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$PtCl_2$- and $PtCl_4$-Catalyzed Cycloisomerization of Polyunsaturated Precursors

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The $PtCl_2$- and $PtCl_4$-catalyzed cycloisomerization of polyunsaturated precursors with different *O*-protecting groups at the propargylic position is reported. The free hydroxy, *O*-(bromomethyl)dimethylsilyl, *O*-methyl and *O*-propenyl derivatives **1a–f** have afforded mixtures of skeletal rearrangement products and/or polycyclic molecules incorporating a cyclopropyl ring system in variable chemical yields. Other parameters such as the variation of the alkenyl chains and the triple-bond substitution have been examined and gave new mechanistic elements. Very interestingly, for analogous compounds containing an ester moiety, such as the *O*-4-nitrobenzoyl or acetate group (**1g–j**, and **22**) bicyclo[4.1.0]hept-2-enyl derivatives were obtained in good yields. These products are formally the result of a 1,2-migration of an *O*-acyl group, coupled to a cyclopropanation step. Related propargylic acetates with a pendant aromatic group (**25**) or substituted at the terminal acetylenic carbon with a methoxycarbonyl group (**24**) did not afford this class of rearranged compounds. This type of reaction seems restricted to propargylic derivatives, because the suitably functionalized homopropargylic acetate **24** only afforded 1,3-dienes.

Introduction

In the last few years, our groups have been actively working on the Pauson–Khand reaction[1] and free radical chemistry[2] of diversely functionalized 1,6-enynes, and in this context, we have recently investigated the reactivity of substrates of type **1** (Figure 1).

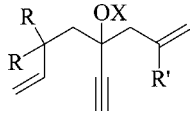

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Figure 1. General 1,6-enyne framework.

Continuing with our interest in the straightforward assembly of complex polycyclic structures from readily available precursors, we have concentrated on the $PtCl_2$-catalyzed cycloisomerization of these polyunsaturated precursors. In fact, transition-metal-catalyzed cycloisomerization of 1,6-enynes[3,4] constitutes one of the best-known examples of what have been called *full atom economy reactions*.[5] Since the pioneering work of Trost with electrophilic palladium catalysts,[6] some novel reactions featuring skeletal rearrangements,[7] and cyclopropanation processes have been reported.[8] With $PtCl_2$,[9,10] or Au^I and Au^{III} catalysis,[11–14] and very recently Cu^I,[15,16] $FeCl_3$[17] and In^{III},[18,19] a number of reports from different laboratories have highlighted the scope and limitations of this new synthetic opportunity for the preparation of carbocycles and/or heterocycles.

Very pleasantly, the $PtCl_2$-mediated cycloisomerization of the substrates **1** (Figure 1) gave new and surprising results.[20] Subsequent chemical developments of these results,[21–23] as well as our theoretical contributions to this area have also been recently reported.[24–26] Now, in this paper, we would like to describe in full some of the preliminary results[20] of the $PtCl_2$-promoted cycloisomerization of precursors **1**, as well as new substrates for this reaction, which illustrate the synthetic power of these transformations.

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Results and Discussion

1. Preliminary Results

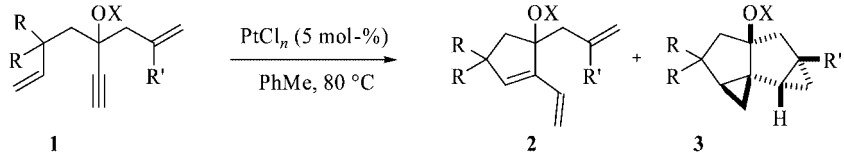
The choice of substrates **1** relied on several features: an easily accessible branched structure, with two pendant ole-

fins connected by distinct tethers and a functionalized, easily modified and stereogenic propargylic position. When submitted to typical reaction conditions (5 mol-% $PtCl_2$, toluene, 80 °C for 2.5 h), precursor **1a** provided a mixture of the expected formal metathesis adduct **2a** as a minor fraction and a larger amount of a fairly complex structure, compound **3a** (48% yield, Scheme 1).

Inspection of the NMR spectrum of **3a** clearly showed us that no olefinic protons were present, but the high density of protons at high field suggested that these molecules were possibly polycyclic derivatives incorporating one or more cyclopropyl ring systems. Several structural hypotheses were raised, but a definitive structure was impossible to propose at this point. Finally, the solution to this problem was obtained by X-ray diffraction analysis[20] of the 4-nitrobenzoyl derivative of compound **3a** (**4**), easily prepared by the standard method in an unoptimized reaction (Scheme 2).

The structure of compound **3a** (Scheme 1) corresponds to the octahydro-2,2-dimethyl-1*H*-dicyclopropa[*a*,*g*]pentalene skeleton, which had not been described previously in the literature. Moreover, the formation of compound **3a** that involves the formation of four C–C and four new stereocontrolled centers, is spectacular in terms of chemo-, regio- and stereoselectivity, featuring a synthetically simple and efficient operation. Additionally, this reaction involves the transformation of the alkyne moiety into a bis-carbene entity that accomplishes a bis-cyclopropanation, leading to two fused bicyclo[3.0.1]hexane systems. Such bis-cyclopropanation had been previously found by Chatani and Murai with a linear dienyne.[27] Our branched system leads to a particularly strained structure, which illustrates the synthetic power of these reactions. Recently, gold[28] and ruthenium[29] catalyses have also given interesting entries into bis-cyclopropyl derivatives.

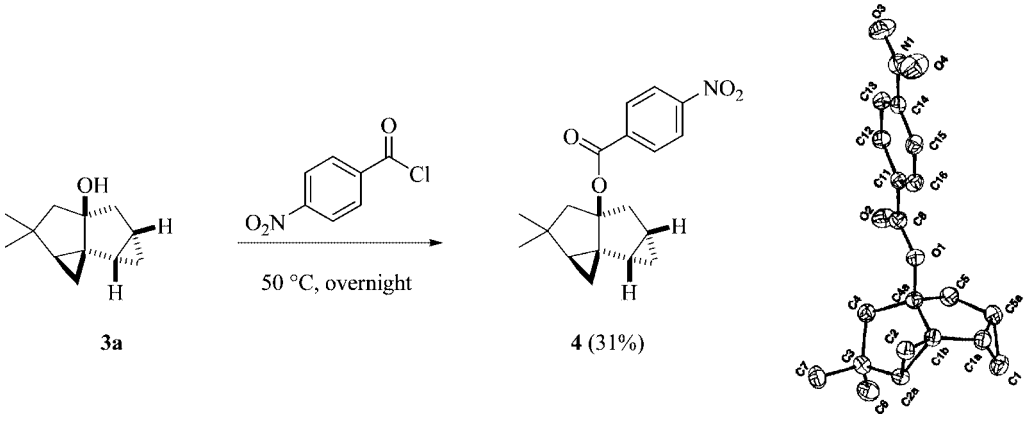
The observed spectroscopic data of compounds **3b** and **3c**, similar to that of the analogous derivative **3a**, prompted us to assign the same structure to these molecules, as well as the same relative configuration at the newly formed stereocenters. As an additional proof of structure, the reaction of silyl derivative **3b** with tetrabutylammonium fluoride in THF at room temperature afforded a compound identical to polycycle **3a** in quantitative yield (Scheme 1). Interestingly, methyl ether **1c** gave diastereomerically pure **3c**, in a very clean reaction (73% yield), with no detectable metathesis adduct **2c**. The use of $PtCl_4$ also proved to be very rewarding for this reaction, since tetracycle **3c** was isolated in 77% yield. In contrast, methallyl precursor **1d** underwent



1 **2** **3**

Entry	X	R,R'	Catalyst	2	3
1, **1a**	H	Me, H	$PtCl_2$	**2a**, 20%	**3a**, 48%
2, **1b**	$SiMe_2Br$	Me, H	$PtCl_2$	**2b**, 8%	**3b**, 38%
3, **1c**	Me	Me, H	$PtCl_2$	-	**3c**, 73%
4, **1c**	Me	Me, H	$PtCl_4$	-	**3c**, 77%
5, **1d**	Me	Me, Me	$PtCl_2$	-	**3d**, 34%
6, **1d**	Me	Me, Me	$PtCl_4$	-	**3d**, 40%
7, **1e**	Me	H, H	$PtCl_2$	-	**3e**, 54%
8, **1e**	Me	H, H	$PtCl_4$	-	**3e**, 20%

Scheme 1.

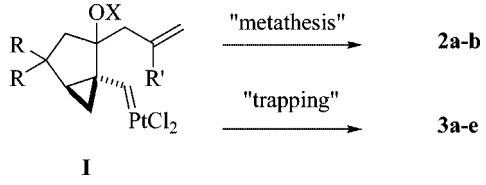


3a **4** (31%)

Scheme 2.

in a clean reaction from which **3d** was isolated as a single product in 34% yield with $PtCl_2$ and in a slightly better yield (40%) with $PtCl_4$ (Scheme 1, entries 5 and 6). We could also show that the presence of a dimethyl group on the butenyl chain was not necessary, since we could isolate **3e** in 54% yield consistently as a single diastereomer from precursor **1e**. In that case, the use of $PtCl_4$ did not result in any improvement of the yield.

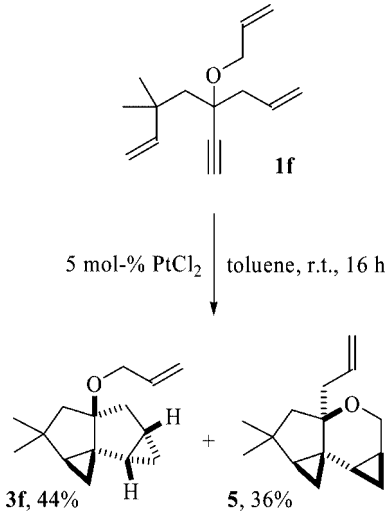
These promising findings prompted us to expand and explore this chemistry by preparing new precursors for the Pt^{II}-mediated cycloisomerization, as well as to define a mechanistic rationale.[20,24–26] Thus, all these results were consistent with the intervention of a platinacyclo-propyl intermediate[7–9,29–31] of type **I** that can evolve into a formal metathesis pathway or can be further trapped to give the tetracyclic structures **3a**–**e** (Scheme 3).



Scheme 3.

Additional information was collected by examining the behavior of *O*-allyl precursor **1f**, which contains an additional unsaturation (Scheme 4) and is easily prepared from precursor **1a**.

Despite all the possible interventions of the unsaturations, a clean reaction (room temp. for 16 h) was observed, since two major adducts (**3f** and **5**) were isolated in good overall yield (44% and 36% yield, respectively, Scheme 4) and in both cases as single diastereoisomers. The structure of product **3f** was proposed by analogy with spectroscopic data of the products **3a**–**e**. Structural assignment of product **5** was secured by derivatization and X-ray analysis of **6** (Scheme 5).[32] These findings are supported by recent mechanistic studies carried out by Soriano and Marco-Contelles[33] and represent an interesting possibility for forming oxygenated heterocycles.



Scheme 4.

2. Variations on the *O*-Methyl Substrates

Starting from the general framework **1**, we enlarged our study, now considering 1,6-enynes **7**, which feature the easily modifiable groups R, R′ and R″(Figure 2).

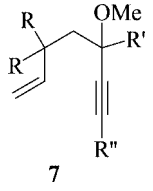
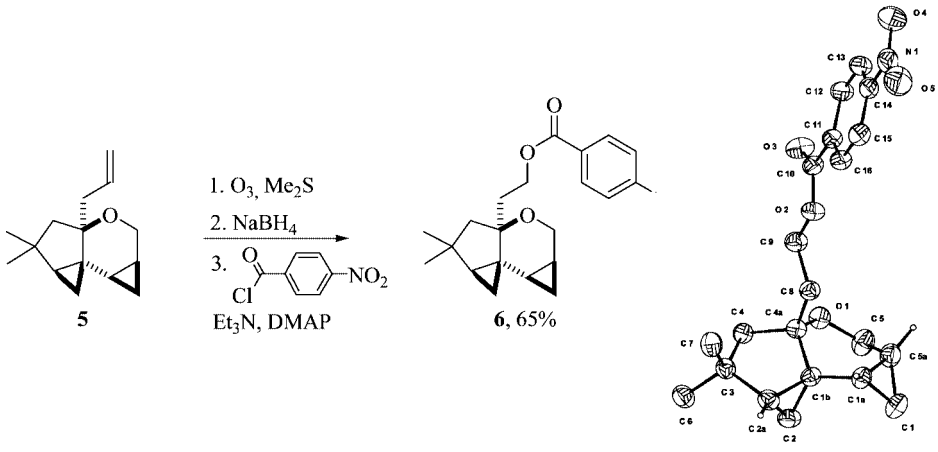


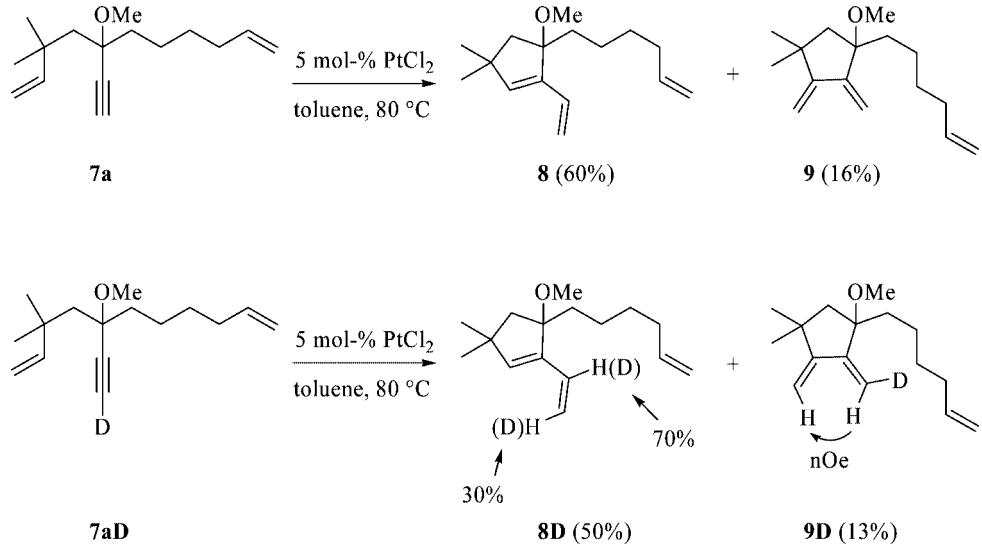
Figure 2. 1,6-Enynes bearing a propargylic OMe group.

