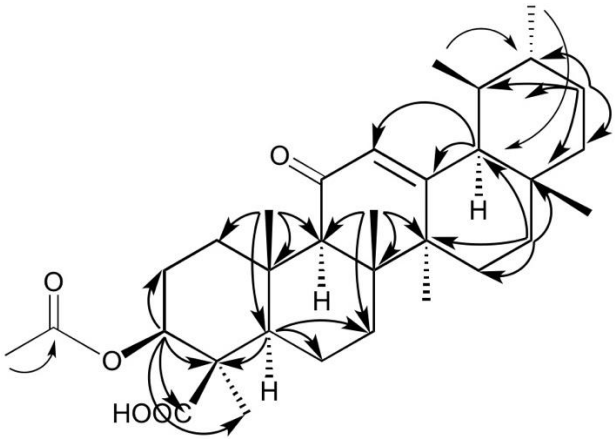

Figure 2. Most important C,H-coupling from HMBC experiments for compound **4**.

β-Boswellic acid [β-BA, (1)]
From **2**
Compound **2** (0.5, 0.80 mmol) was stirred at 25 °C with aq. sodium hydroxide solution (0.5 M, 15 mL) overnight. Usual workup followed by chromatography (silica gel, hexane/diethyl ether, 3:1, + 0.1% of acetic acid) yielded **1** (340 mg, 93%) as a colorless solid; m.p. 233-235 °C (lit.: 232-235 °C [14]), $[\alpha]_D$ = +109.3° (*c* = 0.85, $CHCl_3$) (lit.: +86° (*c* = 0.54, $CHCl_3$) [14]).

From **3**:
In an autoclave (Parr, glass insert) to a solution of **3** (2.0 g, 4.25 mmol) in acetic acid (75 mL) PtO_2 (0.5 g, 2.2 mmol) was added, and the mixture was hydrogenated for 12 h at 85 bar. The catalyst was filtered off (over a short path of silica gel), the solvent was evaporated under diminished pressure, and the crude product was purified by chromatography (silica gel, hexane/ diethylether, 3:1, + 0.1% of acetic acid) to yield **1** (1.68 g, 87%) as a colorless solid; m.p. 234-236 °C (lit.: 232-236 °C [14]), $[\alpha]_D$ = +107.9° (*c* = 0.9, $CHCl_3$) (lit.: +86° (*c* = 0.54, $CHCl_3$) [14]).

β-3-O-Acetyl-boswellic acid [β-ABA, (2)]
From **1**:
Acetylation of **1** (2.0 g, 4.38 mmol) in dry pyridine (20 mL) in the presence of DMAP (98 mg, 0.8 mmol) with acetyl chloride (0.5 g, 6.37 mmol) for 6 h at 25 °C followed by usual aq. work-up gave **2** (1.98 g, 91%) as a colorless solid; m.p. 256-258 °C (lit.: 251-253 °C [14]), $[\alpha]_D$ = +59.3° (*c* = 0.8, $CHCl_3$) (lit.: +54° (*c* = 1.0, $CHCl_3$) [14]).

From **4**:
Following the procedure for the synthesis of **1**, by hydrogenolysis of **4** (1.88 g, 4.0 mmol) compound **2** (1.69 g, 87%) was obtained as a colorless solid; m.p. 255-257 °C (lit.: 251-253 °C [14]), $[\alpha]_D$ = +58.7° (*c* = 0.75, $CHCl_3$) (lit.: +54° (*c* = 1.0, $CHCl_3$) [14]).

(3α, 4β) 3-Hydroxy-11-oxo-urs-12-en-24-oic acid (= 11-keto-β-boswellic acid) [KBA, (3)]
AKBA (**4**, 10.0 g, 19.5 mmol) was dissolved in ethanol (200 mL) and an aq. solution of sodium hydroxide (4 M, 100 mL) was added. After stirring at 25 °C for 12 h, the pH was adjusted (aq. HCl), the product was extracted with $CHCl_3$ (5 x 100 mL), and the crude product was purified by chromatography (silica gel, hexane/ethyl acetate, 98:2) to afford pure **KBA** in almost quantitative yield (9.25 g, 98%) as a colorless solid; mp 192-195 °C (lit.: 194-195 °C [14]); $[\alpha]_D$ = +118.2° (*c* = 3.72, $CHCl_3$), lit.: +121° (*c* = 1.11, $CHCl_3$) [14]).

3-*O*-Acetyl-11-keto-β-boswellic acid [AKBA, (4)]
By isolation from frankincense
AKBA was isolated following a modified Jauch's procedure [14] and obtained as a colorless solid; m.p. 268-270 °C (lit.: 271-276 °C [14]), $[\alpha]_D$ = +81.1° (*c* = 1.0, $CHCl_3$) (lit.: +82 (*c* = 1.25, $CHCl_3$) [14]).

From **3**
Acetylation of **3** (2.0 g, 3.90 mmol) as described above for the synthesis of **2** from **1** gave **4** (1.63 g, 89%) as a colorless solid; m.p. 269-272 °C (lit.: 271-276 °C [14]), $[\alpha]_D$ = +82.5° (*c* = 0.9, $CHCl_3$) (lit.: +82° (*c* = 1.25, $CHCl_3$) [14]).

(3α, 4β, 11β) 3,11-Dihydroxy-urs-12-en-24-oic acid (5), (3α, 4β, 11α) 3,11-dihydroxy-urs-12-en-24-oic acid (6), (3α, 4β, 11β) urs-12-en-3,11,24-triol (7), (3α, 4β, 11α) urs-12-en-3,11,24-triol (8)

A suspension of lithium borohydride (0.11 g, 5.0 mmol) and **KBA** (0.47 g, 1.00 mmol) was allowed to react in the microwave (Anton Paar, Monowave, 140 °C, 1 h). For work-up the mixture was carefully diluted with ice-water; extraction with diethylether and chromatography (silica gel, hexane/ diethylether, 1:1, + 0.1% acetic acid) gave **5** (140 mg, 47%), **6** (82 mg, 28%), **7** (46 mg, 10%) and **8** (27 mg, 6%).

Data for **5**: colorless solid; m.p. 124-127 °C; $[\alpha]_D$: +123.1° (*c* = 0.7, $CHCl_3$);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.32 (*d*, *J* = 4.3 Hz, 1H, H-12), 4.47 (*t*, *J* = 4.7 Hz, 1H, H-11), 3.99 (*t*, *J* = 2.4 Hz, 1H, H-3), 2.29 (*m*, 1H, H-2a), 2.08 (*m*, 1H, H-16a), 1.94 (*m*, 2H, H-6b, H-15b), 1.80 (*m*, 1H, H-1b), 1.74 (*m*, 1H, H-6a), 1.65 (*m*, 2H, H-1a, H-7a), 1.55 (*m*, 3H, H-2a, H-5. H-9), 1.45 (*m*, 1H, H-22a), 1.43 (*s*, 3H, H-25), 1.39 (*m*, 3H, H-18. H-19, H-21b), 1.34 (*m*, 3H, H-7b, H-21a, H-22b), 1.32 (*s*, 3H, H-26), 1.29 (*s*, 3H, H-23), 1.13 (*m*, 1H, H-15a), 1.10 (*s*, 3H, H-27), 1.07 (*m*, 1H, H-16b), 0.95 (*s*, 3H, H-30), 0.91 (*m*, 1H, H-20), 0.87 (*s*, 3H, H-28), 0.83 (*d*, *J* = 5.9 Hz, 3H, H-29) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 180.0 (C-24), 142.2 (C-13), 131.5 (C 12), 71.7 (C-3), 66.6 (C-11), 60.9 (C-18), 53.7 (C-9), 51.5 (C-5), 48.5 (C-4), 44.3 (C-14), 43.1 (C-22), 41.7 (C-8), 41.2 (C-19), 41.3 (C-20), 40.4 (C-10), 35.3 (C-1), 35.6 (C-17), 35.3 (C-7), 32.8 (C-21), 30.5 (C-28), 29.6 (C-16), 29.1 (C-15), 28.0 (C-2), 25.7 (C-23), 23.8 (C-27), 22.1 (C-30), 22.0 (C-6), 20.5 (C-26), 18.6 (C-29), 17.6 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 473.4 ($[M+H]^+$); analysis calcd for $C_{30}H_{48}O_4$ (472.70): C 76.23. H 10.24; found: C 76.11, H 10.42.

Data for **6**: m.p. 165-168 °C; $[\alpha]_D$ = + 59.3° (*c* = 0.9, $CHCl_3$);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.20 (*d*, *J* = 2.1 Hz, 1H, H-12), 4.20 (*d*, *J* = 9.1 Hz, 1H, H-11), 3.99 (*bs*, 1H, H-3), 2.13 (*m*, 3H, H-1b, H-2b, H-16a), 1.90 (*m*, 1H, H-6b), 1.80 (*m*, 1H, H-15b), 1.71 (*m*, 2H, H-6a, H-9), 1.65 (*m*, 2H, H-1a, H-5), 1.56 (*m*, 1H, H-7a), 1.43 (*m*, 8H, H-2a, H-7b, H-18, H-19, H-21a, H-21b, H-22a, H-22b), 1.29 (*s*, 3H, H-23), 1.23 (*bs*, 4H, H-15a, H-27), 1.16 (*s*, 3H, H-26), 1.10 (s, 3H, H-25), 0.95 (*bs*, 5H, H-16b, H-20, H-30), 0.92 (*d*, *J* = 6.2 Hz, 3H, H-29), 0.85 (*s*, 3H, H-28) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 180.1 (C-24), 142.0 (C-13), 132.9 (C-12), 71.7 (C-3), 69.5 (C-11), 60.1 (C-18), 55.6 (C-9), 50.8 (C-5), 49.1 (C-4), 45.1 (C-8), 44.3 (C-14), 43.2 (C-22), 41.3 (C-19), 41.2 (C-20), 40.4 (C-10), 37.9 (C-1), 36.0 (C-7), 35.7 (C-17), 33.1 (C-21), 30.0 (C-28), 29.9 (C-16), 28.3 (C-15), 28.1 (C-2), 26.0 (C-23), 24.2 (C-27), 22.7 (C-30), 21.8 (C-6), 19.6 (C-26), 18.7 (C-29), 15.7 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 473.3 ($[M+H]^+$); analysis calcd for $C_{30}H_{48}O_4$ (472.70): C 76.23. H 10.24; found: C 75.97. H 10.39.

Data for **7**: amorphous solid; $[\alpha]_D$ = +58.1° (*c* = 0.3, $CHCl_3$);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.29 (*d*, *J* = 4.2 Hz, 1H, H-12), 4.47 (*m*, 1H, H-11), 3.81 (*bs*, 1H, H-3), 3.74 (*d*, *J* = 10.8 Hz, 1H, H-24b), 3.44 (*d*, *J* = 10.8 Hz, 1H, H-24a), 2.05 (*m*, 1H, H-16a), 1.98 (*m*, 1H, H-2b), 1.90 (*m*, 1H, H-15b), 1.79 (*m*, 1H, H-1b), 1.67 (*m*, 2H, H-1a, H-7a), 1.56 (*m*, 3H, H-2a, H-6b, H-9), 1.47 (*s*, 3H, H-25), 1.41 (*m*, 5H, H-5, H-18, H-19, H-21b, H-22a), 1.32 (*m*, 4H, H-6a, H-7b, H-21a, H-22b), 1.27 (*s*, 3H, H-26), 1.09 (*s*, 3H, H-27), 1.05 (*s*, 3H, H-23), 1.03 (*m*, 2H, H-15a, H-16b), 0.95 (*bs*, 4H, H-20, H-30), 0.85 (*s*, 3H, H-28), 0.82 (*d*, *J* = 5.9 Hz, 3H, H-29) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 141.8 (C-13), 131.8 (C-12), 71.4 (C-3), 66.8 (C-11), 67.2 (C-24), 60.5 (C-18), 54.3 (C-9), 52.1 (C-5), 44.6 (C-4), 44.3 (C-14), 43.1 (C-22), 41.7 (C-8), 41.2 (C-19), 41.1 (C-20), 39.8 (C-10), 35.4 (C-17), 35.3 (C-7), 34.8 (C-1), 32.8 (C-2), 30.1 (C-28), 29.7 (C-16), 29.6 (C-15), 27.2 (C-2), 24.0 (C-27), 23.8 (C-23), 22.6 (C-30), 20.6 (C-6), 20.3 (C-26), 19.9 (C-25), 18.7 (C-29) ppm;
MS (ESI, MeOH): *m/z* = 459.4 ($[M+H]^+$); analysis calcd for $C_{30}H_{50}O_3$ (458.72): C 78.55, H 10.99; found: C 78.40, H 11.13.

Data for **8**: amorphous solid; $[\alpha]_D$ = +50.4° (*c* = 0.2, $CHCl_3$);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.21 (*d*, *J* = 3.1 Hz, 1H, H-12), 4.21 (*m*, 1H, H-11), 3.79 (*bs*, 1H, H-3), 3.72 (*d*, *J* = 10.8 Hz, 1H, H-24b), 3.45 (*d*, *J* = 10.8 Hz, 1H, H-24a), 2.07 (*m*, 1H, H-16a), 1.98 (*m*, 1H, H-1b), 1.89 (*m*, 1H, H-2b), 1.76 (*m*, 3H, H-1a, H-9, H-15b), 1.55 (*m*, 2H, H-6b, H-7a), 1.43 (*m*, 7H, H-2a, H-5, H-6a, H-18, H-19, H-21b, H-22a), 1.34-1.23 (*m*, 3H, H-7b, H-21a, H-22b), 1.21 (*s*, 3H, H-27), 1.12 (*s*, 3H, H-25), 1.05 (*s*, 6H, H-23, H-26), 1.00 (*m*, 1H, H-15a), 0.92 (*bs*, 5H, H-16b, H-20, H-30), 0.90 (*d*, *J* = 6.1 Hz, 3H, H-29), 0.81 (*s*, 3H, H-28) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 142.1 (C-13), 132.2 (C-12), 71.1 (C-3), 69.5 (C-11), 67.1 (C-24), 60.0 (C-18), 565 (C-9), 51.2 (C-5), 45.0 (C-8), 44.7 (C-4), 43.6 (C-14), 43.1 (C-22), 41.5 (C-20), 41.3 (C-19), 39.9 (C-10), 37.1 (C-1), 36.2 (C-7), 35.6 (C-17), 32.6 (C-21), 30.1 (C-28), 29.9 (C-16), 28.2 (C-15), 27.3 (C-2), 24.4 (C-27), 24.0 (C-23), 22.8 (C-30), 20.1 (C-6), 19.3 (C-26), 18.7 (C-29), 18.2 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 459.3 ($[M+H]^+$); analysis calcd for $C_{30}H_{50}O_3$ (458.72): C 78.55, H 10.99; found: C 78.38, H 11.17.

