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PAPER

Vinylogous anionic processes in the formation and interconversion of tetracyclic ring systems†

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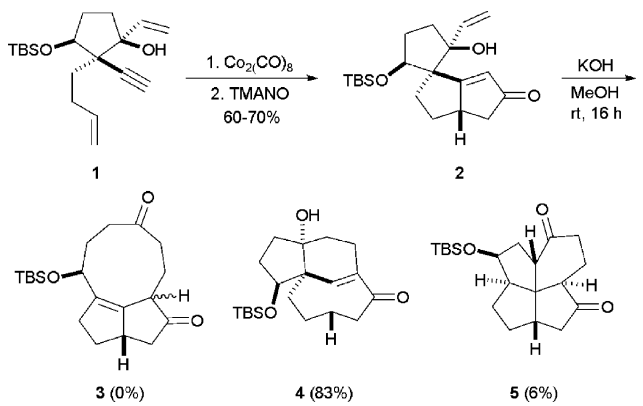
Tandem oxy-Cope and transannular vinylogous aldol reactions and/or vinylogous *retro*-aldol, conjugate addition, and transannular vinylogous aldol reactions transformed some tricyclic vinyl enones into fused tetracycles under basic conditions. Mesylates derived from similar tetracyclic products underwent efficient skeletal reorganization *via* transannular ring-opening but then different modes of transannular ring-closure upon treatment with *tert*-butoxide.

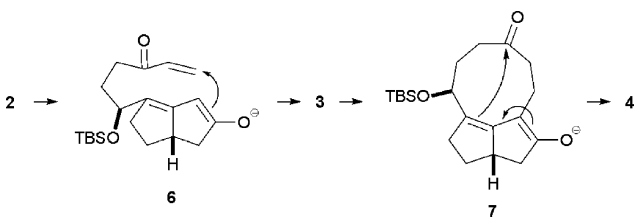
Introduction

In the course of the preparation of the ring-system of the aquariolide diterpenes, a Pauson–Khand reaction of **1** was carried out with high diastereoselectivity to give **2** when trimethylamine *N*-oxide (TMANO) was used as the promoter.[1] Efforts to initiate anionic oxy-Cope rearrangement of **2** to **3** with a variety of bases produced, instead, tetracycle **4** in high yield along with a small amount of the fenestrane **5** (Scheme 1). A concerted, [3.3] sigmatropic process would require propinquity of the termini of the two alkenes of **2**, but the *trans* relationship of these alkenes on the five-membered ring renders this geometry difficult. Reduction of the ketone of **2** stopped the reaction, but would very likely not have inhibited the sigmatropic process, although there are a few instances in which the introduction of another, conjugating double bond has enhanced anionic oxy-Cope reactivity.[2]

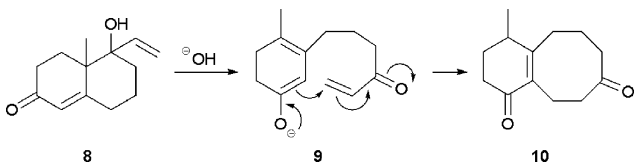


Scheme 1 Pauson–Khand cyclization of **1** and treatment of **2** with base.

The mechanism for the formation of **4** was suggested to be *via* a step-wise process of vinylogous *retro*-aldol reaction, followed by conjugate addition of intermediate **6** to give **3** as a transient species, deprotonation once again and a transannular vinylogous aldol cyclization *via* conjugated enolate **7** (Scheme 2). Vinylogous *retro*-aldol ring-opening and then vinylogous aldol reclosure, but involving a six-membered ring, has been shown by Gribble[3] to be the mechanism by which some chiral Robinson annulation products racemize. While the conjugate addition to form a nine-membered ring is very unusual, a related process was reported by Swaminathan,[4] who had observed the formation of an eight-membered product **10** when the hydroxyketone **8** was treated with base. The transformation was suggested to occur *via* conjugate addition to a vinylogous *retro*-aldol product **9** (Scheme 3) and double-bond isomerization.



Scheme 2 Suggested pathway for the formation of **4** from **2**.



Scheme 3 Ring expansion of **8** to **10**.[4]

In the case of the formation of **4** from **2**, the rigidity of the diquinane moiety reduces the number of degrees of freedom in

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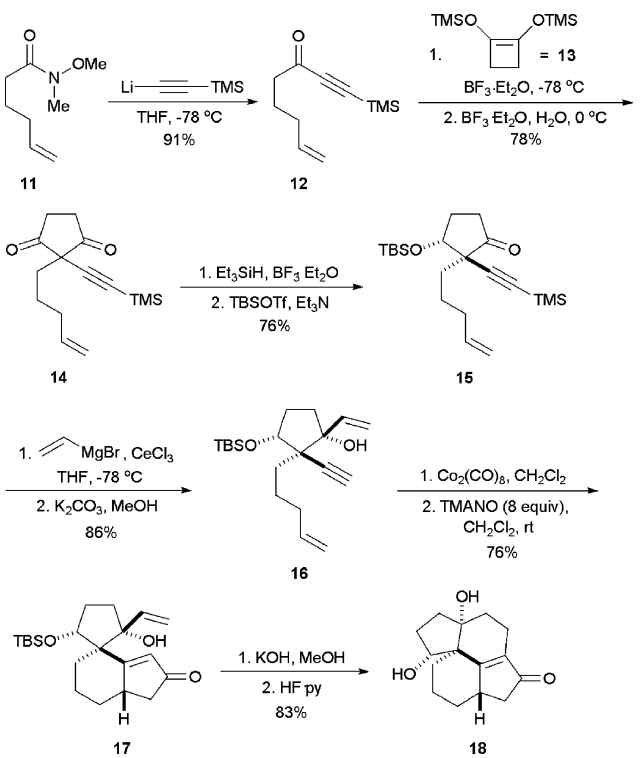
† Electronic supplementary information (ESI) available: NMR spectra, ORTEPs and CIFs for **18**, **37** and **41**. CCDC reference numbers 804296 (**18**), 804297 (**37**) and 804298 (**41**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob01152e

the nine-membered chain. The complexity of this ring-closing process suggested that modification of the structure of **2** might easily draw the reaction pathway in a different direction. If, however, the reaction pathway were not significantly altered, then other tetracyclic systems with architectures related to **4** might be accessed in a similar way. We present here evidence that a change in the ring-size still allows this complex cyclization to proceed, and we show that the ring systems of the tetracyclic products can be reorganized in different ways by tandem anionic processes.

Results and discussion

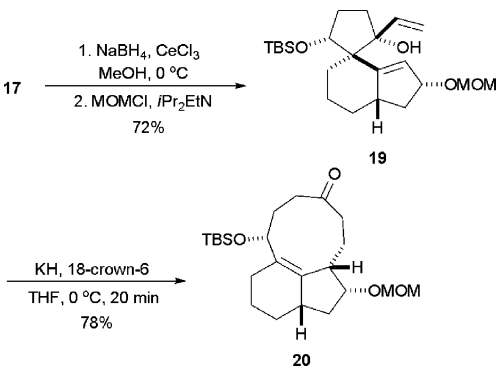
Replacing the butenyl chain of the Pauson–Khand substrate **1** with a pentenyl chain should give a product with a spiroannulated hydrindenone ring-system. The Weinreb amide **11**[5] derived from 5-hexenoic acid was treated with TMS-acetylide to give the ynone **12** (Scheme 4). Geminal acylation[6] of **12** with the four-membered acyloin **13** provided the 1,3-diketone **14** in good yield. Reduction of only one ketone with triethylsilane/$BF_3{\cdot}Et_2O$ was carried out with a *dr* of over 20 : 1, and the monoalcohol was protected as the silyl ether **15**. The stereochemistry of reduction was consistent with the reduction of an analogue[1] and this was corroborated by the X-ray structure of the final tetracyclic product (**18**). Addition of vinylmagnesium bromide in the presence of $CeCl_3$[7] gave a single diastereomer, and the TMS group was removed from the alkyne by basic methanolysis to provide **16**. Pauson–Khand cyclization of **16** took place in good yield when TMANO was employed as the promoter.[8] The crude product appeared to be a mixture of diastereomers with a *dr* of 5 : 1. Nevertheless, the yield of the major diastereomer **17** was somewhat higher than that of **2**, which suggested that the greater conformational mobility of the developing six-membered ring may allow for a more facile



Scheme 4 Synthesis of **17** and its cyclization to **18**.

cyclization in the context of these sterically demanding substrates. Furthermore, the yield of **17** was good in spite of reports of Pauson–Khand cyclizations in which the tether forms a six-membered ring having widely different yields.[9] The vinyl alcohol **17** was now ready for the cyclization. Compound **17** was consumed within two hours in methanolic KOH at room temperature, and treatment of the product with HF gave a tetracyclic product **18** amenable to X-ray crystallographic analysis.

