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Conversion of chiral unsaturated cyanohydrins into chiral carba- and heterocycles via ring-closing metathesis

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Abstract—Aliphatic unsaturated cyanohydrins **1–3** served as starting materials in the synthesis of a set of new chiral unsaturated cyclic 1,2-ethanolamines. Combining a Grignard addition–$NaBH_4$ reduction sequence with a ring-closing metathesis afforded unsaturated cyclic 1,2-ethanolamines **7–11** and **22–25** in good yields and high ee (96–99%). The conversion of cyanohydrins **1–3** via a DIBAL reduction–transimination–$NaBH_4$ reduction sequence, using allylamine, followed by ring-closing metathesis yielded tetrahydropyridines **28**, tetrahydroazepinols **33** and tetrahydroazocinols **34** in high yields and excellent ee (97–99%).

1. Introduction

Chiral non-racemic cyanohydrins have proven to be expedient starting materials for the synthesis of several classes of compounds.[1–6] Over the past twenty years our research has focussed on the synthesis and application of chiral cyanohydrins with high enantiomeric purity, employing the enzyme hydroxynitrile lyase (*Pa*HNL, E.C. 4.1.2.10) from almonds. In previous communications we reported on the synthesis of several aliphatic unsaturated cyanohydrins.[7–9] Three particular examples are depicted in Figure 1.

It was envisioned that cyanohydrins **1–3**, after conversion to bis-olefinic compounds, would be excellent starting materials for the ring-closing metathesis (RCM) mediated synthesis of a unique set of chiral unsaturated carba- and heterocyclic compounds.[10] Conversion of cyanohydrin **1** via a one-pot Grignard addition–$NaBH_4$ reduction[11] sequence, using an olefinic Grignard reagent, followed by subsequent *N*-protection and RCM, would provide an efficient methodology for the synthesis of chiral unsaturated cyclic 1,2-ethanolamines (Scheme 1, path a).

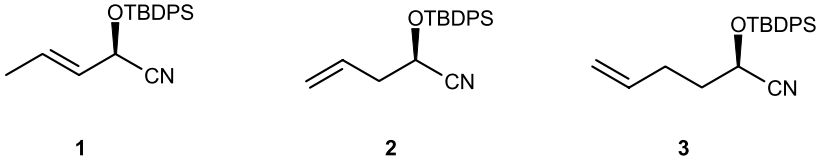
In a similar fashion, a DIBAL reduction–transimination–$NaBH_4$ reduction[12] sequence, using allylamine, would lead to a bis-olefinic secondary amine after *N*-protection, an obvious precursor for a RCM using the now readily available Grubbs' catalyst.[13,14] In this way, 3-hydroxy-tetrahydropyridines could be obtained (Scheme 1, path b).

Applying the same chemistry to cyanohydrins **2** and **3** should lead to a set of compounds depicted in Figure 2. This report presents our results in the exploration of these routes.

2. Results and discussion

2.1. Cyclic unsaturated 1,2-ethanolamines

Our attention was first focussed on the conversion of



1 2 3

Figure 1. Unsaturated *O*-protected cyanohydrins **1–3**: starting materials for the synthesis of chiral carba- and heterocyclic compounds.

Keywords: Cyanohydrins; Ring-closing metathesis; Cyclic ethanolamines; Heterocycles.
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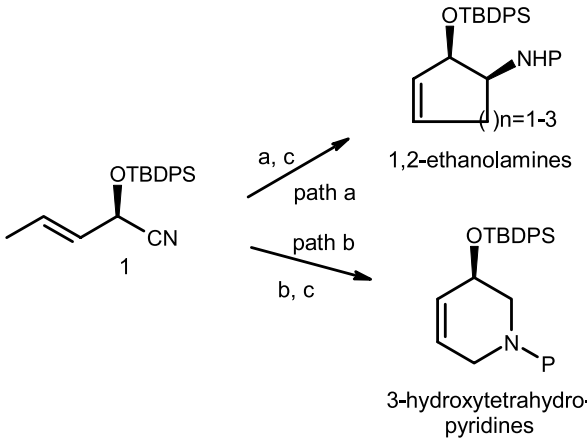


Scheme 1. General pathways for the conversion of cyanohydrin **1** into cyclic derivatives. (a) Grignard addition–$NaBH_4$ reduction. (b) DIBAL reduction–transimination–$NaBH_4$ reduction; (c) Grubbs catalyst.

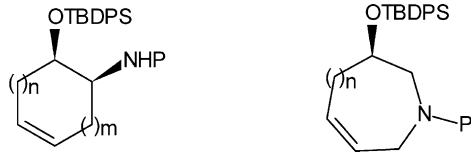
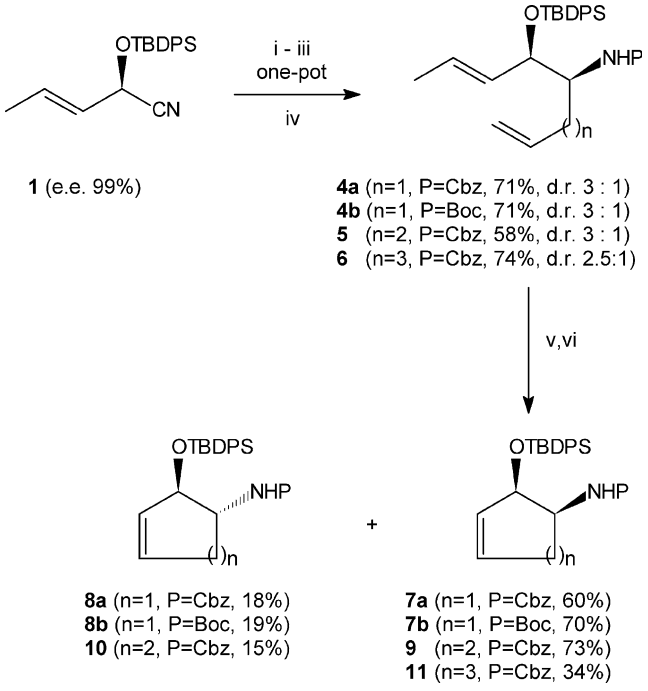
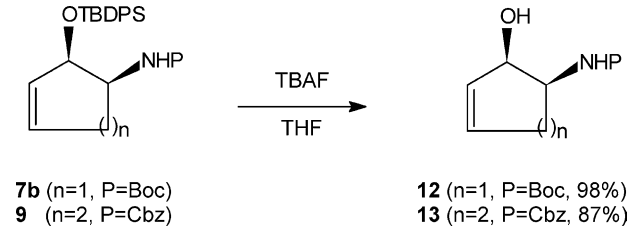


Figure 2. Set of compounds (n, $m=1$, 2) obtainable from *O*-protected cyanohydrins **2** and **3**.

protected cyanohydrin **1** into cyclic 1,2-ethanolamines. Starting from cyanohydrin **1**, addition of 1.5 equiv of the appropriate Grignard reagent led, after quenching with methanol, to the formation of a primary imine. Subsequent in situ $NaBH_4$ reduction, followed by *N*-protection, afforded



Scheme 2. Conversion of cyanohydrin **1** into *O*,*N*-protected unsaturated cyclic 1,2-ethanolamines. For compounds **4**–**6** the major diastereoisomer is depicted. Reagents: (i) $H_2C{=}CH(CH_2)_mMgBr$; (ii) MeOH; (iii) $NaBH_4$; (iv) Cbz-Cl or Boc_2O; (v) Grubbs catalyst; (vi) silicagel column separation.

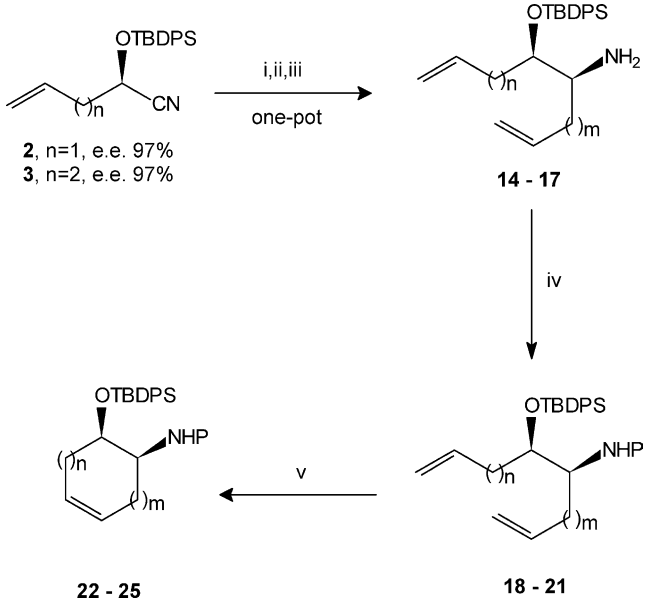


Scheme 3. *O*-deprotection of compounds **7b** and **9** to obtain the previously described compounds **12** and **13**.

bis-olefinic compounds **4**–**6** in yields of 72–85%. During the reduction a mixture of two diastereoisomers was formed with the depicted erythro isomers **4**–**6** as the predominant products (Scheme 2). It was not possible to separate the diastereoisomers at this stage.

RCM reactions were performed in refluxing dichloromethane using 4 mol% of Grubbs catalyst.[14] For the 5- and 6-membered rings the RCM proceeded with good yields (78–89%). The diastereoisomers were readily separated by silicagel column chromatography, affording pure ethanolamines **7**–**10**. In the case of the 7-membered ring **11**, dimerization at the terminal double bond was the prominent reaction. Ethanolamine **11** was obtained in 34% yield as a mixture of two unseparable diastereoisomers. To be able to determine the enantiomeric excess (ee) of these compounds, the racemic forms were also synthesized. Chiral HPLC of compounds **7**–**10** showed that all these cyclic ethanolamines were obtained with excellent enantiomeric purity (ee 96–98%).

Additional proof of the stereochemistry of these ethanolamines was obtained by *O*-deprotection of compounds **7b** and **9** resulting in the formation of the known compounds **12**[15] and **13**[16] (Scheme 3). For both compounds spectral and physical data were in agreement with the literature.



Scheme 4. Conversion of cyanohydrins **2** and **3** into *O*,*N*-protected cyclic 1,2-ethanolamines. For compounds **14**–**25** the major diastereoisomer is depicted. Reagents: (i) $H_2C{=}CH(CH_2)_mMgBr$; (ii) MeOH; (iii) $NaBH_4$; (iv) Cbz-Cl or Boc_2O; (v) Grubbs catalyst (4 mol%).

Extension of our strategy to cyanohydrins **2** and **3** afforded *O*,*N*-protected ethanolamines **14**–**17** (Scheme 4). The Grignard addition–$NaBH_4$ reduction sequence generally afforded diastereomeric mixtures (dr $\pm$2.5:1), with the depicted compounds as the major diastereoisomers. Subsequent *N*-protection of the crude amines **14**–**17**, followed by RCM afforded new cyclic 1,2-ethanolamines **22**–**25** in good overall yields (Table 1). Attempts to separate the obtained diastereomeric mixtures remained without success.