9,11-Dehydro-β-boswellic acid (9)
To a solution of **5** or **6** (100 mg, 0.21 mmol) in methanol, ion exchange resin IR120H$^+$ was added, and the mixture was stirred at 60 °C for 1 h. Filtration followed by usual workup and chromatography (silica gel, hexane/ diethylether, 1:1, + 0.1% acetic acid) gave **9** (87 mg, 91%) as a colorless solid; m.p. 231-234 °C; $[\alpha]_D$: +339.7° (*c* = 0.5, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.67 (*d*, *J* = 5.8 Hz, 1H, H-11), 5.45 (*d*, *J* = 5.9 Hz, 1H, H-12), 4.07 (*t*, *J* = 2.7 Hz, 1H, H-3), 2.26 (*m*, 1H, H-2b), 2.02 (*m*, 1H, H-16a), 1.91 (*m*, 2H, H-6b, H-15b), 1.78 (*m*, 2H, H-1b, H-6a), 1.67 (*m*, 3H, H-1a, H-2a, H-7a), 1.59 (*dd*, *J* = 12.0, 1.5 Hz, 1H, H-9), 1.48 (*m*, 2H, H-18, H-22a), 1.43-1.39 (*m*, 2H, H-7b, H-21b), 1.38 (*s*, 3H, H-23), 1.35-1.21 (*m*, 3H, H-19, H-21a, H-22b), 1.20 (*s*, 3H, H-26), 1.11 (*s*, 3H, H-25), 1.07 (*m*, 1H, H-15a), 0.95 (*bs*, 8H, H-16b, H-20, H-27, H-30), 0.84 (*s*, 3H, H-28), 0.81 (*d*, *J* = 6.5 Hz, 3H, H-29) ppm;
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 182.7 (C-24), 152.6 (C-9), 141.6 (C-13), 123.1 (C-12), 116.3 (C-11.), 70.1 (C-3), 57.2 (C-18), 47.0 (C-4), 46.2 (C-5), 43.4 (C-8), 41.4 (C-22), 40.5 (C-14), 39.3 (C-20), 39.3 (C-10), 39.1 (C-19), 33.5 (C-17), 32.5 (C-1), 31.7 (C-7), 31.4 (C-21), 28.5 (C-28), 28.2 (C-16), 26.2 (C-15), 27.2 (C-2), 24.0 (C-23), 23.1 (C-25), 21.5 (C-26), 21.5 (C-30), 19.5 (C-6), 17.4 (C-27), 17.1 (C-29) ppm;
MS (ESI, MeOH): *m/z* = 455.4 ($[M+H]^+$); analysis calcd for $C_{30}H_{46}O_3$ (454.68): C 79.24, H 10.19; found: C 79.02, H 10.34.

(3α, 4β) 3-Acetoxy-11-oxo-urs-12-en-24-ol (10)
A solution of **4** (2.0 g, 4.0 mmol) and thionyl chloride (10 mL) was heated for 3 h at 90 °C. The volatiles were removed under reduced pressure, and the residue was dissolved in dry THF (50 mL). Sodium borohydride (606 mg, 16.0 mmol) was added, and stirring at 25 °C was continued overnight. After usual aq. work-up, extraction with diethyl ether and chromatography (silica gel, hexane, 7:3) **10** (1.43 g, 72%) was obtained as colorless solid; m.p. 211-213°C; $[\alpha]_D$ = 48.4° (*c* = 4.48, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.02 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 3.75 (*d*, *J* = 11.2 Hz, 1H, H-24), 3.52 (*d*, *J* = 11.2 Hz, 1H, H-24), 2.53 (*virt. dt*, *J* = 3.3, 3.3, 13.3 Hz,1H, H-1b), 2.42 (*s*, 1H, H-9), 2.08 (*virt dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 2.06 (*s*, 3H, H-32), 1.91 (*m*, 1H, H-2a), 1.86 (*virt. dt*, *J* = 13.7, 5.0 Hz, 13.7 Hz, 1H, H-15a), 1.66 (*m*, 1H, H-7a), 1.62 (*m*, 1H, H-2b), 1.58 (*m*, 1H, H-6a), 1.52 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.45 (*m*, 2H, H-21), 1.40 (*m*, 1H, H-6b), 1H, H-7b), 1.39 (*m*, 1H, H-19), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.26 (*m*, 1H, H-5, 1H, H-1a), 1.20 (*m*, 1H, H-15b), 1.14 (*s*, 6H, H-25, H-26), 0.99 (*virt. dt*, *J* = 13.7, 2.5, 2.5 Hz, 1H, H-16b), 0.97 (*s*, 3H, H-23), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.80 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.6 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.6 (C-11), 170.6 (C-31), 165.9 (C13), 130.3 (C-12), 73.3 (C-3), 65.5 (C-24), 61.4 (C-9), 59.0 (C-18), 50.3 (C-5), 45.2 (C-8), 43.6 (C-14), 42.2 (C-4), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 36.7 (C-10), 34.3 (C-1), 33.9 (C-17), 33.1 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 22.7 (C-2), 21.8 (C-23), 21.3 (C-30), 21.1 (C-32), 20.6 (C-27), 18.4 (C-26), 17.7 (C-6), 17.4 (C-29), 16.8 (C-25) ppm; MS (ESI, MeOH): *m/z* = 499.6 ($[M+H]^+$); analysis calcd for $C_{32}H_{50}O_4$ (498.74): C 77.06, H 10.10; found: C 76.87, H 10.31.

(3α, 4β) 3-Acetoxy-11-oxo-urs-12-en-24-al (11)
To a solution of **10** (900 mg, 1.81 mmol) in dry DCM (20 mL) PCC (977 mg, 4.53 mmol) was added, and stirring at 25 °C was continued for 5 h. Usual aq. work-up, extraction with DCM followed by chromatography (silica gel, hexanes/ethyl acetate, 9:1) gave **11** (280 mg, 31%) as a white solid; m.p. 147 °C; $[\alpha]_D$ = 49.2° (*c* = 4.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (*s*, 1H, H-24), 5.54 (*s*, 1H, H-12), 5.31 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 2.51 (*ddd*, *J* = 13.3, 3.3, 3.7 Hz, 1H, H-1b), 2.43 (*s*, 1H, H-9), 2.09 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 2.07 (*s*, 3H, H-32), 1.88 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.78 (*m*, 2H, H-6), 1.72 (*m*, 1H, H-7a), 1.63 (*m*, 2H, H-2), 1.53 (*dd*, *J* = 10.8, 1.7 Hz, 1H, H-18), 1.51 (*dd*, *J* = 2.9, 9.1 Hz, 1H, H-5), 1.49 (*m*, 1H, H-7b), 1.47 (*m*, 1H, H-22b), 1.40 (*m*, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.35 (*s*, 3H, H-27), 1.25 (*m*, 1H, H-22a), 1.20 (*m*, 1H, H-1a, 1H, H-15b), 1.17 (*s*, 3H, H-26), 1.06 (*s*, 3H, H-25), 1.00 (*s*, 3H, H-23), 0.99 (*m*, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.4 (C-24), 199.1 (C-11), 170.2 (C-31), 165.0 (C-13), 130.4 (C-12), 72.1 (C-3), 59.8 (C-9), 59.0 (C-18), 51.2 (C-4), 50.6 (C-5), 45.0 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.0 (C-10), 34.0 (C-1), 33.9 (C 17), 32.9 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.1 (C-2), 21.3 (C-30), 21.1 (C-32), 20.6 (C-27), 19.3 (C-23), 18.6 (C-26), 17.4 (C-29), 17.0 (C-6), 14.6 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 497.5 ($[M+H]^+$); analysis calcd for $C_{32}H_{48}O_4$ (496.72): C 77.38, H 9.74; found: C 77.12, H 9.89.

(3α, 4β) 3-Acetoxy-24-hydroximino-urs-12-en-11-one (12)
A solution of **11** (200 mg, 0.4 mmol) and hydroxylammonium chloride (157 mg, 2.0 mmol) in dry pyridine (5 mL) was stirred for 3 h at 50 °C; the solvents were removed under diminished pressure, and the residue subjected to chromatography (silica gel, hexane/ethyl acetate, 8:2) to afford **12** (160 mg, 78%) as a white solid; m.p. 204 °C; $[\alpha]_D$ = 40.4° (*c* = 3.60, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (*s*, 1H, H-24), 5.53 (*s*, 1H, H-12), 5.30 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 2.52 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz 1H, H-1b), 2.42 (*s*, 1H, H-9), 2.10 (*m*, 1H, H-2a, 1H, H-16a), 2.07 (*s*, 3H, H-32), 1.87 (*ddd*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.72 (*virt. dt*, *J* = 12.9, 3.7, 12.9 Hz, 1H, H-7a), 1.58 (*m*, 1H, H-6a), 1.55 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.2, 1.7 Hz, 1H, H-18), 1.48 (*m*, 1H, H-6b, 1H, H-22b), 1.44 (*m*, 1H, H-7b, 1H, H-21a), 1.38 (*m*, 1H, H-19), 1.37 (*dd*, *J* = 2.5, 9.5 Hz, 1H, H-5), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.26 (*m*, 1H, H-21b), 1.19 (*m*, 1H, H-1a), 1.17 (*m*, 1H, H-15b), 1.16

(*s*, 3H, H-26), 1.09 (*s*, 3H, H-25), 1.02 (*s*, 3H, H-23), 0.97 (*m*, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.80 (*s*, 3H, H-28), 0.78 (*d*, *J* = 6.6 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.3 (C-11), 170.3 (C-31), 164.8 (C-13), 154.5 (C-24), 130.4 (C-12), 73.4 (C-3), 60.2 (C-9), 59.0 (C-18), 50.2 (C-5), 45.0 (C-8), 43.7 (C-14), 42.0 (C-4), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.0 (C-10), 34.1 (C-1), 33.9 (C-17), 32.5 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C15), 23.9 (C-23), 22.7 (C-2), 21.3 (C-30), 21.1 (C-32), 20.6 (C-27), 18.6 (C-26), 17.4 (C-29), 17.0 (C-6), 15.0 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 512.3 ($[M+H]^+$); analysis calcd for $C_{32}H_{49}NO_4$ (511.74): C 75.11, H 9.65, N 2.74; found: C 74.91, H 9.84, N 2.53.

(3α, 4β) 3-Acetoxy-4-methylamino-urs-12-en-11-one (13)

To a solution of **12** (110 mg, 0.22 mmol) and ammonium acetate (172 mg, 2.2 mmol) in dry methanol (10 mL) containing sodium cyanoborohydride (420 mg, 6.6 mmol), $TiCl_3$ (solution, 12% in aqu. HCl, 1.39 mL, 1.67 mmol) was added, and stirring at 25 °C was continued overnight. Usual workup (2 N NaOH) followed by extraction with DCM and chromatography (silica gel, DCM/MeOH/aq. NH_3, 95:5:1) gave **13** (106 mg, 96%) as a white amorphous solid; $[\alpha]_D$ = +50.3° (*c* = 4.58, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.04 (*dd*, *J* = 2.4, 2.9 Hz, 1H, H-3), 2.85 (*d*, *J* = 13.7 Hz, 1H, , H-24), 2.63 (*d*, *J* = 13.7 Hz, 1H, H-24), 2.53 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.42 (*s*, 1H, H-9), 2.08 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 2.06 (*s*, 3H, H-32), 1.90 (*m*, 1H, H-2a), 1.85 (*m*, 1H, H-15a), 1.68 (*virt. dt*, 1H, *J* = 12.5 Hz, 4.6 Hz, 12.5 Hz, H-7a), 1.60 (*m*, 1H, H-2b), 1.56 (*m*, 2H, H-6), 1.52 (*d*, *J* = 11.2 Hz, 1H, H-18), 1.40 (*m*, 2H, H-22), 1.39 (*m*, 1H, H-19), 1.37 (*m*, 2H, H-21), 1.34 (*m*, 1H, H-7b), 1.33 (*s*, 3H, H-27), 1.27 (*m*, 1H, H-1a), 1.20 (*m*, 1H, H-5), 1.18 (*m*, 1H, H-15b), 1.16 (*s*, 3H, H-25), 1.14 (*s*, 3H, H-26), 0.99 (*virt. dt*, *J* = 15.4, 2.5, 2.5 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.90 (*s*, 3H, H-23), 0.88 (*m*, 1H, H-20), 0.80 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.6 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.6 (C-11), 170.7 (C-31), 164.8 (C-13), 130.4 (C-12), 73.6 (C-3), 61.6 (C-9), 59.0 (C-18), 50.7 (C-5), 45.3 (C-24), 45.2 (C-8), 43.6 (C-14), 41.4 (C-4), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 36.8 (C-10), 34.3 (C-1), 33.9 (C-17), 33.0 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 22.5 (C-2), 22.1 (C-23), 21.4 (C-30), 21.1 (C-32), 20.6 (C-27), 18.4 (C-26), 17.5 (C-6), 17.4 (C-29), 16.9 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 498.4 ($[M+H]^+$); analysis calcd for $C_{32}H_{51}NO_3$ (497.75): C 77.22, H 10.33 N 2.81; found: C 77.03, H 10.54, N 2.56.

3-*O*-Acetyl-11-keto-β-boswellic acid methyl ester (14)

Following the procedure as described for the synthesis of **26** (*vide infr*a), compound **14** was obtained in 95% yield as a colorless solid; m.p. 181-184 °C (lit.: 203-204 °C [6], $[\alpha]_D$ = +73.0° (*c* = 4.2, $CHCl_3$) (Lit.: +51.7° (*c* = 3.8, $CHCl_3$) [6] ;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (*s*, 1H, H-12), 5.30 (*dd*, 1H, *J* = 2.7, 3.0 Hz, H-3), 3.65 (*s*, 3H, H-33)), 2.50 (*ddd*, *J* = 13.4, 2.8, 4.4 Hz, 1H, H-1b), 2.38 (*s*, 1H, H-9), 2.18 (*dddd*, *J* = 15.5, 2.7, 4.4, 14.2 Hz, 1H, H-2a), 2.07 (*ddd*, 1H, *J* = 15.0, 4.4, 14.7 Hz, H-16a), 2.05 (*s*, 3H, H-32)), 1.87 (*ddd*, 1H, *J* = 13.0, 5.2, 14.7 Hz, H-15a), 1.80 (*dddd*, 1H, *J* = 14.2, 4.2 12.6, 13.6 Hz, H-6a), 1.72 (*dddd*, 1H, *J* = 14.2, 2.0, 3.6, 4.3 Hz, H-6b), 1.65 (*ddd*, 1H, *J* = 12.2, 3.6, 13.6 Hz, H-7a), 1.58 (*dddd*, 1H, *J* = 15.5, 2.8, 3.0, 3.1 Hz, H-2b), 1.51 (*dd*, 1H, *J* = 11.6, 2.2 Hz, H-18), 1.46 (*ddd*, 1H, *J* = 14.3, 0.4, 4.5 Hz, H-22b), 1.44 (*ddd*, 1H, *J* = 12.2, 4.2, 4.3 Hz, H-7b), 1.42 (*dddd*, 1H, *J* = 14.5, 0.4, 10.7, 13.8 Hz, H-21a), 1,41 (*ddd*, 1H, *J* = 7.9, 9.8, 11.6 Hz, H-19), 1.36 (*dd*, 1H, *J* = 2.0, 12.6 Hz, H-5), 1.33 (*s*, 3H, H-27), 1.30 (*dddd*, 1H, *J* = 14.5, 1.0, 4.5, 7.0 Hz, H-21b), 1.28 (*ddddd*, 1H, *J* = 14.3, 7.0, 10.7, 2.2, 3.9 Hz, H-22a), 1.21 (*ddd*, 1H, *J* = 13.0, 1.8, 4.4 Hz, H-15b), 1.18 (*ddd*, 1H, *J* = 13.4, 3.1, 14.2 Hz, H-1a), 1.15 (*s*, 3H, H-26), 1.15 (*s*, 3H, H-23), 1.01 (*s*, 3H, H-25), 0.99 (*dddd*, 1H, *J* = 15.0, 1.8, 5.2, 3.9 Hz, H-16b), 0.92 (*d*, 3H, *J* = 3.7 Hz, H-30), 0.92 (*dddd*, 1H, *J* = 1.0, 3.7, 9.8, 13.8 Hz, H-20), 0.80 (*s*, 3H, H-28), 0.77 (*d*, 3H, *J* = 7.9 Hz, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 176.1 (C-24), 170.2 (C-31), 164.8 (C-13), 130.5 (C-12), 73.3 (C-3), 60.2 (C-9), 59.0 (C-18), 51.5 (C-33), 50.4 (C-5), 46.6 (C-4), 45.0 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.1 (C-10), 34.6 (C-1), 33.9 (C-17), 32.8 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.8 (C-23), 23.6 (C-2), 21.3 (C-30), 21.1 (C-32), 20.5 (C-27), 18.7 (C-6), 18.3 (C-26), 17.4 (C-29), 13.1 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 527.5 ($[M+H]^+$) ; analysis calcd for $C_{33}H_{50}O_5$ (526.75) : C 75.25, H 9.57; found : C 75.03, H 9.69.

