The unexpected formation of bicyclo[2.2.1]heptane derivatives by Lewis acid-catalyzed transannular double cyclization

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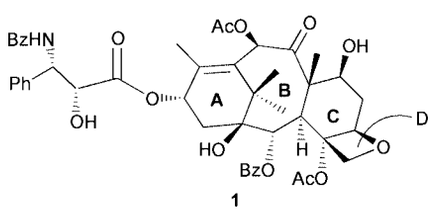
Attempted synthesis of the cyclooctanoid skeleton of taxane molecules, by an intramolecular Lewis acid catalyzed Hosomi–Sakurai cyclization of the allylsilane with the aldehyde moiety in **17**, unexpectedly led to the formation of bicyclo[2.2.1]heptane derivatives **18** and **19a**. Since the formation of spiro compounds by allylsilane terminated domino reaction has no precedent in literature, we extended the reaction conditions to unactivated olefins. Spontaneous aromatization accompanied by bicyclic ring formation was observed in these cases. Bicyclo[2.2.1]-heptane derivative **11** was also formed in high yield by an intramolecular SmI_2 mediated ketyl–olefin coupling of aldehyde in the hydroxysulfone **10**.

Introduction

Taxol **1** and its analogues have been the focus of organic



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research in the past decade owing to their unique structural features and significant biological activities.[1,2] After the isolation of Taxol from the barks of the Pacific yew trees and its structural elucidation,[3] synthetic approaches toward the structurally complex polycyclic diterpenoids of *Taxus* family have provided a valuable forum for assessing the current state-of-the-art of organic methodology.[4] Although the efforts of six groups have so far culminated in the total synthesis of Taxol,[5] the fascinating array of contiguous stereocentres, functionality embellished skeleton and the sterically encumbered eight membered ring of this molecule continue to cast its spell over synthetic organic chemists.[5] Undoubtedly, the emergence of Taxol as a potent anticancer drug has served to spearhead a recent spurt in synthetic activity directed towards cyclooctanoid systems.[6] On our part, we have reported a quantitative construction of the BC ring system through a KHMDS mediated intramolecular Michael addition of a sulfone stabilized carbanion to a dienone moeity.[7] However, due to preliminary difficulties encountered in adopting this useful methodology for the construction of a highly functionalized ABC skeleton from a preformed AC ring system, we undertook studies on some alternative convergent synthetic approaches in this direction. These include an intramolecular Lewis acid catalyzed Hosomi–Sakurai cyclization[8] of the aldehyde with the allylsilane in compound **17** and a SmI_2 mediated intramolecular cyclization of the aldehyde with activated olefins.[9] However, these strategies, which were envisaged to bring about the tactical eight membered ring closure of advanced AC ring precursor, led to the exclusive formation of bicyclo[2.2.1]heptane rings. The unique features of the allylsilane terminated domino reaction,[10] which furnished spirocyclization resulting in the formation of bicyclo[2.2.1]heptane derivative, prompted us to extend this useful methodology for the reaction of unactivated olefins. To our delight, spontaneous aromatization accompanied by bicyclic ring formation was observed in these cases. A detailed report of this useful synthetic methodology is disclosed in this paper.[11]

Results and discussion

The prerequisite allyl silane **17**, which was anticipated to undergo the key Lewis acid catalyzed transformation to give the cyclooctanoid framework, was prepared by the following sequence of reactions. The known compound **4** was prepared by an alternative strategy from the reported procedure,[12] using Diels–Alder reaction as the key step (Scheme 1). Thus, acetate **2**[13] on treatment with acrolein at −78 °C in the presence of a stoichiometric amount of $BF_3{\cdot}Et_2O$ gave the carbaldehyde **3** in 82% yield. The aldehyde **3** was reduced using $NaBH_4$ in methanol and protected as the TBDMS ether using TBDMSCl and Et_3N in the presence of 4-dimethylaminopyridine (DMAP). The acetate functionality was then reduced to the corresponding hydroxy group by diisobutylaluminium hydride (DIBAL-H) at 0 °C to yield the alcohol **4** in an overall yield of 89% for three steps from **3**. Sulfenylation of **4** was carried out by adopting Hata's protocol using $(PhS)_2$ and Bu_3P in pyridine.[14] The selective oxidation of the sulfide **5** to the corresponding sulfone, without cleaving the TBDMS ether, could not be achieved by Oxone in a reasonable yield, even under buffered conditions in the presence of Na_2HPO_4.[15] The best results were achieved by carrying out the oxidation with Oxone followed by reintroducing the TBDMS protection into the crude hydroxysulfone using TBDMSCl and Et_3N to furnish the sulfone **6** in 96% overall yield for 2 steps.

After securing a high yield route to the A ring precursor **6**, various conditions were examined to effectively carry out coupling of the sulfone with 1-methylcyclohexa-2,5-diene-1-carbaldehyde **7**.[16] BuLi failed to effect the desired reaction even in the presence of HMPA or mild Lewis acids. However, the sulfonyl carbanion generated using lithium diisopropylamide (LDA) at 0 °C could be efficiently coupled with cyclohexadiene carbaldehyde **7** at −78 °C to furnish the hydroxysulfone **8** in 80% yield as a mixture of two diastereoisomers in the ratio of 2.2 : 1. The reverse quenching of the reaction mixture by pouring into a suspension of saturated NH_4Cl in Et_2O was critical to achieve product formation in a reasonable yield, presumably, due to the reversibility of the reaction. Based on the steric

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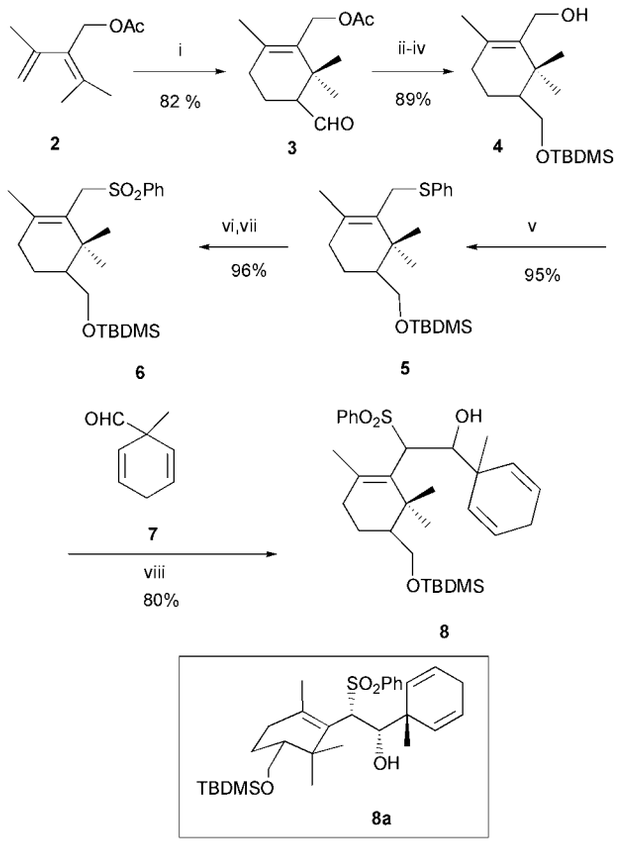
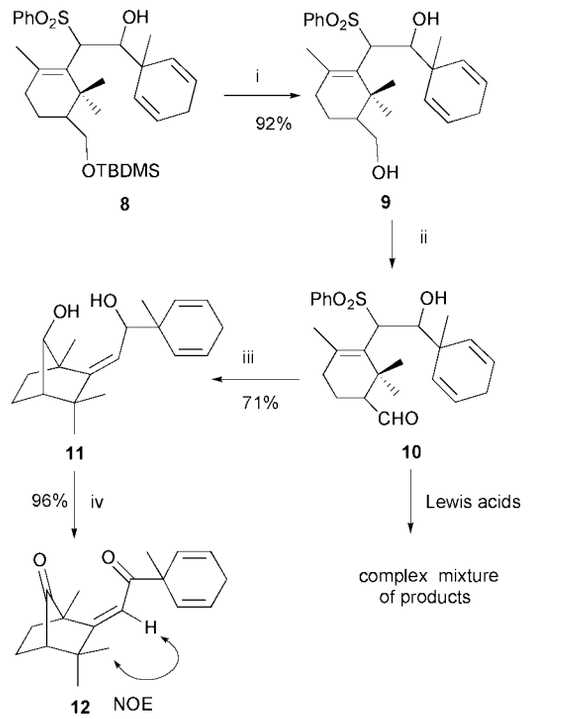


