

Supporting Information

Macrocycle Formation by Ring-Closing Metathesis (RCM). Application to the Syntheses of Novel Macrocyclic Taxoids

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Synthesis and characterization data for synthetic intermediates.

General Methods: ^1H and ^{13}C NMR spectra were measured on a Bruker AC-250 NMR spectrometer or a Varian 300 or 500 NMR spectrometer using tetramethylsilane as the internal standard. Melting points were measured on a Thomas Hoover Capillary melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. IR spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. TLC was performed on Merck DC-alufolien with Kieselgel 60F-254 and column chromatography was carried out on silica gel 60 (Merck; 230-400 mesh ASTM). Chiral HPLC analysis for the determination of enantiomeric excess was carried out with a Waters HPLC assembly consisting of a Waters M45 solvent delivery system, a Waters Model 680 gradient controller, and a Waters M440 detector (at 254 nm), equipped with a Spectra Physics Model SP4270 integrator using a DAICEL-CHIRACEL OD chiral column (25 x 0.46 cm i.d.), employing hexane/2-propanol (99.5/0.5, v/v) as the solvent system with a flow rate of 1.0 mL/min. Elemental analysis were performed at M-H-W Laboratory, Phoenix, AZ. High resolution mass spectra were obtained at the University of California, Riverside Mass Spectrometry Facility, Riverside, CA or the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.

Materials: The chemicals were purchased from Aldrich Co. and Sigma and purified before use by standard methods. Tetrahydrofuran was freshly distilled from sodium metal and benzophenone. Dichloromethane was also distilled immediately prior to use under nitrogen from calcium hydride. (3*R*,4*S*)-1-PMP-3-TIPSO-4-(2-methylprop-1-enyl)azetindin-2-one (**15**) was prepared following the procedure previously reported from these laboratories.^{38,44} 10-Deacetylbaecatin III (DAB) was donated by Indena, SpA, Italy.

7,10,13-Tri(triethylsilyl)-2-debenzoyl-10-deacetylbaecatin III (10**).**⁵³ To a solution of DAB (900 mg, 1.652 mmol) and imidazole (674.8 mg, 9.912 mmol) in dry *N,N*-dimethylformamide (DMF, 3 mL) was added chlorotriethylsilane (1.386 mL, 8.260 mmol) dropwise *via* syringe at room temperature. The reaction mixture was stirred for 47 h at room temperature and diluted with ethyl acetate

(150 mL). The mixture was then washed with water (20 mL x 3), brine (20 mL), dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was purified on a silica gel column using hexane/ethyl acetate (10/1) as the eluant to give 7,10,13-tri(triethylsilyl)-DAB⁵³ as a white solid (1.408 g, 96%): mp 187-189 °C; $[\alpha]_{\text{D}}^{20}$ -38.8 (c 0.28, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.65 (m, 18 H), 0.99 (m, 27 H), 1.11 (s, 3 H), 1.18 (s, 3 H), 1.64 (s, 3 H), 1.87 (m, 1 H), 1.97 (s, 3 H), 2.08 (dd, J = 15.2, 8.8 Hz, 1 H), 2.21 (dd, J = 15.1, 8.2 Hz, 1 H), 2.27 (s, 3 H), 2.51 (m, 1 H), 3.84 (d, J = 7.0 Hz, 1 H), 4.13 (d, J = 8.3 Hz, 1 H), 4.27 (d, J = 8.3 Hz, 1 H), 4.40 (dd, J = 10.5, 6.6 Hz, 1 H), 4.92 (m, 2 H), 5.18 (s, 1 H), 5.61 (d, J = 7.0 Hz, 1 H), 7.44 (t, J = 7.3 Hz, 2 H), 7.57 (t, J = 7.3 Hz, 1 H), 8.07 (d, J = 7.4 Hz, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.7, 5.2, 5.9, 6.9, 10.4, 14.8, 20.5, 22.4, 26.3, 37.3, 19.8, 42.4, 46.8, 58.2, 68.3, 72.6, 75.4, 75.7, 76.6, 79.5, 80.7, 83.9, 128.5, 129.6, 130.0, 133.4, 135.7, 139.3, 167.1, 169.7, 205.6.

To a solution of 7,10,13-tri(triethylsilyl)-DAB thus obtained (870 mg, 0.980 mmol) in dry THF (45 mL) at -10 °C was added dropwise a solution of Red-Al in toluene (0.589 mL, 65% wt), and the reaction mixture was stirred for 20 min at -10 °C. The reaction was quenched with saturated aqueous ammonium chloride (20 mL), and the aqueous layer was extracted with ethyl acetate (50 mL x 3). The combined extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified on a silica gel column using hexane/ethyl acetate (8/1 followed by 3/1) as the eluant to afford **10** as a white solid (768 mg, 100% yield): mp 68-70 °C; $[\alpha]_{\text{D}}^{20}$ -35.6 (c 0.87, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.57 (m, 18 H), 0.94 (m, 27 H), 1.11 (s, 3 H), 1.55 (s, 3 H), 1.87 (m, 1 H), 1.88 (s, 3 H), 1.94 (m, 1 H), 2.00 (m, 1 H), 2.12 (s, 3 H), 2.47 (m, 1 H), 3.42 (d, J = 6.6 Hz, 1 H), 3.80 (d, J = 6.6 Hz, 1 H), 4.31 (dd, J = 10.4, 6.5 Hz, 1 H), 4.50 (d, J = 9.0 Hz, 1 H), 4.57 (d, J = 9.1 Hz, 1 H), 4.63 (s, 1 H), 4.89 (d, J = 8.3 Hz, 1 H), 4.91 (m, 1 H), 5.08 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.7, 5.1, 5.8, 6.7, 6.8, 10.5, 14.4, 20.5, 22.3, 37.3, 40.3, 42.5, 58.1, 65.0, 66.3, 72.6, 74.6, 75.7, 77.9, 78.5, 81.9, 83.7, 126.8, 127.4, 128.4, 135.9, 138.9, 169.6, 206.3. HRMS (FAB, DCM/NBA) *m/z* calcd for C₄₀H₇₄O₉Si₃·H⁺: 783.4719. Found: 783.4726 (Δ = -0.9 ppm).

Compounds **12a,c-g** were synthesized in a similar manner to compound **12b**. Their characterization data are shown below.

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-(but-3-enoyl)-10-deacetylbaecatin III (12a): 67% (52% conversion); white solid; mp 98-100 °C; $[\alpha]_{\text{D}}^{20}$ -42.9 (c 0.12, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.60 (m, 18 H), 0.96 (m, 27 H), 1.09 (s, 6 H), 1.58 (s, 3 H), 1.86 (m, 1 H), 1.92 (s, 3 H), 2.02 (m, 2 H), 2.15 (s, 3 H), 2.49 (m, 1 H), 3.08 (d, J = 6.0 Hz, 1 H), 3.70 (d, J = 7.0 Hz, 1 H), 4.13 (d, J = 8.0 Hz, 1 H), 4.35 (dd, J = 10.5, 6.6 Hz, 1 H), 4.42 (d, J = 8.0 Hz, 1 H), 4.88 (t, J = 8.7 Hz, 1 H), 4.92 (d, J = 8.2 Hz, 1 H), 5.13 (s, 1 H), 5.17 (m, 2 H), 5.35 (d, J = 7.0 Hz, 1 H), 5.89 (m, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.8, 5.1, 5.9, 6.8, 6.9, 10.3, 14.5, 20.5, 22.3, 26.3, 37.2, 39.5, 39.7, 42.9, 46.7, 58.2, 68.2, 72.5, 75.4, 75.7, 76.6, 79.4, 80.4, 84.1, 118.9, 129.7, 135.6, 139.4, 170.0, 172.4, 205.6. HRMS (FAB, DCM/NBA/PEG) *m/z* calcd for C₄₄H₇₈O₁₀Si₃·H⁺: 851.4981. Found: 851.4946 (Δ = 4.1 ppm).

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-(hex-5-enoyl)-10-deacetylbaecatin III (12c): 92% yield; colorless film; ^1H NMR (250 MHz, CDCl_3) δ 0.47-0.65 (m, 18 H), 0.87-0.98 (m, 27 H), 1.06 (s, 6 H), 1.53 (s, 3 H), 1.69 (m, 3 H), 1.89 (s, 3 H), 2.00 (m, 2 H), 2.11 (s, 3 H), 2.32 (m, 4 H), 2.46 (s, 1 H), 3.67 (d, J = 6.8 Hz, 1 H), 4.08 (d, J = 8.0 Hz, 1 H), 4.31 (dd, J = 10.4, 6.6 Hz, 1 H), 4.37 (d, J = 8.0 Hz, 1 H), 4.81-5.02 (m, 4 H), 5.10 (s, 1 H), 5.31 (d, J = 6.9 Hz, 1 H), 5.71 (m, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.7, 5.1, 5.9, 6.7, 6.8, 10.3, 14.4, 20.4, 22.2, 23.6, 24.4, 24.6, 25.2, 25.4, 26.2, 26.3, 30.8, 32.6, 32.7, 33.0, 34.0, 34.8, 37.1, 39.4, 42.9, 46.7, 49.7, 55.7, 58.1, 68.2, 72.5, 74.8, 75.6, 76.5, 79.2, 80.4, 84.0, 115.3, 135.6, 137.5, 139.4, 169.9, 174.5, 205.6.

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-[(*R*)-3-methylhept-6-enoyl]-10-deacetylbaecatin III (12e): 93% yield; white solid, mp 137.5-138.5 °C; ^1H NMR (250 MHz, CDCl_3) δ 0.51-0.68 (m, 18 H), 0.91-1.02 (m, 30 H), 1.31 (m, 2 H), 1.40 (m, 1 H), 1.57 (s, 3 H), 1.85 (m, 1 H), 1.92 (s, 3 H), 1.91-2.11 (m, 5 H), 2.35 (d, J = 10.9 Hz, 1 H), 2.50 (m, 1 H), 3.71 (d, J = 6.9 Hz, 1 H), 4.12 (d, J = 7.9 Hz, 1 H), 4.35 (dd, J = 10.5, 6.6 Hz, 1 H), 4.43 (d, J = 7.9 Hz, 1 H), 4.91 (m, 4 H), 5.14 (s, 1 H), 5.34 (d, J = 6.9 Hz, 1 H), 5.77 (m, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.8, 5.2, 5.9, 6.85, 6.92, 10.3, 14.5, 19.7, 20.4, 22.3, 26.4, 29.4, 31.1, 35.6, 37.2, 39.4, 42.3, 43.0, 46.9, 58.2, 68.3, 72.5, 74.7, 75.7, 76.8, 79.4, 80.4, 84.1, 114.6, 135.7, 138.4, 139.3, 170.0, 174.2, 205.6. HRMS (FAB) m/z calcd for $\text{C}_{48}\text{H}_{86}\text{O}_{10}\text{Si}_3\cdot\text{H}^+$: 907.5607. Found: 907.5611 (Δ = -0.4 ppm).

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-[*N*-methyl-*N*-(pent-4-enoyl)aminoacetyl]-10-deacetylbaecatin III (12g): 78% yield; white solid, mp 82-84 °C; $[\alpha]_{\text{D}}^{20}$ -26.7 (c 0.09, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.63 (m, 18 H), 0.97 (m, 27 H), 1.06 (s, 3 H), 1.10 (s, 3 H), 1.49 (bs, 1 H), 1.58 (s, 3 H), 1.86 (m, 1 H), 1.93 (s, 3 H), 2.00 (s, 1 H), 2.04 (s, 1 H), 2.16 (s, 3 H), 2.40-2.51 (m, 4 H), 3.16 (s, 3 H), 3.84 (d, J = 7.0 Hz, 1 H), 4.14 (d, J = 7.9 Hz, 1 H), 4.28 (d, J = 10.4, 6.6 Hz, 1 H), 4.29-4.33 (m, 2 H), 4.40 (d, J = 7.9 Hz, 1 H), 4.91-4.95 (m, 2 H), 5.01-5.12 (m, 2 H), 5.42 (d, 1 H), 5.80 (m, 1H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.8, 4.9, 5.2, 5.9, 6.8, 6.9, 10.2, 14.6, 20.7, 22.4, 26.4, 28.8, 29.7, 32.5, 33.2, 37.3, 40.8, 42.7, 46.5, 51.2, 58.3, 68.4, 72.5, 75.8, 76.5, 80.7, 84.2, 115.5, 136.2, 136.9, 138.9, 169.5, 169.6, 173.6, 205.5. HRMS (FAB, $\text{MeOH}/\text{NBA}/\text{PPG}$) m/z calcd for $\text{C}_{48}\text{H}_{85}\text{NO}_{11}\text{Si}_3\cdot\text{H}^+$: 936.5509. Found: 936.5508 (Δ = 0.1 ppm).

Compounds **8a,c-k** were synthesized in a similar manner to compound **8b**. Their characterization data are shown below.

7-Triethylsilyl-2-debenzoyl-2-(but-3-enoyl)baecatin III (8a): 76% yield from **12a** (3 steps); white solid; mp 105-107 °C; $[\alpha]_{\text{D}}^{20}$ -49.3 (c 0.39, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.55 (m, 6 H), 0.90 (m, 9 H), 1.00 (s, 3 H), 1.00 (s, 3 H), 1.60 (s, 3 H), 1.86 (m, 1 H), 2.02 (s, 3 H), 2.14 (s, 3 H), 2.15 (s, 3 H), 2.11 (m, 2 H), 2.50 (m, 1 H), 3.10 (d, J = 6.7 Hz, 2 H), 3.73 (d, J = 7.1 Hz, 1 H), 4.14 (d, J = 7.5 Hz, 1 H), 4.41 (m, 1 H), 4.45 (d, J = 7.5 Hz, 1 H), 4.78 (t, J = 10.6 Hz, 1 H), 4.93 (d, J = 9.2 Hz, 1 H), 5.15 (m, 2 H), 5.36 (d, J = 7.1 Hz, 1 H), 5.90 (m, 1 H), 6.40 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.2, 6.7, 9.8, 14.1, 14.8, 19.9, 20.9, 22.5, 26.8, 37.2, 38.0, 39.6, 42.6,

47.0, 58.6, 60.4, 67.8, 72.4, 72.8, 74.7, 75.7, 78.6, 80.5, 84.3, 119.1, 129.6, 132.4, 144.1, 169.2, 170.8, 172.3, 202.2. HRMS (FAB, DCM/NBA/NaCl/PEG) m/z calcd for $C_{34}H_{52}O_{10}Si\cdot Na^+$: 687.3177. Found: 687.3165 ($\Delta = 1.7$ ppm).

7-Triethylsilyl-2-debenzoyl-2-(hex-5-enoyl)baccatin III (8c): 82% yield from **12c** (3 steps); white solid; 1H NMR (250 MHz, $CDCl_3$) δ 0.54 (m, 6 H), 0.89 (m, 9 H), 0.99 (s, 3 H), 1.09 (s, 3 H), 1.59 (s, 3 H), 1.73 (m, 2 H), 1.83 (m, 1 H), 2.01-2.15 (m, 11 H), 2.29 (m, 4 H), 2.49 (m, 1 H), 3.72 (d, $J = 7.0$ Hz, 1 H), 4.12 (d, $J = 8.1$ Hz, 1 H), 4.41 (m, 2 H), 4.77 (bt, 1 H), 4.91-5.06 (m, 3 H), 5.33 (d, $J = 7.0$ Hz, 1 H), 5.74 (m, 1 H), 6.39 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 5.3, 6.7, 9.8, 14.9, 20.0, 20.9, 22.6, 23.7, 26.8, 32.8, 34.0, 37.2, 37.9, 42.8, 47.1, 58.6, 67.8, 72.3, 74.2, 75.8, 78.6, 80.5, 84.4, 115.5, 132.5, 137.5, 144.2, 169.3, 170.8, 174.6, 202.3. HRMS (FAB) m/z calcd for $C_{36}H_{56}O_{10}Si\cdot H^+$: 693.3670. Found: 693.3667 ($\Delta = 0.5$ ppm).

7-Triethylsilyl-2-debenzoyl-2-allyloxyacetyl baccatin III (8d): 62% yield from **12d** (3 steps); white solid; 1H NMR (300 MHz, $CDCl_3$) δ 0.57 (m, 6 H), 0.98 (m, 9 H), 0.98 (s, 3 H), 1.17 (s, 3 H), 1.24 (s, 3 H), 1.63 (s, 3 H), 2.13 (s, 3 H), 2.19 (s, 3 H), 2.45 (m, 1 H), 3.74 (d, $J = 6.9$ Hz, 1 H), 4.11 (m, 2 H), 4.44 (m, 1 H), 4.79 (m, 1 H), 4.94 (d, $J = 8.1$ Hz, 1 H), 5.28 (m, 2 H), 5.42 (d, $J = 6.9$ Hz, 1 H), 5.91 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.37, 5.44, 5.55, 7.02, 10.20, 15.23, 20.25, 20.94, 21.23, 22.92, 27.14, 37.53, 38.44, 43.03, 47.34, 59.06, 67.70, 69.17, 72.65, 76.19, 78.93, 80.95, 84.77, 118.55, 132.96, 134.15, 144.85, 169.92, 171.50, 172.37, 202.86.

