Supplementary data:

Synthesis of macrocyclic precursors of phomactins using [2,3]-Wittig rearrangements

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Experimental

General

Flash column chromatography was performed using Merck silica gel (60H; 40-60μ, 230-240 mesh). Petrol refers to light petroleum which was redistilled before use and refers to the fraction boiling between 40 and 60 °C. Tetrahydrofuran was dried over sodium-benzophenone and was distilled prior to use. Dichloromethane was dried over CaH₂ and was distilled before use. Ether refers to diethyl ether. Reactions under non-aqueous conditions were carried out under an atmosphere of nitrogen or argon.

Electron impact (EI) or chemical ionisation using ammonia (CI) mass spectra were recorded using a Micromass Trio 200 spectrometer and high resolution mass spectra on a Kratos Concept IS spectrometer. Infra-red spectra were measured using a Genesis FTIR spectrometer on NaBr plates, either neat or as evaporated films unless otherwise stated. Nuclear magnetic resonance spectra were recorded in deuteriated chloroform unless otherwise indicated on either a Varian Unity 500 (500 MHz), Varian INOVA 400 (300 MHz), or a Varian INOVA 300 (300 MHz) spectrometer. Coupling constants (J) are given in Hertz (Hz) and chemical shifts are relative to tetramethylsilane.

6-tert-Butyldimethylsilyloxyhex-4-yn-1-ol 13

n-Butyllithium (1.6 M in hexanes, 9.2 cm³, 148 mmol) was added dropwise at -78 °C to the propyne 12 (21 g, 124 mmol) in THF (150 cm³) and the solution stirred at -78 °C for 0.5 h. Oxetane (9.64 cm³, 148 mmol) in THF (100 cm³) was added, followed immediately by boron trifluoride etherate (18.9 cm³, 150 mmol). The mixture was stirred for a further 2 h and saturated aqueous ammonium chloride (200 cm³) was added. The organic phase was washed with water (2x200 cm³) and brine (200 cm³), dried (MgSO₄), and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 20 – 40% ether in petrol afforded the title compound 13 as a pale yellow oil (24 g, 85%), Rf = 0.2 (20% ether in petrol) (Found: M⁺ + NH₄, 246.1884. C₁₂H₂₈O₂NSi requires M, 246.1889); νmax/cm⁻¹
3357 (br), 2930, 2858, 1465, 1057 and 1014; δH (300 MHz, CDCl₃) 4.3 (2 H, s, 6-H₂), 3.76 (2 H, br t, J, 6, 1-H₂), 2.35 (2 H, m, 2-H₂), 1.77 (2 H, t, J, 7, 3-H₂), 1.46 (1 H, br s, OH), 0.92 [9 H, s, Si(CH₃)₃] and 0.12 [6 H, s, Si(CH₃)₂]; δC (75 MHz, CDCl₃) 79.2, 61.7, 51.9, 31.1, 25.8, 22.5, 18.3, 15.3 and -5.2; m/z (CI) 246 (M⁺ + 18, 100%), 229 (40), 97 (80) and 91 (25).

**Ethyl (2E)-8-tert-butyldimethylsilyloxy-2-methyloct-2-en-6-ynoate 14**

Dimethyl sulfoxide (12.5 cm³, 240 mmol) in dichloromethane (100 cm³) was added dropwise at -78 °C to oxalyl chloride (11.4 cm³, 132 mmol) in dichloromethane (250 cm³). The solution was stirred for 20 min, then the alcohol 13 (20 g, 88 mmol) in dichloromethane (150 cm³) was added dropwise. After stirring for 1 h, triethylamine (49 cm³, 350 mmol) was added, and the reaction allowed to stir at room temperature for a further 1 h before being cooled to -78 °C. 1-Carbethoxyethylidenetriphenylphosphorane (36.5 g, 100 mmol) in dichloromethane (100 cm³) was added and the suspension warmed to room temperature. After 16 h, saturated aqueous ammonium chloride (250 cm³) was added and the organic layer was washed with water (300 cm³) and brine (300 cm³), dried (MgSO₄), and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 10 – 20% ether in petrol, afforded the title compound 14 as a pale yellow oil (24.5 g, 90%), Rf = 0.6 (20% ether in petrol) (Found: M⁺ + H, 311.2049. C₁₇H₃₁O₃Si requires M, 311.2043); νmax/cm⁻¹ 2925, 2876, 1739, 1466, 1110 and 1035; δH (300 MHz, CDCl₃) 6.77 (1 H, m, 3-H), 4.30 (2 H, s, 8-H₂), 4.2 (2 H, q, J, 7, CO₂CH₂CH₃), 2.37 (4 H, m, 4-H₂ and 5-H₂), 1.86 (3 H, s, 2-CH₃), 1.30 (3 H, t, J, 7, CO₂CH₂CH₃), 0.92 [9 H, s, Si(CH₃)₃] and 0.12 [6 H, s, Si(CH₃)₂]; δC (75 MHz, CDCl₃) 167.9, 139.7, 129.0, 83.9, 79.3, 60.4, 51.8, 27.8, 25.8, 22.5, 18.1, 14.2, 12.5 and -5.2; m/z (EI) 311 (M⁺ + 1, 10%), 253 (100) and 75 (80).

**(2E)-8-tert-Butyldimethylsilyloxy-2-methyloct-2-en-6-yn-1-ol 15**

Super-Hydride™ (1.0 M in THF, 42 cm³, 42 mmol) was added dropwise at -78 °C to ester 14 (5.62 g, 18 mmol) in THF (100 cm³) and the solution stirred for 1 h then water (200 cm³) was added. On warming to room temperature, the organic phase was diluted with ether (100 cm³), separated and washed with water (150 cm³) and brine (150 cm³), dried (MgSO₄) and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 20 – 50% ether in petrol, afforded the title compound 15 as a colourless oil (4 g, 84%), Rf = 0.25 (20% ether in petrol) (Found: M⁺ 268.1862. C₁₅H₂₉O₂Si requires M, 268.1859); νmax/cm⁻¹ 3426 (br), 2955, 2880, 1723, 1462 and 1340; δH (300 MHz, CDCl₃) 5.47 (1 H, m, 3-H), 4.31 (2 H, s, 8-H₂), 4.02 (2 H, s, 1-H₂), 2.27 (4 H, m, 4-H₂ and 5-H₂), 1.69 (3 H, s, 2-CH₃), 1.4 (1 H, br s, OH), 0.92 [9 H, s, Si(CH₃)₃] and 0.13 [6 H, s, Si(CH₃)₂]; δC (75 MHz, CDCl₃) 136.1, 124.2, 84.7, 78.9, 68.7, 51.9, 26.8, 25.8, 18.9, 18.3, 13.7 and -5.2; m/z 286 (M⁺ + 18, 100%), 269 (M⁺ + 1, 34%), 251 (59), 246 (95), 229 (30), 200 (27), 195 (25), 184 (25), 97 (40), 92 (40) and 91 (40).
(2E)-8-tert-Butyldimethylsilyloxy-1-tert-butyldiphenylsilyloxy-2-methyloct-2-en-6-yne 16

