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$PtCl_2$-mediated cycloisomerization of unsaturated propargylic carboxylates

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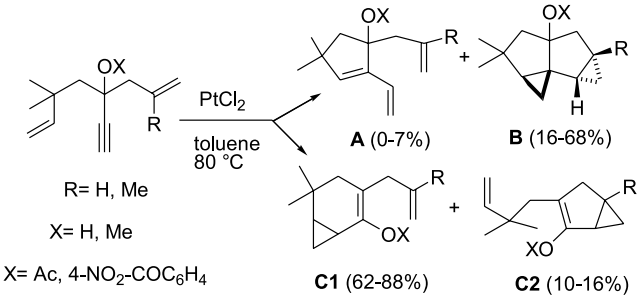
Abstract—The $PtCl_2$-mediated cycloisomerization of unsaturated propargylic carboxylates yields differently functionalized bicyclo[4.1.0]-heptane enol esters from moderate to good yield, in a very diastereoselective manner. We have prepared and submitted to $PtCl_2$-catalyzed cycloisomerization a series of differently substituted hept-1-en-6-ynes with different *O*-acyl (acetyl, trichloroacetyl, 3,4,5-trimethoxy-benzoyl, etc.) protecting groups at propargylic positions, investigating also the effect of the geometry at the double bond, as well as the effect of the number of substituents at the alkene moiety. As a result, we have found that the *O*-acetyl migrating group is the best one in terms of simplicity and chemical yields. In this reaction we have isolated mixtures of compounds formed by minor 1-acetoxy-allenes and major bicyclo[4.1.0]heptane derivatives. Major products are the result of a sequential process involving steps of cycloisomerization plus cyclopropanation, followed by acyl migration. The basic methanolysis (K_2CO_3, MeOH) of these intermediates gave mixtures of *cis* and *trans*-caran-2-ones. This two-step protocol (cycloisomerization plus basic methanolysis) for the syntheses of α,β-unsaturated cyclopropyl ketones constitutes a synthetic alternative to the usual unfriendly, intramolecular cyclopropanation of unsaturated α-diazocarbonyl derivatives. The formation of these bicyclo[4.1.0]heptane derivatives is a simple, but efficient entry into the skeleton of the 'carane' family of natural products.

1. Introduction

Transition-metal catalyzed cycloisomerization of 1,6-enynes[1] constitutes one of the best known examples of what has been called 'full atom economy' reactions.[2] Particularly attractive has been the use of the readily available and stable platinum salts and complexes as catalysts. Since the pioneer work by Trost,[3a–c] a number of reports from different laboratories have highlighted the mechanism of these isomerizations, as well as the scope and limitations of this synthetic procedure for the preparation of carbocycles and/or heterocycles.[3,4] In this context, Fensterbank, Malacria and Marco-Contelles[4a] have reported the critical effect that the type of the substituents at propargylic positions in differently functionalized 1,6-enynes have on the course of their $PtCl_2$-mediated 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 (Scheme 1).[4a] Compounds of type **A** and **B** were obtained after skeletal rearrangement, and sequential cycloisomerization plus cyclopropanation reactions, respectively, while products of type **C** were the formal result of a cycloisomerization and cyclopropanation followed by acyl migration, both transformations involving possibly Pt cyclopropyl carbenes. More recently Malacria and co-workers have reported the $PtCl_2$-catalyzed cycloisomerization of 5-en-1-yn-3-ol systems,[4b] as well as the tandem $PtCl_2$ catalyzed-thermal [3,3] rearrangements of enyne acetates.[4c]



Scheme 1.

A careful revision of the current literature has shown that this attractive $PtCl_2$-mediated cycloisomerization reaction[4a] has precedent on a work published by Ohloff et al. some

Keywords: Propargylic carboxylates; $PtCl_2$-mediated cycloisomerization; Hept-1-en-6-ynes; Cyclopropanes; Bicyclo[4.1.0]heptanes; Carane natural products.
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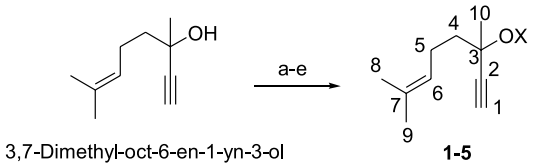
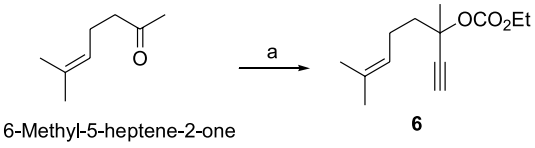


Scheme 2. Reagents: (a) Ac_2O, py, DMAP, rt, 12 h [(**1**): X=$COCH_3$, 81%]. (b) $(Cl_3CCO)_2O$, py, DMAP, rt, 45 min [(**2**): X=$COCCl_3$, 79%]. (c) C_6H_5COCl, py, DMAP, reflux, 46 h [(**3**): X=COC_6H_5, 64%]. (d) $C_6H_2(OCH_3)_3COCl$, py, DMAP, reflux, 24 h {(**4**): X=CO[3,4,5-$(OCH_3)_3C_6H_2$], 49%}. (e) 4-$(NO_2)C_6H_4COCl$, py, DMAP, 80 °C, 16 h [(**5**): X=CO[4-$(NO_2)C_6H_4$], 70%].



Scheme 3. Reagents: (a) Ethynylmagnesium bromide, 2 h, rt; then $ClCO_2Et$, py, DMAP, 5 h, rt (68%).

years ago.[5a] In 1984 Rautenstrauch described the same reaction,[5b] and found that from related precursors, but using $PdCl_2(CH_3CN)_2$ as catalyst, similar products were obtained in better yields (10–40%). 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 until was have rediscovered it by serendipity (Scheme 1).[4a] Ohe and Uemura have recently reported the intermolecular version[5c] of this reaction.

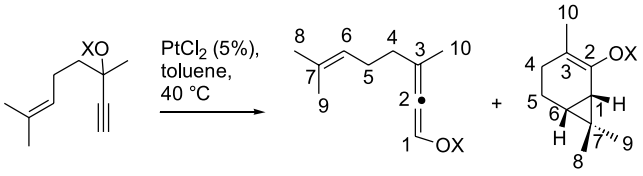
2. Results and discussion

The unexplored and high synthetic potential of these results led us to start a research program aimed at establishing the scope and generality of the $PtCl_2$-catalyzed cycloisomerization of unsaturated propargylic carboxylates. In order to do this, we have prepared new 1,6-enyne derivatives, simplifying the structure of our former precursors, with a methyl substituent at the quaternary propargylic center, fixing in two methylene carbons the tether connecting the unsaturated double bond with the quaternary center, and moving the gem-dimethyl groups at the allylic position to the terminal carbon of the alkene moiety. Then, compounds **1**–**6**, incorporating different acyloxy groups to operate in the presumed key isomerization process, were designed. These precursors were readily prepared in two steps, after Grignard reaction of commercial 6-methyl-5-heptene-2-one with ethynylmagnesium bromide, followed by O-acylation of the resulting 3,7-dimethyl-oct-6-en-1-yn-3-ol[6a] (Schemes 2 and 3).

Precursor **1**,[6a] under the standard conditions [$PtCl_2$ (5%), toluene, 40 °C], afforded the known 1-acetoxy allene **7**[6a,7] and the bicyclo[4.1.0]heptane enol acetate **8**[5a] (Table 1, entry a). Compound **8** has been already described in literature[5a] and the reported spectroscopic data are in good agreement with the ones that we have observed in our sample. The formation of the allenyl esters has not been detected in our previous experiments,[4a] but they are routinely found in the transition metal-catalyzed isomerization of propargylic acetates.[8] However, it has been reported that heating propargylic acetates in benzene or toluene with $PtCl_2$ or silver trifluoroacetate as catalyst gives a diene type of product, instead of the allenyl acetate, the product obtained with copper chloride as catalyst.[7b] Very interestingly, compound **1**, without catalyst, at 60 °C for 72 h, in toluene as solvent, was recovered unreacted, and when $PdCl_2$ (5% mol) was used as catalyst, no reaction was observed at 40 °C for 15 h, or after 44 h at 80 °C. Using gold trichloride ($AuCl_3$), in the same conditions, we were able to isolate compounds **7** and **8** in 33 and 29% yields, respectively. Regarding the solvent, with $PtCl_2$ as catalyst, in methylene chloride, only product **8** was isolated in 25%, after 70 h at 40 °C.