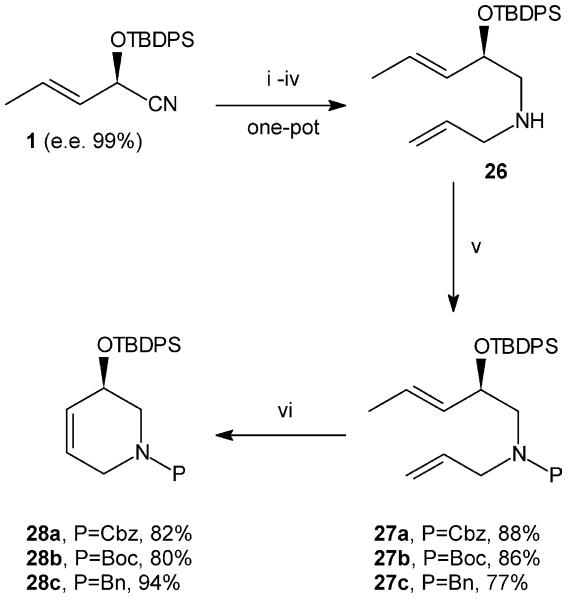
Table 1. Results for the conversion of cyanohydrins **2** and **3** into *O*,*N*-protected cyclic 1,2-ethanolamines **22**–**25**

Comp.	*n*	*m*	P	Yield (%)
18a	1	1	Cbz	69
18b	1	1	Boc	89
19a	1	2	Cbz	79
19b	1	2	Boc	81
20a	2	1	Cbz	68
20b	2	1	Boc	56
21	2	2	Cbz	68
22a	1	1	Cbz	87
22b	1	1	Boc	77
23a	1	2	Cbz	96
23b	1	2	Boc	66
24a	2	1	Cbz	94
24b	2	1	Boc	86
25	2	2	Cbz	66[a]

[a] Yield based on 55% converted starting material.

2.2. Unsaturated *N*-heterocycles

Next, our efforts were directed towards the synthesis of *O*,*N*-protected (*R*)-3-hydroxy-2*H*−1,2,3,6-tetrahydro-pyridines **28a**–**c** (Scheme 5).

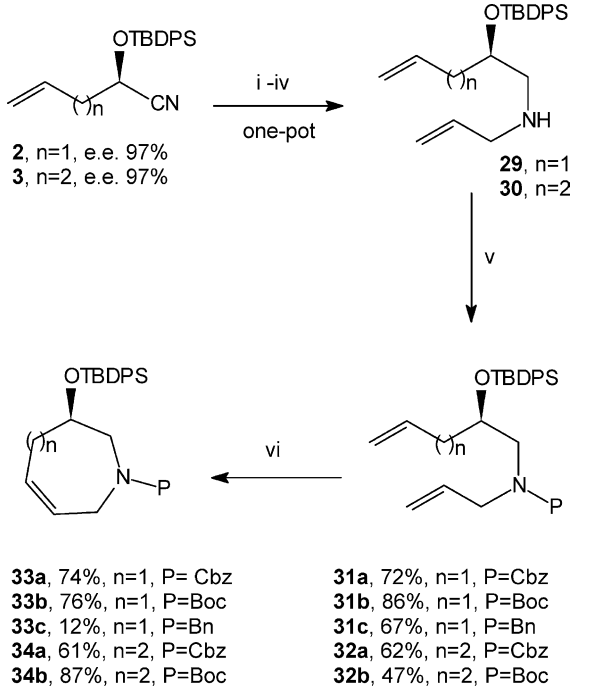


Scheme 5. Synthesis of (*R*)-*N*-protected 3-[(*t*-butyldiphen-ylsilyl)oxy]-2*H*-1,2,3,6-tetrahydropyridines. Reagents: (i) DIBAL; (ii) MeOH; (iii) Allylamine; (iv) $NaBH_4$; (v) Cbz-Cl or Boc_2O or BnBr; (vi) Grubbs catalyst (4 mol%).

Employing the previously described[12] DIBAL reduction–transimination–$NaBH_4$ reduction sequence to cyanohydrin **1**, using allylamine in the transimination step, afforded the secondary amine **26** in quantitative yield. Crude **26** was protected with a Cbz-, Boc- or Bn-group to give *N*-protected dienes **27a**–**c** in good yields (77–88%). Tetrahydropyridines **28a**–**c** were obtained in 80–94% (69–72% overall based on 1) yields via a ring- closing metathesis reaction with Grubbs' catalyst in refluxing dichloromethane.[13,14]

The smooth transformation of **27c** into **28c** is remarkable, as the Grubbs catalyst is generally ineffective for the conversion of tertiary amines.[13] The ee of **28c** was determined by chiral HPLC and found to be 99%. *O*-TBDPS-protected tetrahydropyridine **28a** was deprotected to afford benzyl (*R*)-3-hydroxy-3,6-dihydropyridine-1(2*H*)-carboxylate, an earlier described compound.[17] The spectroscopic and physical data were in complete agreement. It should be noted that the authors assigned the configuration of this compound incorrectly as *S*.[17] The ee (98%) was determined by chiral HPLC. Recently the *O*-MOM-protected analog of **28b** served as the starting compound in a synthesis of 5-des-(hydroxymethyl)-1-deoxynojir-mycin, reportedly a potent glycosidase inhibitor.[18]

Application of the same chemistry to cyanohydrins **2** and **3** led to the synthesis of the new *O*,*N*-protected tetrahydro-azepinols **33a**–**c** and azocinols **34a**,**b** (Scheme 6). In general, the yields were slightly lower than in the synthesis of the tetrahydropyridines. Carbamate protected 7- and 8-membered heterocycles **33a**,**b** and **34a**,**b** were obtained in 53–65% and 38–41% overall yields respectively. RCM with the tertiary amine **31c** failed completely. Using the HCl salt of **31c** in a RCM afforded azepinol **33c** in 12% yield.



Scheme 6. Transformation of cyanohydrins **2** and **3** into *O*,*N*-protected tetrahydroazepinols (**33a**–**c**) and tetrahydro-azocinols (**34a**,**b**). Reagents: (i) DIBAL; (ii) MeOH; (iii) allylamine; (iv) $NaBH_4$; (v) Cbz-Cl or Boc_2O or BnBr; (vi) Grubbs catalyst (4 mol%).

3. Conclusion

Cyanohydrins **1**–**3** were found to be excellent starting materials for the enantioselective synthesis of a number of new chiral *N*-heterocycles and cyclic 1,2-ethanolamines. The combination of either a DIBAL reduction–transimination–$NaBH_4$ reduction or a Grignard addition–$NaBH_4$ reduction sequence with ring-closing metathesis employing the Grubbs' catalyst, proved to be a powerful methodology for the preparation of these compounds in only three steps and high yields.

4. Experimental

4.1. General procedures and remarks

Reactions were carried out in an inert nitrogen or argon atmosphere. For reactions involving DIBAL or Grignard reagents flame dried equipment was used. All compounds were synthesized in both racemic and non-racemic form. ees were determined by comparing racemic with non-racemic compounds on chiral HPLC employing a Daicel CHIRALCEL OD or ODH column, using hexane (HEX) 2-propanol (IPA) mixtures as the eluent, and UV detection at 254 nm. Eluents are specified in each case. TLC-analyses were performed on Merck plastic silica gel 60 F_{254} plates. Detection by UV (254 nm); ammonium molybdate (50 g L^{-1}) and cerium(IV) sulfate (1 g L^{-1}) in aqueous 10% H_2SO_4, followed by heating to 150 °C; or 5% (w/v) aqueous $KMnO_4$. Column chromatography was performed on Fluka silica gel (0.063–0.200 mm). Solvents for chromatography were distilled before use (PE = petroleum ether 40–60; DEE = diethyl ether; EtOAc = ethyl acetate). Other solvents were of p.a. quality and stored over molecular sieves (3 Å). Commercial chemicals were used as received. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker AC-200 instrument. Samples were measured in $CDCl_3$, using TMS as an internal standard for ^1H NMR, and $CDCl_3$ as internal standard for ^{13}C NMR. Optical rotations were measured on a Propol automatic polarimeter (Sodium D line, $\lambda = 589$ nm). ESI-MS was performed on a Perkin Elmer SCIEX API 165 instrument. ESI-HRMS was performed on a Finnigan LTQ FTMS instrument.

General procedure for the one-pot Grignard addition–$NaBH_4$ reduction reactions. Under an argon atmosphere the appropriate *O*-TBDPS-protected cyanohydrin (3.0 mmol) was dissolved in dry DEE (30 mL). At room temperature a solution of Grignard reagent (4.5 mmol) was added dropwise. The reaction was stirred at room temperature for 1 h, cooled to −20 °C and quenched with dry MeOH (5.0 mL). After a few minutes the mixture was cooled to −80 °C and $NaBH_4$ (0.29 g, 7.5 mmol) added. The mixture was slowly warmed to room temperature at which it was stirred for 2 h. Then the reaction was poured into water (50 mL) and extracted with DEE (3×30 mL). The combined DEE layers were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo to afford the crude amines as colorless oils in quantitative yield.

General procedure for the one-pot DIBAL reduction–transimination–$NaBH_4$ reductions. Under an argon atmosphere the appropriate *O*-TBDPS-protected cyanohydrin (3.0 mmol) was dissolved in dry DEE (30 mL). At −78 °C DIBAL (4.5 mL, 4.5 mmol, 1.0 M in hexanes) was added. The reaction was allowed to warm up slowly to 0 °C. After recooling to −90 °C anhydrous methanol (5.0 mL) was added at once followed after 5 min, by allyl amine (1.20 mL, 16 mmol). The cooling bath was removed and the reaction was stirred for 2 h at room temperature. The resulting suspension was cooled to −20 °C and $NaBH_4$ (0.28 g, 7.4 mmol) was added in three portions. After stirring for 2 h at room temperature the suspension was poured into an aqueous 0.4 M NaOH (40 mL) solution. The layers were separated and the water layer was extracted with DEE (2×20 mL). After washing the combined organic layers with brine (20 mL), drying ($MgSO_4$), filtration and evaporation of the solvent in vacuo the crude amines were obtained as colorless oils in quantitative yield.

General procedure for carbobenzyloxy (Cbz) protections. The crude amine (1.0 mmol) was dissolved in an ice cold mixture of CH_2Cl_2 (5.0 mL) and saturated aqueous $NaHCO_3$ solution (10 mL). Benzyl chloroformate (0.30 mL, 2.0 mmol) was added dropwise and the reaction stirred vigorously overnight while warming to room temperature. The layers were separated and the water layer was extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo to afford the crude *N*-Cbz-protected product.

General procedure for butyloxycarbonyl (Boc) protections. The crude amine (1.0 mmol) was dissolved in CH_2Cl_2 (5.0 mL). Triethylamine (TEA, 0.16 mL, 1.1 mmol) and di-*t*-butyl dicarbonate (654 mg, 3.0 mmol) were added. After stirring overnight at room temperature the solvent was evaporated at reduced pressure to obtain the crude *N*-Boc-protected product.

General procedure for benzyl (Bn) protections. The amine (1.0 mmol) was dissolved in CH_2Cl_2 (4.0 mL) and $Na_2CO_3 \cdot 10H_2O$ (0.60 g, 2.1 mmol), water (2.0 mL) and benzyl bromide (0.16 mL, 1.3 mmol) were added. The reaction was stirred vigorously overnight. After separation of the layers the water layer was extracted with CH_2Cl_2 (2×2 mL). All organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo to afford the crude benzylated product.

General procedure for ring closing metathesis reactions. The appropriate diene was dissolved in CH_2Cl_2 (1 mmol/10 mL) and argon was bubbled through the solution for 3 min. Grubbs' catalyst (4 mol%) was added and the mixture refluxed (maximum 24 h). Progress of reaction was monitored by TLC with the new cyclic products running slightly lower. Upon completion, the solvent was evaporated to obtain the crude product.