Imidazole (2.96 g, 43 mmol) and tert-butyldiphenylsilyl chloride (5.3 cm$^3$, 21 mmol) were added to the alcohol 15 (4.6 g, 17 mmol) in dichloromethane (100 cm$^3$) at 0 °C. The mixture was stirred for 16 h and diluted with ether (100 cm$^3$). The solution was washed with saturated aqueous ammonium chloride (200 cm$^3$), water (150 cm$^3$) and brine (150 cm$^3$), dried (MgSO$_4$) and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 10% ether in petrol, afforded the title compound 16 as a colourless oil (5.85 g, 67%), $R_f$ = 0.95 (20% ether in petrol) (Found: M$^+$ 506.3050. C$_{31}$H$_{46}$O$_2$Si$_2$ requires M, 506.3036); $\nu_{\max}$/cm$^{-1}$ 2930, 2857, 1727, 1460, 1364, 1256, 1219, 1111 and 1079; $\delta$H (300 MHz, CDCl$_3$) 7.69 (4 H, m, Ar-H), 7.41 (6 H, m, Ar-H), 5.52 (1 H, m, 3-H), 4.30 (2 H, s, 8-H$_2$), 4.07 (2 H, s, 1-H$_2$), 2.25 (4 H, m, 4-H$_2$ and 5-H$_2$), 1.62 (3 H, s, 2-CH$_3$), 1.07 and 0.93 [each 9 H, s, SiC(CH$_3$)$_3$] and 0.12 [6 H, s, Si(C$_3$H$_3$)$_2$]; $\delta$C (75 MHz, CDCl$_3$) 135.5, 133.8, 129.5, 127.5, 122.6, 99.9, 85.0, 68.7, 51.9, 26.8, 25.8, 19.2, 19.1, 18.3, 18.1, 13.5, 3.2 and -5.2; m/z (CI) 524 (M$^+$ + 18, 100%), 449 (40), 375 (5), 251 (15) and 197 (25).

(6E)-8-tert-Butyldiphenylsilyloxy-7-methyloct-6-en-2-yn-1-ol 17

Alkyne 16 (4.3 g, 9 mmol) was dissolved in a mixture of methanol and carbon tetrachloride (1 : 1 , 100 cm$^3$), and the solution sonicated for 4 h at 50 °C then concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 20 – 50% ether in petrol, afforded the title compound 17 as a clear oil (3.2 g, 86%), $R_f$ = 0.3 (50% ether in petrol) (Found: M$^+$ + NH$_4$, 410.2515. C$_{23}$H$_{36}$O$_2$NSi requires M, 410.2513); $\nu_{\max}$/cm$^{-1}$ 3406 (br), 2930, 2857, 1730, 1461, 1429 and 1108; $\delta$H (300 MHz, CDC$_3$) 7.77 (4 H, m, Ar-H), 7.45 (6 H, m, Ar-H), 5.52 (1 H, m, 6-H), 4.26 (2 H, s, 1-H$_2$), 4.10 (2 H, s, 8-H$_2$), 2.29 (4 H, m, 4-H$_2$ and 5-H$_2$), 1.74 (1 H, br s, OH), 1.65 (3 H, s, 7-CH$_3$) and 1.11 [9 H, s, SiC(CH$_3$)$_3$]; $\delta$C (75 MHz, CDC$_3$) 135.5, 135.4, 133.8, 129.5, 127.5, 122.6, 99.9, 85.0, 68.7, 51.9, 26.8, 25.8, 19.2, 19.1, 18.3, 18.1, 13.5, 3.2 and -5.2; m/z (CI) 410 (M$^+$ + 18, 13%), 197 (90) and 137 (100).

Methyl (8SR,9RS)-7-{(6E)-8-tert-Butyldiphenylsilyloxy-7-methyloct-6-en-2-yn-1-yloxy}methyl-8,9-dimethyl-1,4-dioxaspiro[4.5]dec-6-ene-8-carboxylate 19

tetra-n-Butylammonium iodide (0.23 g, 0.6 mmol), 15-crown-5 (1.37 cm$^3$, 7 mmol) and sodium hydride (60% dispersion in mineral oil, 0.28 g, 7 mmol) were added to the alcohol 17 (2.7 g, 6.9 mmol) in THF (50 cm$^3$) at 0 °C. The solution was stirred until effervescence had ceased (approximately 5 min) then the bromide 18 (2 g, 6.3 mmol) in THF (50 cm$^3$) was added using a cannula. The mixture was stirred at room temperature for 16 h and then saturated aqueous ammonium chloride (100 cm$^3$) and ether (50 cm$^3$) were added. The organic extracts were washed with water (150 cm$^3$) and brine (150 cm$^3$), dried (MgSO$_4$) and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted
with 5 – 20% ether in petrol, afforded the title compound 19 as a clear, viscous oil (1.7 g, 42%), $R_f = 0.2$ (50% ether in petrol) (Found: $M^+ = 630.3389$. $C_{38}H_{50}O_{6}Si$ requires $M = 630.3376$; $\nu_{\text{max}}/\text{cm}^{-1}$ 2933, 2881, 2343, 1731, 1667, 1455, 1428, 1254 and 1112; $\delta_H$ (500 MHz, CDCl$_3$) 7.69 (4 H, m, Ar-$H$), 7.40 (6 H, m, Ar-$H$), 5.72 (1 H, s, 6-$H$), 5.48 (1 H, m, 6´-$H$), 4.06 (4 H, m, 1´-$H_2$ and 7-$CH_2$), 3.92 – 4.03 (6 H, m, 2-$H_2$, 3-$H_2$ and 8´-$H_2$), 3.68 (3 H, s, 8-CO$_2$CH$_3$), 2.56 (1 H, m, 9-$H$), 2.25 (4 H, m, 8´-$H_2$ and 5´$-H_2$), 1.73 (2 H, m, 10-$H_2$), 1.62 (3 H, s, 7´-$CH_3$), 1.19 (3 H, s, 8-$CH_3$), 1.07 $\delta_H$ (9 H, s, SiC(CH$_3$)$_3$) and 0.88 (3 H, d, $J$ 7, 9-$CH_3$); $m/z$ (El) 630 ($M^+$, 5%), 573 (50), 437 (25), 335 (60) and 199 (100).

