Supporting Information
Stereoselective Synthesis of the Monomeric Unit of Actin Binding Macrolide Rhizopodin
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3. Spectra (1H and 13C NMR) of compounds: S23-S44
1. General Experimental Procedures:
All reactions were carried out in oven or flame-dried glassware with magnetic stirring under nitrogen atmosphere using dry, freshly distilled solvents, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel plates with UV light, I₂, 7% ethanolic phosphomolybdic acid-heat and 2.5% ethanolic anisaldehyde (with 1% AcOH and 3.3% conc. H₂SO₄)-heat as developing agents. Silica gel finer than 200 mesh was used for flash column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. Optical rotations were measured using Autopol III manufactured by Rudolph using sodium (589, D line) lamp and are reported as follows: [α]D²⁵ (c = g/100 ml, solvent). Analytical HPLC analyses were performed on a Waters 515 HPLC system equipped with a 5 µ Daniel Chiralpak 1A column (25 × 0.46 cm) and photodiode array detector setting of λ =274 nm. IR spectra were recorded as neat liquids or KBr pellets. High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Agilent 6520- Q-TofMS/MS system and JEOL-AccuTOF JMST100LC. Mass spectra were obtained under electron impact ionisation (EI), liquid secondary ion mass spectrometric (LSIMS) technique, electron spray ionisation (ESI) and MALDI techniques. ¹H NMR spectra were recorded on 400, 300 and 200 MHz spectrometers in appropriate solvents and calibrated using residual undeuterated solvent as an internal reference, and the chemical shifts are shown in δ ppm scales. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad), m (multiplet, for unresolved lines), etc. ¹³C NMR spectra were recorded on 100, 75 and 50 MHz spectrometers with complete proton decoupling.
1. Experimental procedures and data for the compounds:

Methyl Ether 11:
TiCl₄ (0.88 mL, 8.1 mmol) was added dropwise to a solution of auxiliary 10 (1.76 g, 8.1 mmol) in CH₂Cl₂ (60 mL) at 0 °C. The yellow rigid suspension was stirred for 5 min at 0 °C and cooled to −78 °C. After 10 min, a solution of i-Pr₂NEt (1.4 mL, 8.1 mmol) in CH₂Cl₂ (10 mL) was added. The dark red enolate solution thus obtained was stirred for 2 h at −40 °C, a solution of SnCl₄ (0.63 mL, 5.4 mmol) in CH₂Cl₂ (10 mL) followed by dimethyl acetal 9 (3 g, 5.4 mmol), as a solution in CH₂Cl₂ (10 mL), were added in dropwise manner at −78 °C. After stirring for 30 min, the resulting mixture was brought to −50 °C and stirred at the same temperature for 4 h, then the reaction mixture was quenched with saturated aqueous NH₄Cl (20 mL) at the same temperature. After warming to room temperature, the mixture was extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (50 mL), brine (50 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 10% EtOAc in hexanes) provided the optically pure methyl ether in 11 (3.05 g, 79%) as yellow oil.

Rₛ: 0.6 (silica gel, 20% EtOAc in hexane); [α]D²⁷: +88.3 (c 0.9, CHCl₃); IR (neat): νmax 3162, 2936, 1695, 1460, 1368, 1220, 1100, 769 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.68 - 7.64 (m, 4H), 7.44 - 7.34 (m, 6H), 5.27 (ddd, J = 7.9, 5.9, 1.4 Hz, 1H), 5.08 - 4.99 (m, 1H), 3.70 - 3.62 (m, 3H), 3.42 (dd, J = 11.5, 8.7 Hz, 1H), 3.27 (s, 3H), 2.95 (dd, J = 11.5, 1.5 Hz, 1H), 2.37 - 2.31 (m, 1H), 1.82 - 1.70 (m, 1H), 1.68 - 1.59 (m, 2H), 1.56 - 1.45 (m, 1H), 1.08 - 1.02 (m, 15H), 0.96 (d, J = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 202.50, 177.05, 135.53, 133.92, 133.90, 129.54, 127.62, 82.40, 71.78, 63.95, 57.26, 41.78, 30.49, 29.01, 27.31, 26.86, 25.76, 19.18, 19.04, 17.06, 13.38; HRMS (ESI): Calcd for C₃₀H₄₃NO₃NaS₂Si [M+Na]+ 580.2351, found 580.2340.
Keto phosphonate 6:

n-BuLi (1.6 M solution in hexane, 7.83 mL, 12.54 mmol) was added to flask with MeP(O)(OMe)$_2$ (1.56 mL, 14.4 mmol) in THF (55 mL) at -78 °C and allowed to stir for 30 min. A solution of compound 11 (2 g, 3.6 mmol) in THF (10 mL × 2) was added to the reaction flask and allowed to stir for additional 30 min. Then the reaction mixture was quenched with saturated aqueous NH$_4$Cl (20 mL) at the same temperature. After warming to room temperature, the mixture was extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (50 mL), brine (50 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 50% EtOAc in hexanes) provided the pure phosphonate 6 (1.7 g, 92%) as clear oil.

$R_f$: 0.6 (silica gel, EtOAc); $[\alpha]_D^{27}$: -51.1 (c 0.5, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3009, 2947, 1712, 1463, 1254, 1217, 1106, 1037, 762 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.67 - 7.65 (m, 4H), 7.43 - 7.36 (m, 6H), 3.79 - 3.75 (m, 6H), 3.68 (t, $J = 6.1$ Hz, 2H), 3.37 (ddd, $J = 9.3$, 5.0, 3.7 Hz, 1H), 3.31 (dd, $J = 22.7$, 14.5 Hz, 1H), 3.23 (s, 3H), 3.09 (dd, $J = 21.7$, 14.3 Hz, 1H), 3.02 - 2.97 (m, 1H), 1.76 - 1.68 (m, 1H), 1.67 - 1.58 (m, 2H), 1.54 - 1.43 (m, 1H), 1.08 (s, 9H), 1.01 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 206.15, 206.10, 135.89, 134.24, 134.23, 129.92, 127.96, 83.47, 64.12, 57.68, 53.32, 53.25, 53.24, 53.17, 50.19, 50.18, 43.13, 41.84, 27.19, 27.16, 26.55, 19.53, 12.83; HRMS (ESI): Calcd for C$_{27}$H$_{41}$O$_6$PNaSi [M+Na]$^+$ 580.2351, found 580.2340.

Homo propargyl alcohol 14:

To a solution of indium (467 mg, 4.08 mmol, 2 eq), chiral amino alcohol 13 (1.96 g, 9.2 mmol) and pyridine (0.75 mL, 9.2 mmol) in THF (60 mL) under argon at RT was slowly added
propargyl bromide (2.73 mL, 18.4 mmol). The cloudy suspension was stirred for 60 min with formation of a coin of indium. Then the reaction was cooled to -78 °C. A solution of aldehyde 12 (1 g, 4.6 mmol) in THF (5 mL) was added dropwise over a period of 30 min and the reaction was stirred for 30 min at -78 °C and then 16 h during a slow warming to RT. After stirring for another 12 h at RT, the reaction mixture was quenched with 1N HCl (20 mL) at the same temperature. The mixture was extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (50 mL), brine (50 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. Purification by column chromatography (silica, 20% EtOAc in hexanes) afforded alcohol 14 as a 10:1 mixture of diastereomers (0.981 g, 83%) as a clear oil.

