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TETRAHEDRON: *ASYMMETRY*

Chemoenzymatic synthesis of enantiomerically enriched aminoalkenols and glycosides thereof†

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Abstract

1-*t*-Butoxycarbonylamido-3-pentene-1-ol **3** and 2-azido-4-phenyl-3-butene-1-ol **4** were enantiomerically enriched by enzymatic acetylation using various lipases and esterases (CHIRAZYM) to give acetylated compounds **5** and **7**, respectively. Compound **3** gave the best results ($E=94$) with *Candida antarctica A* lipase (CHIRAZYM L-5), whereas **4** could not be separated into the enantiomers with satisfactory E values. The absolute configurations were proven for both compounds via independently prepared derivatives. Both enantiomers of **5**, as well as racemic **7**, were *N*-deblocked and condensed with octonic acid derivatives **14** to give the corresponding *C*-glycosides **17** and **22** after deprotection of the intermediates in good overall yield. Compound **4** was similarly condensed with glucose imidate **11** to give the diastereomeric *O*-glycosides **13** after deprotection. The latter glycosides were prepared as precursors for the generation of the corresponding aldehydes as substrates for aldolase catalyzed reactions. © 2000 Published by Elsevier Science Ltd.

1. Introduction

As part of a project towards the synthesis of enantiomerically pure alkenyl glycosides, we recently prepared a series of optically active alkene diol derivatives by lipase and esterase catalyzed saponification and esterification reactions, respectively, of racemic precursors **1** and **2**.[1] These enantiomerically pure alkene diols were subsequently glycosylated to afford the corresponding alkenyl glycosides after deblocking of the protected intermediates.[1] The diastereomerically pure alkenyl glycosides obtained were useful precursors for the generation of glycosylated aldehydes, which in turn were substrates for aldolase catalyzed syntheses of unnatural oligosaccharides.[2]

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† Dedicated to James Reed Harris.

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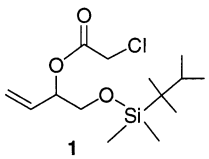
In continuation of this project we extended the enzymatic resolution of alkenols to 1-*t*-butoxycarbamido-3-pentene-2-ol **3** and 2-azido-4-phenyl-3-butene-1-ol **4** in order to prepare the corresponding glycosides as useful precursors for substrates for aldolase catalyzed reactions. Furthermore, optically active aminoalkenols of type **3** and **4** are important building blocks for the synthesis of pyrrolidine and indolicine alkaloids,[3,4] (+)-galantinic acid,[5] polyamino acids,[6] and acromelinic acid derivatives.[7]



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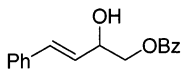

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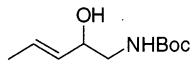

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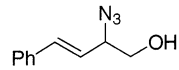

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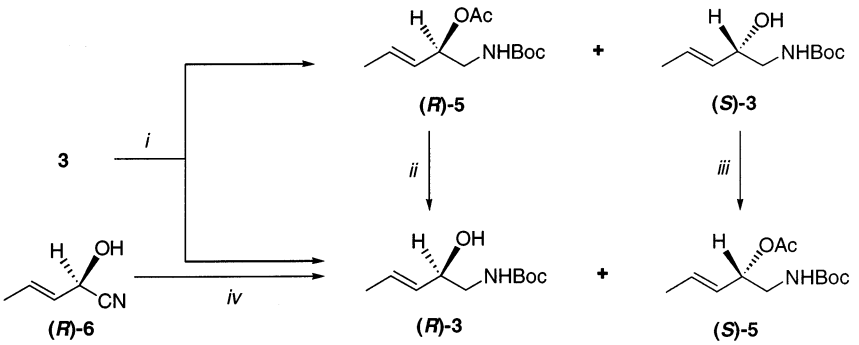
2. Results and discussion

Both racemic aminoalkenol derivatives **3** and **4** that were used in this study were prepared according to known procedures[8–11] from crotonaldehyde and cinnamaldehyde, respectively, as follows. First, trimethylsilyl cyanide was quantitatively added to crotonaldehyde using a catalytic amount of $ZnCl_2$.[8] Next, the intermediate silylated cyanohydrin was reduced with $LiAlH_4$ without further purification[9] to afford 1-amino-3-pentene-2-ol, which was condensed with Boc_2O in dichloromethane according to a slightly modified literature procedure[9] to give racemic aminoalkenol **3** in a 95% yield. Starting from cinnamaldehyde, condensation with trimethyl sulfonium iodide according to Märkl[10] gave first styryl oxirane, which was regioselectively opened[11] with NaN_3 to afford aminoalkenol derivative **4** (82%). Both racemic aminoalkenol derivatives **3** and **4** were subsequently used as substrates for enzymatic acetylations with various lipases and esterases.

First, **3** was used as the substrate for enzymatic esterification using some CHIRAZYM lipases and esterases (Table 1) in combination with vinyl acetate in *t*-butylmethylether as the solvent (Scheme 1). Although several racemic saturated 1-amino-2-alkanols have been previously resolved by enzymatic esterification and saponification of acylated derivatives,[12] to the best of our knowledge no resolution of aminoalkenol **3** or similar 1-amino-3-alkene-2-ol derivatives have been previously described. Only 1-*t*-butoxycarbamido-4-pentene-3-ol has been previously enzymatically acylated with lipases in good enantiomeric excess.[13]



Scheme 1. *i*: Lipase or esterase, vinyl acetate, *t*-butyl methyl ether (Table 1). *ii*: Cat. NaOMe in MeOH. *iii*: Acetic anhydride in pyridine. *iv*: (a) Crotonaldehyde, HCN, almond oxynitrilase, Ref. 14 (→**(*R*)-6**); (b) $LiAlH_4$, Ref. 15; (c) Boc_2O, Et_3N, Ref. 9

For our study of the enzymatic resolution of aminoalkenols we used the Boc protecting group in **3** for the amino function, because the latter can be easily cleaved after the resolution of the enantiomers without affecting the double bond. As shown in Scheme 1, enzymatic esterifications of **3** led to the acetylated aminoalkenol **(*R*)-5** and the non-acetylated enantiomer **(*S*)-3**, respectively, or vice versa. Both products could be separated by simple column chromatography. Furthermore, **(*S*)-3** was conventionally acetylated to give **(*S*)-5** and **(*R*)-5** was saponified without any loss of enantiomeric excess to afford **(*R*)-3**. Thus, both enantiomers of **3** and **5** could be prepared this way and their enantiomeric purity determined by gas chromatography of acetates **5** on chiral stationary phases (see Section 3). The absolute configuration of **(*R*)-3** and **(*R*)-5** was also proven by an independent preparation via oxynitrilase catalyzed addition[14] of HCN to crotonaldehyde followed by subsequent reduction[15] and *N*-protection[9] of the intermediate cyanohydrin **(*R*)-6**.

The various *Pseudomonas* species lipases (Table 1, entries 1–3, 6, and 10), which previously gave excellent results for the resolution of alkene diols,[1] resulted in poor resolutions of compound **3** in this case. Similarly, other lipases and esterses could not be used efficiently for the resolution of aminoalcohol **3**. Only the *Candida antarctica A* lipase (CHIRAZYM L-5, entry 7) gave good results, which could be improved further by immobilisation of the lipase on Celite (entries 8 and 9).[16] Interestingly, all *Pseudomonas* species lipases, as well as some *Candida* lipases and the *porcine*

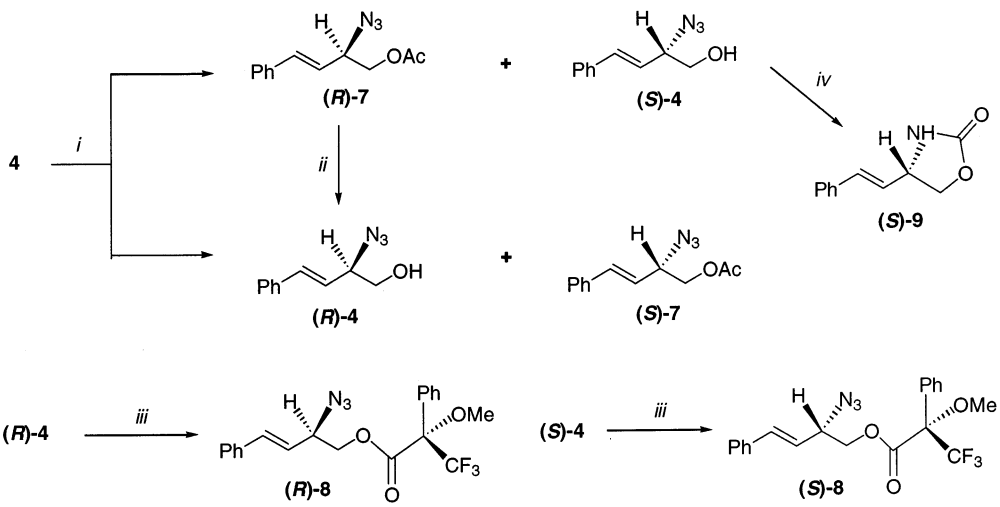
Table 1
Enzymatic resolution of **3** using various lipases under esterification conditions[a]