Alkenyl Chain (R′ Group)

We first looked at the possibility of obtaining tetracycles incorporating medium-sized rings that would result from the trapping of carbene **I** with a long pendant alkene chain. For this purpose, we prepared dienyne **7a**, expecting that it would lead to a bis-cyclopropyl-substituted 5,8-bicyclic

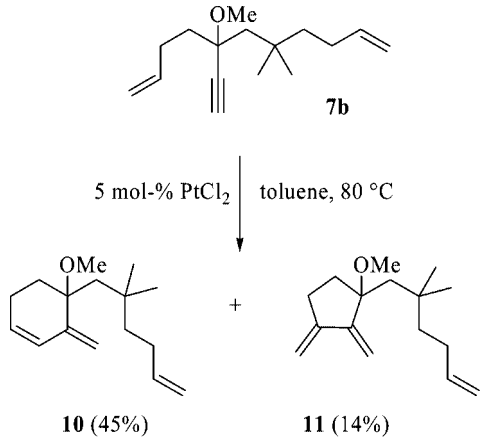


Scheme 5.

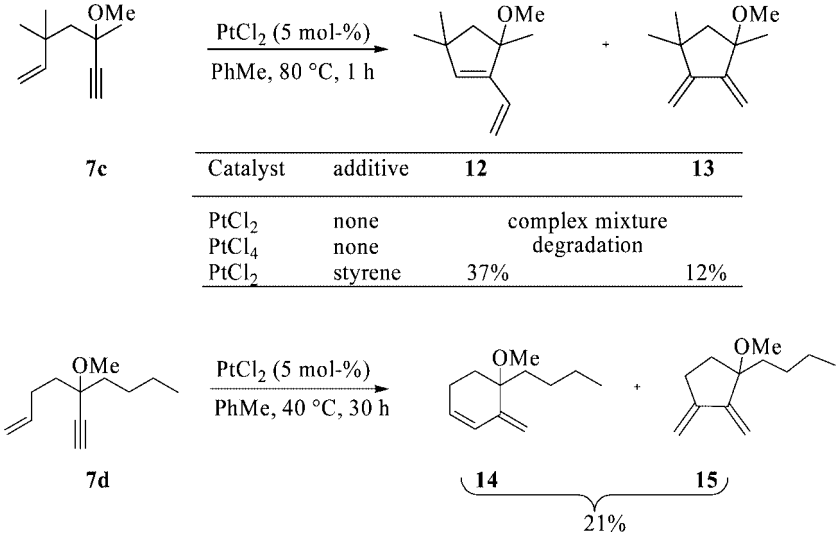


Scheme 6.

system. When we submitted this compound to typical conditions, we did not observe any polycyclic compound but a mixture of two products. Metathesis adduct **8** was obtained in 60% yield, along with diene **9** in 16% yield (Scheme 6). To the best of our knowledge, although frequently occurring when other metals are used,[4] this is the first report of the formation of a diene of type **9** in a Pt-catalyzed cycloisomerization. Only the 1,6-enyne moiety was involved in this reaction, most probably because the R′ alkene is too remote. Consequently, in contrast to the findings shown in Scheme 1, the formal metathesis product was the major one. We decided to test the reactivity of deuterated compound **7aD** for evidence of atom scrambling, as previously described by Murai[34] and Oi and Inoue[35] in this kind of cycloisomerization.[36] When this compound was submitted to the same experimental conditions, it led to deuterated



Scheme 7.



Scheme 8.

dienes **8D** in a 7:3 ratio in favor of the abnormal metathesis product. It should be noted that the stereochemistry of the deuterium incorporation was fully consistent with literature reports.[3,35,37] The stereochemical assignment of *exo* diene **9D** was based on nOe measurements (Scheme 6).

We then prepared a new precursor that possessed a *gem*-dimethyl moiety on the R′ chain. We hoped that a Thorpe–Ingold effect would favor the formation of the cyclooctane product.[38] We were confident, from the results obtained with **7a**, that the first cyclopropanation would take place easily, generating the platinacyclopropyl carbene species. When we submitted **7b** to cycloisomerization conditions, we did not obtain the expected product but a mixture of two compounds, cyclohexene **10** in 45% yield and cyclopentane **11** in 25% yield, analogous to **9**. No trace of the metathesis product was observed (Scheme 7).

Eventually, we supressed the pendant allylic chain to focus on the 1,6-enyne reactivity. Substrate **7c** reacted sluggishly with $PtCl_2$ and even worse with $PtCl_4$. Addition of an olefin[39,40] to the reaction medium allowed for the formation of metathesis adduct **12** as the major compound, along with diene **13** in a moderate overall yield.

Substrate **7d**, which does not bear the *gem*-dimethyl moiety, gave a complex mixture from which no metathesis product was observed and **14** and **15** could be isolated, albeit in low yield (Scheme 8).

Triple Bond Substitution (R′′ Group)

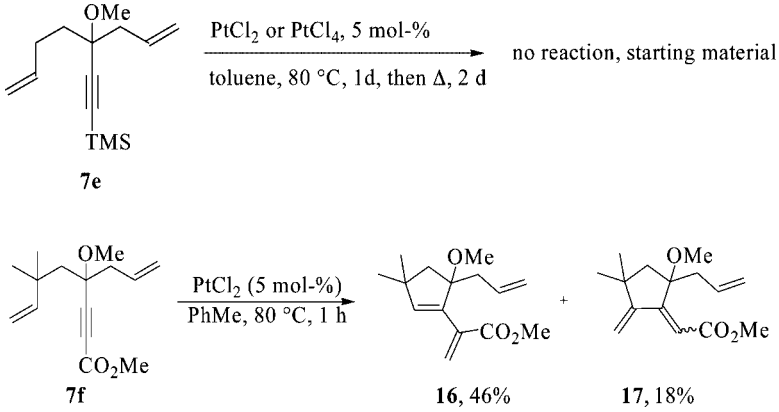
To gain more insight into this highly substrate-dependent reaction, we also examined the substitution of the triple bond. The easily synthesized compound **7e**, which that features a TMS group on the alkyne, showed no reaction towards $PtCl_2$ or $PtCl_4$ catalysis. This lack of reactivity has already been described with other silylated systems[23,41] (Scheme 9). In the same vein, alkyl substitution gave a very low yield of cycloisomerization products (<15%). So, we turned our attention to precursors bearing an electron-withdrawing group. Methoxyester derivative **7f** reacted readily with a good overall yield. Major product **16** came from a formal metathesis reaction, and minor product **17** was the dimethylenecyclopentane. No reaction was observed with the pendant allylic moiety (Scheme 9).

All this led us to refine our mechanistic proposal. All of our findings and those reported in the literature urged us to consider cyclopropylplatinacarbene **I** as the key intermediate in these transformations. Trapping of this species by a pendant unsaturation would lead to polycycles **3**.

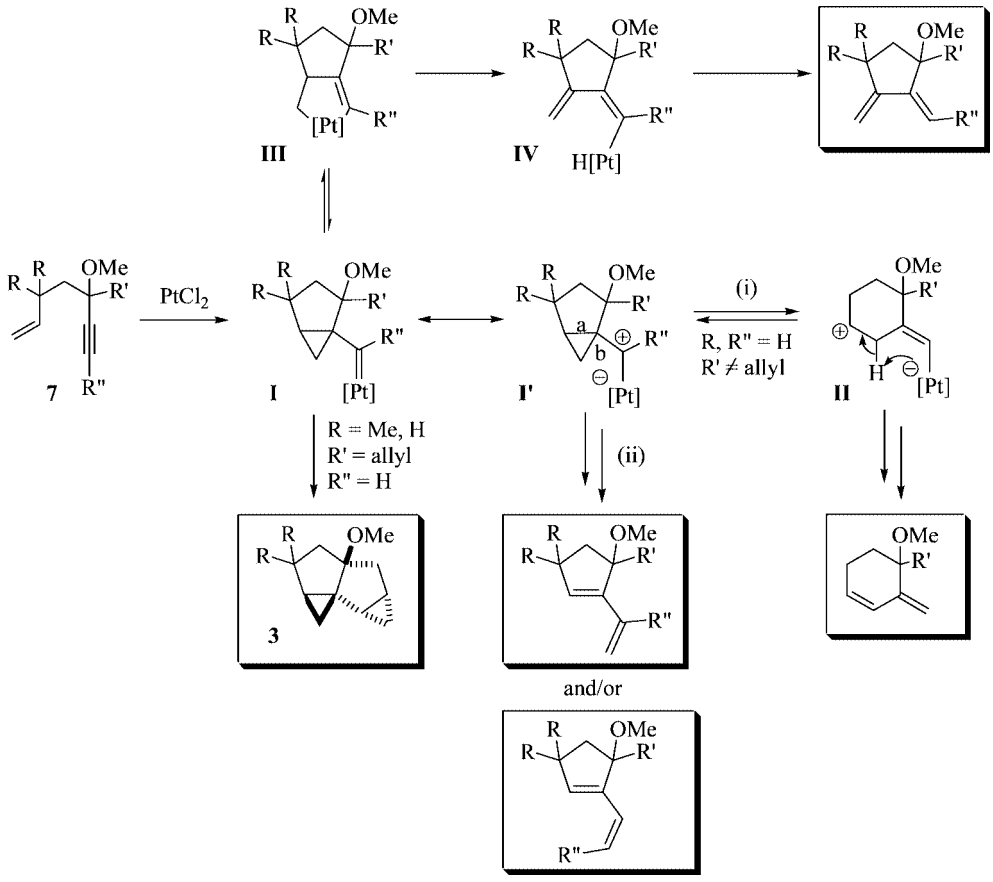
Other evolutions are possible. Metallacarbene **I** can also be viewed as a metallic zwitterion **I′**, which corresponds to a metalated non-classical homoallylic cation.[9,31] Zwitterionic cyclohexyl intermediate **II** would contribute significantly only when R = H, which alleviates severe 1,3-diaxial interactions. Consecutive proton eliminations, possibly assisted by platinum, affords methylenecyclohexene adducts **10** and **14**. The formation of dienes **9**, **11**, **13**, **15**, and **17** (and notably **9D**) is a signature of platinacyclopentene **III**. This intermediate can originate from cyclopropylplatinacarbene **I** through a vinylcyclopropane to cyclopentene type of mechanism or by direct oxidative cyclization after coordination of both unsaturations of the 1,6-enyne moiety. However, this possibility has not been supported by DFT calculations,[30] and the observation of products deriving from this intermediate is generally scarce. Therefore, we favor the intervention of platinacyclopentene **III** as an evolution of cyclopropylplatinacarbene **I**. β-hydride elimination gives birth to intermediate **IV**, which leads to dimethylenecyclopentane adducts after reductive elimination.

The formation of formal metathesis adducts **8**, **12**, and **16** from intermediate **I** has been fully studied recently. Calculations by Soriano and Marco-Contelles on $PtCl_2$ and by Echavarren on gold complexes corroborate the initial mechanism proposal by Murai, Inoue and Oi.[25,34–36] Single cleavage or double cleavage of the cyclopropyl moiety explain the formation of both isomers.

If the triple bond is substituted by a TMS group or an alkyl chain, unproductive and unselective catalyses are observed. In contrast, substitution by an electron-withdrawing group (precursor **7f**) restores a decent level of reactivity, as evidenced by the formation of dienes **16** and **17**, but does not allow the formation of tetracyclic adducts, probably due to unfavorable steric interactions.



Scheme 9.



Scheme 10.

Finally, an interesting observation stems from the difference of reactivity between **7a** and **7c** and **7b** and **7d**, the latter giving more sluggish results. To account for this, we suspect that an additional coordination of the metal by the remote unsaturation would somehow stabilize intermediate **I** and favor its evolution through other pathways (e.g. diene formation) when the second cyclization is too difficult to take place. The same process would take place in the presence of an additional olefin.

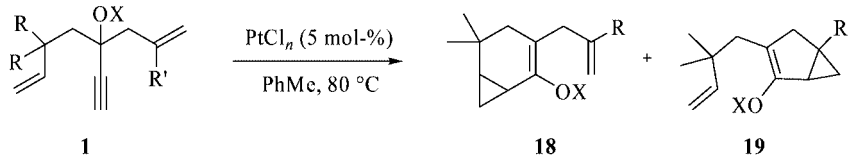
All these considerations are summarized in Scheme 10.

In conclusion, we have carried out several experiments on 1,6-enynes possessing a methoxy moiety on the propargylic position, making subtle variations on the general framework. The study of the influence of these parameters (*gem*-dimethyl on the enyne, additional unsaturation, triple bond substitution) allowed us to draw an overview of the different mechanistic pathways involved from a single common carbene intermediate. DFT calculations to support these conclusions are ongoing and will be reported in due course.

3. Variations on the *O*-Acyl Substrates

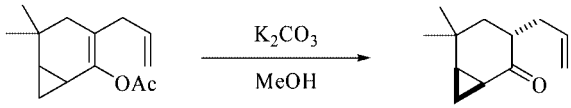
Next, we considered precursors **1g**–**i**, where a 4-nitrobenzoyloxy group or an acetate has been located at the propargylic position. These compounds were easily synthesized by standard *O*-acylation (Et_3N, DMAP in CH_2Cl_2) of the corresponding free alcohols. In fact, for correlation purposes, we wanted to prepare product **4** (Scheme 2), which we had previously obtained by acylation of polycycle **3a**, by direct $PtCl_2$-cycloisomerization from the corresponding open precursor **1g**. In Scheme 11, we show the results we observed in this $PtCl_2$-catalyzed cycloisomerization reaction. Contrary to our expectations, esters **1g**, **1h** and **1i** gave the bicyclo[4.1.0]hept-2-en-2-yl 4-*O*-acyl derivatives **18a** (76%), **18b** (88%) and **18c** (62%), respectively, in good yields and in shorter reaction times than those of the *O*-alkyl derivatives. These compounds were accompanied by minor amounts of cyclopentene derivatives **19a**, **19b** and **19c**, whose structure assignment was based on ^1H NMR spectra. No pure sample of **19** could be obtained, as it was always in a mixture with the corresponding product **18**. Unmethylated precursor **1j** could also efficiently undergo the cycloisomerization process to provide **18d** with $PtCl_2$ or $PtCl_4$. In that case, no five-membered ring was detected. Additional proof of structure was obtained when compound **18b** was transformed into *trans* ketone **20** after methanolysis (Scheme 11). The stereochemical assignment of **20** was deduced from nOe studies.

