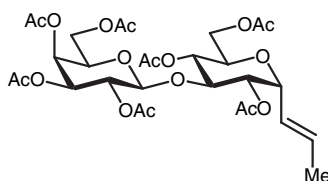


Supporting Information



Compound 12. (1,5-Cyclooctadiene)bis(methyldiphenylphosphine) iridium (I) hexafluorophosphate (0.03 g, 0.03 mmol, 10 mol %) was stirred in degassed THF (3 mL) and activated under a H₂ atmosphere (1 atm) until the opaque red suspension became a clear, slightly orange solution. Ar was then bubbled through the solution for 5 minutes to remove any H₂. The activated catalyst was then added to peracetylated α -allyl lactoside **11** (0.21 g, 0.31 mmol) in degassed THF (3 mL) and stirred for 24 hrs. The orange mixture was then concentrated under reduced pressure and subjected to column chromatography (SiO₂, R_f 0.30) using 55:45 pet. ether/EtOAc as the eluent to afford a foam (0.17 g, 80%, 10:1 α : β).

Yield = 80% (10:1 α : β) (10 mol%, 1 day, unoptimized)

R_f = 0.30 (50% EtOAc/pet. ether)

m.p. = 68-70°C

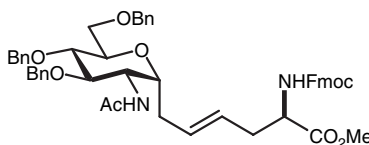
IR (film, NaCl) 2969, 2943, 1763, 1449, 1379, 1230, 1055, 898, 767, 610 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) (major isomer) δ 1.72 (d, J = 6.7 Hz, 3H), 1.90 (s, 3H), 1.96 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.002 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H), 3.63 (m, 2H), 3.79 (ddd, J = 2.3, 5.1, 9.6 Hz, 1H), 3.83 (m, 1H), 4.04 (m, 7H), 4.32 (m, 1H), 4.43 (m, 1H), 4.52 (m, 1H), 4.89 (m, 3H), 5.05 (dd, J = 7.7, 10.3, 1H), 5.28 (m, 3H), 5.44 (m, 1H), 5.62 (ddd, J = 1.6, 6.4, 15.4, 1H), 5.81 (m, 1H)

¹³C NMR (500 MHz) (CDCl₃) δ 20.4, 20.5, 20.8, 20.81, 60.8, 62.3, 66.6, 69.0, 70.0, 70.3, 70.5, 70.6, 70.9, 72.8, 76.9, 101.1, 123.0, 133.8, 169.1, 169.6, 169.9, 169.94, 170.1, 170.2, 170.4

HRMS Calcd for C₂₉H₄₀O₁₇ (M⁺): 660.2266. Found: 660.2241

General Procedure for Olefin Metathesis. To a stirring solution of the olefinic glycoside and allyl amino acid or allyl peptide in dry CH₂Cl₂ (0.6 M) was added Grubbs' catalyst **A** or **B** (see specific mol % below) and refluxed for 1-2 days. The solution was concentrated *in vacuo* and subjected to column chromatography.



Compound 6 (R¹ = Bn, R² = Fmoc).

Yield = 74% (10 mol%, 16 h)

R_f = 0.19 (40% EtOAc/pet. ether)

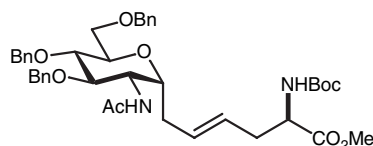
m.p. = 149-152°C

IR (film, NaCl) 3318, 3074, 3039, 2952, 2908, 1754, 1702, 1658, 1545, 1449, 1274, 1213, 1099, 1055, 750, 697 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) δ 1.86 (s, 3H), 2.13 (m, 1H), 2.21 (m, 1H), 2.49 (m, 2H), 3.55 (s, 1H), 3.62 (s, 3H), 3.71 (m, 2H), 3.87 (br t, 2H), 4.23 (m, 3H), 4.34 (d, J = 8.0 Hz, 2H), 4.46 (m, 5H), 4.57 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 5.37 (m, 1H), 5.47 (m, 1H), 6.07 (d, J = 8.7 Hz, 1H), 6.58 (d, J = 9.9 Hz, 1H), 7.29 (m, 17H), 7.38 (t, J = 7.4 Hz, 2H), 7.65 (t, J = 8.0 Hz, 2H), 7.75 (d, J = 7.4 Hz, 2H)

¹³C NMR (500 MHz) (CDCl₃) δ 23.4, 34.5, 34.9, 46.7, 47.2, 52.2, 67.0, 67.5, 71.7, 72.0, 73.1, 74.2, 75.1, 119.9, 125.3, 126.9, 127.0, 127.4, 127.6, 127.65, 127.7, 127.8, 128.1, 128.35, 128.4, 128.5, 130.2, 137.3, 137.6, 138.1, 141.2, 143.9, 144.1, 156.1, 169.5, 172.1

HRMS Calcd for C₅₁H₅₄N₂O₉ (M⁺): 838.3829. Found: 838.3842



Compound **6** ($R^1 = \text{Bn}$, $R^2 = \text{Boc}$).

