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Selective transformations of differently functionalized 4-ethynyl-octa-1,7-dienes and 5-ethynyl-nona-1,8-dienes via intramolecular Pauson–Khand reaction: preparation of new and useful building blocks for the synthesis of angularly fused triquinanes

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Abstract—The intramolecular Pauson–Khand (PK) reaction of 4-bromomethyldimethylsilyloxy-4-ethynyl-6,6-dimethyloct-1-en-7-yne (**1**), the differently functionalized 4-ethynyl-octa-1,7-dienes (**2**–**6**), and 5-ethynyl-5-hydroxy-2,4,4-trimethyl-nona-1,8-diene (**7**) is reported. The resulting bicyclo[3.3.0]oct-1-en-3-ones (**22**–**29**) and (**33**–**35**) have been obtained in good yield, with moderate stereoselectivity. Major isomers (**22**, **24**, **26**, **28**) have the free or protected hydroxyl group *cis* to H-6a at the fused ring carbon. In dienyne compound **7** the *gem*-dimethyl functional group, with the same length for both alkenyl chains, dictates the regiochemistry of the PK reaction, affording major bicyclo derivatives **33** and **34** (in a 4.6:1 ratio, the major isomer (**33**) having the free hydroxyl group *cis* to the methyl group at C-6a), and compound **35** with the hydroxyl group *trans* to proton H-6a at ring junction. All new adducts are potential useful building blocks for the total synthesis of angularly fused triquinanes. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the last times the Pauson–Khand (PK) reaction[1] has been an extremely useful tool for the synthesis[2] of the complex carbocyclic assemblies present in the fascinating group of polyquinane natural products.[3] Some of us have recently developed cobalt-mediated cycloisomerization[4] and free radical based[5] approaches for the synthesis of different types of triquinanes. On the other hand, some of us have reported on the PK reaction of sugar enynes for the synthesis of cyclopentannulated-pyranosides en route to iridoids,[6] or have used the free radical chemistry for the synthesis of complex polycyclic arrays on sugar templates.[7] Based on this background, we have recently started a collaborative effort aimed at the analysis of the synthetic potential of highly functionalized dienyne or enediyne structures using highly selective organometallic-based transformations.[8]

As a result, in this article we report the intramolecular PK reaction of 4-bromomethyldimethylsilyloxy-4-ethynyl-6,6-dimethyloct-1-en-7-yne (**1**), the diversely functionalized 4-ethynyl-octa-1,7-dienes (**2**–**6**), and 5-ethynyl-5-hydroxy-2,4,4-trimethyl-nona-1,8-diene (**7**) (Fig. 1) for the synthesis of bicyclo[3.3.0]oct-1-en-3-ones as potential new and useful intermediates for the preparation of angularly fused triquinanes. In fact, a detailed survey of the available literature on the selected PK substrates for the synthesis of polyquinanes has shown that the structural motif '5-hydroxy-3,3-dimethyl' in compounds of type **A** (Scheme 1) has not been usually incorporated in the hept-1-en-6-yne functional theme; obviously, this fact has added an additional bonus of interest and novelty to the present project. The control of the *n* value in the branched-chain (see compound of type **A**, Scheme 1) will also dictate the course of the reaction; we were confident that for $n=1$, the double bond at C-1/C-2 would not participate in the PK reaction. Conversely, for $n=2$, a competition between the double bond at C-1/C-2 and at C-7/C-8 would take place, but we speculated that the presence of the *gem*-dimethyl group at C-6 close to C-7/C-8 bond could be critical for the final result of the reaction due to the Thorpe–Ingold effect.[9] In addition, and for future synthetic developments on this subject, we plan to use the pendant 3-butenyl chain installed at C-4 in compounds of

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Keywords: selective transformations; Pauson–Khand reaction; angularly fused triquinanes.

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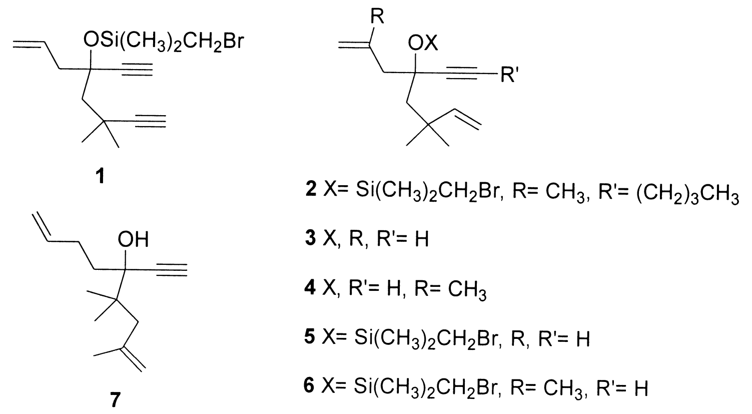


1

7

2 X= $Si(CH_3)_2CH_2Br$, R= CH_3, R'= $(CH_2)_3CH_3$

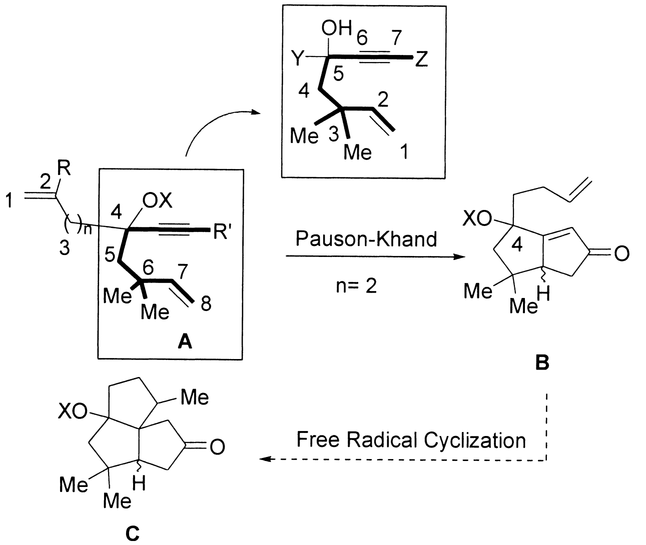
3 X, R, R'= H

4 X, R'= H, R= CH_3

5 X= $Si(CH_3)_2CH_2Br$, R, R'= H

6 X= $Si(CH_3)_2CH_2Br$, R= CH_3, R'= H

Figure 1.



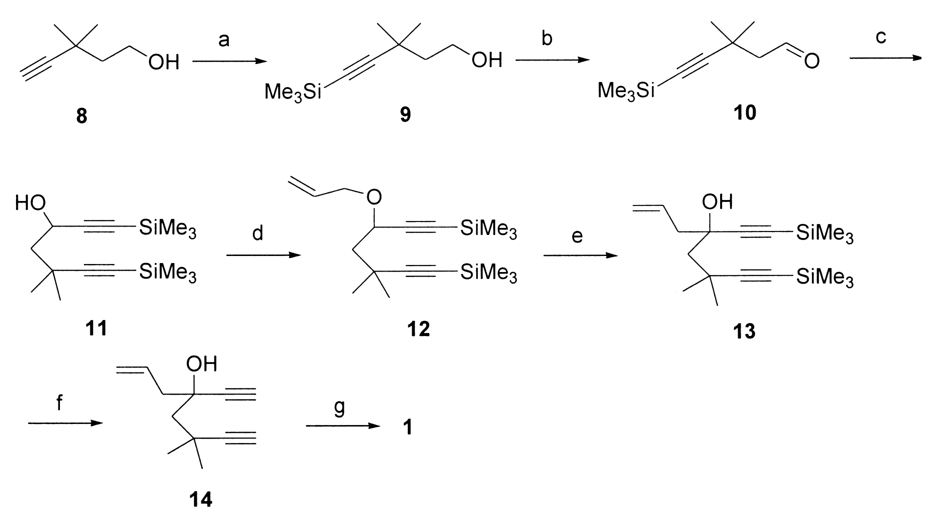
Scheme 1. PK reaction of dienynes (**A**) for the synthesis of bicyclo[3.3.0]oct-1-en-ones (**B**) intermediates for the synthesis of angularly fused triquinanes (**C**).

type **B** (Scheme 1) for the second key cyclopentannulation, possibly via a free radical cyclization reaction,[10,11] to give the angularly fused triquinanes of type (**C**) (Scheme 1).

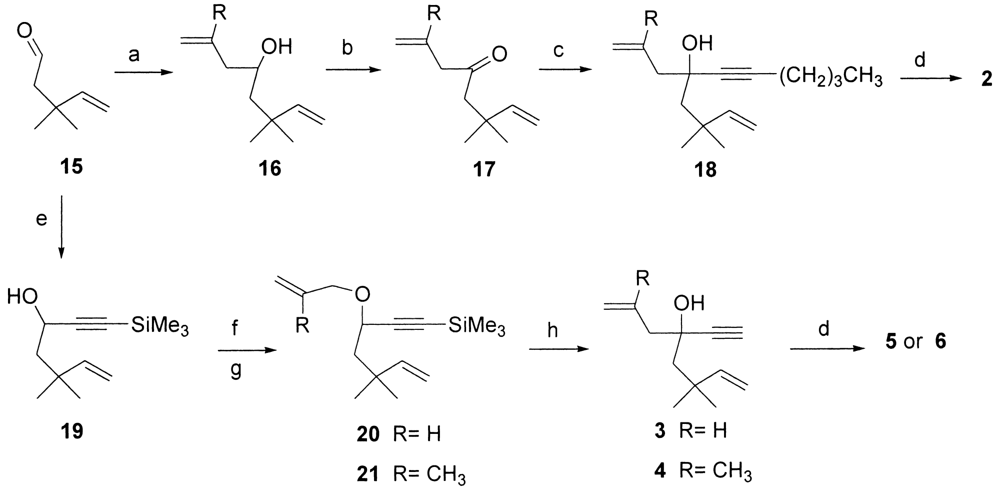
2. Results and discussion

The PK precursors (**1–6**) (Fig. 1) were prepared as shown in Schemes 2 and 3. For the synthesis of precursor **1** (Fig. 1) the starting material was the known alcohol **8**[12] (Scheme 2). After *C*-silylation at the terminal acetylenic position under Denmark's conditions,[13] oxidation, reaction with lithium trimethylsilylacetylide, *O*-alkylation with allyl chloride,[14] [2,3]-Wittig rearrangement,[15] desilylation and *O*-silylation (bromomethyldimethylsilylchloride, imidazole, DMF), compound **1** was finally isolated, via intermediates **9–14**, in good overall yield. All new compounds showed excellent spectroscopic and analytical data (Section 3).