For 8-membered rings the RCM reactions were performed at 0.005 M concentration of diene in toluene at 60 °C.

4.1.1. (2*R*,3*E*)-2-[(*t*-Butyldiphenylsilyl)oxy]pent-3-ene nitrile (1). Prepared as described earlier,[7] $[\alpha]_D^{20} = -4.2$ ($c = 1$, $CHCl_3$). ee 99%, Chiralcel OD, HEX/IPA = 99.75:0.25, 1.0 mL/min, RT 7.3 min (*R*-enantiomer), RT

11.0 min (*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H, *t*-Bu); 1.68 (d, 3H, J=5.9 Hz, CH_3); 4.75 (d, 1H, J=5.8 Hz, CHO); 5.50 (m, 1H, =CH); 5.72 (m, 1H, =CH); 7.35 (m, 6H, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.3, 19.1, 26.5, 63.3, 118.4, 125.8, 127.7, 127.8, 130.1, 130.2, 131.3, 131.5, 131.9, 135.6.

4.1.2. (2*R*)-2-[(*t*-Butyldiphenylsilyl)oxy]pent-4-ene nitrile (2). Prepared as described earlier,[8] $[\alpha]_D^{25}=+30.3$ (c=1.2, CH_2Cl_2). ee 97%, Chiralcel ODH, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 5.9 min (*R*-enantiomer), RT 8.6 min (*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, *t*-Bu); 2.35–2.61 (m, 2H, CH_2); 4.35 (dd, 1H, J=5.5, 7.0 Hz, CHO); 5.16 (m, 2H, =CH_2); 5.77 (m, 1H, =CH); 7.42 (m, 6H, SiPh); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 18.6, 26.4, 40.1, 62.4, 118.6, 119.9, 127.7, 130.1, 130.3, 131.2, 131.6, 135.4, 135.5.

4.1.3. (2*R*)-2-[(*t*-Butyldiphenylsilyl)oxy]hex-5-ene nitrile (3). Prepared as described earlier,[9] $[\alpha]_D^{20}=+29.0$ (c=1, $CHCl_3$). ee 97%, Chiralcel ODH, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 5.4 min (*R*-enantiomer), RT 7.3 min (*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, *t*-Bu); 1.84 (m, 2H, CH_2); 2.21 (m, 2H, CH_2); 4.35 (t, 1H, J=6.2 Hz, CHO); 4.97 (m, 2H, =CH_2); 5.63 (m, 1H, =CH); 7.42 (m, 6H, Ph); 7.68 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.5, 28.2, 35.0, 62.2, 115.9, 119.7, 127.5, 127.8, 129.3, 129.9, 130.2, 131.6, 134.7, 135.1, 135.5.

4.2. Preparation of cyclic unsaturated 1,2-ethanolamines

4.2.1. (5*R*,6*E*)-5-(*t*-Butyldiphenylsilyl)oxyocta-1,6-diene-4-amine. Prepared from cyanohydrin **1** and allylmagnesium bromide as a mixture of two diastereoisomers in a 3:1=(4*S*,5*R*)–(4*R*,5*R*) ratio as determined by ^{1}H NMR. ESI-MS m/z 380.0 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.44 (d, 3H, J=6.2 Hz, CH_3, minor isomer); 1.52 (d, 3H, J=5.2 Hz, CH_3 major isomer); 1.93–2.17 (m, 2H, CH_2); 2.73–2.84 (m, 1H, CHN); 3.54–3.68 (m, 2H, NH_2); 3.96 (m, 1H, CHO); 4.94–5.74 (m, 5H, CH=CH+CH=CH_2); 7.37 (m, 6H, Ph); 7.67 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.4, 19.0, 26.8, 37.1, 55.3, 77.3, 116.7, 127.0, 127.2, 127.4, 128.7, 128.9, 129.2, 129.3, 129.8, 130.3, 133.7, 133.9, 134.7, 135.2, 135.5, 135.7, 136.2. Observed for minor isomer: 18.7, 26.5, 55.7, 78.4, 117.8.

4.2.2. (6*R*,7*E*)-6-(*t*-Butyldiphenylsilyl)oxynona-1,7-diene-5-amine. Prepared from cyanohydrin **1** and but-3-en-1-ylmagnesium bromide as a mixture of two diastereoisomers in a 3:1=(5*S*,6*R*)–(5*R*,6*R*) ratio as determined by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.19–1.69 (m, 5H, CH_3 and CH_2); 1.87–2.21 (m, 2H, CH_2); 2.66–2.75 (m, 1H, CHN); 3.97 (dd, 1H, J=4.4, 7.3 Hz CHO); 4.86–5.10 (m, 3H, CH=CH_2); 5.36 (m, 1H, =CH); 5.62–5.83 (m, 1H, =CH); 7.38 (m, 6H, Ph); 7.66 (m, 4H, Ph). Observed for minor isomer: 3.86 (dd, 1H, J=5.2, 7.3 Hz, CHO). ^{13}C NMR ($CDCl_3$): δ 17.6, 19.3, 27.1, 30.3, 32.1, 55.6, 77.7, 114.4, 127.3, 127.5, 127.6, 128.8, 129.4, 129.5, 129.6, 134.0, 135.4, 135.7, 135.9, 138.2. Observed for minor isomer: 26.7, 30.0, 55.9, 79.1, 115.5.

4.2.3. (7*R*,8*E*)-7-(*t*-Butyldiphenylsilyl)oxydeca-1,8-diene-6-amine. Prepared from cyanohydrin **1** and pent-4-en-1-ylmagnesium bromide as a mixture of two diastereoisomers in a 3:1=(6*S*,7*R*)–(6*R*,7*R*) ratio as determined by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.16–1.66 (m, 7H, CH_3 and CH_2); 1.80–2.05 (m, 2H, CH_2); 2.54–2.72 (m, 1H, CHN); 3.96 (dd, 1H, J=5.1, 10.2 Hz, CHO); 4.92 (m, 2H, =CH_2); 5.15–5.41 (m, 2H, CH=CH); 5.62–5.79 (m, 1H, =CH); 7.39 (m, 6H, Ph); 7.66 (m, 4H, Ph). Observed for minor isomer: 3.86 (dd, 1H, J=5.1, 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ 17.6, 19.2, 25.3, 27.0, 32.3, 33.6, 55.9, 77.7, 114.4, 127.3, 127.5, 127.8, 128.5, 128.7, 128.8, 129.4, 129.6, 131.0, 134.0, 134.9, 135.1, 135.7, 135.9, 138.4, 138.5. Observed for minor isomer: 17.4, 25.7, 32.4, 33.8, 56.4, 79.2.

4.2.4. Benzyl [(2*R*,3*E*)-1-allyl-2-(*t*-butyldiphenylsilyl)-oxy-pent-3-en-1-yl]carbamate (4a). Obtained as a mixture of two diastereoisomers in a 3:1=(1*S*,2*R*)–(1*R*,2*R*) ratio as determined by ^{1}H NMR. Yield 71% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS m/z 514.3 $[M+H]^+$; 536.2 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.42 (d, 3H, J=7.7 Hz, CH_3, minor isomer); 1.48 (d, 3H, J=4.6 Hz, CH_3 major isomer); 2.02–2.44 (m, 2H, CH_2); 2.64 (m, 1H, CHN); 4.18 (m, 1H, CHO); 4.63 (m, 1H, NH); 4.90–5.08 (m, 5H, CH=CH_2, CH_2Ph); 5.35 (m, 1H, =CH); 5.61 (m, 1H, =CH); 7.30 (m, 11H, SiPh, Ph); 7.62 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.5, 19.3, 27.0, 34.4, 55.6, 66.3, 76.4, 117.2, 127.4, 127.5, 127.8, 128.3, 128.8, 129.0, 129.3, 129.4, 129.6, 133.6, 134.7, 135.5, 135.8, 135.9, 136.6, 155.9. Observed for minor isomer: 18.9, 26.5, 36.2, 66.5, 76.1, 118.5, 156.1.

4.2.5. *t*-Butyl [(2*R*,3*E*)-1-allyl-2-(*t*-butyldiphenylsilyl)-oxypent-3-en-1-yl]carbamate (4b). Obtained as a mixture of two diastereoisomers in a 3:1=(1*S*,2*R*)–(1*R*,2*R*) ratio as determined by ^{1}H NMR. Yield 71% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=97:3). ESI-MS m/z 480.1 $[M+H]^+$; 502.4 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.40 (s, 9H, *t*-Bu); 1.48 (d, 3H, J=4.4 Hz, CH_3); 2.24 (m, 2H, CH_2); 3.63 (m, 1H, CHN); 4.12 (m, 1H, CHO); 4.51 (m, 1H, NH); 5.00 (m, 2H, =CH_2); 5.32 (m, 2H, =CH); 5.59–5.76 (m, 1H, =CH); 7.40 (m, 6H, SiPh); 7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.4, 19.2, 26.9, 28.2, 34.5, 54.9, 76.0, 78.5, 116.8, 127.2, 127.4, 128.4, 128.6, 129.3, 129.5, 129.7, 130.1, 133.5, 133.6, 133.8, 134.9, 135.7, 155.3. Observed for minor isomer: 36.2, 75.5, 155.4.

4.2.6. Benzyl [(2*R*,3*E*)-1-(but-3-enyl)-2-(*t*-butyl-diphenylsilyl)oxypent-3-en-1-yl]carbamate (5). Obtained as a mixture of two diastereoisomers in a 3:1=(1*S*,2*R*)–(1*R*,2*R*) ratio as determined by ^{1}H NMR. Yield 58% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 1.41–1.61 (m, 5H, CH_3 and CH_2); 1.81–2.25 (m, 2H, CH_2); 3.65 (m, 1H, CHN); 4.12 (m, 1H, CHO); 4.66 (d, 1H, J=9.5 Hz, NH); 4.90–5.10 (m, 5H, $PhCH_2$, CH=CH_2); 5.34 (m, 1H, =CH); 5.75–5.92 (m, 1H, =CH); 7.34 (m, 11H, Ph); 7.63 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.7, 19.4, 27.1, 29.5, 30.3, 56.0, 66.4, 76.6, 114.7, 127.4, 127.6, 127.9, 128.3, 128.4, 128.7, 129.6, 129.8, 133.9, 134.9, 135.9, 136.0, 138.0, 156.2.

4.2.7. Benzyl [(2*R*,3*E*)-1-(pent-4-enyl)-2-(*t*-butyl-diphenylsilyl)oxypent-3-en-1-yl]carbamate (6). Obtained as a mixture of two diastereoisomers in a 2.5:1=(1*S*,2*R*)–(1*R*,2*R*) ratio as determined by ^{1}H NMR. Yield 74% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 1.26–1.56 (m, 7H, CH_3 and CH_2); 1.96 (m, 2H, CH_2); 3.60 (m, 1H, CHN); 4.07–4.16 (m, 1H, CHO); 4.63 (d, 1H, J=9.5 Hz, NH); 4.79–5.18 (m, 4H, $PhCH_2$, =CH_2); 5.34 (m, 2H, CH=CH); 5.72 (m, 1H, =CH); 7.36 (m, 11H, Ph); 7.62 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.6, 19.4, 25.2, 27.1, 29.6, 33.5, 56.2, 66.3, 76.5, 114.7, 126.6, 127.4, 127.6, 127.9, 128.4, 128.6, 128.8, 129.3, 129.7, 130.4, 133.7, 133.9, 134.9, 135.9, 136.0, 136.9, 138.5, 156.3. Observed for minor isomer: 25.4, 26.7, 31.2, 66.5, 76.1.

