Supporting Information

Synthesis of the C17-C30 Fragment of Amphidinol 3.

Nicolas Rival, Damien Hazelard, Gilles Hanquet, Thomas Kreuzer, Charlelie Bensoussan,
Sebastien Reymond, Janine Cossy, and Françoise Colobert*

Laboratoire de stéréochimie (UMR CNRS 7509), CNRS/Université de Strasbourg (ECPM),
25 Rue Becquerel, F-67087 Strasbourg, France.

Laboratoire de Chimie Organique, ESPCI ParisTech, CNRS, 10 Rue Vauquelin, 75231 Paris Cedex 05, France

francoise.colobert@unistra.fr

Table of contents

General procedures S2

Preparation of compounds 3-8, 10-17, 19-24, 26, 28 and intermediate compounds S3

1H and 13C NMR Spectra for 5-8, 11-17, 19-24, 26, 28 and intermediate compounds S23
General Methods

Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note:
Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Dichloromethane was distilled over CaH₂ and acetonitrile over P₂O₅. Flash column chromatography (FC) was performed using silica gel 60 for preparative column chromatography (40–63 mm), unless specifically noted otherwise. Demetalled silica gel was prepared according to published procedure. ¹Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F254 (otherwise stated), visualization by UV light or through staining with phosphomolybdic acid, KMnO₄ or Vanillin. Optical rotations were measured on a polarimeter with a sodium lamp and are reported as follows: αD (c g/100 mL, solvent). NMR spectra (¹H and ¹³C) were recorded on a 300 MHz or 400 MHz. Chemical shifts are reported in ppm with the solvent (CDCl₃) resonance as the δ 7.26 ppm (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, s ap=apparent singlet, mc=multiplet center, coupling constants Hz, integration). Carbon NMR (¹³C NMR) spectra were also run at various field strengths as indicated. Spectra were recorded in CDCl₃ using residual undeuterated solvent (77 ppm) as an internal reference. Infra red (IR) spectra were recorded on a diamond ATR spectrometer using neat simples. Infra red frequencies are reported in wavenumbers (cm⁻¹), intensities were determined qualitatively and are reported as strong (s), medium (m) or weak (w). Solid Lewis acids were flamed-dried in the reaction flask under vacuum and under Argon before use.

Synthesis of (+)-(R)-1-methyl-4-(methylsulfinyl)benzene\(^2\)

A solution of methyl iodide (4.17 g, 29.4 mmol) in 26 mL of Et\(_2\)O was added slowly at room temperature to magnesium (650 mg, 26.7 mmol) and stirred at room temperature for 2 h. The resulting mixture was transferred via transfer syringe to a solution of (-)-(1R,2S,3R,3S)-menthyl-p-tolyl-sulfinate\(^3\) (6.56 g, 22.3 mmol) in 26 mL of toluene at 0 °C. After the addition, the mixture is stirred at room temperature for 3 h and then hydrolyzed with aqueous saturated solution of NH\(_4\)Cl (30 mL). The aqueous phase is extracted with Et\(_2\)O (3x30 mL) and the combined organic layers were washed with brine (30 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue was crystallized in hot petroleum ether and overnight storage at -10 °C. After filtration, the mother liquid was subsequently purified by flash chromatography on silica gel (Et\(_2\)O → EtOAc) giving the (+)-(R)-1-methyl-4-(methylsulfinyl)benzene as white crystals (2.84 g, 18.41 mmol, 83%): m.p. 72 - 74 °C; \([\alpha]^{25}\)\(_D\) +197.2° (c = 1.03 in CHCl\(_3\)); R\(_f\): 0.36 (EtOAc); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.41 (A\(_2\)B\(_2\), \(J_{AB}\) = 8.1 Hz, \(\Delta\nu\) = 62.9 Hz, 4H), 2.68 (s, 3H), 2.39 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.4, 141.4, 129.9, 123.4, 43.9, 21.3; IR 3052, 3020, 2997, 2907, 1595, 1494, 1455, 1422, 1398, 1387, 1299, 1209, 1178, 1104, 1087, 1046, 1013, 970, 947, 848, 815, 707, 686 cm\(^{-1}\).

Synthesis of sodium 4-hydroxybutanoate \(^3\)

Sodium hydroxide (7.57 g, 0.19 mol) was dissolved in 112 mL of EtOH at room temperature and stirred for 30 min, prior to the addition of \(\delta\)-butyrolactone (16.0 g, 0.19 mol). The resulting mixture was stirred for 2 h at room temperature, while a white precipitate has been formed. The solution was concentrated under reduced pressure and the resultant white solid was suspended in 300 mL of benzene and heated for 2 h using a Dean Stark device to remove traces of water. After evaporation of the solvent the white solid was dried under reduced pressure. Recrystallization of the crude product in EtOH furnished sodium salt \(^3\) (22.2 g, 0.176 mol, 95%) as white crystals: \(^1\)H NMR (300 MHz, D\(_2\)O) \(\delta\) 3.58 (t, \(J = 6.7\) Hz, 2H), 2.22 (t, \(J = 7.6\) Hz, 2H), 1.78 (q, \(J = 7.0\) Hz, 2H); \(^{13}\)C NMR (75 MHz) (D\(_2\)O) \(\delta\) 183.7, 62.1, 34.7, ...
29.0; IR 3318, 2960, 2944, 2878, 1555, 1475, 1450, 1437, 1407, 1361, 1329, 1248, 1273, 1228, 1173, 1157, 1066, 1052, 1015, 946, 920, 881, 869, 775, 751, 697 cm\(^{-1}\).

**Synthesis of methyl 4-(tert-butyldiphenylsilyloxy) butanoate 4**

![Schema](image)

Iodomethane (6.5 mL, 104.13 mmol) in 12 mL of dry DMF was added to a stirred solution of sodium 4-hydroxybutanoate 3 (2.02 g, 16.02 mmol) in 44 mL of DMF. The resulting solution was stirred for 24 h prior to the addition of imidazole (2.40 g, 35.2 mmol) and tert-butyldiphenylchlorosilane (5.28 g, 19.2 mmol). Stirring was continued for 16 h, and the mixture was diluted with 100 mL of EtOAc, washed subsequently with distilled water, aqueous saturated Na\(_2\)S\(_2\)O\(_3\) and brine (40 mL each), dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/10) to afford the protected ester 4 as a colorless oil (5.18 g, 14.52 mmol, 91%): \(\text{Rf} 0.60\) (EtOAc/Cyclohexane: 1/10); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.64-7.71\) (m, 4H), 7.37-7.47 (m, 6H), 3.71 (t, \(J = 6.1\) Hz, 2H), 3.67 (s, 3H), 2.49 (t, \(J = 7.5\) Hz, 2H), 1.87-1.96 (m, 2H), 1.08 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 174.0, 135.5, 133.7, 129.6, 127.6, 62.8, 51.4, 30.6, 27.76, 26.8, 19.2\); IR 3072, 3051, 2953, 2932, 2858, 1738, 1590, 1473, 1463, 1428, 1390, 1362, 1256, 1192, 1168, 1105, 998, 967, 822, 738, 700, 688 cm\(^{-1}\).

**Synthesis of (R)-5-(tert-butyldiphenylsilyloxy)-1-(p-tolylsulfinyl)pentan-2-one 5**

![Schema](image)