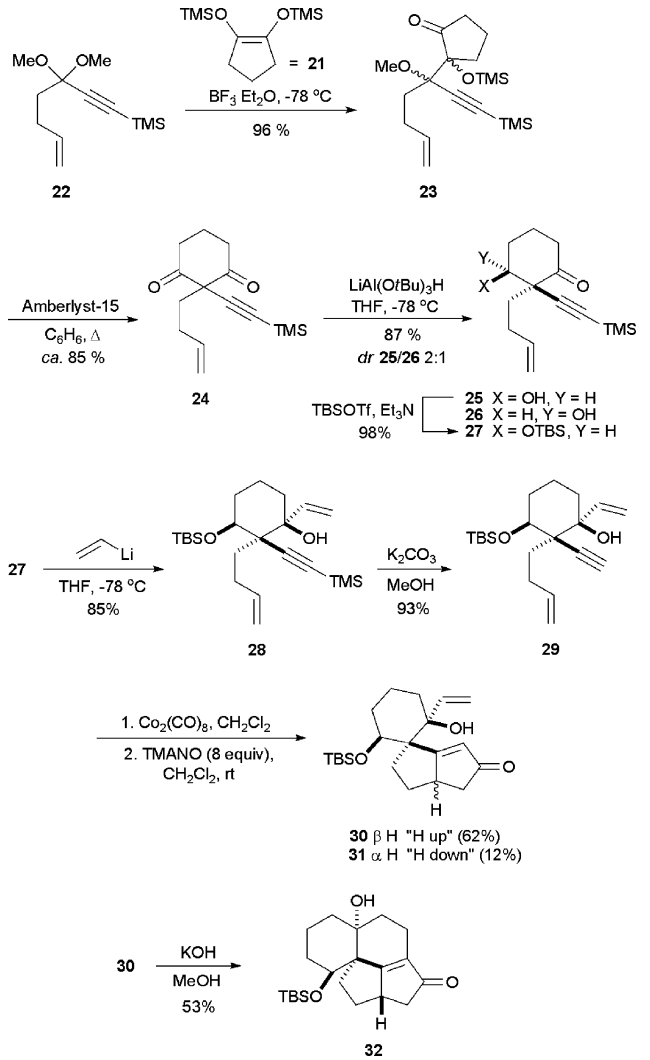
The larger ring in **17**, relative to **2**, appeared to have no effect on the cyclization. However, unlike in **2**, the alkene moieties in **17** are *syn* with respect to the five-membered ring, and so **17** will have a geometry that would easily allow a [3.3] sigmatropic pathway to a nine-membered-ring intermediate. The likelihood of the cyclization to **18** involving a concerted, anionic oxy-Cope rearrangement, instead of, or in addition to, a step-wise, vinylogous *retro*-aldol and conjugate recyclization, was demonstrated in the following way. Reduction of the ketone of **17** and protection of the resulting alcohol gave **19**, for which intramolecular carbonyl chemistry would be obviated. Nevertheless, treatment of **19** at 0 °C with base gave the nine-membered-ring product **20** (Scheme 5).



Scheme 5 Anionic oxy-Cope rearrangement of **19**.

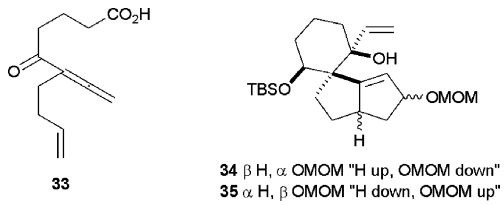
A sterner test for the formation of a tetracycle would be to use a substrate for which a larger, ten-membered ring would need to close in the Michael addition step while disfavoring the formation of the ten-membered ring intermediate by a sigmatropic process. This required a spiroannulated six-membered ring and a *trans* relationship between the alkene moieties. Attempts to carry out a geminal acylation directly on an alkynyl ketone using the acyloin **21** led mainly to decomposition, but an acceptable yield of **24** was obtained by carrying out the geminal acylation in two steps from the ketal[10] **22** (Scheme 6).

The initial step, a Mukaiyama aldol reaction of **21** with **22**, gave the diastereomeric cyclopentanones **23** in remarkably high yield. Then, **23** was treated with Amberlyst-15[11] in refluxing benzene to produce **24**. This diketone was very sensitive to ring-opening; exposure of **24** to silica gel led rapidly to ring-opened material, of which the allene **33** was a major component. Therefore, **24** was used immediately without purification. Monoreduction with triethylsilane and acid was not compatible with **24**. Monoreduction with $NaBH_4$ took place in excellent yield but with no facial selectivity. $LiAl(O\textit{t}\text{-}Bu)_3H$ provided the epimers **25** and **26** with some modest diastereoselectivity. The alcohol function of the major isomer **25** was protected as its TBS ether **27**. Reactions of **27** with vinylmagnesium bromide, with and without $CeCl_3$, showed



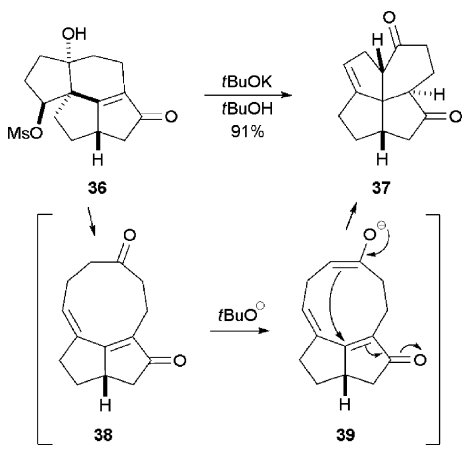
Scheme 6 Synthesis of **30** and its cyclization.

no stereoselectivity, but the reaction with vinyllithium yielded **28** with very good facial discrimination. This product was consistent with axial attack on the lowest-energy conformer of **27**. After removal of the TMS from the alkyne, **29** underwent Pauson–Khand cyclization using the same conditions as before to give stereoisomer **30** along with some of the minor epimer **31**. In the presence of methanolic KOH, the vinyl alcohol **30** was transformed slowly into tetracycle **32**. After 28 h at room temperature the yield of **32** was only 53%, and there was a significant amount of decomposition. The poorer yield was consistent with the removal of a [3.3] sigmatropic pathway for the opening the six-membered ring as well as the added difficulty of closure of a ten-membered ring *via* a Michael addition. In order to rule out the Cope rearrangement, **30** and **31** were reduced and protected to give **34** and **35**,[12] respectively. In contrast with **19**, neither **34** nor **35** underwent Cope rearrangement under basic conditions. Compounds **34** and **35**, just like **2**, have their alkene moieties *trans* with respect to the ring that will undergo opening, and therefore these compounds would require considerable energy to overcome the strain required to attain a geometry in which a concerted Cope process could occur.



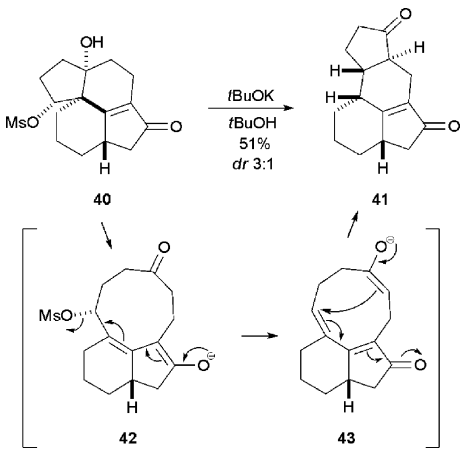
The original cyclization of **2** had yielded a small amount of an intriguing fenestrane **5**. It was proposed that **5** arose from an alternate transannular cyclization pathway from **3**.[1] It was obvious that cyclization as shown with **7** was favoured over any other cyclization because **4** was the predominant product. However, if the transannular cyclization represented by **7** could be rendered less favorable, and if the tetracyclic products **4**, **18**, and **32** could be returned to nine- or ten-membered tricyclics by cleavage of the central bond, then reclosure across the medium-sized ring could be diverted towards compounds resembling **5**. To this end, mesylates were obtained from **4**, **18**, and **32**.

Mesylate **36** derived from **4** was in hand,[1] and the idea was that a Grob fragmentation would rupture the central bond forming a nine-membered intermediate in the presence of base. When **36** was added to *tert*-butoxide the unsaturated fenestrane **37** was produced very efficiently (Scheme 7). The structure of **37** was established by X-ray crystallography. Transannular cyclization of enolate **39**, likely derived from **38**, would have produced **37**. Enolate **39** can attain the geometry required for the transannular 1,4-reaction with little strain.



Scheme 7 Proposed base-mediated elimination and skeletal reorganization of mesylate **36**.

The mesylate derived from tetracycle **32** gave intractable material under the same basic conditions. Given the fate of the mesylate from **32**, mesylate **40**, prepared from **18**, was treated with base for a shorter period of time (Scheme 8). Instead of producing a fenestrane, **40** yielded the tetracycle **41** along with a byproduct that appeared to be epimeric with **41** α to the carbonyl, in a ratio of 3 : 1. Although the yield of **41** plus the byproduct was only 51%, 40% of the starting mesylate **40** was recovered. The byproduct was inseparable from **41** by flash chromatography, but crystallization provided a few crystals of **41**, from which the structure was elucidated by X-ray crystallography. The skeleton of **41** is the core of the sesterterpene bolivianine.[13]



Scheme 8 Base-mediated elimination and skeletal reorganization of mesylate **40**.

The relative stereochemistry of the alcohol and the mesylate in **40** was not suited to the Grob fragmentation, unlike in **36** where these groups were antiperiplanar.[14] Nevertheless, ejection of the mesylate from the enolate **42**, which would have arisen from the vinylogous *retro*-aldol of **40**, would have led to the nine-membered diketone. (Indeed, a similar mechanism might have operated in the conversion of **36** to **38**.) In the basic medium this diketone could have enolized and undergone a transannular 1,4-reaction with little strain in the same way as was seen for **39**, but a fenestrane was not isolated. Instead, the product **41** must have arisen *via* the 1,6-transannular reaction of enolate **43**. It is remarkable that the small difference in geometry and the minor increase in flexibility imparted by the six-membered ring in **40**, relative to the five-membered ring in **39**, must have been sufficient to favor the formation of tetracycle **41** through a geometrically more difficult transannular 1,6-reaction.

Conclusions

A number of tetracyclic systems have been accessed from spirocyclic precursors resembling **1**. Successful Pauson–Khand cyclizations were followed by the transformation of the tricyclic products into tetracyclic compounds under basic conditions. Two pathways were available to the tetracycles, either an anionic oxy-Cope reaction followed by a transannular conjugate addition or a vinylogous *retro*-aldol, an extraordinary conjugate addition to form a nine- or a ten-membered intermediate, and transannular vinylogous aldol cyclization. Conversion of **4** and **18** to the mesylates **36** and **40** allowed the reopening of their central carbon–carbon bonds under basic conditions and then reclosure of central bonds *via* different modes of transannular aldol reaction to give different ring systems. These findings offer potential for synthetic exploitation in the construction and rearrangement of polycyclic systems.