3-*O*-Acetyl-11-keto-β-boswellic acid ethyl ester (15) and 3-*O*-acetyl-11-keto-β-boswellic acid-*N*, *N´*-diisopropylcarbaminimidanhydride (16)

To a solution of **4** (200 mg, 0.4 mmol) in dry DCM (15 mL), DIC (76 mg, 0.6 mmol), DMAP (50 mg, 0.4 mmol) and dry ethanol (1.5 mL) were added. After stirring for 12 h at 25 °C, the solvents were removed under diminished pressure, and the residue subjected to chromatography (silica gel, hexane/ethyl acetate, 95:5) to yield **15** (150 mg, 69%) as a white solid; m.p. 211-214 °C; $[\alpha]_D$ = +71.0° (*c* = 5.32, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.31 (*dd*, 1H, H-3, *J* = 2.4, 2.7 Hz), 4.12 (*m*, 2H, H-33), 2.51 (*virt. dt*, *J* = 13.4 Hz, 3.4, 3.4 Hz, 1H, H-1b), 2.39 (*s*, 1H, H-9), 2.19 (*m*, 1H, H-2a), 2.07 (*virt. dt*, *J* = 13.7, 4.9, 13.7 Hz, 1H, H-16a), 2.06 (*s*, 3H, H-32), 1.87 (*virt. dt*, *J* = 13.4, 4.9, 13.4 Hz, 1H,

H-15a), 1.84 (*m*, 1H, H-6a), 1.73 (*m*, 1H, H-6b), 1.65 (*virt. dt*, *J* = 12.8 Hz, 4.0, 12.8 Hz, 1H, H-7a), 1.59 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.0 Hz, 1.2 Hz, 1H, H-18), 1.47 (*m*, 1H, H-22b), 1.42 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.36 (*dd*, *J* = 2.1, 12.2 Hz, 1H, H-5), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.26 (*t*, *J* = 7.0 Hz, 3H, H-34), 1.20 (*virt. dt*, *J* = 13.4 Hz, 4.0, 13.4,1H, H-15b), 1.18 (*m*, 1H, H-1a), 1.16 (*s*, 6H, H-23, H-26), 1.05 (*s*, 3H, H-25), 0.99 (*virt. dt*, *J* = 13.4, 2.4, 2.4 Hz, 1H, H-16b), 0.94 (*m*, 1H, H-20), 0.93 (*s*, 3H, H-30), 0.80 (*s*, 3H, H-28), 0.78 (*d*, *J* = 6.4 Hz, H, H-29) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.3 (C-11), 175.5 (C-24), 170.2 (C-31), 164.8 (C-13), 130.5 (C-12), 73.3 (C-3), 60.6 (C-33), 60.3 (C-9), 59.0 (C-18), 50.5 (C-5), 46.6 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.3 (C-10), 34.7 (C-1), 34.0 (C-17), 32.9 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.7 (C-2), 21.3 (C-32), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 14.0 (C-34),13.4 (C-25) ppm;

MS (ESI, MeOH): *m/z* = 541.4 ($[M+H]^+$); analysis calcd for $C_{34}H_{52}O_5$ (540.77): C 75.51, H 9.69; found: C 75.43, H 9.80.

Data for **16**: yield: 18 mg (7%), amorphous, white solid; $[\alpha]_D$ = -23.5° (*c* = 6.32, $CHCl_3$);

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.70 (*br s*, 1H, N*H*), 5.53 (*s*, 1H, H-12), 5.48 (*br s*, 1H, H-3), 4.07 (*m*, 1H, H-34), 3.74 (*m*, 1H, H-37), 2.50 (*ddd*, *J* = 13.3, 2.9, 3.3 Hz, 1H, H-1b), 2.39 (*s*, 1H, H-9), 2.18 (*m*, 1H, H-2a), 2.11 (*virt. dt*, *J* = 13.7, 4.6, 13.7 Hz, 1H, H-16a), 2.04 (*s*, 3H, H-32), 1.87 (*virt. dt*, *J* = 13.7, 4.6, 13.7 Hz, 1H, H-15a), 1.80 (*m*, 2H, H-6), 1.70 (*m*, 1H, H-7a), 1.58 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.6, 1.7 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.46 (*m*, 2H, H-21), 1.44 (*m*, 1H, H-7b), 1.41 (*s*, 3H, H-27), 1.39 (*m*, 1H, H-19), 1.34 (*dd*, *J* = 2.9, 12.5 Hz, 1H, H-5), 1.30 (*d*, *J* = 7.9 Hz, 12H, H-35, H-36, H-38, H-39)), 1.29 (*m*, 1H, H-22a), 1.22 (*m*, 1H, H-15b), 1.19 (*m*, 1H, H-1a), 1.18 (*s*, 6H, H-23, H-26), 1.08 (*s*, 3H, H-25), 0.99 (*virt. dt*, *J* = 13.7, 3.3, 3.7 Hz, 1H, H-16b), 0.94 (*m*, 1H, H-20), 0.93 (*s*, 3H, H-30), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0 (C-11), 174.0 (C-24), 170.2 (C-31), 164.6 (C-13), 154.8 (C-33), 130.6 (C-12), 73.6 (C-3), 60.4 (C-9), 59.0 (C-18), 53.5 (C-34), 50.4 (C-5), 48.1 (C-37), 46.5 (C-4), 45.0 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.5 (C-10), 34.8 (C-1), 34.0 (C-17), 32.9 (C-7), 30.9 (C-21), 28.9 (C-38 and C-39), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 24.9 (C-35 and C-36), 24.0 (C-23), 23.8 (C-2), 21.3 (C-30), 21.1 (C-32), 20.5 (C-27), 19.5 (C-6), 18.3 (C-26), 17.4 (C-29), 13.6 (C-25) ppm;

MS (ESI, MeOH): *m/z* = 639.3 ($[M+H]^+$); analysis calcd for $C_{39}H_{62}N_2O_5$ (638.78): C 73.31, H 9.78, N 4.38; found: C 73.09, H 9.98, N 4.11.

11-Keto-β-boswellic acid ethyl ester (17)

Zemplén deacetylation of **15** (270 mg, 0.5 mmol) in EtOH (10 mL) and cat. NaOEt followed by usual workup and chromatography (silica gel, hexane/ethyl acetate, 95:5), gave **17** (224 mg, 90%) as a white solid; m.p. 230-233°C; $[\alpha]_D$ = +116.9° (*c* = 4.4, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (*s*, 1H, H-12), 4.10 (*m*, 1H, H-3, 2H, H-31), 2.47 (*ddd*, *J* = 13.7, 3.3, 3.7 Hz, 1H, H-1b), 2.40 (*s*, 1H, H-9), 2.27 (*m*, 1H, H-2a), 2.07 (*virt. dt*, *J* = 13.7, *J* = 5.0, 13.7 Hz, 1H, H-16a), 1.87 (*virt. dt*, *J* = 13.7, 4.6 Hz, 13.7 Hz, 1H, H-15a), 1.82 (*m*, 1H, H-6a), 1.72 (*m*, 1H, H-6b), 1.64 (*virt. dt*, *J* = 13.3, 4.2, 13.3 Hz, 1H, H-7a), 1.54 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 1.2, 11.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.47 (*dd*, *J* = 12.0, 2.1 Hz, 1H, H-5), 1.42 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.32 (*m*, 1H, H-1a), 1.29 (*s*, 3H, H-27), 1.28 (*m*, 1H, H-22a), 1.27 (*s*, 3H, H-23), 1.26 (*t*, *J* = 7.3 Hz, 3H, H-32), 1.20 (*m*, 1H, H-15b), 1.15 (*s*, 3H, H-26), 1.04 (*s*, 3H, H-25), 0.99 (*ddd*, *J* = 13.7, 2.1, 2.9 Hz, 1H, H-16b), 0.92 (*s*, 3H, H-30), 0.90 (*m*, 1H, H-20), 0.80 (*s*, 3H, H-28), 0.78 (*d*, *J* = 6.6 Hz 3H, H-29) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.5 (C-11), 176.7 (C-24), 164.9 (C-13), 130.5 (C-12), 70.7 (C-3), 60.4 (C-9), 60.2 (C-31) 59.0 (C-18), 48.8 (C-5), 47.3 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.4 (C-10), 34.0 (C-1), 33.9 (C-17), 32.9 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 26.3 (C-2), 24.3 (C-23), 21.1 (C-30), 20.5 (C-27), 18.9 (C-6), 18.3 (C-26), 17.4 (C-29), 14.0 (C-32) 13.1 (C-25) ppm;

MS (ESI, MeOH): *m/z* = 499.5 ($[M+H]^+$); analysis calcd for $C_{32}H_{50}O_4$ (498.74): C 77.06, H 10.10; found: C 76.80, H 10.34.

3-*O*-Acetyl-11-keto-β-boswellic acid propyl ester (18)

Following the procedure given for the synthesis of **15**, from **4** (150 mg, 0.3 mmol), DIC (57 mg, 0.45 mmol) und DMAP (45 mg, 0.37 mmol) in dry DCM and *n*-propanol (1 mL) followed by chromatography (silica gel, hexane/ethyl acetate, 95:5), **18** (115 mg, 69%) was obtained as a white amorphous solid; $[\alpha]_D$ = +75.5° (*c* = 4.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.48 (*s*, 1H, H-12), 5.27 (*virt. t*, *J* = 2.7, 2.7 Hz, 1H, H-3), 4.00 (*m*, 1H, H-33), 3.93 (*m*, 1H, H-33), 2.46 (*ddd*, *J* = 13.3, 3.0, 3.2 Hz, 1H, H-1b), 2.35 (*s*, 1H, H-9), 2.15 (*m*, 1H, H-2a), 2.03 (*virt. dt*, *J* = 13.6, 5.0, 13.6 Hz, 1H, H-16a), 2.02 (*s*, 3H, H-32), 1.83 (*virt. dt*, *J* = 13.6, 5.0, 13.6 Hz, 1H, H-15a), 1.78 (*m*, 1H, H-6b), 1.70 (*m*, 1H, H-6a), 1.62 (*m*, 2H, H-34), 1.60 (*m*, 1H, H-7a), 1.54 (*m*, 1H, H-2b), 1.48 (*d*, *J* = 10.9 Hz, 1H, H-18), 1.45 (*m*, 1H, H-22b), 1.41 (*m*, 1H, H-7b, 2H, H-21), 1.36 (*m*, 1H, H-19), 1.32 (*dd*, *J* = 1.6, 12.4 Hz, 1H, H-5), 1.28 (*s*, 3H, H-27), 1.25 (*m*, 1H, H-22a), 1.18 (*m*, 1H, H-1a and 1H, H-15b), 1.12 (*s*, 6H, 2 H-23, H-26), 1.00 (*s*, 3H, H-25), 0.95 (*ddd*, *J* = 13.6, 2.0, 2.5 Hz, 1H, H-16b), 0.91 (*t*, *J* = 7.4 Hz, 3H, H-35), 0.89 (*m*, 1H,

H-20), 0.88 (*s*, 3H, H-30), 0.76 (*s*, 3H, H-28), 0.74 (*d*, *J* = 6.4 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 175.6 (C-24), 170.2 (C-31), 164.8 (C-13), 130.5 (C-12), 73.3 (C-3), 66.3 (C33), 60.2 (C-9), 59.0 (C-18), 50.4 (C-5), 46.7 (C-4), 45.0 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.2 (C-10), 34.6 (C-1), 33.9 (C-17), 32.8 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.6 (C-2), 21.7 (C-34), 21.3 (C-30), 21.1 (C-32), 20.5 (C-27), 18.7 (C-6), 18.3 (C-26), 17.4 (C-29), 13.1 (C-25), 10.7 (C-35) ppm;
MS (ESI, MeOH): *m/z* = 555.5 ([M+H]$^+$); analysis calcd for $C_{35}H_{54}O_5$ (554.80): C 75.77, H 9.81; found: C 75.46, H 9.99.

3-*O*-Acetyl-11-keto-β-boswellic acid butyl ester (19)
Following the procedure given for the synthesis of **15**, from **4** (150 mg, 0.3 mmol), DIC (57 mg, 0.45 mmol), DMAP (45 mg, 0.37 mmol) and *n*-butanol (1 mL) followed by chromatography (silica gel, hexane/ethyl acetate, 98:2), **19** (150 mg, 87%) was obtained as a white, amorphous solid; $[\alpha]_D$ = +68.9° (*c* = 3.88, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.31 (*dd*, *J* = 2.4, 2.7 Hz, 1H, H-3), 4.10 (*m*, 1H, H-33), 4.02 (*m*, 1H, H-33), 2.51 (*virt. dt*, *J* = 13.1, 3.4, 3.4 Hz, 1H, H-1b), 2.39 (*s*, 1H, H-9), 2.20 (*m*, 1H, H-2a), 2.08 (*virt. dt*, *J* = 13.7, 4.9, 13.7 Hz, 1H, H-16a), 2.06 (*s*, 3H, H-32), 1.88 (*ddd*, *J* = 13.4, 4.9, 13.4 Hz, 1H, H-15a), 1.83 (*m*, 1H, H-6a), 1.73 (*m*, 1H, H-6b), 1.66 (*m*, 1H, H-7a), 1.62 (*m*, 2H, H-34), 1.60 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.0, 1.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.43 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.36 (*m*, 2H, H-35), 1.34 (*m*, 1H, H-5), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.20 (*m*, 1H, H-1a, 1H, H-15b), 1.17 (*s*, 3H, H-26), 1.16 (*s*, 3H, H-23), 1.05 (*s*, 3H, H-25), 0.98 (*ddd*, *J* = 13.7, 2.1, 2.7 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*t*, *J* = 7.3 Hz, 3H, H-36), 0.92 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.4 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.3 (C-11), 175.6 (C-24), 170.2 (C-31), 164.8 (C-13), 130.5 (C-12), 73.3 (C-3), 64.5 (C-33), 60.3 (C-9), 59.0 (C-18), 50.5 (C-5), 46.7 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.2 (C-10), 34.7 (C-1), 34.0 (C-17), 32.9 (C-7), 30.9 (C-21), 30.4 (C-34), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.7 (C-2), 21.3 (C-30), 21.1 (C-32), 20.5 (C-27), 19.4 (C35), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.7 (C-36), 13.3 (C-25) ppm;
MS (ESI, MeOH) *m/z* = 569.4 M+H]$^+$; analysis calcd for $C_{36}H_{56}O_5$ (568.83): C 76.01, H 9.92; found: C 75.80, H 10.03.

