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Highly diastereoselective Henry reaction of nitro compounds with chiral derivatives of glyoxylic acid

Iwona Kudyba,[a] Jerzy Raczko,[a,b] Zofia Urbańczyk-Lipkowska[a] and Janusz Jurczak[a,c,*]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b]*ZD CHEMIPAN, Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[c]*Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

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Abstract—*N*-Glyoxyloyl-(2*R*)-bornane-10,2-sultam and (1*R*)-8-phenylmenthyl glyoxylate react stereoselectively with simple nitro compounds giving diastereoisomeric nitroalcohols with high asymmetric induction. *N*-Glyoxyloyl-(2*R*)-bornane-10,2-sultam **1a** is shown to be a highly efficient chiral inducer, superior to (1*R*)-8-phenylmenthyl glyoxylate **1b**. In all cases, the absolute (2*S*) configuration at the center bearing the hydroxy group and the relative *syn* configuration for the major diastereoisomers were determined.

1. Introduction

The nitroaldol addition is one of the basic methods for the construction of carbon–carbon bonds.[1] The nitroalcohols formed in this reaction offer an easy access to a variety of interesting intermediates such as 2-aminoalcohols, 2-nitroketones and nitroalkenes,[2] which are useful for the synthesis of biologically important compounds.[3] Currently, there is a substantial interest in the development of a stereocontrolled version of the Henry reaction. The chiral building block approach has been widely investigated,[4] however, particular attention was paid to application of chiral catalysts, providing nitroalcohols in good yield and with high enantioselectivity.[5] On the other hand, there are only two examples of the diastereoselective Henry reaction using substrates containing a chiral auxiliary, namely (1*R*)-8-phenylmenthol, in the literature.[6]

In the course of our search for synthetic applications of chiral derivatives of α-oxo acids, we have synthesised *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**1a**)[7] and examined its applicability in a number of diastereoselective reactions.[8] High asymmetric induction obtained during these studies prompted us to extend our investigations on addition of **1a** to nitromethane (**2**) and five other simple nitro compounds of type **3**, and to compare the efficiency of **1a** with that of the glyoxylic ester of (1*R*)-8-phenylmenthol (**1b**) (Scheme 1).

2. Results and discussion

Initial investigations on the reaction of **1a** with nitromethane (**2**), carried out under conditions described by Solladié-Cavallo et al.[6] for glyoxylate **1b** failed completely giving only products from fragmentation of bornane-10-2-sultam despite the temperature of the reaction. Due to these results, we excluded potassium fluoride, common mediator of the nitroaldol reaction. To overcome this problem, we resolved to check two other procedures using either neutral Al_2O_3 (Method A) or tetrabutylammonium fluoride trihydrate (TBAF·$3H_2O$, Method B).

As revealed in Table 1, only moderate yields were obtained for the reactions promoted by both Al_2O_3 and TBAF·$3H_2O$ (Table 1, entries 1 and 3), and substantial amounts of sultam auxiliary were found in reaction mixtures. However, these reactions proceeded with high diastereoselectivity. Encouraged by these results, we decided to improve the reaction yields by using Al_2O_3 activated by heating at 120 °C under reduced pressure (Method A′) or anhydrous TBAF dried at 80 °C in vacuum (Method B′).

Indeed, we obtained much better yields for the reactions under investigation. We also checked the influence of high pressure on the reaction course. Unfortunately, we did not observed an increase of the chemical yield as we expected (entry 5). At the next stage of our studies, we studied five other nitro compounds, namely 1-nitrohexane (**3a**), 2-nitroacetaldehyde diethyl acetal (**3b**), 1-nitro-1-phenylmethane (**3c**), 2-nitro-1-phenylethane (**3d**) and ethyl nitroacetate (**3e**). We have chosen them among others as a representative group made of simple aliphatic, benzylic or

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* Corresponding author. Tel.: +48-22-6320578; fax: +48-22-6326681; e-mail address: jurczak@icho.edu.pl

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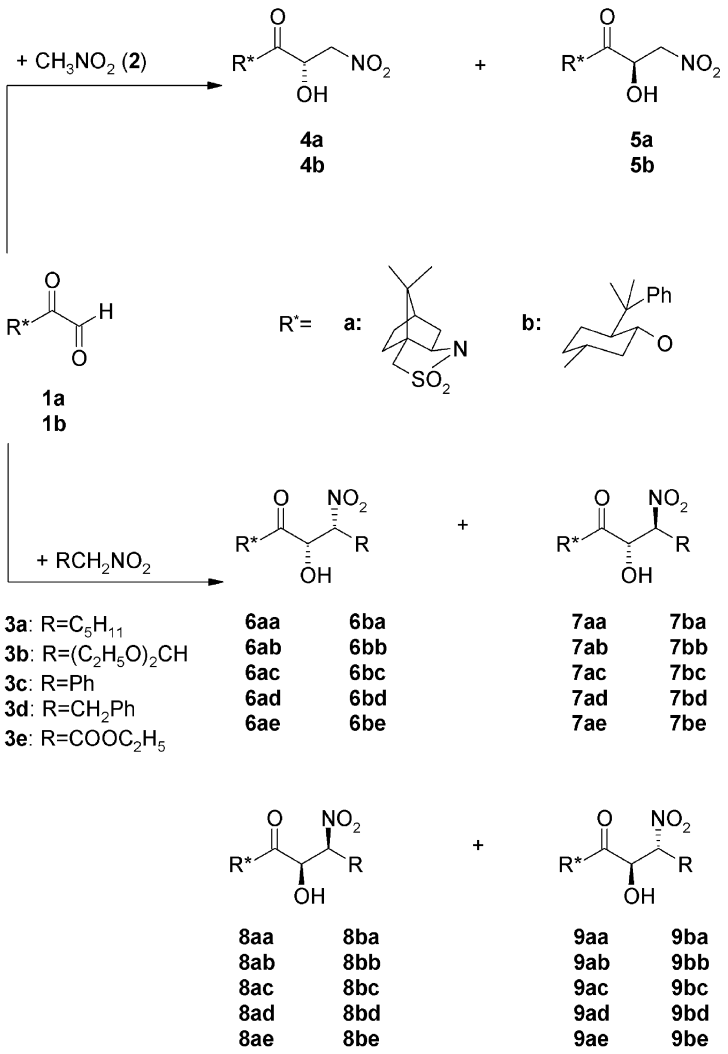


Scheme 1.

having functional groups, which open routes to further functionalisation of the obtained products. Four diastereoisomeric nitroalcohols were formed upon their reaction with **1a** (Scheme 1, Table 2).

Similarly to the reactions of **1a** with **2** (Table 1), application of the activated catalysts highly improved the yield of reactions of **3a-e** with **1a**, although unfortunately were accompanied by a slight decrease of diastereoselectivity (Table 2, Methods A′ and B′). The only exception is the product **6ab** which was detected to be a single diastereoisomer (entries 8–10). The reactions of **3b** and **3c** carried out under high pressure provided the nitroalcohols with much higher yields (entries 10 and 15). As regards diastereoselectivity, we observed formation of four possible diastereoisomers; in most cases we were able to isolate and characterise them in a chromatographically pure form. The best results were obtained for the reaction of **1a** with **3b**, when a single diastereoisomer was formed (entry 9).

Table 1. Reactions of chiral aldehyde **1a** with **2**

Entry	Method[a]	Time (h)	Yield[b] (%)	Diastereoisomeric ratio[c] **4a**:**5a**
1	A	48	30	83:17
2	A′	4	80	77:23
3	B	2	38	97:3
4	B′	8	50	98:2
5	C	2.5	28	90:10

[a] Method A: Al_2O_3, rt; A′: activated Al_2O_3, rt, B: TBAF·$3H_2O$, −78 °C; B′: anhydrous TBAF, −78 °C; C: TBAF·$3H_2O$, 10 kbar, 0 °C.
[b] Yield given for isolated products.
[c] Calculated by both HPLC and ^{1}H NMR analysis

The second chiral auxiliary applied by us was (1*R*)-8-phenylmenthol which earlier proved to be very effective in many other processes, especially in aldol condensations which is similar to the Henry reaction.[9] Its glyoxylate **1b**, being an ester, was supposed to be more stable than glyoximide **1a** under the reaction conditions. Presumably for the initial reactions of glyoxylate **1b** with nitromethane (**2**) we did not notice any influence of the way of preparing catalysts on the chemical yield; the ester moiety did not hydrolyse. Both TBAF and Al_2O_3 led to the desired nitroalcohols in high yields, however, the use of activated catalysts improved slightly their efficiency (Table 3).

Table 2. Reactions of chiral aldehyde **1a** with nitro compounds **3a-e**

Entry	Nitro compound	Method[a] used	Time (h)	Yield[b] (%)	Diastereoisomeric ratio[c] **6**:**7**:**8**:**9**
1	**3a**	A	26	5	74:26:0:0
2	**3a**	A′	8	93	68:14:12:6
3	**3a**	B	2	29	90:10:0:0
4	**3a**	B′	2,5	38	54:33:7:7
5	**3a**	C	2.5	28	88:12:0:0
6	**3b**	A	26	0	—
7	**3b**	A′	1	78	64:16:15:5
8	**3b**	B	5	45	>99:1:0:0
9	**3b**	B′	2.5	80	>99:1:0:0
10	**3b**	C	3	70	>99:1:0:0
11	**3c**	A	2.5	46	84:16:0:0
12	**3c**	A′	0.5	90	75:20:5:0
13	**3c**	B	2.5	42	93:7:0:0
14	**3c**	B′	1.5	82	88:7:5:0
15	**3c**	C	3	60	92:8:0:0
16	**3d**	A′	1	91	59:19:16:6
17	**3d**	B	1	6	—
18	**3d**	B′	8	50	57:20:13:10
19	**3e**	A	24	55	38:30:21:11
20	**3e**	A′	1.5	83	39:26:23:12
21	**3e**	B	2	43	34:26:25:15
22	**3e**	B′	2	70	35:30:21:14
23	**3e**	C	2	41	31:23:28:18

[a] Method A: Al_2O_3, RT; A′: activated Al_2O_3, rt, B: TBAF·$3H_2O$, −78 °C; B′: anhydrous TBAF, −78 °C; C: TBAF·$3H_2O$, 10 kbar, 0 °C.
[b] Calculated by both HPLC and ^1H NMR analysis.
[c] Yield given for isolated products.

The same relationships were observed for reactions of **1b** with other nitro compounds **3a-e** (Table 4). As far as diastereoselectivity is concerned, we found that (1*R*)-8-phenylmenthol is a less efficient chiral auxiliary compared to (2*R*)-bornane-10,2-sultam. In most cases, we observed formation of four possible diastereoisomers. Additionally, the reactions catalysed by TBAF provided the products in lower diastereoselectivity than the corresponding reactions catalysed by Al_2O_3. Similarly to the reactions of **1a**, application of activated Al_2O_3 resulted in a slight decrease of diastereoselectivity (Table 4, Method A′). Lowering the temperature of the above processes resulted in formation of nitroalcohols with better chiral induction as well as high chemical yields (entries 16–18). In general, the use of **1a**, as compared with **1b**, led to better stereochemical results.

The configuration of major diastereoisomer **4a** was established on the basis of correlation between optical rotations of nitrodiol **10**, the product of reductive removal of chiral auxiliary, and the analogous nitrodiol of known stereochemistry, which was obtained from reduction of adduct **4b** (Scheme 2). The configuration of compound **4b** was set up as (2*S*) via its chemical correlation to L-isoserine, as described later.

Table 3. Reactions of chiral aldehyde **1b** with **2**

Entry	Method[a]	Time (h)	Yield[b] (%)	Diastereoisomeric ratio[c] **4b**:**5b**
1	A	17	78	85:15
2	A′	24	90	73:27
3	B	5.5	43	53:47
4	B′	2.5	86	75:25
5	C	3	75	73:27

[a] Method A: Al_2O_3, rt; A′: activated Al_2O_3, rt, B: TBAF·$3H_2O$, −78 °C; B′: anhydrous TBAF, −78 °C; C: TBAF·$3H_2O$, 10 kbar, 0 °C.
[b] Yield given for the isolated products.
[c] Calculated by both HPLC and ^1H NMR analysis.

An X-ray analysis was made for the major adduct **6aa**, showing the absolute (2*S*) configuration at the center bearing the hydroxy group, and the relative *syn* configuration of hydroxy and nitro groups (Fig. 1).

The configuration of the minor diastereoisomer **7aa** was estimated by comparison of optical rotations and NMR spectra of two nitrodiols **11a** and **11b** obtained by reductive hydrolysis of sultam from diastereoisomerical diols (2*S*)-**6aa** and **7aa** (Scheme 3). Nitrodiols **11a** and **11b** were in diastereoisomeric relationship, that is, the relative configuration of compound **7aa** is *anti*.

The configuration of major adduct **6ab**, was determined by the X-ray crystal structure. As revealed in Figure 2, it has the absolute (2*S*)-hydroxy-(3*R*)-nitro configuration, which constitutes a relative *syn* relation (Fig. 2).

In the case of the adduct obtained in the reaction of **1a** with 1-nitro-1-phenylmethane (**3c**), the major diastereoisomer **6ac** shows the (2*S*)-hydroxy-(3*R*)-nitro absolute configuration and the relative *syn* configuration as established earlier by X-ray analysis.[10] Configurations of minor products were assigned on analogous way as in the case of nitroalcohols **6aa** and **7aa** (Scheme 3).

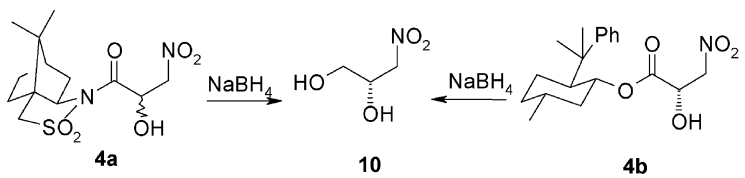
The configuration of compound **4b** was established as (2*S*) from its chemical correlation to (−)-isoserine (**14**) (Scheme 4).[6] Nitroalcohol **4b**, after protecting its hydroxy group with *t*-butyldimethylsilyl chloride, was catalytically reduced to give amine **13**, which was converted to (−)-**14** by simultaneous hydrolysis of chiral auxiliary and protecting group.

The configuration of two major products formed in the reaction of **1b** with 1-nitrohexane (**3a**) were estimated by measurements of NOE for H-2 and H-3 hydrogens of

Table 4. Reactions of chiral aldehyde **1b** with nitro compounds **3a-e**

Entry	Nitro compound	Method[a] used	Time (h)	Yield[b] (%)	Diasteroisomeric ratio[c] **6**:**7**:**8**:**9**
1	**3a**	A	17	60	62:22:10:6
2	**3a**	A′	24	85	58:24:12:6
3	**3a**	B	22	43	34:30:24:12
4	**3a**	B′	1	90	33:28:23:16
5	**3a**	C	2	73	42:24:20:14
6	**3b**	A	17	39	88:7:5:0
7	**3b**	A′	6	96	68:21:8:3
8	**3b**	B	2	47	62:17:15:6
9	**3b**	B′	1	64	66:24:10:0
10	**3b**	C	2	62	61:17:15:7
11	**3c**	A	3	90	89:8:3:0
12	**3c**	A′	1	97	83:13:0:0
13	**3c**	B″	1.5	90	63:23:14
14	**3c**	B	20	86	51:35:14
15	**3c**	C	2	77	66:23:11
16	**3d**	A	48	60	47:32:14:7
17	**3d**	A′	7	98	62:19:13:6
18	**3d**	A″	24	89	71:19:6:5
19	**3d**	B	2.5	97	28:27:26:18
20	**3e**	A	20	95	54:46:0:0
21	**3e**	B	5	96	50:50:0:0
22	**3e**	C	2	98	50:50:0:0

[a] Method A: Al_2O_3, RT; A′: activated Al_2O_3, RT, A″: activated Al_2O_3, −20 °C, B: TBAF·3H_2O, −78 °C; B′: 0.5 anhydrous TBAF, −78 °C; B″: TBAF·3H_2O, −20 °C; C: TBAF·3H_2O, 10 kbar, 0 °C.
[b] Calculated by HPLC analysis and ^{1}H NMR.
[c] Yield given for isolated products.