Interestingly, a careful re-examination of the current literature showed that this $PtCl_2$-mediated cycloisomerization reaction of propargyl acetates was not entirely new, as some precedent was established by Ohloff in 1976 with Zn^{II}.[42] Some years later, Rautenstrauch also described the same



1 18 19

Entry	X	R,R'	Catalyst	18	19
1, **1g**	p-$COC_6H_4NO_2$	Me, H	$PtCl_2$	**18a**, 76%	**19a**, 4%
2, **1h**	$COCH_3$	Me, H	$PtCl_2$	**18b**, 88%	**19b**, 3%
3, **1i**	p-$COC_6H_4NO_2$	Me, Me	$PtCl_2$	**18c**, 62%	**19c**, 16%
4, **1j**	$COCH_3$	H,H	$PtCl_2$	**18d**, 93%	-
5, **1j**	$COCH_3$	H,H	$PtCl_4$	**18d**, 98%	-

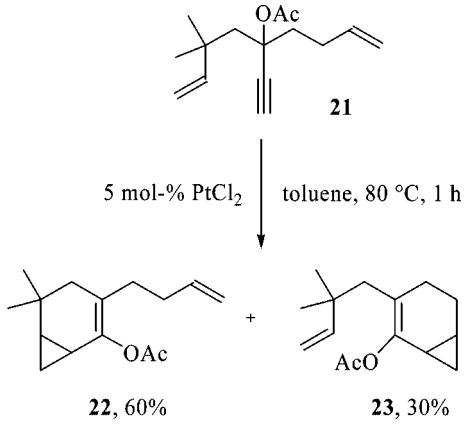


18b **20**, 93%

Scheme 11.

reaction,[43] and found that similar products were obtained in moderate yields (10–40%) from related precursors, with $PdCl_2(CH_3CN)_2$ as a catalyst,. After this preliminary communication, no further reports from this laboratory were available, and the potential interest of this new mode of cycloisomerization reaction, as well as the potential synthetic applications of the resulting building blocks, remained unexplored. Recently, after we recently rediscovered this reactivity,[20] Ohe and Uemura have reported the intermolecular version[44,45] of this reaction. Further reports from our laboratories,[46,47] as well as the development of gold(I) or gold(III) catalyses,[48,49] have established the versatility of this transformation and have enlarged its scope to even include asymmetric transformations.[15,50–52]

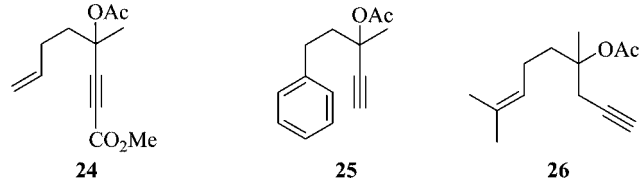
Interestingly, a *gem*-dimethyl effect[38] was observed in the case of **21**, which preferably gave **22** over **23** (Scheme 12).



Scheme 12.

In summary, we have observed the important effect that the type of the substituents at propargylic centers in differently functionalized 1,6-enynes have on the course of their $PtCl_2$-catalyzed cycloisomerization reactions. It was noticed that on going from the free alcohol (or ethers) to *O*-acyl derivatives, the major final resulting products were completely different. For the *O*-acyl migration, the mechanism may involve an initial cycloisomerization followed by a migration, with the initial 1,2-migration being followed by intramolecular cyclopropanation or cyclization of a half-rearranged intermediate.[15,50–51] DFT calculations on our substrates have not allowed us to discern an obvious pathway so far.[24] This result urged us to extend these observations to other enynes, in order to explore the scope and generality of the process. We could notably show that the substitution on the alkyne favors the formation of allenyl esters that can further undergo a thermal [3,3] rearrangement.[23]

We have also prepared and submitted to cyclization precursors **24**, **25** and **26** (Figure 3). In compound **24**, we have incorporated a propargylic acetate and a methoxycarbonyl group at the terminal position of the acetylenic moiety. Propargylic acetate **25** has been designed to determine if the presumed Pt carbene intermediate could be trapped by the pendant aromatic ring. Finally, we wanted to know if this cycloisomerization, as shown in Scheme 8, is still possible with the homopropargylic acetate **26** or is it limited to propargylic carboxylates.

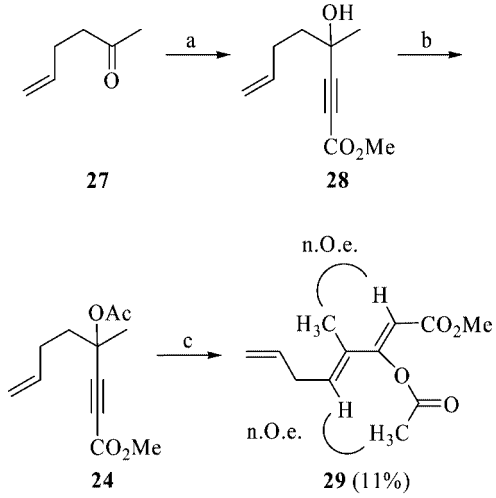


24 **25** **26**

Figure 3. Different enynes bearing an OAc group.

Precursor **24** was prepared from commercial 5-hexene-2-one (**27**), via alcohol **28**, as shown in Scheme 13. Under the usual catalysis conditions, we only isolated the acyclic

product **29** in low yield (11%). The structure of this compound was firmly established based on its spectroscopic and analytical data. The assigned configuration at the double bonds rests on selective nOe Experiments. As observed before,[23] the formation of compound **29** could simply be explained by hydrogen abstraction by Pt to form a dienylplatinum hydride that undergoes reductive elimination. The reasons why the expected product from a Rautenstrauch isomerization[20,43] have not been detected in this case are still obscure and demand further investigation. In fact, the reaction of terminal substituted alkynes seems to be very substrate-dependent, as recent results have shown that conveniently functionalized 5-en-1-yn-3-ol derivatives substituted with methoxycarbonyl[21] groups at the terminal alkyne moiety efficiently cyclize to give bicyclic adducts.

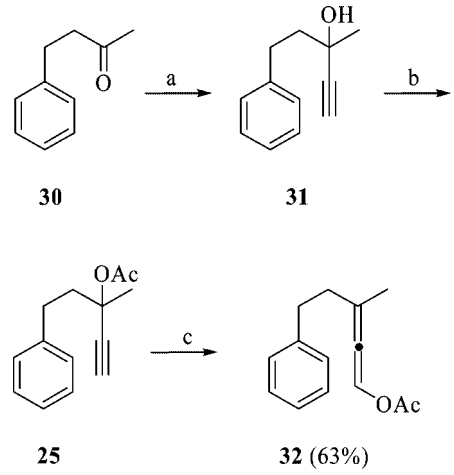


a: methyl propiolate, LDA, THF, -78 °C (71%)
b: Ac_2O, py, DMAP, r.t., 2.5 h (73%)
c: $PtCl_2$ (5 mol-%), toluene, 80 °C, 11 h

Scheme 13.

We have prepared precursor **25**[53] from commercially available 4-phenyl-2-butanone (**30**), via propargylic alcohol **31** using standard protocols (Scheme 14). After $PtCl_2$-mediated cycloisomerization, we were able to isolate and characterize only the 1-acetoxyallene **32** that would originate from a 1,3-acetate migration (Scheme 14). Formal C–H activation products consisting of an indene motif have been obtained with ruthenium,[44] platinum[54] and gold catalysis[55] when the aromatic group is at the propargylic substitution.

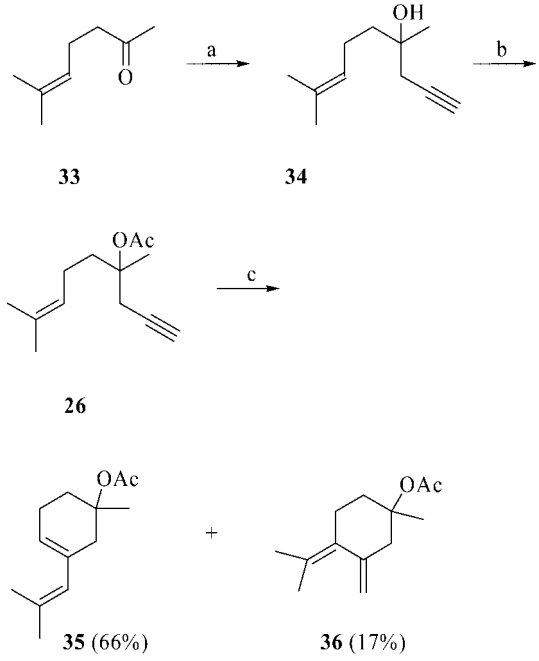
Similarly, we have synthesized compound **26** from 6-methylhept-6-ene-2-one (**33**), via known alcohol **34**.[56] The $PtCl_2$-promoted cycloisomerization of precursor **26** gave an inseparable mixture of products **35** and **36** (Scheme 15) in good yield. The structure of these molecules was clearly established after careful spectroscopic analysis. Major isomer **35** is the skeletal rearrangement product,[12] while compound **36** is a typical 1,3-diene obtained in transition-metal promoted reactions.[4] In no case was a cyclopropyl-derived



a: ethynylmagnesium bromide, r.t., 12 h (86%)
b: Ac_2O, py, DMAP, r.t., 12 h (70%)
c: $PtCl_2$ (5 mol-%), toluene, r.t., 5 h

Scheme 14.

product detected and isolated, implying that the Rautenstrauch isomerization[43] seems restricted to propargylic carboxylates.



a: propargyl bromide, Zn, r.t., 19 h (12%)
b: Ac_2O, py, DMAP, r.t., 16 h (44%)
c: $PtCl_2$ (5 mol-%), toluene, 40 °C, 40 h

Scheme 15.

Conclusions

In conclusion, the $PtCl_2$- and $PtCl_4$-catalyzed cycloisomerization of polyunsaturated precursors with different *O*-protecting groups at the propargylic position has been re-

ported. As a result, from free hydroxy, *O*-(bromomethyl)-dimethylsilyl or *O*-alkyl derivatives, we have isolated mixtures of skeletal rearrangement products and/or polycyclic molecules incorporating a cyclopropyl ring system in variable yields. Although some of these reactions have no preparative impact, they allowed for the isolation of new cycloisomerization products, which strongly support the intermediacy of cyclopropylplatinacarbene and platinacyclopentene intermediates and give new mechanistic insight. Very interestingly, for analogous compounds containing an ester moiety, bicyclo[4.1.0]hept-2-en-yl 4-*O*-acyl compounds were obtained in good yields. These products are formally the result of a sequential process of cycloisomerization and a 1,2-migration of the benzoyloxy group, the exact order of the events being still under scrutiny. A related propargylic acetate substituted at the terminal acetylenic carbon with a methoxycarbonyl group or with a pendant aromatic group did not afford this class of rearranged compounds. Similarly, this type of reaction seems restricted to propargylic derivatives, because a suitably functionalized homopropargylic acetate only afforded 1,3-dienes.

Experimental Section

General: Reactions were carried out under an anhydrous atmosphere of Ar. Glassware was flame-dried under an argon gas flow prior to use. Anhydrous THF and Et_2O were obtained by distillation over sodium/benzophenone under nitrogen and used immediately. Triethylamine, pyridine and diisopropylamine were dried and then distilled from KOH; toluene and CH_2Cl_2 were dried and then distilled from CaH_2. *n*-Butyllithium was purchased as 2.5 M solutions in hexanes and titrated before use. Other reagents were commercially available and used without further purification, unless otherwise indicated. TLC was performed on Silica F254 (Merck) and detection by UV light at 254 nm or by charring with phosphomolybdic-H_2SO_4 reagent, and *p*-anisaldehyde. Column chromatography was performed on Silica Gel 60 (Merck, 230 mesh). ^{1}H and ^{13}C NMR spectra were recorded at room temperature, either at 200 MHz and 50 MHz with an AC200 Bruker spectrometer, at 250 MHz and 63 MHz with an AC250 Bruker spectrometer, at 300 MHz and 75 MHz with a Bruker Avance-300 spectrometer, or at 400 MHz and 100 MHz, respectively, with an ARX400 AVANCE Bruker spectrometer. Chemical shifts are given in ppm and referenced to the residual solvent signal (δ = 7.26 ppm for $CDCl_3$) for ^{1}H NMR spectroscopy. For ^{13}C NMR, shifts are referenced to the central solvent peak (δ = 77.3 ppm for $CDCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, q, and hept stand for multiplet, singlet, doublet, triplet, quadruplet, and heptuplet, respectively. IR spectra were recorded with a Tensor 27 (ATR diamond) Bruker spectrometer. IR data is reported as characteristic bands (cm^{-1}) in their maximal intensity. The melting points were measured with an SMP3 Stuart Scientific melting point apparatus or with a digital melting point apparatus (Electrothermal) and are uncorrected. Elemental analysis was performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie.

Synthesis of the Precursors: The synthesis of **1a** and **1b** and their spectroscopic data have already been described.[1] *O*-Methylation of the tertiary alcohols with NaH and MeI provided **1c** and **1d** in good yields (>80%). Precursor **1e** was prepared by a similar route, which was also applied to obtain precursors **7**.[1] Similarly, *O*-allylation of **1a** with NaH and allyl bromide gave **1f**. *O*-Acyl precursors **1g**–**j** and **22** were prepared from the corresponding alcohol with acetic anhydride, or *p*-nitrobenzoyl chloride in pyridine with DMAP, or in CH_2Cl_2 with Et_3N and DMAP.

4-Ethynyl-4-methoxy-6,6-dimethylocta-1,7-diene (1c): IR (neat): $\tilde{\nu}$ = 3300, 3100, 2950, 2350, 1650, 1460, 1390 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.99 (dd, *J* = 17.7, 10.9 Hz, 1 H), 5.82 (m, 1 H), 5.12–4.80 (m, 4 H), 3.31 (s, 3 H, OMe), 2.53 (s, 1 H), 2.44 (d, *J* = 7.4 Hz, 2 H), 1.71 (s, 2 H), 1.18 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.3 (CH), 133.4 (CH), 118.3 (CH_2, CH=*C*H_2), 109.2 (CH_2, CH=*C*H_2), 84.1 (C), 76.7 (CH), 75.3 (C), 51.1 (CH_3, OMe), 49.6 (CH_2), 44.6 (CH_2), 36.7 (C), 28.5 (CH_3), 28.2 (CH_3) ppm. $C_{13}H_{20}O$ (192.30): calcd. C 81.20, H 10.48; found C 80.91, H 10.72.

4-Ethynyl-4-methoxy-2,6,6-trimethylocta-1,7-diene (1d): IR (neat): $\tilde{\nu}$ = 3300, 3050, 2950, 2320, 1630, 1450, 1380 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.00 (dd, *J* = 17.7, 10.3 Hz, 1 H), 4.92–4.77 (m, 4 H), 3.31 (s, 3 H, OMe), 2.53 (s, 1 H), 2.39 (s, 2 H), 1.79 (s, 3 H), 1.73 (s, 2 H), 1.17 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.5 (CH), 141.6 (C), 115.3 (CH_2, CH=*C*H_2), 109.0 (CH_2, CH=*C*H_2), 84.4 (C), 76.9 (CH), 75.4 (C), 51.1 (CH_3, OMe), 49.7 (CH_2), 47.9 (CH_2), 36.6 (C), 28.2 (2 CH_3), 24.1 (CH_3) ppm.

4-Ethynyl-4-methoxy-3,3-octa-1,7-diene (1e): IR (neat): $\tilde{\nu}$ = 3309, 3078, 2922, 2853, 2109, 1642 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91–5.76 (m, 2 H), 5.12 (m, 2 H), 4.93 (m, 2 H), 3.35 (s, 3 H, OMe), 2.50 (s, 1 H), 2.47 (d, *J* = 7.0 Hz, 2 H), 2.28–2.13 (m, 2 H), 1.75 (t, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5 (CH), 133.1 (CH), 118.6 (CH_2, CH=*C*H_2), 114.8 (CH_2, CH=*C*H_2), 83.9 (C), 75.9 (C), 75.1 (C), 51.7 (CH_2), 42.5 (CH_2), 37.4 (CH_2), 28.3 (CH_2) ppm.

