

A Stereoselective *cis*-Enyne Synthesis Using Vinyl Sulfone Chemistry[§]

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Abstract: The *trans*-sulfonyl enyne **8** was deprotonated using lithium diisopropylamide to provide a *cis*-enyne anion which was coupled with a variety of carbonyl compounds to provide, in high yields, a range of silyl-protected phenylsulfonyl enynes. These were desulfonlated in good yields to provide silyl protected terminal *cis*-enyne. Both these processes were shown to proceed with very good *cis*-selectivity.

The *cis*-enyne functionality can be found in a wide range of natural products that have been extracted from a number of sources. One of the largest groups of compounds is found within the secondary metabolites of various species of the *Laurencia* red alga.¹ Other sources of this type of compound include sponges,² sea-hares³ and the South American "poison arrow" frogs.⁴ More recently, fermentation broths of soil microorganisms have yielded the potent antitumour antibiotics esperamycin,⁵ calicheamycin⁶ and dynemycin.⁷ All these compounds have, as a common feature, a *cis*-double bond directly bonded to an acetylene (Figure 1), often at the end of a chain ($R^2 = H$).



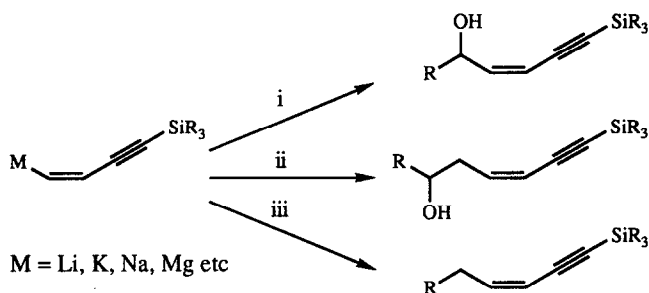
Figure 1

The methods which are available for the synthesis of this type of functionality are varied, but can be conveniently divided into groups, according to how the *cis*-double bond is introduced. The Peterson olefination reaction has been used to introduce the *cis*-enyne side chain into a number of natural products.⁸

[§]Dedicated to Professor Charles W. Rees in recognition of his many chemical contributions and personal inspiration.

We have used the partial hydrogenation of diynes⁹ to achieve analogous transformations and other groups¹⁰ have used similar reductive methods. The Wittig reaction has been used successfully in several natural product syntheses.¹¹ Many more recent methods involve the coupling of a metal acetylide with a *cis*-vinyl halide.¹² Conversely, methods exist which couple a vinyl organometallic reagent with an acetylenic halide.¹³ Other, less easily classified examples, have also produced *cis*-enyne.¹⁴

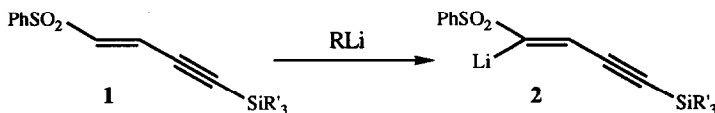
In our work towards the synthesis of a small group of the above natural products, we wished to prepare a nucleophilic synthon, which would introduce the *cis*-enyne functionality directly. The terminal *cis*-enyne found in nature are either unsubstituted, or substituted at the allylic or homoallylic positions with a halogen atom. In order to have a common precursor to all these structures we required the stereospecific formation of a *cis*-enyne anion, silylated on the terminal acetylenic carbon, which would (i) attack aldehydes, (ii) open epoxides, and (iii) undergo alkylation. The products of the proposed *cis*-enyne anion additions (Scheme 1) would then need only the relatively simple transformations of halide displacement and desilylation to give the desired natural product unsaturated side-chains.



Scheme 1

Reagents: (i) $RCHO$; (ii) Epoxide; (iii) RCH_2X

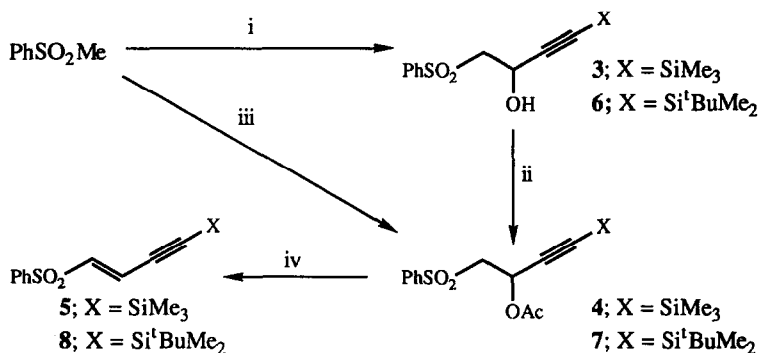
The Julia olefin synthesis is well known for the efficient introduction of double bonds in which the *E*-configuration is usually preferred.¹⁵ Some groups have successfully deprotonated the resulting vinyl sulfone at the α position to furnish a vinyl anion with fixed stereochemistry.¹⁶ Thus, if a *trans*-phenylsulfonyl enyne **1** could be synthesised and deprotonated in the same fashion, the resulting enyne sulfone anion **2** would be a *cis*-enyne synthon (Scheme 2). This process would of course be dependent on the stereochemical outcome of the addition and subsequent desulfonylation steps. In this paper we describe our work on the synthesis of the vinyl sulfone **1**, its metallation to **2** and subsequent reaction with various carbonyl compounds to prepare *cis*-enyne allylic alcohols.



Scheme 2

RESULTS AND DISCUSSION

The required *trans*-enynes **5** and **8** were obtained by elimination of acetate from the precursors **4** and **7** (Scheme 3). Phenyl methyl sulfone was deprotonated to form the α -sulfonyl anion, which was reacted with trimethylsilylpropynal to form the β -hydroxy sulfone **3**. This was either isolated at this stage in 85% yield, or acylated in a one-pot procedure to form the acetate **4** in 83% yield over the two steps. Acetylation of the addition product **3** with acetic anhydride, triethylamine and a catalytic quantity of dimethylaminopyridine furnished the acetate **4** in 95%. Previous work by Julia had indicated that the elimination of β -sulfonyl acetates and tosylates could be controlled to give either *E*- or *Z*-double bond geometry.¹⁷ Attempts to use the literature conditions (powdered NaOH, dioxane) for the production of the *E*-alkene resulted in decomposition. Attempted elimination with DBU resulted in desilylation and subsequent base-promoted polymerisation. Success was achieved with triethylamine, a base weaker than DBU, over longer reaction times. Thus when the acetate **4** was heated overnight in refluxing THF containing triethylamine (20 equiv.) the trimethylsilyl-(TMS)-protected *trans*-enyn sulfone **5** was obtained in 81% yield. NMR data showed no trace of the *cis*-isomer. Several attempts to deprotonate the TMS-(*E*)-enyn sulfone were unsuccessful, the only identifiable product being that due to desilylation, not deprotonation.