The common starting material for the synthesis of compounds **2–6** was aldehyde **15**[16] (Scheme 3), whose reaction with 2-methylallylmagnesium bromide afforded alcohol **16** (68%). The oxidation of compound **16** to give ketone **17** (55%) followed by reaction with



Scheme 2. *Reagents*: (a) BuLi, trimethylsilylchloride (88%). (b) Swern oxidation. (c) Lithium trimethylsilylacetylide, THF, −78°C (81%, for two steps from **9**). (d) (i) EtMgBr, THF; 0°C; (ii) allyl chloride, HMPA (99%). (e) BuLi, THF, −78°C (90%). (f) KF, DMSO (91%). (g) $BrCH_2SiMe_2Cl$, imidazole, DMF (99%).



Scheme 3. *Reagents*: (a) 2-Methylallylmagnesium bromide, THF, 0°C (68%). (b) Swern oxidation (55%). (c) C_6H_9Li, $CeCl_3$, −78°C (80%). (d) $BrCH_2SiMe_2Cl$, imidazole, DMF (**18** to **2**: 87%, **3** to **5**: 90%, **4** to **6**: 93%). (e) Lithium trimethylsilylacetylide, THF, −78°C (90%). (f) (i) EtMgBr, THF, 0°C; (ii) allyl bromide, HMPA (88%). (g) (i) EtMgBr, THF 0°C; (ii) 2-methylallyl chloride, HMPA (90%). (h) (i) BuLi, THF, −78°C; (ii) KF, DMSO (**20** to **3**: 81%, **21** to **4**: 73%).

1-hexynyllithium, at −78°C, in the presence of cerium salts,[17] gave tertiary alcohol **18** in 80% yield. Silylation under the standard conditions (given earlier) afforded finally precursor **2** in 87% yield. For the synthesis of compounds **3** and **4**, the reaction of product **15** with lithium trimethylsilylacetylide gave alcohol **19** in 90% yield (Scheme 3). Subsequent *O*-alkylation with allyl bromide[14] or 2-methylallyl chloride provided the allyl, propargyl ethers **20** and **21**, in 88 and 90% yield, respectively. Finally, a [2,3]-Wittig sigmatropic rearrangement[15] allowed us to obtain the desired products in convenient chemical yields (**3**: 81%; **4**: 73%). As before, standard silylation of these substrates gave precursors **5** and **6**, in 90 and 93% yield, respectively (Scheme 3). All new compounds showed excellent spectroscopic and analytical data (Section 3).

With the desired compounds in hand we studied the PK reaction. In the standard 'one-pot' experimental conditions (Section 3) using chemical decomposition[18] of the intermediate cobalt-complex with NMO, compound **1**, an enediyne (Fig. 1), and precursor **2**, a dienyne with a disubstituted triple bond (Fig. 1), cleanly afforded the intermediate cobalt-complex, but after decomposition of the cobalt-adduct a complex reaction mixture resulted giving a series of unidentified products. In the case of precursor **2** this reactivity was unexpected, but for product **1** these results are in sharp contrast with the tandem PK reaction reported for similar substrates, affording polycyclic derivatives.[19]

These deceiving results prompted us to submit the free or bromomethyldimethylsilyl-protected 4-ethynyl-4-hydroxy-6,6-dimethyl-octa-1,7-dienes (**3**–**6**) (Fig. 1) to similar PK reaction conditions.

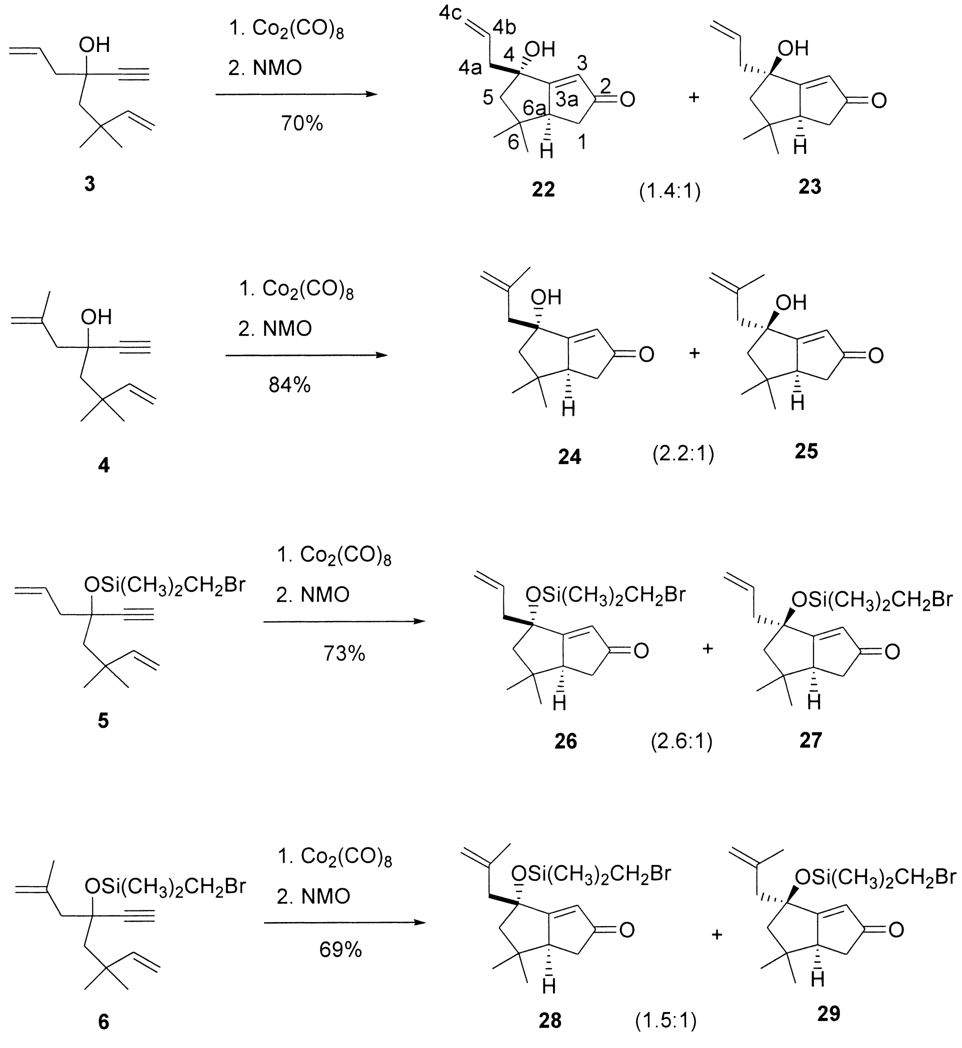
The NMO-induced PK reaction of this material gave adducts **22**/**23** (70% yield), **24**/**25** (84% yield), **26**/**27** (73% yield) and **28**/**29** (69% yield) (Scheme 4).

In all these cases, the stereoselectivity was rather low, in the range of 1.4:1–2.6:1 (Scheme 4), as we could determine in the crude reaction mixture by integrating the clearly differentiated H-6a signals of each isomer on the ^{1}H NMR spectra. On a general basis, H-6a signals for the major isomers appeared more deshielded than in the minor ones (see for instance for **22** (3.22 ppm) and for **23** (2.86 ppm)).

After chromatography we were able to separate these compounds, and isolate pure major products **22**, **24**, **26** and **28**, along with pure minor isomers **23** and **25**.