4.2.8. Benzyl (1*S*,2*R*)-(2-[*t*-butyldiphenylsilyl]oxycyclopent-3-en-1-yl)carbamate (7a). Major isomer, obtained from diastereomeric mixture **4a**. Yield 60% (colorless oil, purified by silicagel column chromatography, first fraction, eluent PE/EtOAc=96:4). $[\alpha]_D^{25}=-19.6$ (c=0.53, CH_2Cl_2). ESI-MS m/z 472.2 $[M+H]^+$; 494.2 $[M+Na]^+$; 965.3 $[M_2+Na]^+$; 1437.0 $[M_3+Na]^+$; ee 96%, Chiralcel OD, HEX/IPA=99:1, 1.0 mL/min, RT 9.4 min (1*S*,2*R*-enantiomer), RT 10.4 min (1*R*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 2.33 (m, 1H, CH_2); 2.62 (m, 1H, CH_2); 4.17 (m, 1H, CHN); 4.66 (m, 1H, CHO); 5.12 (s, 2H, CH_2Ph); 5.46 (m, 1H, =CH); 5.64 (d, 1H, J=10.1 Hz, NH); 5.82 (m, 1H, =CH); 7.39 (m, 11H, Ph, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 37.8, 52.4, 66.1, 75.7, 127.4, 127.5, 127.6, 128.2, 129.6, 131.7, 132.9, 133.0, 133.5, 135.4, 135.5, 136.6, 155.8. HRMS calculated for $[M+H]^+$ 472.23025, found: 472.23090.

4.2.9. *t*-Butyl (1*S*,2*R*)-(2-[*t*-butyldiphenylsilyl]oxycyclopent-3-en-1-yl)carbamate (7b). Major isomer, obtained from diastereomeric mixture **4b**. Yield 70% (colorless oil, purified by silicagel column chromatography, first fraction, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-27.0$ (c=1.0, CH_2Cl_2). ESI-MS m/z 438.1 $[M+H]^+$; 460.0 $[M+Na]^+$; 875.5 $[M_2+H]^+$; 897.6 $[M_2+Na]^+$; ee 98%, Chiralcel ODH, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 7.0 min (1*S*,2*R*-enantiomer), RT 8.8 min (1*R*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, *t*-Bu); 1.46 (s, 9H, *t*-Bu); 2.30 (m, 1H, CH_2); 2.60 (dd, 1H, J=7.3, 16.8 Hz, CH_2); 4.11 (m, 1H, CHN); 4.65 (d, 1H, J=6.6 Hz, CHO); 5.40 (m, 2H, =CH, NH); 5.82 (m, 1H, =CH); 7.41 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 26.9, 28.3, 38.1, 51.9, 75.8, 78.8, 127.5, 127.7, 129.7, 131.6, 131.9, 132.5, 133.1, 133.4, 133.9, 135.7, 155.6. HRMS calculated for $[M+H]^+$ 438.24590, found: 438.24622.

4.2.10. Benzyl (1*R*,2*R*)-(2-[*t*-butyldiphenylsilyl]-oxycyclo-pent-3-en-1-yl)carbamate (8a). Minor isomer, obtained from diastereomeric mixture **4a**. Yield 18% (colorless solid, purified by silicagel column chromatography, second fraction, eluent PE/EtOAc=96:4). $[\alpha]_D^{25}=-16.5$ (c=0.51, CH_2Cl_2). ESI-MS m/z 494.2 $[M+Na]^+$; 965.2 $[M_2+Na]^+$; 1436.5 $[M_3+Na]^+$; ee 98%, Chiralcel OD, HEX/IPA=97:3, 1.0 mL/min, RT 8.0 min (1*R*,2*R*-enantiomer), RT 17.6 min (1*S*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 2.04 (m, 1H, CH_2); 2.88 (m, 1H, CH_2); 4.17 (m, 1H, CHN); 4.52 (m, 1H, NH); 4.61 (m, 1H, CHO); 5.02 (d, 1H, J=12.5 Hz, CH_2Ph); 5.08 (d, 1H, J=12.5 Hz, CH_2Ph); 5.54 (m, 1H, =CH); 5.78 (m, 1H, =CH); 7.38 (m, 11H, Ph, SiPh); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 37.9, 60.1, 66.4, 83.2, 127.5, 127.9, 128.3, 129.6, 131.5, 132.5, 133.5, 133.9, 135.7, 136.5, 155.7. HRMS calculated for $[M+H]^+$ 472.23025, found: 472.23062.

4.2.11. *t*-Butyl (1*R*,2*R*)-(2-[*t*-butyldiphenylsilyl]-oxycyclo-pent-3-en-1-yl)carbamate (8b). Minor isomer, obtained from diastereomeric mixture **4b**. Yield 19% (colorless oil, purified by silicagel column chromatography, second fraction, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-17.4$ (c=0.94, CH_2Cl_2). ESI-MS m/z 460.1 $[M+Na]^+$; HPLC Chiralcel ODH, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 8.7 min (1*S*,2*S*-enantiomer), RT 9.3 min (1*R*,2*R*-enantiomer), no base line separation. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.42 (s, 9H, *t*-Bu); 2.03 (m, 1H, CH_2); 2.84 (dd, 1H, J=6.6, 16.8 Hz, CH_2); 4.11 (m, 1H, CHN); 4.28 (m, 1H, NH); 4.59 (m, 1H, CHO); 5.50 (m, 1H, =CH); 5.75 (m, 1H, =CH); 7.41 (m, 6H, SiPh); 7.68 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.9, 28.4, 38.3, 59.8, 79.0, 83.4, 127.6, 129.6, 131.7, 131.9, 132.5, 133.4, 133.6, 134.1, 135.7, 135.9, 155.3. HRMS calculated for $[M+H]^+$ 438.24590, found: 438.24640.

4.2.12. Benzyl (1*S*,2*R*)-(2-[-*t*-butyldiphenylsilyl]-oxycyclo-hex-3-en-1-yl)carbamate (9). Major isomer, obtained from diastereomeric mixture **5**. Yield 73% (colorless oil, purified by silicagel column chromatography, first fraction, eluent PE/EtOAc=95:5). $[\alpha]_D^{25}=-71.4$ (c=1.0, CH_2Cl_2). ee 97%, Chiralcel OD, HEX/IPA=99:1, 1.0 mL/min, RT 7.7 min (1*R*,2*S*-enantiomer), RT 10.3 min (1*S*,2*R*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.85–2.35 (m, 4H, CH_2); 3.73 (m, 1H, CHN); 4.21 (m, 1H, CHO); 5.06 (d, 1H, J=12.4 Hz, CH_2Ph); 5.13 (d, 1H, J=12.4 Hz, CH_2Ph); 5.32 (m, 2H, =CH and NH); 5.66 (m, 1H, =CH); 7.15–7.45 (m, 11H, Ph, SiPh); 7.69 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 24.1 (C5 and C6), 27.1, 50.8, 66.4, 67.1, 127.6, 127.8, 127.9, 128.5, 129.3, 129.8, 129.9, 130.3, 133.4, 133.9, 134.9, 135.8, 135.9, 136.9, 155.9. HRMS calculated for $[M+H]^+$ 486.24590, found: 486.24658.

4.2.13. Benzyl (1*R*,2*R*)-(2-[-*t*-butyldiphenylsilyl]-oxycyclo-hex-3-en-1-yl)carbamate (10). Minor isomer, obtained from diastereomeric mixture **5**. Yield 15% (colorless solid, purified by silicagel column chromatography, first fraction, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-23.0$ (c=1.0, CH_2Cl_2). ee 97%, Chiralcel OD, HEX/IPA=99:1, 1.0 mL/min, RT 9.8 min (1*R*,2*R*-enantiomer), RT 14.8 min (1*S*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 2.10 (m, 4H, CH_2); 3.85 (m, 1H, CHN); 3.95 (broad s, 1H, NH); 4.39 (d, 1H, J=8.0 Hz, CHO); 4.96 (d, 1H, J=11.7 Hz, CH_2Ph); 5.07 (d, 1H, J=11.7 Hz, CH_2Ph); 5.47 (d, 1H, J=10.2 Hz, =CH); 5.68 (d, 1H, J=9.5 Hz, =CH); 7.31–7.45 (m, 11H, Ph, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 23.1, 25.5, 26.8, 52.9, 66.4, 70.4, 126.6 127.5, 127.6, 127.9, 128.4, 129.2, 129.6, 133.4, 135.8, 135.9, 136.5, 155.6. HRMS calculated for $[M+H]^+$ 486.24590, found: 486.24649.

4.2.14. Benzyl (2*R*)-(2-[-*t*-butyldiphenylsilyl]-oxycyclo-hept-3-en-1-yl)carbamate (11). Obtained as a

diastereomeric mixture, (1*S*,2*R*)–(1*R*,2*R*)=2.5:1, from diastereomeric mixture **6** in 34% yield as a colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.25–1.62 (m, 2H, CH_2); 1.78–2.42 (m, 4H, CH_2); 3.60–3.95 (m, 1H, CHN); 4.44 (m, 1H, CHO); 4.84–5.11 (m, 2H, CH_2Ph); 5.38 (m, 1H, NH); 5.56 (m, 1H, =CH); 5.83 (m, 1H, =CH); 7.15–7.45 (m, 11H, Ph, SiPh); 7.69 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 21.7, 26.9, 28.1, 32.3, 53.9, 66.4, 73.7, 125.9, 127.5, 127.6, 127.9, 128.4, 129.6, 129.7, 129.9, 133.4, 135.8, 136.0, 156.0. Observed for minor isomer: 27.0, 28.0, 52.8.

4.2.15. *t*-Butyl (1*S*,2*R*)-(2-hydroxycyclopent-3-en-1-yl)-carbamate (12). Compound **7b** (172 mg, 0.394 mmol) was dissolved in THF (6 mL) and excess TBAF (3 equiv) was added. After 2 h the reaction was completed as monitored by TLC. The solvent was evaporated and the residue purified by column chromatography. Yield 77 mg (98%). (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5→1:1). $[\alpha]_D^{20}=-41.4$ ($c=1.0$, CH_2Cl_2). Enantiomers could not be separated by chiral HPLC on Daicel Chiralcel ODH, OJ and Chiralpak AD columns. ^{1}H NMR ($CDCl_3$) lit[15b]: δ 1.46 (s, 9H, *t*-Bu); 2.01 (broad s, 1H, OH); 2.23 (m, 1H, CH_2); 2.70 (m, 1H, CH_2); 4.12 (m, 1H, CHN); 4.58 (broad d, 1H, CHO); 5.17 (broad s, 1H, NH); 5.88 (m, 1H, CH=CH); 6.00 (m, 1H, CH=CH). ^{13}C NMR ($CDCl_3$) lit[15b]: δ 28.3, 37.4, 52.2, 74.2, 79.3, 131.7, 134.5, 156.1.