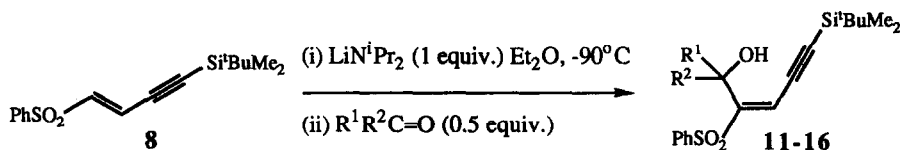


Scheme 3

Reagents: X = SiMe₃: (i) (a) ⁿBuLi, (b) TMS-C≡C-CHO (85%), (iii) (CH₃CO)₂O, Et₃N, DMAP (95%), (iii) (a) ⁿBuLi, (b) TMS-C≡C-CHO, (c) (CH₃CO)₂O (83%), (iv) Et₃N (20 equiv.), reflux (81%); X = ^tBuMe₂ (i) (a) ⁿBuLi, (b) ^tBuMe₂Si-C≡C-CHO (94%), (ii) (CH₃CO)₂O, Et₃N, DMAP (95%), (iii) (a) ⁿBuLi, (b) ^tBuMe₂Si-C≡C-CHO, (c) (CH₃CO)₂O (49%), (iv) Et₃N (20 equiv.), reflux, 8 h (94%) or DBU (1.1 equiv.), 0 °C, 5 mins (99%).

It was anticipated that a more robust silicon protecting group would be able to withstand the required deprotonation conditions. The sequence which had been used to generate the TMS-*trans*-enyn sulfone was repeated for the TBDMS analogue (Scheme 3). It is noteworthy that most of the steps involved in producing the TBDMS-*trans*-enyn sulfone occurred in better yields, fulfilling the hope that a TBDMS-protected acetylene would be more robust to a wide range of conditions. The elimination process was further improved employing 1.1 equivalents of DBU at 0 °C for five minutes, which gave the product **8** in 99% yield. This compound was easily recrystallised from hexane and showed no trace of the *Z*-isomer (by NMR). The TBDMS-*trans*-enyn

sulfone is a stable crystalline solid, and can be stored under normal laboratory conditions without any decomposition or loss of stereoisomeric purity.

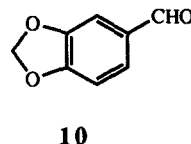
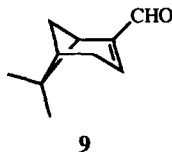


Scheme 4

The *trans*-enyne sulfone **8** was deprotonated using freshly prepared lithium diisopropylamide. An excess of the anion from **8** was treated (Scheme 4) with a variety of aldehydes and one ketone (Table 1) to give a range of sulfonylenynes. These products showed excellent retention of the double bond geometry, as detected by the absence of any trace of the other isomer in their NMR spectra.

Table 1 - Reactions of the Sulfonylenyne Anion with Aldehydes (Scheme 4)

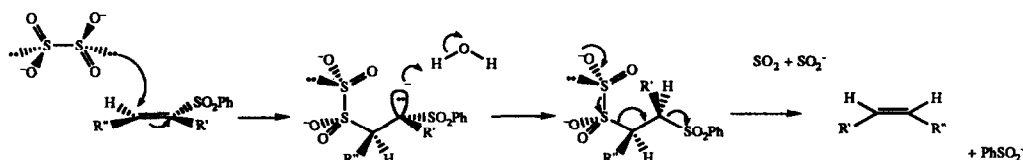
Entry	R ¹	R ²	Product	Yield
1	Ph	H	11	92%
2	$i\text{C}_3\text{H}_7$	H	12	97%
3	$n\text{C}_6\text{H}_{13}$	H	13	73%
4 ^a	$n\text{C}_6\text{H}_{13}$	H	13	95%
5	$(\text{CH}_2)_4$	H	14	92%
6	(-) - Myrtenal 9	H	15	85%
7	Heliotropin 10	H	16	96%



^aMgBr₂ added

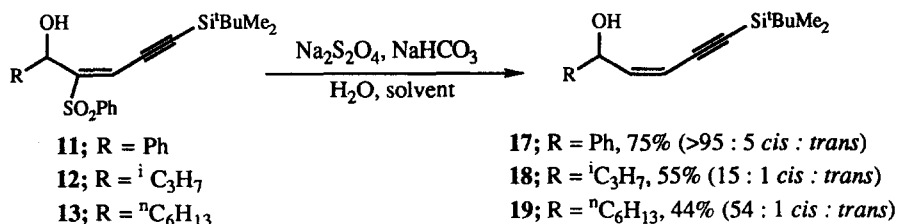
It can be seen from Table 1 that the addition of the anion of the *trans*-enyne sulfone **8** to carbonyl compounds is a highly efficient process. Initially problems were encountered with more enolisable aldehydes, such as *n*-heptanal (entry 3). The yield was improved by the addition of magnesium dibromide to the anion before the addition of the carbonyl compound (entry 4), thus reducing the basicity of the reagent and enhancing the nucleophilic process.

There are several literature methods for the desulfonylation of both alkyl and vinyl sulfones. The common amalgam methods¹⁸ were felt to be too severe, and were not attempted. Radical methods, employing tri-*n*-butyltin hydride, have been successful for some specific compounds, namely β -keto sulfones¹⁹ and α -fluoro vinyl sulfones.²⁰ This method was attempted; treatment of a solution of the benzaldehyde adduct **11**



Scheme 5 - Mechanism for Desulfonylation of Vinyl Sulfones with Sodium Dithionite

with tributyltin hydride and a catalytic amount of AIBN in refluxing toluene overnight gave no desulfonylated products. Success was achieved by modifying a Julia method,²¹ which involves using sodium dithionite as the reducing agent. The mechanism is believed to follow an addition-elimination process (Scheme 5).¹⁸ When this procedure was applied to the enyne sulfones **11-13** the desulfonylated enynes **17-19** respectively were obtained in variable yields with good *cis*-selectivity (Scheme 6).



Scheme 6

Table 2 Desulfonylation of the Enyne Sulfones **11-13**

Entry	Material	Na ₂ S ₂ O ₄	NaHCO ₃	Temp.	Time	Solvents	Product	Yield	Z:E
1	11	4 equiv. ^a	6 equiv.	50° C	4 h	c	17	50%	>95:5
2 ^b	11	4 equiv.	6 equiv.	50° C	18 h	c	17	60%	>95:5
3	12	4 equiv.	6 equiv.	120° C	1 h	d	18	39%	2:1
4	12	6 equiv.	12 equiv.	80° C	1 h	c	18	55%	15:1
5	13	6 equiv.	12 equiv.	60° C	2 h	c	19	57%	33:1
6	13	6 equiv. ^a	12 equiv.	80° C	4 h	e	19	44%	54:1

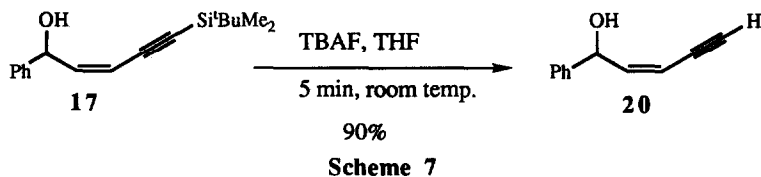
^a Added in two or more portions; ^b20% starting material isolated; ^cDMF : Water : THF (1 : 1 : 1);

^dDMF : Water (1 : 1); ^eTHF : Water (1 : 1)

It can be seen (Table 2) that the outcome of the desulfonylation process is quite dependent on the choice of the relative quantities of sodium dithionite and sodium bicarbonate, as well as solvents and reaction times. Improved yields could be obtained under optimised conditions, but at the expense of stereoselectivity. The literature conditions²¹ (entry 3) gave both a poor yield (39%) and a poor *Z* : *E*-selectivity (2:1). Lowering the reaction temperature improved the selectivity and the yield of the process (entry 4). Each substrate for this reaction required slightly different conditions. Different solvent mixtures had to be employed to ensure that each particular reactant dissolved well, and there was no clear guide to the choice of optimum conditions. However, reasonable yields and good selectivities could be obtained. The best result was obtained with the

phenyl-substituted alcohol **11**, which was desulfonylated in 75% yield (based on unrecovered starting material), and showed no trace of the *trans*-isomer (by NMR).

