Synthesis of Imino Sugar Scaffolds for the Generation of Glycosidase Inhibitor Libraries

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Dedicated to the memory of Professor Christian Pedersen

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We have synthesized imino sugar scaffolds bearing two points of diversity — the stereocenters located in α positions relative to the nitrogen atom — and three points of orthogonal derivatization — a carboxylic function, the primary hydroxy group, and the ring nitrogen atom. The key steps in the synthetic approach are the chain elongation of aldehyde **5** with the formation of an α,β-unsaturated ester, the Michael addition of an amine, and the final cyclization. This strategy leads to the preparation of different *N*-substituted imino sugar analogues having both α and β structures and of both D and L stereochemistry. Different derivatives have been prepared from the scaffolds we obtained. The carboxymethyl group was coupled to the amino function of different amino acids to afford compounds **30**–**34**, while the selectively accessible primary hydroxy group has been substituted with an azido group to afford compounds **24**–**26**.

Introduction

The significant role that carbohydrates play in a variety of biological processes, particularly cell−cell and cell−pathogen recognition phenomena, has stimulated great interest in compounds that interfere in carbohydrate metabolism and in carbohydrate-based recognition phenomena. In this context, great efforts have been devoted to the synthesis of glycomimetics,[1] such as imino sugars[2] and C-glycosides,[3] which can act as inhibitors of carbohydrate processing enzymes and/or as stable analogues of glycidic entities. In particular, imino sugars, in which the ring oxygen atom of the natural sugar is replaced by a nitrogen atom that, when protonated, assumes a positive charge, mimic the oxonium ion transition state of glycosidases and, therefore, act as competitive inhibitors. The natural imino sugar nojirimycin (**1**; Figure 1), discovered in 1966 as the first glucose mimic,[4] has shown inhibitory activity towards α- and β-glucosidases,[2,4] but because of the lability of the hemiaminal function, chemists' interest shifted to the stable, and even more powerful, inhibitor, 1-deoxynojirimycin (DNJ, **2**) and to a variety of its derivatives.[2] The multitude of publications on the synthesis of imino sugars reported so far outlines the growing interest in finding inhibitors that have improved activities and specificities. Particular attention has been devoted to the preparation of numerous *N*-alkylated derivatives of 1-deoxynojirimycin;[5] indeed, the presence of a lipophilic appendage on the nitrogen atom strongly enhances the biological activity.[6] In addition, the design and synthesis of imino sugar C-glycosides[7] has attracted attention since α-homonojirimycin (**3**), first synthesized by Liu[8] and thereafter isolated from a natural source,[9] has proven to be a potent and, more significantly, selective inhibitor of α-glycosidases from the mouse gut and human intestine. In addition, properly functionalized and protected imino sugar C-glycosides could be useful building blocks for the synthesis of more complex imino sugar conjugates.

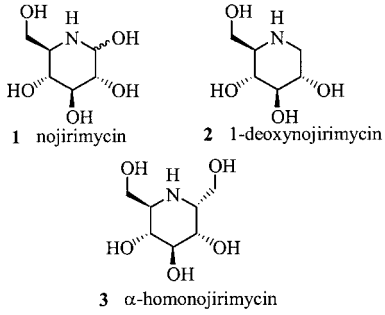

Figure 1. Natural imino sugars

Since the rational design of specific inhibitors is frequently difficult, in part because of the lack of information regarding the structures of most enzymes' active sites, we

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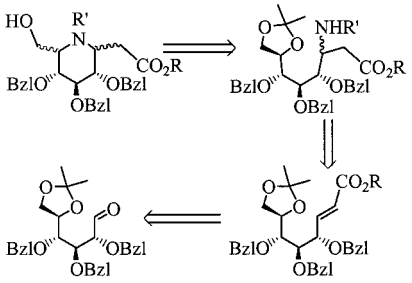
believed that the synthesis of an imino sugar library could represent a better strategy in the search for specificity. An interesting example of a "dynamic" library of imino sugars, reported by Vogel et al.,[10] is based on the imines obtained from an imino sugar bearing a carboxaldehyde function and different amines. Recently, Wong et al.,[11] in search of selective α-fucosidase inhibitors, reported the synthesis of a library of fuconojirimycin derivatives generated from a single core structure. We aimed, instead, to generate a library from imino sugar scaffolds having various points of diversity, functional groups, and orthogonal protections. While contemplating the kind of diversity sites that should be introduced into our library, we considered some structural features of previously cited imino sugars that have been proven to correlate with and to enhance the inhibitory potency and enzyme selectivity: the presence of an alkyl chain on the ring nitrogen atom and the presence of a substituent at C(1).

To allow easy derivatization at these positions, we chose to synthesize imino-C-glycosides having a carboxylic function; this unit allows further elongation/derivatization by well-established peptide synthesis procedures.

Results and Discussion

Retrosynthetic Scheme

We planned a retrosynthesis (Scheme 1) that allows imino sugars to be obtained having a methylenecarboxylic appendage at C(1) for further elongation. Furthermore, the synthesis allows the preparation of analogues of both α- and β-glycosides and both the D and L series of sugars. The obtained imino sugars present three points for orthogonal derivatization: the carboxylic group, the primary hydroxy group, and the ring nitrogen atom.



Scheme 1

Formation of the α,β-Unsaturated Ester and Michael Addition of the Amino Group

The synthetic strategy, outlined in Scheme 2, starts from aldehyde **5** and requires, as key reactions, elongation to form α,β-unsaturated esters, the introduction of an amino group by Michael addition, and, finally, the cyclization. Aldehyde **5**,[12] obtained from commercially available 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose, was treated with [(ethoxycarbonyl)- and (benzyloxycarbonyl)methylene]triphenylphosphorane (Scheme 2) to afford the α,β-unsaturated esters **6** and **7**. It is noteworthy that, in a combinatorial approach, the use of different stabilized ylides allows the introduction of different substituents at C(1).

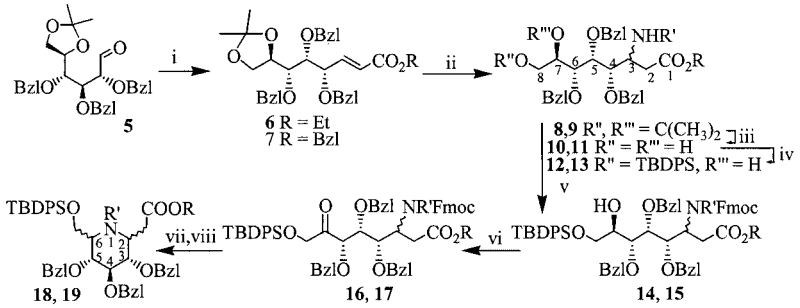
The Michael acceptors **6** and **7** represent key intermediates for the introduction of a range of substituted amines and, thus, affords, once again in a combinatorial fashion, different *N*-substituted imino sugars as final products. We used butylamine, allylamine, and benzylamine — the latter two to permit deprotection of the amino group for further derivatization. The Michael addition afforded two diastereoisomers **8** [(3*S*) configuration] and **9** [(3*R*) configuration], whose ratios are listed in Table 1. The configuration at the newly formed stereocenter was determined, by ^{1}H NMR coupling constants and the NOESY 1D experiments discussed below, only after cyclization.

Since we were interested in the production of both diastereoisomers, no chelating agent or chiral auxiliaries were adopted to improve the diastereoselectivity. We rationalize the predominance of the (*S*) product over the (*R*) one in

Table 1. Products of the Michael addition

Compound	R′NH$_2$	Products **8**, **9**	**8**/**9** ratio	Yield [%]
6	allyl	**8a**, **9a**	63:37	50 (**8**), 30 (**9**)
6	benzyl	**8b**, **9b**	63:37	33 (**8**), 19 (**9**)[a]
6	butyl	**8c**, **9c**	63:37	50 (**8**), 30 (**9**)
7	allyl	**8d**, **9d**	60:40	43 (**8**), 28 (**9**)

[a] 28% of the starting material was recovered.



Scheme 2. Reagents and conditions: i) PPh_3=CHCOOR, toluene, reflux; ii) R′NH_2 R′ = All, Bu, Bzl; iii) PTSOH, CH_3CN, H_2O, reflux; iv) TBDPSiCl, imidazole, CH_2Cl_2; v) FmocCl, Na_2CO_3, dioxane/H_2O; vi) PCC, CH_2Cl_2; vii) piperidine, DMF; viii) CH_2Cl_2, Na_2SO_4, AcOH, $NaBH(OAc)_3$

terms of a slightly more favorable nucleophilic attack from the less hindered side of the double bond, according to the Cram transition state model depicted in Figure 2. The two diastereoisomers obtained from the conjugate additions were readily separated by flash chromatography.

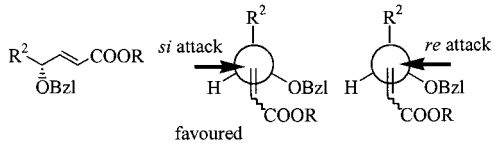


Figure 2. Diastereoselection of the conjugate addition

Cyclization

To obtain their cyclic imino sugar structures, the open chain compounds **8** and **9** can by cyclized by nucleophilic attack of the amino group on an electrophilic center at C(7). We performed this cyclization by intramolecular reductive amination, which requires oxidation of the secondary hydroxy group at C(7). To perform this transformation, the isopropylidene protecting groups of compounds **8** and **9** were hydrolyzed (*p*-toluenesulfonic acid or camphorsulfonic acid, $MeCN/H_2O$, reflux) and the products were treated with *tert*-butyldiphenylsilyl chloride (imidazole, CH_2Cl_2) to protect the primary hydroxy groups selectively. Oxidation of the free hydroxy groups of compounds **12** and **13** required protection of the secondary amino groups to avoid their oxidation to the corresponding *N*-oxides. Therefore, compounds **12** and **13** were converted into the Fmoc derivatives **14** and **15** and then treated with PCC to afford the ketones **16** and **17**. Finally, cleavage of the Fmoc protecting group and immediate intramolecular reductive amination, performed using $NaBH(OAc)_3$ under acidic conditions (1,2-dichloroethane, Na_2SO_4, AcOH) afforded the imino sugars **18** and **19** (Figure 3) in variable yields [40−98% for the last three steps (Table 2)]. ^{1}H NMR spectroscopic analysis on the cyclized products allowed us to determine the absolute configurations of the C(2) stereocenter formed during the Michael addition and at C(6).

The values of the coupling constants ($J_{5,4}$ = 9.5, $J_{4,3}$ = 9.5, and $J_{3,2}$ = 8.4 Hz) of compound **18d** (Figure 4) are indicative for a *trans*-diaxial disposition of the protons, which, thus, indicates a $^4C_1$ conformation; moreover, the diaxial disposition of C(2)-H/C(3)-H allows us to determine the absolute (*S*) configuration of the C(2) center. In addition, the coupling constant $J_{5,6}$ = 5.9 Hz indicates an equatorial disposition of the C-6−H proton and consequently the (*S*) absolute configuration at the C(6) center. This data are supported by monodimensional NOE difference experiments and are confirmed by bidimensional NOESY; a strong NOE was observed between C(2)-H/C(4)-H while NOEs were absent for C(2)-H/C(6)-H and C(4)-H/C(6)-H. In compound **19d**, the coupling constants $J_{5,6}$ = 9.6, $J_{5,4}$ = 9.6, and $J_{4,3}$ = 9.5 Hz are indicative of a $^4C_1$ conformation and a *trans*-diaxial disposition of the C(3)-H/C(4)-H, C(4)-H/C(5)-H, and C(5)-H/C(6)-H units; the latter disposition is also indicative of the absolute (*R*) configuration at C-6. In a similar manner, $J_{3,2}$ = 5.2 Hz is diagnostic of the equatorial disposition of C(2)-H and the absolute (*R*) configuration at C(2). Moreover, an NOE was found between C(4)-H and C(6)-H. The absolute configurations of the C(2) and C(6) centers of the other compounds were determined similarly. The stereochemical outcome of the newly formed stereocenter C(6) of products **18** and **19** is somehow correlated to the configuration of the carbon atom bearing the amine in precursors **16** and **17**. As outlined in Table 2, the cyclization affords, as the major products, compounds having the substituent at C(6) positioned *trans* with respect to the one at C(2) (Entries 1, 3−8). The only compound that behaves differently is **16b** (Entry 2), which afforded as its major product the imino sugar **18b** that has its C(2) and C(6) substituents in a *cis* configuration. In this compound, the coupling constants $J_{3,4}$ = 9.6, and $J_{3,2}$ = 8.4 Hz confirm a *trans*-diaxial disposition of the C(2)-H/C(3)-H and C(3)-H/C(4)-H units, which, thus, indicates an absolute (*S*) configuration of the C(2) center, and an NOE between the C(2)-H and C(6)-H protons indicates the axial disposition of the C(6)-H unit and, consequently, the (*R*) configuration at C(6).

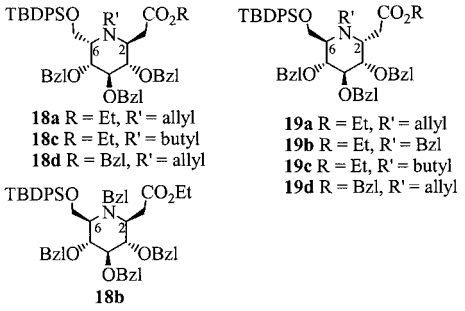


Figure 3. Cyclization major products

Table 2. Stereochemical outcome of the reductive amination

Entry	Substrate	C(2)/C(6), *trans*/*cis* ratio	Major product	Yield [%][a]
1	**16a**	95:5	**18a**	82
2	**16b**	20:80	**18b**	65
3	**16c**	100:0	**18c**	45
4	**16d**	95:5	**18d**	55
5	**17a**	95:5	**19a**	98
6	**17b**	85:25	**19b**	40
7	**17c**	95:5	**19c**	68
8	**17d**	87:13	**19d**	55

[a] Yield of the isolated major product; calculated from the alcohols **14/15**.

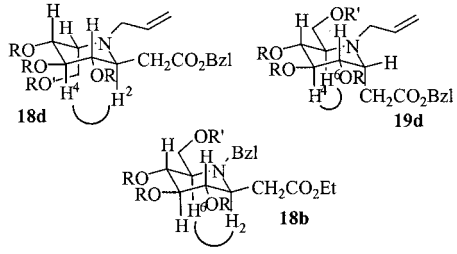
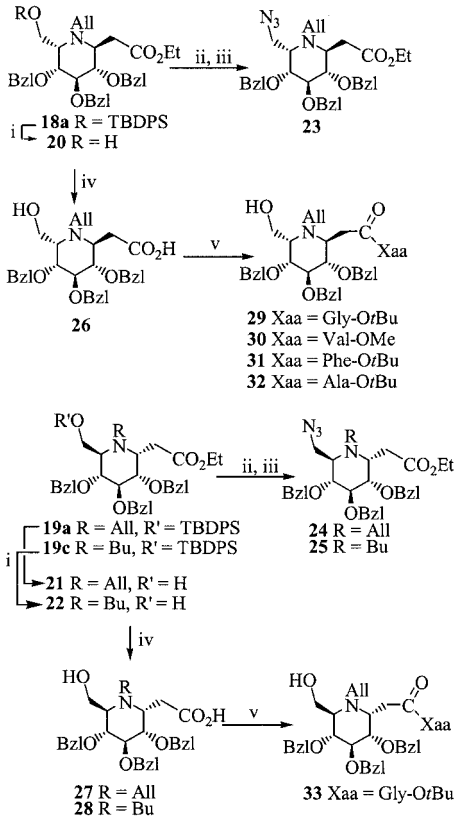


Figure 4. NOE correlations

Derivatization

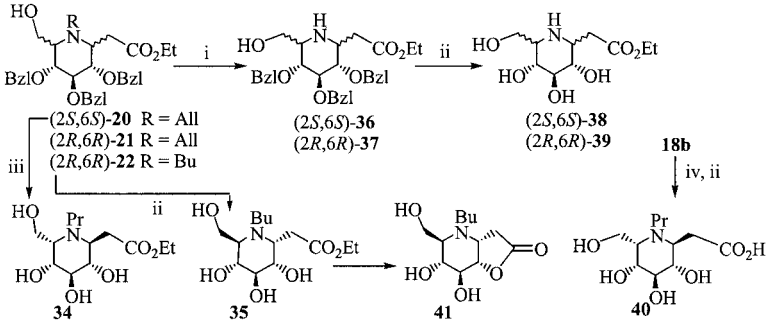
Imino sugars **18a**, **19a**, and **19c** (major isomers) were deprotected at their primary hydroxy groups by treatment with tetrabutylammonium fluoride to afford compounds **20**, **21**, and **22**, respectively (Scheme 3); these free primary hydroxy groups can be derivatized or modified. These compounds were converted into the corresponding azides **23**, **24**, and **25** by transformation to the intermediate mesylates and subsequent treatment with sodium azide. Furthermore, compounds **20**, **21**, and **22** were converted into the corresponding carboxylic acids **26**−**28** to allow easy derivatization of the "anomeric" appendage. We coupled compounds **26** and **27** with different amino acids under typical peptide coupling conditions (HBTU, HOBT, DIPEA, DMF) to obtain the iminoglycosyl amino acids **29**−**33** (50−78% yield), which, to the best of our knowledge, are among only a few examples[13,14] of imino sugars linked to amino acids.



Scheme 3. Reagents and conditions: i) TBAF, THF; ii) MsCl, Py, CH_2Cl_2; iii) NaN_3, DMF; iv) LiOH, MeOH/H_2O/THF; v) HBTU, HOBT, DIPEA, DMF, Xaa

Deprotection

Compound **22** was debenzylated by performing catalytic hydrogenation with $Pd(OH)_2$/C in acidic methanol, affording the deprotected imino sugar **35** (Scheme 4). Not surprisingly, compound **35**, in D_2O, spontaneously began to convert into its corresponding lactone **41** in the NMR tube, as evidenced by the ^1H NMR spectroscopic signals of the lactone, the most significant of which are those of the C(3)-H unit, shifted downfield from $\delta = 3.62$ to 4.33 ppm, and the C(2)-H proton, which shifts from $\delta = 3.75$ to 4.05 ppm, with respect to **35**. Compound **41** can be used for selective derivatization or modification of the hydroxy group at C(2); e.g., the formation of mimics of *N*-acetylglucosamine. Debenzylation of compound **20** afforded a mixture of the desired *N*-propyl derivative **34** and the deallylated compound **38**; this problem, which is due to partial deallylation caused by the palladium catalyst, was overcome by hydrogenation of **20** using Raney nickel as catalyst, which afforded pure compound **34**. Compounds **38** and **39** were obtained from **20** and **21** by deallylation with $[Pd(PPh_3)_4]$ and dimethylbarbituric acid (DMBA) and subsequent debenzylation $[Pd(OH)_2/C, H_2, MeOH, AcOH)]$. Compound **18b** was desilylated (TBAF, THF) at the primary hydroxy group and debenzylated to afford the carboxylic acid **40**.



Scheme 4. Reagents and conditions: i) $Pd(PPh_3)_4$, DMBA; ii) H_2, $Pd(OH)_2$/C, AcOH, MeOH; iii) Raney Ni, MeOH, H_2; iv) TBAF, THF

Conclusion

A ductile strategy for the synthesis of imino sugar libraries is described. The stereochemical outcome of the Michael addition and of the cyclization by reductive amination generates two points of diversity that determine the absolute configurations at the C(2) and C(6) centers (α or β; D or L) of the final imino sugars. Although the stereochemical outcome of the cyclization depends on the stereochemistry obtained in the Michael addition, we observed, in the case of the Michael adduct having a (*S*) configuration, that the result can be reversed by changing the substituent at the nitrogen atom from butyl or allyl to benzyl.

The imino sugars obtained according to this strategy present different sites for ready derivatization. In particular, the carboxylic function at the "anomeric" substituent allows further elongation; for instance, we functionalized it by coupling with amino acids. The selectively deprotected primary hydroxy group, which allows elongation at the "non-reducing" end of the sugar mimic, was converted into azide functions, i.e., masked precursors of the amino groups. Furthermore, with proper choice of the primary amine employed in the Michael reaction, the amino group of the ring nitrogen atom also can be varied or deprotected to allow further derivatization.

Experimental Section

General Remarks: All solvents were dried with molecular sieves, for at least 24 h prior to use. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Merck) with detection using UV light when possible, or by charring with a solution of concd. H_2SO_4/EtOH/H_2O (5:45:45) or a solution of $(NH_4)_6Mo_7O_{24}$ (21 g), $Ce(SO_4)_2$ (1 g), concd. H_2SO_4 (31 mL) in water (500 mL). Flash column chromatography was performed on silica gel 230−400 mesh (Merck). ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Varian Mercury 400 MHz instrument using $CDCl_3$ as the solvent unless otherwise stated. Chemical shift assignments, reported in ppm, are referenced to the corresponding solvent peaks. Mass spectra were recorded with a MALDI2 Kompakt Kratos instrument, using gentisic acid (DHB) as the matrix. Optical rotations were measured at room temperature using a Krüss P3002 electronic polarimeter and are reported in units of 10^{-1} deg·cm^2·g^{-1}. Elemental analyses were performed using a Perkin−Elmer Series II Analyzer 2400.

Ethyl (2*E*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-7,8-bis(isopropylidenoxy)-2-octenoate (6): Aldehyde **5** (1.574 g, 3.74 mmol) was dissolved in toluene (20 mL) and [(ethoxycarbonyl)methylene]triphenylphosphorane (2.18 g, 5.61 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at 80 °C for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to provide compound **6** (1.50 g, 86%, *de* 100%) as a colorless oil. $[\alpha]_D^{20} = +4.7$ (c = 0.4, $CHCl_3$). ^1H NMR: δ = 1.29 [s, 3 H, (CH_3)$_2$C], 1.31 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$CH_3), 1.40 [s, 3 H, (CH_3)$_2$C], 3.64 [dd, $^3J_{H,H}$ = 6.2, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(5)-H], 3.84 [br. t, $^3J_{H,H}$ = 3.9 Hz, 1 H, C(6)-H], 3.92 [dd, $^2J_{H,H}$ = 8.1, $^3J_{H,H}$ = 6.7 Hz, 1 H, C(8a)-H], 4.00 [br. t, 1 H, C(8b)-H], 4.12−4.20 [m, 3 H, C(7)-H, OCH_2CH$_3$], 4.27 [t, $^3J_{H,H}$ = 6.2 Hz, 1 H, C(4)-H], 4.41 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.76 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 6.04 [d, $^3J_{H,H}$ = 15.8 Hz, 1 H, C(2)-H], 6.93 [dd, $^3J_{H,H}$ = 15.8, $^3J_{H,H}$ = 5.9 Hz, 1 H, C(3)-H], 7.29−7.37 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.71 (OCH$_2$*C*H$_3$), 25.31 [(*C*H$_3$)$_2$C], 26.93 [(*C*H$_3$)$_2$C], 60.88, 66.12 [C(8), O*C*H$_2$CH$_3$], 72.20, 74.43, 75.19 (3 *C*H$_2$Ph), 77.28, 78.78, 79.31, 81.66 [C(4), C(5), C(6), C(7)], 108.4 [(CH$_3$)$_2$*C*], 123.4 [C(2)], 127.8−128.6 (*C*HAr), 137.8, 138.1, 138.4 (3 *C*qAr), 144.7 [C(3)], 166.0 [C(1)] ppm. MS (MALDI-TOF): m/z = 584 [M + Na]$^+$, 600 [M + K]$^+$. $C_{34}H_{40}O_7$ (560.7): calcd. C 72.83, H 7.19; found C 72.53, H 7.17.

