Tetrahedron 67 (2011) 1448–1455

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Allylsilane and diallylsilane reactions with functionalized ethylene ketals or benzodioxoles

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ARTICLE INFO

Article history:
Received 18 October 2010
Received in revised form 13 December 2010
Accepted 14 December 2010
Available online 21 December 2010

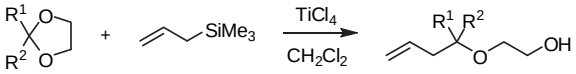
Keywords:
Allylsilane
Diallylsilane
Ethylene ketals
Benzodioxoles
Diastereoselectivity

ABSTRACT

The bis-allylation of ethylene ketal and catechol ketal derivatives of 2,5-hexanedione occurred with a great stereoselectivity. The tetraallylation of bis-catechol ketal derivatives of 2,5-hexanedione and 2-methyl-1,3-cyclohexanedione or the diallylation of 4-phenylbutan-2-one derivatives arise in good yields and these compounds were suitable substrates for ring-closing metathesis leading to 4,4-dialkylcyclopentenes. Condensation of 1,8-bistrimethylsilyl-2,6-octadiene (Bistro) with 4-phenylbutan-2-one catechol ketal derivatives or 2-methylcyclohexan-1,3-dione mono catechol ketal afforded in good yields cyclic and tricyclic products **12** or **23**, respectively.

1. Introduction

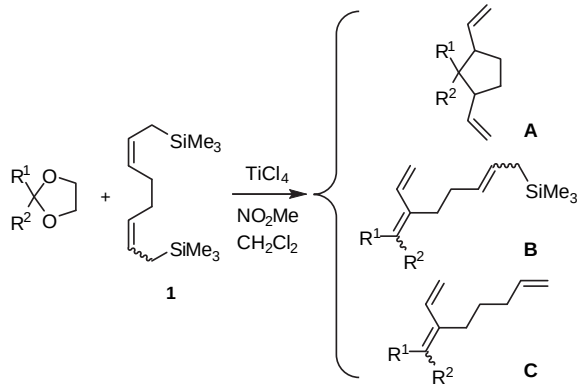
The allylation of electrophilic reagents has gained in importance since the development of the allylsilane chemistry from the seventies.[1] In particular, formation of homoallyl alkyls ethers by allylation of acetals (Hosomi reaction) is well documented (Scheme 1).[2,3]



Scheme 1. Reaction of allyltrimethylsilane with ethylene ketals (Hosomi reaction).

For about fifteen years, we have developed the use of 1,8-bis (trimethylsilyl)-2,6-octadiene (Bistro) **1** as nucleophilic reagent.[4] In the course of the titanium tetrachloride mediated reaction of Bistro with an ethylene ketal, three products could be obtained, the very interesting corresponding divinylcyclopentane **A** and two by-product trienes **B** and **C**. Valuable yields of **A** have been observed with benzylic ethylene ketals (R^1=Ph),[5] but **B** and **C** were major products with aliphatic ethylene ketals (Scheme 2).[6]

These results suggested that the titanium glycolate ether is not enough leaving group to allow the substitution reaction with the second allylsilane moiety. In the benzylic case, the formation of a benzylic cation could explain the formation of **A**. Increasing the leaving group ability by using catechol ketals (2,2-dialkylbenzodioxoles) instead of ethylene ketals should enhance the reactivity of the titanium specie (pK_a of catechol, 9.45 and 12.8,[7] 9.31 and 12.49,[8] 9.21 and 11.0,[9] 9.20,[10] 9.34 and 12.6,[11] glycol, 15.1)[11] and therefore enhance its reactivity. The ^{13}C NMR displacement of the functional carbon atom of catechol ketals (δ: 118–125 ppm/TMS) was ~10 ppm downfield compared to these of ethylene ketals (δ: 107–112 ppm/TMS).



Scheme 2. Reaction of Bistro 1 with ethylene ketals.

Indeed, the complex titanium dichloride catecholate **D** could be more stable than its glycolate counterpart. The diallylation involved

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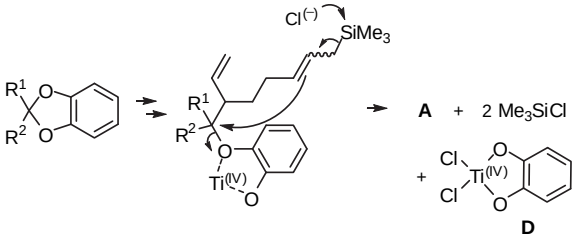
doi:10.1016/j.tet.2010.12.045

the formation of the titanium complex, which underwent a substitution reaction by the second allylsilane moiety to release complex **D**. This titanium complex is a stable, well known compound (CAS number, 13523-46-1)(Scheme 3).[12]

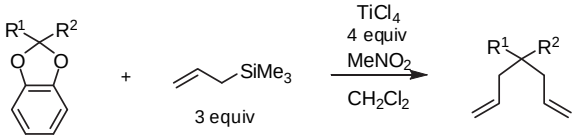


Scheme 3. Postulated reaction of Bistro with 2,2-dialkylbenzodioxoles.

The chemistry of 2,2-dialkylbenzodioxoles are weakly developed. Some results confirmed the easy substitution of the ether linkage. In particular, treatment with boron tribromide exclusively led to *gem*-dibromo derivatives in excellent yields,[13] and the dichloroalane provoked reductive opening to give phenolic ethers.[14]

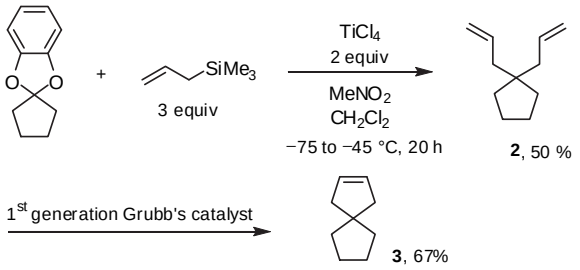
2. Results and discussion

Consequently, we prepared various benzodioxoles[15] to confirm this hypothesis. With 2,2-dialkyl-1,3-benzodioxoles, we have recently shown that allyltrimethylsilane cleanly reacts to give 4,4-dialkylhepta-1,6-dienes resulting from a diallylation process (Scheme 4).[16]



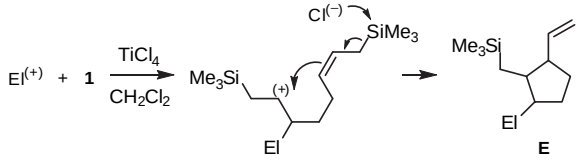
Scheme 4. Diallylation of 2,2-dialkyl-1,3-benzodioxoles.

Moreover, these 4,4-dialkylhepta-1,6-dienes can be used in the ring-closing metathesis to give 4,4-dialkylcyclopentenes, as in the following example from cyclopentanone (Scheme 5).



Scheme 5. Conversion of cyclopentanone catechol ketal to the doubly homologated product **2** followed by ring-closing metathesis.