To ensure that these desulfonylated products could be desilylated efficiently to produce the required terminal *cis*-enyne, a prototype desilylation was carried out. The phenyl-substituted silylated enyne **17** was treated with tetra-*n*-butyl ammonium fluoride (TBAF) for five minutes to produce the desilylated *cis*-enyne **20** in 90% yield (Scheme 7). There was no sign of the *E*-isomer (by NMR).



In this way, the sulfone methodology has been shown to be efficient in the introduction of the *cis*-enyne group to produce allylic alcohols. Both the addition and the desilylation processes proceed with high retention of geometrical configuration. Thus, starting from benzaldehyde, the *cis*-enyne **20** was produced in 62% overall yield, with no trace of the *trans*-isomer. Work is proceeding to apply this method to produce homoallylic alcohols, via epoxide opening (Scheme 1, route ii), and unsubstituted enynes, via alkylation (Scheme 1, route iii).

EXPERIMENTAL

NMR spectra were recorded using Bruker WM250 and WM400 instruments. IR spectra were determined on a Perkin-Elmer 1310 spectrophotometer, calibrated relative to polystyrene. Low and high resolution electron impact (EI) mass spectra were recorded on AEI MS902 and MS30 instruments, respectively. Chemical ionisation (CI) and some EI mass spectra were recorded by Dr. J. Ballantine and co-workers at the S.E.R.C. Mass Spectrometry Service, Swansea. Microanalyses were performed by Mr D. Flory and staff at the University Chemical Laboratory, Cambridge. Melting points were determined on a Büchi 510 apparatus. Flash chromatography²² was carried out on Merck Kieselgel 60 (230-400 mesh) and thin layer chromatography was carried out on Merck Kieselgel 60 GF254 plates, coated to a thickness of 0.25 mm. THF refers to tetrahydrofuran distilled from potassium in a recycling still. Ether refers to diethyl ether distilled from sodium in a recycling still. Other solvents were purified by standard techniques.²³

3-Hydroxy-4-phenylsulfonyl-1-trimethylsilyl-but-1-yne 3.

Butyl lithium (6.7 cm³ of a 1.5 M solution in hexanes, 10 mmol) was added to a solution of the phenyl methyl sulfone (1.56 g, 10 mmol) in THF (25 cm³) at 0 °C. After one hour the solution was cooled to -78 °C and a solution of trimethylsilylpropynal (1.00 g, 7.9 mmol) in THF (15 cm³) was added. After one hour at this temperature the reaction was allowed to warm to room temperature and a saturated aqueous solution of ammonium chloride (20 cm³) was added, the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (20 cm³), dried over magnesium sulphate and evaporated. The product was purified by flash column chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **3**, which was recrystallised from ethyl acetate / hexane (2.4 g, 85%) to give a white solid, m.p. 92-93 °C; *R*_f (1 : 1 hexane / ethyl acetate) 0.54; (Found: C, 55.1; H, 6.6. C₁₃H₁₈O₃SiS requires C, 55.3; H, 6.4%); *v*_{max} (CHCl₃) / cm⁻¹ 3580 (m), 3520 (brm), 2950 (m), 2860 (m), 2180 (m), 1590 (w), 1440 (m), 1380 (m), 1310 (vs), 1310 (vs), 1140 (vs);

δ_H (80 MHz; CDCl₃) 8.00-7.55 (5H, m, ArH), 4.93 (1H, dd, *J* 7.4, CHOH), 3.50 (1H, d, *J* 7, PhSO₂CH_a), 3.48 (1H, d, *J* 4, PhSO₂CH_b), 0.12 (9H, s, Si(CH₃)₃); δ_C (100 MHz; CDCl₃) 139.1, 134.1, 129.4, 128.1 (aryl C), 101.9, 91.7 (alkyne C), 62.0 (PhSO₂CH₂), 57.8 (CHOH), -0.4 (Si(CH₃)₃); *m/z* (EI) 282 (M⁺, 3%), 267 ((M-Me)⁺, 100), 264 ((M-H₂O)⁺, 8), 140 (32), 135 (68), 125 (43), 77 (Ph⁺, 47) and 73 (TMS⁺, 60) (Found: M⁺, 282.0671. C₁₃H₁₈SiO₃ requires *M*, 282.0746).

3-Acetoxy-4-phenylsulfonyl-1-trimethylsilyl-but-1-yne 4.

Methyl lithium / lithium bromide complex (1.35 cm³ of a 1.5 M solution in ether, 2 mmol) was added to a solution of phenyl methyl sulfone (313 mg, 2 mmol) in THF (20 cm³) at 0 °C. After twenty minutes the solution was cooled to -78 °C and a solution of trimethylsilylpropynal (126 mg, 1 mmol) in THF (5 cm³) was added. After half an hour acetic anhydride (0.4 cm³, 4.2 mmol) was added and the reaction was allowed to warm to room temperature. The reaction was quenched with water (2 cm³) and then a saturated aqueous solution of sodium bicarbonate (10 cm³) was added, the phases were separated and the aqueous layer was extracted with ethyl acetate (3 x 75 cm³). The combined organic phases were washed with brine (20 cm³), dried over magnesium sulphate and the solvents were removed *in vacuo*. The product was purified by flash

column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the sulfonyl acetate **4**, which was recrystallised from ether / hexane (270 mg, 83%) to give a white solid, m.p. 76-76.5 °C; R_f (4 : 1 hexane / ethyl acetate) 0.33; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 2930 (m), 2180 (m), 1740 (vs) 1370 (s), 1310 (vs), 1140 (vs); δ_H (80 MHz; CDCl₃) 7.91-7.54 (5H, m, ArH), 5.77 (1H, dd, J 9, 3, CH₂OAc), 3.70 (1H, dd, J 15, 9, PhSO₂CH₂a), 3.50 (1H, dd, J 15, 3, PhSO₂CH₂b), 1.85 (3H, s, CH₃CO₂), 0.11 (9H, s, Si(CH₃)₃); δ_C (100 MHz; CDCl₃) 166.8 (MeCO₂), 139.2, 134.0, 129.3, 128.3 (aryl C), 98.8, 92.6 (alkyne C), 59.5 (PhSO₂CH₂), 58.4 (CH₂OAc), 20.5 (CH₃CO₂), -0.5 (Si(CH₃)₃); m/z (CI) 309 ((M-CH₃)⁺, 95%), 281 ((M-CH₃CO)⁺, 4), 265 ((M-OAc)⁺, 9), 264 ((M-AcOH)⁺, 12), 215 (54), 199 (69), 183 ((M-PhSO₂)⁺, 62), 141 ((PhSO₂)⁺, 35), 135 (50), 125 (45), 117 (100), 77 (Ph, 97), 75 (31) and 73 (TMS⁺, 45) (Found: (M-Me)⁺, 309.0617. C₁₄H₁₇SiSO₄ requires (M-Me), 309.0617); (Found: C, 55.4; H, 6.4. C₁₅H₂₀O₄SiS requires C, 55.5; H, 6.2%).