Scheme 1 *Reagents and conditions*: i, acrolein, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 °C; ii, $NaBH_4$, MeOH, 0 °C; iii, TBDMSCl, DMAP, Et_3N, CH_2Cl_2, 0 °C–RT; iv, DIBAL-H, Et_2O, 0 °C; v, $(PhS)_2$, Bu_3P, Py, RT; vi, Oxone, THF–MeOH–H_2O, 0 °C–RT; vii, TBDMSCl, DMAP, Et_3N, CH_2Cl_2, 0 °C–RT; viii, LDA, THF, −78 °C.



Scheme 2 *Reagents and conditions*: i, HF–Py, THF–Py, RT; ii, 5 mol% TPAP, NMO, 4 Å MS, CH_2Cl_2, RT; iii, SmI_2, HMPA, THF, 0 °C; iv, 5 mol% TPAP, NMO, 4 Å MS, CH_2Cl_2, RT.

interactions in the Felkin–Ahn model, it could be presumed that the major diastereoisomer would be **8a**, in which the bulky $CH_2OTBDMS$ group occupies an equatorial position in the cyclohexene ring and the hydroxy and phenyl sulfonyl groups are oriented *syn* to each other.

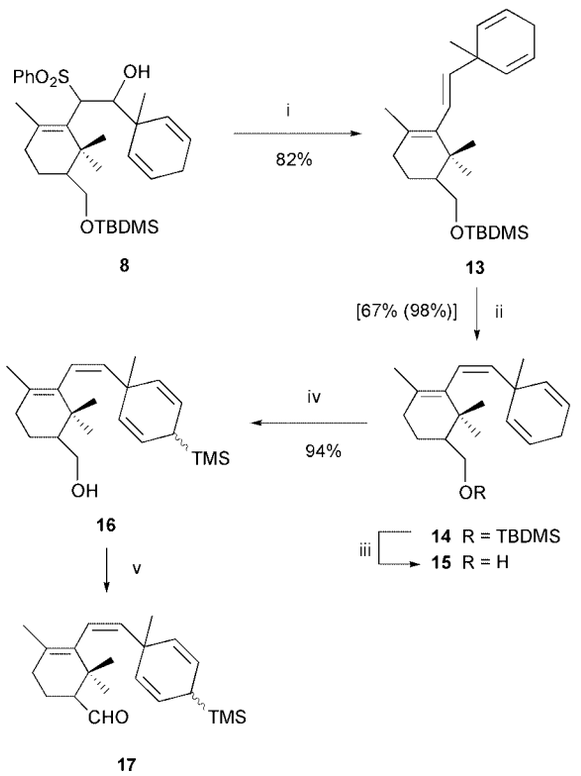
At this stage, we decided to explore the feasibility of ketyl–olefin reductive coupling using Lewis acids to construct the B ring, as represented in Scheme 2. For this purpose, attempts were made to cleave the TBDMS ether of **8** using TBAF in THF, which resulted in the cleavage of the hydroxysulfone moiety in a retro-aldol fashion. Aqueous acetic acid also failed to furnish the desired dihydroxy sulfone in good yield. However, the TBDMS ether could be cleaved in excellent yield by using 70% HF in pyridine buffered with pyridine according to Trost's procedure.[17] The selective oxidation of the primary alcohol in compound **9** to give **10** was achieved in quantitative yield using 5 mol% of tetrapropylammonium perruthenate (TPAP)[18] in the presence of 4-methylmorpholine *N*-oxide as the reoxidant in CH_2Cl_2 and quenching the reaction after 10 min. Interestingly, when the reaction is carried out over a longer duration, allylic oxidation of the cyclohexadiene moiety is observed in considerable yields.[19]

With the desired aldehyde **10** in hand, several attempts were made to carry out the cyclization in the presence of Lewis acids. However, all these efforts were thwarted by the presence of the hydroxysulfone moiety and an inseparable mixture of products was obtained under these conditions. Since, a Lewis acid catalyzed reaction failed to induce the formation of the eight-membered B ring, it was intriguing to check the reactivity of this aldehyde towards SmI_2.[20] Interestingly, the reaction exclusively furnished bicyclo[2.2.1]heptanol derivative **11** in 71% yield. Oxidation of the alcohol using TPAP quantitatively furnished the corresponding ketoenone **12**, which exhibited a characteristic carbonyl absorption of five-membered ketones at 1776 cm^{-1}. The geometry about the double bond of the ketone was established by NOE measurements. Although sulfone terminated ketyl–olefin couplings are documented in the literature,[21] there is no precedent for the efficient construction of bicyclo[2.2.1]heptanol derivatives under these conditions.[22] Also, the exclusive ketyl–olefin reductive coupling using SmI_2 in the presence of HMPA to give a bicyclo[2.2.1]heptane system is in marked contrast with the Julia–Lythgoe olefination of a hydroxysulfone under similar conditions in the absence of a carbonyl moiety (*vide infra*).[23]

A closer examination of the molecular model of compound **8** revealed that the olefinic moiety of the cyclohexadiene and the carbaldehyde on the A-ring are brought to close proximity by the introduction of a *cis*-double bond between the A and C ring. Accordingly, attempts were made to protect the secondary hydroxy group of **8** as its acetate to carry out the Julia–Lythgoe elimination (Scheme 3). However, the neopentyl environment of the neighbourhood spoiled all the efforts in this direction and the protection of the alcohol could not be achieved even under drastic conditions. Using Birch conditions, the elimination of hydroxysulfone could be carried out to furnish the *trans*-isomer **14**, *albeit*, in low yield. SmI_2 in THF also failed to induce the elimination of hydroxy sulfone.[24] Fortunately, under modified conditions developed by us,[25] Julia–Lythgoe elimination could be effected in high yield by SmI_2 in the presence of HMPA.[26] The best results were obtained by the rapid addition of a solution of the hydroxysulfone in THF to 0.1 M solution of SmI_2 in THF containing 6 equivalents of HMPA at RT.