Yield = 78% (10 mol%, 16 h)

R_f = 0.19 (40% EtOAc/pet. ether)

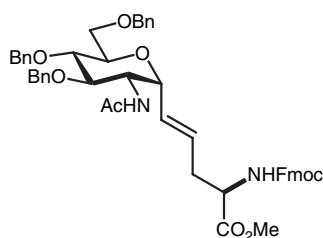
m.p. = 120-122°C

IR (film, NaCl) 3319, 2943, 2908, 1763, 1685, 1641, 1519, 1379, 1177, 1134, 1099, 1055, 750, 706 cm^{-1}

¹H NMR (500 MHz) (CDCl_3) δ 1.41 (s, 9H), 1.82 (s, 3H), 2.09 (m, 1H), 2.17 (m, 1H), 2.41 (t, $J = 6.1$ Hz, 2H), 3.56 (m, 1H), 3.64 (s, 3H), 3.65 (m, 1H), 3.73 (dd, $J = 7.1, 9.9$ Hz, 1H), 3.84 (m, 2H), 4.15 (br d, $J = 9.6$ Hz, 1H), 4.23 (br t, $J = 7.1$ Hz, 1H), 4.31 (m, 1H), 4.46 (m, 4H), 4.58 (dd, $J = 11.9, 19.6$ Hz, 2H), 5.24 (d, $J = 8.3$ Hz, 1H), 5.32 (m, 1H), 5.48 (m, 1H), 6.50 (d, $J = 9.9$, 1H), 7.27 (m, 15H)

¹³C NMR (500 MHz) (CDCl_3) δ 23.3, 28.3, 34.6, 35.3, 47.1, 52.1, 67.7, 67.8, 71.8, 72.1, 73.0, 73.1, 74.3, 75.0, 79.7, 126.5, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5, 130.4, 137.3, 137.6, 138.2, 155.3, 169.6, 172.5

HRMS Calcd for $\text{C}_{41}\text{H}_{52}\text{N}_2\text{O}_9$ (M^+): 716.3673. Found: 716.3665



Compound **9** ($R^1 = \text{Bn}$, $R^2 = \text{Fmoc}$).

Yield = 82% (10 mol%, 24 h)

R_f = 0.17 (50% EtOAc/pet. ether)

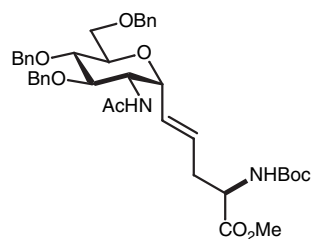
m.p. = 165-167°C

IR (film, NaCl) 3336, 3039, 2952, 2873, 1728, 1667, 1536, 1457, 1221, 1073, 916, 750, 706 cm^{-1}

¹H NMR (500 MHz) (CDCl_3) δ 1.81 (s, 3H), 2.49 (m, 1H), 2.60 (m, 1H), 3.58 (m, 1H), 3.66 (m, 1H), 3.72 (m, 4H), 3.80 (m, 1H), 4.22 (m, 3H), 4.47 (m, 10H), 5.51 (dd, $J = 5.5, 15.7$, 1H), 5.61 (m, 1H), 5.76 (d, $J = 8.3$, 1H), 6.46 (d, $J = 9.3$, 1H), 7.27 (m, 17H), 7.37 (t, $J = 7.4$, 2H), 7.63 (d, $J = 7.4$, 2H), 7.74 (d, $J = 7.4$, 2H)

¹³C NMR (500 MHz) (CDCl_3) δ 23.3, 35.2, 47.1, 48.9, 52.4, 67.1, 67.7, 68.8, 72.2, 72.4, 73.2, 73.3, 74.8, 119.9, 125.2, 126.5, 127.1, 127.6, 127.7, 127.8, 127.9, 128.1, 128.4, 128.5, 128.6, 131.4, 137.3, 137.5, 138.1, 141.2, 143.8, 156.0, 170.0, 172.0

HRMS Calcd for $\text{C}_{50}\text{H}_{52}\text{N}_2\text{O}_9$ (M^+): 824.3673. Found: 824.3676



Compound **9** ($R^1 = \text{Bn}$, $R^2 = \text{Boc}$).

