Supporting information

Asymmetric total synthesis of Paecilomycin E, 10’-epi-Paecilomycin E and 6’-epi-Cochliomycin C

Pratik Pal, Nandan Jana and Samik Nanda*

Department of Chemistry, Indian Institute of Technology, Kharagpur, 721302, India

snanda@chem.iitkgp.ernet.in

Content

Experimental details for the synthesis of few compounds  PP2-PP18
NMR spectrum of compounds  PP 19-PP 188
HPLC chromatogram  PP 189- PP 191
**General Information:** Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. THF and diethylether were distilled from sodiumbenzophenone ketyl. Dichloromethane (CH$_2$Cl$_2$), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were distilled from CaH$_2$. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (Merck) with UV light, ethanolic anisaldehyde and phosphomolybdic acid/heat as developing agents. Silicagel 100-200 mesh was used for column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. Proton nuclear magnetic resonance ($^1$H-NMR) and carbon nuclear magnetic resonance ($^{13}$C-NMR) spectra were acquired in CDCl$_3$ unless otherwise mentioned. Chemical shifts are reported in parts per million (ppm, $\delta$), downfield from tetramethylsilane (TMS, $\delta = 0.00$ ppm), and are referenced to residual solvent (CDCl$_3$, $\delta = 7.26$ ppm ($^1$H), 77.16 ppm ($^{13}$C) and CD$_3$COCD$_3$, $\delta = 2.09$ ppm ($^1$H)). Coupling constants ($J$) are reported in hertz (Hz) and the resonance multiplicity abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet; comp, overlapping multiplets of magnetically non-equivalent protons. Optical rotations were measured on a JASCO P1020 digital polarimeter. Mass spectrometric analysis was performed in the CRF, IIT-Kharagpur (TOF analyzer). HPLC analysis was performed with the help of PDA detector (200-800 nm)

**(R)-6-(4-methoxybenzyloxy)hexan-2-yl acetate (12)**

In a typical resolution experiment, a solution of racemic alcohol 11 (4.0 g, 16.8 mmol) in anhydrous diisopropyl ether (75 ml) was stirred with vinyl acetate (1 equiv, 1.7 mL) and powdered molecular sieves (25 mg, 4 Å) followed by the addition of CAL-B (1.0 g). The reaction mixture was stirred in an orbit shaker (250 rpm) at room temperature for 1 h. After 50% conversion (by TLC analysis), the reaction mixture was filtered through a pad of celite and evaporated to dryness. The alcohol and the acetate were isolated by column chromatography. The undesired acetate (12) was deprotected and converted to the desired alcohol 13 by Mitsunobu inversion. The spectral ($^1$H/$^{13}$C-NMR, HRMS) and optical data for (R)-12 is in perfect agreement with those of reported one.$^{12a}$
(S)-6-(4-methoxybenzyloxy)hexan-2-ol (13)

To a stirring solution of (R)-acetate (12) (5.9 g, 21 mmol) in 50 mL MeOH was added K₂CO₃ (869 mg, 6.3 mmol) and stirred for 4 h. Methanol was evaporated in vacuo and 300 mL diethyl ether was added to it. The organic part was washed with water (50 mL), saturated NH₄Cl solution (50 mL) and then with brine solution (50 mL). The organic part was dried over anhydrous MgSO₄ and solvent was removed in vacuo to afford the crude alcohol which was used for the next step without further purification.

**Mitsunobu inversion:** To the stirring solution of the alcohol (5.0 g, 21 mmol) in 90 mL of anhydrous THF was added TPP (8.0 g, 31 mmol), DIAD (6.18 mL, 31 mmol) and benzoic acid (3.7 g, 31 mmol) at 0 ºC. The reaction was stirred overnight at room temperature. THF was removed in vacuo and the residue was taken in ethyl acetate (200 mL). The organic part was washed with saturated NaHCO₃ (2 × 30 mL) and brine (50 mL) solution and then dried over anhydrous MgSO₄. The organic solvent was evaporated in vacuo and purification was accomplished by flash column chromatography eluting with EtOAc/hexane (1:15) to afford the (S)-benzoate (6.1 g, 17.8) as a colorless liquid in 85% yield.

Rᵣ = 0.20 (EtOAc/hexane, 1:15).

**¹H NMR of benzoate derivative of compound (S)-13 (400 MHz, CDCl₃):** δ: 7.97-7.95 (m, 2H), 7.48-7.47 (m, 1H), 7.37-7.33 (m, 2H), 7.18-7.15 (m, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 5.12-5.01 (m, 1H), 4.33 (s, 2H), 3.71 (s, 3H), 3.36 (t, J = 6.4 Hz, 2H), 1.71-1.50 (m, 4H), 1.45-1.34 (m, 2H), 1.26 (d, J = 6.4 Hz, 3H).

**¹³C NMR of benzoate derivative of compound (S)-13 (100 MHz, CDCl₃):** δ: 166.4, 159.3, 132.9, 131.0, 130.8, 129.7, 129.4, 128.4, 113.9, 72.7, 71.8, 69.9, 55.45, 36.0, 29.8, 22.3, 20.3.

**Benzoate hydrolysis:** To the stirring solution of the benzoate (6.1 g, 17.8 mmol) in 200 mL MeOH was added NaOH (2.2 g, 53 mmol) at room temperature and stirred for 12 h at room temperature. After completion of the reaction MeOH was evaporated in vacuo and the crude residue was diluted with 250 mL diethyl ether. The organic part was washed with (2 × 50 mL) water, brine solution (50 mL) and then dried over anhydrous MgSO₄. The organic solvent was evaporated in vacuo and purification through flash column chromatography eluting with
EtOAc/hexane (1:5) to afford the (S)-alcohol (13) (4.2 g, 17.8) as a colorless liquid in 100% yield.

(S)-tert-butyl(6-(4-methoxybenzoyloxy)hexan-2-yloxy)dimethylsilane (14)

To a stirred solution of alcohol (S)-13 (7.29 g, 30.65 mmol) and imidazole (4.16 g, 61.3 mmol) in dry CH₂Cl₂ (91 mL), TBSCl (4.62 g, 36.78 mmol) was added portion wise at 0°C. The reaction mixture was stirred at the same temperature for 2 h and then quenched with water (50 mL). The dichloromethane (CH₂Cl₂) layer was separated, and the aqueous layer was extracted with additional CH₂Cl₂ (2 × 60 mL). The combined organic layers were washed with water, saturated Na₂CO₃ solution and brine solution and then dried over anhydrous MgSO₄. The organic solvent was removed in vacuo, and purification was accomplished by flash column chromatography eluting with EtOAc/hexane (1:20) to afford the (S)-14 (10.24 g, 95%) as a colorless liquid.

R_f = 0.55 (EtOAc/hexane, 1:10).

¹H NMR (200 MHz, CDCl₃): \( \delta \): 7.26 (d, \( J = 8.6 \) Hz, 2H), 6.88 (d, \( J = 8.8 \) Hz, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.75-3.69 (m, 1H), 3.43 (t, \( J = 6.4 \) Hz, 2H), 1.63-1.53 (m, 2H), 1.44-1.36 (m, 4H), 1.12 (d, \( J = 6 \) Hz, 3H), 0.892 (s, 9H), 0.05 (s, 6H).

¹³C NMR (50 MHz, CDCl₃, 77.23): \( \delta \): 159.3, 129.4, 113.9, 72.7, 70.3, 68.8, 55.4, 39.7, 30.0, 26.1, 23.9, 22.6, 18.3, -4.2, -4.5.

\([\alpha]_D^{28} = -6.62 \) (c = 1.26, CHCl₃).

HRMS (ESI) for C₂₀H₃₆O₃SiNa [M + Na]+, calculated: 375.2331, found: 375.2325.