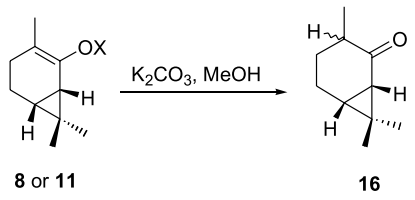
Trichloroacetate **2**, under the standard conditions for the cycloisomerization reaction, gave a complex reaction mixture, in a very slow reaction. After work-up and isolation, only product **9** was isolated in poor yield (20%) (Table 1, entry b). This result shows the importance of the anchimeric assistance of the acyloxy group at the propargylic position for the success of this process. Very clearly, the efficiency of the cycloisomerization reaction was hampered by the low anchimeric assistance ability of

Table 1. $PtCl_2$-mediated cycloisomerization reaction of compounds **1**–**6**



Entry	Precursor	Time (h)	Isolated yields (%)	
a	**1**[6a] X=$COCH_3$	72	**7**[6a,7] (8)	**8**[5a] (54)
b	**2** X=$COCCl_3$	46		**9** (20)
c	**3** X=COC_6H_5	26[a]	**10** (11)	**11** (40)
d	**4** X=CO[3,4,5-$(OCH_3)_3C_6H_2$]	62[a]		**12** (39)[a,b]
e	**5** X=CO[4-$(NO_2)C_6H_4$]	46[a]		**13** (34)
f	**6** X=$CO_2C_2H_5$	22[a]	**14**(3)	**15** (11)

[a] For **3**: Plus 4.5 h at 60 °C. For **4**: Plus 23 h at 60 °C. For **5**: At 60 °C. For **6**: Plus 19 h at 60 °C.
[b] 80% pure (glc).



Scheme 4. Conditions: From **8** (X=$COCH_3$): 15 min, rt (*cis/trans*: 1/3; 66%). From **11** (X=COC_6H_5): 24 h, rt (*only trans*; 50%).

the *O*-trichloroacetyl group due to the electron-withdrawing chlorine atoms.

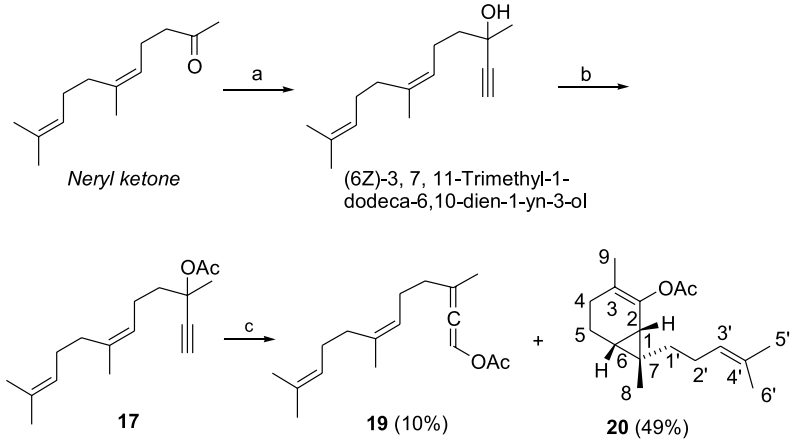
With this result in mind we tested new substrates containing differently substitued benzoyl groups (**3**–**5**). From compound **3**, after $PtCl_2$ catalyzed rearrangement, the allenyl ester **10** (11%) and product **11** (40%) (Table 1, entry c) were isolated, confirming the suitability of the unsubstituted benzoyl group to participate in this cycloisomerization reaction. In order to explore the influence of donor or electron-withdrawing substituents at the aromatic moiety we submitted to cyclization precursors **4** and **5**, with three methoxy and with one nitro groups, respectively, at the aromatic ring. As we can see, precursors **4** and **5** gave products **12** (39% yield) (Table 1, entry d) and **13** (34% yield) (Table 1, entry e) in moderate yield, and no traces of the allenyl derived molecules were detected. All these new compounds gave excellent analytical and spectroscopic data, similar to those described for the parent derivative **8**. In overall, and in good agreement with what has been reported,[8a] even an electron-withdrawing group, as the 4-nitrobenzoyl, promotes the cycloisomerization reaction, but less efficiently than the benzoyl or the substituted trimethoxybenzoyl group; in addition, the benzoyl behaves less efficiently than the acetyl group, probably due to a steric effect.

In this context, the analysis of the reactivity of a carbonate group seemed to us very promising. Thus, we prepared precursor **6** (Scheme 3). Unfortunately, this compound gave a complex reaction mixture, and we only could isolate products **14** and **15** in poor yield (Table 1, entry f).

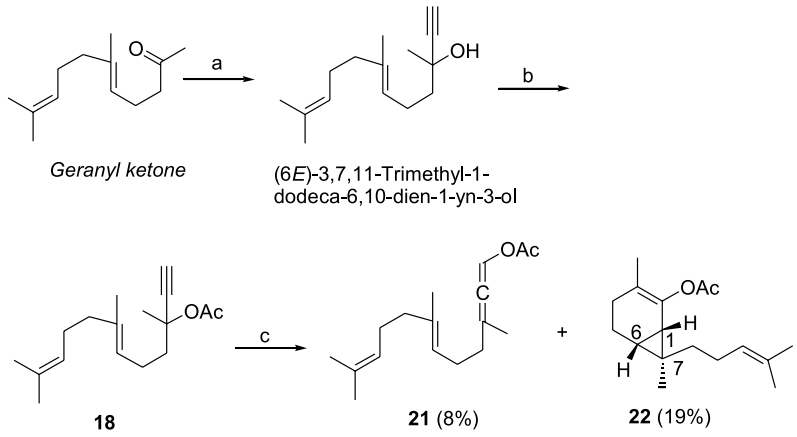
From these results we conclude that the acetyl group is the best migrating group in terms of simplicity and efficiency and, by comparison with the substrates having *gem*-dimethyl groups at the allylic position (Scheme 1),[4a] the presence of two methyl groups at the terminal double bond retards the speed of the reaction, giving moderate to low yields of the cycloisomerization reaction products. This is possibly a consequence of the higher steric hinderance at the transition state, due to the presence of the methyl groups at the terminal position, and points out to an accelerating factor due to the Thorpe-Ingold effect of the *gem*-dimethyl groups in the precursors shown in Scheme 1.[4a] Regarding the different tested acyl groups and their different anchimeric assistance properties, it seems that groups having functional moieties directly bonded to the carbonyl group, with a strong -I effect, as the trichloromethyl or the ethoxy in the carbonate, do not favour the Rautenstrauch isomerization, while electron-donating groups as the methyl or the phenyl accelerate it.

The formation of compounds **8**, **9**, **11**–**13** and **15** constitutes a simple, but efficient entry into the skeleton of the 'carane' family of natural products.[9] As expected, after treatment with K_2CO_3, MeOH, acetate **8** afforded a mixture of *cis* and *trans*-caran-2-one (**16**) in a 1/3 ratio (Scheme 4), that we were unable to separate by chromatography. The ^1H NMR analysis and the comparison of these data with those reported for these compounds[9a] clearly showed that our major compound was the *trans* isomer. The formation of major *trans*-isomer **16** is in good agreement with the reported base isomerization of mixtures of *cis* and *trans*-caran-2-one leading to the major, thermodynamically more stable *trans* isomer.[9b] Similarly, compound **11**, after a long base-mediated methanolysis, gave only *trans*-isomer **16** (Scheme 4).

Next we submitted to cycloisomerization the known precursors **17**[10] (Scheme 5) and **18**[10] (Scheme 6) in order to test the influence of a proximal triple substituted alkene, the stereochemistry at this double bond, as well as the presence of a second, terminal trisubstituted double bond. Compounds **17** (Scheme 5) and **18** (Scheme 6) have been synthesized using the same synthetic sequence, as previously shown for compounds **1**–**6** (Schemes 2 and 3), starting from commercial neryl and geranyl acetones, respectively.



Scheme 5. Reagents: (a) Ethynylmagnesium bromide, THF/Et_2O (1:1), rt, 4 h (80%); (b) Ac_2O, py, DMAP, rt, 40 h (63%); (c) $PtCl_2$ (5%), toluene, 40 °C, 32 h.



Scheme 6. Reagents: (a) Ethynylmagnesium bromide, THF/Et_2O (1:1), rt, 4 h (70%); (b) Ac_2O, py, DMAP, rt, 24 h (63%); (c) $PtCl_2$ (5%), toluene, 80 °C, 32 h.

Acetate **17**[10] gave the known allene **19**[11] and compound **20** (Scheme 5). After selective NOE experiments in the ^1H NMR spectrum we could determine that in acetate **20** the methyl at C-7 was *cis* to the cyclopropyl protons at C-1 and C-6.

