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 CaH_2 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 cm^3, 148 mmol) was added dropwise at -78 °C to the propyne **12** (21 g, 124 mmol) in THF (150 cm^3) and the solution stirred at -78 ^{o}C for 0.5 h. Oxetane (9.64 cm^3, 148 mmol) in THF (100 cm^3) was added, followed immediately by boron trifluoride etherate (18.9 cm^3, 150 mmol). The mixture was stirred for a further 2 h and saturated aqueous ammonium chloride (200 cm^3) was added. The organic phase was washed with water (2x200 cm^3) and brine (200 cm^3), dried ($MgSO_4$), 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%), R_f = 0.2 (20% ether in petrol) (Found: $M^+ + NH_4$, 246.1884. $C_{12}H_{28}O_2NSi$ requires *M*, 246.1889); ν_{max}/cm^{-1}

3357 (br), 2930, 2858, 1465, 1057 and 1014; δ_H (300 MHz, $CDCl_3$) 4.3 (2 H, s, 6-*H*$_2$), 3.76 (2 H, br t, *J*, 6, 1-*H*$_2$), 2.35 (2 H, m, 2-*H*$_2$), 1.77 (2 H, t, *J*, 7, 3-*H*$_2$), 1.46 (1 H, br s, O*H*), 0.92 [9 H, s, SiC(C*H*$_3$)$_3$] and 0.12 [6 H, s, Si(C*H*$_3$)$_2$]; δ_C (75 MHz, $CDCl_3$) 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 (2*E*)-8-*tert*-butyldimethylsilyloxy-2-methyloct-2-en-6-ynoate 14

Dimethyl sulfoxide (12.5 cm^3, 240 mmol) in dichloromethane (100 cm^3) was added dropwise at -78 °C to oxalyl chloride (11.4 cm^3, 132 mmol) in dichloromethane (250 cm^3). The solution was stirred for 20 min, then the alcohol **13** (20 g, 88 mmol) in dichloromethane (150 cm^3) was added dropwise. After stirring for 1 h, triethylamine (49 cm^3, 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 cm^3) was added and the suspension warmed to room temperature. After 16 h, saturated aqueous ammonium chloride (250 cm^3) was added and the organic layer was washed with water (300 cm^3) and brine (300 cm^3), dried ($MgSO_4$), 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%), R_f = 0.6 (20% ether in petrol) (Found: M^+ + H, 311.2049. $C_{17}H_{31}O_3Si$ requires M, 311.2043); ν_{max}/cm^{-1} 2925, 2876, 1739,1466, 1110 and 1035; δ_H (300 MHz, $CDCl_3$) 6.77 (1 H, m, 3-*H*), 4.30 (2 H, s, 8-*H*$_2$), 4.2 (2 H, q, *J*, 7, $CO_2CH_2CH_3$), 2.37 (4 H, m, 4-*H*$_2$ and 5-*H*$_2$), 1.86 (3 H, s, 2-C*H*$_3$), 1.30 (3 H, t, *J*, 7, $CO_2CH_2CH_3$), 0.92 [9 H, s, SiC(C*H*$_3$)$_3$] and 0.12 [6 H, s, Si(C*H*$_3$)$_2$]; δ_C (75 MHz, $CDCl_3$) 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).

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

Super-Hydride™ (1.0 M in THF, 42 cm^3, 42 mmol) was added dropwise at -78 °C to ester **14** (5.62 g, 18 mmol) in THF (100 cm^3) and the solution stirred for 1 h then water (200 cm^3) was added. On warming to room temperature, the organic phase was diluted with ether (100 cm^3), separated and 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 20 – 50% ether in petrol, afforded the *title compound* **15** as a colourless oil (4 g, 84%), R_f = 0.25 (20% ether in petrol) (Found: M^+ 268.1862. $C_{15}H_{28}O_2Si$ requires *M*, 268.1859); ν_{max}/cm^{-1} 3426 (br), 2955, 2880, 1723, 1462 and 1340; δ_H (300 MHz, $CDCl_3$) 5.47 (1 H, m, 3-*H*), 4.31 (2 H, s, 8-*H*$_2$), 4.02 (2 H, s, 1-*H*$_2$), 2.27 (4 H, m, 4-*H*$_2$ and 5-*H*$_2$), 1.69 (3 H, s, 2-C*H*$_3$), 1.4 (1 H, br s, O*H*), 0.92 [9 H, s, SiC(C*H*$_3$)$_3$] and 0.13 [6 H, s, Si(C*H*$_3$)$_3$]; δ_C (75 MHz, $CDCl_3$) 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).

