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ORIGINAL PAPER

# Addition of allylzinc to α-amino acid-derived imines: synthesis of diamino alcohols by hydroboration

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**Abstract** Imines obtained by condensation of Z-protected or Boc-protected α-amino aldehydes with α-amino *tert*-butyl esters or with *O*-silyl-protected amino alcohols were reacted with preformed allyl zinc yielding homoallylamines with yields around 50% and selectivities ranging from 50:50 to 90:10. Hydroboration of the terminal double bond furnished diamino alcohols with yields up to 97%. The configuration of the substrates was determined by X-ray-crystallographic analysis of a hydroboration product and comparison of physical data.

**Keywords** Amino acids · Schiff bases · Allyl addition · Nucleophilic additions · Amino alcohols

## Introduction

Amino acids have widely been used as starting materials in stereoselective synthesis [1]. Astonishingly, this pool of chiral substances [2, 3] has never been used for addition of C-nucleophiles to amino acid-derived α-amino imines (Scheme 1), most probably because of the rather poor reactivity of imines as compared with, e.g., aldehydes [4]. Similarly reactive α-amino hydrazones [5, 6] and α-amino nitrones [7–9, and references cited therein] have been used occasionally in the addition of C-nucleophiles. The addition of cyanide to α-amino imines has been reported once [10].

In the course of our studies on the synthesis of peptidomimetics [11–17] we needed allyl adducts to α-amino imines and the resulting alcohols obtained by subsequent hydroboration. Here we report the synthesis of these compounds, which should be useful starting materials in organic synthesis.

## Results and discussion

### *Preparation of α-amino acid-derived imines*

We decided to use *N*-Boc (*tert*-butyloxycarbonyl)-protected and *N*-Z (benzyloxycarbonyl)-protected α-amino acids as starting materials to enable deprotection of the compounds obtained by standard procedures [18]. *N*-Protected amino aldehydes used for the preparation of imines were obtained via two routes (Scheme 2). Route A was used for the preparation of Z-protected products [18] and included protection, esterification [19], and reduction of thus obtained Z-protected amino esters with lithium aluminum hydride [20]. In route B we started with reduction of an α-amino acid yielding an amino alcohol [21] and subsequent *N*-protection with Boc [22] or Z [23]. Route A proved to be more effective, because fewer by-products were obtained during this three-step procedure and chromatographic purification of the protected amino alcohols was often dispensable. In both routes a final oxidation with either Dess–Martin periodinane [24] or with sodium hypochlorite and catalytic amounts of 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) [25] furnished *N*-protected amino aldehydes with yields ranging from 50 to 80%.

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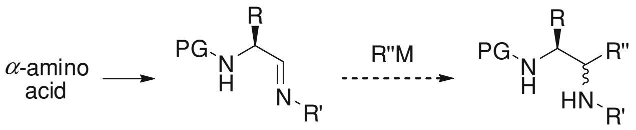
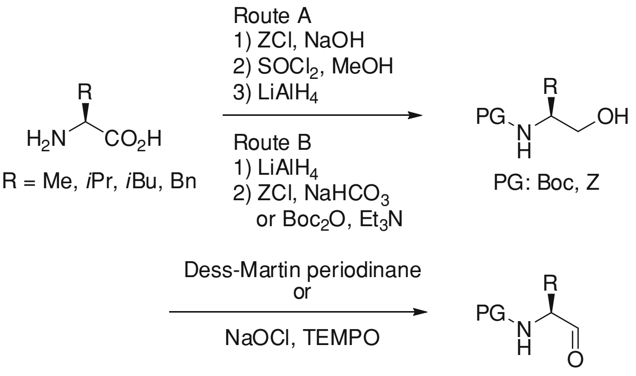


**Scheme 1**



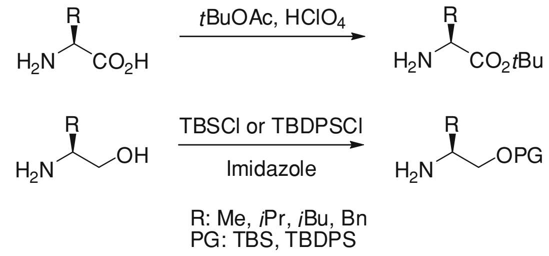
**Scheme 2**

Amino components used for the preparation of imines were similarly prepared from α-amino acids (Scheme 3). Amino acid *tert*-butyl esters were obtained by transesterification with *tert*-butyl acetate [26] and *O*-silyl-protected amino alcohols were obtained by silylation of amino alcohols with *tert*-butyldimethylsilyl chloride (TBSCl) or *tert*-butyldiphenylsilyl chloride (TBDPSCl) [27].

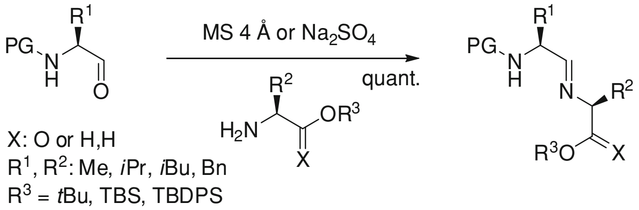
Imines were obtained by mixing stoichiometric amounts of an aldehyde and an amine component together with either molecular sieves (4 Å) or with anhydrous sodium sulfate (Scheme 4).

### *Addition of organozinc compounds to amino acid-derived imines*

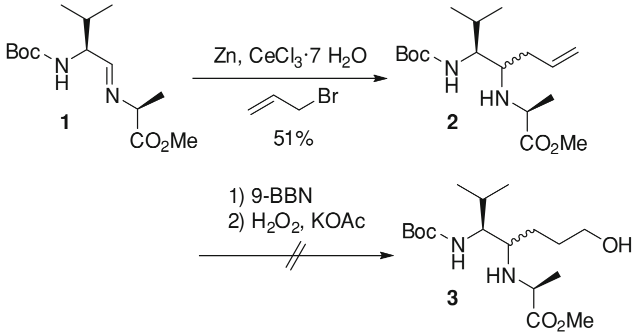
When we applied a method reported by Bocoum et al. [28], in which a mixture of imine **1** and allyl bromide was added to a suspension of zinc and cerium chloride ($CeCl_3 \cdot 7H_2O$) in tetrahydrofuran at 0 °C, no consumption of the zinc and no reaction was observed. But when we added imine **1** at 0 °C to a preformed organozinc compound obtained by reaction of allyl bromide with zinc and cerium chloride, a 51% yield of the homoallylamine was obtained (Scheme 5). In this variation it was mandatory to keep the reaction temperature for the formation of the organozinc compound below 20 °C to prevent decomposition of the reagent. Oxidative work-up in the subsequent hydroboration of alkene **2** had to be performed without sodium hydroxide, to prevent saponification of the methyl ester. Nevertheless, utilization of potassium acetate as base [29] did not prove reactive enough to achieve formation of the terminal alcohol **3**.



**Scheme 3**



**Scheme 4**



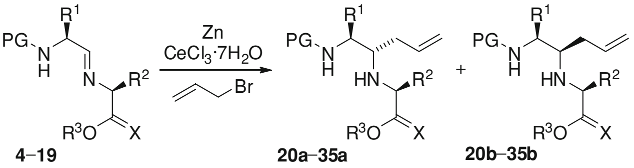
**Scheme 5**

To obtain compounds suitable for a hydroboration by an oxidative workup in the presence of sodium hydroxide we used either *tert*-butyl ester derivatives or silyl-protected amino alcohol-derived imines **4**–**19** in further experiments.

Allyl addition under conditions as applied to the methyl ester **1** gave homoallylamines **20**–**35** (Table 1) as mixtures of isomers, which could be separated by conventional chromatography except for product **35**. The allyl adducts were obtained in yields up to 66%, where differing amounts of side products were observed. Small amounts (up to 30%) of homoallylalcohols **36** resulted from allyl addition to amino aldehydes present, because of partial imine hydrolysis during the reaction. Degradation products were observed after imine formation in up to 10% yield.

Products **37** and **38** given in Fig. 1 resulted after attempted condensation of Z-leucinal and valine *tert*-butyl ester. These compounds were unambiguously identified by comparison with published spectra [30]. A similar reaction has previously been reported by Lethinen and Brunow [31]; no explanation or mechanism was

**Table 1** Allyl addition to α-amino acid-derived imines



| No. | Imine | PG | R$^1$ | R$^2$ | X | R$^3$ | Product[a] | Yield (%) | d.r.[b] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **4** | Boc | *i*Pr | Me | H,H | TBS | **20a, 20b** | 48 | 70:30[c] |
| 2 | **5** | Z | *i*Bu | Me | H,H | TBDPS | **21a, 21b** | 27 | 60:40[d] |
| 3 | **6** | Z | *i*Pr | Me | H,H | TBDPS | **22a, 22b** | 59 | 90:10[d] |
| 4 | **7** | Boc | *i*Pr | *i*Pr | H,H | TBDPS | **23a, 23b** | 57 | 43:57[c] |
| 5 | **8** | Boc | *i*Pr | Bn | H,H | TBS | **24a, 24b** | 44 | 53:47[d,e] |
| 6 | **9** | Z | *i*Bu | Bn | H,H | TBS | **25a, 25b** | 55 | n.d.[f] |
| 7 | **10** | Z | *i*Bu | Me | H,H | TBS | **26a, 26b** | 32 | 66:34 |
| 8 | **11** | Z | *i*Pr | Me | H,H | TBS | **27a, 27b** | 36 | n.d.[f] |
| 9 | **12** | Z | *i*Pr | *i*Bu | H,H | TBS | **28a, 28b** | 50 | 65:35[c] |
| 10 | **13** | Z | *i*Bu | *i*Pr | O | *t*Bu | **29a, 29b** | 38 | 37:63[c] |
| 11 | **14** | Z | *i*Pr | Me | O | *t*Bu | **30a, 30b** | 66 | 80:20[d] |
| 12 | **15** | Z | *i*Pr | *i*Bu | O | *t*Bu | **31a, 31b** | 40 | 37:63[d] |
| 13 | **16** | Z | *i*Bu | Bn | O | *t*Bu | **32a, 32b** | 49 | 47:53[d] |
| 14 | **17** | Z | *i*Pr | *i*Pr | O | *t*Bu | **33a, 33b** | 31 | 49:51[d] |
| 15 | **18** | Z | *i*Pr | Bn | O | *t*Bu | **34a, 34b** | 64 | 87:13[d] |
| 16 | **19** | Z | Me | *i*Bu | O | *t*Bu | **35a, 35b** | 33 | 67:33[c,g] |

[a] Conditions: Zn (2 eq.), $CeCl_3·7H_2O$ (0.1 eq.), allyl bromide (1.9 eq.), THF, 0 °C to r.t., overnight

[b] Assignment of the stereoisomers was made on the basis of retention times, optical rotation, and NMR spectroscopic data

[c] Determination of diastereomeric ratio by NMR spectroscopy

[d] Determination of diastereomeric ratio by HPLC

[e] Configuration unambiguously determined by X-ray crystallographic analysis of subsequent product **44a** (53:47 *S*:*R*)

[f] Diastereomeric ratio could not be determined

[g] Not separable by chromatography. Assignment of configuration was not possible

given for this reaction. To prevent this side reaction several dehydrating agents (sodium sulfate, alumina, molecular sieves) were tested and the reaction was performed with strict exclusion of oxygen and light, but its appearance could not be prevented.

Diastereoselectivities in the allyl addition ranged from 50:50 to 90:10. In the reactions of amino alcohol derivatives **4–12** the best selectivities were obtained for alanine-derived substrates (entries 1–3 and 7), whereas bulkier side chains led to reduced selectivities. No general trend was observed for *tert*-butyl ester derivatives **13–19**.

Assignment of the isomers was accomplished on the basis of tendencies in the retention times (thin-layer chromatography), in optical rotation, and in NMR spectroscopic data (Table 2). Generally, the isomer eluting first has a significantly lower optical rotation, generally a smaller vicinal coupling constant (${}^3J$) between hydrogen atoms 4′-H and 5′-H, and a somewhat lower shift for C-4′. The relative configuration of the isomers was assigned with the help of these data and because of unambiguous assignment of the configuration in isomer **24a** obtained after X-ray crystallographic analysis of its derivative **44a** (vide infra) suggesting a 4′*S* configuration for isomers **20–34a**.

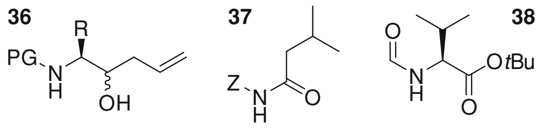


**Fig. 1** Side products observed during allyl addition and imine formation

The best results in the allyl additions were obtained at 0 °C. Selectivities in the allyl addition to aldimine **14** (c.f. Table 1, entry 11) dropped from 80:20 at 0 °C to 60:40 at −78 °C, whereas yields were essentially the same. The effect of Lewis acids and other additives on the outcome of the reaction was tested (Table 3). Allyl addition to imine **17** gave a poor 47:53 selectivity without Lewis acid. Selectivities and yields did not improve significantly in the presence of $CeCl_3·7H_2O$, $Sm(OTf)_3$, or $ZnCl_2$. Addition of Schreiner's catalyst **39** (Fig. 2) [32–34, and references cited therein] as a hydrogen bond donor led to a comparable 50:50 selectivity and a slightly improved 56% yield. Nevertheless, the reactions were performed in the presence of cerium chloride despite the reduced yields, because the allylzinc reagent was preferentially obtained with this salt present.

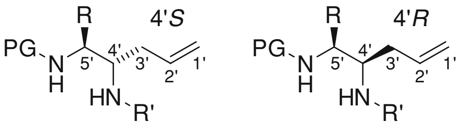
Permutation of both amino acid moieties' configurations revealed an insignificant match–mismatch interaction (Scheme 6). The selectivities, if any, seem to be ruled by the stereogenic centres in the amino ester-based moiety.

### *Hydroboration of homoallylamines*

Hydroboration of homoallylamines **20–35** with 9-borabicyclo[3.3.1]nonane (9-BBN) and subsequent oxidative work-up [35] furnished terminal alcohols **42–52** with high regioselectivities [36] and with good yields (Scheme 7, Table 4).

Compound **35** was carried on as a mixture of isomers, although only one isomer of the alcohol **52a** was isolated after transformation and chromatography (entry 14). The structure of diamino alcohol **44a** was determined by X-ray-crystallographic analysis (Fig. 3, Table 5) giving further unambiguous evidence for the structure of alkene **24a**.

**Table 2** Assignment of isomers according to physical data



| Compound | Config. C-4′ | $[\alpha]^{20}_{D}$ ($10^{-1}$ deg cm$^2$ g$^{-1}$) | $R_f^a$ | $^1$H NMR $^3J_{4'-5'}$ (Hz) | $^{13}$C NMR $\delta$ (C-4′) (ppm) |
|---|---|---|---|---|---|
| **20a** | *S* | −3.8 | 0.44 | 1.7 | 54.3 |
| **20b** | *R* | +16.1 | 0.35 | 2.1 | 54.7 |
| **21a** | *S* | −6.5 | 0.41 | 1.8 | n.d. |
| **21b** | *R* | +18.5 | 0.36 | 2.0 | n.d. |
| **22a** | *S* | −7.8 | 0.37 | 1.6 | n.d. |
| **22b** | *R* | +20.0 | 0.30 | 1.7 | n.d. |
| **23a** | *S* | −17.3 | 0.52 | 1.6 | n.d. |
| **23b** | *R* | −1.9 | 0.52 | 2.4 | 54.7 |
| **24a** | *S*[b] | −40.6 | 0.44 | 1.7 | 54.6 |
| **24b** | *R* | +4.0 | 0.35 | n.d. | 55.7 |
| **25a** | *S* | −18.0 | 0.53 | 1.7–2.2 | 57.6 |
| **25b** | *R* | +17.6 | 0.43 | 3.2 | 58.2 |
| **26a** | *S* | −4.6 | 0.45 | 1.8 | 57.4 |
| **26b** | *R* | +37.9 | 0.35 | n.d. | 57.5 |
| **27a** | *S* | −1.1 | 0.26 | 2.0 | 54.5 |
| **27b** | *R* | +19.7 | 0.15 | n.d. | 55.7 |
| **28a** | *S* | −10.9 | 0.51 | 1.5 | 54.2 |
| **28b** | *R* | +14.3 | 0.37 | n.d. | 55.7 |
| **29a** | *S* | −31.6 | 0.44 | 1.9 | 58.9 |
| **29b** | *R* | ±0.0 | 0.40 | 3.1 | 60.1 |
| **30a** | *S* | −27.8 | 0.33 | 1.5 | 55.4 |
| **30b** | *R* | −1.0 | 0.15 | 4.2 | 55.7 |
| **31a** | *S* | −31.9 | 0.43 | 1.4 | 55.6 |
| **31b** | *R* | −8.8. | 0.30 | 4.3 | 56.1 |
| **32a** | *S* | −15.6 | 0.41 | 1.6 | 58.7 |
| **32b** | *R* | +8.5 | 0.34 | 3.3 | 59.8 |
| **33a** | *S* | −28.5 | 0.47 | 1.5 | 55.9 |
| **33b** | *R* | −7.0 | 0.38 | 4.3 | 56.6 |
| **34a** | *S* | −43.2 | 0.33 | 1.5 | 55.6 |
| **34b** | *R* | −21.3 | 0.15 | 5.7 | 57.3 |
| **35a** | *S* | n.d. | 0.41 | n.d. | n.d. |
| **35b** | *R* | n.d. | 0.41 | n.d. | n.d. |

Numbering differs in the respective compounds

n.d., not determined

[a] Retention factor: Eluent *n*-hexane–AcOEt, 6:1

[b] Unambiguously assigned by X-ray-crystallographic analysis of derivative **44a**

**Table 3** Allyl addition in the presence of additives

| No. | Additive | Yield (%) | d.r.[a] |
|---|---|---|---|
| 1 | – | 49 | 47:53 |
| 2 | $CeCl_3 \cdot 7H_2O$ | 31 | 49:51 |
| 3 | $Sm(OTf)_3$ | 53 | 48:52 |
| 4 | $ZnCl_2$ | 51 | 50:50 |
| 5 | **39** | 56 | 50:50 |

Allyl addition to imine **17**; Further conditions as given in Table 1

[a] Determination of diastereomeric ratio by HPLC

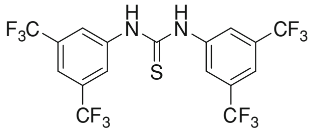
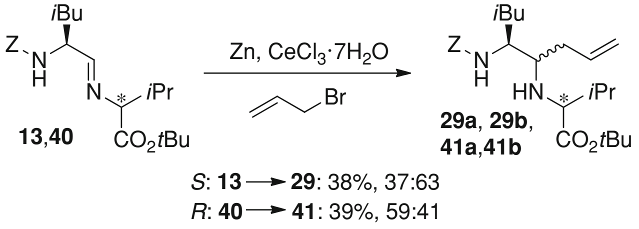
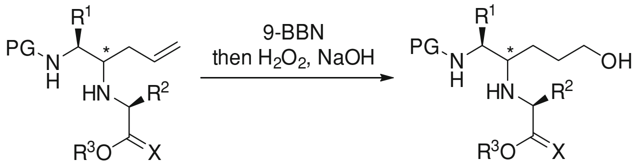


**Fig. 2** Schreiner's catalyst **39** used as hydrogen bond donor



**Scheme 6**



**Scheme 7**

## Conclusion

Allyl addition to α-amino acid-derived imines using organozinc compounds, a type of reaction not published before, has been achieved with reasonable yields and selectivities up to 90:10. The thus obtained homoallylamines were transformed, by hydroboration, to diamino alcohols bearing a terminal hydroxy function. These highly functionalized substrates have been used in the preparation of peptidomimetics. These investigations will be reported elsewhere.

## Experimental

Tetrahydrofuran (THF) and $Et_2O$ were distilled from sodium benzophenone ketyl radical; $CH_2Cl_2$ was distilled from $CaH_2$. Abbreviations: TBS, *tert*-butyldimethylsilyl; TBDPS, *tert*-butyldiphenylsilyl; 9-BBN, 9-borabicyclo[3.3.1] nonane; TEMPO, tetramethylpiperidine-*N*-oxide. All moisture-sensitive reactions were carried out under oxygen-free argon or $N_2$ using oven-dried glassware and a vacuum line.

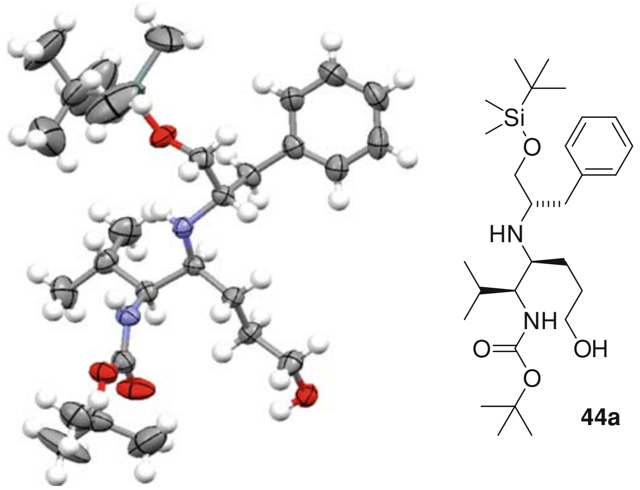
**Table 4** Synthesis of diamino alcohols by hydroboration

| No. | Alkene | PG | $R^1$ | $R^2$ | X | $R^3$ | Product | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | **20a** | Boc | *i*Pr | Me | H,H | TBS | **42a** | 87 |
| 2 | **22a** | Z | *i*Pr | Me | H,H | TBDPS | **43a** | 97 |
| 3 | **24a** | Boc | *i*Pr | Bn | H,H | TBS | **44a** | 83 |
| 4 | **25a** | Z | *i*Bu | Bn | H,H | TBS | **45a** | 79 |
| 5 | **25b** | Z | *i*Bu | Bn | H,H | TBS | **45a** | 81 |
| 6 | **27a** | Z | *i*Pr | Me | H,H | TBS | **46a** | 89 |
| 7 | **30b** | Z | *i*Pr | Me | O | *t*Bu | **47b** | 62 |
| 8 | **31a** | Z | *i*Pr | *i*Bu | O | *t*Bu | **48a** | 94 |
| 9 | **31b** | Z | *i*Pr | *i*Bu | O | *t*Bu | **48b** | 84 |
| 10 | **32a/32b**[a] | Z | *i*Bu | Bn | O | *t*Bu | **49a**, **49b**[b] | 52 |
| 11 | **33b** | Z | *i*Pr | *i*Pr | O | *t*Bu | **50b** | 71 |
| 12 | **34a** | Z | *i*Pr | Bn | O | *t*Bu | **51a** | 73 |
| 13 | **34b** | Z | *i*Pr | Bn | O | *t*Bu | **51b** | 94 |
| 14 | **35a** | Z | Me | *i*Bu | O | *t*Bu | **52a**[c] | 64 |

[a] As a mixture of isomers

[b] Isomers could be separated

[c] Only one isomer was obtained after purification by chromatography



**44a**

**Fig. 3** Structure of **44a** in the crystal

Flash column chromatography [37] was carried out using Merck silica gel 60 (230–400 mesh), and thin-layer chromatography (TLC) was carried out using commercially available Merck $F_{254}$ pre-coated sheets. Medium-pressure liquid chromatography (MPLC): Pump (Labomatic MD-50), detection by UV absorption (Latek UVIS 200); Merck LiChroprep Si 60 (15–25 $\mu$m). HPLC: Analyses of diastereoisomer distributions were carried out with a Merck-Hitachi LaChrom D7000 apparatus with a L7100 mixer and diode-array detection (L7455) on a Merck LiChrospher Si 60 chromatographic column (5 $\mu$m, flow: 1–1.5 $cm^3\ min^{-1}$). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Cryospek WM-250, an AM-400, or a DRX 500. Chemical shifts are given in ppm downfield of tetramethylsilane. $^{13}$C NMR spectra were recorded with broadband proton decoupling and were assigned using DEPT 135 and DEPT 90 experiments. Melting points were measured on a Büchi apparatus. IR spectra were recorded on a Bruker IFS-88 spectrometer. Elemental analyses were performed on a Heraeus CHN–O-rapid or on an elementar vario MICRO and were in good agreement with calculated values. Electron-impact high-resolution mass spectra were recorded on a Finnigan MAT-90. Optical rotations were recorded on a Perkin Elmer 241 polarimeter (using the sodium D line, 589 nm) and specific optical rotations [α] are given in units of $10^{-1}$ deg $cm^2$ $g^{-1}$.