11-Keto-β-boswellic acid butyl ester (20)
Zemplen deacetylation of **19** (100 mg, 0.18 mmol) in *n*-butanol (3.0 mL) with catal. amounts of sodium butanolate as described above gave **20** (79 mg, 86%) as a white solid; m.p. 185-188 °C; $[\alpha]_D$ = +98.1° (*c* = 4.24, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (*s*, 1H, H-12), 4.07 (*dd*, *J* = 2.5, 2.5 Hz, 1H, H-3), 4.05 (*m*, 1H, H-31), 3.99 (*m*, 1H, H-31), 2.47 (*ddd*, *J* = 13.3, 2.9, 4.1 Hz, 1H, H-1b), 2.40 (*s*, 1H, H-9), 2.26 (*m*, 1H, H-2a), 2.07 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.86 (*virt. dt*, *J* = 13.7, 5.4, 13.7 Hz 1H, H-15a), 1.81 (*m*, 1H, H-6a), 1.72 (*m*, 1H, H-6b), 1.64 (*m*, 1H, H-7a), 1.62 (*m*, 2H, H-32), 1.58 (*m*, 1H, H-2b), 1.52 (*m*, 1H, H-18), 1.46 (*m*, 1H, H-22b), 1.44 (*m*, 1H, H-5, and 1H, H-7a, and 2H, H-21), 1.42 (*m*, 2H, H-33), 1.39 (*m*, 1H, H-19), 1.30 (*m*, 1H, H-1a), 1.29 (*s*, 3H, H-27), 1.28 (*m*, 1H, H-22a), 1.26 (*s*, 3H, H-23), 1.19 (*ddd*, *J* = 13.7, 2.1, 2.9 Hz, 1H, H-15b), 1.15 (*s*, 3H, H-26), 1.03 (*s*, 3H, H-25), 0.98 (*ddd*, *J* = 13.7, 2.1, 2.9 Hz, 1H, H-16b), 0.94 (*m*, 1H, H-20), 0.93 (*s*, 3H, H-30), 0.92 (*t*, *J* = 7.5 Hz, 3H, H-34), 0.79 (*s*, 3H, H-28), 0.77 (*d*, *J* = 6.6 Hz 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.5 (C-11), 176.8 (C-24), 164.9 (C-13), 130.5 (C-12), 70.7 (C-3), 64.1 (C-31), 60.4 (C-9), 59.0 (C-18), 48.8 (C-5), 47.4 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.4 (C-10), 34.8 (C-17), 34.0 (C-1), 32.9 (C-7), 30.9 (C-21), 30.5 (C-32), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 26.3 (C-2), 24.3 (C-23), 21.1 (C-30), 20.5 (C-27), 19.4 (C-33), 18.9 (C-6), 18.3 (C-26), 17.4 (C-29), 13.8 (C-34), 13.6 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 527.5 ([M+H]$^+$); analysis calcd for $C_{34}H_{54}O_4$ (526.79): C 77.52, H 10.33; found: C 77.37, H 10.50.

3-*O*-Acetyl-11-keto-β-boswellic acid 2-(2-hydroxyethoxy)-ethyl ester (21)
Following the procedure as described above, from **4** (200 mg, 0.4 mmol) and thionyl chloride (1 mL) and sodium diethyleneglycolate [from diethyleneglycole (1 mL) + sodium (100 mg)] followed by chromatography (silica gel, hexane/ethyl acetate, 95:5), **21** (160 mg, 60%) was obtained as a white amorphous solid; $[\alpha]_D$ = +56.1° (*c* = 6.36, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.32 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 4.22 (*m*, 2H, H-36), 3.70 (*m*, 4H, 2 H-33, H-34), 3.57 (*m*, 2H, H-35), 2.52 (*ddd*, *J* = 13.3, 3.3, 3.7 Hz, 1H, H-1b), 2.39 (*s*, 1H, H-9), 2.20 (*m*, 1H, H-2a), 2.08 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 2.06 (*s*, 3H, H-32), 1.89 (*m*, 1H, H-6a), 1.86 (*m*, 1H, H-15a), 1.73 (*m*, 1H, H-6b), 1.66 (*m*, 1H, H-7a), 1.59 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.49 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b), 2H, H-21), 1.39 (*m*, 1H, H-19), 1.37 (*dd*, *J* = 1.7, 12.0 Hz, 1H, H-5), 1.34 (*m*, 1H, H-22a), 1.33 (*s*, 3H, H-27), 1.18 (*m*, 1H, H-1a, 1H, H-15b), 1.17 (*s*, 3H, H-23), 1.16 (*s*, 3H, H-26), 1.06 (*s*, 3H, H-25), 0.99 (*ddd*, *J* = 13.7, 2.4, 2.9 Hz, 1H, H-16b), 0.94 (*m*, 1H, H 20), 0.93 (*s*, 3H, H-30), 0.80 (*s*, 3H, H-28), 0.78 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.1 (C-11), 175.5 (C-24), 170.1 (C-31), 164.8 (C-13), 130.5 (C-12), 73.2 (C-3), 72.2 (C-35), 68.8 (C-34), 63.4 (C-36), 61.8 (C-33), 60.2 (C-9), 59.1 (C-18), 50.5 (C-5), 46.8

(C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.3 (C-10), 34.7 (C-1), 34.0 (C-17), 32.9 (C-7), 30.9 (C-21), 28.9 (C-28), 27.6 (C-16), 27.3 (C-15), 23.8 (C-23), 23.6 (C-2), 21.3 (C-30), 21.1 (C-32), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.3 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 601.4 /$[M+H]^+$); analysis calcd for $C_{36}H_{56}O_7$ (600.83): C 71.97, H 9.39; found: C 71.69, H 9.47.

3-*O*-Acetyl-11-keto-boswellic acid 4-(N-tert-butyloxycarbonylamino)]-butyl ester (22)
Following the procedure as described above, from **4** (200 mg, 0.4 mmol), thionyl chloride (1 mL) and 4-aminobutan-1-ol (356 mg, 4.0 mmol) the crude ester was prepared, followed by dissolving the residue in 1,4-dioxane (8 mL) and water (4 mL). An aq. solution of sodium hydroxide (1 N, 4 mL) and di-*tert*-butyl-dicarbonate (960 mg, 4.4 mmol) were added at 0 °C, and stirring at 25 °C was continued overnight. Usual workup followed by an extraction with ethyl acetate and chromatography (silica gel, hexane/ethyl acetate, 4:1) gave **22** (160 mg, 58%) as a white amorphous solid; $[\alpha]_D$ = +48.2° (*c* = 4.42, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.54 (*s*, 1H, H-12), 5.31 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 4.10 (*m*, 1H, H-33), 4.03 (*m*, 1H, H-33), 3.14 (*virt. d*, *J* = 6.2, 6.2 Hz, 2H, H-36), 2.52 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.40 (*s*, 1H, H-9), 2.19 (*m*, 1H, H-2a), 2.09 (*virt. dt*, *J* = 13.7, 4.6, 13.7 Hz, 1H, H-16a), 2.07 (*s*, 3H, H-32), 1.89 (*virt. dt*, *J* = 13.7, 4.6, 13.7 Hz, 1H, H-15a), 1.82 (*m*, 1H, H-6a), 1.77 (*m*, 1H, H-6b), 1.70 (*m*, 2H, H-35), 1.66 (*m*, 1H, H-7a), 1.60 (*m*, 1H, H-2b), 1.55 (*m*, 2H, H-34), 1.53 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b, 2H, H-21), 1.43 (*s*, 9H, H-39, H-40, H-41), 1.40 (*m*, 1H, H-19), 1.37 (*dd*, *J* = 2.5, 12.0 Hz, 1H, H-5), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.20 (*m*, 1H, H-1a, 1H, H-15b), 1.17 (*s*, 6H, H-23, H-26), 1.04 (*s*, 3H, H-25), 1.01 (*virt. dt*, *J* = 13.7, 2.5, 2.5 Hz, 1H, H-16b), 0.95 (*m*, 1H, H-20), 0.94 (*s*, 3H, H-30), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.6 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 175.5 (C-24), 170.1 (C-31), 164.8 (C-13), 155.9 (C-37), 130.5 (C-12), 79.5 (C-38), 73.2 (C-3), 64.3 (C-33), 60.2 (C-9), 59.0 (C-18), 50.4 (C-5), 46.7 (C-4), 45.0 (C-8), 43.7 (C-14), 40.9 (C-22), 40.0 (C36), 39.3 (C-19), 39.3 (C-20), 37.2 (C-10), 34.6 (C-1), 33.9 (C-17), 32.8 (C-7), 30.9 (C-21), 28.8 (C-28), 28.4 (C39; C-40 and C-41), 27.5 (C-16), 27.2 (C-15), 26.9 (C-34), 25.8 (C-35), 23.9 (C-23), 23.6 (C-2), 21.4 (C-30), 21.1 (C-32), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.3 (C-25) ppm;
MS (ESI, methanol): *m/z* = 706.4 ($[M+Na]^+$); analysis calcd for $C_{41}H_{65}NO_7$ (683.96): C 71.99, H 9.58, N 2.05; found: C 71.74, H 9.82, N 1.86.

3-*O*-Acetyl-11-keto-β-boswellic acid difluoromethyl ester (23)
A solution of **4** (200 mg, 0.4 mmol) in dry glyme (10 mL) was heated to 190°C, and a solution of sodium chlorodifluoroacetate (610 mg, 4.0 mmol) in dry glyme (15 mL) was slowly added within 1 h. Heating and stirring at this temperature was continued for 2 h, the mixture was cooled to room temperature and diluted with water (200 mL). Extraction with DCM (4 x 50 mL) followed by chromatography (silica gel, hexane/ethyl acetate, 95:5) gave **23** (160 mg, 71%) as a colorless solid; m.p. 135 °C; $[\alpha]_D$ = +66.7° (*c* = 4.52, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (*t*, $J_{H,F}$ = 71.2 Hz, 1H, C*H*F_2), 5.54 (*s*, 1H, H-12), 5.29 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 2.56 (*ddd*, *J* = 13.3, 2.9, 3.7 Hz, 1H, H-1b), 2.40 (*s*, 1H, H-9), 2.16 (*m*, 1H, H-2a), 2.08 (*s*, 3H, H-32), 2.07 (*m*, 1H, H-16a), 1.89 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.80 (*m*, 2H, H-6), 1.75 (*m*, 1H, H-7a), 1.65 (*m*, 1H, H-2b), 1.53 (*d*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.50 (*m*, 2H, H-7b, H-22b), 1.48 (*m*, 2H, H-21), 1.44 (*dd*, *J* = 2.1, 12.0 Hz, 1H, H-5), 1.39 (*m*, 1H, H-19), 1.33 (*s*, 3H, H-27), 1.28 (*m*, 1H, H-22a), 1.25 (*s*, 3H, H-23), 1.20 (*m*, 1H, H-1a, 1H, H-15b), 1.18 (*s*, 3H, H-26), 1.10 (*s*, 3H, H-25), 1.01 (*m*, 1H, H-16b), 0.94 (*m*, 1H, H-20), 0.93 (*s*, 3H, H-30), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.9 (C-11), 172.4 (C-24), 169.9 (C-31), 165.0 (C-13), 130.4 (C-12), 112.4 (*t*, $J_{C,F}$ = 258.2 Hz, C-33), 72.4 (C-3), 60.2 (C-9), 59.0 (C-18), 50.5 (C-5), 47.0 (C-4), 45.0 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.3 (C-10), 34.4 (C-1), 33.9 (C-17), 32.7 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.3 (C-2), 23.1 (C-23), 21.2 (C-30), 21.1 (C-32), 20.5 (C-27), 18.6 (C-6), 18.2 (C-26), 17.4 (C-29), 13.2 (C-25) ppm; ^{19}F-NMR (188 MHz, $CDCl_3$): δ = -92.7 (*d*, $J_{F,F}$ = 92 Hz, F), -92.3 (*d*, $J_{F,F}$ = 92 Hz, F) ppm;
MS (ESI, MeOH) *m/z* = 563.4 ($[M+H]^+$); analysis calcd for $C_{33}H_{48}F_2O_5$ (562.73): C 70.43, H 8.60; found: C 70.14, H 8.45.

(3α, 4β) 3-Acetyloxy-4-isocyanato-24-norurs-12-en-11-one (24)
To a solution of **AKBA** (200 mg, 0.4 mmol) in *tert*-butanol (1.5 mL) and triethylamine (60 mg, 0.6 mmol) at 70 °C under argon, diphenylphosphorylazide (260 mg, 0.96 mmol) was slowly added, and the mixture was stirred for 3 h. The solvents were evaporated under diminished pressure, and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate, 95:5 → 8:2) to yield **24** (120 mg, 59%) as a white solid; m.p. 175°C (lit.: 170-176 °C [28]); $[\alpha]_D$ = +63.8° (*c* = 5.0, $CHCl_3$), lit.: +64.7° (*c* = 5.26, $CHCl_3$) [28].
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.54 (*s*, 1H, H-12), 4.76 (*dd*, *J* = 2.5 Hz, 2.7 Hz, 1H, H-3), 2.58 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.38 (*s*, 1H, H-9), 2.08 (*m*, 1H, H-2a, 1H, H-16a), 2.07 (*s*, 3H, H-32), 1.90 (*virt. dt*, *J* = 13.5, 4.6, 13.5 H, 1H, H-15a), 1.73 (*virt. dt*, *J* = 12.5, 4.3, 12.5 Hz, 1H, H-7a), 1.65 (*m*, 1H, H-6a), 1.60 (*m*, 1H, H-2b, 1H, H-6b), 1.58 (*d*, *J* = 12.5 Hz, 1H, H-18), 1.50 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.32

(*s*, 6H, H-23, H-27), 1.30 (*s*, 3H, H-25), 1.28 (*m*, 1H, H-22a), 1.20 (*s*, 3H, H-26), 1.18 (*m*, 1H, H-1a, 1H, H-5, 1H, H-15b), 1.00 (*ddd*, *J* = 13.0, 2.5, 2.9 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.4 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.1 (C-11), 169.8 (C-31), 165.0 (C-13), 130.4 (C-12), 122.7 (C-24), 75.4 (C-3), 60.4 (C-9), 60.1 (C-4), 58.9 (C-18), 49.2 (C-5), 45.0 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 36.8 (C-10), 33.9 (C-1), 33.4 (C -17), 32.1 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 27.9 (C-23), 22.4 (C-2), 21.3 (C-30), 21.1 (C-32), 20.7 (C-27), 18.8 (C-26), 17.4 (C-29), 17.1 (C-6), 14.8 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 510.6 ($[M+H]^+$); analysis calcd for $C_{32}H_{47}NO_4$: (509.72): C 75.40, H 9.29, N 2.75; found: C 75.19, H 9.46, N 2.50.

