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The nucleophilic addition of α-metallated 1,3-dioxanes to planar chiral cationic η^3-allylmolybdenum complexes. Synthesis of (2*E*,5*S*,6*R*,7*E*)-6-methyl-8-phenylocta-2,7-dienoic acid methyl ester, a key component of the Cryptophycins

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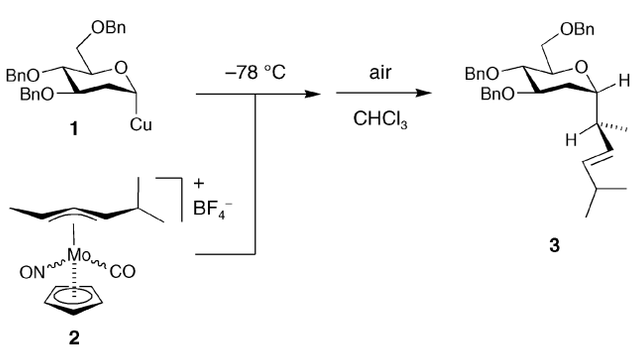
Two adjacent stereogenic centres and a pendant alkene were constructed *via* nucleophilic addition of a 1,3-dioxan-4-ylcopper(I) reagent to a cationic η^3-allylmolybdenum complex as part of a synthesis of (2*E*,5*S*,6*R*,7*E*)-6-methyl-8-phenylocta-2,7-dienoic acid, a key component of the Cryptophycins. Oxidative addition of $Mo(CO)_4(THF)_2$ to allyl benzoates provides an efficient synthesis of η^3-allylmolybdenum(dicarbonyl) complexes.

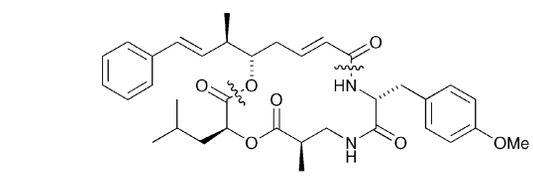
Introduction

We recently showed that the nucleophilic addition of tetrahydropyran-2-ylcopper(I) reagents to planar chiral η^3-allylmolybdenum complexes offers a powerful method for the stereoselective appendage of a chain to an oxacyclic ring.[1] The method, illustrated in Scheme 1 for the synthesis of *C*-glycosides,[2] entails the construction of two adjacent stereogenic centres with a pendant alkene. The high level of stereocontrol is a consequence of the reaction of the organocopper(I) nucleophile with retention of configuration and preferential attack at the allyl ligand *anti* to the molybdenum.[3] The one burr under the saddle is the issue of regioselectivity: a combination of steric and electronic factors governs the site of attack. In the case of complex **2**, the steric effect predominates (≥15 : 1).[4]

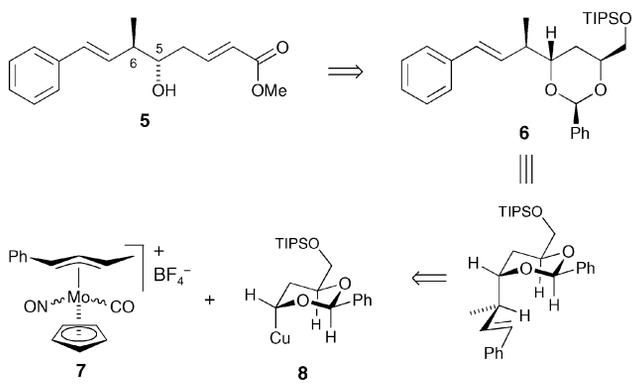


Scheme 1

We now show that 1,3-dioxan-4-ylcopper(I) reagents are effective nucleophilic partners in the reaction providing a method for the stereoselective appendage of 1,3-diol chains.[5] The strategy is exemplified for the synthesis of the methyl ester (**5**) of (2*E*,5*S*,6*R*,7*E*)-6-methyl-8-phenylocta-2,7-dienoic acid, a key component of the Cryptophycins (Scheme 2).[6–10] The Cryptophycins are cyclodepsipeptides with pronounced antitumour activity owing to their inhibition of tubulin polymerisation.[11,12] Our synthesis of **5** is a vehicle for exploring the effect of a conjugating substituent on the regioselectivity of nucleophilic addition to η^3-allylmolybdenum complex **7** using the α-metallated dioxane **8** as the nucleophile leading to the dioxane derivative **6** which fixes the *anti* stereochemistry between C5 and C6 in the target.



Cryptophycin 4 (**4**)

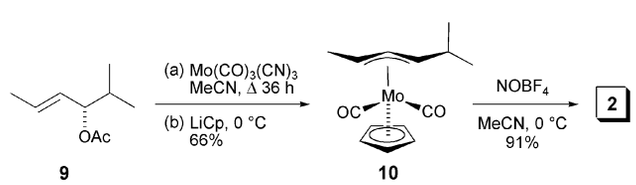


Scheme 2

Results and discussion

Synthesis of the cationic η^3-allylmolybdenum complex 7

The first practical and general synthesis of cationic η^3-allylmolybdenum complexes (Scheme 3) was reported in 1988 by Faller and Linebarrier[13,14] who showed that the scalemic allylic acetate **9** derived from Sharpless kinetic resolution of the corresponding allylic alcohol, underwent oxidative addition of the complex $Mo(CO)_3(MeCN)_3$[15] with retention of configuration to give the neutral complex **10** after reaction with lithium cyclopentadienide. Activation of the planar chiral neutral

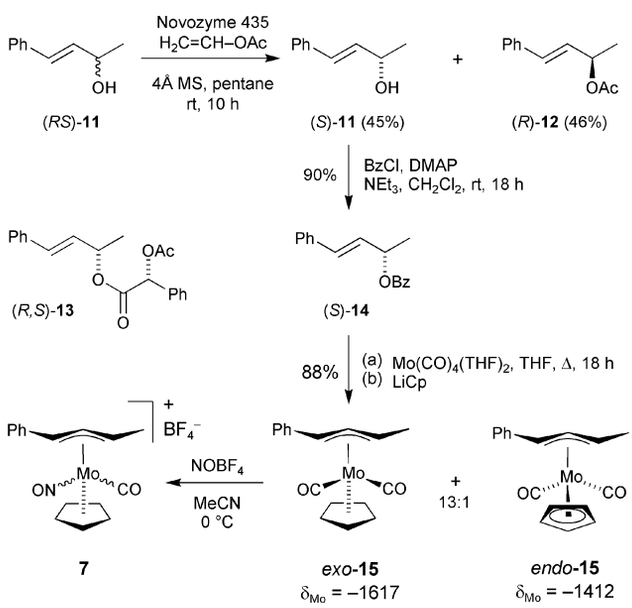


Scheme 3

DOI: 10.1039/b400242c

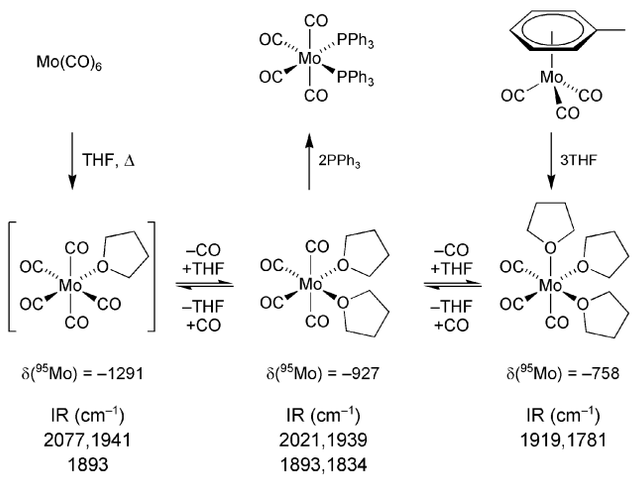
complex with nitrosonium tetrafluoroborate gave the cationic complex **2** as a mixture of diastereoisomers owing to the stereorandom nature of the ligand exchange.

The Faller protocol was substantially modified for the synthesis of the complex **7** (Scheme 4). Easy and efficient kinetic resolution of the racemic allylic alcohol (*RS*)-**11** was accomplished using Novozyme 435, a recombinant immobilised B-component lipase from *Candida antarctica*, and vinyl acetate, to give (*S*)-**11** and the acetate ester (*R*)-**12** in 45% and 46% yield respectively.[16,17] The enantiomeric ratio of the allylic alcohol (*S*)-**11** was assayed at 97 : 3 by NMR spectroscopic analysis of the corresponding (*R*)-acetoxyphenylacetic ester **13**. Initial attempts to perform oxidative addition on the acetate ester of (*S*)-**11** using $Mo(CO)_3(MeCN)_3$ were disappointing. The reaction was very slow in refluxing acetonitrile, requiring five days to go to completion, and the isolated yield of the neutral complex **15** was 35% at best after ligand exchange with lithium cyclopentadienide. A parallel study established that the rate of oxidative addition depended on the ester leaving group, with benzoate giving the optimum yield and rate.[18] When benzoate (*S*)-**14** was treated with $Me(CO)_3(MeCN)_3$ in refluxing acetonitrile, the reaction was complete in just 28 h and the yield of the isolated neutral complex **15** improved to 76%. A further improvement attended the oxidative addition of $Mo(CO)_4(Py)_2$[19,20] to the benzoate ester (*S*)-**14** in refluxing THF: the reaction was complete in 18 h and the yield of the neutral complex **15** climbed to 88%. The neutral complex **15** was obtained as fine yellow needles (mp 85–88 °C) after recrystallisation from ether–pentane but ^{95}Mo NMR spectroscopic analysis revealed the presence of *exo* and *endo* isomers (*exo* : *endo* = 13 : 1) that were easily distinguished by the large difference in chemical shifts.[21] Finally, ligand exchange with nitrosonium tetrafluoroborate in acetonitrile at 0 °C gave initially two isomeric cationic complexes **7** (*ca.* 1 : 1) owing to the stereorandom introduction of central chirality at molybdenum. Although the cationic complex **7** could be isolated as a solid by precipitation, it was usually generated and used in solution without purification.



Scheme 4

The dramatic improvement in speed and yield observed with $Mo(CO)_4(Py)_2$ and the allyl benzoate begged the question as to whether further improvements could be wrested from ligand substitutions on the molybdenum reagent. $Mo(CO)_4(Py)_2$ was easily synthesised by refluxing $Mo(CO)_6$ in THF for 12 h in the presence of 2 equivalents of pyridine.[19] When the reaction was followed by ^{95}Mo NMR spectroscopy, a complex mixture of Mo species was observed in time dependent ratio which included $Mo(CO)_5(THF)$ and *cis*-$Mo(CO)_4(THF)_2$. A clearer picture emerged when $Mo(CO)_6$ was heated in degassed THF (0.08 M) for 22 h in the absence of pyridine and the reaction was followed by ^{95}Mo NMR and IR spectroscopy (Scheme 5). A compound with a signal at −1291 ppm with infrared absorptions at 2077, 1941 and 1893 cm^{-1} was rapidly formed which we ascribed to $Mo(CO)_5(THF)$. This signal gradually disappeared and was replaced by a major signal at −927 ppm with $\Delta\omega_{1/2}$ = 120 Hz (in THF) due to *cis*-$Mo(CO)_4(THF)_2$ and a minor component (*ca.* 4%) with a signal at −750 ppm, $\Delta\omega_{1/2}$ = 65 Hz and IR absorptions at 1919 and 1781 cm^{-1} which we ascribed to *fac*-$Mo(CO)_3(THF)_3$.[22] The stereochemistry of *cis*-$Mo(CO)_4(THF)_2$ was assigned from the infrared signals at 2021, 1939, 1893 and 1834 cm^{-1} and its rapid and quantitative transformation to *cis*-$Mo(CO)_4(PPh_3)_2$ on addition of two equivalents of PPh_3.[23,24] *cis*-$Mo(CO)_4(THF)_2$ was stable in THF, in the absence of light and oxygen, and could be precipitated from pentane at −100 °C as a yellow solid but it was too labile to be isolated and characterised by X-ray crystallography.



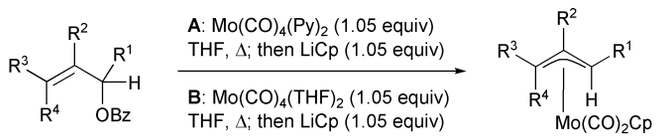
Scheme 5

A mixture of benzoate (*S*)-**14** and $Mo(CO)_4(THF)_2$ was refluxed in THF for 14 h whereupon TLC analysis indicated complete consumption of the benzoate. On addition of LiCp, the neutral complex **15** was obtained in 88% yield.[25] Hence the THF complex reacted slightly faster than its pyridine analogue though the yield in this case was identical. In order to explore the scope and synthetic advantages of the novel $Mo(CO)_4(THF)_2$ complex, we prepared a series of η^3-allylmolybdenum complexes **17a**–**h** from allylic benzoates **16a**–**h** using $Mo(CO)_4(Py)_2$ (Procedure A) and $Mo(CO)_4(THF)_2$ (Procedure B) under identical conditions. The data presented in Table 1 shows that the $Mo(CO)_4(THF)_2$ reagent gave faster reactions though the yields were only marginally better (4–12%). TLC analysis of the progress of the reaction also indicated that the $Mo(CO)_4(THF)_2$ reagent gave cleaner reactions, especially in the synthesis of trisubstituted systems such as **17e** and **17f**.