7-Triethylsilyl-2-debenzoyl-2-[(R)-3-methylhept-6-enoyl]baccatin III (8e): 80% yield from **12e** (3 steps); white solid; mp 85-87 °C; 1H NMR (250 MHz, $CDCl_3$) δ 0.58 (m, 6 H), 0.97 (m, 15 H), 1.09 (s, 3 H), 1.22 (m, 2 H), 1.30 (m, 1 H), 1.58 (s, 3 H), 1.83 (m, 1 H), 2.00 (s, 3 H), 2.08 (m, 5 H), 2.12 (s, 6 H), 2.34 (d, $J = 10.5$ Hz, 1 H), 2.47 (m, 1 H), 3.72 (d, $J = 6.9$ Hz, 1 H), 4.12 (d, $J = 7.9$ Hz, 1 H), 4.43 (d, $J = 7.9$ Hz, 1 H), 4.76 (bt, 1 H), 4.93 (d, $J = 10.0$ Hz, 1 H), 4.98 (d, $J = 19.6$ Hz, 1 H), 5.32 (d, $J = 6.9$ Hz, 1 H), 5.77 (m, 1 H), 6.38 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 5.2, 6.7, 9.8, 14.8, 19.7, 19.9, 20.9, 22.5, 26.8, 29.4, 31.1, 35.6, 37.1, 37.9, 42.1, 42.8, 47.2, 58.6, 67.8, 72.2, 74.0, 75.7, 76.7, 78.6, 80.4, 84.3, 114.6, 132.4, 138.4, 144.1, 169.3, 170.8, 174.2, 202.3. HRMS (FAB) m/z calcd for $C_{38}H_{60}O_{11}Si\cdot H^+$: 721.3983. Found: 721.3986 ($\Delta = -0.4$ ppm).

7-Triethylsilyl-2-debenzoyl-2-[(Z)-3-methylhepta-2,6-dienoyl]baccatin III (8f): 58% yield from **12f** (3 steps); white solid; mp 70 -72 °C; $[\alpha]_D^{20} -50.0$ (c 0.18, $CHCl_3$); 1H NMR (250 MHz, $CDCl_3$) δ 0.56 (m, 6 H), 0.93 (m, 15 H), 1.00 (s, 3 H), 1.12 (s, 3 H), 1.30 (m, 1 H), 1.56 (s, 3 H), 1.82 (s, 6 H), 1.83 (m, 1 H), 2.12 (s, 6 H), 2.21 (m, 5 H), 2.43 (m, 1 H), 2.80 (m, 2 H), 3.01 (dd, 2 H), 3.72 (m, 2 H), 4.15 (m, 2 H), 4.42 (m, 2 H), 4.78 (bt, 1 H), 4.98 (m, 4 H), 5.33 (d, 1 H), 5.37 (t, 1 H), 5.74 (m, 1 H), 6.39 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 5.2, 6.7, 9.9, 14.9, 20.0, 20.9, 22.5, 24.1, 26.8, 32.4, 37.2, 38.2, 42.7, 47.1, 58.6, 67.8, 72.3, 74.9, 75.8, 84.4, 115.1, 126.5, 128.5, 132.5, 135.8, 143.9, 169.3, 170.5, 172.1, 202.2. HRMS (FAB, DCM/NBA) m/z calcd for $C_{38}H_{58}O_{11}Si\cdot H^+$: 719.3827. Found: 719.3827 ($\Delta = 0.0$ ppm).

7-Triethylsilyl-2-debenzoyl-2-[N-methyl-N-(pent-4-enoyl)aminoacetyl]baccatin III (8g): 50% yield from **12g** (3 steps); white solid; mp 118-120 °C; $[\alpha]_D^{20} -30.0$ (c 0.10, $CHCl_3$); 1H

NMR (250 MHz, CDCl_3) δ 0.53 (m, 6 H), 0.92 (m, 9 H), 1.00 (s, 3 H), 1.23 (s, 3 H), 1.68 (s, 3 H), 1.84-2.20 (m, 4 H), 2.01 (s, 3 H), 2.41-2.67 (m, 4 H), 3.18 (s, 3 H), 3.78-3.83 (m, 4 H), 4.23-4.33 (m, 4 H), 4.80 (t, 1 H); 4.95 (m, 2 H), 5.10, (s, 1 H), 5.40 (d, 1 H), 5.83 (m, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.2, 6.7, 9.8, 23.4, 28.7, 32.5, 37.5, 40.0, 42.1, 46.8, 50.1, 67.7, 72.0, 84.6, 115.0, 133.5, 136.2, 144.0, 156.5, 168.0, 169.2, 171.0, 174.0, 202.0. HRMS (FAB, DCM/NBA) m/z calcd for $\text{C}_{38}\text{H}_{59}\text{NO}_{12}\text{Si}\cdot\text{H}^+$: 750.3885. Found: 750.3883 ($\Delta = 0.2$ ppm).

7-Triethylsilyl-2-debenzoyl-2-(2-but-3-enylbenzoyl)baccatin III (8h): 55% yield from **12h** (3 steps); white solid; mp 222-224 °C; $[\alpha]_{\text{D}}^{20} -77.8$ (c 0.18, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.58 (m, 6 H), 0.91 (m, 9 H), 1.04 (s, 3 H), 1.19 (s, 3 H), 1.67 (s, 3 H), 1.84 (m, 1 H), 2.17 (s, 3 H), 2.21 (s, 3 H), 2.22-2.60 (m, 5 H), 3.14 (m, 1 H), 3.85 (d, $J = 6.9$ Hz, 1 H), 4.13 (d, $J = 8.2$ Hz, 1 H), 4.21 (d, $J = 8.2$ Hz, 1 H), 4.46 (dd, $J = 6.6, 10.3$ Hz, 1 H), 4.83 (t, $J = 6.8$ Hz, 1 H), 5.04-4.90 (m, 3 H), 5.59 (d, $J = 6.9$ Hz, 1 H), 5.86 (m, 1 H), 7.26 (m, 2 H), 7.45 (m, 1 H), 8.06 (d, $J = 7.0$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.3, 6.8, 10.0, 14.9, 20.1, 20.1, 21.0, 22.6, 26.9, 33.2, 33.8, 35.4, 37.3, 38.4, 42.9, 47.4, 58.7, 68.0, 72.3, 74.5, 75.8, 76.5, 78.8, 80.8, 84.2, 115.0, 126.0, 128.1, 131.3, 131.4, 132.7, 138.1, 144.0, 145.3, 167.6, 169.4, 171.6, 202.3. HRMS (FAB, MeOH/NBA/PPG) m/z calcd for $\text{C}_{41}\text{H}_{58}\text{O}_{11}\text{Si}\cdot\text{H}^+$: 755.3830 Found: 755.3827 ($\Delta = -0.4$ ppm).

7-Triethylsilyl-2-debenzoyl-2-(2-allyloxybenzoyl)baccatin III (8i): 56% yield from **12i** (3 steps); white solid; mp 223 °C; ^1H NMR (250 MHz, CDCl_3) δ 0.55 (m, 6 H), 0.90 (m, 9 H), 1.04 (s, 3 H), 1.20 (s, 3 H), 1.69 (s, 3 H), 1.85 (m, 1 H), 2.12 (m, 2 H), 2.15 (6, 6 H), 2.25 (m, 2 H), 2.49 (m, 1 H), 2.57 (s, 1 H), 3.78 (d, $J = 6.8$ Hz, 1 H), 4.23 (d, $J = 8.3$ Hz, 1 H), 4.30 (d, $J = 8.3$ Hz, 1 H), 4.44 (dd, $J = 10.2, 6.6$ Hz, 1 H), 4.69 (d, $J = 4.7$ Hz, 2 H), 4.82 (m, 1 H), 4.88 (m, 1 H), 6.42 (s, 1 H), 6.94 (d, $J = 8.3$ Hz, 1 H), 7.00 (d, $J = 7.6$ Hz, 1 H), 7.44 (t, $J = 7.1$ Hz, 1 H), 7.79 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.2, 6.7, 9.9, 14.9, 20.1, 20.9, 22.6, 26.7, 37.3, 39.2, 42.5, 47.1, 58.8, 67.9, 69.2, 72.3, 75.3, 75.9, 77.7, 80.8, 84.3, 113.4, 118.3, 120.7, 131.7, 132.3, 133.7, 144.0, 167.7, 166.5, 170.8, 202.4; HRMS (FAB, MeOH/NBA/PPG) m/z calcd for $\text{C}_{40}\text{H}_{57}\text{O}_{12}\text{Si}\cdot\text{H}^+$: 757.3619. Found: 757.3622 ($\Delta = -0.4$ ppm).

Compounds **8m,o** were synthesized in a similar manner to compound **8l**. Their characterization data are shown below.

7-Triethylsilyl-2-debenzoyl-2-(3-methyl-3-allyloxybutanoyl)baccatin (8m): 60% yield from **14** (2 steps); white solid; ^1H NMR (300 MHz, CDCl_3) δ 0.57 (q, $J = 6.6$ Hz, 6 H), 0.88 (t, $J = 6.6$ Hz, 9 H), 1.05 (s, 3 H), 1.17 (s, 3 H), 1.23 (s, 3 H), 1.30 (s, 3 H), 1.38 (s, 3 H), 1.66 (s, 3 H), 2.04 (s, 3 H), 2.18 (s, 3 H), 2.62 (m, 4 H), 3.69 (d, $J = 6.6$ Hz, 1 H), 3.96 (m, 1 H), 4.26 (d, $J = 7.8$ Hz, 1 H), 4.41 (m, 2 H), 4.79 (t, $J = 7.8$ Hz, 1 H), 4.94 (d, $J = 8.1$ Hz, 1 H), 5.15 (d, $J = 11.7$ Hz, 1 H), 5.40 (d, $J = 6.6$ Hz, 1 H), 5.91 (m, 1 H), 6.39 (s, 1 H).

7-Triethylsilyl-2-debenzoyl-2-(3,3-dimethylpent-4-enoyl)baccatin (8o): 65% yield from **14** (2 steps); white solid; ^1H NMR (300 MHz, CDCl_3) δ 0.56 (q, $J = 9.9$ Hz, 6 H), 0.89 (t, $J = 9.9$ Hz, 9 H), 1.01 (s, 3 H), 1.06 (s, 3 H), 1.14 (s, 3 H), 1.18 (s, 3 H), 1.23 (s, 3 H), 1.65 (s, 3 H), 2.04 (s, 3 H), 2.17 (s, 3 H), 2.31 (d, $J = 3.6$ Hz, 1 H), 2.42 (m, 1 H), 3.82 (d, $J = 6.9$ Hz, 1 H), 4.15 (m, 1

H) 4.36 (dd, $J = 6.6, 4.5$ Hz, 1H), 4.84 (t, $J = 7.2$ Hz, 1 H), 4.97 (m, 2 H), 5.32 (d, $J = 6.9$ Hz, 1 H) 5.92 (dd, $J = 10.5, 6.9$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 5.74, 7.02, 10.15, 14.5, 15.19, 20.31, 21.24, 22.93, 27.08, 36.66, 37.57, 38.77, 43.18, 47.65, 47.97, 59.04, 68.36, 72.71, 74.56, 76.20, 78.71, 81.02, 84.84, 111.78, 133.19, 144.43, 147.57, 169.94, 171.48, 173.27, 202.87.

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-[(E)-2-methylhexa-1,5-dienyl]azetidin-2-one (17b). To a solution of diisopropylamine (0.4 mL, 3.25 mmol) in dry THF (10 mL) was added *n*-BuLi (1.3 mL, 3.25 mmol, 2.5 M-hexane solution) at 0 °C with stirring. After 30 min, the reaction mixture was cooled to -84 °C, and a solution of (-)-*trans*-2-phenylcyclohexyl triisopropylsiloxyacetate **19** (975 mg, 2.5 mmol) in dry THF (5 mL) was added slowly *via* cannula. The mixture was stirred for an additional 1 h, and a solution of *N*-(4-methoxyphenyl)-(E)-3-methylhepta-2,6-dienaldimine (3 mmol) in dry THF (10 mL) was added slowly *via* cannula at -84 °C. The imine used was prepared from 3-methylhepta-2,6-dienal and *p*-anisidine, and used as obtained. The reaction mixture was stirred for 4 h and then allowed to warm to room temperature overnight with stirring. The reaction mixture was then diluted with ethyl acetate, poured into a saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with a 3% hydrochloric acid and brine, dried over anhydrous magnesium sulfate and evaporated to dryness. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 40/1) gave **17b** as a white solid (700 mg, 63 % yield): $[\alpha]_{\text{D}}^{22} +39.9$ (c 1.43, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 1.08 (m, 21 H), 1.85 (s, 3 H), 2.18 (bs, 4 H), 3.72 (s, 3 H), 4.82 (dd, $J = 4.8, 9.9$ Hz, 1 H), 4.90-5.04 (m, 2 H), 5.06 (d, $J = 5.1$ Hz, 1 H), 5.37 (dd, $J = 1.2, 9.9$ Hz, 1 H), 5.77 (m, 1 H), 6.83 (d, $J = 9.0$ Hz, 2H), 7.32 (d, $J = 9.0$ Hz, 2 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.9, 16.6, 17.5, 31.8, 39.2, 55.4, 57.5, 114.3, 114.9, 118.5, 118.6, 120.3, 121.3, 138.1, 142.4, 165.7. MS m/z 443 (M^+); HRMS (EI) m/z calcd for $\text{C}_{26}\text{H}_{41}\text{NO}_3\text{Si}^+$: 443.2856. Found: 443.2860 ($\Delta = -0.9$ ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-[(E)-2-methylhexa-1,5-dienyl]azetidin-2-one (18b). To a solution of **17b** (234 mg, 0.59 mmol) in acetonitrile (30 mL) and water (20 mL) was added dropwise a solution of CAN (1.14 g, 2.0 mmol) in water (10 mL) at -15 °C. After stirring for 3 h at the same temperature, the reaction mixture was diluted with ethyl acetate, poured into saturated aqueous sodium sulfate and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous magnesium sulfate and evaporated to dryness. The residue was dissolved in dichloromethane (3 mL), and to this solution were added triethylamine (0.15 mL, 1.1 mmol), di-*tert*-butyl dicarbonate (0.2 mL, 0.7 mmol) and DMAP (catalytic amount). After stirring for 15 h, the reaction mixture was diluted with ethyl acetate, poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous magnesium sulfate and evaporated to dryness. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 40/1) gave **18b** as a colorless oil (228 mg, 88 % yield for two steps): ^1H NMR (300 MHz, CDCl_3) δ 1.04 (m, 21 H), 1.47 (s, 9 H), 1.77 (s, 3 H), 2.16 (s, 4 H), 4.76 (dd, $J = 9.8, 5.6$ Hz, 1 H), 4.94 (d, $J = 11.7$ Hz, 1 H), 5.01 (d, $J = 15.1$ Hz, 1 H), 5.32-5.29 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR

(62.9 MHz, CDCl₃) δ 11.8, 16.7, 17.6, 28.0, 31.9, 39.3, 53.4, 56.7, 77.3, 82.9, 114.7, 118.2, 138.1, 142.9, 148.0, 166.5.

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triethylsiloxy-4-[(E)-2-methylhexa-1,5-dienyl]azetidin-2-one (9b). To a solution of β -lactam **18b** (171 mg, 0.39 mmol) in pyridine-acetonitrile (1/1, 4 mL) was added dropwise HF/pyridine (70/30, 1 mL) at 0 °C, and the mixture was allowed to warm to room temperature. Then, the mixture was stirred for 20 h at room temperature. The reaction was quenched with saturated aqueous sodium carbonate (10 mL) and the reaction mixture was diluted with ethyl acetate (80 mL), washed with saturated aqueous copper sulfate (15 mL x 3), water and brine, dried over anhydrous magnesium sulfate and evaporated to dryness. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 9/1) gave (3R,4S)-1-(tert-butoxycarbonyl)-3-hydroxy-4-[(E)-2-methylhexa-1,5-dienyl]azetidin-2-one as a colorless oil (107 mg, 97 % yield). To a solution of the 3-OH- β -lactam thus obtained (81 mg, 0.29 mmol) in dichloromethane (6 mL) was added dropwise chlorotriethylsilane (58 μ L, 0.43 mmol), triethylamine (42 μ L, 0.57 mmol) and a catalytic amount of DMAP at room temperature, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated aqueous ammonium chloride (10 mL), and the reaction mixture was extracted with dichloromethane (30 mL x 3). The combined extracts were dried over anhydrous magnesium sulfate and evaporated to dryness. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 20/1) gave **9b** as a colorless oil (104 mg, 91% yield, 97% ee): $[\alpha]_D^{22} +48.8$ (c 0.43, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 0.64 (t, J = 7.2 Hz, 6 H), 0.95 (t, J = 7.2 Hz, 9 H), 1.48 (s, 9 H), 1.77 (d, J = 1.2 Hz, 3 H), 2.17 (m, 4 H), 4.74 (dd, J = 9.6, 5.7 Hz, 1 H), 4.88 (d, J = 5.7 Hz, 1 H), 5.05-4.93 (m, 3 H), 5.28 (d, J = 9.6 Hz, 1 H), 5.81 (m, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.4, 6.3, 27.9, 31.8, 39.0, 56.3, 76.6, 82.7, 114.6, 118.0, 137.8, 142.6, 147.9, 166.3. HRMS (DCI/NH₃) *m/z* calcd for C₂₁H₃₇NO₄Si-NH₄⁺: 413.2836. Found: 413.2830 (Δ = -0.6 ppm).

Compound **9c** was synthesized from the chiral TIPS-ester **19** and pentenaldimine *via* **17c** and **18c** in a similar manner to compound **9b**.