4.2.16. Benzyl (1*S*,2*R*)-(2-hydroxycyclohex-3-en-1-yl)-carbamate (13). Silyl ether **9** (422 mg, 0.866 mmol) was dissolved in THF (8 mL) and excess TBAF (3 equiv) was added. TLC showed complete conversion after 1 h. The solvent was evaporated and the residue purified by silicagel column chromatography, eluent PE/EtOAc=95:5→3:1→2:3 to afford the title compound (188 mg, 87%) as a colorless oil. $[\alpha]_D^{20}=-100.6$ ($c=1.0$, CH_2Cl_2, [lit.[16], $[\alpha]_D^{20}=-55.6$ ($c=1.0$, CH_2Cl_2 for ee=58%]). ee 98%, Chiralcel ODH, HEX/IPA=90:10, 1.0 mL/min, RT 10.9 min (1*S*,2*R*-enantiomer), RT 19.0 min (1*R*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$) lit[16]: δ 1.62 (d, 1H, $J=5.1$ Hz, OH); 1.57–1.69 (m, 1H, CH_2); 1.73–1.84 (m, 1H, CH_2); 2.15 (m, 2H, CH_2); 3.79 (m, 1H, CHN); 4.14 (m, 1H, CHO); 5.11 (s, 2H, CH_2Ph); 5.31 (m, 1H, NH); 5.77–5.95 (m, 2H, CH=CH); 7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) lit[16]: δ 23.1, 24.4, 50.4, 64.5, 66.4, 127.0, 127.8, 128.2, 129.1, 131.0, 136.2, 155.9.

4.2.17. (5*R*)-5-(*t*-Butyldiphenylsilyl)oxyocta-1,7-diene-4-amine (14). Obtained as a mixture of two diastereoisomers in a (4*S*,5*R*)–(4*S*,5*R*)=2.5:1 ratio as determined by ^{1}H NMR. ESI-MS *m*/*z* 380.0 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.91–2.41 (m, 4H, CH_2); 2.79 (m, 1H, CHN); 3.73 (m, 1H, CHO); 4.77–5.09 (m, 4H, =CH_2); 5.49–5.72 (m, 2H, =CH); 7.39 (m, 6H, SiPh); 7.70 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 36.6, 36.8, 54.0, 76.0, 116.4, 116.8, 127.1, 127.2, 127.6, 128.7, 129.0, 129.2, 129.3, 133.3, 133.5, 134.1, 134.6, 135.5. Observed for minor isomer: 18.6, 26.4, 37.2, 37.8, 52.8, 75.4, 115.7, 117.7.

4.2.18. (4*R*)-4-(*t*-Butyldiphenylsilyl)oxynona-1,8-diene-5-amine (15). Obtained as a mixture of two diastereoisomers in a (4*R*,5*S*)–(4*R*,5*R*)=2:1 ratio as determined by ^{1}H NMR. ESI-MS *m*/*z* 394.2 $[M+H]^+$, 787.6 $[M_2+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.16–1.61 (m, 2H, CH_2); 1.86–2.51 (m, 4H, CH_2); 2.60–2.76 (m, 1H, CHN); 3.61–3.74 (m, 1H, CHO); 4.82–4.99 (m, 4H, =CH_2); 5.44–5.82 (m, 2H, =CH); 7.40 (m, 6H, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 18.9, 26.7, 31.3, 33.3, 36.1, 54.2, 76.5, 114.1, 116.2, 127.0, 127.1, 129.1, 129.3, 129.9, 130.9, 132.8, 133.2, 133.6, 134.7, 134.9, 135.4. Observed for minor isomer: 18.6, 26.1, 35.1, 37.7, 52.6, 75.7, 113.9, 116.5.

4.2.19. (5*R*)-5-(*t*-Butyldiphenylsilyl)oxynona-1,8-diene-4-amine (16). Obtained as a mixture of two diastereoisomers in a (4*S*,5*R*)–(4*R*,5*R*)=2.4:1 ratio as determined by ^{1}H NMR. ESI-MS *m*/*z* 394.3 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.26–2.27 (m, 6H, CH_2); 2.79 (m, 1H, CHN); 3.66 (m, 1H, CHO); 4.77–4.96 (m, 2H, =CH_2); 5.02–5.18 (m, 2H, =CH_2); 5.47–5.70 (m, 2H, =CH); 7.41 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.8, 29.5, 30.6, 37.1, 54.3, 76.2, 114.1, 116.6, 127.2, 127.3, 128.8, 129.3, 129.4, 133.5, 133.8, 134.6, 135.6 135.8, 137.6, 137.9. Observed for minor isomer: 26.4, 29.4, 31.3, 38.7, 53.1, 75.6, 117.9.

4.2.20. (6*R*)-6-(*t*-Butyldiphenylsilyl)oxydeca-1,9-diene-5-amine (17). Obtained as a mixture of two diastereoisomers in a (5*S*,6*R*)–(5*R*,6*R*)=2:1 ratio as determined by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.10–2.27 (m, 8H, CH_2); 2.61–2.79 (m, 1H, CHN); 3.42–3.66 (m, 1H, CHO); 4.77–4.99 (m, 4H, =CH_2); 5.42–5.83 (m, 2H, =CH); 7.40 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 18.9, 26.6, 29.1, 30.1, 31.4, 33.0, 54.2, 76.4, 113.8, 114.1, 126.9, 127.0, 129.1, 133.1, 133.5, 133.8, 134.4, 135.3 137.3, 137.7, 137.9. Observed for minor isomer: 29.5, 30.4, 31.7, 52.6, 75.6, 113.5.

4.2.21. Benzyl [(2*R*)-1-allyl-2-(*t*-butyldiphenylsilyl)oxy-pent-4-en-1-yl]carbamate (18a). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 69% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 514.3 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 2.04–2.35 (m, 4H, CH_2); 3.70 (m, 1H, CHN); 3.90 (m, 1H, CHO); 4.71–5.09 (m, 6H, =CH_2, $PhCH_2$); 5.49–5.78 (m, 2H, =CH); 7.38 (m, 11H, SiPh, $PhCH_2$); 7.63 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 27.0, 32.8, 38.8, 53.5, 66.2, 75.0, 117.1, 117.5. 127.5, 127.9, 128.3, 129.6, 129.7, 133.5, 134.6, 135.0, 135.8, 155.6. Observed for minor isomer: 37.5, 52.4, 66.5, 74.1, 118.1, 156.0.

4.2.22. *t*-Butyl [(2*R*)-(1-allyl-*t*-butyldiphenylsilyl)-oxy-pent-4-en-1-yl]carbamate (18b). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 89% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 480.2 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.37 (s, 9H, *t*-Bu); 1.95–2.45 (m, 4H, CH_2); 3.64 (m, 1H, CHN); 3.91 (m, 1H, CHO); 4.59 (br d, 1H, NH); 4.83–5.09 (m, 4H, =CH_2); 5.43–5.61 (m, 1H, =CH); 5.67–5.79 (m, 1H, =CH); 7.40 (m, 6H, SiPh);

7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 18.5, 26.4, 26.9, 32.1, 38.1, 52.0, 74.3, 77.9, 115.7, 116.0. 126.7, 126.8, 128.9, 129.0, 131.5, 131.8, 132.6, 132.9, 134.0, 134.4, 135.0, 135.2, 154.3. Observed for minor isomer: 36.8, 51.0, 73.6, 115.4, 116.5, 154.8.

4.2.23. Benzyl [(2*R*)-(1-but-3-en-1-yl)-2-(*t*-butyl-diphenylsilyl)oxypent-4-en-1-yl]carbamate (19a). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2:1 ratio as determined by ^{1}H NMR. Yield 79% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). ESI-MS *m*/*z* 528.3 $[M+H]^+$; 550.4 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.43–1.68 (m, 2H, CH_2); 1.92–2.22 (m, 4H, CH_2); 3.65 (m, 1H, CHN); 3.86 (m, 1H, CHO); 4.71–5.13 (m, 6H, $=CH_2$, CH_2Ph); 5.28–5.83 (m, 2H, =CH); 7.37 (m, 11H, SiPh, $PhCH_2$); 7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 26.9, 27.5, 30.0, 38.7, 53.6, 66.1, 75.4, 114.6, 117.4. 127.4, 127.6, 127.9, 128.2, 129.6, 129.7, 129.8, 133.5, 135.7, 136.6, 137.7, 137.9, 155.7. Observed for minor isomer: 32.4, 52.4, 66.4, 74.7, 114.4, 118.0, 156.1.

4.2.24. *t*-Butyl [(2*R*)-(1-but-3-en-1-yl)-2-(*t*-butyl-diphenyl-silyl)oxypent-4-en-1-yl]carbamate (19b). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2:1 ratio as determined by ^{1}H NMR. Yield 81% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 494.3 $[M+H]^+$; 516.2 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.39 (s, 9H, *t*-Bu); 1.30–1.60 (m, 2H, CH_2); 1.84–2.19 (m, 4H, CH_2); 3.45–3.65 (m, 1H, CHN); 3.86 (m, 1H, CHO); 4.57 (d, 1H, J=10.2 Hz, NH); 4.66–5.07 (m, 4H, $=CH_2$); 5.39–5.60 (m, 1H, =CH); 5.64–5.92 (m, 1H, =CH); 7.41 (m, 6H, SiPh); 7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 26.9, 28.2, 30.1, 32.5, 38.8, 52.8, 76.4, 78.4, 114.7, 117.2, 127.4, 127.5, 129.5, 129.8, 132.7, 133.3, 133.5, 133.7, 134.0, 135.6, 137.8, 138.0, 155.1. Observed for minor isomer: 27.1, 52.5, 75.5, 78.6, 114.5, 117.8, 155.5.

4.2.25. Benzyl [(2*R*)-(1-allyl-*t*-butyldiphenylsilyl)-oxyhex-5-en-1-yl]carbamate (20a). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 68% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 528.3 $[M+H]^+$; 550.3 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.37–2.04 (m, 4H, CH_2); 2.18–2.45 (m, 2H, CH_2); 3.69–3.85 (m, 2H, CHN, CHO); 4.70–5.17 (m, 6H, $=CH_2$, CH_2Ph); 5.31–5.84 (m, 2H, =CH); 7.37 (m,11H, SiPh, CH_2Ph); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 26.8, 29.3, 32.9, 37.1, 53.6, 66.0, 75.1, 114.5, 117.0, 127.3, 127.5, 127.7, 128.0, 128.1, 128.9, 129.4, 129.5, 133.2, 133.4, 134.4, 134.6, 134.8, 135.6, 137.1, 137.2, 155.4. Observed for minor isomer: 18.8, 26.4, 33.1, 52.5, 66.3, 73.5, 118.0, 156.0.

4.2.26. *t*-Butyl [(2*R*)-(1-allyl-*t*-butyldiphenylsilyl)-oxyhex-5-en-1-yl]carbamate (20b). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 56% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 494.4 $[M+H]^+$; 516.4 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, *t*-Bu); 1.41 (s, 9H, *t*-Bu); 1.30–1.59 (m, 2H, CH_2); 1.77–1.92 (m, 2H, CH_2); 2.33 (m, 2H, CH_2); 3.69 (m, 1H, CHN); 3.86 (m, 1H, CHO); 4.61–5.12 (m, 4H, $=CH_2$); 5.46–5.82 (m, 2H, =CH); 7.42 (m, 6H, SiPh); 7.68 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 27.1, 28.3, 29.5, 33.1, 37.6, 53.2, 75.5, 78.6, 114.5, 116.8, 127.5, 127.6, 129.6, 129.7, 133.5, 133.9, 135.0, 135.3, 135.8, 137.7, 155.2. Observed for minor isomer: 27.3, 33.4, 52.0, 73.8, 78.8.

