# Total synthesis of (±)-furoscrobiculin B

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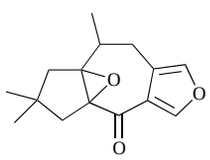
1 PERKIN

**Total synthesis of (±)-furoscrobiculin B, a lactarane sesquiterpene isolated from basidiomycetes of mushrooms, has been achieved *via* an improved synthetic route of our previous work based on a Furan Ring Transfer (FRT) reaction and base-catalysed pinacol-type rearrangement.**

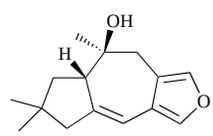


## Introduction

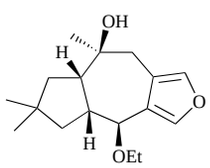
Furoscrobiculins are a series of lactarane sesquiterpenes that were isolated from basidiomycetes of mushrooms including *Lactarius* and *Russula*.[1] Sesquiterpenes of *Lactarius* constitute those mushrooms' chemical defence against various predators such as bacteria, fungi, animals and insects,[2] and also show antifeedant properties against the storage pests *Tribolium confusum* Duv., *Trogoderma granarium* Ev. and *Sitophilus granarius* L.[3] These compounds have a complex hydroazulene framework with a 3,4-disubstituted furan ring. Owing to their unique structure, only a limited number of synthetic studies on the lactarane skeleton have been reported,[4] in contrast to illudane and marasmane sesquiterpenes that are metabolites of mushrooms and related basidiomycetes.



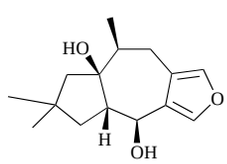
Furoscrobiculin A



Furoscrobiculin B **1**



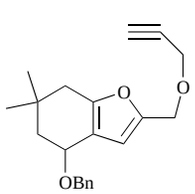
Furoscrobiculin C



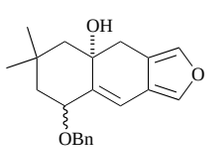
Furoscrobiculin D

Furoscrobiculins

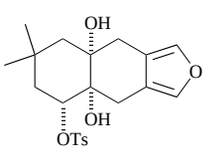
The first total synthesis of furoscrobiculin B **1** in racemic form was reported by us,[4d] in which a novel strategy was performed to construct the lactarane skeleton by using the Furan Ring Transfer (FRT) reaction[5] of intermediates **A** into **B** and base-catalysed pinacol-type rearrangement of glycol **C** into ketone **D**. However, in this synthetic route, there were some disadvantages regarding the chemical yields and the number of steps. Herein we report the details of a new total synthetic route to racemate (±)-**1** *via* prop-2-ynyl ether **4** instead of intermediate **A** using our strategy for the construction of the azuleno[5,6-*c*]furan ring system.[4d]



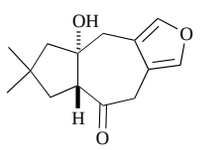
**A**



**B**



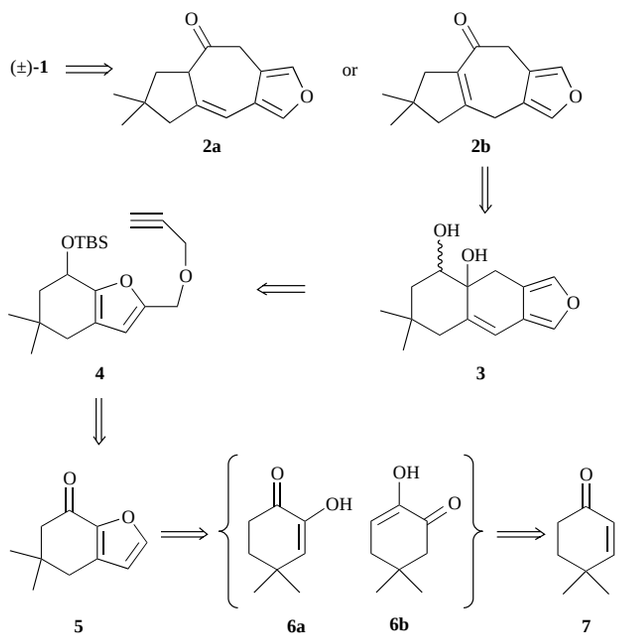
**C**



**D**

Synthetic intermediates of our previous route[4d]

Retrosynthetic analysis is outlined in Scheme 1. A key step for the synthesis of (±)-furoscrobiculin B **1** is the easy formation of a lactarane skeleton **2a** or **2b** from naphtho[2,3-*c*]furandiol **3** with appropriate stereochemistry *via* a pinacol-type rearrangement. Compound **3** would be constructed by the FRT reaction from prop-2-ynyl ether **4**, which would be provided from benzofuran derivative **5**. Compound **5** could be obtained from 1,2-diketones **6a**,**b** by modified Feist–Beniary furanation. Therefore we chose commercially available 4,4-dimethylcyclohex-2-en-1-one **7** as the starting material to prepare compounds **6a**,**b**.



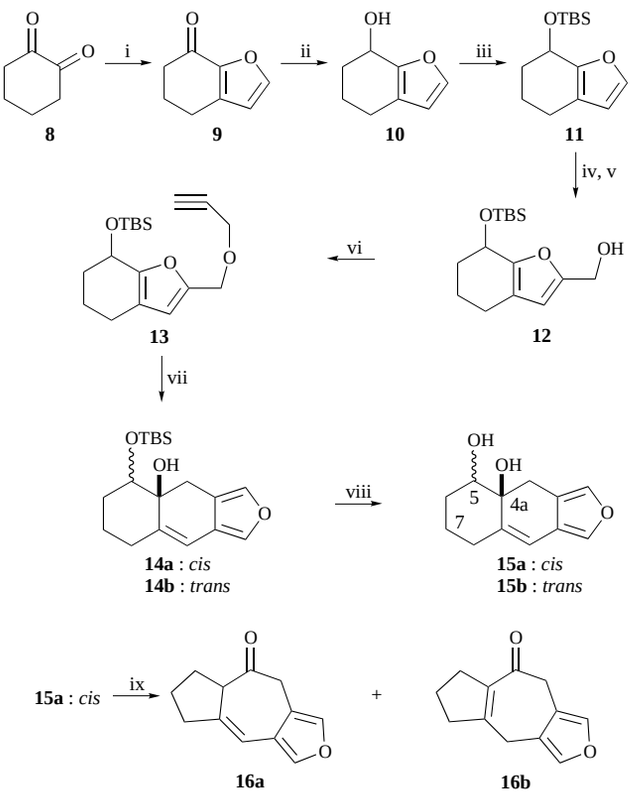
**Scheme 1** Retrosynthetic analysis of (±)-**1**

## Results and discussion

### Model study

As a model study for the construction of the azuleno[5,6-*c*]-furan ring system, we employed benzofuran derivative **9** as the starting material, which was easily prepared from cyclohexane-1,2-dione **8** by modified Feist–Beniary furanation.[6] Compound **9** was converted into *tert*-butyldimethylsilyl ether **11** in 64% yield by reduction with $LiAlH_4$ and subsequent protection of the resulting hydroxy group in intermediate **10**. The prop-2-ynyl ether **13**, which was required for the FRT reaction, was prepared from compound **11** by a three-step sequence in 69% yield [i,

formylation of the C(2)-position; ii, reduction of the formyl group to the primary alcohol **12**; iii, propynylation of alcohol **12** into ether **13**]. Treatment of compound **13** with Bu$^t$OK in Bu$^t$OH at 80 °C resulted in a smooth FRT reaction to afford a separable diastereomeric mixture of naphtho[2,3-*c*]furans **14a** and **14b** in the ratio 1:2 in 93% yield. Removal of the protecting group of compounds **14a**,**b** gave the diols **15a** and **15b** in 85 and 90% yield, respectively. Stereochemistry of diols **15a**,**b** was confirmed by $^1$H NMR and nuclear Overhauser effect (NOESY) spectra as depicted in Scheme 2. According to the




**Scheme 2** *Reagents and conditions* (*and yields*): i, $ClCH_2CHO$, aq. $NaHCO_3$, room temp.; aq. $H_2SO_4$ (42%); ii, $LiAlH_4$, THF, room temp. (67%); iii, TBSCl, imidazole, DMF, room temp. (96%); iv, BuLi, THF, 0 °C; DMF, −78 °C; v, $NaBH_4$, MeOH, room temp. (78% for 2 steps); vi, prop-2-ynyl bromide, $Bu_4NHSO_4$, aq. NaOH, $Et_2O$, room temp. (89%); vii, Bu$^t$OK, Bu$^t$OH, 80 °C (93%) (**14a**:**14b** = 1:2); viii, TBAF, THF, room temp., **15a** (85%), **15b** (90%); ix, TsCl, Py, room temp. (68%) (**16a**:**16b** = 5:2)

Dreiding stereomodel and MM2 calculations, the skeleton of compounds **15a**,**b** was considered to have a conformationally rigid structure, in which the angular C(4a)-hydroxy group has an axial orientation (Fig. 1). In the $^1$H NMR spectrum of *cis*-diol **15a**, C(5)-H was observed at $\delta_H$ 3.32 (dd, *J* 5.8 and 10.1 Hz). These coupling constants suggest that the C(5)-hydroxy group has an equatorial orientation. Furthermore, an NOE was observed between the C(5)-axial proton and the C(7)-axial proton in the NOESY spectrum. On the other hand, in the spectra of compound **15b**, C(5)-H was observed at $\delta_H$ 3.78 (dd, *J* 2.6 and 2.6 Hz), and no NOE between C(5)-H and C(7)-H was observed, which suggests that the C(5)-hydroxy group of compound **15b** has an axial orientation.

These stereochemical assignments were also supported by the next pinacol rearrangement. The stereochemistry of the C(5)-hydroxy group of *cis*-diol **15a** with an equatorial orientation was considered to be suitable because of the coplanarity for the desired pinacol rearrangement.[7] In fact, treatment of compound **15a** with toluene-*p*-sulfonyl chloride in pyridine at room temperature gave the azuleno[5,6-*c*]furans **16a** and **16b** in 48 and 20% yield, respectively. On the other hand, the same reaction of *trans*-diol **15b** gave a complex mixture.