Experimental

Reactions were conducted under inert atmosphere (dry N_2). Dichloromethane was distilled from calcium hydride. Ethyl acetate and hexanes were distilled. Flash chromatography employed silica gel (40–63 μm particle size, 230–240 mesh). Melting points were acquired using a Fisher–Johns apparatus and are uncorrected. IR spectra were recorded with an FT instrument using CsI plates. ^{1}H NMR spectra were acquired at 500 MHz and ^{13}C NMR spectra at 125 MHz as $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR chemical shifts are often followed by the number of attached hydrogens (DEPT) in parentheses.

N-Methoxy-*N*-methyl-5-hexenamide (11)

After the procedure of Snapper *et al.*,[5] 1,1-carbonyldiimidazole (CDI) (0.850 g, 5.24 mmol) was added to a solution of 5-hexenoic acid (0.500 g, 4.37 mmol) in CH_2Cl_2 (22 mL) at 0 °C. The mixture was stirred at this temperature for 1 h. *N*,*O*-Dimethylhydroxylamine hydrochloride was added, and the mixture was stirred at rt for 4 h. The suspension was filtered through a plug of cotton to remove the precipitate, and the cotton plug was rinsed twice with CH_2Cl_2. The filtrate was washed with 1 M aqueous HCl and brine and was then dried over $MgSO_4$. Evaporation of the solvent gave **11** (0.538 g, 78%): IR (neat) 3077 (w), 2937 (s), 1667 (s) cm^{-1}; ^{1}H NMR δ 5.81 (1H, ddt, J = 17.0, 10.2, 6.6 Hz), 5.03 (1H, d, J = 17.0 Hz), 4.98 (1H, d, J = 10.2 Hz), 3.68 (3H, s), 3.18 (3H, s), 2.43 (2H, t, J = 7.6 Hz), 2.11 (2H, q, J = 7.6 Hz), 1.74 (2H, pentet, J = 7.6 Hz); ^{13}C NMR δ 174.8 (0), 138.4 (1), 115.3 (2), 61.4 (3), 33.6 (2), 32.5 (3), 31.4 (2), 29.7 (2); HRMS (ESI TOF) m/z 180.1002, $[C_8H_{15}NO_2 + Na]^+$ requires 180.0995.

1-(Trimethylsilyl)oct-7-en-1-yn-3-one (12)

A 1.5 M solution of *n*-BuLi in hexane (9.8 mL, 15 mmol) was added to a solution of ethynyltrimethylsilane (1.45 g, 14.8 mmol) in THF (45 mL) at −78 °C. The solution was stirred at this temperature for 30 min. A solution of **11** (1.55 g, 9.86 mmol) in THF (15 mL) was added dropwise over 5 min. The solution was stirred at −78 °C for 1 h after which time TLC analysis indicated that none of the amide remained. The mixture was warmed to rt. Saturated aqueous NH_4Cl was added, and the solution became yellow. The mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under vacuum left a residue that was purified by flash chromatography (5% EtOAc/hexanes) to give **12** (1.73 g, 91%): ^{1}H NMR δ 5.77 (1H, ddt, J = 16.9, 10.3, 6.8 Hz), 5.03 (1H, dq, J = 16.9, 1.6 Hz), 5.00 (1H, m), 2.57 (2H, t, J = 7.4 Hz), 2.09 (2H, qt, J = 6.8, 1.3 Hz), 1.76 (2H, pentet, J = 7.4 Hz), 0.24 (9H, s); ^{13}C NMR δ 187.9 (0), 137.7 (1), 115.6 (2), 102.2 (0), 97.8 (0), 44.6 (2), 33.0 (2), 23.1 (2), –0.6 (3C, 3); HRMS (ESI TOF) m/z 195.1203, $[C_{11}H_{19}OSi]^+$ requires 195.1200.

2-(Pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentane-1,3-dione (14)

$BF_3{\cdot}OEt_2$ (1.65 mL, 13.1 mmol) was added to a solution of **12** (1.70 g, 8.76 mmol) in CH_2Cl_2 (67 mL) at −78 °C. The solution became yellow and was stirred at this temperature for 15 min. Neat acyloin **13**[15] (2.42 g, 10.5 mmol) was added dropwise at −78 °C, and the mixture was stirred for 1 h. The mixture was warmed to 0 °C and was treated sequentially with H_2O (1.6 mL, 89 mmol) and $BF_3{\cdot}OEt_2$ (11 mL, 88 mmol). The mixture was allowed to warm to rt. After 30 min TLC revealed that rearrangement was complete. The solution was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and

dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash chromatography (10% EtOAc/hexanes) gave **14** (1.78 g, 78%): mp 57–58 °C; IR (neat) 3078 (m), 2958 (s), 2173 (m), 1732 (s), 1641 (m) cm^{-1}; ^1H NMR δ 5.74 (1H, ddt, J = 17.0, 10.3, 6.7 Hz), 5.00 (1H, br d, J = 17.0 Hz), 4.96 (1H, m), 2.99 (2H, m), 2.74 (2H, m), 2.04 (2H, br q, J = 7.3 Hz), 1.80 (2H, m), 1.48 (2H, qt, J = 7.5, 4.6 Hz), 0.15 (9H, s); ^{13}C NMR δ 207.8 (2C, 0), 137.8 (1), 115.4 (2), 98.1 (0), 92.0 (0), 56.9 (0), 35.2 (2C, 2), 33.6 (2), 33.4 (2), 23.7 (2), –0.1 (3C, 3); HRMS (ESI TOF) m/z 285.1270, $[C_{15}H_{22}O_2Si + Na]^+$ requires 285.1281.

(2*R**,3*S**)-3-(*tert*-Butyldimethylsilyl)oxy-2-(pent-4-enyl)-2-((trimethylsilyl)ethynyl)cyclopentanone (15)

Triethylsilane (1.05 mL, 6.56 mmol) was added to a solution of **14** (1.50 g, 5.73 mmol) in CH_2Cl_2 (60 mL) at rt. $BF_3{\cdot}OEt_2$ (0.82 mL, 6.54 mmol) was added, and the solution became bright yellow. The mixture was stirred for 16 h after which time TLC analysis indicated that some of the starting material still remained. Additional amounts of triethylsilane (0.20 mL, 1.3 mmol) and $BF_3{\cdot}OEt_2$ (0.16 mL, 1.3 mmol) were added, and the solution was stirred for 4 h. The mixture was poured into saturated aqueous $NaHCO_3$. The mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified using flash chromatography (CH_2Cl_2) to provide (2*R**,3*S**)-3-hydroxy-2-(pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentanone (**14a**) (1.21 g, 80%): IR (neat) 3463 (br m), 3077 (w), 2958 (s), 2161 (m), 1743 (s), 1641 (w) cm^{-1}; ^1H NMR δ 5.83 (1H, ddt, J = 17.0, 10.2, 6.7 Hz), 5.04 (1H, br d, J = 17.0 Hz), 4.98 (1H, br d, J = 10.2 Hz), 4.41 (1H, narrow m), 2.51–2.39 (4H, m), 2.13 (2H, m), 1.97 (1H, m), 1.81–1.70 (2H, m), 1.58 (1H, m), 1.48 (1H, m), 0.14 (9H, s); ^{13}C NMR δ 212.7 (0), 138.7 (1), 115.1 (2), 102.9 (0), 91.1 (0), 76.1 (1), 55.5 (0), 34.0 (2), 33.4 (2), 28.4 (2), 28.3 (2), 24.4 (2), 0.1 (3C, 3); HRMS (ESI TOF) m/z 287.1442, $[C_{15}H_{24}O_2Si + Na]^+$ requires 287.1438.

Triethylamine (0.69 mL, 5.0 mmol) was added to a solution of **14a** (1.05 g, 3.98 mmol) in THF (40 mL) at 0 °C. TBSOTf (1.04 mL, 4.54 mmol) was added, and the mixture was stirred for 1 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the layers were separated. The aqueous layer was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under vacuum followed by flash chromatography (3% EtOAc/hexanes) of the residue gave **15** (1.44 g, 95%): IR (neat) 3078 (m), 2955 (s), 2162 (s), 1756 (s), 1641 (m) cm^{-1}; ^1H NMR δ 5.82 (1H, ddt, J = 17.1, 10.0, 6.9 Hz), 5.01 (1H, br d, J = 17.1 Hz), 4.94 (1H, br d, J = 10.0 Hz), 4.34 (1H, narrow m), 2.47–2.31 (3H, m), 2.08 (2H, m), 1.89 (1H, m), 1.76–1.63 (2H, m), 1.58 (1H, m), 1.43 (1H, m), 0.86 (9H, s), 0.13 (9H, s), 0.10 (3H, s), 0.09 (3H, s); ^{13}C NMR δ 213.1 (0), 138.8 (1), 114.8 (2), 103.5 (0), 90.8 (0), 76.9 (1), 56.1 (0), 34.3 (2), 33.5 (2), 29.1 (2), 28.7 (2), 25.9 (3C, 3), 24.4 (2), 18.2 (0), 0.2 (3C, 3), –4.2 (3), –4.7 (3); HRMS (ESI TOF) m/z 401.2287, $[C_{21}H_{38}O_2Si_2 + Na]^+$ requires 401.2303.