Synthesis of the 1,3-dioxan-4-ylcopper(I) reagent 8

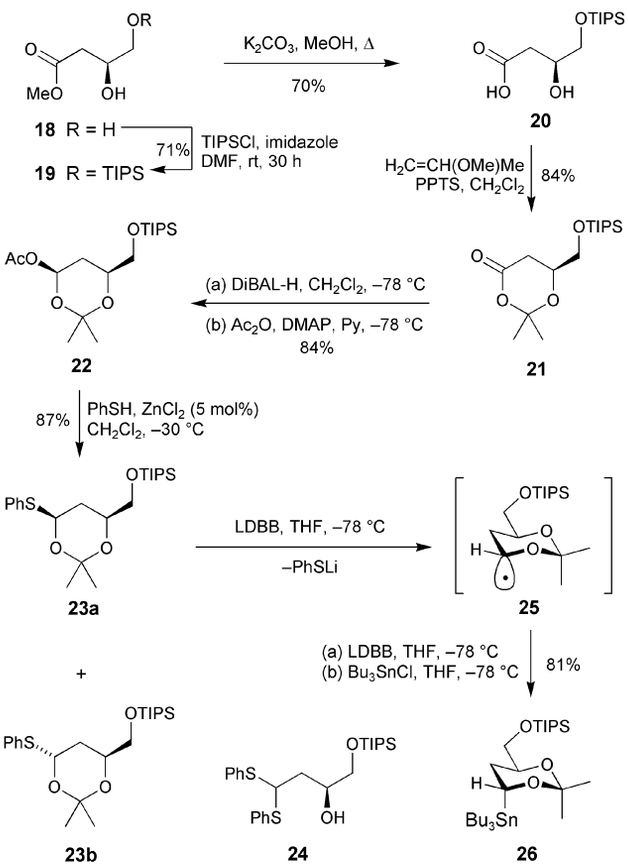
We planned to generate the key 1,3-dioxan-4-ylcopper(I) reagent by transmetallation of the corresponding stannane to its lithium derivative followed by a second transmetallation to the copper reagent using a Cu(I) salt. The isopropylidene protected 1,3-dioxan-4-ylstannane **25** (Scheme 6) was our initial choice of stereodefined tin precursor because a six-step synthesis from dimethyl (*S*)-malate had been reported.[26] We were unable to implement the published procedure or any of its subsequent renditions[27–29] but a reliable variation was eventually found and is summarised in Scheme 6. The sequence began with the selective reduction of dimethyl (*S*)-malate with BH_3·

Table 1 The oxidative addition of $Mo(CO)_2(Py)_2$ and $Mo(CO)_4(THF)_2$ to allylic benzoates



16a-h 17a-h

16	R^1	R^2	R^3	R^4	Procedure A		Procedure B	
					Time	Yield **17**	Time	Yield **17**
a	H	H	H	H	12 h	86%	9 h	86%
b	H	Me	H	H	20 h	82%	16 h	85%
c	H	H	Me	Me	56 h	58%	44 h	65%
d	Me	H	CO_2Et	H	72 h	70%	16 h	82%
e	Me	Me	Me	H	59 h	80%	44 h	86%
f	Me	H	Me	Me	82 h	50%	68 h	58%
g	H	Me	iPr	H	—	—	96 h	95%
h	Me	H	CO_2Et	Me	—	—	24 h	88%



Scheme 6

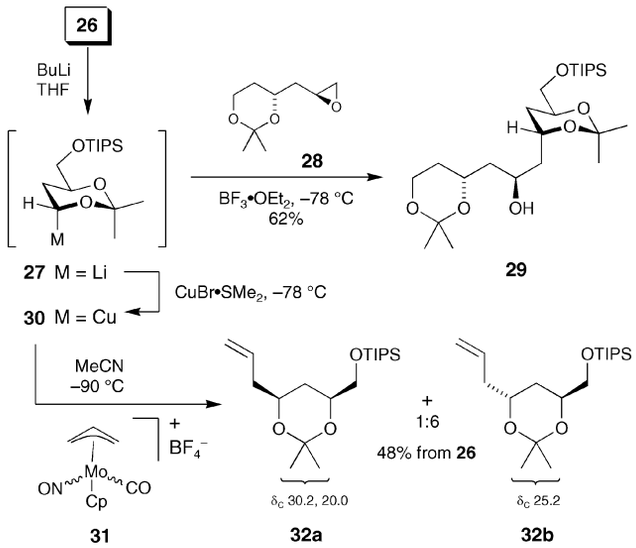
SMe_2 as described by Moriwake[30] to give the 1,2-diol **18** in 89% yield. The terminal hydroxyl was selectively protected as the triisopropylsilyl (TIPS) ether **19** and the methyl ester was hydrolysed to give carboxylic acid **20**. The hydroxyl and carboxyl groups were protected as the 1,3-dioxan-4-one derivative **21** in 94% yield on treatment of **20** with 2-methoxypropene in the presence of pyridinium *p*-toluenesulfonate (PPTS). Reduction of the dioxanone to the lactol with DiBAL-H at −78 °C followed immediately by *in situ* acetylation with acetic anhydride in the presence of DMAP gave the (4*S*,6*S*)-acetoxydioxane **22** in 84% yield as a single isomer. The high stereoselectivity in the reduction-acetylation sequence was precedented in similar transformations on dioxanones reported by Rychnovsky.[31,32]

The conversion of the acetoxydioxane **22** to the *O,S*-acetal **23a**,**b** was the most vexatious step in the sequence. Initial attempts to exploit precedent[32] by using thiophenol and $BF_3{\cdot}OEt_2$ in dichloromethane at a variety of temperatures and times invariably returned the *S,S*-acetal **24** as the sole product. Use of $PhSSiMe_3$ in place of thiophenol gave trace amounts of **23a**,**b** at −78 °C using $BF_3{\cdot}OEt_2$ as promoter but the combination of $PhSSiMe_3$ and $ZnCl_2$ at −60 °C in dichloromethane gave the desired *O,S*-acetals **23a**,**b** (a : b = 1 : 3) in 81% yield after only 5 min. Finally, the best results were obtained by simply treating **22** with thiophenol in the presence of 4 mol% $ZnCl_2$ at −30 °C for 5 min whereupon **23a**,**b** was obtained in 87% yield (a : b = 9 : 1) with only a trace of **24** being formed by TLC. The diastereoisomeric acetals **23a**,**b** were separable by column chromatography and their relative stereochemistry was easily determined by the characteristic signals for the acetal methyl groups in the ^{13}C NMR spectra. The *syn*-isomer **23a** revealed signals at 30.1 and 20.9 ppm in accord with the expected chair conformation whereas the *anti*-diastereoisomer **23b** gave corresponding signals at 28.1 and 24.6 ppm indicative of the expected twist-boat conformation.[33]

The reductive lithiation[34] of the mixture of *O,S*-acetals **23a**,**b** using lithium di-*tert*-butylbiphenylide (LDBB)[35,36] in THF at −78 °C followed by quenching the reaction mixture with excess chlorotributylstannane gave the known[26] 1,3-dioxan-4-yl-stannane **26** as a single diastereoisomer. The stereoconvergent formation of a single stannane from the mixture of *O,S*-acetals is a consequence of the radical anomeric effect[37–39] stabilising the conformation of the SOMO in **25**. Rapid donation of a second electron from the LDBB gave the axial organolithium, which is configurationally stable at low temperature,[28,29] and thence the axial stannane on transmetallation.

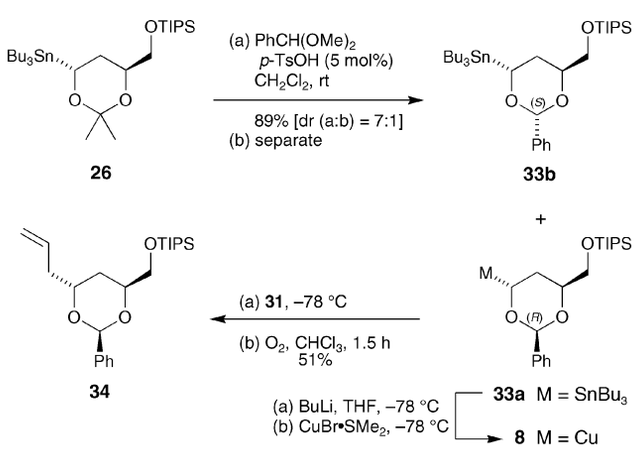
It was our original intention to use the 1,3-dioxan-4-yl-copper(I) reagent **30** (Scheme 7) as the nucleophilic partner in our synthesis of Cryptophycin 4. Rychnovsky had shown that the lithium reagent **27**, derived from transmetallation of the stannane **26** with BuLi, reacted with the terminal oxirane **28** in the presence of $BF_3{\cdot}OEt_2$ to give the alkylation product **29** as a single diastereoisomer (62%) with clean retention of configuration.[26] However, a model study of the key alkylation reaction discovered an unexpected stereochemical problem. When the lithium reagent **27** was converted to its copper(I) derivative **30** at −78 °C and then added to a solution of the simple cationic η^3-allylmolybdenum complex **31** in acetonitrile at −90 °C, the adducts **32a**,**b** were obtained as a mixture of separable diastereoisomers in 48% overall yield from **26**.

The formation of a significant proportion of the inversion product **32a** did not bode well for the Cryptophycin synthesis and it was the first example in our programme in which stereochemistry had been compromised in the addition of an α-heteroalkylcopper(I) nucleophile to a cationic η^3-allylmolyb-



Scheme 7

denum complex. We surmised that the origin of the problem lay in the repulsive 1,3-diaxial interaction between the Cu atom and the axial isopropylidene methyl group in **30**. To test this hypothesis, the isopropylidene group was transacetalised in 89% yield to the separable benzylidene acetals **33a**,**b** (a : b = 7 : 1) by treatment of **26** with benzaldehyde dimethylacetal in the presence of *p*-toluenesulfonic acid (Scheme 8). Equilibration of the minor diastereoisomer **33b** under the same reaction conditions returned a mixture of **33a** : **33b** in the ratio 11 : 1. The stereochemistry of the diastereoisomers was deduced from ^{1}H NMR spectroscopic data summarised in Table 2. The major diastereoisomer **33a** was identified by the strong NOE interactions between C2H and C4H whilst the minor diastereoisomer **33b** displayed a strong NOE interaction between C2H and C6H in accord with the twist-boat conformation depicted.



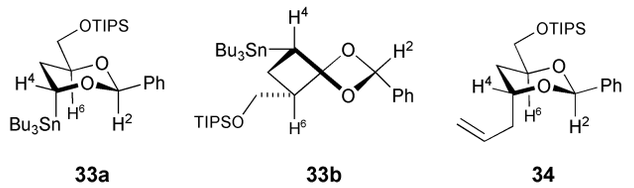
Scheme 8

Our suspicion that the configurational stability of the copper(I) reagent **30** was a consequence of steric destabilisation was lent some credence when the 1,3-dioxan-4-ylcopper(I) reagent **8** prepared from **33a** was treated with cationic complex **31** (Scheme 8). The adduct **34** was obtained as a single diastereoisomer in 51% yield after oxidative decomplexation. However, in the next section we will show that reagent **8** does not preserve its stereochemical integrity in its reactions with cationic complexes.

Union of fragments 7 and 8 and completion of the synthesis

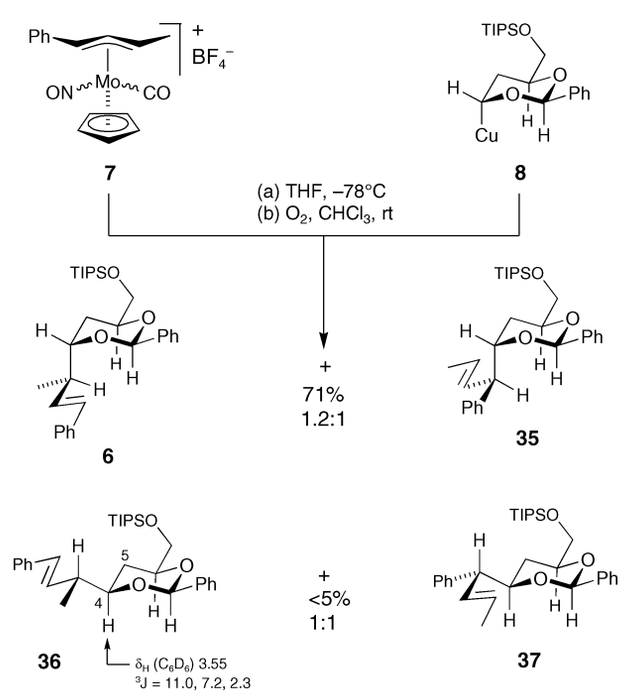
Stannane **33a** was converted to the 1,3-dioxan-4-ylcopper(I) reagent **8** on an 8.5 mmol scale whilst carefully maintaining

Table 2 NOE data for dioxanes **33a**,**b** and **34**



		δ (ppm)	Multiplicity, ^3J (Hz)	NOE
	H^2	5.81	s	16% ⟶ H^6
33a	H^4	5.15	apparent d, 6.4	—
	H^6	4.26	dddd, 10.7, 6.9, 5.2, 2.4	10% ⟶ H^2
	H^2	5.73	s	13% ⟶ H^4
33b	H^4	4.59	13.7, 2.3	14% ⟶ H^2
	H^6	4.17–4.12	m	10% ⟶ H^5
	H^2	5.84	s	16% ⟶ H^6
34	H^4	4.35	apparent q, 6.9	—
	H^6	4.18	dddd, 11.0, 2.5, 5.9, 5.9	10% ⟶ H^2

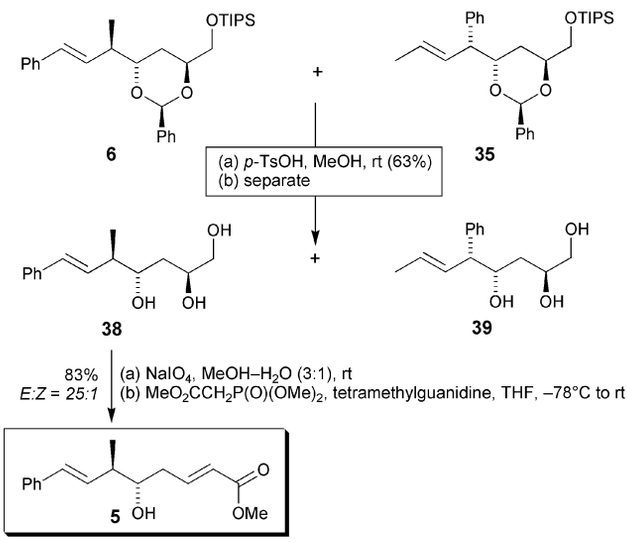
the temperature at ≤ −78 °C. A solution of the freshly prepared cationic complex **7** in acetonitrile, generated by adding nitrosonium tetrafluoroborate to the neutral complex **15** at 0 °C, was added in one portion to the copper reagent and after 1 h, aqueous workup was followed by oxidative decomplexation (O_2, $CHCl_3$). Column chromatography returned an inseparable mixture of regioisomeric olefins **6** and **35** in 71% yield whose relative proportion (1.2 : 1) was determined by integration of the alkene signals at 6.51 (d) and 6.26 (dd) ppm attributed to **6** and a multiplet at 5.64–5.50 attributed to **35** (Scheme 9). A further pair of inseparable regioisomeric olefins (*ca.* 1 : 1) were also obtained in < 5% yield which were tentatively assigned structures **36** and **37**. Evidence for the stereochemistry in **36** derived from the signal for C4H with a large ^3J coupling (11 Hz) with the axial proton at C5, and strong NOE interactions between the protons at C2, C4 and C6 indicative of their axial relationship.