(2*E*)-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. $C_{31}H_{46}O_2Si_2$ requires *M*, 506.3036); ν_{max}/cm^{-1} 2930, 2857, 1727, 1460, 1364, 1256, 1219, 1111 and 1079; δ_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(CH_3)$_2$]; δ_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).

(6*E*)-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. $C_{23}H_{36}O_2NSi$ requires *M*, 410.2513); ν_{max}/cm^{-1} 3406 (br), 2930, 2857, 1730, 1461, 1429 and 1108; δ_H (300 MHz, $CDCl_3$) 7.77 (4 H, m, Ar-*H*), 7.45 (6 H, m, Ar-*H*), 5.55 (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)$_3$]; δ_C (75 MHz, $CDCl_3$) 135.5, 135.4, 133.8, 129.6, 127.6, 122.4, 86.0, 78.5, 68.7, 51.2, 26.8, 26.7, 19.3, 19.1 and 13.5; *m/z* (CI) 410 (M^+ + 18, 13%), 197 (90) and 137 (100).

Methyl (8*SR*,9*RS*)-7-[(6*E*)-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 effervesence 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. $C_{38}H_{50}O_6Si$ requires *M*, 630.3376); ν_{max}/cm^{-1} 2933, 2881, 2343, 1731, 1667, 1455, 1428, 1254 and 1112; δ_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_2CH_3), 2.56 (1 H, m, 9-*H*), 2.25 (4 H, m, 4′-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 [9 H, s, SiC(CH_3)$_3$] and 0.88 (3 H, d, *J* 7, 9-CH_3); *m/z* (EI) 630 (M^+, 5%), 573 (50),437 (25), 335 (60) and 199 (100).

(8*SR*,9*RS*)-7-[(6*E*)-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™ (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 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. $C_{37}H_{51}O_5Si$ requires *M*, 603.3505); ν_{max}/cm^{-1} 3439 (br), 2930, 2857, 1656, 1428, 1112 and 1060; δ_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-C*H* and 8′-H_2), 4.05 – 3.71 (5 H, m, 1′-H_2, 2-H_2 and 7-C*H*′), 3.64 and 3.43 (each 1 H, d, *J* 12, 8-C*H*), 2.82 (1 H, br s, O*H*), 2.47 (1 H, m, 9-*H*), 2.30 (4 H, m, 4′-H_2 and 5′-H_2), 1.76 (2 H, *m*, 10-H_2), 1.66 (3 H, s, 8-CH_3), 1.11 [9 H, s, SiC(CH_3)$_3$] and 0.92 (3 H, d, *J* 7, 9-CH_3); δ_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* (EI) 602 (M^+, 0.5%), 572 (2.5), 545 (5), 471 (2.5), 335 (20), 333 (16) and 199 (100).

(8*SR*,9*RS*)-8-*tert*-Butyldimethylsilyloxymethyl-7-[(6*E*)-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 trifluoromethanesulfonate (58 μL, 0.253 mmol) was added to the alcohol **20** (100 mg, 0.166 mmol) and triethylamine (50 μL, 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); δ_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-C*H*), 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′-

CH_3), 1.03 and 0.84 [each 9 H, s, SiC(CH_3)$_3$], 0.84 (3 H, s, 8-CH_3), 0.81 (3 H, d, *J* 7.5, 9-CH_3), 0.00 [6 H, s, Si(CH_3)$_2$]; δ_C (75 MHz, $CDCl_3$) 144.7, 135.5, 135.3, 133.8, 130.8, 129.5, 127.5, 124.5, 122.5, 105.6, 86.4, 76.1, 69.4, 68.7, 65.2, 64.4, 64.2, 57.7, 42.2, 38.0, 30.8, 26.8, 25.8, 25.6, 19.2, 18.1, 15.4, 14.9, 13.4, -3.6 and -5.6; *m/z* (CI) 734 (M^++18, 3%). Some of the analogous enone (*ca.* 12 mg, 10%) was also isolated.