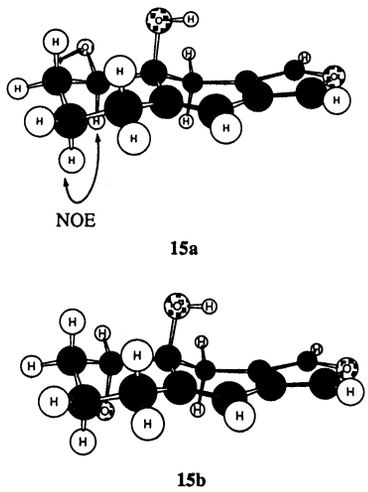
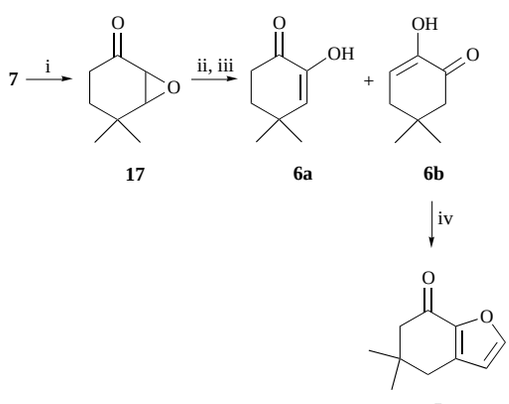



**Fig. 1** Relative configuration of naphthofuran diols **15a** and **15b**

**Total synthesis of (±)-furoscrobiculin B**

The above success of the model study prompted us to synthesize (±)-furoscrobiculin B according to the aforementioned retrosynthetic analysis. First, we prepared compound **5** from 1,2-diketones **6a**,**b** *via* modified Feist–Beniary furanation. That is to say, after conversion of 4,4-dimethylcyclohex-2-en-1-one **7** into the epoxide **17**, epoxide-ring opening under basic conditions followed by hydrolysis of the enol ether gave an inseparable 1:1 mixture of compounds **6a**,**b**.[8] Furanation of a mixture of compounds **6a**,**b** gave a single product **5** in 68% yield (Scheme 3).




**Scheme 3** *Reagents and conditions* (*and yields*): i, aq. $H_2O_2$, aq. NaOH, MeOH, room temp. (86%); ii, aq. NaOH, MeOH, reflux (74%); iii, aq. $H_2SO_4$, THF, reflux (89%); iv, $ClCH_2CHO$, aq. $NaHCO_3$, MeOH, room temp.; aq. $H_2SO_4$, room temp. (68%)

Next, preparation of the prop-2-ynyl ether **4** from compound **5** was accomplished by a similar sequence to that described in the model study: i, reduction of the ketone of **5**; ii, protection of the hydroxy group of alcohol **18**; iii, formylation of compound **19** followed by reduction of the aldehyde; iv, propynylation of the primary alcohol **20**. FRT reaction of compound **4** (Bu$^t$OK in Bu$^t$OH at 80 °C) gave separable diastereomers **21a** (*cis*, 11% yield) and **21b** (*trans*, 77% yield). The stereochemistry of compounds **21a**,**b** was determined by $^1$H NMR and NOESY spectra after conversion into the corresponding diols **3a** (*cis*) and **3b** (*trans*), respectively (Scheme 4). In the $^1$H NMR and NOESY spectra of *cis*-diol **3a**, C(5)-H was observed at $\delta_H$ 3.68 (dd, *J* 6.9, 9.9 Hz), and an NOE was observed between one of the *gem*-methyl groups and C(5)-H. The NMR spectroscopic data were similar to those of model compound **15a**. Taking into consideration the change in the *cis*-*trans* ratio in compounds **14** and **21**, the diastereoselectivity of this FRT reaction was believed to be affected by the steric inter-

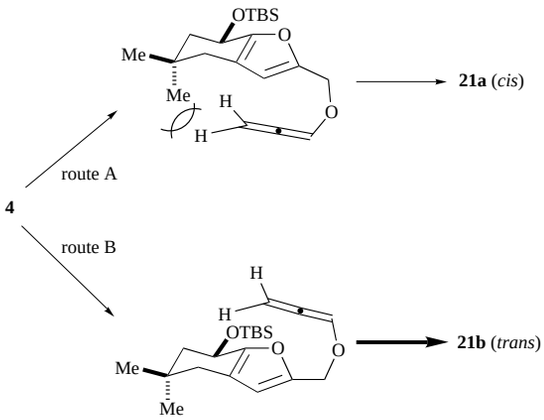
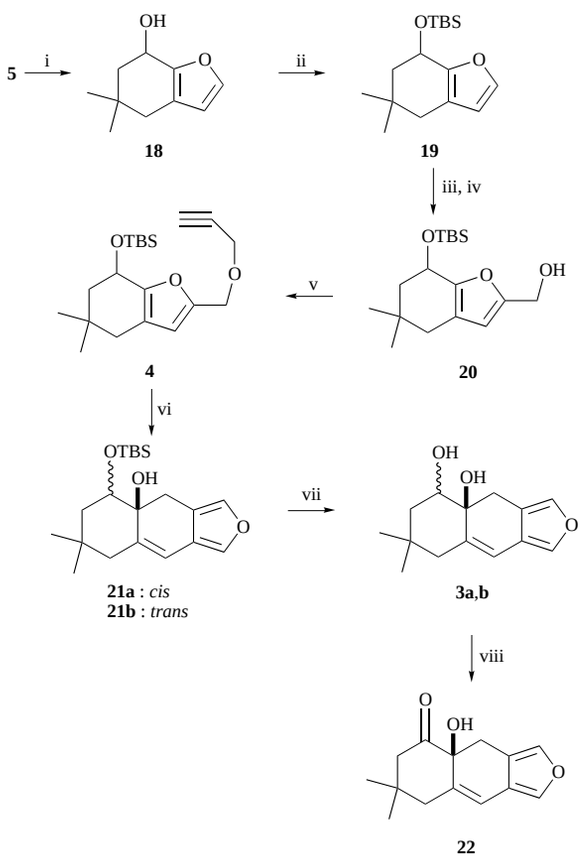



**Fig. 2** Diastereoselectivity of FRT reaction

action between the terminal hydrogen of the allene and the C(5)-*gem*-methyl group in the reaction intermediate (Fig. 2, route A). Sterically favoured β-face approach of the allenyl ether (route B) might lead to *trans*-product **21b**.




**Scheme 4** *Reagents and conditions* (*and yields*): i, $NaBH_4$, EtOH, room temp. (93%); ii, TBSCl, imidazole, DMF, room temp. (92%); iii, BuLi, THF, 0 °C; DMF, −78 °C; iv, $NaBH_4$, EtOH, room temp. (87% for 2 steps); v, prop-2-ynyl bromide, $Bu_4NHSO_4$, aq. NaOH, $Et_2O$ (92%); vi, $Bu^tOK$, $Bu^tOH$, 80 °C (88%) (**21a**:**21b** = 1:7); vii, TBAF, THF, **3a** (76%), **3b** (quant.); viii, Dess–Martin periodinane, $CH_2Cl_2$, room temp. (78% from **3b**)

For preparation of the sterically desired compound **3a** from its diastereomer **3b**, we at first tried epimerization of the C(5)-hydroxy group *via* the corresponding tosyl ester, which did not, however, afford satisfactory results owing to the instability of the tosyl derivative of alcohol **3b**. Next, we studied diastereoselective reduction of α-hydroxy ketone **22**, which was obtained from diol **3b** by the Dess–Martin periodinane[9] oxidation in 78% yield.

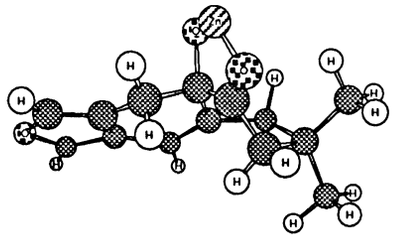
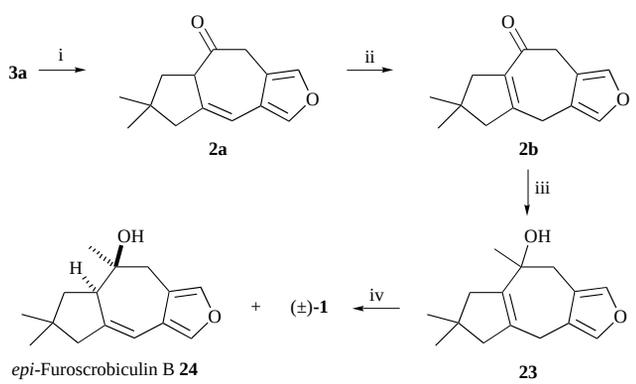


**Fig. 3** Chelation model for the reduction of compound **22** with $Zn(BH_4)_2$ showing a more favourable α-attack

Results of the reduction of the acyloin **22** with several reducing agents are summarized in Table 1. Sterically bulky reagents such as K-Selectride and $LiAlH(OBu^t)_3$ (entries 1 and 2) were not effective at all, and $NaBH_4$ (entry 3) showed high *trans*-selectivity. However, diisobutylaluminium hydride (DIBALH) (entries 4 and 5) and $Zn(BH_4)_2$ (entries 6 and 7) showed *cis*-selectivity. Among these the best result (98% yield, 93% diastereoselectivity) was obtained when using $Zn(BH_4)_2$ at −100 °C (entry 7). The remarkable difference in diastereoselectivity between entries 6 and 7 might be explained by the formation of a chelation intermediate (Fig. 3) and preferential α-attack of the reagent.