The *trans*-double bond was then isomerized under photochemical conditions. The isomerization was induced by irradiating a solution of the *trans*-isomer **13** in benzene in a Pyrex glass apparatus, using 2-acetylnaphthalene as the sensitizer and using a 450 W Hg lamp as the source of light, maintaining the reaction temperature below 5 °C. Other sensitizers such as benzophenone and 1-acetylnaphthalene did not give satisfactory results for the reaction. The ^1H NMR spectrum of the *cis*-isomer **14** revealed that the compound exists as two conformational isomers as in the case of *cis*-β-ionol derivatives.[27]

After the successful installation of the desired *cis*-double bond, we focussed our attention on introducing a suitable

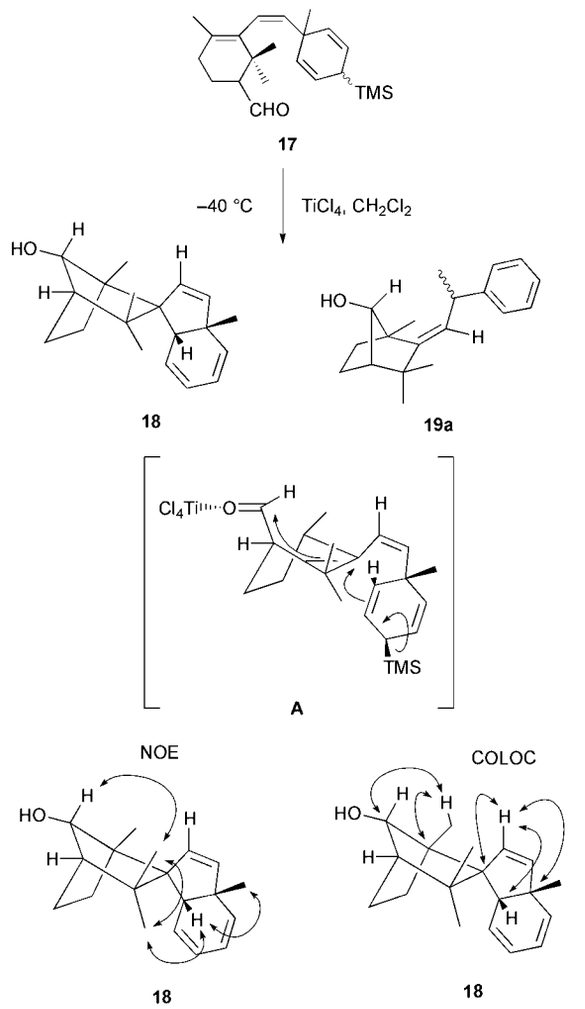


Scheme 3 *Reagents and conditions*: i, SmI_2, HMPA, THF, RT; ii, *hv* (450 W), 2-acetylnaphthalene, benzene, 0–5 °C; iii, TBAF, THF, 0 °C–RT; iv, BuLi, TMEDA, TMSCl, THF, 0 °C; then 0.5 M H_2SO_4–THF; v, 3 mol% TPAP, NMO, 4 Å MS, CH_2Cl_2, RT.

functional group at the allylic position of the cyclohexadiene moiety, which could facilitate an intramolecular ketyl–olefin coupling to provide the eight membered ring. Initially, an intramolecular SmI_2 mediated coupling of the aldehyde with the dienone moiety was attempted. After deprotection of the silyl group, the alcohol **15** was subjected to a double oxidation using TPAP in a mixed solvent system of CH_3CN and CH_2Cl_2 to provide the corresponding keto–dienone precursor in 45% yield which was treated without further purification with SmI_2 in the presence of HMPA. Unfortunately, the reaction furnished a complex mixture of products, which could not be characterized by conventional techniques of analysis. Various attempts made to introduce a leaving group such as a sulfone or a chloride at the allylic position of the cyclohexadiene moiety also met with failure.

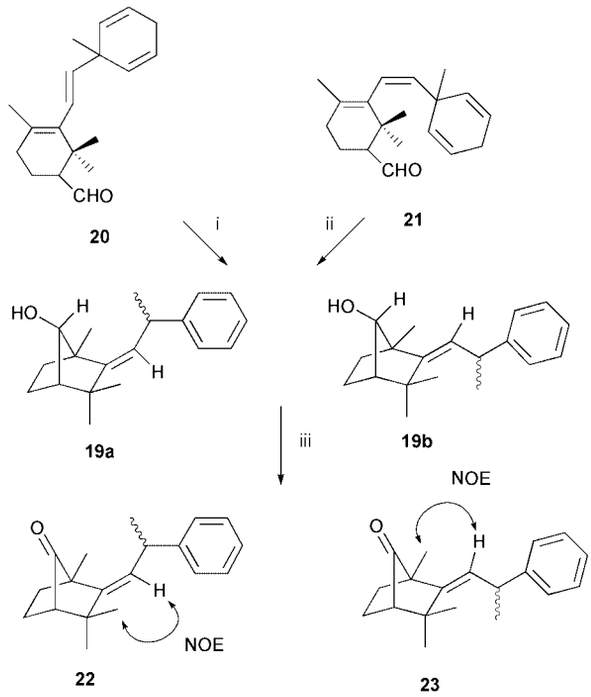
We then planned to attempt a Hosomi–Sakurai coupling of the allylsilane in the hope of forming the elusive eight-membered ring. The allyl silane **17** was prepared by the following sequence of reactions. The dianion derived from alcohol **15** by treatment with BuLi in the presence of tetramethylethylenediamine (TMEDA) was subjected to disilylation with TMSCl. The silyl protection of the hydroxy group was then selectively cleaved in a 1 : 1 mixture of 0.5 M H_2SO_4–THF to give **16** in 94% overall yield as a complex mixture of two diastereoisomers and the corresponding atropisomers. Oxidation of the resultant diastereoisomeric mixture of alcohols using Ley's method [18] afforded **17** quantitatively.

Next, Lewis-acid catalyzed cyclization of **17** was investigated under a variety of reaction conditions (Scheme 4). When **17** was treated with $TiCl_4$ (1.2 equiv) in CH_2Cl_2 at −40 °C, the spiro compound **18** was obtained in 28% yield as a single stereoisomer along with **19a** in 5% yield as a mixture of two isomers. The structure and the relative stereochemistry of the compound were established on the basis of its NOESY spectrum and the long range coupling observed in the COLOC spectrum. Since the S_E2' reaction of allylsilanes is mechanism-controlled, loss of the silyl group and the subsequent reaction with the electrophile should take place in an anti fashion; *i.e.* with a simple 1,3-transfer of chirality.[28] Therefore, it could be expected that only one of the diastereoisomers of **2** in which the silyl substituent is oriented *trans* to the angular methyl group could lead to the observed product as represented in the transition state **A** whereas the other isomer might undergo decomposition on treatment with a Lewis acid. The formation of spiro compound **18** as a single isomer further indicates the concerted nature of the cyclization *via* the transition state **A**. Unfortunately, various efforts to separate the two diastereoisomers of **17** and investigate the reactivity of aldehydes derived from the individual isomers towards Lewis acid were not successful. To the best of our knowledge, an allylsilane terminated domino reaction to accomplish spirocyclization is unprecedented in the literature. In addition, the reaction provides an expeditious assembly of bicyclo[2.2.1]heptane derivatives combined with spirocyclization in a sterically encumbered environment.



Scheme 4 Lewis acid-catalysed cyclization yielding bicyclo[2.2.1]-heptane derivatives.

