# Stereoselective construction of optically active bicyclo[3.3.0]octenone derivatives based on the Pauson–Khand reaction

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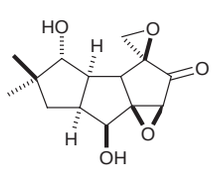
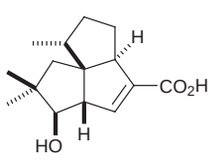
**A new procedure for synthesis of optically active bicyclo[3.3.0]octenone derivatives possessing two distinguishable hydroxy groups was developed based on the intramolecular Pauson–Khand reaction of optically active enynes, which were easily prepared from dimethyl L-tartrate. (4*S*,5*S*)-4,5-Bis(*tert*-butyldimethylsiloxy)-7-(trimethylsilyl)hept-1-en-6-yne, for example, afforded (5*S*,7*S*,8*S*)-7,8-bis(*tert*-butyldimethylsiloxy)-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one exclusively, whereas (3*S*,4*S*)-3,4-dihydroxy-7-(trimethylsilyl)hept-1-en-6-yne produced (5*R*,6*S*,7*S*)-6,7-dihydroxy-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one in a highly stereoselective manner.**

## Introduction

Triquinane sesquiterpenes can be mainly divided into two groups, the linear and the angular, on the basis of the fusion pattern of three five-membered rings.[1] Coriolin is a representative compound of the former group, and the basic carbon framework of pentalenic acid exhibits the structure of typical angular sesquiterpenes. An optically active bicyclo[3.3.0]octane nucleus can be regarded as the common structural feature of these two types of triquinane sesquiterpenes. Therefore, much effort[2] has so far been devoted to development of efficient and stereoselective synthesis of the bicyclo[3.3.0]octane framework with suitable functionalities.

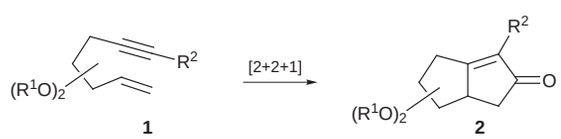


Coriolin



Pentalenic Acid

The Pauson–Khand reaction,[3] a formal [2+2+1] cyclisation of three components (alkyne moiety, olefin portion and carbon monoxide), is well known to be one of the most powerful methods for the construction of cyclopentenone derivatives. During the course of our programme directed towards the development of stereoselective carbon–carbon bond-formation reactions mediated by alkyne-dicobalthexacarbonyl complexes,[4] we envisaged that intramolecular Pauson–Khand reaction of optically active enyne derivatives such as **1** possessing an ether functionality at the propynyl or allylic position would stereoselectively afford the corresponding optically active bicyclo[3.3.0]octenone derivatives **2** (Scheme 1). By taking



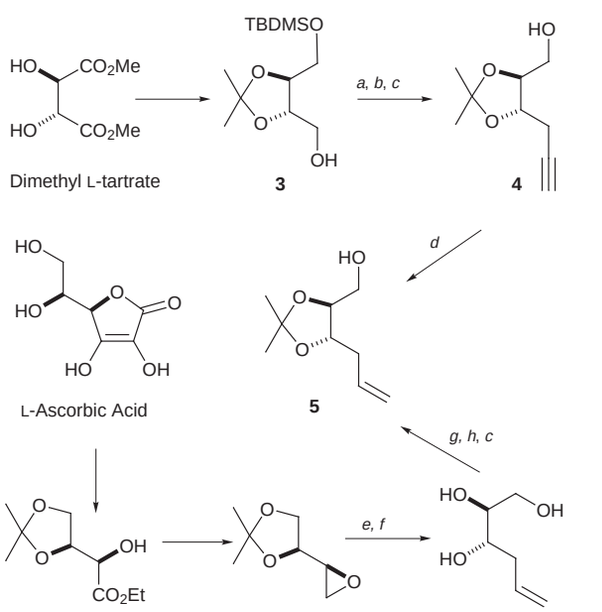
**Scheme 1**

compounds **2** as the key intermediate, both types of triquinane sesquiterpenes would be synthesised in an optically active form. We describe here a highly diastereoselective construction of optically active bicyclo[3.3.0]octenone derivatives *via* intramolecular Pauson–Khand reaction.

## Results and discussion

### Intramolecular Pauson–Khand reaction of (4*S*,5*S*)-4,5-bis-(oxygenated)-hept-1-en-6-yne derivatives[5]

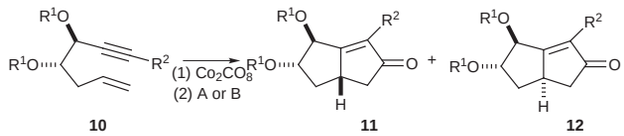
At the inception of this programme, dimethyl L-tartrate was taken as a starting material for the preparation of starting optically active enyne derivatives (Scheme 2). Treatment of



**Scheme 2** *Reagents*: *a*, $Tf_2O$, $Et_3N$; *b*, LiC≡CTMS, THF; *c*, TBAF; *d*, $H_2$, Lindlar cat.; *e*, $CH_2$=$CHMgBr$, CuI; *f*, conc. HCl, MeOH; *g*, TBDMSCl, $Et_3N$, DMAP; *h*, $Me_2C(OMe)_2$, PPTS

alcohol **3**, derived from dimethyl L-tartrate according to Kibayashi's procedure,[6] with triflic anhydride gave the corresponding triflate,[7] which was subsequently exposed to lithium (trimethylsilyl)acetylide[8] at −20 °C to provide, after desilylation with TBAF, ynol **4** in 47% yield. Half-reduction of the triple

**Table 1** Pauson–Khand reaction of compounds **10**




**a**; $R^1 = R^2 = H$ **b**; $R^1 = H$, $R^2 = Ph$ **c**; $R^1 = H$, $R^2 = Bu$ **d**; $R^1 = H$, $R^2 = TMS$
**e**; $R^1 = TBDMS$, $R^2 = H$ **f**; $R^1 = TBDMS$, $R^2 = Ph$ **g**; $R^1 = TBDMS$, $R^2 = Bu$
**h**; $R^1 = TBDMS$, $R^2 = TMS$ **i**; $R^1 = Ac$, $R^2 = H$ **j**; $R^1 = Ac$, $R^2 = Ph$
**k**; $R^1 = Ac$, $R^2 = Bu$ **l**; $R^1 = Ac$, $R^2 = TMS$

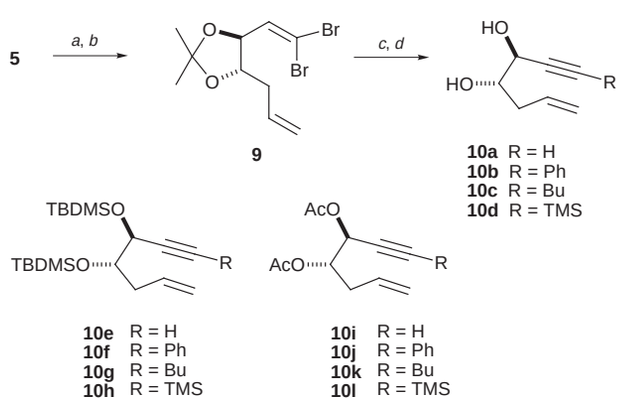
| Entry | Substrate | $R^1$ | $R^2$ | Condition | Product (ratio)[a] **11:12** | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **10b** | H | Ph | A | 81:19 | 57 |
| 2 | **10b** | H | Ph | B | 92:8 | 84 |
| 3 | **10c** | H | Bu | A | 84:16 | 68 |
| 4 | **10c** | H | Bu | B | 83:17 | 70 |
| 5 | **10d** | H | TMS | A | 100:0 | 62 |
| 6 | **10d** | H | TMS | B | — | 0[d] |
| 7 | **10e** | TBDMS | H | A | 50:50[c] | 92 |
| 8 | **10e** | TBDMS | H | B | 45:55[c] | 69 |
| 9 | **10f** | TBDMS | Ph | A | 83:17[c] | 89 |
| 10 | **10f** | TBDMS | Ph | B | 92:8[c] | 85 |
| 11 | **10g** | TBDMS | Bu | A | 90:10[c] | 80 |
| 12 | **10g** | TBDMS | Bu | B | 96:4[c] | 84 |
| 13 | **10h** | TBDMS | TMS | A | 100:0[c] | 93 |
| 14 | **10h** | TBDMS | TMS | B | 100:0[c] | 6[e] |
| 15 | **10i** | Ac | H | A | 76:24 | 60 |
| 16 | **10i** | Ac | H | B | 65:35 | 86 |
| 17 | **10j** | Ac | Ph | A | 87:13 | 96 |
| 18 | **10j** | Ac | Ph | B | 88:12 | 98 |
| 19 | **10k** | Ac | Bu | A | 88:12 | 98 |
| 20 | **10k** | Ac | Bu | B | 91:9 | 96 |
| 21 | **10l** | Ac | TMS | A | 100:0 | 86 |
| 22 | **10l** | Ac | TMS | B | 100:0 | 30[f] |

Condition A: (i) $Co_2CO_8$, (ii) $CH_3CN$, 70–75 °C. Condition B: (i) $Co_2CO_8$, (ii) THF, TMANO, rt.
[a] Ratio between products **11** and **12** was determined on the basis of $^1H$ NMR spectral analysis. [b] Total yield of compounds **11** and **12**. [c] Compounds **11** and **12** could be isolated in pure form. Ratio indicated refers to isolated amounts of each isomer. [d] The starting material **10d** was recovered (35%). [e] The starting material **10h** was recovered (34%). [f] The starting material **10l** was recovered (51%).

bond of compound **4** was undertaken in the presence of Lindlar catalyst to give enol **5** in 88% yield. An alternative procedure was also developed starting from commercially available L-ascorbic acid. According to Abushanab's method,[9] ethyl ester **6** derived from L-ascorbic acid was reduced with LAH to give the diol, which was subsequently converted into the known epoxide **7**[9] under Mitsunobu conditions. Ring opening of the epoxy functionality in epoxide **7** was realised by Grignard reaction with vinylmagnesium bromide in the presence of copper(I) iodide to afford, after acid treatment, enetriol **8** in 80% overall yield. Protection of the primary alcohol of triol **8** with TBDMSCl was followed by successive acetonisation and desilylation to furnish compound **5** in 88% yield.

Introduction of an alkyne moiety was performed according to Corey's procedure[10] (Scheme 3). Primary alcohol **5** was oxidised under Swern conditions to give the aldehyde, which was treated with triphenylphosphine and carbon tetrabromide to leave the dibromoolefin **9** in 79% yield. Treatment of dibromide **9** with *n*-butyllithium effected conversion of the dibromoolefin moiety into a triple bond to provide, after deketalisation, the alkyne derivative **10a** in 75% yield. The other eleven enyne derivatives **10b–l** for intramolecular Pauson–Khand cyclisation were prepared from compound **10a** as a common synthetic intermediate by conventional means (see Experimental section).

The Pauson–Khand reaction was investigated under two different conditions. Treatment of a compound **10** with dicobaltoctacarbonyl [$Co_2(CO)_8$] in methylene dichloride at room

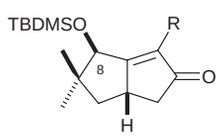



**Scheme 3** *Reagents*: *a*, $(COCl)_2$, DMSO, $Et_3N$; *b*, $PPh_3$, $CBr_4$; *c*, BuLi, 0 °C; *d*, conc. HCl, MeOH

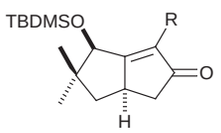
temperature (rt) gave the corresponding cobalt-complexed derivative. This complex was then heated in acetonitrile at 70–75 °C (condition A)[11] or exposed to trimethylamine *N*-oxide (TMANO) at rt (condition B).[12] The results obtained are summarised in Table 1. In the case of compound **10a**, cobalt-complexed **10a** provided two new products under both A and B conditions in a ratio of ~1:1 (monitored by TLC), but these cyclised products could not be isolated, presumably due to their instability. On exposure to thermal conditions (condition A), however, phenyl derivative **10b** afforded cyclised products **11b** and **12b** in a stereoselective manner (**11b**:**12b** = 81:19) in

57% yield (entry 1). Highly stereoselective formation of product **11b** over isomer **12b** (92 : 8) was observed under condition B (entry 2). Similar selectivity and chemical yield were obtained when compound **10c** was treated under conditions A and B (entries 3,4). In addition, exclusive formation of compound **11d** in 62% yield could be attained in the case of substrate **10d** under thermal conditions (entry 5). Treatment of cobalt-complexed compound **10d** with TMANO led to decomplexation to leave the starting **10d** in 35% yield (entry 6). In a series of TBDMS derivatives **10e**–**h** (entries 7–14), compounds **11** were formed predominantly except for the case of compound **10e** ($R^2$ = H; entries 7,8) where products **11e** and **12e** were obtained nonselectively. Similar behaviour was recorded when acetoxy derivatives **10i**–**l** were submitted to intramolecular Pauson–Khand conditions (entries 15–22), although moderately preferential formation of isomer **11i** over isomer **12i** was observed in the case of substrate **10i** ($R^2$ = H, entries 15,16).

Structures of cyclised products **11** and **12** were determined by comparison of $^1$H NMR spectra with the known racemic compounds[13] **13** and **14**, whose structures were unambiguously established by chemical transformation as well as spectral evidence. The C-8 protons of *cis*-bicycles **13a** and **13b** resonate at $\delta$ 4.16 and 4.03, respectively, whereas those of their *trans*-isomers **14a** and **14b** appear at rather lower field ($\delta$ 4.72 and 4.47, respectively) in their $^1$H NMR spectra. These diagnostic differences in chemical shift could be successfully applied to stereochemical assignment of our products **11** and **12**. $^1$H NMR spectra of compounds **11f** and **11g**, for example, show C-8 protons at $\delta$ 4.59 and 4.45, while C-8 protons of the corresponding isomers **12f** and **12g** appear at $\delta$ 4.88 and 4.75 in their $^1$H NMR spectra.



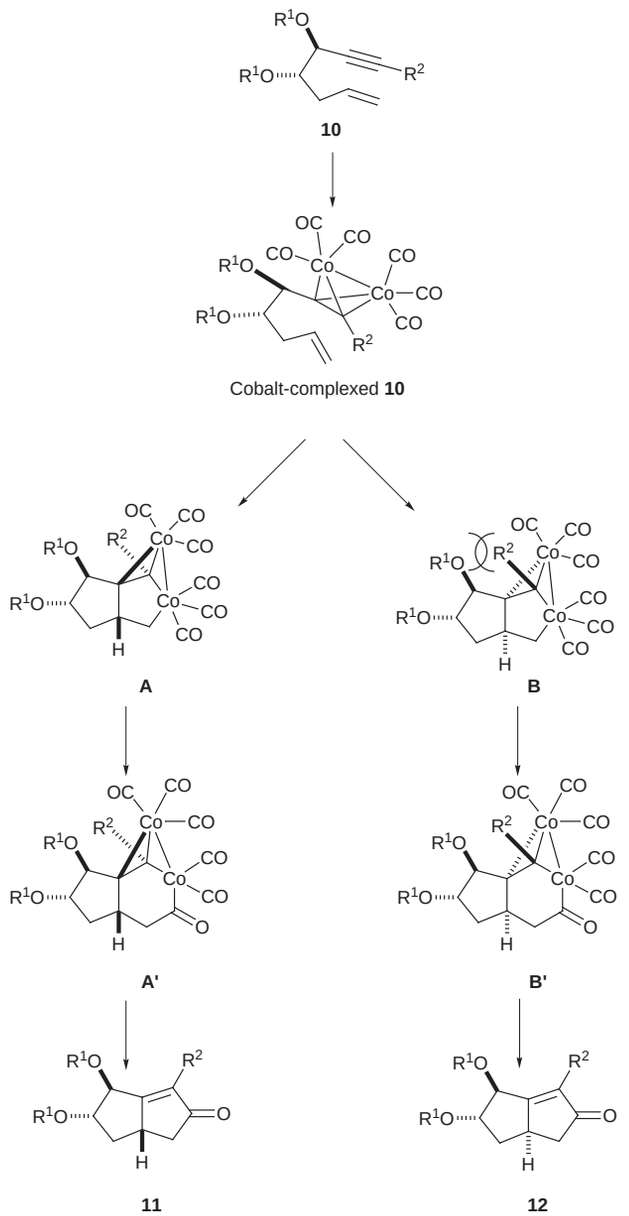

**13a** R = TMS
**13b** R = Me




**14a** R = TMS
**14b** R = Me

Several significant features deserve comment. Enyne derivatives having a substituent at the acetylenic terminus constantly produced the corresponding isomer **11** in a diastereoselective fashion. Although moderate selectivity was observed as aforementioned in the case of substrate **10i** ($R^1$ = Ac, $R^2$ = H), a substituent at the acetylenic terminus seems to be mandatory for high stereoselectivity in this Pauson–Khand reaction. In particular, a considerably bulky terminal substituent like the TMS group completely governs the stereochemical outcome under thermal conditions (condition A in Table 1), resulting in exclusive formation of products **11d**,**h**,**l**. This observation is in good accord with the results obtained by Magnus[13,14] during a series of studies on the intramolecular Pauson–Khand reaction. Interestingly, TMS derivatives **10d**,**h**,**l** afforded mainly starting materials along with small amounts of cyclised products when exposed to TMANO (condition B; entries 6, 14, 22). It should be mentioned that although compounds **10a**,**e**,**i** without any substituents at the triple bond terminus gave the cyclised products nonselectively this is actually not a serious drawback to this cyclisation, since the terminal TMS group of these enynes can serve as a surrogate for the acetylenic hydrogen. Bulky substituents on the two hydroxy groups of substrates **10** were found not always to affect significantly the degree of stereoselectivity in the formation of products **11**. It is, however, obvious that the most bulky TBDMS group on these two hydroxy groups constantly provided high stereoselectivity except for the case of substrate **10e**.