To a solution of diisopropylamine (1.59 mL, 11.35 mmol) in 15 mL of THF cooled at -78 °C was added dropwise \(n\)-BuLi (6.48 mL, 1.60 M in hexane, 10.37 mmol). The resulting solution was stirred for 1 h at -78 °C, prior to the addition of a solution of (+)-(R)-1-methyl-4-(methylsulfinyl)benzene (1.52 g, 9.87 mmol) in 12 mL of THF at -78 °C. After stirring for 1 h at -78 °C, the anion solution was transferred via transfer syringe to a -78 °C cold solution of the ester 4 (1.76 g, 4.94 mmol) in 18 mL of THF and stirred for 1 h. The reaction mixture was then diluted with 20 mL of Et\(_2\)O, hydrolyzed with aqueous saturated NH\(_4\)Cl (20 mL) and washed with brine (20 mL). The organic layer was dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on demetalled silica gel (Et\(_2\)O) to furnish the \(\beta\)-ketosulfoxide 5 as a colorless

oil (2.34 g, 4.89 mmol, 99%): $[\alpha]^{25}_D +90.6^\circ$ (c = 1.43 in CHCl$_3$) and recovered 40% of the excess of (+)-(R)-1-methyl-4-(methylsulfinyl)benzene, R$_f$ 0.63 (Et$_2$O), $^1$H NMR (300 MHz, CDCl$_3$) δ 7.61-7.64 (m, 4H), 7.52 (B of A$_2$B$_2$, $J_{AB} = 8.1$ Hz, $\Delta\nu = 63.3$ Hz, 2H), 7.35-7.45 (m, 6H), 7.31 (A of A$_2$B$_2$, $J_{AB} = 8.1$ Hz, $\Delta\nu = 63.3$ Hz, 2H), 3.79 (t, $J = 6.1$ Hz, 2H), 2.49-2.68 (m, 2H), 2.40 (s, 3H), 1.74-1.83 (m, 2H), 1.04 (s, 9H); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62-7.66 (m, 4H), 7.51-7.53 (m, 2H), 7.32-7.45 (m, 8H), 4.17-4.24 (m, 1H), 3.61-3.69 (m, 2H), 2.85 (AB of ABX, $J_{AB} = 13.4$ Hz, $J_{AX} = 9.8$ Hz, $J_{BX} = 2.0$ Hz, $\Delta\nu = 102.9$ Hz, 2H), 2.42 (s, 3H), 1.54 - 1.68 (m, 4H), 1.03 (s, 9H); $^1$C NMR (75 MHz, CDCl$_3$) δ 141.5, 139.9, 135.55, 135.5, 133.65, 133.6, 130.1, 130.0, 129.6, 127.6, 124.0, 124.0, 66.6, 63.8, 61.7, 34.0, 28.3, 26.8, 21.4, 19.2; IR 3365, 2930, 2858, 1472, 1428, 1390, 1362, 1110, 1056, 963, 823, 810, 741, 705, 688 cm$^{-1}$; HRMS ES m/z (M+Li)$^+$ Calcd for C$_{28}$H$_{34}$LiO$_3$SSi 485.2152, found 485.2100.

**Synthesis of (S)-5-(tert-butyldiphenylsilyloxy)-1-((R)-p-tolylsulfinyl)pentan-2-ol 6**

To a solution of $\beta$-ketosulfoxide 5 (614 mg, 1.28 mmol) in 10 mL of THF cooled at -78 °C was added dropwise DIBAL-H (1.60 mL, 1.0 M in toluene, 1.60 mmol). The resulting solution was stirred for 5 h at -78 °C, quenched with 2 mL of MeOH, diluted with 10 mL of EtOAc, hydrolyzed with an aqueous saturated solution of sodium-potassium tartrate (10 mL) and stirred overnight until a clear phase-separation occurred. The aqueous phase was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on demetalled silica gel (EtOAc/cyclohexane: 1/1) gave the $\beta$-hydroxysulfoxide 6 as a colorless oil (611 mg, 1.27 mmol, 99%): $[\alpha]^{25}_D$: +120.0° (c = 1.15 in CHCl$_3$); R$_f$ 0.37 (EtOAc/Cyclohexane: 1/1); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62-7.66 (m, 4H), 7.51-7.53 (m, 2H), 7.32-7.45 (m, 8H), 4.17-4.24 (m, 1H), 3.61-3.69 (m, 2H), 2.85 (AB of ABX, $J_{AB} = 13.4$ Hz, $J_{AX} = 9.8$ Hz, $J_{BX} = 2.0$ Hz, $\Delta\nu = 102.9$ Hz, 2H), 2.42 (s, 3H), 1.54 - 1.68 (m, 4H), 1.03 (s, 9H); $^1$C NMR (75 MHz, CDCl$_3$) δ 141.5, 139.9, 135.55, 135.5, 133.65, 133.6, 130.1, 130.0, 129.6, 127.6, 124.0, 124.0, 66.6, 63.8, 61.7, 34.0, 28.3, 26.8, 21.4, 19.2; IR 3365, 2930, 2858, 1472, 1428, 1390, 1110, 1056, 963, 823, 810, 741, 705, 688 cm$^{-1}$; HRMS ES m/z (M+Li)$^+$ Calcd for C$_{28}$H$_{34}$LiO$_3$SSi 487.2310, found 487.2274.

**Synthesis of ((S)-4-(benzyl oxy)-5-((R)-p-tolylsulfinyl)pentyloxy)(tert-butyl)diphenylsilane 7**

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2012
A solution of alcohol 6 (958 mg, 1.99 mmol) in 5 mL of THF was added dropwise at 0°C to a solution of (96 mg, 3.99 mmol) oil-free sodium hydride in 20 mL of THF. The reaction mixture was stirred for 30 min, prior to the addition of (592 μl, 4.98 mmol) benzyl bromide. After 30 min at 0°C and 3 h at room temperature the resulting solution was carefully hydrolyzed by adding 5 mL of an aqueous saturated solution of NH₄Cl. The aqueous layer was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 2/5) to give the benzylether 7 (854 mg, 1.49 mmol, 75%) as a colorless oil: [α]D +91.2° (c = 1.43 in CHCl₃); Rf 0.60 (EtOAc/Cyclohexane: 1/1); ¹H NMR (300 MHz, CDCl₃) δ 7.62-7.67 (m, 4H), 7.46-7.47 (m, 2H), 7.27-7.43 (m, 13H), 4.67 (AB, JAB = 11.0 Hz, Δν = 11.5 Hz, 2H), 4.07-4.14 (X of ABX, m, 1H), 3.65 (t, J = 6.1 Hz, 2H), 2.82-2.91 (AB of ABX, m, 2H), 2.42 (s, 3 H), 1.52-1.85 (m, 4 H), 1.04 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 141.6, 141.3, 138.0, 135.5, 133.8, 130.0, 129.6, 128.4, 128.1, 127.8, 127.6, 123.8, 73.2, 72.3, 64.6, 63.6, 30.2, 27.6, 26.9, 21.4, 19.2; IR 2930, 2857, 1494, 1472, 1455, 1428, 1105, 1086, 1045, 1016, 998, 938, 822, 807, 738, 699 cm⁻¹; HRMS ES m/z (M+Na)+ Calcd for C₃₅H₄₂NaO₃SSi 593.2516, found 593.2472.

Synthesis of (S)-2-(benzyloxy)-5-(tert-butyldiphenylsilyloxy)pentanal 8

To a solution of sulfoxide 7 (850 mg, 1.49 mmol) in 12 mL of MeCN cooled at 0°C was added dropwise subsequently 2,4,6-collidine (595 μl, 4.47 mmol) and trifluoroacetic anhydride (1.04 mL, 7.45 mmol). The reaction mixture was stirred 30 min, prior to the addition of 12 mL of an aqueous saturated solution of NaHCO₃, warmed to room temperature and stirred for 1 h at this temperature. The aqueous layer was extracted with EtOAc (3x15 mL) and the combined organic layers were washed with brine (15 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9) gave the aldehyde 8 (585 mg, 1.31 mmol, 88%) as a colorless oil: [α]D -30.6° (c = 1.03 in CHCl₃); Rf 0.46 (EtOAc/Cyclohexane: 1/10); ¹H NMR (300 MHz, CDCl₃) δ 9.65 (d, J = 2.0 Hz, 1H); 7.65-7.68 (m, 4H), 7.29-7.47 (m, 11H), 4.59 (AB, JAB = 11.7 Hz, Δν = 41.7 Hz, 2H), 3.78 (ddd, J = 7.4 Hz, J = 5.2 Hz, J = 2.0 Hz, 1H), 3.64 (t, J = 6.0 Hz, 2H), 1.57-1.93 (m, 4H), 1.06 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 203.5, 137.3, 135.5, 133.8, 129.6, 128.5, 128.0, 128.0, 127.6, 83.2, 72.4, 63.2, 27.7, 26.9, 26.419, 19.209; IR 2858, 1733, 1472, 1455, 1428, 1106, 1090,
1028, 1007, 998, 937, 823, 794, 738, 699 cm\(^{-1}\), Anal. Calcd for C\(_{28}\)H\(_{34}\)O\(_3\)Si C, 75.29; H, 7.67; Found: C, 75.23; H, 7.598.

**Synthesis of ethyl-3-oxohept-6-enoate\(^5\)**

To a stirred solution of 4-pentenoic acid 9 (6.0 g, 59.3 mmol) in THF (60 mL) was added portion wise carbonyldiimidazole (9.62 g, 59.3 mmol). The mixture was stirred 1 h at room temperature.