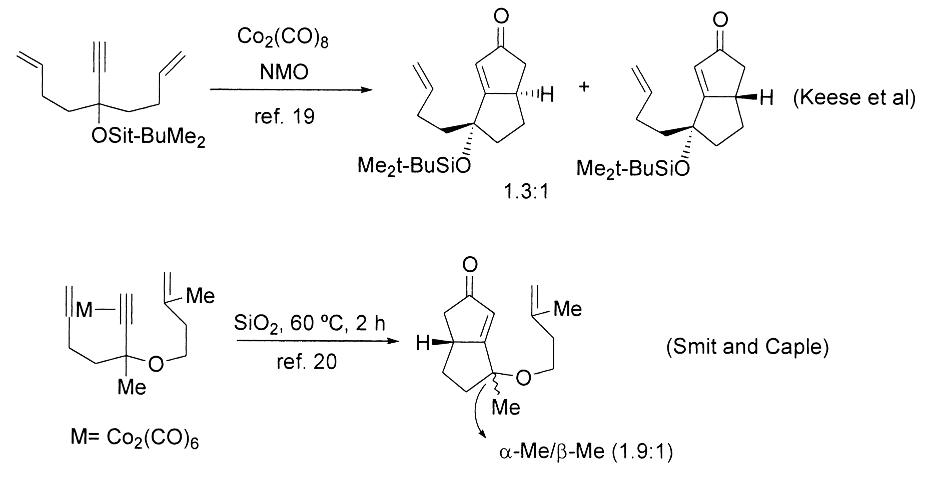
The chemical yield was good, but the stereoselectivity moderate. A detailed analysis of the ^{1}H/^{13}C NMR, DEPT, HMQC, 2D COSY spectra allowed us to assign all the observed signals to the protons and carbons of these molecules. As a matter of case, in the ^{1}H NMR spectrum of major compound **22** we could observe protons H-1 and H-1′ at 2.41 and 2.14 ppm with vicinal coupling constants of 6.6 and 2.7 Hz with H-6a, the proton at the ring junction; the protons at C-5 (56.0 ppm) appeared as a singlet at 2.02 ppm; H-3 at 5.98 ppm showed a small coupling constant (2.7 Hz) with H-6a. Very interestingly, in the ^{13}C NMR spectra we could observe C-6a in compound **22** at 53.8 ppm, while in product **23** this carbon appears more deshielded, at 54.8 ppm ($\Delta\delta=+1$ ppm). As noted earlier, in the cyclization of compound **5** and **6** we have isolated pure only major isomers **26** and **28**, respectively, along with mixtures of the major and minor isomers (**26**+**27** (1:1 ratio) and **28**+**29** (1.2:1 ratio)). In the NMR spectra of these mixtures we were able to analyze the specific signals for the minor isomers **27** and **29** (**27**: ^{1}H NMR (δ) 2.73 (dt, $J_{6a,1'}=6.5$ Hz, $J_{6a,1}=2.6$ Hz, 1H, H-6a), 2.05 and 1.92 (2d) ($J_{5,5'}=14.0$ Hz, 1H, 2×H-5); ^{13}C NMR (δ) 192.6 (C-3a), 80.5 (C-4), 55.7 (C-5); **29**: ^{1}H NMR (δ) 2.76–2.74 (m, 1H, H-6a); ^{13}C NMR (δ) 193.2 (C-3a), 80.8 (C-4), 55.7 (C-5), 53.4 (C-6a), 50.8 (C-4a), 38.0 (C-6)).

The *cis* relative stereochemistry at (OH)C-4/C-H6a in the major isomer **22** was determined by nOe analysis and has been assigned as shown, as no effect was detected between H-6a (3.22 ppm) and H-4a (2.61 ppm); conversely, a nOe effect was observed between H-6a (3.22 ppm) and the

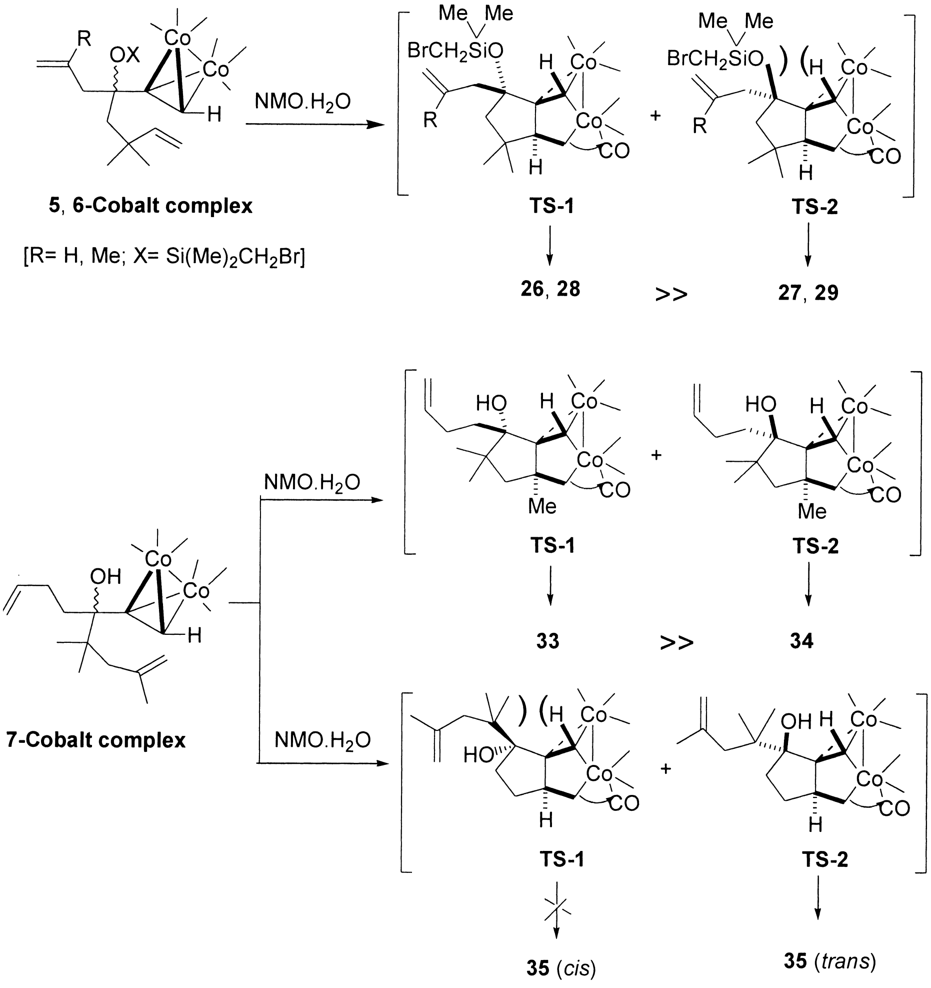


Scheme 4. PK reaction of dienynes **3**–**6**.

signals between 2.49 and 2.34 ppm, this range including protons H-4a, OH and H-1; in addition, as expected, other nOe effects were evident with H-1′ (2.14 ppm) and 2×H-5 (2.02 ppm). Thus, in the major isomer **22** H-6a and the hydroxyl group are *cis* orientated. On the other hand, minor isomer **23** showed a nOe effect between protons H-6a (2.86 ppm) and 2×H-4a (2.48 ppm), 2.40 ppm (H-1)/2.22 ppm (H-1′)/2.04 ppm (H-5). Similar spectroscopic data were also observed in the other adducts, and the corresponding nOe experiments also confirmed these assignments.



Scheme 5. PK reaction on cobalt complexes of 1-en-6-yn-5-ol derivatives (Refs. 19 and 20).

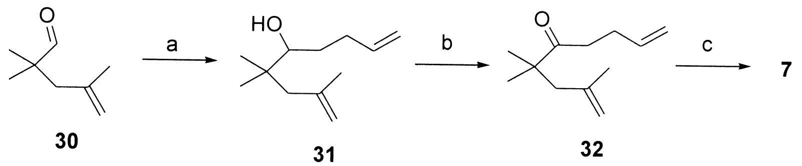


Scheme 6. Proposed transition states for the PK reaction of dienynes **5**, **6** and **7**.

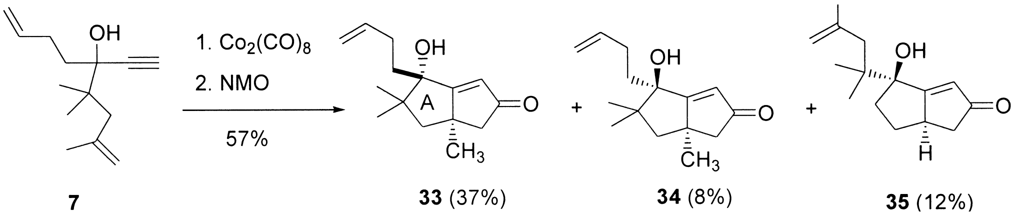
Consequently, we conclude that in the PK reaction of precursors **3**–**6** major *cis* H-6a/(OH)–C4 isomers have been formed.

All these results are in good agreement with the qualitative and quantitative diastereomeric results reported by Keese for the PK reaction of related substrates (Scheme 5).[19] In addition, in a very interesting report on the synthesis of fenestrane derivatives, Smit and Caple[20] described the PK reaction of some very closely related substrates to ours, affording adducts in which the proton at the ring junction and the 3-butenyloxy group were *cis* in the major isomer showing a moderate stereoselectivity (*cis*/*trans* 1.9:1) (Scheme 5).

A possible explanation for these results could be advanced applying the mechanism suggested by Magnus[21] for the intramolecular PK reaction, as shown in Scheme 6. Regarding precursors **5** and **6**, the unfavorable steric interaction between the 'bromomethyldimethylsilyloxy' group and the 'acetylenic proton', compared with a similar interaction with the less sterically demanding 2-substituted allyl chain and the 'acetylenic proton', clearly favors the more stable transition state TS-1, predicting that the experimentally observed major isomers should have the C(4)-*O*-silyl branch and H-6a *cis*, as it is the case. What it is more interesting, and apparently anomalous, is that on going from these substrates (**5** and **6**) to the similar free hydroxy substituted precursors (**3** and **4**) the same stereochemical outcome results affording major isomers with the groups at C(4)–OH and H-6b in a *cis* orientation. As the hydroxyl group seems *smaller* than the 2-substituted allyl chain, the Magnus' mechanism being valid,[21] we hypothesize that other simultaneous effect should be operating—a possible



Scheme 7. *Reagents*: (a) 3-Butenylmagnesium bromide (42%). (b) Swern oxidation (90%). (c) (i) Lithium trimethylsilylacetylide, THF, −78°C; (ii) KF, DMSO (74%).



Scheme 8. PK reaction of precursor **7**.

strong and efficient coordination between the free hydroxyl group with the cobalt atom—to account for these results, but we cannot give still a convenient explanation for this, and new experiments should be designed and carried out.

The good yields obtained in the synthesis of compounds of type **22–29** is of synthetic interest, because these products are possible intermediates for the synthesis of natural products of the angularly fused triquinane type, as described by Paquette.[22]

Next we studied the PK reaction of precursor 5-ethynyl-5-hydroxy-2,4,4-dimethyl-nona-1,8-diene (**7**) (Fig. 1). This compound was synthesized as shown in Scheme 7. The reaction of the known aldehyde **30**[23] with 3-butenyl-magnesium bromide afforded alcohol **31**, which after Swern oxidation and reaction of the resulting ketone **32** with lithium trimethylsilylacetylide gave the desired precursor. All new compounds showed excellent spectroscopic and analytical data (Section 3).

