6.1 General Experimental Methods

Unless otherwise noted, all chemicals and materials were used as received from Aldrich Chemical Co. without further purification. Grubbs catalysts were purchased from Acros Organics Chemical Co. Moisture-sensitive reactions were performed in oven–dried glassware under argon atmospheres. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. Dichloromethane was distilled from calcium hydride. Thin layer chromatography (TLC) plates (silica gel 60 GF, with aluminum support) from E. Merck were used for monitoring progress of a reaction and visualized with 254 nm UV light with vanillin/sulfuric acid spray in some cases by dipping in an ethanolic phosphomolybdic acid solution. Silica gel for column chromatography was purchased from E. Merck (230–400 mesh). Preparative thin layer chromatography (PTLC) plates (silica gel 60 GF) were purchased from Analtech. $^1$H and $^{13}$C NMR spectra were obtained from a Varian Unity 400 spectrometer in CDCl$_3$ at 399.951 and 100.578 MHz frequency respectively. Chemical shifts are reported as $\delta$–values relative to tetramethylsilane (TMS) as internal reference. Mass spectra (HRFAB and LRFAB) were obtained at Nebraska Center for Mass Spectrometry, University of Nebraska, and the Analytical Services in the Department of Chemistry at Virginia Tech. The phrase “worked–up in usual way” refers to addition of an excess amount of a suitable organic solvent and water to the reaction mixture and washing the organic layer with water and brine. The collected organic phase is then dried over anhydrous sodium sulfate and evaporated. Known intermediates and starting materials were prepared following procedures that are reported in the literature. NMR and other characterization data of the known compounds were compared to reported values and were identical.
2–Debenzoyl–2–(p–fluorobenzoyl)–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (2.7).

To a solution of of p–fluorobenzoic acid (757 mg, 5.40 mmol) in dry toluene (10 mL) was added 1,3–diisopropylcarbodiimide (0.85 mL, 5.40 mmol) and (660 mg, 5.40 mmol) and the heterogenous solution was stirred at room temperature for 5 min, and then 7,10,13–tri(triethylsilyl)–2–debenzoyl–10–deacetylbaccatin (200 mg, 0.255 mmol) in 5 mL of toluene was added dropwise and stirred for 10 min. at room temperature and heated to 55 °C for 24 h. The reaction mixture was diluted with ethyl acetate and washed with water and sodium bicarbonate. The combined organic phase was washed with water, brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Purification of the crude product by PTLC (EtOAc : hexanes 2.5:7.5), gave 2–debenzoyl–2–(p–fluorobenzoyl)–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (2.7) as a white solid in 75% yield.

$^1$H NMR δ 0.61 (m, 18H), 0.98 (m, 27H), 1.09 (s, 3H), 1.19 (s, 3H), 1.32 (s, 3H), 1.63 (m, 2H), 1.90 (s, 3H), 2.14 (s, 3H), 2.18 (m, 2H), 2.83 (m, 3H), 3.60 (d, J = 6 Hz), 3.80 (d, J = 10 Hz), 3.82 (d, J = 10 Hz), 4.54 (m, 1H), 4.97 (t, J = 4, 1H), 5.07 (s, 1H), 5.65 (dd, J = 5.2 Hz, J = 5.2 Hz, 1H), 7.13 (t, J = 8.4 Hz, 2H), 7.96 (ddd, J = 4, 2H); $^{13}$C NMR δ 5.05, 5.44, 5.76, 14.03, 14.59, 21.13, 22.53, 25.40, 37.99, 40.85, 43.12, 55.78, 68.74, 70.94, 72.56, 73.02, 77.03, 86.60, 90.22, 115.99, 116.21, 132.32, 132.41, 137.90, 139.51, 164.37, 171.25, 206.66. HRFABMS m/z calculated for C$_{47}$H$_{77}$FO$_{10}$Si$_3$ (M+H)$^+$ 903.4730, found 903.4752, Δ = 2.4 ppm.


To a stirred solution of 2–debenzoyl–2–(p–fluorobenzoyl)–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (2.7, 169 mg, 0.186 mmol) in 1.1 mL of DMF was added imidazole (67 mg, 0.98 mmol) and chlorodimethylsilane (54 µL, 0.49 mmol) and stirred at room temperature for 1 h. After TLC (2:8, EtOAc:hexanes) showed the completion of the reaction, the reaction mixture was quenched with saturated sodium bicarbonate (solution in methanol) of and stirred for additional 10 min. then extracted with ethyl acetate and washed with water and brine. The combined organic phase was dried over anhydrous...
sodium sulfate and concentrated under reduced pressure. Purification of the crude product by PTLC (2:8, EtOAc:hexanes) gave the desired product in 94% yield.

$^1$H NMR $\delta$ –0.29(d, $J = 4$, 3H), 0.06(d, $J = 4$, 3H), 0.55(m, 6H), 0.67(m, 6H), 0.90(t, $J = 8$, $J = 8$, 9H), 1.01(t, $J = 8$, $J = 8$, 9H), 1.05(s, 3H), 1.64(s, 3H), 1.84(m, 1H), 2.09(s, 3H), 2.15(s, 3H), 2.26(m, 4H), 2.34(m, 1H), 2.48(m, 1H), 3.78(d, $J = 8$, 1H), 4.18(dd, $J = 8$, 1H), 4.42(dd, $J = 4$, $J = 4$, 1H), 4.51(m, 1H), 4.93(m, 2H), 5.67(d, $J = 8$, 1H), 6.43(s, 1H), 7.13(t, $J = 8$, $J = 8$, 2H), 8.04(m, 2H), $^{13}$C NMR $\delta$ 0.18, 0.60, 4.97, 5.47, 6.96, 7.11, 10.22, 14.40, 14.96, 21.17, 21.24, 22.13, 22.60, 27.62, 37.41, 39.37, 44.20, 46.82, 58.44, 68.69, 72.36, 75.84, 76.09, 76.64, 76.94, 77.26, 77.58, 81.17, 82.14, 84.51, 115.80, 116.02, 131.92, 132.75, 132.84, 144.94, 164.58, 164.80, 169.51, 169.98, 202.36.

LRFABMS m/z calculated for (M+H)$^+$ C$_{45}$H$_{72}$FO$_{11}$Si$_3$ 891, found 891.


To a cooled solution of 2–Debenzoyl–(2–p–fluorobenzoyl)–1–dimethylsilyl–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (167 mg, 0.173 mmol) in 4 mL of THF at 0 °C was added Red–Al® (65 wt. % solution of sodium bis(2–methoxyethoxy)aluminum hydride in toluene, 0.32 mL, 1.53 mmol). After 45 min. the reaction mixture was carefully quenched with saturated potassium sodium tartrate solution and extracted with ethyl acetate, and then washed with water and brine. The resulting organic layer was dried and concentrated under reduced pressure. The residue was subjected to a preparative chromatography (3:7, EtOAc:hexanes) to afford 75 mg (47%) of the desired product 2.8. 62 mg of unreacted starting material was also recovered from the reaction.

$^1$H NMR $\delta$ –0.3 (d, $J = 2.4$ Hz, 3H), 0.01 (d, $J = 2.8$ Hz, 3H), 0.57 (m, 6H), 0.66 (m, 6H), 0.80 (m, 6H), 0.98 (m, 27H), 1.17 (s, 3H), 1.53 (s, 3H), 1.54 (m, 2H), 2.44 (m, 1H), 2.55 (m, 1H), 2.77 (dd, $J = 12.8$ Hz, $J = 2.4$ Hz, 1H), 3.59 (d, $J = 6$ Hz, 1H), 3.79 (b, 1H), 4.01 (dd, $J = 5.6$ Hz, $J = 6.0$ Hz, 1H), 4.17 (d, $J = 8$ Hz, 1H), 4.28 (d, $J = 8$ Hz, 1H), 4.55 (m, 1H), 4.66 (m, 1H), 5.22 (s, 1H), 5.56 (d, $J = 4.8$ Hz, 1H), 7.10 (t, $J = 8.4$ Hz, 2H), 8.14 (ddd, $J = 2$H), $^{13}$C NMR $\delta$ 0.59, 0.97, 4.87, 5.43, 6.24, 7.04, 10.22, 17.44, 18.54, 30.24, 33.73, 37.88, 38.58, 43.25, 51.81, 59.51, 70.22, 73.25, 74.98, 76.71, 79.68, 80.47, 88.68,

A solution of 2–debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–1–dimethylsilyl–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (0.159 mg, 0.172 mmol) in 3.6 mL of THF at 0 °C was treated with LHMDS (0.234 mL, 1 M, 0.234 mmol) followed by acetyl–d$_3$–chloride (0.06 mL, 0.9 mmol). The reaction mixture was stirred for 3 h and quenched with saturated NH$_4$Cl solution. The reaction mixture was extracted with ethyl acetate and washed with water and brine. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification of the crude residue with PTLC (2:8, EtOAc:hexanes) gave 2–debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d$_3$–acetyl)–1–dimethylsilyl–7,10,13–tris(triethylsilyl)–10–deacetylbaccatin (2.9, 110 mg, 66%).