A solution of diisopropylamine (33.5 mL, 237.2 mmol) in THF (30 mL) was cooled to \(-78 \, ^\circ\text{C}\) and was subsequently treated with a solution of n-butyllithium (148.3 mL, 1.60 M in hexane, 237.2 mmol). After 30 min at \(-78 \, ^\circ\text{C}\) a solution of EtOAc (11.61 mL, 118.6 mmol) in 30 mL of THF was added dropwise. After 30 min at \(-78 \, ^\circ\text{C}\) this solution was added to the imidazolide solution cooled at \(-78 \, ^\circ\text{C}\). After 15 min at \(-78 \, ^\circ\text{C}\) the reaction was warmed to room temperature and stirred 3 h. The reaction mixture was quenched with 300 mL of aqueous saturated solution of NH\(_4\)Cl. The mixture was extracted with Et\(_2\)O (2x200 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO\(_4\), filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9 \(\rightarrow\) 2/8) yielding the \(\beta\)-keto ester as a colorless oil (7.4 g, 43.68 mmol, 74%): R\(_f\) 0.47 (EtOAc/Cyclohexane: 1/3); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.42-5.89 (m, 1 H), 5.04 (d, \(J = 17.1 \, \text{Hz}\), 1 H), 5.00 (d, \(J = 9.3 \, \text{Hz}\), 1 H), 4.21 (q, \(J = 7.2 \, \text{Hz}\), 2 H), 3.44 (s, 2 H), 2.65 (d, \(J = 7.2 \, \text{Hz}\), 2 H), 2.30-2.40 (m, 2 H), 1.28 (t, \(J = 7.2 \, \text{Hz}\), 3 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 201.8, 167.0, 136.4, 115.4, 61.2, 49.2, 41.9, 27.3, 14.0.

**Synthesis of ethyl 3,3-ethylenedioxy-hept-6-enoate\(^6\)**

\(\beta\)-keto ester (vide supra) (6.23 g, 36.6 mmol) was diluted in ethylene glycol (26.5 mL, 475.8 mmol) and treated subsequently at room temperature with triethyl orthoformate (15 mL, 91.5 mmol) and (±)-10-camphorsulfonic acid (860 mg, 3.7 mmol). The resulting mixture was stirred for 24 h, prior to addition of a NaHCO\(_3\) saturated solution (100 mL). The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO\(_4\), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel

---


(EtOAc/Cyclohexane: 1/9) afforded acetal 10 as a colorless oil (7.56 g, 35.46 mmol, 97%): Rf 0.26 (EtOAc/Cyclohexane: 1/5); 1H NMR (300 MHz, CDCl3) δ 5.75-3.91 (m, 1H), 5.03 (dq, J = 18.0, J = 1.8 Hz, 1H), 4.95 (dq, J = 9.0, J = 1.5 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.93-4.05 (m, 4H), 2.66 (s, 2H), 2.12-2.23 (m, 2H), 1.88-1.96 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 169.4, 138.1, 114.4, 109.0, 65.1, 60.5, 42.7, 36.8, 27.7, 14.1

Synthesis of 1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-one

To a solution of diisopropylamine (6.4 mL, 45.4 mmol) in 50 mL of THF cooled at -78 °C was added dropwise n-BuLi (28.4 mL, 1.60 M in hexane, 45.4 mmol). The resulting solution was stirred for 1 h at -78 °C, prior to the addition of a solution of (+)-(R)-1-methyl-4-(methylsulfinyl)benzene (7.0 g, 45.4 mmol) in 40 mL of THF at -78 °C. After stirring for 1 h at -78 °C, a solution of ester 10 (4.31 g, 20.17 mmol) in 40 mL of THF was added dropwise. The reaction mixture was stirred for 5 h at -78 °C, hydrolyzed with an aqueous saturated solution of NH4Cl (150 mL) and warmed to room temperature. The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over Na2SO4, filtered and concentrated in vacuo. Purification of the crude by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1→7/3) afforded the sulfoxide as a yellow oil (4.61 g, 14.25 mmol, 72%): [α]25D +135.7° (c = 0.79 in CHCl3); Rf 0.25 (EtOAc/Cyclohexane: 1/1); 1H NMR (300 MHz, CDCl3) δ 7.52 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 5.65-5.82 (m, 1H), 4.97 (dq, J = 17.1 Hz, J = 2.4 Hz, 1H), 4.91 (dq, J = 10.2 Hz, J = 2.7 Hz, 1H), 3.90-3.98 (m, 6H), 2.84 (AB, JAB = 13.5 Hz, Δν = 29.7 Hz, 2H), 2.40 (s, 3 H), 2.00-2.12 (m, 2 H), 1.63-1.72 (m, 2 H); 13C NMR (75 MHz, CDCl3) δ 199.2, 142.0, 139.7, 137.8, 130.0, 124.1, 114.6, 109.1, 69.0, 64.9, 51.8, 37.0, 27.5, 21.4; IR 2922, 1708, 1641, 1494, 1359, 1306, 1085, 1035, 950, 911, 809 cm⁻¹; HRMS ES m/z (M+Li): Calcd for C17H22LiO4S 329.1394, found 329.1385

Synthesis of (S)-1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-ol 11
Dibal-H (17 mL, 1.0 M in toluene, 17 mmol) was added dropwise to β-ketosulfoxide (vide supra) (2.2 g, 6.83 mmol) dissolved in 100 mL of THF cooled at -78 °C. The resulting solution was stirred for 2 h at -78 °C, quenched with 20 mL of MeOH, diluted with 65 mL of EtOAc, hydrolyzed with a saturated sodium-potassium tartrate solution (65 mL) and stirred overnight. The aqueous phase was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1→6/4) affording the β-hydroxysulfoxide 11 as a white solid (2.19 g, 6.75 mmol, 99%): [α]$_{D}^{25}$ +206.7° (c = 1.00 in CHCl₃); R$_f$ 0.46 (EtOAc/Cyclohexane: 4/1); $^1$H NMR (300 MHz, CDCl₃) δ 7.54 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 5.69-5.85 (m, 1H), 4.99 (d, $J$ = 18.3, 1H), 4.94 (d, $J$ = 10.2, 1H), 4.42-4.53, (m, 1H), 3.89-3.99 (m, 4H), 2.77-2.93 (m, 2 H), 2.41 (s, 3 H), 2.01-2.13 (m, 2 H), 1.82-1.89 (m, 2 H), 1.61-1.73 (m, 2 H); $^{13}$C NMR (75 MHz, CDCl₃) δ 141.2, 140.5, 137.8, 129.8, 123.7, 114.4, 110.7, 64.6, 64.5, 62.7, 42.6, 36.3, 27.7, 21.2; IR 3359, 2927, 1710, 1641, 1492, 1398, 1305, 1085, 1030, 911, 810cm$^{-1}$; HRMS ES m/z (M+Na)$^+$ Calcd for C$_{17}$H$_{24}$NaO$_4$S 347.1288, found 347.1247.

Synthesis of (25)-2-Hydroxy-1((R)-p-tolylsulfinyl)-oct-7-en-4-one

Acetal 11 (1.09 g, 3.36 mmol) in 35 mL of acetone was treated with (±)-10-camphorsulfonic acid (170 mg, 0.73 mmol). The reaction was stirred 24 h and diluted with 20 mL of CH$_2$Cl$_2$. The organic phase was washed with a saturated NaHCO$_3$ solution (2x10 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated under reduced pressure affording hydroxyketone as a solid, which was directly used for the next step without further purification. For analysis, a sample was recrystallized in ether to give a white solid: m.p. 73 - 75 °C; [α]$_{D}^{25}$ +228.6° (c = 0.61 in CHCl₃); R$_f$ 0.45 ((EtOAc/Cyclohexane: 4/1); $^1$H NMR (300 MHz, CDCl₃) δ 7.53 (d, $J$ = 8.1 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 5.69-5.86 (m, 1H), 5.01 (d, $J$ = 17.1, 1H), 4.98 (d, $J$ = 10.2, 1H), 4.57-4.68 (m, 1H), 2.90 (AB of ABX, $J_{AB}$ = 13.5, $J_{AX}$ = 9.5 Hz, $J_{BX}$ = 2.7 Hz, Δν = 86.24 Hz, 2H), 2.64-2.70 (m, 2H), 2.45-2.56 (m, 2 H), 2.43 (s, 3 H), 2.26-2.36 (m, 2 H); $^{13}$C NMR (75 MHz, CDCl₃) δ 209.0, 141.6, 136.6,
130.1, 123.9, 123.9, 115.5, 65.8, 63.4, 48.6, 42.6, 27.3, 21.4; IR 3361, 2907, 1710, 1641, 1494, 1376, 1049, 1038, 905, 808 cm\(^{-1}\); HRMS ES m/z (M+Na)\(^+\) Calcd for C\(_{15}\)H\(_{20}\)NaO\(_3\)S 303.1025, found 303.0989.