In Scheme 8 we show the results of the PK reaction of precursor **7**. Three compounds (**33–35**) were isolated and characterized in good combined chemical yield (57%). Products **33** and **34** were obtained in 37 and 8% yield, respectively. These two molecules are the cyclization products with 3-methyl-3-butenyl group as the alkenyl part in the PK reaction, while product **35** (12% yield) is the PK reaction product resulting from the cyclization with the 3-butenyl side chain. Thus, major product(s) have been obtained from the reaction with the alkenyl part incorporating the *gem*-dimethyl in the chain. Thus, this example shows the power of the Thorpe–Ingold[9] effect in the PK reaction, a fact that to the best of our knowledge has not been previously demonstrated in this type of cyclizations. This effect appears to be very strong, driving the PK reaction, for a similar length in the tether, to the bicyclo[3.3.0]oct-1-en-3-one with the *gem*-dimethyl substitution in the ring A. All these products showed excellent spectroscopic and analytical data, in good agreement with these structures (Section 3). The stereochemical assignments were carried out by selective nOe experiments irradiating the methyl at the quaternary center (C-6a) (1.27 ppm) and observing the effect on the methylene protons at C-4a (1.86 ppm) in the branched side chain: a clear nOe was observed in compound **34**, establishing the *cis* orientation of these functional groups, while in product **33** this effect was absent. Compound **35** showed H-6a at 2.96–2.86 ppm, a value which is similar to the chemical shift of this proton in the minor isomer in the cyclization of precursors **3–6**; in consequence, we have tentatively assigned the *trans* OH/H(C6a) stereochemistry at these stereocenters. Additional confirmation was obtained upon selective positive nOe experiments between proton H-6a and methyls on C-4 (1.05 and 0.99 ppm).

The formation of major isomer **33** is coherent with the formation of the major *cis* isomers in the cyclization of precursors **3–6**, but a satisfactory explanation for this result has not been yet found. The formation of the exclusive *trans* isomer **35** in this PK reaction can be explained using also the Magnus' mechanism.[21] In this case the strong steric interaction between the 'acetylenic proton' and the '*gem*-dimethyl branched chain' clearly favors the transition state TS-2 versus the transition state TS-1, where this interaction is avoided resulting in the formation of a *trans* product between H-6a and C4–OH (Scheme 6).

To summarize, we have described the PK reaction of a series of dienynes (**3–7**). This reaction has afforded good yields of the corresponding bicyclo[3.3.0]oct-1-en-3-ones (**22–29**, **33–35**), with moderate stereoselectivity. The formation of major *cis* C-4(OH)/H-6a adducts in these processes is of interest and completely unexpected, taking account into the Magnus mechanism[21] into account for the intramolecular PK reaction. The cyclization of compound **7** also shows the strong directing influence of the Thorpe–Ingold effect, for the first time, to the best of our knowledge, that such a reactivity has been documented in the PK reactions. Finally, these molecules are potential useful building blocks for further development. This work is now in progress and will be reported in due course.

3. Experimental

3.1. General methods

Reactions were monitored by TLC using precoated silica gel aluminum plates containing a fluorescent indicator (Merck, 5539). Detection was done by UV (254 nm) followed by charring with sulfuric–acetic acid spray, 1% aqueous potassium permanganate solution or 0.5% phosphomolybdic acid in 95% EtOH. Anhydrous Na_2SO_4 was used to dry organic solutions after washing the organic extract with brine, unless otherwise noted, and the removal of solvents was carried out under vacuum with a rotary evaporator. Column chromatography was performed using silica gel 60 (230–400 mesh, Merck). ^1H and ^{13}C NMR spectra were recorded with Varian VXR spectrometers. Values with (*) can be interchanged. PE refers to petroleum-ether, EA to ethyl acetate, EE to ethyl ether. Compounds **8**,[12] **15**,[14] and **30**[23] were synthesized as described. Cerium chloride heptahydrate has been previously dried under vacuum for an entire week as described.[24]

3.2. General method for the Swern oxidation

To a cold (−78°C) solution of oxalyl chloride (1.2 equiv.) in CH_2Cl_2 was added a solution of DMSO (2.3 equiv.) in CH_2Cl_2. After 5 min of stirring at this temperature, a solution of the alcohol in CH_2Cl_2 was added dropwise. After 15 min, triethylamine (5 equiv.) was added and the mixture was allowed to warm slowly to rt. The reaction was then diluted in ether and treated with a saturated solution of NH_4Cl. After extraction with ether, purification of the reaction mixture by chromatography gave the aldehyde.

3.3. General method for the reaction of lithium trimethylsilylacetylide with aldehydes

To a cooled (−78°C) solution of trimethylsilylacetylene (1.37 equiv.) in THF was added BuLi (1 equiv., 2 M solution in hexane). The mixture was stirred for 30 min at this temperature, then crude aldehyde in THF was added dropwise. The mixture was allowed to warm to rt and treated with excess of a saturated ammonium chloride solution. The aqueous layer was extracted with ether, chromatographic purification of the organic extract gave the alcohol.

3.4. General method for the *O*-alkylation

To an ice-cold solution of alcohol and *ortho*-phenanthrolin (a few mg) in THF was added dropwise ethylmagnesium bromide (ca. 1 equiv.) until a persistent dark-red color was perceived. After addition of HMPA (4.0 equiv.), and the appropriate allyl halide (1.5 equiv.), the mixture was refluxed until completion of the reaction (ca. 3.5 h). The reaction mixture was then allowed to cool to rt and treated with an excess of a saturated ammonium chloride solution and water. The aqueous layer was extracted with ether. Purification by chromatography afforded the corresponding ethers.

3.5. General method for the Wittig rearrangement followed by potassium fluoride promoted desilylation

(a) *Wittig rearrangement*. To a cooled (−78°C) solution of allylic ether in THF was added BuLi (1.2 equiv., 2.4 M solution in hexane). The reaction was monitored by TLC and quenched after completion at this temperature with an excess of a saturated ammonium chloride solution. The aqueous layer was extracted with Et_2O. The combined organic layers were then washed with brine and dried over Na_2SO_4. (b) *Potassium fluoride promoted desilylation*. The crude alcohol was dissolved in DMSO at rt and treated with potassium fluoride (1.5 equiv.) and water (a few drops). After 2 h, the reaction was diluted in water, extracted with ether. Chromatography gave the desired product.

3.6. General method for the silylation reaction

To a solution of the alcohol and imidazole (2.0 equiv.) in freshly distilled DMF (1 M) at 0°C was added dropwise bromomethyldimethylsilylchloride (0.95 equiv.). The mixture was stirred for 0.5 h under N_2. The organic layer was then washed with a saturated solution of NH_4Cl, and the aqueous phase was extracted with ether (3×10 mL). The crude product was subjected to chromatography.

3.6.1. 3,3-Dimethyl-5-trimethylsilylpent-4-yn-1-ol (9). To a cooled (−78°C) solution of alcohol **8**[12] (11.15 g, 99.4 mmol) in THF (200 mL) was added dropwise BuLi (110 mL, 2.2 equiv., 2 M solution in hexane). The mixture was stirred for 1.25 h at rt, and then cooled in dry ice before addition of trimethylsilylchloride (32 mL, 250 mmol, 2.5 equiv.). The mixture was allowed to warm slowly and refluxed for 1.5 h. Hydrolysis with an aqueous solution of H_2SO_4 (107 mL, 1.5 equiv., 1.4 M) of the hot mixture was followed by an extraction with ether. The combined organic layers were then washed with a saturated solution of $KHCO_3$, brine and dried over $MgSO_4$. Chromatography (PE/EA, 85:15) gave **9** (16.18 g, 88%) of a slightly yellow oil: IR (neat) 3330, 2960, 2150, 1450, 1240, 840, 750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (q, J=6.4 Hz, 2H), 2.88 (d, J=6.4 Hz, 1H, OH), 1.65 (t, J=6.4 Hz, 2H), 1.17 (s, 6H), 0.08 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 114.3, 84.8, 60.4, 45.3, 30.1, 29.7 (2C), 0.2 (3C).

3.6.2. 1,7-Bis-(trimethylsilyl)-5,5-dimethyl-1,6-heptadiyn-3-ol (11). Following the general method for the Swern oxidation, alcohol **9** (5.53 g, 30 mmol) gave product **10**, which was used in the next step without purification (oil; ^1H NMR (400 MHz, $CDCl_3$) δ 9.75 (t, J=3.0 Hz, 1H), 2.20 (d, J=3.0 Hz, 2H), 1.16 (s, 6H), 0.0 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 111.5, 85.8, 54.9, 29.7, 29.4 (2C), 0.0 (3C)). Following the general method for the reaction of lithium trimethylsilylacetylide with carbonyl derivatives, the above aldehyde **10** (2.77 g, ca. 15 mmol) in THF (15 mL) gave product **11** (3.40 g, 81% yield over two steps from compound **9**) after purification by chromatography (PE/EA 95:5): oil; IR (neat) 3590, 3490, 2950, 2890, 2860, 2240, 1245, 840 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.60 (dt, J=8.7, 3.5 Hz, 1H), 2.99 (s, 1H, OH), 1.86 (d, J=3.5 Hz, 1H), 1.65 (d, J=3.5 Hz, 1H), 1.18 (s, 3H), 1.17 (s, 3H), 0.06 (s, 9H), 0.04 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 113.8, 106.9, 88.6, 85.9, 61.0, 50.4, 30.6, 30.4, 28.8, 0.0 (6C). Anal. calcd for $C_{15}H_{28}OSi_2$: C, 64.22; H, 10.06. Found: C, 64.23; H, 10.08.