Pinacol-type rearrangement of *cis*-diol **3a** by esterification with toluene-*p*-sulfonyl chloride in pyridine at room temperature readily proceeded to afford an azulenofuran **2a** in 64% yield accompanied by a small amount of isomerized product **2b** in 2% yield. Preliminary methylation of compound **2a** using MeLi gave unsatisfactory results. That is to say, the major product of the reaction was the undesired *epi*-furoscrobiculin B **24**, and the desired furoscrobiculin B **1** was obtained only as a minor product (**1**:**24** = 2:9), which might be caused by attack of the nucleophile from the convex face of substrate **2a**. We then selected compound **2b** as a precursor to target furoscrobiculin B **1**. Isomerization of βγ-enone **2a** into αβ-enone **2b** was accomplished by using triethylamine in pyridine at room temperature in 35% yield from compound **3a** (Scheme 5). The conversion of enone **2b** into (±)-furo-




**Scheme 5** *Reagents and conditions* (*and yields*): i, TsCl, Py, DMAP, room temp.; ii, TEA, Py, room temp. (35% for 2 steps); iii, MeLi, $CeCl_3$, −78 °C (79%); iv, $Bu^tOK$, DMF, room temp. (68%) (**1**:**24** = 7:2)

scrobiculin B was accomplished according to our previous synthetic route.[4d] That is to say, methylation of enone **2b** with MeLi in the presence of $CeCl_3$ gave the alcohol **23** in 79% yield.[10] Treatment of alcohol **23** with $Bu^tOK$ in dimethylformamide (DMF) at room temperature gave the target molecule **1** (53% yield) and its epimer **24** (15% yield) in the ratio 7:2, which were very unstable, as reported by Battaglia *et al*.[11] The structure of compound **1** was confirmed by IR, $^1H$ NMR, $^{13}C$ NMR, $^1H$–$^1H$ chemical-shift correlation (COSY), NOESY and mass spectroscopic analyses, comparing their data with those of Battaglia *et al*.

**Table 1** Reduction of α-hydroxy ketone **22**

| Entry | Reducing agent (mol equiv.) | Solvent | Temp. (*T*/°C) | Yield (%)[a] [**3a**:**3b**] |
|---|---|---|---|---|
| 1 | K-Selectride (3) | THF | 60 | *b* |
| 2 | $LiAlH(OBu^t)_3$ (6) | THF | 60 | no reaction |
| 3 | $NaBH_4$ (1) | EtOH | −78 | 64 [3:97] |
| 4 | DIBALH (4) | $CH_2Cl_2$ | −78 | 60 [64:36] |
| 5 | DIBALH (4) | THF | −78 | 82 [71:29] |
| 6 | $Zn(BH_4)_2$ (1.5) | $Et_2O$ | 0 | 89 [60:40] |
| 7 | $Zn(BH_4)_2$ (1.5) | $Et_2O$ | −100 | 98 [93:7] |

[a] Isolated yield. [b] Only decomposition products were obtained.

## Experimental

Unless otherwise stated the following generalizations apply. $^1$H NMR spectra were determined using a JEOL JNM-GX 270 spectrometer (270 MHz) for solutions in $CDCl_3$ with $Me_4Si$ as internal standard. Chemical shifts are expressed in δ-values, and *J*-values are given in Hz. $^{13}$C NMR spectra were recorded for solutions in $CDCl_3$, using a 67.8 MHz JEOL JNM-GX 270 spectrometer. Chemical shifts were assigned using residual $CDCl_3$ as internal standard. IR spectra were obtained with a JASCO A-100 infrared spectrophotometer. Mass spectra and high-resolution mass spectra (HRMS) were determined on JEOL D-300 or JEOL DX-300 instruments. Analytical TLC was performed on precoated Kieselgel 60 $F_{254}$, with inspection under UV light or visualization by conc. sulfuric acid–*p*-anisaldehyde spray or potassium permanganate spray reagents. Non-flash chromatography separations were performed on Kieselgel 60 (70–230 mesh) and flash chromatography on Kieselgel 60 (230–400 mesh). All solvents were purified and dried prior to use. All reactions sensitive to moisture or air were performed under Ar. All extracted solutions were dried over anhydrous $Na_2SO_4$ or $MgSO_4$ prior to evaporation.

### 4,5,6,7-Tetrahydrobenzofuran-7-one 9

Aq. cyclohexane-1,2-dione **8** (10.2 g, 90.9 mmol in 70 $cm^3$) was added dropwise at 0 °C to aq. chloroacetaldehyde (40%; 18.0 $cm^3$, 91.7 mmol) and aq. $NaHCO_3$ (9.0 g, 107 mmol in 70 $cm^3$). The reaction mixture was stirred for 12 h at room temperature. Ethyl acetate (90 $cm^3$) was added and the resulting solution was acidified (pH 1: tested with pH paper) with aq. 10% $H_2SO_4$, then was stirred for 1 h at room temperature. The reaction mixture was neutralized with solid $NaHCO_3$, then was extracted twice with ethyl acetate. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (3:2)] gave title compound **9** (5.25 g, 42%) as needles, mp 49 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1660 (C=O); $\delta_H$ 7.54 (1 H, d, $J_{2,3}$ 1.7, 2-H), 6.40 (1 H, d, $J_{2,3}$ 1.7, 3-H), 2.76 (2 H, t, *J* 6.0, 6-$H_2$), 2.52–2.57 (2 H, m, 4-$H_2$) and 2.09–2.18 (2 H, m, 5-$H_2$); *m/z* (EI) 136 ($M^+$, 100%), 108 (81) and 52 (58).

### 4,5,6,7-Tetrahydrobenzofuran-7-ol 10

To a solution of ketone **9** (433 mg, 3.17 mmol) in dry THF (4.0 $cm^3$) was added $LiAlH_4$ (121 mg, 3.18 mmol) at 0 °C. The reaction mixture was stirred for 0.5 h at room temperature, then was quenched with aq. 2 M NaOH and filtered. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (1:1)] gave the alcohol **10** (293 mg, 67%) as an oil; $\nu_{max}$(neat)/$cm^{-1}$ 3320 (OH) and 880 (furan); $\delta_H$ 7.31 (1 H, d, $J_{2,3}$ 1.7, 2-H), 6.21 (1 H, d, $J_{2,3}$ 1.7, 3-H), 4.78 (1 H, t, $J_{6,7}$ 4.0, 7-H), 2.32–2.56 (2 H, m, 4-$H_2$) and 1.69–1.97 (5 H, m, 5- and 6-$H_2$, OH); *m/z* (EI) 138 ($M^+$, 18%), 120 (92) and 91 (100).

### 7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydrobenzofuran 11

To a solution of alcohol **10** (3.54 g, 25.6 mmol) in dry DMF (20 $cm^3$) were added imidazole (4.36 g, 64.1 mmol) and *tert*-butyldimethylsilyl chloride (TBSCl) (5.02 g, 33.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight. The resulting mixture was poured into water and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (40:1)] gave the title silyl ether **11** (6.18 g, 96%) as an oil; $\nu_{max}$(neat)/$cm^{-1}$ 880 (furan); $\delta_H$ 7.28 (1 H, d, $J_{2,3}$ 1.7, 2-H), 6.17 (1 H, d, $J_{2,3}$ 1.7, 3-H), 4.75 (1 H, br t, $J_{6,7}$ 4.6, 7-H), 2.44–2.52 (1 H, m, 4-$H^B$), 2.31–2.39 (1 H, m, 4-$H^A$), 1.83–1.96 (3 H, m, 6-$H_2$ and 5-$H^B$), 1.66–1.74 (1 H, m, 5-$H^A$), 0.91 [9 H, s, $C(CH_3)_3$], 0.15 (3 H, s, $SiCH_3$) and 0.09 (3 H, s, $SiCH_3$); *m/z* (EI) 252 ($M^+$, 5%), 237 (58) and 197 (100).

### 7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydro-2-(hydroxymethyl)benzofuran 12

Butyllithium (1.65 M solution in hexane; 20 $cm^3$, 32.5 mmol) was added dropwise to a solution of compound **11** (2.74 g, 10.8 mmol) in dry THF (20 $cm^3$) over a period of 10 min at −78 °C. The reaction mixture was stirred for 0.5 h at the same temperature, then was warmed to 0 °C gradually over a period of 0.5 h. After being stirred for 0.5 h at 0 °C, the whole was cooled to −78 °C again. As soon as the reaction mixture had been added dropwise to a solution of dry DMF (8.4 $cm^3$, 108 mmol) in dry THF (10 $cm^3$) at −78 °C over a period of 10 min, the resulting mixture was quenched with saturated aq. $NH_4Cl$, and extracted three times with diethyl ether. The combined extracts were washed with brine and dried. After removal of the solvent *in vacuo*, the residue was dissolved in dry methanol (20 $cm^3$). To the solution was added $NaBH_4$ (410 mg, 10.8 mmol) at 0 °C. After being stirred for 0.5 h at room temperature, the reaction mixture was quenched with saturated aq. $NH_4Cl$, and extracted three times with diethyl ether. The combined extacts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (3:1)] gave the *alcohol* **12** (2.39 g, 78%) as an oil (Found: $[M - H]^+$, 281.1597. $C_{15}H_{25}O_3Si$ requires *m/z*, 281.1573); $\nu_{max}$(neat)/$cm^{-1}$ 3300 (OH) and 870 (furan); $\delta_H$ 6.09 (1 H, s, 3-H), 4.74 (1 H, br t, $J_{6,7}$ 4.6, 7-H), 4.54 (2 H, s, $CH_2OH$), 2.41–2.49 (1 H, m, 4-$H^B$), 2.25–2.36 (1 H, m, 4-$H^A$), 1.82–1.97 (2 H, m, 6-H, 5-$H^B$), 1.63–1.73 (2 H, m, 5-$H^A$, OH), 0.91 [9 H, s, $C(CH_3)_3$], 0.15 (3 H, s, $SiCH_3$) and 0.10 (3 H, s, $SiCH_3$); *m/z* [(+)FAB] 281 ($[M - H]^+$, 44%), 265 (100), 225 (51) and 151 (98).