$^1$H NMR δ = 0.28(d, J = 2.8, 3H), 0.070(d, J = 2.8, 3H), 0.56(m, 6H), 0.67(m, 6H), 0.92(m, 9H), 1.01(m, 12H), 1.18(s, 3H), 1.65(s, 3H), 1.82(m, 1H), 2.56(s, 3H), 2.24(m, 1H), 2.38(m, 1H), 2.45(m, 1H), 3.79(d, J = 7.2), 4.20(dd, J = 5.2), 4.52(m, 1H), 4.94(bd, J = 7.6, 1H), 5.68(d, J = 6.8, 1H), 6.44(s, 1H), 7.14(t, J = 12, 2H), 8.10(m, 2H). $^{13}$C NMR δ 0.20, 0.69, 5.00, 6.07, 7.12, 7.16, 10.25, 14.97, 22.14, 37.43, 39.38, 44.20, 46.84, 58.46, 68.69, 72.37, 75.83, 76.11, 76.67, 81.17, 82.15, 84.53, 115.81, 116.03, 126.87, 126.89, 131.94, 132.75, 132.85, 144.95, 164..60, 169.55, 202.37. LRFABMS $m/z$ calculated for C$_{47}$H$_{82}$FO$_9$Si$_4$(M+Na)$^+$ 943, found 943.

2–Debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d$_3$–acetyl)–10–deacetylbaccatin (2.9)

To a solution of 2–debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d$_3$–acetyl)–1–dimethylsilyl–7,10,13–tris(triethylsilyl)baccatin III (2.9) (80 mg, 0.082 mmol) in 1.5 mL of THF was added HF–pyridine (2 mL, large excess) and the solution was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate and washed with sodium bicarbonate solution. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue
was purified with PTLC (7:3, EtOAc:hexanes) to afford the desired product (41 mg, 88%).

\[ ^1H \text{NMR } \delta \]

-1.09(s, 3H), 1.66(s, 3H), 1.85(m, 1H), 2.04(bs, 4H), 2.45(s, 3H), 2.56(m, 1H), 3.86(d, J = 6.8, 1H), 4.13(d, J = 7.6, 1H), 4.27(d, J 8.4, 1H), 4.45(dd, J = 8.4, 1H), 4.88(bt, 1H), 4.98(bd, J = 7.6, 1H), 5.59(d, J = 7.2, 1H), 6.31(s, 1H), 7.15(t, J = 7.2, 2H), 8.11(dd, J = 7.2, J = 4.2, 2H). LRFABMS m/z calculated for C_{29}H_{33}D_{3}FO_{10}(M+H)^+ 566, found 566.

**2–Debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d_{3}–acetyl)–baccatin III (2.10)**

To a solution of 2–debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d_{3}–acetyl)–10–deacetylbaccatin (40 mg, 0.070 mmol) in 1.5 mL of THF was added a catalytic amount (0.1equiv) of CeCl_{3} and stirred at room temperature for 10 min. Then, acetic anhydride (0.21 mL, 2.1 mmol) was added and stirred for 2 h. After the reaction is completed, the mixture was diluted with ethyl acetate and washed with sodium bicarbonate solution followed by water and brine. After drying over anhydrous sodium sulfate the solvent was evaporated and the residue was purified by preparative TLC (3:7, EtOAc:hexanes) to give 41 mg of **2.10** (96%) yield.

\[ ^1H \text{NMR } \delta \]

1.10 (s, 3H), 1.66 (s, 3H), 1.85 (m, 1H), 2.04 (s, 3H), 2.23 (s, 3H), 2.27 (m, 3H), 2.56 (m, 1H), 3.87 (d, J = 6.8 Hz, 1H), 4.13 (d, J = 7.6 Hz, 1H), 4.27 (d, J = 8.4 Hz, 1H), 4.45 (dd, J = 8.4 Hz, J = 4 Hz, 1H), 4.89 (t, J = 6.8 Hz, 1H), 4.98 (d, 7.6 Hz, 1H), 5.59 (d, J = 7.2 Hz, 1H), 6.31 (s, 1H), 7.15 (t, J = 9.2 Hz, 2H), 8.10 (dd, J = Hz, 2H), \[ ^{13}C \text{NMR } \delta \]

15.84, 21.12, 27.17, 35.79, 38.73, 42.89, 46.34, 58.90, 68.11, 72.50, 75.29, 76.42, 76.57, 79.32, 80.96, 84.69, 116.01, 116.23, 131.98, 132.83, 146.68, 166.29, 171.58, 204.32. LRFABMS m/z calculated for C_{31}H_{35}D_{3}FO_{11}(M+H)^+ 608, found 608.

**2–Debenzoyl–(2–p–fluorobenzoyl)–4–deacetyl–(4–d_{3}–acetyl)–7–O–triethylsilylbaccatin III (2.3)**

2–Debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d_{3}–acetyl)–baccatin III (2.10, 40 mg, 0.066 mmol was dissolved in 1.5 mL of dry DMF and treated with imidazole (42 mg, 0.61 mmol) and chlorotriethylsilane (0.05 mL, 0.3 mmol) and stirred for 30 minutes and at this point the TLC showed the completion of the reaction. The reaction mixture was
diluted with methanol solution saturated with sodium bicarbonate and stirred for 10 minutes. The mixture was diluted and extracted with ethyl acetate, washed with water and brine. The dried organic phase was concentrated under reduced pressure and purified by preparative TLC (6:4, EtOAc:hexanes) to give 2–debenzoyl–2–(p–fluorobenzoyl)–4–deacetyl–4–(d₃–acetyl)–7–triethylsilylbaccatin III (2.3, 45 mg, 94%).

\[ \text{1}^1 \text{H NMR } \delta \text{ 0.57(m, 18H), 0.87(m, 12H), 1.10(s, 3H), 1.87(s, 4H), 1.58(s, 3H), 1.67(s, 3H), 1.87(m, 1H), 2.06(d, J = 4.8, 1H), 2.18(bs, 4H), 2.53(m, 1H), 3.87(d, J = 8, 1H), 4.28(d, J = 8, 1H), 4.48(dd, J = 6.8, J = 4, 1H), 4.83(m, 1H), 4.97(d, J = 9.6, 1H), 5.60(d, J = 7.2, 1H), 6.50(s, 1H), 7.15(t, J = 8, 2H), 8.12(m, 2H).} \]

\[ \text{1}^3 \text{C NMR } \delta \text{ 5.50, 6.97, 10.16, 15.19, 27.05, 37.44, 38.37, 42.98, 47.47, 58.87, 68.17, 72.56, 75.10, 75.94, 76.67, 78.99, 81.07, 84.47, 115.97, 116.19, 132.84, 132.93, 144.13, 166.36, 202.34.} \]

LRFABMS m/z calculated for C₃₇H₄₈D₃FO₁₁Si (M+Na)^+ 744, found 744.

7,13–bis(triethylsilyl)–2–debenzoyl–2–(p–fluorobenzoyl)–baccatin III

\[ \text{1}^1 \text{H NMR } \delta \text{ 0.57(m, 6H), 0.65(m, 6H), 0.91(t, J = 8, J = 8, 9H), 1.00(t, J = 8, J = 8, 9H), 1.10(s, 3H), 1.17(s, 3H), 1.65(s, 3H), 1.83(m, 1H), 2.10(s, 3H), 2.16(s, 3H), 2.7(s, 3H), 2.50(m, 1H), 3.80(d, J = 4, 1H), 4.12(d, J = 8, 1H), 4.46(dd, J = , J = , 1H), 4.93(t, J = 16, J = 8, 2H), 5.59(d, J = 8, 1H), 6.45(s, 1H), 7.13(t, J = 8, J = 8, 3H), 8.01(dd, J = 4, J = 4, 3H),} \]

\[ \text{1}^3 \text{C NMR } \delta \text{ 5.05, 5.47, 6.96, 7.16, 10.29, 15.03, 21.17, 21.40, 22.56, 26.66, 37.36, 40.05, 43.21, 47.11, 58.47, 68.64, 72.34, 75.68, 75.89, 76.61, 76.93, 77.24, 77.56, 79.73, 80.95, 84.44, 115.94, 116.16, 125.98, 131.76, 132.78, 132.87, 132.92, 145.74, 166.36, 169.47, 170.05, 202.51.} \]

6.2 Typical Procedures for the Preparation of β–lactams:

i) To a solution of o–allyloxy benzaldehyde in dichloromethane was added 1.1 equiv of p–anisidine and large excess of anhydrous magnesium sulfate and stirred at room temperature for 12 hours. The yellowish slurry was filtered and concentrated under reduced pressure and the crude imine was taken to the next step without purification (quantitative yields were obtained).
ii) To the crude imine dissolved in anhydrous dichloromethane was added 3 equiv of triethylamine (Hünig’s base improved yields) and cooled to –78 °C. To this solution 1.2 equivalents of acetoxyacetyl chloride was added dropwise and the thick reaction mixture was allowed slowly to warm–up to room temperature and stirred for 12 h. The dark crude reaction mixture was concentrated without aqueous work–up and purified by a normal phase column chromatograph (4:6, EtOAc:hexanes). One more short column chromatograph was done to get sufficiently pure lactams (yields range 65–76%).

iii) The racemic β–lactam was then dissolved in acetonitrile, and to this solution a phosphate buffer at pH 7.2 was mixed and stirred vigorously. Immobilized Lipase PS Amano enzyme (one to one weight ratio to the lactam) was added and stirred for 2–3 days. The progress of the reaction was monitored by TLC, and after the completion of the reaction, the lipase was filtered off and the solution was worked–up in the usual way. Purification by column chromatography (4:6 EtOAc:hexanes) gave the less polar, enantiomerically pure acetoxy–β–lactam (48–50% yield based on the required isomer).

iv) The solution of acetoxy–β–lactam in THF was added slowly to a 1 M KOH solution at 0 °C. The solution was stirred 45 min and the deacetylation reaction was completed. The THF in the reaction mixture was evaporated under reduced pressure and at low temperature and diluted with ethyl acetate and worked–up in the usual way. The product of the reaction was used for the next step without purification (quantitative yield).

v) To a solution of hydroxy lactam in minimum amount of DMF was added 3 equiv of imidazole and 1.1 equiv of triisopropyl chloride and stirred for 3 h. The reaction mixture was diluted with ethyl acetate and worked–up as usual. Column chromatography (2:8, EtOAc:hexanes) of the crude product gave protected β–lactams in yields ranging from 72% to 84%.

vi) To a solution of TIPS protected lactam in acetonitrile at –5 °C, was dropwise added CAN (ceric ammonium nitrate) (3 equiv) dissolved in water. The reaction mixture was stirred for 45 min and TLC indicated the consumption of the starting material it was
diluted with ethyl acetate and washed with water, saturated solution of sodium metabisulfite and saturated sodium bicarbonate and worked–up as usual. The crude product was chromatographed (4:6, EtOAc:hexanes) to give the PMP deprotected lactam in 69–75% yield.

vii) To a solution of the deprotected β–lactam in dichloromethane at 0 °C was added catalytic amount of DMAP, 3 equiv of triethylamine, and acid chloride. The mixture was then stirred at room temperature for 1 h and diluted with ethyl acetate and worked up in the usual way. The acylated lactam was purified by chromatography (2:8, EtOAc:hexanes) to give the final β–lactam (87–90% yield).

