**General Procedures**

All non-aqueous reactions were conducted in flame or oven-dried glassware under an argon atmosphere and were stirred magnetically unless otherwise noted. Air sensitive reagents and solutions were transferred *via syringe* (unless noted otherwise) and were introduced to the reaction vessel through rubber septa. Solids were introduced under a positive pressure of argon. Temperature, other than room temperature, refers to bath temperature unless otherwise indicated. All distillations were performed under an argon atmosphere or at reduced pressure attained by either a water aspirator (15-30 mm Hg) or an oil pump (<1 mm Hg). The phrase “concentrated in *vacuo*” refers to removal of solvents by means of a Buchi rotary-evaporator attached to a water aspirator (15-30 mm Hg) followed by pumping to constant weight (<1 mm Hg).

**Chromatography**

Purification by flash chromatography was performed following the procedure by Stille66 using the indicated solvent system on EM Reagent silica gel 60 (230-400) mesh. Analytical thin layer chromatography (TLC) was performed using EM silica gel 60 F-254 pre-coated glass plates (0.25 mm). Visualization was effected by short-wave UV illumination or by dipping into a stain solution followed by heating on a hot plate.

**Reagents and Solvents**

Reagent-grade solvents were used without purification for all extractions and work-up procedures. Deionized water was used for all aqueous reactions and for the preparation of all aqueous solutions. Reaction solvents and reagents were dried and purified according to published literature procedures by distillation under argon or vacuum from the appropriate drying agent:

- Distilled from sodium benzophenone ketyl:
  - Tetrahydrofuran (THF), diethyl ether (Et₂O), and xylenes.
Distilled from calcium hydride:
Methylene chloride (CH₂Cl₂), toluene, triethylamine (Et₃N), pyridine,
diisopropylethylamine, dimethyl formamide (DMF), 2,6-lutidine.
Distilled from sodium metal:
Benzene, methanol.
Stock solutions of "BuLi in hexanes or 'BuLi in pentane were titrated using
diphenylacetic acid.¹¹⁸ Diphenylacetic acid was recrystallized from hexanes.

Physical Data
Proton nuclear magnetic resonance (NMR) spectra were obtained on Avance 500
(500 MHz) or Avance 400 (400 MHz) spectrometer. Carbon NMR spectra were
obtained on an Avance 400 (100 MHz). Chemical shifts are reported in ppm (δ)
downfield relative to tetramethylsilane and are referenced to the deuterated solvent
(CHCl₃ at 7.27 ppm, benzene at 7.15 ppm). Data are reported as follows: chemical
shift (multiplicity, coupling constants in Hertz, number of hydrogens). Multiplicity is
designated using the following abbreviations and combinations thereof: s (singlet), d
(doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet), m
(multiplet and/or multiple resonances).

Infrared (IR) spectra were recorded on a Perkin Elmer 1610 FT-IR spectrophotometer
and are reported in wave numbers (cm⁻¹) with polystyrene as a standard. Low
resolution mass spectra were obtained using a Hewlett Packard Series 1100 MSD
mass spectrometer.
**Synthesis of compound 190.**

A 50 mL round bottom flask was charged with a solution of bisalkyne 189 in THF (3 g, 6.87 mmol, 1 eq in 50 mL). A stock solution of trityl lithium in THF was added until color of the solution remained rosy red. The rosy red solution was stirred for 30 min. Neat MeI (0.79 mL, 12 mmol, 1.8 eq, d = 2.275 g/cc) was added dropwise to the reaction mixture. The rosy red solution turned into a lemon yellow solution instantly. After 30 min the reaction mixture was quenched with 20 mL of saturated NH₄Cl and diluted with 100 mL of Et₂O. After separating the phases, the organic layer was washed with brine (1 x 50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. Both triphenylmethane and the product were too close moving on TLC. As a result the crude mixture was taken to the next step without purification.

**Preparation of trityl lithium solution:** A 100 mL of round bottom flask was charged with a solution of triphenylmethane in THF (2.7 g, 11 mmol, 1.6 eq in 20 mL). A 2.5 M solution of "BuLi (0.527 g, 8.24 mmol, 1.2 eq) in hexane was added dropwise at RT. The colorless solution turned into a rosy red solution. This rosy red solution was stirred for 30 min to ensure complete deprotonation.

Please refer Katie’s thesis for characterization data
Synthesis of compound 132.

A 50 mL round bottom flask was charged with azeotropically dried zirconocene dichloride (1.55 g, 5.28 mmol, 1.4 eq). It was dissolved in 24 mL of THF. The flask was covered with aluminum foil owing to the light sensitive nature of Schwartz reagent. 1M solution of super hydride in THF (5.28 mL, 5.28 mmol, 1.4 eq) was added dropwise for a period of 20 min. The reaction contents were stirred for an hr at which point it turned into a white suspension. A solution of azeotropically dried bisalkyne 193 in THF (1.110 g, 3.175 mmol, 1 eq in 2 mL) was added dropwise for a period of 10 min. The reaction contents were stirred for an hr. The white suspension turned into a clear orange yellow solution during the course of the reaction.

A freshly sublimed iodine in THF (1.34 g, 5.28 mmol, 1.4 eq in 4 mL) was stirred for 30 min in the presence of oven dried K$_2$CO$_3$ (app 60 mg). This solution was then added dropwise to the vinyl zirconium solution. The reaction mixture was stirred for 10 min and quenched with 4 mL of saturated NaHCO$_3$ and 4 mL of saturated Na$_2$S$_2$O$_3$. This biphasic solution was then passed through celite and the phases were separated. The aqueous layer was extracted twice with ether (2 x 10 mL) and the combined organic layers were washed with brine (1 x 40 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes- CH$_2$Cl$_2$, 10:1) to yield 1.45 g (91%) of the title compound 132 as a clear oil.

Please refer Katie’s thesis for characterization data
**Synthesis of compound 195.** A flame dried 250 mL 3 neck round bottom flask with an immersion thermometer was charged with alcohol 198 (3 g, 12.3 mmol, 1 eq). It was dissolved in 125 mL of dry THF. The reaction mixture was cooled to -5°C (internal). The reaction mixture was treated with neat MeI (3.83 mL, 61.5 mmol, 5 eq, d = 2.28 g/cc). After 10 min, KOtBu (2.7 g, 21.6 mmol, 2 eq) was added in one portion. The reaction mixture turned to a yellow suspension. After 1h the reaction mixture was quenched with 40 mL of water. The reaction mixture was diluted with 150 mL of ether and the phases were separated. The aqueous layer was extracted with ether (3 x 100 mL). The combined organic layers were washed with brine (1 x 250 mL), dried over MgSO₄, filtered and concentrated in vacuo to afford 3.0 g of the title compound 195 as a pale yellow oil. The material was not stable to column chromatography. As a result it was carried to the next step without purification.

\[ \text{R}_f = 0.92 \text{ (hexanes-ether 1:1)} \]

UV, CAM, KMnO₄ active

**\(^1\)H NMR (400 MHz, CDCl₃, ppm)**

\[ \delta 6.19 \text{ (dd, } J = 6.08, 1.21 \text{ Hz, 1H)}, 4.54 \text{ (dd, } J = 6.10, 2.46 \text{ Hz, 1H)}, 4.30-4.09 \text{ (m, 1H)}, 3.92-3.75 \text{ (m, 1H)}, 3.50 \text{ (s, 3H)}, 2.98 \text{ (dd, } J = 8.88, 6.46 \text{ Hz, 1H)}, 1.31 \text{ (d, } J = 6.47 \text{ Hz, 3H)}, 0.86 \text{ (s, 9H)}, 0.06 \text{ (d, 6H)} \]

**\(^{13}\)C NMR (100 MHz, CDCl₃, ppm)**

\[ \delta 143.37, 103.76, 84.08, 73.80, 69.42, 60.44, 25.83, 17.98, 17.25, -4.52, -4.73 \]
| IR (film)        | 2932, 2857, 1649, 1250, 1113, 1072, 1049 cm<sup>-1</sup> |
Synthesis of compound 200.

A 100 mL round bottom flask was charged with glucal 195 (0.530 g, 2.05 mmol, 1 eq). It was diluted with 8 mL of DCE. The reaction mixture was cooled to 0°C (external). A solution of DMDO in acetone was added and the reaction was monitored by TLC. After the consumption of glucal, freshly distilled cyclohexene (0.21 mL, 2.05 mmol, 1 eq, d = 0.811 g/cc) was added. The reaction was stirred at 0°C for 45 min after which dry Et₂N (0.57 mL, 4.1 mmol, 2 eq, d = 0.726 g/cc) was added followed by PhSH (0.42 mL, 4.1 mmol, 2 eq, d = 1.073 g/cc). After 2h, the reaction mixture was concentrated to 10 mL. The reaction mixture was diluted with 20 mL of CH₂Cl₂, dried over MgSO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 40:1) to yield 0.512 g (65%) of the title compound 200 as a pale yellow oil.

R<sub>f</sub> = 0.77 (hexanes-ether 1:1)  
UV, CAM, KMnO₄ active

<sup>1</sup>H NMR (400 MHz, CDCl₃, ppm)  
δ 7.82-7.49 (m, 2H), 7.49-7.24 (m, 3H), 4.52 (t, <i>J</i> = 8.07, 8.07 Hz, 1H), 3.79-3.48 (m, 4H), 3.48-3.23 (m, 2H), 2.80 (t, <i>J</i> = 9.12, 9.12 Hz, 1H), 2.34 (dd, <i>J</i> = 12.28, 2.31 Hz, 1H), 1.51-1.32 (d, 3H), 1.08-0.80 (s, 9H), 0.16 (s, 6H)
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
$\delta$ 132.29, 128.88, 127.79, 88.32, 85.77, 78.41, 77.29, 76.97, 76.65, 75.90, 73.26, 61.24, 25.88, 18.28, -4.45

IR (film)  
3700, 2930, 2856, 1440, 1250, 1116, 1130, 1077 cm$^{-1}$

$[\alpha]_D^{25}$  
(+) 45.66 (C = 3.9, C$_6$H$_6$)
Synthesis of compound 194.

A 10 mL round bottom flask was charged with thioglycoside 200 (0.512 g, 1.33 mmol, 1 eq). It was dissolved in 1.3 mL of CH₂Cl₂. The reaction mixture was cooled to 0°C. After 10 min, dry Et₃N (0.56 mL, 3.99 mmol, 3 eq, d = 0.726 g/cc) was added followed by dropwise addition of TBSOTf (0.37 mL, 1.60 mmol, 1.2 eq, d = 1.151 g/cc). After 5h, the reaction mixture was quenched with 3 mL of saturated NaHCO₃. The organic layer was diluted with 15 mL of ether. After separating the phases, the aqueous phase was extracted with CH₂Cl₂ (2 x 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by chromatography (hexanes-ether, 60:1) to yield 0.64 g (96%) of the title compound 194 as a pale yellow oil.

Rᵥ = 0.79 (hexanes-ether 4:1)  UV, CAM, KMnO₄ active

¹H NMR (500 MHz, CDCl₃, ppm)  δ 7.63-7.47 (m, 2H), 7.32 (ddd, J = 26.60, 10.92, 4.48 Hz, 3H), 4.88-4.73 (m, 1H), 3.85-3.44 (m, 2H), 3.57-3.66 (m, 1H), 3.42-3.34 (s, 3H), 3.05 (ddd, J = 7.26, 5.22, 1.81 Hz, 1H), 1.48 (d, 3H), 1.19-0.82 (m, 18H), 0.18 (m, J = 11.83, 12H)

¹³C NMR (101 MHz, CDCl₃, ppm)  δ 135.82, 130.62, 128.72, 126.73, 88.60, 85.72, 76.82, 75.24, 74.91, 59.54, 26.32,
26.22, 19.65, 18.15, 18.12, -2.70, -3.22, -3.35, -3.68

IR (film) 2930, 2890, 1472, 1386, 1254, 1141, 1104, 1065 cm$^{-1}$

$[\alpha]^0_{25}$ (+) 57.22 (C = 4.6, C$_6$H$_6$)
Synthesis of compound 122.

A 25 mL round bottom flask was charged with fully protected thioglycoside 194 (0.600 g, 1.20 mmol, 1eq). It was dissolved in 6 mL of CH₂Cl₂. The reaction mixture was cooled to 0°C (external). Finely grounded NaHCO₃ (1 g, 12.0 mol, 10 eq) and freshly recrystallized m-CPBA (0.208 g, 1.20 mol, 1 eq) were added sequentially. After stirring for 30 min, the reaction mixture was quenched with 5 mL saturated NaHCO₃. The contents were warmed to room temperature. 2 mL of water was added to ensure complete solubility of the inorganic salts. After separating the phases the aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The combined organic layers were washed with brine (1 x 15 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude mixture was purified by chromatography (hexanes-ether, 10:1 to elute the first diastereomer then 3:1 to elute the second diastereomer) to afford 0.402 g (65%) of the title compound

\[ R_f = 0.48 \text{ (hexanes-ether 3:1)} \]

UV, CAM, KMnO₄ active

\(^1\)H NMR (500 MHz, CDCl₃, ppm)  
δ 7.87-7.69 (m, 2H), 7.67-7.47 (m, 3H), 4.68-4.47 (m, 1H), 4.26 (s, 1H), 4.01 (dd, \( J = 3.79, \ 2.45 \text{ Hz, 1H} \)), 3.94 (qd, \( J = 9.48, \ 6.17, \ 6.17, \ 6.16 \text{ Hz, 1H} \)), 3.56-3.50 (s, 3H), 3.18 (dd, \( J = 9.46, \ 2.32 \text{ Hz, 1H} \)), 1.27 (d, \( J = 6.17, \text{ Hz, 3H} \)), 1.05 (s, \( J = 9H \)), 0.96-0.89 (s, 9H), 0.29 (s, 3H), 0.25 (s, 3H), 0.21 (s, 3H), 0.18 (s, 3H)
$^1$H NMR (500 MHz, CDCl$_3$, ppm)  
\[ \delta 7.66 (dd, J = 6.51, 2.94 \text{ Hz}, 2\text{H}), 7.57-7.42 \text{ (m, 3H)}, 3.95 (d, J = 6.09 \text{ Hz}, 1\text{H}), 3.82 (t, J = 5.87, 5.87 \text{ Hz}, 1\text{H}), 3.62 (t, J = 6.11, 6.11 \text{ Hz}, 1\text{H}), 3.49-3.38 \text{ (m, 4H)}, 2.94 (dd, J = 8.86, 6.67 \text{ Hz}, 1\text{H}), 1.29 (d, J = 8.92 \text{ Hz}, 3\text{H}), 0.97 (s, 9\text{H}), 0.91-0.82 (s, 9\text{H}), 0.12 (d, 6\text{H}), 0.04 (d, 6\text{H}) \]

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
\[ \delta 141.59, 135.81, 131.22, 128.86, 125.61, 97.08, 85.72, 76.92, 74.58, 70.97, 65.83, 59.97, 26.41, 26.04, 18.75, 18.39, 18.18, 18.12, -2.90, -3.03, -3.58, -3.81 \]

IR (film)  
2929, 2856, 1470, 1387, 1259, 1137, 1112, 1091 cm$^{-1}$

Diastereomer 2:

$R_f = 0.09 \text{ (hexanes-ether 3:1)}$  
UV, CAM, KMnO$_4$ active

$^1$H NMR (500 MHz, CDCl$_3$, ppm)  
\[ \delta 7.66 (dd, J = 6.51, 2.94 \text{ Hz}, 2\text{H}), 7.57-7.42 \text{ (m, 3H)}, 3.95 (d, J = 6.09 \text{ Hz}, 1\text{H}), 3.82 (t, J = 5.87, 5.87 \text{ Hz}, 1\text{H}), 3.62 (t, J = 6.11, 6.11 \text{ Hz}, 1\text{H}), 3.49-3.38 \text{ (m, 4H)}, 2.94 (dd, J = 8.86, 6.67 \text{ Hz}, 1\text{H}), 1.29 (d, J = 8.92 \text{ Hz}, 3\text{H}), 0.97 (s, 9\text{H}), 0.91-0.82 (s, 9\text{H}), 0.12 (d, 6\text{H}), 0.04 (d, 6\text{H}) \]

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
\[ \delta 143.84, 130.78, 128.51, 125.12, 96.69, 87.79, 76.65, 74.21, 70.32, 70.11, 58.31, 25.74, 25.55, 19.45, 17.95, 17.76, -4.25, -4.66, -4.76, -4.86 \]

IR (film)  
2929, 2857, 1470, 1256, 1131, 1085, 1043 cm$^{-1}$

$[\alpha]_D^{25}$  
(+) 159.30 (C = 3.7, C$_6$H$_6$)

A 25 mL round bottom flask was charged with allylic alcohol 216 (1.9 g, 12 mmol, 1 eq). It was dissolved in 10 mL of CH₂Cl₂ and cooled to 0°C (external). The reaction mixture was treated with 2,6-lutidine (4.2 mL, 36 mmol, 3 eq, d = 0.920 g/cc) followed by dropwise addition of TBSOTf (2.76 mL, 12 mmol, 1 eq, d = 1.151 g/cc). After stirring for 40 min, the reaction mixture was quenched with 5 mL of saturated NaHCO₃. After separating the phases the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were washed with water (1 x 10 mL), brine (1 x 10 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 12:1) to yield 3.12 g (98%) of the title compound 210 as a colorless oil.