Entry	Enzyme (mg)	Time	Yield of products (ee)		*E* value
			Alcohol **3**	Ester **5**	
1	*Pseudomonas* species[b] (40)	66 h	48% **(*R*)-3** (64%)	42% **(*S*)-5** (71%)	11
2	*Pseudomonas* species[b,c] (40)	27 h	48% **(*R*)-3** (53%)	44% **(*S*)-5** (58%)	6
3	*Pseudomonas* species[d] (10)	26 h	34% **(*R*)-3** (66%)	62% **(*S*)-5** (36%)	4
4	*Candida antarctica* B[e] (3)	30 d	–	Traces **(*S*)-5** (96%)	–
5	*Candida cyclindracea*[f] (20)	15 d	–	Traces **(*S*)-5** (69%)	–
6	*Pseudomonas* species[g] (10)	5.5 h	46% **(*R*)-3** (41%)	46% **(*S*)-5** (37%)	3
7	*Candida antarctica* A[h] (10)	96 h	44% **(*S*)-3** (93%)	46% **(*R*)-5** (86%)	45
8	*Candida antarctica* A[h,i] (40)	29 h	44% **(*S*)-3** (96%)	48% **(*R*)-5** (92%)	94
9	*Candida antarctica* A[h,j] (440)	29 h	44% **(*S*)-3** (99%)	49% **(*R*)-5** (93%)	94
10	*Pseudomonas* species[k] (10)	8.5 h	60% **(*R*)-3a** (46%)	34% **(*S*)-5** (73%)	10
11	*Porcine pancreas*[l] (20)	15 d	–	Traces **(*S*)-5** (77%)	–
12	*Humicola* species[m] (10)	30 d	–	–	–

[a] **3** (100 mg, 497 μmol) was treated with the respective lipase and vinyl acetate (5 ml) in *t*-butyl methyl ether (9 ml) until ca. 50% conversion was obtained, followed by chromatographic separation of the products.
[b] Amano PS lipase immobilized on Celite.
[c] In *n*-pentane as the solvent.
[d] CHIRAZYM L-1, similar to *Burkholderia cepacia*.
[e] CHIRAZYM L-2
[f] CHIRAZYM L-3.
[g] CHIRAZYM L-4, cholesterine esterase.
[h] CHIRAZYM L-5.
[i] Immobilized on Celite.
[j] **3a** (1.5 g, 7.46 mmol).
[k] CHIRAZYM L-6.
[l] CHIRAZYM L-7.
[m] CHIRAZYM L-8.

pancreas lipase acetylated the (*S*)-enantiomer of **3**, whereas the *Candida antarctica A* lipase showed an inverted enantioselectivity and consumed the (*R*)-isomer faster. A similar observation was recently made by Oshida et al.[17] for the enantioselective acylation of a cholesterine derivative. This significant deviation from the Katzlauskas rule[18] for the preferred reaction of one enantiomer during enzymatic acylations with *Pseudomonas* and *Candida* lipases may be interpreted in terms of a similar bulkiness of the two substituents in compound **3** (i.e. the (*E*)-propenyl residue vs. the *t*-butoxycarbamidomethyl residue). Obviously, *Candida antarctica A* lipase recognizes the *t*-butoxycarbamidomethyl residue as the larger residue, whereas all other enzymes recognize the (*E*)-propenyl residue as the larger one. However, since the *E* values in the second case are significantly lower, this finding may not be interpreted as an exception from the Katzlauskas rule.2

Next, (*E*)-2-azido-4-phenyl-3-butene-1-ol **4** was used as a substrate for the enzymatic resolution of the enantiomers. All attempts to kinetically resolve the enantiomers of racemic **7** by saponification with various *Pseudomonas* species lipases failed. In all cases, 100% conversion was found for enzymatic deacetylation without any discrimination of enantiomers (no details are shown in Section 3). Thus, the enzymatic acetylation was used next for separation of the enantiomers. Although many examples of the resolution of 1-azido-alkane-2-ols by enzymatic esterification are in the literature[12f] no examples of 2-azido-alkane-1-ols are described. Only for (*E*)-1-amino-2-azido-4-phenyl-3-butene has it been shown that enzymatic esterification with Amano PS lipase in ethyl acetate led to the corresponding (*S*)-enantiomer in 80% ee.[19] Therefore, compound **4** was used as a substrate for several lipases as similarly performed above for aminoalcohol **3** (Table 2). The enantiomeric excess of the formed acetates **7** and the recovered alcohols **4** was determined by HPLC after derivatisation with Moshers acid[20] to give compounds **8** because a direct separation of enantiomers of **7** or **4** on chiral stationary phases was not possible. For the determination of the absolute configuration of the obtained esters **(*R*)-7** and of the remaining alcohols **(*S*)-4**, the latter was first reduced to the corresponding aminoalcohol by a variation of the Staudinger reaction,[11] followed by condensation of the intermediate with phosgene to afford oxazolidinone **(*S*)-9**. The specific rotation of the latter was compared to the one of the enantiomer, which was independently prepared from L-serine (Scheme 2).[21]



Scheme 2. *i*: Lipase or esterase, vinyl acetate, *t*-butyl methyl ether (Table 2). *ii*: Cat. NaOMe in MeOH. *iii*: (*R*)-2-Methoxy-2-phenyl-2-trifluoromethyl-acetyl chloride, pyridine. *iv*: (a) PPh_3, THF, 2 days then H_2O, 1 day, Ref. 11; (b) $COCl_2$ in toluene, pyridine, −30°C, 2.5 h

In sharp contrast to the results of the enzymatic acylation of compound **3**, the azidoalcohol **4** gave only useless *E* values with various enzymes (Table 2). The best results (ee values of ca. 20%) were solely obtained from acylations of **4** with *Candida cyclindracea* (CHIRAZYM L-3, entry 4) and *Humicola* species (CHIRAZYM L-8, entry 10). *Candida antarctica A* lipase (CHIRAZYM L-5, entries 5–7) gave **(*S*)-4** and **(*R*)-7** up to 16% ee. Thus, due to the low *E* values in these cases no further optimizations were performed[22] and racemic **4** was used for glycosylations (see below).

Previously, 1-azido-3-butene-2-yl β-D-glucopyranoside has been prepared from the corresponding benzoylated 1-*p*-toluenesulfonyloxy-3-butene-2-yl glucoside by nucleophilic substitution with sodium azide, followed by debenzoylation of the intermediate and was found to be unstable at room temperature.[1a] Here, we glycosylated racemic **4** with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate **11**, prepared from 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose[23] **10** in 86% yield, to give glucoside **12** (86%) as a 1:1 mixture of diastereomers,

Table 2
Enzymatic resolution of **4** using various lipases under esterification conditions[a]

Entry	Enzyme (mg)	Time	Yield of products (ee)		*E* value
			Alcohol **4**	Ester **7**	
1	*Pseudomonas* species[b] (40)	24 h	–	100% ***rac*-7** (0%)	–
2	*Pseudomonas* species[c] (10)	5.5 h	–	100% ***rac*-7** (0%)	–
3	*Candida antarctica* B[d] (5)	4.5 h	42% **(*S*)-4** (18%)	51% **(*R*)-7** (12%)	1.5
4	*Candida cyclindracea*[e] (100)	51 h	47% **(*S*)-4** (20%)	40% **(*R*)-7** (20%)	1.8
5	*Candida antarctica* A[f] (50)	100 h	42% **(*S*)-4** (13%)	47% **(*R*)-7** (10%)	1.4
6	*Candida antarctica* A[f,g] (40)	10 h	57% **(*S*)-4** (<5%)	42% **(*R*)-7** (<5%)	–
7	*Candida antarctica* A[f,g,h] (200)	62 h	52% **(*S*)**-4 (16%)	45% **(*R*)-7** (16%)	1.0
8	*Pseudomonas* species[i] (25)	1.2 h	45% **(*R*)-4** (<5%)	49% **(*S*)-7** (8%)	1.2
9	*Pocine pancreas*[j] (100)	3.3 h	28% **(*R*)-4** (<5%)	59% **(*S*)-7** (<5%)	–
10	*Humicola* species[k] (100)	42 h	38% **(*R*)-4** (21%)	49% **(*S*)-7** (20%)	1.8
11	*Mucor miehei*[l] (9)	17.5 h	44% **(*S*)-4** (10%)	53% **(*R*)-7** (5%)	1.2
12	*Alcaligines* species[m] (50)	4 h	–	100% ***rac*-7** (0%)	–

[a] **4** (100 mg, 528 μmol) was treated with the respective lipase and vinyl acetate (5 ml) in *t*-butyl methyl ether (9 ml) until ca. 50% conversion was obtained, followed by chromatographic separation of the products and derivatisation with Mosher's acid.

[b] Amano PS lipase immobilized on Celite.

[c] CHIRAZYM L-1, similar to *Burkholderia cepacia*.

[d] CHIRAZYM L-2.

[e] CHIRAZYM L-3.

[f] CHIRAZYM L-5.

[g] Immobilized on Celite.

[h] **4** (1.0 g, 5.28 mmol).

[i] CHIRAZYM L-6.

