Supporting Information:

General information

Reactions were generally performed under inert atmosphere (argon) in flame-dried flasks. Solvents and reagents were added by syringe. Solvents were dried using standard procedures and were purified with a MB SPS-800-dry solvent system. Commercially available reagents were used as received without further purification unless otherwise stated. Products were purified by flash chromatography on silica gel (230–400 mesh, MACHERY-NAGEL). Unless otherwise stated, yields refer to analytical pure samples. Hydrogenolyses were performed with hydrogen from Air Liquide (Alphagaz 2). TLC-analyses were performed on silica gel coated aluminum plates purchased from Merck. Products were detected by UV-activity and by using staining reagents (cer/molybdenum reagent, KMnO₄ and ninhydrine). NMR spectra were recorded on BRUKER (AV 400, AV 500, AV 700) and JEOL (ECP 500) instruments. Chemical shifts (δ) are listed in parts per million (ppm) and are reported relative to solvent residual signals: CDCl₃ (¹H: δ = 7.26 ppm, ¹³C: δ = 77.2 ppm), CD₃OD (¹H: δ = 3.31 ppm, ¹³C: δ = 49.0 ppm) or CD₂Cl₂ (¹H: δ = 5.32 ppm, ¹³C: δ = 54.0 ppm). Integrals are in accordance with assignments; coupling constants (J) are given in Hz. All ¹³C NMR spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), s br (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), m c (centered multiplet). For detailed peak assignments 2D spectra were recorded (COSY and HMQC). IR spectra were measured with a Jasco spectrometer (FT/IR-4100 with DLATGS Detector). HRMS analyses were performed with Agilent 6210 (ESI–TOF, 10 μL/min, 1.0 bar, 4 kV) and Varian/Agilent Ionspec QFT-7 (ESI–FTICR, 4 μL/min, 1.0 bar, 4kV) instruments. Elemental analyses were carried out with instruments from Elementar (Vario EL, Vario EL III). Melting points were determined with a Reichert apparatus (Thermovar) and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at the temperatures given.
(3S,4’S)-2-Benzyl-4-[2-(trimethylsilyl)ethoxy]-3-(2′-vinyl-1,3´-dioxolan-4’-yl)-3,6-
dihydro-2H-1,2-oxazine (2)

Acrolein dimethyl acetal (6.75 mL, 56.9 mmol) and ceric ammonium nitrate (31 mg, 57 μmol) were dissolved in dichloromethane (10 mL) and stirred for 15 min. Then 1,2-oxazine 1 (2.00 g, 5.69 mmol) was added and the solution was stirred for 3 days at rt. The reaction was quenched with water (10 mL) and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc 20:1) to yield 2a and 2b (1.98 g, 89%, d.r. 63:37) as colorless oils.

Major diastereomer 2a: [α]D₂² = -6.7 (c = 1.35, CHCl₃); ¹H NMR (500 MHz, CD₂Cl₂): δ = 0.07 [s, 9 H, Si(CH₃)₃], 1.00-1.11 [m, 2 H, CH₂Si(CH₃)₃], 3.26 (d, J = 7.6 Hz, 1 H, 3-H), 3.76 (ddd, J = 5.5, 9.6, 10.3 Hz, 1 H, CH₂CH₂Si(CH₃)₃), 3.01-3.84 (m, 1 H, CH₂CH₂Si(CH₃)₃), 3.85, 4.00, 4.53 (ABX system, J₀ₓ = 6.5 Hz, J₁ₓ = 7.6 Hz, J₂ₓ = 8.2 Hz, 3 H, 5´-H, 4´-H), 4.10-4.17 (m, 3 H, 6-H, NCH₂), 4.38 (dd, J = 1.9, 14.6 Hz, 1 H, 1-H, 6-H), 4.75 (dd, J = 1.9, 3.5 Hz, 1 H, 1-H, 5-H), 5.28 (dbr, J = 6.1 Hz, 1 H, 2´-H), 5.32 (dbr, J = 0.7, 1.4, 10.3 Hz, 1 H, 2´´-H), 5.46 (dbr, J = 1.4, 17.2 Hz, 1 H, 2´´-H), 5.82 (dbr, J = 6.1, 10.3, 17.2 Hz, 1 H, 1´´-H), 7.24-7.28 (m, 1 H, Ph), 7.31-7.34 (m, 2 H, Ph), 7.41-7.42 (m, 2 H, Ph) ppm; ¹³C NMR (125 MHz, CD₂Cl₂): δ = -1.18 [q, Si(CH₃)₃], 17.9 [t, CH₂Si(CH₃)₃], 58.5 (t, NCH₂), 64.20 (d, C-3), 64.26 (t, C-6), 65.1 [t, CH₂CH₂Si(CH₃)₃], 67.5 (t, C-5´), 76.7 (d, C-4´), 93.7 (d, C-5), 104.3 (d, C-2´), 120.0 (t, C-2´´), 127.6, 128.7, 129.2 (3 d, Ph), 136.0 (d, C-1´´), 138.9 (s, Ph), 150.5 (s, C-4) ppm; IR (ATR): ν = 3070 (=C-H), 2940-2870 (C-H), 1595 (C=C), 1420 (C-H), 1200 (C-O) cm⁻¹; HRMS (ESI-TOF): m/z calcd for C₂₁H₃₂NO₄Si [M + H]+: 390.2101; found: 390.2103; calcd for C₂₁H₃₁NNaO₄Si [M + Na]+: 412.1920; found: 412.1922.