This prompted us to explore further the generality of the cyclization, in order to firmly establish the role played by the silyl group. For this purpose, the olefinic aldehydes **20** and **21** carrying no silyl groups were treated with various Lewis acids (Scheme 5). The aldehydes in turn were prepared by desilylation followed by TPAP oxidation of the corresponding alcohols. Treatment of **20** with $SnCl_4$ in CH_2Cl_2 provided the aromatized products **19a** and **19b** in 90% yield as a 1 : 1 : 6 : 6 mixture of four isomers. On the other hand, similar treatment of the *cis* isomer **21** gave **19a** and **19b** in 50% yield, again as a mixture of four stereoisomers. The mixtures were oxidized using Ley's method [18] to quantitatively give a mixture of two stereoisomers **22** and **23**. Geometry about the double bond of these ketones was unequivocally established by NOE measurements.



Scheme 5 *Reagents and conditions*: i, $SnCl_4$, CH_2Cl_2, −30 °C; ii, $SnCl_4$, CH_2Cl_2, −30 to −10 °C; iii, 3 mol% TPAP, NMO, 4 Å MS, CH_2Cl_2, RT.

In conclusion, in pursuit of a synthetic methodology for the construction of the ABC skeleton of taxoid molecules, we have unravelled some novel methods for the assembly of bicyclo-[2.2.1]heptane derivatives. These methods include an intramolecular SmI_2 mediated ketyl–olefin coupling and a Lewis acid catalyzed Hosomi–Sakurai reaction of an olefin with an aldehyde. Especially noteworthy is the domino reaction in which an allylsilane terminated spirocyclization is triggered by Lewis acid catalyzed ketyl–olefin coupling to yield a bicyclo-[2.2.1]heptane derivative.

Experimental

General

All moisture and air sensitive reactions were carried out in an atmosphere of argon. Diisopropylamine and triethylamine were freshly distilled from calcium hydride prior to use. TMEDA and HMPA were distilled from calcium hydride and stored over 4 Å molecular sieves. All other reagents and solvents were used as obtained from commercial suppliers. Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a JEOL GX-500 at 500 MHz, a Hitachi R-3000 or Varian Gemini-2000 at 300 MHz for samples in $CDCl_3$ using tetramethylsilane as the internal standard. ^{1}H NMR data are presented in the following order: chemical shift, multiplicity [s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broadened)], coupling constant(s) (*J*/Hz) and integration. ^{13}C NMR spectra were recorded using a Varian Gemini-2000 at 75 MHz for samples in $CDCl_3$. IR spectra were recorded with a JASCO IR Report-100 or Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were taken on JEOL-DX-300 spectrometer. Flash column chromatography was carried out on neutral silica gel (230–400 mesh).

5-*tert*-Butyldimethylsiloxymethyl-1-phenylthiomethyl-2,6,6-trimethylcyclohex-1-ene 5

A solution of the alcohol **4** (18.0 g, 60.4 mmol) in pyridine (49 cm^3) was treated with Bu_3P (45 cm^3, 181 mmol) followed by $(PhS)_2$ (39.5 g, 180 mmol) at RT. After stirring for 9 h at ambient temperature, the reaction mixture was diluted with Et_2O. The resultant solution was vigorously stirred with 10% aq. NaOH for 30 min. The phases were separated and the organic layer was washed with water, brine, dried over $MgSO_4$ and concentrated under vacuum. The crude product was column chromatographed (hexane–AcOEt 50 : 1) to provide the sulfide as a colourless liquid (22.4 g, 95%) (Found C, 70.8; H, 9.8; S, 8.0. $C_{23}H_{38}OSSi$ requires C, 70.7; H, 9.8; S, 8.2%); ν_{max}(neat)/cm^{-1} 1580, 1465, 1250; δ_H (300 MHz, $CDCl_3$) 0.05 (6H, s, 2 × CH_3Si), 0.90 (9H, s, ^{t}Bu), 0.94 (3H, s, 6-CH_3), 1.19 (3H, s, 6-CH_3), 1.36–1.52 (2H, m, 4-H_2), 1.77 (3H, s, 2-CH_3), 1.78–1.87 (1H, m, 5-H), 1.95–2.05 (2H, m, 3-H_2), 3.38 (1H, dd, *J* = 9.5, 8.4 Hz, C*H*HOTBDMS), 3.55–3.64 (2H, m, CH_2SPh), 3.78 (1H, dd, *J* = 9.5, 3.7 Hz, CH*H*OTBDMS), 7.11–7.18 (1H, m, ArH), 7.23–7.34 (4H, m, ArH); *m*/*z* 390 (M$^+$).

5-*tert*-Butyldimethylsiloxymethyl-1-phenylsulfonylmethyl-2,6,6-trimethylcyclohex-1-ene 6

Oxone (4.0 g, 6.5 mmol) was added in portions to a solution of the sulfide **5** (900 mg, 2.31 mmol) in THF–MeOH–H_2O (3 : 1 : 1, 22.5 cm^3) at 0 °C. After stirring for 4 h at RT, the reaction mixture was concentrated under vacuum, the residue was dissolved in water, and repeatedly extracted with AcOEt. The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The crude residue was dissolved in CH_2Cl_2 (20 cm^3) and treated with TBDMSCl (491 mg, 3.26 mmol), DMAP (27 mg, 0.22 mmol) followed by Et_3N (910 mm^3, 6.53 mmol) at 0 °C. The reaction mixture was allowed to warm to RT and stirred further for 12 h. The reaction mixture was diluted with Et_2O, washed with water, brine, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography (hexane–AcOEt 95 : 5) to give a colourless solid (880 mg, 96%). Mp 77–78 °C (Found C, 65.2; H, 8.8; S, 7.3. $C_{23}H_{38}O_3SSi$ requires C, 65.4; H, 9.1; S, 7.6%); ν_{max}($CHCl_3$)/cm^{-1} 1305, 1155; δ_H (300 MHz, $CDCl_3$) 0.05 (6H, s, 2 × CH_3Si), 0.89 (9H, s, ^{t}Bu), 0.93 (3H, s, 6-CH_3), 1.12 (3H, s, 6-CH_3), 1.53–1.55 (2H, m, 4-H_2), 1.68 (3H, s, 2-CH_3), 1.79–1.88 (1H, m, 5-H), 2.04–2.12 (2H, m, 3-H_2), 3.38 (1H, dd, *J* = 9.5, 8.8 Hz, CH*H*OTBDMS), 3.76 (1H, dd, *J* = 9.5, 3.7 Hz, C*H*HOTBDMS), 3.91–4.02 (2H, m, CH_2SO_2Ph), 7.50–7.65 (3H, m, ArH), 7.88–7.95 (2H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 18.3, 20.9, 22.0, 23.3, 26.0, 28.3, 31.7, 36.7, 47.0, 57.8, 63.5, 126.0, 127.8, 129.1, 133.2, 139.5, 141.8; *m*/*z* 281 (M$^+$ − SO_2Ph).