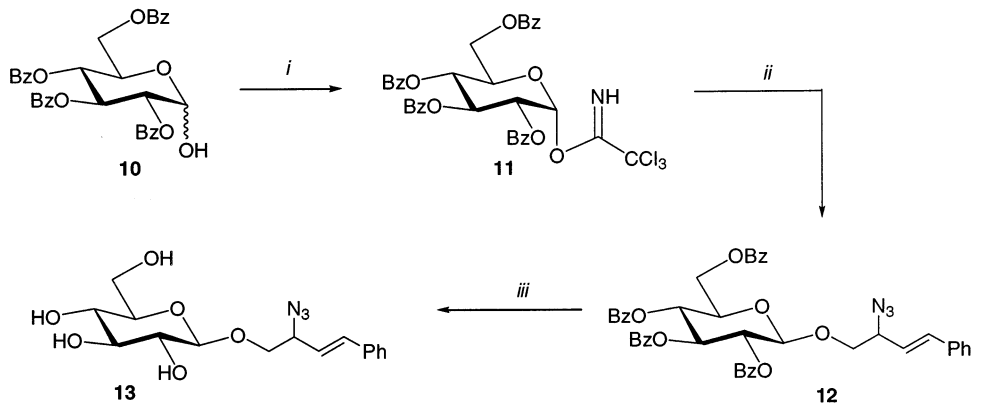
[j] CHIRAZYM L-7.

[k] CHIRAZYM L-8.

[l] CHIRAZYM L-9.

[m] CHIRAZYM L-10.

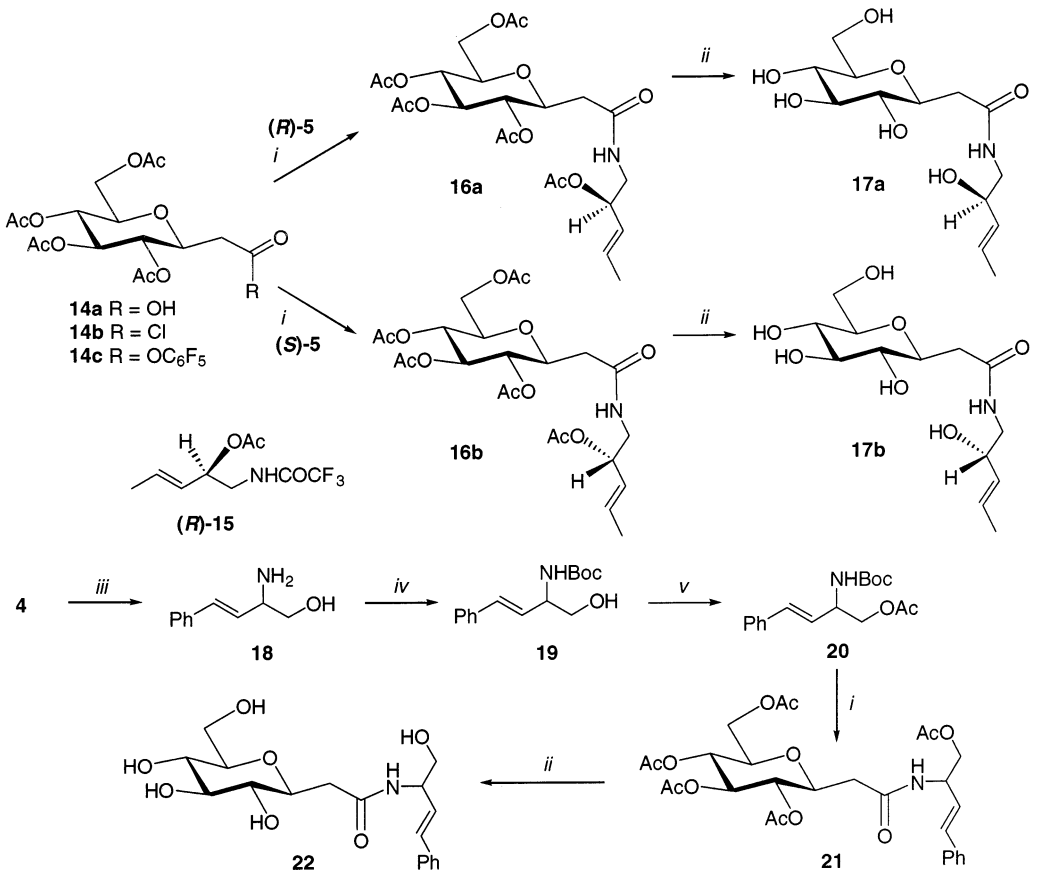
which could not separated by preparative chromatography. Final debenzoylation of the latter afforded glucoside **13** (88%), which was completely stable at room temperature and thus was useful for generation of the corresponding glycosylated aldehyde for aldolase catalyzed preparation of disaccharides (Scheme 3).[2]



Scheme 3. *i*: Cl_3CCN, K_2CO_3, CH_2Cl_2, 20°C, 6 days, 86%. *ii*: **4**, cat. TMSOTf, CH_2Cl_2, −30°C, 3.5 h, 86%. *iii*: Cat. NaOMe, MeOH, 20°C, 1 day, 88%

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-2-deoxy-D-*glycero*-D-*gulo*-octonic acid **14a** was chosen as the glycon fragment for aminoalcohols **5**. The latter can be prepared by condensation of acetobromoglucose and dibenzyl malonate using Hanessian's procedure,[24] by oxidation of an allyl *C*-glycoside[25] or by Mata's procedure[26] via condensation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose with Meldrum's acid. The latter procedure worked best in our hands for the preparation of larger amounts of **14a**. Direct condensation of **14a** with intermediately *N*-deblocked racemic **5** (treatment of **5** with trifluoacetic acid in dichloromethane at 20°C for 1 h, followed by concentration of the solution) and dicyclohexyl carbodiimide (DCC) afforded only racemic **15**. Therefore, crude chloride **14b**, which was prepared from **14a** by treatment with thionyl chloride[25,27] was used. Reaction of the latter with *N*-deblocked **(*R*)-5** afforded **16a** (57%) and **(*R*)-15** (20%) as a byproduct formed by condensation of the intermediate trifluoroacetic acid salt derived in situ from **(*R*)-5**. No such byproduct was found when **14b** was condensed with in situ *N*-deblocked **20** obtained from racemic **4** by subsequent Staudinger reaction,[11] *N*-protection with Boc_2O, and *O*-acetylation (see Scheme 4). Here, the corresponding octonic amide **21** was obtained in 84% yield as an inseparable 1:1 mixture of diastereomers.

Next, pentafluorophenyl ester **14c** was used as the glycosyl donor, which was prepared from **14a** by condensation with trifluorophenol and DCC in 91% yield. Reaction of **14c** with both enantiomers of in situ *N*-deblocked **5** proceeded smoothly at 80°C and afforded **16a** (72%) and **16b** (68%) without formation of undesired **15**. Finally, all three glycosides **16a**, **16b** and **21** were deacetylated to give the free *C*-glycosides **17a**, **17b**, and **22**, respectively, which are in turn precursors for the generation of aldehydes as substrates for aldolase catalyzed reactions as previously described.[2]



Scheme 4. *i*: (a) F_3CCOOH, CH_2Cl_2, 20°C, 1.5 h; (b) **(*R*)-5**+**14b**→**16a** (57%)+**(*R*)-15** (20%), **(*R*)-5**+**14c**→**16a** (72%), **(*S*)-5**+**14c**→**16b** (68%), **20**+**14b**→**21** (84%). *ii*: Cat. NaOMe, MeOH, 1–2 days, **17a** (87%), **17b** (96%), **22** (94%). *iii*: Ref. 11. *iv*: Boc_2O, CH_2Cl_2, 20°C, 31 h (73%). *v*: Ac_2O, pyridine, CH_2Cl_2, 20°C, 1.5 days (97%)

3. Experimental

3.1. General

The NMR data were obtained from spectra measured in $CDCl_3$ solutions (with Me_4Si as the internal standard) at 25°C with a Bruker AMX 300 spectrometer. ^1H NMR signal assignments were made by first-order analysis of the spectra and by HH-COSY spectra. Of the two magnetically non-equivalent geminal protons at C-6 of the sugar residues of compounds **12**, **13**, **16**, **17**, **21**, and **22**, the one resonating at lower field was allocated H-6a and the one resonating at higher field H-6b. ^{13}C NMR assignments were made by mutual comparison of the spectra by DEPT spectra and CH-COSY spectra. Proton and carbon signals of diastereomers of compounds **12**, **13**, **21**, and **22** were allocated non-italic and italic, respectively. Optical rotations were measured at 25°C with a Perkin–Elmer automatic polarimeter, Model 241. TLC was performed on precoated plastic sheets, Polygram SIL UV_{254}, 40×80 mm (Macherey–Nagel) using appropriately adjusted mixtures of toluene/acetone and *n*-hexane/ethyl acetate. Detection was affected by UV light, where applicable, and by charring with 5% H_2SO_4 in ethanol. CC was

performed by eluting from columns of silica gel 60 (Merck) with appropriately adjusted mixtures of toluene/acetone, *n*-hexane/ethyl acetate, and CCl_4/acetone, respectively. Solutions in organic solvents were dried with anhydrous Na_2SO_4 and concentrated at 2 kPa, <40°C. The enantiomeric excess (ee) of compounds **5** were determined with a Hewlett–Packard HP 6890 series gas chromatograph with a FID detector at 200°C and a split injector at 150°C using H_2 at 10^5 Pa and a 23 m glass capillar column with a diameter of 0.25 mm packed with heptakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin as the stationary phase. Compound **3** was acetylated (see below) to give **5** prior to the determination of the ee value, as described above. The ee values of compound **4** were determined by esterification with (–)-Mosher's acid (see below) and separation of the formed diastereomers **8** by HPLC using a Sykam S1100 pump with a Linear Instruments UV–vis 206 multiple wavelength detector, a 200 mm Macherey–Nagel column with a diameter of 4 mm packed with Nucleosil 100-5 (Macherey–Nagel) and 50:1 *n*-hexane/ethyl acetate at a flow rate of 0.4 ml/min for elution. Compound **7** was deacetylated (see below) to give **4** prior to the determination of the ee value, as described above.