Highly preferential formation of compounds **11** over isomers **12** can be tentatively interpreted on the basis of a mechanistic hypothesis for the intramolecular Pauson–Khand reaction as proposed by Magnus[13] (Scheme 4). Cobalt complexation of

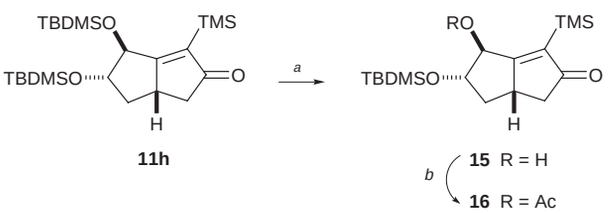



**Scheme 4**

enyne **10** with $Co_2(CO)_8$ gave the corresponding dicobalt-hexacarbonyl-complexed **10**, which would in turn result in formation of two possible cobalt-metallocycles **A** and **B** *via* consecutive ligand exchange between one of six carbon monoxides on the cobalt atoms and the internal olefin moiety, followed by alkene insertion into a carbon–cobalt bond. The intermediate **A** can undergo carbon monoxide insertion to give the second intermediate **A′** which would collapse to compound **11** by the following two steps, (i) migration of a carbon–cobalt bond to an adjacent carbonyl moiety and (ii) reductive elimination of the dicobalt moiety, whereas the intermediate **B** must produce the corresponding second intermediate **B′** which would undertake a similar transformation to afford product **12**. Therefore, the first step (formation of intermediates **A** and **B**) would be considered to be the process determining the reaction's stereochemical outcome. In the cobalt-metallocycle **B**, the C-8 hydroxy functionality ($R^1$O group) at the propynyl position should have a nonbonding interaction with the substituent at

the acetylenic terminus ($R^2$ group) due to a kind of 1,3-pseudo-diaxial relationship in the sterically congested concave face of the transient cobaltabicyclo[3.3.0]octanone skeleton; thereby a seriously unfavourable interaction might occur. This would not be the case in the intermediate **A** where the $R^1O$ group and $R^2$ substituent have a *trans* relationship. As a result, the cyclisation pathway through **A** would be preferred over that through **B**, giving rise to predominant formation of products **11**. These simple analyses, therefore, help us to explain the diastereoselective bias observed in the above intramolecular Pauson–Khand reaction where exclusive or stereoselective construction of products **11** over isomers **12** could be realised. The fact that the bulkier the substituents on the hydroxy group and/or triple bond terminus the higher the diastereoselectivity may reflect an increase of instability of **B** due to nonbonding interaction between the $R^1O$ group and the $R^2$ moiety.[13]

We could develop the procedure for stereoselective construction of optically active bicyclo[3.3.0]octenone derivatives **11** from enynes **10**, which have two distinguishable hydroxy groups at allylic and homoallylic positions. Compound **11h**, for instance, gave the allylic alcohol derivative **15** in 75% yield on treatment with TBAF. Introduction of an acetyl group on the allylic hydroxy group of compound **15** was easily realised under standard conditions to provide acetate **16** in 79% yield as shown in Scheme 5. Thus, compound **11h** would be expected to be an



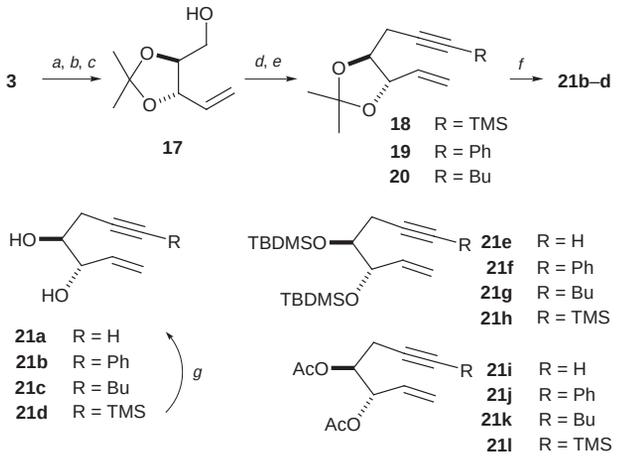

**Scheme 5** *Reagents*: *a*, TBAF, THF; *b*, $Ac_2O$, $Et_3N$, DMAP, $CH_2Cl_2$

important intermediate for further manipulation aiming at synthesis of optically active triquinane sesquiterpene natural products. The next phase of our programme was to investigate the Pauson–Khand reaction of the regioisomers of compound **10**, which would be prepared from the same starting material, dimethyl L-tartrate.

### Intramolecular Pauson–Khand reaction of (3*S*,4*S*)-3,4-bis(oxygenated)-hept-1-en-6-yne derivatives

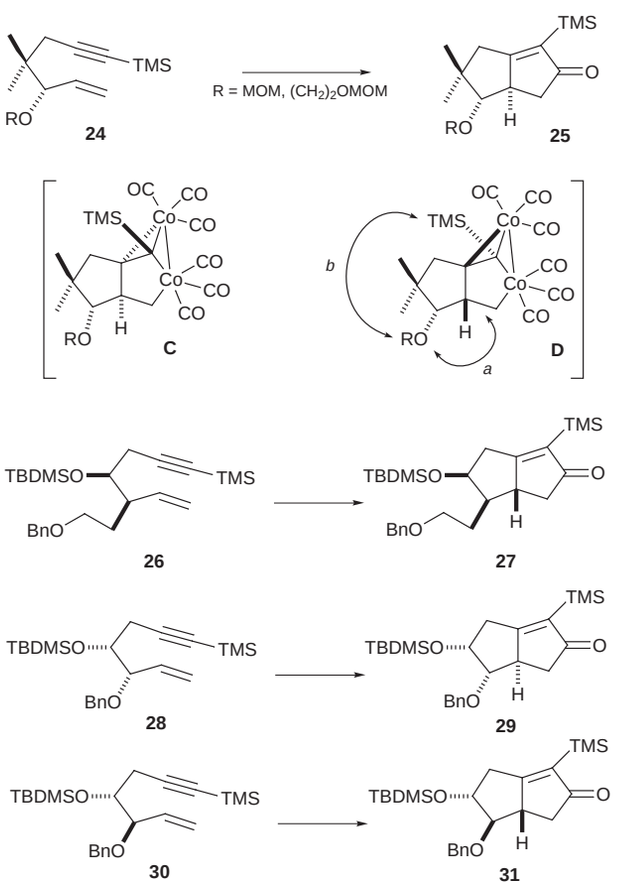
The acetonide derivative **3**,[6] derived from dimethyl L-tartrate, was oxidised under Swern conditions to give the aldehyde, which was then exposed to Wittig reaction with methylidenetriphenylphosphorane to afford, after deprotection with TBAF, the alkene derivative **17** in 80% overall yield. Activation of the hydroxy group of compound **17** as a triflate was followed by displacement with lithium (trimethylsilyl)acetylide[8] to furnish compound **18** in 45% yield. The corresponding phenyl and butyl derivatives **19** and **20** were also prepared from alcohol **17** by changing the nucleophile from lithium (trimethylsilyl)acetylide to lithium phenylacetylide and lithium hexylide, respectively. Deketalisation of compound **18** under conventional conditions gave the dihydroxy derivative **21d** in 97% yield, treatment of which with potassium carbonate in methanol effected removal of the terminal TMS group to afford terminal alkyne **21a** in 83% yield. Compounds **19** and **20** could be easily converted into the corresponding dihydroxy derivatives **21b**,**c**. The TBDMS-protected and acetylated congeners **21e**–**l** as substrates for intramolecular Pauson–Khand reaction were derived from diols **21a**–**d** according to procedures described for the preparation of their regioisomeric analogues **10e**–**l** (Scheme 6; see Experimental section).

Prior to our present investigation, Magnus[13a] disclosed complete control of stereoselectivity in a synthesis of 6-substituted-2-TMS-bicyclo[3.3.0]octenone skeletons by intra-



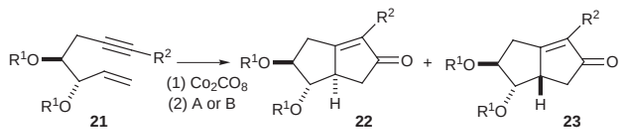

**Scheme 6** *Reagents*: *a*, $(COCl)_2$, DMSO, $Et_3N$; *b*, $Ph_3PCH_2$, THF; *c*, TBAF, THF; *d*, $Tf_2O$, $Et_3N$, $CH_2Cl_2$; *e*, LiC≡CTMS, DMPU, THF; *f*, TsOH, MeOH; *g*, $K_2CO_3$, MeOH

molecular Pauson–Khand reaction where racemic enyne derivatives **24** possessing bulky substituents at the allylic position were found to produce exclusively the corresponding bicyclic compounds **25** in good yields (68 and 78% yield). This high stereochemical bias could be tentatively and understandably explained in terms of the intermediacy of cobalt-metallocycles **C** and **D**.[13] The intermediate **C** leading to product **25** has a *cis* arrangement between the oxygen functionality (OR) and ring-junction hydrogen, and a *trans* alignment with the TMS group as well. In the intermediate **D**, the OR appendage is placed in the concave face and therefore suffers from not only an unfavourable *cis*-1,2-relationship with the carbon–carbon framework of the five-membered metallocyclic ring (interaction *a*), but also a 1,4-pseudo-nonbonding interaction with the TMS group (interaction *b*) as depicted in Scheme 7.




**Scheme 7**

**Table 2** Pauson–Khand reaction of compounds **21**




**a**; $R^1 = R^2 = H$ **b**; $R^1 = H$, $R^2 = Ph$ **c**; $R^1 = H$, $R^2 = Bu$ **d**; $R^1 = H$, $R^2 = TMS$
**e**; $R^1 = TBDMS$, $R^2 = H$ **f**; $R^1 = TBDMS$, $R^2 = Ph$ **g**; $R^1 = TBDMS$, $R^2 = Bu$
**h**; $R^1 = TBDMS$, $R^2 = TMS$ **i**; $R^1 = Ac$, $R^2 = H$ **j**; $R^1 = Ac$, $R^2 = Ph$
**k**; $R^1 = Ac$, $R^2 = Bu$ **l**; $R^1 = Ac$, $R^2 = TMS$

| Entry | Substrate | $R^1$ | $R^2$ | Condition | Product (ratio)[a] **22:23** | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **21b** | H | Ph | A | 60:40[c] | 61 |
| 2 | **21b** | H | Ph | B | 82:18[c] | 75 |
| 3 | **21c** | H | Bu | A | 67:33[c] | 67 |
| 4 | **21c** | H | Bu | B | 94:6[c] | 70 |
| 5 | **21d** | H | TMS | A | 93:7[c] | 74 |
| 6 | **21d** | H | TMS | B | — | 0[d] |
| 7 | **21e** | TBDMS | H | A | 49:51[e] | 84 |
| 8 | **21e** | TBDMS | H | B | 65:35[e] | 81 |
| 9 | **21f** | TBDMS | Ph | A | 43:57[e] | 91 |
| 10 | **21f** | TBDMS | Ph | B | 53:47[e] | 82 |
| 11 | **21g** | TBDMS | Bu | A | 38:62 | 88 |
| 12 | **21g** | TBDMS | Bu | B | 70:30 | 63 |
| 13 | **21h** | TBDMS | TMS | A | 70:30 | 80 |
| 14 | **21h** | TBDMS | TMS | B | 83:17 | 62[f] |
| 15 | **21j** | Ac | Ph | A | 56:44 | 60 |
| 16 | **21j** | Ac | Ph | B | 59:41 | 73 |
| 17 | **21k** | Ac | Bu | A | 52:48 | 85 |
| 18 | **21k** | Ac | Bu | B | 57:43 | 83 |
| 19 | **21l** | Ac | TMS | A | 77:23 | 79 |
| 20 | **21l** | Ac | TMS | B | 67:33 | 57 |

Condition A: (i) $Co_2CO_8$, (ii) $CH_3CN$, 70–75 °C. Condition B: (i) $Co_2CO_8$, (ii) THF, TMANO, rt.
[a] Ratio between products **22** and **23** was determined on the basis of $^1H$ NMR spectral analysis. [b] Total yield of compounds **22** and **23**. [c] Isolated as the corresponding diacetate derivatives **22j–l** and **23j–l**. [d] The starting material **21d** was recovered (49%). [e] Compounds **22** and **23** could be isolated in pure form. Ratio indicated refers to isolated amounts of each isomer. [f] In addition, the starting material **21h** was recovered (29%).

Thus exclusive formation of compounds **25** could be rationalised from the above considerations.[13] Mulzer[15] also reported an exclusive formation of optically active bicyclo[3.3.0]derivative **27** in 43% yield from the optically active enyne **26** having a bulky (benzyloxy)ethyl functionality at the allylic position (Scheme 7). Therefore, we anticipated that Pauson–Khand reaction of the *O*-TBDMS-protected enynes **21f–h** would proceed in a highly stereoselective way to afford products **22f–h** in line with the literature precedents.[13–15]

Pauson–Khand reaction of (3*S*,4*S*)-3,4-bis(oxygenated)-hept-1-en-6-yne derivatives **21** was carried out under two different conditions[11,12] as described for the cyclisation of analogues **10**. The results obtained are presented in Table 2. Contrary to our expectation, however, compounds **21f–h** didn't provide the corresponding bicycles **22f–h** in a stereoselective fashion (entries 9–14). In addition, acetyl derivatives **21j–l** afforded cyclised products nonselectively (entries 15–20). It should be emphasised here that highly preferential construction of compounds **22** over **23** *could* be observed in a series of dihydroxy compounds **21b–d** (entries 1–6). In particular, when compound **21c** with a butyl group at the acetylenic terminus was exposed to condition B, compound **22c** was obtained in a highly stereoselective manner (entry 4, **22c**:**23c** = 94:6). Similar high selectivity (93:7) was recognised in the case of TMS derivative **21d** under condition A (entry 5). Phenyl derivative **21b** also showed high selectivity in production of compound **22b** (entry 2). Compounds **21a** and **21i** ($R^2 = H$) could be converted into the corresponding cobalt-complexed ones, but attempted further conversion into the cyclised products was fruitless presumably due to decomposition of cyclised products during column chromatography. The structures of the cyclised products were determined by spectral evidence and comparison with known compounds[15] whose stereochemistry was already unambiguously established.

Enyne derivatives **21b–d** with the smaller substituent (a free hydroxy group) at the allylic position revealed the higher diastereoselectivity. This phenomenon is in sharp contrast to the prediction based on Magnus' working hypothesis.[13] Enyne **24** (R = H; Scheme 7) had been shown to furnish cyclised products **25** and its C-5 epimer in the ratio 72:28 when submitted to Pauson–Khand conditions. The diastereoselectivity was obviously decreased by changing the allylic substituent from sterically bulkier ones [MOM, $(CH_2)_2OMOM$] to a less bulky one (H). An additional two examples resulting in unsatisfactory selectivity were also disclosed by Mulzer[15] (Scheme 7). Namely, optically active enyne **28** produced the cyclised product **29** in 31% yield under Pauson–Khand conditions in moderate selectivity (**29**: its C-5 epimer = 75:25). Furthermore, optically active enyne **30**, having a very similar relative structure to that of compounds **21**, gave optically active bicycle **31** and its C-5 epimer nonselectively in rather lower yield again. Although these two compounds have the relatively bulky benzyloxy functionality at the allylic position, acceptable stereoselectivity could not be achieved. It is apparent that high stereoselectivity observed in the cases of substrates **21c**, **21d** (and **21b**) (Table 2, entries 4, 5, 2) can never be rationalised by Magnus' working hypothesis[13] alone. The free hydroxy group at the allylic position would play an important role in governing the stereochemical outcome, although details of the mechanism still remain unclear.