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(3-butenyl)azetidin-2-one (17c): 56% yield; colorless oil; $[\alpha]_D^{25} +10.1$ (c 1.39, CHCl₃); IR (neat) 2944, 2867, 1749, 1513 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.14 (m, 21 H), 1.97 (m, 2 H), 2.17 (m, 2 H), 3.78 (s, 3 H), 4.16 (m, 1 H), 5.06-4.97 (m, 3 H), 5.82 (ddt, J = 13.1, 10.4, 6.3 Hz, 1 H), 6.86 (d, J = 8.9 Hz, 2 H), 7.33 (d, J = 8.9 Hz, 2 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 12.1, 17.8, 26.4, 29.8, 55.5, 57.9, 76.0, 114.4, 115.2, 118.5, 131.0, 137.7, 156.1, 165.6, 170.6. MS *m/z* 404 (M-H⁺), 360 (M⁺-i-Pr); HRMS (DCI/NH₃) *m/z* calcd for C₂₃H₃₇NO₃Si-H⁺: 404.2621. Found: 404.2606 (Δ = -3.8 ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-(3-butenyl)azetidin-2-one (18c): 72% yield (two steps); colorless oil; $[\alpha]_D^{28} +16.3$ (c 4.37, CHCl₃); IR (neat) 2945, 2867, 1808, 1725, 1463 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.09 (m, 21 H), 1.51 (s, 9 H), 1.93 (m, 2 H), 2.20 (m, 2 H), 4.07 (q, J = 5.9 Hz, 1 H), 5.08-4.96 (m, 3 H), 5.82 (ddt, J = 17.0, 10.3, 6.5 Hz, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 11.9, 17.7, 27.1, 28.0, 29.9, 58.0, 76.1, 83.2, 115.0, 137.7, 166.3, 169.0.

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triethylsiloxy-4-(3-butenyl)azetidin-2-one

(9c): 90% yield (two steps); colorless oil; 97% ee; $[\alpha]_D^{30} +17.4$ (c 0.23, CHCl_3); IR (neat) 2956, 2914, 1809, 1725 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 0.69 (t, $J = 7.9$ Hz, 6 H), 0.97 (t, $J = 7.0$ Hz, 9 H), 1.50 (s, 9 H), 1.90 (m, 2 H), 2.15 (m, 2 H), 4.03 (dt, $J = 7.6, 5.1$ Hz, 1 H), 4.85 (d, $J = 5.9$ Hz, 1 H), 5.08–4.97 (m, 1 H), 5.82 (ddt, $J = 16.9, 10.3, 6.6$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 6.6, 26.9, 28.0, 29.9, 57.7, 75.6, 83.3, 115.0, 137.7, 166.2, 169.1. MS m/z 373 ($\text{M}\cdot\text{NH}_3^+$); 317 ($\text{M}\cdot\text{NH}_3^+ - t\text{-Bu}$); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{18}\text{H}_{33}\text{NO}_4\text{Si}\cdot\text{NH}_4^+$: 373.2523. Found: 373.2528 ($\Delta = 1.4$ ppm).

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(1-acetoxyp-2-enyl)azetidin-2-one (20a). To a stirred solution of aldehyde **16** (413 mg, 1.1 mmol) in 50 mL THF at -78°C was added dropwise 1.2 mL (1M in THF, 1.2 mmol) of vinylmagnesium bromide. The solution was allowed to stir for 30 min, and 4.2 mL (4.4 mmol) of Ac_2O was added dropwise and the temperature was allowed to slowly warm to room temperature. The mixture was then quenched with water, extracted with EtOAc three times, and washed with brine. The combined organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The resulting crude oil was purified on silica gel (hexanes/EtOAc = 5/1) to yield **20a** as a colorless oil (480 mg, 98% yield): ^1H NMR (250.133 MHz, CDCl_3) δ 1.14 (m, 21 H), 3.76 (s, 3 H), 4.33 (dd, $J = 6.1, 5.6$ Hz, 1 H), 5.09 (d, $J = 5.2$ Hz, 1 H), 5.24 (d, $J = 11.3$ Hz, 1 H), 5.26 (d, $J = 16.1$ Hz, 1 H), 5.55 (dd, $J = 6.6, 6.2$ Hz, 1 H); 6.84 (d, $J = 8.9$ Hz, 2 H), 7.38 (d, $J = 8.9$ Hz, 2 H); ^{13}C NMR (62.896 MHz, CDCl_3) δ 11.9, 17.7, 17.8, 20.8, 55.4, 60.1, 73.0, 75.8, 114.0, 118.4, 119.6, 156.3, 169.4.

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(prop-2-enyl)azetidin-2-one (17d). To a mixture of $\text{Pd}(\text{dba})_3\cdot\text{CHCl}_3$ (28.5 mg, 0.028 mmol) and HCO_2NH_4 (138.7 mg, 2.20 mmol) under argon was added dioxane (3 mL) and PBU_3 (0.03 mL, 0.11 mmol). After heating the mixture to reflux with stirring, β -lactam **20a** (492 mg, 1.10 mmol) was added in dioxane (3 mL), and allowed to react for 18 h. The reaction mixture was then diluted with EtOAc, quenched with a saturated aqueous solution of KF, extracted three times with EtOAc, and washed with saturated aqueous KF solution and brine until the aqueous layer is no longer black. The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The resulting crude oil was purified by column chromatography on silica gel (hexanes/EtOAc = 9/1) to yield **17d** as a colorless oil (278.5 mg, 65% yield): ^1H NMR (250.133 MHz, CDCl_3) δ 1.04 (m, 21 H), 2.65 (m, 2 H), 3.77 (s, 3 H), 4.19 (m, 1 H), 5.05 (d, $J = 10.3$ Hz, 1 H), 5.06 (d, $J = 5.2$ Hz, 1 H), 5.09 (d, $J = 17.2$ Hz, 1 H), 6.85 (d, $J = 8.9$ Hz, 2 H), 7.33 (d, $J = 8.9$ Hz, 2 H); ^{13}C NMR (62.896 MHz, CDCl_3) δ 12.0, 17.7, 17.8, 17.9, 41.9, 55.4, 58.7, 74.7, 76.1, 114.3, 117.8, 118.7, 131.0, 134.1, 156.1, 169.9. HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{35}\text{NO}_3\text{Si}\cdot\text{H}^+$: 390.2464. Found: 390.2463 ($\Delta = 0.4$ ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-(prop-2-enyl)azetidin-2-one (9d). β -Lactam **9d** was prepared from **17d** in the same procedure as that described above for **18b**. 96% yield (two steps); colorless oil; ^1H NMR (250.133 MHz, CDCl_3) δ 1.05 (m, 21 H), 1.44 (s, 9 H), 2.56 (m, 2 H), 4.08 (dd, 1 H), 4.93 (d, $J = 5.2$ Hz, 1 H), 5.08 (m, 2 H), 5.82 (m, 1 H); ^{13}C NMR (62.896 MHz, CDCl_3) δ 11.9, 17.6, 17.7, 27.9, 32.6, 58.3, 76.1, 83.1, 117.9, 133.8, 148.3, 166.0.

HRMS (FAB) m/z calcd for $C_{20}H_{37}NO_4Si \cdot H^+$: 384.2574. Found: 384.2570 ($\Delta = -1.0$ ppm).

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-vinylazetidin-2-one (17e).

To a suspension of methyltriphenylphosphonium bromide (568 mg, 1.59 mmol) in 20 mL anhydrous THF at $-78^\circ C$ was added *n*-BuLi (0.64 mL, 2.5 M in hexane, 1.60 mmol) under nitrogen. The solution was allowed to warm to room temperature and stirred for 20 min, and cooled to $-78^\circ C$. A solution of 4-formyl- β -lactam **16** (400 mg, 1.06 mmol) in 15 mL THF was added dropwise at that temperature, stirred for 1.5 h and warmed to room temperature. The reaction was quenched with saturated aqueous ammonium chloride (15 mL), and the aqueous layer was extracted with dichloromethane (30 mL x 3). The combined extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified on a silica gel column using hexane/ethyl acetate (10/1) as the eluant to afford **17e** as a colorless oil (358 mg, 90% yield): 1H NMR ($CDCl_3$) δ 1.09 (m, 21 H), 3.77 (s, 3 H), 4.56 (dd, $J = 8.3, 5.0$ Hz, 1 H), 5.09 (d, $J = 5.1$ Hz, 1 H), 5.45 (d, $J = 9.5$ Hz, 1 H), 5.51 (d, $J = 16.3$ Hz, 1 H), 5.97 (ddd, $J = 17.3, 9.9, 8.4$ Hz, 1 H), 6.83 (d, $J = 9.0$ Hz, 2 H), 7.38 (d, $J = 9.0$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 17.65, 17.71, 55.4, 62.4, 77.5, 114.2, 118.4, 121.4, 131.5, 133.6, 155.1, 165.3. Anal. Calcd for $C_{21}H_{33}NO_3Si$: C, 67.16; H, 8.86; N, 3.73. Found: C, 67.37; H, 8.61; N, 3.79.

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-vinylazetidin-2-one (9e).

β -Lactam **9e** was prepared from **17e** in the same procedure as that described for **18b**: 86% yield for two steps; colorless oil; 1H NMR ($CDCl_3$) δ 1.06 (m, 21 H), 1.49 (s, 9 H), 4.49 (dd, $J = 8.3, 5.7$ Hz, 1 H), 5.00 (d, $J = 4.6$ Hz, 1 H), 5.40 (d, $J = 16.8$ Hz, 1 H), 5.44 (d, $J = 6.0$ Hz, 1 H), 5.90 (ddd, $J = 17.6, 10.2, 8.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 17.54, 17.59, 28.0, 61.4, 77.3, 83.3, 119.4, 121.3, 131.7, 148.1, 165.7. Anal. Calcd for $C_{19}H_{35}NO_4Si$: C, 61.75; H, 9.55; N, 3.79. Found: C, 62.00; H, 9.36; N, 3.84.

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(1-tert-butyldimethylsiloxy-2-propenyl)azetidin-2-one (17f). β -Lactam **17f** was prepared from **16** in the same procedure as that described for **20a**: 82% yield for two steps; colorless oil; 1H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.05 (s, 3 H), 0.86 (s, 9 H), 1.11 (m, 21 H), 3.77 (s, 3 H), 4.30 (dd, $J = 5.0, 2.6$ Hz, 1 H), 4.61 (s, 1 H), 5.10 (m, 2 H), 5.30 (m, 1 H), 5.90 (m, 1 H), 6.80 (d, $J = 9.0$ Hz, 2 H), 7.37 (d, $J = 9.0$ Hz, 2 H). HRMS (CI/ NH_3) m/z calcd for $C_{28}H_{49}NO_4Si_2 \cdot H^+$: 520.3278. Found: 520.3273 ($\Delta = 1.0$ ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-[(R)-1-tert-butyldimethylsiloxy-2-propenyl]azetidin-2-ones (18f). β -Lactam **18f** was prepared from **17f** in the same procedure as that described for **18b**: 82% yield for two steps; colorless oil; 1H NMR (250 MHz, $CDCl_3$) δ 0.02 (s, 3 H), 0.05 (s, 3 H), 0.86 (s, 9 H), 1.08 (m, 21 H), 1.49 (s, 9 H), 4.01 (dd, $J = 5.7, 3.7$ Hz, 1 H), 4.60 (dd, $J = 8.1, 3.6$ Hz, 1 H), 4.93 (d, $J = 6.0$ Hz, 1 H), 5.14 (d, $J = 10.9$ Hz, 1 H), 5.18 (d, $J = 17.0$ Hz, 1 H), 6.18 (m, 1 H); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ -5.0, -4.1, 11.9, 17.7, 25.8, 28.0, 61.7, 72.0, 75.5, 82.9, 116.7, 139.2, 166.2. HRMS (FAB) m/z calcd for $C_{26}H_{51}NO_4Si_2 \cdot Na^+$: 536.3204. Found: 536.3196 ($\Delta = 1.4$ ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triethylsiloxy-4-[(R)-1-triethylsiloxybut-3-enyl]azetidin-2-ones (9f). To a solution of β -lactam **18f** (250 mg, 0.487 mmol) in 6 mL of pyridine/acetonitrile (1/1) was added dropwise HF/pyridine (70/30, 1.50 mL) at 0 °C, and the mixture was allowed to warm to room temperature. Then, the mixture was stirred at room temperature for 36 h. The reaction was quenched with saturated aqueous sodium carbonate solution (10 mL) and the reaction mixture was diluted with ethyl acetate (70 mL), washed with saturated aqueous copper sulfate solution (15 mL x 3), water and brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was purified on a silica gel column using hexane/ethyl acetate (1/1 followed by 1/2) as the eluant to afford (3R,4S)-1-(tert-butoxycarbonyl)-3-hydroxy-4-(1-hydroxyprop-2-enyl)azetidin-2-one as a white solid (106.5 mg, 90% yield): mp 121-123 °C; ^1H NMR (250 MHz, CDCl_3) δ 1.45 (s, 9 H), 3.34 (bs, 1 H), 4.11 (dd, J = 4.8, 3.0 Hz, 1 H), 4.49 (dd, J = 4.1, 1.2 Hz, 1 H), 4.88 (d, J = 6.0 Hz, 1 H), 5.17 (d, J = 10.8 Hz, 1 H), 5.32 (dd, J = 17.1, 0.9 Hz, 1 H), 6.00 (m, 1 H); ^{13}C NMR (62.896 MHz, CDCl_3) δ 27.8, 61.2, 71.0, 75.8, 84.0, 116.1, 136.7, 148.6, 167.8. HRMS (CI/NH_3) m/z calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_5\cdot\text{NH}_4^+$: 261.1450. Found: 261.1461 (Δ = -4.0 ppm).

To a solution of the 3-OH- β -lactam thus obtained (85 mg, 0.349 mmol) and DMAP (21.3 mg, 0.175 mmol) in dichloromethane (4 mL) was added chlorotriethylsilane (0.24 mL, 1.40 mmol) and triethylamine (0.29 mL, 2.10 mmol) at room temperature, and the mixture was stirred for 8 h at the same temperature. The reaction was quenched with saturated aqueous ammonium chloride solution (10 mL), and the reaction mixture was extracted with dichloromethane (20 mL x 3). The combined extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Column chromatography of the residue on silica gel using hexane/ethyl acetate (8/1) as the eluant afforded **9f** as a colorless oil (164 mg, 99.5% yield): ^1H NMR (250.133 MHz, CDCl_3) δ 0.34-0.71 (m, 12 H), 0.87- 1.00 (m, 18 H), 1.49 (s, 9 H), 3.99 (dd, J = 5.5, 4.9 Hz, 1 H), 4.56 (dd, J = 7.7, 4.6 Hz, 1 H), 4.82 (d, J = 6.0 Hz, 1 H), 5.12 (d, J = 10.1 Hz, 1 H), 5.16 (d, J = 17.3 Hz, 1 H), 6.10 (m, 1 H); ^{13}C NMR (62.896 MHz, CDCl_3) δ 4.4, 4.9, 6.4, 6.7, 28.0, 61.4, 72.0, 75.2, 82.9, 116.6, 138.9, 148.5, 166.3. HRMS (FAB) m/z calcd for $\text{C}_{23}\text{H}_{45}\text{NO}_5\text{Si}_2^+$: 494.2734. Found: 494.2723 (Δ = 2.2 ppm).

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(3-iodophenyl)azetidin-2-one (20b). β -Lactam **20b** was prepared from **19** in a procedure similar to that described for **17b**: 79% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 0.92 (m, 21 H), 3.75 (s, 3 H), 5.05 (d, J = 5.1 Hz, 1 H), 5.22 (dd, J = 1.2, 4.8 Hz, 1 H), 6.79 (d, J = 9.3 Hz, 2 H), 7.07 (t, J = 7.8 Hz, 1 H), 7.26 (d, J = 9.0 Hz, 2 H), 7.28 (t, J = 7.8 Hz, 1 H), 7.64 (d, J = 8.1 Hz, 1 H), 7.69 (d, J = 1.5 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 11.7, 17.5, 55.4, 62.4, 77.8, 94.1, 114.4, 118.6, 127.5, 130.0, 130.7, 136.6, 137.2, 137.4, 156.3, 165.3. HRMS (FAB) m/z calcd for $\text{C}_{25}\text{H}_{34}\text{INO}_3\text{Si}\cdot\text{H}^+$: 552.1431. Found: 552.1432 (Δ = -0.2 ppm).

(3R,4S)-1-(4-Methoxyphenyl)-3-triisopropylsiloxy-4-(3-ethenylphenyl)azetidin-2-one (17g). To a solution of **20b** (575 mg, 1.10 mmol) in dry dioxane (40 mL) at room temperature under nitrogen was added triphenylphosphine (115 mg, 0.44 mmol), $\text{Pd}_2(\text{dba})_3$ (40 mg, 0.044 mmol), and tributylvinyltin (0.453 mL, 1.55 mmol). The mixture was then heated to 80 °C with stirring

overnight. The mixture was diluted with ethyl acetate and the mixture was passed through a short pad of silica. The organic layer was washed with 1M KF, dried over anhydrous magnesium sulfate, and purified on silica gel using 20% ethyl acetate in hexane to afford **17g** as a white solid (420 mg, 87% yield): ^1H NMR (300 MHz, CDCl_3) δ 0.92 (m, 21 H), 3.72 (s, 3 H), 5.12 (d, $J = 5.1$ Hz, 1 H), 5.22 (m, 2 H), 5.61 (d, $J = 17.1$ Hz, 1 H), 6.68 (dd, $J = 11.1, 17.7$ Hz, 1 H), 6.77 (d, $J = 9$ Hz, 2 H), 7.23 (t, $J = 7.2$ Hz, 1 H), 7.28 (d, $J = 8.7$ Hz, 2 H), 7.29 (m, 2 H), 7.34 (m, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 11.7, 17.5, 55.4, 63.2, 77.8, 114.1, 114.3, 118.6, 126.1, 126.2, 127.8, 128.4, 131.0, 134.4, 136.5, 137.6, 156.1, 165.6. HRMS (FAB) m/z calcd for $\text{C}_{27}\text{H}_{37}\text{NO}_3\text{Si}\cdot\text{H}^+$: 452.2621. Found: 452.2622 ($\Delta = -0.2$ ppm).