3.2. (E)-1-t-Butoxycarbonylamido-3-pentene-2-ol **3**

A solution of (*E*)-1-amino-3-pentene-2-ol[9] (5.76 g, 56.9 mmol), Boc_2O (13.66 g, 62.6 mmol) and Et_3N (25 ml) in CH_2Cl_2 (100 ml) was stirred for 16 h at 0°C, while the temperature was brought to room temp. Concentration of the solution and recrystallisation of the residue from aq. MeOH afforded **3** (10.88 g, 95%). The physical data were in accordance to the literature data.[9]

3.3. Analytic kinetic resolution of **3**

A mixture of racemic **3** (150 mg, 0.745 mmol), vinyl acetate (5 ml) and enzyme (see Table 1) in *t*-butylmethylether (9 ml) was stirred at room temp. until TLC showed about 50% conversion. The mixture was filtered and the filtrate was concentrated. Chromatography of the residue with 2:1 *n*-hexane/ethyl acetate afforded first **(*R*)-5** or **(*S*)-5**, the ee value of which was determined by GC (see above).

Eluted next was **(*R*)-3** or **(*S*)-3**, the ee value of which was determined by GC (see above), as described above for compound **5** after treatment of the sample of **3** with pyridine (10 ml) and Ac_2O (1 ml) at room temp. for 24 h, followed by concentration and filtration of the residue with CH_2Cl_2 over a short column of silica gel.

3.4. Preparative kinetic resolution of **3**

A mixture of racemic 3 (1.50 g, 7.45 mmol), vinyl acetate (55 ml) and *Candida antarctica A* lipase (440 mg, CHIRAZYM L-5, immobilized on Celite[16]) in *t*-butylmethylether (120 ml) was stirred at room temp. for 24 h. The mixture was filtered and the filtrate was concentrated. Chromatography of the residue with 2:1 *n*-hexane:ethyl acetate afforded first **(*R*)-5** (895 mg, 49%, ee = 93%); $[\alpha]_D = -22.0$ ($c = 1.8$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 5.80$ (m, 1H, H-4, $J_{3,4} = 15.3$ Hz, $J_{4,5} = 6.5$ Hz, $J_{2,3} = 0.9$ Hz), 5.40 (ddd, 1H, H-3, $J_{2,3} = 7.2$ Hz, $J_{3,5} = 1.6$ Hz), 5.25 (dd, 1H, H-2, $J_{1,2} = 11.6$ Hz), 4.68 (s, 1H, NH), 3.39–3.21 (m, 2H, H-1), 2.06 (s, 2H, $COCH_3$), 1.72–1.69 (m, 3H, H-5), 1.44 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz): $\delta = 170.2$ (CO), 155.7 (CONH), 130.8 (C-4), 126.5 (C-3), 79.5 ($C(CH_3)_3$), 73.8 (C-2), 43.8 (C-1), 28.3 ($C(CH_3)_3$), 21.2

($CO\mathit{C}H_3$), 17.8 (C-5); anal. calcd for $C_{12}H_{21}NO_4$ (243.3): C, 59.24; H, 8.70; N, 5.76; found: C, 59.34; H, 8.83; N, 5.74.

Eluted next was **(*S*)-3** (661 mg, 44%, ee = 99%); $[\alpha]_D = +13.9$ ($c = 1.1$, $CHCl_3$); physical data were in accordance with the data of the racemate.

3.5. (R)-1-t-Butoxycarbonylamido-3-pentene-2-ol (R)-3

(a) A solution of **(*R*)-5** (0.20 g, 0.822 mmol, ee = 89%) and a catalytic amount of NaOMe in MeOH (5 ml) was stirred at room temp. for 16 h. The mixture was neutralized by addition of Dowex 1X8 H^+ resin and filtered. Concentration of the filtrate afforded **(*R*)-3** (161 mg, 97%, ee = 89%); $[\alpha]_D = -7.8$ ($c = 0.6$, $CHCl_3$); physical data were in accordance with the data of the racemate.

(b) A mixture of (*R*)-2-hydroxy-3-pentenenitrile[14] **(*R*)-6** (1.94 g, 20.0 mmol, ee = 94%) and $LiAlH_4$ (0.84 g, 22.0 mmol) in Et_2O (20 ml) was refluxed for 2 h. Workup as described[28] afforded crude (*R*)-1-amino-3-pentene-1-ol (1.14 g), which was treated with Boc_2O as described under Section 3.2 to give **(*R*)-3** (107 mg, 27%, ee = 74%); $[\alpha]_D = -9.5$ ($c = 1.5$, $CHCl_3$); physical data were in accordance with the data of the racemate.

3.6. (R)-2-Acetoxy-1-t-butoxycarbonylamido-3-pentene (R)-5

A solution of **(*R*)-3** (0.20 g, 0.994 mmol, ee = 74%), pyridine (2 ml) and Ac_2O (1.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temp. for 16 h, washed subsequently with aq. HCl and aq. $NaHCO_3$ solution, dried and concentrated. Chromatography of the residue with 3:2 *n*-hexane: ethyl acetate afforded **(*R*)-5** (0.22 g, 90%, ee = 74%).

3.7. (S)-2-Acetoxy-1-t-butoxycarbonylamido-3-pentene (S)-5

A solution of **(*S*)-3** (0.71 g, 3.53 mmol, ee = 93%), pyridine (4 ml) and Ac_2O (3 ml) in CH_2Cl_2 (15 ml) was treated as described under Section 3.6 to give **(*S*)-5** (0.62 g, 73%, ee = 93%).

3.8. Analytic kinetic resolution of 4

A mixture of racemic **4**[10,11] (100 mg, 0.528 mmol), vinyl acetate (5 ml) and enzyme (see Table 2) in *t*-butylmethylether (9 ml) was stirred at room temp. until TLC showed about 50% conversion. The mixture was filtered and the filtrate was concentrated. Chromatography of the residue with 3:1 *n*-hexane:ethyl acetate afforded first **(*R*)-7** or **(*S*)-7**, the ee value of which was determined by treatment of a sample (2–3 mg) with a catalytic amount of NaOMe in MeOH (5 ml) at room temp. for 16 h, neutralisation with Dowex H^+ resin, filtration and concentration, followed by redissolving the residue (2–3 mg) in CH_2Cl_2 (1 ml) and treatment with pyridine (10 μl) and (*R*)-(−)-2-methoxy-2-trifluoromethyl-2-phenyl acetyl chloride[20] (3 μl) at room temp. for 16 h, filtration of the mixture with CH_2Cl_2 over a short column of silica gel and determination of the diastereomers by HPLC (see above).

Eluted next was **(*R*)-4** or **(*S*)-4**, the ee value of which was determined as described above for compound **7**.

3.9. Preparative kinetic resolution of **4**

A mixture of racemic **4**[10,11] (1.0 g, 5.28 mmol), vinyl acetate (55 ml) and *Candida antarctica A* lipase (200 mg, CHIRAZYM L-5, immobilized on Celite[16]) in *t*-butylmethylether (90 ml) was stirred at room temp. for 62 h. The mixture was filtered and the filtrate was concentrated. Chromatography of the residue with 6:1 *n*-hexane:ethyl acetate afforded first **(*R*)-7** (543 mg, 45%, ee = 16%); $[\alpha]_D = -13.6$ ($c = 1.1$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 7.42$–7.25 (m, 5H, H–Ph), 6.73 (d, 1H, H-4, $J_{3,4} = 15.9$ Hz), 6.09 (dd, 1H, H-3, $J_{2,3} = 7.6$ Hz), 4.35 (dt, 1H, H-2, $J_{1a,2} = 4.4$ Hz, $J_{1b,2} = 7.6$ Hz), 4.26 (dd, 1H, H-1a, $J_{1a,1b} = -11.4$ Hz), 4.11 (dd, 1H, H-1b), 2.11 (s, 3H, $COCH_3$); ^{13}C NMR (75.5 MHz): $\delta = 170.6$ (CO), 135.5–126.7 (Ph), 135.4 (C-4), 122.3 (C-3), 65.7 (C-2), 62.5 (C-1), 20.7 ($COCH_3$); anal. calcd for $C_{12}H_{13}N_3O_2$ (231.3): C, 62.33; H, 5.67; N, 18.17; found: C, 62.61; H, 5.63; N, 17.98.

