Ruthenium-catalysed *ortho* vinylation of aromatic ketones with alkynes; unexpected cyclopentaannulation

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Abstract

Ruthenium-catalysed coupling of aromatic ketones with alkynylsilanes yielded in most cases *ortho* vinylation adducts in high yield. The predominant stereochemistry of the newly introduced double bond was *E* in all but a few cases. In contrast, 1-acetylnaphthalene underwent a one-pot insertion–cyclisation sequence yielding cyclopenta[*a*]naphthalene derivatives. A bis acetylene gave both mono and bis insertion products. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

We have reported previously on the use of η^2-tetracarbonylmanganese complexes of podocarpic acid derivatives to effect cyclopentaannulation of the arene ring, leading to ring C aromatic steroidal analogues in excellent yield. The *ortho* manganated derivative **2** can be prepared by refluxing the free diterpenoid **1** with $PhCH_2Mn(CO)_5$ in heptane to give the η^2-tetracarbonylmanganese complex (**2**) in 95% yield [1]. A coupling reaction with either an alkene [2] or an alkyne [3] leads directly to the required tetracyclic skeleton (Scheme 1) via an insertion–cyclisation sequence.
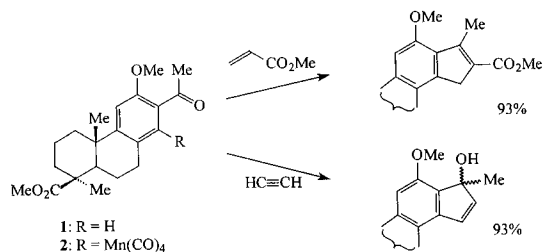
Scheme 1.

While benefiting practically from the one-pot transformation, these reactions require an initial stoichiometric cyclometallation step before any coupling can proceed. We [4,5] and others [6,7] have reported on the use of a ruthenium complex in catalytic quantities to effect aryl ketone *ortho* C–H/olefin (optimally an ethenylsilane) coupling reactions, resulting in alkylation but not proceeding to cyclopentaannulation (compare Scheme 1). The resulting *ortho* 2-(trialkoxysilyl)ethyl adducts require further functional group manipulations before cyclopentaannulation can be accomplished. The ruthenium-catalysed coupling of an aryl ketone *ortho* C–H bond with an alkyne has been reported [6,7]. When an alkynylsilane was used this reaction affords vinylsilanes, which have been demonstrated by us to undergo cyclisation in a separate step, leading to the construction of five-membered rings, including benzofulvenes [8]. We now report our results of the application of the $RuH_2CO(PPh_3)_3$-catalysed *ortho* C–H/alkyne coupling reaction to a range of aromatic ketones.

2. Results and discussion

1-Phenyl-2-trimethylsilylethyne (**3**) and dimethylbis(phenylacetylene)silane (**4**) were used as representative mono- and diynes.

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Table 1
Reactions of model substrates catalysed by $RuH_2(CO)(PPh_3)_3$

Substrate	Alkyne (molar equivalents)	Cat. mol%	Time (h)	E/Z	Product (%) [a]
5	$PhC\equiv CSiMe_3$, 2	6	22	7.25/1	**6**, 95
7	$PhC\equiv CSiMe_3$, 3	6	49	10/1	**8**, 95
9	$PhC\equiv CSiMe_3$, 2	6	23	1/1	**10**, 93

[a] Isolated yield.

$PhC\equiv C-R$

3: R = $SiMe_3$

4: R = $Si(Me)_2C\equiv CPh$

2-Methylacetophenone (**5**) and 2-*t*-butyldimethylsiloxy-acetophenone (**7**) were used as model substrates for the diterpenoid **11**, and 6-methoxy-1-tetralone (**9**) as surrogate for the diterpenoid **13**. The bulky *t*-butyldimethylsilyl group was required to protect the *ortho* oxygen in order to inhibit catalyst quenching by chelation during the coupling sequence [4,5].

5: R^1 = Me, R^2 = H
6: R^1 = Me, R^2 = C(Ph)=CHSiMe₃
7: R^1 = OSiMe₂^{t}Bu, R^2 = H
8: R^1 = OSiMe₂^{t}Bu, R^2 = C(Ph)=CHSiMe₃

9: R^1 = OMe, R^2 = H
10: R^1 = OMe, R^2 = C(Ph)=CHSiMe₃
29: R^1 = H, R^2 = H
30: R^1 = H, R^2 = C(Ph)=CHSi(Me₂)C≡CPh
31: R^1 = H, R^2 = C(Ph)=CHSi(Me₂)OH

The results of the coupling of these model aryl carbonyl substrates with 1-phenyl-2-trimethylsilylethyne catalysed by $RuH_2(CO)(PPh_3)_3$ are given in Table 1.

All reactions were performed in refluxing toluene. Since 1-phenyl-2-trimethylsilylethyne is not symmetrical, four isomers (two regio- and two stereo-isomers) of the coupled product are possible. In the event, 2-methylacetophenone gave the vinylsilane **6** (95%), in which the largest appended substituent was remote from the main body of the molecule. The stereochemistry in the newly introduced sidechain was determined from analysis of the ^{1}H-NMR spectrum. Thus, for a range of 1,2-dialkylvinylsilanes Chan and coworkers [9] have reported that a vinyl proton of an *E* isomer consistently resonates at higher field (ca. 0.3 ppm) than a vinyl proton for the corresponding *Z* isomer. In the present work the signal due to the vinyl proton of the *E* isomer of **6** occurred at 5.97 ppm while that due to the *Z* isomer appeared at 6.43 ppm in the ^{1}H-NMR spectrum. Integration of these peaks provided the E/Z ratio (7.25/1); this method was used to calculate the isomer ratio in all subsequent coupling products. The high *E* selectivity results from the requirement of a concerted insertion of the alkyne into the ruthenium hydride bond [10]. Not surprisingly, the E/Z ratio in the 1,2,3-trisubstituted *ortho* TBDMS

ether **8** was higher (10/1) than that in the less bulky analogue **6**. In contrast to acetophenones **5** and **7**, however, 6-methoxy-1-tetralone (**9**) gave a 93% yield of the coupled adduct (**10**) in which the E/Z ratio was 1:1.

The optimum yield from these coupling reactions required a scale of ≥ 2 mmol of the aryl ketone. If the reaction of **5** was performed on a 0.7 mmol scale very little product was formed. Similarly, reaction of **7** on a 1.5 mmol scale gave **8** in only 45% yield after a comparable reflux time. These observations suggest that the use of this methodology for organic synthesis on a very small scale may be limited.

Since the coupling reaction had proceeded smoothly for the model monocyclic and bicyclic substrates, attention was turned to the diterpenoid analogues **11** and **13**. The results from coupling reactions of methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**13**) with 1-phenyl-2-trimethylsilylethyne (**3**) are given in Table 2.
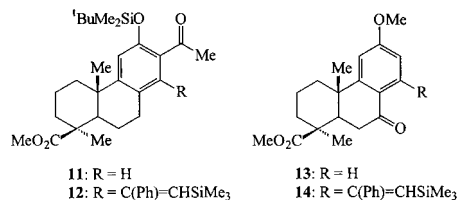
11: R = H
12: R = C(Ph)=CHSiMe₃

13: R = H
14: R = C(Ph)=CHSiMe₃

On a 1 mmol scale reaction the yield of the C14-alkylated product (**14**) was only 68% even with a prolonged reaction time of 68 h, whereas on a 2 mmol scale the yield was improved significantly (88%). However, since both of these reactions had been run using a two-fold excess of the alkynylsilane, a reaction was attempted with only a slight excess of the alkyne. Gratifyingly, a near-quantitative yield (94%) of **14** was isolated after chromatography. These data suggest that intermolecular coordination of the alkyne to the active catalyst competes significantly with the required cycloruthenation of the arene carbonyl substrate; a lower concentration of alkyne in the reaction mixture apparently facilitates intramolecular coordination and subsequent *ortho* C–H insertion. In contrast, this effect was not observed during the ruthenium-catalysed insertion reactions of alkenes, in which five molar equivalents of alkene were used routinely and without detriment to the yield of alkylated product [4,5]. This could be attributed

to the smaller size of the unsubstituted terminal alkene as opposed to the disubstituted alkyne, or to different coordinating abilities of the unsaturated ligands. Despite the increased complexity of the diterpenoid substrate **13**, equal amounts of the *E* and *Z* isomers were formed. Interconversion between these isomers during the course of the reaction cannot be discounted.

The NMR spectra of the crude alkylation mixture from diterpenoid **13** contained three sets of peaks, perhaps suggesting that a regioisomer of **14** had also been formed. However, this possibility was dismissed on the basis of an electrophilic protiodesilylation of the vinylsilane (treatment with HI), which gave only a single 1,1-disubstituted ethene in high yield. Variable-temperature NMR spectra (298–413 K) revealed that the *Z* isomer was in fact a mixture of two rotamers due to restricted rotation around the C(14)–C(vinyl) bond as a consequence of interaction between the SiMe$_3$ group and the tricyclic diterpenoid. Analysis [11] of the coalescence data yielded $\Delta S^+ = 142 \pm 10$ J K mol^{-1}, $\Delta H^+ = 29.6 \pm 1.0$ kJ mol^{-1} and $\Delta G^+ = 72.1 \pm 1.0$ kJ mol^{-1}. These figures are comparable with those applicable to rotation barriers in a series of 1-vinylnaphthalenes [12].

The coupling of methyl 13-acetyl-12-(((1,1-dimethylethyl)dimethylsilyl) - oxy)podocarpa - 8,11,13 - trien-19-oate (**11**) with 1-phenyl-2-trimethylsilylethyne did not proceed as smoothly as had the vinylation reaction of **13**. Initial results are given in Table 3.