(3R, 4S)–1–Benzoyl–3–TIPSO–4–(p–deuterophenyl)azetidin–2–one (2.4)

\[
{^1}H \text{ NMR } \delta 0.90(\text{m, 18H}), 0.98(\text{t, 3H}), 5.25(\text{d, J = 4, 1H}), 5.43(\text{d, J = 4, 1H}), 7.37(\text{dd, J = 8, J = 12, 4H}), 7.48(\text{t, J = 8, 2H}), 7.59(\text{m, 1H}), 8.04(\text{d, J = 8, 2H}), 11.89, 17.58, 17.67, 61.41, 76.82, 128.28, 128.38, 130.10, 133.57, 134.01, 165.70, 166.50. \]

LRFABMS \text{ m/z calculated for } C_{25}H_{33}DNO_3Si (M+H)^+ 425, found 425.


To a heterogenous mixture of NaH (67.20 mg, 2.8 mmol) in THF was added 2.3 (42 mg, 0.058 mmol) and stirred for 10 min. Then, a THF solution of β–lactam (47.5 mg, 0.112 mmol) was added slowly. The reaction mixture was stirred for 4 h and the TLC showed the completion of the starting material. The reaction mixture was cooled to 0 °C and quenched with acetic acid and extracted with ethyl acetate. After washing the organic layer with large quantities of water and saturated sodium bicarbonate and brine the layer was dried and concentrated under reduced pressure. The crude reaction product was purified on preparative TLC (4:6, EtOAc:hexanes) and gave the protected labeled taxol in 84% yield.

\[
{^1}H \text{ NMR } \delta 0.59(\text{m, 6H}), 0.94(\text{m, 30H}), 1.03(\text{s, 3H}), 1.21(\text{s, 3H}), 1.70(\text{s, 3H}), 1.91(\text{m, 1H}), 2.05(\text{s, 3H}), 2.18(\text{m, 2H}), 2.53(\text{m, 1H}), 3.84(\text{d, J = 6.8, 1H}), 4.20(\text{d, J = 8.4, 1H}), 4.28(\text{d, J = 8.4, 1H}), 4.48(\text{dd, J = 6.4, J = 4.0, 1H}), 4.94(\text{m, 2H}), 5.67(\text{d, J = 7.2, 1H}),
\]
5.74 (d, J = 8.8, 1H), 6.24 (t, J = 8.4, 1H), 6.46 (s, 1H), 7.12 (d, J = 8.8, 1H), 7.18 (t, J = 8.4, 2H), 7.38 (m, 7H), 7.74 (d, J = 7.2, 2H), 8.16 (m, 2H). LRFABMS m/z calculated for C₆₂H₈₀D₄FNO₁₄Si₂ (M+Na)⁺ 1169, found 1169.

\[3'-(p\text{-deuterophenyl})-2\text{-debenzoyl}-2-(p\text{-fluorobenzoyl})-4\text{-deacetyl}-4-(d₃\text{-acetyl})-\text{taxol}-\text{(2.2)}\]

To 54 mg of 2'-(triisopropyl)-3'-(p-deuterophenyl)-7-O-triethylsilyl-2-debenzoyl-2-(p-fluorobenzoyl)-4-deacetyl-4-(d₃-acetyl)-paclitaxel (0.032 mmol) in 1.0 mL of THF was added HF/pyridine (1.5 mL, large excess) and the solution was stirred at room temperature for 3 h. The reaction mixture was diluted with ethyl acetate and washed with sodium bicarbonate solution. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by preparative TLC (7:3, EtOAc:hexanes) to afford the desired product (2.2, 40 mg, 97%).

\[^{1}H\text{ NMR \ \delta 1.13(s, 3H), 1.24(s, 3H), 1.25(bs, 3H), 1.59(bs, 1H), 1.68(s, 4H), 1.81(s, 3H), 1.89(m, 1H), 2.24(s, 1H), 2.33(m, 2H), 2.45(d, J = 4, 1H), 2.55(m, 1H), 3.50(d, J = 4, 1H), 3.80(d, J = 7.2, 1H), 4.19(d, J = 8.4, 1H), 4.28(d, J = 8.4, 1H), 4.41(m, 1H), 4.81(bs, 1H), 4.94(d, J = 7.6, 1H), 5.64(d, J = 7.2, 1H), 5.81(dd, J = 2.4, J = 6.8, 1H), 6.25(m, 1H), 6.27(s, 1H), 6.95(d, J = 8.8, 1H), 7.19(t, J = 8, 2H), 7.47(m, 7H), 7.72(d, J = 8.4, 1H), 8.16(m, 2H), 9.79, 15.09, 27.07, 35.90, 43.37, 45.80, 55.05, 58.81, 72.40, 72.58, 73.29, 75.36, 79.40, 81.32, 84.67, 116.13, 116.35, 127.19, 128.95, 129.18, 132.25, 133.04, 133.13, 133.83, 138.15, 142.27, 167.28, 173.02, 203.81.\]

HRFABMS m/z calculated for C₄₇H₄₆D₄FNO₁₄ (M+Na)⁺ 898.3364, found 898.3377, Δ = -1.5 ppm.

\((3R, 4S)-1\text{-Benzoyl}-3\text{-TIPSO}-4\text{-(m-allyloxyphenyl)azetidin-2-one (3.7a).}\)

\[3.7a, [\alpha]^{20}_D = +40.2 \text{ (c 0.0146, CHCl}_3); \]

\[^{1}H\text{ NMR \ \delta 0.92 (m, 18 H), 0.99 (m, 3H), 4.52 (m, 2H), 5.24 (d, J = 6 Hz, 1H), 5.26 (dd, J = 12 Hz, J = 1.6 Hz, 1H), 5.40 (d, J = 6 Hz, 1H), 5.4 (dd, J = 1.6 Hz, 1H), 6.04 (m, 1H), 6.87 (dd, J = 8.4 Hz, J = 3.6 Hz, J = 1.2 Hz, 1H), 6.98 (m, 2H), 7.27 (dd, J = 8 Hz, J = 15.5 Hz, 1H), 7.48 (m, 2H), 7.59 (m, 1H), 8.04 (dd, J = 1.2 Hz, J = 2.1 Hz, 2H) \text{^{13}C NMR \ \delta 11.77, 17.55, 61.14, 68.94, 114.71, 117.68, 120.90, 128.23, 129.25, 129.95, 132.16, 133.36, 133.42, 135.44, 158.66, 165.45, 166.32;} \]
HRFABMS m/z calc'd for C$_{28}$H$_{37}$NO$_4$Si(M+Li)$^+$, 486.2652, found 486.2669, $\Delta = -3.6$ ppm.

(3R , 4S)-1–Benzoyl–3–TIPSO–4–(m–vinylphenyl)azetidin–2–one (3.7b)

[ 3.7b. [ $\alpha$ ]$^2_0$ = +117.8 (c 2.567, CHCl$_3$); $^1$H NMR $\delta$ 0.92 (m, 18 H), 0.97–1.04 (m, 3H), 5.24 (dd, J= 0.8 Hz, J = 8 Hz, 1H), 5.26 (d, J = 6 Hz, 1H), 5.43 (d, J= 6 Hz, 1H), 5.74 (dd, J = 0.8 Hz, J = 16.8 Hz, 1H), 6.72 (dd, J = 6.8 Hz, J = 17.6 Hz, 1H), 7.29–7.38 (m, 3H), 7.41 (bs, 1H), 7.48 (t, J = 5.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 8.04 (d, J = 7.2 Hz, 2H) $^{13}$C NMR $\delta$ 11.60, 17.35, 61.01, 76.52, 114.05, 126.16, 127.58, 128.12, 128.30, 129.82, 132.00, 133.32, 134.04, 136.56, 137.49, 165.35, 166.20. HRFABMS m/z calculated for C$_{27}$H$_{36}$NO$_3$Si (M+H)$^+$ 450.2464, found 450.2503, $\Delta = 8.6$ ppm.