(8*RS*,9*SR*)-8-*tert*-Butyldimethylsilyloxymethyl-6-[(6*E*)-1-hydroxy-8-*tert*-butyldiphenylsilyloxy-7-methyl-oct-6-en-2-yn-1-yl]-8,9-dimethyl-7-methylene-1,4-dioxaspiro[4.5]decane 22

n-Butyllithium (2 M in hexanes, 241 μL, 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. $C_{43}H_{64}O_5Si_2$ requires *M*, 716.4292); ν_{max}/cm^{-1} 3500 (br), 2959, 2932, 2857, 2216, 1684, 1465, 1281 and 1112; δ_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*H*), 5.47 (0.3 H, s, 7-C*H*), 5.42 (1 H, m, 6′-*H*), 5.21 (0.3 H, s, 7-C*H*′), 5.18 (0.7 H, s, 7-C*H*′), 4.95 (0.7 H, m, 1′-*H*), 4.86 (0.3 H, m, 1′-*H*), 4.30 – 3.56 (7 H, 2-H_2, 3-H_2, 8′-H_2, O*H*), 3.51 and 3.44 (each 1 H, d, *J* 9.5, 8-C*H*), 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_2), 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)$_2$]; δ_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* (CI) 734 (M^++18, 3%).

(8*RS*,9*SR*)-8-*tert*-Butyldimethylsilyloxymethyl-6-[(6*E*)-8-*tert*-butyldiphenylsilyloxy-7-methyl-1-oxo-oct-6-en-2-yn-1-yl]-8,9-dimethyl-7-methylene-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. $C_{43}H_{62}O_5Si_2$ requires *M*, 714.4136); ν_{max}/cm^{-1} 2958, 2930, 2859, 2213, 1729, 1681, 1465, 1283 and 1114; δ_H (300 MHz, C_6D_6) 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-C*H*), 4.02 (1 H, m, 2-C*H*), 3.96 (2 H, m, 2-C*H*, 3-C*H*), 3.83 (3 H, 3-C*H*, 8′-H_2), 3.70 (1 H, s, 6-*H*), 3.59 and 3.50 (each 1 H, d, *J* 10.5, 8-C*H*), 2.26 (4 H, m, 4′-H_2, 5′-H_2), 1.90 (1 H, m, 9-*H*), 1.52 (3 H, s, 7′-CH_3), 1.60 and 1.45 (each 1 H, m, 10-*H*), 0.98 [9 H, s, SiC(CH_3)$_3$], 0.84 (3 H, s, 8-CH_3), 0.80 [9 H, s, SiC(CH_3)$_3$], 0.76 (3 H, d, *J* 7, 9-CH_3), 0.01 and 0.02 (each 3 H, s, SiCH_3); δ_C (75 MHz, $CDCl_3$) 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. $C_{43}H_{62}O_5Si_2$ requires *M*, 714.4136); ν_{max}/cm^{-1} 2958, 2930, 2859, 2213, 1729, 1681, 1465, 1283 and 1114; δ_H (500 MHz, $CDCl_3$) 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-C*H*), 4.01 (2 H, m, 2-C*H*, 3-C*H*), 3.86 (5 H, m, 2-C*H*, 3-C*H*, 6-*H*, and 8′-H_2), 3.59 and 3.49 (each 1 H, d, *J* 10, 8-C*H*), 2.30 (4 H, m, 4′-H_2, 5′-H_2), 2.02 (1 H, m, 9-*H*), 1.57 (3 H, s, 7′-CH_3), 1.20 (2 H, m, 10-H_2), 1.01 [9 H, s, SiC(CH_3)$_3$], 0.84 [12 H, s, 8-CH_3 and SiC(CH_3)$_3$], 0.79 (3 H, d, *J* 7.5, 9-CH_3) and 0.00 [6 H, s, Si(CH_3)$_2$]; δ_C (75 MHz, $CDCl_3$) 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*SR*,3*SR*,5*RS*,6*SR*)-2-[(1*RS*,6*E*)-(8-*tert*-Butyldiphenylsilyloxy-1-tri-isopropylsilyloxy-7-methyloct-6-en-2-yn-1-yl]-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) ν_{max}/cm^{-1} 3070, 2944, 2893, 1463, 1428, 1383, 1320, 1249, 1151, 1107, 1055, 883, 860, 834, 741 and 709; δ_H (300 MHz, $CDCl_3$) 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-C*H*), 5.39 (1 H, br t, *J* 7, 6′-*H*), 5.30 (1 H, s, 1-C*H*′), 4.80 (1 H, m, 1′-*H*), 4.80 and 4.70 (each 1 H, d, *J* 7, OCH*H*O), 4.04 (2 H, s, 8′-H_2), 3.78 (1 H, m, 3-*H*), 3.74 (1 H, td, *J* 10, 7.5, CH*H*CH_2Si), 3.50 (1 H, m, CH*H*′CH_2Si), 3.49 and 3.34 (each 1 H, d, *J* 14.5, 6-C*H*), 2.58 (1 H, m, 2-*H*), 2.18 (4 H, m, 4′-H_2 and 5′-H_2), 2.08 (1 H, m), 2.02 (1 H, m), 1.61 (3 H, s, 7′-CH_3), 1.54 (1 H, m), 1.36 (3 H, s, 6-CH_3), 1.01 – 1.04 [30 H, m, SiC(CH_3)$_3$ and Si(C*H*(CH_3)$_2$)$_3$], 0.95 (3 H, d, *J* 6.5, 5-CH_3), 0.91 (2 H, m, CH_2Si) and 0.02 [9 H, s, Si(CH_3)$_3$]; δ_C (75 MHz, $CDCl_3$) 146.9,