(8SR,9RS)-7-[(6E)-8-tert-Butyldiphenylsilyloxy-7-methyloct-6-en-2-yn-1-yloxy]methyl-8,9-dimethyl-8-hydroxymethyl-1,4-dioxaspiro[4.5]dec-6-ene 20

Super-Hydride$^\text{TM}$ (1.0 M in THF, 3.14 cm$^3$, 3.14 mmol) was added dropwise at 0 °C to ether 19 (0.9 g, 1.4 mmol) in THF (50 cm$^3$) and the mixture stirred for 50 min. Water (100 cm$^3$) and ether (50 cm$^3$) were added and the organic extract was washed with water (100 cm$^3$) and brine (100 cm$^3$), dried (MgSO$_4$) and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel, eluted with 5 – 20% ether in petrol, afforded the title compound 20 as a clear, viscous oil (0.8 g, 93%), $R_f = 0.1$ (50% ether in petrol) (Found: $M^+ + H = 603.3498$. $C_{37}H_{51}O_{6}Si$ requires $M = 603.3505$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3439 (br), 2930, 2857, 1656, 1428, 1112 and 1060; $\delta_H$ (300 MHz, CDCl$_3$) 7.73 (4 H, m, Ar-$H$), 7.44 (6 H, m, Ar-$H$), 5.80 (1 H, s, 6-H), 5.54 (1 H, m, 6´-$H$), 4.24 – 4.06 (5 H, m, 3-$H_2$, 7-$CH$ and 8´-$H_2$), 4.05 – 3.71 (5 H, m, 1´-$H_2$, 2-$H_2$ and 7-$CH$), 3.64 and 3.43 (each 1 H, d, $J$ 12, 8-CH), 2.82 (1 H, br s, $OH$), 2.47 (1 H, m, 9-$H$), 2.30 (4 H, m, 8´-$H_2$ and 5´-$H_2$), 1.76 (2 H, m, 10-$H_2$), 1.66 (3 H, s, 8-$CH_3$), 1.11 $\delta_H$ (9 H, s, SiC(CH$_3$)$_3$) and 0.92 (3 H, d, $J$ 7, 9-$CH_3$); $\delta_C$ (75 MHz, CDCl$_3$) 143.8, 135.5, 133.7, 132.4, 130.1, 129.5, 127.5, 122.3, 105.2, 87.6, 76.6, 76.4, 74.9, 64.7, 64.3, 58.3, 57.6, 45.4, 43.1, 37.7, 30.1, 26.8, 19.0, 15.4, 13.5 and 7.9; $m/z$ (El) 602 ($M^+$, 0.5%), 572 (2.5), 545 (5), 471 (2.5), 335 (20), 333 (16) and 199 (100).

(8SR,9RS)-8-tert-Butyldimethylsiloxymethyl-7-[(6E)-8-tert-butyldiphenylsilyloxy-7-methyloct-6-en-2-yn-1-yloxy]methyl-8,9-dimethyl-1,4-dioxaspiro[4.5]dec-6-ene 21

tert-Butyldimethylsilyl trifluoromethanesulphonate (58 $\mu$L, 0.253 mmol) was added to the alcohol 20 (100 mg, 0.166 mmol) and triethylamine (50 $\mu$L, 0.359 mmol) in dichloromethane (2 cm$^3$) at room temperature and the mixture stirred for 45 min. Saturated aqueous ammonium chloride (10 cm$^3$) was added and the mixture extracted with ether (3x10 cm$^3$). The organic extracts were washed with water (10 cm$^3$) and brine (10 cm$^3$), dried, and concentrated under reduced pressure. Column chromatography of the residue, eluting with 10 – 25% ether in petrol, gave the title compound 21 (80 mg, 67%) as a colourless oil, $R_f = 0.7$ (50% ether in petrol); $\delta_H$ (300 MHz, CDCl$_3$) 7.72 – 7.55 (4 H, m, Ar-$H$), 7.42 – 7.23 (6 H, m, Ar-$H$), 5.64 (1 H, s, 6-$H$), 5.44 (1 H, m, 6´-$H$), 4.17 – 3.78 (10 H, m, 1´-$H_2$, 2-$H_2$, 3-$H_2$, 7-$CH_2$, 8´-$H_2$), 3.51 and 3.40 (each 1 H, d, $J$ 10.5, 8-CH), 2.21 (4 H, m, 4´-$H_2$ and 5´-$H_2$), 1.82 – 1.60 (3 H, m, 9-$H$, 10-$H_2$), 1.58 (3 H, s, 7´-
\((8R,9SR)-8\)-tert-Butyldimethylsilyloxyethyl-6-\((6E)-1\)-hydroxy-8-tert-butylidiphenylsilyloxy-7-methyl-oct-6-en-2-yn-1-yl\)-8,9-dimethyl-1,4-dioxaspiro[4.5]decane 22

\(n\)-Butyllithium (2 M in hexanes, 241 \(\mu\)L, 0.482 mmol) was added to the propargylic ether 21 (69 mg, 0.096 mmol) in tetrahydrofuran (1 cm\(^3\)) at -78 °C and the mixture stirred for 3 h. Saturated aqueous ammonium chloride (5 cm\(^3\)) was added and the mixture extracted with ether (3x5 cm\(^3\)). The organic extracts were washed with water (5 cm\(^3\)) and brine (5 cm\(^3\)), dried and concentrated under reduced pressure. Chromatography of the residue, eluting with 15% ether in petrol, gave the title compound 22 (57 mg, 83%), a mixture of two diastereoisomers (70 : 30), as a colourless oil, \(R_f = 0.66\) (50% ether in petrol) (Found: M\(^+\), 716.4315. C\(_{43}\)H\(_{64}\)O\(_5\)Si\(_2\) requires M\(^+\), 716.4292); \(\nu_{\text{max}}/\text{cm}^{-1}\) 3500 (br), 2959, 2932, 2857, 2216, 1684, 1465, 1281 and 1112; \(\delta_H\) (300 MHz, CDCl\(_3\)) 7.66 (4 H, m, Ar-\(H\)), 7.36 (6 H, m, Ar-\(H\)), 5.74 (0.7 H, s, 7-\(C_\text{H}3\)), 5.47 (0.3 H, s, 7-\(C_\text{H}3\)), 5.42 (1 H, m, 6´-\(H\)), 5.21 (0.3 H, s, 7-\(C_\text{H}3\´)), 5.18 (0.7 H, s, 7-\(C_\text{H}3\´)), 4.95 (0.7 H, m, c-H), 4.86 (0.3 H, m, c-H), 4.30 – 3.56 (7 H, 2-\(H_2\), 3-\(H_2\), 8´-\(H_2\), OH), 3.51 and 3.44 (each 1 H, d, J 7.5, 8-CH\(_3\)), 2.82 (0.7 H, m, 6-H), 2.77 (0.3 H, m, 6-H), 2.22 (4 H, m, 4´-\(H_2\), 5´-\(H_2\)), 2.00 (1 H, m, 9-H), 1.58 (3 H, s, 7´-CH\(_3\)), 1.30 (2 H, m, 10-H), 1.04 [9 H, s, SiC(CH\(_3\)\(_3\))], 0.95 (2.1 H, s, 8-CH\(_3\)), 0.86 [12.9 H, m, SiC(CH\(_3\)\(_3\)), 8-CH\(_3\), 9-CH\(_3\)], 0.04 [1.8 H, s, Si(CH\(_3\)\(_2\))] and 0.00 [4.2 H, s, Si(CH\(_3\)\(_2\))] \(\delta_C\) (75 MHz, CDCl\(_3\)) 147.2, 146.3, 135.5, 130.9, 130.6, 129.6, 128.8, 128.5, 127.3, 121.6, 115.9, 111.4, 109.3, 108.3, 93.4, 84.7, 84.3, 82.5, 80.9, 68.6, 68.3, 67.2, 67.0, 66.0, 65.2, 64.9, 64.8, 63.6, 62.2, 52.3, 51.5, 44.2, 44.0, 37.7, 42.3, 31.3, 26.8, 26.1, 25.9, 25.8, 25.6, 19.4, 19.1, 17.2, 16.5, 15.8, 15.5, 13.6, 13.3, -5.6 and -5.8; \(m/z\) (Cl) 734 (M\(^+\)+18, 3%).