(3R,4S)-1-(tert-Butoxycarbonyl)-3-triisopropylsiloxy-4-(3-ethenylphenyl)azetidin-2-one (9g). β -Lactam **9g** was prepared from **17g** in the same procedure as that described for **18b**: 70% yield for two steps; colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.86 (m, 21 H), 1.39 (s, 9 H), 5.04 (d, $J = 5.4$ Hz, 1 H), 5.15 (d, $J = 5.7$ Hz, 1 H), 5.21 (d, $J = 10.8$ Hz, 1 H), 5.70 (d, $J = 17.4$ Hz, 1 H), 6.67 (dd, $J = 10.8, 17.4$ Hz, 1 H), 7.17 (d, $J = 7.5$ Hz, 1 H), 7.27 (m, 2 H), 7.31 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 11.6, 17.3, 27.8, 62.2, 77.6, 83.3, 113.9, 126.0, 126.1, 127.5, 128.1, 134.2, 136.5, 137.4, 147.8, 166.2. HRMS (FAB) m/z calcd for $\text{C}_{25}\text{H}_{39}\text{NO}_4\text{Si}\cdot\text{H}^+$: 446.2727. Found: 446.2741 ($\Delta = -3.1$ ppm).

Compounds **7b-t** were synthesized in a similar manner to compound **7a**. Their characterization data are shown below.

2-Debenzoyl-2-(pent-4-enoyl)-7-triethylsilyl-13-[(2R,3S,E)-3-tert-butoxycarbonylamino-2-triethylsiloxyocta-4,6-dienoyl]baccatin III (7b): 84% yield from **8b** and **9a-E**; white solid; $[\alpha]_{\text{D}}^{20} -70.0$ (c 0.20, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.60 (m, 12 H), 0.96 (m, 18 H), 1.15 (s, 6 H), 1.41 (s, 9 H), 1.62 (s, 3 H), 1.88 (m, 1 H), 1.95 (s, 3 H), 2.18 (s, 3 H), 2.20 (m, 2 H), 2.27 (s, 3 H), 2.41 (m, 4 H), 2.50 (m, 1 H), 2.79 (t, $J = 6.1$ Hz, 2 H), 3.69 (d, $J = 6.9$ Hz, 1 H), 4.19 (d, $J = 7.9$ Hz, 1 H), 4.29 (d, $J = 1.8$ Hz, 1 H), 4.41 (dd, $J = 10.5, 6.6$ Hz, 1 H), 4.45 (d, $J = 7.9$ Hz, 1 H), 4.94 (m, 3 H), 5.03-5.14 (m, 4 H), 5.43 (m, 2 H), 5.61 (m, 2 H), 5.80 (m, 2 H), 6.10 (t, $J = 8.5$ Hz, 1 H), 6.41 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.4, 5.2, 6.4, 6.6, 9.9, 14.1, 20.7, 21.0, 22.7, 26.3, 28.2, 28.4, 29.6, 33.9, 35.0, 36.2, 37.1, 43.2, 46.5, 55.3, 58.4, 71.1, 72.1, 74.0, 74.5, 75.0, 78.5, 80.9, 84.4, 116.0, 116.1, 128.2, 130.8, 133.5, 135.9, 136.7, 140.8, 155.4, 169.4, 170.1, 171.7, 174.0, 202.1. HRMS (FAB, $\text{CHCl}_3/\text{NBA}/\text{NaCl}/\text{PPG}$) m/z calcd for $\text{C}_{54}\text{H}_{87}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1068.5512. Found: 1068.5520 ($\Delta = -0.7$ ppm).

2-Debenzoyl-2-(but-3-enoyl)-7-triethylsilyl-13-[(2R,3S,E)-3-tert-butoxycarbonylamino-2-triethylsiloxy-5-methylnona-4,8-dienoyl]baccatin III (7c): 69% yield from **8a** and **9b**; white solid; ^1H NMR (250 MHz, CDCl_3) δ 0.60 (m, 12 H), 0.94 (m, 18 H), 1.15 (s, 6 H), 1.40 (s, 9 H), 1.62 (s, 3 H), 1.73 (s, 3 H), 1.86 (m, 1 H), 1.95 (s, 3 H), 2.10 – 2.19 (m, 6 H), 2.15 (s, 3 H), 2.23 (s, 3 H), 2.48 (m, 1 H), 3.16 (t, $J = 7.5$ Hz, 2 H), 3.69 (d, $J = 6.8$ Hz, 1 H), 4.17 (d, $J = 8.0$ Hz, 1 H), 4.22 (d, $J = 2.3$ Hz, 1 H), 4.41 (m, 1 H), 4.46 (d, $J = 8.0$ Hz, 1 H), 4.71 (t, $J = 8.2$ Hz, 1 H), 4.84 – 5.07 (m, 4 H), 5.17 – 5.30 (m, 3 H), 5.75 (m, 1 H), 5.94 (m, 1 H), 6.06 (t, $J =$

8.8 Hz, 1 H), 6.42 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 5.3, 6.7, 9.9, 14.1, 16.9, 20.8, 21.1, 22.5, 26.3, 28.2, 31.8, 35.0, 37.1, 38.8, 39.6, 43.2, 46.5, 51.4, 58.4, 71.3, 72.1, 74.4, 75.0, 78.7, 79.4, 80.7, 84.3, 114.8, 119.2, 121.7, 129.6, 133.2, 137.9, 139.4, 140.9, 155.1, 169.2, 169.9, 171.7, 172.2, 201.8. HRMS (FAB, MeOH/NBA/NaCl/PEG) m/z calcd for $\text{C}_{55}\text{H}_{89}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1082.5668. Found: 1082.5721 ($\Delta = -4.9$ ppm).

2-Debenzoyl-2-(pent-4-enoyl)-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triethylsiloxyhept-6-enoyl]baccatin III (7d): 86% yield from **8b** and **9c**; white solid, mp 78-80 °C; $[\alpha]_{\text{D}}^{20}$ -40.0 (c 0.20, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.58 (m, 12 H), 0.93 (m, 18 H), 1.12 (s, 6 H), 1.37 (s, 9 H), 1.48 (m, 2 H), 1.60 (s, 3 H), 1.85 (m, 1 H), 1.93 (s, 3 H), 2.06 (m, 1 H), 2.12 (s, 3 H), 2.17 (m, 2 H), 2.22 (s, 3 H), 2.39 (m, 4 H), 2.51 (m, 1 H), 3.66 (d, $J = 6.8$ Hz, 1 H), 4.00 (m, 1 H), 4.16 (d, $J = 7.9$ Hz, 1 H), 4.21 (d, $J = 1.0$ Hz, 1 H), 4.38 (dd, $J = 10.5, 6.7$ Hz, 1 H), 4.73 (d, $J = 10.2$ Hz, 1 H), 4.90 (d, $J = 8.5$ Hz, 1 H), 4.95 – 5.12 (m, 4 H), 5.40 (d, $J = 6.8$ Hz, 1 H), 5.70 – 5.91 (m, 2 H), 6.04 (t, $J = 9.0$ Hz, 1 H), 6.39 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 5.2, 6.7, 9.9, 14.1, 20.8, 21.0, 22.7, 26.3, 28.2, 28.4, 30.1, 32.0, 34.0, 35.0, 37.1, 43.2, 46.5, 53.0, 58.4, 71.1, 72.1, 73.5, 74.5, 75.0, 76.6, 78.4, 79.4, 80.8, 84.3, 115.4, 115.9, 133.3, 136.6, 137.4, 140.7, 155.6, 169.2, 169.8, 171.9, 173.7, 201.8. HRMS (FAB, DCM/NBA/NaCl) m/z calcd for $\text{C}_{53}\text{H}_{87}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1056.5512. Found: 1056.5527 ($\Delta = -1.4$ ppm).

2-Debenzoyl-2-[(R)-3-methylhept-6-enoyl]-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triethylsiloxyhept-6-enoyl]baccatin III (7e): 96% yield from **8e** and **9c**; white solid, mp 72-74 °C; ^1H NMR (250 MHz, CDCl_3) δ 0.49-0.67 (m, 12 H), 0.86-1.00 (m, 21 H), 1.13 (s, 6 H), 1.22 (m, 2 H), 1.32 (m, 1 H), 1.38 (s, 9 H), 1.60 (s, 3 H), 1.65 (m, 2 H), 1.86 (m, 1 H), 1.94 (s, 3 H), 2.05 (m, 5 H), 2.13 (s, 3 H), 2.23 (s, 3 H), 2.45 (m, 2 H), 3.67 (d, $J = 6.8$ Hz, 1 H), 4.00 (m, 1 H), 4.17 (d, $J = 7.9$ Hz, 1 H), 4.22 (d, $J = 1.5$ Hz, 1 H), 4.39 (dd, $J = 10.5, 6.4$ Hz, 1 H), 4.45 (d, $J = 8.1$ Hz, 1 H), 4.74 (d, $J = 10.2$ Hz, 1 H), 4.98 (m, 5 H), 5.39 (d, $J = 6.8$ Hz, 1 H), 5.80 (m, 2 H), 6.05 (t, $J = 8.6$ Hz, 1 H), 6.40 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 5.2, 6.7, 9.9, 14.1, 19.7, 20.8, 21.0, 22.7, 26.4, 28.2, 29.2, 30.1, 31.1, 32.0, 34.7, 35.7, 37.1, 42.0, 43.3, 46.6, 53.0, 58.4, 71.2, 72.1, 73.5, 74.1, 75.0, 76.7, 78.6, 79.4, 80.8, 84.3, 114.6, 115.3, 133.3, 137.4, 138.5, 140.8, 155.6, 169.2, 169.9, 172.0, 174.0, 201.9. MS (FAB) m/z calcd for $\text{C}_{56}\text{H}_{93}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1076.6. Found: 1076.5.

2-Debenzoyl-2-(3,3-dimethylhepta-6-enoyl)-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triethylsiloxy-hept-6-enoyl]baccatin III (7f): 84% yield from **8l** and **9c**; white solid, mp 68-71 °C; $[\alpha]_{\text{D}}^{20}$ -46.7 (c 0.3, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.55-0.68 (m, 12 H), 0.87-1.06 (m, 27 H), 1.14 (s, 3 H), 1.38 (s, 9 H), 1.40 (m, 4 H), 1.60 (s, 3 H), 1.86 (m, 1 H), 1.95 (s, 2 H), 2.03 (s, 3 H), 2.07 (m, 2 H), 2.14 (s, 3 H), 2.23 (m, 2 H), 2.50 (m, 1 H), 3.68 (s, $J = 6.7$ Hz, 1 H), 4.00 (m, 1 H), 4.16 (d, $J = 8.0$ Hz, 1 H), 4.23 (m, 1 H), 4.50 (d, $J = 8.0$ Hz, 1 H), 4.72 (d, $J = 10.1$ Hz, 1 H), 4.90-5.10 (m, 5 H), 5.38 (d, $J = 6.7$ Hz, 1 H), 5.81 (m, 2 H), 6.06 (m, 1 H), 6.41 (s, 1 H); ^{13}C NMR (63 MHz, CDCl_3) δ 4.7, 5.3, 6.7, 10.0, 14.2, 20.9, 21.1, 22.8, 26.5, 27.0, 27.3, 28.3, 28.6, 30.2, 32.1, 37.2, 41.2, 43.4, 46.4, 46.8, 53.0, 58.4, 71.2, 72.2, 73.6, 74.0,

75.1, 78.7, 79.4, 80.8, 84.4, 87.6, 114.2, 115.4, 133.3, 137.5, 139.2, 140.8, 155.5, 169.2, 170.0, 172.0, 202.2. FAB-HRMS (FAB, NBA-NaCl) m/e calcd for $C_{57}H_{95}NO_{15}Si_2 \cdot H^+$: 1090.6319. Found: 1090.6319 ($\Delta = 0.0$ ppm).

2-Debenzoyl-2-(2-allyloxybenzoyl)-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triethylsiloxyhept-6-enoyl]baccatin III (7g): 64% yield from **8i** and **9c**; white solid, mp 95-97 °C; 1H NMR (250 MHz, $CDCl_3$) δ 0.59 (m, 12 H), 0.94 (m, 18 H), 1.22 (s, 3 H), 1.22 (3 H), 1.37 (s, 9 H), 1.73 (s, 3 H), 1.98 (s, 3 H), 2.16 (s, 3 H), 2.19 (s, 1 H), 1.45-2.60 (m, 8 H), 2.91 (s, 1 H), 3.75 (d, $J = 6.5$ Hz), 4.02 (m, 1 H), 4.21 (s, 1 H), 4.26 (d, $J = 8.1$ Hz, 1 H), 4.40 (d, $J = 8.1$ Hz, 1 H), 4.59 (m, 1 H), 4.73 (d, $J = 10.3$ Hz, 1 H), 4.84 (m, 2 H), 4.89 (d, $J = 8.6$ Hz, 1 H), 4.99 (d, $J = 9.2$ Hz, 1 H), 5.04 (d, $J = 16.5$ Hz, 1 H), 5.28 (d, $J = 10.7$ Hz, 1 H), 5.39 (d, $J = 16.5$ Hz, 1 H), 5.68 (d, $J = 6.5$ Hz, 1 H), 5.79 (m, 1 H), 6.02 (m, 1 H), 6.09 (t, $J = 9.0$ Hz, 1 H), 6.45 (s, 1 H), 6.96 (d, $J = 8.5$ Hz, 1 H), 7.02 (t, $J = 7.6$ Hz, 1 H), 7.45 (t, $J = 8.3$ Hz, 1 H), 7.79 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 4.7, 5.3, 6.8, 10.1, 14.2, 20.9, 21.2, 22.8, 26.4, 28.2, 30.2, 32.2, 36.1, 37.4, 43.0, 46.6, 52.9, 58.6, 69.1, 71.5, 72.2, 73.7, 75.3, 76.0, 77.5, 79.3, 81.1, 84.3, 113.5, 115.5, 118.0, 120.9, 132.0, 132.7, 133.7, 137.5, 140.8, 155.6, 157.2, 167.0, 169.3, 169.8, 172.0, 202.1.

2-Debenzoyl-2-allyloxyacetyl-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triethylsiloxyhept-6-enoyl]baccatin III (7i): 69% yield from **8d** and **9c**; white solid; 1H NMR (300 MHz, $CDCl_3$) δ 0.62 (m, 12 H), 0.98 (m, 18 H), 1.14 (s, 3 H), 1.39 (s, 9 H), 1.59 (s, 3 H), 1.65 (s, 3 H), 1.98 (s, 3 H), 2.19 (s, 3 H), 2.21 (s, 1 H), 2.43 (m, 1 H), 3.63 (d, $J = 6.9$ Hz, 1 H), 3.98-4.22 (m, 3 H), 4.41 (m, 2 H), 4.78 (d, $J = 10.2$ Hz, 1 H), 4.89-5.11 (m, 4 H), 5.29 (m, 1 H), 5.45 (d, $J = 6.9$ Hz, 1 H), 5.62-6.09 (m, 3 H), 6.41 (s, 1 H).

2-Debenzoyl-2-(pent-4-enoyl)-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triisopropylsiloxy-3-(3-vinylphenyl)propanoyl]baccatin III (7j): 66% yield from **8b** and **9g**; white solid; 1H NMR (300 MHz, $CDCl_3$) δ 0.56 (m, 6 H), 0.90 (t, $J = 7.8$ Hz, 9 H), 1.08 (m, 21H), 1.18 (s, 3 H), 1.25 (s, 3H), 1.38 (s, 9 H), 1.63 (s, 3 H), 1.89 (m, 1 H), 1.98 (s, 3 H), 2.16 (s, 3 H), 2.21 (m, 2 H), 2.40 (s, 3 H), 2.42 (m, 4 H), 2.49 (m, 1 H), 3.71 (d, $J = 6.9$ Hz, 3 H), 4.16 (d, $J = 8.1$ Hz, 1 H), 4.44 (m, 2 H), 4.73 (d, $J = 1.5$ Hz, 1 H), 4.95 (d, $J = 8.1$ Hz, 1 H), 5.05 (d, $J = 11.4$ Hz, 1 H), 5.26 (d, $J = 6.9$ Hz, 1H), 5.41 (m, 1 H), 5.71 (d, $J = 17.7$ Hz, 1 H), 5.76 (d, $J = 10.8$ Hz, 1 H), 5.83 (m, 1H), 6.14 (t, $J = 8.7$ Hz, 1 H), 6.43 (s, 1 H), 6.69 (dd, $J = 11.1, 17.7$, 1 H), 7.13 (d, $J = 6.6$ Hz, 1 H), 7.29 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.3, 6.7, 10.0, 12.5, 13.6, 14.2, 17.5, 17.8, 19.9, 20.8, 21.2, 23.0, 25.8, 26.4, 26.8, 27.8, 28.23, 28.4, 34.0, 35.2, 37.1, 43.2, 46.6, 58.4, 69.5, 71.1, 74.6, 75.0, 75.7, 78.6, 80.9, 84.4, 114.2, 116.0, 124.4, 125.6, 125.9, 128.7, 133.4, 136.6, 137.9, 140.6, 169.2, 169.7, 173.9, 201.8. HRMS (FAB) m/z calcd for $C_{60}H_{93}NO_{15}Si_2 \cdot H^+$: 1124.6162. Found: 1124.6100 ($\Delta = 5.0$ ppm).