3.6.3. 1,7-(Bistrimethylsilyl)-5,5-dimethyl-3-(2-propenyl)-1,6-heptadiyn-3-ol (13). Following the general method for the *O*-alkylation, alcohol **11** (3.32 g, 11.8 mmol) and allyl bromide (1.5 mL, 18.2 mmol) afforded crude **12** (3.9 g, quantitative yield) which was used in the next step without further purification. Following the general method for the Wittig rearrangement, crude allylic ether **12** (0.99 g, 3.1 mmol) gave product **13** (0.89 g, 90%) after purification by chromatography (PE/EE 95:5): oil; IR (neat) 3480, 2950, 2240, 1635, 1360, 1245, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (ddt, J=17.3, 9.6, 6.7 Hz, 1H), 5.15 (dd, J=9.6, 3.0 Hz, 1H), 5.10 (dd, J=17.3, 3.0 Hz, 1H), 4.40 (s, 1H, OH), 2.43 (ABX, 2H), 1.77 (AB, 2H), 1.50 (s, 3H), 1.25 (s, 3H), 0.16 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 118.4, 114.2, 108.4, 90.1, 87.2, 69.2, 52.2, 48.5, 33.0, 29.8, 19.9, 0.0 (6C). Anal. calcd for $C_{18}H_{32}OSi_2$: C, 81.75; H, 9.15. Found: C, 81.65; H, 9.20.

3.6.4. 5,5-Dimethyl-3-(2-propenyl)-1,6-heptadiyn-3-ol (14). Following the general method for potassium fluoride promoted desilylation, product **13** (2.36 g, 7.36 mmol) yielded compound **14** (1.18 g, 91%) after purification by chromatography (PE/EA 4:1): oil; IR (neat) 3520, 3400, 3290, 3070, 2960, 2910, 2860, 2100, 1635, 1360 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (m, 1H), 5.15 (m, 2H), 3.77 (s, 1H, OH), 2.54 (s, 1H), 2.44 (d, J=6.5 Hz, 2H), 2.31 (s, 1H), 1.80 (AB, 2H), 1.48 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 119.2, 91.7, 86.6, 74.4, 71.1, 69.0, 51.8, 48.8, 32.6, 30.0, 29.4.

3.6.5. 4-Bromomethyldimethylsilyloxy-4-ethynyl-6,6-dimethyloct-1-en-7-yne (1). Following the general method for the silylation reaction, alcohol **14** (0.41 g, 2.3 mmol) gave compound **1** (0.70 g, 99%) after chromatography (PE/EE 9:1) as a slightly yellow oil: IR (neat) 3285, 3060, 2950, 2910, 2850, 2090, 1660, 1245, 830, 725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.87 (ddt, J=17.3, 9.6, 7.0 Hz, 1H), 5.13 (d, J=9.6 Hz, 1H), 5.11 (d, J=17.3 Hz, 1H), 2.58 (m, 5H), 2.07 (s, 1H), 1.81 (AB, 2H), 1.33 (s, 3H), 1.30 (s, 3H), 0.33 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 113.3, 118.6, 92.0, 86.7, 75.4, 71.4, 68.7, 51.9, 48.5, 31.1, 30.4, 29.6, 17.3, −0.3 (2C).

3.6.6. 6,6-Dimethyl-2-methyl-octa-1,7-dien-4-ol (16). To an ice-cold solution of aldehyde **15**[14] (3.37 g, 30 mmol) and 1,10-phenanthroline (3 mg) in THF (27 mL) was added dropwise a solution of 2-methylallylmagnesium bromide in THF (2 M solution, ca. 1 equiv.) until a persistent dark-red color was perceived. The reaction mixture was then warmed to rt for the completion of the reaction. Acid hydrolysis was done at 0°C with a 10% HCl solution. The aqueous layer was extracted with ether. Purification by chromatography (PE/EA 95:5) gave alcohol **17** (3.20 g, 68%) as an oil: IR (neat) 3420, 3070, 2950, 2930, 2860, 1740, 1725, 1640 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, J=17.6, 10.7 Hz, 1H), 4.98 (d, J=17.6 Hz, 1H), 4.96 (d, J=10.7 Hz, 1H), 4.83 (s, 1H), 4.74 (s, 1H), 3.83 (m, 1H), 2.26–2.10 (m, 2H), 1.96 (s, 1H, OH), 1.72 (s, 3H), 1.45 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.8, 113.3, 110.9, 66.6, 49.7, 47.5, 36.3, 28.2, 26.6, 22.5.

3.6.7. 6,6-Dimethyl-2-methyl-octa-1,7-dien-4-one (17). Following the general method for the Swern oxidation, compound **16** (3.20 g, 19 mmol) gave ketone **17** (1.75 g, 55%) after purification by chromatography (PE/EA 94:6), as a slightly yellow oil: IR (neat) 3070, 2950, 2920, 2860, 1710, 1580, 905, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, J=17.7, 10.3 Hz, 1H), 4.98–4.93 (m, 3H), 4.78 (s, 1H), 3.08 (s, 2H), 2.45 (s, 2H), 1.73 (s, 3H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 147.2, 139.4, 115.0, 111.0, 54.0, 53.1, 36.4, 27.0 (2C), 22.7.

3.6.8. 5-(2-Methylallyl)-3,3-dimethylundec-1-en-6-yn-5-ol (18). To a vigorously stirred suspension of dried cerium chloride[24] (3.8 g, 15.6 mmol, 1.5 equiv.) in THF (45 mL) was added dropwise unsaturated ketone **17** (1.73 g, 10.4 mmol) in THF (10 mL). This mixture was stirred for 1 h at rt. BuLi (8 mL, 15.6 mmol, 1.5 equiv., 1.95 M in hexane) was added at −78°C to a solution of hexyne (2.2 mL, 19 mmol, 1.8 equiv.) in THF (20 mL) and the mixture was left at this temperature for 1.25 h. This solution was then added dropwise to the suspension of cerium chloride and ketone **18** cooled in a dry ice bath. The mixture was allowed to warm to rt, and then treated with ether and ammonium chloride. The aqueous layer was extracted with ether, and filtration through a path of celite laid a brown-rose paste that was carefully washed with ether. Chromatography (PE/EA 95:5) gave alcohol **18** (2.07 g, 80%) as a colorless oil: IR (neat) 3450, 3070, 2950, 2920, 2860, 1670, 1455 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.10 (dd, J=17.6, 10.7 Hz, 1H), 5.06–4.80 (m, 4H), 2.54 (s, 1H, OH), 2.35 (s, 2H), 2.18 (t, J=7.0 Hz, 2H), 1.91 (s, 3H), 1.76 (s, 2H), 1.50–1.39 (m, 4H), 1.28 (s, 3H), 1.12 (s, 3H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.5, 142.1, 115.5, 110.5, 86.3, 83.9, 69.0, 53.7, 52.8, 37.0, 30.5, 29.9, 27.3, 24.7, 22.1, 18.6, 13.7. Anal. calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.15; H, 11.42.

3.6.9. [1-(2-Methylallyl)-1-(2,2-dimethylbut-3-enyl)hept-2-ynyloxy]bromomethyldimethylsilane (2). Following the general method for the silylation reaction, alcohol **18** (2.03 g, 8.2 mmol) gave product **2** (2.70 g, 87%) as an oil: IR (neat) 3070, 2950, 2920, 2860, 1640, 1250, 810 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.02 (dd, J=17.6, 10.7 Hz, 1H), 4.85–4.75 (m, 4H), 2.62 (s, 2H), 2.39 (AB, 2H), 2.21 (t, J=7.0 Hz, 2H), 1.84 (s, 3H), 1.73 (AB, 2H), 1.55–1.37 (m, 4H), 1.16 (s, 3H), 1.12 (s, 3H), 0.94 (t, J=7.2 Hz, 3H), 0.30 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.8, 142.0, 115.5, 108.8, 87.6, 84.3, 72.0, 53.6, 53.5, 36.9, 30.4, 29.0, 28.2, 24.6, 22.3, 18.6, 18.1, 13.7, −1.0 (2C). Anal. calcd for $C_{20}H_{35}BrOSi$: C, 60.13; H, 8.83. Found: C, 60.23; H, 8.86.

3.6.10. 5,5-Dimethyl-1-trimethylsilylhept-6-en-1-yn-3-ol (19). Following the general method for the reaction of lithium trimethylsilylacetylide with carbonyl derivatives, compound **15**[14] (16.83 g, 150 mmol) gave alcohol **19** (28.32 g, 90%) after purification by chromatography (PE/EA 9:1): oil; IR (neat) 3350, 2950, 2920, 2890, 2870, 2160, 2075, 1635, 1245, 755 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (d, J=17.0, 10.8 Hz, 1H), 4.91 (d, J=17.0 Hz, 1H), 4.89 (d, J=10.8 Hz, 1H), 4.31 (dd, J=11.1, 6.1 Hz, 1H), 2.02 (bs, 1H, OH), 1.70 (d, J=6.1 Hz, 2H), 1.00 (s, 6H), 0.08 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.0, 111.4, 108.0, 89.2, 60.7, 50.5, 36.3, 28.0, 26.8, 0.0 (3C). Anal. calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found: C, 68.46; H, 10.58.

3.6.11. (3-Allyloxy-5,5-dimethylhept-6-en-1-ynyl)trimethylsilane (20). Following the general method for the *O*-alkylation, alcohol **19** (6.31 g, 30 mmol) afforded the desired product **20** (6.63 g, 88%) after purification by chromatography (PE/EE 95:5): oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.89 (m, 1H), 5.79 (dd, J=17.7, 10.3 Hz, 1H), 5.25 (dq, J=17.7, 1.5 Hz, 1H), 5.15 (dq, J=10.3, 1.5 Hz, 1H), 4.91 (d, J=16.2 Hz, 1H), 4.90 (d, J=11.8 Hz, 1H), 4.19 (ddt, J=12.8, 5.4, 1.5 Hz, 1H), 4.00 (dd, J=6.9, 5.9 Hz, 1H), 3.85 (ddt, J=12.8, 5.4, 1.5 Hz, 1H), 1.76 (dd, J=6.9, 5.9 Hz, 2H), 1.06 (s, 6H), 0.14 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.7, 134.5, 117.2, 110.9, 105.8, 90.1, 69.4, 67.0, 48.2, 36.2, 27.6, 27.1, −0.1 (3C).