4-deacetyl-(4-(4-pentenoyl))-1-O-dimethylsilyl-7,10,13-tirs-(O-triethylsilyl)-10-deacetylbaccatin (3.9)

To a solution of 3.8 (500 mg, 0.55 mmol) in dry THF (5 mL) at 0 °C was added LHMDS (0.60 mL, 0.60 mmol) and stirred for 30 min. followed by the addition 4–pentenoyl chloride (71 $\mu$L, 0.60 mmol) and stirred for 1.5 h. The reaction mixture was quenched with saturated solution of NH$_4$Cl and the aqueous phase was extracted with ethyl acetate (25 mL x 3). The combined organic phase is washed with water and brine and dried over anhydrous sodium sulfate and concentrated under vacuo. Purification on PTLC (1.5:8.5 EtOAc/Hexanes) afforded the desired intermediate C–4 modified compound as a white solid in 78% (425 mg) yield. A minor product with a loss of dimethylsilyl group was also isolated and used in the subsequent step.

$^1$H NMR $\delta$ –0.29(d, J = 4, 3H), 0.06(d, J = 2.8 Hz, 3H), 0.66(m, 18H), 0.98(m, 27H), 1.10(s, 3H), 1.19(s, 3H), 1.65(s, 3H), 1.96(s, 3H), 2.29(m, 2H), 2.55(m, 3H), 2.68(m, 2H), 3.83(d, J = 8, 1H), 4.23(dd, J = 8, 2H), 4.38(dd, J = 8 Hz, 4, 1H), 4.54(m, 1H), 4.89(d, J = 8), 5.09(d, 12, 1H), 5.15(s, 1H), 5.17(d, J = 18, 1H), 5.71(d, J = 8, 1H), 5.91(m, 1H), 7.46(t, J = 8, 2H), 7.58(t, J = 8, 1H), 8.10(d, J = 8, 2H), HRFABMS m/z calculated for C$_{52}$H$_{88}$O$_{10}$Si$_4$ (M+Na)$^+$ 1007.5352, found 1007.5329, $\Delta = -2.3$ ppm.
4-deacetyl-(4-(4-pentenoyl))-10-deacetylbaccatin (3.10)
To a solution of 3.9 (417 mg, 0.42 mmol), in 10 mL of THF at 0 °C was added 1 mL of pyridine and 2.1 mL of HF/Py dropwise and stirred for 15 min and allowed to stir further for 12 h at room temperature. The reaction mixture is diluted with ethyl acetate and washed with saturated NaHCO₃ solution. The organic phase is then washed with water and brine and concentrated under reduced pressure. The crude product is then purified on PTLC (6.5:3.5, EtOAc/Hexanes) and gave the desired deprotected product in 91% (225 mg) yield.

$^1$H NMR $\delta$ 1.09(s, 6H), 0.96(d, $J = 8$, 1H), 1.61(s, 1H), 1.74(s, 3H), 1.82(m, 1H),
2.04(bs, 2H), 2.06(s, 3H), 2.27(m, 2H), 2.48(bs, 2H), 2.59(m, 1H), 2.70(m, 2H), 4.00(d, $J = 4$, 1H), 4.17(d, $J = 4$, 1H), 4.32(d, $J = 8$, 1H), 4.86(m, 1H), 4.93(d, $J = 8$, 1H), 5.09(d, $J = 4$, 1H), 5.16(d, $J = 16$, 1H), 5.24(d, $J = 4$, 1H), 5.63(d, $J = 8$, 1H), 5.90(m, 1H), 7.48(t, $J = 8$, 2H), 7.61(t, $J = 8$, 1H), 8.1(d, $J = 8$, 2H), $^{13}$C NMR $\delta$ 10.01, 14.41, 15.29, 20.00, 26.91, 28.75, 34.57, 37.16, 38.92, 42.82, 47.23, 57.88, 60.68, 68.01, 72.26, 75.07, 75.20, 76.83, 79.06, 81.00, 84.53, 116.06,128.85, 129.58, 130.32, 134.94, 136.85, 142.69, 167.27, 172.87, 211.91, HRFABMS m/z calculated for C$_{32}$H$_{40}$O$_{10}$ (M+Na)$^+$ 607.2519, found 607.2511, Δ = −1.3 ppm.

4-deacetyl-(4-(4-pentenoyl))-baccatin III (3.11)
To a solution of 3.10 (220 mg, 0.38 mmol) in THF and 0.1 equiv CeCl$_3$ at room temperature was stirred for 5 min and 10 equivalents of acetic anhydride was added and reacted for 3 h and after the completion of the reaction by TLC analysis the reaction mixture was diluted with ethyl acetate and washed twice with NaHCO$_3$ and the combined organic phase was washed with water, brine, dried over sodium sulfate and concentrated under vacuo. Purification of the crude product on PTLC (5:5, EtOAc/Hexanes) yielded the desired a white solid product (222 mg, 94%).

$^1$H NMR $\delta$ 1.07(s, 6H), 1.66(bs, 4H), 1.85(m, 1H), 2.04(bs, 4H), 2.21(d, 1H), 2.23(s, 3H),
2.28(m, 2H), 2.52(m, 4H), 2.68(m, 2H), 3.87(d, $J = 8$, 1H), 4.15(d, $J = 8$, 1H), 4.30(d, 1H), 4.48(m, 1H), 4.87(m, 1H), 4.95(d, $J = 8$, 1H), 5.07(d, $J = 12$, 1H), 5.13(d, $J = 16$, 1H), 5.61(d, $J = 8$, 1H), 5.90(m, 1H), 6.31(s, 1H), 7.48(t, $J = 8$, 2H), 7.61(t, $J = 8$, 1H), 8.10(d, $J = 4$, 2H), $^{13}$C NMR $\delta$ 9.68, 14.41, 15.78, 21.19, 27.16, 28.73, 34.56, 35.77,
38.87, 42.91, 46.40, 58.89, 60.65, 68.10, 72.51, 75.17, 76.44, 76.66, 79.32, 81.03, 84.80, 116.05, 128.84, 129.54, 130.32, 131.97, 133.92, 136.86, 146.72, 167.26, 171.61, 172.74, 204.40. LRFABMS m/z calculated for C_{34}H_{43}O_{11} (M+H)^+ 627, found 627.

4-deacetyl-(4-(4-pentenoyl))-7-O-triethylsilyl-baccatin III (3.6)

To a solution of 3.10 (215 mg, 0.34 mmol) in anhydrous 2 mL of DMF at 0°C and imidazole (69 mg, 1.02 mmol) was added chlorotriethylsilane (86 µL, 0.51 mmol) dropwise, via syringe. The reaction mixture was stirred for 4 h and after TLC analysis indicated the completion of the reaction, 3 mL of saturated methanol/NaHCO₃ solution was added and stirred for 10 min. The reaction mixture was then diluted with ethylacetate (75 mL), washed with water (15 mL x 2), brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified with PTLC (3:7, EtOAc/Hexanes) afforded the desired product as a white solid in 92% yield.

^1H NMR (CDCl₃) δ 0.58 (m, 6H), 0.92 (m, 9H), 1.03 (s, 3H), 1.19 (s, 3H), 1.62 (s, 3H), 1.87 (dt, J = 2 Hz, 12.4 Hz, 1H), 2.03(d, J = 5.2, 1H), 2.17 (s, 3H), 2.26 (m, 2H), 2.51 (m, 3H), 2.68 (t, J = 8 Hz, 2H), 3.87 (d, J = 7.2 Hz, 1H), 4.14 (d, J = 8.0 Hz, 1H), 4.30 (d, J = 8.0, 1H), 4.49 (dd, J = 6.8 Hz, 1H), 4.82 (m, 1H), 4.91 (d, J = 7.6 Hz, 1H), 5.07 (dd, J = 1.2 Hz, J = 9.2 Hz, 1H), 5.14 (d, J = 14 Hz, 1H), 5.63 (d, J = 7.2, 1H), 5.91 (m, 1H), 6.45 (s, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 8.11 (d, J = 7.2 Hz, 2H); ^13C NMR δ 5.49, 6.98, 10.17, 15.13, 20.32, 21.19, 27.04, 28.96, 34.90, 37.47, 38.48, 43.01, 47.56, 58.90, 68.20, 72.56, 74.97, 76.00, 76.77, 78.97, 81.09, 84.54, 116.07, 128.79, 129.61, 130.34, 132.92, 133.87, 136.88, 144.14, 167.33, 169.60, 172.66, 202.39; HRFABMS m/z calcd for C_{40}H_{56}O_{11}Si (M+Li)^+, 747.3752, found 747.3747, Δ = 0.6 ppm.