Scheme 9

Hydrolysis of the triisopropylsilyl and benzylidene acetal protecting groups from the mixture of **6** and **35** gave triols **38** and **39** which could be separated, albeit with some difficulty, by column chromatography (Scheme 10). Sodium periodate oxidation of triol **38** revealed a *β*-hydroxy aldehyde which

underwent a Wadsworth–Horner–Emmons olefination using trimethylphosphonoacetate and tetramethylguanidine in THF at low temperature to give ester **5** in 83% overall yield from **38** as a single isomer.[40] Comparison of spectroscopic data for **5** with those reported by Moore and Tius[41] together with the conversion of **5** to Cryptophycin 4 confirmed the structure and stereochemistry of the target.[5]



Scheme 10

The formation of the diastereoisomers **36** and **37** in the key addition step was a minor vexation compared with the lack of regioselectivity in the formation of **6** and **35**. The contrast with the good steric discrimination between the methyl and isopropyl termini observed in complex **2**[1,2] suggests that the methyl and phenyl groups have similar steric requirements in complex **7** thereby allowing the electronic directing effect of the nitrosyl ligand to predominate.[4,13] Tangential evidence for this argument was gleaned by following the ligand exchange reaction (**15** to **7**) by ^{1}H NMR spectroscopy in CD_3CN: two major *endo* isomers (the kinetic products)[21,42] were observed in the ratio 1.2 : 1, paralleling the observed ratio of olefin products following alkylation. Upon standing in CD_3CN solution for 24 h, the two *endo* isomers isomerised to a mixture of four compounds, presumably two pairs of *exo* and *endo* isomers, in the ratio 2.3 : 2 : 1 : 1.2, as estimated from the intensities of cyclopentadienyl singlets at 5.69, 6.11, 6.22, and 6.02 ppm respectively.

Conclusions

The synthesis of (2*E*,5*S*,6*R*,7*E*)-6-methyl-8-phenylocta-2,7-dienoic acid (**5**) with the correct relative and absolute stereochemistry at C5 and C6 proved that (a) the key coupling step had occurred *anti* to the molybdenum in **7**; (b) the nucleophile **8** added predominantly with retention of configuration; and (c) the oxidative addition of $Mo(CO)_4(THF)_2$ to allylic benzoates occurred with clean retention. The complete retention of stereochemistry in the addition of 1,3-dioxan-4-ylcopper(I) reagent **8** to the simple cationic complex **31** and the formation of epimeric adducts from the addition of **8** and **30** to cationic complexes **7** and **31** respectively shows that erosion in the stereochemical integrity of the nucleophile, though a rare event, may be influenced by the structure of the cationic complex, and by adverse steric interactions in the nucleophile. $Mo(CO)_4(THF)_2$ has been developed as an easily prepared and highly reactive reagent for the formation of η^3-allylmolybdenum complexes from allylic benzoates, including trisubstituted systems which have hitherto been inaccessible by conventional reagents. Finally, we have established that 1,3-dioxan-4-ylcopper(I) reagents are effective nucleophilic partners that form adducts rapidly and stereoselectively with cationic η^3-allylmolybdenum complexes.[43]

Experimental

Organic extracts were dried using magnesium sulfate ($MgSO_4$) unless otherwise specified, and were concentrated using a rotary evaporator. Diethyl ether and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. Eluants used in the purification of the Mo complexes were degassed by sparging with dry nitrogen for 20–30 minutes before use. $CuBr{\cdot}SMe_2$ was prepared by the procedure of Taylor[44] and purified by recrystallisation before use. Commercial *n*-butyllithium was titrated against 1,3-diphenylacetone-*p*-tosylhydrazone prior to use.[45]

Specific optical rotations ($[\alpha]_D$) were measured at ambient temperature (21±3 °C) on an Optical Activity polAAr 2000 polarimeter using a 5 mL cell with a 1 dm path length or a 0.5 mL cell with a 0.05 dm path length. Infra-red (IR) spectroscopic details are reported as ν_{max} in cm^{-1}, followed by an intensity descriptor: s = strong, m = medium, br = broad; weak absorptions are not recorded. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, C_6D_6 or CD_3CN solution in 5 mm diameter tubes, and the chemical shift in ppm is quoted relative to the residual signals of chloroform (δ_H 7.27, δ_C 77.2), benzene (δ_H 7.27, δ_C 128.4) or acetonitrile (δ_H 2.00, δ_C 117.7) unless specified otherwise. Coupling constants (*J*) are reported in Hz. ^{1}H NMR signal assignments are based on COSY and HMQC correlations. ^{13}C NMR signal assignments are based on DEPT and C–H correlation experiments. ^{95}Mo NMR (13 MHz) spectra were recorded on a Bruker WP200SY spectrometer and were referenced externally to $Na_2[MoO_4]$.[46,47] Low and high resolution mass spectra were run on a JEOL MStation JMS-700 spectrometer. Ion mass/charge (*m*/*z*) ratios are reported as values in atomic mass units followed, in parenthesis, by the peak intensity relative to the base peak (100%). GCMS was performed on the above spectrometer, using a Chrompack WCOT Fused Silica column (25 m × 0.25 mm, CP-SIL 8CB-MS stationary phase), initial temperature and heating rates are specified for individual cases.

(2*S*,3*E*)-4-Phenylbut-3-en-2-ol (11) and (1*R*,2*E*)-acetic acid 1-methyl-3-phenylallyl ester (12)

A suspension of Novozyme 435 (66 mg), crushed activated 4 Å molecular sieves (330 mg), (*RS*)-**11** (660 mg, 4.45 mmol) and vinyl acetate (10.3 mL, 111 mmol) in pentane (20 mL) was shaken gently at rt for 10 h. ^{1}H NMR spectroscopy of the crude reaction mixture indicated ≥ 50% conversion. After filtration and concentration *in vacuo*, the residue was purified by column chromatography (SiO_2, ether : hexanes = 2 : 8 ⟶ 4 : 6) to give acetate (*R*)-**12** (390 mg, 2.05 mmol, 46%) as a colourless oil, and alcohol (*S*)-**11** (300 mg, 2.02 mmol, 45%) as a colourless oil which solidified upon standing. Alcohol (*S*)-**11** gave mp 29–30 °C (hexanes–dichloromethane); lit.[48] mp 31–33 °C; $[\alpha]_D$ = −34.1 (*c* 2.34, $CHCl_3$); lit.[49] $[\alpha]_D$ (enantiomer) = +34.2 (*c* 1.77, $CHCl_3$). ^{1}H and ^{13}C NMR spectroscopic data were in accordance with literature data.[50,51] The enantiomeric ratio for alcohol **11** was estimated as 97 : 3 *via* formation of the corresponding (*R*)-acetoxyphenylacetic ester **13** by an analogous procedure to that detailed above.

Acetate (*R*)-**12** gave $[\alpha]_D$ = +143.1 (*c* 3.38, $CHCl_3$); lit.[52] $[\alpha]_D$ = +151.1 (*c* 5.27, $CHCl_3$). ^{1}H NMR and IR spectroscopic data were in accordance with literature data.[53] ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (*C*OMe), 136.5 (C, Ph), 131.7 (CH, Ph), 129.0 (CH, Ph), 128.7 (2CH, Ph), 128.0 (CH, Ph), 126.7 (2CH, Ph), 71.1 (C1H), 21.5 (CO*Me*), 20.5 (C1-*Me*). The enantiomeric ratio for acetate (*R*)-**12** was estimated as 96 : 4 by cleavage of the acetate (10 wt% K_2CO_3, MeOH, rt, 15 h) and formation of the corresponding (*R*)-acetoxyphenylacetic ester.

(*R*)-Acetoxyphenylacetic acid (1*S*)-1-methyl-3-phenylallyl ester [(*R,S*)-13]

To a solution of alcohol (*S*)-**11** (41 mg, 0.28 mmol), (*R*)-acetoxyphenylacetic acid (59 mg, 0.30 mmol) and DMAP (2 mg, 0.01 mmol) in CH_2Cl_2 (10 mL) at 0 °C under N_2 was added DCC (86 mg, 0.41 mmol). The mixture was stirred at 0 °C for 10 min and at rt for 50 min before filtering through Celite and washing with Et_2O. After drying, filtration and concentration *in vacuo*, the residue was purified by column chromatography (SiO_2, ether : hexanes = 3 : 7) to give the title compound (76 mg, 0.23 mmol, 84%) as a colourless oil. The diastereoisomeric ratio at C1 was estimated as 97 : 3 *via* integration of the C3H signals in the ^{1}H NMR spectrum: δ = 6.56 (d, J = 16.0, (1*S*)-diastereoisomer), δ = 6.26 (d, J = 16.0, (1*R*)-diastereoisomer), with reference to a sample prepared from (*RS*)-**11**.

$[\alpha]_D = -107.7$ (*c* 2.32, $CHCl_3$).

IR (film): ν = 1755 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ referenced to added TMS): δ = 7.50–7.19 (10H, m, Ph), 6.58 (1H, d, J = 16.0 Hz, PhC*H*), 6.16 (1H, dd, J = 16.0, 6.4 Hz, PhCH=C*H*), 5.95 (1H, s, CHOAc), 5.55 (1H, ddq, J = 6.4, 1.1, 6.5 Hz, C*H*CH$_3$), 2.17 (3H, s, OAc), 1.27 (3H, d, J = 6.5 Hz, CHC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3 (C=O), 168.2 (C=O), 136.3 (C, Ph), 134.0 (C, Ph), 131.9 (CH), 129.2 (CH or Ph), 128.8 (2CH, Ph), 128.6 (2CH, Ph), 128.0 (2CH), 127.7 (2CH, Ph), 126.7 (2CH, Ph), 74.8 (*C*HOAc), 72.6 (CH), 20.8 (*C*H$_3$CO), 20.0 (*C*H$_3$CH).

LRMS (EI$^+$ mode): m/z = 324.2 [M$^{+\bullet}$, 2%], 264.2 (7), 131.1 (100), 118.1 (40), 107.1 (32), 91.1 (20), 43.0 (17).

HRMS (EI$^+$ mode): found M$^{+\bullet}$, 324.1359. $C_{20}H_{20}O_4$ requires M, 324.1362.

(*R*)-Acetoxyphenylacetic acid (1*R*)-1-methyl-3-phenylallyl ester [(*R,R*)-13]

$[\alpha]_D = -2.6$ (*c* 1.40, $CHCl_3$).

IR (film): ν = 1763 s, 1743 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ referenced to added TMS): δ = 7.49–7.18 (10H, Ph), 6.26 (1H, d, J = 16.0 Hz, PhC*H*), 5.98 (1H, dd, J = 16.0, 6.2 Hz, PhCH=C*H*), 5.95 (1H, s, C*H*OAc), 5.55 (1H, ddq, J = 6.4, 1.2, 6.2 Hz, C*H*CH$_3$), 2.19 (3H, s, OAc), 1.42 (3H, d, J = 6.4 Hz, CHC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (C=O), 168.2 (C=O), 136.3 (C), 134.0 (C), 131.4 (CH), 129.4 (CH), 128.9 (2CH), 128.6 (3CH), 128.0 (3CH), 127.9 (CH), 126.6 (CH), 74.8 (CHOAc), 72.4 (CH–O), 20.9 (CH$_3$CO), 20.4 (*C*H$_3$CH).

LRMS (CI$^+$ mode, NH_3): m/z = 342.1 [(M + NH$_4$)$^+$, 14%], 212.1 (14), 131.1 (100).

(1*S*,2*E*)-Benzoic acid 1-methyl-3-phenylallyl ester [(*S*)-14]

To a solution of alcohol (*S*)-**11** (3.82 g, 25.8 mmol) and 4-dimethylaminopyridine (10 mg) in CH_2Cl_2 (30 mL) at rt under N_2 was added benzoyl chloride (3.3 mL, 28.4 mmol) and triethylamine (4.0 mL, 28.4 mmol). The solution was stirred at rt for 18 h before the addition of HCl (2 M, 30 mL). The phases were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine (50 mL), dried, filtered and concentrated *in vacuo*. The pale yellow solid residue was purified by recrystallisation from hexanes to give the title compound (5.89 g, 23.3 mmol, 90%) as a white solid: mp = 79–80 °C; $[\alpha]_D = +1.46$ (*c* 7.56, $CDCl_3$); lit.[49] $[\alpha]_D = +0.42$ (*c* 8.16 $CHCl_3$).