4-Phenylsulfonyl-1-trimethylsilyl-but-3-(E)-en-1-yne **5**.

Triethylamine (3.5 cm³, 25 mmol) was added to a solution to the acetoxysulfone **4** (410 mg, 1.26 mmol) in dry THF (50 cm³) and the reaction was heated at reflux overnight. The cooled reaction mixture was poured into 2M HCl (30 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 75 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to afford the enyne sulfone **5** (270 mg, 81%), which was recrystallised from hexane as a white solid, m.p. 59-60 °C; R_f (4 : 1 hexane / ethyl acetate) 0.46; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 2960 (m), 2900 (m), 1590 (s), 1310 (s), 1140 (s), 1070 (s); δ_H (250 MHz; CDCl₃) 7.89-7.52 (5H, m, ArH), 6.77 (1H, d, J 15, alkene CH), 6.69 (1H, d, J 15, alkene CH), 0.18 (9H, s, Si(CH₃)₃); δ_C (100 MHz; CDCl₃) 139.7 (alkene C), 139.6, 133.8, 129.4, 127.7 (aryl C), 123.1 (alkene C), 108.3, 98.3 (alkyne C), -0.6 (Si(CH₃)₃); m/z (CI) 249 ((M-Me)⁺, 44%), 199 (3), 185 (5), 167 (6), 159 (14), 135 (24), 125 (50), 107 (100), 97 (23) and 77 (Ph⁺, 86) (Found: (M+NH₄)⁺, 282.0984. C₁₃H₂₀SiSNO₂ requires (M+NH₄), 282.0984); (Found: C, 58.9; H, 6.0. C₁₃H₁₆O₂SiS requires C, 59.1; H, 6.1%).

1-Butyldimethylsilyl-3-hydroxy-4-phenylsulfonyl-but-1-yne **6**.

Butyl lithium (50 cm³ of a 1.5M solution in hexanes, 75 mmol) was added to a solution of phenyl methyl sulfone (13.8 g, 88 mmol) in THF (150 cm³) at 0 °C. After ten minutes the solution was cooled to -78 °C and a solution of TBDMS-propynal (10.0 g, 59 mmol) in THF (20 cm³) was added by cannula. The reaction was then allowed to warm to room temperature, by which time all the aldehyde had been consumed (by TLC). Saturated aqueous ammonium chloride solution (50 cm³) was added, the phases were separated and the aqueous layer was extracted with ether (3 x 80 cm³). The combined organic phases were washed with 2 M HCl (20 cm³) and with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 2 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **6** (17.94 g, 94%) as a white solid, m.p. 47-49 °C; R_f (1 : 1 hexane / ethyl acetate) 0.70; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3580 (m), 3530 (br.m), 2940 (s), 2900 (m), 2870 (s), 2180 (m), 1590 (m), 1450 (m), 1390 (m), 1330 (m), 1310 (s), 1140 (s); δ_H (250 MHz; CDCl₃) 7.95-7.91 (2H, m, ArH), 7.68-7.54 (3H, m, ArH), 4.95 (1H, m, CHOH), 3.55 (1H, dd, J 9, 15, PhSO₂CH₂a), 3.42 (1H, dd, J 3, 15, PhSO₂CH₂b), 3.14 (1H, d,

J 4, OH), 0.88 (9H, s, Si(CH₃)₃), 0.05 (6H, s, Si(CH₃)₂); δ_C (100 MHz; CDCl₃) 139.1, 134.2, 129.4, 128.1 (aryl C), 102.7, 90.0 (alkyne C), 62.1 (PhSO₂CH₂), 57.8 (CHOH), 26.0 (Si(CH₃)₃), 16.4 (Si(CH₃)₃), -4.9 Si(CH₃)₂; *m/z* (CI) 342 ((M+NH₄)⁺, 100%), 325 ((M+H)⁺, 11), 307 ((M-OH)⁺, 4), 284 (6), 267 ((M-^tBu)⁺, 4), 241 (2), 199 (2), 184 (5), 167 (13) and 152 (2) (Found: (M+NH₄)⁺, 342.1559. C₁₆H₂₈SiNO₃ requires (M+NH₄), 342.1559); (Found: C, 59.1; H, 7.5. C₁₆H₂₄O₃SiS requires C, 59.2; H, 7.5%).

3-Acetoxy-1-*t*-Butyldimethylsilyl-4-phenylsulfonyl-but-1-yne 7.

Method 1. Methyl lithium /lithium bromide complex (100 cm³ of a 1.5 M solution in ether, 0.15 mol) was added through a dropping funnel to a solution of the phenyl methyl sulfone (23.5 g, 0.15 mol) in THF (200 cm³) at 0 °C. After twenty minutes the solution was cooled to -78 °C and a solution of TBDMS-propynal (16.9 g, 0.1 mol) in THF (20 cm³) was added. After forty-five minutes acetic anhydride (20 cm³, 0.22 mol) was added and the reaction was allowed to warm to room temperature. The reaction was quenched with water (50 cm³) and then neutralised with a saturated aqueous solution of sodium bicarbonate. The phases were separated and the aqueous layer was extracted with ether (3 x 150 cm³). The combined organic phases were washed with brine (30 cm³), dried over magnesium sulphate and evaporated. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the acetate (7), which was recrystallised from hexane to yield a highly crystalline white solid (18 g, 49%), m.p. 71-72°C; *R*_f (4 : 1 hexane / ethyl acetate) 0.31; ν_{max} (CHCl₃) / cm⁻¹ 2750 (m), 2175 (w), 1750 (vs) 1370 (m), 1330 (s), 1310 (s), 1140 (s); δ_H (250 MHz; CDCl₃) (CDCl₃) 7.89 (2H, d, *J* 8, ArH), 7.67-7.54 (3H, m, ArH), 5.76 (1H, dd, *J* 9, 3, CHOAc), 3.71 (1H, ddd, *J* 15, 9, 1, PhSO₂CH₂a), 3.49 (1H, dd, *J* 15, 3 Hz, PhSO₂CH₂b), 1.82 (3H, s, CH₃CO₂), 0.87 (9H, s, Si(CH₃)₃), 0.04 (6H, s, Si(CH₃)₂); δ_C (100 MHz; CDCl₃) 168.8 (MeCO₂), 139.3, 134.0, 129.3, 128.2 (aryl C), 99.5, 91.1 (alkyne C), 59.5 (PhSO₂CH₂), 58.5 (CHOAc), 25.9 (Si(CH₃)₃), 20.5 (CH₃CO₂), 16.4 (Si(CH₃)₃), -5.0 Si(CH₃)₂; *m/z* (CI) 384 ((M+NH₄)⁺, 56%), 324 (100), 307 (4), 291 (5), 266 (2), 223 (3) and 199 (2) (Found: (M+NH₄)⁺, 384.1665. C₁₈H₃₀SiNO₄ requires (M+NH₄), 384.1665); (Found: C, 59.1; H, 7.3. C₁₈H₂₆O₄SiS requires C, 59.0; H, 7.2%).