Preparation of compound 3.5a

To a solution of 3.6 (120 mg, 0.16 mmol) in anhydrous THF (1.5 mL) at −40 °C was added LHMDS ( 0.18 mL, 0.18 mmol) and stirred for 5 min and then β–lactam 3.7a (153 mg, 0.32 mmol) was added and allowed to stir for 45 min. and the reaction mixture was quenched with saturated solution of NH₄Cl and diluted with ethyl acetate (40 mL). The aqueous phase was extracted twice and the organic layer was washed with water, brine, dried over anhydrous sodium sulfate and concentrated under vacuo. The crude coupled
product then is purified with PTLC (2.5:7.5, EtOAc/Hexanes) to afford the taxoid–ω,ω′–diene 3.5a (182 mg, 92%) as a white solid:

\[ \text{\textsuperscript{1}H NMR (CDCl}_3) \delta 0.59 (m, 6H), 0.91 (m, 30H), 1.17 (s, 3H), 1.21 (s, 3H), 1.70 (s, 3H), 1.89 (dt, J = 2 Hz, 12 Hz, 1H), 2.04 (s, 3H), 2.17 (s, 3H), 2.39 (m, 2H), 2.48–2.71 (m, 4H), 3.05 (m, 1H), 3.83 (d, J = 7.2 Hz, 1H), 4.20 (d, J = 8.4 Hz, 1H), 4.31 (d, J = 8.4 Hz, 1H), 4.48 (dd, J = 6.8 Hz, J = 4 Hz, 1H), 4.54 (d, J = 2.4 Hz, 2H), 4.88 (m, 1H), 4.90 (s, 1H), 5.04 (d, J = 10.4 Hz, 1H), 5.13 (d, J = 15.6 Hz, 1H), 5.28 (dd, J = 9.2 Hz, J = 1.6 Hz, 1H), 5.39 (d, J = 16 Hz, 1H), 5.64 (d, J = 9.2 Hz, 1H), 5.70 (d, J = 7.2 Hz, 1H), 5.85 (m, 1H), 6.03 (m, 1H), 6.17 (t, J = 10 Hz), 6.46 (s, 1H), 6.84 (d, J = 5.6 Hz, 1H), 6.94 (s, 1H), 7.08 (d, J = 8.8 Hz, 1H), 7.29 (t, J = 8 Hz, 1H), 7.34–7.63 (m, 7H), 7.74 (d, J = 7.2 Hz, 2H), 8.16 (d, J = 7.2 Hz, 1H); \text{\textsuperscript{13}C NMR} \delta 5.52, 6.97, 10.34, 12.81, 14.58, 17.98, 18.03, 18.12, 21.10, 26.75, 30.01, 35.76, 37.44, 43.55, 47.00, 56.30, 58.63, 69.01, 72.13, 72.46, 75.14, 75.21, 75.70, 79.09, 81.43, 84.61, 113.30, 114.58, 117.06, 117.90, 119.12, 127.17, 128.051, 129.49, 129.92, 131.98, 133.86, 135.96, 140.24, 140.49, 159.28, 167.01, 167.23, 169.55, 172.11, 172.23, 210.81; HRFABMS \text{m/z calcd for C}_{68}H_{93}NO_{15}Si_2 (M+Li)^+, 1226.6141, found, 1226.6192, \Delta = –4.2 ppm.}

**Ring Closing Metathesis –preparation of 3.3**

To a solution of 3.5a (70 mg, 0.06 mmol) in 30 mL of anhydrous CH\textsubscript{2}Cl\textsubscript{2} at room temperature was added bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (Grubbs catalyst) (7.4 mg, 15 mol%) in 15 mL of CH\textsubscript{2}Cl\textsubscript{2} using a Harvard Apparatus syringe pump at 0.08 mL/min flow rate. The reaction mixture was stirred for 20 h and the solvent was removed under reduced pressure and the concentrated residue was purified with PTLC (2.5:7.5, EtOAc/Hexanes) to give the protected intermediate macrocyclic compound in 72% yield. HRFABMS \text{m/z calcd for C}_{66}H_{89}NO_{15}Si_2 (M+Li)^+, 1198.5931, found 1198.5757, \Delta = 2.2 ppm.

To a solution of silyl protected intermediate (45 mg, 0.038 mmol), in 4 mL THF at 0 °C was added 0.1 mL of pyridine and 0.23 mL of HF/Py dropwise and allowed to stir further for 12 h at room temperature. The reaction mixture was diluted with ethyl acetate and washed with saturated NaHCO\textsubscript{3} solution. The organic phase was then washed with water and brine and concentrated under reduced pressure. The crude product was
purified on PTLC (6:4, EtOAc/hexanes) and gave the desired macrocyclic taxoid 3.3 in 78% yield.

\[ ^1H\text{ NMR} \ \delta \ 1.16 \ (s, \ 3H), \ 1.30 \ (s, \ 3H), \ 1.69 \ (s, \ 3H), \ 1.84 \ (s, \ 3H), \ 1.89 \ (m, \ 1H), \ 2.41 \ (s, \ 3H), \ 2.34–2.56 \ (m, \ 5H), \ 2.68 \ (m, \ 1H), \ 2.88 \ (dt, \ J = 3.6 \ Hz, \ J = 7.2 \ Hz, \ 1H), \ 3.77 \ (d, \ J = 6.8 \ Hz, \ 1H), \ 4.22 \ (d, \ J = 8.4 \ Hz, \ 1H), \ 4.34 \ (d, \ J = 8.4 \ Hz, \ 1H), \ 4.41 \ (m, \ 1H), \ 4.68 \ (dd, \ J = 6 \ Hz, \ 1H), \ 4.78 \ (bd, \ 1H), \ 4.9 \ (d, \ J = 9.6 \ Hz, \ 1H), \ 5.57 \ (d, \ J = 8.8 \ Hz, \ 1H), \ 5.71 \ (d, \ J = 7.2 \ Hz, \ 1H), \ 5.75 \ (m, \ 1H), \ 5.84 \ (m, \ 1H), \ 6.27 \ (bs, \ 2H), \ 6.81 \ (d, \ J = 8.4 \ Hz, \ 1H), \ 6.96 \ (d, \ J = 5.2 \ Hz, \ 1H), \ 7.06 \ (bs, \ 1H), \ 7.30–7.56 \ (m, \ 7H), \ 7.67 \ (d, \ J = 6.4 \ Hz, \ 1H), \ 7.71 \ (d, \ J = 7.2 \ Hz, \ 2H), \ 8.18 \ (d, \ J = 7.2 \ Hz, \ 2H);\ ^{13}C\text{ NMR} \ \delta \ 9.6, \ 14.71, \ 20.95, \ 22.36, \ 26.99, \ 29.26, \ 29.74, \ 35.50, \ 35.79, \ 36.07, \ 37.58, \ 43.35, \ 45.71, \ 55.55, \ 58.57, \ 70.09, \ 72.26, \ 72.77, \ 72.84, \ 75.15, \ 75.59, \ 76.34, \ 79.41, \ 81.17, \ 84.61, \ 116.39, \ 119.06, \ 119.32, \ 119.52, \ 127.13, \ 127.86, \ 128.75, \ 128.80, \ 129.31, \ 130.29, \ 130.41, \ 132.00, \ 133.14, \ 133.74, \ 133.80, \ 133.90, \ 139.23, \ 142.43, \ 158.44, \ 167.00, \ 171.37, \ 173.38, \ 203.71; \text{ HRFABMS} \ m/z \ \text{calcd for } C_{51}H_{55}NO_{15} (M+Li)^+, \ 928.3732, \ \text{found} \ 928.3746, \ \Delta = -1.6 \ ppm.\]

**Macrocyclic taxoid 3.4**

Macrocyclic taxoid 3.4 was prepared using similar procedure for compound 3.3.

\[ ^1H\text{ NMR} \ \delta \ 1.14 \ (s, \ 3H), \ 1.31 \ (s, \ 3H), \ 1.61 \ (s, \ 3H), \ 1.69 \ (s, \ 3H), \ 1.78 \ (m, \ 1H), \ 1.89 \ (m, \ 1H), \ 2.1 \ (m, \ 2H), \ 2.23 \ (s, \ 3H), \ 2.53 \ (m, \ 3H), \ 2.64–2.86 \ (m, \ 3H), \ 3.70 \ (d, \ J = 7.2 \ Hz, \ 2H), \ 4.19 \ (d, \ J = 8.4 \ Hz, \ 1H), \ 4.29 \ (d, \ J = 8.4 \ Hz, \ 1H), \ 4.37 \ (m, \ 1H), \ 4.52 \ (t, \ J = 5.6 \ Hz), \ 4.88 \ (d, \ J = 8 \ Hz, \ 1H), \ 5.60 \ (m, \ 1H), \ 5.69 \ (d, \ J = 7.2 \ Hz, \ 1H), \ 5.88 \ (m, \ 1H), \ 6.25 \ (s, \ 1H), \ 6.27 \ (m, \ 1H), \ 6.70 \ (d, \ J = 11.6 \ Hz, \ 1H), \ 7.03 \ (d, \ J = 7.6 \ Hz, \ 1H), \ 7.19 \ (d, \ J = 7.6 \ Hz, \ 1H), \ 7.27 \ (m, \ 1H), \ 7.35–7.55 \ (m, \ 7H), \ 7.63 \ (t, \ J = 7.6 \ Hz, \ 1H), \ 7.81 \ (d, \ J = 7.2, \ 2H), \ 8.07 \ (d, \ J = 7.2 \ Hz, \ 2H); \ ^{13}C\text{ NMR} \ \delta \ 9.89, \ 14.51, \ 21.09, \ 22.84, \ 24.09, \ 27.50, \ 34.97, \ 35.79, \ 35.95, \ 43.55, \ 46.12, \ 71.76, \ 72.48, \ 75.33, \ 75.67, \ 76.04, \ 79.61, \ 82.00, \ 84.94, \ 125.12, \ 126.38, \ 127.38, \ 128.82, \ 128.92, \ 129.30, \ 129.74, \ 131.48, \ 132.33, \ 132.84, \ 133.79, \ 134.067, \ 138.19, \ 138.87, \ 142.88, \ 167.38, \ 168.24, \ 171.63, \ 172.08, \ 173.22, \ 203.86; \text{ HRFABMS} \ m/z \ \text{calcd for } C_{50}H_{53}NO_{14} (M+Na)^+, \ 914.3364, \ \text{found} \ 914.3382, \ \Delta = 2.0 \ ppm.\]
(3R, 4S)-1-Benzyol-3-TIPSO-4-(O-allyloxyphenyl)azetidin-2-one (3.17)

$^1$H NMR $\delta$ 0.95(m, 18H), 1.00(m, 3H), 5.30(dd, J = 12, J = 5.6, 2H), 5.41(d, J = 16, 1H), 5.85(d, J = 5.6, 1H), 6.09(ddd, J = 4.2, 1H), 6.87(d, J = 7.6, 1H), 6.94(t, J = 8, 1H), 7.25(m, 2H), 7.47(t, J = 8.2, 2H), 7.57(t, J = 8, 1H), 8.04(d, J = 8, 1H); $^1^3$C NMR $\delta$ 12.02, 17.62, 57.22, 69.25, 76.81, 111.66, 117.763, 120.65, 122.41, 128.32, 128.41, 129.31, 130.09, 132.65, 133.38, 133.55, 157.17, 166.01, 166.60. LRFABMS $m/z$ calculated for C$_{28}$H$_{38}$NO$_4$Si (M+H)$^+$ 480, found 480.