IR (KBr): ν = 1709 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ referenced to added TMS): δ = 8.10–8.06 (2H, m, Ph), 7.55–7.21 (8H, m, Ph), 6.69 (1H, d, J = 16.0 Hz, PhC*H*), 6.30 (1H, dd, J = 16.0, 6.6 Hz, PhCH=C*H*), 5.79 (1H, ddq, J = 6.5, 1.1, 6.5 Hz, C*H*CH$_3$), 1.54 (3H, d, J = 6.5 Hz, CHC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (*C*OPh), 136.5 (C), 133.0 (CH), 131.8 (CH), 131.1 (CH), 129.7 (2CH), 129.0 (CH), 128.7 (2CH), 128.5 (2CH), 128.0 (CH), 126.7 (2CH), 71.7 (CH), 20.6 (CH$_3$).

***syn-syn*-Dicarbonyl(η^5-cyclopentadienyl)-[(1,2,3-η)-(1*R*,2*S*,3*S*)-1-phenyl-2-but-2-en-1-yl]molybdenum (15)**

Procedure A. To a solution of $Mo(CO)_6$ (512 mg, 1.94 mmol) in degassed THF (25 mL) under N_2 was added pyridine (0.31 mL, 3.88 mmol) and the solution brought to reflux. After refluxing for 12 h, a solution of benzoate (*S*)-**14** (465 mg, 1.84 mmol) in degassed THF (1.5 mL) was added dropwise *via* syringe to the red-orange solution, which was refluxed for a further 18 h before cooling to rt over 1 h. Freshly prepared LiCp (7.1 mL of a 0.29 M solution in THF was added and the dark red-brown solution stirred at rt under N_2 for 1 h. The solution was transferred *via* syringe to a round-bottomed flask and concentrated *in vacuo* to a volume of approximately 10 mL, before purification by column chromatography (Al_2O_3, degassed hexanes–Et_2O, 2 : 1, under N_2) and concentration *in vacuo*. The title compound was obtained as a fine yellow crystalline solid (597 mg, 1.71 mmol, 88%).

Procedure B. A solution of $Mo(CO)_6$ (0.804 g, 3.04 mol) in degassed THF (25 mL) was heated to reflux under N_2 whereupon benzoate (*S*)-**14** (0.732 g, 2.9 mmol) in degassed THF (2 mL) was added dropwise *via* syringe. After addition was complete the mixture was refluxed for a further 12 h. The mixture was allowed to cool to rt and a freshly prepared solution of LiCp (0.3 M, 10 mL) was added. After stirring at rt for 1 h, workup as described above gave the title complex (0.939 g, 2.9 mmol, 93%).

Neutral complex **15** was generally used without further purification, but for analytical purposes it could be purified by recrystallisation from pentane to give fine yellow needles: mp 85–88 °C; $[\alpha]_D = +8.0$ (*c* 0.67, $CHCl_3$).

IR (KBr): ν = 1917 s, 1839 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ referenced to added TMS): δ = 7.30–7.19 (3H, m, Ph), 7.12–7.08 (2H, m, Ph), 5.10 (5H, s, Cp), 4.88 (1H, t, J = 9.6 Hz, PhCH–C*H*–CH), 2.35 (1H, d, J = 10.0 Hz, PhC*H*–CH–CH), 1.86 (3H, d, J = 6.0 Hz, CHC*H*$_3$), 1.78–1.73 (1H, m, PhCH–CH–C*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 239.7 (CO), 239.6 (CO), 142.1 (C, Ph), 128.6 (2CH, Ph), 125.9 (CH, Ph), 125.1 (2CH, Ph), 93.9 (5CH, Cp), 68.5 (PhCH–*C*H–CH), 58.8 (PhCH–CH–*C*H), 58.4 (Ph*C*H–CH–CH), 21.2 (CH$_3$).

^{95}Mo NMR (13 MHz, THF): $\delta_{exo} = -1617$, $\delta_{endo} = -1412$. *exo* : *endo* = 13 : 1.

LRMS (EI mode): m/z = 350.2 [(M(^{98}Mo))$^{+\bullet}$, 25%], 322.2 [(M(^{98}Mo)-CO)$^{+\bullet}$, 20], 292.2 (100).

Found: C, 58.60; H, 4.69. $C_{17}H_{16}O_2Mo$ requires C, 58.63; H, 4.63%.

***syn-syn*-Carbonyl-(nitrosyl)-(η^5-cyclopentadienyl)-[(1,2,3-η)-(1*R*,2*S*,3*S*)-1-phenyl-2-but-2-en-1-yl]molybdenum tetrafluoroborate (7)**

Cationic complex **15** was routinely prepared in a minimum volume (*ca.* 2–3 mL mmol^{-1}) of freshly distilled MeCN at 0 °C under N_2 by the addition of $NOBF_4$ (1.1 eq.) and transferred directly *via* cannula to a solution of the nucleophile. However, for characterisation purposes the title compound was prepared on a 3.4 mmol scale and transferred to Et_2O (200 mL) at 0 °C under N_2 to yield a light-brown solid after cooling to −60 °C for 15 min. Cationic complex **7** (518 mg, 1.20 mmol, 36%) was isolated by filtration under an atmosphere of N_2: IR (solution in CD_3CN): ν = 2080 s, 1720 s cm^{-1}. Complex **7** was initially isolated as a mixture of two major isomers (presumably a pair of *endo* isomers), in the approximate ratio 1.2 : 1. On standing at rt for 24 h, a mixture of four isomers was obtained in a ratio

of approximately 2.3 : 2 : 1 : 1.2, as estimated by the integrations of Cp singlets at 5.69, 6.11, 6.22 and 6.02 ppm respectively.

^{1}H NMR (360 MHz, CD_3CN) data for the initial (*endo*) isomers: δ = 7.54–7.35 (10H, m, Ph), 6.11 (5H, s, Cp), 5.69 (5H, s, Cp), 6.23–5.93 (2H, m, PhCH–C*H*–CH), 5.28 (1H, d, *J* = 11.7 Hz, PhC*H*–CH–CH), 5.20 (1H, d, *J* = 13.4 Hz, PhC*H*–CH–CH), 3.95 (1H, dq, *J* = 12.9, 6.2 Hz, PhCH–CH–C*H*), 3.76 (1H, dq, *J* = 12.3, 6.2 Hz, PhCH–CH–C*H*), 2.47 (3H, d, *J* = 5.9 Hz, CHCH_3), 2.30 (3H, d, *J* = 6.3 Hz, CHCH_3); partial data for the *exo*-isomers: δ = 6.22 (5H, s, Cp), 6.02 (5H, s, Cp), 4.77 (1H, d, *J* = 13.8 Hz, PhC*H*–CH–CH), 4.51–4.44 (2H, m, PhCH–CH–C*H*), 4.40 (1H, d, *J* = 13.0 Hz, PhC*H*–CH–CH), 2.42 (3H, d, *J* = 6.4 Hz, CHCH_3). Signals for C2H and the second C4H doublet obscured by major isomer peaks at 6.23–5.93 ppm and 2.30 ppm respectively.

^{13}C NMR (100 MHz, CD_3CN, equilibrium mixture of four isomers): δ = 214.9 (C), 213.9 (C), 211.0 (C), 209.5 (C), 136.8 (C), 135.8 (C), 135.4 (C), 134.0 (C), 131.4 (2CH), 130.7 (2CH), 130.0 (2CH), 129.8 (2CH), 129.7 (2CH), 129.5 (2CH), 129.4 (2CH), 128.0 (2CH), 127.7 (2CH), 127.6 (2CH), 106.7 (CH), 106.5 (CH), 104.2 (CH), 103.3 (5CH), 102.5 (5CH), 102.4 (5CH), 101.8 (5CH), 101.0 (CH), 94.6 (CH), 93.4 (CH), 92.3 (CH), 88.0 (CH), 83.3 (CH), 80.6 (CH), 76.8 (CH), 74.6 (CH), 21.1 (CH_3), 19.6 (CH_3), 18.9 (CH_3), 18.2 (CH_3).

^{95}Mo NMR (13 MHz, MeCN): δ = −1293, −1339, −1383 ppm, in the approximate ratio 1 : 2.5 : 4, with approximate line widths of 210 Hz, 206 Hz, 290 Hz respectively.

HRMS (FAB mode, nitrobenzyl alcohol matrix): found $M^{+\bullet}$, 352.0235. $C_{16}H_{16}O_2N^{98}Mo$ requires M, 352.0238. Found $M^{+\bullet}$, 350.0246. $C_{16}H_{16}O_2N^{96}Mo$ requires M, 350.0235.

Benzoic acid 1,2-dimethyl-2-butenyl ester (16e)

To a solution of 1,2-dimethyl-2-butenol (1.46 g, 14.6 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added DMAP (0.1 g, 0.73 mmol), NEt_3 (3.1 mL, 21.9 mmol) and benzoyl chloride (1.9 mL, 16 mmol). The cooling bath was removed and the reaction mixture allowed to stir at ambient temperature for 12 h whereupon the excess benzoyl chloride was destroyed by the addition of 3-dimethylaminopropylamine (1 mL). The reaction mixture was washed with HCl (1 M, 2 × 45 mL) and $NaHCO_3$ (1 M, 2 × 45 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, Et_2O : hexanes = 1 : 4) to give the title compound (1.82 g, 8.9 mmol, 61%) as a colourless oil.

IR (film): ν = 1720 s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–8.08 (2H, m, *o*-ArH), 7.53–7.58 (1H, m, *p*-ArH), 7.41–7.47 (2H, m, *m*-ArH), 5.64 (1H, qq, *J* = 6.7, 0.3 Hz, C3H), 5.52 (1H, q, *J* = 6.5 Hz, C1H), 1.72 (3H, s, C2CH_3), 1.63 (3H, d, *J* = 6.5 Hz, C4H_3), 1.43 (3H, d, *J* = 6.5 Hz, C1CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2 (CO), 135.5 (C2), 133.1 (CH), 131.3 (C), 129.7 (2CH), 128.7 (2CH), 122.1 (C3H), 76.1 (C1H), 19.6 (C1*C*H_3), 13.5 (C2*C*H_3), 12.1 (C4H_3).

Found: C, 76.41; H, 7.88. $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%.

(4*S*,2*E*)-2-Methyl-4-(benzoyloxy)-pent-2-enoic acid ethyl ester (16h)

Benzoate **16h**, prepared from (4*S*,2*E*)-ethyl-4-hydroxy-2-methylpent-2-enoate[54,55] (0.18 g, 1.2 mmol) in 84% yield by the procedure described for **16e**, was isolated as a colourless oil after purification by column chromatography (SiO_2, hexanes : Et_2O = 10 : 1).

$[a]_D$ = 74.9 (*c* 0.91, $CHCl_3$).

IR (film): ν = 1717 s, 1659 m cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (2H, dd, *J* = 8.5, 1.3 Hz, *o*-ArH), 7.48 (1H, td, *J* = 7.2, 1.2 Hz, *p*-ArH), 7.35 (2H, t, *J* = 7.2 Hz, *m*-ArH), 6.66 (1H, dd, *J* = 8.6 Hz, 1.4 Hz, C3H), 5.82 (1H, dq, *J* = 8.2, 6.7 Hz, C4H), 4.14 (2H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 1.91 (3H, d, *J* = 1.1 Hz, C2CH_3), 1.4 (3H, d, *J* = 6.4 Hz, C5H_3), 1.23 (3H, t, *J* = 7.2 Hz, OCH$_2$CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1 (C), 166.2 (C), 139.9 (CH), 133.5 (CH), 130.6 (C), 130.1 (CH), 130.0 (2CH), 128.8 (2CH), 68.7 (CH), 61.3 (CH_2), 20.2 (CH_3), 14.6 (CH_3), 13.3 (CH_3).

LRMS (FAB mode): *m*/*z* = 263 [(M^+ + H), 12%], 141 (100), 105 (51), 77 (7).

HRMS (ES mode): Found (M^+ + H), 263.1280. $C_{15}H_{18}O_4$ + H) requires M, 263.1283.

Dicarbonyl(η^5-cyclopentadienyl)-(η^3-propenyl)-molybdenum (17a)

Complex **17a**, prepared from benzoate **16a**[56,57] in 86% yield by procedure A (10.8 mmol scale) and 86% yield by procedure B (5.5 mmol scale), was obtained as yellow needles: mp 136–139 °C (Et_2O–pentane); lit.[58] mp 135–138 °C (Et_2O–heptane). ^{1}H NMR spectroscopy indicated that **17a** was a mixture of *exo* and *endo* isomers (3.3 : 1) in good agreement with literature data.[21,58] ^{95}Mo NMR (13 MHz, THF): δ_{exo} = −1856, δ_{endo} = −1648.[21]

Dicarbonyl(η^5-cyclopentadienyl)-(η^3-2-methylallyl)-molybdenum (17b)

Complex **17b**, prepared from benzoate **16b**[59] in 82% yield by procedure A (3.3 mmol scale) and 85% yield by procedure B (4.6 mmol scale), was obtained as a yellow solid: mp 76–78 °C (Et_2O–pentane); lit.[60] mp 79–81 °C. The IR, ^{1}H NMR and ^{95}Mo NMR spectroscopic data agreed with those reported by Faller and co-workers.[21,60]

^{13}C NMR (75 MHz, $CDCl_3$): δ = 105.4 (C), 90.5 (5CH, Cp), 38.6 (2CH_2), 23.6 (CH_3).