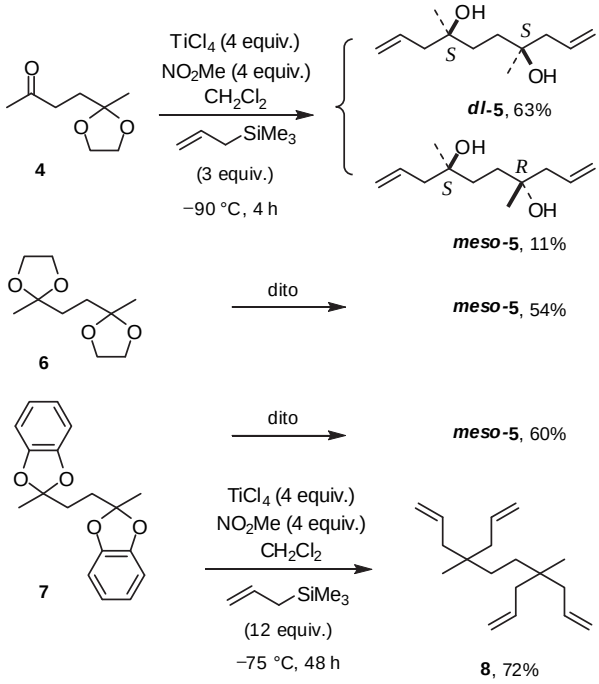
In this preliminary report, the importance of the presence of nitromethane (4 M equiv) was determining. This additive reduced or prevented the formation of by-products **E**. It's resulted from a participation reaction of the second allylsilane moiety in the first addition step of the electrophilic reagent $El^{(+)}$ (Scheme 6).[17,18] The $TiCl_4$ mediated dialkylation reaction of acyl chlorides or ethylene ketals by Bistro is altered by the presence of a nitro group, either in the co-solvent (nitromethane) or in the aliphatic chain. This effect is due to a complexation between the nitro group and titanium, making easier the release of chloride anions essential to the restitution of the allylic moiety with rearrangement.[19]



Scheme 6. Participation reaction in the course of the reaction of Bistro with an electrophilic reagent in the absence of nitromethane.

Then, we investigated the reaction of allyltrimethylsilane and Bistro with various ethylene and catechol ketals.

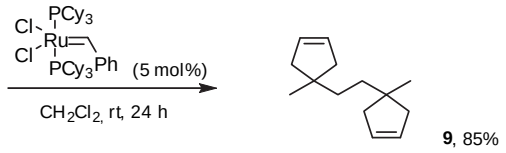
From the synthetic point of view, it was very important to obtain alcohols, which are more suitable for further manipulation than homoallyl ethers. So we studied the reaction of allyltrimethylsilane with the hexan-2,4-dione mono ethylene ketal **4**, diethylene ketal **6**, and dicatechol ketal **7**. In each case, reactions gave rise to diols resulting from a twice allylation. More interestingly, reactions are stereoselective, the hexan-2,4-dione mono ethylene ketal **4** affording mainly *dl*-**5** while **6** and **7** gave rise to *meso*-**5** (Scheme 7). These results demonstrated that a stereo-cooperativity should occur between the two functional groups with, probably, the formation of $TiCl_4$ mediated cyclic intermediates.[17c,20a] The only comparable result deals with allylstannation of hexan-2,4-dione with allyldibutyltin chloride in the presence of water, which led to a 1:1 mixture of ***dl*-5** and ***meso*-5** (no yield given).[21]



Scheme 7. Allylation of the 2,5-hexanedione derivatives.

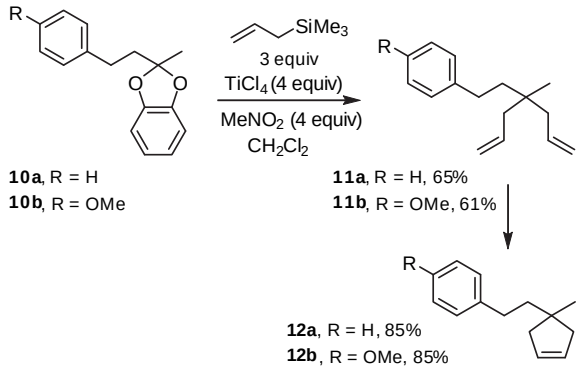
Interestingly, the tetraallylation of the dicatechol ketal **7** giving rise to **8** was performed in a very good yield to give only one product by using a large excess of allyltrimethylsilane.

The structure of the tetraene **8** resulting from a tetraallylation is confirmed by a ring-closing metathesis reaction using the 'first-generation' Grubbs catalyst[22] giving bis-cyclopentene **9** in good yields (Scheme 8).



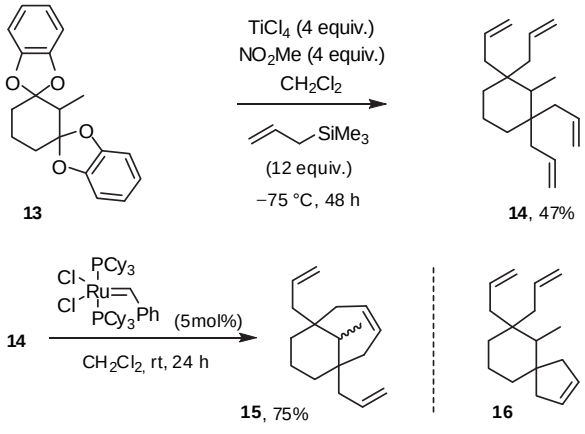
Scheme 8. Ring-closing metathesis reaction of **8**.

The diallylation still occured with functionalized ketone catechol ketals as **10a** or **10b** (Scheme 9). The ring-closing metathesis afforded valuable cyclopentenes **12a** and **12b** in good yields.



Scheme 9. Diallylation reaction of 4-arylbutan-2-one derivatives **10a** and **10b**.

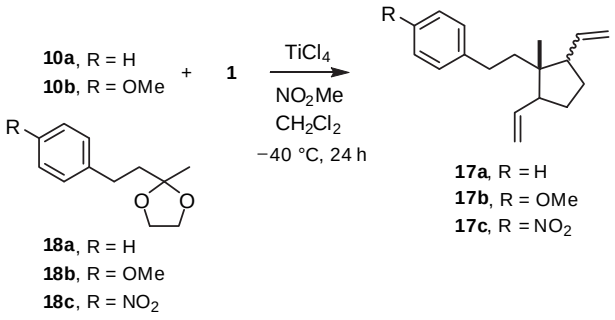
The diallylation of the dicatechol ketal **13** led to a mainly mixture containing the product of tetrallylation **14** in 47% yield (Scheme 10). Again, the structure was confirmed by a ring-closing reaction producing **15** (75% yield, two isomers, *syn* and *anti*). Surprisingly, we observed the formation of a cycloheptene ring instead of a cyclopentene (Scheme 10). Indeed, the isomeric spiro[4.5]decene **16** is slightly less stable than **15**, at the B3LYP/G.311G++(d,p) level of the theory[23] by $\delta\Delta G$=0.7 kcal/mol (for **15**, E=−663.572032 a.u., ZPE=0.388711 a.u., ΔG=−663.227682 a.u.; for spiro isomer **16**: E=−663.570196 a.u., ZPE=0.388289 a.u., ΔG=−663.226559 a.u.).