Minor diastereomer 2b: [α]D₂² = +16.4 (c = 1.10, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ = 0.04 [s, 9 H, Si(CH₃)₃], 0.98-1.08 [m, 2 H, CH₂Si(CH₃)₃], 3.29 (dbr, J = 7.5 Hz, 1 H, 3-H), 3.66-3.74 [m, 1 H, CH₂CH₂Si(CH₃)₃], 3.77-3.87 [m, 1 H, CH₂CH₂Si(CH₃)₃], 3.86, 3.99 (AB of ABX system, J₀ₓ = 6.4, J₁ₓ = J₂ₓ = 8.1 Hz, 1 H, 5´-H), 4.14, 4.41, 4.71 (ABX system, J₀ₓ = 1.9 Hz, J₁ₓ = 3.2 Hz, J₂ₓ = 14.5 Hz, 3 H, 6-H, 5-H), 4.15 (s, 2 H, NCH₂), 4.56 (m₁, 1 H, 4´-H), 5.29 (d, J = 6.0 Hz, 1 H, 2´-H), 5.31 (d, J = 10.3 Hz, 1 H, 2´´-H), 5.45 (d, J = 17.2 Hz, 1 H, 2´´-H), 5.81 (ddd, J = 6.0, 10.3, 17.2 Hz, 1 H, 1´´-H), 7.23-7.25 (m, 1 H, Ph), 7.29-7.32 (m, 2 H, Ph), 7.41-7.42 (m, 2 H, Ph) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = -1.3 [q, Si(CH₃)₃], 17.5 [t, CH₂Si(CH₃)₃], 58.3
(t, NCH₂), 63.5 (d, C-3), 64.6 [t, C-6, CH₂CH₂Si(CH₃)₃], 67.0 (t, C-5′), 76.1 (d, C-4′), 93.2 (d, C-5), 103.9 (d, C-2′), 119.9 (t, C-2′′), 127.2, 128.3, 128.8 (3 d, Ph), 135.1 (d, C-1′′), 138.0 (s, Ph), 150.2 (s, C-4) ppm; IR (ATR): v = 3070 (–C-H), 2840 (C-H), 1595 (C=C), 1420 (C-H), 1245 (C-O) cm⁻¹; HRMS (ESI-TOF): m/z calcd for C₂₁H₃₂NO₄Si [M + H]⁺: 390.2101; found: 390.2099; calcd for C₂₁H₃₁NNaO₄Si [M + Na]⁺: 412.1921; found: 412.1921.

(3S,4′S)-2-Benzyl-3-[2´-(but-3´-enyl)-1´,3´-dioxolan-4´-yl]-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2H-1,2-oxazine (3)

Pent-4-enal (1.00 mL, 10.1 mmol) was added to a mixture of ytterbium(III) triflate hydrate (79 mg, 127 μmol) in dichloromethane (1.2 mL). After 30 min, a solution of diol 1 (402 mg, 1.14 mmol) in dichloromethane (1 mL) was added and the reaction mixture was stirred for 25 h at rt. The reaction was quenched with sat. aqueous sodium hydrogen carbonate solution (2 mL) and the aqueous phase was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc 20:1) to yield 3a (249 mg, 52%) and 3b (62 mg, 13%) as colorless oils (d.r. 80:20).