Yield = 77% (10 mol%, 48 h)

R_f = 0.18 (50% EtOAc/pet. ether)

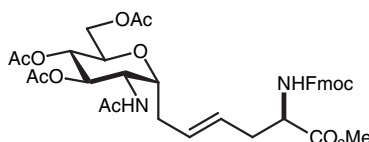
m.p. = 67-69°C

IR (film, NaCl) 3310, 2943, 2873, 1719, 1667, 1536, 1466, 1370, 1169, 1090, 750, 706 cm^{-1}

^1H NMR (500 MHz) (CDCl_3) δ 1.43 (s, 9H), 1.85 (s, 3H), 2.49 (m, 2H), 3.59 (t, $J = 3.0$ Hz, 1H), 3.67 (t, $J = 3.9$ Hz, 1H), 3.71 (s, 3H), 3.72 (m, 1H), 3.80 (dd, $J = 6.5, 10.1$, 1H), 4.20 (m, 2H), 4.36 (m, 1H), 4.24 (m, 1H), 4.52 (m, 5H), 4.62 (d, $J = 11.5$, 1H), 5.18 (d, $J = 8.0$, 1H), 5.49 (dd, $J = 5.2, 15.5$, 1H), 5.62 (m, 1H), 6.30 (d, $J = 9.0$, 1H), 7.29 (m, 15H)

^{13}C NMR (500 MHz) (CDCl_3) δ 23.3, 28.3, 35.4, 48.7, 52.3, 67.8, 68.9, 72.3, 72.5, 73.2, 73.7, 74.9, 75.0, 79.9, 127.1, 127.6, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5, 130.6, 137.4, 137.7, 138.1, 155.3, 169.9, 172.3

HRMS Calcd for $\text{C}_{40}\text{H}_{50}\text{N}_2\text{O}_9$ (M^+): 702.3516. Found: 702.3494



Compound **6** ($\text{R}^1 = \text{Ac}$, $\text{R}^2 = \text{Fmoc}$).

Yield = 65% (6.5:1 *trans:cis*-) (10 mol % each day, 2 days)

R_f = 0.25 (70% EtOAc/pet. ether)

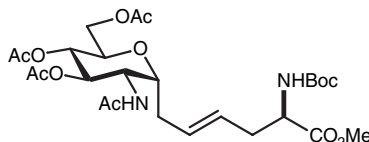
m.p. = n/a

IR (film, NaCl) 3345, 3021, 2960, 1754, 1676, 1545, 1457, 1379, 1248, 1047, 767 cm^{-1}

^1H NMR (500 MHz) (CDCl_3) δ 1.99 (s, 3H), 2.04 (s, 3H), 2.076 (s, 3H), 2.083 (s, 3H), 2.21 (m, 1H), 2.36 (m, 1H), 2.53 (m, 2H), 3.76 (s, 3H), 3.88 (m, 1H), 4.13 (m, 2H), 4.25 (m, 2H), 4.41 (m, 4H), 4.93 (t, $J = 6.2$ Hz, 1H), 5.02 (t, $J = 7.0$ Hz, 1H), 5.46 (m, 2H), 5.64 (d, $J = 8.3$ Hz, 1H), 5.93 (d, $J = 8.7$, 1H), 7.31 (m, 2H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.61 (m, 2H), 7.76 (d, $J = 7.4$ Hz, 2H)

^{13}C NMR (500 MHz) (CDCl_3) δ 20.7, 20.8, 20.82, 23.2, 30.1, 31.1, 35.3, 47.1, 49.8, 52.4, 53.5, 60.8, 61.2, 67.0, 67.5, 69.6, 70.5, 71.1, 120.0, 125.0, 125.1, 125.2, 125.8, 127.0, 127.7, 128.6, 129.6, 141.3, 143.8, 143.9, 155.8, 168.9, 169.6, 170.6, 170.7, 172.1

HRMS Calcd for $\text{C}_{36}\text{H}_{42}\text{N}_2\text{O}_{12}$ (M^+): 694.2738. Found: 694.2726



Compound **6** ($\text{R}^1 = \text{Ac}$, $\text{R}^2 = \text{Boc}$).

Yield = 60% (12.5:1 *trans:cis*-) (10 mol % each day, 2 days)

R_f = 0.25 (70% EtOAc/pet. ether)

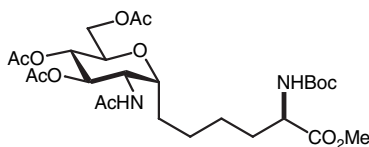
m.p. = n/a

IR (film, NaCl) 3358, 2986, 2952, 1754, 1527, 1440, 1379, 1239, 1169, 1065 cm^{-1}

^1H NMR (500 MHz) (CDCl_3) (major isomer) δ 1.42 (s, 9H), 1.97 (s, 3H), 2.06 (m, 9H), 2.20 (m, 1H), 2.36 (m, 1H), 2.45 (m, 2H), 3.73 (s, 3H), 3.76 (m, 1H), 3.88 (m, 1H), 4.10 (m, 3H), 4.24 (m, 2H), 4.33 (m, 1H), 4.39 (dd, $J = 6.2, 12.2$ Hz, 1H), 4.94 (t, $J = 6.5$ Hz, 1H), 5.02 (t, $J = 7.5$ Hz, 1H), 5.12 (d, $J = 8.0$ Hz, 1H), 5.44 (m, 2H), 5.91 (d, $J = 8.5$ Hz, 1H)