(S)-5-(tert-Butyl-dimethyl-silanyloxy)-hexan-1-ol (15)

Compound 14 (10.24 g, 29.09 mmol) was dissolved in 116 mL of CH₂Cl₂/phosphate buffer (pH = 7; 19:1) and the solution was cooled to 0 °C. DDQ (7.92g, 34.91mmol) was added portion wise to the solution and the mixture was stirred at this temperature for 1 h. Then, the reaction mixture was filtered through a pad of celite. The residue was then washed with 70 mL of CH₂Cl₂. The combined organic solution was washed successively with 5% NaHCO₃ solution, water and brine solution. The organic layer was then dried with anhydrous MgSO₄ and evaporated in vacuo.
Purification by flash column chromatography (EtOAc:hexane = 1:12) afforded compound 15 (6.47 g, 27.92 mmol) as colorless oil in 96% yield.

\[ R_f = 0.45 \text{ (EtOAc/hexane, 1:5).} \]

\(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \): 3.82-3.74 (m, 1H), 3.63 (t, \( J = 6.4 \) Hz, 2H), 1.59-1.52 (m, 4H), 1.44-1.35 (m, 4H), 1.11 (d, \( J = 6 \) Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \( \delta \): 68.7, 62.9, 39.5, 32.9, 26.1, 23.9, 22.0, 18.3, -4.2, -4.5.

\([\alpha]_D^{28} = -8.53 \text{ (c = 0.8, CHCl}_3\)).

HRMS (ESI) for C\(_{12}\)H\(_{28}\)O\(_2\)SiNa [M + Na]\(^+\), calculated: 255.1756, found: 255.1750.

\((S)-5-(\text{tert}-\text{butyldimethylsilyloxy})\text{hexyl methanesulfonate (16)}\)

To a cooled solution (0 °C) of the alcohol 15 (6.47 g, 27.92 mmol) in 111 mL of dry CH\(_2\)Cl\(_2\) was added 4.6 mL (33.5 mmol) of Et\(_3\)N and 2.6 mL (33.5 mmol) of methanesulfonyl chloride and the mixture was stirred for 12 h. The reaction was then quenched with addition of 50 mL of cold water. The CH\(_2\)Cl\(_2\) layer was separated and the aqueous layer was extracted with additional CH\(_2\)Cl\(_2\) (2×50 mL). The combined organic layer was washed with saturated NaHCO\(_3\) and brine solution and dried over anhydrous MgSO\(_4\). Total solvent was evaporated in \textit{vacuo} to afford the crude product, which was then purified by flash column chromatography (EtOAc/hexane, 1:10) to yield compound 16 (8.31 g, 26.80 mmol) as colorless oil.

\[ R_f = 0.45 \text{ (EtOAc/hexane, 1:5).} \]

\(^1\)H NMR (200 MHz, CDCl\(_3\), 7.26): \( \delta \): 4.22 (t, \( J = 6.6 \) Hz, 2H), 3.83-3.74 (m, 1H), 3.00 (s, 3H), 1.78-1.71 (m, 2H), 1.41.41 (m, 4H), 1.12 (d, \( J = 6 \) Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\), 77.23): \( \delta \): 77.2, 68.4, 39.1, 37.5, 29.3, 26.1, 23.9, 21.8, 18.3, -4.1, -4.6.

\([\alpha]_D^{28} = -7.82 \text{ (c = 1.06, CHCl}_3\)).

HRMS (ESI) for C\(_{13}\)H\(_{30}\)O\(_4\)SSiNa [M + Na]\(^+\), calculated: 333.1532, found: 333.1525.

\((S)-\text{tert}-\text{butyl}(6\text{-iodohexan-2-yloxy})\text{dimethylsilane (17)}\)
The mesylate 16 (8.31 g, 26.80 mmol) was dissolved in 170 mL anhydrous acetone. To this solution was added 36 g of anhydrous NaI, 1.48 g of NaHCO₃, and few drops of diisopropylethylamine. After protecting the reaction from light by aluminum foil, the reaction was allowed to stir at room temperature for 6 h. The acetone was then removed in vacuo and the residue was taken up in diethyl ether. After filtration through celite the solvent was removed in vacuo. Purification through flash chromatography (EtOAc/hexane, 1:30) furnished the iodo compound 17 (8.43 g, 24.65 mmol) as colorless liquid.

Rᵣ = 0.25 (EtOAc/hexane, 1:40).

¹H NMR (200 MHz, CDCl₃): δ: 3.83-3.74 (m, 1H), 3.19 (t, J = 7 Hz, 3H), 1.89-1.79 (m, 2H), 1.49-1.42 (m, 4H), 1.13 (d, J = 6 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H).

¹³C NMR (50 MHz, CDCl₃): δ: 68.5, 38.7, 33.8, 27.0, 26.1, 24.0, 18.3, 7.2, -4.1, -4.5.

[α]D²⁸ = -7.74 (c = 1.2, CHCl₃).


(S)-2-(5-(tert-butyldimethylsilyloxy)hexylthio)pyridine (18)

To a cooled solution (0 ºC) of the 2-mercaptopyridine (203 mg, 1.83 mmol) in 3.0 mL anhydrous DMF was added 73.2 mg NaH (60 % in mineral oil, 1.83 mmol) portion wise and stirred for 20 minute at same temperature. Mesylate 16 (633 mg, 2 mmol) in 2.0 mL anhydrous DMF was added drop wise to the previous solution at 0 ºC. The reaction solution was then stirred for 10 h. Saturated solution of ammonium chloride was added to it and then it was poured into 150 mL diethyl ether. The organic layer was washed with (3×50 mL) water and then with 40 mL brine solution. The organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. Purification was done by flash column chromatography (EtOAc/hexane = 1:10) to afford the sulfide 18 (552 mg, 1.7 mmol) in 83% yield.

Rᵣ = 0.45 (EtOAc/hexane, 1:15).

¹H NMR (200 MHz, CDCl₃): δ: 8.43-8.39 (m, 1H); 7.49-7.41 (m, 1H); 7.17-7.13 (m, 1H); 6.98-6.92 (m, 1H); 3.78 (q, J = 6.0 Hz, 2H); 3.16 (t, J = 7.2 Hz, 1H); 1.74-1.63 (m, 2H); 1.49-1.40 (m, 4H); 1.11 (d, J = 6.2 Hz, 3H); 0.88 (s, 9H); 0.04 (s, 6H).
\(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta\): 159.5, 149.6, 135.7, 122.1, 119.1, 68.3, 39.1, 29.9, 29.3, 25.8, 25.1, 23.8, 18.1, -4.5, -4.8.

\([\alpha]_D^{28} = -15.8\) (c = 0.9, CHCl\(_3\)).

HRMS (ESI) for C\(_{17}\)H\(_{31}\)NOSSiNa [M + Na]\(^+\), calculated: 348.1793, found: 348.1787.

(S)-2-(5-(tert-butyldimethylsilyloxy)hexylsulfonyl)pyridine (8)

To a stirring solution of sulfide 18 (425 mg, 1.31 mmol) in ethanol (11.0 mL) was added a mixture of (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)4H\(_2\)O (242 mg, 0.2 mmol) and 30\% H\(_2\)O\(_2\) solution (1.1 mL) at 0 \(^\circ\)C. The mixture was stirred at room temperature for 6 h, and after that the reaction mixture was poured into 10\% Na\(_2\)S\(_2\)O\(_3\) solution and extracted with ethyl acetate (100 mL). The organic layer was washed with saturated NaHCO\(_3\) solution and brine, dried over anhydrous MgSO\(_4\) and concentrated in vacuo. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to give sulphone 8 (420 mg, 1.17 mmol) as colorless gummy oil in 90\% yield.

R\(_f\) = 0.45 (EtOAc/hexane, 1:15).

\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\): 8.74 (d, \(J = 4.4\) Hz, 1H); 8.11-8.06 (m, 1H); 8.01-7.92 (m, 1H); 7.58-7.52 (m, 1H); 3.77-3.67 (m, 1H); 3.37 (t, \(J = 8\) Hz, 2H); 1.77-1.69 (m, 2H); 1.43-1.36 (m, 4H); 1.07 (d, \(J = 6\) Hz, 3H); 0.84 (s, 9H); 0.00 (s, 6H).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta\): 154.2, 150.2, 138.1, 127.2, 122.1, 67.9, 51.8, 38.8, 25.8, 24.4, 23.7, 22.1, 17.9, -4.5, -4.9.

\([\alpha]_D^{28} = -17\) (c = 0.6, CHCl\(_3\)).

HRMS (ESI) for C\(_{17}\)H\(_{31}\)NO\(_3\)SSiNa [M + Na]\(^+\), calculated: 380.1691, found: 380.1686.