Rₚ = 0.76 (hexanes-ether 1:1)   UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm)    δ 5.14 (s, 1H), 4.88 (s, 1H), 4.73 (t, J = 2.55, 2.55 Hz, 1H), 3.72 (d, J = 9.01 Hz, 1H), 3.68-3.58 (m, 1H), 3.35 (s, 3H), 2.50 (s, J = 6.52, 6.52 Hz, 2H), 1.27 (d, J = 6.19 Hz, 3H), 1.08-0.87 (s, 9H), 0.13 (d, 6H)

¹³C NMR (100 MHz, CDCl₃, ppm)    δ 143.21, 108.15, 98.26, 75.27, 70.97, 54.51, 39.64, 25.76, 18.63, 18.07, -4.46, -4.85
IR (film)  
2992, 2955, 2930, 2896, 2857, 1471, 1378, 1360, 1255, 1206, 1128, 1100 cm$^{-1}$

$[\alpha]_D^{25}$  
(-) 173.89 ($C = 7.17, C_6H_6$)
Synthesis of compound 209.

A 1L flask was charged with protected allylic alcohol 210 (2g, 7.34 mmol). It was dissolved in 12 mL of CH₂Cl₂. After cooling the reaction mixture to 0°C, a solution of DMDO in acetone was added (approximately 520 mL). The reaction mixture was allowed to warm to room temperature without removing the ice bath and the contents were stirred for 6 h at room temperature. The reaction mixture was concentrated to 20 mL at room temperature at which point it turned turbid. It was diluted with 100 mL of CH₂Cl₂ and washed with brine (2 x 50 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated at room temperature. Care was taken not to overheat the sample or connect to a high vacuum owing to high volatility of the title compound. The crude mixture was taken to the next step without purification.

R_f = 0.70 (hexanes-ether 1:1) UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm) δ 4.82 (d, J = 3.64 Hz, 1H), 3.78 (qd, J = 9.11, 6.35, 6.28, 6.28 Hz, 1H), 3.52 (t, J = 7.86, 7.86 Hz, 1H), 3.36 (s, 3H), 3.05 (dd, J = 5.61, 1.16 Hz, 1H), 2.60 (d, J = 5.62 Hz, 1H), 2.37-2.21 (m, 1H), 1.68-1.53 (m, 1H), 1.43-1.25 (d, 3H), 0.95-0.89 (s, 9H), 0.12 (s, 6H)
\(^{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) \(\delta 98.46, 72.84, 69.15, 57.51, 54.51, 49.36, 37.94, 25.80, 18.49, 18.18, -4.57, -5.02\)

IR (film) \(2931, 2897, 2857, 1252, 1114, 1052\) cm\(^{-1}\)

\([\alpha]_D^{25}\) \((-) 99.59 \text{ (C= 4.4, C}_6\text{H}_6\)
Synthesis of compound 218.

A 50 mL three neck round bottom flask with immersion thermometer was charged with the crude mixture (approximately 2.3 g, 7.97 mmol, 1 eq) obtained from the previous experiment. It was dissolved in 15 mL of dry ether and cooled to 0°C (internal). Lithium aluminum hydride (0.757 g, 19.9 mmol, 2.5 eq) was added in one portion and the reaction mixture was allowed to warm to 20°C (internal) without removing ice bath. It took an hr to reach 20°C after which the reaction was proven to be complete by TLC. The reaction mixture was cooled to 0°C (internal) and quenched carefully with 0.8 mL of deionized water, 0.8 mL of 4N NaOH and 1.6 mL of deionized water (the aqueous solutions were added dropwise). During this process the grey suspension turned into a white suspension. The ice bath was removed and the white suspension was stirred for an hr at room temperature. The reaction mixture was diluted with 50 mL of ether and the contents were filtered. The white precipitate was washed with copious amount of ether. The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes–ether, 5:1) to yield 1.72 g (81% for 2 steps) of the title compound 218 as a clear oil.

\[ R_f = 0.41 \] (hexanes-ether 1:1) UV, CAM, KMnO₄ active

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, \text{ ppm)} \]

\[ \delta 4.69 \text{ (d, } J = 3.90 \text{ Hz, 1H), 3.58 (qd, } J = 9.36, 6.27, 6.25, 6.25 \text{ Hz, 1H), 3.40-3.19 (m, 4H), 1.96 (dd, } J = 13.66, 1.17 \text{ Hz, 1H), 1.84 (dd, } J = 13.95, 4.25 \text{ Hz, 1H), 1.66 (s, 1H),} \]
1.37 (s, 3H), 1.27-1.19 (d, 3H), 0.99-0.87 (s, 9H), 0.12 (d, 6H)

\[ \text{\(^{13}\text{C NMR (101 MHz, CDCl}_3, \text{ppm)}\)} \]
\[ \delta \ 98.15, \ 80.54, \ 71.76, \ 67.10, \ 54.52, \ 42.90, \ 25.95, \ 22.82, \ 18.71, \ 18.26, \ -3.77, \ -4.59 \]

\[ \text{IR (film)} \]
3488, 2953, 2931, 2896, 2857, 1461, 1383, 1362, 1326, 1251, 1199, 1133, 1110, 1074, 1054, 1006 cm\(^{-1}\)

\[ \text{[\(\alpha\)]\text{D}^{25}} \]
(-) 101.67 (C = 6.17, C\(_6\)H\(_6\))
Synthesis of compound 125.

A 50 mL round bottom flask was charged with the alcohol 218 (1.6 g, 5.5 mmol, 1 eq). It was dissolved in 4 mL of THF and cooled to 0°C (external). A 1M solution of TBAF in THF (16.5 mL, 16.5 mmol, 3 eq) was added to the reaction mixture. The ice bath was removed and the contents were warmed to room temperature and stirred for 2 h. Owing to the high solubility of the product in water a non aqueous work up was employed. The reaction mixture was concentrated and the crude mixture was purified by column chromatography (hexanes-ethyl acetate, 2:1) to yield 1g of the title compound 125 as a colorless oil in quantitative yield.

\[ R_f = 0.03 \text{(hexanes-ether 1:1)} \]

UV, CAM, KMnO\(_4\) active

\( ^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \( \delta 4.74 \text{ (d, } J = 4.16 \text{ Hz, } 1\text{H}), 3.64 \text{ (qd, } J = 9.62, 6.20, 6.20, 6.19 \text{ Hz, } 1\text{H}), 3.34 \text{ (s, } 3\text{H}), 3.29 \text{ (d, } J = 9.53 \text{ Hz, } 1\text{H}), 2.99 \text{ (s, } 1\text{H}), 2.71 \text{ (s, } 1\text{H}), 2.01 \text{ (d, } J = 11.93 \text{ Hz, } 1\text{H}), 1.95-1.81 \text{ (m, } 1\text{H}), 1.42 \text{ (s, } 3\text{H}), 1.33 \text{ (d, } J = 6.20 \text{ Hz, } 3\text{H}) \)

\( ^{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) \( \delta \) 98.25, 79.53, 71.78, 66.51, 54.72, 43.08, 22.03, 18.05

IR (film) \ 3419, 2974, 2933, 2901, 1452, 1382, 1199, 1129, 1054 cm\(^{-1}\)
$[\alpha]_D^{25}$

(-) 124.41 (C = 6.1, C₆H₆)
Synthesis of compound 225.

A 25 mL round bottom flask was charged with alcohol 221 (5 g, 22.9 mmol, 1 eq). It was dissolved in 25 mL of CH₂Cl₂. The reaction mixture was cooled to 0°C (external). Et₃N (9.57 mL, 68.7 mmol, 3 eq, d = 0.726 g/cc) was added followed by dropwise addition of TBSOTf (5.78 mL, 25.2 mmol, 1.1 eq, d = 1.151 g/cc). After stirring for 2 h, the reaction mixture was quenched with 10 mL of saturated NaHCO₃. After separating the phases the organic layer was washed with 0.1N HCl (3 x 10 mL), saturated NaHCO₃ (1 x 25 mL) and brine (1 x 25 mL). It was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 40:1) to afford 6.78 g of the title compound 225 as a colorless oil.

Rᵣ = 0.63 (hexanes-ether 2:1) CAM active

¹H NMR (400 MHz, CDCl₃, ppm) δ 4.88 (s, 1H), 4.14 (d, J = 5.71 Hz, 1H), 4.09-3.95 (m, 1H), 3.61 (qd, J = 9.74, 6.23, 6.23, 6.19 Hz, 1H), 3.43 (s, 3H), 3.37 (dd, J = 9.67, 7.10 Hz, 1H), 1.55 (s, 3H), 1.38 (s, 3H), 1.28 (d, J = 6.29 Hz, 3H), 0.98-0.90 (s, 9H), 0.19 (s, 3H), 0.12 (s, 3H)
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) \[ \delta 108.86, 98.08, 79.08, 76.02, 75.85, 65.74, 54.65, 28.06, 26.35, 25.83, 18.03, 17.70, -4.02, -4.95 \]

IR (film) \[ 2987, 2953, 2933, 2857, 1383, 1247, 1219, 1169, 1121, 1093, 1063 \text{ cm}^{-1} \]

$[\alpha]_D^{25}$ \[ (+) 0.766 (C = 4.6, C_6H_6) \]
**Synthesis of compound 225b.**

A 10 mL round bottom flask was charged with alcohol 221 (0.2 g, 0.916 mmol, 1 eq). It was dissolved in 1 mL of CH$_2$Cl$_2$. The reaction mixture was cooled to 0°C (external). 2,6-lutidine (0.32 mL, 2.75 mmol, 3 eq, d = 0.926 g/cc) was added followed by dropwise addition of TIPSOTf (0.25mL, 0.916 mmol, 1 eq, d = 1.140 g/cc). After stirring for 2 h the reaction mixture was quenched with 3 mL of saturated NaHCO$_3$. It was diluted with 15 mL of CH$_2$Cl$_2$. After separating the phases the organic layer was washed with 0.1N HCl (1 x 5 mL), saturated NaHCO$_3$ (2 x 5 mL), and brine (1 x 10 mL). It was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 15:1) to afford 0.313 g (91%) of the title compound as a colorless oil.

R$_f$ = 0.67 (hexanes-ether 2:1)  
CAM active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
$\delta$ 4.86 (s, 1H), 4.15 (d, $J = 5.96$ Hz, 1H), 4.06 (t, $J = 6.14$, 6.14 Hz, 1H), 3.67-3.52 (m, 2H), 3.42 (s, 3H), 1.52 (s, 3H), 1.39-1.33 (m, 6H), 1.27-1.16 (m, 3H), 1.12 (dd, $J = 7.07$, 2.12 Hz, 18H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
$\delta$ 108.79, 98.18, 79.18, 76.33, 75.96, 66.03, 54.66, 27.86, 26.17, 18.07, 17.86, 12.64
<table>
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<th>Property</th>
<th>Values</th>
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<td>IR (film)</td>
<td>2940, 1463, 1382, 1245, 1218, 1124, 1094, 1063, 1022 cm$^{-1}$</td>
</tr>
<tr>
<td>$[^{25}\alpha]$</td>
<td>(+) 24.44 (C = 3.85, C$_6$H$_6$)</td>
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Synthesis of compound 235.

A 50 mL round bottom flask was charged with alcohol 221 (1.7 g, 7.789 mmol, 1 eq). It was dissolved in 8 mL of CH$_2$Cl$_2$. Catalytic amount of DMAP (0.095 g, 0.779 mmol, 0.1 eq) and imidazole (1.6 g, 23.5 mmol, 3 eq) were added. It took 10 min for the solid to go into solution. Neat TBDPSCI (2.66 mL, 10.2 mmol, 1.3 eq, d = 1.052 g/cc) was added to the reaction mixture. After 10 min the clear solution turned into a white suspension. After stirring for 48 h the reaction mixture was quenched with 10 mL of saturated NaHCO$_3$. After separating the phases the organic layer was washed with brine (1 x 10 mL), dried over Na$_2$SO$_4$ filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 10:1) to afford 2.8 g (80%) of the title compound 235 as a colorless oil.