Scheme 2.

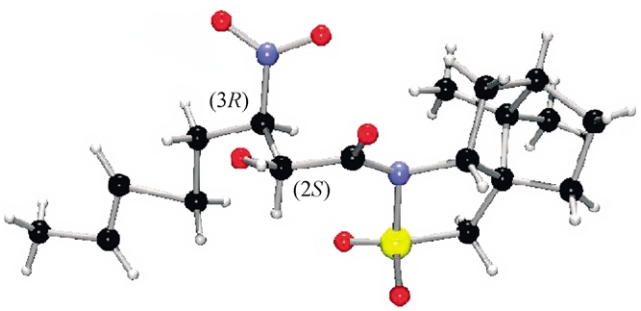
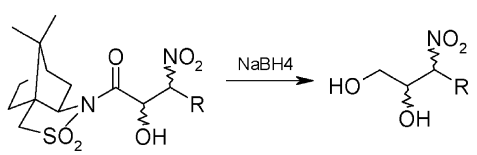


Figure 1. X-ray structure of (2′R)-*N*-[(2*S*)-hydroxy-(3*R*)-nitrooctanoyl]-bornane-10′,2′-sultam (**6aa**).



6aa	R=C_5H_{11}	**11a**
7aa	R=C_5H_{11}	**11b**
6ac	R=Ph	**12a**
7ac	R=Ph	**12b**
8ac	R=Ph	**12c**

Scheme 3.

isopropylidene derivatives **18a** and **18b**, produced from adducts **6ba** and **7ba**, respectively (Scheme 5). Positive NOE was observed for the oxazolidine **18b** (10.0% for H-2, 7.6% for H-3) indicating the relative *syn* configuration of H-2 and H-3 hydrogens, which determine relative configuration *anti* for compound **7ba**. The positive NOE was not seen for the oxazolidine **18a**, pointing out the relative *anti* configuration of H-2 and H-3, which states the relative *syn* configuration for compound **6ba**.

The same procedure was applied for assignment of the relative configuration of nitroalcohols **6bb**, **7bb** and **7bc** (Scheme 5).

In the case of the adduct obtained in the reaction of **1b** with 1-nitro-1-phenylmethane (**3c**), the major diastereoisomer **6bc** shows the (2*S*)-hydroxy-(3*R*)-nitro configuration and the relative *syn* configuration for these groups established earlier by X-ray analysis.[10] That compound was used in the total synthesis of Taxotere® side chain.[11]

In the case of the adduct obtained in the reaction of **1b** with 2-nitro-1-phenylethane (**3d**), the configuration of the major diastereoisomer **6bd** was established as (2*S*,3*R*) by total synthesis of (−)-bestatin.[11] The configuration of the minor diastereoisomer **7bd**, assigned earlier by X-ray analysis, is

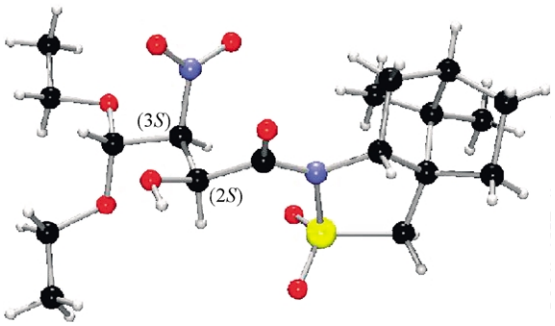


Figure 2. X-ray structure of (2′*R*)-N-[4,4-Diethoxy-(2*S*)-hydroxy-(3*R*)-nitrobutanoyl]-bornane-10′,′2-sultam (**6ab**).

(2*S*)-hydroxy-(3*S*)-nitro and the relative configuration of these groups is *anti*.[10]

On the basis of structural analysis referring to relationship of configurations of new stereogenic centres, we have noticed the occurrence of some distinct regularities. The most important one is that the major diastereoisomer obtained in the above-discussed reactions has the relative *syn* configuration of nitro and hydroxy groups, and the absolute (2*S*)-hydroxy-(3*R*)-nitro configuration. The second diastereoisomer formed also possess the absolute configuration (2*S*), however the relative relation of C-2 and C-3 substituents was in all cases *anti*.

3. Conclusions

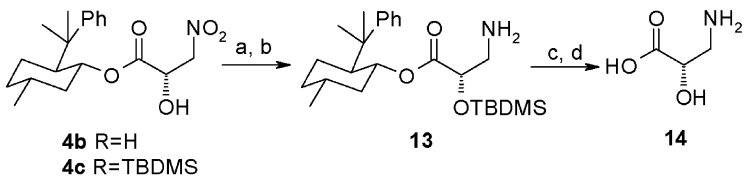
On the basis of the above-mentioned analyses, we conclude that the major diastereoisomers **4** and **6** possess the absolute (2*S*) configuration of the hydroxy-bearing stereogenic centre in all cases. The relative configuration of nitro and hydroxy groups is *syn* for all major diastereoisomers **6**, contrary to the *anti* configuration found in products obtained via the chiral-pool approach. Thus, our methodology seems to be complementary to the chiral pool as concerns the relative configuration of newly created stereogenic centres.

In summary, we have shown that the derivatives of glyoxylic acid, bearing (2*R*)-bornane-10,2-sultam and (1*R*)-8-phenylmenthol as chiral auxiliaries, are very convenient substrates for preparation of optically pure nitro-alcohols that could be used as starting materials in the synthesis of various natural products.

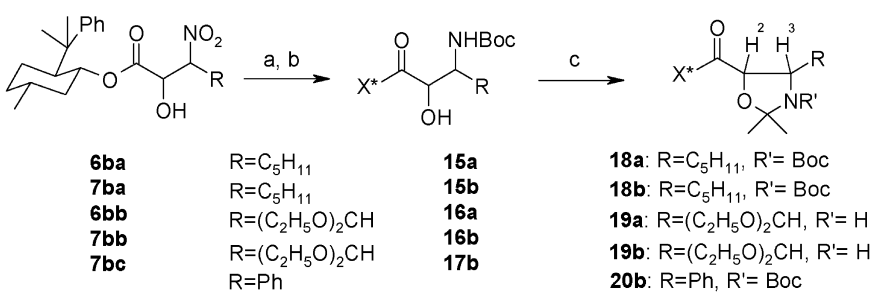
4. Experimental

4.1. General methods

All reactions were carried out under argon atmosphere with anhydrous solvents dried according to standard laboratory methods. ^{1}H and ^{13}C NMR spectra were measured on Bruker AM-500 (500 and 125 MHz, respectively) and Varian Gemini (200 and 50 MHz, respectively) spectrometers using residual $CHCl_3$ as internal reference. Mass spectra were carried out with AMD-604 Intectra instrument. Optical rotations were measured on a JASCO DIP-360 polarimeter with a thermally jacketed 10 cm cell. Infrared spectra were recorded on a Perkin–Elmer 1640 FT-IR. Melting points were determined with Kofler hot stage apparatus and are uncorrected. Flash-column chromatography was performed on silica gel (Kieselgel-60, Merck, 200–400 mesh). TLC was performed on Merck aluminum plates (Kieselgel 60 F_{254}) and compounds were visualized with a solution of MoO_3 and $Ce_2(SO_4)_3$ in 15% H_2SO_4. All high-pressure reactions were carried out in a piston-cylinder type apparatus with an initial working volume of about 5 mL. The X-ray measurements were run on a Nonius MACH3 diffractometer using Express software, without absorption corrections. The structures were solved by the SHELXS86[12] and refined with the SHELXL93[13] programs. The known configuration of the asymmetric centres has been confirmed by the Flack parameter refinement. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers **6aa**: CCDC 228305 and **6ab**: CCDC 228306. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2



Scheme 4. Reagents: (a) TBDMSCl, (b) H_2, Raney Ni, (c) HCl, (d) epoxypropane



Scheme 5. Reagents: (a) H_2, Raney Ni, (b) Boc_2O, (c) DMP, H^+.

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4.2. General procedures for the reactions of 1 with 2 or 3

4.2.1. General procedure for the neutral Al_2O_3 (Method A) or activated Al_2O_3 (Method A′) catalysed reaction. A carbonyl compound (1 mmol) and a nitro compound (2 mmol) were added to a solution of a catalyst (2 mmol) in THF (5 mL) at rt under argon atmosphere. Activated Al_2O_3 was prepared before the reaction by heating at 120 °C under reduced pressure (0.2 mm Hg) for 2 h. The reaction was monitored by TLC, and when finished, it was filtered and evaporated. All products were purified by column chromatography (hexane/AcOEt 9:1–6:4).

4.2.2. General procedure for the TBAF·3H$_2$O (Method B) and TBAF (Methods B′ and B″) catalysed reaction. A catalyst (0.5 mmol) was added to a solution of a carbonyl compound (1 mmol) in dry THF (5 mL) under argon atmosphere. The reaction mixture was cooled to −78 °C and a nitro compound (2 mmol) was added. Anhydrous TBAF was prepared just before the reaction by heating at 80 °C at reduced pressure (0.2 mm Hg) for 2 h. The reaction was monitored by TLC, and when finished, it was quenched by addition of saturated aqueous NaCl and extracted with AcOEt. The combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated. All products were purified by column chromatography (hexane–AcOEt 9:1–6:4).

4.2.3. General procedure for the TBAF·3H$_2$O catalysed reaction under high pressure (10 kbar) (Method C). A catalyst (0.5 mmol) was added to a precooled (0 °C) solution of a carbonyl compound (1 mmol) in dry THF (5 mL), followed by addition of a nitro compound (2 mmol). The reaction was carried out in high pressure apparatus at the indicated temperature and time. When finished, it was quenched by addition of saturated aqueous NaCl and extracted with AcOEt. The combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated. All products were purified by column chromatography (hexane/AcOEt 9:1–6:4).

4.2.4. (2′*R*)-*N*-[(2*S*)-Hydroxy-3-nitropropanoyl]-bornane-10′,2′-sultam (4a). Colourless crystals, mp=160–161 °C (MeOH); HRMS-EI: Calcd for $C_{13}H_{20}O_6N_2SNa$ $(M+Na)^+$: 355.0939, found 355.0942. Anal Calcd C. 46.97, H. 6.08, N. 8.42, S. 9.64, found C. 47.18, H. 6.14, N. 8.33, S. 9.71; IR (KBr): 3492, 2964, 2884, 1694, 1549, 1329, 1296, 1222, 1138, 1101, 1064, 769, 611, 533 cm^{-1}; $[\alpha]_D^{20}=-103.6$ (c=0.90; $CHCl_3$); R_f=0.5 (hexane/AcOEt 6:4); ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.11 (ddd, $J_{2,3A}$=3.9 Hz, $J_{2,3B}$=4.0 Hz, $J_{2,OH}$=5.9 Hz, 1H, H-2), 5.01 (dd_{AB}, $J_{3A,3B}$=13.3 Hz, $J_{2,3A}$=3.9 Hz, 1H, H_A-3), 4.88 (dd_{AB}, $J_{3A,3B}$=13.3 Hz, $J_{2,3B}$=4.0 Hz, 1H, H_B-3), 4.00 (dd, $J_{2',3'A}$=4.7 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.77 (d, $J_{2,OH}$=5.9 Hz, 1H, OH), 3.56 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.52 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 2.21 (ddd, $J_{2',3'A}$=4.7 Hz, $J_{3'A,3'B}$=13.8 Hz, $J_{3'A,4}$=7.3 Hz, 1H, H_A-3′), 2.09 (dd, $J_{2',3'B}$=7.8 Hz, $J_{3'A,3'B}$=$J_{3'A,4}$=13.8 Hz, 1H, H_B-3′), 2.00–1.84 (m, 3H, H-4′, H-6′), 1.51–1.25 (m, 2H, H-5′), 1.13 (s, 3H, H-8′), 0.99 (s, 3H, H-9′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 169.9 (C-1), 78.3 (C-3), 68.4 (C-2), 65.4 (C-2′), 52.8 (C-10′), 49.3 (C-1′), 48.0 (C-7′), 44.4 (C-4′), 37.3 (C-3′), 32.6 (C-6′), 26.3 (C-5′), 20.3 (C-8′), 19.8 (C-9′).

4.2.5. (2′*R*)-*N*-[(2′*R*)-Hydroxy-3-nitropropanoyl]-bornane-10′,2′-sultam (5a). Selected signals from differential NMR spectra: ^{1}H (400 MHz; $CDCl_3$): δ 5.33 (ddd, $J_{2,3A}$=4.0 Hz, $J_{2,3B}$=8.0 Hz, $J_{2,OH}$=6.4 Hz, 1H, H-2), 4.90 (dd_{AB}, $J_{3A,3B}$=14.0 Hz, $J_{2,3A}$=4.0 Hz, 1H, H_A-3), 4.69 (dd_{AB}, $J_{3A,3B}$=14.0 Hz, $J_{2,3B}$=8.0 Hz, 1H, H_B-3), 3.93 (dd, $J_{2',3'A}$=4.8 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.84 (d, $J_{2,OH}$=6.4 Hz, 1H, OH), 3.59 (d_{AB}, $J_{10'A,10'B}$=13.9 Hz, 1H, H_A-10′), 3.55 (d_{AB}, $J_{10'A,10'B}$=13.9 Hz, 1H, H_A-10′), 1.14 (s, 3H, H-8′), 0.93 (s, 3H, H-9′); ^{13}C (50 MHz; $CDCl_3$): δ 168.8 (C-1), 75.6 (C-3), 68.1 (C-2), 65.2 (C-2′), 52.6 (C-10′), 49.5 (C-1′), 47.9 (C-7′), 44.6 (C-4′), 37.4 (C-3′), 32.7 (C-6′), 26.4 (C-5′), 20.4 (C-8′), 19.9 (C-9′).

4.2.6. (2′*R*)-*N*-[(2*S*)-Hydroxy-(3*R*)-nitrooctanoyl]-bornane-10′,2′-sultam (6aa). Colourless crystals, mp=79–80 °C (hexane/AcOEt); HRMS-EI: Calcd $C_{18}H_{31}N_2O_6S$ $(M+H)^+$: 403.1902, found 403.1923. Anal Calcd C. 53.71, H. 7.51, N. 6.96, S. 7.97, found C. 53.71, H. 7.54, N. 7.00, S. 7.89; IR (KBr): 3493, 3291, 2959, 2932, 2877, 1696, 1555, 1334, 1292, 1216, 1136, 1051, 765, 627, 536 cm^{-1}; $[\alpha]_D^{20}=-66.7$ (c=1.05; $CHCl_3$); R_f=0.6 (hexane/AcOEt 7:3); ^{1}H NMR δ (500 MHz; $CDCl_3$): δ 5.02 (ddd, $J_{2,3}$=2.4 Hz, $J_{3,4A}$=5.9 Hz, $J_{3,4B}$=8.4 Hz, 1H, H-3), 4.91 (dd, $J_{2,3}$=2.4 Hz, $J_{2,OH}$=7.8 Hz, 1H, H-2), 3.97 (dd, $J_{2',3'A}$=4.7 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.55 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.50 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_B-10′), 3.44 (d, $J_{2,OH}$=7.8 Hz, 1H, OH), 2.31–2.23 (m, 2H, H-4), 2.20 (ddd, $J_{2',3'A}$=4.7 Hz, $J_{3'A,4}$=7.8 Hz, $J_{3'A,3'B}$=14.0 Hz, 1H, H_A-3′), 2.20 (dd, $J_{2',3'B}$=$J_{3'A,4}$=7.8 Hz, $J_{3'A,3'B}$=14.0 Hz, 1H, H_B-3′), 2.00–1.85 (m, 3H, H-4′, H-6′), 1.51–1.28 (m, 8H, H-5, H-6, H-7, H-5′), 1.22 (s, 3H, H-8′), 1.00 (s, 3H, H-9′), 0.89 (t, 3H, $J_{7,8}$=7.0 Hz, H-8); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.3(C-1), 89.4 (C-3), 71.4 (C-2), 65.2 (C-2′), 52.8 (C-10′), 49.1 (C-1′), 47.9 (C-7′), 44.3 (C-4′), 37.3 (C-3′), 35.9 (C-6′), 31.2 (C-4), 29.2 (C-5), 26.7 (C-5′), 24.9 (C-6), 22.1 (C-7), 20.3 (C-8′), 19.8 (C-9′), 13.8 (C-8).

