Torquoselectivity in the Cationic Cyclopentannelation of (2*Z*)-Hexa-2,4,5-trienal Acetals

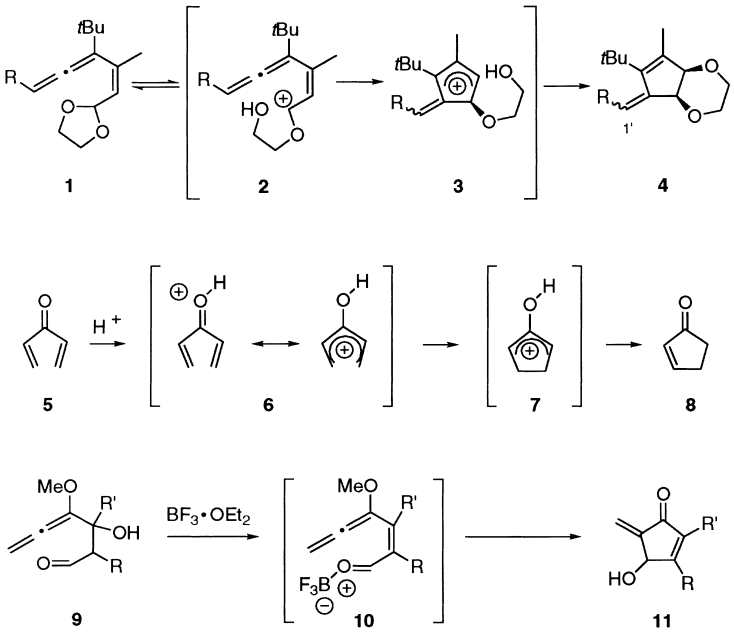
Beatriz Iglesias,[a] Angel R. de Lera,*[a] Jesús Rodríguez-Otero,[b] and Susana López[c]

Abstract: Inter- and intramolecular trapping experiments and density functional theory ab initio calculations for model systems are consistent with the acid-catalyzed rearrangement of 2-[(1*Z*)-hexa-1,3,4-trienyl]dioxolanes **1** to tetrahydroalkylidenecyclopenta-1,4-dioxins **4**; this involves the electrocyclic ring closure of substituted hydroxypentadienyl carbocations. The reaction, which may be considered a variant of the Nazarov cyclization, occurs much more readily than the standard Nazarov cyclization, proceeding rapidly even at $-30\,^{\circ}C$. B3LYP/6-31G**//HF/6-31G** calculations for models **36**, **38** and **40** predict that the two alternative conrotations at the cyclization termini are associated with activation energies differing by 0.55, 0.56 and 1.60 kcal mol^{-1}, respectively, in favour of the R-outwards rotation. This last value corresponds to an *E*-**41**/*Z*-**41** product ratio of >99:1 at $-60\,^{\circ}C$, in consonance with the experimental observation that divinylallene **1a** rearranges exclusively to *E*-**4a** at temperatures below $-30\,^{\circ}C$. At higher temperatures the torquoselectivity of the reaction **1a** $\rightarrow$ **4a** is masked by subsequent isomerization to the *Z* isomer, the greater stability of which is attributable to steric interaction between the substituent at the exocyclic double bond and the bulky neighbouring *t*Bu group in the *E* isomer.

Keywords: ab initio calculations · acetals · cyclizations · hexa-2,4,5-trienal acetals · selectivity

Introduction

We recently reported that treatment of 2-[(1*Z*)-hexa-1,3,4-trienyl]dioxolanes **1** with *p*-toluenesulfonic acid (*p*-TsOH) at room temperature affords tetrahydroalkylidenecyclopenta-1,4-dioxins **4** (Scheme 1).[1] If this process proceeds by the generation of the charged ring **3** via carbocation **2**, followed by trapping of the resident hydroxyl, then as the electrocyclic annelation of a (substituted) hydroxypentadienyl carbocation it may be regarded as a variant of the Nazarov cyclization, the standard version of which is currently understood to be the acid-catalysed 4π-e^- electrocyclic ring closure of divinyl ketones **5** to cyclopentenones **8** via 3-hydroxypentadienyl and hydroxycyclopentenyl cations (**6** and **7**, respectively; Scheme 1).[2]



Scheme 1. Ring closure reactions.

The variant **1** $\rightarrow$ **2** $\rightarrow$ **3** $\rightarrow$ **4** (in which the charge is developed at the 1-position of a 2,4-pentadiene system instead of the

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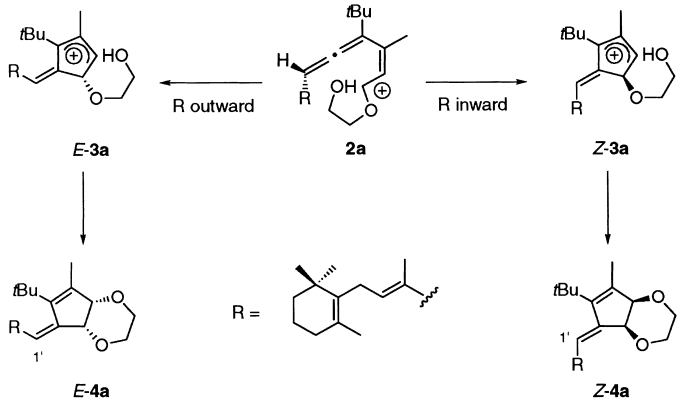
3-position of a 1,4-system, and the uncharged cyclization terminus forms part of an allene system[3–5]) has a precedent[6] in the Lewis acid induced cyclization of alcohols **9** to 4-hydroxy-5-methylenecyclopentenones **11** via the (2*Z*)-4-methoxyhexa-2,4,5-trienals **10** (Scheme 1).[7] However, being substituted at both termini, the conrotatory thermal cyclization of vinylallenes **1** can give rise to either *Z* or *E* isomers with respect to the exocyclic double bond of **4**, depending on whether the substituent R rotates inwards or outwards (Scheme 2). This therefore gives rise to the possibility of



Scheme 2. Reaction scheme for the formation of *Z*- and *E*-**4**, depending on whether the substituent R rotates inwards or outwards.

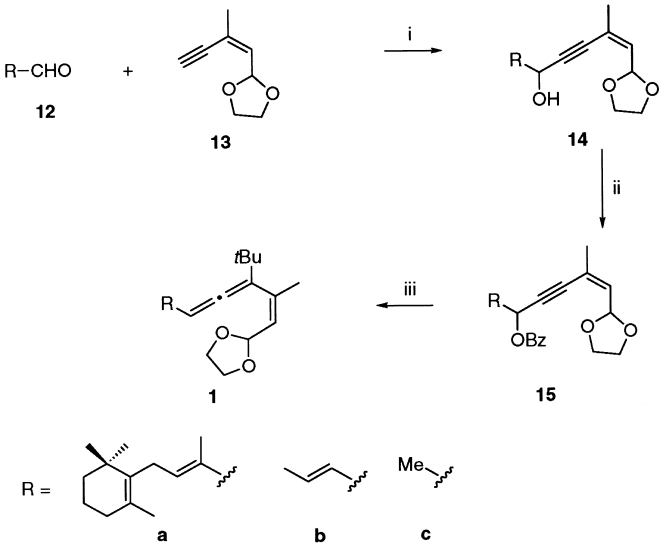
torquoselectivity,[8, 9] that is, diastereoselectivity that arises as a result of a preference for one or the other rotation mode. Of further synthetic interest, not explored in this work, is the fact that a selective mode of rotation in these systems would transfer the configuration of their axial chirality into a certain double bond configuration in a stereoconvergent way. By the same token, the use of enantiomerically pure allenes should result in the transfer of the allene axis chirality to the two newly generated stereocenters at the angular carbons of the dioxolane/cyclopentene ring during the torquoselective, electrocyclic ring closure. As a result, enantiomeric cyclized products **4a** should be obtained from the enantiomers of the starting (2*Z*)-hexa-2,4,5-trienal acetals **2a**.

In our earlier work[1] we observed very little torquoselectivity in the cyclization of **1a**, obtaining a 60:40 mixture of the 1′*E* and 1′*Z* isomers of **4a**. This was surprising in view of the total torquoselectivity of the related electrocyclic closure of vinylallenes to alkylidenecyclobutenes,[10] and it prompted us to further investigate the process. In this article we describe in full our work with vinylallenes **1**, including density functional theory (DFT) ab initio calculations for the analysis of the torquoselectivity of the electrocyclization process and the results of attempts to broaden the synthetic utility of the reaction by intermolecular trapping of the intermediate cation.

Abstract in Spanish: *Los experimentos de atrapado inter- e intramolecular y los cálculos ab initio DFT realizados con sistemas modelo concuerdan con un mecanismo de reordenamiento por catálisis ácida para la transformación de los 2-[(1Z)-hexa-1,3,4-trienil]dioxolanos **1** en las tetrahidroalquilidenciclopenta-1,4-dioxinas **4**, a través de la electrociclación de carbocationes hidroxipentadienílicos sustituidos intermedios. Esta reacción puede, por tanto, ser considerada como una variante de la ciclación de Nazarov, aunque transcurre a mayor velocidad que ésta última, incluso a −30 °C. Los cálculos B3LYP/6−31G**//HF/6−31G** realizados sobre los sistemas modelo **36**, **38** y **40** predicen que los dos posibles modos de conrotación alternativos están asociados a valores de energías de activación que difieren en 0.55, 0.56 y 1.60 kcal mol^{-1}, respectivamente, a favor del modo de rotación R-hacia afuera. Este último valor corresponde a una relación de productos E-**41**/Z-**41** de >99:1 a −60 °C, lo que corrobora la observación experimental de que el divinilaleno **1a** se transforma únicamente en E-**4a** a temperaturas inferiores a −30 °C. A temperaturas más elevadas la torqueselectividad de la reacción **1a** → **4a** se ve enmascarada por la posterior isomerización del producto al isómero Z, cuya mayor estabilidad se atribuye a la interacción estérica entre el sustituyente sobre el doble enlace exocíclico y el voluminoso grupo tBu vecino en el isómero E.*

Results and Discussion

Preparation of vinylallene acetals 1: A versatile approach to the required vinylallenes that is based on the displacement of propargyl benzoates by cuprates has been described elsewhere.[10b] It proceeds uneventfully provided care is taken to prevent propargyl and allenyl derivatives from encountering acidic conditions during work-up and purification. With these precautions, the protected enynal **13**[11a] was deprotonated with *n*BuLi and then coupled to aldehydes **12a–c**[11b] to afford propargyl alcohols **14a–c** (Scheme 3). Benzoates **15a–c** were prepared by quenching the alkoxide derivatives of **14a–c** with benzoyl chloride, and were then treated with the cuprate obtained upon treatment of *t*BuLi (2 mol equiv) with CuCN. This afforded the *tert*-butyl-substituted vinylallenes **1a–c** in good overall yields, presumably through a regioselective S_N2' displacement reaction.



Scheme 3. i) *n*BuLi, THF, −78 °C, 1 h; 25 °C, 1 h; ii) *n*BuLi, BzCl, THF, −78 °C to 25 °C in 2 h; iii) *t*BuLi, CuCN, Et_2O, −78 °C, 1 h; 0 °C, 1 h.

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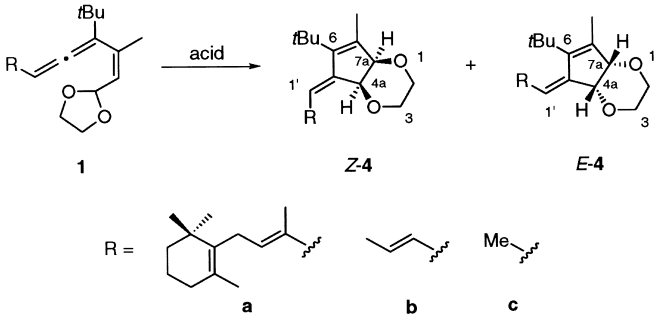
Cyclization of vinylallene acetals 1: When acetals **1a–c** were cyclized under deprotection/activation conditions,[12] which involved a variety of Brønsted or Lewis acids in solution or linked to insoluble polymers (Scheme 4), best yields were



Scheme 4. Reaction scheme for the cyclization of acetals **1a–c** under deprotection/activation conditions.

obtained using the Brønsted acid *p*-TsOH,[13] the hard Lewis acid $FeCl_3 \cdot SiO_2$,[14] $LiBF_4$ (thought to act by generation of the Lewis acid $B(OH)_3$ and the nucleophile F^-)[15] and the soft Lewis acids $LiClO_4$ (in ether)[16] and $PdCl_2(CH_3CN)_2$[17] (Table 1).[18] The *Z* and *E* products of these reactions were separated chromatographically and identified by ^1H and

Table 1. Cationic cyclopentannelation of **1a–c**.

Acetal	Acid[a]	Product	*Z*/*E* ratio[b]	*Z*/*E* ratio[c]	Yield [%][d]
1a	*p*-TsOH[13]	**4a**	42:58	> 99:1	99
	$FeCl_3 \cdot SiO_2$[14]		> 99:1		96
	$LiBF_4$[15]		66:34	66:34	99
	$LiClO_4$[16]		> 99:1		92
	$PdCl_2(CH_3CN)_2$[17]		> 99:1		99
1b	*p*-TsOH[13]	**4b**	35:65	25:75	99
	$FeCl_3 \cdot SiO_2$[14]		48:52	80:20	99
	$LiBF_4$[15]		43:57	45:55	96
	$LiClO_4$[16]	NR[e]			
	$PdCl_2(CH_3CN)_2$[17]		80:20	> 99:1	97
1c	*p*-TsOH[13]	**4c**	35:65	25:75	50
	$FeCl_3 \cdot SiO_2$[14]		42:58	50:50	85
	$LiBF_4$[15]		42:58	34:66	55
	$LiClO_4$[16]		36:64	32:68	65
	$PdCl_2(CH_3CN)_2$[17]		45:55	50:50	39

[a] Reaction conditions: *p*-TsOH, 0.1 mol equiv, acetone/H_2O; $FeCl_3 \cdot SiO_2$, 1.3 mol equiv, $CHCl_3$; $LiBF_4$, 1.0 mol equiv, CH_3CN (2% H_2O); $LiClO_4$, 1.5 mol equiv, Et_2O; $PdCl_2(CH_3CN)_2$, 0.2 mol equiv, acetone/H_2O. All reactions proceeded for 30 min at 25 °C except where otherwise stated. All experiments were performed in triplicate. [b] Isomer ratio determined by weighing the purified products. [c] Isomer ratio after 46 h at 25 °C, determined by integration of the ^1H NMR spectra. [d] Purified products. [e] NR, no reaction.