### *Allyl additions*

#### General procedure (GP 1) for preparation of amino alcohols

The amino acid (1.00 mmol) was added in portions at 0 °C to a suspension of 57 mg $LiAlH_4$ (1.50 mmol) in 10 $cm^3$ anhydrous $Et_2O$ and the mixture was heated to reflux for 3 h. The reaction was stopped by careful addition of 1.50 $cm^3$ $H_2O$, 1.50 $cm^3$ aqueous NaOH (3 M), and 4.50 $cm^3$ $H_2O$ at 0 °C with vigorous stirring. The obtained suspension was stirred for 1 h and filtered. The filtrate was dried ($Na_2SO_4$), concentrated, and purified by distillation or recrystallization.

#### General procedure (GP 2) for preparation of *N*-Z-protected amino alcohols

Benzyl chloroformate (148 $mm^3$, 1.05 mmol) was added at 0 °C to a mixture of amino alcohol (1.00 mmol), 5 $cm^3$ $CH_2Cl_2$, and 5 $cm^3$ aqueous saturated $NaHCO_3$ solution. The mixture was stirred for 3 h at room temperature and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 10 $cm^3$). The combined organic layers were dried ($Na_2SO_4$), concentrated, and purified by distillation or recrystallization.

#### General procedure (GP 3) for preparation of *N*-Boc-protected amino alcohols

$Boc_2O$ (229 mg, 1.05 mmol) was added at 0 °C to a solution of amino alcohol (1.00 mmol) and 153 $mm^3$ $Et_3N$ (1.10 mmol) in 10 $cm^3$ THF. The mixture was stirred for 18 h at room temperature and the solvent was removed. The residue was diluted in 50 $cm^3$ EtOAc and the solution was washed with 25 $cm^3$ $H_2O$ and 25 $cm^3$ brine, dried ($Na_2SO_4$), concentrated, and purified by column chromatography (silica gel).

#### General procedure (GP 4) for preparation of *O*-TBS-protected or *O*-TBDPS-protected amino alcohols

TBSCl (301 mg, 2.00 mmol) or TBDPSCl (550 mg, 2.00 mmol) was added portionwise at 0 °C to a mixture

**Table 5** Crystal data and structure refinement for *tert*-butyl (3*S*,4*S*,2′*S*)-4-[1-(*tert*-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate (**44a**)

| | |
|---|---|
| Identification code | pod08 and CCDC-721237 |
| Empirical formula | $C_{28}H_{52}N_2O_4Si$ |
| Formula weight | 508.81 g $mol^{-1}$ |
| Temperature | 203(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | *P*21 |
| Unit cell dimensions | $a = 11.433(2)$ Å, $\alpha = 90^\circ$<br>$b = 9.824(2)$ Å, $\beta = 108.80(3)^\circ$<br>$c = 15.575(3)$ Å, $\gamma = 90^\circ$ |
| Volume, *Z* | 1,656.0(6) $Å^3$, 2 |
| Density (calculated) | 1.020 Mg $m^{-3}$ |
| Absorption coefficient | 0.101 $mm^{-1}$ |
| *F*(000) | 560 |
| Crystal size | 0.4 × 0.06 × 0.08 $mm^3$ |
| $2\Theta_{max}$ | 48.02° |
| Limiting indices | $-13 \le h \le 13, -10 \le k \le 10, -17 \le l \le 17$ |
| Reflections collected | 9,579 |
| Independent reflections | 4,969 [*R*(int) = 0.0540] |
| Refinement method | Full-matrix least squares on $F^2$ |
| Data/restraints/parameters | 4,969/1/328 |
| Goodness-of-fit on $F^2$ | 0.958 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0468$, $\omega R_2 = 0.0911$ |
| *R* indices (all data) | $R_1 = 0.0933$, $\omega R_2 = 0.1078$ |
| Largest diff. peak and hole (e/$Å^3$) | 0.15 and −0.17 |
| Structure solution SHELXS-97 | [38] |
| Structure refinement SHELXL-97 | [38] |

Details of the crystallographic analysis of *tert*-butyl (3*S*,4*S*,2′*S*)-4-[1-(*tert*-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate (**44a**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-721237. Data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)

of amino alcohol (1.00 mmol) and 150 mg imidazole (2.20 mmol) in 20 $cm^3$ $CH_2Cl_2$. The mixture was stirred overnight at room temperature and the reaction was stopped by addition of 10 $cm^3$ aqueous saturated $NaHCO_3$ solution. The aqueous layer was extracted with $CH_2Cl_2$ (2 × 20 $cm^3$). The combined organic layers were dried ($Na_2SO_4$), concentrated, and purified by column chromatography (silica gel).

### General procedure (GP 5) for preparation of amino acid *tert*-butyl esters

$HClO_4$ (70%, 3.60 $cm^3$, 15.0 mmol) was added slowly at 0 °C to a suspension of the amino acid (10.0 mmol) in 24 $cm^3$ AcO*t*Bu. The mixture was stirred for 24 h at room temperature, diluted with $H_2O$, and brought to pH 12 by careful addition of $K_2CO_3$. The aqueous layers were extracted with $Et_2O$ (2 × 50 $cm^3$) and the combined organic layers were washed with brine, dried ($Na_2SO_4$), concentrated, and used without further purification.

### General procedure (GP 6) for preparation of *N*-protected amino aldehydes

*Variation A:* 530 mg Dess–Martin periodinane (1.25 mmol) was added to a solution of the *N*-protected amino alcohol (1.00 mmol) in 10 $cm^3$ $CH_2Cl_2$. The mixture was stirred for 2–4 h (monitoring with TLC) and further periodinane was added if necessary. A solution of 1 g $NaHCO_3$ and 1 g $Na_2S_2O_3$ in 15 $cm^3$ $H_2O$ was added at room temperature with vigorous stirring and stirring was continued for 45 min. The aqueous layer was extracted with $CH_2Cl_2$ (2 × 10 $cm^3$) and the combined organic layers were washed with 20 $cm^3$ brine, dried ($Na_2SO_4$), concentrated, and used without purification.

*Variation B:* An aqueous solution of 0.71 $cm^3$ NaOCl (1.14 mmol) and 252 mg $NaHCO_3$ (3.00 mmol) was added at 0 °C within 1–2 h to a mixture of the *N*-protected amino alcohol (1.00 mmol), 108 mg NaBr (1.00 mmol), and 0.39 mg TEMPO (0.02 mmol) in 3 $cm^3$ toluene, 3 $cm^3$ EtOAc, and 0.5 $cm^3$ $H_2O$. The aqueous layer was extracted with $Et_2O$ (2 × 5 $cm^3$) and the organic layers were washed successively with 8 mg KI in 2 $cm^3$ 10% $KHSO_4$ solution, with 1 $cm^3$ 10% $Na_2S_2O_3$ solution, and with 2 $cm^3$ brine. Drying ($Na_2SO_4$) and concentration yielded the aldehyde, which was used without purification.

### General procedure (GP 7) for preparation of amino acid-derived imines

The amino acid-derived amine (1.00 mmol) was added to a mixture of the *N*-protected amino aldehyde (1.00 mmol), 500 mg molecular sieves (4 Å), and 10 $cm^3$ $CH_2Cl_2$. After stirring for 3 h at room temperature, filtration, and concentration, a crude product was obtained, which was used without purification.

### General procedure (GP 8) for allyl addition to amino acid-derived imines

Allyl bromide (165 $mm^3$, 1.90 mmol) was added slowly at 0 °C under an argon atmosphere to a suspension of 130 mg Zn (2.00 mmol) and 37 mg $CeCl_3 \cdot 7H_2O$ (0.10 mmol) in 3 $cm^3$ anhydrous THF. Stirring was continued for 30–60 min at 0 °C until complete consumption of the zinc and a solution of the aldimine in 3 $cm^3$ anhydrous THF was added slowly. The mixture was warmed to room temperature, stirred for 15 h, and the reaction was stopped by addition of 904 mg $Na_4EDTA \cdot 4H_2O$ (2.00 mmol) in 10 $cm^3$ $H_2O$. The mixture was extracted with $Et_2O$ (4 × 10 $cm^3$). The combined organic layers were washed with 25 $cm^3$ brine, dried ($Na_2SO_4$), and concentrated, and the residue was separated and purified by chromatography (silica gel).

*tert-Butyl (3S,4S,2′S) and (3S,4R,2′S)-4-[1-(tert-butyldimethylsilyloxy)-2-propylamino]-2-methylhept-6-en-3-ylcarbamate* (**20a**, **20b**, $C_{22}H_{46}N_2O_3Si$)

Aldimine **4** (1.49 g, 4.00 mmol), 524 mg Zn (8.00 mmol), 149 mg $CeCl_3 \cdot 7H_2O$ (0.40 mmol), and 662 mm$^3$ allyl bromide (7.60 mmol) were reacted according to GP 8 in 5 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 8:1 → 6:1) yielded 561 mg adduct **20a** (1.35 mmol, 34%) and 238 mg adduct **20b** (0.57 mmol, 14%) as colourless oils.

**20a**: $R_f = 0.44$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -3.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.17$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.06$ (s, 3H, SiCH$_3$), 0.06 (s, 3H, SiCH$_3$), 0.90 (s, 9H, SiC(CH$_3$)$_3$), 0.89–0.93 (m, 6H, 3′-H$_3$, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.92 (d, $^3J = 6.8$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.20–1.50 (bs, 1H, CHN$H$CH), 1.44 (s, 9H, OC(C$H_3$)$_3$), 1.66 (dsept, $^3J = 9.3$ Hz, $^3J = 6.9$ Hz, 1H, 2-H), 2.05 (dt, $^2J = 13.8$ Hz, $^3J = 7.9$ Hz, 1H, 5-H$_a$), 2.15–2.23 (m, 1H, 5-H$_b$), 2.71 (ddd, $^3J = 8.2$ Hz, $^3J = 4.8$ Hz, $^3J = 1.5$ Hz, 1H, 4-H), 2.79 ($\varphi$-quintd, $^3J = 6.4$ Hz, $^3J = 4.2$ Hz, 1H, 2′-H), 3.21 (ddd, $^3J = 10.3$ Hz, $^3J = 9.3$ Hz, $^3J = 1.7$ Hz, 1H, 3-H), 3.32 (dd, $^2J = 9.8$ Hz, $^3J = 7.0$ Hz, 1H, 1′-H$_a$), 3.53 (dd, $^2J = 9.8$ Hz, $^3J = 4.2$ Hz, 1H, 1′-H$_b$), 4.80 (d, $^3J = 10.2$ Hz, 1H, NHCO), 5.05 (ddt, $^3J = 10.2$ Hz, $^3J = 2.2$ Hz, $^3J = 1.0$ Hz, 1H, 7-H$_{cis}$), 5.06–5.13 (m, 1H, 7-H$_{trans}$), 5.84 (ddt, $^3J = 17.2$ Hz, $^3J = 10.1$ Hz, $^3J = 7.3$ Hz, 1H, 2-H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.4$ (q, SiCH$_3$), $-5.3$ (q, SiCH$_3$), 17.7 (q, C-3′), 18.3 (s, Si$C$(CH$_3$)$_3$), 19.4 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 25.9 (q, SiC($C$H$_3$)$_3$), 28.4 (q, OC($C$H$_3$)$_3$), 30.3 (d, C-2), 37.7 (t, C-5), 52.4 (d, C-2′), 54.3 (d, C-4), 58.1 (d, C-3), 67.4 (t, C-1′), 78.4 (s, O$C$(CH$_3$)$_3$), 117.4 (t, C-7), 135.5 (d, C-6), 156.3 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}446$ (N–H), 1,719 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 415 (100) [(M + H)$^+$]; HRMS ($C_{22}H_{47}N_2O_3Si$): calcd. 415.3356, found 415.3360.

**20b**: $R_f = 0.35$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +16.1 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.50$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.05$ (s, 6H, Si(CH$_3$)$_2$), 0.70–0.90 (bs, 1H, CHN$H$CH), 0.90 (s, 9H, SiC(CH$_3$)$_3$), 0.92 (d, $^3J = 6.7$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.93 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.02 (d, $^3J = 6.4$ Hz, 3H, 3′-H$_3$), 1.44 (s, 9H, OC(C$H_3$)$_3$), 1.67 (dsept, $^3J = 9.3$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 2.09–2.17 (m, 2H, 5-H$_2$), 2.70 (qt, $^3J = 6.4$ Hz, $^3J = 5.1$ Hz, 1H, 2′-H), 2.83 (td, $^3J = 6.6$ Hz, $^3J = 2.1$ Hz, 1H, 4-H), 3.17 (td, $^3J = 9.7$ Hz, $^3J = 2.1$ Hz, 1H, 3-H), 3.40 (dd, $^2J = 9.8$ Hz, $^3J = 5.4$ Hz, 1H, 1′-H$_a$), 3.45 (dd, $^2J = 9.8$ Hz, $^3J = 4.7$ Hz, 1H, 1′-H$_b$), 4.97 (d, $^3J = 10.0$ Hz, 1H, NHCO), 5.03–5.10 (m, 2H, 7-H$_2$), 5.81 (ddt, $^3J = 17.7$ Hz, $^3J = 9.6$ Hz, $^3J = 7.3$ Hz, 1H, 6-H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.4$ (q, Si($C$H$_3$)$_2$), 18.4 (s, Si$C$(CH$_3$)$_3$), 18.8 (q, C-3′), 19.5 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 25.9 (q, SiC($C$H$_3$)$_3$), 28.5 (q, OC($C$H$_3$)$_3$), 30.7 (d, C-2), 38.6 (t, C-5), 53.3 (d, C-2′), 54.7 (d, C-4), 58.9 (d, C-3), 67.4 (t, C-1′), 78.5 (s, O$C$(CH$_3$)$_3$), 117.5 (t, C-7), 135.6 (d, C-6), 156.4 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}438$, 3,353 (N–H), 1,718 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 415 (100) [(M + H)$^+$]; HRMS ($C_{22}H_{47}N_2O_3Si$): calcd. 415.3356, found 415.3352.

*Benzyl (4S,5S,2′S) and (4S,5R,2′S)-5-[1-(tert-butyldiphenylsilyloxy)-2-propylamino]-2-methyloct-7-en-4-ylcarbamate* (**21a**, **21b**, $C_{36}H_{50}N_2O_3Si$)

Aldimine **5** (1.09 g, 2.00 mmol), 262 mg Zn (4.00 mmol), 76 mg $CeCl_3 \cdot 7H_2O$ (0.20 mmol), and 331 mm$^3$ allyl bromide (3.80 mmol) were reacted according to GP 8 in 5 cm$^3$ THF within 16 h. Chromatography (hexanes–EtOAc 6:1) yielded 180 mg adduct **21a** (0.31 mmol, 15%) and 135 mg adduct **21b** (0.23 mmol, 12%) as colourless oils.

**21a**: $R_f = 0.41$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -6.5 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.79$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.90$ (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 0.91 (d, $^3J = 6.5$ Hz, 3H, CHC$H_3$), 0.92 (d, $^3J = 6.4$ Hz, 3H, CHC$H_3$), 1.05 (s, 9H, C(CH$_3$)$_3$), 1.24 (ddd, $^2J = 13.7$ Hz, $^3J = 8.7$ Hz, $^3J = 5.3$ Hz, 1H, 3-H$_a$), 1.37 (ddd, $^2J = 13.8$ Hz, $^3J = 9.4$ Hz, $^3J = 5.5$ Hz, 1H, 3-H$_b$), 1.45 (bs, 1H, CHN$H$CH), 1.60 ($\varphi$-doct, $^3J = 8.2$ Hz, $^3J = 6.2$ Hz, 1H, 2-H), 2.12 ($\varphi$-t, $^3J = 7.0$ Hz, 2H, 6-H$_2$), 2.52 (td, $^3J = 6.9$ Hz, $^3J = 1.9$ Hz, 1H, 5-H), 2.82 ($\varphi$-quintd, $^3J = 6.4$ Hz, $^3J = 4.0$ Hz, 1H, 2′-H), 3.40 (dd, $^2J = 10.0$ Hz, $^3J = 6.5$ Hz, 1H, 1′-H$_a$), 3.57 (dd, $^2J = 9.9$ Hz, $^3J = 4.2$ Hz, 1H, 1′-H$_b$), 3.75 (tdd, $^3J = 9.5$ Hz, $^3J = 5.2$ Hz, $^3J = 1.7$ Hz, 1H, 4-H), 4.93 (d, $^3J = 9.7$ Hz, 1H, NHCO), 5.03 (dd, $^3J = 10.2$ Hz, $^2J = 2.1$ Hz, 1H, 8-H$_{cis}$), 5.07 (dd, $^3J = 17.0$ Hz, $^2J = 1.8$ Hz, 1H, 8-H$_{trans}$), 5.08 (d, $^2J = 12.3$ Hz, 1H, C$H_a$H$_b$Ph), 5.11 (d, $^2J = 12.3$ Hz, 1H, CH$_a$$H_b$Ph), 5.81 (ddt, $^3J = 17.2$ Hz, $^3J = 10.1$ Hz, $^3J = 7.2$ Hz, 1H, 7-H), 7.26–7.45 (m, 11H, 3 Ph), 7.62–7.67 (m, 4H, 3 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.0$ (q), 19.2 (s), 22.3 (q), 23.2 (q), 24.9 (d), 26.9 (q), 37.4 (t), 42.4 (t), 51.3 (d), 53.0 (d), 57.3 (d), 66.5 (t), 67.9 (t), 117.6 (t), 127.7 (d, 4 C), 128.0 (d), 128.0 (d, 2C), 128.5 (d), 129.6 (d), 129.7 (d), 133.5 (s), 133.6 (s), 134.8 (d), 135.2 (s), 135.5 (d), 135.6 (d, 2C), 135.6 (d, 2C), 156.3 (s) ppm; IR (KBr): $\bar{\nu} = 3{,}418$, 3,336 (N–H), 1,721 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 587 (97) [(M + H)$^+$]; HRMS ($C_{36}H_{51}N_2O_3Si$): calcd. 587.3669, found 587.3666.

**21b**: $R_f = 0.36$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +18.5 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.74$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.85$ (d, $^3J = 6.6$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.86 (d, $^3J = 6.5$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 1.05 (s, 9H, C(CH$_3$)$_3$), 1.06 (d, $^3J = 6.5$ Hz, 3H, 3′-H$_3$), 1.19 (ddd, $^2J = 13.3$ Hz, $^3J = 9.4$ Hz, $^3J = 4.8$ Hz, 1H, 3-H$_a$), 1.30 (ddd, $^2J = 13.6$ Hz, $^3J = 9.6$ Hz, $^3J = 5.5$ Hz, 1H, 3-H$_b$), 1.15–1.45 (m, 1H, CHN*H*CH), 1.47–1.61 (m, 1H, 2-H), 2.00 (dtt, $^2J = 13.8$ Hz, $^3J = 7.6$ Hz, $^4J = 1.1$ Hz, 1H, 6-H$_a$), 2.16 (dtt, $^2J = 13.6$ Hz, $^3J = 6.2$ Hz, $^4J = 1.2$ Hz, 1H, 6-H$_b$), 2.61 (ddd, $^3J = 7.9$ Hz, $^3J = 6.1$ Hz, $^3J = 2.0$ Hz, 1H, 5-H), 2.72–2.82 (m, 1H, 2-H), 3.45 (dd, $^2J = 9.8$ Hz, $^3J = 5.4$ Hz, 1H, 1′-H$_a$), 3.51 (dd, $^2J = 9.8$ Hz, $^3J = 4.7$ Hz, 1H, 1′-H$_b$), 3.70 (tdd, $^3J = 9.6$ Hz, $^3J = 4.8$ Hz, $^3J = 2.0$ Hz, 1H, 4-H), 4.99–5.08 (m, 3H, 8-H$_2$, NHCO), 5.07 (d, $^2J = 12.6$ Hz, 1H, C*H$_a$*H$_b$Ph), 5.10 (d, $^2J = 12.6$ Hz, 1H, CH$_a$*H$_b$*Ph), 5.77 (dddd, $^3J = 16.8$ Hz, $^3J = 10.5$ Hz, $^3J = 7.9$ Hz, $^3J = 6.5$ Hz, 1H, 7-H), 7.28–7.45 (m, 11H, 3 Ph), 7.63–7.70 (m, 4H, 3 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.1$ (q), 19.3 (s), 22.2 (q), 23.3 (q), 24.9 (d), 26.9 (q), 37.9 (t), 42.2 (t), 51.6 (d), 53.3 (d), 57.1 (d), 66.5 (t), 68.6 (t), 117.6 (t), 127.8 (d, 4 C), 128.0 (d), 128.1 (d, 2C), 128.5 (d, 2C), 129.6 (d), 129.7 (d), 133.7 (s, 2C), 135.6 (d, 4 C), 135.7 (d), 136.9 (s), 156.3 (s) ppm; IR (KBr): $\bar{\nu} = 3{,}412$, 3,339 (N–H), 1,720 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 587 (100) [(M + H)$^+$]; HRMS ($C_{36}H_{51}N_2O_3Si$): calcd. 587.3669, found 587.3666.

*Benzyl (3S,4S,2′S) and (3S,4R,2′S)-4-[1-(tert-butyldiphenylsilyloxy)-2-propylamino]-2-methylhept-6-en-3-ylcarbamate* (**22a**, **22b**, $C_{35}H_{48}N_2O_3Si$)
Aldimine **6** (5.55 g, 10.5 mmol), 1.37 g Zn (20.9 mmol), 398 mg CeCl$_3$·7H$_2$O (1.05 mmol), and 1.73 cm$^3$ allyl bromide (19.9 mmol) were reacted according to GP 8 in 20 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 5:1) yielded 3.07 g adduct **22a** (5.36 mmol, 51%) and 493 mg adduct **22b** (0.86 mmol, 8%) as colourless oils.