5-*tert*-Butyldimethylsiloxymethyl-1-[2-(1-methylcyclohexa-2,5-dien-1-yl)-2-hydroxy-1-phenylsulfonylethyl]-2,6,6-trimethylcyclohex-1-ene 8

A solution of diisopropylamine (2.32 cm^3, 16.6 mmol) in THF (60 cm^3) was treated with BuLi (1.56 M solution in hexane, 9.10 cm^3, 14.2 mmol) and stirred for 30 min at 0 °C. A solution of sulfone **6** (5.00 g, 11.8 mmol) in THF (25 cm^3) was added dropwise at 0 °C and stirred for further 30 min. The reaction mixture was cooled to −78 °C and a solution of the aldehyde **7** (1.88 g, 15.4 mmol) in THF (15 cm^3) was added dropwise and stirred for further 1 h. The reaction was quenched by pouring into a suspension of saturated NH_4Cl in Et_2O. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash column chromatography (hexane–Et_2O–CH_2Cl_2 10 : 1 : 1) to give a colourless solid (5.13 g, 80%). Mp 109 °C (decomp.) (Found C, 68.4; H, 8.9; S, 5.8. $C_{31}H_{48}O_4SSi$ requires C, 68.3; H, 8.9; S, 5.9%); ν_{max}($CHCl_3$)/cm^{-1} 3400; δ_H (500 MHz, $CDCl_3$) 0.03 (1.88H, s, CH_3Si), 0.05 (2.06H, s, CH_3Si), 0.06 (2.06H, s, CH_3Si), 0.88 (2.81H, s, ^{t}Bu), 0.90 (6.19H, s, ^{t}Bu), 0.98 (0.94H, s, CH_3), 1.02 (2.06H, s, CH_3), 1.11 (2.06H, s, CH_3), 1.14 (0.94H, s, CH_3), 1.16 (2.06H, s, CH_3), 1.18 (0.94H, s, CH_3), 1.43 (0.94H, s, 2-CH_3), 1.44–1.60 (1H, m, 4-*H*H), 1.62 (2.06H, s, 2-CH_3), 1.64–1.81(2H, m, 4-H*H* and 5-H), 1.96–2.14 (2H, m, 3-H_2), 2.60–2.67 (2H, m, 4′-H_2), 3.24 (0.31H, dd, *J* = 9.7, 9.2 Hz,

C*H*HOTBDMS), 3.44 (0.69H, dd, J = 9.8, 9.8 Hz, C*H*HOTBDMS), 3.67 (0.31H, dd, J = 9.7, 3.7 Hz, C*H*HOTBDMS), 3.72 (0.69H, dd, J = 9.8, 4.3 Hz, CH*H*OTBDMS), 3.96 (0.31H, d, J = 4.9 Hz, C*H*OH), 4.05 (0.69H, d, J = 4.9 Hz, C*H*OH), 4.38–4.43 (1H, m, $CHSO_2Ph$), 5.39–5.79 (4H, m, olefinic H), 7.47–7.51 (2H, m, ArH), 7.57–7.61 (1H, m, ArH), 7.90–7.92 (2H, m, ArH); *m*/*z* 487 ($M^+ - {}^tBu$).

5-Hydroxymethyl-1-[2-(1-methylcyclohexa-2,5-dien-1-yl)-2-hydroxy-1-phenylsulfonylethyl]-2,6,6-trimethylcyclohex-1-ene 9

The TBDMS ether **8** (200 mg, 0.367 mmol) was dissolved in a solution of HF–pyridine in THF–pyridine in a Teflon vial prepared according to the method of Trost.[17] After stirring for 5 h at RT, the reaction mixture was diluted with Et_2O, washed with 1 M HCl, water, brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography (hexane–AcOEt 1 : 1) to give a colourless solid (145 mg, 92%). Mp 87 °C (decomp.) (Found C, 69.9; H, 8.1; S, 7.7. $C_{25}H_{34}O_4S$ requires C, 69.7; H, 8.0, S, 7.45%); ν_{max}(KBr)/cm^{-1} 3509, 1278, 1130; δ_H (300 MHz, $CDCl_3$) 1.05–1.24 (9H, m, 3 × CH_3), 1.46 (0.9H, s, 2-CH_3), 1.48–1.59 (1H, m, 4-H*H*), 1.68–1.77 (1H, m, 4-*H*H), 1.78 (2.1H, s, 2-CH_3), 1.89–2.00 (1.6H, m), 2.03–2.14 (0.7H, m), 2.19–2.35 (0.7H, m), 2.54–2.59 (1.3H, m, 4′-H_2), 2.62–2.67 (0.7H, m, 4′-H_2), 3.24–3.30 (0.3 H, m, CH*H*OH), 3.65–3.72 (0.7H, m, CH*H*OH), 3.73–3.81 (1H, m, C*H*HOH), 3.96–3.99 (0.3H, d, J = 5.4 Hz, C*H*OH), 4.11–4.14 (0.7H, d, J = 5.7 Hz, C*H*OH), 4.38–4.43 (1H, d, J = 5.7 Hz, $CHSO_2Ph$), 5.32–5.45 (1.7H, m, olefinic H), 5.46–5.52 (0.7H, m, olefinic H), 5.68–5.73 (1.3H, m, olefinic H), 5.75–5.80 (0.3H, m, olefinic H), 7.46–7.53 (2H, m, ArH), 7.54–7.62 (1H, m, ArH), 7.90–7.94 (2H, m, ArH); *m*/*z* 337.1475 (M^+ − C ring).

1,3,3-Trimethyl-2-[2-hydroxy-2-(1-methylcyclohexa-2,5-dien-1-yl)ethylidene]bicyclo[2.2.1]heptan-7-ol 11

To a suspension of the alcohol **9** (50 mg, 0.116 mmol), 4-methylmorpholine *N*-oxide (34 mg, 0.290 mmol) and 4 Å molecular sieves (50 mg) in CH_2Cl_2 (3 cm^3) was added TPAP (2.2 mg, 5 mol%) and the reaction mixture was stirred at RT for 15 min. The reaction mixture was loaded onto a short column of silica gel, and washed down with Et_2O (40 cm^3). The crude aldehyde **10** was concentrated under vacuum and used for the next step without further purification.

A 0.1 M solution of SmI_2 was prepared by the addition of a solution of 1,2-diiodoethane (229 mg, 0.81 mmol) in THF (5 cm^3) to a stirred suspension of Sm (131 mg, 0.87 mmol) in THF (4 cm^3). After stirring the suspension for 1 h, deaerated HMPA (1 cm^3, 6 mmol) was added to the resultant dark blue solution and stirred for a further 10 min. A solution of the crude aldehyde **10** in THF (3 cm^3) was added slowly to the reaction mixture using a syringe pump at 0 °C. After stirring for an additional 30 min, the reaction was quenched by the addition of satd. NH_4Cl. The reaction mixture was then diluted with Et_2O, and treated with a saturated aqueous solution of sodium potassium tartrate. After separating the phases, the aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (hexane–AcOEt 7 : 3) to give pure diol **11** as a colourless solid (23.4 mg, 71%). Mp 112–113 °C (Found (M^+ − 18) 270.1949. $C_{19}H_{26}O$ requires *m*/*z* 270.1984); ν_{max}(neat)/cm^{-1} 3382, 1455; δ_H (300 MHz, $CDCl_3$) 1.04 (3H, s, CH_3), 1.05 (3H, s, CH_3), 1.06 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.56–1.63 (2H, m, 5-*H*H and 6-H*H*), 1.64–1.74 (1H, m, 5-*H*H), 1.77–1.79 (1H, m, 4-H), 1.80–1.86 (1H, m, 6-H*H*), 2.62–2.67 (2H, m, 4′-H_2), 3.86 (1H, s, 7-H), 4.36 (1H, d, J = 10.2, C*H*OH), 5.10 (1H, d, J = 10.2, 2-C=CH), 5.51–5.56 (2H, m, olefinic H), 5.82–5.92 (2H, m, olefinic H); δ_C (75 MHz, $CDCl_3$) 17.2, 22.1, 25.5, 26.6, 27.0, 29.4, 31.4, 40.5, 41.6, 51.3, 52.8, 72.9, 80.8, 117.9, 125.5, 125.9, 130.1, 131.6, 158.5.