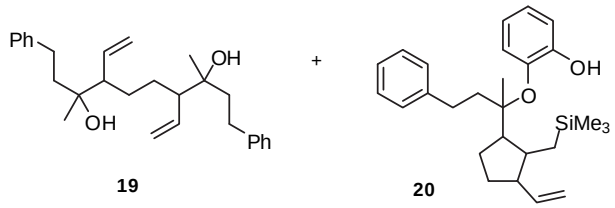
Scheme 10. Allylation of the bis-dioxole **13** and the ring-closing metathesis reaction.

The poor solubility of dicatechol ketal of the 1,4-cyclohexanedione in both CH_2Cl_2 and $CHCl_3$ at low temperature do not allowed any reaction with allyltrimethylsilane.

With Bistro **1** as allylsilane reagent, the catechol ketal **10a**, or the ethylene ketal **18a** of the 4-phenylbutan-2-one, or the same corresponding ketals of 4-*p*-anisylbutan-2-one **10b** and **18b**, provided the expected 1,3-divinylcyclopentane derivatives **17** in fair yields from **10a,b** (along with **10a**, 5% of diol **19**) and moderate yields from **18a,b** (Scheme 11). Without nitromethane and from **10a**, the yield of **17a** decreased to 25% and a new minor product, **20** (3%, only two isomers, ~60:40) appeared. Compound **20** came from a participation reaction of the second allylsilane moiety (product **E**) (Scheme 11). These results showed unambiguously the major role of nitromethane in this process. As in the previous results concerning the reaction of Bistro with several aliphatic ethylene ketals,[6] the major isomer was the *dl*, and then the *meso-anti*.

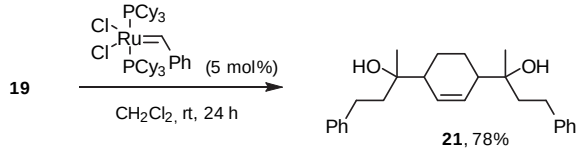


From **10a**: 70% yield; **(±)-17a** : ***meso-anti*-17a** : ***meso-syn*-17a** = 63:23:14
From **10b**: 57% yield; **(±)-17b** : ***meso-anti*-17b** : ***meso-syn*-17b** = 62:22:16
From **18a**: 46% yield; **(±)-17a** : ***meso-anti*-17a** : ***meso-syn*-17a** = 66:23:11
From **18b**: 41% yield; **(±)-17b** : ***meso-anti*-17b** : ***meso-syn*-17b** = 62:23:15
From **18c**: 42% yield; **(±)-17c** : ***meso-anti*-17c** : ***meso-syn*-17c** = 62:23:15



Scheme 11. Reactions of Bistro **1** with 4-phenylbutan-2-one derivatives.

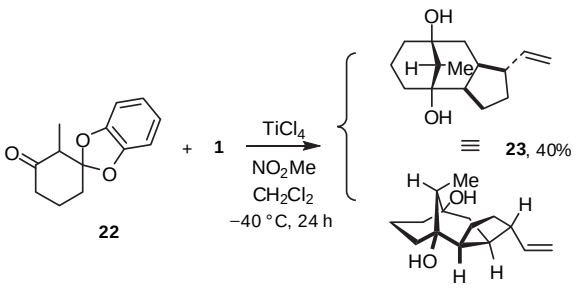
The structure of **19** was confirmed by a ring-closing metathesis reaction[22] giving cyclohexene **21** as only one isomer as revealed by the ^{13}C NMR spectrum (Scheme 12).



Scheme 12. Ring-closing metathesis reaction of **19**.

Surprisingly, the reaction with 2-methylcyclohexan-1,3-dione mono catechol ketal **22** stereoselectively afforded the tricyclic diol **23** (Scheme 13).

The relative stereochemistry of **23** was assigned through extensive NMR analysis. To sum up, ^1H (500 MHz) and ^{13}C (125 MHz)



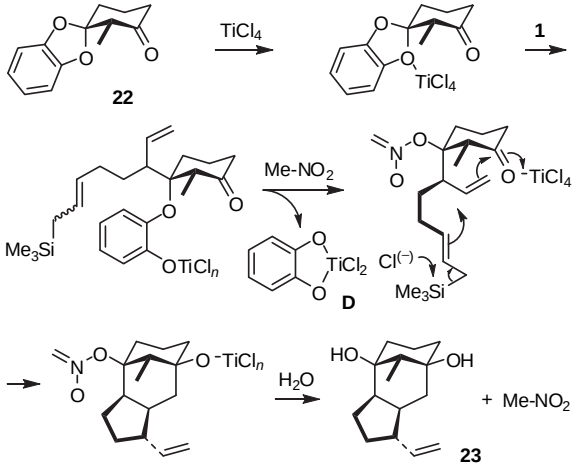
Scheme 13. Reaction of Bistro **1** with 2-methylcyclohexan-1,3-dione mono catechol ketal **22**.

resonances were assigned from *J*-resolve, DEPT, COSYGP, HMBC, HMQC gradient, NOESY (see Experimental section).

The formation of diols **5**, **19**, and **23**, instead of phenolic ethers, is difficult to explain. This unexpected finding seemingly defies our long understanding of the mechanism of allysilane substitution. A careful study of various products of the reaction (in organic and water phases) showed that the only phenolic compound present was the catechol. Clearly, the formation of alcohol instead of homoallyl ether involves a hydrolysis step. As phenoxy ethers are stable compounds under reaction conditions, we consider the formation of an intermediate product, which gives rise to an alcohol during the work-up. In two experiments, we have obtained diol **23** even though the crude reaction mixture was added to a solution of sodium methylate (excess) in anhydrous methanol instead of the usual hydrolysis. Taking into account solvent properties of nitromethane,[24–27] the catechol–chlorotitanium complex may be substituted to its aci-form with release of titanium dichloride catecholate **D** to give nitronate.[28]

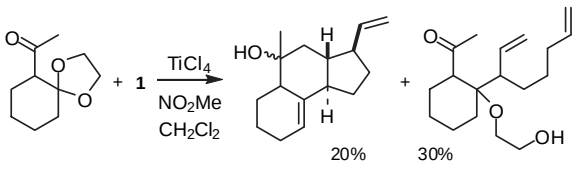
Next, a cascade reaction induced by the addition of chlorine anion to the silicon atom provoked a bicyclization beginning with a nucleophilic attack on the internal carbon atom of the vinyl group and its addition to the carbonyl group (push–pull mechanism).[29]