Taxoid-α,ω-diene 3.16

$^1$H NMR $\delta$ 0.61(m, 9H), 0.88(m, 27H), 1.23(s, 6H), 2.00(m, 2H), 2.08(s, 3H), 2.20(bs, 5H), 2.34(m, 2H), 2.54(m, 4H), 2.86(qt, J = 7.2, 1H), 3.29(qt, J = 7.2, 1H), 3.84(d, J = 7.2), 4.21(d, J = 8, 1H), 4.29(d, J = 8.4, 1H), 4.60(m, 2H), 4.89(m, 3H), 4.99(d, J = 15.6, 1H), 5.36(bs, 1H), 5.38(d, J = 10.4, 1H), 5.52(d, J = 16, 1H), 5.69(d, J = 7.2, 1H), 5.76(m, 1H), 6.03(dd, J = 7.2, J = 2.0, 1H), 6.29(t, J = 9.2, 1H), 6.38(m, 1H), 6.48(s, 1H), 6.54(d, J = 8.4, 1H), 6.96(m, 2H), 7.13(d, J = 9.2, 1H), 7.32(m, 3H), 7.49(m, 4H), 7.72(d, J = 9.2, 2H), 8.21(d, J = 8.4, 2H) HRFABMS $m/z$ calcd for C$_{68}$H$_{94}$NO$_{15}$Si$_2$(M+H)$_2$, 1220.6162, found 1220.6136, $\Delta$ = 2.1 ppm.

7,13-O-bis-(triethylsilyl)-10-deacetyl-10-(4-penenoyl)-baccatin III (4.7)

To a solution of 10-deacetylbaccatin (500 mg, 0.92 mmol) in 12 mL of THF was added 1.2 mol% of CeCl$_3$ and acetic anhydride (1.1 mL, 12 mmol) and stirred at room temperature for 3 h. The reaction mixture was diluted with ethyl acetate and quenched with saturated solution of NaHCO$_3$ and worked up in the usual way. After purification on column chromatography, the product was characterized and was identical to baccatin III.

To a solution of baccatin III (500 mg, 0.85 mmol) in 10 mL of DMF was added imidazole (2.6 g, 39 mmol) and stirred for 5 minunates and cooled to 0°C. To the reaction mixture chloroethylsilane (1.6 mL, 9.4mmol) was added and stirred for 4 h. After completion of the reaction the reaction was stopped and worked up in the usual way. Column chromatography (EtOAc:hexanes 5:5) of the crude product gave the desired
product in 85% for the two steps. The characterization data for this compound was identical to previous reports.

To a solution of the 7,13–bis(triethylsily)baccatin III (435 mg, 0.7 mmol) in ethanol 20 mL was added 8 mL of hydrazine monohydrate and stirred for 3 h. After the reaction was completed, the solvent was evaporated under reduced pressure and the crude reaction product was diluted with ethyl acetate and worked up in the usual way. The desired product showed a higher R_f value than the starting material. Purification on PTLC (EtOAc:hexanes 3:7) gave the desired 10–deacetylated product in 87% yield.

HRFABMS m/z calculated for C_{41}H_{65}O_{10}Si_{2} (M+H)^+ 773.4116, found 773.40918, Δ = -3.2 ppm.

To a cooled solution of 7,13–bis(triethylsily)–10–deacetylbaccatin (321 mg, 0.42 mmol) in 10 mL of pyridine at 0 °C was added 4–pentenoyl chloride (0.23 mL, 2.1 mmol) and stirred for 12 h. The reaction mixture was diluted with ethyl acetate and washed with (2 x 25 mL) of saturated copper sulfate and worked–up in the usual way. The crude product was purified on PTLC (EtOAc:hexanes, 2:8) and the desired product (4.7) was obtained in 74% yield.

HRFABMS m/z calculated for C_{46}H_{71}O_{11}Si_{2} (M+H)^+ 855.4535, found 855.44904, Δ = - 5.3 ppm.

10–(4–Pentenoyl)–10–deacetylbaccatin.

To a solution of 10–deacetylbaccatin (600mg, 1.1 mmol) in 15 mL of THF was added 1.1 mol % of CeCl₃ at room temperature and stirred for 5 minutes and 4–pentenoic anhydride (2 mL, 11 mmol) was added slowly and stirred at room temperature for 3 h. The reaction mixture then is diluted with ethyl acetate and washed with saturated sodium bicarbonate and worked–up as usual. The crude product was purified by column chromatography (1:1, EtOAc:hexanes) and gave the desired product in 89% yield.

^1H NMR δ 1.10(s, 6H), 1.67(bs, 3H), 1.86(t, J = 16 Hz, J = 12 Hz, 1H), 2.04(s, 3H), 2.28(s, 5H), 2.46(dd, J = 8 Hz, J = 4 Hz, 2H), 2.60(m, 3H), 3.88(d, J = 8 Hz, 1H), 4.15(d, J = 8Hz, 1H), 4.30(d, J = 8 Hz, 1H), 4.46(dd, J = 8 Hz, J = 4 Hz, 1H), 4.88(s, 1H),
5.05(m, 3H), 5.62(d, J = 8 Hz, 1H), 5.88(dd, J = 8 Hz, J = 12 Hz, 1H), 6.33(s, 1H), 7.26(s, 1H), 7.48(t, J = 8 Hz, J = 8 Hz, 2H), 7.60(t, J = 8 Hz, J = 8 Hz, 1H), 8.10(d, J = 8 Hz, 2H) HRFABMS \textit{m/z} calculated for C$_{34}$H$_{43}$NO$_{11}$ (M+H)$^+$ 627.2805, found 627.2812, $\Delta = 1.0$ ppm.

10–(4–pentenoyl)–7–triethylsilyl–10–deacetylbaccatin (4.3)

To a solution of 10–(4–pentenoyl)–10–deacetylbaccatin (500 mg, 0.80 mmol) at 0 °C in 4 mL DMF was added imidazole (163 mg, 2.4 mmol) and stirred for 5 minutes. To this solution chlorotriethylsilane (0.15 mL, 0.88 mmol) was added and the reaction mixture was stirred for 4 hours. The progress of the reaction was carefully monitored to avoid the side reaction on the 13–OH position. After the reaction was completed the mixture was quenched with saturated MeOH/sodium bicarbonate solution and worked–up as usual. The crude product was purified by PTLC (4:6, EtOAc:hexanes) and the desired product was isolated in 92% yield.

$^1$H NMR $\delta$ 0.58(m, 6H), 0.91(t, J = 8 Hz, J = 8 Hz, 9H), 1.02(s, 3H), 1.18(s, 3H), 1.67(s, 4H), 1.86(m, 1H), 2.17(s, 3H), 2.27(s, 5H), 2.44(m, 2H), 2.52(m, 3H), 3.87(d, J = 8Hz, 1H), 4.13(d, J = 12 Hz, 1H), 4.29(d, J = 8 Hz, 1H), 4.48(dd, J = 8 Hz, J = 16 Hz, 1H), 4.95(d, J = 8 Hz, 1H), 5.01(d, J = 8Hz, 1H), 5.07(d, J = 16 Hz, 1H), 5.62(d, J = 8 Hz, 1H), 5.86(dd, J = 8 Hz, J = 8 Hz, 1H), 6.47(s, 1H), 7.46(t, J = 8 Hz, J = 8 Hz, 2H), 7.59(t, J = 8 Hz, J = 4 Hz, 1H), 8.09(t, J = 4 Hz, J = 4 Hz, 2H), $^{13}$C NMR $\delta$ 128.80, 129.64, 130.30, 132.95, 133.81, 136.79, 144.20, 167.30, 170.92, 171.53, 202.42. HRFABMS \textit{m/z} calculated for C$_{40}$H$_{57}$O$_{11}$Si (M+H)$^+$ 741.3670, found 741.36542, $\Delta = 2.2$ ppm.

(3R, 4S)–1–(m–(pent–4–en–oxy)–benzoyl)–3–TIPSO–4–phenyl-azetidin–2–one (4.4)

$^1$H NMR $\delta$ 0.91(m, 18H), 0.98(m, 3H), 1.90(ddd, J = 8, 2H), 2.24(q, J= 8, 2H), 4.01(t, J = 4, 2H), 5.00(d, J = 12, 1H), 5.07(d, J = 16, 1H), 5.24(d, J = 6, 1H), 5.41(d, J = 6, 1H), 5.85(m, 1H), 7.11(dd, J = 8, J= 4, 1H), 7.37(m, 6H), 7.54(bs, 1H), 7.66(d, J = 8, 1H), $^{13}$C NMR $\delta$ 11.90, 17.58, 28.52, 30.30, 61.48, 67.66, 76.74, 115.191, 115.50, 120.61, 122.51, 128.38, 129.40, 133.41, 134.06, 137.95, 159.02, 165.57, 166.33. HRFABMS \textit{m/z} calculated for C$_{30}$H$_{42}$NO$_{4}$Si (M+H)$^+$ 508.2883, found 508.28500, $\Delta = 6.2$ ppm.
(3R, 4S)−1−(m−allyloxy)−benzoyl−3−TIPSO−4−phenyl−azetidin−2−one (4.9)

$^1$H NMR $\delta$ 0.91(m, 18), 1.00(m, 3H), 4.59(dt, J = 4, 2H), 5.24(d, J = 4, 1H), 5.31(d, J = 12, 1H), 5.41(d, J = 4, 1H), 5.45(m, 1H), 6.05(m, 1H), 7.14(m, 1H), 7.34(m, 6H), 7.57(m, 1H), 7.67(d, J = 8, 1H), 11.89, 17.58, 61.47, 69.26, 76.74, 115.50, 118.23, 120.79, 122.77, 128.38, 128.44, 129.45, 133.13, 134.03, 158.55, 165.57. HRFABMS m/z calculated for C$_{28}$H$_{38}$O$_4$NSi (M+H)$^+$ 480.2570, found 480.2579, $\Delta$ = 1.9 ppm.