Benzyl (2*E*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-7,8-bis(isopropylidenoxy)-2-octenoate (7): Aldehyde **5** (385 mg, 0.78 mmol) was dissolved in toluene (2 mL) and [(benzyloxycarbonyl)methylene]triphenylphosphorane (480 mg, 1.5 equiv.) dissolved in toluene (2 mL) was added. The reaction mixture was heated at 80 °C. After 7 h, the solvent was evaporated under reduced pressure and purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded compound **7** (473 mg, 98% yield) as a colorless oil. $[\alpha]_D^{20}$ = +6.3 (c = 0.9, $CHCl_3$). ^1H NMR: δ = 1.26 [s, 3 H, (CH_3)$_2$C], 1.41 [s, 3 H, (CH_3)$_2$C], 3.64 [dd, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(5)-H], 3.84 [t, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(6)-H], 3.93 [dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(8a)-H], 4.00 [br. t, 1 H, C(8b)-H], 4.17 [dt, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(7)-H], 4.28 [dt, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(4)-H], 4.42 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.59 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.65 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.76 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 5.15 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 5.19 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 6.09 [dd, $^3J_{H,H}$ = 16.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(2)-H], 7.00 [dd, $^3J_{H,H}$ = 16.2, $^3J_{H,H}$ = 6.4 Hz, 1 H, C(3)-H], 7.22−7.38 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 25.32 [(*C*H$_3$)$_2$C], 26.94 [(*C*H$_3$)$_2$C], 66.16, 66.71, 72.30, 74.43, 75.20 [C(8), 4 *C*H$_2$Ph], 77.38, 78.78, 79.30, 81.65 [C(4), C(5), C(6), C(7)], 108.5 [(CH$_3$)$_2$*C*], 122.9 [C(2)], 128.0−128.8 (*C*HAr), 136.0, 137.8, 138.0, 138.4 (4 *C*qAr), 145.5 [C(3)], 165.8 [C(1)] ppm. MS (MALDI-TOF): m/z = 645 [M + Na]$^+$, 661 [M + K]$^+$. $C_{39}H_{40}O_7$ (620.7): calcd. C 75.22, H 6.80; found C 75.15, H 6.62.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)octanoate (8a) and Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)-octanoate (9a): Compound **6** (725 mg, 1.29 mmol) was dissolved in allylamine (1.94 mL, 25.86 mmol, 12 equiv.) and the reaction mixture was stirred at room temperature for 5 d. The excess allylamine was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to yield **8a** and **9a** (652 mg, 82%, **8a**/**9a**, 63:37) as colorless oils. **8a:** $[\alpha]_D^{20}$ = −3.5 (c = 0.8, $CHCl_3$). ^1H NMR: δ = 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$CH_3), 1.30 [s, 3 H, (CH_3)$_2$C], 1.42 [s, 3 H, (CH_3)$_2$C], 2.46−2.57 [m, 2 H, C(2a)-H, C(2b)-H], 2.95 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CH=CH$_2$), 3.02 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CH=CH$_2$), 3.15 [m, 1 H, C(3)-H], 3.69 [dd, $^3J_{H,H}$ = 7.3, $^3J_{H,H}$ = 3.5 Hz, 1 H, C(5)-H], 3.84 [br. t, $^3J_{H,H}$ = 3.7 Hz, 1 H, C(6)-H], 3.92 [dd, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 3.1 Hz, 1 H, C(4)-H], 3.95 [dd, $^2J_{H,H}$ = 8.2, $^3J_{H,H}$ = 6.6 Hz, 1 H, C(8a)-H], 4.04 [m, 1 H, C(8b)-H], 4.08 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.21 [ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 4.3 Hz, 1 H, C(7)-H], 4.61 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.80 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.82 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.86 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.97 [dd, $^3J_{H,H}$ = 10.3, $^4J_{H,H}$ =

1.4 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.01 (dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.70 [ddt, $^3J_{H,H}$ = 17.0, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.9 Hz, 1 H, $CH_2CH{=}CH_2$], 7.25−7.34 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.68 (OCH_2CH_3), 25.34 [$(CH_3)_2C$], 26.97 [$(CH_3)_2C$], 36.20 ($-CH_2CH{=}CH_2$), 49.87 [C(2)], 56.20 [C(3)], 60.72, 66.35 [C(8), CH_2CH_3], 74.49, 74.91, 75.32 (3 CH_2Ph), 77.32, 79.38, 79.46, 81.28 [C(4), C(5), C(6), C(7)], 108.5 [$(CH_3)_2C$], 115.7 ($CH_2CH{=}CH_2$), 127.8−128.6 (*C*HAr), 137.2 ($CH_2CH{=}CH_2$), 138.4, 138.5, 138.7 (3 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 619 $[M + H]^+$, 641 $[M + Na]^+$, 657 $[M + K]^+$. $C_{37}H_{47}NO_7$ (617.8): calcd. C 71.94, H 7.67, N 2.27; found C 71.72, H 7.65, N 2.26. **9a:** $[\alpha]_D^{20}$ = +5.7 (*c* = 1.8, $CHCl_3$). ^{1}H NMR: δ = 1.08 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3); 1.21 [s, 3 H, $(CH_3)_2C$], 1.35 [s, 3 H, $(CH_3)_2C$], 2.37 [dd, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 6.9 Hz, 1 H, C(2a)-H], 2.49 [dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 5.2 Hz, 1 H, C(2b)-H], 3.00−3.05 [m, 2 H, C(3)-H, $CHCH{=}CH_2$], 3.28 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.8 Hz, 1 H, $CHCH{=}CH_2$), 3.72−3.77 [m, 2 H, C(4)-H, C(6)-H], 3.82−3.84 [m, $^3J_{H,H}$ = 5.1, 1 H, C(8a)-H], 3.88 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 3.96 [dd, $^2J_{H,H}$ = 8.2, $^3J_{H,H}$ = 7.0 Hz, 1 H, C(8b)-H], 4.07 [dd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 2.2 Hz, 1 H, C(5)-H], 4.16 (br. t, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 4.3 Hz, 1 H, C(7)-H]], 4.47 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.57 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.74 (d, $^2J_{H,H}$ = 11.3 Hz, 2 H, 2 C*H*Ph), 4.78 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 5.00 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.7 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.10 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.7 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.72−5.82 (m, 1 H, $CH_2CH{=}CH_2$), 7.12−7.28 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.62 (OCH_2CH_3), 25.29 [$(CH_3)_2C$], 27.00 [$(CH_3)_2C$], 30.14 ($-CH_2CH{=}CH_2$), 49.99 [C(2)], 55.21 [C(3)], 60.77, 66.45 [C(8), OCH_2CH_3], 74.29, 75.16, 75.24 (3 CH_2Ph), 77.51, 77.51, 78.91, 80.77 [C(4), C(5), C(6), C(7)], 108.3 [$(CH_3)_2C$], 116.7 ($CH_2CH{=}CH_2$), 127.7−129.1 (*C*HAr), 137.2 ($CH_2CH{=}CH_2$), 138.5, 138.6, 138.8 (3 *C*qAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 619 $[M + H]^+$, 641 $[M + Na]^+$, 657 $[M + K]^+$. $C_{37}H_{47}NO_7$ (617.8): calcd. C 71.94, H 7.67, N 2.27; found C 71.75, H 7.64, N 2.28.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Benzylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)-octanoate (8b) and Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Benzylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)-octanoate (9b): Under an inert gas, compound **6** (779 mg, 1.39 mmol) was dissolved in benzylamine (500 μL, 3.6 equiv.) and the reaction mixture was stirred for 7 d. Excess benzylamine was evaporated under reduced pressure and then purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded pure compound **8b** (303 mg, 33% yield) as a yellow oil and a mixture of **9b** and **6**, which was separated by flash chromatography (toluene/ethyl acetate, 9:1) to afford **9b** (177 mg, 19% yield) as a yellow oil and unchanged **6** (222 mg). **8b:** $[\alpha]_D^{20}$ = −15.0 (*c* = 1.6, $CHCl_3$). ^{1}H NMR: δ = 1.11 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 1.15 [s, 3 H, $(CH_3)_2C$], 1.20 [s, 3 H, $(CH_3)_2C$], 2.52−2.59 [m, 2 H, C(2a)-H, C(2b)-H], 3.19−3.22 [m, 1 H, C(3)-H], 3.42 (d, $^3J_{H,H}$ = 12.8 Hz, 1 H, C*H*Ph), 3.49 (d, $^3J_{H,H}$ = 12.8 Hz, 1 H, C*H*Ph), 3.60 [dd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(5)-H], 3.74 [br. t, 1 H, C(6)-H], 3.84 [dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(8a)-H], 3.90−3.94 [m, 1 H, C(4)-H], 3.92 [dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(8b)-H], 3.94−4.40 (m, 2 H, OCH_2CH_3), 4.13 [dt, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(7)-H], 4.49 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.51 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.72 (br. d, 2 H, 2 C*H*Ph), 7.00−7.24 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.72 (OCH_2CH_3), 25.40 [$(CH_3)_2C$], 27.00 [$(CH_3)_2C$], 36.30 [C(2)], 56.78 [C(3)], 51.45, 60.75, 66.41, 74.55, 74.90, 75.34 [C(8), 4 CH_2Ph, OCH_2CH_3], 77.33, 79.46, 79.51, 81.34 [C(4), C(5), C(6), C(7)], 108.5 [$(CH_3)_2C$], 127.8−128.6 (*C*HAr), 138.4, 138.6, 138.7, 140.5 (4 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 669 $[M + H]^+$, 691 $[M + Na]^+$. $C_{41}H_{49}NO_7$ (667.8): calcd. C 73.74, H 7.40, N 2.10; found C 74.00, H 7.21, N 2.03. **9b:** $[\alpha]_D^{20}$ = +0.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR: δ = 1.15 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 1.31 [s, 3 H, $(CH_3)_2C$], 1.45 [s, 3 H, $(CH_3)_2C$], 2.49 [dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 7.0 Hz, 1 H, C(2a)-H], 2.65 [dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 4.5 Hz, 1 H, C(2b)-H], 3.02−3.08 [m, 1 H, C(3)-H], 3.62−3.68 (m, 2 H, CH_2Ph), 3.80 [br. d, 1 H, C(4)-H], 3.88−4.00 [m, 5 H, C(8a)-H, C(8b)-H, C*H*Ph, OCH_2CH_3], 4.18−4.24 [m, 2 H, C(5)-H, C(7)-H], 4.50 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.57 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, C*H*Ph), 4.61−4.69 (m, 2 H, 2 C*H*Ph), 4.80−4.89 (m, 2 H, 2 C*H*Ph), 7.20−7.38 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.63 (OCH_2CH_3), 25.37 [$(CH_3)_2C$], 27.03 [$(CH_3)_2C$], 36.20 [C(2)], 55.14 [C(3)], 51.30, 60.76, 65.93, 66.71, 74.19, 75.25 [C(8), 4 CH_2Ph, OCH_2CH_3], 77.27, 78.97, 81.02, 81.89 [C(4), C(5), C(6), C(7)], 108.2 [$(CH_3)_2C$], 128.3−136.3 (*C*HAr), 138.6, 138.7, 138.9, 140.5 (4 *C*qAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 669 $[M + H]^+$, 691 $[M + Na]^+$, 707 $[M + K]^+$. $C_{41}H_{49}NO_7$ (667.8): calcd. C 73.74, H 7.40, N 2.10; found C 73.98, H 7.12, N 2.32.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-7,8-bis(isopropylidenoxy)octanoate (8c) and Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-7,8-bis(isopropylidenoxy)-octanoate (9c): Compound **6** (350 mg, 0.62 mmol) was dissolved in butylamine (913 mg, 12.48 mmol) under an inert gas and the reaction mixture was stirred at room temperature for 8 h. The excess butylamine was evaporated under reduced pressure and then the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to yield **8c** and **9c** (324 mg, 84%; **8c**/**9c** = 63:37) as colorless oils. **8c:** $[\alpha]_D^{20}$ = +3.4 (*c* = 1.7, $CHCl_3$). ^{1}H NMR: δ = 0.81 [t, $^3J_{H,H}$ = 6.9 Hz, 3 H, $(CH_2)_3CH_3$], 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.16−1.28 (m, 4 H, $CH_2CH_2CH_3$), 1.30 [s, 3 H, $(CH_3)_2C$], 1.43 [s, 3 H, $(CH_3)_2C$], 2.29−2.37 [m, 2 H, $NCH_2(CH_2)_2CH_3$], 2.48−2.53 [m, 2 H, C(2a)-H, C(2b)-H], 3.10−3.14 [m, 1 H, C(3)-H], 3.67 [dd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(5)-H], 3.87 [br. t, $^3J_{H,H}$ = 3.8 Hz, 1 H, C(6)-H], 3.92 [dd, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(4)-H], 3.95 [dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 6.6 Hz, 1 H, C(8a)-H], 4.03−4.10 [m, 3 H, OCH_2CH_3, C(8b)-H], 4.23 [dt, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 4.2 Hz, 1 H, C(7)-H], 4.61 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.78, (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.88 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph, 7.27−7.38 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.45, 14.67 [$N(CH_2)_3CH_3$, OCH_2CH_3], 20.79 ($CH_2CH_2CH_2CH_3$), 25.30 [$(CH_3)_2C$], 26.94 [$(CH_3)_2C$], 30.14 ($CH_2CH_2CH_2CH_3$), 36.44 [C(2)], 47.37 ($CH_2CH_2CH_2CH_3$), 57.11 [C(3)], 60.66, 66.27 [OCH_2CH_3, C(8)], 74.55, 74.87, 75.28 (3 CH_2Ph), 77.38, 79.38, 79.45, 81.35 [C(4), C(5), C(6), C(7)], 108.4 [$(CH_3)_2C$], 127.8−128.5 (*C*HAr), 138.4, 138.5, 138.7 (3 *C*qAr), 172.8 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 634 $[M + H]^+$. $C_{38}H_{51}NO_7$ (633.8): calcd. C 72.01, H 8.11, N 2.21; found C 72.24, H 8.38, N 2.01. **9c:** $[\alpha]_D^{20}$ = −0.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR: δ = 0.91 [t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $N(CH_2)_3CH_3$], 1.16 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.26−1.41 (m, 4 H, $CH_2CH_2CH_3$), 1.29 [s, 3 H, $(CH_3)_2C$], 1.43 [s, 3 H, $(CH_3)_2C$], 2.35−2.45 [m, 2 H, C(2a)-H, $NCH(CH_2)_2CH_3$], 2.58 [dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 5.4 Hz, 1 H, C(2b)-H], 2.68−2.74 [m, 1 H, $NCH(CH_2)_2CH_3$], 3.01−3.05 [m, 1 H, C(3)-H], 3.79 [dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 2.2 Hz, 1 H, C(4)-H], 3.84 [dd, $^3J_{H,H}$ = 3.8, $^3J_{H,H}$ = 2.9 Hz, 1 H, C(6)-H], 3.93 [dd, $^2J_{H,H}$ = 7.7, $^3J_{H,H}$ = 6.7 Hz, 1 H, C(8a)-H], 3.97 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 4.06 [br. t, 1 H, C(8b)-H], 4.14 [dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 2.6 Hz, 1 H, C(5)-H], 4.24 [dt, $^3J_{H,H}$ = 4.4,

$^3J_{H,H}$ = 4.2 Hz, 1 H, C(7)-H], 4.55 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.82, (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.83 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.85 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 7.26−7.40 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.53, 14.64 [N(CH$_2$)$_3$*C*H$_3$, OCH$_2$*C*H$_3$], 20.93 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 25.29 [(*C*H$_3$)$_2$C], 26.99 [(*C*H$_3$)$_2$C], 33.14 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 36.58 [C(2)], 47.28 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 56.17 [C(3)], 60.69, 66.42 [O*C*H$_2$CH$_3$, C(8)], 74.27, 75.16, 75.22 (3 *C*H$_2$Ph), 77.56, 78.98, 80.91, 81.77 [C(4), C(5), C(6), C(7)], 108.2 [(CH$_3$)$_2$*C*], 127.6−128.5 (*C*HAr), 138.7, 138.8, 138.9 (3 *C*qAr), 172.6 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 634 [M + H]$^+$. $C_{38}H_{51}NO_7$ (633.8): calcd. C 72.01, H 8.11, N 2.21; found C 72.36, H 8.33, N 2.12.

Benzyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)octanoate (8d) and Benzyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-bis(isopropylidenoxy)-octanoate (9d): Under an inert gas, compound **7** (353 mg, 0.566 mmol) was dissolved in allylamine (424 μL, 10 equiv.) and then the reaction mixture was stirred for 72 h. The excess allylamine was evaporated under reduced pressure and then purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded pure compounds **8d** (163 mg, 42% yield) and **9d** (110 mg, 29% yield) as yellowish oils. **8d:** $[\alpha]_D^{20}$ = −2.1 (*c* = 2.9, CHCl$_3$). ^{1}H NMR: δ = 1.10 [s, 3 H, (C*H*$_3$)$_2$C], 1.13 [s, 3 H, (C*H*$_3$)$_2$C], 2.44−2.53 [m, 2 H, C(2a)-H, C(2b)-H], 2.85 [br.dd, 1 H, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 8.0 Hz, 1 H, C*H*CH=CH$_2$], 2.91 [br. dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CH=CH$_2$], 3.05−3.11 [m, 1 H, C(3)-H,], 3.59 [dd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 3.2 Hz, 1 H, C(5)-H], 3.73 [br. t, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(6)-H], 3.82−3.87 [m, 2 H, C(8a)-H, C(4)-H], 3.92 [dd, $^2J_{H,H}$ = 8.0, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(8b)-H], 4.12 [dt, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(7)-H], 4.50 (br. d, $^2J_{H,H}$ = 11.6 Hz, 3 H, 3 C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.69 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.73 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.85 [dd, $^3J_{H,H}$ = 12.0, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 4.89 [dd, $^3J_{H,H}$ = 19.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 4.95 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 4.98 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 5.53−5.62 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.22−7.38 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 25.33 [(*C*H$_3$)$_2$C], 26.95 [(*C*H$_3$)$_2$C], 30.14 [C(2)], 49.80 (*C*H$_2$CH=CH$_2$), 56.39 [C(3)], 66.40, 66.58, 74.46, 74.94, 75.26 [C(8), 4 *C*H$_2$Ph], 77.28, 77.35, 79.36, 81.19 [C(4), (5), (6), (7)], 108.4 [(CH$_3$)$_2$*C*], 108.5 (CH$_2$CH=*C*H$_2$), 127.8−128.7 (CH$_2$*C*H=CH$_2$, *C*HAr), 136.1, 138.3, 138.5, 138.6 (4 *C*qAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 680 [M + H]$^+$, 702 [M + Na]$^+$, 718 [M + K]$^+$. $C_{42}H_{49}NO_7$ (679.9): calcd. C 74.20, H 7.26, N 2.06; found C 73.98, H 7.33, N 1.80. **9d:** $[\alpha]_D^{20}$ = +3.2 (*c* = 1.5, CHCl$_3$). ^{1}H NMR: δ = 1.30 [s, 3 H, (C*H*$_3$)$_2$C], 1.44 [s, 3 H, (C*H*$_3$)$_2$C], 2.49 [dd, $^2J_{H,H}$ = 15.6, $^3J_{H,H}$ = 7.6 Hz, 1 H, C(2a)-H], 2.61 [dd, $^2J_{H,H}$ = 15.6, $^3J_{H,H}$ = 5.2 Hz, 1 H, C(2b)-H], 3.07−3.12 [m, 2 H, C(3)-H, C*H*CH=CH$_2$], 3.35 [br. dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CH=CH$_2$], 3.81−3.85 [m, 2 H, C(5)-H, C(6)-H], 3.94 [dd, $^2J_{H,H}$ = 8.0, $^3J_{H,H}$ = 6.4 Hz, 1 H, C(8a)-H], 4.05 [dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 7.2 Hz, 1 H, C(8b)-H], 4.15 [dd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 2.4 Hz, 1 H, C(4)-H], 4.23−4.27 [m, 1 H, C(7)-H], 4.50 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.65 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.82 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.83 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.91 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 4.97 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 5.07 [dd, $^3J_{H,H}$ = 10.0, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.16 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 2.0 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.78−5.88 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.22−7.38 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 25.30 [(*C*H$_3$)$_2$C], 27.01 [(*C*H$_3$)$_2$C], 30.15 [C(2)], 50.00 (*C*H$_2$CH=CH$_2$), 55.22 [C(3)], 66.45, 66.60, 74.27, 75.19, 77.36 [C(8), 4 *C*H$_2$Ph], 77.53, 78.88, 80.79, 81.98 [C(4), C(5), C(6), C(7)], 108.3 [(CH$_3$)$_2$*C*], 116.1 (CH$_2$CH=*C*H$_2$), 127.6−128.8 (CH$_2$*C*H=CH$_2$, *C*HAr), 135.9−138.6 (*C*qAr), 172.2 [C(1)] ppm.. MS (MALDI-TOF): *m*/*z* = 680 [M + H]$^+$, 702 [M + Na]$^+$, 718 [M + K]$^+$. $C_{42}H_{49}NO_7$ (679.9): calcd. C 74.20, H 7.26, N 2.06; found C 74.10, H 7.51, N 1.90.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (10a): Compound **8a** (359 mg, 0.58 mmol) was dissolved in CH$_3$CN (3 mL) and H$_2$O (100 μL) was added. The reaction solution was acidified using PTSA and then stirred at 60 °C for 20 min. The mixture was neutralized using NaHCO$_3$ (saturated solution), the two layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 5 mL); the combined organic layers were dried with Na$_2$SO$_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:5) yielding **10a** (267 mg, 80%) as a colorless oil. $[\alpha]_D^{20}$ = −7.1 (*c* = 0.7, CHCl$_3$). ^{1}H NMR: δ = 1.21 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.50−2.53 [m, 2 H, C(2a)-H, C(2b)-H], 3.05 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 6.0 Hz, 1 H, C*H*CH=CH$_2$), 3.14 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.8 Hz, 1 H, C*H*CH=CH$_2$), 3.32 [dd, $^3J_{H,H}$ = 10.9, $^3J_{H,H}$ = 6.5 Hz, 1 H, C(3)-H], 3.66 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(8a)-H], 3.70 [dd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(6)-H], 3.74 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 3.4 Hz, 1 H, C(8b)-H], 3.84 [t, $^3J_{H,H}$ = 4.1 Hz, 1 H, C(5)-H], 3.88 [br. dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 4.2 Hz, 1 H, C(7)-H], 3.92 [br. t, $^3J_{H,H}$ = 4.8 Hz, 1 H, C(4)-H], 4.06 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.58 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.61 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.76 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 5.01 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.07 [dd, $^3J_{H,H}$ = 17.1, $^4J_{H,H}$ = 1.7 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.76 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.9 Hz, 1 H, CH$_2$C*H*=CH$_2$), 7.25−7.36 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.64 (OCH$_2$*C*H$_3$), 36.20 [C(2)], 50.24 (−*C*H$_2$CH=CH$_2$), 56.12 [C(3)], 60.79, 63.92 [C(8), O*C*H$_2$CH$_3$], 71.95, 77.01, 78.98, 79.71 [C(4), C(5), C(6), C(7)], 73.58, 74.42, 74.44 (3 *C*H$_2$Ph), 116.1 (CH$_2$CH=*C*H$_2$), 128.0−128.8 (*C*HAr), 137.0 (CH$_2$*C*H=CH$_2$), 137.8, 137.9, 138.2 (3 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 579 [M + H]$^+$, 601 [M + Na]$^+$, 617 [M + K]$^+$. $C_{34}H_{43}NO_7$ (577.7): calcd. C 70.69, H 7.50, N 2.42; found C 70.44, H 7.47, N 2.43.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Benzylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (10b): Compound **8b** (108 mg, 0.16 mmol) was dissolved in CH$_3$CN (2 mL); H$_2$O (300 μL) and PTSA (95 mg, 0.3 equiv.) were added. The reaction mixture was heated to 70 °C for 3 h. After cooling to room temp., the reaction mixture was diluted with EtOAc, washed with a saturated solution of NaHCO$_3$, dried with Na$_2$SO$_4$, and filtered; the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 1:1) afforded pure compound **10b** (98 mg, 97% yield) as a colorless oil. $[\alpha]_D^{20}$ = −7.8 (*c* = 1.8, CHCl$_3$). ^{1}H NMR: δ = 1.17 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.48−2.50 [m, 2 H, C(2a)-H, C(2b)-H], 3.30−3.36 [m, 1 H, C(3)-H], 3.50−3.65 [m, 5 H, C(7)-H, C(8a)-H, C(8b)-H, 2 C*H*Ph], 3.70−3.75 [m, 2 H, C(5)-H, C(6)-H], 3.86−3.88 [m, 1 H, C(4)-H], 3.93−4.03 (m, 2 H, OC*H*$_2$CH$_3$), 4.47 (s, 2 H, C*H*$_2$Ph), 4.49 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 7.00−7.24 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.68 (OCH$_2$*C*H$_3$), 36.25 [C(2)], 56.47 [C(3)], 51.79, 60.83, 63.92, 73.94, 74.39, 74.41 [C(8), 4 *C*H$_2$Ph, O*C*H$_2$CH$_3$], 71.99, 77.09, 79.07, 79.73 [C(4), C(5), C(6), C(7)], 128.0−128.7 (*C*HAr), 137.8, 137.9, 138.3, 140.4 (4