### 7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydro-2-(2-oxapent-4-ynyl)benzofuran 13

To a solution of compound **12** (4.73 g, 16.7 mmol) in diethyl ether (20 $cm^3$) were added aq. 50% NaOH (100 $cm^3$), tetrabutylammonium hydrogen sulfate (568 mg, 1.67 mmol) as a phase-transfer catalyst, and prop-2-ynyl bromide (3.8 $cm^3$, 50.2 mmol). The reaction mixture was stirred for 1.5 h at room temperature. The resulting mixture was extracted three times with diethyl ether. The combined extracts were washed successively with water and brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (20:1)] gave *compound* **13** (4.77 g, 89%) as an oil (Found: $M^+$, 320.1793. $C_{18}H_{28}O_3Si$ requires M, 320.1808); $\nu_{max}$(neat)/$cm^{-1}$ 3300 (≡C–H) and 880 (furan); $\delta_H$ 6.16 (1 H, s, 3-H), 4.73 (1 H, t, $J_{6,7}$ 4.0, 7-H), 4.51 (2 H, s, $CH_2O$), 4.15 (2 H, d, *J* 2.3, $OCH_2C{\equiv}CH$), 2.41–2.49 (1 H, m, 4-$H^B$), 2.44 (1 H, t, *J* 2.3, $OCH_2C{\equiv}CH$), 2.25–2.36 (1 H, m, 4-$H^A$), 1.81–1.94 (3 H, m, 6-$H_2$ and 5-$H^B$), 1.63–1.73 (1 H, m, 5-$H^A$), 0.90 [9 H, s, $C(CH_3)_3$], 0.15 (3 H, s, $SiCH_3$) and 0.09 (3 H, s, $SiCH_3$); $\delta_C$ 152.0 (s, C-2), 149.6 (s, C-7a), 120.3 (s, C-3a), 110.7 (d, C-3), 79.4 (d, $OCH_2C{\equiv}CH$), 74.4 (s, $OCH_2C{\equiv}CH$), 63.2 (t, 2-$CH_2O$), 62.9 (d, C-7), 56.4 (t, $OCH_2C{\equiv}CH$), 33.5 (t, C-6), 25.8 [q, $C(CH_3)_3$], 22.2 (t, C-4), 19.1 (t, C-5), 18.2 [s, $C(CH_3)_3$], −4.7 (q, $SiCH_3$) and −4.9 (q, $SiCH_3$); *m/z* [(+)FAB] 319 ($[M - H]^+$, 74%), 265 (100) and 189 (98).

**(4a*SR*,5*RS*)-5-(*tert*-Butyldimethylsilyloxy)-4,4a,5,6,7,8-hexahydronaphtho[2,3-*c*]furan-4a-ol 14a and (4a*SR*,5*SR*)-5-(*tert*-butyldimethylsilyloxy)-4,4a,5,6,7,8-hexahydronaphtho[2,3-*c*]-furan-4a-ol 14b**

A solution of the ether **13** (406 mg, 1.27 mmol) in *tert*-butyl alcohol (5 $cm^3$) was added dropwise to a solution of potassium *tert*-butoxide (569 mg, 5.07 mmol) in *tert*-butyl alcohol (10 $cm^3$) at room temperature. The reaction mixture was heated to 80 °C for 2 h. The resulting mixture was cooled to room temperature, poured into saturated aq. $NH_4Cl$ and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (10:1)] gave a mixture of *cis*-**14a** (140 mg, 33%) and *trans*-**14b** (252 mg, 60%) as an oil; the cis-*naphtho*[2,3-c]*furanol* **14a** (Found: $[M + H]^+$, 321.1881. $C_{18}H_{29}O_3Si$ requires *m/z*, 321.1886); $\nu_{max}$(neat)/$cm^{-1}$ 3550 (OH) and 880 (furan); $\delta_H$ 7.25 (1 H, s, 1-H), 7.16 (1 H, t, *J* 1.0, 3-H), 6.34 (1 H, d, $J_{8B,9}$ 2.3, 9-H), 3.59 (1 H, dd, $J_{5,6B}$ 6.9, $J_{5,6A}$ 8.6, 5-H), 3.0 (1 H, d, $J_{4A,4B}$ 16.5, 4-$H^A$), 2.66 (1 H, dd, $J_{3,4B}$ 2.0, $J_{4A,4B}$ 16.5, 4-$H^B$), 2.57 (1 H, br s, OH), 2.47 (1 H, dm, $J_{8A,8B}$ 14.2, 8-$H^B$), 2.20 (1 H, dt, $J_{8B,9}$ 2.3, $J_{8A,8B}$ 14.2, 8-$H^A$), 1.72–1.82 (3 H, m, 6-$H_2$ and 7-$H^B$), 1.25–1.35 (1 H, m, 7-$H^A$), 0.94 [9 H, s, $C(CH_3)_3$], 0.12 (3 H, s, $SiCH_3$) and 0.11 (3 H, s, $SiCH_3$); $\delta_C$ 138.8 (s, C-8a), 137.6 (d, C-1), 136.2 (d, C-3), 120.8 (s, C-9a), 117.8 (s, C-3a), 116.5 (d, C-9), 77.8 (d, C-5), 73.2 (s, C-4a), 31.8 (t, C-4), 31.1 (t, C-6 or -8), 31.1 (t, C-8 or -6), 25.9 [q, $C(CH_3)_3$], 23.8 (t, C-7), 18.1 [s, $C(CH_3)_3$], −4.0 (q, $SiCH_3$) and −4.8 (q, $SiCH_3$); *m/z* [(+)FAB] 319 ($[M - H]^+$, 20%), 303 (100) and 263 (60); the trans-*naphtho*[2,3-c]*furanol* **14b** (Found: $[M + H]^+$, 321.1878. $C_{18}H_{29}O_3Si$ requires *m/z*, 321.1886); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3600 (OH) and 900 (furan); $\delta_H$ 7.24 (1 H, s, 1-H), 7.15–7.17 (1 H, m, 3-H), 6.28 (1 H, d, *J* 2.3, 9-H), 3.77 (1 H, dd, $J_{5,6B}$ 2.0, $J_{5,6A}$ 3.3, 5-H), 3.22 (1 H, dd, $J_{3,4B}$ 2.1, $J_{4A,4B}$ 16.5, 4-$H^B$), 2.60 (1 H, d, $J_{4A,4B}$ 16.5, 4-$H^A$), 2.49 (1 H, dm, $J_{8A,8B}$ 14.9, 8-$H^B$), 2.29 (1 H, dm, $J_{8A,8B}$ 14.9, 8-$H^A$), 2.04 (1 H, ddd, $J_{5,6B}$ 2.0, *J* 4.0, $J_{6A,6B}$ 13.0, 6-$H^B$), 1.86 (1 H, tt, $J_{5,6A}$ 3.3, $J_{6A,6B}$ 13.0, 6-$H^A$), 1.74 (1 H, br s, OH), 1.62–1.76 (1 H, m, 7-$H^B$), 1.47–1.57 (1 H, m, 7-$H^A$), 0.83 [9 H, s, $C(CH_3)_3$] and 0.07 (6 H, s, $SiCH_3$); $\delta_C$ 139.2 (s, C-8a), 137.9 (d, C-1), 135.8 (d, C-3), 120.8 (s, C-9a), 117.9 (s, C-3a), 115.9 (d, C-9), 74.2 (d, C-5), 73.2 (s, C-4a), 30.7 (t, C-4 or -6), 30.6 (t, C-6 or -4), 29.0 (t, C-8), 25.8 [q, $C(CH_3)_3$], 19.5 (t, C-7), 18.0 [s, $C(CH_3)_3$], −4.3 (q, $SiCH_3$) and −4.9 (q, $SiCH_3$); *m/z* [(+)FAB] 319 ($[M - H]^+$, 18%), 303 (86), 263 (83) and 171 (100).

**(4a*SR*,5*RS*)-4,4a,5,6,7,8-Hexahydronaphtho[2,3-*c*]furan-4a,5-diol 15a**

To a solution of silyl ether **14a** (127 mg, 0.40 mmol) in dry THF (0.8 $cm^3$) was added tetrabutylammonium fluoride (TBAF) (1.0 M solution in THF; 0.8 $cm^3$, 0.8 mmol). The reaction mixture was stirred for 2 h at room temperature. The resulting mixture was extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (1:1)] gave *title compound* **15a** (69.7 mg, 85%) as needles, mp 158–159 °C (from MeOH) (Found: C, 69.89; H, 6.84. $C_{12}H_{14}O_3$ requires C, 69.67; H, 6.80%); $\nu_{max}$(KBr)/$cm^{-1}$ 3350 (OH) and 890 (furan); $\delta_H$($CD_3OD$) 7.10–7.19 (1 H, m, 1-H), 7.09 (1 H, d, *J* 2.6, 3-H), 6.19 (1 H, d, *J* 2.3, 9-H), 4.50 (2 H, br s, OH), 3.32 (1 H, dd, $J_{5,6B}$ 5.8, $J_{5,6A}$ 10.1, 5-H), 2.97 (1 H, d, $J_{4A,4B}$ 16.8, 4-$H^A$), 2.73 (1 H, dd, $J_{3,4B}$ 1.7, $J_{4A,4B}$ 16.8, 4-$H^B$), 2.40 (1 H, ddt, *J* 2.0, *J* 4.3, $J_{8A,8B}$ 13.9, 8-$H^B$), 2.10 (1 H, dm, $J_{8A,8B}$ 13.9, 8-$H^A$), 1.65–1.78 (3 H, m, 6-$H_2$ and 7-$H^B$) and 1.19–1.32 (1 H, m, 7-H); $\delta_C$($CD_3OD$) 141.1 (s, C-8a), 138.8 (d, C-1), 137.3 (d, C-3), 122.6 (s, C-9a), 119.3 (s, C-3a), 116.5 (d, C-9), 77.7 (d, C-5), 74.3 (s, C-4a), 32.1 (t, C-4), 31.5 (t, C-6 or -8), 31.4 (t, C-8 or -6) and 25.4 (t, C-7); *m/z* [(+)FAB] 206 ($M^+$, 100%) and 189 (10).

