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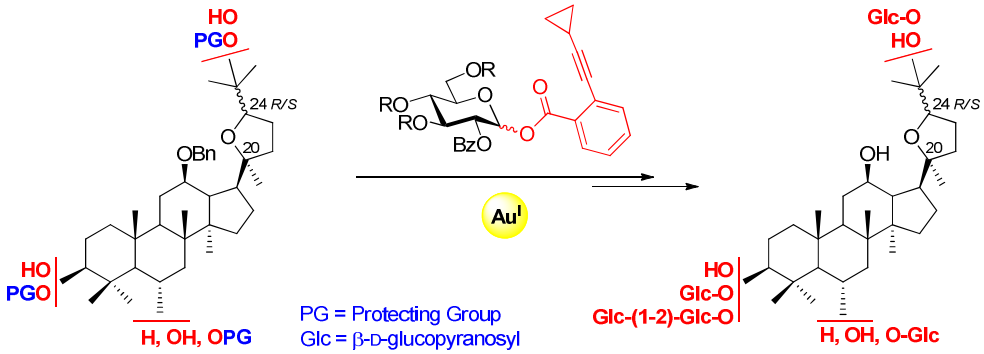


ABSTRACT: A total of 14 ocotillol-type ginsenosides were conveniently synthesized employing glycosylation of ocotillol sapogenin derivatives with glucosyl *ortho*-alkynylbenzoate donors under the promotion of a gold(I) catalyst as the key step. Relying on a rational protecting group strategy and the unexpected regioselectivity of the glycosylation of the 3,25-diol sapogenins (**2a**/**2b**, **5a**/**5b**) for the tertiary 25-OH, mono 3-*O*-glucosyl ocotillol-PPD, 6-*O*-glucosyl ocotillol-PPT, 25-*O*-glucosyl ocotillol-PPD/PPT and 3,25-di-*O*-glucosyl ocotillol-PPD/PPT ginsenosides were prepared in which the configuration at the C-24 is either *R* or *S*.

INTRODUCTION

Ocotillol-type ginsenosides represent a small group of triterpenoid saponins derived from dammarane ginsenosides.[1] Their characteristic triterpenoid aglycone consists of either a 20(*S*)-protopanaxadiol (PPD) or 20(*S*)-protopanaxatriol (PPT) featuring a hydroxyisopropyl-tetrahydrofuran side chain at the C-20. Naturally, they mainly occur in *Panax* species (Araliaceae family), but some have also been isolated from *Neoalsomitra integrifoliola* vine and *Gynostemma pentaphyllum* herb (Cucurbitaceae family).[2,3] Thus far, less than 20 naturally occurring ocotillol-type ginsenosides have been characterized and reported, namely majonoside R1, R2, pseudo-ginsenoside F11 (24-*R*/*S* epimers), RT2, RT4, RT5, vina-ginsenoside R1 (24-*R*/*S* epimers), R2, R5, R6, neoalsoside D1, E1 and gynoside A, B, C.[1-4] For all these compounds, the C-20 of the sapogenin aglycone has a *S*-configuration and the sugar units which are D-glucose, L-rhamnose and D-xylose are attached onto the aglycone either at the 3β-OH (PPD) or 6α-OH (PPT). Recently, the 20(*R*)-epimer of 24(*R*)-pseudo-ginsenoside F11 was isolated from red American ginseng and novel structures will probably continue to be reported with the aid of modern and more sensitive characterization techniques.[5]

The variability in the type of sugars and the degree of glycosylation determine their biological properties. For instance, majonoside R2, the major constituent of the Vietnamese ginseng, exhibits antinociceptive,[6] anti-tumor-promoting,[7] hepatoprotective,[8] antioxidant,[9] and anti-inflammatory activities,[10] whereas 24(*R*)-pseudo-ginsenoside F11, present in American ginseng, enhances neuronal activity,[11] attenuates nephrotoxicity induced by Cisplastin,[12] and can be effective for the treatment of type-2 diabetes.[13] In addition to their own biological properties, some ocotillol-type ginsenosides have been identified as metabolites of the corresponding dammarane saponins, implying that they might be involved in their beneficial effects.[14]

The wide range of biological activities of ocotillol-type ginsenosides recently renewed their interest as potential pharmacophores. However, molecular mechanistic study is hampered by the fact that they are naturally produced in heterogeneous complex mixtures and in low yield. Tissue and cell cultures,[15] as well as biotechnology and gene regulation methods,[16] have been studied to produce ginsenosides, however, improvements are required since the content of ginsenosides remains low. Alternatively, chemical synthesis appears attractive for the preparation of homogeneous natural and synthetic ginsenosides in appreciable amounts with the aim of studying structure-activity relationship and discovering novel therapeutic targets.[17]

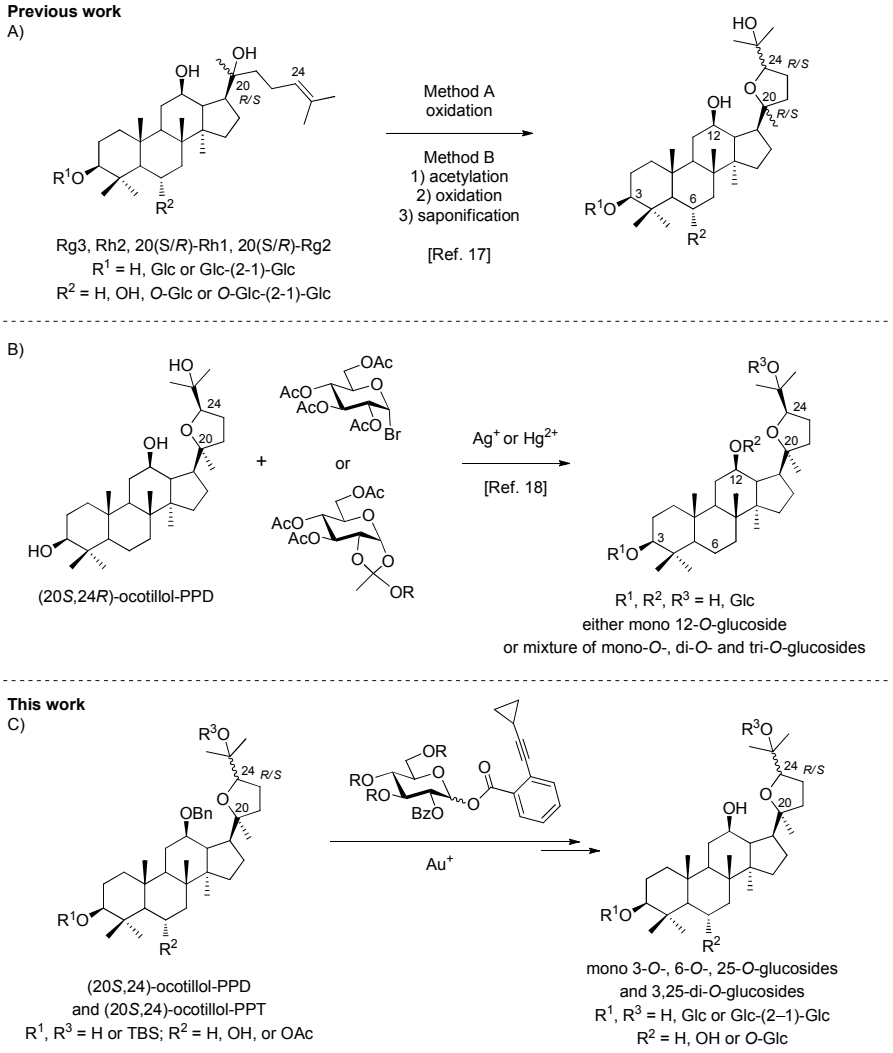
Biosynthetically, it is assumed that ocotillol-type ginsenosides are derived from dammarane ginsenosides after epoxidation of the C-24–C-25 double bond followed by an intramolecular cyclization of the 20-OH.[16] Based on this consideration, semi-synthesis of ocotillol-type ginsenosides have been described by oxidation of the corresponding dammarane saponins. The oxidation is usually carried out with *m*-CPBA, H_2O_2, or oxone either on the natural or partially protected dammarane saponins.[18] The cyclization then provides a 1:1 mixture of C-24 epimers while the configuration at the C-20 remains unchanged (Scheme 1, A). However, this method suffers from undesired oxidized byproducts and is limited by the availability of the starting dammarane saponins. Indeed, synthetic ocotillol-type ginsenosides bearing a sugar moiety at the C-25 cannot be synthesized under these conditions.

Direct glycosylation between an ocotillol aglycone and a sugar donor appears as the most straightforward approach to synthesize various ocotillol-type saponins. In this regard, Atopkina *et al.* reported the synthesis of ocotillol-type ginsenosides by coupling between (20*S*,24*R*)-ocotillol-PPD acceptor and α-acetobromoglucose and orthoester donors under the promotion of silver or mercury salts (Scheme 1, B).[19] Although, ocotillol-type ginsenosides bearing a glucose unit at the sterically hindered 25-OH could be

synthesized, the low to moderate regioselectivity and yields as well as the use of toxic promoter clearly represent a limitation. Accordingly, the development of an alternative glycosylation protocol is still of great interest.

For several years now, our group has devoted much effort on the chemical synthesis of triterpenoid saponins.[20] The preparation of the sterically hindered and acid-labile dammarane ginsenosides have been successfully achieved through the selective protection of the hydroxyl groups of the sapogenins as well as the development of a gold(I)-catalyzed glycosylation protocol which proceeds under neutral conditions.[21,22] Herein, we report the synthesis of mono 3-*O*-, 6-*O*-, 25-*O*- and 3,25-di-*O*-glucosyl ocotillol-type PPD and PPT ginsenosides by glycosylation between a partially protected ocotillol sapogenin and a glucosyl *ortho*-alkynylbenzoate donor (Scheme 1, C).

Scheme 1. Synthetic access to ocotillol-type ginsenosides. Ac = acetyl; Bn = benzyl; Glc = β-D-glucopyranosyl; TBS = *tert*-butyldimethylsilyl.

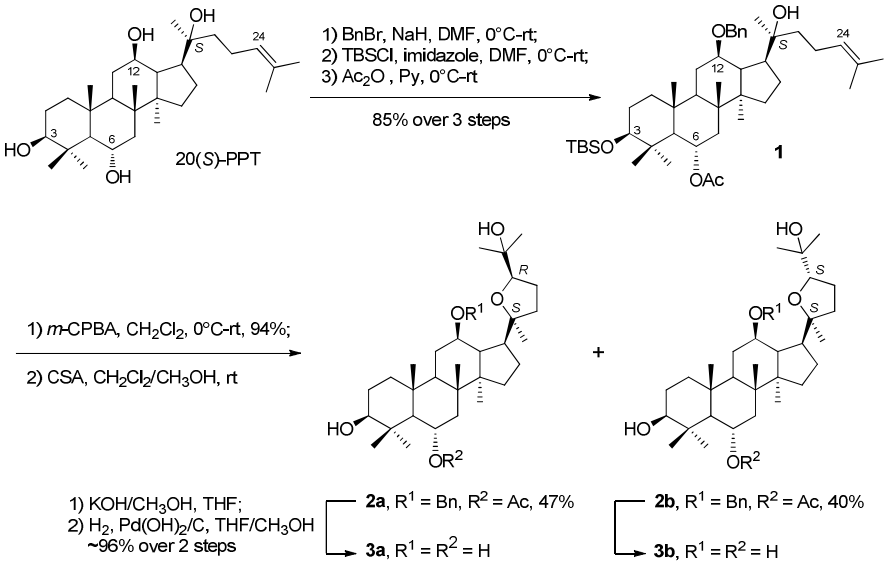


RESULTS AND DISCUSSION

Initially, four ocotillol-PPT and PPD sapogenins were prepared from 20(*S*)-PPT and 20(*S*)-PPD, respectively. Relying on our previous results which clearly established the reactivity sequence of the four hydroxyl groups of 20(*S*)-PPT (12-OH > 3-OH > 6-OH >> 20-OH) and demonstrated that an ether protecting group at the 12-OH increases the nucleophilicity of the 20-OH by intramolecular H-bonding,[21] 20(*S*)-PPT

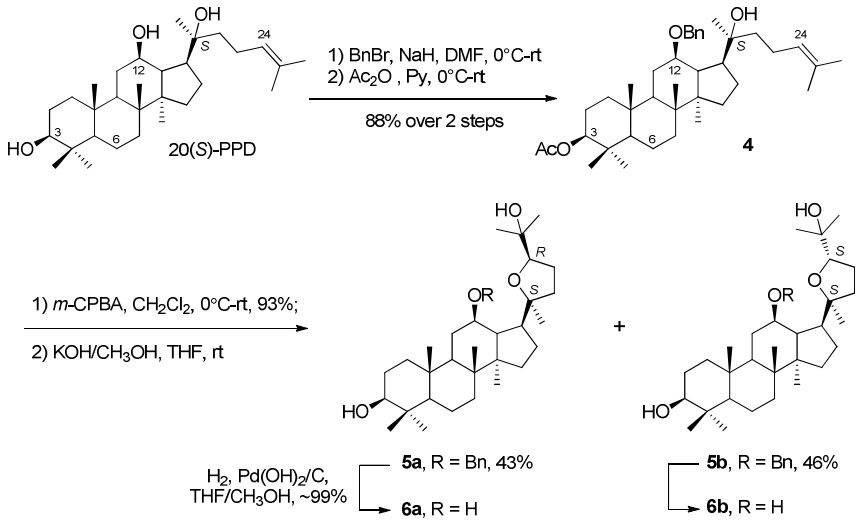
was orthogonally protected as depicted in Scheme 2. The 12-, 3- and 6-OHs were protected, in this order, as benzyl ether, *tert*-butyldimethyl-silyl ether (TBS), and acetyl, respectively, providing the 20(*S*)-OH PPT derivative **1** in 85% yield (3 steps). Then, the construction of the THF-ring in a stereoselective manner was attempted by using *t*-BuOOH and a catalytic amount of $VO(acac)_2$ in CH_2Cl_2.[23] However, no stereoselectivity was observed and the corresponding ocotillol-PPT was isolated in a moderate 55% yield and in a 1:1 mixture of cis/trans-THF ring. Thus, standard *m*-CPBA in CH_2Cl_2 was employed and provided the corresponding ocotillol-PPT in a high 94% yield,[18] albeit in an 1:1 mixture of 24(*R/S*)-epimers, inseparable at this stage. Several functionalizations of the 25-OH were carried out in order to separate the two diastereoisomers. Fortunately, they could be cleanly separated at the next step, that is after removal of the TBS group with camphorsulfonic acid (CSA), providing the two 3,25-diol PPT sapogenins **2a** (47%) and **2b** (40%). In order to confirm the configuration of the C-24, the acetyl and benzyl groups were removed under basic and hydrogenolytic conditions and the NMR spectra of the corresponding fully deprotected ocotillol-PPT were compared with the literature. Based on the difference of chemical shifts between the C-27 and C-26,[24] **3a** was found to have the *R*-configuration ($\Delta_{C27\text{-}C26}$ = 0.5 ppm) and **3b** the *S*-configuration ($\Delta_{C27\text{-}C26}$ = 2.2 ppm). As expected, the configuration of the C-20(*S*) remained unchanged. Furthermore, a single crystal of **3b** was subjected to X-ray diffraction analysis and confirmed unambiguously the configuration of C-20 and C-24 (Supporting Info).[25]

Scheme 2. Synthesis of ocotillol-PPT sapogenins **2a** and **2b**.