Then, the hydrolysis (or methanolysis) afforded alcohol (with retention of configuration) and nitromethane (Scheme 14). Although the acyclic alkyl nitronates are unstable,[28] ethyl methanenitronate is a known compound.[30] In superacid solutions, the methylation of nitromethane led to the corresponding onium ion.[31]



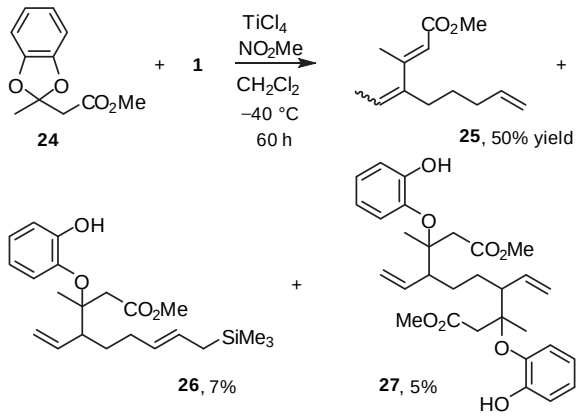
Scheme 14. Formation of tricyclic diol **23**.

Previously, in the course of the Bistro addition to 2-acetylcyclohexanone mono ethylene ketal, a similar reaction giving a tricyclic alcohol was observed, but in the last step an elimination of glycolate occurred (Scheme 15).[32]



Scheme 15. Reaction of Bistro with 2-acetylcyclohexanone mono ethylene ketal.

We next investigated the reactivity of methyl acetylacetate catechol ketal **24**, but, in this case, the main product **25** came from an elimination reaction of catecholate. Minor compounds **26** and **27** appeared as only one stereoisomer according to the ^{13}C NMR spectra (Scheme 16).



Scheme 16. Reaction of Bistro with methyl acetylacetate catechol ketal **24**.

These results showed that the substitution of catecholate by the aci-form of nitromethane depends on subtle structural parameters (the increase of the concentration of nitromethane drastically reduced the reaction rate).

3. Conclusions

The use of dioxoles instead of ethylene ketals notably increased the reactivity of the functional carbon atom and allowed the diallylation even with Bistro **1**, the reactivity of which is strongly reduced compared to the trimethylallylsilane.

4. Experimental section

4.1. General

All reactions were performed under an argon atmosphere in oven-dried glassware. CH_2Cl_2, was freshly distilled from P_2O_5. Other reagents and solvents were obtained from commercial sources and used as received. Flash column chromatography (FC): *Merck* 230–400 mesh silica gel; EtOAc, Et_2O, and petroleum ether as eluents. Thin-layer chromatography (TLC): *Macherey–Nagel* silica gel UV_{254} analytical plates; detection either with UV, or by dipping in revealing solution. ^1H and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions at 500 or 300, and 1250 or 75 MHz, respectively, using a Bruker Advance DPX 500 or AC300 spectrometers. Chemical shift δ in parts per million relative to $CDCl_3$ (signals for residual $CHCl_3$ in the $CDCl_3$: 7.24 ppm for ^1H NMR and 77.16 ppm (central) for ^{13}C NMR). Carbon-proton couplings were determined by DEPT sequence experiments.

4.2. Synthesis of ethylene ketals and dioxoles. General procedure

A 500 mL flask equipped with a Dean–Stark apparatus was charged with ketone (0.1 mol), ethylene glycol (31 g, 0.5 mol) or catechol (16.5 g, 0.15 mol), camphor-10-sulfonic acid (1 g, 4.3 mmol), and toluene (200 mL). The mixture was refluxing, and completion of the reaction was followed by TLC. Then, for the preparation of ethylene ketals, the solution was washed with saturated aqueous solution of $NaHCO_3$, and dried over $MgSO_4$. For the preparation of dioxoles, the solution was stirred for 2 h with anhydrous K_2CO_3 (15 g)

and then filtered. The solvent was evaporated in vacuo, and the residue was flash chromatographed on silica gel.

4.2.1. Cyclopentanone catechol ketal (CAS number, 183-32-4). ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.86–6.77 (m, 4H), 2.19–2.11 (m, 4H), 1.92–1.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.50 (s), 125.43 (s), 121.09 (d) (2C), 108.27 (d) (2C), 37.16 (t) (2C), 23.41 (t) (2C).

*4.2.2. Hexan-2,5-dione mono ethylene ketal (**4**) (CAS number, 33528-35-7).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.83–3.88 (m, 4H), 2.44 (t, J=7.5 Hz, 2H), 2.08 (s, 3H), 1.90 (t, J=7.5 Hz, 2H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=208.4 (s), 109.3 (s), 64.7 (t), 38.3 (q), 32.9 (t), 30.0 (t), 24.0 (q).

*4.2.3. Hexan-2,5-dione bis-ethylene ketal (**6**) (CAS number, 944-26-3).* Mp 63 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.89 (br s, 8H), 1.7 (s, 4H), 1.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=109.7 (s), 64.6 (t), 33.3 (t), 23.8 (q).

*4.2.4. 2,2′-Dimethyl-2,2′-ethylenebis(1,3-benzodioxole) (**7**) (CAS number, 219787-12-9).* Mp 121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.77–6.72 (m, 4H), 2.14 (s, 4H), 1.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.5 (s), 121.2 (d), 118.3 (s), 108.5 (d), 32.8 (t), 24.8 (q).

*4.2.5. 2-Methyl-1,3-cyclohexanedione mono catechol ketal (**22**).* Mp 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.72–6.78 (m, 4H), 2.93 (q, J=6.6 Hz, 1H), 2.50–2.58 (m, 1H), 2.31–2.40 (m, 2H), 2.02–2.17 (m, 1H), 1.80–1.98 (m, 2H), 1.09 (d, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=207.0 (s), 147.6 (s), 147.3 (s), 121.5 (d), 119.8 (s), 108.5 (d), 108.2 (d), 54.4 (d), 40.0 (t), 34.6 (t), 19.2 (t), 6.6 (q). $C_{13}H_{14}O_3$ (218.25): C 71.54, H 6.47; found C 71.65, H 6.31.

*4.2.6. 2-Methyl-1,3-cyclohexanedione dicatechol ketal (**13**).* After completion of the reaction according to the general procedure, the solution was stirred with pentane (250 mL) for 15 min. After settling, the pentane phase was concentrated and the solid was crystallized in a mixture pentane–diethyl ether to give **13** (65%). **13**, mp 76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.85–6.89 (m, 2H), 6.78–6.81 (m, 6H), 2.52 (q, J=6.7 Hz, 1H), 2.25–2.32 (m, 2H), 1.89–2.05 (m, 1H), 1.69–1.83 (m, 3H), 1.09 (d, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.1 (s), 147.3 (s), 147.3 (s), 121.3 (d), 121.2 (d), 118.5 (s), 108.7 (d), 108.1 (d), 47.3 (d), 34.9 (t), 17.8 (t), 5.2 (q). $C_{19}H_{18}O_4$ (310.34): C 73.53, H 5.85; found C 73.55, H 5.81.