(8R,S9R)-8-tert-Butyldimethylsilyloxyethyl-6-\((6E)-1\)-hydroxy-8-tert-butylidiphenylsilyloxy-7-methyl-oct-6-en-2-yn-1-yl\)-8,9-dimethyl-1,4-dioxaspiro[4.5]decanes 23a,b

Dess-Martin periodinane (150 mg, 0.354 mmol) was added to the mixture of diastereoisomeric alcohols 22 (57 mg, 0.080 mmol) in dichloromethane (2 cm\(^3\)) at room temperature and the mixture stirred for 30 min. Saturated aqueous sodium hydrogen carbonate (10 cm\(^3\)) containing sodium thiosulfate (2.5 g) was added and the mixture extracted with ether (3x5 cm\(^3\)). The ethereal extracts were washed with saturated aqueous sodium hydrogen carbonate (10 cm\(^3\)), water (10 cm\(^3\)) and brine (10 cm\(^3\)), dried, and concentrated under reduced pressure. Column chromatography of the residue, eluting with 15% ether in petrol, gave the title compound 23a (19 mg, 33%), as a colourless oil \(R_f = 0.75\) (50% ether in petrol) (Found: M\(^+\),
714.4128. \( \text{C}_{43}\text{H}_{62}\text{O}_{5}\text{Si}_{2} \) requires \( M, 714.4136 \); \( \nu_{\text{max}}/\text{cm}^{-1} \) 2958, 2930, 2859, 2213, 1729, 1681, 1465, 1283 and 1114; \( \delta_{\text{H}} \) (300 MHz, \( \text{CDCl}_{3} \)) 7.58 (4 H, m, Ar-H), 7.32 (6 H, m, Ar-H), 5.35 (1 H, m, 6'-H), 5.09 and 4.83 (each 1 H, s, 7-CH), 4.02 (1 H, m, 2-CH), 3.96 (2 H, m, 2-CH, 3-CH), 3.83 (3 H, 3-CH, 8'-H), 3.70 (1 H, s, 6-H), 3.59 and 3.50 (each 1 H, d, \( J 10.5, 8-\text{CH} \)), 2.26 (4 H, m, 4'-H, 5'-H), 1.90 (1 H, m, 9-H), 1.52 (3 H, s, 7'-CH3), 1.60 and 1.45 (each 1 H, m, 10-H), 0.98 [9 H, s, Si(CH3)3], 0.84 (3 H, s, 8-CH3), 0.80 [9 H, s, Si(CH3)3], 0.76 (3 H, d, \( J 7, 9-\text{CH3} \)), 0.01 and 0.02 (each 3 H, s, SiCH3); \( \delta_{\text{C}} \) (75 MHz, \( \text{CDCl}_{3} \)) 185.8, 147.2, 135.5, 130.9, 129.6, 128.8, 127.6, 121.6, 111.4, 109.3, 93.2, 82.5, 68.6, 67.0, 65.2, 64.9, 62.2, 44.2, 40.7, 32.3, 26.8, 26.1, 25.9, 19.4, 16.5, 15.8, 13.6 and -5.6; \( m/z \) (CI) 715 (\( M^+ + 1 \), 4%) and 419 (100). The second fraction was the title compound 23b (31 mg, 55%), as a colourless oil \( R_f = 0.70 \) (50% ether in petrol) (Found: \( M^+, 714.4150 \). \( \text{C}_{43}\text{H}_{62}\text{O}_{5}\text{Si}_{2} \) requires \( M, 714.4136 \); \( \nu_{\text{max}}/\text{cm}^{-1} \) 2958, 2930, 2859, 2213, 1729, 1681, 1465, 1283 and 1114; \( \delta_{\text{H}} \) (500 MHz, \( \text{CDCl}_{3} \)) 7.62 (4 H, m, Ar-H), 7.32 (6 H, m, Ar-H), 5.40 (1 H, m, 6'-H), 5.21 and 5.10 (each 1 H, s, 7-CH), 4.01 (2 H, m, 2-CH, 3-CH), 3.86 (5 H, m, 2-CH, 3-CH, 6-H, and 8'-H), 3.59 and 3.49 (each 1 H, d, \( J 10, 8-\text{CH} \)), 2.30 (4 H, m, 4'-H, 5'-H), 2.02 (1 H, m, 9-H), 1.57 (3 H, s, 7'-CH3), 1.20 (2 H, m, 10-H), 1.01 [9 H, s, Si(CH3)3], 0.84 [12 H, s, 8-CH3 and SiC(CH3)3], 0.79 (3 H, d, \( J 7.5, 9-\text{CH3} \)) and 0.00 [6 H, s, Si(CH3)2]; \( \delta_{\text{C}} \) (75 MHz, \( \text{CDCl}_{3} \)) 185.6, 146.3, 135.2, 130.6, 129.3, 128.5, 127.3, 121.3, 115.9, 108.3, 93.7, 80.9, 68.3, 67.2, 66.0, 64.8, 63.6, 44.2, 37.7, 31.3, 26.6, 25.8, 25.6, 19.1, 17.2, 15.5, 13.3, -5.8 and -5.9; \( m/z \) (CI) 715 (\( M^+ + 1 \), 6%) and 419 (100).