(3α, 4β) 3-Acetyloxy-4-amino-24-norurs-12-en-11-one (25)

To a solution of **24** (obtained from **4** (400 mg, 0.8 mmol) as described above) in $CHCl_3$ (20 mL), conc. aq. hydrochloric acid (5 mL) was added, and the mixture was stirred for 5 h at 60 °C. Usual work-up followed by extraction with $CHCl_3$ (5 x 20 mL) followed by chromatography (silica gel, DCM/MeOH/aq. NH_3, 95:5:1) gave **25** (280 mg, 72%) as an off-white solid; m.p. 168-170 °C (lit.: 169-171 °C [28], $[\alpha]_D$ = +50.9° (*c* = 7.92, $CHCl_3$) lit.: +8° (*c* = 1.0, $CHCl_3$) [28].
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 4.57 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 2.54 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.41 (*s*, 1H, H-9), 2.10 (*m*, 1H, H-2a, 1H,H-16a), 2.05 (*s*, 3H, H-32), 1.88 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.72 (*virt. dt*, *J* = 12.5, 5.0, 12.5 Hz, 1H, H-7a), 1.58 (*m*, 2H, H-6), 1.54 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.48 (*m*,1H, H-22b), 1.45 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.33 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.28 (*s*, 3H, H-23), 1.22 (*m*, 1H, H-1a, 1H, H-15b), 1.18 (*s*, 3H, H-25), 1.17 (*s*, 3H, H-26), 1.14 (*dd*, *J* = 2.9,11.2 Hz, 1H, H-5), 0.99 (*virt. dt*, *J* = 14.1, 2.1, 2.1 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.80 (*s*, 3H, H-28), 0.79 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.6 (C-11), 170.3 (C-31), 164.9 (C-13), 130.4 (C-12), 78.3 (C-3), 61.0 (C-9), 59.0 (C-18), 53.7 (C-4), 49.1 (C-5), 45.2 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 36.7 (C-10), 34.0 (C-1), 33.9 (C-17), 32.4 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 22.0 (C-2), 21.4 (C-30), 21.1 (C-32), 20.7 (C-27), 18.6 (C-26), 17.4 (C-29), 16.8 (C-6), 16.0 (C-23), 15.2 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 470.4 ($[M+H]^+$); analysis calcd for $C_{31}H_{51}NO_2$: (469.74): C 79.26, H 10.94, N 2.98; found: C 79.01, H 11.14, N 2.69.

11-Keto-β-boswellic acid methyl ester (26)

A suspension of **KBA** (4.73 g, 10.0 mmol) and Cs_2CO_3 (9.8 g, 30 mmol) in THF (50 mL) was stirred at 0 °C for 30 min, then MeI (6.23 mL, 100 mmol) was added, and stirring continued for 12 h. The mixture was diluted with ether (500 mL), washed with water and brine (2 x 50 mL each), dried (Na_2SO_4), and the solvents were evaporated to yield **26** (4.60 g, 95%) as an off-white solid (sufficiently pure for the next reactions); an analytical sample showed m.p. 223-225 °C (lit.: 220-225 °C [29], $[\alpha]_D$ = +111.2° (*c* = 4.34, $CHCl_3$) (lit.: +111.2 (*c* = 4.34, $CHCl_3$) [29].

3-O-Methyl-11-keto-β-boswellic acid methyl ester (27)

A suspension of **26** (300 mg, 0.62 mmol) and sodium hydride (60%; dispersion in mineral oil; 248 mg, 6.2 mmol) in dry THF (20 mL) was heated under reflux for 15 min. The mixture was cooled to 25 °C, and methyl iodide (390 µl, 6.2 mmol) was added. After stirring overnight, usual workup and chromatography (silica gel, chloroform) **27** (280 mg, 91%) was obtained as a colorless solid; m.p. 243-244 °C; $[\alpha]_D$ = +104.2° (*c* = 4.60, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (*s*, 1H, H-12), 3.63 (*s*, 3H, H-31), 3.47 (*virt. t*, *J* = 2.5, 2.5 Hz, 1H, H-3), 3.29 (*s*, 3H, H-32), 2.39 (*virt. dt*, *J* = 12.9, 3.3, 3.3 Hz, 1H, H-1b), 2.38 (*s*, 1H, H-9), 2.06 (*ddd*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.96 (*m*, 1H, H-2a), 1.85 (*ddd*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.76 (*m*, 1H, H-6a), 1.72 (*m*, 1H, H-2b, 1H, H-6b), 1.64 (*ddd*, *J* = 12.9, 3.7 Hz, 12.9 Hz, 1H, H-7a), 1.50 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.46 (*m*, 1H, H-22b), 1.42 (*m*, 2H, H-21), 1.40 (*m*, 1H, H-7b), 1.39 (*m*, 1H, H-19), 1.38 (*m*, *J* = 2.1, 12.0 Hz, 1H, H-5), 1.30 (*m*, 1H, H-22a), 1.28 (*s*, 3H, H-27), 1.22 (*s*, 3H, H-23), 1.20 (*m*, 1H, H-1a), 1.18 (*m*, 1H, H-15b), 1.14 (*s*, 3H, H-26), 1.00 (*s*, 3H, H-25), 0.98 (*m*, 1H, H-16b), 0.93 (*m*, 1H, H-20), 0.91 (*s*, 3H, H-30), 0.79 (*s*, 3H, H-28), 0.76 (*d*, *J* = 6.6 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.6 (C-11), 177.5 (C-24), 164.8 (C-13), 130.5 (C-12), 80.1 (C-3), 60.3 (C-9), 59.0 (C-18), 57.0 (C-32), 51.2 (C-31), 49.5 (C-5), 47.8 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19 and C-20), 37.2 (C-10), 34.2 (C-17), 34.0 (C-1), 32.8 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 24.0 (C-23), 21.1 (C-30), 20.7 (C-2), 20.6 (C-27), 18.9 (C-6), 18.3 (C-26), 17.4 (C-29), 13.2 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 499.5 $M+H]^+$; analysis calcd for $C_{32}H_{50}O_4$: (498.74): C 77.06, H 10.10; found: C 76.83, H 10.24.

3-*O*-*tert*-Butyl-11-keto-β-boswellic acid methyl ester (28)

To a solution of **26** (388 mg, 0.8 mmol) in dry DCM (20 mL), magnesium perchlorate (605 mg, 2.8 mmol) and di-*tert*-butyl-dicarbonate (2.5 g, 11.7 mmol) were added within 2 days. After an additional stirring for one day at 25 °C, aq. hydrochloric acid (1%, 20 mL) was added, the organic layer was separated, the aq. phase was extracted with DCM (3 x 30 mL), and the combined organic phases were dried ($MgSO_4$).

The solvent was evaporated under diminished pressure, and the residue was subjected to chromatography (silica gel, chloroform) to yield **28** (370 mg, 86%) as an oil; $[\alpha]_D$ = +102.0° (*c* = 4.60, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (*s*, 1H, H-12), 3.83 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 3.61 (*s*, 3H, H-31), 2.38 (*s*, 1H, H-9), 2.33 (*virt. dt*, *J* = 12.9, 3.3, 3.3 Hz, 1H, H-1b), 2.06 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.98 (*m*, 1H, H-2a), 1.85 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.76 (*m*, 1H, H-6a), 1.68 (*m*, 1H, H-2b, 1H, H-6b), 1.64 (*m*, 1H, H-7a), 1.49 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.46 (*m*, 1H, H-22b), 1.44 (*m*, 2H, H-21), 1.42 (*m*, 1H, H-1a), 1.41 (*dd*, *J* = 2.1, 12.9 Hz, 1H, H-5), 1.39 (*m*, 1H, H-19), 1.36 (*m*, 1H, H-7b), 1.30 (*s*, 3H, H-27), 1.28 (*m*, 1H, H-22a), 1.18 (*m*, 1H, H-15b), 1.15 (*s*, 15H, H-23, H-26, H-33, H-34, H-35), 0.98 (*s*, 3H, H-25), 0.97 (*m*, 1H, H-16b), 0.92 (*m*, 1H, H-20), 0.91 (*s*, 3H, H-30), 0.79 (*s*, 3H, H-28), 0.78 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.7 (C-11), 178.1 (C-24), 164.5 (C-13), 130.6 (C-12), 69.9 (C-3), 60.5 (C-9), 59.0 (C-18), 51.0 (C-31), 48.9 (C-5), 48.1 (C-4), 45.0 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C19 and C-20), 37.2 (C-10), 34.4 (C-1), 33.9 (C-17), 33.0 (C-7), 30.9 (C-21), 29.0 (C-33, C-24 and C-35), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 25.6 (C-2), 24.8 (C-23), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.4 (C-26), 17.4 (C-29), 13.4 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 541.4 ($[M+H]^+$); analysis calcd for $C_{35}H_{56}O_4$: (540.82): C 77.73, H 10.44; found: C 77.51, H 10.67.

3-*O*-Octanoyl-11-keto-β-boswellic acid methyl ester (29)
To a solution of **26** (194 mg, 0.4 mmol) and DMAP (98 mg, 0.8 mmol) in dry pyridine (10 mL) and dry DCM (10 mL), at 0 °C capryloyl chloride (650 mg, 452 µl, 4.0 mmol) was slowly added. The mixture was allowed to warm to 25 °C, and stirring was continued overnight. After usual workup and chromatography (silica gel, hexane/ethyl acetate, 8:2) **29** (240 mg, 98%) was obtained as an off-white, amorphous solid; $[\alpha]_D$ = +48.5° (*c* = 5.26. $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.30 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 3.66 (*s*, 1H, H-39), 2.51 (*virt. dt*, 1H, *J* = 13.3, 3.3, 3.3 Hz, H-1b), 2.38 (*s*, 1H, H-9), 2.30 (*ddd*, *J* = 7.5, 9.1, 1.7 Hz, 2H, H-32), 2.18 (*m*, 1H, H-2a), 2.08 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.88 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.82 (*m*, 1H, H-6a), 1.75 (*m*, 1H, H-6b), 1.62 (*m*, 2H, H-33)), 1.60 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.45 (*m*, 2H, H-7), 2H, H-21), 1.39 (*m*, 1H, H-19), 1.37 (*dd*, *J* = 2.5, 12.0 Hz, 1H, H-5), 1.32 (*s*, 3H, H-27), 1.30 (*m*, 1H, H-22a), 1.28 (*m*, 4H, H-34, H-35)), 1.26 (*m*, 2H, H-37), 1.24 (*m*, 2H, H-36), 1.16 (*s*, 3H, H-23), 1.15 (*s*, 3H, H-26), 1.18 (*m*, 1H, H-1a, 1H, H-15b), 1.02 (*s*, 3H, H-25), 1.00 (*m*, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.92 (*m*, 1H, H-20), 0.85 (*t*, *J* = 6.8 Hz, 3H, H-38), 0.80 (*s*, 3H, H-28), 0.78 (*dd*, *J* = 6.6 Hz, 1H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 176.1 (C-24), 172.8 (C-31), 164.8 (C-13), 130.5 (C-12), 73.0 (C-3), 60.4 (C-9), 59.0 (C-18), 51.6 (C-39), 50.5 (C-5), 46.7 (C-4), 45.1 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.1 (C-10), 34.8 (C32), 34.7 (C-1), 34.0 (C-17), 32.9 (C-7), 31.6 (C36), 30.9 (C-21), 29.1 (C-34), 29.0 (C-35), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 25.1 (C33), 23.9 (C-23), 23.7 (C-2), 22.6 (C37), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 14.0 (C-38), 13.1 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 611.5 ($[M+H]^+$); analysis calcd for $C_{39}H_{62}O_5$: (610.91): C 76.68, H 10.23; found: C 76.50, H 10.40.

3-*O*-Pivaloyl-11-keto-β-boswellic acid methyl ester (30)
Following the procedure given for **29**, from **26** (194 mg, 0.4 mmol), DMAP (98 mg, 0.8 mmol), dry pyridine, dry DCM (10 mL) and pivaloyl chloride (480 mg, 0.4 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 9:1), **30** (210 mg, 93%) was obtained as a white, amorphous solid; $[\alpha]_D$ = +61.4° (*c* = 5.04, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (*s*, 1H, H-12), 5.24 (*dd*, *J* = 2.5, 2.9 Hz, 1H, H-3), 3.67 (*s*, 3H, H-33), 2.52 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.38 (*s*, 1H, H-9), 2.18 (*m*, 1H, H-2a), 2.08 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.87 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.80 (*m*, 1H, H-6a), 1.73 (*m*, 1H, H-6b), 1.64 (*virt. dt*, *J* = 12.9, 3.7, 12.9 Hz, 1H, H-7a), 1.58 (*m*, 1H, H-2b), 1.52 (*dd*, *J* = 11.2, 1.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b), 1.42 (*m*, 1H, H-21a), 1.40 (*dd*, *J* = 2.1, 12.0, 1H, H-5, Hz), 1.36 (*m*, 1H, H-19), 1.32 (*m*, 1H, H-22a), 1.30 (*s*, 3H, H-27), 1.28 (*m*, 1H, H-21b), 1.20 (*s*, 9H, H-34, H-35, H-36)), 1.19 (*m*, 1H, H-1a, 1H, H-15b), 1.17 (*s*, 6H, 2 H-23, H-26), 1.03 (*s*, 3H, H-25), 1.00 (*virt. dt*, *J* = 13.3, 2.5, 2.5 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.91 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.80 (*d*, *J* = 7.1 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.3 (C-11), 176.0 (C-24), 177.1 (C-31), 164.9 (C-13), 130.5 (C-12), 73.0 (C-3), 60.5 (C-9), 59.0 (C-18), 51.5 (C-33), 50.7 (C-5), 46.8 (C-4), 45.0 (C-8), 43.6 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.1 (C-10), 34.8 (C-1), 33.9 (C-17), 33.1 (C-7), 30.8 (C-21), 28.8 (C-28), 27.5 (C-16), 27.3 (C-34, C-35 and C-36), 27.2 (C-15), 24.0 (C-23), 23.4 (C-2), 21.1 (C-30), 20.2 (C-27), 18.8 (C-6), 18.3 (C-26), 17.5 (C-29), 13.1 (C-25) ppm;
MS (ESI, methanol): *m/z* = 569.5 ($[M+H]^+$); analysis calcd for $C_{36}H_{56}O_5$ (568.83): C 76.01, H 9.92; found: C 75.83, H 10.14.