\[ R_f: 0.5 \text{ (silica gel, 30% EtOAc in hexane)}; \ \left[\alpha\right]_{D}^{27} : +6.1 \text{ (c 1.2, CHCl}_3\right); \ \textbf{IR (neat):} \ \nu_{\text{max}} \text{ 3441, 3308, 2980, 2116, 1656, 1319, 1170, 769 cm}^{-1}\text{; } \textbf{¹H NMR (400 MHz, DMSO-D}_6\text{ at } 90 ^\circ\text{C):} \delta 4.86 \text{ (d, } J = 5.6 \text{ Hz, 1H), 4.03 - 3.79 \text{ (m, 4H), 2.58 (t, } J = 2.4 \text{ Hz, 1H), 2.32} - 2.21 \text{ (m, 2H), 1.49 (s, 3H), 1.45 (s, 12H); } \textbf{¹³C NMR (75 MHz, CDCl}_3\right) \text{ a mixture of carbamate rotamers: } \delta 154.02, 94.32, 81.21, 80.50, 71.49, 70.6, 70.1, 64.63, 64.0, 61.32, 60.20, 28.35, 26.67, 24.01, 23.6; \ \textbf{HRMS (ESI):} \text{ Calcd for C}_{14}H_{23}NO_4Na [M+Na]+ 292.1524, found 292.1511.}

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\[ \text{Vinyl iodide 15:} \]

To a solution of alcohol 14 (0.9 g, 3.5 mmol) in THF (20 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 210 mg, 5.25 mmol). The reaction mixture was stirred at 0 °C for 10 min, then MeI (0.7 mL, 10.5 mmol) followed by Tetra n-butyl ammonium iodide (TBAI) (129 mg, 0.35 mmol) was added. The resultant mixture was stirred at room temperature for 1 h. Then the reaction mixture was cooled to 0 °C , then quenched with saturated aqueous NH₄Cl (10 mL) at the same temperature. After warming to room temperature, the mixture was extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (20 mL), brine (10 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. Purification by column chromatography
(silica, 10% EtOAc in hexanes) allowed the separation of the two diastereoisomers anti/syn and permitted to isolate the major anti methyl ether intermediate A (851 mg, 86%) as a clear oil.

**Rf:** 0.6 (silica gel, 20% EtOAc in hexane); \( \alpha \) : +22.8 (c 1.1, CHCl₃); IR (neat): \( \nu_{\text{max}} \) 3438, 3308, 2980, 2120, 1693, 1389, 1097, 769 cm\(^{-1} \);

**\( ^1H \text{ NMR} \):**

- **(400 MHz, C₆D₆ at 70 °C)**
  - A mixture of carbamate rotamers: \( \delta \) 4.0 - 3.97 (m, 2H), 3.77 (m, 1H), 3.68 (dd, \( J = 8.1, 6.3 \) Hz, 1H), 3.24 (s, 3H), 2.33 (ddd, \( J = 17.1, 5.8, 2.9 \) Hz, 1H), 2.24 (ddd, \( J = 17.1, 6.1, 1.7 \) Hz, 1H), 1.80 (t, \( J = 2.5 \) Hz, 1H), 1.66 (s, 3H), 1.53 (s, 3H), 1.41 (s, 9H);
  - **\( ^{13}C \text{ NMR} \):** A mixture of carbamate rotamers: \( \delta \) 153.06, 95.11, 82.10, 50.29, 80.22, 70.88, 64.64, 61.23, 59.25, 29.14, 27.37, 25.36, 22.47;

**HRMS (ESI):**

- Calcd for C₁₅H₂₅NO₄NaSi [M+Na]+ 306.1681, found 306.1687.

To a solution of Cp₂ZrCl₂ (1.31 g, 4.5 mmol) in THF (18 mL) at 0 °C was added slowly a solution of DIBAL-H in toluene (4.5 mL, 4.5 mmol) under argon. The resultant suspension was stirred for 30 min at 0 °C, followed by addition of a solution of the above methyl ether A (850 mg, 3 mmol) in THF (2 mL). The mixture was warmed to room temperature and stirred until a homogeneous solution resulted (ca. 1 h) and then cooled to –78 °C, followed by addition of I₂ (990 mg, 3.9 mmol) in THF (3 mL). After 30 min at –78 °C, the reaction mixture was quenched with 1N HCl. After warming to RT, the mixture was extracted with diethyl ether (150 mL × 2). The combined organic extracts were washed with Na₂S₂O₃, (10 mL), NaHCO₃, (10 mL), water (10 mL), brine (10 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. Purification by column chromatography (silica, 10% EtOAc in hexanes) afforded E-vinyl iodide 15 (1.035 mg, 91%) as a light yellow oil.

**Rf:** 0.3 (silica gel, 10% EtOAc in hexane); \( \alpha \) : +15.1 (c 0.4, CHCl₃); IR (neat): \( \nu_{\text{max}} \) 3020, 2976, 1683, 1458, 1392, 1217, 765 cm\(^{-1} \);

**\( ^1H \text{ NMR} \):**

- (400 MHz, C₆D₆ at 70 °C) a mixture of carbamate rotamers: \( \delta \) 6.47 (dt, \( J = 14.7, 7.9 \) Hz, 1H), 5.87 (d, \( J = 14.7 \) Hz, 1H) 3.94 - 3.90 (m, 1H), 3.75 (m, 1H), 3.60 (dd, \( J = 8.6, 6.8 \) Hz, 1H), 3.53 (m, 1H), 3.13 (s, 3H), 2.05 - 1.90 (m, 2H), 1.63 (s, 3H), 1.51 (s, 3H), 1.40 (s, 9H);
  - **\( ^{13}C \text{ NMR} \):** A mixture of carbamate rotamers: \( \delta \) 153.18, 143.65, 95.03, 80.36, 80.25, 77.31, 64.89, 64.65, 61.27, 61.07, 59.24, 59.14, 38.88, 29.14, 27.48, 25.49;

**HRMS (ESI):**

**Amino alcohol 7:** A solution of 4 M hydrochloric acid in dioxane (2 ml) was added to the vinyl iodide 15 (35 mg, 0.081 mmol) at 0 °C under argon atmosphere. The solution was stirred for 3 h at room temperature, then toluene (5 ml) was added and the solution was concentrated in vacuo. Two subsequent additions of toluene (2 × 5 ml) followed by concentration in vacuo afforded the crude hydrochloride salt of the amino alcohol 7 as a yellow residue, which was used without further purification. The formation of the product was confirmed by $^1$H NMR of crude reaction mixture and formation of single spot in TLC ($R_f$: 0.5 60% MeOH in EtOAc).

**Alcohol 18:** To a stirred solution of compound 17 (3.0 g, 5.93 mmol) in dry CH$_2$Cl$_2$: H$_2$O (20:1, 20 mL), DDQ (2.02 g, 8.9 mmol) was added at room temperature and stirred at the same temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NaHCO$_3$ (20 mL), extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (25 mL), brine (10 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 20% EtOAc in hexanes) gave alcohol 18 (2.15 g, 94%) as clear oil.