^{13}C NMR (500 MHz) (CDCl_3) δ 20.7, 20.8, 23.2, 26.8, 28.3, 30.1, 30.9, 34.6, 35.4, 49.6, 50.2, 52.3, 53.0, 53.4, 60.6, 61.3, 62.3, 67.1, 67.5, 68.6, 69.3, 69.8, 70.2, 70.8, 71.9, 74.1, 74.3, 75.6, 79.9, 126.1, 127.2, 128.5, 129.4, 155.2, 168.9, 169.6, 170.6, 170.9, 172.5

HRMS Calcd for $\text{C}_{26}\text{H}_{40}\text{N}_2\text{O}_{12}$ (M^+): 572.2581. Found: 572.2581



Yield = 89%

R_f = 0.20 (70% EtOAc:pet. ether)

m.p. = n/a

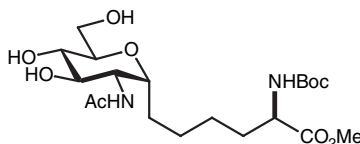
IR (film, NaCl) 3362, 2961, 2873, 1754, 1536, 1449, 1379, 1239, 1178, 1055, 924, 741

¹H NMR (300 MHz) (CDCl₃) δ 1.30 (m, 4H), 1.43 (s, 9H), 1.56 (m, 3H), 1.77 (m, 1H), 1.96 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 3.73 (s, 3H), 3.84 (m, 1H), 4.09 (m, 2H), 4.28 (m, 3H), 4.98 (m, 3H), 5.83 (d, *J* = 8.1 Hz, 1H)

¹³C NMR (300 MHz) (CDCl₃) δ 20.7, 20.8, 23.2, 24.6, 25.0, 26.6, 28.3, 32.7, 50.8, 52.3, 53.1, 61.6, 67.8, 70.2, 71.4, 155.3, 169.0, 169.6, 170.6, 171.1, 173.3

HRMS Calcd for C₂₆H₄₂N₂O₁₂ (M⁺): 574.2738. Found: 574.2714

To a stirring solution of **FSI-242** (65 mg, 0.114 mmol) in MeOH (0.6 mL) and EtOAc (0.6 mL) under H₂ (1 atm) was added Pd(OH)₂/C (20%) (7 mg). The reaction mixture was filtered through Celite after stirring overnight. The filtrate was concentrated under reduced pressure and subjected to column chromatography (SiO₂, R_f 0.20, 70% EtOAc:pet. ether) to give **TBIII-245** as a film (58 mg, 89%).



Compound **7**.

Yield = (qu)

m.p. = n/a

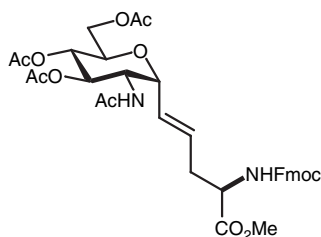
IR (film, NaCl) 3537, 2960, 2873, 1658, 1449, 1379, 1222, 1178, 1055 cm⁻¹

¹H NMR (300 MHz) (CDCl₃) δ 1.24 (m, 4H), 1.34 (s, 9H), 1.52 (m, 4H), 1.88 (s, 3H), 3.19 (m, 1H), 3.29 (m, 1H), 3.49 (m, 1H), 3.56 (m, 1H), 3.61 (s, 3H), 3.70 (dd, *J* = 2.0, 12.0 Hz, 1H), 3.87 (m, 2H), 3.99 (m, 1H)

¹³C NMR (300 MHz) (CDCl₃) δ 22.6, 26.1, 26.2, 26.7, 28.7, 32.7, 52.6, 55.0, 63.1, 72.4, 72.9, 74.3, 74.7, 128.3, 129.3, 158.2, 173.5, 175.1

HRMS Calcd for C₂₀H₃₆N₂O₉ (M⁺): 448.2421. Found: 448.2424

To a stirring solution of Na⁺ (5 mg) in MeOH (1 mL) was added **TBIII-245** (30 mg, 0.05 mmol). After stirring for 2 hrs, the reaction mixture was quenched by careful addition of Amberlite IR-120 to ensure that the pH did not become acidic and cause cleavage of the Boc-group. The mixture was then filtered, and the filtrate concentrated under a reduced pressure to give **TBIII-253** as a white glass (23 mg, qu).



Compound **9** (R¹ = Ac, R² = Fmoc).