R$_f$ = 0.57 (hexanes-ether 2:1)  

UV, CAM active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  

$\delta$ 7.76 (ddd, $J = 27.26, 7.95, 1.51$ Hz, 4H), 7.57-7.38 (m, 6H), 4.81 (s, 1H), 4.41-4.16 (m, 1H), 4.13 (d, $J = 5.77$ Hz, 1H), 3.74 (qd, $J = 9.58, 6.26, 6.26, 6.24$ Hz, 1H), 3.58-3.28 (m, 4H), 1.29 (s, 3H), 1.13 (m, 15H)

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  

$\delta$ 136.54, 136.02, 134.25, 132.82, 129.62, 129.36, 127.34, 127.29, 108.84, 98.01,
78.82, 76.61, 75.83, 65.84, 54.76, 27.38, 27.05, 26.28, 19.70, 18.04

IR (film) 2933, 2907, 2857, 1471, 1427, 1383, 1244, 1219, 1169, 1142, 1093, 1024 cm\(^{-1}\)

\([\alpha]_D^{25}\) (+) 18.87 (C = 6.20, C\(_6\)H\(_6\))
**General procedure:**

A 100 mL flask was charged with anhydrous ZnI₂ (52 g, 16.2 mmol, 2 eq). Addition of DCE (162 mL) led to the formation of white suspension. TBAI (26.11 g, 81 mmol, 1 eq) was added to this white suspension. After 5 min, a solution of silyl protected monoacetonide in DCE (81 mmol, 1 eq in 15 mL) was added dropwise to the reaction mixture. The white suspension turned to a yellow suspension. After 5 min, neat PhSTMS (24.3 mmol, 3 eq) was added dropwise. The yellow suspension turned back to a white suspension. The reaction mixture was stirred for 16 h at which point TLC revealed complete consumption of starting material. The reaction mixture was quenched with 20 mL of saturated NaHCO₃. The biphasic solution was then passed through celite to filter of zinc salts. After separating the phases, the aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layer was washed with brine (1 x 100 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude mixture was purified on a column chromatography (100% hexanes to elute PhSH, then switched to 40:1 hexanes-ether) to yield thioglycoside in 70% yield.
**Synthesis of compound 229a.**

\[ \text{R}_f = 0.70 \text{ (hexanes-ether 2:1)} \]  
UV, CAM, KMnO\textsubscript{4} active

\[^{1}\text{H} \text{NMR (400 MHz, C}_{6}\text{D}_{6}, \text{ppm)} \]
\[ \delta 7.60-7.55 \text{ (m, 2H), 7.38-7.27 \text{ (m, 3H), 5.09 (d, } J = 2.14 \text{ Hz, 1H), 4.45 \text{ (dd, } J = 5.63, 2.14 \text{ Hz, 1H), 4.12-3.94 \text{ (m, 1H), 3.55 \text{ (dd, } J = 8.81, 6.70 \text{ Hz, 1H), 3.34 \text{ (qd, } J = 8.80, 6.23, 6.22, 6.22 \text{ Hz, 1H), 1.64 \text{ (s, 3H), 1.49-1.41 \text{ (s, 3H), 1.41-1.32 \text{ (d, 3H), 1.03-0.89 \text{ (s, 9H), 0.21 \text{ (s, 3H), 0.16 \text{ (s, 3H)}}}} \]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3, \text{ppm))} \]
\[ \delta 135.44, 130.49, 128.86, 127.10, 110.19, 83.91, 80.52, 77.37, 77.05, 76.73, 76.38, 75.98, 75.30, 27.99, 26.45, 25.84, 18.38, 18.02, -4.05, -4.90 \]

IR (film)  
2954, 2931, 2856, 1473, 1379, 1245, 1216, 1110, 1063 cm\textsuperscript{-1}

\[^{[\alpha]}_D^{25}\]  
(-) 117.16 (C = 5.0, C\textsubscript{6}H\textsubscript{6})
Synthesis of compound 229b.

\[ \text{R}_f = 0.68 \text{ (hexanes-ether 2:1)} \quad \text{UV, CAM , KMnO}_4 \text{ active} \]

\[ ^1\text{H NMR (400 MHz, C}_6\text{D}_6, \text{ppm}) \quad \delta \text{ 7.56-7.41 (m, 2H), 7.36-7.15 (m, 3H), 5.11 (dd, } J = 19.95, 2.10 \text{ Hz, 1H), 4.44 (dd, } J = 6.26, 2.08 \text{ Hz, 1H), 4.17 (t, } J = 5.86, 5.86 \text{ Hz, 1H), 3.88-3.69 (m, 1H), 3.55 (p, } J = 6.40, 6.40, 6.39, 6.39 \text{ Hz, 1H), 1.58 (s, 3H), 1.44-1.36 (m, 6H), 1.11 (m, 21H)} \]

\[ ^1\text{C NMR (100 MHz, CDCl}_3, \text{ppm}) \quad \delta \text{ 135.76, 129.94, 128.82, 126.79, 110.48, 83.78, 79.51, 77.48, 75.99, 73.81, 27.31, 26.03, 19.31, 18.07, 12.40} \]

\[ \text{IR (film)} \quad 2941, 2866, 1584, 1462, 1380, 1242, 1216, 1157, 1113, 1063, 1016 \text{ cm}^{-1} \]
Synthesis of compound 236.

\[ R_f = 0.56 \text{ (hexanes-ether 2:1)} \]

\[ \text{UV, CAM, KMnO}_4 \text{ active} \]

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm)

\[ \delta 7.92 \text{ (td, } J = 6.75, 3.12, 3.12 \text{ Hz, } 2H), \]
\[ 7.88-7.82 \text{ (m, } 2H), 7.75-7.68 \text{ (m, } 2H), 7.39- \]
\[ 7.29 \text{ (m, } 6H), 7.23-7.16 \text{ (m, } 2H), 7.15-7.07 \]
\[ (m, 1H), 5.08 \text{ (d, } J = 2.10 \text{ Hz, } 1H), 4.39 \text{ (dd, } \]
\[ J = 5.93, 2.12 \text{ Hz, } 1H), 4.20 \text{ (t, } J = 6.00, \]
\[ 6.00 \text{ Hz, } 1H), 3.83 \text{ (dd, } J = 7.69, 6.11 \text{ Hz, } \]
\[ 1H), 3.44-3.25 \text{ (m, } 1H), 1.36 \text{ (s, } 3H), 1.33 \]
\[ (m, J = 2.06 \text{ Hz, } 9H, 3H), 1.27 \text{ (d, } J = 6.28 \]
\[ \text{Hz, } 3H) \]

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)

\[ \delta 136.90, 136.44, 136.04, 134.14, 132.84, \]
\[ 130.51, 129.92, 129.68, 128.80, 126.72, \]
\[ 110.15, 84.30, 80.00, 76.31, 76.27, 75.70, \]
\[ 27.23, 27.05, 26.16, 19.56, 19.08 \]

IR (film)

\[ 2931, 2856, 1474, 1379, 1241, 1217, 1156, \]
\[ 1064 \text{ cm}^{-1} \]

$[^{25}\alpha]_D$

\[ (+) 18.87 \text{ (C = 6.2, C}_6\text{H}_6) \]
Synthesis of compound 237.

A 50 mL round bottom flask was charged with thioester 236 (2 g, 3.73 mmol, 1 eq). It was dissolved in 20 mL of THF and the contents were cooled to 0°C. A solution of lithium napthalide in THF was added dropwise at 0°C. The reaction mixture turned from colorless to yellow to orange to dark brown. When the color of the solution remained dark green, addition of lithium napthalide was stopped. The reaction mixture was quenched with 10 mL of deionized water and the contents were allowed to warm to room temperature. After separating the phases the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine (1 x 25 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 10:1) to yield 0.7 g (51%) of the title compound 237 as a colorless oil.

Rₛ = 0.30 (hexanes-ether 2:1) UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.82 (dd, J = 7.72, 1.55 Hz, 2H), 7.79-7.73 (m, 2H), 7.52-7.41 (m, 6H), 6.27 (dd, J = 6.00, 1.31 Hz, 1H), 4.60 (dd, J = 6.02, 2.49 Hz, 1H), 4.32 (t, J = 5.73, 5.73 Hz, 1H), 3.99 (qd, J = 8.83, 6.40, 6.40, 6.40 Hz, 1H), 3.58 (dd, J = 9.00, 6.51 Hz, 1H), 1.52 (d, J = 5.41 Hz, 1H), 1.37 (d, J = 7.80 Hz, 3H), 1.13 (s, 9H)
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 144.45, 136.21, 135.61, 134.90, 134.47, 132.70, 130.14, 130.08, 128.08, 127.98, 102.57, 76.85, 74.92, 70.12, 27.24, 26.68, 19.66, 17.85

IR (film) 3557, 3069, 2932, 2893, 2857, 1649, 1471, 1427, 1389, 1231, 1111, 1046 cm$^{-1}$

$[\alpha]_D^{25}$ (-) 4.61 (C = 4.125, C$_6$H$_6$)
**Synthesis of compound 238.**

A 25 mL two neck round bottom flask with immersion thermometer was charged with allylic alcohol 237 (0.565 g, 2.257 mmol, 1 eq). It was dissolved in 3 mL of ether. The contents were cooled to 0°C (internal). Neat MeI (0.7 mL, 11.3 mmol, 5 eq, d = 2.275 g/cc) was added. After 10 min, KOtBu (0.758 g, 6.772 mmol, 3 eq) was added. The white suspension immediately turned into a yellow suspension and the internal temperature elevated to 8°C. The ice bath was removed and the reaction mixture was allowed to attain room temperature. After stirring at room temperature for an hr, the reaction mixture was quenched with 3 mL deionized water. The reaction mixture was diluted with 15 mL ether and the phases were separated. The aqueous layer was extracted with ether (2 x 5 mL) and the combined organic layers were washed with brine (1 x 15 mL), dried over MgSO4 filtered and concentrated at room temperature to obtain a pale yellow oil. Attempts to purify the crude mixture either on silica or alumina resulted in extensive decomposition. As a result the crude mixture was carried to the next step.

Rf = 0.65 (hexanes-ether 2:1) UV, CAM, KMnO4 active

$^1$H NMR (400 MHz, CDCl3, ppm) δ 7.79 (dt, $J = 7.61$, 7.46, 1.55 Hz, 4H), 7.52-7.41 (m, 6H), 6.23 (dd, $J = 6.17$, 0.97 Hz, 1H), 4.52 (dd, $J = 6.20$, 3.23 Hz, 1H), 4.39-4.33 (m, 1H), 4.03 (dq, 1H), 3.45 (s, 3H), 3.27 (dd, $J = 6.89$, 5.21 Hz, 1H), 1.50 (d, $J = 6.63$ Hz, 3H), 1.15 (s, 9H)
\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta \) 143.05, 135.89, 134.22, 133.64, 129.67, 129.63, 127.61, 127.51, 102.62, 83.47, 73.19, 67.89, 59.44, 26.93, 19.20, 17.00

IR (film) 3069, 2932, 2891, 2857, 1646, 1470, 1427, 1388, 1247, 1196, 1170, 1110 cm\(^{-1}\)

\([\alpha]_D^{25}\) (-) 24.32 (C = 4.1, C\(_6\)H\(_6\))
**Synthesis of compound 240.**

A 100 mL round bottom flask was charged with a solution of olefin 238 in DCE (0.517 g, 1.35 mmol, 1 eq in 10 mL). The reaction mixture was cooled to -5°C. A solution of DMDO in acetone was added (21 mL). After an hr TLC revealed complete consumption of starting material. Freshly distilled cyclohexene (0.14 mL, 1.35 mmol, 1 eq, d = 0.811 g/cc) was added and the contents were stirred for 45 min. Triethylamine (0.14 mL, 2.70 mmol, 2 eq, d = 0.726 g/cc) and thiophenol (0.5 mL, 4.89 mmol, 4 eq, d = 1.073 g/cc) were added sequentially and the reaction flask was transferred to an ice bath. After stirring at 0°C (external) for 2 h, the reaction mixture was concentrated to 10 mL at which point it turned turbid. The reaction mixture was diluted with 50 mL of CH₂Cl₂ and washed with brine (1 x 15 mL). It was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (100% hexane to remove thiophenol then to 25:1 hexanes-ether) to afford 0.370 g (55% for two steps) of the title compound 240 as a colorless oil.

**Rf** = 0.40 (hexanes-ether 2:1)  
UV, CAM, KMnO₄ active

**¹H NMR (400 MHz, CDCl₃, ppm)**  
δ 7.85 (dd, J = 8.48, 6.86 Hz, 2H), 7.83-7.74 (m, 2H), 7.56-7.40 (m, 9H), 7.38-7.31 (m, 3H), 4.40 (d, J = 9.76 Hz, 1H), 3.78 (t, J = 8.60, 8.60 Hz, 1H), 3.56-3.44 (m, 4H), 3.39-3.27 (m, 1H), 3.01 (dd, J = 12.01, 6.25 Hz,
$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 1.95 (d, $J = 6.00$, 6.00 Hz, 1H), 1.42 (d, 6.17 Hz, 3H), 1.15 (s, 9H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 136.15, 135.48, 134.69, 133.05, 132.65, 132.34, 129.61, 129.57, 128.79, 127.70, 127.61, 127.51, 87.36, 85.81, 79.12, 75.59, 73.33, 60.51, 26.99, 19.67, 18.55
Synthesis of compound 241.

A 10 mL round bottom flask was charged with alcohol 240 (0.9 g, 1.83 mmol, 1 eq). It was dissolved in 2 mL of CH₂Cl₂. Catalytic amount of DMAP (0.041 g, 0.366 mmol, 0.2 eq) and pyridine (0.44 mL, 5.49 mmol, 3 eq, d = 0.978 g/cc) were added sequentially. After 10 min neat acetic anhydride (0.2 mL, 2.2 mmol, 1.2 eq, d = 1.082 g/cc) was added dropwise. After stirring 3h at room temperature the reaction mixture was quenched with 3 mL of saturated NaHCO₃. After separating the phases the aqueous layer was extracted with CH₂Cl₂ (3 x 5 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was redissolved in 15 mL of heptane and concentrated in vacuo. This process was repeated twice to remove residual pyridine and acetic acid. The crude mixture was purified by column chromatography (hexanes-ether, 30:1) to afford 0.740 g (74%) of the title compound 241 as a white crystalline solid.

R<sub>f</sub> = 0.50 (hexanes-ether 2:1) UV, CAM, KMnO₄ active

<sup>1</sup>H NMR (400 MHz, CDCl₃, ppm) δ 7.83 (dd, J = 7.73, 1.69 Hz, 2H), 7.70 (dd, J = 7.83, 1.59 Hz, 2H), 7.50-7.40 (m, 8H), 7.30 (dq, J = 4.55, 4.19, 4.19, 2.71 Hz, 3H), 5.10-5.01 (m, 1H), 4.45 (d, J = 9.99 Hz, 1H), 3.88 (t, J = 8.94, 8.94 Hz, 1H), 3.36-3.25 (m, 4H), 3.08 (t, J = 9.12, 9.12 Hz, 1H), 1.57 (s, 3H), 1.41 (d, J = 6.19 Hz, 3H), 1.09 (s, 9H)
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) \[ \delta 169.95, 136.24, 135.87, 134.50, 133.76, \\
130.98, 129.64, 129.34, 128.72, 127.50, \\
127.37, 127.18, 86.55, 85.99, 76.09, 75.76, \\
72.98, 60.04, 26.76, 20.67, 19.59, 18.78 \]

IR (film) \[ 2934, 2893, 1751, 1475, 1223, 1167, 1136, \\
1108, 1064, 1039 \text{ cm}^{-1} \]

$[\alpha]_D^{25}$ \[ (-) 34.91 \text{ (C = 3.2, C}_6\text{H}_6) \]
Synthesis of compound 242.

A 50 mL round bottom flask containing freshly activated 4Å molecular sieves (5 g) was charged with a solution of azeotropically dried (twice) thioglycoside 241 (0.235 g, 0.43 mmol, 1.2 eq) and diol 125 (0.130 g, 0.740 mmol, 1.0 eq) in 23 mL of CH₂Cl₂. The reaction mixture was cooled to -5°C. NIS (0.036 g, 0.0159 mmol, 2.2 eq) was added in one portion followed by dropwise addition of AgOTf (0.013 g, 0.051 mmol, 0.1 eq). After an hr, the reaction mixture was quenched with saturated thiosulfate (3 mL) and NaHCO₃ (3 mL). The cooling bath was removed and the contents were allowed to warm to RT. The reaction mixture was diluted with 25 mL of CH₂Cl₂ and the phases were separated. The aqueous layer was extracted twice with ether (2 x 5mL) and the combined organic layers were washed with brine (1 x 25 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 5:1) to afford 0.09 g (34%) of the title compound 242 as a colorless oil.

13C NMR (100 MHz, CDCl₃, ppm) δ 169.62, 136.12, 135.85, 133.73, 132.83, 129.61, 129.34, 127.45, 127.35, 101.86, 98.04, 86.31, 85.77, 75.02, 74.77, 72.23, 71.18, 65.87, 59.75, 54.61, 43.06, 26.72, 22.78, 20.87, 19.57, 18.47, 18.28
Synthesis of compound 248.