1,3,3-Trimethyl-2-[2-oxo-2-(1-methylcyclohexa-2,5-dien-1-yl)-ethylidene]bicyclo[2.2.1]heptan-7-one 12

To a suspension of the alcohol **11** (20 mg, 0.069 mmol), 4-methylmorpholine *N*-oxide (33 mg, 0.278 mmol) and 4 Å molecular sieves (50 mg) in CH_2Cl_2 (3 cm^3) was added TPAP (2.4 mg, 10 mol%) and the reaction mixture was stirred at RT for 15 min. The reaction mixture was loaded onto a short column of silica gel, and washed down with Et_2O (40 cm^3). The crude product was purified by column chromatography (hexane–Et_2O 8 : 2) to give a colourless solid (19 mg, 96%). Mp 81 °C (Found C, 80.6; H, 8.6. $C_{19}H_{24}O_2$ requires C, 80.2; H, 8.5); ν_{max}(neat)/cm^{-1} 1776, 1689; δ_H (500 MHz, $CDCl_3$) 1.00 (3H, s, 3-CH_3), 1.06 (3H, s, 1-CH_3), 1.18 (3H, s, 3-CH_3), 1.19 (3H, s, 1′-CH_3), 1.65–1.70 (1H, m, 6-H*H*), 1.77–1.72 (1H, m, 5-*H*H), 1.78–1.79 (1H, m, 5-*H*H), 1.80–1.83 (1H, m, 4-H), 1.88–1.93 (1H, m, 6-H*H*), 2.64–2.73 (2H, m, 4′-H_2), 5.46–5.49 (1H, m, olefinic H), 5.53–5.56 (1H, m, olefinic H), 5.77–5.78 (1H, m, olefinic H), 5.79–5.90 (1H, m, olefinic H), 6.31 (1H, s, =CHCO); δ_C (125 MHz, $CDCl_3$) 12.14 (1-CH_3), 17.72 (5-C), 22.62 (3-CH_3), 24.31 (1′-CH_3), 26.09 (4′-C), 28.96 (3-CH_3), 30.25 (6-C), 41.98 (3-C), 50.63 (1′-C), 50.74 (4-C), 50.86 (1-C), 118.04 (=*C*HCO) [124.86, 125.14, 129.44, 130.08 (4 × olefinic C)], 167.31 (2-C), 202.48 (1′-CO), 215.40 (7-C); *m*/*z* 191.1080 (M^+ − C ring).

(*E*)-5-*tert*-Butyldimethylsiloxymethyl-1-[2-(1-methylcyclohexa-2,5-dien-1-yl)ethenyl]-2,6,6-trimethylcyclohex-1-ene 13

A 0.1 M solution of SmI_2 in THF (6.43cm^3, 0.643 mmol) was treated with HMPA (0.23 cm^3) and stirred at RT for 10 min. A solution of sulfone **8** (100 mg, 0.184 mmol) in THF (3 cm^3) was added rapidly and the reaction mixture was stirred for 30 min. The reaction mixture was diluted with Et_2O, washed with 1 M HCl, satd. $NaHCO_3$, water and brine, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography (hexane–Et_2O 500 : 1) to give a colourless liquid (58 mg, 82%) (Found C, 77.5; H, 11.0. $C_{25}H_{42}OSi$ requires C, 77.65; H, 10.95%); ν_{max}(neat)/cm^{-1} 1470, 1460, 1360; δ_H (300 MHz, $CDCl_3$) 0.04 (6H, s, 2 × CH_3Si), 0.80 (3H, s, CH_3), 0.89 (9H, s, ^tBu), 1.02 (3H, s, CH_3), 1.17 (3H, s, CH_3), 1.35–1.50 (2H, m, 4-H_2), 1.63 (3H, s, 2-CH_3), 1.78–1.85 (1H, m, 5-H), 1.94–1.99 (2H, m, 3-H_2), 2.59–2.64 (2H, m, 4′-H_2), 3.36 (1H, dd, J = 9.9, 9.2 Hz, CH*H*OTBDMS), 3.76 (1H, dd, J = 9.9, 4.0 Hz, C*H*HOTBDMS), 5.30 (1H, d, J = 16.1 Hz, *trans*-olefinic H), 5.53–5.57 (2H, m, olefinic H), 5.65–5.75 (3H, m, olefinic H); δ_C (75 MHz, $CDCl_3$) −5.1, 18.4, 21.6, 22.6, 26.1, 27.9, 28.5, 31.4, 36.4, 38.9, 46.9, 64.0, 121.9, 125.0, 127.7, 133.2, 137.7, 142.4; *m*/*z* 386 (M^+).

(*Z*)-5-*tert*-Butyldimethylsiloxymethyl-1-[2-(1-methylcyclohexa-2,5-dien-1-yl)ethenyl]-2,6,6-trimethylcyclohex-1-ene 14

A solution of *trans*-**13** (535 mg, 1.39 mmol) and 2-acetylnaphthalene (470 mg, 2.76 mmol) in benzene (55 cm^3) in a Pyrex vessel was irradiated with a 450 W high pressure Hg lamp for 3 h, maintaining the temperature of the reaction mixture below 5 °C. The reaction mixture was concentrated under vacuum and the *cis*–*trans* mixture was separated by flash column chromatography (hexane) to give the *cis*-isomer **14** as a colourless liquid [360 mg, 67% (98% based on recovered starting material)] (Found C, 77.7; H, 10.9. $C_{25}H_{42}OSi$ requires C, 77.65; H, 10.95%). ν_{max}(neat)/cm^{-1} 1472, 1465, 1360, 1260; δ_H (300 MHz, $CDCl_3$, RT) 0.05 (6H, s, 2 × CH_3Si), 0.83 (1.5H, s, CH_3), 0.86 (1.5H, s, CH_3), 0.90 (9H, s, ^tBu), 1.05 (1.5H, s, CH_3), 1.08 (1.5H, s, CH_3), 1.11 (3H, s, CH_3), 1.35–1.50 (2H, m, 4-H_2), 1.54 (3H, br s, 2-CH_3), 1.75–1.97 (3H, m, 3-H_2 and 5-H), 2.45–2.69 (2H, m, 4′-H_2), 3.30–3.43 (1H, m, CH*H*OTBDMS), 3.71–3.83 (1H, m, C*H*HOTBDMS), 5.25 (1H, br d, J = 12.5 Hz, *cis*-olefinic H), 5.45–5.72 (5H, m, olefinic H); δ_H (500 MHz, DMSO-d_6, 90 °C) 0.05 (6H, s, 2 × CH_3Si), 0.87 (3H, s, CH_3),

0.90 (9H, s, ^{t}Bu), 1.06 (3H, s, CH_3), 1.10 (3H, s, CH_3), 1.36–1.48 (2H, m, 4-CH_2), 1.54 (3H, s, 2-CH_3), 1.69–1.95 (3H, m, CH_2 and CH), 2.46-2.71 (2H, m, 4′-CH_2), 3.33–3.46 (1H, m, C*H*HOTBDMS), 3.76 (1H, dd, J = 9.8, 3.7 Hz, CH*H*OTBDMS), 5.30 (1H, d, J = 12.8 Hz, *cis*-olefinic H), 5.46–5.68 (5H, m, olefinic H); *m*/*z* 386 (M^+).