4.2.27. Benzyl [1-but-3-enyl-(2*R*)-(*t*-butyldiphenylsilyl)-oxyhex-5-en-1-yl]carbamate (21). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 68% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 564.3 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.25–2.05 (m, 5H, CH_2); 2.31 (m, 1H, CH_2); 3.76 (m, 1H, CHN); 3.90 (m, 1H, CHO); 4.70 (m, 2H, $=CH_2$); 4.83–5.18 (m, 4H, $=CH_2$, $PhCH_2$); 5.45–5.82 (m, 2H, =CH); 7.37 (m, 11H, SiPh, $PhCH_2$); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.5, 27.1, 29.6, 30.2, 33.1, 33.4, 53.9, 66.3, 75.9, 114.6, 115.1, 127.5, 127.7, 127.9, 128.0, 128.4, 129.7, 129.8, 129.9, 133.5, 133.8, 135.9, 137.5, 138.0, 155.8. Observed for minor isomer: 18.8, 26.4, 32.4, 52.5, 66.6, 74.1, 156.3.

4.2.28. Benzyl (6*R*)-6-[(*t*-butyldiphenylsilyl)-oxycyclohex-3-en-1-yl]carbamate (22a). Obtained as a mixture of two diastereoisomers in a (1*S*,6*R*)–(1*R*,6*R*)=2.5:1 ratio as determined by HPLC. Yield 87% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 486.7 $[M+H]^+$. ee 96%, Chiralcel OD, HEX/IPA=99.5:0.5, 1.0 mL/min, major diastereoisomer RT 16.4 min (1*S*,6*R*-enantiomer), RT 25.6 min (1*R*,6*S*-enantiomer). Minor diastereoisomer RT 33.5 min (1*S*,6*S*-enantiomer), RT 35.3 min (1*S*,6*S*-enantiomer) no baseline separation. ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 2.04–2.24 (m, 4H, CH_2); 3.84 (m, 1H, CHN); 4.08 (m, 1H, CHO); 4.79–5.02 (m, 2H, $PhCH_2$); 5.48 (m, 1H, =CH); 5.61 (m, 1H, =CH); 7.35 (m, 11H, SiPh, $PhCH_2$); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 26.8, 28.3, 32.3, 50.3, 66.2, 69.0, 123.4, 124.5, 127.4, 127.6, 127.8, 128.2, 129.1, 129.5, 129.6, 133.3, 134.0, 134.6, 135.6, 136.5, 155.7. Observed for minor isomer: 19.0, 26.4, 30.1, 51.2, 69.5, 124.2. HRMS calculated for $[M+H]^+$ 486.24649, found: 486.24590.

4.2.29. *t*-Butyl (6*R*)-6-[(*t*-butyldiphenylsilyl)-oxycyclohex-3-en-1-yl]carbamate (22b). Obtained as a mixture of two diastereoisomers in a (1*S*,6*R*)–(1*R*,6*R*)=2.5:1 ratio as determined by HPLC. Yield 77% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m*/*z* 474.4 $[M+H]^+$. ee 98%, Chiralcel OD, HEX/IPA=99.75:0.25, 1.0 mL/min, major diastereoisomer RT 10.4 min (1*S*,6*R*-enantiomer), RT 12.3 min (1*R*,6*S*-enantiomer). Minor diastereoisomer RT 8.3 min (1*S*,6*S*-enantiomer), RT 13.9 min (1*R*,6*R*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.43 (s, 9H, *t*-Bu); 1.94–2.24 (m, 4H, CH_2); 3.76 (m, 1H, CHN); 4.10 (m, 1H, CHO); 4.77 (br s, 1H, NH); 5.46 (m, 1H, =CH); 5.63 (m, 1H, =CH); 7.39 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 26.9, 28.3, 32.5 (C2 and C5), 49.7, 69.2, 78.9, 123.4, 124.8, 127.4, 127.6, 129.6, 129.7, 133.5, 133.6, 134.3, 135.6, 155.3. Observed for minor isomer:

27.3, 50.8, 69.5, 124.2. HRMS calculated for $[M+H]^+$ 452.26155, found: 452.26230.

4.2.30. Benzyl (2*R*)-[(*t*-butyldiphenylsilyl)oxycyclohept-4-en-1-yl]carbamate (23a). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.8:1 ratio as determined by HPLC. Yield 96% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=92:8). ESI-MS *m/z* 500.3 $[M+H]^+$; 522.6 $[M+Na]^+$. Chiral HPLC, ee 98%, Chiralcel OD, HEX/IPA=99.5:0.5, 1.0 mL/min, major diastereoisomer RT 16.8 min (1*R*,2*S*-enantiomer); RT 26.1 min (1*S*,2*R*-enantiomer). Minor diastereoisomer RT 15.4 min (1*R*,2*R*-enantiomer), RT 27.4 min (1*S*,2*S*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.51–1.88 (m, 2H, CH_2); 1.95–2.38 (m, 4H, CH_2); 3.71 (m, 1H, CHN); 4.02 (m, 1H, CHO); 4.52 (d, 1H, J=8.0 Hz, NH); 5.02 (s, 2H, $PhCH_2$); 5.39 (m, 1H, =CH); 5.68–5.91 (m, 1H, =CH); 7.36 (m, 11H, SiPh, $PhCH_2$); 7.66 (m, 4H, SiPh). Observed for minor isomer: 3.52 (m, CHN); 3.89 (m, CHO). ^{13}C NMR ($CDCl_3$): δ 19.1, 24.5, 26.9, 27.7, 31.9, 58.0, 66.2, 71.1, 126.0, 127.4, 127.6, 127.7, 128.0, 128.3, 129.6, 132.3, 133.1, 133.5, 133.6, 134.1, 135.6, 135.8, 136.6, 155.3. Observed for minor isomer: 23.5, 30.2, 59.0, 66.4, 73.7, 155.5. HRMS calculated for $[M+H]^+$ 500.26155, found: 500.26172.

4.2.31. *t*-Butyl (2*R*)-2-[(*t*-butyldiphenylsilyl)-oxycyclohept-4-en-1-yl]carbamate (23b). Obtained as a mixture of two diastereoisomers in a (1*S*,2*R*)–(1*R*,2*R*)=2.5:1 ratio as determined by HPLC. Yield 66% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m/z* 466.2 $[M+H]^+$; 488.2 $[M+Na]^+$. Chiral HPLC, Chiralcel OD, HEX/IPA=99.75:0.25, 1.0 mL/min, major diastereoisomer, RT 7.9 min (1*S*,2*R*- and 1*R*,2*S*-enantiomers), minor diastereoisomer RT 9.3 min (1*S*,2*S*- and 1*R*,2*R*-enantiomers). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, *t*-Bu); 1.40 (s, 9H, *t*-Bu); 1.72–2.27 (m, 6H, CH_2); 3.45–3.76 (m, 1H, CHN); 3.83–4.05 (m, 1H, CHO); 4.84 (br s, 1H, NH); 5.36 (m, 1H, =CH); 5.71–90 (m, 1H, =CH); 7.40 (m, 6H, SiPh); 7.68 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 26.9, 27.0, 27.8, 28.3, 32.0, 58.9, 71.5, 78.7, 125.9, 126.2, 127.5, 127.6, 129.6, 132.4, 133.3, 133.7, 133.9, 134.3, 135.7, 135.9, 154.9. Observed for minor isomer: 19.2, 30.5, 34.0, 57.6, 73.8, HRMS calculated for $[M+H]^+$ 466.27720, found: 466.27753.

4.2.32. Benzyl (7*R*)-[(*t*-butyldiphenylsilyl)oxycyclohept-3-en-1-yl]carbamate (24a). Obtained as a mixture of two diastereoisomers in a (1*S*,7*R*)–(1*R*,7*R*)=2.8:1 ratio as determined by HPLC. Yield 94% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). ESI-MS *m/z* 500.2 $[M+H]^+$; 522.4 $[M+Na]^+$. ee 98%, Chiralcel OD, HEX/IPA=99.5:0.5, 1.0 mL/min, RT 10.3 min (1*R*,7*R*-enantiomer), RT 11.4 min (1*R*,7*S*-enantiomer), RT 16.1 (1*S*,7*R*- and 1*S*,7*S*-enantiomers). ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, *t*-Bu); 1.38–1.58 (m, 2H, CH_2); 1.65–2.17 (m, 2H, CH_2); 2.26–2.45 (m, 1H, CH_2); 2.50–2.88 (m, 1H, CH_2); 3.77 (m, 1H, CHN); 4.01 (m, 1H, CHO); 4.79 (d, 1H, J=8.8 Hz, NH); 5.00 (s, 2H, $PhCH_2$); 5.68 (m, 1H, =CH); 5.81 (m, 1H, =CH); 7.35 (m, 11H, SiPh, $PhCH_2$); 7.69 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 21.8, 27.0, 28.8, 32.3, 53.1, 66.1, 75.3, 127.5, 127.7, 128.3, 129.3, 129.7, 133.3, 133.6, 133.7, 134.7, 135.7, 135.8, 136.6, 155.3. Observed for minor isomer: 19.0, 21.6, 26.5, 29.6, 32.1, 52.5, 66.4 HRMS calculated for $[M+H]^+$ 500.26155, found: 500.26215.

4.2.33. *t*-Butyl (7*R*)-[(*t*-butyldiphenylsilyl)oxycyclohept-3-en-1-yl]carbamate (24b). Obtained as a mixture of two diastereoisomers in a (1*S*,7*R*)–(1*R*,7*R*)=2.5:1 ratio as determined by ^{1}H NMR. Yield 86% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). ESI-MS *m/z* 466.2 $[M+H]^+$; 488.2 $[M+Na]^+$. Chiral HPLC, ee 98%, Chiralcel OD, HEX/IPA=99.75:0.25, 0.6 mL/min, Major diastereoisomer RT 10.8 min (1*S*,7*R*-enantiomer); RT 14.4 min (1*R*,7*S*-enantiomer). Minor diastereoisomer RT 8.1 min (1*S*,7*S*-enantiomer), RT 8.6 min (1*R*,7*R*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H, *t*-Bu); 1.39 (s, 9H, *t*-Bu); 1.46–1.65 (m, 2H, CH_2); 1.70–2.17 (m, 2H, CH_2); 2.22–2.40 (m, 1H, CH_2); 2.65–2.84 (m, 1H, CH_2); 3.66–3.85 (m, 1H, CHN); 3.93–4.08 (m, 1H, CHO); 4.85 (d, 1H, J=9.5 Hz, NH); 5.60–5.95 (m, 2H, =CH); 7.41 (m, 6H, SiPh); 7.69 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 21.7, 27.1, 28.3, 29.0, 32.3, 52.6, 75.5, 78.6, 127.5, 127.7, 128.0, 129.7, 130.6, 130.7, 133.1, 133.7, 135.8, 154.9. HRMS calculated for $[M+H]^+$ 466.27720, found: 466.27728.

4.2.34. Benzyl (8*R*)-[(*t*-butyldiphenylsilyl)oxycycloocta-4-en-1-yl]carbamate (25). Obtained as a mixture of two diastereoisomers in a (1*S*,8*R*)–(1*R*,8*R*)=2.2:1 ratio as determined by HPLC. Yield 66% at 55% conversion. (Colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). ESI-MS *m/z* 514.2 $[M+H]^+$; 536.6 $[M+Na]^+$. Chiral HPLC, Chiralcel OD, HEX/IPA=99.5:0.5, 1.0 mL/min, major diastereoisomer RT 24.2 min (1*S*,8*R*-enantiomer and 1*R*,8*S*-enantiomer). Minor diastereoisomer RT 10.6 min (1*S*,8*S*-enantiomer and 1*R*,8*R*-enantiomer). ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, *t*-Bu); 1.41–1.63 (m, 2H, CH_2); 1.77–2.04 (m, 4H, CH_2); 2.28–2.65 (m, 1H, CH_2); 2.75–2.86 (m, 1H, CH_2); 3.77–3.89 (m, 1H, CHN); 4.06 (m, 1H, CHO); 4.32 (d, 1H, J=8.8 Hz, NH); 4.93 (s, 2H, $PhCH_2$); 5.51–5.78 (m, 2H, =CH); 7.33 (m, 11H, SiPh, $PhCH_2$); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.4, 21.8, 22.8, 27.1, 31.0, 34.3, 53.4, 66.1, 77.5, 127.5, 127.7, 127.8, 128.3, 128.5, 129.7, 129.9, 131.2, 134.0, 134.7, 135.8, 135.9, 136.7, 155.2. HRMS calculated for $[M+H]^+$ 514.27720, found: 514.27783.