A flame dried 10 mL round bottom flask was charged with a solution of disaccharide 242 in CH$_2$Cl$_2$ (84 mg, 0.136 mmol, 1 eq in 1 mL). The contents were cooled to 0°C. 2,6-Lutidine (50 µL, 0.408 mmol, 3 eq, d = 0.926 g/cc) was added followed by TBSOTf (31 µL, 0.136 mmol, 1 eq, d = 1.151 g/cc). The ice bath was removed and the reaction mixture was stirred at RT for 12 h. The reaction mixture was quenched with 1 mL of saturated NaHCO$_3$ and diluted with 5 mL of CH$_2$Cl$_2$. After separating the phases, organic layer was washed with brine (1 x 5 mL), dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (hexanes-ether, 10:1) to yield 64 mg (64%) of the title compound as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  δ 7.83 (dd, $J$ = 7.45, 1.69 Hz, 2H), 7.73-7.65 (m, 2H), 7.48-7.38 (m, 6H), 4.92 (dd, $J$ = 9.52, 8.21 Hz, 1H), 4.67 (dd, $J$ = 10.74, 6.02 Hz, 2H), 3.80 (t, $J$ = 9.21, 9.21 Hz, 1H), 3.51 (tt, $J$ = 8.31, 8.31, 4.18, 4.18 Hz, 1H), 3.36 (d, $J$ = 9.84 Hz, 1H), 3.32 (s, 3H), 3.29 (s, 3H), 3.17 (qd, $J$ = 9.49, 6.20, 6.15, 6.15 Hz, 1H), 3.03 (t, $J$ = 9.08, 9.08 Hz, 1H), 1.97 (d, $J$ = 13.45 Hz, 1H), 1.84 (dd, $J$ = 13.48, 4.28 Hz, 1H), 1.42 (s, 3H), 1.36 (d, $J$ = 6.11 Hz, 3H), 1.29-1.24 (m, 6H), 1.06 (s, 9H), 0.76 (s, 9H), 0.07 (s, 3H), -0.06 (s, 3H)
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) \( \delta \) 169.50, 136.22, 135.81, 133.94, 132.29, 129.60, 129.20, 127.54, 127.30, 100.11, 97.90, 86.71, 82.55, 75.65, 74.62, 74.49, 71.01, 65.45, 59.98, 54.47, 44.63, 26.70, 25.76, 22.95, 20.68, 19.62, 18.46, 18.30, 17.74, -1.74, -1.97
Synthesis of compound 250.

A 50 mL round bottom flask was charged with protected thioester 235 (4g, 7.49 mmol, 1 eq). It was dissolved in 4 mL of THF. The reaction mixture was cooled to 0°C (external). A 1M solution of TBAF in THF (22.4 mL) was added to the reaction mixture. The reaction mixture turned dark yellow. The ice bath was removed and the reaction was allowed to attain room temperature. After stirring at room temperature for 5 h the reaction mixture was quenched with 10 mL of saturated NaHCO₃. After separating the phases the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were washed with brine (1 x 25 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 2:1) to yield mixture of epimers in 94% yield.

\[ R_f = 0.09 \text{ (hexanes-ether 2:1)} \]

UV, CAM, KMnO₄ active – Major diastereomer

\[ ^1\text{H NMR (400 MHz, CDCl}_3, \text{ ppm)} \]
\[ \delta 7.62-7.53 \text{ (m, 2H), 7.41-7.27 (m, 3H), 5.08 (d, } J = 2.18 \text{ Hz, 1H), 4.47 (dd, } J = 5.49, \]
\[ 2.19 \text{ Hz, 1H), 4.06 (dd, } J = 7.13, 5.59 \text{ Hz, 1H), 3.61-3.51 (m, 1H), 3.34 (qd, } J = 9.60, \]
\[ 6.15, 6.15, 6.15 \text{ Hz, 1H), 2.78 (d, } J = 3.76 \text{ Hz, 1H), 1.63 (s, 3H), 1.46 (s, 3H), 1.42 (d, } J = 6.16 \text{ Hz, 3H)} \]
$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
\[ \delta \ 135.02, 130.86, 128.91, 127.36, 110.66, 83.82, 80.26, 76.34, 74.80, 74.60, 28.12, 26.33, 17.72 \]

IR (film)  
3471, 2895, 1439, 1382, 1267, 1247, 1157, 1129 cm$^{-1}$

$[\alpha]_D^{25}$  
(-) 182.93 (C = 1.33, C$_6$H$_6$)

$R_f = 0.40$ (hexanes-ether 2:1)  
UV, CAM, KMnO$_4$ active – Minor diastereomer

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
\[ \delta \ 7.60-7.48 \text{ (m, 2H)}, 7.42-7.27 \text{ (m, 3H)}, 5.82 \text{ (s, 1H)}, 4.40 \text{ (d, } J = 5.57 \text{ Hz, 1H)}, 4.26-4.05 \text{ (m, 2H)}, 3.57-3.44 \text{ (m, 2H)}, 1.59 \text{ (s, 3H)}, 1.48-1.40 \text{ (s, 3H), 1.30 (dd, } J = 6.16, 3H) \]

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
\[ \delta \ 133.41, 131.83, 128.94, 127.54, 109.66, 83.66, 78.50, 76.56, 74.95, 67.01, 28.11, 26.35, 17.15 \]

IR (film)  
3457, 2985, 1478, 1440, 1380, 1242, 1219, 1161, 1120, 1064, 1012 cm$^{-1}$

$[\alpha]_D^{25}$  
(+ ) 276.50 (C = 1.40, C$_6$D$_6$)
Synthesis of compound 251.

A 50 mL two neck round bottom flask with immersion thermometer was charged with 95% NaH (0.324 g, 13.48 mmol, 2 eq). 8 mL of THF was added and the white suspension was vigorously stirred. The reaction mixture was cooled to 0°C (internal). A solution of alcohol 250 (2 g, 6.74 mmol, 1 eq in 2 mL of THF) was added dropwise to the white suspension. During this period, there was constant evolution of H₂. The white suspension turned yellow after addition was complete. Neat PMBBr (1.3 mL, 8.09 mmol, 1.2 eq, d = 1.379 g/cc) was added. The reaction mixture was allowed to attain room temperature without removing ice bath. After stirring for 6 h at room temperature, the reaction was cooled back to 0°C and quenched with 3 mL of deionized water. The reaction mixture was diluted with 40 mL of ether and the phases were separated. The aqueous phase was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine (1 x 50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 15:1 to 10:1) to afford 2.02 g (72%) of the title compound 251 as a mixture of diasteromers.

Rᵢ = 0.42 (hexanes-ether 1:1)  UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm)  δ 7.57 (dd, J = 16.85, 9.98 Hz, 2H), 7.44-7.25 (m, 5H), 7.08-6.86 (m, 2H), 5.06 (dd, J = 6.01, 2.12 Hz, 1H), 4.85 (dd, J = 15.73, 9.16 Hz, 1H), 4.77-4.58 (m, 1H), 4.55-4.43
(m, 1H), 4.34-4.24 (m, 1H), 3.87 (s, 3H), 3.51-3.34 (m, 2H), 1.65 (s, 3H), 1.48 (s, 3H), 1.40 (d, J = 6.16, 3H)

\(^\text{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) \(\delta\) 159.30, 135.24, 130.78, 130.19, 129.68, 128.88, 127.25, 113.71, 110.39, 84.00, 80.15, 80.05, 76.33, 74.56, 72.62, 55.25, 27.93, 26.38, 18.50

IR (film) 2932, 1611, 1515, 1440, 1378, 1246, 1062, 1033 cm\(^{-1}\)

\([\alpha]_D^{25}\) (-) 103.93 (C = 2.467, C\(_6\)H\(_6\))
Synthesis of compound 252.

A 50 mL 2 neck round bottom flask with immersion thermometer was charged with thioester 251 (3.3 g, 7.92 mmol, 1 eq). It was dissolved in 13 mL of THF and the contents were cooled to -75°C (internal). A solution of lithium napthalide in THF was added dropwise at -75°C. During the course of addition the internal temperature was strictly kept below -70°C. The reaction mixture turned from colorless to yellow to orange to dark brown. When the color of the solution remained dark green, addition of lithium napthalide was stopped. The reaction mixture was quenched with 5 mL of methanol followed by 10 mL of deionized water and the contents were allowed to warm to room temperature. After separating the phases the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 6:1 to 4:1) to yield 1.922 g (97%) of the title compound 252 as a white waxy solid.

R_f = 0.18 (hexanes-ether 1:1) UV, CAM, KMnO₄ active

^1H NMR (400 MHz, CDCl₃, ppm) δ 7.47-7.26 (m, 2H), 7.07-6.84 (m, 2H), 6.36 (dd, J = 5.97, 1.51 Hz, 1H), 4.79 (d, J = 1.70 Hz, 2H), 4.74 (dd, J = 6.00, 2.34 Hz, 1H), 4.37 (m, 1H), 3.93 (qd, J = 9.65, 6.38, 6.38, 6.37 Hz, 1H), 3.85 (s, 3H), 3.31 (dd, J
\[ \begin{align*} \text{1H NMR} &= 9.65, 6.99 \text{ Hz, 1H), 1.91 \ (d, J = 5.86 \text{ Hz,} \\ &1 \text{H), 1.45 \ (d, J = 6.41 \text{ Hz, 3H)}} \\

^{13}\text{C NMR (101 MHz, CDCl}_3, \text{ ppm)} &= \delta 159.31, 144.51, 130.28, 129.65, 113.94, \\ &103.13, 81.98, 74.09, 73.92, 69.92, 55.26, \\ &17.62 \\

\text{IR (film)} &= 3192, 2903, 1648, 1513, 1278, 1247, 1113, \\ &1096 \text{ cm}^{-1} \\

[\alpha]_D^{25} &= (+) 16.30 \ (C = 0.54, \text{C}_6\text{H}_6) 
\end{align*} \]
Synthesis of compound 253.

A 25 mL two neck round bottom flask with immersion thermometer was charged with allylic alcohol 253 (0.565 g, 2.257 mmol, 1 eq). It was dissolved in 3 mL of ether. The contents were cooled to 0°C (internal). Neat MeI (0.7 mL, 11.3 mmol, 5 eq, d = 2.275 g/cc) was added. After 10 min, KOtBu (0.758 g, 6.772 mmol, 3 eq) was added. The white suspension immediately turned into a yellow suspension and the internal temperature elevated to 8°C. The ice bath was removed and the reaction mixture was allowed to attain room temperature. After stirring at room temperature for an hr, the reaction mixture was quenched with 3 mL deionized water. The reaction mixture was diluted with 15 mL ether and the phases were separated. The aqueous layer was extracted with ether (2 x 5 mL) and the combined organic layers were washed with brine (1 x 15 mL), dried over MgSO₄ filtered and concentrated at room temperature to obtain a pale yellow oil. Attempts to purify the crude mixture either on silica or alumina resulted in extensive decomposition. As a result the crude mixture was carried to the next step.

Rₛₜ = 0.60 (hexanes-ether 1:1) UV, CAM, KMnO₄ active
Synthesis of compound 255.

A 250 mL round bottom flask with immersion thermometer was charged with 45 mL of DMDO in acetone. The solution was cooled to -45°C (internal). A solution of olefin 253 in DCE (0.43 g, 1.63 mmol, 1eq in 6 mL) was added dropwise (flow rate: 14 mL/h). After an hr TLC revealed complete consumption of starting material. Freshly distilled cyclohexene (0.44 mL, 6.61 mmol, 4 eq, d = 0.811 g/cc) was added and the contents were stirred for 45 min. Triethylamine (0.45 mL, 3.26 mmol, 2 eq, d = 0.726 g/cc) and thiophenol (0.5 mL, 4.89 mmol, 3 eq, d = 1.073 g/cc) were added sequentially and the reaction flask was transferred to an ice bath. After stirring at 0°C (external) for 2 h, the reaction mixture was concentrated to 10 mL at which point it turned turbid. The reaction mixture was diluted with 50 mL of CH₂Cl₂ and washed with brine (1 x 15 mL). It was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (100% hexane to remove thiophenol then to 8:1 hexanes-ether) to afford 0.380 g (63% for two steps) of the title compound 255 as a colorless oil.

Rᵣ = 0.17 (hexanes-ether 1:1)  UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm)  δ  7.56-7.48 (m, 2H), 7.35-7.24 (m, 5H), 6.92-6.84 (m, 2H), 4.77 (d, J = 10.51 Hz, 1H), 4.56 (d, J = 10.51 Hz, 1H), 4.47 (d, J = 9.72 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.47-3.33 (m, 2H), 3.26 (t, J = 8.82, 8.82 Hz, 1H), 3.06 (t, J = 9.15, 9.15 Hz, 1H),
2.54 (d, $J = 2.18$ Hz, 1H), 1.31 d, $J = 9.21$Hz, 3H)

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
$\delta$ 159.20, 132.77, 132.00, 130.11, 129.79, 129.00, 128.09, 113.88, 88.12, 87.63, 82.50, 75.87, 74.87, 72.89, 61.18, 55.31 18.20

IR (film)  
3435, 2933, 2901, 2835, 1612, 1513, 1249, 1075, 1033 cm$^{-1}$

$[\alpha]_D^{25}$  
(-) 40.88 (C = 3.075, C$_6$H$_6$)
Synthesis of compound 256.

A 10 mL round bottom flask was charged with alcohol 255 (0.3 g, 0.768 mmol, 1 eq). It was dissolved in 1 mL of CH\(_2\)Cl\(_2\). Catalytic amount of DMAP (0.017 g, 0.154 mmol, 0.2 eq) and pyridine (0.19 mL, 2.304 mmol, 3 eq, d = 0.978 g/cc) were added sequentially. After 10 min neat acetic anhydride (0.087 mL, 0.922 mmol, 1.2 eq, d = 1.082 g/cc) was added dropwise. After stirring 3h at room temperature the reaction mixture was quenched with 3 mL of saturated NaHCO\(_3\). After separating the phases the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3 x 5 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated \textit{in vacuo}. The crude mixture was redissolved in 15 mL of heptane and concentrated \textit{in vacuo}. This process was repeated twice to remove residual pyridine and acetic acid. The crude mixture was purified by column chromatography (hexanes-ether, 3:1) to afford 0.305 g (92%) of the title compound 256 as a white crystalline solid.

\( \text{R}_f = 0.30 \text{ (hexanes-ether 1:1)} \)

\( ^1\text{H NMR (400 MHz, CDCl}_3\text{, ppm)} \)

\( \delta 7.67-7.45 \text{ (m, 2H), 7.46-7.20 \text{ (m, 5H), 6.94 \text{ (d, J = 8.48 Hz, 2H), 4.98 \text{ (t, J = 9.61, 9.61 Hz, 1H), 4.83 \text{ (d, J = 10.55 Hz, 1H), 4.64 \text{ (t, J = 9.67, 9.67 Hz, 2H), 3.94-3.77 \text{ (s, 3H), 3.58 \text{ (s, 3H), 3.55-3.35 \text{ (m, 2H), 3.22 \text{ (t, J = 9.18, 9.18 Hz, 1H), 2.18 \text{ (s, 3H), 1.34 \text{ (d, 10.87 Hz, 3H)}}) \) \) \) \) \) \)
$^{13}$C NMR (101 MHz, CDCl$_3$, ppm) \quad \delta \ 169.50, 159.39, 133.25, 132.01, 130.13, \\
129.79, 128.81, 127.63, 113.84, 86.22, \\
85.87, 82.24, 75.70, 74.84, 72.25, 60.63, \\
55.25, 21.06, 18.04

IR (film) \quad \text{2937, 2898, 2842, 1738, 1614, 1516, 1376,} \\
1127, 1071, 1045 \text{ cm}^{-1}

$[\alpha]_D^{25}$ \quad (-) 21.20 (C = 2.90, C$_6$H$_6$)
**Synthesis of compound 257.**

A 25 mL round bottom flask was charged with a solution of thioglycoside 255 in CH$_2$Cl$_2$ (1.7 g, 4.35 mmol, 1 eq in 10 mL). DMAP was added (1.6 g, 13.05 mmol, 3 eq). After stirring for the reaction mixture for 15 min, neat pivalic anhydride was added dropwise (1.7 mL, 8.7 mmol, 2 eq). After stirring at RT for 2 h, the reaction mixture was quenched with saturated NaHCO$_3$ (3 mL). After separating the phases, the organic layer was washed with brine (1 x 10 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. To remove pivalic acid and pyridine, the crude mixture was diluted with heptane and distilled. This process was repeated until no odor of pivalic acid was detected. The crude mixture was purified by column chromatography (hexanes-ether, 5:1) to afford 1.7 g (82%) of the title compound 257 as a colorless oil.