Major diastereoisomer 3a: [α]D²² = +16.5 (c = 1.10, CHCl₃); ¹H NMR (500 MHz, CD₂Cl₂): δ = 0.09 [s, 9 H, Si(CH₃)₃], 1.02-1.13 [m, 2 H, CH₂Si(CH₃)₃], 1.73-1.77 (m, 2 H, 1˝-H), 2.18-2.22 (m, 2 H, 2˝-H), 3.25 (d, J = 7.5 Hz, 1 H, 3-H), 3.74-3.79 [m, 1 H, CH₂CH₂Si(CH₃)₃], 3.80-3.87 [m, 1 H, CH₂CH₂Si(CH₃)₃], 3.86, 4.00 (AB part of ABX system, Jₓₓ = 7.5 Hz, Jₓₓ = 8.2 Hz, Jₓₓ = 13.2 Hz, 2 H, 5˝-H), 4.13, 4.40, 4.75 (ABX system, Jₓₓ = 2.0 Hz, Jₓₓ = 3.4 Hz, Jₓₓ = 14.6 Hz, 3 H, 6-H, 5-H), 4.16 (s, 2 H, NCH₂), 4.50 (mc, 1 H, 4˝-H), 4.99 (mc, 1 H, 4˝-H), 5.07 (ddd, J = 1.2, 3.3, 5.0 Hz, 1 H, 4˝-H), 5.89 (ddd, J = 6.6, 10.2, 17.0 Hz, 1 H, 3˝-H), 7.26-7.29 (m, 1 H, Ph), 7.33-7.35 (m, 2 H, Ph), 7.43-7.44 (m, 2 H, Ph) ppm; ¹³C NMR (125 MHz, CD₂Cl₂): δ = -1.14 [q, Si(CH₃)], 17.9 [t, CH₂Si(CH₃)₃], 28.8 (t, C-2˝), 34.1 (t, C-1˝), 58.6 (t, NCH₂), 64.3 (t, d, C-6, C-3), 65.1 [t, CH₂CH₂Si(CH₃)₃], 67.5 (t, C-5˝), 76.5 (d, C-4˝), 93.6 (d, C-5), 104.5 (d, C-2˝), 114.9 (t, C-4˝), 127.6, 128.7, 129.2 (3 d, Ph), 139.0 (d, C-3˝), 150.7 (s, C-4) ppm; IR (ATR): v = 3080–3030 (=C-H), 2955-2840 (C-H), 1670 (C=C), 1250 (C-O) cm⁻¹; HRMS (ESI-TOF): m/z calcd for C₂₃H₃₈NO₄Si [M + H]⁺: 418.2408, found: 418.2410, calcd for C₂₃H₃₈NNaO₄Si [M + Na]⁺: 440.2228, found: 440.2228; elemental
Minor diastereoisomer 3b: \([\alpha]_d^{22} = +32.3\) (c = 0.99, CHCl_3); \(^1\)H NMR (500 MHz, CD_2Cl_2): \(\delta = 0.09\) [s, 9 H, Si(CH_3)_3], 1.01-1.12 [m, 2 H, \(\text{CH}_2\text{Si}(\text{CH}_3)_3\)], 1.73-1.78 (m, 2 H, 1\(^{'-}\)-H), 2.22 (mc, 2 H, 2\(^{''-}\)-H), 3.24 (d, \(J = 7.0\) Hz, 1 H, 3-H), 3.74-3.79 [m, 1 H, \(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3\)], 3.82-3.87 [m, 1 H, \(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3\)], 3.92, 4.01, 4.50 (ABX system, \(J_{AX} = 6.2\) Hz, \(J_{BX} = 8.0\) Hz, \(J_{AB} = 8.8\) Hz, 3 H, 5\(^{-}\)-H, 4\(^{-}\)-H), 4.12, 4.39, 4.76 (ABX system, \(J_{AX} = 2.0\) Hz, \(J_{BX} = 3.5\) Hz, \(J_{AB} = 14.6\) Hz, 3 H, 6-H, 5-H), 4.13, 4.16 (AB system, \(J_{AB} = 14.3\) Hz, 2 H, NCH_2), 4.98 (mc, 1 H, 2\(^{-}\)-H), 4.99 (ddd, \(J = 1.3, 1.9, 10.2\) Hz, 1 H, 4\(^{-}\)-H), 5.08 (ddd, \(J = 1.9, 3.6, 17.0\) Hz, 1 H, 4\(^{-}\)-H), 5.90 (ddd, \(J = 6.6, 10.2, 17.0\) Hz, 1 H, 3\(^{-}\)-H), 7.25-7.28 (m, 1 H, Ph), 7.32-7.35 (m, 2 H, Ph), 7.42-7.43 (m, 2 H, Ph) ppm; \(^{13}\)C NMR (125 MHz, CD_2Cl_2): \(\delta = -1.1\) [q, Si(CH_3)_3], 18.0 [t, \(\text{CH}_2\text{Si}(\text{CH}_3)_3\)], 28.9 (t, C-2\(^{''}\)), 34.2 (t, C-1\(^{-}\)), 58.7 (t, NCH_2), 64.1 (d, C-3), 65.1 [t, C-6, \(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3\)], 68.6 (t, C-5\(^{-}\)), 75.6 (d, C-4\(^{-}\)), 93.7 (d, C-5), 104.3 (d, C-2\(^{-}\)), 114.9 (t, C-4\(^{-}\)), 127.6, 128.7, 129.2 (3 d, Ph), 138.9, 139.0 (d, s, C-3\(^{-}\), Ph), 150.8 (s, C-4) ppm; IR (ATR): \(\tilde{\nu} = 3065-3035\) (=C-H), 2955-2845 (C-H), 1670 (C=C), 1455 (C-H), 1250 (C-O) cm\(^{-1}\); HRMS (ESI-TOF): \(m/z\) calcd for \(\text{C}_{23}\text{H}_{35}\text{NNaO}_4\text{Si}\) \([\text{M} + \text{Na}]^+\): 440.2228, found: 440.2298; calcd for \(\text{C}_{23}\text{H}_{35}\text{KNO}_4\text{Si}\) \([\text{M} + \text{K}]^+\); 456.1972, found: 456.1994; elemental analysis calcd (%) for \(\text{C}_{23}\text{H}_{35}\text{NO}_4\text{Si}\) (417.6): C, 66.15; H, 8.45; N, 3.35; found: C, 66.14; H, 8.12; N, 3.40.