$R_f$: 0.6 (silica gel, 30% EtOAc in hexane); $[\alpha]_D^{27}$: $-16.6$ (c 0.5, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3446, 3073, 2932, 1467, 1428, 1388, 1107, 757 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.69 – 7.63 (m, 4H), 7.42 – 7.34 (m, 6H), 3.74 – 3.66 (m, 3H), 3.56 – 3.45 (m, 2H), 3.33 (s, 3H), 1.96 – 1.88 (m, 1H), 1.73 – 1.65 (m, 2H), 1.06 (s, 9H), 0.93 (d, $J = 7.1$ Hz, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 135.72, 133.91, 129.72, 127.74, 81.92, 65.47, 61.42, 58.02, 38.67, 33.41, 27.01, 19.38, 12.47; HRMS (ESI): Calcd for C$_{23}$H$_{34}$O$_3$NaSi [M+Na]$^+$ 409.2174, found 409.2174.
Alcohol 20:

To a stirred solution of alcohol 18 (2 g, 5.18 mmol) in CH$_2$Cl$_2$ (15 mL) at 0 °C, t-BuOH (1.5 mL) was added followed by Dess–Martin periodinane (3.3 g, 7.8 mmol) under nitrogen atmosphere. The reaction mixture was warmed to RT and stirred for 1 h. Saturated aqueous Na$_2$S$_2$O$_3$ (15 mL) and saturated aqueous NaHCO$_3$ (15 mL) solutions were added. The resultant biphasic mixture was stirred for 15 min and then extracted with EtOAc (100 mL × 2). The combined organic extracts were washed with water (25 mL), brine (10 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. The crude residue obtained was directly used for the next reaction without any further characterization.

To a stirred solution of the above aldehyde (2 g, 5.18 mmol) in 20 mL of CH$_2$Cl$_2$ at -78 °C prenyl stannane 19 (1.96 mL, 5.7 mmol) was added followed by slow addition of TiCl$_4$ (0.56 mL, 5.18 mmol) at –78 °C. Reaction mixture was maintained at the same temperature for 10 min, quenched with saturated aqueous NaHCO$_3$ (10 mL). After warming to RT the mixture was extracted with EtOAc (100 mL × 2). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 10% EtOAc in hexanes) gave alcohol (anti isomer) 20 (1.841g, 78%) as clear oil.

$R_f$: 0.4 (silica gel, 15% EtOAc in hexane); [α]$_D^{27}$ : -10.4 (c 0.4, CHCl$_3$); IR (neat): $\nu_{max}$ 3415, 3018, 2960, 1634, 1466, 1107, 769, 702 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 – 7.64 (m, 4H), 7.42 – 7.35 (m, 6H), 5.79 (dd, $J = 17.4$, 11.0 Hz, 1H), 5.05 – 4.96 (m, 2H), 3.65 (dd, $J = 9.8$, 5.1 Hz, 1H) 3.55 – 3.47 (m, 3H), 3.36 (s, 3H), 2.30 (bs, 1H), 1.92 (sep, $J = 6.0$ Hz, 1H), 1.73 – 1.27 (m, 2H), 1.06 (s, 9H), 1.00 - 0.98 (m, 6H), 0.95 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 145.44, 135.75, 135.72, 133.95, 133.89, 129.70, 127.73, 113.16, 80.66, 75.01, 65.62, 58.63, 41.50, 39.04, 32.41, 27.03, 22.98, 22.45, 19.42, 13.05; HRMS (ESI): Calcd for C$_{28}$H$_{42}$O$_3$NaSi $[M+Na]^+$ 477.2800, found 477.2821.
PMB Ether 21:
To a stirred solution of alcohol 20 (1.80 g, 3.96 mmol) and PMBOC(=NH)CCl₃ (2.23 g, 7.93 mmol) in dry toluene (35 mL), La(OTf)₃ (117 mg, 0.2 mmol) was added at room temperature. The reaction was allowed to stir for 24 h, and then concentrated in vacuo. In order to precipitate trichloroacetamide, the residual oil was taken up in n-pentane/CH₂Cl₂ mixture (3/1, 50 mL) and filtered. The filtrate was concentrated and purification by column chromatography (silica gel, 6% EtOAc in hexane) gave PMB ether 21 (2.1 g, 92%) as clear oil.

Rᶠ: 0.4 (silica gel, 10% EtOAc in hexane); [α]D²⁷ : -10.4 (c 0.4, CHCl₃); IR (neat): ν max 3078, 2987, 2864, 1562, 1458, 1208, 1136, 1058, 756 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.68 – 7.64 (m, 4H), 7.41 – 7.34 (m, 6H), 7.27 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 7.1 Hz, 2H), 5.93 (dd, J = 17.1, 11.3 Hz, 1H), 5.03 – 4.99 (m, 2H), 4.59 (d, J = 11.1 Hz, 1H), 4.53 (d, J = 11.1 Hz, 1H), 3.79 (s, 3H), 3.68 (dd, J = 10.3, 6.2 Hz, 1H) 3.57 – 3.47 (m, 2H), 3.32 (dd, J = 10.0, 1.9 Hz, 1H), 3.29 (s, 3H), 2.02 - 1.94 (m, 1H), 1.72 – 1.42 (m, 2H), 1.05 - 1.04 (m, 15H), 0.91 (d, J = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 159.07, 146.23, 135.74, 135.70, 134.05, 131.57, 129.61, 129.59, 128.97, 127.68, 113.79, 111.76, 83.97, 79.50, 74.86, 65.36, 57.21, 55.35, 42.47, 38.47, 33.73, 27.03, 24.16, 23.09, 19.36, 12.48; HRMS (ESI): Calcd for C₃₆H₅₀O₄NaSi [M+Na]⁺ 574.3375, found 574.3375.

Hydroxy Ester 23:
To a solution of the alkene 21 (1 g, 1.74 mmol) in THF:H₂O (3:1, 12 mL) was added NMO (408 mg, 3.48 mmol), a 0.04 M solution of OsO₄ in toluene (4.35 mL, 0.174 mmol) at 0 °C. The reaction was stirred at rt for 12 h. H₂O (10 mL) and CH₂Cl₂ (50 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (100 mL × 2). The organic layers were combined, dried using Na₂SO₄, filtered and concentrated in vacuo. The crude diol was used for the next step without further purification.
To a solution of the above crude diol in THF:pH=7 buffer (1:1, 12 mL) was added NaIO₄ (556 mg, 2.61 mmol) at 0 °C. The reaction was stirred at rt for 0.5 h, quenched with saturated aqueous NaHCO₃ (1 mL) and extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na₂SO₄) filtered and concentrated in vacuo. The crude aldehyde was used for the next step without further purification.

To a stirred solution of the above crude aldehyde in 10 mL of dry toluene at -78 °C, enol silane 22 (0.57 mL, 2.61 mmol) was added followed by slow addition of BF₃·Et₂O (0.194 mL, 1.56 mmol) at –78 °C. Reaction mixture was maintained at the same temperature for 5 min, quenched with saturated aqueous NaHCO₃ (5 mL). After warming to RT the mixture was extracted with EtOAc (100 mL × 2). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na₂SO₄) filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 20% EtOAc in hexanes) gave β-hydroxy ester 23 (927 mg, 82%) as a 76:23 mixture of inseparable mixture of diastereoisomers.

Rₛ: 0.4 (silica gel, 30% EtOAc in hexane); [α]D²⁷: -18.5 (c 0.4, CHCl₃); IR (neat): νmax 3078, 2987, 2864, 1562, 1458, 1208, 1136, 1058, 756 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ 7.67 - 7.65 (m, 4H), 7.43 - 7.35 (m, 6H), 7.21 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.60 (d, J = 11.0 Hz, 1H), 4.57 (d, J = 11.0 Hz, 1H), 4.18 - 4.14 (m, 2H), 3.77 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 173.38, 159.25, 135.65, 133.81, 130.25, 129.63, 129.09, 127.69, 113.85, 85.03, 82.46, 80.90, 79.35, 75.41, 74.18, 73.02, 72.55, 65.04, 57.40, 55.26, 51.78, 42.49, 41.10, 38.30, 37.35, 33.53, 33.12, 26.94, 22.38, 19.99, 19.29, 18.43, 12.42; HRMS (ESI): Calcd for C₃₈H₅₄O₇Si [M+Na]+ 673.3513, found 673.3536.