3.6.12. 6,6-Dimethyl-4-ethynyl-octa-1,7-dien-4-ol (3). Following the general method for the Wittig rearrangement followed by potassium fluoride promoted desilylation, allylic ether **20** (6.63 g, 26.5 mmol) gave product **3** (3.81 g, 81% from **20**) after purification by chromatography (PE/EA 9:1): oil; IR (neat) 3550, 3450, 3300, 3080, 2960, 2930, 2910, 1840, 1725, 1635 cm^{-1}; ^{1}H NMR (200 MHz,

$CDCl_3$) δ 6.15–5.75 (m, 2H), 5.20–4.95 (m, 4H), 2.67 (s, 1H, OH), 2.48 (s, 1H), 2.40–2.25 (m, 2H), 1.73 (s, 2H), 1.25 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.0, 133.1, 119.2, 111.3, 87.2, 74.0, 69.2, 52.4, 49.4, 37.0, 30.2, 26.7. Anal. calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.48. Found: C, 80.77; H, 10.23.

3.6.13. 6,6-Dimethyl-2-methyl-4-ethynyl-octa-1,7-dien-4-ol (4). Following the general method for the *O*-alkylation, alcohol **19** (6.31 g, 30 mmol) and 2-methallylchoride (4.4 mL, 45 mmol, 1.5 equiv.) afforded *[3-(2-methylallyloxy)-5,5-dimethylhept-6-en-1-ynyl]trimethylsilane* (**21**) (7.13 g, 90%), that was directly engaged in the next step. Following the general method for the Wittig rearrangement followed by potassium fluoride promoted desilylation, the above crude allylic ether **21** (7.13 g, 27.1 mmol) yielded product **4** (3.80 g, 73% from **21**) after purification by chromatography (PE/EA 94:6): oil; IR (neat) 3540, 3460, 3300, 3070, 2950, 2920, 2870, 1720, 1635, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (dd, J=17.6, 10.7 Hz, 1H), 5.09 (dd, J=17.6, 1.3 Hz, 1H), 5.02 (dd, J=10.7, 1.3 Hz, 1H), 4.98 (m, 1H), 4.85 (t, J=1.1 Hz, 1H), 2.73 (s, 1H), 2.53 (s, 1H, OH), 2.40 (s, 2H), 1.92 (s, 3H), 1.82 (d, J=3.3 Hz, 2H), 1.32 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.0, 141.5, 115.7, 111.1, 88.2, 74.1, 68.9, 52.9, 52.3, 37.2, 30.0, 26.8, 24.5.

3.6.14. 5-Bromomethyldimethylsilyloxy-3,3-dimethyl-5-ethynyl-octa-1,7-diene (5). Following the general method for the silylation reaction, alcohol **3** (1.90 g, 10.7 mmol) gave product **5** (3.17 g, 90%) as an oil: IR (neat) 3300, 3080, 2960, 2930, 2910, 2870, 1830, 1640, 1250, 815, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dd, J=17.6, 10.7 Hz, 1H), 5.90 (m, 1H), 5.20–5.05 (m, 2H), 4.88 (m, 2H), 2.60 (s, 2H), 2.58 (s, 1H), 2.47 (d, J=6.6 Hz, 2H), 1.75 (AB, 2H), 1.18 (s, 3H), 1.12 (s, 3H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 133.7, 118.6, 109.4, 87.6, 75.4, 71.8, 53.0, 49.9, 37.0, 29.2, 28.0, 17.9, −0.8 (2C). Anal. calcd for $C_{15}H_{25}BrOSi$: C, 54.70; H, 7.65. Found: C, 54.68; H, 7.69.

3.6.15. 5-Bromomethyldimethylsilyloxy-3,3-dimethyl-5-ethynyl-7-methyl-octa-1,7-diene (6). Following the general method for the silylation reaction, alcohol **4** (1.90 g, 9.9 mmol) gave product **6** (3.16 g, 93%) as an oil: IR (neat) 3300, 3070, 2960, 2920, 2870, 1640, 1250, 840, 815, 790 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, J=17.6, 10.7 Hz, 1H), 4.95–4.80 (m, 4H), 2.62 (AB, 2H), 2.44 (AB, 2H), 1.85 (s, 3H), 1.80 (AB, 2H), 1.18 (s, 3H), 1.14 (s, 3H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 141.4, 115.9, 109.3, 88.1, 75.7, 71.9, 53.1, 53.0, 36.9, 29.2, 28.0, 24.6, 17.8, −0.9 (2C). Anal. calcd for $C_{16}H_{27}BrOSi$: C, 55.98; H, 7.93. Found: C, 56.20; H, 7.68.

3.7. General method for the Pauson–Khand reaction

To a solution of the corresponding precursor in dry methylene chloride (0.025 M), under argon and at rt, was added Co_2CO_8 (1.1 equiv.) and the mixture was stirred until complete reaction (~30 min). Then the mixture was cooled at 0°C and commercially available NMO (6.3 equiv.) was added in one pot. After 3 h at rt the crude was filtered over Celite 545, washed with methylene chloride, and the solvent was evaporated. The residue was purified by chromatography eluting with hexane/EA mixtures.

3.7.1. Pauson–Khand reaction of precursor (3). Following the general method for PK reaction, compound **3** (88 mg, 0.49 mmol) gave products **22** and **23** (71 mg, 70%) in 1.4:1 ratio, after chromatography (hexane/EA 3:1).

(4R)-4,5,6,6aα-Tetrahydro-4-hydroxy-6,6-dimethyl-4-(2-propenyl)-2(1H)-pentalenone* (**22**): oil; IR (neat) 3397, 2958, 1698, 1629, 1246, 1184 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (d, $J_{3,6a}$=2.7 Hz, 1H, H-3), 5.93 (ddt, $J_{4b,4c}$=16.7 Hz, $J_{4b,4c'}$=10.5 Hz, $J_{4a,4b}$=7.2 Hz, 1H, H-4b), 5.29–5.24 (m, 1H, H-4c), 5.21 (dm, 1H, $J_{4b,4c'}$=10.5 Hz, H-4c′), 3.22 (dt, $J_{6a,1}$=6.6 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.7 Hz, 1H, H-6a), 2.61 (dd, $J_{4a,4a'}$=14.0 Hz, $J_{4a,4b}$=7.2 Hz, 1H, H-4a), 2.49–2.34 (m, 2H, H-4a′, OH), 2.41 (dd, $J_{1,1'}$=18.6 Hz, $J_{1,6a}$=6.6 Hz, 1H, H-1), 2.14 (dd, $J_{1,1'}$=18.6 Hz, $J_{1',6a}$=2.7 Hz, 1H, H-1), 2.02 (s, 2H, 2×H-5), 1.18 (s, 3H, CH_3), 0.70 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7 (C-2), 189.8 (C-3a), 132.5 (C-4b), 123.6 (C-3), 120.3 (C-4c), 74.6 (C-4), 56.0 (C-5), 53.8 (C-6a), 44.3 (C-4a), 36.9 (C-6), 36.6 (C-1), 29.3 (CH_3), 22.5 (CH_3); MS (70 eV) *m/z* 206 (39), 165 (100), 150 (27), 137 (66), 81 (841), 53 (36), 41 (42). Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.49; H, 9.05.

(4S)-4,5,6,6aα-Tetrahydro-4-hydroxy-6,6-dimethyl-4-(2-propenyl)-2(1H)-pentalenone* (**23**): mp 77–80°C; IR (KBr) ν 3426, 2960, 2920, 1687, 1631, 1232, 1187, 917, 858 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, $J_{3,6a}$=2.5 Hz, 1H, H-3), 5.83 (ddt, $J_{4b,4c}$=17.0 Hz, $J_{4b,4c'}$=10.3 Hz, $J_{4b,4a}$=7.3 Hz, 1H, H-4b), 5.30–5.19 (m, 2H, 2×H-4c), 2.86 (dt, $J_{6a,1}$=6.4 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.5 Hz, 1H, H-6a), 2.48 (dd, $J_{4a,4b}$=7.3 Hz, $J_{4a,4c}$=3.8 Hz, 2H, 2×H-4a), 2.40 (dd, $J_{1',1}$=18.4 Hz, $J_{1,6a}$=6.4 Hz, 1H, H-1), 2.22 (dd, $J_{1,1'}$=18.4 Hz, $J_{1',6a}$=2.7 Hz, 1H, H-1′), 2.20 (s, 1H, OH), 2.04 (d, $J_{5',5}$=14.2 Hz, 1H, H-5), 1.88 (d, $J_{5,5'}$=14.2 Hz, 1H, H-5′), 1.13 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.6 (C-2), 193.0 (C-3a), 132.0 (C-4b), 125.0 (C-3), 120.7 (C-4c), 76.7 (C-4), 55.9 (C-5), 54.8 (C-6a), 46.0 (C-4a), 38.4 (C-6), 37.0 (C-1), 28.5 (CH_3), 21.7 (CH_3); MS (70 eV) *m/z* 206 (3), 165 (100), 137 (59), 81 (24), 53 (24), 41 (32). Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 76.08; H, 8.90.

3.7.2. Pauson–Khand reaction of precursor (4). Following the general method for PK reaction, compound **4** (84 mg, 0.44 mmol) gave products **24** and **25** (80 mg, 84%) in 2.2:1 ratio, after chromatography (hexane/EA 6:4).