3-*O*-Oxalyl-β-boswellic acid (31)
To a solution of **1** (150 mg, 0.33 mmol) in dry THF (5 mL), oxalyl chloride (0.3 mL, 3.5 mmol) was slowly added, and stirring at 25 °C was continued for 1 h.

Usual workup followed by extraction (diethyl ether) and chromatography (silica gel, hexane/ethyl acetate, 9:1 → 7:3 → 3:2) gave **31** (148 mg, 85%) as a white solid; m.p. 211-214 °C; $[\alpha]_D$ = +54.1° (*c* = 0.5, acetone);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.41 (*t*, *J* = 2.6 Hz, 1H, H-3), 5.22 (*t*, *J* = 3.5 Hz, 1H, H-12), 2.25 (*m*, 1H, H-2b), 2.12 (*m*, 1H, H-16a), 1.93 (*m*, 4H, H-6b, H-11a, H-11b, H-15b), 1.79 (*m*, 1H, H-6a), 1.69 (*m*, 2H, H-2a, H-9), 1.58 (*m*, 3H, H-1b, H-5, H-7a), 1.39 (*m*, 7H, H-1a, H-7b, H-18, H-19, H-21b, H-22a, H-22b), 1.27 (*bs*, 4H, H-21a, H-23), 1.14 (*s*, 3H, H-27), 1.12 (*s*, 3H, H-26), 1.06 (*m*, 1H, H-15a), 0.99 (*s*, 3H, H-25), 0.95 (*bs*, 4H, H-20, H-30), 0.81 (*s*, 3H, H-28), 0.80 (*t*, *J* = 6.0 Hz, 3H, H-29) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 178.3 (C-24), 160.1 (C-32, COOH of oxalyl), 160.2 (C-31), 141.2 (C-13), 126.6 (C-12), 78.3 (C-3), 61.1 (C-18), 52.0 (C-5), 48.4 (C-9), 48.1 (C-4), 44.1 (C-8), 43.3 (C-22), 41.6 (C-14), 41.7 (C-19), 41.4 (C-20), 39.2 (C-10), 36.4 (C-1), 35.3 (C-17), 34.6 (C-7), 32.7 (C-21), 30.2 (C-28), 29.9 (C-16), 28.1 (C-15), 25.0 (C-2 and C-11), 25.1 (C-23), 24.6 (C-27), 22.4 (C-30), 21.4 (C-6), 18.7 (C-29), 18.3 (C-26), 14.9 (C-25);
MS (ESI, MeOH): *m/z* = 529.4 [(M+H]$^+$); analysis calcd for $C_{32}H_{48}O_6$ for: (528.72): C 72.45, H 9.37; found: C 72.69, H 9.15.

3-*O*-Oxalyl-11-keto-β-boswellic acid (32)
Following the procedure given for **31**, from **3** (250 mg, 0.53 mmol) **32** (234 mg, 84%) was obtained as an off-white solid; m.p. 186-189 °C; $[\alpha]_D$ = +65.2° (*c* = 1.04, acetone);
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.56 (*s*, 1H, H-12), 5.44 (*bs*, 1H, H-3), 2.57 (*m*, 1H, H-1b), 2.44 (*s*, 1H, H-9), 2.30 (*m*, 1H, H-2b), 2.09 (*m*, 1H, H-16a), 1.91 (*m*, 2H, H-6b, H-15b), 1.72 (*m*, 3H, H-2a, H-6a, H-7a), 1.47 (*m*, 6H, H-5, H-7b, H-18, H-19, H-21b, H-22a), 1.35 (*s*, 3H, H-27), 1.31 (*s*, 3H, H-23), 1.30-1.22 (*m*, 3H, H-1a, H-21a, H-22b), 1.20 (*bs*, 4H, H-15a, H-26), 1.15 (*s*, 3H, H-25), 1.05-0.96 (*m*, 1H, H-16b), 0.95 (*bs*, 4H, H-20, H-30), 0.81 (*s*, 3H, H-28), 0.80 (*d*, *J* = 6.3 Hz, 3H, H-29) ppm;
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 200.3 (C-11), 180.5 (C-24), 165.7 (C-13), 158.7 (C-32 of oxalyl), 157.6 (C-31), 130.4 (C-12), 77.6 (C-3), 60.0 (C-9), 59.0 (C-18), 50.3 (C-5), 46.5 (C-4), 45.0 (C-8), 43.6 (C-14), 40.7 (C-22), 39.3 (C-19), 39.2 (C-20), 37.1 (C-10), 34.1 (C-1), 34.2 (C-17), 32.5 (C-7), 30.8 (C-21), 28.9 (C-28), 27.4 (C-16), 27.4 (C-15), 23.7 (C-23), 23.2 (C-2), 21.0 (C-30), 20.3 (C-27), 18.5 (C-6), 18.3 (C-26), 17.1 (C-29),13.1 (C-25) ppm;
MS (ESI; MeOH): *m/z* = 527.3 ([M+H]$^+$); analysis calcd for $C_{32}H_{46}O_7$ for: (526.70): C 72.97, H 8.80; found: C 72.77, H 8.98.

Bis[3-*O*-β-boswellic acid]malonate (33)
A solution of **1** (500 mg, 1.09 mmol) in dry THF (15 mL) was slowly added to a solution of malonyl chloride (1.0 g, 7.0 mmol) in dry THF (1.0 mL), and stirring at 25 °C was continued for 10 min. The mixture was poured into cold water (5 °C, 100 mL). Extraction with diethyl ether (5 x 50 mL) followed by usual work-up and chromatography (silica gel, hexane/diethyl ether 1:1 + 1% HOAc) gave **33** (251 mg, 47%) as a colorless solid; m.p. 237-240 °C; $[\alpha]_D$ = +61.7° (*c* = 0.55, $CHCl_3$);
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.40 (*bs*, 2H, H-3), 5.16 (*bs*, 2H, H-12), 3.45 (*s*, 2H, H-32 of malonyl), 2.17 (*m*, 2H, H-2b), 2.01 (*m*, 2H, H-16a), 1.92 (*m*, 4H, H-11a, H-11b), 1.81 (*m*, 4H, H-6b, H-15b), 1.68 (*m*, 4H, H-2a, H-6a), 1.54 (*m*, 6H, H-1B, H-7a, H-9), 1.40 (*m*, 8H, H-5. H-7b, H-21b, H-22a), 1.32 (*m*, 4H, H-18. H-19), 1.29 (*s*, 6H, H-23), 1.21 (*m*, 6H, H-1a, H-21a, H-22b), 1.11 (*s*, 6H, H-27), 1.06 (*s*, 6H, H-26), 1.05-0.99 (*m*, 2H, H-15a), 0.91 (*m*, 16H, H-16b, H-20, H-25, H-30), 0.79 (*bs*, 12H, H-28. H-29) ppm;
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 182.1 (C-24), 165.5 (C-31 of malonyl), 139.4 (C-13), 124.5 (C-12), 74.5 (C-3), 59.1 (C-18), 50.5 (C-5), 46.8 (C-9), 46.9 (C-4), 42.1 (C-14), 42.1 (C-32, CH_2 of malonyl), 41.6 (C-22), 40.1 (C-8), 39.6 (C-19), 39.3 (C-20), 37.4 (C-10), 34.5 (C-1), 33.8 (C-17), 33.0 (C-7), 31.0 (C-21), 28.9 (C-28), 28.0 (C-16), 26.3 (C-15), 23.6 (C-23), 23.5 (C-2), 23.3 (C-11), 23.3 (C-27), 21.3 (C-30), 19.6 (C-6), 17.6 (C-29), 16.7 (C-26), 13.1 (C-25) ppm;
MS (ESI; MeOH): *m/z* = 981.9 ([M+H]$^+$); analysis calcd for $C_{63}H_{96}O_8$ (981.43): C 77.10, H 9.86; found: C 76.83, H 9.97.

Bis[3-O-11-keto-β-boswellic acid]malonate (34)
Following the procedure given for **33**, from **3** (500 mg, 1.06 mmol) **34** (303 mg, 57%) was obtained as a colorless solid; m.p. 234-238 °C (decomp.); $[\alpha]_D$ = +90.3° (*c* = 0.65, $CHCl_3$);
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.55 (*s*, 2H, H-12), 5.37 (*bs*, 2H, H-3), 3.45 (*s*, 2H, H-32 of malonyl), 2.56 (*m*, 2H, H-1b), 2.42 (*s*, 2H, H-9), 2.26 (*m*, 2H, H-2b), 2.09 (*m*, 2H, H-16a), 1.87 (*m*, 4H, H-6b, H-15b), 1.68 (*m*, 6H, H-2a, H-6a, H-7a), 1.46 (*m*, 12H, H-5, H-7b, H-18, H-19, H-21b, H-22a), 1.33 (*s*, 6H, H-27), 1.30 (*m*, 4H, H-21a, H-22b), 1.24 (*s*, 6H, H-23), 1.20 (*m*, 4H, H-1a, H-15a), 1.17 (*s*, 6H, H-26), 1.12 (*s*, 6H, H-25), 1.03 (*m*, 2H, H-16b), 0.95 (*bs*, 8H, H-20. H-30), 0.85 (*s*, 6H, H-28), 0.81 (*d*, *J* = 5.9 Hz, 6H, H-29) ppm;
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 199.5 (C-11), 181.4 (C-24), 165.5 (C-31 of malonyl), 165.1 (C-13), 130.3 (C-12), 74.5 (C-3), 60.1 (C-9), 59.0 (C-18), 50.6 (C-5), 46.7 (C-4), 45.2 (C-8), 43.7 (C-14), 42.0 (C-32 of malonyl)), 40.7 (C-22), 39.0 (C-19, C-20), 37.5 (C-10), 34.3 (C-1), 34.1 (C-17), 32.6 (C-7), 30.8 (C-21), 28.7 (C-28), 27.3 (C-16), 27.0 (C-15), 24.1 (C-23), 23.5 (C-2), 21.0 (C-30), 20.3 (C-27), 18.5 (C-6), 18.6 (C-26), 17.5 (C-29), 13.1 (C-25) ppm;
MS (ESI; MeOH): *m/z* = 1009.8 ([M+H]$^+$); analysis calcd for $C_{63}H_{92}O_{10}$ (1009.4): C 74.96, H 9.19; found: C 74.73, H 9.32.

3-*O*-Succinyl-β-boswellic acid (35)
To a solution of **1** (200 mg, 0.44 mmol) in dry DCM

(20 mL) succinic anhydride (400 mg, 4.0 mmol), dry triethylamine (1.0 mL) and DMAP (60 mg, 0.49 mmol) were added, and the mixture was stirred at 25 °C for one day. Usual aq. work-up followed by chromatography (silica gel, hexane/ ethyl acetate, 9:1 → 7:3 → 3:2) furnished **35** (181 mg, 81%) as a colorless solid; m.p. 175-178 °C; $[\alpha]_D$ = +59.3° (*c* = 1.75, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.34 (*t, J* = 2.3 Hz, 1H, H-3), 5.17 (*t, J* = 3.4 Hz, 1H, H-12), 2.79-2.60 (*m*, 4H, H-32, H-33), 2.17-2.11 (*m*, 1H, H-2a), 2.04-1.97 (*m*, 1H, H-16a), 1.95-1.91 (*m*, 2H, H-11a, H-11b), 1.89-1.75 (*m*, 2H, H-6, H-15), 1.70-1.67 (*m*, 1H, H-6), 1.65-1.57 (*m*, 2H, H-2b, H-9), 1.55-1.48 (m, 2H, H-1b, H-7a), 1.46-1.35 (*m*, 4H, H-5, H-7b, H-21a, H-22a), 1.35-1.31 (*m*, 2H, H-18, H-19), 1.30-1.22 (*m*, 2H, H-21b, H-22b), 1.22 (*bs*, 4H, H-1b, H-23), 1.11 (*s*, 3H, H-27), 1.06 (*s*, 3H, H-26), 1.05-0.96 (*m*, 1H, H-15), 0.94-0.85 (*m*, 8H, H-16b, H-20, H-25, H-30), 0.80 (*s*, 3H, H-28), 0.79 (*bs*, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.4 (C-24), 177.7 (C-34), 171.0 (C-31), 139.4 (C-13), 124.3 (C-12), 73.9 (C-3), 59.0 (C-18), 50.5 (C-5), 46.8 (C-9), 46.7 (C-4), 42.1 (C-14), 41.5 (C-22), 40.0 (C-8), 39.6 (C-19), 39.5 (C-20), 37.2 (C-10), 34.5 (C-1), 33.6 (C-17), 33.0 (C-7), 31.5 (C-21), 29.1 (C-32 or C-33), 29.1 (C-32or C-33), 28.9 (C-28), 28.0 (C-16), 26.5 (C-15), 23.6 (C-23), 23.5 (C-2), 23.3 (C-11), 23.0 (C-27), 21.1 (C-30), 19.4 (C-6), 17.5 (C-29), 16.8 (C-26), 13.3 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 509.4 ($[M+H]^+$); analysis calcd for $C_{34}H_{52}O_6$ (508.73): C 70.83, H 10.30; found: C 70.61, H 10.45.

3-*O*-Succinyl-11-keto-β-boswellic acid (36)
Following the procedure for the synthesis of **35**, from **3** (188 mg, 0.4 mmol), compound **36** (162 mg, 71%) was obtained as a colorless solid; m.p. 180-184 °C (lit.: 172-176 °C [21]); $[\alpha]_D$ = 50.6° (*c* = 5.20, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (*s*, 1H, H-12), 5.33 (*virt. t, J* = 2.5, 2.5 Hz, 1H, H-3), 2.67 (*m*, 4H, H-32, H-33), 2.53 (*m*, 1H, H-1b), 2.42 (*s*, 1H, H-9), 2.20 (*m*, 1H, H-2a), 2.08 (*virt. dt, J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.88 (*virt. dt, J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.70 (*m*, 2H, H-6), 1.64 (*m*, 1H, H-7a), 1.56 (*m*, 1H, H-2b), 1.53 (*dd, J* = 11.0, 1.7 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.36 (*m*, 1H, H-5), 1.33 (*s*, 3H, H-27), 1.25 (*m*, 1H, H-22a), 1.22 (*m*, 1H, H-15b), 1.20 (*s*, 3H, H-26), 1.18 (*m*, 1H, H-1a), 1.17 (*s*, 3H, H-23), 1.13 (*s*, 3H, H-25), 0.99 (*m*, 1H, H-16b), 0.94 (*m*, 1H, H-20), 0.93 (*s*, 3H, H-30), 0.81 (*s*, 3H, H-28), 0.80 (*d, J* = 7.5 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.7 (C-11), 182.0 (C-24), 178.1 (C34), 170.7 (C-31), 165.6 (C-13), 130.3 (C-12), 73.6 (C-3), 60.2 (C-9), 59.0 (C-18), 50.4 (C-5), 46.5 (C4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.3 (C-10), 34.5 (C-1), 33.9 (C-17), 32.8 (C-7), 30.9 (C-21), 29.4 + 29.0 (C32 + C33), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.8 (C-23), 23.5 (C-2), 21.1 (C-30), 20.4 (C-27), 18.7 (C-6), 18.3 (C-26), 17.4 (C-29), 13.3 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 571.4 ($[M+H]^+$); analysis calcd for $C_{34}H_{50}O_7$ (570.76): C 71.55, H 8.83; found: C 71.31, H 8.98.