Method 2. Triethylamine (11 cm³, 79 mmol), 4,4-dimethylaminopyridine (0.65 g, 5.3 mmol) and acetic anhydride (7.5 cm³, 79 mmol) were added to a solution of the sulfone alcohol 6 (17.11 g, 53 mmol) in THF (250 cm³) at 0 °C. The mixture was stirred at room temperature for four hours. The reaction was quenched with 2M HCl (150 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (40 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the acetate 7 as a white solid which was recrystallised from hexane to yield a highly crystalline white solid (18.37 g, 95%), which was identical in all respects to the material produced by the two-step route.

1-*t*-Butyldimethylsilyl-4-phenylsulfonyl-but-3-(*E*)-en-1-yne 8.

Method 1. Triethylamine (82 cm³, 0.59 mol) was added to a solution to the acetoxy sulfone 7 (10.8 g, 29.5 mmol) in dry THF (250 cm³) and the reaction was heated at reflux for eight hours. The cooled reaction mixture was poured into 2M HCl (500 cm³), the phases were separated and the aqueous layer was extracted with ether

(3 x 250 cm³). The combined organic phases were washed with brine (50 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the enyne sulfone **8**, which was recrystallised from hexane to give a highly crystalline white solid (8.47 g, 94%), m.p. 89-91°C; *R_f* (4 : 1 hexane / ethyl acetate) 0.51; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 2930 (m), 2860 (m), 1590 (m), 1320 (s), 1150 (s), 1070 (s); δ_{H} (250 MHz; CDCl₃) 7.90-7.86 (2H, m, ArH), 7.62-7.52 (3H, m, ArH), 6.78 (1H, d, *J* 15, alkene CH_a), 6.69 (1H, d, *J* 15, alkene CH_b), 0.92 (9H, s, SiC(CH₃)₃), 0.12 (6H, s, Si(CH₃)₂); δ_{C} (100 MHz; CDCl₃) 139.6 (aryl C and alkene C), 133.8, 129.4, 127.9 (aryl C), 123.1 (alkene C), 107.0, 99.0 (alkyne C), 26.0 (SiC(CH₃)₃), 16.6 (SiC(CH₃)₃), -5.0 (Si(CH₃)₂). *m/z* (CI) 324 ((M+NH₄)⁺, 100%), 307 ((M+H)⁺, 2), 291 ((M-Me)⁺, 3) and 266 (5) (Found: (M+NH₄)⁺, 324.1454. C₁₆H₂₆SiSNO₂ requires (M+NH₄), 324.1454); (Found: C, 62.9; H, 7.2. C₁₆H₂₂O₂SiS requires C, 62.7; H, 7.2%).

Method 2. DBU (1.8 cm³, 12 mmol) was added to a solution of the acetoxy sulfone **7** (4.0 g, 10.9 mmol) in THF (30 cm³) at 0 °C. The reaction was stirred at this temperature for five minutes. The reaction was quenched with 2M HCl (50 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 50 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel using 4 : 1 hexane / ethyl acetate as eluent to yield the enyne sulfone **8**, which was recrystallised from hexane to yield a highly crystalline white solid (3.32 g, 99%), which was identical in all respects to the material produced from the triethylamine elimination.

1-Butyldimethylsilyl-5-phenyl-4-phenylsulfonyl-pent-3-(E)-en-1-yn-5-ol 11.

LDA was prepared by the addition of butyl lithium (2.50 cm³ of a 1.45 M solution in hexanes, 3.6 mmol) to a solution of diisopropylamine (0.50 cm³, 3.6 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (1.041 g, 3.40 mmol) in dry ether (100 cm³) at -95 °C. After five minutes freshly distilled benzaldehyde (0.18 cm³, 1.77 mmol) was added and the reaction was stirred at -95 °C for one hour, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 50 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **11** as a white solid (762 mg, 92%), m.p. 82-83 °C; *R_f* (4 : 1 hexane / ethyl acetate) 0.45; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3520 (m), 2940 (s), 2860 (s), 1590 (m), 1320 (s), 1140 (s), 1100 (s); δ_{H} (250 MHz; CDCl₃) 7.50-7.40 (3H, m, ArH), 7.30-7.18 (4H, m, ArH), 7.12-7.10 (3H, m, ArH), 6.98 (1H, s, alkene CH), 6.06 (1H, s, CHOH), 0.88 (9H, s, SiC(CH₃)₃), 0.11 (3H, s, Si(CH₃)), 0.10 (3H, s, Si(CH₃)); δ_{C} (100 MHz; CDCl₃) 153.5 (PhSO₂C=CH), 140.0, 139.2, 133.2, 128.8, 128.1, 127.7, 127.5, 125.5 (aryl C), 122.4 (PhSO₂C=CH), 112.4, 98.2 (acetylene C), 71.2 (CHOH), 25.9 (SiC(CH₃)₃), 16.5 (SiC(CH₃)₃), -5.1 (Si(CH₃)₂); *m/z* (CI) 430 ((M+NH₄)⁺, 100%), 412 (M⁺, 26), 395 ((M-OH)⁺, 11) and 355 ((M-tBu)⁺, 3) (Found: (M+NH₄)⁺, 430.1872. C₁₆H₂₆SiSNO₃ requires (M+NH₄), 430.1872); (Found: C, 67.1; H, 6.9. C₂₃H₂₈O₃SiS requires C, 67.0; H, 6.8%).

1'-Butyldimethylsilyl-6-methyl-4-phenylsulfonyl-hept-3-(E)-en-1-yn-5-ol 12.

LDA was prepared by the addition of butyl lithium (2.70 cm³ of a 1.45 M solution in hexanes, 3.92 mmol) to a solution of diisopropylamine (0.55 cm³, 3.93 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (1.172 g, 3.83 mmol) in dry ether (100 cm³) at -95 °C. After five minutes freshly distilled isobutyraldehyde (0.175 cm³, 1.93 mmol) was added and the reaction was stirred at -95 °C for one hour, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) was added, the phases were separated and the aqueous layer was extracted with ether (3 x 75 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **12**, which was recrystallised from hexane to give a white solid (705 mg, 97%), m.p. 74-75 °C; *R_f* (4 : 1 hexane / ethyl acetate) 0.42; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3550 (m), 2950 (s), 2880 (s), 2180 (w), 1590 (m), 1320 (s), 1140 (s), 1100 (s); δ_{H} (250 MHz; CDCl₃) 7.90-7.87 (2H, m, ArH), 7.61-7.49 (3H, m, ArH), 6.78 (1H, s, alkene CH), 4.37 (1H, d, *J* 9, CHOH), 1.62 (1H, br, OH), 1.25-1.10 (1H, m, CHMe₂), 1.01, 0.74 (1:1, 6H, d, *J* 7, CH(CH₃)₂), 0.92 (9H, s, SiC(CH₃)₃), 0.13 (6H, s, Si(CH₃)₃); δ_{C} (100 MHz; CDCl₃) 154.4 (PhSO₂C=CH), 140.4, 133.7, 129.3, 128.2 (aryl C), 121.6 (PhSO₂C=CH), 112.2, 98.5 (alkyne C), 76.6 (CHOH), 33.7 (CHMe₂), 26.0 (SiC(CH₃)₃), 19.0, 18.9 (CHMe₂), 16.6 (SiC(CH₃)₃), -5.0 (Si(CH₃)₂); *m/z* (CI) 396 ((M+NH₄)⁺, 100%), 378 (M⁺, 20), 361 ((M-OH)⁺, 70), 276 ((M-^tBu)⁺, 3), 237 (2), 199 (5), 152 (2) and 91 (1) (Found: (M+NH₄)⁺, 396.2029. C₂₀H₃₄SiNO₃ requires (M+NH₄), 396.2029); (Found: C, 63.4; H, 7.9. C₂₀H₃₀O₃SiS requires C, 63.5; H, 8.0%).