**22a**: $R_f = 0.37$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -7.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.77$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.90$ (d, $^3J = 6.4$ Hz, 3H, 3′-H$_3$), 0.91 (d, $^3J = 6.7$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.91 (d, $^3J = 6.7$ Hz, 3H, H(CH$_3$)$_a$(C*H$_3$*)$_b$), 1.04 (s, 9H, C(CH$_3$)$_3$), 1.15–1.60 (bs, 1H, CHN*H*CH), 1.70 (dsept, $^3J = 9.6$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 2.05 (dddt, $^2J = 13.6$ Hz, $^3J = 8.3$ Hz, $^3J = 7.3$ Hz, $^4J = 1.2$ Hz, 1H, 5-H$_a$), 2.15–2.24 (m, 1H, 5-H$_b$), 2.73 (ddd, $^3J = 8.4$ Hz, $^3J = 4.9$ Hz, $^3J = 1.6$ Hz, 1H, 4-H), 2.83 ($\varphi$-quintd, $^3J = 6.4$ Hz, $^3J = 4.2$ Hz, 1H, 2′-H), 3.28 (ddd, $^3J = 10.2$ Hz, $^3J = 9.6$ Hz, $^3J = 1.6$ Hz, 1H, 3-H), 3.40 (dd, $^2J = 9.9$ Hz, $^3J = 6.7$ Hz, 1H, 1′-H$_a$), 3.56 (dd, $^2J = 9.9$ Hz, $^3J = 4.3$ Hz, 1H, 1′-H$_b$), 5.00–5.11 (m, 3H, 7-H, NHCO), 5.09 (d, $^2J = 12.3$ Hz, 1H, C*H$_a$*H$_b$Ph), 5.13 (d, $^2J = 12.2$ Hz, 1H, CH$_a$*H$_b$*Ph), 5.79 (ddt, $^3J = 17.2$ Hz, $^3J = 10.1$ Hz, $^3J = 7.2$ Hz, 1H, 6-H), 7.27–7.44 (m, 11H, 3 Ph), 7.62–7.67 (m, 4H, 3 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 17.7$ (q), 19.2 (s), 19.5 (q), 20.0 (q), 26.9 (q), 30.9 (d), 37.7 (t), 52.5 (d), 54.1 (d), 58.9 (d), 66.5 (t), 68.2 (t), 117.6 (t), 127.7 (d, 4 C), 128.0 (d), 128.0 (d, 2C), 128.5 (d, 2C),129.6 (d), 129.7 (d), 133.5 (s), 133.5 (s), 135.5 (d), 135.6 (d, 2C), 135.7 (2d), 137.0 (s), 156.8 (s) ppm; IR (KBr): $\bar{\nu} = 3{,}423$, 3,300 (N–H), 1,726 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 573 (100) [(M + H)$^+$]; HRMS ($C_{35}H_{49}N_2O_3Si$): calcd. 573.3512, found 573.3515.

**22b**: $R_f = 0.30$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +20.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.80$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.84$ (d, $^3J = 6.7$ Hz, 3H, H(CH$_3$)$_a$ (C*H$_3$*)$_b$), 0.87 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 1.05 (s, 9H, C(CH$_3$)$_3$), 1.07 (d, $^3J = 6.4$ Hz, 3H, 3′-H$_3$), 1.26 (bs, 1H, CHN*H*CH), 1.59 (dsept, $^3J = 9.6$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 2.00–2.18 (m, 2H, 5-H$_2$), 2.69 (qdd, $^3J = 6.4$ Hz, $^3J = 5.7$ Hz, $^3J = 4.3$ Hz, 1H, 2′-H), 2.78 (td, $^3J = 6.7$ Hz, $^3J = 1.7$ Hz, 1H, 4-H), 3.17 (td, $^3J = 9.8$ Hz, $^3J = 1.7$ Hz, 1H, 3-H), 3.43 (dd, $^2J = 9.9$ Hz, $^3J = 5.7$ Hz, 1H, 1′-H$_a$), 3.50 (dd, $^2J = 9.9$ Hz, $^3J = 4.4$ Hz, 1H, 1′-H$_b$), 5.00–5.08 (m, 2H, 7-H$_2$), 5.08 (d, $^2J = 12.4$ Hz, 1H, C*H$_a$*H$_b$Ph), 5.12 (d, $^2J = 12.2$ Hz, 1H, CH$_a$*H$_b$*Ph), 5.23 (d, $^3J = 10.0$ Hz, 1H, NHCO), 5.75 (dddd, $^3J = 17.0$ Hz, $^3J = 10.2$ Hz, $^3J = 7.8$ Hz, $^3J = 6.7$ Hz, 1H, 6-H), 7.28–7.44 (m, 11H, 3 Ph), 7.63–7.69 (m, 4H, 3 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.6$ (q), 19.3 (s), 19.7 (q), 20.0 (q), 26.9 (q), 30.7 (d), 38.9 (t), 53.7 (d), 54.3 (d), 59.9 (d), 66.5 (t), 68.4 (t), 117.8 (t), 127.7 (d, 4 C), 128.0 (d), 128.1 (d, 2C), 128.5 (d, 2C), 129.7 (2d), 133.7 (s, 2C), 135.3 (d), 135.6 (4d), 137.0 (s), 156.8 (s) ppm; IR (KBr): $\bar{\nu} = 3{,}418$, 3,341 (N–H), 1,726 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 573 (99) [(M + H)$^+$]; HRMS ($C_{35}H_{49}N_2O_3Si$): calcd. 573.3512, found 573.3510.

*tert-Butyl (3S,4S,2′S) and (3S,4R,2′S)-4-[1-(tert-butyldiphenylsilyloxy)-3-methyl-2-butylamino]-2-methylhept-6-en-3-ylcarbamate* (**23a**, **23b**, $C_{34}H_{54}N_2O_3Si$)
Aldimine **7** (1.57 g, 3.00 mmol), 392 mg Zn (6.00 mmol), 114 mg CeCl$_3$·7H$_2$O (0.30 mmol), and 496 mm$^3$ allyl bromide (5.70 mmol) were reacted according to GP 8 in 5 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 8:1 → 5:1) yielded 416 mg adduct **23a** (0.73 mmol, 24%) and 552 mg adduct **23b** (0.97 mmol, 32%) as colourless oils.

**23a**: $R_f = 0.52$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -17.3 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.82$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.79$ (d, $^3J = 6.9$ Hz, 3H, CHC*H$_3$*), 0.82 (d, $^3J = 7.0$ Hz, 3H, CHC*H$_3$*), 0.87 (d, $^3J = 6.6$ Hz, 3H, CHC*H$_3$*), 0.91 (d, $^3J = 6.7$ Hz, 3H, CHC*H$_3$*), 1.06 (s, 9H, SiC(CH$_3$)$_3$), 1.10–1.40 (bs, 1H, CHN*H*CH), 1.45 (s, 9H, OC(CH$_3$)$_3$), 1.72 (dsept, $^3J = 9.3$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 1.80 (septd, $^3J = 7.0$ Hz, $^3J = 4.3$ Hz, 1H, 3′-H), 2.02 (ddd, $^2J = 13.6$ Hz, $^3J = 8.4$ Hz, $^3J = 7.6$ Hz, 1H, 5-H$_a$), 2.16 (ddd, $^2J = 13.3$ Hz, $^3J = 6.8$ Hz, $^3J = 4.8$ Hz, 1H, 5-H$_b$), 2.47 (dt, $^3J = 6.5$ Hz, $^3J = 4.5$ Hz, 1H, 2′-H), 2.68

(ddd, $^3J = 8.7$ Hz, $^3J = 4.7$ Hz, $^3J = 1.6$ Hz, 1H, 4-H), 3.18 (td, $^3J = 10.0$ Hz, $^3J = 1.6$ Hz, 1H, 3-H), 3.50 (dd, $^2J = 10.3$ Hz, $^3J = 6.5$ Hz, 1H, 1′-H$_a$), 3.62 (dd, $^2J = 10.3$ Hz, $^3J = 4.6$ Hz, 1H, 1′-H$_b$), 4.83 (d, $^3J = 10.2$ Hz, 1H, NHCO), 5.00 (dd, $^3J = 10.2$ Hz, $^2J = 2.2$ Hz, 1H, 7-H$_{cis}$), 5.02 (dd, $^3J = 17.1$ Hz, $^2J = 1.8$ Hz, 1H, 7-H$_{trans}$), 5.75 (ddt, $^3J = 17.3$ Hz, $^3J = 10.2$ Hz, $^3J = 7.2$ Hz, 1H, 6-H), 7.36–7.47 (m, 6H, 2 Ph), 7.63–7.69 (m, 4H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.0$ (q), 18.8 (q), 19.2 (s), 19.6 (q), 20.2 (q), 26.9 (q), 28.5 (d), 28.9 (q), 30.3 (d), 38.0 (t), 54.7 (d), 58.7 (d), 62.5 (d), 63.3 (t), 78.5 (s), 117.4 (t), 127.7 (d, 4 C), 129.7 (d), 129.7 (d), 133.5 (2s), 135.6 (d), 135.7 (2d), 135.7 (d, 2C), 156.3 (s) ppm; IR (KBr): $\bar{\nu} = 3{,}437$ (N–H), 1,719 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 567 (100) [(M + H)$^+$]; HRMS ($C_{34}H_{55}N_2O_3Si$): calcd. 567.3982, found 567.3979.

**23b**: $R_f = 0.52$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -1.9 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.84$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.78$ (d, $^3J = 6.6$ Hz, 3H, CHC*H$_3$*), 0.82 (d, $^3J = 6.7$ Hz, 3H, CHC*H$_3$*), 0.85 (d, $^3J = 7.5$ Hz, 3H, CHC*H$_3$*), 0.87 (d, $^3J = 6.9$ Hz, 3H, CHC*H$_3$*), 1.05 (s, 9H, SiC(CH$_3$)$_3$), 1.42 (s, 9H, OC(CH$_3$)$_3$), 1.63 (dsept, $^3J = 9.1$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 1.92 (septd, $^3J = 6.9$ Hz, $^3J = 4.3$ Hz, 1H, 3′-H), 2.00–2.15 (m, 3H, 5-H$_2$, CHN*H*CH), 2.45 (dt, $^3J = 5.6$ Hz, $^3J = 4.6$ Hz, 1H, 2′-H), 2.73 (ddd, $^3J = 7.6$ Hz, $^3J = 5.3$ Hz, $^3J = 2.4$ Hz, 1H, 4-H), 3.15 (ddd, $^3J = 9.8$ Hz, $^3J = 9.0$ Hz, $^3J = 2.3$ Hz, 1H, 3-H), 3.50 (dd, $^2J = 10.5$ Hz, $^3J = 4.9$ Hz, 1H, 1-H$_a$), 3.55 (dd, $^2J = 10.5$ Hz, $^3J = 5.8$ Hz, 1H, 1-H$_b$), 4.87 (d, $^3J = 10.0$ Hz, 1H, NHCO), 5.01–5.08 (m, 2H, 7-H$_2$), 5.77 (ddt, $^3J = 16.7$ Hz, $^3J = 9.4$ Hz, $^3J = 7.2$ Hz, 1H, 6-H), 7.36–7.46 (m, 6H, 2 Ph), 7.64–7.69 (m, 4H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.3$ (s, Si*C*(CH$_3$)$_3$), 19.0 (q, *C*HCH$_3$), 19.2 (q, *C*HCH$_3$), 19.3 (q, *C*HCH$_3$), 20.1 (q, *C*HCH$_3$), 26.9 (q, SiC(*C*H$_3$)$_3$), 28.4 (q, OC(*C*H$_3$)$_3$), 29.3 (d, C-3′), 30.3 (d, C-2), 37.7 (t, C-5), 54.7 (d, C-4), 58.4 (d, C-2′), 61.8 (d, C-3), 64.3 (t, C-1′), 78.5 (s, O*C*(CH$_3$)$_3$), 117.5 (t, C-7), 127.7 (d, 4C, Ph), 129.6 (d, Ph), 129.7 (d, Ph), 133.6 (2s, Ph), 135.4 (d, C-2′), 135.6 (4d, Ph), 156.4 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}437$ (N–H), 1,718 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 567 (94) [(M + H)$^+$]; HRMS ($C_{34}H_{55}N_2O_3Si$): calcd. 567.3982, found 567.3985.

*tert-Butyl (3S,4S,2′S) and (3S,4R,2′S)-4-[1-(tert-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-2-methylhept-6-en-3-ylcarbamate* (**24a**, **24b**, $C_{28}H_{50}N_2O_3Si$)

Aldimine **8** (247 mg, 0.55 mmol), 72 mg Zn (1.10 mmol), 21 mg CeCl$_3$·7H$_2$O (0.06 mmol), and 91 mm$^3$ allyl bromide (1.05 mmol) were reacted according to GP 8 in 3 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 8:1 → 6:1) yielded 60 mg adduct **24a** (0.12 mmol, 22%) and 60 mg adduct **24b** (0.12 mmol, 22%) as colourless oils.

**24a**: $R_f = 0.44$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -40.6 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.61$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.03$ (s, 3H, SiCH$_3$), 0.03 (s, 3H, SiCH$_3$), 0.78 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.83 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.91 (s, 9H, SiC(CH$_3$)$_3$), 1.26 (bs, 1H, CHN*H*CH), 1.36–1.45 (m, 1H, 2-H), 1.44 (s, 9H, OC(C*H$_3$*)$_3$), 2.03–2.19 (m, 2H, 5-H$_2$), 2.60 (dd, $^2J = 13.4$ Hz, $^3J = 7.4$ Hz, 1H, 3′-H$_a$), 2.65 (dd, $^2J = 13.6$ Hz, $^3J = 6.6$ Hz, 1H, 3′-H$_b$), 2.75–2.81 (m, 2H, 2′-H, 4-H), 3.09 (td, $^3J = 9.9$ Hz, $^3J = 1.7$ Hz, 1H, 3-H), 3.40 (dd, $^2J = 9.9$ Hz, $^3J = 4.7$ Hz, 1H, 1′-H$_a$), 3.52 (dd, $^2J = 9.9$ Hz, $^3J = 4.1$ Hz, 1H, 1′-H$_b$), 4.77 (d, $^3J = 10.1$ Hz, 1H, NHCO), 5.03–5.11 (m, 2H, 7-H$_2$), 5.82 (ddt, $^3J = 17.3$ Hz, $^3J = 10.1$ Hz, $^3J = 7.2$ Hz, 1H, 6-H) 7.14–7.35 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.5$ (q, SiCH$_3$), −5.4 (q, Si*C*H$_3$), 18.2 (s, Si*C*(CH$_3$)$_3$), 19.5 (q, CH*C*H$_3$), 20.0 (q, CH*C*H$_3$), 25.9 (q, SiC(*C*H$_3$)$_3$), 28.5 (q, OC(*C*H$_3$)$_3$), 30.5 (d, C-2), 38.2 (t, C-5), 39.1 (t, C-3′), 54.6 (d, C-4), 59.8 (d, C-2′), 58.6 (d, C-3), 64.2 (t, C-1′), 78.3 (s, O*C*(CH$_3$)$_3$), 117.5 (t, C-7), 126.0 (d, Ph), 128.2 (d, 2C, Ph), 129.3 (d, 2C, Ph), 135.5 (d, C-6), 139.8 (s, Ph), 156.2 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}426$ (N–H), 1,718 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 491 (43) [(M + H)$^+$]; HRMS ($C_{28}H_{51}N_2O_3Si$): calcd. 491.3669, found 491.3665.

**24b**: $R_f = 0.35$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +4.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.91$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.02$ (s, 3H, SiCH$_3$), 0.02 (s, 3H, SiCH$_3$), 0.86 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.90 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.91 (s, 9H, SiC(CH$_3$)$_3$), 1.47 (s, 9H, OC(C*H$_3$*)$_3$), 1.60 (bs, 1H, CHN*H*CH), 1.86 ($\varphi$-oct, $^3J = 6.6$ Hz, 1H, 2-H), 2.13 (dt, $^2J = 13.9$ Hz, $^3J = 7.0$ Hz, 1H, 5-H$_a$), 2.26 (ddd, $^2J = 13.6$ Hz, $^3J = 6.6$ Hz, $^3J = 5.4$ Hz, 1H, 5-H$_b$), 2.60 (dd, $^2J = 13.3$ Hz, $^3J = 8.6$ Hz, 1H, 3′-H$_a$), 2.73 (dd, $^2J = 13.3$ Hz, $^3J = 5.3$ Hz, 1H, 3′-H$_b$), 2.77–2.84 (m, 1H, 4-H), 2.92–3.01 (m, 1H, 2′-H), 3.34 (dd, $^2J = 10.0$ Hz, $^3J = 5.2$ Hz, 1H, 1′-H$_a$), 3.50 (dd, $^2J = 10.0$ Hz, $^3J = 3.9$ Hz, 1H, 1′-H$_b$), 3.44–3.51 (m, 1H, 3-H), 4.55 (d, $^3J = 10.5$ Hz, 1H, NHCO), 5.09 (ddd, $^3J = 10.1$ Hz, $^2J = 2.1$ Hz, $^4J = 1.1$ Hz, 1H, 7-H$_{cis}$), 5.14 (ddd, $^3J = 17.1$ Hz, $^2J = 2.0$ Hz, $^4J = 1.5$ Hz, 1H, 7-H$_{trans}$), 5.88 (ddt, $^3J = 17.2$ Hz, $^3J = 10.1$ Hz, $^3J = 7.1$ Hz, 1H, 6-H), 7.17–7.32 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.5$ (q, SiCH$_3$), −5.4 (q, SiCH$_3$), 18.2 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 18.2 (s, Si*C*(CH$_3$)$_3$), 20.7 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 25.9 (q, SiC(*C*H$_3$)$_3$), 28.5 (q, OC(*C*H$_3$)$_3$), 28.8 (d, C-2), 35.4 (t, C-5), 38.9 (t, C-3′), 55.7 (d, C-4), 57.2 (d, C-3), 58.4 (d, C-2′), 63.4 (t, C-1′), 78.8 (s, O*C*(CH$_3$)$_3$), 117.4 (t, C-7), 126.0 (d, Ph), 128.2 (d, 2C, Ph), 129.4 (d, 2C, Ph), 135.8 (d, C-6), 139.7 (s, Ph), 156.3 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}357$ (N–H), 1,702 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 491 (74) [(M + H)$^{+}$]; HRMS ($C_{28}H_{51}N_2O_3Si$): calcd. 491.3669, found 491.3672.

*Benzyl (4S,5S,2′S) and (4S,5R,2′S)-5-[1-(tert-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-2-methyloct-7-en-4-ylcarbamate* (**25a**, **25b**, $C_{32}H_{50}N_2O_3Si$)

Aldimine **9** (6.21 g, 12.5 mmol), 1.63 g Zn (25.0 mmol), 473 mg $CeCl_3{\cdot}7H_2O$ (1.25 mmol), and 1.79 cm$^3$ allyl bromide (23.8 mmol) were reacted according to GP 8 in 10 cm$^3$ THF within 16 h. Chromatography (hexanes–EtOAc 10:1) yielded 1.86 g adduct **25a** (3.46 mmol, 28%) and 1.16 g adduct **25b** (2.16 mmol, 17%) as colourless oils.

**25a**: $R_f = 0.53$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -18.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 1.00, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.03 (2s, 6H, $Si(CH_3)_2$), 0.82 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.84 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.91 (s, 9H, $C(CH_3)_3$), 1.05 (ddd, $^2J$ = 13.7 Hz, $^3J$ = 9.1 Hz, $^3J$ = 5.2 Hz, 1H, 3-H$_a$), 1.10 (ddd, $^2J$ = 13.4 Hz, $^3J$ = 9.4 Hz, $^3J$ = 5.5 Hz, 1H, 3-H$_b$), 1.31 (bs, 1H, CHN*H*CH), 1.47 (dsext, $^3J$ = 8.7 Hz, $^3J$ = 6.7 Hz, 1H, 2-H), 2.06 (dt, $^2J$ = 14.1 Hz, $^3J$ = 7.4 Hz, 1H, 6-H$_a$), 2.13 (dt, $^2J$ = 13.7 Hz, $^3J$ = 6.8 Hz, 1H, 6-H$_b$), 2.60 (ddd, $^3J$ = 7.2 Hz, $^3J$ = 5.6 Hz, $^3J$ = 2.2 Hz, 1H, 5-H), 2.63 (dd, $^2J$ = 12.9 Hz, $^3J$ = 7.0 Hz, 1H, 3′-H$_a$), 2.66 (dd, $^2J$ = 13.3 Hz, $^3J$ = 6.8 Hz, 1H, 3′-H$_b$), 2.77 (tt, $^3J$ = 7.1 Hz, $^3J$ = 3.9 Hz, 1H, 2′-H), 3.40 (dd, $^2J$ = 10.0 Hz, $^3J$ = 4.0 Hz, 1H, 1′-H$_a$), 3.52 (dd, $^2J$ = 10.0 Hz, $^3J$ = 4.1 Hz, 1H, 1′-H$_b$), 3.64 (tdd, $^3J$ = 9.6 Hz, $^3J$ = 5.1 Hz, $^3J$ = 1.7 Hz, 1H, 4-H), 4.92 (d, $^3J$ = 9.5 Hz, 1H, NHCO), 5.05 (dd, $^3J$ = 10.3 Hz, $^2J$ = 1.6 Hz, 1H, 8-H$_{cis}$), 5.06 (d, $^2J$ = 12.5 Hz, 1H, $OCH_aH_bPh$), 5.08 (dd, $^3J$ = 17.3 Hz, $^2J$ = 1.6 Hz, 1H, 8-H$_{trans}$), 5.09 (d, $^2J$ = 12.5 Hz, 1H, $OCH_aH_bPh$), 5.80 (ddt, $^3J$ = 17.2 Hz, $^3J$ = 10.1 Hz, $^3J$ = 7.2 Hz, 1H, 7-H), 7.11–7.46 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = −5.4 (q, $Si(CH_3)_a(CH_3)_b$), −5.4 (q, $Si(CH_3)_a(CH_3)_b$), 18.3 (s, $C(CH_3)_3$), 22.2 (q, $CH(CH_3)_a(CH_3)_b$), 23.2 (q, $CH(CH_3)_a(CH_3)_b$), 24.9 (d, C-2), 26.0 (q, $C(CH_3)_3$), 37.7 (t, C-6), 39.4 (t, C-3′), 42.2 (t, C-3), 51.5 (d, C-4), 57.6 (d, C-5), 60.2 (d, C-2′), 63.5 (t, C-1′), 66.4 (t, O*C*H$_2$Ph), 117.2 (t, C-8), 126.1 (d, Ph), 128.0 (d, 3C, Ph), 128.3 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.5 (2d, Ph), 135.6 (d, C-7), 137.0 (s, Ph), 140.0 (s, Ph), 156.3 (s, NHCO) ppm; IR (DRIFT): $\bar{\nu} = 3{,}412$, 3,338 (N–H), 1,721 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 539 (76) [(M + H)$^{+}$]; HRMS ($C_{32}H_{51}N_2O_3Si$): calcd. 539.3669, found 539.3671.

**25b**: $R_f = 0.43$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +17.6 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 0.65, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.01 (s, 3H, $Si(CH_3)_a(CH_3)_b$), 0.02 (s, 3H, $Si(CH_3)_a(CH_3)_b$), 0.87 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.87 (d, $^3J$ = 6.6 Hz, 3H, $Si(CH_3)_a(CH_3)_b$), 0.89 (s, 9H, $C(CH_3)_3$), 1.03–1.25 (m, 2H, 3-H$_2$), 1.48 (bs, 1H, CHN*H*CH), 1.50–1.60 (m, 1H, 2-H), 1.97–2.08 (m, 1H, 6-H$_a$), 2.24 (dtt, $^2J$ = 13.9 Hz, $^3J$ = 6.8 Hz, $^3J$ = 1.5 Hz, 1H, 6-H$_b$), 2.53 (dd, $^2J$ = 13.5 Hz, $^3J$ = 7.3 Hz, 1H, 3′-H$_a$), 2.62 (dd, $^2J$ = 13.5 Hz, $^3J$ = 6.4 Hz, 1H, 3′-H$_b$), 2.73 (td, $^3J$ = 7.1 Hz, $^3J$ = 3.2 Hz, 1H, 5-H), 2.83–2.91 (m, 1H, 2′-H), 3.35 (dd, $^2J$ = 10.0 Hz, $^3J$ = 6.2 Hz, 1H, 1′-H$_a$), 3.49 (dd, $^2J$ = 10.0 Hz, $^3J$ = 4.2 Hz, 1H, 1′-H$_b$), 3.70 (tt, $^3J$ = 10.0 Hz, $^3J$ = 3.2 Hz, 1H, 4-H), 4.76 (d, $^3J$ = 9.3 Hz, 1H, NHCO), 4.91 (dd, $^3J$ = 17.2 Hz, $^2J$ = 1.6 Hz, 1H, 8-H$_{trans}$), 4.96 (dd, $^3J$ = 10.2 Hz, $^2J$ = 1.9 Hz, 1H, 8-H$_{cis}$), 5.05 (d, $^2J$ = 12.2 Hz, 1H, $OCH_aH_bPh$), 5.09 (d, $^2J$ = 11.7 Hz, 1H, $OCH_aH_bPh$), 5.79 (ddt, $^3J$ = 17.2 Hz, $^3J$ = 9.9 Hz, $^3J$ = 7.3 Hz, 1H, 7-H), 7.11–7.37 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = −5.5 (q, $Si(CH_3)_a(CH_3)_b$), −5.4 (q, $Si(CH_3)_a(CH_3)_b$), 18.2 (s, $C(CH_3)_3$), 21.6 (q, $CH(CH_3)_a(CH_3)_b$), 24.0 (q, $CH(CH_3)_a(CH_3)_b$), 24.5 (d, C-2), 25.9 (q, $C(CH_3)_3$), 37.2 (t, C-6), 37.6 (t, C-3), 39.3 (t, C-3′), 51.3 (d, C-4), 58.2 (d, C-5), 59.9 (d, C-2′), 64.6 (t, C-1′), 66.4 (t, O*C*H$_2$Ph), 117.2 (t, C-8), 126.0 (d, Ph), 127.9 (d, 3C, Ph), 128.3 (d, 2C, Ph), 128.4 (d, 2C, Ph), 129.4 (2d, Ph), 135.4 (d, C-7), 136.9 (s, Ph), 139.7 (s, Ph), 156.1 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}402$, 3,337 (N–H), 1,722 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 539 (76) [(M + H)$^{+}$]; HRMS ($C_{32}H_{51}N_2O_3Si$): calcd. 539.3669, found 539.3666.