Starting from precursor **18**,[10] after $PtCl_2$-mediated cycloisomerization, we isolated the known allene **21**[11] and compound **22** (Scheme 6), in lower yields compared with the results obtained form its isomer **17**. The relative configuration in compound **22**, around the fused rings, was proved to be as shown in Scheme 6, as no NOE effect was observed between the methyl group at C-7 and the cyclopropyl protons at C-1 and C-6 in the ^1H NMR spectrum.

From these results we conclude that the $PtCl_2$ -promoted cycloisomerization process of trisubstitued alkenes is possible, proceeds stereospecifically giving *cis*- or *trans*-products, depending on the stereochemistry at the double bond on the precursor, the *Z* isomer affording the *cis* isomer, while the *E* isomer leads to the corresponding *trans* derivative. Finally, note that the terminal double bond was not involved in the cyclization reaction. These results show also that the efficiency of the reaction is critically dependent on the stereochemistry at the central double bond: the *Z*-isomer provided a moderate yield of the bicyclic derivative, the *E* isomer giving a complex reaction mixture and the final products in poor overall chemical yields.

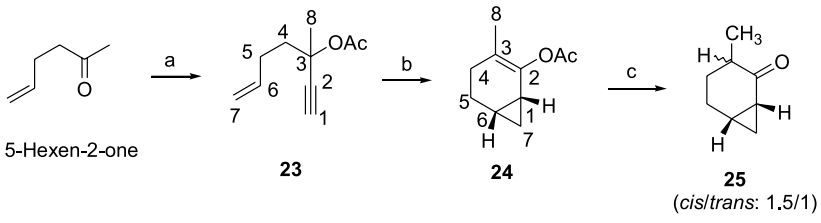
Our next precursor was acetate **23** (Scheme 7), where we have eliminated the methyl groups on the double bond or at allylic positions. Compound **23**[6b] has been synthesized from commercial 5-hexen-2-one following the standard sequence. The isomerization of precursor **23** afforded product **24** (Scheme 7) in a quick reaction and in quantitative chemical yield (99%). The clean and high yielding reaction of precursor **23**, compared with the results obtained in the previously reported results[4a] (Scheme 1) or the results obtained from precursors **1**–**6** (Table 1) clearly show the importance of steric interactions in the transition state in transition-metal catalyzed reactions.[12]

Next, product **24** was submitted to the basic methanolysis to give the known ketone **25**[13] (Scheme 7), isolated as a mixture of isomers *cis*/*trans* in 1.5:1 ratio, in 61% yield. The spectroscopic data of this mixture were in good agreement with the reported values for these compounds.[13a]

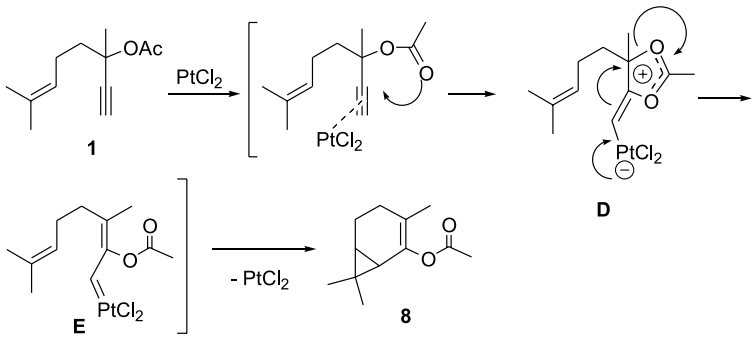
Finally, note that as an added bonus of the present cycloisomerization reaction of readily available propargylic carboxylates, the synthesis of α,β-unsaturated cyclopropyl ketones **16** and **25**, in a two-step protocol ($PtCl_2$-mediated cycloisomerization plus basic methanolysis), constitutes an alternative to the usual unfriendly, intramolecular cyclopropanation of unsaturated α-diazocarbonyl derivatives, prepared by reaction of carboxylic acid chlorides and diazomethane.[14]

Regarding the mechanism of this $PtCl_2$-madiated cycloisomerization reaction, in Scheme 8 we show a tentative proposal based on previous findings.[3g,4a,15] The intramolecular ester attack to the polarized metal-alkyne complex should give intermediate **D** that evolves to Pt carbene **E**, whose final reaction with the terminal double bond results in the formation of compound **8**.

In summary, in this paper we have presented additional synthetic details on the scope and generality of the $PtCl_2$-catalyzed cycloisomerization of unsaturated propargylic



Scheme 7. Reagents: (a) Ethynylmagnesium bromide, THF/Et_2O (1:1), rt, 3 h (50%); then, Ac_2O, py, DMAP, rt, 12 h (67%); (b) $PtCl_2$ (5%), toluene, rt, 18 h (99%); (c) K_2CO_3, MeOH, rt , 18 h (61%).



Scheme 8. Proposed mechanism for the $PtCl_2$-mediated cycloisomerization of compound **1**.

carboxylates.[4,5] This reaction yields differently functionalized bicyclo[4.1.0]heptane enol esters from moderate to good yield, in a very diastereoselective and stereospecific manner. Basic metanolysis (K_2CO_3, MeOH) of these intermediates gave mixtures of *cis*- and *trans*-caran-2-ones. The formation of these bicyclo[4.1.0]heptane derivatives is a simple but efficient entry into the skeleton of the 'carane' family of natural products.[16]

3. Experimental

3.1. General methods

Melting points were determined on a digital melting-point apparatus (Electrothermal) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, at 300.13 and at 75.47 MHz (Bruker Avance-300). TLC was performed on Silica F254 (Merck) and detection by UV light at 254 nm or by charring with phosphomolybdic-H_2SO_4 reagent. Column chromatography was effected on Silica Gel 60 (Merck, 230 mesh). The assignment of chemical shifts are based on standard NMR experiments (^{1}H, ^{13}C, DEPT, ^{1}H–^{1}H COSY, HMQC, HMBC). In the NMR spectra values with (*) can be interchanged.

3.2. General procedure for the $PtCl_2$-catalyzed cycloisomerization reaction

To a degassed solution of the precursor in dry toluene (0.025 M) $PtCl_2$ (0.05 equiv) was added at room temperature (rt), under argon. The reaction mixture was stirred at 40–80 °C until complete reaction. Then, the reaction mixture was filtered and the solvent was evaporated under vacuum. Purification by flash chromatography, eluting with mixtures of EtOAc/hexane gave the corresponding products.

3.3. General procedure for the esterification reaction

To a solution of the respective alcohol in dry pyridine, DMAP (0.2 equiv) and the required acid chloride (or acid anhydride) (1.5 equiv) were added. The reaction mixture was refluxed until complete reaction. Then, the solvent was evaporated under vacuum, the crude was dissolved in dichloromethane and washed with an aqueous saturated solution of $NaHCO_3$, brine and water. Purification by flash chromatography eluting with mixtures of EtOAc/hexane gave the corresponding products.

3.4. General procedure for methanolysis of enol esters

Solid potassium carbonate (2.0 equiv) was added to a solution of the respective enol ester in methanol (0.05 M). The reaction mixture, stirred at rt until complete reaction, was quenched by adding brine. The reaction mixture was extracted by diethyl ether and dried over anhydrous Na_2SO_4. Purification by flash column chromatography (EtOAc/hexane) afforded the corresponding ketones.

3.4.1. 3,7-Dimethyl-oct-6-en-1-yn-3-yl acetate ('dehydrodehydrolinalyl acetate') (1).[6a] A solution of 6-methyl-5-heptene-2-one (0.86 g, 6.8 mmol) in a mixture of dry THF/diethyl ether (1:1) (4 mL) was added dropwise, at rt, to a solution of ethynylmagnesium bromide (16 mL, 8.16 mmol, 0.5 M in THF) in anhydrous diethyl ether (16 mL), under argon. The reaction mixture was stirred at rt for 3 h. Then, water (25 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (25×3 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. Purification by flash chromatography (EtOAc/hexane, 5:95) gave 3,7-dimethyl-oct-6-en-1-yn-3-ol ('dehydrolinalool') (0.75 g, 72% yield) [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.18 (tm, J=7.4 Hz, 1H, H-6), 2.47 (s, 1H, H-1), 2.30–2.17 (m, 2H, H-5), 2.20 (br s, 1H, OH), 1.72 (s, 3H, H-8)*, 1.71 (s, 3H, H-9)*, 1.72–1.56 (m, 2H, H-4), 1.51 (s, 3H, H-10)]. Following the general procedure for the esterification reaction, to a solution of 'dehydrolinalool' (337 mg, 2.21 mmol) in dry pyridine (4 mL), DMAP (120 mg, 0.98 mmol) and acetic anhydride (339.2 mg, 5 mL, 3.32 mmol) were added. The reaction mixture was stirred 12 h at rt. The solvent was evaporated under vacuum and the crude was purified by flash chromatography (EtOAc/hexane, 2:98) to furnish (**1**) (350 mg, 81% yield) as a colorless oil, that showed spectroscopic data [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.08 (tm, J=7.0 Hz, 1H, H-6), 2.53 (s, 1H, H-1), 2.15–2.08 (m, 2H, H-5), 1.99 (s, 3H, $OCOCH_3$), 1.95–1.69 (m, 2H, H-4), 1.65 (s, 6H, H-8*, H-10), 1.31 (s, 3H, H-9*)] in agreement with the structure of this known product.[6a]