**Synthesis of (2S,4S)-7-(4-methoxybenzoyloxy)-1-((R)-p-tolylsulfinyl)octane-2,4-diol 12**

![Chemical structure](image)

Diethylmethoxy borane (4 mL, 1.0 M in THF, 4 mmol) was added dropwise to crude hydroxyketone (vide supra) (874 mg, 3.12 mmol) in 40 mL of THF/MeOH (4/1) at –78 °C. The resulting mixture was stirred for 20 min, prior to the addition of sodium borohydride (138 mg, 4.06 mmol). The reaction was stirred 4 h at –78 °C and was quenched with 38 mL of acetic acid, warmed up to room temperature, diluted with EtOAc (50 mL) and treated with an saturated NaHCO\(_3\) solution up to pH = 6. The aqueous phase was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was taken up in MeOH, heated and concentrated *in vacuo*. This procedure was repeated four times. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane : 6/4) affording the diol 12 as a white solid (704 mg, 2.49 mmol, 80% over two steps): m.p. 110-114°C; \([\alpha]\)\(^{25}\)_D +230.3° (c = 1.00 in CHCl\(_3\)), R\(_f\) 0.33 (EtOAc/Cyclohexane: 4/1); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.52 (d, \(J\) = 8.4 Hz, 2H), 7.35 (d, \(J\) = 8.1 Hz, 2H), 5.71-5.88 (m, 1H), 5.01 (dd, \(J\) = 17.3, \(J\) = 1.7, 1H), 4.95 (d, \(J\) = 10.7 Hz, 1H), 4.38-4.55 (m, 1H), 3.81-3.97 (m, 1H), 3.61 (s broad, 2 H), 2.87 (ABX, \(J_{AB}\) = 13.4 Hz, \(J_{AX}\) = 9.8 Hz, \(J_{BX}\) = 2.0 Hz, \(\Delta\nu\) = 126.3 Hz, 2H), 2.42 (s, 3 H), 2.02-2.24 (m, 2 H), 1.41-1.75 (m, 4 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.7, 139.4, 138.3, 130.1, 124.0, 114.9, 71.3, 67.4, 62.2, 42.7, 36.9, 29.6, 21.4; IR 3284, 2907, 1641, 1494, 1450, 1318, 1105, 1084, 1034, 910, 810 cm\(^{-1}\); HRMS ES m/z (M+Li)\(^+\) Calcd for C\(_{15}\)H\(_{22}\)LiO\(_3\)S 289.1445, found 289.1407.

**Synthesis of (4S,6S)-4-(3-(4-methoxybenzoyloxy)butyl-2,2-dimethyl-6((R)-p-tolylsulfinylmethyl)-1,3-dioxane**

![Chemical structure](image)

Dimethoxypropane (4.5 mL, 36.7 mmol) and PPTS (109 mg, 433 μmol) were added to diol 12 (608 mg, 1.45 mmol) in 14 mL of acetone at room temperature. The reaction was
stirred for 16 h, hydrolyzed with 10 mL of a saturated NaHCO₃ solution and poured in 30 mL of EtOAc. The aqueous layer was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 2/1) gave the acetal as a solid (351.8 mg, 1.09 mmol, 95%): m.p. 59 - 61 °C; [α]²⁵D +204.7° (c = 0.51 in CHCl₃); Rf 0.76 ((EtOAc/Cyclohexane: 4/1); ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.72-5.87 (m, 1H), 4.93-5.06 (m, 2 H), 4.42-4.57 (m, 1H), 3.85-3.97 (m, 1H), 2.70-2.86 (m, 2 H), 2.41 (s, 3 H), 2.01-2.25 (m, 2 H), 1.52 (s, 3 H), 1.45-1.70 (m, 2 H), 1.44 (s, 3 H), 1.17 (s, 3 H), 1.17-1.38 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 141.3, 138.0, 130.0, 123.8, 114.8, 99.2, 67.9, 65.0, 63.5, 36.4, 35.2, 30.0, 29.0, 21.3, 21.3, 19.8; IR: 2993, 2937, 1638, 1494, 1436, 1376, 1263, 1195, 1170, 1053, 1033, 807 cm⁻¹; HRMS ES m/z (M+Li)⁺ Calcd for C₁₈H₁₆LiO₃S 329.1758, found 329.1711.

Synthesis of (4S,6S)-6-[(3-(4-methoxybenzyl)oxy)butyl]-2,2-dimethyl-1,3-dioxane-4-carbaldehyde 13

2,4,6-collidine (0.72 mL, 5.54 mmol) and trifluoroacetic anhydride (1.2 mL, 8.63 mmol) were added dropwise subsequently to a solution of sulfoxide (vide supra) (568 mg, 1.76 mmol) in 20 mL of MeCN cooled at 0 °C. The reaction mixture was stirred 45 min, prior to the addition of 20 mL of a saturated NaHCO₃ solution, warmed to room temperature and stirred for 1 h 30. The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 5/95→20/80) gave the aldehyde 13 as a colorless oil (325 mg, 1.58 mmol, 90%): [α]²⁵D -37.9° (c = 0.33 in CHCl₃); Rf 0.37 (EtOAc/Cyclohexane: 1/3); ¹H NMR (300 MHz, CDCl₃) δ 9.59 (s, 1H), 5.72-5.88 (m, 1H), 4.93-5.09 (m, 2H), 4.28 (dd, J = 12.3 Hz, 3.0 Hz, 1H), 3.53-4.00 (m, 1H), 2.03-2.25 (m, 2H), 1.49-1.68 (m, 2H), 1.47 (s, 3H), 1.46 (s, 3H), 1.31 (q, J = 12.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 201.3, 137.9, 115.0, 99.1, 74.1, 67.5, 35.2, 31.0, 29.8, 28.9, 19.5; IR: 2993, 2927, 1739, 1641, 1435, 1380, 1267, 1201, 1111, 911 cm⁻¹; HRMS ES m/z (M+Li)⁺ Calcd for C₁₁H₁₆LiO₃ 205.1411, found 205.1395.

Synthesis of (4S,6S)-6-(but-3-enyl)-N-methoxy-N,2,2-trimethyl-1,3-dioxane-4-carboxamide 14
To aldehyde 13 (148 mg, 0.75 mmol) in 14 mL of t-BuOH and 14 mL of water was added subsequently KH$_2$PO$_4$ (605 mg, 4.45 mmol), 2-methyl-2-butene (6.4 mL, 56.0 mmol) and NaClO$_2$ (227 mg, 2.51 mmol). The reaction mixture was stirred 5 h 30 min and organic solvents were removed under reduced pressure. The aqueous layer was extracted 3 times with EtOAc and the combined organic layers were washed with brine dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure to give the crude acid, which was used for the next step without purification.

To a solution of the crude acid in 4 mL of CH$_2$Cl$_2$ was added portionwise carbonyldiimidazole (184 mg, 1.14 mmol). The reaction mixture was stirred 1 h at room temperature, prior to the addition of N,O-dimethylhydroxylamine hydrochloride (110 mg, 1.13 mmol). The reaction mixture was stirred overnight at room temperature filtered to remove insoluble materials and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 20/80) gave the amide 14 as a colorless oil (146.7 mg, 0.57 mmol, 76%): [α]$^{25}_D$ -24.1° (c = 0.86 in CHCl$_3$); R$_f$ 0.4 (EtOAc/Cyclohexane: 1/1); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.71-5.88 (m, 1H), 4.91-5.07 (m, 2H), 4.82 (d, J = 10.2 Hz, 1 H), 3.84-3.97 (m, 1H), 3.73 (s, 3H), 3.19 (s, 3 H), 2.03-2.24 (m, 2 H), 1.49-1.87 (m, 4H), 1.47 (s, 3 H), 1.44 (s, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.9, 138.0, 114.8, 99.2, 67.8, 67.0, 61.6, 35.2, 32.3, 32.0, 30.0, 29.0, 19.4; IR 2992, 2937, 1671, 1642, 1440, 1380, 1258, 1199, 1165, 1115, 972, 912 cm$^{-1}$; HRMS ES m/z (M+Li)$^+$ Calcd for C$_{13}$H$_{23}$LiO$_4$ 264.1782, found 264.1768.