(1\(^{S}\),5\(^{R}\),6\(^{S}\),8\(^{S}\))-2-Benzyl-8-(hydroxymethyl)-6-vinyl-3,7-dioxo-2-azabicyclo[3.3.1]nonan-9-on (4)

1,2-Oxazine 2 (552 mg, 1.42 mmol) was dissolved in acetonitrile (10 mL) and cooled to 0 °C. Then trimethylsilyl triflate (1.23 mL, 1.00 g, 4.50 mmol) was slowly added and the mixture was stirred for one hour at this temperature, then for 18 h at rt. The reaction was quenched with 5% aqueous ammonia solution (10 mL) and the aqueous phase was extracted with diethyl ether (5 x 10 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc 10:1) to yield bicyclic ketone 4 (310 mg, 76%) as colorless oil and tricyclic compound 5 (9 mg, 2%) as yellow oil.

Data for 4 (the compound is fairly instable and was not fully characterized): \(^1\)H NMR (400 MHz, CD_3OD): \(\delta = 2.70\) (ddd, \(J = 1.9, 3.3, 6.9\) Hz, 1 H, 5-H), 3.45 (mc, 1 H, 1-H), 3.69-3.75 (m, 2 H, 8-H, 8-CH_2), 3.87 (dd, \(J = 8.6, 13.2\) Hz, 1 H, 8-CH_2), 3.94, 4.10 (AB system, \(J_{AB} = 14.0\) Hz, 2
H, NCH2), 4.33-4.30 (m, 1 H, 6-H), 4.34, 4.52 (AB part of ABX system, JAX = 3.3 Hz, JBX = 6.9 Hz, JAB = 11.9 Hz, 2 H, 4-H), 5.27 (dbr, J = 10.8 Hz, 1 H, 2'-H), 5.47 (dbr, J = 17.4 Hz, 1 H, 2'-H), 5.87 (ddd, J = 4.4, 10.8, 17.4 Hz, 1 H, 1'-H), 7.19-7.35 (m, 5 H, Ph) ppm.

Data of (2aR,4S,4aR,7aS,7bS)-7-Benzyl-7b-(2-trimethylsiloxy)-4-vinylhexahydro-2H,4H-1,3,6-trioxa-7-azacyclopenta[cd]indene (5):