3-*O*-Glutaroyl-β-boswellic acid (37)
To a solution of **1** (500 mg, 1.09 mmol) in dry pyridine (15 mL), glutaric anhydride (1.83 g, 16.0 mmol) and DMAP (60 mg, 0.49 mmol) were added, and the mixture was heated under reflux for 12 h. Usual aq. work-up followed by chromatography (silica gel, hexane/diethylether 2:1 + 1% HOAc) gave **37** (519 mg, 83%) as a colorless solid; m.p. 135-138 °C; $[\alpha]_D$ = +59.1° (*c* = 0.51, $CHCl_3$);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.33 (*t, J* = 2.4 Hz, 1H, H-3), 5.22 (*t, J* = 3.4 Hz, 1H, H-12), 2.45 (*t, J* = 7.4 Hz, 2H, H-34 of glutaroyl), 2.41 (*t, J* = 7.4 Hz, 2H, of glutaroyl), 2.20-2.12 (*m*, 1H, H-2b), 2.11-2.05 (*m*, 1H, H-16a), 2.01-1.85 (*m*, 6H, H-6b, H-11a, H-11b, H-15b, of glutaroyl), 1.77-1.75 (*m*, 1H, H-6a), 1.70- 1.65 (*m*, 1H, H-9), 1.64-1.56 (*m*, 2H, H-2a, H-7a), 1.55-1.48 (*m*, 2H, H-1b, H-5), 1.46-1.26 (*m*, 8H, H-1a, H-7b, H-18, H-19, H-21a, H-21b, H-22a, H-22b), 1.24 (*s*, 3H, H-23), 1.16 (*s*, 3H, H-27), 1.09 (*s*, 3H, H-26), 1.06-1.00 (*m*, 1H, H-15a), 0.99 (*s*, 3H, H-25), 0.96-0.88 (*m*, 5H, H-16b, H-20, H-30), 0.85 (*s*, 3H, H-28), 0.83 (*d, J* = 5.8 Hz, 3H, H-29) ppm; ^{13}C NMR (acetone-d_6, 125 MHz): δ = 179.3 (C-24), 175.1 (C-35, COOH of glutaroyl), 173.4 (C-31, CO of glutaroyl), 141.3 (C-13), 126.5 (C-12), 75.1 (C-3), 61.1 (C-18), 52.5 (C-5), 48.6 (C-9), 48.1 (C-4), 44.1 (C-8), 43.5 (C-22), 42.1 (C-14), 41.7 (C-19), 41.3 (C-20), 39.0 (C-10), 36.6 (C-1), 35.5 (C-17), 35.2 (C-34 of glutaroyl), 34.7 (C-7), 34.3 (C-32 of glutaroyl), 32.7 (C-21), 30.2 (C-28), 29.9 (C-16), 28.5 (C-15), 25.0 (C-23), 25.2 (C-2), 25.2 (C-11), 24.6 (C-27), 22.5 (C-30), 22.3 (C-33 of glutaroyl), 21.8 (C-6), 18.7 (C-29), 18.6 (C-26), 14.7 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 571.4 ($[M+H]^+$); analysis calcd for $C_{35}H_{54}O_6$ (570.80): C 73.65, H 9.54; found: C 73.46, H 9.70.

3-*O*-Glutaroyl-11-keto-β-boswellic acid (38)
Following the procedure given for the synthesis of **37**, from **3** (700 mg, 1.5 mmol), compound **38** (658 mg, 75%) was obtained as a colorless solid; m.p. 136-139 °C; $[\alpha]_D$ = 65.1° (*c* = 0.5, acetone);
^{1}H NMR (500 MHz, acetone-d_6): δ = 5.51 (*s*, 1H, H-12), 5.27 (*t, J* = 2.6 Hz, 1H, H-3), 2.52-2.49 (*m*, 2H, H-1a, H-9), 2.45 (*t, J* = 7.4 Hz, 2H, H-34), 2.41 (*t, J* = 7.4 Hz, 2H, H-32), 2.287-2.15 (*m*, 2H, H-2a, H-16a), 1.98-1.86 (*m*, 4H, H-6a, H-15a, H-33), 1.80-1.75 (*m*, 2H, H-6b, H-7a), 1.60-1.42 (*m*, 7H, H-2bα, H-5, H-7b, H-18, H-19, H-21a, H-22a), 1.40 (s, 3H, H-27), 1.39-1.34 (*m*, 2H, H-21b, H-22b), 1.34-1.25 (*m*, 2H, H-1b, H-15b), 1.24 (*s*, 3H, H-23), 1.20 (*s*, 3H, H-26), 1.19 (*s*, 3H, H-25), 1.08-1.00 (*m*, 1H, H-16b), 0.95 (*bs*, 4H, H-20, H-30), 0.85 (*s*, 3H, H-28), 0.84 (*d, J* = 6.4 Hz, 3H, H-29) ppm;

^{13}C NMR (125 MHz, acetone-d_6): δ = 199.7 (C-11), 178.6 (C-24), 175.3 (C-35), 173.5 (C-31), 165.7 (C-13), 132.0 (C-12), 74.8 (C-3), 62.1 (C-9), 60.8 (C-18), 52.1 (C-5), 48.1 (C-4), 46.5 (C-8), 45.4 (C-14), 42.6 (C-22), 41.01 (C-19), 40.8 (C-20), 39.3 (C-10), 36.2 (C-1), 35.6 (C-17), 35.0 (C-34), 34.5 (C-7), 34.1 (C-32), 32.5 (C-21), 30.0 (C-28), 29.1 (C-16), 29.1 (C-15), 25.1 (C-23), 25.2 (C-2), 22.1 (C-30), 22.0 (C-33), 22.2 (C-27), 21.8 (C-6), 19.9 (C-26), 18.6 (C-29), 14.7 (C-25);
MS (ESI, MeOH): *m/z* = 585.4 ([M+H]$^+$); analysis calcd for $C_{35}H_{52}O_7$ (584.78): C 71.89, H 19.15; found: C 71.64, H 19.32.

3-*O*-[3,4,5-Tris(benzyloxy)benzoyl]-β-boswellic acid (40)

To a suspension of 3,4,5-tri-*O*-benzyl-benzoic acid (0.34 g, 2.0 mmol) in dry DCM (10 ml) containing dry DMF (2 drops) oxalyl chloride (0.38 g, 3.0 mmol) was added, and the mixture was stirred at 30 °C for 2 h. The solvents were removed under diminished pressure, dry toluene (2 mL) was added and removed under diminished pressure. The residue (crude **39**) was dissolved in dry pyridine (2 mL), and a solution of **1** (410 mg, 0.90 mmol) in dry pyridine (5 mL) was added. After stirring for two days at 25 °C, water (0.5 mL) was added, and the mixture was stirred for several minutes. Usual aq. work-up followed by extraction with DCM (5 x 30 mL) and chromatography (silica gel, hexane/diethyl ether 4:1 + 1% acetic acid) gave **40** (493 g, 63%) as a colorless solid m.p. 140-143 °C; $[\alpha]_D$ = +19.3° (*c* = 1.10, $CHCl_3$);
^{1}H NMR (500 MHz, acetone-d_6): δ = 7.46-7.31 (*m*, 15H, Ar-H), 7.30-7.20 (*m*, 2H, aryl), 5.55 (*t*, *J* = 2.7 Hz, 1H, H-3), 5.19-5.10 (*m*, 1H, H-12), 5.14 (*s*, 4H, benzyl), 5.10 (*s*, 2H, benzyl), 2.34-2.21 (*m*, 1H, H-2a), 2.07-1.83 (*m*, 5H, H-6a, H-11a, H-11b, H-15a, H-16a), 1.83-1.70 (*m*, 2H, H-2b, H-6b), 1.70-1.65 (*m*, 1H, H-9), 1.65-1.54 (*m*, 3H, H-1a, H-5, H-7a), 1.52-1.45 (*m*, 1H, H-7b), 1.45-1.34 (*m*, 3H, H-1b, H-21a, H-22a), 1.34-1.27 (*m*, 2H, H-18, H-19), 1.26 (*bs*, 4H, H-22b, H-23), 1.24-1.14 (*m*, 1H, H-21b), 1.09 (*s*, 3H, H-26), 1.07 (*s*, 3H, H-27), 1.02-0.97 (*m*, 1H, H-15b), 0.96 (*s*, 3H, H-25), 0.92 (*s*, 3H, H-30), 0.92-0.82 (*m*, 2H, H-16b, H-20), 0.81 (*s*, 3H, H-28), 0.70 (*d*, *J* = 6.4 Hz, 3H, H-29) ppm;
^{13}C NMR (125 MHz, acetone-d_6): δ = 181.5 (C-24), 164.7 (C-31), 152.5 (aryl), 142.4 (aryl, 139.7 (C-13), 137.3 (aryl), 136.2 (aryl), 128.4 (aryl), 128.1 (aryl), 128.0 (aryl), 127.7 (aryl), 127.6 (aryl), 125.5 (aryl), 124.4 (C-12), 108.5 (aryl), 75.1 (benzyl), 73.8 (C-3), 71.0 (benzyl), 59.0 (C-18), 51.2 (C-5), 47.2 (C-9), 47.0 (C-4), 42.0 (C-14), 41.6 (C-22), 40.0 (C-8), 39.7 (C-19), 39.4 (C-20), 37.5 (C-10), 35.1 (C-1), 33.9 (C-7), 33.5 (C-17), 31.5 (C-21), 28.6 (C-28), 28.1 (C-16), 26.2 (C-15), 24.1 (C-23), 23.9 (C-2), 23.4 (C-11), 23.3 (C-27), 21.2 (C-30), 19.6 (C-6), 17.3 (C-29), 16.9 (C-26), 13.3 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 879.5 ([M+H]$^+$); analysis calcd for $C_{58}H_{70}O_7$ (879.17): C 79.24, H 8.03; found: C 79.02, H 8.27.

3-*O*-[3,4,5-Tris(benzyloxy)benzoyl]-11-keto-β-boswellic acid (41)

Following the procedure given for the synthesis of **40**, from **3** (200 mg, 0.44 mmol), compound **41** (270 mg, 69%) was obtained as a colorless solid; m.p. 117-120 °C; $[\alpha]_D$ = +27.9° (*c* = 1.3, acetone);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.54 (*m*, 4H, aryl), 7.53 (*s*, 2H, aryl), 7.40 (*m*, 8H, aryl), 7.26 (*m*, 3H, aryl), 5.55 (*t*, *J* = 2.7 Hz, 1H, H-3), 5.46 (*s*, 1H, H-12), 5.25 (*s*, 2H, benzyl), 5.24 (*s*, 2H, benzyl), 5.13 (*s*, 2H, benzyl), 2.69 (*s*, 1H, H-9), 2.58 (*m*, 1H, H-1a), 2.36 (*m*, 1H, H-2a), 2.02 (*m*, 2H, H-6a, H-16a), 1.94 (*m*, 2H, H-7a, H-15a), 1.85 (*m*, 1H, H-6b), 1.70 (*m*, 1H, H-5), 1.62 (*m*, 1H, H-2b), 1.54 (*m*, 4H, H-1b, H-7b, H-18, H-22a), 1.44 (*m*, 1H, H-21a), 1.39 (*s*, 3H, H-27), 1.32 (*m*, 3H, H-19, H-21b, H-22b), 1.23 (*s*, 3H, H-23), 1.22 (*s*, 3H, H-25), 1.21 (*bs*, 4H, H-15b, H-26), 0.99 (*m*, 1H, H-16b), 0.96 (*bs*, 4H, H-20, H-30), 0.86 (*s*, 3H, H-28), 0.74 (*d*, *J* = 6.5 Hz, 3H, H-29) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 199.7 (C-11), 178.6 (C-24), 166.5 (C-31), 165.5 (C-13), 154.7 (aryl), 144.1 (aryl), 139.6 (aryl), 138.7 (aryl), 132.0 (C-12), 130.4 (aryl), 130.0 (aryl), 129.8 (aryl), 129.7 (aryl), 127.5 (aryl), 110.4 (aryl), 76.6 (benzyl), 75.5 (C-3), 72.4 (benzyl), 62.3 (C-9), 60.7 (C-18), 52.4 (C-5), 48.3 (C-4), 46.7 (C-8), 45.5 (C-14), 42.4 (C-22), 41.0 (C-19), 40.8 (C-20), 39.4 (C-10), 36.8 (C-1), 35.4 (C 17), 34.8 (C-7), 32.6 (C-21), 30.1 (C-28), 29.0 (C-16), 28.9 (C-15), 25.5 (C-24), 25.3 (C-2), 22.6 (C-30), 22.1 (C-27), 20.8 (C-6), 19.8 (C-26), 18.5 (C-29), 14.8 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 893.8 ([M+H]$^+$); analysis calcd for $C_{58}H_{68}O_8$ (893.16): C 78.00, H 7.67; found: C 77.72, H 7.91.

3-*O*-(3,4,5-Trihydroxybenzoyl)-β-boswellic acid (42)

A solution of **40** (250 mg, 0.30 mmol) in dry THF (10 mL) was hydrogenated (atmospheric pressure in the presence of Pd/C (10%, 50 mg) for 6 h. The catalyst was filtered off, the solvent removed under diminished pressure, and the residue was subjected to chromatography (silica gel, hexane/diethyl ether 1:1 + 1% acetic acid) to afford **42** (164 mg, 87%) as an off-white solid; m.p. 202-204 °C; $[\alpha]_D$ = 49.7° (*c* = 0.5, acetone);
^{1}H NMR (500 MHz, acetone-d_6): δ = 7.16 (s, 2H, aryl), 5.44 (*t*, *J* = 2.7 Hz, 1H, H-3), 5.22 (*t*, *J* = 3.4 Hz, 1H, H-12), 2.31-2.21 (*m*, 1H, H-2a), 2.15-2.01 (*m*, 1H, H-16a), 2.01-1.87 (*m*, 4H, H-6a, H-11a, H-11b, H-15a), 1.86-1.80 (*m*, 1H, H-6b), 1.79-1.62 (*m*, 4H, H-2b, H-5, H-7a, H-9), 1.61-1.52 (*m*, 1H, H-1b), 1.51-1.42 (*m*, 2H, H-7b, H-22a), 1.42-1.34 (*m*, 4H, H-1b, H-18, H-19, H-21a), 1.34-1.29 (*m*, 2H, H-21b, H-22b), 1.27 (*s*, 3H, H-23), 1.20 (*s*, 3H, H-27), 1.14 (*s*, 3H, H-26), 1.11-1.03 (*m*, 1H, H-15b), 1.01 (*s*, 3H, H-25), 0.95 (*s*, 3H, H-30), 0.94-0.85 (*m*, 2H, H-16b,

H-20), 0.83 (*s*, 3H, H-28), 0.82 (*d*, *J* = 6.2 Hz, 3H, H-29) ppm;
^{13}C-NMR (125 MHz, acetone-d6): δ = 179.3 (C-24), 166.7 (C-31), 147.2 (aryl), 141.4 (C-13), 139.7 (aryl), 126.5 (C-12), 123.4 (aryl), 110.7 (aryl), 75.2 (C-3), 61.01 (C-18), 52.6 (C-5), 49.0 (C-9), 48.7 (C-4), 44.1 (C-8), 43.1 (C-22), 41.7 (C-14), 41.4 (C-19), 41.3 (C-20), 39.1 (C-10), 36.9 (C-1 -), 35.4 (C-17), 35.0 (C-7), 32.7 (C-21), 30.1 (C-28), 29.9 (C-16), 28.4 (C-15), 25.3 (C-23), 25.2 (C-2), 25.0 (C-11), 24.8 (C-27), 22.8 (C-30), 21.5 (C-6), 19.2 (C-29), 18.6 (C-26), 15.1 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 607.6 ([M-H]$^-$); analysis calcd for $C_{37}H_{52}O_7$ (608.80): C 72.99, H 8.61; found: C 72.77, H 8.81.