Thus, refluxing **11** with 1.2 molar equivalents of the alkyne and 6 mol% catalyst for 17 h (run 1) gave the insertion product **12** in only 22% yield. Surprisingly, the *E* isomer was favoured only slightly (*E*/*Z* = 1.20/1) in spite of the relative congestion due to the 1,2,3-substitution pattern in the vinylated aromatic product. Although the *Z* isomer again consisted of a set of rotamers, determination of the activation parameters by variable temperature NMR studies in DMSO-d_6 was thwarted by in situ cleavage of the TBDMS ether. Increasing the amount of catalyst to 8 mol% and extending the reflux time to 89 h (run 2) resulted in the yield doubling to 43%, but the reaction was far from being optimised. An increase in the molar ratio of either the alkyne (run 3) or of both the alkyne and the ruthenium catalyst (run 4) afforded yields of only 22 and 27%, respectively. These low yields could be due to competitive coordination of

the alkyne to the active catalyst in preference to the carbonyl group, as discussed previously.

In the earlier study [4,5], coupling of triethoxyvinylsilane with the diterpenoid **11** was investigated by adding 2 mol% RuH$_2$(CO)(PPh$_3$)$_3$ initially, then adding a further 2 mol% after 24 h; a quantitative yield of the adduct resulted. Although it has been discovered subsequently that such sequential additions of the catalyst are not mandatory, application of this protocol to the alkyne insertion chemistry was nevertheless studied (Table 4).

Thus, refluxing **11** with three molar equivalents PhC≡CSiMe$_3$ in the presence of 6 mol% RuH$_2$-CO(PPh$_3$)$_3$ for 48 h, followed by the addition of another 2 mol% of the catalyst and refluxing for a further 43 h (run 5), gave the adduct (**12**) in 36% yield. Increasing the initial reflux time, the amount of catalyst added in the second addition, and the second reflux time (run 6) improved the yield only slightly (40%). However, a significant improvement to 67% was obtained by using 8 mol% catalyst initially, and refluxing for 4 days; an additional 2 mol% catalyst was then added and refluxing continued for a further 48 h (run 7). A reaction similar to run 5 in which the catalyst was added in two 6 mol% portions but decreasing the total reaction time (run 8) resulted in further improvement of the yield, to 79%. Thus, the optimised conditions for vinylation of the diterpenoid **11** with PhC≡CSiMe$_3$ requires (i) portionwise addition (2 × 6 mol%) of RuH$_2$CO(PPh$_3$)$_3$; (ii) three molar equivalents of the alkyne; and (iii) a total reflux time of at least 69 h.

The vinylated diterpenoids **12** and **14** underwent cyclisation on treatment with trimethyl orthoformate to afford tetracyclic molecules in good yield [8].

Bis alkylated adducts, in which both aromatic *ortho* C–H bonds (if present) couple with an unsaturated substrate, have been isolated from catalysed insertion reactions of alkenes. In order to determine if bis vinylation could be achieved similarly, the reaction of 4-methoxyacetophenone (**15**) with 1-phenyl-2-trimethyl-silylethyne was attempted.
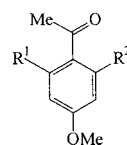
15: R^1 = R^2 = H
16: R^1 = H, R^2 = C(Ph)=CHSiMe$_3$
17: R^1 = R^2 = C(Ph)=CHSiMe$_3$

Table 2
Vinylation reactions of methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**13**)

Mmol	Alkyne (molar equivalents)	Cat. mol%	Time (h)	*E*/*Z*	Product (%) [a]
1	PhC≡CSiMe$_3$, 2	6	68	1/1	**14**, 68
2	PhC≡CSiMe$_3$, 2	6	20	1/1	**14**, 88
2	PhC≡CSiMe$_3$, 1.3	6	20	1/1	**14**, 94

[a] Isolated yield.

Table 3
Vinylation reactions of the methyl 12-OTBDMS-podocarpa-8,11,13-trien-19-oate (11)

Run	Substrate (mmol)	Alkyne 3 (mmol)	Cat. mol%	Time (h)	Product (%) [a]
1	2	1.2	6	17	12, 22
2	2	1.2	8	89	12, 43
3	2	4	6	46	12, 27
4	2	10	8	48	12, 22

[a] Isolated yield.

Treatment of 15 with PhC≡CSiMe₃ (1.1 molar equivalents) in the presence of 6 mol% RuH₂(CO)(PPh₃)₃ gave a mixture of coupled products in a total yield of 69%. Surprisingly, the mono adduct 16 consisted predominantly of the Z isomer, and in this case both the E and Z isomers were separable by flash chromatography. Consequently, the ¹H- and ¹³C-NMR spectra for each stereoisomer could be assigned fully on the basis of 2-D experiments. This data proved invaluable for assignments of signals individually to E/Z isomers for the usual cases when the mixtures could not be separated. The bis adduct 17 was a mixture of all three stereoisomers (ZZ/EZ/EE = 1/1.4/17). As expected, the symmetrical E/E isomer predominated. The E/Z geometry of the two introduced double bonds results in the adduct becoming unsymmetrical, as evident in the ¹H-NMR spectrum. As expected, the ZZ isomer was present in the smallest amount, alkenyl products resulting from alkyne/C–H coupling being usually of E stereochemistry predominantly. The ¹H-NMR signals due to the ZZ isomer were very broad, indicating that a rotational barrier existed for this compound.

Attempts to induce bis cyclopentaannulation of the adducts 17b, potentially leading to novel bicyclo[3,3,0] fused tricyclic arenes (Scheme 2), by the method used by us for other vinylsilanes [8] were unsuccessful.
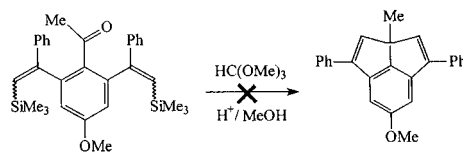
Murai and co-workers [13] have reported that both 1-acetylnaphthalene (18) and 2-acetylnaphthalene (20) undergo a ruthenium-catalysed reaction with alkenes to give 1:1 coupled adducts in high yields. Therefore, the coupling of these acetylnaphthalenes was examined with 1-phenyl-2-trimethylsilylethyne in order to confirm that this class of compounds was amenable to the ruthenium catalysed vinylation reaction. Indeed, 2-acetylnaphthalene (20) gave the insertion adduct 21 in 75% yield after refluxing for 48 h with 1.1 molar equivalents of PhC≡CSiMe₃ in the presence of 6 mol% RuH₂CO(PPh₃)₃.
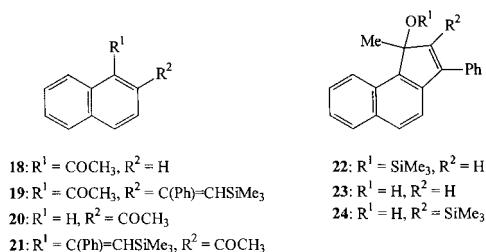
There are two possible sites in 2-acetylnaphthalene (20) for ortho C–H bond activation to occur, leading to either a 1,2- or a 2,3-disubstituted naphthalene. The regiochemistry of arene activation at C1 was confirmed by examination of ¹H-NMR spectra. Thus, the singlet at 8.30 ppm due to H(1) in the ¹H-NMR spectrum of 2-acetylnapthalene (20) was absent in the ¹H-NMR spectrum of the C1-vinylated product 21. In agreement with this assignment, Murai and co-workers [13] have reported that coupling of triethoxyvinylsilane with 2-acetylnaphthalene gave the C1-alkylated product in quantitative yield. In the present work and, in contrast to all the previously studied examples, the E/Z ratio in 21 was 1/11; i.e. the Z isomer predominated.

1-Acetylnaphthalene (18) also possesses two sites (ortho and peri) for C–H bond activation. It was expected that this substrate would give rise to a 1,2-substituted product rather than a 1,8-substituted product in accordance with the work of Murai and co-workers [13]. In the event, refluxing 18 with 1.1 molar equivalents PhC≡CSiMe₃ and 6 mol% catalyst for 36 h resulted in quantitative conversion of the starting material into four products. One of these was the expected C2-alkyne coupling product (19) (45%, 1/1 mixture with 24), which was predominantly the E isomer (E/Z = 7/1). Interestingly, there were peaks in the ¹³C-NMR spectrum of the crude reaction mixture between 80 and 90 ppm, indicative of oxygenated and/or benzylic or acetylenic carbons. Similarly, a group of signals from 1.9 to 2.0 ppm in the ¹H-NMR spectrum indicated either a methyl group on a carbon–carbon double bond or a methyl group on saturated carbon. That is, the carbonyl group was no longer present in some of the products.

The structures of these three compounds were determined by a combination of 2-D NMR experiments and, in the case of 24, by X-ray crystallographic analysis (Fig. 1). All of the products were derived from an intermediate in the catalytic cycle that underwent insertion into the carbonyl group, resulting overall in the formation of a

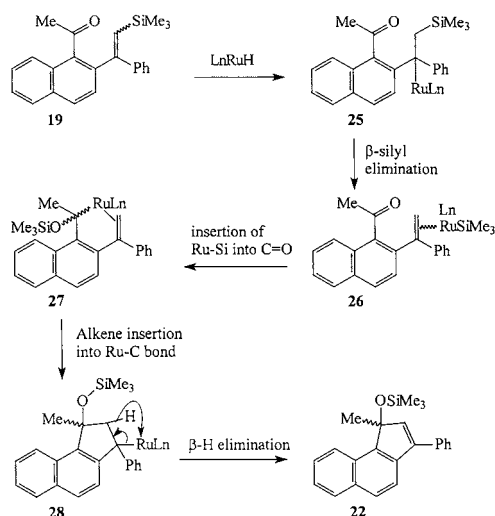18: R¹ = COCH₃, R² = H
19: R¹ = COCH₃, R² = C(Ph)=CHSiMe₃
20: R¹ = H, R² = COCH₃
21: R¹ = C(Ph)=CHSiMe₃, R² = COCH₃

22: R¹ = SiMe₃, R² = H
23: R¹ = H, R² = H
24: R¹ = H, R² = SiMe₃

Scheme 2.