4-Ethynyl-6,6-dimethyl-4-*O*-propenyl-1,7-octadien-4-ol (1f): To a cold (0 °C) solution of 4-ethynyl-6,6-dimethyl-1,7-octadien-4-ol (**1a**, 220 mg, 1.24 mmol) in dry THF (10 mL), NaH (99 mg, 2.48 mmol) was added, and the reaction mixture was stirred at the same temperature for 10 min. Allyl bromide (0.15 mL, 2.48 mmol) and a catalytic amount of tetrabutylammonium iodide were added. The mixture was stirred for 18 h at room temp., until the reaction was complete. The excess of NaH was destroyed by adding AcOH (0.5 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography (CH_2Cl_2/hexane, 4:96) afforded **1f** (202 mg, 81% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3304, 3081, 2985, 1640, 1460, 1381, 1290, 1250 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92 (dd, *J* = 17.5, 10.5 Hz, 1 H), 5.80 (m, 2 H), 5.27–5.18 (m, 2 H), 5.18–4.91 (m, 2 H), 4.72–4.76 (m, 2 H), 4.11 (ddt, *J* = 12.3, 4.9, 1.7 Hz, 1 H), 3.91 (ddt, *J* = 12.3, 4.9, 1.7 Hz, 1 H), 2.43 (s, 1 H), 2.38 (m, 2 H), 1.66 (m, 2 H), 1.06 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8 (CH), 135.6 (CH), 133.8 (CH), 118.6 (CH_2, CH=*C*H_2), 116.2 (CH_2, CH=*C*H_2), 109.5 (CH_2, CH=*C*H_2), 84.8 (C), 76.9 (C), 75.4 (CH), 65.4 (CH_2), 50.5 (CH_2), 45.7 (CH_2), 37.1 (C), 28.9 (CH_3), 28.6 (CH_3) ppm. MS (70 eV): *m*/*z* (%) = 218 (1) [M]$^+$, 177 (3), 135 (13), 107 (12), 91 (20), 79 (16), 69 (100), 55 (19), 41 (80). $C_{15}H_{22}O$ (218.33): calcd. C 82.52, H 10.16; found C 82.33, H 10.09.

5-Ethynyl-5-methoxy-3,3-dimethylundeca-1,10-diene (7a): IR (neat): $\tilde{\nu}$ = 3305, 3080, 2940, 2105, 1640 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (dd, *J* = 17.3, 10.7 Hz, 1 H), 5.82 (ddt, *J* = 17.1, 10.5, 6.6 Hz, 1 H), 5.02 (dd, *J* = 17.3, 1.0 Hz, 1 H), 5.01 (dd, *J* = 17.1, 1.5 Hz, 1 H), 4.96 (dd, *J* = 10.7, 1.0 Hz, 1 H), 4.94 (dd, *J* =

10.5, 1.5 Hz, 1 H), 3.32 (s, 3 H, OMe), 2.52 (s, 1 H), 2.07 (m, 2 H), 1.76 (m, 2 H), 1.69 (m, 2 H), 1.50–1.30 (m, 4 H), 1.18 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6 (CH), 139.3 (CH), 114.7 (CH_2, CH=*C*H_2), 109.6 (CH_2, CH=*C*H_2), 85.1 (C), 76.3 (C), 76.2 (CH), 51.2 (CH_3, OMe), 49.7 (CH_2), 40.1 (CH_2), 37.0 (C), 34.1 (CH_2), 29.4 (CH_2), 23.8 (CH_2), 28.8 (CH_3), 28.7 (CH_3) ppm; **7aD** ($C_{16}H_{25}DO$): ^1H NMR (400 MHz, $CDCl_3$): the same spectrum as that of **7a**, except no signal at δ = 2.52 ppm. ^{13}C NMR (100 MHz, $CDCl_3$): the same spectrum as that of **7a**, except δ = 85.1 (t, *J* = 7 Hz) and 76.2 (t, *J* = 39 Hz) ppm. CIMS: (NH_3) *m*/*z* (%) = 253 (15) $[M + NH_4]^+$, 236 (21) $[M + H]^+$, 221 $[M - 15]^+$, 204 $[M - 31]^+$.

5-Ethynyl-5-methoxy-7,7-dimethylundeca-1,10-diene (7b): IR (neat): $\tilde{\nu}$ = 3300, 3070, 2940, 2100, 1640, 1460, 1075 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.81 (m, 2 H), 5.02 (d, *J* = 17.3 Hz, 1 H), 4.98 (d, *J* = 17.7 Hz, 1 H), 4.95 (d, *J* = 11.5 Hz, 1 H), 4.89 (d, *J* = 10.2 Hz, 1 H), 3.29 (s, 3 H, OMe), 2.53 (s, 1 H), 2.15 (m, 2 H), 2.02 (m, 2 H), 1.76 (m, 2 H), 1.65 (d, *J* = 14.2 Hz, 1 H), 1.59 (d, *J* = 14.2 Hz), 1.44 (m, 2 H), 1.04 (s, 3 H), 1.03 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8 (CH), 138.3 (CH), 114.5 (CH_2, CH=*C*H_2), 113.6 (CH_2, CH=*C*H_2), 84.4 (C), 76.2 (CH), 75.5 (C), 50.8 (CH_3, OMe), 48.1 (CH_2), 42.9 (2 CH_2), 39.7 (CH_2), 33.5 (C), 28.7 (CH_2), 28.5 (CH_3), 28.3 (CH_3) ppm. $C_{16}H_{26}O$ (234.38): calcd. C 81.99, H 11.18; found C 81.84, H 11.35.

5-Methoxy-3,3,5-trimethylhept-1-en-6-yne (7c): IR (neat): $\tilde{\nu}$ = 3309, 3083, 2923, 2854, 2109, 1639 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.01 (dd, *J* = 17.7, 10.8 Hz, 1 H), 4.92 (dd, *J* = 17.7, 1.3 Hz, 1 H), 4.87 (dd, *J* = 10.8, 1.3 Hz, 1 H), 3.33 (s, 3 H, OMe), 2.48 (s, 1 H), 1.83 (d, *J* = 14.6 Hz, 1 H), 1.76 (d, *J* = 14.6 Hz, 1 H), 1.42 (s, 3 H), 1.16 (s, 3 H), 1.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6 (CH), 109.7 (CH_2, CH=*C*H_2), 85.8 (C), 74.9 (CH), 73.4 (C), 52.7 (CH_2), 51.2 (CH_3, OMe), 37.0 (C), 28.9 (CH_3), 28.4 (CH_3), 28.0 (CH_3) ppm.

5-Ethynyl-5-methoxy-non-1-ene (7d): IR (neat): $\tilde{\nu}$ = 3310, 3078, 2926, 2856, 1642 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.84 (ddt, *J* = 17.4, 10.4, 6.6 Hz, 1 H), 5.05 (dd, *J* = 17.4, 1.5 Hz, 1 H), 4.96 (dd, *J* = 10.4, 1.5 Hz, 1 H), 3.33 (s, 3 H, OMe), 2.46 (s, 1 H), 2.17 (m, 2 H), 1.75 (t, *J* = 8.4 Hz, 2 H), 1.67 (t, *J* = 7.8 Hz, 2 H), 1.43–1.30 (m, 4 H), 0.92 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3 (CH), 114.5 (CH_2, CH=*C*H_2), 77.2 (CH), 76.1 (C), 74.1 (C), 51.2 (CH_3, OMe), 37.5 (CH_2), 36.9 (CH_2), 28.1 (CH_2), 25.9 (CH_2), 22.9 (CH_2), 14.0 (CH_3) ppm.

(3-Allyl-3-methoxy-hept-6-en-1-ynyl)trimethylsilane (7e): IR (neat): $\tilde{\nu}$ = 3078, 2956, 2928, 2856, 2165, 1642 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (m, 2 H), 5.10 (m, 2 H), 5.05–4.93 (m, 2 H), 3.35 (s, 3 H), 2.45 (d, *J* = 7.4 Hz, 2 H), 2.18 (m, 2 H), 1.71 (t, *J* = 8.3 Hz, 2 H), 0.18 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8 (CH), 133.5 (CH), 118.4 (CH_2, CH=*C*H_2), 114.8 (CH_2, CH=*C*H_2), 105.8 (C), 91.8 (C), 76.4 (C), 51.8 (CH_3, OMe), 42.6 (CH_2), 37.5 (CH_2), 28.6 (CH_2), 0.30 (3 CH_3, TMS) ppm.

Methyl 4-Allyl-4-methoxy-6,6-dimethyloct-7-en-2-ynoate (7f): To a solution of **1a** (384 mg, 2 mmol, 1 equiv.) in dry THF (10 mL) was added *n*BuLi (0.95 mL of a 2.2 M solution, 2.1 mmol, 1.05 equiv.) at –78 °C. Methyl chloroformate (0.46 mL, 6 mmol, 3 equiv.) was added, and the mixture was allowed to warm to room temp. The reaction was quenched with a saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated to give **7f** (495 mg, 99% yield). IR (neat): $\tilde{\nu}$ = 3081, 2955, 2873, 2230, 1717, 1639 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.94 (dd, *J* = 17.4, 10.6 Hz, 1 H), 5.78 (m, 1 H), 5.11 (m, 2 H), 4.90 (dd, *J* = 17.4, 1.3 Hz, 1 H), 4.84 (dd, *J* = 10.6, 1.3 Hz, 1 H), 3.76 (s, 3 H, CO_2Me), 3.33 (s, 3 H, OMe), 2.47 (m, 2 H), 1.75 (s, 2 H), 1.12 (s, 3 H), 1.10 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7 (C), 148.6 (CH), 132.2 (CH), 119.1 (CH_2, CH=*C*H_2), 109.8 (CH_2, CH=*C*H_2), 87.9 (C), 80.3 (C), 75.3 (C), 52.7 (CH_3), 51.5 (CH_3, OMe), 49.5 (CH_2), 43.8 (CH_2), 36.6 (C), 28.6 (CH_3), 27.9 (CH_3) ppm.

1-Allyl-1-ethynyl-3,3-dimethylpent-4-enyl 4′-Nitrobenzoate (1g): IR (neat): $\tilde{\nu}$ = 3300, 3080, 2960, 2115, 1730, 1640, 1610, 1530, 1350 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 9.0 Hz, 2 H, Ar), 8.16 (d, *J* = 9.0 Hz, 2 H, Ar), 6.00 (dd, *J* = 17.4, 10.6 Hz, 1 H), 5.92 (m, 1 H), 5.18 (d, *J* = 16.2 Hz, 1 H *trans*), 5.16 (d, *J* = 11.2 Hz, 1 H *cis*), 4.95 (dd, *J* = 17.4, 1.0 Hz, 1 H *trans*), 4.84 (dd, *J* = 10.6, 1.0 Hz, 1 H *cis*), 3.07 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.90 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.76 (s, 1 H), 2.40 (d, *J* = 15.0 Hz, 1 H), 2.11 (d, *J* = 15.0 Hz, 1 H), 1.23 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.0 (C, C=O), 148.4 (CH), 136.5 (C, Ar), 132.0 (CH), 130.8 (2 CH, Ar), 128.5 (C, Ar), 123.6 (2 CH, Ar), 119.7 (CH_2, CH=*C*H_2), 110.4 (CH_2, CH=*C*H_2), 82.8 (C), 79.1 (C), 77.0 (CH), 49.2 (CH_2), 44.8 (CH_2), 36.9 (C), 29.0 (CH_3), 28.0 (CH_3) ppm. GCMS (EI): *m*/*z* (%) = 286 (9) [M–C_3H_5], 150 (100). $C_{19}H_{21}NO_4$ (327.38): calcd. C 69.71, H 6.47, N 4.28; found C 69.65; H, 6.60; N, 4.18.

1-Allyl-1-ethynyl-3,3-dimethylpent-4-enyl Acetate (1h): IR (neat): $\tilde{\nu}$ = 3300, 3100, 2950, 2350, 1750, 1640, 1440, 1370 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.93 (dd, *J* = 17.2, 10.3 Hz, 1 H), 5.81 (m, 1 H), 5.13–5.04 (m, 2 H), 4.90 (dd, *J* = 17.7, 1.5 Hz, 1 H *trans*), 4.86 (dd, *J* = 10.3, 1.5 Hz, 1 H *cis*), 2.87 (dd, *J* = 14.3, 7.4 Hz, 1 H), 2.69 (dd, *J* = 14.3, 7.4 Hz, 1 H), 2.60 (s, 1 H), 2.15 (d, *J* = 15.3 Hz, 1 H), 1.95 (s, 3 H, OAc), 1.86 (d, *J* = 15.3 Hz, 1 H), 1.15 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.4 (C, C=O), 148.7 (CH), 132.3 (CH), 119.1 (CH_2, CH=*C*H_2), 109.7 (CH_2, CH=*C*H_2), 83.5 (C), 77.0 (C), 75.9 (CH), 49.1 (CH_2), 44.6 (CH_2), 36.8 (C), 28.9 (CH_3), 27.7 (CH_3), 22.2 (CH_3, OAc) ppm.

1-Methallyl-1-ethynyl-3,3-dimethylpent-4-enyl 4′-Nitrobenzoate (1i): IR (neat): $\tilde{\nu}$ = 3300, 3080, 2960, 2115, 1730, 1640, 1610, 1530, 1350 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 9.2 Hz, 2 H, Ar), 8.18 (d, *J* = 9.2 Hz, 2 H, Ar), 6.02 (dd, *J* = 17.4, 10.6 Hz, 1 H), 4.97 (dd, *J* = 10.6, 1.0 Hz, 1 H *cis*), 4.86 (d, *J* = 1.2 Hz, 2 H), 4.85 (dd, *J* = 17.4, 1.0 Hz, 1 H *trans*), 3.06 (d, *J* = 14.4 Hz, 1 H), 2.87 (d, *J* = 14.4 Hz, 1 H), 2.77 (s, 1 H), 2.42 (d, *J* = 15.0 Hz, 1 H), 2.11 (d, *J* = 15.0 Hz, 1 H), 1.82 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, CDCl3): δ = 163.1 (C, C=O), 148.5 (CH), 140.2 (C), 136.6 (C, Ar), 130.8 (2 CH+C, Ar), 126.6 (2 CH, Ar), 116.7 (CH_2, CH=CH_2), 110.3 (CH_2, CH=CH_2), 83.1 (C), 79.0 (C), 77.5 (CH), 49.8 (CH_2), 48.2 (CH_2), 36.9 (C), 29.2 (CH_3), 27.9 (CH_3), 24.1 (CH_3) ppm. GCMS (EI): *m*/*z* (%) = 286 (5) [M – C_4H_7], 150 (100).