3.4.2. 3,7-Dimethyl-octa-1,2,6-trien-1-yl acetate (7)[6a,7] **and 3,7,7-trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl acetate ('2-acetoxy-2-carene') (8).**[5a] Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound (**1**) (130.7 mg, 0.55 mmol) in dry toluene (27 mL) $PtCl_2$ (7.32 mg, 0.027 mmol) was added. The reaction mixture was stirred

for 72 h at 40 °C. Purification by flash chromatography (EtOAc/hexane, 0.5:99.5) afforded (**7**)[6a,7] (10.3 mg, 8% yield) and 2-acetoxy-2-caren (**8**)[5a] (70.7 mg, 54% yield). Both compounds (**7**[6a,7] and **8**[5a]) and are known and showed analytical and spectroscopic data, in good agreement with those described in literature. **7**: Oil; IR (film) ν 3065, 2919, 2857, 1976, 1750 ($OCOCH_3$), 1445, 1368, 1216, 1148 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 1H, H-1), 5.12 (tm, $J=7.1$ Hz, 1H, H-6), 2.15 (m, 2H, H-5), 2.13 (s, 3H, $OCOCH_3$), 2.10–2.01 (m, 2H, H-4), 1.78 (d, $J=2.0$ Hz, 3H, H-10), 1.62 (s, 3H, H-8)*, 1.59 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7 (C-2), 169.2 ($OCOCH_3$), 132.5 (C-7), 123.6 (C-6), 116.2 (C-3), 110.1 (C-1), 35.6 (C-4), 26.3 (C-5), 26.0 (C-9), 21.3 ($OCOCH_3$), 20.9 (C-10), 18.1 (C-8); MS (70 eV) *m/z* 195 ($M^+ +1$, 4), 151 (30), 134 (21), 123 (30), 109 (42), 84 (71), 69 (43), 49 711), 43 (100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.30; H, 9.18. **8**: Oil; IR (film) ν 2926, 2864, 1756 ($OCOCH_3$), 1698, 1450, 1368, 1213, 1165 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33–2.20 (m, 1H, H-4), 2.16 (s, 3H, $OCOCH_3$), 1.85–1.75 (m, 1H, H-5), 1.75–1.65 (m, 1H, H-4′), 1.65–1.59 (m, 1H, H-5′), 1.55 (s, 3H, H-10), 1.12–1.06 (m, 2H, H-1, H-6), 1.07 (s, 3H, H-9)*, 1.00 (s, 3H, H-8)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8 ($OCOCH_3$), 141.7 (C-2), 119.4 (C-3), 29.9 (C-4), 28.3 (C-8)*, 25.2 (C-7), 24.9 (C-6)**, 24.1 (C-1)**, 21.3 ($OCOCH_3$), 17.9 (C-5), 16.4 (C-10), 16.1 (C-9)*; MS (70 eV) *m/z* 194 (M^+, 4), 193 (M^+-1, 4), 166 (6), 152 (49), 137 (38), 123 (22), 109 (100), 91 (27), 83 (13), 77 (16), 69 (29), 55 (17), 43 (83). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.96; H, 9.60.

3.4.3. 3,7-Dimethyloct-6-en-1-yn-3-yl trichloroacetate (2). Following the general procedure for the esterification reaction, to a solution of 'dehydrolinalool' (115.8 mg, 0.76 mmol) in dry pyridine (3 mL) DMAP (18.6 mg, 0.15 mmol) and trichloroacetic anhydride (0.35 mL, 1.14 mmol) were added. The reaction mixture was stirred at rt for 45 min. After usual workup, flash chromatography (EtOAc/hexane, 0.5:99.5) gave compound **2** (178.5 mg, 79% yield) as a colorless oil: IR (film) ν 3305, 2971, 2927, 2123, 1771 (OCO), 1673, 1449, 1377, 1343, 1238, 1165 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.16 (tm, $J=7.0$ Hz, 1H, H-6), 2.71 (s, 1H, H-1), 2.38–2.13 (m, 2H, H-5), 2.08–1.82 (m, 2H, H-4), 1.82 (s, 3H, H-10), 1.71 (s, 3H, H-8)*, 1.65 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4 ($OCOCCl_3$), 132.8 (C-7), 122.4 (C-6), 91.5 ($OCOCCl_3$), 81.2 (C-2), 80.3 (C-3), 75.4 (C-1), 41.2 (C-4), 25.7 (C-10), 25.6 (C-9), 22.7 (C-5), 17.5 (C-8); MS (70 eV) *m/z* 134, 135 (5, 5), 119 (88), 105 (21), 91 (40), 84 (36), 77 (15), 69 (100), 55 (19), 49 (44), 41 (63). Anal. Calcd for $C_{12}H_{15}Cl_3O_2$: C, 48.43; H, 5.08. Found: C, 48.36; H, 4.75.

3.4.4. 3,7,7-Trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl trichloroacetate (9). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of 3,7-dimethyl-1-octyn-6-en-3-trichloroacetate (**2**) (105.7 mg, 0.37 mmol) in dry toluene (15 mL), $PtCl_2$ (4.98 mg, 0.18 mmol) was added. The reaction mixture was stirred for 46 h at 40 °C until complete the reaction. After flash chromatography (EtOAc/hexane, 1:99) (9) (14.7 mg, 20% yield) was isolated as a colorless oil: IR (film) ν 2923, 2865, 1774 (OCO), 1702, 1450, 1376, 1354, 1230, 1218, 1077 cm^{-1}; ^1H NMR (75 MHz, $CDCl_3$) δ 2.38–2.20 (m, 1H, H-4), 1.98–1.80 (m, 2H, H-4′, H-5), 1.78–1.68 (m, 1H, H-5′;), 1.66 (s, 3H, H-10), 1.28–1.10 (m, 2H, H-1, H-6), 1.10 (s, 3H, H-9)*, 1.05 (s, 3H, H-8)*; ^{13}C NMR (300 MHz, $CDCl_3$) δ 160.4 ($OCOCCl_3$), 142.7 (C-2), 121.2 (C-3), 90.5 ($OCOCCl_3$), 30.3 (C-4), 28.2 (C-8)*, 25.9 (C-7), 25.4 (C-6)**, 23.2 (C-1)**, 18.0 (C-5), 16.1 (2C, C-10, C-9*); MS (70 eV) *m/z* 296, 298 (M^+, 6, 6), 281, 283 (M^+-15, 4, 4), 189, 191 (8, 8), 151 (9), 135 (18), 123 (21), 119 (100), 117 (34), 91 (38), 81 (31), 69 (24). Anal. Calcd for $C_{12}H_{15}Cl_3O_2$: C, 48.43; H, 5.08. Found: C, 48.66; H, 5.28.

3.4.5. 3,7-Dimethyloct-6-en-1-yn-3-yl benzoate (3). Following the general procedure for the esterification reaction, to a solution of 'dehydrolinalool' (250.1 mg, 1.65 mmol) in dry pyridine (5 mL), DMAP (40.2 mg, 0.33 mmol) and benzoyl chloride (0.46 mL, 3.29 mmol) were added. The reaction mixture was refluxed for 46 h. After standard work-up, flash chromatography (EtOAc/hexane, 2:98) gave (**3**) (272.0 mg, 64% yield) as a colorless thick oil: IR (film) ν 3301, 3062, 2971, 2926, 2117, 1725 (OCOPh), 1601, 1585, 1491, 1451, 1375, 1314, 1279, 1168 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.55 (m, 1H), 7.49 (m, 2H) (5H, $OCOC_6H_5$), 5.16 (tm, $J=7.4$ Hz, 1H, H-6), 2.61 (s, 1H, H-1), 2.35–2.22 (m, 2H, H-5), 2.15–2.06 (ddd, $J=6.1$ Hz, $J=10.7$ Hz, $J=13.4$ Hz, 1H, H-4), 2.01–1.92 (ddd, $J=5.4$ Hz, $J=10.7$ Hz, $J=13.4$ Hz 1H, H-4′), 1.82 (s, 3H, H-10), 1.68 (s, 3H, H-8)*, 1.63 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 ($OCOC_6H_5$), 132.8 (C-7), 132.9, 132.3, 130.8, 128.3 (COC_6H_5), 123.1 (C-6), 83.6 (C-2), 75.2 (C-3), 73.5 (C-1), 41.6 (C-4), 26.5 (C-10), 25.6 (C-9), 22.9 (C-5), 17.6 (C-8); MS (70 eV) *m/z* 256 (M^+, 12), 134 (25), 119 (78), 105 (100), 91 (38), 77 (61), 69 (29), 51 (21), 41 (28). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.36; H, 8.14.