^{13}C NMR spectroscopy. Initial elucidation of the structures of *Z*- and *E*-**4a–c** (obtained by using *p*-TsOH for deprotection/activation) was based on the replacement of the acetal and vicinal vinyl proton signals (which for **1a** lie at $\delta = 5.41$ and 5.31, respectively) by signals in the region $\delta = 4.0–4.5$ region suggestive of a tetrahydro-1,4-dioxin,[19] on the appearance of ^{13}C NMR signals for ring-fusing tertiary carbons in the region $\delta = 72.0–80.0$[19c] and on the difference, between one product and the other, in the chemical shift of one of these signals ($\delta = 74.5$ and 78.7 for **4a**, $\delta = 72.1$ and 77.9 for **4b**, and $\delta = 71.9$ and 78.5 for **4c**). This difference in chemical shift was interpreted as being due to the shielding of C4a by the allyl substituent through steric compression in the *Z* isomer but not in the *E* isomer (γ-effect).[20] The γ-effect was also assumed to be responsible for the signal of the exocyclic allyl methyl group which lies at higher field in the spectrum of *Z*-**4c** than in that of *E*-**4c**, at $\delta = 13.4$ versus $\delta = 17.7$. The structures were further confirmed by the results of NOE experiments; enhancement of absorption by the exocyclic vinyl proton upon saturation of the *t*Bu substituent was observed in the products tentatively identified as *Z* isomers but not in the *E* isomers.

With *p*-TsOH as deprotection/activation agent, the product of reaction of **1a** for 30 min at 25 °C (hereinafter, "standard conditions") was an almost quantitative yield of a 42:58 mixture of the *Z* and *E* isomers (Table 1). The contrast between this ratio and the much greater torquoselectivity of the analogous processes for four-membered rings,[10] and the finding that $LiBF_4$, $FeCl_3 \cdot SiO_2$, $LiClO_4$ and $PdCl_2(CH_3CN)_2$ all favoured the *Z* rather than the *E* isomer under standard conditions (the latter three affording the *Z* isomer almost exclusively; see Table 1), suggested that the true torquoselectivity of the cyclization process might be being masked by subsequent isomerization. To investigate this possibility **1a** was treated with *p*-TsOH in [D_6]acetone/D_2O at −60 °C, and ^1H NMR spectra were run every 20 min as the temperature was increased stepwise to 0 °C in 10 °C intervals, and finally to 25 °C. Between −60 °C and −40 °C there was a significant build-up of *E*-**4a**, and no significant amount of the *Z* isomer had appeared even when all **1a** had been consumed (after 20 min at −30 °C). At room temperature, however, *Z*-**4a** was formed at the expense of the *E* isomer, *Z*/*E* ratios of 55:45, 66:34, 75:25, 91:9 and 99:1 being estimated from the spectra run after 65, 113, 161, 257 and 400 h respectively. It was concluded that the *Z* isomer is thermodynamically more stable than the *E* isomer, and that under the standard reaction conditions the initial cyclization product *E*-**4a** had undergone partial isomerization to the more stable form. Furthermore, the involvement of the acid in the isomerization process was shown by the results of separate experiments carried out at 25 °C with pure *E*-**4a**; this substrate was recovered unaltered after 48 h when stirred in acetone/water, but was cleanly converted to the *Z* isomer in 46 h when *p*-TsOH was added to the reaction medium. At the same temperature, stirring in hexane with a catalytic amount of iodine also brought about total isomerization (within 30 min), as it does with other polyenes,[21] whilst stirring in hexane for 2 h permited recovery of unaltered *E*-**4a**. Finally, it was found that the extent of isomerization might be limited by the nature of the acid; whereas the 66:34 *Z*/*E* ratio obtained with $LiBF_4$ in CH_3CN/water under standard conditions was unchanged after stirring for 46 h (Table 1), total isomerization was achieved by stirring for a further 15 h after addition of a catalytic amount (0.2 mol equivalents) of the soft Lewis acid Pd^{II}.

The results obtained with the simpler divinylallene **1b** were more complex. Firstly, there was no reaction with $LiClO_4$, a fact that seems unlikely to be totally due to the attenuation of the Lewis acidity of Li^+ by complexation with the solvent and

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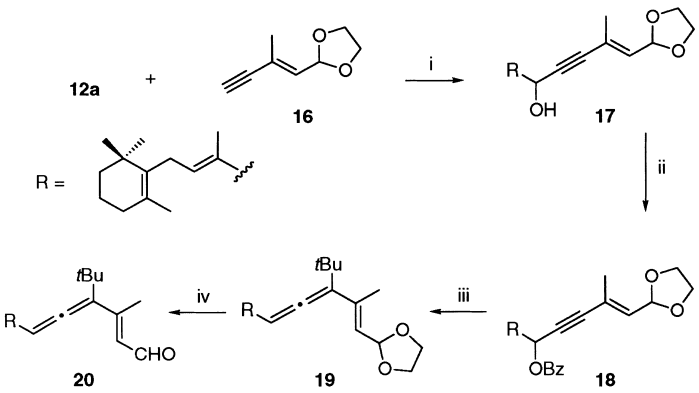
the counterion.[22] Secondly, prolonged exposure to the acid increased the *Z*/*E* ratio as expected when Pd^{II} and $FeCl_3 \cdot SiO_2$ were used (to >99:1 and 80:20, respectively), but prolonged exposure to *p*-TsOH or $LiBF_4$ did not significantly alter the *Z*/*E* ratio. Furthermore, treatment of pure *E*-**4b** with *p*-TsOH in acetone/water for 48 h at 25 °C gave a 25:75 *Z*/*E* ratio (together with unidentified minor products). When **1b** was stirred at −60 °C in [D_6]acetone/D_2O with a catalytic amount of *p*-TsOH, the *Z*/*E* ratio obtained after 30 min was 35:65 (effectively the same as that obtained under the standard conditions); this suggests incomplete torquoselectivity. Upon progressively raising the temperature, compound **1b** was consumed before −30 °C was reached; at −30 °C signals attributed to the deprotected aldehyde were detected, but at no temperature did they ever account for more than 15% of the product mixture. In summary, the cyclization of **1b** to **4b** appeared to be incompletely torquoselective, and subsequent equilibration appeared to depend on the nature of the acid present in the medium.

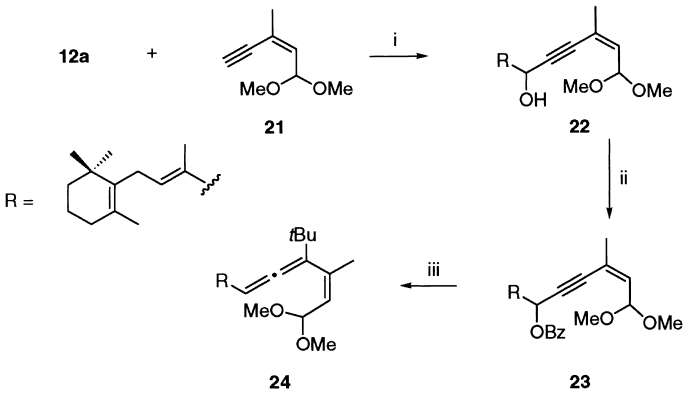
The results obtained with **1c** were inconclusive because the yield of **4c** was always significantly less than 100% due to its volatility (Table 1). The *Z*/*E* ratio was slightly less than unity for all the reagents used under standard conditions, and was essentially unaltered by prolonged exposure to the reagent up to 46 h (Table 1). Pure *E*-**4c** and pure *Z*-**4c** were both unaffected by 48 h treatment with *p*-TsOH in acetone/water at 25 °C. As in the case of **1b**, treatment of **1c** with *p*-TsOH in [D_6]acetone/D_2O at low temperature (−80 °C) rapidly gave a 35:65 *Z*/*E* mixture of **4c** (within 15 min); at −40 °C all **1c** had been consumed, but the 35:65 *Z*/*E* ratio remained essentially unaltered even after 46 h at 25 °C.

Reaction of (2*E*)-divinylallene 19: As expected, the 2*Z* geometry of the starting vinylallenes is essential for cyclization to proceed: when the 2*E* isomer **19** was prepared as shown in Scheme 5 and then subjected to the standard conditions listed in Table 1, the octa-2,4,5,7-tetraenal **20**[10b] was obtained cleanly in quantitative yield in all cases.

Cyclization of (2*Z*)-octa-2,4,5,7-tetraenal dimethyl acetal 24: To investigate whether an analogue of cation **3** could be trapped by an external nucleophile (which would provide both support for the assumed mechanism and broaden the synthetic potential of the reaction), we prepared the dimethyl acetal **24**, by using the same steps as for the dioxolane analogue (Scheme 6). Compound **24** was chosen because cleavage of one of the MeO-C1 bonds during generation of the carbocation under acidic conditions would eliminate both competition from a resident nucleophile and the need for addition of a nucleophilic reagent to the medium, since the methanol formed would itself act as an external nucleophile.



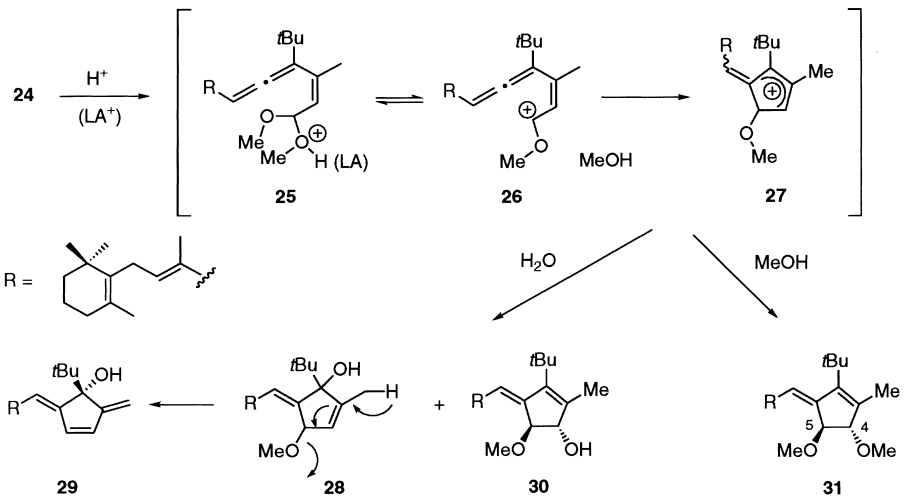
Scheme 5. i) *n*BuLi, THF, −78 °C, 1 h; 25 °C, 1 h; ii) *n*BuLi, BzCl, THF, −78 °C to 25 °C in 2 h; iii) *t*BuLi, CuCN, Et_2O, −78 °C, 1 h; 0 °C, 1 h; iv) *p*-TsOH, acetone/H_2O, 25 °C, 30 min.



Scheme 6. i) *n*BuLi, THF, −78 °C, 1 h; 25 °C, 1 h; ii) *n*BuLi, BzCl, THF, −78 °C to 25 °C in 2 h; iii) *t*BuLi, CuCN, Et_2O, −78 °C, 1 h; 0 °C, 1 h.

It was envisaged that the methanol produced as described above would trap cation **27** to afford compound **31**, an analogue of **4a** (Scheme 7). In the event, however, treatment of **24** under the conditions listed in Table 2 led to complex mixtures from which compounds **29**, **30** and **31** were isolated in yields listed in Table 2.[23]

Identification of **31** followed from the correspondence between its ^1H NMR signals and those of **4a**, and the *trans*



Scheme 7. Reaction scheme for the formation of compounds **28**–**31**.

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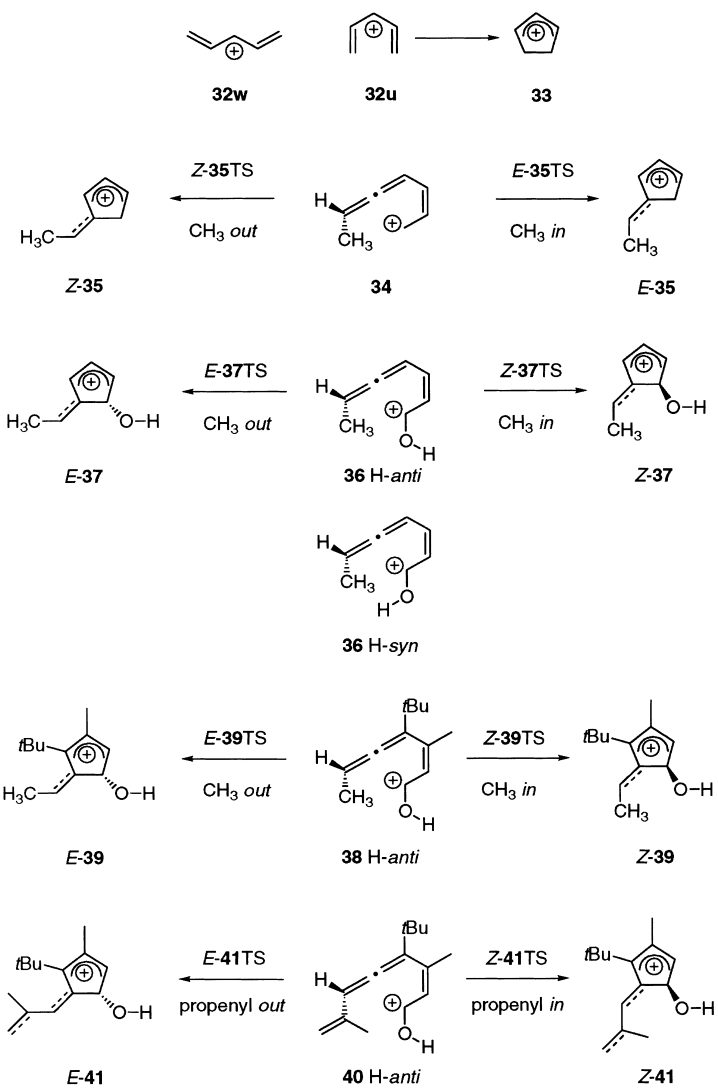
Table 2. Cyclization of dimethyl acetal **24**.