Dicarbonyl-(η^5-cyclopentadienyl)-(2,3,4-η-2-methyl-3-butenyl)-molybdenum (17c)

Complex **17c**, prepared from benzoate **16c**[61] in 58% yield by procedure A (2.1 mmol scale) and 65% yield by procedure B (3.2 mmol scale), was obtained as a yellow solid: mp 61–63 °C (Et_2O–pentane); lit.[60] mp 65–69 °C (Et_2O–hexane). The IR, ^{1}H NMR and ^{95}Mo NMR spectroscopic data agreed with those reported by Faller and co-workers.[21,60]

^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.2 (5CH, Cp), 81.5 (C2), 68.6 (C3H), 31.1 (C4H_2), 30.8 (CH_3), 14.4 (CH_3).

syn,syn-Dicarbonyl-(η^5-cyclopentadienyl)-[2,3,4-η-(2*R*,3*S*,4*S*)-1-ethoxy-1-oxopent-2-enyl]molybdenum (17d)

Complex **17d**, prepared from benzoate **16d** in 70% yield by procedure A (3.2 mmol scale) and 82% yield by procedure B (0.3 mmol scale), was obtained as an air-sensitive viscous yellow-orange oil. The ^{1}H and ^{13}C NMR spectroscopic data agreed with those reported.[62]

Dicarbonyl-(η^5-cyclopentadienyl)-(2,3,4-η-3-methyl-3-pentenyl)-molybdenum (17e)

The title complex **17e**, prepared from benzoate **16e** in 80% yield by procedure A (1.7 mmol scale) and 85% yield by procedure B (3.7 mmol scale), was obtained as a yellow solid: mp 136–137 °C (Et_2O–pentane).

IR (film): ν = 1930 s, 1850 s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (5H, s, CpH), 2.21 (2H, q, *J* = 6.0 Hz, C2H and C4H), 2.02 (6H, d, *J* = 6.0 Hz, C1H_3 and C5H_3), 1.82 (3H, s, C3H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 105.7 (C3), 91.0 (5CH, Cp), 51.8 (C2H and C4H), 16.8 (2CH_3), 13.3 (CH_3).

^{95}Mo NMR (13 MHz, $CDCl_3$): δ = −1487.

HRMS (EI$^+$ mode): found $M^{+\bullet}$, 300.2010. $C_{12}H_{14}O_2Mo$ requires M, 300.2088.

Dicarbonyl-(η^5-cyclopentadienyl)-(2,3,4-η-2-methyl-3-pentenyl)-molybdenum (17f)

Complex **17f**, prepared from benzoate **16f**[63] in 50% yield by procedure A (1.4 mmol scale) and 58% yield by procedure B (1.7 mmol scale), was obtained as a dark yellow oil.

IR (film): ν = 1931 s, 1848 s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (5H, s, CpH), 4.05 (1H, d, J = 9.8 Hz, C3H), 1.93 (1H, m, C4H), 1.78 (3H, d, J = 6.3 Hz, $C5H_3$), 1.74 (3H, s, $C1H_3$), 0.99 (3H, s, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 93.4 (5CH, Cp), 72.5 (C3H), 72.3 (C2), 55.7 (C4H), 31.2 (C2-*Me*), 23.1 ($C1H_3$), 21.6 ($C5H_3$). The sample deteriorated before the weak and broad carbonyl signals could be recorded.

^{95}Mo NMR (13 MHz, $CDCl_3$): δ = −1654.

HRMS (EI$^+$ mode): found M$^{+\bullet}$, 300.2010. $C_{12}H_{14}O_2Mo$ requires M, 300.2088.

Dicarbonyl-(η^5-(cyclopentadienyl)-(1,2,3-η-2,4-dimethyl-2-pentenyl)-molybdenum (17g)

Complex **17g**, prepared from benzoate **16g**[64] in 95% yield (2.15 mmol scale) by procedure B, was obtained as a yellow oil.

IR (film): ν = 1941 s, 1866 s cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.58 (5H, s, CpH), 2.55 (1H, s, $C1H_{trans}$), 2.40–2.25 (1H, m, C4H), 2.11 (1H, d, J = 9.7 Hz, C3H), 1.67 (3H, s, C2Me), 1.27 (1H, s, $C1H_{cis}$), 1.06–1.01 (6H, m, $C4Me_2$).

^{13}C NMR (75 MHz, C_6D_6): δ = 242.8 (CO), 242.3 (CO), 103.2 (C2), 91.1 (5CH, Cp), 71.4 (C3H), 36.6 ($C1H_2$), 30.2 (C4H), 25.9 (CH_3), 25.2 (CH_3), 19.3 (CH_3).

Satisfactory HRMS (electrospray) or microanalytical data could not be obtained for **17g**.

Dicarbonyl-(η^5-cyclopentadienyl)-(2,3,4-η-2-methyl-1-ethoxy-1-oxopent-2-enyl)molybdenum (17h)

Complex **17g**, prepared from benzoate **16g** in 88% yield (0.76 mmol scale) by procedure B, was obtained as a yellow-orange oil:

$[\alpha]_D$ = +41.3 (c 0.21, $CHCl_3$).

IR (film): ν = 1949 s, 1868 s, 1693 s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.97 (1H, d, J = 10.7 Hz, C3H), 4.73 (5H, s, CpH), 4.07 (1H, dq, J = 10.75, 7.2 Hz, $CH_AH_BCH_3$), 3.96 (1H, dq, J = 10.75, 7.2 Hz, $CH_AH_BCH_3$), 2.34 (1H, dq, J = 10.7, 6.3 Hz, C4H), 1.51 (3H, d, J = 6.3 Hz, $C5H_3$), 1.18 (3H, s, $C2CH_3$), 1.02 (3H, t, J = 7.1 Hz, OCH_2CH_3).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 238.1 (CO), 237.7 (CO), 173.5 (CO), 93.2 (5CH, Cp), 73.4 (C4H), 62.9 (C2), 59.6 (C3H), 58.9 (CH_2), 19.5 ($C2CH_3$), 15.9 ($C5H_3$), 13.8 (CH_3).

LRMS (EI mode): m/z = 360.2 (M$^{+\bullet}$, 8%), 332.2 (M − CO, 20), 304.2 (M − 2CO, 37), 228.1 (100)

(3*S*)-3,4-Dihydroxybutyric acid methyl ester (18)

Diol **18**, prepared in 89% yield on an 89 mmol scale by the method of Moriwake and co-workers, gave $[\alpha]_D$ = −23.2 (c 1.22, $CHCl_3$); lit. $[\alpha]_D$ = −24.6 (c 1.00, $CHCl_3$).[30,65] ^{1}H and ^{13}C NMR spectroscopic data were in accordance with literature data.[65]

(3*S*)-3-Hydroxy-4-(triisopropylsilyloxy)butyric acid methyl ester (19)

To a solution of diol **18** (12.0 g, 89.3 mmol) and imidazole (12.2 g, 178.6 mmol) in *N*,*N*-dimethylformamide (100 mL) at 0 °C under N_2 was added triisopropylsilyl chloride (20.1 mL, 93.8 mmol). The solution was stirred at rt for 30 h and then poured into hexanes (250 mL) and H_2O (75 mL). The phases were separated and the organic phase washed with H_2O (2 × 50 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, ethyl acetate : hexanes = 1 : 9) to give the title compound (18.5 g, 63.6 mmol, 71%) as a colourless oil.

$[\alpha]_D$ = −7.2 (c 1.06, $CHCl_3$).

IR (film): ν = 3481 br m, 2944 s, 2867 s, 1736 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (1H, ddq, J = 7.6, 5.8, 4.8 Hz, C3H), 3.72 (1H, dd, J = 9.8, 4.9 Hz, $C4H_AH_B$), 3.71 (3H, s, CO_2Me), 2.91 (1H, d, J = 4.8 Hz, OH), 3.66 (1H, dd, J = 9.8, 5.8 Hz, $C4H_AH_B$), 2.58 (1H, dd, J = 16.0, 4.8 Hz, $C2H_AH_B$), 2.52 (1H, dd, J = 16.0, 7.6 Hz, $C2H_AH_B$), 1.06 (18H, d, J = 5.6 Hz, $SiCHMe_2$), 1.15–1.04 (3H, m, $SiCHMe_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7 (C1), 68.8 (C3H), 66.6 ($C4H_2$), 51.9 (CO_2Me), 38.0 ($C2H_2$), 18.1 ($6CH_3$, $SiCHMe_2$), 12.0 (3CH, $SiCHMe_2$).

LRMS (CI mode, isobutane): m/z = 291.2 [(M + H)$^+$, 100%], 247.1 (15).

Found: C, 57.81; H, 10.37. $C_{14}H_{30}O_4Si$ requires: C, 57.89; H, 10.41%.

(3*S*)-3-Hydroxy-4-(triisopropylsilyloxy)butyric acid (20)

To a solution of ester **19** (38.6 g, 133 mmol) in MeOH (600 mL) was added 10% aqueous potassium carbonate solution (270 mL) and the mixture refluxed for 1.5 h. After cooling to rt, the mixture was acidified to pH 2 with 2 M HCl. After extraction with Et_2O (2 × 250 mL) and washing with brine (200 mL), the organic phase was dried, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, ethyl acetate : hexanes = 2 : 8 ⟶ 1 : 1) to give the title compound (27.1 g, 98 mmol, 74%) as a colourless oil.

$[\alpha]_D$ = −7.2 (c 0.83, $CHCl_3$).

IR (film): ν = 3460 br, 1713 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50 (1H, br s, OH), 4.17–4.07 (1H, m, C3H), 3.73 (1H, dd, J = 9.8, 4.9 Hz, $C4H_AH_B$), 3.68 (1H, dd, J = 9.8, 5.7 Hz, $C4H_AH_B$), 2.63 (1H, dd, J = 16.2, 4.6 Hz, $C2H_AH_B$), 2.56 (1H, dd, J = 16.2, 7.9 Hz, $C2H_AH_B$), 1.05 (18H, d, J = 5.7 Hz, $SiCHMe_2$), 1.15–1.05 (3H, m, $SiCHMe_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6 (C1), 68.7 (C3H), 66.4 ($C4H_2$), 38.1 ($C2H_2$), 18.0 ($6CH_3$, $SiCHMe_2$), 12.0 (3CH, $SiCHMe_2$).

LRMS (CI mode, isobutane): m/z = 277 [(M + H)$^+$, 100%], 259 (14), 233 (23), 173 (19).

Found: C, 56.22; H, 10.03. $C_{13}H_{28}O_4Si$ requires: C, 56.48; H, 10.21%.

(6*S*)-6-[(Triisopropylsilyloxy)methyl]-2,2-dimethyl-1,3-dioxan-4-one (21)

To a solution of acid **20** (7.45 g, 27.0 mmol) and 2-methoxypropene (3.10 mL, 32.3 mmol) in CH_2Cl_2 (250 mL) at rt under N_2 was added pyridinium *p*-toluenesulfonate (339 mg, 1.35 mmol). The clear solution was stirred at rt for 3 h before concentration *in vacuo*. The residue was purified by column chromatography (SiO_2, ether : hexanes = 4 : 6) to give the title compound (7.15 g, 22.6 mmol, 84%) as a clear oil: $[\alpha]_D$ = −38.4 (c 1.10, $CHCl_3$). Further elution yielded acid **20** (730 mg, 2.64 mmol, 10%).

IR (film): ν = 2945 s, 2864 s, 1746 s cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (1H, tt, J = 7.1, 4.8 Hz, C6H), 3.81 (1H, dd, J = 10.4, 4.8 Hz, CH_AH_BOTIPS), 3.74 (1H, dd, J = 10.4, 4.8 Hz, CH_AH_BOTIPS), 2.59 (2H, apparent d, J = 7.1 Hz, $C5H_2$), 1.59 and 1.57 (3H each, s, CMe_2), 1.05 (18H, d, J = 5.2 Hz, $SiCHMe_2$), 1.14–1.03 (3H, m, $SiCHMe_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (C4), 106.1 (C2), 68.7 (C6H), 65.6 (CH_2OTIPS), 31.8 ($C5H_2$), 29.1 (CH_3), 25.0 (CH_3), 18.0 ($6CH_3$, $SiCHMe_2$), 12.0 (3CH, $SiCHMe_2$).

LRMS (CI mode, isobutane): m/z = 317.3 [(M + H)$^+$, 100%], 259.2 (16).

Found: C, 60.71; H, 10.07. $C_{16}H_{32}O_4Si$ requires: C, 60.72; H, 10.19%.

(4*S*,6*S*)-4-Acetoxy-2,2-dimethyl-6-(triisopropylsilyloxymethyl)-1,3-dioxane (22)

To a solution of dioxanone **21** (19.1 g, 60.4 mmol) in CH_2Cl_2 (180 mL) at −78 °C under N_2 was added neat DIBAL-H (11.3 mL, 63.4 mmol) dropwise. After stirring −78 °C for 1 h, pyridine (14.6 mL, 181 mmol), 4-dimethylaminopyridine (8.11 g, 66.4 mmol) in CH_2Cl_2 (50 mL) and acetic anhydride (22.8 mL, 241 mmol) were added and the clear solution stirred at −78 °C for a further 1.5 h before the addition of aqueous NH_4Cl (100 mL) and aqueous sodium potassium tartrate (100 mL). The solution was allowed to warm to rt with vigorous stirring over 1 h. The phases were separated, and the aqueous phase extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with ice-cold 1 M $NaHSO_4$ (3 × 100 mL), aqueous $NaHCO_3$ (2 × 100 mL) and brine (100 mL), dried, filtered and concentrated *in vacuo* to yield the crude product as a colourless oil. The residue was purified by column chromatography (SiO_2, ether : hexanes = 1 : 9) to give the title compound (18.3 g, 50.7 mmol, 84%) as a clear oil. ^{13}C NMR spectroscopy indicated that acetate **22** was a single diastereoisomer, identified as the *syn*-1,3-diol acetonide isomer by reference to the shifts of the acetonide methyl signals, and to the coupling constants of C4H.[66,67]

$[a]_D = -5.1$ (*c* 1.26, $CHCl_3$).