4.3. Preparation of *N*-heterocycles

4.3.1. (2*R*,3*E*)-1-Allylamino-2-[(*t*-butyldiphenylsilyl)-oxy]-pent-3-ene-2-ol (26). $[\alpha]_D^{20}=-14.2$ (c=1.0, CH_2Cl_2). ESI-MS *m/z*=380.2 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.50 (d, 3H, J=5.9 Hz, CH_3); 2.51–2.73 (m, 2H, CH_2); 3.12 (d, 2H, J=5.8 Hz, CH_2); 4.23 (m, 1H, CHO); 5.07 (m, 2H, $=CH_2$); 5.19–5.45 (m, 2H, =CH); 5.72–5.91 (m, 1H, =CH); 7.35 (m, 6H, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$); δ 17.3, 19.1, 26.9, 51.8, 55.3, 73.7, 115.6, 127.1, 127.3, 127.5, 129.3, 129.4, 132.0, 134.0, 135.6, 135.8, 136.5.

4.3.2. Benzyl 1-allyl[(2*R*,3*E*)-2-(*t*-butyldiphenylsilyl)-oxy-pent-3-en-1-yl]carbamate (27a). Yield 88% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). $[\alpha]_D^{25}=-14.8$ (c=1.0, CH_2Cl_2). ESI-MS

m/z=414.3 $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.03 (s, 9H, *t*-Bu); 1.43 (d, 3H, J=5.9 Hz, CH_3); 3.14–3.40 (m, 2H, CH_2); 3.78 (m, 2H, CH_2); 4.19–4.39 (m, 1H, CHO); 4.91–5.13 (m, 5H, $PhCH_2$, $CH{=}CH_2$); 5.26 (m, 1H, =CH); 5.59–5.76 (m, 1H, =CH); 7.28 (m, 11H, SiPh, $PhCH_2$); 7.60 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.4, 19.1, 26.9, 50.7, 52.6, 66.9, 73.0, 116.3, 127.2, 127.4, 127.7, 128.0, 128.3, 129.4, 131.3, 133.4, 133.6, 133.9, 135.8, 136.0, 156.0.

4.3.3. *t*-Butyl 1-allyl[(2*R*,3*E*)-2-(*t*-butyldiphenylsilyl)-oxy-pent-3-en-1-yl]carbamate (27b). Yield 86% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). $[\alpha]_D^{25}=-17.0$ (c=1.0, CH_2Cl_2). ESI-MS m/z=480.2 $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.38 (d, 3H, J=5.9 Hz, CH_3); 1.41 (s, 9H, *t*-Bu); 3.07–3.40 (m, 2H, CH_2); 3.63–3.84 (m, 2H, CH_2); 4.25 (m, 1H, CHO); 5.00 (m, 2H, $=CH_2$); 5.12–5.37 (m, 2H, =CH); 5.58–5.75 (m, 1H, =CH); 7.35 (m, 6H, SiPh); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.4, 19.0, 26.9, 28.1, 50.4, 52.4, 73.3, 79.1, 115.6, 127.1, 127.3, 129.3, 131.6, 133.8, 135.6, 135.8, 155.0.

4.3.4. (2*R*,3*E*)-1-[Allyl(benzyl)amino-2-(*t*-butyl-diphenylsilyl)oxypent-3-en-2-ol (27c). Yield 77% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=100:0→90:10). $[\alpha]_D^{25}=+15.2$ (c=1.0, CH_2Cl_2). ESI-MS m/z=470.2 $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.03 (s, 9H, *t*-Bu); 1.52 (d, 3H, J=6.6 Hz, CH_3); 2.50 (m, 2H, CH_2); 2.92 (d, 2H, J=6.6 Hz, $C{=}CCH_2$); 3.43 (s, 2H, $PhCH_2$); 4.14 (m, 1H, CHO); 5.04 (m, 2H, $=CH_2$); 5.20–5.47 (m, 2H, $=CH_2$); 5.62–5.79 (m, 1H, =CH); 7.21 (s, 5H, $PhCH_2$); 7.37 (m, 6H, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 17.6, 19.2, 27.1, 57.3, 58.8, 60.4, 73.1, 116.9, 126.2, 126.6, 127.2, 127.4, 127.9, 128.1, 128.3, 128.7, 128.9, 129.3, 129.4, 133.3, 134.3, 134.4, 135.9, 136.0, 139.7.

4.3.5. Benzyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-3,6-dihydropyridine-1(2*H*)-carboxylate (28a). Yield 82% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{25}=-18.8$ (c=1.0, CH_2Cl_2). ESI-MS m/z=472.5 $[M+H]^+$, 943.5 $[M_2+H]^+$. Chiralcel OD, HEX/IPA=99.8:0.2, 1.0 mL/min, RT 16.7 min (*R*-enantiomer) and 18.3 min (*S*-enantiomer) no baseline separation. ^1H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 3.29 (m, 1H, CH_2); 3.67 (m, 1H, CH_2); 3.96 (m, 2H, CH_2); 4.23 (m, 1H. CHO); 5.06 (m, 2H, $PhCH_2$); 5.71 (m, 2H, CH=CH); 7.32 (m, 11H, Ph, SiPh); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.9, 43.2, 47.4, 64.9, 67.0, 124.9, 125.9, 127.6, 127.9, 128.4, 129.2, 129.8, 132.3, 133.7, 135.7, 136.6, 155.1. HRMS calculated for $[M+Na]^+$ 494.21219, found: 494.21271.

4.3.6. *t*-Butyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-3,6-dihydropyridine-1(2*H*)-carboxylate (28b). Yield 80% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). $[\alpha]_D^{25}=-25.4$ (c=1.0, CH_2Cl_2). ESI-MS m/z=438.0 $[M+H]^+$. Chiralcel OD, HEX/IPA=99.8:0.2, 1.0 mL/min, RT 10.0 min (*R*-enantiomer) and 10.6 min (*S*-enantiomer) no baseline separation. ^1H NMR ($CDCl_3$): δ 1.07 (s, 9H, *t*-Bu); 1.41 (s, 9H, *t*-Bu); 3.21 (dd, 1H, J=7.2, 12.9 Hz, CH_2); 3.68–3.93 (m, 3H, CH_2); 4.27 (m, 1H, CHO); 5.65 (m, 2H, CH=CH); 7.38 (m, 6H, SiPh); 7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.9, 28.3, 42.9, 48.7, 65.2, 79.3, 125.8, 127.4, 127.5, 127.7, 129.4, 129.5, 129.6, 133.9, 134.1, 135.6, 154.4. HRMS calculated for $[M+Na]^+$ 460.22812, found: 460.22784.

4.3.7. (3*R*)-1-Benzyl-3-[(*t*-butyldiphenylsilyl)oxy]-1,2,3,6-tetrahydropyridin-3-ol (28c). Yield 94% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). $[\alpha]_D^{25}=-18.2$ (c=1.0, CH_2Cl_2). ESI-MS m/z=428.0 $[M+H]^+$. ee >99%, Chiralcel OD, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 9.8 min (*R*-enantiomer), RT 12.2 min (*S*-enantiomer). ^1H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 2.36 (dd, 1H, J=6.6, 11.0 Hz, CH_2); 2.68 (dd, 1H, J=5.1, 11.0 Hz, CH_2); 2.90 (m, 2H, CH_2); 3.53 (m, 2H, CH_2); 4.36 (m, 1H, CHO); 5.69 (m, 2H, CH=CH); 7.23–7.41 (m, 11H, Ph, SiPh); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.9, 52.4, 57.2, 62.1, 66.9, 127.0, 127.5, 128.2, 128.9, 129.3, 129.6, 134.1, 135.7, 135.8, 138.0. HRMS calculated for $[M+H]^+$ 428.24042, found: 428.24097.

4.3.8. Benzyl (3*R*)-3-hydroxy-3,6-dihydropyridine-1(2*H*)-carboxylate. Compound **28a** (132 mg, 0.280 mmol) was dissolved in THF (5.0 mL) and an excess of tetrabutylammonium fluoride (3 equiv) was added. After 2 h TLC showed complete conversion of **28a**. The solvent was evaporated in vacuo and the residue purified by silicagel column chromatography, eluent PE/EtOAc=3:1→1:3, to give the title compound (56 mg) in 99% yield as a colorless oil. $[\alpha]_D^{21}=-65.4$ (c=1.0, $CHCl_3$, lit.[17], $[\alpha]_D^{30}=-67.0$ (c=0.96, $CHCl_3$)). ee 98%, Chiralcel ODH, HEX/IPA=85:15, 1.0 mL/min, RT 8.3 min (*R*-enantiomer), 10.5 min (*S*-enantiomer). ^1H NMR ($CDCl_3$): δ 2.19 (broad s, 1H, OH); 3.63 (m, 2H, CH_2); 3.92 (m, 2H, CH_2); 4,21 (m, 1H, CHO); 5.15 (s, 2H, $PhCH_2$); 5.90 (m, 2H, CH=CH); 7.35 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 43.1, 47.4, 63.1, 67.2, 125.9, 126.8, 127.8, 127.9, 128.4, 136.3, 155.6.

4.3.9. (2*R*)-1-Allylamino-2-[(*t*-butyldiphenylsilyl)-oxy]-pent-4-en-2-ol (29). $[\alpha]_D^{20}=-9.4$ (c=1.0, CH_2Cl_2). ESI-MS m/z=380.1 $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 2.26 (m, 2H, CH_2); 2.61 (d, 2H, J=5.1 Hz, CH_2); 3.08 (d, 2H, J=5.8 Hz, CH_2); 3.89 (m, 1H, CHO); 4.96 (m, 4H, $=CH_2$); 5.57–5.85 (m, 2H, =CH); 7.40 (m, 6H, SiPh); 7.66 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 26.9, 39.9, 52.1, 53.9, 72.4, 115.3, 117.0, 125.2, 127.5, 128.1, 128.9, 129.6, 134.0, 134.4, 135.8, 136.8.

4.3.10. (2*R*)-1-Allylamino-2-[(*t*-butyldiphenylsilyl)-oxy]-hex-5-en-2-ol (30). $[\alpha]_D^{20}=-3.0$ (c=1.0, CH_2Cl_2). ESI-MS m/z=394.0 $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.43–1.64 (m, 2H, CH_2); 1.77–2.03 (m, 2H, CH_2); 2.60 (d, 2H, J=5.1 Hz, CH_2); 3.07 (d, 2H, J=5.8 Hz, CH_2); 3.84–3.93 (m, 1H, CHO); 4.80–4.91 (m, 2H, $=CH_2$); 4.99–5.11 (m, 2H, $=CH_2$); 5.50–5.88 (m, 2H, 2×=CH); 7.38 (m, 6H, SiPh); 7.69 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 27.0, 29.4, 34.4, 52.2, 54.2, 72.4, 114.3, 115.4, 127.5, 129.5, 129.6, 134.1, 135.7, 135.8, 136.8, 138.2.