2-Debenzoyl-2-(2-but-3-enylbenzoyl)-7-triethylsilyl-13-[(2R,3S)-3-tert-butoxycarbonylamino-2-triisopropylsiloxyhex-5-enoyl]baccatin III (7k): 92% yield from **8h** and **9d**; white solid; mp 96-97 °C; $[\alpha]_D^{22}$ -65 (c 0.23, $CHCl_3$); 1H NMR (250 MHz, $CDCl_3$) δ 0.60

(m, 6 H), 0.93 (m, 6 H), 1.14 (s, 27 H), 1.24 (s, 3 H), 1.26 (s, 3H), 1.34 (s, 9 H), 1.70 (s, 3 H), 1.89 (m, 1 H), 2.02 (s, 3 H), 2.18 (s, 1 H), 2.30 (s, 3 H), 2.36-2.59 (m, 7 H), 3.12 (m, 2 H), 3.81 (d, $J = 6.7$ Hz, 1 H), 4.11-4.28 (m, 2 H), 4.46 (m, 1 H), 4.51 (s, 1 H), 4.79 (d, $J = 10.4$ Hz, 1 H), 4.90-5.21 (m, 5 H), 5.66 (d, $J = 6.3$ Hz, 1 H), 5.74-5.90 (m, 2 H), 6.12 (m, 1 H), 6.48 (s, 1 H), 7.26-7.37 (m, 2 H), 7.45-7.50 (m, 1 H), 8.13 (d, $J = 7.9$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.3, 6.7, 10.1, 12.5, 12.9, 14.4, 18.2, 20.9, 21.3, 22.8, 26.4, 28.2, 29.7, 33.8, 35.4, 37.0, 37.2, 43.3, 46.8, 53.9, 58.4, 71.7, 72.3, 73.4, 75.1, 78.9, 79.5, 81.0, 84.2, 115.0, 118.2, 126.3, 127.9, 131.3, 131.6, 132.6, 133.3, 134.1, 138.1, 140.9, 145.2, 155.5, 167.3, 169.3, 169.8, 172.3, 201.9. HRMS (FAB) m/z calcd for $\text{C}_{61}\text{H}_{95}\text{NO}_{15}\text{Si}_2\cdot\text{H}^+$: 1138.6319. Found: 1138.6313 ($\Delta = 0.5$ ppm).

2-Debenzoyl-2-[(*R*)-3-methylhept-6-enoyl]-7-triethylsilyl-13-[(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxyhex-5-enoyl]baccatin III (7l): 97% yield from **8e** and **9d**; white solid; ^1H NMR (250 MHz, CDCl_3) δ 0.53 (m, 6 H), 0.89 (m, 9 H), 0.96 (d, $J = 6.2$ Hz, 3 H), 1.10 (m, 27 H), 1.37 (s, 6 H), 1.38 (m, 3 H), 1.60 (s, 3 H), 1.85 (m, 1 H), 1.94 (s, 3 H), 2.06 (m, 5 H), 2.13 (s, 3 H), 2.19 (s, 3 H), 2.22 (m, 1 H), 2.33 (m, 2 H), 2.45 (m, 1 H), 3.66 (d, $J = 6.6$ Hz, 1 H), 4.03 (m, 1 H), 4.17 (d, $J = 7.9$ Hz, 1 H), 4.41 (m, 3 H), 4.75 (d, $J = 10.1$ Hz, 1 H), 4.91 (m, 2 H), 5.06 (m, 2 H), 5.39 (d, $J = 6.6$ Hz, 1 H), 5.75 (m, 2 H), 6.0 (t, $J = 9.1$ Hz, 1 H), 6.40 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.3, 6.7, 9.9, 12.8, 14.3, 18.1, 18.15, 19.7, 20.8, 21.0, 22.9, 26.3, 28.2, 29.1, 31.1, 34.8, 35.6, 36.9, 37.1, 41.9, 43.2, 46.5, 54.0, 58.4, 71.7, 72.1, 73.2, 74.1, 75.1, 76.7, 78.6, 79.5, 80.8, 84.3, 114.6, 118.2, 133.2, 134.0, 138.5, 140.9, 155.6, 169.2, 169.8, 172.3, 174.0, 201.9. HRMS (FAB) m/z calcd for $\text{C}_{58}\text{H}_{97}\text{NO}_{15}\text{Si}_2\cdot\text{H}^+$: 1104.6475. Found: 1104.6475 ($\Delta = 0$ ppm).

2-Debenzoyl-2-(3,3-dimethylhept-6-enoyl)-7-triethylsilyl-13-[(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxyhex-5-enoyl]baccatin III (7m): 90% yield from **8l** and **9d**; white solid; ^1H NMR (250 MHz, CDCl_3) δ 0.56 (m, 6 H), 0.89 (m, 9 H), 1.03 (s, 3 H), 1.04 (s, 3 H), 1.10 (m, 21 H), 1.13 (s, 6 H), 1.37 (s, 9 H), 1.45 (m, 2 H), 1.59 (s, 3 H), 1.85 (m, 1 H), 1.95 (s, 3 H), 2.03 (m, 4 H), 2.13 (s, 3 H), 2.20 (s, 3 H), 2.26 (m, 2 H), 2.33 (m, 2 H), 2.49 (m, 1 H), 3.67 (d, $J = 6.5$ Hz, 1 H), 4.02 (m, 1 H), 4.16 (d, $J = 8.0$ Hz, 1 H), 4.39 (dd, $J = 10.3, 6.7$ Hz, 1 H), 4.45 (s, 1 H), 4.48 (d, $J = 8.0$ Hz, 1 H), 4.74 (d, $J = 10.1$ Hz, 1 H), 4.93 (m, 3 H), 5.08 (m, 2 H), 5.38 (d, $J = 6.5$ Hz, 1 H), 5.79 (m, 2 H), 6.01 (t, $J = 8.9$ Hz, 1 H), 6.41 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.3, 6.7, 9.9, 12.9, 14.3, 18.1, 18.15, 20.8, 21.0, 22.9, 26.4, 27.0, 27.2, 28.2, 28.6, 33.2, 34.7, 36.9, 37.1, 41.0, 43.3, 46.2, 46.7, 54.0, 58.4, 71.7, 72.1, 73.2, 73.9, 75.1, 76.8, 78.5, 79.5, 80.7, 84.3, 114.2, 118.3, 133.2, 134.1, 139.2, 140.9, 155.5, 169.2, 169.8, 172.3, 173.2, 201.9. HRMS (FAB) m/z calcd for $\text{C}_{59}\text{H}_{99}\text{NO}_{15}\text{Si}_2\cdot\text{H}^+$: 1118.6632. Found: 1118.6629 ($\Delta = 0.2$ ppm).

2-Debenzoyl-2-(3-methyl-3-allyloxybutanoyl)-7-triethylsilyl-13-[(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxy-hex-5-enoyl]baccatin III (7n): 92% yield from **8m** and **9d**; white solid; ^1H NMR (300 MHz, CDCl_3) δ 0.54 (m, 6 H), 0.89 (m, 9 H), 1.12 (m, 18 H), 1.37 (m, 9 H), 1.62 (s, 3 H), 1.98 (s, 3 H), 2.12 (s, 3 H), 2.15 (s, 3 H), 2.30-2.65 (m, 3 H), 3.64 (d, $J = 6.6$ Hz, 1 H), 3.95 (m, 2 H), 4.27 (d, $J = 8.1$ Hz, 1 H), 4.34 (m, 2 H), 4.74 (d, $J = 10.2$ Hz, 1 H),

4.93 (d, $J = 9.9$ Hz, 1 H), 4.93 (m, 2 H), 5.45 (d, $J = 6.6$ Hz, 1 H), 5.73 (m, 1 H), 5.96 (m, 1 H), 6.40 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 5.28, 6.69, 9.88, 12.50, 12.85, 14.17, 14.40, 17.90, 18.08, 18.16, 20.84, 21.01, 22.90, 25.32, 25.69, 26.36, 28.19, 36.23, 37.04, 37.25, 42.75, 46.40, 47.39, 54.05, 58.45, 60.35, 63.77, 79.37, 80.94, 84.45, 117.11, 118.09, 133.72, 134.20, 135.34, 140.58, 155.42, 169.29, 169.26, 170.48, 172.31, 201.99. HRMS (FAB) m/z calcd for $\text{C}_{58}\text{H}_{97}\text{NO}_{16}\text{Si}_2\cdot\text{H}^+$: 1120.6424. Found: 1120.6398 ($\Delta = 2.3$ ppm).

2-Debenzoyl-2-[*N*-methyl-*N*-(pent-4-enoyl)aminoacetyl]-7-triethylsilyl-13-[(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxy-hex-5-enoyl]baccatin III (7o): 62% yield from **8g** and **9d**; white solid; mp 30-32 °C; $[\alpha]_{\text{D}}^{20}$ -25.0 (c 0.10, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.53 (m, 6 H), 0.96 (m, 9 H), 1.11 (s, 3 H), 1.14 (s, 21 H), 1.37 (s, 9 H), 1.68 (s, 3 H), 1.95 (s, 3 H), 2.13 (d, 3 H), 2.43-2.46 (m, 4 H), 3.18 (s, 3 H), 3.67 (d, 2 H), 3.78 (m, 1 H), 4.23-4.33 (m, 4 H), 4.73 (d, 1 H), 4.92-4.99 (m, 2 H); 4.95 (d, 2 H), 5.40 (d, 1 H), 5.83 (m, 1 H), 6.00 (t, 1 H), 6.40 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 5.3, 6.7, 9.8, 12.9, 18.0, 18.1, 20.1, 21.0, 27.0, 28.2, 28.6, 30.2, 33.0, 33.9, 36.0, 38.0, 42.1, 43.5, 46.0, 51.0, 54.5, 58.0, 71.0, 71.8, 74.0, 79.0, 80.2, 82.3, 83.5, 95.2, 103.0, 115.0, 119.0, 133.0, 134.0, 137.2, 141.0, 171.0, 174.0, 202.0. HRMS (FAB, DCM/NBA) m/z calcd for $\text{C}_{58}\text{H}_{96}\text{N}_2\text{O}_{16}\text{Si}_2\cdot\text{H}^+$: 1133.6323. Found: 1133.6318 ($\Delta = 0.4$ ppm).

Macrocyclic taxoids **21b-o** were synthesized from **7b-o** in a similar manner to compound **21a**. Their characterization data are shown below. Toluene was used as the solvent instead of dichloromethane wherever higher reaction temperature (> 40 °C) was necessary. Catalyst loading ranges from 20 mol% to 60 mol%.

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,4*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-1,11-diketoundeca-4,7-dienylene]baccatin III (21b): 80% yield; white solid; $E/Z = 3/1$ based on ^1H NMR; ^1H NMR (500 MHz, CDCl_3) δ 0.57 (m, 6 H), 0.65 (m, 6 H), 0.92 (m, 9 H), 0.98 (m, 9 H), 1.14 (s, 3 H), 1.18 (s, 3 H), 1.44 (s, 9 H), 1.62 (s, 3 H), 1.89 (m, 1 H), 2.00 (s, 3 H), 2.16 (s, 3 H), 2.12-2.20 (m, 2 H), 2.26 (s, 3 H), 2.45-2.71 (m, 4 H), 2.81 (m, 2 H), 2.95 (m, 1 H), [3.74 (major), 3.76 (minor)] (d, $J = 7.5$ Hz, 1 H), 4.05 (m, 1 H), 4.17 (d, $J = 8.0$ Hz, 1 H), 4.14-4.24 (m, 1 H), 4.42 (d, $J = 7.5$ Hz, 1 H), 4.46 (dd, $J = 10.6, 6.5$ Hz, 1 H), 4.67 (s, 1 H), 4.91 (d, $J = 9.0$ Hz, 1 H), 5.33 (m, 1 H), 5.42 (d, $J = 7.5$ Hz, 1 H), 5.53 (m, 3 H), [5.73 (major), 5.77 (minor)] (dt, $J = 15.0, 5.0$ Hz, 1 H), [6.20 (minor), 6.31 (major)] (t, $J = 8.5$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.8, 5.3, 6.7, 10.2, 14.2, 20.9, 21.4, 21.6, 22.0, 23.2, 26.4, 28.4, 29.7, 30.5, 35.0, 36.4, 37.0, 43.1, 46.6, 58.1, 58.4, 70.0, 71.9, 73.6, 74.8, 76.3, 77.2, 79.3, 80.7, 84.6, 125.1, 127.6, 129.8, 132.2, 133.4, 139.9, 155.0, 169.2, 170.1, 172.8, 201.5. HRMS (FAB, $\text{CHCl}_3/\text{NBA}/\text{NaCl}/\text{PPG}$) m/z calcd for $\text{C}_{52}\text{H}_{83}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1040.5199. Found: 1040.5171 ($\Delta = 2.7$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,4*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-5-methyl-1,11-diketoundeca-4,8-dienylene]baccatin III (21c): 78% yield (90% conversion); white solid; $E/Z = 3/1$ as indicated by ^1H NMR; ^1H NMR (500 MHz, CDCl_3) δ 0.57 (m, 6 H), 0.66 (m, 6 H), 0.92 (m, 9 H), 0.99 (m, 9 H), [1.10 (minor), 1.11 (major)] (s, 3 H), 1.14 (s, 3