**(4a*SR*,5*SR*)-4,4a,5,6,7,8-Hexahydronaphtho[2,3-*c*]furan-4a,5-diol 15b**

TBAF (1.0 M solution in THF; 1.6 $cm^3$, 1.6 mmol) was added to silyl ether **14b** (255 mg, 0.80 mmol). The reaction mixture was stirred for 7 days at room temperature. The resulting mixture was extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (1:1)] gave *title compound* **15b** (148 mg, 90%) as a viscous oil (Found: $M^+$, 206.0944. $C_{12}H_{14}O_3$ requires M, 206.0943); $\nu_{max}$(neat)/$cm^{-1}$ 3450 (OH) and 890 (furan); $\delta_H$ 7.26 (1 H, d, *J* 1.3, 1-H), 7.16–7.18 (1 H, m, 3-H), 6.36 (1 H, d, $J_{8B,9}$ 2.0, 9-H), 3.78 (1 H, dd, $J_{5,6B}$ 2.6, $J_{5,6A}$ 2.6, 5-H), 3.31 (1 H, dd, *J* 2.0, $J_{4A,4B}$ 17.0, 4-$H^B$), 2.73 (1 H, d, $J_{4A,4B}$ 17.0, 4-$H^A$), 2.49–2.62 (1 H, m, 8-$H^B$), 2.23–2.31 (1 H, m, 8-$H^A$), 2.08–2.22 (1 H, m, 6-$H^B$), 1.89 (2 H, br s, OH) and 1.60–1.79 (3 H, m, 6-$H^A$ and 7-$H_2$); $\delta_C$ 138.1 (s, C-8a), 138.0 (d, C-1), 136.3 (d, C-3), 120.4 (s, C-9a), 117.4 (s, C-3a), 117.0 (d, C-9), 73.9 (d, C-5), 72.9 (s, C-4a), 30.4 (t, C-4 or -6), 30.2 (t, C-6 or -4), 28.4 (t, C-8) and 19.8 (t, C-7); *m/z* [(+)FAB] 206 ($M^+$, 54%) and 189 (100).

**5,6,7,7a-Tetrahydroazuleno[5,6-*c*]furan-8(9*H*)-one 16a and 4,5,6,7-tetrahydroazuleno[5,6-*c*]furan-8(9*H*)-one 16b**

To a solution of diol **15a** (46.9 mg, 0.23 mmol) in dry pyridine (0.5 $cm^3$) was added toluene-*p*-sulfonyl chloride (87 mg, 0.45 mmol). The whole was stirred for 2 h at room temperature. The resulting mixture was poured into water and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (10:1)] gave a mixture of βγ-*enone* **16a** (20.6 mg, 48%) and αβ-*enone* **16b** (8.7 mg, 20%) as an oil; βγ-*enone* **16a** (Found: $M^+$, 188.0841. $C_{12}H_{12}O_2$ requires M, 188.0837); $\nu_{max}$(neat)/$cm^{-1}$ 1720 (C=O) and 880 (furan); $\delta_H$ 7.36 (1 H, s, 3-H), 7.27 (1 H, dd, *J* 1.7 and 2.3, 1-H), 6.49 (1 H, dd, *J* 2.1 and 4.5, 4-H), 3.73 (1 H, d, $J_{9A,9B}$ 19.1, 9-$H^A$), 3.49–3.53 (1 H, m, 7a-H), 3.39 (1 H, ddd, *J* 1.3, $J_{1,9B}$ 1.7, $J_{9A,9B}$ 19.1, 9-$H^B$), 2.28–2.49 (3 H, m, 7-$H^B$ and 5-$H_2$), 1.57–1.86 (3 H, m, 6-$H_2$ and 7-$H^A$); $\delta_C$ 206.4 (s, C-8), 143.4 (s, C-4a), 139.7 (d, C-3), 138.8 (d, C-1), 124.0 (s, C-3a), 117.8 (s, C-9a), 112.7 (d, C-4), 56.6 (d, C-7a), 39.1 (t, C-9), 34.0 (t, C-7), 26.9 (t, C-5) and 25.3 (t, C-6); *m/z* [(+)FAB] 188 ($M^+$, 100%); αβ-*enone* **16b** (Found: $[M + H]^+$, 189.0911. $C_{12}H_{13}O_2$ requires *m/z*, 189.0916); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1640 and 1610 (conj. C=O) and 880 (furan); $\delta_H$ 7.24 (1 H, s, 1- or 3-H), 7.23 (1 H, d, *J* 0.7, 3- or 1-H), 3.66 (2 H, s, 9-$H_2$), 3.49 (2 H, d, *J* 1.0, 4-$H_2$), 2.62–2.77 (4 H, m, 5- and 7-H) and 1.76–1.87 (2 H, m, 6-$H_2$); $\delta_C$ 194.2 (s, C-8), 156.7 (s, C-7a), 139.4 (d, C-1 or -3), 138.2 (d, C-3 or -1), 138.1 (s, C-4a), 122.8 (s, C-3a or -9a), 118.7 (s, C-9a or -3a), 41.7 (t, C-9), 40.1 (t, C-4), 33.8 (t, C-7), 26.4 (t, C-5) and 20.8 (t, C-6); *m/z* [(+)FAB] 189 ($[M + H]^+$, 100%).

**4,5,6,7-Tetrahydro-5,5-dimethylbenzofuran-7-one 5**

A solution of diones **6a** and **6b**[8] (5.30 g, 37.8 mmol) in methanol (30 $cm^3$) was added dropwise at 0 °C to aq. chloroacetaldehyde (40%; 7.8 $cm^3$, 49.1 mmol) and aq. $NaHCO_3$ (3.8 g, 45.4 mmol in 35 $cm^3$). The reaction mixture was stirred for 60 h at room temperature. Ethyl acetate (50 $cm^3$) was added and the resulting solution was acidified (pH 1: tested with pH paper) with aq. 10% $H_2SO_4$, then was stirred for 3 h at room temperature. The reaction mixture was neutralized with solid $NaHCO_3$, then extracted twice with ethyl acetate. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (3:1)] gave title ketone **5** (4.21 g, 68%) as an oil; $\nu_{max}$(neat)/$cm^{-1}$ 1670 (C=O) and 890 (furan); $\delta_H$ 7.59 (1 H, d, $J_{2,3}$ 1.7, 2-H), 6.39 (1 H, d, $J_{2,3}$ 1.7, 3-H), 2.65 (2 H, s, 6-$H_2$), 2.44 (2 H, s, 4-$H_2$) and 1.12 (6 H, s, 5-$Me_2$); $\delta_C$ 185.5 (s, C-7), 147.7 (d, C-2), 147.0 (s, C-7a), 138.3 (s, C-3a), 112.0 (d, C-3), 52.2 (t, C-6), 36.9 (t, C-4), 36.5 (s, C-5) and 28.4 (q, 5-$Me_2$); *m/z* (EI) 164 ($M^+$, 48%), 149 (39) and 108 (100).

**4,5,6,7-Tetrahydro-5,5-dimethylbenzofuran-7-ol 18**

To a solution of ketone **5** (530 mg, 3.23 mmol) in dry ethanol (10 $cm^3$) was added $NaBH_4$ (122 mg, 3.23 mmol) at 0 °C. The reaction mixture was stirred for 2 h at room temperature, then was quenched with saturated aq. $NH_4Cl$ and extracted with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by column chromatography [hexane–ethyl acetate (3:1)] gave *compound* **18** (496 mg, 93%) as an oil (Found: $[M - H]^+$, 165.0901. $C_{10}H_{13}O_2$ requires *m/z*, 165.0916); $\nu_{max}$(neat)/$cm^{-1}$ 3350 (OH) and 890 (furan); $\delta_H$ 7.33 (1 H, dd, *J* 0.7 and 2.0, 2-H), 6.18 (1 H, d, *J* 1.7, 3-H), 4.78 (1 H, br t, $J_{6,7}$ 6.3, 7-H), 2.37 (1 H, dd, $J_{4B,3}$ 2.0, $J_{4A,4B}$ 15.8, 4-$H^B$), 2.19 (1 H, dt, $J_{4A,6B}$ 1.3, $J_{4A,4B}$ 15.8, 4-$H^A$), 2.09 (1 H, br s, OH), 1.95 (1 H, ddd, $J_{4A,6B}$ 1.3, $J_{6B,7}$ 6.3, $J_{6A,6B}$ 13.2, 6-$H^B$), 1.63 (1 H, dd, $J_{6A,7}$ 7.3, $J_{6A,6B}$ 13.2, 6-$H^A$), 1.10 (3 H, s, 5-Me) and 0.96 (3 H, s, 5-Me); $\delta_C$ 149.8 (s, C-7a), 142.3 (d, C-2), 119.0 (s, C-3a), 110.6 (d, C-3), 63.0 (d, C-7), 46.1 (t, C-6), 36.3 (t, C-4), 32.6 (s, C-5), 30.1 (q, 5-Me) and 27.0 (q, 5-Me); *m/z* [(+)FAB] 165 ($[M - H]^+$, 23%) and 149 (100).