(1*R**,2*S**,3*S**)-3-(*tert*-Butyldimethylsilyl)oxy-2-ethynyl-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (16)

A 1.0 M solution of vinylmagnesium bromide in THF (4.5 mL, 4.5 mmol) was added to a suspension of anhydrous $CeCl_3$ (1.11 g, 4.50 mmol) in THF (10 mL) at –78 °C. The mixture was stirred at this temperature for 2 h. A solution of **15** (0.850 g, 2.25 mmol) in THF (5.0 mL) was added, and the mixture was stirred at –78 °C for 1 h. After this time, TLC analysis indicated that no starting material remained. The mixture was warmed to rt, and the reaction was quenched with 5% aqueous citric acid. The mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified using flash chromatography (2% EtOAc/hexanes) to give (1*R**,2*S**,3*R**)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (**15a**) (0.816 g, 89%): IR (neat) 3504 (br), 3077 (m), 2956 (s), 2161 (s), 1641 (s) cm^{-1}; ^1H NMR δ 6.14 (1H, ddd, J = 17.3, 10.9, 1.6 Hz), 5.82 (1H, ddt, J = 17.1, 10.3, 6.8 Hz), 5.40 (1H, dd, J = 17.3, 2.1 Hz), 5.17 (1H, dd, J = 10.9, 2.1 Hz), 5.00 (1H, dd, J = 17.1, 1.7 Hz), 4.93 (1H, dd, J = 10.3, 1.2 Hz), 4.26 (1H, d, J = 4.8 Hz), 4.09 (1H, d, J = 1.3 Hz, OH), 2.40–2.28 (2H, m), 2.06 (2H, m), 1.92 (1H, m), 1.78 (1H, m), 1.70 (2H, m), 1.46–1.31 (2H, m), 0.90 (9H, s), 0.14 (9H, s), 0.13 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 140.5 (1), 139.1 (1), 114.5 (2), 114.2 (2), 108.4 (0), 90.3 (0), 85.3 (0), 80.9 (1), 56.1 (0), 38.8 (2), 34.6 (2), 32.4 (2), 27.3 (2), 26.0 (3C, 3), 25.2 (2), 18.0 (0), 0.2 (3C, 3), –4.2 (3), –5.0 (3); HRMS (ESI TOF) m/z 429.2607, $[C_{23}H_{42}O_2Si_2 + Na]^+$ requires 429.2616.

Anhydrous K_2CO_3 (0.380 g, 2.56 mmol) was added to a solution of **15a** (0.800 g, 1.97 mmol) in MeOH (17 mL) at 0 °C. The mixture was allowed to warm to rt and stirred for 18 h. The mixture was then diluted with water, and the MeOH was removed under reduced pressure. The resulting suspension was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. Removal of the solvent under vacuum followed by flash chromatography (2% EtOAc/hexanes) gave **16** (0.641 g, 97%): IR (neat) 3504 (br), 3308 (m), 3076 (m), 2932 (s), 2860 (m), 2106 (w), 1641 (m) cm^{-1}; ^1H NMR δ 6.15 (1H, ddd, J = 17.2, 10.7, 1.8 Hz), 5.82 (1H, ddt, J = 17.1, 10.3, 6.8 Hz), 5.41 (1H, dd, J = 17.2, 2.1 Hz), 5.18 (1H, dd, J = 10.7, 2.1 Hz), 5.00 (1H, br d, J = 17.1 Hz), 4.93 (1H, d, J = 10.3 Hz), 4.30 (1H, d, J = 4.9 Hz), 4.05 (1H, d, J = 1.8 Hz, OH), 2.42–2.29 (2H, m), 2.22 (1H, s), 2.06 (2H, m), 1.95 (1H, m), 1.81 (1H, m), 1.73 (2H, m), 1.49–1.33 (2H, m), 0.91 (9H, s), 0.13 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 140.2 (1), 138.9 (1), 114.6 (2), 114.5 (2), 85.8 (0), 85.1 (1), 80.8 (1), 73.7 (0), 55.1 (0), 38.7 (2), 34.6 (2), 32.2 (2), 27.4 (2), 25.9 (3C, 3), 25.1 (2), 18.0 (0), –4.2 (3), –5.0 (3); HRMS (ESI TOF) m/z 357.2197, $[C_{20}H_{34}O_2Si + Na]^+$ requires 357.2220.

(1*R**,2*R**,7a′*R**,5*R**)-5-(*tert*-Butyldimethylsilyl)oxy-5′,6′,7′,7a′-tetrahydro-2-hydroxy-2-vinylspiro[cyclopentane-1,4′-inden]-2′(1′*H*)-one (17)

Dicobalt octacarbonyl (0.350 g, 1.02 mmol) was added to a solution of alcohol **16** (0.308 g, 0.922 mmol) in CH_2Cl_2 (4.0 mL). The resulting red solution was stirred at rt for 18 h, after which time TLC analysis indicated that none of the starting material remained. The mixture was diluted with CH_2Cl_2 (60 mL) and treated with a solution of anhydrous TMANO (0.575 g, 7.65 mmol) in CH_2Cl_2 (20 mL) at rt. The solution was stirred for a further 16 h during which time a deep blue precipitate formed. The mixture was filtered through a plug of silica gel

(EtOAc eluent), and the solvent was removed under reduced pressure. Flash chromatography (12% EtOAc/hexanes) of the crude product gave **17** (0.232 g, 76%) and some material that appeared to be epimeric at the bridgehead position (14%). For **17**: mp 114–116 °C; IR (neat) 3484 (br), 2951 (s), 2931 (s), 2858 (m), 1714 (s), 1691 (s), 1597 (m) cm^{-1}; ^1H NMR δ 6.07 (1H, dd, J = 17.6, 11.0 Hz), 6.00 (1H, d, J = 1.3 Hz), 5.48 (1H, dd, J = 17.6, 1.7 Hz), 5.26 (1H, dd, J = 11.0, 1.7 Hz), 4.45 (1H, s, OH), 4.39 (1H, d, J = 4.9 Hz), 2.81 (1H, m), 2.54 (1H, dd, J = 18.9, 6.6 Hz), 2.44 (1H, br d, J = 13.9 Hz), 2.37 (1H, ddd, J = 14.8, 12.0, 4.9 Hz), 2.25 (1H, ddd, J = 15.5, 9.9, 5.9 Hz), 2.13 (1H, m), 1.97 (1H, dd, J = 18.9, 2.6 Hz), 1.94 (1H, m), 1.90–1.82 (2H, m), 1.53 (1H, qt, J = 13.5, 3.5 Hz), 1.41 (1H, td, J = 13.9, 4.2 Hz), 1.15 (1H, qd, J = 12.5, 3.7 Hz), 0.93 (9H, s), 0.16 (6H, s); ^{13}C NMR δ 208.6 (0), 181.6 (0), 138.2 (1), 131.0 (1), 117.1 (2), 84.5 (0), 79.1 (1), 60.8 (0), 41.7 (2), 41.5 (1), 37.1 (2), 34.3 (2), 31.7 (2), 25.9 (3C, 3), 25.6 (2), 22.7 (2), 18.1 (0), –4.1 (3), –4.9 (3); HRMS (ESI TOF) m/z 385.2162, $[C_{21}H_{34}O_3Si + Na]^+$ requires 385.2169.

(3a*R**,7a*R**,10*S**,10a*R**)-2,3,3a,4,6,7,7a,8,9,10-Decahydro-7a,10-dihydroxycyclopenta[*f*]acenaphthalen-5(1*H*)-one (18)

Compound **17** (120 mg, 0.33 mmol) was dissolved in MeOH (3.0 mL) with KOH (25 mg, 0.45 mmol), and this was stirred for 2 h at rt at which time TLC indicated the complete disappearance of **17**. Saturated aqueous NH_4Cl was added followed by water, and the mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent gave a residue (94 mg) that was added to HF·pyridine (0.4 mL) in CH_2Cl_2 (2.5 mL) at 0 °C. The mixture was stirred for 1 h, after which time TLC analysis indicated that none of the starting material remained. The mixture was poured into cold saturated aqueous $NaHCO_3$, which was extracted thoroughly with a 1 : 1 $CHCl_3/CH_2Cl_2$ solution. The combined organic layers were washed with brine and then dried over Na_2SO_4. Removal of the solvent *in vacuo* gave **18** (68 mg, 83%): mp 122–124 °C; IR (neat) 3404 (br), 2929 (s), 2858 (m), 1686 (s), 1638 (s) cm^{-1}; ^1H NMR δ 4.43 (1H, narrow m), 2.70 (1H, narrow m), 2.58 (1H, m), 2.51 (1H, m, OH), 2.37 (2H, narrow m), 2.29 (1H, narrow m), 2.15–1.93 (4H, m), 1.86 (3H, narrow m), 1.80–1.62 (2H, m), 1.54 (1H, m), 1.24 (1H, m), 1.04 (1H, qd, J = 12.8, 4.2 Hz); ^{13}C NMR δ 207.2 (0), 179.7 (0), 136.2 (0), 82.2 (0), 76.3 (1), 56.1 (0), 42.4 (2), 37.3 (2), 37.0 (1), 35.8 (2), 32.2 (2), 30.2 (2), 28.7 (2), 22.7 (2), 18.1 (2); HRMS (ESI TOF) m/z 271.1314, $[C_{15}H_{20}O_3 + Na]^+$ requires 271.1305.

X-Ray crystal structure determination for 18

Measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Ka radiation (λ = 0.71070 Å). The crystal was a colourless plate of dimensions 0.23 × 0.22 × 0.06 mm, formula $C_{15}H_{20}O_3$, M = 248.32, monoclinic, a = 11.2484(9) Å, b = 8.5765(5) Å, c = 12.9938(9) Å, α = 90.00°, β = 105.921(3)°, γ = 90.00°, V = 1205.45(15) $Å^3$, $P21/c$ (#14), Z = 4, $F(000)$ = 536, T = 120.1 K, μ(Mo-Kα) 0.094 mm^{-1}, 2825 observed reflections ($I > 3.00\sigma(I)$) and 183 variable parameters; $R(F_o)$ = 0.0364, $wR_2(F^2)$ = 0.0452, goodness of fit = 1.014.