Table 4
Sequential additions of RuH$_2$(CO)(PPh$_3$)$_3$ during vinylation of **11**

| Run	Alkyne **3** (molar equivalents)	Ru mol% (first addition)	Time (h)	Ru mol% (second addition)	Time (h)	Product (%) [a]
5	3	6	48	2	43	**12**, 36
6	5	6	168	6	96	**12**, 40
7	3	8	96	2	48	**12**, 64
8	3	6	26	6	43	**12**, 79

[a] Isolated yield.

five-membered ring in situ. This is the first reported example of cyclopentaannulation catalysed by RuH$_2$CO(PPh$_3$)$_3$. The formation of **22** (12%) and **23** (38%) can be explained by the mechanism outlined in Scheme 3. Insertion of a ruthenium hydride species into the double bond of **19** followed by a β-silyl migration [14] yields the intermediate **26**. Ru–Si insertion into the proximal carbonyl [15] gives the σ-bonded π-coordinated ruthenium complex **27**, in which the alkene inserts into the Ru–C(alkyl bond) [16] to form the indanol derivative **28**. Subsequent β-hydride elimination yields the trimethylsilyl ether **22**. Silica gel chromatography caused partial acid-catalysed cleavage of the trimethylsilyl group give to the alcohol **23**. The mechanism leading to **24** is not clear. In an independent experiment, refluxing **19** with two molar equivalents PhC≡CSiMe$_3$ for 24 h in the presence of 20 mol% RuH$_2$CO(PPh$_3$)$_3$ resulted in the formation of **22** and **23** only; no **24** was detected, indicating that this compound arises by a different pathway. Some **19** was also recovered, but had isomerised completely into the E isomer.

The reactions reported above have utilised alkynes containing only one triple bond. Weber and co-workers [17] have reported that 1,3-divinyldisiloxane couples with acetophenone under ruthenium catalysis to give copoly-

mers. We have found that a 1,4-divinylsilane inserts readily into the ortho C–H bond of 1-tetralone to give both monoaryl and diaryl adducts. Thus, refluxing 1-tetralone (**29**) with RuH$_2$CO(PPh$_3$)$_3$ (6 mol%) and 1.3 molar equivalents dimethylbis(phenylacetylene)silane (**4**) [18] resulted in quantitative conversion of the aryl ketone. The major product **30** (55%) arises from insertion of one alkyne into the ortho C–H bond, giving an alkenylalkynylsilane. Alkynylsilanes are known to undergo rapid cleavage to yield functionalised silanes and the acetylene [19]. The silanol **31** was isolated (15%) after chromatography and probably results from acidic cleavage.
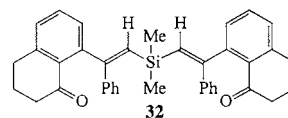
Compound **32** (8%) arises from double insertion of the bis acetylene (**4**). An X-ray crystallographic analysis of **32** (Fig. 2) revealed a rigid EE stereochemistry of the new double bonds. Thus dimethylbis(phenylacetylene)silane (**4**) may find use in polymer synthesis if two ortho C–H bonds are present in the ketone starting material, as in acetophenone itself. In connection with this result, Weber [20] has reported that 1,4-bis((trimethylsilyl)ethynyl)benzene inserts into both ortho C–H bonds of acetophenone promoted by RuH$_2$CO(PPh$_3$)$_3$, giving cross conjugated polymers.

In summary, the ortho alkylation of various aromatic ketones with alkynylsilanes catalysed by a ruthenium complex resulted in a high yield of ortho vinylation products, in which the double bond showed a preference for E geometry. The reaction was applicable to two diterpenoid ketones that have been cyclised to afford tetracyclic molecules [8]. 1-Acetylnaphthalene gave products containing a five-membered ring formed in situ. The use of a bis acetylenylsilane did not suppress the catalysed reaction, and resulted in the formation of a single stereoisomer of a diarylated 1,4-divinylsilane, as well as products derived from reaction at one alkyne centre only.

2.1. X-ray crystal structures for 24 and 32

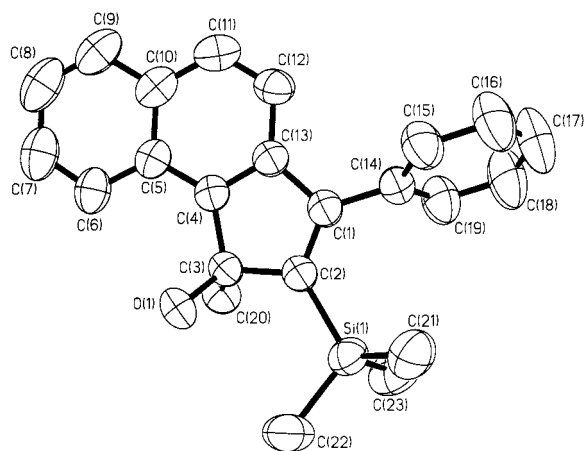Data were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo–K$_\alpha$

Scheme 3.

Fig. 1. The atomic arrangement in **24**. Only one independent molecule is shown.

radiation ($\lambda = 0.71073$ Å). Data collection covered a nominal sphere of reciprocal space for **24**, or a hemisphere for **32**, by a combination of exposures. Each set of exposures had a different ϕ angle for the crystal and covered 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing duplicate reflections; no evidence of decay was evident. Unit cell parameters were obtained by least-squares fit to 5896 reflections for **24** and 7397 for **32** which had $I > 10\sigma(I)$. Absorption corrections were applied by the method of Blessing [21] and equivalent reflections averaged. Details of crystal data and collection parameters are given in Table 5.

2.2. Structure solution and refinement

The structures were solved by direct methods using SHELXS [22] and refined by least squares on F^2 using SHELXL [23]. The asymmetric unit of **24** contains three independent molecules and there is some evidence of disorder in the methyl groups of these molecules. Where the electron density could be resolved into two parts, the atoms have been treated as two half-weighted atoms. All non-hydrogen atoms have been allowed to refine anisotropically, and hydrogen atoms were placed geometrically and allowed to refine with a riding model (including free rotation for methyl groups) with U_{iso} 20% greater than the carrier atom. Final atomic coordinates and selected bond lengths are given in Tables 6–9.

The structure of **24** establishes the structure and the relative stereochemistry and for **32** shows the rigid *EE* stereochemistry of the double bonds. The Figures show the observed stereochemistry and give the numbering scheme. All bond lengths are within the normally accepted range.

Table 5
Data collection and processing parameters

	24	**32**
Formula	$C_{23}H_{24}Osi$	$C_{38}H_{36}O2Si$
Molecular weight	344.51	552.76
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	14.4788(3)	15.7866(2)
b (Å)	14.9316(2)	10.9248(1)
c (Å)	15.1827(3)	18.2333(2)
α (°)	88.478(1)	
β (°)	69.482(1)	98.068(1)
γ (°)	82.518(1)	
V (Å^3)	3047.3(1)	3113.49(6)
Z	6	4
D_{obs} (g cm^{-3})	1.126	1.179
$F(000)$	1104	1176
μ (mm^{-1})	0.122	0.107
Radiation Mo–K_α (monochromatic) λ (Å)	0.71073	0.71073
Temperature (K)	291	291
Diffractometer	Siemens SMART	Siemens SMART
Scan technique	Area detector	Area detector
2θ (min./max.) (°)	2.6–52.6	2.6–52.6
Reflections collected/unique	27 671/12 146	17 835/6309
	R_{int} 0.0242	R_{int} 0.0290
No. of observed reflections $I > 2\sigma(I)$	7752	4202
Crystal size (mm)	$0.40 \times 0.38 \times 0.36$	$0.40 \times 0.35 \times 0.20$
A (min./max.)	0.953–0.957	0.958–0.979
Goodness of fit on F^2	1.045	1.032
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
R [a] (observed data)	0.0654	0.0556
wR_2 [b] (all data)	0.1904	0.1535

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, weight $= 1.0/[\sigma^2(F_o^2) + a*P^2 + b*P]$, $P = (F_o^2 + 2F_c^2)/3$.
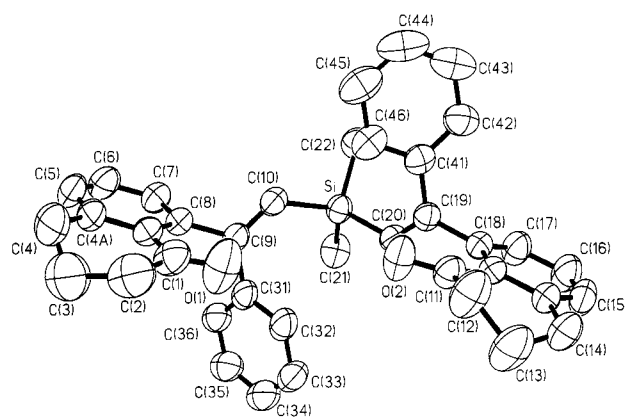

Fig. 2. The atomic arrangement in **32**.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **24**