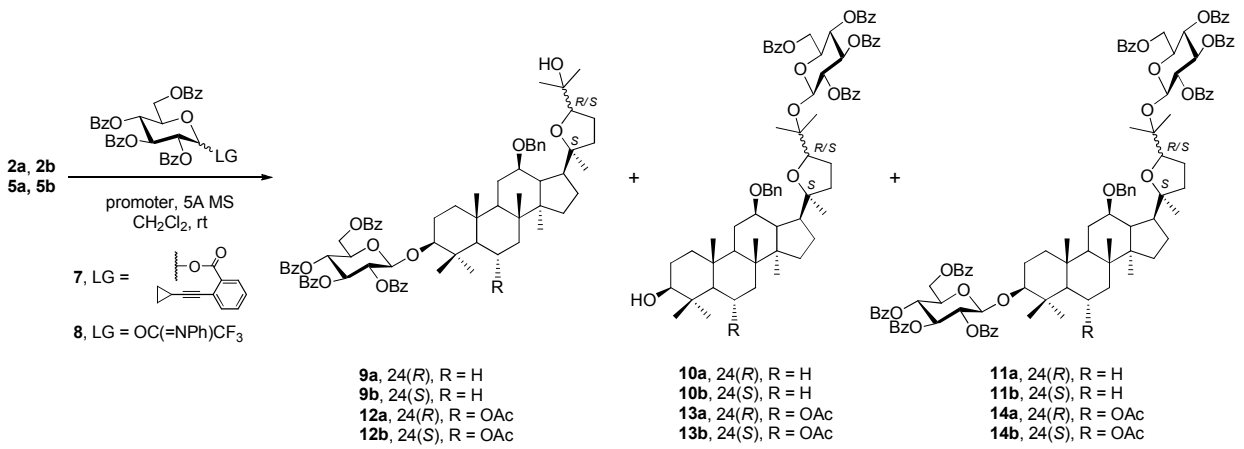
Following a similar approach, the 3- and 12-OHs of 20(*S*)-PPD were protected as acetyl and benzyl ether, respectively, affording the 20-OH PPD **4** in 88% yield over 2 steps (Scheme 3). Then, treatment with *m*-CPBA afforded the corresponding ocotillol-PPD in a 1:1 mixture of C-24 epimers (93%), inseparable at this stage. Like previously, the removal of the acetyl group under basic conditions (KOH/CH_3OH in THF) allowed us to isolate the two diastereoisomers **5a** (43%) and **5b** (46%). After hydrogenolysis of the benzyl group at the 12-position, NMR analysis demonstrated that **6a** and **6b** corresponded to the 24(*R*)- and 24(*S*)-forms, respectively, without modification of the configuration of the C-20(*S*).[26,27] In addition, the structure of **6a** was unequivocally confirmed by X-ray crystallography analysis (Supporting Info).[27]

Scheme 3. Synthesis of ocotillol-PPD sapogenins **5a** and **5b**.



Assuming that the secondary 3-OH would be more reactive than the sterically hindered tertiary 25-OH,[19] regioselective glycosylation of the four ocotillol sapogenins (**2a**/**2b**, **5a**/**5b**) with two perbenzoyl glucosyl donors, namely 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (**7**) and *N*-phenyl trifluoroacetimidate (**8**),[28] was investigated (Table 1). The reactions were performed with 1.0 equiv. of acceptor, 1.0 equiv. of donor, 5Å molecular sieves in CH_2Cl_2 at room temperature and proceeded smoothly with the donor being totally consumed after 4h. Depending on the promotion conditions, mono 3-*O*- (**9a**/**9b**, **12a**/**12b**), 25-*O*- (**10a**/**10b**, **13a**/**13b**) and 3,25-di-*O*-glucosides (**11a**/**11b**, **14a**/**14b**) were isolated, in complete 1,2-trans configuration due to the neighboring participation of the benzoyl protecting group.

Table 1. Glycosylation between ocotillol sapogenins (**2a**/**2b**, **5a**/**5b**) and perbenzoyl glucopyranosyl donors (**7**-**8**).[a]



Entry	Acceptor	Donor	Promoter (equiv.)	3-*O*-glucoside[b]	25-*O*-glucoside[b]	3,25-di-*O*-glucoside[b]
1	**5a**	**7**	$Ph_3PAuNTf_2$ (0.2)	**9a**, 12%	**10a**, 47%	**11a**, 17%
2	**5a**	**7**	$Ph_3PAuNTf_2$ (0.5)	**9a**, trace	**10a**, 61%	**11a**, 23%
3	**5a**	**8**[c]	TMSOTf (0.2)	**9a**, trace	**10a**, 36%	**11a**, 37%
4	**5b**	**7**	$Ph_3PAuNTf_2$ (0.2)	**9b**, 4%	**10b**, 59%	**11b**, 12%
5	**2a**	**7**	$Ph_3PAuNTf_2$ (0.2)	**12a**, 6%	**13a**, 58%	**14a**, 16%
6	**2b**	**7**	$Ph_3PAuNTf_2$ (0.2)	**12b**, trace	**13b**, 67%	**14b**, 14%

[a] Conditions: donor (1.0 equiv.), acceptor (1.0 equiv.), promoter, 5Å molecular sieves, CH_2Cl_2, rt, unless otherwise stated. [b] Yield% refers to the pure isolated product and is calculated based on the acceptor. [c] 1.1 equiv. of donor **8** is used. TMSOTf = trimethylsilyl trifluoromethanesulfonate.

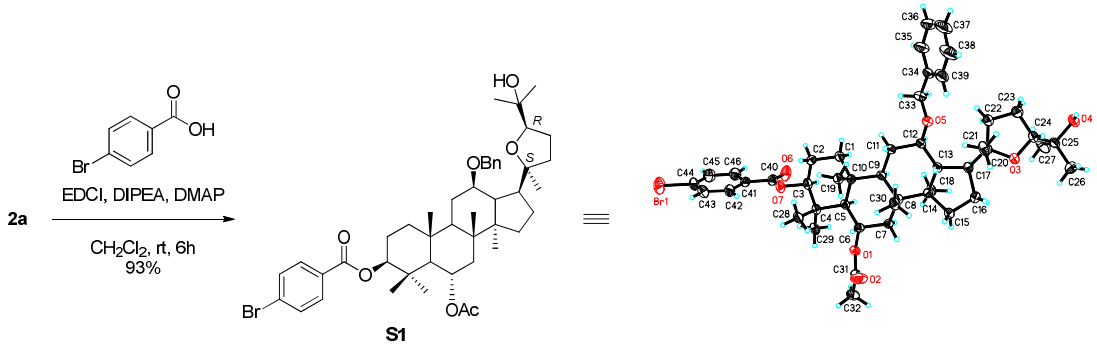
To our surprise, when coupling 3,25-diol acceptor **5a** with donor **7** under the promotion of $Ph_3PAuNTf_2$ (0.2 equiv.), 25-*O*-glycoside **10a** was isolated as the main product (47%) along with the 3-*O*-glucoside **9a** (12%) and 3,25-di-*O*-glucoside **11a** (17%, entry 1). Increasing the amount of gold(I) catalyst to 0.5 equiv. did not improve the regioselectivity of the glycosylation, although glucosides **10a** and **11a** were isolated in slightly better yields (61% and 23%, respectively). Only traces of the 3-*O*-glycoside **9a** was detected on TLC in that case (entry 2). When performing the reaction with donor **8** under the promotion of TMSOTf (0.2 equiv.), the regioselectivity of the glycosylation decreased significantly. Indeed, glucosides

10a and **11a** were isolated in 36% and 37% yields, respectively, while only traces of **9a** were detected on TLC (entry 3). The conditions employing donor **7** promoted by $Ph_3PAuNTf_2$ (0.2 equiv.) were then applied to sapogenins **5b**, **2a**, and **2b** (entries 4-6). In these cases, the 25-*O*-glycosides (**10b**, **13a**, **13b**) were also isolated as the main products in moderate yields ranging from 58% to 67%. The corresponding 3-*O*- (**9b**, **12a**, **12b**) and 3,25-di-*O*-glucosides (**11b**, **14a**, **14b**) remained as minor products, with less than 10% and 20% yields, respectively.

These results imply that the sterically hindered tertiary 25-OH of the four ocotillol sapogenin derivatives **2a**/**2b** and **5a**/**5b** is more reactive than the secondary 3-OH. A similar observation was reported by Atopkina *et al.* during the glycosylation of the 12β-OAc derivative of betulafolienetriol oxide acceptor, the 3α-epimer of ocotillol-PPD, with α-acetobromoglucose donor.[29] Based on IR analysis of the acceptor, they postulated the presence of a weak intramolecular H-bond between the proton of the 25-OH and the oxygen of the 12-OAc, resulting in an increased nucleophilicity of the 25-OH. A similar intramolecular H-bond was also suggested to explain the anomalous catalytic rearrangement of 1,2-orthoacetates of α-D-glucose and ocotillol-PPD.[30] In our case, an analogous intramolecular H-bond may explain the higher nucleophilicity of the 25-OH. In order to characterize and confirm the intramolecular H-bond, crystallization of the sapogenins **2a**/**2b** and **5a**/**5b** were attempted but have failed, due to their amorphous nature. The introduction of a 4-bromobenzoyl protecting group at the 3-OH of **2a** enabled us to obtain a single crystal of the corresponding 25-OH ocotillol-PPT sapogenin **S1** which was then analyzed by X-ray crystallography (Scheme 4). The X-ray structure did not show any intramolecular H-bond. Thus, we assume that the conformation of the ocotillol sapogenin, which depends on the protecting group pattern and the solvent in which the reaction is performed, might render the 25-OH more accessible for glycosylation. The match/mismatch of the two chiral

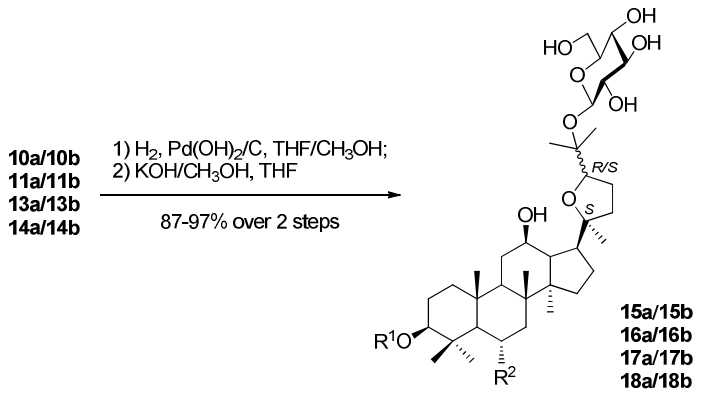
acceptor and donor might explain these results, although further study is needed.[31] It is also worth noting that the 24(*S*)-isomers provided slightly better yields than their corresponding 24(*R*)-forms under these glycosylation conditions.

Scheme 4. Synthesis and X-ray structure of sapogenin **S1**. ORTEP figure with thermal ellipsoids shown at 30% probability.



This unexpected regioselectivity provided readily synthetic ocotillol-type ginsenosides bearing a glucose unit either at the 25-position (**10a**/**10b**, **13a**/**13b**) or the 3,25-positions (**11a**/**11b**, **14a**/**14b**). Full deprotection of these 8 glycosides by a sequential removal of the benzyl group (H_2, $Pd(OH)_2/C$ in THF/CH_3OH) and the ester groups (KOH/CH_3OH in THF) afforded in excellent yields the corresponding ocotillol-type ginsenosides **15-18**, that we have named pseudo-ginsenoside OT1-OT8 (Scheme 5).

Scheme 5. Synthetic 25-*O*- and 3,25-di-*O*-glucosyl ocotillol-type ginsenosides (**15a**/**15b** – **18a**/**18b**). Glc = β-D-glucopyranosyl.

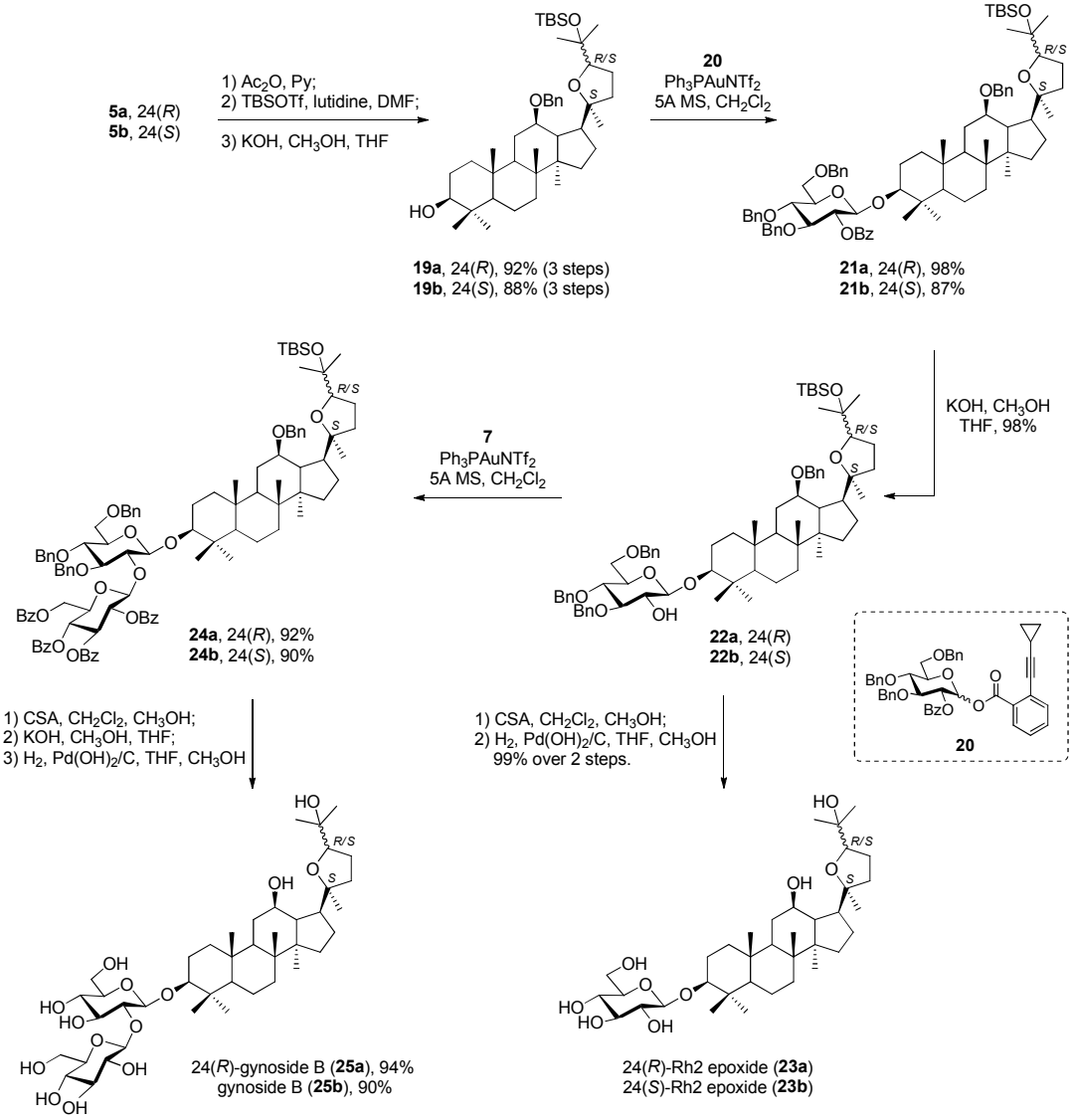


Name	C-20,C-24	R^1	R^2
pseudo-ginsenoside OT1 (**15a**)	*S,R*	H	H
pseudo-ginsenoside OT2 (**15b**)	*S,S*	H	H
pseudo-ginsenoside OT3 (**16a**)	*S,R*	Glc	H
pseudo-ginsenoside OT4 (**16b**)	*S,S*	Glc	H
pseudo-ginsenoside OT5 (**17a**)	*S,R*	H	OH
pseudo-ginsenoside OT6 (**17b**)	*S,S*	H	OH
pseudo-ginsenoside OT7 (**18a**)	*S,R*	Glc	OH
pseudo-ginsenoside OT8 (**18b**)	*S,S*	Glc	OH

Because the glycosylation prevails at the 25-OH, alternative route was designed to access natural and synthetic mono 3-*O*-glucosyl ocotillol-PPD ginsenosides. As depicted in Scheme 6, the two separated diastereoisomers **5a** and **5b** were, in parallel experiments, acetylated with Ac_2O in pyridine at room temperature. Under these reaction conditions, the secondary 3-OHs were selectively protected in excellent yields (>90%) whereas the sterically hindered tertiary 25-OHs remained free, thus corroborating the likely match/mismatch of the two chiral acceptor and donor during the glycosylation reaction. The successful protection of the 25-OHs with a TBS group was achieved using *tert*-butyldimethylsilyl triflate (TBSOTf) and 2,6-lutidine in DMF, and subsequent removal of the 3-*O*-acetyl groups under basic conditions provided the

two 3-OH ocotillol-PPD sapogenins **19a** and **19b** in excellent yields (>88% over 3 steps). Due to the low reactivity of the 3-OH observed in the previous glycosylation reactions (Table 1), the "super armed" 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (**20**) was used as donor.[32] The coupling of **19a** and **19b** with **20** proceeded smoothly and almost quantitatively under the promotion of $Ph_3PAuNTf_2$. The corresponding 3-*O*-glucosides **21a** and **21b** were obtained in excellent yields (>87%) and complete β-selectivity due to the neighboring participation of the benzoyl protecting group. Then, removal of the benzoyl group under basic conditions afforded the intermediates **22a** and **22b** (98%). On the one hand, **22a** and **22b** were fully deprotected by desilylation with CSA and hydrogenolysis of the 4 benzyl groups, thus yielding 24(*R*)-Rh2 epoxide (**23a**) and its 24(*S*)-isomer (**23b**) (99% over 2 steps).[18] On the other hand, **22a** and **22b** were coupled with donor **7** under the promotion of $Ph_3PAuNTf_2$ and provided **24a** and **24b** in high yield (>90%) and complete β-selectivity ensured by the benzoyl protecting group at the 2-position of the glucosyl donor. After full deprotection, including desilylation, saponification of the 4 benzoyl groups, and hydrogenolysis of the 4 benzyl groups, gynoside B (**25b**) and its 24(*R*)-epimer (**25a**) were isolated in 90% and 94% yields, respectively, over 3 steps. Gynoside B has also been named Rg3 oxide/epoxide or pseudo-ginsenoside GQ in the literatures.[18,26,33] It is worth mentioning that a stepwise glycosylation strategy was adopted in order to control the 1,2-trans configuration of the two glycosidic bonds, and that the NMR data of **23a**/**23b** and **25a**/**25b** were in agreement with those reported in the literature (Supporting Info).[18,26]