Thus a highly stereoselective procedure for syntheses of (5*S*,7*S*,8*S*)-2-substituted-7,8-dioxygenated-bicyclo[3.3.0]oct-1-en-3-one and (5*R*,6*S*,7*S*)-2-substituted-6,7-dihydroxybicyclo-[3.3.0]oct-1-en-3-one derivatives from (4*S*,5*S*)-4,5-dioxygenated-hept-1-en-6-yne and (3*S*,4*S*)-3,4-dihydroxy-6-substituted-hept-1-en-6-yne derivatives, respectively, on the basis of the Pauson-Khand reaction was developed. This method would provide useful starting materials with two distinguishable hydroxy groups as well as an enone moiety for synthesis of optically active triquinane sesquiterpenes. Further studies on the mechanism and application of this methodology to stereoselective construction of bicyclo[4.3.0]nonenone and bicyclo[5.3.0]decenone skeletons are now in progress.

## Experimental

Mps were determined on a Yanagimoto micro melting-point apparatus and are uncorrected. IR spectra were measured with a JASCO A-102 spectrometer for solutions in $CHCl_3$, mass spectra with Hitachi M-80 and JEOL JMS-SX 102 A mass spectrometers, optical rotations with a Horiba SEPA-300 high sensitivity polarimeter, $^1$H NMR spectra with JEOL EX-270 and JEOL JNM-GX 500 spectrometers for solutions in $CDCl_3$ with either tetramethylsilane as an internal standard for compounds that have no silyl group or $CHCl_3$ ($\delta_H$ 7.26) for compounds possessing the silyl group, and $^{13}$C NMR spectra with JEOL EX-270 and JEOL JNM-GX 500 spectrometers for samples in $CDCl_3$ with $CDCl_3$ ($\delta_C$ 77.0) as an internal reference. All *J*-values are in Hz and $[\alpha]_D$-values in $10^{-1}$ deg cm$^2$ g$^{-1}$. $CH_2Cl_2$ was freshly distilled from $P_2O_5$, and THF from sodium/benzophenone prior to use. All reactions were carried out under nitrogen. Silica gel (Silica gel 60, 230–400 mesh, Merck) was used for chromatography. Organic extracts were dried over anhydrous $Na_2SO_4$.

**(2*S*,3*S*)-2,3-(Isopropylidenedioxy)hex-5-yn-1-ol (−)-4**

To a solution of the silyl ether **3** (305 mg, 1.10 mmol) and $Et_3N$ (335 mg, 3.31 mmol) in $CH_2Cl_2$ (13 cm$^3$) was added a solution of trifluoromethanesulfonic anhydride ($Tf_2O$) (466 mg, 1.65 mmol) in $CH_2Cl_2$ (7.0 cm$^3$) at −20 °C. The reaction mixture was stirred for 30 min at the same temperature, washed successively with saturated aq. $NaHCO_3$, water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (10:1) to give the triflate. BuLi in hexane (1.65 mol dm$^{-3}$; 0.67 cm$^3$, 1.10 mmol) was added to a solution of (trimethylsilyl)acetylene (130 mg, 1.32 mmol) in THF (6.0 cm$^3$) at 0 °C. The resulting solution of acetylide in THF was cooled to −20 °C, to which a solution of the crude triflate in a combined solution of THF and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone (DMPU) (12 and 3.0 cm$^3$, respectively) was added. The reaction mixture was stirred for 1 h, quenched by addition of saturated aq. $NH_4Cl$ and extracted with diethyl ether. The extract was washed successively with water and brine, dried and concentrated to dryness. The residue was dissolved in THF (5.0 cm$^3$) and a solution of TBAF in THF (1.00 mol dm$^{-3}$; 2.40 cm$^3$, 2.40 mmol) was added. The reaction mixture was stirred at rt for 1 h and diluted with ethyl acetate and the solution was washed successively with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (5:1) to give *title compound* (−)-**4** (88.0 mg, 47%) as an oil (Found: C, 63.0; H, 8.2. $C_9H_{14}O_3$ requires C, 63.5; H, 8.3%); $[\alpha]_D^{18}$ −3.0 (*c* 0.50, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 3610 (OH), 3480 (OH), 3320 (C≡C–H) and 2100 (C≡C); $\delta_H$ 4.08–3.86 (3 H, m, 1-, 2- and 3-H), 3.71 (1 H, ddd, *J* 11.5, 7.3 and 4.3, 1-H), 2.62 (1 H, ddd, *J* 17.2, 5.0 and 2.6, 4-H), 2.51 (1 H, ddd, *J* 17.0, 6.6 and 2.6, 4-H), 2.07 (1 H, t, *J* 2.6, 6-H), 2.02 (1 H, dd, *J* 7.3 and 5.0, OH), 1.44 (3 H, s, Me) and 1.43 (3 H, s, Me); $\delta_C$ 109.2, 81.0, 79.3, 74.4, 70.9, 62.19, 27.1 and 22.8; *m*/*z* 169 ($M^+$ − 1, 2.1%), 155 (91), 59 (91) and 43 (100).

**(2*S*,3*S*)-2,3-(Isopropylidenedioxy)hex-5-en-1-ol (−)-5**

A suspension of ynol **4** (83 mg, 0.49 mmol) and pyridine (293 mg, 3.70 mmol) in hexane (20 cm$^3$) was hydrogenated in the presence of Lindlar catalyst (23.5 mg) under hydrogen at rt for 2 h. The catalyst was filtered off and the filtrate was concentrated to dryness. Chromatography of the residual oil with hexane–AcOEt (10:1) afforded *title compound* (−)-**5** (74.0 mg, 88%) as an oil (Found: C, 62.5; H, 9.5. $C_9H_{16}O_3$ requires C, 62.8; H, 9.4%); $[\alpha]_D^{26}$ −23.1 (*c* 0.49, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 3610 (OH), 3460 (OH) and 1645 (C=C); $\delta_H$ 5.84 (1 H, ddt, *J* 17.2, 10.2 and 6.9, 5-H), 5.20–5.08 (2 H, m, 6-$H_2$), 4.14–3.54 (4 H, m, 1-$H_2$, 2- and 3-H), 2.42–2.34 (2 H, m, 4-$H_2$), 1.86 (1 H, m, OH), 1.43 (3 H, s, Me) and 1.42 (3 H, s, Me); $\delta_C$ 133.5, 117.8, 108.7, 81.0, 75.8, 61.9, 37.3, 27.3 and 27.0; *m*/*z* 157 ($M^+$ − 15, 87%), 141 (20), 131 (62), 83 (41), 79 (28), 59 (100) and 43 (29).

**(2*S*,3*S*)-Hex-5-ene-1,2,3-triol (−)-8**

To a suspension of copper(I) iodide (351 mg, 1.85 mmol) in THF (30 cm$^3$) was added a solution of vinylmagnesium bromide in THF (0.87 mol dm$^{-3}$; 14 cm$^3$, 1.38 mmol) at −78 °C. After stirring of this mixture for 5 min, a solution of epoxide **7** (877 mg, 6.08 mmol) in THF (10 cm$^3$) was added to the reaction mixture, which was further stirred for an additional hour before being quenched by addition of saturated aq. $NH_4Cl$, and extracted with $Et_2O$ four times. The extracts were washed successively with water and brine, dried and concentrated to dryness. The residue was dissolved in MeOH (60 cm$^3$) to which conc. HCl (4.0 cm$^3$) was added. The reaction mixture was heated under reflux for 3 h. MeOH was evaporated off and the residue was diluted with water, and extracted with AcOEt four times. The extracts were washed with water, dried and concentrated to dryness. Chromatography of the residual oil with AcOEt gave *title compound* (−)-**8** (640 mg, 80%) as an oil (Found: C, 54.0; H, 9.0. $C_6H_{12}O_3$ requires C, 54.5; H, 9.2%); $[\alpha]_D^{25}$ −4.8 (*c* 0.21, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 3390 (OH) and 1645 (C=C); $\delta_H$ 5.85 (1 H, m, 5-H), 5.22–5.12 (2 H, m, 6-$H_2$), 3.83–3.45 (4 H, m, 1-$H_2$, 2- and 3-H), 2.69 (1 H, br s, OH), 2.45–2.15 (4 H, m, 4-$H_2$ and OH); $\delta_C$ 134.3, 118.0, 73.4, 71.6, 64.3 and 38.0; *m*/*z* 132 ($M^+$, 0.6%), 91 (46), 78 (26), 63 (30), 55 (22) and 43 (100).

**Conversion of triol (−)-8 into alcohol (−)-5**

TBDMSCl (991 mg, 6.57 mmol) was added to a solution of triol **8** (825 mg, 6.24 mmol), $Et_3N$ (944 mg, 9.33 mmol) and DMAP (146 mg, 1.20 mmol) in $CH_2Cl_2$ (10 cm$^3$) at rt. After being stirred for 2 h, the reaction mixture was quenched by addition of saturated aq. $NH_4Cl$ and extracted with $CH_2Cl_2$. The extract was washed successively with water and brine, dried and concentrated to leave the crude mono-TBDMS-protected product. This residue was dissolved in acetone (15 cm$^3$) to which 2,2-dimethoxypropane (8.47 g, 81.3 mmol) and PPTS (270 mg, 1.07 mmol) were successively added. The reaction mixture was stirred at rt for 3 h and acetone was evaporated off. A solution of TBAF in THF (1.00 mol dm$^{-3}$; 7.0 cm$^3$, 7.00 mmol) was added to a solution of the residue in THF (15 cm$^3$). After being stirred for 30 min at rt, the reaction mixture was quenched by addition of water and extracted with AcOEt. The extract was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (4:1) afforded alcohol (−)-**5** (949 mg, 88%).

**(3*S*,4*S*)-1,1-Dibromo-3,4-(isopropylidenedioxy)hepta-1,6-diene (−)-9**

A solution of DMSO (1.28 g, 16.3 mmol) in $CH_2Cl_2$ (6.0 cm$^3$) was gradually added to a solution of oxalyl dichloride (1.04 g, 8.16 mmol) in $CH_2Cl_2$ (6.0 cm$^3$) at −78 °C. After stirring of the $CH_2Cl_2$ solution for 15 min, a solution of the alcohol **5** (611 mg, 3.55 mmol) in $CH_2Cl_2$ (6.0 cm$^3$) was added and the reaction mixture was stirred at −78 °C for 1 h. $Et_3N$ (2.16 g, 21.3 mmol) was added to the reaction mixture, which was then gradually

warmed to rt and diluted with $CH_2Cl_2$. The $CH_2Cl_2$ solution was washed successively with water and brine, dried and concentrated to dryness.

To a solution of $PPh_3$ (7.45 g, 28.4 mmol) in $CH_2Cl_2$ (12 $cm^3$) was added a solution of $CBr_4$ (4.71 g, 14.2 mmol) in $CH_2Cl_2$ (12 $cm^3$) at 0 °C and the solution was stirred for an additional 10 min. A solution of the crude aldehyde derived from alcohol **5** in $CH_2Cl_2$ (18 $cm^3$) was then added to a solution of the ylide in $CH_2Cl_2$ at 0 °C and stirring was continued for 3 h at rt. The reaction mixture was quenched by addition of saturated aq. $NaHCO_3$ and extracted with $CH_2Cl_2$, which was washed successively with water and brine, dried and concentrated to dryness. The residual solids were washed with hexane several times and the filtrate was concentrated to leave a residue, which was chromatographed with hexane–AcOEt (40 : 1) to give *dibromide* (−)-**9** (914 mg, 79%) as a pale yellow oil (Found: C, 37.0; H, 4.4. $C_{10}H_{14}Br_2O_2$ requires C, 36.8; H, 4.3%), $[\alpha]_D^{24}$ −3.2 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1645 (C=C) and 1620 (C=C); $\delta_H$ 6.44 (1 H, d, *J* 8.3, 2-H), 5.84 (1 H, ddt, *J* 17.2, 10.2 and 6.9, 6-H), 5.22–5.11 (2 H, m, 7-$H_2$), 4.33 (1 H, t, *J* 8.3, 3-H), 3.86 (1 H, ddd, *J* 8.3, 6.6 and 5.0, 4-H), 2.51–2.32 (2 H, m, 5-$H_2$), 1.42 (3 H, s, Me) and 1.40 (3 H, s, Me); $\delta_C$ 135.5, 133.0, 118.0, 109.6, 94.1, 80.2, 79.2, 40.0, 27.1 and 26.7; *m*/*z* 313 ($M^+$ − 15, 3.3%), 311 ($M^+$ − 15, 6.6), 309 ($M^+$ − 15, 3.5), 258 (16), 96 (49) and 43 (100).

**(3*S*,4*S*)-Hept-6-en-1-yne-3,4-diol (−)-10a**

To a solution of dibromide **9** (205 mg, 0.63 mmol) in dry $Et_2O$ (4.0 $cm^3$) was added BuLi in hexane (1.62 mol $dm^{-3}$; 0.78 $cm^3$, 1.26 mmol) at 0 °C and the reaction mixture was stirred for 30 min before being diluted with MeOH (8.0 $cm^3$), to which conc. HCl (0.5 $cm^3$) was added. The reaction mixture was heated under reflux for 3 h and then MeOH was evaporated off. The residue was taken up with AcOEt, which was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (5 : 1) afforded *diol* (−)-**10a** (58 mg, 75%) as an oil (Found: C, 66.9; H, 7.9. $C_7H_{10}O_2$ requires C, 66.7; H, 8.0%); $[\alpha]_D^{18}$ −11.8 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3590 (OH), 3400 (OH), 3310 (C≡C–H) and 1645 (C=C); $\delta_H$ 5.87 (1 H, ddt, *J* 17.2, 9.6 and 7.6, 6-H), 5.23–5.15 (2 H, m, 7-$H_2$), 4.24 (1 H, dd, *J* 5.9 and 2.0, 3-H), 3.74 (1 H, ddd, *J* 7.9, 5.9 and 4.3, 4-H), 2.60–2.22 (4 H, m, 5-$H_2$ and OH) and 2.52 (1 H, d, *J* 2.0, 1-H); $\delta_C$ 133.7, 118.6, 82.0, 74.6, 73.7, 65.3 and 36.9; *m*/*z* 71 ($M^+$ − 55, 6.2%), 56 (17) and 43 (14).

**(3*S*,4*S*)-1-Phenylhept-6-en-1-yne-3,4-diol (−)-10b**

To a solution of terminal alkyne **10a** (25 mg, 0.20 mmol) and iodobenzene (49 mg, 0.24 mmol) in THF (2.0 $cm^3$) were successively added $Pd(PPh_3)_2Cl_2$ (4.2 mg, $6.0 \times 10^{-3}$ mmol), CuI (2.3 mg, $1.2 \times 10^{-2}$ mmol) and diisopropylamine (203 mg, 2.01 mmol) at rt. The reaction mixture was stirred for 2 h and filtered. The filtrate was concentrated to leave a residual oil, which was chromatographed with hexane–AcOEt (5 : 1) to afford *title compound* (−)-**10b** (34 mg, 84%) as an oil (Found: C, 76.8; H, 7.0. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); $[\alpha]_D^{20}$ −36.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3590 (OH), 3400 (OH) and 2210 (C≡C); $\delta_H$ 7.45–7.40 (2 H, m, ArH), 7.32–7.25 (3 H, m, ArH), 5.90 (1 H, ddt, *J* 16.8, 9.6 and 7.6, 6-H), 5.22–5.11 (2 H, m, 7-$H_2$), 4.45 (1 H, d, *J* 6.6, 3-H), 3.82 (1 H, m, 4-H), 3.32 (1 H, s, OH), 3.01 (1 H, s, OH), 2.57 (1 H, m, 5-H) and 2.34 (1 H, m, 5-H); $\delta_C$ 133.9, 131.7, 128.6, 128.3, 122.1, 118.2, 87.1, 86.5, 74.1, 66.1 and 37.1; *m*/*z* 202 ($M^+$, 1.3%), 158 (18), 132 (48), 115 (25), 104 (24), 77 (33) and 41 (15).