Reaction conditions	**29** [%]	**30** [%]	**31** [%]
p-TsOH (0.1 equiv), acetone, H_2O (32 equiv), 25 °C, 30 min	51	27	–
$LiBF_4$ (1.0 equiv) 4% H_2O in CH_3CN, 25 °C, 1 h	–	5–16	21
$FeCl_3 \cdot SiO_2$ (2.0 equiv) 0% MeOH in $CHCl_3$, 25 °C, 2 h	–	–	31
$PdCl_2(CH_3CN)_2$ (0.2 equiv) 10% MeOH in acetone, 25 °C, 2 h	–	–	40

arrangement of the methoxy groups was deduced from the negligible coupling constant between H4 and H5 of the alkylidenecyclopentene ring (cf. 4.2 Hz for **4a**); this corresponded to the same O-C-C-O angle as predicted by MMX calculations,[24] 109.5° (36.1° for the *cis* isomer). The structure of **30** was determined by analogous reasoning, together with an NOE experiment that confirmed the position of the methoxy group and the geometry of the side chain relative to the exocyclic double bond. Identification of **29** was based on its ^{1}H NMR spectrum [which shows signals for the exocyclic methylene at $\delta = 5.00$ and 5.09, and additional doublets for the double bond of the cyclopentene ring at $\delta = 6.32$ and 6.87 ($J =$ 6.0 Hz)], on the ^{13}C NMR signal for a bis-allyl tertiary alcohol at $\delta = 85.5$ and on a NOE experiment that confirmed the geometry at the exocyclic double bond and the connectivity shown in Scheme 7.

The production of compound **30** when water is present in the medium is attributable to direct competition between MeOH and water for the electron-deficient positions of cation **27**. Under the same conditions, compound **29** could arise through attack by water at the *t*Bu terminus of the allyl system, followed by elimination of MeOH from the resulting alcohol, **28** (Scheme 7). However, attempts to increase yields of **29** and **30** by increasing the water content of the medium were unsuccessful.[25]

Ab initio calculations: We sought the origin of the facility and torquoselectivity of the above reactions by using Gaussian 94 programs[26] to perform density functional calculations of the cyclization of successively more complete models of cation **2**, all with the charge at one cyclization terminus and an allene at the other (Scheme 8). The geometries, energies and normal-mode vibrational frequencies of the starting cations, the *E* and *Z* products and the corresponding transition structures were computed by using the hybrid density functional method Becke3LYP.[27–30] Entropies and free energies of reaction were calculated by using the Gaussian 94 vibrational analysis program (vibrational frequencies were scaled by a factor of 0.9181 for thermochemical analysis[31]). The density functional method was chosen in view of the previous successful application of density functional theory (DFT)[27] to the description of the transition structures of other pericyclic reactions,[32] and of previous DFT ab initio calculations for the Nazarov cyclizations of cation **6** (Scheme 1), of the dication analogue with a diprotonated oxygen and of 1-phenyl-2-propen-1-ones.[33]



Scheme 8. Models for cation **2** used in DFT calculations.

We began by investigating the cyclization of the s-*cis*-2,3,5-heptatrienyl cation **34** so as to allow comparison with results[33] for cyclization of **32**, an unsubstituted pentadienyl cation with the charge on the central carbon. The s-*cis* conformer of **34** was chosen as the starting structure because, although the most stable conformer of **32** is the w-shaped **32w** rather than the u-shaped **32u**,[34] it is the u-shaped series that are the direct substrates for cyclization. After optimizing the geometry of **34**, we searched for the transition structures *E*-**35**TS and *Z*-**35**TS that led to the ethylidenecyclopentenyl cations *E*-**35** and *Z*-**35**. Table 3 lists the corresponding energies, the distance between the cyclization termini in each structure, the energies of activation required to attain each transition structure and the absolute value of the difference between these energies of activation, together with analogous data for the other cyclizations investigated in this work and for the transition states reported for the electrocyclizations of **32u** to **33**[33] and of **6** to **7**.[33, 34a] The results for the process **34** → **35** agree with the latter in predicting a rather early transition state; *E*-**35**TS and *Z*-**35**TS show only 42% of the total shortening of the distance between the termini. Moreover, both the kinetic and the thermodynamic selectivities of

Table 3. Total energies and distances between cyclization termini of vinylallenium cations **34**, **36**, **38** and **40**, their cyclization products *E*-**35**/*Z*-**35**, *E*-**37**/*Z*-**37**, *E*-**39**/*Z*-**39** and *E*-**41**/*Z*-**41**, and the transition structures of the alternative conrotatory processes, with the corresponding activaction energies and the absolute difference $|\Delta Ea|$ between these last. Non-allenyl systems (**33**TS and **7**TS) are also included for comparison.

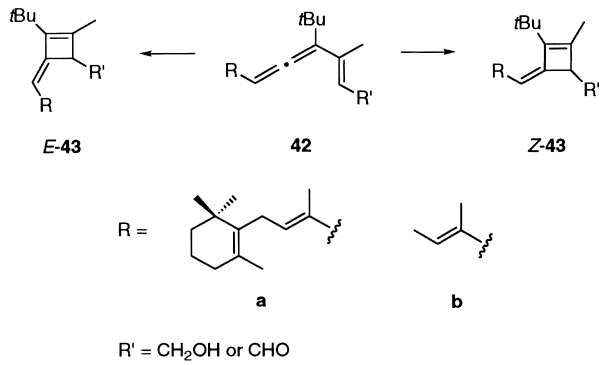
Structure	Computational Level[a]	Total Energies [a.u.]	r_{C-C} [Å]	Ea [kcal mol^{-1}]	$\|\Delta Ea\|$ [kcal mol^{-1}]
33TS[3]	A		2.31	5.0	
7TS[33]	A		2.11	18.89	
34	A	– 271.80721	3.06		
***E*-35TS**	A	– 271.80141	2.40	3.64	0.49
***Z*-35TS**	A	– 271.80220	2.41	3.15	
***E*-35**	A	– 271.87294	1.51		
***Z*-35**	A	– 271.87106	1.51		
36	A	– 347.04837	3.20		
***E*-37TS**	A	– 347.03583	2.14	7.86	0.55
***Z*-37TS**	A	– 347.03495	2.15	8.41	
***E*-37**	A	– 347.06692	1.53		
***Z*-37**	A	– 347.06925	1.53		
38	B	– 543.65490	3.03		
***E*-39TS**	B	– 543.64964	2.08	2.42	0.56
***Z*-39TS**	B	– 543.64870	2.09	2.98	
***E*-39**	B	– 543.67061	1.53		
***Z*-39**	B	– 543.67969	1.52		
40	B	– 621.05920	3.04		
***E*-41TS**	B	– 621.05558	2.07	2.12	1.60
***Z*-41TS**	B	– 621.05298	2.10	3.72	
***E*-41**	B	– 621.07334	1.54		
***Z*-41**	B	– 621.08699	1.52		

[a] A, B3LYP/6 – 31G*; B, B3LYP/6 – 31G**.

34 → **35** are of the same sign as those observed experimentally for **1** → **4**, the R-inward rotation having a higher activation energy but leading to a more stable product than the R-outward rotation. The activation energies for **34** → **35** (3.15 kcal mol^{-1} **34** → *Z*-**35** and 3.64 kcal mol^{-1} for **34** → *E*-**35**) are similar to that reported for **32u** → **33** (5.0 kcal mol^{-1})[33] and, as for **32u** → **33**, they are much lower than values calculated for the standard Nazarov cyclization **6** → **7** (18.89 kcal mol^{-1} according to DFT/6-31G*[33] calculations and 15.9 kcal mol^{-1} according to MP2/6-31G*).[34, 35]

The large energy of activation of **6** → **7** relative to **32u** → **33** is attributed to stabilization of the cationic centre of **6** by the electron-donating hydroxyl oxygen.[33] To investigate the effect of the analogous oxygen in vinylallenes **2**, we performed calculations for the process **36** → **37** after optimizing the starting structure (the conformation with the O–H bond *anti* to the forming C–C bond, denoted in Scheme 8 as **36** H-*anti*, which was 0.51 kcal mol^{-1} more stable than the conformation with O–H *syn* to the forming bond). As expected, the activation energies were higher than for **34** → **35** (Table 3), but they were still about 10 kcal mol^{-1} less than for **6** → **7**,[36] possibly because the linear allene carbon of the vinylallenes offers less steric hindrance to bond formation than the sp^2 terminal carbons of **6**. Also, in keeping with the stabilization of the starting cation, the transition state was attained later than for **34** → **35**, when bond formation was already about 62% complete (cf. r_{C-C} = 2.14 Å; 2.11 Å for **7**-TS at the B3LYP/6-31G* level[33]).

In the electrocyclization of (2*E*)-vinylallenes to alkylidenecyclobutenes,[10] R-inward rotation is favoured when, as in vinylallenes **1**, R is subject to steric interaction with a *tert*-butyl group adjacent to the cyclization terminus (Scheme 9; the experimental *Z*-**43a**/*E*-**43a** ratio is 17:83 when R′ = CH_2OH and < 1:99 when R′ = CHO). Calculations for the cyclization of **38**, which likewise bears a *tert*-butyl group in this



Scheme 9. Reaction scheme for the cyclization of **42**.

position (and also an adjacent methyl, making it identical to **2c** except for the smaller substituent at the charged terminus) showed stabilization of the product of R-inward rotation relative to the R-outward product, *Z*-**39** being 5.7 kcal mol^{-1} more stable than *E*-**39**, whereas *Z*-**37** is only 1.5 kcal mol^{-1} more stable than *E*-**37**. Thus the presence of the *tert*-butyl and methyl groups affords the R-inward product a thermodynamic advantage. It also lowers the activation energies of both conrotations relative to the process **36** → **37**, possibly because steric interaction between the *tert*-butyl and the neighbouring methyl forces the cyclization termini closer together (3.03 Å in **38** versus 3.20 Å in **36**). However, in the case of process **38** → **39** the barrier to R-inward rotation at 25 °C is 0.56 kcal mol^{-1} higher than the barrier to R-outward rotation; this corresponds to a *Z*/*E* ratio of 28:72, which is close to the ratio of 35:65 observed experimentally for cyclization of **1c** to **4c**. Changing the temperature had little effect, and in any case had very similar effects on the R-inward and R-outward processes (Table 4 lists ZPVE values and thermal energies at 25 °C and – 60 °C, and Table 5 contains enthalpies of reaction and energies of activation at 25 °C, – 60 °C and 0 K).

Table 4. Relative energies, ZPVE and thermal energies for vinylallenylium cations **38** and **40**, their alternative cyclization products *E*-**39**/*Z*-**39** and *E*-**41**/*Z*-**41**, and the transition structures of the corresponding conrotatory processes.[a]

Structure	E[b]	ZPE[c]	E_{th} (25 °C)[c]	E_{th} (– 60 °C)[c]
38	0.00	173.25	10.73	6.07
***E*-39TS**	3.30	173.01	9.50	5.61
***Z*-39TS**	3.89	173.00	9.48	5.59
***E*-39**	– 9.86	174.88	9.35	5.50
***Z*-39**	– 15.56	174.95	9.41	5.56
40	0.00	193.85	12.07	6.80
***E*-41TS**	2.27	193.74	11.44	6.35
***Z*-41TS**	3.90	193.79	11.35	6.27
***E*-41**	– 8.87	195.36	11.42	6.32
***Z*-41**	– 17.44	196.02	11.24	6.20

[a] Computed at the B3LYP/6 – 31G**//HF/6 – 31G** level. [b] Relative energies in kcal mol^{-1}. [c] In kcal mol^{-1}, from HF/6 – 31G** vibrational frequencies scaled by a factor of 0.9181.

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Table 5. Enthalpies of reaction and activation energies [kcal mol^{-1}] for cyclization of vinylallenylium cations **38** and **40** to the alkylidenecyclopentenium cations ***E*-39**/***Z*-39** and ***E*-41**/***Z*-41**, at 298, 213 and 0 K.

	298 K	213 K	0 K
$\Delta\Delta H$ (***E*-39**)	−9.61	−8.80	−8.23
$\Delta\Delta H$ (***Z*-39**)	−15.18	−14.37	−13.86
E_a (***E*-39TS**)[a]	2.42	3.02	3.06
E_a (***Z*-39TS**)[a]	2.98	3.58	3.64
$\Delta\Delta H$ (***E*-41**)	−8.01	−7.84	−7.36
$\Delta\Delta H$ (***Z*-41**)	−16.10	−15.87	−15.27
E_a (***E*-41TS**)[a]	2.12	2.14	2.16
E_a (***Z*-41TS**)[a]	3.72	3.74	3.84

[a] $E_a = \Delta H^{\neq} + RT$.

Assuming that the relative stabilities of *Z* and *E* isomers are maintained following entrapment of the cation, the finding that *Z*-**39** is appreciably more stable than *E*-**39** is formally in keeping with the experimental observation that the R-inward product *Z*-**4a** is more stable than *E*-**4a**. Where the R-inward rotation is thermodynamically favoured but kinetically disadvantaged, as in **38** → **39** and **1a** → **4a**, the causes responsible for relative destabilization of the R-inward transition state must disappear between transition state and product. Inspection of structures **1** to **4** therefore suggests that steric hindrance between R and the substituent at the other cyclization terminus may be relevant. The latter appears likely to be initially better placed for hindrance of an R-inward rotation than the *tert*-butyl for hindrance of an R-outward rotation. However, in the products in which these two substituents are located on either side of the alkylidene, their relative effects depend only on their relative bulks and orientations.