$R_f = 0.46$ (hexanes-ether 1:1)  

UV, CAM, KMnO$_4$ active

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.45 (dd, $J = 7.56$, 1.72 Hz, 2H), 7.36-7.20 (m, 5H), 6.88 (d, $J = 8.55$ Hz, 2H), 4.93 (t, $J = 9.63$, 9.63 Hz, 1H), 4.77 (d, $J = 10.57$ Hz, 1H), 4.58 (dd, $J = 10.33$, 7.44 Hz, 2H), 3.82 (s, 3H), 3.58 (s, 3H), 3.45-3.29 (m, 2H), 3.18 (t, $J = 9.17$, 9.17 Hz, 1H), 1.29 (m, 12H)

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm) $\delta$ 176.81, 159.42, 133.77, 131.95, 129.89, 128.89, 127.68, 113.89, 86.56, 86.31, 82.47,
IR (film)  
2973, 1738, 1612, 1513, 1278, 1249, 1171, 1150, 1071 cm$^{-1}$

$[\alpha]_{D}^{25}$  
(-) 27.46 (C = 4.6, C$_6$H$_6$)
Synthesis of compound 260.

A 100 mL round bottom flask was charged with a solution of thioglycoside 257 in CH₂Cl₂ (1 g, 2.1 mmol, 1 eq in 40 mL). Deionized water (2 mL) was added to the reaction mixture. This was followed by addition of DDQ (480 mg, 2.1 mmol, 1 eq). The reaction mixture slowly turned to a dark greenish black solution. The reaction was stirred at RT for 3 h at which point the reaction turned to a brownish red solution. The reaction mixture was quenched with saturated NaHCO₃ (1 x 10 mL). After separating the phases, the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layer was washed with brine (1 x 50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 4:1) to afford 0.597 g (80%) of the title compound 260 as a white waxy solid.

Rₛₜ = 0.10 (hexanes-ether 1:1)  
UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm)  
7.50 (td, J = 4.63, 2.54, 2.54 Hz, 2H), 7.37-7.29 (m, 3H), 4.99 (dd, J = 9.97, 8.96 Hz, 1H), 4.68 (d, J = 10.08 Hz, 1H), 3.55 (s, 3H), 3.51-3.42 (m, 1H), 3.39-3.29 (m, 2H), 2.69 (d, J = 2.64 Hz, 1H), 1.42 (d, J = 6.04 Hz, 3H), 1.32 (s, 9H)
$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  \[ \delta 176.72, 133.63, 131.91, 128.82, 127.66, \\
86.66, 85.63, 75.76, 74.62, 71.40, 60.11, \\
38.73, 27.14, 17.88 \]

IR (film)  \[ 3466, 2974, 1736, 1583, 1478, 1396, 1278, \\
1158 \text{ cm}^{-1} \]

$\left[ \alpha \right]_D^{25}$  \[ (-) 38.25 \text{ (C = 3.13, C$_6$H$_6$)} \]
Synthesis of compound 261.

A 25 mL round bottom flask fitted with condenser was charged with a solution of thioglycoside 260 in DMF (0.5 g, 1.41 mmol, 1 eq, in 10 mL). DMAP (34 mg, 0.282 mmol, 0.2 eq) and imidazole (190 mg, 2.82 mmol, 2 eq) were added to the reaction mixture. TBSOTf (0.4 g 1.55 mmol, 1.1 eq) was added dropwise and the contents were warmed to 60°C and stirred overnight. The reaction mixture was quenched with saturated NaHCO₃ (1 x 10 mL). After separating the phases, the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layer was washed with water (2 x 15 mL) brine (2 x 20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 40:1) to afford 0.5 g (82%) of the title compound 261 as a colorless oil.

Rᵥ = 0.79 (hexanes-ether 1:1) UV, CAM, KMnO₄ active

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.54-7.46 (m, 2H), 7.39-7.27 (m, 3H), 5.04-4.92 (m, 1H), 4.73-4.61 (m, 1H), 3.48 (s, 3H), 3.44-3.21 (m, 3H), 1.42-1.29 (m, 12H), 1.02-0.89 (s, 9H), 0.15 (d, J = 13.43, 2.97 Hz, 6H)

¹³C NMR (101 MHz, CDCl₃, ppm) δ 176.71, 134.00, 131.63, 128.78, 127.46, 86.64, 86.24, 75.75, 72.31, 60.79, 38.73, 27.19, 25.88, 18.48, 17.99, -3.98, -4.54
IR (film)  
2956, 2886, 1739, 1477, 1277, 1170, 1147, 1108, 1070 cm$^{-1}$

$[\alpha]_D^{25}$  
(-) 27.32 (C = 5, C$_6$H$_6$)
A 50 mL round bottom flask containing freshly activated 4Å molecular sieves (700 mg) was charged with a solution of azeotropically dried (twice) thioglycoside 262 (0.32 g, 0.683 mmol, 1.2 eq) and diol 125 (0.1 g, 0.5689 mmol, 1 eq) in 19 mL of CH$_2$Cl$_2$. The reaction mixture was cooled to -70°C. NIS (0.153 g, 0.682 mmol, 1.4 eq) was added in one portion followed by a solution of AgOTf in toluene (7.3 mg, 0.0285 mmol, 0.05 eq in 0.3 mL). The reaction mixture was removed from -70°C bath and placed in a cryocool maintained at -36°C. After 6 h, the reaction mixture was quenched with saturated thiosulfate (5 mL) and NaHCO$_3$ (5 mL). The cooling bath was removed and the contents were allowed to warm to RT. The reaction mixture was diluted with 40 mL of ether and the phases were separated. The aqueous layer was extracted twice with ether (2 x 10 mL) and the combined organic layers were washed with brine (1 x 25 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 10:1) to afford 2.5:1 mixture of regioisomers in 74 % yield.

**Compound 264.**

R$_f$ = 0.62 (hexanes-ether 1:1)  
CAM, KMnO$_4$ active
\[ \text{\(^1\)H NMR (400 MHz, CDCl}_3, \text{ppm)} \]
\[ \delta 4.93 (dd, J = 9.25, 7.92 \text{ Hz, 1H}), 4.77 (d, J = 7.88 \text{ Hz, 1H}), 4.73 (d, J = 3.69 \text{ Hz, 1H}), 3.68-3.59 (m, 1H), 3.46 (s, 3H), 3.39-3.29 (m, 6H), 3.21 (ddd, J = 13.47, 6.78, 3.47 Hz, 1H), 1.96 (dd, J = 13.59, 1.21 Hz, 1H), 1.88 (dd, J = 13.57, 4.08 Hz, 2H), 1.38 (s, 3H), 1.33-1.27 (m, 16H), 0.95-0.91 (s, 9H), 0.17 (s, 3H), 0.12 (s, 3H) \]

\[ \text{\(^{13}\)C NMR (101 MHz, CDCl}_3, \text{ppm)} \]
\[ \delta 177.00, 101.39, 98.11, 85.19, 85.02, 75.99, 74.15, 72.31, 65.93, 60.74, 54.61, 42.95, 38.89, 27.44, 27.08, 25.86, 23.15, 18.35, 1808, 17.93, -3.99, -4.37 \]

IR (film)  
3518, 2929, 1739, 1463, 1382, 1257 cm\(^{-1}\)

\([\alpha]\)\(_D\)\(^{25}\) \((-) 56.05 (C = 8.1, C_6H_6)\)

**Compound 263.**

\(R_f = 0.39 \) (hexanes-ether 1:1) \hspace{1cm} CAM active

\[ \text{\(^1\)H NMR (400 MHz, CDCl}_3, \text{ppm)} \]
\[ \delta 4.87 (dd, J = 9.21, 8.02 \text{ Hz, 1H}), 4.74 (d, J = 4.21 \text{ Hz, 1H}), 4.65 (d, J = 7.93 \text{ Hz, 1H}), 3.76-3.63 (m, 1H), 3.51 (s, 3H), 3.41-3.19 (m, 7H), 2.73 (s, 1H), 2.03 (dd, J = 13.71, 4.48 Hz, 1H), 1.89 (d, J = 13.63 Hz, 1H), 1.39 (s, 3H), 1.31 (d, J = 6.14 Hz, 3H), \]
1.29-1.24 (m, 12H), 0.93 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H)

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
$\delta$ 177.05, 98.14, 94.50, 84.94, 78.76, 76.18, 75.78, 73.86, 72.39, 65.96, 60.76, 54.67, 40.34, 38.77, 27.35, 25.86, 19.71, 18.22, 18.15, 17.94, -4.01, -4.53

IR (film)  
3539, 2934, 2894, 2858, 1732, 1461, 1382, 1277, 1254, 1197, 1157, 1132, 1097 cm$^{-1}$

$[^{[\alpha]}]_{D}^{25}$  
(-) 47.47 (C = 4.15, C$_6$H$_6$)
Synthesis of compound 265.

A 25 mL round bottom flask was charged with a solution of disaccharide 263 in CH$_2$Cl$_2$ (75 mg, 0.14 mmol, 1eq in 1 mL). DMAP (5 mg) and Et$_3$N (60 µL, 0.42 mmol, 3 eq, d = 0.726 g/cc) were added to the reaction mixture. TBSOTf (40 µL, 0.168 mmol, 1.2 eq, d = 1.151 g/cc) was added dropwise and the contents were stirred at RT overnight. The reaction mixture was quenched with 1 mL of saturated NaHCO$_3$. After separating the phases, the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 2 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 40:1) to afford 55 mg (61%) of the title compound 265 as a colorless oil.

R$_f$ = 0.86 (hexanes-ether 1:1)  
CAM active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
δ 5.05 (d, $J$ = 7.89 Hz, 1H), 4.88 (dd, $J$ = 9.50, 7.94 Hz, 1H), 4.70 (d, $J$ = 3.53 Hz, 1H), 3.66-3.50 (m, 2H), 3.50-3.43 (s, 3H), 3.40-3.19 (m, 5H), 3.14-3.04 (m, 1H), 2.04 (d, $J$ = 13.26 Hz, 1H), 1.93 (dd, $J$ = 13.39, 4.24 Hz, 1H), 1.44 (s, 3H), 1.39-1.20 (m, 18H), 1.00-0.88 (m, 21H), 0.15 (m, 12H)

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm)  
δ 177.07, 99.04, 97.92, 85.39, 81.23, 76.30, 75.93, 74.29, 72.17, 65.60, 60.80, 54.51,
44.73, 38.81, 27.49, 25.91, 23.57, 22.28, 18.42, 18.01, 17.98, 14.00, -1.63, -1.70, -3.94, -4.38

IR (film) 2955, 2932, 2890, 2857, 1741, 1461, 1383, 1364, 1275, 1255, 1195, 1155, 1135, 1101, 1057, 1022, 1001 cm$^{-1}$

$[\alpha]_D^{25}$  (-) 56.13 (C = 5.6, C$_6$H$_6$)
Synthesis of compound 266.

A 10 mL round bottom flask was charged with a solution of disaccharide 265 (60 mg, 0.0924 mmol, 1 eq in 1 mL of toluene). The reaction mixture was cooled to -78°C. After stirring for 20 min at -78°C, a solution of DIBAL-H in toluene (28 mg, 0.194 mmol, 2.1 eq, in 0.3 mL) was added dropwise along the walls for 30 min to the reaction mixture. After addition, the reaction mixture was stirred for 30 min at which point TLC revealed complete consumption of pivalate. The reaction mixture was quenched with 0.3 mL of MeOH. This was followed by addition of 2 mL of saturated Na$_2$SO$_4$. The cooling bath was removed and the reaction mixture was allowed to warm to RT. The reaction mixture was diluted with 4 mL of Et$_2$O and stirred at RT for an hr. The contents were dried over MgSO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 10:1) to afford 40 mg (84%) of the title compound 266 as a colorless oil.

R$_f$ = 0.75 (hexanes-ether 1:1) CAM active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)

$\delta$ 4.72 (d, $J = 3.93$ Hz, 1H), 4.63 (d, $J = 7.87$ Hz, 1H), 3.70-3.59 (m, 4H), 3.43 (t, $J = 7.85$, 7.85 Hz, 2H), 3.36-3.17 (m, 5H), 3.00 (t, $J = 8.74$, 8.74 Hz, 1H), 2.68 (s, 1H), 2.10 (d, $J = 13.35$ Hz, 1H), 1.94 (dd, $J = 13.39$, 4.13 Hz, 1H), 1.52 (s, 3H), 1.33 (d, $J = 6.22$ Hz, 3H), 1.29 (d, $J = 6.01$ Hz, 3H), 0.99-
0.90 (s, 18H), 0.21-0.14 (m, 9H), 0.12 (s, 3H)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) δ 103.73, 97.95, 86.26, 86.14, 76.19, 75.80, 72.73, 65.71, 60.57, 54.62, 44.65, 26.01, 25.98, 23.57, 18.27, 18.21, 18.12, 18.05, -1.68, -1.89, -3.94, -4.67

IR (film) 2931, 2893, 2856, 1462, 1381, 1255, 1195, 1108, 1057, 1021 cm\(^{-1}\)

\([\alpha]_D^{25}\) (-) 64.91 (C = 2.2, C\(_6\)H\(_6\))
Synthesis of compound 267.

A 10 mL round bottom flask was charged with freshly prepared LiHMDS (12 mg, 0.071 mmol, 2 eq). 0.25 mL of THF was added. The reaction mixture was cooled to -78°C with the aid of dry ice acetone bath. After stirring for 20 min, a solution of azeotropically dried (twice) alcohol 266 in THF (20 mg, 0.035 mmol, 1 eq in 0.4 mL) was added dropwise to LiHMDS solution. The reaction mixture was stirred for an hr. Neat CS$_2$ (20 µL, 0.354 mmol, 10 eq, d = 1.266 g/cc) was added to lithium alkoxide. The reaction mixture turned to a lemon yellow solution. After stirring at -78°C for 2 h, neat MeI (10 µL, 0.176 mmol, 5 eq, d = 2.28 g/cc) was added to the reaction mixture. Cooling bath was removed and the contents were allowed to warm to RT. After stirring for an hr at RT, the reaction mixture was quenched with saturated NaHCO$_3$. The reaction mixture was diluted with 5 mL of Et$_2$O. After separating the phases the aqueous layer was extracted twice with Et$_2$O (2 x 5 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na$_2$SO$_4$ filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 20:1) to yield 17 mg (73%) of the title compound 267 as a colorless oil.

$R_f = 0.81$ (hexanes-ether 1:1)  

CAM active

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm) δ 5.87 (dd, $J = 9.26, 8.08$ Hz, 1H), 5.13 (d, $J = 8.04$ Hz, 1H), 4.69 (d, $J = 3.63$ Hz, 1H), 3.59-3.50 (m, 1H), 3.47 (m, 4H), 3.37-3.21 (m, 6H), 2.65 (s, 3H), 2.04 (d, $J = 13.43$ Hz,
1H), 1.92 (dd, $J = 13.41, 4.29$ Hz, 1H), 1.39 (s, 3H), 1.31 (d, $J = 5.94$ Hz, 3H), 1.27 (d, $J = 6.03$ Hz, 3H), 0.96 (d, 18H), 0.23 (s, 3H), 0.16 (d, 6H), 0.13 (s, 3H)

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, ppm) δ 99.81, 97.94, 85.44, 83.08, 82.84, 76.33, 75.94, 72.44, 65.38, 60.57, 54.30, 44.79, 25.82, 25.69, 22.99, 19.38, 18.16, 17.98, 17.95, 17.89, -1.77, -2.01, -4.17, -4.82

IR (film) 2929.7, 1225, 1061 cm$^{-1}$

$[\alpha]_D^{25}$ (-) 67.69 (C = 1.6, C$_6$H$_6$)
Synthesis of compound 268.