(S)-5-(tert-butyldimethylsilyloxy)hexyl)triphenylphosphonium iodide (9)

To a solution of the iodide (8.43 g, 24.65 mmol) in anhydrous toluene (66 mL) was added TPP (12.9 g, 49.3 mmol) and Hünig’s base (21.6 mL, 123.25 mmol). The mixture was refluxed for 12 h. The solution was then cooled to room temperature and concentrated under reduced pressure to afford the crude phosphonium salt 9. It is then trititated with anhydrous pentane (5×20 mL) and
dried under high vacuum to get the Wittig salt 9 (13.5 g, 22.43 mmol) as a off white solid which was used without farther purification.

$R_f = 0.15$ (EtOAc).

**(S)-**tert-**butyl**(5-**(4-methoxybenzyloxy)**pent-1-en-3-yloxy)**diphenylsilane (20)

To a cooled (0 °C) solution of optically pure alcohol (S)-19 (5.55 g, 25 mmol) in dry CH$_2$Cl$_2$ (100 mL) was added imidazole (2.55 g, 37.5 mmol) and TBDPSCI (7.71 mL, 30 mmol). The mixture was stirred for 6 h at room temperature and then quenched with 50 mL of water. The organic layer was separated and the aqueous part was extracted with CH$_2$Cl$_2$ (2×30 mL). The combined organic part was washed with saturated NaHCO$_3$ solution and brine solution and then dried over anhydrous MgSO$_4$. The solution was then concentrated in vacuo and purified via flash chromatography (EtOAc:hexane = 1:20) to yield compound 20 (10.92 g, 23.75 mmol) as colorless oil in 95% yield.

$R_f = 0.30$ (EtOAc/hexane, 1:15).

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$: 7.78-7.72 (m, 4H), 7.45-7.38 (m, 6H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.2$ Hz, 2H), 5.88 (ddd, $J = 17.4$, 10.4, 6.8 Hz, 1H), 5.16-5.03 (m, 1H), 4.9 (s, 1H), 4.44-4.41(m, 1H), 4.36 (s, 2H), 3.8 (s,3H), 3.56-3.50 (m, 2H), 1.98-1.77 (m, 2H), 1.14 (s, 9H).

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$: 159.2, 140.7, 136.2, 136.1, 134.4, 134.3, 130.8, 129.7, 129.6, 129.4, 127.8, 127.7, 127.5, 114.7, 113.8, 72.5, 72.5, 66.3, 55.4, 37.8, 27.2, 19.5.

$[\alpha]_D^{28} = 11.76$ (c = 0.86, CHCl$_3$).

HRMS (ESI) for C$_{29}$H$_{36}$O$_3$SiNa [M + Na]$^+$, calculated: 483.2331, found: 483.2321.

**(S)-2-(**tert-**butyldiphenylsilyloxy)**-4-**(4-methoxybenzyloxy)**butanal (10)

To a stirring solution of the olefin 20 (10.92 g, 23.75 mmol) in 92 mL of THF/H$_2$O (3:1) at room temperature was sequentially added NMO (3.33 g, 28.5 mmol), 0.05 M solution of OsO$_4$ in toluene (47.5 mL, 2.37 mmol) and NaIO$_4$ (1.12 g, 47.5 mmol). The mixture was stirred vigorously at room temperature for 12 h. The reaction was quenched by the addition of saturated aq. Na$_2$SO$_3$ solution (18 mL) and further stirred for 1 h at room temperature. The reaction mixture is then filtered through a celite pad and washed with150 mL of EtOAc. The organic
layer was separated and the aqueous part was washed with EtOAc (2×50 mL). The combined organic layers were successively washed with 5% aq.NaHCO₃ solution, saturated aq. Na₂SO₃ and with brine solution. Total organic solution was then dried over anhydrous MgSO₄ and concentrated under reduced pressure to furnish the crude product, which on purification by flash chromatography (EtOAc/hexane = 1:15) afforded the aldehyde 10 (8.77 g, 19 mmol) in 80% yield.

Rᵣ = 0.35 (EtOAc/hexane, 1:10).

¹H NMR (200 MHz, CDCl₃): δ: 9.58 (s, 1H), 7.65- 7.62 (m, 4H), 7.44- 7.32 (m, 6H), 7.21 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.36 (s, 2H), 4.22- 4.17 (m, 1H), 3.81 (s, 3H), 2.10-1.90 (m, 1H), 1.90-1.77 (m, 1H), 1.11 (s, 9H).

¹³C NMR (50 MHz, CDCl₃): δ: 203.4, 159.2, 136.2, 136.1, 134.5, 132.7, 130.93, 130.3, 129.6, 129.6, 129.2, 127.7, 127.5, 113.8, 72.5, 68.6, 67.3, 66.8, 55.5, 39.5, 38.5, 31.3, 29.9, 27.6, 27.2, 26.1, 25.8, 23.9, 19.5, 18.3, -4.2, -4.5.

[α]D²⁸ = 15.21 (c = 1.06, CHCl₃).


2-bromo-3,5-dimethoxybenzaldehyde (27)

To a solution of compound 26 (5.04 g, 30.2 mmol) in acetic acid (140 mL) was added a solution of bromine (1.56 mL, 30.2 mmol) in acetic acid (20 mL) dropwise at 0 ºC. The reaction mixture was stirred at room temperature for 8 h. The reaction mixture was poured into 300 mL ice water and the crude product got precipitated. The precipitate was collected by filtration and washed by ice cold water. The crude product was then purified by recrystallization from hexane to afford compound 27 (6.26 g, 25.67 mmol) in 85% yield as white solid.

Rᵣ = 0.35 (EtOAc/hexane, 1:10).

¹H NMR of compound 27 (200 MHz, CDCl₃): δ: 10.45, 7.07 (d, J = 2.8 Hz, 1H), 6.75 (d, J = 2.8 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).

¹³C NMR of compound 27 (50 MHz, CDCl₃): δ: 191.9, 159.8, 156.9, 134.6, 108.9, 105.7, 103.3, 56.5, 55.7.

HRMS (ESI) for C₉H₉BrO₃Na [M + Na]⁺, calculated: 266.9632, found: 266.9625.
**2-(2-bromo-3,5-dimethoxyphenyl)-1,3-dioxolane (28)**

A solution of compound 27 (5.5 g, 22.5 mmol), p-toluenesulfonic acid (0.5 g) and 1,2 ethanediol (6.15 mL, 112.25 mmol) were taken in 75 mL anhydrous benzene and refluxed in Dean-stark apparatus for 3 h. The benzene was then removed in *vacuo* and the residue was purified by flash column chromatography (EtOAc/hexane/ triethylamine = 1:7: 0.07) to furnish compound 28 (6.35g, 22.05 mmol) in 98% yield.

\[ R_f = 0.25 \ (\text{EtOAc/hexane, 1:10}). \]

\[ ^1 \text{H NMR of compound 28 (200 MHz, CDCl}_3\text{): } \delta: 6.80 \ (d, J = 2.8 \text{ Hz, 1H}), 6.51 \ (d, J = 2.8 \text{ Hz, 1H}), 6.12 \ (s, 1H), 4.16-4.12 \ (m, 2H), \]

\[ 4.09-4.01 \ (m, 2H), 3.86 \ (s, 3H), 3.74 \ (s, 3H). \]

\[ ^13 \text{C NMR of compound 28 (50 MHz, CDCl}_3\text{): } \delta: 159.8, 156.7, 138.4, 128.2, 103.5, 103.4, 102.5, \]

\[ 100.6, 65.4, 56.4, 55.6. \]

HRMS (ESI) for C\(_{11}\)H\(_{13}\)BrO\(_4\)Na [M + Na]+, calculated: 310.9894, found: 310.9899.