1'-Butyldimethylsilyl-4-phenylsulfonyl-undec-3-(E)-en-1-yn-5-ol 13.

Method 1. LDA was prepared by the addition of butyl lithium (2.2 cm³ of a 1.43 M solution in hexanes, 3.19 mmol) to a solution of diisopropylamine (0.45 cm³, 3.21 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (937 mg, 3.06 mmol) in dry ether (100 cm³) at -95 °C. After fifteen minutes freshly distilled n-heptanal (0.22 cm³, 1.58 mmol) was added and the reaction was stirred at -95 °C for fifteen minutes, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **13** as a white solid (485 mg, 73%), m.p. 50-51 °C; *R_f* (4 : 1 hexane / ethyl acetate) 0.35; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3550 (brw), 2930 (m), 2860 (m), 1590 (w), 1310 (m), 1150 (m), 1090 (m); δ_{H} (250 MHz; CDCl₃) 7.87 (2H, dd, *J* 2, 7, ArH_O), 7.64-7.49 (3H, m, ArH_{m+p}), 6.77 (1H, s, alkene CH), 4.66 (1H, dd, *J* 9, 5, CHOH), 2.57 (1H, brs, OH), 1.84-1.62 (2H, m, CH₂CHOH), 1.38-1.18 (8H, m, 4xCH₂), 0.93 (9H, s, SiC(CH₃)₃), 0.84 (3H, t, *J* 6, CH₃), 0.11 (6H, s, Si(CH₃)₃); δ_{C} (100 MHz; CDCl₃) 155.2 (PhSO₂C=CH), 140.2, 133.6, 129.2, 128.2 (aryl C), 120.1 (PhSO₂C=CH), 112.3, 98.3 (alkyne C), 70.8 (CHOH), 36.8, 31.6, 28.8 (3xCH₂), 26.0 (SiC(CH₃)₃), 25.7, 22.5 (2xCH₂), 16.6 (SiC(CH₃)₃), 14.0 (CH₃), -5.0 (Si(CH₃)₂); *m/z* (CI) 438 ((M+NH₄)⁺, 100%), 420 (M⁺, 11), 403 ((M-OH)⁺, 26), 324 (2), 281 (5), 261 (25), 246 (5) 132 (2) and 91

(5) (Found: $(M+NH_4)^+$, 438.2498. $C_{23}H_{40}SiSNO_3$ requires $(M+NH_4)$, 438.2498); (Found: C, 65.9; H, 8.7. $C_{23}H_{36}SiSO_3$ requires C, 65.7; H, 8.6%).

Method 2. LDA was prepared by the addition of butyl lithium (4.7 cm³ of a 1.45 M solution in hexanes, 6.82 mmol) to a solution of diisopropylamine (0.95 cm³, 6.78 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (2.023 g, 6.61 mmol) in dry ether (100 cm³) at -95 °C. After fifteen minutes magnesium dibromide (8 cm³ of a 1 M solution in 1 : 4 ether / benzene, 8 mmol) was added. The reaction was warmed to -78 °C for five minutes and then recooled to -95 °C. Freshly distilled n-heptanal (0.50 cm³, 3.58 mmol) was added and the reaction was stirred at -95 °C for fifteen minutes, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **13** as a white solid (1.423 g, 95%), which was identical in all respects to the material produced above.

1-Hydroxy-1-(5'-*t*-butyldimethylsilyl-1'-hydroxy-2'-phenylsulfonyl-pent-2'-(*E*)-en-4'-ynyl)-cyclohexane **14**

LDA was prepared by the addition of butyl lithium (2.25 cm³ of a 1.43 M solution in hexanes, 3.22 mmol) to a solution of diisopropylamine (0.45 cm³, 3.21 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (964 mg, 3.15 mmol) in dry ether (100 cm³) at -95 °C. After five minutes cyclohexanone (0.17 cm³, 1.64 mmol) was added and the reaction was stirred at -95 °C for fifteen minutes, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 50 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **14** as a white solid (609 mg, 92%), m.p. 56-57 °C; R_f (4 : 1 hexane / ethyl acetate) 0.44; ν_{max} (CHCl₃) / cm⁻¹ 3560 (m), 2940 (s), 2860 (s), 1580 (m), 1300 (s), 1140 (s), 1110 (s); d_H (250 MHz; CDCl₃) 7.82 (2H, d, J 8, ArH_O), 7.61-7.47 (3H, m, ArH_{m+p}), 7.06 (1H, s, alkene CH), 2.45-2.33 (2H, m, 2xCH_aH_bCOH), 1.64-1.48 (7H, m, 2xCH₂, 2xCH_aH_bCOH, CH_aH_bCH₂CH₂COH), 1.24-1.13 (1H, m, CH_aH_bCH₂CH₂COH), 0.96 (9H, s, SiC(CH₃)₃), 0.18 (6H, s, Si(CH₃)); d_C (100 MHz; CDCl₃) 158.6 (PhSO₂C=CH), 141.3, 133.0, 128.9, 127.6 (aryl C), 119.1 (PhSO₂C=CH), 113.5, 99.5 (alkyne C), 74.4 (COH), 35.8 (CH₂), 26.0 (SiC(CH₃)₃), 24.7, 21.1 (CH₂), 16.7 (SiC(CH₃)₃), -5.0 (Si(CH₃)₂); m/z (CI) 422 ((M+NH₄)⁺, 48%), 404 (M⁺, 100), 387 ((M-OH)⁺, 22), 324 (5), 282 (4), 265 (5) and 247 (22) (Found: $(M+NH_4)^+$, 422.2185. $C_{22}H_{36}SiSNO_3$ requires $(M+NH_4)$, 422.2185); (Found: C, 65.1; H, 7.9. $C_{22}H_{32}SiSO_3$ requires C, 65.3; H, 8.0%).