\( (2\text{SR,}3\text{SR,}5\text{RS,}6\text{SR})-2-[(1\text{RS,}6\text{E})-(8\text{-tert-Butyldiphenylsilylxylo}-1\text{-tri-isopropylsilylxylo}-7\text{-methyloct-6-en-2-yn-1-yl}]\text{-5,6-dimethyl-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylene-cyclohexane} \) 45

2,6-Lutidine (0.29 cm\(^3\), 2.5 mmol) and tri-iso-propylsilyl methanesulphonate (0.29 cm\(^3\), 1.07 mmol) were added to the alcohol 37 (0.58 g, 0.713 mmol) in dichloromethane (9.7 cm\(^3\)) at 0 °C and the solution stirred for 30 min prior to the addition of water (10 cm\(^3\)) and ethyl acetate (10 cm\(^3\)). The aqueous layer was extracted with ethyl acetate (3x10 cm\(^3\)) and the organic extracts washed with brine (15 cm\(^3\)), dried (MgSO\(_4\)), and concentrated under reduced pressure. Column chromatography of the residue, eluting with 1 – 20% ether in petrol, afforded the title compound 45 (0.59 g, 87%) as a clear oil, \( R_f = 0.6 \) (50% ether in petrol) \( \nu_{\text{max}}/\text{cm}^{-1} \) 3070, 2944, 2893, 1463, 1428, 1383, 1320, 1249, 1151, 1107, 1055, 883, 860, 834, 741 and 709; \( \delta_{\text{H}} \) (300 MHz, \( \text{CDCl}_{3} \)) 7.91 (2 H, m, Ar-H), 7.68 (4 H, m, Ar-H), 7.59 (1 H, m, Ar-H), 7.53 (2 H, m, Ar-H), 7.33 – 7.43 (6 H, m, Ar-H), 5.41 (1 H, s, 1-CH), 5.39 (1 H, br t, \( J 7, 6'-\text{H} \)), 5.30 (1 H, s, 1-CH'), 4.80 (1 H, m, 1'-H), 4.80 and 4.70 (each 1 H, d, \( J 7, \text{OCH}_2\text{O} \)), 4.04 (2 H, s, 8'-H), 3.78 (1 H, m, 3-H), 3.74 (1 H, td, \( J 10, 7.5, \text{CHHCH}_2\text{Si} \)), 3.50 (1 H, m, CHH'CH2Si), 3.49 and 3.34 (each 1 H, d, \( J 14.5, 6-\text{CH} \)), 2.58 (1 H, m, 2'-H), 2.18 (4 H, m, 4'-H and 5'-H), 2.08 (1 H, m), 2.02 (1 H, m), 1.61 (3 H, s, 7'-CH3), 1.54 (1 H, m), 1.36 (3 H, s, 6-CH3), 1.01 – 1.04 [30 H, m, SiC(CH3)3 and SiC(CH(CH3)2)3], 0.95 (3 H, d, \( J 6.5, 5-\text{CH3} \)), 0.91 (2 H, m, CH2Si) and 0.02 [9 H, s, Si(CH3)3]; \( \delta_{\text{C}} \) (75 MHz, \( \text{CDCl}_{3} \)) 146.9,
142.7, 135.5, 133.8, 129.5, 129.1, 128.3, 127.6, 122.9, 115.5, 94.6, 86.3, 81.2, 76.4, 68.9, 64.9, 54.9, 44.5, 35.9, 35.8, 35.4, 26.9, 19.9, 19.3, 19.1, 18.2, 18.1, 17.7, 17.0, 13.5, 12.5, 12.3 and -1.42.

(2RS,3SR,5RS,6SR)-5,6-Dimethyl-2-[(1RS,6E)-(1,8-dihydroxy-7-methyloct-6-en-2-yn-1-yl]-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylene cyclohexane 46

tetra-n-Butylammonium fluoride (1.0 M solution in tetrahydrofuran, 1.16 cm³, 1.16 mmol) was added to the bis-silyl ether 45 (0.56 g, 0.578 mmol) in tetrahydrofuran (3.6 cm³) at room temperature and the solution was stirred for 1.5 h before being concentrated under reduced pressure. Column chromatography of the residue, eluted with 5 – 60% ether in petrol, afforded the title compound 46 (0.31 g, 93%) as an oil, Rf = 0.05 (50% ether in petrol) (Found; M⁺ + NH₄, 594.3294. C₃₁H₅₂O₆NSSi requires M⁺, 594.3284); νmax/cm⁻¹ 3467 (br), 2951, 2924, 1447, 1317, 1248, 1150, 1025, 859 and 836; δH (500 MHz, CDCl₃) 7.96 (2 H, d, J 7, Ar-H), 7.67 (1 H, t, J 7.5, Ar-H), 7.58 (2 H, m, Ar-H), 5.49 (1 H, m, 6’-H), 5.37 and 5.17 (each 1 H, s, 1-C₃H₃), 4.92 and 4.80 (each 1 H, d, J 7, OCH₂O), 4.63 (1 H, br d, J 10, 1’-H), 4.10 (1 H, d, J 10, 1’-OH), 3.98 (2 H, br d, J 7, 8’-H₂), 3.94 (1 H, td, J 10, 5, 3-H), 3.77 and 3.59 (each 1 H, td, J 11.5, 5.5, CH₃CH₂Si), 3.50 and 3.38 (each 1 H, d, J 15, 6-CH), 2.69 (1 H, br d, J 10, 2-H), 2.50 (1 H, br t, J 6.5, 8’-OH), 2.32 – 2.41 (5 H, m, 4’-H₂, 5’-H₂ and 4-H), 2.06 (1 H, dt, J 13, 4.5, 4-H’), 1.92 (1 H, m, 5-H), 1.59 (3 H, s, 7’-CH₃), 1.24 (3 H, s, 6-CH₃), 0.97 (2 H, m, CH₂Si), 0.92 (3 H, d, J 6.5, 5-CH₃) and 0.03 [9 H, s, Si(CH₃)₃]; δC (75 MHz, CDCl₃) 147.8, 142.7, 137.0, 133.7, 129.7, 127.6, 123.6, 111.7, 94.6, 87.1, 80.2, 79.9, 68.4, 66.0, 64.8, 63.4, 51.2, 45.8, 37.3, 36.2, 26.8, 19.6, 19.4, 18.2, 16.8, 14.1 and -1.2; m/z (CI) 594 (M⁺ + 18, 1%), 277 (70), 172 (74), 170 (87), 135 (92) and 90 (100).