3.4.6. 3,7-Dimethyl-octa-1,2,6-trien-1-yl benzoate (10) and 3,7,7-trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl benzoate (11). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound (**3**) (130.7 mg, 0.55 mmol) in dry toluene (20 mL), $PtCl_2$ (6.79 mg, 0.027 mmol) was added. The reaction mixture was stirred for 26 h at 40 °C and for 4.5 h at 60 °C. Purification by flash chromatography (EtOAc/hexane, 0.5:99.5) afforded compounds **10** (14.4 mg, 11% yield) and **11** (52.3 mg, 40% yield). **10**: Oil; IR (film) ν 3065, 2919, 2857, 1976, 1750 (OCOPh), 1445, 1368, 1216, 1148 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–7.99 (m, 2H), 7.59–7.46 (m, 1H), 7.40–7.35 (m, 2H) (5H, $OCOC_6H_5$), 7.59–7.46 (m, 1H, H-1), 5.15 (tm, $J=7.2$ Hz, 1H, H-6), 2.18–1.98 (m, 4H, H-4, H-5), 1.80 (d, $J=1.8$ Hz, 3H, H-10), 1.64 (s, 3H, H-8)*, 1.58 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4 (C-2), 165.1 ($OCOC_6H_5$), 133.6, 132.5, 130.2, 128.8 ($OCOC_6H_5$), 130.0 (C-7), 123.9 (C-6), 116.3 (C-3), 110.4 (C-1), 35.7 (C-4), 26.3 (C-5), 26.0 (C-9), 21.0 (C-10), 18.2 (C-8); MS (70 eV) *m/z* 256 (M^+, 1), 187 (7), 151 (11), 119 (5), 105 (100), 77 (38), 51 (10), 41 (15). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.72; H, 8.01. **11**: Oil; IR (film) ν 3066, 2922, 1729 (OCOPh), 1601, 1584, 1492, 1451, 1375, 1314, 1272, 1176, 1106, 1069, 1026 cm^{-1}; ^1H

NMR (300 MHz, $CDCl_3$) δ 8.14 (m, 2H), 7.58 (m, 1H), 7.49 (m, 2H) (5H, $OCOC_6H_5$), 2.35–2.00 (m, 1H, H-4), 1.87–1.65 (m, 2H, H-5, H-4′), 1.60–1.55 (m, 1H, H-5′), 1.62 (s, 3H, H-10), 1.40–1.15 (m, 2H, H-1, H-6), 1.11 (s, 3H, H-9)*, 1.09 (s, 3H, H-8)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3 ($OCOC_6H_5$), 142.0 (C-2), 135.1, 130.3, 129.9, 128.7 ($OCOC_6H_5$), 119.6 (C-3), 30.1 (C-4), 28.4 (C-8)*, 25.3 (C-7), 25.1 (C-6)**, 24.3 (C-1)**, 18.1 (C-5), 16.5 (C-10), 16.2 (C-9)*; MS (70 eV) *m/z* 256 (M^+, 38), 151 (3), 134 (7), 105 (100), 77 (56), 41 (12). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.54; H, 7.69.

3.4.7. 3,7-Dimethyloct-6-en-1-yn-3-yl(3′,4′,5′)-trimethoxy benzoate (4). Following the general procedure for the esterification reaction a solution of 'dehydrolinalool' (290.0 mg, 1.92 mmol) in dry pyridine (5 mL), DMAP (46.8 mg, 0.38 mmol) and 3,4,5-trimethoxybenzoyl chloride (886 mg, 3.84 mmol) were added. The reaction mixture was refluxed for 24 h. After usual workup, purification by flash chromatography (EtOAc/hexane, 4:96) furnished product **4** (272.0 mg, 49% yield) as white crystals: mp 45–47 °C; IR (film) ν 3234, 2973, 2936, 2111, 1721 (OCOAr), 1687, 1590, 1504, 1455, 1413, 1372, 1335, 1247, 1222, 1162 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 [s, 2H, $OCOC_6H_2(OCH_3)_3$], 5.18 (tm, J=7.0 Hz, 1H, H-6), 3.90 (s, 9H, 3×CH_3O), 2.62 (s, 1H, H-1), 2.40–2.21 (m, 2H, H-5), 2.20–1.95 (m, 2H, H-4), 1.82 (s, 3H, H-10), 1.65 (s, 3H, H-8)*, 1.61 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5 (*O*COAr), 152.9, 132.5, 125.9, 106.9 [$OCOC_6H_2(OCH_3)_3$], 132.1 (C-7), 123.2 (C-6), 83.7 (C-2), 75.5 (C-3), 73.7 (C-1), 61.0 (OCH_3), 56.2 (2×CH_3O), 41.9 (C-4), 26.6 (C-10), 25.7 (C-9), 23.1 (C-5), 17.6 (C-8); MS (70 eV) *m/z* 346 (M^+, 2), 212 (46), 195 (100), 134 (16), 119 (78), 91 (17), 41 (20). Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.56. Found: C, 69.15; H, 7.48.

3.4.8. 3,7,7-Trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl 3′,4′,5′-trimethoxybenzoate (12). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound **4** (101.6 mg, 0.29 mmol) in dry toluene (12 mL), $PtCl_2$ (3.9 mg, 0.14 mmol) was added. The reaction mixture was stirred for 62 h at 40 °C and for 23 h at 60 °C. Flash chromatography (EtOAc/hexane, 4:96) gave compound **12** [39.3 mg, 39% yield, (80% purity by glc)], as a light yellow oil: IR (film) ν 2925, 2853, 1727 (OCO), 1591, 1504, 1463, 1416, 1337, 1106 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 [s, 2H, $OCOC_6H_2(OCH_3)_3$], 3.95 (s, 6H, 2×CH_3O), 3.94 (s, 3H, CH_3O), 2.40–2.18 (m, 1H, H-4), 2.00–180 (m, 2H, H-5, H-4′), 1.79–1.66 (m, 1H, H-5′), 1.61 (s, 3H, H-10), 1.25–1.18 (m, 2H, H-1, H-6), 1.10 (s, 3H, H-8)*, 1.09 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 [*O*COC_6H_2-$(OCH_3)_3$], 153.3, 135.0, 125.6, 107.5 [$OCOC_6H_2(OCH_3)_3$], 142.0 (C-2), 119.3 (C-3), 61.3 (CH_3O), 56.6 (2×CH_3O), 30.0 (C-4), 28.4 (C-8)*, 26.0 (C-7), 25.4 (C-6)**, 24.5 (C-1)**, 17.9 (C-5), 16.5 (C-10), 16.2 (C-9)*; MS (70 eV) *m/z* 346 (M^+, 1), 229 (8), 212 (11), 209 (4), 195 (100), 167 (5), 152 (8), 137 (8), 123 (5), 111 (5), 95 (8), 85 (15), 77 (12), 69 (16), 51 (7), 43 (19). Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.56. Found: C, 69.30; H, 7.95.

3.4.9. 3,7-Dimethyloct-6-en-1-yn-3-yl 4-nitrobenzoate (5). Following the general procedure for the esterification reaction, to a solution of 'dehydrolinalool' (500.0 mg, 3.29 mmol) in dry pyridine (5 mL), DMAP (80.28 mg, 0.65 mmol) and 4-nitrobenzoyl chloride (915.3 mg, 4.93 mmol) were added. The reaction mixture was heated at 80 °C for 16 h until complete reaction. Purification by flash column chromatography (EtOAc/hexane, 4:96) afforded (**5**) (660.0 mg, 70% yield) as white crystals: mp 73–74 °C; IR (KBr) ν 3298, 3119, 2971, 2921, 1726 (OCOAr), 1607, 1590, 1526, 1446, 1377, 1351, 1323, 1290, 1166 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (dm, J=9.0 Hz, 2H, $OCOC_6H_4NO_2$), 8.19 (d, J=9.0 Hz, 2H, $OCOC_6H_4NO_2$), 5.19 (tm, J=7.1 Hz, 1H, H-6), 2.69 (s, 1H, H-1), 2.40–2.20 (m, 2H, H-5), 2.18–1.76 (m, 2H, H-4), 1.87 (s, 3H, H-10), 1.71 (s, 3H, H-8)*, 1.66 (s, 3H, H-9)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 ($OCOC_6H_4NO_2$), 153.0, 138.8, 135.1, 126.0 ($OCOC_6H_4NO_2$), 133.2 (C-7), 125.4 (C-6), 85.5 (C-2), 79.0 (C-3), 76.8 (C-1), 43.9 (C-4), 28.9 (C-10), 28.1 (C-9), 25.5 (C-5), 20.1 (C-8); MS (70 eV) *m/z* 301 (M^+, 1), 150 (70), 134 (8), 119 (100), 104 (29), 91 (42), 79 (9), 76 (21), 41 (37). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.42; H, 6.59; N, 4.77.