142.7, 135.5, 133.8, 133.1, 129.5, 129.1, 128.3, 127.6, 127.5, 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.

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

tetra-n-Butylammonium fluoride (1.0 M solution in tetrahydrofuran, 1.16 cm^3, 1.16 mmol) was added to the bis-silyl ether **45** (0.56 g, 0.578 mmol) in tetrahydrofuran (3.6 cm^3) 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, R_f = 0.05 (50% ether in petrol) (Found; $M^+ + NH_4$, 594.3294. $C_{31}H_{52}O_6NSSi$ requires *M*, 594.3284); ν_{max}/cm^{-1} 3467 (br), 2951, 2924, 1447, 1317, 1248, 1150, 1025, 859 and 836; δ_H (500 MHz, $CDCl_3$) 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-C*H*), 4.92 and 4.80 (each 1 H, d, *J* 7, OCH*H*O), 4.63 (1 H, br d, *J* 10, 1′-*H*), 4.10 (1 H, d, *J* 10, 1′-O*H*), 3.98 (2 H, br d, *J* 7, 8′-H_2), 3.94 (1 H, td, *J* 10, 5, 3-*H*), 3.77 and 3.59 (each 1 H, td, *J* 11.5, 5.5, CH*H*CH_2Si), 3.50 and 3.38 (each 1 H, d, *J* 15, 6-C*H*), 2.69 (1 H, br d, *J* 10, 2-*H*), 2.50 (1 H, br t, *J* 6.5, 8′-O*H*), 2.32 – 2.41 (5 H, m, 4′-H_2 , 5′-H_2 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′-CH_3), 1.24 (3 H, s, 6-CH_3), 0.97 (2 H, m, CH_2Si), 0.92 (3 H, d, *J* 6.5, 5-CH_3) and 0.03 [9 H, s, Si(CH_3)$_3$]; δ_C (75 MHz, $CDCl_3$) 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).

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

Imidazole (8 mg, 0.117 mmol) was added to the diol **46** (45 mg, 0.078 mmol) in dichloromethane (0.4 cm^3) 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 cm^3) and ethyl acetate (2 cm^3) were added. The aqueous layer was extracted with ethyl acetate (3x2 cm^3) and the organic extracts were washed with brine (4 cm^3), dried ($MgSO_4$) 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, R_f 0.4 (50% ether in petrol) (Found; $M^+ + NH_4$, 708.4140. $C_{37}H_{66}O_6NSSi_2$ requires *M*, 708.4149); ν_{max}/cm^{-1} 3497 (br), 2952, 2929, 2894, 2858, 1638, 1584, 1465, 1449, 1379, 1316, 1250, 1150, 1105, 1027, 836 and 775; δ_H (300 MHz, $CDCl_3$) 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-C*H*), 4.84 and 4.81 (each 1 H, d, *J* 7, OCH*H*O), 4.62 (1 H, br d, *J* 10, 1′-*H*), 4.09 (1 H, d, *J* 10, O*H*), 4.01 (2 H, s, 8′-H_2), 3.89 (1 H, td, *J* 10, 5, 3-*H*), 3.81 and 3.58 (each 1 H, m,