(4R)-4,5,6,6aα-Tetrahydro-4-hydroxy-6,6-dimethyl-4-(2-methyl-2-propenyl)-2(1H)-pentalenone* (**24**): oil; IR (neat) 3445, 2955, 1694, 1626, 1180, 886 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 (d, $J_{3,6a}$=2.6 Hz, 1H, H-3), 5.00 (qt, $J_{4c,4c'}$=$J_{4c,CH3}$=1.0 Hz, H-4c), 4.87 (q, 1H, $J_{4c,4c'}$=$J_{4c',2(4a)}$=1.0 Hz, 1H, H-4c′), 3.22 (dt, $J_{6a,1}$=6.6 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.6 Hz, 1H, H-6a), 2.70 (d, $J_{4a,4a'}$=14.1 Hz, 1H, H-4a), 2.44 (dd, $J_{1,1'}$=18.6 Hz, $J_{1,6a}$=6.6 Hz, 1H, H-1), 2.33 (dd, $J_{4a,4a'}$=14.1 Hz, J=0.7 Hz, 1H, H-4a′), 2.24 (br s, 1H, OH), 2.17 (dd, $J_{1,1'}$=18.6 Hz, $J_{1',6a}$=2.6 Hz, 1H, H-1′), 2.16 (d, $J_{5,5'}$=14.0 Hz, 1H, H-5), 2.00 (d, $J_{5,5'}$=14.0 Hz, 1H, H-5′), 1.88 (d, 3H, J=0.9 Hz, $CH_3C{=}CH_2$), 1.20 (s, 3H,

CH_3), 0.73 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5 (C-2), 190.0 (C-3a), 141.6 (C-4b), 123.4 (C-3), 115.8 (C-4c), 74.9 (C-4), 56.4 (C-5), 53.4 (C-6a), 47.3 (C-4a), 36.9 (C-6), 36.8 (C-1), 29.5 (CH_3), 24.5 ($\mathit{C}H_3C{=}CH_2$), 22.6 (CH_3); MS (70 eV) *m/z* 220 (6), 192 (13), 165 (100), 149 (51), 137 (81), 121 (27), 109 (37), 108 (63), 95 (27). Anal. calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.41; H, 8.99.

(4S)-4,5,6,6aα-Tetrahydro-4-hydroxy-6,6-dimethyl-4-(2-methyl-2-propenyl)-2(1H)-pentalenone* (**25**): oil; IR (neat) 3442, 2954, 1697, 1626, 1230, 895 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.02 (d, $J_{3,6a}$=2.5 Hz, 1H, H-3), 5.02 (dq, $J_{4c,CH3}$=0.5 Hz, $J_{4c,4c'}$=1.0 Hz, 1H, H-4c), 4.86 (q, $J_{4c,4c'}$=$J_{4c',CH2(4a)}$=1.0 Hz, 1H, H-4c′), 2.89 (dt, $J_{6a,1}$=6.4 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.5 Hz, 1H, H-6a), 2.48 (s, 2H, 2×H-4a), 2.41 (dd, $J_{1,1'}$=18.6 Hz, $J_{1,6a}$=6.4 Hz, 1H, H-1′), 2.37 (s, 1H, OH), 2.23 (dd, $J_{1,1'}$=18.6 Hz, $J_{1',6a}$=2.5 Hz, 1H, H-1′), 2.09 (d, $J_{5,5'}$=14.1 Hz, 1H, H-5′), 1.90 (d, $J_{5,5'}$=14.1 Hz, 1H, H-5), 1.81 (dt, *J*=0.9, 0.5 Hz, 3H, $C\mathit{H}_3C{=}CH_2$), 1.14 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.4 (C-2), 193.7 (C-3a), 141.2 (C-4b), 125.1 (C-3), 116.3 (C-4c), 76.6 (C-4), 56.5 (C-5), 54.5 (C-6a), 49.5 (C-4a), 38.3 (C-6), 36.9 (C-1), 28.7 (CH_3), 24.4 ($\mathit{C}H_3C{=}CH_2$), 21.7 (CH_3); MS (70 eV) *m/z* 220 (6), 192 (9), 165 (100), 164 (22), 149 (24), 137 (77), 109 (42), 108 (30), 95 (24). Anal. calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.08; H, 9.40.

3.7.3. Pauson–Khand reaction of precursor (5). Following the general method for PK reaction, compound **5** (73 mg, 0.22 mmol) gave products **26** and **27** (58 mg, 73%) in 2.6:1 ratio, after chromatography (hexane/EA 95:5). *(4R*)-4-(Bromomethyldimethylsilyloxy)-4,5,6,6aα-tetrahydro-6,6-dimethyl-4-(2-propenyl)-2(1H)-pentalenone* (**26**): oil; IR (neat) 2959, 1713, 1629, 1253, 1145, 1070, 816 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.03 (d, $J_{3,6a}$=2.6 Hz, 1H, H-3), 5.88 (ddt, $J_{4b,4c}$=17.0 Hz, $J_{4b,4c'}$=9.9 Hz, $J_{4b,4a}$=7.0 Hz, 1H, H-4b), 5.18–5.09 (m, 2H, 2×H-4c), 3.19 (dt, $J_{6a,1}$=6.6 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.6 Hz, 1H, H-6a), 2.67 (d br d, $J_{4a,4a'}$=14.3 Hz, $J_{4a,4b}$=7.0 Hz, 1H, H-4a), 2.44 (dd, $J_{1,1'}$=18.8 Hz, $J_{1,6a}$=6.6 Hz, 1H, H-1), 2.41 (s, 2H, CH_2Br), 2.31 (ddt, $J_{4a,4a'}$=14.3 Hz, $J_{4a',4b}$=7.0 Hz, $J_{4a',4c}$=1.1 Hz, 1H, H-4a), 2.16 (dd, $J_{1,1'}$=18.8 Hz, $J_{1,6a}$=2.6 Hz, 1H, H-1), 2.09 (d, $J_{5,5'}$=14.2 Hz, 1H, H-5), 2.03 (d, $J_{5,5'}$=14.2 Hz, 1H, H-5′), 1.18 (s, 3H, CH_3), 0.67 (s, 3H, CH_3), 0.27, 0.25 ($Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9 (C-2), 188.9 (C-3a), 133.2 (C-4b), 125.0 (C-3), 118.8 (C-4c), 77.7 (C-4), 57.0 (C-5), 54.0 (C-6a), 44.8 (C-4a), 36.6 (2C, C-1, C-6), 29.7 (CH_3), 22.6 (CH_3), 17.2 (CH_2Br), −0.73 ($Si(CH_3)_2$); MS (70 eV) *m/z* 317 (100), 315 (100), 275 (20), 273 (22), 260 (36), 258 (37), 152 (52), 150 (53), 124 (45), 122 (42), 91 (24), 75 (37), 41 (24). Anal. calcd for $C_{16}H_{25}O_2BrSi$: C, 53.78; H, 7.05. Found: C, 54.00; H, 7.30. Product **27** could not be isolated in a pure state.

3.7.4. Pauson–Khand reaction of precursor (6). Following the general method for PK reaction, compound **6** (79 mg, 0.23 mmol) gave products **28** and **29** (59 mg, 69%) in 1.5:1 ratio, after chromatography (hexane/EA 9:1). *(4R*)-4-(Bromomethyldimethylsilyloxy)-4,5,6,6aα-tetrahydro-6,6-dimethyl-4-(2-methyl-2-propenyl)-2(1H)-pentalenone* (**28**): oil; IR (neat) 2958, 1714, 1627, 1253, 1090, 1067, 814 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.02 (d, $J_{3,6a}$=2.6 Hz, 1H, H-3), 4.89 (s, 1H, H-4c), 4.75 (s, 1H, H-4c′), 3.15 (dt, $J_{6a,1}$=6.6 Hz, $J_{6a,1'}$=$J_{6a,3}$=2.6 Hz, 1H, H-6a), 2.68 (br d, $J_{4a,4a'}$=14.7 Hz, 1H, H-4a), 2.41 (dd, $J_{1,1'}$=18.6 Hz, $J_{1,6a}$=6.6 Hz, 1H, H-1), 2.36 (s, 2H, CH_2Br), 2.22 (d, $J_{5,5'}$=14.1 Hz, 1H, H-5), 2.15 (d, $J_{4a,4a'}$=14.7 Hz, 1H, H-4a), 2.14 (dd, $J_{1,1'}$=18.6 Hz, $J_{1',6a}$=2.6 Hz, 1H, H-1′), 2.01 (d, $J_{5,5'}$=14.1 Hz, 1H, H-5′), 1.79 (s, 3H, $C\mathit{H}_3C{*}CH_2$), 1.14 (s, 3H, CH_3), 0.64 (s, 3H, CH_3), 0.22 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0 (C-2), 189.5 (C-3a), 141.8 (C-4b), 125.2 (C-3), 115.3 (C-4c), 78.0 (C-4), 56.9 (C-5), 54.2 (C-6a), 48.2 (C-4a), 36.7 (C-1), *29.7* (*C-6*), 29.5 (CH_3), 24.3 ($\mathit{C}H_3C{*}CH_2$), 22.2 (CH_3), 17.1 (CH_2Br), −0.82 ($Si(CH_3)_2$); MS (70 eV) *m/z* 317 (99), 315 (100), 275 (22), 273 (27), 260 (39), 258 (39), 152 (51), 150 (53), 124 (46), 122 (42), 91 (26), 79 (16), 77 (18), 75 (33), 55 (21), 41 (21). Anal. calcd for $C_{17}H_{27}O_2BrSi$: C, 54.98; H, 7.33. Found: C, 55.06; H, 7.63. Product **29** could not be isolated in a pure state.