(3R, 4S)−1−(m−(vinyl)−benzoyl)−3−TIPSO−4−phenyl−azetidin−2−one (4.10)

$^1$H NMR $\delta$ 0.94(m, 18H), 1.03(m, 3H), 5.28(dd, J = 4.8, J = 1.2, 1H), 3.5(d, J = 10.8, 1H), 5.45(d, J = 6, 1H), 5.84(d, J = 17.6, 1H), 6.79(dd, J = 10.8, 6.8, 1H), 7.40(m, 6H), 7.64(d, J = 6.8, 1H), 7.97(d, 6.8, 1H), 8.07(bs, 1H); $^{13}$C NMR $\delta$ 11.27, 17.37, 61.28, 76.65, 115.38, 127.66, 128.17, 128.23, 128.34, 129.11, 130.84, 132.42, 135.89, 137.77, 165.42, 166.16. HRFABMS m/z calculated for C$_{27}$H$_{35}$NO$_3$Si (M+H)$^+$ 450.2464, found 450.2479, $\Delta$ = 3.3 ppm.

Compound 4.11

$^1$H NMR $\delta$ 0.86(m, 18H), 0.96(m, 3H), 2.34(m, 2H), 4.19(m, 2H), 5.05(m, 2H), 5.10(d, J = 4, 1H), 5.19(d, J = 4, 1H), 5.65(m, 1H), 7.30(m, 6H), $^{13}$C NMR $\delta$ 11.85, 17.54, 17.64, 33.17, 62.60, 65.89, 76.94, 77.26, 77.58, 78.19, 117.91, 128.32, 128.36, 128.64, 133.43, 133.75, 149.39, 166.31. HRFABMS m/z calculated for C$_{23}$H$_{36}$NO$_4$Si (M+H)$^+$ 418.2414, found 418.2416, $\Delta$ = 0.4 ppm.

Taxoid -ω-ω-diene 4.2

$^1$H NMR $\delta$ 0.59(m, 6H), 0.93(m, 30H), 1.17(s, 3H), 1.22(s, 3H), 1.61(s, 3H), 1.78(m, 3H), 1.85(m, 1H), 2.05(s, 3H), 2.16(bs, 4H), 2.44(m, 3H), 2.56(bs, 6H), 3.77(m, 2H), 3.84(m, 2H), 4.21(d, J = 8, 1H), 4.30(d, J = 5.6, 1H), 5.01(m, 6H), 5.83(m, 4H), 6.23(t, J = 8.8, 9.2, 1H), 6.48(s, 1H), 7.02(d, J = 5.6, 1H), 7.10(d, J = 8.8, 1H), 7.34(m, 8H), 7.54(m, 3H), 8.16(d, J = 4, 2H); $^{13}$C NMR $\delta$ 5.55, 7.01, 12.78, 14.49, 18.02, 23.29, 26.79, 28.53, 29.03, 30.23, 35.96, 43.53, 46.94, 56.16, 58.63, 67.35, 67.35, 71.87, 72.46, 75.13, 75.93, 76.76, 79.11, 81.40, 84.51, 105.60, 112.75, 114.35, 115.81, 118.681, 119.14,
126.57, 128.17, 128.98, 129.50, 129.93, 130.52, 133.84, 135.61, 136.75, 137.94, 138.44, 140.39, 159.62, 167.00, 167.24, 170.36, 171.56, 171.93, 201.95. HRFABMS m/z calculated for C\textsubscript{70}H\textsubscript{97}NO\textsubscript{15} (M+Na)\textsuperscript{+} 1270.6294, found 1270.6289, \(\Delta = -0.4\) ppm.

**Taxoid-\(\omega\omega\)-diene 4.15**

\(^{1}\)H NMR \(\delta\) 0.58(m, 6H), 0.92(m, 30H), 1.24(bs, 6H), 1.65(s, 5H), 1.90(t, \(J = 4, J = 12, 1H\)), 2.00(s, 3H), 2.15(m, 1H), 2.31(m, 4H), 2.51(m, 8H), 3.84(d, \(J = 8, 1H\)), 3.95(dd, \(J = 8, J = 2H\)), 4.18(d, \(J = 8, 1H\)), 4.30(d, \(J = 8, 1H\)), 4.48(dd, \(J = 4, J = 4, 1H\)), 4.81(s, 1H), 4.95(m, 4H), 5.02(d, \(J = 12, 1H\)), 5.09(d, \(J = 16, 1H\)), 5.30(d, \(J = 8, 1H\)), 5.53(d, \(J = 12, 2H\)), 5.69(d, \(J = 4, 1H\)), 5.88(m, 1H), 6.27(t, \(J = 4, 1H\)), 6.48(s, 1H), 7.28(t, \(J = 8, J = 8, 2H\)), 7.48(t, \(J = 8, J = 4, 2H\)), 7.58(t, \(J = 8, J = 8, 1H\)), 8.13(d, \(J = 8, 2H\)). \(^{13}\)C NMR \(\delta\) 5.54, 7.03, 10.41, 12.72, 14.46, 18.02, 18.04, 23.18, 26.79, 29.05, 33.52, 33.75, 43.54, 46.94, 58.58, 64.56, 72.43, 75.03, 75.18, 79.34, 84.50, 115.82, 117.35, 126.59, 128.89, 129.44, 130.51, 136.76, 140.66, 167.37, 171.52, 171.71, 202.00. HRFABMS m/z calculated for C\textsubscript{63}H\textsubscript{91}NO\textsubscript{15}Si\textsubscript{2} (M+Na)\textsuperscript{+} 1180.5825, found 1180.5879, \(\Delta = 4.57\) ppm.

**Protected macrocyclic taxoid analog 4.13**

\(^{1}\)H NMR \(\delta\) 0.56(m, 9H), 0.92(m, 27H), 1.00(s, 3H), 1.25(bs, 3H), 1.69(s, 6H), 1.78(m, 2H), 1.86(m, 1H), 2.07(m, 2H), 2.2(m, 2H), 2.41(m, 1H), 2.43(s, 3H), 2.53(m, 1H), 2.63(m, 1H), 3.81(d, \(J = 6.8, 1H\)), 4.05(m, 1H), 4.20(d, \(J = 8.4, 1H\)), 4.30(m, 1H), 4.35(d, \(J = 8.4, 1H\)), 4.46(dd, \(J = 6.8, J = 4.0, 1H\)), 4.92(d, \(J = 2, 1H\)), 4.99(d, \(J = 8, 1H\)), 5.37(m, 2H), 5.60(d, \(J = 9.2, 1H\)), 5.70(d, \(J = 6.8, 1H\)), 5.82(t, \(J = 8, 1H\)), 6.57(s, 1H), 6.95(d, \(J = 8.8, 1H\)), 7.01(m, 1H), 7.29(m, 7H), 7.39(m, 2H), 7.51(m, 1H), 7.61(m, 1H), 8.09(d, \(J = 5.2, 2H\)), \(^{13}\)C NMR \(\delta\) 5.50, 6.89, 10.08, 12.61, 14.49, 18.00, 21.60, 22.70, 26.62, 28.20, 28.75, 29.40, 34.04, 35.62, 43.64, 46.99, 57.34, 58.87, 67.83, 72.59, 74.62, 75.35, 76.21, 78.21, 84.35, 110.40, 120.14, 120.64, 126.66, 126.79, 127.84, 128.18, 128.94, 130.33, 130.52, 131.21, 133.84, 134.31, 140.55, 158.74, 169.59, 171.89, 173.82, 202.11. HRFABMS m/z calculated for C\textsubscript{66}H\textsubscript{93}NO\textsubscript{15}Si\textsubscript{2} (M+Na)\textsuperscript{+}: 1242.5981, 1242.5903, \(\Delta = 6.2\) ppm.
Macrocyclic taxoid analog 4.1

$^1$H NMR δ 1.12(s, 3H), 1.23(s, 3H), 1.67(s, 3H), 1.90(s, 3H), 2.14(m, 2H), 2.35(s, 3H)
2.61(m, 6H), 3.81(d, J = 6.4 Hz), 4.03(m, 2H), 4.17(d, J = 8 Hz, 1H), 4.28(d, J = 8 Hz, 1H), 4.42 (m, 1H), 4.77(m, 2H), 4.94(d, J = 8 Hz, 1H), 5.43(m, 2H), 5.64(d, J = 8 Hz, 1H), 5.69(d, J = 7.2 Hz, 1H), 6.20(m, 1H), 6.22(s , 1H), 7.07(m, 1H), 7.12(d, J = 8 Hz, 1H), 7.23–7.48(m,10H), 7.60(t, J = 8 Hz, J = 4 Hz), 8.04(d, J = 8 Hz, 2H).  $^{13}$C NMR δ 9.64, 15.64, 21.53, 22.56, 27.28, 27.35, 28.64, 28.79, 33.73, 33.85, 36.23, 43.14, 45.88, 57.17, 59.01, 87.01, 71.52, 72.69, 74.93, 75.10, 75.67, 76.82, 79.27, 81.51, 84.57, 112.98, 119.34, 119.68, 127.14, 128.29, 128.62, 128.89, 129.12, 129.28, 130.10, 130.24, 130.95, 133.54, 134.01, 134.96, 138.92, 142.48, 159.31, 167.11, 167.56, 170.69, 171.30, 173.33, 203.95. HRFABMS m/z calcd for C$_{53}$H$_{60}$NO$_{15}$ (M+H)$^+$: 950.3963 found for C$_{53}$H$_{60}$NO$_{15}$ (M+H)$^+$ 950.4005, Δ = 4.4 ppm.