CH*H*CH$_2$Si), 3.49 and 3.38 (each 1 H, d, *J* 14.5, 6-C*H*), 2.69 (1 H, br d, *J* 10, 2-*H*), 2.27 (4 H, m, 4′-*H*$_2$ and 5′-*H*$_2$), 2.10 (1 H, dt, *J* 13, 4.2, 4-*H*), 1.85 (1 H, m, 5-*H*), 1.61 (3 H, s, 7′-C*H*$_3$), 1.53 (1 H, m, 4-*H*′), 1.27 (3 H, s, 6-C*H*$_3$), 0.84 – 0.99 [14 H, m, SiC(C*H*$_3$)$_3$, 5-C*H*$_3$ and C*H*$_2$Si], 0.01 (3 H, s, SiC*H*$_3$) and 0.01 (12 H, s, 4 x SiC*H*$_3$); δ_C (75 MHz, $CDCl_3$) 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, 45.4, 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* (CI) 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).

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

2,6-Lutidine (0.0054 cm^3, 0.0462 mmol) and tri-isopropylsilyl methanesulfonate (0.0117 cm^3, 0.0435 mmol) were added to the alcohol **47** (29 mg, 0.0414 mmol) in dichloromehane (0.3 cm^3) at 0 °C and the solution stirred for 30 min. Water (0.5 cm^3) and ethyl acetate (1 cm^3) were added, the aqueous phase was extracted with ethyl acetate (3x2 cm^3), and the organic extracts were washed with brine (3 cm^3), dried ($MgSO_4$), 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, R_f = 0.8 (50% ether in petrol) ν_{max}/cm^{-1} 2928, 2894, 2864, 1528, 1461, 1321, 1249, 1150, 1054, 836 and 775; δ_H (300 MHz, $CDCl_3$) 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-C*H*), 5.39 (1 H, br t, *J* 5.5, 6′-*H*), 5.33 (1 H, s, 1-C*H*′), 4.82 (2 H, m, 1′-*H* and OCH*H*O), 4.72 (1 H, d, *J* 7, OCH*H*′O), 4.02 (2 H, s, 8′-*H*$_2$), 3.81 (1 H, m, 3-*H*), 3.75 and 3.49 (each 1 H, m, CH*H*CH$_2$Si), 3.52 and 3.36 (each 1 H, d, *J* 14.5, 6-C*H*), 2.59 (1 H, t, *m*, 3-*H*), 2.20 (4 H, m, 4′-*H*$_2$ and 5′-*H*$_2$), 2.06 (2 H, m, 4-*H* and 5-*H*), 1.62 (3 H, s, 7′-C*H*$_3$), 1.56 (1 H, m, 4-*H*′), 1.23 (3 H, s, 6-C*H*$_3$), 1.06 [21 H, m, 3 x SiC*H*(C*H*$_3$)$_2$], 0.97 (3 H, d, *J* 6.5, 5-C*H*$_3$), 0.90 [11 H, m, C*H*$_2$Si and SiC(C*H*$_3$)$_3$], 0.08 and 0.05 (each 3 H, s, SiC*H*$_3$) and 0.04 [9 H, s, Si(C*H*$_3$)$_3$]; δ_C (75 MHz, $CDCl_3$) 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).

(2*SR*,3*SR*,5*RS*,6*SR*)-5,6-Dimethyl-2-[(1*RS*,6*E*)-(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 cm^3) were added to the bis-silyl ether **48** (0.15 g, 0.177 mmol) in tetrahydrofuran (1.07 cm^3) 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 cm^3) followed by ethyl acetate (2 cm^3). The aqueous phase was extracted with ethyl acetate (4x5 cm^3) and the organic