(R)-MTPA ester: To a solution of (R)-Mosher’s acid (30 mg, 0.12 mmol) in dry toluene (1 mL) were added DMAP (16 mg, 0.13 mmol), triethylamine (18 µL, 0.13 mmol) and 2,4,6-
trichlorobenzoyl chloride (19 µL, 0.12 mmol), successively. After stirring for 30 minutes, a solution of alcohol 23 (25 mg, 0.04 µmol) in dry toluene (0.5 mL) was added. After stirring for 6h, the reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL) and extracted with EtOAc (30 mL × 2). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na₂SO₄) and concentrated in vacuo. Purification by column chromatography (silica gel, 18% EtOAc in hexanes) gave (R)-MTPA ester (26 mg, 75%) as a 76:23 mixture of diastereoisomers. 

**Rf:** 0.4 (silica gel, 20% EtOAc in hexane); [α]D²⁷: -5.4 (c 0.8, CHCl₃); **IR (neat):** νmax 3064, 2924, 2867, 1743, 1368, cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 7.67 - 7.64 (m, 4H), 7.58 - 7.55 (m, 2H), 7.43 - 7.33 (m, 9H), 7.23 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.61 (dd, J = 9.1, 3.0 Hz, 1H), 4.47 (d, J = 11.0 Hz, 1H), 4.40 (d, J = 11.0 Hz, 1H), 3.79 (s, 3H), 3.67 (dd, J = 10.1, 6.2 Hz, 1H), 3.59 (s, 3H), 3.54 - 3.36 (m, 5H), 3.35 (dd, J = 6.6, 5.5 Hz, 1H), 3.23 (s, 3H), 2.97 (d, J = 16.0, 0.2Hz), 2.78 (dd, J = 16.1, 2.4 Hz, 0.8Hz), 2.57 (dd, J = 16.1, 9.0 Hz, 1H), 2.0 - 1.95 (m, 1H), 1.55 - 1.52 (m, 2H), 1.05 (s, 9H), 0.90 (d, J = 6.8 Hz, 3H), 0.85 (s, 3H), 0.84 (s, 3H); **¹³C NMR (75 MHz, CDCl₃):** δ 171.35, 165.81, 159.10, 135.72, 135.66, 133.94, 132.17, 131.03, 129.66, 129.64, 129.55, 128.93, 128.32, 127.71, 127.59, 113.80, 80.89, 79.53, 78.02, 74.79, 65.28, 57.41, 55.45, 55.33, 51.92, 42.83, 38.66, 35.97, 33.69, 27.00, 20.08, 19.47, 19.34, 12.41; **HRMS (ESI):** Calcd for C₄₈H₆₁F₃O₆NaSi [M+Na]+ 889.3934, found 889.3925.

(−)-MTPA ester: To a solution of (S)-Mosher’s acid (30 mg, 0.12 mmol) in dry toluene (1 mL) were added DMAP (16 mg, 0.13 mmol), triethylamine (18 µL, 0.13 mmol) and 2,4,6-trichlorobenzoyl chloride (19 µL, 0.12 mmol), successively. After stirring for 30 minutes, a solution of alcohol 23 (25 mg, 0.04 µmol) in dry toluene (0.5 mL) was added. After stirring for 15 min, the reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL) and extracted with EtOAc (30 mL × 2). The combined organic extracts were washed with water (10 mL), brine...
(10 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. Purification by column chromatography (silica gel, 18% EtOAc in hexanes) gave (S)-MTPA ester (13 mg, 38%) as a 76:23 mixture of diastereoisomers.

$R_f$: 0.4 (silica gel, 20% EtOAc in hexane); $[\alpha]_D^{27}$ : $-14.7$ (c 0.1, CHCl$_3$); IR (neat): $v_{max}$ 3064, 2925, 2868, 1742, 1696, 1460, 1370, 1108, 767 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 - 7.64 (m, 4H), 7.57 - 7.55 (m, 2H), 7.42 - 7.34 (m, 9H), 7.24 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.64 (dd, $J = 8.6$, 2.5 Hz, 1H), 4.51 (d, $J = 11.0$ Hz, 1H), 4.46 (d, $J = 11.0$ Hz, 1H), 3.78 (s, 3H), 3.68 (dd, $J = 9.9$, 6.5 Hz, 1H), 3.61 - 3.50 (m, 5H), 3.47 (s, 3H), 3.42 (dd, $J = 7.7$, 2.3 Hz, 1H), 3.26 (s, 3H), 2.98 (d, $J = 16.1$, 0.2H), 2.74 (dd, $J = 15.9$, 2.6 Hz, 0.8H), 2.50 (dd, $J = 15.9$, 8.8 Hz, 1H), 2.01 - 1.94 (m, 1H), 1.60 - 1.56 (m, 2H), 1.04 (s, 9H), 0.91 (s, 3H), 0.90 (d, $J = 6.8$ Hz, 3H), 0.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.13, 165.78, 159.01, 135.64, 135.58, 133.86, 131.73, 130.99, 129.57, 129.55, 129.52, 129.47, 128.88, 128.35, 127.88, 127.63, 127.62, 113.71, 80.79, 79.49, 77.89, 74.48, 65.17, 57.35, 55.27, 51.85, 42.70, 38.52, 35.68, 33.54, 29.70, 26.92, 20.03, 19.45, 19.26, 12.36; HRMS (ESI): Calcd for C$_{48}$H$_{65}$F$_3$O$_9$NSi [M+NH$_4$]+ 884.4420, found 884.4385.

**Determination of the absolute configuration:** The $\Delta \delta$ values ($\delta_S - \delta_R$) for these MTPA esters described below:

The $\Delta \delta$ values ($\delta_S - \delta_R$) for MTPA esters in ppm (400 MHz) proves that the S-isomer is the major product (see. Seco, J. M.; Quinoa, E.; Riguera, R. Chem. Rev. 2004, 104, 17.)

**TBS Ether 8a:**
To a solution of alcohol 23 (1.7 g, 2.61 mmol) in CH₂Cl₂ (10 mL), 2,6-lutidine (0.92 mL, 7.84 mmol) followed by TBSOTf (0.9 mL, 3.91 mmol) were added at 0 ºC. After stirring for 15 min, the reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL) and extracted with EtOAc (100 mL × 2). The combined organic extracts were washed with saturated aqueous CuSO₄ (10 mL), water (10 mL), brine (10 mL), dried (Na₂SO₄) and concentrated in vacuo. Purification by column chromatography (silica gel, 10% EtOAc in hexanes) gave silyl ether 8a (1.970 g, 97%) as a 76:23 mixture of diastereoisomers.