2-(5'-*t*-butyldimethylsilyl-1'-hydroxy-2'-phenylsulfonyl-pent-2'-(*E*)-en-4'-ynyl)-6,6-dimethyl bicyclo[3.3.1]-hept-2-ene **15**

LDA was prepared by the addition of butyl lithium (2.2 cm³ of a 1.45 M solution in hexanes, 3.15 mmol) to a solution of diisopropylamine (0.45 cm³, 3.21 mmol) in dry ether (15 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (925 mg, 3.02 mmol) in dry ether (100 cm³)

at -95 °C. After fifteen minutes a solution of (1*R*)-(-)-myrtenal **9** (230 cm³, 1.53 mmol) in ether (50 cm³) was added and the reaction was stirred at -95 °C for fifteen minutes, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by rotary chromatography (Chromatotron®) on silica gel, using 6 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **15**, which was recrystallised from hexane to give a white solid (591 mg, 85%), which was a 1 : 1 mixture of diastereomers, m.p. 102-103°C; *R*_f (4 : 1 hexane / ethyl acetate) 0.49; ν_{max} (CHCl₃) / cm⁻¹ 3560 (brm), 2860 (m), 1740 (m), 1590 (m), 1310 (s), 1140 (s), 1090 (s); δ_{H} (250 MHz; CDCl₃) 7.88-7.83 (2H, ArH_o), 7.62-7.46 (3H, m, ArH_{m+p}), 6.90, 6.89 (1H, s, side chain alkene CH), 5.51, 5.44 (1H, brd, *J* 1, ring alkene CH), 5.04, 4.97 (1H, brd, *J* 2, CHOH), 2.98 (1H, brs, OH), 2.37-1.94 (6H, m, 2xCH and 2xCH₂), 1.23, 1.19 (3H, s, CH₃), 0.91 (9H, s, SiC(CH₃)₃), 0.77, 0.75 (3H, s, CH₃), 0.11 (6H, s, Si(CH₃)₃); δ_{C} (100 MHz; CDCl₃) 153.6, 152.4 (PhSO₂C=CH), 145.3, 144.8 (ring C=C-CHOH), 140.1, 140.0, 133.7, 133.6, 129.2, 129.1, 128.4, 128.3 (aryl C), 122.0, 121.1, 120.9, 119.8 (ring C=CH, PhSO₂C=CH), 112.9, 112.5, 98.8, 98.6 (alkyne C), 72.3, 72.1 (CHOH), 43.1, 42.5, 40.5 (2xring CH), 38.2, 38.0 (CMe₂), 31.4, 31.2, 31.1, 30.5 (2xCH₂), 26.1, 26.0 (CH₃), 26.0 (SiC(CH₃)₃), 21.2, 21.1 (CH₃), 16.6 (SiC(CH₃)₃), 14.0 (CH₃), -5.0 (Si(CH₃)₂); *m/z* (CI) 474 ((M+NH₄)⁺, 67%), 456 (M⁺, 18), 439 ((M-OH)⁺, 100), 397 (3), 383 (2), 299 (7), 160 (13) and 132 (4) (Found: (M+NH₄)⁺, 474.2498. C₂₆H₄₀SiSNO₃ requires (M+NH₄), 474.2498); (Found: C, 68.4; H, 8.0. C₂₆H₃₆SiSO₃ requires C, 68.4; H, 8.0%).

4-(5'-*t*-Butyldimethylsilyl-1'-hydroxy-2'-phenylsulfonyl-pent-2'-(*E*)-en-4'-ynyl)-1,2-methylene-dioxabenzene **16**

LDA was prepared by the addition of butyl lithium (2.40 cm³ of a 1.43 M solution in hexanes, 3.43 mmol) to a solution of diisopropylamine (0.48 cm³, 3.42 mmol) in dry ether (20 cm³) at 0 °C. After 10 minutes the LDA solution was added dropwise to a solution of the enyne sulfone **8** (1.00g, 3.27 mmol) in dry ether (100 cm³) at -95 °C. After five minutes heliotropin **10** (250 mg, 1.67 mmol) was added and the reaction was stirred at -95 °C for thirty minutes, then allowed to warm to room temperature. Saturated aqueous ammonium chloride solution (50 cm³) and then water (10 cm³) were added, the phases were separated and the aqueous layer was extracted with ether (3 x 50 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by flash column chromatography on silica gel, using 5 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **16** as a very thick oil (730 mg, 96%), *R*_f (4 : 1 hexane / ethyl acetate) 0.32; ν_{max} (CHCl₃) / cm⁻¹ 3520 (brm), 2940 (m), 2900 (m), 2870 (s), 1594 (m), 1310 (s), 1145 (s), 1095 (s); δ_{H} (250 MHz; CDCl₃) 7.55-7.28 (5H, m, SO₂C₆H₅), 6.95 (1H, s, alkene CH), 6.70 (1H, ddd, *J* 8, 2, 1, H₅), 6.59 (1H, d, *J* 1, H₃), 6.54 (1H, d, *J* 8, H₆), 5.94 (1H, brs, CHOH), 5.82, 5.81 (2H, d, *J* 8, CH₂O₂), 3.77 (1H, br, OH) 0.87 (9H, s, SiC(CH₃)₃), 0.10 (6H, s, Si(CH₃)₃); δ_{C} (100 MHz; CDCl₃) 153.5 (PhSO₂C=CH), 147.5, 147.0 (ArC-O), 140.1 (ArC-SO₂), 133.4 (ArC-CHOH), 133.2, 128.8, 127.8 (PhSO₂ C), 122.1 (PhSO₂C=CH), 119.1 (aryl C), 112.5 (alkyne C), 107.9, 106.4 (aryl C), 101.0 (CH₂O₂), 98.2 (alkyne C), 71.0 (CHOH), 26.0 (SiC(CH₃)₃), 16.6 (SiC(CH₃)₃), -5.1 (Si(CH₃)₂); *m/z* (CI) 474 ((M+NH₄)⁺, 28%), 456 ((M-Me)⁺, 12), 439 ((M-OH)⁺, 100) and 299 (2) (Found: M⁺, 456.1427. C₂₄H₂₈SiSO₅ requires M, 456.1427).

1-(4-Butyldimethylsilyl-5-phenyl-pent-3-(Z)-en-1-yn-5-ol 17.

Sodium dithionite (209 mg, 1.2 mmol) and sodium bicarbonate (303 mg, 3.6 mmol) were added to a solution of the sulfone **11** (124 mg, 0.3 mmol) in DMF / THF / water (1:1:1, 60 cm³) and stirred at 50 °C overnight. The reaction was quenched with aqueous ammonium chloride solution (30 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 75 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by preparative thin layer chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield some undesulfonylated starting material (25 mg, 20%) and the alcohol **17** as a white solid (49 mg, 60%), m.p. 73-74 °C; *R_f* (4 : 1 hexane / ethyl acetate) 0.53; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3600 (m), 2940 (s), 2900 (m), 2870 (s), 2170 (m), 1610 (w), 1420 (m); δ_{H} (250 MHz; CDCl₃) 7.45-7.25 (5H, m, ArH), 6.11 (1H, dd, *J* 11, 8, CH(OH)CH=CH), 5.83 (1H, brd, *J* 8, CHOH), 5.62 (1H, dd, *J* 11, 1, CH(OH)CH=CH), 0.97 (9H, s, SiC(CH₃)₃), 0.16 (3H, s, Si(CH₃)₂); δ_{C} (100 MHz; CDCl₃) 145.4 (CH(OH)CH=CH), 142.4, 128.6, 127.7, 125.8 (aryl C), 109.9 (CH(OH)CH=CH), 101.5, 99.4 (alkyne C), 72.1 (CHOH), 26.1 (SiC(CH₃)₃), 16.6 (SiC(CH₃)₃), -4.7 (Si(CH₃)₂); *m/z* (CI) 273 ((M+H)⁺, 3%), 255 ((M-OH)⁺, 100), 232 (2) and 215 (3) (Found: (M-OH)⁺, 255.1569. C₁₇H₂₃Si requires (M-OH), 255.1569); (Found: C, 75.0; H, 9.0. C₁₇H₂₄OSi requires C, 74.9; H, 8.9%).