(1*R**,2*R**,7a′*R**,5*R**)-5-(*tert*-Butyldimethylsilyl)oxy-2-hydroxy-2-vinyl-5′,6′,7′,7a′-tetrahydro-2′-(methoxymethoxy)spiro[cyclopentane-1,4′-inden]-2′-ol (19)

$CeCl_3 \cdot 7H_2O$ (128 mg, 0.344 mmol) was added to a solution of **17** (112 mg, 0.309 mmol) in MeOH (3.0 mL) at 0 °C. $NaBH_4$ (12 mg, 0.32 mmol) was added, and the mixture was stirred for 30 min. The reaction was quenched by the addition of saturated aqueous NH_4Cl, and the MeOH was then removed under vacuum. The mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a solid residue that was dissolved in CH_2Cl_2 (2.0 mL). *N*,*N*-Diisopropylethylamine (0.60 mL, 0.35 mmol) and MOMCl (0.33 mL, 0.35 mmol) were sequentially added at 0 °C. The mixture was allowed to warm to rt and was stirred for 5 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over Na_2SO_4. Removal of the solvent under vacuum gave a residue that was purified by flash chromatography (8% EtOAc/hexanes) to give the single diastereomer **19** (90 mg, 72%): IR (neat) 3468 (br m), 3086 (w) cm^{-1}; ^1H NMR δ 6.23 (1H, dd, J = 17.2, 10.8 Hz), 5.51 (1H, s), 5.44 (1H, dd, J = 17.2, 2.0 Hz), 5.20 (1H, dd, J = 10.8, 1.8 Hz), 4.69 (1H, d, J = 6.8 Hz) 4.66 (1H, d, J = 6.8 Hz), 4.57 (1H, m), 4.42 (1H, s, OH), 4.22 (1H, d, J = 5.0 Hz), 3.37 (3H, s), 2.49–2.36 (3H, m), 2.25 (1H, br d, J = 13.8 Hz), 2.19 (1H, ddd, J = 15.6, 10.0, 6.0 Hz), 2.00 (1H, m), 1.92 (1H, m), 1.80–1.71 (2H, m), 1.40 (1H, qt, J = 13.4, 3.2 Hz), 1.33–1.27 (2H, m), 1.07 (1H, dt, J = 12.6, 3.2 Hz), 0.91 (9H, s), 0.13 (3H, s), 0.12 (3H, s); ^{13}C NMR δ 147.9 (0), 139.3 (1), 128.0 (1), 115.6 (2), 96.3 (2), 84.9 (0), 83.2 (1), 79.1 (1), 58.8 (0), 55.5 (3), 43.6 (1), 38.3 (2), 38.2 (2), 35.1 (2), 31.6 (2), 25.9 (3C, 3), 25.2 (2), 23.2 (2), 18.1 (0), –4.1 (3), –4.9 (3); HRMS (ESI TOF) m/z 431.2595, $[C_{23}H_{40}O_4Si + Na]^+$requires 431.2588.

(1*R**,2a*S**,6*R**,11a*S**)-6-(*tert*-Butyldimethylsilyl)oxy-2a,3,4,5,6,7,8,10,11,11a-decahydro-1-(methoxymethoxy)-1*H*-cyclonona[*cd*]inden-9(2*H*)-one (20)

18-Crown-6 (50 mg, 0.19 mmol) was added to a solution of **19** (69 mg, 0.17 mmol) in THF (1.5 mL) at 0 °C. KH (9 mg, 0.2 mmol) was added and the mixture was stirred for 20 min. The reaction was quenched by the addition of saturated aqueous NH_4Cl, and the mixture was then extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (8% EtOAc/hexanes) to give **20** (54 mg, 78%): IR (neat) 1700 (s) cm^{-1}; ^1H NMR δ 4.72 (1H, d, J = 6.5 Hz), 4.68 (1H, d, J = 6.5 Hz), 4.40 (1H, dd, J = 11.5, 3.0 Hz), 4.03 (1H, ddd, J = 11.5, 8.6, 6.0 Hz), 3.39 (3H, s), 2.93 (1H, m), 2.68 (1H, td, J = 12.1, 5.3 Hz), 2.37–2.01 (9H, m), 1.90 (1H, m), 1.81–1.73 (3H, m), 1.42 (1H, m), 1.31 (1H, q, J = 11.5 Hz), 1.18 (1H, qd, J = 12.0, 3.0 Hz), 0.86 (9H, s), 0.02 (3H, s), –0.03 (3H, s); ^{13}C NMR δ 214.0 (0), 139.5 (0), 133.8 (0), 96.1 (2), 78.6 (1), 72.2 (1), 55.7 (3), 45.0 (2), 41.2 (1), 38.9 (1), 38.2 (2), 35.6 (2), 32.5 (2), 27.0 (2), 26.0 (3C, 3), 24.9 (2), 22.6 (2), 20.9 (2), 18.3 (0), –4.5 (3), –4.9 (3); HRMS (ESI TOF) m/z 431.2591, $[C_{23}H_{40}O4Si + Na]^+$ requires 431.2588.

3,3-Dimethoxy-1-(trimethylsilyl)hept-6-en-1-yne (22)

Trimethyl orthoformate (20 mL) was added to a solution of 1-(trimethylsilyl)hept-6-en-1-yn-3-one (4.65 g, 25.8 mmol) in MeOH (20 mL) at rt. *p*-TsOH hydrate (0.05 g, 0.3 mmol) was added, and the mixture was stirred for 20 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the bulk of the organic solvent was removed under reduced pressure. The mixture was then extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent gave an oil that was purified by passage through a plug of silica gel (5% EtOAc/hexanes) to give **22** (5.53 g, 95%): IR (neat) 3081 (w), 2961 (s), 2153 (w) cm^{-1}; ^1H NMR δ 5.87 (1H, ddt, J = 10.2, 16.7, 5.5 Hz), 5.05 (1H, dq, J = 16.7, 1.7 Hz), 4.97 (1H, dq, J = 10.2, 1.7 Hz), 3.31 (6H, s), 2.24 (2H, m), 1.87 (2H, m), 0.20 (9H, s); ^{13}C NMR δ 138.2 (1), 114.7 (2), 101.4 (0), 99.2 (0), 90.8 (0), 50.2 (2C, 3), 36.5 (2), 28.8 (2), 0.0 (3C, 3); HRMS (ESI TOF) m/z 249.1279, $[C_{12}H_{22}O_2Si + Na]^+$ requires 249.1281.

2-(But-3-enyl)-2-((trimethylsilyl)ethynyl)cyclohexane-1,3-dione (24)

$BF_3{\cdot}OEt_2$ (22.1 mL, 0.179 mol) was added to a solution of **22** (20.00 g, 0.0885 mol) and **21**[10b,15] (25.55 g, 0.105 mol) in CH_2Cl_2 (580 mL) at −78 °C. The solution became dark. The mixture was stirred at this temperature for 3 h, and then it was warmed to rt. The reaction was quenched with saturated aqueous $NaHCO_3$. The solution became pale yellow. The mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was eluted through a plug of silica (10% EtOAc/hexanes) to give an inseparable diastereomeric mixture **23** (31.19 g, 96%). A portion of this mixture (6.00 g, 16.4 mmol) was dissolved in benzene (340 mL) and Amberlyst-15 (3.00 g) was added. The vessel was fitted with a Dean–Stark apparatus and reflux condenser, and the mixture was heated at reflux for 16 h. The mixture was cooled and filtered through sintered glass. The filtrate was washed with saturated aqueous $NaHCO_3$, and this aqueous solution was back-extracted thoroughly with EtOAc. The combined organic solutions were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent gave crude **24** (3.68 g, 85% mass recovery) as a yellow oil that largely decomposed upon chromatography. (The crude product was used directly for the preparation of **25** and **26**.) Chromatography resulted in greatly reduced yields (< 20%) but did provide **24** as a colourless solid: mp: 32–35 °C; IR (neat) 2954 (s), 1711 (s) cm^{-1}; ^1H NMR δ 5.86 (1H, ddt, J = 17.1, 10.2, 6.6 Hz), 5.05 (1H, ddd, J = 17.1, 3.5, 1.7 Hz), 4.96 (1H, ddd, J = 10.2, 3.5, 1.0 Hz), 3.27 (2H, dt, J = 15.0, 11.9 Hz), 2.52 (2H, dt, J = 15.0, 4.7 Hz), 2.21 (1H, m), 2.16 (2H, m), 1.97 (2H, m), 1.61 (1H, m), 0.17 (9H, s); ^{13}C NMR δ 201.7 (2C, 0), 138.5 (1), 114.7 (2), 101.3 (0), 94.1 (0), 67.2 (0), 37.6 (2C, 2), 29.4 (2), 28.8 (2), 18.0 (2), –0.2 (3C, 3); HRMS (EI) m/z 262.1399, $[C_{15}H_{22}O_2Si]^+$ requires 262.1389.

(2*R,3*R**)-2-(But-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)-cyclohexanone (25) and (2*R**,3*S**)-2-(but-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)cyclohexanone (26)**

A 1.0 M solution of $LiAl(O\textit{t}\text{-}Bu)_3H$ (9.0 mL, 9.0 mmol) was added to a solution of diketone **24** (2.20 g, 8.40 mmol) in THF (100 mL) at −78 °C. When TLC analysis indicated that none of the starting material remained (less than 10 min), the mixture was warmed rapidly to 0 °C, and saturated aqueous NH_4Cl was added. After addition of more water, the mixture was extracted thoroughly with EtOAc/Et_2O. The organic layers were combined and washed with brine and then dried over Na_2SO_4. Removal of the solvent under reduced pressure gave 1.92 g (87%) of a 2 : 1 mixture of **25** (major) and **26** (minor). Repeated flash chromatography (60% CH_2Cl_2/hexanes) separated these epimers. For **25**: mp 45–46 °C; IR (neat) 3506 (br s), 3075 (m), 2956 (s), 2162 (m), 1708 (s), 1640 (m) cm^{-1}; ^1H NMR δ 5.86 (1H, ddt, J = 10.2, 17.1, 6.7 Hz), 5.05 (1H, dq, J = 17.1, 1.8 Hz), 4.96 (1H, d, J = 10.2 Hz), 3.56 (1H, td, J = 9.0, 4.6 Hz), 2.83 (1H, ddd, J = 13.3, 12.0, 6.0 Hz), 2.28 (1H, dt, J = 13.3, 4.9 Hz), 2.22–2.14 (3H, m), 2.15 (1H, d, J = 9.0 Hz, OH), 2.09–1.98 (3H, m), 1.88 (1H, m), 1.50 (1H, m), 0.20 (9H, s); ^{13}C NMR δ 206.2 (0), 138.7 (1), 114.8 (2), 103.4 (0), 94.1 (0), 76.2 (1), 59.9 (0), 37.9 (2), 32.0 (2), 30.7 (2), 29.9 (2), 20.9 (2), 0.2 (3C, 3); HRMS (ESI TOF) m/z 287.1438, $[C_{15}H_{24}O_2Si + Na]^+$ requires 287.1438.