Eluted next was **(*S*)-4** (516 mg, 52%, ee = 16%); $[\alpha]_D = +22.5$ ($c = 1.0$, $CHCl_3$); physical data were in accordance with the data of the racemate.[11]

3.10. (R)-2-Azido-4-phenyl-3-butene-1-ol **(R)-4**

A solution of **(*R*)-7** (170 mg, 0.735 mmol, ee = 16%) in MeOH (5 ml) was treated with a catalytic amount of NaOMe as described in Section 3.5 (a). Chromatography of the residue with 4:1 *n*-hexane:ethyl acetate afforded **(*R*)-4** (131 mg, 94%, ee = 16%); $[\alpha]_D = -27.0$ ($c = 1.0$, $CHCl_3$); physical data were in accordance with the data of the racemate.[11]

3.11. (S)-4-(2-Phenyethenyl)-2-oxazolidinone **(S)-9**

A solution of Ph_3P (253 mg, 0.97 mmol) in THF (6 ml) was added at room temp. to a solution of **(*S*)-4** (166 mg, 0.88 mmol, ee = 16%) in THF (10 ml) and the mixture was stirred for 2 d. Water (1 ml) was added and stirring was continued for 1 day. The mixture was concentrated, redissolved in Et_2O (6 ml) and extracted three times with a 5% aq. HCl solution (5 ml). The combined aq. extracts were brought to pH 13 by addition of a 1 M aq. NaOH solution and extracted with CH_2Cl_2. Pyridine (2 ml) and a 20% solution of phosgene (2 ml) were added at −30°C to the dried extracts and the solution was stirred for 2.5 h at 5°C. Water (2 ml) was added, the mixture was diluted with CH_2Cl_2, washed subsequently with aq. HCl and aq. $NaHCO_3$ solution, dried and concentrated. Chromatography of the residue with 2:1 *n*-hexane: ethyl acetate afforded **(*S*)-9** (79 mg, 55%); mp = 110°C (*n*-hexane); $[\alpha]_D = +1.3$ ($c = 1.5$, EtOH); Ref. 21 $[\alpha]_D = -6.5$ ($c = 2.4$, EtOH) for **(*R*)-9**; ^{1}H NMR (300 MHz): $\delta = 7.40$–7.29 (m, 5H, H–Ph), 6.61 (d, 1H, H-2′, $J_{1',2'} = 15.8$ Hz), 6.13 (dd, 1H, H-1′, $J_{1',4} = 7.6$ Hz), 5.74 (s, 1H, NH), 4.63–4.52 (m, 2H, H-5), 4.20–4.10 (m, 1H, H-4); ^{13}C NMR (75.5 MHz): $\delta = 159.4$ (C-2), 135.3–126.7 (Ph), 133.9 (C-2′), 126.3 (C-1′), 70.2 (C-5), 55.1 (C-4; anal. calcd for $C_{11}H_{11}NO_2$ (189.2): C, 69.83; H, 5.86; N, 7.40; found: C, 69.68; H, 5.72; N, 7.27.

3.12. 2,3,4,6-Tetra-O-benzoyl-α-D-glucopyranosyl trichloroacetimidate **11**

K_2CO_3 (8.43 g, 60.9 mmol) was added to a solution of 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose[23] **10** (7.29 g, 12.2 mmol), CCl_3CN (7.4 ml, 73.45 mmol) in CH_2Cl_2 (100 ml), the mixture was stirred at room temp. for 6 days, filtered and concentrated. Chromatography of the residue with 20:1 CCl_4:acetone afforded **11** (7.78 g, 86%); $[\alpha]_D = +82.0$ ($c = 1.0$, $CHCl_3$); ^{1}H

NMR (300 MHz): $\delta = 8.64$ (s, 1H, NH), 8.06–7.25 (m, 20H, Ph), 6.85 (d, 1H, H-1, $J_{1,2} = 3.7$ Hz), 6.29 (t, 1H, H-3, $J_{2,3} = J_{3,4} = 10.0$ Hz), 5.83 (t, 1H, H-4, $J_{4,5} = 9.8$ Hz), 5.63 (dd, 1H, H-2), 4.65 (dd, 1H, H-6a, $J_{5,6a} = 2.6$ Hz, $J_{6a,6b} = -12.9$ Hz), 4.69–4.62 (m, 1H, H-5), 4.49 (dd, 1H, H-6b, $J_{5,6b} = 5.5$ Hz); ^{13}C NMR (75.5 MHz): $\delta = 166.0$, 165.6, 165.4, 165.2 (4 CO), 160.5 (CNH), 133.6–128.4 (4 Ph), 93.1 (C-1), 90.7 (CCl_3), 70.7 (2C, C-3,5), 70.2 (C-2), 68.6 (C-4), 62.5 (C-6); anal. calcd for $C_{36}H_{28}NO_{10}Cl_3$ (741.0): C, 58.36; H, 3.81; N, 1.89; Cl, 14.35; found: C, 58.22; H, 3.83; N, 1.83; Cl, 14.00.

3.13. 2-Azido-4-phenyl-3-butene-1-yl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside **12**

TMSOTf (29 μl, 0.16 mmol) was added at −30°C to a solution of racemic **4**[10,11] (0.29 g, 1.50 mmol) and **11** (1.19 g, 1.61 mmol) in CH_2Cl_2 (20 ml), the mixture was stirred for 3 h and neutralized by addition of pyridine. The mixture was washed with aq. HCl and aq. $NaHCO_3$ solutions, dried and concentrated. Chromatography of the residue with a gradient of 60:1 to 50:1 toluene:ethyl acetate afforded **12** (0.99 g, 86%) as a 1:1 mixture of diastereomers; $[\alpha]_D = +5.4$ ($c = 1.5$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 8.04$–7.16 (m, 50H, Ph, *Ph*), 6.58 (d, 1H, H-4′, $J_{3',4'} = 15.9$ Hz), 6.57 (d, 1H, *H-4′*, $J_{3',4'} = 15.3$ Hz), 6.03 (dd, 1H, H-3′, $J_{3',4'} = 15.9$ Hz, $J_{2',3'} = 7.8$ Hz), 5.96 (dd, 1H, *H-3′*, $J_{3',4'} = 16.0$ Hz, $J_{2',3'} = 7.6$ Hz), 5.93 (t, 1H, H-3, $J_{2,3} = J_{3,4} = 9.6$ Hz), 5.92 (t, 1H, *H-3*, $J_{2,3} = J_{3,4} = 9.6$ Hz), 5.70 (t, 1H, H-4, $J_{3,4} = J_{4,5} = 9.6$ Hz), 5.69 (t, 1H, *H-4*, $J_{3,4} = J_{4,5} = 9.7$ Hz), 5.58 (dd, 1H, H-2, $J_{2,3} = 9.7$ Hz, $J_{1,2} = 7.8$ Hz), 5.57 (dd, 1H, *H-2*, $J_{2,3} = 9.7$ Hz, $J_{1,2} = 7.8$ Hz), 4.98 (d, 1H, H-1, $J_{1,2} = 7.8$ Hz), 4.97 (d, 1H, *H-1*, $J_{1,2} = 7.8$ Hz), 4.67 (dd, 1H, H-6a, $J_{6a,6b} = -12.1$ Hz, $J_{5,6a} = 2.9$ Hz), 4.66 (dd, 1H, *H-6a*, $J_{6a,6b} = -12.1$ Hz, $J_{5,6a} = 2.8$ Hz), 4.52 (dd, 2H, H-6b, *H-6b*, $J_{6a,6b} = -12.2$ Hz, $J_{5,6b} = 5.2$ Hz), 4.29–4.15 (m, 4H, H-2′, H-5, *H-2′*, *H-5*), 4.02 (dd, 1H, H-1′a, $J_{1'a,1'b} = -10.7$ Hz, $J_{1'a,2'} = 3.8$ Hz), 3.98 (dd, 1H, *H-1′a*, $J_{1'a,1'b} = -10.7$ Hz, $J_{1'a,2'} = 5.9$ Hz), 3.73 (dd, 1H, H-1′b, $J_{1'a,1'b} = -10.4$ Hz, $J_{1'b,2'} = 5.1$ Hz), 3.63 (dd, 1H, *H-1′b*, $J_{1'a,1'b} = -10.6$ Hz, $J_{1'b,2'} = 8.1$ Hz); ^{13}C NMR (75.5 MHz): $\delta = 166.1$–165.0 (Ph), 135.6–125.3 (Ph), 134.9 (C-4′), 134.5 (*C-4′*), 123.0 (C-3′), 122.7 (*C-3′*), 101.5 (C-1), 101.2 (*C-1*), 72.8 (C-3,*3*), 72.4 (C-5,*5*), 71.9 (C-1′), 71.71 (C-2), 71.66 (*C-2*), 71.0 (*C-1′*), 69.6 (C-4,*4*), 63.6 (C-2′), 63.2 (*C-2′*), 63.0 (C-6,*6*); anal. calcd for $C_{44}H_{37}N_3O_{10}$ (767.8): C, 68.83; H, 4.86; N, 5.47; found: C, 68.61; H, 5.01; N, 5.41.