(2RS,3SR,5RS,6SR)-2-[(1RS,6E)-(8-tert-Butyldimethylsilyloxy-1-hydroxy-7-methyloct-6-en-2-yn-1-yl]-5,6-dimethyl-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylene cyclohexane 47

Imidazole (8 mg, 0.117 mmol) was added to the diol 46 (45 mg, 0.078 mmol) in dichloromethane (0.4 cm³) at room temperature, the solution was cooled to 0 °C and tert-butyldimethylsilyl chloride (12 mg, 0.078 mmol) was added. After 30 min, water (1 cm³) and ethyl acetate (2 cm³) were added. The aqueous layer was extracted with ethyl acetate (3x2 cm³) and the organic extracts were washed with brine (4 cm³), dried (MgSO₄) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 1 – 30% ether in petrol, afforded the title compound 47 (48 mg, 89%) as a clear oil, Rf 0.4 (50% ether in petrol) (Found; M⁺ + NH₄, 708.4140. C₃₇H₆₆O₆NSSi₂ requires M⁺, 708.4149); νmax/cm⁻¹ 3497 (br), 2952, 2929, 2894, 2858, 1638, 1584, 1465, 1449, 1379, 1316, 1250, 1150, 1105, 1027, 836 and 775; δH (300 MHz, CDCl₃) 7.94 (2 H, d, J 8, Ar-H), 7.64 (1 H, m, Ar-H), 7.57 (2 H, t, J 7.5, Ar-H), 5.42 (1 H, br s, 6’-H), 5.34 and 5.18 (each 1 H, s, 1-CH), 4.84 and 4.81 (each 1 H, d, J 7, OCH₂O), 4.62 (1 H, br d, J 10, 1’-H), 4.09 (1 H, d, J 10, OH), 4.01 (2 H, s, 8’-H₂), 3.89 (1 H, td, J 10, 5, 3-H), 3.81 and 3.58 (each 1 H, m,
CHHCH₂Si), 3.49 and 3.38 (each 1 H, d, J 14.5, 6-CH), 2.69 (1 H, br d, J 10, 2-H), 2.27 (4 H, m, 4’-H₂ and 5’-H₂), 2.10 (1 H, dt, J 13, 4.2, 4-H), 1.85 (1 H, m, 5-H), 1.61 (3 H, s, 7’-CH₃), 1.53 (1 H, m, 4’-H’), 1.27 (3 H, s, 6-CH₃), 0.84 – 0.99 [14 H, m, SiC(CH₃)₃, 5-CH₃ and CH₂Si], 0.01 (3 H, s, SiCH₃) and 0.01 (12 H, s, 4 x SiCH₃); δC (75 MHz, CDCl₃) 133.4, 129.4, 127.4, 122.7, 117.8, 111.7, 106.9, 98.8, 94.7, 90.0, 79.6, 76.6, 73.1, 68.5, 65.7, 64.5, 58.3, 51.1, 39.4, 36.9, 36.2, 32.0, 27.2, 26.6, 19.2, 18.1, 16.6, 13.6, -1.4 and -5.2; m/z (Cl) 708 (M⁺ + 18, 20%), 647 (10), 575 (10), 442 (24), 365 (21), 294 (40), 277 (76), 269 (100), 242 (39), 135 (41) and 90 (77).

(2SR,3SR,5RS,6SR)-2-[(1RS,6E)-(8-tert-Butyldimethylsilyloxy-1-tri-isopropylsilyloxy-7-methyloct-6-en-2-yn-1-yl)-5,6-dimethyl-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylenecyclohexane 48

2,6-Lutidine (0.0054 cm³, 0.0462 mmol) and tri-isopropylsilyl methanesulfonate (0.0117 cm³, 0.0435 mmol) were added to the alcohol 47 (29 mg, 0.0414 mmol) in dichloromethane (0.3 cm³) at 0 °C and the solution stirred for 30 min. Water (0.5 cm³) and ethyl acetate (1 cm³) were added, the aqueous phase was extracted with ethyl acetate (3 x 2 cm³), and the organic extracts were washed with brine (3 cm³), dried (MgSO₄), and concentrated under reduced pressure. Column chromatography of the residue, eluted with 1 – 20% ether in petrol, afforded the title compound 48 (34 mg, 97%) as a clear oil, Rf = 0.8 (50% ether in petrol) νmax/cm⁻¹ 2928, 2894, 2864, 1528, 1461, 1321, 1249, 1150, 1054, 836 and 775; δH (300 MHz, CDCl₃) 7.94 (2 H, d, J 7.5, Ar-H), 7.62 (1 H, 6, J 7, Ar-H), 7.55 (2 H, t, J 7.5, Ar-H), 5.43 (1 H, s, 1-CH), 5.39 (1 H, br t, J 5.5, 6’-H), 5.33 (1 H, s, 1-CH’), 4.82 (2 H, m, 1’-H and OCH₂), 4.72 (1 H, d, J 7, OCH₂), 4.02 (2 H, s, 8’-H₂), 3.81 (1 H, m, 3-H), 3.75 and 3.49 (each 1 H, m, 2-H and 5-H), 1.62 (3 H, s, 7’-CH₃), 1.56 (1 H, m, 4-H’), 1.23 (3 H, s, 6-CH₃), 1.06 [21 H, m, 3 x SiCH(CH₃)₂], 0.97 (3 H, d, J 6.5, 5-CH₃), 0.90 [11 H, m, CH₂Si and SiCH(CH₃)₃], 0.08 and 0.05 (each 3 H, s, SiCH₃) and 0.04 [9 H, s, Si(CH₃)₃]; δC (75 MHz, CDCl₃) 146.8, 142.6, 135.6, 133.1, 129.0, 127.4, 122.9, 115.3, 99.9, 94.5, 86.2, 81.1, 68.4, 64.8, 63.9, 54.8, 44.4, 35.9, 35.7, 26.7, 25.9, 23.7, 20.7, 19.7, 18.9, 18.1, 18.0, 16.9, 13.4, 12.4, -1.5 and -5.4; m/z (ES⁺) 870 (M⁺ + 23, 68%), 869 (72%), 729 (19) and 145 (14).

(2SR,3SR,5RS,6SR)-5,6-Dimethyl-2-[(1RS,6E)-(8-hydroxy-1-tri-isopropylsilyloxy-7-methyloct-6-en-2-yn-1-yl)-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylenecyclohexane 49