3-*O*-(3,4,5-Trihydroxybenzoyl)-11-keto-β-boswellic acid (43)
Following the procedure given for the synthesis of **42**, hydrogenation of **41** (200 mg, 0.22 mmol) gave **43** (113 mg, 81%) as a colorless solid; m.p. 224-227 °C (decomp.); $[\alpha]_D$ = +38.3° (*c* = 0.9, acetone);
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.16 (*s*, 2H, Ar-H), 5.51 (*s*, 1H, H-12), 5.45 (*t*, *J* = 2.7 Hz, 1H, H-3), 2.58 (*s*, 1H, H-9), 2.59-2.51 (*m*, 1H, H-1a), 2.36-2.25 (*m*, 1H, H-2a), 2.21 (*dt*, *J* = 13.7 Hz, 4.8 Hz, H-16a), 2.01-1.88 (*m*, 2H, H-6a, H-15a), 1.87-1.80 (*m*, 2H, H-6b, H-7a), 1.70-1.62 (*m*, 2H, H-5, H-2b), 1.64-1.56 (*m*, 1H, H-18), 1.55-1.47 (*m*, 3H, H-7b, H-19, H-22a), 1.44 (*bs*, 4H, H-21a, H-27), 1.43-1.34 (*m*, 3H, H-1b, H-21b, H-22b), 1.33-1.26 (*m*, 1H, H-15b), 1.26 (*s*, 3H, H-23), 1.23 (*s*, 3H, H-26), 1.21 (*s*, 3H, H-25), 1.08-1.00 (*m*, 1H, H-16b), 0.98 (*bs*, 4H, H-20, H-30), 0.85 (*s*, 3H, H-28), 0.82 (*d*, *J* = 6.4 Hz, 3H, H-29) ppm;
^{13}C NMR (acetone-d_6, 125 MHz): δ = 199.7 (C-11), 178.9 (C-24, COOH), 166.7 (C-31), 165.7 (C-13), 147.1 (C_{ar}), 139.9 (C_{ar}), 132.0 (C-12), 123.2 (C_{ar}), 110.7 (C_{ar}), 75.1 (C-3), 62.4 (C-9), 60.7 (C-18), 52.4 (C-5), 48.4 (C-4), 46.7 (C-8), 45.3 (C-14), 42.6 (C-22), 41.0 (C-20), 40.8 (C-19), 39.3 (C-10), 36.5 (C-1), 35.7 (C-17), 34.8 (C-7), 32.7 (C-21), 30.0 (C-28), 29.0 (C-16), 28.9 (C-15), 25.4 (C-23), 25.2 (C-2), 22.3 (C-30), 22.1 (C-27), 20.8 (C-6), 20.1 (C-26), 18.9 (C-29), 14.89 (C-25);
MS (ESI, MeOH): *m*/*z* = 623.6 ([M+H]$^+$); analysis calcd for $C_{37}H_{50}O_8$ (622.78): C 71.36, H 8.09; found: C 71.17, H 8.35.

3-*O*-(*trans*-3-Phenylpropenoyl)-11-keto-β-boswellic acid methyl ester (45)
To a solution of *trans* cinnamic acid chloride (668 mg, 4.0 mmol) in dry DCM (20 mL), a solution of **26** (300 mg, 0.62 mmol) containing DMAP (cat.) in dry pyridine (5 mL) and dry DCM (15 mL) was added. After stirring at 25 °C overnight, the solvents were removed under diminished pressure, and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 9:1 → 7:1) to afford **45** (278 mg, 73%) as an off-white amorphous solid; $[\alpha]_D$ = 36.3° (*c* = 2.20, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (*d*, *J* = 15.8 Hz, 1H, H-34), 7.52 (*m*, 2H, H-37 + H-39), 7.36 (*m*, 3H, H-36, H-38, H-40), 6.46 (*d*, *J* = 15.8 Hz, 1H, H-33), 5.54 (*s*, 1H, H-12), 5.46 (*virt. t*, *J* = 2.5, 2.5 Hz, 1H, H-3), 3.69 (*s*, 3H, H-31), 2.56 (*virt. dt*, *J* = 13.3, 3.3, 3.3 Hz, 1H, H-1b), 2.45 (*s*, 1H, H-9), 2.27 (*m*, 1H, H-2a), 2.10 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-16a), 1.90 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.82 (*m*, 1H, H-6a), 1.77 (*m*, 1H, H-6b), 1.68 (*m*, 1H, H-7a, 1H, H-2b), 1.53 (*dd*, 1H, *J* = 11.2, 1.2 Hz, H-18), 1.50 (*m*, 1H, H-22b), 1.45 (*m*, 1H, H-7b, 1H, H-21a), 1.39 (*m*, 1H, H-19), 1.37 (*s*, 3H, H-27), 1.35 (*m*, 1H, H-5), 1.30 (*m*, 1H, H-22a), 1.25 (*m*, 1H, H-1a, 1H, H-21b), 1.21 (*s*, 3H, H-23), 1.20 (*m*, 1H, H-15b), 1.18 (*s*, 3H, H-26), 1.06 (*s*, 3H, H-25), 0.99 (*m*, 1H, H-16b), 0.94 (*s*, 3H, H-30), 0.91 (*m*, 1H, H-20), 0.82 (*s*, 3H, H-28), 0.79 (*d*, 3H, H-29, *J* = 6.6 Hz) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 176.1 (C-24), 166.1 (C-31), 164.8 (C-13), 144.8 (C34), 134.4 (C35), 130.5 (C-12), 130.2 (C-38), 128.8 (C-36 + C-40), 128.0 (C-37 + C-39), 118.5 (C-33), 73.3 (C-3), 60.4 (C-9), 59.0 (C-18), 51.6 (C-31), 50.6 (C-5), 46.8 (C-4), 45.1(C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.2 (C-10), 34.8 (C-1), 34.0 (C-17), 32.9 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.7 (C-2), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.1 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 615.6 ([M+H]$^+$); analysis calcd for $C_{40}H_{54}O_5$ (614.85): C 78.14, H 8.85; found: C 78.00, H 8.98.

3-*O*-[*trans*-3-(3,4-Diallyloxyphenyl)-propenoyl]-11-keto-β-boswellic acid methyl ester (47)
A solution of *trans*-3-(3,4-diallyloxyphenyl)-propenoic acid (521 mg, 2.0 mmol) and thionyl chloride (0.6 g, 5.0 mmol) in dry DCM (10 mL) was stirred at 25 °C for 4 h. The volatiles were removed under reduced pressure, and the residue (**46**) was dissolved in dry DCM (20 mL). This solution was added to a solution containing **26** (386 mg, 0.4 mmol), DMAP (98 mg, 0.8 mmol) and dry pyridine (5 mL) in dry DCM (10 mL). Usual aq. workup after stirring overnight at 25 °C, followed by chromatography (silica gel, hexane/ethyl acetate, 8:2) gave **47** (200 mg, 69%) as an amorphous white solid; $[\alpha]_D$ = 20.3° (*c* = 5.40, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (*d*, *J* = 15.8 Hz, 1H, H-34)), 7.07 (*dd*, *J* = 8.3, 2.1 Hz, 1H, H-40), 7.05 (*d*, *J* = 2.1 Hz, 1H, H-39), 6.85 (*d J* = 8.3 Hz, 1H, H-36), 6.27 (*d*, *J* = 15.8 Hz, 1H, H-33)), 6.05 (*m*, 2H, H-42, H-45), 5.53 (*s*, 1H, H-12), 5.44 (*virt. t*, *J* = 2.5, 2.5 Hz, 1H, H-3), 5.40 + 5.23 (*m*, 4H, H-43, H-46)), 4.61 (*m*, 4H, H-41, H-44), 3.68 (*s*, 3H, H-31)), 2.54 (*ddd*, *J* = 13.3, 3.3 Hz, 3.7 Hz, 1H, H-1b), 2.44 (*s*, 1H, H-9), 2.24 (*m*, 1H, H-2a), 2.09 (*virt. dt*, *J* = 13.7, 5.0 Hz,13.7 Hz, 1H, H-16a), 1.89 (*virt. dt*, *J* = 13.7, 5.0, 13.7 Hz, 1H, H-15a), 1.84 (*m*, 1H, H-6a), 1.76 (*m*, 1H, H-6b), 1.68 (*m*, 1H, H-7a, 1H, H-2b), 1.53 (*d*, *J* = 11.2 Hz, 1H, H-18), 1.48 (*m*, 1H, H-22b), 1.46 (*dd*, *J* =

2.1, 12.0 Hz, 1H, H-5), 1.44 (*m*, 1H, H-7b, 2H, H-21), 1.39 (*m*, 1H, H-19), 1.36 (*s*, 3H, H-27), 1.32 (*m*, 1H, H-22a), 1.25 (*m*, 1H, H-1a), 1.22 (*m*, 1H, H-15b), 1.20 (*s*, 3H, H-23), 1.18 (*s*, 3H, H-26), 1.05 (*s*, 3H, H-25), 0.98 (*virt. dt*, *J* = 13.3, 2.5, 2.5 Hz, 1H, H-16b), 0.93 (*s*, 3H, H-30), 0.90 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.79 (*d*, 3H, H-29, *J* = 6.6 Hz) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.2 (C-11), 176.1 (C-24), 166.3 (C-32), 164.7 (C-13), 150.7 ($C_{arom.}$), 148.5 ($C_{arom.}$), 144.6 ($C_{arom.}$), 133.1 (*C*H=CH_2), 132.9 (*C*H=CH_2), 130.5 (C-12), 127.6 ($C_{arom.}$), 122.6 (C-40), 117.9 (CH=*C*H_2), 117.9 (CH=*C*H_2), 116.3 (*C*H=CH), 113.5 ($C_{aromat.}$), 113.1 ($C_{aromat.}$), 73.1 (C-3), 70.1 (C41), 69.7 (C44), 60.4 (C-9), 59.0 (C-18), 51.6 (C-31), 50.6 (C-5), 46.9 (C-4), 45.1 (C-8), 43.7 (C-14), 40.9 (C-22), 39.3 (C-19), 39.3 (C-20), 37.2 (C-10), 34.9 (C-1), 33.9 (C-17), 32.9 (C-7), 30.9 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.8 (C-2), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.1 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 727.4 ($[M+H]^+$); analysis calcd for $C_{46}H_{62}O_7$ (726.98): C 76.00, H 8.60; found C 75.78, H 8.83.

3-*O*-[*trans*-3-(3,4-Dihydroxyphenyl)-propenoyl]-11-keto-β-boswellic acid methyl ester (48)

A solution of **47** (100 mg, 0,14 mmol), morpholine (122 mg, 1,4 mmol) and $Pd(PPh_3)_4$ (20 mg) in dry DCM (20 mL) was stirred at 25 °C for 1 h. The solvents were removed under reduced pressure, and the residue was subjected to chromatography (hexane/ethyl acetate, 7:3) to yield **48** (70 mg, 78%) as an off white, amorphous solid; $[\alpha]_D$ = 35.6° (*c* = 6.64, MeOH);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (*d*, 1H, *J* = 15.8 Hz H-34), 7.07 (*d*, 1H, *J* = 2.1 H-36), 6.97 (*dd*, 1H, *J* = 8.3, 2.1 Hz, H-40), 6.84 (*d*, 1H, *J* = 8.3 Hz, H-39), 6.26 (*d*, 1H, *J* = 15.8 Hz, H-33), 5.54 (*s*, 1H, H-(12), 5.44 (*dd*, 1H, *J* = 2.5, 2.9 Hz H-3), 3.68 (*s*, 3H, H-31), 2.55 (*ddd*, 1H, *J* = 13.3, 2.9, 3.3 Hz, H-1b), 2.46 (*s*, 1H, H-9), 2.24 (*m*, 1H, H-2a), 2.09 (*virt. dt*, 1H, *J* = 13.7, 5.0, 13.7 Hz, H-16a), 1.89 (*virt. dt*, 1H, *J* = 13.7, 5.0, 13.7, H-15a), 1.84 (*m*, 1H, H-6a), 1.76 (*m*, 1H, H-6b), 1.66 (*m*, 2H, H-2b, H-7a), 1.53 (*d*, 1H, *J* = 11.2 Hz, H-18), 1.48 (*m*, 1H, H-22b), 1.46 (*dd*, 1H, *J* = 2.5 , 9.1 Hz, H-5), 1.44 (*m*, 3H, H-7b, H-21a,b), 1.38 (*m*, 1H, H-19), 1.36 (*s*, 3H, H-27)), 1.31 (*m*, 1H, H-22a), 1.26 (*m*, 1H, H-1a), 1.22 (*m*, 1H, H-15b), 1.19 (*s*, 3H, H-23), 1.18 (*s*, 3H, H-26), 1.05 (*s*, 3H, H-25), 0.99 (*ddd*, 1H, *J* = 13.3, 2.1, 2.5 Hz, H-16b), 0.92 (*s*, 3H, H-30), 0.90 (*m*, 1H, H-20), 0.81 (*s*, 3H, H-28), 0.77 (*d*, 3H, *J* = 6,2 Hz, H-29) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.2 (C-24), 166.8 (C-32), 165.9 (C-13), 146.5 (C-38), 145.1 (C-34), 144.1 (C-37), 130.2 (C-12), 127.4 (C-35), 122.2 (C-40), 115.8 (C-33), 115.3 (C-39), 114.3 (C-36), 73.3 (C-3), 60.4 (C-9), 59.1 (C-18), 51.6 (C-31), 50.6 (C-5), 46.9 (C-4), 45.1 (C-8), 43.8 (C-14), 40.9 (C-22), 39.3 (C-19), 39.2 (C-20), 37.2 (C-10), 34.8 (C-1), 34.0 (C-17), 30.8 (C-7), 30.3 (C-21), 28.8 (C-28), 27.5 (C-16), 27.2 (C-15), 23.9 (C-23), 23.7 (C-2), 21.1 (C-30), 20.5 (C-27), 18.8 (C-6), 18.3 (C-26), 17.4 (C-29), 13.2 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 647.4 ($[M+H]^+$); analysis calcd for $C_{40}H_{54}O_7$ (646.85): C 74.27, H 8.41; found: C 74.01, H 8.57.

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