**Synthesis of (45,5S)-5-(benzyloxy)-2-8-(tert-butylidiphenylsilyloxy)oct-1-en-4-ol 15**

To a solution of aldehyde 8 (460 mg, 1.03 mmol) in 8 mL of CH$_2$Cl$_2$ was added dropwise at -78 °C a solution of TiCl$_4$ (1.03 mL, 1.0 M in CH$_2$Cl$_2$, 1.03 mmol), followed by the dropwise addition of 2-bromo-3-((trimethylsilyl)propene (199 mg, 1.03 mmol). The reaction mixture was stirred for 2 h 30 min at -78°C, 30 min at 0 °C and hydrolyzed with an aqueous saturated solution of NH$_4$Cl (8 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3x10 mL) and the combined organic layers were washed with brine (10 mL), dried over
Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/6) to give the alcohol 15 (495 mg, 0.87 mmol, 85%) as a colourless oil as the favoured diastereomer (8.5/1): [α]²⁵°D +7.6° (c = 1.10 in CHCl₃); Rf 0.48 (EtOAc/Cyclohexane: 1/5); ¹H NMR (300 MHz, CDCl₃) δ 7.67-7.71 (m, 4H), 7.28-7.47 (m, 11H), 5.63 (d, J = 1.6 Hz, 1H), 5.50 (d, J = 1.6 Hz, 1H), 4.57 (AB, J_AB = 11.4 Hz, Δν = 47.7 Hz, 2H), 3.93-3.98 (X of ABX, m, 1H), 3.71 (t, J = 5.9 Hz, 2H), 3.39 (dt as q, J = 5.2 Hz, 1H), 2.51-2.68 (AB of ABX, m, 2H), 2.09 (s, br., 1H), 1.59-1.87 (m, 4H), 1.08 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 138.1, 135.6, 133.9, 130.7, 129.6, 128.5, 127.9, 127.8, 127.6, 119.2, 80.2, 72.0, 70.1, 63.8, 45.5, 28.2, 26.9, 26.2, 19.2; IR 3461, 2931, 2858, 1472, 1455, 1428, 1390, 1207, 1105, 1088, 1070, 1028, 998, 938, 889, 797, 738, 699 cm⁻¹; HRMS ES m/z (M+Li)+ Calcd for C₃₁H₃₉BrLiO₃Si 573.2007, found 573.1943.

Synthesis of (S,S)-6-(benzyloxy)-5-(2-bromoallyl)-2,2,3,3,6,6-hexamethyl-11,11-diphenyl-4,10-dioxa-3,11-disilatridecane 16

A solution of alcohol 15 (300 mg, 532 μmol) in 3 mL of DMF was treated subsequently with imidazole (72 mg, 1.06 mmol, N,N-dimethylaminopyridine (2 mg, 16.4 μmol) and TBSCl (120 mg, 798 mmol) at room temperature. After 16 h the reaction mixture was poured on diethylether/H₂O (1:1) (20 mL). The organic layer was washed with distilled water (3x10 mL). The aqueous layer was extracted with Et₂O (3x20 mL) and the combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/40) afforded the silyl ether 16 (347 mg, 0.51 mmol, 96%) as a colorless oil: [α]²⁵°D –16.5° (c = 1.00 in CHCl₃); Rf 0.46 (EtOAc/Cyclohexane: 1/40); ¹H NMR (300 MHz, CDCl₃) δ 7.67-7.70 (m, 4H), 7.67-7.70 (m, 4H), 7.27-7.46 (m, 11H), 5.61 (s, 1H), 5.45 (d, J = 1.2 Hz, 1H), 4.57 (AB, J_AB = 11.5 Hz, Δν = 44.4 Hz, 2H), 4.18 - 4.23 (X of ABX, m, 1H), 3.62-3.76 (m, 2H), 3.34-3.39 (m, 1H), 2.29-2.75 (AB of ABX, m, 2H), 1.26-1.88 (m, 4H), 1.07 (s, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.5, 135.6, 134.1, 132.5, 129.5, 128.3, 128.0, 127.6, 127.6, 119.2, 81.3, 72.1, 69.3, 64.2, 43.7, 29.9, 26.9, 25.8, 25.1, 19.2, 18.0, -4.5, -4.5; IR 2954, 2929, 2893, 2857, 1472, 1463, 1428, 1389, 1361, 1251, 1091, 1028, 1006, 957, 936, 885, 826, 810, 776, 738, 699 cm⁻¹; HRMS ES m/z (M+Li)+ Calcd for C₃₁H₃₉BrLiO₃Si₂ 687.2871, found 687.2845.
Synthesis of (4S,5S)-5-(benzyloxy)-1-((4S,6S)-6-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)-4-((tert-butyldimethylsilyl)oxy)-8-((tert-butylidiphenylsilyl)oxy)-2-methyleneoctan-1-one 17

To a solution of vinylbromide 16 (243 mg, 0.36 mmol) in 3.5 mL of Et₂O cooled at -78 °C was added dropwise t-BuLi (0.46 mL, 1.7 M in pentane, 0.78 mmol). The reaction mixture was stirred 40 min at -78 °C and a solution of amide 14 (50 mg, 0.19 mmol) in 2.5 mL of Et₂O was added via cannula. The temperature was gradually increased until 0 °C during 3 h and the reaction mixture was quenched with aqueous saturated solution of NH₄Cl. The mixture was extracted 3 times with Et₂O and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/30) yielding the coupling compound 17 (106 mg, 0.133 mmol, 70 %) as a colourless oil: [α]²⁵_D -21.6° (c = 1.0 in CHCl₃); Rf 0.65 ((EtOAc/Cyclohexane: 1/6); ¹H NMR (300 MHz, CDCl₃) δ 7.64-7.69 (m, 5H), 7.28-7.44 (m, 10H), 6.25 (d, J = 0.6 Hz, 1H), 5.90 (s, 1H), 5.71-5.89 (m, 1H), 4.94-5.08 (m, 2H), 4.87 (dd, J = 10.8 Hz, J = 3.6 Hz, 1H), 4.59 (AB, J_AB = 11.4 Hz, Δν = 79.6 Hz, 2H), 3.98-4.06 (m, 1H), 3.82-3.97. (m, 1H), 3.55-3.76 (m, 2H), 3.28-3.36 (m, 1H), 2.83 (dd, J = 12.9 Hz, J = 2.7 Hz, 1H), 2.05-2.24 (m, 3H), 1.75-1.87 (m, 2H), 1.50-1.71 (m, 6H), 1.49 (s, 3H), 1.45 (s, 3H), 1.05 (s, 9H), 0.83 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 198.1, 143.2, 138.8, 138.1, 135.6, 134.1, 129.6, 129.5, 128.3, 128.0, 127.55, 127.5, 114.9, 99.2, 81.5, 71.6, 71.5, 70.3, 67.9, 64.3, 35.3, 34.2, 33.1, 30.0, 29.99, 29.0, 26.9, 25.9, 24.7, 19.3, 19.2, 17.9, -4.4; IR 2929, 2856, 1683, 1641, 1380, 1255, 1201, 1106, 1085, 936, 826, 775, 738, 700 cm⁻¹; HRMS ES m/z (M+Li)⁺ Calcd for C₄₈H₇₀LiO₆Si₂ 805.4866, found 805.4823.

Synthesis of tert-butyl((S)-4-(4-methoxybenzyloxy)-5-((R)-p-tolylsulfinyl)pentyloxy)diphenylsilane 19

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2012
To a solution of β-hydroxysulfoxide 6 (1.84 g, 3.83 mmol) in 20 mL of THF at room temperature was added methoxybenzyl-trichloracetimidate\(^7\) (1.53 g, 5.74 mmol) and Yb(OTf)\(_3\)-H\(_2\)O (124 mg, 0.20 mmol). The resulting mixture was stirred for 16 h at room temperature and hydrolyzed with 15 mL of distilled water. The aqueous layer was extracted with EtOAc (3x 15 mL) and the combined organic layers were washed with brine (15 mL) dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1) gave the protected alcohol 22 as a yellow oil (2.01 g, 3.41 mmol, 80%): \([\alpha]^{25}_D +55.73^\circ\) (c = 1.50 in CHCl\(_3\)); R\(_f\) 0.29 (EtOAc/Cyclohexane: 1/2); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 6.7-7.6 (m, 18H), 4.52 (AB, J_{AB} = 8.7 Hz, \Delta \nu = 8.95 Hz, 2H), 3.97 (m, 1H), 3.71 (s, 3H), 3.56 (t, J = 6.3 Hz, 2H), 2.76 (m, 2H), 2.32 (s, 3H), 1.40-1.70 (m, 4H), 0.95 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 159.4, 141.6, 141.3, 135.5, 133.9, 130.2, 130.0, 129.7, 129.6, 127.6, 123.8, 113.9, 72.9, 72.0, 64.6, 63.6, 55.3, 30.2, 27.7, 26.9, 21.4, 19.20; IR: 2931, 2857, 1726, 1612, 1587, 1513, 1494, 1463, 1427, 1390, 1302, 1246, 1174, 1109, 1085, 1033, 937, 821, 808, 741, 701, 687 cm\(^-1\); HRMS ES m/z (M+Na)\(^+\) Calcd for C\(_{36}\)H\(_{44}\)NaO\(_4\)Si 623.262, found 623.262.