Acetic acid, tetrahydrofuran and water (3 : 1 : 1 v/v, 3.1 cm³) were added to the bis-silyl ether 48 (0.15 g, 0.177 mmol) in tetrahydrofuran (1.07 cm³) at 0 °C and the solution stirred for 30 min at 0 °C and then at room temperature for 24 h. Saturated aqueous sodium bicarbonate was added at 0 °C (2.5 cm³) followed by ethyl acetate (2 cm³). The aqueous phase was extracted with ethyl acetate (4 x 5 cm³) and the organic
extracts washed with brine (10 cm³), dried (MgSO₄) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 1 – 50% ether in petrol, afforded the title compound 49 (0.106 g, 82%) as a clear oil, Rf = 0.2 (50% ether in petrol) (Found; M⁺ + NH₄, 750.4623. C₄₀H₇₂O₇Si₂SN requires M, 750.4619); νmax/cm⁻¹ 3487 (br), 2895, 2857, 1447, 1377, 1320, 1249, 1151, 1027 and 836; δH (300 MHz, CDCl₃) 7.95 (2 H, d, J 7, Ar-H), 7.64 (1 H, t, J 7.5, Ar-H), 7.40 (2 H, t, J 7.5, Ar-H), 5.51 (1 H, br t, J 6.5, 6´-H), 5.41 and 5.35 (each 1 H, s, 1-CH), 4.88 (1 H, d, J 7, OCH₂O), 4.81 (1 H, m, 1´-H), 4.71 (1 H, d, J 7, OCH₂H'), 4.01 (2 H, s, 8´-H₂), 3.79 (2 H, m, 3-H and CH₂H₂Si), 3.53 (1 H, d, J 14.5, 6-CH), 3.51 (1 H, m, CH₂H'CH₂Si), 3.38 (1 H, d, J 14.5, 6-CH'), 2.62 (1 H, dd, J 7, 4, 2-H), 2.27 (4 H, m, 4´-H₂ and 5´-H₂), 2.08 (1 H, dt, J 13.5, 4.5, 4-H), 1.97 (1 H, m, 5-H), 1.67 (3 H, s, 7´-CH₃), 1.60 (1 H, m, 4´-H'), 1.40 (3 H, s, 6-CH₃), 1.07 [21 H, m, 3 x SiCH(CH₃)₂], 0.97 (3 H, d, J 6.5, 5-CH₃), 0.94 (2 H, m, CH₂Si) and 0.05 [9 H, s, Si(CH₃)₃]; δC (75 MHz, CDCl₃) 147.2, 142.6, 136.3, 133.1, 129.1, 127.4, 123.4, 114.6, 94.6, 86.3, 81.3, 76.9, 68.1, 64.9, 64.3, 63.8, 54.4, 44.6, 36.2, 35.4, 26.4, 19.2, 18.9, 18.1, 17.9, 16.9, 13.7, 12.4 and -1.5; m/z (Cl) 750 (M⁺ + 18, 0.3%), 294 (42), 277 (82) and 90 (100).

(2R,3SR,5RS,6SR)-2-[(1RS,6E)-(8-Bromo-1-tri-isopropylsilyloxy-7-methyloct-6-en-2-yn-1-yl)-5,6-di-methyl-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylene-cyclohexane 50
Triethylamine (0.097 cm³, 0.7 mmol) and methanesulfonyl chloride (0.033 cm³, 0.44 mmol) were added to the alcohol 49 (0.19 g, 0.175 mmol) in dichloromethane (2.8 cm³) at 0 °C and the solution allowed to warm to room temperature and stirred for 30 min. After cooling to 0 °C, lithium bromide (0.23 g, 2.63 mmol) in acetonitrile (1.4 cm³) was added and the mixture stirred for 30 min at ambient temperature then filtered through a pad of celite. The filter-cake was washed with dichloromethane and the filtrate was concentrated under reduced pressure. The residue was taken up in ethyl acetate (5 cm³) and washed with saturated aqueous sodium bicarbonate (5 cm³). The aqueous phase was washed with ethyl acetate (4x5 cm³) and the organic extracts were washed with brine (10 cm³), dried (MgSO₄) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 1 – 15% ether in petrol, afforded the title compound 50 (0.159 g, 86%) as a clear oil, Rf = 0.65 (50% ether in petrol) (Found; M⁺ - Br, 715.4237. C₄₀H₇₂O₇Si₂SN requires M, 715.4248); νmax/cm⁻¹ 2943, 2896, 2865, 1465, 1446, 1320, 1248, 1150, 1106, 1052, 1033, 861 and 835; δH (400 MHz, CDCl₃) 7.94 (2 H, d, J 7, Ar-H), 7.63 (1 H, t, J 7.5, Ar-H), 7.56 (2 H, dd, J 8, 7, Ar-H), 5.65 (1 H, m, 6´-H), 5.47 and 5.34 (each 1 H, s, 1-CH), 4.85 (1 H, br d, J 4, 1´-H), 4.81 and 4.71 (each 1 H, d, J 7, OCH₂O), 3.96 (2 H, s, 8´-H₂), 3.76 (2 H, m, 3-H and CH₂H₂Si), 3.50 (2 H, m, 6-CH and CH₂H'CH₂Si), 3.36 (1 H, d, J 14.5, 6-CH'), 2.57 (1 H, dd, J 7, 4.5, 2-H), 2.22 (4 H, m, 4´-H₂ and 5´-H₂), 2.07 (1 H, dt, J 13.5, 4.5, 4-H), 1.98 (1 H, m, 5-H), 1.77 (3 H, d, J 1, 7´-CH₃), 1.54 (1 H, m, 4´-H'), 1.36 (3 H, s, 6-CH₃), 1.05 [21 H, m, 3 x SiCH(CH₃)₂], 0.95 (3 H, d, J 7, 5-CH₃), 0.89 (2 H, m, CH₂Si), 0.03 [9 H, s, Si(CH₃)₃]; δC (75 MHz, CDCl₃) 146.8, 142.7, 133.1, 129.5,
129.1, 127.4, 114.9, 94.7, 85.5, 81.6, 76.6, 64.9, 63.9, 54.3, 44.6, 41.2, 36.2, 36.0, 27.3, 23.7, 19.4, 18.5, 18.1, 18.0, 16.9, 15.7, 14.7, 12.4 and -1.5; m/z (CI) 715 (M+ - 79, 0.04%), 277 (29) and 90 (100).


Sodium hexamethyldisilazide (1.0 M solution in tetrahydrofuran, 0.125 cm³, 0.125 mmol) was added to the bromide 50 (33 mg, 0.0415 mmol) in tetrahydrofuran (0.25 cm³) at 0°C over 30 min using a syringe pump and the solution stirred for 30 min. Saturated aqueous ammonium chloride (1.5 cm³) and ethyl acetate were added. The aqueous layer was extracted into ethyl acetate (3x3 cm³) and the organic extracts were washed with brine (5 cm³), dried (MgSO₄) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 0 – 5% ether in petrol, afforded the title compound 51 (19 mg, 64%) as a clear oil, Rf = 0.65 (50% ether in petrol) (Found: M+ + NH₄, 732.4525. C₄₀H₇₀O₅NSSi₂ requires M+, 732.4513); \( \nu_{\text{max}}/\text{cm}^{-1} \) 2927, 2865, 1718, 1652, 1540, 1463, 1373, 1309, 1145 and 1045; \( \delta_H \) (300 MHz, CDCl₃) 7.98 (2 H, d, J 8, Ar-H), 7.62 (3 H, d, m, Ar-H), 6.19 (1 H, s, 15-CH), 6.02 (1 H, s, 15-CH'), 5.55 (1 H, m, 7-H), 5.00 (1 H, m, 2-H), 4.79 and 4.75 (each 1 H, d, J 6.5, OCH₂), 3.82 (1 H, td, J 9.5, 5.5, CH₂CH₂Si), 3.62 (2 H, m, 10-H and 14-H), 3.46 (1 H, td, J 9, 6.5, CHH'CH₂Si), 3.23 (1 H, t, J 10.5, 9-H), 2.95 (1 H, m, 12-H), 2.22 – 1.95 (7 H, m), 1.57 (1 H, m, 13-H), 1.43 (3 H, s, 8-CH₃), 1.17 – 1.05 (24 H, m, 11-CH₃ and 3 x SiCH(CH₃)₂), 0.97 – 0.90 (5 H, m, 12-CH₃ and C₂H₅Si) and 0.06 (9 H, s, Si(CH₃)₃); m/z (CI) 732 (M+ + 18, 1.3%), 567 (15), 428 (10), 425 (15), 269 (12), 253 (18), 251 (22), 215 (11), 160 (13) and 90 (100).