*C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 628 [M + H]$^+$, 650 [M + Na]$^+$, 666 [M + K]$^+$. $C_{38}H_{45}NO_7$ (627.8): calcd. C 72.70, H 7.23, N 2.23; found C 72.35, H 7.15, N 2.01.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-7,8-dihydroxyoctanoate (10c): The same procedure was used as that for the synthesis of **10a**, starting from **8c** (1.98 g, 3.20 mmol). Purification by flash chromatography (petroleum ether/EtOAc, 1:1) afforded **10c** (1.34 g, 72%) as colorless oil. $[\alpha]_D^{20}$ = −5.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR: δ = 0.85 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, N(CH$_2$)$_3$C*H*$_3$], 1.27 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.25−1.38 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 2.36−2.42 [m, 1 H, C*H*(CH$_2$)$_2$CH$_3$], 2.47−2.58 [m, 3 H, C(2a)-H, C(2b)-H, C*H*(CH$_2$)$_2$CH$_3$], 3.30 [dd, $^3J_{H,H}$ = 10.9, $^3J_{H,H}$ = 5.9 Hz, 1 H, C(3)-H], 3.68 [dd, $^2J_{H,H}$ = 11.5, $^3J_{H,H}$ = 4.5 Hz, 1 H, C(8a)-H], 3.72 [dd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 4.5 Hz, 1 H, C(6)-H], 3.75 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 3.5 Hz, 1 H, C(8b)-H], 3.85 [br. t, $^3J_{H,H}$ = 4.2 Hz, 1 H, C(5)-H], 3.90 [dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 4.2 Hz, 1 H, C(7)-H], 3.92 [br. t, $^3J_{H,H}$ = 5.0 Hz, 1 H, C(4)-H], 4.06 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.60 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.71 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.76 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 7.30−7.35 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.47, 14.65 [*C*H$_2$(CH$_2$)$_2$CH$_3$, OCH$_2$*C*H$_3$], 20.84 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 32.82 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 36.84 [C(2)], 47.66 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 57.25 [C(3)], 60.75, 64.00 [O*C*H$_2$CH$_3$, C(8)], 73.91, 74.42, 74.45 (3 *C*H$_2$Ph), 71.93, 77.34, 79.00, 79.84 [C(4), C(5), C(6), C(7)], 127.9−128.7 (*C*HAr), 137.8, 137.9, 138.3 (3 *C*qAr), 172.8 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 595 [M + H]$^+$. $C_{35}H_{47}NO_7$ (593.8): calcd. C 70.80, H 7.98, N 2.36; found C 70.94, H 7.95, N 2.35.

Benzyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (10d): Compound **8d** (158 mg, 0.23 mmol) was dissolved in CH_3CN (2 mL); H_2O (300 μL) and CSA (5 mg, 0.1 equiv.) were added. The reaction mixture was heated to 70 °C for 6 h. After cooling to room temp., the reaction mixture was diluted with EtOAc, washed with a saturated solution of $NaHCO_3$, dried with Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 4:6) afforded pure compound **10d** (130 mg, 88% yield) as a colorless oil. $[\alpha]_D^{20}$ = −9.1 (*c* = 1.8, $CHCl_3$). ^{1}H NMR: δ = 2.43−2.50 [m, 2 H, C(2a)-H, C(2b)-H], 2.94 [dd, 1 H, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CH=CH$_2$], 3.04 [dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 6.0 Hz, 1 H, C*H*CH=CH$_2$], 3.23−3.27 [m, 1 H, C(3)-H], 3.55 [dd, $^2J_{H,H}$ = 11.3, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(8a)-H], 3.59 [dd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(6)-H], 3.63 [dd, $^2J_{H,H}$ = 8.0, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(8b)-H], 3.72 [dd, $^3J_{H,H}$ = 5.2, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(5)-H], 3.74−3.78 [m, 1 H, C(7)-H,], 3.81−3.84 [m, 1 H, C(4)-H], 4.45 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.48 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.50 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.54 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.91 [d, $^3J_{H,H}$ = 10.2 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 4.94 (s, 2 H, C*H*$_2$Ph), 4.89 [d, $^3J_{H,H}$ = 16.0 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.63 [ddt, $^3J_{H,H}$ = 16.0, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 5.6 Hz, 1 H, CH$_2$C*H*=CH$_2$], 7.22−7.38 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 36.13 [C(2)], 50.18 (*C*H$_2$CH=CH$_2$), 56.25 [C(3)], 63.93, 66.62, 73.89, 74.38, 74.52 [C(8), 4 *C*H$_2$Ph], 71.92, 76.89, 78.97, 79.71 [C(4), C(5), C(6), C(7)], 116.2 (CH$_2$CH=*C*H$_2$), 128.0−128.7 (CH$_2$*C*H=CH$_2$, *C*HAr), 136.0, 137.6, 137.7, 138.2 (4 *C*qAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 640 [M + H]$^+$, 662 [M + Na]$^+$. $C_{39}H_{45}NO_7$ (639.8): calcd. C 73.22, H 7.09, N 2.19; found C 73.58, H 7.39, N 1.90.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (11a): The same procedure was used as that for the synthesis of **10a**, starting from **9a** (213 mg, 0.34 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 5:5) afforded **11a** (170 mg, 85%) as a colorless oil. $[\alpha]_D^{20}$ = +3.2 (*c* = 0.9, $CHCl_3$). ^{1}H NMR: δ = 1.21 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.51 [dd, $^2J_{H,H}$ = 15.3, $^3J_{H,H}$ = 6.1 Hz, 1 H, C(2a)-H], 2.59 [dd, $^2J_{H,H}$ = 15.4, $^3J_{H,H}$ = 6.9 Hz, 1 H, C(2b)-H], 3.09 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.7 Hz, 1 H, C*H*CH=CH$_2$), 3.26−3.33 [m, 2 H, C(3)-H, C*H*CH=CH$_2$], 3.65−3.69 [m, 2 H, C(8a)-H, C(5)-H], 3.75 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 3.7 Hz, 1 H, C(8b)-H], 3.88 [dd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 2.7 Hz, 1 H, C(6)-H], 3.92 [dd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 3.8 Hz, 1 H, C(4)-H], 4.05 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.27 [dd, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 3.2 Hz, 1 H, C(7)-H], 4.56 (d, $^2J_{H,H}$ = 11.8 Hz, 1 H, C*H*Ph), 4.59 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.71 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.83 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 5.07 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.16 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.7 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.83 (ddt, $^3J_{H,H}$ = 17.0, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.9 Hz, 1 H, CH$_2$C*H*=CH$_2$), 7.26−7.34 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.68 (OCH$_2$*C*H$_3$), 36.01 [C(2)], 49.96 (−*C*H$_2$CH=CH$_2$), 54.62 [C(3)], 60.87, 64.27 [O*C*H$_2$CH$_3$, C(8)], 73.44, 74.30, 74.91 (3 *C*H$_2$Ph), 72.11, 76.83, 78.59, 80.27 [C(4), C(5), C(6), C(7)], 116.3 (CH$_2$CH=*C*H$_2$), 127.9−128.7 (*C*HAr), 136.8 (CH$_2$*C*H=CH$_2$), 138.0, 138.0, 138.5 (3 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 579 [M + H]$^+$, 601 [M + Na]$^+$, 617 [M + K]$^+$. $C_{34}H_{43}NO_7$ (577.7): calcd. C 70.69, H 7.50, N 2.42, O 19.39; found C 70.83, H 7.48, N 2.38.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Benzylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (11b): Same procedure as that used for **10b**, starting from **9b** (81 mg, 0.12 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 1:1) afforded pure compound **11b** (60 mg, 79% yield) as a yellow oil. **11b** $[\alpha]_D^{20}$ = +3.0 (*c* = 1.6, $CHCl_3$). ^{1}H NMR: δ = 1.19 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.57 [dd, $^2J_{H,H}$ = 15.3, $^3J_{H,H}$ = 6.5 Hz, 1 H, C(2a)-H], 2.63 [dd, $^2J_{H,H}$ = 15.36, $^3J_{H,H}$ = 6.7 Hz, 1 H, C(2b)-H], 3.26−3.29 [m, 1 H, C(3)-H], 3.56 [dd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 3.37 Hz, 1 H, C(6)-H], 3.62 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 4.7 Hz, 1 H, C(8a)-H], 3.64 (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, C*H*Ph), 3.70 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(8b)-H], 3.83−3.92 [m, 3 H, C(4)-H, C(7)-H, C*H*Ph], 4.00−4.05 (m, 2 H, OC*H*$_2$CH$_3$), 4.29 [dd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 3.3 Hz, 1 H, C(5)-H], 4.48 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.54 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.74 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 7.20−7.40 (m, 20 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.64 (OCH$_2$*C*H$_3$), 30.14 [C(2)], 54.83 [C(3)], 51.36, 60.88, 64.21, 73.42, 74.18, 74.81 [C(8), 4 *C*H$_2$Ph, O*C*H$_2$CH$_3$], 71.91, 76.82, 78.15, 80.00 [C(4), C(5), C(6), C(7)], 127.3−128.7 (*C*HAr), 137.8, 137.9, 137.9, 138.3 (4 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 628 [M + H]$^+$, 650 [M + Na]$^+$, 666 [M + K]$^+$. $C_{38}H_{45}NO_7$ (627.8): calcd. C 72.70, H 7.23, N 2.23; found C 72.95, H 7.24, N 2.42.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-7,8-dihydroxyoctanoate (11c): The same procedure was used as that for the synthesis of **10a**, starting from **9c** (1.419 g, 2.29 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 5:5) afforded **11c** (1.147 g, 86%) as a colorless oil. $[\alpha]_D^{20}$ = +5.4 (*c* = 0.2, $CHCl_3$). ^{1}H NMR: δ = 0.90 [t, $^3J_{H,H}$ = 7.3 Hz, 3 H, N(CH$_2$)$_3$C*H*$_3$], 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.26−1.44 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 2.36−2.43 [m, 1 H, NC*H*(CH$_2$)$_2$CH$_3$], 2.54−2.58 [m, 2 H, C(2a)-H, C(2b)-H], 2.60−2.69 [m, 1 H,

NC*H*$(CH_2)_2CH_3$], 3.26 [dt, $^3J_{H,H}$ = 6.2, $^3J_{H,H}$ = 2.5 Hz, 1 H, C(3)-H], 3.68 [dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 3.8 Hz, C(5)-H], 3.69 [dd, $^2J_{H,H}$ = 10.5, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(8a)-H], 3.77 (dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 2.7 Hz, 1 H, C(8b)-H], 3.88 [dd, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 2.2 Hz, 1 H, C(6)-H], 3.93 [dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 3.8 Hz, 1 H, C(4)-H], 4.06 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, O$CH_2$$CH_3$), 4.27 [dd, $^3J_{H,H}$ = 6.00, 2.8 Hz, 1 H, C(7)-H], 4.59 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.61 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.77 (s, 2 H, 2 C*H*Ph), 4.84 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 7.29−7.35 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR (100.57 MHz, $CDCl_3$, 25 °C): δ = 14.53, 14.68 [N$(CH_2)_3$*C*H_3, OCH_2*C*H_3), 20.94 (CH_2CH_2*C*H_2CH_3), 32.96 (CH_2*C*$H_2CH_2CH_3$), 47.27 [C(2)], 55.57 [C(3)], 60.83, 64.38 [O*C*H_2CH_3, C(8)], 73.43, 74.27, 74.84 (3 *C*H_2Ph), 72.16, 76.94, 78.67, 80.38 [C(4), C(5), C(6), C(7)], 127.9−128.8 (*C*HAr), 138.0, 138.5, 138.5 (3 *C*qAr), 172.8 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 595 $[M + H]^+$. $C_{35}H_{47}NO_7$ (593.8): calcd. C 70.80, H 7.98, N 2.36; found C 70.90, H 8.00, N 2.36.

Benzyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-7,8-dihydroxyoctanoate (11d): Same procedure as that used for **10d**, starting from **9d** (110 mg, 0.16 mmol); purification by flash chromatography (petroleum ether/ethyl acetate, 1:1 to 4:6) afforded pure compound **11d** (83 mg, 81% yield) as a yellowish oil. $[\alpha]_D^{20}$ = +5.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.54 [dd, $^2J_{H,H}$ = 15.4, $^3J_{H,H}$ = 6.0 Hz, 1 H, C(2a)-H], 2.64 [dd, $^2J_{H,H}$ = 15.6, $^3J_{H,H}$ = 6.7 Hz, 1 H, C(2b)-H], 3.06 [br. dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 5.8 Hz, 1 H, C*H*CH=CH_2], 3.25−3.32 [m, 1 H, C(3)-H], 3.63−3.67 [m, 2 H, C(6)-H, C(8a)-H], 3.73 [dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 3.7 Hz, 1 H, C(8b)-H], 3.86−3.91 [m, 2 H, C(4)-H, C(7)-H], 4.23 [dd, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 3.5 Hz, 1 H, C(5)-H], 4.54 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.67 (s, 2 H, CH_2Ph), 4.78 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 5.00 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 5.03 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 5.05 [dd, $^3J_{H,H}$ = 10.2, $^2J_{H,H}$ = 1.3 Hz, 1 H, CH_2CH=CH_2(*cis*)], 5.11 [d, $^3J_{H,H}$ = 17.2 Hz, 1 H, CH_2CH=CH_2(*trans*)], 5.75−5.82 [m, 1 H, CH_2C*H*=CH_2], 7.20−7.40 (m, 20 H, *H*Ar) ppm. ^{13}C NMR (100.57 MHz, $CDCl_3$, 25 °C): δ = 35.81 [C(2)], 49.91 (*C*H_2CH=CH_2), 54.80 [C(3)], 64.24, 66.73, 73.43, 74.19, 74.79 [C(8), 4 *C*H_2Ph], 72.06, 76.69, 78.36, 79.93 [C(4), C(5), C(6), C(7)], 116.3 (CH_2CH=*C*H_2), 128.0−130.0 (CH_2*C*H=CH_2, *C*HAr), 135.9, 137.8, 137.9, 138.3 (4 *C*qAr), 172.3 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 640 $[M + H]^+$. $C_{39}H_{45}NO_7$ (639.8): calcd. C 73.22, H 7.09, N 2.19; found C 72.95, H 7.12, N 2.01.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (12a): 10a (267 mg, 0.46 mmol) was dissolved in CH_2Cl_2 (3 mL) and then *tert*-butyldiphenylsilyl chloride (TBDPSCl) (191 mg, 0.69 mmol, 1.5 equiv.) and imidazole (94 mg, 1.39 mmol, 3 equiv.) were added. The reaction mixture was stirred at room temperature for 6 h before CH_3OH (500 μL) and H_2O (3 mL) were added. The two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) yielding **12a** (350 mg, 93%) as a colorless oil. $[\alpha]_D^{20}$ = −11.8 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.00 [s, 9 H, (CH_3)$_3$C], 1.11 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 2.35−2.48 [m, 2 H, C(2a)-H, C(2b)-H], 2.87−2.98 (m, 2 H, C*H*CH=CH_2), 3.13−3.17 [m, 1 H, C(3)-H], 3.69−3.86 [m, 5 H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H], 3.91 [dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 3.8 Hz, 1 H, C(4)-H], 3.96 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OC$H_2$$CH_3$), 4.42 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.47 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.55 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.74 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.86 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.6, 1 H, CH_2CH=CH_2(*cis*)], 4.92 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH_2CH=CH_2(*trans*)], 5.61 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.8 Hz, 1 H, CH_2C*H*=CH_2), 7.04−7.35 (m, 21 H, *H*Ar), 7.55−7.60 (m, 4 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.70 (OCH_2*C*H_3), 19.79 [(CH_3)$_3$*C*], 27.40 [(*C*H_3)$_3$C], 36.16 [C(2)], 49.96 (*C*H_2CH=CH_2), 55.91 [C(3)], 60.68, 65.27 [O*C*H_2CH_3, C(8)], 73.56, 75.01, 75.06 (3 *C*H_2Ph), 71.89, 77.66, 79.36, 80.39 [C(4), C(5), C(6), C(7)], 115.9 (CH_2CH=*C*H_2), 127.8−130.0 (*C*HAr), 133.3, 133.4 (2 *C*qAr), 135.9 (CH_2*C*H=CH_2), 138.2, 138.3, 138.8 (3 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 817 $[M + H]^+$, 839 $[M + Na]^+$, 855 $[M + K]^+$. $C_{50}H_{61}NO_7Si$ (816.1): calcd. C 73.59, H 7.53, N 1.72; found C 73.37, H 7.55, N 1.71.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Benzylamino)-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (12b): Compound **10b** (98 mg, 0.16 mmol) was dissolved in dry CH_2Cl_2 (2 mL) under an inert gas. Imidazole (42 mg, 4 equiv.) and TBDPSCl (80 μL, 2 equiv.) were added. After 2 h, the reaction mixture was quenched with MeOH (2 drops), diluted with H_2O, and extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4 and filtered and then the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded pure compound **12b** (130 mg, 96% yield). $[\alpha]_D^{20}$ = −17.5 (*c* = 1.3, $CHCl_3$). ^{1}H NMR: δ = 1.14 [s, 9 H, (CH_3)$_3$C], 1.23 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 2.55−2.66 [m, 2 H, C(2a)-H, C(2b)-H], 3.25−3.39 [m, 1 H, C(3)-H], 3.59 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, C*H*Ph), 3.65 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, C*H*Ph), 3.80−4.20 [m, 5 H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H], 4.00−4.15 [m, 3 H, C(4)-H, OC$H_2$$CH_3$], 4.51 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.57 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.73 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.88 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 7.20−7.80 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.71 (OCH_2*C*H_3), 19.76 [(CH_3)$_3$*C*], 27.42 [(*C*H_3)$_3$C], 36.22 [C(2)], 56.47 [C(3)], 51.54, 60.72, 65.30, 73.56, 74.98, 75.04 [C(8), 4 *C*H_2Ph, O*C*H_2CH_3], 71.95, 77.71, 79.54, 80.40 [C(4), C(5), C(6), C(7)], 126.9−135.9 (*C*HAr), 133.3, 133.4, 138.2, 138.3, 138.8, 140.6 (*C*qAr), 172.8 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 867 $[M + H]^+$, 889 $[M + Na]^+$, 905 $[M + K]^+$. $C_{54}H_{63}NO_7Si$ (866.2): calcd. C 74.88, H 7.33, N 1.62; found C 74.53, H 7.12, N 1.78.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (12c): The same procedure was used as that for the synthesis of **12a**, starting from **10b** (1.59 g, 2.74 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded **12c** (1.86 g, 83%) as a colorless oil. $[\alpha]_D^{20}$ = −10.0 (*c* = 0.7, $CHCl_3$). ^{1}H NMR: δ = 0.84 [t, $^3J_{H,H}$ = 7.0 Hz, 3 H, N$(CH_2)_3$CH_3], 1.13 [s, 9 H, (CH_3)$_3$C], 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.20−1.32 (m, 4 H, CH_2CH_2CH$_3$), 2.35−2.42 [m, 2 H, CH_2(CH_2)$_2$CH_3], 2.50 [dd, $^2J_{H,H}$ = 15.4, $^3J_{H,H}$ = 7.7 Hz, 1 H, C(2a)-H], 2.56 [dd, $^2J_{H,H}$ = 15.4, $^3J_{H,H}$ = 4.8 Hz, 1 H, C(2b)-H], 3.23 [dt, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 4.1 Hz, 1 H, C(3)-H], 3.83−4.04 [m, 6 H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H], 4.08 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OC$H_2$$CH_3$), 4.55 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.61 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.80 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.85 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 7.18−7.45 (m, 21 H, C*H*Ar), 7.68−7.72 (m, 4 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.50, 14.70 [N$(CH_2)_3$*C*H_3, OCH_2*C*H_3], 19.78

[$(CH_3)_3C$], 20.85 ($CH_2CH_2CH_2CH_3$), 27.40 [$(CH_3)_3C$], 32.95 ($CH_2CH_2CH_2CH_3$), 36.36 [C(2)], 47.47 ($CH_2CH_2CH_2CH_3$), 56.94 [C(3)], 60.61, 65.30 [OCH_2CH_3, C(8)], 72.98, 73.53, 75.03 (3 CH_2Ph), 71.90, 77.77, 79.40, 80.51 [C(4), C(5), C(6), C(7)], 127.8−130.0 (*C*HAr), 133.3, 133.4 (2 *C*qAr), 135.8, 135.9 (*C*HAr), 138.2, 138.4, 138.9 (3 *C*qAr), 172.9 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 833 $[M + H]^+$, 855 $[M + Na]^+$. $C_{51}H_{65}NO_7Si$ (832.2): calcd. C 73.61, H 7.87, N 1.68; found C 73.46, H 7.88, N 1.67.

Benzyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (12d): Compound **10d** (105 mg, 0.16 mmol) was dissolved in dry CH_2Cl_2 (2 mL) under an inert gas. Imidazole (33 mg, 3 equiv.) and TBDPSCl (45 μL, 1.5 equiv.) were added. After 2.5 h, the reaction mixture was quenched with MeOH (2 drops), diluted with H_2O, and extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4 and filtered and then the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded pure compound **12d** (137 mg, 96% yield) as a colorless oil. $[\alpha]_D^{20}$ = −8.4 (*c* = 2.1, $CHCl_3$). ^1H NMR: δ = 1.10 [s, 9 H, $(CH_3)_3C$], 2.52−2.62 [m, 2 H, C(2a)-H, C(2b)-H], 2.87−3.17 (m, 2 H, -$CH_2CH{=}CH_2$), 3.24−3.29 [m, 1 H, C(3)-H], 3.76−3.88 [m, 4 H, C(5)-H, C(6)-H, C(8a)-H, C(8b)-H], 3.93−3.97 [m, 1 H, C(7)-H], 4.01 [dd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 3.6 Hz, 1 H, C(4)-H], 4.48 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.53 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.75 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.93 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 4.97−5.03 [m, 2 H, C*H*Ph, $CH_2CH{=}CH_2$(*trans*)], 5.05 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 5.61−5.73 (m, 1 H, $CH_2CH{=}CH_2$), 7.12−7.72 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 19.76 [$(CH_3)_3C$], 27.38 [$(CH_3)_3C$], 36.03 [C(2)], 49.88 ($CH_2CH{=}CH_2$), 56.04 [C(3)], 60.79, 65.26, 66.51, 73.53, 74.95 [C(8), 4 CH_2Ph], 71.89, 75.05, 77.68, 81.35 [C(4), C(5), C(6), C(7)], 127.8−130.0 ($CH_2CH{=}CH_2$, *C*HAr), 133.2, 133.4, 136.2, 138.0, 138.0, 138.2, 138.7 (*C*qAr), 135.8−135.9 (*C*HAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 879 $[M + H]^+$. $C_{55}H_{63}NO_7Si$ (878.2): calcd. C 75.22, H 7.23, N 1.59; found C 75.02, H 7.51, N 1.80.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-8-(*tert*-butyldiphenylsilyl)oxy-7-hydroxyoctanoate (13a): Same procedure as that used for the synthesis of **12a**, starting from **11a** (164 mg, 0.284 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded **13a** (222 mg, 96%) as a colorless oil. $[\alpha]_D^{20}$ = +4.0 (*c* = 0.7, $CHCl_3$). ^1H NMR: δ = 1.15 [s, 9 H, $[(CH_3)_3C]$], 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.54 [dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 7.6, 1 H, C(2a)-H], 2.62 [dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.4 Hz, 1 H, C(2b)-H], 3.11 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.8 Hz, 1 H, C*H*CH=CH_2), 3.26−3.30 [m, 1 H, C(3)-H], 3.36 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CH=CH_2), 3.86−4.18 [m, 7 H, C(4)-H, C(5)-H, C(6)-H, C(8a)-H, C(8b)-H, OCH_2CH_3], 4.44 [dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 2.4 Hz, 1 H, C(7)-H], 4.54 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.63 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.65 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.76 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.84 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.96 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 5.08 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)] 5.20 [dd, $^3J_{H,H}$ = 17.1, $^4J_{H,H}$ = 1.7 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.87 (ddt, $^3J_{H,H}$ = 17.2, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.8 Hz, 1 H, $CH_2CH{=}CH_2$), 7.23−7.47 (m, 21 H, *H*Ar), 7.71−7.78 (m, 4 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.71 (OCH_2CH_3), 19.83 [$(CH_3)_3C$], 27.10 [$(CH_3)_3C$], 36.32 [C(2)], 50.00 (−$CH_2CH{=}CH_2$), 55.34 [C(3)], 60.80, 65.43 [OCH_2CH_3, C(8)], 73.29, 74.86, 75.32 (3 CH_2Ph), 72.12, 77.31, 79.42, 81.22 [C(4), C(5), C(6), C(7)], 116.1 ($CH_2CH{=}CH_2$), 127.7−130.0 (*C*HAr), 133.4, 133.6 (2 *C*qAr), 135.7−137.3 (*C*HAr), 138.4, 138.5, 138.9 (3 *C*qAr), 172.6 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 817 $[M + H]^+$, 839 $[M + Na]^+$, 855 $[M + K]^+$. $C_{50}H_{61}NO_7Si$ (816.1): calcd. C 73.59, H 7.53, N 1.72; found C 73.39, H 7.51, N 1.74.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*) 3-(Benzylamino)-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (13b): Same procedure as that used for the synthesis of **12b**, starting from **11b** (72 mg, 0.11 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded pure compound **13b** (83 mg, 87% yield) as a colorless oil. $[\alpha]_D^{20}$ = 0.0 (*c* = 2.3, $CHCl_3$). ^1H NMR: δ = 1.09 [s, 9 H, $(CH_3)_3C$], 1.75 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.54 [dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 7.7 Hz, 1 H, C(2a)-H], 2.65 [dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 5.2 Hz, 1 H, C(2b)-H], 3.21−3.26 [m, 1 H, C(3)-H], 3.62 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, C*H*Ph), 3.69 [dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 2.3 Hz, 1 H, C(6)-H], 3.79 [dd, $^2J_{H,H}$ = 10.4, $^3J_{H,H}$ = 5.4 Hz, 1 H, C(8a)-H], 3.85−3.92 [m, 3 H, C(4)-H, C(8b)-H, C*H*Ph], 3.96−4.04 [m, 3 H, C(7)-H, OCH_2CH_3], 4.42 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.42−4.46 [m, 1 H, C(5)-H], 4.48 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.72 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.90 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 7.15−7.80 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.65 (OCH_2CH_3), 19.77 [$(CH_3)_3C$], 27.38 [$(CH_3)_3C$], 36.32 [C(2)], 55.43 [C(3)], 60.75, 65.59, 73.27, 74.84, 75.24 [C(8), 4 CH_2Ph, OCH_2CH_3], 71.99, 77.56, 79.26, 81.24 [C(4), C(5), C(6), C(7)], 127.1−135.9 (*C*HAr), 133.4, 133.5, 138.3, 138.6, 138.9, 140.6 (*C*qAr), 172.6 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 867 $[M + H]^+$, 889 $[M + Na]^+$. $C_{54}H_{63}NO_7Si$ (866.2): calcd. C 74.88, H 7.33, N 1.62; found C 74.84, H 7.19, N 1.43.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-4,5,6-Tris(benzyloxy)-3-(butylamino)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (13c): Same procedure as that used for the synthesis of **12a**, starting from **11c** (175 mg, 0.30 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded **13c** (233 mg, 93%) as a colorless oil. $[\alpha]_D^{20}$ = +9.5 (*c* = 0.4, $CHCl_3$). ^1H NMR: δ = 0.90 [t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $N(CH_2)_3CH_3$], 1.13 [s, 9 H, $(CH_3)_3C$], 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.26−1.48 (m, 4 H, $CH_2CH_2CH_3$), 2.37 [ddd, $^2J_{H,H}$ = 10.8, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 6.1 Hz, 1 H, $NCH(CH_2)_2CH_3$], 2.52 [dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 7.4 Hz, 1 H, C(2a)-H], 2.62 [dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 5.5 Hz, 1 H, C(2b)-H], 2.69 [ddd, $^2J_{H,H}$ = 10.9, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 6.0 Hz, 1 H, $NCH(CH_2)_2CH_3$], 3.22−3.25 [m, 1 H, C(3)-H], 3.87−4.09 [m, 7 H, C(4)-H, C(5)-H, C(6)-H, C(8a)-H, C(8b)-H, OCH_2CH_3], 4.41 [dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 2.5 Hz, 1 H, C(7)-H], 4.57 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.75 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.93 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 7.23−7.45 (m, 21 H, CHAr), 7.69−7.73 (m, 4 H, CHAr) ppm. ^{13}C NMR: δ = 14.57, 14.70 [$N(CH_2)_3CH_3$, OCH_2CH_3], 19.80 [$(CH_3)_3C$], 20.97 ($CH_2CH_2CH_2CH_3$), 27.41 [$(CH_3)_3C$], 30.17 ($CH_2CH_2CH_2CH_3$), 36.35 [C(2)], 56.14 [C(3)], 60.72, 65.39 [OCH_2CH_3, C(8)], 73.24, 74.78, 75.28 (3 CH_2Ph), 72.22, 77.24, 79.48, 81.40 [C(4), C(5), C(6), C(7)], 127.7−129.9 (*C*HAr), 133.4, 133.6 (2 *C*qAr), 135.9, 135.9 (*C*HAr), 138.5, 138.6, 139.0 (3 *C*qAr), 172.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 833 $[M + H]^+$, 855 $[M + Na]^+$, 871 $[M + K]^+$. $C_{51}H_{65}NO_7Si$ (832.2): calcd. C 73.61, H 7.87, N 1.68; found C 73.51, H 7.85, N 1.68.

Benzyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-(Allylamino)-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (13d): Same procedure as that used for the synthesis of **12d**, starting from **11d**

(73 mg, 0.11 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded pure compound **13d** (78 mg, 78% yield) as a colorless oil. **13d:** $[\alpha]_D^{20}$ 0 (c = 0.4, $CHCl_3$). ^1H NMR: δ = 0.99 [s, 9 H, (CH_3)$_3$C], 2.43 [dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 7.3 Hz, 1 H, C(2a)-H], 2.50 [dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 5.6 Hz, 1 H, C(2b)-H], 2.93 [dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 5.7 Hz, 1 H, C*H*CH=CH$_2$], 3.11−3.15 [m, 1 H, C(3)-H], 3.19 [dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CH=CH$_2$], 3.70 [dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 6.5 Hz, 1 H, C(6)-H], 3.74−3.75 [m, 2 H, C(8a)-H, C(8b)-H], 3.80 [dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 2.3 Hz, 1 H, C(4)-H], 3.85−3.89 [m, 1 H, C(7)-H], 4.27 [dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 2.8 Hz, 1 H, C(5)-H], 4.40 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.43 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.48 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.59 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.67 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.77 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.84 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.89 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.91 [dd, $^3J_{H,H}$ = 10.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.02 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.64−5.73 [m, 1 H, CH$_2$C*H*=CH$_2$], 7.05−7.60 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 19.83 [(CH$_3$)$_3$*C*], 27.45 [(*C*H$_3$)$_3$C], 36.29 [C(2)], 50.01 (*C*H$_2$CH=CH$_2$), 55.35 [C(3)], 65.40, 66.64, 73.27, 74.83, 75.24 [C(8), 4 *C*H$_2$Ph], 72.11, 77.31, 79.34, 81.20 [C(4), C(5), C(6), C(7)], 116.1 (CH$_2$CH=*C*H$_2$), 127.7−128.7 (*C*HAr), 130.0 (CH$_2$*C*H=CH$_2$), 133.4, 133.6, 136.0, 138.4, 138.5, 138.9 (*C*qAr), 135.8−135.9 (*C*HAr), 172.4 [C(1)] ppm. MS (MALDI-TOF): m/z = 879 [M + H]$^+$, 901 [M + Na]$^+$. $C_{55}H_{63}NO_7Si$ (878.2): calcd. C 75.22, H 7.23, N 1.59; found C 75.39, H 7.12, N 1.80.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-{Allyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (14a): 12a (413 mg, 0.51 mmol) was dissolved in dioxane (3 mL) and then FmocCl (200 mg, 0.76 mmol, 1.5 equiv.) dissolved in dioxane (1 mL) was added. Na_2CO_3 (10% aqueous sol., 1.3 mL) was added and after 2 h the solvent was evaporated under reduced pressure. The crude product was dissolved in ethyl acetate (5 mL) and then the solution washed with H_2O (2 × 5 mL) and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 8:2) yielding **14a** (488 mg, 90%) as a colorless oil. $[\alpha]_D^{20}$ = −10.5 (c = 1.4, $CHCl_3$). ^1H NMR: δ = 1.08−1.18 [m, 12 H, (CH_3)$_3$C, OCH$_2$CH_3], 2.72−2.80 [m, 2 H, CH_2CH=CH$_2$], 2.82−3.00 [m, 2 H, C(2a)-H, C(2b)-H], 3.60−4.20, 4.38−4.78 [2m, 17 H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, 5 C*H*Ph, OCH_2CH$_3$, C*H*-Fmoc, CH_2-Fmoc), 4.79−5.00 (m, 3 H, C*H*Ph, CH$_2$CH=CH_2), 5.47−5.58 (m, 1 H, CH$_2$C*H*=CH_2), 7.05−7.38 (m, 25 H, C*H*Ar), 7.52−7.79 (m, 8 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.63 (OCH$_2$*C*H$_3$), 19.82 [(CH$_3$)$_3$*C*], 27.45 [(*C*H$_3$)$_3$C], 30.21, 34.00 [C(2), *C*H$_2$CH=CH_2], 47.76 [C(3)], 60.89, 65.47, 67.47, 74.23, 74.73, 74.74 [C(8), 3 *C*H$_2$Ph, O*C*H$_2$CH$_3$, *C*H$_2$-Fmoc], 50.75, 72.37, 74.73, 77.77, 80.05 [C(4), C(5), C(6), C(7), *C*H-Fmoc], 116.3 (CH$_2$CH=*C*H$_2$), 120.3−130.0 (*C*HAr), 133.4, 133.5 (*C*qAr), 139.9 (CH$_2$*C*H=CH$_2$), 138.3−144.4 (*C*qAr), 156.2 (*C*=O Fmoc), 171.6 [C(1)] ppm. MS (MALDI-TOF): m/z = 1061 [M + Na]$^+$, 1077 [M + K]$^+$. $C_{65}H_{71}NO_9Si$ (1038.4): calcd. C 75.19, H 6.89, N 1.35; found C 74.96, H 6.90, N 1.35.

Benzyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-{Benzyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (14b): Compound **12b** (130 mg, 0.15 mmol) was dissolved in dioxane (600 μL) then a 10% aqueous solution of Na_2CO_3 (488 μL, 2.6 equiv.) and a solution of FmocCl (47 mg, 1.2 equiv.) in dioxane (300 μL) were added. After 30 min, the reaction mixture was diluted with H_2O and extracted with EtOAc. The organic layer was dried with Na_2SO_4 and filtered and then the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded pure compound **14b** (132 mg, 81% yield) as a colorless oil. $[\alpha]_D^{20}$ = −16.0 (c = 0.9, $CHCl_3$). ^1H NMR: δ = 1.02−1.18 [m, 12 H, (CH_3)$_3$C, OCH$_2$CH_3), 2.68−2.79 [m, 1 H, C(2a)-H], 2.80−2.85 [m, 1 H, C(2b)-H], 3.65−3.80 [m, 2 H CH_2 (Fmoc)], 3.80−4.00 [m, 4 H, C(8a)-H, C(8b)-H, OCH_2CH$_3$], 4.02−4.18 [m, 2 H, C(6)-H, C(7)-H], 4.20−4.38 [C*H*(Fmoc)], 4.38−4.78 [m, 9 H, C(4)-H, C(5)-H, 7 C*H*Ph], 4.82−4.96 [m, 2 H, C(3)-H, C*H*Ph], 6.98−7.80 (m, 38 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.44 (OCH$_2$*C*H$_3$), 19.79 [(CH$_3$)$_3$*C*], 27.42 [(*C*H$_3$)$_3$C], 30.18 [C(2)], 47.59 [C(3)], 60.84, 65.44, 67.46, 67.88, 74.22, 74.67, 74.71 [C(8), 4 *C*H$_2$Ph, O*C*H$_2$CH$_3$, *C*H$_2$(Fmoc)], 72.35, 72.35, 77.88, 80.22 [C(4), C(5), C(6), C(7)], 120.1−135.9 (*C*HAr), 133.3, 133.5, 138.3, 138.4, 138.7, 141.4, 144.0, 144.1 (*C*qAr), 156.5 [C=O (Fmoc)], 171.6 [C(1)] ppm. MS (MALDI-TOF): m/z = 1111 [M + Na]$^+$, 1127 [M + K]$^+$. $C_{69}H_{73}NO_9Si$ (1088.4): calcd. C 76.14, H 6.76, N 1.29; found C 75.88, H 6.91, N 1.11.

Ethyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-{Butyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (14c): Same procedure as that used for the synthesis of **14a**, starting from **12c** (529 mg, 0.64 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded **14c** (650 mg, 97%) as a colorless oil. $[\alpha]_D^{20}$ = −6.0 (c = 1.2, $CHCl_3$). ^1H NMR: δ = 0.73 [br. t, 3 H, N(CH$_2$)$_3$CH_3], 0.79−0.95 (m, 4 H, CH_2CH_2CH$_3$), 1.13 [s, 9 H, (CH_3)$_3$C], 1.17 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$CH_3), 2.73−3.08 [m, 4 H, C(2a)-H, C(2b)-H, NCH_2(CH$_2$)$_2$CH$_3$], 3.70−4.20 [m, 11 H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, C*H*Fmoc, CH_2Fmoc, OCH_2CH$_3$], 4.44−4.70 [m, 6 H, C(3)-H, 5 C*H*Ph), 4.85 (br. d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 7.23−7.41 (m, 25 H, C*H*Ar), 7.71−7.77 (m, 8 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.61 [N(CH$_2$)$_3$*C*H$_3$, OCH$_2$*C*H$_3$), 19.79 [(CH$_3$)$_3$*C*], 23.89 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 27.41 [(*C*H$_3$)$_3$C], 27.43 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 30.06, 32.03 [C(2), *C*H$_2$CH$_2$CH$_2$CH$_3$], 47.84 [C(3)], 60.80, 65.45, 66.73, 73.00, 73.10, 74.68 [C(8), O*C*H$_2$CH$_3$, *C*H$_2$Fmoc, 3 *C*H$_2$Ph], 72.47, 72.99, 73.39, 77.71, 79.77 [C(4), C(5), C(6), C(7), *C*HFmoc], 127.2−141.6 (*C*HAr, *C*qAr), 172.1 [C(1)] ppm. MS (MALDI-TOF): m/z = 1077 [M + Na]$^+$, 1093 [M + K]$^+$. $C_{66}H_{75}NO_9Si$ (1054.4): calcd. C 75.18, H 7.17, N 1.33; found C 74.98, H 7.18, N 1.36.