For **26**: IR (neat) 3441 (br s), 3076 (m), 2959 (s), 2161 (m), 1722 (s), 1641 (m) cm^{-1}; ^1H NMR δ 5.89 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.08 (1H, dq, J = 16.9, 1.7 Hz), 4.98 (1H, d, J = 10.2 Hz), 4.20 (1H, br s, OH), 3.00 (1H, td, J = 12.8, 6.2 Hz), 2.44 (1H, m), 2.31–2.11 (3H, m), 2.05 (1H, m), 1.97 (1H, m), 1.87 (2H, m), 1.70–1.62 (2H, m), 0.17 (9H, s); ^{13}C NMR δ 207.5 (0), 138.8 (1), 114.9 (2), 105.2 (0), 92.3 (0), 76.5 (1), 55.9 (0), 38.4 (2), 30.3 (2), 29.2 (2), 28.9 (2), 21.6 (2), 0.2 (3C, 3); HRMS (ESI TOF) m/z 287.1442, $[C_{15}H_{24}O_2Si + Na]^+$ requires 287.1438.

(2*R,3*R**)-2-(But-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)cyclohexanone (27)**

Triethylamine (1.60 mL, 11.4 mmol) was added to a solution of **25** (2.06 g, 7.78 mmol) in THF (75 mL) at 0 °C. TBSOTf (1.9 mL, 8.4 mmol) was added and the solution was stirred for 1 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (5% EtOAc/hexanes) gave **27** (2.88 g, 98%): IR (neat) 3078 (m), 2957 (s), 2160 (m), 1729 (s), 1641 (m) cm^{-1}; ^1H NMR δ 5.85 (1H, ddt, J = 17.0, 10.2, 6.3 Hz), 5.02 (1H, ddd, J = 17.0, 3.4, 1.8 Hz), 4.94 (1H, dd, J = 10.2, 1.8 Hz), 3.55 (1H, dd, J = 9.8, 3.7 Hz), 2.91 (1H, dt, J = 12.4, 6.3 Hz), 2.24–2.08 (4H, m), 1.99–1.84 (2H, m), 1.80 (2H, m), 1.43 (1H, qt, J = 12.7, 4.1 Hz), 0.90 (9H, s), 0.16 (9H, s), 0.07 (3H, s), 0.06 (3H, s); ^{13}C NMR δ 206.9 (0), 139.2 (1), 114.3 (2), 105.1 (0), 91.7 (0), 77.2 (1), 59.9 (0), 37.9 (2), 32.1 (2), 31.2 (2), 29.6 (2), 25.9 (3C, 3), 20.9 (2), 18.3 (0), 0.2 (3C, 3), –3.7 (3), –4.5 (3); HRMS (ESI TOF) m/z 401.2304, $[C_{21}H_{38}O_2Si_2 + Na]^+$ requires 401.2303.

(1*R,2*R**,3*R**)-2-(But-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-1-vinylcyclohexanol (28)**

A 1.6 M solution of *n*-BuLi (2.4 mL, 3.8 mmol) was added to a solution of tetravinyltin (217 mg, 0.956 mmol) in THF (1.8 mL) at −78 °C. The mixture, which had become cloudy, was stirred at

this temperature for 30 min and then allowed to warm to rt for 15 min during which time the mixture clarified. The mixture was then cooled back to –78 °C, and ketone **27** (242 mg, 0.64 mmol) in THF (4.2 mL) was added dropwise. TLC revealed that reaction was complete in 10 min. The mixture was allowed to warm to rt, and saturated aqueous NH_4Cl was added. The mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (3% EtOAc/hexanes) to give **28** (221 mg, 85%) and a small amount of the epimer (*1R*,2S*,3S**)-*2-(but-3-enyl)-3-(tert-butyldimethylsilyl)oxy-2-((trimethylsilyl)-ethynyl)-1-vinylcyclohexanol* (**28a**) (24 mg, 9%). For **28**: IR (neat) 3502 (br m), 3079 (w) cm^{-1}; ^1H NMR δ 6.00 (1H, dd, J = 17.3, 10.8 Hz), 5.79 (1H, ddt, J = 17.0, 13.2, 6.6 Hz), 5.33 (1H, dd, J = 17.3, 1.7 Hz), 5.16 (1H, dd, J = 10.8, 1.7 Hz), 5.00 (1H, dq, J = 17.0, 1.7 Hz), 4.94 (1H, d, J = 10.1 Hz), 3.97 (1H, br s), 2.34 (1H, m), 2.06 (1H, m), 1.96 (1H, m), 1.76–1.58 (4H, m), 1.55 (2H, m), 1.44 (1H, m), 0.94 (9H, s), 0.16 (3H, s), 0.15 (9H, s), 0.11 (3H, s); ^{13}C NMR δ 140.6 (1), 139.0 (1), 114.9 (2), 114.4 (2), 108.1 (0), 89.0 (0), 75.6 (1), 73.8 (0), 49.6 (0), 34.1 (2), 32.7 (2), 29.7 (2), 28.2 (2), 25.9 (3C, 3), 18.1 (0), 15.6 (2), 0.22 (3C, 3), –4.5 (3), –4.9 (3); HRMS (ESI TOF) m/z: 429.2630, $[C_{23}H_{42}O_2Si_2 + Na]^+$ requires 429.2616.

For **28a**: IR (neat) 3500 (m), 3078 (w) cm^{-1}; ^1H NMR δ 6.42 (1H, dd, J = 17.4, 10.8 Hz), 5.78 (1H, ddt, J = 17.0, 10.3, 6.7 Hz), 5.23 (1H, dd, J = 17.4, 1.1 Hz), 5.11 (1H, dd, J = 10.8, 1.1 Hz), 4.96 (1H, dq, J = 17.0, 1.7 Hz), 4.88 (1H, d, J = 10.3 Hz), 3.83 (1H, dd, J = 10.8, 3.9 Hz), 2.34 (1H, m), 2.21 (1H, m), 2.05 (1H, td, J = 13.4, 4.6 Hz), 1.85 (1H, m), 1.76–1.59 (4H, m), 1.55 (1H, m), 1.25 (1H, br d, J = 14.0 Hz), 0.89 (9H, s), 0.15 (9H, s), 0.07 (3H, s), 0.04 (3H, s); ^{13}C NMR δ 144.5 (1), 139.8 (1), 113.6 (2), 111.8 (2), 107.7 (0), 90.6 (0), 78.4 (0), 74.2 (1), 50.8 (0), 35.8 (2), 32.0 (2), 31.9 (2), 31.6 (2), 25.9 (3C, 3), 19.5 (2), 18.1 (0), 0.18 (3C, 3), –3.7 (3), –4.5 (3); HRMS (ESI TOF) m/z 429.2592, $[C_{23}H_{42}O_2Si_2 + Na]^+$ requires 429.2616.

(1*R**,2*R**,3*R**)-2-(But-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-ethynyl-1-vinylcyclohexanol (29)

K_2CO_3 (194 mg, 1.40 mmol) was added to a solution of **28** (477 mg, 1.17 mmol) in MeOH (10 mL) at 0 °C. The mixture was stirred at rt for 14 h. Water was added, and MeOH was removed under reduced pressure. The mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography (5% EtOAc/hexanes) to give **29** (364 mg, 93%): IR (neat) 3262 (s) cm^{-1}; ^1H NMR δ 6.06 (1H, dd, J = 17.3, 10.9 Hz), 5.79 (1H, ddt, J = 17.0, 13.2, 6.6 Hz), 5.36 (1H, dd, J = 17.3, 1.7 Hz), 5.20 (1H, dd, J = 10.9, 1.7 Hz), 5.03 (1H, dq, J = 17.0, 1.6 Hz), 4.96 (1H, d, J = 10.1 Hz), 4.06 (1H, br s), 2.38 (1H, m), 2.21 (1H, s), 2.12–1.96 (2H, m), 1.82–1.54 (6H, m), 1.49 (1H, m), 0.96 (9H, s), 0.19 (3H, s), 0.14 (3H, s); ^{13}C NMR δ 140.7 (1), 138.5 (1), 115.0 (2), 114.8 (2), 85.6 (0), 75.7 (1), 73.7 (1), 72.8 (0), 48.3 (0), 33.7 (2), 32.2 (2), 29.4 (2), 27.8 (2), 25.8 (3C, 3), 18.0 (0), 15.2 (2), –4.7 (3), –4.8 (3); HRMS (ESI TOF) m/z 357.2231, $[C_{20}H_{34}O_2Si + Na]^+$ requires 357.2220.