Atom	x	y	z	U_{eq} [a]
Si(1)	4910(1)	7966(1)	267(1)	63(1)
O(1)	4652(1)	6666(1)	2222(1)	57(1)
C(1)	3494(2)	6674(2	586(2)	51(1)
C(2)	4268(2)	6952(2)	762(2)	50(1)
C(3)	4583(2)	6260(2)	1404(2)	49(1)
C(4)	3792(2)	5626(2)	1640(2)	49(1)
C(5)	3653(2)	4872(2)	2243(2)	56(1)
C(6)	4239(2)	4602(2)	2805(2)	71(1)
C(7)	4023(3)	3889(3)	3395(2)	89(1)
C(8)	3223(3)	3427(2)	3460(3)	98(1)
C(9)	2660(3)	3657(2)	2923(3)	85(1)
C(10)	2850(2)	4382(2)	2295(2)	65(1)
C(11)	2263(2)	4634(2)	1737(2)	71(1)
C(12)	2415(2)	5357(2)	1161(2)	62(1)
C(13)	3181(2)	5863(2)	1132(2)	52(1)
C(14)	3007(2)	7055(2)	−78(2)	57(1)
C(15)	2031(2)	7451(2)	237(2)	76(1)
C(16)	1585(3)	7790(3)	−393(3)	101(1)
C(17)	2114(4)	7735(3)	−1339(3)	118(2)
C(18)	3076(4)	7339(3)	−1659(3)	111(1)
C(19)	3527(3)	6994(2)	−1036(2)	80(1)
C(20)	5613(2)	5757(2)	854(2)	62(1)
C(21)	3969(3)	8953(2)	308(3)	94(1)
C(22)	5680(3)	8250(2)	953(3)	87(1)
C(23)	5781(3)	7748(3)	−964(3)	111(1)
Si(2)	8559(1)	6093(1)	−8514(1)	80(1)
O(2)	6207(1)	5793(1)	−7139(1)	67(1)
C(31)	7385(2)	7700(2)	−7424(2)	63(1)
C(32)	7536(2)	6793(2)	−7563(2)	59(1)
C(33)	6703(2)	6385(2)	−6793(2)	56(1)
C(34)	6014(2)	7208(2)	−6283(2)	56(1)
C(35)	6075(2)	7256(2)	−5554(2)	60(1)
C(36)	4583(2)	6500(2)	−5180(2)	77(1)
C(37)	3674(3)	6608(3)	−4477(3)	96(1)
C(38)	3208(3)	7457(4)	−4117(3)	101(1)
C(39)	3643(3)	8199(3)	−4453(3)	90(1)
C(40)	4589(2)	8129(2)	−5193(2)	70(1)
C(41)	5050(3)	8896(2)	−5580(3)	85(1)
C(42)	5942(3)	8836(2)	−6285(3)	78(1)
C(43)	6436(2)	7970(2)	−6648(2)	61(1)
C(44)	8040(2)	8379(2)	−7919(2)	75(1)
C(45)	7893(6)	8943(5)	−8579(6)	81(2)
C(45′)	7558(6)	9169(5)	−8275(5)	75(2)
C(46)	8324(5)	9716(4)	−8858(4)	151(2)
C(47)	9247(5)	9683(4)	−8791(3)	130(2)
C(48)	9560(3)	9034(3)	−8287(3)	104(1)
C(49)	8969(2)	8377(3)	−7855(2)	81(1)
C(50)	7146(2)	5835(2)	−6140(2)	77(1)
C(51)	8220(3)	4968(3)	−8662(4)	122(2)
C(52)	9714(3)	5893(3)	−8223(4)	129(2)
C(53)	8798(4)	6688(4)	−9648(3)	148(2)
Si(3)	678(1)	6784(1)	4861(1)	80(1)
O(3	2895(1)	7603(1)	3671(1)	70(1)
C(61)	865(2)	8541(2)	5513(2)	60(1)
C(62)	1170(2)	7896(2)	4825(2)	62(1)
C(63)	1996(2)	8237(2)	3981(2)	62(1)
C(64)	2157(2)	9122(2)	4351(2)	59(1)
C(65)	2874(2)	9708(2)	3936(2)	64(1)
C(66)	3617(2)	9574(2)	3032(2)	77(1)
C(67)	4288(3)	10 167(3)	2680(3)	92(1)
C(68)	4271(3)	10 927(3)	3212(3)	97(1)

Table 6 (Continued)

Atom	x	y	z	U_{eq} [a]
C(69)	3583(3)	11 074(2)	4087(3)	86(1)
C(70)	2856(2)	10 487(2)	4475(2)	69(1)
C(71)	2124(3)	10 646(2)	5383(2)	74(1)
C(72)	1434(2)	10 075(2)	5764(2)	70(1)
C(73)	1467(2)	9295(2)	5242(2)	59(1)
C(74)	51(2)	8548(2)	6444(2)	64(1)
C(75)	224(4)	8617(4)	7278(4)	55(1)
C(76)	−538(5)	8612(5)	8140(5)	57(2)
C(75′)	−275(7)	8118(7)	7214(6)	101(2)
C(76′)	−463(7)	8119(7)	8109(7)	110(3)
C(77)	−1459(3)	8568(3)	8184(3)	108(1)
C(78)	−1676(3)	8714(3)	7394(3)	112(2)
C(79)	−924(2)	8718(3)	6528(2)	89(1)
C(80)	1661(3)	8385(3)	3131(2)	83(1)
C(81)	1719(7)	5903(7)	4231(7)	111(3)
C(81′)	1469(7)	6022(7)	3884(7)	107(3)
C(82)	402(4)	6294(3)	6076(3)	132(2)
C(83)	−512(3)	6949(3)	4638(4)	127(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

3. Experimental

For general experimental details see Ref. [5].

3.1. Ruthenium-catalysed coupling of 1-phenyl-2-trimethylsilylethyne with various aromatic ketones

3.1.1. 2-Methylacetophenone

2-Methylacetophenone (0.268 g, 2 mmol), 1-phenyl-2-trimethylsilylethyne (0.696 g, 4 mmol) and carbonyldihydrotris(triphenylphosphine)ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 22 h. Distillation (Kugelrohr) gave 1-(2-methyl-6-(1-phenyl-2-trimethylsilylethenyl)phenyl)ethanone (**6**) (0.6 g, 97%) as a yellow oil, b.p. 167°C (0.9 mmHg). v_{max} 1698 (C=O), 1598, 1468 (C=C), 1247, 835 (Si–C) cm^{-1}. δ_H − 0.040, s, 9H, SiMe$_3$(Z); 0.002, s, 9H, SiMe$_3$(E); 2.08, s, 3H, CH$_3$; 2.29, s, 3H, CH$_3$; 2.31, s, 3H, CH$_3$; 2.31, s, 3H, CH$_3$; 5.97, s, 1H, 2-C(Ph)=CH(E); 6.43, s, 1H, 2-C(Ph)=CH(Z); 6.96, dd, J = 7.28, 1.32 Hz, 1H, Ar-H; 7.12–7.36, m, 7H, Ar-H. δ_C − 0.57, SiMe$_3$(Z); 0.08, SiMe$_3$(E); 19, 5, ArCH$_3$; 31.6, COCH$_3$(Z); 32.0, COCH$_3$(E); 127.0, 127.1, 127.9, 128.06, 128.1, 128.4, 129.6, 129.9, 131.9, 135.7, 138.5, 141.6, 141.8, 142.3, 142.4, 154.4, 156.3, Ar-C; 205.7, (C=O)(E); 206.9, (C=O)(Z). m/z 308 (3, M$^+$), 235 (100, M − SiMe$_3$). Found: M$^+$ 308.1596. C$_{20}$H$_{24}$OSi Calc.: M 308.1596.

3.1.2. 1-(2-(((1,1-Dimethylethyl)dimethylsilyl)oxy)-phenyl)ethanone

1 - (2 - (((1,1 - Dimethylethyl)dimethylsilyl)oxy)phenyl)-ethanone (0.5 g, 2 mmol), 1-phenyl-2-trimethylsi-

lylethyne (1.044 g, 6 mmol) and carbonyldihydrotris-(triphenylphosphine)ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 49 h. Flash chromatography (silica gel, 20:1 hexanes–ether) followed by distillation (Kugelrohr) gave 1-(2-(((1,1-dimethylethyl)dimethylsilyl)oxy)-6-(1-phenyl-2-trimethylsilylethenyl)phenyl)-ethanone (**8**) (95%) as a colourless oil, b.p. 230°C (0.4 mmHg). ν_{max} 1701 (C=O), 1458, 1568 (C=C), 1275, 836 cm^{-1} (Si–C). δ_H − 0.07, 9H, SiMe$_3$; 0.19, 9H, SiMe$_2$; 0.94, s, 9H, CMe$_3$; 1.88, s, 3H, COCH$_3$(Z); 2.0, s, 3H, COCH$_3$(E); 5.94, s, 1H, 6-C(Ph)=CH(E); 6.24, s, 1H, 6-C(Ph)=CH(Z); 6.73, d, J = 8.1 Hz, 1H, H(5); 6.84, d, J = 8.1 Hz, 1H, H(3); 7.09–7.32, m, 6H, Ar-H. δ_C − 4.38, SiMe$_2$; − 0.80, SiMe$_3$; 17.9, CMe$_3$; 25.5, CMe$_3$; 31.7, COCH$_3$; 117.9, C(5); 122.7, C(3); 127.6, 128.9, 129.9, 134.4, 133.6, 142.3, 144.6, 151.5, 156.5 Ar-C; 205.2, COCH$_3$. m/z 424 (< 1, M$^+$), 351 (100, M − SiMe$_3$), 73 (48, SiMe$_3$). Found: M$^+$ 424.2255. C$_{25}$H$_{36}$O$_2$Si$_2$ Calc.: M 424.2253.

3.1.3. 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone

3,4-Dihydro-6-methoxy-1(2H)-naphthalenone (0.352 g, 2 mmol), 1-phenyl-2-trimethylsilylethyne (0.696 g, 4 mmol) and carbonyldihydrotris(triphenylphosphine-ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 23 h. Flash chromatography (silica gel, 4:1 hexanes–ether) gave 3,4-dihydro-6-methoxy-8-(1-phenyl-2-trimethylsilylethenyl)-1(2H)-naphthalenone (**10**) (0.652 g, 93%) as a yellow oil. ν_{max} 1677 (C=O), 1589 (C=C), 1247, 836 cm^{-1} (Si–C). δ_H − 0.152, s, 9H, SiMe$_3$(Z); 0.015, s, 9H, SiMe$_3$(E); 2.03, m, 6H, H(3) both isomers; 2.43, t, J = 6.8 Hz, 2H, H(2)(Z); 2.47, t, J = 6.8 Hz, 2H, H(2)(E); 2.90, t, J = 6.1 Hz, 2H, H(4)(E); 2.98, t, J = 6.3 Hz, 2H, H(4)(Z); 3.9, s, 3H, OMe(Z); 3.91, s, 3H, OMe(E); 5.70, s, 1H, 8-C(Ph)=CH(E); 6.21, s, 1H, 8-C(Ph)=CH(Z); 6.68, d, J = 2.4 Hz, 2H, H(5) or H(7); 6.78, d, J = 2.4 Hz, 2H, H(5) or H(7); 7.20–7.34, m, 10H, Ar-H. δ_C − 0.507, SiMe$_3$(Z); 0.106, SiMe$_3$(E); 22.6, C(3)

both isomers; 30.8, C(2)(E); 30.9, C(2)(Z); 39.4, C(4)(E); 39.6, C(4)(Z); 54.9, OMe both isomers; 111.3, C(5)(E); 112.2, C(5)(Z); 116.7, C(7)(E); 116.8, C(7)(Z); 123.7, 124.4, 124.7, 125.7, 126.7, 127.5, 128.4, 128.9, 141.9, 142.2, 145.5, 147.6, 149.8, 158.1, 160.2, 161.4, 161.5 Ar-C; 194.9, C(1)(Z); 195.4, C(1)(E). m/z 350 (< 1, M$^+$), 277 (100, M − SiMe$_3$). Found: M$^+$ 350.1703. C$_{22}$H$_{26}$O$_2$Si Calc.: M 350.1702.