3.14. 2-Azido-4-phenyl-3-butene-1-yl β-D-glucopyranoside **13**

A solution of **12** (0.50 g, 0.64 mmol) and a catalytic amount of NaOMe in MeOH (10 ml) and toluene (2 ml) was stirred at room temp. for 24 h, neutralized with Dowex H^+ resin, filtered and concentrated. Chromatography of the residue with 20:1 CH_2Cl_2:MeOH, followed by filtration with water over a column of Biogel P2 and lyophilisation afforded **13** (0.20 g, 88%) as a 1:1 mixture of diastereomers; $[\alpha]_D = -16.3$ ($c = 1.5$, MeOH); ^{1}H NMR (300 MHz, CD_3OD): $\delta =$ 7.38–7.15 (m, 10H, Ph, *Ph*), 6.68 (d, 2H, H-4′,*4′*, $J_{3',4'} = 15.9$ Hz), 6.18 (dd, 1H, H-3′, $J_{3',4'} = 15.8$ Hz, $J_{2',3'} = 7.5$ Hz), 6.17 (dd, 1H, *H-3′*, $J_{3',4'} = 15.9$ Hz, $J_{2',3'} = 7.6$ Hz), 4.39–4.31 (m, 2H, H-2′,*2′*), 4.29 (d, 1H, H-1, $J_{1,2} = 7.7$ Hz), 4.28 (d, 1H, *H-1*, $J_{1,2} = 7.7$ Hz), 3.94 (dd, 1H, H-1′a, $J_{1'a,1'b} = -10.7$ Hz, $J_{1'a,2'} = 4.2$ Hz), 3.90 (dd, 1H, *H-1′a*, $J_{1'a,1'b} = -10.8$ Hz, $J_{1'a,2'} = 7.5$ Hz), 3.82 (d, 2H, H-6a,*6a*, $J_{6a,6b} = -12.0$ Hz), 3.69–3.57 (m, 4H, H-1′b,6b,*1′b*,*6b*), 3.34–3.14 (m, 8H, H-2,3,4,5,*2*,*3*,*4*,*5*); ^{13}C NMR (75.5 MHz, CD_3OD): $\delta = 137.5$–127.7 (Ph, *Ph*), 135.5 (C-4′,*4′*), 124.9 (C-3′), 124.8 (*C-3′*), 104.9 (C-1), 104.3 (*C-1*), 78.0 (C-3,5,3,*5*), 75.1 (C-2), 75.0 (*C-2*), 73.0 (C-1′), 72.5 (*C-1′*), 71.6 (C-4), 71.5 (*C-4*), 65.3 (C-2′), 64.7 (*C-2′*), 62.8 (C-6), 62.7 (*C-6*); FAB-MS calcd for $C_{16}H_{21}N_3O_6$ ($m/z = 351.143$); found: 352.150 ($[M+H]^+$).

3.15. 4,5,6,8-Tetra-O-acetyl-3,7-anhydro-2-deoxy-D-glycero-D-gulo-octonoyl chloride **14b**

A solution of 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-2-deoxy-D-*glycero*-D-*gulo*-octonic acid[26] **14a** (0.3 g, 0.77 mmol) in thionyl chloride (10 ml) was stirred for 2 h at 80°C. Concentration of the solution afforded crude **14b**,[25,27] which was used without further purification.

3.16. Pentafluorophenyl 4,5,6,8-tetra-O-acetyl-3,7-anhydro-2-deoxy-D-glycero-D-gulo-octonoate **14c**

DCC (88 mg, 0.43 mmol) was added at 0°C to a solution of 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-2-deoxy-D-*glycero*-D-*gulo*-octonic acid[26] **14a** (0.15 g, 0.38 mmol) and pentafluorophenol (78 mg, 0.42 mmol) in ethyl acetate (3 ml), the mixture was stirred for 2 h, filtered and the filtrate was concentrated. Chromatography of the residue with 3:1 *n*-hexane:ethyl acetate afforded **14c** (194 mg, 91%); mp = 115–116°C; $[\alpha]_D = -3.6$ ($c = 1.3$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 5.25$ (t, 1H, H-5, $J_{4,5} = J_{5,6} = 9.3$ Hz), 5.09 (t, 1H, H-6, $J_{5,6} = J_{6,7} = 9.7$ Hz), 4.99 (t, 1H, H-4, $J_{3,4} = J_{4,5} = 9.7$ Hz), 4.27 (dd, 1H, H-8a, $J_{8a,8b} = -12.3$ Hz, $J_{7,8a} = 5.1$ Hz), 4.08 (dd, 1H, H-8b, $J_{8a,8b} = -12.5$ Hz, $J_{7,8b} = 2.2$ Hz), 4.08–4.01 (m, 1H, H-3), 3.75 (ddd, 1H, H-7, $J_{6,7} = 10.0$ Hz, $J_{7,8a} = 5.0$ Hz, $J_{7,8b} = 2.2$ Hz), 2.90–2.87 (m, 2H, H-2), 2.08, 2.07, 2.04, 2.02 (12H, $COCH_3$); ^{13}C NMR (75.5 MHz): $\delta = 170.7$, 170.2, 169.7, 169.4 (4 CO), 166.0 (C-1), 165.9, 149.4, 149.2, 139.3, 134.5, 123.9 (C_6F_5), 76.0 (C-7), 74.2, 73.9 (C-3,5), 71.3 (C-4), 68.3 (C-6), 62.0 (C-8), 36.6 (C-2), 20.6 (4 CH_3); FAB-MS calcd for $C_{22}H_{21}F_5O_{11}$ ($m/z = 556.100$); found: 557.110 ($[M+H]^+$).

3.17. N-[(R)-2-Acetoxy-3-pentene-1-yl] 4,5,6,8-tetra-O-acetyl-3,7-anhydro-2-deoxy-D-glycero-D-gulo-octo-noyl amide **16a**

(a) A solution of **(*R*)-5** (173 mg, 0.71 mmol) and CF_3COOH (1 ml) in CH_2Cl_2 (10 ml) was stirred at room temp. for 1 h, concentrated and redissolved in CH_2Cl_2 (20 ml). The solution was cooled to 0°C, pyridine (2 ml) and a solution of crude **14b** (freshly prepared from 0.3 g of **14a** as described in Section 3.15) in CH_2Cl_2 (20 ml) was added and the mixture was stirred at room temp. for 40 h. The solution was washed subsequently with aq. HCl and aq. $NaHCO_3$ solutions, dried and concentrated. Chromatography of the residue with 3:1 *n*-hexane:ethyl acetate afforded first **(*R*)-15** (33 mg, 20%); $[\alpha]_D = -15.3$ ($c = 0.8$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 6.60$ (s, 1H, NH), 5.85 (dq, 1H, H-4, $J_{3,4} = 15.4$ Hz, $J_{4,5} = 6.6$ Hz), 5.46–5.31 (m, 2H, H-2,3), 3.60 (dd, 1H, H-1a, $J_{1a,1b} = -14.4$ Hz, $J_{1a,2} = 4.7$ Hz), 3.52 (dd, 1H, H-1b, $J_{1a,1b} = -14.2$ Hz, $J_{1b,2} = 6.3$ Hz), 2.09 (s, 3H, $COCH_3$), 1.73 (ddd, 3H, H-5, $J_{4,5} = 6.5$ Hz, $J_{3,5} = 1.6$ Hz, $J_{2,5} = 0.6$ Hz); ^{13}C NMR (75.5 MHz): $\delta = 170.6$ (CO), 157.3 (q, $J_{C,F} = 37$ Hz, $COCF_3$), 131.9 (C-4), 125.4 (C-3), 115.7 (q, $J_{C,F} = 288$ Hz, $COCF_3$), 72.5 (C-2), 43.1 (C-1), 21.0 ($COCH_3$) 17.7 (C-5); anal. calcd for $C_9H_{12}F_3NO_3$ (239.2): C, 45.19; H, 5.06; N, 5.86; found: C, 45.08; H, 5.09; N, 5.83.

Eluted next was **16a** (209 mg, 57%); $[\alpha]_D = -17.6$ ($c = 1.4$, $CHCl_3$); ^{1}H NMR (300 MHz): $\delta = 6.15$ (bt, 1H, NH, $J_{1',NH} = 5.6$ Hz), 5.78 (dd, 1H, H-4′, $J_{3',4'} = 15.1$ Hz, $J_{4',5'} = 6.6$ Hz), 5.37 (ddd, 1H, H-3′, $J_{3',4'} = 15.3$ Hz, $J_{2',3'} = 7.1$ Hz, $J_{3',5'} = 1.6$ Hz), 5.29–5.23 (m, 1H, H-2′), 5.16 (t, 1H, H-5, $J_{4,5} = J_{5,6} = 9.3$ Hz), 5.02 (t, 1H, H-6, $J_{5,6} = J_{6,7} = 9.7$ Hz), 4.84 (t, 1H, H-4, $J_{3,4} = J_{4,5} = 9.6$ Hz), 4.17, 4.16 (2 s, 2H, H-8a,8b), 3.83 (td, 1H, H-3, $J_{3,4} = J_{2b,3} = 9.4$ Hz, $J_{2a,3} = 2.9$ Hz), 3.67 (ddd, 1H, H-7, $J_{6,7} = 10.0$ Hz, $J_{7,8a} = 3.9$ Hz, $J_{7,8b} = 2.9$ Hz), 3.46 (ddd, 1H, H-1′a, $J_{1'a,1'b} = -14.1$ Hz, $J_{1'a,NH} = 5.7$ Hz $J_{1'a,2'} = 4.4$ Hz), 3.41–3.32 (m, 1H, H-1′b), 2.38 (dd, 1H, H-2a, $J_{2a,2b} = -15.1$ Hz, $J_{2a,3} = 2.9$ Hz), 2.29 (dd, 1H, H-2b, $J_{2a,2b} = -15.2$ Hz, $J_{2b,3} = 8.9$ Hz), 2.05, 2.03, 2.00, 1.99,

1.96 (5 s, 15H, COCH_3), 1.67 (d, 3H, H-5′, $J_{4',5'}=6.5$ Hz); ^{13}C NMR (75.5 MHz): $\delta=170.6$, 170.4, 170.2, 169.8, 169.5, 169.1 (*C*OCH$_3$, C-1), 131.0 (C-4′), 126.4 (C-3′), 75.8 (C-7), 74.7 (C-3), 73.9 (C-5), 73.3 (C-2′), 71.3 (C-4), 68.2 (C-6), 61.9 (C-8), 42.9 (C-1′), 38.9 (C-2), 21.2, 20.7, 20.6, 20.5 (CO*C*H$_3$), 17.8 (C-5′); anal. calcd for $C_{23}H_{33}NO_{12}$ (515.5): C, 53.59; H, 6.45; N, 2.72; found: C, 53.34; H, 6.60; N, 2.66.