R₉: 0.4 (silica gel, 10% EtOAc in hexane); [α]D²⁷ : −17.3 (c 0.4, CHCl₃); IR (neat): νmax 2958, 2858, 1734, 1460, 1250, 1082, 769 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.68 - 7.64 (m, 4H), 7.44 - 7.34 (m, 6H), 7.27 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 4.57 (s, 2H), 4.20 (dd, J = 7.4, 3.0 Hz, 1H), 3.79 (s, 3H), 3.69 (dd, J = 10.2, 6.4 Hz, 1H), 3.62 (s, 3H), 3.57 - 3.48 (m, 3H), 3.31 (s, 3H), 2.86 (dd, J = 16.3, 2.0 Hz, 0.2H), 2.69 (dd, J = 16.3, 2.9 Hz, 0.8H), 2.36 (dd, J = 16.3, 7.6 Hz, 1H), 2.05 - 1.95 (m, 1H), 1.63 - 1.50 (m, 2H), 1.04 (s, 9H), 0.92 - 0.87 (m, 18H), 0.06 (s, 3H), -0.03 (s, 3H); ¹³C NMR (50 MHz, CDCl₃): δ 173.21, 158.99, 135.76, 135.72, 134.03, 131.57, 129.65, 129.63, 129.02, 128.76, 127.73, 113.79, 81.53, 79.63, 74.64, 74.33, 65.49, 57.44, 55.39, 51.60, 44.07, 38.89, 38.77, 33.49, 27.06, 26.20, 20.64, 19.94, 19.39, 18.47, 12.50, -3.95, -4.39; HRMS (ESI): Calcd for C₄₄H₆₈O₇NaSi₂ [M+Na]+ 787.4401, found 787.4374.

Carboxylic Acid 8: To a solution of silyl ether (1.9 g, 2.43 mmol) in THF:i-PrOH:H₂O (1:4:1, 10 mL) at 60 ºC, LiOH·H₂O (614 mg, 14.6 mmol) was added and continued to stir at same temperature for 24 h. The reaction mixture was cooled to 0 ºC, then acidified to pH ~ 2 with 20% citric acid and extracted with EtOAc (150 mL × 2). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na₂SO₄) filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 20% EtOAc in hexane) gave carboxylic acid 8 (1.69 g, 93%) as a 76:23 mixture of diastereoisomers.
$R_f$: 0.4 (silica gel, 30% EtOAc in hexane); $[\alpha]_D^{27} = -14.2$ (c 2.2, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3472, 3024, 2947, 1718, 1087, 768 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 - 7.69 (m, 4H), 7.44 - 7.34 (m, 6H), 7.31 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.64 (s, 2H), 4.23 (dd, $J = 7.4$, 3.3 Hz, 1H), 3.81 (s, 3H), 3.74 (dd, $J = 9.7$, 5.8 Hz, 1H), 3.63 - 3.54 (m, 3H), 3.35 (s, 3H), 2.99 (dd, $J = 16.0$, 2.7 Hz, 0.2H), 2.82 (dd, $J = 16.3$, 3.1 Hz, 0.8H), 2.46 (dd, $J = 16.0$, 7.1 Hz, 1H), 2.07 - 2.00 (m, 1H), 1.71 - 1.57 (m, 2H), 1.11 (s, 3H), 1.10 (s, 9H), 0.99 (s, 3H), 0.96 - 0.92 (m, 12H), 0.11 (s, 3H), 0.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.11, 178.48, 159.01, 158.98, 135.72, 135.67, 135.28, 134.88, 133.96, 134.44, 131.35, 129.69, 129.63, 129.61, 128.74, 127.77, 127.69, 113.79, 81.64, 81.21, 79.72, 79.52, 74.67, 74.41, 74.32, 74.21, 65.46, 65.32, 57.54, 55.30, 44.08, 43.80, 39.36, 38.85, 38.75, 38.43, 33.77, 27.03, 26.64, 26.22, 26.19, 20.66, 19.99, 19.35, 18.42, 12.37, -3.81, -3.90, -4.40, -4.67; HRMS (ESI): Calcd for C$_{43}$H$_{67}$O$_7$Si$_2$ [M+H]$^+$ 751.4426, found 751.4417.

**Hydroxy Amide 24:**

NEt$_3$ (0.05 mL, 0.243 mmol) was added in one portion to a stirred solution of the crude aminoalcohol 7 (0.081 mmol) in THF (2 ml) at 0 °C under a nitrogen atmosphere. The solution was stirred at 0 °C for 15 min and then carboxylic acid 8 (67 mg, 0.081 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (24 mg, 0.121 mmol) and 1-hydroxybenzotriazole (17 mg, 0.121 mmol) were added separately, each in one portion. After stirring for 12 h at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated NH$_4$Cl solution (5 mL), saturated NaHCO$_3$ solution (5 mL), water (5 mL), brine (5 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 25% EtOAc in hexanes) allowed the separation of the two diastereoisomers anti/syn and permitted to isolate the major anti hydroxyamide 24 (48 mg, 58%), along with the corresponding minor syn diastereoisomer (14 mg, 18%).
Major Isomer:

$R_f$: 0.5 (silica gel, 40% EtOAc in hexane); [α]$_D$$^27$ : $-16.2$ (c 0.6, CHCl$_3$); IR (neat): $v_{max}$ 3368, 3019, 2983, 1646, 1465, 1216, 769 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 - 7.64 (m, 4H), 7.43 - 7.33 (m, 6H), 7.27 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.52 (dt, $J = 14.6$, 7.3 Hz, 1H), 6.30 (d, $J = 7.7$ Hz, 1H), 6.16 (d, $J = 14.6$ Hz, 1H), 4.61 (d, $J = 11.0$ Hz, 1H), 4.56 (d, $J = 11.0$ Hz, 1H), 4.09 (t, $J = 4.7$ Hz, 1H), 3.94 - 3.87 (m, 1H), 3.82 - 3.75 (m, 4H), 3.69 (dd, $J = 10.1$, 6.3 Hz, 1H), 3.57 - 3.49 (m, 4H), 3.43 - 3.38 (m, 1H), 3.34 (s, 3H), 3.31 (s, 3H), 2.70 (dd, $J = 15.6$, 4.1 Hz, 1H), 2.46 (bs, 1H), 2.39 - 2.19 (m, 3H), 2.04 - 1.93 (m, 1H), 1.58 (t, $J = 5.8$ Hz, 2H), 1.04 (s, 9H), 0.95 (s, 3H), 0.93 - 0.88 (m, 15H), 0.07 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 172.29, 159.05, 141.53, 135.73, 135.69, 134.01, 131.53, 129.65, 128.79, 127.72, 113.86, 82.27, 81.62, 79.97, 74.83, 74.59, 65.51, 61.98, 58.51, 57.80, 55.39, 52.76, 44.40, 41.01, 39.01, 37.39, 34.18, 27.05, 26.24, 21.33, 20.77, 19.38, 18.41, 12.51, -3.67, -4.55; HRMS (ESI): Calcd for C$_{50}$H$_{78}$NO$_8$NaSi$_2$ [M+Na]$^+$ 1026.4208, found 1026.4216.