3.1.4. Methyl 12-methoxy-7-oxopodocarpa-9,11,13-trien-19-oate

Methyl 12-methoxy-7-oxopodocarpa-9,11,13-trien-19-oate (0.632 g, 2 mmol), 1-phenyl-2-trimethylsi-

Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **32**

Atom	x	y	z	U_{eq} [a]
Si	1259(1)	3810(1)	1185(1)	52(1)
O(1)	3654(2)	1276(2)	2111(2)	116(1)
O(2)	3250(1)	4426(2)	3338(1)	81(1)
C(1)	3724(2)	234(3)	1916(2)	77(1)
C(2)	4463(2)	− 524(4)	2278(2)	108(1)
C(3)	4612(3)	− 1686(4)	1887(3)	141(2)
C(4)	3821(3)	− 2375(3)	1656(2)	106(1)
C(4A)	3141(2)	− 1614(2)	1217(2)	75(1)
C(5)	2541(2)	− 2156(3)	691(2)	87(1)
C(6)	1912(2)	− 1488(3)	282(2)	87(1)
C(7)	1861(2)	− 240(2)	397(2)	71(1)
C(8)	2446(2)	349(2)	922(1)	56(1)
C(8A)	3101(2)	− 341(2)	1338(1)	61(1)
C(9)	2344(2)	1715(2)	980(1)	54(1)
C(10)	1679(2)	2207(2)	1250(1)	56(1)
C(11)	3362(2)	5397(2)	3652(1)	58(1)
C(12)	4037(2)	5532(3)	4312(2)	88(1)
C(13)	4513(2)	6692(3)	4280(2)	99(1)
C(14)	3924(2)	7777(3)	4264(2)	77(1)
C(14A)	3125(2)	7650(2)	3699(1)	59(1)
C(15)	2667(2)	8691(2)	3449(2)	78(1)
C(16)	1968(2)	8615(2)	2911(2)	83(1)
C(17)	1702(2)	7484(2)	2622(2)	70(1)
C(18)	2128(1)	6421(2)	2865(1)	51(1)
C(18A)	2852(1)	6505(2)	3410(1)	50(1)
C(19)	1782(1)	5233(2)	2526(1)	49(1)
C(20)	1826(1)	4980(2)	1819(1)	52(1)
C(21)	1292(2)	4453(3)	241(1)	73(1)
C(22)	119(2)	3685(3)	1342(2)	71(1)
C(31)	2949(1)	2477(2)	610(2)	58(1)
C(32)	3395(2)	3433(2)	985(2)	74(1)
C(33)	3914(2)	4181(2)	603(2)	86(1)
C(34)	3976(2)	3949(3)	− 131(2)	89(1)
C(35)	3541(2)	3009(2)	− 502(2)	79(1)
C(36)	3033(2)	2263(2)	− 127(2)	66(1)
C(41)	1305(1)	4444(2)	2994(1)	53(1)
C(42)	673(2)	4930(3)	3361(2)	74(1)
C(43)	178(2)	4181(4)	3741(2)	95(1)
C(44)	324(2)	2953(4)	3775(2)	97(1)
C(45)	959(2)	2451(3)	3434(2)	87(1)
C(46)	1455(2)	3194(2)	3043(1)	67(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 7
Selected bond lengths (Å) for **24**

	Molecule 1	Molecule 2	Molecule 3
Si(1)–C(21)	1.859(4)	1.851(4)	1.859(9)
Si(1)–C(23)	1.861(4)	1.859(5)	1.855(9)
Si(1)–C(22)	1.862(3)	1.861(4)	1.893(3)
Si(1)–C(2)	1.880(3)	1.844(3)	1.883(3)
O(1)–C(3)	1.436(3)	1.423(3)	1.443(3)
C(1)–C(2)	1.356(3)	1.353(4)	1.354(4)
C(1)–C(13)	1.478(4)	1.478(4)	1.475(4)
C(1)–C(14)	1.482(4)	1.484(4)	1.489(4)
C(2)–C(3)	1.537(3)	1.536(4)	1.543(4)
C(3)–C(4)	1.520(3)	1.514(4)	1.526(4)
C(3)–C(20)	1.534(3)	1.528(4)	1.531(4)
C(4)–C(13)	1.374(4)	1.372(4)	1.378(4)

lylethyne (0.452 g, 2.6 mmol) and carbonyldihydro-tris(triphenylphosphine)-ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 20 h. Flash chromatography (silica gel, 4:1 hexanes–ether) gave methyl 12-methoxy-7-oxo-14-(1-phenyl-2-trimethylsi-lylethenyl)podocarpa-9,11,13-trien-19-oate (**14**) (0.928 g, 94%) as a yellow oil. v_{max} 1725 (C=O ester), 1675 (C=O ketone), 1587 (C=C), 1265, 862 (Si–C), 738 cm^{-1}. δ_H − 0.175, s, 3H, SiMe_3(Z); 0.012, s, 3H, SiMe_3(E); 1.06, s, 3H, H(20)(E); 1.12 and 1.14, s, 3H, H(20)(Z); 1.18, s, 3H, H(18)(E); 1.19 and 1.23, s, 3H, H(18)(Z), H(3 ax) underneath; 1.50–1.64, m, 2H, H(1 ax) both isomers; 1.67–1.76, 2H, H(2 eq) both isomers; 1.90–2.11, m, 4H, H(5), H(2 ax) both isomers; 2.29, t, $J = 12.5$ Hz, 3H, H(3 eq) both isomers, H(1 eq)(Z); 2.38, d, $J = 12.8$ Hz, 11H, H(3 eq)(Z); 2.65, dd, $J = 17.8, 3.9$ Hz, 1H, H(6 eq)(E); 2.75, dt, $J = 17.6, 4.4$ Hz, 1H, H(6 eq)(Z); 2.98–3.12, m, 2H, H(6 ax) both iso-mers; 3.66, s, 3H, 19-OMe(E); 3.67 and 3.69, s, 3H, 19-OMe(Z); 3.88 and 3.90, s, 3H, 12-OMe(Z); 3.91, s, 3H, 12-OMe(E); 5.49, s, 1H, 14-C(Ph)=CH(E); 6.09 and 6.11, s, 1H, 14-C(Ph)=CH(Z); 6.54, d, $J = 2.5$ Hz, 1H, H(13)(Z); 6.58, d, $J = 2.5$ Hz, 1H, H(13)(Z); 6.67, d, $J = 2.5$ Hz, 1H, H(13)(E); 6.96, d, $J = 2.5$ Hz, 1H, H(11)(E); 7.06, d, $J = 2.5$ Hz, 1H, H(11)(Z); 7.08, d, $J = 2.5$ Hz, 1H, H(11)(Z); 7.18–7.28, m 5H, Ar-H. δ_C − 0.4, SiMe_3(Z); 0.27, SiMe_3(E); 19.62, C(2)(E); 19.68, C(2)(Z); 21.4, H(20)(E); 21.44, H(20)(Z); 27.64, H(18)(E); 27.71 and 27.79 H(18)(Z); 37.2, C(3)(Z); 37.36, C(3)(E); 38.08, C(6)(E); 38.26, C(6)(Z); 38.72, C(1)(E); 39.04, C(1)(Z); 39.09 and 39.16, C(10)(Z); 39.23, C(10)(E); 43.8, C(4) both isomers; 49.34, C(5)(E); 49.44 and 49.64, C(5)(Z); 51.38, 19-OMe(E);

51.45, 19-OMe(Z); 55.3, 12-OMe both isomers; 108.9, C(11)(E); 110.02 and 110.07, C(11)(Z); 115.4, C(13)(E); 115.62 and 115.86, C(13)(Z); 122.47, C(8)(E); 123.13 and 123.49, C(8)(Z); 124.18 and 124.67, 14-C(Ph)=CH(Z); 125.95, 126.88, 126.92, 127.05, 127.76, Ar-CH; 128.80, 14-C(Ph)=CH(E); 129.2, Ar-CH; 142.15, 14-C(Ph)=CH($ipso$)(E); 142.19 and 142.47, 14-C(Ph)=CH($ipso$)(Z); 145.8, C(14)(Z); 149.9, C(14)(E); 157.6, C(9)(E); 157.86, C(9)(Z); 158.52 and 158.67, 14-C(Ph)=CH(Z); 160.7, 14-C(Ph)=CH(E); 162.2, C(12) both isomers; 176.9, C(19)(E); 177.0, C(19)(Z); 195.71 and 195.78, C(7)(Z); 196.55, C(7)(E). m/z 490 (< 1, M$^+$), 417 (100, M − SiMe$_3$). Found: M$^+$ 490.25315. C$_{30}$H$_{38}$O$_4$Si. Calc.: M 490.2539.