Preparation of compound 5.15

To a solution of 1,8–naphthaldehydic acid (5 g, 25 mmol) in 200 mL of DMF was added (17.3 g, 0.125 mol) potassium carbonate and vigorously stirred. Iodomethane (7.8 mL, 0.125 mol) was then slowly added to the heterogeneous mixture and refluxed for 3 h. The reaction mixture was cooled and poured onto 500 mL of ice–water and washed twice with water and worked–up in the usual way. Purification of the crude product on column chromatography (EtOAc:hexanes, 1.5:8.5) gave the desired esterification product in 73% yield.

To a solution of (carboethoxymethyl)triphenylphosphonium bromide (4.4 g, 10.2 mmol) in 100 mL of THF at 0°C was added LHMDS (10.2 mL, 1M) and stirred for 1 h and treated with 1,8–naphtaldehydic methyl ester (2 g, 10.2 mmol) and allowed to react for 12 h. The reaction mixture was then quenched with saturated NH$_4$Cl and worked up in the usual way. Purification of the crude olefin product on column (EtOAc:hexanes, 2:8) gave the desired E–olefin in 67% yield.

$^1$H NMR δ 1.35(t, J = 7.2, 3H), 3.93(s, 3H), 4.28(q, J = 6.8, J = 7.2, 2H), 6.33(d, J = 15.6, 1H), 7.51(m, 2H), 7.69(d, J = 7.2, 1H), 7.95(d, J = 9.2, 1H), 8.06(d, J = 14.6, 1H). $^{13}$C NMR δ 14.59, 52.88, 60.79, 119.91, 125.31, 126.29, 128.23, 128.36, 128.70, 130.77,
132.10, 132.50, 134.47, 144.70, 166.90, 171.21. LRFABMS $m/z$ calculated for $C_{17}H_{16}O_4$ (M+H)$^+$ 285, found 285.

(3R, 4S)–1–(4–pentenoyl)–3–TIPSO–4–phenyl–azetidin–2–one (5.17)

$^1$H NMR $\delta$ 0.89(m, 18), 0.96(m,3H), 2.43(m, 2H), 2.89(m, 2H), 5.00(d, $J = 8.8$, 1H), 5.07(d, $J = 14.6$, 1H), 5.16(d, $J = 6$, 1H), 5.21(d, $J = 6$, 1H), 5.71(d, $J = 16.8$, 1H), 6.68(dd, $J = 9.2$, $J = 6.8$, 1H), 7.15(m, 1H), 7.30(m, 3H); $^{13}$C NMR $\delta$ 11.86, 17.63, 28.20, 36.36, 61.33, 114.31, 116.09, 126.23, 126.43, 127.71, 128.53, 133.89, 136.56, 136.81, 137.75, 166.97, 170.67. HRFABMS $m/z$ calculated for $C_{25}H_{37}NO_3Si$ (M+H)$^+$ 428.2621, found 428.2616, $\Delta$ -1.2 ppm.

Compound 5.20

$^1$H NMR $\delta$ 0.57(m, 6H), 0.92(m, 30H), 1.24(bs, 6H), 1.70(s, 3H), 1.76(bs, 2H), 1.85(m, 1H), 2.03(bs, 4H), 2.18(bs, 5H), 2.33(m, 5H), 2.50(m, 4H), 3.83(d, $J = 8$, 1H), 4.21(d, $J = 8$, 1H), 4.31(d, $J = 8$, 1H), 4.47(dd, $J = 4$, 1H), 4.81(d, $J = 4$, 1H), 4.94(d, $J = 8$, 1H), 4.98(d, $J = 12$, 1H), 5.03(d, $J = 16$, 1H), 5.55(d, $J = 8$, 1H), 5.76(m, 3H), 6.20(t, $J = 8$, 1H), 6.40(d, $J = 12$, 1H), 6.46(s, 1H), 6.71(dd, $J = 12$, $J = 8$, 1H), 7.16(d, $J = 8$, 1H), 7.29(m, 3H), 7.48(m, 2H), 7.59(t, $J = 8$, 1H), 8.13(d, $J = 4$, 1H); $^{13}$C NMR $\delta$ 5.52, 6.97, 10.36, 12.76, 14.48, 18.06, 21.12, 21.76, 23.23, 26.76, 29.50, 35.81, 37.43, 43.61, 46.89, 55.61, 58.63, 72.01, 72.45, 75.16, 75.24, 75.68, 76.79, 78.97, 79.14, 81.45, 84.49, 114.64, 115.99, 124.58, 126.06, 128.94, 129.08, 129.49, 130.47, 133.82, 133.86, 136.75, 137.03, 138.26, 138.81, 140.46, 167.23, 169.59, 170.17, 171.90, 172.21, 202.01. HRFABMS $m/z$ calculated for $C_{62}H_{89}NO_{14}Si_2$ (M+Na)$^+$ 1150.5719, found 1150.5724, $\Delta$ = 4.34 ppm.

Compound 5.21

$^1$H NMR $\delta$ 0.58(m, 6H), 0.91(m, 39H), 1.24(s, 6H), 1.70(bs, 5H), 1.85(m, 1H), 2.01(s, 3H), 2.19(bs, 4H), 2.24(m, 3H), 2.35(m, 1H), 2.52(bs, 4H), 3.84(d, $J = 4$, 1H), 3.95(m, 2H), 4.19(d, $J = 8$, 1H), 4.30(d, $J = 8$, 1H), 4.48(dd, $J = 4$, 1H), 4.80(d, $J = 4$, 1H), 4.95(m, 3H), 5.29(d, $J = 8$, 1H), 5.56(m, 2H), 5.70(d, $J = 8$, 1H), 5.74(d, $J = 16$, 1H), 6.28(t, $J = 8$, 1H), 6.46(s, 1H), 6.71(dd, $J = 8$, 1H), 7.18(b, 1H), 7.33(m, 4H), 7.49(t, $J = 8$, 2H), 7.58(t, $J = 8$, 1H), 8.13(d, $J = 8$, 2H); $^{13}$C NMR $\delta$ 5.06, 5.52, 6.98, 7.18, 10.38,
11.91, 12.73, 14.45, 17.63, 18.00, 21.13, 23.20, 26.77, 33.51, 37.40, 43.58, 46.94, 58.58, 59.76, 64.60, 72.43, 75.18, 75.93, 79.28, 80.10, 81.37, 84.50, 114.68, 117.38, 124.54, 126.00, 128.23, 128.90, 129.07, 129.45, 130.50, 136.00, 138.28, 140.66, 149.54, 167.00, 169.55, 171.68, 202.01. HRFABMS \textit{m/z} calculated for C_{62}H_{89}NO_{15}Si_{2} (M+Na)^{+} 1166.5668, found 1166.5660, \Delta = 0.6 \text{ ppm.}

\textbf{Compound 5.22}

$^1$H NMR $\delta$ 0.89(m, 18H), 0.95(m, 3H), 5.25(d, $J = 10.8$, 1H), 5.31(d, $J = 6$, 1H), 5.37(d, $J = 6$, 1H), 5.74(d, $J = 18.4$, 1H), 6.72(dd, $J = 11.2$, 1H), $J = 6.8$, 1H), 7.17(dt, $J = 2$, $J = 5.6$, 1H), 7.32–7.46(m, 6H), 7.88(d, $J = 8$, 1H), $^{13}$C NMR $\delta$ 11.85, 17.55, 62.21, 76.96, 92.24, 114.42, 126.62, 126.68, 128.16, 128.25, 128.58, 128.76, 132.19, 133.60, 136.81, 137.77, 139.83, 140.02, 165.96, 166.09. HRFABMS \textit{m/z} calculated for C_{27}H_{34}NO_{3}Si (M+H)^{+} 576.1431, found 576.1426, \Delta = 0.8 \text{ ppm.}

\textbf{Compound 5.23}

$^1$H NMR $\delta$ 0.85(m, 18H), 0.92(m, 3H), 3.79(s, 3H), 4.75(d, $J = 2$, 1H), 5.23(d, $J = 8$, 1H), 5.61(dd, $J = 7.2$, 1H), $J = 1.6$, 1H), 5.75(dd, $J = 16.8$, 1H), $J = 0.8$, 1H), $^{13}$C NMR $\delta$ 12.48, 17.86, 52.62, 56.46, 75.89, 92.71, 114.39, 125.93, 126.44, 128.44, 128.86, 131.51, 136.89, 138.0, 138.82, 140.39, 142.02, 168.77, 172.33. HRFABMS \textit{m/z} calculated for C_{28}H_{38}NO_{4}Si (M+H)^{+} 608.1693, found 608.1689, \Delta = -0.7 \text{ ppm.}
$^1$H and $^{13}$C NMR spectra of key intermediates and final products are shown.