3.4.10. 3,7,7-Trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl 4-nitrobenzoate (13). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound (**5**) (303.9 mg, 1.06 mmol) in dry toluene (43 mL), $PtCl_2$ (14.08 mg, 0.053 mmol) was added. The reaction mixture was stirred for 46 h at 60 °C. Purification by flash chromatography (EtOAc/hexane, 4:96) gave compound **13** (103.3 mg, 34% yield) as yellow crystals: mp 78–80 °C; IR (KBr) ν 2918, 1724 (OCOAr), 1605, 1529, 1449, 1349, 1320, 1276, 1166 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 4H, $OCOC_6H_4NO_2$), 2.41–2.24 (m, 1H, H-4), 2.00–1.80 (m, 2H, H-5, H-4′), 1.78–1.69 (m, 1H, H-5′), 1.61 (s, 3H, H-10), 1.24–1.18 (m, 2H, H-1, H-6), 1.09 (s, 2×3H, 6H, H-8, H-9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1 ($OCOC_6H_4NO_2$), 153.7, 144.7, 134.2, 126.7 ($OCOC_6H_4NO_2$), 142.4 (C-2), 117.2 (C-3), 32.9 (C-4), 28.3 (C-8)*, 28.3 (C-7), 27.9 (C-6)**, 26.9 (C-1)**, 20.7 (C-5), 19.3 (C-10), 18.9 (C-9)*; MS (70 eV) *m/z* 301 (M^+, 55), 286 (6), 258 (5), 231 (4), 150 (100), 134 (12), 119 (17), 104 (34), 92 (15), 81 (7), 76 (16). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.52; H, 6.60; N, 4.98.

3.4.11. Carbonic acid (3,7-dimethyl-1-octyn-6-en-3-yl) ethyl ester (6). A solution of of 6-methyl-5-heptene-2-one (1.0 g, 7.94 mmol) in a mixture of THF/diethyl ether (1:1) (20 mL) was added dropwise, at rt, to a solution of ethynylmagnesium bromide (20 mL, 9.53 mmol, 0.5 M in THF), under argon. The reaction mixture was stirred at rt for 2 h. After completion of reaction, ethyl chloroformiate (1.12 g, 10.32 mmol) was added at 0 °C and the reaction was stirred at rt for 5 h. Then reaction was quenched by adding cold water (100 mL), and the organic layer was extracted with diethyl ether (100×3 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, purification by flash chromatography (EtOAc/hexane, 0.5:99.5) gave (**6**) (1.22 g, 68% yield) as a yellow oil: IR (film) ν 3290, 2981, 2930, 2120, 1754 [OC(O)OEt], 1447, 1371, 1261, 1167 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08 (m, 1H, H-6), 4.15 (q, J=7.0 Hz, 2H, $OCO_2CH_2CH_3$), 2.58 (s, 1H,

H-1), 2.25–2.08 (m, 2H, H-5), 2.05–1.90 (m, 1H, H-4), 1.90–1.75 (m, 1H, H-5′), 1.69 (s, 3H, H-10), 1.66 (s, 3H, H-8)*, 1.60 (s, 3H, H-9)*, 1.27 (t, $J=7.0$ Hz, 3H, $OCO_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3 ($OCO_2CH_2CH_3$), 132.8 (C-7), 123.3 (C-6), 83.6 (C-2), 77.5 (C-3), 74.2 (C-1), 63.9 ($OCO_2CH_2CH_3$), 41.5 (C-4), 26.6 (C-10), 26.0 (C-9), 23.2 (C-5), 18.0 (C-8), 14.6 ($OCO_2CH_2CH_3$); MS (70 eV) *m/z* 165 (4), 152 (10), 137 (23), 119 (100), 109 (19), 105 (16), 91 (49), 81 (8), 79 (12), 69 (58), 55 (13), 49 (55), 41 (35). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.50; H, 9.02.

3.4.12. Carbonic acid-(3,7-dimethyl-octa-1,2,6-trien-1-yl) ethyl ester (14) and carbonic acid-(3,7,7-trimethyl-bicyclo[4.1.0.]hept-2-en-2-yl) ethyl ester (15). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerization reaction, to a degassed solution of compound **6** (224 mg, 1.0 mmol) in dry toluene (25 mL), $PtCl_2$ (13.3 mg, 0.05 mmol) was added. The reaction mixture was stirred for 7 h at rt, heated at 40 °C for 22 h and at 60 °C for 19 h. After usual workup, purification by flash chromatography (EtOAc/hexane, 0.2:99.8) afforded compounds **14** (9.9 mg, 3%) and **15** (25.2 mg, 11% yield, 80% purity) as colorless oils. **14**: IR (film) ν 3068, 2927, 2855, 1981, 1754, 1452, 1370, 1254, 1094 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (br s, 1H, H-1), 5.32 (m, 1H, H-6), 4.26 (q, $J=7.1$ Hz, 2H, $OCO_2CH_2CH_3$), 2.20–2.06 (m, 4H, H-4, H-5), 1.85 (d, $J=1.8$ Hz, 3H, H-10), 1.70 (s, 3H, H-9)*, 1.62 (s, 3H, H-8)*, 1.28 (t, $J=7.1$ Hz, 3H, $OCO_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6 (C-2), 153.4 ($OCO_2CH_2CH_3$), 132.6 (C-7), 123.9 (C-6), 117.4 (C-3), 112.3 (C-1), 64.9 ($OCO_2CH_2CH_3$), 35.7 (C-4), 26.3 (C-5), 26.1 (C-9), 21.1 (C-10), 18.1 (C-8), 14.6 ($OCO_2CH_2CH_3$); MS (70 eV) *m/z* 224 (M^+, 2), 151 (25), 137 (18), 134 (38), 123 (37), 119 (50), 109 (62), 105 (78), 95 (31), 91 (47), 77 (37), 69 (84), 41 (100). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.50; H, 9.02. **15**: IR (film) ν 2983, 2929, 2865, 1755 ($OCO_2CH_2CH_3$), 1701, 1450, 1369, 1245, 1169, 1135, 1094, 1045, 1003 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (q, $J=7.2$ Hz, 2H, $OCO_2CH_2CH_3$), 2.35–2.20 (m, 1H, H-4), 1.95–1.70 (m, 3H, H-5, H-4′), 1.61 (s, 3H, H-10), 1.37 (t, $J=7.2$ Hz, 3H, $OCO_2CH_2CH_3$), 1.30–1.12 (m, 2H, H-1, H-6), 1.09 (s, 3H, H-9)*, 1.01 (s, 3H, H-8)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 ($OCO_2CH_2CH_3$), 142.1 (C-2), 119.8 (C-3), 65.1 ($OCO_2CH_2CH_3$), 30.2 (C-4), 28.2 (C-8)*, 25.4 (C-7), 25.0 (C-6)**, 23.8 (C-1)**, 17.9 (C-5), 16.1 (C-10), 16.0 (C-9)*, 14.6 ($OCO_2CH_2CH_3$); MS (70 eV) *m/z* 224 (M^+, 20), 165 (12), 152 (37), 137 (98), 123 (23), 119 (38), 109 (100), 105 (25), 91 (50), 81 (40), 69 (30), 51 (8), 41 (53). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.70; H, 8.74.