3.1.5. Methyl 13-acetyl-12-(((1,1-dimethylethyl)di-methylsilyl)oxy)podocarpa-8,11,13-trien-19-oate

Methyl 13-acetyl-12-(((1,1-dimethylethyl)dimethyl-silyl)oxy)podocarpa-8,11,13-trien-19-oate (0.888 g, 2 mmol), 1-phenyl-2-trimethylsilylethyne (10.44 g, 6 mmol) and carbonyldihydrotris(triphenylphosphine)-ruthenium(II) (0.110 g, 0.12 mmol) were refluxed in toluene (3 ml) for 26 h. Further carbonyldihydrotris-(triphenylphosphine)ruthenium(II) (0.110 g, 0.12 mmol) was added and refluxing continued for a further 43 h. Flash chromatography (silica gel, hexanes, then ben-zene) gave methyl 13-acetyl-12-(((1,1-dimethylethyl)-dimethylsilyl)oxy)-14-(1-phenyl-2-trimethylsilylethenyl)-podocarpa-8,11,13-trien-19-oate (**12**) (0.986 g, 79%) as a brown oil. v_{max} 1726 (C=O ester), 1702 (C=O ketone), 1248, 862, 839 cm^{-1} (Si–C). δ_H − 0.115 and − 0.109, s, 9H, SiMe_3(Z); − 0.016 and 0.011, s, 9H, SiMe_3(E); 0.160, 0.188, 0.192, 0.207, 0.216, 0.227, 0.235, 0.255, s, 6H, SiMe_2Bu; 0.963, 0.968, 0.976, 0.984, s, 9H, SiMe$_2$CMe_3; 1.01, 1.03, 1.04, 1.11, s, 3H, H(20; 1.17, 1.23, 1.27, s, 3H, H(18), H(3 ax) underneath; 1.30–1.46, m, 2H, H(5), H(1 ax); 1.53, d, $J = 9.3$ Hz, 1H, H(5); 1.64–1.72, m, 1H, H(2 eq); 1.73–1.88, m, 1H, H(6 ax); 2.04, 2.08, 2.11, s, 3H, 13-COCH_3; 1.96–2.30, m, 4H, H(2 ax), H(6 eq), H(1 eq), H(3 eq); 2.40, s, 3H, 13-COCH_3; 2.45–2.67, m, 1H, H(7 ax); 2.73–2.78, m, 1H, H(7 eq); 3.63 and 3.64, s, 3H, 19-OMe; 5.68, s, 1H, 14-C(Ph)=CH(E); 6.47 and 6.50, s, 1H, 14-C(Ph)=CH(Z); 6.68, s, 1H, H(11)(E); 6.76 and 6.28, s, 1H, H(11)(Z); 7.17–7.36, m, 5H, Ar-H. δ_C − 4.57, − 4.4, − 4.0, − 3.96, − 3.86, SiMe_2Bu; − 1.2 and − 1.1, SiMe_3(E); 0.88 and 0.2, SiMe_3(Z); 18.05, SiMe$_2$CMe_3; 20.0, 20.6, 20.8, 21.1, C(2), C(6); 22.9, H(20); 25.7, SiMe$_2$CMe_3; 28.3, H(18); 29.4, 29.7, 29.8, C(7); 31.9, 32.1, 32.3, 33.1, 13-COCH_3; 37.4, C(3); 38.7, 38.8, C(10); 39.4, 39.7, 39.9, C(1); 43.8, C(4); 51.1, 51.2, 19-OMe; 51.9, 52.2, 52.8, C(5); 115.2, C(11)(E); 115.5 and 115.8, C(11)(Z); 125.8, 126.0, 126.2, 126.5, 127.1, C(8); 127.5, 128.7, 129.3, 129.4, Ar-CH; 130.0 and 130.5, 14-C(Ph)=CH (Z); 132.2, 132.4, C(13); 133.8 and

Table 9
Selected bond lengths (Å) for **32**

Si–C(20)	1.865(2)
Si–C(22)	1.866(3)
Si–C(21)	1.867(3)
Si–C(10)	1.871(2)
O(1)–C(1)	1.203(3)
O(2)–C(11)	1.207(3)
C(1)–C(8A)	1.477(4)
C(1)–C(2)	1.505(4)
C(2)–C(3)	1.492(6)
C(3)–C(4)	1.469(6)
C(4)–C(4A)	1.498(4)
C(8)–C(9)	1.506(3)
C(9)–C(10)	1.333(3)
C(9)–C(31)	1.498(3)
C(11)–C(18A)	1.487(3)
C(11)–C(12)	1.498(3)
C(12)–C(13)	1.479(4)
C(13)–C(14)	1.503(4)
C(14)–C(14A)	1.519(4)
C(18)–C(19)	1.507(4)
C(19)–C(20)	1.329(3)
C(19)–C(41)	1.489(3)

134.4, 14-C(Ph)=CH(*E*); 138.7, 140.5, 141.7, 142.6, 149.3, 149.5, 149.6, 149.9, 150.2, Ar-*C*(quaternary); 155.4, 156.9, 14-*C*(Ph)=CH(*E*); 177.7, C(19); 203.5, 203.7, 204.9, 13-*C*OCH₃. *m/z* 618 (< 1, M⁺), 545 (100, M − SiMe₃). Found: M⁺ 618.35702. C₃₇H₄₄O₄Si₂ Calc.: M 618.35606.

3.1.6. 4-Methoxyacetophenone

4-Methoxyacetophenone (300 mg, 2 mmol), 1-phenyl-2-trimethylsilylethyne (0.365 g, 2.1 mmol) and carbonyldihydrotris(triphenylphosphine)ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 48 h. Flash chromatography (silica gel, 1:1 then 2:1 hexanes–benzene) gave (i) a mixture (330 mg) of *EE*, *ZZ*, *EZ* isomers (1.7/1/1.4) of 1-(4-methoxy-2,5-bis(1-phenyl-2-trimethylsilylethenyl)phenylethanone (**17**) as a brown oil. *ν*max 1693 (C=O), 1587 (C=C), 1245, 859, 838, cm⁻¹ (Si–C). *δ*H 0.004, s, 9H, SiMe₃(*EE*); 0.028, s, 9H, SiMe₃(*EZ*); 0.031, s, 9H, SiMe₃(*EZ*); 1.63, s, 3H, CO*Me*(*ZZ*); 1.73, s, 3H, CO*Me* (*EZ*); 1.83, s, 3H, CO*Me*(*EE*); 3.74, s, 3H, 4-O*Me*(*E*); 3.84, s, 3H, 4-O*Me*(*EZ*); 3.98, s, 3H, 4-O*Me*(*Z*); 5.96, s, 2H, 2,6-C(Ph)=C*H*(*E*); 5.98, s, 1H, 2-C(Ph)=C*H*(*EZ*); 6.34, s, 2H, 2,6-C(Ph)=C*H*(*Z*); 6.37, s, 1H, 6-C(Ph)=C*H*(*EZ*); 6.67, s, 2H, H(3,5)(*EE*); 6.76, d, *J* = 2.52 Hz, 1H, H(3)(*EZ*); 6.81, d, *J* = 2.52 Hz, 1H, H(5)(*EZ*); 6.95, bs, 1H, H(3,5)(*ZZ*); 7.22–7.04, m, 10H, Ar-*H* all isomers. *δ*C 0.073, SiMe₃(*ZZ*); 0.159, SiMe₃(*EE* and *EZ*); 0.365, SiMe₃(*EZ*); 30.7, COCH₃(*ZZ*); 31.3, COCH₃(*EZ*); 31.7, COCH₃(*EE*); 55.2, 4-OMe(*EE*); 55.3, 4-OMe(*EZ*); 55.4, 4-OMe(*ZZ*); 114.2, C(3,5)(*EE*); 114.7, C(3)(*EZ*); 115.3, C(5)(*EZ*); 116.1, C(3,5) (*ZZ*); 127.0, 127.2, 127.6, 127.7, 127.75, 128.9, 128.05, 128.3, 129.76, 129.83, Ar-*C*H all isomers; 130.7, 2,6-C(Ph)=CH)(*ZZ*); 131.3, 6-C(Ph)=CH)(*EZ*); 134.2, C(1)(*ZZ* and *EE*); 134.6, C(1)(*EZ*); 135.1, 2-C(Ph)=CH)(*EZ*); 135.15, 2,6-C(Ph)=CH)(*EE*); 141.22, C(2)(*EZ*); 141.97, 2-C(*Ph*)=CH)(*EE*); 142.06, 142.2, 142.16, Ar-C-(quaternary); 145.07, C(2,6)(*EE*); 145.6, C(6) 155.0, 6-*C*(Ph)=CH)(*EZ*); 155.0, 6-*C*(Ph)=CH)(*ZZ*); 155.8, 2,6-*C*(Ph)=CH)(*ZZ*); 156.5, 2,6-*C*(Ph)=CH)(*EE*); 156.6, 2-*C*(Ph)=CH)(*EZ*); 158.5, C(4)(*EE*); 158.7, C(4)(*EZ*); 159.2, C(4)(*ZZ*); 202.4, *C*OMe(*ZZ*); 204.4, *C*OMe-(*EZ*); 206.5, *C*OMe(*EE*); two quaternary carbon signals not detected. *m/z* 498 (1, M⁺), 425 (100, M − SiMe₃), 73 (55, SiMe₃). Found: M⁺ 498.2405. C₃₁H₃₈O₂Si₂ Calc.: M 498.2410; (ii) 1-(4-methoxy-2-(*Z*-1-phenyl-2-trimethylsilylethenyl)phenylethanone (**16**) (177 mg) as a brown oil. *ν*max 1681 (C=O), 1595, 1562 (C=C), 1235, 862, 847, cm⁻¹ (Si–C). *δ*H − 0.072, s, 9H, SiMe₃; 2.38, s, 3H, CO*Me*; 3.9, s, 3H, 4-OMe; 6.43, s, 1H, 2-C(Ph)=C*H*; 6.82, d, *J* = 2.4 Hz, 1H, H(3); 6.98, dd, *J* = 8.8, 2.4 Hz, 1H, H(5); 7.24–7.34, m, 5H, Ar-*H*; 7.87, d, *J* = 8.8 Hz, 1H, H(6). *δ*C − 0.42, SiMe₃; 29.0, COCH₃; 55.4, 4-OMe; 112.8, C(5); 117.6, C(3); 126.3, C(9), C(13); 127.6, C(*meta*); 127.9, 2-C(Ph)=CH; 128.1,