*Benzyl (4S,5S,2′S) and (4S,5R,2′S)-5-[1-(tert-butyldimethylsilyloxy)-2-propylamino]-2-methyloct-7-en-4-ylcarbamate* (**26a**, **26b**, $C_{26}H_{46}N_2O_3Si$)

Aldimine **10** (2.88 g, 6.86 mmol), 897 mg Zn (13.7 mmol), 256 mg $CeCl_3{\cdot}7H_2O$ (0.69 mmol), and 0.98 cm$^3$ allyl bromide (13.0 mmol) were reacted according to GP 8 in 10 cm$^3$ THF within 16 h. Chromatography (hexanes–$Et_2O$ 9:1 → 5:1) yielded 619 mg adduct **26a** (1.34 mmol, 19%) and 428 mg adduct **26b** (0.92 mmol, 13%) as colourless oils.

**26a**: $R_f = 0.45$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -4.6 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 0.62, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.04 (2s, 6H, $Si(CH_3)_2$), 0.89 (s, 9H, $C(CH_3)_3$), 0.89 (d, $^3J$ = 6.5 Hz, 3H, $CHCH_3$), 0.91 (d, $^3J$ = 7.0 Hz, 3H, $CHCH_3$), 0.93 (d, $^3J$ = 6.6 Hz, 3H, $CHCH_3$), 1.28 (ddd, $^2J$ = 13.7 Hz, $^3J$ = 8.5 Hz, $^3J$ = 5.0 Hz, 1H, 3-H$_a$), 1.28 (ddd, $^2J$ = 13.6 Hz, $^3J$ = 9.4 Hz, $^3J$ = 5.5 Hz, 1H, 3-H$_b$), 1.44 (bs, 1H, CHN*H*CH), 1.57 ($\varphi$-doct, $^3J$ = 8.8 Hz, $^3J$ = 6.5 Hz, 1H, 2-H), 2.11 ($\varphi$-t, $^3J$ = 7.0 Hz, 2H, 6-H$_2$), 2.55 (td, $^3J$ = 6.7 Hz, $^3J$ = 1.9 Hz, 1H, 5-H), 2.77 ($\varphi$-quintd, $^3J$ = 6.4 Hz, $^3J$ = 3.9 Hz, 1H, 2′-H), 3.32 (dd, $^2J$ = 9.8 Hz, $^3J$ = 6.4 Hz, 1H, 1′-H$_a$), 3.53 (dd, $^2J$ = 9.8 Hz, $^3J$ = 4.1 Hz, 1H, 1′-H$_b$), 3.75 (tdd, $^2J$ = 9.4 Hz, $^3J$ = 5.1 Hz, $^3J$ = 1.8 Hz, 1H, 4-H), 4.97 (d, $^3J$ = 9.5 Hz, 1H, NHCO), 5.05 (ddv, $^2J$ = 1.8 Hz, 1H, 8-H$_{cis}$), 5.07 (d, $^2J$ = 12.2 Hz, 1H, $CH_aH_bPh$), 5.05 (dd, $^3J$ = 17.2 Hz, $^2J$ = 1.8 Hz, 1H, 8-H$_{trans}$), 5.11 (d, $^2J$ = 12.3 Hz, 1H,

$CH_a\mathit{H_b}Ph$), 5.82 (ddt, $^3J = 17.3$ Hz, $^3J = 10.1$ Hz, $^3J = 7.2$ Hz, 1H, 7-H), 7.26–7.37 (m, 5H, Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = -5.4$ (q, $Si(\mathit{C}H_3)_a(CH_3)_b$), −5.3 (q, $Si(CH_3)_a(\mathit{C}H_3)_b$), 18.6 (q, C-3′), 18.3 (s, $\mathit{C}(CH_3)_3$), 22.3 (q, $CH(\mathit{C}H_3)_a(CH_3)_b$), 23.3 (q, $CH(CH_3)_a(\mathit{C}H_3)_b$), 24.9 (d, C-2), 25.9 (q, $C(\mathit{C}H_3)_3$), 37.3 (t, C-6), 42.3 (t, C-3), 51.3 (d, C-4), 53.1 (d, C-2′), 57.4 (d, C-5), 66.4 (t, $\mathit{C}H_2Ph$), 66.8 (t, C-1′), 117.5 (t, C-8), 128.0 (d, 3C, Ph), 128.5 (2d, Ph), 135.5 (d, C-7), 136.9 (s, Ph), 156.3 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}436$, 3,335 (N–H), 1,723 (C=O) $cm^{-1}$; MS (FAB pos.): *m/z* (%) = 463 (100) [$(M + H)^+$]; HRMS ($C_{26}H_{47}N_2O_3Si$): calcd. 463.3356, found 463.3354.

**26b**: $R_f = 0.35$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +37.9 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c = 0.87$, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 3H, $Si(C\mathit{H_3})_a(CH_3)_b$), 0.04 (s, 3H, $Si(CH_3)_a(C\mathit{H_3})_b$), 0.83 (d, $^3J = 6.2$ Hz, 3H, $CH(C\mathit{H_3})_a(CH_3)_b$), 0.89 (s, 9H, $C(CH_3)_3$), 0.88–0.94 (m, 6H, $CH(CH_3)_a(C\mathit{H_3})_b$, 3′-$H_3$), 1.15–1.22 (m, 2H, 3-$H_2$), 1.54 (bs, 1H, $CHN\mathit{H}CH$), 1.59–1.72 (m, 1H, 2-H), 1.95–2.09 (m, 1H, 6-$H_a$), 2.33 (dtt, $^2J = 13.9$ Hz, $^3J = 6.2$ Hz, $^3J = 1.5$ Hz, 1H, 6-$H_b$), 2.68–2.76 (m, 1H, 5-H), 2.78–2.88 (m, 1H, 2′-H), 3.40 (dd, $^2J = 9.8$ Hz, $^3J = 5.3$ Hz, 1H, 1′-$H_a$), 3.46 (dd, $^2J = 9.7$ Hz, $^3J = 4.9$ Hz, 1H, 1′-$H_b$), 3.72–3.82 (m, 1H, 4-H), 5.02–5.14 (m, 4H, 8-$H_2$, $C\mathit{H_2}Ph$), 5.28 (d, $^3J = 9.1$ Hz, 1H, NHCO), 5.73–5.86 (m, 1H, 7-H), 7.27–7.40 (m, 5H, Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = -5.4$ (q, $Si(\mathit{C}H_3)_a(CH_3)_b$), −5.4 (q, $Si(CH_3)_a(\mathit{C}H_3)_b$), 17.2 (q, C-3′), 18.2 (s, $\mathit{C}(CH_3)_3$), 21.6 (q, $CH(\mathit{C}H_3)_a(CH_3)_b$), 24.0 (q, $CH(CH_3)_a(\mathit{C}H_3)_b$), 24.6 (d, C-2), 25.9 (q, $C(\mathit{C}H_3)_3$), 37.6 (t, C-3 or C-6), 37.8 (t, C-3 or C-6), 50.5 (d, C-4), 52.1 (d, C-2′), 57.2 (d, C-5), 66.3 (t, $\mathit{C}H_2Ph$), 67.5 (t, C-1′), 117.2 (t, C-8), 127.9 (d, 3C, Ph), 128.4 (d, 2C, Ph), 135.3 (d, C-7), 137.0 (s, Ph), 156.3 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}417$, 3,332 (N–H), 1,723 (C=O) $cm^{-1}$; MS (FAB pos.): *m/z* (%) = 463 (100) [$(M + H)^+$]; HRMS ($C_{26}H_{47}N_2O_3Si$): calcd. 463.3356, found 463.3354.

*Benzyl (3S,4S,2′S) and (3S,4S,2′S)-4-[1-(tert-butyldimethylsilyloxy)-2-propylamino]-2-methylhept-6-en-3-ylcarbamate* (**27a**, **27b**, $C_{25}H_{44}N_2O_3Si$)

Aldimine **11** (5.10 g, 14.3 mmol), 1.87 g Zn (28.6 mmol), 533 mg $CeCl_3{\cdot}7H_2O$ (1.43 mmol), and 2.36 $cm^3$ allyl bromide (27.2 mmol) were reacted according to GP 8 in 20 $cm^3$ THF within 16 h. Chromatography (hexanes–$Et_2O$ 8:1 → 3:1) yielded 1.85 g adduct **27a** (4.12 mmol, 29%) as colourless oil and 440 mg adduct **27b** (0.98 mmol, 7%) as a colourless solid.

**27a**: $R_f = 0.26$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +19.7 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c = 1.00$, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H, $Si(CH_3)_2$), 0.88 (s, 9H, $C(CH_3)_3$), 0.93 (d, $^3J = 6.6$ Hz, 3H, $CH(C\mathit{H_3})_a(CH_3)_b$), 0.95 (d, $^3J = 6.6$ Hz, 3H, $CH(CH_3)_a(C\mathit{H_3})_b$), 1.00 (d, $^3J = 6.4$ Hz, 3H, 3′-$H_3$), 0.50–1.50 (bs, 1H, $CHN\mathit{H}CH$), 1.72 (dsept, $^3J = 9.5$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 2.05–2.19 (m, 2H, 5-$H_2$), 2.69 (qt, $^3J = 6.5$ Hz, $^3J = 4.9$ Hz, 1H, 2′-H), 2.87 (td, $^3J = 6.7$ Hz, $^3J = 2.0$ Hz, 1H, 4-H), 3.23 (td, $^3J = 9.6$ Hz, $^3J = 2.0$ Hz, 1H, 3-H), 3.39 (dd, $^2J = 9.8$ Hz, $^3J = 5.2$ Hz, 1H, 1′-$H_a$), 3.43 (dd, $^2J = 9.8$ Hz, $^3J = 4.7$ Hz, 1H, 1′-$H_b$), 4.97–5.07 (m, 2H, 7-H), 5.05 (d, $^2J = 12.3$ Hz, 1H, $C\mathit{H_a}H_bPh$), 5.09 (d, $^2J = 12.3$ Hz, 1H, $CH_a\mathit{H_b}Ph$), 5.29 (d, $^3J = 9.9$ Hz, 1H, NHCO), 5.75 (ddt, $^3J = 16.8$ Hz, $^3J = 10.8$ Hz, $^3J = 7.3$ Hz, 1H, 6-H), 7.24–7.36 (m, 5H, Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = -5.4$ (q, $Si(\mathit{C}H_3)_a(CH_3)_b$), −5.3 (q, $Si(CH_3)_a(\mathit{C}H_3)_b$), 18.3 (s, $\mathit{C}(CH_3)_3$), 18.6 (q, C-3′), 19.6 (q, $CH(\mathit{C}H_3)_a(CH_3)_b$), 20.0 (q, $CH(CH_3)_a(\mathit{C}H_3)_b$), 25.9 (q, $C(\mathit{C}H_3)_3$), 30.7 (d, C-2), 38.6 (t, C-5), 53.3 (d, C-2′), 54.5 (d, C-4), 59.7 (d, C-3), 66.4 (t, $\mathit{C}H_2Ph$), 67.4 (t, C-1′), 117.7 (t, C-7), 127.9 (d, Ph), 128.0 (d, 2C, Ph), 128.5 (2d, Ph), 135.3 (d, C-6), 137.0 (s, Ph), 156.8 (s, NHCO) ppm; IR (DRIFT): $\bar{\nu} = 3{,}341$ (N–H), 1,726 (C=O) $cm^{-1}$; MS (FAB pos.): *m/z* (%) = 449 (100) [$(M + H)^+$]; HRMS ($C_{25}H_{45}N_2O_3Si$): calcd. 449.3199, found 449.3195.

**27b**: $R_f = 0.15$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +18.0 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c = 0.73$, $CHCl_3$); m.p.: 48–50 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H, $Si(CH_3)_2$), 0.85 (d, $^3J = 6.8$ Hz, 3H, $CH(C\mathit{H_3})_a(CH_3)_b$), 0.94 (d, $^3J = 6.8$ Hz, 3H, $CH(CH_3)_a(C\mathit{H_3})_b$), 0.89 (s, 9H, $C(CH_3)_3$), 0.89 (d, $^3J = 6.6$ Hz, 3H, 3′-$H_3$), 1.50 (bs, 1H, $CHN\mathit{H}CH$), 1.99 (septd, $^3J = 6.9$ Hz, $^3J = 5.2$ Hz, 1H, 2-H), 2.10–2.27 (m, 2H, 5-$H_2$), 2.73 (q, $^3J = 6.0$ Hz, 1H, 4-H), 2.84 (dqd, $^3J = 7.3$ Hz, $^3J = 6.6$ Hz, $^3J = 4.3$ Hz, 1H, 2′-H), 3.31 (dd, $^2J = 9.7$ Hz, $^3J = 7.3$ Hz, 1H, 1′-$H_a$), 3.49 (dd, $^2J = 9.7$ Hz, $^3J = 4.4$ Hz, 1H, 1′-$H_b$), 3.55 (dt, $^3J = 10.3$ Hz, $^3J = 5.6$ Hz, 1H, 3-H), 4.93 (d, $^3J = 10.4$ Hz, 1H, NHCO), 5.03–5.12 (m, 2H, 7-$H_2$), 5.08 (d, $^2J = 12.1$ Hz, 1H, $C\mathit{H_a}H_bPh$), 5.12 (d, $^2J = 12.1$ Hz, 1H, $CH_a\mathit{H_b}Ph$), 5.85 (ddt, $^3J = 17.3$ Hz, $^3J = 10.1$ Hz, $^3J = 7.1$ Hz, 1H, 6-H), 7.25–7.38 (m, 5H, Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = -5.4$ (q, $Si(CH_3)_a(CH_3)_b$), −5.4 (q, $Si(CH_3)_a(\mathit{C}H_3)_b$), 17.4 (q, C-3′), 17.7 (q, $CH(\mathit{C}H_3)_a(CH_3)_b$), 18.3 (q, $CH(CH_3)_a(\mathit{C}H_3)_b$), 18.3 (s, $\mathit{C}(CH_3)_3$), 25.9 (q, $C(\mathit{C}H_3)_3$), 28.5 (d, C-2), 35.2 (t, C-5), 51.8 (d, C-2′), 55.7 (d, C-4), 57.8 (d, C-3), 66.6 (t, $\mathit{C}H_2Ph$), 67.6 (t, C-1′), 117.5 (t, C-7), 128.0 (d, 3C, Ph), 128.5 (2d, Ph), 135.4 (d, C-2′), 136.9 (s, Ph), 156.8 (s, NHCO) ppm; IR (DRIFT): $\bar{\nu} = 3{,}326$ (N–H), 1,712, 1,691 (C=O) $cm^{-1}$; MS (FAB pos.): *m/z* (%) = 449 (100) [$(M + H)^+$]; HRMS ($C_{25}H_{45}N_2O_3Si$): calcd. 449.3199, found 449.3202.

*Benzyl (3S,4S,2′S) and (3S,4R,2′S)-4-[1-(tert-butyldimethylsilyloxy)-4-methyl-2-pentylamino]-2-methylhept-6-en-3-ylcarbamate* (**28a**, **28b**, $C_{28}H_{50}N_2O_3Si$)

Aldimine **12** (3.42 g, 7.62 mmol), 994 mg Zn (15.2 mmol), 288 mg $CeCl_3{\cdot}7H_2O$ (0.76 mmol), and 1.09 $cm^3$ allyl bromide (14.5 mmol) were reacted according to GP 8 in

15 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 8:1 → 5:1) yielded 1.42 g adduct **28a** (2.89 mmol, 38%) as a colourless oil and 466 mg adduct **28b** (0.95 mmol, 12%) as a colourless solid.

**28a**: $R_f = 0.51$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -10.9 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.89$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.03$ (s, 3H, Si(C$H_3$)$_a$(CH$_3$)$_b$), 0.04 (s, 3H, Si(CH$_3$)$_a$(C$H_3$)$_b$), 0.86 (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.86–0.90 (m, 3H, CH$_2$CH(CH$_3$)$_a$(C$H_3$)$_b$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.94 (d, $^3J = 6.7$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.94 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.15 ($\varphi$-t, $^3J = 6.7$ Hz, 2H, 3′-H$_2$), 1.05–1.40 (bs, 1H, CHN$H$CH), 1.64 ($\varphi$-oct, $^3J = 6.7$ Hz, 1H, 2-H), 1.65–1.76 (m, 1H, 4′-H), 2.07 ($\varphi$-dt, $^2J = 14.2$ Hz, $^3J = 7.1$ Hz, 1H, 5-H$_a$), 2.15 (dddt, $^2J = 13.7$ Hz, $^3J = 7.0$ Hz, $^3J = 5.5$ Hz, $^4J = 1.3$ Hz, 1H, 5-H$_b$), 2.53–2.64 (m, 1H, 2′-H), 2.81 (ddd, $^3J = 7.9$ Hz, $^3J = 5.4$ Hz, $^3J = 1.5$ Hz, 1H, 4-H), 3.23 (td, $^3J = 9.8$ Hz, $^3J = 1.5$ Hz, 1H, 3-H), 3.36 (dd, $^2J = 10.0$ Hz, $^3J = 4.9$ Hz, 1H, 1′-H$_a$), 3.62 (dd, $^2J = 10.0$ Hz, $^3J = 3.7$ Hz, 1H, 1′-H$_b$), 5.00–5.15 (m, 4H, 7-H$_2$, C$H_2$Ph), 5.26 (d, $^3J = 10.1$ Hz, 1H, NHCO), 5.81 (dtt, $^3J = 17.2$ Hz, $^3J = 10.1$ Hz, $^3J = 7.2$ Hz, 1H, 6-H), 7.27–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.5$ (q, Si($C$H$_3$)$_a$(CH$_3$)$_b$), −5.4 (q, Si(CH$_3$)$_a$($C$H$_3$)$_b$), 18.2 (s, $C$(CH$_3$)$_3$), 19.7 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.0 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 22.8 (q, CH$_2$CH($C$H$_3$)$_a$(CH$_3$)$_b$), 23.2 (q, CH$_2$CH(CH$_3$)$_a$($C$H$_3$)$_b$), 24.9 (d, C-4′), 25.9 (q, C($C$H$_3$)$_3$), 30.6 (d, C-2), 38.4 (t, C-5), 42.3 (t, C-3′), 54.2 (d, C-4), 56.0 (d, C-2′), 59.3 (d, C-3), 64.9 (t, C-1′), 66.4 (t, $C$H$_2$Ph), 117.5 (t, C-7), 128.0 (d, Ph), 128.0 (d, 2C, Ph), 128.5 (2d, Ph), 135.3 (d, C-6), 137.0 (s, Ph), 156.8 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}430$, 3,343 (N–H), 1,727 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 491 (100) [(M + H)$^+$]; HRMS (C$_{28}$H$_{51}$N$_2$O$_3$Si): calcd. 491.3669, found 491.3671.

**28b**: $R_f = 0.37$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +14.3 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.75$, CHCl$_3$); m.p.: <45 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.04$ (s, 6H, Si(CH$_3$)$_2$), 0.87 (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 0.86–0.91 (m, 3H, CHC$H_3$), 0.89 (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 0.89 (s, 9H, C(CH$_3$)$_3$), 0.94 (d, $^3J = 6.8$ Hz, 3H, CHC$H_3$), 1.15 ($\varphi$-t, $^3J = 6.7$ Hz, 2H, 3′-H$_2$), 1.40 (bs, 1H, CHN$H$CH), 1.60 ($\varphi$-nonet, $^3J = 6.6$ Hz, $^3J = 6.6$ Hz, 1H, 4′-H), 1.96 (septd, $^3J = 6.7$ Hz, $^3J = 5.5$ Hz, 1H, 2-H), 2.10–2.26 (m, 2H, 5-H$_2$), 2.70 (qd, $^3J = 6.7$ Hz, $^3J = 4.2$ Hz, 1H, 2′-H), 2.75 (q, $^3J = 6.0$ Hz, 1H, 4-H), 3.32 (dd, $^2J = 10.0$ Hz, $^3J = 6.2$ Hz, 1H, 1′-H$_a$), 3.54 (dt, $^3J = 10.2$ Hz, $^3J = 5.6$ Hz, 1H, 3-H), 3.61 (dd, $^2J = 9.9$ Hz, $^3J = 3.8$ Hz, 1H, 1′-H$_b$), 4.97 (d, $^3J = 10.2$ Hz, 1H, NHCO), 5.03–5.13 (m, 4H, 7-H$_2$, C$H_2$Ph), 5.84 (ddt, $^3J = 17.2$ Hz, $^3J = 10.2$ Hz, $^3J = 7.2$ Hz, 1H, 6-H), 7.25–7.38 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.5$ (q, Si($C$H$_3$)$_a$(CH$_3$)$_b$), −5.4 (q, Si(CH$_3$)$_a$($C$H$_3$)$_b$), 18.0 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.9 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 18.3 (s, $C$(CH$_3$)$_3$), 22.8 (q, CH$_2$CH($C$H$_3$)$_a$(CH$_3$)$_b$), 23.5 (q, CH$_2$CH(CH$_3$)$_a$($C$H$_3$)$_b$), 24.5 (d, C-1), 24.9 (d, C-4′), 25.9 (q, C($C$H$_3$)$_3$), 28.7 (d, C-2), 35.6 (t, C-5), 41.9 (t, C-3′), 54.6 (d, C-2′), 55.7 (d, C-4), 57.7 (d, C-3), 65.2 (t, C-1′), 66.5 (t, $C$H$_2$Ph), 117.4 (t, C-7), 128.0 (d, 3C, Ph), 128.5, (2d, Ph), 135.6 (d, C-6), 136.9 (s, Ph), 156.7 (s, NHCO) ppm; IR (DRIFT): $\bar{\nu} = 3{,}301$ (N–H), 1,721, 1,692 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 491 (100) [(M + H)$^+$]; HRMS (C$_{28}$H$_{51}$N$_2$O$_3$Si): calcd. 491.3669, found 491.3666.

*tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-7-methyloct-1-en-4-ylamino]-3-methylbutanoate* (**29a**, **29b**, C$_{26}$H$_{42}$N$_2$O$_4$)

Aldimine **13** (404 mg, 1.00 mmol), 131 mg Zn (2.00 mmol), 37 mg CeCl$_3$·7H$_2$O (0.10 mmol), and 170 mm$^3$ allyl bromide (1.90 mmol) were reacted according to GP 8 in 4 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 10:1 → 8:1) yielded 98 mg adduct **29a** (0.22 mmol, 22%) as a colourless solid and 72 mg adduct **29b** (0.16 mmol, 16%) as a colourless oil.