To investigate this hypothesis, we carried out calculations for the cyclization of **40**, in which R is larger than in **38** and contains the methyl-substituted vinyl group present in **1a.** With this R, the thermodynamic advantage of the R-inward product increased to 8.6 kcal mol^{-1} and the kinetic disadvantage to 1.60 kcal mol^{-1} (Table 3). This is equivalent to *Z*/*E* ratios of about 1:99 at 25 °C and about 2:998 at −60 °C, which is in keeping with the experimental results for **1a** → **4a**. Examination of the transition structures for the R-inward rotation (Figure 1) shows that steric interaction between the methyl group of the propenyl substituent and the hydrogen atom of the carbinol twists the exocyclic diene about the C1′–C2′ hinge to form a C5-C1′-C2′-C3′ dihedral angle of 165°, thereby reducing stabilization by conjugation. In contrast, an angle of 180°, which ensures full conjugation of the exocyclic diene (and eventually extended conjugation to include the carbenium ion) is maintained throughout the R-outward rotation from **40** to *E*-**41**TS. The fact that the reactions of **1b** and **1c** are less torquoselective than that of **1a**, giving *Z*/*E* ratios of about 35:65 at −60 °C, may be attributed to the weaker steric interactions of their smaller R groups.

It is interesting to note that in the electrocyclic ring closure of divinylallene **42** (Scheme 9), the fact that torquoselectivity is greater when R′ = CHO than when R′ = CH_2OH is also attributable to the influence of an exocyclic π system, though in a different way. Whereas for **40** → **41** (and presumably for

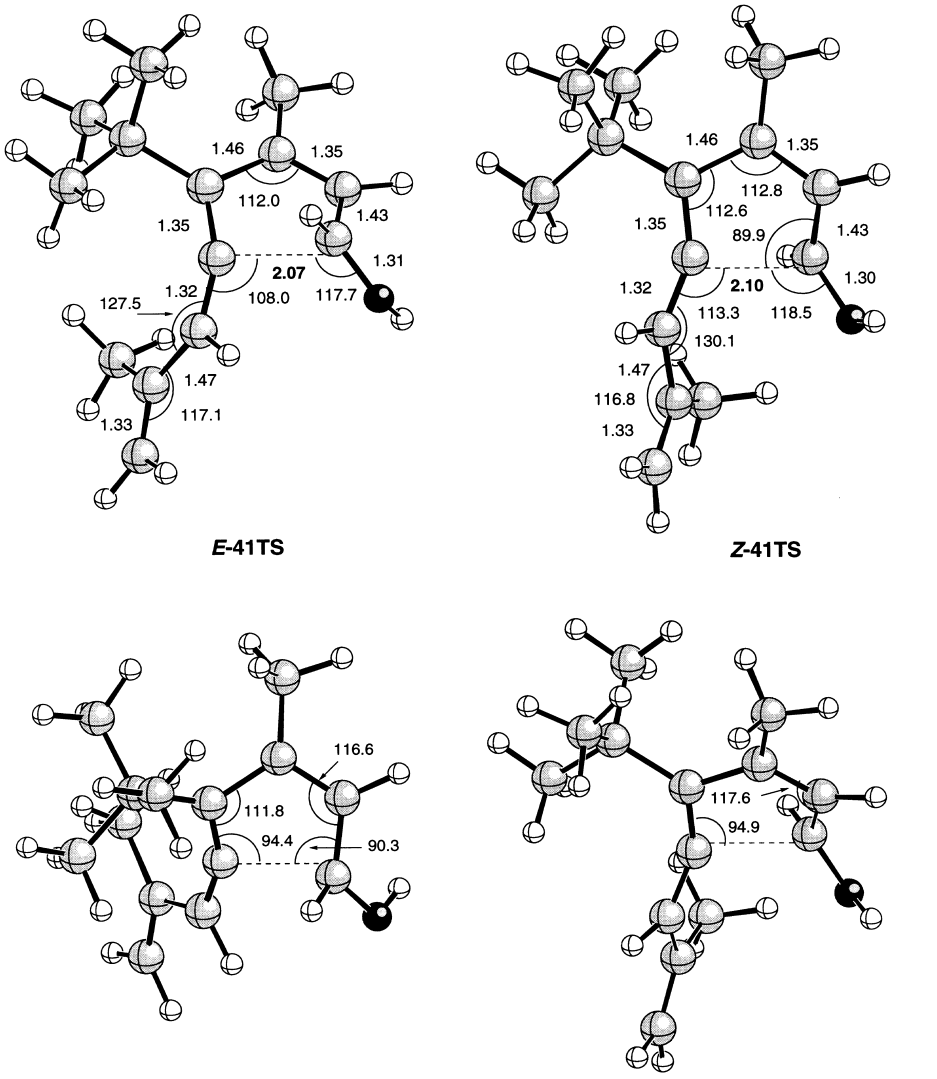

Figure 1. Main geometric features of **41**TS computed at the B3LYP/6–31G** level. Bond lengths and angles are given in Å and degrees, respectively. The lower representation (corresponding to a 30° rotation of the upper figures) highlights the steric interactions thought to be responsible for the diminished conjugation of the exocyclic diene in *Z*-**41**TS relative to *E*-**41**TS.

1a → **4a**) the R-inward rotation is disfavoured by entailing a weakening of the existing exocyclic conjugation and of the nascent extended π system embracing the ring and the R group, in the case of **42** → **43** the R-inward rotation, which has an earlier transition state, is favoured by reluctance to relinquish the existing extended conjugation between the 2,4-diene and the carbonyl. This difference apart, the findings reported in ref. [10] and those presented here jointly highlight the importance of stereoelectronic effects in electrocyclic reactions.

Conclusions

The rearrangement of 2-[(1*Z*)-hexa-1,3,4-trienyl]dioxolanes to tetrahydroalkylidenecyclopenta-1,4-dioxins under acidic conditions occurs with great facility. It seems likely to proceed through the mechanism advanced in Scheme 1, in which the 1-oxypentadienyl carbocation **2** rearranges to a conjugated ion **3**, which is then trapped by the resident hydroxyl. This last step is presumably facilitated by delocalization of the positive charge of **3**, which must be enhanced by the exocyclic extension of its π system and must counteract the stabilization of localized charge by the C1 oxygen in **2**. As the electrocyclic annelation of a (substituted) hydroxypentadienyl carbocation, this mechanism may be looked on as a variant of the Nazarov cyclization. It is supported by the intermolecular trapping processes inferred in experiments with analogue **24** and also by the finding that the reaction proceeds at considerable rates at temperatures below −30 °C. This is consistent with the substantial decrease in the energy of activation expected for molecular rearrangements[37] that proceed through the mediation of charged atoms. Ab initio calculations support the experimental findings by predicting low activation energies for the rearrangement of model systems (the 1-hydroxyhepta-2,4,5-trienyl cations **34**, **36** and **38**, and the 1-hydroxyocta-2,4,5,7-tetraenyl cation **40**). Moreover the theoretically predicted stereoselectivity is also consistent with the experimental findings; DFT calculations at the B3LYP/6-31G**//HF/6-31G** level suggest that the torquoselectivity of the reaction, which with **1a** is 100 % in favour of the R-outward rotation at temperatures impeding acid-induced equilibration, is attributable to steric hindrance between R and the C1 substituent and that the R-inward reaction products (the *Z*-tetrahydroalkylidenecyclopenta-1,4-dioxins) are considerably more stable than the R-outward isomers. This post-transition reversal of relative stabilities is attributed to strong steric interactions between the R group and the neighbouring *tert*-butyl group, which under acid conditions leads to equilibration between the *Z* and *E* isomers of products **4**. The extent of this $E \rightarrow Z$ transition appears to depend on both the bulk of R and the acid present in the medium.

Experimental Section

General: Solvents were dried according to published methods and distilled before use. HPLC grade solvents were used for the HPLC purification. All other reagents were commercial compounds of the highest purity available. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel (60 F-254) plates (0.25 mm) precoated with a fluorescent indicator. Column chromatography was performed with Merck silica gel 60 (particle size 0.040–0.063 μm). Proton (^{1}H) and carbon (^{13}C) magnetic resonance spectra (NMR) were recorded on Bruker WM 250 [250 MHz (63 MHz for ^{13}C)], Bruker AMX 300 [300 MHz (75 MHz for ^{13}C)] and Bruker AMX 400 [400 MHz (100 MHz for ^{13}C)] Fourier transform spectrometers, and chemical shifts are expressed in parts per million (δ) relative to tetramethylsilane (TMS, $\delta = 0$), benzene (C_6H_6, $\delta = 7.20$ for ^{1}H) or chloroform ($CHCl_3$, $\delta = 7.24$ for ^{1}H and $\delta = 77.00$ for ^{13}C) as internal reference. ^{13}C multiplicities (s = singlet, d = doublet, t = triplet, q = quartet) were assigned with the aid of the DEPT pulse sequence. Infrared spectra (IR) were obtained on a MIDAC Prospect Model FT-IR spectrophotometer. UV/Vis spectra were recorded on an HP5989A spectrophotometer with MeOH as solvent. Low-resolution mass spectra were taken on an HP59970 instrument operating at 70 eV. High-resolution mass spectra were taken on a VG Autospec M instrument.

(2*E*,7*Z*)-8-{[1,3]-Dioxolan-2-yl}-3,7-dimethyl-1-(2,6,6-trimethylcyclohex-1-en-1-yl)octa-2,7-dien-5-yn-4-ol (14a)

General procedure for the preparation of propargyl alcohols: *n*-Butyllithium (5.7 mL, 2.77 M in hexanes, 15.79 mmol) was added dropwise, at −78 °C, to a solution of alkyne **13** (2.0 g, 14.48 mmol) in THF (49 mL), and the mixture was stirred for 40 min. A solution of aldehyde **12a** (2.71 g, 13.16 mmol) in THF (53 mL) was then added through a cannula. After stirring at −78 °C for 1 h and at 25 °C for an additional 1 h a saturated aqueous NH_4Cl solution (50 mL) was added and the mixture was stirred for 5 min. It was then extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine (3 × 200 mL), dried over Na_2SO_4 and evaporated. Chromatography (SiO_2, 65:33:2 hexane/EtOAc/Et_3N) of the residue afforded compound **14a** (3.96 g, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (s, 3H; C6″-CH_3), 0.97 (s, 3H; C6″-CH_3), 1.53 (s, 3H; C2″-CH_3), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.81 (d, $J = 0.8$ Hz, 3H; CH_3), 1.93 (m, 5H; 2H3″, CH_3), 2.00 (s, 1H; OH), 2.75 (d, $J = 6.5$ Hz, 2H; 2H1), 3.8–4.0 (m, 4H; 2H4′, 2H5′), 4.87 (s, 1H; H4), 5.44 (t, $J = 6.5$ Hz, 1H; H2), 5.64 (s, 2H; H8, H2′); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 12.2$ (q), 19.5 (t), 19.7 (q), 23.4 (q), 27.1 (t), 28.2 (q, 2×), 32.9 (t), 34.9 (s, C6″), 39.7 (t), 65.0 (t, 2×), 68.5 (d, C4), 82.8 (s), 94.3 (s), 101.5 (d, C2′), 125.2 (s), 128.3 (s), 129.6 (d), 132.5 (d), 134.1 (s), 135.9 (s); IR (NaCl): $\tilde{\nu} = 3600$–3100 (br, O–H), 2914 (s, C–H), 2218 (w, C≡C), 1643 (s), 1451 (s), 1388 (s), 1150 (s), 1068 (s), 952 cm^{-1} (s); UV/Vis (MeOH): $\lambda_{max} = 228$ nm; MS: *m*/*z* (%): 344 (3) $[M]^+$, 326 (15), 204 (36), 203 (84), 166 (50), 135 (52), 123 (100), 122 (35), 121 (60), 107 (44), 95 (41), 93 (54), 91 (56), 79 (41), 77 (31); HRMS for $C_{22}H_{32}O_3$: calcd 344.2351; found 344.2355.

(4*Z*)-5-{[1,3]-Dioxolan-2-yl}-4-methyl-1-[(1*E*)-1-methyl-3-(2,6,6-trimethylcyclohex-1-en-1-yl)prop-1-en-1-yl]pent-4-en-2-ynyl benzoate (15a)

General procedure for the preparation of propargyl benzoates: A cooled (−78 °C) solution of propargyl alcohol **14a** (3.78 g, 10.98 mmol) in THF (100 mL) was treated with *n*-butyllithium (7.5 mL, 1.6 M in hexanes, 12.08 mmol). The solution was stirred at this temperature for 30 min and at 0 °C for an additional 5 min before cooling down to −78 °C, at which temperature benzoyl chloride (1.5 mL, 12.08 mmol) was added dropwise. The reaction mixture was slowly warmed up to 25 °C for 2 h, a saturated aqueous NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution (2 × 50 mL) and brine (2 × 50 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel (83:15:2 hexane/EtOAc/Et_3N) to afford a yellow oil identified as compound **15a** (4.69 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (s, 3H; C6‴-CH_3), 0.97 (s, 3H; C6‴-CH_3), 1.4–1.6 (m, 4H; 2H4‴, 2H5‴), 1.53 (s, 3H; C2‴-CH_3), 1.91 (m, 8H; 2H3‴, C1″-CH_3, C4-CH_3), 2.78 (d, $J = 6.5$ Hz, 2H; 2H3″), 3.8–4.1 (dm, 4H; 2H4′, 2H5′), 5.6–5.7 (m, 3H; H5, H2′, H2″), 6.15 (s, 1H; H1), 7.4–7.5 (m, 2H; 2× ArH), 7.5–7.6 (m, 1H; ArH), 8.0–8.1 (m, 2H; 2× ArH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 12.6$ (q), 19.5 (t), 19.7 (q), 23.3 (q), 27.2 (t), 28.2 (q, 2×), 32.9 (t), 34.9 (s), 39.7 (t), 65.0 (t, 2×), 70.4 (d, C1), 83.7 (s), 91.1 (s), 101.5 (d, C2′), 125.0 (s), 128.4 (d, 2×), 128.7 (s), 129.0 (s), 129.8 (d, 2×), 130.3 (s), 132.6 (d), 133.1 (d), 133.2 (d), 135.6 (s), 165.4 (s, C=O); IR (NaCl): $\tilde{\nu} = 2960$ (s, C–H), 2935 (s, C–H), 2867 (s, C–H), 2224 (w, C≡C), 1722 (s, C=O), 1646 (w), 1452 (m), 1260 (s), 1151 (m), 1088 (s), 940 (m), 706 cm^{-1} (s); UV/Vis (MeOH): $\lambda_{max} = 230$ nm; MS: *m*/*z* (%): 448 (0.2) $[M]^+$, 375 (1), 343 (5), 311 (5), 207 (4), 149 (57), 137 (8), 122 (13), 119 (7), 106 (9), 105 (100), 95 (10), 91 (13), 77 (24), 73 (14); HRMS for $C_{29}H_{36}O_4$: calcd 448.2614; found 448.2617.