**Synthesis of (S)-5-(tert-butyldiphenylsilyloxy)-2-(4-methoxybenzyloxy)-pentanal 20**

To a solution of sulfoxide 19 (950 mg, 1.62 mmol) in 16 mL of MeCN cooled at 0 °C was added dropwise subsequently 2,4,6-collidine (0.60 mL, 4.88 mmol) and trifluoroacetic anhydride (1.20 mL, 8.1 mmol). The reaction mixture was stirred for 30 min, prior to the addition of 65 mL of saturated solution of NaHCO\(_3\), warmed to room temperature and stirred for 1 h. The aqueous layer was extracted with EtOAc (3x50 mL) and the combined organic layers were washed with brine (50 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9) to give the aldehyde 20 (683 mg, 1.42 mmol, 88%) as a brown oil: \([\alpha]^{25}_D -19.6^\circ\) (c = 1.00 in CHCl\(_3\)); R\(_f\) 0.21 (EtOAc/Cyclohexane: 1/3); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 9.65 (d, J=2.1 Hz, 1H), 6.8-7.7 (m, 14H), 4.50 (AB, J_{AB} = 9 Hz; \Delta \nu = 34.15 Hz, 2H), 3.80 (s, 3H), 3.70 (m, 1H), 3.64 (t, J = 6 Hz, 2H), 1.57-1.98 (m, 4H), 1.04 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 203.7, 159.5, 135.6, 133.8, 129.7, 129.6, 129.4, 127.5, 113.9, 82.9, 72.1, 63.2, 55.3, 27.7, 26.9, 26.4, 19.2; IR: 3071, 2931, 2857, 1732, 1612, 1530.

---

To a solution of aldehyde 20 (253 mg, 0.53 mmol) in 4 mL of CH₂Cl₂ was added dropwise at -78 °C a solution of TiCl₄ (0.5 mL, 1.0 M in CH₂Cl₂, 0.53 mmol), followed by the dropwise addition of 2-bromo-3-(trimethylsilyl)propene (100 mg, 0.53 mmol). The reaction mixture was stirred for 3 h at -78 °C and hydrolyzed with a saturated solution of NH₄Cl (4 mL). The aqueous layer was extracted with CH₂Cl₂ (3x5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo.

The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/6) giving the diol 21 as a colorless oil as the only syn diastereomer (215 mg, 0.45 mmol, 85%): [α]²⁵ D -3.23° (c = 1.07, CHCl₃); Rf 0.53 (EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.25-7.55 (m, 10H); 5.59 (d, J = 1.08 Hz, 1H), 5.40 (d, J = 1.59 Hz, 1H), 3.66 (m, 1H), 3.59 (t, J = 3.27 Hz, 2H), 3.40 (m, 1H), 2.87 (m, 1H), 2.51 (m, 2H), 2.25 (m, 1H, OH), 1.45-1.68 (m, 4H), 0.93 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 135.6, 133.5, 130.6, 129.8, 127.7, 119.6, 72.9, 71.7, 64.2, 46.0, 31.0, 28.7, 26.9, 19.2; IR 3397, 2930, 2856, 1738, 1631, 1472, 1427, 1389, 1245, 1106, 889, 822, 739, 700, 687 cm⁻¹; HRMS ES m/z (M+Na)⁺ Calcd for C₂₉H₃₆NaO₄Si 499.228, found 499.225.

Synthesis of (4S,5S)-2-bromo-8-(tert-butyldiphenylsilyloxy)oct-1-ene-4,5-diol 21

To a solution of aldehyde 20 (253 mg, 0.53 mmol) in 4 mL of CH₂Cl₂ was added dropwise at -78 °C a solution of TiCl₄ (0.5 mL, 1.0 M in CH₂Cl₂, 0.53 mmol), followed by the dropwise addition of 2-bromo-3-(trimethylsilyl)propene (100 mg, 0.53 mmol). The reaction mixture was stirred for 3 h at -78 °C and hydrolyzed with a saturated solution of NH₄Cl (4 mL). The aqueous layer was extracted with CH₂Cl₂ (3x5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo.

The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/6) giving the diol 21 as a colorless oil as the only syn diastereomer (215 mg, 0.45 mmol, 85%): [α]²⁵ D -3.23° (c = 1.07, CHCl₃); Rf 0.53 (EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.25-7.55 (m, 10H); 5.59 (d, J = 1.08 Hz, 1H), 5.40 (d, J = 1.59 Hz, 1H), 3.66 (m, 1H), 3.59 (t, J = 3.27 Hz, 2H), 3.40 (m, 1H), 2.87 (m, 1H), 2.51 (m, 2H), 2.25 (m, 1H, OH), 1.45-1.68 (m, 4H), 0.93 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 135.6, 133.5, 130.6, 129.8, 127.7, 119.6, 72.9, 71.7, 64.2, 46.0, 31.0, 28.7, 26.9, 19.2; IR 3397, 2930, 2856, 1738, 1631, 1472, 1427, 1389, 1245, 1106, 889, 822, 739, 700, 687 cm⁻¹; HRMS ES m/z (M+Na)⁺ Calcd for C₂₉H₃₆NaO₄Si 499.228, found 499.225.

Synthesis of (3-((4S,5S)-5-(2-bromoallyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propoxy)(tert-butyl)diphenylsilane 22

To a solution of diol 21 (120 mg, 0.25 mmol) in 3 mL of acetone and 0.9 mL of dimethoxypropane was added PPTS (22 mg, 0.093 mmol) at room temperature. The reaction mixture was stirred for 16 h, hydrolyzed with 2 mL of a saturated solution of NaHCO₃ and poured on 30 mL of EtOAc. The aqueous layer was extracted with EtOAc (3x6 mL) and the combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel (EtOAc/ Cyclohexane: 2/98) gave the acetal 22 (127 mg, 0.25 mmol, 98%) as a colorless oil: [α]²⁵ D -12.37° (c = 1.03 , CHCl₃); Rf 0.81 (EtOAc/Cyclohexane: 1/4); ¹H NMR (300
MHz, CDCl$_3$) $\delta$ 7.26-7.68 (m, 10H), 5.72 (d, $J$ = 0.9 Hz, 1H), 5.50 (d, $J$ = 1.5 Hz, 1H), 3.95 (td, $J$ = 4.68 Hz, 1H), 3.7 (m, 3H), 2.65 (AB (ABX), $J_{AB}$ = 15 Hz, $J_{AX}$ = 7.5 Hz, $J_{BX}$ = 4.5 Hz, $\Delta \nu$ = 43.88 Hz, 2H), 1.5-1.8 (m, 4H), 1.39 (s, 3H), 1.37 (s, 3H), 1.05 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.6, 134.0, 129.6, 129.4, 127.6, 119.1, 108.5, 80.4, 78.1, 63.6, 45.3, 29.3, 29.0, 27.3, 27.2, 26.9, 19.2; HRMS m/z (M+Na)$^+$ Calcd for C$_{27}$H$_{37}$BrNaO$_3$Si 539.159, found 539.159.