4.3.11. Benzyl 1-allyl[(2*R*)-2-(*t*-butyldiphenylsilyl)-oxy-pent-4-en-1-yl]carbamate (31a). Yield 72% (colorless oil,

purified by silicagel column chromatography, eluent PE/EtOAc=97:3→95:5). $[\alpha]_D^{20}=-20.2$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=514.4$ $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 2.10 (m, 2H, CH_2); 3.16 (m, 1H, CH_2); 3.29–3.61 (m, 1H, CH_2); 3.75 (m, 2H, CH_2); 4.02 (m, 1H, CHO); 4.77–5.07 (m, 6H, $=CH_2$, $PhCH_2$); 5.67 (m, 2H, 2×=CH); 7.35 (m, 11H, SiPh, $PhCH_2$); 7.63 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.9, 39.2, 50.6, 51.5, 66.9, 71.1, 116.3, 117.2, 127.5, 127.7, 127.9, 128.2, 129.6, 130.0, 130.3, 133.3, 133.4, 133.7, 135.7, 135.8, 136.5, 155.9.

4.3.12. *t*-Butyl 1-allyl[(2*R*)-2-(*t*-butyldiphenylsilyl)-oxy-pent-4-en-1-yl]carbamate (31b). Yield 86% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-19.6$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=480.3$ $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.40 (s, 9H, *t*-Bu); 2.06 (dd, 2H, $J=6.6$, 13.9 Hz, CH_2); 3.00–3.88 (m, 4H, 2×CH_2); 4.00 (m, 1H, CHO); 4.83–5.05 (m, 4H, $=CH_2$); 5.65 (m, 2H, =CH); 7.40 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 28.1, 39.3, 50.6, 51.3, 71.4, 79.0, 115.6, 117.0, 127.4, 129.5, 133.7, 133.9, 135.1, 135.6, 155.1.

4.3.13. (2*R*)-1-Allyl-1-benzyl-2-[(*t*-butyldiphenylsilyl)-oxy]-1-aminopent-4-ene-2-ol (31c). Yield 67% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=100:0→90:10). $[\alpha]_D^{20}=+30.8$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=470.3$ $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 2.18 (m, 1H, CH_2); 2.35 (m, 2H, CH_2); 2.54 (m, 1H, CH_2); 2.83 (m, 2H, CH_2); 3.33 (dd, 2H, $J=2.2$, 13.9 Hz, $PhCH_2$); 3.85 (m, 1H, CHO); 4.80–5.05 (m, 4H, $=CH_2$); 5.61–5.85 (m, 2H, =CH); 7.20–7.43 (m, 11H, $PhCH_2$, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.3, 27.1, 33.2, 39.4, 57.4, 58.9, 71.5, 116.9, 117.2, 126.7, 127.5, 128.0, 128.3, 128.7, 128.9, 129.6, 134.2, 134.4, 135.1, 135.7, 136.0, 136.5, 139.6.

4.3.14. Benzyl 1-allyl[(2*R*)-2-(*t*-butyldiphenylsilyl)-oxy-hex-5-en-1-yl]carbamate (32a). Yield 62% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-12.2$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=528.2$ $[M+H]^+$. ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 1.25–1.56 (m, 2H, CH_2); 1.84–2.05 (m, 2H, CH_2); 3.13 (m, 1H, CH_2); 3.31–3.83 (m, 3H, CH_2); 3.94 (m, 1H, CHO); 4.71–5.18 (m, 6H, $=CH_2$, $PhCH_2$); 5.40–5.71 (m, 2H, =CH); 7.36 (m, 11H, SiPh, $PhCH_2$); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 28.6, 33.6, 50.3, 51.3, 66.8, 70.8, 114.2, 116.1, 127.3, 127.6, 128.1, 129.4, 133.1, 133.7, 135.6, 136.3, 137.8, 155.8.

4.3.15. *t*-Butyl 1-allyl[(2*R*)-2-(*t*-butyldiphenylsilyl)-oxy-hex-5-en-1-yl]carbamate (32b). Yield 47% (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=98:2→95:5). $[\alpha]_D^{20}=-18.6$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=494.6$ $[M+H]^+$, 516.3 $[M+Na]^+$. ^1H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.40 (s, 9H, *t*-Bu); 1.25–1.53 (m, 2H, CH_2); 2.00 (m, 2H, CH_2); 3.02 (m, 1H, CH_2); 3.55 (m, 2H, CH_2); 3.77 (m, 1H, CH_2); 3.92 (m, 1H, CHO); 4.80–5.03 (m, 4H, 2×$=CH_2$); 5.47–5.68 (m, 2H, 2×=CH); 7.40 (m, 6H, SiPh); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 26.9, 28.2, 28.7, 33.7, 50.2, 51.2, 71.2, 79.3, 114.1, 115.6, 127.5, 127.8, 129.5, 133.8, 134.0, 135.7, 136.7, 138.1, 138.3, 155.2.

4.3.16. Benzyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (33a). Yield 74% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-12.6$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=486.3$ $[M+H]^+$, 508.3 $[M+Na]^+$. ee 98%, Chiralcel OD, HEX/IPA=99.75:0.25, 1.2 mL/min, RT 24.1 min (*S*-enantiomer); RT 25.8 min (*R*-enantiomer). ^1H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 2.25 (dd, 2H, $J=5.1$, 5.9 Hz, CH_2); 3.32 (m, 1H, CH_2); 3.68–4.24 (m, 4H, CH_2, CHO); 5.06 (m, 2H, $PhCH_2$); 5.55 (m, 1H, =CH); 5.74 (m, 1H, =CH); 7.32 (m, 11H, SiPh, $PhCH_2$); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.0, 26.8, 34.8, 46.6, 54.5, 66.7, 69.8, 126.7, 127.2, 127.5, 127.7, 128.2, 129.2, 129.3, 129.6, 133.7, 135.6, 155.5. HRMS calculated for $[M+H]^+$ 486.24590, found: 486.24637.

4.3.17. *t*-Butyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (33b). Yield 76% (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=-23.4$ ($c=1.0$, CH_2Cl_2). ESI-MS $m/z=452.2$ $[M+H]^+$, 474.3 $[M+Na]^+$. ee 97%, Chiralcel OD, HEX/IPA=99.8:0.2, 1.0 mL/min, RT 9.3 min (*R*-enantiomer), 10.9 min (*S*-enantiomer). ^1H NMR ($CDCl_3$): δ 1.06 (s, 9H, *t*-Bu); 1.37 (s, 9H, *t*-Bu); 2.25 (m, 2H, CH_2); 3.19 (dd, 1H, $J=8.0$, 13.9 Hz, CH_2); 3.45–4.09 (m, 3H, CH_2); 4.24 (m, 1H, CHO); 5.53 (m, 1H, =CH); 5.68 (m, 1H, =CH); 7.39 (m, 6H, SiPh), 7.65 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.2, 27.2, 28.3, 34.5, 46.8, 54.3, 70.4, 79.5, 126.2, 126.9, 127.6, 129.6, 129.7, 133.8, 135.7, 154.8. HRMS calculated for $[M+H]^+$ 452.26155, found: 452.26239.

4.3.18. (3*R*)-1-Benzyl-3-[(*t*-butyldiphenylsilyl)oxy]-2,3,4,7-tetrahydroazepine (33c). For this reaction diene **31c** (184 mg, 0.392 mmol) was dissolved in CH_2Cl_2 (40 mL) and HCl (4 M in dioxane, 0.11 mL, 0.440 mmol) was added. Argon was bubbled through the solution for 5 min and the Grubbs catalyst (13 mg, 4 mol%) was added. The reaction was refluxed for 24 h, cooled, washed with an aqueous saturated $NaHCO_3$ solution, dried ($MgSO_4$) and concentrated to afford the crude product. Purification gave the title compound (20 mg) in 12% yield. (colorless oil, purified by silicagel column chromatography, eluent PE/EtOAc=95:5). $[\alpha]_D^{20}=+161$ ($c=0.4$, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.02 (s, 9H, *t*-Bu); 2.42 (m, 2H, CH_2); 2.84 (dd, 1H, $J=8.0$, 13.2 Hz, CH_2); 3.14 (m, 3H, CH_2); 3.54 (d, 1H, $J=13.2$ Hz, CH_2Ph); 3.62 (d, 1H, $J=13.2$ Hz, CH_2Ph); 3.94 (m, 1H, CHO); 5.61 (m, 2H, CH=CH); 7.25 (s, 5H, Ph); 7.39 (m, 6H, SiPh); 7.61 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): 19.2, 26.9, 36.5, 52.4, 56.6, 59.9, 68.2, 127.4, 127.6, 128.3, 128.7, 129.3, 129.7, 135.7, 137.2.

4.3.19. Benzyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-3,4,5,8-tetrahydroazocine-1(2*H*)-carboxylate (34a). Yield 61%, based on converted starting material, conversion 50% after 24 h. (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=9:1). $[\alpha]_D^{21}=+20.4$ ($c=1$, CH_2Cl_2). ESI-MS $m/z=500.2$ $[M+H]^+$, 522.4 $[M+Na]^+$. ee 97%, Chiralcel OD, HEX/IPA=99.75:0.25, 1.0 mL/min, RT 22.6 min (*S*-enantiomer), 25.1 min (*R*-enantiomer). ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H, *t*-Bu); 1.55–2.27 (m, 4H, CH_2); 3.30–4.13 (m, 5H, CH_2, CHO); 5.01 (s, 2H, $PhCH_2$); 5.11 (s, 2H, $PhCH_2$); 5.30 (m, 1H, =CH); 5.63

(m, 1H, =CH); 7.15–7.41 (m, 11H, SiPh, $PhCH_2$); 7.64 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 21.5, 26.9, 34.9, 47.4, 52.9, 67.0, 69.7, 125.0, 126.3, 127.5, 127.8, 128.0, 128.3, 129.6, 130.9, 133.9, 134.3, 134.9, 135.7, 136.8, 155.8. HRMS calculated for $[M+H]^+$ 500.26155, found: 500.26251.

4.3.20. *t*-Butyl (3*R*)-3-[(*t*-butyldiphenylsilyl)oxy]-3,4,5,8-tetrahydroazocine-1(2*H*)-carboxylate (34b). Yield 87%, based on converted starting material, conversion 52% after 24 h. (colorless oil, purified by silicagel column chromatography, eluent PE/DEE=95:5). $[\alpha]_D^{21}=+23.4$ ($c=1$, CH_2Cl_2). ESI-MS m/z=466.2 $[M+H]^+$, 488.2 $[M+Na]^+$, 954.0 $[M_2+Na]^+$. Chiral HPLC, Chiralcel OD, no separation. ^1H NMR ($CDCl_3$): δ 1.05 (s, 9H, *t*-Bu); 1.38 (s, 9H, *t*-Bu); 1.66–1.94 (m, 3H, CH_2); 2.21 (m, 1H, CH_2); 3.12–3.54 (m, 2H, CH_2); 3.70–3.92 (m, 2H, CH_2); 4.01–4.13 (m, 1H, CHO); 5.27 (m, 1H, =CH); 5.60 (m, 1H, =CH); 7.40 (m, 6H, SiPh,); 7.67 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$): δ 19.1, 21.3, 26.9, 28.9, 35.1, 47.5, 53.0, 69.7, 79.4, 125.9, 127.5, 128.4, 129.6, 129.9, 133.9, 134.2, 134.3, 135.7, 155.1. HRMS calculated for $[M+H]^+$ 466.27720, found: 466.27924.

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