Yield = 69% (10 mol % each day, 2 days)

R_f = 0.25 (70% EtOAc:pet. ether)

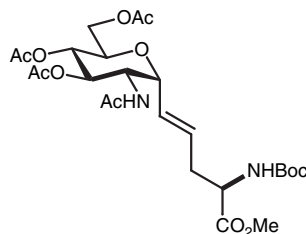
m.p. = n/a

IR (film, NaCl) 3345, 3021, 2960, 1754, 1676, 1536, 1457, 1379, 1239, 1055, 767 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) δ 1.96 (s, 3H), 1.97 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H), 2.62 (m, 2H), 3.80 (s, 3H), 3.94 (m, 1H), 4.10 (m, 1H), 4.23 (m, 2H), 4.40 (m, 2H), 4.47 (m, 2H), 4.57 (m, 1H), 5.05 (m, 2H), 5.58 (d, *J* = 8.0 Hz, 1H), 5.75 (m, 2H), 5.91 (d, *J* = 9.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 7.0 Hz, 2H)

¹³C NMR (500 MHz) (CDCl₃) δ 20.7, 23.0, 36.0, 47.1, 51.2, 52.7, 53.8, 62.3, 67.1, 68.5, 70.3, 70.8, 73.8, 120.0, 125.0, 126.3, 127.1, 127.8, 131.6, 141.3, 143.7, 155.6, 169.1, 170.1, 170.8, 171.5, 171.7

HRMS Calcd for C₃₅H₄₀N₂O₁₂ (M⁺): 680.2581. Found: 680.2600



Compound **9** (R¹ = Ac, R² = Boc).

Yield = 77% (10 mol % each day, 2 days)

R_f = 0.24 (70% EtOAc/pet. ether)

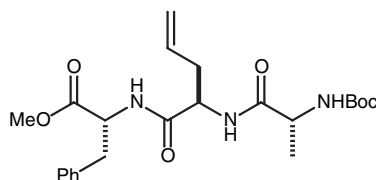
m.p. = n/a

IR (film, NaCl) 3336, 2986, 2943, 1754, 1536, 1379, 1239, 1169, 1047 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) δ 1.42 (s, 9H), 1.96 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 2.55 (m, 2H), 3.76 (s, 3H), 3.91 (m, 1H), 4.06 (dd, *J* = 2.0, 12.3 Hz, 1H), 4.20 (dd, *J* = 5.1, 12.2 Hz, 1H), 4.36 (m, 2H), 4.52 (t, *J* = 5.5 Hz, 1H), 5.02 (m, 2H), 5.22 (d, *J* = 6.7 Hz, 1H), 5.72 (m, 2H), 5.95 (d, *J* = 8.3 Hz, 1H)

¹³C NMR (500 MHz) (CDCl₃) δ 20.6, 20.7, 23.0, 28.2, 35.9, 51.1, 52.5, 53.3, 62.3, 68.6, 70.1, 70.9, 74.0, 80.2, 125.8, 132.2, 154.9, 169.1, 170.1, 170.8, 171.4, 172.0

HRMS Calcd for C₂₅H₃₈N₂O₁₂ (M⁺): 558.2425. Found: 558.2422



Compound **14**.

Experimental: Fmoc-Allyl-Gly (200 mg, 0.57 mmol, 1eq), H₂N-Phe-Ome (136 mg, 0.57mmol, 1eq), PyBop® (328 mg, 0.63 mmol, 1.1eq) and DIEA (0.2 mL, 148 mg, 1.14 mmol) were stirred in dry THF (10 mL) for 5 h. The reaction mixture was then concentrated, redissolved in EtOAc (25 mL), and extracted sequentially with 5% citric acid (25 mL), 2 times with 5% sodium bicarbonate (25 mL), and 2 times with water (25 mL). The organic layer was dried with sodium sulfate and concentrated under reduced pressure. The white solid was then redissolved in 10% diethylamine in DMF (5 mL). This mixture was stirred at room temperature for 1 hour. The resulting solution was concentrated under high vacuum to a residue. This residue was then dissolved in a 1:1 solution of THF and DMF (30 mL). Boc-protected alanine (108 mg, 0.572 mmol, 1 eq) and PyBop (328 mg, 0.628 mmol, 1.1 eq) was added to this solution and stirred at room temperature under argon. Diisopropylethylamine (0.1mL, 0.572mmol, 1eq) was added, and the reaction was allowed to stir for 16 hours. The mixture was concentrated under reduced pressure and redissolved in ethyl acetate (50 mL). The resulting solution was extracted sequentially with 5% citric acid (25 mL), 2 times with 5% sodium bicarbonate (25 mL), and 2 times with water (25 mL). The organic layer was dried with sodium sulfate and concentrated under reduced pressure. The white solid was subjected to column chromatography (SiO₂, R_f 0.25, 50% EtOAc/pet. ether) to give **FSI-209** as a pale yellow solid (153 mg, 60%, overall)

Yield = 60% (overall)