(*Z*)-5-Hydroxymethyl-1-[2-(1-methylcyclohexa-2,5-dien-1-yl)-ethenyl]-2,6,6-trimethylcyclohex-1-ene 15

Bu_4NF (1.0 M solution in THF, 0.78 cm^3, 0.78 mmol) was added to a solution of **14** (150 mg, 0.388 mmol) in THF (2.2 cm^3) at 0 °C and the reaction mixture was stirred for 16 h at RT. After addition of water, the reaction mixture was extracted with AcOEt, the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography (hexane–AcOEt 5:1) to give the corresponding alcohol **15** (100 mg, 95%) (Found C, 83.4; H, 10.3. $C_{19}H_{28}O$ requires C, 83.8; H, 10.4%). ν_{max}(neat)/cm^{-1} 3300; δ_H (300 MHz, $CDCl_3$) 0.85 (1.5H, s, CH_3), 0.88 (1.5H, s, CH_3), 1.07 (1.5H, s, CH_3), 1.09 (1.5H, s, CH_3), 1.12 (3H, s, CH_3), 1.22–1.29 (1H, m, 4-*H*H), 1.41–1.52 (1H, m, 4-H*H*), 1.55 (1.5H, br s, 2-CH_3), 1.57 (1.5H, br s, 2-CH_3), 1.76–2.05 (3H, m, 3-H_2 and 5-H), 2.58–2.64 (2H, m, 4′-H_2), 3.34–3.52 (1H, m, CH_2OH), 3.78–3.93 (1H, m, CH_2OH), 5.23–5.34 (1H, m, olefinic H), 5.43–5.73 (5H, m, olefinic H); *m*/*z* 272.2141.

(*Z*)-5-Hydroxymethyl-1-[2-(1-methyl-4-trimethylsilylcyclohexa-2,5-dien-1-yl)ethenyl]-2,6,6-trimethylcyclohex-1-ene 16

To a solution of the alcohol **15** (59 mg, 0.22 mmol) and TMEDA (165 mm^3, 1.09 mmol) in THF (2 cm^3) at 0 °C was added BuLi (1.56 M solution in hexane, 300 mm^3, 0.468 mmol). The reaction mixture was stirred for 1 h at the same temperature and the resultant dianion was trapped by the addition of TMSCl (140 cm^3, 1.10 mmol). After stirring for 30 min at the same temperature, the reaction mixture was diluted with Et_2O, washed with H_2O, 0.5 M H_2SO_4, and brine, dried over $MgSO_4$ and concentrated under vacuum. The crude disilyl derivative was dissolved in THF (1.5 cm^3) and treated with 0.5 M H_2SO_4 (1.5 cm^3) at 0 °C. The mixture was stirred for 30 min at RT. The reaction mixture was then diluted with Et_2O, washed with H_2O, saturated $NaHCO_3$, saturated NaCl, dried ($MgSO_4$) and concentrated under vacuum. The crude product was purified by column chromatography (hexane–AcOEt 15:1) to give the allylsilane **16** (70 mg, 94%) (Found C, 76.2; H, 10.3. $C_{22}H_{36}OSi$ requires C, 76.7; H, 10.5); ν_{max}(neat)/cm^{-1} 3320; δ_H (300 MHz, $CDCl_3$) −0.01 (1.8H, s, CH_3), 0.01 (4.2H, s, CH_3), 0.03 (0.9H, s, CH_3), 0.05 (2.1H, s, CH_3), 0.81–0.92 (3H, m, CH_3), 1.02–1.17 (6H, m, 2 × CH_3), 1.17–1.26 (1H, m, 4-H*H*), 1.39–1.48 (1H, m, 4-*H*H), 1.56 (0.6H, s, CH_3), 1.57 (1.4H, s, CH_3), 1.63 (0.3 H, s, CH_3), 1.66 (0.7 H, s, CH_3), 1.78–2.04 (3H, m, 3-H_2 and 5-H), 2.13–2.21 (1H, m, 4′-H), 3.36–3.49 (1H, m, C*H*OH), 3.79–3.92 (1H, m, C*H*OH), 5.22–5.41 (2H, m, olefinic H), 5.42–5.47 (1H, m, olefinic H), 5.48–5.72 (3H, m, olefinic H); *m*/*z* 344.2535.

(±)-(1*R**,2*S**,4*S**,7*S**,3a′*R**,7a′*R**)-1,3,3,3a′-Tetramethyl-spiro[bicyclo[2.2.1] heptane-2,1′-(*cis*-3a′,7a′-dihydroinden)]-7-ol 18 and 1,3,3-trimethyl-2-(2-methyl-2-phenylethylidene)bicyclo-[2.2.1]heptan-7-ol 19a

To a suspension of the alcohol **16** (32 mg, 0.93 mmol), NMO (22 mg, 0.19 mmol), 4 Å molecular sieves (50 mg) in CH_2Cl_2 (1 cm^3), was added TPAP (3.2 mg, 0.0091 mmol) and the reaction mixture was stirred at RT for 15 min. The reaction mixture was then loaded onto a short column of silica gel and washed down with Et_2O and concentrated. The crude aldehyde was used as such without further purification for the next step.

A solution of the aldehyde **17** in CH_2Cl_2 (1.7 cm^3) was treated with $TiCl_4$ (12 mm^3, 0.11 mmol) in CH_2Cl_2 (0.1 cm^3) at −40 °C. After stirring the reaction mixture for 2 h at the same temperature, it was quenched by the addition of satd. NH_4Cl. The reaction mixture was then extracted with Et_2O. The combined organic layer was washed with water and brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel (hexane–AcOEt 9:1) to give a mixture of **18** and **19a**. The separation of the mixture was achieved by HPLC (hexane–AcOEt 15:1) to give the alcohol **19a** (1.2 mg, 5%) (Found M^+ 270.1976. $C_{19}H_{26}O$ requires *m*/*z* 270.1984); ν_{max}(neat)/cm^{-1} 3380; δ_H (500 MHz, $CDCl_3$) 1.01–1.06 (6H, m, 2 × CH_3), 1.23–1.38 (6H, m, 2 × CH_3), 1.54–1.62 (2H, m, 6-*H*H and 5-H*H*), 1.63–1.74 (1H, m, 5-*H*H), 1.76–1.86 (2H, m, 6-H*H* and 4-H), 3.84–3.92 (1H, m, CHAr), 3.96–4.04 (1H, m, CHOH), 5.12 (1H, d, J = 9.8, olefinic H), 7.13–7.31 (5H, m, ArH).

Further elution yielded the spiro compound **18** (7.0 mg, 28%) (Found M^+ 270.1995. $C_{19}H_{26}O$ requires *m*/*z* 270.1984); ν_{max}(neat)/cm^{-1} 3420; δ_H (400 MHz, $CDCl_3$) 0.77 (3H, s, 1-CH_3), 0.87 (3H, s, 3-CH_3), 1.03 (3H, s, 3-CH_3), 1.10 (3H, s, 3a′-CH_3), 1.12–1.18 (1H, m, 6-H*H*), 1.65–1.78 (3H, m, 5-H_2 and 4-H), 2.27–2.36 (1H, m, 6-*H*H), 2.51 (1H, dd, J = 5.9, 1.3 Hz, 7a′-H), 4.00 (1H, br s, 7-H), 5.48 (1H, br d, J = 9.3 Hz, olefinic H), 5.52 (1H, d, J = 6.1 Hz, olefinic H), 5.59 (1H, d, J = 6.1 Hz, olefinic H), 5.68–5.73 (1H, m, olefinic H), 5.81–5.87 (1H, m, olefinic H), 5.93–5.99 (1H, m, olefinic H); δ_C (100 MHz, $CDCl_3$) 16.0, 22.2, 25.3, 26.7, 28.3, 28.4, 39.8, 46.8, 48.9, 53.4, 53.8, 70.7, 79.4, 119.2, 122.0, 129.1, 132.8, 135.4, 137.1.