extracts washed with brine (10 cm^3), dried ($MgSO_4$) 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, R_f = 0.2 (50% ether in petrol) (Found; $M^+ + NH_4$, 750.4623. $C_{40}H_{72}O_6Si_2SN$ requires *M*, 750.4619); ν_{max}/cm^{-1} 3487 (br), 2895, 2857, 1447, 1377, 1320, 1249, 1151, 1027 and 836; δ_H (300 MHz, $CDCl_3$) 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-C*H*), 4.88 (1 H, d, *J* 7, OCH*H*O), 4.81 (1 H, m, 1′-*H*), 4.71 (1 H, d, *J* 7, OCH*H*′O), 4.01 (2 H, s, 8′-H_2), 3.79 (2 H, m, 3-*H* and CH*H*CH_2Si), 3.53 (1 H, d, *J* 14.5, 6-C*H*), 3.51 (1 H, m, CH*H*′CH_2Si), 3.38 (1 H, d, *J* 14.5, 6-C*H*′), 2.62 (1 H, dd, *J* 7, 4, 2-*H*), 2.27 (4 H, m, 4′-H_2 and 5′-H_2), 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′-CH_3), 1.60 (1 H, m, 4-*H*′), 1.40 (3 H, s, 6-CH_3), 1.07 [21 H, m, 3 x SiC*H*(CH_3)$_2$], 0.97 (3 H, d, *J* 6.5, 5-CH_3), 0.94 (2 H, m, CH_2Si) and 0.05 [9 H, s, Si(CH_3)$_3$]; δ_C (75 MHz, $CDCl_3$) 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* (CI) 750 (M^+ + 18, 0.3%), 294 (42), 277 (82) and 90 (100).

(2*SR*,3*SR*,5*RS*,6*SR*)-2-[(1*RS*,6*E*)-(8-Bromo-1-tri-isopropylsilyloxy-7-methyloct-6-en-2-yn-1-yl]-5,6-di-methyl-6-phenylsulfonylmethyl-3-(2-trimethylsilylethoxy)methoxy-1-methylenecyclohexane 50

Triethylamine (0.097 cm^3, 0.7 mmol) and methanesulfonyl chloride (0.033 cm^3, 0.44 mmol) were added to the alcohol **49** (0.19 g, 0.175 mmol) in dichloromethane (2.8 cm^3) 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 acetone (1.4 cm^3) 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 cm^3) and washed with saturated aqueous sodium bicarbonate (5 cm^3). The aqueous phase was washed with ethyl acetate (4x5 cm^3) and the organic extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography of the residue, eluted with 1 – 15% ether in petrol, afforded the *title compound* **50** (0.159g, 86%) as a clear oil, R_f = 0.65 (50% ether in petrol) (Found; M^+ - Br^{79}, 715.4237. $C_{40}H_{67}O_5Si_2S$ requires *M*, 715.4248); ν_{max}/cm^{-1} 2943, 2896, 2865, 1465, 1446, 1320, 1248, 1150, 1106, 1052, 1033, 861 and 835; δ_H (400 MHz, $CDCl_3$) 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-C*H*), 4.85 (1 H, br d, *J* 4, 1′-*H*), 4.81 and 4.71 (each 1 H, d, *J* 7, OCH*H*O), 3.96 (2 H, s, 8′-H_2), 3.76 (2 H, m, 3-*H* and CH*H*CH_2Si), 3.50 (2 H, m, 6-C*H* and CH*H*′CH_2Si), 3.36 (1 H, d, *J* 14.5, 6-C*H*′), 2.57 (1 H, dd, *J* 7, 4.5, 2-*H*), 2.22 (4 H, m, 4′-H_2 and 5′-H_2), 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′-CH_3), 1.54 (1 H, m, 4-*H*′), 1.36 (3 H, s, 6-CH_3), 1.05 [21 H, m, 3 x SiC*H*(CH_3)$_2$], 0.95 (3 H, d, *J* 7, 5-CH_3), 0.89 (2 H, m, CH_2Si), 0.03 [9 H, s, Si(CH_3)$_3$]; δ_C (75 MHz, $CDCl_3$) 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).