(1RS,2RS,7E,11SR,12RS,14SR)-15-Methylene-10-phenylsulfonyl-8,11,12-trimethyl-14-(2-trimethylsilyloxy)methoxybicyclo[9.3.1]pentadec-7-en-3-yn-2-ol 52

tetra-n-Butylammonium fluoride (1.0 M solution in tetrahydrofuran, 0.026 cm³, 0.026 mmol) was added to the silyl ether 51 (17 mg, 0.0238 mmol) in tetrahydrofuran (0.3 cm³) at room temperature. The solution was stirred for 1.5 h then concentrated under reduced pressure. Column chromatography of the residue, eluting with 1 – 25% ether in petrol, afforded the title compound 52 (7.5 mg, 73%) as a clear oil, Rf = 0.25 (50% ether in petrol) \( \nu_{\text{max}}/\text{cm}^{-1} \) 3465 (br), 2952, 2922, 2865, 1718, 1652, 1540, 1463, 1373, 1309, 1145 and 1045; \( \delta_H \) (300 MHz, CDCl₃) 7.97 (2 H, d, J 7.5, Ar-H), 7.60 (3 H, m, Ar-H), 6.14 and 6.02 (each 1 H, s, 15-CH), 5.57 (1 H, m, 7-H), 4.92 (1 H, m, 2-H), 4.74 and 4.69 (each 1 H, d, J 6.5, OCH₂), 3.83 (1 H, d, 4.5, OH), 3.75 (1 H, m, CHH₂CH₂Si), 3.64 – 3.52 (3 H, m, 10-H, 14-H and CHH'CH₂Si), 3.16 (1 H, dd, J 13.5, 10.5, 9-H), 2.93 (1 H, quin, J 7, 12-H), 2.38 (2 H, m, 5-H₂), 2.30 (1 H, m, 1-H), 2.17 – 2.00 (4 H, m, 6-H₂, 9-H' and 13-H), 1.46 (3 H, s, 8-CH₃), 1.42 (1 H, m, 13-H'), 1.13 (3 H, d, J 6.5, 12-CH₃), 1.09 (3 H, s, 11-CH₃), 1.01 (2 H, m, CH₂Si) and 0.05 (9 H, s, Si(CH₃)₃); \( \delta_C \) (75 MHz, CDCl₃) 145.5, 142.0, 133.5, 133.1, 129.6, 129.0, 128.1, 115.3, 95.4, 85.1, 83.1, 80.5, 72.2, 65.9, 61.1, 53.2, 53.0,
39.2, 39.0, 37.7, 26.2, 18.3, 18.1, 17.9, 17.2 and -1.6; \( m/z \) (ES-) 593 (\( M^+ + 35 \), 99%), 157 (89) and 111 (100).

\((1SR,2RS,7E,11SR,12RS,14SR)\)-15-Methylene-8,11,12-trimethyl-2-tri-isopropylsilyloxy-14-(2-trimethylsilylethoxy)methoxybicyclo[9.3.1]pentadec-7-en-3-yn-15-Methylene phosphate (0.05 g, 0.35 mmol) was added to the sulfone 51 (25 mg, 0.035 mmol) in tetrahydrofuran (0.2 cm\(^3\)) and methanol (0.2 cm\(^3\)) and the resulting suspension cooled to 0 °C. Sodium-mercury amalgam (5% sodium, 0.16 g, 0.35 mmol) was added and the suspension allowed to warm to room temperature and stirred for 2 h. Saturated aqueous ammonium chloride (1 cm\(^3\)) was added and the mixture diluted with ethyl acetate (2 cm\(^3\)) and decanted from the residue. The aqueous phase was extracted with ethyl acetate (3x2 cm\(^3\)) and the organic extracts washed with brine (4 cm\(^3\)), dried (Na\(_2\)SO\(_4\)) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 0 – 5% ether in petrol, afforded the title compound 53 (14 mg, 69%) as a clear oil, \( R_f = 0.8 \) (50% ether in petrol) \( \nu_{\text{max}}/\text{cm}^{-1} \) 2928, 2866, 1463, 1379, 1249, 1162, 1106, 1052, 1035, 859 and 836; \( \delta_H \) (300 MHz, CDCl\(_3\)) 6.15 (1 H, s, 15-CH), 5.01 (1 H, d, J 9, 7-H), 4.94 (1 H, s, 15-CH'), 4.90 (1 H, d, J 3.5, 2-H), 4.79 and 4.73 (each 1 H, d, J 6.5, OCH/O), 3.85 (1 H, m, CHHCH\(_2\)Si), 3.57 (1 H, td, J 10, 5.5, 14-H), 3.44 (1 H, m, CHHCH\(_2\)Si), 2.50 (1 H, dd, J 10.5, 3.5, 1-H), 2.25 – 1.95 (7 H, m, 5-H\(_2\), 6-H\(_2\), 9-H\(_2\) and 13-H\(_2\)), 1.62 (3 H, s, 8-CH\(_3\)), 1.48 (1 H, m, 13-H'), 1.29 (3 H, m, 10-H\(_2\) and 12-H), 1.14 (18 H, d, J 6, 3 x SiCH(CH\(_3\))\(_2\)), 1.05 (3 H, s, 11-CH\(_3\)), 0.91 [5 H, 3 x SiCH(CH\(_3\))\(_2\) and CH\(_2\)Si], 0.79 (3 H, d, J 6.5, 12-CH\(_3\)) and 0.06 [9 H, s, Si(CH\(_3\))\(_3\)]; \( \delta_C \) (75 MHz, CDCl\(_3\)) 151.7, 136.1, 126.8, 108.8, 96.3, 83.9, 81.6, 65.1, 62.5, 53.0, 44.9, 43.4, 40.4, 35.6, 30.4, 30.0, 27.5, 19.0, 18.53, 18.5, 18.3, 18.2, 16.5, 15.9, 12.8 and -1.2; \( m/z \) (ES+) 597 (\( M^+ + \text{Na} \), 96%), 575 (\( M^+ + 1 \), 12%), 464 (25), 242 (100); (ES-) 573 (\( M^+ - 1 \), 11%), 339 (27), 247 (37), 230 (66), 219 (20) and 113 (100).