R_f = 0.25 (50% EtOAc/pet. ether)

m.p. = 98-100°C

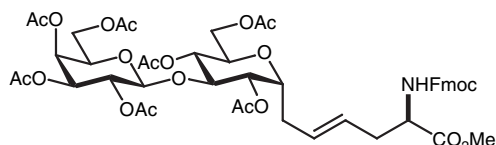
IR (film, NaCl) 3310, 3065, 2986, 1754, 1650, 1527, 1457, 1379, 1256, 1178, 1038, 933, 863, 758, 697 cm⁻¹

¹H NMR (300 MHz) (CDCl₃) δ 1.32 (d, *J* = 7.3 Hz, 3H), 1.45 (s, 9H), 2.48 (t, *J* = 6.7 Hz, 2H), 3.11 (ddd, *J* = 6.0, 13.9, 26.5 Hz, 2H), 3.72 (s, 3H), 4.12 (q, *J* = 6.9 Hz, 1H), 4.41 (q, *J* = 6.6 Hz, 1H), 4.84 (m, 2H), 5.09 (m, 2H), 5.66 (m, 1H), 6.51 (br s, 1H), 6.59 (d, *J* = 7.3 Hz, 1H), 7.10 (m, 2H), 7.28 (m, 3H)

¹³C NMR (500 MHz) (CDCl₃) δ 18.0, 28.3, 36.2, 37.7, 50.2, 52.2, 52.3, 53.2, 80.3, 119.1, 127.1, 128.6, 129.2, 132.6, 135.7, 155.7, 170.3, 171.5, 172.5

HRMS Calcd for C₂₃H₃₃N₃O₆ (M⁺): 447.2369. Found: 447.2370

Literature: 1. Coste, J.; Le-Nguyen, D.; Castro, B. *Tetrahedron Lett.* **1990**, *31*, 205-208. 2. Walkup, R.; Cole, D.; Whittlesey, B. J. *Org. Chem.* **1995**, *60*, 2630-2634. 3. Høeg-Jensen, T.; Jakobsen, M.; Olsen, C.; Holm, A.; *Tetrahedron Lett.* **1991**, *32*, 7617-7620.



Compound **12** (R² = Fmoc).

Yield = 57% (10 mol % each day, 2 days)

R_f = 0.14 (50% EtOAc/pet. ether)

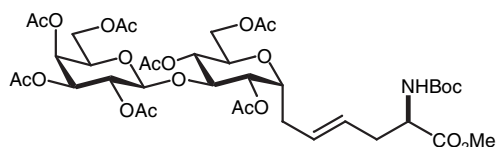
m.p. = n/a

IR (film, NaCl) 3380, 3021, 2952, 1754, 1519, 1457, 1379, 1230, 1064, 758 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) (major isomer) δ 1.96 (s, 3H), 2.07 (m, 19H), 2.23 (m, 1H), 2.50 (m, 2H), 3.67 (m, 1H), 3.77 (m, 3H), 3.90 (m, 1H), 4.15 (m, 6H), 4.43 (m, 5H), 4.98 (m, 2H), 5.15 (m, 1H), 5.44 (m, 5H), 7.31 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.61 (m, 2H), 7.76 (d, *J* = 7.4 Hz, 2H)

¹³C NMR (500 MHz) (CDCl₃) (major isomer) δ 20.5, 20.6, 20.8, 20.9, 29.74, 69.7, 69.8, 70.7, 71.0, 101.4, 120.0, 125.1, 126.9, 127.0, 129.7, 141.2, 143.7, 143.9, 155.7, 169.2, 169.6, 169.9, 170.0, 170.4

HRMS Calcd for C₄₈H₅₇NO₂₁ (M⁺): 983.3423. Found: 983.3458



Compound **12** (R² = Boc).

Yield = 73% (10 mol % each day, 2 days) (TBIII-221)

R_f = 0.21 (50% EtOAc/pet. ether)

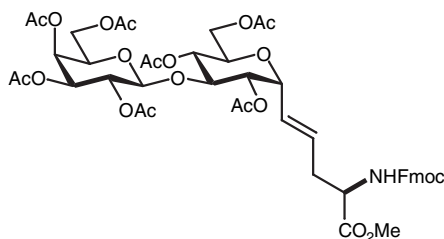
m.p. = n/a

IR (film, NaCl) 3371, 3021, 2986, 1754, 1510, 1449, 1379, 1239, 1178, 1064, 767 cm⁻¹

¹H NMR (500 MHz) (CDCl₃) (major isomer) δ 1.43 (s, 9H), 2.07 (m, 22H), 2.26 (m, 1H), 2.48 (m, 2H), 3.66 (m, 1H), 3.73 (s, 3H), 3.81 (m, 1H), 3.88 (m, 1H), 4.13 (m, 4H), 4.34 (m, 2H), 4.50 (m, 1H), 4.95 (m, 2H), 5.06 (m, 2H), 5.34 (m, 2H), 5.46 (m, 2H)