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2-[(1*Z*,6*E*)-3-*tert*-Butyl-2,6-dimethyl-8-(2,6,6-trimethylcyclohex-1-en-1-yl)octa-1,3,4,6-tetraen-1-yl]-[1,3]-dioxolane (1a)

General procedure for the preparation of vinylallenes: *tert*-Butyllithium (5.65 mL, 1.5 M in pentane, 8.48 mmol) was added dropwise to a cooled (−78 °C), stirred suspension of CuCN (0.38 g, 4.24 mmol) in Et_2O (40 mL). The mixture was stirred at −78 °C for 5 min and at 0 °C for an additional 15 min, before cooling down again to −78 °C. The solution of propargyl benzoate **15a** (1.0 g, 2.23 mmol) in Et_2O (20 mL) was then added through a cannula, and the resulting mixture was stirred at −78 °C for 1 h, and at 0 °C for an additional 1 h. Water (10 mL) was added and the heterogeneous mixture was filtered and extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with water (3 × 50 mL), dried over Na_2SO_4 and evaporated. The product was purified by chromatography on silica gel (90:8:2 hexane/EtOAc/Et_3N) to afford a colourless oil identified as compound **1a** (0.58 g, 70% yield). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.95$ (s, 3H; C6″-CH_3), 0.96 (s, 3H; C6″-CH_3), 1.11 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.53 (s, 3H; C2″-CH_3), 1.71 (d, $J = 0.9$ Hz, 3H; C6′-CH_3), 1.92 (t, $J = 6.6$ Hz, 2H; 2H3″), 1.96 (d, $J = 1.3$ Hz, 3H; C2′-CH_3), 2.78 (d, $J = 6.3$ Hz, 2H; 2H8′), 3.7–4.0 (dm, 4H; 2H4, 2H5), 5.20 (t, $J = 6.3$ Hz, 1H; H7′), 5.31 (dq, $J = 8.1$, 1.3 Hz, 1H; H1′), 5.41 (d, $J = 8.1$ Hz, 1H; H2), 5.85 (s, 1H; H5′); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.6$ (q), 19.5 (t), 19.7 (q), 26.0 (q), 27.7 (t), 28.2 (q), 28.3 (q), 30.3 (q, 3 ×, *t*Bu), 32.9 (t), 34.2 (s), 34.9 (s), 39.8 (t), 65.0 (t, 2 ×), 100.3 (d), 101.8 (d), 115.3 (s), 124.5 (d), 128.0 (s), 128.7 (s), 130.0 (d), 136.4 (s), 141.5 (s), 200.4 (s); IR (NaCl): $\tilde{\nu} = 2965$ (s, C−H), 2948 (s, C−H), 2869 (s, C−H), 1940 (w, C=C=C), 1655 (m), 1455 (m), 1380 (m), 1131 (s), 1054 (s), 950 cm^{-1} (m); UV/Vis (MeOH): $\lambda_{max} = 234$ nm; MS: *m*/*z* (%): 384 (20) $[M]^+$, 369 (7), 327 (20), 279 (12), 248 (23), 247 (75), 191 (100), 187 (21), 177 (24), 175 (29), 161 (36), 147 (34), 119 (36), 107 (26), 105 (41), 95 (28), 91 (47), 81 (24), 79 (28), 77 (23), 73 (62), 57 (47); HRMS for $C_{26}H_{40}O_2$: calcd 384.3028; found 384.3027.

(2*E*,7*Z*)-8-{[1,3]-Dioxolan-2-yl}-7-methylocta-2,7-dien-5-yn-4-ol (14b): Following the general procedure for the preparation of propargyl alcohols, the reaction of alkyne **13** (1.0 g, 7.24 mmol) and crotonaldehyde **12b** (0.56 g, 7.96 mmol) afforded compound **14b** (1.42 g, 95% yield) as a colourless oil after purification by chromatography (SiO_2, 75:22:3 hexane/EtOAc/Et_3N). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.73$ (d, $J = 6.4$ Hz, 3H; 3H1), 1.91 (s, 3H; C7-CH_3), 2.20 (br s, 1H; OH), 3.9–4.0 (m, 4H; 2H4′, 2H5′), 4.95 (d, $J = 5.6$ Hz, 1H; H4), 5.63 (dd, $J = 13.2$, 5.6 Hz, 1H; H3), 5.65 (s, 2H; H8, H2′), 5.89 (dq, $J = 13.2$, 6.4 Hz, 1H; H2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.5$ (q), 23.5 (q), 63.2 (d, C4), 65.1 (t, 2 ×), 83.1 (s), 94.2 (s), 101.4 (d, C2′), 125.1 (s, C7), 128.9 (d), 130.0 (d), 132.6 (d); IR (NaCl): $\tilde{\nu} =$ 3600–3100 (br, O−H), 3034 (w, C−H), 2981 (w, C−H), 2892 (m, C−H), 2219 (w, C=C), 1448 (s), 1395 (s), 1326 (m), 1152 (m), 1063 (m), 1028 (m), 962 cm^{-1} (s); MS: *m*/*z* (%): 208 (83) $[M]^+$, 193 (58), 167 (27), 151 (22), 137 (43), 135 (38), 123 (27), 121 (71), 109 (45), 107 (38), 95 (50), 93 (77), 91 (100), 87 (23), 79 (54), 77 (80), 73 (35), 69 (47), 65 (39); HRMS for $C_{12}H_{16}O_3$: calcd 208.1099; found 208.1100.

(4*Z*)-5-{[1,3]-Dioxolan-2-yl}-4-methyl-1-[(1*E*)-prop-1-en-1-yl]pent-4-en-2-ynyl benzoate (15b): Following the general procedure for the preparation of propargyl benzoates, alcohol **14b** was transformed into benzoate **15b** in 90% yield, after purification by chromatography on silica gel (90:7:3 hexane/EtOAc/Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.78$ (dd, $J = 6.5$, 0.9 Hz, 3H; 3H3″), 1.94 (d, $J = 1.1$ Hz, 3H; C4-CH_3), 3.8–4.0 (dm, 4H; 2H4′, 2H5′), 5.6–5.7 (m, 3H; H5, H2′, H1″), 6.08 (dq, $J = 13.5$, 6.5 Hz, 1H; H2″), 6.23 (d, $J = 6.5$ Hz, 1H; H1), 7.4–7.5 (m, 2H; 2 × ArH), 7.5–7.6 (m, 1H; ArH), 8.0–8.1 (m, 2H; 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 17.6 (q), 23.3 (q), 65.1 (t, 2 ×), 65.2 (d, C1), 84.0 (s), 90.7 (s), 101.4 (d, C2′), 124.8 (s), 126.1 (d), 128.3 (d, 2 ×), 129.8 (d, 2 ×), 130.0 (s), 131.8 (d), 133.1 (d), 133.3 (d), 165.3 (s, C=O); IR (NaCl): $\tilde{\nu} = 3038$ (m, C−H), 2959 (s, C−H), 2887 (s, C−H), 2228 (w, C=C), 1723 (s, C=O), 1599 (m), 1448 (s), 1391 (m), 1314 (s), 1262 (s), 1153 (m), 1100 (m), 1066 (m), 923 (s), 714 cm^{-1} (s); MS: *m*/*z* (%): 312 (0.02) $[M]^+$, 239 (5), 207 (10), 149 (10), 147 (6), 117 (6), 106 (9), 105 (100), 91 (14), 79 (5), 78 (6), 77 (31), 73 (6), 65 (4), 51 (9); HRMS for $C_{19}H_{20}O_4$: calcd 312.1362; found 312.1361.

2-[(1*Z*,6*E*)-3-*tert*-Butyl-2-methylocta-1,3,4,6-tetraen-1-yl]-[1,3]-dioxolane (1b): Following the general procedure for the preparation of vinylallenes, starting with propargyl benzoate **15b**, vinylallene **1b** was prepared in 65% yield, after purification by chromatography on silica gel (90:7:3 hexane/EtOAc/Et_3N). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (s, 9H; *t*Bu), 1.73 (d, $J = 1.3$ Hz, 3H; 3H8′), 1.95 (d, $J = 6.4$ Hz, 3H; C2′-CH_3), 3.8–4.0 (m, 4H; 2H4, 2H5), 5.31 (dq, $J = 8.0$, 1.3 Hz, 1H; H1′), 5.38 (d, $J = 8.0$ Hz, 1H; H2), 5.6–5.8 (m, 3H; H5′, H6′, H7′); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 18.5$ (q), 25.8 (q), 30.3 (q, 3 ×, *t*Bu), 34.1 (s), 64.9 (t, 2 ×), 94.4 (d), 101.7 (d), 114.5 (s), 124.8 (d), 126.9 (d), 127.1 (d), 141.2 (s), 202.3 (s, C4′); IR (NaCl): $\tilde{\nu} =$ 2961 (s, C−H), 2881 (s, C−H), 1935 (m, C=C=C), 1455 (s), 1371 (s), 1140 (m), 1064 (m), 954 (s), 838 cm^{-1} (m); MS: *m*/*z* (%): 248 (11) $[M]^+$, 233 (15), 192 (33), 191 (59), 147 (25), 133 (26), 119 (26), 105 (46), 91 (38), 77 (32), 73 (100), 58 (41), 57 (45); HRMS for $C_{16}H_{24}O_2$: calcd 248.1776; found 248.1777.

(5*Z*)-6-{[1,3]-Dioxolan-2-yl}-5-methylhex-5-en-3-yn-2-ol (14c): Following the general procedure for the preparation of propargyl alcohols, the reaction of alkyne **13** (1.0 g, 7.24 mmol) and acetaldehyde **12c** (0.35 g, 7.96 mmol) afforded compound **14c** (1.17 g, 90% yield) as a colourless oil, after purification by chromatography on silica gel (75:22:3 hexane/EtOAc/Et_3N). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.47$ (d, $J = 6.6$ Hz, 3H; 3H1), 1.63 (br s, 1H; OH), 1.90 (s, 3H; C5-CH_3), 3.8–4.0 (m, 4H; 2H4′, 2H5′), 4.66 (m, 1H; H2), 5.65 (s, 2H; H6, H2′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.5$ (q), 24.2 (q), 58.6 (d, C2), 65.1 (t, 2 ×), 81.2 (s), 96.7 (s), 101.4 (d, C2′), 125.1 (s, C5), 132.3 (d, C6); IR (NaCl): $\tilde{\nu} = 3600$–3100 (br, O−H), 2985 (s, C−H), 2890 (s, C−H), 2221 (w, C=C), 1643 (s), 1450 (m), 1392 (m), 1329 (s), 1290 (m), 1151 (m), 1067 (m), 948 (s), 870 cm^{-1} (m); MS: *m*/*z* (%): 182 (46) $[M]^+$, 167 (79), 136 (17), 125 (15), 121 (14), 111 (23), 109 (41), 95 (100), 93 (35), 91 (25), 79 (33), 77 (47), 73 (38); HRMS for $C_{10}H_{14}O_3$: calcd 182.0943; found 182.0944.

(4*Z*)-5-{[1,3]-Dioxolan-2-yl}-1,4-dimethylpent-4-en-2-yn-1-yl benzoate (15c): Following the general procedure for the preparation of propargyl benzoates, alcohol **14c** was transformed into benzoate **15c** in 90% yield, after purification by chromatography on silica gel (90:7:3 hexane/EtOAc/Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.64$ (d, $J = 6.6$ Hz, 3H; C1-CH_3), 1.92 (d, $J = 1.0$ Hz, 3H; C4-CH_3), 3.8–4.0 (dm, 4H; 2H4′, 2H5′), 5.65 (m, 2H; H5, H2′), 5.85 (q, $J = 6.6$ Hz, 1H; H1), 7.4–7.5 (m, 2H; 2 × ArH), 7.5–7.6 (m, 1H; ArH), 8.0–8.1 (m, 2H; 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.5$ (q), 23.3 (q), 61.3 (d, C1), 65.1 (t, 2 ×), 82.2 (s), 93.0 (s), 101.4 (d, C2′), 124.8 (s), 128.3 (d, 2 ×), 129.8 (d, 2 ×), 130.0 (s), 133.1 (d), 165.5 (s, C=O); IR (NaCl): $\tilde{\nu} = 3070$ (w, C−H), 2992 (m, C−H), 2956 (m, C−H), 2891 (m, C−H), 2226 (w, C=C), 1726 (s, C=O), 1451 (m), 1391 (m), 1318 (s), 1266 (s), 1104 (m), 1063 (m), 950 (m), 715 cm^{-1} (s); MS: *m*/*z* (%): 286 (1) $[M]^+$, 181 (9), 165 (8), 164 (12), 149 (5), 106 (9), 105 (100), 93 (7), 91 (13), 79 (5), 78 (5), 77 (33), 73 (5), 65 (5), 51 (9); HRMS for $C_{17}H_{18}O_4$: calcd 286.1205; found 286.1205.