3.4.13. Caran-2-one (16).[9] Following the general procedure for hydrolysis of enol esters, to a solution of '2-acetoxy-2-carene' (**8**) (70 mg, 0.36 mmol) in methanol (2 mL, 0.05 M), solid potassium carbonate (70.5 mg, 0.72 mmol) was added. The reaction mixture was stirred at rt. After complete reaction (15 min) the reaction was quenched by adding brine (5 mL), extracted with diethyl ether and dried over anhydrous Na_2SO_4. Purification by flash column chromatography (EtOAc/hexane, 2:98) afforded caran-2-one (**16**)[9] (35.6 mg, 66% yield), isolated as an inseparable mixture of *cis/trans* isomers in a 1:3 ratio, which showed identical spectroscopic data to those described for these isomers in literature[9a]: Oil; IR (film) ν 2931, 2869, 1682, 1454, 1376, 1225, 1179 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (major *trans* isomer) 1.99 (m, 1H, H-3), 1.82 (m, 2H, H-4), 1.57 (m, 2H, H-5), 1.44 (m, 1H, H-1), 1.22 (s, 3H, H-8), 1.17 (m, 1H, H-6), 1.16 (s, 3H, H-9), 1.06 (d, $J=6.6$ Hz, 3H, H-10); (minor *cis* isomer)[9d] 1.13 (s, 3H, H-8), 1.12 (s, 3H, H-9), 1.04 (d, $J=6.6$ Hz, 3H, H-10); ^{13}C NMR (300 MHz, $CDCl_3$) δ (major *trans* isomer) 212.2 (C-2), 43.7 (C-3), 35.9 (C-4), 35.7 (C-1), 32.4 (C-9), 29.8 (C-6), 28.2 (C-7), 19.3 (C-5), 17.0 (C-8), 15.9 (C-10); (minor isomer *cis*)[9d] 211.8 (C-2), 43.1 (C-3), 34.6 (C-1), 30.3 (C-9), 28.8 (C-4), 26.1 (C-6), 24.1 (C-7), 19.7 (C-5), 18.2 (C-8), 14.6 (C-10); MS (70 eV) *m/z* 152 (M^+, 2) 149 (77), 135 (40), 111 (37), 97 (55), 84 (95), 69 (92), 57 (100), 49 (75), 43 (75). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.65; H, 10.32.

3.5. Methanolysis of enol ester 11

Following the general procedure for the methanolysis of enol esters compound **11** (200 mg, 0.78 mmol), dissolved in methanol (15 mL, 0.05 M), was treated with solid potassium carbonate (153.1 mg, 1.56 mmol). The reaction mixture was stirred at rt for 24 h. Purification by flash column chromatography (EtOAc/hexane, 2:98) afforded *trans*-2-caranone (**16**)[9a] (59.3 mg, 50% yield), which showed identical spectroscopic to those observed for the major isomer obtained in the methanolysis of compound **8**.

3.5.1. (6*Z*)-3,7,11-Trimethyl-6,10-dodecadien-1-yn-3-yl acetate (17).[10] To a solution of neryl acetone (0.5 g, 2.6 mmol) in dry THF/diethyl ether (1:1) (2 mL) was added dropwise ethynylmagnesium bromide (6.5 mL, 3.1 mmol, 0.5 M in THF), at rt, in anhydrous diethyl ether (5 mL), under argon. The reaction mixture was stirred at rt for 4 h. Then water (20 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2×3 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. Purification by flash chromatography (EtOAc/hexane, 2:98) gave (6*Z*)-3,7,11-trimethyl-1-dodeca-6,10-dien-1-yn-3-ol (0.451 g, 80%) [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.06–5.01 (m, 2H), 2.35 (s, 1H), 2.35–1.90 (m, 8H), 2.01 (br s, 1H), 1.59 (s, 6H), 1.51 (s, 3H), 1.39 (s, 3H)]. Following the General Protocol for the Esterification to a solution of compound (6*Z*)-3,7,11-trimethyl-1-dodeca-6,10-dien-1-yn-3-ol (0.2 g, 0.91 mmol) in dry pyridine (3 mL), DMAP (21.96 mg, 0.18 mmol) and acetic anhydride (139.2 mg, 0.19 mL, 1.37 mmol) were added. The reaction mixture was stirred 40 h at rt. The solvent was evaporated under vacuum and the crude was purified by flash chromatography (EtOAc/hexane, 0.4:99.6) to give compound **17** (150 mg, 63% yield) as a colorless oil, that showed analytical and spectroscopic data [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.02 (tm, $J=7.1$ Hz, 2H), 2.46 (s, 1H), 2.20–2.00 (m, 2H), 1.98–1.94 (m, 4H), 1.93 (s, 3H), 1.90–1.65 (m, 4H), 1.58 (s, 9H), 1.51 (s, 3H)] in agreement with the structure of this known product.[10]

3.5.2. (6*Z*)-3,7,11-Trimethyl-1,2,6,10-dodecatetraen-1-yl acetate (19) and (1*S,6*R**,7*R**)-3,7-dimethyl-7-(4-methyl-3-pentenyl)bicyclo[4.1.0]hept-2-en-2-yl acetate (20).** Following the general procedure for the

$PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound **17** (100 mg, 0.382 mmol) in dry toluene (15 mL) $PtCl_2$ (5.1 mg, 0.19 mmol) was added. The reaction mixture was stirred for 32 h at 40 °C. Purification by flash chromatography (EtOAc/hexane, 0.4:99.6) afforded compounds (**19**) {(13 mg, 10% yield, 80% pure)][^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 1H, H-1), 5.02 (m, 2H), 2.15–1.90 (m, 8H), 2.03 (s, 3H), 1.73 [d, J=2.0 Hz, 3H], 1.58 (s, 2×3H, 6H), 1.50 (s, 3H)] that showed spectroscopic data in good agreement with those described in literature[11]} and (**20**) (49 mg, 49% yield). **20**: Oil; IR (film) ν 2959, 2925, 2856, 1756 ($OCOCH_3$), 1451, 1368, 1260, 1213, 1098 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (tm, J=7.1 Hz, 1H, H-3′), 2.20–2.00 (m, 2H), 2.05 (s, 3H, $OCOCH_3$), 2.00–1.64 (m, 2H), 1.58 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H), 1.30–1.13 (m, 4H), 1.06–0.98 (m, 2H, H-1, H-6), 0.93 (s, 3H, H-8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9 ($OCOCH_3$), 141.4 (C-2), 131.7 (C-4′), 125.4 (C-3′), 122.9 (C-3), 30.4 (C-4), 30.2 (C-2′), 29.0 (C-7), 26.1 (C-9), 25.7 (C-1′), 25.6 (C-6), 25.5 (C-8), 24.4 (C-1), 21.3 ($OCOCH_3$), 18.3 (C-5), 17.8 (C-6′), 16.4 (C-5′); MS (70 eV) m/z 262 (M^+, 12), 220 (63), 177 (17), 164 (13), 151 (42), 135 (100), 133 (5), 123 (18), 109 (44), 95 (20), 83 (11), 43 (38). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.81; H, 9.99. Found: C, 77.76; H, 10.03.

3.5.3. (6*E*)-3,7,11-Trimethyl-6,10-dodecadien-1-yn-3-yl acetate (18).[10] To a solution of geranyl acetone (0.5 g, 2.6 mmol) in dry THF/diethyl ether (1:1) (2 mL) was added dropwise ethynylmagnesium bromide (6.5 mL, 3.1 mmol, 0.5 M in THF), at rt, in anhydrous diethyl ether (5 mL), under argon. The reaction mixture was stirred at rt for 4 h. Then water (20 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2×3 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. Purification by flash chromatography (EtOAc/hexane, 2:98) gave unreacted starting material (91 mg) and the known derivative (6*E*)-3,7,11-trimethyl-1-dodeca-6,10-dien-1-yn-3-ol (0.325 g, 70% yield) [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.08 (m, 2H), 2.36 (d, J=2.0 Hz, 1H), 2.30–1.82 (m, 8H), 1.60 (s, 3H), 1.59 (s, 3H), 1.55 (s, 1H, OH), 1.50 (s, 3H), 1.39 (s, 3H)]. Following the general protocol for the esterification reaction, to a solution of (6*E*)-3,7,11-trimethyl-1-dodeca-6,10-dien-1-yn-3-ol (0.3 g, 1.36 mmol) in dry pyridine (5 mL), DMAP (32.2 mg, 0.27 mmol) and acetic anhydride (208.1 mg, 0.28 mL, 2.04 mmol) were added. The reaction mixture was stirred 24 h at rt. The solvent was evaporated under vacuum and the crude was purified by flash chromatography (EtOAc/hexane, 0.4:99.6) to give compound **18** (150 mg, 63% yield) as a colorless oil, that showed spectroscopic data [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.03 (m, 2H, H-6, H-10), 2.46 (d, J=1.7 Hz, 1H, H-1), 2.18–1.60 (m, 8H), 1.93 (s, 3H, $OCOCH_3$), 1.58 (s, 6H), 1.52 (s, 6H)] in agreement with the structure of this known product.[10]