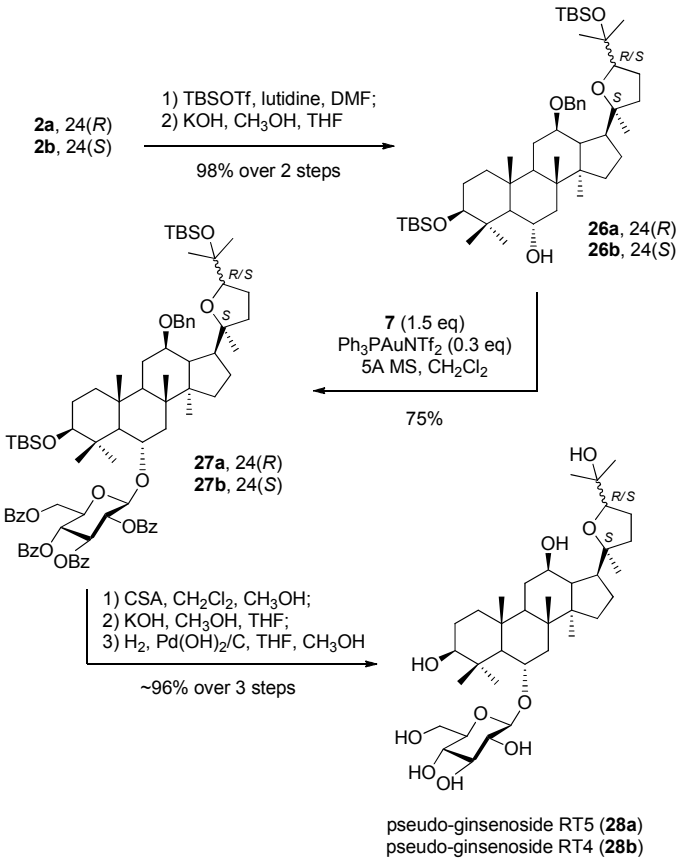
Scheme 6. Synthesis of natural and synthetic 3-*O*-glucosyl ocotillol-PPD ginsenosides (**23a**/**23b**, **25a**/**25b**).



Finally, mono 6-*O*-glucosyl ocotillol-PPT ginsenosides were conveniently synthesized starting from the two separated diastereoisomers **2a** and **2b** (Scheme 7). TBS protection (TBSOTf, 2,6-lutidine, DMF) of the 3,25-OHs followed by deacetylation (KOH/CH_3OH, THF) provided the corresponding 6-OH sapogenins **26a** and **26b** in 98% yields over 2 steps. Then, glycosylations between **26a**/**26b** and donor **7** required a slight excess of donor (1.5 equiv.) and a higher loading of $Ph_3PAuNTf_2$ (0.3 equiv./donor) to attain 75% yields of

the corresponding 6-*O*-glucosides **27a** and **27b**. Sequential removal of the TBS, benzoyl, and benzyl groups was achieved under conventional conditions and yielded the natural pseudo-ginsenosides RT5 (**28a**) and RT4 (**28b**) (95-97% over 3 steps). Their NMR data were in agreement with those reported in the literature (Supporting Info).[4,26,34]

Scheme 7. Synthesis of natural 6-*O*-glucosyl ocotillol-PPT ginsenosides (**28a**/**28b**).



CONCLUSION

In conclusion, 14 ocotillol-type ginsenosides were chemically synthesized via direct glycosylation of partially protected ocotillol sapogenins and glycosyl *ortho*-alkynylbenzoate donors under the catalysis of

$Ph_3PAuNTf_2$. The unexpected regioselectivity of the glycosylation occurring at the tertiary 25-OH of sapogenins **2a**/**2b** and **5a**/**5b** allowed us to synthesize 8 ocotillol-type ginsenosides (PPD and PPT), named pseudo-ginsenoside OTn (n = 1-8) (**15a**/**15b**-**18a**/**18b**), bearing a glucosyl unit either at the 25-position or the 3,25-positions, and in which the C-24 was either *R*- or *S*-form. Following a rational protecting group approach, 6 natural 3-*O*-glycosyl ocotillol-PPD and 6-*O*-glycosyl ocotillol-PPT ginsenosides, namely 24(*R*)-gynoside B (**25a**)/gynoside B (**25b**), 24(*R*/*S*)-Rh2 epoxide (**23a**/**23b**), and pseudo-ginsenoside RT5/RT4 (**28a**/**28b**) were also prepared conveniently and effectively. We assume that this straightforward approach represents a valuable alternative in order to access natural and synthetic ocotillol-type ginsenosides in appreciable amounts with the aim of accelerating their structure-activity relationship study.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under nitrogen or argon atmosphere with anhydrous solvents in flame-dried glassware, unless otherwise noted. All glycosylation reactions were performed in the presence of 5Å molecular sieves, which were flame-dried immediately before use in the reaction under high vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. The chemicals used were reagent grade as supplied, except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) and by heating with a solution of 10% H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.23 ppm), or C_5D_5N (^{1}H NMR δ = 7.22 ppm, ^{13}C NMR δ = 123.87 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HSQC experiments. Splitting

patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. High-resolution mass spectra were recorded on ESI-TOF and MALDI-FT spectrometers. Optical rotations were measured on a polarimeter using either $CHCl_3$ or CH_3OH as solvent.

Protopanaxadiol (PPD) *and protopanaxatriol* (PPT) were prepared readily from the crude extract of ginseng following the known procedure.[21,35] Glucosyl donors **7**, **8**, and **20** were synthesized according to literature procedures.[22,36]

General Procedure for Gold(I)-catalyzed Glycosylation with *ortho*-alkynylbenzoate Donors. To a flask were added the glucosyl donor, the sapogenin acceptor, PPh_3AuNTf_2, and freshly activated 5Å molecular sieves (weight equal to the combined weight of the donor and acceptor). The flask was evacuated and refilled with Ar, and this process was repeated for 3 times. Then, dry CH_2Cl_2 was added, and the resulting mixture was stirred at room temperature for 4h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated under vacuum (workup). The resulting residue was purified by silica gel column chromatography to provide the coupled glycosides.

General debenzylation procedure. To a solution of the benzylated compound in CH_3OH and THF was added $Pd(OH)_2/C$ (Pd 20 wt.% on carbon) and the suspension was stirred under hydrogen pressure (1 atm). After complete consumption of the benzylated compound (TLC), the suspension was filtered through a pad of Celite® and the filtrate was concentrated *in vacuo* (workup). The resulting residue was finally purified by column chromatography to provide the desired alcohol.

General saponification procedure. To a solution of the esterified compound in CH_3OH and THF was added KOH, and the mixture was stirred at room temperature overnight. After complete consumption of the esterified compound (TLC), the solvents were evaporated under reduced pressure (workup). The resulting residue was then purified by column chromatography to provide the desired alcohol.

General desilylation procedure. To a solution of the silylated (TBS) compound in a solvent mixture of CH_3OH and CH_2Cl_2 was added camphorsulfonic acid (CSA). The mixture was stirred at room temperature for 48h, and TLC showed that the TBS-compound was completely consumed. NEt_3 was added to quench the reaction and the solvents were then evaporated under reduced pressure (workup). The resulting residue was finally purified by silica gel column chromatography to provide the desired alcohol.

*3β-O-tert-Butyldimethylsilyl-6α-O-acetyl-12β-O-benzyl-20(S)-protopanaxatriol (**1**).* To a mixture of PPT (200 mg, 0.42 mmol) and 60% NaH (50 mg, 1.26 mmol) in dry DMF (25 mL) was added BnBr (56 μL, 0.50 mmol) at 0 ^oC. The ice bath was removed and the mixture was stirred at room temperature for 2h. Saturated aqueous NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with EtOAc (200 mL×3). The organic layers were combined, washed with water and brine, and dried over Na_2SO_4. The solvent was removed under vacuum to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 2:1) to afford 12β-OBn-PPT-3β,6α,20-triol **C1** as a white solid.

To a solution of **C1** and imidazole (57 mg, 0.84 mmol) in dry DMF (1.5 mL) was added TBSCl (126 mg, 0.84 mmol) at room temperature. After being stirred for 24h, the reaction mixture was diluted with EtOAc (300

mL) and washed with water and brine. The organic layer was dried over Na_2SO_4 and filtered, the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to afford 3β-OTBS,12β-OBn-PPT-6α,20-diol **C2** as a white solid.

To a solution of **C2** in dry pyridine (5 mL) was added dropwise Ac_2O (5 mL) at 0 ^oC. The resulting mixture was stirred at room temperature overnight, whereupon the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to give **1** (258 mg, 85% over 3 steps) as a white solid: $[\alpha]^{25}_D$ = +27.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.19 (m, 5H), 5.33 (dt, *J* = 10.6, 7.6 Hz, 1H), 5.09 (t, *J* = 6.4 Hz, 2H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.43 (d, *J* = 11.3 Hz, 1H), 3.45 (td, *J* = 10.2, 4.7 Hz, 1H), 3.18 (dd, *J* = 11.3, 4.5 Hz, 1H), 2.03 (s, 3H), 1.67 (s, 3H), 1.53 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 0.99 (s, 3H), 0.89 (s, 12H), 0.80 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 137.0, 130.9, 128.5, 128.0, 127.9, 125.4, 79.1, 78.8, 77.3, 77.0, 76.8, 72.6, 70.7, 69.8, 58.7, 54.0, 51.7, 49.4, 45.8, 42.4, 40.7, 39.4, 39.3, 38.7, 35.5, 30.9, 30.7, 27.3, 26.9, 26.5, 25.91, 25.85, 25.76, 22.1, 22.0, 18.1, 17.6, 17.2, 17.01, 16.98, 16.1, -3.6, -5.0; HRMS (ESI) calcd for $C_{45}H_{74}O_5SiNa$ $[M+Na]^+$ 745.5198, found 745.5187.

(20S,24R)-Epoxy-6α-O-acetyl-12β-O-benzyl-dammarane-3β,25-diol ***(2a)*** *and (20S,24S)-Epoxy-6α-O-acetyl-12β-O-benzyl-dammarane-3β,25-diol* ***(2b)***. To a solution of **1** (211 mg, 0.29 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise a solution of *m*-CPBA (100 mg, 0.58 mmol) in dry CH_2Cl_2 (5 mL) at 0 ^oC. The ice bath was removed and the mixture was stirred at room temperature overnight (control TLC showed that **1** was completely consumed). Saturated aqueous $NaHSO_3$ was added to quench the reaction, and the resulting mixture was extracted with EtOAc (100 mL×3). The organic layers were combined, washed

with water and brine, and dried over Na_2SO_4. The solvent was removed under vacuum to give a residue, which was purified by silica gel column chromatography (toluene/EtOAc, 20:1) to afford (20*S*,24)-Epoxy-3β-OTBS-6α-OAc-12β-OBn-dammarane-25-ol **C3** (203 mg, 94%) in a 1:1 mixture of C-24 isomers, as white solids.

Ocotillol sapogenin **C3** (234 mg, 0.32 mmol) was then subjected to the general desilylation procedure with CH_3OH (25 mL), CH_2Cl_2 (25 mL), and CSA (147 mg, 0.63 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 2:1) afforded ocotillol sapogenins **2a** (93 mg, 47%) and **2b** (79 mg, 40%) as white solids.

2a: $[\alpha]^{25}_D$ = +11.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.03 (m, 5H), 5.33 (td, *J* = 10.8, 4.0 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.46 (d, *J* = 12.6 Hz, 1H), 3.64 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.27 (td, *J* = 10.4, 4.6 Hz, 1H), 3.18 (dd, *J* = 11.8, 4.4 Hz, 1H), 2.04 (s, 3H), 1.21 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H), 0.83 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 139.0, 128.1, 127.7, 127.2, 86.0, 83.7, 78.9, 78.0, 70.8, 70.3, 70.2, 58.7, 51.9, 49.9, 49.3, 47.7, 42.4, 40.6, 39.4, 38.8, 38.6, 32.0, 30.4, 28.4, 28.3, 27.4, 27.0, 26.4, 24.6, 22.0, 18.3, 17.2, 16.7, 15.6; HRMS (ESI) calcd for $C_{39}H_{60}O_6Na$ $[M+Na]^+$ 647.4282 , found 647.4274.

2b: $[\alpha]^{25}_D$ = +15.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.15 (m, 5H), 5.35 (dt, *J* = 11.2, 7.3 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.36 (d, J = 11.6 Hz, 1H), 3.62 (t, *J* = 7.4 Hz, 1H), 3.35 (td, *J* = 10.2, 5.0 Hz, 1H), 3.20 (dd, *J* = 11.7, 4.5 Hz, 1H), 2.05 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 138.9, 128.1, 127.5, 127.2, 86.2, 84.4, 79.3, 78.1, 70.8, 70.7, 70.2, 58.7, 51.6, 50.3, 49.4, 47.9, 42.4, 40.6, 40.0, 39.5, 38.8, 38.6, 30.9, 30.4, 27.7, 27.5, 27.0, 26.9, 25.6, 23.9, 22.7, 22.0, 17.6, 17.0, 16.9, 15.6; HRMS (ESI) calcd for $C_{39}H_{60}O_6Na$ $[M+Na]^+$

647.4282, found 647.4271.

*(20S,24R)-Epoxy-dammarane-3β,6α,12β,25-tetraol (**3a**).*[24,25] Ocotillol sapogenin **2a** (18 mg, 0.029 mmol) was subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (8.0 mg, 0.014 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 5:3) provided (20*S*,24*R*)-epoxy-12β-OBn-dammarane-3β,6α,25-triol **C4** as a white solid (17 mg, >99%).

Ocotillol sapogenin **C4** was subjected to the general debenzylation procedure with CH_3OH (0.5 mL), THF (0.5 mL) and $Pd(OH)_2/C$ (17 mg, 0.024 mmol Pd) for 6h. After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 1:1) provided compound **3a** (13 mg, 97% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +3.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, pyridine-d5) δ 4.41 (td, *J* = 9.7, 5.3 Hz, 1H), 3.96 (t, *J* = 7.4 Hz, 1H), 3.73 (td, *J* = 10.3, 4.4 Hz, 1H), 3.51 (dt, *J* = 11.4, 4.8 Hz, 1H), 1.98 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.12 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 86.8, 85.8, 78.5, 71.3, 70.5, 67.8, 62.1, 55.2, 52.3, 50.6, 49.5, 48.5, 47.6, 41.2, 40.5, 39.6, 39.4, 33.0, 32.5, 32.0, 31.8, 28.9, 28.2, 27.8, 27.3, 27.1, 25.6, 18.5, 17.9, 17.3, 16.6; HRMS (ESI) calcd for $C_{30}H_{52}O_5Na$ $[M+Na]^+$ 515.3707, found 515.3701.

*(20S,24S)-Epoxy-dammarane-3β,6α,12β,25-tetraol (**3b**).*[24,25] Following the procedure described above for **3a**, **2b** (39 mg, 0.062 mmol) led to **3b** (31 mg, 96% over 2 steps), isolated as a white solid: $[\alpha]^{25}_D$ = +0.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, pyridine-d5) δ 4.50 – 4.40 (m, 1H), 4.20 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.80 (td, *J* = 10.1, 4.6 Hz, 1H), 3.56 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.01 (s, 3H), 1.47 (s, 6H), 1.34 (s, 3H), 1.33 (s, 3H), 1.19 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 88.6, 87.2, 78.6, 71.0, 70.1, 67.9, 62.1, 52.4,

50.4, 49.7, 49.3, 47.7, 41.3, 40.5, 39.6, 39.5, 32.83, 32.77, 32.4, 32.1, 29.2, 28.8, 28.3, 27.2, 26.8, 25.9, 18.2, 18.0, 17.4, 16.6; HRMS (ESI) calcd for $C_{30}H_{52}O_5Na$ $[M+Na]^+$ 515.3707, found 515.3707. (X-ray analysis provided in the Supporting Info).