**(4*S*,5*S*)-4,5-Bis(*tert*-butyldimethylsiloxy)hept-1-en-6-yne (−)-10e**

To a solution of diol **10a** (58.5 mg, 0.47 mmol) and $Et_3N$ (291 mg, 2.87 mmol) in $CH_2Cl_2$ (2.0 $cm^3$) was added TBDMSOTf (0.33 $cm^3$, 1.44 mmol) at 0 °C. The reaction mixture was stirred for 20 min at rt, quenched by addition of water, and extracted with $CH_2Cl_2$ four times. The extracts were washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane afforded *title compound* (−)-**10e** (161 mg, 98%) as an oil (Found: C, 64.0; H, 10.9. $C_{19}H_{38}O_2Si_2$ requires C, 64.3; H, 10.8%); $[\alpha]_D^{20}$ −8.1 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3310 (C≡C–H) and 1645 (C=C); $\delta_H$ 5.86 (1 H, ddt, *J* 17.2, 9.9 and 7.3, 2-H), 5.13–5.01 (2 H, m, 1-$H_2$), 4.31 (1 H, dd, *J* 5.3 and 2.3, 5-H), 3.62 (1 H, ddd, *J* 7.6, 5.3 and 4.0, 4-H), 2.54–2.29 (2 H, m, 3-$H_2$), 2.35 (1 H, d, *J* 2.3, 7-H), 0.91 (9 H, s, $^t$Bu), 0.89 (9 H, s, $^t$Bu), 0.14 (3 H, s, Me), 0.10 (3 H, s, Me), 0.06 (3 H, s, Me) and 0.05 (3 H, s, Me); $\delta_C$ 135.6, 116.9, 83.1, 74.8, 73.4, 66.7, 36.8, 25.8, 25.8, 18.2, 18.1, −4.5, −4.7 and −4.9; *m*/*z* 354 ($M^+$, 29%), 313 (13), 297 (89), 189 (21), 147 (99), 115 (21), 91 (30) and 73 (100).

**(4*S*,5*S*)-4,5-Bis(*tert*-butyldimethylsiloxy)-7-phenylhept-1-en-6-yne (−)-10f**

According to the procedure described for preparation of compound **10e** from diol **10a**, compound **10b** (96 mg, 0.48 mmol) was treated with TBDMSOTf (0.24 $cm^3$, 1.05 mmol) and $Et_3N$ (218 mg, 2.15 mmol) to give *title compound* (−)-**10f** (200 mg, 98%) as an oil (Found: $M^+$, 430.2711. $C_{23}H_{42}O_2Si_2$ requires *M*, 430.2723); $[\alpha]_D^{20}$ −10.2 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1640 (C=C); $\delta_H$ 7.43–7.38 (2 H, m, ArH), 7.32–7.27 (3 H, m, ArH), 5.91 (1 H, ddt, *J* 17.2, 9.9 and 7.3, 2-H), 5.13–5.03 (2 H, m, 1-H), 4.53 (1 H, d, *J* 5.3, 5-H), 3.72 (1 H, ddd, *J* 7.3, 5.3 and 4.3, 4-H), 2.58–2.36 (2 H, m, 3-$H_2$), 0.94 (9 H, s, $^t$Bu), 0.91 (9 H, s, $^t$Bu), 0.19 (3 H, s, Me), 0.14 (3 H, s, Me), 0.09 (3 H, s, Me) and 0.08 (3 H, s, Me); $\delta_C$ 135.6, 131.5, 128.2, 128.0, 123.3, 116.8, 89.0, 85.4, 75.2, 67.3, 37.3, 25.9, 18.3, 18.1, −4.4, −4.5 and −4.7; *m*/*z* 430 ($M^+$, 56%), 373 (39), 185 (100), 147 (49), 115 (14) and 73 (62).

**(4*S*,5*S*)-4,5-Bis(*tert*-butyldimethylsiloxy)undec-1-en-6-yne (−)-10g**

To a solution of terminal alkyne **10e** (385 mg, 1.09 mmol) in THF (5.0 $cm^3$) was added BuLi in hexane (1.60 mol $dm^{-3}$; 0.81 $cm^3$, 1.30 mmol) at 0 °C. After being stirred at the same temperature for 30 min, a solution of butyl iodide (602 mg, 3.27 mmol) in a combined solution of THF and DMPU (1.0 and 1.0 $cm^3$, respectively) was added to the reaction mixture, which was then stirred for 9 h at rt, quenched by addition of saturated aq. $NH_4Cl$ and extracted with $Et_2O$. The extract was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane afforded *title compound* (−)-**10g** (322 mg, 72%) as an oil (Found: C, 66.9; H, 11.3. $C_{23}H_{46}O_2Si_2$ requires C, 67.3; H, 11.3%); $[\alpha]_D^{24}$ −5.5 (*c* 0.20, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2220 (C≡C) and 1645 (C=C); $\delta_H$ 5.88 (1 H, ddt, *J* 17.2, 10.2 and 7.3, 2-H), 5.10–4.99 (2 H, m, 1-$H_2$), 4.29 (1 H, dt, *J* 5.3 and 2.0, 5-H), 3.60 (1 H, ddd, *J* 7.6, 5.3 and 4.3, 4-H), 2.50–2.28 (2 H, m, 3-$H_2$), 2.20 (2 H, dt, *J* 6.6 and 2.0, 8-$H_2$), 1.51–1.35 (4 H, m, 9- and 10-$H_2$), 0.94–0.86 (21 H, m, $^t$Bu × 2 and Me), 0.12 (3 H, s, Me), 0.09 (3 H, s, Me), 0.06 (3 H, s, Me) and 0.05 (3 H, s, Me); $\delta_C$ 136.0, 116.5, 85.8, 79.3, 75.3, 67.0, 37.1, 30.7, 25.9, 25.9, 21.9, 18.4, 18.3, 18.1, 13.6, −4.4, −4.5, −4.5 and −4.7; *m*/*z* 410 ($M^+$, 30%), 353 (40), 185 (84), 147 (87), 115 (17) and 73 (84).

**(4*S*,5*S*)-4,5-Bis(*tert*-butyldimethylsiloxy)-1-(trimethylsilyl)hept-1-en-6-yne (−)-10h**

According to the procedure described for preparation of compound **10g** and terminal alkyne **10e**, the same substrate **10e** (385 mg, 1.09 mmol) was successively treated with BuLi in hexane (1.60 mol $dm^{-3}$; 0.81 $cm^3$, 1.30 mmol) and TMSCl (237 mg, 2.18 mmol) to give, after chromatography with hexane, *title compound* (−)-**10h** (451 mg, 97%) as an oil (Found: $M^+$, 426.2818. $C_{22}H_{46}O_2Si_3$ requires *M*, 426.2806); $[\alpha]_D^{25}$ −1.0 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2160 (C≡C) and 1640 (C=C); $\delta_H$ 5.86 (1 H, ddt, *J* 17.2, 9.9 and 7.3, 2-H), 5.11–5.00 (2 H, m, 1-H), 4.28 (1 H, d, *J* 5.3, 5-H), 3.62 (1 H, m, 4-H), 2.50–2.28 (2 H, m,

3-$H_2$), 0.91 (9 H, s, $^t$Bu), 0.89 (9 H, s, $^t$Bu), 0.15 (9 H, s, TMS), 0.13 (3 H, s, Me), 0.10 (3 H, s, Me), 0.06 (3 H, s, Me) and 0.05 (3 H, s, Me); $\delta_C$ 136.6, 116.8, 105.5, 90.2, 74.9, 67.1, 37.3, 25.9, 25.8, 18.3, 18.1, −0.2, −4.4, −4.4, −4.5 and −4.6; *m*/*z* 426 ($M^+$, 19%), 369 (33), 147 (79), 115 (17) and 73 (98).

**(4*S*,5*S*)-Undec-1-en-6-yne-4,5-diol (−)-10c**

A solution of compound **10g** (86 mg, 0.21 mmol) and PTSA (40 mg, 0.23 mmol) in MeOH (4.0 $cm^3$) was stirred for 9 h at rt. The reaction mixture was concentrated to leave a residual oil, which was chromatographed with hexane–AcOEt (3:1) to afford *title diol* (−)-**10c** (39 mg, 100%) as an oil (Found: C, 72.1; H, 10.1. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%); $[\alpha]_D^{20}$ −20.0 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3600 (OH), 3410 (OH), 2220 (C≡C) and 1645 (C=C); $\delta_H$ 5.89 (1 H, ddt, *J* 17.2, 10.2 and 7.3, 2-H), 5.21–5.12 (2 H, m, 1-$H_2$), 4.24 (1 H, dt, *J* 6.3 and 2.0, 5-H), 3.66 (1 H, ddd, *J* 7.9, 6.3 and 4.0, 4-H), 2.55–2.20 (6 H, m, 3- and 8-$H_2$ and OH × 2), 1.56–1.34 (4 H, m, 9- and 10-$H_2$) and 0.91 (3 H, t, *J* 7.3, Me); $\delta_C$ 134.1, 118.1, 87.6, 78.1, 74.3, 65.9, 37.1, 30.6, 21.9, 18.4 and 13.5; *m*/*z* 182 ($M^+$, 30%), 155 (20), 142 (49), 131 (96), 115 (77), 77 (44) and 43 (100).

**(3*S*,4*S*)-1-(Trimethylsilyl)hept-6-en-1-yne-3,4-diol (−)-10d**

According to the procedure described for preparation of diol **10c** from compound **10g**, substrate **10h** (164 mg, 0.38 mmol) was treated with PTSA (84 mg, 0.44 mmol) in MeOH (7.0 $cm^3$) to give *title diol* (−)-**10d** (75 mg, 98%) as an oil [fast-atom bombardment (FAB) mass: Found: $M^+ - 1$, 197.1004. $C_{10}H_{17}O_2Si$ requires *m*/*z*, 197.0998]; $[\alpha]_D^{20}$ −22.1 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3600 (OH), 3400 (OH), 2160 (C≡C) and 1645 (C=C); $\delta_H$ 5.87 (1 H, ddt, *J* 17.2, 9.9 and 7.3, 6-H), 5.21–5.12 (2 H, m, 7-$H_2$) 4.20 (1 H, br t, *J* 5.9, 3-H), 3.70 (1 H, m, 4-H), 2.61–2.41 (3 H, m, 5-H and OH × 2), 2.23 (1 H, m, 5-H) and 0.18 (9 H, s, TMS); $\delta_C$ 133.9, 118.2, 103.5, 91.7, 74.0, 66.1, 37.0 and −0.3; chemical ionisation (CI) mass: *m*/*z* 199 ($M^+ + 1$, 13%), 181 (100), 128 (18), 109 (18), 91 (18) and 73 (72).

**(4*S*,5*S*)-4,5-Diacetoxyhept-1-en-6-yne (+)-10i**

To a solution of diol **10a** (63 mg, 0.50 mmol), $Et_3N$ (200 mg, 1.98 mmol) and DMAP (6.0 mg, 0.05 mmol) in $CH_2Cl_2$ (10 $cm^3$) was added acetic anhydride (207 mg, 2.03 mmol) at 0 °C. The reaction mixture was stirred for 1 h at rt, diluted with water and extracted with $CH_2Cl_2$. The extract was washed successively with water (several times) and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (3:1) afforded *title compound* (+)-**10i** (102 mg, 98%) as an oil (Found: C, 62.6; H, 6.7. $C_{11}H_{14}O_4$ requires C, 62.9; H, 6.7%); $[\alpha]_D^{20}$ +58.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3330 (C≡C–H) and 1745 (CO); $\delta_H$ 5.75 (1 H, dddd, *J* 14.2, 9.8, 7.3 and 6.3, 2-H), 5.45 (1 H, dd, *J*, 5.1 and 2.4, 5-H), 5.18–5.11 (3 H, m, 4-H and 1-$H_2$), 2.57–2.41 (2 H, m, 3-$H_2$), 2.50 (1 H, d, *J* 2.4, 7-H), 2.11 (3 H, s, Ac) and 2.08 (3 H, s, Ac); $\delta_C$ 170.4, 169.8, 132.6, 119.3, 78.0, 75.8, 72.5, 64.4, 35.1, 21.2 and 21.1; CI mass *m*/*z* 211 ($M^+ + 1$, 75%), 201 (41) and 151 (100).

**(4*S*,5*S*)-4,5-Diacetoxy-7-phenylhept-1-en-6-yne (+)-10j**

According to the procedure described for preparation of diacetate **10i** from compound **10a**, diol **10b** (82 mg, 0.41 mmol) was treated with $Et_3N$ (164 mg, 1.62 mmol), DMAP (4.9 mg, 0.04 mmol) and acetic anhydride (170 mg, 1.66 mmol) to give *title diacetate* (+)-**10j** (110 mg, 96%) as an oil (Found: C, 71.5; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); $[\alpha]_D^{21}$ +92.1 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2250 (C≡C), 1740 (CO) and 1650 (C=C); $\delta_H$ 7.45–7.29 (5 H, m, ArH), 5.79 (1 H, dddd, *J* 14.2, 10.3, 7.8 and 6.6, 2-H), 5.69 (1 H, d, *J* 6.4, 5-H), 5.26 (1 H, ddd, *J* 7.8, 6.4 and 4.4, 4-H), 5.18–5.11 (2 H, m, 1-$H_2$), 2.61 (1 H, m, 3-H), 2.50 (1 H, m, 3-H), 2.13 (3 H, s, Ac) and 2.09 (3 H, s, Ac); $\delta_C$ 170.1, 169.5, 132.3, 131.9, 128.9, 128.3, 121.7, 118.7, 86.9, 83.0, 72.5, 64.8, 34.9 and 20.9; CI mass *m*/*z* 287 ($M^+ + 1$, 0.4%), 245 (16), 227 (100), 199 (14) and 185 (24).

**(4*S*,5*S*)-4,5-Diacetoxyundec-1-en-6-yne (+)-10k**

According to the procedure described for the preparation of compound **10i** from diol **10a**, substrate **10c** (140 mg, 0.77 mmol) was treated with $Et_3N$ (311 mg, 3.07 mmol), DMAP (9.4 mg, 0.08 mmol) and acetic anhydride (322 mg, 3.15 mmol) to give *title compound* (+)-**10k** (196 mg, 96%) as an oil (Found: C, 67.8; H, 8.3. $C_{15}H_{22}O_4$ requires C, 67.6; H, 8.3%); $[\alpha]_D^{20}$ +72.9 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2250 (C≡C), 1740 (CO) and 1650 (C=C); $\delta_H$ 5.73 (1 H, dddd, *J* 14.2, 10.3, 7.8 and 6.4, 2-H), 5.42 (1 H, dt, *J* 4.4 and 2.5, 5-H), 5.11–5.06 (3 H, m, 1-$H_2$ and 4-H), 2.51 (1 H, m, 3-H), 2.38 (1 H, m, 3-H), 2.18 (2 H, td, *J* 7.8 and 2.5, 8-$H_2$), 2.06 (3 H, s, Ac), 2.04 (3 H, s, Ac), 1.49–1.32 (4 H, m, 9- and 10-$H_2$) and 0.88 (3 H, t, *J* 7.3, Me); $\delta_C$ 170.0, 169.6, 132.4, 118.5, 88.2, 74.1, 72.7, 64.8, 34.9, 30.3, 21.8, 20.8, 18.3 and 13.5; CI mass *m*/*z* 267 ($M^+ + 1$, 7.0%), 207 (100) and 165 (12).

**(4*S*,5*S*)-4,5-Diacetoxy-7-(trimethylsilyl)hept-1-en-6-yne (+)-10l**

According to the procedure described for preparation of compound **10i** from substrate **10a**, diol **10d** (206 mg, 1.04 mmol) was treated with $Et_3N$ (421 mg, 4.16 mmol), DMAP (13 mg, 0.10 mmol) and acetic anhydride (436 mg, 4.27 mmol) to give *title diacetate* (+)-**10l** (279 mg, 95%) as an oil (Found: C, 59.5; H, 7.8. $C_{14}H_{22}O_4Si$ requires C, 59.5; H, 7.9%); $[\alpha]_D^{18}$ +80.8 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2200 (C≡C), 1740 (CO) and 1650 (C=C); $\delta_H$ 5.74 (1 H, dddd, *J* 14.2, 10.3, 7.8 and 6.4, 2-H), 5.46 (1 H, d, *J* 6.4, 5-H), 5.17–5.09 (3 H, m, 4-H and 1-$H_2$), 2.51 (1 H, m, 3-H), 2.41 (1 H, m, 3-H), 2.08 (3 H, s, Ac), 2.06 (3 H, s, Ac) and 0.16 (9 H, s, TMS); $\delta_C$ 170.0, 161.4, 132.2, 118.7, 98.9, 92.6, 72.5, 64.6, 34.8, 20.8 and −0.5; CI mass *m*/*z* 283 ($M^+ + 1$, 29%), 223 (47), 200 (11) and 199 (100).