3.5.4. (6*E*)-3,7,11-Trimethyl-1,2,6,10-dodecatetraen-1-yl acetate (21).[11] and (1*S**,6*R**,7*S**)-3,7-dimethyl-7-(4-methyl-3-pentenyl)bicyclo[41.0]hept-2-en-2-yl acetate (22). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of compound (**18**) (120 mg, 0.458 mmol) in dry toluene (18 mL) $PtCl_2$ (6.1 mg, 0.023 mmol) was added. The reaction mixture was stirred for 32 h at 80 °C. Purification by flash chromatography (CH_2Cl_2/hexane, 1:9) afforded products **21**[11] (9.4 mg, 8% yield) and **22** (23.1 mg, 19% yield). **21**[11]: Oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (m, 1H, H-1), 5.12 (m, 2H, H-6, H-10), 2.13 (s, 3H, $OCOCH_3$), 2.11–1.98 (m, 8H), 2.03 (s, 3H), 1.83 (d, J=1.8 Hz, 3H, H-15), 1.68 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 169.2, 136.1, 131.7, 124.7, 124.5, 116.3, 110.2, 40.0, 35.9, 26.9, 26.2, 26.0, 23.7, 21.0, 18.0, 16.4; MS (70 eV) m/z 262 (32), 151 (73), 133 (91), 109 (90), 69 (100), 43 (80). **22**: Oil; IR (film) ν 2961, 2918, 2855, 1756 ($OCOCH_3$), 1448, 1368, 1214, 1099 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.98 (tm, J=7.1 Hz, 1H, H-3′), 2.20–1.65 (m, 2H, H-2′), 2.25–2.08 (m, 1H), 2.06 (s, 3H, $OCOCH_3$), 2.00–1.85 (m, 2H),1.78–1.62 (m, 1H), 1.57 (s, 3H, H-5′), 1.50 (s, 3H, H-6′), 1.44 (s, 3H, H-9), 1.22–1.05 (m, 2H), 1.03–0.98 (m, 2H, H-1, H-6), 0.86 (s, 3H, H-8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0 ($OCOCH_3$), 140.7 (C-2), 130.7 (C-4′), 124.1 (C-3′), 118.8 (C-3), 41.6 (C-4), 29.2 (C-2′), 28.5 (C-7), 25.2 (C-1′), 25.0 (C-9), 23.5 (C-6), 22.7 (C-1), 20.4 ($OCOCH_3$), 17.1 (C-5), 17.0 (C-5′), 15.6 (C-6′), 12.4 (C-8); MS (70 eV) m/z 262 (M^+, 4), 220 (47), 177 (13), 164 (10), 149 (27), 135 (100), 121 (30), 109 (56), 41 (82). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.58; H, 9.67.

3.5.5. 3-Methyl-hept-6-en-1-yn-3-yl acetate (23).[6b] A solution of of 6-hexene-2-one (0.50 g, 5.1 mmol) in a mixture of dry THF/diethyl ether (1:1) (4 mL) was added dropwise, at rt, to a solution of ethynylmagnesium bromide (13 mL, 6.1 mmol, 0.5 M in THF) in anhydrous diethyl ether (15 mL), under argon. The reaction mixture was stirred at rt for 3 h. Then water (20 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2×3 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. Purification by flash chromatography (EtOAc/hexane, 5: 95) gave 3-methyl-hept-6-en-1-yn-3-ol (0.32 g, 50% yield) [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.76 (ddt, J=6.6 Hz, J=10.0 Hz, J=17.2 Hz, 1H), 5.01 (dm, J=17.2 Hz, 1H), 4.86 (dm, J=10 Hz, 1H), 2.35 (s, 1H), 2.34–2.09 (m, 2H), 2.07 (br s, 1H), 1.69–1.61 (m, 2H), 1.39 (s, 3H)]. Following the general method for the esterification reaction, to a solution of 3-methyl-hept-6-en-1-yn-3-ol (200 mg, 1.60 mmol) in dry pyridine (4 mL), DMAP (39 mg, 0.32 mmol) and acetic anhydride (0.32 mg, 0.36 mL, 2.42 mmol) were added. The reaction mixture was stirred 12 h at rt. The solvent was evaporated under vacuum and the crude was purified by flash chromatography (EtOAc/hexane, 0.8:99.2) to furnish acetate **23** (180 mg, 67% yield) as a colorless oil, that spectroscopic data [^{1}H NMR (200 MHz, $CDCl_3$) δ 5.72 (ddt, J=6.6 Hz, J=10.0 Hz, J=17.2 Hz, 1H, H-6), 4.96 (dm, J=17.2 Hz, 1H, H-7), 4.87 (dm, J=10 Hz, 1H, H-7′), 2.45 (s, 1H, H-1), 2.25–2.06 (m, 2H, H-5), 1.92 (s, 3H, $OCOCH_3$), 2.00–1.86 (m, 1H, H-4), 1.84–1.69 (m, 1H, H-4′), 1.57 (s, 3H, H-8)] in good agreement with the structure of this known product.[6b]

3.5.6. 3-Methylbicyclo[4.1.0] hept-2-en-2-yl acetate (24). Following the general procedure for the $PtCl_2$-catalyzed cycloisomerisation reaction, to a degassed solution of 1-ethynyl-1-methyl-4-pentenyl acetate (**23**) (140.8 mg,

0.81 mmol) in dry toluene (32 mL), $PtCl_2$ (10.8 mg, 0.04 mmol) was added. The reaction mixture was stirred for 18 h at rt. Purification by flash chromatography (EtOAc/hexane, 0.8:99.2) afforded the expected product **24** (140.0 mg, 99% yield): Oil; IR (film) ν 3074, 3005, 2919, 2859, 1755 ($OCOCH_3$), 1698, 1445, 1368, 1320, 1228, 1214 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H, $OCOCH_3$), 1.84–1.54 (m, 4H, H-4, H-5), 1.38 (br s, 3H, H-8), 1.38–1.18 (m, 1H, H-6), 1.07 (td, $J=4.6$ Hz, $J=8.5$ Hz, 1H, H-1), 0.67 (dt, $J=4.6$ Hz, $J=8.0$ Hz, 1H, H-7), 0.59 (m, 1H, H-7′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 ($OCOCH_3$), 143.4 (C-2), 115.3 (C-3), 26.2 (C-4), 21.1 ($OCOCH_3$), 19.6 (C-5), 16.5 (C-8), 14.6 (C-6), 12.3 (C-1), 10.4 (C-7). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.25.

3.5.7. 2-Methyl bicyclo[4.1.0]heptan-2-one (25).[13] Following the general method for the methanolysis of the enol esters, to a solution of 3-methylbicyclo[4.1.0]hept-2-en-2-yl acetate (**24**) (200 mg, 1.15 mmol) in methanol (22 mL, 0.05 M) solid potassium carbonate (225.3 mg, 2.29 mmol) was added. The reaction mixture was stirred at rt for 18 h, quenched by adding brine (25 mL), extracted with diethyl ether and dried over anhydrous Na_2SO_4. Purification by flash column chromatography (EtOAc/hexane, 2:98) afforded 2-methyl bicycle[4.1.0]heptan-2-one (**25**) (87 mg, 61% yield), isolated as an inseparable mixture of *cis/trans* diastereomers in a 1.5:1 ratio, which showed identical spectroscopic to those described for these isomers in literature:[13] Oil; IR (film) ν 3081, 3015, 2960, 2931, 2872, 1688, 1456, 1376, 1351, 1214, 1192 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.20–1.72 (m, 2H), 1.70–15.2 (m, 3H), 1.32–1.12 (m, 2H), 0.98 (d, $J=7.0$ Hz, H-8, major *trans* isomer), 0.91 (d, $J=7.0$ Hz, H-8, minor *trans* isomer), 0.94–0.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (major *cis* isomer) 211.3 (C-2), 42.5 (C-3), 25.5 (C-6), 25.0 (C-4), 21.8 (C-5), 16.6 (C-1), 16.6 (C-8), 8.5 (C-7); (minor *trans* isomer) 212.8 (C-2), 39.2 (C-3), 30.0 (C-4), 20.9 (C-5), 19.6 (C-6), 14.2 (C-1), 16.4 (C-8), 15.6 (C-7); GLC/MS *m/z* (major *cis* isomer) (retention time: 10.99 min) 124 (M^+, 36) 109 (15), 95 (12), 81 (62), 67 (25), 54 (100), 51 (7) 39 (50); (minor *trans* isomer) (retention time: 11.22 min) *m/z* 124 (M^+, 34) 109 (13), 97 (8), 95 (11), 81 (60), 67 (21), 54 (100), 39 (50).

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16. During the preparation of this manuscript we were aware of a communication (Fürstner, A.; Hannen, P. *Chem. Commun.* **2004**, 2546–2547) on the same subject, describing the $AuCl_3$-catalyzed cycloisomerization reaction of similar propargylic carboxylates.