*3β-O-Acetyl-12β-O-benzyl-20(S)-protopanaxadiol (**4**).* To a mixture of PPD (300 mg, 0.65 mmol) and 60% NaH (52 mg, 2.0 mmol) in dry DMF (45 mL) was added BnBr (109 μL, 0.78 mmol) at 0 ^oC. The ice bath was removed and the mixture was stirred at room temperature for 2h. Saturated aqueous NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with EtOAc (200 mL×3). The organic layers were combined, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to afford 12β-OBn-PPD-3β,20-diol **C5** as a white solid.

To a solution of **C5** in dry pyridine (5 mL) was added dropwise Ac_2O (5 mL) at 0 ^oC. The ice bath was removed and the resulting mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure and the resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) to give compound **4** (340 mg, 88% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +34.3 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 5H), 5.19 (brs, 1H), 5.10 (t, J = 6.6 Hz, 1H), 4.67 (d, J = 11.3 Hz, 1H), 4.54 – 4.36 (m, 2H), 3.44 (td, J = 10.3, 4.7 Hz, 1H), 2.04 (s, 3H), 1.67 (s, 3H), 1.54 (s, 3H), 1.08 (s, 3H), 0.99 (s, 3H), 0.89 (s, 3H), 0.85 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 137.1, 130.8, 128.4, 128.1, 127.8, 125.5, 80.7, 79.2, 72.5, 69.8, 55.9, 54.0, 51.9, 49.9, 46.2, 39.8, 38.6, 37.8, 37.2, 35.6, 34.6, 31.0, 28.0, 27.1, 26.6, 26.0, 25.8, 23.6, 22.2, 21.3, 18.1, 17.6, 17.0, 16.5, 16.2, 15.8; HRMS (ESI) calcd for $C_{39}H_{60}O_4Na$ $[M+Na]^+$ 615.4384, found 615.4373.

(20S,24R)-Epoxy-12β-O-benzyl-dammarane-3β,25-diol ***(5a)*** *and* *(20S,24S)-Epoxy-12β-O-benzyl-dammarane-3β,25-diol* ***(5b)***. Following the procedure described for **2a/2b**, **4** (340 mg, 0.57 mmol) led to (20S,24)-epoxy-3β-OAc-12β-OBn-dammarane-25-ol **C6** (324 mg, 93%, 1:1 mixture of C-24 isomers), isolated as a white solid.

Sapogenin **C6** (324 mg, 0.53 mmol) was subjected to the general saponification procedure with CH_3OH (5.0 mL), THF (5.0 mL) and KOH (160 mg, 2.85 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 7:1 to 5:1) afforded ocotillol sapogenins **5a** (132 mg, 43%) and **5b** (142 mg, 46%) as white solids.

5a: $[\alpha]^{25}_D$ = -14.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.10 (m, 5H), 4.62 (d, *J* = 12.7 Hz, 1H), 4.46 (d, *J* = 12.6 Hz, 1H), 3.64 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.26 (td, *J* = 10.3, 4.2 Hz, 1H), 3.18 (dd, *J* = 11.3, 4.3 Hz, 1H), 1.22 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H), 0.98 (s, 3H), 0.96 (s, 3H), 0.86 (s, 3H), 0.79 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 128.1, 127.7, 127.1, 86.0, 83.8, 79.2, 78.8, 70.2, 70.1, 55.9, 52.1, 50.5, 49.4, 48.2, 39.7, 39.0, 38.9, 37.2, 34.7, 32.0, 28.5, 28.3, 28.0, 27.5, 27.3, 26.4, 24.6, 18.4, 18.3, 16.2, 15.5, 15.3; HRMS (ESI) calcd for $C_{37}H_{58}O_4Na$ $[M+Na]^+$ 589.4227 , found 589.4221.

5b: $[\alpha]^{25}_D$ = -13.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.16 (m, 5H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 3.62 (t, *J* = 7.3 Hz, 1H), 3.35 (td, *J* = 10.3, 5.0 Hz, 1H), 3.20 (dd, *J* = 11.4, 4.6 Hz, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 1.06 (s, 3H), 0.98 (s, 3H), 0.98 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 128.1, 127.6, 127.2, 86.3, 84.4, 79.7, 78.9, 70.7, 70.1, 55.9, 51.9, 50.3, 50.0, 48.3, 40.0, 39.7, 38.9, 37.2, 34.7, 31.0, 28.0, 27.9, 27.5, 27.3, 27.0, 25.7, 23.9, 22.7, 18.3, 17.7, 16.1, 15.7, 15.3; HRMS (ESI) calcd for $C_{37}H_{58}O_4Na$ $[M+Na]^+$ 589.4227, found 589.4223.

*(20S,24R)-Epoxy-dammarane-3β,12β,25-triol (**6a**).*[26,27] Ocotillol sapogenin **5a** (14 mg, 0.025 mmol) was subjected to the general debenzylation procedure with CH_3OH (0.5 mL), THF (0.5 mL) and $Pd(OH)_2/C$ (14 mg, 0.020 mmol Pd) for 6h. After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 1:1) provided **6a** (12 mg, 99%) as a white solid: $[\alpha]^{25}_D$ = +5.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, pyridine-d5) δ 4.19 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.78 (td, *J* = 10.0, 4.5 Hz, 1H), 3.46 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.47 (s, 3H), 1.33 (s, 6H), 1.25 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 88.6, 87.2, 78.2, 70.9, 70.1, 56.6, 52.4, 50.9, 49.70, 49.68, 40.2, 39.75, 39.70, 37.6, 35.4, 32.9, 32.8, 32.4, 29.2, 28.8, 28.5, 27.1, 26.8, 26.0, 19.0, 18.3, 16.9, 16.5, 15.9; HRMS (ESI) calcd for $C_{30}H_{52}O_4Na$ $[M+Na]^+$ 499.3758, found 499.3764. (X-ray analysis provided in the Supporting Info).

*(20S,24S)-Epoxy-dammarane-3β,12β,25-triol (**6b**).*[26,27] Following the procedure described above for **6a**, **5b** (16 mg, 0.028 mmol) led to **6b** (13 mg, 99%) as a white solid: $[\alpha]^{25}_D$ = +0.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, pyridine-d5) δ 3.96 (t, *J* = 7.4 Hz, 1H), 3.72 (td, *J* = 10.1, 4.0 Hz, 1H), 3.43 (dd, *J* = 10.7, 5.3 Hz, 1H), 1.48 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 86.9, 85.8, 78.1, 71.3, 70.4, 56.6, 52.4, 51.0, 49.9, 48.6, 40.2, 39.7, 39.6, 37.6, 35.4, 33.0, 32.6, 31.8, 30.2, 29.0, 28.8, 28.4, 27.8, 27.4, 27.1, 25.6, 18.9, 18.5, 16.8, 16.4, 15.7; HRMS (ESI) calcd for $C_{30}H_{52}O_4Na$ $[M+Na]^+$ 499.3758, found 499.3761.

*3β-O-(2',3',4',6'-Tetra-O-benzoyl-β-D-glucopyranosyl)-12β-O-benzyl-(20S,24R)-epoxydammarane-25-ol (**9a**) and 12β-O-benzyl-25-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24R)-epoxydammarane-3β-ol*

*(**10a**)* *and*

*12β-O-benzyl-3,25-di-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24R)-epoxydammarane (**11a**).*

The general glycosylation procedure was used with donor **7** (134 mg, 0.176 mmol), acceptor **5a** (100 mg, 0.176 mmol) and PPh_3AuNTf_2 (26 mg, 0.035 mmol). After work-up, purification by silica gel column chromatography (toluene/EtOAc, 15:1 to 10:1) afforded saponins **9a** (24 mg, 12%), **10a** (95 mg, 47%) and **11a** (53 mg, 17%) as white solids.

9a: $[\alpha]^{25}_D$ = +9.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J = 7.6 Hz*, 2H), 7.93 (t, *J = 8.4 Hz*, 4H), 7.83 (d, *J = 7.7 Hz*, 2H), 7.54 – 7.22 (m, 17H), 5.91 (t, *J = 9.6 Hz*, 1H), 5.62 – 5.54 (m, 1H), 4.85 (d, *J = 7.9 Hz*, 1H), 4.70 – 4.59 (m, 2H), 4.59 – 4.42 (m, 2H), 4.18 – 4.11 (m, 1H), 3.64 (dd, *J = 8.4, 6.5 Hz*, 1H), 3.25 (td, *J = 10.2, 4.1 Hz*, 1H), 3.07 (dd, *J = 11.7, 4.2 Hz*, 1H), 1.21 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H), 0.93 (s, 3H), 0.80 (s, 3H), 0.76 (s, 3H), 0.66 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.9, 165.3, 165.0, 139.2, 133.4, 133.2, 133.1, 133.0, 129.84, 129.78, 129.75, 129.71, 129.4, 128.85, 128.78, 128.4, 128.31, 128.28, 128.26, 128.1, 127.7, 127.2, 103.3, 90.6, 86.0, 83.8, 79.3, 77.3, 77.2, 77.0, 76.8, 73.0, 72.1, 72.0, 70.3, 70.2, 70.0, 63.4, 56.1, 52.0, 50.4, 49.4, 48.1, 39.6, 38.9, 38.8, 36.8, 34.7, 31.9, 28.34, 28.30, 27.5, 27.4, 26.4, 26.0, 24.6, 18.3, 18.0, 16.1, 15.9, 15.5; HRMS (ESI) calcd for $C_{71}H_{85}O_{13}$ $[M+H]^+$ 1145.5985 , found 1145.5990.

10a: $[\alpha]^{25}_D$ = +9.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.20 (m, 17H), 5.88 (t, *J* = 9.6 Hz, 1H), 5.61 (t, *J* = 9.6 Hz, 1H), 5.47 (t, *J* = 8.8 Hz, 1H), 5.24 (d, *J* = 7.9 Hz, 1H), 4.60 (dd, *J* = 11.8, 2.4 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.46 (dd, *J* = 11.9, 5.8 Hz, 1H), 4.24 (d, *J* = 11.5 Hz, 1H), 4.15-4.05 (m, 1H), 3.76 (t, *J* = 6.6 Hz, 1H), 3.31 (td, *J* = 10.1, 5.0 Hz, 1H), 3.21 (dd, *J* = 11.2, 4.2 Hz, 1H), 1.13 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H), 0.99 (s,

3H), 0.98 (s, 3H), 0.90 (s, 3H), 0.86 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.9, 165.3, 164.9, 139.0, 133.3, 133.1, 133.00, 132.96, 129.8, 129.74, 129.70, 129.67, 129.0, 128.9, 128.4, 128.3, 128.2, 128.1, 127.5, 127.1, 96.2, 86.6, 82.1, 80.1, 79.6, 78.9, 77.2, 73.3, 72.2, 72.0, 70.2, 70.0, 63.6, 55.9, 51.5, 51.4, 50.0, 48.0, 39.7, 39.05, 38.96, 37.2, 34.7, 31.9, 31.0, 29.4, 28.0, 27.9, 27.8, 27.3, 25.9, 23.2, 23.1, 22.7, 21.2, 18.3, 17.6, 16.1, 15.7, 15.3, 14.1; HRMS (ESI) calcd for $C_{71}H_{84}O_{13}Na$ $[M+Na]^+$ 1167.5804, found 1167.5793.

11a: $[\alpha]^{25}_D$ = +16.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 8.03 – 8.00 (m, 2H), 8.00 – 7.95 (m, 4H), 7.95 – 7.90 (m, 4H), 7.88 – 7.81 (m, 4H), 7.58 – 7.22 (m, 29H), 5.94 (t, *J* = 9.7 Hz, 1H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.67 – 5.55 (m, 3H), 5.48 (dd, *J* = 9.7, 8.1 Hz, 1H), 5.26 (d, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 7.9 Hz, 1H), 4.66 – 4.52 (m, 4H), 4.47 (dd, *J* = 12.0, 5.9 Hz, 1H), 4.27 (d, *J* = 11.4 Hz, 1H), 4.2-4.15 (m, 1H), 4.15 – 4.07 (m, 1H), 3.77 (t, *J* = 7.0 Hz, 1H), 3.31 (td, *J* = 10.2, 5.1 Hz, 1H), 3.11 (dd, *J* = 11.7, 4.4 Hz, 1H), 1.14 (s, 3H), 1.09 (s, 3H), 1.03 (s, 3H), 0.94 (s, 3H), 0.87 (s, 3H), 0.80 (s, 3H), 0.71 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 166.0, 165.9, 165.32, 165.28, 165.0, 164.9, 138.9, 134.2, 134.1, 133.5, 133.4, 133.2, 133.14, 133.11, 133.04, 132.99, 132.00, 131.98, 129.85, 129.81, 129.75, 129.70, 129.65, 129.63, 129.4, 129.3, 129.2, 128.95, 128.90, 128.82, 128.76, 128.44, 128.38, 128.30, 128.26, 128.2, 127.5, 127.2, 103.3, 96.2, 90.6, 86.6, 82.1, 80.1, 79.7, 73.3, 72.9, 72.2, 72.1, 72.0, 70.3, 70.1, 69.9, 63.6, 63.4, 56.1, 51.5, 51.3, 49.9, 48.0, 39.7, 39.1, 38.9, 38.8, 36.8, 34.7, 31.0, 27.8, 27.7, 27.6, 26.0, 23.2, 23.1, 21.3, 18.0, 17.5, 15.9, 15.6; HRMS (ESI) calcd for $C_{105}H_{110}O_{22}Na$ $[M+Na]^+$ 1745.7381, found 1745.7361.

3β-O-(2',3',4',6'-Tetra-O-benzoyl-β-D-glucopyranosyl)-12β-O-benzyl-(20S,24S)-epoxydammarane-25-ol ***(9b)*** *and 12β-O-benzyl-25-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24S)-epoxydammarane-3β-ol* ***(10b)*** *and*

12β-O-benzyl-3,25-di-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24S)-epoxydammarane ***(11b)***.

The general glycosylation procedure was used with donor **7** (134 mg, 0.176 mmol), acceptor **5b** (100 mg, 0.176 mmol) and PPh_3AuNTf_2 (26 mg, 0.035 mmol). After work-up, purification by silica gel column chromatography (toluene/EtOAc, 15:1 to 10:1) provided saponins **9b** (8 mg, 4%), **10b** (120 mg, 59%) and **11b** (38 mg, 12%) as white solids.

9b: $[\alpha]^{25}_D$ = +10.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J = 7.7 Hz*, 2H), 7.97 – 7.90 (m, 4H), 7.83 (d, *J = 7.7 Hz*, 2H), 7.55 – 7.22 (m, 17H), 5.92 (t, *J = 9.6 Hz*, 1H), 5.62 – 5.54 (m, 2H), 4.85 (d, *J = 7.9 Hz*, 1H), 4.66 – 4.57 (m, 2H), 4.54 (dd, *J = 11.8, 6.7 Hz*, 1H), 4.37 (d, *J = 11.4 Hz*, 1H), 4.18 – 4.11 (m, 1H), 3.62 (t, *J = 7.1 Hz*, 1H), 3.33 (td, *J = 9.9, 4.8 Hz*, 1H), 3.09 (dd, *J = 11.6, 4.0 Hz*, 1H), 1.15 (s, 3H), 1.14 (s, 3H), 1.06 (s, 3H), 0.93 (s, 3H), 0.84 (s, 3H), 0.79 (s, 3H), 0.68 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.8, 165.3, 165.0, 138.9, 133.4, 133.2, 133.1, 132.9, 129.83, 129.78, 129.75, 129.70, 129.4, 128.82, 128.76, 128.4, 128.3, 128.2, 127.5, 127.2, 103.3, 90.6, 86.3, 84.4, 79.7, 77.3, 77.2, 77.0, 76.7, 72.9, 72.1, 71.9, 70.6, 70.3, 70.0, 63.4, 56.1, 51.8, 50.3, 50.0, 48.3, 40.0, 39.6, 38.9, 38.8, 36.8, 34.6, 31.9, 30.9, 29.3, 27.7, 27.5, 27.0, 26.0, 25.6, 23.9, 22.7, 18.0, 17.6, 15.9, 15.6, 14.1; HRMS (ESI) calcd for $C_{71}H_{85}O_{13}$ $[M+H]^+$ 1145.5985 , found 1145.5987.