\[
\begin{align*}
\alpha_{D}^{22} & = +0.30 \ (c = 0.90, \text{ CHCl}_3) ; \\
\text{1H NMR (700 MHz, CDCl}_3): \delta & = 0.18 \ [s, 9 \text{ H, Si(CH}_3)_3], 2.45 \ (\text{ddd, J = 3.6, 6.5, 7.5 Hz, 1 H, 4a-H}), 3.89 \ (d, J = 14.1 \text{ Hz, 1 H, NCH}_2), 3.90, 4.00 \ (\text{AB part of ABX system, JAX = 3.6 Hz, JBX = 7.5 Hz, JAB = 13.2 Hz, 2 H, 5-H}), 3.98, 4.09, 4.38 \ (\text{ABX system, JAX = 2.3 Hz, JBX = 4.7 Hz, JAB = 11.5 Hz, 3 H, 2-H, 2a-H}), 4.22 \ (d, J = 14.1 \text{ Hz, 1 H, NCH}_2), 4.40 \ (s, 1 \text{ H, 7a-H}), 4.75 \ (t, J = 7.5 \text{ Hz, 1 H, 4-H}), 5.22 \ (d, J = 10.5 \text{ Hz, 1 H, 2'-H}), 5.27 \ (d, J = 17.3 \text{ Hz, 1 H, 2'-H}), 6.08 \ (\text{ddd, J = 7.5, 10.5, 17.3 Hz, 1 H, 1'-H}), 7.25-7.27 \ (m, 1 \text{ H, Ph}), 7.31-7.34 \ (m, 2 \text{ H, Ph}), 7.38-7.39 \ (m, 2 \text{ H, Ph}) \ ppm; \ \\
\text{13C NMR (175 MHz, CDCl}_3): \delta & = 2.19 \ [q, \text{ Si(CH}_3)_3], 48.3 \ (d, \text{ C-4a}), 57.7 \ (t, \text{ NCH}_2), 65.9 \ (t, \text{ C-5}), 70.6 \ (t, \text{ C-2}), 85.9 \ (d, \text{ C-4}), 88.9 \ (s, \text{ C-7b}), 90.0 \ (d, \text{ C-2a}), 96.0 \ (d, \text{ C-7a}), 118.4 \ (t, \text{ C-2'}), 127.3, 128.4, 128.8 \ (3 \ d, \text{ Ph}), 135.5 \ (d, \text{ C1'}), 137.4 \ (s, \text{ Ph}) \ ppm; \ \\
\text{IR (ATR): } \tilde{\nu} & = 3020 \ (=C-H), 2955-2850 \ (C-H), 1735 \ (C=C), 1465 \ (C-H) \ 1215 \ (C-O) \ \text{cm}^{-1}; \ \\
\text{HRMS (ESI-TOF): m/z calcd for C}_{19}H_{28}NO_4Si \ [M + H]^+: 362.1782; \ \\
& \text{found: 362.1819; calcd for C}_{19}H_{27}NNaO_4Si \ [M + Na]^+: 384.1602; \ \\
& \text{found: 384.1646.}
\end{align*}
\]

(1S,5R,6S,8S)-2-Benzyl-8-[(tert-butyldimethylsiloxy)-methyl]-6-vinyl-3,7-dioxa-2-azabicyclo[3.3.1]nonan-9-on (6)

\[
\begin{align*}
\text{1,2-Oxazine 2 (885 mg, 2.27 mmol) was dissolved in acetonitrile (18 mL) and cooled to -30 °C. Tin(IV) chloride (1.77 g, 0.79 mL, 6.81 mmol) was added and the solution was stirred for 18 h and allowed to warm to rt. The reaction was quenched with water (20 mL) and extracted with dichloromethane (5 x 30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was dissolved in dichloromethane (4.5 mL) and cooled to 0 °C, then 2,6-lutidine (449 mg, 4.09 mmol) and tert-butyldimethylsilyl triflate (779 mg, 2.95 mmol) were added and the mixture was stirred for 2 h}
\end{align*}
\]
at rt. The reaction was quenched with aqueous ammonium chloride solution (5 mL) and the aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc 30:1) to yield 6 (447 mg, 49%) as a colorless oil.