**ethyl 2-formyl-4,6-dimethoxybenzoate (5)**

To a stirring solution of compound 28 (1.44 g, 5 mmol) in 20 mL anhydrous THF was added n-BuLi (1.6 M in hexane, 3.1 mL, 5 mmol) at -78 ºC drop wise and stirred for further 1 h. Ethyl chloroformate (0.7 mL, 7.5 mmol) in 5 mL anhydrous THF was slowly added to the reaction mixture and stirred for 1 h. The reaction solution was then quenched by adding water (25 mL) and p-toluenesulfonic acid (1 g). The resulting solution was stirred for 4 h at 40 ºC and extracted with EtOAc. The combined organic extracts was dried over anhydrous MgSO\(_4\) and concentrated in *vacuo*. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to afford compound 5 (952 mg, 4 mmol) as white solid in 80% yield.

\[ R_f = 0.4 \ (\text{EtOAc/hexane, 1:10}). \]

\[ ^1 \text{H NMR of compound 5 (200 MHz, CDCl}_3\text{): } \delta: 9.94 \ (s, 1H), 6.93 \ (d, J = 2.2 \text{ Hz, 1H}), 6.68 \ (d, J = 2.2 \text{ Hz, 1H}), 4.39 \ (q, J = 7.2 \text{ Hz, 2H}), 3.84 \ (s, 3H), 3.82 \ (s, 3H), 1.35 \ (t, J = 7.2 \text{ Hz, 1H}). \]

\[ ^13 \text{C NMR of compound 5 (50 MHz, CDCl}_3\text{): } \delta: 189.9, 166.3, 161.7, 158.2, 135.5, 118.1, 104.5, \]

\[ 104.2, 61.8, 56.2, 55.6, 14.0. \]


**Ethyl 3-chloro-2-formyl-4,6-dimethoxybenzoate (6)**

To a stirring solution of compound 5 (952 mg, 4 mmol) in 26 mL anhydrous CH\(_2\)Cl\(_2\) at 0 ºC was added sulfuryl chloride (0.32 mL, 4 mmol, dissolved in 3 mL of CH\(_2\)Cl\(_2\)). After 20 min the reaction was quenched by addition of water (10 mL). The organic layer was then separated and
the aqueous layer was further washed by CH$_2$Cl$_2$. The combined extract was dried over anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to give compound 6 (783 mg, 2.88 mmol) as off white solid in 72% yield.

$R_f = 0.35$ (EtOAc/hexane, 1:10).

$^1$H NMR of compound 6 (200 MHz, CDCl$_3$): $\delta$: 10.48 (s, 1H), 6.72 (s, 1H), 4.40 (q, $J = 7.2$ Hz, 2H), 3.98 (s, 3H), 3.89 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H),

$^{13}$C NMR of compound 6 (50 MHz, CDCl$_3$): $\delta$: 189.5, 166.6, 157.6, 156.2, 131.2, 117.9, 116.7, 101.6, 61.9, 56.8, 56.6, 14.0.

HRMS (ESI) for C$_{12}$H$_{13}$ClO$_5$Na $[M + Na]^+$, calculated: 295.0349, found: 295.0344.

(5$S$,11$R$,$Z$)-5-(2-(4-methoxybenzyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-4,12-dioxa-3,13-disilapentadec-6-ene (36)

Compound 36 was prepared from the Witting reaction between enantiomer of 9 and the aldehyde 10 in 76% yield as described earlier.

$R_f = 0.65$ (EtOAc/hexane, 1:20).

$^1$H NMR of compound 36 (400 MHz, CDCl$_3$): $\delta$: 7.70-7.63 (m, 4H), 7.41-7.30 (m, 6H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.40-5.35 (m, 1H), 5.19-5.13 (m, 1H), 4.65-4.57 (m, 1H), 4.35 (s, 2H), 3.80 (s, 3H), 3.65-3.61 (m, 1H), 3.50-3.38 (m, 2H), 1.95-1.94 (m, 1H), 1.87 (m, 1H), 1.74-1.66 (m, 1H), 1.58-1.51 (m, 3H), 1.25-1.17 (m, 3H), 1.03 (comp. 3H), 1.03 (s, 9H), 0.87 (s, 9H), 0.01 (s, 6H).

$^{13}$C NMR of compound 36 (50 MHz, CDCl$_3$): $\delta$: 159.2, 136.2, 136.1, 134.5, 132.7, 130.9, 130.3, 129.6, 129.5, 129.2, 127.6, 127.5, 113.8, 72.5, 68.6, 67.2, 66.7, 55.3, 39.5, 38.5, 27.6, 27.2, 26.1, 25.9, 23.9, 19.5, 18.3, -4.2, -4.5.

$[\alpha]_D^{28} = -2.2$ (c = 0.05, CHCl$_3$).

HRMS (ESI) for C$_{40}$H$_{60}$O$_4$Si$_2$Na $[M + Na]^+$, calculated: 683.3927, found: 683.3923.

(5$S$,6$S$,7$S$,11$R$)-5-(2-(4-methoxybenzyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-3,3-diphenyl-4,12-dioxa-3,13-disilapentadecane-6,7-diol (37)

The dihydroxylation reaction of compound 36 was performed as described previously to afford compound 37 and 38 in 1:9 ratio.

$R_f$ of 37 = 0.32 (EtOAc/hexane, 1:5).
$^1$H NMR of compound 37 (400 MHz, CDCl$_3$): $\delta$: 7.71-7.65 (m, 4H), 7.46-7.35 (m, 6H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.21 (s, 2H), 4.15-4.13 (m, 1H), 3.80 (s, 3H), 3.79-3.76 (m, 1H), 3.51-3.49 (m, 1H), 3.35-3.34 (m, 1H), 3.27-3.25 (m, 1H), 3.21-3.19 (m, 1H), 2.10-2.01 (m, 1H), 1.78-1.73 (m, 2H), 1.67-1.66 (m, 2H), 1.46-1.44 (m, 2H), 1.32-1.35 (m, 4H), 1.11 (d, $J = 6$ Hz, 3H), 1.03 (s, 9H), 0.91 (s, 9H), 0.04 (s, 6H).

$^{13}$C NMR of compound 37 (50 MHz, CDCl$_3$): $\delta$: 159.2, 136.0, 133.6, 132.9, 130.2, 130.0, 129.3, 128.0, 127.7, 113.8, 75.0, 72.48, 72.2, 72.0, 68.7, 66.3, 55.3, 39.8, 33.8, 27.2, 26.1, 24.0, 21.91, 19.0, 18.2, -4.2, -4.5.

$[\alpha]_{D}^{28} = 12.0$ (c = 0.8, CHCl$_3$).

HRMS (ESI) for C$_{40}$H$_{62}$O$_5$Si$_2$Na [M + Na]$^+$, calculated: 717.3982, found: 717.3988.

(5S,6R,7R,11R)-5-(2-(4-methoxybenzylxyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-3,3-diphenyl-4,12-dioxo-3,13-disilapentadecane-6,7-diol (38)

$^1$H NMR of compound 38 (200 MHz, CDCl$_3$): $\delta$: 7.67-7.60 (m, 4H), 7.44-7.37 (m, 6H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 4.28 (s, 2H), 4.21-4.00 (m, 1H), 3.80 (s, 3H), 3.59-3.56 (m, 3H), 3.19-3.15 (m, 1H), 1.86-1.83 (m, 2H), 1.42-1.32 (m, 6H), 1.11 (comp. 3H), 1.08 (s, 9H), 0.88 (s, 9H), 0.04 (s, 6H).

$^{13}$C NMR of compound 38 (50 MHz, CDCl$_3$): $\delta$: 159.3, 135.9, 133.9, 133.4, 130.0, 129.9, 129.6, 129.5, 127.8, 127.7, 113.9, 72.8, 72.5, 71.8, 68.8, 66.3, 55.2, 39.9, 32.6, 32.3, 27.2, 26.1, 23.7, 21.9, 19.4, 18.2, -4.3, -4.5.

$[\alpha]_{D}^{28} = -1.1$ (c = 1.6, CHCl$_3$).

HRMS (ESI) for C$_{40}$H$_{62}$O$_5$Si$_2$Na [M + Na]$^+$, calculated: 717.3982, found: 717.3991.

$\text{tert-buty}l((S)-1-((4R,5R)-5-((R)-4-(\text{tert-butyldimethylsilyloxy})pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-methoxybenzylxyloxy)propoxy)diphenylsilane$ (39)

Compound 39 was prepared in 94% yield when the diol 38 was treated with catalytic amount of PPTS and 2,2-DMP in acetone as described earlier.