10b: $[\alpha]^{25}_D$ = +3.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (t, *J* = 7.3 Hz, 4H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.18 (m, 17H), 5.92 – 5.80 (m, 1H), 5.57 (t, *J* = 9.7 Hz, 1H), 5.54 – 5.35 (m, 2H), 4.65 – 4.55 (m, 2H), 4.48 (dd, *J* = 11.9, 6.6 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 4.14 – 4.10 (m, 1H), 3.60 (dd, *J* = 9.4, 5.1 Hz, 1H), 3.34 (td, *J* = 10.2, 4.9 Hz, 1H), 3.22 (dd, *J* = 11.3, 4.5 Hz, 1H), 1.19 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H), 1.02 (s, 3H), 1.00 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.8, 165.3, 165.0, 139.0, 133.3, 133.1, 133.0, 132.9, 129.84, 129.81, 129.73, 129.69, 129.0,

128.9, 128.4, 128.3, 128.2, 128.1, 127.6, 127.2, 96.6, 86.8, 84.6, 80.2, 79.7, 78.9, 77.3, 77.0, 76.8, 73.3, 72.2, 71.9, 70.3, 70.1, 63.7, 55.9, 51.9, 51.0, 50.0, 48.3, 39.7, 39.5, 39.0, 37.2, 34.7, 31.1, 29.7, 29.0, 28.0, 27.8, 27.3, 26.2, 24.2, 22.3, 21.0, 18.3, 17.6, 16.1, 15.7, 15.4; HRMS (ESI) calcd for $C_{71}H_{84}O_{13}Na$ $[M+Na]^+$ 1167.5804, found 1167.5793.

11b: $[\alpha]^{25}_D$ = +14.0 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 8.03 – 7.98 (m, 4H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.93 (t, *J* = 7.4 Hz, 4H), 7.84 (t, *J* = 6.6 Hz, 4H), 7.58 – 7.24 (m, 29H), 5.94 (t, *J* = 9.7 Hz, 1H), 5.87 (t, *J* = 9.5 Hz, 1H), 5.63-5.53 (m, 3H), 5.54 – 5.36 (m, 2H), 4.87 (d, *J* = 8.8 Hz, 1H), 4.65 – 4.52 (m, 4H), 4.48 (dd, *J* = 11.9, 6.6 Hz, 1H), 4.31 (d, *J* = 8.4 Hz, 1H), 4.18 – 4.14 (m, 1H), 4.15 – 4.03 (m, 1H), 3.60-3.58(m, 1H), 3.31 (td, *J* = 10.1, 4.9 Hz, 1H), 3.11 (dd, *J* = 11.7, 4.2 Hz, 1H), 1.19 (s, 3H), 1.06 (s, 6H), 0.97 (s, 3H), 0.88 (s, 3H), 0.81 (s, 3H), 0.71 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 166.0, 165.9, 165.8, 165.34, 165.31, 165.02, 164.96, 138.9, 134.2, 134.1, 133.5, 133.3, 133.2, 133.1, 133.0, 132.9, 132.0, 129.84, 129.80, 129.76, 129.73, 129.68, 129.4, 129.3, 129.2, 129.0, 128.9, 128.84, 128.77, 128.43, 128.37, 128.30, 128.26, 128.23, 128.21, 127.6, 127.3, 103.3, 96.6, 90.6, 86.8, 84.6, 80.2, 79.8, 77.3, 77.0, 76.8, 73.3, 72.9, 72.2, 72.1, 72.0, 71.9, 70.3, 70.1, 63.7, 63.4, 56.1, 51.9, 50.9, 50.0, 48.2, 39.7, 39.5, 38.9, 38.8, 36.8, 34.7, 31.1, 29.7, 28.9, 27.7, 27.6, 26.2, 26.0, 24.1, 22.3, 21.0, 18.0, 17.6, 15.97, 15.96, 15.6; HRMS (ESI) calcd for $C_{105}H_{110}O_{22}Na$ $[M+Na]^+$ 1745.7381, found 1745.7364.

3β-O-(2',3',4',6'-Tetra-O-benzoyl-β-D-glucopyranosyl)-6α-O-acetyl-12β-O-benzyl-(20S,24R)-epoxydammarane-25-ol ***(12a)*** *and*

6α-O-acetyl-12β-O-benzyl-25-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24R)-epoxydammarane-3β-ol ***(13a)*** *and*

*6α-O-acetyl-12β-O-benzyl-3,25-di-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24R)-epoxydammarane (**14a**).* The general glycosylation procedure was used with donor **7** (122 mg, 0.16 mmol), acceptor **2a** (100 mg, 0.16 mmol) and PPh_3AuNTf_2 (23 mg, 0.032 mmol). After work-up, purification by silica gel column chromatography (petroleum ether/EtOAc, 5:2 to 2:1) provided saponins **12a** (12 mg, 6%), **13a** (112 mg, 58%) and **14a** (46 mg, 16%) as white solids.

12a: $[\alpha]^{25}_D$ = +13.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J = 7.6 Hz*, 2H), 7.95 – 7.90 (m, 4H), 7.83 (d, *J = 7.7 Hz*, 2H), 7.55 – 7.22 (m, 17H), 5.91 (t, *J = 9.6 Hz*, 1H), 5.63 – 5.53 (m, 2H), 5.20 (td, *J = 10.6, 3.2 Hz*, 1H), 4.84 (d, *J = 7.9 Hz*, 1H), 4.68 – 4.60 (m, 1H), 4.53 (dd, *J = 11.9, 6.5 Hz*, 1H), 4.46 (d, *J = 12.5 Hz*, 1H), 4.22 – 4.08 (m, 1H), 3.66 – 3.60 (m, 1H), 3.25 (td, *J = 10.2, 4.3 Hz*, 1H), 3.05 (dd, *J = 11.8, 4.4 Hz*, 1H), 1.83 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H), 0.78 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 166.0, 165.9, 165.3, 165.0, 139.1, 133.5, 133.2, 133.1, 133.0, 129.9, 129.8, 129.5, 128.9, 128.8, 128.4, 128.35, 128.32, 128.2, 127.7, 127.3, 103.5, 89.9, 86.0, 83.8, 79.1, 72.9, 72.2, 72.0, 70.5, 70.3, 70.2, 63.4, 59.0, 51.8, 49.8, 49.6, 47.8, 42.4, 40.6, 39.0, 38.9, 38.5, 36.5, 31.9, 31.8, 29.9, 29.4, 28.25, 28.19, 27.2, 26.4, 25.6, 25.0, 24.6, 22.7, 21.8, 18.2, 17.0, 16.8, 16.1, 14.1; HRMS (ESI) calcd for $C_{73}H_{86}O_{15}Na$ $[M+Na]^+$ 1225.5859 , found 1225.5847.

13a: $[\alpha]^{25}_D$ = +20.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.21 (m, 17H), 5.89 (t, *J* = 9.6 Hz, 1H), 5.61 (t, *J* = 9.7 Hz, 1H), 5.47 (t, *J* = 9.4 Hz, 1H), 5.37 (td, *J* = 10.3, 5.0 Hz, 1H), 5.24 (d, *J* = 7.9 Hz, 1H), 4.60 (dd, *J* = 11.9, 2.4 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.47 (dd, *J* = 11.9, 5.9 Hz, 1H), 4.25 (d, *J* = 11.5 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.75 (t, *J* = 6.7 Hz, 1H), 3.32 (td, *J* = 10.1, 5.1 Hz, 1H), 3.22 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.08 (s, 3H), 1.20 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H), 1.02 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.86 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 166.1, 165.9, 165.3, 164.9, 138.9, 133.4, 133.1, 133.03, 132.98, 129.8, 129.74, 129.73, 129.69, 129.66, 129.6, 129.0, 128.9, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 96.2, 86.5, 82.1, 80.0, 79.3, 78.3, 73.3, 72.2, 71.9, 70.8, 70.2, 70.0, 63.6, 58.7, 51.3, 49.3, 47.6, 42.5, 40.7, 39.5, 39.1, 38.8, 38.6, 30.9, 30.4, 29.7, 27.72, 27.68, 26.9, 25.8, 23.3, 23.1, 22.1, 21.1, 17.5, 17.0, 16.9, 15.6; HRMS (ESI) calcd for $C_{73}H_{86}O_{15}Na$ $[M+Na]^+$ 1225.5859, found 1225.5857.

14a: $[\alpha]^{25}_D$ = +18.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.97 – 7.88 (m, 8H), 7.83 (t, *J* = 7.0 Hz, 4H), 7.54 – 7.23 (m, 29H), 5.93 (t, *J* = 9.7 Hz, 1H), 5.88 (t, *J* = 9.7 Hz, 1H), 5.63 – 5.55 (m, 3H), 5.46 (t, *J* = 8.8 Hz, 1H), 5.23 – 5.20 (m, 2H), 4.86 (d, *J* = 7.8 Hz, 1H), 4.67 – 4.51 (m, 4H), 4.46 (dd, *J* = 11.9, 5.9 Hz, 1H), 4.25 (d, *J* = 11.3 Hz, 1H), 4.20 – 4.13 (m, 1H), 4.13 – 4.02 (m, 1H), 3.73 (t, *J* = 6.6 Hz, 1H), 3.29 (td, *J* = 14.6, 9.9 Hz, 1H), 3.08 (dd, *J* = 11.7, 4.1 Hz, 1H), 1.86 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 166.1, 165.93, 165.87, 165.28, 165.27, 165.0, 164.9, 138.7, 133.5, 133.3, 133.2, 133.1, 133.02, 132.98, 132.96, 129.84, 129.81, 129.79, 129.76, 129.74, 129.68, 129.6, 129.4, 129.0, 128.9, 128.81, 128.76, 128.43, 128.37, 128.3, 128.24, 128.21, 127.4, 127.3, 103.5, 96.2, 89.8, 86.4, 82.0, 79.9, 79.3, 73.3, 72.8, 72.2, 72.1, 72.0, 71.9, 70.5, 70.3, 70.2, 69.9, 63.6, 63.3, 58.9, 51.35, 51.28, 49.3, 47.5, 42.4, 40.6, 39.1, 39.0, 38.8, 38.4, 31.9, 30.8, 29.9, 29.7, 29.3, 27.7, 27.5, 25.8, 25.6, 23.3, 23.1, 22.7, 21.8, 21.1, 17.5, 16.9, 16.8, 16.1, 14.1; HRMS (ESI) calcd for $C_{107}H_{112}O_{24}Na$ $[M+Na]^+$ 1803.7436, found 1803.7410.

6α-O-Acetyl-12β-O-benzyl-25-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24S)-epoxydammara ne-3β-ol ***(13b)*** *and* *6α-O-acetyl-12β-O-benzyl-3,25-di-O-(2',3',4',6'-tetra-O-benzoyl-β-D-glucopyranosyl)-(20S,24S)-epoxydam*

*marane (**14b**).* The general glycosylation procedure was used with donor **7** (122 mg, 0.16 mmol), acceptor **2b** (100 mg, 0.16 mmol) and PPh_3AuNTf_2 (23 mg, 0.032 mmol). After work-up, purification by silica gel column chromatography (petroleum ether/EtOAc, 5:2 to 2:1) afforded saponins **13b** (130 mg, 67%) and **14b** (40 mg, 14%) as white solids.

13b: $[\alpha]^{25}_D$ = +24.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.1 Hz, 4H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.14 (m, 17H), 5.85 (t, *J* = 9.2 Hz, 1H), 5.56 (t, *J* = 9.7 Hz, 1H), 5.49 – 5.40 (m, 2H), 5.41 – 5.29 (m, 1H), 4.64 – 4.53 (m, 2H), 4.47 (dd, *J* = 11.9, 6.6 Hz, 1H), 4.31 (d, *J* = 11.5 Hz, 1H), 4.13 – 4.10 (m, 1H), 3.58 (dd, *J* = 9.2, 4.7 Hz, 1H), 3.33 (td, *J* = 10.1, 5.2 Hz, 1H), 3.21 (dd, *J* = 11.5, 4.0 Hz, 1H), 2.07 (s, 3H), 1.19 (s, 3H), 1.18 (s, 3H), 1.14 (s, 3H), 1.05 (s, 6H), 0.98 (s, 3H), 0.93 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 166.1, 165.8, 165.4, 165.0, 138.8, 133.4, 133.1, 133.03, 132.96, 129.84, 129.81, 129.72, 129.69, 129.0, 128.9, 128.4, 128.3, 128.24, 128.18, 127.6, 127.2, 96.6, 86.6, 84.5, 80.1, 79.4, 78.2, 73.3, 72.2, 72.0, 70.8, 70.3, 70.2, 63.7, 58.7, 51.7, 51.0, 49.4, 47.8, 42.5, 40.7, 39.55, 39.52, 38.9, 38.6, 31.0, 30.4, 29.7, 28.9, 27.7, 26.9, 26.1, 24.1, 22.2, 22.0, 21.0, 17.5, 17.0, 16.9, 15.6; HRMS (ESI) calcd for $C_{73}H_{86}O_{15}Na$ $[M+Na]^+$ 1225.5859, found 1225.5854.

14b: $[\alpha]^{25}_D$ = +15.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 8.00 (t, *J* = 7.3 Hz, 4H), 7.97 – 7.89 (m, 6H), 7.85 (t, *J* = 8.1 Hz, 4H), 7.58 – 7.24 (m, 29H), 5.94 (t, *J* = 9.7 Hz, 1H), 5.86 (t, *J* = 9.4 Hz, 1H), 5.67 – 5.54 (m, 3H), 5.51 – 5.41 (m, 2H), 5.25 (td, *J* = 10.4, 4.1 Hz, 1H), 4.87 (d, *J* = 7.8 Hz, 1H), 4.67 – 4.52 (m, 4H), 4.48 (dd, *J* = 11.8, 6.6 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 4.21 – 4.15 (m, 1H), 4.15 – 4.10 (m, 1H), 3.59 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.35 – 3.28 (m, 1H), 3.09 (dd, *J* = 11.7, 4.1 Hz, 1H), 1.88 (s, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.87 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 166.1, 165.95, 165.88, 165.8, 165.35, 165.29, 165.0, 164.9, 138.7, 133.5, 133.4, 133.3,

133.09, 133.06, 133.03, 132.98, 132.9, 129.84, 129.80, 129.76, 129.73, 129.68, 129.4, 129.0, 128.9, 128.8, 128.7, 128.45, 128.39, 128.32, 128.28, 128.25, 128.23, 127.5, 127.3, 103.5, 96.5, 89.9, 86.6, 84.4, 80.2, 79.4, 73.3, 72.8, 72.2, 72.1, 72.0, 71.9, 70.4, 70.3, 70.2, 70.1, 63.7, 63.3, 58.9, 51.6, 51.0, 49.4, 47.7, 42.4, 40.6, 39.5, 39.0, 38.8, 38.4, 30.9, 29.9, 29.7, 28.9, 27.5, 26.1, 25.6, 24.0, 22.2, 21.8, 21.1, 17.5, 16.9, 16.1; HRMS (ESI) calcd for $C_{107}H_{112}O_{24}Na$ $[M+Na]^+$ 1803.7436, found 1803.7420.

25-O-β-D-Glucopyranosyl-(20S,24R)-epoxydammarane-3β,12β-diol ***(15a)***. The general debenzylation procedure was used with **10a** (38 mg, 0.033 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (38 mg, 0.054 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (18 mg, 0.33 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 5:1) provided **15a** (20 mg, 97% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +11.4 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.84 (d, J = 7.6 Hz, 1H), 4.45 (dd, J = 10.3, 2.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 4.11 (t, J = 9.2 Hz, 1H), 3.89 – 3.85 (m, 3H), 3.66 – 3.61 (m, 1H), 3.40 – 3.34 (m, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.22 (s, 3H), 1.16 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H), 0.83 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 99.1, 86.6, 85.3, 78.5, 78.22, 78.16, 76.9, 75.7, 72.1, 70.9, 63.3, 56.6, 52.5, 50.5, 49.1, 48.7, 40.1, 39.7, 39.3, 37.4, 35.3, 32.2, 32.1, 30.5, 30.1, 28.9, 28.8, 28.5, 26.0, 24.8, 24.6, 24.1, 18.9, 17.9, 16.6, 16.4, 15.8; HRMS (ESI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4284.