Benzyl (3*S*,4*S*,5*R*,6*R*,7*R*)-3-{Allyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (14d): Compound **12d** (110 mg, 0.13 mmol) was dissolved in dioxane (700 μL) and then a 10% aqueous solution of Na_2CO_3 (407 μL, 2.6 equiv.) and a solution of FmocCl (39 mg, 1.2 equiv.) in dioxane (300 μL) were added. After 30 min, the reaction mixture was diluted with H_2O and extracted with EtOAc. The organic layer was dried with Na_2SO_4 and filtered and then the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 85:15) afforded pure compound **14d** (115 mg, 84% yield) as a colorless oil. $[\alpha]_D^{20}$ = −11.2 (c = 2.0, $CHCl_3$). ^1H NMR: δ = 1.05 [s, 9 H, (CH_3)$_3$C], 2.83−3.00 [m, 2 H, C(2a)-H, C(2b)-H], 3.60−4.21 [m, 10 H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, C*H*Ph -CH_2CH=CH$_2$], 4.35−4.88 [m, 7 H, 4 C*H*Ph, CH_2(Fmoc), C*H*(Fmoc)], 4.70−4.88 [m, 3 H, C*H*Ph, CH$_2$CH=CH_2], 4.90−5.20 [m, 2 H, 2 C*H*Ph], 7.02−7.80 (m, 38 H, *H*Ar) ppm.^{13}C NMR: δ = 19.77 [(CH$_3$)$_3$*C*], 27.40 [(*C*H$_3$)$_3$C], 34.20 [C(2)], 47.70 [C(3)], 60.81, 65.42, 66.74, 67.45, 74.17, 74.70 [C(8), 4 *C*H$_2$Ph, *C*H$_2$CH=CH$_2$], 72.34, 72.34, 80.01, 80.19 [C(4), C(5), C(6), C(7)], 116.3 (CH$_2$CH=*C*H$_2$), 125.2−130.0 (CH$_2$*C*H=CH$_2$, *C*HAr), 133.3, 133.5, 138.2, 138.3, 138.6, 141.5, 144.1, 144.3 (*C*qAr), 156.1 [C=O (Fmoc)], 171.4

[C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 1123 [M + Na]$^+$, 1139 [M + K]$^+$. $C_{70}H_{73}NO_9Si$: calcd. C 76.40, H 6.69, N 1.27; found C 76.20, H 6.77, N 1.60.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-{Allyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (15a): Same procedure as that used for the synthesis of **14a**, starting from **13a** (350 mg, 0.43 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded **15a** (400 mg, 96%) as a colorless oil. $[\alpha]_D^{20}$ = +32.8 (*c* = 0.8, $CHCl_3$). ^{1}H NMR: δ = 1.12 [s, 9 H, (C*H*$_3$)$_3$C], 1.18 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.18−2.22 [m, 1 H, C(2a)-H], 2.60−2.80 [m, 1 H, C(2b)-H], 3.73−4.48 [m, 14 H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, NC*H*$_2$CH=CH$_2$, C*H*$_2$Fmoc, C*H*Fmoc, OC*H*$_2$CH$_3$, C*H*Ph], 4.56−4.72 [m, 4 H, 3 C*H*Ph, C(3)-H], 4.76 (br. d, 1 H, C*H*Ph), 4.85 (br. d, 1 H, C*H*Ph), 4.90−5.00 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.64−5.78 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.23−7.39 (m, 25 H, C*H*Ar), 7.56−7.76 (m, 8 H, C*H*Ar). ^{13}C NMR: δ = 14.67 (OCH$_2$*C*H$_3$), 19.83 [(CH$_3$)$_3$*C*], 27.41 [(*C*H$_3$)$_3$C], 30.17, 35.71 [C(2), *C*H$_2$CH=CH$_2$], 47.67 [C(3)], 60.89,65.02, 67.93, 74.19, 74.19, 75.86 [C(8), O*C*H$_2$CH$_3$, *C*H$_2$Fmoc, 3 *C*H$_2$Ph], 71.51, 77.63, 77.63, 79.52 [C(4), C(5), C(6), C(7)], 116.7 (CH$_2$CH=*C*H$_2$), 120.2−128.0 (*C*HAr), 133.3, 133.5 (2 *C*qAr), 135.9 (CH$_2$*C*H=CH$_2$), 138.7, 141.5, 144.2 (3 *C*qAr), 157.0 (*C*=OFmoc), 170.9 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 1061 [M + Na]$^+$, 1077 [M + K]$^+$. $C_{65}H_{71}NO_9Si$: calcd. C 75.19, H 6.89, N 1.35; found C 74.98, H 6.87, N 1.36.

Benzyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-{Benzyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate Acid (15b): Same procedure as that used for the synthesis of **14b**, starting from **13b** (60 mg, 0.07 mmol). Purification by flash chromatography (toluene/ethyl acetate, 95:5) afforded pure compound **15b** (61 mg, 81% yield) as a yellowish oil. $[\alpha]_D^{20}$ = +41.8 (*c* = 0.5, $CHCl_3$). ^{1}H NMR: δ = 0.80−1.08 [m, 12 H, (C*H*$_3$)$_3$C, OCH$_2$C*H*$_3$], 2.10−2.18 [m, 1 H, C(2a)-H], 2.44−2.54 [m, 1 H, C(2b)-H], 3.62−3.95, 3.96−4.15, 4.20−4.38 [3m, 13 H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, C*H*$_2$(Fmoc), C*H*(Fmoc), C*H*Ph, OC*H*$_2$CH$_3$], 4.40−4.62 [m, 6 H, 6 C*H*Ph], 4.76−4.80 (m, 1 H, C*H*Ph), 7.05−7.75 (m, 38 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.56 (OCH$_2$*C*H$_3$), 19.71 [(CH$_3$)$_3$*C*], 27.36 [(*C*H$_3$)$_3$C], 35.85 [C(2)], 47.59 [C(3)], 60.84, 65.08, 68.00, 73.13, 73.26, 74.21, 75.13 [C(8), 4 *C*H$_2$Ph, O*C*H$_2$CH$_3$, *C*H$_2$ (Fmoc)], 71.58, 77.81, 79.23, 80.93 [C(4), C(5), C(6), C(7)], 120.2−135.9 (*C*HAr), 133.2, 133.2, 137.9, 138.1, 138.2, 138.3, 141.4, 144.1 (*C*qAr), 166.0 [C=O (Fmoc)], 170.9 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 1111 [M + Na]$^+$, 1127 [M + K]$^+$. $C_{69}H_{73}NO_9Si$ (1088.4): calcd. C 76.14, H 6.76, N 1.29; found C 76.03, H 6.55, N 1.30.

Ethyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-{Butyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (15c): Same procedure as that used for the synthesis of **14c**, starting from **13c** (158 mg, 0.19 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded **15c** (180 mg, 90%) as a colorless oil. $[\alpha]_D^{20}$ = +25.3 (*c* = 1.2, $CHCl_3$). ^{1}H NMR: δ = 0.67 [t, $^3J_{H,H}$ = 6.9 Hz, 3 H, N(CH$_2$)$_3$C*H*$_3$], 1.04−1.08 [m, 12 H, (C*H*$_3$)$_3$C, OCH$_2$C*H*$_3$], 0.77−1.17 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 2.14−2.18 [m, 1 H, C(2a)-H], 2.62−2.64 [m, 1 H, C(2b)-H], 2.85−2.87 [m, 1 H, NC*H*(CH$_2$)$_2$CH$_3$], 3.00−3.13 [m, 1 H, NC*H*(CH$_2$)$_2$CH$_3$], 3.61−4.70 [m, 18 H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, C*H*$_2$(Fmoc), C*H*(Fmoc), 6 C*H*Ph, OC*H*$_2$CH$_3$], 7.11−7.47 (m, 25 H, C*H*Ar), 7.61−7.66 (m, 8 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.69 [N(CH$_2$)$_3$*C*H$_3$, OCH$_2$*C*H$_3$), 19.87 [(CH$_3$)$_3$*C*], 20.89 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 23.41 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 27.47 [(*C*H$_3$)$_3$C], 30.20, 35.80 [C(2), *C*H$_2$CH$_2$CH$_2$CH$_3$], 47.80 [C(3)], 60.88, 67.35, 71.90, 74.03, 76.00 [C(8), O*C*H$_2$CH$_3$, 3 *C*H$_2$Ph], 73.20, 77.63, 77.63, 79.60 [C(4), C(5), C(6), C(7)], 127.2−141.6 (*C*HAr, *C*qAr), 172.1 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 1077 [M + Na]$^+$, 1093 [M + K]$^+$. $C_{66}H_{75}NO_9Si$ (1054.4): calcd. C 75.18, H 7.17, N 1.33; found C 75.21, H 7.15, N 1.32.

Benzyl (3*R*,4*S*,5*R*,6*R*,7*R*)-3-{Allyl[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}-4,5,6-tris(benzyloxy)-8-[(*tert*-butyldiphenylsilyl)oxy]-7-hydroxyoctanoate (15d): Same procedure as that used for the synthesis of **14d**, starting from **13d** (71 mg, 0.08 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 85:15) afforded pure compound **15d** (87 mg, 98% yield) as a yellowish oil. $[\alpha]_D^{20}$ = +28.9 (*c* = 1.8, $CHCl_3$). ^{1}H NMR: δ = 1.03 [s, 9 H, (C*H*$_3$)$_3$C], 2.54−2.67 [m, 2 H, C(2a)-H, C(2b)-H], 4.13 [br. t, 1 H, C(4)-H], 3.62−4.38 [m, 10 H, C(5)-H, C(6)-H, C(7)-H, C(8a)-H, C(8b)-H, C*H*$_2$CH=CH$_2$, C*H*$_2$(Fmoc), C*H*(Fmoc)], 4.21 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.47−4.53 (m, 3 H, 3 C*H*Ph), 4.53−4.61 [m, 1 H, C(3)-H], 4.65 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.73 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.81 [br. d, $^3J_{H,H}$ = 11.1 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 4.82 [br. d, $^3J_{H,H}$ = 16.3 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 4.88 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, C*H*Ph), 4.93 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, C*H*Ph), 5.51−5.61 [m, 1 H, CH$_2$C*H*=CH$_2$], 7.05−7.60 (m, 38 H, *H*Ar) ppm. ^{13}C NMR: δ = 19.81 [(CH$_3$)$_3$*C*], 27.41 [(*C*H$_3$)$_3$C], 35.52 [C(2)], 47.67 [C(3)], 61.00, 65.03, 66.71, 67.89, 74.15, 75.87 [C(8), 4 *C*H$_2$Ph, *C*H$_2$CH=CH$_2$], 71.54, 77.58, 77.73, 79.43 [C(4), C(5), C(6), C(7)], 116.6 (CH$_2$CH=*C*H$_2$), 127.7−128.7 (*C*HAr), 129.9 (CH$_2$*C*H=CH$_2$), 135.6−135.9 (*C*HAr), 133.3, 133.5, 138.6, 141.5, 141.5, 144.3 (*C*qAr), 157.3 [C=O (Fmoc)], 170.7 [C(1)] ppm. MS (MALDI-TOF): *m*/*z* = 1123 [M + Na]$^+$, 1139 [M + K]$^+$. $C_{70}H_{73}NO_9Si$ (1100.4): calcd. C 76.40, H 6.69, N 1.27; found C 76.05, H 6.73, N 1.39.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2-yl]acetate (18a): Compound **14a** (418 mg, 0.40 mmol) was dissolved in CH_2Cl_2 (4 mL) under an inert gas, and added to a flask containing PCC (345 mg, 1.60 mmol, 4 equiv.), previously dried with powdered molecular sieves (4 Å). After 12 h, the reaction mixture was filtered through silica gel (petroleum ether/ethyl acetate, 9:1) to remove the PCC. The solvent was then evaporated, crude **16a** was dissolved in dry DMF (3 mL) under an inert gas, and piperidine (600 μL) was added. After 20 min, the solvent was evaporated under reduce pressure. The crude product was dissolved in dry 1,2-dichloroethane (10 mL) under an inert gas and then Na_2SO_4 (2.17 g, 15.32 mmol, 40 equiv.), AcOH (230 mg, 3.83 mmol, 10 equiv.), and NaBH(OAc)$_3$ (324 mg, 1.53 mmol, 4 equiv.) were added. After 6 h, the reaction mixture was neutralized using $NaHCO_3$ (satd. solution); the two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 15:1) yielding **18a** [263 mg, 82% for the three steps) as a colorless oil. The (6*R*) stereoisomer was detectable only by TLC]. $[\alpha]_D^{20}$ = −52.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR: δ = 1.10 [s, 9 H, (C*H*$_3$)$_3$C], 1.15 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.48 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.3 Hz, 1 H, C*H*CO$_2$Et), 2.77 (dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 5.0 Hz, 1 H, C*H*CO$_2$Et), 3.24−3.26 [m, 1 H, C(6)-H], 3.28 (dd, $^2J_{H,H}$ = 15.3, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CH=CH$_2$), 3.38−3.42 (m, 1 H, C*H*CH=CH$_2$), 3.41 [dd, $^3J_{H,H}$ = 9.4, $^3J_{H,H}$ = 8.7 Hz, 1 H, C(3)-H], 3.76−3.82 [m, 2 H, C(2)-H, C(5)-H], 3.88−4.10 (m, 2 H, C*H*$_2$OTBDPS), 4.01 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.12 [dd, $^3J_{H,H}$ = 9.1, $^3J_{H,H}$ = 8.7 Hz, 1 H, C(4)-H], 4.57 (s, 2 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.68

(d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.90 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.98 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, C*H*Ph), 5.00−5.05 (m, 2 H, $CH_2CH{=}CH_2$), 5.69 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 5.8 Hz, 1 H, $CH_2CH{=}CH_2$), 7.21−7.43 (m, 21 H, CHAr), 7.75−7.78 (m, 4 H, CHAr) ppm. ^{13}C NMR: δ = 14.67 (OCH_2CH_3), 19.58 [$(CH_3)_3C$], 27.36 [$(CH_3)_3C$], 36.60 (CH_2CO_2Et), 51.66 ($CH_2CH{=}CH_2$), 57.29, 58.72 [C(2), C(6)], 60.69 (OCH_2CH_3), 72.95, 74.84, 75.58 (3 CH_2Ph), 79.11, 81.29, 84.16 [C(3), C(4), C(5)], 116.8 ($CH_2CH{=}CH_2$), 127.5−129.8 (CHAr), 133.4, 133.5 (2 CqAr), 136.0 ($CH_2CH{=}CH_2$), 138.7, 138.9, 139.0 (3 CqAr), 172.2 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 799 [M + H]$^+$ 821 [M + Na]$^+$. $C_{50}H_{59}NO_6Si$ (798.1): calcd. C 75.25, H 7.45, N 1.76; found C 75.33, H 7.21, N 1.80.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*R*)-1-Benzyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2-yl]acetate (18b): Compound **14b** (117 mg, 0.11 mmol) was dissolved in dry CH_2Cl_2 (4 mL) under an inert gas, and added to a flask containing PCC (48 mg, 2 equiv.) previously dried with powdered molecular sieves (4 Å). After 12 h, more PCC (24 mg, 1 equiv.) was added and then, after 1 h, the mixture was concentrated and filtered through silica gel (petroleum ether/ethyl acetate, 9:1) to remove PCC and molecular sieves. The solvent was then evaporated and the crude product was dissolved in dry DMF (1 mL) under an inert gas. Piperidine (10 μL) was added and the reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure without heating and then the crude product was dried in vacuo for 3 h. This material was dissolved in dry 1,2-dichloroethane (3 mL) under an inert gas and then Na_2SO_4 (632 mg, 40 equiv.), AcOH (63 μL, 10 equiv.), and $NaBH(OAc)_3$ (94 mg, 4 equiv.) were added in sequence. The reaction mixture was stirred overnight before being neutralized with a saturated solution of $NaHCO_3$, extracted with CH_2Cl_2, dried with Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure. Purification by flash chromatography (toluene) afforded compound **18b** (75 mg, 81% for the three steps) as a mixture of diastereoisomers [(6*R*)/(6*S*) = 8:2, determined by NMR spectroscopy] as a colorless oil. $[\alpha]_D^{20}$ = −16.8 (*c* = 2.3, $CHCl_3$). ^{1}H NMR: δ = 1.02−1.08 [m, 12 H, $(CH_3)_3C$, OCH_2CH_3], 2.54 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 7.6 Hz, 1 H, C*H*COOEt), 2.84 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 4.4 Hz, 1 H, C*H*COOEt), 3.06−3.12 [m, 1 H, C(6)-H], 3.53 [dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(3)-H], 3.78−3.84 [m, 4 H, C(2)-H, C(5)-H, C*H*OTBDPS, C*H*Ph], 3.85−410 [m, 5 H, C(4)-H, C*H*OTBDPS, C*H*Ph, OCH_2CH_3], 4.37 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.42 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.65 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.69 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.89 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 5.00 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 7.19−7.80 (m, *H*Ar) ppm. ^{13}C NMR: δ = 14.57 (OCH_2CH_3), 19.57 [$(CH_3)_3C$], 27.33 [$(CH_3)_3C$], 31.00 (CH_2COOEt), 57.03, 58.52 [C(2), (6)], 52.12, 60.75, 65.94, 72.58, 75.03, 75.64 ($CH_2OTBDPS$, 4 CH_2Ph, OCH_2CH_3), 78.72, 81.39, 84.43 [C(3), C(4), C(5)], 126.5−136.0 (CHAr), 132.5, 133.3, 133.5, 138.4, 138.9, 140.1 (CqAr), 172.0 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 849 [M + H]$^+$. $C_{54}H_{61}NO_6Si$ (848.2): calcd. C 76.47, H 7.25, N 1.65; found C 76.12, H 7.00, N 1.70.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Butyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2yl]acetate (18c): Compound **14c** (30 mg, 0.028 mmol) was dissolved in CH_2Cl_2 (4 mL) under an inert gas, and added to a flask containing PCC (24 mg, 0.11 mmol, 4 equiv.), previously dried with powdered molecular sieves (4 Å). After 3 h, the reaction mixture was filtered through silica gel (petroleum ether/ethyl acetate, 8:2) to remove PCC. The solvent was evaporated and then the crude product was dissolved in dry DMF (0.25 mL) under an inert gas and piperidine (2.5 μL) was added. After 2 h, the solvent was evaporated under reduce pressure. The crude product was dissolved in dry 1,2-dichloroethane (1 mL) under an inert gas and then Na_2SO_4 (159 mg, 1.12 mmol, 40 equiv.), AcOH (16.8 mg, 0.28 mmol, 10 equiv.), and $NaBH(OAc)_3$ (24 mg, 0.112 mmol, 4 equiv.) were added. The reaction mixture was stirred overnight and then neutralized by adding $NaHCO_3$ (satd. solution); the two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) yielding **18c** (10 mg, 45%) as a colorless oil. $[\alpha]_D^{20}$ = −15.0 (*c* = 1.1, $CHCl_3$). ^{1}H NMR: δ = 0.90 [t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $N(CH_2)_3CH_3$], 1.11 [s, 9 H, $(CH_3)_3C$], 1.17 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.27−1.31 (m, 4 H, $CH_2CH_2CH_3$), 2.48 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.3 Hz, 1 H, C*H*CO_2Et), 2.54−2.63 [m, 1 H, NC*H*$(CH_2)_2CH_3$], 2.70−2.75 [m, 1 H, NC*H*$(CH_2)_2CH_3$], 2.76 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.0 Hz, 1 H, C*H*CO_2Et), 3.27 [td, $^3J_{H,H}$ = 5.5, $^3J_{H,H}$ = 3.1 Hz, 1 H, C(6)-H], 3.39 [dd, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(3)-H], 3.63 [ddd, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 7.3, $^3J_{H,H}$ = 5.0 Hz, 1 H, C(2)-H], 3.78 [dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 5.8 Hz, 1 H, C(5)-H], 3.95 [dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(4)-H], 3.97−4.11 (m, 2 H, OCH_2TBDPS), 4.01 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 4.64 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, C*H*Ph), 4.66 (s, 2 H, 2 C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.91 (d, $^2J_{H,H}$ = 10.6 Hz, 1 H, C*H*Ph), 4.99 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 7.26−7.38 (m, 21 H, *H*Ar), 7.77−7.79 (m, 4 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.57, 14.64 [$N(CH_2)_3CH_3$, OCH_2CH_3], 19.57 [$(CH_3)_3C$], 20.76 ($CH_2CH_2CH_2CH_3$), 27.29 [$(CH_3)_3C$], 31.81 ($CH_2CH_2CH_2CH_3$), 36.69 (CH_2CO_2Et), 48.10 ($CH_2CH_2CH_2CH_3$) 57.35, 59.33 [C(2), C(6)], 60.63, 60.72 (CH_2OTBDPS, OCH_2CH_3), 73.08, 74.94, 75.54 (3 CH_2Ph), 79.43, 81.45, 84.25 [C(3), C(4), C(5)], 127.6−129.8 (CHAr), 133.5, 133.6 (2 CqAr), 135.9, 136.0 (CHAr), 138.7, 138.9, 138.97 (3 CqAr), 172.3 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 815 [M + H]$^+$. $C_{51}H_{63}NO_6Si$ (814.1): calcd. C 75.24, H 7.80, N 1.72; found C 75.33, H 7.69, N 1.70.

Benzyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2-yl]acetate (18d): Compound **14d** (100 mg, 0.09 mmol) was dissolved in dry CH_2Cl_2 (5 mL) under an inert gas, and added to a flask containing PCC (293 mg, 1.5 equiv.) previously dried with powdered molecular sieves (4 Å). After 2 h, the mixture was concentrated and filtered through silica gel (petroleum ether/ethyl acetate, 8:2) to remove PCC and molecular sieves. The solvent was then evaporated and the crude product was dissolved in dry DMF (2 mL) under an inert gas. Piperidine (100 μL) was added and the reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure without heating and the crude product was dried in vacuo for 3 h. The material was dissolved in dry 1,2-dichloroethane (2 mL) under an inert gas and then Na_2SO_4 (392 mg, 40 equiv.), AcOH (40 μL, 10 equiv.), and $NaBH(OAc)_3$ (59 mg, 4 equiv.) were added in sequence. The reaction mixture was stirred overnight before it was neutralized with a saturated solution of $NaHCO_3$, extracted with CH_2Cl_2, dried with Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded pure compound **18d** (42 mg, 55% yield for the three steps) as a colorless oil. The (6*R*) stereoisomer was detectable only by TLC. $[\alpha]_D^{20}$ = −9.0 (*c* = 1.5, $CHCl_3$). ^{1}H NMR: δ = 1.09 [s, 9 H, $(CH_3)_3C$], 2.45 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.2 Hz, 1 H, C*H*COOBn), 2.71 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.2 Hz, 1 H, C*H*COOBn), 3.12−3.19 [m, 2 H, C(6)-H, C*H*CH=CH_2), 3.26 [dd, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 6.4 Hz, 1 H, C*H*CH=CH_2], 3.35 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(3)-

H], 3.67 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 5.9 Hz, 1 H, C(5)-H], 3.72−3.78 [m, 1 H, C(2)-H], 3.84 (dd, $^2J_{H,H}$ = 11.1, $^3J_{H,H}$ = 8.0 Hz, 1 H, C*H*OTBDPS), 3.93 (dd, $^2J_{H,H}$ = 11.1, $^3J_{H,H}$ = 5.0 Hz, 1 H, C*H*OTBDPS), 4.05 [t, $^3J_{H,H}$ = 9.5 Hz, 1 H, C(4)-H], 4.45 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, C*H*Ph), 4.49 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, C*H*Ph), 4.53 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.58 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.84 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, C*H*Ph), 4.88 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.87−4.92 (m, 2 H, $CH_2CH{=}CH_2$), 4.99 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, C*H*Ph), 5.50−5.57 (m, 1 H, $CH_2CH{=}CH_2$), 7.19−7.80 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 19.55 [$(CH_3)_3C$], 27.32 [$(CH_3)_3C$], 36.51 (CH_2COOBn), 51.82 ($CH_2CH{=}CH_2$), 57.33, 58.74 [C(2), C(6)], 60.95, 66.49, 72.95, 74.75, 75.52 ($CH_2OTBDPS$, 4 CH_2Ph), 79.12, 81.21, 84.04 [C(3), C(4), C(5)], 116.8 ($CH_2CH{=}CH_2$), 127.4−129.8, (*C*HAr), 133.3, 133.4, 136.2, 138.6, 138.9, 139.0 (*C*qAr), 136.0−136.1 (*C*HAr), 171.9 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 861 [M + H]$^+$. $C_{55}H_{61}NO_6Si$ (860.2): calcd. C 76.80, H 7.15, N 1.63; found C 76.51, H 6.95, N 1.33.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2yl]acetate (19a): Same procedure as that used for the synthesis of **18a**, starting from **15a** (184 mg, 0.18 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 15:1) afforded **19a** (140 mg, 98% for the three steps) as a colorless oil. $[\alpha]_D^{20}$ = +21.6 (*c* = 0.5, $CHCl_3$). ^{1}H NMR: δ = 0.98 [s, 9 H, $(CH_3)_3C$], 1.07 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.46 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 6.2 Hz, 1 H, C*H*CO_2Et), 2.62 (dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 6.6 Hz, 1 H, C*H*CO_2Et), 2.67 [dd, $^3J_{H,H}$ = 9.9, $^3J_{H,H}$ = 2.4 Hz, 1 H, C(6)-H], 3.13 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.7 Hz, 1 H, -C*H*CH=CH_2), 3.37 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.6 Hz, 1 H, -C*H*CH=CH_2), 3.46 [dd, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 3.60 [dd, $^3J_{H,H}$ = 8.9, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(4)-H], 3.65 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 5.0, 1 H, C(3)-H], 3.94−3.80 [m, 5 H, OCH_2CH_3, $CH_2OTBDPS$, C(2)-H], 4.40 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.48 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.60 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.79 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.84 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.99 [d, $^3J_{H,H}$ = 15.4 Hz, $CH_2CH{=}CH_2$(*trans*)], 5.00 [d, $^3J_{H,H}$ = 11.6 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.64 (ddt, $^3J_{H,H}$ = 11.6 Hz, 1 H, $CH_2CH{=}CH_2$), 6.95−7.36 (m, 21 H, *H*Ar), 7.43−7.64 (m, 4 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.61 (OCH_2CH_3), 19.79 [$(CH_3)_3C$], 27.44 [$(CH_3)_3C$], 30.17 (CH_2CO_2Et), 52.27 ($CH_2CH{=}CH_2$), 54.59 [C(2)], 60.38 [C(6)], 60.66 (OCH_2CH_3), 72.66, 75.14, 75.90 (3 CH_2Ph), 78.49, 80.03, 84.08 [C(3), C(4), C(5)], 117.0 ($CH_2CH{=}CH_2$), 127.6−132.5 (*C*HAr), 133.3, 133.5 (2 *C*qAr), 135.9 ($CH_2CH{=}CH_2$), 138.6, 138.6, 138.9 (3 *C*qAr), 172.8 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 799 [M + H]$^+$ 821 [M + Na]$^+$. $C_{50}H_{59}NO_6Si$ (798.1): calcd. C 75.25, H 7.45, N 1.76; found C 75.22, H 7.49, N 1.75.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Benzyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2-yl]acetate (19b): Same procedure as that used for the synthesis of **18b**, starting from **15b** (63 mg, 0.06 mmol). Purification by flash chromatography (toluene) afforded two diastereoisomeric compounds **19b** (28 mg, 57% global yield for the three steps) in the ratio (6*R*)/(6*S*) = 7:3. **Major Isomer (6*R*):** $[\alpha]_D^{20}$ = +16.3 (*c* = 2.0, $CHCl_3$). ^{1}H NMR: δ = 0.80 (t, 3 H, OCH_2CH_3), 0.85 [s, 9 H, $(CH_3)_3C$], 2.21 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*COOEt), 2.41 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*COOEt), 2.64−2.66 [m, 1 H, C(6)-H], 3.38 [t, $^3J_{H,H}$ = 9.2 Hz, 1 H, C(5)-H], 3.41−3.54 [m, 3 H, C(3)-H, C(4)-H, C*H*Ph], 3.56−3.64 (m, 2 H, OCH_2CH_3), 3.65−3.72 [m, 1 H, C(2)-H], 3.73−3.83 (m, 2 H, $CH_2OTBDPS$), 3.94 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, C*H*Ph), 3.97 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.13 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.26 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.42 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.74 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, C*H*Ph), 6.80−7.40 (m, *H*Ar) ppm. ^{13}C NMR: δ = 14.26 (OCH_2CH_3), 19.53 [$(CH_3)_3C$], 27.34 [$(CH_3)_3C$], 30.28 (CH_2COOEt), 54.39, 61.01 [C(2), C(6)], 52.81, 60.24, 62.68, 72.09, 74.73, 75.33 ($CH_2OTBDPS$, 4 CH_2Ph, OCH_2CH_3), 78.78, 80.00, 83.96 [C(3), C(4), C(5)], 127.0−129.9 (*C*HAr), 133.3, 133.4, 138.7, 139.3, 139.6, 140.3 (*C*qAr), 172.0 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 849 [M + H]$^+$. $C_{54}H_{61}NO_6Si$ (848.2): calcd. C 76.47, H 7.25, N 1.65; found C 76.58, H 7.13, N 1.76.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-1-butyl-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2yl]acetate (19c): Same procedure as that used for the synthesis of **18c**, starting from **15c** (80.7 mg, 0.077 mmol) to afford **19c** (43 mg, 68% for the three steps). The (6*S*) stereoisomer was detectable only by TLC. $[\alpha]_D^{20}$ = +16.9 (*c* = 0.7, $CHCl_3$). ^{1}H NMR: δ = 0.93 [t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $N(CH_2)_3CH_3$], 1.13 [s, 9 H, $(CH_3)_3C$], 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.48−1.51 (m, 4 H, $CH_2CH_2CH_2CH_3$), 2.52 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CO_2Et), 2.56−2.63 [m, 1 H, NC*H*$(CH_2)_2CH_3$], 2.67 (dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 6.5 Hz, 1 H, C*H*CO_2Et), 2.72 [ddd, $^3J_{H,H}$ = 9.9, $^3J_{H,H}$ = 4.1, $^3J_{H,H}$ = 2.5 Hz, 1 H, C(6)-H], 2.80−2.89 [m, 1 H, NC*H*$(CH_2)_2CH_3$], 3.55 [dd, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 3.73 [dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 9.6 Hz, 1 H, C(4)-H], 3.75 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 5.2, 1 H, C(3)-H], 3.91−4.14 [m, 5 H, C(2)-H, OCH_2CH_3, $CH_2OTBDPS$), 4.50 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.73 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.77 (d, $^2J_{H,H}$ = 10.5 Hz, 1 H, C*H*Ph), 4.90 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.97 (d, $^2J_{H,H}$ = 10.6 Hz, 1 H, C*H*Ph), 7.24−7.26 (m, 21 H, CHAr), 7.66−7.77 (m, 4 H, CHAr) ppm. ^{13}C NMR: δ = 14.64, 14.78 [$N(CH_2)_3CH_3$, OCH_2CH_3], 19.82 [$(CH_3)_3C$], 21.01 ($CH_2CH_2CH_2CH_3$), 27.48 [$(CH_3)_3C$], 29.23 ($CH_2CH_2CH_2CH_3$), 31.28 (CH_2CO_2Et), 48.87 ($CH_2CH_2CH_2CH_3$), 54.54, 61.33 [C(2), C(6)], 60.73, 62.51, 72.83, 75.11, 75.87 ($CH_2OTBDPS$, OCH_2CH_3, 3 CH_2Ph), 78.68, 80.45, 84.22 [C(3), C(4), C(5)], 127.6−129.9 (*C*HAr), 133.5, 133.6 (2 *C*qAr), 136.0, 136.0 (*C*HAr), 138.7, 138.7, 139.0 (3 *C*qAr), 173.2 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 815 [M + H]$^+$. $C_{51}H_{63}NO_6Si$ (814.1): calcd. C 75.24, H 7.80, N 1.72; found C 75.41, H 7.55, N 1.69.

Benzyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-3,4,5-tris(benzyloxy)-6-{[(*tert*-butyldiphenylsilyl)oxy]methyl}piperidin-2-yl]acetate (19d): Same procedure as that used for the synthesis of **18d**, starting from **15d** (69 mg, 0.06 mmol). Purification by flash chromatography (toluene/ethyl acetate, 95:5) afforded two diastereoisomeric compounds **19d** (32 mg, 62% global yield for the three steps) in the ratio (6*R*)/(6*S*) = 7:1. **Major Isomer (6*R*):** $[\alpha]_D^{20}$ = +16.6 (*c* = 1.2, $CHCl_3$). ^{1}H NMR: δ = 1.06 [s, 9 H, $(CH_3)_3C$], 2.50 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*COOBn), 2.68 (dd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.8 Hz, 1 H, C*H*COOBn), 2.71−2.74 [m, 1 H, C(6)-H], 3.18 [dd, $^2J_{H,H}$ = 14.6, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*CH=CH_2], 3.45 [dd, $^2J_{H,H}$ = 14.6, $^3J_{H,H}$ = 5.2 Hz, 1 H, C*H*CH=CH_2], 3.54 [t, $^3J_{H,H}$ = 9.6 Hz, 1 H, C(5)-H], 3.69 [t, $^3J_{H,H}$ = 9.5 Hz, 1 H, C(4)-H], 3.74 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 5.2 Hz, 1 H, C(3)-H], 3.89 (br. d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*OTBDPS), 3.95 (dd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 4.5 Hz, 1 H, C*H*OTBDPS), 3.95−4.00 [m, 1 H, C(2)-H], 4.47 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.55 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.72 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.85 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, C*H*Ph), 4.86 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.91 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H,

C*H*Ph), 4.96 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, C*H*Ph), 5.04−5.07 (m, 2 H, $CH_2CH{=}CH_2$), 5.65−5.75 (m, 1 H, $CH_2CH{=}CH_2$), 7.00−7.40 (m, 30 H, *H*Ar) ppm. ^{13}C NMR: δ = 19.76 [$(CH_3)_3C$], 27.41 [$(CH_3)_3C$], 29.45 (CH_2COOBn), 51.28 ($CH_2CH{=}CH_2$), 54.70, 60.43 [C(2), C(6)], 62.01, 66.55, 72.71, 75.10, 75.87 ($CH_2OTBDPS$, 4 CH_2Ph), 78.44, 80.10, 83.94 [C(3), C(4), C(5)], 117.1 ($CH_2CH{=}CH_2$), 127.6−128.6, (CHAr), 129.9 ($CH_2CH{=}CH_2$), 133.3, 133.4, 136.1, 138.5, 138.6, 138.9 (CqAr), 135.5−135.6 (CHAr), 172.6 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 861 [M + H]$^+$. $C_{55}H_{61}NO_6Si$ (860.2): calcd. C 76.80, H 7.15, N 1.63; found C 76.81, H 7.30, N 1.88.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetate (20): Compound **18a** (140 mg, 0.18 mmol) was dissolved in THF (1 mL) and TBAF (0.35 mmol, 2 equiv., 1 M in THF, 350 μL) was added. The reaction mixture was stirred at room temperature for 8 h and then more TBAF (0.09 mmol, 0.5 equiv., 1 M in THF, 90 μL) was added. After 4 h, the reaction mixture was quenched with buffer phosphate (pH = 7; 3 mL), the two layers were separated, the aqueous layer was extracted with ethyl acetate (3 × 3 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 8:2) yielding **20** (81 mg, 83%) as a colorless oil. $[\alpha]_D^{20}$ = −24.3 (*c* = 0.9, $CHCl_3$). ^{1}H NMR: δ = 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.37 (dd, $^2J_{H,H}$ = 15.5, $^3J_{H,H}$ = 7.4 Hz, 1 H, C*H*CO_2Et), 2.86−2.91 (m, 1 H, C*H*CO_2Et), 2.97 (dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 8.2 Hz, 1 H, C*H*$CH{=}CH_2$), 3.33 [ddd, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 6.2 Hz, 1 H, C(6)-H], 3.38−3.40 [m, 2 H, C(2)-H, C(3)-H], 3.44 (dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 4.2 Hz, 1 H, C*H*$CH{=}CH_2$), 3.72−3.83 [m, 3 H, C(4)-H, CH_2OH], 3.87 [dd, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = 6.2 Hz, 1 H, C(5)-H], 4.11 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 4.55 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.63 (s, 2 H, CH_2Ph), 4.79 (d, $^2J_{H,H}$ = 10.5 Hz, 1 H, C*H*Ph), 4.91 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.92 (d, $^2J_{H,H}$ = 10.5 Hz, 1 H, C*H*Ph), 5.02 [br. d, $^3J_{H,H}$ = 17.1 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.05 [br. d, $^3J_{H,H}$ = 10.5 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.51−5.61 (m, 1 H, $CH_2CH{=}CH_2$), 7.25−7.34 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.66 (OCH_2CH_3), 34.60 (CH_2CO_2Et), 50.02 ($-CH_2CH{=}CH_2$), 53.49, 57.65 [C(2), C(6)], 56.94, 61.18 (OCH_2CH_3, CH_2OH), 73.25, 75.54, 76.16 (3 CH_2Ph), 77.47, 79.13, 84.98 [C(3), C(4), C(5)], 117.9 ($CH_2CH{=}CH_2$), 127.9−128.7 (CHAr), 136.3 ($CH_2CH{=}CH_2$), 138.0, 138.2, 138.7 (3 CqAr), 171.8 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 561 [M + H]$^+$, 583 [M + Na]$^+$, 599 [M + K]$^+$. $C_{34}H_{41}NO_6$ (559.7): calcd. C 72.96, H 7.38, N 2.50; found C 73.00, H 7.36, N 2.49.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetate (21): Same procedure as that used for the synthesis of **20**, starting **19a** (735 mg, 0.92 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 8:2) afforded **21** (375 mg, 73%) as a colorless oil. $[\alpha]_D^{20}$ = +29.9 (*c* = 1.2, $CHCl_3$). ^{1}H NMR: δ = 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.53 (dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 7.1 Hz, 1 H, C*H*CO_2Et), 2.69 (dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 6.1 Hz, 1 H, C*H*CO_2Et), 2.84 [ddd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 4.7, $^3J_{H,H}$ = 4.4, 1 H, C(6)-H], 3.24 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.1 Hz, 1 H, C*H*$CH{=}CH_2$), 3.31 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.3 Hz, 1 H, C*H*$CH{=}CH_2$), 3.59 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 3.71−3.78 [m, 3 H, C(3)-H, C(4)-H, C*H*OH], 3.84 (dd, $^2J_{H,H}$ = 11.8, $^3J_{H,H}$ = 3.7 Hz, 1 H, C*H*OH), 3.95 [dd, $^3J_{H,H}$ = 11.4, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(2)-H], 4.02 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 4.61 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.64 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.69 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.93 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.97 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 5.17 [d, $^3J_{H,H}$ = 10.3 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.20 [d, $^3J_{H,H}$ = 16.7 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.81 (ddt, $^3J_{H,H}$ = 16.8, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 6.1 Hz, 1 H, $CH_2CH{=}CH_2$), 7.30−7.34 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.64 (OCH_2CH_3), 30.74 (CH_2CO_2Et), 51.16 ($CH_2CH{=}CH_2$), 55.43, 59.65 [C(2), C(6)], 59.63, 60.88 (CH_2OH, OCH_2CH_3), 72.85, 75.56, 72.75 (3 CH_2Ph), 78.29, 79.25, 83.45 [C(3), C(4), C(5)], 117.6 ($CH_2CH{=}CH_2$), 127.8−128.7 (CHAr), 136.1 ($CH_2CH{=}CH_2$), 138.3, 138.4, 138.8 (3 CqAr), 172.5 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 561 [M + H]$^+$, 583 [M + Na]$^+$, 599 [M + K]$^+$. $C_{34}H_{41}NO_6$ (559.7): calcd. C 72.96, H 7.38, N 2.50; found C 72.99, H 7.36, N 2.49.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-1-butyl-6-(hydroxymethyl)piperidin-2-yl]acetate (22): The reaction was carried out as described in the preparation of **20**, starting from **19c** (376 mg, 0.46 mmol) to afford **22** (228 mg, 86%) as a colorless oil. $[\alpha]_D^{20}$ = +7.6 (*c* = 1.1, $CHCl_3$). ^{1}H NMR: δ = 0.93 [t, $^3J_{H,H}$ = 7.3 Hz, 1 H, $N(CH_2)_3CH_3$], 1.22 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, OCH_2CH_3), 1.40−1.48 (m, 4 H, $CH_2CH_2CH_3$), 2.44−2.52 [m, 1 H, NC*H*$(CH_2)_2CH_3$], 2.49 (dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 7.5 Hz, 1 H, C*H*CO_2Et), 2.57 [dd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 6.1 Hz, 1 H, NC*H*$(CH_2)_2CH_3$], 2.66 (dd, $^2J_{H,H}$ = 15.0, $^3J_{H,H}$ = 5.9 Hz, 1 H, C*H*CO_2Et), 2.74−2.80 [m, 1 H, C(6)-H], 3.55 [dd, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 3.68−3.82 (m, 1 H, C*H*OH), 3.71 [dd, $^3J_{H,H}$ = 9.3, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(4)-H], 3.75 [dd, $^3J_{H,H}$ = 9.4, $^3J_{H,H}$ = 5.3 Hz, 1 H, C(3)-H], 3.82−3.85 [m, 2 H, C(2)-H, C*H*OH), 4.03−4.10 (m, 2 H, OCH_2CH_3), 4.62 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.69 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.81 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.92 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.96 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 7.30−7.34 (m, 15 H, *H*Ar) ppm. ^{13}C NMR: δ = 14.51, 14.62 [$N(CH_2)_3CH_3$, OCH_2CH_3], 20.86 ($CH_2CH_2CH_2CH_3$), 30.54, 31.25 ($CH_2CH_2CH_2CH_3$, CH_2CO_2Et), 47.65 ($CH_2CH_2CH_2CH_3$), 54.94, 60.02 [C(2), C(6)], 59.54, 60.92 (CH_2OH, OCH_2CH_3), 73.04, 75.64, 75.77 (3 CH_2Ph), 75.77, 78.53, 79.43 [C(3), C(4), C(5)], 127.8−128.7 (CHAr), 138.3, 138.8, 138.8 (3 CqAr), 172.7 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 577 [M + H]$^+$, 599 [M + Na]$^+$. $C_{35}H_{45}NO_6$ (575.7): calcd. C 73.02, H 7.88, N 2.43; found C 73.29, H 7.61, N 2.20.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-6-(azidomethyl)-3,4,5-tris(benzyloxy)piperidin-2-yl]acetate (23): Compound **20** (91 mg, 0.163 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and pyridine (77 mg, 0.98 mmol, 6 equiv.) and MsCl (56 mg, 0.49 mmol, 3 equiv.) were added. The mixture was stirred at room temperature for 6 h, then H_2O (2 mL) was added. The two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and then the crude product was dissolved in DMF (1.5 mL); NaN_3 (16 mg, 0.25 mmol, 1.5 equiv.) was added and the mixture was stirred at 80 °C for 4 h. H_2O (5 mL) was added, the mixture was extracted with ethyl acetate (4 × 5 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to afford **23** (45 mg, 47%) as a colorless oil. $[\alpha]_D^{20}$ = +3.0 (*c* = 1.7, $CHCl_3$). ^{1}H NMR: δ = 1.21 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.35 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 10.4 Hz, 1 H, C*H*CO_2Et), 2.75 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.2 Hz, 1 H, C*H*CO_2Et), 3.11 (dd, $^2J_{H,H}$ = 14.2, $^3J_{H,H}$ = 4.5 Hz, 1 H, C*H*N_3), 3.21−3.31 (m, 3 H, $CH_2CH{=}CH_2$, C*H*N_3), 3.47 [br. d, $^3J_{H,H}$ = 10.0 Hz, 1 H, C(3)-H], 3.77 [dd, $^3J_{H,H}$ = 11.1, $^3J_{H,H}$ = 4.4 Hz, 1 H, C(6)-H], 3.93−4.16 [m, 5 H, C(2)-H, OCH_2CH_3, C(4)-H, C(5)-