**29a**: $R_f = 0.44$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -31.6 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.20$, CHCl$_3$); m.p.: 48–50 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.91$ (d, $^3J = 6.3$ Hz, 3H, CHC$H_3$), 0.92 (d, $^3J = 6.5$ Hz, 3H, CHC$H_3$), 0.93 (d, $^3J = 6.5$ Hz, 3H, CHC$H_3$), 0.93 (d, $^3J = 6.8$ Hz, 3H, CHC$H_3$), 1.26 (bs, 1H, CHN$H$CH), 1.32 (ddd, $^2J = 13.7$ Hz, $^3J = 8.2$ Hz, $^3J = 5.6$ Hz, 1H, 6′-H$_a$), 1.37 (ddd, $^2J = 14.0$ Hz, $^3J = 8.6$ Hz, $^3J = 5.5$ Hz, 1H, 6′-H$_b$), 1.47 (s, 9H, C(C$H_3$)$_3$), 1.64 (dsept, $^3J = 7.9$ Hz, $^3J = 6.5$ Hz, 1H, 7′-H), 1.77 ($\varphi$-oct, $^3J = 6.7$ Hz, 1H, 3-H), 2.03–2.12 (m, 1H, 3′-H$_a$), 2.16 (dtt, $^2J = 13.9$ Hz, $^3J = 6.9$ Hz, $^3J = 1.9$ Hz, 1H, 3′-H$_b$), 2.48 (td, $^3J = 7.0$ Hz, $^3J = 1.9$ Hz, 1H, 4′-H), 2.89 (d, $^3J = 6.6$ Hz, 1H, 2-H), 3.72 (tdd, $^3J = 9.2$ Hz, $^3J = 5.6$ Hz, $^3J = 1.9$ Hz, 1H, 5′-H), 5.03 (d, $^3J = 9.5$ Hz, 1H, NHCO), 5.04–5.11 (m, 2H, 1′-H), 5.07 (d, $^2J = 12.2$ Hz, 1H, OC$H_a$H$_b$), 5.11 (d, $^2J = 12.2$ Hz, 1H, OCH$_a$$H_b$), 5.78 (dddd, $^3J = 17.0$ Hz, $^3J = 9.5$ Hz, $^3J = 7.6$ Hz, $^3J = 6.8$ Hz, 1H, 2′-H), 7.27–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.9$ (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 19.5 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 22.3 (q, CH$_2$CH($C$H$_3$)$_a$(CH$_3$)$_b$), 23.3 (q, CH$_2$CH($C$H$_3$)$_a$(CH$_3$)$_b$), 24.9 (d, C-7′), 28.2 (q, C($C$H$_3$)$_3$), 32.2 (d, C-3), 37.7 (t, C-3′), 42.4 (t, C-6′), 51.2 (d, C-5′), 58.9 (d, C-4′), 66.5 (t, OCH$_2$), 68.0 (d, C-2), 81.0 (s, $C$(CH$_3$)$_3$), 117.8 (t, C-1′), 128.1 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 135.3 (d, C-2′), 136.9 (s, Ph), 156.2 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}346$ (N–H), 1,721, 1,704 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 447 (86) [(M + H)$^+$]; HRMS (C$_{26}$H$_{43}$N$_2$O$_4$): calcd. 447.3223, found 447.3226.

**29b**: $R_f = 0.40$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = \pm 0.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.84$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.89$ (d, $^3J = 6.3$ Hz, 3H, CHC$H_3$), 0.90 (d, $^3J = 6.5$ Hz, 3H, CHC$H_3$), 0.91 (d, $^3J = 6.5$ Hz, 3H, CHC$H_3$), 0.92 (d, $^3J = 6.8$ Hz, 3H, CHC$H_3$), 1.15–1.40 (m, 2H, 6′-H), 1.46 (s, 9H, C(C$H_3$)$_3$), 1.55–1.72 (m, 2H, CHN*H*CH, 7′-H), 1.80 (φ-oct, $^3J = 6.6$ Hz, 1H, 3-H), 2.11 (t, $^3J = 7.1$ Hz, 2H, 3′-H$_2$), 2.57 (td, $^3J = 6.6$ Hz, $^3J = 3.1$ Hz, 1H, 4′-H), 2.91 (d, $^3J = 7.3$ Hz, 1H, 2-H), 3.77–3.86 (m, 1H, 5′-H), 5.00–5.13 (m, 5H, 1′-H, NHCO, OCH$_2$), 5.67–5.79 (m, 1H, 2′-H), 7.26–7.39 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.4$ (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 19.3 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 21.9 (q, CH$_2$CH($C$H$_3$)$_a$(CH$_3$)$_b$), 23.6 (q, CH$_2$CH(CH$_3$)$_a$($C$H$_3$)$_b$), 24.7 (d, C-7′), 28.1 (q, C($C$H$_3$)$_3$), 32.4 (d, C-3), 36.3 (t, C-3′), 38.8 (t, C-6′), 50.3 (d, C-5′), 60.1 (d, C-4′), 66.2 (d, C-2), 66.4 (t, O$C$H$_2$), 81.0 (s, $C$(CH$_3$)$_3$), 117.6 (t, C-1′), 127.9 (d, 3C, Ph), 128.4 (2d, Ph), 135.0 (d, C-2′), 136.9 (s, Ph), 156.3 (s, NHCO), 175.1 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}346$ (N–H), 1,725 (bs, C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 447 (30) [(M + H)$^+$]; HRMS ($C_{26}H_{43}N_2O_4$): calcd. 447.3223, found 447.3221.

### *tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-6-methylhept-1-en-4-ylamino]propanoate* (**30a**, **30b**, $C_{23}H_{36}N_2O_4$)

Aldimine **14** (1.45 g, 4.00 mmol), 523 mg Zn (8.00 mmol), 149 mg CeCl$_3$·7H$_2$O (0.40 mmol), and 661 mm$^3$ allyl bromide (7.60 mmol) were reacted according to GP 8 in 5 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 8:1 → 3:1) yielded 860 mg adduct **30a** (2.13 mmol, 53%) and 216 mg adduct **30b** (0.53 mmol, 13%) as colourless oils.

**30a**: $R_f = 0.33$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -27.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 0.82, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.94$ (d, $^3J = 6.7$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.95 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.17 (d, $^3J = 6.9$ Hz, 3H, 3-H$_3$), 1.46 (s, 9H, C(C$H_3$)$_3$), 1.44–1.50 (m, 1H, CHN*H*CH), 1.67 (dsept, $^3J = 9.8$ Hz, $^3J = 6.7$ Hz, 1H, 6′-H), 2.06–2.20 (m, 2H, 3′-H$_2$), 2.76 (ddd, $^3J = 7.7$ Hz, $^3J = 6.4$ Hz, $^3J = 1.5$ Hz, 1H, 4′-H), 3.22 (q, $^3J = 6.9$ Hz, 1H, 2-H), 3.17–3.24 (m, 1H, 5′-H), 5.03–5.14 (m, 3H, 1′-H$_2$, NHCO), 5.08 (d, $^2J = 12.3$ Hz, 1H, OC$H_a$H$_b$), 5.13 (d, $^2J = 12.2$ Hz, 1H, OCH$_a H_b$), 5.77 (ddt, $^3J = 15.9$ Hz, $^3J = 11.2$ Hz, $^3J = 7.2$ Hz, 1H, 2′-H), 7.28–7.41 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.7$ (q, CHC$H_3$), 19.8 (q, CHC$H_3$), 19.9 (q, CHC$H_3$), 28.1 (q, C($C$H$_3$)$_3$), 31.2 (d, C-6′), 38.7 (t, C-3′), 55.4 (d, C-4′), 57.4 (d, C-2 or C-5′), 59.4 (d, C-2 or C-5′), 66.5 (t, OCH$_2$), 81.0 (s, $C$(CH$_3$)$_3$), 117.9 (t, C-1′), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (2d, Ph), 135.0 (d, C-2′), 136.9 (s, Ph), 156.7 (s, NHCO), 175.4 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}337$ (N–H), 1,727 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 405 (100) [(M + H)$^+$]; HRMS ($C_{23}H_{37}N_2O_4$): calcd. 405.2753, found 407.2751.

**30b**: $R_f = 0.15$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -1.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 1.00, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.93$ (d, $^3J = 6.7$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.93 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.18 (d, $^3J = 6.8$ Hz, 3H, 3-H$_3$), 1.45 (s, 9H, C(C$H_3$)$_3$), 1.60–1.90 (bs, 1H, CHN*H*CH), 1.76 (dsept, $^3J = 7.9$ Hz, $^3J = 6.7$ Hz, 1H, 6′-H), 1.98 (dt, $^2J = 14.0$ Hz, $^3J = 8.6$ Hz, 1H, 3′-H$_a$), 2.24 (dddt, $^2J = 14.0$ Hz, $^4J = 8.6$ Hz, $^3J = 5.6$ Hz, $^3J = 3.6$ Hz, 1H, 3′-H$_b$), 2.72 (dt, $^3J = 8.5$ Hz, $^3J = 4.1$ Hz, 1H, 4′-H), 3.44 (q, $^3J = 6.9$ Hz, 1H, 2-H), 3.55 (ddd, $^3J = 10.3$ Hz, $^3J = 8.1$ Hz, $^3J = 4.3$ Hz, 1H, 5′-H), 4.66 (d, $^3J = 10.9$ Hz, 1H, NHCO), 5.06 (d, $^2J = 12.3$ Hz, 1H, OC$H_a$H$_b$), 5.14 (d, $^2J = 12.3$ Hz, 1H, OCH$_a H_b$), 5.08–5.18 (m, 2H, 1′-H), 5.83 (dddd, $^3J = 16.7$ Hz, $^3J = 10.3$ Hz, $^3J = 8.4$ Hz, $^3J = 6.0$ Hz, 1H, 2′-H), 7.27–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.3$ (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.3 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 19.5 (q, C-3), 28.1 (q, C($C$H$_3$)$_3$), 29.5 (d, C-6′), 34.5 (t, C-3′), 54.7 (d, C-2), 55.7 (d, C-4′), 57.2 (d, C-5′), 66.6 (t, O$C$H$_2$), 80.7 (s, $C$(CH$_3$)$_3$), 118.1 (t, C-1′), 128.0 (d, 3C, Ph), 128.5 (d, 2C, Ph), 135.2 (d, C-2′), 136.8 (s, Ph), 156.9 (s, NHCO), 175.4 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}335$ (N–H), 1,726 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 405 (100) [(M + H)$^+$]; HRMS ($C_{23}H_{37}N_2O_4$): calcd. 405.2753, found 407.2751.

### *tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-6-methylhept-1-en-4-ylamino]-4-methylpentanoate* (**31a**, **31b**, $C_{26}H_{42}N_2O_4$)

Aldimine **15** (29.7 g, 73.5 mmol), 9.61 g Zn (147 mmol), 2.74 g CeCl$_3$·7H$_2$O (7.35 mmol), and 10.5 cm$^3$ allyl bromide (140 mmol) were reacted according to GP 8 in 40 cm$^3$ THF within 16 h. Chromatography (hexanes–Et$_2$O 6:1 → 3:1) yielded 6.58 g adduct **31a** (14.7 mmol, 20%) and 6.70 g adduct **31b** (15.0 mmol, 20%) as colourless oils.

**31a**: $R_f = 0.43$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -31.9 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 0.70, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.88$ (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.90 (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(CH$_3$)$_a$(C$H_3$)$_b$), 0.95 (d, $^3J = 6.7$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.96 (d, $^3J = 6.7$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.26–1.34 (m, 1H, 3-H$_a$), 1.30–1.55 (bs, 1H, CHN*H*CH), 1.35 (dt, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, 2H, 3-H$_b$), 1.41 (s, 9H, C(C$H_3$)$_3$), 1.60–1.77 (m, 2H, 4-H, 6′-H), 2.11 (tt, $^3J = 7.0$ Hz, $^4J = 1.3$ Hz, 2H, 3′-H$_2$), 2.76 (td, $^3J = 6.9$ Hz, $^3J = 1.5$ Hz, 1H, 4′-H), 3.13 (dd, $^3J = 7.5$ Hz, $^3J = 7.0$ Hz, 1H, 2-H), 3.20 (td, $^3J = 9.9$ Hz, $^3J = 1.4$ Hz, 1H, 5′-H), 5.04 (ddt, $^3J = 10.4$ Hz, $^2J = 2.0$ Hz, $^4J = 1.3$ Hz, 1H, 1′-H$_{cis}$), 5.01–5.09 (m, 1H, 1′-H$_{trans}$), 5.09 (d, $^2J = 12.1$ Hz, 1H, OC$H_a$H$_b$), 5.13 (d, $^2J = 12.1$ Hz, 1H, OCH$_a H_b$), 5.30 (d, $^3J = 9.9$ Hz, 1H, NHCO), 5.76 (ddt, $^3J = 17.6$ Hz, $^3J = 10.4$ Hz, $^3J = 7.2$ Hz, 1H, 2′-H), 7.14–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.7$ (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 22.5 (q,

$CH_2CH(CH_3)_a(CH_3)_b$), 22.7 (q, $CH_2CH(CH_3)_a(CH_3)_b$), 24.8 (d, C-4), 28.1 (q, $C(CH_3)_3$), 31.4 (d, C-6′), 38.9 (t, C-3′), 43.7 (t, C-3), 55.6 (d, C-4′), 59.5 (d, C-5′), 61.0 (d, C-2), 66.5 (t, $OCH_2$), 81.0 (s, $C(CH_3)_3$), 118.0 (t, C-1′), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (2d, Ph), 134.9 (d, C-2′), 137.0 (s, Ph), 156.7 (s, NHCO), 175.7 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,337 (N–H), 1,727 (C=O) $cm^{-1}$; MS (FAB pos.): *m*/*z* (%) = 447 (97) [$(M + H)^+$]; HRMS ($C_{26}H_{43}N_2O_4$): calcd. 447.3223, found 447.3221.

**31b**: $R_f = 0.30$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -8.8 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c$ = 0.63, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.87 (d, $^3J$ = 6.7 Hz, 3H, $CH_2CH(CH_3)_a(CH_3)_b$), 0.91 (d, $^3J$ = 6.7 Hz, 3H, $CH_2CH(CH_3)_a(CH_3)_b$), 0.93 (d, $^3J$ = 6.8 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.94 (d, $^3J$ = 6.8 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 1.30 (dt, $^2J$ = 13.4 Hz, $^3J$ = 7.3 Hz, 1H, 3-$H_a$), 1.39 (dt, $^2J$ = 13.6 Hz, $^3J$ = 6.9 Hz, 1H, 3-$H_b$), 1.46 (s, 9H, $C(CH_3)_3$), 1.60–1.72 (m, 2H, 4-H, CHN*H*CH), 1.79 ($\varphi$-oct, $^3J$ = 6.8 Hz, 1H, 6′-H), 1.92–2.03 (m, 1H, 3′-$H_a$), 2.22 (dddt, $^2J$ = 14.0 Hz, $^3J$ = 5.9 Hz, $^3J$ = 4.2 Hz, $^4J$ = 1.6 Hz, 1H, 3′-$H_b$), 2.69 (dt, $^3J$ = 8.6 Hz, $^3J$ = 4.2 Hz, 1H, 4′-H), 3.33 (t, $^3J$ = 7.3 Hz, 1H, 2-H), 3.57 (ddd, $^3J$ = 10.2 Hz, $^3J$ = 8.0 Hz, $^3J$ = 4.4 Hz, 1H, 5′-H), 4.68 (d, $^3J$ = 10.0 Hz, 1H, NHCO), 5.04–5.17 (m, 4H, 1′-H, $OCH_2$), 5.79 (dddd, $^3J$ = 16.9 Hz, $^3J$ = 10.9 Hz, $^3J$ = 8.4 Hz, $^3J$ = 6.0 Hz, 1H, 2′-H), 7.27–7.39 (m, 5H, Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 19.3 (q, $CH(CH_3)_a(CH_3)_b$), 20.3 (q, $CH(CH_3)_a(CH_3)_b$), 22.6 (q, $CH_2CH(CH_3)_a(CH_3)_b$), 22.8 (q, $CH_2CH(CH_3)_a(CH_3)_b$), 24.9 (d, C-4), 28.1 (q, $C(CH_3)_3$), 29.6 (d, C-6′), 34.7 (t, C-3′), 43.5 (t, C-3), 56.1 (d, C-4′), 57.2 (d, C-5′), 58.4 (d, C-2), 66.6 (t, $OCH_2$), 80.7 (s, $C(CH_3)_3$), 118.1 (t, C-1′), 128.0 (d, 3C, Ph), 128.5 (d, 2C, Ph), 135.2 (d, C-2′), 136.9 (s, Ph), 156.8 (s, NHCO), 175.7 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,335 (N–H), 1,726 (C=O) $cm^{-1}$; MS (FAB pos.): *m*/*z* (%) = 447 (100) [$(M + H)^+$]; HRMS ($C_{26}H_{43}N_2O_4$): calcd. 447.3223, found 447.3221.

*tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-7-methyloct-1-en-4-ylamino]-3-phenylpropanoate* (**32a**, **32b**, $C_{30}H_{42}N_2O_4$)

Aldimine **16** (2.26 g, 5.00 mmol), 654 mg Zn (10.0 mmol), 186 mg $CeCl_3{\cdot}7H_2O$ (0.50 mmol), and 720 $mm^3$ allyl bromide (9.50 mmol) were reacted according to GP 8 in 15 $cm^3$ THF within 16 h. Chromatography (hexanes–$Et_2O$ 8:1 → 4:1) yielded 537 mg adduct **32a** (1.09 mmol, 22%) and 672 mg adduct **32b** (1.36 mmol, 27%) as colourless oils.

**32a**: $R_f = 0.41$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -15.6 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c$ = 1.17, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.81 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.83 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.95–1.15 (m, 2H, 6′-H), 1.38 (s, 9H, $C(CH_3)_3$), 1.33–1.52 (m, 2H, 7′-H, CHN*H*CH), 2.06 (dddt, $^2J$ = 13.7 Hz, $^3J$ = 7.9 Hz, $^3J$ = 6.9 Hz, $^4J$ = 1.4 Hz, 1H, 3′-$H_a$), 2.14 (dtt, $^2J$ = 13.6 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1H, 3′-$H_b$), 2.50 (td, $^3J$ = 7.0 Hz, $^3J$ = 1.8 Hz, 1H, 4′-H), 2.71 (dd, $^2J$ = 13.4 Hz, $^3J$ = 8.0 Hz, 1H, 3-$H_a$), 2.83 (dd, $^2J$ = 13.4 Hz, $^3J$ = 6.3 Hz, 1H, 3-$H_b$), 3.35 (dd, $^3J$ = 8.0 Hz, $^3J$ = 6.3 Hz, 1H, 2-H), 3.62 (tdd, $^3J$ = 9.3 Hz, $^3J$ = 5.7 Hz, $^3J$ = 1.5 Hz, 1H, 5′-H), 4.72 (d, $^3J$ = 9.7 Hz, 1H, NHCO), 5.02–5.10 (m, 4H, 1′-$H_2$, $OCH_2$), 5.75 (dddd, $^3J$ = 17.5 Hz, $^3J$ = 9.4 Hz, $^3J$ = 7.8 Hz, $^3J$ = 6.5 Hz, 1H, 2′-H), 7.15–7.40 (m, 10H, 2 Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 22.2 (q, $CH(CH_3)_a(CH_3)_b$), 23.1 (q, $CH(CH_3)_a(CH_3)_b$), 24.8 (d, C-7′), 28.0 (q, $C(CH_3)_3$), 37.9 (t, C-3′), 40.5 (t, C-3), 42.6 (t, C-6′), 51.3 (d, C-5′), 58.7 (d, C-4′), 63.9 (d, C-2), 66.4 (t, $OCH_2$), 81.3 (s, $C(CH_3)_3$), 118.0 (t, C-1′), 126.5 (d, Ph), 128.0 (d, 3C, Ph), 128.2 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.5 (2d, Ph), 135.2 (d, C-2′), 137.0 (s, Ph), 138.0 (s, Ph), 156.2 (s, NHCO), 174.4 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,339 (N–H), 1,724 (C=O) $cm^{-1}$; MS (FAB pos.): *m*/*z* (%) = 495 (21) [$(M + H)^+$]; HRMS ($C_{30}H_{43}N_2O_4$): calcd. 495.3223, found 495.3227.

**32b**: $R_f = 0.34$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = +8.5 \times 10^{-1}$ deg $cm^2$ $g^{-1}$ ($c$ = 1.19, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.86 (d, $^3J$ = 6.5 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 0.88 (d, $^3J$ = 6.6 Hz, 3H, $CH(CH_3)_a(CH_3)_b$), 1.04–1.24 (m, 2H, 6′-$H_2$), 1.35 (s, 9H, $C(CH_3)_3$), 1.49–1.60 (m, 2H, 7′-H, CHN*H*CH), 2.05–2.15 (m, 2H, 3′-$H_2$), 2.56 (td, $^3J$ = 7.2 Hz, $^3J$ = 3.3 Hz, 1H, 4′-H), 2.73 (dd, $^2J$ = 13.4 Hz, $^3J$ = 7.8 Hz, 1H, 3-$H_a$), 2.81 (dd, $^2J$ = 13.4 Hz, $^3J$ = 6.6 Hz, 1H, 3-$H_b$), 3.43 (dd, $^3J$ = 7.7 Hz, $^3J$ = 6.5 Hz, 1H, 2-H), 3.70–3.80 (m, 1H, 5′-H), 4.57 (d, $^3J$ = 9.2 Hz, 1H, NHCO), 5.03–5.14 (m, 4H, 1′-$H_2$, $OCH_2$), 5.71 (ddt, $^3J$ = 17.4 Hz, $^3J$ = 10.4 Hz, $^3J$ = 7.2 Hz, 1H, 2′-H), 7.15–7.40 (m, 10H, 2 Ph) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.8 (q, $CH(CH_3)_a(CH_3)_b$), 23.7 (q, $CH(CH_3)_a(CH_3)_b$), 24.6 (d, C-7′), 28.0 (q, $C(CH_3)_3$), 36.4 (t, C-3′), 38.6 (t, C-3), 40.7 (t, C-6′), 50.4 (d, C-5′), 59.8 (d, C-4′), 62.8 (d, C-2), 66.4 (t, $OCH_2$), 81.2 (s, $C(CH_3)_3$), 117.7 (t, C-1′), 126.4 (d, Ph), 128.0 (d, 2C, Ph), 128.0 (d, Ph), 128.2 (d, 2C, Ph), 128.4 (d, 2C, Ph), 129.5 (2d, Ph), 134.9 (d, C-2′), 136.9, 138.0 (2s, 2 Ph), 156.2 (s, NHCO), 174.8 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,341 (N–H), 1,722 (C=O) $cm^{-1}$; MS (FAB pos.): *m*/*z* (%) = 495 (45) [$(M + H)^+$]; HRMS ($C_{30}H_{43}N_2O_4$): calcd. 495.3223, found 495.3220.

*tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-6-methylhept-1-en-4-ylamino]-3-methylbutanoate* (**33a**, **33b**, $C_{25}H_{40}N_2O_4$)

Aldimine **17** (5.86 g, 15.0 mmol), 1.96 g Zn (30.0 mmol), 559 mg $CeCl_3{\cdot}7H_2O$ (1.50 mmol), and 2.43 $cm^3$ allyl bromide (28.5 mmol) were reacted according to GP 8 in 30 $cm^3$ THF within 16 h. Chromatography (hexanes–$Et_2O$ 8:1 → 4:1) yielded 878 mg adduct **33a** (2.00 mmol, 14%)

and 1.09 g adduct **33b** (2.50 mmol, 17%) as colourless oils.