\[\text{at \( \alpha \)}_{D}^{22} = +75.3 \ (c = 0.83, \text{CHCl}_3); \quad \text{'H NMR (500 MHz, CDCl}_3): \delta = 0.02, 0.04 \ [2 s, 6 \text{ H, Si(CH}_3)_3], 0.85 \ (s, 9 \text{ H, Sit-Bu}), 2.68 \ (\text{m}, 1 \text{ H, 5-H}), 3.57 \ (\text{m}, 1 \text{ H, 1-H}), 3.74, 3.86, 3.99 \ (\text{ABM part of ABMX system, } J_{AX} = 1.3 \text{ Hz, } J_{AM} = 5.2 \text{ Hz, } J_{BM} = 8.6 \text{ Hz, } J_{AB} = 9.6 \text{ Hz, 3 H, 8-H, 8-CH}_2), 3.99, 4.14 \ (\text{AB system, } J_{AB} = 14.1 \text{ Hz, 2 H, NCH}_2), 4.30 \ (\text{d, } J = 5.0 \text{ Hz, 1 H, 6-H}), 4.31, 4.45 \ (\text{AB part of ABX system, } J_{AX} = 3.2 \text{ Hz, } J_{BX} = 5.3 \text{ Hz, } J_{AB} = 11.8 \text{ Hz, 2 H, 4-H}), 5.29 \ (\text{d br, } J = 10.8 \text{ Hz, 1 H, 2'-H}), 5.43 \ (\text{d br, } J = 17.3 \text{ Hz, 1 H, 2'-H}), 5.81 \ (\text{ddd, } J = 5.0, 10.8, 17.3 \text{ Hz, 1 H, 1'-H}), 7.25-7.28 \ (\text{m, 1 H, Ph}), 7.31-7.34 \ (\text{m, 2 H, Ph}), 7.35-7.37 \ (\text{m, 2 H, Ph}) \text{ ppm; } ^{13}\text{C NMR (125 MHz, CDCl}_3): \delta = -5.4, -5.3 \ [2 \text{ q, Si(CH}_3)_3], 18.3, 25.9 \ (\text{q, s, Sit-Bu}), 53.8 \ (\text{d, C-5), 61.2 \ (\text{t, 8-CH}_2), 61.5 \ (\text{t, NCH}_2), 67.4 \ (\text{t, C-4), 72.0 \ (\text{d, C-1), 80.8 \ (\text{d, C-6), 81.6 \ (\text{d, C-8), 117.7 \ (\text{t, C-2'), 127.6, 128.5, 128.9 \ (3 \text{ d, Ph), 134.3 \ (d, C-1'), 136.7 \ (s, Ph), 207.4 \ (s, C-9) ppm; IR (ATR): } \tilde{\nu} = 3080 \ (\text{C=H}), 2950-2830 \ (\text{C-H}), 1730 \ (\text{C=O), 1595 \ (C=C), 1250 \ (C-O \text{ cm}^{-1}; \quad \text{HRMS (ESI-TOF): } m/z \text{ calcd for } C_{22}H_{34}NO_4Si [M + H]^+: 404.2257; \text{ found: 404.2259; calcd for } C_{22}H_{33}NNaO_4Si [M + Na]^+: 426.2077; \text{ found: 426.2078; elemental analysis calcd (% for } C_{22}H_{33}NNaO_4Si (403.6): C, 65.47, H, 8.24, N, 3.47; \text{ found: C, 64.77, H, 8.20, N, 3.49.}}}

(2S,3R,4R,5S,6S)-(3-Amino-6-ethyl-4-hydroxytetrahydro-2H-pyran-2,5-diyl)dimethanol (9a)

A suspension of Pd/C (10% Pd, 150 mg) and MeOH (3 mL) was saturated with hydrogen for 15 min. The bicyclic compound 7a (150 mg, 515 μmol) was dissolved in MeOH (1 mL), and added to the suspension. The mixture was stirred for 18 h under hydrogen pressure (balloon). The mixture was then filtrated through a pad of Celite® and the solvent was removed in vacuo. The crude material was purified by column chromatography (silica gel, CH₂Cl₂/MeOH 10:1) to yield 9a (37 mg, 35%) as a colorless solid.

m.p. 156-158 °C; [\alpha]_{D}^{22} = +85.6 \ (c = 0.95, \text{CH}_3\text{OH}); \quad \text{'H NMR (700 MHz, CD}_3\text{OD): } \delta = 1.05 \ (\text{t, } J = 7.4 \text{ Hz, 3 H, 2'-H}), 1.66-1.72 \ (\text{m, 1 H, 1'-H}), 1.87-1.93 \ (\text{m, 1 H, 1'-H}), 1.97 \ (\text{m}, 1 \text{ H, 5-H}), 3.53 \ (\text{m}, 2 \text{ H, 3-H, 6-H}), 3.60, 3.82, 3.86 \ (\text{ABX system, } J_{AX} = 5.0 \text{ Hz, } J_{BX} = 8.2 \text{ Hz, } J_{AB} = 11.9 \text{ Hz, 3 H, 2-H, 2-CH}_2), 3.86, 3.95 \ (\text{AB system, } J_{AB} = 11.5 \text{ Hz, 2 H, 5-CH}_2), 4.30 \ (\text{dd, } J = 4.5, 6.8
Hz, 1 H, 4-H) ppm;\(^{13}\)C NMR (175 MHz, CD\(_3\)OD): \(\delta = 11.2\) (q, C-2\(^\prime\)), 26.0 (t, C-1\(^\prime\)), 43.6 (d, C-5), 52.4 (d, C-6), 55.0 (t, 5-CH\(_2\)), 63.2 (t, 2-CH\(_2\)), 69.0 (d, C-4), 76.7 (d, C-3), 82.3 (d, C-2) ppm; IR (ATR): \(\tilde{\nu} = 3235\) (O-H, N-H), 2950-2845 (C-H), 1465 (C-H), 1255 (C-O) cm\(^{-1}\); HRMS (ESI-TOF): \(m/z\) calcd for C\(_9\)H\(_{20}\)NO\(_4\) \([M + H]^+\): 206.1392; found: 206.1387.