H], 4.34 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 4.49 (d, $^2J_{H,H}$ = 12.6 Hz, 1 H, C*H*Ph), 4.56 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.71 (d, $^2J_{H,H}$ = 11.6 Hz, 2 H, 2 C*H*Ph), 5.07 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.13 [d, $^3J_{H,H}$ = 17.2 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.62−5.68 (m, 1 H, $CH_2CH{=}CH_2$), 7.25−7.34 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.73 (OCH_2CH_3), 30.15 (CH_2CO_2Et), 38.64, 50.15 ($-CH_2CH{=}CH_2$, CH_2N_3), 55.34, 61.04 [C(2), C(6)], 60.47 (OCH_2CH_3), 72.55, 72.60, 73.10 (3 CH_2Ph), 78.37, 80.00, 85.18 [C(3), C(4), C(5)], 116.7 ($CH_2CH{=}CH_2$), 127.7−128.8 (*C*HAr), 137.16 ($CH_2CH{=}CH_2$), 137.7, 137.9, 138.0 (3 *C*qAr), 172.3 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 586 [M + H]$^+$, 608 [M + Na]$^+$. $C_{34}H_{40}N_4O_5$ (584.7): calcd. C 69.84, H 6.90, N 9.58; found C 70.01, H 6.95, N 9.39.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-6-(azidomethyl)-3,4,5-tris(benzyloxy)piperidin-2-yl]acetate (24): The reaction was carried out as described for the preparation of **23**, starting from **21** (94 mg, 0.17 mmol) to afford **24** (50 mg, 51%) as a colorless oil. $[\alpha]_D^{20}$ = −8.3 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.21 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.47 (dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CO_2Et), 2.63 (dd, $^2J_{H,H}$ = 15.3, $^3J_{H,H}$ = 6.7 Hz, 1 H, C*H*CO_2Et), 2.88 [dt, $^3J_{H,H}$ = 9.3, $^3J_{H,H}$ = 3.0 Hz, 1 H, C(6)-H], 3.17 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 7.2 Hz, 1 H, C*H*CH=CH_2), 3.45 (dd, $^2J_{H,H}$ = 13.9, $^3J_{H,H}$ = 5.6 Hz, 1 H, C*H*CH=CH_2), 3.65 (dd, $^3J_{H,H}$ = 9.1, $^3J_{H,H}$ = 8.5 Hz, 1 H, C*H*N_3), 3.69−3.76 [m, 2 H, C(3)-H, C(4)-H], 3.79 [dd, $^3J_{H,H}$ = 12.5, $^3J_{H,H}$ = 2.8 Hz, 1 H, C(5)-H], 3.95−3.98 (m, 1 H, C*H*N_3), 4.03 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2CH_3), 4.08 [dd, $^3J_{H,H}$ = 11.7, $^3J_{H,H}$ = 5.0 Hz, 1 H, C(2)-H], 4.58 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.68 (d, $^2J_{H,H}$ = 10.6 Hz, 1 H, C*H*Ph), 4.71 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.80 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.98 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.99 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 5.19 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.22 [d, $^3J_{H,H}$ = 16.7 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.88 (dddd, $^3J_{H,H}$ = 17.3, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 5.5 Hz, $CH_2CH{=}CH_2$), 7.28−7.35 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.59 (OCH_2CH_3), 29.24 (CH_2CO_2Et), 43.27 ($-CH_2CH{=}CH_2$), 50.00 (CH_2N_3), 54.93, 59.07 [C(2), C(6)], 60.82 (OCH_2CH_3), 72.73, 75.74, 75.87 (3 CH_2Ph), 78.89, 80.20, 83.26 [C(3), C(4), C(5)], 118.1 ($CH_2CH{=}CH_2$), 127.7−128.7 (*C*HAr), 135.5 ($CH_2CH{=}CH_2$), 138.4, 138.9, 138.9 (3 *C*qAr), 172.5 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 586 [M + H]$^+$, 608 [M + Na]$^+$, 624 [M + K]$^+$. $C_{34}H_{40}N_4O_5$ (584.7): calcd. C 69.84, H 6.90, N 9.58; found C 69.98, H 6.99, N 9.38.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-6-(Azidomethyl)-3,4,5-tris(benzyloxy)-1-butylpiperidin-2-yl]acetate (25): The reaction was carried out as described in the preparation of **23**, starting from compound **22** (67 mg mg, 0.12 mmol) to afford **25** (54 mg, 77%) as a colorless oil. $[\alpha]_D^{20}$ = −7.7 (*c* = 1.2, $CHCl_3$). ^{1}H NMR: δ = 0.96 [t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $N(CH_2)_3CH_3$], 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.32 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 1.40−1.60 (m, 2 H, $CH_2CH_2CH_3$), 2.40−2.50 [m, 2 H, NC*H*$(CH_2)_2CH_3$, C*H*CO_2Et], 2.59−2.66 [m, 2 H, NC*H*$(CH_2)_2CH_3$, C*H*CO_2Et], 2.74 [ddd, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 4.5, $^3J_{H,H}$ = 2.9 Hz, 1 H, C(6)-H], 3.48 [dd, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 8.6 Hz, 1 H, C(5)-H], 3.54 (dd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 4.8 Hz, 1 H, C*H*N_3), 3.64 (dd, $^2J_{H,H}$ = 13.5, $^3J_{H,H}$ = 3.0 Hz, 1 H, C*H*N_3), 3.70 [dd, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = 8.5 Hz, 1 H, C4)-H], 3.76 [dd, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = 5.3 Hz, 1 H, C(3)-H], 3.94−4.02 [m, 1 H, C(2)-H], 4.06 (q, $^3J_{H,H}$ = 7.1 Hz, OCH_2CH_3), 4.60 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.62 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.80 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 4.98 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.99 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 7.28−7.39 (m, 15 H, CHAr) ppm. ^{13}C NMR: δ = 14.55, 14.60 [$N(CH_2)_3CH_3$, OCH_2CH_3], 20.98, 29.44, 30.69 (CH_2CO_2Et, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$), 48.44, 49.32 (CH_2N_3, $CH_2CH_2CH_2CH_3$), 54.83, 58.75 [C(2), C(6)], 60.89 (OCH_2CH_3), 72.93, 75.63, 75.72 (3 CH_2Ph), 78.96, 79.87, 83.63 [C(3), C(4), C(5)], 127.8−128.7 (*C*HAr), 138.3, 138.4, 138.8 (3 *C*qAr), 172.7 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 602 [M + H]$^+$, 624 [M + Na]$^+$, 640 [M + K]$^+$. $C_{35}H_{44}N_4O_5$ (600.8): calcd. C 69.98, H 7.38, N 9.33; found C 70.12, H 7.45, N 9.59.

[(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)-piperidin-2-yl]acetic Acid (26): Compound **20** (100 mg, 0.18 mmol) was dissolved in a mixture of THF/CH_3OH/H_2O (1:1:1; 1.5 mL) and then LiOH (42 mg, 0.27 mmol, 1.5 equiv.) was added. The mixture was stirred at room temperature for 3 h and then acidified with HCl (5%). The two layers were separated; the aqueous layer was extracted with ethyl acetate (3 × 3 mL) and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:9) yielding **26** (90 mg, 94%) as an amorphous solid. $[\alpha]_D^{20}$ = −21.4 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (CD_3COCD_3): δ = 2.60−2.66 (m, 1 H, C*H*CO_2H), 2.80−2.83 (m, 1 H, C*H*CO_2H), 3.26−3.36 (m, 1 H, C*H*CH=CH_2), 3.40−3.96 [m, 8 H, C(2)-H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C*H*$_2$OH, C*H*CH=CH_2], 4.64−4.69 (m, 3 H, 3 C*H*Ph), 4.77 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.85 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, C*H*Ph), 4.89 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, C*H*Ph), 5.07 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 5.17 [d, $^3J_{H,H}$ = 17.2 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.66−5.79 (m, 1 H, $CH_2CH{=}CH_2$), 7.20−7.42 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR (CD_3COCD_3): δ = 32.19 (CH_2CO_2H), 50.15, 53.92, 56.88, 57.42 [C(2), C(6), $CH_2CH{=}CH_2$, CH_2OH], 57.46, 72.60, 74.58 74.99, 77.33, 79.06 [C(3), C(4), C(5), 3 CH_2Ph], 117.2 ($CH_2CH{=}CH_2$), 127.5−129.0 (*C*HAr), 136.9 ($CH_2CH{=}CH_2$), 138.8, 138.98, 139.4 (3 *C*qAr), 173.2 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 533 [M + H]$^+$. $C_{32}H_{37}NO_6$ (531.6): calcd. C 72.29, H 7.01, N 2.63; found C 72.31, H 7.04, N 2.61.

[(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetic Acid (27): Same procedure as that used for the synthesis of **26**, starting from **21** (86 mg, 0.15 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 1:9) afforded **27** (77 mg, 97%) as an amorphous solid. $[\alpha]_D^{20}$ = −11.7 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3COCD_3): δ = 3.03 (t, dd, $^3J_{H,H}$ = 16.8, $^3J_{H,H}$ = 9.3 Hz, 1 H, C*H*CO_2H), 3.33−3.36 (m, 1 H, C*H*CO_2H), 3.80−4.31 [m, 8 H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C*H*$_2$OH, C*H*$_2$CH=CH_2], 4.37−4.39 [m, 1 H, C(2)-H], 4.54 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, C*H*Ph), 4.60−4.68 (m, 4 H, 4 C*H*Ph), 4.70 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 5.29 [d, $^3J_{H,H}$ = 18.6 Hz, 1 H, $CH_2CH{=}CH_2$(*trans*)], 5.33 [d, $^3J_{H,H}$ = 10.3 Hz, 1 H, $CH_2CH{=}CH_2$(*cis*)], 6.02−6.12 (m, 1 H, $CH_2CH{=}CH_2$), 7.21−7.32 (m, 15 H, CHAr) ppm. ^{13}C NMR (100.57 MHz, CD_3COCD_3, 25 °C): δ = 30.17 (CH_2CO_2OH), 50.21, 53.33, 54.03, 57.95 [C(2), C(6), -$CH_2CH{=}CH_2$, CH_2OH], 64.12, 72.53, 73.14 73.76, 74.52, 74.90 [C(3), C(4), C(5), 3 CH_2Ph], 124.3 ($CH_2CH{=}CH_2$), 127.8−129.3 (*C*HAr), 137.9 ($CH_2CH{=}CH_2$), 170.8 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 533 [M + H]$^+$, 555 [M + Na]$^+$. $C_{32}H_{37}NO_6$ (531.6): calcd. C 72.29, H 7.01, N 2.63; found C 72.27, H 7.00, N 2.61.

[(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-1-butyl-6-(hydroxymethyl)piperidin-2-yl]acetic Acid (28): Same procedure as that used for the synthesis of **26**, starting from **22** (19 mg, 0.033 mmol). Purification by flash chromatography (petroleum ether/ethyl acetate, 1:9) afforded **22** (18 mg, 100%) as an amorphous solid. $[\alpha]_D^{20}$ = −12.5 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (CD_3COCD_3): δ = 0.73 [t, $^3J_{H,H}$ = 7.4 Hz, 3 H, $N(CH_2)_3CH_3$], 1.07−1.23 (m, 4 H,

$CH_2CH_2CH_3$), 2.81 (dd, $^2J_{H,H}$ = 17.3, $^3J_{H,H}$ = 5.3 Hz, 1 H, $CHCO_2H$), 2.90−3.01 [m, 3 H, $CHCO_2H$, $NCH_2(CH_2)_2CH_3$], 3.53−4.00 [m, 7 H, C(2)-H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, CH_2OH], 4.55 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, $CHPh$), 4.56 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, $CHPh$), 4.61 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, $CHPh$), 4.62 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, $CHPh$), 4.69 (d, $^2J_{H,H}$ = 11.3 Hz, 1 H, $CHPh$), 4.72 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, $CHPh$), 7.14−7.24 (m, 15 H, $CHAr$) ppm. ^{13}C NMR (CD_3COCD_3): δ = 13.63 [$N(CH_2)_3CH_3$], 20.20 ($CH_2CH_2CH_2CH_3$), 29.90 ($CH_2CH_2CH_2CH_3$), 34.60, 48.84, 55.88, 56.92, 58.57 [CH_2CO_2H, C(2), C(6), $NCH_2(CH_2)_2CH_3$, CH_2OH], 64.01, 72.95, 74.12 75.97, 77.76, 79.37 [C(3), C(4), C(5), 3 CH_2Ph], 126.6−129.0 ($CHAr$), 138.4, 138.5, 138.8 (3 $CqAr$), 172.5 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 549 [M + H]$^+$, 571 [M + Na]$^+$. $C_{33}H_{41}NO_6$ (547.7): calcd. C 72.37, H 7.55, N 2.56; found C 72.33, H 7.56, N 2.55.

{2-[(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetyl}glycine *tert*-Butyl Ester (29): Compound **26** (80 mg 0.15 mmol) was dissolved in DMF (2 mL) and then H-Gly-O*t*Bu·AcOH (86 mg, 0.45 mmol, 3 equiv.), HBTU (171 mg, 0.45 mmol, 3 equiv.), HOBt (57 mg, 0.42 mmol, 2.8 equiv.), and DIPEA (96 mg, 0.75 mmol, 5 equiv.) were added. The mixture was stirred at room temperature for 3 h and then water (3 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were back-extracted with brine and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:4) yielding **29** (71 mg, 73%) as a colorless oil. $[\alpha]_D^{20}$ = −12.8 (*c* = 1.6, $CHCl_3$). ^1H NMR (CD_3COCD_3): δ = 1.44 [s, 9 H, $(CH_3)_3C$], 2.58 (dd, $^2J_{H,H}$ = 15.9, $^3J_{H,H}$ = 10.3 Hz, 1 H, $CHCONH$), 2.79 (dd, $^2J_{H,H}$ = 16.1, $^3J_{H,H}$ = 3.7 Hz, 1 H, $CHCONH$), 3.18 (dd, $^2J_{H,H}$ = 14.2, $^3J_{H,H}$ = 8.2 Hz, 1 H, $CHCH=CH_2$), 3.32 (dd, $^2J_{H,H}$ = 9.6, $^3J_{H,H}$ = 2.1 Hz, 1 H, $CHOH$), 3.39 [m, 1 H, C(6)-H], 3.45−3.52 [m, 2 H, C(2)-H, C(3)-H], 3.61 (dd, $^3J_{H,H}$ = 14.2, $^3J_{H,H}$ = 4.4, 1 H, $CHCH=CH_2$), 3.68−3.79 [m, 2 H, C(4)-H, $CHOH$], 3.80−3.84 [m, 2 H, $NHCH_2CO_2tBu$], 3.94 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 6.1 Hz, 1 H, C(5)-H], 4.64 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.65 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, $CHPh$), 4.69 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, $CHPh$), 4.79 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.79 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.88 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.92 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 5.04 [d, $^3J_{H,H}$ = 9.9 Hz, 1 H, $CH_2CH=CH_2(cis)$], 5.16 [dd, $^3J_{H,H}$ = 17.1, $^4J_{H,H}$ = 0.7 Hz, 1 H, $CH_2CH=CH_2(trans)$], 5.78 (ddt, $^3J_{H,H}$ = 18.1, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 4.4 Hz, 1 H, $CH_2CH=CH_2$), 7.24−7.40 (m, 15 H, $CHAr$), 7.86 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, N*H*) ppm. ^{13}C NMR (CD_3COCD_3): δ = 32.93 [$(CH_3)_3C$], 39.52 [$(CH_3)_3C$], 47.10 (CH_2CONH), 54.93, 61.91 ($NHCH_2CO tBu$, $CH_2CH=CH_2$), 58.74, 62.93 [C(2), C(6)], 77.72, 79.96, 80.41, 86.11 (CH_2OH, 3 CH_2Ph), 82.82, 84.70, 89.98 [C(3), C(4), C(5)], 121.6 ($CH_2CH=CH_2$), 132.6−133.6 ($CHAr$), 143.0 ($CH_2CH=CH_2$), 144.4, 144.5, 144.7 (3 $CqAr$), 174.4, 176.3 (2 C=O) ppm. MS (MALDI-TOF): *m*/*z* = 646 [M + H]$^+$, 668 [M + Na]$^+$. $C_{38}H_{48}N_2O_7$ (644.8): calcd. C 70.78, H 7.50, N 4.34; found C 70.66, H 7.36, N 4.49.

{2-[(2*S*,3*S*,4*S*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetyl}valine Methyl Ester (30): Compound **26** (37 mg 0.07 mmol) was dissolved in DMF (700 μL) and then L-Val-OMe·HCl (70 mg, 0.42 mmol, 6 equiv.), HBTU (159 mg, 0.42 mmol, 6 equiv.), HOBt (53 mg, 0.392 mmol, 5.6 equiv.), and DIPEA (90 mg, 0.70 mmol, 10 equiv.) were added. The mixture was stirred at room temperature for 3 h and then water (3 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were back-extracted with brine (5 mL) and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/EtOAc 6:4) yielding **30** (35 mg, 78%) as a colorless oil. $[\alpha]_D^{20}$ = −14.5 (*c* = 0.9, $CHCl_3$). ^1H NMR (CD_3COCD_3) δ = 0.93 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, $(CH_3)_2C$], 0.94 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, $(CH_3)_2C$], 2.09−2.14 [m, 1 H, $CH(CH_3)_2$], 2.64 (dd, $^2J_{H,H}$ = 16.1, $^3J_{H,H}$ = 10.3 Hz, 1 H, $CHCONH$), 2.82 (dd, $^2J_{H,H}$ = 16.4, $^3J_{H,H}$ = 3.6 Hz, 1 H, $CHCONH$), 3.23 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 8.1 Hz, 1 H, $CHCH=CH_2$), 3.31 (br. d, $^3J_{H,H}$ = 8.8 Hz, 1 H, $CHOH$), 3.36−3.42 [m, 1 H, C(6)-H], 3.47−3.54 [m, 2 H, C(2)-H, C(3)-H], 3.62−3.65 (m, 1 H, $CHCH=CH_2$), 3.67 (s, 3 H, OCH_3), 3.73−3.79 [m, 1 H, C(4)-H], 3.94 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 6.0 Hz, 1 H, C(5)-H], 4.40 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 5.7 Hz, 1 H, $NHCHCO_2CH_3$), 4.63 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, $CHPh$), 4.69 (d, $^2J_{H,H}$ = 11.7 Hz, 2 H, 2 $CHPh$), 4.79 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.87 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, $CHPh$), 4.93 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, $CHPh$), 5.07 [d, $^3J_{H,H}$ = 10.1 Hz, $CH_2CH=CH_2(cis)$], 5.19 [d, $^3J_{H,H}$ = 16.4 Hz, 1 H, $CH_2CH=CH_2(trans)$], 5.71−5.81 (m, 1 H, $CH_2CH=CH_2$), 7.29−7.36 (m, 15 H, CHAr), 7.86 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, NH) ppm. ^{13}C NMR (CD_3COCD_3): δ = 23.35, 24.24 [$(CH_3)_2C$], 36.23 [$CH(CH_3)_2$], 39.49 (CH_2CONH), 54.93, 62.18 (CH_2OH, $CH_2CH=CH_2$), 56.72, 58.89, 62.77, 63.05 [C(2), C(6), OCH_3, $NHCHCO$], 77.72, 80.02, 80.39 (3 CH_2Ph), 82.76, 84.69, 89.85 [C(3), C(4), C(5)], 122.0 ($CH_2CH=CH_2$), 132.6−133.6 ($CHAr$), 142.6 ($CH_2CH=CH_2$), 144.1, 144.2, 144.7 (3 $CqAr$), 176.2, 177.4 (2 C=O) ppm. MS (MALDI-TOF): *m*/*z* = 646 [M + H]$^+$, 668 [M + Na]$^+$. $C_{38}H_{48}N_2O_7$ (644.8): calcd. C 70.78, H 7.50, N 4.34; found C 70.71, H 7.65, N 4.30.

{2-[(2*S*,3*S*,4*S*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetyl}phenylalanine *tert*-Butyl Ester (31): Compound **26** (32 mg 0.06 mmol) was dissolved in DMF (500 μL) and then L-Phe-O*t*Bu·HCl (93 mg, 0.361 mmol, 6 equiv.), HBTU (137 mg, 0.361 mmol, 6 equiv.), HOBt (45 mg, 0.336 mmol, 5.8 equiv.), and DIPEA (78 mg, 0.60 mmol, 10 equiv.) were added. The mixture was stirred at room temperature for 3 h and then water (3 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were back-extracted with brine (5 mL) and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:4) to yield **31** (31 mg, 70%) as a colorless oil. $[\alpha]_D^{20}$ = +12.4 (*c* = 0.7, $CHCl_3$). ^1H NMR (CD_3COCD_3): δ = 1.36 [s, 9 H, $(CH_3)_3C$], 2.56 (dd, $^2J_{H,H}$ = 16.3, $^3J_{H,H}$ = 10.3 Hz, 1 H, $CHCONH$), 2.77 (dd, $^2J_{H,H}$ = 16.5, $^3J_{H,H}$ = 3.7 Hz, 1 H, $CHCONH$), 2.98−3.04 (m, 2 H, CH_2Ph), 3.15 (dd, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 8.2 Hz, 1 H, $CHCH=CH_2$), 3.35−3.50 [m, 3 H, C(2)-H, C(3)-H, C(6)-H], 3.52−3.57 (m, 1 H, $CHCH=CH_2$), 3.72−3.77 [m, 2 H, C(4)-H, $CHOH$], 3.86 (br. t, $^3J_{H,H}$ = 10.5 Hz, 1 H, $CHOH$), 3.92 [dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 6.0 Hz, 1 H, C(5)-H], 4.58−4.62 (m, 1 H, $NHCHCO_2tBu$), 4.62 (d, $^2J_{H,H}$ = 11.0, 1 H, $CHPh$), 4.65 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, $CHPh$), 4.69 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H, $CHPh$), 4.78 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 4.86 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, $CHPh$), 4.92 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, $CHPh$), 5.00 [d, $^3J_{H,H}$ = 10.1 Hz, 1 H, $CH_2CH=CH_2(cis)$], 5.14 [d, $^3J_{H,H}$ = 17.2 Hz, 1 H, $CH_2CH=CH_2(trans)$], 5.60−5.70 (m, 1 H, $CH_2CH=CH_2$), 7.28−7.33 (m, 15 H, *H*Ar), 7.90 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, N*H*) ppm. ^{13}C NMR (CD_3COCD_3): δ = 32.80 [$(CH_3)_3C$], 39.38 [$(CH_3)_3C$], 43.30, 55.00, 62.10 ($CH_2CH=CH_2$, CH_2Ph, CH_2CONH), 58.74, 59.77, 63.06 [C(2), C(6), $NHCHCO_2tBu$], 77.72, 79.97, 80.35, 86.34 (CH_2OH, 3 CH_2Ph), 82.83, 84.74, 89.77 [C(3), C(4), C(5)], 121.7 ($CH_2CH=CH_2$), 131.9−134.6 ($CHAr$), 142.7 ($CqAr$), 142.8 ($CH_2CH=CH_2$), 144.1, 144.2, 144.7 (3 $CqAr$), 175.8, 176.2 (2 C=O) ppm. MS:

m/*z* = 736 [M + H]$^+$, 758 [M + Na]$^+$, 774 [M + K]$^+$. $C_{45}H_{54}N_2O_7$ (734.9): calcd. C 73.54, H 7.41, N 3.81; found C 73.22, H 7.48, N 3.93.