4.2.7. 1,4-Cyclohexanedione dicatechol ketal. Mp 270 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.78 (br s, 8H), 2.21 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.2 (s), 121.4 (d), 108.9 (d), 31.7 (t). $C_{19}H_{18}O_4$ (310.34): C 72.96, H 5.44; found C 73.05, H 5.38.

*4.2.8. 2-Methyl-(2-phenylethyl)-1,3-benzodioxole (**10a**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.26–7.36 (m, 5H), 6.85 (s, 4H), 2.84–2.89 (m, 2H), 2.28–2.34 (m, 2H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.6 (s), 141.3 (s), 128.5 (d), 128.4 (d), 126.1 (d), 121.2 (d), 118.4 (s), 108.5 (d), 41.1 (t), 29.5 (t), 24.6 (q). $C_{16}H_{16}O_2$ (240.30): C 79.97, H 6.71; found C 79.85, H 6.61.

*4.2.9. 2-Methyl-[2-(p-anisyl)ethyl]-1,3-benzodioxole (**10b**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, J=8.6 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 6.82 (s, 4H), 3.80 (s, 3H), 2.84–2.75 (m, 2H), 2.30–2.22 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9 (s), 147.6 (s), 133.3 (s), 129.3 (d), 121.1 (d), 118.5 (s), 113.9 (d), 108.4 (d), 55.3 (q), 41.3 (t), 28.5 (t), 24.6 (q). $C_{17}H_{18}O_3$ (270.32): C 75.53, H 6.71; found C 75.55, H 6.68.

*4.2.10. 4-Phenylbutan-2-one ethylene ketal (**18a**) (CAS number, 69246-00-0).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.20–7.33 (m, 5H), 3.98–4.01 (m, 4H), 2.73–2.78 (m, 2H), 1.97–2.03 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=142.2 (s), 128.4 (d), 128.35 (d), 125.8 (d), 109.7 (s), 64.8 (t), 41.1 (t), 33.3 (t), 24.0 (q).

*4.2.11. 4-Anisylbutan-2-one ethylene ketal (**18b**) (CAS number, 290309-44-3).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.10 (d, J=8.7 Hz, 2H), 6.81 (d, J=8.7 Hz, 2H), 3.95 (m, 4H), 3.76 (s, 3H), 2.65 (m, 2H), 1.91 (m, 2H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.8 (s), 134.3 (s), 129.2 (d)(2C), 113.8 (d)(2C), 109.7 (s), 64.8 (t), 55.3 (q), 41.3 (t), 29.4 (t), 24.0 (q). $C_{13}H_{18}O_3$ (222.28): C 78.24, H 8.16; found C 78.15, H 8.21.

*4.2.12. 4-(p-Nitrophenyl)butan-2-one ethylene ketal (**18c**)*[33]. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.11 (d, J=8.7 Hz, 2H), 7.32 (d, J=8.7 Hz, 2H), 3.99–3.93 (m, 4H), 2.83–2.77 (m, 2H), 2.00–1.94 (m, 2H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.3 (s), 146.3 (s), 129.2 (d)(2C), 123.7 (d)(2C), 109.3 (s), 64.9 (s)(2C), 40.4 (t), 30.2 (t), 24.1 (q).

*4.2.13. 2-Methyl-2-(methoxycarbonylmethyl)-1,3-benzodioxole (**24**) (CAS number, 50836-24-3).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.77 (m, 4H), 3.67 (s, 3H), 2.94 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=168.8 (s), 146.9 (s), 121.6 (d), 115.6 (s), 108.8 (d), 52.0 (q), 43.7 (t), 24.4 (q).

4.3. Allylation of ethylene ketals and dioxoles. General procedure

A 50 mL three-necked flask equipped with a thermometer, a septum cap, a magnetic stirring bar, and argon outlet was charged with anhydrous CH_2Cl_2 (25 mL) and anhydrous nitromethane (1.1 mL, 20 mmol). The solution was cooled to −60 °C, and $TiCl_4$ was added (2.2 mL, 20 mmol) followed by the ethylene ketal or the dioxole (5 mmol). Then, the solution was cooled to −90 °C, and allyltrimethylsilane (2.40 mL, 15 mmol for **5**, or 9.6 mL, 60 mmol for **8** and **14**) in anhydrous CH_2Cl_2 (10 mL). For **5**, the solution was stirred at −90 °C for 4 h, and for **8** and **14**, the solution was warmed to −75 °C for 48 h. The completion of the reaction was followed by TLC. Then, the solution was poured onto aqueous saturated NH_4Cl solution and extracted with CH_2Cl_2. The extract was washed until neutrality and possibly filtrated on Celite®. The solution was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel, eluting with a gradient of petroleum ether–diethyl ether.

*4.3.1. 1,1-Diallylcyclopentane (**2**) (CAS number, 1187741-04-3).* Yield 50%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.82 (ddt, J=15.8, 11.2, 7.4 Hz, 2H), 5.04 (br s, 2H), 5.02–4.98 (m, 2H), 2.06 (d, J=7.5 Hz, 4H), 1.65–1.55 (m, 4H), 1.45–1.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=136.2 (d)(2C), 116.8 (t)(2C), 45.2 (s), 43.6 (t)(2C), 36.9 (t)(2C), 24.9 (t)(2C).

4.3.2. (4R,7R*)-4,7-dimethyl-1,9-decadien-4,7-diol (**dl-5**)*[21]. ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.81–5.95 (m, 2H), 5.06–5.17 (m, 4H), 2.55 (½AB d, J=14.1, 7.1 Hz, 1H), 2.48 (½AB d, J=14.1, 7.1 Hz, 1H), 1.84–1.99 (m, 4H), 1.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=133.4 (d), 119.1 (t), 72.6 (s), 48.7 (t), 48.6 (t), 38.6 (t), 29.8 (q).

4.3.3. (4R,7S*)-4,7-dimethyl-1,9-decadien-4,7-diol (meso-**5**)*[21]. ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.77–5.94 (2H, m), 5.06–5.13 (4H, m), 2.53 (1H, ½AB d, J=14.1, 6.9 Hz), 2.46 (1H, ½AB d, J=14.1, 7.1 Hz), 2.21 (2H, d, J=7.5 Hz), 1.75–1.85 (2H, m), 1.58–1.65 (4H, m), 1.49 (3H, s), 1.15 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ=133.8 (d), 133.6 (d), 119.1 (t), 118.8 (t), 73.2 (s), 71.9 (s), 48.5 (t), 46.4 (t), 37.8 (t), 36.3 (t), 29.8 (q), 26.9 (q).