1-Allyl-1-ethynylpent-4-enyl Acetate (1j): IR (neat): $\tilde{\nu}$ = 3295, 3079, 2980, 2928, 2857, 2118, 1742, 1642 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.84–5.76 (m, 2 H), 5.15–4.94 (m, 4 H), 2.79–2.75 (m, 2 H), 2.59 (s, 1 H), 2.23–2.21 (m, 2 H), 2.06–2.04 (m, 1 H), 2.00 (s, 3 H, OAc), 1.91–1.82 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5 (C, C=O), 137.8 (CH), 132.1 (CH), 119.5 (CH_2, CH=*C*H_2), 115.3 (CH_2, CH=*C*H_2), 82.8 (C), 78.2 (C), 75.0 (CH), 42.8 (CH_2), 37.7 (CH_2), 28.5 (CH_2), 22.1 (CH_3, OAc) ppm.

1-But-3-enyl-1-ethynyl-3,3-dimethylpent-4-enyl Acetate (21): IR (neat): $\tilde{\nu}$ = 3306, 3081, 2965, 2931, 2873, 2117, 1743, 1642 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.94 (dd, *J* = 17.4, 10.6 Hz, 1 H), 5.78 (m, 1 H), 5.04–4.86 (m, 4 H), 2.61 (s, 1 H), 2.23–2.17 (m, 4 H), 2.03 (m, 1 H), 1.99 (s, 3 H, OAc), 1.93–1.90 (m, 1 H), 1.16 (s, 3 H), 1.13 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5 (C, C=O), 137.8 (CH), 132.1 (CH), 119.5 (CH_2, CH=*C*H_2),

115.3 (CH_2, CH=*C*H_2), 82.8 (C), 78.2 (C), 75.0 (CH), 42.8 (CH_2), 37.7 (CH_2), 28.5 (CH_2), 22.1 (CH_3, OAc) ppm.

Methyl 4-Acetyloxy-4-methyloct-7-en-2-ynoate (24): To a solution of diisopropylamine (1.07 mL, 7.65 mmol) in THF (40 mL), cooled to –78 °C, *n*BuLi (4.78 mL, 7.65 mmol, 1.6 M in hexane) was added. The solution was warmed to 0 °C for 15 min. Then, to this solution, cooled to –78 °C, methyl propiolate (0.82 mL, 9.18 mmol) was slowly added. After stirring at –78 °C for 1 h, the reaction mixture was treated with 5-hexene-2-one (**27**, 0.5 g, 5.1 mmol), stirred at –78 °C for 30 min, and then warmed to room temp. The reaction mixture was diluted with diethyl ether (40 mL), washed with an aqueous solution of sodium bisulfate (1 N, 2×40 mL), dried with Na_2SO_4 and concentrated in vacuo. Flash chromatography, eluting with EtOAc/hexane (5:95), afforded **28** (660 mg, 71% yield) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3079, 2981, 2953, 2235, 1719, 1642, 1592, 1436, 1372, 1256 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.73 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1 H), 5.03 (dm, *J* = 16.7 Hz, 1 H), 4.85 (dm, *J* = 10.1 Hz, 1 H), 3.67 (s, 3 H, CO_2CH_3), 2.25–2.07 (m, 2 H), 1.77–1.66 (m, 2 H), 1.43 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3 (C=O), 138.1, 115.7, 90.9, 75.3, 68.0, 53.2 (CO_2CH_3), 42.2, 29.5, 29.2 ppm. To a solution of compound **28** (400 mg, 2.19 mmol) in dry pyridine (5 mL), DMAP (53.4 mg, 0.44 mmol) and acetic anhydride (336.3 mg, 3.30 mmol) were added. The reaction mixture was stirred for 2.5 h at room temp. The solvent was evaporated, and the crude material was purified by flash chromatography (EtOAc/hexane, 4:96) to furnish **24** (360 mg, 73% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3080, 2981, 2239, 1747, 1720, 1642, 1435, 1370, 1313, 1262 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.68 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1 H), 4.99 (dm, *J* = 16.7 Hz, 1 H), 4.85 (dm, *J* = 10.1 Hz, 1 H), 3.65 (s, 3 H, CO_2CH_3), 2.17–2.00 (m, 2 H), 1.93 (s, 3 H, $OCOCH_3$), 1.91–1.73 (m, 2 H), 1.59 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4 ($OCOCH_3$), 154.1 (C=O), 137.4, 115.7, 87.2, 77.3, 73.9, 53.2 (CO_2CH_3), 40.3, 28.6, 26.1 (CH_3), 21.9 ($OCOCH_3$). MS (70 eV) *m*/*z* 209 (1) $[M - 15]^+$, 182 (12), 169 (5), 150 (100), 149 (21), 133 (12), 122 (44), 111 (6), 105 (50), 77 (21), 43 (87) ppm. $C_{12}H_{16}O_4$ (224.25): calcd. C 64.27, H 7.19; found C 64.46 H, 7.28.

3-Methyl-5-phenylpent-1-yn-3-yl Acetate (25): A solution of 4-phenyl-2-butanone (**30**, 0.5 g, 3.38 mmol) in a mixture of dry THF/diethyl ether (1:1, 2 mL) was added dropwise, at room temp., to a solution of ethynylmagnesium bromide (8.5 mL, 4.05 mmol, 0.5 M in THF) in anhydrous diethyl ether (8.5 mL), under argon. The reaction mixture was stirred at room temp. for 12 h. Water (25 mL) was added to quench the reaction, and the mixture was extracted with diethyl ether (3×25 mL). The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum. Purification by flash chromatography (EtOAc/hexane, 3:97) gave **31** (510 mg, 86% yield) which showed spectroscopic data identical to those described in the literature[39] [^1H NMR (200 MHz, $CDCl_3$): δ = 7.25–7.10 (m, 5 H, C_6H_5), 2.82–2.76 (m, 2 H), 2.73 (s, 1 H, OH), 2.43 (s, 1 H), 1.95–1.84 (m, 2 H), 1.47 (s, 3 H, CH_3) ppm].

To a solution of compound **31** (400 mg, 2.3 mmol) in dry pyridine (5 mL), DMAP (56.1 mg, 0.46 mmol) and acetic anhydride (351.9 mg, 0.5 mL, 3.45 mmol) were added. The reaction mixture was stirred overnight at room temp. The solvent was evaporated, and the crude was purified by flash chromatography (EtOAc/hexane, 1:99) to furnish **25** (333 mg, 70% yield) as a colorless oil, which showed spectroscopic data identical to those described in the literature[51] [^1H NMR (200 MHz, $CDCl_3$): δ = 7.25–7.10 (m, 5 H, C_6H_5), 2.78–2.69 (m, 2 H), 2.53 (s, 1 H), 2.26–1.98 (m, 2 H), 1.93 (s, 3 H, $OCOCH_3$), 1.65 (s, 3 H, CH_3) ppm].

4,8-Dimethylnon-7-en-1-yn-4-yl Acetate (26): To a solution of 6-methyl-5-heptene-2-one (**33**, 2.0 g, 15.8 mmol) in a mixture of THF/saturated aqueous solution of NH_4Cl (1:5, 70 mL), zinc dust (6.18 g, 95.2 mmol) was added under argon. The mixture was stirred in an ice bath (0 °C). Thereafter, propargyl bromide (5.33 mL, 47.6 mmol) was added, and the reaction was stirred for 19 h at room temp. The mixture was concentrated, and the crude material was extracted with ethyl acetate (3×10 mL). The organic extract was washed with brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography of the crude material, eluting with EtOAc/hexane (0.5:99.5), gave unreacted 6-methyl-5-heptene-2-one (**33**, 883 mg) and known compound **34**[56] (211 mg, 12% yield) as a light yellow oil: [^1H NMR (300 MHz, $CDCl_3$): δ = 5.09 (tm, *J* = 7.1 Hz, 1 H), 2.41 (d, *J* = 2.7 Hz, 2 H), 2.16–2.04 (m, 3 H, 2 H, OH), 1.85 (s, 1 H), 1.71 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.69–1.58 (m, 2 H), 1.31 (s, 3 H, CH_3) ppm].

To a solution of compound **34** (290 mg, 1.75 mmol) in dry pyridine (2 mL), DMAP (42.7 mg, 0.35 mmol) and acetic anhydride (267.3 mg, 2 mL, 2.62 mmol) were added. The reaction mixture was stirred at room temp. for 16 h. Purification by flash column chromatography (EtOAc/hexane, 0.5:99.5) gave **26** (161.2 mg, 44% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3310, 2966, 2925, 2857, 2121, 1736, 1450, 1368, 1247 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.10 (tm, *J* = 7.1 Hz, 1 H), 2.75 (dd, *J* = 12.0, 2.0 Hz, 1 H), 2.55 (dd, *J* = 12.0, 2.0 Hz, 1 H), 1.97 (s, 4 H, $OCOCH_3$, H), 2.00–1.85 (m, 3 H), 1.80–1.65 (m, 1 H), 1.61 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 170.7 ($OCOCH_3$), 132.3 (C), 123.9 (CH), 82.7 (C), 80.5 (C), 70.7 (CH), 38.1 (CH_2), 29.0 (CH_2), 26.0 (CH_3), 23.9 (CH_2), 22.6 (CH_3), 22.5 ($OCOCH_3$), 17.9 (CH_3) ppm. MS (70 eV): *m*/*z* (%) = 208 (9) $[M]^+$, 191 (20), 175 (6), 147 (100), 131 (9), 73 (75), 55 (11), 41 (12). $C_{13}H_{20}O_2$ (298.30): calcd. C 74.96, H 9.68; found C 74.83, H 9.72.

Cycloisomerization Products

General Procedure (GP) for the $PtCl_n$-Catalyzed Cycloisomerization Reaction: To a degassed solution of the precursor in dry toluene (0.025 M), $PtCl_n$ (0.05 equiv.) was added at room temp. under argon. The reaction mixture was stirred at the stated temperature until the reaction was complete. The reaction mixture was filtered, and the solvent was evaporated under vacuum. Purification by flash chromatography gave the corresponding products.

2-Ethenyl-4,4-dimethyl-1-(2-propenyl)-2-cyclopenten-1-ol (2a) and (1a*R,3a*S**,4a*R**,5a*R**,5b*S**)-octahydro-2,2-dimethyl-3a*H*-dicyclopropa[*a*,*g*]pentalen-3a-ol (3a):** Cyclization of precursor **1a** (178 mg, 1 mmol) with $PtCl_2$ (10.4 mg, 0.04 mmol), following the GP (80 °C, 2 h) gave, after purification by flash chromatography (EtOAc/hexane, 5:95), triene **2a** (35 mg, 20%) and compound **3a** (85 mg, 48%). **2a**: IR (neat): $\tilde{\nu}$ = 3400, 2920, 1630, 1450 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.28 (dd, *J* = 18.0, 11.4 Hz, 1 H), 5.80 (m, 1 H), 5.69 (s, 1 H), 5.60 (dd, *J* = 18.0, 2.0 Hz, 1 H *trans*), 5.18–5.09 (m, 3 H, 2H+H *cis*), 2.63 (dd, *J* = 13.7, 8.0 Hz, 1 H), 2.41 (dd, *J* = 13.7, 8.0 Hz, 1 H), 2.17 (br. s, 1 H), 2.13 (d, *J* = 14.0 Hz, 1 H), 1.74 (d, *J* = 14.0 Hz, 1 H), 1.35 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4 (C), 142.2 (CH), 134.2 (CH), 130.4 (CH), 118.6 (CH_2), 116.0 (CH_2), 85.4 (C), 53.5 (CH_2), 44.7 (CH_2), 42.0 (C), 30.7 (CH_3), 28.8 (CH_3) ppm. $C_{12}H_{18}O$ (178.27): calcd. C 80.85, H 10.18; found C 80.62, H 10.23. **3a**: IR (neat): $\tilde{\nu}$ = 3370, 2950, 1460, 1360 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.21 (br. s, 1 H), 2.16 (dd, *J* = 14.1, 6.6 Hz, 1 H), 1.71 (m, 1 H), 1.67 (dd, *J* = 14.1, 3.2 Hz, 1 H), 1.60 (d, *J* = 14.2 Hz, 1 H), 1.36 (td, *J* = 7.9, 4.0 Hz, 1 H), 1.06 (s, 3 H, CH_3), 1.03 (d, *J* = 14.2 Hz, 1 H), 0.92 (s, 3 H, CH_3), 0.89 (td, *J* = 7.9,

4.7 Hz, 1 H), 0.85 (dd, *J* = 8.4, 4.9 Hz, 1 H), 0.78 (dd, *J* = 8.4, 4.2 Hz, 1 H), 0.69 (dd, *J* = 4.9, 4.2 Hz, 1 H), 0.50 (dt, *J* = 4.7, 4.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 99.2 (C), 47.2 (CH_2), 45.9 (C), 44.4 (CH_2), 39.3 (C), 35.4 (CH), 30.2 (CH_3), 28.1 (CH_3), 22.2 (CH_2), 20.5 (CH), 20.1 (CH), 11.5 (CH_2) ppm. GCMS (EI): *m*/*z* (%) = 178 (6) [M], 145 (100). $C_{12}H_{18}O$ (178.27): calcd. C 80.85, H 10.18; found C 80.65, H 9.98.