**Synthesis of 1-((4S,6S)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-one 23**

![Diagram of compound 23]

To a solution of vinylbromide 22 (600 mg, 1.16 mmol) in 15 mL of Et$_2$O cooled at -78 °C was added dropwise t-BuLi (1.36 mL, 1.7 M in pentane, 2.32 mmol). The reaction mixture was stirred 40 min at -78 °C and a solution of amide 14 (150 mg, 0.58 mmol) in 15 mL of Et$_2$O was added via cannula. The temperature was gradually increased until 0°C during 3 h and the reaction mixture was quenched with aqueous saturated solution of NH$_4$Cl. The mixture was extracted 3 times with Et$_2$O and the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (EtOAc/cyclohexane: 1/30) yielding the coupling compound 23 (246 mg, 0.40 mmol, 70%) as a colorless oil: [$\alpha$]$^D_{25}$ -9.41° (c = 0.505 in CHCl$_3$); R$_f$ 0.65 (EtOAc/cyclohexane: 1/6); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.3-7.7 (m, 10H), 6.24 (s, 1H), 6.01 (s, 1H), 5.79 (ddt, $J_{trans}$ = 16.86 Hz, $J_{cis}$ = 10.05 Hz, $^3$J = 6.6 Hz, 1H), 4.97 (m, 2H), 4.91 (dd, $J$ = 11.64 Hz, $J$ = 2.79 Hz, 1H), 3.75 (m, 1H), 3.45-3.7 (m, 4H), 2.45 (AB (ABX), $J_{AB}$ = 22.5 Hz, $J_{AX}$ = 2.7 Hz, $J_{BX}$ = 8.1 Hz; $\Delta \nu$ = 88.95 Hz, 2H), 2.1 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.34 (s 3H), 1.05 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.1, 142.5, 138.1, 135.6, 134.0, 129.5, 128.4, 127.6, 115.0, 108.1, 99.2, 80.6, 78.9, 71.4, 67.9, 63.7, 35.3, 35.1, 32.9, 30.2, 30.0, 29.0, 27.3, 27.3, 27.2, 26.9, 26.9, 19.4, 19.2; IR 3072, 2986, 2931, 2858, 1731, 1684, 1641, 1589, 1428, 1378, 1252, 1200, 1164, 1109, 1088, 996, 962, 938, 912, 865, 822, 740 710, 687 cm$^{-1}$; HRMS m/z (M+Na)$^+$ Calcd for C$_{38}$H$_{54}$NaO$_6$Si 657.358, found 657.360.
Synthesis of \((R)-1-((4S,6S)-6-(\text{but-3-enoyl})-2,2\text{-dimethyl-1,3-dioxan-4-yl})-2-((((4R,5R)-5-(\text{3-tert-butyldiphenylsilyloxy})\text{propyl})-2,2\text{-dimethyl-1,3-dioxolan-4-yl})\text{methyl})\text{prop-2-en-1-ol 24}\)

**Way A: Stereoselective reduction of enone 23**

To a solution of enone 23 (173 mg, 0.27 mmol) in 10 mL of Et₂O cooled at 0 °C was added CeCl₃ (20 mg, 0.08 mmol) and dropwise a freshly prepared solution of Zn(BH₄)₂ (1.15 mL, 0.183 M in Et₂O, 0.210 mmol). The mixture was stirred 20 minutes at 0 °C and quenched with 10 mL of NH₄Cl saturated solution. The mixture was extracted 3 times with Et₂O and the combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/15 then 1/6) giving the alcohol (69 mg, 0.11 mmol, 40%) as a colorless oil as the only trans diastereomer 24.

**Way B: Stereoselective addition of vinyl bromide 22 to aldehyde 13 in the presence of magnesium bromide.**

Dibromomethane (1.25 g, 6.65 mmol) in 1.7 mL of distillated toluene was added dropwise over 30 minutes in a solution of magnesium (173 mg, 7.11 mmol) in 5 mL of distillated Et₂O at RT. The reaction was stirred 30 minutes at RT and was clarified for 1 h 30 (solution supposed at 1 M).

t-BuLi (1.7 M in hexane, 270 μl, 0.457 mmol) wad added dropwise in a solution of vinyl bromide 22 (107.5 mg, 0.21 mmol) in 3 mL of THF at -78 °C. The reaction was stirred 30 minutes at -78°C and turned into deep yellow. MgBr₂ solution (1 M, 210 μl, 0.210 mmol) was added at -78 °C, and the reaction was stirred 30 minutes at -78 °C. Aldehyde 13 (33 mg, 0.166 mmol) in 2 mL of dichloromethane was added via cannula. The reaction was stirred 1 h 30 at -78 °C and allowed to warm to RT.

The reaction was hydrolyzed with NH₄Cl solution, aqueous phase extracted three times with DCM. Organic phases were washed with brine, dried over Na₂SO₄, filtrated and

---

8 J. Am. Chem. Soc. 1960, 82 (23), 6074-6081

S18
evaporated. Diastereoisomers (5.5/1) were separated by flash chromatography (EtOAc/ Cyclohexane 1/6), giving the alcohol 24 (58 mg, 0.091 mmol, 55%) as a colorless oil.

**Way C: Stereoselective addition of vinyl bromide 22 to aldehyde 13**

t-BuLi (1.7M in hexane, 173 μL, 0.29 mmol) was added dropwise in a solution of vinyl bromide 22 (70 mg, 0.14 mmol) in 2 mL of distilled Et₂O at -78°C. The reaction was stirred 45 minutes -78°C, the solution turned to deep yellow. Aldehyde 13 (14 mg, 0.067 mmol) in 2 mL of Et₂O was added via cannula to the reaction, and the reaction was stirred 2h at -78°C. The reaction was allowed to warm to RT and was hydrolyzed with NH₄Cl solution. The aqueous phase was extracted three times with Et₂O, organic phases were washed with brine, dried over Na₂SO₄, filtrated, evaporated. The two diastereoisomers (6/1) were separated by flash chromatography (EtOAc/cyclohexane 1/6), giving the alcohol 26 (27 mg, 0.042 mmol, 62%) as a colorless oil: [α]²⁵D -22.71° (c = 1.035 in CHCl₃), Rᵢ 0.28 (EtOAc/Cyclohexane: 1/6); ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.70 (m, 10H), 5.79 (ddt, Jtrans = 17.01 Hz, Jcis = 10.17 Hz, J = 6.75 Hz, 1H), 5.21 (s, 1H), 5.07 (s, 1H), 4.97 (m, 2H), 4.05 (m, 1H), 3.95 (m, 1H), 3.80 (m, 1H), 3.6-3.75 (m, 4H), 3.15 (m, 1H), 2.27 (d, J = 5.7 Hz, 2H), 2.12 (m, 2H), 1.1-1.18 (m, 20H), 1.05 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 144.1, 138.3, 135.6, 134.0, 129.6, 127.6, 115.5, 114.7, 108.3, 98.6, 81.0, 80.7, 76.6, 70.64, 68.0, 63.6, 35.8, 35.5, 31.1, 30.1, 29.2, 29.0, 28.8, 27.7, 27.2, 26.9, 19.8, 19.2; IR 3473, 3072, 2988, 2930, 2857, 1741, 1641, 1472, 1462, 1428, 1378, 1239, 1199, 1165, 1109, 1089, 1047, 990, 909, 823, 740, 701, 687 cm⁻¹; HRMS m/z (M+Na) Calcd for C₃₈H₅₆NaO₆Si 659.374, found 659.378.

**Minor diastereoisomer:** Rᵢ 0.24 ((EtOAc/Cyclohexane: 1/6); ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.70 (m, 10H), 5.79 (m, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 4.97 (m, 2H), 4.25 (m, 1H), 3.6-3.95 (m, 6H), 3.15 (m, 1H), 2.10-2.32 (m, 4H), 1.1-1.18 (m, 20H), 1.05 (s, 3H).

**Synthesis of 4-((4S,6S)-6-((R)-2-(((4R,5R)-5-((3-(tert-butylidiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-hydroxyallyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 26**

To a solution of alcohol 24 (20 mg, 0.03 mmol) in a mixture of 2 mL of dimethylacetamide and 0.7 mL of water was added Cu(OAc)₂ (13 mg, 0.065 mmol) and PdCl₂ (3 mg, 0.016 mmol). The flask was connected with a balloon of O₂ and the reaction mixture
was stirred 3 days at room temperature. The reaction mixture was extracted 3 times with ethyl acetate and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Hexane 1/4), giving the methyl ketone 26 (16.6 mg, 0.025mmol, 85%) as a colorless oil: [α]²⁵D -21.03° (c = 0.98, CHCl₃); R₁ 0.25 (EtOAc/Cyclohexane 1/4); ¹H NMR (300 MHz, CDCl₃) δ 7.26-7.68 (m, 10H), 5.21 (s, 1H, 17), 5.07 (s, 1H), 4.05 (d, J = 5.01 Hz, 1H), 3.95 (m, 1H), 3.6-3.75 (m, 4H), 2.52 (t, J = 2.47 Hz, 2H), 2.26 (d, J = 5.7 Hz, 2H), 2.13 (s, 3H), 1.5-1.9 (m, 6H), 1.2-1.45 (m, 14H), 1.05 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 208.6, 144.1, 135.6, 133.9, 129.6, 127.6, 115.6, 108.3, 98.6, 81.0, 80.7, 76.6, 70.6, 67.9, 63.6, 39.1, 35.8, 31.1, 30.3, 30.0, 29.9, 29.0, 28.8, 27.3, 27.2, 26.9, 19.8, 19.2; HRMS ES m/z (M+Na)⁺ Calcd for C₃₈H₅₆NaO₆Si 659.374, found 659.378.