2-[(1*Z*)-3-*tert*-Butyl-2-methylhexa-1,3,4-trien-1-yl]-[1,3]-dioxolane (1c): Following the general procedure for the preparation of vinylallenes, starting with propargyl benzoate **15c**, vinylallene **1c** was prepared in 67% yield, after purification by chromatography on silica gel (90:7:3 hexane/EtOAc/Et_3N). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.09$ (s, 9H; *t*Bu), 1.64 (d, $J = 6.9$ Hz, 3H; 3H6′), 1.95 (s, 3H; C2′-CH_3), 3.8–4.0 (m, 4H; 2H4, 2H5), 5.07 (q, $J = 6.9$ Hz, 1H; H5′), 5.30 (d, $J = 8.0$ Hz, 1H; H2), 5.39 (d, $J = 8.0$ Hz, 1H; H1′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$ (q), 25.9 (q), 30.4 (q, 3 ×, *t*Bu), 33.7 (s), 64.9 (t, 2 ×), 85.8 (d, C2), 101.7 (d, C1′), 111.8 (s), 124.4 (d, C5′), 142.1 (s), 200.8 (s, C4′); IR (NaCl): $\tilde{\nu} = 2961$ (s, C−H), 2884 (s, C−H), 1953 (w, C=C=C), 1660 (m), 1459 (m), 1391 (m), 1370 (m), 1135 (s), 1063 (s), 949 (s), 772 cm^{-1} (m); MS: *m*/*z* (%): 222 (20) $[M]^+$, 207 (21), 165 (34), 163 (13), 147 (16), 135 (28), 121 (22), 105 (17), 91 (22), 79 (14), 77 (20), 73 (42), 58 (100), 57 (33), 55 (15); HRMS for $C_{14}H_{22}O_2$: calcd 222.1620; found 222.1618.

(5*Z*)- and (5*E*)-6-*tert*-Butyl-7-methyl-5-[(2*E*)-2-methyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-2-enyliden]-5H-2,3,4a,7a-tetrahydrocyclopenta-1,4-dioxin (*Z*-4a and *E*-4a)

General procedure for the deprotection/activation of acetals: Water (30 μL, 1.56 mmol) and *p*-toluenesulfonic acid (5 mg, 0.03 mmol) were added to a solution of acetal **1a** (0.10 g, 0.26 mmol) in acetone (11.5 mL, 0.16 mol). The reaction mixture was stirred at 25 °C for 30 min, a saturated aqueous $NaHCO_3$ solution (10 mL) was added and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic extracts were washed with water (3 × 25 mL), dried over $MgSO_4$ and evaporated. Purification by chromatography (SiO_2, 90:8:2 hexane/EtOAc/Et_3N) yielded compound **4a** (99 mg, 99%) in a 42:58 *Z*/*E* ratio.

Data for isomer *Z*-4a: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.99$ (s, 3H; C6″-CH_3), 1.00 (s, 3H; C6″-CH_3), 1.33 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.58 (s, 3H; C2″-CH_3), 1.84 (d, $J = 0.9$ Hz, 3H; CH_3), 1.91 (t, $J =$ 6.0 Hz, 2H; 2H3″), 1.96 (d, $J = 1.2$ Hz, 3H; CH_3), 2.79 (d, $J = 6.2$ Hz, 2H;

2H4′), 3.4–3.6 (dm, 4H; 2H2, 2H3), 4.17 (br d, 1H; H4a or H7a), 4.48 (d, $J = 4.2$ Hz, 1H; H7a or H4a), 5.57 (t, $J = 6.2$ Hz, 1H; H3′), 6.11 (s, 1H; H1′); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.4$ (q), 16.7 (q), 19.6 (t), 19.7 (q), 27.8 (t), 28.3 (q, 2×), 30.8 (q, 3×, *t*Bu), 32.9 (t), 34.5 (s), 34.9 (s), 39.8 (t), 61.4 (t), 63.8 (t), 74.5 (d), 79.7 (d), 127.8 (s), 129.2 (d), 131.0 (s), 131.6 (d), 135.8 (s), 136.6 (s), 140.0 (s), 146.4 (s); IR (NaCl): $\tilde{\nu} = 2961$ (s, C–H), 2925 (s, C–H), 2865 (s, C–H), 1676 (m), 1605 (m), 1461 (s), 1368 (m), 1279 (m), 1131 (s), 1063 (m), 898 cm^{-1} (s); UV/Vis (MeOH): $\lambda_{max} = 280$ nm; MS: *m*/*z* (%): 384 (100) $[M]^+$, 369 (19), 265 (19), 248 (18), 247 (83), 203 (23), 191 (55), 175 (37), 119 (27), 105 (28), 95 (16), 93 (24), 91 (34), 81 (17), 79 (23), 77 (16), 57 (23), 55 (18); HRMS for $C_{26}H_{40}O_2$: calcd 384.3028; found 384.3022.

Data for isomer *E*-4a: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.95$ (s, 3H; C6″-CH_3), 0.96 (s, 3H; C6″-CH_3), 1.21 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.52 (s, 3H; C2″-CH_3), 1.58 (s, 3H; C2′-CH_3), 1.89 (t, $J = 6.2$ Hz, 2H; 2H3″), 1.97 (s, 3H; C7-CH_3), 2.74 (d, $J = 6.7$ Hz, 2H; 2H4′), 3.5–3.7 (dm, 4H; 2H2, 2H3), 4.0–4.1 (m, 2H; H4a, H7a), 5.16 (tq, $J = 6.7$, 1.5 Hz, 1H; H3′), 5.65 (s, 1H; H1′); ^{13}C RMN (63 MHz, $CDCl_3$): $\delta = 13.9$ (q), 16.8 (q), 19.5 (t), 19.9 (q), 27.6 (t), 28.3 (q), 28.4 (q), 29.9 (q, 3×, *t*Bu), 31.5 (s), 32.9 (t), 34.8 (s), 39.8 (t), 62.0 (t), 62.1 (t), 78.7 (d), 79.4 (d), 125.2 (d), 128.0 (s), 129.5 (d), 133.2 (s), 135.8 (s), 137.3 (s), 138.5 (s), 149.9 (s); IR (NaCl): $\tilde{\nu} =$ 2956 (s, C–H), 2914 (s, C–H), 2862 (s, C–H), 1638 (m), 1455 (s), 1277 (m), 1133 (s), 1090 (m), 899 cm^{-1} (s); UV/Vis (MeOH): $\lambda_{max} = 264$ nm; MS: *m*/*z* (%): 384 (93) $[M]^+$, 369 (22), 265 (23), 248 (21), 247 (100), 203 (28), 197 (23), 192 (20), 191 (71), 187 (32), 175 (50), 147 (27), 133 (26), 129 (21), 119 (34), 105 (35), 91 (45), 79 (31), 57 (39), 55 (34); HRMS for $C_{26}H_{40}O_2$: calcd 384.3028; found 384.3023.

(5*Z*)- and (5*E*)-5-[(2*E*)-But-2-enyliden]-6-*tert*-butyl-7-methyl-5H-2,3,4a,7a-tetrahydrocyclopenta-1,4-dioxin (*Z*-4b and *E*-4b): Following the general procedure for the deprotection/activation of acetals, treatment of acetal **1b** (60 mg, 0.24 mmol) in acetone (10.5 mL, 0.14 mol) with water (26 μL, 1.44 mmol) and *p*-toluenesulfonic acid (5 mg, 0.02 mmol), afforded compound **4b** (99% yield) as a mixture of isomers in a 35:65 *Z*/*E* ratio.

Data for isomer *Z*-4b: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9H; *t*Bu), 1.81 (d, $J = 6.9$ Hz, 3H; 3H4′), 2.00 (s, 3H; C7-CH_3), 3.5–3.7 (m, 4H; 2H2, 2H3), 4.15 (d, $J = 4.6$ Hz, 1H; H4a or H7a), 4.62 (d, $J = 4.6$ Hz, 1H; H7a or H4a), 5.74 (dq, $J = 14.5$, 6.9 Hz, 1H; H3′), 6.31 (d, $J = 11.0$ Hz, 1H; H1′), 6.41 (ddq, $J = 14.5$, 11.0, 1.6 Hz, 1H; H2′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 13.8 (q), 18.5 (q), 30.8 (q, 3×, *t*Bu), 34.8 (s, *t*Bu), 61.6 (t), 63.4 (t), 72.1 (d), 79.1 (d), 124.5 (d), 128.8 (d), 130.1 (d), 137.1 (s), 140.8 (s), 145.5 (s); IR (NaCl): $\tilde{\nu} = 2954$ (s, C–H), 2913 (s, C–H), 2857 (s, C–H), 1595 (w), 1449 (m), 1365 (m), 1278 (m), 1128 (s), 1061 (m), 965 (m), 891 cm^{-1} (m); MS: *m*/*z* (%): 248 (22) $[M]^+$, 233 (12), 219 (6), 205 (7), 191 (20), 167 (20), 149 (100), 133 (19), 123 (20), 121 (18), 119 (26), 111 (26), 109 (24), 105 (49), 97 (40), 95 (34), 91 (33), 85 (35), 83 (39), 77 (29), 69 (54); HRMS for $C_{16}H_{24}O_2$: calcd 248.1776; found 248.1776.

Data for isomer *E*-4b: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (s, 9H; *t*Bu), 1.81 (d, $J = 6.9$ Hz, 3H; 3H4′), 1.99 (s, 3H; C7-CH_3), 3.5–3.7 (m, 4H; 2H2, 2H3), 3.99 (d, $J = 4.5$ Hz, 1H; H4a or H7a), 4.13 (d, $J = 4.5$ Hz, 1H; H7a or H4a), 5.70 (dq, $J = 14.6$, 6.9 Hz, 1H; H3′), 5.89 (d, $J = 11.4$ Hz, 1H; H1′), 6.44 (ddq, $J = 14.6$, 11.4, 1.6 Hz, 1H; H2′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 15.5 (q), 18.4 (q), 30.6 (q, 3×, *t*Bu), 33.7 (s, *t*Bu), 61.8 (t), 62.2 (t), 77.9 (d), 78.8 (d), 119.8 (d), 130.1 (d), 130.4 (d), 137.8 (s), 138.3 (s), 149.4 (s); IR (NaCl): $\tilde{\nu} = 2954$ (s, C–H), 2909 (s, C–H), 2860 (s, C–H), 1599 (w), 1446 (s), 1339 (m), 1276 (m), 1132 (s), 1088 (m), 973 (m), 893 cm^{-1} (m); MS: *m*/*z* (%): 248 (13) $[M]^+$, 233 (7), 223 (7), 205 (7), 191 (8), 177 (5), 150 (10), 149 (100), 147 (7), 133 (9), 119 (8), 105 (14), 91 (11), 77 (10); HRMS for $C_{16}H_{24}O_2$: calcd 248.1777; found 248.1776.

(5*Z*)- and (5*E*)-6-*tert*-Butyl-5-ethenyliden-7-methyl-5H-2,3,4a,7a-tetrahydrocyclopenta-1,4-dioxin (*Z*-4c and *E*-4c): Following the general procedure for the deprotection/activation of acetals, treatment of acetal **1c** (60 mg, 0.27 mmol) in acetone (12 mL, 0.16 mol) with water (29 μL, 1.62 mmol) and *p*-toluenesulfonic acid (5 mg, 0.03 mmol), afforded compound **4c** (50% yield) as a mixture of isomers in a 35:65 *Z*/*E* ratio.

Data for isomer *Z*-4c: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.31$ (s, 9H; *t*Bu), 1.85 (d, $J = 7.0$ Hz, 3H; 3H2′), 1.96 (s, 3H; C7-CH_3), 3.5–3.7 (m, 4H; 2H2, 2H3), 4.13 (d, $J = 4.2$ Hz, 1H; H4a or H7a), 4.53 (d, $J = 4.2$ Hz, 1H; H7a or H4a), 5.76 (q, $J = 7.0$ Hz, 1H; H1′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.4$ (q), 14.8 (q), 30.8 (q, 3×, *t*Bu), 34.8 (s, *t*Bu), 61.5 (t), 63.5 (t), 71.9 (d), 79.1 (d), 119.5 (d, C1′), 135.1 (s), 142.3 (s), 145.2 (s); IR (NaCl): $\tilde{\nu} = 3063$ (w, C–H), 2956 (s, C–H), 2909 (s, C–H), 2862 (s, C–H), 1603 (w), 1451 (m), 1367 (m), 1340 (m), 1279 (m), 1134 (s), 1103 (m), 1063 (m), 958 (m), 893 (s), 837 (m), 776 cm^{-1} (m); MS: *m*/*z* (%): 222 $[M]^+$, 83), 207 (64), 193 (19), 166 (22), 163 (37), 151 (25), 149 (100), 147 (53), 135 (57), 121 (44), 119 (28), 113 (37), 107 (36), 105 (43), 93 (29), 91 (57), 79 (31), 77 (41); HRMS for $C_{14}H_{22}O_2$: calcd 222.1620; found 222.1618.

Data for isomer *E*-4c: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (s, 9H; *t*Bu), 1.86 (d, $J = 7.6$ Hz, 3H; 3H2′), 1.95 (s, 3H; C7-CH_3), 3.4–3.7 (m, 4H; 2H2, 2H3), 3.96 (d, $J = 4.4$ Hz, 1H; H4a or H7a), 4.05 (d, $J = 4.4$ Hz, 1H; H7a or H4a), 5.34 (q, $J = 7.6$ Hz, 1H; H1′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.2$ (q), 17.7 (q), 30.6 (q, 3×, *t*Bu), 33.6 (s, *t*Bu), 61.9 (t), 62.0 (t), 78.5 (d), 78.7 (d), 114.7 (d, C1′), 137.1 (s), 140.0 (s), 149.0 (s); IR (NaCl): $\tilde{\nu} = 2954$ (s, C–H), 2906 (s, C–H), 2859 (s, C–H), 1651 (w), 1598 (w), 1446 (s), 1366 (m), 1337 (m), 1276 (s), 1198 (m), 1134 (s), 1078 (s), 890 (s), 811 cm^{-1} (m); MS: *m*/*z* (%): 222 (24) $[M]$, 207 (21), 163 (11), 149 (100), 147 (16), 135 (18), 121 (15), 119 (10), 113 (10), 105 (16), 91 (21), 77 (18); HRMS for $C_{14}H_{22}O_2$: calcd 222.1620; found 222.1619.