IR (film): $\nu = 1757$ s cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.18$ (1H, dd $J = 10.0$, 3.0 Hz, C4H), 4.01 (1H, dddd, $J = 11.7$, 6.3, 4.8, 2.5 Hz, C6H), 3.81 (1H, dd, $J = 9.8$, 5.0 Hz, CH_AH$_B$OTIPS), 3.61 (1H, dd, $J = 9.6$, 6.4 Hz, CH$_A$$H_B$OTIPS), 2.11 (3H, s, COMe), 1.96 (1H, dt, $J = 12.4$, 2.8 Hz, C5H_AH$_B$), 1.56–1.43 (1H, m, C5H$_A$$H_B$), 1.52 and 1.44 (3H each, s, CMe$_2$), 1.13–1.01 (3H, m, SiC*H*Me$_2$), 1.05 (18H, d, $J = 4.8$ Hz, SiCH*Me*$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 169.6$ (*C*OMe), 100.7 (C2), 89.6 (C4H), 69.5 (CH$_2$OTIPS), 66.8 (C6H), 33.1 (C5H$_2$), 29.8 (3, CMe$_2$), 21.4 (3, CO*Me*), 20.9 (3, CMe$_2$), 18.1 (6CH$_3$, SiCH*Me*$_2$), 12.1 (3CH, Si*C*HMe$_2$).

LRMS (CI mode, NH_3): *m*/*z* = 378.3 [(M + NH_4)$^+$, 67%], 318.3 (100), 301.2 (92).

Found: C, 59.95; H, 9.88. $C_{18}H_{36}O_5Si$ requires: C, 59.96; H, 10.06%.

(4*R*,6*S*)-2,2-Dimethyl-4-phenylsulfanyl-6-(triisopropylsilyloxymethyl)-1,3-dioxane (23b) and (4*S*,6*S*)-2,2-dimethyl-4-phenylsulfanyl-6-(triisopropylsilyloxymethyl)-1,3-dioxane (23a)

To a solution of acetate **22** (9.90 g, 27.5 mmol) in CH_2Cl_2 (110 mL) at −70 °C under N_2 was added phenylthiotrimethylsilane (5.5 mL, 28.8 mmol) and $ZnCl_2$ (0.82 mL of a 1.0 M solution in ether, 0.82 mmol) dropwise. The light brown solution was stirred at −70 °C for 17 h before addition of 1 M NaOH (50 mL) and warming to rt. The phases were separated, and the aqueous phase extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with 1 M NaOH (50 mL) and brine (50 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, ether : hexanes = 2 : 98 ⟶ 4 : 96) to give a mixture of the title compounds (9.74 g, 23.7 mmol, 86%) as a clear oil. ^1H and ^{13}C NMR spectroscopy indicated a ratio of **23b** : **23a** of approximately 7 : 3.[66,67] For analytical purposes, a sample of isomers **23b** and **23a** was separated by careful column chromatography.

Alternative procedure: $ZnCl_2$ (1.9 mL of a 1.0 M solution in ether, 1.9 mmol) was added dropwise to a solution of acetate **22** (17.4 g, 48.4 mmol) and thiophenol (5.2 mL, 50.8 mmol) in CH_2Cl_2 (240 mL) at −30 °C under N_2. After stirring for 15 min at −30 °C NaOH (1 M, 100 mL) was added and the mixture allowed to warm to rt. Workup and purification as above yielded a mixture of the title compounds (17.3 g, 42.1 mmol) as a colourless oil. ^1H and ^{13}C NMR spectroscopy indicated a ratio of **23b** : **23a** of approximately 1 : 9.[66,67]

Spectroscopic data for thioether **23b**: (R_f = 0.85, Et_2O : PhMe = 2 : 98)

$[a]_D = +85.0$ (*c* 0.22, $CHCl_3$).

IR (film): $\nu = 2942$ s, 2859 s, 1461 m, 1382 m, 1137 m, 1114 m, 873 m, 688 m cm^{-1}.

^1H NMR (360 MHz, $CDCl_3$): $\delta = 7.52$–7.47 (2H, m, Ph), 7.33–7.22 (3H, m, Ph), 5.50 (1H, t, $J = 5.8$ Hz, C4H), 4.17 (1H, ddt, $J = 10.2$, 4.7, 5.5 Hz, C6H), 3.80 (1H, dd, $J = 10.2$, 5.5 Hz, CH_AH$_B$OTIPS), 3.64 (1H, dd, $J = 10.2$, 5.7 Hz, CH$_A$$H_B$OTIPS), 2.08 (1H, ddd, $J = 13.5$, 10.1, 6.0 Hz, C5H_AH$_B$), 1.99 (1H, ddd, $J = 13.5$, 5.7, 4.7 Hz, C5H$_A$$H_B$), 1.61 and 1.38 (3H each, s, CMe$_2$), 1.14–1.04 (3H, m, SiC*H*Me$_2$), 1.07 (18H, d, $J = 4.5$ Hz, SiCH*Me*$_2$).

^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 135.6$ (C, Ph), 131.0 (2CH, Ph), 129.0 (2CH, Ph), 127.1 (CH, Ph), 101.1 (C2), 78.6 (C4H or C6H), 67.8 (C4H or C6H), 66.5 (CH$_2$OTIPS), 34.0 (C5H$_2$), 28.1 (CMe$_2$), 24.6 (CMe$_2$), 18.1 (6CH$_3$, SiCH*Me*$_2$), 12.1 (3CH, Si*C*HMe$_2$).

LRMS (FAB$^+$ mode): *m*/*z* = 433.4 [(M + Na)$^+$, 22%], 335.4 (14), 301.4 (47), 243.3 (82), 173.2 (100), 157.2 (73), 115.3 (43).

HRMS (FAB$^+$ mode, PEG): found [M + Na]$^+$, 433.2210. $C_{22}H_{38}O_3SSiNa$ requires 433.2209.

Compound **23a** (R_f = 0.78, Et_2O : PhMe = 2:98) has been described previously, with only the following ^{13}C NMR data reported: $\delta = 30.0$ (Me), 19.9 (Me) ppm.[66]

$[a]_D = -54.2$ (*c* 0.36, $CHCl_3$).

IR (film): $\nu = 2938$ s, 2859 s, 1138 m, 1117 m, 955 m, 881 m, 689 m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$–7.48 (2H, m, Ph), 7.32–7.23 (3H, m, Ph), 5.31 (1H, dd, $J = 12.0$, 2.5 Hz, C4H), 4.02 (1H, dddd, $J = 11.3$, 6.4, 4.9, 2.4 Hz, C6H), 3.76 (1H, dd, $J = 9.8$, 4.9 Hz, CH_AH$_B$OTIPS), 3.54 (1H, dd, $J = 9.8$, 6.4 Hz, CH$_A$$H_B$OTIPS), 1.98 (1H, dt, $J = 12.9$, 12.5 Hz, C5H_AH$_B$), 1.61–1.52 (1H, m, C5H$_A$$H_B$), 1.55 and 1.52 (3H each, s, CMe$_2$), 1.12–1.04 (3H, m, SiC*H*Me$_2$), 1.04 (18H, d, $J = 4.5$ Hz, SiCH*Me*$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.3$ (C, Ph), 131.4 (2CH, 1, Ph), 129.0 (2CH, 1, Ph), 127.3 (CH, Ph), 100.3 (C2), 77.7 (C4H or C6H), 70.5 (C4H or C6H), 66.9 (CH$_2$OTIPS), 34.0 (C5H$_2$), 30.1 (CMe$_2$), 20.0 (CMe$_2$), 18.1 (6CH$_3$, SiCH*Me*$_2$), 12.1 (3CH, Si*C*HMe$_2$).

LRMS (CI mode, NH_3): *m*/*z* = 428.2 [(M + NH_4)$^+$, 34%], 370.2 (39), 318.2 (69), 301.2 (100), 283.2 (81), 260.2 (31), 151.1 (39).

HRMS (CI$^+$ mode, isobutane): found [M + H]$^+$, 411.2389. $C_{22}H_{39}O_3SSi$ requires 411.2389.

Found (mixture of isomers): C, 64.36; H, 9.41. $C_{22}H_{38}O_3SSi$ requires: C, 64.34; H, 9.33%.

4,4-Bis-phenylsulfanyl-1-(triisopropylsilyloxy)butan-2-ol (24)

The title compound was obtained in an initial attempt to synthesise thioethers **23b** and **23a** by the following procedure: a solution of acetate **22** (57 mg, 0.16 mmol) and thiophenol (0.03 mL, 0.32 mmol) in CH_2Cl_2 (5 mL) was cooled to −78 °C under N_2 and BF_3·OEt_2 (0.02 mL, 0.19 mmol) was added dropwise. After stirring at −78 °C for 1 h, NaOH (1 M, 2 mL) was added, the mixture was warmed to rt and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases washed with NaOH (1 M, 2 × 10 mL), brine (10 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, Et_2O : hexanes = 1 : 9) to give the title compound (55 mg, 0.12 mmol, 75%) as a colourless oil.

$[a]_D = -8.1$ (*c* 0.42, $CHCl_3$).

IR (film): $\nu = 2943$ s, 2866 s, 1582 m, 1477 m, 1464 m, 1117 m, 882 m, 791 m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53$–7.50 (2H, m, Ph), 7.46–7.43 (2H, m, Ph), 7.33–7.23 (6H, m, Ph), 4.74 (1H, dd, $J = 10.5$, 4.1 Hz, H4), 4.16–4.11 (1H, m, H2), 3.70 (1H, dd,

J = 9.8, 3.7 Hz, C1H_AH_B), 3.50 (1H, dd, J = 9.8, 6.4 Hz, C1H_AH_B), 2.50 (1H, d, J = 4.8 Hz, OH), 2.09 (1H, ddd, J = 14.2, 9.9, 4.1 Hz, C3H_AH_B), 1.79 (1H, ddd, J = 14.2, 10.5, 3.1 Hz, C3H_AH_B), 1.07–0.99 (3H, m, SiCHMe$_2$), 1.03 (18H, d, J = 4.8 Hz, SiCHMe_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3 (C, Ph), 134.0 (C, Ph), 133.0 (2CH, Ph), 132.7 (2CH, Ph), 129.1 (4CH, Ph), 127.9 (CH, Ph), 127.8 (CH, Ph), 69.5 (C2H), 67.3 (C1H$_2$), 54.8 (C4H), 39.6 (C3H$_2$), 18.1 (6CH$_3$, SiCHMe_2), 12.0 (3CH, SiCHMe$_2$).

LRMS (CI mode, NH_3): m/z = 480.0 [(M + NH_4)$^+$, 3%], 370.1 (23), 335.1 (100), 174.1 (9).

(4*R*,6*S*)-2,2-Dimethyl-4-tributylstannyl-6-triisopropylsilyloxymethyl-1,3-dioxane (26)

Lithium 4,4′-di-*tert*-butylbiphenylide (LDBB) was prepared by a modification to the method of Freeman and Hutchinson:[36] a mixture of Li (3.24 g, 467 mmol), 4,4′-di-*tert*-butylbiphenyl (12.5 g, 46.7 mmol) and THF (160 mL) was stirred at 0 °C for 48 h under a static Ar atmosphere. The LDBB solution was added dropwise to a solution of sulfides **23a** and **23b** (4.42 g, 10.8 mmol) in THF (120 mL) at −78 °C and the resulting dark blue solution stirred at −78 °C for 10 min before the addition of Bu_3SnCl (3.3 mL, 11.3 mmol) dropwise. After stirring for 10 min, H_2O (100 mL) and Et_2O (100 mL) were added and the cold bath removed. The phases were separated and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phases washed with NaOH (0.5 M, 3 × 50 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes ⟶ ether : hexanes = 1 : 99) to give the title compound (4.96 g, 8.38 mmol, 81%) as a colourless oil. ^{13}C NMR spectroscopy indicated the presence of a single isomer, identified as the expected *trans*-disubstituted 1,3-dioxane by reference to the chemical shifts of the acetonide methyl signals.[66,67] Compound **26** has been previously described, with only the following ^{13}C NMR spectroscopic data reported: δ = 24.7 (Me), 24.5 (Me) ppm.[66]

$[\alpha]_D$ = −17.2 (*c* 1.02, $CHCl_3$).

IR (film): ν = 2949 s, 2928 s, 2870 s, 1465 m, 1382 m, 1225 m, 1143 m, 1101 m, 1002 m, 878 m, 692 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (1H, dd, J = 11.3, 6.3 Hz, C4H), 3.90 (1H, dq, J = 8.8, 5.9 Hz, C6H), 3.75 (1H, dd, J = 10.0, 5.8 Hz, CH_AH_BOTIPS), 3.62 (1H, dd, J = 10.0, 5.8 Hz, CH$_A$$H_B$OTIPS), 2.11 (1H, dt, J = 5.9, 12.1 Hz, C5H_AH_B), 1.69 (1H, ddd, J = 12.7, 8.9, 6.2 Hz, C5H$_A$$H_B$), 1.58–1.46 (6H, m, SnCH$_2$CH$_2$CH_2Me), 1.36–1.26 (6H, m, SnCH$_2$CH_2CH$_2$Me), 1.32 and 1.29 (3H each, s, CMe$_2$), 1.13–1.05 (3H, m, SiCHMe$_2$), 1.07 (18H, d, J = 4.4 Hz, SiCHMe_2), 0.93–0.84 (15H, m, SnCH_2CH$_2$CH$_2$$Me$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.4 (C2), 68.1 (C6H), 66.7 (CH$_2$OTIPS), 59.8 (C4H), 34.1 (C5H$_2$), 29.3 (3CH$_2$, $^3J_{C-Sn}$ = 10.4, SnCH$_2$CH$_2$$CH_2$Me), 27.8 (3CH$_2$, $^2J_{C-Sn}$ = 25.2, SnCH$_2$$CH_2CH_2$Me), 24.9 (CMe$_2$), 24.7 (CMe$_2$), 18.1 (6CH$_3$, SiCH$Me_2$), 13.9 (3CH$_3$, SnCH$_2CH_2$$CH_2$$Me$), 12.2 (3CH, Si$CHMe_2$), 8.8 (3CH$_2$, $^1J_{C-Sn}$ = 161.0, 150.9, SnCH$_2$CH$_2$-CH$_2$Me).

LRMS (EI$^+$ mode): m/z = 591.2 [M$^{+\bullet}$, 0.1%], 535.2 (19), 477.2 (40), 291.1 (100), 243.2 (75), 157.1 (74), 115.0 (38).