25-O-β-D-Glucopyranosyl-(20S,24S)-epoxydammarane-3β,12β-diol ***(15b)***. The general debenzylation procedure was used with **10b** (72 mg, 0.063 mmol), CH_3OH (2.0 mL), THF (2.0 mL) and $Pd(OH)_2/C$ (72 mg

0.10 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (5.0 mL), THF (5.0 mL) and KOH (35 mg, 0.63 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 6:1) furnished **15b** (39 mg, 97% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = -11.7 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.98 (d, *J* = 7.6 Hz, 1H), 4.42 (dd, *J* = 11.8, 2.3 Hz, 1H), 4.31 – 4.16 (m, 3H), 4.12 (t, *J* = 9.2 Hz, 1H), 3.97 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.86 – 3.83 (m, 1H), 3.65 (td, *J* = 10.2, 4.7 Hz, 1H), 3.45 – 3.29 (m, 1H), 1.46 (s, 3H), 1.42 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.83 (s, 6H); ^{13}C NMR (126 MHz, pyridine-d5) δ 99.4, 88.1, 87.0, 78.8, 78.6, 78.25, 78.20, 75.8, 71.9, 71.0, 63.0, 56.6, 52.3, 50.8, 49.5, 49.4, 40.1, 39.73, 39.66, 37.6, 35.3, 32.8, 32.7, 32.2, 29.0, 28.8, 28.6, 28.4, 26.6, 24.8, 20.4, 19.0, 18.2, 16.8, 16.4, 15.8; HRMS (ESI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4284.

3,25-Di-O-β-D-Glucopyranosyl-(20S,24R)-epoxydammarane-12β-ol ***(16a)***. The general debenzylation procedure was used with **11a** (36 mg, 0.021 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (36 mg, 0.051 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (12 mg, 0.21 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 5:1) afforded **16a** (16 mg, 96% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +19.3 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.89 (d, *J* = 7.8 Hz, 1H), 4.85 (d, *J* = 7.6 Hz, 1H), 4.58 (dd, *J* = 11.7, 2.0 Hz, 1H), 4.47 (dd, *J* = 11.8, 2.3 Hz, 1H), 4.38 (dd, *J* = 11.8, 5.5 Hz, 1H), 4.29 – 4.20 (m, 3H), 4.17 (t, *J* = 9.3 Hz, 1H), 4.12 (t, *J* = 9.2 Hz, 1H), 4.04 – 3.95 (m, 2H), 3.92 – 3.87 (m, 3H), 3.65 (td, *J* = 10.0, 4.9 Hz,

1H), 3.30 (dd, *J* = 11.7, 4.4 Hz, 1H), 1.51 (s, 3H), 1.38 (s, 3H), 1.26 (s, 3H), 1.23 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H), 0.87 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 107.1, 99.2, 89.1, 86.5, 85.3, 78.9, 78.6, 78.5, 78.2, 76.9, 76.0, 75.7, 72.1, 72.0, 70.8, 63.3, 56.6, 52.5, 50.5, 49.2, 48.7, 40.1, 39.8, 39.0, 37.0, 35.3, 32.2, 32.1, 30.5, 30.2, 28.9, 28.3, 26.9, 26.1, 24.8, 24.6, 24.1, 18.6, 17.9, 16.9, 16.6, 15.8; HRMS (ESI) calcd for $C_{42}H_{72}O_{14}Na$ $[M+Na]^+$ 823.4814, found 823.4811.

3,25-Di-O-β-D-glucopyranosyl-(20S,24S)-epoxydammarane-12β-ol ***(16b)****.* The general debenzylation procedure was used with **11b** (58 mg, 0.034 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (58 mg, 0.083 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (3.0 mL), THF (3.0 mL) and KOH (20 mg, 0.34 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 4:1) provided **16b** (26 mg, 96% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = -4.9 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.99 (d, *J* = 7.6 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.34 (dd, *J* = 11.9, 5.7 Hz, 1H), 4.29 – 4.19 (m, 4H), 4.14 (q, *J* = 9.3 Hz, 2H), 4.05 – 3.95 (m, 3H), 3.91 – 3.82 (m, 1H), 3.70 – 3.59 (m, 1H), 3.35 (dd, *J* = 11.7, 4.2 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 1.27 (s, 3H), 1.21 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H), 0.86 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 107.1, 99.4, 88.9, 88.1, 87.0, 78.9, 78.8, 78.6, 78.3, 76.0, 75.9, 72.1, 71.9, 71.0, 63.3, 63.0, 56.6, 52.3, 50.7, 49.8, 49.5, 49.4, 40.1, 39.8, 39.5, 37.1, 35.3, 32.8, 32.7, 32.2, 29.0, 28.5, 28.3, 26.9, 26.6, 24.9, 20.3, 18.6, 18.2, 16.9, 16.7, 15.7; HRMS (ESI) calcd for $C_{42}H_{73}O_{14}$ $[M+H]^+$ 801.4995, found 801.4991.

25-O-β-D-Glucopyranosyl-(20S,24R)-epoxydammarane-3β,6α,12β-triol ***(17a)****.* The general debenzylation

procedure was used with **13a** (25 mg, 0.021 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (25 mg, 0.036 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (12 mg, 0.21 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 2:1) afforded **17a** (13 mg, 96% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +31.7 (*c* 1.0, CH_3OH); ^1H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.83 (d, J = 7.4 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.37 – 4.28 (m, 1H), 4.26 – 4.15 (m, 2H), 4.09 (t, J = 9.0 Hz, 1H), 3.93 – 3.81 (m, 3H), 3.68 – 3.60 (m, 1H), 3.43 (dd, J = 10.6, 4.6 Hz, 1H), 1.89 (s, 3H), 1.49 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.20 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, pyridine-d5) δ 99.1, 86.5, 85.2, 78.5, 78.4, 78.1, 76.9, 75.7, 72.0, 70.8, 67.8, 63.2, 61.9, 52.3, 50.0, 48.7, 48.6, 47.5, 41.1, 40.4, 39.3, 39.2, 32.1, 32.0, 31.9, 30.4, 28.8, 28.2, 25.9, 24.7, 24.5, 24.0, 17.8, 17.7, 17.3, 16.5; HRMS (ESI) calcd for $C_{36}H_{62}O_{10}Na$ $[M+Na]^+$ 677.4235, found 677.4237.

*25-O-β-D-Glucopyranosyl-(20S,24S)-epoxydammarane-3β,6α,12β-triol (**17b**)*. The general debenzylation procedure was used with **13b** (20 mg, 0.017 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (20 mg, 0.028 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (2.0 mL), THF (2.0 mL) and KOH (9 mg, 0.17 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 2:1) furnished **17b** (10 mg, 92% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = -1.8 (*c* 1.0, CH_3OH); ^1H NMR (400 MHz, pyridine-d5 + 1 drop of D_2O) δ 5.01 (d, J = 7.6 Hz, 1H), 4.46 (dd, J = 11.7, 1.9 Hz, 1H), 4.41 – 4.35(m, 1H), 4.33 – 4.20 (m, 3H), 4.16 (t, J = 9.2 Hz, 1H), 4.00 (t, J = 10.0 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.67 (td, J = 10.5, 4.9 Hz, 1H), 3.51 (dd, J = 10.9, 5.2 Hz, 1H), 1.96 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.43 (s, 3H),

1.19 (s, 3H), 1.09 (s, 3H), 0.96 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, pyridine-d5) δ 99.3, 88.0, 86.9, 78.8, 78.6, 78.5, 78.2, 75.8, 71.8, 71.0, 67.8, 63.0, 62.0, 52.2, 50.3, 49.4, 49.0, 47.6, 41.2, 40.5, 39.6, 39.4, 32.7, 32.6, 32.2, 32.0, 30.1, 28.9, 28.5, 28.2, 26.5, 24.7, 20.4, 18.1, 17.9, 17.3, 16.6; HRMS (ESI) calcd for $C_{36}H_{62}O_{10}Na$ $[M+Na]^+$ 677.4235, found 677.4223.

*3,25-Di-O-β-D-glucopyranosyl-(20S,24R)-epoxydammarane-6α,12β-diol (**18a**).* The general debenzylation procedure was used with **14a** (15 mg, 0.0086 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (15 mg, 0.021 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (5 mg, 0.086 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 2:1) provided **18a** (6 mg, 87% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +22.4 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.89 (d, J = 7.7 Hz, 1H), 4.84 (d, J = 7.6 Hz, 1H), 4.56 (d, J = 11.4 Hz, 1H), 4.45 (d, J = 11.3 Hz, 1H), 4.37 (dd, J = 11.7, 5.3 Hz, 1H), 4.32 – 4.12 (m, 5H), 4.09 (t, J = 9.2 Hz, 1H), 4.02 (t, J = 9.4 Hz, 1H), 3.96 (brs, 1H), 3.92 – 3.82 (m, 3H), 3.69 – 3.59 (m, 1H), 3.35 (dd, J = 11.5, 4.1 Hz, 1H), 1.99 (s, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 1.01 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (101 MHz, pyridine-d5) δ 107.3, 99.1, 89.7, 86.4, 85.2, 78.9, 78.5, 78.4, 78.1, 76.8, 76.0, 75.6, 72.0, 71.9, 70.8, 67.6, 63.3, 63.2, 62.0, 52.3, 50.0, 48.8, 48.6, 47.5, 41.0, 40.6, 38.9, 38.8, 32.1, 31.9, 31.5, 30.4, 30.1, 28.8, 26.7, 26.0, 24.8, 24.5, 24.1, 17.9, 17.6, 17.3, 17.0; HRMS (ESI) calcd for $C_{42}H_{72}O_{15}Na$ $[M+Na]^+$ 839.4763, found 839.4760.

*3,25-Di-O-β-D-glucopyranosyl-(20S,24S)-epoxydammarane-6α,12β-diol (**18b**).* The general debenzylation

procedure was used with **14b** (22 mg, 0.012 mmol), CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (22 mg, 0.031 mmol Pd), overnight. After workup, the corresponding 12-OH compound was obtained as a crude residue. This latter was then subjected to the general saponification procedure with CH_3OH (2.0 mL), THF (2.0 mL) and KOH (7 mg, 0.12 mmol). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 2:1) provided **18b** (9 mg, 90% over 2 steps) as a white solid: $[\alpha]^{25}_D$ = +0.7 (*c* 1.0, CH_3OH); ^1H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.98 (d, *J* = 7.6 Hz, 1H), 4.92 (d, *J* = 7.7 Hz, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.38 – 4.28 (m, 2H), 4.28 – 4.18 (m, 4H), 4.17 – 4.09 (m, 2H), 4.05 (t, J = 8.4 Hz, 1H), 3.99 – 3.95 (m, 2H), 3.88 – 3.82 (m, 1H), 3.65 (td, *J* = 9.9, 4.7 Hz, 1H), 3.40 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.00 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, pyridine-d5) δ 107.4, 99.3, 89.5, 88.0, 86.9, 78.9, 78.8, 78.5, 78.2, 76.0, 75.8, 72.0, 71.8, 71.0, 67.7, 63.2, 62.9, 62.0, 52.2, 50.2, 49.4, 49.0, 47.5, 41.1, 40.7, 39.3, 38.9, 32.7, 32.5, 32.2, 31.4, 30.1, 28.9, 28.5, 26.7, 26.6, 24.8, 20.2, 18.1, 17.8, 17.2, 17.0; HRMS (ESI) calcd for $C_{42}H_{72}O_{15}Na$ $[M+Na]^+$ 839.4763, found 839.4758.

(20S,24R)-Epoxy-12β-O-benzyl-25-O-tert-butyldimethylsilyl-dammarane-3β-ol ***(19a)***. To a solution of **5a** (156 mg, 0.28 mmol) in dry pyridine (2.0 mL) was added dropwise Ac_2O (2.0 mL) at 0 ^oC. The resulting mixture was stirred at room temperature overnight, whereupon the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) to give the corresponding 3β-OAc ocotillol sapogenin **C7** (163 mg, 98%) as a white solid.

To a solution of **C7** (111 mg, 0.18 mmol) and 2,6-lutidine (42 μl, 0.36 mmol) in dry DMF (1.0 mL) was added TBSOTf (78 μl, 0.36 mmol) at 0 ^oC. The ice bath was removed and the mixture was stirred at room

temperature for 2h (control TLC showed that **C7** was completely consumed). The mixture was diluted with EtOAc and washed with water and brine. The organic layer was dried over Na_2SO_4 and filtered, and the filtrate was concentrated under vacuum. The crude residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to afford the corresponding 3β-OAc-12β-OBn-25-OTBS-ocotillol sapogenin **C8** as a white solid (124 mg, 94%).

Sapogenin **C8** (124 mg, 0.17 mmol) was subjected to the general saponification procedure with CH_3OH (2.0 mL), THF (2.0 mL) and KOH (48 mg, 0.85 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 10:1) provided **19a** (116 mg, 99%) as a white solid: $[\alpha]^{25}_D$ = -10.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 3.56 (t, *J* = 6.0 Hz, 1H), 3.36 (td, *J* = 10.2, 5.0 Hz, 1H), 3.20 (dd, *J* = 11.2, 4.4 Hz, 1H), 1.15 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 0.99 (s, 6H), 0.88 (s, 3H), 0.87 (s, 12H), 0.79 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 128.1, 127.6, 127.1, 86.6, 84.1, 79.8, 78.9, 74.9, 70.1, 55.9, 51.6, 51.5, 50.0, 48.0, 39.7, 39.5, 38.9, 37.2, 34.7, 31.1, 28.0, 27.9, 27.7, 27.3, 27.0, 26.0, 25.9, 25.2, 21.0, 18.3, 18.2, 17.6, 16.1, 15.7, 15.3, -2.1, -2.1; HRMS (ESI) calcd for $C_{43}H_{72}O_4SiNa$ $[M+Na]^+$ 703.5092, found 703.5093.

*3β-O-(2'-O-Benzoyl-3',4',6'-tri-O-benzyl-β-D-glucopyranosyl)-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24R)-epoxydammarane (**21a**).* The general glycosylation procedure was used with donor **20** (109 mg, 0.176 mmol), acceptor **19a** (60 mg, 0.088 mmol) and PPh_3AuNTf_2 (13 mg, 0.018 mmol). After work-up, purification by silica gel column chromatography (petroleum ether/EtOAc, 20:1 to 10:1) afforded **21a** (105 mg, 98%) as a white solid: $[\alpha]^{25}_D$ = +32.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (m, 15H), 7.12 (brs, 5H), 5.32 (t, *J* = 8.7 Hz, 1H), 4.83 (d,

J = 10.9 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.70 – 4.50 (m, 6H), 4.35 (d, *J* = 11.5 Hz, 1H), 3.86 – 3.75 (m, 2H), 3.70 – 3.65 (m, 2H), 3.61 – 3.50 (m, 2H), 3.37 – 3.27 (m, 1H), 3.05 (dd, *J* = 11.4, 3.8 Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H), 0.93 (s, 3H), 0.85 (s, 9H), 0.82 (s, 3H), 0.81 (s, 3H), 0.67 (s, 3H), 0.60 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 139.2, 138.4, 137.9, 137.9, 132.9, 130.1, 129.8, 128.45, 128.35, 128.28, 128.26, 128.14, 128.07, 128.06, 127.9, 127.63, 127.61, 127.5, 127.1, 103.4, 89.8, 86.6, 84.1, 82.9, 79.8, 78.4, 75.1, 75.05, 74.96, 74.2, 73.5, 70.0, 69.3, 56.2, 51.6, 51.5, 50.0, 48.0, 39.7, 39.5, 39.0, 36.9, 34.7, 31.1, 29.7, 27.9, 27.7, 27.6, 27.1, 26.1, 26.0, 25.9, 25.2, 21.0, 18.2, 18.1, 17.5, 16.03, 15.98, 15.7, -2.1; HRMS (ESI) calcd for $C_{77}H_{104}O_{10}SiNa$ $[M+Na]^+$ 1239.7291, found 1239.7292.

*3β-O-(3',4',6'-Tri-O-benzyl-β-D-glucopyranosyl)-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24R)-epoxydammarane (**22a**).* The general saponification procedure was used with **21a** (105 mg, 0.086 mmol), CH_3OH (3.0 mL), THF (3.0 mL) and KOH (29 mg, 0.86 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 10:1) provided **22a** (94 mg, 98%) as a white solid: $[\alpha]^{25}_D$ = +1.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.14 (m, 20H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.83 (dd, *J* = 10.6, 8.1 Hz, 2H), 4.62 – 4.52 (m, 4H), 4.43 – 4.26 (m, 2H), 3.74 (d, *J* = 10.6 Hz, 1H), 3.69 – 3.57 (m, 3H), 3.57 – 3.48 (m, 3H), 3.34 (td, *J* = 10.2, 5.1 Hz, 1H), 3.16 (dd, *J* = 11.6, 3.9 Hz, 1H), 1.14 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.87 (s, 3H), 0.86 (s, 12H), 0.83 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 138.7, 138.4, 138.1, 128.43, 128.41, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 105.0, 89.5, 86.6, 84.8, 84.1, 79.8, 77.8, 75.5, 75.2, 75.1, 75.02, 74.97, 73.4, 70.1, 69.4, 56.2, 51.6, 51.5, 50.0, 48.0, 39.7, 39.5, 39.2, 39.0, 37.0, 34.8, 31.1, 29.7, 28.2, 27.9, 27.7, 27.1, 26.1, 26.0, 25.9, 25.2, 21.0, 18.2, 17.6, 16.5, 16.1, 15.7, -2.1; HRMS (ESI) calcd for $C_{70}H_{100}O_9SiNa$ $[M+Na]^+$ 1135.7029, found

1135.7016.