*4.3.4. 4,7-Diallyl-4,7-dimethyldeca-1,9-diene (**8**).* Yield 72% from **7**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.85–5.70 (m, 4H), 5.05–4.95 (m,

8H), 2.10–1.90 (m, 8H), 1.60–1.00 (m, 4H), 0.8 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=135.4 (d) (4C), 117.1 (t) (4C), 44.0 (t) (4C), 35.8 (s) (2C), 32.3 (t) (2C), 24.8 (s) (2C). $C_{18}H_{30}$ (246.23): C 87.73, H 12.27; found C 87.78, H 12.15.

*4.3.5. 2,2-Diallyl-4-phenylbutane (**11a**).* Yield 65% from **10a**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.28–7.09 (m, 5H), 5.91–5.78 (m, 2H), 5.09–5.02 (m, 4H), 2.58–2.53 (m, 2H), 2.05 (d, *J*=7.5 Hz, 4H), 1.53–1.47 (m, 2H), 0.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.4 (s), 135.2 (d)(4C), 128.4 (d), 125.7 (d), 117.3 (t)(2C), 44.0 (t)(2C), 41.7 (t), 36.1 (s), 30.2 (t), 24.7 (q). $C_{16}H_{22}$ (214.35): C 89.65, H 10.35; found C 89.79, H 10.25.

*4.3.6. 2,2-Diallyl-4-(4-p-methoxyphenyl)butane (**11b**).* Yield 61% from **10b**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.10 (d, *J*=8.2 Hz, 2H), 6.84 (d, *J*=8.2 Hz, 2H), 5.94–5.80 (m, 2H), 5.11–5.05 (m, 4H), 3.79 (s, 3H), 2.56–2.50 (m, 2H), 2.07 (d, *J*=7.4 Hz, 4H), 1.53–1.47 (m, 2H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.8 (s), 135.5 (s), 135.2 (d)(2C), 129.3 (d)(2C), 117.3 (t)(2C), 113.9 (d)(2C), 55.4 (q), 44.0 (t)(2C), 41.9 (t), 36.1 (s), 29.3 (t), 24.7 (q). $C_{17}H_{24}O$ (244.37): C 83.55, H 9.90; found C 83.70, H 9.78.

*4.3.7. 2-Methyl-1,1,3,3-tetraallylcyclohexane (**14**).* Yield 47% from **13**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.92–5.72 (m, 4H), 5.10–4.94 (m, 8H), 2.22–1.78 (m, 8H), 1.74–1.21 (m, 6H), 0.90 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=135.2 (d)(4C), 117.0 (t)(4C), 47.1 (t)(2C), 44.4 (t)(2C), 41.3 (d), 37.1 (s)(2C), 31.4 (t)(2C), 22.2 (t), 8.1 (q). EI-MS: *m*/*z* 217 ($M^+-C_3H_5$), 175 (100), 161, 147, 135, 121, 107, 95.

4.4. Reaction of bistro with ethylene ketals and dioxoles. General procedure

The same procedure that for the allylation is used with $TiCl_4$ (2.2 mL, 20 mmol) followed by the ethylene ketal or the dioxole (5 mmol). Then, the solution was cooled to −90 °C, and Bistro 1 (3.17 g, 12.5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added. For cases of **17**, **19**, **20**, and **23**, the solution was warmed to −40 °C for 24 h. For **25**, **26**, and **27**, the solution was warmed to −40 °C for 60 h.

*4.4.1. 2,5-Divinyl-1-methyl-1-(2-phenylethyl)cyclopentane (**17a**).* Yield 70% from **10a**, and 46% from **18a**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.17–7.37 (5H, m), 5.81–5.97 (2H, m), 4.90–5.17 (4H, m), 2.64–2.75 (2H, m), 2.45–2.49 (2H, m), 1.90–2.15 (2H, m), 1.50–1.72 (4H, m), 1.10, 1.0, 0.75 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$)(*ma*: *meso-anti*; *ms*: *meso-syn*): δ=143.7 (s, *dl*), 143.6 (s, *ms*), 140.6 (d, *dl*), 140.3 (d, *dl*), 139.9 (d, *ms*), 128.4 (d, *dl*), 125.6 (d, *ms*), 115.5 (t, *ms*), 115.1 (t, *dl*), 114.2 (t, *dl*), 56.4 (d, *ms*), 54.1 (d, *dl*), 52.2 (d, *dl*), 52.1 (d, *dl*), 47.4 (s), 41.0 (t, *ms*), 39.8 (t), 30.8 (t, *dl*), 30.2 (t, *ms*), 29.0 (t, *dl*), 28.0 (t, *dl*), 27.6 (t, *ms*), 23.9 (q, *ma*), 21.0 (q, *dl*), 15.5 (q, *ms*). $C_{18}H_{24}$ (240.19): C 89.94, H 10.06; found C 89.85, H 10.01.

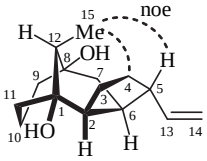
*4.4.2. 2,5-Divinyl-1-methyl-1-(2-p-anisylethyl)cyclopentane (**17b**).* Yield 57% from **10b**, 41% from **18b**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.15 (2H, d, *J*=8.6 Hz), 6.83 (2H, d, *J*=8.6 Hz), 5.70–5.98 (2H, m), 4.9–5.1 (4H, m), 3.78 (3H, s), 2.5–2.7 (m, 2H), 1.80–2.1 (2H, m), 1.5–1.70 (6H, m), 1.07 (3H, s, *ms*), 0.93 (3H, s, *dl*), 0.72 (3H, s, *ma*); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.7 (s), 140.7 (d), 140.4 (d), 139.8 (d), 135.8 (s), 129.3 (d), 115.4 (t), 115.0 (t), 114.0 (t), 113.8 (d), 55.3 (q), 52.1 (d), 52.0 (d), 47.3 (s), 40.0 (t), 29.0 (t), 28.9 (t), 28.0 (t), 23.9 (q, *ma*), 20.9 (q, *dl*), 15.5 (q, *ms*). $C_{19}H_{26}O$ (270.20): C 84.39, H 9.69; found C 84.11, H 9.78.

*4.4.3. 2,5-Divinyl-1-methyl-1-[2-p-nitrophenylethyl]cyclopentane (**17c**).* Yield 42% from **18c**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.09 (d, *J*=8.7 Hz, 2H), 7.26 (d, *J*=8.7 Hz, 2H), 5.92–5.66 (m, 2H), 5.06–4.98 (m, 4H), 2.81–2.62 (m, 2H), 2.41–2.26 (m, 2H), 2.05–1.85 (m, 2H), 1.70–1.40 (m, 4H), 1.06 (s, 0.63H), 0.91 (s, 1.9H), 0.72 (s, 0.48H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=151.7 (s), 146.3 (s), 140.6 (d), 139.9 (d),139.6 (d), 129.2 (d), 123.8 (d), 123.7 (d), 115.8 (t), 115.5 (t), 114.4 (t), 56.1 (d), 54.1 (d), 52.7 (d), 52.3 (d), 47.3 (s), 39.5 (t), 30.8 (t), 29.1 (t), 29.0 (t), 28.1 (t), 27.4 (t), 20.9 (q). $C_{18}H_{28}NO_2$ (285.38): C 75.76, H 8.12; found: C 75.82, H 8.18.