**33a**: $R_f = 0.47$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -28.5 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 0.84, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.90 (d, $^3J$ = 6.7 Hz, 3H, CHC$H_3$), 0.94 (d, $^3J$ = 6.7 Hz, 3H, CHC$H_3$), 0.94 (d, $^3J$ = 6.8 Hz, 3H, CHC$H_3$), 0.95 (d, $^3J$ = 6.8 Hz, 3H, CHC$H_3$), 1.18 (bs, 1H, CHN*H*CH), 1.48 (s, 9H, C(C$H_3$)$_3$), 1.71 (dsept, $^3J$ = 10.0 Hz, $^3J$ = 6.7 Hz, 1H, 6′-H), 1.74 ($\varphi$-oct, $^3J$ = 6.8 Hz, 1H, 3-H), 2.12 (tt, $^3J$ = 7.0 Hz, $^3J$ = 1.3 Hz, 2H, 3′-H$_2$), 2.72 (td, $^3J$ = 6.9 Hz, $^3J$ = 1.5 Hz, 1H, 4′-H), 2.82 (d, $^3J$ = 6.9 Hz, 1H, 2-H), 3.20 (td, $^3J$ = 10.0 Hz, $^3J$ = 1.5 Hz, 1H, 5′-H), 5.02–5.08 (m, 2H, 1′-H$_2$), 5.09 (d, $^2J$ = 12.1 Hz, 1H, OC$H_a$H$_b$), 5.13 (d, $^2J$ = 12.2 Hz, 1H, OCH$_a$$H_b$), 5.27 (d, $^3J$ = 9.9 Hz, 1H, NHCO), 5.76 (ddt, $^3J$ = 17.8 Hz, $^3J$ = 10.6 Hz, $^3J$ = 7.2 Hz, 1H, 2′-H), 7.27–7.41 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1 (q, CHC$H_3$), 19.3 (q, CHC$H_3$), 19.8 (q, CHC$H_3$), 20.1 (q, CHC$H_3$), 28.2 (q, C(C$H_3$)$_3$), 31.2 (d, C-6′), 32.2 (d, C-3), 38.9 (t, C-3′), 55.9 (d, C-4′), 59.6 (d, C-5′), 66.5 (t, O*C*H$_2$), 68.5 (d, C-2), 81.1 (s, *C*(CH$_3$)$_3$), 117.9 (t, C-1′), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 135.0 (d, C-2′), 137.0 (s, Ph), 156.7 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,343 (N–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 433 (100) [(M + H)$^+$]; HRMS (C$_{25}$H$_{41}$N$_2$O$_4$): calcd. 433.3066, found 433.3072.

**33b**: $R_f = 0.38$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -7.0 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 1.00, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.89 (d, $^3J$ = 6.5 Hz, 3H, CHC$H_3$), 0.91 (d, $^3J$ = 6.3 Hz, 3H, CHC$H_3$), 0.92 (d, $^3J$ = 6.6 Hz, 3H, CHC$H_3$), 0.93 (d, $^3J$ = 6.7 Hz, 3H, CHC$H_3$), 1.46 (s, 9H, C(C$H_3$)$_3$), 1.61 (bs, 1H, CHN*H*CH), 1.75 ($\varphi$-oct, $^3J$ = 6.8 Hz, 1H, 3-H), 1.81 ($\varphi$-oct, $^3J$ = 6.7 Hz, 1H, 6′-H), 1.99 (dt, $^2J$ = 13.6 Hz, $^3J$ = 8.0 Hz, 1H, 3′-H$_a$), 2.22 (dddt, $^2J$ = 13.8 Hz, $^3J$ = 6.1 Hz, $^3J$ = 4.3 Hz, $^4J$ = 1.6 Hz, 1H, 3′-H$_b$), 2.65 (dt, $^3J$ = 8.6 Hz, $^3J$ = 4.4 Hz, 1H, 4′-H), 3.00 (d, $^3J$ = 6.6 Hz, 1H, 2-H), 3.55 (ddd, $^3J$ = 10.0 Hz, $^3J$ = 7.5 Hz, $^3J$ = 4.3 Hz, 1H, 5′-H), 4.74 (d, $^3J$ = 10.3 Hz, 1H, NHCO), 5.06 (d, $^2J$ = 12.3 Hz, 1H, OC$H_a$H$_b$), 5.10 (d, $^2J$ = 12.3 Hz, 1H, OCH$_a$$H_b$), 5.09–5.16 (m, 2H, 1′-H), 5.73–5.85 (m, 1H, 2′-H), 7.27–7.38 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 18.8 (q, CH*C*H$_3$), 19.1 (q, CH*C*H$_3$), 19.2 (q, CH*C*H$_3$), 20.4 (q, CH*C*H$_3$), 28.2 (q, C(*C*H$_3$)$_3$), 29.4 (d, C-6′), 32.1 (d, C-3), 34.9 (t, C-3′), 56.6 (d, C-4′), 57.1 (d, C-5′), 65.7 (d, C-2), 66.6 (t, O*C*H$_2$), 80.7 (s, *C*(CH$_3$)$_3$), 118.0 (t, C-1′), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (2d, Ph), 135.3 (d, C-2′), 136.8 (s, Ph), 156.8 (s, NHCO), 175.0 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,343 (N–H), 1,724 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 433 (93), [(M + H)$^+$]; HRMS (C$_{25}$H$_{40}$N$_2$O$_4$): calcd. 433.3066, found 433.3064.

*tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-6-methylhept-1-en-4-ylamino]-3-phenylpropanoate* (**34a**, **34b**, C$_{29}$H$_{40}$N$_2$O$_4$)
Aldimine **18** (6.50 g, 14.8 mmol), 1.94 g Zn (29.6 mmol), 552 mg CeCl$_3$·7H$_2$O (1.48 mmol), and 2.45 cm$^3$ allyl bromide (28.2 mmol) were reacted according to GP 8 in 20 cm$^3$ THF within 16 h. Chromatography (hexanes–EtOAc 6:1) yielded 3.74 g adduct **34a** (7.79 mmol, 53%) and 771 mg adduct **34b** (1.60 mmol, 11%) as colourless oils.

**34a**: $R_f = 0.33$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -43.2 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 0.86, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.79 (d, $^3J$ = 6.7 Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.84 (d, $^3J$ = 6.7 Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.37 (s, 9H, C(C$H_3$)$_3$), 1.33–1.43 (m, 1H, 6′-H), 1.68 (bs, 1H, CHN*H*CH), 2.09 (tq, $^3J$ = 7.2 Hz, $^4J$, $^3J$ = 1.4 Hz, 2H, 3′-H$_2$), 2.72 (dd, $^2J$ = 13.3 Hz, $^3J$ = 8.0 Hz, 1H, 3-H$_a$), 2.74 (dt, $^3J$ = 7.1 Hz, $^3J$ = 1.6 Hz, 1H, 4′-H), 2.81 (dd, $^2J$ = 13.4 Hz, $^3J$ = 6.7 Hz, 1H, 3-H$_b$), 3.11 (td, $^3J$ = 10.0 Hz, $^3J$ = 1.4 Hz, 1H, 5′-H), 3.30 (dd, $^3J$ = 7.9 Hz, $^3J$ = 6.7 Hz, 1H, 2-H), 5.01–5.13 (m, 2H, 1′-H, NHCO), 5.06 (d, $^2J$ = 12.5 Hz, 1H, OC$H_a$H$_b$), 5.12 (d, $^2J$ = 12.3 Hz, 1H, OCH$_a$$H_b$), 5.73 (ddt, $^3J$ = 16.3 Hz, $^3J$ = 10.7 Hz, $^3J$ = 7.2 Hz, 1H, 2′-H), 7.14–7.40 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.7 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 19.9 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 28.0 (q, C(*C*H$_3$)$_3$), 31.1 (d, C-6′), 38.8 (t, C-3′), 40.5 (t, C-3), 55.6 (d, C-4′), 59.5 (d, C-5′), 64.0 (d, C-2), 66.4 (t, O*C*H$_2$), 81.3 (s, *C*(CH$_3$)$_3$), 118.0 (t, C-1′), 126.5 (d, Ph), 127.9 (d, 3C, Ph), 128.2 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.4 (2d, Ph), 134.9 (d, C-2′), 137.1, 137.8 (2s, 2 Ph), 156.6 (s, NHCO), 174.4 (s, C-1) ppm; IR (KBr): $\bar{\nu}$ = 3,400, 3,335 (N–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 481 (100) [(M + H)$^+$]; HRMS (C$_{29}$H$_{41}$N$_2$O$_4$): calcd. 481.3066, found 481.3071.

**34b**: $R_f = 0.15$ (hexanes–EtOAc 6:1); $[\alpha]_D^{20} = -21.3 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c$ = 1.07, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.85 (d, $^3J$ = 6.7 Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.88 (d, $^3J$ = 6.7 Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.35 (s, 9H, C(C$H_3$)$_3$), 1.56 (bs, 1H, CHN*H*CH), 1.88 (septd, $^3J$ = 6.7 Hz, $^3J$ = 6.2 Hz, 1H, 6′-H), 2.03 (dddt, $^2J$ = 14.3 Hz, $^3J$ = 7.2 Hz, $^3J$ = 5.9 Hz, $^4J$ = 1.3 Hz, 1H, 3′-H$_a$), 2.12 (dddt, $^2J$ = 14.1 Hz, $^3J$ = 7.0 Hz, $^3J$ = 5.3 Hz, $^4J$ = 1.4 Hz, 1H, 3′-H$_b$), 2.59 (q, $^3J$ = 5.7 Hz, 1H, 4′-H), 2.80 (dd, $^2J$ = 13.3 Hz, $^3J$ = 7.5 Hz, 1H, 3-H$_a$), 2.90 (dd, $^2J$ = 13.4 Hz, $^3J$ = 6.6 Hz, 1H, 3-H$_b$), 3.51 (dt, $^3J$ = 10.1 Hz, $^3J$ = 5.7 Hz, 1H, 5′-H), 3.52 (dd, $^3J$ = 7.6 Hz, $^3J$ = 6.5 Hz, 1H, 2-H), 4.89 (d, $^3J$ = 10.4 Hz, 1H, NHCO), 4.93 (ddt, $^3J$ = 17.1 Hz, $^2J$ = 1.9 Hz, $^4J$ = 1.3 Hz, 1H, 1′-H$_{trans}$), 4.96 (ddt, $^3J$ = 10.3 Hz, $^2J$ = 2.0 Hz, $^4J$ = 1.0 Hz, 1H, 1′-H$_{cis}$), 5.07 (d, $^2J$ = 12.0 Hz, 1H, OC$H_a$H$_b$), 5.11 (d, $^2J$ = 12.3 Hz, 1H, OCH$_a$$H_b$), 5.73 (ddt,

${}^3J = 17.3$ Hz, ${}^3J = 10.2$ Hz, ${}^3J = 7.1$ Hz, 1H, 2′-H), 7.17–7.38 (m, 10H, 2 Ph) ppm; ${}^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 17.8$ (q, $\mathrm{CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 20.6 (q, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 28.0 (q, $\mathrm{C}(C\mathrm{H_3})_3$), 28.7 (d, C-6′), 34.9 (t, C-3′), 40.1 (t, C-3), 57.3 (d, C-4′), 58.5 (d, C-5′), 61.2 (d, C-2), 66.6 (t, O$C$H$_2$), 81.0 (s, $C(\mathrm{CH_3})_3$), 117.1 (t, C-1′), 126.5 (d, Ph), 128.0 (d, Ph), 128.0 (d, 2C, Ph), 128.3 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.4 (2d, Ph), 135.5 (d, C-2′), 136.8, 137.7 (2s, 2 Ph), 156.8 (s, NHCO), 173.8 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}403$, 3,337 (N–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 481 (35) [(M + H)$^+$]; HRMS ($\mathrm{C_{29}H_{41}N_2O_4}$): calcd. 481.3066, found 481.3061.

*tert-Butyl (2S,4′S,5′S) and (2S,4′S,5′S)-2-[2-(benzyloxycarbonylamino)hex-5-en-3-ylamino]-4-methylpentanoate* (**35a**, **35b**, $\mathrm{C_{24}H_{38}N_2O_4}$)

Aldimine **19** (1.07 g, 2.85 mmol), 373 mg Zn (5.70 mmol), 106 mg $\mathrm{CeCl_3{\cdot}7H_2O}$ (0.29 mmol), and 470 mm$^3$ allyl bromide (5.42 mmol) were reacted according to GP 8 in 4 cm$^3$ THF within 16 h. Chromatography (hexanes–EtOAc 6:1) yielded a mixture of isomers **35a/35b** (395 mg, 0.94 mmol, 33%) as a colourless oil. $R_\mathrm{f} = 0.40$ (hexanes–EtOAc 6:1). Spectroscopic data given for a mixture of isomers: Major isomer, selected data: ${}^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.81$ (d, ${}^3J = 6.6$ Hz, 3H, $\mathrm{CH}(\mathrm{C}H_3)_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 0.86 (d, ${}^3J = 6.7$ Hz, 3H, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(\mathrm{C}H_3)_\mathrm{b}$), 1.05 (d, ${}^3J = 6.7$ Hz, 3H, 6′-H$_3$), 1.48 (s, 9H, $\mathrm{C(CH_3)_3}$), 2.54 (td, ${}^3J = 7.2$ Hz, ${}^3J = 3.7$ Hz, 1H, 4′-H), 3.10 (dd, ${}^3J = 7.7$ Hz, ${}^3J = 6.7$ Hz, 1H, 2-H) ppm; ${}^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 15.3$ (q, C-6′), 22.2 (q, $\mathrm{CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 22.8 (q, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 24.9 (d, C-4), 28.1 (q, $\mathrm{C}(C\mathrm{H_3})_3$), 36.1 (t, C-3′), 43.8 (t, C-3), 47.7 (d, C-5′), 59.4 (d, C-4′), 60.7 (d, C-2), 66.4 (t, OCH$_2$), 81.0 (s, $C(\mathrm{CH_3})_3$), 117.9 (t, C-1′), 134.9 (d, C-2′), 136.8 (s, Ph), 156.1 (s, NHCO), 175.8 (s, C-1) ppm. Minor isomer, selected data: ${}^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.85$ (d, ${}^3J = 6.6$ Hz, 3H, $\mathrm{CH}(\mathrm{C}H_3)_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 0.87 (d, ${}^3J = 6.7$ Hz, 3H, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(\mathrm{C}H_3)_\mathrm{b}$), 1.48 (s, 9H, $\mathrm{C(CH_3)_3}$), 2.44 (td, ${}^3J = 6.9$ Hz, ${}^3J = 2.1$ Hz, 1H, 4′-H), 3.13–3.20 (m, 1H, 2-H) ppm; ${}^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 19.0$ (q, C-6′), 22.5 (q, $\mathrm{CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 22.8 (q, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 24.8 (d, C-4), 28.1 (q, $\mathrm{C}(C\mathrm{H_3})_3$), 37.6 (t, C-3′), 43.7 (t, C-3), 48.7 (d, C-5′), 59.1 (d, C-2), 59.4 (d, C-4′), 66.5 (t, OCH$_2$), 81.0 (s, $C(\mathrm{CH_3})_3$), 117.9 (t, C-1′), 135.1 (d, C-2′), 136.8 (s, Ph), 155.9 (s, NHCO), 175.5 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}339$ (N–H), 1,727 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 419 (100) [(M + H)$^+$]; HRMS ($\mathrm{C_{24}H_{39}N_2O_4}$): calcd. 41.2910, found 419.2908.

*tert-Butyl (2R,4′S,5′S) and (2R,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-7-methyloct-1-en-4-ylamino]-3-methylbutanoate* (**41a**, **41b**, $\mathrm{C_{26}H_{42}N_2O_4}$)

Aldimine **40** (404 mg, 1.00 mmol), 131 mg Zn (2.00 mmol), 37 mg $\mathrm{CeCl_3{\cdot}7H_2O}$ (0.10 mmol), and 170 mm$^3$ allyl bromide (1.90 mmol) were reacted according to GP 8 in 4 cm$^3$ THF within 16 h. Chromatography (hexanes–$\mathrm{Et_2O}$ 10:1 → 8:1) yielded 95 mg adduct **41a** (0.21 mmol, 21%) and 80 mg adduct **41b** (0.18 mmol, 18%) as colourless oils.

**41a**: $R_\mathrm{f} = 0.47$ (hexanes–EtOAc 6:1); $[\alpha]_\mathrm{D}^{20} = +30.5 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.93$, $\mathrm{CHCl_3}$); ${}^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.91$ (d, ${}^3J = 6.4$ Hz, 3H, $\mathrm{CHC}H_3$), 0.92 (d, ${}^3J = 6.5$ Hz, 3H, $\mathrm{CHC}H_3$), 0.93 (d, ${}^3J = 6.0$ Hz, 3H, $\mathrm{CHC}H_3$), 0.94 (d, ${}^3J = 6.8$ Hz, 3H, $\mathrm{CHC}H_3$), 1.32 (ddd, ${}^2J = 13.6$ Hz, ${}^3J = 8.2$ Hz, ${}^3J = 5.5$ Hz, 1H, 6′-H$_\mathrm{a}$), 1.35–1.50 (bs, 1H, CHN$H$CH), 1.37 (ddd, ${}^2J = 14.0$ Hz, ${}^3J = 8.7$ Hz, ${}^3J = 5.4$ Hz, 1H, 6′-H$_\mathrm{b}$), 1.47 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.64 ($\varphi$-dsept, ${}^3J = 8.1$ Hz, ${}^3J = 6.5$ Hz, 1H, 7′-H), 1.77 ($\varphi$-oct, ${}^3J = 6.7$ Hz, 1H, 3-H), 2.08 (ddd, ${}^2J = 13.6$ Hz, ${}^3J = 7.8$ Hz, ${}^3J = 6.8$ Hz, 1H, 3′-H$_\mathrm{a}$), 2.16 (dtt, ${}^2J = 13.9$ Hz, ${}^3J = 6.9$ Hz, ${}^4J = 1.4$ Hz, 1H, 3′-H$_\mathrm{b}$), 2.48 (td, ${}^3J = 7.0$ Hz, ${}^3J = 1.9$ Hz, 1H, 4′-H), 2.89 (d, ${}^3J = 6.4$ Hz, 1H, 2-H), 3.72 (tdd, ${}^3J = 9.2$ Hz, ${}^3J = 5.7$ Hz, ${}^3J = 1.8$ Hz, 1H, 5′-H), 5.03 (d, ${}^3J = 9.3$ Hz, 1H, NHCO), 5.04–5.11 (m, 2H, 1′-H$_2$), 5.07 (d, ${}^2J = 12.3$ Hz, 1H, $\mathrm{OC}H_a\mathrm{H_b}$), 5.11 (d, ${}^2J = 12.2$ Hz, 1H, $\mathrm{OCH_a}H_b$), 5.78 (ddt, ${}^3J = 17.4$ Hz, ${}^3J = 10.1$ Hz, ${}^3J = 7.3$ Hz, 1H, 2′-H), 7.28–7.40 (m, 5H, Ph) ppm; ${}^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 18.9$ (q, $\mathrm{CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 19.5 (q, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 22.3 (q, $\mathrm{CH_2CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 23.3 (q, $\mathrm{CH_2CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 24.9 (d, C-7′), 28.2 (q, $\mathrm{C}(C\mathrm{H_3})_3$), 32.2 (d, C-3), 37.7 (t, C-3′), 42.4 (t, C-6′), 51.2 (d, C-5′), 58.9 (d, C-4′), 66.5 (t, O$C$H$_2$), 68.0 (d, C-2), 81.0 (s, $C(\mathrm{CH_3})_3$), 117.8 (t, C-1′), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 135.3 (d, C-2′), 136.9 (s, Ph), 156.2 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}340$ (N–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 447 (30) [(M + H)$^+$]; HRMS ($\mathrm{C_{26}H_{43}N_2O_4}$): calcd. 447.3223, found 447.3226.

**41b**: $R_\mathrm{f} = 0.43$ (hexanes–EtOAc 6:1); $[\alpha]_\mathrm{D}^{20} = -0.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.88$, $\mathrm{CHCl_3}$); ${}^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.89$ (d, ${}^3J = 6.8$ Hz, 3H, $\mathrm{CHC}H_3$), 0.90 (d, ${}^3J = 6.9$ Hz, 3H, $\mathrm{CHC}H_3$), 0.91 (d, ${}^3J = 7.0$ Hz, 3H, $\mathrm{CHC}H_3$), 0.92 (d, ${}^3J = 7.1$ Hz, 3H, $\mathrm{CHC}H_3$), 1.15–1.45 (m, 3H, 6′-H$_2$, CHN$H$CH), 1.46 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.58–1.71 (m, 1H, 7′-H), 1.80 ($\varphi$-oct, ${}^3J = 6.8$ Hz, 1H, 3-H), 2.11 (t, ${}^3J = 7.1$ Hz, 2H, 3′-H$_2$), 2.57 (td, ${}^3J = 7.1$ Hz, ${}^3J = 3.4$ Hz, 1H, 4′-H), 2.91 (d, ${}^3J = 7.0$ Hz, 1H, 2-H), 3.76–3.86 (m, 1H, 5′-H), 5.01–5.13 (m, 5H, 1′-H$_2$, NHCO, $\mathrm{OC}H_2$), 5.67–5.80 (m, 1H, 2′-H), 7.25–7.38 (m, 5H, Ph) ppm; ${}^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 18.4$ (q, $\mathrm{CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 19.3 (q, $\mathrm{CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 21.9 (q, $\mathrm{CH_2CH}(C\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 23.6 (q, $\mathrm{CH_2CH}(\mathrm{CH_3})_\mathrm{a}(C\mathrm{H_3})_\mathrm{b}$), 24.7 (d, C-7′), 28.1 (q, $\mathrm{C}(C\mathrm{H_3})_3$), 32.4 (d, C-3), 36.3 (t, C-3′), 38.8 (t, C-6′), 50.3 (d, C-5′), 60.1 (d, C-4′), 66.2 (d, C-2), 66.4 (t, O$C$H$_2$), 81.0 (s, $C(\mathrm{CH_3})_3$), 117.6 (t, C-1′), 127.9 (d, 3C, Ph), 128.4 (d, 2C, Ph), 135.1 (d, C-2′), 136.9 (s, Ph), 156.3 (s, NHCO), 175.1 (s, C-1) ppm; IR (KBr):

$\bar{\nu}$ = 3,345 (N–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 447 (65) [(M + H)$^+$]; HRMS (C$_{26}$H$_{43}$N$_2$O$_4$): calcd. 447.3223, found 447.3221.

### *Synthesis of alcohols via hydroboration*

#### General procedure (GP 9) for synthesis of alcohols via hydroboration

A solution of the alkene (prepared according to GP 8, 1 mmol) in 5 cm$^3$ anhydrous THF was added at 0 °C under an argon atmosphere to 4 cm$^3$ 9-BBN (0.5 M in THF, 2 mmol). The mixture was warmed to room temperature and stirred for 3 h. NaOH (3 M, 5.50 cm$^3$), 7.80 cm$^3$ H$_2$O$_2$ (30%), and 1 g NaOH were added at 0 °C and the mixture was extracted with Et$_2$O (3 × 20 cm$^3$). The combined organic layers were washed with 40 cm$^3$ brine, dried (Na$_2$SO$_4$), concentrated, and purified by chromatography (silica gel).