H), 1.42 (s, 9 H), [1.62 (minor), 1.63 (major)] (s, 3 H), [1.66 (major), 1.73 (minor)] (s, 3 H), 1.90 (m, 1 H), 1.99 (s, 3 H), 2.02 (m, 2 H), [2.03 (minor), 2.16 (major)] (s, 3 H), 2.27 (m, 4 H), [2.32 (minor), 2.38 (major)] (s, 3 H), 2.51 (m, 1 H), [3.02 (major), 3.03 (minor)] (d, $J = 7.0$ Hz, 2 H), 3.75 (d, $J = 8.0$ Hz, 1 H), 4.20 (d, $J = 7.5$ Hz, 1 H), 4.27 (m, 1 H), 4.33 (bt, 1 H), 4.44 (m, 1 H), 4.46 (d, $J = 7.5$ Hz, 1 H), 4.70 (bs, 1 H), 4.92 (t, $J = 10.5$ Hz, 1 H), 4.94 (d, $J = 8.5$ Hz, 1 H), 5.29 (d, $J = 8.0$ Hz, 1 H), [5.33 (major), 5.51 (minor)] (m, 1 H), [5.57 (dt, $J = 15.5, 8.0$ Hz), 5.63 (minor) (m)] (1 H), 5.70 (dt, $J = 15.5, 7.0$ Hz, 1 H), [6.11 (minor), 6.17 (major)] (t, $J = 9.0$ Hz, 1 H), [6.39 (minor), 6.40 (major)] (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 4.7, 4.8, 5.3, 6.7, 10.2, 14.3, 18.2, 20.9, 21.3, 23.2, 26.3, 28.4, 28.7, 35.9, 36.9, 37.7, 38.3, 42.9, 46.7, 54.6, 58.1, 69.9, 72.0, 73.7, 74.8, 75.1, 79.5, 79.7, 80.6, 84.4, 117.8, 121.8, 133.4, 134.1, 140.3, 141.2, 154.9, 169.2, 170.0, 171.8, 172.0, 201.5. HRMS (FAB, MeOH/NBA/NaCl/PPG) m/z calcd for $\text{C}_{53}\text{H}_{85}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1054.5355. Found: 1054.5318 ($\Delta = 3.6$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-1,10-diketodec-6-enylene]baccatin III (21d): 67% yield, the reaction was carried out under reflux in dichloromethane; *E* isomer only; white solid; $[\alpha]_{\text{D}}^{20} -38.2$ (c 0.18, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.59 (m, 12 H), 0.92 (m, 18 H), 1.10 (s, 3 H), 1.13 (s, 3 H), 1.39 (s, 9 H), 1.61 (m, 2 H), 1.62 (s, 3 H), 1.86 (m, 1 H), 1.95 (m, 2 H), 2.01 (s, 3 H), 2.15 (s, 3 H), 2.17 - 2.26 (m, 2 H), 2.30 (s, 3 H), 2.31 - 2.50 (m, 5 H), 3.79 (d, $J = 8.0$ Hz, 1 H), 4.15 (d, $J = 8.0$ Hz, 1 H), 4.46 (d, $J = 8.0$ Hz, 1 H), 4.51 (dd, $J = 10.8, 6.6$ Hz, 1 H), 4.73 (bt, 1 H), 4.89 (d, $J = 8.6$ Hz, 1 H), 5.36 (d, $J = 8.0$ Hz, 1 H), 5.57 (dt, $J = 16.0, 4.9$ Hz, 1 H), 5.73 (dt, $J = 16.0, 4.3$ Hz, 1 H), 6.20 (t, $J = 8.7$ Hz, 1 H), 6.37 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.5, 4.6, 5.2, 6.6, 6.7, 10.5, 13.9, 20.8, 21.8, 23.2, 26.0, 27.6, 28.3, 29.7, 35.8, 36.7, 37.8, 43.1, 47.2, 56.0, 57.9, 71.4, 71.6, 74.5, 75.8, 76.2, 79.3, 80.2, 80.6, 84.7, 129.4, 130.2, 133.4, 139.7, 155.1, 169.2, 170.5, 173.0, 174.5, 201.2. HRMS (FAB, DCM/NBA/NaCl/PEG) m/z calcd for $\text{C}_{51}\text{H}_{83}\text{NO}_{15}\text{Si}_2\cdot\text{Na}^+$: 1028.5199. Found: 1028.5113 ($\Delta = -1.4$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,10*R*,*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-10-methyl-1,12-diketododec-6-enylene]baccatin III (21e): 91% yield; *E* isomer only; white solid, mp 116-118 °C; ^1H NMR (250 MHz, CDCl_3) δ 0.59-0.85-1.01 (m, 21 H), 1.08 (s, 3 H), 1.10 (s, 3 H), 1.36 (s, 9 H), 1.50 (m, 5 H), 1.60 (s, 3 H), 1.65 (m, 2 H), 1.85 (m, 1 H), 1.95 (s, 3 H), 2.07 (m, 5 H), 2.12 (s, 3 H), 2.18 (s, 3 H), 2.26 (m, 1 H), 2.47 (m, 1 H), 3.72 (d, $J = 7.5$ Hz, 1 H), 3.98 (t, 1 H), 4.04 (s, 1 H), 4.15 (d, $J = 8.0$ Hz, 1 H), 4.40 (dd, $J = 10.2, 6.5$ Hz, 1 H), 4.49 (d, $J = 8.0$ Hz, 1 H), 4.91 (d, $J = 8.3$ Hz, 1 H), 5.30 (d, $J = 7.5$ Hz, 1 H), 5.35 (m, 1 H), 5.47 (dt, $J = 15.6, 5.2$ Hz, 1 H), 5.83 (t, $J = 9.0$ Hz, 1 H), 6.37 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 4.6, 5.2, 6.7, 10.0, 14.2, 20.5, 20.8, 21.0, 22.8, 26.0, 27.7, 27.8, 28.2, 30.7, 32.5, 30.9, 35.1, 37.0, 43.0, 43.1, 47.0, 51.8, 58.1, 60.3, 72.1, 72.2, 73.9, 74.6, 74.9, 76.4, 79.1, 79.2, 80.7, 84.3, 127.8, 133.0, 134.2, 140.9, 155.3, 169.1, 169.6, 172.4, 174.2, 201.7. HRMS (FAB) m/z calcd for $\text{C}_{54}\text{H}_{89}\text{NO}_{15}\text{Si}_2\cdot\text{H}^+$: 1048.5849. Found: 1048.5840 ($\Delta = 0.9$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-10,10-dimethyl-1,12-diketododec-6-enylene]baccatin III (21f): 58% yield (82% yield at 75% conversion); *E* isomer only; white solid, mp 126-128 °C; $[\alpha]_D^{20}$ -63.9 (c 0.36, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 0.54-0.66 (m, 12 H), 0.90 (m, 9 H), 0.97 (m, 9 H), 0.98 (s, 3 H), 1.00 (s, 3 H), 1.12 (s, 3 H), 1.15 (s, 3 H), 1.38 (s, 9 H), 1.42 (m, 2 H), 1.61 (m, 3 H), 1.70 (m, 2 H), 1.81 (m, 1 H), 1.98 (s, 2 H), 2.04 (s, 3 H), 2.06 (m, 2 H), 2.14 (s, 3 H), 2.18 (s, 3 H), 2.32 (m, 2 H), 2.50 (m, 1 H), 2.68 (m, 1 H), 3.74 (d, *J* = 7.2 Hz, 1 H), 4.06-4.17 (m, 3 H), 4.41 (dd, *J* = 10.8, 6.6 Hz, 1 H), 4.55 (d, *J* = 8.4 Hz, 1 H), 4.66 (d, *J* = 10.2 Hz, 1 H), 4.93 (d, *J* = 7.5 Hz, 1 H), 5.36 (d, *J* = 7.2 Hz, 1 H), 5.40 (m, 1 H), 5.55 (dt, *J* = 15.6, 5.0 Hz, 1 H), 5.76 (t, *J* = 9.6 Hz, 1 H), 6.42 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.7, 5.3, 6.7, 9.9, 14.3, 20.8, 22.9, 26.2, 26.4, 27.3, 27.9, 28.2, 29.0, 32.1, 33.1, 34.1, 35.0, 37.2, 39.6, 43.4, 46.9, 47.2, 51.4, 58.3, 72.2, 74.2, 74.4, 75.1, 78.8, 79.3, 80.8, 84.4, 115.4, 127.7, 132.9, 135.1, 141.3, 155.7, 169.1, 169.6, 172.7, 173.3, 201.9; HRMS (FAB, CHCl₃/NBA/NaCl/PPG) *m/z* calcd for C₅₅H₉₁NO₁₅Si₂·H⁺: 1062.6006. Found: 1062.6003 (Δ = 0.2 ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,*E*)-3-*tert*-butoxycarbonylamino-2-triethylsiloxy-9-oxa-10,11-benzo-1,12-diketododec-6-enylene]baccatin III (21g): 82% yield; *E* isomer only; white solid, mp 110 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.45-0.67 (m, 12 H), 0.87-1.00 (m, 18 H), 1.17 (s, 3 H), 1.21 (s, 3 H), 1.36 (s, 9 H), 1.69 (s, 3 H), 1.72 (m, 1 H), 1.90 (m, 1 H), 2.00 (s, 3 H), 2.03 (s, 1 H), 2.15 (s, 6 H), 2.16 (m, 1 H), 2.31 (m, 2 H), 2.46 (m, 1 H), 2.69 (m, 1 H), 2.97 (s, 1 H), 3.80 (d, *J* = 7.0 Hz, 1 H), 4.13-4.20 (m, 2 H), 4.20 (d, *J* = 8.2 Hz, 1 H), 4.37 (d, *J* = 8.2 Hz, 1 H), 4.45 (dd, *J* = 10.6, 6.5 Hz, 1 H), 4.60-4.90 (m, 4 H), 5.60-5.90 (m, 4 H), 6.41 (s, 1 H), 6.97 (d, *J* = 8.2 Hz, 1 H), 7.02 (d, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.70 (d, *J* = 7.3 Hz, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.6, 5.3, 6.7, 10.2, 14.3, 20.8, 21.3, 23.0, 26.3, 28.2, 29.7, 32.5, 37.2, 42.9, 52.0, 58.4, 70.6, 72.0, 73.6, 74.0, 75.2, 76.7, 77.2, 79.5, 80.9, 84.5, 112.6, 121.0, 128.8, 129.7, 132.3, 133.6, 140.8, 155.7, 157.6, 168.6, 169.2, 172.9, 201.9. HRMS (FAB, CHCl₃/NBA/NaCl/PPG) *m/z* calcd for C₅₆H₈₆NO₁₆Si₂·H⁺: 1084.5485. Found: 1084.5487 (Δ = -0.2 ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxy-4,6-benzo-1,11-diketoundec-7-enylene]baccatin III (21j): 65% yield; white solid; *E/Z* = 3/1 as indicated by ¹H NMR; ¹H NMR (300 MHz, CDCl₃) δ 0.54 (m, 6 H), 0.90 (m, 9 H), 1.08 (m, 21H), 1.18 (s, 3 H), 1.25 (s, 3 H), 1.38 (s, 9 H), 1.63 (s, 3 H), 1.89 (m, 1 H), 1.98 (s, 3 H), 2.16 (s, 3 H), 2.21 (m, 2 H), 2.40 (s, 3 H), 2.42 (m, 4 H), 2.49 (m, 1 H), 3.71 (d, *J* = 6.9 Hz, 3 H), 4.16 (d, *J* = 7.8 Hz, 1H), 4.44 (m, 2 H), 4.73 (d, *J* = 1.5 Hz, 1 H), 4.95 (d, *J* = 8.1 Hz, 1 H), 5.05 (d, *J* = 11.4 Hz, 1 H), 5.26 (d, *J* = 6.9 Hz, 1 H), 5.41 (m, 1 H), 5.71 (d, *J* = 17.7 Hz, 1 H), 5.76 (d, *J* = 10.8 Hz, 1 H), 5.83 (m, 1 H), 6.14 (t, *J* = 8.7 Hz, 1 H), 6.43 (s, 1 H), 6.69 (dd, *J* = 17.7, 11.1 Hz, 1 H), 7.13 (d, *J* = 6.6 Hz, 1 H), 7.29 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 5.3, 6.7, 10.0, 12.5, 13.6, 14.2, 17.5, 17.8, 19.9, 20.8, 21.2, 23.0, 25.8, 26.4, 26.8, 27.8, 28.23, 28.4, 34.0, 35.2, 37.1, 43.2, 46.6, 58.4, 69.5, 71.1, 74.6, 75.0, 75.7, 78.6, 80.9, 84.4, 114.2, 116.0, 124.4, 125.6, 125.9, 128.7,

133.4, 136.6, 137.9, 140.6, 169.2, 169.7, 173.9, 201.8. HRMS (FAB) m/z calcd for $C_{58}H_{89}NO_{15}Si_2H^+$: 1096.5849. Found: 1096.5851 ($\Delta = -0.2$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,9*R*,*E*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxy-9-methyl-1,11-diketoundec-5-enylene]baccatin III (21l): 96% yield (84% conversion); *E* isomer only; white solid; 1H NMR (500 MHz, $CDCl_3$) δ 0.55 (m, 6 H), 0.90 (m, 12 H), 1.08 (m, 27 H), 1.24 (m, 3 H), 1.36 (s, 9 H), 1.61 (s, 3 H), 1.86 (m, 3 H), 1.94 (s, 3 H), 2.03 (m, 5 H), 2.12 (s, 3 H), 2.17 (m, 2 H), 2.21 (s, 3 H), 2.44 (m, 1 H), 2.83 (m, 1 H), 3.75 (d, $J = 8.0$ Hz, 1 H), 3.94 (t, $J = 9.7$ Hz, 1 H), 4.17 (d, $J = 8.0$ Hz, 1 H), 4.32 (s, 1 H), 4.44 (m, 2 H), 4.80 (d, $J = 10.6$ Hz, 1 H), 4.91 (d, $J = 8.3$ Hz, 1 H), 5.26 (d, $J = 8.0$ Hz, 1 H), 5.44 (dt, $J = 16.5, 6.9$ Hz, 1 H), 5.61 (dd, $J = 16.5, 6.8$ Hz, 1 H), 5.82 (t, $J = 8.0$ Hz, 1 H), 6.35 (s, 1 H); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 5.2, 6.7, 10.3, 12.3, 14.3, 17.0, 17.8, 20.8, 21.3, 22.7, 25.9, 28.1, 28.2, 28.4, 29.0, 35.4, 36.0, 36.8, 38.5, 43.0, 45.4, 47.1, 56.5, 57.9, 71.9, 73.2, 74.7, 75.0, 76.1, 79.4, 79.8, 80.7, 84.4, 128.7, 131.1, 133.2, 140.6, 155.6, 169.1, 169.3, 172.6, 172.8, 201.4. HRMS (FAB) m/z calcd for $C_{56}H_{93}NO_{15}Si_2H^+$: 1076.6162. Found: 1076.6167 ($\Delta = -0.5$ ppm).

7-Triethylsilyl-2-debenzoyl-2,13-[(2*R*,3*S*,*E*)-3-*tert*-butoxycarbonylamino-2-triisopropylsiloxy-9,9-dimethyl-1,11-diketoundec-5-enylene]baccatin III (21m): 88% yield (84% conversion); *E* isomer only; white solid; 1H NMR (500 MHz, $CDCl_3$) δ 0.56 (m, 6 H), 0.90 (m, 9 H), 0.96 (s, 3 H), 1.02 (s, 3 H), 1.09 (m, 21 H), 1.11 (s, 6 H), 1.36 (m, 2 H), 1.41 (s, 9 H), 1.60 (s, 3 H), 1.85 (m, 1 H), 1.99 (s, 3 H), 2.04 (m, 2 H), 2.14 (s, 3 H), 2.23 (s, 3 H), 2.35 (m, 6 H), 2.48 (m, 1 H), 3.74 (d, $J = 7.7$ Hz, 1 H), 3.91 (bs, 1 H), 4.10 (d, $J = 8.0$ Hz, 1 H), 4.29 (d, $J = 3.0$ Hz, 1 H), 4.44 (dd, $J = 10.4, 6.4$ Hz, 1 H), 4.52 (d, $J = 8.0$ Hz, 1 H), 4.88 (d, $J = 8.4$ Hz, 1 H), 5.09 (bs, 1 H), 5.30 (d, $J = 7.7$ Hz, 1 H), 5.48 (dt, $J = 16.0, 5.3$ Hz, 1 H), 5.55 (dt, $J = 16.0, 5.3$ Hz, 1 H), 5.84 (t, $J = 8.6$ Hz, 1 H), 6.38 (s, 1 H); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 5.3, 6.7, 10.1, 12.4, 14.4, 17.9, 20.8, 21.2, 22.5, 26.2, 27.1, 28.2, 28.3, 28.7, 34.2, 36.2, 36.6, 36.9, 40.0, 43.1, 46.5, 47.5, 54.4, 58.1, 72.0, 73.5, 74.7, 76.3, 79.3, 80.8, 84.5, 125.0, 133.2, 134.2, 140.4, 155.3, 169.1, 169.6, 172.5, 173.0, 201.4. HRMS (FAB) m/z calcd for $C_{57}H_{95}NO_{15}Si_2H^+$: 1090.6319. Found: 1090.6321 ($\Delta = -0.2$ ppm).

Compounds **6b-t** were synthesized in a similar manner to compound **6a**. Their characterization data are shown below.

2-Debenzoyl-2,13-[(10*R*,9*S*,7*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-1,11-diketoundeca-4,7-dienylene]baccatin III (6b): 74% yield; white solid; *E/Z* = 3/1 as indicated by 1H NMR; 1H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 3 H), [1.15 (minor), 1.22 (major)] (s, 3 H), 1.46 (s, 9 H), 1.60 (s, 3 H), 1.83 (s, 3 H), 1.89 (m, 1 H), 2.05 (m, 2 H), 2.21 (s, 3 H), 2.22 (s, 3 H), 2.51 (m, 4 H), 2.83 (m, 2 H), 2.92 (m, 1 H), 3.41 (bs, 1 H), 3.69 (d, $J = 7.5$ Hz, 1 H), 3.92 (d, $J = 10.0$ Hz, 1 H), 4.18 (d, $J = 8.0$ Hz, 1 H), 4.23 (m, 1 H), 4.40 (dd, $J = 11.0, 6.5$ Hz, 1 H), 4.42 (d, $J = 8.0$ Hz, 1 H), 4.74 (d, $J = 7.0$ Hz, 1 H), 4.94 (d, $J = 8.0$ Hz, 1 H), 5.34 (m, 2 H), 5.39 (d, $J = 7.5$ Hz, 1 H), [5.80 (major), 5.87 (minor)] (dt, $J = 16.0, 5.0$ Hz, 1 H), [6.19 (major), 6.20 (minor)] (s, 1 H), 6.31 (t, $J = 9.0$ Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.7, 14.7, 20.8, 21.6, 22.1, 22.8, 26.7, 28.3, 30.4,

35.0, 35.2, 36.3, 42.9, 45.4, 58.2, 70.6, 71.8, 74.9, 75.1, 75.4, 76.2, 79.6, 80.7, 84.7, 113.1, 124.5, 127.3, 130.2, 133.0, 142.2, 156.4, 169.6, 169.7, 171.3, 172.8, 203.5. HRMS (FAB) m/z calcd for $C_{40}H_{55}NO_{15}\cdot H^+$: 790.3650. Found: 790.3650 ($\Delta = 0$ ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,7*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-7-methyl-1,11-diketoundeca-3,7-dienylene]baccatin III (6c): 68% yield; white solid; $E/Z = 3/1$ as indicated by 1H NMR; 1H NMR (500 MHz, $CDCl_3$) δ 1.01(s, 3 H), 1.19 (s, 3 H), 1.46 (s, 9 H), [1.71 (major), 1.77 (minor)] (s, 3 H), 1.83 (s, 3 H), 1.85 (m, 1 H), 2.00–2.22 (m, 6 H), 2.22 (s, 6 H), 2.30 (s, 3 H), 2.47 (m, 1 H), 2.53 (m, 1 H), [3.03 (major), 3.08 (minor)] (d, $J = 6.5$ Hz, 1 H), [3.66 (minor), 3.70 (major)] (d, $J = 7.4$ Hz, 1 H), 3.99 (t, $J = 8.4$ Hz, 1 H), 4.20 (d, $J = 8.1$ Hz, 1 H), 4.42 (m, 1 H), 4.46 (d, $J = 8.1$ Hz, 1 H), 4.60(m, 1 H), 4.64 (d, $J = 6.6$ Hz, 1 H), 4.89 – 5.03 (m, 2 H), [5.27 (major), 5.31 (minor)] (d, $J = 7.4$ Hz, 1 H), 5.53 – 5.74 (m, 2 H), 6.16 (m, 1 H), 6.18 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 9.7, 14.7, 18.3, 20.8, 22.2, 22.9, 26.6, 28.3, 35.1, 36.0, 37.5, 38.5, 39.2, 42.8, 45.4, 53.6, 58.1, 70.2, 70.7, 71.8, 75.4, 76.2, 77.2, 80.2, 80.7, 84.6, 114.2, 116.9, 120.1, 122.0, 133.8, 142.7, 153.1, 169.5, 171.4, 171.7, 172.4, 203.5. HRMS (FAB, MeOH/NBA/NaCl/PPG) m/z calcd for $C_{41}H_{57}NO_{15}\cdot Na^+$: 826.3626. Found: 826.3654 ($\Delta = -3.4$ ppm).

