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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



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

instances in which the introduction of another, conjugating double bond has enhanced anionic oxy-Cope reactivity.²

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 Gribble³ 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 11⁵ derived from 5-hexenoic acid was treated with TMS-acetylide to give the ynone 12 (Scheme 4). Geminal acylation⁶ of 12 with the four-membered acyloin 13 provided the 1,3-diketone 14 in good yield. Reduction of only one ketone with triethylsilane/BF3·Et2O 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 analogue¹ and this was corroborated by the X-ray structure of the final tetracyclic product (18). Addition of vinylmagnesium bromide in the presence of CeCl₃⁷ 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

OTMS TMSC = 13 1. OMe TMS BF3.Et2O, -78 °C Li Ŵғ TMS THF, -78 °C 2. BF3 Et2O, H2O, 0 °C 91% 78% 12 11 TBSC 0 C Ω 1. Et₃SiH, BF₃ Et₂O TMS TMS 2. TBSOTf, Et₃N 76% 14 15 / TBSO 'OH MgBr , CeCl₃ THF. -78 °C 1. Co₂(CO)8, CH₂Cl₂ 2. TMANO (8 equiv), 2. K₂CO₃, MeOH CH2Cl2, rt 86% 76% 16 OH TBSO ΌH 1. KOH, MeOH HC 2. HF py 83% 17 18

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 sixmembered 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 signatropic 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 ketal¹⁰ **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-15¹¹ 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 NaBH₄ took place in excellent yield but with no facial selectivity. LiAl(Ot-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 CeCl₃, 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 sixmembered 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 ninemembered 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 1,4reaction 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. ¹H NMR spectra were acquired at 500 MHz and ¹³C NMR spectra at 125 MHz as CDCl₃ solutions unless otherwise noted. ¹³C 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 5hexenoic acid (0.500 g, 4.37 mmol) in CH₂Cl₂ (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 CH₂Cl₂. The filtrate was washed with 1 M aqueous HCl and brine and was then dried over MgSO₄. Evaporation of the solvent gave 11 (0.538 g, 78%): IR (neat) 3077 (w), 2937 (s), 1667 (s) cm⁻¹; ¹H 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); ¹³C 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 NH₄Cl was added, and the solution became yellow. The mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. 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%): ¹H 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); ¹³C 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-1,3dione (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 NaHCO₃. The aqueous layer was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and

dried over MgSO₄. 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); ¹³C 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, [C₁₅H₂₂O₂Si + 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 CH₂Cl₂ (60 mL) at rt. BF₃·OEt₂ (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 BF₃·OEt₂ (0.16 mL, 1.3 mmol) were added, and the solution was stirred for 4 h. The mixture was poured into saturated aqueous NaHCO₃. The mixture was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and dried over Na₂SO₄. Evaporation of the solvent gave a residue that was purified using flash chromatography (CH₂Cl₂) to provide $(2R^*, 3S^*)$ -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); ¹³C 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, [C₁₅H₂₄O₂Si + 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 NaHCO₃, and the layers were separated. The aqueous layer was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. 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); ¹³C 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/z401.2287, $[C_{21}H_{38}O_2Si_2 + Na]^+$ 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 CeCl₃ (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 Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was evaporated, and the residue was purified using flash chromatography (2% EtOAc/hexanes) to give (1R*,2S*,3R*)-3-(tert-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-2-(pent-4enyl)-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); ¹³C 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 K₂CO₃ (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 Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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); ¹³C 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 CH₂Cl₂ (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 CH₂Cl₂ (60 mL) and treated with a solution of anhydrous TMANO (0.575 g, 7.65 mmol) in CH₂Cl₂ (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); ¹³C 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 NH₄Cl was added followed by water, and the mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. Evaporation of the solvent gave a residue (94 mg) that was added to HF·pyridine (0.4 mL) in CH₂Cl₂ (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 NaHCO₃, which was extracted thoroughly with a 1:1 CHCl₃/CH₂Cl₂ solution. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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); ¹³C 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, [C₁₅H₂₀O₃ + 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 ($\lambda = 0.71070$ Å). The crystal was a colourless plate of dimensions $0.23 \times 0.22 \times 0.06$ 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, $\alpha = 90.00^{\circ}$, $\beta = 105.921(3)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 1205.45(15) Å³, P21/c (#14), Z = 4, F(000) = 536, T = 120.1 K, μ (Mo-K α) 0.094 mm⁻¹, 2825 observed reflections ($I > 3.00\sigma(I)$) and 183 variable parameters; $R(F_{\circ}) = 0.0364$, w $R_2(F^2) = 0.0452$, 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[cyclo-pentane-1,4'-inden]-2'-ol (19)

CeCl₃·7H₂O (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. NaBH₄ (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 NH₄Cl, and the MeOH was then removed under vacuum. The mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. Evaporation of the solvent gave a solid residue that was dissolved in CH₂Cl₂ (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 NaHCO₃, and the mixture was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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); ¹³C 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 NH₄Cl, and the mixture was then extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and then dried over MgSO4. 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); ¹³C 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, [C₂₃H₄₀O4Si + 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 NaHCO₃, and the bulk of the organic solvent was removed under reduced pressure. The mixture was then extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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); ¹³C 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)