*3β-O-β-D-Glucopyranosyl-(20S,24R)-epoxydammarane-12β,25-diol (**23a, 24(R)-Rh2 epoxide**).*[18] Compound **22a** (20 mg, 0.018 mmol) was subjected to the general desilylation procedure with CH_3OH (1.0 mL), CH_2Cl_2 (1.0 mL) and CSA (8 mg, 0.036 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 5:1) provided the corresponding 25-OH glucoside **C9** as a white solid (18 mg, >99%).

Glucoside **C9** (18 mg, 0.018 mmol) was subjected to the general debenzylation procedure with CH_3OH (1.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (18 mg, 0.026 mmol Pd). After workup, purification by silica gel column chromatography (CH_2Cl_2/CH_3OH, 8:1) afforded **23a** (11 mg, 99%) as a white solid: $[\alpha]^{25}_D$ = +11.1 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.91 (d, J = 7.8 Hz, 1H), 4.56 (dd, J = 11.8, 2.3 Hz, 1H), 4.35 (dd, J = 11.8, 5.6 Hz, 1H), 4.26 (t, J = 9.0 Hz, 1H), 4.17 (t, J = 9.2 Hz, 1H), 4.06 – 3.92 (m, 3H), 3.69 (td, J = 10.4, 4.6 Hz, 1H), 3.35 (dd, J = 11.8, 4.4 Hz, 1H), 1.46 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 0.95 (s,3H), 0.95 (s, 3H), 0.89 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 106.8, 88.8, 86.7, 85.5, 78.4, 78.2, 75.6, 71.6, 71.0, 70.4, 62.8, 56.4, 52.1, 50.7, 49.5, 48.3, 40.0, 39.6, 39.2, 36.9, 35.1, 32.8, 32.3, 31.6, 28.7, 28.1, 27.2, 27.0, 26.9, 26.6, 25.4, 18.4, 18.3, 16.7, 16.5, 15.5; HRMS (ESI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4289.

*3β-O-[2”,3”,4”,6”-Tetra-O-benzoyl-β-D-glucopyranosyl-(1→2)-3’,4’,6’-tri-O-benzyl-β-D-glucopyranosyl]-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24R)-epoxydammarane (**24a**).* The general glycosylation procedure was used with donor **7** (65 mg, 0.086 mmol), acceptor **22a** (48 mg, 0.043 mmol) and PPh_3AuNTf_2

(6 mg, 0.008 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 10:1) furnished **24a** (67 mg, 92%) as a white solid: $[\alpha]^{25}_{D}$ = +4.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.16 (m, 30H), 7.12 – 7.04 (m, 2H), 5.84 (t, *J* = 9.7 Hz, 1H), 5.69 (t, *J* = 9.7 Hz, 1H), 5.56 (t, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 7.9 Hz, 1H), 4.72 – 4.24 (m, 11H), 4.08 – 3.98 (m, 1H), 3.88 (t, *J* = 8.2 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.65 – 3.57 (m, 1H), 3.57–3.45 (m, 3H), 3.44 – 3.25 (m, 2H), 3.09 (dd, *J* = 11.6, 4.2 Hz, 1H), 1.16 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.09 (s, 3H), 0.96 (s, 3H), 0.86 (s, 12H), 0.76 (s, 6H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.8, 165.1, 165.0, 139.2, 138.3, 138.2, 137.8, 134.2, 134.1, 133.3, 133.15, 133.09, 132.9, 130.9, 129.9, 129.80, 129.78, 129.7, 129.3, 129.2, 128.9, 128.8, 128.6, 128.4, 128.33, 128.31, 128.2, 128.1, 127.83, 127.78, 127.60, 127.59, 127.56, 127.5, 127.1, 103.7, 100.6, 90.3, 86.7, 85.6, 84.1, 79.8, 78.7, 78.1, 75.4, 75.0, 74.8, 74.6, 73.4, 73.2, 72.4, 72.0, 70.0, 69.9, 69.2, 65.6, 63.2, 56.3, 51.6, 51.5, 50.0, 48.0, 39.7, 39.5, 39.4, 39.1, 36.9, 34.8, 31.1, 30.6, 29.7, 27.85, 27.75, 27.69, 27.1, 26.1, 26.0, 25.9, 25.2, 21.0, 19.2, 18.2, 18.0, 17.6, 16.1, 16.0, 15.7, 13.7, -2.1, -2.1; HRMS (ESI) calcd for $C_{104}H_{126}O_{18}SiNa$ $[M+Na]^+$ 1713.8606, found 1713.8609.

3β-O-[β-D-Glucopyranosyl-(1→2)-β-D-glucopyranosyl]-(20S,24R)-epoxydammarane-12β,25-diol ***(25a, 24(R)-gynoside B)***.[18,26] Compound **24a** (52 mg, 0.031 mmol) was subjected to the general desilylation procedure with CH_3OH (1.0 mL), CH_2Cl_2 (1.0 mL) and CSA (14 mg, 0.062 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 2:1) provided the corresponding 25-OH glucoside **C10** as a white solid (44 mg, 94%).

Glucoside **C10** (44 mg, 0.029 mmol) was subjected to the general saponification procedure with CH_3OH

(2.0 mL), THF (2.0 mL) and KOH (16 mg, 0.29 mmol). After workup, purification by silica gel column chromatography (CH_2Cl_2/CH_3OH, 15:1) provided debenzoylated glucoside **C11** as a white solid (33 mg, >99%).

Glucoside **C11** (33 mg, 0.028 mmol) was subjected the general debenzylation procedure with CH_3OH (2.0 mL), THF (2.0 mL) and $Pd(OH)_2/C$ (33 mg, 0.047 mmol Pd), overnight. After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 4:1) provided **25a** (23 mg, >99%) as a white solid: $[\alpha]^{25}_D$ = +6.8 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 5.35 (d, J = 7.7 Hz, 1H), 4.85 (d, J = 7.5 Hz, 1H), 4.56 – 4.44 (m, 2H), 4.40 – 4.14 (m, 6H), 4.12 – 4.02 (m, 2H), 3.95 (t, *J = 8.3 Hz*, 1H), 3.93 – 3.82 (m, 2H), 3.67 (td, J = 10.4, 4.5 Hz, 1H), 3.24 (dd, J = 11.7, 4.3 Hz, 1H), 1.45 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H), 0.87 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 106.2, 105.2, 88.9, 86.8, 85.7, 83.6, 78.4, 78.3, 78.2, 78.0, 77.3, 71.75, 71.70, 71.2, 70.4, 62.9, 62.8, 56.5, 52.3, 50.8, 49.8, 48.5, 40.1, 39.8, 39.3, 37.0, 35.2, 32.9, 32.5, 31.7, 28.9, 28.1, 27.8, 27.3, 27.0, 26.8, 25.6, 18.5, 18.4, 16.6, 15.6; HRMS (MALDI) calcd for $C_{42}H_{72}O_{14}Na$ $[M+Na]^+$ 823.4814, found 823.4825.

(20S,24S)-Epoxy-12β-O-benzyl-25-O-tert-butyldimethylsilyl-dammarane-3β-ol ***(19b)***. Following the procedure described above for **19a**, **5b** (171 mg, 0.30 mmol) led to the corresponding 3β-OAc ocotillol sapogenin **C12** (165 mg, 90%). TBSOTf-silylation of **C12** (143 mg, 0.23 mmol) led to the corresponding 3β-OAc-12β-OBn-25-OTBS-ocotillol sapogenin **C13** (169 mg, 99%). Finally, saponification of sapogenin **C13** (169 mg, 0.23 mmol) led to **19b** (157 mg , 99%), isolated as a white solid: $[\alpha]^{25}_D$ = -18.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5H), 4.59 (d, J = 11.6 Hz, 1H), 4.37 (d, J = 11.6 Hz, 1H), 3.55 (t, J = 7.4 Hz, 1H), 3.34 (td, J = 10.1, 5.2 Hz, 1H), 3.20 (dd, J = 11.3, 4.4 Hz, 1H), 1.14 (s, 3H), 1.13 (s, 3H), 1.10

(s, 3H), 0.98 (s, 6H), 0.88 (s, 3H), 0.85 (s, 3H), 0.83 (s, 9H), 0.78 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 128.1, 127.5, 127.1, 86.0, 85.0, 79.7, 78.9, 74.7, 70.1, 55.9, 51.9, 50.0, 49.6, 48.2, 39.7, 39.3, 38.9, 37.2, 34.7, 31.0, 28.0, 27.9, 27.7, 27.35, 27.33, 25.9, 25.6, 24.7, 22.5, 18.3, 18.1, 17.7, 16.1, 15.6, 15.3; HRMS (ESI) calcd for $C_{43}H_{72}O_4SiNa$ $[M+Na]^+$ 703.5092, found 703.5089.

*3β-O-(2'-O-Benzoyl-3',4',6'-tri-O-benzyl-β-D-glucopyranosyl)-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24S)-epoxydammarane (**21b**).* Following the procedure described above for **21a**, **19b** (95 mg, 0.14 mmol) led to **21b** (147 mg, 87%), isolated as a white solid: $[\alpha]^{25}_D$ = +20.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.21 (m, 15H), 7.15 (brs, 5H), 5.34 (t, *J* = 8.7 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 11.1 Hz, 1H), 4.74 – 4.53 (m, 6H), 4.39 (d, *J* = 11.4 Hz, 1H), 3.90 – 3.78 (m, 2H), 3.77 – 3.65 (m, 2H), 3.60 – 3.50 (m, 2H), 3.41 – 3.24 (m, 1H), 3.08 (dd, *J* = 11.5, 3.9 Hz, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 0.95 (s, 3H), 0.86 (s, 12H), 0.84 (s, 3H), 0.69 (s, 3H), 0.62 (s, 3H), 0.08 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 139.1, 138.4, 137.9, 137.8, 132.9, 130.1, 129.7, 128.4, 128.34, 128.27, 128.24, 128.14, 128.06, 128.04, 127.9, 127.62, 127.60, 127.54, 127.52, 127.1, 103.4, 89.8, 86.0, 84.9, 82.9, 79.7, 78.4, 75.1, 75.0, 74.7, 74.1, 73.5, 70.0, 69.3, 56.2, 51.9, 50.0, 49.6, 48.2, 39.7, 39.3, 39.0, 36.9, 34.7, 31.0, 29.7, 27.8, 27.6, 27.4, 26.1, 25.9, 25.7, 25.6, 24.7, 22.5, 18.15, 18.06, 17.6, 16.02, 15.96, 15.6, -2.1; HRMS (ESI) calcd for $C_{77}H_{108}NO_{10}Si$ $[M+NH_4]^+$ 1234.7737, found 1234.7733.

*3β-O-(3',4',6'-Tri-O-benzyl-β-D-glucopyranosyl)-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24S)-epoxydammarane (**22b**).* Following the procedure described above for **22a**, **21b** (147 mg, 0.12 mmol) led to **22b** (132 mg, 98%), isolated as a white solid: $[\alpha]^{25}_D$ = -4.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 –

7.09 (m, 20H), 4.95 (d, J = 11.2 Hz, 1H), 4.83 (t, J = 9.5 Hz, 2H), 4.64 – 4.50 (m, 4H), 4.37 (d, J = 11.5 Hz, 1H), 4.31 (brs, 1H), 3.74 (d, J = 10.5 Hz, 1H), 3.69 – 3.45 (m, 6H), 3.35 – 3.30 (m, 1H), 3.20 – 311 (m, 1H), 1.14 (s, 3H), 1.13 (s, 3H), 1.10 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.87 (s, 6H), 0.83 (s, 12H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 138.7, 138.4, 138.1, 128.42, 128.40, 128.3, 128.1, 128.0, 127.9, 127.8, 127.65, 127.58, 127.52, 127.49, 127.1, 104.9, 89.5, 86.0, 85.0, 84.7, 79.8, 77.8, 75.5, 75.2, 75.1, 75.0, 74.7, 73.4, 70.0, 69.4, 56.2, 52.0, 50.0, 49.6, 48.2, 39.7, 39.3, 39.2, 39.0, 36.9, 34.7, 31.0, 29.7, 28.2, 27.84, 27.77, 27.4, 26.1, 25.9, 25.6, 24.7, 22.6, 18.1, 17.7, 16.5, 16.1, 15.7, -2.1; HRMS (ESI) calcd for $C_{70}H_{100}O_9SiNa$ $[M+Na]^+$ 1135.7029, found 1135.7033.

*3β-O-β-D-Glucopyranosyl-(20S,24S)-epoxydammarane-12β,25-diol (**23b, 24(S)-Rh2 epoxide**).*[26] Following the procedure described above for **23a**, **22b** (28 mg, 0.025 mmol) led to **23b** (16 mg, 99% over 2 steps), isolated as a white solid: $[\alpha]^{25}_D$ = +8.3 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.86 (d, J = 7.8 Hz, 1H), 4.46 (d, J = 11.8 Hz, 1H), 4.31 – 4.20 (m, 2H), 4.17 – 4.04 (m, 2H), 3.99 – 3.93 (m, 2H), 3.66 (td, J = 9.8, 4.7 Hz, 1H), 3.29 (dd, J = 11.7, 4.1 Hz, 1H), 1.44 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H), 1.21 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H), 0.83 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (101 MHz, pyridine-d5) δ 106.8, 88.6, 88.2, 86.9, 78.6, 78.2, 75.6, 71.7, 70.6, 69.8, 62.9, 56.3, 52.1, 50.4, 49.30, 49.27, 39.8, 39.5, 39.1, 36.8, 35.0, 32.5, 32.4, 32.0, 28.8, 28.5, 27.9, 26.8, 26.6, 26.4, 25.6, 18.3, 17.9, 16.6, 16.4, 15.4; HRMS (ESI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4271.

*3β-O-[2",3",4",6"-Tetra-O-benzoyl-β-D-glucopyranosyl-(1→2)-3',4',6'-tri-O-benzyl-β-D-glucopyranosyl]-12β-O-benzyl-25-O-tert-butyldimethylsilyl-(20S,24S)-epoxydammarane (**24b**).* Following the procedure

described above for **24a**, **22b** (66 mg, 0.059 mmol) led to **24b** (90 mg, 90%), isolated as a white solid: $[\alpha]^{25}_{D}$ = +6.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.90 – 7.75 (m, 6H), 7.57 – 7.13 (m, 30H), 7.09 (brs, 2H), 5.85 (t, *J* = 9.6 Hz, 1H), 5.70 (t, *J* = 9.5 Hz, 1H), 5.56 (t, *J* = 8.8 Hz, 1H), 5.40 (d, *J* = 7.8 Hz, 1H), 4.75 – 4.26 (m, 11H), 4.05 (brs, 1H), 3.88 (t, *J* = 7.9 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.64 – 3.44 (m, 4H), 3.44 – 3.27 (m, 2H), 3.09 (d, *J* = 7.9 Hz, 1H), 1.15 (s, 6H), 1.13 (s, 3H), 1.09 (s, 3H), 0.96 (s, 3H), 0.86 (s, 9H), 0.76 (s, 6H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.8, 165.1, 165.0, 139.2, 138.4, 138.2, 137.8, 133.3, 133.15, 133.09, 132.9, 129.9, 129.8, 129.7, 129.2, 128.9, 128.8, 128.7, 128.4, 128.33, 128.31, 128.2, 128.1, 127.83, 127.78, 127.61, 127.56, 127.53, 127.48, 127.1, 103.7, 100.6, 90.3, 86.0, 85.6, 84.9, 79.8, 78.7, 78.1, 75.4, 74.8, 74.7, 74.6, 73.4, 73.2, 72.4, 72.0, 70.0, 69.9, 69.2, 63.2, 60.4, 56.3, 52.0, 50.0, 49.6, 48.3, 39.7, 39.4, 39.3, 39.1, 36.9, 34.8, 31.0, 29.4, 27.8, 27.7, 27.4, 26.1, 25.9, 25.6, 24.7, 22.6, 18.2, 18.0, 17.7, 16.1, 16.0, 15.7, 14.2, 0.0, -2.1; HRMS (ESI) calcd for $C_{104}H_{126}O_{18}SiNa$ $[M+Na]^+$ 1713.8606, found 1713.8604.