Found: C, 56.90; H, 9.98. $C_{28}H_{60}O_3SiSn$ requires: C, 56.85; H, 10.22%.

(4*RS*,6*S*)-4-Allyl-2,2-dimethyl-6-triisopropylsilyloxymethyl-1,3-dioxane (32a,b)

BuLi (0.15 mL of a 2.29 M solution in hexanes, 0.35 mmol) was added to a solution of stannane **26** (190 mg, 0.32 mmol) in THF (20 mL) at −78 °C under N_2. The solution was stirred at −78 °C for 5 min and then cooled to −90 °C. A solution of CuBr·SMe$_2$ (79 mg, 0.39 mmol) in diisopropyl sulfide (0.3 mL) and THF (0.3 mL) was added *via* cannula maintaining the reaction temperature below −80 °C. The orange solution was stirred at −78 °C for 30 min before cooling to −90 °C and dropwise addition of a solution of complex **31** (which had been freshly prepared from neutral complex **17a** (91 mg, 0.35 mmol) and $NOBF_4$ (45 mg, 0.39 mmol) in MeCN (4 mL), 0 °C, 20 min). The brown solution was allowed to warm to −78 °C over 30 min before addition of aqueous NH_3 (5 mL), aqueous NH_4Cl (10 mL) and Et_2O (25 mL) and removal of the cooling bath. After warming to room temperature, the mixture was filtered through Celite, rinsing with Et_2O (3 × 25 mL). The phases were separated, the aqueous phase was extracted with Et_2O (3 × 25 mL) and the combined organic phases were washed with brine (50 mL), dried, filtered and concentrated *in vacuo*. The crude products were dissolved in analytical grade chloroform (50 mL), and stirred at rt with a stream of O_2 bubbling through the solution for 17 h. The solvent was removed *in vacuo* and the residue purified by column chromatography (SiO_2, Et_2O : hexanes = 2 : 98) to give the title compound (53 mg, 0.15 mmol, 48%) as a colourless oil. ^{1}H NMR spectroscopy indicated that olefin **32a**,**b** was present as a mixture of epimers (inseparable by column chromatography) at the C4 position. The major isomer was determined to be the (6*S*)-epimer by the large (^3J 11.6) coupling of H6 to H5 (C_6D_6). ^{13}C NMR spectroscopic data confirmed the assignment, acetonide methyl carbon shifts at 30.2 and 20.0 ppm being indicative of the stereochemistry.[66,67] The minor (6*R*)-isomer exhibited acetonide methyl carbon shifts at 25.2 ppm (2C, 3). The ratio of equatorial : axial isomers was estimated from ^{1}H NMR spectroscopy ($CDCl_3$) comparing the integration of signals at: 3.79–3.72 (2 overlapping dd, 1 each from (6*R*)- and (6*S*)-isomers) and 3.63 (1H, dd, (6*R*)-isomer).

$[\alpha]_D$ = −12.8 (*c* 1.06, $CHCl_3$).

IR (film): ν = 2943 s, 2866 s, 1642 w, 1464 m, 1379 m, 1261 m, 1200 m, 1172 m, 1114 s, 994 m, 883 m cm^{-1}.

(6*S*)-isomer only ^{1}H NMR (400 MHz, C_6D_6): δ = 5.90–5.80 (1H, m, CH=CH$_2$), 5.06–5.01 (2H, m, CH=CH_2), 3.88 (1H, ddt, J = 11.6, 2.5, 5.5 Hz, C4H), 3.80 (1H, dd, J = 9.7, 5.2 Hz, CH$_2$OTIPS), 3.69 (1H, ddt, J = 11.6, 2.4, 6.0 Hz, C6H), 3.57 (1H, dd, J = 9.7, 2.2 Hz, CH$_2$OTIPS), 2.34–2.27 (1H, m, CH_AH_BCH=CH$_2$), 2.14–2.07 (1H, m, CH$_A$$H_B$CH=CH$_2$), 1.50 (3H, s, Me_ACMe$_B$), 1.45 (1H, dt, J = 12.8, 2.6 Hz, C5H_AH_B), 1.30 (3H, s, Me$_A$CMe_B), 1.26–1.17 (1H, m, C5H$_A$$H_B$), 1.11 (18H, d, J = 2.8 Hz, SiCHMe_2), 1.15–1.08 (3H, m, SiCHMe$_2$).

(6*S*)-isomer (major) ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4 (CH=CH$_2$), 117.2 (CH=CH$_2$), 98.6 (CMe$_2$), 70.2 (C4H), 68.7 (C6H), 67.4 (CH$_2$OTIPS), 41.1 (CH$_2$CH=CH$_2$), 33.9 (C5H$_2$), 30.2 (Me_ACMe$_B$), 20.0 (Me$_A$CMe_B), 18.1 (6CH$_3$, SiCHMe_2), 12.2 (3CH, SiCHMe$_2$).

(6*R*)-isomer (minor) ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.7 (CH=CH$_2$), 117.0 (CH=CH$_2$), 100.3 (CMe$_2$), 68.1 (C6H or C4H), 66.7 (CH$_2$OTIPS), 66.5 (C6H or C4H), 40.4 (CH$_2$CH=CH$_2$), 34.4 (C5H$_2$), 25.2 (2C, CMe_2), 18.1 (6CH$_3$, SiCHMe_2), 12.2 (3CH, SiCHMe$_2$).

LRMS (CI$^+$ mode): m/z = 343.2 [(M + H)$^+$, 5], 285.2 (100), 267.2 (26), 241.2 (20), 217.2 (7), 173.1 (13), 111.1 (32).

Found: C, 66.75; H, 11.09. $C_{19}H_{38}O_3Si$ requires: C, 66.61; H, 11.18%.

(2*R*,4*R*,6*S*)-2-Phenyl-4-tributylstannanyl-6-triisopropylsilyloxymethyl-1,3-dioxane (33a) and (2*S*,4*R*,6*S*)-2-phenyl-4-tributylstannanyl-6-triisopropylsilyloxymethyl-1,3-dioxane (33b)

To a solution of stannane **26** (4.32 g, 7.30 mmol), methanol (0.9 mL, 21.9 mmol) and benzaldehyde dimethylacetal (5.5 mL, 36.5 mmol) in CH_2Cl_2 (120 mL) at rt under N_2 was added *p*-TsOH (69 mg, 0.37 mmol). The solution was stirred at rt for 7 h before concentration *in vacuo*. The residue was purified by column chromatography (SiO_2, Et_2O : hexanes = 2 : 98) to give the title compounds (4.17 g, 6.52 mmol, 89%) as a colourless oil. ^{1}H NMR spectroscopy indicated a mixture of **33a** and **33b**

in the approximate ratio 7 : 1, based on the integration of C2H singlets at 5.81 and 5.73 ppm respectively. Separation of isomers was possible by careful column chromatography (SiO_2, PhMe : hexanes = 1 : 3). The major isomer was identified as the (2*R*)-isomer **33a** by NOE studies.

Data for the (2*R*)-isomer (**33a**): (R_f = 0.13, PhMe : hexanes = 1 : 3)

$[a]_D$ = +20.6 (*c* 1.61, $CHCl_3$).

IR (film): ν = 2922 s, 2860 s, 1460 m, 1107 m, 755 m, 687 m cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.93–7.90 (2H, m, Ph), 7.36–7.22 (3H, m, Ph), 5.81 (1H, s, C2H), 5.15 (1H, apparent d, *J* = 6.4 Hz, C4H), 4.26 (1H, dddd, *J* = 10.7, 6.9, 5.2, 2.4 Hz, C6H), 4.18 (1H, dd, *J* = 9.7, 5.0 Hz, CH_AH$_B$OTIPS), 3.89 (1H, dd, *J* = 9.7, 7.2 Hz, CH$_A$$H_B$OTIPS), 2.56 (1H, ddd, *J* = 13.3, 10.8, 6.4 Hz, C5H_AH$_B$), 2.07 (1H, br dd, *J* = 13.3, 1.4 Hz, C5H$_A$$H_B$), 1.76–1.63 (6H, m, SnCH$_2$CH$_2$CH_2Me), 1.49 (6H, sextet, *J* = 7.3 Hz, SnCH$_2$CH_2CH$_2$Me), 1.27–1.12 (12H, m, SnCH$_2$CH$_2$CH$_2$*Me* + SiC*H*Me$_2$), 1.22 (18H, d, *J* = 2.8 Hz, SiCH*Me*$_2$), 1.04 (6H, t, *J* = 7.2 Hz, SnCH_2CH$_2$CH$_2$Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1 (C, Ph), 128.8 (CH, Ph), 128.4 (2CH, Ph), 126.2 (2CH, Ph), 100.6 (C2H), 77.4 (C6H), 74.4 (C4H), 66.6 (CH$_2$OTIPS), 33.9 (C5H$_2$), 29.3 (3CH$_2$, $^3J_{C–Sn}$ = 10.2, SnCH$_2$CH$_2$*C*H$_2$Me), 27.7 (3CH$_2$, $^2J_{C–Sn}$ = 27.8, SnCH$_2$*C*H$_2$CH$_2$Me), 18.2 (6CH$_3$, SiCH*Me*$_2$), 13.8 (3CH$_3$, Sn(CH$_2$)$_3$*Me*), 12.1 (3CH, Si*C*HMe$_2$), 10.3 (3CH$_2$, $^1J_{C–Sn}$ 150.1, 143.6, Sn*C*H$_2$CH$_2$CH$_2$Me).

LRMS (CI$^+$ mode): *m*/*z* = 641.2 [(M + H)$^+$, 35], 583.1 (100), 581.1 (76), 533.2 (32), 475.1 (18), 291.1 (44), 289.1 (34), 243.2 (22), 107.1 (86).

Found: C, 60.17; H, 9.41. $C_{32}H_{60}O_3SiSn$ requires: C, 60.09; H, 9.46%.

Data for the (2*S*)-isomer (**33b**): (R_f = 0.22, PhMe : hexanes = 1 : 3).

$[a]_D$ = −2.14 (*c* 1.54, $CHCl_3$).

IR (film): ν = 2960 s, 2864 s, 1460 s, 1380 m, 1114 m, 1073 m, 1018 m, 881 m, 798 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (2H, m, Ph), 7.36–7.28 (3H, m, Ph), 5.73 (1H, s, C2H), 4.59 (1H, dd, *J* = 13.7, 2.3 Hz, C4H), 4.35 (1H, t, *J* = 9.0 Hz, CH_AH$_B$OTIPS), 4.17–4.12 (1H, m, C6H), 4.01 (1H, dd, *J* = 9.5, 5.2 Hz, CH$_A$$H_B$-OTIPS), 2.59 (1H, dt, *J* = 6.1, 13.8 Hz, C5H_AH$_B$), 1.85 (1H, ddd, *J* = 13.8, 2.3, 1.1 Hz, C5H$_A$$H_B$), 1.61–1.51 (6H, m, SnCH$_2$CH$_2$CH_2Me), 1.31 (6H, sextet, *J* = 7.2 Hz, SnCH$_2$CH_2-CH$_2$Me), 1.18–1.08 (3H, m, SiC*H*Me$_2$), 1.10 (18H, d, *J* = 5.2 Hz, SiCH*Me*$_2$), 0.99–0.94 (6H, m, SnCH_2CH$_2$CH$_2$Me), 0.90 (9H, t, *J* = 7.4 Hz, SnCH$_2$CH$_2$CH$_2$*Me*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0 (C, Ph), 128.5 (CH, Ph), 128.2 (2CH, Ph), 126.2 (2CH, Ph), 97.9 (C2H), 73.1 (C4H), 68.1 (C6H), 61.8 (CH$_2$OTIPS), 30.1 (C5H$_2$), 29.3 (3CH$_2$, $^3J_{C–Sn}$ = 10.2 Hz, SnCH$_2$CH$_2$*C*H$_2$Me), 27.9 (3CH$_2$, $^2J_{C–Sn}$ = 26.8 Hz, SnCH$_2$*C*H$_2$CH$_2$Me), 18.2 (6CH$_3$, SiCH*Me*$_2$), 13.9 (3CH$_3$, Sn(CH$_2$)$_3$*Me*), 12.1 (3CH, Si*C*HMe$_2$), 8.6 (3CH$_2$, $^1J_{C–Sn}$ = 160.6, 153.6 Hz, Sn*C*H$_2$CH$_2$CH$_2$Me).

LRMS (CI$^+$ mode): *m*/*z* = 641.0 [(M + H)$^+$, 49%], 583.0 (100), 581.0 (75), 533.0 (31), 351.1 (42), 291.0 (69), 289.0 (53).

Found: C, 60.07; H, 9.36. $C_{32}H_{60}O_3SiSn$ requires: C, 60.09; H, 9.46%.

(2*S*,4*R*,6*S*)-4-Allyl-2-phenyl-6-triisopropylsilyloxymethyl-1,3-dioxane (34)

Olefin **34** was prepared in an analogous fashion to olefin **32** on a scale of 0.25 mmol of stannane **33a** and 0.28 mmol of neutral complex **31**. Purification by column chromatography (SiO_2, Et_2O : hexanes = 3 : 97) gave the title compound (50 mg, 0.13 mmol, 51%) as a clear oil. ^{1}H and ^{13}C NMR spectroscopy indicated the presence of a single isomer, identified as the (6*S*)-isomer on the basis of the small (*J* = 6.9) coupling between C6H and C5H. NOE experiments confirmed the assignment, with large (12–16%) enhancements observed between C6H and C2H, and no enhancement observed between C4H and C6H when either position was irradiated.

$[a]_D$ = +17.5 (*c* 0.59 $CHCl_3$).