$^1$H NMR of compound 39 (400 MHz, CDCl$_3$): 7.68-7.63 (m, 4H), 7.42-7.33 (m, 6H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 4.26 (s, 2H), 4.06-4.03 (m, 1H), 3.97-3.89 (m, 2H), 3.80 (s, 3H), 3.67-3.62 (m, 1H), 3.52-3.47 (m, 2H), 1.99-1.77 (m, 2H), 1.36 (s, 3H), 1.26 (s, 3H), 1.22-1.15 (comp. 4H), 1.05-1.01 (comp. 4H), 1.01 (s, 9H), 0.88 (s, 9H), 0.01 (s, 6H).
$^{13}$C NMR of compound 39 (50 MHz, CDCl$_3$): δ: 159.1, 136.1, 133.9, 133.9, 130.9, 129.9, 129.8, 127.7, 127.7, 113.8, 107.6, 80.6, 77.8, 72.5, 69.8, 68.7, 66.5, 35.3, 39.6, 34.9, 29.9, 27.9, 27.1, 26.1, 25.7, 23.7, 22.4, 21.1, 19.5, 18.3, -4.2, -4.5.

$[\alpha]_D^{28} = -0.1$ (c = 0.05, CHCl$_3$).

HRMS (ESI) for C$_{43}$H$_{66}$O$_5$Si$_2$Na [M + Na]$^+$, calculated: 757.4295, found: 757.4287.

(S)-3-(((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butyldiphenylsilyloxy)propan-1-ol (40)

Compound 40 was prepared in 96% yield from compound 39 as presented earlier.

$^1$H NMR of compound 40 (200 MHz, CDCl$_3$): δ: 7.68-7.64 (m, 4H), 7.48-7.36 (m, 6H), 4.18-4.10 (m, 2H), 3.89-3.86 (m, 1H), 3.74-3.66 (m, 2H), 3.55-3.43 (m, 1H), 1.91-1.82 (comp. 5H), 1.37 (s, 3H), 1.33 (s, 3H), 1.30-1.15 (m, 3H), 1.08 (d, $J$ = 6 Hz, 3H), 1.03 (s, 9H), 0.88 (s, 9H), -0.04 (s, 6H).

$[\alpha]_D^{28} = -2.23$ (c = 0.5, CHCl$_3$).

HRMS (ESI) for C$_{35}$H$_{58}$O$_5$Si$_2$Na [M + Na]$^+$, calculated: 637.3720, found: 637.3715.

5-(((S)-3-(((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butyldiphenylsilyloxy)propylthio)-1-phenyl-1H-tetrazole (41)

Compound 41 was prepared from primary alcohol 40 in the same way as compound 25 was prepared.

$^1$H NMR of compound 41 (200 MHz, CDCl$_3$): δ: 7.67-7.63 (m, 4H), 7.55-7.54 (m, 5H), 7.41-7.32 (m, 6H), 4.16-4.10 (m, 1H), 4.04-3.99 (m, 1H), 3.89-3.86 (m, 1H), 3.71-3.62 (m, 1H), 3.59-3.43 (m, 2H), 2.20-1.99 (m, 2H), 1.35 (s, 3H), 1.29 (s, 3H), 1.17-1.16 (m, 3H), 1.07 (comp. 3H), 1.04 (s, 9H), 0.87 (s, 9H), 0.03 (s, 6H).

$[\alpha]_D^{28} = +1.5$ (c = 0.3, CHCl$_3$).

HRMS (ESI) for C$_{42}$H$_{62}$N$_4$O$_4$SSi$_2$Na [M + Na]$^+$, calculated: 797.3927, found: 797.3932.
5-((S)-3-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butylidiphenylsilyloxy)propylsulfonyl)-1-phenyl-1H-tetrazole (42)

Sulfone 42 was prepared from sulfide 41 as described earlier.

$^{1}$H NMR of compound 42 (400 MHz, CDCl$_3$): $\delta$: 7.65-7.59 (m, 9H), 7.58-7.36 (m, 6H), 4.08-4.00 (m, 1H), 3.98-3.96 (m, 1H), 3.89-3.38 (m, 2H), 3.66-3.63 (m, 2H), 2.23-2.15 (m, 2H), 1.33 (s, 3H), 1.29 (s, 3H), 1.25 (comp. 3H), 1.08 (d, $J = 6.8$ Hz, 3H), 1.05 (s, 9H), 0.88 (s, 9H), 0.01 (s, 6H).

$^{13}$C NMR of compound 42 (50 MHz, CDCl$_3$): $\delta$: 153.4, 135.9, 135.9, 133.2, 133.0, 132.8, 131.4, 130.3, 130.2, 129.7, 128.0, 127.9, 125.2, 108.0, 80.4, 77.5, 69.7, 68.6, 52.5, 39.4, 32.0, 30.0, 29.7, 27.9, 27.5, 27.1, 26.0, 25.7, 23.7, 22.2, 19.3, 18.2, -4.3, -4.6. 

[$\alpha$]$_D^{28}$ = 2.5 (c = 0.3, CHCl$_3$).

HRMS (ESI) for C$_{42}$H$_{62}$N$_4$O$_6$SSi$_2$Na [M + Na]$^+$, calculated: 829.3826, found: 829.3819.

Ethyl 2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butylidiphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzoate (43)

The olefin 43 was prepared by JK-olefination reaction of aldehyde 5 and sulfone 42 in 82% yield as described previously.

$^{1}$H NMR of compound 43 (400 MHz, CDCl$_3$): $\delta$: 7.68-7.66 (m, 4H), 7.41-7.33 (m, 6H), 6.45 (s, 1H), 6.34 (s, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 6.25-6.20 (m, 2H), 4.36-4.28 (m, 2H), 4.10-4.07 (m, 1H), 4.04-4.02 (m, 1H), 3.89-3.86 (m, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.69-3.64 (m, 1H), 2.47-2.44 (m, 2H), 1.39 (comp. 3H), 1.36 (s, 3H), 1.28 (s, 3H), 1.19-1.09 (m, 3H), 1.06 (comp. 3H), 1.04 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H).

$^{13}$C NMR of compound 43 (100 MHz, CDCl$_3$): $\delta$: 167.9, 161.3, 158.1, 137.6, 136.1, 135.9, 133.8, 133.6, 129.9, 129.9, 129.8, 129.0, 127.7, 127.7, 115.9, 107.6, 101.4, 97.6, 79.8, 77.7, 71.8, 68.7, 61.0, 55.9, 55.3, 39.6, 68.4, 30.2, 28.2, 26.0, 25.9, 23.7, 22.2, 19.4, 18.2, 14.4, -4.3, -4.6. 

[$\alpha$]$_D^{28}$ = 6.2 (c = 0.03, CHCl$_3$).

HRMS (ESI) for C$_{47}$H$_{70}$O$_6$Si$_2$Na [M + Na]$^+$, calculated: 841.4506, found: 841.4498.

Ethyl 2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butylidiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzoate (44)


The olefin 44 was prepared by JK-olefination reaction between aldehyde 6 and sulfone 42 in 78% yield as described earlier.

$^1$H NMR of compound 44 (400 MHz, CDCl$_3$): δ: 7.73-7.52 (m, 4H), 7.52-7.34 (m, 6H), 6.46 (d, $J$ = 16.8 Hz, 1H), 6.44 (s, 1H), 6.14-6.07 (m, 1H), 4.30-4.20 (m, 1H), 4.18-4.11 (m, 1H), 4.04-4.02 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.67-3.63 (m, 1H), 2.45 (s, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 1.34-1.22 (comp. 4H), 1.20-1.16 (m, 2H), 1.09 (comp. 3H), 1.05 (s, 9H), 0.93 (s, 9H), 0.07 (s, 6H).

$^{13}$C NMR of compound 44 (100 MHz, CDCl$_3$): δ: 167.4, 156.4, 155.9, 136.4, 136.2, 133.6, 133.6, 132.8, 129.9, 129.9, 127.9, 127.7, 127.7, 117.0, 113.6, 107.8, 95.2, 79.2, 77.8, 71.1, 68.8, 61.4, 56.5, 56.3, 39.7, 38.9, 30.4, 28.4, 27.2, 27.1, 26.2, 26.0, 23.8, 23.7, 22.2, 19.4, 18.2, 14.3, -4.2, -4.5.

$[\alpha]_D^{28} = 5.2$ (c = 0.03, CHCl$_3$).