**7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydro-5,5-dimethylbenzofuran 19**

The alcohol **18** (220 mg, 1.32 mmol) was used as a starting material. By the same procedure as that described for the synthesis of compound **11** and purification by column chromatography [hexane–ethyl acetate (40:1)], compound **19** (340 mg, 92%) was obtained as an oil; $\nu_{max}$(neat)/$cm^{-1}$ 880 (furan); $\delta_H$ 7.29 (1 H, dd, *J* 0.7 and 2.0, 2-H), 6.12 (1 H, d, *J* 1.7, 3-H), 4.73 (1 H, br t, $J_{6,7}$ 6.3, 7-H), 2.33 (1 H, dd, $J_{3,4B}$ 1.7, $J_{4A,4B}$ 15.8, 4-$H^B$), 2.14 (1 H, dd, $J_{4A,6B}$ 1.3, $J_{4A,4B}$ 15.8, 4-$H^A$), 1.79 (1 H, ddd, $J_{4A,6B}$ 1.3, $J_{6B,7}$ 6.3, $J_{6A,6B}$ 13.2, 6-$H^B$), 1.64 (1 H, dd, $J_{6A,7}$ 6.9, $J_{6A,6B}$ 13.2, 6-$H^A$), 1.06 (3 H, s, 5-Me), 0.93 (3 H, s, 5-Me), 0.91 [9 H, s, $C(CH_3)_3$], 0.14 (3 H, s, $SiCH_3$) and 0.13 (3 H, s, $SiCH_3$); $\delta_C$ 150.2 (s, C-7a), 141.8 (d, C-2), 118.5 (s, C-3a), 110.4 (d, C-3), 63.5 (d, C-7), 46.9 (t, C-6), 36.4 (t, C-4), 32.6 (s, C-5), 29.9 (q, 5-Me), 27.5 (q, 5-Me), 25.9 [q, $C(CH_3)_3$], 18.3 [s, $C(CH_3)_3$], −4.7 (q, $SiCH_3$) and −4.8 (q, $SiCH_3$).

**7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydro-2-hydroxymethyl-5,5-dimethylbenzofuran 20**

Compound **19** (3.10 g, 11.0 mmol) was used as a starting material. By the same procedure as described for the synthesis of compound **12** and purification by column chromatography [hexane–ethyl acetate (3:1)], *compound* **20** (2.99 g, 87%) was obtained as an oil (Found: $[M - H]^+$, 309.1891. $C_{17}H_{29}O_3Si$ requires *m/z*, 309.1886); $\nu_{max}$(neat)/$cm^{-1}$ 3350 (OH); $\delta_H$ 6.06 (1 H, s, 3-H), 4.74 (1 H, t, $J_{6,7}$ 6.4, 7-H), 4.54 (2 H, s, $CH_2OH$), 2.32 (1 H, dd, $J_{4B,6B}$ 1.3, $J_{4A,4B}$ 15.8, 4-$H^B$), 2.13 (1 H, d, $J_{4A,4B}$ 15.8, 4-$H^A$), 1.81 (1 H, ddd, $J_{4B,6B}$ 1.3, $J_{6,7}$ 6.4, $J_{6A,6B}$ 13.2, 6-$H^B$), 1.77 (1 H, br s, OH), 1.64 (1 H, dd, $J_{6,7}$ 6.4, $J_{6A,6B}$ 13.2, 6-$H^A$), 1.08 (3 H, s, 5-Me), 0.95 (3 H, s, 5-Me), 0.92 [9 H, s, $C(CH_3)_3$], 0.15 (6 H, s, $SiCH_3$); $\delta_C$ 153.4 (s, C-2), 150.3 (s, C-7a), 119.4 (s, C-3a), 108.7 (d, C-3), 63.5 (d, C-7), 57.9 (t, $CH_2OH$), 46.8 (t, C-6), 36.3 (t, C-4), 32.4 (s, C-5), 29.9 (q, 5-$CH_3$), 27.5 (q, 5-$CH_3$), 25.8 [q, $C(CH_3)_3$], 18.3 [s, $C(CH_3)_3$], −4.6 (q, $SiCH_3$) and −4.8 (q, $SiCH_3$); *m/z* [(+)FAB] 309 ($[M - H]^+$, 35%) and 293 (99).

**7-(*tert*-Butyldimethylsilyloxy)-4,5,6,7-tetrahydro-5,5-dimethyl-2-(2-oxapent-4-ynyl)benzofuran 4**

Compound **20** (2.11 g, 6.81 mmol) was used as starting material. By the same procedure as described for the synthesis of analogue **13** and purification by column chromatography [hexane–ethyl acetate (20:1)], *compound* **4** (2.18 g, 92%) was obtained as an oil (Found: $[M - H]^+$, 347.2067. $C_{20}H_{31}O_3Si$ requires *m/z*, 347.2042); $\nu_{max}$(neat)/$cm^{-1}$ 3300 (≡C–H); $\delta_H$ 6.13 (1 H, s, 3-H), 4.73 (1 H, t, $J_{6,7}$ 6.4, 7-H), 4.50 (2 H, s, 2-$CH_2O$), 4.16 (2 H, d, *J* 2.6, $OCH_2C{\equiv}CH$), 2.44 (1 H, t, *J* 2.3, $OCH_2C{\equiv}CH$), 2.32 (1 H, dd, $J_{4B,6B}$ 1.7, $J_{4A,4B}$ 15.8, 4-$H^B$), 2.13 (1 H, d, $J_{4A,4B}$ 15.8, 4-$H^A$), 1.80 (1 H, ddd, $J_{4B,6B}$ 1.3, $J_{6,7}$ 6.4, $J_{6A,6B}$ 13.2, 6-$H^B$), 1.64 (1 H, dd, $J_{6,7}$ 6.4, $J_{6A,6B}$ 13.2, 6-$H^A$), 1.07 (3 H, s, 5-Me), 0.95 (3 H, s, 5-Me), 0.92 [9 H, s, $C(CH_3)_3$], 0.15 (3 H, s, $SiCH_3$) and 0.15 (3 H, s, $SiCH_3$); $\delta_C$ 150.8 (s, C-2), 150.3 (s, C-7a), 119.4 (s, C-3a), 111.0 (d, C-3), 79.6 (d, $OCH_2C{\equiv}CH$), 74.5 (s, $OCH_2$-$C{\equiv}CH$), 63.4 (d, C-7), 63.3 (t, 2-$CH_2O$), 56.6 (t, $OCH_2C{\equiv}CH$), 46.7 (t, C-6), 36.3 (t, C-4), 32.4 (s, C-5), 29.9 (q, 5-$CH_3$), 27.6 (q, 5-$CH_3$), 25.9 [q, $C(CH_3)_3$], 18.3 [s, $C(CH_3)_3$], −4.6 (q, $SiCH_3$) and −4.8 (q, $SiCH_3$); *m/z* [(+)FAB] 347 ($[M - H]^+$, 74%), 293 (100) and 217 (92).

**(4a*SR*,5*RS*)-5-(*tert*-Butyldimethylsilyloxy)-4,4a,5,6,7,8-hexahydro-7,7-dimethylnaphtho[2,3-*c*]furan-4a-ol 21a and (4a*SR*,5*SR*)-5-(*tert*-butyldimethylsilyloxy)-4,4a,5,6,7,8-hexahydro-7,7-dimethylnaphtho[2,3-*c*]furan-4a-ol 21b**

Compound **4** (111 mg, 0.32 mmol) was used as starting material. By the same procedure as described for the synthesis of compounds **14a**,**b** and purification by flash column chromatography [hexane–ethyl acetate (20:1)], compounds **21a** (12.4 mg, 11%) and **21b** (85.0 mg, 77%) were obtained as an oil; the cis-*naphtho*[2,3-c]*furanol* **21a** (Found: $M^+$, 348.2106. $C_{20}H_{32}O_3Si$ requires M, 348.2121); $\nu_{max}$(neat)/$cm^{-1}$ 3550 (OH) and 890 (furan); $\delta_H$ 7.26 (1 H, s, 1-H), 7.17 (1 H, d, $J_{3,4B}$ 2.0, 3-H), 6.33 (1 H, d, $J_{8B,9}$ 2.3, 9-H), 3.74 (1 H, dd, $J_{5,6B}$ 5.0, $J_{5,6A}$ 11.5, 5-H), 3.01 (1 H, d, $J_{4A,4B}$ 16.5, 4-$H^A$), 2.65 (1 H, dd, $J_{3,4B}$ 2.0, $J_{4A,4B}$ 16.5, 4-$H^B$), 2.61 (1 H, br s, OH), 2.50 (1 H, d, $J_{8A,8B}$ 13.9, 8-$H^A$), 1.87 (1 H, dd, $J_{8B,9}$ 2.3, $J_{8A,8B}$ 13.9, 8-$H^B$), 1.68 (1 H, dd, $J_{5,6A}$ 11.5, $J_{6A,6B}$ 12.9, 6-$H^A$), 1.43 (1 H, ddd, $J_{6B,8B}$ 2.6, $J_{5,6B}$ 5.0, $J_{6A,6B}$ 12.9, 6-$H^B$), 1.00 (3 H, s, 7-Me), 0.94 [9 H, s, $C(CH_3)_3$], 0.87 (3 H, s, 7-Me), 0.12 (3 H, s, $SiCH_3$) and 0.11 (3 H, s, $SiCH_3$); $\delta_C$ 137.6 (d, C-1), 137.0 (s, C-8a), 136.2 (d, C-3), 120.8 (s, C-9a), 118.0 (d, C-9), 117.7 (s, C-3a), 75.1 (d, C-5), 72.0 (s, C-4a), 44.5 (t, C-4 or -6), 44.0 (t, C-6 or -4), 32.0 (t, C-8), 31.8 (q, 7-Me), 31.7 (s, C-7), 25.9 [q, $C(CH_3)_3$], 25.1 (q, 7-Me), 18.0 [s, $C(CH_3)_3$], −4.0 (q, $SiCH_3$) and −4.7 (q, $SiCH_3$); *m/z* [(+)FAB] 347 ($[M - H]^+$, 31%), 331 (98), 291 (54) and 199 (100); the trans-*naphtho*[2,3-c]*furanol* **21b** (Found: $[M - H]^+$, 347.2051. $C_{20}H_{31}O_3Si$ requires *m/z*, 347.2042); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3600 (OH) and 890 (furan); $\delta_H$ 7.26 (1 H, s, 1-H), 7.21 (1 H, d, $J_{3,4B}$ 1.7, 3-H), 6.25 (1 H, d, *J* 2.0, 9-H), 3.97 (1 H, dd, $J_{5,6B}$ 3.3, $J_{5,6A}$ 8.6, 5-H), 2.88 (1 H, dd, $J_{3,4B}$ 1.7, $J_{4A,4B}$ 16.8, 4-$H^B$), 2.77 (1 H, d, $J_{4A,4B}$ 16.8, 4-$H^A$), 2.43 (1 H, d, $J_{8A,8B}$ 13.5, 8-$H^B$), 1.85 (1 H, d, $J_{8A,8B}$ 13.5, 8-$H^A$), 1.75 (1 H, br s, OH), 1.60 (1 H, dd, $J_{5,6B}$ 3.3, $J_{6A,6B}$ 13.9, 6-$H^B$), 1.33 (1 H, dd, $J_{5,6A}$ 8.6, $J_{6A,6B}$ 13.9, 6-$H^A$), 1.05 (3 H, s, 7-Me), 0.95 (3 H, s, 7-Me), 0.87 [9 H, s, $C(CH_3)_3$], 0.11 (3 H, s, $SiCH_3$) and 0.09 (3 H, s, $SiCH_3$); $\delta_C$ 139.5 (s, C-8a), 138.5 (d, C-1), 136.1 (d, C-3), 120.9 (s, C-9a), 117.9 (s, C-3a), 116.2 (d, C-9), 75.4 (d, C-5), 74.6 (s, C-4a), 43.3 (t, C-4 or -6), 42.8 (t, C-6 or -4), 31.5 (q, 7-Me), 31.1 (s, C-7), 29.4 (q, 7-Me), 27.8 (t, C-8), 25.8 [q, $C(CH_3)_3$], 18.0 [s, $C(CH_3)_3$], −4.4 (q, $SiCH_3$) and −4.8 (q, $SiCH_3$); *m/z* [(+)FAB] 347 ($[M - H]^+$, 32%), 331 (80), 291 (64) and 199 (100).