BF₃·OEt₂ (22.1 mL, 0.179 mol) was added to a solution of 22 (20.00 g, 0.0885 mol) and 2110b,15 (25.55 g, 0.105 mol) in CH2Cl2 (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 NaHCO₃. The solution became pale yellow. The mixture was extracted thoroughly with CH2Cl2. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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 NaHCO₃, 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); ¹³C 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, [C₁₅H₂₂O₂Si]⁺ 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(Ot-Bu) $_{3}$ H (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 NH₄Cl was added. After addition of more water, the mixture was extracted thoroughly with EtOAc/Et₂O. The organic layers were combined and washed with brine and then dried over Na₂SO₄. 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% CH₂Cl₂/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); ¹³C 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); ¹³C 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, [C₁₅H₂₄O₂Si + 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 NaHCO₃, and the mixture was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and then dried over MgSO₄. 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); ¹³C 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 NH₄Cl was added. The mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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-envl)-3-(tert-butyldimethylsilvl)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); ¹³C 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); ¹³C 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, [C₂₃H₄₂O₂Si₂ + Na]⁺ requires 429.2616.

(1*R**,2*R**,3*R**)-2-(But-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2ethynyl-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 Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. 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**,3*a*′*R**,6*R**)-6-(*tert*-Butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*′,4′-dihydro-2′*H*-spiro[cyclohexane-1,1′-pentalen]-5′(3′*H*)-one (30) and (1*R**,2*R**,3*a*′*S**,6*R**)-6-(*tert*-butyl-dimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*′,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 CH₂Cl₂ (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 CH₂Cl₂ (70 mL) and anhydrous TMANO (740 mg, 9.90 mmol) in CH₂Cl₂ (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); ¹³C 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); ¹³C 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, [C₂₁H₃₄O₃Si + 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 NH4Cl was added, and the mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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 $(3H, s), -0.08 (3H, s); {}^{13}C NMR \delta 209.5 (0), 188.8 (0), 133.4 (0),$ 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 SiO₂ (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/CH₂Cl₂) 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); ¹³C 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, [C₁₂H₁₆O₃ + Na]⁺ requires 207.1027.

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

NaBH₄ (12 mg, 0.32 mmol) was added to a solution of 30 (53 mg, 0.15 mmol) and CeCl₃·7H₂O (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 NH₄Cl. The MeOH was removed under reduced pressure, and the aqueous mixture was extracted thoroughly with Et₂O. The organic layers were combined and washed with brine and then dried over Na₂SO₄. 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); ¹³C 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 CH₂Cl₂ (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 NaHCO₃, and the mixture was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and dried over Na₂SO₄. 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);¹³C 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, [C₂₃H₄₀O₄Si + 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); ¹³C 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, [C₂₃H₄₀O₄Si + 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)

KOt-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 NH₄Cl, and the mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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 (C₆D₆) 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); ¹³C NMR (C₆D₆) 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, [C₁₄H₁₆O₂ + 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 ($\lambda = 0.71069$ Å). The crystal was a colourless needle of dimensions 0.32 × 0.19 × 0.11 mm, formula C₁₄H₁₆O₂, M = 216.28, triclinic, a = 8.5532(17) Å, b = 18.428(5) Å, c = 8.1080(17) Å, $\alpha = 93.05(2)^{\circ}$, $\beta = 118.249(14)^{\circ}$, $\gamma = 94.88(2)^{\circ}$, V = 1115.3(5) Å³, $P\bar{1}(\#2)$, Z = 4, F(000) = 464, T = 296.1 K, μ (Mo-K α) 0.085 mm⁻¹, 3193 observed reflections ($I > 3.00\sigma(I)$) and 291 variable parameters; $R(F_{\circ}) = 0.0448$, w $R_2(F^2) = 0.0563$, goodness of fit = 1.127.

(*3aR**,7*aR**,10*S**,10*aR**)-2,3,3a,4,6,7,7a,8,9,10-Decahydro-7ahydroxy-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 CH₂Cl₂ (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 NaHCO₃. and the mixture was extracted thoroughly with CH₂Cl₂. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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); ¹³C 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*bS**)-2,3,3a,4,6,6a,9,9a-Octahydro-1*H*cyclopenta[*e*]acenaphthalene-5,7(8*H*,9b*H*)-dione (41)

KOt-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 NH₄Cl, and the mixture was extracted thoroughly with Et₂O. The combined organic layers were washed with brine and then dried over Na₂SO₄. 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 ($\lambda = 0.71070$ Å). The crystal was a colourless needle of dimensions $0.25 \times 0.28 \times 0.33$ 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, $\alpha = 82.616(11)^\circ$, $\beta = 76.245(9)^\circ$, $\gamma = 83.941(14)^\circ$, V = 1199.33(12) Å³, $P\bar{1}(\#2)$, Z = 4, F(000) = 496, T = 120.1 K, μ (Mo-K α) 0.0828 mm⁻¹, 4302 observed reflections ($I > 3.00\sigma(I)$) and 343 variable parameters; $R(F_{\circ}) = 0.0442$, w $R_2(F^2) = 0.0555$, goodness of fit = 1.051.

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