C(*ortho*), C(*para*); 130.9, C(1); 131.9, C(6); 141.9, 2-C(*Ph*)=CH(*ipso*).; 144.3, C(2); 156.6, 2-*C*(Ph)=CH; 161.8, C(4); 197.9, (C=O). *m/z* 324 (1, M⁺), 251 (100, M − SiMe₃). Found: M⁺ 324.1538. C₂₀H₂₄O₂Si Calc.: M 324.1545: (iii) a mixture (4/5) (56 mg) of the mono arylated *E* and *Z* isomers which was subjected to PLC (2:1 hexanes–benzene) to give 1-(4-methoxy-2-(*E*-1-phenyl-2-trimethylsilyl-ethenyl))phenylethanone (**16**) (16 mg) as a brown oil. *ν*max 1682 (C=O), 1597, 1562 (C=C), 1248, 855, 841, cm⁻¹ (Si–C). *δ*H − 0.013, s, 9H, SiMe₃; 2.35, s, 3H, CO*Me*; 3.81, s, 3H, 4-OMe; 5.86, s, 1H, 7=C*H*; 6.70, d, *J* = 2.4 Hz, 1H, H(3); 6.83, dd, *J* = 8.8, 2.4 Hz, 1H, H(5); 7.26–7.32, m, 5H, Ar-*H*; 7.50, d, *J* = 8.4 Hz, 1H, H(6). *δ*C − 0.24, SiMe₃; 29.5, COCH₃; 55.2, 4-OMe; 111.8, C(5); 116.0, C(3); 127.5, C(*ortho*); 129.3, C(*meta*); 130.0, C(*para*); 133.1, C(1); 134.7, 2-C(Ph)=CH or C(6); 141.8, 2-C(*Ph*)=CH(*ipso*); 147.2, C(2); 156.9, 2-*C*(Ph)=CH; 160.4, C(4); 202.1, (C=O) one Ar-*C*H not detected. *m/z* 324 (< 1, M⁺), 251(100, M − SiMe₃). Found: M⁺ 324.1540. C₂₀H₂₄O₂Si Calc.: M 324.1545.

3.1.7. 2-Acetylnaphthalene

2-Acetylnaphthalene (0.340 g, 2 mmol), 1-phenyl-2-trimethylsilylethyne (0.365 g, 2.1 mmol) and carbonyl-dihydrotris(triphenylphosphine)ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 48 h. Flash chromatography (silica gel, 2:1, 1:1 hexanes–benzene, then benzene) gave 2-acetyl-8-(1-phenyl-2-trimethylsilylethenyl)naphthalene (**21**) (519 mg, 75%) as a golden oil. *ν*max 1690 (C=O ketone), 1681 (C=O ketone), 1245, 858, 836 cm⁻¹ (Si–C). *δ*H − 0.29, s, 9H, SiMe₃(*Z*); 0.71, s, 9H, SiMe₃(*E*); 2.53, s, 3H, 2-COC*H*₃(*E*); 2.54, s, 3H, 2-COC*H*₃(*Z*); 6.04, s, 1H, 1-C(Ph)=C*H*(*E*); 6.95, s, 1H, 1-C(Ph)=C*H*(*Z*); 7.24–7.32, m, 3H, Ar-*H*; 7.42–7.48, m, 3H, Ar-*H*; 7.56, t, *J* = 7.16 Hz, 1H, Ar-*H*; 7.86–7.97, m, 3H, Ar-*H*; 8.04, d, *J* = 8.5 Hz, 1H, Ar-*H*(*Z*); 8.10, d, *J* = 8.24 Hz, 1H, Ar-*H*(*E*). *δ*C − 1.008, SiMe₃(*Z*); 0.276, SiMe₃(*E*); 30.4, 2-COCH₃(*Z*); 30.7, 2-COCH₃(*E*); 124.0, 125.1, 126.4, 126.8, 127.6, 127.9, 128.0, 128.2, 128.5, Ar-*C*H; 131.3, 1-C(Ph)=CH(*Z*); 132.8, 134.6, 136.1, Ar-*C*(quaternary); 136.9, 1-C(Ph)=C*H*(*E*); 139.6, 141.6, 152.2, Ar-*C*(quaternary); 201.4, 2-*C*OCH₃. *m/z* 344 (< 1, M⁺), 271 (100, M − SiMe₃). Found: M⁺ 344.15934. C₂₃H₂₄OSi Calc.: M 344.15964.

3.1.8. 1-Acetylnaphthalene

1-Acetylnaphthalene (0.340 g, 2 mmol), 1-phenyl-2-trimethylsilylethyne (0.365 g, 2.1 mmol) and carbonyl-dihydrotris(triphenylphosphine)ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 36 h. Flash chromatography (silica gel, hexanes, 9:1 hex-anes–ether) gave (i) 1-methyl-3-phenyl-1-*O*-trimethylsi-lylcyclopenta[*a*]-1*H*-naphthalene (**22**) (84 mg) as a brown oil. *ν*max 1435 (C=C), 1249 (Si–C), 1119 (Si–O),

1095 (C–O), 841 (Si–C), 824 (C–H, two adjacent hydrogens), 748 (C–H, four adjacent hydrogens), 696 cm^{-1} (C–H, five adjacent hydrogens). δ_H −0.125, 1-OSiMe$_3$; 1.84, 1-CH$_3$; 6.59, s, C(2); 7.43–7.55, m, H(7), H(meta), H(para); 7.58–7.62, m, 1H, H(8); 7.64, d, J = 8.4, 1H, H(4); 7.66–7.69, m, 2H, H(ortho); 7.86, d, J = 8.4 Hz, H(5); 7.94, d, J = 8.2 Hz, 1H, H(6); 8.40, d, J = 8.4 Hz, 1H, H(9). δ_H 1.28, 1-OSiMe$_3$; 27.2, 1-CH$_3$; 83.9, C(1); 119.1, C(4); 124.5, C(9); 124.8, C(7); 125.9, C(8); 127.5, C(ortho), 127.9, C(para); 128.5, C(5); 128.6, C(meta); 128.7, C(6); 128.8, C(9a); 132.8, C(5a); 135.2, 3-Ph(ipso); 137.4, C(3a); 140.7, C(2); 142.3, C(3); 145.5, C(9b). m/z 344 (100, M$^+$), 329 (40, M − 15), 277 (60), 73 (65, SiMe$_3$). Found: M$^+$ 344.15926. C$_{23}$H$_{24}$OSi Calc.: M 344.15964: (ii) a mixture of three compounds which was separated further by flash chromatography (1:1, 1:3 hexanes–benzene, then benzene) to give (a) a two-component mixture (312 mg) which was subjected to radial chromatography (10:1 hexanes–ether) to give: (b) 1-acetyl-2-(1-phenyl-2-trimethylsilylethenyl)naphthalene (**19**) (36 mg) as a colourless oil. v_{max} 1697 (C=O ketone), 1248, 862, 836 (Si–C), 750, (C–H, four adjacent hydrogens), 702 cm^{-1} (C–H, five adjacent hydrogens). δ_H −0.112 s, 3H, SiMe$_3$(Z); 0.021, s, 3H, SiMe$_3$(E); 2.29, s, 3H, COCH$_3$(Z); 2.53, s, 3H, COCH$_3$(E); 6.10, s, 1H, 2-C(Ph)=CH(E); 6.57, s, 1H, 2-C(Ph)=CH(Z); 7.18, d, J = 8.5 Hz, 1H, H(3)(E); 7.28–7.38, m, 5H, Ar-H; 7.51, td, J = 6.9, 1.4 Hz, 1H, H(6) or H(7); 7.54, td, J = 6.3, 1.1 Hz, 1H, H(6) or H(7); 7.74, d, J = 8.6 Hz, 1H, H(4); 7.82–7.85, m, 2H, H(5), H(8). δ_C −0.79, SiMe$_3$(Z); −0.27, SiMe$_3$(E); 32.34, COCH$_3$(Z); 32.76, COCH$_3$(E); 124.9, C(5) or C(8); 126.2, C(6) or C(7); 126.9, C(3); 127.1, C(6) or C(7); 127.9, C(ortho); 128.06, C(para); 128.11, C(5) or C(8); 128.2, C(8a); 128.4, C(4); 129.7, C(meta); 132.6, C(4a); 137.0, 2-C(Ph)=CH(E); 138.6, C(1); 139.6, C(2); 142.1, 2-C(Ph)=CH (ipso); 153.4, 2-C(Ph)=CH(Z); 155.9, 2-C(Ph)=CH(E); 206.7, 1-COCH$_3$(E). m/z 344 (4, M$^+$), 271 (100, M − SiMe$_3$). Found: M$^+$ 344.1596. C$_{23}$H$_{24}$OSi Calc.: M, 344.1596; (c) a mixture (159 mg) of (a) and (b); (d) 1-hydroxy-1-methyl-3-phenyl-2-trimethylsilylcyclopenta[a]-1H-naphthalene (**24**) (46 mg) as brown crystals m.p. 60–65°C. v_{max} 3559 (OH), 1247 (Si–C), 839 (Si–C), 823 (C–H 2 adjacent hydrogens), 750 (C–H 4 adjacent hydrogens), 702 (C–H 5 adjacent hydrogens) cm^{-1}. δ_H 0.15, s, 9H, 2-SiMe$_3$; 1.94, 1-CH$_3$; 2.00, bs, 1H, 1-OH; 7.08, d, J = 8.3, 1H, H(4); 7.35–7.38, m, 2H, H(ortho); 7.44–7.51, m, 4H, H(7), H(meta), H(para); 7.59, td, J = 8.4, 1.3 Hz, 1H, H(8); 7.56, d, J = 8.3, H(6); 7.91, d, J = 8.2 Hz, 1H, H(5); 8.46, d, J = 8.4 Hz, 1H, H(9). δ_C 0.90, 2-SiMe$_3$; 25.3, 1-CH$_3$; 88.9, C(1); 124.3, C(4); 124.9, C(9); 126.2, C(7); 127.6, C(8); 127.9, C(9a); 128.1, C(para), C(meta); 128.64, C(5); 128.88, C(ortho), 129.1, C(6); 133.0, C(5a); 136.9, 3-Ph(ipso); 140.2, C(3a); 146.0, C(9b);