4.2.7. (2′*R*)-*N*-[*anti*-(2ξ)-Hydroxy-(3ξ)-nitrooctanoyl]-bornane-10′,2′-sultam (7aa). Colourless oil, $[\alpha]_D^{20}=-63.6$ (c=0.845; $CHCl_3$); R_f=0.5 (hexane/AcOEt 7:3); ^{1}H NMR (500 MHz; $CDCl_3$): δ 5.26 (dd, $J_{2,3}$=5.4 Hz, $J_{2,OH}$=6.3 Hz, 1H, H-2), 4.92 (ddd, $J_{2,3}$=5.4 Hz, $J_{3,4A}$=3.3 Hz, $J_{3,4B}$=9.1 Hz, 1H, H-3), 3.96 (dd, $J_{2',3'A}$=4.9 Hz, $J_{2',3'B}$=7.7 Hz, 1H, H-2′), 3.58 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.51 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_B-10′), 3.50 (d, $J_{2,OH}$=6.3 Hz, 1H, OH), 2.18–1.70 (m, 7H, H-4, H-3′, H-4′, H-6′), 1.49–1.23 (m, 8H, H-5, H-6, H-7, H-5′), 1.15 (s, 3H, H-8′), 1.01 (s, 3H, H-9′), 0.87 (t, 3H, $J_{7,8}$=6.8 Hz, H-8); ^{13}C NMR (125 MHz; $CDCl_3$): δ 169.5 (C-1), 87.3 (C-3), 70.8 (C-2), 65.3 (C-2′), 52.9 (C-10′), 49.2 (C-1′), 47.9 (C-7′), 44.5 (C-4′), 37.9 (C-3′), 32.8 (C-6′), 31.2 (C-4), 27.8 (C-5), 26.3 (C-5′), 25.1 (C-6), 22.2 (C-7), 20.6 (C-8′), 19.8 (C-9′), 13.8 (C-8).

4.2.8. (2′*R*)-*N*-[4,4-Diethoxy-(2*S*)-hydroxy-(3*S*)-nitrobutanoyl]-bornane-10′,′2-sultam (6ab). Colourless crystals, mp=98–100 °C (hexane/Et_2O); HRMS-EI: Calcd

for $C_{18}H_{30}N_2O_8SNa$ $(M+Na)^+$ 457.1620, found 457.1608. Anal Calcd C. 49.76, H. 6.96, N. 6.45, S. 7.38, found C. 49.95, H. 7.25, N. 6.53, S. 7.54; IR (KBr): 3527, 3291, 2966, 1686, 1553, 1333, 1142, 1064 cm^{-1}; $[\alpha]_D{}^{20}=-75.6$ (c=1.03; $CHCl_3$); R_f=0.6 (hexane/AcOEt 7:3); ^1H NMR (200 MHz; $CDCl_3$): δ 5.24 (d, $J_{3,4}$=8.2 Hz, 1H, H-4), 5.23 (dd, $J_{2,OH}$=8.2 Hz, $J_{2,3}$=2.4 Hz, 1H, H-2), 5.08 (dd, $J_{3,4}$=8.2 Hz, $J_{2,3}$=2.4 Hz, 1H, H-3), 3.95 (dd, $J_{2',3'A}$=5.1 Hz, $J_{2',3'B}$=7.5 Hz, 1H, H-2′), 3.79 (q, $J_{5,6}$=7.4 Hz, 2H, H-5), 3.78 (q, $J_{5'',6''}$=7.1 Hz, 2H, H-5″), 3.16 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 2H, H_A-10′), 3.08 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 2H, H_B-10′), 2.15–2.03 (m, 2H, H3′), 2.20–1.83 (m, 3H, H-4′, H-6′), 1.55-1.32 (m, 2H, H-5′), 1.26 (t, $J_{5,6}$=7.1 Hz, 3H, H-6), 1.18 (t, $J_{5'',6''}$=7.4 Hz, 3H, H-6″), 0.99 (s, 3H, H-8′), 0.93 (s, 3H, H-9′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 169.8 (C-1), 99.2 (C-4), 89.4 (C-3), 69.4 (C-2), 65.2 (C-2′), 63.3 (C-5, C-5″), 52.8 (C-10′), 49.1 (C-1′), 47.9 (C-7′), 44.4 (C-4′), 37.5 (C-3′), 32.7 (C-6′), 26.4 (C-5′), 20.4 (C-8′), 19.9 (C-9′), 15.1 (C-6), 14.9 (C-6″).

4.2.9. (2′*R*)-*N*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-bornane-10′,′2-sultam (7ab). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 5.57 (dd, $J_{2,OH}$=6.2 Hz, $J_{2,3}$=6.6 Hz, 1H, H-2), 3.50 (dd, $J_{2',3'A}$=4.6 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′); ^{13}C (125 MHz; $CDCl_3$): δ 170.6 (C-1), 99.6 (C-4), 89.6 (C-3), 71.6 (C-2), 52.2 (C-10′), 48.6 (C-1′), 47.6 (C-7′), 44.3 (C-4′), 26.0 (C-5′), 13.7 (C-6).

4.2.10. (2′*R*)-*N*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-bornane-10′,′2-sultam (8ab). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 5.44 (dd, $J_{3,4}$=8.4 Hz, $J_{2,3}$=6.0 Hz, 1H, H-2), 3.97 (d, $J_{2,3}$=6.0 Hz, 1H, OH), 3.31 (dd, $J_{2',3'A}$=4.8 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′); ^{13}C (125 MHz; $CDCl_3$): δ 47.5 (C-7′), 44.3 (C-4′), 26.1 (C-5′).

4.2.11. (2′*R*)-*N*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-bornane-10′,′2-sultam (9ab). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 3.82 (d, $J_{2,3}$=7.8 Hz, 1H, OH), 3.48 (dd, $J_{2',3'A}$=4.6 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′); ^{13}C (50 MHz; $CDCl_3$): δ 168.4 (C-1), 96.1 (C-4), 65.1 (C-2′), 52.0 (C-10′), 47.4 (C-7′), 44.2 (C-4′), 14.9 (C-6).

4.2.12. (2′*R*)-*N*-[(2*S*)-Hydroxy-(3*R*)-nitro-3-phenylpropanoyl]-bornane-10′,2′-sultam (6ac). Colourless crystals, mp=169–170 °C (hexane/AcOEt); HRMS-EI: Calcd for $C_{19}H_{25}N_2O_6S$ $(M+H)^+$ 409.1433, found 409.1432. Anal. Calcd for $C_{19}H_{24}N_2O_6S$: C. 55.87, H. 5.92, N. 6.86, S. 7.85, found C. 55.79, H. 6.08, N. 6.80, S. 7.87; IR (KBr): 3496, 3291, 2999, 2944, 2909, 1682, 1561, 1367, 1320, 1214, 1137, 1072, 719, 532 cm^{-1}; $[\alpha]_D{}^{20}=-68$ (c=1.39; $CHCl_3$); R_f=0.4 (hexane/AcOEt 7:3); ^1H NMR (500 MHz; $CDCl_3$): δ 7.60–7.35 (m, 5H, Ar), 5.95 (d, $J_{2,3}$=6.6 Hz, 1H, H-3), 5.55 (dd, $J_{2,3}$=6.6 Hz, $J_{2,OH}$=6.5 Hz, 1H, H-2), 3.97 (dd, $J_{2',3'A}$=4.7 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.66 (d, $J_{2,OH}$=6.5 Hz, 1H, OH), 3.51 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.46 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_B-10′), 1.95–1.85 (m, 4H, H-4′, H-6′), 1.78–1.74 (m, 1H, H_A-3′), 1.67–1.60 (m, 1H, H_B-3′), 1.42–1.36 (m, 1H, H_A-5′), 1.33–1.23 (m, 1H, H_B-5′), 0.92 (s, 3H, H-8′), 0.79 (s, 3H, H-9′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 168.7 (C-1), 130.3 (i-Ar),130.1 (Ar), 129.2 (Ar), 128.8 (Ar), 92.0 (C-3), 72.0 (C-2), 65.1 (C-2′), 52.9 (C-10′), 48.9 (C-1′), 47.7 (C-7′), 44.5 (C-4′), 37.4 (C-3′), 32.7 (C-6′), 26.3 (C-5′), 20.4 (C-8′), 19.7 (C-9′).

4.2.13. (2′*R*)-*N*-[*anti*-(2ξ)-Hydroxy-(3ξ)-nitro-3-phenylpropanoyl]-bornane-10′,2′-sultam (7ac). Colourless oil, ^1H NMR (500 MHz; $CDCl_3$): δ 7.46–7.38 (m, 5H, Ar), 5.93 (d, $J_{2,3}$=6.7 Hz, 1H, H-3), 5.69 (dd, $J_{2,3}$=6.7 Hz, $J_{2,OH}$=5.8 Hz, 1H, H-2), 3.93 (dd, $J_{2',3'A}$=4.8 Hz, $J_{2',3'B}$=8.2 Hz, 1H, H-2′), 3.38 (d, $J_{2,OH}$=6.5 Hz, 1H, OH), 3.61 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.52 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_B-10′), 2.01–1.50 (m, 6H, H-4′, H-6′, H-3′), 1.46–1.40 (m, 1H, H_A-5′), 1.38–1.31 (m, 1H, H_B-5′), 1.22 (s, 3H, H-8′), 1.01 (s, 3H, H-9′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 171.2 (C-1), 130.1 (i-Ar),130.0 (Ar), 129.1 (Ar), 128.3 (Ar), 89.2 (C-3), 70.9 (C-2), 64.2 (C-2′), 52.8 (C-10′), 49.1 (C-1′), 47.8 (C-7′), 44.6 (C-4′), 37.7 (C-3′), 32.8 (C-6′), 26.7 (C-5′), 20.8 (C-8′), 19.0 (C-9′).

4.2.14. (2′*R*)-*N*-[(2*R*)-Hydroxy-(3*S*)-nitro-3-phenylpropanoyl]-bornane-10′,2′-sultam (8ac). Colourless oil, $[\alpha]_D{}^{20}=-41$ (c=1.11; $CHCl_3$); ^1H NMR (500 MHz; $CDCl_3$): δ 7.50–7.38 (m, 5H, Ar), 5.85 (d, $J_{2,3}$=9.0 Hz, 1H, H-3), 5.49 (dd, $J_{2,3}$=9.0 Hz, $J_{2,OH}$=6.1 Hz, 1H, H-2), 3.97 (dd, $J_{2',3'A}$=4.9 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.57 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_A-10′), 3.55 (d_{AB}, $J_{10'A,10'B}$=13.8 Hz, 1H, H_B-10′), 3.51 (d, $J_{2,OH}$=6.5 Hz, 1H, OH), 2.23–2.18 (m, 1H, H_A-3′), 2.10–2.04 (m, 1H, H_B-3′), 1.99–1.85 (m, 4H, H-4′, H-6′), 1.50–1.45 (m, 1H, H_A-5′), 1.39–1.33 (m, 1H, H_B-5′), 1.12 (s, 3H, H-8′), 0.98 (s, 3H, H-9′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 168.2 (C-1), 131.5 (i-Ar),130.0 (Ar), 128.9 (Ar), 128.3 (Ar), 87.9 (C-3), 70.8 (C-2), 65.0 (C-2′), 52.6 (C-10′), 49.5 (C-1′), 47.8 (C-7′), 44.3 (C-4′), 37.4 (C-3′), 32.5 (C-6′), 26.3 (C-5′), 20.4 (C-8′), 19.7 (C-9′).

4.2.15. (2′*R*)-*N*-[(2*S*)-Hydroxy-(3*R*)-nitro-4-phenylbutanoyl]-bornane-10′,2′-sultam (6ad). Colourless oil, HRMS-ESI: Calcd for $C_{20}H_{26}N_2O_6SNa$ $(M+Na)^+$ 445.1404, found 445.1415. Anal. Calcd C. 56.86, H. 6.20, N. 6.63, S. 7.59, found C. 57.09, H. 6.31, N. 6.46, S. 7.71; IR (film): 3470, 2961, 1694, 1555, 1335, 1294, 1167, 1138, 1061, 753, 700, 535 cm^{-1}; $[\alpha]_D{}^{20}=-60$ (c=1.10; $CHCl_3$); R_f=0.4 (hexane/AcOEt 7:3); ^1H NMR (500 MHz; $CDCl_3$): δ 7.34–7.25 (m, 5H, Ar), 5.34 (ddd, $J_{2,3}$=2.2 Hz, $J_{3,4A}$=5.8 Hz, $J_{3,4B}$=9.1 Hz, 1H, H-3), 4.92 (dd, $J_{2,3}$=2.2 Hz, $J_{2,OH}$=7.1 Hz, 1H, H-2), 3.96 (dd, $J_{2',3'A}$=4.8 Hz, $J_{2',3'B}$=7.9 Hz, 1H, H-2′), 3.58 (dd_{AB}, $J_{3,4B}$=9.1 Hz, $J_{4A,4B}$=14.5 Hz, 1H, H_B-4), 3.27 (dd_{AB}, $J_{3,4A}$=5.8 Hz, $J_{4A,4B}$=14.5 Hz, 1H, H_A-4), 3.13 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_A-10′), 3.08 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_B-10′), 2.01–1.81 (m, 3H, H-3′, H-4′), 1.49–1.29 (m, 2H, H-6′), 1.20–1.08 (m, 1H, H-5′), 1.19 (s, 3H, H-8′), 0.97 (s, 3H, H-9′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.3 (C-1), 134.9 (i-Ar),129.3 (Ar), 128.6 (Ar), 127.3 (Ar), 90.2 (C-3), 71.3 (C-2), 65.3 (C-2′), 52.8 (C-10′), 49.2 (C-1′), 47.9 (C-7′), 44.3 (C-4′), 37.2 (C-3′), 35.4 (C-4), 32.5 (C-6′), 26.4 (C-5′), 20.2 (C-8′), 19.8 (C-9′).

4.2.16. (2′*R*)-*N*-[(2ξ)-Hydroxy-(3ξ)-nitro-4-phenylbutanoyl]-bornane-10′,2′-sultam (7ad). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ

5.32 (dd, $J_{2,3}$=4.9 Hz, $J_{2,OH}$=5.8 Hz, 1H, H-2), 5.21 (ddd, $J_{2,3}$=4.9 Hz, $J_{3,4A}$=4.0 Hz, $J_{3,4B}$=8.8 Hz, 1H, H-3), 3.92 (dd, $J_{2',3'A}$=4.4 Hz, $J_{2',3'B}$=7.9 Hz, 1H, H-2′), 3.55 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_A-10′), 3.49 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_B-10′), 3.43 (dd_{AB}, $J_{3,4B}$=8.8 Hz, $J_{4A,4B}$=15.0 Hz, 1H, H_B-4), 3.14 (dd_{AB}, $J_{3,4A}$=4.0 Hz, $J_{4A,4B}$=15.0 Hz, 1H, H_A-4), 1.06 (s, 3H, H-8′), 0.95 (s, 3H, H-9′); ^{13}C (125 MHz; $CDCl_3$): δ 169.3 (C-1), 134.8 (i-Ar), 129.0 (Ar), 128.7 (Ar), 127.3 (Ar), 88.2 (C-3), 70.4 (C-2), 65.3 (C-2′), 52.8 (C-10′), 49.1 (C-1′), 47.8 (C-7′), 44.4 (C-4′), 37.7 (C-3′), 35.4 (C-4), 32.7 (C-6′), 26.2 (C-5′), 20.7 (C-8′), 19.7 (C-9′).