(1*R**,2*R**,3a′*R**,6*R**)-6-(*tert*-Butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3a′,4′-dihydro-2′*H*-spiro[cyclohexane-1,1′-pentalen]-5′(3′*H*)-one (30) and (1*R**,2*R**,3a′*S**,6*R**)-6-(*tert*-butyl-dimethylsilyloxy)-2-hydroxy-2-vinyl-3a′,4′-dihydro-2′*H*-spiro[cyclohexane-1,1′-pentalen]-5′(3′*H*)-one (31)

Dicobalt octacarbonyl (446 mg, 1.30 mmol) was added to a solution of **29** (0.364 g, 1.09 mmol) in CH_2Cl_2 (8.0 mL) at rt. The mixture was stirred for 20 h. At this time the TLC analysis showed complete consumption of **29** and the formation of a new, less polar, red compound. The mixture was diluted with CH_2Cl_2 (70 mL) and anhydrous TMANO (740 mg, 9.90 mmol) in CH_2Cl_2 (10 mL) was added. After 16 h a deep blue precipitate had formed. The mixture was filtered through a plug of silica gel (EtOAc eluent). Removal of the solvent under reduced pressure followed by flash chromatography (5% EtOAc/hexanes) provided **30** (247 mg, 62%) and **31** (48 mg, 12%). For **30**: IR (neat) 3453 (br s), 1705 (s) cm^{-1}; ^1H NMR δ 6.43 (1H, d, J = 2.3 Hz), 5.68 (1H, ddd, J = 17.2, 10.9, 0.9 Hz), 5.36 (1H, br s, OH), 5.25 (1H, dd, J = 17.2, 1.6 Hz), 5.05 (1H, dd, J = 10.9, 1.6 Hz), 3.83 (1H, t, J = 2.6 Hz), 2.91 (1H, m), 2.55 (1H, dd, J = 17.9, 6.3 Hz), 2.16–1.96 (3H, m), 2.04 (1H, dd, J = 17.9, 3.2 Hz), 1.81–1.52 (6H, m), 1.13 (1H, ddd, J = 20.0, 11.8, 8.0 Hz), 0.91 (9H, s), 0.05 (3H, s), –0.06 (3H, s); ^{13}C NMR δ 211.1 (0), 189.2 (0), 140.3 (1), 129.8 (1), 115.4 (2), 76.0 (0), 75.9 (1), 53.9 (0), 45.2 (1), 41.4 (2), 35.9 (2), 34.6 (2), 30.5 (2), 28.0 (2), 25.8 (3C), 17.9 (0), 14.8 (2), –4.9 (3), –5.0 (3); HRMS (ESI TOF) m/z 385.2160, $[C_{21}H_{34}O_3Si + Na]^+$ requires 385.2169.

For **31**: IR (neat) 3443 (br w), 1704 (s) cm^{-1}; ^1H NMR δ 6.22 (1H, d, J = 2.3 Hz), 5.83 (1H, dd, J = 17.1, 10.9 Hz), 5.28 (1H, d, J = 17.1 Hz), 5.14 (1H, dd, J = 10.9, 1.5 Hz), 3.78 (1H, t, J = 3.5 Hz), 2.91 (1H, m), 2.55 (1H, dd, J = 17.5, 6.4 Hz), 2.10–1.99 (3H, m), 1.99 (1H, dd, J = 17.5, 3.8 Hz), 1.85–1.79 (3H, m), 1.74–1.61 (2H, m), 1.56 (1H, m), 1.16 (1H, m), 0.95 (9H, s), 0.10 (3H, s), 0.03 (3H, s); ^{13}C NMR δ 210.9 (0), 190.4 (0), 141.1 (1), 128.9 (1), 115.7 (2), 75.8 (1), 75.2 (0), 54.6 (0), 49.2 (1), 42.3 (2), 35.5 (2), 33.5 (2), 29.9 (2), 29.6 (2), 26.0 (3C, 3), 18.0 (0), 15.4 (2), –4.27 (3), –4.29 (3); HRMS (ESI TOF) m/z 385.2173, $[C_{21}H_{34}O_3Si + Na]^+$ requires 385.2169.

(4*aR**,8*R**,8*aR**,10*aR**)-8-(*tert*-Butyldimethylsilyl)oxy-3,4,4*a*,5,6,7,8,9,10,10*a*-decahydro-4*a*-hydroxy-1*H*-pentaleno[1,6-*ja*]naphthalene-2(1*H*)-one (32)

KOH (4 mg, 0.08 mmol) was added to a solution of **30** (19 mg, 0.052 mmol) in MeOH (1.0 mL) at rt. The mixture was stirred for 28 h. Saturated aqueous NH_4Cl was added, and the mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified by flash chromatography to give **32** (10 mg, 53%): IR (neat) 3427 (br m), 1701 (s) cm^{-1}; ^1H NMR δ 3.77 (1H, m), 3.02 (1H, m), 2.68 (1H, dd, J = 18.6, 6.0 Hz), 2.41–2.26 (3H, m), 2.23–2.14 (2H, m), 2.10 (1H, dd, J = 18.6, 1.6 Hz), 1.94 (1H, dd, J = 13.0, 8.8 Hz), 1.71–1.53 (5H, m), 1.37 (2H, m), 0.91 (1H, m), 0.88 (9H, s), 0.02 (3H, s), –0.08 (3H, s); ^{13}C NMR δ 209.5 (0), 188.8 (0), 133.4 (0), 75.1 (1), 72.9 (0), 54.0 (0), 43.1 (2), 42.1 (1), 36.1 (2), 32.0 (2), 31.9 (2), 29.7 (2), 27.1 (2), 25.9 (3C, 3), 20.1 (2), 18.0 (0), 17.1 (2), –4.3 (3), –4.6 (3); HRMS (ESI TOF) m/z 385.2150, $[C_{21}H_{34}O_3Si + Na]^+$ requires 385.2169.

5-Oxo-6-vinylidenedec-9-enoic acid (33)

Chromatography-grade SiO_2 (200 mg) was added to a solution of crude diketone **24** (50 mg, 0.19 mmol) in EtOAc (3.0 mL). The slurry was stirred for 6 h, and was then filtered through a plug of Celite (EtOAc eluent). Evaporation of the solvent left a residue that was purified using flash chromatography (5% MeOH/CH_2Cl_2) to give **33** (0.018 g, 51%): IR (neat) 3302 (very br s), 2922 (s), 1710 (s) cm^{-1}; ^1H NMR δ 5.80 (1H, ddt, J = 16.9, 10.2, 6.7 Hz), 5.22 (2H, t, J = 2.9 Hz), 5.02 (1H, dq, J = 16.9, 1.7 Hz), 4.96 (1H, d, J = 10.2 Hz), 2.75 (2H, t, J = 7.2 Hz), 2.40 (2H, t, J = 7.2 Hz), 2.28 (2H, m), 2.16 (2H, q, J = 7.1 Hz), 1.93 (2H, pentet, J = 7.2 Hz); ^{13}C NMR δ 216.4 (0), 200.2 (0), 177.0 (0), 137.9 (1), 115.3 (2), 108.0 (0), 80.4 (2), 38.0 (2), 32.8 (2), 31.9 (2), 25.7 (2), 19.8 (2); HRMS (ESI TOF) m/z 207.1019, $[C_{12}H_{16}O_3 + Na]^+$ requires 207.1027.

(1*R,2*R**,3a′*R**,5′*S**,6*R**)-6-(*tert*-Butyldimethylsilyloxy)-5′-(methoxymethoxy)-2-vinyl-3′,3a′,4′,5′-tetrahydro-2′*H*-spiro[cyclohexane-1,1′-pentalen]-2-ol (34)**

$NaBH_4$ (12 mg, 0.32 mmol) was added to a solution of **30** (53 mg, 0.15 mmol) and $CeCl_3 \cdot 7H_2O$ (82 mg, 0.22 mmol) in MeOH (1.5 mL) at 0 °C. The mixture was stirred for 20 min, and the reaction was then quenched by the addition of saturated aqueous NH_4Cl. The MeOH was removed under reduced pressure, and the aqueous mixture was extracted thoroughly with Et_2O. The organic layers were combined and washed with brine and then dried over Na_2SO_4. Evaporation of the solvent gave (*1R*,2R*,3a′R*,5′S*,6R**) - *6* - (*tert* - *butyldimethylsilyloxy*) - *2* - *vinyl-3′,3a′,4′,5′-tetrahydro-2′H-spiro*[*cyclohexane-1,1′-pentalene*]-*2,5′-diol* (**30a**) (49 mg, 92%) that was used without further purification: IR (neat) 3406 (br s) cm^{-1}; ^1H NMR δ 5.88 (1H, dd, J = 17.3, 10.9 Hz), 5.87 (1H, s), 5.36 (1H, br s, OH), 5.24 (1H, dd, J = 17.3, 1.9 Hz), 5.08 (1H, dd, J = 10.9, 1.9 Hz), 5.02 (1H, br t, J = 7.4 Hz), 3.62 (1H, t, J = 2.8 Hz), 2.67 (1H, m), 2.58 (1H, dt, J = 12.3, 5.7 Hz), 2.07 (1H, qt, J = 13.1, 4.6 Hz), 1.90 (1H, dd, J = 13.9, 8.1 Hz), 1.81 (1H, dt, J = 11.7, 7.3 Hz), 1.75–1.59 (5H, m), 1.51–1.46 (2H, m), 1.18 (1H, dt, J = 12.3, 7.5 Hz), 1.08 (1H, ddd, J = 19.9, 11.7, 8.3 Hz), 0.91 (9H, s), 0.03 (3H, s), –0.04 (3H, s); ^{13}C NMR δ 154.2 (0), 141.7 (1), 128.0 (1), 114.2 (2), 83.2 (1), 76.3 (0), 75.8 (1), 50.9 (0), 49.0 (1), 42.5 (2), 37.0 (2), 34.4 (2), 32.1 (2), 27.9 (2), 25.9 (3C, 3), 17.9 (0), 15.0 (2), –4.8 (3), –5.0 (3); HRMS (ESI TOF) m/z 387.2329, $[C_{21}H_{36}O_3Si + Na]^+$ requires 387.2326.