IR (film): ν = 2866 s, 1463 m, 1383 m, 1216 m, 1118 s, 1069 m, 1027 m, 995 s, 918 m, 883 s, 754 s, 697 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (2H, m, Ph), 7.38–7.30 (3H, m, Ph), 5.88 (1H, ddt, *J* = 16.8, 10.0, 7.3 Hz, C*H*=CH$_2$), 5.84 (1H, s, C2H), 5.21–5.13 (2H, m, CH=CH_2), 4.35 (1H, m, apparent q, *J* = 6.9 Hz, C6H), 4.18 (1H, ddt, *J* = 11.0, 2.5, 5.9 Hz, C4H), 3.93 (1H, dd, *J* = 9.9, 5.4 Hz, CH_AH$_B$OTIPS), 3.69 (1H, dd, *J* = 9.9, 6.4 Hz, CH$_A$$H_B$OTIPS), 2.87 (1H, dt, *J* = 14.4, 7.3 Hz, CH_AH$_B$CH=CH$_2$), 2.55 (1H, dt, *J* = 14.4, 7.3 Hz, CH$_A$$H_B$CH=CH$_2$), 2.00 (1H, ddd, *J* = 13.8, 11.2, 6.2 Hz, C5H_AH$_B$), 1.74 (1H, ddd, *J* = 13.5, 2.5, 1.3 Hz, C5H$_A$$H_B$), 1.15–1.03 (3H, m, SiC*H*Me$_2$), 1.08 (18H, d, *J* = 5.2 Hz, SiCH*Me*$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1 (C, Ph), 134.7 (*C*H=CH$_2$), 128.8 (CH, Ph), 128.3 (2CH, Ph), 126.3 (2CH, Ph), 117.6 (CH=*C*H$_2$), 94.4 (*C*HPh), 73.2 (C4H), 72.3 (C6H), 66.9 (CH$_2$OTIPS), 35.6 (*C*H$_2$CH=CH$_2$), 30.3 (C5H$_2$), 18.2 (6CH$_3$, SiCH*Me*$_2$), 12.1 (3CH, Si*C*HMe$_2$).

LRMS (CI$^+$ mode): *m*/*z* = 391.1 [(M + H)$^+$, 100], 347.1 (8), 285.1 (50), 261.1 (11), 241.1 (11), 111.1 (13), 107.1 (12).

Found: C, 70.65; H, 9.73. $C_{23}H_{38}O_3Si$ requires: C, 70.72; H, 9.81%.

(2*S*,4*S*,6*S*)-4-[(1*R*,2*E*)-1-Methyl-3-phenyl-2-propenyl]-2-phenyl-6-triisopropylsilyloxymethyl-1,3-dioxane (6) and (2*S*,4*S*,6*S*)-4-[(1*S*,2*E*)-1-phenyl-2-butenyl]-2-phenyl-6-triisopropylsilyloxymethyl-1,3-dioxane (35)

n-BuLi (5.4 mL of a 1.7 M solution in hexanes) was added dropwise to a solution of stannane **33a** (5.40 g, 8.45 mmol) in THF (150 mL) at −80 °C under N_2. After the light-yellow solution was stirred at −80 °C for 1 h, a solution of CuBr·SMe$_2$ (2.08 g, 10.14 mmol) in di-*iso*-propylsulfide (7 mL) and THF (8.5 mL) was added *via* cannula, maintaining the internal solution temperature below −80 °C. The orange-brown solution was stirred at −80 °C for 1 h under N_2 before the addition of cationic complex **7** (freshly prepared: nitrosonium tetrafluoroborate (1.28 g, 11.0 mmol) was added to a solution of neutral complex **15** (3.53 g, 10.1 mmol, prepared by procedure A above) in MeCN (20 mL) at 0 °C and the yellow solution stirred at 0 °C under N_2 for 15 min) *via* cannula. The light-brown solution was stirred at −80 °C for 1 h before the addition of aqueous NH_4Cl (40 mL) and aqueous NH_3 (10 mL) and removal of the cooling bath. After reaching room temperature, the mixture was filtered through Celite, washing thoroughly with Et_2O (50 mL). The phases were separated, and the aqueous phase extracted with Et_2O (2 × 50 mL), and the combined organic phases washed with brine (100 mL), dried, filtered and concentrated *in vacuo*. The crude material was dissolved in $CHCl_3$ (250 mL) and stirred at rt for 17 h with a stream of O_2 bubbling through the brown solution. Removal of solvent *in vacuo* yielded a dark brown oil which was purified by column chromatography (SiO_2, Et_2O : hexanes = 2 : 98) to give a mixture of the title compounds (2.90 g, 6.03 mmol, 71% from stannane **33a**) as a pale yellow oil. ^{1}H NMR spectroscopy revealed a ratio of **6** : **35** of approximately 1.2 : 1 (in favour of the desired isomer), estimated by integration of the vinylic proton peaks at 6.51 and 6.28 ppm (**6**) and 5.64–5.50 ppm (**35**).

$[a]_D$ (1.2 : 1 mixture of **6** : **35**) = +23.3 (*c* 1.50, $CHCl_3$).

IR (film) ν = 2942 s, 2866 s, 1462 m, 1117 s, 1069 m, 1028 m, 1014 m, 995 m, 882 m, 748 m, 696 s, 660 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.17 (19H, m, Ph), 7.05–7.04 (1H, m, Ph), 6.51 [1H, d, *J* = 15.9 Hz, PhC*H*=CHR, (**6**)], 6.28 [1H, dd, *J* = 15.9, 8.4 Hz, PhCH=C*H*R, (**6**)], 5.85 [1H, s, C*H*Ph, (**6**)], 5.76 [1H, s, C*H*Ph, (**35**)], 5.64–5.50 [2H, m, MeC*H*=C*H*R, (**35**)], 4.44 [1H, dd, *J* = 11.1, 5.0 Hz, (**35**)], 4.27–

3.90 (6H, m), 3.72 [2H, ddd, J = 10.0, 6.6, 1.4 Hz, (**6**)], 3.19 (1H, q, J = 8.3 Hz), 2.11 [1H, ddd, J = 13.5, 2.5, 1.5 Hz, (**35**)], 2.02–1.90 (3H, m), 1.66 [3H, dd, J = 5.6, 0.8 Hz, (**35**)], 1.13 [3H, d, J = 6.4 Hz, Me (**6**)], 1.12–1.00 (42H, m, $SiCHMe_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9 (C, Ph), 139.1 (C, Ph), 138.9 (C, Ph), 137.8 (C, Ph), 133.5 [PhCH=*C*HR (**6**)], 132.2 [*C*H=CH, (**35**)], 130.1 [Ph*C*H=CHR (**6**)], 128.8 (2CH, Ph), 128.7 (2CH, Ph), 128.6 [CH, Ph or CH=CH, (**35**)], 128.4 [CH, Ph or CH=CH, (**35**)], 128.3 (2CH, Ph), 128.2 (2CH, Ph), 128.1 (2CH, Ph), 127.9 [CH, Ph or CH=CH, (**35**)], 127.2 [CH, Ph or CH=CH, (**35**)], 126.6 [CH, Ph or CH=CH, (**35**)], 126.3 (2CH, Ph), 126.2 (2CH, Ph), 125.9 (2CH, Ph), 94.8 [*C*HPh (**6**)], 94.3 [*C*HPh, (**35**)], 76.6 (CH), 74.8 (CH), 73.3 (CH), 73.1 (CH), 66.8 ($2CH_2$), 50.0 (CH), 37.6 [PhCH=CH*C*HMeR, (**6**)], 28.9 (CH_2), 28.7 (CH_2), 18.2 ($14CH_3$, Me + $SiCHMe_2$), 12.2 (6CH, $SiCHMe_2$).

LRMS (CI mode, isobutane): m/z = 481 [$(M + H)^+$, 17%], 393 (21), 375 (58), 351 (100), 307 (25), 245 (44).

Found: C, 74.86; H, 9.41. $C_{30}H_{44}O_3Si$ requires: C, 74.95; H, 9.22%.

(2*R*,4*S*,5*R*,6*E*)-5-Methyl-7-phenyl-hept-6-ene-1,2,4-triol (38) and (2*R*,4*S*,5*S*,6*E*)-5-phenyl-oct-6-ene-1,2,4-triol (39)

To a solution of dioxanes **6** and **35** (**6** : **35** = 1.2 : 1, 2.77 g, 5.76 mmol) in MeOH (100 mL) at rt was added *p*-toluenesulfonic acid monohydrate (164 mg, 0.86 mmol). The pale yellow solution was stirred at rt for 1 d before solvent removal *in vacuo*. The residue was purified by column chromatography (SiO_2, EtOAc) to give a mixture of the title compounds (861 mg, 3.64 mmol, 63%) as a pale yellow oil. Careful repetitive column chromatography allowed the separation of isomers. Triol **38**, a viscous oil, gave : $[a]_D$ = +103.6 (c 1.10, MeOH).

IR (film): ν = 3465 br s, 2935 m, 2873 m, 1452 m, 1388 m, 1365 m, 1329 m, 1082 m, 992 m, 972 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.23 (5H, m, Ph), 6.49 (1H, d, J = 16.1 Hz, C7H), 6.12 (1H, dd, J = 16.1, 8.7 Hz, C6H), 4.05–3.99 (1H, m, C2H), 3.80–3.76 (1H, m, C4H), 3.67 (1H, dd, J = 11.1, 3.6 Hz, C1H_AH$_B$), 3.54 (1H, dd, J = 11.1, 7.0 Hz, C1H$_A$$H_B$), 2.41 (1H, br sextet, J = 7.3 Hz, C5H), 1.75 (1H, ddd, J = 14.4, 8.7, 2.5 Hz, C3H_AH$_B$), 1.60 (1H, ddd, J = 14.4, 9.3, 3.5 Hz, C3H$_A$$H_B$), 1.12 (3H, d, J = 6.8 Hz, C5–Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1 (C, Ph), 132.3 (C6H or C7H), 131.6 (C6H or C7H), 128.8 (2CH, Ph), 127.7 (CH, Ph), 126.4 (2CH, Ph), 72.3 (C2H), 69.6 (C4H), 66.9 ($C1H_2$), 44.2 (C5H), 36.4 ($C3H_2$), 16.9 (C5–*Me*).

LRMS (CI mode, NH_3): m/z = 254.2 [$(M + NH_4)^+$, 100%], 237.1 (28), 219.1 (22).

Found: C, 71.15; H, 8.70. $C_{14}H_{20}O_3$ requires: C, 71.16; H, 8.53%.

Triol **39** solidified upon standing and was recrystallised from Et_2O to give fine white needles, mp 110–111 °C.

$[a]_D$ = −69.1 (c 1.65, MeOH).

IR (KBr): ν = 3397 br s, 1112 m, 1082 m, 1070 s, 1025 s, 963 m, 702 m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.30 (2H, m, Ph), 7.26–7.17 (3H, m, Ph), 5.65–5.53 (2H, m, C6H and C7H), 4.13 (1H, dt, J = 2.5, 8.8 Hz, C4H), 4.07–4.01 (1H, m, C2H), 3.65 (1H, dd, J = 11.1, 3.5 Hz, C1H_AH$_B$), 3.53 (1H, dd, J = 11.1, 7.0 Hz, C1H$_A$$H_B$), 3.30 (1H, t, J = 8.2 Hz, C5H), 2.94 (1H, br s, OH), 2.18 (1H, br s, OH), 1.88 (1H, ddd, J = 14.5, 8.7, 2.6 Hz, C3H_AH$_B$), 1.68 (3H, d, J = 5.0 Hz, C8H_3), 1.63 (1H, br s, OH), 1.55 (1H, ddd, J = 14.5, 9.1, 3.5 Hz, C3H$_A$$H_B$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4 (C, Ph), 130.8 (Ph, C6H or C7H), 129.2 (2CH, Ph), 128.5 (2CH, Ph), 128.4 (Ph, C6H or C7H), 127.2 (Ph, C6H or C7H), 72.1 (C4H), 69.7 (C2H), 67.1 ($C1H_2$), 56.7 (C5H), 36.8 ($C3H_2$), 18.3 (C8H_3).

LRMS (CI mode, NH_3): m/z = 254.2 [$(M + NH_4)^+$, 100%], 236.2 (30), 219.2 (8), 116.1 (12).

Found: C, 71.27; H, 8.73. $C_{14}H_{20}O_3$ requires: C, 71.16; H, 8.53%.

(2*E*,5*S*,6*R*,7*E*)-5-Hydroxy-6-methyl-8-phenylocta-2,7-dienoic acid methyl ester (5)

To a solution of triol **38** (125 mg, 0.53 mmol) in MeOH (15 mL) and H_2O (5 mL) at rt was added sodium periodate (170 mg, 0.79 mmol). The clear solution was stirred at rt for 1.5 h, after which time a white precipitate was present. Methanol was removed *in vacuo* and H_2O (30 mL) and CH_2Cl_2 (20 mL) were added. The phases were separated and the aqueous phase extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried, filtered and concentrated *in vacuo* to afford a crude aldehyde as a colourless oil (103 mg, 0.50 mmol). The crude aldehyde was twice dissolved in PhMe (20 mL) and the solvent evaporated. To a solution of the crude aldehyde in THF (17 mL) was added trimethylphosphonoacetate (0.17 mL, 1.17 mmol) and the mixture cooled to −78 °C under N_2 whereupon *N*,*N*,*N*′,*N*′-tetramethylguanidine (0.15 mL, 1.17 mmol) in THF (5 mL) was added dropwise over 2 min. The clear solution was allowed to warm to rt over 16 h and stirred at rt for 42 h before the addition of H_2O (20 mL) and Et_2O (20 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic phases were dried, filtered and concentrated *in vacuo* to afford a pale yellow oil. The residue was purified by column chromatography (SiO_2, Et_2O : cyclohexane = 2 : 8 ⟶ 4 : 6) to give the title compound (114 mg, 0.44 mmol, 83%) as a colourless oil. $[a]_D$ = +71.7 (c 1.20, $CHCl_3$); lit. $[a]_D$ = +55.2 (c 0.31, $CHCl_3$).[41] Spectroscopic data were in accordance with literature data.[41]

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