**General procedure for Pauson–Khand reaction of enynes 10**

**Condition A.** $Co_2(CO)_8$ (0.60 mmol) was added to a solution of an enyne **10** (0.50 mmol) in $CH_2Cl_2$ (5.0 $cm^3$) at rt. After being stirred for 2 h, the $CH_2Cl_2$ solution was evaporated to leave a residue, which was taken up in MeCN (5.0 $cm^3$). A solution of crude cobalt-complexed enyne **10** in MeCN was heated at 70–75 °C until complete disappearance of the starting material (*ca.* 0.3–5 h). The reaction mixture was passed through a short pad of Celite and the filtrate was concentrated to dryness. Chromatography of the residue with hexane–AcOEt gave products **11** and **12**.

**Condition B.** The crude cobalt-complexed enyne **10** was dissolved in THF (10 $cm^3$) to which $TMANO{\cdot}2H_2O$ (3.00 mmol) was added at 0 °C. The reaction mixture was stirred at rt until complete disappearance of the starting material (*ca.* 1–5 h). Work-up and chromatography as described in Condition A gave products **11** and **12**. Chemical yield and product ratio between **11** and **12** are summarised in Table 1.

**(5*S*,7*S*,8*S*)- and (5*R*,7*S*,8*S*)-7,8-Dihydroxy-2-phenylbicyclo-[3.3.0]oct-1-en-3-one 11b and 12b**

A *mixture of stereoisomers* **11b** and **12b** was obtained in the ratio 81:19 (entry 1) as an oil (Found: $M^+$, 230.0932. $C_{14}H_{14}O_3$ requires *M*, 230.0943); $\nu_{max}/cm^{-1}$ 3650 (OH), 3400 (OH) and 1705 (CO); selected data for $\delta_H$ 7.74–7.30 (5 H, m, ArH), 5.10 (19/100 H, m, 8-H), 4.49 (81/100 H, s, 8-H), 4.37 (19/100 H, m, 7-H), 4.25 (81/100 H, m, 7-H), 3.41 (19/100 H, m, 5-H) and 3.22 (81/100 H, m, 5-H); selected data for $\delta_C$ 208.6, 176.8, 138.4, 130.6, 128.9, 128.7, 128.5, 82.5, 76.3, 43.0, 39.9 and 38.3; *m*/*z* 230 ($M^+$, 42%), 212 (38), 196 (32), 186 (55), 170 (45), 142 (31), 129 (100), 115 (63) and 77 (35).

**(5*S*,7*S*,8*S*)- and (5*R*,7*S*,8*S*)-2-Butyl-7,8-dihydroxybicyclo-[3.3.0]oct-1-en-3-ones 11c and 12c**

A *mixture of stereoisomers* **11c** and **12c** was obtained in a ratio 84:16 (entry 3) as an oil (Found: $M^+$, 210.1256. $C_{12}H_{18}O_3$ requires *M*, 210.1256); $\nu_{max}/cm^{-1}$ 3520 (OH), 3370 (OH), 1700 (CO) and 1665 (C=C); selected data for $\delta_H$ 4.85 (16/100 H, s,

8-H), 4.61 (84/100 H, m, 8-H), 4.41 (84/100 H, ddd, *J* 8.6, 6.6 and 3.6, 7-H), 4.32 (16/100 H, m, 7-H), 3.17 (16/100 H, m, 5-H), 3.06 (84/100 H, m, 5-H) and 0.90 (84/100 × 3 H, t, *J* 8.7, Me); selected data for $\delta_C$ 210.5, 175.9, 140.2, 82.2, 75.2, 42.1, 39.6, 38.4, 30.3, 23.6, 22.7 and 13.8; *m*/*z* 210 ($M^+$, 49%), 192 (28), 166 (73), 150 (48), 137 (40), 109 (45), 95 (71), 79 (42) and 43 (100).

**(5*S*,7*S*,8*S*)-7,8-Dihydroxy-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (−)-11d**

*Compound* (−)-**11d** was obtained (entry 5) as a solid, mp 126–127 °C (from hexane–AcOEt) (Found: C, 58.6; H, 8.0. $C_{11}H_{18}O_3Si$ requires C, 58.4; H, 8.0%); $[a]_D^{17}$ −211.6 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3610 (OH), 3400 (OH), 1695 (CO) and 1620 (C=C); $\delta_H$ 4.59 (1 H, s, 8-H), 4.40 (1 H, m, 7-H), 3.14 (1 H, m, 5-H), 2.66–2.51 (4 H, m, 4- and 6-H and OH × 2), 2.11 (1 H, dd, *J* 17.8 and 4.0, 4-H), 1.19 (1 H, td, *J* 11.9 and 8.6, 6-H) and 0.19 (9 H, s, TMS); $\delta_C$ 214.0, 190.2, 140.2, 81.7, 76.3, 43.4, 43.3, 38.2 and −1.2; *m*/*z* 226 ($M^+$, 9.0%), 193 (100), 182 (32), 166 (34), 151 (50) and 73 (86).

**(5*S*,7*S*,8*S*)-7,8-Bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (−)-11e**

*Compound* (−)-**11e** was obtained as an oil (Found: $M^+$, 382.2387. $C_{20}H_{38}O_3Si_2$ requires *M*, 382.2360); $[a]_D^{20}$ −101.6 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1705 (CO) and 1640 (C=C); $\delta_H$ 5.98 (1 H, d, *J* 2.3, 2-H), 4.43 (1 H, m, 8-H), 4.27 (1 H, ddd, *J* 6.9, 6.6 and 2.3, 7-H), 3.17 (1 H, m, 5-H), 2.65 (1 H, dd, *J* 17.8 and 6.6, 4-H), 2.49 (1 H, ddd, *J* 12.5, 8.3 and 6.6, 6-H), 2.11 (1 H, dd, *J* 17.8 and 3.3, 4-H), 1.14 (1 H, ddd, *J* 12.5, 10.6 and 6.9, 6-H), 0.89 (9 H, s, ᵗBu), 0.87 (9 H, s, ᵗBu), 0.13 (3 H, s, Me), 0.08 (3 H, s, Me), 0.07 (3 H, s, Me) and 0.06 (3 H, s, Me); $\delta_C$ 210.6, 185.5, 126.7, 82.5, 76.4, 43.0, 41.4, 39.1, 25.8, 25.7, 18.0, 17.9, −4.3, −4.6, −4.7 and −4.7; *m*/*z* 382 ($M^+$, 13%), 339 (12), 325 (66), 209 (18), 147 (93), 91 (12) and 73 (100).

**(5*R*,7*S*,8*S*)-7,8-Bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (+)-12e**

*Compound* (−)-**12e** was obtained as a solid, mp 41–42 °C (from hexane–AcOEt) (Found: C, 62.4; H, 10.1. $C_{20}H_{38}O_3Si_2$ requires C, 62.8; H, 10.0%); $[a]_D^{20}$ +185.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1705 (CO) and 1645 (C=C); $\delta_H$ 6.01 (1 H, t, *J* 2.0, 2-H), 4.73 (1 H, m, 8-H), 4.13 (1 H, m, 7-H), 3.24 (1 H, m, 5-H), 2.67 (1 H, dd, *J* 18.2 and 6.9, 4-H), 2.07 (1 H, dd, *J* 18.2 and 3.0, 4-H), 2.05 (1 H, m, 6-H), 1.75 (1 H, ddd, *J* 13.5, 9.6 and 8.3, 6-H), 0.92 (9 H, s, ᵗBu), 0.90 (9 H, s, ᵗBu), 0.13 (3 H, s, Me), 0.12 (3 H, s, Me), 0.09 (3 H, s, Me) and 0.07 (3 H, s, Me); $\delta_C$ 209.3, 189.4, 125.1, 80.6, 79.8, 43.9, 39.3, 38.6, 25.8, 25.7, 18.1, 17.9, −4.6, −4.7 and −4.8; *m*/*z* 382 ($M^+$, 12%), 325 (93), 224 (20), 147 (100), 91 (15) and 73 (56).

**(5*S*,7*S*,8*S*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-phenylbicyclo-[3.3.0]oct-1-en-3-one (−)-11f**

*Compound* (−)-**11f** was obtained as an oil (Found: $M^+$, 458.2697. $C_{26}H_{42}O_3Si_2$ requires *M*, 458.2673); $[a]_D^{20}$ −70.1 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1705 (CO); $\delta_H$ 7.53–7.48 (2 H, m, ArH), 7.42–7.29 (3 H, m, ArH), 4.59 (1 H, s, 8-H), 4.34 (1 H, ddd, *J* 6.3, 4.3 and 1.7, 7-H), 3.19 (1 H, m, 5-H), 2.88 (1 H, dd, *J* 17.9 and 6.6, 4-H), 2.64 (1 H, ddd, *J* 13.2, 9.2 and 6.3, 6-H), 2.28 (1 H, dd, *J* 17.9 and 3.3, 4-H), 1.22 (1 H, ddd, *J* 13.2, 8.6 and 4.3, 6-H), 0.88 (9 H, s, ᵗBu), 0.81 (9 H, s, ᵗBu), 0.05 (3 H, s, Me), 0.04 (3 H, s, Me), 0.03 (3 H, s, Me) and 0.02 (3 H, s, Me); $\delta_C$ 208.7, 179.1, 137.0, 131.3, 128.7, 128.2, 128.1, 81.7, 76.1, 44.0, 39.3, 38.6, 25.7, 17.9, 17.8, −4.3, −4.4, −4.8 and −4.8; *m*/*z* 458 ($M^+$, 27%), 401 (21), 300 (49), 284 (40), 167 (28), 147 (25), 73 (81) and 57 (100).

**(5*R*,7*S*,8*S*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-phenylbicyclo-[3.3.0]oct-1-en-3-one (+)-12f**

*Compound* (+)-**12f** was obtained as an oil (Found: C, 67.7; H, 9.2. $C_{26}H_{42}O_3Si_2$ requires C, 68.1; H, 9.2%); $[a]_D^{20}$ +2.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1700 (CO); $\delta_H$ 7.44–7.24 (5 H, m, ArH), 4.88 (1 H, s, 8-H), 4.24 (1 H, d, *J* 4.3, 7-H), 3.34 (1 H, m, 5-H), 2.84 (1 H, dd, *J* 17.7 and 6.6, 4-H), 2.32 (1 H, dd, *J* 17.7 and 3.3, 4-H), 2.08 (1 H, m, 6-H), 1.57 (1 H, m, 6-H), 0.92 (9 H, s, ᵗBu), 0.57 (9 H, s, ᵗBu), 0.14 (3 H, s, Me), 0.13 (3 H, s, Me), 0.02 (3 H, s, Me) and −0.32 (3 H, s, Me); $\delta_C$ 208.5, 183.7, 138.4, 131.6, 129.2, 128.2, 128.0, 81.4, 78.0, 43.2, 40.8, 38.6, 25.8, 25.5, 17.9, 17.7, −4.2, −4.4, −4.5 and −5.6; *m*/*z* 458 ($M^+$, 29%), 401 (52), 300 (65), 284 (53), 147 (100), 73 (75) and 57 (24).

**(5*S*,7*S*,8*S*)-2-Butyl-7,8-bis(*tert*-butyldimethylsiloxy)bicyclo-[3.3.0]oct-1-en-3-one (−)-11g**

*Compound* (−)-**11g** was obtained as an oil (Found: C, 65.5; H, 10.6. $C_{24}H_{46}O_3Si_2$ requires C, 65.7; H, 10.6%); $[a]_D^{19}$ −101.0 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1700 (CO) and 1670 (C=C); $\delta_H$ 4.45 (1 H, s, 8-H), 4.24 (1 H, m, 7-H), 3.05 (1 H, m, 5-H), 2.67 (1 H, dd, *J* 17.8 and 6.6, 4-H), 2.54 (1 H, ddd, *J* 13.2, 9.2 and 6.6, 6-H), 2.30–2.13 (2 H, m, $CH_2$), 2.06 (1 H, dd, *J* 17.8 and 3.0, 4-H), 1.52–1.21 (4 H, m, $CH_2$), 1.06 (1 H, ddd, *J* 13.2, 9.2 and 4.6, 6-H), 0.89 (3 H, t, *J* 7.3, Me), 0.88 (9 H, s, ᵗBu), 0.85 (9 H, s, ᵗBu), 0.14 (3 H, s, Me), 0.06 (6 H, s, Me × 2) and 0.04 (3 H, s, Me); $\delta_C$ 211.1, 177.5, 137.8, 82.2, 75.4, 43.2, 39.7, 38.6, 30.5, 25.8, 25.7, 24.0, 22.8, 18.0, 17.9, 13.9, −4.4, −4.5, −4.6 and −4.7; *m*/*z* 438 ($M^+$, 59%), 381 (48), 280 (44), 264 (38), 147 (20) and 73 (15).

**(5*R*,7*S*,8*S*)-2-Butyl-7,8-bis(*tert*-butyldimethylsiloxy)bicyclo-[3.3.0]oct-1-en-3-one (+)-12g**

*Compound* (+)-**12g** was obtained as an oil (Found: C, 65.4; H, 10.7%); $[a]_D^{20}$ +15.6 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1700 (CO) and 1660 (C=C); $\delta_H$ 4.75 (1 H, s, 8-H), 4.15 (1 H, dt, *J* 6.3 and 2.0, 7-H), 3.09 (1 H, m, 5-H), 2.62 (1 H, dd, *J* 17.8 and 6.3, 4-H), 2.36–2.18 (2 H, m, $CH_2$), 2.02 (1 H, dd, *J* 17.8 and 3.0, 6-H), 1.98 (1 H, m, 6-H), 1.53 (1 H, ddd, *J* 12.9, 11.9 and 6.3, 4-H), 1.46–1.22 (4 H, m, $CH_2$), 0.93–0.86 (21 H, m, ᵗBu × 2 and Me), 0.17 (3 H, s, Me), 0.15 (3 H, s, Me), 0.10 (3 H, s, Me) and 0.09 (3 H, s, Me); $\delta_C$ 210.4, 179.2, 139.0, 81.5, 79.8, 42.3, 39.3, 38.6, 31.1, 25.9, 25.8, 23.0, 18.0, 17.9, 14.0, −4.1, −4.2, −4.5 and −4.8; *m*/*z* 438 ($M^+$, 57%), 381 (46), 280 (43), 264 (38), 147 (20) and 73 (13).

**(5*S*,7*S*,8*S*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (−)-11h**

*Compound* (−)-**11h** was obtained as an oil (Found: $M^+$, 454.2757. $C_{23}H_{46}O_3Si_3$ requires *M*, 454.2755); $[a]_D^{21}$ −114.5 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1690 (CO) and 1620 (C=C); $\delta_H$ 4.49 (1 H, s, 8-H), 4.16 (1 H, m, 7-H), 3.21 (1 H, m, 5-H), 2.67 (1 H, dd, *J* 17.5 and 6.9, 4-H), 2.55 (1 H, ddd, *J* 13.5, 10.6 and 5.9, 6-H), 2.05 (1 H, dd, *J* 17.5 and 4.0, 4-H), 1.13 (1 H, ddd, *J* 13.5, 7.3 and 2.3, 6-H), 0.87 (9 H, s, ᵗBu), 0.82 (9 H, s, ᵗBu), 0.22 (9 H, s, TMS), 0.14 (3 H, s, Me), 0.07 (3 H, s, Me), 0.04 (3 H, s. Me) and 0.03 (3 H, s, Me); $\delta_C$ 215.5, 192.5, 137.4, 79.9, 75.6, 45.4, 41.2, 38.7, 25.7, 25.6, 17.9, 17.8, −1.0, −4.3, −4.3, −4.6 and −4.8; *m*/*z* 454 ($M^+$, 16%), 397 (14), 296 (43), 147 (31), 133 (16), 73 (99) and 57 (100).