A 5 mL bottom flask fitted with condenser was charged with AIBN (4 mg, 0.0244 mmol, 1 eq) and neat Bu$_3$SnH (13.3 µL, 0.049 mmol, 2 eq, d = 1.082 g/cc). The contents were diluted with 0.8 mL of degassed toluene (30 min). The reaction mixture was refluxed for an hr. A solution of xanthate 267 in degassed toluene (16 mg, 0.0244 mmol, 1 eq in 0.4 mL) was added for an hr through syringe pump. The reaction mixture was refluxed for 14 h at which point TLC revealed complete consumption of xanthate. The reaction mixture was concentrated and the crude mixture was purified by column chromatography (pentane-ether, 40:1) to yield 13 mg (98%) of the title compound 268 as a colorless oil.

$R_f = 0.86$ (hexanes-ether 1:1)  
CAM active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
δ 4.79 (dd, $J = 9.85$, 1.87 Hz, 1H), 4.66 (d, $J = 3.92$ Hz, 1H), 3.57 (qd, $J = 9.91$, 6.15, 6.15, 6.15 Hz, 1H), 3.36-3.24 (m, 7H), 3.20-3.05 (m, 2H), 2.98 (ddd, $J = 12.82$, 8.00, 4.86 Hz, 1H), 2.38 (ddd, $J = 12.36$, 4.81, 1.85 Hz, 1H), 2.02 (d, $J = 13.38$ Hz, 1H), 1.88 (dd, $J = 13.40$, 4.33 Hz, 1H), 1.41 (s, 3H), 1.40-1.32 (m, 1H), 1.29 (d, $J = 6.21$ Hz, 3H), 1.27-1.22 (d, 2H), 0.92-0.85 (m, 18H), 0.11 (d, 6H), 0.07 (d, 6H)
$^{13}$C NMR (101 MHz, CDCl$_3$, ppm) $\delta$ 101.13, 98.03, 86.34, 81.27, 76.70, 75.58, 72.45, 65.76, 58.02, 54.59, 44.60, 35.64, 25.99, 25.84, 23.24, 18.47, 18.40, 18.29, 17.94, -1.83, -1.89, -3.99, -4.79

IR (film) 2930, 2856, 1462, 1381, 1255, 1101, 1056 cm$^{-1}$
Synthesis of compound 281.

A 250 mL three neck round bottom flask fitted with an immersion thermometer was charged with a solution of acylated thioxazolidinone in CH$_2$Cl$_2$ (6.08 g, 23.2 mmol, 1.05 eq, in 100 mL). The reaction mixture was cooled to 0°C (external). TiCl$_4$ (2.68 mL, 0.0232 mol, 1.05 eq, d = 1.72 g/cc) was added dropwise to the reaction mixture which resulted in the formation of brownish orange crystals. After 30 min, neat sparteine (5.33 mL, 0.0232 mol, 1.05 eq, d = 1.02 g/cc) was added dropwise to the reaction mixture. The solution turned dark purple color and the crystals slowly dissolved over the period of time. After 1 h, the reaction mixture was cooled to -55°C (internal temp) with the help of CHCl$_3$/ dry ice bath. NMP (2.35 mL, 0.0244 mol, 1.05 eq, d = 1.028 g/cc) was added dropwise. After 30 min, a solution of aldehyde (6 g in 20 mL of CH$_2$Cl$_2$, 0.0232 mol, 1eq) was added dropwise via a syringe pump (30 mL/h). Care was taken that the internal temperature never exceeded -50°C. After stirring at -55°C for 2 h, the reaction mixture was quenched with 50 mL of half saturated NH$_4$Cl and diluted with 200 mL of CH$_2$Cl$_2$. After separating the phases the organic layer was washed with water (2 x 100 mL), brine (1 x 100 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was taken to the next step without purification.

$R_f = 0.32$ (hexanes-ether 1:2)  
UV, CAM, KMnO$_4$, Vanillin active
$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
\( \delta 7.92-7.85 \) (m, 4H), 7.53 (ddd, \( J = 9.25, 5.33, 1.69 \) Hz, 3H), 7.42-7.31 (m, 3H), 7.29-7.23 (m, 2H), 5.00-4.90 (m, 2H), 4.85-4.79 (m, 1H), 4.72 (tq, \( J = 7.42, 7.42, 7.42, 3.69, 3.69 \) Hz, 1H), 4.38-4.25 (m, 3H), 3.99 (dt, \( J = 9.01, 8.98, 4.90 \) Hz, 1H), 3.66-3.54 (m, 2H), 3.48-3.42 (m, 3H), 3.34-3.25 (m, 2H), 2.85-2.76 (m, 1H), 1.93-1.74 (m, 2H), 1.38 (d, \( J = 6.93 \) Hz, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
\( \delta 185.00, 177.67, 135.97, 135.13, 133.25, 132.93, 129.36, 128.98, 128.10, 127.89, 127.62, 127.41, 126.46, 126.03, 125.84, 75.70, 75.12, 72.48, 70.13, 68.73, 60.03, 59.24, 42.84, 37.51, 36.67, 11.04

IR (film)  
3696, 3660, 3468, 2923, 1692, 1601, 1549, 1453, 1366, 1319, 1191, 1154, 1018 cm$^{-1}$

\([\alpha]_D^{25}\)  
(+) 62.73 (C = 4.1, C$_6$H$_6$)
**Synthesis of compound 282.**

A 250 mL round bottom flask with immersion thermometer was charged with a solution of aldol adduct 281 in CH₂Cl₂ (11 g, 21.6 mmol, 1 eq, in 65 mL). The reaction mixture was cooled to 0°C (internal). Neat 2,6 lutidine (7.6 mL, 65.2 mmol, 3 eq, d = 0.92 g/cc) was added followed by dropwise addition of TESOTf (4.89 mL, 21.6 mmol, 1 eq, d = 1.169 g/cc). After stirring at 0°C for 2 h, the reaction mixture was quenched with 20 mL of saturated NaHCO₃ and diluted with 40 mL of CH₂Cl₂. After separating the phases the organic layer was washed with water (1 x 40 mL), brine (1 x 50 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (hexanes-ether, 8:1) to yield 10.7 g (94% for 2 steps) of the title compound 282 as a pale yellow viscous oil.

\[ R_f = 0.80 \text{(hexanes-ether 1:2)} \]

UV, CAM, KMnO₄, Vanillin active

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, \text{ ppm) } \delta \begin{align*} 7.9-8.0 \text{ (m, 4H), } 7.5-7.6 \text{ (m, 3H), } 7.2-7.4 \text{ (m, 5H), } 5.0 \text{ (d, 1H), } 4.9 \text{ (m, 1H), } 4.8 \text{ (d, 1H), } 4.4 \text{ (m, 1H), } 4.3 \text{ (dd, 1H), } 4.13 \text{ (t, 1H), } 3.87 \text{ (m, 1H), } 3.60 \text{ (d, 2H), } 3.4 \text{ (s, 3H), } 3.30 \text{ (m, 1H), } 2.80 \text{ (dd, 1H), } 1.9-2.1 \text{ (m, 2H), } 1.4 \text{ (d, 3H), } 0.98 \text{ (m, 9 H), } 0.62 \text{ (q, 6H) } \end{align*} \]
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm) $\delta$ 185, 176, 136, 135, 133.4, 132.9, 129.5, 129, 127.9, 127.6, 127.3, 125.98, 125.91, 125.7, 125.6, 75.6, 75.3, 71.4, 71.3, 69.9, 60, 59, 44, 38, 37.00, 12.00, 7.5

IR (film) 2954, 2875, 1696, 1454, 1363, 1350, 1188, 1151, 1016 cm\textsuperscript{-1}

$[\alpha]_D^{25}$ (+) 64.30 (C = 2.75, C\textsubscript{6}H\textsubscript{6})
Synthesis of compound 176.

A 250 mL round bottom flask was charged with TES product aldol adduct 282 in CH₂Cl₂ (10.4 g, 16.7 mmol, 1 eq, in 50 mL). The solution was cooled to 0°C. Ethane thiol (3.7 mL, 50.1 mmol, 3 eq, d = 0.839 g/cc) and DBU (2.5 mL, 16.7 mmol, 1 eq, d = 1.018 g/cc) were added sequentially to the reaction mixture. The solution turned dark yellow. After stirring at 0°C for 2 h, the reaction mixture was diluted with 150 mL of CH₂Cl₂ and washed with 0.1M HCl (2 x 50 mL), saturated NaHCO₃ (1 x 100 mL), brine (1 x 100 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified immediately by column chromatography (hexanes-ether, 50:1) to yield 6.23 g (81%) of the title compound 176 as a pale yellow oil.

Please look into Gabe’s thesis for the characterization data of this compound
Synthesis of compound 177.

A 100 mL 2 neck round bottom flask with immersion thermometer was charged with a solution of thioester 176 in toluene (3 g, 6.12 mmol, 1 eq, in 30 mL). It was cooled to -76°C (internal). After 20 min, neat DIBAL-H (1 mL, 6.12 mmol, 1 eq, d = 0.798 g/cc) was added dropwise (addition rate 2 mL/h). After 15 min, the reaction mixture was quenched with 1 mL of dry acetone followed by 2 mL of saturated Na$_2$SO$_4$. The cooling bath was removed and the contents were warmed to RT. At RT, the reaction mixture was diluted with 100 mL of ether and MgSO$_4$ was added until it was free flowing. After stirring for 30 min, the reaction mixture was filtered and concentrated in vacuo. Owing to the instability of the aldehyde, the material was immediately carried to the next step.

Please look into Gabe’s thesis for the characterization data of this compound.
**Synthesis of compound 283.**

A flame dried three neck round bottom flask fitted with an immersion thermometer was charged with a solution of acylated thioxazolidinone 278 in CH₂Cl₂ (1.43 g, 5.73 mmol, 1.05 eq. in 21 mL). The reaction mixture was cooled to 0°C (external). TiCl₄ (63 mL, 5.73 mmol, 1.05 eq, d = 1.72 g/cc) was added dropwise to the reaction mixture which resulted in the formation of brownish orange crystals. After 30 min, neat (-)-sparteine (1.30 mL, 5.734 mmol, 1.05 eq, d = 1.02 g/cc) was added dropwise to the reaction mixture. The solution turned dark purple color and the crystals slowly dissolved over the period of time. After 1 h, the reaction mixture was cooled to -73°C (internal temp). NMP (0.56 mL, 5.73 mmol, 1.05 eq, d = 1.028 g/cc) was added dropwise. After 30 min, a solution of aldehyde 177 in CH₂Cl₂ (2.33 g, 5.5 mmol, 1 eq. in 50 mL) was added dropwise. After addition, the reaction mixture was transferred to a cryocool kept at -30°C. After stirring at -30°C for 14 h, the reaction mixture was poured into a beaker containing sat NaHCO₃ (30 mL) and stirred vigorously. It formed an emulsion. To this emulsion was added celite until both phases were visible. The reaction mixture was diluted with 50 mL of CH₂Cl₂ and the contents were filtered through a fritted funnel (C). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 30 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated *in vacuo*. The reaction mixture was purified by column chromatography (hexanes-ether, 5:1) to yield 2.43 g (65%) of the title compound 283 as a pale yellow cloudy oil.
$R_f = 0.68$ (hexanes-ether 1:2)  UV, CAM, KMnO$_4$, Vanillin active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
\begin{align*}
\delta & 7.83 \text{ (dd, } J = 7.42, 2.39 \text{ Hz, 4H), 7.51-7.45} \\
& (m, 3H), 7.37-7.20 \text{ (m, 5H), 4.95} \text{ (dd, } J = \\
& 12.12, 5.23 \text{ Hz, 1H), 4.91-4.83} \text{ (m, 2H), 4.70} \\
& \text{ (dd, } J = 12.10, 3.81 \text{ Hz, 1H), 4.36 (s, 1H),} \\
& 4.28 \text{ (dd, } J = 7.39, 4.14 \text{ Hz, 2H), 4.23-4.13} \\
& \text{ (m, 2H), 3.76 (dt, } J = 8.05, 7.97, 4.46 \text{ Hz,} \\
& 1H), 3.59-3.50 \text{ (m, 2H), 3.42-3.37} \text{ (m, 4H),} \\
& 2.75 \text{ (dd, } J = 13.17, 10.34 \text{ Hz, 1H), 1.95-} \\
& 1.79 \text{ (m, 2H), 1.77-1.67} \text{ (m, 1H), 1.23 (t, } J = \\
& 7.59, 7.59 \text{ Hz, 3H), 0.98-0.88} \text{ (m, 12H), 0.59} \\
& \text{ (dt, } J = 6.9, 6H) \\
\end{align*}

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
\begin{align*}
\delta & 185.19, 176.71, 136.48, 135.47, 133.31, \\
& 132.87, 129.42, 128.94, 127.98, 127.83, \\
& 127.64, 127.30, 126.01, 125.87, 125.70, \\
& 125.53, 75.70, 75.34, 74.01, 72.87, 71.36, \\
& 70.06, 65.65, 60.99, 59.13, 40.95, 40.45, \\
& 37.47, 35.03, 12.68, 12.46, 8.65, 6.81, 4.94 \\
\end{align*}

IR (film)  
3453, 2954, 2876, 1705, 1455, 1352, 1319, 
1191, 1153, 1121, 1015 cm$^{-1}$

$[\alpha]_D^{25}$  
(+)$ 16.57$ (C = 1.6, C$_6$H$_6$)
Synthesis of compound 284.

In a 25 ml round bottom flask was taken a solution of aldol adduct 283 in DMF (3.650 g, 5.367 mmol, 1 eq in 5 mL). The reaction mixture was flushed with argon and then cooled to 0°C (external). After 10 min, Et$_3$N (3.7 mL, 26.8 mmol, 5 eq, d = 0.726 g/cc) was added dropwise to the reaction mixture. After 10 min, neat TBSOTf (3.1 mL, 13.4 mmol, 2.5 eq, d = 1.151 g/cc) was added dropwise. The reaction mixture was allowed to attain room temperature without removing ice bath. The reaction mixture was quenched with 10 ml saturated NaHCO$_3$. The reaction mixture was diluted with 50 mL of Et$_2$O, washed with water (4 x 5 mL), brine (1 x 50 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified on a silica column (hexanes-ether, 30: 1) to yield 2.90 g (68%) of the title compound 284 as a pale yellow oil.

R$_f$ = 0.88 (hexanes-ether 1:2) UV, CAM, KMnO$_4$, Vanillin active

$^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.89-7.79 (m, 3H), 7.73 (d, $J$ = 8.47 Hz, 1H), 7.56-7.46 (m, 3H), 7.37-7.29 (m, 3H), 7.13 (dd, $J$ = 7.49, 1.78 Hz, 2H), 4.94 (d, $J$ = 11.74 Hz, 1H), 4.91-4.82 (m, 1H), 4.75-4.62 (m, 2H), 4.37 (t, $J$ = 4.97, 4.97 Hz, 1H), 3.90 (dd, $J$ = 9.28, 2.16 Hz, 1H), 3.85-3.68 (s, 3H), 3.57 (ddd, $J$ = 14.14, 10.26, 4.64 Hz, 2H), 3.47-3.39 (s, 3H), 2.97 (dd, $J$
= 13.36, 3.23 Hz, 1H), 2.68 (dd, $J = 13.36, 9.55$ Hz, 1H), 2.03 (ddd, $J = 13.80, 8.24, 5.33$ Hz, 1H), 1.76 (dd, $J = 11.97, 6.22$ Hz, 1H), 1.70-1.58 (m, 1H), 1.28-1.20 (m, 3H), 1.07-0.97 (m, 12H), 0.97-0.91 (m, 9H), 0.69 (td, $J = 15.97, 6.09, 6.09$ Hz, 6H), 0.14 (s, 3H), 0.09 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)

$\delta$ 184.49, 176.52, 136.49, 135.22, 133.18, 132.79, 129.40, 128.82, 127.90, 127.56, 127.80, 127.56, 127.26, 126.23, 126.05, 126.02, 125.76, 75.79, 75.42, 72.25, 71.50, 70.81, 69.41, 59.91, 59.06, 46.50, 40.25, 39.34, 37.13, 26.00, 18.25, 13.62, 11.02, 7.17, 5.93, -3.98, -4.49

IR (film) 2954, 2878, 1694, 1603, 1456, 1365, 1320, 1252, 1188, 1151, 1071, 1008 cm$^{-1}$

$[\alpha]_{D}^{25}$ (-) 8.125 (C = 1.6, C$_6$H$_6$)
Synthesis of compound 285.
A 10 mL round bottom flask was charged with TBS product aldol adduct 284 in CH₂Cl₂ (0.866 g, 1.09 mmol, 1 eq in 5 mL). The solution was cooled to -5°C. Ethanethiol (0.25 mL, 3.27 mmol, 3 eq, d=0.839 g/cc) and DBU (0.163 mL, 1.09 mmol, 1 eq, d=1.018 g/cc) were added sequentially to the reaction mixture. The solution turned dark yellow. After stirring at -5°C for 2 h, the reaction mixture was diluted with 20 mL of CH₂Cl₂ and washed with 0.1M HCl (2 x 5 mL), saturated NaHCO₃ (1 x 5 mL), brine (1 x 20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified immediately by column chromatography (hexanes-ether, 30:1) to yield 0.491 g (88%) of the title compound 285 as a pale yellow oil.