(2*E*,7*E*)-8-{[1,3]-Dioxolan-2-yl}-3,7-dimethyl-1-(2,6,6-trimethylcyclohex-1-en-1-yl)octa-2,7-dien-5-yn-4-ol (17): Following the general procedure for the preparation of propargyl alcohols, the reaction of alkyne **16** (1.0 g, 7.24 mmol) and aldehyde **12a** (1.36 g, 6.59 mmol) afforded 2.17 g (95% yield) of compound **17** as a colourless oil, after purification by chromatography on silica gel (85:10:5 hexane/EtOAc/Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.93$ (s, 3H; C6″-CH_3), 0.94 (s, 3H; C6″-CH_3), 1.50 (s, 3H; C2″-CH_3), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.75 (s, 3H; CH_3), 1.87 (s, 3H; CH_3), 1.88 (t, $J = 6.2$ Hz, 2H; 2H3″), 2.71 (d, $J = 6.4$ Hz, 2H; 2H1), 3.8–4.0 (dm, 4H; 2H4′, 2H5′), 4.78 (s, 1H; H4), 5.39 (tq, $J = 6.4$, 1.0 Hz, 1H; H2), 5.49 (d, $J = 6.9$ Hz, 1H; H2′), 5.72 (dq, $J = 6.9$, 1.4 Hz, 1H; H8); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.0$ (q), 17.7 (q), 19.4 (t), 19.5 (q), 26.9 (t), 28.1 (q, 2×), 32.8 (t), 34.7 (s), 39.6 (t), 64.8 (t, 2×), 68.1 (d, C4), 86.8 (s), 88.7 (s), 99.4 (d), 124.6 (s), 128.1 (s), 129.0 (d), 132.3 (d), 132.6 (s), 135.8 (s); IR (NaCl): $\tilde{\nu} = 3600-3100$ (br, O–H), 2953 (s, C–H), 2923 (s, C–H), 2863 (s, C–H), 2212 (w, C≡C), 1641 (m), 1460 (m), 1380 (m), 1221 (w), 1148 (m), 1071 (m), 936 cm^{-1} (s); MS: *m*/*z* (%): 344 (3) $[M]^+$, 326 (2), 287 (3), 271 (19), 203 (27), 177 (27), 149 (23), 135 (51), 123 (86), 93 (79), 91 (100), 79 (71), 77 (71), 73 (90), 55 (56); HRMS for $C_{22}H_{32}O_3$: calcd 344.2351; found 344.2350.

(4*E*)-5-{[1,3]-Dioxolan-2-yl}-4-methyl-1-[(1*E*)-1-methyl-3-(2,6,6-trimethylcyclohex-1-en-1-yl)prop-1-en-1-yl]pent-4-en-2-ynyl benzoate (18): Following the general procedure for the preparation of propargyl benzoates, alcohol **17** was transformed into benzoate **18** in 93% yield, after purification by chromatography on silica gel (90:5:5 hexane/EtOAc/Et_3N). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.95$ (s, 3H; C6‴-CH_3), 0.96 (s, 3H; C6‴-CH_3), 1.53 (s, 3H; C2‴-CH_3), 1.4–1.6 (m, 4H; 2H4‴, 2H5‴), 1.87 (s, 3H; C1″-CH_3), 1.91 (d, $J = 1.4$ Hz, 3H; C4-CH_3), 1.94 (t, $J = 7.0$ Hz, 2H; 2H3‴), 2.77 (d, $J = 6.4$ Hz, 2H; 2H3″), 3.8–4.0 (m, 4H; 2H4′, 2H5′), 5.53 (d, $J = 7.0$ Hz, 1H; H2′), 5.60 (tq, $J = 6.4$, 1.3 Hz, 1H; H2″), 5.80 (dq, $J = 7.0$, 1.4 Hz, 1H; H5), 6.11 (s, 1H; H1), 7.4–7.5 (m, 2H; 2×ArH), 7.5–7.6 (m, 1H; ArH), 8.0–8.1 (m, 2H; 2×ArH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta =$ 12.6 (q), 17.7 (q), 19.4 (t), 19.6 (q), 27.2 (t), 28.2 (q, 2×), 32.9 (t), 34.8 (s), 39.7 (t), 64.9 (t, 2×), 70.3 (d), 85.3 (s), 87.7 (s), 99.5 (d), 124.3 (s), 128.3 (d, 2×), 128.6 (s), 129.1 (s), 129.8 (d, 2×), 130.3 (s), 132.4 (d), 133.0 (d), 133.2 (d), 135.6 (s), 165.3 (s, C=O); IR (NaCl): $\tilde{\nu} = 2928$ (s, C-H), 2867 (s, C–H), 2220 (w, C≡C), 1724 (s, C=O), 1641 (m), 1597 (m), 1460 (m), 1079 (s), 1028 (s), 927 (s), 712 cm^{-1} (s); MS: *m*/*z* (%): 448 (1) $[M]^+$, 375 (2), 343 (2), 311 (5), 149 (34), 119 (6), 105 (100), 95 (11), 81 (11), 77 (18), 73 (44); HRMS for $C_{29}H_{36}O_4$: calcd 448.2614; found 448.2616.

2-[(1*E*,6*E*)-3-*tert*-Butyl-2,6-dimethyl-8-(2,6,6-trimethylcyclohex-1-en-1-yl)octa-1,3,4,6-tetraen-1-yl]-[1,3]-dioxolane (19): Following the general procedure for the preparation of vinylallenes, starting with propargyl benzoate **18**, vinylallene **19** was prepared in 64% yield, after purification by chromatography on silica gel (95:5 hexane/Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (s, 6H; C6″-2CH_3), 1.13 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.54 (s, 3H; C2″-CH_3), 1.70 (d, $J = 1.0$ Hz, 3H; C6′-CH_3), 1.92 (d, $J = 1.3$ Hz, 3H; C2′-CH_3), 1.92 (t, $J = 6.4$ Hz, 2H; 2H3″), 2.79 (d, $J =$ 6.7 Hz, 2H; 2H8′), 3.8–4.0 (dm, 4H; 2H4, 2H5), 5.18 (tq, $J = 6.7$, 1.0 Hz, 1H; H7′), 5.42 (dq, $J = 6.9$, 1.3 Hz, 1H; H1′), 5.50 (d, $J = 6.9$ Hz, 1H; H2), 5.87 (s, 1H; H5′); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.7$ (q), 19.4 (q), 19.6 (t), 19.8 (q), 27.8 (t), 28.3 (q), 30.2 (q, 3×, *t*Bu), 32.9 (t), 34.4 (s), 34.9 (s), 39.8 (t), 64.8 (t, 2×), 100.4 (d), 100.9 (d), 119.6 (s), 124.6 (d), 127.9 (s), 128.7 (s), 129.7 (d), 136.4 (s), 139.9 (s), 201.8 (s, C4′); IR (NaCl): $\tilde{\nu} = 2924$ (s, C–H), 2857 (s, C–H), 1931 (m, C=C=C), 1656 (s), 1463 (s), 1381 (s), 1144

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(m), 1064 (m), 939 (m), 866 (m), 732 cm^{-1} (s); MS: *m*/*z* (%): 384 (2) $[M]^+$, 327 (3), 247 (8), 233 (2), 191 (16), 147 (6), 119 (10), 105 (70), 93 (9), 91 (9), 81 (11), 73 (100); HRMS for $C_{26}H_{40}O_2$: calcd 384.3028; found 384.3026.

(2*E*,7*E*)-4-*tert*-Butyl-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,5,7-tetraenal (20): Following the general procedure for the deprotection/activation of acetals, treatment of acetal **19** (60 mg, 0.16 mmol) in acetone (6.9 mL, 93.6 mmol) with water (17 μL, 0.94 mmol) and *p*-toluenesulfonic acid (2 mg, 0.02 mmol), afforded aldehyde **20** (50 mg 94%).[10b]

(2*Z*)-3-Methylpent-2-en-4-ynal dimethyl acetal (21): A solution of (2*Z*)-3-methylpent-2-en-4-ynal (0.95 g, 10.10 mmol) in dry methanol (19 mL) was treated with hydrogen chloride (10.10 mL, 1.0 M in Et_2O, 10.10 mmol). The reaction mixture was stirred at 25 °C for 15 min and then MeOH (19 mL) was added. After stirring for an additional 20 min a new portion of MeOH (24 mL) was added and the final mixture was stirred for 10 min. It was then poured over a saturated aqueous $NaHCO_3$ solution and the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (2 × 200 mL), water (200 mL) and brine (200 mL), dried (Na_2SO_4) and evaporated. Purification by chromatography on silica gel (elution gradient: from 1:1 CH_2Cl_2/hexane to 100% CH_2Cl_2) afforded compound **21** (1.24 g, 88%), which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.94$ (d, $J =$ 1.1 Hz, 3H; C3-CH_3), 3.19 (s, 1H; H5), 3.38 (s, 6H; 2 × OCH_3), 5.17 (d, $J =$ 7.5 Hz, 1H; H1), 5.79 (dq, $J = 7.5$, 1.1 Hz, 1H; H2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.1$ (q), 53.4 (q, 2 ×), 81.4 (d, C5), 82.4 (s, C4), 101.9 (d, C1), 122.2 (s, C3), 134.6 (d, C2); IR (NaCl): $\tilde{\nu} = 3288$ (m, C≡C–H), 2932 (m, C–H), 2830 (m, C–H), 1449 (m), 1378 (m), 1130 (s), 1074 (s), 1054 (s), 956 cm^{-1} (m); MS: *m*/*z* (%): 140 (12) $[M]^+$, 132 (6), 125 (15), 110 (6), 109 (100), 94 (21), 77 (13), 75 (12), 70 (5), 66 (6), 65 (8); HRMS for $C_8H_{12}O_2$: calcd 140.0837; found 140.0836.

(2*Z*,7*E*)-3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,7-dien-4-yn-6-ol-1-al dimethyl acetal (22): Following the general procedure for the preparation of propargyl alcohols, the reaction of alkyne **21** (0.28 g, 1.98 mmol) and aldehyde **12a** (0.37 g, 1.80 mmol) afforded, in order of elution, unreacted starting aldehyde **12a** (0.14 g, 61% conversion) and compound **22** (0.35 g, 92% yield), after purification by chromatography (SiO_2, elution gradient: from 93:5:2 hexane/EtOAc/Et_3N to 78:20:2 hexane/EtOAc/Et_3N). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (s, 3H; C6′-CH_3), 0.98 (s, 3H; C6′-CH_3), 1.4–1.6 (m, 4H; 2H4′, 2H5′), 1.55 (s, 3H; C2′-CH_3), 1.83 (s, 3H; CH_3), 1.92 (m, 5H; 2H3′, CH_3), 2.76 (d, $J = 6.4$ Hz, 2H; 2H9), 3.36 (s, 6H; C1-2OMe), 4.90 (s, 1H; H6), 5.10 (d, $J = 7.5$ Hz, 1H; H1), 5.46 (t, $J = 6.4$ Hz, 1H; H8), 5.71 (dq, $J = 7.5$, 1.4 Hz, 1H; H2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.2$ (q), 19.4 (t), 19.6 (q), 23.2 (q), 27.0 (t), 28.2 (q, 2 ×), 32.8 (t), 34.8 (s, C6′), 39.6 (t), 53.2 (q, 2x), 68.3 (d, C6), 83.2 (s), 94.2 (s), 101.9 (d, C1), 122.8 (s), 128.1 (s), 129.2 (d), 132.4 (s), 132.8 (d), 135.8 (s); IR (NaCl): $\tilde{\nu} = 3600-3100$ (br, O–H), 2927 (s, C–H), 2865 (m, C–H), 1449 (m), 1380 (m), 1192 (m), 1133 (s), 1054 (s), 947 (m), 755 cm^{-1} (w); MS: *m*/*z* (%): 315 (57) $[M - OCH_3]^+$, 314 (100) $[M - CH_3OH]^+$, 191 (42), 177 (89), 165 (95), 150 (70), 137 (66), 136 (93), 123 (94), 121 (83), 107 (55), 105 (46), 95 (75), 93 (52), 91 (59), 81 (67), 79 (45), 69 (54); HRMS ($[M - CH_3OH]^+$) for $C_{21}H_{30}O_2$: calcd 314.2246; found 314.2255.

(4*Z*)-6,6-Dimethoxy-4-methyl-1-[(1*E*)-1-methyl-3-(2,6,6-trimethylcyclohex-1-en-1-yl)prop-1-en-1-yl]hex-4-en-2-ynyl benzoate (23): According to the general procedure for the preparation of propargyl benzoates, propargyl alcohol **22** (0.14 g, 0.40 mmol) was transformed into benzoate **23** (0.18 g, 99% yield), after chromatography (SiO_2, 90:8:2 hexane/EtOAc/Et_3N). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.98$ (s, 6H; C6″-2CH_3), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.55 (s, 3H; C2″-CH_3), 1.9 (m, 8H; 2H3″, C1′-CH_3, C4-CH_3), 2.80 (d, $J = 6.4$ Hz, 2H; 2H3′), 3.32 (s, 3H; C6-OMe), 3.35 (s, 3H; C6-OMe), 5.09 (d, $J = 7.6$ Hz, 1H; H6), 5.64 (t, $J = 6.4$ Hz, 1H; H2′), 5.72 (dq, $J = 7.6$, 1.4 Hz, 1H; H5), 6.15 (s, 1H; H1), 7.44 (m, 2H; 2 × ArH), 7.56 (m, 1H; ArH), 8.05 (m, 2H; 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 12.6 (q), 19.4 (t), 19.6 (q), 23.0 (q), 27.2 (t), 28.2 (q, 2 ×), 32.8 (t), 34.8 (s, C6″), 39.6 (t), 53.7 (q, 2 ×), 70.3 (d, C1), 84.1 (s), 90.5 (s), 102.4 (d, C6), 122.4 (s), 128.3 (d, 2 ×), 128.5 (s), 128.8 (s), 129.6 (d, 2 ×), 130.1 (s), 132.5 (d), 133.0 (d), 133.7 (d), 135.4 (s), 165.2 (s, C=O); IR (NaCl): $\tilde{\nu} = 2928$ (s, C–H), 1724 (s, C=O), 1452 (m), 1257 (s), 1095 (s), 1069 (s), 952 (m), 711 cm^{-1} (m); MS: *m*/*z* (%): 450 (0.9) $[M]^+$, 418 (4) $[M - CH_3OH]^+$, 313 (10), 178 (7), 177 (26), 137 (8), 106 (7), 105 (100), 95 (8), 77 (13), 75 (10); HRMS for $C_{29}H_{38}O_4$: calcd 450.2770; found 450.2771.