¹³C NMR (500 MHz) (CDCl₃) (major isomer) δ 20.5, 20.51, 20.6, 20.7, 20.8, 20.9, 23.8, 28.2, 29.7, 35.5, 41.8, 52.2, 53.0, 60.8, 62.1, 63.5, 66.6, 66.7, 68.7, 69.0, 69.6, 69.8, 70.1, 70.4, 70.5, 70.7, 70.71, 70.9, 71.0, 71.6, 73.2, 76.4, 79.9, 96.2, 96.5, 101.3, 102.2, 127.1, 128.4, 128.7, 129.2, 155.1, 169.1, 169.5, 169.9, 170.0, 170.3, 170.7, 172.4

HRMS Calcd for C₃₈H₅₅NO₂₁ (M⁺): 861.3267. Found: 861.3279



Compound **13** (R^2 =Fmoc).

Yield = 60% (10 mol %, 2 days)

R_f = 0.11 (60% EtOAc/pet. ether)

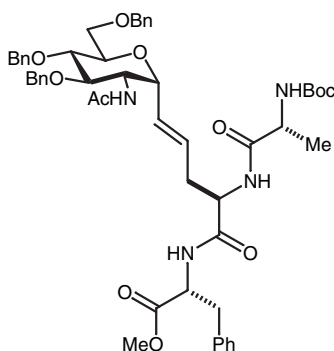
m.p. = n/a

IR (film, NaCl) 3362, 2934, 2855, 1754, 1527, 1449, 1379, 1230, 1055, 915, 750 cm^{-1}

¹H NMR (500 MHz) (CDCl_3) (major product) δ 1.96 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.11 (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 2.65 (m, 2H), 3.78 (m, 6H), 4.14 (m, 5H), 4.45 (m, 5H), 4.62 (m, 1H), 4.97 (m, 2H), 5.10 (m, 1H), 5.23 (m, 1H), 5.36 (d, J = 6.3 Hz, 1H), 5.47 (m, 1H), 5.76 (d, J = 3.3 Hz, 1H)

¹³C NMR (500 MHz) (CDCl_3) (major product) δ 20.4, 20.6, 20.7, 20.8, 29.7, 30.9, 35.7, 47.1, 52.8, 53.4, 60.8, 62.4, 66.6, 67.0, 68.9, 69.0, 70.0, 70.2, 70.4, 70.7, 71.0, 72.0, 76.8, 101.2, 120.0, 125.0, 126.5, 127.0, 127.7, 131.0, 141.3, 143.8, 155.5, 169.2, 169.7, 169.9, 170.0, 170.1, 170.3, 170.5, 171.9

HRMS Calcd for $\text{C}_{47}\text{H}_{55}\text{NO}_{21}$ (M^+): 969.3267. Found: 969.3250



Compound **15**.

Yield = 60% (10 mol % each day, 2 days)

R_f = 0.28 (70% EtOAc/pet. ether)

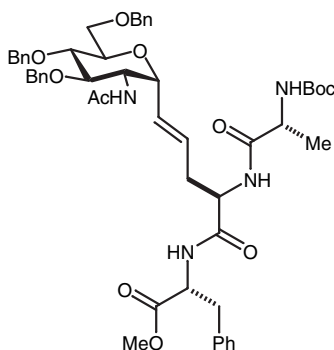
m.p. = 122-124°C

IR (film, NaCl) 3319, 3039, 2978, 2933, 1737, 1658, 1536, 1510, 1466, 1379, 1256, 1178, 1099, 916, 741, 697 cm^{-1}

¹H NMR (300 MHz) (CDCl_3) δ 1.30 (d, J = 6.8 Hz, 3H), 1.41 (s, 9H), 1.85 (m, 2H), 1.89 (s, 3H), 2.25 (m, 1H), 2.71 (dt, J = 4.7, 14.1 Hz, 1H), 3.04 (dd, J = 5.7, 13.8 Hz, 1H), 3.12 (dd, J = 6.5, 13.8 Hz, 1H), 3.65 (s, 3H), 3.73 (m, 4H), 4.23 (m, 3H), 4.48 (m, 8H), 4.82 (m, 1H), 5.47 (dd, J = 6.9, 15.9 Hz, 1H), 5.56 (m, 1H), 5.67 (d, J = 5.7 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.24 (m, 20H)

¹³C NMR (300 MHz) (CDCl_3) δ 18.7, 23.3, 28.3, 29.6, 34.4, 38.0, 49.7, 51.8, 52.2, 53.2, 67.6, 69.6, 72.1, 72.2, 72.6, 73.2, 74.5, 74.7, 79.5, 127.0, 127.5, 127.7, 127.8, 127.9, 128.1, 128.4, 128.5, 128.6, 129.2, 131.6, 135.9, 137.2, 137.9, 155.5, 170.3, 171.4, 173.7

HRMS Calcd for $\text{C}_{52}\text{H}_{64}\text{N}_4\text{O}_{11}$ (M^+): 920.4572. Found: 920.4541



Compound **16**.