R_f = 0.42 (hexanes-ether 4:1)

UV, CAM, KMnO₄, Vanillin active

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.87 (dd, J = 7.99, 3.93 Hz, 4H), 7.51 (tt, J = 6.30, 6.30, 3.14, 3.14 Hz, 3H), 4.92 (d, J = 12.08 Hz, 1H), 4.76 (d, J = 12.09 Hz, 1H), 4.34 (dd, J = 6.31, 2.10 Hz, 1H), 4.04 (ddd, J = 7.43, 5.91, 3.42 Hz, 1H), 3.71-3.62 (m, 1H), 3.57-3.51 (m, 2H), 3.44 (s, 3H), 2.94-2.77 (m, 3H), 1.99 (td, J = 14.22, 7.18, 7.18 Hz, 1H), 1.86-1.68 (m, 2H), 1.29-1.22 (t, 3H), 1.17 (d, J = 6.44, 6.44 Hz, 3H),
1.05-0.96 (m, 9H), 0.96-0.86 (m, 12H), 0.67 (q, $J = 8.05$, 7.94, 7.94 Hz, 6H), 0.07 (s, 3H), -0.00 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
$\delta$ 202.67, 136.31, 133.28, 132.87, 127.92, 127.79, 127.59, 126.06, 125.90, 125.69, 125.62, 75.60, 75.35, 73.87, 71.50, 70.84, 59.10, 51.14, 44.22, 38.12, 26.00, 23.06, 18.23, 14.52, 10.57, 9.76, 7.08, 5.87, -4.29, -4.40

IR (film)  
3055, 2953, 2930, 2877, 1688, 1509, 1460, 1382, 1251, 1194, 1121, 1079, 1006 cm$^{-1}$
A 2 neck round bottom flask fitted with immersion thermometer was charged with a suspension of 95% NaH in THF (0.203 g, 8.45 mmol, 1.1 eq in 10 mL). It was cooled to 0°C. Neat β-ketoester 296 was added dropwise (1 g, 7.68 mmol, 1 eq) for a period of 30 min such that the internal temperature did not exceed beyond 5°C. After addition was complete, the reaction was stirred for 10 min at 0°C and then cooled to -88°C (internal).

A 2 neck round bottom flask with immersion thermometer was charged with a solution of TBSOTf in THF (1.94 mL, 8.45 mmol, 1.1 eq in 12 mL). The solution was cooled to -88°C (internal) with the aid of dry ice / acetone / liquid N₂. The solution of sodium enolate was then cannulated dropwise to the solution of TBSOTf such that internal temperature always stayed below -82°C*. After addition, the reaction mixture was allowed to warm to -50°C without removing the cooling bath. At -50°C it was quenched with 10 mL of saturated NH₄Cl and the reaction contents were allowed to warm to RT. The reaction mixture was diluted with 50 mL of ether and the phases were separated. The aqueous layer was extracted with ether (2 x 10 mL) and the combined organic layer was washed with brine (1 x 50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was repeatedly purified on a column chromatography (hexanes-benzene, 10:1) to obtain the major diastereomer.

* It was observed that when the internal temperature was kept between -65°C to -70°C during the addition of enolate solution to TBSOTf, a 1:1 mixture was obtained.
General procedure for the synthesis of diene:

A 2 neck flask with immersion thermometer was charged with a solution of KHMDS in ether (30.50 mmol, 1.5 eq in 70 mL). After cooling the reaction mixture to 0°C (external), neat enone (20.5 mmol, 1 eq) was added dropwise for a period of 30 min. After addition, the reaction mixture was stirred for 10 min at which point it was cooled to -76°C (internal). Freshly distilled TMSCl or TBSOTf (30.50 mmol, 1.5 eq for TMSCl, 21 mmol, 1.05 eq for TBSOTf) was added dropwise at -76°C. Care was taken such that the internal temperature never rose beyond -72°C. The reaction mixture was allowed to warm to RT in an 8 h period without removing the cooling bath. The reaction mixture was concentrated with the aid of special vacuum adapter (figure 32). After flushing with argon, the reaction mixture was diluted with dry pentane and transferred into a centrifuge tube. After centrifugation, the supernatant solution was transferred into a dry flask and the contents were concentrated with the aid of special vacuum adapter. 

1HNMR of the crude mixture indicated that the material was 95% pure and the diene is used in the next step without purification.
Synthesis of compound 289.

\[ \text{Synthesis of compound 289.} \]

\[ \text{OTBS} \]

\[ \text{299} \]

\[ \text{KHMDS, Et}_2\text{O, 0°C then -78°C then TBSOTf} \]

\[ \text{OTBS} \]

\[ \text{289} \]

\[ \text{^1H NMR (400 MHz, CDCl}_3, \text{ ppm)} \quad \delta \quad 4.68 \text{ (q, } J = 7.4 \text{ Hz, 1H), } 3.55 \text{ (s, } 3\text{H), } 1.65 \text{ (s, } 3\text{H), } 1.56 \text{ (d, } J = 7.4 \text{ Hz, } 3\text{H), } 0.95 \text{ (s, } 9\text{H), } 0.93 \text{ (s, } 9\text{H), } 0.17 \text{ (s, } 3\text{H), } 0.10 \text{ (s, } 3\text{H)} \]

\[ \text{^13C NMR (100 MHz, CDCl}_3, \text{ ppm)} \quad \delta \quad 191.2, 182.8, 90.4, 73.5, 59.4, 19.1, 19.0, 9.1, 3.4, -4.7 \]
Synthesis of compound 307.

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
$\delta$ 4.68 (q, J = 7.4 Hz, 1H), 3.55 (s, 3H), 1.65 (s, 3H), 1.56 (d, J = 7.4 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H), 0.09 (s, 9H)
Synthesis of compound 320.

$^{1}H$ NMR (400 MHz, CDCl$_3$, ppm)  
$\delta$ 4.81-4.72 (m, 1H), 4.00 (s, 1H), 3.63 (s, 3H), 1.54 (d = 6.02 Hz, 3H), 0.96 (s, 9H), 0.25 (s, 9H), 0.14 (s, 6H)

$^{13}C$ NMR (101 MHz, CDCl$_3$, ppm)  
$\delta$ 157.37, 146.03, 103.48, 73.93, 54.96, 25.84, 18.14, 12.93, 5.40, 0.52, -4.37
Synthesis of compound 323.

$^1\text{H}$ NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 4.73 (q, $J = 6.99, 6.99, 6.97$ Hz, 1H), 3.91 (s, 1H), 3.59-3.51 (s, 3H), 1.48 (d, 3H), 0.94-0.87 (d, 18H), 0.17-0.12 (s, 6H), 0.08 (s, 6H)

$^{13}\text{C}$ NMR (101 MHz, CDCl$_3$, ppm) $\delta$ 157.30, 145.83, 103.90, 74.18, 54.88, 25.79, 18.06, 13.12, -4.04, -4.30
Synthesis of compound 306.

A 10 mL round bottom flask was charged with a solution of oxazaborolidine in CH$_2$Cl$_2$ (0.158 g, 0.39 mmol, 0.5 eq in 3 mL). The pale yellow solution was cooled to -78°C and stirred for 30 min. Neat TfOH was added (34 µL, 0.38 mmol, 0.49 eq) dropwise to the reaction mixture. During the addition, the solution turned from pale yellow to bright yellow and then back to pale yellow. After 30 min, a solution of aldehyde in CH$_2$Cl$_2$ (0.2 g, 0.77 mmol, 1 eq in 1 mL) was added dropwise for a period of 15 min. After addition, the reaction mixture was stirred for 15 min after which neat diene (0.45 g, 1.2 mmol, 1.5 eq) was added dropwise for a period of 30 min. The reaction flask was then transferred to cryocool kept at -55°C and stirred for 6 h. The reaction mixture was quenched with 3 mL of saturated NaHCO$_3$ and the contents were allowed to warm to RT. At RT the reaction mixture was diluted with CH$_2$Cl$_2$ and the phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 5 mL) and the combined organic layers were washed with brine (1 x 25 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 20:1) to yield title compound 306 as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 8.06-7.71 (m, 4H), 7.64-7.40 (m, 3H), 4.94 (d, $J$ = 12.20 Hz, 1H), 4.72 (d, $J$ = 12.21 Hz, 1H), 4.41-4.22 (m, 1H), 3.97-3.83 (m, 1H), 3.80 (s, 3H), 3.55 (dq, $J$ = 10.27,
10.26, 10.26, 4.89 Hz, 2H), 3.46-3.35 (3, 3H), 3.27-3.14 (m, 1H), 1.84-1.71 (m, 4H), 1.67-1.58 (m, 2H), 1.11 (d, J = 6.79 Hz, 3H), 0.93-0.87 (s, 9H), 0.05 (d, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 201.53, 159.57, 136.76, 133.36, 132.81, 127.87, 127.63, 125.91, 125.57, 125.47, 125.37, 117.40, 76.11, 75.25, 70.99, 70.98, 61.20, 59.14, 47.02, 36.03, 25.92, 18.10, 11.37, 8.81, -4.23, -4.50
General procedure for hetero Diels-Alder reaction:

A flame dried 10 mL round bottom flask was charged with a solution of oxazaborolidine in CH$_2$Cl$_2$ (0.328 g, 0.929 mmol, 0.2 eq in 4 mL). The pale yellow solution was cooled to -78°C and stirred for 30 min. Neat TfOH (62 µL, 0.69 mmol, 0.15 eq) was added dropwise to the reaction mixture. During the addition, the solution turned from pale yellow to bright yellow and then back to pale yellow. After 30 min, a solution of aldehyde in CH$_2$Cl$_2$ (1.2g, 4.64 mmol, 1 eq in 1 mL) was added dropwise for a period of 15 min. After addition, the reaction mixture was stirred for 15 min after which neat diene (3.5 mL, 10.6 mmol, 2.3 eq) was added dropwise for a period of 30 min. After addition the contents were stirred at -78°C for 6 h at which point it was quenched with 3 mL of saturated NaHCO$_3$ and warmed to RT. At RT the reaction mixture was diluted with 10 mL of CH$_2$Cl$_2$ and the phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 5 mL) and the combined organic layers were washed with brine (1 x 15 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 20:1) to yield the title compound as a pale yellow oil.
**Synthesis of compound 308.**

\[ R_f = 0.30 \text{ (hexane-ether, 3:1) } \]

UV, Vanilin active, double elution

$^1$H NMR (400 MHz, CDCl$_3$, ppm)

\[ \delta 7.82-7.66 \text{ (m, 4H), 7.38 (ddt, } J = 11.38, 11.38, 7.82, 3.29 \text{ Hz, 3H), 4.84 (d, } J = 11.94 \text{ Hz, 1H), 4.64 (t, } J = 9.82, 9.82 \text{ Hz, 1H), 4.23-4.07 (m, 1H), 3.76 (dq, } J = 6.53, 6.53, 6.39, 3.45 \text{ Hz, 1H), 3.71-3.56 (m, 4H), 3.49-3.38 (m, 2H), 3.33-3.26 (s, 3H), 1.86-1.71 (m, 4H), 1.50-1.38 (m, 1H), 1.05-0.96 (d, 3H), 0.93-0.87 (s, 9H), 0.14 (d, 6H), 0.01 (s, 9H) \]

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)

\[ \delta 170.15, 165.48, 136.65, 133.31, 132.79, 127.81, 127.74, 127.56, 125.77, 125.66, 125.53, 125.47, 109.79, 75.96, 75.35, 71.62, 71.23, 59.07, 51.20, 43.81, 37.39, 26.52, 19.19, 14.61, 13.86, 0.72, -2.22, -2.76 \]
IR (film) 2952, 2859, 1709, 1605, 1462, 1362, 1272, 1188, 1108 cm$^{-1}$
Synthesis of compound 327.

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm)  
\(\delta 7.85 \) (ddd, \( J = 13.39, 7.16, 3.94 \) Hz, 4H),  
7.58-7.41 (m, 3H), 5.15 (s, 1H), 4.93 (d, \( J = 10.19 \) Hz, 1H),  
4.76 (d, \( J = 10.19 \) Hz, 1H), 4.28 (ddd, \( J = 9.47, 5.57, 2.03 \) Hz, 1H),  
4.21-4.05 (m, 1H), 3.96-3.81 (m, 1H), 3.78-3.61 (s, 3H), 3.60-3.47 (m, 2H), 3.46-3.38 (s, 3H), 1.88-1.74 (m, 1H), 1.73-1.60 (m, 1H), 1.13-1.05 (d, 3H), 1.04-0.99 (s, 9H), 0.94 (m 12H), 0.37-0.26 (d, 6H), 0.24-0.18 (s, 3H), 0.09 (s, 3H)
Synthesis of compound 309.

A 5 mL round bottom flask was charged with a solution of cycloaddition product in THF (0.08 g, 0.13 mmol, 1 eq in 1 mL). 0.1 mL of 1N HCl was added to the solution. The reaction mixture was stirred vigorously for a min and immediately neutralized with pH = 7 buffer capsule and the pH of the solution was monitored. The reaction mixture was diluted with 10 mL of ether and the phases were separated. The aqueous layer was extracted with ether and the combined organic layers were washed with brine (1 x 5 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 3:1) to yield the title compound 309 as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.82-7.62 (m, 4H), 7.50-7.28 (m, 3H), 4.81 (d, $J = 11.69$ Hz, 1H), 4.69 (d, $J = 11.70$ Hz, 1H), 3.99 (dtd, $J = 7.05, 4.70, 4.46, 2.72$ Hz, 1H), 3.83-3.66 (m, 1H), 3.62 (s, 3H), 3.50-3.36 (m, 2H), 3.35-3.18 (m, 5H), 1.92-1.77 (m, 1H), 1.74 (s, 3H), 1.37 (ddd, $J = 12.01, 7.30, 2.10$ Hz, 1H), 0.98-0.89 (d, 3H), 0.89-0.81 (s, 9H), 0.09 (d, $J = 6.56$, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 172.22, 166.25, 136.58, 133.34, 132.94, 127.92, 127.64, 126.36, 126.11, 125.87, 125.63, 110.54, 75.88, 75.43, 72.86, 69.66,
59.24, 51.75, 44.20, 38.86, 26.19, 18.96, 15.07, 13.93, -2.72, -3.20

IR (film) 3788, 3454, 2931, 2858, 1682, 1604, 1461, 1361, 1274, 1190, 1112 cm\(^{-1}\)

\([\alpha]_\text{D}^{25}\) (+) 39.99 (C = 11.2, C\(_6\)H\(_6\))
Synthesis of compound 310.