**(5*S*,7*S*,8*S*)- and (5*R*,7*S*,8*S*)-7,8-Diacetoxybicyclo[3.3.0]oct-1-en-3-one 11i and 12i**

A mixture of *title diacetates* **11i** and **12i** was obtained in the ratio 76 : 24 (entry 15) as an oil (Found: $M^+$, 238.0830. $C_{12}H_{14}O_5$ requires *M*, 238.0841); $\nu_{max}/cm^{-1}$ 1740 (CO), 1715 (CO) and 1645 (C=C); selected data for $\delta_H$: 6.23 (76/100 H, d, *J* 2.4, 2-H), 6.03 (24/100 H, t, *J* 2.0, 2-H), 5.84 (24/100 H, m, 8-H), 5.61 (76/100 H, m, 8-H), 5.42 (76/100 H, ddd, *J* 8.8, 7.3 and 3.9, 7-H), 5.29 (24/100 H, m, 7-H), 3.33 (24/100 H, m, 5-H), 3.19 (76/100 H, m, 5-H), 2.15 (24/100 × 3 H, s, Ac), 2.12 (76/100 × 3 H, s, Ac), 2.11 (76/100 × 3 H, s, Ac) and 2.08 (24/100 × 3 H, s, Ac); *m*/*z* 238 ($M^+$, 12%), 196 (78), 154 (100), 136 (83), 110 (61), 91 (24) and 43 (86).

**(5*S*,7*S*,8*S*)- and (5*R*,7*S*,8*S*)-7,8-Diacetoxy-2-phenylbicyclo-[3.3.0]oct-1-en-3-one 11j and 12j**

A mixture of *title diacetates* **11i** and **12i** was obtained in the ratio 87:13 (entry 17) as an oil (Found: C, 68.7; H, 5.8. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.8%); $\nu_{max}$/cm$^{-1}$ 1740 (CO) and 1715 (CO); selected data for $\delta_H$: 7.49–7.32 (5 H, m, Ph), 6.28 (13/100 H, s, 8-H), 5.73 (87/100 H, m, 8-H), 5.46 (87/100 H, ddd, *J* 8.3, 7.3 and 3.4, 7-H), 5.26 (13/100 H, m, 7-H), 3.37 (13/100 H, m, 5-H), 3.30 (87/100 H, m, 5-H), 2.18 (87/100 × 3 H, s, Ac), 2.13 (13/100 × 3 H, s, Ac), 2.04 (13/100 × 3 H, s, Ac) and 2.03 (87/100 × 3 H, s, Ac); *m*/*z* 314 (M$^+$, 7.0%), 254 (44), 230 (46), 212 (85), 194 (85), 186 (39) and 166 (24).

**(5*S*,7*S*,8*S*)- and (5*R*,7*S*,8*S*)-7,8-Diacetoxy-2-butylbicyclo-[3.3.0]oct-1-en-3-ones 11k and 12k**

A mixture of *title diacetates* **11k** and **12k** was obtained in the ratio 88:12 (entry 19) as an oil (Found: C, 65.2; H, 7.6. $C_{16}H_{22}O_5$ requires C, 65.3; H, 7.5%); $\nu_{max}$/cm$^{-1}$ 1740 (CO), 1710 (CO) and 1675 (C=C); selected data for $\delta_H$: 5.98 (12/100 H, s, 8-H), 5.71 (88/100 H, m, 8-H), 5.37 (88/100 H, td, *J* 7.3 and 3.4, 7-H), 5.22 (12/100 H, m, 7-H), 3.15 (12/100 H, m, 5-H), 3.07 (88/100 H, m, 5-H), 2.13 (12/100 × 3 H, s, Ac), 2.09 (12/100 × 3 H, s, Ac), 2.08 (88/100 × 3 H, s, Ac), 2.05 (88/100 × 3 H, s, Ac) and 0.87 (88/100 × 3 H, t, *J* 7.3, Me); selected data for $\delta_C$: 209.7, 170.9, 170.5, 170.0, 141.8, 80.7, 73.4, 42.5, 40.0, 36.8, 30.7, 24.1, 23.0, 21.3, 21.2 and 14.3; *m*/*z* 294 (M$^+$, 8.0%), 252 (27), 210 (76), 192 (35), 166 (26) and 43 (100).

**(5*S*,7*S*,8*S*)-7,8-Diacetoxy-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (−)-11l**

*Compound* (−)-**11l** was obtained as an oil (Found: C, 58.1; H, 7.2. $C_{15}H_{22}O_5Si$ requires C, 58.0; H, 7.1%); $[\alpha]_D^{19}$ −130.0 (*c* 0.50, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 1740 (CO), 1705 (CO) and 1630 (C=C); $\delta_H$ 5.65 (1 H, d, *J* 3.4, 8-H), 5.37 (1 H, td, *J* 7.3 and 3.4, 7-H), 3.18 (1 H, m, 5-H), 2.72–2.62 (2 H, m, 4- and 6-H), 2.10 (3 H, s, Ac), 2.09 (3 H, s, Ac), 2.15–1.96 (1 H, m, 4-H), 1.26 (1 H, m, 6-H) and 0.20 (9 H, s, TMS); $\delta_C$ 212.9, 184.9, 170.0, 169.5, 141.6, 79.7, 74.3, 43.3, 43.2, 35.8, 20.9, 20.8 and −1.5; *m*/*z* 310 (M$^+$, 1.5%), 295 (28), 253 (15), 211 (16), 193 (85), 117 (30), 75 (22) and 43 (100).

**(5*S*,7*S*,8*S*)-7-(*tert*-Butyldimethylsiloxy)-8-hydroxy-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (−)-15**

To a solution of bis-silyl ether **11h** (41.4 mg, 0.09 mmol) in THF (2.0 cm$^3$) was added a solution of TBAF in THF (1.0 mol dm$^{-3}$; 0.10 cm$^3$, 0.10 mmol) at 0 °C. After being stirred for 15 min at 0 °C, the reaction mixture was diluted with AcOEt, washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10:1) gave the *title compound* (−)-**15** (23.2 mg, 75%) as an oil (Found: C, 60.3; H, 9.4. $C_{17}H_{32}O_3Si_2$ requires C, 60.0; H, 9.5%); $[\alpha]_D^{20}$ −137.6 (*c* 0.51, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 3675 (OH), 3425 (OH), 1695 (CO) and 1620 (C=C); $\delta_H$ 4.51 (1 H, s, 8-H), 4.30 (1 H, m, 7-H), 3.01 (1 H, m, 5-H), 2.60 (1 H, dd, *J* 17.8 and 6.6, 4-H), 2.46 (1 H, dt, *J* 12.2 and 7.6, 6-H), 2.08 (1 H, dd, *J* 17.8 and 4.0, 4-H), 1.94 (1 H, s, OH), 1.18 (1 H, td, *J* 12.2 and 7.6, 6-H), 0.90 (9 H, s, $^t$Bu), 0.24 (9 H, s, TMS), 0.12 (3 H, s, Me) and 0.10 (3 H, s, Me); $\delta_C$ 214.0, 190.7, 139.7, 81.9, 76.6, 43.6, 43.0, 38.9, 25.8, 18.0, −1.2 and −4.7; *m*/*z* 340 (M$^+$, 1.4%), 283 (100), 267 (15), 193 (20), 149 (12) and 75 (80).

**(5*S*,7*S*,8*S*)-8-Acetoxy-7-(*tert*-butyldimethylsiloxy)-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (−)-16**

According to the procedure described for the preparation of diacetate **10i** from diol **10a**, the *title compound* (−)-**16** (40.2 mg, 79%) was obtained from the alcohol **15** (45.2 mg, 0.13 mmol) as an oil (Found: C, 59.6; H, 9.0. $C_{19}H_{34}O_4Si_2$ requires C, 59.6; H, 9.0%); $[\alpha]_D^{17}$ −88.0 (*c* 0.50, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 1745 (CO), 1695 (CO) and 1625 (C=C); $\delta_H$ 5.44 (1 H, d, *J* 2.6, 8-H), 4.39 (1 H, td, *J* 6.3 and 2.6, 7-H), 3.15 (1 H, m, 5-H), 2.65 (1 H, dd, *J* 17.5 and 6.6, 4-H), 2.52 (1 H, ddd, *J* 12.9, 8.9 and 6.3, 6-H), 2.10 (1 H, dd, *J* 17.5 and 4.0, 4-H), 2.08 (3 H, s, Ac), 1.23 (1 H, ddd, *J* 12.9, 10.2 and 6.3, 6-H), 0.86 (9 H, s, $^t$Bu), 0.21 (9 H, s, TMS), 0.08 (3 H, s, Me) and 0.05 (3 H, s, Me); $\delta_C$ 213.8, 186.8, 169.4, 140.9, 78.9, 76.5, 44.3, 42.8, 39.3, 25.7, 21.0, 17.9, −1.3, −4.9 and −5.0; *m*/*z* 382 (M$^+$, 0.2%), 367 (22), 325 (87), 307 (18), 117 (100), 75 (90) and 43 (50).

**(2*S*,3*S*)-2,3-(Isopropylidenedioxy)pent-4-en-1-ol (−)-17**

A solution of DMSO (7.89 g, 101 mmol) in $CH_2Cl_2$ (35 cm$^3$) was gradually added to a solution of oxalyl dichloride (6.41 g, 50.5 mmol) in $CH_2Cl_2$ (35 cm$^3$) at −78 °C. After stirring of the $CH_2Cl_2$ solution for 15 min, a solution of the threitol derivative **3** (6.97 g, 25.3 mmol) in $CH_2Cl_2$ (35 cm$^3$) was added and the reaction mixture was stirred at the same temperature for 1 h. $Et_3N$ (15.3 g, 151 mmol) was added to the reaction mixture, which was then gradually warmed to rt and diluted with $CH_2Cl_2$. The solution was washed successively with water and brine, dried and concentrated to leave the crude aldehyde.

To a suspension of potassium *tert*-butoxide (8.50 g, 75.8 mmol) in THF (120 cm$^3$) was added portionwise methyltriphenylphosphonium bromide (27.1 g, 75.8 mmol) and the THF solution was stirred at rt for 2 h. A solution of the crude aldehyde in THF (50 cm$^3$) was added to this THF solution of the resulting methylenetriphenylphosphorane at rt. After being stirred for 1 h, the reaction mixture was quenched by addition of water and extracted with $Et_2O$. The extract was washed successively with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (50:1) to give the corresponding olefin derivative (5.78 g).

TBAF as a solution in THF (1.0 mol dm$^{-3}$; 25.4 cm$^3$, 25.4 mmol) was added to a solution of the crude olefin derivative (5.78 g, 21.2 mmol) in THF (260 cm$^3$) at 0 °C. After being stirred for 2.5 h at rt, the reaction mixture was quenched by addition of saturated aq. $NH_4Cl$ and extracted with $Et_2O$. The extract was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:2) afforded *title alcohol* (−)-**17** (3.18 g, 80%) as a pale yellow oil (Found: C, 60.7; H, 8.8. $C_8H_{14}O_3$ requires C, 60.7; H, 8.9%); $[\alpha]_D^{18}$ −3.1 (*c* 0.51, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 3650 (OH) and 3450 (OH); $\delta_H$ 5.82 (1 H, ddd, *J* 17.2, 10.2 and 7.6, 4-H), 5.37 (1 H, d, *J* 17.2, 5-H), 5.25 (1 H, d, *J* 10.2, 5-H), 4.29 (1 H, m, 3-H), 3.90–3.70 (2 H, m, 1- and 2-H), 3.60 (1 H, m, 1-H), 2.21 (1 H, s, OH) and 1.43 (6 H, s, Me × 2); $\delta_C$ 135.0, 119.0, 109.2, 81.1, 78.3, 60.8, 26.9 and 26.9; *m*/*z* 158 (M$^+$, 1.9%), 143 (26), 127 (6.7), 113 (1.4) and 43 (100).

**(3*S*,4*S*)-3,4-Isopropylidenedioxy-7-(trimethylsilyl)hept-1-en-6-yne (+)-18**

According to the procedure described for the preparation of the hexynol **4** from the threitol derivative **3**, compound **17** (1.00 g, 6.32 mmol) was successively treated with $Tf_2O$ and lithium (trimethylsilyl)acetylide to give *title compound* (+)-**18** (680 mg, 45%) as a pale yellow oil (Found: C, 65.6; H, 9.3. $C_{13}H_{22}O_2Si$ requires C, 65.5; H, 9.3%); $[\alpha]_D^{19}$ +8.6 (*c* 0.51, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 2160 (C≡C) and 1645 (C=C); $\delta_H$ 5.87 (1 H, ddd, *J* 17.1, 10.7 and 7.3, 2-H), 5.42 (1 H, d, *J* 17.1, 1-H), 5.26 (1 H, d, *J* 10.7, 1-H), 4.30 (1 H, m, 3-H), 3.79 (1 H, ddd, *J* 8.3, 5.9 and 4.4, 4-H), 2.61 (1 H, dd, *J* 17.1 and 5.9, 5-H), 2.55 (1 H, dd, *J* 17.1 and 4.4, 5-H), 1.44 (3 H, s, Me), 1.43 (3 H, s, Me) and 0.15 (9 H, s, TMS); $\delta_C$ 135.1, 118.7, 109.0, 101.7, 87.4, 81.5, 78.2, 27.1, 27.0, 22.9 and −0.1; *m*/*z* 165 (M$^+$ − TMS, 4.1%), 152 (0.8), 135 (3.8), 127 (14), 109 (3.3) and 43 (100).

**(3*S*,4*S*)-3,4-Isopropylidenedioxy-7-phenylhept-1-en-6-yne (+)- 19**

According to the procedure described for the preparation of the hexynol **4** from the threitol **3**, compound **17** (1.20 g, 7.60 mmol) was successively treated with $Tf_2O$ and lithium phenylacetylide

to give *title compound* (+)-**19** (819 mg, 44%) as a pale yellow oil (Found: C, 79.4; H, 7.6. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%); $[\alpha]_D^{20}$ +4.2 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1645 (C=C); $\delta_H$ 7.43–7.36 (2 H, m, ArH), 7.31–7.24 (3 H, m, ArH), 5.90 (1 H, ddd, *J* 17.1, 10.3 and 6.8, 2-H), 5.45 (1 H, d, *J* 17.1, 1-H), 5.28 (1 H, d, *J* 10.3, 1-H), 4.36 (1 H, m, 3-H), 3.89 (1 H, ddd, *J* 7.8, 5.9 and 4.9, 4-H), 2.79 (1 H, dd, *J* 17.1 and 5.9, 5-H), 2.74 (1 H, dd, *J* 17.1 and 4.9, 5-H), 1.48 (3 H, s, Me) and 1.45 (3 H, s, Me); $\delta_C$ 135.0, 131.5, 128.2, 127.8, 123.4, 118.8, 109.2, 85.0, 82.8, 81.7, 78.5, 27.0 and 22.5; *m*/*z* 242 ($M^+$, 3.3%), 227 (57), 199 (1.5), 185 (23), 167 (73), 156 (37), 127 (55) and 115 (100).

**(3*S*,4*S*)-3,4-(Isopropylidenedioxy)undec-1-en-6-yne (+)-20**

According to the procedure described for the preparation of the hexynol **4** from threitol derivative **3**, compound **17** (1.60 g, 10.1 mmol) was successively treated with $Tf_2O$ and lithium hexylide to give *title compound* (+)-**20** (970 mg, 43%) as a pale yellow oil (Found: C, 75.4; H, 9.9. $C_{14}H_{22}O_2$ requires C, 75.6; H, 10.0%); $[\alpha]_D^{27}$ +11.3 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1645 (C=C); $\delta_H$ 5.85 (1 H, ddd, *J* 17.1, 10.3 and 6.8, 2-H), 5.39 (1 H, d, *J* 17.1, 1-H), 5.23 (1 H, d, *J* 10.3, 1-H), 4.24 (1 H, m, 3-H), 3.76 (1 H, ddd, *J* 8.3, 5.9 and 4.9, 4-H), 2.51 (1 H, ddt, *J* 16.6, 5.9 and 2.4, 5-H), 2.46 (1 H, ddt, *J* 16.6, 4.9 and 2.4, 5-H), 2.15 (2 H, tt, *J* 6.8 and 2.4, 8-$H_2$), 1.49–1.33 (4 H, m, 9- and 10-$H_2$), 1.43 (3 H, s, Me), 1.41 (3 H, s, Me) and 0.86 (3 H, t, *J* 7.3, Me); $\delta_C$ 135.2, 118.5, 109.0, 82.8, 81.6, 78.8, 74.8, 30.9, 27.0, 21.9, 21.8, 18.4 and 13.5; *m*/*z* 222 ($M^+$, 0.6%), 207 (32), 175 (1.0), 147 (6.5), 127 (74), 98 (86) and 43 (100).