HRMS (ESI) for C$_{47}$H$_{69}$ClO$_8$Si$_2$Na $[M + Na]^+$, calculated: 875.4116, found: 875.4110.

(2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxyphenyl)methanol (45)

Compound 43 was reduced to compound 45 with DIBAL-H in 95% yield as presented earlier.

$^1$H NMR of compound 45 (400 MHz, CDCl$_3$): δ: 7.77-7.67 (m, 4H), 7.46-7.36 (m, 6H), 6.65 (d, $J$ = 15.6 Hz, 1H), 6.47 (s, 1H), 6.38 (d, $J$ = 2.0 Hz, 1H), 6.20-6.16 (m, 1H), 6.68 (d, $J$ = 4.0 Hz, 2H), 4.19-4.17 (m,1H), 4.15-4.10 (m, 1H), 3.97-3.96 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.74-3.68 (m, 1H), 2.54 (s, 2H), 1.51 (s, 3H), 1.39-1.33 (m, 1H), 1.33 (s, 3H), 1.29-1.18 (comp. 4H), 1.13-1.11 (m,1 H), 1.10 (comp. 3H), 1.08 (s, 9H), 0.91 (s, 9H), 0.06 (s, 6H).

$^{13}$C NMR of compound 45 (100 MHz, CDCl$_3$): δ: 160.3, 159.3, 139.6, 136.2, 136.2, 134.0, 133.8, 130.1, 130.0, 129.7, 127.9, 127.8, 119.4, 107.9, 102.5, 97.6, 80.0, 78.0, 71.9, 68.9, 55.8, 55.4, 39.8, 38.8, 30.4, 28.4, 27.3, 26.2, 23.9, 22.4, 19.6, 18.4, -4.1, -4.4.

$[\alpha]_D^{28} = 6.2$ (c = 0.05, CHCl$_3$).

HRMS (ESI) for C$_{45}$H$_{68}$O$_7$Si$_2$Na $[M + Na]^+$, calculated: 799.4401, found: 799.4395.

(2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxyphenyl)methanol (46)

The ester functionality in compound 44 was reduced with DIBAL-H to afford compound 46 in 92% yield as stated previously.
$^1$H NMR of compound 46 (400 MHz, CDCl$_3$): $\delta$: 7.77-7.68 (m, 4H), 7.42-7.35 (m, 6H), 6.46 (s, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.06 (td, $J = 15.2$, 6.8 Hz, 1H), 4.67 (d, $J = 3.6$ Hz, 1H), 4.24-4.21 (m, 1H), 4.11-4.07 (m, 1H), 3.95 (s, 3H), 3.68 (q, $J = 6.0$ Hz, 1H), 2.59-2.57 (m, 2H), 1.48-1.41 (m, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.19-1.11 (m, 3H), 1.08-1.06 (comp. 3H), 1.05 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H).

$^{13}$C NMR of compound 46 (100 MHz, CDCl$_3$): $\delta$: 157.8, 155.2, 139.3, 136.2, 136.1, 133.8, 133.6, 130.0, 129.9, 127.7, 121.0, 113.7, 167.9, 95.1, 79.8, 78.0, 71.3, 67.9, 58.0, 56.5, 56.0, 39.7, 39.0, 30.2, 28.5, 27.1, 26.1, 23.7, 22.2, 19.4, 18.3.

$[\alpha]_D^{28} = 7.2$ (c = 0.04, CHCl$_3$).

HRMS (ESI) for C$_{45}$H$_{67}$ClO$_7$Si$_2$Na [M + Na]$^+$, calculated: 833.4011, found: 833.4016.

2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzaldehyde (47)

Compound 45 was oxidized to aldehyde 47 by MnO$_2$ in 95% yield as stated earlier.

$^1$H NMR of compound 47 (400 MHz, CDCl$_3$): $\delta$: 10.43 (s, 1H), 7.70-7.69 (m, 4H), 7.41-7.33 (m, 6H), 7.27 (d, $J = 15.6$ Hz, 1H), 6.47 (d, $J = 2.0$ Hz, 1H), 6.35 (d, $J = 2.4$ Hz, 1H), 6.19 (ddd, $J = 15.6$, 8.8, 4.4 Hz, 1H), 4.15-4.09 (m, 1H), 4.08-4.06 (m, 1H), 4.05-4.04 (m, 1H), 3.91 (s, 3H), 3.71-3.67 (m, 1H), 2.62-2.49 (m, 2H), 1.80 (s, 3H), 1.21 (s, 3H), 1.19-1.10 (comp. 4H), 0.89 (comp. 3H), 0.88 (s, 9H), 0.03 (s, 6H).

$^{13}$C NMR of compound 47 (100 MHz, CDCl$_3$): $\delta$: 190.4, 164.7, 164., 143.6, 136.1, 136.1, 133.9, 133.8, 131.2, 131.0, 129.9, 129.9, 127.7, 127.7, 116.1, 107.8, 104.0, 96.9, 80.0, 77.8, 71.9, 68.8, 55.9, 55.5, 39.7, 38.5, 30.3, 28.3, 27.2, 28.1, 28.0, 23.7, 22.3, 19.54, 18.3, -4.2, -4.5.

$[\alpha]_D^{28} = 5.1$ (c = 0.1, CHCl$_3$).

HRMS (ESI) for C$_{45}$H$_{66}$O$_7$Si$_2$Na [M + Na]$^+$, calculated: 797.4244, found: 797.4235.

2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzaldehyde (48)

Alcohol 46 was oxidized by MnO$_2$ to afford aldehyde 48 in 90% yield as presented earlier.

$^1$H NMR of compound 48 (400 MHz, CDCl$_3$): $\delta$: 10.05 (s, 1H), 7.73-7.61 (m, 4H), 7.42-7.34 (m, 6H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.46 (s, 1H), 5.92-5.84 (m, 1H), 4.18-4.15 (m, 1H), 4.08-4.06 (m, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.97 (comp. 1H), 3.69-3.64 (m, 1H), 2.59-2.56 (m, 2H), 1.42-1.41 (m, 1H), 1.37 (s, 3H), 1.29 (s, 3H), 1.26-1.25 (m, 1H), 1.11-1.06 (m, 3H), 1.05 (comp. 3H), 1.05 (comp. 1H), 1.02 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H).
\[ ^{13}C \text{ NMR of compound 48 (100 MHz, CDCl}_3\]: } \delta: 189.7, 160.6, 159.3, 142.7, 137.4, 136.1, 136.1, 133.7, 133.6, 130.0, 129.9, 127.7, 120.5, 118.7, 114.0, 107.9, 94.7, 79.6, 77.9 71.1, 68.9, 56.5, 56.4, 39.7, 39.0, 30.0, 28.4, 27.1, 26.2, 26.1, 23.7, 22.2, 19.4, 18.3, -4.2, -4.5.

\[ \alpha D^28 = 5.1 \text{ (c = 0.1, CHCl}_3) \].

HRMS (ESI) for C_{45}H_{65}ClO_7Si_2Na [M + Na]^+, calculated: 831.3854, found: 831.3859.

**2-((S,E)-4-((4R,SR)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxol-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzoic acid (49)**

Pinnick oxidation of aldehyde 47 was performed to furnish the acid 49 in 80% yield as described earlier.

\[ ^1H \text{ NMR of compound 49 (400 MHz, CDCl}_3\]: } \delta: 7.69-7.67 (m, 4H), 7.41-7.35 (m, 6H), 7.38 (s, 1H), 6.46-6.15 (m, 1H), 6.13-5.91 (m, 1H), 4.14-4.11 (m, 1H), 3.90 (s, 3H), 3.68-3.65 (m, 1H), 2.50-2.46 (m, 2H), 1.48-1.46 (m, 2H), 1.36 (s, 3H), 1.31 (s, 3H), 1.29-1.27 (m, 2H), 1.06 (s, 3H), 0.02 (s, 6H).

\[ \alpha D^28 = 6.9 \text{ (c = 0.03, CHCl}_3) \].

HRMS (ESI) for C_{45}H_{66}O_8Si_2Na [M + Na]^+, calculated: 813.4193, found: 813.4187.