*4.4.4. 3,8-Dimethyl-1,10-diphenyl-4,7-divinyldecan-3,6-diol (**19**).* Yield 5% from **18a**; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.1–7.3 (m, 10H), 5.5–5.85 (m, 2H), 4.9–5.25 (m, 4H), 2.6–2.8 (m, 2H), 2.0–2.07 (m, 2H), 1.70–1.82 (m, 1H), 1.30–1.65 (m, 3H), 1.20 (s, 3H), 1.15 (s, 3H), 0.85–0.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.0 (s), 139.0 (d), 138.95 (d), 138.9 (d), 138.8 (d), 128.5 (d), 125.8 (d), 119.2 (t), 119.6 (t), 118.6 (t), 114.7 (t), 114.6 (t), 73.8 (s), 73.4 (s), 55.4 (d), 54.6 (d), 42.1 (t), 33.9 (t), 33.8 (t), 29.9 (t), 29.8 (t), 28.5 (t), 28.1 (t), 28.5 (t), 27.48 (t), 24.3 (q), 24.1 (q), 24.0 (q). $C_{16}H_{28}O_2$ (252.21): C 76.14, H 11.18; found C 76.23, H 11.28.

*4.4.5. 2-(2-Hydroxyphenoxy)-4-phenyl-2-[2-(trimethylsilylmethyl)-3-vinylcyclopentyl]butane (**20**).* Yield 5% from **10a** in the absence of nitromethane; ^{1}H NMR (300 MHz, $CDCl_3$)(M, major isomer; m, minor isomer): δ=7.35–7.15 (m, 9H), 5.85 (ddd, *J*=17.1, 10.4, 8.2 Hz, 1H), 5.07–4.95 (m, 4H), 2.80–2.55 (m, 4H), 1.0–0.85 (m, 4H), 0.12 (q, m), 0.05 (q, M); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.1 (d), 142.9 (s) (2C), 140.5 (d), 128.5 (d)(4C), 125.8 (d)(2C), 114.8 (t, M), 113.1 (t, m), 75.7 (s, M), 75.0 (s, m), 59.2 (d, m), 55.4 (d, M), 51.8 (d, m), 49.1 (d, M), 44.0 (t, M), 43.95 (t, m), 41.8 (d, m), 40.0 (d, M), 32.0 (t, m), 30.7 (t, M), 30.3 (t, m), 30.0 (t, M), 29.9 (t,M), 27.6 (t, m), 26.7 (t,M), 26.2 (t, m), 24.3 (q, m), 23.5 (q, M), 19.7 (t), 0.02 (q, m), −0.3 (q, M). $C_{27}H_{38}O_2Si$ (422.26): C 76.72, H 9.06; found C 76.73, H 9.15.

4.4.6. (1R,2R*,5S*,6S*,8S*,12S*)-12-Methyl-5-vinyltricyclo[6.3.1.0^{2,6}]-dodecan-1,8-diol (**23**).*



Yield 40% from **22**; ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.75 (ddd, *J*=17.1, 10.2, 9.8 Hz, H13), 4.91 (d, *J*=17.1 Hz, H14), 4.85 (d, *J*=10.2 Hz, H14), 2.32 (m, H6), 2.26 (m, H5), 2.21 (q, *J*=7.1 Hz, H12), 2.15 (m, H2, H9), 1.93 (m, H4), 1.89 (m, H9), 1.86 (m, H3, H10), 1.85 (m, H7), 1.82 (m, H11), 1.85 (m, H7), 1.64 (m, H3, H10), 1.40 (m, H4, H11), 1.18 (d, *J*=7.1 Hz, Me15); ^{13}C NMR (125 MHz, $CDCl_3$): δ=142.9 (C13), 112.5 (C14), 77.1 (C8), 75.7 (C1), 52.3 (C5), 50.7 (C2), 48.6 (C7), 44.8 (C12), 44.0 (C6), 34.1 (C9), 33.4 (C11), 29.0 (C4), 26.5 (C3), 21.8 (C10), 9.6 (C15). $C_{15}H_{24}O_2$ (236.18): C 76.23, H 10.24; found C 76.15, H 10.32.

*4.4.7. Methyl 3-methyl-4-ethylidenenona-2,8-dienoate (**25**).* Yield 50% from **24**; ^{1}H NMR (300 MHz, $CDCl_3$) (M, major isomer; m, minor isomer): δ 5.71–5.78 (m, 1H), 5.26 (d, *J*=8.5 Hz, 1H), 5.18 (d, *J*=8.8 Hz, 1H), 4.91 (d, *J*=17.1 Hz, 1H), 4.82 (d, *J*=10.1 Hz, 1H), 3.62 (s, 3H), 3.00 (s, 2H, m), 2.92 (s, 2H, M), 2.72–2.81 (m, 1H, M), 2.56 (q, *J*=7.2 Hz, 1H, m), 1.80–1.89 (m, 2H), 1.72 (s, 3H, m), 1.65 (s, 3H, M), 1.42–1.64 (m, 2H), 1.20–1.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6 (s), 143.7 (d), 135.3 (t, M), 134.9 (d, m), 127.0 (s, M), 126.6 (s, m), 112.3 (t), 51.8 (d), 44.9 (t, M), 43.2 (q, M), 39.5 (t), 37.9 (t, m), 37.6 (q, m), 33.7 (t), 33.0 (t), 24.1 (q, m), 16.6 (q, M). $C_{13}H_{20}O_2$ (208.15): C 74.96, H 9.68; found C 75.05, H 9.58.

*4.4.8. Methyl 3-methyl-3-(2-hydroxyphenoxy)-9-trimethylsilyl-4-vinylnon-7-enoate (**26**).* Yield 7% from **24**; ^{1}H NMR (300 MHz, $CDCl_3$):

δ 6.91–7.00 (m, 3H), 6.72 (t, *J*=7 Hz, 1H), 5.40–5.60 (m, 2H), 5.05–5.28 (m, 3H), 3.74 (s, 3H), 2.89 (½AB, *J*=15.9 Hz, 1H), 2.52 (½AB, *J*=16.1 Hz, 1H), 2.08–2.15 (m, 2H), 1.90–1.98 (m, 1H), 1.41–1.50 (m, 2H), 1.24–1.33 (m, 1H), 1.16 (s, 3H), −0.01 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.5 (s), 151.9 (s), 141.4 (s), 137.7 (d), 128.2 (s), 126.8 (d), 126.5 (d), 125.1 (d), 123.3 (d), 119.7 (t), 119.2 (d), 116.2 (d), 83.4 (s), 53.5 (d), 52.3 (d), 40.0 (t), 27.9 (t), 27.8 (s), 25.0 (t), 20.8 (q), 18.8 (t), 1.6 (q). $C_{22}H_{34}O_4Si$ (390.22): C 67.65, H 8.77; found C 67.72, H 8.78.