3β-O-[β-D-Glucopyranosyl-(1→2)-β-D-glucopyranosyl]-(20S,24S)-epoxydammarane-12β,25-diol ***(25b, gynoside B)***.[18,26] Following the procedure described above for **25a**, **24b** (55 mg, 0.032 mmol) led to **25b** (23 mg, 90% over 3 steps), isolated as a white solid: $[\alpha]^{25}_{D}$ = -5.0 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 5.38 (d, *J* = 7.3 Hz, 1H), 4.90 (d, *J* = 6.9 Hz, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.45 – 4.36 (m, 1H), 4.36 – 4.21 (m, 5H), 4.20 – 4.15 (m, 1H), 4.11 (brs, 1H), 3.93 (brs, 1H), 3.74 (brs, 1H), 3.28 (d, *J* = 7.7 Hz, 1H), 1.47 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 106.2, 105.2, 89.0, 88.5, 87.2, 83.6, 78.5, 78.4, 78.2, 78.1, 77.3, 71.8, 71.7, 70.9, 70.1, 63.0, 62.8, 56.6, 52.4, 50.7, 49.63, 49.61, 40.1, 39.8,

39.4, 37.1, 35.3, 32.8, 32.7, 32.3, 29.1, 28.8, 28.2, 27.1, 26.9, 26.7, 25.9, 18.6, 18.2, 16.7, 15.7; HRMS (MALDI) calcd for $C_{42}H_{72}O_{14}Na$ $[M+Na]^+$ 823.4814, found 823.4820.

*(20S,24R)-Epoxy-3β,25-di-O-tert-butyldimethylsilyl-12β-O-benzyl-dammarane-6α-ol (**26a**).* To a solution of **2a** (71 mg, 0.11 mmol) and 2,6-lutidine (59 μl, 0.44 mmol) in dry DMF (0.3 mL) was added TBSOTf (0.1 ml, 0.44 mmol) at 0 ^oC. The ice bath was removed and the mixture was stirred at room temperature for 4h (control TLC showed that **2a** was completely consumed). The reaction mixture was diluted with EtOAc and washed with water and brine. The organic layer was dried over Na_2SO_4 and filtered, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to afford the corresponding 3,25-di-OTBS sapogenin **C14** as a white solid (95 mg, 98%).

Sapogenin **C14** (57 mg, 0.067 mmol) was subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (18 mg, 0.33 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 20:1) provided **26a** (53 mg, 98%) as a white solid: $[\alpha]^{25}_D$ = +6.3 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.04 (m, 5H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.54 (t, *J* = 6.0 Hz, 1H), 3.34 (td, *J* = 10.1, 5.0 Hz, 1H), 3.16 (dd, *J* = 11.1, 4.4 Hz, 1H), 1.23 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.05 (s, 3H), 0.95 (s, 3H), 0.90 (s, 15H), 0.85 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.04 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 128.1, 127.5, 127.1, 86.5, 84.1, 79.6, 79.2, 77.3, 77.0, 76.7, 74.9, 70.1, 68.7, 61.3, 51.5, 51.4, 49.5, 47.6, 47.0, 40.8, 39.9, 39.5, 39.1, 38.8, 31.1, 31.0, 29.7, 27.8, 27.7, 27.4, 27.0, 25.95, 25.90, 25.2, 20.9, 18.1, 17.5, 17.2, 17.1, 16.0, -2.09, -2.10, -3.6, -4.9; HRMS (ESI) calcd for $C_{49}H_{86}O_5Si_2Na$ $[M+Na]^+$ 833.5906, found 833.5890.

*6α-O-(2',3',4',6'-Tetra-O-benzoyl-β-D-glucopyranosyl)-3β,25-di-O-tert-butyldimethylsilyl-12β-O-benzyl-(20 S, 24R)-epoxydammarane (**27a**).* The general glycosylation procedure was used with donor **7** (76 mg, 0.099 mmol), acceptor **26a** (54 mg, 0.066 mmol) and PPh_3AuNTf_2 (24 mg, 0.033 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 10:1 to 8:1) provided **27a** (68 mg, 75%) as a white solid: $[\alpha]^{25}_D$ = +9.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.91 (t, *J* = 7.7 Hz, 4H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.22 (m, 17H), 5.91 (t, *J* = 9.6 Hz, 1H), 5.72 – 5.56 (m, 2H), 5.13 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 10.3 Hz, 1H), 4.54 – 4.47 (m, 2H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.04 (t, *J* = 8.9 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.33 – 3.20 (m, 1H), 2.97 (dd, *J* = 11.2, 4.2 Hz, 1H), 1.15 (s, 3H), 1.12 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H), 0.88 (s, 3H), 0.86 (s, 12H), 0.82 (s, 3H), 0.72 (s, 9H), 0.66 (s, 3H), 0.09 (s,3H), 0.08 (s, 3H), -0.07 (s, 3H), -0.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.8, 165.2, 165.1, 139.0, 133.3, 133.1, 133.0, 129.78, 129.75, 129.69, 129.5, 129.4, 128.81, 128.78, 128.34, 128.26, 128.2, 128.08, 128.07, 127.5, 127.1, 102.4, 86.4, 84.0, 80.6, 79.6, 79.5, 74.9, 73.5, 72.2, 70.0, 69.6, 63.4, 60.0, 51.5, 51.3, 49.3, 47.5, 44.9, 40.8, 39.5, 39.3, 39.2, 38.7, 30.6, 30.4, 29.6, 27.7, 27.5, 27.1, 25.9, 25.8, 25.2, 20.8, 18.1, 17.9, 17.3, 17.2, 17.1, 15.9, -2.12, -2.15, -3.8, -5.2; HRMS (ESI) calcd for $C_{83}H_{112}O_{14}Si_2Na$ $[M+Na]^+$ 1411.7483, found 1411.7470.

*6α-O-β-D-Glucopyranosyl-(20S,24R)-epoxydammarane-3β,12β,25-triol (**28a, pseudo-ginsenoside RT5**).*[4,26,34] Compound **27a** (66 mg, 0.047 mmol) was subjected to the general desilylation procedure with CH_3OH (1.0 mL), CH_2Cl_2 (1.0 mL) and CSA (45 mg, 0.19 mmol). After workup, purification by silica gel column chromatography (petroleum ether/EtOAc, 1:1) provided the corresponding 3,25-OHs **C15** as a white solid (55 mg, 99%).

Compound **C15** (55 mg, 0.047 mmol) was subjected to the general saponification procedure with CH_3OH (1.0 mL), THF (1.0 mL) and KOH (28 mg, 0.49 mmol). After workup, purification by silica gel column chromatography (CH_2Cl_2/CH_3OH, 8:1) afforded the corresponding 12-OBn compound **C16** a white solid (36 mg, 99%).

Compound **C16** (36 mg, 0.049 mmol) was subjected to the general debenzylation procedure with CH_3OH (2.0 mL), THF (1.0 mL) and $Pd(OH)_2/C$ (36 mg, 0.051 mmol Pd). After workup, purification by RP-18 column chromatography (CH_3OH/H_2O, 5:1) provided **28a** (32 mg, >99%) as a white solid: $[\alpha]^{25}_D$ = +20.3 (*c* 1.0, CH_3OH); ^{1}H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 4.94 (d, *J* = 7.8 Hz, 1H), 4.47 (dd, *J* = 11.6, 2.4 Hz, 1H), 4.37 (td, *J* = 10.6, 3.1 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.13 (t, *J* = 9.2 Hz, 1H), 4.02 (t, *J* = 8.2 Hz, 1H), 3.96 – 3.90 (m, 2H), 3.65 (td, *J* = 10.4, 4.6 Hz, 1H), 3.47 (dd, *J* = 11.4, 5.0 Hz, 1H), 1.98 (s, 3H), 1.52 (s, 3H), 1.44 (s, 3H), 1.28 (s, 3H), 1.22 (s, 3H), 1.15 (s, 3H), 0.94 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 106.0, 86.7, 85.6, 80.1, 79.7, 78.6, 78.2, 75.5, 71.9, 71.2, 70.3, 63.1, 61.5, 52.2, 50.6, 49.4, 48.4, 45.1, 41.0, 40.4, 39.6, 39.5, 32.7, 32.4, 31.7, 28.8, 27.9, 27.7, 27.2, 27.0, 25.5, 18.0, 17.9, 17.1, 16.3; HRMS (ESI) calcd for $C_{36}H_{62}O_{10}Na$ $[M+Na]^+$ 677.4235, found 677.4240.

*(20S,24S)-Epoxy-3β,25-di-O-tert-butyldimethylsilyl-12β-O-benzyl-dammarane-6α-ol (**26b**).* Following the procedure described above for **26a**, **2b** (52 mg, 0.083 mmol) led firstly to the corresponding 3,25-di-OTBS derivative **C17**, isolated as a white solid (70 mg, 98%). Then, saponification of **C17** (53 mg, 0.062 mmol) led to **26b** (49 mg , 98%), isolated as a white solid: $[\alpha]^{25}_D$ = +6.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.09 (td, *J* = 10.3, 3.3 Hz, 1H), 3.55 (t, *J* = 7.4 Hz, 1H), 3.33 (td, *J* = 10.2, 5.0 Hz, 1H), 3.16 (dd, *J* = 11.2, 4.5 Hz, 1H), 1.23 (s, 3H), 1.14 (s, 3H), 1.12

(s, 3H), 1.09 (s, 3H), 1.05 (s, 3H), 0.95 (s, 3H), 0.90 (s, 15H), 0.83 (s, 9H), 0.05 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 128.1, 127.5, 127.1, 85.9, 85.0, 79.6, 79.2, 74.6, 70.0, 68.7, 61.3, 51.7, 49.6, 49.5, 47.8, 46.9, 40.8, 39.9, 39.3, 39.1, 38.8, 31.1, 30.9, 29.7, 27.8, 27.7, 27.4, 27.3, 25.94, 25.87, 25.6, 24.7, 22.5, 18.15, 18.13, 17.6, 17.2, 17.1, 16.0, -2.10, -2.11, -3.6, -4.9; HRMS (ESI) calcd for $C_{49}H_{86}O_5Si_2Na$ $[M+Na]^+$ 833.5906, found 833.5894.

*6α-O-(2',3',4',6'-Tetra-O-benzoyl-β-D-glucopyranosyl)-3β,25-di-O-tert-butyldimethylsilyl-12β-O-benzyl-(20 S,24S)-epoxydammarane (**27b**).* Following the procedure described above for **27a**, **26b** (56 mg, 0.070 mmol) led to **27b** (72 mg, 75%), isolated as a white solid: $[\alpha]^{25}_D$ = +8.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.90 (t, *J* = 7.3 Hz, 4H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.58 – 7.18 (m, 17H), 5.91 (t, *J* = 9.4 Hz, 1H), 5.70 – 5.55 (m, 2H), 5.12 (d, *J* = 7.4 Hz, 1H), 4.63 – 4.46 (m, 3H), 4.33 (d, *J* = 11.5 Hz, 1H), 4.24 (brs, 1H), 4.04 (t, *J* = 9.1 Hz, 1H), 3.53 (t, *J* = 7.1 Hz, 1H), 3.31 – 3.22 (m, 1H), 3.01 – 2.94 (m, 1H), 1.15 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 0.92 (s, 3H), 0.87 (s, 3H), 0.85 (s, 12H), 0.82 (s, 3H), 0.71 (s, 9H), 0.65 (s, 3H), 0.07 (s, 6H), -0.08 (s, 3H), -0.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.8, 165.2, 165.1, 139.0, 133.3, 133.1, 133.0, 129.77, 129.74, 129.67, 129.5, 129.3, 128.8, 128.3, 128.25, 128.16, 128.1, 127.4, 127.0, 102.5, 85.7, 84.8, 80.8, 79.5, 77.2, 77.0, 76.7, 74.6, 73.5, 72.2, 70.0, 69.6, 63.5, 60.0, 51.6, 49.5, 49.3, 47.7, 44.9, 40.8, 39.33, 39.29, 39.2, 38.6, 30.4, 29.6, 27.7, 27.5, 27.3, 27.0, 25.8, 25.4, 24.8, 22.3, 18.1, 17.9, 17.4, 17.2, 17.1, 15.9, -2.1, -3.8, -5.2; HRMS (ESI) calcd for $C_{83}H_{112}O_{14}Si_2Na$ $[M+Na]^+$ 1411.7483, found 1411.7468.

*6α-O-β-D-Glucopyranosyl-(20S,24S)-epoxydammarane-3β,12β,25-triol (**28b, pseudo-ginsenoside RT4**).*[4,26,34] Following the procedure described above for **28a**, **27b** (70 mg, 0.050 mmol) led to **28b** (31 mg, 95% over 3

steps), isolated as a white solid: $[\alpha]^{25}_D$ = +8.9 (*c* 1.0, CH_3OH); ^1H NMR (500 MHz, pyridine-d5 + 1 drop of D_2O) δ 5.06 (d, *J* = 7.7 Hz, 1H), 4.56 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.48 (td, *J* = 10.4, 2.6 Hz, 1H), 4.39 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.33 – 4.16 (m, 3H), 4.12 (t, *J* = 8.2 Hz, 1H), 4.02 – 3.99 (m, 1H), 3.77 (td, *J* = 10.1, 4.7 Hz, 1H), 3.56 (dd, *J* = 11.6, 4.5 Hz, 1H), 2.10 (s, 3H), 1.63 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.25 (s, 3H), 1.10 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, pyridine-d5) δ 106.1, 88.5, 87.1, 80.2, 79.7, 78.6, 78.3, 75.5, 71.9, 70.9, 70.0, 63.1, 61.6, 52.3, 50.4, 49.5, 49.2, 45.2, 41.1, 40.4, 39.7, 39.6, 32.7, 32.6, 32.3, 31.7, 29.0, 28.7, 28.0, 27.0, 26.6, 25.8, 17.9, 17.8, 17.2, 16.4; HRMS (ESI) calcd for $C_{36}H_{62}O_{10}Na$ $[M+Na]^+$ 677.4235, found 677.4239.

*(20S,24R)-Epoxy-3β-O-para-bromobenzoyl-6α-O-acetyl-12β-O-benzyl-dammarane-25-ol (**S1**).* To a solution of **2a** (30 mg, 0.048 mmol), 4-bromobenzoic acid (15 mg, 0.075 mmol), and DMAP (9.0 mg, 0.074 mmol) in dry CH_2Cl_2 (1.0 mL) were successively added EDCI (18 mg, 0.094 mmol) and DIPEA (18 μL, 0.096 mmol). The reaction mixture was stirred at room temperature for 6h, and was then diluted with EtOAc (100 mL). The mixture was washed with water and saturated brine, and was then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 5:1) to provide **S1** (36mg, 93%) as a white solid: $[\alpha]^{25}_D$ = +33.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J = 8.4 Hz*, 2H), 7.58 (d, *J = 8.4 Hz*, 2H), 7.38 (d, *J = 7.3 Hz*, 1H), 7.32 (t, *J = 7.4 Hz*, 1H), 7.29 – 7.21 (m, 1H), 5.37 (td, *J = 10.7, 3.7 Hz*, 1H), 4.68 (dd, *J = 11.7, 4.7 Hz*, 1H), 4.62 (d, *J = 12.6 Hz*, 1H), 4.48 (d, *J = 12.6 Hz*, 1H), 3.64 (dd, *J = 8.4, 6.5 Hz*, 1H), 3.29 (td, *J = 10.3, 4.3 Hz*, 1H), 2.02 (s, 3H), 1.22 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 1.07 (s, 6H), 1.06 (s, 3H), 1.03 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 165.6, 139.0, 131.7, 131.0, 129.6, 128.1, 128.0, 127.8, 127.3, 85.9, 83.8, 81.2, 78.9,

77.3, 77.2, 77.0, 76.8, 70.5, 70.34, 70.26, 58.8, 51.9, 49.8, 49.4, 47.8, 42.4, 40.6, 39.3, 38.2, 38.1, 32.0, 31.6, 30.4, 28.5, 28.3, 27.4, 26.4, 24.6, 23.2, 22.7, 22.0, 18.3, 17.3, 17.0, 16.8, 14.1; HRMS (ESI) calcd for $C_{46}H_{63}O_7BrNa$ $[M+Na]^+$ 829.3649, found 829.3651.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for compounds **3b**, **6a** and **S1** (CIF)

Crystal structure data for compounds **3b**, **6a** and **S1**, comparison of the ^{13}C NMR data of **23a**, **23b**, **25a**, **25b**, **28a** and **28b** with those reported in the literature, and ^{1}H and ^{13}C NMR spectra of all numbered compounds (PDF)

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Notes

The authors declare no competing financial interest.

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