(b) A solution of **(*R*)-5** (243 mg, 1.0 mmol) and CF_3COOH (1.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temp. for 1 h, concentrated and redissolved in DMF (8 ml). Et_3N (0.153 ml, 1.1 mmol) and a solution of crude **14c** (0.56 g, 1.0 mmol) in DMF (5 ml) was added and the solution was stirred for 6 h at 80°C. The mixture was concentrated, the residue redissolved in CH_2Cl_2, washed subsequently with aq. HCl and aq. $NaHCO_3$ solutions, dried and concentrated. Chromatography of the residue with 1:3 *n*-hexane:ethyl acetate afforded **16a** (373 mg, 72%).

3.18. N-*[(*S*)-2-Acetoxy-3-pentene-1-yl] 4,5,6,8-tetra*-O-*acetyl-3,7-anhydro-2-deoxy-*D*-glycero-*D*-gulo-octo-noyl amide* ***16b***

Treatment of **(*S*)-5** (243 mg, 1.0 mmol) as described in Section 3.17 (b) afforded **16b** (352 mg, 68%); $[\alpha]_D=0.0$ ($c=1.4$, $CHCl_3$); mp = 123°C; ^{1}H NMR (300 MHz): $\delta=6.16$ (bt, 1H, NH, $J_{1',NH}=5.7$ Hz), 5.81 (dd, 1H, H-4′, $J_{3',4'}=15.1$ Hz, $J_{4',5'}=6.5$ Hz), 5.41 (ddd, 1H, H-3′, $J_{3',4'}=15.2$ Hz, $J_{2',3'}=7.0$ Hz, $J_{3',5'}=1.6$ Hz), 5.33–5.27 (m, 1H, H-2′), 5.20 (t, 1H, H-5, $J_{4,5}=J_{5,6}=9.3$ Hz), 5.06 (t, 1H, H-6, $J_{5,6}=J_{6,7}=9.7$ Hz), 4.89 (t, 1H, H-4, $J_{3,4}=J_{4,5}=9.7$ Hz), 4.24 (dd, 1H, H-8a, $J_{8a,8b}=-12.4$ Hz, $J_{7,8a}=4.9$ Hz), 4.12 (dd, 1H, H-8b, $J_{8a,8b}=-12.4$ Hz, $J_{7,8b}=2.2$ Hz), 3.90 (ddd, 1H, H-3, $J_{3,4}=9.9$ Hz, $J_{2b,3}=8.5$ Hz, $J_{2a,3}=3.3$ Hz), 3.68 (ddd, 1H, H-7, $J_{6,7}=10.0$ Hz, $J_{7,8a}=4.8$ Hz, $J_{7,8b}=2.2$ Hz), 3.50 (ddd, 1H, H-1′a, $J_{1'a,1'b}=-14.1$ Hz, $J_{1'a,NH}=5.7$ Hz $J_{1'a,2'}=4.3$ Hz), 3.44–3.35 (m, 1H, H-1′b), 2.43 (dd, 1H, H-2a, $J_{2a,2b}=-15.0$ Hz, $J_{2a,3}=3.3$ Hz), 2.34 (dd, 1H, H-2b, $J_{2a,2b}=-15.1$ Hz, $J_{2b,3}=8.6$ Hz), 2.09, 2.07, 2.04, 2.03, 2.00 (5 s, 15H, $COCH_3$), 1.71 (dd, 3H, H-5′, $J_{4',5'}=6.3$ Hz, $J_{3',5'}=1.2$ Hz); ^{13}C NMR (75.5 MHz): $\delta=170.5$, 170.3, 170.1, 169.8, 169.4, 169.1 (*C*OCH_3, C-1), 131.0 (C-4′), 126.4 (C-3′), 75.8 (C-7), 74.7 (C-3), 73.9 (C-5), 73.3 (C-2′), 71.2 (C-4), 68.3 (C-6), 61.9 (C-8), 42.9 (C-1′), 39.0 (C-2), 21.1, 20.7, 20.6, 20.5 (CO*C*H$_3$), 17.8 (C-5′); anal. calcd for $C_{23}H_{33}NO_{12}$ (515.5): C, 53.59; H, 6.45; N, 2.72; found: C, 53.75; H, 6.58; N, 2.82.

3.19. N-*[(*R*)-2-Hydroxy-3-pentene-1-yl] 3,7-anhydro-2-deoxy-*D*-glycero-*D*-gulo-octonoyl amide* ***17a***

Treatment of **16a** (281 mg, 0.545 mmol) as described in Section 3.14 afforded **17a** (144 mg, 87%); $[\alpha]_D=-9.5$ ($c=1.0$, MeOH); ^{1}H NMR (300 MHz, CD_3OD): $\delta=5.66$ (dqd, 1H, H-4′, $J_{3',4'}=15.4$ Hz, $J_{4',5'}=6.5$ Hz, $J_{2',4'}=1.0$ Hz), 5.39 (ddd, 1H, H-3′, $J_{3',4'}=15.3$ Hz, $J_{2',3'}=6.7$ Hz, $J_{3',5'}=1.6$ Hz), 4.02 (dd, 1H, H-2′, $J_{1',2'}=12.4$ Hz, $J_{2',3'}=6.5$ Hz), 3.75 (dd, 1H, H-8a, $J_{8a,8b}=-12.0$ Hz, $J_{7,8a}=2.0$ Hz), 3.57 (dd, 1H, H-8b, $J_{8a,8b}=-11.9$ Hz, $J_{7,8b}=5.0$ Hz), 3.46 (dt, 1H, H-3, $J_{3,4}=J_{2b,3}=9.2$ Hz, $J_{2a,3}=2.8$ Hz), 3.29–3.16 (m, 4H, H-1′a,5,6,7), 3.07 (dd, 1H, H-1′b, $J_{1'a,1'b}=-13.5$ Hz, $J_{1'b,2'}=7.3$ Hz), 3.01 (t, 1H, H-4, $J_{3,4}=J_{4,5}=9.0$ Hz), 2.66 (dd, 1H, H-2a, $J_{2a,2b}=-14.7$ Hz, $J_{2a,3}=2.8$ Hz), 2.28 (dd, 1H, H-2b, $J_{2a,2b}=-14.8$ Hz, $J_{2b,3}=9.0$ Hz), 1.63 (d, 3H, H-5′, $J_{4',5'}=6.5$ Hz); ^{13}C NMR (75.5 MHz): $\delta=174.1$ (C-1), 132.7 (C-3′), 128.7 (C-4′), 81.6, 79.6 (C-5,7), 78.0 (C-3), 75.0 (C-4), 72.1, 71.6 (C-2′,6), 62.8 (C-8), 46.4 (C-1′), 40.1 (C-2), 18.0 (C-5′); FAB-MS calcd for $C_{13}H_{23}NO_7$ ($m/z=305.147$); found: 306.150 ([M+H]$^+$).

3.20. N-[(S)-2-Hydroxy-3-pentene-1-yl] 3,7-anhydro-2-deoxy-D-glycero-D-gulo-octonoyl amide **17b**

Treatment of **16b** (187 mg, 0.363 mmol) as described in Section 3.14 afforded **17b** (106 mg, 96%); $[\alpha]_D = -11.8$ ($c = 1.0$, MeOH); ^{1}H NMR (300 MHz, CD_3OD): $\delta = 5.66$ (dqd, 1H, H-4′, $J_{3',4'} = 15.4$ Hz, $J_{4',5'} = 6.5$ Hz, $J_{2',4'} = 1.0$ Hz), 5.39 (ddd, 1H, H-3′, $J_{3',4'} = 15.4$ Hz, $J_{2',3'} = 6.7$ Hz, $J_{3',5'} = 1.6$ Hz), 4.03 (dd, 1H, H-2′, $J_{1',2'} = 12.3$ Hz, $J_{2',3'} = 6.6$ Hz), 3.76 (d, 1H, H-8a, $J_{8a,8b} = -12.6$ Hz), 3.55 (dd, 1H, H-8b, $J_{8a,8b} = -12.0$ Hz, $J_{7,8b} = 5.1$ Hz), 3.46 (dt, 1H, H-3, $J_{3,4} = J_{2b,3} = 9.3$ Hz, $J_{2a,3} = 2.8$ Hz), 3.30–3.11 (m, 4H, H-1′a,5,6,7), 3.06 (dd, 1H, H-1′b, $J_{1'a,1'b} = -13.5$ Hz, $J_{1'b,2'} = 7.4$ Hz), 3.01 (t, 1H, H-4, $J_{3,4} = J_{4,5} = 9.0$ Hz), 2.66 (dd, 1H, H-2a, $J_{2a,2b} = -14.7$ Hz, $J_{2a,3} = 2.8$ Hz), 2.27 (dd, 1H, H-2b, $J_{2a,2b} = -14.7$ Hz, $J_{2b,3} = 9.1$ Hz), 1.63 (d, 3H, H-5′, $J_{4',5'} = 6.5$ Hz); ^{13}C NMR (75.5 MHz): $\delta = 174.1$ (C-1), 132.7 (C-3′), 128.7 (C-4′), 81.7, 79.5 (C-5,7), 78.0 (C-3), 75.1 (C-4), 72.0, 71.7 (C-2′,6), 62.9 (C-8), 46.5 (C-1′), 40.1 (C-2), 18.0 (C-5′); FAB-MS calcd for $C_{13}H_{23}NO_7$ ($m/z = 305.147$); found: 306.150 ($[M+H]^+$).