2-Debenzoyl-2,13-[(9*R*,8*S*,*E*)-8-*tert*-butoxycarbonylamino-9-hydroxy-1,10-diketodec-4-enylene]baccatin III (6d): 60% yield; *E* isomer only; white solid, mp 164–166 °C; $[\alpha]_D^{20} -51.4$ (c 0.12, $CHCl_3$); 1H NMR (250 MHz, $CDCl_3$) δ 0.97 (s, 3 H), 1.11 (s, 3 H), 1.34 (m, 2 H), 1.37 (s, 9 H), 1.55 (s, 3 H), 1.75 (m, 1 H), 1.80 (s, 3 H), 2.03(m, 2 H), 2.16 (s, 3 H), 2.20 (s, 3 H), 2.23 (m, 2 H), 2.32 – 2.50 (m, 5 H), 3.65 (m, 1 H), 3.69 (d, $J = 8.1$ Hz, 1 H), 3.91 (d, $J = 6.7$ Hz, 1 H), 4.18 (d, $J = 8.1$ Hz, 1 H), 4.38 (dd, $J = 10.5, 6.5$ Hz, 1 H), 4.42 (d, $J = 8.1$ Hz, 1 H), 4.88 (d, $J = 7.9$ Hz, 1 H), 5.31 (d, $J = 8.1$ Hz, 1 H), 5.48 (dt, $J = 15.6, 5.5$ Hz, 1 H), 5.73 (bdt, $J = 15.6$ Hz, 1 H), 6.09 (t, $J = 8.6$ Hz, 1 H), 6.14 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 9.8, 14.0, 14.4, 20.7, 22.4, 22.7, 26.0, 26.6, 28.1, 31.3, 34.9, 35.4, 38.1, 42.9, 45.8, 53.9, 57.9, 71.1, 72.5, 73.5, 75.3, 75.9, 76.1, 79.6, 80.7, 84.9, 129.6, 130.7, 132.9, 141.5, 156.7, 170.1, 170.6, 171.3, 173.9, 203.4. HRMS (EI) m/z calcd for $C_{39}H_{55}NO_{15}\cdot H^+$: 778.3650. Found: 778.3648 ($\Delta = 0.3$ ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*,3*R*,*E*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3-methyl-1,12-diketododec-6-enylene]baccatin III (6e): 94.5% yield; *E* isomer only; white solid, mp 184–186 °C; 1H NMR (250 MHz, $CDCl_3$) δ 0.99 (d, $J = 6.2$ Hz, 3 H), 1.03 (s, 3 H), 1.16 (s, 3 H), 1.38 (s, 9 H), 1.53 (m, 3 H), 1.60 (s, 3 H), 1.84 (s, 3 H), 1.86 (m, 1 H), 2.02 (s, 3 H), 2.10 (m, 7 H), 2.18 (s, 3 H), 2.20 (s, 3 H), 2.30 (m, 1 H), 2.45–2.71 (m, 3 H), 3.11 (bs, 1 H), 3.71 (d, $J = 7.5$ Hz, 1 H), 3.99 (s, 1 H), 4.17 (d, $J = 8.3$ Hz, 1 H), 4.39 (m, 1 H), 4.50 (m, 2 H), 4.95 (d, $J = 8.1$ Hz, 1 H), 5.30 (d, $J = 7.5$ Hz, 1 H), 5.35 (m, 1 H), 5.43 (dt, $J = 15.5, 5.0$ Hz, 1 H), 5.92 (t, $J = 7.5$ Hz, 1 H), 6.20 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 9.5, 14.2, 15.0, 20.5, 20.8, 21.7, 22.5, 26.3, 27.9, 27.95, 28.1, 30.6, 32.1, 35.0, 35.3, 43.0, 45.8, 51.5, 58.3, 60.4, 72.0, 73.2, 73.7, 74.8, 75.6, 76.2, 79.6, 79.65, 80.7, 84.5, 127.6, 132.4, 134.1, 142.8, 155.3, 169.5, 171.3, 174.1, 174.2, 203.6. HRMS (EI) m/z calcd for $C_{42}H_{61}NO_{15}\cdot H^+$: 820.4119. Found: 820.4121 ($\Delta = -0.2$ ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*,*E*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3,3-dimethyl-1,12-diketododec-6-enylene]baccatin III (6f): 83% yield; *E* isomer only; white solid, mp 178 °C; $[\alpha]_{\text{D}}^{22}$ -80 (c 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.96 (s, 3 H), 1.04 (s, 3 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 1.38 (s, 9 H), 1.58 (s, 3 H), 1.68-1.87 (m, 3 H), 1.87 (s, 3 H), 1.90-2.14 (m, 4 H), 2.15 (d, *J* = 2.4 Hz, 3 H), 2.20 (d, *J* = 1.2 Hz, 3 H), 2.27-2.37 (m, 2 H), 2.47-2.55 (m, 2 H), 2.76 (dd, *J* = 15.6, 9.0 Hz, 1 H), 2.90 (ddd, *J* = 24.9, 17.7, 1.8 Hz, 1 H), 3.72 (d, *J* = 7.2 Hz, 1 H), 3.96 (d, *J* = 7.2 Hz, 1 H), 4.10 (t, *J* = 10.2 Hz, 1 H), 4.14 (d, *J* = 7.8 Hz, 1 H), 4.37 (m, 1 H), 4.43 (d, *J* = 9.6 Hz, 1 H), 4.55 (d, *J* = 7.8 Hz, 1 H), 4.95 (d, *J* = 7.2 Hz, 1 H), 5.34-5.45 (m, 2 H), 5.85 (t, *J* = 9.0 Hz, 1 H), 6.23 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 9.4, 15.2, 20.8, 21.5, 22.7, 26.7, 27.8, 28.2, 29.1, 32.6, 34.0, 35.4, 39.6, 43.2, 46.0, 46.8, 51.1, 58.1, 58.4, 72.2, 73.1, 74.5, 74.6, 75.7, 79.0, 79.7, 80.8, 84.6, 127.3, 132.3, 135.1, 143.1, 169.6, 171.3, 173.3, 174.7, 203. HRMS (FAB, CHCl₃/NBA/NaCl/PPG) *m/z* calcd for C₄₃H₆₃NO₁₅·H⁺: 834.4276. Found: 834.4279 (Δ = -0.4 ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*,*E*)-10-*tert*-butoxycarbonylamino-11-hydroxy-4-oxa-2,3-benzo-1,12-diketododec-6-enylene]baccatin III (6g): 79% yield; *E* isomer only; white solid, mp 190-192 °C; $[\alpha]_{\text{D}}^{22}$ -109 (c 0.11, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.14 (s, 3 H), 1.26 (s, 3 H), 1.38 (s, 9 H), 1.55 (m, 1 H), 1.70 (s, 3 H), 1.89 (m, 1 H), 1.91 (s, 3 H), 2.14 (s, 3 H), 2.23 (s, 3 H), 2.25-2.55 (m, 4 H), 2.77 (m, 1 H), 2.99 (d, *J* = 8.0 Hz, 1 H), 3.03 (s, 1 H), 3.79 (d, *J* = 7.1 Hz, 1 H), 4.00 (d, *J* = 7.7 Hz, 1 H), 4.07 (m, 1 H), 4.24 (d, *J* = 8.3 Hz, 1 H), 4.42 (m, 1 H), 4.42 (d, *J* = 8.3 Hz, 1 H), 4.55 (d, *J* = 9.7 Hz, 1 H), 4.67 (d, *J* = 15.0 Hz, 1 H), 4.72 (d, *J* = 15.0 Hz, 1 H), 4.90 (d, *J* = 8.1 Hz, 1 H), 5.69 (m, 3 H), 5.69 (t, *J* = 6.7 Hz, 1 H), 6.26 (s, 1 H), 6.98 (d, *J* = 8.5 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 9.8, 15.3, 20.9, 22.0, 22.9, 26.6, 28.2, 28.4, 29.7, 32.2, 35.5, 37.7, 42.7, 45.7, 51.7, 58.6, 70.4, 71.9, 73.1, 75.5, 75.8, 76.4, 77.8, 80.0, 80.9, 84.8, 113.6, 121.3, 128.7, 129.0, 132.1, 133.0, 133.7, 142.8, 155.6, 168.6, 169.7, 171.4, 203.9. HRMS (FAB, CHCl₃/NBA/NaCl/PPG) *m/z* calcd for C₄₄H₅₇NO₁₆·H⁺: 856.3757. Found: 856.3756 (Δ = 0.1 ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*,*E*)-10-*tert*-butoxycarbonylamino-11-hydroxy-7,8,9-benzo-1,12-diketododec-5-enylene]baccatin III (6h): 67% yield from **7h** (two steps); *E* isomer only; white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.19 (s, 3 H), 1.23 (s, 3 H), 1.43 (s, 9 H), 1.53 (s, 3 H), 1.60-1.75 (m, 4 H), 1.78 (s, 3 H), 1.92 (m, 2 H), 1.99 (m, 2 H), 2.19 (s, 6 H), 2.32 (m, 2 H), 2.37 (m, 1 H), 2.46 (m, 1 H), 3.55 (d, *J* = 7.5 Hz, 1 H), 4.03 (m, 1 H), 4.30 (dd, *J* = 11.0, 6.5 Hz, 1 H), 4.37 (d, *J* = 8.0 Hz, 1 H), 4.83 (d, *J* = 8.5 Hz, 1 H), 4.91 (m, 1 H), 5.20 (d, *J* = 7.5 Hz, 1 H), 5.28 (s, 1 H), 6.16 (s, 1 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 7.45 (d, *J* = 4.5 Hz, 1 H). HRMS (FAB) *m/z* calcd for C₄₄H₅₇NO₁₅·H⁺: 840.3807. Found: 840.3804 (Δ = 0.4 ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3-oxa-1,11-diketoundec-5-enylene]baccatin III (6i): 94% yield from **7i** (two steps); *E* isomer only; white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.01 (s, 3 H), 1.18 (s, 3 H), 1.39 (s, 9 H), 1.65 (s, 3 H), 1.84 (s, 3 H), 2.19 (s, 3 H), 2.21 (s, 3 H), 2.45 (m, 2 H), 3.67 (d, *J* = 6.9 Hz, 1 H), 3.98-4.20 (m, 3 H), 4.25 (d, *J* = 8.1 Hz, 1 H), 4.41 (m, 2 H), 4.60 (d, *J* = 10.4 Hz, 1 H), 4.97 (d, *J* = 8.1 Hz, 1 H),

5.39 (d, $J = 6.9$ Hz, 1 H), 5.51 (s, 2 H), 5.85 (t, $J = 6.9$ Hz, 1 H), 6.17 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 9.18, 13.64, 14.63, 20.28, 21.52, 22.12, 25.55, 27.40, 27.69, 32.08, 34.66, 36.09, 42.27, 44.97, 50.33, 52.42, 57.75, 68.87, 71.36, 71.77, 72.33, 74.53, 75.19, 75.64, 76.15, 76.57, 78.93, 79.68, 80.18, 84.29, 128.9, 130.07, 132.45, 142.20, 155.38, 169.31, 170.28, 171.09, 174.30, 203.31. HRMS (FAB) m/z calcd for $\text{C}_{39}\text{H}_{55}\text{NO}_{16}\cdot\text{H}^+$: 794.3599. Found: 794.3593 ($\Delta = 0.8$ ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*)-9-*tert*-butoxycarbonylamino-10-hydroxy-6,7,8-benzo-1,11-diketoundec-4-enylene]baccatin III (6j): 80% yield; white solid; $E/Z = 3/1$ as indicated by ^1H NMR; ^1H NMR (300 MHz, CDCl_3) δ 1.23 (s, 3 H), 1.25 (s, 3 H), 1.44 (m, 6 H), [1.53 (major), 1.56 (minor)] (s, 1 H), [1.73 (major), 1.76 (minor)] (s, 1 H), 1.79 (m, 2 H), 2.20 (m, 3 H), [3.48 (major), 3.59 (minor)] (d, $J = 7.0$ Hz, 1 H), 3.91 (d, $J = 10.2$ Hz, 1 H), 4.07 (d, $J = 8.0$ Hz, 1 H), 4.14 (d, $J = 8.0$ Hz, 1 H), 4.34 (m, 2 H), 4.49 (d, $J = 8.0$ Hz, 0.25 H) (minor), 4.81 (m, 2 H), 4.91 (d, $J = 8.1$ Hz, 0.25 H) (minor), [5.16 (minor), 5.34 (major)] (d, $J = 7.5$ Hz, 1 H), 5.40 (d, $J = 5.4$ Hz, 1 H), [5.60 (major), 5.84 (minor)] (dt, $J = 8.7, 3.6$ Hz, 1 H), [6.12 (major), 6.13 (minor)] (s, 1 H), [6.17 (minor), 6.32 (major)] (t, $J = 8.4$ Hz, 1 H), 6.46 (m, 1 H), [6.90 (major), 7.02 (minor)] (s, 1 H), 7.20 (m, 2 H), 7.41 (t, $J = 7.5$ Hz, 1 H). HRMS (FAB) m/z calcd for $\text{C}_{43}\text{H}_{55}\text{NO}_{15}\cdot\text{H}^+$: 826.3650. Found: 826.3646 ($\Delta = 0.5$ ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*)-9-*tert*-butoxycarbonylamino-10-hydroxy-2,3-benzo-1,11-diketoundec-6-enylene]baccatin III (6k): 64% yield; white solid, mp 199–201 °C; $E/Z = 3/1$ as indicated by ^1H NMR; ^1H NMR (500 MHz, CDCl_3) δ 1.12 (s, 3 H), 1.25 (s, 3 H), 1.47 (s, 9 H), 1.63 (s, 3 H), 1.82–1.90 (m, 1 H), 1.91 (s, 3 H), 2.21 (s, 3 H), 2.25 (s, 3 H), 2.26–2.35 (m, 1 H), 2.39–2.55 (m, 5 H), 2.60–2.69 (m, 1 H), 2.85–2.99 (m, 1 H), 3.15–3.27 (m, 1 H), 3.78–3.86 (m, 1 H), 3.96 (d, $J = 8.5$ Hz, 1 H), 4.02 (s, 1 H), 4.10 (d, $J = 8.0$ Hz, 1 H), 4.44 (m, 1 H), 4.84 (dd, $J = 12.5, 10.0$ Hz, 1 H), 5.53 (dt, $J = 17.0, 5.0$ Hz, 1 H), 5.69 (m, 2 H), 6.18 (t, $J = 9.0$ Hz, 1 H), 6.23 (s, 1 H), 7.25 (m, 2 H), 7.50 (m, 1 H), 7.71 (m, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.8, 14.8, 20.9, 21.9, 22.6, 26.6, 28.3, 32.3, 33.3, 35.2, 37.6, 46.3, 54.0, 71.3, 71.7, 75.5, 76.5, 79.5, 80.7, 81.0, 84.7, 123.3, 126.4, 128.6, 131.2, 132.4, 135.9, 155.5, 169.8, 169.3, 170.2, 171.6, 203.5. HRMS (FAB) m/z calcd for $\text{C}_{44}\text{H}_{57}\text{NO}_{15}\cdot\text{H}^+$: 840.3806. Found: 840.3811 ($\Delta = -0.5$ ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,3*R*,*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3-methyl-1,11-diketoundec-6-enylene]baccatin III (6l): 96% yield; white solid; E isomer only; ^1H NMR (250 MHz, CDCl_3) δ 0.93 (d, $J = 5.5$ Hz, 3 H), 1.01 (s, 3 H), 1.15 (s, 3 H), 1.40 (s, 9 H), 1.59 (s, 3 H), 1.66 (m, 3 H), 1.86 (s, 3 H), 1.89 (m, 1 H), 2.15 (m, 3 H), 2.21 (s, 3 H), 2.22 (s, 3 H), 2.26 (m, 2 H), 2.51 (m, 3 H), 3.57 (bs, 1 H), 3.74 (d, $J = 7.9$ Hz, 1 H), 3.98 (m, 1 H), 4.04 (d, $J = 4.5$ Hz, 1 H), 4.16 (d, $J = 8.3$ Hz, 1 H), 4.41 (dd, $J = 10.0, 5.8$ Hz, 1 H), 4.47 (d, $J = 8.3$ Hz, 1 H), 4.69 (d, $J = 8.5$ Hz, 1 H), 4.94 (d, $J = 8.4$ Hz, 1 H), 5.25 (d, $J = 7.9$ Hz, 1 H), 5.55 (m, 2 H), 5.96 (t, $J = 7.5$ Hz, 1 H), 6.18 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.7, 15.0, 20.8, 22.0, 22.5, 26.3, 28.2, 28.9, 29.2, 35.1, 35.8, 35.9, 36.6, 42.9, 44.3, 45.8, 55.1, 58.1, 71.8, 73.5, 74.6, 74.9, 75.5, 76.0, 80.1, 80.4, 80.6, 84.7, 126.4, 132.7, 133.3, 142.5, 156.2, 169.5, 171.3, 173.1, 173.5, 203.4. HRMS (FAB) m/z calcd for $\text{C}_{41}\text{H}_{59}\text{NO}_{15}\cdot\text{H}^+$: 806.3963. Found: 806.3960 ($\Delta = 0.4$ ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3,3-dimethyl-1,11-diketoundec-6-enylene]baccatin III (6m): 92% yield; *E* isomer only; white solid; $[\alpha]_D^{20}$ -83.8 (c 0.80, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.96 (s, 3 H), 1.02 (s, 3 H), 1.18 (s, 3 H), 1.45 (s, 9 H), 1.52 (m, 2 H), 1.57 (s, 3 H), 1.83 (m, 1 H), 1.88 (s, 3 H), 2.12 (m, 2 H), 2.20 (m, 2 H), 2.21 (s, 3 H), 2.23 (s, 3 H), 2.32 (m, 2 H), 2.52 (m, 3 H), 3.75 (d, *J* = 7.7 Hz, 1 H), 3.97 (d, *J* = 8.1 Hz, 1 H), 4.09 (m, 1 H), 4.32 (bs, 1 H), 4.41 (t, *J* = 7.8 Hz, 1 H), 4.52 (d, *J* = 7.8 Hz, 1 H), 4.79 (d, *J* = 7.0 Hz, 1 H), 4.93 (d, *J* = 7.8 Hz, 1 H), 5.28 (d, *J* = 7.7 Hz, 1 H), 5.37 (ddd, *J* = 15.7, 7.0, 4.7 Hz, 1 H), 5.49 (dt, *J* = 15.5, 5.5 Hz, 1 H), 6.06 (t, *J* = 8.6 Hz, 1 H), 6.19 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 9.6, 14.7, 20.8, 22.0, 22.5, 26.5, 27.1, 27.3, 28.3, 28.8, 34.2, 35.1, 35.7, 36.8, 39.5, 43.0, 46.1, 47.2, 53.6, 58.2, 71.3, 71.8, 75.0, 75.4, 76.2, 79.9, 80.6, 80.9, 84.8, 123.3, 132.6, 135.9, 142.3, 169.7, 171.3, 171.5, 172.9, 203.4. HRMS (FAB) *m/z* calcd for C₄₂H₆₁NO₁₅·H⁺: 820.4119. Found: 820.4116 (Δ = 0.4 ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,*E*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3,3-dimethyl-4-oxa-1,11-diketoundeca-6-enylene]baccatin III (6n): 50% yield from **7n** (two steps); white solid; *E* isomer only; ¹H NMR (300 MHz, CDCl₃) δ 1.01 (s, 3 H), 1.23 (m, 9 H), 1.39 (s, 9 H), 1.59 (s, 3 H), 1.88 (s, 3 H), 2.09 (s, 3 H), 2.21 (m, 4 H), 2.45 (m, 2 H), 3.68 (d, *J* = 6.9 Hz, 1 H), 3.81-4.19 (m, 3 H), 4.32 (m, 2 H), 4.67 (d, *J* = 8.1 Hz, 1 H), 4.97 (d, *J* = 8.1 Hz, 1 H), 5.36 (d, *J* = 6.9 Hz, 1 H), 5.39-5.62 (m, 2 H), 6.17 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 9.76, 14.18, 14.58, 20.83, 22.45, 24.53, 26.50, 26.59, 28.29, 29.68, 35.10, 37.12, 42.81, 45.74, 47.61, 58.12, 62.48, 71.15, 71.76, 74.76, 75.41, 75.53, 76.18, 79.70, 80.57, 84.79, 125.35, 132.71, 133.22, 142.20, 170.23, 171.37, 172.05, 203.55. HRMS (FAB) *m/z* calcd for C₄₁H₅₉NO₁₆·H⁺: 822.3912. Found: 822.3914 (Δ = -0.2 ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3-aza-3-methyl-1,4,12-triketododec-7-enylene]baccatin III (6o): 81% yield from **7o** (two steps); white solid; *E/Z* ~ 4/1 based on ¹H NMR; *Major isomer (E)*: ¹H NMR (250 MHz, CDCl₃) δ 1.06 (s, 3 H), 1.24 (s, 6 H), 1.41 (s, 9 H), 1.64 (s, 3 H), 1.82 (s, 3 H), 2.03 (s, 3 H), 2.21 (s, 3 H), 2.36 (m, 3 H), 2.50 (m, 1 H), 3.18 (s, 3 H), 3.65 (d, 1 H), 3.82 (m, 1 H), 4.41 (dd, 2 H), 4.43 (m, 2 H), 4.44 (m, 2 H), 4.67 (m, 1 H), 4.95 (d, 1 H), 5.40 (m, 2 H), 6.20 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 5.1, 8.7, 9.7, 10.1, 10.6, 16.3, 16.8, 18.5, 19.3, 20.3, 22.1, 23.7, 25.2, 28.6, 30.8, 31.4, 32.1, 38.2, 40.8, 47.3, 50.1, 53.9, 55.5, 67.0, 67.8, 68.9, 70.9, 71.5, 73.7, 74.6, 76.2, 77.5, 80.2, 121.2, 126.6, 128.6, 137.5, 164.7, 165.1, 166.7, 166.8, 168.2, 169.3, 198.9. HRMS (FAB, DCM/NBA) *m/z* calcd for C₄₁H₅₈N₂O₁₆·H⁺: 835.3865. Found: 835.3863 (Δ = 0.2 ppm).