**2-((S,E)-4-((4R,SR)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxol-4-yl)-4-(tert-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzoic acid (50)**

Pinnick oxidation of aldehyde 48 was performed as described earlier to furnish acid 50 in 80% yield.

\[ ^1H \text{ NMR of compound 50 (400 MHz, CDCl}_3\]: } \delta: 7.69-7.66 (m, 4H), 7.40-7.33 (m, 6H), 6.46 (d, J = 15.6 Hz, 1H), 6.44 (s, 1H), 4.18-4.16 (m, 1H), 4.15-4.12 (m, 1H), 3.99 (s, 1H), 3.99 (comp. 1H), 3.68-3.63 (m, 1H), 2.50-2.47 (m, 2H), 1.31 (s, 3H), 1.31 (s, 3H), 1.29-1.21 (comp. 5H), 1.06 (s, 3H), 1.04 (s, 9H), 0.08 (s, 9H), 0.02 (s, 6H).

\[ \alpha D^28 = 6.9 \text{ (c = 0.03, CHCl}_3) \].
HRMS (ESI) for C_{45}H_{65}ClO_{8}Si_{2}Na [M + Na]^+, calculated: 831.3854, found: 831.3859.

2-((S,E)-4-((tert-butylidiphenylsilyloxy)-4-((4R,5R)-5-((R)-4-hydroxypentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)but-1-enyl)-4,6-dimethoxybenzoic acid (51)

Seco-acid 51 was prepared from 49 in 85% yield as stated earlier.

1H NMR of compound 51 (400 MHz, CDCl3): δ: 7.69-7.67 (m, 4H), 7.41-7.35 (m, 6H), 6.66 (d, J = 15.6 Hz, 1H), 6.50 (d, J = 2 Hz, 1H), 6.38 (d, J = 1.6 Hz, 1H), 6.25-6.17 (m, 1H), 4.13-4.10 (m, 1H), 4.05-4.02 (m, 1H), 3.90-3.84 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.71-3.65 (m, 1H), 2.56-2.42 (m, 2H), 1.39 (s, 3H), 1.36-1.33 (m, 2H), 1.28 (s, 3H), 1.25-1.21 (comp. 4H), 1.10 (d, J = 6.0 Hz, 3H), 1.05 (s, 9H).

13C NMR of compound 51 (100 MHz, CDCl3): δ: 169.7, 161.8, 158.6, 139.6, 136.1, 136.1, 133.8, 133.6, 130.1, 130.0, 129.9, 127.8, 127.7, 107.8, 102.5, 97.7, 79.9, 77.6, 72.2, 68.0, 56.3, 55.6, 38.8, 38.4, 30.1, 28.0, 27.4, 27.2, 27.1, 25.8, 23.2, 23.1, 22.2, 19.5.

[α]_{D}^{28} = 5.1 (c = 0.02, CHCl3).

HRMS (ESI) for C_{39}H_{52}O_{8}SiNa [M + Na]^+, calculated: 699.3328, found: 699.3323.

2-((S,E)-4-((tert-butylidiphenylsilyloxy)-4-((4R,5R)-5-((R)-4-hydroxypentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)but-1-enyl)-3-chloro-4,6-dimethoxybenzoic acid (52)

Selective deprotection of TBS group in compound 50 was performed as stated earlier to afford seco-acid 52 in 82% yield.

1H NMR of compound 52 (400 MHz, CDCl3): δ: 7.69-7.68 (m, 4H), 7.41-7.35 (m, 6H), 6.46 (d, J = 16.4 Hz, 1H), 6.44 (s, 1H), 6.19-6.14 (m, 1H), 4.18-4.16 (m, 1H), 4.05-4.03 (m, 1H), 3.92 (s, 3H), 3.88 (comp. 1H), 3.85 (s, 3H), 3.66-3.65 (m, 1H), 2.51-2.50 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 1.25-1.23 (m, 2H), 1.18-1.16 (m, 3H), 1.11 (d, J = 6.0 Hz, 3H), 1.07-1.06 (m, 1H), 1.03 (s, 9H).

13C NMR of compound 52 (50 MHz, CDCl3): δ: 169.9, 156.6, 156.1, 136.9, 136.3, 130.2, 134.0, 133.7, 130.0, 129.8, 127.9, 127.7, 116.5, 113.9, 107.9, 95.3, 79.7, 77.9, 71.6, 68.3, 56.6, 56.5, 39.1, 38.8, 30.2, 28.1, 27.1, 25.9, 23.4, 22.1, 19.5.

[α]_{D}^{28} = 5.1 (c = 0.02, CHCl3).

HRMS (ESI) for C_{39}H_{51}ClO_{8}SiNa [M + Na]^+, calculated: 733.2939, found: 733.2932.
$^1$H- NMR of Benzoate of compound (S)-13 (400MHz, CDCl$_3$)
$^{13}$C- NMR of Benzoate of compound (S)-13 (100MHz, CDCl$_3$)
DEPT- NMR of Benzoate of compound (S)-13 (100MHz, CDCl₃)
$^1$H-NMR of compound 14 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 14 (50MHz, CDCl$_3$)
DEPT- NMR of compound 14 (50MHz, CDCl₃)
$^1$H-NMR of compound 15 (200MHz, CDCl$_3$)
\[^{13}\text{C}\text{-NMR of compound 15 (50MHz, CDCl}_3\text{ )}\]
DEPT- NMR of compound 15 (50MHz, CDCl₃)
$^{13}$C-NMR of compound 16 (50MHz, CDCl$_3$)
DEPT- NMR of compound 16 (50MHz, CDCl₃)
$^1$H-NMR of compound 18 (200MHz, CDCl$_3$)
DEPT-NMR of compound 18 (50MHz, CDCl₃)
$^1$H- NMR of compound 8 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 8 (50MHz, CDCl$_3$)
DEPT-NMR of compound 8 (50MHz, CDCl$_3$)

\[
\text{OTBS} \quad \text{8}
\]

- 150.23
- 138.17
- 127.35
- 122.17
- 68.00
- 51.92
- 38.90
- 25.84
- 24.52
- 23.76
- 22.19
$^1$H- NMR of compound 17 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 17 (50MHz, CDCl$_3$)
DEPT- NMR of compound 17 (50MHz, CDCl$_3$)
$^1$H- NMR of compound 20 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 20 (50MHz, CDCl$_3$)

[Diagram of $^{13}$C-NMR spectrum with peaks labeled]

OTBDPS

20

OPMB
DEPT- NMR of compound 20 (50MHz, CDCl₃)
$^1$H- NMR of compound 10 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 10 (50MHz, CDCl$_3$)
DEPT- NMR of compound 10 (50MHz, CDCl₃)
$^1$H- NMR of compound 7 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 7 (50MHz, CDCl$_3$)
DEPT- NMR of compound 7 (50MHz, CDCl₃)
$^1$H- NMR of compound 22 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 22 (50MHz, CDCl$_3$)
DEPT- NMR of compound 22 (50MHz, CDCl₃)
$^1$H- NMR of compound 21 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 21 (100MHz, CDCl$_3$)
DEPT- NMR of compound 21 (100MHz, CDCl₃)
$^1$H-NMR of compound 23 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 23 (50MHz, CDCl$_3$)
DEPT- NMR of compound 23 (50MHz, CDCl₃)
$^1$H-NMR of compound 24 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 24 (50MHz, CDCl$_3$)
DEPT- NMR of compound 24 (50MHz, CDCl₃)
$^1$H- NMR of compound 25 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 25 (50MHz, CDCl$_3$)
DEPT- NMR of compound 25 (50MHz, CDCl₃)
$^1$H- NMR of compound 4 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 4 (50MHz, CDCl$_3$)
DEPT- NMR of compound 4 (50MHz, CDCl₃)
$^1$H- NMR of compound 26 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 26 (50MHz, CDCl$_3$)
$^{13}$C-NMR of compound 27 (100MHz, CDCl$_3$)
$^1$H- NMR of compound 28 (200MHz, CDCl$_3$)
$^{13}$C- NMR of compound 28 (50MHz, CDCl$_3$)
$^1$H- NMR of compound 5 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 5 (50MHz, CDCl$_3$)
DEPT-NMR of compound 5 (50MHz, CDCl₃)
$^1$H-NMR of compound 6 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 6 (50MHz, CDCl$_3$)
DEPT- NMR of compound 6 (50MHz, CDCl₃)
NOE spectra of compound 5 (500 MHz, CDCl₃)
NOE spectra of compound 6 (500 MHz, CDCl₃)
$^{13}$C-NMR of compound 29 (50MHz, CDCl$_3$)
DEPT- NMR of compound 29 (50MHz, CDCl₃)
$^1$H- NMR of compound 30 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 30 (50MHz, CDCl$_3$)
DEPT- NMR of compound 30 (50MHz, CDCl₃)