4.2.17. (2′R)-*N*-[(2ξ)-Hydroxy-(3ξ)-nitro-4-phenylbutanoyl]-bornane-10′,2′-sultam (8ad). Colourless crystals, mp=176–178 °C; ^{1}H (500 MHz; $CDCl_3$): δ 7.15–5.40 (m, 5H, Ar), 5.35 (dd, $J_{2,3}$=11.0 Hz, $J_{2,OH}$=6.0 Hz, 1H, H-2), 5.20–5.32 (m, 1H, H-3), 3.97 (dd, $J_{2',3'A}$=4.5 Hz, $J_{2',3'B}$=7.8 Hz, 1H, H-2′), 3.68 (d, J=6.0 Hz, 1H, OH), 3.61 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_A-10′), 3.52 (d_{AB}, $J_{10'A,10'B}$=13.7 Hz, 1H, H_B-10′), 3.49 (dd_{AB}, $J_{3,4B}$=8.5 Hz, $J_{4A,4B}$=15.0 Hz, 1H, H_B-4), 3.19 (dd_{AB}, $J_{3,4A}$=4.0 Hz, $J_{4A,4B}$=15.0 Hz, 1H, H_A-4), 1.84–2.15 (m, 5H), 1.30–1.55 (m, 2H), 1.13 (s, 3H, H-8′), 1.01 (s, 3H, H-9′); ^{13}C (125 MHz; $CDCl_3$): δ 168.2 (C-1), 134.6 (i-Ar), 128.9 (Ar), 128.8 (Ar), 127.5 (Ar), 89.4 (C-3), 70.7 (C-2), 65.3 (C-2′), 52.7 (C-10′), 49.3 (C-1′), 47.8 (C-7′), 44.6 (C-4′), 37.6 (C-3′), 35.9 (C-4), 32.6 (C-6′), 26.7 (C-5′), 20.4 (C-8′), 20.3 (C-9′).

4.2.18. (2′*R*)-*N*-[(2ξ)-Hydroxy-(3ξ)-nitro-4-phenylbutanoyl]-bornane-10′,2′-sultam (9ad). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.19–5.16 (m, 1H, H-3), 5.11–5.08 (m, 1H, H-2), 1.13 (s, 3H, H-8′); ^{13}C (125 MHz; $CDCl_3$): δ 171.0 (C-1), 135.0 (i-Ar), 89.5 (C-3), 70.2 (C-2), 64.9 (C-2′), 52.4 (C-10′), 49.2 (C-1′), 47.2 (C-7′), 44.6 (C-4′), 37.5 (C-3′), 35.0 (C-4), 31.1 (C-6′).

4.2.19. (2′*R*)-*N*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitro-propanoyl]-bornane-10′,2′-sultam (6ae). Colourless oil, HRMS-LSIMS(+): Calcd for $C_{16}H_{25}N_2O_8S$ $(M+H)^+$ 405.1331, found 405.1316. Anal Calcd C. 47.52, H. 5.98, N. 6.93, S. 7.93, found C. 47.82, H. 6.16, N. 6.62, S. 7.87; IR (film): 3476, 2963, 1752, 1695, 1567, 1335, 1320, 1297, 1221, 1168, 1138, 1062, 1023, 857, 765, 536 cm^{-1}; R_f=0.6 (hexane/AcOEt 7:3); ^{1}H NMR (500 MHz; $CDCl_3$): δ 5.84 (d, $J_{2,3}$=5.2 Hz, 1H, H-3), 5.40 (d, $J_{2,3}$=$J_{2,OH}$=5.2 Hz, 1H, H-2), 4.36–4.25 (m, 2H, H-5), 4.00–3.93 (m, 1H, H-2′), 4.39–3.62 (m, 2H, H-10′), 2.19–1.84 (m, 5H, H-3′, H-4′, H-6′), 1.75–1.25 (m, 8H, H-5′, H-6), 1.15 (s, 3H, H-8′), 0.99 (s, 3H, H-9′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 167.6 (C-1), 161.6 (C-1), 88.7 (C-3), 69.6 (C-2), 65.1 (C-2′), 63.6 (C-5), 52.8 (C-10′), 49.3 (C-1′), 47.9 (C-7′), 44.4 (C-4′), 37.4 (C-3′), 32.6 (C-6′), 26.3 (C-5′), 20.4 (C-8′), 19.7 (C-9′) 13.7 (C-6).

4.2.20. (2′*R*)-*N*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitropropanoyl]-bornane-10′,2′-sultam (7ae). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.70 (d, $J_{2,3}$=3.4 Hz, 1H, H-3), 5.51 (d, $J_{2,3}$=$J_{2,OH}$=3.4 Hz, 1H, H-2), 1.13 (s, 3H, H-8′), 0.95 (s, 3H, H-9′); ^{13}C (125 MHz; $CDCl_3$): δ 167.8 (C-1), 161.8 (C-1), 87.6 (C-3), 69.5 (C-2), 65.3 (C-2′), 63.5 (C-5), 52.7 (C-10′), 49.4 (C-1′), 48.0 (C-7′), 44.5 (C-4′), 37.2 (C-3′), 32.5 (C-6′), 26.9 (C-5′), 20.3 (C-8′), 19.6 (C-9′) 13.6 (C-6).

4.2.21. (2′*R*)-*N*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitropropanoyl]-bornane-10′,2′-sultam (8ae). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.64 (d, $J_{2,3}$=8.3 Hz, 1H, H-3), 5.39 (d, $J_{2,3}$=$J_{2,OH}$=8.3 Hz, 1H, H-2), 1.12 (s, 3H, H-8′), 0.94 (s, 3H, H-9′); ^{13}C (125 MHz; $CDCl_3$): δ 167.4 (C-1), 161.8 (C-1), 87.8 (C-3), 70.0 (C-2), 65.0 (C-2′), 63.5 (C-5), 52.7 (C-10′), 49.4 (C-1′), 47.8 (C-7′), 44.3 (C-4′), 37.5 (C-3′), 32.4 (C-6′), 26.6 (C-5′), 20.3 (C-8′), 19.6 (C-9′) 13.6 (C-6).

4.2.22. (2′*R*)-*N*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitropropanoyl]-bornane-10′,2′-sultam (9ae). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.60 (d, $J_{2,3}$=7.1 Hz, 1H, H-3), 5.51 (d, $J_{2,3}$=$J_{2,OH}$=7.1 Hz, 1H, H-2), 1.10 (s, 3H, H-8′), 0.90 (s, 3H, H-9′); ^{13}C (125 MHz; $CDCl_3$): δ 167.2 (C-1), 162.5 (C-1), 85.5 (C-3), 69.8 (C-2), 65.3 (C-2′), 63.3 (C-5), 52.9 (C-10′), 49.4 (C-1′), 47.6 (C-7′), 44.6 (C-4′), 37.6 (C-3′), 32.6 (C-6′), 26.7 (C-5′), 20.4 (C-8′), 19.8 (C-9′) 13.6 (C-6).

4.2.23. *O*-[(2*S*)-Hydroxy-3-nitropropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (4b). Colourless oil, HRMS-LSIMS(+): Calcd for $C_{19}H_{27}O_5NNa$ $(M+Na)^+$: 372.1786, found 372.1790. Anal Calcd C. 65.31, H. 7.79, N. 4.01, found C. 65.28, H. 8.03, N. 3.94; IR (film): 3486, 2957, 2924, 1732, 1557, 1376, 1224, 1124, 978, 766, 702 cm^{-1}; $[\alpha]_D^{20}$=−6.40 (c=1.15; $CHCl_3$); R_f=0.4 (hexane/AcOEt 8:2); ^{1}H NMR (200 MHz; $CDCl_3$): δ 7.32–7.08 (m, 5H, Ar), 4.85 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.3 Hz, 1H, H-1′), 4.11 (dd_{AB}, $J_{3A,3B}$=14.5 Hz, $J_{2,3A}$=3.4 Hz, 1H, H_A-3), 3.83 (dd_{AB}, $J_{3A,3B}$=14.5 Hz, $J_{2,3B}$=4.3 Hz, 1H, H_B-3), 3.42 (t, $J_{2,3A}$=3.8 Hz, 1H, H-2), 2.40 (bs, 1H, OH), 2.40–2.08 (m, 1H, H-2′), 2.06–1.88 (m, 2H, H_A-6′, H_A-3′), 1.82–1.68 (m, 1H, H_A-4′), 1.62–1.38 (m, 1H, H_A-5′), 1.25–1.18 (m, 1H, H_B-3′), 1.27 (s, 3H, H-9′), 1.15 (s, 3H, H-10′), 1.10–0.90 (m, 2H, H_B-4′, H_B-6′), 0.90 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 169.8 (C-1), 152.4 (i-Ar), 127.9 (Ar), 125.0 (Ar), 124.9 (Ar), 77.2 (C-2), 76.1 (C-1′), 75.8 (C-3), 66.6 (C-2′), 40.5 (C-6′), 39.0 (C-8′), 34.2 (C-4′), 31.0 (C-5′), 30.8 (C-9′), 25.8 (C-3′), 21.5 (C-7′), 20.9 (C-10″).

4.2.24. *O*-[(2*R*)-Hydroxy-3-nitropropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (5b). Selected signals from differential NMR spectra: ^{1}H (200 MHz; $CDCl_3$): δ 4.93 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.9 Hz, $J_{1',6'B}$=4.5 Hz, 1H, H-1′), 4.18 (dd_{AB}, $J_{3A,3B}$=15.4 Hz, $J_{2,3A}$=5.3 Hz, 1H, H_A-3), 4.06 (dd_{AB}, $J_{3A,3B}$=15.4 Hz, $J_{2,3B}$=6.1 Hz, 1H, H_B-3), 1.30 (s, 3H, H-9′), 1.19 (s, 3H, H-10′); ^{13}C (50 MHz; $CDCl_3$): δ 169.1 (C-1), 152.3 (i-Ar), 128.0 (Ar), 127.5 (Ar), 125.0 (Ar), 77.3 (C-2), 67.9 (C-2′), 40.8 (C-6′), 39.1 (C-8′), 31.1 (C-5′), 26.0 (C-3′), 21.4 (C-7′).

4.2.25. *O*-[*syn*-(2ξ)-Hydroxy-(3ξ)-nitrooctanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (6ba). Colourless oil, HRMS-LSIMS(+): Calcd for $C_{24}H_{38}O_5N$ $(M+H)^+$: 420.2750, found 420.2745. Anal Calcd C. 68.71, H. 8.89, N. 3.34, found C. 68.71, H. 9.10, N. 3.35; IR (film): 3497, 2957, 2927, 2870, 1732, 1555, 1458, 1258, 1130, 1094, 976,

766 cm^{-1}; $[\alpha]_D{}^{20}$=26.4 (c=1.42; $CHCl_3$); R_f=0.6 (hexane/AcOEt 8:2); ^1H NMR (500 MHz; $CDCl_3$): δ 7.33–7.23 (m, 4H, Ar), 7.21–7.09 (m, 1H, Ar), 4.90 (dt, $J_{1',6'A}=J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 4.00 (ddd, $J_{2,3}$=3.0 Hz, $J_{3,4A}$=10.9 Hz, $J_{3,4B}$=6.8 Hz, 1H, H-3), 3.10 (dd, $J_{2,3}$=3.0 Hz, $J_{2,OH}$=6.5 Hz, 1H, H-2), 2.88 (d, $J_{2,OH}$=6.5 Hz, 1H, OH), 2.31–2.12 (m, 1H, H-2′), 2.10–2.00 (m, 1H, H_A-3′), 1.99–1.84 (m, 3H, H-4, H_A-6′), 1.76–1.71 (m, 3H, H-5, H_A-4′), 1.56–1.29 (m, 6H, H-6, H-7, H-3′, H_A-5′), 1.28 (s, 3H, H-9′), 1.16 (s, 3H, H-10′), 1.01–0.86 (m, 8H, H_B-4′, H_B-6′, H-7′, H-8); ^{13}C NMR (125 MHz; $CDCl_3$): δ 168.2 (C-1), 152.5 (i-Ar), 127.9 (Ar), 125.2 (Ar), 125.0 (Ar), 87.6 (C-3), 76.9 (C-1′), 71.7 (C-2), 50.1 (C-2′), 40.6 (C-6′), 39.2 (C-8′), 34.3 (C-4′), 31.0 (C-9′), 30.5 (C-5′), 30.4 (C-5), 28.3 (C-4), 26.0 (C-3′), 25.6 (C-6), 22.3 (C-7), 21.8 (C-7′), 21.7 (C-10′), 13.8 (C-8).

4.2.26. *O*-[*anti*-(2ξ)-Hydroxy-(3ξ)-nitrooctanoyl]-(1′*R*, 2′*S*,5′*R*)-8′-phenylmenthol (7ba). Colourless oil, ^1H NMR (500 MHz; $CDCl_3$): δ 4.92 (dt, $J_{1',6'A}=J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.4, 1H, H-1′), 4.19 (dt, $J_{2,3}=J_{3,4B}$=3.2 Hz, $J_{3,4A}$= 7.3 Hz, 1H, H-3), 3.72 (dd, $J_{2,3}$=3.2 Hz, $J_{2,OH}$=4.8 Hz, 1H, H-2), 2.95 (d, $J_{2,OH}$ Hz=4.8, 1H), OH, 1.24 (s, 3H, H-9′), 1.15 (s, 3H, H-10′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.3 (C-1), 152.4 (i-Ar), 127.9 (Ar), 125.2 (Ar), 125.0 (Ar), 87.5 (C-3), 76.8 (C-1′), 69.6 (C-2), 50.0 (C-2′), 40.6 (C-6′), 39.1 (C-8′), 34.3 (C-4′), 31.1 (C-9′), 30.9 (C-5), 30.8 (C-5′), 28.2 (C-4), 26.0 (C-3′), 25.5 (C-6), 22.1 (C-7), 21.7 (C-7′), 21.6 (C-10′), 13.7 (C-8).

4.2.27. *O*-[(2ξ)-Hydroxy-(3ξ)-nitrooctanoyl]-(1′*R*, 2′*S*,5′*R*)-8′-phenylmenthol (8ba). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 4.97 (dt, $J_{1',6'A}=J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.5 Hz, 1H, H-1′), 4.22 (dt, $J_{2,3}=J_{3,4B}$=3.8 Hz, $J_{3,4A}$=9.9 Hz, 1H, H-3), 3.37 (dd, $J_{2,3}$= 3.8 Hz, $J_{2,OH}$=4.0 Hz, 1H, H-2), 3.03 (d, $J_{2,OH}$=4.0 Hz, 1H, OH), 1.24 (s, 3H, H-9′), 1.15 (s, 3H, H-10′); ^{13}C (125 MHz; $CDCl_3$): δ 170.3 (C-1), 151.7 (i-Ar), 128.0 (Ar), 125.1 (Ar), 125.0 (Ar), 89.2 (C-3), 77.0 (C-1′), 70.2 (C-2), 50.2 (C-2′), 41.2 (C-6′), 39.2 (C-8′), 34.2 (C-4′), 31.1 (C-9′), 30.9 (C-5′), 30.3 (C-5), 28.2 (C-4), 26.0 (C-3′), 25.5 (C-6), 22.1 (C-7), 21.7 (C-7′), 21.6 (C-10′), 13.7 (C-8).