**(4a*SR*,5*SR*)-4,4a,5,6,7,8-Hexahydro-7,7-dimethylnaphtho-[2,3-*c*]furan-4a,5-diol 3b**

Compound **21b** (1.84 g, 5.27 mmol) was used as starting material. By the same procedure as described for the synthesis of compound **15b**, and purification by column chromatography [hexane–ethyl acetate (1:1)], *compound* **3b** (1.39 g; quant.) was obtained as a viscous oil (Found: $M^+$, 234.1254. $C_{14}H_{18}O_3$ requires M, 234.1256); $\nu_{max}$(neat)/$cm^{-1}$ 3400 (OH) and 880 (furan); $\delta_H$ 7.30 (1 H, s, 1-H), 7.25 (1 H, s, 3-H), 6.29 (1 H, d, $J_{8B,9}$ 2.0, 9-H), 4.06 (1 H, dd, $J_{5,6B}$ 3.6, $J_{5,6A}$ 10.2, 5-H), 2.92 (1 H, d, $J_{4A,4B}$ 16.3, 4-$H^A$), 2.84 (1 H, dd, *J* 1.8, $J_{4A,4B}$ 16.3, 4-$H^B$), 2.44 (1 H, dd, $J_{8B,9}$ 2.0, $J_{8A,8B}$ 13.5, 8-$H^B$), 1.95 (2 H, br s, OH), 1.84 (1 H, d, $J_{8A,8B}$ 13.5, 8-$H^A$), 1.67 (1 H, dd, $J_{5,6B}$ 3.6, $J_{6A,6B}$ 13.5, 6-$H^B$), 1.34 (1 H, dd, $J_{5,6A}$ 10.2, $J_{6A,6B}$ 13.5, 6-$H^A$), 1.09 (3 H, s, 7-Me) and 0.96 (3 H, s, 7-Me); $\delta_C$ 139.3 (s, C-8a), 138.8 (d, C-1), 136.4 (d, C-3), 120.7 (s, C-9a), 117.3 (s, C-3a), 116.6 (d, C-9), 74.6 (d, C-5), 74.5 (s, C-4a), 42.9 (t, C-4 or -6), 41.8 (t, C-6 or -4), 31.3 (q, 7-Me), 31.0 (s, C-7), 29.5 (q, 7-Me) and 26.6 (t, C-8); *m/z* [(+)FAB] 234 ($M^+$, 33%) and 217 (100).

**4,4a,7,8-Tetrahydro-4a-hydroxy-7,7-dimethylnaphtho[2,3-*c*]-furan-5(6*H*)-one 22**

Dess–Martin reagent was prepared according to Dess and Martin's procedure.[9] A solution of compound **3b** (497 mg, 2.12 mmol) in dry $CH_2Cl_2$ (8 $cm^3$) was added dropwise to the solution of Dess–Martin periodinane (1.35 g, 3.18 mmol) in dry $CH_2Cl_2$ (10 $cm^3$). The reaction mixture was stirred for 0.5 h at room temperature. The resulting mixture was diluted with diethyl ether, and poured into saturated aq. $NaHCO_3$ containing $Na_2S_2O_4$. The ethereal layer was separated and extracted twice with diethyl ether. The combined extracts were washed successively with saturated aq. $NaHCO_3$ and water. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (3:1)] gave *acyloin* **22** (382 mg, 78%) as an oil (Found: $M^+$, 232.1099. $C_{14}H_{16}O_3$ requires M, 232.1099); $\nu_{max}$(neat)/$cm^{-1}$ 3400 (OH), 1720 (C=O) and 890 (furan); $\delta_H$ 7.34 (1 H, s, 1-H), 7.25–7.26 (1 H, m, 3-H), 6.48 (1 H, d, $J_{8B,9}$ 2.3, 9-H), 2.98 (1 H, dd, $J_{4B,3}$ 2.0, $J_{4A,4B}$ 16.5, 4-$H^B$), 2.89 (1 H, d, $J_{4A,4B}$ 16.5, 4-$H^A$), 2.74 (1 H, d, $J_{6A,6B}$ 13.2, 6-$H^A$), 2.65 (1 H, d, $J_{8A,8B}$ 14.4, 8-$H^A$), 2.53 (1 H, br s, OH), 2.30 (1 H, dd, *J* 2.0, $J_{6A,6B}$ 13.2, 6-$H^B$), 2.16 (1 H, dd, *J* 1.7, $J_{8A,8B}$ 14.4, 8-$H^B$), 1.12 (3 H, s, 7-Me) and 0.93 (3 H, s, 7-Me); $\delta_C$ 209.8 (s, C-5), 138.7 (d, C-1), 136.9 (d, C-3), 136.7 (s, C-8a), 120.2 (s, C-9a), 119.0 (d, C-9), 116.3 (s, C-3a), 74.3 (s, C-4a), 50.3 (t, C-6), 44.2 (t, C-4), 34.5 (s, C-7), 30.8 (q, 7-Me), 27.7 (t, C-8) and 26.9 (q, 7-Me); *m/z* [(+)FAB] 232 ($M^+$, 36%) and 215 (100).

**(4a*SR*,5*RS*)-4,4a,5,6,7,8-Hexahydro-7,7-dimethylnaphtho-[2,3-*c*]furan-4a,5-diol 3a**

Zinc borohydride [$Zn(BH_4)_2$] was prepared according to Gensler's procedure.[12] To a solution of acyloin **22** (107 mg, 0.46 mmol) in dry diethyl ether (7 $cm^3$) was added the reagent (~1.34 M solution in diethyl ether; 5.1 $cm^3$, 0.69 mmol) at −100 °C. The reaction mixture was stirred for 0.5 h at the same temperature. The resulting mixture was warmed to room temperature, quenched with saturated aq. $NH_4Cl$, and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (3:2)] gave diols **3a** (98.1 mg, 91%) and **3b** (7.4 mg, 7%); cis-*diol* **3a**: crystals, mp 128–129 °C (Found: $M^+$, 234.1256. $C_{14}H_{18}O_3$ requires M, 234.1256); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3550 (OH) and 880 (furan); $\delta_H$ 7.27 (1 H, s, 1-H), 7.19 (1 H, d, *J* 1.0, 3-H), 6.31 (1 H, d, *J* 2.3, 9-H), 3.68 (1 H, dd, $J_{5,6B}$ 6.9, $J_{5,6A}$ 9.9, 5-H), 3.20 (1 H, d, $J_{4A,4B}$ 17.0, 4-$H^A$), 2.79 (1 H, dd, $J_{3,4B}$ 2.0, $J_{4A,4B}$ 17.0, 4-$H^B$), 2.43 (1 H, d, $J_{8A,8B}$ 14.2, 8-$H^A$), 2.13 (2 H, br s, OH), 1.92 (1 H, d, $J_{8A,8B}$ 14.2, 8-$H^B$), 1.56–1.67 (2 H, m, 6-$H_2$), 1.02 (3 H, s, 7-Me) and 0.89 (3 H, s, 7-Me); $\delta_C$ 138.0 (d, C-1), 137.7 (s, C-8a), 136.3 (d, C-3), 120.7 (s, C-9a), 117.6 (d, C-9), 117.2 (s, C-3a), 74.1 (d, C-5), 71.6 (s, C-4a), 44.5 (t, C-4 or -6), 43.9 (t, C-6 or -4), 31.7 (q, 7-Me), 31.7 (s, C-7), 31.2 (t, C-8) and 24.9 (q, 7-Me); *m/z* [(+)FAB] 234 ($M^+$, 42%) and 217 (100).