(2*Z*,7*E*)-4-*tert*-Butyl-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,5,7-tetraenal dimethyl acetal (24): Following the general procedure for the preparation of vinylallenes, propargyl benzoate **23** (50 mg, 0.11 mmol) was transformed into vinylallene **24** (42 mg, 98% yield), after chromatography (SiO_2, 94:4:2 hexane/EtOAc/Et_3N). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (s, 3H; C6′-CH_3), 0.98 (s, 3H; C6′-CH_3), 1.12 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4′, 2H5′), 1.54 (s, 3H; C2′-CH_3), 1.73 (s, 3H; C7-CH_3), 1.93 (t, $J = 6.1$ Hz, 2H; 2H3′), 1.97 (d, $J = 1.2$ Hz, 3H; C3-CH_3), 2.80 (d, $J =$ 6.5 Hz, 2H; 2H9), 3.31 (s, 3H; C1-OMe), 3.34 (s, 3H; C1-OMe), 4.88 (d, $J = 8.0$ Hz, 1H; H1), 5.20 (t, $J = 6.5$ Hz, 1H; H8), 5.42 (dq, $J = 8.0$, 1.2 Hz, 1H; H2), 5.82 (s, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.8$ (q), 19.5 (t), 19.7 (q), 26.1 (q), 27.7 (t), 28.3 (q, 2 ×), 30.3 (q, 3 ×, *t*Bu), 32.8 (t), 34.4 (s), 34.9 (s), 39.8 (t), 53.0 (q, OMe), 53.1 (q, OMe), 100.1 (d), 101.9 (d), 115.6 (s), 124.5 (d), 127.9 (s), 128.5 (s), 129.9 (d), 136.3 (s), 138.6 (s), 200.1 (s, C5); IR (NaCl): $\tilde{\nu} = 2962$ (s, C-H), 2866 (s, C–H), 2828 (s, C–H), 1933 (w, C=C=C), 1463 (s), 1361 (m), 1127 (s), 1078 (s), 1055 (s), 946 cm^{-1} (m); MS: *m*/*z* (%): 386 (12) $[M]^+$, 371 (31), 355 (11), 329 (68), 249 (43), 217 (22), 193 (52), 119 (24), 95 (27), 91 (25), 81 (26), 75 (100), 69 (21); HRMS for $C_{26}H_{42}O_2$: calcd 386.3185; found 386.3182.

(5*E*)-1-*tert*-Butyl-2-methyliden-5-[(2*E*)-2-methyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-2-enyliden]cyclopent-3-en-1-ol (29) and (4*Z*)-3-*tert*-butyl-5-methoxy-2-methyl-4-[(2*E*)-2-methyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-2-enyliden]cyclopent-2-en-1-ol (30): Following the general procedure for the deprotection/activation of acetals, treatment of divinylallenylacetal **24** (65 mg, 0.17 mmol) in acetone (7.4 mL, 0.10 mol) with H_2O (0.1 mL, 5.5 mmol) and *p*-toluenesulfonic acid monohydrate (3.2 mg, 0.02 mmol), afforded, after purification by chromatography on silica gel (elution gradient: from 98:2 hexane/EtOAc to 80:20 hexane/EtOAc), compound **29** (29 mg, 51% yield) and compound **30** (17 mg, 27% yield).

Data for compound 29: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$ (s, 9H; *t*Bu), 0.97 (s, 3H; C6″-CH_3), 0.99 (s, 3H; C6″-CH_3), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.55 (s, 3H; C2″-CH_3), 1.9 (m, 2H; 2H3″), 1.94 (d, $J = 1.0$ Hz, 3H; C2′-CH_3), 2.83 (d, $J = 6.5$ Hz, 2H; 2H4′), 5.00 (s, 1H; H1‴), 5.09 (s, 1H; H1‴), 5.40 (t, $J = 6.5$ Hz, 1H; H3′), 5.92 (s, 1H; H1′), 6.32 (d, $J = 6.0$ Hz, 1H; H3), 6.87 (d, $J = 6.0$ Hz, 1H; H4); ^{1}H NMR (400 MHz, CD_3COCD_3): $\delta = 0.90$ (s, 9H; *t*Bu), 0.99 (s, 3H; C6″-CH_3), 1.00 (s, 3H; C6″-CH_3), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.56 (s, 3H; C2″-H_3), 1.9 (m, 2H; 2H3″), 1.94 (d, $J =$ 1.0 Hz, 3H; C2′-CH_3), 2.88 (d, $J = 6.5$ Hz, 2H; 2H4′), 4.95 (d, $J = 0.9$ Hz, 1H; H1‴), 5.07 (s, 1H; H1‴), 5.36 (t, $J = 6.5$ Hz, 1H; H3′), 5.90 (s, 1H; H1′), 6.36 (d, $J = 6.0$ Hz, 1H; H3 or H4), 6.89 (d, $J = 6.0$ Hz, 1H; H4 or H3); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.90$ (s, 6H; C6″-2CH_3), 0.95 (s, 9H; *t*Bu), 1.2–1.5 (m, 4H; 2H4″, 2H5″), 1.40 (s, 3H; C2″-CH_3), 1.70 (s, 3H; C2′-CH_3), 1.8 (m, 2H; 2H3′), 2.73 (d, 2H; 2H4′), 4.81 (s, 1H; H1‴), 4.88 (s, 1H; H1‴), 5.49 (t, 1H; H3′), 6.0 (m, 2H; H1′, H3 or H4), 6.70 (d, 1H; H4 or H3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.9$ (q), 19.9 (t), 20.2 (q), 25.4 (q, 3 ×, *t*Bu), 27.2 (t), 28.1 (q, 2 ×), 33.3 (t), 35.4 (s), 37.8 (s), 40.1 (t), 85.5 (s, C1), 106.9 (t, C1‴), 127.6 (d, C1′), 128.5 (s), 132.4 (s), 134.1 (d, C4), 135.4 (d, 2 ×), 136.6 (s), 144.9 (s), 156.6 (s); ^{13}C NMR (100 MHz, CD_3COCD_3): $\delta =$ 16.2 (q), 19.5 (q), 19.7 (t), 25.0 (q, 3 ×, *t*Bu), 27.8 (t), 28.1 (q, 2 ×), 33.9 (t), 35.1 (s), 37.4 (s), 40.0 (t), 84.6 (s, C1), 106.2 (t, C1‴), 127.1 (d), 128.1 (s), 132.7 (s), 133.8 (d), 133.9 (d), 135.7 (d), 136.7 (s), 145.6 (s), 157.0 (s); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 16.7$ (q), 20.0 (t), 25.4 (q, 3x, *t*Bu), 28.2 (t), 28.6 (q), 33.2 (t), 35.3 (s), 37.7 (s), 40.1 (t), 85.4 (s, C1), 106.8 (t, C1‴), 127.6 (d), 128.0 (s), 132.9 (s), 133.9 (d), 135.0 (d), 135.5 (d), 136.6 (s), 145.4 (s), 156.7 (s); IR (NaCl): $\tilde{\nu} = 3600-3100$ (br, O–H), 2958 (s, C–H), 1697 (m), 1464 (m), 1362 (m), 1216 (m), 1071 (w), 1013 (w), 758 cm^{-1} (s); MS: *m*/*z* (%): 340 (26) $[M]^+$, 283 (55), 203 (21), 159 (100), 147 (33), 137 (75), 123 (33), 109 (23), 95 (47), 91 (28), 81 (33), 79 (21), 69 (44); HRMS for $C_{24}H_{36}O$: calcd 340.2766; found 340.2754.

Data for compound 30: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.00$ (s, 6H; C6″-2CH_3), 1.34 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4″, 2H5″), 1.58 (s, 3H; C2″-CH_3), 1.89 (s, 3H; C2′-CH_3), 1.9 (m, 2H; 2H3″), 2.05 (s, 3H; C2-CH_3), 2.8 (m, 2H; 2H4′), 3.36 (s, 3H; C5-OMe), 4.07 (s, 1H; H5), 4.18 (s, 1H; H1), 5.45 (t, $J = 6.4$ Hz, 1H; H3′), 6.31 (s, 1H; H1′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.5$ (q), 14.8 (q), 18.3 (t), 18.7 (q), 26.7 (t), 27.1 (q, 2 ×), 29.8 (q, 3 ×, *t*Bu), 31.6 (t), 33.2 (s), 33.7 (s), 38.4 (t), 53.8 (q), 81.0 (d), 83.3 (d), 126.7 (s), 130.2 (d), 130.3 (s), 131.8 (d), 135.2 (s), 135.8 (s), 139.1 (s), 146.1 (s); IR (NaCl): $\tilde{\nu} = 3600-3100$ (br, O–H), 2928 (s, C–H), 2868 (m, C–H), 1697 (m), 1460 (m), 1363 (m), 1085 (m), 757 cm^{-1} (s); MS: *m*/*z* (%): 372 (66) $[M]^+$, 340 (39), 235 (44), 219 (61), 203 (66), 179 (61), 162 (54), 147 (45),

137 (69), 123 (72), 121 (62), 119 (56), 109 (56), 107 (69), 105 (61), 95 (100), 93 (64); HRMS for $C_{25}H_{40}O_2$: calcd 372.3028; found 372.3022.

2-[(2*E*)-4-[(1*Z*)-2-*tert*-Butyl-4,5-dimethoxy-3-methylcyclopent-2-enylidene]-3-methylbut-2-en-1-yl]-1,3,3-trimethylcyclohex-1-ene (31): A solution of lithium tetrafluoroborate (19 mg, 0.20 mmol) in 4% aqueous CH_3CN (0.2 mL) was added to divinylallenylacetal **24** (77 mg, 0.20 mmol). A second portion of solvent 4% aq. CH_3CN (0.2 mL) was added and the reaction mixture was stirred at 25 °C for 1 h. It was then diluted with EtOAc (0.5 mL) and washed with a saturated aqueous $NaHCO_3$ solution (1 mL), dried over Na_2SO_4 and evaporated. Purification by chromatography on silica gel (elution gradient: from 98:2 hexane/EtOAc to 85:15 hexane/EtOAc) afforded compound **31** (16 mg, 21% yield) and compound **30** (10 mg, 13% yield). Data for compound **31**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.00$ (s, 3H; C3-CH_3), 1.01 (s, 3H; C3-CH_3), 1.35 (s, 9H; *t*Bu), 1.4–1.6 (m, 4H; 2H4, 2H5), 1.59 (s, 3H; C1-CH_3), 1.87 (s, 3H; C3′-CH_3), 1.93 (t, $J = 6.3$ Hz, 2H; 2H6), 2.00 (s, 3H; C3″-CH_3), 2.7–2.9 (m, 2H; 2H1′), 3.32 (s, 3H; OMe), 3.37 (s, 3H; OMe), 3.77 (s, 1H; H4″ or H5″), 4.08 (s, 1H; H5″ or H4″), 5.46 (t, $J = 6.3$ Hz, 1H; H2′), 6.26 (s, 1H; H4′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.9$ (q), 16.5 (q), 19.6 (t), 19.9 (q), 27.9 (t), 28.5 (q, 2×), 30.9 (q, 3×, *t*Bu), 32.9 (t), 34.4 (s), 35.0 (s), 39.7 (t), 54.4 (q), 56.3 (q), 80.0 (d), 90.3 (d), 127.8 (s), 130.7 (d), 131.5 (s), 132.0 (d), 135.3 (s), 136.7 (s), 141.4 (s), 148.2 (s); IR (NaCl): $\tilde{\nu} = 2928$ (s, C–H), 2826 (m, C–H), 1703 (w), 1458 (m), 1362 (m), 1089 (s), 757 cm^{-1} (s); MS: *m*/*z* (%): 387 (25) $[M+1]^+$, 386 (86) $[M]^+$, 371 (37), 354 (23), 249 (56), 218 (21), 217 (100), 193 (36), 161 (34), 137 (26), 95 (20), 75 (23); HRMS for $C_{26}H_{42}O_2$: calcd 386.3185; found 386.3186.

2-[(2*E*)-4-[(1*Z*)-2-*tert*-Butyl-4,5-dimethoxy-3-methylcyclopent-2-enylidene]-3-methylbut-2-en-1-yl]-1,3,3-trimethylcyclohex-1-ene (31): Dry $CHCl_3$ (0.5 mL) followed by MeOH (11.5 μL, 0.30 mmol) were added to a mixture of divinylallenylacetal **24** (11 mg, 0.03 mmol) and $FeCl_3 \cdot SiO_2$ (9.5 mg, 0.04 mmol). The final mixture was stirred at 25 °C for 45 min. The solvent was evaporated and the residue chromatographed (SiO_2, 97:3 hexane/EtOAc) to afford compound **31** (3.4 mg, 31% yield).

2-[(2*E*)-4-[(1*Z*)-2-*tert*-Butyl-4,5-dimethoxy-3-methylcyclopent-2-enylidene]-3-methylbut-2-en-1-yl]-1,3,3-trimethylcyclohex-1-ene (31): MeOH (7 μL, 0.17 mmol) was added to the solution of divinylallenylacetal **24** (6.4 mg, 0.02 mmol) in acetone (0.3 mL), followed by Pd^{II} chloride bis(acetonitrile) (1 mg, 0.003 mmol) and the mixture was stirred at 25 °C for 20 min. The solvent was evaporated and the residue purified by chromatography on silica gel (97:3 hexane/EtOAc) to afford compound **31** (2.6 mg, 40% yield).

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[24] MMX calculations were carried out with the MacSpartan software package from Wavefunction, Irvine, CA.
[25] The yield of products decreased with increasing amount of H_2O; use of 32 equivalents afforded compounds **29** and **30** in 18% and 17% yield, respectively, whereas 358 equivalents led to product **30** in < 5% yield.
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