4.2.28. *O*-[(2ξ)-Hydroxy-(3ξ)-nitrooctanoyl]-(1′*R*, 2′*S*,5′*R*)-8′-phenylmenthol (9ba). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 4.94 (dt, $J_{1',6'A}=J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.5 Hz, 1H, H-1′), 4.49 (dt, $J_{2,3}=J_{3,4B}$=4.5 Hz, $J_{3,4A}$=9.0 Hz, 1H, H-3), 1.30 (s, 3H, H-9′), 1.17 (s, 3H, H-10′); ^{13}C (125 MHz; $CDCl_3$): δ 169.5 (C-1), 152.5 (i-Ar), 87.0 (C-3), 76.6 (C-1′), 70.8 (C-2), 49.5 (C-2′), 40.9 (C-6′), 39.3 (C-8′), 34.4 (C-4′), 31.2 (C-9′), 30.4 (C-5′), 30.3 (C-5), 28.8 (C-4), 26.2 (C-3′), 25.4 (C-6), 22.1 (C-7), 21.7 (C-7′), 21.5 (C-10′), 13.8 (C-8).

4.2.29. *O*-[4,4-Diethoxy-*syn*-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (6bb). Colourless oil, HRMS-LSIMS(+): Calcd for $C_{24}H_{38}O_7N$ $(M+H)^+$: 452.2648, found 452.2643. Anal. Calcd C. 63.87, H. 8.26, N. 3.10, found C. 63.62, H. 8.45, N. 3.10; IR (film): 3492, 2961, 2926, 1737, 1556, 1445, 1327, 1278, 1120, 1066, 766, 702 cm^{-1}; $[\alpha]_D{}^{20}$=−13.5 (c=0.98; $CHCl_3$); R_f=0.5 (hexane/AcOEt 8:2); ^1H NMR (500 MHz; $CDCl_3$): δ 7.29–7.10 (m, 5H, Ar), 4.97 (d, $J_{3,4}$=8.0 Hz, 1H, H-4), 4.93 (dt, $J_{1',6'A}=J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.5 Hz, 1H, H-1′), 4.28 (dd, $J_{2,3}$=2.5 Hz, $J_{3,4}$=8.0 Hz, 1H, H-3), 3.63 (dd, $J_{5A,5B}$=9.2 Hz, $J_{5,6}$=7.1 Hz, 2H, H-5), 3.56 (dd, $J_{5''A,5''B}$=9.2 Hz, $J_{5'',6''}$=7.1 Hz, 2H, H-5″), 3.40 (dd, $J_{2,3}$= 2.5 Hz, $J_{2,OH}$=7.3 Hz, 1H, H-2), 2.91 (d, $J_{2,OH}$=7.3 Hz, 1H, OH), 2.12 (ddd, $J_{1',2'}$=10.8 Hz, $J_{2',3'A}$=12.3 Hz, $J_{2',3'B}$= 3.7 Hz, 1H, H-2′), 1.98–1.92 (m, 1H, H_A-3′), 1.89–1.84 (m, 1H, H_A-6′), 1.75–1.70 (m, 1H, H_A-4′), 1.52–1.40 (m, 1H, H_A-5′), 1.30 (s, 3H, H-9′), 1.29 (t, $J_{5,6}$=7.1 Hz, 3H, H-6), 1.20–1.14 (m, 1H, H_B-3′), 1.10–0.91 (m, 2H, H_B-4′, H_B-6′), 1.18 (s, 3H, H-10′), 1.15 (t, $J_{5'',6''}$=7.1 Hz, 3H, H-6″), 0.90 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.1 (C-1), 151.7 (i-Ar), 127.9 (Ar), 125.3 (Ar), 125.2 (Ar), 99.5 (C-4), 88.5 (C-3), 76.9 (C-1′), 68.4 (C-2), 64.8 (C-5), 64.5 (C-5″), 50.3 (C-2′), 40.8 (C-6′), 39.2 (C-8′), 34.4 (C-4′), 31.3 (C-5′), 30.4 (C-9′), 26.1 (C-3′), 21.8 (C-7′), 21.7 (C-10′), 15.3 (C-6), 15.0 (C-6″).

4.2.30. *O*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (7bb). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 5.01 (d, $J_{3,4}$=8.1 Hz, 1H, H-4), 4.41 (dd, $J_{2,3}$=1.7 Hz, $J_{3,4}$=8.1 Hz, 1H, H-3), 3.40 (dd, $J_{2,3}$=1.7 Hz, $J_{2,OH}$= 3.9 Hz, 1H, H-2); ^{13}C (125 MHz; $CDCl_3$): δ 169.5 (C-1), 151.3 (i-Ar), 128.0 (Ar), 125.5 (Ar), 125.0 (Ar), 99.3 (C-4), 88.9 (C-3), 77.0 (C-1′), 68.9 (C-2), 65.3 (C-5), 64.6 (C-5″), 50.1 (C-2′), 41.0 (C-6′), 39.4 (C-8′), 34.4 (C-4′), 31.3 (C-5′), 30.2 (C-9′), 26.1 (C-3′), 22.6 (C-7′), 21.7 (C-10′), 15.1 (C-6), 15.0 (C-6″).

4.2.31. *O*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (8bb). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 5.01 (d, $J_{3,4}$=7.7 Hz, 1H, H-4), 4.59 (dd, $J_{2,3}$=2.2 Hz, $J_{3,4}$=7.7 Hz, 1H, H-3), 4.11 (dd, $J_{2,3}$=2.2 Hz, $J_{2,OH}$= 3.9 Hz, 1H, H-2), 3.05 (d, $J_{2,OH}$=3.9 Hz, 1H, OH); ^{13}C (125 MHz; $CDCl_3$): δ 168.8 (C-1), 152.1 (i-Ar), 127.9 (Ar), 99.2 (C-4), 87.6 (C-3), 77.0 (C-1′), 69.6 (C-2), 64.7 (C-5), 64.4 (C-5″), 49.8 (C-2′), 39.2 (C-8′), 34.4 (C-4′), 31.2 (C-5′), 29.6 (C-9′), 26.3 (C-3′), 22.8 (C-7′), 22.1 (C-10′), 15.2 (C-6), 14.1 (C-6″).

4.2.32. *O*-[4,4-Diethoxy-(2ξ)-hydroxy-(3ξ)-nitrobutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (9bb). Selected signals from differential NMR spectra: ^1H (500 MHz; $CDCl_3$): δ 5.15 (d, $J_{3,4}$=8.1 Hz, 1H, H-4), 4.73 (dd, $J_{2,3}$=2.9 Hz, $J_{3,4}$=8.1 Hz, 1H, H-3), 4.01 (dd, $J_{2,3}$=2.9 Hz, $J_{2,OH}$= 2.3 Hz, 1H, H-2); ^{13}C (125 MHz; $CDCl_3$): δ 167.9 (C-1), 152.9 (i-Ar), 128.0 (Ar), 89.2 (C-3), 77.2 (C-1′), 70.2 (C-2), 66.7 (C-5), 64.1 (C-5″), 49.8 (C-2′), 39.4 (C-8′), 34.4 (C-4′), 30.9 (C-5′), 29.8 (C-9′), 26.3 (C-3′), 22.5 (C-7′), 22.2 (C-10′).

4.2.33. *O*-[(2*S*)-Hydroxy-(3*R*)-nitro-3-phenylpropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (6bc). Colourless crystals, mp=179–180 °C (hexane/AcOEt); HRMS-LSIMS (+): Calcd for $C_{25}H_{31}O_5NNa$ $(M+Na)^+$ 448.2099, found 448.2087. Anal. Calcd C. 70.57, H. 7.34, N. 3.29, found C. 70.10, H. 7.55, N. 3.32; IR (KBr): 3479 2958, 2924, 1730, 1556, 1496, 1456, 1366, 1258, 1121, 957, 766, 701 cm^{-1}; $[\alpha]_D{}^{20}$=7.2 (c=0.93; $CHCl_3$); R_f=0.5 (hexane/AcOEt 8:2)^1H NMR (500 MHz; $CDCl_3$): δ 7.50–7.06 (m, 10H, 2xAr), 5.14 (d, $J_{2,3}$=5.1 Hz, 1H, H-3), 4.87 (dt,

$J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.5$ Hz, 1H, H-1′), 3.63 (dd, $J_{2,3}=5.1$ Hz, $J_{2,OH}=6.1$ Hz, 1H, H-2), 3.05 (d, $J_{2,OH}=6.1$ Hz, 1H, OH), 2.07 (ddd, $J_{1',2'}=10.8$ Hz, $J_{2',3'A}=3.6$ Hz, $J_{2',3'B}=12.1$ Hz, 1H, H-2′), 1.99 (dd, $J_{2',3'A}=J_{4'A,3'A}=3.6$ Hz, $J_{3'A,3'B}=13.5$ Hz, 1H, H_A-3′), 1.78–1.71 (m, 1H, H_A-6′), 1.67–1.62 (m, 1H, H_A-4′), 1.52–1.41 (m, 1H, H_A-5′), 1.30 (s, 3H, H-9′), 1.26–1.19 (m, 1H, H_B-3′), 1.15 (s, 3H, H-10′), 1.00–0.89 (m, 2H, H_B-4′, H_B-6′), 0.87 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 169.9 (C-1), 152.3 (i-Ar), 131.0 (i-Ar), 129.9 (Ar), 129.1 (Ar), 128.6 (Ar), 127.9 (Ar), 125.4 (Ar), 124.2 (Ar), 91.1 (C-3), 76.9 (C-1′), 71.1 (C-2), 50.1 (C-2′), 40.5 (C-6′), 39.1 (C-8′), 34.2 (C-4′), 31.1 (C-5′), 30.8 (C-9′), 25.9 (C-3′), 21.6 (C-7′), 21.3 (C-10′).

4.2.34. *O*-[*anti*-(2ξ)-Hydroxy-(3ξ)-nitro-3-phenylpropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (7bc). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.25 (d, $J_{2,3}=4.5$ Hz, 1H, H-3), 4.94 (dt, $J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.2$ Hz, 1H, H-1′), 4.21 (dd, $J_{2,3}=4.5$ Hz, $J_{2,OH}=4.8$ Hz, 1H, H-2), 3.05 (d, $J_{2,OH}=4.8$ Hz, 1H, OH), 1.34 (s, 3H, H-9′), 1.20 (s, 3H, H-10′), 0.86 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C (125 MHz; $CDCl_3$): δ 169.7 (C-1), 152.0 (i-Ar), 131.3 (i-Ar), 129.9 (Ar), 129.8 (Ar), 128.3 (Ar), 128.2 (Ar), 125.3 (Ar), 125.0 (Ar), 89.6 (C-3), 77.5 (C-1′), 70.5 (C-2), 50.3 (C-2′), 40.9 (C-6′), 39.3 (C-8′), 34.4 (C-4′), 31.2 (C-5′), 30.4 (C-9′), 26.0 (C-3′), 21.6 (C-7′), 21.5 (C-10′).

4.2.35. *O*-[(2ξ)-Hydroxy-(3ξ)-nitro-3-phenylpropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (8bc). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 5.39 (d, $J_{2,3}=5.2$ Hz, 1H, H-3), 4.73 (dt, $J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.4$ Hz, 1H, H-1′), 4.60 (dd, $J_{2,3}=5.1$ Hz, $J_{2,OH}=3.8$ Hz, 1H, H-2), 2.95 (d, $J_{2,OH}=3.8$ Hz, 1H, OH), 1.25 (s, 3H, H-9′), 1.15 (s, 3H, H-10′), 0.78 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C (125 MHz; $CDCl_3$): δ 168.7 (C-1), 152.5 (i-Ar), 129.8 (Ar), 129.2(Ar), 128.0 (Ar), 125.4 (Ar), 125.0 (Ar), 89.5 (C-3), 77.4 (C-1′), 72.3 (C-2), 49.8 (C-2′), 40.8 (C-6′), 39.2 (C-8′), 34.2 (C-4′), 31.1 (C-5′), 30.2 (C-9′), 26.3 (C-3′), 22.3 (C-7′), 21.0 (C-10′).

4.2.36. *O*-[(2*S*)-Hydroxy-(3*R*)-nitro-4-phenylbutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (6bd). Colourless crystals, mp=85 °C (hexane/Et2O); HRMS-ESI: Calcd for $C_{26}H_{33}O_5NNa$ $(M+Na)^+$ 462.2251, found 462.2251. Anal. Calcd C. 71.05, H. 7.57, N. 3.19, found C. 70.90, H. 7.61, N. 3.03; IR (KBr): 3567, 2960, 2920, 1718, 1546, 1367, 1282, 1126, 986, 758, 695, 491 cm^{-1}; $[\alpha]_D{}^{20}=26$ (c=1.11; $CHCl_3$); R_f=0.5 (hexane/AcOEt 8:2); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.40–7.30 (m, 3H, Ar), 7.22–7.19 (m, 4H, Ar), 7.07–7.02 (m, 2H, Ar), 6.75–6.71 (m, 1H, Ar), 4.92 (dt, $J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.5$ Hz, 1H, H-1′), 4.35 (ddd, $J_{2,3}=2.7$ Hz, $J_{3,4A}=6.9$ Hz, $J_{3,4B}=8.5$ Hz, 1H, H-3), 4.31 (dd_{AB}, $J_{4A,4B}=13.9$ Hz, $J_{3,4A}=6.9$ Hz, 1H, H_A-4), 3.07 (dd_{AB}, $J_{4A,4B}=13.9$ Hz, $J_{3,4B}=6.9$ Hz, 1H, H_B-4), 3.01 (dd, $J_{2,3}=2.7$ Hz, $J_{2,OH}=6.9$ Hz, 1H, H-2), 2.95 (d, $J_{2,OH}=6.9$ Hz, 1H, OH), 2.10 (ddd, $J_{1',2'}=10.6$ Hz, $J_{2',3'A}=12.1$ Hz, $J_{2',3'B}=3.7$ Hz, 1H, H-2′), 1.96 (dq, $J_{3'A,3'B}=13.5$ Hz, $J_{2',3'B}=J_{3',4'A}=3.7$ Hz, 1H, H_A-3′), 1.87–1.84 (m, 1H, H_A-6′), 1.75–1.70 (m, 1H, H_A-4′), 1.52–1.41 (m, 1H, H_A-5′), 1.23–1.16 (m, 1H, H_B-3′), 1.24 (s, 3H, H-9′), 1.12 (s, 3H, H-10′), 1.00–0.90 (m, 2H, H_B-4′, H_B-6′), 0.89 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.3 (C-1), 151.8 (i-Ar), 135.0 (i-Ar), 129.3 (Ar), 128.8 (Ar), 127.6 (Ar), 127.4 (Ar), 125.1 (Ar), 125.0 (Ar), 88.5 (C-3), 76.9 (C-1′), 68.7 (C-2), 50.1 (C-2′), 40.7 (C-6′), 39.1 (C-8′), 35.4 (C-4), 34.4 (C-4′), 31.2 (C-5′), 30.6 (C-9′), 26.0 (C-3′), 21.6 (C-7′), 21.3 (C-10′).