1-(4-Butyldimethylsilyl-6-methyl-hept-3-(Z)-en-1-yn-5-ol 18.

Sodium dithionite (570 mg, 3.27 mmol) and sodium bicarbonate (555 mg, 6.6 mmol) were added to a solution of the sulfone **12** (124 mg, 0.3 mmol) in DMF / THF / water (1:1:1, 60 cm³) and stirred at 50 °C; after two hours there was no sign of reaction (by TLC) and so a further similar amount of sodium dithionite and sodium bicarbonate were added and the reaction was heated to 80 °C. The reaction was complete (by TLC) after one hour. The reaction was quenched with aqueous ammonium chloride solution (30 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 75 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by preparative thin layer chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **18** as a light yellow oil (72 mg, 55%), which was a 15:1 mixture of *cis*- and *trans*-isomers (by ¹H NMR). Data for **18**: *R_f* (4 : 1 hexane / ethyl acetate) 0.56; $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3610 (m), 2930 (s), 2890 (s), 2860 (s), 2160 (m), 1940 (w), 1600 (w), 1365 (m), 985 (m); δ_{H} (250 MHz; CDCl₃) 5.93 (1H, dd, *J* 11, 8, CH(OH)CH=CH), 5.60 (1H, dd, *J* 11, 1, CH(OH)CH=CH), 4.42 (1H, brdd, *J* 8, 6, CHOH), 1.87-1.70 (1H, m, CHMe₂), 1.96, 0.90 (1:1, 6H, d, *J* 7, CH(CH₃)₂), 0.94 (9H, s, SiC(CH₃)₃), 0.11 (6H, s, Si(CH₃)₂); δ_{C} (100 MHz; CDCl₃) 145.1 (CH(OH)CH=CH), 110.7 (CH(OH)CH=CH), 101.8, 98.7 (alkyne C), 75.1 (CHOH), 33.9 (CHMe₂), 26.1 (SiC(CH₃)₃), 18.0, 17.9 (CHMe₂), 16.6 (SiC(CH₃)₃), -4.7 (Si(CH₃)₂); *m/z* (CI) 256 ((M+NH₄)⁺, 10%), 238 (M⁺, 80), 221 ((M-OH)⁺, 100), 198 (7) 181 ((M-^tBu)⁺, 10), 163 (9) and 91 (30) (Found: (M+NH₄)⁺, 256.2097. C₁₄H₃₀SiNO requires (M+NH₄), 256.2097).

1-(4-Butyldimethylsilyl-undec-3-(Z)-en-1-yn-5-ol 19.

Sodium dithionite (4 x 95 mg, 1.85 mmol) was added in four portions to a solution of the sulfone **13** (130 mg, 0.309 mmol) and sodium bicarbonate (312 mg, 3.71 mmol) in THF / water (1:1, 100 cm³) and stirred at 80 °C for four hours, adding each portion at hourly intervals. The reaction was quenched with aqueous ammonium

chloride solution (50 cm³), the phases were separated and the aqueous layer was extracted with ether (3 x 100 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by preparative thin layer chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the alcohol **19** as a light yellow oil (38 mg, 44%), which was a 54:1 mixture of *cis* and *trans* isomers (by ¹H NMR). Data for **19**: $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3500 (brm), 2860 (s), 2160 (s), 1950 (m), 1660 (m), 990 (m); δ_{H} (250 MHz; CDCl₃) 5.92 (1H, dd, *J* 11, 8, CH(OH)CH), 5.54 (1H, dd, *J* 11, 1, CHCCSi), 4.70-4.62 (1H, m, CHOH), 1.84 (1H, brs, OH), 1.66-1.17 (10H, m, 5 x CH₂), 0.94 (9H, s, SiC(CH₃)₃), 0.92-0.84 (3H, m, CH₃), 0.11 (6H, s, Si(CH₃)₃); δ_{C} (100 MHz; CDCl₃) 146.9 (CH(OH)CH=CH), 109.7 (CH(OH)C=CH), 101.5, 98.7 (alkyne C), 70.3 (CHOH), 36.6, 31.8, 29.1 (3xCH₂), 26.1 (SiC(CH₃)₃), 25.1, 22.5 (2xCH₂), 16.6 (SiC(CH₃)₃), 14.1 (CH₃), -4.7 (Si(CH₃)₂); *m/z* (CI) 298 ((M+NH₄)⁺, 3%), 280 ((M+NH₄-H₂O)⁺, 73), 263 ((M-OH)⁺, 100), 240 (12), 223 (25), 147 (32), 132 (60) and 91 (42) (Found: (M+NH₄-H₂O)⁺, 280.2460. C₁₇H₃₄SiN requires (M+NH₄-H₂O), 280.2460).

5-phenyl-pent-3-(*Z*)-en-1-yn-5-ol **20**.

Tetra-*n*-butyl ammonium fluoride (0.7 cm³ of a 1.0 M solution in THF, 0.7 mmol) was added dropwise to a solution of the silyl enyne **17** (152 mg, 0.55 mmol) in THF (20 cm³) and stirred for five minutes at room temperature. A saturated aqueous solution of sodium bicarbonate (20 cm³) was added, the phases were separated and the aqueous layer was extracted with ether (3 x 50 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulphate and the solvents were removed *in vacuo*. The product was purified by preparative thin layer chromatography on silica gel, using 4 : 1 hexane / ethyl acetate as eluent, to yield the terminal enyne **20** as a yellow oil (784 mg, 90%), $\nu_{\max}$ (CHCl₃) / cm⁻¹ 3600 (m), 2420 (brw), 3300 (s), 2880 (m), 2110 (m), 1605 (w), 1010 (m); δ_{H} (250 MHz; CDCl₃) 7.46-7.25 (5H, m, ArH), 6.16 (1H, ddd, *J* 11, 9, 1, CH(OH)CH=CH), 5.81 (1H, brd, *J* 9, CHOH), 5.59 (1H, ddd, *J* 11, 2, 1, CH(OH)CH=CH), 3.22 (1H, dd, *J* 1, 2, acetylene H), 2.38 (1H, brs, OH); δ_{C} (100 MHz; CDCl₃) 146.2 (CH(OH)CH=CH), 142.2, 128.6, 127.8, 125.8 (aryl C), 108.9 (CH(OH)CH=CH), 83.2 (alkyne C), 79.5 (acetylene CH), 71.8 (CHOH); *m/z* (CI) 158 ((M+NH₄-H₂O)⁺, 29), 141 ((M-OH), 100), 130 (6), 115 (2) and 105 (5) (Found: (M+NH₄-H₂O), 158.0970. C₁₁H₁₂N requires (M+NH₄-H₂O), 158.0970).

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