**(3*S*,4*S*)-7-(Trimethylsilyl)hept-1-en-6-yne-3,4-diol (−)-21d**

A solution of compound **18** (1.10 g, 4.60 mmol) and PTSA (175 mg, 0.92 mmol) in MeOH (45 $cm^3$) was stirred at rt for 24 h, and MeOH was evaporated off. The residue was chromatographed with hexane–AcOEt (2:1) to give *title diol* (−)-**21d** (887 mg, 97%) as an oil (Found: C, 60.5; H, 9.0. $C_{10}H_{18}O_2Si$ requires C, 60.6; H, 9.2%); $[\alpha]_D^{27}$ −25.9 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3580 (OH), 3430 (OH), 2160 (C≡C) and 1645 (C=C); $\delta_H$ 5.88 (1 H, ddd, *J* 17.1, 10.7 and 6.4, 2-H), 5.38 (1 H, d, *J* 17.1, 1-H), 5.26 (1 H, d, *J* 10.7, 1-H), 4.13 (1 H, m, 3-H), 3.65 (1 H, m, 4-H), 2.55 (1 H, dd, *J* 17.1 and 5.4, 5-H), 2.54 (1 H, s, OH), 2.51 (1 H, s, OH), 2.46 (1 H, dd, *J* 17.1 and 6.8, 5-H) and 0.15 (9 H, s, TMS); $\delta_C$ 136.9, 117.6, 102.5, 87.8, 74.7, 72.2, 24.8 and −0.3; *m*/*z* 198 ($M^+$, 0.2%), 130 (35) and 73 (100).

**(3*S*,4*S*)-Hept-1-en-6-yne-3,4-diol (−)-21a**

A suspension of the above silane **21d** (627 mg, 3.16 mmol) and $K_2CO_3$ (873 mg, 6.32 mmo) in MeOH (30 $cm^3$) was stirred at rt overnight, and MeOH was evaporated off. The residue was diluted with water and extracted with AcOEt, which was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded the *title diol* (−)-**21a** (330 mg, 83%), as an oil (FAB mass: Found: $M^+ + 1$, 127.0762. $C_7H_{11}O_2$ requires *m*/*z*, 127.0759); $[\alpha]_D^{18}$ −22.4 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3600 (OH), 3440 (OH), 3340 (C≡C–H), 2110 (C≡C) and 1645 (C=C); $\delta_H$ 5.88 (1 H, ddd, *J* 17.1, 10.3 and 5.9, 2-H), 5.40 (1 H, d, *J* 17.1, 1-H), 5.28 (1 H, d, *J* 10.3, 1-H), 4.16 (1 H, m, 3-H), 3.68 (1 H, m, 4-H), 2.56 (1 H, br d, *J* 4.9, OH), 2.53 (1 H, ddd, *J* 17.1, 5.4 and 2.9, 5-H), 2.44 (1 H, m, OH), 2.43 (1 H, ddd, *J* 17.1, 6.8 and 2.9, 5-H) and 2.07 (1 H, t, *J* 2.9, 7-H); $\delta_C$ 136.8, 117.8, 80.4, 74.7, 72.2, 70.9 and 23.2; CI mass *m*/*z* 127 ($M^+ + 1$, 29%) and 109 (100).

**(3*S*,4*S*)-7-Phenylhept-1-en-6-yne-3,4-diol (−)-21b**

According to the procedure described for the preparation of diol **21d** from compound **18**, the *title compound* (−)-**21b** (674 mg, 88%) was obtained from its protected form **19** (919 mg, 3.80 mmol) as a solid, mp 60.0–62.0 °C (from hexane–AcOEt) (Found: C, 77.3; H, 7.1. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); $[\alpha]_D^{26}$ −11.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3590 (OH), 3450 (OH) and 1650 (C=C); $\delta_H$ 7.45–7.36 (2 H, m, ArH), 7.33–7.25 (3 H, m, ArH), 5.93 (1 H, ddd, *J* 17.1, 10.7 and 4.4, 2-H), 5.44 (1 H, d, *J* 17.1, 1-H), 5.30 (1 H, d, *J* 10.7, 1-H), 4.24 (1 H, m, 3-H), 3.76 (1 H, m, 4-H), 2.75 (1 H, dd, *J* 17.1 and 5.4, 5-H), 2.67 (1 H, dd, *J* 17.1 and 6.8, 5-H), 2.51 (1 H, d, *J* 4.9, OH) and 2.42 (1 H, d, *J* 4.4, OH); $\delta_C$ 137.0, 131.6, 128.3, 128.0, 123.2, 117.8, 85.4, 83.2, 74.8, 72.5 and 24.4; *m*/*z* 202 ($M^+$, 0.8%), 173 (8.0) and 115 (100).

**(3*S*,4*S*)-Undec-1-en-6-yne-3,4-diol (−)-21c**

According to the procedure described for the preparation of diol **21d** from its protected form **18**, the *title compound* (−)-**21c** (718 mg, 96%) was obtained from the precursor **20** (917 mg, 4.12 mmol) as a solid, mp 40.0–41.0 °C (from hexane–AcOEt) (Found: C, 72.7; H, 9.8. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%); $[\alpha]_D^{28}$ −32.4 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3590 (OH), 3450 (OH) and 1645 (C=C); $\delta_H$ 5.87 (1 H, ddd, *J* 17.1, 10.3 and 5.9, 2-H), 5.38 (1 H, d, *J* 17.1, 1-H), 5.25 (1 H, d, *J* 10.3, 1-H), 4.13 (1 H, m, 3-H), 3.60 (1 H, m, 4-H), 2.53 (1 H, d, *J* 4.4, OH), 2.49 (1 H, d, *J* 5.4, OH), 2.48 (1 H, ddt, *J* 16.6, 5.4 and 2.4, 5-H), 2.38 (1 H, ddt, *J* 16.6, 6.4 and 2.4, 5-H), 2.16 (2 H, tt, *J* 6.8 and 2.4, 8-$H_2$), 1.51–1.33 (4 H, m, 9- and 10-$H_2$) and 0.90 (3 H, t, *J* 7.3, Me); $\delta_C$ 137.0, 117.5, 83.7, 75.2, 74.8, 72.5, 31.0, 23.7, 21.9, 18.4 and 13.6; *m*/*z* 182 ($M^+$, 2.3%), 164 (1.8), 153 (11), 135 (11) and 125 (40).

**(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)hept-1-en-6-yne (−)-21e**

According to the procedure described for the preparation of bis-silyl ether **10e** from diol **10a**, *title compound* (−)-**21e** (248 mg, 89%) was obtained from diol **21a** (100 mg, 0.79 mmol) as an oil (Found: C, 64.1; H, 10.9. $C_{19}H_{38}O_2Si_2$ requires C, 64.3; H, 10.8%); $[\alpha]_D^{21}$ −79.9 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3340 (C≡C–H), 2110 (C≡C) and 1645 (C=C); $\delta_H$ 5.94 (1 H, ddd, *J* 17.1, 10.7 and 4.4, 2-H), 5.28 (1 H, d, *J* 17.1, 1-H), 5.15 (1 H, d, *J* 10.7, 1-H), 4.20 (1 H, m, 3-H), 3.79 (1 H, ddd, *J* 8.8, 4.4 and 3.4, 4-H), 2.48 (1 H, ddd, *J* 17.1, 3.4 and 2.9, 5-H), 2.09 (1 H, ddd, *J* 17.1, 8.8 and 2.9, 5-H), 1.91 (1 H, t, *J* 2.9, 7-H), 0.91 (18 H, s, $^t$Bu × 2), 0.14 (3 H, s, Me), 0.10 (3 H, s, Me), 0.07 (3 H, s, Me) and 0.04 (3 H, s, Me); $\delta_C$ 136.3, 115.5, 83.4, 74.6, 69.1, 25.8, 21.6, 18.2, 18.1, −4.4, −4.6, −4.8 and −5.0; *m*/*z* 354 ($M^+$, 0.8%), 339 (0.9), 297 (56), 241 (10), 189 (14), 147 (100), 133 (12) and 115 (19).

**(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)-7-phenylhept-1-en-6-yne (−)-21f**

According to the procedure described for the aforementioned preparation (**10a**→**10e**), *title compound* (−)-**21f** (409 mg, 96%) was obtained from diol **21b** (200 mg, 0.99 mmol) as an oil (Found: C, 69.4; H, 9.9. $C_{25}H_{42}O_2Si_2$ requires C, 69.7; H, 9.8%); $[\alpha]_D^{30}$ −70.9 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1650 (C=C); $\delta_H$ 7.45–7.37 (2 H, m, ArH), 7.30–7.22 (3 H, m, ArH), 5.99 (1 H, ddd, *J* 17.1, 10.3 and 4.4, 2-H), 5.32 (1 H, d, *J* 17.1, 1-H), 5.19 (1 H, d, *J* 10.3, 1-H), 4.26 (1 H, m, 3-H), 3.88 (1 H, ddd, *J* 9.3, 4.4 and 2.9, 4-H), 2.72 (1 H, dd, *J* 17.1 and 2.9, 5-H), 2.35 (1 H, dd, *J* 17.1 and 9.3, 5-H), 0.94 (9 H, s, $^t$Bu), 0.93 (9 H, s, $^t$Bu), 0.18 (3 H, s, Me), 0.14 (3 H, s, Me), 0.11 (3 H, s, Me) and 0.08 (3 H, s, Me); $\delta_C$ 136.4, 131.5, 128.1, 127.4, 124.2, 115.5, 89.2, 81.3, 74.7, 25.8, 25.8, 22.5, 18.2, 18.1, −4.4, −4.6, −4.7 and −4.9; *m*/*z* 430 ($M^+$, 9.5%), 415 (1.1), 373 (54), 315 (11), 259 (48), 147 (78), 115 (31) and 73 (100).

**(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)undec-1-en-6-yne (−)-21g**

According to the procedure described for the aforementioned preparation (**10a**→**10e**), *title compound* (−)-**21g** (436 mg, 96%) was obtained from diol **21c** (200 mg, 1.10 mmol) as an oil (Found: C, 67.1; H, 11.3. $C_{23}H_{46}O_2Si_2$ requires C, 67.3; H, 11.3%); $[\alpha]_D^{18}$ −65.7 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1645 (C=C); $\delta_H$ 5.93 (1 H, ddd, *J* 17.6, 10.7 and 4.4, 2-H), 5.25 (1 H, d, *J* 17.6 1-H), 5.13 (1 H, d, *J* 10.7, 1-H), 4.18 (1 H, m, 3-H), 3.72 (1 H, ddd, *J* 8.8, 4.4 and 3.9, 4-H), 2.43 (1 H, ddt, *J* 17.1, 3.9 and 2.4,

5-H), 2.13 (2 H, ddt, *J* 7.3, 6.8 and 2.4, 8-$H_2$), 2.06 (1 H, ddt, *J* 17.1, 8.8 and 2.4, 5-H), 1.50–1.35 (4 H, m, 9- and 10-$H_2$), 0.90 (21 H, m, $^t$Bu × 2 and Me), 0.12 (3 H, s, Me), 0.09 (3 H, s, Me), 0.06 (3 H, s, Me) and 0.03 (3 H, s, Me); $\delta_C$ 136.8, 115.1, 81.0, 78.5, 75.0, 74.8, 31.1, 25.8, 22.0, 21.9, 18.6, 18.2, 18.1, 13.6, −4.5, −4.7, −4.8 and −5.0; *m/z* 410 ($M^+$, 6.2%), 395 (1.6), 353 (63), 315 (16), 239 (64), 147 (97), 115 (16) and 73 (100).

**(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)-7-(trimethylsilyl)hept-1-en-6-yne (−)-21h**

According to the procedure described for the aforementioned preparation (**10a→10e**), *title compound* (−)-**21h** (101 mg, 94%) was obtained from diol **21d** (50.0 mg, 0.25 mmol) as an oil (Found: $M^+$, 426.2830. $C_{22}H_{46}O_2Si_3$ requires *M*, 426.2805); $[a]_D^{18}$ −75.7 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2160 (C≡C) and 1645 (C=C); $\delta_H$ 5.92 (1 H, ddd, *J* 17.1, 10.3 and 4.4, 2-H), 5.25 (1 H, d, *J* 17.1, 1-H), 5.14 (1 H, d, *J* 10.3, 1-H), 4.19 (1 H, m, 3-H), 3.77 (1 H, ddd, *J* 8.8, 4.4 and 3.4, 4-H), 2.51 (1 H, dd, *J* 17.1 and 3.4, 5-H), 2.14 (1 H, dd, *J* 17.1 and 8.8, 5-H), 0.91 (18 H, s, $^t$Bu × 2), 0.15 (3 H, s, Me), 0.14 (9 H, s, Me), 0.11 (3 H, s, Me), 0.07 (3 H, s, Me) and 0.04 (3 H, s, Me); $\delta_C$ 136.4, 115.4, 106.2, 85.2, 74.6, 74.5, 25.8, 23.0, 18.2, 18.1, 0.09, −4.3, −4.6, −4.8 and −4.9; *m/z* 426 ($M^+$, 0.4%), 411 (1.4), 369 (44), 315 (9.4), 255 (38), 199 (13), 147 (76), 115 (14) and 73 (100).

**(3*S*,4*S*)-3,4-Diacetoxyhept-1-en-6-yne (−)-21i**

According to the procedure described for the preparation of diacetate **10i** from diol **10a**, *title compound* (−)-**21i** (166 mg, 100%) was obtained from diol **21a** (100 mg, 0.79 mmol) as a pale yellow oil (Found: C, 63.0; H, 6.8. $C_{11}H_{14}O_4$ requires C, 62.9; H, 6.7%); $[a]_D^{21}$ −17.1 (*c* 0.52, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3340 (C≡C–H), 1740 (CO) and 1650 (C=C); $\delta_H$ 5.73 (1 H, ddd, *J* 17.1, 10.3 and 6.4, 2-H), 5.50 (1 H, m, 3-H), 5.36 (1 H, d, *J* 17.1, 1-H), 5.28 (1 H, d, *J* 10.3, 1-H), 5.10 (1 H, q, *J* 5.9, 4-H), 2.52 (1 H, ddd, *J* 17.1, 5.9 and 2.4, 5-H), 2.45 (1 H, ddd, *J* 17.1, 6.4 and 2.4, 5-H), 2.08 (3 H, s, Ac), 2.06 (3 H, s, Ac) and 2.01 (1 H, t, *J* 2.4, 7-H); $\delta_C$ 170.0, 169.6, 131.9, 119.5, 78.4, 73.6, 71.2, 70.9, 20.8, 20.7 and 20.7; CI mass *m/z* 211 ($M^+$ + 1, 20%), 169 (1.4), 151 (100), 129 (1.0) and 109 (3.7).

**(3*S*,4*S*)-3,4-Diacetoxy-7-phenylhept-1-en-6-yne (+)-21j**

According to the procedure described for the aforementioned preparation (**10a→10i**), *title compound* (+)-**21j** (283 mg, 100%) was obtained from diol **21b** (200 mg, 0.99 mmol) as a pale yellow oil (Found: C, 71.6; H, 6.3. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); $[a]_D^{24}$ +12.8 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1740 (CO) and 1645 (C=C); $\delta_H$ 7.42–7.36 (2 H, m, ArH), 7.31–7.25 (3 H, m, ArH), 5.80 (1 H, ddd, *J* 17.6, 10.7 and 6.3, 2-H), 5.61 (1 H, m, 3-H), 5.40 (1 H, d, *J* 17.6, 1-H), 5.32 (1 H, d, *J* 10.7, 1-H), 5.21 (1 H, td, *J* 6.3 and 5.9, 4-H), 2.76 (1 H, dd, *J* 17.1 and 5.9, 5-H), 2.71 (1 H, dd, *J* 17.1 and 6.3, 5-H), 2.12 (3 H, s, Ac) and 2.10 (3 H, s, Ac); $\delta_C$ 170.0, 169.6, 132.0, 131.5, 128.1, 127.9, 123.0, 119.2, 83.9, 82.8, 73.7, 71.5, 21.6, 20.8 and 20.7; *m/z* 286 ($M^+$, 8.5%), 211 (6.1), 184 (80), 165 (25), 115 (32) and 43 (100).