(Bromomethyl){[2-ethenyl-4,4-dimethyl-1-(2-propenyl)-2-cyclopenten-1-yl]oxy}dimethylsilane (2b) and (Bromomethyl)dimethyl-{[(1a*R,3a*S**,4a*R**,5a*R**,5b*S**)-octahydro-2,2-dimethyl-3a*H*-dicyclopropa[*a*,*g*]pentalen-3a-yl]oxy}silane (3b):** Cyclization of precursor **1b** (308 mg, 0.94 mmol) with $PtCl_2$ (12 mg, 0.047 mmol), following the GP (80 °C, 4 h) gave, after purification by flash chromatography (hexane/CH_2Cl_2, 9:1), triene **2b** (26 mg, 8%) and compound **3b** (188 mg, 61%). **2b**: Oil. IR (neat): $\tilde{\nu}$ = 3080, 2940, 1630, 1440, 1250 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.25 (dd, *J* = 17.8, 11.2 Hz, 1 H), 5.77 (m, 1 H), 5.61 (s, 1 H), 5.59 (dd, *J* = 18.0, 1.6 Hz, 1 H *trans*), 5.18–5.02 (m, 3 H, 2 H+H *cis*), 2.66 (dd, *J* = 13.4, 7.0 Hz, 1 H), 2.49 (s, 2 H, CH_2–Br), 2.33 (dd, *J* = 13.4, 7.0 Hz, 1 H), 2.15 (d, *J* = 13.0 Hz, 1 H), 1.80 (d, *J* = 13.0 Hz, 1 H), 1.17 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 0.28 [s, 6 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.0 (C), 140.7 (CH), 134.8 (CH), 130.6 (CH), 117.5 (CH_2), 115.9 (CH_2), 88.5 (C), 52.5 (CH_2), 46.3 (CH_2), 41.7 (C), 30.4 (CH_3), 28.5 (CH_3), 17.6 (CH_2, CH_2–Br), –0.9 [2 CH_3, $Si(CH_3)_2$] ppm. **3b**: IR (neat): $\tilde{\nu}$ = 3060, 2990, 2960, 2870, 1740, 1450, 1350 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.54 (s, 2 H, CH_2–Br), 2.21 (dd, *J* = 15.0, 7.4 Hz, 1 H), 1.70 (m, 1 H), 1.69 (d, *J* = 9.4 Hz, 1 H), 1.63 (d, *J* = 14.0 Hz, 1 H), 1.37 (td, *J* = 7.4, 4.0 Hz, 1 H), 1.11 (d, *J* = 14.0 Hz, 1 H), 1.07 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 0.90 (m, 2 H), 0.76 (m, 2 H), 0.49 (q, *J* = 4.0 Hz, 1 H), 0.32 [s, 3 H, $Si(CH_3)_2$], 0.31 [s, 3 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 102.7 (C), 48.9 (CH_2), 45.9 (C), 45.5 (CH_2), 38.9 (C), 36.0 (CH), 30.3 (CH_3), 28.5 (CH_3), 22.5 (CH_2), 20.9 (2 CH), 18.3 (CH_2, CH_2–Br), 13.0 (CH_2), –0.7 [2 CH_3, $Si(CH_3)_2$] ppm. GCMS (EI): *m*/*z* (%) = 330 (21) [M(^{81}Br)], 328 (21) [M(^{79}Br)], 145 (100). $C_{15}H_{25}BrOSi$ (329.36): calcd. C 54.70, H 7.65; found C 55.00 H, 7.87.

(1a*R,3a*S**,4a*R**,5a*R**,5b*S**)-Octahydro-3a-methoxy-2,2-dimethyl-1*H*-dicyclopropa[*a*,*g*]pentalene (3c):** Cyclization of precursor **1c** (97 mg, 0.5 mmol) with $PtCl_2$ (6.5 mg, 0.025 mmol), following the GP (80 °C, 3 h) gave, after purification by flash chromatography (Et_2O/pentane: 2:98), compound **3c** (71 mg, 73%). Alternatively, cyclization of precursor **1c** (137 mg, 0.71 mmol) was conducted with $PtCl_4$ (12 mg, 0.036 mmol), following the same procedure (80 °C, 1 h) and gave, after purification by flash chromatography (Et_2O/pentane, 2:98), compound **3c** (105 mg, 77%). **3c**: IR (neat): $\tilde{\nu}$ = 2950, 1480, 1380 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.28 (s, 3 H, OMe), 2.36 (dd, *J* = 14.3, 7.0 Hz, 1 H), 1.61 (m, 1 H), 1.52 (dd, *J* = 14.3, 2.5 Hz, 1 H), 1.52 (d, *J* = 14.3 Hz, 1 H), 1.33 (td, *J* = 7.4, 3.4 Hz, 1 H), 1.08 (d, *J* = 14.3 Hz, 1 H), 1.06 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 0.89 (td, *J* = 8.4, 4.4 Hz, 1 H), 0.82–0.70 (m, 3 H), 0.47 (q, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 104.0 (C), 51.9 (CH_3, OMe), 46.2 (CH_2), 43.8 (C), 39.2 (C, CH_2), 35.8 (CH), 30.7 (CH_3), 28.3 (CH_3), 22.1 (CH_2), 21.7 (CH), 21.2 (CH), 12.2 (CH_2) ppm. $C_{13}H_{20}O$ (192.30): C 81.20, H 10.48; found C 81.07, H 10.59.

(1a*R,3a*S**,4a*R**,5a*R**,5b*R**)-Octahydro-3a-methoxy-2,2,4a-trimethyl-1*H*-dicyclopropa[*a*,*g*]pentalene (3d):** Cyclization of precursor **1d** (86 mg, 0.4 mmol) with $PtCl_2$ (5 mg, 0.02 mmol), following the GP (80 °C, 3 h) gave, after purification by flash chromatography (Et_2O/pentane, 2:98), compound **3d** (29 mg, 34%). Alternatively, cyclization of precursor **1d** (80 mg, 0.39 mmol) was conducted with $PtCl_4$ (7 mg, 0.02 mmol), following the same procedure (80 °C, 2 h) and gave, after purification by flash chromatography (Et_2O/pentane, 2:98), compound **3d** (32 mg, 40%). **3d**: IR (neat): $\tilde{\nu}$ = 3040, 2950, 1460 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.28 (s, 3 H, OMe), 2.19 (d, *J* = 14.6 Hz, 1 H), 1.72 (d, *J* = 14.6 Hz, 1 H), 1.53 (d, *J* = 13.8 Hz, 1 H), 1.30 (s, 3 H, CH_3), 1.13 (d, *J* = 13.8 Hz, 1 H), 1.12 (m, 1 H), 1.09 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 0.91 (m, 1 H), 0.85–0.70 (m, 3 H), 0.64 (t, *J* = 3.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 103.2 (C), 52.3 (CH_3, OMe), 46.5 (CH_2), 45.3 (C), 45.2 (CH_2), 39.6 (C), 36.0 (CH), 31.0 (CH_3), 30.0 (C), 28.9 (CH, CH_2), 28.6 (CH_3), 23.8 (CH_3), 12.8 (CH_2) ppm.

(1a*R,3a*S**,4a*R**,5a*R**,5b*S**)-Octahydro-3a*H*-dicyclopropa[*a*,*g*]-pentalen-3a-ol (3e):** Cyclization of precursor **1e** (83 mg, 0.5 mmol) with $PtCl_2$ (6.5 mg, 0.025 mmol), following the GP (80 °C, 2 h) gave, after purification by flash chromatography (Et_2O/pentane, 2:98), compound **3e** (45 mg, 53%). Alternatively, cyclization of precursor **1e** (102 mg, 0.62 mmol) was conducted with $PtCl_4$ (10 mg, 0.03 mmol), following the same procedure (80 °C, 2 h) and gave, after purification by flash chromatography (Et_2O/pentane, 5:95), compound **3e** (20 mg, 20%). IR (neat): $\tilde{\nu}$ = 3060, 2930, 1460 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (s, 3 H, OMe), 2.30 (dd, *J* = 14.6, 7.5 Hz, 1 H), 1.80 (m, 1 H), 1.70–1.60 (m, 3 H), 1.38 (td, *J* = 7.6, 3.3 Hz, 1 H), 1.29 (dd, *J* = 14.6, 3.0 Hz, 1 H), 1.21 (m, 1 H), 1.02 (m, 1 H), 0.93–0.83 (m, 3 H), 0.39 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.5 (C), 52.2 (CH_3, OMe), 41.3 (C), 37.7 (CH_2), 30.0 (CH_2), 26.2 (CH_2), 22.98 (CH_2), 22.97 (CH), 20.9 (CH), 20.3 (CH), 12.7 (CH_2) ppm.

***p*-Nitrobenzoate 4:** To a solution of compound **3a** (89 mg, 0.5 mmol, 1 equiv.) in CH_2Cl_2 (2.5 mL) was added 4-nitrobenzoyl chloride (371 mg, 2 mmol, 4 equiv.). The mixture was heated to 50 °C overnight and quenched with 10% aqueous HCl. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. Purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 9:1) gave the pure ester **4** (51 mg, 31% yield). The solid product was recrystallized from hexane/Et_2O. **4**: Solid, m.p. 135 °C. IR (in $CDCl_3$ solution): $\tilde{\nu}$ = 3040, 2940, 1700, 1600, 1520, 1450 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.23 (m, 4 H, Ar), 2.74 (dd, *J* = 15.7, 7.4 Hz, 1 H), 2.26 (d, *J* = 14.8 Hz, 1 H), 1.83 (dd, *J* = 15.7, 2.5 Hz, 1 H), 1.64 (m, 1 H), 1.49 (td, *J* = 7.4, 3.4 Hz, 1 H), 1.16 (d, *J* = 14.8 Hz, 1 H), 1.14 (s, 3 H, CH_3), 1.06 (m, 1 H), 0.93 (s, 3 H, CH_3), 0.96–0.84 (m, 3 H), 0.58 (q, *J* = 3.9 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.0 (C, C=O), 150.7 (C, Ar), 137.5 (C, Ar), 131.0 (2 CH, Ar), 123.8 (2 CH, Ar), 109.9 (C), 46.3 (CH_2), 45.2 (C), 41.9 (CH_2), 40.2 (C), 35.2 (CH), 30.7 (CH_3), 28.9 (CH_3), 22.7 (CH_2), 21.0 (2 CH), 12.9 (CH_2) ppm.

(1a*R,3a*S**,4a*R**,5a*R**,5b*R**)-Octahydro-3a-allyloxy-2,2,4a-trimethyl-1*H*-dicyclopropa[*a*,*g*]pentalene (3f) and Tetracycle 5:** Cyclization of **1f** with $PtCl_2$ (85 mg, 0.39 mmol), following the GP (16 h at room temp.) gave, after purification by flash chromatography (CH_2Cl_2/hexane, 1:4), compounds **3f** (38 mg, 44% yield) and **5** (31 mg, 36% yield). **3f**: Oil. IR (neat): $\tilde{\nu}$ = 3060, 2950, 1650, 1450, 1360, 1290 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.97 (dddd, *J* = 17.3, 10.5, 5.6, 5.4 Hz, 1 H), 5.30 (dq, *J* = 17.3, 1.7 Hz, 1 H *trans*), 5.12 (dq, *J* = 10.5, 1.3 Hz, 1 H *cis*), 4.05 (m, 2 H, 2H), 2.37 (dd, *J* = 15.1, 7.4 Hz, 1 H), 1.64 (m, 3 H), 1.38 (td, *J* = 7.5, 3.6 Hz, 1 H), 1.19 (d, *J* = 13.9 Hz, 1 H), 1.10 (s, 3 H, CH_3), 0.95 (m, 1 H), 0.94 (s, 3 H, CH_3), 0.86 (m, 2 H), 0.78 (m, 1 H), 0.50 (q, *J* = 3.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7 (CH), 116.0 (CH_2), 104.5 (C), 65.9 (CH_2), 47.6 (CH_2), 44.2 (C), 40.9 (CH_2), 39.5 (C), 36.5 (CH), 31.1 (CH_3), 28.6 (CH_3), 22.3 (CH, CH_2), 21.6 (CH), 12.8 (CH_2) ppm. MS (70 eV): *m*/*z* (%) = 218 (1) [M]$^+$, 207

(6), 183 (16), 168 (51), 105 (21), 91 (100), 79 (12), 77 (29). $C_{15}H_{22}O$ (218.33): calcd. C 82.52, H 10.16; found C 82.67, H 10.38. **5**: IR (neat): $\tilde{\nu}$ = 3060, 2950, 1650, 1450, 1360, 1290 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.95 (m, 1 H), 5.13 (d, J = 10.1 Hz, 1 H *cis*), 5.12 (d, J = 17.2 Hz, 1 H *trans*), 4.26 (dd, J = 11.8, 7.3 Hz, 1 H), 3.55 (dd, J = 11.8, 7.0 Hz, 1 H), 3.13 (m, 1 H), 2.37 (dd, J = 14.4, 9.2 Hz, 1 H), 1.62 (d, J = 13.5 Hz, 1 H), 1.50 (dd, J = 8.0, 3.2 Hz, 1 H), 1.45 (m, 1 H), 1.34 (m, 1 H), 1.19 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.90 (d, J = 13.5 Hz, 1 H), 0.88 (m, 1 H), 0.49 (t, J = 4.1 Hz, 1 H), 0.39 (q, J = 4.6 Hz, 1 H), 0.21 (dd, J = 7.9, 4.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1 (CH), 117.0 (CH_2), 81.0 (C), 66.4 (CH_2), 43.4 (CH_2), 42.3 (CH_2), 38.5 (C), 35.5 (CH), 34.7 (C), 29.0 (CH_3), 28.5 (CH_3), 16.4 (CH_2), 15.0 (CH_2), 13.5 (CH), 10.6 (CH) ppm. MS (70 eV): *m*/*z* (%) = 218 (1) $[M]^+$, 183 (5), 161 (9), 135 (11), 105 (22), 97 (44), 69 (87), 43 (88). $C_{15}H_{22}O$ (218.33): calcd. C 82.52, H 10.16; found C 82.47, H 10.27.

Ester 6: A solution of compound **5** (82 mg, 0.4 mmol, 1 equiv.) in CH_2Cl_2/methanol (1:1, 8 mL) was cooled to –78 °C. Ozone was bubbled into the solution until a persistent blue color was perceived. The excess of ozone was then removed by bubbling argon into the reaction vessel. Sodium borohydride (29 mg, 0.8 mmol, 2 equiv.) was added, and the mixture was slowly warmed to 0 °C. After 1 h of stirring at 0 °C, the reaction was quenched with a saturated ammonium chloride solution for 30 min. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$, and the solvents were removed under vacuum. To a cold (0 °C) solution of the resulting crude alcohol (0.4 mmol, 1 equiv.) in CH_2Cl_2 (3 mL) were added triethylamine (110 µL, 0.8 mmol, 2 equiv.), DMAP (10 mg, 0.08 mmol, 0.2 equiv.) and 4-nitrobenzoyl chloride (82 mg, 0.44 mmol, 1.1 equiv.). After a 15 min of stirring at room temp., the reaction was quenched with a saturated ammonium chloride solution. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. Purification by flash chromatography on silica gel (Et_2O/pentane, 2:8) gave the desired ester **6** (87 mg, 65% yield over 2 steps). The solid product was recrystallized from hexane/Et_2O. Solid, m.p. 94 °C. IR (film): $\tilde{\nu}$ = 2960, 1720, 1600, 1520, 1280 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 9.1 Hz, 2 H, Ar), 8.23 (d, J = 9.1 Hz, 2 H, Ar), 4.58 (m, 2 H), 4.25 (dd, J = 11.9, 7.3 Hz, 1 H), 3.51 (dd, J = 11.9, 7.6 Hz, 1 H), 2.78 (m, 1 H), 2.17 (m, 1 H), 1.60 (d, J = 13.6 Hz, 1 H), 1.53 (dd, J = 8.1, 3.3 Hz, 1 H), 1.47 (m, 1 H), 1.37 (m, 1 H), 1.22 (s, 3 H, CH_3), 1.03 (d, J = 13.6 Hz, 1 H), 1.00 (s, 3 H, CH_3), 0.89 (td, J = 7.6, 5.1 Hz, 1 H), 0.50 (t, J = 4.0 Hz, 1 H), 0.40 (q, J = 4.6 Hz, 1 H), 0.23 (dd, J = 8.1, 4.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8 (C, C=O), 150.4 (C, Ar), 136.0 (C, Ar), 130.7 (2 CH, Ar), 123.5 (2 CH, Ar), 79.7 (C), 66.7 (CH_2), 63.7 (CH_2), 42.9 (CH_2), 38.5 (C), 37.3 (CH_2), 35.3 (CH), 34.5 (C), 29.0 (CH_3), 28.2 (CH_3), 16.5 (CH_2), 14.7 (CH_2), 13.4 (CH), 10.5 (CH) ppm.