*4.4.9. Dimethyl 3,6-di[3-(2-hydroxyphenoxy)-3-butyrate]-1,7-octadiene (**27**).* Yield 5% from **24**; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92–6.96 (m, 4H), 8.38 (s, 2H, OH), 6.85 (dd, *J*=8.1, 1.3 Hz, 2H), 6.73 (td, *J*=9.1, 1.7 Hz, 2H), 5.72–5.83 (m, 2H), 4.89–5.01 (m, 4H), 3.73 (s, 6H), 2.84 (½AB, *J*=15.7 Hz, 2H), 2.54 (½AB, *J*=15.7 Hz, 2H), 2.29 (dd, *J*=6.6, 2.5 Hz, 2H), 1.77–1.1.84 (m, 10H), 1.21 (s, 6H), 1.11–1.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8 (s), 151.9 (s), 143.9 (d), 141.4 (s), 124.9 (d), 123.3 (d), 119.1 (d), 116.2 (d), 112.3 (t), 84.2 (s), 52.2 (d), 47.1 (d), 41.7 (d), 40.0 (t), 32.6 (t), 32.3 (t), 27.9 (t), 26.5 (t), 20.3 (q). $C_{30}H_{38}O_8$ (526.26): C 68.42, H 7.27; found C 68.52, H 7.38.

4.5. Ring-closing metathesis of diallyl derivatives. General procedure

In a 100 mL double-necked flask equipped with and argon outlet was charged with anhydrous CH_2Cl_2, (80 mL), diallyl derivative (0.4 mmol) 15 mg (0.02 mmol) of first generation Grubbs catalyst. The solution was stirred for 24 h at room temperature. Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel, eluting with *n*-pentane (or petroleum ether/diethyl ether 80:20, for **21**).

*4.5.1. Spiro[4.4]non-2-ene (**3**).* Yield 67%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.69 (br s, 2H), 2.29 (br s, 4H), 1.75–1.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=129.9 (d), 45.9 (t), 45.1 (s), 40.5 (t), 24.1 (t). C_9H_{14} (122.21): C 88.45, H 11.55; found C 88.55, H 11.68.

*4.5.2. 1,2-Bis-(1-methylcyclopent-3-enyl)ethane (**9**).* Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.0 (m, 4H), 2.30–2.00 (m, 8H), 1.40–1.20 (m, 4H), 1.00 (s, 6H); ^{13}C NMR (7 Hz, $CDCl_3$): δ=129.4 (d)(4C), 46.4 (t)(4C), 41.1 (s)(2C), 38.1 (t)(2C), 27.9 (q)(2C). $C_{14}H_{22}$ (190.17): C 88.35, H 11.65; found C 88.45, H 11.55.

*4.5.3. 4-Methyl-4-(2-phenylethyl)cyclopentene (**12a**).* Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$): 7.38–7.18 (m, 5H), 5.72 (br s, H), 2.70–2.64 (m, 2H), 2.20–2.00 (4H), 1.83–1.77 (m, 2H), 1.21 (s, 3H); ^{13}C NMR: 143.5 (s), 129.4 (d) (2C), 128.4 (d) (4C), 125.7 (d), 46.4 (t) (2C), 45.2 (t), 41.4 (s), 32.2 (t), 27.8 (q). $C_{14}H_{18}$ (186.29): C 90.26, H 9.74; found C 89.98, H 9.68.

*4.5.4. 4-Methyl-4-(2-anisylethyl)cyclopentene (**12b**).* Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$): 7.11 (d, *J*=8.7 Hz, 2H), 6.83 (d, *J*=8. Hz, 2H), 5.63 (br s, 2H), 3.78 (s, 3H), 2.56–2.50 (m, 2H), 2.31–2.08 (m, 4H), 1.71–1.65 (m, 2H), 1.12 (s, 3H); ^{13}C NMR: 157.7 (s), 135.6 (s), 129.4 (d)(2C), 129.3 (d)(2C), 113.9 (d)(2C), 55.4 (q), 46.4 (t)(2C), 45.4 (t), 41.4 (s), 31.2 (t), 27.8 (q). $C_{15}H_{20}O$ (216.32): C 83.28, H 9.32; found C 83.39, H 9.42.

*4.5.5. 1,6-Diallyl-10-methylbicyclo[4.3.1]dec-3-ene (**15**).* Yield 75%, two isomers, 2:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.85–5.73 (m, 1H), 5.63–5.54 (m, 1H), 5.42–5.37 (½AB, d, *J*=15.4, 6.0 Hz, 1H, minor isomer), 5.37–5.32 (½AB, d, *J*=15.2, 6.3 Hz, 1H, major isomer), 5.20–5.15 (½AB, d, *J*=15.2, 8.7 Hz, 1H, major isomer), 2.34 (m, 1H), 2.31 (m, 1H), 2.25 (m, 1H), 2.21 (m, 1H), 2.11–2.03 (m, 4H), 1.70–1.1 (m, 7H), 0.78 (d, *J*=7.0 Hz, 3H, minor isomer); 0.68 (d, *J*=6.7 Hz, 3H, major isomer); ^{13}C NMR (75 MHz, $CDCl_3$): δ=138.7 (d)(2C), 129.2 (d) (2C), 114.6 (t)(2C), 47.7 (t)(2C), 44.7 (s), 41.5 (t), 37.8 (t), 22.9 (t), 14.2 (q). EI-MS: *m*/*z* 230 (M^+), 215, 201, 189, 173, 161, 147 (100), 133, 93.

*4.5.6. 3,6-Bis(2-hydroxy-4-phenyl-2-butyl)cyclohexene (**21**).* Yield 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24–7.15 (m, 10H), 5.83 (br s, 2H), 2.74–2.66 (m, 4H), 2.34–2.25 (m, 2H), 1.97–1.72 (m, 10H), 1.24 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=142.8 (s), 129.9 (d), 129.6 (d), 128.4 (d)(4C), 127.4 (d), 127.3 (d), 125.8 (d), 74.6 (s), 74.4 (s), 45.8 (d), 45.2 (d), 42.5 (t), 41.0 (t), 30.1 (t), 30.0 (t), 25.2 (t), 24.8 (d), 24.6 (t), 24.0 (t), 23.3 (d) 22.41 (t), 22.36 (t). $C_{26}H_{34}O_2$ (378.26): C 82.49, H 9.05; found C 82.55, H 9.15.

Acknowledgements

D.M. is grateful to the MEN for a grant and N.G. is grateful to the *CNRS* and the *Région Provence-Alpes-Côte d'Azur* for a grant. We thank Dr. R. Faure for the preparation of 2D NMR spectra and Dr. V. Heran for mass analysis. This work has been financially supported by the *CNRS* and the *Ministère de l'Education Nationale*. We are indebted to Dr. B. Vacher (Pierre Fabre Médicaments, Castres, Fr) for helpful comments.

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