**(3*S*,4*S*)-3,4-Diacetoxyundec-1-en-6-yne (−)-21k**

According to the procedure described for the aforementioned preparation (**10a→10i**), *title compound* (−)-**21k** (289 mg, 99%), was obtained from diol **21c** (200 mg, 1.10 mmol) as a pale yellow oil (Found: C, 67.6; H, 8.2. $C_{15}H_{22}O_4$ requires C, 67.7; H, 8.3%); $[a]_D^{19}$ −4.9 (*c* 0.50, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1740 (CO) and 1645 (C=C); $\delta_H$ 5.74 (1 H, ddd, *J* 17.1, 10.8 and 6.4, 2-H), 5.51 (1 H, m, 3-H), 5.33 (1 H, d, *J* 17.1, 1-H), 5.26 (1 H, d, *J* 10.8, 1-H), 5.05 (1 H, td, *J* 6.4 and 5.4, 4-H), 2.47 (1 H, ddt, *J* 16.6, 6.4 and 2.4, 5-H), 2.41 (1 H, ddt, *J* 16.6, 6.4 and 2.4, 5-H), 2.11 (2 H, ddt, *J* 7.3, 6.3 and 2.4, 8-$H_2$), 2.08 (3 H, s, Ac), 2.05 (3 H, s, Ac), 1.47–1.31 (4 H, m, 9- and 10-$H_2$) and 0.88 (3 H, t, *J* 7.3, Me); $\delta_C$ 170.0, 169.7, 132.2, 119.0, 83.0, 73.9, 73.8, 72.0, 30.8, 21.8, 21.0, 20.9, 20.8, 18.3 and 13.5; CI mass *m/z* 267 ($M^+$ + 1, 16%), 207 (100), 165 (7.2), 147 (4.1) and 105 (1.3).

**(3*S*,4*S*)-3,4-Diacetoxy-7-(trimethylsilyl)hept-1-en-6-yne (−)-21l**

According to the procedure described for the aforementioned preparation (**10a→10i**), *title compound* (−)-**21l** (199 mg, 93%) was obtained from diol **21d** (150 mg, 0.76 mmol) as a pale yellow oil (Found: C, 59.5; H, 7.8. $C_{14}H_{22}O_4Si$ requires C, 59.5; H, 7.9%); $[a]_D^{27}$ −13.1 (*c* 0.49, $CHCl_3$); $\nu_{max}/cm^{-1}$ 2160 (C≡C), 1740 (CO) and 1645 (C=C); $\delta_H$ 5.74 (1 H, ddd, *J* 17.1, 10.8 and 6.4, 2-H), 5.49 (1 H, m, 3-H), 5.34 (1 H, d, *J* 17.1, 1-H), 5.27 (1 H, d, *J* 10.8, 1-H), 5.11 (1 H, td, *J* 6.3 and 5.9, 4-H), 2.53 (1 H, dd, *J* 17.1 and 5.9, 5-H), 2.49 (1 H, dd, *J* 17.1 and 6.3, 5-H), 2.08 (3 H, s, Ac), 2.06 (3 H, s, Ac) and 0.12 (9 H, s, TMS); $\delta_C$ 169.9, 169.6, 132.0, 119.2, 100.8, 87.6, 73.8, 71.4, 22.1, 20.9, 20.7 and −0.2; *m/z* 282 ($M^+$, 1.0%), 267 (3.4), 222 (11), 207 (16), 180 (44), 165 (24) and 117 (100).

**General procedure for the Pauson–Khand reaction of enynes 21**

According to the procedure described for the Pauson–Khand reaction of enynes **10**, enynes **21** were exposed to two conditions (Conditions A and B). Chemical yields and product ratios between the stereoisomeric products **22** and **23** are summarised in Table 2.

**(5*R*,6*S*,7*S*)- and (5*S*,6*S*,7*S*)-6,7-Diacetoxy-2-phenylbicyclo-[3.3.0]oct-1-en-3-one 22j and 23j**

A *mixture of diacetates* **22j** and **23j** (82:18) was obtained from diol **21b** after acetylation (entry 2) as an oil (FAB mass: Found: $M^+$ + 1, 315.1268. $C_{18}H_{19}O_5$ requires *m/z*, 315.1235); $\nu_{max}/cm^{-1}$ 1740 (CO), 1710 (CO) and 1660 (C=C); selected data for $\delta_H$ 7.60 (18/100 × 2 H, d, *J* 7.3, ArH), 7.52 (82/100 × 2 H, d, *J* 7.3, ArH), 7.44–7.31 (3 H, m, ArH), 5.51 (82/100 H, ddd, *J* 10.3. 6.4 and 5.4, 7-H), 5.30 (18/100 H, d, *J* 4.9, 7-H), 5.27 (18/100 H, m, 6-H), 4.93 (82/100 H, dd, *J* 10.1 and 6.4, 6-H), 3.47 (18/100 H, m, 5-H), 3.15 (82/100 H, m, 5-H), 2.14 (3 H, s, Ac), 2.03 (82/100 × 3 H, s, Ac) and 2.02 (18/100 × 3 H, s, Ac); FAB mass *m/z* 315 ($M^+$ + 1, 15%), 255 (65), 195 (100), 149 (69) and 136 (61).

**(5*R*,6*S*,7*S*)- and (5*S*,6*S*,7*S*)-6,7-Diacetoxy-2-butylbicyclo-[3.3.0]oct-1-en-3-one 22k and 23k**

A *mixture of diacetates* **22k** and **23k** (67:33) was obtained from diol **21c** after acetylation (entry 3) as a pale yellow oil (Found: $M^+$, 294.1478. $C_{16}H_{22}O_5$ requires *M*, 294.1468); $\nu_{max}/cm^{-1}$ 1740 (CO), 1710 (CO) and 1670 (C=C); selected data for $\delta_H$ 5.42 (67/100 H, ddd, *J* 10.3, 6.4 and 5.4, 7-H), 5.24–5.19 (33/100 × 2 H, m, 6- and 7-H), 4.84 (67/100 H, dd, *J* 10.3 and 6.4, 6-H), 2.09 (3 H, s, Ac), 2.06 (67/100 × 3 H, s, Ac), 1.98 (33/100 × 3 H, s, Ac), 0.88 (67/100 × 3 H, t, *J* 7.3, Me) and 0.87 (33/100 × 3 H, t, *J* 7.3, Me); *m/z* 294 ($M^+$, 1.6%), 252 (8.8), 234 (15), 192 (36), 174 (100), 149 (35) and 132 (85).

**(5*R*,6*S*,7*S*)- and (5*S*,6*S*,7*S*)-6,7-Diacetoxy-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one 22l and 23l**

A *mixture of diacetates* **22l** and **23l** (93:7) was obtained from diol **21d** after acetylation (entry 5) as a pale yellow oil (Found: C, 58.1; H, 7.3. $C_{15}H_{22}O_5Si$ requires C, 58.0; H, 7.1%); $\nu_{max}/cm^{-1}$ 1740 (CO), 1690 (CO) and 1620 (C=C); selected data for $\delta_H$ 5.42 (93/100 H, ddd, *J* 10.3, 6.8 and 5.9, 7-H), 5.26–5.20 (7/100 × 2 H, 6- and 7-H), 4.89 (93/100 H, dd, *J* 10.3 and 6.8, 6-H), 3.34 (7/100 H, m, 5-H), 3.04 (93/100 H, m, 5-H), 2.09 (3 H, s, Ac), 2.07 (93/100 × 3 H, s, Ac), 2.02 (7/100 × 3 H, s, Ac), 0.20 (7/100 × 9 H, s, TMS) and 0.18 (93/100 × 9 H, s, TMS); selected data for $\delta_C$ 212.0, 185.4, 170.6, 170.5, 139.6, 80.2, 77.3, 50.5, 41.6, 34.4, 20.9, 20.9 and −1.4; *m/z* 310 ($M^+$, 0.3%), 295 (3.1), 250 (29), 207 (13), 190 (100), 175 (67) and 147 (14).

**(5*R*,6*S*,7*S*)-6,7-Bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (+)-22e**

*Compound* (+)-**22e** was obtained as a pale yellow oil (Found: C, 62.6; H, 10.3. $C_{20}H_{38}O_3Si_2$ requires C, 62.8; H, 10.0%); $[a]_D^{17}$ +190.1 (*c* 0.51, $CHCl_3$); $\nu_{max}/cm^{-1}$ 1705 (CO) and 1635

(C=C); $\delta_H$ 5.88 (1 H, m, 2-H), 4.32 (1 H, dt, *J* 9.8 and 5.9, 7-H), 3.61 (1 H, dd, *J* 9.8 and 5.9, 6-H), 3.12 (1 H, br dd, *J* 19.1 and 9.8, 8-H), 2.94 (1 H, m, 5-H), 2.57 (1 H, dd, *J* 18.2 and 6.4, 4-H), 2.41 (1 H, br dd, *J* 19.1 and 5.9, 8-H), 2.21 (1 H, dd, *J* 18.2 and 3.4, 4-H), 0.90 (18 H, s, ᵗBu × 2), 0.09 (9 H, s, Me × 3) and 0.07 (3 H, s, Me); $\delta_C$ 209.1, 182.9, 126.7, 84.2, 79.7, 51.2, 41.1, 36.0, 25.8, 17.9, −4.2, −4.6 and −4.6; *m*/*z* 382 ($M^+$, 0.7%), 367 (1.6), 325 (60), 297 (10), 250 (5.4), 193 (44), 147 (100) and 119 (13).

**(5*S*,6*S*,7*S*)-6,7-Bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (−)-23e**

*Compound* (−)-**23e** was obtained as a pale yellow oil (Found: C, 62.5; H, 10.1%); $[\alpha]_D^{17}$ −139.8 (*c* 0.50, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 1700 (CO) and 1635 (C=C); $\delta_H$ 5.91 (1 H, m, 2-H), 4.21 (1 H, d, *J* 4.9, 7-H), 3.89 (1 H, d, *J* 3.9, 6-H), 3.33 (1 H, m, 5-H), 2.90 (1 H, ddd, *J* 19.0, 4.9 and 1.0, 8-H), 2.44 (1 H, br d, *J* 19.0, 8-H), 2.40 (1 H, ddd, *J* 17.1, 6.4 and 1.0, 4-H), 2.30 (1 H, dd, *J* 17.1 and 3.9, 4-H), 0.89 (9 H, s, ᵗBu), 0.81 (9 H, s, ᵗBu), 0.10 (3 H, s, Me), 0.09 (3 H, s, Me), 0.07 (3 H, s, Me) and 0.04 (3 H, s, Me); $\delta_C$ 211.4, 188.0, 126.0, 79.7, 76.2, 49.3, 36.3, 36.2, 25.7, 25.6, 18.0, 17.9, −4.5, −4.7, −4.8 and −5.0; *m*/*z* 382 ($M^+$, 0.8%), 367 (2.5), 325 (73), 297 (9.7), 250 (3.5), 193 (63), 147 (100) and 119 (17).

**(5*R*,6*S*,7*S*)-6,7-Bis(*tert*-butyldimethylsiloxy)-2-phenylbicyclo-[3.3.0]oct-1-en-3-one (+)-22f**

*Compound* (+)-**22f** was obtained as a solid, mp 94–95 °C (from hexane) (Found: C, 68.0; H, 9.3. $C_{26}H_{42}O_3Si_2$ requires C, 68.1; H, 9.2%); $[\alpha]_D^{22}$ +68.1 (*c* 0.50, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 1700 (CO) and 1650 (C=C); $\delta_H$ 7.54 (2 H, d, *J* 7.3, ArH), 7.40 (2 H, t, *J* 7.3, ArH), 7.31 (1 H, t, *J* 7.3, ArH), 4.41 (1 H, dt, *J* 9.8 and 6.4, 7-H), 3.65 (1 H, dd, 9.8 and 6.4, 6-H), 3.36 (1 H, br dd, *J* 18.1 and 9.8, 8-H), 2.99 (1 H, m, 5-H), 2.77 (1 H, dd, *J* 18.1 and 6.4, 4-H), 2.51 (1 H, ddd, *J* 18.1, 6.4 and 2.0, 8-H), 2.39 (1 H, dd, *J* 18.1 and 3.4, 4-H), 0.92 (9 H, s, ᵗBu), 0.88 (9 H, s, ᵗBu), 0.11 (3 H, s, Me), 0.10 (6 H, s, Me × 2) and 0.09 (3 H, s, Me); $\delta_C$ 206.8, 176.2, 136.3, 131.1, 128.4, 128.2, 128.0, 84.0, 79.7, 49.0, 41.8, 36.8, 25.8, 17.9, 17.9, −4.2, −4.5 and −4.6; *m*/*z* 458 ($M^+$, 0.1%), 443 (1.8), 401 (80), 326 (19), 269 (44), 195 (67), 167 (25), 147 (100) and 133 (9.3).

**(5*S*,6*S*,7*S*)-6,7-Bis(*tert*-butyldimethylsiloxy)-2-phenylbicyclo-[3.3.0]oct-1-en-3-one (−)-23f**

*Compound* (−)-**23f** was obtained as an oil (Found: C, 68.0; H, 9.4%); $[\alpha]_D^{24}$ −29.9 (*c* 0.21, $CHCl_3$); $\nu_{max}$/cm$^{-1}$ 1700 (CO) and 1650 (C=C); $\delta_H$ 7.56 (2 H, d, *J* 7.3, ArH), 7.39 (2 H, t, *J* 7.3, ArH), 7.30 (1 H, t, *J* 7.3, ArH), 4.24 (1 H, d, *J* 4.9, 7-H), 3.94 (1 H, d, *J* 3.9, 6-H), 3.39 (1 H, m, 5-H), 3.00 (1 H, br dd, *J* 19.0 and 4.9, 8-H), 2.67 (1 H, br d, *J* 19.0, 8-H), 2.59 (1 H, dd, *J* 17.1 and 6.3, 4-H), 2.48 (1 H, dd, *J* 17.1 and 3.4, 4-H), 0.92 (9 H, s, ᵗBu), 0.78 (9 H, s, ᵗBu), 0.13 (6 H, s, Me × 2), 0.06 (3 H, s, Me) and 0.05 (3 H, s, Me); $\delta_C$ 208.9, 181.5, 136.0, 132.0, 128.3, 128.1, 127.6, 76.5, 75.9, 47.1, 37.2, 36.8, 25.8, 25.6, 17.9, −4.4, −4.7, −4.7 and −4.9; *m*/*z* 458 ($M^+$, 0.6%), 443 (4.4), 401 (100), 326 (21), 269 (33), 195 (74), 147 (96) and 133 (10).

**(5*R*,6*S*,7*S*)- and (5*S*,6*S*,7*S*)-2-Butyl-6,7-bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one 22g and 23g**

A *mixture of bicyclic enones* **22g** and **23g** (70:30) was obtained from enyne **21g** (entry 12) as a pale yellow oil (Found: $M^+$, 438.2963. $C_{24}H_{46}O_3Si_2$ requires *M*, 438.2985); $\nu_{max}$/cm$^{-1}$ 1700 (CO) and 1660 (C=C); selected data for $\delta_H$ 4.31 (70/100 H, dt, *J* 9.8 and 6.4, 7-H), 4.20 (30/100 H, d, *J* 5.4, 7-H), 3.86 (30/100 H, d, *J* 3.9, 6-H), 3.54 (70/100 H, dd, *J* 9.8 and 6.4, 6-H), 3.20 (30/100 H, m, 5-H), 2.70 (70/100 H, m, 5-H), 0.90 (70/100 × 9 H, s, ᵗBu), 0.89 (70/100 × 9 H, s, ᵗBu), 0.88 (30/100 × 9 H, s, ᵗBu) and 0.79 (30/100 × 9 H, s, ᵗBu); *m*/*z* 438 ($M^+$, 0.8%), 423 (4.9), 381 (87), 353 (8.6), 325 (26), 306 (4.2), 249 (20), 175 (80), 147 (100) and 133 (24).

**(5*R*,6*S*,7*S*)- and (5*S*,6*S*,7*S*)-6,7-Bis(*tert*-butyldimethylsiloxy)-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one 22h and 23h**

A *mixture of bicyclic enones* **22h** and **23h** (70:30) was obtained from enyne **21h** (entry 13) as a pale yellow oil (Found: C, 61.0; H, 10.3. $C_{23}H_{46}O_3Si_3$ requires C, 60.7; H, 10.2%); $\nu_{max}$/cm$^{-1}$ 1690 (CO) and 1610 (C=C); selected data for $\delta_H$ 4.30 (70/100 H, dt, *J* 9.8 and 6.4, 7-H), 4.19 (30/100 H, d, *J* 5.4, 7-H), 3.86 (30/100 H, d, *J* 3.4, 6-H), 3.58 (70/100 H, dd, *J* 9.8 and 6.4, 6-H), 3.28 (30/100 H, m, 5-H), 2.88 (70/100 H, m, 5-H), 0.90 (9 H, s, ᵗBu), 0.89 (70/100 × 9 H, s, ᵗBu), 0.79 (30/100 × 9 H, s, ᵗBu), 0.18 (70/100 × 9 H, s, TMS) and 0.17 (30/100 × 9 H, s, TMS); *m*/*z* 454 ($M^+$, 1.2%), 439 (13), 423 (0.5), 398 (100), 323 (5.2), 265 (17), 191 (24), 147 (93) and 119 (15).

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