N,*N*-Diisopropylethylamine (40 μL, 0.24 mmol) was added to a solution of **30a** (30 mg, 0.082 mmol) in CH_2Cl_2 (0.7 mL) at 0 °C. MOMCl (12 μL, 0.15 mmol) was added, and the mixture was allowed to warm to rt. After 6 h the reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure, followed by flash chromatography (10% EtOAc/hexanes) afforded **34** (27 mg, 81%): IR (neat) 3390 (br s), 1038 (s) cm^{-1}; ^1H NMR δ 5.93 (1H, dd, J = 17.3, 11.0 Hz), 5.92 (1H, m), 5.30 (1H, br s, OH), 5.22 (1H, dd, J = 17.3, 1.8 Hz), 5.07 (1H, dd, J = 11.0, 1.8 Hz), 4.88 (1H, m), 4.71 (1H, d, J = 6.7 Hz), 4.69 (1H, d, J = 6.7 Hz), 3.61 (1H, t, J = 2.7 Hz), 3.38 (3H, s), 2.63 (1H, m), 2.50 (1H, dt, J = 12.3, 6.8 Hz), 2.07 (1H, qt, J = 13.1, 4.8 Hz), 1.88 (1H, dd, J = 13.8, 8.3 Hz), 1.79 (1H, dt, J = 11.7, 6.9 Hz), 1.74–1.55 (4H, m), 1.50–1.42 (2H, m), 1.36 (1H, dt, J = 12.2, 8.0 Hz), 1.10 (1H, ddd, J = 19.9, 11.7, 8.3 Hz), 0.91 (9H, s), 0.03 (3H, s), –0.04 (3H, s);^{13}C NMR δ 154.1 (0), 142.0 (1), 126.5 (1), 114.5 (2), 96.1 (2), 88.8 (1), 76.6 (0), 76.1 (1), 55.4 (3), 51.4 (0), 48.4 (1), 39.7 (2), 37.3 (2), 34.6 (2), 32.2 (2), 28.3 (2), 26.1 (3C, 3), 18.2 (0), 15.4 (2), –4.5 (3), –4.7 (3); HRMS (ESI TOF) m/z 431.2549, $[C_{23}H_{40}O_4Si + Na]^+$ requires 431.2588.

(1*R,2*R**,3a′*S**,5′*R**,6*R**)-6-(*tert*-Butyldimethylsilyloxy)-5′-(methoxymethoxy)-2-vinyl-3′,3a′,4′,5′-tetrahydro-2′*H*-spiro[cyclohexane-1,1′-pentalen]-2-ol (35)**

Following the procedure for **34**, **31** (40 mg, 0.11 mmol) gave **35** (30 mg, 67%). For **35**: ^1H NMR δ 5.82 (1H, d, J = 0.5 Hz), 5.79 (1H, dd, J = 17.4, 10.9 Hz), 5.18 (1H, dd, J = 17.4, 1.6 Hz), 5.07 (1H, dd, J = 10.9, 1.7 Hz), 5.00 (1H, dd, J = 7.9, 6.6 Hz), 4.70 (1H, d, J = 5 Hz), 4.65 (1H, d, J = 5 Hz), 3.82 (1H, t, J = 3.0 Hz), 3.37 (3H, s), 2.61 (1H, m), 2.44 (1H, m), 2.05 (1H, m), 1.88 (1H, m) 1.82–1.70 (4H, m) 1.66 (1H, dt, J = 15.0, 5.0 Hz), 1.57 (1H, ddd, J = 15.0, 9.8, 5.0 Hz), 1.49 (1H, m), 1.25 (1H, m), 1.07 (1H, m), 0.97 (9H, s), 0.14 (3H, s), 0.12 (3H, s); ^{13}C NMR δ 155.2 (0), 142.2 (2), 125.6 (1), 114.5 (2), 95.7 (2), 88.0 (1), 76.2 (1), 76.0 (0), 55.2 (3), 51.6 (1), 51.3 (0), 40.3 (2), 37.3 (2), 32.6 (2), 31.0 (2), 29.7 (2), 26.1 (3, 3C), 18.0 (0), 15.3 (2), –4.17 (3), –4.21 (3); HRMS (ESI TOF) m/z 431.2598, $[C_{23}H_{40}O_4Si + Na]^+$ requires 431.2588.

(2*aR,6*aS**,9*aR**,9*bR**)-2,2*a*,3,4,6,6*a*,9,9*a*-Octahydro-1*H*-pentaleno[1,6-*dc*]indene-1,7(8*H*)-dione (37)**

KO*t*-Bu (7 mg, 0.06 mmol) was added to a solution of mesylate **36**[1] (15.8 mg, 0.050 mmol) in *t*-BuOH (0.5 mL) at 0 °C. The mixture was warmed to rt and stirred for 4 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded a residue that was purified by flash column chromatography to give **37** (10 mg, 91%): mp 97–100 °C; ^1H-NMR (C_6D_6) δ 4.94 (1H, s), 2.70 (1H, t, J = 9.5 Hz), 2.58 (1H, m), 2.49 (1H, m), 2.12 (3H, m), 1.80 (6H, m), 1.61 (1H, m), 1.54 (1H, m), 1.04 (1H, m); ^{13}C NMR (C_6D_6) δ 216.9 (0), 209.9 (0), 154.3 (0), 117.3 (1), 66.8 (0), 57.5 (1), 49.7 (1), 44.2 (2), 42.7 (1), 41.8 (2), 34.83 (2), 34.78 (2), 22.6 (2), 19.7 (2); HRMS (ESI TOF) m/z 239.1040, $[C_{14}H_{16}O_2 + Na]^+$ requires 239.1043.

X-Ray crystal structure determination for 37

Measurements were made on a Rigaku AFC5R instrument with graphite monochromated Mo-Ka radiation (λ = 0.71069 Å). The crystal was a colourless needle of dimensions 0.32 × 0.19 × 0.11 mm, formula $C_{14}H_{16}O_2$, M = 216.28, triclinic, a = 8.5532(17) Å, b = 18.428(5) Å, c = 8.1080(17) Å, α = 93.05(2)°, β = 118.249(14)°, γ = 94.88(2)°, V = 1115.3(5) Å^3, $P\bar{1}$(#2), Z = 4, $F(000)$ = 464, T = 296.1 K, μ(Mo-Kα) 0.085 mm^{-1}, 3193 observed reflections ($I > 3.00\sigma(I)$) and 291 variable parameters; $R(F_o)$ = 0.0448, $wR_2(F^2)$ = 0.0563, goodness of fit = 1.127.

(3*aR,7*aR**,10*S**,10*aR**)-2,3,3a,4,6,7,7a,8,9,10-Decahydro-7a-hydroxy-5-oxocyclopenta[*f*]acenaphthalen-10-yl methanesulfonate (40)**

Triethylamine (50 μL, 0.39 mmol) was added to a solution of **18** (65 mg, 0.26 mmol) in CH_2Cl_2 (2.5 mL). MsCl (23 μL, 0.30 mmol) was added, and the mixture was allowed to warm to rt. After 5 h the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were washed with brine and then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified using flash chromatography (75% EtOAc/hexanes) to give **40** (0.068 g, 81%): IR (neat) 3443 (br), 2934 (s), 2859 (m), 1693 (s), 1644 (m) cm^{-1}; ^1H NMR δ 5.32 (1H, dd, J = 4.4, 1.9 Hz), 3.11 (3H, s), 2.77 (1H, m), 2.59 (1H, dd, J = 19.1, 6.4 Hz), 2.40 (1H, ddd, J = 17.9, 5.6, 2.1 Hz), 2.31–2.11 (4H, m), 2.07–1.98 (3H, m), 1.94–1.63 (5H, m), 1.34 (1H, td, J = 13.0, 5.1 Hz), 1.05 (1H, qd, J = 13.0, 5.1 Hz); ^{13}C NMR δ 206.6 (0), 176.6 (0), 137.9 (0), 86.4 (1), 81.4 (0), 55.6 (0), 42.3 (2), 39.4 (1), 37.2 (3), 36.4 (2), 36.3 (2), 31.3 (2), 30.5 (2), 28.7 (2), 22.0 (2), 17.8 (2); HRMS (ESI TOF) m/z 349.1086, $[C_{16}H_{22}O_5S + Na]+$ requires 349.1080.

(3*aR,6*aR**,9*aR**,9*bS**)-2,3,3a,4,6,6a,9,9a-Octahydro-1*H*-cyclopenta[*e*]acenaphthalene-5,7(8*H*,9b*H*)-dione (41)**

KO*t*-Bu (13 mg, 0.12 mmol) was added to a solution of **40** (20 mg, 0.061 mmol) in *t*-BuOH (1 mL) at 0 °C. The mixture was allowed to warm to rt after 1 h and was maintained at this temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted thoroughly with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue that was purified by flash chromatography (15% EtOAc/hexanes) to yield **41** along with a compound that appeared to be epimeric (7 mg, 51%) in a ratio of approximately 3 : 1, and 8 mg (40%) of **40** was recovered. Crystallization from EtOAc/hexanes gave a small amount of homogeneous **41**: mp 117–120 °C; IR (neat): 2929 (s), 1738 (s), 1696 (s) cm^{-1}; ^1H NMR δ 2.79–2.44 (5H, m), 2.52 (3H, m), 2.09–1.88 (6H, m), 1.79 (1H, m), 1.61 (1H, m), 1.27 (1H, m), 1.05 (1H, m); ^{13}C NMR δ 216.8 (0), 207.0 (0), 181.2 (0), 135.1 (0), 48.0 (1), 42.52 (2), 42.48 (2), 40.1 (2), 39.6 (2), 38.5 (1), 36.5 (1), 28.4 (2), 25.2 (1), 22.7 (2), 20.5 (2); HRMS (ESI TOF) m/z 253.1205, $[C_{15}H_{18}O_2 + Na]^+$ requires 253.1199.

X-Ray crystal structure determination for 41

Measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Ka radiation (λ = 0.71070 Å). The crystal was a colourless needle of dimensions 0.25 × 0.28 × 0.33 mm, formula $C_{15}H_{18}O_2$, M = 230.31, triclinic, a = 8.3858(2) Å, b = 8.9432(4) Å, c = 16.6524(14) Å, α = 82.616(11)°, β = 76.245(9)°, γ = 83.941(14)°, V = 1199.33(12) Å^3, $P\bar{1}$(#2), Z = 4, $F(000)$ = 496, T = 120.1 K, μ(Mo-Kα) 0.0828 mm^{-1}, 4302 observed reflections ($I > 3.00\sigma(I)$) and 343 variable parameters; $R(F_o)$ = 0.0442, w$R_2(F^2)$ = 0.0555, goodness of fit = 1.051.

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