5-(Hex-5-enyl)-5-methoxy-3,3-dimethyl-1-vinylcyclopentene (8) and 1-(Hex-5-enyl)-1-methoxy-4,4-dimethyl-2,3-dimethylenecyclopentane (9): Cyclization of precursor **7a** (92 mg, 0.4 mmol) with $PtCl_2$ (5 mg, 0.02 mmol), following the GP (50 °C, 6 h) gave, after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 9:1), cyclopentene **8** (55 mg, 60%) and cyclopentane **9** (15 mg, 16%). **8**: IR (neat): $\tilde{\nu}$ = 3080, 2930, 1640, 1465 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.29 (dd, J = 17.8, 11.2 Hz, 1 H), 5.82 (ddt, J = 17.1, 10.5, 6.6 Hz, 1 H), 5.70 (s, 1 H), 5.59 (dd, J = 17.8, 1.8 Hz, 1 H), 5.09 (dd, J = 11.2, 1.8 Hz, 1 H), 5.01 (dd, J = 17.1, 1.5 Hz, 1 H), 4.94 (dd, J = 10.5, 1.5 Hz, 1 H), 3.13 (s, 3 H, O–CH_3), 2.09 (m, 2 H, CH_2), 1.91 (d, J = 14.8 Hz, 1 H), 1.85 (d, J = 14.8 Hz, 1 H), 1.42–1.25 (m, 6 H, 3CH_2), 1.15 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3 (CH), 139.9 (C), 139.4 (CH), 131.3 (CH), 115.7 (CH_2), 114.6 (CH_2), 92.7 (C), 50.6 (CH_3, O–Me), 46.6 (CH_2), 41.7 (C), 39.8 (CH_2), 34.1 (CH_2), 30.1 (CH_3), 29.8 (CH_2), 29.7 (CH_3), 24.1 (CH_2) ppm. $C_{16}H_{26}O$ (234.38): calcd. C 81.99, H 11.18; found C 81.85, H 11.38. **8D**, deuterated at C-2: ^1H NMR (400 MHz, $CDCl_3$): the same spectrum as that of **8**, except no signal at δ = 6.29 ppm and δ = 5.59 (d, J = 1.8 Hz, 1 H), 5.09 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): same spectrum as that of **8**, except δ = 131.3 (t, J = 22 Hz) ppm; deuterated at C-1: ^1H NMR (400 MHz, $CDCl_3$): the same spectrum as that of **8**, except no signal at δ = 5.59 ppm and δ = 6.29 (d, J = 11.4 Hz, 1 H), 5.09 (d, J = 11.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): the same spectrum as that of **8**, except δ = 115.7 (t, J = 24 Hz) ppm. ESI-MS: *m*/*z* (%) = 274 (30) $[M + K]^+$, 258 (100) $[M + Na]^+$, 236 (10) $[M + H]^+$. **9**: IR (neat): $\tilde{\nu}$ = 3080, 2930, 1640, 1460 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.82 (ddt, J = 17.1, 10.5, 6.6 Hz, 1 H), 5.58 (s, 1 H), 5.40 (s, 1 H), 5.01 (dd, J = 17.1, 1.5 Hz, 1 H), 4.94 (dd, J = 10.5, 1.5 Hz, 1 H), 4.93 (s, 1 H), 4.85 (s, 1 H), 3.07 (s, 3 H, O–CH_3), 2.09 (m, 2 H), 1.91 (d, J = 13.6 Hz, 1 H), 1.91 (m, 1 H), 1.59 (d, J = 13.6 Hz, 1 H), 1.46–1.25 (m, 5 H), 1.23 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 (C), 150.4 (C), 139.3 (CH), 114.7 (CH_2), 107.5 (CH_2), 104.3 (CH_2), 84.4 (C), 50.7 (CH_3), 49.7 (CH_2), 40.1 (C), 34.7 (CH_2), 34.2 (CH_2), 31.7 (CH_3), 31.1 (CH_3), 29.8 (CH_2), 23.7 (CH_2) ppm. **9D**: ^1H NMR (400 MHz, $CDCl_3$): the same spectrum as that of **9**, except no signal at δ = 4.85 ppm. ^{13}C NMR (100 MHz, $CDCl_3$): the same spectrum as that of **9**, except δ = 104.3 (t, J = 23 Hz) ppm.

4-(2,2-Dimethylhex-5-enyl)-4-methoxy-3-methylenecyclohexene (10) and 1-(2,2-Dimethylhex-5-enyl)-1-methoxy-2,3-dimethylenecyclopentane (11): Cyclization of precursor **7b** (80 mg, 0.34 mmol) with $PtCl_2$ (5 mg, 0.02 mmol), following the GP (50 °C, 6 h) gave, after purification by flash chromatography on silica gel (pentane/Et_2O, 98:2), cyclohexene **10** (36 mg, 45%) and cyclopentane **11** (11 mg, 14%). **10**: IR (neat): $\tilde{\nu}$ = 3080, 2940, 1640, 1460 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.08 (d, J = 10.2 Hz, 1 H), 5.79 (ddt, J = 16.8, 10.2, 6.6 Hz, 1 H), 5.67 (m, 1 H), 5.13 (s, 1 H), 4.97 (d, J = 16.8 Hz, 1 H), 4.95 (s, 1 H), 4.88 (d, J = 10.2 Hz, 1 H), 3.15 (s, 3 H), 2.25 (m, 2 H), 2.03–1.90 (m, 3 H), 1.76 (dt, J = 12.2, 4.1 Hz, 1 H), 1.55 (m_{AB}, 2 H), 1.42 (m, 1 H), 1.35 (m, 1 H), 1.00 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1 (C), 140.5 (CH), 130.2 (CH), 128.2 (CH), 113.8 (CH_2), 112.1 (CH_2), 79.2 (C), 49.4 (CH_3), 46.0 (CH_2), 44.0 (CH_2), 34.5 (C), 30.9 (CH_2), 29.2 (2 CH_3), 29.0 (CH_2), 25.3 (CH_2) ppm. **11**: IR (neat): $\tilde{\nu}$ = 3080, 2930, 1640, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddt, J = 16.8, 10.2, 6.6 Hz, 1 H), 5.59 (s, 1 H), 5.41 (t, J = 2.5 Hz, 1 H), 5.02 (d, J = 10.2 Hz, 1 H), 4.97 (d, J = 16.8 Hz, 1 H), 4.95 (s, 1 H), 4.92 (t, J = 2.0 Hz, 1 H), 3.05 (s, 3 H), 2.55 (m, 1 H), 2.36 (m, 1 H), 2.14 (ddd, J = 12.7, 8.1, 3.0 Hz, 1 H), 2.05 (m, 2 H), 1.98 (d, J = 15.2 Hz, 1 H), 1.72 (m, 1 H), 1.43 (m, 2 H), 1.29 (d, J = 15.2 Hz, 1 H), 1.05 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7 (C), 147.5 (C), 139.8 (CH), 113.8 (CH_2), 106.6 (CH_2), 105.0 (CH_2), 86.0 (C), 50.0 (CH_3), 43.8 (CH_2), 42.8 (CH_2), 36.2 (CH_2), 34.0 (C), 29.8 (CH_2), 28.8 (CH_2), 28.6 (CH_3), 28.1 (CH_3) ppm.

5-Methoxy-3,3,5-trimethyl-1-vinylcyclopentene (12) and 1-Methoxy-1,4,4-trimethyl-2,3-dimethylenecyclopentane (13): Cyclization of precursor **7c** (166 mg, 1.0 mmol) with $PtCl_2$ (14 mg, 0.05 mmol) and styrene (580 µL, 5 mmol), following the GP (80 °C, 1 h) gave, after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 9:1), a mixture of **12** and **13** (3:1, 82 mg, 49% yield). **12**: ^1H NMR (400 MHz, $CDCl_3$): δ = 6.25 (dd, J = 18.2, 11.8 Hz, 1 H), 5.62 (s, 1 H), 5.60 (d, J = 18.2 Hz, 1 H), 5.09 (d, J = 11.8 Hz,

1 H), 3.11 (s, 3 H, OMe), 2.06 (d, *J* = 14.1 Hz, 1 H), 1.67 (d, *J* = 14.1 Hz, 1 H), 1.47 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6 (CH), 141.1 (C), 131.1 (CH), 115.8 (CH_2, CH=*C*H_2), 89.3 (C), 50.7 (CH_3, OMe), 49.7 (CH_2), 41.6 (C), 29.8 (CH_3), 29.7 (CH_3), 28.3 (CH_3) ppm. **13**: ^1H NMR (400 MHz, $CDCl_3$): δ = 5.54 (s, 1 H), 5.39 (s, 1 H), 4.98 (s, 1 H), 4.84 (1s, 1 H), 3.11 (s, 3 H, OMe), 1.97 (d, *J* = 13.6 Hz, 1 H), 1.58 (d, *J* = 13.6 Hz, 1 H), 1.47 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7 (C), 107.2 (CH_2), 104.3 (CH_2), 82.2 (C), 51.9 (CH_2), 50.9 (CH_3, OMe), 40.2 (C), 31.1 (CH_3), 31.0 (CH_3), 22.9 (CH_3) ppm.

4-Butyl-4-methoxy-3-methylenecyclohexene (14) and 1-Butyl-1-methoxy-2,3-dimethylenecyclopentane (15): Cyclization of precursor **7d** (180 mg, 1.0 mmol, 1 equiv.) following the GP (40 °C, 30 h) gave, after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 95:5), a mixture of **14** and **15** (**14/15**, 4:1, 38 mg, 21% yield). **14**: ^1H NMR (400 MHz, $CDCl_3$): δ = 6.07 (d, *J* = 9.6 Hz, 1 H), 5.71 (m, 1 H), 5.06 (s, 1 H), 4.98 (s, 1 H), 3.17 (s, 3 H, OMe), 2.56–2.51 (m, 1 H), 2.35–2.23 (m, 1 H), 1.98–1.93 (m, 1 H), 1.62–1.56 (m, 1 H), 1.38–1.24 (br. m, 6 H), 0.86–0.93 (m, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1 (C), 129.3 (CH), 128.4 (CH), 111.5 (CH_2), 77.2 (C), 49.4 (CH_3, OMe), 36.1 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 25.0 (CH_2), 24.1 (CH_2), 14.1 (CH_3) ppm. **15**: ^1H NMR (400 MHz, $CDCl_3$): 5.59 (s, 1 H), 5.41 (s, 1 H), 4.93 (s, 1 H), 4.91 (s, 1 H), 3.08 (s, 3 H, OMe), 2.56–2.51 (m, 1 H), 2.29 (m, 1 H), 1.95 (m, 1 H), 1.59 (m, 1 H), 1.38–1.24 (m, 6 H), 0.89 (m, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8 (C), 147.8 (C), 106.2 (CH_2), 105.0 (CH), 85.5 (C), 49.6 (CH_3, OMe), 30.3 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 25.8 (CH_2), 23.2 (CH_2), 14.2 (CH_3) ppm.

Methyl 2-(5-Allyl-5-methoxy-3,3-dimethylcyclopent-1-enyl)acrylate (16) and Methyl (2-Allyl-2-methoxy-4,4-dimethyl-5-methylenecyclopentylidene)acetate (17): Cyclization of precursor **7f** (125 mg, 0.5 mmol, 1 equiv.) following the GP (80 °C, 1 h) gave, after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 9:1), a mixture of **16** and **17** (**16/17**, 2.5:1, 80 mg, 64% yield). **16**: IR (neat): $\tilde{\nu}$ = 3076, 2954, 2933, 2864, 1726, 1639 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.21 (s, 1 H), 6.20 (s, 1 H), 6.07 (s, 1 H), 5.67 (m, 1 H), 5.02 (m, 2 H), 3.77 (s, 3 H, CO_2Me), 3.12 (s, 3 H, OMe), 2.50 (m, 2 H), 1.88 (m, 2 H), 1.13 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (C=O), 148.4 (CH), 134.6 (C), 134.4 (CH), 133.0 (C), 124.2 (CH_2, CH=*C*H_2), 117.8 (CH_2, CH=*C*H_2), 93.5 (C), 52.0 (CH_3), 50.3 (CH_3), 44.9 (CH_2), 43.8 (CH_2), 41.5 (C), 29.4 (CH_3), 28.9 (CH_3) ppm. **17**: IR (neat): $\tilde{\nu}$ = 3076, 2954, 2933, 2864, 1726, 1639 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.56 (s, 1 H), 5.85 (m, 1 H), 5.72 (s, 1 H), 5.34 (s, 1 H), 5.12 (m, 2 H), 3.77 (s, 3 H, CO_2Me), 3.04 (s, 3 H, OMe), 2.74 (m, 1 H), 2.26 (m, 1 H), 1.88 (m, 2 H), 1.19 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (C=O), 149.2 (CH), 139.1 (C), 134.0 (CH), 126.3 (C), 117.7 (CH_2, CH=*C*H_2), 115.1 (CH_2, CH=*C*H_2), 76.5 (C), 51.7 (CH_3), 49.7 (CH_3), 44.7 (CH_2), 38.3 (CH_2), 33.1 (C), 31.2 (CH_3), 29.9 (CH_3) ppm.

5,5-Dimethyl-3-(2-propenyl)bicyclo[4.1.0]hept-2-en-2-yl 4-Nitrobenzoate (18a): Cyclization of **1g** (228 mg, 0.7 mmol) with $PtCl_2$ (9 mg, 0.035 mmol) following the GP (2 h at 80 °C) gave, after purification by flash chromatography (EtOAc/hexane, 2:98), a mixture of **18a** and **19a** (95:5, 183 mg, 80% yield). **18a**: solid, m.p. 73–75 °C. IR (KBr): $\tilde{\nu}$ = 3115, 3000, 2950, 2850, 1725, 1610, 1530 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.33 (m, 4 H, Ar), 5.63 (m, 1 H), 4.99 (dd, *J* = 17.2, 1.6 Hz, 1 H *trans*), 4.98 (dd, *J* = 11.0, 1.6 Hz, 1 H *cis*), 2.72 (dd, *J* = 14.6, 6.0 Hz, 1 H), 2.60 (dd, *J* = 14.6, 6.0 Hz, 1 H), 1.82 (d, *J* = 16.4 Hz, 1 H), 1.68 (d, *J* = 16.4 Hz, 1 H), 1.37 (td, *J* = 8.4, 4.2 Hz, 1 H), 1.15 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.06–0.76 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.3 (C, C=O), 150.8 (C, Ar), 143.6 (C), 135.4 (C, Ar), 135.0 (CH), 131.1 (2 CH, Ar), 123.8 (2 CH, Ar), 116.2 (CH_2), 115.6 (C), 38.2 (CH_2), 35.0 (CH_2), 29.6 (CH_3), 28.5 (CH_3), 28.1 (C), 26.9 (CH), 13.7 (CH), 10.2 (CH_2) ppm. GCMS (EI): *m*/*z* (%) = 327 (4) [M], 150 (100). $C_{19}H_{21}NO_4$ (327.37): calcd. C 69.71, H 6.47, N 4.28; found C 70.02, H 6.65, N 4.48. **19a**: characteristic signals: ^1H NMR (200 MHz, $CDCl_3$): δ = 5.79 (dd, *J* = 17.4, 10.6 Hz, 1 H), 0.99 (s, 6 H, 2 CH_3), 0.39 (m, 1 H) ppm.