Minor Isomer:

$R_f$: 0.6 (silica gel, 40% EtOAc in hexane); [α]$_D$$^27$ : $-9.8$ (c 1.5, CHCl$_3$); IR (neat): $v_{max}$ 3300, 2982, 1641, 1219, 1083, 767 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 - 7.65 (m, 4H), 7.41 - 7.34 (m, 6H), 7.28 (d, $J = 8.2$ Hz, 2H), 6.85 (d, $J = 8.2$ Hz, 2H), 6.54 (dt, $J = 14.6$, 7.3 Hz, 1H), 6.21 (d, $J = 6.7$ Hz, 1H), 6.18 (d, $J = 14.6$ Hz, 1H), 4.61 (d, $J = 11.0$ Hz, 1H), 4.56 (d, $J = 11.0$ Hz, 1H), 4.21 (dd, $J = 6.4$, 3.2 Hz, 1H), 3.94 (dd, $J = 12.3$, 2.8 Hz, 1H), 3.85 (dd, $J = 7.5$, 3.6 Hz, 1H), 3.79 (s, 3H), 3.73 (dd, $J = 9.9$, 6.3 Hz, 1H), 3.63 - 3.49 (m, 5H), 3.35 (s, 3H), 3.31 (s, 3H), 2.75 (dd, $J = 15.8$, 3.1 Hz, 1H), 2.38 - 2.20 (m, 3H), 2.06 - 1.98 (m, 1H), 1.70 - 1.49 (m, 3H), 1.05 (s, 9H), 0.95 (s, 3H), 0.94 (s, 3H), 0.9 - 0.88 (m, 12H), 0.09 (s, 3H), 0.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.19, 159.00, 141.51, 135.72, 135.67, 134.00, 131.55, 129.61, 129.59, 128.94, 127.68, 113.81, 81.88, 80.88, 79.50, 77.74, 74.60, 74.22, 65.45, 61.86, 58.86, 57.41, 55.34, 52.46, 43.75, 41.28, 38.68, 37.65, 33.60, 29.77, 27.01, 26.29, 22.76, 21.20, 19.35, 18.40, 14.19, 12.51, -3.86, -4.79; HRMS (ESI): Calcd for C$_{50}$H$_{79}$NO$_8$Si$_2$ [M+H]$^+$ 1004.4388, found 1004.4376.

S15
Oxazole 25:

To a solution of hydroxy amide 24 (47 mg, 0.047 mmol) in CH$_2$Cl$_2$ (2 mL) were added $t$-BuOH (0.2 mL), NaHCO$_3$ (40 mg, 0.473 mmol) and Dess-Martin periodinane (100 mg, 0.236 mmol). The mixture was stirred for 45 min then filtered through a plug of silica gel, eluting with hexanes–ethyl acetate (5:1 to 3:2). Concentration of the eluant gave the crude aldehyde.

To a stirred solution of the crude aldehyde in CH$_2$Cl$_2$ (2 mL) at 0 °C under a nitrogen atmosphere, 2,6-di-tert-butyl-4-methylpyridine (100 mg, 0.474 mmol), triphenylphosphine (62 mg, 0.236 mmol) and dibromotetrachloroethane (77 mg, 0.236 mmol) were added successively, each in one portion. The reaction mixture was stirred at room temperature for 1 h and then 1,8-diazabicyclo[5.4.0]undec-7-ene (0.036 mL, 0.236 mmol) in acetonitrile (1 mL) was added dropwise, over a period of 10 min. After stirring for 3 h at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated NH$_4$Cl solution (5 mL), water (5 mL), brine (5 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 10% EtOAc in hexanes) afforded the oxazole 25 (35 mg, 74%) as light yellow oil.

$R_f$: 0.6 (silica gel, 20% EtOAc in hexane); $\left[\alpha\right]_D^{27}$: $-26.3$ ($c$ 0.8, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3016, 2934, 1515, 1464, 1216, 1101, 765 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 - 7.64 (m, 4H), 7.41 - 7.34 (m, 7H), 7.26 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 6.52 (dt, $J = 14.4$, 7.2 Hz, 1H), 6.08 (d, $J = 14.4$ Hz, 1H), 4.58 (s, 2H), 4.21 (dd, $J = 7.6$, 2.6 Hz, 1H), 4.17 (t, $J = 6.5$ Hz, 1H), 3.79 (s, 3H), 3.71 (dd, $J = 10.1$, 6.0 Hz, 1H), 3.60 - 3.49 (m, 3H), 3.31 (s, 3H), 3.29 (s, 3H), 3.07 (dd, $J = 15.8$, 2.9 Hz, 1H), 2.86 (dd, $J = 15.8$, 7.8 Hz, 1H), 2.53 (t, $J = 6.5$ Hz, 2H), 2.06 - 1.98 (m, 1H), 1.66 - 1.57 (m, 2H), 1.05 (s, 9H), 0.94 - 0.89 (m, 9H), 0.84 (s, 9H), -0.02 (s, 3H), -3.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.11, 158.98, 142.03, 140.20, 135.55, 135.69, 135.17, 134.03, 133.99, 134.54, 129.64, 129.62, 128.75, 127.71, 113.77, 81.58, 79.73, 77.34, 75.56, 75.48, 74.64, 65.38, 57.46, 57.05, 55.37, 44.29, 41.00, 38.64, 33.44, 32.85, 27.02, 26.15,
20.74, 19.87, 19.35, 18.38, 12.55, -4.32, -4.47; **HRMS (ESI):** Calcd for C\textsubscript{50}H\textsubscript{74}INO\textsubscript{7}NaSi\textsubscript{2} [M+Na]+ 1006.3945, found 1006.3940.

**Alcohol 26:** AcOH (0.042 mL, 0.074 mmol) was added to a solution of TBAF (1.0 M in THF, 0.072 mL, 0.072 mmol) in DMF (1.0 mL) at room temperature and the mixture was stirred at room temperature for 1h, then a solution of 25 (35 mg, 0.036 mmol) in DMF (1.0 mL) was added dropwise over a period of 5 min at 0 °C. After stirring for 6 h at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated NaHCO\textsubscript{3} solution (5 mL), water (5 mL), brine (5 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 25% EtOAc in hexanes) afforded the alcohol 26 (23 mg, 84%).

\(R_f\): 0.3 (silica gel, 40% EtOAc in hexane); [\(\alpha\)]\textsubscript{D}\textsuperscript{27} : -41.7 (c 0.2, CHCl\textsubscript{3}); **IR (neat):** \(\nu_{\text{max}}\) 3478, 3010, 2986, 1460, 1217, 770 cm\textsuperscript{-1}; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.46 (s, 1H), 7.28 (d, \(J = 8.7\) Hz, 2H), 6.84 (d, \(J = 8.7\) Hz, 2H), 6.53 (dt, \(J = 14.7, 7.3\) Hz, 1H), 6.10 (d, \(J = 14.7\) Hz, 1H), 4.64 (d, \(J = 11.0\) Hz, 1H), 4.50 (d, \(J = 11.0\) Hz, 1H), 4.22 - 4.17 (m, 2H), 3.80 (s, 3H), 3.74 - 3.69 (m, 1H), 3.64 - 3.62 (m, 1H), 3.54 (dd, \(J = 10.9, 4.8\) Hz, 1H), 3.45 - 3.41 (m, 1H), 3.37 (s, 3H), 3.32 (s, 3H), 3.10 (dd, \(J = 15.8, 2.1\) Hz, 1H), 2.85 (dd, \(J = 15.8, 7.9\) Hz, 1H), 2.55 (t, \(J = 6.7\) Hz, 2H), 2.35 - 2.27 (m, 1H), 1.83 – 1.74 (m, 3H), 0.96 (s, 3H), 0.95 (s, 3H), 0.86 (s, 9H), 0.83 (d, \(J = 7.2\) Hz, 3H), 0.01 (s, 3H), -0.34 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 164.31, 159.16, 142.06, 140.41, 135.26, 134.45, 128.85, 113.89, 82.92, 81.49, 77.31, 76.00, 75.53, 75.00, 65.30, 57.11, 57.08, 55.43, 44.35, 41.06, 35.00, 32.85, 31.10, 26.18, 20.84, 20.17, 18.41, 13.19, -4.31, -4.51; **HRMS (ESI):** Calcd for C\textsubscript{34}H\textsubscript{56}INO\textsubscript{7}NaSi [M+Na]+ 768.2768, found 768.2765.
Enone 27:

To a solution of alcohol 26 (23 mg, 0.030 mmol) and \( i\text{-Pr}_2\text{NEt} \) (0.08 mL, 0.45 mmol) in \( \text{CH}_2\text{Cl}_2:\text{DMSO} \) (10:1, 2 mL) at 0 \( ^\circ \text{C} \) was added \( \text{SO}_3\cdot\text{Py} \) (24 mg, 0.15 mmol) and the reaction mixture was stirred at 0 \( ^\circ \text{C} \) for 30 min. A solution of saturated \( \text{NH}_4\text{Cl} \) solution (5 mL) was added and the mixture was extracted with EtOAc (30 mL × 2). The combined organic extracts were washed with water (5 mL), brine (5 mL), dried (\( \text{Na}_2\text{SO}_4 \)), filtered and concentrated in vacuo. The crude aldehyde was used for the next step without further purification.