*tert-Butyl (3S,4S,2′S)-4-[1-(tert-butyldimethylsilyloxy)-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate*
(**42a**, C$_{22}$H$_{48}$N$_2$O$_4$Si)
Alkene **20a** (237 mg, 0.57 mmol) and 2.30 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 1.14 mmol) in 5 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 216 mg alcohol **42** (0.50 mmol, 87%) as a colourless oil. $R_f$ = 0.51 (hexanes–EtOAc 1:1); $[\alpha]_D^{20}$ = +0.4 × 10$^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 1.14, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.06 (s, 3H, Si(C$H_3$)$_a$(CH$_3$)$_b$), 0.06 (s, 3H, Si(CH$_3$)$_a$(C$H_3$)$_b$), 0.90 (s, 9H, SiC(CH$_3$)$_3$), 0.91 (d, $^3J$ = 6.3 Hz, 3H, CH(C$H_3$)$_a$ (CH$_3$)$_b$), 0.94 (d, $^3J$ = 6.3 Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 0.92 (d, $^3J$ = 6.3 Hz, 3H, 3′-H$_3$), 1.43 (s, 9H, OC(CH$_3$)$_3$), 1.35–1.87 (m, 7H, 7-H$_2$, 6-H$_2$, 3-H, OH, CHN$H$CH), 2.64 (ddd, $^3J$ = 8.3 Hz, $^3J$ = 4.0 Hz, $^3J$ = 2.9 Hz, 1H, 5-H), 2.79 ($\varphi$-dquint, $^3J$ = 6.4 Hz, $^3J$ = 4.3 Hz, 1H, 2′-H), 3.27 (ddd, $^3J$ = 10.4 Hz, $^3J$ = 8.6 Hz, $^3J$ = 2.7 Hz, 1H, 4-H), 3.36 (dd, $^3J$ = 9.8 Hz, $^3J$ = 6.8 Hz, 1H, 1′-H$_a$), 3.53 (dd, $^2J$ = 9.8 Hz, $^3J$ = 4.4 Hz, 1H, 1′-H$_b$), 3.53 (ddd, $^2J$ = 10.9 Hz, $^3J$ = 7.4 Hz, $^3J$ = 4.9 Hz, 1H, 1-H$_a$), 3.66 (dt, $^2J$ = 11.0 Hz, $^3J$ = 5.7 Hz, 1H, 1-H$_b$), 4.76 (d, $^3J$ = 10.3 Hz, 1H, NHCO) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = −5.4 (q, Si($C$H$_3$)$_a$(CH$_3$)$_b$), −5.3 (q, Si(CH$_3$)$_a$ ($C$H$_3$)$_b$), 17.5 (q, C-3′), 18.2 (s, Si$C$(CH$_3$)$_3$), 19.1 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.2 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 25.9 (q, SiC($C$H$_3$)$_3$), 28.4 (q, OC($C$H$_3$)$_3$), 28.8 (t, C-6), 29.4 (t, C-7), 29.6 (d, C-3), 52.3 (d, C-2′), 54.4 (d, C-5), 58.2 (d, C-4), 62.7 (t, C-8), 67.4 (t, C-1′), 78.9 (s, Si$C$(CH$_3$)$_3$), 156.8 (s, NHCO) ppm; IR (KBr): $\bar{\nu}$ = 3,341 (N–H, O–H), 1,697 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 433 (100) [(M + H)$^+$]; HRMS (C$_{22}$H$_{49}$N$_2$O$_4$Si): calcd. 433.3462, found 433.3458.

*Benzyl (3S,4S,2′S)-4-[1-(tert-butyldiphenylsilyloxy)-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate*
(**43a**, C$_{35}$H$_{50}$N$_2$O$_4$Si)
Alkene **22a** (1.22 g, 2.13 mmol) and 8.50 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 4.26 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 1.23 g alcohol **43a** (2.08 mmol, 97%) as a colourless oil. $R_f$ = 0.50 (hexanes–EtOAc 1:1); $[\alpha]_D^{20}$ = −5.0 × 10$^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 0.67, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.90 (d, $^3J$ = 6.3 Hz, 3H, CHC$H_3$), 0.91 (d, $^3J$ = 6.6 Hz, 3H, CHC$H_3$), 0.92 (d, $^3J$ = 6.7 Hz, 3H, CHC$H_3$), 1.04 (s, 9H, SiC(CH$_3$)$_3$), 1.30–1.41 (m, 1H, 5-H$_a$), 1.41–1.77 (m, 5H, 6-H$_2$, 5-H$_b$, OH, CHN$H$CH), 1.77–1.87 (m, 1H, 2-H), 2.65 (ddd, $^3J$ = 8.5 Hz, $^3J$ = 4.2 Hz, $^3J$ = 2.3 Hz, 1H, 4-H), 2.80 (td, $^3J$ = 6.4 Hz, $^3J$ = 4.3 Hz, 1H, 2′-H), 3.30 (ddd, $^3J$ = 10.4 Hz, $^3J$ = 9.0 Hz, $^3J$ = 2.3 Hz, 1H, 3-H), 3.42 (dd, $^2J$ = 9.9 Hz, $^3J$ = 6.6 Hz, 1H, 1′-H$_a$), 3.53 (ddd, $^2J$ = 10.6 Hz, $^3J$ = 7.0 Hz, $^3J$ = 5.4 Hz, 1H, 7-H$_a$), 3.58 (dd, $^2J$ = 9.8 Hz, $^3J$ = 4.2 Hz, 1H, 1′-H$_b$), 3.54–3.63 (m, 1H, 7-H$_b$), 5.02 (d, $^3J$ = 10.2 Hz, 1H, NHCO), 5.07 (d, $^2J$ = 12.3 Hz, 1H, C$H_a$H$_b$Ph), 5.12 (d, $^2J$ = 12.3 Hz, 1H, CH$_a$$H_b$Ph), 7.26–7.45 (m, 11H, 3 Ph), 7.62–7.66 (m, 4H, 3 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 17.7 (q, C-3′), 19.3 (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 26.9 (s, $C$(CH$_3$)$_3$), 29.1 (t, C-3′), 29.5 (t, C-6), 29.9 (d, C-2), 52.5 (d, C-2′), 54.2 (d, C-4), 59.0 (d, C-3), 62.8 (t, C-7), 66.7 (t, $C$H$_2$Ph), 68.2 (t, C-1′), 127.7 (d, 4C, Ph), 128.0 (d, 3C, Ph), 128.5 (d, 2C, Ph), 129.7 (d, 2C, Ph), 133.5 (s, Ph), 133.5 (s, Ph), 135.6 (d, 2C, Ph), 135.6 (2d, Ph), 136.8 (s, Ph), 157.1 (s, NHCO) ppm; IR (KBr): $\bar{\nu}$ = 3,420 (N–H, O–H), 1,708 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 591 (100) [(M + H)$^+$]; HRMS (C$_{35}$H$_{51}$N$_2$O$_4$Si): calcd. 591.3618, found 591.3616.

*tert-Butyl (3S,4S,2′S)-4-[1-(tert-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate* (**44a**, C$_{28}$H$_{52}$N$_2$O$_4$Si)
Alkene **24a** (1.18 g, 2.40 mmol) and 9.60 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 4.80 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 1.02 g alcohol **44a** (2.00 mmol, 83%) as a colourless solid. $R_f$ = 0.62 (hexanes–EtOAc 1:1); $[\alpha]_D^{20}$ = +38.5 × 10$^{-1}$ deg cm$^2$ g$^{-1}$ (*c* = 1.03, CHCl$_3$); m.p.: 117–119 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.03 (s, 3H, Si(C$H_3$)$_a$(CH$_3$)$_b$), 0.04 (s, 3H, Si(CH$_3$)$_a$(C$H_3$)$_b$), 0.79 (d, $^3J$ = 6.7 Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.85 (d, $^3J$ = 6.6 Hz, 3H, CH(CH$_3$)$_a$ (C$H_3$)$_b$), 0.91 (s, 9H, SiC(CH$_3$)$_3$), 1.43 (s, 9H, OC(CH$_3$)$_3$), 1.38–1.72 (m, 7H, 6-H$_2$, 5-H$_2$, 2-H, OH, CHN$H$CH), 2.63 ($\varphi$-d, $^3J$ = 7.0 Hz, 2H, 3′-H$_2$), 2.71 (ddd, $^3J$ = 7.5 Hz,

$^3J = 5.1$ Hz, $^3J = 2.3$ Hz, 1H, 4-H), 2.80 ($\varphi$-tt, $^3J = 6.9$ Hz, $^3J = 4.6$ Hz, 1H, 2′-H), 3.14 (ddd, $^3J = 10.1$ Hz, $^3J = 9.1$ Hz, $^3J = 2.3$ Hz, 1H, 3-H), 3.42 (dd, $^3J = 10.0$ Hz, $^3J = 4.8$ Hz, 1H, 1′-H$_a$), 3.53 (dd, $^2J = 9.9$ Hz, $^3J = 4.2$ Hz, 1H, 1′-H$_b$), 3.59 (ddd, $^2J = 10.6$ Hz, $^3J = 7.1$ Hz, $^3J = 5.3$ Hz, 1H, 7-H$_a$), 3.64 ($\varphi$-td, $^3J = 5.5$ Hz, $^3J$, $^2J = 11.1$ Hz, 1H, 7-H$_b$), 4.65 (d, $^3J = 10.2$ Hz, 1H, NHCO), 7.15–7.33 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.5$ (q, Si(*C*H$_3$)$_a$(CH$_3$)$_b$), −5.4 (q, Si(CH$_3$)$_a$(*C*H$_3$)$_b$), 18.2 (s, Si*C*(CH$_3$)$_3$), 19.4 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 25.9 (q, SiC(*C*H$_3$)$_3$), 28.5 (q, OC(*C*H$_3$)$_3$), 29.5 (t, C-6 or C-5), 29.6 (t, C-6 or C-5), 29.9 (d, C-2), 38.9 (t, C-3′), 54.7 (d, C-4), 58.6 (d, C-3), 59.6 (d, C-2′), 62.7 (t, C-7), 64.3 (t, C-1′), 78.7 (s, O*C*(CH$_3$)$_3$), 126.1 (d, Ph), 128.3 (d, 2C, Ph) 129.3 (d, 2C, Ph), 139.7 (s, Ph), 156.7 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}367$, 3,183 (N–H, O–H), 1,709 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 509 (100) [(M + H)$^+$]; HRMS ($C_{28}H_{53}N_2O_4Si$): calcd. 509.3775, found 509.3777.

*Benzyl (4S,5S,2′S)-5-[1-(tert-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-8-hydroxy-2-methyl-4-octylcarbamate* (**45a**, $C_{32}H_{52}N_2O_4Si$)

Alkene **25a** (1.50 g, 2.79 mmol) and 11.2 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 5.58 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 1.23 g alcohol **45a** (2.21 mmol, 79%) as a colourless oil. $R_f = 0.61$ (hexanes–EtOAc 1:1); $[\alpha]_D^{20} = -57.6 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.685$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.04$ (s, 3H, Si(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.05 (s, 3H, Si(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.80 (d, $^3J = 6.6$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.82 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.91 (s, 9H, C(CH$_3$)$_3$), 1.09 (ddd, $^2J = 13.0$ Hz, $^3J = 9.7$ Hz, $^3J = 4.8$ Hz, 1H, 3-H$_a$), 1.34 (ddd, $^2J = 13.9$ Hz, $^3J = 6.9$ Hz, $^3J = 2.9$ Hz, 1H, 3-H$_b$), 1.39–1.74 (m, 5H, 7-H$_2$, 6-H$_2$, 2-H), 1.89 (bs, 2H, CHN*H*CH, OH), 2.55 (td, $^3J = 6.6$ Hz, $^3J = 2.2$ Hz, 1H, 5-H), 2.59 (dd, $^2J = 13.3$ Hz, $^3J = 7.4$ Hz, 1H, 3′-H$_a$), 2.71 (dd, $^2J = 13.3$ Hz, $^3J = 6.5$ Hz, 1H, 3′-H$_b$), 2.81 (tt, $^3J = 6.9$ Hz, $^3J = 4.2$ Hz, 1H, 2′-H), 3.47 (dd, $^2J = 10.0$ Hz, $^3J = 4.0$ Hz, 1H, 1′-H$_a$), 3.54 (dd, $^2J = 10.0$ Hz, $^3J = 4.4$ Hz, 1H, 1′-H$_b$), 3.59 ($\varphi$-t, $^3J = 6.1$ Hz, 2H, 8-H$_2$), 3.66 (tdd, $^3J = 9.9$ Hz, $^3J = 4.4$ Hz, $^3J = 2.0$ Hz, 1H, 4-H), 4.83 (d, $^3J = 9.6$ Hz, 1H, NHCO), 5.05 (d, $^2J = 12.3$ Hz, 1H, OC*H$_a$*H$_b$Ph), 5.08 (d, $^2J = 12.5$ Hz, 1H, OCH$_a$*H$_b$*Ph), 7.17–7.39 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.4$ (q, Si(CH$_3$)$_2$), 18.3 (s, Si*C*(CH$_3$)$_3$), 22.0 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 23.3 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 24.8 (d, C-2), 25.9 (q, SiC(*C*H$_3$)$_3$), 29.5 (t, C-6), 29.9 (t, C-7), 39.2 (t, C-3′), 41.6 (t, C-3), 51.3 (d, C-4), 57.9 (d, C-5), 59.8 (d, C-2′), 62.7 (t, C-8), 63.8 (t, C-1′), 66.5 (t, O*C*H$_2$Ph) ppm; IR (KBr): $\bar{\nu} = 3{,}408$, 3,340 (N–H, O–H), 1,705 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 557 (100) [(M + H)$^+$]; HRMS ($C_{32}H_{53}N_2O_4Si$): calcd. 557.3775, found 557.3771.

*Benzyl (4S,5S,2′S)-5-[1-(tert-butyldimethylsilyloxy)-3-phenyl-2-propylamino]-8-hydroxy-2-methyloct-4-ylcarbamate* (**45b**, $C_{32}H_{52}N_2O_4Si$)

Alkene **25a** (940 mg, 1.74 mmol) and 7.00 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 3.48 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 788 mg alcohol **45b** (1.42 mmol, 81%) as a colourless oil. $R_f = 0.54$ (hexanes–EtOAc 1:1); $[\alpha]_D^{20} = +11.9 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.06$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.01$ (s, 3H, Si(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.02 (s, 3H, Si(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.87 (d, $^3J = 6.3$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.88 (d, $^3J = 6.3$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.89 (s, 9H, C(CH$_3$)$_3$), 1.04 (ddd, $^2J = 14.5$ Hz, $^3J = 9.5$ Hz, $^3J = 3.5$ Hz, 1H, 3-H$_a$), 1.14 (ddd, $^2J = 13.7$ Hz, $^3J = 10.7$ Hz, $^3J = 4.2$ Hz, 1H, 3-H$_b$), 1.23–1.36 (m, 1H, 6-H$_a$), 1.44–1.74 (m, 4H, 6-H$_b$, 2-H$_2$, 2-H), 2.45 (bs, 2H, OH, CHN*H*CH), 2.55 (dd, $^2J = 13.4$ Hz, $^3J = 7.2$ Hz, 1H, 3′-H$_a$), 2.66 (dd, $^2J = 13.4$ Hz, $^3J = 6.7$ Hz, 1H, 3′-H$_b$), 2.72 (ddd, $^3J = 8.2$ Hz, $^3J = 5.2$ Hz, $^3J = 3.2$ Hz, 1H, 5-H), 2.96–3.04 (m, 1H, 2′-H), 3.47 (dd, $^2J = 10.1$ Hz, $^3J = 5.6$ Hz, 1H, 1′-H$_a$), 3.52 (dd, $^2J = 10.1$ Hz, $^3J = 4.5$ Hz, 1H, 1′-H$_b$), 3.56 (ddd, $^2J = 10.7$ Hz, $^3J = 7.4$ Hz, $^3J = 4.9$ Hz, 1H, 8-H$_a$), 3.65 (dt, $^2J = 11.0$ Hz, $^3J = 5.5$ Hz, 1H, 8-H$_b$), 3.80 (tt, $^3J = 10.1$ Hz, $^3J = 3.2$ Hz, 1H, 4-H), 4.52 (d, $^3J = 10.1$ Hz, 1H, NHCO), 5.03 (d, $^2J = 12.4$ Hz, 1H, OC*H$_a$*H$_b$Ph), 5.06 (d, $^2J = 12.2$ Hz, 1H, OCH$_a$*H$_b$*Ph), 7.14–7.37 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.4$ (q, Si(*C*H$_3$)$_a$(CH$_3$)$_b$), −5.4 (q, Si(CH$_3$)$_a$(*C*H$_3$)$_b$), 18.2 (s, *C*(CH$_3$)$_3$), 21.8 (q, C-1), 23.7 (q, C-1), 24.7 (d, C-2), 25.9 (q, SiC(*C*H$_3$)$_3$), 29.1 (t, C-7), 30.1 (t, C-6), 39.1 (t, C-3), 39.3 (t, C-3′), 50.9 (d, C-4), 58.3 (d, C-5), 59.1 (d, C-2′), 62.7 (t, C-8), 65.0 (t, C-1′), 66.6 (t, O*C*H$_2$Ph), 126.2 (d, Ph), 128.0 (d, 2C, Ph), 128.0 (d, Ph), 128.4 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.4 (2d, Ph), 136.7 (s, Ph), 139.2 (s, Ph), 156.2 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}400$, 3,331 (N–H, O–H), 1,718 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 557 (10) [(M + H)$^+$]; HRMS ($C_{32}H_{53}N_2O_4Si$): calcd. 557.3775, found 557.3770.

*Benzyl (3S,4S,2′S)-4-[1-(tert-butyldimethylsilyloxy)-2-propylamino]-7-hydroxy-2-methyl-3-heptylcarbamate* (**46b**, $C_{25}H_{46}N_2O_4Si$)

Alkene **27a** (1.85 g, 4.12 mmol) and 16.5 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 8.24 mmol) in 20 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 3:1 → 2:1) yielded 1.71 g alcohol **46b** (3.67 mmol, 89%) as a colourless oil. $R_f = 0.46$

(hexanes–EtOAc 1:1); $[\alpha]_D^{20} = +0.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.95$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.04$ (s, 6H, Si(CH$_3$)$_2$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.91 (d, $^3J = 6.3$ Hz, 3H, CHC*H*$_3$), 0.92 (d, $^3J = 6.8$ Hz, 3H, CHC*H*$_3$), 0.95 (d, $^3J = 6.6$ Hz, 3H, CHC*H*$_3$), 1.33–1.45 (m, 1H, 5-H$_a$), 1.47–1.87 (m, 5H, 5-H$_b$, 6-H$_2$, OH, CHN*H*CH), 1.78 ($\varphi$-dquint, $^3J = 8.8$ Hz, $^3J = 6.7$ Hz, 1H, 2-H), 2.69 (ddd, $^3J = 8.0$ Hz, $^3J = 4.6$ Hz, $^3J = 2.5$ Hz, 1H, 4-H), 2.76 ($\varphi$-quintd, $^3J = 6.4$ Hz, $^3J = 4.2$ Hz, 1H, 2′-H), 3.30 (ddd, $^3J = 10.3$ Hz, $^3J = 8.7$ Hz, $^3J = 2.5$ Hz, 1H, 3-H), 3.34 (dd, $^2J = 9.8$ Hz, $^3J = 6.4$ Hz, 1H, 1′-H$_a$), 3.52 (dd, $^2J = 9.8$ Hz, $^3J = 4.2$ Hz, 1H, 1′-H$_b$), 3.56 (ddd, $^2J = 10.7$ Hz, $^3J = 7.1$ Hz, $^3J = 5.5$ Hz, 1H, 7-H$_a$), 3.63 (dt, $^2J = 10.6$ Hz, $^3J = 5.9$ Hz, 1H, 7-H$_b$), 5.07 (d, $^2J = 12.3$ Hz, 1H, C*H*$_a$H$_b$Ph), 5.10 (d, $^3J = 9.1$ Hz, 1H, NHCO), 5.11 (d, $^2J = 12.3$ Hz, 1H, CH$_a$*H*$_b$Ph), 7.27–7.37 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.4$ (q, Si(*C*H$_3$)$_a$(CH$_3$)$_b$), $-5.3$ (q, Si(CH$_3$)$_a$(*C*H$_3$)$_b$), 17.7 (q, C-3′), 18.2 (s, *C*(CH$_3$)$_3$), 19.2 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 20.2 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 25.9 (q, C(*C*H$_3$)$_3$), 29.3 (t, C-6 or C-5), 29.4 (t, C-6 or C-5), 29.9 (d, C-2), 52.7 (d, C-2′), 54.3 (d, C-4), 59.1 (d, C-3), 62.8 (t, C-7), 66.6 (t, *C*H$_2$Ph), 67.2 (t, C-1′), 128.0 (d, 2C, Ph), 128.0 (d, Ph), 128.5 (2d, Ph), 136.9 (s, Ph), 157.1 (s, NHCO) ppm; IR (KBr): $\bar{\nu} = 3{,}326$ (N–H, O–H), 1,703 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 467 (100) [(M + H)$^+$]; HRMS (C$_{25}$H$_{47}$N$_2$O$_4$Si): calcd. 467.3305, found 467.3308.

*tert-Butyl (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]propanoate*
(**47b**, C$_{23}$H$_{38}$N$_2$O$_5$)

Alkene **30b** (309 mg, 0.76 mmol) and 3.10 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 1.52 mmol) in 5 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 1:1) yielded 200 mg alcohol **47b** (0.47 mmol, 62%) as a colourless oil. $R_f = 0.30$ (hexanes–EtOAc 2:1); $[\alpha]_D^{20} = -1.4 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.74$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.91$ (d, $^3J = 6.7$ Hz, 3H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.95 (d, $^3J = 6.7$ Hz, 3H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 1.16 (ddt, $^3J = 6.7$ Hz, $^3J = 9.8$ Hz, $^2J = 13.7$ Hz, 1H, 3′-H$_a$), 1.21 (d, $^3J = 6.8$ Hz, 3H, 3-H$_3$), 1.46 (s, 9H, C(CH$_3$)$_3$), 1.59 (ddt, $^2J = 13.8$ Hz, $^3J = 7.0$ Hz, $^3J = 2.7$ Hz, 1H, 3′-H$_b$), 1.67 (dsept, $^3J = 7.7$ Hz, $^3J = 6.7$ Hz, 1H, 6′-H), 1.67–1.76 (m, 2H, 2′-H$_2$), 2.68 (bs, 2H, OH, CHN*H*CH), 2.68 (dt, $^3J = 9.8$ Hz, $^3J = 3.1$ Hz, 1H, 4′-H), 3.45–3.67 (m, 2H, 1′-H$_a$, 5′-H), 3.53 (q, $^3J = 6.8$ Hz, 1H, 2-H), 3.69 (dt, $^2J = 10.6$ Hz, $^3J = 5.2$ Hz, 1H, 1′-H$_b$), 4.61 (d, $^3J = 10.3$ Hz, 1H, NHCO), 5.07 (d, $^2J = 12.2$ Hz, 1H, C*H*$_a$H$_b$Ph), 5.12 (d, $^2J = 12.2$ Hz, 1H, CH$_a$*H*$_b$Ph), 7.28–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.4$ (q, C-3), 19.7 (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 20.0 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 27.0 (t, C-3′), 28.0 (q, C(*C*H$_3$)$_3$), 29.8 (t, C-2′), 30.1 (d, C-6′), 54.3 (d, C-2), 56.5 (d, C-4′), 57.3 (d, C-5′), 62.8 (t, C-1′), 66.8 (t, *C*H$_2$Ph), 80.8 (s, *C*(CH$_3$)$_3$), 128.1 (d, 2C, Ph), 128.1 (d, Ph), 128.5 (d, 2C, Ph), 136.6 (s, Ph), 157.1 (s, NCHO), 174.6 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}331$ (N–H, O–H), 1,724 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 423 (100) [(M + H)$^+$]; HRMS (C$_{23}$H$_{39}$N$_2$O$_5$): calcd. 423.2859, found 423.2863.