4.2.37. *O*-[(2*S*)-Hydroxy-(3*S*)-nitro-4-phenylbutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (7bd). Colourless crystals, mp=91–93 °C (hexane/AcOEt); $[\alpha]_D{}^{20}=-21$ (c=1.27; $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.31–7.21 (m, 7H, Ar), 7.16–7.12 (m, 1H, Ar), 7.08–7.025 (m, 2H, Ar), 4.94 (dt, $J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.4$ Hz, 1H, H-1′), 4.46 (ddd, $J_{2,3}=3.9$ Hz, $J_{3,4A}=9.7$ Hz, $J_{3,4B}=4.5$ Hz, 1H, H-3), 3.47 (dd, $J_{2,3}=3.9$ Hz, $J_{2,OH}=4.6$ Hz, 1H, H-2), 3.19 (dd_{AB}, $J_{4A,4B}=14.9$ Hz, $J_{3,4A}=9.7$ Hz, 1H, H_A-4), 3.01 (d, $J_{2,OH}=4.6$ Hz, 1H, OH), 2.73 (dd_{AB}, $J_{4A,4B}=14.9$ Hz, $J_{3,4B}=4.5$ Hz, 1H, H_B-4), 2.16 (ddd, $J_{1',2'}=10.8$ Hz, $J_{2',3'A}=12.2$ Hz, $J_{2',3'B}=3.6$ Hz, 1H, H-2′), 1.96 (dq, $J_{3'A,3'B}=13.5$ Hz, $J_{2',3'B}=J_{3',4'A}=3.6$ Hz, 1H, H_A-3′), 1.80–1.71 (m, 1H, H_A-6′, H_A-4′), 1.53–1.41 (m, 1H, H_A-5′), 1.23–1.16 (m, 1H, H_B-3′), 1.29 (s, 3H, H-9′), 1.18 (s, 3H, H-10′), 1.10–0.91 (m, 2H, H_B-4′, H_B-6′), 0.90 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.0 (C-1), 151.7 (i-Ar), 135.4 (i-Ar), 128.9 (Ar), 128.7 (Ar), 128.1 (Ar), 127.4 (Ar), 125.4 (Ar), 125.1 (Ar), 90.2 (C-3), 77.4 (C-1′), 70.2 (C-2), 50.2 (C-2′), 41.2 (C-6′), 39.3 (C-8′), 34.3 (C-4), 34.2 (C-4′), 31.3 (C-5′), 30.4 (C-9′), 26.1 (C-3′), 21.8 (C-7′), 21.6 (C-10′).

4.2.38. *O*-[(2ξ)-Hydroxy-(3ξ)-nitro-4-phenylbutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (8bd). Colourless crystals, mp=126–127 °C; $[\alpha]_D{}^{20}=13$ (c=0.92; $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.39–7.35 (m, 2H, Ar), 7.33–7.29 (m, 1H, Ar), 7.26–7.24 (m, 3H, Ar), 7.20–7.13 (m, 4H, Ar), 4.90 (dt, $J_{1',6'A}=J_{1',2'}=10.8$ Hz, $J_{1',6'B}=4.4$ Hz, 1H, H-1′), 4.52 (ddd, $J_{2,3}=2.33$ Hz, $J_{3,4A}=5.8$ Hz, $J_{3,4B}=10.3$ Hz, 1H, H-3), 3.45 (dd, $J_{2,3}=2.3$ Hz, $J_{2,OH}=4.4$ Hz, 1H, H-2), 3.43 (dd_{AB}, $J_{4A,4B}=13.6$ Hz, $J_{3,4A}=5.8$ Hz, 1H, H_A-4), 3.12 (dd_{AB}, $J_{4A,4B}=13.6$ Hz, $J_{3,4B}=10.3$ Hz, 1H, H_B-4), 2.21 (ddd, $J_{1',2'}=10.7$ Hz, $J_{2',3'A}=12.2$ Hz, $J_{2',3'B}=3.6$ Hz, 1H, H-2′), 1.96 (dq, $J_{3'A,3'B}=13.5$ Hz, $J_{2',3'B}=J_{3',4'A}=3.6$ Hz, 1H, H-3′), 1.94–1.90 (m, 1H, H_A-6′), 1.75–1.71 (m, 1H, H_A-4′), 1.53–1.44 (m, 1H, H_A-5′), 1.25–1.16 (m, 1H, H_B-3′), 1.26 (s, 3H, H-9′), 1.14 (s, 3H, H-10′), 1.05–0.90 (m, 2H, H_B-4′, H_B-6′), 0.89 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 169.6 (C-1), 152.5 (i-Ar), 135.5 (i-Ar), 129.3 (Ar), 128.9 (Ar), 127.9 (Ar), 127.4 (Ar), 125.2 (Ar), 125.2 (Ar), 87.2 (C-3), 76.8 (C-1′), 69.2 (C-2), 49.7 (C-2′), 40.8 (C-6′), 39.3 (C-8′), 34.6 (C-4), 34.4 (C-4′), 31.3 (C-5′), 30.7 (C-9′), 26.2 (C-3′), 21.6 (C-7′), 21.5 (C-10′).

4.2.39. *O*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitropropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (6be). Colourless oil, HRMS-ESI: Calcd for $C_{22}H_{31}O_7NNa$ $(M+Na)^+$: 444.1993, found 444.1960. Anal. Calcd C. 62.69, H. 7.41, N. 3.32, found C. 62.77, H. 7.41, N. 3.37; 3493, 2961, 2927, 2871, 1754, 1567, 1496, IR (film): 1444, 1368, 1257, 1199, 1129, 1029, 767, 703, 532 cm^{-1}; R_f=0.5 (hexane/AcOEt 8:2); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.35–7.25 (m, 4H, Ar), 7.17–7.08 (m, 1H, Ar), 4.94 (dt, $J_{1',6'A}=J_{1',2'}=10.7$ Hz, $J_{1',6'B}=4.5$ Hz, 1H, H-1′), 4.84 (d, $J_{2,3}=2.6$ Hz, 1H, H-3), 4.35–4.16 (m, 2H, H-5), 3.79 (dd, $J_{2,3}=2.6$ Hz, $J_{2,OH}=5.0$ Hz,

1H, H-2), 3.19 (d, $J_{2,OH}$=5.2 Hz, 1H, OH), 2.20–2.07 (m, 1H, H-2′), 2.02–1.94 (m, 1H, H_A-3′), 1.86–1.77 (m, 1H, H_A-6′), 1.77–1.71 (m, 1H, H_A-4′), 1.56–1.44 (m, 1H, H_A-5′), 1.37–1.18 (m, 1H, H_B-3′), 1.19 (s, 3H, H-9′), 1.18 (s, 3H, H-10′), 1.00–0.89 (m, 3H, H_B-4′, H_B-6′, H-6), 0.88 (d, $J_{5',7'}$=6.6 Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 168.4 (C-1), 161.6 (C-4), 151.8 (i-Ar), 128.0 (Ar), 125.5 (Ar), 125.4 (Ar), 88.2 (C-3), 77.5 (C-1′), 68.4 (C-2), 63.2 (C-5), 50.3 (C-2′), 40.8 (C-6′), 39.1 (C-8′), 34.3 (C-4′), 31.1 (C-5′), 30.3 (C-9′), 25.9 (C-3′), 21.5 (C-7′), 21.5 (C-10′), 13.7 (C-6).

4.2.40. *O*-[(2ξ)-Hydroxy-3-carboxyethyl-(3ξ)-nitropropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (7be). Selected signals from differential NMR spectra: ^{1}H (500 MHz; $CDCl_3$): δ 4.88 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.3 Hz, 1H, H-1′), 4.45 (d, $J_{2,3}$=3.4 Hz, 1H, H-3), 3.70 (dd, $J_{2,3}$=3.4 Hz, $J_{2,OH}$=7.8 Hz, 1H, H-2), 3.11 (d, $J_{2,OH}$=7.8 Hz, 1H, OH), 1.18 (s, 3H, H-9′), 1.15 (s, 3H, H-10′), 0.90 (d, $J_{5',7'}$=6.6, 3H, H-7′); ^{13}C (125 MHz; $CDCl_3$): δ 168.2 (C-1), 161.8 (C-4), 152.6 (i-Ar), 128.0 (Ar), 125.4 (Ar), 125.2 (Ar), 87.7 (C-3), 77.4 (C-1′), 68.6 (C-2), 63.2 (C-5), 50.0 (C-2′), 40.2 (C-6′), 39.0 (C-8′), 34.3 (C-4′), 31.0 (C-5′), 30.4 (C-9′), 25.8 (C-3′), 21.6 (C-7′), 21.6 (C-10′), 13.8 (C-6).

4.3. General procedure for the synthesis of nitrodiols

To a precooled solution (0 °C) of nitroalcohol (1 mmol) in THF (1 mL), $NaBH_4$ (1.1 mmol) was portionwise added. Progress of the reaction was monitored by TLC, and when finished, it was quenched by addition of saturated aqueous NaCl and extracted with AcOEt. The combined organic extracts were dried over $MgSO_4$ and evaporated. All products were purified by column chromatography (hexane/AcOEt 8:2–4:6).

4.3.1. 3-Nitropropane-(1,2*S*)-diol (10). The title compound was obtained in 85% yield from 4a, and 87% from 4b: colourless oil, HRMS-ESI: Calcd for $C_3H_8NO_4$ $(M+H)^+$ 122.1005; found 122.1008. Anal. Calcd C. 29.75, H. 5.82, N. 11.56, found C. 29.60, H. 5.92, N. 11.31; IR (film): 3366, 1552, 1384, 1111, 1048, 875 cm^{-1}; $[\alpha]_D{}^{20}$=−6.7 (*c*=0.99; $CHCl_3$); R_f=0.1 (hexane/AcOEt 1:1); ^{1}H NMR (500 MHz; D_2O): δ 4.75 (dd_{AB}, $J_{2,3A}$=3.2 Hz, $J_{3A,3B}$=13.0 Hz, 1H, H_A-3), 4.59 (dd_{AB}, $J_{2,3B}$=9.0 Hz, $J_{3A,3B}$=13.0 Hz, 1H, H_B-3), 4.43 (dddd, $J_{2,3A}$=3.2 Hz, $J_{2,3B}$=9.0 Hz, $J_{2,1A}$=5.0 Hz, $J_{2,1B}$=5.6 Hz, 1H, H-2), 3.69 (dd_{AB}, $J_{2,1A}$=5.0 Hz, $J_{1A,1B}$=11.9 Hz, 1H, H_A-1), 3.65 (dd_{AB}, $J_{2,1B}$=5.6 Hz, $J_{1A,1B}$=11.9 Hz, 1H, H_B-1); ^{13}C NMR (125 MHz; $CDCl_3$): δ 77.7 (C-3), 68.8 (C-2), 63.4 (C-1).

4.3.2. (3*R*)-Nitrooctane-(1,2*S*)-diol (11a). The title compound was obtained with 88% yield; colourless oil, HRMS-ESI: Calcd for $C_8H_{17}NO_4Na$ $(M+Na)^+$: 214.1050, found 214.1054. Anal. Calcd C. 50.25, H. 8.96, N. 7.32, found C. 50.03, H. 8.83, N. 7.20; IR (film): 3371, 2958, 2931, 2863, 1554, 1464, 1377, 1099, 1039, 833 cm^{-1}; R_f=0.2 (hexane/AcOEt 1:1); $[\alpha]_D{}^{20}$=10.5 (*c*=1.74; MeOH); ^{1}H NMR (200 MHz; $CDCl_3$): δ 4.64 (ddd, $J_{2,3}$=8.3 Hz, $J_{3,4A}$=3.9 Hz, $J_{3,4B}$=10.4 Hz, 1H, H-3), 4.15 (dd, $J_{2,3}$=8.3 Hz, $J_{2,1A}$=3.0 Hz, $J_{2,1B}$=5.5 Hz, 1H, H-2), 3.79 (dd_{AB}, $J_{2,1A}$=3.0 Hz, $J_{1A,1B}$=11.9 Hz, 1H, H_A-1), 3.61 (dd_{AB}, $J_{2,1B}$=5.5 Hz, $J_{1A,1B}$=11.9 Hz, 1H, H_B-1), 2.10–1.87 (m, 1H, H_A-4), 1.83–1.63 (m, 1H, H_B-4), 1.50–1.10 (m, 6H, H-5, H-6, H-7), 0.88–082 (m, 3H, H-8); ^{13}C NMR (50 MHz; $CDCl_3$): δ 90.3 (C-3), 72.5 (C-2), 62.9 (C-1), 30.9 (C-4), 29.9 (C-5), 25.2 (C-6), 22.2 (C-7), 13.8 (C-8).

4.3.3. *anti*-(3ξ)-Nitrooctane-(1,2ξ)-diol (11b). The title compound was obtained with 85% yield; colourless oil, HRMS-ESI: Calcd for $C_8H_{17}NO_4Na$ $(M+Na)^+$: 214.1050, found 214.1052. Anal. Calcd C. 50.25, H. 8.96, N. 7.32, found C. 50.10, H. 8.89, N. 7.19; IR (film): 3370, 2958, 2932, 2865, 1552, 1464, 1378, 1098, 1038, 834 cm^{-1}; $[\alpha]_D{}^{20}$=−21.0 (*c*=1.70; MeOH); ^{1}H NMR (200 MHz; $CDCl_3$): δ 4.63 (ddd, $J_{2,3}$=5.8 Hz, $J_{3,4A}$=3.5 Hz, $J_{3,4B}$=10.3 Hz, 1H, H-3), 4.09 (dd, $J_{2,3}$=$J_{2,1A}$=5.8 Hz, $J_{2,1B}$=3.8 Hz, 1H, H-2), 3.76 (dd_{AB}, $J_{2,1B}$=3.8 Hz, $J_{1A,1B}$=11.7 Hz, 1H, H_B-1), 3.66 (dd_{AB}, $J_{2,1A}$=5.8 Hz, $J_{1A,1B}$=11.7 Hz, 1H, H_A-1), 2.30–1.80 (m, 21H, H-4), 1.60–1.30 (m, 6H, H-5, H-6, H-7), 0.99–082 (m, 3H, H-8); ^{13}C NMR (50 MHz; $CDCl_3$): δ 89.4 (C-3), 72.2 (C-2), 62.7 (C-1), 31.0 (C-4), 29.0 (C-5), 25.4 (C-6), 22.2 (C-7), 13.8 (C-8).

4.3.4. (3*R*)-Nitro-3-phenylpropane-(1,2*S*)-diol (12a). The title compound was obtained with 90% yield. Colourless crystals, mp=83 °C (hexane/AcOEt); HRMS-ESI: Calcd for $C_9H_{11}NO_4$ $(M+Na)^+$ 220.0580; found 220.0572. Anal. Calcd C. 54.82, H. 5.62, N. 7.10, found C. 55.00, H. 5.78, N. 7.21; IR (KBr): 3541, 3400, 2928, 1649, 1539, 1370, 1320, 1100, 1049, 903, 732, 692, 632, 497 cm^{-1}; $[\alpha]_D{}^{20}$=−11.1 (*c*=0.51; ^{i}PrOH); R_f=0.2 (hexane/AcOEt 1:1); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.60–7.35 (m, 5H, Ar), 5.60 (d, $J_{2,3}$=9.9 Hz, 1H, H-3), 4.64 (ddd, $J_{2,3}$=9.9 Hz, $J_{2,1A}$=2.9 Hz, $J_{2,1B}$=4.6 Hz, 1H, H-2), 3.73 (bs, 1H, OH-2), 3.56 (dd_{AB}, $J_{2,1A}$=2.9 Hz, $J_{1A,1B}$=11.7 Hz, 1H, H_A-1), 3.29 (dd_{AB}, $J_{2,1B}$=4.6 Hz, $J_{1A,1B}$=11.7 Hz, 1H, H_B-1), 2.79 (bs, 1H, OH-1); ^{13}C NMR (125 MHz; $CDCl_3$): δ 131.2 (i-Ar),130.4 (Ar), 129.3 (Ar), 128.0 (Ar), 93.3 (C-3), 72.9 (C-2), 62.1 (C-1).