1,3,3-Trimethyl-2-(2-methyl-2-phenylethylidene)bicyclo[2.2.1]-heptan-7-ol 19a and 19b

Bu_4NF (1.0 M solution in THF, 520 mm^3, 0.520 mmol) was added to a solution of the TBDMS ether **13** (100 mg, 0.259 mmol) in THF (1 cm^3) at 0 °C and the reaction mixture was stirred for 16 h at RT. After addition of water, the reaction mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography (hexane–AcOEt 5:1) to give the corresponding alcohol (61 mg, 87%) (Found M^+ 272.2123. $C_{19}H_{28}O$ requires *m*/*z* 272.2140); ν_{max}(neat)/cm^{-1} 3350; δ_H (300 MHz, $CDCl_3$) 0.82 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.17 (3H, s, CH_3), 1.24–1.39 (1H, m, 4-*H*H), 1.41–1.54 (1H, m, 4-H*H*), 1.63 (3H, s, 2-CH_3), 1.80–1.93 (1H, m, 5-H), 1.95–2.07 (2H, m, 3-H_2), 2.57–2.68 (2H, m, 4′-H_2), 3.34–3.50 (1H, m, CH*H*OH), 3.78–3.92 (1H, m, C*H*HOH), 5.32 (1H, d, J = 15.9 Hz, *trans*-olefinic H), 5.49–5.79 (5H, m, olefinic H); δ_C (75 MHz; $CDCl_3$) 21.4, 21.6, 22.5, 26.0, 27.6, 28.4, 31.1, 36.3, 38.3, 47.2, 64.0, 122.1, 124.9, 127.9, 133.2, 137.7, 142.7.

To a suspension of this alcohol (20 mg, 0.074 mmol), NMO (17 mg, 0.15 mmol), 4 Å molecular sieves (30 mg) in CH_2Cl_2 (1 cm^3), was added TPAP (1.3 mg, 0.0037 mmol) and the reaction mixture was stirred at RT for 15 min. The reaction mixture was then loaded onto a short column of silica gel and washed down with Et_2O and concentrated. A solution of the crude aldehyde in CH_2Cl_2 (1.4 cm^3) was treated with $SnCl_4$ (10mm^3, 0.085 mmol) in CH_2Cl_2 (0.1 cm^3) at −30 °C. After stirring the reaction mixture for 1.5 h at the same temperature, it was quenched by the addition of satd. NH_4Cl. The reaction mixture was then extracted with Et_2O. The combined organic layer was washed with water and brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel (hexane–AcOEt 9:1) to give a 6:6:1:1 mixture of **19a** and **19b** (17.8 mg, 90%).

Similarly, the crude aldehyde obtained by oxidation of the alcohol **15** (21.5 mg, 0.0790 mmol) with TPAP (1.4 mg, 0.0040 mmol) and NMO (18.5 mg, 0.158 mmol), was dissolved in CH_2Cl_2 (1.5 cm^3), and treated with $SnCl_4$ (11 mm^3, 0.094

mmol) in CH_2Cl_2 (0.1 cm^3) at −30 °C. The reaction mixture was allowed to warm to −10 °C over 4.5 h. The usual workup furnished a 7.5:7.5:1:1 mixture of **19a** and **19b** (10.6 mg, 50%).

1,3,3-Trimethyl-2-(2-methyl-2-phenylethylidene)bicyclo[2.2.1]-heptan-7-one 22 and 23

A 7.5:7.5:1:1 mixture of the bicyclic alcohol **19a** and **19b** (10 mg, 0.037 mmol) in CH_2Cl_2 (300 mm^3) was stirred with 4 Å molecular sieves (30 mg), NMO (9.0 mg, 0.077 mmol) and TPAP (1.3 mg, 0.0037 mmol) at RT for 30 min. The reaction mixture was loaded onto a short column of silica gel and washed down with Et_2O. The residue was concentrated to furnish a 7.5:7.5:1:1 mixture of the ketones **22** and **23** (9.6 mg, 97%). The separation of the isomers by HPLC (hexane–Et_2O 20:1) gave the two *Z*-isomers **22**.

(1) (Found M^+ 268.1846. $C_{19}H_{24}O$ requires *m*/*z* 268.1827), $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H (500 MHz, $CDCl_3$) 1.04 (3H, s, 3-CH_3), 1.20 (3H, s, 1-CH_3), 1.30 (3H, d, J = 6.7 Hz, CH_3CH), 1.35 (3H, s, 3-CH_3), 1.54–1.63 (2H, m, CH_2), 1.65–1.86 (3H, m, CH_2 and 4-H), 3.83–3.92 (1H, m, CHAr), 5.37 (1H, d, J = 9.8 Hz, olefinic H), 7.17–7.33 (5H, m, ArH).

(2) (Found M^+ 268.1870. $C_{19}H_{24}O$ requires *m*/*z* 268.1827); $\nu_{max}(CHCl_3)/cm^{-1}$ 1770; δ_H (500 MHz, $CDCl_3$) 1.01 (3H, s, 3-CH_3), 1.25 (3H, s, 1-CH_3), 1.28 (3H, s, 3-CH_3), 1.32 (3H, d, J = 7.3 Hz, CH_3CH), 1.52–1.62 (2H, m, CH_2), 1.78–1.97 (3H, m, CH_2 and 4-H), 3.84–3.92 (1H, m, CHAr), 5.36 (1H, d, J = 10.3Hz, olefinic H), 7.15–7.33 (5H, m, ArH).

Further elution with hexane–Et_2O (80:1 v/v) gave the corresponding two *E*-isomers **23**.

(1) (Found M^+ 268.1807. $C_{19}H_{24}O$ requires *m*/*z* 268.1827); $\nu_{max}(CHCl_3)/cm^{-1}$ 1760; δ_H (500 MHz, $CDCl_3$) 1.06 (3H, s, 3-CH_3), 1.21 (3H, s, 1-CH_3), 1.31 (3H, d, J = 6.7 Hz, CH_3CH), 1.41 (3H, s, 3-CH_3), 1.56–1.62 (1H, m, 6-H*H*), 1.66–1.79 (3H, m, 5-H_2 and 6-*H*H), 1.88–1.96 (1H, m, 4-H), 3.80–3.90 (1H, m, CHAr), 5.19 (1H, d, J = 11.0 Hz, olefinic H), 7.19–7.34 (5H, m, ArH).

(2) (Found M^+ 268.1863. $C_{19}H_{24}O$ requires *m*/*z* 268.1827); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H (500 MHz, $CDCl_3$) 1.03 (3H, s, 3-CH_3), 1.14 (3H, s, 1-CH_3), 1.36 (3H, d, J = 6.7 Hz, CH_3CH), 1.49 (3H, s, 3-CH_3), 1.56–1.82 (4H, m, 5-H_2 and 6-H_2), 1.96–2.04 (1H, m, 4-H), 3.82–3.90 (1H, m, CHAr), 5.20 (1H, d, J = 10.4 Hz, olefinic H), 7.16–7.34 (5H, m, ArH).

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