152.68, 152.7, C(2), C(3). m/z 344 (100, M$^+$), 329 (20, M − 15), 313 (35, M − 31), 73 (90, SiMe$_3$). Found: M$^+$ 344.15978. C$_{23}$H$_{24}$OSi Calc.: M 344.15964: and (iii) 1-methyl-3-phenyl-1-hydroxycyclopenta[a]-1H-naphthalene (84 mg) as a brown oil. v_{max} 3354 (OH), 1514 (C=C), 1444 (C=C), 1072 (C–O), 822 (C–H, two adjacent hydrogens), 749 (C–H, four adjacent hydrogens), 697 cm^{-1} (C–H, five adjacent hydrogens). δ_H 1.87, 1-CH$_3$; 2.72, s, 1H, 1-OH; 6.49, s, C(2); 7.42–7.53, m, H(7), H(meta), H(para); 7.58–7.62, m, 1H, H(8); 7.64–7.67, m, 3H, H(4), H(ortho); 7.94, d, J = 8.2 Hz, H(5); 7.94, d, J = 8.2 Hz, 1H, H(6); 8.40, d, J = 8.4 Hz, 1H, H(9). δ_C 24.2, 1-CH$_3$; 82.5, C(1); 119.5, C(4); 124.2, C(9); 125.0, C(7); 126.4, C(8); 127.7, C(ortho), 128.1, C(para); 128.3, C(9a); 128.7, C(meta); 128.8, C(5); 129.0, C(6); 132.8, C(5a); 135.0, 3-Ph(ipso); 137.9, C(3a); 140.7, C(2); 142.5, C(3); 144.4, C(9b). m/z 272 (100, M$^+$), 257 (35, M − 15). Found: M$^+$ 272.11957. C$_{20}$H$_{16}$O Calc.: M 272.1201.

3.2. Ruthenium-catalysed coupling of dimethylbis-(2-phenylacetylene)silane with 3,4-dihydro-1(2H)-naphthalenone

3,4-Dihydro-1(2H)-naphthalenone (0.292 g, 2 mmol), dimethylbis(2-phenylacetylene)silane (0.674 g, 1.6 mmol) and carbonyldihydrotris(triphenylphosphine)-ruthenium(II) (0.110 g, 0.06 mmol) were refluxed in toluene (3 ml) for 26 h. Flash chromatography (4:1, 2:1 hexanes–ether) gave (i) 3,4-dihydro-8-(1-(2-(dimethyl-(phenylethynyl)silyl)phenylethenyl))-2(1H)-naphthalenone (**30**) (538 mg) as a brown oil. v_{max} 2247, 2157 (C≡C), 1685 (C=O), 1488 (C=C), 1250 (Si–C), 909, 848 (Si–C), 732 cm^{-1}. δ_H 0.12, s, 6H, SiMe$_2$(Z); 0.15, s, 6H, SiMe$_2$(Z); 0.33, s, 6H, SiMe$_2$(E); 2.03, t, J = 6.1 Hz, 2H, H(3); 2.50, t, J = 6.5 Hz, 2H, H(2); 2.94, t, J = 6.0 Hz, 2H, H(4); 5.91, s, 1H, 8-C(Ph)=CH(SiMe$_2$R) E); 6.38, s, 1H, 8-C(Ph)=CH(SiMe$_2$R) Z); 7.24–7.57, m, 23H, Ar-H. δ_C −0.31, SiMe$_2$ Z); 0.35, SiMe$_2$ E); 22.809, C(3) Z); 22.857, C(3) E); 30.5, C(2) E); 30.6, C(2) Z); 39.9, C(4) E); 40.0, C(4) Z); 93.7, C≡CPh(Z); 94.2, C≡CPh(E); 105.3, C≡CPh(Z); 105.6, C≡CPh(E); 121.4, 8-C(Ph)=CH(Z); 123.3, C≡CPh-(ipso)(Z); 123.34, C≡CPh(ipso)(E); 125.4, 8-C(Ph)=CH-(E); 126.3, 127.2, 127.4, 127.48, 127.9, 128.14, 128.2, 128.36, 128.4, 128.5, 129.0, 129.4, 130.1, 130.6, 131.1, 131.4, Ar-C; 131.9, C≡CPh(ortho)(Z); 132.0, C≡CPh(ortho)(E); 142.04, 142.6, 145.4, 145.6, 147.0, Ar-C(quaternary); 160.3, 8-C(Ph)=CH(Z); 162.4, 8-C(Ph)=CH(E); 196.8, C(1)(Z); 197.4, C(1)(E). m/z 406 (5, M$^+$), 247 (100, M-SiMe$_2$C≡CPh). Found: M$^+$ 406.17514. C$_{28}$H$_{26}$OSi Calc.: M 406.17529; (ii) a mixture (1/4.6) (42 mg) of an unidentified compound and 3,4-dihydro-8-(2-dimethylhydroxysilyl-1-phenyl-ethenyl)-2(1H)naphthalenone (**31**); (iii) 3,4-dihydro-8-(2-dimethylhydroxysilyl-1-phenylethenyl)-2(1H)-naph-

thalenone (**31**) (52 mg) as a brown oil. ν_{max} 3439 (OH), 1683 (C=O), 1467 (C=C), 1250, 848 (Si–C), 699 cm^{-1}. δ_H − 0.296, s, 6H, Si*Me*$_2$OH; 2.0–2.06, m, 2H, H(3); 2.44–2.50, m, 2H, H(2); 2.93, t, $J = 6.1$ Hz, 2H, H(4)(*Z*); 2.98, t, $J = 6.1$ Hz, 2H, H(4)(*E*); 5.49, s, 1H, 8-C(Ph)=C*H*(*E*); 6.18, s, 1H, 8-C(Ph)=C*H*(*Z*); 7.16–7.30, m, 7H, Ar-H; 7.42, t, $J = 7.5$ Hz, 1H, H(6). δ_C − 0.82, Si*Me*$_2$OH(*Z*); − 0.29, Si*Me*$_2$OH(*E*); 22.76, C(3)(*E*); 22.79, C(3)(*Z*); 30.44, C(2)(*Z*); 30.61, C(2) (*E*); 39.81, C(4)(*Z*); 40.07, C(4)(*E*); 125.0, 8-C(Ph)=CH; 131.8, C(6)(*E* and *Z*); 142.25, C(*Ph*)=CH(*ipso*)(*E*); 142.93, C(*Ph*)=CH(*ipso*)(*Z*); 143.2, C(8)(*Z*); 145.13, 145.19, C(4a)(*E* and *Z*); 147.5, C(8)(*E*); 157.6, 8-*C*(Ph)=CH(*Z*); 159.4, 8-*C*(Ph)=CH(*E*); 196.6, C(1)(*Z*); 197.3, C(1)(*E*). m/z 322 (< 1, M$^+$), 305 (100, M − OH), 247 (100, M − SiMe$_2$OH), 231 (45). Found: M$^+$ + H 323.1458. C$_{20}$H$_{23}$O$_2$Si Calc.: M + H 323.14673; (iv) a mixture (1/1.7, 37 mg) of 3,4-dihydro-8-(2-dimethylhydroxysilyl - 1 - phenylethenyl) - 2(1*H*)naphth - alenone (**31**) and bis (2-(3,4-dihydro-2(1*H*)-naph-thalenone)-2-phenylethenyl)dimethylsilyl (**32**); and (v) bis(2-(8-(3,4-dihydro-2(1*H*)-naphthalenone))-2-phenyl-ethenyl)dimethylsilane (**32**) (61 mg) as golden rods m.p. 140–141°C. ν_{max} 1683 (C=O), 1587 (C=C), 849 cm^{-1} (Si–C). δ_H 0.034, s, 6H, Si*Me*$_2$; 2.01, p, $J = 6.5$ Hz, 4H, H(3); 2.45, t, $J = 6.5$ Hz, 4H, H(2); 2.91, t, $J = 6.5$ Hz, 4H, H(4); 5.69, s, 2H, 8-C(Ph)=C*H*(*E*); 7.0, d, $J = 7.5$ Hz, 2H, H(7); 7.18, d, $J = 7.60$ Hz, 2H, H(5); 7.20–7.33, m, 10H, Ar-*H*; 7.40, t, $J = 7.5$ Hz, 2H, H(6). δ_C 0.71, Si*Me*$_2$R(*E*); 22.8, C(3); 30.4, C(2); 39.8, C(4); 126.8, C(*para*); 126.9, C(*ortho*); 127.8, C(5); 129.1, 8-C(Ph)=CH(*E*); 129.3, C(*meta*); 130.2, C(7); 130.5, C(8a); 131.7, C(6); 142.4, 8-C(*Ph*)=CH(*ipso*); 145.1, C(4a); 147.5, C(8); 159.6, 8-*C*(Ph)=CH(*ipso*); 197.3, C(1). m/z 553 (5, M$^+$ + H), 247 (70, M − SiMe$_2$R), 231 (100). Found: M$^+$ + H 553.25471. C$_{38}$H$_{37}$O$_2$Si Calc.: M + H 553.25314.

4. Supplementary material

Lists of hydrogen coordinates, anisotropic thermal parameters and full bond lengths and angles for complexes **24** and **32** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 120656 and CCDC 120657, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.-ac.uk).

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