To a solution of ketophosphonate 6 (31.2 mg, 0.060 mmol) in THF (2 mL) and \( \text{H}_2\text{O} \) (0.05 mL) at room temperature, \( \text{Ba(OH)}_2\cdot8\text{H}_2\text{O} \) (10 mg, 0.030 mmol) was added and allowed to stir for 30 min. A solution of the above aldehyde in THF (1 mL) was added to the reaction flask. After stirring for 6 h at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated \( \text{NH}_4\text{Cl} \) solution (5 mL), saturated \( \text{NaHCO}_3 \) solution (5 mL), water (5 mL), brine (5 mL), dried (\( \text{Na}_2\text{SO}_4 \)), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 15\% EtOAc in hexanes) afforded the enone 27 (30 mg, 86\%) as a colorless oil.

\( R_f \): 0.5 (silica gel, 20\% EtOAc in hexane); \([\alpha]_D^{27} \) : -38.1 (c 0.8, \( \text{CHCl}_3 \)); \( \text{IR (neat)} \): \( \nu_{\text{max}} \) 3010, 2926, 1686, 1514, 1463, 1376, 1216, 1094, 910, 764 cm\(^{-1} \); \( ^1\text{H NMR (400 MHz, CDC}_3\text{)} \): \( \delta \) 7.68 - 7.64 (m, 4H), 7.48 (s, 1H), 7.44 - 7.35 (m, 6H), 7.29 (d, \( J = 8.4 \) Hz, 2H), 6.96 (dd, \( J = 16.1, 6.6 \) Hz, 1H), 6.90 (d, \( J = 8.4 \) Hz, 2H), 6.53 (dt, \( J = 14.4, 7.2 \) Hz, 1H), 6.18 (d, \( J = 16.1 \) Hz, 1H), 6.09 (d, \( J = 14.4 \) Hz, 1H), 4.65 (d, \( J = 11.1 \) Hz, 1H), 4.50 (d, \( J = 11.1 \) Hz, 1H), 4.21 - 4.14 (m, 2H), 3.80 (s, 3H), 3.67 (t, \( J = 6.0 \) Hz, 2H), 3.63 (dd, \( J = 8.9, 1.9 \) Hz, 1H), 3.51 - 3.47 (m, 1H), 3.40 (dt, \( J = 9.8, 3.5 \) Hz, 1H), 3.34 (s, 3H), 3.31 (s, 3H), 3.24 (s, 3H), 3.08 (dd, \( J = 16.1, 2.9 \) Hz, 1H), 3.02 (t, \( J = 7.5 \) Hz, 1H), 2.87 (dd, \( J = 15.8, 7.9 \) Hz, 1H), 2.79 (dd, \( J = 11.7, 6.1 \) Hz, 1H), 2.55 (t, \( J = 6.8 \) Hz, 2H), 1.74 - 1.44 (m, 6H), 1.07 - 1.04 (m, 12H), 0.99 (d, \( J = 7.1 \) Hz, 3H), 0.92 (s, 3H), 0.92 (s, 3H).
0.91 (s, 3H), 0.85 (s, 9H), -0.01 (s, 3H), -3.33 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 202.68, 163.98, 159.11, 148.51, 142.06, 140.24, 135.64, 135.32, 134.10, 131.48, 129.62, 128.91, 128.73, 127.69, 113.86, 82.46, 81.62, 81.16, 77.28, 75.66, 75.46, 74.84, 64.06, 63.92, 57.75, 57.01, 55.37, 47.13, 44.24, 41.00, 38.17, 33.06, 32.93, 27.61, 26.97, 26.74, 26.15, 20.87, 20.06, 19.29, 18.38, 14.60, 13.01, -4.34, -4.44; HRMS (ESI): C$_{59}$H$_{88}$INO$_9$NaSi$_2$ [M+Na]$^+$ 1160.4939, found 1160.4943.

Ketone 3a:

To a stirred solution of enone 27 (30 mg, 0.013 mmol) in degassed benzene (2 mL) at room temperature was added [{Ph$_3$PCuH)$_6$} (75 mg, 0.04 mmol). After stirring for 6 h at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated NH$_4$Cl solution, water (5 mL), brine (5 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 18% EtOAc in hexanes) gave keto compound 3a (24 mg, 82%) as clear oil.

$R_f$: 0.6 (silica gel, 20% EtOAc in hexane); [\(\alpha\)]$_D^{27}$: -33.7 (c 0.5, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3020, 2934, 1712, 1519, 1465, 1216, 1096, 910, 765 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 - 7.64 (m, 4H), 7.48 (s, 1H), 7.42 - 7.36 (m, 6H), 7.29 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.54 (dt, $J = 14.4$, 7.3 Hz, 1H), 6.10 (d, $J = 14.4$ Hz, 1H), 4.63 (d, $J = 11.1$ Hz, 1H), 4.52 (d, $J = 11.1$ Hz, 1H), 4.22 - 4.17 (m, 2H), 3.86 (s, 3H), 3.67 (t, $J = 6.3$ Hz, 2H), 3.62 (dd, $J = 8.8$, 2.7 Hz, 1H), 3.46 - 3.42 (m, 1H), 3.34 - 3.30 (m, 7H), 3.23 (s, 3H), 3.09 (dd, $J = 15.9$, 2.8 Hz, 1H), 2.87 (dd, $J = 15.8$, 8.0 Hz, 1H), 2.76 (dd, $J = 8.5$, 7.2 Hz, 1H), 2.59 - 2.47 (m, 4H), 1.89 - 1.67 (m, 3H), 1.64 - 1.52 (m, 4H), 1.49 - 1.41 (m, 1H), 1.34 - 1.28 (m, 1H), 1.04 (s, 9H), 0.96 - 0.93 (m, 9H), 0.86 (s, 3H), 0.85 (s, 9H), 0.01 (s, 3H), -3.33 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 213.96, 164.14, 159.05, 142.11, 140.28, 135.66, 135.23, 134.09, 131.69, 129.65, 128.75, 127.70, 113.82, 82.52, 82.42, 81.52, 77.28, 75.75, 75.33, 74.82, 64.03, 57.52, 57.04, 56.78, 55.38, 49.38,
Vinyl iodide 3:

To a stirred solution of compound 3a (24 mg, 0.021 mmol) in CH$_2$Cl$_2$: pH=7 buffer (20:1, 2 mL), DDQ (181 mg, 0.79 mmol) was added at room temperature. After stirring for 4 h at the same temperature, the reaction mixture was diluted with EtOAc, washed with saturated NaHCO$_3$ solution, water (5 mL), brine (5 mL), dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 25% EtOAc in hexanes) gave alcohol 3 (20 mg, 95%) as colorless oil.