Compounds **6'd** - **6'g**, **6'l**, **6'm**, and **6'o** were synthesized in a similar manner to compound **6'a**. Their characterization data are shown below.

2-Debenzoyl-2,13-[(9*R*,8*S*)-8-*tert*-butoxycarbonylamino-9-hydroxy-1,10-diketodecylene]baccatin III (6'd): 92% yield; white solid, mp 187-189 °C; $[\alpha]_D^{20}$ -60.0 (c 0.15, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.97 (s, 3 H), 1.14 (s, 3 H), 1.18 - 1.62 (m, 8 H), 1.37 (s, 9 H), 1.53 (s, 3 H), 1.79 (m, 1 H), 1.82 (s, 3 H), 2.10 - 2.22 (m, 2 H), 2.16 (s, 3 H), 2.17 (s, 3 H), 2.29

– 2.49 (m, 5 H), 3.60 (t, $J = 6.8$ Hz, 1 H), 3.68 (d, $J = 8.0$ Hz, 1 H), 3.81 (d, $J = 6.1$ Hz, 1 H), 4.13 (d, $J = 8.0$ Hz, 1 H), 4.37 (m, 2 H), 4.85 (d, $J = 8.0$ Hz, 1 H), 5.32 (d, $J = 8.0$ Hz, 1 H), 6.13 (s, 1 H), 6.22 (t, $J = 8.6$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.9, 14.2, 20.6, 22.5, 22.7, 24.7, 24.9, 26.1, 28.1, 28.7, 29.5, 32.4, 34.9, 37.9, 43.0, 45.7, 55.0, 57.9, 71.0, 71.4, 74.4, 75.2, 75.7, 76.1, 79.7, 80.8, 80.9, 132.8, 141.5, 157.1, 170.2, 171.3, 173.5, 174.1, 203.4. HRMS (FAB, DCM/NBA/NaCl/PPG) m/z calcd for $\text{C}_{39}\text{H}_{57}\text{NO}_{15}\cdot\text{Na}^+$: 802.3626. Found: 802.3665 ($\Delta = -4.9$ ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*,3*R*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3-methyl-1,12-diketododecylene]baccatin III (6'e): 95% yield; white solid, mp 172–174 °C; ^1H NMR (250 MHz, CDCl_3) δ 0.96 (d, $J = 6.1$ Hz, 3 H), 1.04 (s, 3 H), 1.20 (s, 3 H), 1.40 (s, 9 H), 1.44 (m, 11 H), 1.60 (s, 3 H), 1.83 (s, 3 H), 1.86 (m, 1 H), 1.99 (m, 2 H), 2.21 (s, 6 H), 2.27 (m, 2 H), 2.50 (m, 3 H), 3.18 (bs, 1 H), 3.72 (d, $J = 7.4$ Hz, 1 H), 3.95 (m, 2 H), 4.18 (d, $J = 8.1$ Hz, 1 H), 4.39 (m, 1 H), 4.53 (m, 2 H), 4.94 (d, $J = 8.1$ Hz, 1 H), 5.32 (d, $J = 7.4$ Hz, 1 H), 6.06 (t, 1 H), 6.21 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.6, 14.2, 14.9, 20.5, 20.8, 22.0, 22.6, 24.1, 26.4, 26.5, 28.2, 28.4, 28.6, 30.3, 31.3, 35.2, 35.5, 36.1, 42.9, 43.1, 45.7, 52.9, 58.3, 71.9, 73.0, 73.8, 74.6, 75.5, 76.2, 79.6, 80.0, 80.8, 84.6, 132.6, 142.3, 156.0, 169.6, 171.3, 174.0, 174.1, 203.6. HRMS (FAB) m/z calcd for $\text{C}_{42}\text{H}_{63}\text{NO}_{15}\cdot\text{H}^+$: 822.4263. Found: 822.4265 ($\Delta = -0.3$ ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3,3-dimethyl-1,12-diketododecylene]baccatin III (6'f): 93% yield; white solid, mp 157–159 °C; $[\alpha]_{\text{D}}^{22} -90$ (c 0.10, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 0.94 (s, 3 H), 1.01 (s, 3 H), 1.22 (s, 3 H), 1.25 (s, 3 H), 1.39 (s, 9 H), 1.20–1.85 (m 10 H), 1.88 (s, 3 H), 1.88 (m, 1 H), 2.03 (s, 2 H), 2.01 (d, $J = 11.7$ Hz, 1 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 2.33 (d, $J = 11.2$ Hz, 1 H), 2.45–2.70 (m, 3 H), 3.08 (m, 1 H), 4.00 (m, 1 H), 4.08–4.16 (m, 3 H), 4.40 (m, 1 H), 4.48–4.58 (m, 2 H), 4.96 (d, $J = 9.9$ Hz, 1 H), 5.40 (d, $J = 6.9$ Hz, 1 H), 6.01 (m, 1 H), 6.24 (s, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.5, 15.0, 20.8, 21.8, 22.6, 23.6, 25.0, 26.5, 26.9, 28.2, 28.8, 29.1, 29.7, 30.5, 32.4, 34.1, 35.3, 35.7, 40.3, 43.3, 45.9, 47.7, 52.7, 58.4, 72.0, 73.6, 73.4, 74.6, 75.6, 77.2, 79.2, 80.0, 80.8, 84.7, 132.4, 143.0, 155.9, 169.6, 171.4, 173.6, 174.5, 203.7. HRMS (FAB, $\text{CHCl}_3/\text{NBA}/\text{NaCl}/\text{PPG}$) m/z calcd for $\text{C}_{43}\text{H}_{65}\text{NO}_{15}\cdot\text{H}^+$: 836.4432. Found: 836.4435 ($\Delta = -0.3$ ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*)-10-*tert*-butoxycarbonylamino-11-hydroxy-4-oxa-2,3-benzo-1,12-diketododecylene]baccatin III (6'g): 66% yield; white solid, mp 170–172 °C; $[\alpha]_{\text{D}}^{22} -109$ (c 0.11, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 1.16 (s, 3 H), 1.32 (s, 3 H), 1.43 (s, 9 H), 1.45–1.91 (m 7 H), 1.62 (s, 3 H), 1.92 (s, 3 H), 2.18 (s, 3 H), 2.24 (s, 3 H), 2.50 (m, 5 H), 2.65 (s, 1 H), 3.12 (d, $J = 8.5$ Hz, 1 H), 3.79 (d, $J = 6.7$ Hz, 1 H), 4.00 (m, 1 H), 4.13 (m, 4 H), 4.27 (d, $J = 8.4$ Hz, 1 H), 4.42 (m, 1 H), 4.61 (d, $J = 8.4$ Hz, 1 H), 4.86 (d, $J = 8.1$ Hz, 1 H), 5.76 (d, $J = 6.7$ Hz, 1 H), 6.15 (m, 1 H), 6.27 (s, 1 H), 6.96–7.03 (m, 2 H), 7.46 (t, $J = 8.8$ Hz, 1 H), 7.73 (d, $J = 6.5$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 9.8, 15.0, 20.8, 22.1, 22.7, 23.4, 24.5, 26.7, 28.1, 28.3, 29.7, 31.7, 35.5, 37.7, 43.1, 45.7, 53.7, 58.7, 68.9, 71.9, 73.8, 74.0, 75.7, 76.7, 77.8, 80.3, 81.1, 82.9, 84.8, 112.4, 114.6, 120.3, 120.7, 132.9, 133.0, 134.0, 142.6, 145.6, 156.4, 157.0, 168.9, 169.7,

171.4, 174.7, 203.9. HRMS (FAB, CHCl₃/NBA/NaCl/PPG) m/z calcd for C₄₄H₅₉NO₁₆·H⁺: 858.3912. Found: 858.3904 (Δ = 0.9 ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*,3*R*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3-methyl-1,11-diketoundecylene]baccatin III (6'1): 94% yield; white solid; ¹H NMR (250 MHz, CDCl₃) δ 0.97 (d, J = 6.2 Hz, 3 H), 1.02 (s, 3 H), 1.13 (s, 3 H), 1.35 (m, 6 H), 1.39 (s, 3 H), 1.60 (s, 3 H), 1.69 (m, 3 H), 1.81 (s, 3 H), 1.86 (m, 1 H), 2.21 (s, 3 H), 2.22 (s, 3 H), 2.26 (m, 4 H), 2.51 (m, 2 H), 2.65 (m, 1 H), 3.19 (bs, 1 H), 3.75 (d, J = 7.8 Hz, 1 H), 4.02 (s, 1 H), 4.18 (d, J = 8.0 Hz, 1 H), 4.42 (dd, J = 10.3, 5.9 Hz, 1 H), 4.47 (d, J = 8.0 Hz, 1 H), 4.56 (d, J = 9.4 Hz, 1 H), 4.93 (d, J = 7.9 Hz, 1 H), 5.25 (d, J = 7.8 Hz, 1 H), 5.97 (t, J = 8.9 Hz, 1 H), 6.18 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 9.8, 14.2, 15.0, 19.0, 20.8, 22.1, 22.6, 24.8, 25.6, 26.3, 28.0, 28.2, 29.2, 33.3, 35.1, 35.9, 36.3, 43.0, 44.3, 45.8, 52.4, 58.1, 71.8, 73.9, 74.1, 74.8, 75.5, 76.1, 80.0, 80.1, 80.7, 84.7, 132.8, 142.5, 156.1, 169.6, 171.4, 173.4, 174.3, 203.5. HRMS (FAB) m/z calcd for C₄₁H₆₁NO₁₅·H⁺: 808.4119. Found: 808.4118 (Δ = 0.2 ppm).

2-Debenzoyl-2,13-[(10*R*,9*S*)-9-*tert*-butoxycarbonylamino-10-hydroxy-3,3-dimethyl-1,11-diketoundecylene]baccatin III (6'm): 96% yield; white solid; $[\alpha]_D^{20}$ -66.4 (c 0.47, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.95 (s, 3 H), 1.03 (s, 3 H), 1.05 (s, 3 H), 1.20 (s, 3 H), 1.39 (m, 8 H), 1.44 (s, 9 H), 1.57 (s, 3 H), 1.86 (m, 1 H), 1.87 (s, 3 H), 2.17 (m, 3 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 2.35 (d, J = 12.0 Hz, 1 H), 2.52 (m, 3 H), 3.77 (d, J = 7.6 Hz, 1 H), 3.88 (m, 1 H), 3.98 (m, 1 H), 4.09 (d, J = 8.0 Hz, 1 H), 4.42 (m, 1 H), 4.51 (d, J = 8.0 Hz, 1 H), 4.66 (d, J = 7.5 Hz, 1 H), 4.93 (d, J = 8.0 Hz, 1 H), 5.29 (d, J = 7.6 Hz, 1 H), 6.13 (t, J = 8.6 Hz, 1 H), 6.19 (s, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 9.6, 14.8, 20.8, 22.1, 22.6, 23.9, 24.5, 26.4, 28.3, 29.0, 31.5, 32.9, 34.4, 35.1, 36.1, 41.0, 43.1, 46.2, 46.3, 55.0, 58.2, 71.8, 72.0, 74.8, 75.4, 75.7, 76.2, 77.2, 79.5, 80.8, 84.8, 132.7, 142.3, 156.6, 169.7, 170.7, 173.2, 173.25, 203.4. HRMS (FAB) m/z calcd for C₄₂H₆₃NO₁₅·H⁺: 822.4276. Found: 822.4281 (Δ = 0.6 ppm).

2-Debenzoyl-2,13-[(11*R*,10*S*)-10-*tert*-butoxycarbonylamino-11-hydroxy-3-aza-3-methyl-1,4,12-triketododecylene]baccatin III (6'o): 100% yield; white solid; ¹H NMR (250 MHz, CDCl₃) δ 1.09 (s, 3 H), 1.24 (s, 3 H), 1.28 (s, 9 H), 1.44 (s, 3 H), 1.66 (s, 3 H), 1.86 (s, 3 H), 2.02 (s, 1 H), 2.03 (s, 3 H), 2.21 (s, 3 H), 2.36 (m, 4 H), 2.50 (m, 1 H), 3.21 (s, 3 H), 3.60 (d, 1 H), 3.82 (m, 1 H), 4.3 (m, 2 H), 4.6 (m, 1 H), 4.95 (d, 1 H), 5.50 (d, 1 H), 6.23 (m, 2 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 4.9, 10.2, 16.3, 17.7, 18.0, 18.8, 19.2, 22.2, 25.2, 26.6, 29.3, 30.9, 32.6, 33.2, 38.3, 40.6, 47.2, 54.1, 67.4, 69.9, 71.7, 73.5, 76.7, 80.3, 128.0, 137.8, 152.0, 164.0, 165.0, 167.2, 169.0, 170.0, 199.0. HRMS (FAB, DCM/NBA) m/z calcd for C₄₁H₆₀N₂O₁₆·H⁺: 837.4021. Found: 837.4022 (Δ = -0.1 ppm).