A 10 mL round bottom flask was charged with a solution of mixed hemi-orthoester in CH$_2$Cl$_2$ (0.042g, 0.082 mmol, 1 eq in 0.8 mL). Solid 2,6-ditert-butyl-4-methyl pyridine was added (0.033g, 0.16 mmol, 2 eq) to the reaction mixture and the contents were stirred for 2 d. The reaction mixture was concentrated in vacuo and the crude mixture was purified by column chromatography (hexanes-ether, 5:1) to yield 0.035 g (89%) of the title compound 310 as a pale yellow oil.

R$_f$ = 0.30 (hexane-ether 1:1)  

UV, CAM, Vanilin active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
δ 7.82 (d, $J = 9.21$ Hz, 4H), 7.61-7.37 (m, 3H), 4.90 (d, $J = 11.58$ Hz, 1H), 4.75 (d, $J = 11.58$ Hz, 1H), 4.34 (ddd, $J = 10.00$, 4.49, 2.90 Hz, 1H), 4.00 (ddd, $J = 11.15$, 7.04, 4.27 Hz, 1H), 3.57-3.49 (m, 1H), 3.44 (dd, $J = 10.33$, 4.60 Hz, 1H), 3.38 (s, 3H), 2.35-2.21 (m, 1H), 1.95 (ddd, $J = 14.36$, 10.06, 2.68 Hz, 1H), 1.88-1.73 (m, 4H), 1.24-1.16 (d, 3H), 1.05-0.91 (s, 9H), 0.16 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
δ 167.45, 166.06, 136.02, 133.26, 132.94, 128.08, 127.88, 127.61, 126.54, 125.98, 125.78, 106.67, 74.80, 72.96, 59.24, 38.82,
36.94, 25.47, 18.22, 16.46, 10.07, -3.55, -3.75

IR (film) 2929, 1704, 1647, 1462, 1383, 1347, 1254, 1120 cm\(^{-1}\)

\([\alpha]_D^{25}\) (+) 124.80 (C = 1.7, C\(_6\)H\(_6\))
Synthesis of compound 286.

A 50 mL flask was charged with a solution of enone / hemi orthoester in THF (0.475g, 0.81 mmol in 18 mL). 12 mL of 1N HCl was added to the solution. The biphasic solution was stirred vigorously for 3 h. The reaction mixture was neutralized with pH = 7 buffer capsule and the pH of the solution was monitored. The reaction mixture was diluted with 20 mL of ether and the phases were separated. The aqueous layer was extracted with ether (3 x 10 mL) and the combined organic layers were washed with brine (1 x 20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (hexanes-ether, 1:1) to yield 0.209 g (70%) of the title compound 286 as a pale yellow oil.

Rₛ = 0.19 (hexanes-ether 1:1)  
UV, CAM, Vanillin active

¹H NMR (400 MHz, CDCl₃, ppm)  
δ 7.81 (dd, J = 8.65, 3.78 Hz, 4H), 7.62-7.35 (m, 3H), 4.96 (d, J = 12.18 Hz, 1H), 4.59 (d, J = 12.20 Hz, 1H), 4.03 (ddd, J = 10.26, 5.82, 4.19 Hz, 2H), 3.58 (dd, J = 10.13, 3.92 Hz, 1H), 3.51-3.41 (m, 4H), 2.59 (q, J = 6.54, 6.54, 6.54 Hz, 1H), 2.10 (qd, J = 10.72, 7.22, 7.20, 7.20 Hz, 1H), 2.00-1.88 (m, 1H), 1.68-1.55 (m, 1H), 1.20 (t, J =
7.01, 7.01 Hz, 1H), 1.06 (d, $J = 7.25$ Hz, 3H), 0.97 (d, $J = 6.56$ Hz, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm)  
δ 204.34, 169.05, 133.08, 132.86, 128.17, 127.95, 127.57, 127.38, 126.67, 126.44, 126.29, 75.58, 74.84, 73.34, 73.09, 59.38, 49.87, 46.45, 35.28, 12.15, 7.50

IR (film)  
3790, 3055, 2927, 2247, 1760, 1721, 1663, 1509, 1454, 1391, 1361, 1332, 1232, 1117 cm$^{-1}$
Synthesis of compound 338.

A 100 mL 2 neck round bottom flask with immersion thermometer was charged with a solution of thioester 285 in toluene (2.265 g, 3.41 mmol, 1 eq, in 25 mL). It was cooled to -76°C (internal). After 20 min, a solution of DIBAL-H in toluene (0.61 mL, 3.41 mmol, 1 eq, d = 0.798 g/cc in 10 mL) was added dropwise along the walls (addition rate 10 mL/h). Care was taken such that the internal temperature never exceeded beyond -75°C. After addition the reaction mixture was stirred for 15 min and then quenched with 1 mL of dry acetone followed by 2 mL of saturated Na$_2$SO$_4$. The cooling bath was removed and the contents were warmed to RT. At RT, the reaction mixture was diluted with 100 mL of ether and MgSO$_4$ was added until it was free flowing. After stirring for 30 min, the reaction mixture was filtered and concentrated in vacuo. The crude mixture was purified immediately by column chromatography (100% CH$_2$Cl$_2$) to yield 1.80 g (88%) of the title compound 338 as a pale yellow oil.

$R_f = 0.30$ (hexanes-ether 4:1)  
UV, CAM, KMnO$_4$, vanillin active

$^1$H NMR (400 MHz, CDCl$_3$, ppm)  
$\delta$ 9.65 (s, 1H), 7.8-7.9 (m, 4H), 7.3-7.5 (m, 3H), 4.8-4.9 (d, 1H), 4.65-4.70 (d, 1H), 4.30 (d, 1H), 4.0 (m, 1H), 3.6 (m, 1H), 3.45 (d, 2H), 3.29 (s, 3H), 2.49 (m, 1H), 1.90 (m, 1H), 1.7-1.8 (m, 2H), 1.05 (d, 3H), 0.97 (m,
$^1$H NMR (600 MHz, CDCl$_3$, ppm) δ 2.08 (s, 3H), 9.87 (m, 12H), 0.56 (q, 6H), 0.02 (s, 3H), -0.10 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 205.5, 136.0, 133.5, 133.1, 125.8, 126.2, 127.8, 128.1, 128.3, 75.7, 75.2, 71.9, 71.6, 70.9, 59.2, 50.1, 43.2, 37.9, 26.1, 10.0, 7.2, 7.0, 5.9, -4.1, -4.3

IR (film) 2954, 2929, 2876, 2856, 1734, 1726, 1471, 1454, 1251, 1123, 1111, 1084 cm$^{-1}$
Synthesis of compound 337.

A 25 mL round bottom flask was charged with azeotropically dried vinyl iodide in ether (0.418 g, 0.991 mmol, 1.3 eq in 9 mL). It was cooled to -78°C. A solution of tBuLi in pentane (0.122 g, 1.91 mmol, 2.5 eq) was added dropwise to the reaction mixture and the contents were stirred for 20 min at -78°C. A solution of ZnI₂·Et₂O (0.316 g, 0.99 mmol, 1.3 eq) in ether was added dropwise to lithiated alkyne and the contents were allowed to 0°C without removing the cooling bath. During this time the white suspension turned into a colorless solution. A solution of azeotropically dried aldehyde in ether (0.460 g, 0.762 mmol, 1 eq in 1 mL) was added to the reaction mixture at 0°C and the contents were stirred at 0°C for 8 h. The reaction mixture was quenched with saturated NH₄Cl solution and the reaction mixture was warmed to RT. The reaction mixture was diluted with 10 mL of ether and the phases were separated. The aqueous layer was extracted with ether (2 x 5 mL) and the combined organic layer was washed with brine (1 x 10 ml), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography to yield 0.474 g of the title compound 337 in 69% yield.

R<sub>f</sub> = 0.10 (hexanes-ether 4:1) UV, Vanilin, CAM active
Synthesis of compound 131.

A 25 mL round bottom flask was charged with a solution of azeotropically dried allylic alcohol 337 in CH₂Cl₂ (0.47 g, 0.527 mmol, 1 eq in 6 mL). The reaction mixture was cooled to 0°C. Neat pyridine (2.13 mL, 26.36 mmol, 50 eq) was added followed by addition of DMP (1.1 g, 2.636 mmol, 5 eq) in one portion. The reaction mixture was allowed to warm to RT without removing ice bath and stirred for 8 h at RT. Additional DMP was added if the reaction did not proceed to completion. The reaction mixture was diluted with 25 mL of anhydrous ether and cooled to 0°C. It was then filtered through celite and concentrated in vacuo. The crude mixture was purified by column chromatography (pentane-ether: 10:1) to yield the title compound 131 in 65-75% yield.

Please refer Katie’s thesis for characterization data
Synthesis of compound 336.

A 10 mL round bottom flask was charged with K$_3$Fe(CN)$_6$ (0.429 g, 1.302 mmol, 3 eq), K$_2$CO$_3$ (0.179 g, 1.302 mmol, 3 eq) and NaHCO$_3$ (0.121 g, 1.932 mmol, 3.3 eq). It was dissolved in 3.2 mL of deionized water. The aqueous solution turned into a pale yellow solution.

A 10 mL round bottom flask was charged with (DHQ)$_2$AQN (0.187 mg, 0.217 mmol, 0.5 eq) and potassium osomate (0.016 g, 0.0434 mmol, 0.1 eq). 3.2 mL of tBuOH was added. The reaction mixture was stirred vigorously for 30 min. The pale yellow aqueous solution was transferred into the flask containing a solution of osomate. The biphasic solution was then stirred for an hr and then cooled to 0°C. A precooled solution of olefin (0.370 g, 0.412 mmol, 1 eq) and methane sulfonamide solution (0.062 g, 0.653 mmol, 1.5 eq) in tBuOH (0.4 mL) was added to the biphasic solution at 0°C. The reaction mixture was stirred for 2.5 days at 0°C.

The reaction mixture was quenched by adding a solution of Na$_2$SO$_3$ (0.383 g in 6 mL). The reaction mixture was allowed to warm to RT and stirred for an hr. The crude mixture was diluted with 15 mL of EtOAc and the phases were separated. The aqueous layer was extracted with EtOAc (5 x 10 mL) and the combined organic layer was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was taken to the next step without purification.

Please refer Katie’s thesis for characterization data
**Synthesis of compound 130.**

A 10 mL flask was charged with a solution of diol 336 in anhydrous MeOH (0.12 g, 0.129 mmol, 1 eq, in 2 mL). Solid PPTS (0.011 g, 0.044 mmol, 0.3 eq) was added in one portion and the reaction mixture stirred for 6 h. The reaction mixture was quenched with saturated NaHCO₃ (0.5 mL). The biphasic solution was salted with NaCl until it became one layer. It was then filtered and the salts were thoroughly washed with ethyl acetate. The combined filtrate was then concentrated in vacuo. The crude mixture was purified by column chromatography to yield 0.083 g (78%) of the title compound 130 as a 5:1 mixture of diasteromers.

Please refer Katie’s thesis for characterization data
Synthesis of compound 353.

A 10 mL round bottom flask was charged with a solution of diol in toluene (0.021 g, 0.0253 mmol, 1 eq in 3 mL). Solid phenyl boroxine (0.004 g, 0.00128 mmol, 0.5 eq) was added in one portion. A Dean Stark apparatus was fitted to this flask and the contents were refluxed for 6 h. After 6 h the heating was discontinued and the Dean Stark apparatus was dismantled. The reaction flask was fitted to a special vacuum adapter (figure 33) and the contents were concentrated in vacuo. Attempts to purify the crude mixture on silica resulted in the partial hydrolysis of boronate.

Figure 33. Dean Stark apparatus

R_f = 0.77 (hexanes-ether 1:1)  UV, CAM, Vanilin active
$^1$H NMR (400 MHz, CD$_2$Cl$_3$, ppm) δ 7.92-7.75 (m, 1H), 7.49 (ddd, $J = 7.31$, 5.37, 2.61 Hz, 1H), 7.38 (t, $J = 7.36$, 7.36 Hz, 1H), 4.94 (d, $J = 11.68$ Hz, 1H), 4.86-4.73 (m, 1H), 4.65 (d, $J = 11.71$ Hz, 1H), 4.33 (d, $J = 6.08$ Hz, 1H), 4.15-4.03 (m, 1H), 3.99 (d, $J = 9.88$ Hz, 1H), 3.93-3.82 (m, 1H), 3.83-3.72 (m, 1H), 3.69-3.46 (m, 1H), 3.39 (s, 1H), 3.26 (s, 1H), 2.36-2.23 (m, 1H), 2.22-2.09 (m, 1H), 2.09-1.96 (m, 1H), 1.96-1.83 (m, 1H), 1.83-1.70 (m, 1H), 1.54 (s, 1H), 1.43 (s, 1H), 1.37-1.24 (m, 1H), 1.01 (d, $J = 6.55$ Hz, 1H), 0.87 (t, $J = 8.11$, 8.11 Hz, 1H), 0.16 (s, 1H), 0.13 (s, 1H), 0.04 (d, $J = 5.21$ Hz, 1H)
Synthesis of compound 365.

A 10 mL round bottom flask was charged with a solution of diol 130 in CH₂Cl₂ (0.02 g, 0.024 mmol, 1 eq). It was cooled to -78°C. Pyridine (37 µL, 0.456 mmol, 19 eq, d = 0.982 g/cc) was added followed by a solution of diphosgene in CH₂Cl₂ (0.0081 g, 0.049 mmol, 1.7 eq in 0.1 mL). The reaction mixture was allowed to warm to 0°C without removing the cooling bath (took approximately 4 h to reach 0°C). At 0°C, the reaction mixture was stirred for an hr and then quenched with 3 mL of saturated NaHCO₃. The crude mixture was diluted with 10 mL of CH₂Cl₂ and the phases were separated. The organic layer was washed with brine (1 x 10 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (pentane-ether 5:1) to yield 0.019 g (92%) of the title compound as a colorless oil.

Rₛₜ = 0.67 (hexanes-ether 1:1)  
UV, CAM, Vanilin active

¹H NMR (400 MHz, CD₂Cl₂, ppm)  
δ 7.90 (td, J = 22.82, 10.41, 10.41 Hz, 4H),  
7.69-7.42 (m, 3H), 5.02 (ddd, J = 11.59, 9.60, 7.30 Hz, 2H), 4.67 (d, J = 11.75 Hz, 1H), 4.44 (d, J = 5.37 Hz, 1H), 4.21-4.12 (m, 1H), 4.07 (d, J = 9.70 Hz, 1H), 3.93-3.78 (m, 2H), 3.60 (dq, J = 10.32, 10.30,
10.30, 4.48 Hz, 2H), 3.53–3.46 (m, 4H), 3.44 (s, 3H), 3.22 (s, 3H), 2.41-2.29 (m, 1H), 2.28-2.16 (m, 1H), 2.13–1.95 (m, 2H), 1.90–1.63 (m, 8H), 1.53–1.41 (m, 3H), 1.03 (t, J = 7.15, 7.15 Hz, 3H), 0.96 (t, J = 6.41, 6.41 Hz, 21H), 0.20 (d, J = 1.91 Hz, 6H), 0.11 (d, J = 10.70 Hz, 6H)

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$ ppm)  
\[ \delta \] 153.74, 136.42, 133.23, 132.81, 127.82, 127.67, 127.53, 126.02, 125.77, 125.73, 125.56, 99.98, 80.57, 79.09, 78.51, 75.78, 75.54, 75.33, 75.25, 73.27, 71.40, 68.74, 68.29, 58.86, 57.85, 48.45, 39.17, 35.74, 35.29, 34.32, 30.01, 29.85, 25.51, 17.88, 17.78, 15.33, 11.42, 4.78, 2.98, -4.57, -4.78, -5.10, -5.22

IR (film)  
2928, 2856, 1812, 1462, 1384, 1254, 1073 cm$^{-1}$
References


Appendix

$^1\text{H-NMR, } ^{13}\text{C-NMR and IR Spectra}$