*tert-Butyl (2S,4′S,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]-4-methylpentanoate*
(**48a**, C$_{26}$H$_{44}$N$_2$O$_5$)

Alkene **31a** (5.36 g, 12.0 mmol) and 48.0 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 24.0 mmol) in 50 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 3:2) yielded 5.25 g alcohol **48a** (11.3 mmol, 94%) as a colourless oil. $R_f = 0.27$ (hexanes–EtOAc 2:1); $[\alpha]_D^{20} = -29.7 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.32$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.88$ (d, $^3J = 6.6$ Hz, 3H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.91 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 0.92 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 0.95 (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 1.17 (ddt, $^2J = 13.7$ Hz, $^3J = 9.7$ Hz, $^3J = 6.7$ Hz, 1H, 3′-H$_a$), 1.23–1.31 (m, 1H, 3-H$_a$), 1.46 (s, 9H, C(CH$_3$)$_3$), 1.44–1.75 (m, 6H, 6′-H, 3′-H$_b$, 2′-H$_2$, 4-H, 3-H$_b$), 2.41 (bs, 2H, OH, CHN*H*CH), 2.63 (dt, $^3J = 9.3$ Hz, $^3J = 3.2$ Hz, 1H, 4′-H), 3.45 (t, $^3J = 7.1$ Hz, 1H, 2-H), 3.54 (dt, $^2J = 10.8$ Hz, $^3J = 5.9$ Hz, 1H, 1′-H$_a$), 3.60 (ddd, $^3J = 10.4$ Hz, $^3J = 8.5$ Hz, $^3J = 3.9$ Hz, 1H, 5′-H), 3.66 (dt, $^2J = 10.7$ Hz, $^3J = 5.3$ Hz, 1H, 1′-H$_b$), 4.68 (d, $^3J = 10.3$ Hz, 1H, NHCO), 5.07 (d, $^2J = 13.0$ Hz, 1H, C*H*$_a$H$_b$Ph), 5.10 (d, $^2J = 12.9$ Hz, 1H, CH$_a$*H*$_b$Ph), 7.28–7.39 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.5$ (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 22.6 (q, CH$_2$CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 22.8 (q, CH$_2$CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 25.0 (d, C-4), 27.1 (t, C-3′), 28.1 (q, C(*C*H$_3$)$_3$), 29.7 (t, C-2′), 30.1 (d, C-6′), 43.4 (t, C-3), 56.6 (d, C-4′), 57.2 (d, C-5′), 58.0 (d, C-2), 62.7 (t, C-1′), 66.7 (t, *C*H$_2$Ph), 80.9 (s, *C*(CH$_3$)$_3$), 128.0 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 136.7 (s, Ph), 157.0 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}420$ (N–H, O–H), 1,725 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 465 (100) [(M + H)$^+$]; HRMS (C$_{26}$H$_{45}$N$_2$O$_5$): calcd. 465.3328, found 465.3325.

*tert-Butyl (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]-4-methylpentanoate*
(**48b**, C$_{26}$H$_{44}$N$_2$O$_5$)

Alkene **31b** (6.27 g, 14.0 mmol) and 56.2 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 28.1 mmol) in 50 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 1:1) yielded 5.49 g alcohol **48b** (11.8 mmol, 84%) as a colourless oil. $R_f = 0.32$ (hexanes–

EtOAc 1:1); $[\alpha]_D^{20} = -25.7 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.81$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.88$ (d, $^3J = 6.6$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.90 (d, $^3J = 6.6$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.96 (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.97 (d, $^3J = 6.6$ Hz, 3H, CH$_2$CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 1.22–1.38 (m, 2H, 3-H), 1.46 (s, 9H, C(CH$_3$)$_3$), 1.38–1.78 (m, 8H, 6′-H, 3′-H$_2$, 2′-H$_2$, 4-H, OH, CHN*H*CH), 2.69 (ddd, $^3J = 7.4$ Hz, $^3J = 5.9$ Hz, $^3J = 1.4$ Hz, 1H, 4′-H), 3.12 (dd, $^3J = 7.6$ Hz, $^3J = 6.8$ Hz, 1H, 2-H), 3.19 (td, $^3J = 10.0$ Hz, $^3J = 1.4$ Hz, 1H, 5′-H), 3.51–3.64 (m, 2H, 1′-H$_2$), 5.07 (d, $^2J = 12.2$ Hz, 1H, C*H$_a$*H$_b$Ph), 5.12 (d, $^2J = 12.2$ Hz, 1H, CH$_a$*H$_b$*Ph), 5.28 (d, $^3J = 10.0$ Hz, 1H, NHCO), 7.28–7.40 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.8$ (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 20.1 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 22.5 (q, CH$_2$CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 22.7 (q, CH$_2$CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 24.7 (d, C-4), 28.1 (q, C(*C*H$_3$)$_3$), 29.6 (t, C-2′), 30.5 (t, C-3′), 31.0 (d, C-6′), 43.7 (t, C-3), 55.8 (d, C-4′), 59.7 (d, C-5′), 61.1 (d, C-2), 62.5 (t, C-1′), 66.6 (t, *C*H$_2$Ph), 81.1 (s, *C*(CH$_3$)$_3$), 128.0 (d, 2C, Ph), 128.1 (d, Ph), 128.6 (d, 2C, Ph), 136.8 (s, Ph), 157.0 (s, NHCO), 176.1 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}342$ (N–H, O–H), 1,723 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 465 (100) [(M + H)$^+$]; HRMS (C$_{26}$H$_{45}$N$_2$O$_5$): calcd. 465.3328, found 465.3326.

*tert-Butyl (2S,4′S,5′S) and (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-7-methyl-4-octylamino]-3-phenylpropanoate* (**49a**, **49b**, C$_{30}$H$_{44}$N$_2$O$_5$)

Alkene **32a/32b** (2.42 g, 4.89 mmol) and 19.6 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 9.78 mmol) in 20 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 1:1) yielded 581 mg alcohol **49a** (1.13 mmol, 23%) and 728 mg alcohol **49b** (1.42 mmol, 29%) as colourless oils.

**49a**: $R_f = 0.20$ (hexanes–EtOAc 2:1); $[\alpha]_D^{20} = -24.2 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.07$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.80$ (d, $^3J = 6.6$ Hz, 3H, CH(C*H$_3$*)$_a$(CH$_3$)$_b$), 0.83 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C*H$_3$*)$_b$), 0.97 (ddd, $^2J = 13.5$ Hz, $^3J = 8.7$ Hz, $^3J = 4.9$ Hz, 1H, 6′-H$_a$), 1.05 (ddd, $^2J = 13.5$ Hz, $^3J = 9.8$ Hz, $^3J = 5.5$ Hz, 1H, 6′-H$_b$), 1.39 (s, 9H, C(CH$_3$)$_3$), 1.30–1.70 (m, 7H, 2′-H$_2$, 3′-H$_2$, 7′-H, CHN*H*CH, OH), 2.40 (td, $^3J = 6.8$ Hz, $^3J = 1.7$ Hz, 1H, 4′-H), 2.71 (dd, $^2J = 13.4$ Hz, $^3J = 8.2$ Hz, 1H, 3-H$_a$), 2.84 (dd, $^2J = 13.4$ Hz, $^3J = 6.1$ Hz, 1H, 3-H$_b$), 3.34 (dd, $^3J = 8.3$ Hz, $^3J = 6.1$ Hz, 1H, 2-H), 3.53–3.60 (m, 2H, 1′-H$_2$), 3.62 (tdd, $^3J = 9.6$ Hz, $^3J = 4.8$ Hz, $^3J = 1.6$ Hz, 1H, 5′-H), 4.89 (d, $^3J = 9.7$ Hz, 1H, NHCO), 5.05 (d, $^2J = 12.6$ Hz, 1H, OC*H$_a$*H$_b$Ph), 5.08 (d, $^2J = 12.8$ Hz, 1H, OCH$_a$*H$_b$*Ph), 7.15–7.40 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 22.1$ (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 23.2 (q, CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 24.8 (d, C-7′), 28.0 (q, C(*C*H$_3$)$_3$), 29.6 (t, C-2′ or C-3′), 29.7 (t, C-2′ or C-3′), 40.5 (t, C-3), 42.4 (t, C-6′), 51.4 (d, C-5′), 59.5 (d, C-4′), 62.6 (t, C-1′), 64.1 (d, C-2), 66.5 (t, O*C*H$_2$Ph), 81.5 (s, *C*(CH$_3$)$_3$), 126.6 (d, Ph), 128.0 (d, 2C, Ph), 128.0 (d, Ph), 128.3 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.5 (2d, Ph), 136.8 (s, Ph), 137.9 (s, Ph), 156.4 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}344$ (N–H, O–H), 1,719 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 513 (100) [(M + H)$^+$]; HRMS (C$_{30}$H$_{45}$N$_2$O$_5$): calcd. 513.3328, found 513.3331.

**49b**: $R_f = 0.11$ (hexanes–EtOAc 2:1); $[\alpha]_D^{20} = +4.8 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.83$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.87$ (d, $^3J = 6.6$ Hz, 6H, CH(C*H$_3$*)$_2$), 1.05 (ddd, $^2J = 13.5$ Hz, $^3J = 9.2$ Hz, $^3J = 3.6$ Hz, 1H, 6′-H$_a$), 1.20 (ddd, $^2J = 13.9$ Hz, $^3J = 11.0$ Hz, $^3J = 4.3$ Hz, 1H, 6′-H$_b$), 1.37 (s, 9H, C(CH$_3$)$_3$), 1.25–1.65 (m, 5H, 2′-H$_2$, 3′-H$_2$, 7′-H), 2.10 (bs, 2H, OH, CHN*H*CH), 2.50 (ddd, $^3J = 8.4$ Hz, $^3J = 5.7$ Hz, $^3J = 3.1$ Hz, 1H, 4′-H), 2.71 (dd, $^2J = 13.3$ Hz, $^3J = 8.1$ Hz, 1H, 3-H$_a$), 2.86 (dd, $^2J = 13.3$ Hz, $^3J = 6.4$ Hz, 1H, 3-H$_b$), 3.52 (dd, $^3J = 8.0$ Hz, $^3J = 6.3$ Hz, 1H, 2-H), 3.54–3.60 (m, 1H, 1′-H$_a$), 3.64 (dt, $^2J = 11.0$ Hz, $^3J = 5.9$ Hz, 1H, 1′-H$_b$), 3.74–3.83 (m, 1H, 5′-H), 4.46 (d, $^3J = 9.6$ Hz, 1H, NHCO), 5.04 (s, 2H, OC*H$_2$*Ph), 7.10–7.40 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9$ (q, CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 23.6 (q, CH(CH$_3$)$_a$(CH$_3$)$_b$), 24.7 (d, C-7′), 28.0 (q, C(*C*H$_3$)$_3$), 28.3 (t, C-3′), 29.8 (t, C-2′), 39.2 (t, C-3), 40.6 (t, C-6′), 50.4 (d, C-5′), 60.1 (d, C-4′), 62.6 (d, C-2), 62.7 (t, C-1′), 66.5 (t, O*C*H$_2$Ph), 81.4 (s, *C*(CH$_3$)$_3$), 126.5 (d, Ph), 128.0 (d, 2C, Ph), 128.0 (d, Ph), 128.3 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.6 (2d, Ph), 136.7 (s, Ph), 136.8 (s, Ph), 156.2 (s, NHCO), 174.5 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}398$, 3,341 (N–H, O–H), 1,720 (C=O) cm$^{-1}$; MS (FAB pos.): *m/z* (%) = 513 (100) [(M + H)$^+$]; HRMS (C$_{30}$H$_{45}$N$_2$O$_5$): calcd. 513.3328, found 513.3,331.

*tert-Butyl (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]-3-methylbutanoate* (**50b**, C$_{25}$H$_{42}$N$_2$O$_5$)

Alkene **33b** (995 mg, 2.30 mmol) and 9.20 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 4.60 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 1:1) yielded 731 mg alcohol **50b** (1.62 mmol, 71%) as a colourless oil. $R_f = 0.45$ (hexanes–EtOAc 1:1); $[\alpha]_D^{20} = -24.9 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.11$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.91$ (d, $^3J = 6.8$ Hz, 9H, 3 CHC*H$_3$*), 0.94 (d, $^3J = 6.6$ Hz, 3H, CHC*H$_3$*), 1.20 (ddt, $^2J = 14.8$ Hz, $^3J = 9.1$ Hz, $^3J = 6.7$ Hz, 1H, 3′-H$_a$), 1.47 (s, 9H, C(CH$_3$)$_3$), 1.59 (dtd, $^2J = 14.4$ Hz, $^3J = 7.5$ Hz, $^3J = 3.1$ Hz, 1H, 3′-H$_b$), 1.64–1.72 (m, 2H, 2′-H$_2$), 1.73 (dsept, $^3J = 8.3$ Hz, $^3J = 6.8$ Hz, 1H, 3-H), 1.82 ($\varphi$-oct, $^3J = 6.7$ Hz, 1H, 6′-H), 2.53 (bs, 2H, OH, CHN*H*CH), 2.60 (dt, $^3J = 9.2$ Hz, $^3J = 3.3$ Hz, 1H, 4′-H), 3.15 (d, $^3J = 6.6$ Hz, 1H, 2-H), 3.55 (dt, $^2J = 10.8$ Hz, $^3J = 6.0$ Hz, 1H, 1′-H$_a$), 3.54–3.62 (m, 1H, 5′-H), 3.67 (dt, $^2J = 10.7$ Hz, $^3J = 5.3$ Hz, 1H, 1′-H$_b$), 4.70 (d, $^3J = 10.5$ Hz, 1H, NHCO), 5.08 (s, 2H, C$H_2$Ph), 7.28–7.37 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.8$ (q, CH$C$H$_3$), 19.1 (q, CH$C$H$_3$), 19.5 (q, CH$C$H$_3$), 20.1 (q, CH$C$H$_3$), 27.1 (t, C-3′), 28.1 (q, C($C$H$_3$)$_3$), 29.7 (d, C-2′), 30.0 (d, C-3), 31.9 (d, C-6′), 56.9 (d, C-4′ or C-5′), 57.0 (d, C-4′ or C-5′), 62.7 (t, C-1′), 65.3 (d, C-2), 66.7 (t, $C$H$_2$Ph), 80.9 (s, $C$(CH$_3$)$_3$), 128.1 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 136.7 (s, Ph), 156.9 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}340$ (N–H, O–H), 1,722 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 451 (64) [(M + H)$^+$]; HRMS (C$_{25}$H$_{43}$N$_2$O$_5$): calcd. 451.3172, found 451.3171.

*tert-Butyl (2S,4′S,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]-3-phenylpropanoate*
(**51a**, C$_{29}$H$_{42}$N$_2$O$_5$)

Alkene **34a** (3.53 g, 7.34 mmol) and 29.4 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 14.7 mmol) in 30 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 3:2) yielded 3.44 g alcohol **51a** (6.90 mmol, 94%) as a colourless oil. $R_f = 0.22$ (hexanes–EtOAc 2:1); $[\alpha]_D^{20} = -36.5 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.82$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.79$ (d, $^3J = 6.6$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.83 (d, $^3J = 6.6$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.37 (s, 9H, C(CH$_3$)$_3$), 1.29–1.45 (m, 5H, 3′-H$_2$, 6′-H, OH, CHN$H$CH), 1.45–1.69 (m, 2H, 2′-H$_2$), 2.66 (td, $^3J = 6.7$ Hz, $^3J = 1.6$ Hz, 1H, 4′-H), 2.72 (dd, $^2J = 13.3$ Hz, $^3J = 7.9$ Hz, 1H, 3-H$_a$), 2.82 (dd, $^2J = 13.4$ Hz, $^3J = 6.6$ Hz, 1H, 3-H$_b$), 3.11 (td, $^3J = 10.0$ Hz, $^3J = 1.6$ Hz, 1H, 1′-H$_a$), 3.30 (dd, $^3J = 8.0$ Hz, $^3J = 6.6$ Hz, 1H, 2-H), 3.51–3.62 (m, 2H, 1′-H$_2$), 5.04 (d, $^2J = 12.3$ Hz, 1H, OC$H_a$H$_b$Ph), 5.10 (d, $^3J = 10.1$ Hz, 1H, NHCO), 5.11 (d, $^2J = 12.3$ Hz, 1H, OCH$_a$$H_b$Ph), 7.14–7.41 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.7$ (q, CH($C$H$_3$)$_a$(CH$_3$)$_b$), 19.9 (q, CH(CH$_3$)$_a$($C$H$_3$)$_b$), 28.0 (q, C($C$H$_3$)$_3$), 29.5 (t, C-2′), 30.4 (t, C-3′), 30.7 (d, C-6′), 40.5 (t, C-3), 56.0 (d, C-4′), 59.6 (d, C-5′), 62.6 (t, C-1′), 64.1 (d, C-2), 66.5 (t, O$C$H$_2$Ph), 81.5 (s, $C$(CH$_3$)$_3$), 126.6 (d, Ph), 127.9 (d, 2C, Ph), 128.0 (d, Ph), 128.3 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.4 (2d, Ph), 136.9 (s, Ph), 137.7 (s, Ph), 157.0 (s, NHCO), 174.9 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}399$ (N–H, O–H), 1,722 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 499 (100) [(M + H)$^+$]; HRMS (C$_{29}$H$_{43}$N$_2$O$_5$): calcd. 499.3172, found 499.3170.

*tert-Butyl (2S,4′R,5′S)-2-[5-(benzyloxycarbonylamino)-1-hydroxy-6-methyl-4-heptylamino]-3-phenylbutanoate*
(**51b**, C$_{29}$H$_{42}$N$_2$O$_5$)

Alkene **34b** (797 mg, 1.66 mmol) and 6.65 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 3.32 mmol) in 10 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (hexanes–EtOAc 2:1 → 1:1) yielded 600 mg alcohol **51b** (1.20 mmol, 73%) as a colourless oil. $R_f = 0.51$ (hexanes–EtOAc 1:1); $[\alpha]_D^{20} = -21.4 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 1.32$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.87$ (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 0.90 (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 1.12 (ddt, $^2J = 13.6$ Hz, $^3J = 9.6$ Hz, $^3J = 6.6$ Hz, 1H, 3′-H$_a$), 1.33 (s, 9H, C(CH$_3$)$_3$), 1.53–1.78 (m, 4H, 2′-H$_2$, 3′-H$_b$, 6′-H), 2.33 (bs, 2H, OH, CHN$H$CH), 2.66 (dt, $^3J = 9.4$ Hz, $^3J = 3.1$ Hz, 1H, 4′-H), 2.77 (dd, $^2J = 13.2$ Hz, $^3J = 7.1$ Hz, 1H, 1′-H$_a$), 2.87 (dd, $^2J = 13.1$ Hz, $^3J = 7.6$ Hz, 1H, 3-H$_b$), 3.55 (ddd, $^2J = 10.9$ Hz, $^3J = 7.4$ Hz, $^3J = 4.7$ Hz, 1H, 1′-H$_a$), 3.59 (ddd, $^3J = 10.5$ Hz, $^3J = 8.7$ Hz, $^3J = 3.4$ Hz, 1H, 5′-H), 3.68 (ddd, $^2J = 10.7$ Hz, $^3J = 5.8$ Hz, $^3J = 4.5$ Hz, 1H, 1′-H$_b$), 3.74 (dd, $^3J = 7.4$ Hz, $^3J = 6.9$ Hz, 1H, 2-H), 4.49 (d, $^3J = 10.5$ Hz, 1H, NHCO), 5.01 (d, $^2J = 12.2$ Hz, 1H, C$H_a$H$_b$Ph), 5.09 (d, $^2J = 12.2$ Hz, 1H, CH$_a$$H_b$Ph), 7.15–7.38 (m, 10H, 2 Ph) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.6$ (q, CH$C$H$_3$), 20.0 (q, CH$C$H$_3$), 27.0 (t, C-3′), 27.9 (q, C($C$H$_3$)$_3$), 29.9 (t, C-2′), 30.0 (d, C-6′), 40.2 (t, C-3), 56.5 (d, C-4′), 57.0 (d, C-5′), 60.8 (d, C-2), 62.7 (t, C-1′), 66.8 (t, $C$H$_2$Ph), 81.1 (s, $C$(CH$_3$)$_3$), 126.5 (d, Ph), 128.1 (d, 2C, Ph), 128.1 (d, Ph), 128.2 (d, 2C, Ph), 128.5 (d, 2C, Ph), 129.6 (2d, Ph), 136.6 (s, Ph), 137.2 (s, Ph), 156.9 (s, NHCO), 173.6 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}341$ (N–H, O–H), 1,720 (C=O) cm$^{-1}$; MS (FAB pos.): $m/z$ (%) = 499 (100) [(M + H)$^+$]; HRMS (C$_{29}$H$_{43}$N$_2$O$_5$): calcd. 499.3172, found 499.3169.

*tert-Butyl (2S,4′S,5′S)-2-[2-(benzyloxycarbonylamino)-6-hydroxy-3-hexylamino]-4-methylpentanoate*
(**52a**, C$_{24}$H$_{40}$N$_2$O$_5$)

Alkene **35** as a mixture of isomers (322 mg, 0.77 mmol) and 3.10 cm$^3$ of a solution of 9-BBN (0.5 M in THF, 1.54 mmol) in 5 cm$^3$ anhydrous THF were reacted according to GP 9 within 3 h at room temperature. Purification by chromatography (CH$_2$Cl$_2$–MeOH 40:1) yielded 215 mg alcohol **52a** as a single isomer (0.49 mmol, 64%) as a colourless oil. $R_f = 0.31$ (CH$_2$Cl$_2$–MeOH 40:1); $[\alpha]_D^{20} = -13.2 \times 10^{-1}$ deg cm$^2$ g$^{-1}$ ($c = 0.69$, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.90$ (d, $^3J = 6.5$ Hz, 3H, CH(C$H_3$)$_a$(CH$_3$)$_b$), 0.91 (d, $^3J = 6.5$ Hz, 3H, CH(CH$_3$)$_a$(C$H_3$)$_b$), 1.16 (d, $^3J = 6.8$ Hz, 3H, 6′-H$_3$), 1.28–1.70 (m, 8H, 3-H$_2$, 2′-H$_2$, 3′-H$_2$, OH, CHN$H$CH), 1.46 (s, 9H, C(CH$_3$)$_3$), 1.71–1.80 (m, 1H, 4-H), 2.39 (td, $^3J = 6.6$ Hz, $^3J = 2.0$ Hz, 1H, 4′-H), 3.20 (dd, $^3J = 7.8$ Hz, $^3J = 6.6$ Hz, 1H, 2-H), 3.59 ($\varphi$-t, $^3J = 6.2$ Hz, 2H, 1′-H$_2$), 3.75 (ddd, $^3J = 9.2$ Hz, $^3J = 6.7$ Hz, $^3J = 2.0$ Hz, 1H, 5′-H), 5.06 (d, $^2J = 12.2$ Hz, 1H, C$H_a$H$_b$Ph), 5.10 (d, $^2J = 12.2$ Hz, 1H, CH$_a$$H_b$Ph), 5.17 (d, $^3J = 8.4$ Hz, 1H, NHCO), 7.28–7.38 (m, 5H, Ph) ppm; $^{13}$C NMR (100 MHz,

$CDCl_3$): $\delta = 19.0$ (q, C-6′), 22.4 (q, $CH(\mathit{C}H_3)_a(CH_3)_b$), 22.8 (q, $CH(CH_3)_a(\mathit{C}H_3)_b$), 24.8 (d, C-4), 28.1 (q, 3C, $C(\mathit{C}H_3)_3$), 29.4 (t, C-2′ or C-3′), 29.5 (t, C-2′ or C-3′), 43.7 (t, C-3), 48.8 (d, C-4′), 60.1 (d, C-5′), 61.0 (d, C-2), 62.6 (t, C-1′), 66.6 (t, $\mathit{C}H_2Ph$), 81.1 (s, $\mathit{C}(CH_3)_3$), 128.1 (d, Ph), 128.1 (d, 2C, Ph), 128.5 (d, 2C, Ph), 136.7 (s, Ph), 156.2 (s, NHCO), 176.0 (s, C-1) ppm; IR (KBr): $\bar{\nu} = 3{,}342$ (N–H, O–H), 1,724 (bs, C=O) $cm^{-1}$; MS (FAB pos.): *m/z* (%) = 437 (100) [$(M + H)^+$]; HRMS ($C_{24}H_{41}N_2O_5$): calcd. 437.3015, found 437.3013.

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