3-Allyl-5,5-dimethylbicyclo[4.1.0]hept-2-en-2-yl Acetate (18b): Cyclization of **1h** (230 mg, 1.04 mmol) with $PtCl_2$ (14 mg, 0.05 mmol) following the GP (2 h at 80 °C) gave, after purification by flash chromatography (Et_2O/PE, 5:95) a mixture of **18b** and **19b** (**18b/19b**, 97:3, 209 mg, 91% yield). **18b**: IR (neat): $\tilde{\nu}$ = 3090, 2950, 1750, 1690, 1640, 1450, 1360 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.56 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1 H), 4.95 (d, *J* = 17.0 Hz, 1 H *trans*), 4.93 (d, *J* = 10.0 Hz, 1 H *cis*), 2.63 (dd, *J* = 14.8, 6.4 Hz, 1 H), 2.50 (dd, *J* = 14.8, 6.4 Hz, 1 H), 2.13 (s, 3 H, OAc), 1.61 (m_{AB}, 2 H), 1.21 (m, 1 H), 1.05 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 0.96 (m, 1 H), 0.77 (m, 1 H), 0.66 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.4 (C, C=O), 143.4 (C), 135.4 (CH), 115.8 (CH_2), 114.6 (C), 37.9 (CH_2), 34.9 (CH_2), 29.5 (CH_3), 28.5 (CH_3), 28.0 (C), 26.6 (CH), 20.8 (CH_3, OAc), 13.6 (CH), 9.8 (CH_2) ppm. $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found C 76.29, H 9.28. **19b**: characteristic signals: ^1H NMR (200 MHz, $CDCl_3$): δ = 5.76 (dd, *J* = 17.2, 10.5 Hz, 1 H), 2.12 (s, 3 H, OAc), 0.94 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 0.21 (m, 1 H) ppm.

3-Methallyl-5,5-dimethylbicyclo[4.1.0]hept-2-en-2-yl 4′-Nitrobenzoate (18c): Cyclization of **1i** (243 mg, 0.7 mmol) with $PtCl_2$ (9 mg, 0.034 mmol) following the GP (2 h at 80 °C) gave, after purification by flash chromatography (EtOAc/hexane, 1:99), a mixture of **18c** and **19c** (**18c/19c**, 7:3, 213 mg, 88% yield). **18c**: Solid, m.p. 57–59 °C. IR (KBr): $\tilde{\nu}$ = 3110, 3070, 2960, 1730, 1610, 1525, 1350 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.31 (m, 4 H, Ar), 4.72, (s, 1 H), 4.67 (s, 1 H), 2.63 (s, 2 H), 1.71 (m_{AB}, 2 H), 1.63 (s, 3 H, CH_3), 1.39 (td, *J* = 8.4, 4.4 Hz, 1 H), 1.13 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.12 (m, 1 H), 0.94–0.75 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.2 (C, C=O), 150.8 (C, Ar), 144.2 (C), 142.5 (C), 135.4 (C, Ar), 131.1 (2 CH, Ar), 123.8 (2 CH, Ar), 115.3 (C), 112.3 (CH_2), 39.1 (CH_2), 38.0 (CH_2), 29.6 (CH_3), 28.7 (CH_3), 28.0 (C), 27.0 (CH), 22.0 (CH_3), 13.6 (CH), 10.2 (CH_2) ppm. GCMS (EI): *m*/*z* (%) = 341 (10) [M], 150 (100). $C_{20}H_{23}NO_4$ (321.40): calcd. C 70.36, H 6.79, N 4.10; found C 70.65, H 7.00, N 4.40. **19c**: characteristic signals: ^1H NMR (200 MHz, $CDCl_3$): δ = 5.78 (dd, *J* = 17.4, 10.6 Hz, 1 H), 4.90 (d, *J* = 10.6 Hz, 1 H), 4.86 (d, *J* = 17.4 Hz, 1 H), 1.30 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 0.51 (t, *J* = 3.5 Hz, 1 H) ppm.

3-Allylbicyclo[4.1.0]hept-2-en-2-yl Acetate (18d): Cyclization of **1j** (192 mg, 1.0 mmol) with $PtCl_2$ (14 mg, 0.05 mmol) following the GP (1 h at 80 °C) gave, after purification by simple filtration through silica gel, compound **18d** (178 mg, 93% yield). Alternatively, cyclization of precursor **1j** (192 mg, 1.0 mmol) was conducted with $PtCl_4$ (17 mg, 0.05 mmol), following the same procedure (80 °C, 2 h) and gave compound **18d** (190 mg, 98%) as an oil. IR (neat): $\tilde{\nu}$ = 3076, 3006, 2977, 2922, 2859, 1754, 1638 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.62 (m, 1 H), 4.91 (m, 2 H), 2.62 (m, 2 H), 2.17 (s, 3 H), 1.96–1.67 (m, 4 H), 1.42 (m, 1 H), 1.20 (m, 1 H), 0.75 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7 (C, C=O), 144.4 (C), 135.7 (CH), 116.8 (C), 115.9 (CH_2),

35.1 (CH_2), 23.8 (CH_2), 21.2 (CH_3, OAc), 19.7 (CH_2), 14.8 (CH), 12.5 (CH), 10.2 (CH_2) ppm.

3-Allyl-5,5-dimethylbicyclo[4.1.0]heptan-2-one (20): To a solution of acetate **18b** (85 mg, 0.4 mmol, 1 equiv.) in methanol (3 mL) was added potassium carbonate (113 mg, 0.8 mmol, 2 equiv.), and the mixture was stirred for 10 min at room temp. The reaction was quenched with a saturated ammonium chloride solution. The aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. Purification by flash chromatography on silica gel (Et_2O/pentane, 5:95) gave the desired ketone **20** (64 mg, 93% yield) as a single diastereomer, the relative stereochemistry of which was determined by NOESY experiments. **20**: Oil. IR (neat): $\tilde{\nu}$ = 3080, 2950, 1680, 1470, 1360 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.60 (m, 1 H), 4.99–4.93 (m, 2 H), 2.35 (m, 1 H), 2.23–2.01 (m, 2 H), 1.72 (m, 1 H), 1.37–1.14 (m, 3 H), 1.06 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 1.07–0.89 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 210.3 (C, C=O), 135.7 (CH), 117.1 (CH_2), 42.3 (CH), 36.0 (CH_2), 35.8 (CH_2), 30.2 (CH, CH_3), 29.0 (C), 27.7 (CH_3), 26.5 (CH), 9.7 (CH_2) ppm. $C_{12}H_{18}O$ (178.27): calcd. C 80.84, H 10.18; found C 80.72, H 10.26.

3-But-3-enyl-5,5-dimethylbicyclo[4.1.0]hept-2-en-2-yl Acetate (22) and 3-(2,2-Dimethylbut-3-enyl)bicyclo[4.1.0]hept-2-en-2-yl Acetate (23): Cyclization of precursor **21** (40 mg, 0.17 mmol) with $PtCl_2$ (2.3 mg, 0.008 mmol), following the GP (80 °C, 1 h) gave, after purification by flash chromatography (Et_2OAc/pentane, 8:92), compound **22** (24 mg, 60%) and compound **23** (12 mg, 30%). **22**: IR (neat): $\tilde{\nu}$ = 3076, 3002, 2953, 2865, 1753, 1694, 1640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.75 (m, 1 H), 4.96 (d, J = 18.8 Hz, 1 H), 4.93 (d, J = 9.1 Hz, 1 H), 2.16 (s, 3 H), 2.02 (m, 2 H), 1.93 (m, 2 H), 1.66 (d, J = 16.2 Hz, 1 H), 1.57 (d, J = 16.2 Hz, 1 H), 1.21 (m, 1 H), 1.09 (s, 3 H), 1.06 (m, 1 H), 1.02 (s, 3 H), 0.77 (m, 1 H), 0.66 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8 (C=O), 143.4 (C), 138.8 (CH), 116.5 (C), 114.8 (CH_2, CH=CH_2), 38.5 (CH_2), 31.8 (CH_2), 30.0 (CH_2), 29.9 (CH_3), 28.8 (CH_3), 28.3 (C), 26.8 (CH), 21.2 (CH_3), 13.8 (CH), 10.0 (CH_2) ppm. $C_{15}H_{22}O_2$ (234.33): calcd. C 76.88, H 9.46; found C 76.85, H 9.54. **23**: IR (neat): $\tilde{\nu}$ = 3080, 3003, 2959, 2926, 2859, 1755, 1682, 1639 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.80 (dd, J = 17.7, 10.8 Hz, 1 H), 4.96 (m, 2 H), 2.15 (s, 3 H), 2.05–1.78 (m, 4 H), 1.65–1.58 (m, 1 H), 1.42–1.37 (m, 1 H), 1.28–1.24 (m, 2 H), 0.96 (s, 6 H), 0.73 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3 (C=O), 148.8 (CH), 145.4 (C), 116.8 (C), 109.7 (CH_2, CH=CH_2), 43.7 (CH_2), 38.2 (C), 27.2 (CH_3), 27.0 (CH_3), 26.6 (CH_2), 21.1 (CH_3), 19.5 (CH_2), 14.4 (CH), 12.4 (CH), 9.2 (CH_2) ppm. $C_{15}H_{22}O_2$ (234.33): calcd. C 76.88, H 9.46; found C 76.97, H 9.69.

Methyl (2*Z*,4*Z*)-3-Acetyloxy-4-methyl-2,4,7-octatrienoate (29): Cyclization of precursor **24** (166 mg, 0.74 mmol) with $PtCl_2$ (9.7 mg, 0.036 mmol), following the GP (80 °C, 11 h) afforded, after purification by flash chromatography (EtOAc/hexane, 5:95), product **29** (17 mg, 11% yield). Oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.03 (t, J = 7.5 Hz, 1 H), 5.80– 5.59 (m, 1 H), 5.71 (s, 1 H), 4.91–4.88 (m, 2 H), 3.58 (s, 3 H), 2.84 (t, J = 7.7 Hz, 2 H), 2.22 (s, 3 H), 1.73 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 165.4, 159.6, 135.1, 133.2, 128.9, 116.4, 105.0, 51.9, 33.1, 21.0, 14.1 ppm. MS (70 eV): m/z (%) = 224 (4) $[M]^+$, 201 (10), 197 (13), 185 (26), 183 (22), 141 (100), 97 (41), 43 (83). $C_{12}H_{16}O_4$ (224.25): calcd. C 64.27, H 7.19; found C 64.19, H 7.33.

3-Methyl-5-phenyl-1,2-pentadien-1-yl Acetate (32): Cyclization of precursor **25** (156 mg, 0.72 mmol) with $PtCl_2$ (10.1 mg, 0.038 mmol), following the GP (5 h at room temp. and then 21 h at 40 °C) afforded, after purification by flash chromatography (EtOAc/hexane, 0.5:99.5), the unreacted starting material **25** (22 mg) and compound **32** [101.1 mg, 63% (74% taking into account the recovered starting material)]. Oil. IR (neat): $\tilde{\nu}$ = 3063, 3027, 2985, 2922, 1976, 1747, 1603, 1497, 1453, 1368, 1215 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.05 (m, 6 H), 2.67 (t, J = 8.0 Hz, 2 H), 2.38–2.20 (m, 2 H), 2.04 (s, 3 H), 1.77 (d, J = 2.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.9, 169.1, 141.9, 128.8 (2 C), 128.7 (2 C), 126.3, 115.9, 110.6, 37.1, 33.9, 21.4, 21.3 ppm. MS (70 eV): m/z (%) = 216 (1) $[M]^+$, 173 (42), 156 (84), 145 (48), 129 (46), 91 (100), 43 (81). $C_{14}H_{16}O_2$ (216.28): calcd. C 77.75, H 7.46; found C 77.65, H 7.24.

1-Methyl-3-(2-methylpropenyl)cyclohex-3-en-1-yl Acetate (35) and 1-Methyl-3-methylene-4-[(methyl)ethylidene]cyclohex-1-yl Acetate (36): Cyclization of precursor **26** (154.0 mg, 0.74 mmol) with $PtCl_2$ (9.84 mg, 0.037 mmol), following the GP (40 h at 40 °C) afforded, after purification by flash chromatography (EtOAc/hexane, 4:96), a mixture of compounds **35** and **36** (**35/36**, 4:1 (determined by GLC), 127.8 mg, 83% yield) that we were unable to separate by chromatography. **35** + **36**: IR (neat): $\tilde{\nu}$ = 2968, 2853, 1732, 1651, 1436, 1367, 1236, 1209 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) (major isomer **35**): δ = 5.53 (br. s, H-4), 5.47 (br. s, H-7), 2.53 (d, J = 17.5 Hz, H-2), 2.28 (d, J = 17.5 Hz, H-2′), 2.20–2.05 (m, H-5, 2 H-6), 1.97 (s, $OCOCH_3$), 1.76 (br. s, H-5′, H-9, H-10), 1.53 (s, H-11) ppm; (minor isomer **36**): δ = 4.96 (br. s, H-10), 4.61 (br. d, J = 2.1 Hz, H-10′), 3.12 (d, J = 13.5 Hz, H-2), 1.95 (s, $OCOCH_3$), 1.70 (s, H-5′, H-8, H-9), 1.52 (s, H-11) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = (major isomer **35**) 169.6, 133.5, 132.1, 125.7, 122.5, 79.4, 39.9, 30.9, 25.6, 23.3, 22.2, 21.2, 18.5 ppm; (minor isomer **36**) 169.5, 146.2, 128.6, 126.0, 109.7, 81.3, 39.6, 37.7, 28.6, 25.6, 23.3, 20.9, 18.9 ppm. GLC/MS: (70 eV, major isomer **35**, retention time: 13.0 min) m/z (%) = 208 (5) $[M]^+$, 148 (70), 133 (100), 119 (12), 105 (80), 91 (89), 43 (180); (minor isomer **36**, retention time: 11.0 min) 148 (98), 133 (96), 119 (21), 105 (49), 91 (47), 43 (100). $C_{13}H_{20}O_2$ (208.30): calcd. C 74.96, H 9.68; found C 74.74, H 9.74.

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