![NMR spectrum of compound 30](image)
$^1$H- NMR of compound 31 (400MHz, CDCl$_3$)

![NMR Spectrum](image_url)
\(^{13}\)C- NMR of compound 31 (50MHz, CDCl\(_3\))
DEPT- NMR of compound 31 (50MHz, CDCl₃)
$^{13}$C-NMR of compound 32 (50MHz, CDCl$_3$)
DEPT- NMR of compound 32 (50MHz, CDCl₃)
$^1$H- NMR of compound 3 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 3 (100MHz, CDCl$_3$)
DEPT- NMR of compound 3 (50MHz, CDCl₃)
$^1$H- NMR of compound 33 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 33 (100MHz, CDCl$_3$)
DEPT- NMR of compound 33 (100MHz, CDCl₃)
$^1$H-NMR of compound 34 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 34 (50MHz, CDCl$_3$)
DEPT- NMR of compound 34 (50MHz, CDCl₃)
$^{1}H$-NMR of compound 35 (400MHz, CDCl$_3$)

[Diagram of the NMR spectrum with chemical shifts and assignments]
$^{13}$C-NMR of compound 35 (100MHz, CDCl$_3$)
DEPT- NMR of compound 35 (100MHz, CDCl₃)
$^1$H- NMR of 10'-epi-Paecilomycin E (400MHz, CDCl$_3$)

10'-epi-Paecilomycin E

1H NMR spectrum with annotations and resonance peaks.
$^{13}$C-NMR of 10'-opi-Paecilomycin E (100MHz, CDCl$_3$)
DEPT- NMR of 10'-opi-Paecilomycin E (100MHz, CDCl₃)
$^1$H- NMR of compound 36 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 36 (50MHz, CDCl$_3$)
DEPT-NMR of compound 36 (50 MHz, CDCl₃)
$^1$H- NMR of compound 37 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 37 (50MHz, CDCl$_3$)
DEPT-NMR of compound 37 (50MHz, CDCl₃)
$^1$H- NMR of compound 38 (400MHz, CDCl$_3$)
$^{13}$C- NMR of compound 38 (50MHz, CDCl$_3$)
DEPT- NMR of compound 38 (50MHz, CDCl₃)
$^1$H- NMR of compound 39 (400MHz, CDCl$_3$)
$^{13}$C- NMR of compound 39 (50MHz, CDCl$_3$)
DEPT- NMR of compound 39 (50MHz, CDCl$_3$)
$^1$H- NMR of compound 40 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 40 (50MHz, CDCl$_3$)
DEPT- NMR of compound 40 (50MHz, CDCl$_3$)
$^1$H- NMR of compound 41 (200MHz, CDCl$_3$)
$^{13}$C-NMR of compound 41 (50MHz, CDCl$_3$)
DEPT- NMR of compound 41 (50MHz, CDCl₃)
$^1$H- NMR of compound 42 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 42 (50MHz, CDCl$_3$)
DEPT- NMR of compound 42 (50MHz, CDCl$_3$)
$^1$H- NMR of compound 43 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 43 (100MHz, CDCl₃)
DEPT- NMR of compound 43 (100MHz, CDCl₃)
$^1$H- NMR of compound 45 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 45 (100MHz, CDCl$_3$)
DEPT-NMR of compound 45 (100MHz, CDCl$_3$)
$^{1}$H- NMR of compound 47 (400MHz, CDCl$_3$)
$^{13}$C- NMR of compound 47 (100MHz, CDCl$_3$)
DEPT- NMR of compound 47 (100MHz, CDCl₃)
$^1$H-NMR of compound 49 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 49 (100MHz, CDCl$_3$)
DEPT-NMR of compound 49 (100MHz, CDCl₃)
$^1$H- NMR of compound 51 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 51 (100MHz, CDCl$_3$)
DEPT-NMR of compound 51 (100MHz, CDCl₃)
$^1$H-NMR of compound 53 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 53 (100MHz, CDCl$_3$)
DEPT- NMR of compound 53 (100MHz, CDCl₃)
$^1$H- NMR of compound 55 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 55 (100MHz, CDCl$_3$)
DEPT-NMR of compound 55 (100MHz, CDCl₃)
$^1$H-NMR of compound 57 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 57 (100MHz, CDCl$_3$)
DEPT- NMR of compound 57 (100MHz, CDCl₃)
$^1$H-NMR of Paecilomycin E (100MHz, CDCl$_3$)
C-NMR of Paecilomycin E (400MHz, CDCl₃)
DEPT-NMR of Paecilomycin E (100MHz, CDCl₃)
$^1$H- NMR of Paecilomycin E (600MHz, Acetone-d$_6$)
Expanded $^1$H-NMR of Paecilomycin E (600 MHz, Acetone-d$_6$)
$^{1}\text{H}^{1}\text{H~COSY}$ of paecilomycin E (600 MHz, CDCl$_3$)
HSQC of paecilomycin E (600 MHz, CDCl$_3$)

Paecilomycin E
$^1$H- NMR of compound 44 (400MHz, CDCl$_3$)
$^{13}$C- NMR of compound 44 (100MHz, CDCl$_3$)
DEPT- NMR of compound 44 (100MHz, CDCl₃)
$^1$H- NMR of compound 46 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 46 (100MHz, CDCl$_3$)
DEPT- NMR of compound 46 (100MHz, CDCl₃)
$^1$H- NMR of compound 48 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 48 (100MHz, CDCl$_3$)
DEPT- NMR of compound 48 (100MHz, CDCl$_3$)
$^1$H- NMR of compound 50 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 50 (100MHz, CDCl$_3$)
DEPT- NMR of compound 50 (100MHz, CDCl₃)
$^1$H-NMR of compound 52 (200MHz, CDCl$_3$)
$^{13}$C- NMR of compound 52 (50MHz, CDCl$_3$)
DEPT- NMR of compound 52 (50MHz, CDCl₃)
$^1$H- NMR of compound 54 (400MHz, CDCl$_3$)
$^{13}\text{C}$-NMR of compound 54 (50MHz, CDCl$_3$)
DEPT- NMR of compound 54 (50MHz, CDCl₃)
$^1$H- NMR of compound 56 (400MHz, CDCl$_3$)
$^{13}$C-NMR of compound 56 (100MHz, CDCl$_3$)
DEPT- NMR of compound 56 (100MHz, CDCl₃)
$^1$H-NMR of compound 58 (400MHz, CDCl$_3$)
$^1$H NMR of compound 58 (100MHz, CDCl$_3$)
DEPT-NMR of compound 58 (100MHz, CDCl$_3$)
$^1$H-NMR of 6'-epi-cochliomycin C (400MHz, CDCl$_3$)
$^{13}\text{C} \text{- NMR of 6'-epi-cochliomycin C (100MHz, CDCl}_3$)
DEPT- NMR 6'-epi-cochliomycin C (100MHz, CDCl₃)
$^1$H-NMR of 6'-epi-cochliomycin C (600MHz, Acetone-$d_6$)
HSQC of 6'-epi-cochliomycin C (600 MHz, CDCl₃)
HPLC chromatogram of racemic 11
HPLC chromatogram of (R)-12

Department of Chemistry, IIT-Kharagpur

Sample Information
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Sample ID: transesterification
Valve:
Injection Volume: 5 ul
Data Filename: pratik resolution RAL intermediate alcohol.lcm
Method Filename: pda.lcm
Batch Filename: 
Report Filename: Default.lcr
Date Acquired: 7/1/2014 4:32:14 PM
Data Processed: 7/1/2014 4:47:11 PM

Chromatogram
pratik resolution RAL intermediate alcohol C:\LabSolutions\Data\Project1\pratik resolution RAL intermediate alcohol.lcm

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$\epsilon = 98\%$
HPLC chromatogram of (S)-13