**5,6,7,7a-Tetrahydro-6,6-dimethylazuleno[5,6-*c*]furan-8(9*H*)-one 2a**

To a solution of compound **3a** (23.1 mg, 0.099 mmol) in dry pyridine (2 $cm^3$) were added 4-(dimethylamino)pyridine (2.4 mg, 0.02 mmol) and toluene-*p*-sulfonyl chloride (56 mg, 0.30 mmol). The whole was stirred for 4 h at room temperature. The resulting mixture was poured into water and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (15:1)] gave title compound **2a** (13.6 mg, 64%) and αβ-enone **2b** (1.1 mg, 2%) as an oil; βγ-*enone* **2a** (Found: $[M + H]^+$, 217.1227. $C_{14}H_{17}O_2$ requires *m/z*, 217.1229); $\nu_{max}$($CH_3Cl_3$)/$cm^{-1}$ 1700 (C=O) and 870 (furan); $\delta_H$ 7.36 (1 H, s, 3-H), 7.28 (1 H, d, $J_{1,9B}$ 1.7, 1-H), 6.48 (1 H, d, *J* 0.7, 4-H), 3.74 (1 H, d, $J_{9A,9B}$ 19.0, 9-$H^A$), 3.56 (1 H, t, $J_{7,7a}$ 8.4, 7a-H), 3.39 (1 H, dt, $J_{1,9B}$ 1.7, $J_{9A,9B}$ 19.0, 9-$H^B$), 2.14–2.29 (3 H, m, 7-$H^B$ and 5-$H_2$), 1.59 (1 H, ddd, *J* 1.7, $J_{7,7a}$ 8.4, $J_{7A,7B}$ 13.2, 7-$H^A$), 1.11 (3 H, s, 6-Me) and 0.93 (3 H, s, 6-Me); $\delta_C$ 207.1 (s, C-8), 143.1 (s, C-4a), 139.7 (d, C-3), 138.9 (d, C-1), 123.8 (s, C-3a), 117.8 (s, C-9a), 113.6 (d, C-4), 55.1 (d, C-7a), 48.6 (t, C-9), 40.3 (t, C-7), 39.2 (t, C-5), 37.6 (s, C-6), 28.0 (q, 6-Me) and 27.1 (q, 6-Me); *m/z* [(+)FAB] 217 ($[M + H]^+$, 100%).

**4,5,6,7-Tetrahydro-6,6-dimethylazuleno[5,6-*c*]furan-8(9*H*)-one 2b**

To a solution of crude βγ-enone **2a** derived from diol **3a** (93.9 mg, 0.40 mmol) in dry pyridine (3.0 $cm^3$) was added triethylamine (0.06 $cm^3$, 0.40 mmol) at room temperature. After being stirred for 12 h at the same temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (8:1)] gave *title ketone* **2b** (30.6 mg, 35% from **3a**) as an oil (Found: $[M + H]^+$, 217.1227. $C_{14}H_{17}O_2$ requires *m/z*, 217.1229); $\nu_{max}$(neat)/$cm^{-1}$ 1650 and 1610 (conj. C=O) and 870 (furan); $\delta_H$ 7.24 (1 H, s, 1- or 3-H), 7.22 (1 H, s, 3- or 1-H), 3.65 (2 H, s, 9-$H_2$), 3.44 (2 H, s, 4-$H_2$), 2.54 (2 H, br s, 7-$H_2$), 2.47 (2 H, t, *J* 2.0, 5-$H_2$) and 1.08 (6 H, s, 2 × 6-Me); $\delta_C$ 194.3 (s, C-8), 155.4 (s, C-7a), 139.4 (d, C-1 or -3), 138.2 (d, C-3 or -1), 136.9 (s, C-4a), 122.7 (s, C-3a or -9a), 118.7 (s, C-9a or -3a), 56.1 (t, C-9), 48.2 (t, C-4), 40.1 (t, C-7), 35.5 (s, C-6), 29.4 (q, 6-Me) and 26.7 (t, C-5); *m/z* [(+)FAB] 217 ($[M + H]^+$, 100%).

**4,5,6,7,8,9-Hexahydro-6,6,8-trimethylazuleno[5,6-*c*]furan-8-ol 23**

The organocerium reagent was prepared according to Imamoto's procedure from methyllithium (1.06 M solution in diethyl ether; 0.14 $cm^3$, 0.14 mmol) and cerium(III) chloride heptahydrate (55.9 mg, 0.15 mmol).[10] A solution of compound **2b** (15.5 mg, 0.072 mmol) in dry tetrahydrofuran (THF) (1.0 $cm^3$) was added dropwise to a solution of organocerium reagent in THF at −78 °C. After being stirred for 1 h at the same temperature, the reaction mixture was warmed to room temperature, quenched with saturated aq. $NH_4Cl$, and filtered through Celite. The filtrate was extracted with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (5:1)] gave *alcohol* **23** (13.2 mg, 79%) as an oil (Found: $M^+$, 232.1469. $C_{15}H_{20}O_2$ requires M, 232.1463); $\nu_{max}$(neat)/$cm^{-1}$ 3400 (OH) and 860 (furan); $\delta_H$ 7.27 (1 H, s, 1- or 3-H), 7.15 (1 H, s, 3- or 1-H), 3.11 (2 H, br s, 4-$H_2$), 2.85 (2 H, s, 9-$H_2$), 2.24–2.44 (4 H, m, 5- and 7-$H_2$), 1.62 (1 H, br s, OH), 1.27 (3 H, s, 8-Me), 1.06 (3 H, s, 6-Me) and 1.04 (3 H, s, 6-Me); $\delta_C$ 140.2 (d, C-1 or -3), 138.5 (s, C-7a), 137.6 (d, C-1 or -3), 131.9 (s, C-4a), 124.2 (s, C-3a or -9a), 121.8 (s, C-9a or -3a), 71.1 (s, C-8), 55.1 (t, C-9), 49.2 (t, C-4), 37.6 (t, C-7), 35.3 (s, C-6), 29.3 (q, 6-Me), 29.3 (q, 6-Me), 27.5 (q, 8-Me) and 24.8 (t, C-5); *m/z* [(+)FAB] 232 ($M^+$, 49%) and 215 (100).

**(7a*SR*,8*SR*)-5,6,7,7a,8,9-Hexahydro-6,6,8-trimethylazuleno-[5,6-*c*]furan-8-ol (furoscrobiculin B: 1) and (7a*SR*,8*RS*)-5,6,7,7a,8,9-hexahydro-6,6,8-trimethylazuleno[5,6-*c*]furan-8-ol (*epi*-furoscrobiculin B: 24)**

To a solution of alcohol **23** (44.0 mg, 0.19 mmol) in dry DMF (2.0 $cm^3$) was added potassium *tert*-butoxide (42 mg, 0.38 mmol). The reaction mixture was stirred overnight at room temperature. The resulting mixture was diluted with diethyl ether, poured into water, and extracted three times with diethyl ether. The combined extracts were washed with brine. After removal of the solvent *in vacuo*, purification of the residue by flash column chromatography [hexane–ethyl acetate (5:1)] gave furoscrobiculin B **1** (23.3 mg, 53%) and *epi*-furoscrobiculin B **24** (6.6 mg, 15%); furoscrobiculin B **1** (lit.,[11]) as a viscous oil

(Found: $M^+$, 232.1459. Calc. for $C_{15}H_{20}O_2$: M, 232.1463); $\nu_{max}$(neat)/cm$^{-1}$ 3400 (OH) and 890 (furan); $\delta_H(C_6D_6)$ 7.02 (1 H, s, 3-H), 6.90 (1 H, s, 1-H), 5.97 (1 H, d, *J* 2.3, 4-H), 2.95–3.03 (1 H, br m, 7a-H), 2.70 (2 H, s, 9-$H_2$), 2.15 (2 H, s, 5-$H_2$), 1.62 (1 H, dd, $J_{7B,7a}$ 7.8, $J_{7A,7B}$ 12.2, 7-$H^B$), 1.46 (1 H, t, $J_{7A,7a} = J_{7A,7B}$ = 12.2, 7-$H^A$), 1.06 (3 H, s, 8-Me), 1.0 (3 H, s, 6-Me), 0.92 (3 H, s, 6-Me); $\delta_C(C_6D_6)$ 142.3 (s, C-4a), 141.2 (d, C-3), 140.6 (d, C-1), 123.9 (s, C-3a), 119.0 (s, C-9a), 112.8 (d, C-4), 71.2 (s, C-8), 55.4 (d, C-7a), 50.4 (t, C-9), 44.0 (t, C-7), 41.6 (t, C-5), 35.8 (s, C-6), 29.2 (q, 6-Me), 27.5 (q, 6-Me) and 20.7 (q, 8-Me); *m/z* [(+)FAB] 232 ($M^+$, 100%) and 215 (81); epi-*furoscrobiculin* B **24** as crystals, mp 67–68 °C (from pentane–diethyl ether) (Found: C, 77.59; H, 8.53. $C_{15}H_{20}O_2$ requires C, 77.54; H, 8.68); $\nu_{max}(CHCl_3)$/cm$^{-1}$ 3550, 3400 (OH) and 860 (furan); $\delta_H(C_6D_6)$ 7.03 (1 H, s, 3-H), 6.92 (1 H, t, $J_{1,9B}$ 2.0, 1-H), 6.03 (1 H, d, *J* 2.0, 4-H), 2.70–2.76 (1 H, m, 7a-H), 2.70 (1 H, dd, $J_{7a,9A}$ 0.66, $J_{9A,9B}$ 15.8, 9-$H^A$), 2.50 (1 H, dd, $J_{1,9B}$ 2.0, $J_{9A,9B}$ 15.8, 9-$H^B$), 2.11 (2 H, s, 5-$H_2$), 1.76 (1 H, t, $J_{7A,7a} = J_{7A,7B}$ = 11.9, 7-$H^A$), 1.45 (1 H, dd, $J_{7B,7a}$ 7.3, $J_{7A,7B}$ 11.9, 7-$H^B$), 1.19 (3 H, s, 8-Me), 0.99 (3 H, s, 6-Me) and 0.88 (3 H, s, 6-Me); $\delta_C(C_6D_6)$ 142.2 (s, C-4a), 142.0 (d, C-3), 140.7 (d, C-1), 123.4 (s, C-3a), 119.2 (s, C-9a), 113.5 (d, C-4), 68.9 (s, C-8), 54.2 (d, C-7a), 50.3 (t, C-9), 44.3 (t, C-7), 40.1 (t, C-5), 35.7 (s, C-6), 29.1 (q, 6-Me), 28.2 (q, 6-Me) and 27.4 (q, 8-Me); *m/z* [(+)FAB] 232 ($M^+$, 100%) and 215 (65).

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