Yield = 39% (10 mol % each day, 2 days)

R_f = 0.09 (80% EtOAc/pet. ether)

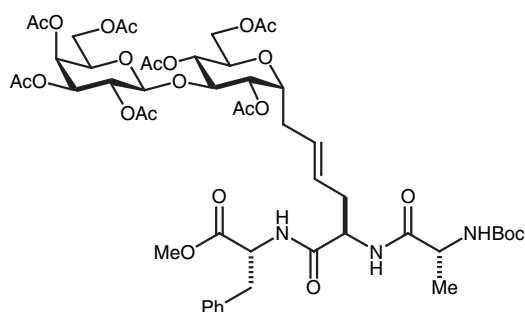
m.p. = n/a

IR (film, NaCl) 3301, 2925, 2855, 1754, 1667, 1536, 1440, 1379, 1239, 1178, 1047, 767 cm^{-1}

^1H NMR (300 MHz) (CDCl_3) (major isomer) δ 1.44 (s, 9H), 1.99 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.43 (m, 4H), 3.10 (m, 2H), 3.71 (s, 3H), 3.93 (m, 1H), 4.15 (m, 5H), 4.39 (q, $J = 6.6$ Hz, 1H), 4.50 (dd, $J = 7.0, 12.0$ Hz, 1H), 4.78 (m, 1H), 4.89 (t, $J = 5.4$ Hz, 1H), 5.01 (t, $J = 6.6$ Hz, 1H), 5.25 (d, $J = 6.6$ Hz, 1H), 5.42 (m, 2H), 6.02 (d, $J = 7.5$, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 6.9$ Hz, 1H), 7.11 (m, 2H), 7.27 (m, 3H)

^{13}C NMR (300 MHz) (CDCl_3) (major isomer) δ 18.4, 20.8, 23.3, 28.3, 29.7, 31.7, 35.2, 37.7, 49.3, 50.1, 52.3, 52.6, 53.3, 61.1, 67.5, 69.3, 70.2, 71.8, 80.0, 127.1, 127.8, 128.6, 129.2, 135.8, 155.4, 168.9, 169.7, 170.4, 170.8, 171.6, 172.7

HRMS Calcd for $\text{C}_{53}\text{H}_{66}\text{N}_4\text{O}_{11}$ (M^+): 790.3637 Found: 790.3651



Compound 17.

Yield = 57% (10 mol %, 2 days)

R_f = 0.17 (70% EtOAc/pet. ether)

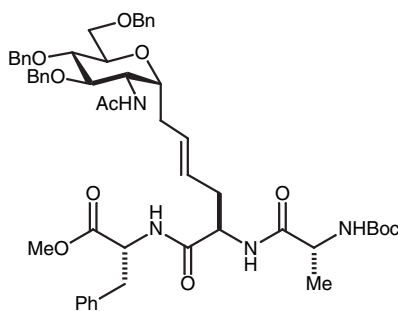
m.p. = n/a

IR (film, NaCl) 3353, 2978, 2934, 1754, 1667, 1510, 1449, 1379, 1230, 1064, 924, 741 cm^{-1}

^1H NMR (300 MHz) (CDCl_3) (major isomer) δ 1.29 (d, $J = 7.2$ Hz, 3H), 1.42 (s, 9H), 1.95 (s, 3H), 2.01 (s, 3H), 2.04 (s, 6H), 2.08 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.35 (m, 4H), 3.08 (m, 2H), 3.69 (m, 5H), 3.90 (m, 1H), 4.10 (m, 5H), 4.31 (m, 2H), 4.54 (m, 1H), 4.79 (m, 1H), 4.94 (m, 2H), 5.14 (m, 2H), 5.41 (m, 4H), 6.53 (dd, $J = 7.5, 23.4$ Hz, 1H), 6.70 (dd, $J = 7.5, 15.3$ Hz, 1H), 7.10 (m, 2H), 7.25 (m, 3H)

^{13}C NMR (300 MHz) (CDCl_3) (major isomer) δ 18.1, 20.5, 20.6, 20.7, 20.8, 28.3, 29.8, 35.4, 37.6, 50.2, 52.3, 52.5, 53.2, 60.8, 62.1, 66.7, 68.7, 69.6, 70.7, 70.9, 71.5, 76.3, 101.4, 127.1, 127.5, 128.6, 129.1, 129.4, 135.7, 169.1, 169.4, 169.5, 169.9, 170.0, 170.2, 170.4, 170.5, 170.7, 171.5, 172.6

HRMS Calcd for $\text{C}_{53}\text{H}_{66}\text{N}_4\text{O}_{11}$ (M^+): 1079.4322. Found: 1079.4336



*Unable to be purified due to tripeptide dimer being present.