(1*SR*,2*RS*,7*E*,11*SR*,12*RS*,14*SR*)-15-Methylene-10-phenylsulfonyl-8,11,12-trimethyl-2-tri-isopropyl-silyloxy-14-(2-trimethylsilylethoxy)methoxybicyclo[9.3.1]pentadec-7-en-3-yne 51

Sodium hexamethyldisilazide (1.0 M solution in tetrahydrofuran, 0.125 cm^3, 0.125 mmol) was added to the bromide **50** (33 mg, 0.0415 mmol) in tetrahydrofuran (0.25 cm^3) at 0 °C over 30 min using a syringe pump and the solution stirred for 30 min. Saturated aqueous ammonium chloride (1.5 cm^3) and ethyl acetate were added. The aqueous layer was extracted into ethyl acetate (3x3 cm^3) and the organic extracts were washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated unde 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, R_f = 0.65 (50% ether in petrol) (Found; $M^+ + NH_4$, 732.4525. $C_{40}H_{70}O_5NSSi_2$ requires *M*, 732.4513); ν_{max}/cm^{-1} 2927, 2865, 1718, 1652, 1540, 1463, 1373, 1309, 1145 and 1045; δ_H (300 MHz, $CDCl_3$) 7.98 (2 H, d, *J* 8, Ar-*H*), 7.62 (3 H, d, m, Ar-*H*), 6.19 (1 H, s, 15-C*H*), 6.02 (1 H, s, 15-C*H′*), 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, OCH*H*O), 3.82 (1 H, td, *J* 9.5, 5.5, CH*H*CH_2Si), 3.62 (2 H, m, 10-*H* and 14-*H*), 3.46 (1 H, td, *J* 9, 6.5, CH*H′*CH_2Si), 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-CH_3), 1.17 – 1.05 [24 H, m, 11-CH_3 and 3 x SiC*H*(CH_3)$_2$], 0.97 – 0.90 [5 H, m, 12-CH_3 and CH_2Si) and 0.06 [9 H, s, Si(CH_3)$_3$]; *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).

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

tetra-n-Butylammonium fluoride (1.0 M solution in tetrahydrofuran, 0.026 cm^3, 0.026 mmol) was added to the silyl ether **51** (17 mg, 0.0238 mmol) in tetrahydrofuran (0.3 cm^3) 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, R_f = 0.25 (50% ether in petrol) ν_{max}/cm^{-1} 3465 (br), 2952, 2922, 1733, 1644, 1446, 1369, 1304, 1249, 1142, 1030, 921, 860 and 836; δ_H (300 MHz, $CDCl_3$) 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-C*H*), 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, OCH*H*O), 3.83 (1 H, d, 4.5, O*H*), 3.75 (1 H, m, CH*H*CH_2Si), 3.64 – 3.52 (3 H, m, 10-*H*, 14-*H* and CH*H′*CH_2Si), 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-H_2), 2.30 (1 H, m, 1-*H*), 2.17 – 2.00 (4 H, m, 6-H_2, 9-*H′* and 13-*H*), 1.46 (3 H, s, 8-CH_3), 1.42 (1 H, m, 13-*H′*), 1.13 (3 H, d, *J* 6.5, 12-CH_3), 1.09 (3 H, s, 11-CH_3), 1.01 (2 H, m, CH_2Si) and 0.05 [9 H, s, Si(CH_3)$_3$]; δ_C (75 MHz, $CDCl_3$) 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, 22.6, 18.3, 18.1, 17.9, 17.2 and -1.6; *m/z* (ES-) 593 (M^+ + 35, 99%), 157 (89) and 111 (100).

(1*SR*,2*RS*,7*E*,11*SR*,12*RS*,14*SR*)-15-Methylene-8,11,12-trimethyl-2-tri-isopropylsilyloxy-14-(2-trimethylsilylethoxy)methoxybicyclo[9.3.1]pentadec-7-en-3-yne 53

Sodium dihydrogen 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_2SO_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) ν_{max}/cm^{-1} 2928, 2866, 1463, 1379, 1249, 1162, 1106, 1052, 1035, 859 and 836; δ_H (300 MHz, $CDCl_3$) 5.61 (1 H, s, 15-C*H*), 5.01 (1 H, d, *J* 9, 7-H), 4.94 (1 H, s, 15-C*H*′), 4.90 (1 H, d, *J* 3.5, 2-*H*), 4.79 and 4.73 (each 1 H, d, *J* 6.5, OCH*H*O), 3.85 (1 H, m, CH*H*CH_2Si), 3.57 (1 H, td, *J* 10, 5.5, 14-*H*), 3.44 (1 H, m, CH*H*′CH_2Si), 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*), 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 SiC*H*$(CH_3)_2$ and CH_2Si], 0.79 (3 H, d, *J* 6.5, 12-CH_3) and 0.06 [9 H, s, Si(CH_3)$_3$]; δ_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^+ + 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).