4.3.5. *anti*-(3ξ)-Nitro-3-phenylpropane-(1,2ξ)-diol (12b). The title compound was obtained with 87% yield. Colourless oil, $[\alpha]_D{}^{20}$=−8.8 (*c*=0.70; ^{i}PrOH); R_f=0.2 (hexane/AcOEt 1:1); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.55–7.40 (m, 5H, Ar), 5.61 (d, $J_{2,3}$=7.1 Hz, 1H, H-3), 4.65 (m, 1H, H-2), 3.77 (dd_{AB}, $J_{2,1A}$=3.8 Hz, $J_{1A,1B}$=11.5 Hz, 1H, H_A-1), 3.68 (dd_{AB}, $J_{2,1B}$=4.9 Hz, $J_{1A,1B}$=11.5 Hz, 1H, H_B-1); ^{13}C NMR (125 MHz; $CDCl_3$): δ 131.2 (i-Ar),130.4 (Ar), 129.3 (Ar), 128.0 (Ar), 93.3 (C-3), 72.9 (C-2), 62.1 (C-1).

4.3.6. (3*S*)-Nitro-3-phenylpropane-(1,2*R*)-diol (12c). The title compound was obtained in 86% yield. Colourless crystals, mp=82–84 °C (hexane/AcOEt); R_f=0.2 (hexane/AcOEt 1:1); $[\alpha]_D{}^{20}$=12.0 (*c*=0.63; ^{i}PrOH).

4.3.7. *O*-[(2*S*)-*t*-Butyldimethylsilyloxy-3-nitropropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (4c). To a solution of nitroalcohol 4b (797 mg, 2.27 mmol) in DMF (3 mL) TBDMSCl (375 mg, 2.49 mmol) and imidazole were added (617 mg, 9.08 mmol). The progress of reaction was monitored by TLC. After stirring at rt for 17 h, solvents were evaporated and purification was achieved on silica-gel column using hexane/AcOEt to give compound 4c (970 mg, 92%), (R_f=0.8 hexane/AcOEt 8:2). Colourless oil, HRMS-LSIMS(+): Calcd for $C_{25}H_{45}O_5SiNNa$ $(M+Na)^+$ 486.2651, found 486.2677. Anal. Calcd C. 64.62, H. 9.11,

N. 3.01, found C. 64.76, H. 9.17, N. 2.88; IR (film): 2956, 2929, 2857, 1752, 1562, 1472, 1379, 1254, 1207, 1154, 969, 838, 766, 782, 701 cm^{-1}; $[\alpha]_D{}^{20}=-3.0$ (c=1.11; $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$): δ 7.40–7.05 (m, 5H, Ar), 4.92 (dt, $J_{1,6A}=J_{1,2}=10.8$ Hz, $J_{1,6B}=4.5$ Hz, 1H, H-1′), 4.18 (dd_{AB}, $J_{3A,3B}=14.5$ Hz, $J_{2,3A}=10.8$ Hz, 1H, H_A-3), 3.42 (dd, $J_{2,3A}=10.8$ Hz, $J_{2,3B}=7.2$ Hz, 1H, H-2), 4.15 (dd_{AB}, $J_{3A,3B}=14.5$ Hz, $J_{2,3B}=7.2$ Hz, 1H, H_B-3), 2.12–2.05 (m, 1H, H-2′), 2.02–1.80 (m, 2H, H_A-6′, H_A-3′), 1.74–1.59 (m, 2H, H_A-4′, H_A-5′), 1.35–1.22 (m, 1H, H_B-3′), 1.32 (s, 3H, H-9′), 1.24 (s, 3H, H-10′), 1.15–1.07 (m, 2H, H_B-4′, H_B-6′), 0.89 (s, 9H, $(CH_3)_3$), 0.86 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′), 0.08 (s, 6H, 2xCH_3); ^{13}C NMR (50 MHz; $CDCl_3$): δ 156.8 (C-1), 150.5 (i-Ar), 128.4 (Ar), 127.9 (Ar), 125.7 (Ar), 77.5 (C-1′), 72.9 (C-2), 62.9 (C-3), 50.2 (C-2′), 40.9 (C-6′), 39.7 (C-8′), 34.2 (C-4′), 31.3 (C-5′), 27.4 (C-9′), 26.5 (C-3′), 25.6 (3xCH_3), 21.9 (C-7′), 21.6 (C-10′), 17.9 ($C(CH_3)_3$), −3.6 (2xCH_3).

4.3.8. *O*-[3-Amino-(2*S*)-*t*-butyldimethylsilyloxy-propanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (13). Through a solution of 2-nitroalcohol 4c (227 mg, 0.49 mmol) in MeOH (5 mL) in the presence of catalytic amounts of Raney Ni, hydrogen was bubled. Progress of the reaction was monitored by TLC. After stirring at rt for 24 h, catalyst was separated, solvents evaporated and purification was achieved on silica-gel column using hexane/AcOEt to give compound 13 (206 mg, 91%). Colourless oil, (R_f=0.1 hexane/AcOEt 8:2). Colourless oil, HRMS-ESI: Calcd for $C_{25}H_{44}O_5SiN$ $(M+H)^+$ 434.3085, found 434.3093. Anal. Calcd C. 69.07, H. 10.20, N. 3.22, found C. 69.06, H. 10.09, N. 3.24; IR (film): 3392, 2954, 2928, 2857, 1745, 1600, 1496, 1471, 1389, 1363, 1252, 1172, 1134, 1082, 985, 915, 837, 779, 700 cm^{-1}; $[\alpha]_D{}^{20}=-28.0$ (c=1.31; $CHCl_3$); ^1H NMR (400 MHz; $CDCl_3$): δ 7.25–7.20 (m, 4H, Ar), 7.16–7.11 (m, 4H, Ar), 4.76 (dt, $J_{1,6A}=J_{1,2}=10.7$ Hz, $J_{1,6B}=4.3$ Hz, 1H, H-1′), 3.44 (dd, $J_{2,3B}=5.1$ Hz, $J_{2,3A}=3.9$ Hz, 1H, H-2), 2.58 (dd_{AB}, $J_{3A,3B}=13.4$ Hz, $J_{2,3A}=3.9$ Hz, 1H, H_A-3), 2.53 (dd_{AB}, $J_{3A,3B}=13.4$ Hz, $J_{2,3B}=5.1$ Hz, 1H, H_B-3), 2.11–2.04 (m, 1H, H-2′), 2.00–1.91 (m, 1H, H_A-3′), 1.75–1.60 (m, 3H, H_B-3′, H_A-4′, H_A-6′,), 1.56–1.41 (m, 1H, H_A-5′), 1.29 (s, 3H, H-9′), 1.19 (s, 3H, H-10′), 1.16–1.07 (m, 2H, H_B-4′, H_B-6′), 0.92 (s, 9H, $(CH_3)_3$), 0.86 (d, $J_{5',7'}=6.5$ Hz, 3H, H-7′), 0.12 (s, 3H, CH_3), 0.05 (s, 3H, CH_3); ^{13}C NMR (50 MHz; $CDCl_3$): δ 171.5 (C-1), 151.9 (i-Ar), 127.8 (Ar), 125.1 (Ar), 124.8 (Ar), 75.3 (C-1′), 73.6 (C-2), 50.0 (C-2′), 46.6 (C-3), 41.4 (C-6′), 39.4 (C-10′), 34.4 (C-4′), 31.1 (C-5′), 28.9 (C-9′), 26.4 (C-3′), 25.6 (3xCH_3), 24.5 (C-7′), 21.6 (C-10′), 18.2 ($C(CH_3)_3$), −4.6 (CH_3), −5.3 (CH_3).

4.3.9. 3-Amino-(2*S*)-hydroxypropionic acid ((−)-isoserin) (14). The solution of ester 13 (150 mg, 0.35 mmol) in 6N HCl aq. (5 mL) was heated at 80 °C. Progress of the reaction was monitored by TLC, and when finished (24 h) acid was removed under reduced pressure. To the residue, dry EtOH (2 mL) and epoxypropane (49 μL, 0.7 mmol) were added. The compound 14 spontaneously precipitated from the reaction mixture (49 mg, 89%). Colourless crystals, mp=187–189 °C (MeOH/H_2O); LRMS-ESI: found for $(M+Na)^+$ 128.0; $[\alpha]_D{}^{20}=-32.0$ (c=0.52; H_2O); ^1H NMR (400 MHz; H_2O): δ 4.27–4.21 (m, 1H, H-2), 3.36 (dd_{AB}, $J_{3A,3B}=12.6$ Hz, $J_{2,3A}=2.8$ Hz, 1H, H_A-3), 3.14 (dd_{AB}, $J_{3A,3B}=12.6$ Hz, $J_{2,3B}=5.1$ Hz, 1H, H_B-3); ^{13}C NMR (50 MHz; $CDCl_3$): δ 177.3 (C-1), 68.7 (C-2), 42.8 (C-3).

4.3.10. General procedure for the synthesis of *N*-Boc-aminoalcohols. Through a solution of a nitroalcohol (0.39 mmol) in MeOH (5 mL) H_2 was bubbled in the presence of catalytic amounts of Raney Ni. Progress of the reaction was monitored by TLC, and when finished, the catalyst was filtered off, solvents were evaporated and the residue was redissolved in a mixture of AcOEt and saturated aq. $NaHCO_3$ (10 mL, 1:1), followed by addition of $(Boc)_2O$ (0.43 mmol). After 2h stirring the layers were separated, and water phase was extracted with CH_2Cl_2. After drying of combined organic layers ($MgSO_4$), solvents were removed under reduced pressure. Purification was achieved on silica gel using hexane/AcOEt (9:1–7:3).

4.3.11. *O*-[*syn*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxyoctanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (15a). The title compound was obtained in 90% yield: colourless oil, HRMS-ESI: Calcd for $C_{29}H_{48}O_5N$ $(M+H)^+$: 490.3527, found 490.3542; IR (film): 3449, 2957, 2928, 2870, 1718, 1498, 1456, 1366, 1243, 1172, 764, 700 cm^{-1}; R_f=0.55 (hexane/AcOEt 7:3); $[\alpha]_D{}^{20}=-13.0$ (c=0.48; $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$): δ 7.33–7.20 (m, 5H, Ar), 4.85 (dt, $J_{1',6'A}=J_{1',2'}=10.6$ Hz, $J_{1',6'B}=4.2$ Hz, 1H, H-1′), 4.78 (d, $J_{2,3}=10.4$ Hz, 1H, H-2), 3.62–3.44 (m, 1H, H-3), 3.02 (d, $J_{3,NH}=2.8$ Hz, 1H, NH), 2.30–2.23 (m, 1H, H-2′), 2.15–2.06 (m, 1H, H_A-3′), 2.03–1.85 (m, 3H, H-4, H_A-6′), 1.78–1.71 (m, 3H, H-5, H_A-4′), 1.56–1.25 (m, 6H, H-6, H-7, H-3′, H_A-5′), 1.38 (s, 9H, 3xCH_3), 1.30 (s, 3H, H-9′), 1.18 (s, 3H, H-10′), 1.01–0.92 (m, 5H, H_B-4′, H_B-6′, H-8), 0.91 (d, $J_{5',7'}=7.3$ Hz); ^{13}C NMR (50 MHz; $CDCl_3$): δ 155.4 (C=O Boc), 152.4 (i-Ar), 128.3 (Ar), 125.7 (Ar), 96.6 ($C(CH_3)_3$), 79.7 (C-1′), 72.0 (C-2), 52.6 (C-3), 50.3 (C-2′), 41.2 (C-6′), 39.8 (C-8′), 34.9 (C-4′), 33.4 (C-4), 32.1 (C-5′), 31.9 (C-5), 30.7 (C-9′), 28.9 (3xCH_3 Boc), 26.7 (C-3′), 26.3 (C-6), 23.2 (C-7′), 22.8 (C-10′), 22.3 (C-7), 14.6 (C-8).

4.3.12. *O*-[*anti*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxyoctanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (15b). The title compound was obtained as a colourless oil, in 92% yield: (R_f=0.50 hexane/AcOEt 7:3); $[\alpha]_D{}^{20}=-10.0$ (c=0.1; $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$): δ 7.35–7.22 (m, 5H, Ar), 4.92 (dt, $J_{1',6'A}=J_{1',2'}=10.7$, $J_{1',6'B}=4.3$, 1H, H-1′), 4.60 (d, $J_{2,3}=9.5$ Hz, 1H, H-2), 3.75–3.50 (m, 1H, H-3), 3.21 (d, $J_{3,NH}=2.8$ Hz, 1H, NH), 2.30–2.25 (m, 1H, H-2′), 2.18–2.08 (m, 1H, H_A-3′), 2.03–1.84 (m, 3H, H-4, H_A-6′), 1.79–1.73 (m, 3H, H-5, H_A-4′), 1.54–1.23 (m, 6H, H-6, H-7, H-3′, H_A-5′), 1.45 (s, 9H, 3xCH_3), 1.30 (s, 3H, H-9′), 1.25 (s, 3H, H-10′), 1.11–0.98 (m, 5H, H_B-4′, H_B-6′, H-8), 0.90 (d, $J_{5',7'}=7.2$ Hz, 3H, H-7′), ^{13}C NMR (50 MHz; $CDCl_3$): δ 172.7 (C-1), 155.9 (C=O Boc), 151.7 (i-Ar), 128.8 (Ar), 125.7 (Ar), 79.7 ($C(CH_3)_3$), 76.2 (C-1′), 73.3 (C-2), 53.3 (C-3), 50.8 (C-2′), 42.1 (C-6′), 41.1 (C-8′), 34.9 (C-4′), 32.0 (C-4), 31.8 (C-5′), 29.9 (C-5), 29.6 (C-9′), 28.9 (3xCH_3 Boc), 26.8 (C-3′), 25.8 (C-6), 24.2 (C-7′), 23.0 (C-10′), 22.3 (C-7), 14.5 (C-8).

4.3.13. *O*-[syn-(3ξ)-*t*-Butoxycarbonylamino-4,4-diethoxy-(2ξ)-hydroxybutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (16a). The compound 16a was obtained as a

colourless oil in 92% yield, (R_f=0.50 hexane/AcOEt 7:3). HRMS-LSIMS(+): Calcd for $C_{29}H_{47}O_7NNa$ $(M+Na)^+$: 544.3250, found 544.3234; IR (film): 3450, 3386, 2973, 2927, 1723, 1501, 1367, 1247, 1171, 1124, 1063, 764, 701 cm^{-1}; $[\alpha]_D{}^{20}$=−4.4 (c=1.61; $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$): δ 7.40–7.10 (m, 5H, Ar), 5.05–4.75 (m, 1H, H-1′), 4.41 (d, $J_{3,4}$=6.5 Hz, 1H, H-4), 3.80–3.50 (m, 4H, H-5, H-5″, H-3), 3.11–3.05 (m, 1H, H-2), 2.14–2.02 (m, 1H, H-2′), 1.98–1.84 (m, 2H, H_A-3′, H_A-6′), 1.75–1.70 (m, 1H, H_A-4′), 1.52–1.41 (m, 1H, H_A-5′), 1.40 (s, 9H, 3xCH_3), 1.31 (s, 3H, H-9′), 1.28 (t, $J_{5,6}$=7.1 Hz, 3H, H-6), 1.22–1.15 (m, 1H, H_B-3′), 1.10–0.91 (m, 2H, H_B-4′, H_B-6′), 1.17 (t, $J_{5'',6''}$=7.1 Hz, 3H, H-6″), 1.16 (s, 3H, H-10′), 0.90 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 172.7 (C-1), 155.4 (C=O Boc), 151.9 (i-Ar), 128.5 (Ar), 126.0 (Ar), 125.7 (Ar), 101.9 (C-4), 79.7 ($C(CH_3)_3$), 76.7 (C-1′), 70.0 (C-2), 64.2 (C-5), 61.6 (C-5″), 53.5 (C-3), 50.6 (C-2′), 41.4 (C-6′), 40.1 (C-8′), 34.9 (C-4′), 31.9 (C-5′), 29.4 (C-9′), 28.9 (3xCH_3), 27.0 (C-8′), 24.4 (C-3′), 22.3 (C-7′, C-10′), 15.8 (C-6), 15.6 (C-6″).