\((E,1R,5R,6S,8S,9R)-2\)-Benzy1-9-benzyloxy-8-(benzyloxymethyl)-6-[3\(^\prime\)-(trimethylsilyl)-prop-1\(^\prime\)-enyl]-3,7-dioxoa-2-azabicyclo[3.3.1]nonane (10)

Bicyclic compound 8 (110 mg, 233 \(\mu\)mol) was dissolved in degassed dichloromethane (1.5 mL) and allyltrimethylsilane (266 mg, 2.33 mmol) was added. Over a period of 6 h Grubbs II catalyst (21 mg, 23 \(\mu\)mol) was added in 3 portions and then stirred for additional 18 h at 40 °C. The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel, hexanes/EtOAc 10:1) to yield 10 (82 mg, 63%) as brownish oil.

\([\alpha]_D^{22} = +45.1\) (c = 0.91, CHCl\(_3\)); \(^1\)H NMR (700 MHz, CDCl\(_3\)): \(\delta = 0.01\) [s, 9 H, Si(CH\(_3\))\(_3\)], 1.50 (d, \(J = 8.2\) Hz, 2 H, 3\(^\prime\)-H), 1.81 (m, 1 H, 5-H), 3.12 (s, 1 H, 1-H), 3.67 (t, \(J = 2.8\) Hz, 1 H, 9-H), 3.76, 3.82, 3.94 (ABX system, \(J_{AB} = 5.2\) Hz, \(J_{AX} = 6.9\) Hz, \(J_{BX} = 9.0\) Hz, 3 H, 8-H, 8-CH\(_2\)), 3.78 (d, \(J = 11.7\) Hz, 1 H, 4-H), 4.23 (d, \(J = 7.0\) Hz, 1 H, 6-H), 4.36 (d, \(J = 13.8\) Hz, 1 H, NCH\(_2\)Ph), 4.51, 4.56 (AB system, \(J_{AB} = 11.8\) Hz, 2 H, OCH\(_2\)Ph), 4.59 (td, \(J = 1.8, 11.7\) Hz, 1 H, 4-H), 4.64, 4.67 (AB system, \(J_{AB} = 11.8\) Hz, 2 H, OCH\(_2\)Ph), 4.65 (d, \(J = 13.8\) Hz, 1 H, NCH\(_2\)Ph), 5.53 (dd, \(J = 7.0, 15.4\) Hz, 1 H, 1\(^\prime\)-H), 5.75 (ddd, \(J = 0.8, 8.2, 15.4\) Hz, 1 H, 2\(^\prime\)-H), 720-7.22 (m, 1 H, Ph), 7.25-7.28 (m, 5 H, Ph), 7.30-7.35 (m, 5 H, Ph), 7.39-7.43 (m, 4 H, Ph) ppm;\(^{13}\)C NMR (175 MHz, CDCl\(_3\)): \(\delta = -1.8\) [q, Si(CH\(_3\))\(_3\)], 23.1 (t, C-3\(^\prime\)), 38.7 (d, C-5), 55.2 (d, C-1), 57.9 (t, C-4), 58.4 (t, NCH\(_2\)Ph), 70.6 (t, OCH\(_2\)Ph, 8-CH\(_2\)), 73.7 (t, OCH\(_2\)Ph), 76.4 (d, C-9), 78.2 (d, C-8), 79.7 (d, C-6), 126.6 (d, C-1\(^\prime\)), 127.0, 127.5, 127.7, 127.9, 128.1, 128.2, 128.5, 128.7, 128.9 (9 d, Ph), 130.2 (d, C-2\(^\prime\)), 138.3, 138.4, 139.0 (3 s, Ph) ppm; IR (ATR): \(\tilde{\nu} = 3060-3030\) (\(=\)C-H), 2920-2860 (C-H), 1720 (C=C), 1455 (C-H), 1245 (C-O) cm\(^{-1}\); HRMS (ESI-TOF): \(m/z\) calcd for C\(_{34}\)H\(_{44}\)NO\(_4\)Si \([M + H]^+\): 558.3040; found: 558.3053; calcd for C\(_{34}\)H\(_{43}\)NNaO\(_4\)Si \([M + Na]^+\): 580.2859; found: 580.2888.
(Z,1'S,3'S,4'R,5'S)-1-[2'-Benzyl-4'-benzyloxy-5'-(buta-1'',3''-dien-1''-yl)-1',2'-oxazinan-3'-yl]-2-(benzyloxy)ethan-1-ol (12)