3.7.5. 2,4,4-Trimethyl-nona-1,8-dien-5-ol (31). To a cold (−78°C) solution of aldehyde **30**[23] (856 mg, 6.8 mmol) in THF (8 mL) was added dropwise 3-butenylmagnesium bromide (6.7 mL, 10.2 mmol, 1.5 equiv., 1.5 M solution of in THF). The reaction mixture was then warmed to rt for the completion of the reaction and treated with a saturated solution of NH_4Cl. After extraction with ether, the organic layers were washed with brine and dried over $MgSO_4$. Purification by chromatography (PE/EE 90:10) gave product **31** (525 mg, 42% yield): IR (neat) 3400, 3080, 2950, 1640, 1460, 1390 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.82 (ddt, *J*=16.7, 9.8, 6.9 Hz, 1H), 5.08–4.68 (m, 4H), 3.28 (dd, *J*=10, 1.5 Hz, 1H), 2.30 (m, 1H), 2.13 (m, 1H), 1.98 (AB, *J*=13 Hz, 2H), 1.78 (s, 3H), 1.68–1.53 (m, 1H), 1.47–1.27 (m, 1H), 0.89 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.0, 138.9, 114.8, 114.6, 78.5, 46.6, 38.5, 31.4, 30.5, 25.4, 24.1, 23.3.

3.7.6. 2,4,4-Trimethyl-nona-1,8-dien-5-one (32). Following the general method for the Swern oxidation, alcohol **31** (2.43 g, 13.3 mmol) gave ketone **32** (2.17 g, 90% yield) after purification by chromatography (PE/EE 9:1): IR (neat) 3080, 2950, 1700, 1640, 1460, 1360 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.80 (ddt, *J*=16.7, 9.8, 6.9 Hz, 1H), 4.99–4.59 (m, 4H), 2.58 (t, *J*=7.4 Hz, 2H), 2.29 (m, 4H), 1.62 (s, 3H), 1.12 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 214.6, 142.3, 137.6, 115.0, 114.2, 47.5, 47.3, 36.6, 27.9, 25.0 (2C), 24.3.

3.7.7. 5-Ethynyl-2,4,4-trimethyl-nona-1,8-dien-5-ol (7). Following the general method for the reaction of lithium trimethylsilylacetylide with carbonyl derivatives, compound **32** (2.17 g, 12 mmol) gave a crude alcohol (3.35 g, quantitative yield), which was submitted to the general method for the potassium fluoride promoted desilylation to give alcohol **7** (1.84 g, 74% yield over two steps) after purification by chromatography (PE/EE 95:5): oil; IR (neat) 3500, 3300, 3080, 2980, 1640, 1450, 1350 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.91 (ddt, *J*=16.7, 9.8, 6.9 Hz, 1H), 5.10–4.80 (m, 4H), 2.52 (s, 1H), 2.47–2.12 (m, 4H), 1.84 (s, 3H), 1.70 (m, 2H), 1.08 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.6, 139.13, 115.5, 115.0, 85.6, 77.9, 74.6, 45.1, 42.4, 34.7, 29.4, 25.6, 23.0, 22.0.

3.7.8. Pauson–Khand reaction of precursor (7). Following the general method for PK reaction, compound **7** (233 mg, 1.13 mmol) gave products **33** (99 mg, 37%), **34** (21 mg, 8%) and **35** (33 mg, 12%) after chromatography (hexane/EA from 9:1 to 6:4).

(4S*)-4-(3-Butenyl)-4,5,6,6a-tetrahydro-4-hydroxy-5,5,6aα-trimethyl-2(1H)-pentalenone (**33**): oil; IR (neat) 3458, 2957, 2869, 2246, 1702, 1621, 1451, 913, 734 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.90 (s, 1H, H-3), 5.97–5.83 (m, 1H, H-4c), 5.10 (dd, $J_{4d,4c}$=17.2 Hz, $J_{4d,4d'}$=1.5 Hz, 1H, H-4d), 5.02 (dd, $J_{4d',4c}$=10.0 Hz, $J_{4d,4d'}$=1.5 Hz, 1H, H-4d′), 2.48 (d, $J_{1,1'}$=16.6 Hz, 1H, H-1), 2.33 (d, $J_{1',1}$=16.6 Hz, 1H, H-1′), 2.36–2.25 (m, 2H, 2×H-4b), 1.85 (br s, 1H, OH), 1.91 (d, $J_{6,6'}$=13.3 Hz, 1H, H-6), 1.71 (ddd, J=9.9, 6.5, 2.9 Hz, 2H, 2×H-4a), 1.63 (d, $J_{6,6'}$=13.3 Hz, 1H, H-6′), 1.41 (s, 3H, CH$_3$), 1.13 and 0.76 (2s, 2×3H, C(5)(CH$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 210.9 (C-2), 193.3 (C-3a), 138.6 (C-4c), 124.9 (C-3), 115.5 (C-4d), 82.1 (C-4), 57.0 (C-1), 50.6 (C-6), 47.5 (C-6a)*, 46.7 (C-5)*, 32.0 (CH$_3$), 31.7 (C-4b), 28.9 (C-4a), 26.8 and 22.2 (2C, C(5)(*C*H$_3$)$_2$); MS (70 eV) *m/z* 206 (44), 192 (26), 178 (62), 151 (100), 135 (45), 122 (68), 109 (38), 95 (30), 81 (34), 67 (40), 55 (43), 41 (38). Anal. calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.64. Found: C, 76.58; H, 9.47.

(4S*)-4-(3-Butenyl)-4,5,6,6a-tetrahydro-4-hydroxy-5,5,6aα-trimethyl-2(1H)-pentalenone (**34**): oil; IR (neat) 3438, 2962, 2870, 1698, 1622, 1169, 909 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.05 (s, 1H, H-3), 5.88 (ddt, $J_{4c,4d'}$=17.1 Hz, $J_{4c,4d}$=10.3 Hz, $J_{4c,4b}$=6.5 Hz, 1H, H-4c), 5.06 (dm, $J_{4d,4c}$=17.1 Hz, 1H, H-4d), 5.01 (dm, $J_{4d',4c}$=10.3 Hz, 1H, H-4d′), 2.52 (d, 1H, $J_{1,1'}$=16,3 Hz, H-1), 2.42 (d, 1H, $J_{1',1}$=16.3 Hz, H-1′), 2.41–2.31 (m, 1H, H-4b), 1.99–1.90 (m, 1H, H-4b′), 1.86–183 (m, 2H, 2×H-4a), 1.80 (d, $J_{6,6'}$=14.2 Hz, 1H, H-6), 1.72 (br s, 1H, OH), 1.70 (d, $J_{6',6}$=14.2 Hz, 1H, H-6′), 1.27 (s, 3H, CH$_3$), 1.08 and 0.84 (2s, 2×3H, C(5)(CH$_3$)$_2$); ^{13}C NMR (CDCl$_3$) δ 208.6 (C-2), 196.9 (C-3a), 138.1 (C-4c), 125.8 (C-3), 115.3 (C-4d), 83.9 (C-4), 57.8 (C-1), 48.5 (C-6), 46.1 (C-6a)*, 43.4 (C-5)*, 34.0 (C-4a), 30.9 (CH$_3$), 29.7 (C-4b), 25.1 and 22.7 (2C, C(5)(*C*H$_3$)$_2$); MS (70 eV) *m/z* 206 (35), 192 (19), 178 (46), 151 (100), 135 (39), 122 (57), 109 (37), 79 (36), 67 (45), 55 (54), 41 (56). Anal. calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.64. Found: C, 76.75; H, 9.51.

(4S*)-4,5,6,6aα-Tetrahydro-4-hydroxy-4-(1,1,3-trimethyl-3-butenyl)-2(1H)-pentalenone (**35**): oil; IR (neat) 3426, 2968, 2869, 1698, 1618, 1373, 1181, 892 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.09 (d, $J_{3,6a}$=2.2 Hz, 1H, H-3), 4.93 (m, 1H, H-4d), 4.73 (m, 1H, H-4d′), 2.96–2.86 (m, 1H, H-6a), 2.64 (dd, $J_{1,1'}$=18.2 Hz, $J_{1,6a}$=6.3 Hz, 1H, H-1), 2.35 (ddd, $J_{5,5'}$=14.0 Hz, $J_{5,6}$=12.2 Hz, $J_{5,6'}$=7.0 Hz, 1H, H-5), 2.25 (br d, $J_{4b,4b'}$=12.8 Hz, 1H, H-4b), 2.17 (dd, $J_{1',1}$=18.4 Hz, $J_{1',6a}$=2.8 Hz, 1H, H-1′), 2.10 (br d, $J_{4b',4b}$=12.8 Hz, 1H, 4b′), 2.1–2.0 (m, 1H, H-6), 1.87 (td, $J_{5',5}$=$J_{5',6}$=14.0 Hz, $J_{5',6'}$=7.3 Hz, 1H, H-5′), 1.83 (s, 3H, CH$_3$), 1.82 (s, 1H, OH), 1.41 (qd, $J_{6',6}$=$J_{6',6a}$=$J_{6',5}$=12.2 Hz, $J_{6',5'}$=7.3 Hz, 1H, H-6′), 1.05 and 0.99 (2s, 2×3H, C(4a)(CH$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 210.4 (C-2), 194.4 (C-3a), 143.3 (C-4c), 126.9 (C-3), 115.5 (C-4d), 84.2 (C-4), 47.6 (C-6a), 44.1 (C-4b), 42.6 (C-1), 40.9 (C-4a), 37.8 (C-5)*, 29.6 (C-6)*, 22.7 (CH$_3$), 25.5 and 22.1 (C(4a)(*C*H$_3$)$_2$); MS (70 eV) *m/z* 219 (7), 162 (22), 138 (100), 95 (38), 55 (53), 43 (34). Anal. calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.64. Found: C, 76.89; H, 9.85.

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