4.3.14. *O*-[*anti*-(3ξ)-*t*-Butoxycarbonylamino-4,4-diethoxy-(2ξ)-hydroxybutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenyl-menthol (16b). The title compound was obtained as a colourless oil in 88% yield, (R_f=0.6 hexane/AcOEt 6:4). ^1H NMR (200 MHz; $CDCl_3$): δ 7.50–7.00 (m, 5H, Ar), 5.00–4.80 (m, 1H, H-1′), 4.41 (d, $J_{3,4}$=5.5 Hz, 1H, H-4), 3.90–3.75 (m, 1H, 1, H-3), 3.70–3.36 (m, 4H, 2H-5, H-5″), 3.20–3.02 (m, 1H, H-2), 2.13–2.01 (m, 1H, H-2′), 1.96–1.80 (m, 2H, H_A-3′, H_A-6′), 1.77–1.71 (m, 1H, H_A-4′), 1.54–1.42 (m, 1H, H_A-5′), 1.45 (s, 9H, 3xCH_3), 1.30 (s, 3H, H-9′), 1.29 (t, $J_{5,6}$=7.1 Hz, 3H, H-6), 1.23–1.15 (m, 1H, H_B-3′), 1.11–0.90 (m, 2H, H_B-4′, H_B-6′), 1.19 (t, $J_{5'',6''}$=7.1 Hz, 3H, H-6″), 1.17 (s, 3H, H-10′), 0.89 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 172.1 (C-1), 155.5 (C=O Boc), 151.9 (i-Ar), 128.5 (Ar), 125.7 (Ar), 125.5 (Ar), 101.5 (C-4), 79.9 ($C(CH_3)_3$), 76.0 (C-1′), 71.8 (C-2), 64.6 (C-5), 62.0 (C-5″), 53.8 (C-3), 50.7 (C-2′), 41.8 (C-6′), 40.9 (C-9′), 35.0 (C-4′), 31.8 (C-5′), 29.7 (C-9′), 28.9 (3xCH_3), 26.9 (C-8′), 24.0 (C-3′), 22.4 (C-7′, C-10′), 15.8 (C-6), 15.6 (C-6″).

4.3.15. *O*-[*anti*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxy-3-phenylpropanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenyl-menthol (17b). The title compound was obtained as a colourless oil in 88% yield (R_f=0.5 hexane/AcOEt 8:2). HRMS-ESI: Calcd for $C_{30}H_{41}O_5NNa$ $(M+Na)^+$ 518.2882, found 518.2899; IR (KBr): 3445 2967, 1722, 1496, 1456, 1367, 1256, 1169, 700; ^1H NMR (400 MHz; $CDCl_3$): δ 7.35–7.20 (m, 7H, Ar), 7.15–7.04 (m, 3H, Ar), 5.50 (d, $J_{2,3}$=9.1 Hz, 1H, H-2), 5.00 (d, $J_{2,3}$=9.1 Hz, 1H, H-3), 4.93 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 3.91 (bs, 1H, NH), 2.19–2.10 (m, 1H, H-2′), 1.94–1.85 (m, 1H, H_A-3′), 1.80–1.73 (m, 1H, H_A-6′), 1.71–1.66 (m, 1H, H_A-4′), 1.52 (s, 9H, 3xCH_3), 1.50–1.40 (m, 1H, H_A-5′), 1.31 (s, 3H, H-9′), 1.28–1.21 (m, 1H, H_B-3′), 1.19 (s, 3H, H-10′), 1.01–0.89 (m, 2H, H_B-4′, H_B-6′), 0.86 (d, $J_{5',7'}$=6.6 Hz, 3H, H-7′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 170.5 (C-1), 154.7 (C=O Boc), 152.2 (i-Ar), 139.4 (i-Ar), 128.2 (Ar), 127.9 (Ar), 127.3 (Ar), 126.6 (Ar), 125.3 (Ar), 79.3 ($C(CH_3)_3$ Boc), 76.1 (C-1′), 74.3 (C-2), 55.7 (C-3), 49.9 (C-2′), 41.1 (C-6′), 39.4 (C-8′), 34.2 (C-4′), 31.2 (C-5′), 28.3 (C-9′), 27.3 (3xCH_3 Boc), 26.1 (C-3′), 22.5 (C-7′), 21.6 (C-10′).

4.4. General procedure of isopropylidene formation

A solution of *N*-Boc-aminoalcohols (0.19 mmol), dimethoxy-propane (0.21 mmol) and catalytic amounts of TsOH in toluene (2 mL) was heated at 50 °C. Progress of the reaction was monitored by TLC. After 5 h the mixture was cooled, solvents were evaporated and the residue was purified on silica gel using hexane/AcOEt (9:1–7:3).

4.4.1. *O*-[*anti*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxy-2,3-isopropylideneoctanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenyl-menthol (18a). The compound was obtained as a colourless oil in 86%. HRMS-ESI: Calcd for $C_{32}H_{51}O_5NNa$ $(M+Na)^+$: 552.3659, found: 552.3666; IR (film): 2955, 2923, 2860, 1747, 1699, 1456, 1381, 1213, 1104, 1061, 769, 701 cm^{-1}; R_f=0.5 (hexane/AcOEt 8:2); $[\alpha]_D{}^{20}$=8.6 (c=1.70; $CHCl_3$); ^1H NMR (500 MHz; $CDCl_3$): δ 7.30–7.24 (m, 4H, Ar), 7.15–7.09 (m, 1H, Ar), 4.90 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.7 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 3.77–3.74 (m, 1H, H-3), 3.29 (d, $J_{2,3}$=2.7 Hz, 1H, H-2), 2.05–1.98 (m, 1H, H-2′), 2.13–2.04 (m, 1H, H_A-3′), 2.01–1.80 (m, 3H, H-4, H_A-6′), 1.78–1.72 (m, 3H, H-5, H_A-4′), 1.55–1.25 (m, 6H, H-6, H-7, H-3′, H_A-5′), 1.47 (s, 6H, 2xCH_3), 1.42 (s, 9H, 3xCH_3), 1.29 (s, 3H, H-9′), 1.18 (s, 3H, H-10′), 1.02–0.91 (m, 2H, H_B-4′, H_B-6′), 0.91 (t, $J_{7,8}$=7.5 Hz, 3H, H-8), 0.87 (d, $J_{5',7'}$=7.3 Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.7 (C-1), 151.7 (C=O Boc), 128.0 (Ar), 125.3 (Ar), 124.9 (Ar), 95.6 ($C(CH_3)_2$), 80.0 ($C(CH_3)_2$), 74.6 (C-1′), 60.6 (C-2), 50.5 (C-2′), 41.6 (C-6′), 39.4 (C-8′), 34.4 (C-4′), 31.4 (C-5), 31.2 (C-5′), 28.8 (C-9′), 28.3 (5xCH_3), 26.3 (C-3′), 24.8 (C-6), 23.5 (C-7′), 22.6 (C-7), 21.6 (C-10′), 14.0 (C-8).

4.4.2. *O*-[*syn*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxy-2,3-isopropylideneoctanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenyl-menthol (18b). The title compound was obtained in 84% yield. R_f=0.45 (hexane/AcOEt; colourless oil, $[\alpha]_D{}^{20}$=−10.8 (c=0.77; $CHCl_3$); ^1H NMR (500 MHz; $CDCl_3$): δ 7.31–7.24 (m, 4H, Ar), 7.15–7.08 (m, 1H, Ar), 4.97–4.94 (m, 1H, H-1′), 3.54–3.50 (m, 1H, H-3), 3.23–3.20 (m, 1H, H-2), 2.05–1.99 (m, 1H, H-2′), 2.12–2.04 (m, 1H, H_A-3′), 2.04–1.83 (m, 3H, H-4, H_A-6′), 1.79–1.71 (m, 3H, H-5, H_A-4′), 1.58–1.26 (m, 6H, H-6, H-7, H-3′, H_A-5′), 1.48 (s, 6H, 2xCH_3), 1.43 (s, 9H, 3xCH_3), 1.31 (s, 3H, H-9′), 1.19 (s, 3H, H-10′), 1.02–0.90 (m, 5H, H_B-4′, H_B-6′, H-8), 0.89 (d, $J_{5',7'}$=7.6 Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 167.0 (C-1), 152.0 (C=O Boc), 151.6 (*i*-Ar), 127.9 (Ar), 125.2 (Ar), 124.8 (Ar), 93.8 ($C(CH_3)_2$), 79.6 ($C(CH_3)_2$), 74.9 (C-1′), 50.1 (C-2′), 41.4 (C-6′), 40.2 (C-8′), 34.4 (C-4′), 31.9 (C-5), 31.0 (C-5′), 30.3 (C-9′), 28.4 (5xCH_3), 26.4 (C-3′), 24.9 (C-6), 23.5 (C-7′), 22.4 (C-7), 21.7 (C-10′), 13.9 (C-8).

4.4.3. *O*-[*anti*-(3ξ)-Amino-4,4-diethoxy-(2ξ)-hydroxy-2,3-isopropylidenebutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenyl-menthol (19a). The title compound was obtained as a colourless oil in 85% yield, (R_f=0.5 hexane/AcOEt 8:2). HRMS-LSIMS(+): Calcd for $C_{24}H_{43}O_5NNa$ $(M+Na)^+$: 484.6302, found 484.6308; IR (film): 3455, 2957, 2926, 1705, 1496, 1456, 1391, 1366, 1257, 1173, 1150, 1119, 765, 701 cm^{-1}; $[\alpha]_D{}^{20}$=−4.4 (c=1.61; $CHCl_3$); ^1H NMR (500 MHz; C_6D_6): δ 7.20–6.90 (m, 5H, Ar), 5.00 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.8 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 4.74 (d,

$J_{3,4}$=1.5 Hz, 1H, H-4), 3.85 (dd, $J_{3,4}$=1.5 Hz, $J_{3,2}$=8.6 Hz, 1H, H-3), 3.75 (ddd, $J_{5A,5B}$=9.6 Hz, $J_{5A,6}$=7.1 Hz, $J_{5B,6}$= 7.0 Hz, 2H, H-5), 3.42 (dd, $J_{5''A,5''B}$=9.6 Hz, $J_{5A'',6''}$= 7.1 Hz, $J_{5B'',6''}$=7.0 Hz, 2H, H-5″), 3.37 (d, $J_{3,2}$=8.6 Hz, 1H, H-2), 2.00–1.90 (m, 3H, H-2′, H_A-3′, H_A-6′), 1.75–1.68 (m, 1H, H_A-4′), 1.55–1.45 (m, 1H, H_A-5′), 1.24 (s, 6H, 3xCH_3), 1.23–1.17 (m, 1H, H_B-3′), 1.15–0.92 (m, 2H, H_B-4′, H_B-6′), 1.12 (s, 3H, H-9′), 1.00–0.92 (m, 6H, H-6, H-6″), 1.12 (s, 3H, H-10′), 0.69 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′); ^{13}C NMR (50 MHz; $CDCl_3$): δ 168.0 (C-1), 152.9 (i-Ar), 128.7 (Ar), 125.8 (Ar), 125.6 (Ar), 99.9 (C-4), 97.8 ($C(CH_3)_2$), 75.7 (C-1′), 74.9 (C-2), 66.2 (C-5), 62.9 (C-5″), 51.2 (C-3), 42.3 (C-2′), 39.8 (C-6′), 39.1 (C-8′), 35.0 (C-4′), 31.7 (C-5′), 31.2 (C-9′), 29.2 (2xCH_3), 27.0 (C-8′), 26.5 (C-3′), 23.9 (C-7′), 22.3 (C-10′), 15.8 (C-6), 15.6 (C-6″).

4.4.4. *O*-[3-*O*-[*syn*-(3ξ)-Amino-4,4-diethoxy-(2ξ)-hydroxy-2,3-isopropylidenebutanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (19b). The title compound was obtained as a colourless oil in 84% yield (R_f=0.50 hexane/AcOEt 8:2): ^{1}H NMR (500 MHz; C_6D_6): δ 7.20–6.90 (m, 5H, Ar), 5.22 (d, $J_{3,4}$=1.8 Hz, 1H, H-4), 4.92 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.4 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 3.87 (dd, $J_{3,4}$=1.8 Hz, $J_{3,2}$=7.8 Hz, 1H, H-3), 3.70–3.65 (m, 2H, H-5), 3.49–3.41 (m, 2H, H-5″), 3.44 (d, $J_{3,2}$=7.8 Hz, 1H, H-2), 2.01–1.92 (m, 3H, H-2′, H_A-3′, H_A-6′), 1.78–1.69 (m, 1H, H_A-4′), 1.56–1.47 (m, 1H, H_A-5′), 1.25 (s, 6H, 3xCH_3), 1.23–1.16 (m, 1H, H_B-3′), 1.15–0.90 (m, 2H, H_B-4′, H_B-6′), 1.13 (s, 3H, H-9′), 1.00–0.91 (m, 6H, H-6, H-6″), 1.15 (s, 3H, H-10′), 0.70 (d, $J_{5',7'}$=6.5 Hz, 3H, H-7′).

4.4.5. *O*-[*syn*-(3ξ)-*t*-Butoxycarbonylamino-(2ξ)-hydroxy-2,3-isopropylidene-3-phenyl-propanoyl]-(1′*R*,2′*S*,5′*R*)-8′-phenylmenthol (20b). The title compound was obtained as a colourless oil in 90% yield, (R_f=0.6 hexane/AcOEt 8:2). HRMS-ESI: Calcd for $C_{33}H_{45}O_5N$ $(M+H)^+$ 558.3190, found 558.3182; IR (KBr): 2959, 2927, 1730, 1703, 1456, 1378, 1366, 1255, 1177, 1099, 764, 700 cm^{-1}; $[\alpha]_D^{20}$=−1.75 (c=1.17; $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.20–6.80 (m, 10H, Ar), 5.48 (bs, 1H, H-2), 5.01 (dt, $J_{1',6'A}$=$J_{1',2'}$=10.6 Hz, $J_{1',6'B}$=4.4 Hz, 1H, H-1′), 3.89 (bs, 1H, H-3), 2.17–2.10 (m, 1H, H-2′), 1.95–1.88 (m, 1H, H_A-3′), 1.81–1.75 (m, 1H, H_A-6′), 1.72–1.69 (m, 1H, H_A-4′), 1.48–1.40 (m, 1H, H_A-5′), 1.21 (s, 3H, H-9′), 1.17 (bs, 9H, H-10′, 2xCH_3), 1.22–1.19 (m, 1H, H_B-3′), 1.06 (s, 9H, 3xCH_3), 1.01–0.90 (m, 2H, H_B-4′, H_B-6′), 0.67 (d, $J_{5',7'}$=6.3 Hz, 3H, H-7′); ^{13}C NMR (125 MHz; $CDCl_3$): δ 169.9 (C-1), 152.1 (C═O Boc), 151.4 (i-Ar), 128.7 (Ar), 128.4 (Ar), 127.9 (Ar), 125.8 (Ar), 125.5 (Ar), 96.6 ($C(CH_3)_2$), 81.3 (C-2), 80.6 ($C(CH_3)_3$ Boc), 76.2 (C-1′), 62.9 (C-3), 50.6 (C-2′), 41.9 (C-6′), 40.2 (C-8′), 34.9 (C-4′), 31.9 (C-5′), 28.3 (C-9′), 27.1 (C-3′), 25.3 (C-7′), 22.3 (C-10′).

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