3.21. (E)-2-t-Butoxycarbonylamido-4-phenyl-3-butene-1-ol **19**

A solution of (*E*)-2-amino-4-phenyl-3-butene-1-ol[11] **18** (0.3 g, 1.37 mmol), Boc_2O (0.33 g, 1.5 mmol) and Et_3N (0.38 ml) in CH_2Cl_2 (15 ml) was stirred at room temp. for 3 h. Concentration of the solution and chromatography of the residue with 2:1 *n*-hexane:ethyl acetate afforded **19** (0.37 g, 73%). The physical data were in accordance with the literature data.[29]

3.22. (E)-1-Acetoxy-2-t-butoxycarbonylamido-4-phenyl-3-butene **20**

Treatment of **19** (0.8 g, 3.1 mmol) with pyridine (4 ml) and Ac_2O (2 ml) in CH_2Cl_2 (15 ml) at room temp. for 1.5 h and workup as described in Section 3.6 afforded **20** (0.9 g, 97%); mp = 78–79°C; ^{1}H NMR (300 MHz): $\delta = 7.38$–7.22 (m, 5H, Ph), 6.59 (dd, 1H, H-4, $J_{3,4} = 15.9$ Hz, $J_{2,4} = 1.4$ Hz), 6.10 (dd, 1H, H-3, $J_{3,4} = 16.0$ Hz, $J_{2,3} = 5.9$ Hz), 4.81 (bs, 1H, H-2), 4.60 (bs, 1H, NH), 4.25–4.15 (m, 1H, H-1a), 4.18 (dd, 1H, H-1b, $J_{1a,1b} = -11.2$ Hz, $J_{1b,2} = 5.0$ Hz), 2.07 (s, 3H, $COCH_3$), 1.47 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz): $\delta = 170.9$ (CO), 155.2 ($COOC(CH_3)_3$), 136.3–126.5 (Ph), 131.9 (C-4), 126.1 (C-3), 79.9 ($C(CH_3)_3$), 66.1 (C-1), 51.5 (C-2), 28.4 ($C(CH_3)_3$), 20.8 ($COCH_3$); anal. calcd for $C_{17}H_{23}NO_4$ (305.4): C, 66.86; H, 7.59; N, 4.59; found: C, 66.78; H, 7.54; N, 4.51.

3.23. N-[1-Acetoxy-4-phenyl-3-butene-2-yl] 4,5,6,8-tetra-O-acetyl-3,7-anhydro-2-deoxy-D-glycero-D-gulo-octonoyl amide **21**

A solution of **20** (218 mg, 0.72 mmol) and CF_3COOH (1.5 ml) in CH_2Cl_2 (10 ml) was stirred at room temp. for 1.5 h, concentrated and redissolved in CH_2Cl_2 (15 ml). The solution was cooled to 0°C, pyridine (2 ml) and a solution of crude **14b** (freshly prepared from 0.31 g of **14a**) as described in Section 3.15 in CH_2Cl_2 (15 ml) was added and the mixture was stirred at room temp. for 24 h. The solution was washed subsequently with aq. HCl and aq. $NaHCO_3$ solutions, dried and concentrated. Chromatography of the residue with 5:1 toluene:acetone afforded **21** (347 mg, 84%) as a 1:1 mixture of diastereomers; ^{1}H NMR (300 MHz): $\delta = 7.38$–7.16 (m, 10H, Ph, *Ph*), 6.59 (dd, 1H, H-4′, $J_{3',4'} = 16.0$ Hz, $J_{2',4'} = 1.2$ Hz), 6.58 (dd, 1H, *H-4′*, $J_{3',4'} = 16.0$ Hz, $J_{2',4'} = 1.5$ Hz), 6.34 (d, 1H, NH, $J_{2',NH} = 8.7$ Hz), 6.29 (d, 1H, *NH*, $J_{2',NH} = 8.6$ Hz), 6.13 (dd, 1H,

H-3′, $J_{3',4'}=16.0$ Hz, $J_{2',3'}=5.8$ Hz), 6.11 (dd, 1H, *H-3′*, $J_{3',4'}=16.0$ Hz, $J_{2',3'}=6.3$ Hz), 5.22 (t, 1H, H-5, $J_{4,5}=J_{5,6}=9.3$ Hz), 5.21 (t, 1H, *H-5*, $J_{4,5}=J_{5,6}=9.3$ Hz), 5.08 (t, 1H, H-6, $J_{5,6}=J_{6,7}=$ 9.7 Hz), 5.07 (t, 1H, *H-6*, $J_{5,6}=J_{6,7}=9.7$ Hz), 5.01–4.87 (m, 2H, H-2′,*2′*), 4.94 (t, 1H, H-4, $J_{3,4}=J_{4,5}=9.5$ Hz), 4.91 (t, 1H, *H-4*, $J_{3,4}=J_{4,5}=9.5$ Hz), 4.36–4.08 (m, 8H, H-1′a,1′b,8′a,8′b,*1′a*,*1′b*,*8′a*,*8′b*), 3.99–3.88 (m, 2H, H-3,*3*), 3.74 (ddd, 1H, H-7, $J_{6,7}=9.9$ Hz, $J_{7,8a}=4.3$ Hz, $J_{7,8b}=2.5$ Hz), 3.70 (ddd, 1H, H-7, $J_{6,7}=9.9$ Hz, $J_{7,8a}=4.5$ Hz, $J_{7,8b}=2.3$ Hz), 2.55–2.37 (m, 4H, H-2a,2b,*2a*,*2b*), 2.09–1.97 (m, 30H, $COCH_3$); ^{13}C NMR (75.5 MHz): $\delta=171.0$–168.6 (10 CO, C-1,*1*), 136.1–126.4 (Ph, *Ph*) 132.5 (C-4′), 132.2 (*C-4′*) 125.3 (C-3′), 125.2 (*C-3′*), 76.0 (C-7), 75.9 (*C-7*) 74.9 (C-3), 74.7 (*C-3*), 73.9 (C-5,*5*), 71.4 (C-4), 71.1 (*C-4*), 68.2 (C-6,*6*), 65.6 (C-1′), 65.5 (*C-1′*), 61.8 (C-8,*8*), 50.5 (C-2′), 50.3 (*C-2′*), 39.1 (C-2,*2*), 20.8–20.6 (10 $CO\mathit{C}H_3$); anal. calcd for $C_{28}H_{35}NO_{12}$ (577.6): C, 58.23; H, 6.11; N, 2.43; found: C, 58.03; H, 6.06; N, 2.30.

3.24. N-*[1-Hydroxy-4-phenyl-3-butene-2-yl] 3,7-anhydro-2-deoxy-D*-glycero-*D*-gulo-*octonoyl amide* ***22***

Treatment of **21** (150 mg, 0.267 mmol) as described Section 3.14 afforded **22** (91 mg, 94%) as a 1:1 mixture of diastereomers; ^1H NMR (300 MHz, CD_3OD): $\delta=7.35$–7.10 (m, 10H, Ph, *Ph*), 6.52 (d, 2H, H-4′,*4′*, $J_{3',4'}=16.0$ Hz), 6.17 (dd, 1H, H-3′, $J_{3',4'}=16.0$ Hz, $J_{2',3'}=6.0$ Hz), 6.16 (dd, 1H, *H-3′*, $J_{3',4'}=16.0$ Hz, $J_{2',3'}=6.2$ Hz), 4.58–4.52 (m, 2H, H-2′,*2′*), 3.76 (dd, 1H, H-8a, $J_{8a,8b}=-12.0$ Hz, $J_{7,8a}=1.5$ Hz), 3.72 (dd, 1H, *H-8a*, $J_{8a,8b}=-12.1$ Hz, $J_{7,8a}=2.1$ Hz), 3.63–3.48 (m, 8H, H-1′a,1′b,3,8b,*1′a*,*1′b*,*3*,*8b*), 3.32–3.16 (m, 6H, H-5,6,7,*5*,*6*,*7*), 3.05 (t, 2H, H-4,*4*, $J_{3,4}=J_{4,5}=9.1$ Hz), 2.73 (dd, 1H, H-2a, $J_{2a,2b}=-14.6$ Hz, $J_{2a,3}=2.7$ Hz), 2.72 (dd, 1H, *H-2a*, $J_{2a,2b}=-14.4$ Hz, $J_{2a,3}=2.5$ Hz), 2.36 (dd, 1H, H-2b, $J_{2a,2b}=-14.6$ Hz, $J_{2b,3}=9.0$ Hz), 2.35 (dd, 1H, *H-2b*, $J_{2a,2b}=-14.4$ Hz, $J_{2b,3}=9.1$ Hz); ^{13}C NMR (75.5 MHz): $\delta=173.6$ (C-1), 173.5 (*C-1*), 138.3–127.4 (Ph, *Ph*), 132.6 (C-4′), 132.3 (*C-4′*), 127.9 (C-3′), 127.9 (*C-3′*), 81.7, 81.5, 79.6 (C-5,7,*5*,*7*), 78.1 (C-3), 78.0 (*C-3*), 75.2 (C-4), 75.1 (*C-4*), 71.8 (C-6), 71.5 (*C-6*), 65.1 (C-1′,*1′*), 63.0 (C-8), 62.6 (*C-8*), 54.8 (C-2′,*2′*), 40.4 (C-2), 40.3 (*C-2*); FAB-MS calcd for $C_{18}H_{25}NO_7$ ($m/z=367.163$); found: 368.170 ($[M+H]^+$).

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