$R_f$: 0.3 (silica gel, 25% EtOAc in hexane); $[\alpha]_D^{27}$: -38.7 (c 0.4, CHCl$_3$); IR (neat): $\nu_{\text{max}}$ 3410, 3023, 2967, 1720, 1456, 1217, 1085, 769 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 - 7.64 (m, 4H), 7.42 - 7.36 (m, 6H), 6.51 (dt, $J=14.5$, 7.3 Hz, 1H), 6.11 (d, $J=14.5$ Hz, 1H), 4.22 - 4.17 (m, 2H), 3.99 - 3.96 (m, 1H), 3.17 (dd, $J=15.7$, 3.5 Hz, 1H), 3.00 (dd, $J=15.7$, 7.4 Hz, 1H), 2.78 - 2.70 (m, 1H), 2.56 (t, $J=7.1$ Hz, 2H), 2.52 - 2.42 (m, 2H), 1.83 - 1.69 (m, 4H), 1.64 - 1.57 (m, 2H), 1.49 - 1.42 (m, 1H), 1.41 - 1.30 (m, 2H), 1.05 (s, 9H), 0.98 (s, 3H), 0.95 (d, $J=7.0$ Hz, 3H), 0.89 - 0.86 (m, 12H), 0.78 (s, 3H), 0.09 (s, 3H), -0.33 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 214.07, 163.59, 141.89, 140.45, 135.66, 135.39, 134.10, 129.64, 127.70, 82.75, 81.78, 80.70, 77.45, 75.33, 71.61, 64.04, 58.63, 57.53, 57.00, 49.34, 41.55, 41.22, 40.99, 35.62, 33.25, 32.85, 27.20, 26.97, 26.33, 26.05, 25.67, 22.50, 19.98, 19.30, 18.14, 15.36, 12.89, -4.62, -4.99;

HRMS (ESI): Calcd for C$_{51}$H$_{82}$INO$_8$NaSi$_2$ [M+Na]$^+$ 1042.4524, found 1042.4537.
Diene 2:

To a stirred solution of vinyl iodide 3 (20 mg, 0.024 mmol) and vinyl stannane 4 (14.2 mg, 0.024 mmol) in degassed DMF (1 mL) was added a solution of Pd(PPh₃)₄ (1.4 mg, 0.0012 mmol) in degassed THF (1 mL) followed by CuTc (4.6 mg, 0.024 mmol). The mixture was stirred for 0.5 h, then saturated NH₄Cl solution (2 mL) was added and extracted with EtOAc (30 mL × 2). The combined organic extracts were washed with water (5 mL), brine (5 mL), dried (Na₂SO₄) and concentrated in vacuo. Purification by column chromatography (silica gel, 22% EtOAc in hexanes) gave pure compound 2 (21 mg, 88%) as clear oil.

**Rᶠ**: 0.5 (silica gel, 30% EtOAc in hexane); [α]D₂⁷: -30.3 (c 0.1, CHCl₃); **IR (neat):** v max 3375, 3019, 2951, 1712, 1639, 1465, 1365, 1252, 1101, 836, 767 cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 7.67 - 7.64 (m, 4H), 7.46 (s, 1H), 7.42 - 7.35 (m, 6H), 6.16 - 6.07 (m, 2H), 5.69 (dt, J = 14.0, 6.5, Hz, 1H), 5.39 (dd, J = 14.0, 7.5 Hz, 1H), 4.25 (t, J = 5.8 Hz, 1H), 4.22 - 4.17 (m, 2H), 3.98 - 3.15 (m, 1H), 3.87 (bs, 1H), 3.70 - 3.65 (m, 6H), 3.45 - 3.39 (m, 4H), 3.34 - 3.31 (m, 4H), 3.23 (s, 3H), 3.21 (s, 3H), 3.17 (dd, J = 16.1, 3.4 Hz, 1H), 3.00 (dd, J = 15.7, 7.4 Hz, 1H), 2.77 - 2.70 (m, 1H), 2.62 - 2.58 (m, 2H), 2.55 - 2.45 (m, 4H), 1.83 - 1.70 (m, 3H), 1.67 - 1.57 (m, 5H), 1.49 - 1.43 (m, 1H), 1.40 - 1.28 (m, 2H), 1.04 (s, 9H), 0.97 (s, 3H), 0.94 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 7.1 Hz, 3H), 0.86 (s, 9H), 0.85 (s, 9H), 0.79 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H), -0.27 (s, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 214.13, 172.27, 163.44, 140.99, 135.66, 135.26, 134.07, 132.79, 131.98, 131.89, 130.32, 129.65, 127.70, 82.52, 81.70, 80.88, 78.80, 76.32, 71.59, 66.87, 64.01, 58.73, 57.53, 56.99, 56.05, 51.49, 49.30, 43.51, 42.51, 41.58, 41.15, 38.06, 35.62, 33.26, 32.82, 27.14, 26.95, 26.26, 26.06, 25.85, 25.63, 22.64, 19.91, 19.29, 18.15, 18.02, 15.33,
12.90, -4.39, -4.61, -4.70, -5.05; **HRMS (ESI):** Calc'd for $\text{C}_{66}\text{H}_{111}\text{NO}_{12}\text{Na}_{3}$ [M+Na]$^+$ 1216.7306, found 1216.7285.
3. Spectra (\(^1\)H and \(^{13}\)C NMR) of compounds:

\(^1\)H NMR spectra of 11 (300 MHz, CDCl\(_3\))

\(^{13}\)C NMR spectra of 11 (75 MHz, CDCl\(_3\))
$^1$H NMR spectra of 6 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 6 (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 14 (400 MHz, DMSO-$d_6$ at 90 $^\circ$C)

$^{13}$C NMR spectra of 14 (75 MHz, CDCl$_3$)
HPLC spectra of Benzoate derivative of 14:
$^1$H NMR spectra of A (400 MHz, C$_6$D$_6$ at 70 $^\circ$C)

$^{13}$C NMR spectra of A (100 MHz, C$_6$D$_6$ at 70 $^\circ$C)
$^1$H NMR spectra of 15 (400 MHz, $C_6D_6$ at 70 $^\circ$C)

$^{13}$C NMR spectra of 15 (100 MHz, $C_6D_6$ at 70 $^\circ$C)
$^1$H NMR spectra of 18 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 18 (50 MHz, CDCl$_3$)
$^1$H NMR spectra of 20 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 20 (75 MHz, CDCl$_3$)
$^1$H NMR spectra of 21 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 21 (75 MHz, CDCl$_3$)
$^1$H NMR spectra of 23 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 23 (75 MHz, CDCl$_3$)
$^1$H NMR spectra of (R)-MTPA Ester (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of (R)-MTPA Ester (75 MHz, CDCl$_3$)
$^1$H NMR spectra of (S)-MTPA Ester (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of (S)-MTPA Ester (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 8a (300 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 8a (50 MHz, CDCl$_3$)
$^1$H NMR spectra of 8 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 8 (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 24 Major isomer (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 24 Major isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectra of 24 Minor isomer (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 24 Minor isomer (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 25 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 25 (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 26 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 26 (100 MHz, CDCl$_3$)
$^1$H NMR spectra of 27 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 27 (75 MHz, CDCl$_3$)
**$^1$H NMR spectra of 3a (400 MHz, CDCl$_3$)**

![H NMR spectrum](image)

**$^{13}$C NMR spectra of 3a (75 MHz, CDCl$_3$)**

![C NMR spectrum](image)
$^1$H NMR spectra of 3 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 3 (75 MHz, CDCl$_3$)
$^1$H NMR spectra of 2 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 2 (100 MHz, CDCl$_3$)