{2-[(2*S*,3*S*,4*R*,5*R*,6*S*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetyl}alanine *tert*-Butyl Ester (32): Compound **26** (52 mg 0.098 mmol) was dissolved in DMF (700 μL) and then L-Ala-O*t*Bu·HCl (107 mg, 0.587 mmol, 6 equiv.), HBTU (223 mg, 0.587 mmol, 6 equiv.), HOBt (74 mg, 5.6 mmol, 5.6 equiv.), and DIPEA (127 mg, 0.980 mmol, 10 equiv.) were added. The mixture was stirred at room temperature for 3 h and then water (3 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were back-extracted with brine (5 mL) and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:4) to yield **32** (32 mg, 50%) as a colorless oil. $[\alpha]_D^{20} = -10.6$ (*c* = 0.4, $CHCl_3$). ^{1}H NMR: δ = 1.35 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CHC*H*$_3$), 1.47 [s, 9 H, (C*H*$_3$)$_3$C], 2.31−2.37 (m, 1 H, C*H*CONH), 2.89 (dd, $^2J_{H,H}$ = 15.7, $^3J_{H,H}$ = 2.3 Hz, 1 H, C*H*CONH), 3.03 (dd, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 8.6 Hz, 1 H, C*H*CH=CH$_2$), 3.37−3.39; 3.45−3.48; 3.68−3.92 [3m, 8 H, C(2)-H, C(3)-H, C(4)-H, C(5)-H, C(6)-H, C*H*$_2$OH, C*H*CH=CH$_2$], 4.43−4.47 (m, 1 H, NHC*H*CO$_2$*t*Bu), 4.55 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.63 (s, 2 H, C*H*$_2$Ph), 4.78 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.88 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.91 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 5.03 [d, $^3J_{H,H}$ = 18.4 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.07 [d, $^3J_{H,H}$ = 11.3 Hz, 1 H, CH$_2$CH=C*H*$_2$ (*trans*)], 5.63−5.73 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.28−7.35 (m, 15 H, *H*Ar) 7.64 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, N*H*) ppm. ^{13}C NMR: δ = 19.25 (CH*C*H$_3$), 28.35 [(*C*H$_3$)$_3$C], 34.60 [(CH$_3$)$_3$*C*], 49.06, 53.68, 58.07 [C(2), C(6), NH*C*HCO], 49.83, 57.76 (−*C*H$_2$CH=CH$_2$, *C*H$_2$OH), 73.18, 75.61, 75.97 (3 *C*H$_2$Ph), 76.85, 79.28, 84.44 [C(3), C(4), C(5)], 118.3 (CH$_2$CH=*C*H$_2$), 127.9−129.2 (*C*HAr), 136.1 (CH$_2$*C*H=CH$_2$), 137.9, 137.9, 138.6 (3 *C*qAr), 170.2, 173.1 (2 *C*=O) ppm. MS: *m*/*z* = 660 [M + H]$^+$, 682 [M + Na]$^+$, 698 [M + K]$^+$. $C_{39}H_{50}N_2O_7$ (658.8): calcd. C 71.10, H 7.65, N 4.25; found C 71.36, H 7.44, N 4.20.

{2-[(2*R*,3*S*,4*R*,5*R*,6*R*)-1-Allyl-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)piperidin-2-yl]acetyl}glycine *tert*-Butyl Ester (33): Compound **27** (49 mg 0.09 mmol) was dissolved in DMF (1 mL) and then H-Gly-O*t*Bu·AcOH (536 mg, 0.28 mmol, 3 equiv.), HBTU (105 mg, 0.28 mmol, 3 equiv.), HOBt (35 mg, 0.26 mmol, 2.8 equiv.), and DIPEA (79 μL, 0.46 mmol, 5 equiv.) were added. The mixture was stirred at room temperature for 3 h and then water (2 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were back-extracted with brine and dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:4) to yield **33** (33 mg, 56%) as a colorless oil. $[\alpha]_D^{20} = +5.2$ (*c* = 1.0, $CHCl_3$). ^{1}H NMR (CD_3COCD_3): δ = 1.44 [s, 9 H, (C*H*$_3$)$_3$C], 2.64−2.66 (m, 2 H, C*H*$_2$CONH), 3.53−3.54 (m, 2 H, C*H*$_2$CH=CH$_2$), 3.62 [dd, $^3J_{H,H}$ = 9.2, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 3.72 (dd, $^2J_{H,H}$ = 17.7, $^3J_{H,H}$ = 5.5 Hz, 1 H, NHC*H*CO$_2$*t*Bu), 3.77−3.92 [m, 5 H, C(3)-H, C(4)-H, C*H*$_2$OH, NHC*H*CO$_2$*t*Bu], 4.60 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.66 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.73 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, C*H*Ph), 4.77 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.88 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 4.93 (d, $^2J_{H,H}$ = 11.1 Hz, 1 H, C*H*Ph), 5.00 [dd, $^3J_{H,H}$ = 10.3, $^4J_{H,H}$ = 1.8 Hz, 1 H, CH$_2$CH=C*H*$_2$(*cis*)], 5.22 [dd, $^3J_{H,H}$ = 17.2, $^4J_{H,H}$ = 1.9 Hz, 1 H, CH$_2$CH=C*H*$_2$(*trans*)], 5.88 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH$_2$C*H*=CH$_2$), 7.26−7.38 (m, 15 H, C*H*Ar), 7.71−7.77 (m, 1 H, N*H*) ppm. ^{13}C NMR (CD_3COCD_3): δ = 31.66 [(*C*H$_3$)$_3$C], 39.15 [(CH$_3$)$_3$*C*], 41.85 (*C*H$_2$CONH), 51.47, 59.14 (NH*C*H$_2$CO*t*Bu, *C*H$_2$CH=CH$_2$), 54.28, 59.81 [C(2), C(6)], 72.08, 74.57, 74.86, 80.76 (*C*H$_2$OH, 3 *C*H$_2$Ph), 78.05, 78.75, 80.95 [C(3), C(4), C(5)], 117.0 (CH$_2$CH=*C*H$_2$), 124.4−128.9 (*C*HAr), 138.9 (CH$_2$*C*H=CH$_2$), 138.9, 139.2, 139.4 (3 *C*qAr), 169.1, 171.6 (2 *C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 646 [M + H]$^+$, 668 [M + Na]$^+$. $C_{38}H_{48}N_2O_7$ (644.8): calcd. C 70.78, H 7.50, N 4.34; found C 70.62, H 7.39, N 4.51.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-Trihydroxy-6-(hydroxymethyl)-1-propylpiperidin-2-yl]acetate (34): Compound **20** (15 mg, 0.027 mmol) was dissolved in CH_3OH (1 mL); a suspension of Raney nickel (0.1 mg/ mL) (5 mL) was added and the reaction mixture was stirred under H_2 for 3 h. The catalyst was filtered through a pad of Celite (eluting with CH_3OH) and then the solvent was evaporated under reduced pressure to afford pure compound **34** (8 mg, quant. yield) as an amorphous solid. $[\alpha]_D^{20} = -35.5$ (*c* = 0.8, H_2O). ^{1}H NMR (D_2O): δ = 0.67 (br. t, 3 H, NCH$_2$CH$_2$C*H*$_3$), 1.10 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.15−1.32 (m, 2 H, NCH$_2$C*H*$_2$CH$_3$), 2.35 (ddd, $^2J_{H,H}$ = 14.1, $^3J_{H,H}$ = 8.8, $^3J_{H,H}$ = 5.3 Hz, 1 H, NC*H*CH$_2$CH$_3$), 2.43−2.54 (m, 2 H, NC*H*CH$_2$CH$_3$, C*H*COOEt), 2.70 (dd, $^2J_{H,H}$ = 16.2, $^3J_{H,H}$ = 5.1 Hz, 1 H, C*H*COOEt), 2.98 [ddd, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 5.3, $^3J_{H,H}$ = 1.6 Hz, 1 H, C(2)-H], 3.09−3.14 [m, 1 H, C(6)-H], 3.20 [dd, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 9.1 Hz, 1 H, C(3)-H], 3.30 [br. t, $^3J_{H,H}$ = 9.9 Hz, 1 H, C(4)-H], 3.61 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, C*H*$_2$OH), 3.75 [dd, $^3J_{H,H}$ = 9.9, $^3J_{H,H}$ = 3.8 Hz, 1 H, C(5)-H], 3.97−4.08 (m, 2 H, OC*H*$_2$CH$_3$) ppm. ^{13}C NMR (D_2O): δ = 11.03, 13.64 (NCH$_2$CH$_2$*C*H$_3$, OCH$_2$*C*H$_3$), 22.15 (NCH$_2$*C*H$_2$CH$_3$), 35.15 (*C*H$_2$COOEt), 48.88, 55.20, 55.97, 60.40, 62.28, 69.19, 71.96, 75.32 [C(2), C(3), C(4), C(5), C(6), *C*H$_2$OH, O*C*H$_2$CH$_3$, N*C*H$_2$CH$_2$CH$_3$], 174.9 (C=O) ppm. MS (MALDI-TOF): *m*/*z* = 292 [M + H]$^+$, 314 [M + Na]$^+$, 330 [M + K]$^+$. $C_{13}H_{25}NO_6$ (291.3): calcd. C 53.59, H 8.65, N 4.81; found C 53.80, H 8.00, N 4.99.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-*N*-Butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidin-2-yl)acetate (35): Compound **22** (20 mg, 0.035 mmol) was dissolved in CH_3OH (5 mL); a catalytic amount of $Pd(OH)_2$ and acetic acid (1 mL) were added and then the reaction mixture was stirred under H_2 overnight. The catalyst was filtered through a pad of Celite (eluting with CH_3OH) and then the solvent was evaporated under reduced pressure to afford pure compound **35** (6 mg, 60% yield) as an amorphous solid. ^{1}H NMR (D_2O): δ = 0.75 [t, $^3J_{H,H}$ = 7.0 Hz, 3 H, N(CH$_2$)$_3$C*H*$_3$], 1.10 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, OCH$_2$C*H*$_3$), 1.08−1.22 [m, 2 H, N(CH$_2$)$_2$C*H*$_2$CH$_3$], 1.22−1.52 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.40−2.58 [m, 4 H, C(6)-H, NC*H*$_2$(CH$_2$)$_2$CH$_3$, C*H*$_2$COOEt], 2.78−2.85 [m, 1 H, NC*H*$_2$(CH$_2$)$_2$CH$_3$]], 3.30 [br. t, $^3J_{H,H}$ = 9.6 Hz, 1 H, C(5)-H], 3.39 [t, $^3J_{H,H}$ = 9.6 Hz, 1 H, C(4)-H], 3.62 (dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 5.9 Hz, 1 H, C(3)-H], 3.70−3.80 [m, 3 H, C(2)-H, C*H*$_2$OH], 4.01 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, OC*H*$_2$CH$_3$) ppm. ^{13}C NMR (100.57 MHz, D_2O, 25 °C): δ = 13.53, 13.57 [N(CH$_2$)$_3$*C*H$_3$, OCH$_2$*C*H$_3$], 20.51 [N(CH$_2$)$_2$*C*H$_2$CH$_3$], 28.31 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 50.34, 56.99, 57.27, 57.67, 59.85, 62.49, 68.82, 74.64, 81.34 [C(2), C(3), C(4), C(5), C(6), *C*H$_2$OH, O*C*H$_2$CH$_3$, N*C*H$_2$(CH$_2$)$_2$CH$_3$, *C*H$_2$COOEt], 178.7 (*C*=O) ppm. MS (MALDI-TOF): *m*/*z* = 306 [M + H]$^+$, 328 [M + Na]$^+$. Selected data for the lactonized form **41**: ^{1}H NMR (D_2O): δ = 0.75 [t, $^3J_{H,H}$ = 7.0 Hz, 3 H, N(CH$_2$)$_3$C*H*$_3$], 1.10−1.30 [m, 2 H, N(CH$_2$)$_2$C*H*$_2$CH$_3$], 1.30−1.60 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$-CH$_3$), 2.38−2.54 [m, 3 H, C(6)-H, NC*H*(CH$_2$)$_2$CH$_3$, C*H*COOEt], 2.68−2.78 [m, 2 H, NC*H*(CH$_2$)$_2$CH$_3$, C*H*COOEt], 3.35 [t, $^3J_{H,H}$ = 9.4 Hz, 1 H, C(5)-H], 3.52 [br. t, $^3J_{H,H}$ = 9.2 Hz, 1 H, C(4)-H], 3.75−3.80 (m, 2 H, C*H*$_2$OH), 4.00−4.08 [m, 1 H, C(2)-H], 4.34 [dd, $^3J_{H,H}$ = 8.9, $^3J_{H,H}$ = 8.1 Hz, 1 H, C(3)-H] ppm. MS (MALDI-TOF): *m*/*z* = 282 [M + Na]$^+$.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-(hydroxymethyl)-piperidin-2-yl]acetate (36): Compound **20** (79 mg, 0.14 mmol) was dissolved in degassed CH_2Cl_2 (700 μL). Dimethylbarbituric acid (77 mg, 0.49 mmol, 3.5 equiv.) and $Pd(PPh_3)_4$ (3.2 mg, 2.8 μmol, 0.02 equiv.) were added and the mixture was stirred for 2 h at 35 °C. The solution was neutralized with $NaHCO_3$ (satd. solution) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL) and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **36** (72 mg, 99%) as a colorless oil. $[\alpha]_D^{20} = -29.5$ (c = 0.3, $CHCl_3$). ^{1}H NMR: δ = 1.15 (t, $^3J_{H,H}$ = 7.1 Hz, 1 H, OCH_2CH_3), 2.23 (dd, $^2J_{H,H}$ = 16.4, $^3J_{H,H}$ = 8.7 Hz, 1 H, C*H*CO_2Et), 2.71 (dd, $^2J_{H,H}$ = 16.3, $^3J_{H,H}$ = 3.2 Hz, 1 H, C*H*CO_2Et), 3.01 [ddd, $^3J_{H,H}$ = 9.3, $^3J_{H,H}$ = 9.0, $^3J_{H,H}$ = 3.2 Hz, 1 H, C(2)-H], 3.12 [br. t, $^3J_{H,H}$ = 9.0 Hz, 1 H, C(3)-H], 3.22−3.30 [m, 1 H, C(6)-H], 3.62 [t, $^3J_{H,H}$ = 9.3 Hz, 1 H, C(4)-H], 3.68 [dd, $^3J_{H,H}$ = 9.3, $^3J_{H,H}$ = 5.8 Hz, 1 H, C(5)-H], 3.72 (br. d, $^3J_{H,H}$ = 7.9 Hz, 2 H, CH_2OH), 4.02 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, O$CH_2$$CH_3$), 4.48 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.58 (s, 2 H, CH_2Ph), 4.69 (d, $^2J_{H,H}$ = 10.7 Hz, 1 H, C*H*Ph), 4.82 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.83 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, C*H*Ph), 7.13−7.43 (m, 15 H, HAr) ppm. ^{13}C NMR: δ = 14.64 (OCH_2CH_3), 36.67 (CH_2CO_2Et), 50.18, 54.95 [C(2), C(6)], 58.41, 61.17 (CH_2OH, OCH_2CH_3), 73.19, 75.43, 75.91 (3 CH_2Ph), 81.62, 82.49, 83.61 [C(3), C(4), C(5)], 127.9−132.3 (*C*HAr), 138.2, 138.3, 138.7 (3 *C*qAr), 172.5 (*C*=O) ppm. MS (MALDI-TOF): m/z = 521 [M + H]$^+$, 543 [M + Na]$^+$, 559 [M + K]$^+$. $C_{31}H_{37}NO_6$ (519.6): calcd. C 71.65, H 7.18, N 2.70; found C 71.31, H 6.99, N 2.90.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-6-(hydroxymethyl)-piperidin-2-yl]acetate (37): The reaction was carried out as described for the preparation of **36**, starting from **21** (15 mg, 0.027 mmol) to afford **37** (14 mg, 100%) as a colorless oil. $[\alpha]_D^{20}$ = −9.4 (c = 1.0, $CHCl_3$). ^{1}H NMR: δ = 1.15 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 2.50 (dd, $^2J_{H,H}$ = 16.1, $^3J_{H,H}$ = 10.2 Hz, 1 H, C*H*CO_2Et), 2.63 (dd, $^2J_{H,H}$ = 16.1, $^3J_{H,H}$ = 4.01 Hz, 1 H, C*H*CO_2Et), 2.78−2.84 [m, 1 H, C(6)-H], 3.29 [br. t, $^3J_{H,H}$ = 9.0 Hz, 1 H, C(5)-H], 3.52−3.63 [m, 4 H, C(3)-H, C(4)-H, CH_2OH], 3.68−3.73 [m, 1 H, C(2)-H], 3.98−4.70 (m, 2 H, OCH_2CH_3), 4.53 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.56 (s, 2 H, CH_2Ph), 4.68 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 4.82 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, C*H*Ph), 4.83 (d, $^2J_{H,H}$ = 10.9 Hz, 1 H, C*H*Ph), 7.13−7.43 (m, 15 H, C*H*Ar) ppm. ^{13}C NMR: δ = 14.64 (OCH_2CH_3), 30.15 (CH_2CO_2Et), 51.09, 55.05 [C(2), C(6)], 60.97, 62.89 (CH_2OH, OCH_2CH_3), 72.91, 75.32, 75.69 (3 CH_2Ph), 79.51, 80.80, 82.72 [C(3), C(4), C(5)], 127.9−132.3 (*C*HAr), 138.3, 138.4, 138.8 (3 *C*qAr), 172.7 (*C*=O) ppm. MS (MALDI-TOF): m/z = 521 [M + H]$^+$, 543 [M + Na]$^+$, 559 [M + K]$^+$. $C_{31}H_{37}NO_6$ (519.6): calcd. C 71.65, H 7.18, N 2.70; found C 71.30, H 7.05, N 2.88.

Ethyl [(2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-Trihydroxy-6-(hydroxymethyl)piperidin-2-yl]acetate (38): Compound **36** (24 mg, 0.046 mmol) was dissolved in CH_3OH (4 mL); a catalytic amount of $Pd(OH)_2$ and acetic acid (1 mL) were added and the reaction mixture was stirred under H_2 overnight. The catalyst was filtered through a Celite pad (eluent CH_3OH) and then the solvent was evaporated under reduced pressure to afford pure compound **38** (10 mg, 87% yield) as an amorphous solid. Compound **38** exists as a mixture of two conformers: $[\alpha]_D^{20} = -40.1$ (c = 1.0, H_2O). ^{1}H NMR (D_2O): δ = 1.10 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 2.28−2.52 (m, 1 H, C*H*COOEt), 2.62−2.75 (m, 1 H, C*H*COOEt), 2.96−3.12 [m, 2 H, C(2)-H, C(6)-H], 3.16−3.24 [m, 1 H, C(3)-H], 3.36 [t, $^3J_{H,H}$ = 8.8 Hz, 1 H, C(5)-H], 3.58−3.70 [m, 2 H, C*H*OH, C(4)-H], 3.75−3.88 (m, 1 H, C*H*OH), 3.97−4.60 (m, 2 H, OCH_2CH_3) ppm. ^{13}C NMR (D_2O): δ = 13.57, 13.59 (OCH_2CH_3), 35.47, 36.81 (CH_2COOEt), 50.62, 55.71, 56.27, 57.16, 57.43, 62.32, 66.55, 69.56, 71.02, 72.47, 73.88, 74.18, 74.29 [C(2), C(3), C(4), C(5), C(6), CH_2OH, OCH_2CH_3], 173.7, 174.3 (*C*=O) ppm. MS (MALDI-TOF): m/z = 250 [M + H]$^+$, 272 [M + Na]$^+$. $C_{10}H_{19}NO_6$ (249.3): calcd. C 48.19, H 7.68, N 5.62; found C 47.95, H 7.81, N 5.39.

Ethyl [(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Trihydroxy-6-(hydroxymethyl)piperidin-2-yl]acetate (39): Compound **37** (36 mg, 0.069 mmol) was dissolved in CH_3OH (5 mL); a catalytic amount of $Pd(OH)_2$ and acetic acid (1 mL) were added and the reaction mixture was stirred under H_2 overnight. The catalyst was filtered through a Celite pad (eluent CH_3OH) and then the solvent was evaporated under reduced pressure to afford pure compound **39** (17 mg, 98% yield) as an amorphous solid. $[\alpha]_D^{20} = 0.0$ (c = 0.8, H_2O). Major conformer: ^{1}H NMR (D_2O): δ = 1.10 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH_2CH_3), 2.57 (dd, $^2J_{H,H}$ = 17.4, $^3J_{H,H}$ = 8.2 Hz, 1 H, C*H*COOEt), 2.91 (dd, $^2J_{H,H}$ = 17.4, $^3J_{H,H}$ = 3.7 Hz, 1 H, C*H*COOEt), 3.29 [br. t, $^3J_{H,H}$ = 9.2 Hz, 1 H, C(3)-H], 3.45−3.62 [m, 3 H, C(2)-H, C(4)-H, C(5)-H], 3.70−3.80 [m, 3 H, CH_2OH, C(6)-H], 4.03 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OCH_2CH_3) ppm. ^{13}C NMR (D_2O): δ = 13.52 (OCH_2CH_3), 34.18 (CH_2COOEt), 51.11, 55.22, 56.87, 62.72, 68.79, 71.45, 72.60 [C(2), C(3), C(4), C(5), C(6), CH_2OH, OCH_2CH_3], 172.3 (*C*=O) ppm. MS (MALDI-TOF): m/z = 250 [M + H]$^+$, 272 [M + Na]$^+$. $C_{10}H_{19}NO_6$ (249.3): calcd. C 48.19, H 7.68, N 5.62; found C 48.02, H 7.94, N 5.45.

[(2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-Trihydroxy-6-(hydroxymethyl)-1-propyl-piperidin-2-yl]acetic Acid (40): Compound **18b** (100 mg, 0.161 mmol) was dissolved in CH_3OH/CH_2Cl_2 (5:3, 8 mL); a catalytic amount of $Pd(OH)_2$ and acetic acid (1 mL) were added and the reaction mixture was stirred under H_2 overnight. The catalyst was filtered through a pad of Celite (eluent CH_3OH) and then the solvent was evaporated under reduced pressure to afford pure compound **40** (17 mg, 98% yield) as an amorphous solid. $[\alpha]_D^{20} = -62.5$ (c = 0.4, H_2O). ^{1}H NMR (D_2O): δ = 0.83 [t, $^3J_{H,H}$ = 7.0 Hz, 3 H, $N(CH_2)_3CH_3$], 1.45−1.59 [m, 1 H, NCH_2CHCH_3], 1.60−1.73 [m, 1 H, $NCH_2CH_2CH_3$], 2.50−2.61 (m, 1 H, C*H*COOH), 2.70−2.81 (m, 1 H, C*H*COOH), 2.92−3.07 (m, 1 H, N*CH*CH_2CH_3), 3.09−3.29 (m, 1 H, N*CH*CH_2CH_3), 3.43−3.64 [m, 3 H, C(2)-H, C(5)-H, C(6)-H], 3.74−3.98 [m, 4 H, C(3)-H, C(4)-H, CH_2OH] ppm. ^{13}C NMR (D_2O): δ = 9.94 [$N(CH_2)_2CH_3$], 19.12 ($NCH_2CH_2CH_3$), 32.00 (CH_2COOH), 49.07, 54.62, 56.98, 61.62, 66.49, 68.68, 73.38 [C(2), C(3), C(4), C(5), C(6), CH_2OH, $NCH_2CH_2CH_3$], 177.0 (*C*=O) ppm. MS (MALDI-TOF): m/z = 264 [M + H]$^+$, 286 [M + Na]$^+$. $C_{11}H_{21}NO_6$ (263.3): calcd. C 50.18, H 8.04, N 5.32; found C 50.46, H 8.34, N 5.50.

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