Under argon atmosphere bicyclic compound 10 (30 mg, 54 µmol) was dissolved in dichloromethane (1 mL) and boron trifluoride diethyl etherate (8 mg, 7 µL, 54 µmol) was added. The solution was stirred for 72 h at rt and then quenched with sat. aqueous sodium bicarbonate solution (3 mL). The aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc 20:1) to yield 12 (14 mg, 47%) as a colorless oil.

[α]D22 = + 25.6 (c = 12.0, CHCl₃); ¹H NMR (700 MHz, CDCl₃): δ = 2.64 (m, 1 H, 5'-H), 3.10 (dd, J = 5.2, 7.0 Hz, 1 H, 3'-H), 3.56-3.58 (m, 2 H, 2-H, 6'-H), 3.65 (dd, J = 3.3, 10.3 Hz, 1 H, 2-H), 3.65 (sbr, 1 H, OH), 3.74 (t, J = 7.0 Hz, 1 H, 4'-H), 3.99 (dd, J = 4.8, 12.0 Hz, 1 H, 6'-H), 4.07 (d, J = 13.9 Hz, 1 H, NCH₂Ph), 4.21 (sbr, 1 H, 1'H), 4.25 (d, J = 13.9 Hz, 1 H, NCH₂Ph), 4.52, 4.66 (AB system, JAB = 10.9 Hz, 2 H, OCH₂Ph), 4.53 (s, 2 H, OCH₂Ph), 5.07 (dd, J = 1.0, 10.0 Hz, 1 H, 4''-H), 5.16 (dd, J = 1.0, 16.8 Hz, 1 H, 4''-H), 5.65 (dd, J = 8.4, 15.3 Hz, 1 H, 1''-H), 6.20 (dd, J = 10.3, 15.3 Hz, 1 H, 2'''-H), 6.30 (dd, J = 10.3, 16.8 Hz, 1 H, 3''-H), 7.24-7.34 (m, 15 H, Ph) ppm; ¹³C NMR (175 MHz, CDCl₃): δ = 45.5 (d, C-5’), 58.1 (t, NCH₂Ph), 66.4 (t, C-6’), 69.3 (d, C-3’), 71.8 (d, C-1), 72.8 (t, C-2), 73.5, 73.6 (2 t, OCH₂Ph), 117.3 (t, C-4’’), 127.3, 127.9, 128.0, 128.1, 128.4, 128.6, 128.7, 128.8 (8 d, Ph), 131.9 (d, C-1’’), 134.1 (d, C-2’’), 136.6 (d, C-3’’), 137.1, 137.8, 138.2 (3 s, Ph) ppm; one d for Ph could not be detected; IR (ATR): v = 3600-3190 (O-H), 3090-3030 (=C-H), 2925-2865 (C-H), 1720 (C= C), 1455 (C-H), 1270 (C-O) cm⁻¹; HRMS (ESI-TOF): m/z calcd for C₃₁H₃₆NO₄ [M + H]⁺: 486.2639; found: 486.2638; calcd for C₃₁H₃₅NNaO₄ [M + Na]⁺: 508.2458; found: 508.2470.
$^1$H NMR (400 MHz, CD$_2$OD)
\(^1\)H NMR (500 MHz, CDCl\(_3\))

\[
\begin{align*}
X &= \text{OBn} \\
\end{align*}
\]

\(^13\)C NMR (125 MHz, CDCl\(_3\))

\[
\begin{align*}
X &= \text{OBn} \\
\end{align*}
\]
$^1$H NMR (700 MHz, CD$_3$OD)

$^{13}$C NMR (175 MHz, CD$_3$OD)