**Synthesis of (R)-2-(((4S,5S)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-((4S,6S)-2,2-dimethyl-6-(3-oxobutyl)-1,3-dioxan-4-yl)allyl pivalate**

To a solution of 26 (16 mg, 0.025 mmol) and DMAP (1 mg, 0.009 mmol) in pyridine (2 mL) was added pivaloyl chloride (5 μl, 0.038 mmol) at 0°C. The reaction was stirred at 70°C for 24 hours, and then cooled down to RT and MeOH (200 μl), was added. The reaction was stirred 1 h at RT and then concentrated under reduced pressure and diluted with EtOAc. The solution was washed respectively with 1 N HCl, saturated solution of NaHCO₃, and water. The organic layer was dried over Na₂SO₄, filtrated and evaporated. The crude was purified by flash chromatography (EtOAc/Hexane 1/6) affording the corresponding pivalate (16.5 mg, 0.022 mmol, 88%); [α]²⁵D -14.72° (c = 1.03, CHCl₃); R₁ 0.72 (EtOAc/ Cyclohexane 2/3); ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.61 (m, 10H), 5.10 (d, J = 4.8 Hz, 1H), 5.05 (d, J = 3.3 Hz, 2H), 4.01 (m, 1H), 3.55-3.76 (m, 5H), 2.41-2.47 (m, 2H), 2.15-2.25 (m, 2H), 2.07 (s, 3H), 1.4 (m, 8H), 1.05-1.35 (m, 21H), 0.97 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 208.6, 177.0, 141.9, 135.5, 133.9, 129.5, 127.6, 114.3, 108.1, 98.6, 80.8, 79.3, 76.9, 69.3, 67.7, 63.7, 39.0, 38.7, 36.4, 31.9, 30.0, 29.9, 29.7, 29.1, 27.4, 27.3, 27.2, 26.9, 19.6, 19.2; HRMS ES m/z (M+Na)⁺ Calcd for C₄₃H₆₄NaO₈Si 759.424, found 759.426.
Synthesis of 4-((4S,6S)-6-((1R)-3-((4R,5R)-5-(3-((tert-butylidiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-hydroxy-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 28

Pd/C (4 mg, 10% WT) was added to a solution of 26 (32 mg, 0.05 mmol) in 5mL of MeOH in an autoclave. The autoclave was purged three times with H₂ and the reaction was stirred overnight over 80 bars of H₂ at RT. The reaction was filtrated over celite, concentrated and purified by flash chromatography (EtOAc/Hexane 1/4) affording the hydrogenated compound as a mixture of two diastereoisomers 28 and 28' (31 mg, 0.048 mmol, 99%): R_f 0.41-0.44 (EtOAc/ Cyclohexane 2/3); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.68 (m, 10H), 3.5-3.95 (m), 3.31 (t, J = 6.16 Hz), 2.95 (m), 2.54 (m), 2.15 (s, 3H), 1.97 (m), 1.45-1.90 (m), 1.30-1.45 (m, 12H), 1.05 (s, 9H), 1.10 (d, J = 7.04 Hz, 3H), 0.91 (d, J = 6.76 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 208.6, 208.6, 208.6, 135.5, 133.9, 129.5, 127.6, 108.1, 108.2, 98.4, 98.4, 81.0, 81.3, 78.3, 79.5, 77.2, 77.2, 69.1, 69.9, 67.9, 68.1, 63.5, 63.6, 39.1, 39.1, 34.8, 31.9, 32.3, 31.7, 30.3, 30.3, 30.1, 29.9, 29.0, 28.8, 28.9, 27.2, 27.3, 26.8, 19.6, 19.7, 19.2, 14.0, 16.2; HRMS ES m/z (M+Na)+ Calcd for C₄₈H₅₈NaO₇Si 677.391, found 677.384.

Synthesis of 4-((4S,6S)-6-((1R)-(benzyloxy)methoxy)-3-((4S,5S)-5-(3-hydroxypropyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-hydroxy-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one

BOMCl (75%, 25 µl, 0.132 mmol) was added to a solution of 32 (28 mg, 0.044 mmol), DIPEA (50 µl, 0.27 mmol) and Bn₄NI (2 mg, 4.4 µmol) in CH₂Cl₂ (2 mL). The reaction was stirred four days at RT and then quenched with water (2 mL). The aqueous phase was extracted three times with CH₂Cl₂; the organic phases were washed with brine, dried over Na₂SO₄, evaporated giving 33, which was directly used for the next step without further purification.
TBAF (40 μl, 1 M, 0.040 mmol) was added to a solution of 33 (14 mg, 0.019 mmol) in THF (1 mL). The reaction was stirred 6 hours at RT and quenched with brine. The aqueous phase was extracted three times with EtOAc, and the organic phases were dried over Na₂SO₄, filtrated, concentrated and purified by flash chromatography (EtOAc/Hexane 1/6) affording the Paquette’s et al. fragment (15.3 mg, 0.028 mmol, 65%).
(R)-5-(tert-butyldiphenylsilyloxy)-1-(p-tolylsulfinyl)pentan-2-one 5
(S)-5-(tert-butyldiphenylsilyloxy)-1-((R)-p-tolylsulfinyl)pentan-2-ol 6
((S)-4-(benzyl oxy)-5-((R)-p-tolylsulfinyl)pentyloxy)(tert-butyl)diphenylsilane 7
(S)-2-(benzyloxy)-5-(tert-butyldiphenylsilyloxy)pentanal 8
1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-one
(S)-1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-ol 11
(2S)-2-Hydroxy-1((R)-p-tolylsulfinyl)-oct-7-en-4-one
(2S,4S)-7-(4-methoxybenzyloxy)-1-((R)-p-tolylsulfinyl)octane-2,4-diol 12
(4S,6S)-4-(3-(4-methoxybenzyl oxy)butyl-2,2-dimethyl-6((R)-p-tolylsulfinylmethyl)-1,3-dioxane
(4S,6S)-6-(3-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde 13
(4S,6S)-6-(but-3-enyl)-N-methoxy-N,2,2-trimethyl-1,3-dioxane-4-carboxamide 14
(4S,5S)-5-(benzyloxy)-2-8-(tert-butyldiphenylsilyloxy)oct-1-en-4-ol 15
(5S,6S)-6-(benzyloxy)-5-(2-bromoallyl)-2,2,3,3,12,12-hexamethyl-11,11-diphenyl-4,10-dioxa-3,11-disilatridecane 16
(4S,5S)-5-(benzyloxy)-1-((4S,6S)-6-(but-3-en-1-yl))-2,2-dimethyl-1,3-dioxan-4-yl)-4-((tert-butyldimethylsilyl)oxy)-8-((tert-butyldiphenylsilyl)oxy)-2-methyleneoctan-1-one 17
tert-butyl((S)-4-(4-methoxybenzyl)oxy)-5-((R)-p-tolylsulfinyl)pentyloxy)diphenylsilane 19
(S)-5-(tert-butyldiphenylsilyloxy)-2-(4-methoxybenzyloxy)pentanal 20
(4S,5S)-2-bromo-8-(tert-butyldiphenylsilyloxy)oct-1-ene-4,5-diol 21
(3-((4S,5S)-5-(2-bromoallyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propoxy)(tert-butyl)diphenylsilane 22
1-(((4S,6S)-6-(but-3-ynyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-one 23
(R)-1-(((4S,6S)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-ol 24
4-((4S,6S)-6-((R)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-hydroxyallyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 26
(R)-2-(((4S,5S)-5-((3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-(((4S,6S)-2,2-dimethyl-6-(3-oxobutyl)-1,3-dioxan-4-yl)allyl pivalate
4-(((4S,6S)-6-((1R)-3-((4R,5R)-5-(3-(tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-hydroxy-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one
28